Development of High-capacity Cathodes by using Anionic Redox for All-solid-state Fluoride ion batteries

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### **Chapter 1** General Introduction

#### 1.1 Background

The tale of human civilization is closely tied to its pursuit of energy. From the primitive days of burning wood to the modern era's infrastructures based on fossil fuels, our developmental process depended on our ability to utilize energy.<sup>1, 2</sup> However, this relentless pursuit, especially in the last two centuries, has come at a significant environmental cost. The 20th century saw a dramatic surge in energy demand, met predominantly by fossil fuels, including oil, coal, and natural gas.<sup>3</sup> While these resources powered economies and transformed societies, they also released vast amounts of carbon dioxide and other greenhouse gases into the atmosphere, leading to global warming and the consequent climate change.<sup>4, 5</sup>

In response to climate change, in December 2015, 195 countries adopted the *Paris Agreement* at the United Nations Climate Change Conference (COP21).<sup>6</sup> The *Paris Agreement* seeks a significant reduction in global greenhouse gas emissions, aiming to limit the rise in global temperature to 2 °C in this century, while also striving for measures to restrict the temperature increase even further to 1.5 °C. In 2021, the International Energy Agency (IEA) published a roadmap detailing how the global energy sector can achieve net-zero emissions by 2050.<sup>7</sup> This landmark report set out a narrow but feasible pathway to realize the *Paris Agreement*'s goal, if governments can rely on strong growth in clean energy technologies such as solar, electricity, etc. Consequently, the next few years are crucial, and the IEA urges countries to reduce their reliance on fossil fuels while doubling their energy efficiency. Both the G7 and G20 meetings have clearly expressed support for this strategic objective.<sup>8</sup>

Achieving this great goal requires transformative actions in various sectors, notably in transportation. Currently, transportation, largely reliant on fossil fuels, contributes to around 25 % of global CO<sub>2</sub> emissions. Transition to electric vehicles (EVs) offers a dual-pronged solution. Firstly, since EVs have no exhaust emission, they can directly reduce urban pollutants,

mitigating both climate change impacts and health risks from air pollution. Secondly, as the energy grid transitions towards being primarily renewable, the ecological impact of EVs will become even more minimal. Moreover, the extensive uptake of EVs can catalyze innovations in battery storage, grid management, and the integration of renewable energy sources. These advancements not only drive progress in the transportation sector, but also strengthen other sector's ability to align with the goals of the *Paris Agreement*. Essentially, the rise of EVs represents more than just a transportation revolution, it embodies a comprehensive approach toward a sustainable future.

Although a number of companies, with Toyota Motor Corporation at the forefront, have been advancing the development of more efficient, low-cost, and eco-friendly hydrogen energy and fuel cells, these technologies still hold a minor market share due to their current maturity level. Lithium-ion batteries (LIBs) have been widely researched and experienced rapid development since they were commercialized by Sony in 1991.<sup>9, 10</sup> In assessing an EV's performance, energy density and power density of the batteries are crucial parameters, as defined in equation (1–1) and (1–2),

Energy density = Capacity 
$$\times$$
 Operating voltage  $(1-1)$ 

Power density = 
$$\frac{\text{Energy density}}{\text{Charging (Discharging) Time}}$$
 (1 – 2)

Energy density reflects the battery's endurance and power density reflects the battery's output capability. Owing to inherent merits including a light atomic mass (M = 6.94) and the lowest standard electrode potential (-3.04 V vs. standard hydrogen electrode), LIBs exhibit high operating voltage, high specific capacity, leading to a higher energy density than lead-acid and nickel-hydrogen batteries. As a result, LIBs have become the most suitable power source for modern EVs. In recent years, with the continuous implementation of the zero-carbon policies, the EV market is expanding at an amazing rate. New EV companies emerged (*BYD*, *Tesla*, etc.), while traditional automakers (*BMW*, *Volvo*, etc.) are rapidly transitioning to capture a larger market share. Consequently, the demand for LIBs has surged. As reported by *S&P Global*, the global LIB capacity stood at 2.8 TWh in the first quarter of 2023. It is estimated to be 6.5 TWh

in 2030, with the EV transportation sector accounting for a demand of 3.7 TWh.<sup>11</sup>

The energy density of the current commercialized lithium-ion battery package is 220-260 Wh kg<sup>-1</sup>, which is still far from the level of complete replacement of traditional fuel vehicles.<sup>12</sup> The endurance of the LIB will be reduced in winter due to the chemical reaction activity, and EVs are facing the dilemma of range anxiety and long charging time. Countries around the world have set targets for improving the energy density in LIBs to drive the development of EVs and renewable energy technologies. Chinese government issued an Action Plan for Promoting the Development of Automobile Power Battery Industry, with the goal of boosting the energy density of LIBs of 500 Wh kg<sup>-1</sup> by 2025.<sup>13</sup> According to the *New Energy Vehicle* Industry Development Plan 2021-2035, new energy vehicles are expected to comprise approximately 20% of the total vehicle market by 2025.14 The US government issued the Battery Material Research Program and Battery 500 Consortium, which brings together worldclass research teams from national laboratories, top universities, and corporations to develop the next-generation Li-metal batteries with energy densities of 500 Wh kg<sup>-1</sup>.<sup>15</sup> In addition, the development of LIBs has been constrained by other issues. In extreme cases, thermal runaway may occur inside the battery, which may eventually cause a fire or explosion.<sup>16</sup> Secondly, the reserves of key elements such as Li, Co, and Ni are limited and unevenly distributed.<sup>17</sup> Mineral extraction faces geopolitical conflicts and some humanitarian issues, and the resource shortages are likely to be severe as demand for EVs increases in the future.

Driven by the demands for improvements in lithium-ion batteries, scientists have shifted focus towards new battery systems with superior properties. While the transition to all-solid-state LIBs promises higher energy densities and eliminates the flammability concerns of organic electrolytes, they are not free from issues, primarily the persistence of lithium dendrites. To address this, researchers are probing alternatives to the traditional Li-ion carriers. This exploration spans cations like Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, etc., and even anions like F<sup>-</sup>, Cl<sup>-</sup>.<sup>18-28</sup> Notably, fluoride-ion batteries (FIBs), an idea from the 1970s but realized by 2011,<sup>22</sup> stand out due to their potential in energy density and enhanced safety. Fluoride-ion batteries offer several advantages: i) the multi-electron reaction of metal/metal fluoride provides high

capacity; ii) the highest electronegativity of fluorine makes fluoride ion high electrochemical stability; iii) the high redox potential of  $F_2/F^-$  enables the utilization of cathode materials with higher potential. These merits allow FIBs to achieve higher theoretical energy density compared to traditional LIBs. Moreover, the non-flammable inorganic fluoride solid electrolyte mitigates the safety concerns of the fluoride-ion batteries. Consequently, all-solid-state fluoride ion batteries have attracted significant attention in recent years. However, it is undeniable that fluoride ion batteries are still in their infancy, with the paramount challenge centered on the development of high-performance electrode materials.

In this study, we have investigated various high-performance cathode materials for allsolid-state fluoride ion batteries. Building on the intercalation-type cathode materials with better structural stability, we achieved significant capacity and cycle performance using both transition metal cationic and anionic redox reactions for charge compensation. We examined the structural changes and charge compensation mechanisms of the active materials during charging and discharging, thereby elucidating the reaction mechanisms. In addition, we have developed a method for preparing cathode nanocomposite, and the as-prepared cathode composite showed improved performance in both cycle stability and rate capability, showcasing promising potential for future application.

In the following sections, we will start with the working principle of lithium-ion secondary batteries. Based on this, we will sequentially introduce the concept of all-solid-state fluoride ion batteries, the current development, and the unresolved challenges. Finally, the research objectives and outline of this thesis will be briefly explained.

#### **1.2 Lithium-ion batteries**

#### **1.2.1** Working principle of lithium-ion batteries

Lithium-ion batteries are the highest energy density practical batteries available and are the foundation for the development of next-generation battery technology.<sup>29</sup> In order to design and develop fluoride ion battery electrode materials, we first need to know how lithium-ion batteries work. The predecessor of the lithium-ion battery is the lithium metal battery, whose research can be traced back to the 1950s, and became practical in the 1970s by Professor M. S. Whittingham.<sup>30</sup> Lithium metal battery uses TiS<sub>2</sub> as the cathode material and Li metal as the anode material, realizing the conversion of chemical energy to electrical energy:

$$x \text{Li} + \text{TiS}_2 \rightarrow \text{Li}_x \text{TiS}_2$$
 (1-3)

In 1980, Professor J. B. Goodenough first reported LiCoO<sub>2</sub> as a cathode material.<sup>31</sup> In the following year, Professor A. Yoshino invented a secondary battery utilizing LiCoO<sub>2</sub> cathode and polyacetylene anode, which was improved to LiCoO<sub>2</sub>|VGCF (vapor-grown carbon fiber) battery in 1985 for better cycle performance.<sup>32</sup> Following continuous improvement, lithiumion batteries were finally commercialized by Sony in 1991.<sup>9</sup> The commercialization of the lithium-ion battery offered an energy density nearly double those of Ni-Cd or Ni-H batteries, in terms of both weight and volume. This significantly reduced the size and weight of the power supplies for portable devices. Professor M. S. Whittingham, J. B. Goodenough, and A. Yoshino were awarded the Nobel Prize in Chemistry in 2019 for their outstanding contributions to lithium-ion battery technology.

Professor M. Armand described lithium-ion batteries as "rocking chair batteries", where the Li-ions as charge carriers shuttle between the cathode and anode inside the battery, the working principle of a LIB is shown in **Figure 1.2**.<sup>34</sup> In the case of a typical LiCoO<sub>2</sub>|graphite battery, during the charge process, Li<sup>+</sup> ions are driven by an external potential difference between the cathode and the anode, and are detached from the cathode material (LiCoO<sub>2</sub>) and diffuse into the electrolyte. The transition metal Co is oxidized, and electrons are released for charge neutrality. The Li<sup>+</sup> ions pass through the separator and are inserted into the anode material (graphite). As the electronic conductivity of the electrolyte is extremely low, the electrons reach the anode side through the external circuit. During the discharge process, the Li<sup>+</sup> ions are released from the lithiated anode material (Li<sub>x</sub>C<sub>6</sub>) and diffuse towards the cathode material, and the released electrons pass through the external circuit, forming an electric current that provides electricity to external loads. The reaction equations for a LIB are as follows:

$$Cathode: LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- \qquad (1-4)$$

Anode : 
$$C_6 + xLi^+ + xe^- \leftrightarrow Li_xC_6$$
 (1-5)

Overall : 
$$\text{LiCoO}_2 + \text{C}_6 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6$$
 (1-6)

Based on the working principle of LIBs, we generally evaluate the performance of LIBs using the following indicators. Voltage, which is determined by the standard potential of the cathode and anode materials. The potential difference between the two electrodes when the battery is not operating is called the open circuit voltage (OCV). When the battery is connected to the external load and current is passed through, the battery voltage will deviate from the OCV due to internal resistance or other factors, this phenomenon is polarization (known as "voltage hysteresis"). The second is capacity, lithium in a LIB are all from the cathode material, the capacity of the cathode material determines the overall capacity of the battery. Taking LiCoO<sub>2</sub> as an example, the theoretical capacity refers to the capacity provided by the complete detachment of Li<sup>+</sup> ions, but the actual Li utilization rate cannot reach 100%, and the practical capacity for most cathode materials is lower than their theoretical capacity.

Energy density is the product of voltage and capacity (equation 1–1), and is defined as the amount of electrical energy released per unit mass/volume of a battery. Energy density determines the range of an EV on a single charge. Power density is defined as the output power per unit mass/volume of the battery, and is determined by the energy density and charge/discharge time. Rate capability refers to the high current charge and discharge performance, the voltage, capacity, and high current charge/discharge time determines the power density. Power density reflects the output capability of the battery as a power source. Current LIBs for EVs are severely limited in energy density and power density, so the development of high-energy and high-power batteries is essential for the development of EVs. In addition, factors such as the electrode-electrolyte interface, volume expansion and phase transition of the electrode material also contribute to the overall electrochemical performance, all of which need to be considered when designing new electrode materials.

#### **1.2.2** Typical cathode materials

#### (1) Li transition metal oxides (LiTmO<sub>2</sub>, Tm=transition metal)

The most representative cathode material for LIBs is LiCoO<sub>2</sub>, which was developed by Professor J. B. Goodenough and co-workers in 1980, and is the first commercialized cathode material.<sup>31</sup> LiCoO<sub>2</sub> has an  $\alpha$ -NaFeO<sub>2</sub> layered structure (space group:  $R\overline{3}m$ ), with the [CoO<sub>6</sub>] and [LiO<sub>6</sub>] octahedral arranged as highly ordered Li–O and Co–O slabs, as shown in Figure **1.3.** LiCoO<sub>2</sub> has the advantages of high voltage (> 3.5 V vs. Li/Li<sup>+</sup>), reasonable practical capacity (~ 150 mAh  $g^{-1}$  in commercialized LIB), and long cycle life. The lithium in the LiCoO<sub>2</sub> is believed to rapidly diffuse through the two-dimensional diffusion channel along the a-b plane, with a theoretical specific capacity of 274 mAh  $g^{-1}$  (fully delithiated). However, when charged above 4.2 V (corresponding to approximately x > 0.5-0.55 in Li<sub>1-x</sub>CoO<sub>2</sub>), LiCoO<sub>2</sub> undergoes an irreversible structural transformation and partial oxygen release as more than half of the lithium is extracted, leading to a decrease in capacity and cycle stability.<sup>35-37</sup> Considering the low utilization of Co as well as its high cost, other metal elements (Ni, Mn, Al, etc.) can be utilized to substitute Co to achieve improved performance. Ternary layered LiTmO<sub>2</sub> materials are designed to modulate the band structure and the valence state of the transition metals. When Co is replaced by Ni/Mn or Ni/Al, these ternary materials are referred to as NCM and NCA materials. By adjusting the ratios of the the transition metals in ternary cathode materials, NCM or NCA materials with higher capacities of  $\sim 200$  mAh g<sup>-1</sup> and high output voltage similar to those of LiCoO<sub>2</sub> can be obtained, which are also popular choice for commercial LIBs.

By inducing Li<sub>2</sub>MnO<sub>3</sub> phase to the LiTmO<sub>2</sub> cathode, a new Li-rich layered oxide material with improved performance can be obtained. Because of the high compatibility of the Li<sub>2</sub>MnO<sub>3</sub> (monoclinic *C*2/*m* phase) and LiTmO<sub>2</sub> (hexagonal  $R\bar{3}m$  phase) phases, they will form a layered solid solution *x*Li<sub>2</sub>MnO<sub>3</sub>·(1–*x*)LiTmO<sub>2</sub>.<sup>39</sup> The Li-rich cathode materials have a higher manganese content than those of NCM and NCA materials, allowing them lower cost, higher thermal stability, less contamination, and can exhibit specific capacities of over 250 mAh g<sup>-1</sup>.

Nevertheless, the phase transition from layer to spinel during cycling will lead to voltage and capacity degradation, making Li-rich materials currently in the laboratory research stage.<sup>40</sup>

For decades, cation disorder, which involves the mixing of Li and M metals within the layered LiTmO<sub>2</sub> structures, has been considered as detrimental to Li<sup>+</sup> ion transport and, consequently, to the reversible capacity of intercalation-type electrodes.<sup>41</sup> However, by adjusting the ratio of Li/Tm, introducing some d<sup>0</sup> inert metals (Nb<sup>5+</sup>, Ti<sup>4+</sup>, etc.), or tuning the short-range ordering, it is possible to link the isolated Li<sup>+</sup> ions in the lattice, and this is so-called cation-disordered Li-excess rocksalt (DRX) cathode material.<sup>42-44</sup> DRX compounds are capable of delivering greater capacities than currently available commercial cathode materials. Additionally, the three-dimensional host structure in DRX exhibits greater stability, attributed to random cation distribution, which prevents the changes in interlayer spacing.<sup>45, 46</sup>

The capacity of the conventional layered oxide cathode materials is limited by the transition metal valence state, which is unable to provide electrons when the transition metals are oxidized to their highest valence. Studies in recent years have shown that some Li-rich cathode materials can exhibit capacities over 300 mAh g<sup>-1</sup>, attributed not only to transition metal redox reactions, but also to oxygen redox.<sup>47–50</sup> Once the lattice  $O^{2-}$  is oxidized during the charge process, there are generally two outcomes: i) the unstable  $O^{n-}$  (0 < n < 2) is further oxidized to  $O_2$  gas and released, causing lattice collapse and the loss of Coulombic efficiency; ii)  $O^{n-}$  has the potential to be reduced to  $O^{2-}$  or  $O^{m-}$  (0 < m < n), allowing a reversible oxygen redox during cycling.<sup>51–53</sup> The former is detrimental and needs to be minimized, while the latter boosts the capacity of the cathode material, which is expected to be further exploited. In addition, studies in recent years have revealed the reversible generation of the O<sub>2</sub> molecule in Li-rich cathode materials.<sup>54, 55</sup> By using the characterization methods such as resonant inelastic X-ray scattering (RIXS) and neutron pair distribution function (PDF), the progressive vibration behavior of a trapped O<sub>2</sub> molecule and the O–O bonds in the charged state of Li-rich cathode materials can be observed.<sup>56, 57</sup>

#### (2) Polyanionic Li transition metal orthophosphates (LiTmPO<sub>4</sub>)

The representative material of this category is LiFePO<sub>4</sub>, which was developed and applied by Professor J. B. Goodenough's group in 1997, and is one of the most successful commercial LIB cathode materials (theoretical capacity: ~170 mAh g<sup>-1</sup>).<sup>58, 59</sup> LiFePO<sub>4</sub> has an olivine structure (space group: *Pnma*), the structure consists of corner-shared [FeO<sub>6</sub>] octahedra and edge-shared [LiO<sub>6</sub>] octahedra running parallel to the *b*-axis, connected by the [PO<sub>4</sub>] tetrahedra. Because the oxygen atoms are strongly bonded by both Fe and P atoms, LiFePO<sub>4</sub> shows excellent cycle performance and operating safety. However, the robust covalent oxygen bonds also result in limited ionic diffusivity and poor electronic conductivity. The Li<sup>+</sup> diffusion is believed to be one-dimensional along the *c*-axis, and the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox contributes to charge compensation with a two-phase LiFePO<sub>4</sub>/FePO<sub>4</sub> reaction.<sup>60</sup>

#### **1.3 All-solid-state fluoride-ion batteries**

The concept of fluoride ion batteries was first proposed in the 1970s. Metal fluorides (e.g., CaF<sub>2</sub>) were found to have high ionic conductivity at high temperature, thus the fluoride ion batteries were first constructed in solid-state form.<sup>61, 62</sup> In 1976, J. Schoonman reported the Pb| $\beta$ -PbF<sub>2</sub>:AgF|BiO<sub>0.09</sub>F<sub>2.82</sub>|Bi cell, experimentally demonstrating that oxyfluoride could be used as a solid-state electrolyte for fluoride ion batteries.<sup>63</sup> Reversible cycling of Pb| $\beta$ -PbF<sub>2</sub>|Bi/BiF<sub>3</sub> galvanic cells at room temperature was reported by Danto et al. in 1978.<sup>64</sup> In 1981, the term 'solid-state fluoride-ion battery' was first used by Schoonman and Wolfert to report the enhancement in ionic conductivity of CaF<sub>2</sub> by ion doping.<sup>65, 66</sup> Thereafter, there were few reports in the field of fluoride ion batteries based on metal and metal fluoride (M/MF<sub>x</sub>) conversion reactions, with La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> acting as the solid electrolyte (**Figure 1.7**).<sup>22</sup> This study introduced a new battery chemistry, which has opened a new horizon for the development of battery technology. The cathodic and anodic reactions of a cell can be written as the following equations:

$$Cathode: MF_{x} + xe^{-} \leftrightarrow M + xF^{-} \qquad (1-7)$$

Anode : 
$$M' + xF^- \leftrightarrow M'F_x$$
 (1-8)

$$Overall: M' + MF_{x} \leftrightarrow M'F_{x} + M \qquad (1-9)$$

#### 1.3.1 Research progress of all-solid-state fluoride-ion batteries

#### Solid electrolytes

Although the ionic radii of  $F^-$  is relatively large (~1.33 Å), the monovalency and low charge density make fluoride ions show high mobility in the solid state.<sup>67–69</sup> In addition to high ionic conductivity, the solid electrolyte candidates should meet the following requirements: i) The electronic conductivity must be low to prevent self-discharge in the cells; ii) The candidates need to be electrochemically stable within a wide voltage range for battery operation (i.e., wide electrochemical window); iii) The candidates must be compatible with the cathode and anode, there must be no chemical reaction between the electrodes and the solid electrolyte to ensure the ion-exchange in the electrode-electrolyte interfaces; iv) The electrolyte needs to have suitable mechanical properties to meet the requirement for solid-state battery fabrication. Although the single-crystal Ba-doped LaF<sub>3</sub> exhibited an ionic conductivity of  $1.7 \times 10^{-4}$  S cm<sup>-1</sup> at 50 °C, the cost of preparing single crystal was too high and it was difficult to be integrated into an all-solid-state cell.<sup>68</sup> Therefore, the polycrystalline compounds are more appropriate and practical. The current fluoride solid electrolytes can be broadly classified into two types: tysonite-type and fluorite-type. In addition, recent studies also reported on novel solid electrolytes with distinct structural characteristics.<sup>70, 71</sup>

#### (1) Tysonite-type and fluorite-type compounds

The tysonite-type  $\text{Re}_{1-x}M_xF_{3-x}$  (Re = La, Ce, Sm, and M = Ba, Ca, Sr) fluorides are promising solid-state electrolyte candidates for FIBs due to their high ionic conductivities and wide electrochemical stability window.<sup>22, 73</sup> The ionic conductivity of undoped tysonite fluoride is insufficient, and by aliovalent doping, which results in fluoride vacancies in the structure, the ionic conductivity of the doped material can be improved by two orders of magnitude compared to the stoichiometric compound.<sup>74, 75</sup> Fitchner et al. applied tysonite-type La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> ( $0 \le x \le 0.15$ ) (LBF) in their first study of all-solid-state FIBs, the lattice structure of La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> is shown in **Figure 1.8**. Among a series of La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> compositions, La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> was considered a reliable solid-state electrolyte due to its relatively high ionic conductivity ( $2.8 \times 10^{-4}$  S cm<sup>-1</sup> at 160 °C) and high thermal stability. On the other hand, the theoretical decomposition potentials of LaF<sub>3</sub> and BaF<sub>2</sub> were calculated to be 5.73 and 6.0 V, respectively,<sup>76</sup> and the electrochemical window of La<sub>0.95</sub>Ba<sub>0.05</sub>F<sub>2.95</sub> was measured to be over 5 V, making this series of compounds promising electrolytes for FIBs.<sup>77</sup> Further studies have shown that high-temperature calcination can improve the differences in the grain boundary structure. The ionic conductivity of La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> can be significantly increased to  $10^{-5}$  S cm<sup>-1</sup> at room temperature by a sintering step at 800 °C for 2 h.<sup>78</sup> Therefore, high-temperature calcination became a simple and cost-effective method to improve the ionic conductivity.

Besides La-based fluorides, the Sr-doped CeF<sub>3</sub> (Ce<sub>1-x</sub>Sr<sub>x</sub>F<sub>3-x</sub>) and Ca-doped SmF<sub>3</sub> (Sm<sub>1-x</sub>Ca<sub>x</sub>F<sub>3-x</sub>) can also be used as a solid electrolyte.<sup>79, 80</sup> The Sr and Ca dopant created anionic vacancies and decreased cationic coordination, which enhanced mutual repulsions among cations and led to smooth fluoride ion transport. When the ionic sizes are similar, the ionic conductivity reaches its maximum at a low substitution rate. This is primarily due to the network relaxation of the Re<sub>x</sub>M<sub>1-x</sub>F<sub>3-x</sub> slabs in competition with the chemical pressure.<sup>25</sup> The fluorite-type electrolytes use alkaline-earth metal fluorides as the host lattice. In the case of BaF<sub>2</sub>, the ionic conductivity of Ba<sub>x</sub>Ca<sub>1-x</sub>F<sub>2</sub> was lower than those of the tysonite-type systems (1.16 × 10<sup>-5</sup> S cm<sup>-1</sup> at 413 K) when using isovalent doping.<sup>81</sup> On the other hand, when using aliovalent doping (Ca<sub>x</sub>La<sub>1-x</sub>F<sub>2+x</sub>, Ba<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub>), the dopant cations with different sizes increased the cation disorder and strain, which improved the ionic conductivity.<sup>82, 83</sup>

#### (2) Tetragonal interlayer compounds

As a group of fluorite derivatives, the  $SnF_2$ -containing  $M_xSn_{2-x}F_4$  (M = Pb, Ba, Ca, Sr) exhibit high ionic conductivity even at room temperature due to their special structures.<sup>84, 85</sup> The M–M–Sn–Sn–M–M slabs ordered along the *c*-axis are present in the tetragonal structure,

and fluoride ions occupy the metal interlayers. Because of the  $5s^2$  lone pair electrons of the  $Sn^{2+}$ , the fluoride ion sublattice is strongly distorted, generating numerous of fluoride ion sites, and the fluoride ions are considered to transport at high ionic conductivity in these ion pathways.<sup>86</sup> The ionic conductivities of BaSnF<sub>4</sub> and PbSnF<sub>4</sub> are about  $10^{-4}$  and  $10^{-3}$  S cm<sup>-1</sup> at room temperature,<sup>85, 87</sup> respectively, which are capable of driving the advancement of room-temperature all-solid-state FIB applications. However, the high formation potential of Sn leads to a narrow electrochemical window for these SnF<sub>2</sub>-based compounds, which limits their application for the study of high-voltage electrode materials.<sup>88</sup>

#### **Electrodes**

#### Anode

In laboratory studies of LIBs, a lithium metal half-cell is most widely used to evaluate the performance of electrode materials. This is mainly because lithium metal has the lowest potential among solid-state redox pairs (-3.04 V vs. standard H electrode), and that Li<sup>+</sup> can be directly plated on Li for a Li<sup>+</sup>/Li redox. Therefore, lithium is a reference which is well suited for evaluating various electrode materials. By the relative potential vs. Li metal, we can assess which electrodes are suitable for using as cathode materials, and which are suitable for using as anode materials. Similarly, we would like to use a F<sub>2</sub> half-cell in FIB, which can be expressed as the following equations:

$$Cathode: M + xF^- \leftrightarrow MF_x \qquad (1-10)$$

Anode: 
$$F_2 + 2e^- \leftrightarrow 2F^-$$
 (1 - 11)

Overall : 
$$M + \frac{x}{2}F_2 \leftrightarrow MF_x$$
 (1 – 12)

However, because of the gaseous nature of  $F_2$ , such a half-cell has not been applied yet. Metal/metal fluorides (M/MF<sub>x</sub>) are stable electrodes that have been utilized in all-solid-state FIBs. The M/MF<sub>x</sub> conversion reactions are typically accompanied by a high free energy, which makes them a high theoretical voltage in the cells.<sup>22</sup> Since the  $F_2/F^-$  redox has the highest potential (2.866 V vs. standard H electrode) over the M/MF<sub>x</sub> redox couples, electrode materials with slightly lower potentials than that of the  $F_2/F^-$  electrode may be suitable for cathodes, and those with significantly lower potentials than that of the  $F_2/F^-$  electrode shall be appropriate anode materials. The relative potentials of M/MF<sub>x</sub> electrodes are summarized in **Table 1.1**. Li/LiF has the lowest potential among the M/MF<sub>x</sub> couples, which is the most ideal anode material for FIBs. However, the flammability of lithium metal and the toxicity of LiF have made it not been applied in FIBs. The anode materials reported so far are Ce/CeF<sub>3</sub>, Ca/CaF<sub>2</sub>, Mg/MgF<sub>2</sub>, La/LaF<sub>3</sub>, Bi/BiF<sub>3</sub>, Zn/ZnF<sub>2</sub>, Pb/PbF<sub>2</sub>,<sup>22, 89–93</sup> among which Pb/PbF<sub>2</sub> is considered to be the most suitable anode material because of its high ionic conductivity, high capacity, stable fluorination process and safety.<sup>92</sup>

Carbon additives are usually required to improve the electronic conductivity when applying  $M/MF_x$  electrodes. Recently, Clemens et al. reported new considerations about FIB anode materials.<sup>94</sup> They found severe carbide formation side reactions in alkali, alkaline earth, lanthanides and 3d/4d/5d transition metals, but negligible in Sn, Pb, and Zn anodes:

$$MF_{y} + ye^{-} + xC \leftrightarrow MC_{x} + yF^{-} \qquad (1-13)$$

Such side reactions may negatively affect the cycle performance of the anode material, but they can also be utilized for designing new anode materials for FIBs. For example, potassium fluoride KF has considerable potential to be applied as a highly reversible anode for FIBs. The hypothetical  $KC_8/KF + C$  anode shows a quite low potential (0.738 V vs. Li/LiF), and for the reaction:

$$KF + 8C + e^- \leftrightarrow KC_8 + F^- \qquad (1 - 14)$$

It can provide a reasonable theoretical capacity of 174 mAh  $g^{-1}$ . Notably, the volume change of this electrode reaction would be as low as ±2.5%. A thorough understanding of carbide formation side reactions will assist in the future design of cost-effective and highly reversible anode materials.

#### Cathode

#### Conversion-type materials

Electrodes that involve conversion reactions between metals and metal fluorides are referred to as conversion-type materials. As mentioned above,  $M/MF_x$  pairs with potentials slightly lower than  $F_2/F^-$  couple are considered suitable cathode materials for FIBs. The electrode capacity is calculated by Faraday's law:

Capacity = 
$$\frac{n \times F}{C \times M}$$
 (1 - 15)

Where *n* is the number of charge carriers (fluoride ions), *F* is Faraday's constant (96485 C/mol), *C* is a conversion factor (3.6 C/mAh), and *M* is the molecular weight of the active material in g/mol. Based on the molecular mass of the metals, the theoretical capacities of M/MF<sub>x</sub> couples are summarized in **Table 1.1**.

In early reported studies, Bi/BiF<sub>3</sub> was widely used as a cathode material in all-solid-state FIBs. The reversible capacity during the initial cycle was only 80 mAh  $g^{-1}$  (theoretical capacity: 385 mAh  $g^{-1}$ ), and rapid capacity fading was observed within 10 cycles.<sup>89</sup> Cu/CuF<sub>2</sub> was considered a promising cathode material because of it high theoretical capacity and high potential (843 mAh  $g^{-1}$  and 3.54 V vs. Li/LiF). Thieu et al. have reported a CuF<sub>2</sub>|La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>|La cell, which exhibited a capacity of 360 mAh  $g^{-1}$  during the first cycle, but only 40 mAh  $g^{-1}$  remained after 23 cycles.<sup>95</sup>

Recently, Zhang et al. systematically investigated the electrochemical properties and reaction mechanisms of the 3d transition metal (Ni/Co/Cu) cathode materials.<sup>96</sup> Depositing transition metal thin film on the LaF<sub>3</sub> single crystal substrate by radio-frequency magnetron sputtering, the cell achieved nearly 100 % utilization of the active material during the first cycle. Through X-ray absorption spectroscopy (XAS) and electrochemical characterization, the reaction mechanism of the M/MF<sub>x</sub> cathode was clarified as a two-phase reaction process without intermediate phase generation. This mechanism was also supported by theoretical density functional theory (DFT) calculations.<sup>97</sup> The two-phase transition of M/MF<sub>x</sub> is always

accompanied by a large volume change (e.g., 195.6 % for Cu/CuF<sub>2</sub>, 216.5 % for Co/CoF<sub>2</sub>, and 199.3 % for Ni/NiF<sub>2</sub>, as shown in **Figure 1.9**), which leads to a two-phase mismatch and a loss of contact with the solid electrolyte. This explains the rapid capacity fading of the conversion-type cathode materials in all-solid-state FIBs. Based on this fundamental study, Zhang et al. prepared a Cu–Pb nanocomposite, the in-situ generated PbF<sub>2</sub> could serve as a rapid ion conductor, thereby improving the kinetics of the Cu/CuF<sub>2</sub> phase transition process.<sup>98</sup> They also designed a Cu<sub>3</sub>Au alloy cathode, which enabled the buffering of the volumetric change and showed an improved rate performance and cycle stability compared to that of Cu.<sup>99</sup> Although these modification methods are difficult to realize in non-thin-film batteries, they also provide us with some new thoughts on conversion-type cathode modification. Wang et al. fabricated a series of FIB cathode composites using the high-pressure torsion (HPT) process, resulting in a more homogeneous mixture of the active material and the solid electrolyte. The HPT process effectively reduced the impedance in the cathode composite, which in turn reduced the polarization during charge/discharge processes.<sup>100</sup>

#### Intercalation-type host materials

The intercalation-type cathode materials are those that obey a topotactic fluorination process, where the fluoride-ion (de)insertion does not change the fundamental framework of the host material. The topotactic fluorination process requires anionic deficiencies in the material lattice, and previous studies have reported the chemical fluorination (heating with fluorination agents such as XeF<sub>2</sub>, AgF<sub>2</sub>, F<sub>2</sub> gas, polyvinylidene fluoride (PVdF)) processes in perovskite-related, Ruddlesden–Popper, and infinite layer structures.<sup>101–104</sup> For instance, in La<sub>2</sub>NiO<sub>3</sub>F<sub>2</sub> (using La<sub>2</sub>NiO<sub>4+d</sub> and PVdF), the fluoride ions not only occupied the interstitial layers, but also replaced a part of original oxygen atoms.<sup>105</sup> In LaSrMnO<sub>4</sub>F<sub>2-x</sub> (using LaSrMnO<sub>4</sub> and AgF<sub>2</sub> in argon-filled Teflon reactor, the crystal structures are shown in **Figure 1.10**) and La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>F (using La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> and F<sub>2</sub> gas), the fluoride ions occupied only in the interstitial sites, leading to an expansion in c-axis without phase transition.<sup>106, 107</sup> When fluoride ions were inserted into the layered oxides to form oxyfluorides, the functional properties of these materials were significantly changed, and these further affected the development of the

intercalation-type cathode materials for all-solid-state FIBs.

Benefiting from the topotactic fluorination process, the intercalation-type cathode materials show much smaller volume change than those of conversion-type  $M/MF_x$  cathode materials, and have received great attention in recent years. Clemens et al. firstly reported BaFeO<sub>2.5</sub> cathode material, and perovskite BaFeO<sub>2.5</sub>F<sub>0.5</sub> was obtained upon electrochemical fluorination.<sup>101</sup> Furthermore, Schafarzikite-type MSb<sub>2</sub>O<sub>4</sub> (M = Mg, Co, Fe) with topotactic fluorination through tunnel-like structures has been reported.<sup>108</sup> However, their reversible capacity and cycle performance were not attractive.

Ruddlesden–Popper perovskites ( $A_{n+1}B_nX_{3n+1}$ , A is a rare earth or alkaline earth element, B is a transition metal, and X is an anion), as a layered derivative of perovskite family (ABX<sub>3</sub>), are an important class of solid-state materials,<sup>109</sup> and have been expected to be the most appropriate host for the reversible (de)intercalation of fluoride ions due to the presence of interstitial anion sites within the rock-salt-related layers in the structures.<sup>110–112</sup> Nowroozi et al. reported the electrochemical properties of Ruddlesden-Popper-type LaSrMnO<sub>4</sub>, La<sub>2</sub>CoO<sub>4+d</sub>, and La<sub>2</sub>NiO<sub>4+d</sub>,<sup>106, 111, 113</sup> and their reversible topotactic electrochemical fluorination processes were elucidated. Recently, there has been a new understanding towards the topotactic fluorination in Ruddlesden-Popper-type cathode materials. Wang et al. prepared oxyfluoride Sr<sub>2</sub>MnO<sub>3</sub>F via a high-pressure-assisted solid-state reaction, the unique mixed-anion composition varied the electrochemical properties.<sup>114</sup> Unlike the two-phase coexistence reaction mechanism of LaSrMnO<sub>4</sub> (LaSrMnO<sub>4</sub> and LaSrMnO<sub>4</sub> $F_x$ , 0 < x < 1), Sr<sub>2</sub>MnO<sub>3</sub>F exhibited a smooth solid-solution reaction mechanism during electrochemical fluorination process, which resulted in a relatively low volume expansion of 3.08 % (6.22 % of LaSrMnO<sub>4</sub>/LaSrMnO<sub>4</sub>F), and the material exhibited improved rate capability. The substitution from O to F in the apical site in the perovskite units in Sr<sub>2</sub>MnO<sub>3</sub>F reduced Coulomb repulsion during electrochemical fluorination and therefore reduced the volume expansion, which led to better rate capability. Wang et al. prepared Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub> cathode material by chemical fluorination (using Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub> and XeF<sub>2</sub>), where fluoride ions can be (de)inserted into lattice vacancies smoothly via 3D percolation sites, resulting in excellent cycling stability.<sup>115</sup> It exhibited

a reversible capacity of ~117 mAh g<sup>-1</sup> with a volume expansion of only 0.17 %, and achieved stable cycle performance up to 70 cycles. The Ruddlesden–Popper materials have stable host structure however, they always contain heavy elements (e.g., La, Sr) to support the framework, which are electrochemical-inactive, leading to low theoretical capacities. In a recent study, Miki, H. et al. developed a La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7– $\delta$ </sub>F<sub>2</sub> oxyfluoride cathode that used the charge compensation of both Mn and O, allowing the lattice structure to accommodate excessive F<sup>-</sup> ions beyond the theoretical capacity. The fluoride-ion insertion process was accompanied by the reversible formation/disappearance of oxygen molecules, achieving a high capacity of 200 mAh g<sup>-1</sup>.<sup>116</sup> The electrochemical properties of the Ruddlesden–Popper structured cathode materials reported so far are summarized in **Table 1.2**.<sup>93, 101, 106, 108, 111, 113–116</sup>

Another derivative of perovskite, the infinite-layer compounds (e.g., CaCuO<sub>2</sub>, SrFeO<sub>2</sub>, LaNiO<sub>2</sub>)<sup>117, 118</sup> consist of a sequence of infinitely repeating stacking of  $[TmO_2]$  (Tm refers to transition metal) square lattices. Such structure has numerous of anion deficiencies and are promising cathode material candidates for all-solid-state FIBs. The electrochemical properties of SrFeO<sub>2</sub> and Ca<sub>0.85</sub>CuO<sub>2</sub> cathode materials were investigated in our previous studies, and further research on infinite-layer cathode materials is essential.<sup>119, 120</sup> In addition, some oxides with low coordination numbers and anion vacancies, such as CuLnO<sub>2</sub> (Ln = Y, La), also broadens the range of promising cathode materials for FIBs.<sup>121</sup>

#### 1.3.2 Challenges and outlooks for all-solid-state fluoride ion batteries

Since the introduction of the all-solid-state FIBs prototype in 2011, significant advancements have been made in the field over a decade. However, the performance of the current FIBs has not reached a level to rival the dominance of LIBs.

The cathode material plays a crucial role in a battery, which determines the capacity and the cell voltage, directly affecting the energy density and power density. Currently, the conversion-type cathode materials for FIBs are limited by the drastic volume change during the two-phase (de)fluorination processes, which leads to poor cycle performance and rate capability. In LIBs, the silicon anode possesses a similar situation. Silicon anode has high theoretical capacity, however, the alloying reaction between Si and Li-Si alloy also brings huge volume change.<sup>122</sup> By drawing analogies between Si and M/MF<sub>x</sub> materials, we can take the following approaches for modifying the conversion-type cathodes.<sup>122</sup> i) Reducing the particle size to nano scale, or preparing special morphology such as thin films can lead to considerable improvement in the electrochemical performances (e.g., 3d transition metal thin films);<sup>96</sup> ii) Preparing composite materials, which can offer sufficient electronic/ionic diffusion pathway or suppress the volume change (e.g., Cu@LaF<sub>3</sub> core-shell, Cu–Pb composite, Cu–Au alloy).<sup>98, 99, 123</sup> In addition, the intercalation-type cathode materials are limited by heavy element and low capacity, promising candidates for application are few. It is vital important to find cathode candidates with light molecular mass and simple structure. We believe that the design and study of high-performance FIB cathode materials can advance battery technology in the future, and there is an urgent need to deepen our understanding of the fluorination reaction mechanism of the materials.

#### 1.4 Objective

As mentioned in the previous sections, the development of the intercalation-type cathode materials was restrained by their low theoretical capacity. It is vital important to improve the capacity and reversibility when designing new intercalation-type cathode materials.

For conventional intercalation cathode materials for LIBs, expanding beyond one electron per transition metal species to achieve so-called multi-electron reaction allows higher theoretical capacities. Multi-electron reactions in typical oxide cathode materials have been realized by the formation of high valent metals,<sup>124</sup> trapped molecular O<sub>2</sub>,<sup>54</sup> and peroxo-like oxidized oxygen species, etc.<sup>53, 125</sup> In addition, the mixed cationic and anionic redox reactions in some layered sulfide cathode materials have resulted in high capacities. Sulfide cathodes exhibited improved structural stability then oxide cathodes due to the low electronegativity of sulfur.<sup>126–128</sup> Therefore, developing the application of anionic redox reactions in FIB intercalation-type cathode materials can significantly improve the current bottleneck of low energy density. Mixed-anion compounds are single compounds containing multiple anions, and their unique crystal structure and ionic coordination have led to expectations of innovative chemical and physical applications (**Figure 1.11**).<sup>129, 130</sup> Previous researches have applied mixed-anion compounds in cathode materials for LIBs and FIBs.<sup>114, 131, 132</sup> Mixed-anion compounds are expected to suppress the lattice distortion upon charge/discharge processes, or improve the stability of the oxygen redox reaction. Consequently, constructing different mixed-anion systems and investigating their properties and mechanisms will enhance our understanding of fluoride ion batteries.

In this thesis, we focused on the design and analysis of high-performance cathode materials for FIBs. The research project began with modifying a conversion-type cathode material, then progressed to developing an intercalation cathode material utilizing the multielectron reaction of the transition metal, and finally developed a variety of intercalation-type cathode materials utilizing anionic redox reactions for enhanced energy density and power density. The structural evolutions, charge compensation mechanisms and kinetic properties of the cathode materials have been elucidated by electrochemical measurements and synchrotron X-ray spectroscopy. We believe that this thesis will offer novel insights into designing high-performance cathode materials for all-solid-state FIBs.

#### 1.5 Outline of the present thesis

This thesis consists of 7 chapters, which reported the electrochemical performance and charge compensation mechanisms of various mixed-anion cathode materials and a facile preparation method for a nanocomposite cathode.

In Chapter 1, we introduced the countermeasures for global warming and the demands of the electric vehicle (EV) market. We briefly described the fundamental working principles of the lithium-ion batteries (LIBs) and typical cathode materials. Unlike widely used LIBs which utilize cations as charge carriers, FIBs employ anions (F<sup>-</sup>) as charge carriers. The working principles, research progress, and current bottlenecks of FIBs were introduced. Particularly, the bottlenecks that limit the further development of FIBs and efforts to overcome them were

discussed.

In Chapter 2, we developed a facile ball milling method for preparing high-performance Cu/Cu<sub>2</sub>O nanocomposite cathode materials. A sires of cathode composites were prepared under different ball milling rotation speeds. We measured the ionic conductivity and electrochemical performance and selected the optimized cathode composite, then selected the optimized one and analyzed its reaction mechanisms by X-ray absorption spectroscopy (XAS) and Transmission electronic microscopy (TEM) measurement. The active materials were uniformly distributed in the solid electrolyte matrix by ball milling process, and the nanocomposite exhibited high capacity and outstanding rate capability than previously reported Cu thin film cathode and Cu<sub>2</sub>O cathode material.

In Chapter 3, we introduced an intercalation-type cathode material CuLaO<sub>2</sub>. It exhibited stable cycle performance and superior rate capability than most of the reported intercalation-type cathode materials for FIBs so far. XAS measurements revealed the charge compensation mechanism as a multi-electron reaction of  $Cu^+/Cu^{3+}$  species. A reversible phase transition between crystalline/amorphous phases was confirmed by XRD measurement. Moreover, the BVS calculations indicated that  $F^-$  can easily move through the 2D pathway in the Cu-planes. This cathode material broke through the bottleneck of poor rate capability and low capacity of the intercalation-type cathodes for FIBs, and brought us consideration on the potential application.

In Chapter 4, we explored the fluoride ion insertion behaviors the Ruddlesden–Poppertype La<sub>2</sub>NiO<sub>4+d</sub> cathode material. Excessive fluoride ions can be inserted into the host lattice, occupying the interstitial sites and directly bonding with Ni cations. Through electrochemical measurements, structural change and XAS analysis, the mechanism of topotactic insertion/extraction of F<sup>-</sup> anions and phase change involving Ni redox and O redox for charge compensation was confirmed. By using the reversible anionic redox reaction, La<sub>2</sub>NiO<sub>4+d</sub> achieved a reversible capacity of 270 mAh g<sup>-1</sup> and a high volumetric capacity of 1863 mAh cm<sup>-3</sup>, which were competitive to recent reported Li-rich excess cathode materials for LIBs. In Chapter 5, we introduced the LaNiO<sub>2</sub> cathode material with an infinite-layer structure. Structural evolution from infinite layer to perovskite-related structure upon the 1st charge process was confirmed, and the material underwent an amorphous transformation after the 1st cycle. LaNiO<sub>2</sub> exhibited superior energy and power density compared to many energy storage systems, which was associated with the strong Ni 3d–O 2p hybridization after fluorination. Both multi-electron cationic (Ni<sup>+</sup>/Ni<sup>3+</sup>) and anionic (O<sup>2–</sup>/O<sup>0</sup>) redox were involved in charge compensation, and the signals of molecular O–O bonds was clearly observed by Resonant inelastic X-ray scattering (RIXS).

In Chapter 6, besides the oxide cathode materials, we also clarified the interesting fluorination mechanism of novel oxyfluorosulfide cathode  $Sr_2F_2Fe_2OS_2$ . Fluoride ions not only bonded with Fe atoms but also occupied the interstitial sites surrounding Sr atoms. In terms of charge compensation,  $Fe^{2+}/Fe^{3+}$  occurred from the middle state of charge while  $S^{2-}/S^0$  contributed to the whole voltage range. Particularly, S redox was firstly confirmed as charge-compensation contributor in FIB system. The existence of neutral S<sub>2</sub> unit was demonstrated by X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS).

In Chapter 7, general conclusions were presented based on experimental results. Furthermore, expectations for the future development of all-solid-state FIBs were suggested.



Lithium-ion battery capacity by market (GWh)

Figure 1.1 Global lithium-ion battery capacity as of May 31st, 2023.<sup>11</sup>



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Figure 1.2 Working principle of a lithium-ion battery.<sup>33</sup>



LiCoO<sub>2</sub> (Lithium cobaltate)

Figure 1.3 Crystal structure of LiCoO<sub>2</sub>.



Figure 1.4 Crystal structure of the Li-rich layer oxide material.<sup>38</sup>



Figure 1.5 Schematic illustration of the structures of (a) stoichiometric layered oxides, (b) Li-rich layered structure, and (c) Li-rich disordered rocksalt structure.<sup>41</sup>



Figure 1.6 The olivine structure of LiFePO<sub>4</sub>.<sup>58</sup>



Figure 1.7 A schematic illustration of the prototype FIB proposed by Fichtner et al.<sup>22</sup>



Figure 1.8 Lattice structure of La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub>.<sup>72</sup>

	Gravimetric	Volumetric	E vs. Li/LiF /	E vs. $Pb/PbF_2$ /
$M/MF_x$ couples	capacity / mAh g <sup>-1</sup>	capacity / mAh $cm^{-3}$	V	V
Li/LiF	3861	2062	0.00	-2.89
Ca/CaF <sub>2</sub>	1337	2073	0.04	-2.85
Ba/BaF <sub>2</sub>	390	1402	0.10	-2.80
$Sr/SrF_2$	612	1554	0.11	-2.78
Na/NaF	1166	1132	0.46	-2.44
La/LaF <sub>3</sub>	579	3560	0.48	-2.41
K/KF	685	591	0.52	-2.38
Ce/CeF <sub>3</sub>	574	3885	0.53	-2.37
$Mg/MgF_2$	2205	3832	0.55	-2.35
Al/AlF <sub>3</sub>	2980	8052	1.17	-1.73
Ti/TiF4	2240	10167	2.05	-0.84
Cr/CrF <sub>3</sub>	1546	11117	2.33	-0.56
$Zn/ZnF_2$	820	5847	2.40	-0.50
Mn/MnF <sub>3</sub>	1463	10874	2.64	-0.26
V/VF <sub>4</sub>	2105	12859	2.70	-0.20
Fe/FeF <sub>3</sub>	1440	3301	2.73	-0.16
$Sn/SnF_2$	452	2936	2.83	-0.07
Pb/PbF <sub>2</sub>	259	8129	2.89	0.00
Ni/NiF <sub>2</sub>	913	3751	2.96	0.07
Bi/BiF <sub>3</sub>	385	14275	3.21	0.32
Mo/MoF <sub>5</sub>	1396	8095	3.43	0.54
Co/CoF <sub>3</sub>	1364	7558	3.54	0.64
Cu/CuF <sub>2</sub>	843	2608	3.54	0.64
Ag/AgF	248	7887	4.16	1.26
Au/AuF <sub>3</sub>	408	11336	5.08	2.19

**Table 1.1** Theoretical capacities of various  $M/MF_x$  couples and relative potentials



Cu (Fm3m) a, b, c = 3.608, 3.608, 3.608 (Å) a,  $\beta$ ,  $\gamma$  = 90, 90, 90 (°) V = 46.96 Å<sup>3</sup>  $Z_{(Cu)} = 4$ 



CuF2 (P21/c)

V = 69.41 Å<sup>3</sup>

ΔV/V = 195.6% (Cu based)

 $Z_{(Cu)}=2$ 



**Co** (*P*6<sub>3</sub>/*mmc*) a, b, c = 2.507, 2.507, 4.069 (Å)  $\alpha, \beta, \gamma = 90, 90, 120$  (°)  $V = 22.15 Å^3$  $Z_{(Co)} = 2$ 



CoF2 (P42/mnm) a, b, c = 3.309, 4.569, 5.362 (Å) a,  $\beta$ ,  $\gamma$  = 90, 121.11, 90 (°) a, b, c = 4.696, 4.696, 3.179 (Å) a,  $\beta$ ,  $\gamma$  = 90, 90, 90 (°) V = 70.10 Å<sup>3</sup>  $Z_{(Co)}=2$ ΔV/V = 216.5% (Co based)



Ni (Fm3m) a, b, c = 3.545, 3.545, 3.545 (Å) a,  $\beta$ ,  $\gamma$  = 90, 90, 90 (°) V = 44.55 Å<sup>3</sup>  $Z_{(Ni)} = 4$ 



NiF<sub>2</sub> (P4<sub>2</sub>/mnm) a, b, c = 4.650, 4.650, 3.084 (Å) a,  $\beta$ ,  $\gamma$  = 90, 90, 90 (°) V = 66.67 Å<sup>3</sup>  $Z_{(Ni)} = 2$  $\Delta V/V = 199.3\%$  (Ni based)



**CoF**<sub>3</sub> ( $R\overline{3}c$ ) *a*, *b*, *c* = 5.279, 5.279, 5.279 (Å) *a*,  $\beta$ ,  $\gamma$  = 56.97, 56.97, 56.97 (°) *V* = 96.76 Å<sup>3</sup>  $Z_{(Co)} = 2$ ΔV/V = 38.0% (CoF2 based) ΔV/V = 336.8% (Co based)

Figure 1.9 Crystallographic models of Cu, Co, Ni, and their fluorides.<sup>96</sup>



Figure 1.10 The structure models of Ruddlesden–Popper-type (A<sub>2</sub>BX<sub>4</sub>) LaSrMnO<sub>4</sub>, partly fluorinated LaSrMnO<sub>4</sub>F, and fully fluorinated LaSrMnO<sub>4</sub>F<sub>2</sub>.<sup>106</sup>
Cathode/anode	1st discharge capacity / mAh g <sup>-1</sup>	Average discharge voltage range / V	Cycle performance
LaSrMnO <sub>4</sub> /Pb+PbF <sub>2</sub>	36	~1.0-0.2	Not reported
BaFeO <sub>2.5</sub> /MgF <sub>2</sub>	6	~2.5-1.0	3 cycles
$Co_{0.5}Fe_{0.5}Sb_2O_4/Pb+PbF_2$	6	~0.5-0	Not reported
$La_2CoO_{4+d}/Zn+ZnF_2$	40	~1.0-0.3	$8 \text{ mAh g}^{-1} / 50 \text{ cycles}$
$La_2NiO_3F_2/Pb+PbF_2$	12	$\sim 1.0 - 0.4$	$22.5 \text{ mAh g}^{-1} / 50 \text{ cycles}$
La2NiO4+d/Zn+ZnF2	72	~1.3-0.5	$30 \text{ mAh } \text{g}^{-1}$ / $70 \text{ cycles}$
$Sr_2MnO_3F_2/Pb+PbF_2$	83	0.31	$\sim 70 \text{ mAh g}^{-1} / 10 \text{ cycles}$
$LaSrMnO_4F/Pb+PbF_2$	70	-0.29	$\sim 70 \text{ mAh g}^{-1} / 10 \text{ cycles}$
$Sr_3Fe_2O_5F_2/Pb+PbF_2$	117	-0.44	$117 \text{ mAh g}^{-1} / 70 \text{ cycles}$
$La_{1.2}Sr_{1.8}Mn_2O_{7-\delta}F_2/PbF_2$	190	0.15	190 mAh $g^{-1}$ / 30 cycles

Table 1.2 A summary of the electrochemical properties of different intercalation-type

cathode materials reported so far.



Figure 1.11 Characteristics of mixed-anion compounds.<sup>124</sup>

# Reference

- Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* 2017, *16* (1), 16–22.
- Armand, M.; Tarascon, J.-M. Building better batteries. *Nature* 2008, 451 (7179), 652–657.
- Abas, N.; Kalair, A.; Khan, N. Review of fossil fuels and future energy technologies. *Futures* 2015, 69, 31–49.
- Shakun, J. D.; Clark, P. U.; He, F. Marcott, S. A.; Mix, A. C.; Liu, Z.; Otto-Bliesner, B.; Schmittner, A.; Bard, E., Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation. *Nature* 2012, *484* (7392), 49–54.
- Archer, D.; Eby, M.; Brovkin, V.; Ridgwell, A.; Cao, L.; Mikolajewicz, U.; Caldeira, K.; Matsumoto, K.; Munhoven, G.; Montenegro, A. Atmospheric lifetime of fossil fuel carbon dioxide. *Annu. Rev. Earth Planet. Sci.* 2009, *37*, 117–134.
- Agreement, P. In *Paris agreement*, Report of the Conference of the Parties to the United Nations Framework Convention on Climate Change (21st session, 2015: Paris). Retrived December, HeinOnline: 2015; p 2017.
- IEA; Net Zero Roadmap: A Global Pathway to Keep the 1.5°C Goal in Reach. https://www.iea.org/reports/net-zero-roadmap-a-global-pathway-to-keep-the-15-0cgoal-in-reach. 2023.
- IEA; A global target to double efficiency progress is essential to keep net zero on the table. https://www.iea.org/commentaries/a-global-target-to-double-efficiencyprogress-is-essential-to-keep-net-zero-on-the-table. 2023.
- 9. SONY Corp. https://www.sony.com/en/SonyInfo/News/Press\_Archive/ 200412/04-060E/.
- Yoshino, A. Brief History and Future of the Lithium-Ion Battery. *The Nobel Prizes 2019* 2022, 207.
- 11. Marjolin, A. Lithium-ion battery capacity to grow steadily to 2030. *S&P Global* https://www.spglobal.com/marketintelligence/en/news-insights/research/lithiu m-ion-

battery-capacity-to-grow-steadily-to-2030, 2023

- IEA; Global EV Outlook 2023. https://www.iea.org/reports/global-ev-outlook-2023,
   2023.
- 四部委关于印发《促进汽车动力电池产业发展行动方案》的通知, the State Council, the People's Republic of China. https://www.gov.cn/xinwen /2017-03/02/content 5172254.htm#1.
- 14. 国务院办公厅印发《新能源汽车产业发展规划(2021-2035 年)》,
   https://www.gov.cn/xinwen/2020-11/02/content\_5556762.htm.
- Battery Materials Research (BMR) & battery500 Consortium Overview. https://www.energy.gov/sites/default/files/2019/06/f64/bat108\_duong\_2019\_6.4\_10.4 8am\_jl.pdf.
- Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N. A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. *J. Energy Chem.* 2021, *59*, 83–99.
- Fu, X.; Beatty, D. N.; Gaustad, G. G.; Ceder, G.; Roth, R.; Kirchain, R. E.; Bustamante, M.; Babbitt, C.; Olivetti, E. A. Perspectives on cobalt supply through 2030 in the face of changing demand. *Environ. Sci. Technol.* 2020, *54* (5), 2985–2993.
- Delmas, C.; Braconnier, J.-J.; Fouassier, C.; Hagenmuller, P. Electrochemical intercalation of sodium in Na<sub>x</sub>CoO<sub>2</sub> bronzes. *Solid State Ionics* 1981, *3*, 165–169.
- Jian, Z.; Luo, W.; Ji, X. Carbon electrodes for K-ion batteries. J. Am. Chem. Soc. 2015, 137 (36), 11566–11569.
- Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E. Prototype systems for rechargeable magnesium batteries. *Nature* 2000, 407 (6805), 724–727.
- Xu, C.; Li, B.; Du, H.; Kang, F. Energetic zinc ion chemistry: the rechargeable zinc ion battery. *Angew. Chem.* 2012, *124* (4), 957–959.
- Reddy, M. A.; Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem. 2011, 21 (43), 17059–17062.

- Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.; Okado, T.; Huang, Z. D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.; Kageyama, H.; Uchimoto, Y. High energy density rechargeable magnesium battery using earthabundant and non-toxic elements. *Sci. Rep.* 2014, *4*, 5622.
- 24. Zhao, X.; Zhao-Karger, Z.; Wang, D.; Fichtner, M. Metal oxychlorides as cathode materials for chloride ion batteries. *Angew. Chem.* **2013**, *125* (51), 13866–13869.
- Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Reddy, M.; Clemens, O. Fluoride ion batteries-past, present, and future. *J. Mater. Chem. A* 2021, *9* (10), 5980–6012.
- Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen, C.;
   Yang, J.; Hwang, B.-J. An ultrafast rechargeable aluminium-ion battery. *Nature* 2015, 520 (7547), 324–328.
- 27. Ponrouch, A.; Frontera, C.; Bardé, F.; Palacín, M. R. Towards a calcium-based rechargeable battery. *Nat. Mater.* **2016**, *15* (2), 169–172.
- 28. Zhao, X.; Zhao-Karger, Z.; Fichtner, M.; Shen, X. Halide-based materials and chemistry for rechargeable batteries. *Angew. Chem., Int. Ed.* **2020**, *59* (15), 5902–5949.
- 29. Tarascon, J.-M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, *414* (6861), 359–367.
- Whittingham, M. S. Electrical energy storage and intercalation chemistry. *Science* 1976, 192 (4244), 1126–1127.
- Mizushima, K.; Jones, P.; Wiseman, P.; Goodenough, J. B. Li<sub>x</sub>CoO<sub>2</sub> (0 < x ≤ 1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* 1980, 15 (6), 783–789.
- 32. Yoshino, A.; Sanechika, K.; Nakajima, T. Secondary Battery, USP4,668,595. 1985.
- Chapman, B. How does a lithium-Ion battery work? https://letstalkscience.ca/educational-resources/stem-explained/how-does-a-lithium-ion-batterywork. 2019.
- 34. Armand, M. In "Intercalation Electrode" in Materials for Advanced Batteries, NATO

CONFERENCE SERIES, Series VI: Material Science, Plenum Press: 1980.

- 35. Wizansky, A. R.; Rauch, P. E.; Disalvo, F. J. Powerful oxidizing agents for the oxidative deintercalation of lithium from transition-metal oxides. *J. Solid State Chem.* 1989, *81* (2), 203–207.
- Qian, J.; Liu, L.; Yang, J.; Li, S.; Wang, X.; Zhuang, H. L.; Lu, Y. Electrochemical surface passivation of LiCoO<sub>2</sub> particles at ultrahigh voltage and its applications in lithium-based batteries. *Nat.Commun.* 2018, 9 (1), 4918.
- Gupta, R.; Manthiram, A. Chemical extraction of lithium from layered LiCoO<sub>2</sub>. *J. Solid* State Chem. **1996**, *121* (2), 483–491.
- 38. Lee, S. H.; Moon, J.-S.; Lee, M.-S.; Yu, T.-H.; Kim, H.; Park, B. M. Enhancing phase stability and kinetics of lithium-rich layered oxide for an ultra-high performing cathode in Li-ion batteries. *J. Power Sources* 2015, *281*, 77–84.
- Johnson, C. S.; Kim, J-S.; Lefief, C.; Li, N.; Vaughey, J. T.; Thackeray, M. M. The significance of the Li<sub>2</sub>MnO<sub>3</sub> component in 'composite' *x*Li<sub>2</sub>MnO<sub>3</sub>·(1-*x*)LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> electrodes. *Electrochem. Commun.* 2004, 6 (10), 1085–1091.
- Peralta, D.; Colin, J.-F.; Boulineau, A.; Simonin, L.; Fabre, F.; Bouvet, J.; Feydi, P.; Chakir, M.; Chapuis, M.; Patoux, S. Role of the composition of lithium-rich layered oxide materials on the voltage decay. *J. Power Sources* 2015, *280*, 687–694.
- Fan, Y.; Zhang, W.; Zhao, Y.; Guo, Z.; Cai, Q. Fundamental understanding and practical challenges of lithium-rich oxide cathode materials: Layered and disordered-rocksalt structure. *Energy Storage Mater.* 2021, 40, 51–71.
- Clément, R.; Lun, Z.; Ceder, G. Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes. *Energy Environ. Sci.* 2020, *13* (2), 345–373.
- 43. Urban, A.; Abdellahi, A.; Dacek, S.; Artrith, N.; Ceder, G. Electronic-structure origin of cation disorder in transition-metal oxides. *Phys. Rev. Lett.* **2017**, *119* (17), 176402.
- 44. Chen, D.; Ahn, J.; Chen, G. An overview of cation-disordered lithium-excess rocksalt cathodes. *ACS Energy Lett.* **2021**, *6* (4), 1358–1376.

- Lee, J.; Urban, A.; Li, X.; Su, D.; Hautier, G.; Ceder, G. Unlocking the potential of cation-disordered oxides for rechargeable lithium batteries. *Science* 2014, 343 (6170), 519–522.
- 46. Zhao, X.; Tian, Y.; Lun, Z.; Cai, Z.; Chen, T.; Ouyang, B.; Ceder, G. Design principles for zero-strain Li-ion cathodes. *Joule* **2022**, *6* (7), 1654–1671.
- Luo, K.; Roberts, M. R.; Guerrini, N.; Tapia-Ruiz, N.; Hao, R.; Massel, F.; Pickup, D. M.; Ramos, S.; Liu, Y.-S.; Guo, J. Anion redox chemistry in the cobalt free 3*d* transition metal oxide intercalation electrode Li[Li<sub>0.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>]O<sub>2</sub>. *J. Am. Chem. Soc.* 2016, *138* (35), 11211–11218.
- Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C.; Vezin, H.; Sougrati, M. T.; Doublet, M.-L.; Foix, D.; Gonbeau, D.; Walker, W. Reversible anionic redox chemistry in highcapacity layered-oxide electrodes. *Nat. Mater.* 2013, *12* (9), 827–835.
- Seo, D.-H.; Lee, J.; Urban, A.; Malik, R.; Kang, S.; Ceder, G. The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials. *Nat. Chem.* 2016, 8 (7), 692–697.
- 50. Kobayashi, Y.; Sawamura, M.; Kondo, S.; Harada, M.; Noda, Y.; Nakayama, M.; Kobayakawa, S.; Zhao, W.; Nakao, A.; Yasui, A. Activation and stabilization mechanisms of anionic redox for Li storage applications: Joint experimental and theoretical study on Li<sub>2</sub>TiO<sub>3</sub>-LiMnO<sub>2</sub> binary system. *Mater. Today* 2020, *37*, 43–55.
- 51. Luo, K.; Roberts, M. R.; Guerrini, N.; Tapia-Ruiz, N.; Hao, R.; Massel, F.; Pickup, D. M.; Ramos, S.; Liu, Y. S.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Anion Redox Chemistry in the Cobalt Free 3*d* Transition Metal Oxide Intercalation Electrode Li[Li<sub>0.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>]O<sub>2</sub>. *J. Am. Chem. Soc.* 2016, *138* (35), 11211–8.
- 52. Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y. S.; Edstrom, K.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Charge-compensation in 3*d*transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* **2016**, *8* (7), 684–91.
- 53. McCalla, E.; Abakumov, A. M.; Saubanère, M.; Foix, D.; Berg, E. J.; Rousse, G.;

Doublet, M.-L.; Gonbeau, D.; Novák, P.; Van Tendeloo, G.; Dominko, R.; Tarascon, J.-M. Visualization of O–O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries. *Science* **2015**, *350* (6267), 1516–1521.

- House, R. A.; Rees, G. J.; Pérez-Osorio, M. A.; Marie, J.-J.; Boivin, E.; Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3*d* cathodes associated with molecular O<sub>2</sub> trapped in the bulk. *Nat. Energy* 2020, *5* (10), 777–785.
- 55. House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K. J.; Roberts, M. R.; Bruce, P. G. Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes. *Nature* 2020, 577 (7791), 502–508.
- 56. House, R. A.; Playford, H. Y.; Smith, R. I.; Holter, J.; Griffiths, I.; Zhou, K.; Bruce, P. G. Detection of trapped molecular O<sub>2</sub> in a charged Li-rich cathode by Neutron PDF. *Energy Environ. Sci.* 2022, *15* (1), 376–383.
- 57. House, R. A.; Marie, J.-J.; Pérez-Osorio, M. A.; Rees, G. J.; Boivin, E.; Bruce, P. G. The role of O<sub>2</sub> in O-redox cathodes for Li-ion batteries. *Nat. Energy* 2021, 6 (8), 781–789.
- Astuti, F.; Maghfirohtuzzoimah, V. L.; Intifadhah, S. H.; Az-Zahra, P.; Arifin, R.; Klysubun, W.; Zainuri, M. In Local structure and electronic structure of LiFePO<sub>4</sub> as a cathode for lithium-ion batteries, *J. Phys.: Conf. Ser. IOP Publishing:* 2021, p012007.
- Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-olivines as positiveelectrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* 1997, 144 (4), 1188.
- Orikasa, Y.; Maeda, T.; Koyama, Y.; Murayama, H.; Fukuda, K.; Tanida, H.; Arai, H.; Matsubara, E.; Uchimoto, Y.; Ogumi, Z. Transient phase change in two phase reaction between LiFePO<sub>4</sub> and FePO<sub>4</sub> under battery operation. *Chem. Mater.* 2013, 25 (7), 1032–1039.
- 61. Baukal, W. Über reaktionsmöglichkeiten in elektroden von festkörperbatterien.

*Electrochim. Acta* **1974**, *19* (11), 687–694.

- 62. Kennedy, J. H.; Miles, R. C. Ionic Conductivity of Doped Beta-Lead Fluoride. J. Electrochem. Soc. 1976, 123 (1), 47.
- 63. Schoonman, J. A solid-state galvanic cell with fluoride-conducting electrolytes. J. *Electrochem. Soc.***1976**, *123* (12), 1772.
- 64. Danto, Y.; Poujade, G.; Pistré, J.; Lucat, C.; Salardenne, J. A Pb|PbF<sub>2</sub>|BiF<sub>3</sub>|Bi thin solid film reversible galvanic cell. *Thin Solid Films* **1978**, *55* (3), 347–354.
- 65. Schoonman, J.; Wolfert, A. Alloy-anodes in fluoride solid-state batteries. J. *Electrochem. Soc.* **1981**, *128* (7), 1522–1523.
- 66. Schoonman, J.; Wolfert, A. Solid-state galvanic cells with fast fluoride conducting electrolytes. *Solid State Ionics* **1981**, *3*, 373–379.
- 67. Buchinskaya, I.; Teplyakova, T.; Sorokin, N.; Karimov, D. Composition Materials in the CaF<sub>2</sub>-BaF<sub>2</sub> System. *Crystallogr. Rep.* **2023**, *68* (2), 316–322.
- 68. Schoonman, A. R. a. J. ELECTRONIC CONDUCTIVITY IN  $La_{1-x}Ba_xF_{3-x}$  CRYSTALS. *Solid State lonics* **1984**, *13* (3), 205–211.
- 69. Sorokin, N. I.; Sobolev, B. P. Nonstoichiometric fluorides-Solid electrolytes for electrochemical devices: A review. *Crystallogr. Rep.* **2007**, *52* (5), 842–863.
- Wang, J.; Hao, J.; Duan, C.; Wang, X.; Wang, K.; Ma, C. A Fluoride-Ion-Conducting Solid Electrolyte with Both High Conductivity and Excellent Electrochemical Stability. *Small* 2022, *18* (5), e2104508.
- Tachibana, S.; Zhong, C.; Ide, K.; Yamasaki, H.; Tojigamori, T.; Miki, H.; Saito, T.; Kamiyama, T.; Shimoda, K.; Orikasa, Y. Fluorosulfide La<sub>2+x</sub>Sr<sub>1-x</sub>F<sub>4+x</sub>S<sub>2</sub> with a Triple-Fluorite Layer Enabling Interstitial Fluoride-Ion Conduction. *Chem. Mater.* 2023, *35* (11), 4235–4242.
- 72. Chable, J.; Dieudonne, B.; Body, M.; Legein, C.; Crosnier-Lopez, M.-P.; Galven, C.; Mauvy, F.; Durand, E.; Fourcade, S.; Sheptyakov, D. Fluoride solid electrolytes: investigation of the tysonite-type solid solutions La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> (x < 0.15). *Dalton Trans.* 2015, 44 (45), 19625–19635.

- Zhang, L. R.; Fichtner, M.; Maximilian, A. Development of tysonite-type fluoride conducting thin film electrolytes for fluoride ion batteries. *Solid State Ionics* 2015, *272*, 39–44.
- Rongeat, C.; Reddy, M. A; Witter, R.; Fichtner, M. Solid electrolytes for fluoride ion batteries: ionic conductivity in polycrystalline tysonite-type fluorides. *ACS Appl. Mater. Interfaces* 2014, 6 (3), 2103–2110.
- 75. Breuer, S.; Gombotz, M.; Pregartner, V.; Hanzu, I.; Wilkening, M. Heterogeneous F anion transport, local dynamics and electrochemical stability of nanocrystalline La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub>. *Energy Storage Mater.* **2019**, *16*, 481–490.
- 76. Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater*. 2013, 1 (1).
- 77. Grenier, A.; Porras-Gutierrez, A. G.; Body, M.; Legein, C.; Chrétien, F.; Raymundo-Piñero, E.; Dollé, M.; Groult, H.; Dambournet, D. Solid Fluoride Electrolytes and Their Composite with Carbon: Issues and Challenges for Rechargeable Solid State Fluoride-Ion Batteries. *J. Phys. Chem. C* 2017, *121* (45), 24962–24970.
- Wilkening, M.; Düvel, A.; Preishuber-Pflügl, F.; da Silva, K.; Breuer, S.; Šepelák, V.; Heitjans, P. Structure and ion dynamics of mechanosynthesized oxides and fluorides. *Z. Kristallogr. Cryst. Mater.* 2017, 232 (1-3), 107–127.
- Dieudonné, B.; Chable, J.; Body, M.; Legein, C.; Durand, E.; Mauvy, F.; Fourcade, S.;
   Leblanc, M.; Maisonneuve, V.; Demourgues, A. The key role of the composition and structural features in fluoride ion conductivity in tysonite Ce<sub>1-x</sub>Sr<sub>x</sub>F<sub>3-x</sub> solid solutions. *Dalton Trans.* 2017, *46* (11), 3761–3769.
- Bieudonné, B.; Chable, J.; Mauvy, F.; Fourcade, S.; Durand, E.; Lebraud, E.; Leblanc, M.; Legein, C.; Body, M.; Maisonneuve, V. Exploring the Sm<sub>1-x</sub>Ca<sub>x</sub>F<sub>3-x</sub> Tysonite Solid Solution as a Solid-State Electrolyte: Relationships between Structural Features and F–Ionic Conductivity. *J. Phys. Chem. C* 2015, *119* (45), 25170–25179.
- 81. Heise, M.; Scholz, G.; Düvel, A.; Heitjans, P.; Kemnitz, E. Mechanochemical synthesis,

structure, and properties of solid solutions of alkaline earth metal fluorides:  $Ma_{1-x}Mb_xF_2$ (M: Ca, Sr, Ba). *Solid State Sci.* **2016**, *60*, 65–74.

- Sobolev, B. P.; Sviridov, I. A.; Fadeeva, V. I.; Sul'yanov, S. N.; Sorokin, N. I.; Zhmurova, Z. I.; Herrero, P.; Landa-Canovas, A.; Rojas, R. M. Mechanochemical synthesis of nonstoichiometric fluorite Ca<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub> nanocrystals from CaF<sub>2</sub> and LaF<sub>3</sub> single crystals. *Crystallogr. Rep.* 2005, *50*, 478–485.
- 83. Preishuber-Pflügl, F.; Bottke, P.; Pregartner, V.; Bitschnau, B.; Wilkening, M. Correlated fluorine diffusion and ionic conduction in the nanocrystalline F<sup>-</sup> solid electrolyte Ba<sub>0.6</sub>La<sub>0.4</sub>F<sub>2.4</sub>—<sup>19</sup>F $T_{1(\rho)}$  NMR relaxation vs. conductivity measurements. *Phys. Chem. Chem. Phys.* **2014**, *16* (20), 9580–9590.
- Murakami, M.; Morita, Y.; Yonemura, M.; Shimoda, K.; Mori, M.; Koyama, Y.;
   Kawaguchi, T.; Fukuda, K.; Ishikawa, Y.; Kamiyama, T.; Uchimoto, Y.; Ogumi, Z. High
   Anionic Conductive Form of Pb<sub>x</sub>Sn<sub>2-x</sub>F<sub>4</sub>. *Chem. Mater.* 2019, *31* (18), 7704–7710.
- Zhang, D.; Nakaki, H.; Yamamoto, K.;Tanaka, K.; Yahara, T.; Imai, K.; Mori, T.; Miki, H.; Nakanishi, S.; Iba, H.; Watanabe, T.; Uchiyama, T.; Amezawa, K.; Uchimoto, Y. Rate-determining process at electrode/electrolyte interfaces for all-solid-state fluorideion batteries. *ACS Appl. Mater. Interfaces* 2021, *13* (25), 30198–30204.
- Clemens, O.; Kruk, R.; Patterson, E. A.; Loho, C.; Reitz, C.; Wright, A. J.; Knight, K. S.; Hahn, H.; Slater, P. R. Introducing a large polar tetragonal distortion into Ba-doped BiFeO<sub>3</sub> by low-temperature fluorination. *Inorg. Chem.* 2014, *53* (23), 12572–12583.
- Ahmad, M. M.; Yamane, Y.; Yamada, K. Structure, ionic conduction, and giant dielectric properties of mechanochemically synthesized BaSnF<sub>4</sub>. J. Appl. Phys. 2009, 106 (7).
- Fujisaki, F.; Mori, K.; Yonemura, M.; Ishikawa, Y.; Kamiyama, T.; Otomo, T.; Matsubara, E.; Fukunaga, T. Mechanical synthesis and structural properties of the fast fluoride-ion conductor PbSnF<sub>4</sub>. J. Solid State Chem. 2017, 253, 287–293.
- 89. Rongeat, C.; Reddy, M. A.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chemis. A* **2014**, *2* (48),

20861-20872.

- Nakano, H.; Matsunaga, T.; Mori, T.; Nakanishi, K.; Morita, Y.; Ide, K.; Okazaki, K.-i.;
   Orikasa, Y.; Minato, T.; Yamamoto, K.; Ogumi, Z.; Uchimoto, Y. Fluoride-Ion Shuttle Battery with High Volumetric Energy Density. *Chem. Mater.* 2020, *33* (1), 459–466.
- Mohammad, I.; Witter, R.; Fichtner, M.; Anji Reddy, M. Room-temperature, rechargeable solid-state fluoride-ion batteries. ACS Appl. Energy Mater. 2018, 1 (9), 4766–4775.
- 92. Nowroozi, M. A.; Clemens, O. Insights on the behavior of conversion-based anode materials for fluoride ion batteries by testing against an intercalation-based reference cathode. ACS Appl. Energy Mater. 2018, 1 (11), 6626–6637.
- Wissel, K.; Schoch, R.; Vogel, T.; Donzelli, M.; Matveeva, G.; Kolb, U.; Bauer, M.;
  Slater, P. R.; Clemens, O. Electrochemical reduction and oxidation of Ruddlesden–Popper-type La<sub>2</sub>NiO<sub>3</sub>F<sub>2</sub> within fluoride-ion batteries. *Chem. Mater.* 2021, 33 (2), 499–512.
- McTaggart, D.; Warren, S. C.; Clemens, O. Reconsidering Anode Materials for Fluoride-Ion Batteries-The Unexpected Roles of Carbide Formation. *ChemSusChem* 2023, e202300486.
- 95. Thieu, D. T.; Fawey, M. H.; Bhatia, H.; Diemant, T.; Chakravadhanula, V. S. K.; Behm,
  R. J.; Kübel, C.; Fichtner, M. CuF<sub>2</sub> as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* 2017, *27* (31), 1701051.
- 96. Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Amezawa, K.; Uchimoto, Y. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, 9 (1), 406–412.
- 97. Haruyama, J.; Okazaki, K. I.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji, T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. ACS Appl. Mater. Interfaces 2020,

12 (1), 428–435.

- Zhang, D.; Yoshinari, T.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Watanabe, T.; Uchiyama, T.; Orikasa, Y.; Amezawa, K.; Uchimoto, Y. Cu-Pb Nanocomposite Cathode Material toward Room-Temperature Cycling for All-Solid-State Fluoride-Ion Batteries. *ACS Appl. Energy Mater.* 2021, 4 (4), 3352–3357.
- 99. Yoshinari, T.; Zhang, D.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Matsunaga, T.; Amezawa, K.; Uchimoto, Y. Kinetic analysis and alloy designs for metal/metal fluorides toward high rate capability for all-solid-state fluoride-ion batteries. *J. Mater. Chem. A* 2021, *9* (11), 7018–7024.
- 100. Wang, Y.; Lee, S.; Yamamoto, K.; Matsunaga, T.; Miki, H.; Iba, H.; Tsuchiya, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Uchimoto, Y. Properties of Composite Electrodes for All-solid-state Fluoride-ion Secondary Batteries Processed by Highpressure Torsion. *Electrochem.* 2023, *91* (2), 027002.
- 101. Clemens, O.; Rongeat, C.; Reddy, M. A.; Giehr, A.; Fichtner, M.; Hahn, H. Electrochemical fluorination of perovskite type BaFeO<sub>2.5</sub>. *Dalton Trans.* 2014, 43 (42), 15771–8.
- 102. Bashian, N. H.; Zuba, M.; Irshad, A.; Becwar, S. M.; Vinckeviciute, J.; Rahim, W.; Griffith, K. J.; McClure, E. T.; Papp, J. K.; McCloskey, B. D. Electrochemical oxidative fluorination of an oxide perovskite. *Chem. Mater.* 2021, *33* (14), 5757–5768.
- McCabe, E. E.; Greaves, C. Fluorine insertion reactions into pre-formed metal oxides.
   J. Fluorine Chem. 2007, 128 (4), 448–458.
- Clemens, O.; Slater, P. R. Topochemical modifications of mixed metal oxide compounds by low-temperature fluorination routes. *Rev. Inorg. Chem.* 2013, 33 (2-3), 105–117.
- 105. Wissel, K.; Heldt, J.; Groszewicz, P. B.; Dasgupta, S.; Breitzke, H.; Donzelli, M.;Waidha, A. I.; Fortes, A. D.; Rohrer, J.; Slater, P. R; Buntkowsky, G.; Clemens, O.

Topochemical fluorination of  $La_2NiO_{4+d}$ : Unprecedented ordering of oxide and fluoride ions in  $La_2NiO_3F_2$ . *Inorg. Chem.* **2018**, *57* (11), 6549–6560.

- Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O. LaSrMnO4: Reversible Electrochemical Intercalation of Fluoride Ions in the Context of Fluoride Ion Batteries. *Chem. Mater.* 2017, *29* (8), 3441–3453.
- Aikens, L.; Gillie, L.; Li, R.; Greaves, C. Staged fluorine insertion into manganese oxides with Ruddlesden-Popper structures: LaSrMnO<sub>4</sub>F and La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>F. *J. Mater. Chem.* 2002, *12* (2), 264–267.
- Nowroozi, M. A.; de Laune, B.; Clemens, O. Reversible Electrochemical Intercalation and Deintercalation of Fluoride Ions into Host Lattices with Schafarzikite-Type Structure. *ChemistryOpen* 2018, 7 (8), 617–623.
- 109. Wells, A. F. Structural inorganic chemistry. Oxford Classic Texts in the Ph: 2012.
- Ishihara, T. Perovskite oxide for solid oxide fuel cells. Springer Science & Business Media: 2009.
- 111. Nowroozi, M. A.; Wissel, K.; Donzelli, M.; Hosseinpourkahvaz, N.; Plana-Ruiz, S.; Kolb, U.; Schoch, R.; Bauer, M.; Malik, A. M.; Rohrer, J.; Ivlev, S.; Kraus, F.; Clemens, O. High cycle life all-solid-state fluoride ion battery with La<sub>2</sub>NiO<sub>4+d</sub> high voltage cathode. *Commun. Mater.* 2020, *1* (1), 27.
- Aikens, L. D.; Li, R. K.; Greaves, C. The synthesis and structure of a new oxide fluoride, LaSrMnO<sub>4</sub>F, with staged fluorine insertion. *Chem. Commun.* 2000, (21), 2129–2130.
- 113. Nowroozi, M. A.; Ivlev, S.; Rohrer, J.; Clemens, O. La<sub>2</sub>CoO<sub>4</sub>: a new intercalation based cathode material for fluoride ion batteries with improved cycling stability. *J. Mater. Chem. A* 2018, 6 (11), 4658–4669.
- Wang, Y.; Yamamoto, K.; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; Cao, Z.; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion Substitution at Apical Sites of Ruddlesden-Popper-type Cathodes toward High Power Density for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2022, *34* (2), 609–616.

- Wang, Y.; Takami, T.; Li, Z.; Yamamoto, K.; Matsunaga, T.; Uchiyama, T.; Watanabe, T.; Miki, H.; Inoue, T.; Iba, H.; Mizutani, U.; Sato, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Oxyfluoride Cathode for All-Solid-State Fluoride-Ion Batteries with Small Volume Change Using Three-Dimensional Diffusion Paths. *Chem. Mater.* 2022, 34 (23), 10631–10638.
- Miki, H.; Yamamoto, K.; Nakaki, H.; Yoshinari, T.; Nakanishi, K.; Nakanishi, S.; Iba, H.; Miyawaki, J.; Harada, Y.; Kuwabara, A.; Wang, Y.; Watanabe, T.; Matsunaga, T.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Double-Layered Perovskite Oxyfluoride Cathodes with High Capacity Involving O–O Bond Formation for Fluoride-Ion Batteries. J. Am. Chem. Soc. 2024, 146 (6), 3844–3853.
- 117. Tsujimoto, Y.; Tassel, C.; Hayashi, N.; Watanabe, T.; Kageyama, H.; Yoshimura, K.; Takano, M.; Ceretti, M.; Ritter, C.; Paulus, W. Infinite-layer iron oxide with a squareplanar coordination. *Nature* 2007, 450 (7172), 1062–1065.
- 118. Lee, K. W.; Pickett, W. E. Infinite-layer LaNiO<sub>2</sub>: Ni<sup>1+</sup> is not Cu<sup>2+</sup>. *Phys. Rev. B* 2004, 70 (16), 165109.
- Wang, Y. Development of Iron-based Oxyfluoride Cathodes for High Energy Density All-Solid-State Fluoride-ion Batteries. 2023.
- Zhang, D. Study of Cu-based Cathode Materials for High-energy All-solid-state Fluoride-ion Batteries. 2022.
- 121. Cava, R. J.; Zandbergen, H.; Ramirez, A.; Takagi, H.; Chen, C.; Krajewski, J.; Peck Jr, W.; Waszczak, J. V.; Meigs, G.; Roth, R. S.; Schneemeyer, L. F. LaCuO<sub>2.5+x</sub> and YCuO<sub>2.5+x</sub> delafossites: materials with triangular Cu<sup>2+δ</sup> planes. *J. Solid State Chem.* 1993, 104 (2), 437–452.
- Shi, Q.; Zhou, J.; Ullah, S.; Yang, X.; Tokarska, K.; Trzebicka, B.; Ta, H. Q.; Rümmeli,
   M. H. A review of recent developments in Si/C composite materials for Li-ion batteries.
   *Energy Storage Mater.* 2021, *34*, 735–754.
- 123. Davis, V. K.; Bates, C. M.; Omichi, K.; Savoie, B. M.; Momčilović, N.; Xu, Q.; Wolf,W. J.; Webb, M. A.; Billings, K. J.; Chou, N. H. Room-temperature cycling of metal

fluoride electrodes: Liquid electrolytes for high-energy fluoride ion cells. *Science* **2018**, *362* (6419), 1144–1148.

- 124. Radin, M. D.; Vinckeviciute, J.; Seshadri, R.; Van der Ven, A. Manganese oxidation as the origin of the anomalous capacity of Mn-containing Li-excess cathode materials. *Nat. Energy* 2019, *4* (8), 639–646.
- Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vezin, H.; Sougrati, M. T.; Doublet, M. L.; Foix, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J. M. Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. *Nat. Mater.* 2013, *12* (9), 827–35.
- Saha, S.; Assat, G.; Sougrati, M. T.; Foix, D.; Li, H.; Vergnet, J.; Turi, S.; Ha, Y.; Yang, W.; Cabana, J.; Rousse, G.; Abakumov, A. M.; Tarascon, J.-M. Exploring the bottlenecks of anionic redox in Li-rich layered sulfides. *Nat. Energy* 2019, *4* (11), 977–987.
- 127. Wang, T.; Ren, G.; Shadike, Z.; Yue, J.; Cao, M.; Zhang, J.; Chen, M.; Yang, X.; Bak, S. M.; Northrup, P.; Liu, P.; Liu, X.; Fu, Z. Anionic redox reaction in layered NaCr<sub>2/3</sub>Ti<sub>1/3</sub>S<sub>2</sub> through electron holes formation and dimerization of S-S. *Nat. Commun.* 2019, *10* (1), 4458.
- 128. Hansen, C. J.; Zak, J. J.; Martinolich, A. J.; Ko, J. S.; Bashian, N. H.; Kaboudvand, F.; Van der Ven, A.; Melot, B. C.; Nelson Weker, J.; See, K. A. Multielectron, Cation and Anion Redox in Lithium-Rich Iron Sulfide Cathodes. *J. Am. Chem. Soc.* 2020, *142* (14), 6737–6749.
- 129. Maeda, K.; Takeiri, F.; Kobayashi, G.; Matsuishi, S.; Ogino, H.; Ida, S.; Mori, T.; Uchimoto, Y.; Tanabe, S.; Hasegawa, T.; Imanaka, N.; Kageyama, H. Recent Progress on Mixed-Anion Materials for Energy Applications. *Bull. Chem. Soc. Jpn.* 2022, 95 (1), 26–37.
- Kageyama, H.; Hayashi, K.; Maeda, K.; Attfield, J. P.; Hiroi, Z.; Rondinelli, J. M.;
   Poeppelmeier, K. R. Expanding frontiers in materials chemistry and physics with multiple anions. *Nat. Commun.* 2018, 9 (1), 772.

- Yoshinari, T.; Yamamoto, K.; Nishijima, M.; Fukuda, K.; Kuwabara, A.; Tanaka, I.; Maeda, K.; Kageyama, H.; Orikasa, Y.; Uchimoto, Y. High Rate Performance of Dual-Substituted LiFePO<sub>4</sub> Based on Controlling Metastable Intermediate Phase. *ACS Appl. Energy Mater.* 2018, *1* (12), 6736–6740.
- 132. Watanabe, A.; Yamamoto, K.; Uchiyama, T.; Matsunaga, T.; Hayashi, A.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Capacity improvement by nitrogen doping to lithium-rich cathode materials with stabilization effect of oxide ions redox. *ACS Appl. Energy Mater*.
  2020, 3 (5), 4162–4167.

# Chapter 2 High-Performance Copper/Copper Oxide-Based Cathode Prepared by a Facile Ball-Milling Method



Benefiting from the high theoretical volumetric energy density of the metal/metal fluorides ( $M/MF_x$ ) cathodes, all-solid-state fluoride-ion batteries (FIBs) are anticipated to be one of the next-generation energy storage devices. However,  $M/MF_x$ 

electrodes have low rate capability due to the large diffusion overpotential of fluoride ions because the reaction proceeds by a two-phase reaction mechanism between the metal M phase and the metal fluoride  $MF_x$  phase, which has significantly different lattice constants. To address this problem, uniformly distributed nanoparticles should be designed to shorten the diffusion pathway. Herein, we report a facile ball-milling method for preparing Cu-based cathode materials. Our findings reveal that as the ballmilling rotation speed increases, there is a significant decrease in the crystallite size of the solid electrolyte and a transformation of Cu oxides into metallic Cu, accompanied by an increase in crystallite size. Among the as-prepared cathode composites, a fine mixture of metallic Cu and Cu oxides with intermediate rotation speed (300 rpm) exhibits superior electrochemical performance, with a reversible capacity of 400 mAh g<sup>-1</sup>Cu2O after 20 cycles. Furthermore, it exhibits excellent rate capability by combining the high capacity of Cu with the satisfactory rate performance of Cu<sub>2</sub>O, achieving a capacity of 174 mAh  $g^{-1}_{Cu2O}$  at a current density of 550 mA  $g^{-1}_{Cu2O}$ , which is currently the highest reported for Cu-based cathode materials in FIBs. A charge compensation mechanism involving  $Cu^0/Cu^{2+}$  and  $Cu^+/Cu^{2+}$  redox reactions has been confirmed through electrochemical methods, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and Scanning transmission electron microscopy (STEM) measurements. The dominant factors affecting the impedance spectra of the as-prepared composites have also been investigated. It is believed that the cathode composites

prepared by a facile ball-milling method in this work will lead to a forward step in the application of all-solid-state FIBs.

## **2.1 Introduction**

Electric vehicles (EVs) are crucial for achieving carbon neutrality as they significantly reduce our carbon footprint and dependence on fossil fuels in transportation.<sup>1-4</sup> The EV industry has revolutionized over the past two decades, primarily due to the improved energy density of Lithium-ion batteries (LIBs).<sup>5, 6</sup> However, the long-term development of LIBs is restricted by the lower volumetric energy density, poor fast charging performance, as well as severe safety concerns.<sup>7–9</sup> To meet the burgeoning demands for high energy and power densities, batteries utilizing different kinds of charge carriers (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, etc.) have been proposed.<sup>10-18</sup> Among them, fluoride-ion batteries (FIBs), associated with the migration of monovalent fluoride ions with relatively small ionic radii, are expected to show superior potential for solid-state battery application.<sup>15, 19–23</sup> By using the multielectron reaction of metal/metal fluorides (M/MF<sub>x</sub>, M=Ni, Co, Cu, and Bi, etc.), FIBs can theoretically reach high energy density.<sup>22, 23</sup> Nevertheless, the rate capability of FIBs relying on conversion-type  $M/MF_x$  electrodes is not attractive due to the two-phase reaction mechanism occurring between the metal M phase and the metal fluoride  $MF_x$ phase with drastic volume expansion/contraction.<sup>22-25</sup> Fluoride ion migration at the distorted M/MF<sub>x</sub> interface is sluggish, and in many cases, the anion sublattice of MF<sub>x</sub> is so densely packed that there are no diffusion sites for fluoride ions.<sup>22–25</sup>

Previously, we have reported that Cu<sub>2</sub>O was utilized as a high-energy cathode material for all-solid-state FIBs.<sup>26</sup> The non-close-packed Cu–O configuration can exert important effects on fast (de)fluorination, which results in reasonable rate capabilities. Furthermore, the fluoride ion intercalation into Cu<sub>2</sub>O lattice was believed to induce a local mix-anion configuration (Cu–O/F) and lead to enhanced fluoride ion diffusion as well as (de)fluorination reactions.<sup>27</sup> However, limited by the valence state of Cu (I), the theoretical capacity of Cu<sub>2</sub>O was only 375 mAh g<sup>-1</sup> (2 fluoride ions insertion) and it exhibited a reversible capacity of only 131 mAh g<sup>-1</sup> due to the narrow electrochemical

window of solid electrolyte PbSnF<sub>4</sub>, which still has room for further improvement.

Here in, we introduce a series of Cu-based cathode materials for all-solid-state FIBs which were prepared by a facile ball-milling method. Cu<sub>2</sub>O nano powder, solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (LBF), and vapor grown carbon fiber (VGCF) were used as the starting materials, and the active material gradually transformed into metallic Cu with the increase of ball-milling rotation speed. By optimizing the ball-milling conditions, we obtained a hybrid Cu and Cu oxide cathode composite. The cathode composite has a much better rate performance than metallic Cu cathodes and higher capacity than Cu oxide alone due to the presence of nano-dispersed Cu and Cu oxide particles. The charge compensation mechanism was revealed by XRD, XAS, and STEM measurements. Moreover, we discussed the ionic conductivities at different ball-milling rotation speeds by analyzing STEM, XRD, XAS, X-ray computed tomography (CT) and Electrochemical impedance spectroscopy (EIS) results. To the best of our knowledge, the extraordinary rate capability of this ball-milled cathode composite using bulk-type cells seems to be one of the best among Cu-based cathode materials studied in FIBs.

## 2.2 Experimental

#### 2.2.1 Material preparation

Solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (LBF) was prepared by a typical solid-state reaction.<sup>15</sup> A stoichiometric amount of LaF<sub>3</sub> (99.9%, Kojundo) and BaF<sub>2</sub> (99.9%, Kojundo) were mixed and milled by a planetary ball mill (Fritsch Pulverisette7 premium line, Germany) using  $\varphi$ 10 mm ZrO<sub>2</sub> balls at 600 rpm for 12 h, the mixture was then pelletized and annealed at 1000°C for 4 h under Ar atmosphere. The cathode composites were obtained by mixing commercial Cu<sub>2</sub>O nano powder (US Research Nanomaterials, USA) with the solid electrolyte LBF and vapor grown carbon fiber (VGCF, Showa Denko, Japan) in a weight ratio of 25: 70: 5 by ball-milling using a 45

ml ZrO<sub>2</sub> pot and  $\varphi$ 2 mm ZrO<sub>2</sub> balls. The mass ratio of the cathode composite to the ZrO<sub>2</sub> ball was 1:50, and various ball-milling rotation speeds (100, 200, 300, 400, 500, and 600 rpm) were used to prepare different cathode composites. The cathode composites subjected to different ball-milling rotation speeds are hereafter referred to as BM-100, 200, 300, 400, 500, and 600. Similarly, the anode composite was obtained by mixing PbF<sub>2</sub> (99.9%, Kojundo), LBF, and VGCF by ball-milling for 10 h under a rotation speed of 300 rpm. Some Pb powder was added and mixed by an agate pestle and mortar after ball-milling, and the mass ratio of the anode composite was PbF<sub>2</sub>/Pb/LBF/VGCF = 3: 2: 4: 1.

#### 2.2.2 Electrochemical measurements

Electrochemical tests were carried out on bulk-type cells (**Figure 2.1**).<sup>26</sup> 150 mg LBF powder was put into a poly(ether-ether-ketone) (PEEK) insulator (10 mm diameter) and pressed under a pressure of 100 MPa for 5 min. Then, the cathode composite and the anode composite and current collectors were placed on the opposite sides of the LBF pellet. Finally, the cell was compressed under a pressure of 360 MPa for 5 min. The ionic conductivities of the cathode composites synthesized at various ball-milling rotation speeds were measured by using an electron-blocking cell. The as-prepared cathode composite was placed into the PEEK insulator and pressed under a pressure of 100 MPa for 5 min. LBF powder as well as current collectors were then placed on the opposite side of the composite pellet and pressed under a pressure of 180 MPa for 5 min. All the assembling processes were carried out in an argon-filled glove box with oxygen and moisture contents less than 0.2 ppm.

The galvanostatic charge-discharge tests were evaluated by HJ1020mSD8 battery testing systems (Hokuto Denko, Japan) at 140 °C without exposure to air. Based on the previous research on Cu redox species,<sup>26, 28</sup> a voltage range of –0.3 to 1.5 V (vs. Pb/PbF<sub>2</sub>) was selected for galvanostatic charge–discharge measurements. Electrochemical impedance spectra (EIS) were obtained by using a High-frequency Impedance Analyzer

E4990A (KEYSIGHT, USA) with an amplitude of 10 mV and frequency range of 100 MHz to 20 Hz at 140 °C under vacuum condition. The ionic conductivity of LBF solid electrolyte was evaluated by electrochemical impedance spectroscopy (EIS) via a Solartron analytical Modulab XM ECS electrochemical test system within the frequency range of  $10^6$  to  $10^{-1}$  Hz and an amplitude voltage of 50 mV at 25, 50, 75, 100, 125, and 140 °C. The activation energy (*E*<sub>a</sub>) was calculated by the Arrhenius equation:<sup>29</sup>

$$\sigma = A e^{\frac{-E_a}{k_B T}} \tag{2-1}$$

where  $\sigma$ , A,  $E_a$ ,  $k_B$ , and T are the ionic conductivity, pre-exponential factor, activation energy, Boltzmann constant, and temperature (K), respectively. Activation energy  $E_a$ can be determined by linear fitting of log  $\sigma$  vs.  $T^{-1}$ , according to the rearranged Equation (2–1):

$$\log \sigma = -\frac{E_a}{2.30259k_B} \cdot \frac{1}{T} + \log A$$
 (2-2)

The measurement data were fitted by using the ZView4 software. **Figure 2.2** shows the EIS results and the calculated ionic conductivities using Arrhenius models. LBF exhibited a reasonable ionic conductivity of  $\sim 8.7 \times 10^{-4}$  S cm<sup>-1</sup> with an activation energy of 0.516 eV at 140 °C, which was similar to the values in previous researches.<sup>30, 31</sup> The solid electrolyte LBF can offer an extensive electrochemical stability window exceeding 5 V, facilitating a comprehensive assessment of the electrochemical properties of the as-prepared cathode composites from a broad voltage range.<sup>32</sup>

## 2.2.3 Characterization

X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Rigaku Ultima IV, Japan) with Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å). Synchrotron X-ray powder diffraction patterns were measured at the BL02B2 beamline in SPring-8 (Hyogo, Japan) with a wavelength of 0.41391 Å, which was calibrated by using CeO<sub>2</sub>.

The morphology of the as-purchased Cu<sub>2</sub>O and the as-prepared cathode composites were characterized using a SU6600 scanning electron microscope (SEM, Hitachi, Japan). Scanning transmission electron microscopy (STEM) measurements with the aid of energy-dispersive X-ray spectroscopy (EDS) and selective area electron diffraction (SAED) measurements were conducted by using a JEM-ARM200F Monochromated Atomic Resolution Analytical Electron Microscope (JEOL, Japan). Synchrotron X-ray computed tomography (CT) was carried out at the BL20XU beamline in SPring-8, the tortuosity factors were calculated using an open-source application 'Taufactor' in MATLAB. X-ray absorption spectroscopy (XAS) measurements for Cu *K*-edge, Cu  $L_{2,3}$ -edge, and F *K*-edge were carried out at the BL14B2 and BL27SU beamlines in SPring-8, respectively. The measurements were conducted under vacuum condition. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) results were analyzed by using the ATHENA software package.<sup>33</sup>

## 2.3 Results and Discussion

#### 2.3.1 Phase, composition, and morphology

The crystal structures of the cathode composites prepared at different ball-milling rotation speeds were characterized by synchrotron XRD, as shown in **Figure 2.3a**. As evident from Figure 2.3a, the cathode composition changed as the ball-milling rotation speed increased. In the BM-100 composite, although almost all peaks were indexed to Cu<sub>2</sub>O (space group:  $Pn\bar{3}m$ ) and La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (space group:  $P\bar{3}c1$ ), there was a broad peak around 9.39° (101) that could be due to CuO (space group: P42/mmc), as shown in Figure 2.3b. As the rotation speed of the ball mill increased, the peaks attributed to LBF were broadened significantly up to 300 rpm (BM-300) and then were broadened slightly with further increase of the ball milling speed. This suggests that the crystallinity of LBF decreased with increased ball milling rotation speed as the rotation speed increased as the rotation speed increased from 100 rpm (BM-100) to 200 rpm (BM-200). However, it was decreased

as the rotation speed increased from 200 rpm (BM-200) to 300 rpm (BM-300), while new peaks indexed to Cu (space group:  $Fm\overline{3}m$ ) appeared around 11.36° (111), 13.15° (200), and 18.68° (220). Thereafter, the intensity of the Cu-derived peaks increased as the rotation increased from 300 rpm (BM-300) to 600 rpm (BM-600). These results mean that the starting material, including mainly Cu<sub>2</sub>O was reduced more to metallic Cu with an increase in the rotation speed of ball milling. The lattice parameters a and c of the LBF were calculated by Le bail refinement (**Table 2.1**). The lattice constants remained unchanged after the ball-milling process, indicating that the active materials and LBF did not react with each other.

To evaluate the effect of ball-milling rotation speeds on the crystallite sizes of LBF and Cu in the as-prepared cathode composites, Scherrer equation was applied to the LBF 111 peak and Cu 113 peak (Figure 2.3c, **Table 2.2**, and **Table 2.3**). The crystallite size of LBF drastically decreased from 39.9 nm to 9.2 nm from BM-100 to BM-300 and it was slightly reduced in BM-400, 500, and 600 (8.5, 8.3, and 7.2 nm, respectively). On the contrary, the diffraction peaks of Cu first appeared in BM-300, then the crystallite size gradually increased from 8.4 nm to 14.1 nm with the increase of ball-milling speed from 300 rpm (BM-300) to 600 rpm (BM-600). This signified the reduction in the crystallinity of solid electrolyte LBF and the increase in the crystallinity of metallic Cu during the ball-milling process.

It was observed in XRD results that the composition of the cathode composites varied with the increase in the ball-milling rotation speed. The ratio of metallic Cu and Cu oxides was examined by soft-XAS technique and linear combination fitting (Figure 2.3d, **Figure 2.4**, and **Table 2.4**). The as-purchased Cu<sub>2</sub>O showed characteristic peaks at 931.2 and 933.5 eV.<sup>26</sup> Compared to the as-purchased Cu<sub>2</sub>O, the intensity of the peak at 931.2 eV was increased for the BM-100 cathode composite. The energy of the peak corresponded to that of CuO, indicating that the active material was partially oxidized during the low-speed ball-milling process. Then increasing the ball-milling speed from 100 rpm to 600 rpm, the intensity of the peak at 931.2 eV was decreased while the peak

around 933.5 eV was broadened and a new peak appeared around 937 eV. These peak shapes and energy positions corresponded to Cu metal, indicating that the active material was reduced during the high-speed ball-milling process. To evaluate the ratio of copper oxide and copper metal in the active material with different ball-milling speeds, linear combination fitting was performed for the Cu *L*-edge spectra (Figure 2.4). The ratio of CuO in the active material was increased by ball-milling with 100 rpm, compared to as-purchased Cu<sub>2</sub>O. However, a further increase in the ball milling speed > 100 rpm, decreased the ratio of copper oxide, including Cu<sub>2</sub>O and CuO, while increasing the ratio of copper metal in the active material. In the case of BM-400, BM-500, and 600, the ratio of copper oxides was negligible against Cu metal. However, as the spectra of composites cannot be fitted with only the Cu spectrum, they may include some copper species, which were different from copper metal.

The electronic structures of the as-prepared cathode composites, as well as the coordination of Cu atoms, were also examined by Cu K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), as shown in **Figure 2.5**. The edge position, which was defined as the maximum point of the first derivative function of the absorption edge vs. energy, were 8978.5 and 8980.1 eV for Cu foil and Cu<sub>2</sub>O references. The plot of absorption energy vs. ball milling rotation speed (Figure 2.5c) revealed that the average valence state of Cu was between Cu<sup>0</sup> and Cu<sup>+</sup> in BM-300.<sup>34</sup> With the increase of ball-milling rotation speed, a clear tendency of transformation from Cu oxides to metallic Cu can be observed in Cu Kedge XANES (Figure 2.5a). The radial distribution functions of the EXAFS for the BM-100 and BM-200 showed a similar shape to that of Cu oxides, however, a new peak corresponded to Cu-Cu interaction emerged from BM-300 (Figure 2.5d). For the BM-300, there were two peaks representing Cu-O and Cu-Cu interactions in Cu K-edge EXAFS, indicating it a mixture of metallic Cu and Cu oxides. In the cases of BM-400, BM-500, and BM-600, the radial distribution functions were very similar to that of the Cu-foil reference. The XAS results indicated that the starting Cu<sub>2</sub>O was oxidized with low-speed ball milling and then was reduced to Cu metal with high-speed ball milling, in agreement with the XRD results.

The morphologies of the as-prepared cathode composites were analyzed by STEM-EDS measurements, as shown in Figure 2.6. The primary particle size of the as-purchased Cu<sub>2</sub>O nanoparticle was about 200 nm (Figure 2.7). The primary particle sizes of the Cu-based active material and solid electrolyte decreased with increasing the ball milling speed up to 300 rpm, and the primary particle size of the Cu-based active material was less than 20 nm in BM-300 (Figure 2.6c). On the other hand, the primary particle size of the Cu-based active material became larger with increasing the ballmilling rotation speed up to 600 rpm. The primary particle size of the Cu-based active material was larger than 50 nm in BM-600 (Figure 2.6f). Besides, the particle size of solid electrolyte LBF decreased with the increase of ball-milling rotation speed, it was about 500 nm at 100 rpm but decreased to less than 100 nm at high rotation speed (400 to 600 rpm). The tendency of the primary particle size change was consistent with the XRD results. Furthermore, the particle size distributions of the as-prepared cathode composites were obtained from SEM images, as shown in Figure 2.8. The average particle size diminished from BM-100 to BM-300, whereas the tiny primary particles agglomerated into larger secondary particles under strong ball milling conditions (BM-400 to BM-600). The combined insights from XRD, XAS, and microscopy suggested that Cu<sub>2</sub>O was chemically transformed into metallic Cu by the ball-milling process, and the average particle size increased with the increment of ball milling rotation speed (400 to 600 rpm).

In order to clarify the morphology of the cathode composites in the pressed cells, SEM-EDS and X-ray CT were carried out on the as-prepared cathode composites after compressing them into pellets. As shown in the SEM-EDS mapping images (**Figure 2.9**), Cu and La were evenly distributed in BM-100, 200, 300, and 400. However, Cu nanoparticles agglomerated to form secondary particles of about  $1-2 \mu m$  under strong

ball milling conditions (Figure 2.9e–f), and there was no solid electrolyte distribution in Cu areas.

In our previous research, we have proved that a non-close-packed Cu<sub>2</sub>O configuration showed enhanced ion transport than a close-packed Cu bulk.<sup>26</sup> The ionic conductivities of the as-prepared cathode composites were supposed to be different since the ratio of metallic Cu to Cu oxides varies significantly. The electrochemical impedance spectroscopies (EIS) of the as-prepared cathode composites were evaluated by using an electron-blocking cell. As shown in the Nyquist plots for the as-prepared cathode composites (**Figure 2.10b**), the high-frequency semicircle could be assigned to grain-boundary resistance of the solid electrolyte since the fitted capacitance values of this semicircle in each spectrum were in the range of 10<sup>-11</sup> to 10<sup>-8</sup> F (**Table 2.5**).<sup>35</sup> However, according to previous research, the semicircle corresponding to bulk resistance should appear in the high-frequency region, as we measured up to 100 MHz.<sup>35</sup> We considered that the bulk resistance was likely to overlap with the semicircle of the grain boundary impedance, and here we treated the grain boundary impedance as the apparent grain boundary impedance.

**Figure 2.11** shows the apparent ionic conductivity of the as-prepared cathode composites. The ionic conductivity gradually decreased from BM-100 to BM-300 whereas it rapidly decreased from BM-300 to BM-400, and then gradually decreased from BM-400 to BM-600. The gradual decrease of the ionic conductivity from BM-100 to BM-300 was caused by the decrease in crystallinity of LBF (Figure 2.3c) and the decrease of the copper oxide amount (Figure 2.4g). The ionic conductivity of LBF was decreased with a decrease in the crystallite size.<sup>36</sup> Moreover, because the tetrahedral sites in Cu-fcc sub-lattice in Cu<sub>2</sub>O could become diffusion channels for fluoride ions,<sup>26</sup> whereas the fluoride ion diffusion pathway was blocked due to the close-packed structure of Cu lattice,<sup>24, 25</sup> the decrease of the copper oxide amount should decrease the ionic conductivity. The rapid decrease of the ionic conductivity from BM-300 to BM-400 was caused by the absence the copper oxide, which was

confirmed by XAS (Figure 2.4). Additionally, the decrease in ionic conductivity observed from BM-400 to BM-600 can be attributed to the increasing tortuosity of the solid electrolyte LBF. As shown in the 3D reconstruction images of BM-400, 500, and 600 (**Figure 2.12a–c**), the secondary particle size of the active material became larger with the increment of ball milling rotation speed, which increased the tortuosity factor of the solid electrolyte from 1.01 to 1.23 (Figure 2.12d).

#### 2.3.2 Electrochemistry

For the galvanostatic charge–discharge measurements of the as-prepared cathode composites, Pb/PbF<sub>2</sub> composite was chosen as the anode material, mainly because of its remarkable intrinsic conductivity,<sup>37, 38</sup> which helped to evaluate the electrochemical performance on cathode more accurately. In some cases of utilizing Pb/PbF<sub>2</sub> as anode, the discharge cutoff voltage can be negative, which was also called "forced discharge" by Clemens et al.<sup>39</sup> In order to obtain more reversible capacity, a voltage range of -0.3 to 1.5 V against Pb/PbF<sub>2</sub> was employed in this study. The as-prepared cathode composites exhibited reversible capacity after several cycles and different charging behaviors depending on their composition (**Figure 2.13**).

The BM-100 composite during the 20th cycle showed a voltage plateau at 1.2 V (Figure 2.13b). When the rotation speed was increased from 100 rpm to 300 rpm, a new plateau appeared at approximately 0.8 V in addition to 1.2 V, as shown in the dQ/dV curve of BM-300 during the 1st charge process in **Figure 2.14**, and the 0.8 V plateau became longer and the charging capacity increased with the rotation speed increased. On the other hand, the capacity decreased when the rotation speed was further increased from 300 rpm to 600 rpm, especially above 400 rpm, the capacity decreased significantly with large polarization. As a result, BM-300 composite showed the highest charge/discharge capacity (387/384 mAh  $g^{-1}$ ) after the 20th cycle (Figure 2.13c). Furthermore, BM-300 exhibited the highest discharge capacity with high current density (174 mAh  $g^{-1}$  at a current density of 550 mA  $g^{-1}$  cu20, as shown in Figure 2.13d).

As similar voltage plateaus at 0.8 V and 1.2 V were observed in Cu thin film and copper oxide cathodes (**Figure 2.15**),<sup>22, 26</sup> each voltage plateau observed in the ball-milled composites is related to a redox of copper metal and a redox of copper oxide. These results were in agreement with the transition from copper oxide to metallic copper, which was confirmed by XRD and XAFS. Although BM-100 and BM-200 showed relatively high ionic conductivity, their low capacities were due to the absence of Cu, while BM-300 showed the highest capacity due to its relatively high ionic conductivity and the presence of Cu metal with a small crystallite size. Compared to BM-300, BM-400, 500, and 600 showed lower ionic conductivity and larger Cu crystallite size, resulting in larger polarization and lower capacity.

#### 2.3.4 Charge compensation mechanisms

According to the abovementioned results, as the BM-300 cathode composite showed the best electrochemical performance, we focused on clarifying the detail of the reaction mechanism for the BM-300 cathode composite. The electronic and local structural changes during charge/discharge were examined by using XAS (Figure 2.16). In the Cu L<sub>2,3</sub>-edge XAS (Figure 2.16b), although the peaks attributed to Cu<sub>2</sub>O and Cu were observed at 933.5 eV and 937.4 eV at pristine state, the intensity of these peaks was decreased while a new peak appeared and the peak intensity was increased during charging. This peak energy corresponded to the peak energy of CuF<sub>2</sub>, indicating the Cu species in the BM-300 composite was oxidized to Cu<sup>2+</sup>. The shape of the spectrum after full discharge recovered to the pristine state, proving the reversibility of the Cu redox reactions. In the F K-edge XAS results (Figure 2.16e), all the samples showed similar absorption edges ( $\geq$  687 eV) which corresponded to the fluorine in LBF solid electrolyte. A pre-edge peak appeared at approximately 684 eV and gradually increased upon charging, which was associated with the F 2p-Cu 3d hybridization, as was observed in the CuF<sub>2</sub> reference.<sup>40</sup> This indicated that the Cu species in the BM-300 composite formed Cu-F bonds after charging. The shape of the spectrum after full discharge

recovered to the pristine state, proving the reversibility of the Cu fluorination/defluorination reactions.

Furthermore, according to the linear combination fitting results in **Figure 2.17**, the weight ratio of Cu and Cu<sub>2</sub>O at the 1st fully charged state were 9% and 0%, respectively. Based on the change in weight ratio of the active materials from the pristine to fully charged state, the capacities were deduced to be approximately 500 mAh g<sup>-1</sup> for Cu and 62 mAh g<sup>-1</sup> for Cu<sub>2</sub>O. The estimated values agreed with the electrochemical measurement result. These results indicate that the remaining Cu<sub>2</sub>O in the BM-300 sample is electrochemically active.

In the Cu *K*-edge XANES (Figure 2.16c), the absorption peak, which was assigned to  $1s \rightarrow 4p$  transition, was observed at ~8981 eV for BM-300 at pristine state. The intensity of this peak gradually decreased upon charging, then at the fully charged state, a very small pre-edge peak appeared at ~8977 eV and the shape of the spectrum became almost similar to that of the CuF<sub>2</sub> spectrum. This pre-edge peak corresponded to  $1s \rightarrow 3d$  transition, serving as a signature of Cu<sup>2+</sup> species. Because it cannot be observed in Cu<sup>0</sup> and Cu<sup>+</sup> compounds due to their fully occupied 3d orbitals.<sup>26, 34, 41</sup> This XANES change indicated that Cu species in the BM-300 composite was oxidized to Cu<sup>2+</sup>. After discharging, the pre-edge peak corresponded to Cu<sup>2+</sup> disappeared and the shape of the Cu *K*-edge XANES recovered to the pristine state, proving the reversibility of the Cu redox reactions.

To clarify the local structural change during charge/discharge, the radial distribution functions of the Cu *K*-edge EXAFS for BM-300 cathode composite were obtained, as shown in Figure 2.16d. The peaks attributed to Cu–O and Cu–Cu coordination were observed at 1.5 Å and 2.2 Å at pristine state. Upon the 1st charging process, the peak corresponded to Cu–Cu coordination gradually decreased and the intensity of the peak at 1.5 Å increased. As this peak corresponded to the Cu–F of CuF<sub>2</sub> as well as the Cu–O of Cu<sub>2</sub>O, the increasing peak intensity indicated that Cu–F bonding was formed upon charging.<sup>26</sup> This result was in agreement with Cu *L*-edge, F *K*-edge,

and Cu *K*-edge XANES results. After discharging, the peaks attributed to Cu–O and Cu–Cu coordination were recovered as the pristine state, proving the reversibility of the local structure of the BM-300.

To further examine the crystal structure of the BM-300 cathode composite after charging, STEM-EDS and TEM observations were performed. **Figure 2.18a** shows the STEM image and the corresponding EDS mappings of the BM-300 cathode composite. The EDS mappings signified that the solid electrolyte LBF and active material were uniformly distributed after fully charging. TEM analysis was further applied to provide an insight into the crystal structure in the red square region in Figure 2.18a (Figure 2.18b). Two areas were selected from Figure 2.18b for fast Fourier transform (FFT) and inverse fast Fourier transform (IFFT), which are displayed in Figure 2.18d–g. After fully charging, a well-defined crystalline structure of monoclinic CuF<sub>2</sub> can be observed from the FFT and IFFT (Figure 2.18d–e). Moreover, solid electrolyte LBF (La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>) was observed to present with good crystallinity and was uniformly mixed with the active material (Figure 2.18f–g). The observation of CuF<sub>2</sub> corresponded to the XAS results. Moreover, the uniform mixture of the active material and LBF showed a reasonable ionic pathway and electrode-electrolyte interface in the BM-300 cathode composite, leading to one of the reasons for excellent rate capability.

From the abovementioned results, a cathode composite possessing a well-suited metallic Cu/Cu oxides ratio can exhibit remarkable rate capability, which can be achieved by straightforwardly modifying the ball-milling conditions; we believe that this study offers a significant perspective on the utilization of Cu-based cathode materials in FIBs.

## 2.4 Conclusions

In this study, we applied a facile ball-milling process to prepare metallic Cu/Cu oxides-based cathode composites for all-solid-state FIBs and examined their electrochemical properties and reaction compensation mechanism. Cu<sub>2</sub>O was used as

starting material and was transformed into metallic Cu as the ball-milling rotation speed increased. The in-situ generated metallic Cu provided significant capacity. However, the high ball-milling rotation speed significantly increased the particle size of Cu, making a larger tortuosity of the solid electrolyte, which in turn resulted in large grain boundary resistance. The BM-300 composite with a suitable metallic Cu/Cu oxides ratio exhibited a reasonable initial capacity (532/487 mAh g<sup>-1</sup> for charging/discharging), good cycling stability (384 mAh g<sup>-1</sup> after 20 cycles), and excellent rate capability (174 mAh g<sup>-1</sup> at a current density of 550 mAh g<sup>-1</sup>cu<sub>20</sub>). The excellent rate performance of the BM-300 composite was attributed to the Cu<sub>2</sub>O component, which has been demonstrated in our previous research to have good rate capability and a better cycling performance than metallic Cu. The cathode composite prepared by a facile ball-milling process using Cu<sub>2</sub>O as starting material represented a significant advancement over previous researches. We believe that the ball-milling method, as a facile process for electrode preparation, holds immense potential for broader applications in the development of high-performance all-solid-state FIBs.



Figure 2.1 Illustration of bulk-type cells used for evaluation of cathode the as-prepared cathode

composites.



Figure 2.2 (a) Nyquist plots of LBF at temperatures of 25, 50, 75, 100, 125, and 140 °C, respectively. (b) Corresponding linear fitting using Arrhenius models.



Figure 2.3 (a) Synchrotron XRD patterns of as-prepared cathode composites. (b) An enlarged view of 2θ = 8.75–10.25° of the XRD patterns, a broad pattern ascribed to 101 diffraction peak of CuO can be found in BM-100 and BM-200. (c) Crystallite sizes of La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> and Cu in the cathode composites with different ball-milling rotation speeds. The crystalline sizes of La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> and Cu are calculated by the La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> [111] and Cu [113] peaks using Scherrer's equation. (d) Cu *L*-edge X-ray absorption spectroscopy of the as-prepared cathode composites. Cu, Cu<sub>2</sub>O, and CuO are provided as references.

Sample	<i>a</i> / Å	<i>c</i> / Å	V / Å <sup>3</sup>
BM-100	7.244(8)	7.411(9)	336.84
BM-200	7.249(9)	7.407(4)	337.11
BM-300	7.248(2)	7.419(4)	337.56
BM-400	7.240(7)	7.412(0)	336.56
BM-500	7.250(4)	7.412(7)	337.43
BM-600	7.241(2)	7.408(6)	336.44

**Table 2.1** The lattice parameters of the solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> in the as-prepared cathode composites obtained via Le bail refinement.

**Table 2.2** The fitted Full Width at Half Maximum (FWHM) of LBF 111 diffractionpeak and the calculated crystallite size.

Sample	FWHM / LBF111	2 <i>θ</i> / °	Crystallite / nm
BM-100	0.053(2)	7.289	39.9
BM-200	0.077(8)	7.290	27.5
BM-300	0.231(8)	7.291	9.2
BM-400	0.248(7)	7.286	8.5
BM-500	0.255(7)	7.296	8.3
BM-600	0.294(9)	7.290	7.2
Sample	FWHM / Cu113	2 <i>θ</i> / °	Crystallite / nm
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BM-300	0.257(6)	21.844	8.4
BM-400	0.192(4)	21.848	11.2
BM-500	0.167(8)	21.841	12.9
BM-600	0.152(8)	21.846	14.1

**Table 2.3** The fitted Full Width at Half Maximum (FWHM) of Cu 113 diffractionpeak and the calculated crystallite size.

 Table 2.4 Weight ratio obtained from XAS linear combination fitting of the as 

 prepared cathode composites.

Cu / %	Cu2O/ %	CuO / %
0	67	33
6.8	90.5	2.7
84.6	9.2	6.2
100	0	0
100	0	0
100	0	0
	Cu / % 0 6.8 84.6 100 100 100	Cu / %       Cu2O/ %         0       67         6.8       90.5         84.6       9.2         100       0         100       0         100       0         100       0



Figure 2.4 (a)–(f) Linear combination fitting of Cu *L*-edge XAS results for the BM-100, 200, 300, 400, 500, and 600 cathode composites. (g) Weight ratio obtained from XAS linear combination fitting of the as-prepared cathode composites and the as-purchased Cu<sub>2</sub>O.



**Figure 2.5** (a) Cu *K*-edge XANES for the as-prepared cathode composites. (b) Cu *K*-edge XANES for the BM-300 composite. (c) The edge positions of the as-prepared cathode composites. (d)  $k_3$ -Weighted Fourier transformation magnitudes of Cu *K*-edge EXAFS. Cu foil, as-purchased Cu<sub>2</sub>O,

and CuO are provided as references.



**Figure 2.6** Scanning transmission electron microscopy (STEM) images and elemental distributions of La, Ba, F, and Cu from EDS mapping of as-prepared cathode composites. (a)–(f) as-prepared BM-100, 200, 300, 400, 500, and 600 cathode composites, respectively.



Figure 2.7 SEM image of as-purchased Cu<sub>2</sub>O nanopowder.



**Figure 2.8** SEM images and related particle size distributions for as-prepared cathode composites. (a)–(f) as-prepared BM-100, 200, 300, 400, 500, and 600 cathode composites, respectively.



**Figure 2.9** SEM-EDS images of the as-prepared cathode composites after pressing them into pellets. (a)–(f) as-prepared BM-100, 200, 300, 400, 500, and 600 cathode composites,

respectively.



Figure 2.10 (a) The equivalent circuit used for the EIS fitting. (b) Nyquist plots at 140 °C for the as-prepared cathode composites.

Samples	$R_{gb}$ / $\Omega$	CPE <sub>gb</sub> -T	CPE <sub>gb</sub> -P	W <sub>s</sub> -R	Ws-T	W <sub>s</sub> -P	Capacitance <sub>gb</sub> / F
BM-100	288	8.28E-9	0.7700	55690	0.1001	0.8052	1.73E-10
BM-200	340	1.12E-8	0.7500	27258	0.0632	0.7277	1.75E-10
BM-300	419	1.07E-8	0.7197	14542	0.0832	0.6210	8.91E-11
BM-400	805	5.11E-9	0.7109	8399	0.0411	0.6016	3.29E-11
BM-500	1234	8.76E-10	0.8026	15015	0.0758	0.5741	2.98E-11
BM-600	1433	4.47E-9	0.7070	41483	0.0838	0.7389	3.15E-11

 Table 2.5 The fitting parameters of the EIS results of the as-prepared cathode materials with different ball-milling rotation numbers.



**Figure 2.11** Plots for the ionic conductivity of the apparent grain boundary in the cathode composites against ball-milling rotation speed measured at 140°C.



**Figure 2.12** X-ray computed tomography (CT) results of the as-prepared cathode composites. (a) BM-400, (b) BM-500, (c) BM-600; (d) Tortuosity factors of the abovementioned samples.



Figure 2.13 (a) Charge/discharge profiles of as-prepared cathode composites upon the 1st cycle.
(b) Charge/discharge profiles of as-prepared cathode composites upon the 20th cycle. (c) Cycle performance of the as-prepared cathode composites. (d) Capacity at various current densities of BM-100, 200, and 300, 400, and 500 cathode composites. The current density was 11 mA g<sup>-1</sup><sub>Cu20</sub>, and the voltage range was -0.3 to 1.5 V against Pb/PbF<sub>2</sub>.



Figure 2.14 dQ/dV curve of BM-300 during the 1st charge process.



Figure 2.15 Charge/discharge profiles upon the 1st cycle which were measured in our previous work. (a) Cu thin film, the current density is 84.3 mA g<sup>-1</sup> and the voltage range is 0–1.25 V against Pb/PbF<sub>2</sub>, (b) Cu<sub>2</sub>O cathode composite, the current density is 7.5 mA g<sup>-1</sup> and the voltage range is 0.4–1.5 V against Pb/PbF<sub>2</sub>.



Figure 2.16 Charge compensation and structural information of BM-300 obtained from the 1st cycle. (a) Ex-situ points in the 1st cycle. (b) Cu *L*-edge X-ray absorption spectra. (c) Cu *K*-edge XANES. (d) *k*<sub>3</sub>-Weighted Fourier transformation magnitudes of Cu *K*-edge EXAFS. (e) F *K*-edge XAS for BM-300 cathode composite upon the 1st cycle. Solid electrolyte LBF and CuF<sub>2</sub> are provided as references.



**Figure 2.17** Linear combination fitting of Cu *L*-edge XAS result for the 1st fully charged state of BM-300. Cu, Cu<sub>2</sub>O, CuO, and CuF<sub>2</sub> are provided as reference samples.



**Figure 2.18** (a) STEM mapping images of BM-300 cathode composite at 1st fully charged state. (b) TEM micrograph in the red square in Figure 2.18a. (c) Crystal structure of the selected areas in Figure 2.18b. Area 1 refers to CuF<sub>2</sub> and area 2 refers to La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (LaF<sub>3</sub>), only metal atoms are displayed. (d)–(e) Corresponding FFT and IFFT of area 1 in Figure 2.18b. (f)–(g) Corresponding

FFT and IFFT of area 2 in Figure 2.18b.

# References

- Xu, C.; Behrens, P.; Gasper, P.; Smith, K.; Hu, M.; Tukker, A.; Steubing, B. Electric vehicle batteries alone could satisfy short-term grid storage demand by as early as 2030. *Nat. Commun.* 2023, *14* (1), 119.
- Sanguesa, J. A.; Torres-Sanz, V.; Garrido, P.; Martinez, F. J.; Marquez-Barja, J. M., A Review on Electric Vehicles: Technologies and Challenges. *Smart Cities* 2021, 4 (1), 372–404.
- Liu, X.; Zhao, F.; Hao, H.; Liu, Z. Opportunities, Challenges and Strategies for Developing Electric Vehicle Energy Storage Systems under the Carbon Neutrality Goal. *World Electro. Veh. J.* 2023, 14 (7), 170.
- IRENA. Global renewables outlook: Energy transformation 2050. IRENA
   2020.https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/
   Apr/IRENA\_Global\_Renewables\_Outlook\_2020.pdf
- Khan, F. M. N. U.; Rasul, M. G.; Sayem, A. S. M.; Mandal, N. K. Design and optimization of lithium-ion battery as an efficient energy storage device for electric vehicles: A comprehensive review. *J. Energy Storage* 2023, *71*,108033.
- Hasan, M. K.; Mahmud, M.; Ahasan Habib, A. K. M.; Motakabber, S. M. A.; Islam, S. Review of electric vehicle energy storage and management system: Standards, issues, and challenges. *J. Energy Storage* 2021, *41*, 102940.
- Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* 2017, 16 (1), 16–22.
- Goodenough, J. B.; Park, K. S. The Li-ion rechargeable battery: a perspective.
   J. Am. Chem. Soc. 2013, 135 (4), 1167–1176.
- Armand, M.; Tarascon, J.-M. Building better batteries. *Nature* 2008, 451 (7179), 652–657.
- Delmas, C.; Braconnier, J.-J.; Fouassier, C.; Hagenmuller, P. Electrochemical intercalation of sodium in Na<sub>x</sub>CoO<sub>2</sub> bronzes. *Solid State Ionics* 1981, *3*, 165–169.

- Jian, Z.; Luo, W.; Ji, X. Carbon electrodes for K-ion batteries. *J. Am. Chem. Soc.* 2015, *137* (36), 11566–11569.
- Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen,
   Y.; Moshkovich, M.; Levi, E. Prototype systems for rechargeable magnesium
   batteries. *Nature* 2000, 407 (6805), 724–727.
- Xu, C.; Li, B.; Du, H.; Kang, F. Energetic zinc ion chemistry: the rechargeable zinc ion battery. *Angew. Chem.* 2012, *124* (4), 957–959.
- Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen,
   C.; Yang, J.; Hwang, B.-J. An ultrafast rechargeable aluminum-ion battery.
   *Nature* 2015, *520* (7547), 324–328.
- Reddy, M. A.; Fichtner, M. Batteries based on fluoride shuttle. *J. Mater. Chem.* 2011, 21 (43), 17059–17062.
- Masese, T.; Yoshii, K.; Yamaguchi, Y.; Okumura, T.; Huang, Z. D.; Kato, M.; Kubota, K.; Furutani, J.; Orikasa, Y.; Senoh, H.; Sakaebe, H.; Shikano, M. Rechargeable potassium-ion batteries with honeycomb-layered tellurates as high voltage cathodes and fast potassium-ion conductors. *Nat. Commun.* 2018, 9 (1), 3823.
- Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.;
   Okado, T.; Huang, Z. D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.;
   Kageyama, H.; Uchimoto, Y. High energy density rechargeable magnesium battery using earth-abundant and non-toxic elements. *Sci. Rep.* 2014, *4*, 5622.
- Zhao, X.; Zhao-Karger, Z.; Wang, D.; Fichtner, M. Metal oxychlorides as cathode materials for chloride ion batteries. *Angew. Chem.* 2013, 125 (51), 13866–13869.
- Rongeat, C.; Anji Reddy, M.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chem. A* 2014, *2* (48), 20861–20872.
- 20. Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Munnangi, A. R.;

Clemens, O. Fluoride ion batteries–past, present, and future. *J. Mater. Chem. A* **2021**, *9* (10), 5980–6012.

- Nakano, H.; Matsunaga, T.; Mori, T.; Nakanishi, K.; Morita, Y.; Ide, K.; Okazaki, K.-i.; Orikasa, Y.; Minato, T.; Yamamoto, K.; Ogumi, Z.; Uchimoto, Y. Fluoride-Ion Shuttle Battery with High Volumetric Energy Density. *Chem. Mater.* 2020, *33* (1), 459–466.
- 22. Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Amezawa, K.; Uchimoto, Y. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, *9* (1), 406–412.
- Thieu, D. T.; Fawey, M. H.; Bhatia, H.; Diemant, T.; Chakravadhanula, V. S. K.;
   Behm, R. J.; Kübel, C.; Fichtner, M. CuF<sub>2</sub> as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* 2017, *27* (31), 1701051.
- Haruyama, J.; Okazaki, K. I.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji, T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. *ACS Appl. Mater. Interfaces* 2020, *12* (1), 428–435.
- 25. Yoshinari, T.; Zhang, D.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Matsunaga, T.; Amezawa, K.; Uchimoto, Y. Kinetic analysis and alloy designs for metal/metal fluorides toward high rate capability for all-solid-state fluoride-ion batteries. *J. Mater. Chem. A* 2021, 9 (11), 7018–7024.
- Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Reversible and Fast (De)fluorination of High-Capacity Cu<sub>2</sub>O Cathode: One Step Toward Practically Applicable All-Solid-State Fluoride-Ion Battery. *Adv. Energy Mater.* 2021, *11* (45), 2102285.

- Kageyama, H.; Hayashi, K.; Maeda, K.; Attfield, J. P.; Hiroi, Z.; Rondinelli, J. M.; Poeppelmeier, K. R. Expanding frontiers in materials chemistry and physics with multiple anions. *Nat. Commun.* 2018, 9 (1), 772.
- Zhang, D.; Yoshinari, T.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Watanabe, T.; Uchiyama, T.; Orikasa, Y.; Amezawa, K.; Uchimoto, Y. Cu–Pb nanocomposite cathode material toward room temperature cycling for all-solid-state fluoride-ion batteries. *ACS Appl. Energy Mater.* 2021, *4* (4), 3352–3357.
- 29. Mohammad, I.; Chable, J.; Witter, R.; Fichtner, M.; Reddy, M. A. Synthesis of Fast Fluoride-Ion-Conductive Fluorite-Type Ba<sub>1-x</sub>Sb<sub>x</sub>F<sub>2+x</sub> (0.1 ≤ x ≤ 0.4): A Potential Solid Electrolyte for Fluoride-Ion Batteries. *ACS Appl. Mater. Interfaces* 2018, *10* (20), 17249–17256.
- Rongeat, C.; Reddy, M. A; Witter, R.; Fichtner, M. Solid electrolytes for fluoride ion batteries: ionic conductivity in polycrystalline tysonite-type fluorides. *ACS Appl. Mater. Interfaces* 2014, 6 (3), 2103–2110.
- Zhang, L.; Reddy, M. A.; Fichtner, M. Development of tysonite-type fluoride conducting thin film electrolytes for fluoride ion batteries. *Solid State Ionics* 2015, 272, 39–44.
- Grenier, A.; Porras-Gutierrez, A. G.; Body, M.; Legein, C.; Chretien, F.; Raymundo-Piñero, E.; Dollé, M.; Groult, H.; Dambournet, D. Solid fluoride electrolytes and their composite with carbon: issues and challenges for rechargeable solid state fluoride-ion batteries. *J. Phys. Chem. C* 2017, *121* (45), 24962–24970.
- Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537–541.
- 34. Gaur, A.; Shrivastava, B. A comparative study of the methods of speciation using X-ray absorption fine structure. *Acta Phys. Pol., A* **2012**, *121* (3), 647–652.

- Irvine, J. T. S.; Sinclair, D. C.; West, A. R. Electroceramics: Characterization by Impedance Spectroscopy. *Adv. Mater.* 1990, *2* (3), 132–138.
- 36. Yubuchi, S.; Tsukasaki, H.; Sakuda, A.; Mori, S.; Hayashi, A.; Tatsumisago, M. Quantitative analysis of crystallinity in an argyrodite sulfide-based solid electrolyte synthesized via solution processing. *RSC Adv.* 2019, 9 (25), 14465–14471.
- 37. Ito, Y.; Koto, K.; Yoshikado, S.; Ohachi, T.; Kanamaru, F.; Mukoyama, T. Variable-temperature X-ray diffraction analysis of the behavior of the mobile fluorine ions in a superionic conductor, β-PbF<sub>2</sub>. *J. Solid State Chem.* 1991, 95 (1), 94–98.
- Berastegui, P.; Hull, S. Structure and conductivity of some fluoride ion conductors. *Solid State Ionics* 2002, *154*, 605–608.
- Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O. LaSrMnO<sub>4</sub>: Reversible Electrochemical Intercalation of Fluoride Ions in the Context of Fluoride Ion Batteries. *Chem. Mater.* 2017, 29 (8), 3441–3453.
- 40. Nakai, S.; Kawata, A.; Ohashi, M.; Kitamura, M.; Sugiura, C.; Mitsuishi, T.; Maezawa, H. Core-exciton absorption in the F K absorption spectra of 3*d* transition-metal fluorides. *Phys. Rev. B. Condens. Matter.* 1988, 37 (18), 10895–10897.
- Chou, C.; Pong, W.; Lin, I.; Tsai, S. Xray Absorption Fine Structure (XAFS) Study of the High-Tc Superconductor Pb-Bi-Sr-Ca-Cu-O System. *Chin. J. Phys.* 1991, 29 (3), 263-282.

# Chapter 3 Reversible Fluoride-Ion (De)Intercalation of CuLaO<sub>2</sub> Cathodes with Crystalline /Amorphous Phase Transition Involving Multi-Electron Reaction



All-solid-state fluorideion batteries (FIBs) are considered as a promising alternative to lithium-ion batteries (LIBs) for nextgeneration energy storage

devices. Intercalation-type cathode materials for FIBs have been developed in the past. However, they are limited by low theoretical capacities, which fail to meet the high energy density and high rate capability demand. This study reports the first application of the intercalation-type cathode material CuLaO<sub>2</sub> in all-solid-state FIBs. This cathode maintains a high capacity of 184 mAh g<sup>-1</sup> over 50 cycles. Compared to the metal/metal fluoride (M/MF<sub>x</sub>) and the intercalation-type cathode materials reported so far, CuLaO<sub>2</sub> exhibits an outstanding rate capability with a capacity of 102 mAh g<sup>-1</sup> even at a high current density of 200 mA g<sup>-1</sup>. Electrochemical measurements, coupled with X-ray absorption spectroscopy and X-ray diffraction prove that the charge/discharge processes of CuLaO<sub>2</sub> proceed via intercalation reaction with the reversible phase transition between crystalline/amorphous phases, and the charge compensation is responsible for multielectron redox of Cu<sup>+</sup>/Cu<sup>3+</sup>. We believe that this study can bring insight into the all-solid-state FIBs.

## **3.1 Introduction**

Lithium-ion batteries (LIBs) have dominated the portable energy storage devices market for decades, mainly due to their high working voltage, high energy density, and commendable cycle life.<sup>1–3</sup> With the burgeoning demand for electric vehicles (EVs) and advanced energy storage technologies in recent years, there is a growing debate about the long-term availability of the critical elements of LIBs (Li, Co) due to its rocketing price, limited abundance and nonuniform geographical distribution.<sup>4, 5</sup> Furthermore, safety concerns associated with a flammable and toxic organic electrolyte of LIBs call for safer alternatives such as all-solid-state battery technologies for future applications. Therefore, researchers are focusing on developing batteries based on different charge carriers such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, etc.,<sup>6-11</sup> targeting superior energy density, power density, and cycle performances that exceed those of LIBs. Among them, fluoride-ion batteries (FIBs), based on the shuttling of fluoride ions, have been considered as a potential alternative in recent years.<sup>10</sup> Since fluoride-ion (F<sup>-</sup>) has the high redox potential (2.87 V vs. SHE) of  $F^{-}/F_{2}$ , FIBs can provide theoretically high voltage using various metal/metal fluoride (M/MF<sub>x</sub>) combinations.<sup>10, 12, 13</sup> The all-solidstate rechargeable FIBs were first proposed in 2011 by Reddy and Fichtner,<sup>10</sup> in which La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> was utilized as the solid electrolyte and metal fluorides (CuF<sub>2</sub>, BiF<sub>3</sub>, SnF<sub>2</sub>, etc.) based on conversion mechanism were used as active materials. Although the conversion-based  $M/MF_x$  electrode materials have the advantage of high theoretical capacities, they suffer from poor cycling and rate performances.<sup>14, 15</sup> This is because the phase transition mechanism between metal and metal fluoride involves a reorganization of the atoms that can bring significant volume change.<sup>13</sup> Such volume change leads to blockage of the fluoride-ion diffusion pathway, which severely affects the electrodeelectrolyte interfaces.<sup>16, 17</sup>

Besides  $M/MF_x$  electrode materials, intercalation-type cathode materials (e.g., perovskite-type BaFeO<sub>2.5</sub>,<sup>18</sup> schafarzikite-type MSb<sub>2</sub>O<sub>4</sub>,<sup>19</sup> Ruddlesden–Popper-type

LaSrMnO<sub>4</sub>,<sup>20</sup> Sr<sub>2</sub>MnO<sub>3</sub>F<sub>2</sub>,<sup>21</sup> and La<sub>2</sub>CoO<sub>4</sub>,<sup>22</sup> etc.) have received significant attention in recent years. These materials obey the topotactic fluorination/defluorination mechanism, effectively reducing the volume change.<sup>23, 24</sup> It is crucial for intercalationtype materials to have anionic insertion sites in the host lattice, such as the rock-salt interstitial layers in Ruddlesden-Popper-type materials. However, the intercalationtype materials previously reported, such as LaSrMnO4, always contain heavy elements to support the framework, which are electrochemical-inactive, resulting in a low theoretical capacity. In addition, the monoelectron reaction of the transition metal (e.g.,  $Mn^{3+}/Mn^{4+}$  in  $Sr_2MnO_3F/Sr_2MnO_3F_2$ ) also limits the capacities of the current intercalation-type cathode materials.<sup>21</sup> In our recent research on Ruddlesen-Poppertype  $La_{1,2}Sr_{1,8}Mn_2O_{7-\delta}F_2$  cathode, excessive fluoride ions (~4 F<sup>-</sup>) can be inserted into the lattice structure, achieving a capacity of 190 mAh g<sup>-1</sup> through the charge compensation of both Mn redox and oxygen redox.<sup>25</sup> Although the application of anionic redox has unlocked the potential of increased capacity in cathode materials, the oxygen redox in high voltage regions typically causes significant voltage hysteresis and large polarization that are disadvantages for practical applications.<sup>26-28</sup> Therefore, one way to achieve high capacity without anionic redox is to use a multielectron cationic redox reaction in the low formula weight cathodes.

In this study, we introduced a delafossite oxide CuLaO<sub>2</sub>, which is known to easily intercalate extra oxygen in the Cu planes and have a two-dimensional (2D) anion pathway in the host structure,<sup>29, 30</sup> as an intercalation-type cathode material for all-solid-state FIBs. This cathode material exhibited a reversible capacity of 208 mAh g<sup>-1</sup> in the initial cycle, and maintained a stable cycle performance over 50 cycles, which surpassed most of the Ruddlesden–Popper-type cathode materials reported so far. The detailed multielectron redox reaction of Cu<sup>+</sup> species was clarified by X-ray absorption spectroscopy (XAS) measurements. CuLaO<sub>2</sub> underwent an amorphous transformation during the charging process and was restored after discharging, which was confirmed by X-ray diffraction (XRD) measurement and chemical fluorination reactions. This

study broadened the range of promising cathode materials for FIBs.

## **3.2 Experimental**

#### **3.2.1** Material preparation

CuLaO<sub>2</sub> was synthesized by a one-step solid-state reaction.<sup>31</sup> Stoichiometric amounts of La<sub>2</sub>O<sub>3</sub> (FUJIFILM Wako, 99.99%) and Cu<sub>2</sub>O (FUJIFILM Wako, 99.5%) were mixed in a mortar and pestle, which was subsequently pelletized in an Ar-filled glovebox. The pellet was then annealed in argon at 860 °C for 12 h, and ground into a fine powder.

Chemical fluorination was conducted for the as-prepared CuLaO<sub>2</sub> by using XeF<sub>2</sub> (Strem Chemicals, 99.5%) as the fluorination agent. CuLaO<sub>2</sub> and XeF<sub>2</sub> were placed separately in a polytetrafluoroethylene (PTFE) sleeve in a molar ratio of 1:  $\frac{n}{2}$  (n=0, 0.2, 0.6, 1.0, 1.4, and 1.8), and sealed in a steel autoclave. All the operations were carried out in an Ar-filled glovebox. Finally, the reactor was heated to 140 °C for 96 h.

Solid electrolyte  $La_{0.9}Ba_{0.1}F_{2.9}$  (LBF) was prepared by the mechanochemical method as described in Section 2.2.1. The cathode composite (CuLaO<sub>2</sub>/LBF/VGCF = 3: 6: 1 in mass ratio) and anode composite (Pb/PbF<sub>2</sub>/LBF/VGCF = 2 :3: 4: 1 in mass ratio) were prepared by ball milling, which has been mentioned in Section 2.2.1.

#### **3.2.2** Electrochemical measurements

Electrochemical tests were carried out on bulk-type cells, the fabrication method has been mentioned in Section 2.2.2. The galvanostatic charge-discharge tests and Galvanostatic Intermittent Titration Technique (GITT) measurement were evaluated by HJ1020mSD8 battery testing systems (Hokuto Denko, Japan) with a cutoff voltage between  $-1.5\sim1.32$  V vs. Pb/PbF<sub>2</sub>. All the electrochemical measurements were recorded at 140 °C without air exposure. The apparent F<sup>-</sup> diffusion coefficients were calculated from the GITT results using the equation (3–1):

$$D_{F-} = \frac{4}{\pi} \left(\frac{iV_m}{zFS}\right)^2 \left(\frac{dE/d\delta}{dE/d\sqrt{t}}\right)^2 \tag{3-1}$$

where  $D_{\text{F-}}$  is the diffusion coefficient, *i* is the current density applied to GITT pulse,  $V_m$  is the molar volume (cm<sup>3</sup> mol<sup>-1</sup>), *z* is the valence, *F* is Faraday's constant, and *S* is the cell interfacial area. The terms  $dE/d\delta$  and  $dE/d\sqrt{t}$  represent the slopes of the coulometric titration curve at composition  $\delta$  and the transient voltage vs. the square root of time, respectively.<sup>32</sup>

#### 3.2.3 Material characterization

XRD patterns were collected using an X-ray diffractometer with Cu Ka radiation  $(\lambda = 1.54056 \text{ Å}, \text{Rigaku Ultima IV}, \text{Japan})$ . Synchrotron XRD data were collected at room temperature in the Ar atmosphere at the BL02B2 beamline in SPring-8 ( $\lambda$  = 0.4133 Å Hyogo, Japan). Rietveld refinement was performed using Jana 2006 software.<sup>33</sup> Scanning transmission electron microscopy (STEM) measurements with the aid of energy dispersive X-ray spectroscopy (EDS) were conducted using a JEM-ARM200F monochromated atomic resolution analytical electron microscope (JEOL, Japan). X-ray absorption spectroscopy (XAS) measurements for Cu K-edge, Cu L2,3edge, and O K-edge were carried out at the BL14B2 and BL27SU beamlines in SPring-8, respectively. To prepare the samples during the second cycle for measurements, all the cells were charged and discharged at a current density of 10 mA  $g^{-1}\,\text{and}$  then transferred from an Ar-filled glovebox. The measurements were carried out under vacuum conditions. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using the ATHENA software package.<sup>34</sup> In order to simulate the anion sites and diffusion path of the F<sup>-</sup> in the structure, bond valence sum (BVS) calculation was performed using the program PyAbstantia,<sup>35</sup> and the BVS 3D mapping was visualized using VESTA.<sup>36</sup>

## 3.3 Results and discussion

#### 3.3.1 Structure and composition

The crystal structure of as-prepared CuLaO<sub>2</sub> was examined by synchrotron XRD (**Figure 3.1a**). All the peaks were indexed to the CuLaO<sub>2</sub> phase (space group:  $R\bar{3}m$ ) with lattice parameters of a = 3.8253(0) Å and c = 17.0645(4) Å, as shown in **Table 3.1**.<sup>37</sup> CuLaO<sub>2</sub> has a delafossite structure, in which O atoms and La atoms form edge-shared [LaO<sub>6</sub>] octahedral layers, and Cu atoms are linearly coordinated with two O atoms and stacked between octahedral layers (Figure 3.1b).<sup>36</sup> STEM-EDS mapping results (Figure 1c) revealed that the particle size of the as-prepared CuLaO<sub>2</sub> was approximately 1  $\mu$ m, and Cu, La, and O atoms were homogeneously distributed in the particles with an atomic ratio of Cu/La/O = 24: 24: 52, which was almost consistent with the theoretical value.<sup>31</sup>

## 3.3.2 Electrochemistry

The electrochemical performance of CuLaO<sub>2</sub> cathode was examined and shown in **Figure 3.2** and **Figure 3.3**. For the galvanostatic charge-discharge measurements, the Pb/PbF<sub>2</sub> composite was used as the anode mainly because of its outstanding inherent conductivity,<sup>38, 39</sup> which enabled a more precise evaluation of the electrochemical performance of CuLaO<sub>2</sub> cathode. The charge/discharge measurements were cut off at a capacity of 2 F<sup>-</sup> insertion, which assumed a two-electron reaction of Cu<sup>+</sup>/Cu<sup>3+</sup>, and the voltage range was set to  $-1.5\sim1.32$  V because the voltage when the 2 F<sup>-</sup> insertion in the first charge process occurred was about 1.32 V as mentioned immediately afterward. The CuLaO<sub>2</sub> cathode exhibited a capacity of 229 mAh g<sup>-1</sup> corresponding to the capacity of 2 F<sup>-</sup> at 1.32 V with plateaus at 0.5 and 1.0 V in the first charge process, and a capacity of 208 mAh g<sup>-1</sup> with plateaus at 0.65, 0, and -0.5 V in the first discharge process (Figure 3.2). The CuLaO<sub>2</sub> cathode exhibited a capacity of 205 mAh g<sup>-1</sup> with plateaus at 0.4 and 0.9 V in the second charge process, and a capacity of 200 mAh g<sup>-1</sup> with plateaus at 0.65

V, 0 V and -0.5 V in the second discharge process. The charge curve shape of 2nd cycle was different from that of 1st cycle, whereas the discharge curve shape of 2nd cycle was similar to that of 1st cycle. In the subsequent cycles, the shape of the charge/discharge curves was similar to the 2nd cycle. As illustrated in Figure 3.3b, CuLaO<sub>2</sub> maintained 88% capacity of its initial capacity after 50 cycles, with almost 100% Coulombic efficiency at 10 mA g<sup>-1</sup>. It is also noteworthy to point out that CuLaO<sub>2</sub> attained 184 mAh g<sup>-1</sup> of capacity after 10 cycles, which remained well maintained up to 50 cycles. In addition, it showed excellent rate capability with a reversible capacity of 102 mAh g<sup>-1</sup> at a high current density of 200 mA g<sup>-1</sup> (Figure 3.3c), which was quite superior to most of the FIB cathode materials reported so far.<sup>21, 25, 40, 41</sup>

Because the CuLaO<sub>2</sub> exhibited reversible charge/discharge curves after 2nd cycle, we focused on analyzing the reaction mechanism of the CuLaO<sub>2</sub> cathode during the 2nd cycle. The GITT results during the 2nd charge/discharge process are shown in Figure 3.4. The open circuit voltages (OCVs) of the charge process continued to increase with the F<sup>-</sup> insertion. According to our previous studies on 3d transition metal/metal fluoride conversion-type cathodes, the OCVs remained almost constant during the two-phase reaction between metal and metal fluoride.<sup>13</sup> Therefore, the continuous change in the OCVs indicated that the charging process in the CuLaO<sub>2</sub> cathode did not proceed via the two-phase reaction. The polarization of the late charge process was not significantly larger than that of the early charge process (Figure 3.4a), as the Li-rich cathode involves anionic redox.<sup>42, 43</sup> This indicated that the fluorination process might not involve the anionic redox, which will be discussed in detail in the following section by using XAS. Similar to the charge-discharge curve shown in Figure 2a, the magnitude of polarization in GITT differs between charging and discharging, and the polarization is particularly large in the range of x = 0-0.75 during discharge (Figure 3a). The different polarization behavior between charge and discharge was also observed in the Na<sup>+</sup> insertion/extraction processes of the NaFePO<sub>4</sub> cathode for the Na-ion battery.<sup>44</sup> In the NaFePO<sub>4</sub> cathode, an intermediate phase of Na<sub>2/3</sub>FePO<sub>4</sub> appears when charging (Naion extraction) from NaFePO<sub>4</sub>. The volume change ratio from NaFePO<sub>4</sub> to FePO<sub>4</sub> is about 16.6 % whereas the volume change ratios from NaFePO<sub>4</sub> to Na<sub>2/3</sub>FePO<sub>4</sub> and from Na<sub>2/3</sub>FePO<sub>4</sub> to FePO<sub>4</sub> are about 3.8 % and 12.8 %. NaFePO<sub>4</sub> has to pass through the intermediate phase during charging because the volume change ratio from NaFePO<sub>4</sub> to Na<sub>2/3</sub>FePO<sub>4</sub> (3.8 %) is smaller than that from Na<sub>2/3</sub>FePO<sub>4</sub> to FePO<sub>4</sub> (12.8%). On the other hand, it can proceed directly from FePO<sub>4</sub> to NaFePO<sub>4</sub> during discharging because the volume change ratio from FePO<sub>4</sub> to Na<sub>2/3</sub>FePO<sub>4</sub> is larger than that from Na<sub>2/3</sub>FePO<sub>4</sub> to NaFePO<sub>4</sub>. As a result, the charging curve exhibits two plateaus whereas the discharging curve exhibits only one plateau. For CuLaO<sub>2</sub>, a similar phase transition including an intermediate phase might occur during discharging, leading to the asymmetric charge/discharge curves and relatively large polarization around -0.5 V. The calculated apparent F<sup>-</sup> diffusion coefficients for the charging process estimated from the GITT curve were  $\sim 10^{-13}$  to  $\sim 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> at 140 °C (Figure 3.4b), which were comparable to those of LIB cathode materials, such as LiCoO<sub>2</sub> and LiFePO<sub>4</sub> at room temperature.<sup>45, 46</sup>

#### 3.3.3 Structural evolution

To examine the crystal and local structural change of the CuLaO<sub>2</sub> cathode during charging and discharging, the XRD, STEM-EDS and Cu *K*-edge EXAFS measurements were carried out during the 2nd cycle. Due to the high ratio of solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> in the cathode composite and severe amorphization of the active material after charging (see in **Figure 3.5**), we were unable to conduct Rietveld refinement to analyze the precise phase transitions. In the XRD patterns of the cathode composite (Figure 3.5 and **Figure 3.6a**), all the peaks of the 1st discharged state (1st Dischg) can be indexed to CuLaO<sub>2</sub> and solid electrolyte LBF. However, a small peak appeared at ~26°, which might be attributed to the generation of LaOF during the ball milling process, as shown in Figure 3.6b. It can be observed that the diffraction patterns of CuLaO<sub>2</sub> still remained when charging to x = 0.5. No diffraction patterns other than the

solid electrolyte LBF could be observed from x = 1 to the fully charged state. The disappearance of the diffraction peaks can be attributed to the amorphous transformation of the CuLaO<sub>2</sub> structure. The F element homogeneously existed in the secondary particles, including Cu, La, and O elements of the 2nd fully charged sample, which was confirmed by STEM-EDS (Figure 3.6b and 3.7). The discharge process was the opposite. When discharging from the fully charged state to -0.5 V, the diffraction patterns of crystalline CuLaO<sub>2</sub> appeared and it remained in the fully discharged state.

Since the amorphous transformation of the active material during electrochemical fluorination and the large amount of solid electrolyte LBF, it was difficult to determine the structure change of charged CuLaO<sub>2</sub> by XRD measurement. Therefore, we attempted to analyze the crystal structure change of CuLaO<sub>2</sub> by using synchrotron XRD for chemically fluorinated CuLaO<sub>2</sub> instead of electrochemically fluorinated CuLaO<sub>2</sub>. The synchrotron XRD results of the chemical fluorination products are shown in Figure **3.8**. CuLaO<sub>2</sub> can maintain its crystal structure with annealing treatment at 140 °C (n =0) as shown in Figure 3.8a. The Bragg peaks of CuLaO<sub>2</sub> were broadened at n = 0.6, and some weak peaks emerged, such as  $2\theta = 4.48^{\circ}$ ,  $6.99^{\circ}$ ,  $11.92^{\circ}$  and so on, indicating the crystallinity reduction and the generation of a new phase. The diffraction peaks of CuLaO<sub>2</sub> continued to broaden at n = 1.0, and the overall peak intensity decreased. It can be clearly observed that two phases coexisted at n = 1.0, with one being CuLaO<sub>2</sub> (Phase 1) and the other identified as its main fluorination product (Phase 2). In the n =1.4 sample, the diffraction peaks of the CuLaO<sub>2</sub> almost disappeared, and the peak intensity of Phase 2 increased and became further broadened. In addition, a sharp peak emerged at  $2\theta = 7.95^{\circ}$ , which can be attributed to the generation of the La<sub>2</sub>O<sub>3</sub> impurity (Space group:  $P\overline{3}m1$ ).<sup>47</sup> The diffraction patterns of the fluorination products ( $n \ge 1.0$ ) showed larger full width at half-maximum (FWHM) and much lower absolute intensities, indicating an amorphous transformation after fluorination.

To examine the local structure around Cu in the CuLaO<sub>2</sub> cathode during the charge-discharge processes, the Cu *K*-edge EXAFS analysis was performed for the

cathode during the second cycle (**Figure 3.9**). Two peaks were observed around 1.4 Å and 2.2 Å in the 1st discharged state. The intensity of the peak around 1.4 Å increased while the intensity of the peak around 2.2 Å decreased during the charge process. Then, the intensity of two peaks returned to the 1st discharged state after fully discharging (2nd Dischg). The increasing intensity of the peak around 1.4 Å was probably caused by the coordination number increment of Cu with Cu–F bond formation,<sup>41</sup> whereas the decreasing intensity of the peak around 2.2 Å might be caused by the amorphization observed in the XRD measurements (Figure 3.6a). Similar reversible structure change between crystalline and amorphous phases has been reported in cathode materials for LIBs.<sup>48, 49</sup>

These GITT, XRD, STEM-EDS and Cu K-edge EXAFS measurements indicated that the charge/discharge reaction of the CuLaO<sub>2</sub> cathode proceeded via an intercalation reaction with the reversible phase transition between crystalline/amorphous phases. To further examine possible F<sup>-</sup> insertion sites and their conduction pathways in the CuLaO<sub>2</sub> cathode, we performed BVS calculations. As shown in Figure 3.10a, the intercalated F<sup>-</sup> was able to be located in the Coulombic potential holes at the center of Cu-triangles, and the CuLaO<sub>2</sub> pristine could accommodate up to 2 F<sup>-</sup> to form CuLaO<sub>2</sub>F<sub>2</sub>. Furthermore, since the anion sites in the CuLaO<sub>2</sub> are two-dimensionally connected with each other, as illustrated by the blue area in Figure 3.10b, inserted  $F^-$  would move to adjacent F sites through the 2D diffusion path. Similar anion sites and diffusion paths have been reported for oxide-ion intercalation in the delafossite materials CuLnO<sub>2</sub> (Ln = La, Y).<sup>29, 30</sup> Furthermore, it has been clarified that easy  $F^-$  diffusion through 2D latticelike channels in the rock-salt interlayers in Ruddlesden-Popper-type layered oxyfluoride La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>F<sub>2</sub> leads to the high rate performance of the cathode.<sup>25, 50</sup> These studies support the idea that the 2D diffusion pathways in the Cu layer of CuLaO<sub>2</sub> contribute to the high bulk diffusion coefficient (Figure 3.4b) and rate performance (Figure 3.3c).

### 3.3.4 Charge compensation

The XAS measurements were used to reveal the charge compensation mechanism, as shown in **Figure 3.11**. In the case of Cu *L*-edge XAS (Figure 3.11a), an absorption peak at 933.8 eV was observed in the 1st discharged state (1st Dischg), which was in agreement with that of CuLaO<sub>2</sub> pristine, indicating that the Cu existed as Cu<sup>+</sup> after the 1<sup>st</sup> discharge process. As charging proceeded, the peak corresponding to Cu<sup>+</sup> gradually diminished and almost disappeared at x = 1, and a peak A at 930.5 eV gradually increased upon charging. The absorption energy of peak A was consistent with the CuO reference, indicating that the valence state of copper was approximately +2 at x = 1. Moreover, it was observed that a new peak B at approximately 932.8 eV appeared at x = 1.5 and increased until the fully charged state. This peak B was in agreement with that previously found in NaCuO<sub>2</sub> and many Cu<sup>3+</sup> compounds,<sup>51-55</sup> and it was basically assigned to  $2p3d^9$  and  $2p3d^{10}L$  (L refers to ligand hole) states. Hence, the Cu *L*-edge XAS results indicated that a multielectron reaction of Cu<sup>+</sup> species occurred in charge compensation.

On the other hand, in the O *K*-edge spectra, the spectrum of the 1st discharged CuLaO<sub>2</sub> (1st Dischg) showed similar behavior as previously reported (Figure 3.11b).<sup>56</sup> The absorption peaks at 531.7 and 536.6 eV were attributed to the transition from O 1s to La 5d–O 2p hybridized states, which can also be observed in La<sub>2</sub>O<sub>3</sub>.<sup>57</sup> Furthermore, the peak located at 533 eV corresponded to the hybridization of O 2p and Cu 4s/4p, which was the signature of Cu<sup>+</sup> and can also be observed in Cu<sub>2</sub>O reference.<sup>57</sup> Significant changes were observed in the pre-edge region of the O *K*-edge spectra upon electrochemical fluorination. In the charge from 1st Dischg to x = 1.0, a peak  $\beta$  appeared at 529.8 eV and its intensity increased. This peak was attributed to the transition from O 1s to Cu 3d–O 2p hybridized orbital and was similar to that of CuO, indicating that the Cu<sup>+</sup>/Cu<sup>2+</sup> redox reaction occurred.<sup>58</sup> In the charge from x = 1.0 to x = 1.5, a peak  $\alpha$  located at 528.6 eV appeared. This peak was attributed to the transition from O 1s to

Cu 3d–O 2p hybridization state with a doping ligand hole, and it can be observed in Cu<sup>3+</sup> compounds LaCuO<sub>3</sub> and NaCuO<sub>2</sub>.<sup>51, 54, 59</sup> In the further charge to Fullchg, the intensity of peak  $\alpha$  increased and a new peak  $\gamma$  emerged at 531.2 eV. The increasing intensity of peak  $\alpha$  suggests further oxidation of Cu<sup>2+</sup>/Cu<sup>3+</sup>. The energy position of peak  $\gamma$  is in good agreement with that of the peak as observed in charged Li-rich cathodes of LIBs, indicating a hole formation in the oxygen 2p orbital.<sup>42, 60</sup> There were two possibilities for the appearance of the peak  $\gamma$ : i) the formation of O–O bonds, ii) as the Cu 3d (Cu<sup>3+</sup>) and O 2p form a strong covalent bond, the peak could also be attributed to the electron transfer from the O 2p orbital to the Cu 3d orbital (i.e., ligand hole formation).<sup>61</sup> Generally, in the case of the Li-rich cathodes of LIBs using oxygen redox reaction, a large polarization accompanies the formation of O-O bonds in the highvoltage region.<sup>42, 43</sup> The relatively small polarization during the charging process in the GITT measurement (Figure 3.4) indicated that O-O bond formation did not occur in the fluorination processes, and the reaction mechanism of the CuLaO<sub>2</sub> near the fully charged state tended to be the O  $2p \rightarrow Cu$  3d electron transfer. After discharging, the peak y reversibly disappeared, and the O K-edge spectra restored to that before charging, indicating a good reversibility during the 2nd cycle. The O K-edge XAS results were consistent with those in Cu L-edge, suggesting that the multielectron redox reaction of Cu species provided charge compensation.

Based on the above-mentioned results, the charge/discharge processes of CuLaO<sub>2</sub> proceed via intercalation reaction with the phase transition between crystalline/amorphous phases, and the charge compensation is responsible for multielectron redox of  $Cu^+/Cu^{3+}$  without O–O bonds formation. The reversible intercalation reaction with multielectron redox leads to good electrochemical properties such as high capacity and cyclability. The fluoride-ions can be intercalated into the Cu planes and are believed to be conducted through the 2D pathway, leading to excellent rate performance. We believe this study offers a significant perspective for developing intercalation-type cathode materials for FIBs.

## **3.4 Conclusion**

In this study, we applied a layered oxide CuLaO<sub>2</sub> as a cathode material for allsolid-state FIBs and the charge/discharge reaction mechanism was examined in depth by GITT, XAS, and XRD measurements. The electrochemical performance revealed that the CuLaO<sub>2</sub> cathode exhibited outstanding cycle performance (184 mAh g<sup>-1</sup> after 50 cycles) and rate capability (102 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup>). The charge/discharge processes of CuLaO<sub>2</sub> proceeded via an intercalation reaction with the reversible phase transition between crystalline/amorphous phases. The detailed investigations by the XAS and XRD measurements revealed that the charge compensation was responsible for multielectron redox of Cu<sup>+</sup>/Cu<sup>3+</sup> without formation of O–O bonds, where the Cu–O ligand hole was generated due to the strong covalency of Cu 3d and O 2p. BVS calculation implied that F<sup>-</sup> could be intercalated into the Cu-planes and move through the 2D pathway. Although the structure of the fluorinated product still needs to be determined more precisely in future studies, CuLaO<sub>2</sub> represents an intercalation-type cathode material for all-solid-state FIBs with a simple structure and excellent electrochemical performance.



Figure 3.1 (a) Synchrotron XRD pattern and Rietveld refinement of as-prepared CuLaO<sub>2</sub> material, wavelength = 0.4133 Å,  $R_p$  = 3.26 %,  $R_f$  = 4.00 %,  $R_{wp}$  = 4.40 %, GOF = 1.31. (b) Structural model of CuLaO<sub>2</sub>,<sup>36</sup> (c) STEM image showing the distribution of Cu, La and O in CuLaO<sub>2</sub> particle.

Atom	Wyckoff Position	x	у	z	$\mathbf{B}_{\mathrm{iso}}$ / $\mathrm{\AA}^2$	Occupancy
Cu1	3a	0	0	0	2.215(6)	1
La1	3b	0	0	0.5	0.801(2)	1
O1	бс	0	0	0.1068(9)	0.970(9)	1

 Table 3.1 Structural parameters of as-prepared CuLaO2 determined from the Rietveld refinement.

Space group:  $R\overline{3}m$ ;  $R_p = 3.26$  %;  $R_{wp} = 4.40$  %,  $R_f = 4.00$  %; GOF = 1.31;

a = 3.8253(0) Å, c = 17.0645(4) Å.



Figure 3.2 Charge-discharge curves of CuLaO<sub>2</sub> cathode in the 1st and 2nd cycles.



Figure 3.3 (a) Charge-discharge curves of CuLaO<sub>2</sub> cathode during the 2nd cycle, the current density is 10 mA g<sup>-1</sup> and the voltage range is -1.5~1.32 V. (b) Cyclic and stability performance up to 50 cycles. The current density is 10 mA g<sup>-1</sup> and the operating temperature is 140 °C. (c) Rate capability at current densities of 10, 20, 50, 100, and 200 mA g<sup>-1</sup>, and the y axis on the right side shows the capacity retention relative to the current density of 10 mA g<sup>-1</sup>.


Figure 3.4 (a) Voltage/capacity profile of CuLaO<sub>2</sub> obtained by GITT measurement during the 2nd charge/discharge processes. (b) Apparent F<sup>-</sup> diffusion coefficients (D<sub>F</sub>-) calculated from GITT results upon the 2nd charge/discharge processes.



Figure 3.5 (a) XRD results between  $2\theta = 20-60^{\circ}$  at various fluorination states during the 2nd cycle. (b) XRD patterns of the CuLaO<sub>2</sub> cathode composite. CuLaO<sub>2</sub> and solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> are provided as references.



Figure 3.6 (a) XRD results for the CuLaO<sub>2</sub> cathode at various fluorination states during the 2nd cycle. CuLaO<sub>2</sub> and solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> are provided as references. The asterisks represent the Bragg peaks of the active material CuLaO<sub>2</sub> in the cathode composite. (b) STEM mapping images of CuLaO<sub>2</sub> cathode at 2nd fully charged state.



Figure 3.7 EDS spectra of Figure 3.6b.



Figure 3.8 (a) Synchrotron XRD results of the chemical fluorination products between  $2\theta = 2-20^{\circ}$ , wavelength = 0.4133 Å. n refers to the molar ratio of the fluorine in XeF<sub>2</sub> to the CuLaO<sub>2</sub>. (b) An enlarged view of  $2\theta = 3.6-13^{\circ}$  of the n = 1.0, and 1.8 samples. CuLaO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> are provided as references.



Figure 3.9  $k^3$ -Weighted Fourier transform magnitudes of Cu K-edge EXAFS at various

fluorination states during the second cycle.



Figure 3.10 Isosurfaces illustrating the difference from -1, corresponding to the formal charge of fluorine (F), derived through the BVS analysis for CuLaO<sub>2</sub>. The BVS mapping for CuLaO<sub>2</sub> reveals the mobility of F<sup>-</sup> in the structure. (a) Structure model of CuLaO<sub>2</sub> (1 × 1 × 1 unit cell) and BVS mapping illustrated at isosurface = 1.9 V indicate that the intercalated F<sup>-</sup> are located in the deep Coulombic potential holes and form at most CuLaO<sub>2</sub>F<sub>2</sub>. (b) Possible F<sup>-</sup> pathway estimated by BVS analysis (2 × 2 × 1 unit cell). It is considered that F<sup>-</sup> is likely to pass through the Coulombic potential trough near the Cu planes. (c) Top view of Figure 3.10b.



Figure 3.11 XAS patterns of CuLaO<sub>2</sub> cathode at various fluorination states during the 2nd cycle.
(a) Cu *L*-edge XAS. CuLaO<sub>2</sub>, CuO, and NaCuO<sub>2</sub> are provided as references. (b) O *K*-edge XANES.CuLaO<sub>2</sub>, Cu<sub>2</sub>O, CuO, and NaCuO<sub>2</sub> are provided as references.

# Reference

- Goodenough, J. B.; Park, K. S. The Li-ion rechargeable battery: a perspective.
   J. Am. Chem. Soc. 2013, 135 (4), 1167–76.
- Khan, F. M. N. U.; Rasul, M. G.; Sayem, A. S. M.; Mandal, N. K. Design and optimization of lithium-ion battery as an efficient energy storage device for electric vehicles: A comprehensive review. *J. Energy Storage* 2023, *71*, 108033.
- Hasan, M. K.; Mahmud, M.; Ahasan Habib, A. K. M.; Motakabber, S. M. A.; Islam, S. Review of electric vehicle energy storage and management system: Standards, issues, and challenges. *J. Energy Storage* 2021, *41*, 102940.
- 4. Vikström, H.; Davidsson, S.; Höök, M. Lithium availability and future production outlooks. *Appl. Energy* **2013**, *110*, 252–266.
- 5. Tarascon, J. M. Is lithium the new gold? *Nat. Chem.* **2010**, *2* (6), 510–510.
- Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen,
   Y.; Moshkovich, M.; Levi, E. Prototype systems for rechargeable magnesium
   batteries. *Nature* 2000, 407 (6805), 724–727.
- Xu, C.; Li, B.; Du, H.; Kang, F. Energetic zinc ion chemistry: the rechargeable zinc ion battery. *Angew. Chem.* 2012, *124* (4), 957–959.
- Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.; Okado, T.; Huang, Z. D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.; Kageyama, H.; Uchimoto, Y. High energy density rechargeable magnesium battery using earth-abundant and non-toxic elements. *Sci. Rep.* 2014, *4*, 5622.
- Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen, C.; Yang, J.; Hwang, B.-J. An ultrafast rechargeable aluminium-ion battery. *Nature* 2015, 520 (7547), 324–328.
- Reddy, M. A.; Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem.
   2011, 21 (43), 17059–17062.
- 11. Zhao, X.; Zhao-Karger, Z.; Wang, D.; Fichtner, M. Metal oxychlorides as cathode materials for chloride ion batteries. *Angew. Chem.* **2013**, *125* (51),

13866-13869.

- Rongeat, C.; Reddy, M. A.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chem. A* 2014, 2 (48), 20861–20872.
- 13. Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H.; Tomoki, U.; Toshiki, W.; Koji, A.; Yoshiharu, U. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, 9 (1), 406–412.
- Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Munnangi, A. R.; Clemens, O. Fluoride ion batteries–past, present, and future. *J. Mater. Chem. A* 2021, 9 (10), 5980–6012.
- 15. Xiao, A. W.; Galatolo, G.; Pasta, M. The case for fluoride-ion batteries. *Joule* 2021, 5 (11), 2823–2844.
- Yoshinari, T.; Zhang, D.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Matsunaga, T.; Amezawa, K.; Uchimoto, Y. Kinetic analysis and alloy designs for metal/metal fluorides toward high rate capability for all-solid-state fluoride-ion batteries. *J. Mater. Chem. A* 2021, 9 (11), 7018–7024.
- Haruyama, J.; Okazaki, K. I.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji,
   T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and
   Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. ACS Appl.
   Mater. Interfaces 2020, 12 (1), 428–435.
- Clemens, O.; Rongeat, C.; Munnangi, A. R.; Giehr, A.; Fichtner, M.; Hahn, H.
   Electrochemical fluorination of perovskite type BaFeO<sub>2.5</sub>. *Dalton Trans.* 2014, 43 (42), 15771–15778.
- 19. Nowroozi, M. A.; de Laune, B.; Clemens, O. Reversible Electrochemical Intercalation and Deintercalation of Fluoride Ions into Host Lattices with

Schafarzikite-Type Structure. ChemistryOpen 2018, 7 (8), 617-623.

- Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O. LaSrMnO<sub>4</sub>: Reversible Electrochemical Intercalation of Fluoride Ions in the Context of Fluoride Ion Batteries. *Chem. Mater.* 2017, 29 (8), 3441–3453.
- Wang, Y.; Yamamoto, K.; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; Cao, Z.; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion Substitution at Apical Sites of Ruddlesden–Popper-type Cathodes toward High Power Density for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2022, *34* (2), 609–616.
- 22. Nowroozi, M. A.; Ivlev, S.; Rohrer, J.; Clemens, O. La<sub>2</sub>CoO<sub>4</sub>: a new intercalation based cathode material for fluoride ion batteries with improved cycling stability. *J. Mater. Chem. A* **2018**, *6* (11), 4658–4669.
- 23. Liu, C.; Neale, Z. G.; Cao, G. Understanding electrochemical potentials of cathode materials in rechargeable batteries. *Mater. Today* **2016**, *19* (2), 109–123.
- 24. Miki, H.; Yamamoto, K.; Cao, S.; Matsunaga, T.; Kumar, M.; Thakur, N.; Sakaguchi, Y.; Watanabe, T.; Iba, H.; Kageyama, H.; Uchimoto, Y. Accelerated fluoride-ion intercalation/deintercalation in a layered-perovskite cathode by controlling the interlayer distance for fluoride-ion batteries. Solid State Ionics 2024, 406, 116480.
- Miki, H.; Yamamoto, K.; Nakaki, H.; Yoshinari, T.; Nakanishi, K.; Nakanishi, S.; Iba, H.; Miyawaki, J.; Harada, Y.; Kuwabara, A.; Wang, Y.; Watanabe, T.; Matsunaga, T.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Double-Layered Perovskite Oxyfluoride Cathodes with High Capacity Involving O–O Bond Formation for Fluoride-Ion Batteries. J. Am. Chem. Soc. 2024, 146 (6), 3844–3853.
- 26. Assat, G.; Tarascon, J.-M. Fundamental understanding and practical challenges of anionic redox activity in Li-ion batteries. *Nat. Energy* **2018**, *3* (5), 373–386.
- 27. Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y. S.;

Edstrom, K.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Chargecompensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* **2016**, *8* (7), 684–691.

- Kawai, K.; Shi, X.-M.; Takenaka, N.; Jang, J.; de Boisse, B. M.; Tsuchimoto, A.; Asakura, D.; Kikkawa, J.; Nakayama, M.; Okubo, M. Kinetic square scheme in oxygen-redox battery electrodes. *Energy Environ. Sci.* 2022, *15* (6), 2591–2600.
- Van Tendeloo, G.; Garlea, O.; Darie, C.; Bougerol-Chaillout, C.; Bordet, P. The fine structure of YCuO<sub>2+x</sub> delafossite determined by synchrotron powder diffraction and electron microscopy. *J. Solid State Chem.* 2001, *156* (2), 428–436.
- Cava, R. J.; Zandbergen, H.; Ramirez, A.; Takagi, H.; Chen, C.; Krajewski, J.;
   Peck Jr, W.; Waszczak, J. V.; Meigs, G.; Roth, R. S.; Schneemeyer, L. F. LaCuO<sub>2.5+x</sub> and YCuO<sub>2.5+x</sub> delafossites: materials with triangular Cu<sup>2+δ</sup> planes.
   J. Solid State Chem. 1993, 104 (2), 437–452.
- Zhang, N.; Gong, H. P-type transparent LaCuOS semiconductor synthesized via a novel two-step solid state reaction and sulfurization process. *Ceram. Int.* 2017, 43 (8), 6295–6302.
- Heubnera, C.; Heidena, S.; Schneiderb, M.; Michaelisa, A. In-situ preparation and electrochemical characterization of submicron sized NaFePO<sub>4</sub> cathode material for sodium-ion batteries. *Electrochim. Acta* 2017, 233, 78–84.
- Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. Z. Kristallogr. Cryst. Mater. 2014, 229 (5), 345–352.
- Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537–541.

- 35. Nishimura, S., *PyAbstantia*, https://shinichinishimura.github.io/pyabst/ (accessed 2024-05-17).
- 36. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276.
- Marquardt, M. A.; Ashmore, N. A.; Cann, D. P. Crystal chemistry and electrical properties of the delafossite structure. *Thin Solid Films* 2006, 496 (1), 146–156.
- Ito, Y.; Koto, K.; Yoshikado, S.; Ohachi, T.; Kanamaru, F.; Mukoyama, T. Variable-temperature X-ray diffraction analysis of the behavior of the mobile fluorine ions in a superionic conductor, β-PbF<sub>2</sub>. *J. Solid State Chem.* **1991**, *95* (1), 94–98.
- Berastegui, P.; Hull, S. Structure and conductivity of some fluoride ion conductors. *Solid State Ionics* 2002, 154, 605–608.
- Wang, Y.; Takami, T.; Li, Z.; Yamamoto, K.; Matsunaga, T.; Uchiyama, T.; Watanabe, T.; Miki, H.; Inoue, T.; Iba, H.; Mizutani, U.; Sato, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Oxyfluoride Cathode for All-Solid-State Fluoride-Ion Batteries with Small Volume Change Using Three-Dimensional Diffusion Paths. *Chem. Mater.* 2022, *34* (23), 10631–10638.
- Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Reversible and Fast (De)fluorination of High-Capacity Cu<sub>2</sub>O Cathode: One Step Toward Practically Applicable All-Solid-State Fluoride-Ion Battery. *Adv. Energy Mater.* 2021, *11* (45), No. 2102285.
- House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K. J.; Roberts, M. R.; Bruce, P. G. Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes. *Nature* 2020, *577* (7791), 502–508.
- 43. House, R. A.; Rees, G. J.; Pérez-Osorio, M. A.; Marie, J.-J.; Boivin, E.;

Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O<sub>2</sub> trapped in the bulk. *Nat. Energy* **2020**, *5* (10), 777–785.

- 44. Lu, J.; Chung, S. C.; Nishimura, S.; Yamada, A. Phase Diagram of Olivine Na<sub>x</sub>FePO<sub>4</sub> (0 < x < 1). *Chem. Mater.* 2013, 25 (22), 4557–4565.
- Xia, H.; Lu, L.; Ceder, G. Li diffusion in LiCoO<sub>2</sub> thin films prepared by pulsed laser deposition. *J. Power Sources* 2006, *159* (2), 1422–1427.
- 46. Aurbach, D.; Levi, M. D.; Levi, E.; Teller, H.; Markovsky, B.; Salitra, G.; Heider, U.; Heider, L. Common electroanalytical behavior of Li intercalation processes into graphite and transition metal oxides. *J. Electrochem. Soc.* 1998, 145 (9), 3024.
- Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater*. 2013, *1* (1), 011002.
- Sakuda, A.; Ohara, K.; Kawaguchi, T.; Fukuda, K.; Nakanishi, K.; Arai, H.; Uchimoto, Y.; Ohta, T.; Matsubara, E.; Ogumi, Z. A reversible rocksalt to amorphous phase transition involving anion redox. *Sci. Rep.* 2018, 8 (1), 15086.
- 49. Nagao, K.; Nagata, Y.; Sakuda, A.; Hayashi, A.; Deguchi, M.; Hotehama, C.; Tsukasaki, H.; Mori, S.; Orikasa, Y.; Yamamoto, K.; Uchimoto, U.; Tatsumisago M. A reversible oxygen redox reaction in bulk-type all-solid-state batteries. *Sci. Adv.* 2020, *6* (25), eaax7236.
- 50. Miki, H.; Matsunaga, T.; Li, Z.; Cao, Z.; Yamamoto, K.; Kumar, M.; Thakur, N.; Watanabe, T.; Iba, H.; Kobayashi, S.; Kawaguchi, S.; Ikeda, K.; Hagihara, M.; Kamiyama, T.; Kuwabara, A.; Kageyama, H.; Maeda, K.; Uchimoto, Y. Fluoride ion storage and conduction mechanism in fluoride ion battery cathode, Ruddlesden-Popper-type layered perovskite La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> crystal. *Inorg. Chem.* 2024, submitted.

- 51. Kaindl, G.; Strebel, O.; Kolodziejczyk, A.; Schäfer, W.; Kiemel, R.; Lösch, S.; Kemmler-Sack, S.; Hoppe, R.; Müller, H.; Kissel, D. Correlation between oxygen-hole concentration and Tc in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> from Cu-L<sub>III</sub> X-ray absorption. *Phys. B* **1989**, *158* (1-3), 446–449.
- 52. Bianconi, A.; Castellano, A. C.; De Santis, M.; Rudolf, P.; Lagarde, P.; Flank, A.; Marcelli, A. L<sub>2, 3</sub> xanes of the high T<sub>c</sub> superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>≈7</sub> with variable oxygen content. *Solid State Commun.* 1987, 63 (11), 1009–1013.
- 53. Huang, M.-J.; Deng, G.; Chin, Y.; Hu, Z.; Cheng, J.-G.; Chou, F.; Conder, K.; Zhou, J.-S.; Pi, T.-W.; Goodenough, J. Determination of hole distribution in Sr<sub>14-x</sub>Ca<sub>x</sub>Cu<sub>24</sub>O<sub>41</sub> using soft x-ray absorption spectroscopy at the Cu L<sub>3</sub> edge. *Phys. Rev. B* 2013, *88* (1), 014520.
- Ono, Y.; Yui, Y.; Hayashi, M.; Asakura, K.; Kitabayashi, H.; Takahashi, K. I. Electrochemical properties of NaCuO<sub>2</sub> for sodium-ion secondary batteries. *ECS Trans.* 2014, 58 (12), 33.
- 55. De Nadai, C.; Demourgues, A.; Grannec, J.; de Groot, F. L<sub>2,3</sub> x-ray absorption spectroscopy and multiplet calculations for KMF<sub>3</sub> and K<sub>2</sub>NaMF<sub>6</sub> (M = Ni, Cu). *Phys. Rev. B* 2001, *63* (12), 125123.
- 56. Cava, R. J.; Zandbergen, H.; Ramirez, A.; Takagi, H.; Chen, C.; Krajewski, J.;
  Peck Jr, W.; Waszczak, J. V.; Meigs, G.; Roth, R. S. LaCuO<sub>2.5+x</sub> and YCuO<sub>2.5+x</sub> delafossites: materials with triangular Cu<sup>2+δ</sup> planes. *J. Solid State Chem.* 1993, 104 (2), 437–452.
- 57. Frati, F.; Hunault, M. O. J. Y.; de Groot, F. M. F. Oxygen K-edge X-ray Absorption Spectra. *Chem. Rev.* **2020**, *120* (9), 4056–4110.
- 58. Jiang, P.; Prendergast, D.; Borondics, F.; Porsgaard, S. Giovanetti, L.; Pach, E.; Newberg, J.; Bluhm, H.; Besenbacher, F.; Salmeron, M. Experimental an theoretical investigation of the electronic structure of Cu<sub>2</sub>O and CuO thin films on Cu(110) using X-ray photoelectron and absorption spectroscopy. *J. Chem. Phys.* 2013, *138* (2), 024704.

- Mizokawa, T.; Fujimori, A.; Namatame, H.; Takeda, Y.; Takano, M. Electronic structure of tetragonal LaCuO<sub>3</sub> studied by photoemission and x-ray-absorption spectroscopy. *Phys. Rev. B* 1998, *57* (16), 9550.
- 60. Gent, W. E.; Abate, I. I.; Yang, W.; Nazar, L. F.; Chueh, W. C. Design rules for high-valent redox in intercalation electrodes. *Joule* **2020**, *4* (7), 1369–1397.
- Yamamoto, K.; Zhou, Y.; Yabuuchi, N.; Nakanishi, K.; Yoshinari, T.; Kobayashi, T.; Kobayashi, Y.; Yamamoto, R.; Watanabe, A.; Orikasa, Y.; Tsuruta, K.; Park, J.; Byon, H. R.; Tamenori, Y.; Ohta, T.; Uchimoto, Y. Charge Compensation Mechanism of Lithium-Excess Metal Oxides with Different Covalent and Ionic Characters Revealed by *Operando* Soft and Hard X-ray Absorption Spectroscopy. *Chem. Mater.* 2019, *32* (1), 139–147.

# Chapter 4 Extending Exploration on Fluoride-Ion (De)Insertion Behaviors of the Ruddlesden– Popper-Type Cathode Material La<sub>2</sub>NiO<sub>4+d</sub>

All-solid-state fluoride ion batteries (FIBs) have been considered as a potential next-generation energy storage device and have attracted various attention in recent years. Since FIBs are in their nascent stages, it is crucial to develop high-performance electrode materials to advance FIB technology. The intercalation-type cathode materials have received much attention due to their structural stability and relatively small volume change during topotactic fluorination process. Recent research has demonstrated the topotactic fluorination behavior in the Ruddlesden-Popper-type cathode material La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> which exhibits a high capacity of 200 mAh g<sup>-1</sup>. This study proves the high performance of Ruddlesden–Popper-type materials by using oxygen redox reactions. However, the complex structure and low theoretical capacity of La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> (~90 mAh g<sup>-1</sup>) indicate that there is still room for improvement in the capacity of these kind of materials. Herein, we extend our investigation of the fluorination behaviors of Ruddlesden-Popper-type cathode material La<sub>2</sub>NiO<sub>4+d</sub> by using both cationic redox (Ni) and anionic redox (O) for charge compensation, allowing the host lattice to accommodate excess fluoride ions to achieve a reversible capacity over 250 mAh g<sup>-1</sup>. The topotactic (de)fluorination processes are proved by the X-ray diffraction (XRD) measurements. Moreover, the reversible Ni and O redox reaction mechanisms are elucidated by X-ray absorption spectroscopy (XAS) measurements. The excessive fluoride-ion insertion leads to the formation of O-O bond, which is reversible after discharging. We believe that this study can exploit the potential of Ruddlesden–Popper-type cathode materials to realize high-performance applications in all-solid-state FIBs.

# 4.1 Introduction

All-solid-state fluoride-ion batteries (FIBs) have been regarded as one of promising alternates for lithium-ion batteries (LIBs).<sup>1-3</sup> The use of monovalent F anions ( $F^-$ ) as charge carriers enables significant electrochemical stability, owing to the high electronegativity of F element. Furthermore, it is possible to achieve outstanding overall energy density due to the multi-electron reactions of various metal/metal fluorides (M/MF<sub>x</sub>). Previous studies have shown that all-solid-state FIBs using M/MF<sub>x</sub> electrodes could exhibit high theoretical energy capacities.<sup>3-5</sup> However, practical applications have encountered challenges within two-phase-type M/MF<sub>x</sub> conversion reactions, mainly due to the substantial lattice mismatch between metal and metal fluorides. These mismatches result in significant strain energy and sluggish phase-transition kinetics. Moreover, the volumetric changes during phase-transition reactions can lead to delamination between active materials and solid electrolyte, significantly affecting the long-term cycling performance of the all-solid-state FIBs.<sup>5, 6</sup>

Intercalation-type cathode materials, which follow a topotactic fluorination mechanism, have also been intensively researched in recent years.<sup>7, 8</sup> These materials possess robust frameworks that enable highly reversible fluoride-ion (de)intercalation without substantial volumetric changes. In particular, the Ruddlesden–Popper-type materials ( $A_{n+1}B_nO_{3n+1}$ , A = La, Sr, etc., B = transition metals, n = 1, 2, 3, ...) are so far found to be the most suitable host for the reversible intercalation of fluoride ions because of the interstitial anion sites within the rock-salt-related layers in the structure.<sup>9–12</sup> In previous studies, we demonstrated that F<sup>-</sup> can reversibly (de)intercalate within the lattice of the Ruddlesden–Popper-type materials LaSrMnO4F, Sr<sub>2</sub>MnO<sub>3</sub>F<sub>2</sub>, and Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>.<sup>13, 14</sup> However, the limited theoretical capacities (74 mAh g<sup>-1</sup> of LaSrMnO<sub>4</sub>F, 85 mAh g<sup>-1</sup> of Sr<sub>2</sub>MnO<sub>3</sub>F<sub>2</sub>, and 118 mAh g<sup>-1</sup> of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>) have restricted their further applications. Therefore, expanding the capacity of Ruddlesden–Popper-type cathode materials is considered worthy of being further

studied.

Previously, anion redox reactions have been extensively studied in LIBs and sodium-ion batteries (SIBs) as an approach for increasing practical capacity.<sup>15–18</sup> The charge compensation by both the transition metal redox and anion redox allows the electrode to accommodate excessive charge carriers, which results in a higher capacity than that obtained by only metal redox. The electrochemical performances and reaction mechanism of the anion redox have been reported in rigorous studies for LIB and SIB cathodes.<sup>19–22</sup> The oxygen redox behaviors have also been demonstrated in our recent research on La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7–8</sub>F<sub>2</sub> cathode for FIBs.<sup>23</sup> The excessive F<sup>-</sup> are expected to be inserted into the perovskite slabs, and the reversible oxygen redox will elevate the cathode capacity. However, the heavy formula weight of La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7–8</sub>F<sub>2</sub> results in a theoretical capacity of only 90 mAh g<sup>-1</sup> (2 F<sup>-</sup>). In the Mn-based Ruddlesden–Popper-type material LaSrMnO4 (n=1 in A<sub>n+1</sub>B<sub>n</sub>O<sub>3n+1</sub>), although it shows high theoretical capacity (154 mAh g<sup>-1</sup> corresponding to 2 F<sup>-</sup>), it only exhibited a discharge capacity of 30 mAh g<sup>-1</sup> when charged to 3 V.<sup>8</sup> This indicates that LaSrMnO4 may undergo severe irreversible reactions at high voltages, leading to structural degradation.

In this study, we investigated the electrochemical performances of La<sub>2</sub>NiO<sub>4+d</sub> as a cathode material for all-solid-state FIBs. The oxygen redox was observed at a high state of charge, allowing excessive amount of fluoride ions to be inserted into the host lattice, which provided a charge capacity of 275 mAh g<sup>-1</sup> (corresponding to 4.1 F<sup>-</sup>). The fluorination/defluorination processes achieved high reversibility through a forced discharge to -1.5 V against Pb/PbF<sub>2</sub> anode. La<sub>2</sub>NiO<sub>4+d</sub> also exhibited a volumetric capacity of 1863 mAh cm<sup>-3</sup>, surpassing those of recently reported Li-excess oxide cathode materials.<sup>24–27</sup> The XRD measurements revealed that two phase coexisted during the fluorination process. Additionally, XAS measurements demonstrated that the charge compensation mechanism involved both nickel and oxygen redox reactions. The fluoride ions were inserted into not only the rock-salt interstitial layers but also combined with Ni in the perovskite slabs, resulting in the O–O bond formation.

Although the exact structure of charged  $La_2NiO_{4+d}$  and a deeper understanding of the oxygen redox mechanism are required to be clarified by further characterization, our study offered valuable insights for selecting high-capacity FIB cathode materials.

# 4.2 Experimental

#### 4.2.1 Synthesis of the materials

La<sub>2</sub>NiO<sub>4+d</sub> was synthesized by a solid-state reaction as described in previous research, and it has an approximate composition of La<sub>2</sub>NiO<sub>4.12</sub> (d = 0.12).<sup>28</sup> Stoichiometric amounts of La<sub>2</sub>O<sub>3</sub> (Wako, 99.99 %) and NiO (Kojundo, 99.9 %) were mixed in a mortar and pestle, then pelletized in an Argon-filled glovebox. The pellet was then sintered in air at 1200 °C for 12 h, and ground into powder. Twice sintering and grinding steps were performed to achieve a single phase.

Chemical fluorination was carried out to insert fluorine into the as-prepared La<sub>2</sub>NiO<sub>4+d</sub>. Poly(vinylidene fluoride) (CH<sub>2</sub>CF<sub>2</sub>)<sub>n</sub> (PVDF; Sigma-Aldrich) was selected as the fluorination agent. The as-prepared La<sub>2</sub>NiO<sub>4+d</sub> and PVDF were placed in separate alumina boats, covered with a sager in an electric muffle furnace, and heated at 370 °C for 24 h in air.<sup>23</sup> In addition, a mixture of the oxide with the PVDF was also heated under the same condition as previously reported.<sup>29</sup> The ratio of La<sub>2</sub>NiO<sub>4+d</sub> to PVDF was 2:1 and 1:1 (refer to F = 1 and F = 2, respectively). All the operations were carried out in an Ar-filled glove box.

Solid electrolyte  $La_{0.9}Ba_{0.1}F_{2.9}$  (LBF) was synthesized by the mechanochemical method, as described in Section 2.2.1.<sup>3</sup> The cathode composite ( $La_2NiO_{4+d}/LBF/VGCF$  = 3: 6: 1 in weight ratio) and anode composite (Pb/PbF<sub>2</sub>/LBF/VGCF = 2 :3: 4: 1 in weight ratio) were prepared by ball milling, which has been mentioned in Section 2.2.1.

#### 4.2.2 Battery assembly

Electrochemical tests were carried out using bulk-type cells, as described in Section 2.2.2. Firstly, LBF powder was put into a poly(ether-ether-ketone) (PEEK) insulator (10 mm diameter) and pressed under a pressure of 100 MPa for 5 min. Then, cathode composite, anode composite was placed on the opposite sides of the LBF pellet. Finally, the cell was compressed under a pressure of 360 MPa for 5 min. All the assembling processes were carried out in an Ar-filled glove box with oxygen and moisture contents of less than 0.2 ppm. Finally, the cell was compressed under a pressure of 360 MPa for 5 min.

## 4.2.3 Electrochemical measurements

The galvanostatic charge-discharge tests and the Galvanostatic Intermittent Titration Technique (GITT) measurement were evaluated by HJ1020mSD8 battery testing systems (Hokuto Denko, Japan) with a cut-off voltage range of -1.5~2.5 V vs. Pb/PbF<sub>2</sub> at 140 °C without exposed to air. For the GITT, the cell was relaxed at open circuit voltage (OCV) for 12 h to allow it to reach a quasi-equilibrium state after each galvanostatic step, which lasted up to a capacity equal to 0.2 F<sup>-</sup> at a current density of 10 mA g<sup>-1</sup>. The apparent F<sup>-</sup> diffusion coefficients were calculated from the GITT results using the equation mentioned in Chapter 3.

### 4.2.4 Characterizations

XRD profiles of the material were collected using an X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å, Rigaku Ultima IV, Japan). Synchrotron X-ray powder diffraction data were collected at room temperature in Ar atmosphere, at the BL02B2 beamline in SPring-8 ( $\lambda = 0.4133$  Å, Hyogo, Japan). The pristine powder sample was characterized at BL02B2 beamline with an energy of 20 keV. The diffractometer was equipped with six MYTHEN silicon micro-strip photon-counting detectors (Dectris Ltd., Baden, Switzerland), and the measurements were performed in Debye-Scherrer transmission geometry. Rietveld refinement was performed using Jana 2006 software.<sup>30</sup> The crystallographic information was supported by VESTA.<sup>31</sup> The morphology of the as-prepared material and energy dispersive spectroscopy spectra (EDS) were characterized using a SU3400 scanning electron microscope (SEM, Hitachi, Japan).

X-ray absorption spectroscopy (XAS) measurements for Ni K-edge, Ni L-edge, F K-edge, and O K-edge were conducted at the BL14B2 and BL27SU beamlines in SPring-8, respectively. To prepare the samples during the first cycle and the 6th cycle (after activation) for ex-situ measurements, all the cells were charged and discharged at a current density of 10 mA  $g^{-1}$  and then transferred from an Ar-filled glovebox. The measurements were carried out under vacuum condition. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using the ATHENA software package.<sup>32</sup>

## 4.3 Results and discussion

#### 4.3.1 Fluoride ion (de)intercalation behavior of La<sub>2</sub>NiO<sub>4+d</sub> before activation

Rietveld refinement revealed that a pure tetragonal La<sub>2</sub>NiO<sub>4.12</sub> (space group: *I4/mmm*) with Ruddlesden–Popper structure was obtained by solid-state reaction, as shown in **Figure 4.1** with lattice parameters of a = b = 3.8614(0) Å and c = 12.6854(2) Å. There was 0.112 O atom occupying the rock-salt interstitial layers, and the oxygen occupancy of the apical site in the perovskite unit was 0.911, where some anionic vacancies were generated (**Table 4.1**). The oxygen in this structure is considered to show high mobility, so that a portion of oxygen diffused from the apical sites to the interstitial layers.<sup>33, 34</sup> The morphologies of the La<sub>2</sub>NiO<sub>4+d</sub>/LBF/VGCF cathode composite are shown in **Figure 4.2**. The LBF and La<sub>2</sub>NiO<sub>4+d</sub> particles were distributed homogeneously after ball milling, and the carbon fibers were interspersed among the particles, as can be distinguished from SEM-EDS images.

 $La_{0.9}Ba_{0.1}F_{2.9}$  was utilized as a solid electrolyte for the fabrication of all-solid-state fluoride-ion cells, because it could offer a reasonable ionic conductivity of ~8×10<sup>-4</sup> S cm<sup>-1</sup> and an extensive electrochemical stability window exceeding 5 V, which facilitated a comprehensive assessment of the electrochemical properties of La<sub>2</sub>NiO<sub>4+d</sub> cathode material from a broad voltage range.<sup>35</sup> Furthermore, an excessive amount of Pb/PbF<sub>2</sub> was used as anode material for fabricating a "fluoride-ion half-cell" due to its outstanding inherent conductivity.<sup>36-38</sup> The electrochemical properties of La<sub>2</sub>NiO<sub>4+d</sub> were measured between  $-1.5\sim2.5$  V vs. Pb/PbF<sub>2</sub> using bulk-type cells. To optimize both ionic and electronic conductivities, the electrodes were mixed with solid electrolyte LBF and VGCF.

As shown in **Figure 4.3a**, the La<sub>2</sub>NiO<sub>4+d</sub> cathode exhibited a capacity of 292 mAh  $g^{-1}$  with a slope between 0.5 V and 1.3 V and a wide plateau at 1.5 V, following by a plateau at approximately 2.4 V during the 1st charge process. A capacity of 211 mAh  $g^{-1}$  was provided in the subsequent discharge process with two voltage plateaus at 0.7 V and -0.8 V. The irreversible capacity during the first cycle might arise from the partial oxygen release at high voltage, which is supported by Ni *L*-edge XAS discussed later, as reported in La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode for FIBs and some Li-rich cathodes for LIBs.<sup>23, 39, 40</sup> Assuming that all the empty interstitial anion sites and apical vacancies are filled with F<sup>-</sup>, the theoretical capacity of La<sub>2</sub>NiO<sub>4+d</sub> is 126 mAh  $g^{-1}$ , according to the following reaction equation (4–1):

$$La_2NiO_{4.12} + 1.88 F^- \rightarrow La_2NiO_{4.12}F_{1.88} + 1.88 e^-$$
 (4 - 1)

However, La<sub>2</sub>NiO<sub>4+d</sub> exhibited about twice the theoretical capacity and had excellent reversibility during charge-discharge processes. Our recent study on the Ruddlesden–Popper-type La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode for FIBs used reversible oxygen redox reaction to achieve extended capacity.<sup>23</sup> Therefore, we speculated that in addition to the intercalation behavior into the interstitial layers, F<sup>-</sup> can also be inserted into other sites within the structure. Apart from the Ni redox reaction, the reversible oxygen redox reaction also participated in charge compensation.

The La<sub>2</sub>NiO<sub>4+d</sub> cathode showed a charge capacity of 253 mAh  $g^{-1}$  with voltage plateaus at -0.5 V and 1.3 V, and a discharge capacity of 241 mAh  $g^{-1}$  with voltage plateaus at 0.7 V and -0.8 V during the 2nd cycle. The charge curve shape of the 2nd cycle differed from that of the 1st cycle, whereas the discharge curve shape of the 2nd cycle was similar to that of the 1st cycle. The charge/discharge capacities consistently increased during the initial 5th cycles. Notably, the shape of charge/discharge curves

remained consistent with the 2nd cycle. A comparison of the average charge/discharge voltages indicated a significant deviation solely between the 1st and the 2nd charging processes (Figure 4.3b). These findings suggested that some structural distortion occurred during the 1st cycle, which was associated with the irreversible reactions.<sup>41</sup>

For an in-depth understanding the crystal structure evolution upon fluoride-ion insertion and extraction, XRD measurements ( $\lambda = 1.5406$  Å) were carried out during the 1st cycle. As shown in Figure 4.4a, all the diffraction patterns for the cathode composite can be indexed by La<sub>2</sub>NiO<sub>4+d</sub> (space group: I4/mmm) and the solid electrolyte LBF (space group:  $P\overline{3}c1$ ) although some LaOF impurity peaks emerged during the ball milling process. Previous studies revealed that the electrochemical fluorination of La<sub>2</sub>NiO<sub>4+d</sub>, possessing a capacity of 155 mAh g<sup>-1</sup>, underwent a twophase reaction.<sup>10</sup> In this work, after charging up to x = 2, two phases (except LBF) can be observed: the first phase was similar to the original La<sub>2</sub>NiO<sub>4+d</sub> and the second phase (diffraction peaks located at  $2\theta = 29.5^{\circ}$ ,  $37.9^{\circ}$ ,  $41.2^{\circ}$ , and  $42.8^{\circ}$ ) was a fluorine-rich phase  $La_2NiO_{4+d}F_x$  with a orthorhombic space group *Fmmm*, which was derived from the I4/mmm symmetry for a  $\sqrt{2} \times \sqrt{2} \times 1$  supercell, and its large expansion along caxis was indicative for the fluorination of the material (c = 15.1 Å vs. c = 12.7 Å of La<sub>2</sub>NiO<sub>4+d</sub>).<sup>10</sup> The amplified La<sub>2</sub>NiO<sub>4+d</sub> $F_x$  diffraction peaks and the diminished La<sub>2</sub>NiO<sub>4+d</sub> peak intensity upon charging indicated that more active material was involved in the fluorination process. Although the empty sites in the La<sub>2</sub>NiO<sub>4+d</sub> lattice can accommodate up to 1.88 F<sup>-</sup> per unit cell, a surprising capacity of 4.4 F<sup>-</sup> was observed at the 1st fully charged state. A lack of a third phase during the 1st charge process implied that the excessive fluoride ions could be inserted into the perovskite layer, as was found in in the research on La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode material for FIBs,<sup>23</sup> which will be discussed in the following section. Additionally, the portion exceeding the theoretical capacity caused almost no noticeable volume change. After the discharging process, the La<sub>2</sub>NiO<sub>4+d</sub> diffraction patterns recovered, and the peaks attributed to the fluorinated phase disappeared, demonstrating the reversible F<sup>-</sup>

insertion and extraction within the La<sub>2</sub>NiO<sub>4+d</sub> host lattice. Regarding to the fine structure after charging, we tried chemical fluorination method using PVDF as fluorination agent to prepare the pure phase of La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub>. As shown in **Figure 4.5**, no pure phase of the *c*-axis expanded fluorination product was obtained after the chemical fluorination reactions. It has been reported in previous research that the fluorine replaces the apical O in La<sub>2</sub>NiO<sub>4+d</sub> (space group: *I*4/*mmm*) and eventually form La<sub>2</sub>NiO<sub>3</sub>F<sub>2</sub> (space group: *Cccm*),<sup>29</sup> which is different from the composition and configuration of the fluorinated product obtained in this experiment. Therefore, chemical fluorination is a significant issue to be investigated in the future.

### 4.3.2 Charge compensation mechanism of La<sub>2</sub>NiO<sub>4+d</sub> before activation

To investigate the electronic structures during F<sup>-</sup> insertion/extraction, a series of ex-situ electrodes were examined by XAS measurements. Figure 4.6a shows the Ni L3edge XAS results during the 1st cycle. The La M-edge peak at approximately 850.7 eV was regarded as the calibrant because the Lanthanum in both electrode and solid electrolyte didn't participate in charge compensation. The intensity of the absorption peak at 855 eV increased and it shifted towards higher energy at an early state of charge (x = 1), which was related to the Ni<sup>2+</sup>/Ni<sup>3+</sup> oxidation reaction, implying an increase in Ni 3d hole states.<sup>42</sup> Previous studies have demonstrated that the Ni oxidation state can be qualitatively evaluated by the Ni L-edge, where the ratio  $L_3$  (high energy)/ $L_3$  (low energy) is positively correlated with the Ni valence state.<sup>43–45</sup> As shown in Figure 4.6b, the  $L_{3 \text{ high}}/L_{3 \text{ low}}$  ratio significantly increased from pristine state to x = 1, but remained almost constant until the fully-charged state. This suggested that Ni ions were oxidized from  $Ni^{2+}$  to  $Ni^{3+}$  in the early process and remained  $Ni^{3+}$  in the subsequent stages. However, the ratio of  $L_{3 \text{ high}}/L_{3 \text{ low}}$  after discharging was lower than that of the pristine state (Figure 4.6b), indicating the Ni valence were reduced compared to that of the pristine state, which was attributed to partial oxygen release during the 1st cycle.

On the other hand, as shown in Figure 4.6c, there was an absorption peak at 529

eV in the O K-edge spectrum of La<sub>2</sub>NiO<sub>4+d</sub>, which was attributed to the transition from O 1s to the hybridized Ni 3d–O 2p state.<sup>46</sup> This peak shifted towards lower energy and significantly increased at an early state of charge (x = 1). This change was related to the strong hybridization of Ni 3d and O 2p, indicating that Ni was oxidized to Ni<sup>3+</sup> upon charging.<sup>43, 46</sup> Notably, a new peak emerged at 531.2 eV and increased at x = 2. This peak was similar to the O redox behavior in Li-rich cathode materials for LIBs, <sup>18, 21, 47</sup> and in the Ruddlesden-Popper-type La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-δ</sub>F<sub>2</sub> cathode for FIBs, which was attributed to the formation of O-O bonds in the lattice.<sup>23</sup> After discharging, the shape of the O K-edge absorption edge didn't return to the state before charging, especially the absorption peak at 529 eV disappeared, and a weak shoulder peak at 530 eV emerged instead, which was close to the Ni<sup>+</sup> reference LaNiO<sub>2</sub> (Figure 4.6c).<sup>48, 49</sup> The observed change suggested a weakened Ni 3d and O 2p hybridization with a decreased Ni valence state. It was observed in the XRD results (Figure 4.4) that the diffraction patterns of La<sub>2</sub>NiO<sub>4+d</sub> became broader and weaker after the 1st discharge process. The Ni valence state at 1st discharged state was lower than its pristine state (+2.24), and this reduction suggested that some irreversible structural change (e.g. oxygen vacancy formation) occurred during the 1st cycle.

The variation tendency of F *K*-edge XAS results during the 1st cycle is shown in **Figure 4.7**. All the samples exhibited similar absorption edge features ( $\geq 687 \text{ eV}$ ) due to the high fluorine content in LBF solid electrolyte. During charging process, a preedge peak emerged at approximately 686 eV and increased upon charging, corresponding to the formation of Ni–F bond as observed in the NiF<sub>2</sub> reference.<sup>50</sup> This indicated that the excessive F<sup>-</sup> can be inserted into the perovskite slabs, as observed in La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode.<sup>23</sup> Although it was not clear how the O–O bonds and excessive fluoride ions existed in the charged La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub>, the oxygen redox reaction would lead to a decreased ionic radius, which might create some cavities and irregular sites in the structure.<sup>23, 41</sup> The excessive F<sup>-</sup> were likely to be located in these irregular sites, as was elucidated in La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode in La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode material.<sup>23</sup> To examine the local structure around Ni in the La<sub>2</sub>NiO<sub>4+d</sub>, the EXAFS analysis of the Ni *K*-edge was performed during the 1st cycle (**Figure 4.8**). Two peaks were observed around 1.4 Å and 3.0 Å in the La<sub>2</sub>NiO<sub>4+d</sub> pristine. The intensity of the first coordination shell (1.4 Å) slightly increased at the end of charging process, which corresponded to the coordination number increment of Ni with Ni–F bond formation (Figure 4.7b). In addition, the decrease in the peak intensity at 3.0 Å with the insertion of F<sup>-</sup> suggested an increase in the Debye–Waller factor, indicating an increase in local distortion of the Ni–La bonds.<sup>23</sup>

The reaction mechanism of the 1st cycle is shown in **Figure 4.9**. During the 1st charging process, La<sub>2</sub>NiO<sub>4+d</sub> underwent an intercalation reaction, where both the Ni<sup>2+/3+</sup> redox and oxygen redox contributed to the charge compensation. The interstitial layers in La<sub>2</sub>NiO<sub>4+d</sub> lattice can accommodate approximately 1.88 F<sup>-</sup> which expanded the *c*-axis of the crystal lattice (the volume expansion was about 14 %). The excessive F<sup>-</sup> were inserted into the irregular sites created by oxygen redox within the perovskite slabs, accompanying by the formation of O–O bonds. After discharging, the La<sub>2</sub>NiO<sub>4+d</sub> lattice structure could be retained while some structural distortion and amorphization occurred due to the partial oxygen release. The electronic structure of Ni and O underwent an irreversible change after the 1st cycle, leading to variations in the charge/discharge profiles observed in the subsequent cycles. The electrochemical properties and the reaction mechanism of the La<sub>2</sub>NiO<sub>4+d</sub> after activation will be investigated in the following section.

#### 4.3.3 Fluoride ion (de)intercalation behavior of La<sub>2</sub>NiO<sub>4+d</sub> after activation

The La<sub>2</sub>NiO<sub>4+d</sub>, after the activation process, exhibited robust electrochemical performances. As a result of activation, La<sub>2</sub>NiO<sub>4+d</sub> exhibited similar charge/discharge profiles to those of the 2nd cycle (in the activation process) but achieved a superior charge capacity of 275 mAh g<sup>-1</sup> (corresponding to 4.1 F<sup>-</sup>), with plateaus at -0.25 V and 1.5 V during the charging process, as shown in **Figure 4.10a**. Then it provided a

discharge capacity of 268 mAh g<sup>-1</sup>, with two plateaus at 0.6 V and -0.75 V. La<sub>2</sub>NiO<sub>4+d</sub> maintained a reversible capacity of 217 mAh g<sup>-1</sup> (a capacity retention of 80%) after 20 cycles, with nearly 100 % coulombic efficiency for each cycle (**Figure 4.11a**). Moreover, it showed an excellent rate capability (130 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup>), as shown in Figure 4.11b. These results confirmed the reversibility and strong rate performance of La<sub>2</sub>NiO<sub>4+d</sub> in a wide voltage range. As shown in Figure 4.10b, La<sub>2</sub>NiO<sub>4+d</sub> exhibited a gravimetric capacity of 270 mAh g<sup>-1</sup> and an outstanding volumetric capacity of 1863 mAh cm<sup>-3</sup>, which surpassed the commercial LIB cathode materials, the intercalation-type FIB cathode materials, and was comparable to those of recently reported Li-excess oxide cathode materials.<sup>13, 14, 23, 27, 51–54</sup>

After activation, La<sub>2</sub>NiO<sub>4+d</sub> exhibited a charge capacity that was about twice of theoretical capacity (275 mAh g<sup>-1</sup>, corresponded to 4.1 F<sup>-</sup>), and the above-mentioned results during the 1st cycle suggested that the excessive F<sup>-</sup> were supposed to be inserted into the perovskite slabs in the host lattice. La<sub>2</sub>NiO<sub>4+d</sub> reached a maximum capacity after a five-cycle activation process. To investigate the kinetic properties upon fluoride ion insertion, GITT measurement was carried out after activation, as shown in Figure 4.12. The obtained results indicated that the polarization of open circuit voltage (OCV) for x > 2 was significantly larger than those in the low state of charge. A similar large polarization has been observed in some LIB cathodes and the FIB cathode  $La_{1,2}Sr_{1,8}Mn_2O_{7-\delta}F_2$  including the formation of molecular  $O_2$  within the lattice.<sup>23,55</sup> This large polarization was likely due to the local structural distortions originating from the excessive fluoride ion insertion and the formation of O-O bonds.<sup>23</sup> It was observed that the polarization during discharging process significantly increased at -0.5 V, which might be related to the phase transition during the F<sup>-</sup> extraction process, as we recently reported in CuLaO<sub>2</sub> cathode material (Chapter 3).<sup>56</sup> The apparent F<sup>-</sup> diffusion coefficients for the charging process were estimated to be  $\sim 10^{-13}$  to  $\sim 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> at 140 °C (Figure 4.12b), which were comparable to those of LiCoO<sub>2</sub> at room temperature.<sup>57</sup> Therefore, the high rate capability of La<sub>2</sub>NiO<sub>4+d</sub> was probably associated

with rapid fluoride-ion diffusion in the bulk.

The crystal structure after activation was different from that of the initial cycle, as shown in **Figure 4.13**. The diffraction peak intensities of La<sub>2</sub>NiO<sub>4+d</sub> significantly decreased compared to those of 1st discharged state, indicating an increased degree of amorphization during the activation process. Upon charging, the peak intensities (103 and 110) of La<sub>2</sub>NiO<sub>4+d</sub> gradually diminished, while a weak and broad pattern was found at  $2\theta = 29.4^{\circ}$  in the fully charged state. Considering the structural evolution observed in the 1<sup>st</sup> cycle, this broad pattern can be attributed to the fluorinated phase La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub>. Nevertheless, the large full width at half maximum and low intensity of this pattern implied that this fluorination product was transformed into an amorphous phase. After discharging, the intensities of 103 and 110 diffraction peaks of La<sub>2</sub>NiO<sub>4+d</sub> recovered, although they were weaker than those before charging. Similar reversible structural change between crystalline/amorphous phases has been observed in cathode materials for LIBs.<sup>58, 59</sup>

#### 4.3.4 Charge compensation mechanism of La<sub>2</sub>NiO<sub>4+d</sub> after activation

The charge compensation mechanisms of La<sub>2</sub>NiO<sub>4</sub> after activation were also examined by XAS, as shown in **Figure 4.14**. Similar to the 1st cycle, the absorption peak at 855 eV in Ni  $L_3$ -edge gradually increased upon charging (Figure 4.14a). The peak intensity ratio  $L_3$  high/ $L_3$  low increased significantly in the early stage of fluoride ion insertion ( $x \le 2$ ), and remained almost constant in the subsequent charge process (x > 2, Figure 4.14b). In addition, in the O *K*-edge spectra, the spectrum before charging (x =0) was similar to that of LaNiO<sub>2</sub>. This suggested that the valence state of Ni was close to +1, which was characterized by a weak Ni 3d–O 2p hybridization (Figure 4.14c). A broad pre-edge peak, which corresponded to the transitions from O 1s to the hybridized states of the Ni 3d and O 2p orbitals, was observed at 529 eV at an early stage of charge (x = 1), and then shifted towards lower energy with increased intensities. This result signified the oxidation of Ni<sup>+</sup>/Ni<sup>3+</sup> for 0 < x < 2, which was consistent with the Ni XAS results (Figure 4.14a).<sup>60</sup> Additionally, further fluoride-ion insertion (x > 2) increased the intensities of the O *K*-edge peak at 531.2 eV, indicating the O–O bond formation. In the F *K*-edge spectra (Figure 4.14d), a small pre-edge peak attributed to metal-fluoride bonds can be observed upon fluoride ion insertion beyond x > 2, suggesting the Ni–F bonds in the La<sub>2</sub>NiO<sub>4+d</sub> structure. After discharging, the shape of the Ni, O, and F XAS results recovered to their pre-charging states, suggesting the high reversibility of the La<sub>2</sub>NiO<sub>4+d</sub> cathode material after activation.

In previous studies on Li-rich cathode materials for LIBs, O<sub>2</sub> molecules were found to be trapped in the fully charged lattice structure, as was proved by resonant inelastic X-ray scattering (RIXS) and pair distribution function (PDF) analysis.<sup>47, 55, 61</sup> Similar molecular O<sub>2</sub> species were identified in La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode material at fully charged state.<sup>23</sup> La<sub>2</sub>NiO<sub>4+d</sub> has a similar crystal structure as La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub>, which contains rock salt interstitial layers and perovskite slabs. Therefore, they might exhibit similar oxygen redox reaction mechanisms, and this calls for further analysis such as RIXS and PDF in the future.

## 4.4 Conclusion

In summary, we have demonstrated the reversible electrochemical fluorination of the Ruddlesden-Popper-type La<sub>2</sub>NiO<sub>4+d</sub> cathode material; it exhibited commendable cycle performance with a comparable gravimetric capacity (270 mAh g<sup>-1</sup>) and excellent volumetric capacity (1863 mAh cm<sup>-3</sup>) after activation process. F<sup>-</sup> were inserted into the vacancy sites in the rock-salt interstitial layers, while the excessive F<sup>-</sup> (beyond 2 F<sup>-</sup>) formed Ni–F bonds within the perovskite slabs. After the initial 5 activation cycles, the Ni<sup>+1</sup>/Ni<sup>+3</sup> redox reaction contributed to the charge compensation, and the oxygen redox occurred at high state of charge, which led to the formation of O–O bonds. The (de)fluorination processes maintained high reversibility, although the crystallinity of the active material gradually decreased with cycling. Compared to the cathode materials with similar structures, La<sub>2</sub>NiO<sub>4+d</sub> exhibited superior capacity than Ruddlesden-Poppertype  $La_{1.2}Sr_{1.8}Mn_2O_{7-\delta}F_2$  (~200 mAh g<sup>-1</sup>) and  $LaSrMnO_4F$  (~70 mAh g<sup>-1</sup>).<sup>13, 23</sup> Although the electrochemical performances of  $La_2NiO_{4+d}$  still need to be further improved, and the behavior of oxygen redox calls for detailed investigation in the future,  $La_2NiO_{4+d}$  undeniably presents significant potential as an intercalation-type cathode material for all-solid-state FIBs.



Figure 4.1. (a) Rietveld refinement of as-prepared La<sub>2</sub>NiO<sub>4+d</sub>. La<sub>2</sub>NiO<sub>4+d</sub> adopts *I*4/*mmm* space group, wavelength = 0.4133 Å,  $R_p$  = 5.19 %,  $R_f$  = 3.59 %,  $R_{wp}$  = 7.48 %, GOF = 4.74. (b)

Schematic diagram of the crystal structure.

Atom	Wyckoff Position	x	у	Z	B <sub>iso</sub> / Å <sup>2</sup>	Occupancy
La1	4e	0	0	0.361(0)	0.54 (0)	1
Ni1	2a	0	0	0	0.47(2)	1
01	4c	0	0.5	0	1.32(9)	1
O2	4e	0	0	0.174(0)	1.32(9)	0.948
03	4d	0	0.5	0.25(0)	1.32(9)	0.112

**Table 4.1.** Structural parameters of as-prepared  $La_2NiO_{4+d}$  determined from the Rietveld refinement.

Space group: *I*4/*mmm*;  $R_p$  = 5.19 %,  $R_{wp}$  = 7.48 %,  $R_f$  = 3.59 %, GOF = 4.74; a = 3.8614(0) Å, c = 12.6854(2) Å.



Figure 4.2. SEM-EDS images of the as-prepared  $La_2NiO_{4+d}$  cathode composite. The carbon fibers can be found in SEM image, and  $La_2NiO_{4+d}$  and solid electrolyte LBF can be distinguished by

EDS mapping.



Figure 4.3 (a) Charge/discharge curves during the initial five cycles between -1.5 V and 2.5 V (vs. Pb/PbF<sub>2</sub>) at a current density of 10 mA g<sup>-1</sup> at 140 °C. (b) The average voltage of La<sub>2</sub>NiO<sub>4+d</sub> cathode during the initial five cycles.



**Figure 4.4** (a) XRD patterns of La<sub>2</sub>NiO<sub>4+d</sub> cathode composite during the 1st cycle. The cathode composite contains solid electrolyte LBF, and the diffraction patterns of LBF can be regarded as the calibrant. Red and black broken lines correspond to La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub> oxyfluoride and La<sub>2</sub>NiO<sub>4+d</sub>, respectively. (b) Lattice volume changes of La<sub>2</sub>NiO<sub>4+d</sub> during the 1st cycle in the voltage range between -1.5 V and 2.5 V. x = 2 means the composition La<sub>2</sub>NiO<sub>4+d</sub>F<sub>2</sub>. The data include error bars, which are smaller than the symbols and not visible.



Figure 4.5 (a) XRD patterns after chemical fluorination reactions of La<sub>2</sub>NiO<sub>4+d</sub> using PVDF as fluorination agent. La<sub>2</sub>NiO<sub>4+d</sub> and PVDF were mixed and heated in air at 370 °C for 24 h. (b) Chemical fluorination of La<sub>2</sub>NiO<sub>4+d</sub> with PVDF in two separated heating boats at 370 °C for 24 h

in air.


Figure 4.6 (a) Ni L<sub>3</sub>-edge XAS of La<sub>2</sub>NiO<sub>4+d</sub> at various fluorination states upon the 1st cycle. Ni, LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4+d</sub>, and LaNiO<sub>3</sub> are provided as references. (b) The relative intensity ratio between Ni L<sub>3</sub> high energy peak to low energy peak (Ni L<sub>3 high</sub>/L<sub>3 low</sub>) at different fluorination states. (c) O *K*-edge XAS collected at different fluorination states during the 1st cycle. LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4+d</sub>, and LaNiO<sub>3</sub> are provided as references.



**Figure 4.7** (a) F *K*-edge XAS of La<sub>2</sub>NiO<sub>4+d</sub> at various fluorination states during the 1st cycle. NiF<sub>2</sub> and LBF are provided as references. (b) The enlarged spectra between energy of 681 and 688 eV.



**Figure 4.8** *k*<sup>3</sup>-Weighted Fourier transform magnitudes of Ni *K*-edge EXAFS at various fluorination states during the 1st cycle. There are two peaks around 1.4 Å and 3.0 Å, which are attributed to Ni–O/Ni–F bonds and Ni–La bonds.



Figure 4.9 Schematic illustration of the phase transition model of La<sub>2</sub>NiO<sub>4+d</sub> during the 1st cycle. At early state of charge, the interstitial layers in La<sub>2</sub>NiO<sub>4+d</sub> lattice can accept 1.88 F<sup>-</sup> to form La<sub>2</sub>NiO<sub>4+d</sub>F<sub>1.88</sub>, two phase coexisted upon charging.<sup>10</sup> The volume expansion was about 14%. The excessive fluoride-ion insertion resulted in fluorinated phase La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub>, F<sup>-</sup> were inserted into perovskite slabs and formed Ni–F bonds, and O–O bonds generated at high state of charge.



Figure 4.10 Electrochemical properties of La<sub>2</sub>NiO<sub>4+d</sub> after activation process. (a)

Charge/discharge profiles for the initial cycle after activation at a current density of 10 mA g<sup>-1</sup> at 140 °C, the voltage range is -1.5~2.5 V vs. Pb/PbF<sub>2</sub>. (b) Comparison of gravimetric capacity and volumetric capacity for La<sub>2</sub>NiO<sub>4</sub> and cathode materials reported in LIBs and FIBs: 1. LiCoO<sub>2</sub>,<sup>51</sup> 2. LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>,<sup>52</sup> 3. LiFePO<sub>4</sub>,<sup>53</sup> 4. Li<sub>1.25</sub>Nb<sub>0.25</sub>Mn<sub>0.5</sub>O<sub>2</sub>,<sup>54</sup> 5. Li<sub>8/7</sub>Ti<sub>2/7</sub>V<sub>4/7</sub>O<sub>2</sub>,<sup>27</sup> 6. Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>,<sup>14</sup> 7. LaSrMnO<sub>4</sub>F,<sup>13</sup> 8. Sr<sub>2</sub>MnO<sub>3</sub>F<sub>2</sub>,<sup>13</sup> 9. La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub>.<sup>23</sup>



Figure 4.11 (a) Cycle performance of La<sub>2</sub>NiO<sub>4+d</sub> after activation process at a current density of 10 mA g<sup>-1</sup>. (b) Rate capability at current densities of 10, 20, 50, 100, and 200 mA g<sup>-1</sup>, the y axis of the right side shows the capacity retention relative to the current density of 10 mA g<sup>-1</sup>.



Figure 4.12 (a) The voltage/capacity profile of  $La_2NiO_{4+d}$  obtained by GITT measurement after activation process. (b) Apparent F<sup>-</sup> diffusion coefficients ( $D_{F}$ -) calculated from GITT results upon the charge process after activation.



**Figure 4.13** (a) XRD patterns of La<sub>2</sub>NiO<sub>4+d</sub> cathode composite after activation process. (b) The enlarged diffraction patterns between  $2\theta = 26 \sim 34^{\circ}$ . At fully charged state, a weak and broad pattern can be observed at  $2\theta = 29.4^{\circ}$ , corresponding to the fluorination product La<sub>2</sub>NiO<sub>4+d</sub>F<sub>x</sub>.



Figure 4.14 (a) Ni L<sub>3</sub>-edge XAS of La<sub>2</sub>NiO<sub>4+d</sub> at various fluorination states after activation. Ni, LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4+d</sub>, and LaNiO<sub>3</sub> are provided as references. (b) The relative intensity ratio between Ni L<sub>3</sub> high energy peak to low energy peak (Ni L<sub>3 high</sub>/L<sub>3 low</sub>) at different fluorination states. (c) O *K*-edge XAS collected after activation. LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4+d</sub>, and LaNiO<sub>3</sub> are provided as references. (d) F *K*-edge XAS at various fluorination states after activation. NiF<sub>2</sub> and LBF are provided as references.

# Reference

- Xiao, A. W.; Galatolo, G.; Pasta, M. The case for fluoride-ion batteries. *Joule* 2021, 5 (11), 2823–2844.
- Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Reddy, M. A.; Clemens, O. Fluoride ion batteries-past, present, and future. *J. Mater. Chem. A* 2021, 9 (10), 5980–6012.
- Reddy, M. A.; Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem.
   2011, 21 (43), 17059–17062.
- Thieu, D. T.; Fawey, M. H.; Bhatia, H.; Diemant, T.; Chakravadhanula, V. S. K.; Behm, R. J.; Kübel, C.; Fichtner, M. CuF<sub>2</sub> as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* 2017, *27* (31), 1701051.
- Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Amezawa, K.; Uchimoto, Y. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, 9 (1), 406–412.
- Yoshinari, T.; Zhang, D.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Matsunaga, T.; Amezawa, K.; Uchimoto, Y. Kinetic analysis and alloy designs for metal/metal fluorides toward high rate capability for all-solid-state fluoride-ion batteries. *J. Mater. Chem. A* 2021, 9 (11), 7018–7024.
- Clemens, O.; Rongeat, C.; Reddy, M. A.; Giehr, A.; Fichtner, M.; Hahn, H. Electrochemical fluorination of perovskite type BaFeO<sub>2.5</sub>. *Dalton Trans.* 2014, 43 (42), 15771–8.
- Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Reddy, M. A.; Clemens, O. LaSrMnO<sub>4</sub>: Reversible Electrochemical Intercalation of Fluoride Ions in the Context of Fluoride Ion Batteries. *Chem. Mater.* 2017, 29 (8), 3441–3453.
- 9. Ishihara, T. Perovskite oxide for solid oxide fuel cells. Springer Science &

#### Business Media, 2009.

- Nowroozi, M. A.; Wissel, K.; Donzelli, M.; Hosseinpourkahvaz, N.; Plana-Ruiz, S.; Kolb, U.; Schoch, R.; Bauer, M.; Malik, A. M.; Rohrer, J.; Ivlev, S.; Kraus, F.; Clemens, O. High cycle life all-solid-state fluoride ion battery with La<sub>2</sub>NiO<sub>4+d</sub> high voltage cathode. *Commun. Mater.* 2020, *1* (1), 27.
- Aikens, L. D.; Li, R. K.; Greaves, C. The synthesis and structure of a new oxide fluoride, LaSrMnO<sub>4</sub>F, with staged fluorine insertion. *Chem.Commun.* 2000, (21), 2129–2130.
- Miki, H.; Yamamoto, K.; Cao, S.; Matsunaga, T.; Kumar, M.; Thakur, N.; Sakaguchi, Y.; Watanabe, T.; Iba, H.; Kageyama, H.; Uchimoto, U. Accelerated fluoride-ion intercalation/deintercalation in a layered-perovskite cathode by controlling the interlayer distance for fluoride-ion batteries. *Solid State Ionics*, 2024, 406, 116480.
- Wang, Y.; Yamamoto, K.; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; Cao, Z.; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion Substitution at Apical Sites of Ruddlesden-Popper-type Cathodes toward High Power Density for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2022, *34* (2), 609–616.
- Wang, Y.; Takami, T.; Li, Z.; Yamamoto, K.; Matsunaga, T.; Uchiyama, T.; Watanabe, T.; Miki, H.; Inoue, T.; Iba, H.; Mizutani, U.; Sato, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Oxyfluoride Cathode for All-Solid-State Fluoride-Ion Batteries with Small Volume Change Using Three-Dimensional Diffusion Paths. *Chem. Mater.* 2022, *34* (23), 10631–10638.
- Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vezin, H.; Sougrati, M. T.; Doublet, M. L.; Foix, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J. M. Reversible anionic redox chemistry in highcapacity layered-oxide electrodes. *Nat. Mater.* 2013, *12* (9), 827–35.
- 16. Maitra, U.; House, R. A.; Somerville, J. W.; Tapia-Ruiz, N.; Lozano, J. G.;

Guerrini, N.; Hao, R.; Luo, K.; Jin, L.; Perez-Osorio, M. A.; Massel, F.; Pickup, D. M.; Ramos, S.; Lu, X.; McNally, D. E.; Chadwick, A. V.; Giustino, F.; Schmitt, T.; Duda, L. C.; Roberts, M. R.; Bruce, P. G. Oxygen redox chemistry without excess alkali-metal ions in Na<sub>2/3</sub>[Mg<sub>0.28</sub>Mn<sub>0.72</sub>]O<sub>2</sub>. *Nat. Chem.* **2018**, *10* (3), 288–295.

- Seo, D. H.; Lee, J.; Urban, A.; Malik, R.; Kang, S.; Ceder, G. The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials. *Nat. Chem.* 2016, 8 (7), 692–7.
- Luo, K. R., M. R. Hao, R. Guerrini, N. Pickup, D. M. Liu, Y. S. Edstrom, K. Guo, J. Chadwick, A. V. Duda, L. C. Bruce, P. G. Charge-compensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat Chem* 2016, *8* (7), 684–91.
- Li, X. L.; Wang, T.; Yuan, Y.; Yue, X. Y.; Wang, Q. C.; Wang, J. Y.; Zhong, J.; Lin, R. Q.; Yao, Y.; Wu, X. J.; Yu, X. Q.; Fu, Z. W.; Xia, Y. Y.; Yang, X. Q.; Liu, T.; Amine, K.; Shadike, Z.; Zhou, Y. N.; Lu, J. Whole-Voltage-Range Oxygen Redox in P2-Layered Cathode Materials for Sodium-Ion Batteries. *Adv. Mater*. 2021, *33* (13), e2008194.
- 20. House, R. A.; Marie, J. J.; Pérez-Osorio, M. A.; Rees, G. J.; Boivin, E.; Bruce,
  P. G. The role of O<sub>2</sub> in O-redox cathodes for Li-ion batteries. *Nat. Energy* 2021,
  6 (8), 781–789.
- Yamamoto, K.; Zhou, Y.; Yabuuchi, N.; Nakanishi, K.; Yoshinari, T.; Kobayashi, T.; Kobayashi, Y.; Yamamoto, R.; Watanabe, A.; Orikasa, Y.; Tsuruta, K.; Park, J.; Byon, H. R.; Tamenori, Y.; Ohta, T.; Uchimoto, Y. Charge Compensation Mechanism of Lithium-Excess Metal Oxides with Different Covalent and Ionic Characters Revealed by Operando Soft and Hard X-ray Absorption Spectroscopy. *Chem. Mater.* 2019, *32* (1), 139–147.
- Rahman, M. M.; Lin, F. Oxygen Redox Chemistry in Rechargeable Li-Ion and Na-Ion Batteries. *Matter* 2021, 4 (2), 490–527.

- Miki, H.; Yamamoto, K.; Nakaki, H.; Yoshinari, T.; Nakanishi, K.; Nakanishi, S.; Iba, H.; Miyawaki, J.; Harada, Y.; Kuwabara, A.; Wang, Y.; Watanabe, T.; Matsunaga, T.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Double-Layered Perovskite Oxyfluoride Cathodes with High Capacity Involving O–O Bond Formation for Fluoride-Ion Batteries. J. Am. Chem. Soc. 2024, 146 (6), 3844–3853.
- Lee, J.; Papp, J. K.; Clement, R. J.; Sallis, S.; Kwon, D. H.; Shi, T.; Yang, W.; McCloskey, B. D.; Ceder, G. Mitigating oxygen loss to improve the cycling performance of high capacity cation-disordered cathode materials. *Nat. Commun.* 2017, 8 (1), 981.
- Huang, J.; Zhong, P.; Ha, Y.; Kwon, D.-H.; Crafton, M. J.; Tian, Y.; Balasubramanian, M.; McCloskey, B. D.; Yang, W.; Ceder, G. Non-topotactic reactions enable high rate capability in Li-rich cathode materials. *Nat. Energy* 2021, 6 (7), 706–714.
- Nakajima, M.; Yabuuchi, N. Lithium-Excess Cation-Disordered Rocksalt-Type Oxide with Nanoscale Phase Segregation: Li<sub>1.25</sub>Nb<sub>0.25</sub>V<sub>0.5</sub>O<sub>2</sub>. *Chem. Mater.* 2017, 29 (16), 6927–6935.
- Konuma, I.; Goonetilleke, D.; Sharma, N.; Miyuki, T.; Hiroi, S.; Ohara, K.; Yamakawa, Y.; Morino, Y.; Rajendra, H. B.; Ishigaki, T.; Yabuuchi, N. A near dimensionally invariable high-capacity positive electrode material. *Nat. Mater.* 2023, 22 (2), 225–234.
- 28. Takeda, Y.; Kanno, R.; Sakano, M.; Yamamoto, O.; Takano, M.; Bando, Y.; Akinaga, H.; Takita, K.; Goodenough, J. B., Crystal chemistry and physical properties of La<sub>2-x</sub>Sr<sub>x</sub>NiO<sub>4</sub> ( $0 \le x \le 1.6$ ). *Mater. Res. Bull.* **1990**, *25* (3), 293–306.
- Wissel, K.; Heldt, J.; Groszewicz, P. B.; Dasgupta, S.; Breitzke, H.; Donzelli, M.; Waidha, A. I.; Fortes, A. D.; Rohrer, J.; Slater, P. R.; Buntkowsky, G.; Clemens, O. Topochemical Fluorination of La<sub>2</sub>NiO<sub>4+d</sub>: Unprecedented Ordering of Oxide and Fluoride Ions in La<sub>2</sub>NiO<sub>3</sub>F<sub>2</sub>. *Inorg. Chem.* 2018, *57* (11),

6549-6560

- Petříček, V.; Dusěk, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. Z. Kristallogr.-Cryst. Mater. 2014, 229 (5), 345–352.
- 31. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276.
- Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537–541.
- Minervini, L.; Grimes, R. W.; Kilner, J. A.; Sickafus, K. E. Oxygen migration in La<sub>2</sub>NiO<sub>4+δ</sub>. *J. Mater. Chem.* 2000, *10* (10), 2349–2354.
- Halat, D. M.; Dervişoğlu R.; Kim, G.; Dustan, M. T.; Blanc, F.; Middlemiss D.
  S.; Grey, C. P. Probing Oxide-Ion Mobility in the Mixed Ionic-Electronic Conductor La<sub>2</sub>NiO<sub>4+δ</sub> by Solid-State <sup>17</sup>O MAS NMR Spectroscopy. J. Am. Chem. Soc. 2016, 138 (36), 11958–11969.
- 35. Grenier, A.; Porras-Gutierrez, A. G.; Body M.; Legein, C.; Chrétien, F.; Raymundo-Piñero, E.; Dollé, M.; Groult, H.; Dambournet, D. Solid Fluoride Electrolytes and Their Composite with Carbon: Issues and Challenges for Rechargeable Solid State Fluoride-Ion Batteries. J. Phys. Chem. C 2017, 121 (45), 24962–24970.
- Haruyama, J.; Okazaki, K.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji,
   T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and
   Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. ACS Appl.
   Mater. Interfaces 2020, 12 (1), 428–435.
- 37. Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Reversible and Fast (De)fluorination of High-Capacity Cu<sub>2</sub>O Cathode: One Step Toward Practically Applicable All-

Solid-State Fluoride-Ion Battery. Adv. Energy Mater. 2021, 11 (45), 2102285.

- Cao, Z.; Yamamoto, K.; Zhang, D.; Matsunaga, T.; Kumar, M.; Thakur, N.;
   Watanabe, T.; Miki, H.; Iba, H.; Amezawa, K.; Uchimoto, Y. ACS Appl. Energy Mater. 2023, 6 (23), 11906–11914.
- House, R. A.; Maitra, U.; Jin, L.; Lozano, J. G.; Somerville, J. W.; Rees, N. H.; Naylor, A. J.; Duda, L. C.; Massel, F.; Chadwick, A. V.; Ramos, S.; Pickup, D. M.; McNally, D. E.; Lu, X.; Schmitt, T.; Roberts, M. R.; Bruce, P. G. What Triggers Oxygen Loss in Oxygen Redox Cathode Materials? *Chem. Mater.* 2019, *31* (9), 3293–3300.
- Xiao, R.; Li, H.; Chen, L. Density Functional Investigation on Li<sub>2</sub>MnO<sub>3</sub>. *Chem. Mater.* 2012, 24 (21), 4242–4251.
- Cao, Z.; Yamamoto, K.; Matsunaga, T.; Watanabe, T.; Kumar, M.; Thakur, N.; Ohashi, R.; Tachibana, S.; Miki, H.; Ide, K.; Iba, H.; Kiuchi, H.; Harada, Y.; Orikasa, Y.\*; Uchimoto, Y., Revealing the Unusual Mechanism of Mixed Cationic and Anionic Redox in Oxyfluorosulfide Cathode for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2024, *36* (4), 1928–1940.
- Uchimoto, Y.; Sawada, H.; Yao, T. Changes in electronic structure by Li ion deintercalation in LiNiO<sub>2</sub> from nickel *L*-edge and O *K*-edge XANES. *J. Power Sources* 2001, *97*, 326–327.
- 43. Tian, C.; Nordlund, D.; Xin, H.; Xu, Y.; Liu, Y.; Sokaras, D.; Lin, F.; Doeff, M.
  M. Depth-Dependent Redox Behavior of LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub>. *J. Electrochem.* Soc. 2018, 165 (3), A696–A704.
- Lin, F.; Markus, I. M.; Nordlund, D.; Weng, T. C.; Asta, M. D.; Xin, H. L.; Doeff,
  M. M. Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries. *Nat. Commun.* 2014, *5*, 3529.
- Xu, J.; Hu, E.; Nordlund, D.; Mehta, A.; Ehrlich, S. N.; Yang, X.; Tong, W. Understanding the Degradation Mechanism of Lithium Nickel Oxide Cathodes for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* 2016, 8 (46), 31677–31683.

- 46. Frati, F.; Hunault, M. O. J. Y.; De Groot, F. M. F. Oxygen K-edge X-ray Absorption Spectra. *Chem. Rev.* **2020**, *120* (9), 4056–4110.
- House, R. A.; Rees, G. J.; Pérez-Osorio, M. A.; Marie, J.-J.; Boivin, E.; Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3*d* cathodes associated with molecular O<sub>2</sub> trapped in the bulk. *Nat. Energy* 2020, 5 (10), 777–785.
- 48. Lee, K. W.; Pickett, W. E. Infinite-layer LaNiO<sub>2</sub>: Ni<sup>1+</sup> is not Cu<sup>2+</sup>. *Phys. Rev. B* 2004, 70 (16), 165109.
- Hepting, M.; Li, D.; Jia, C. J.; Lu, H.; Paris, E.; Tseng, Y.; Feng, X.; Osada, M.; Been, E.; Hikita, Y.; Chuang, Y. D.; Hussain, Z.; Zhou, K. J.; Nag, A.; Garcia-Fernandez, M.; Rossi, M.; Huang, H. Y.; Huang, D. J.; Shen, Z. X.; Schmitt, T.; Hwang, H. Y.; Moritz, B.; Zaanen, J.; Devereaux, T. P.; Lee, W. S. Electronic structure of the parent compound of superconducting infinite-layer nickelates. *Nat. Mater.* 2020, *19* (4), 381–385.
- Olalde-Velasco, P.; Jimenez-Mier, J.; Denlinger, J. D.; Hussain, Z.; Yang, W. L. Direct probe of Mott-Hubbard to charge-transfer insulator transition and electronic structure evolution in transition-metal systems. *Phys. Rev. B* 2011, *83* (24), 241102.
- Lyu, Y.; Wu, X.; Wang, K.; Feng, Z.; Cheng, T.; Liu, Y.; Wang, M.; Chen, R.;
   Xu, L.; Zhou, J.; Lu, Y.; Guo, B. An Overview on the Advances of LiCoO<sub>2</sub>
   Cathodes for Lithium-Ion Batteries. *Adv. Energy Mater.* 2021, *11* (2), 2000982.
- 52. Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y. K. Comparison of the structural and electrochemical properties of layered Li[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> (*x*=1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries. *J. Power Sources* 2013, 233, 121–130.
- 53. Huang, C. Y.; Kuo, T. R.; Yougbare, S.; Lin, L. Y. Design of LiFePO<sub>4</sub> and porous carbon composites with excellent High-Rate charging performance for Lithium-Ion secondary battery. *J. Colloid Interface Sci.* 2022, 607, 1457–1465.

- 54. Wang, R.; Liu, X.; Liu, L.; Lee, J.; Seo, D. H.; Bo, S. H.; Urban, A.; Ceder, G. A disordered rock-salt Li-excess cathode material with high capacity and substantial oxygen redox activity: Li<sub>1.25</sub>Nb<sub>0.25</sub>Mn<sub>0.5</sub>O<sub>2</sub>. *Electrochem. Commun.* 2015, *60*, 70–73.
- House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K. J.; Roberts, M. R.; Bruce, P. G. Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes. *Nature* 2020, *577* (7791), 502–508.
- 56. Cao, Z.; Yamamoto, K.; Matsunaga, T.; Kumar, M.; Thakur, N.; Watanabe, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Kageyama, H.; Uchimoto, Y. Reversible Fluoride-Ion (de)Intercalation of CuLaO<sub>2</sub> Cathode with Crystalline/Amorphous Phase Transition Involving Multi-Electron Reaction. ACS Appl. Energy Mater. 2024, DOI: 10.1021/acsaem.4c01271.
- Xia, H.; Lu, L.; Ceder, G. Li diffusion in LiCoO<sub>2</sub> thin films prepared by pulsed laser deposition. *J. Power Sources* 2006, *159* (2), 1422–1427.
- 58. Sakuda, A.; Ohara, K.; Kawaguchi, T.; Fukuda, K.; Nakanishi, K.; Arai, H.; Uchimoto, Y.; Ohta, T.; Matsubara, E.; Ogumi, Z. A reversible rocksalt to amorphous phase transition involving anion redox. *Sci. Rep.* 2018, 8 (1), 15086.
- 59. Nagao, K.; Nagata, Y.; Sakuda, A.; Hayashi, A.; Deguchi, M.; Hotehama, C.; Tsukasaki, H.; Mori, S.; Orikasa, Y.; Yamamoto, K.; Uchimoto, U.; Tatsumisago M. A reversible oxygen redox reaction in bulk-type all-solid-state batteries. *Sci. Adv.* 2020, *6* (25), eaax7236.
- Kuiper, P.; Kruizinga, G.; Ghijsen, J.; Sawatzky, G. A.; Verweij, H. Character of holes in Li<sub>x</sub>Ni<sub>1-x</sub>O and their magnetic behavior. *Phys. Rev. Lett.* 1989, *62* (2), 221–224.
- House, R. A.; Playford, H. Y.; Smith, R. I.; Holter, J.; Griffiths, I.; Zhou, K.;
   Bruce, P. G. Detection of trapped molecular O<sub>2</sub> in a charged Li-rich cathode by Neutron PDF. *Energy Environ. Sci.* 2022, *15* (1), 376–383.

# Chapter 5 Infinite Layer Oxide Cathode Material LaNiO<sub>2</sub> toward High Energy Density and Power Density

For batteries used in EVs high energy density and high power density are crucial. All-solid-state FIB is a strong competitor for the next-generation batteries due to its high volumetric energy density and high safety. As introduced in Chapter 4, we successfully exploited the mixed cationic redox (Ni) and anionic redox (O) reactions in the Ruddlesden-Popper-type La<sub>2</sub>NiO<sub>4+d</sub> cathode to achieve a reversible capacity of over 250 mAh g<sup>-1</sup>. The electrochemical properties far exceeded the results reported in preliminary studies. However, the rate capability of the material is not yet satisfactory. Herein, we report a LaNiO<sub>2</sub> cathode material with an infinite layer structure, which can transform to a perovskite-related  $LaNiO_2F_x$  structure after topotactic fluorination. Surprisingly, the LaNiO<sub>2</sub> cathode not only provides a high reversible capacity of over 400 mAh  $g^{-1}$ , but also exhibits an outstanding rate capability of 283 mAh  $g^{-1}$  at a current density of 200 mA  $g^{-1}$ , with a power density that far exceeds those of the other battery systems. The high capacity of the material is attributed to the charge compensation of the multi-electron reaction of the Ni<sup>+</sup> and the oxygen redox reactions. The infinite layer structure can accommodate excessive fluoride ions upon charging, leading to the formation of the molecular O<sub>2</sub>, which is proved to be reversible. The strong hybridization of Ni 3d and O 2p orbitals in the charged states leads to excellent electronic conductivity, which results in outstanding rate performance. Although the amorphous transformation during the charge process causes slight capacity fading, the outstanding performance has opened the way for the application of perovskite-type oxyfluorides as high-performance FIB cathodes.

# **5.1 Introduction**

The advancement of storage batteries is increasingly crucial for achieving a sustainable society. For over 30 years, lithium-ion batteries (LIBs) have been successfully commercialized, thanks to their high capacity and long lifespan. Beginning with the well-known LiCoO<sub>2</sub>,<sup>1</sup> LIBs have evolved through several generations of electrode materials. In recent years, the application of the oxygen redox reaction has further enhanced the capacity of LIB cathode materials.<sup>2, 3</sup> However, with the expanding use of electric vehicles and smart grid systems, there is a growing need for rechargeable batteries with even higher capacities and improved safety.

All-solid-state fluoride-ion batteries (FIBs) were firstly proposed in 2011 and have received wide attentions due to the high electrochemical stability of fluoride anion as charge carriers.<sup>4, 5</sup> Owing to the metal/metal fluoride (M/MF<sub>x</sub>) conversion reactions, fluoride ion batteries can achieve high theoretical energy densities.<sup>6–8</sup> However, the two-phase reaction mechanism between metal and metal fluoride leads to drastic volumetric changes, which severely affects the electrode-solid electrolyte interface, resulting in rapid capacity fading and poor rate performance.

Besides conversion-type materials, intercalation-type materials, like perovskite, schafarzikite, Ruddlesden–Popper-type materials ( $Sr_2MnO_3F$ ,  $Sr_3Fe_2O_3F_2$ ,  $La_{1.2}Sr_{1.8}Mn_2O_{7-\delta}F_2$ ), etc., are becoming attractive due to their high structural stability and tolerance to topotactic (de)fluorination.<sup>9–12</sup> It is of vital importance that the intercalation-type materials have anionic vacancies surrounding cationic coordination centers as  $F^-$  intercalation sites. However, the transition metals in the intercalation-type materials have relatively high starting valence states, which limits the theoretical capacities for charge compensation. Therefore, employing anionic redox reactions to participate in charge compensation is an effective strategy for realizing high energy density, as is widely applied in the studies of LIBs and Sodium-ion batteries (SIBs).<sup>13–15</sup>

In Chapter 4, we achieved a reversible capacity exceeding 250 mAh  $g^{-1}$  in the

 $La_2NiO_{4+d}$  cathode material by using the oxygen redox. In order to obtain a higher capacity, we attempted to study on the perovskite-related cathode materials with a simpler structure than the Ruddlesden-Popper perovskite materials. In this chapter, we introduced LaNiO<sub>2</sub> with an infinite layer structure as cathode material for all-solid-state FIBs. The planar [NiO<sub>4</sub>] configuration offered sufficient room for fluoride ion intercalation. LaNiO<sub>2</sub> exhibited a reversible capacity of 400 mAh  $g^{-1}$  (corresponded to  $\sim$ 3.5 F<sup>-</sup> per unit cell) after a two-cycle activation process. The charge compensation mechanism involving both multi-electron Ni redox and oxygen redox was investigated by X-ray absorption spectroscopies (XAS). Moreover, the reversible (de)formation of molecular oxygen was confirmed by Resonant inelastic X-ray scattering (RIXS) analysis. The anionic redox enabled LaNiO2 to accommodate excess fluoride ions, achieving an energy density of 627 Wh kg<sup>-1</sup> and a power density of 4202 Wh L<sup>-1</sup>. Furthermore, the strong hybridization between Ni 3d and O 2p orbitals in charged states provided LaNiO<sub>2</sub> rate performance superior to that of infinite-layered SrFeO<sub>2</sub>, making it quite attractive as a cathode for all-solid-state applications. We strongly believe that these findings provide novel insights into the design of high-energy and high-power cathodes for all-solid-state FIBs.

# **5.2 Experimental**

## 5.2.1 Material preparation

LaNiO<sub>2</sub> was synthesized by reducing LaNiO<sub>3</sub> using CaH<sub>2</sub> according to previous study.<sup>16</sup> LaNiO<sub>3</sub> was prepared by using molten KOH. 50 g KOH (90 %, Sigma-Aldrich) was placed in an SSA-S crucible and melted at 400°C in air for 6.5 h, in order to sufficiently form strong oxidizer  $O_2^{2^-}$  and  $O_2^{-}$ . Then, stoichiometric amount of La<sub>2</sub>O<sub>3</sub> (99.9 %, Wako, dried at 950 °C) and NiO (99.9 %, Koujundo) were mixed and added into the molten KOH. The crucible was maintained at 400 °C for 12 h and then cooled to room temperature in the furnace. LaNiO<sub>3</sub> was isolated by adding the products in deionized water followed by drying at 100 °C in air. Next, the obtained LaNiO<sub>3</sub> was

finely ground with CaH<sub>2</sub> (99.9 %, Sigma-Aldrich) in a molar ratio of 1:2 in an Ar-filled glove box, pelletized and sealed in an evacuated Pyrex tube with vacuum condition and reacted at 300 °C for 24 h. The residual CaH<sub>2</sub> and the reaction byproduct CaO were removed by washing the products with saturated NH<sub>4</sub>Cl in anhydrous ethanol.

Chemical fluorination was carried out to insert fluorine into the as-prepared LaNiO<sub>2</sub>. XeF<sub>2</sub> (Strem Chemicals, 99.5 %) was selected as the fluorination agent. LaNiO<sub>2</sub> and XeF<sub>2</sub> were placed separately in a polytetrafluoroethylene (PTFE) sleeve in a molar ratio of 1: 0.6 (LaNiO<sub>2</sub>/F = 1: 1.2), and then sealed in a steel autoclave. All the operations were carried out in an Ar-filled glove box. Finally, the reactor was heated at 150, 180, 210, and 240 °C for 48 h.

Solid electrolyte La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (LBF) was synthesized by a solid-state reaction, as described in Section 2.2.1.<sup>4</sup> The cathode composite was obtained by mixing LaNiO<sub>2</sub> with solid electrolyte LBF and vapor grown carbon fiber (VGCF, Showa Denko, Japan) in a weight ratio of 3: 6: 1 by ball-milling for 10 h at 100 rpm using ZrO<sub>2</sub> pot and  $\Phi$ 2 mm ZrO<sub>2</sub> balls. The anode composite was obtained by mixing PbF<sub>2</sub> (99.9 %, Kojundo), LBF and VGCF by ball-milling for 10 h at 300 rpm. Some Pb powder (99.9 %, Kojundo) were added and mixed by an agate pestle and mortar after ball-milling, and the mass ratio of the anode composite was PbF<sub>2</sub>/Pb/LBF/VGCF = 3: 2: 4: 1.

### 5.2.2 Electrochemical measurements

Electrochemical tests were carried out on bulk-type cells. 150 mg LBF powder was put into a PEEK insulator (10 mm diameter) and pressed under a pressure of 100 MPa for 5 min. Then, 100 mg of cathode composite, 500 mg of anode composite as well as two pieces of Au current collectors were placed on the opposite sides of the LBF pellet. Finally, the cell was compressed under a pressure of 360 MPa for 5 min. All the assembling processes were carried out in an argon-filled glove box with oxygen and moisture contents of less than 0.2 ppm. The galvanostatic charge-discharge tests and Galvanostatic Intermittent Titration Technique (GITT) measurement were evaluated by

HJ1020mSD8 battery testing systems (Hokuto Denko, Japan) with a voltage range of -1.5 to 2.5 V vs. Pb/PbF<sub>2</sub> at 140 °C without exposed to air. For GITT, each galvanostatic step was lasted for 2.2 h at 10 mA g<sup>-1</sup>, followed by a relaxation step at open circuit voltage (OCV) for 12 h to allow it to reach a quasi-equilibrium state. The apparent F<sup>-</sup> diffusion coefficients were calculated from the GITT results using the equation mentioned in Chapter 3.

#### 5.2.3 Material Characterization

Synchrotron X-ray diffraction (XRD) data were collected at room temperature in Ar atmosphere, at the BL02B2 and BL19B2 beamlines in SPring-8 (Hyogo, Japan). The pristine powder samples were characterized at BL02B2 beamline with an X-ray energy of 20 keV and the wavelength = 0.4133 Å. The pellet samples after electrochemical tests were conducted at BL19B2 beamline with a wavelength = 1.23981 Å. The diffractometer was equipped with six MYTHEN silicon micro-strip photon-counting detectors (Dectris Ltd., Baden, Switzerland), and the measurements were performed in Debye-Scherrer transmission geometry. Rietveld refinement was performed using Jana 2006 software.<sup>17</sup> Scanning transmission electron microscopy (STEM) measurements with the aid of energy dispersive X-ray spectroscopy (EDS) were conducted by using a JEM-ARM200F Monochromated Atomic Resolution Analytical Electron Microscope (JEOL, Japan). X-ray absorption spectroscopy (XAS) measurements for Ni K-edge, Ni L2.3-edge, F K-edge as well as O K-edge were carried out at the BL14B2 and BL27SU beamlines in SPring-8, respectively. To prepare the samples during the first cycle the third cycle for the measurements, all the cells were charged and discharged at a current density of 10 mA g<sup>-1</sup> and then transferred from an Ar-filled glovebox. The measurements were carried out under vacuum condition. The X-ray absorption near edge structure (XANES) data were analyzed using the ATHENA software package.<sup>18</sup> Resonant inelastic X-ray scattering (RIXS) measurements were performed at BL07LSU in SPring-8 using a grazing flat-field type high resolution soft X-ray emission spectrometer.<sup>19</sup> O *K*-edge soft XAS was proceeded in advance in order to determine the proper excitation energy of RIXS. The pellet samples were supported on the holders by carbon tape in an Argon-filled glovebox and then were transferred to the measurement chamber without any exposures to air and moisture. The sample positions were slowly changed with a speed of 2.4  $\mu$ m/s during the RIXS measurements to avoid radiation damage.

## 5.3 Results and discussion

### 5.3.1 Fluoride ion (de)intercalation behavior of LaNiO<sub>2</sub> before activation

LaNiO<sub>2</sub> was prepared by a soft-chemical method using a distorted perovskite LaNiO<sub>3</sub> as precursor and CaH<sub>2</sub> as reducing agent.<sup>16</sup> The details of its synthesis and characterization are described in Experimental. A typical infinite-layer structure (space group: *P4/mmm*) with lattice parameters of a = 3.9578(7) Å and c = 3.3895(5) Å was determined by Rietveld refinement, as shown in **Figure 5.1a-b** and **Table 5.1**. As shown in Figure 5.1c, LaNiO<sub>2</sub> particle was found to be cubic-like, and the atomic ratio obtained from EDS mapping was La/Ni/O = 27: 23: 50, which was close to the theoretical value. After reduced by CaH<sub>2</sub>, the apical O sites of [NiO<sub>6</sub>] octahedra in the original perovskite absent and such anionic deficiencies could possess high tolerance for F intercalation, as shown in Figure 5.1b.

The electrochemical properties of LaNiO<sub>2</sub> were measured between -1.5 V and 2.5 V against Pb/PbF<sub>2</sub> anode by bulk-type cells. In order to improve the ionic and electronic conductivities, both electrodes were mixed with solid electrolyte LBF and conductive additive VGCF. Since F<sub>2</sub> is not feasible for use as the other electrode due to its gaseous nature and the highest standard electrode potential, we utilized excessive amount of Pb/PbF<sub>2</sub> as anode material for fabricating a "fluoride-ion half-cell" in reference to previous studies.<sup>20, 21</sup> As shown in **Figure 5.2a**, the LaNiO<sub>2</sub> cathode exhibited a capacity of 367 mAh g<sup>-1</sup> with one slope between -0.4 V and 1.5 V and one voltage plateau at

1.5 V during the first charge process, and a capacity of 300 mAh g<sup>-1</sup> was provided in the subsequent discharge process with two voltage plateaus at 0.75 V and -0.8 V, where the irreversible capacity may be generated from partial oxygen release at high voltage as reported in some LIB studies.<sup>22, 23</sup> The 1st cycle was regarded to be an activation process, since a different-shaped charge curve and an obvious capacity increase were observed in the 2nd cycle. As a result of activation, it exhibited a higher charge capacity of 415 mAh g<sup>-1</sup> with voltage plateaus at -0.25 V and 1.5 V, and a discharge capacity of 398 mAh g<sup>-1</sup> with voltage plateaus at 0.75 V and -0.8 V that was similar to the first discharge process. The discharge capacity reached the maximum in the 3rd cycle (400 mAh g<sup>-1</sup>), and it showed the similar charge/discharge curves as in the 2nd cycle. The charge/discharge profiles indicated that the structure of LaNiO<sub>2</sub> changes significantly during the first charge process.

For in-depth understanding the crystal structure evolution upon fluoride ion insertion and extraction, synchrotron powder XRD (wavelength = 0.4133 Å) was carried out during the 1st cycle, as shown in Figure 5.3. Almost the diffraction patterns for LaNiO<sub>2</sub> cathode composite were indexed to LaNiO<sub>2</sub> (space group: P4/mmm) and the solid electrolyte LBF (space group:  $P\overline{3}c1$ ) before charging, although some LaOF impurity (emerged at  $2\theta = 7^{\circ}$ ) was generated during the ball milling process. During the 1st cycle, the patterns of the pristine LaNiO<sub>2</sub> were weakened while a new phase emerged when charging to x = 0.5 (Figure 5.3a). To clarify the structure of this fluorinated phase, chemical fluorination experiments were carried out on LaNiO2 pristine, as shown in Figure 5.4. LaNiO<sub>2</sub> reacted with XeF<sub>2</sub> at different temperatures, and a main phase of perovskite structure (space group:  $Pm\overline{3}m$ ) was generated at 210 °C. This phase had a lattice parameter of a = 3.9531(28) Å, as determined by Rietveld refinement (Figure 5.4b). The fluorination product upon electrochemical fluorination was identified as  $LaNiO_2F_x$  with a perovskite structure, and this behavior was similar to that of SrFeO<sub>2</sub>/SrFeO<sub>2</sub>F in previous studies.<sup>24, 25</sup> The diffraction patterns of the  $LaNiO_2F_x$  became progressively broader and weaker upon charging, indicating a

decrease in crystallinity. The 1st charging process was a phase transition reaction, which was similar to the lithiation process of FePO<sub>4</sub>/LiFePO<sub>4</sub> in LIBs.<sup>26</sup> As shown in Figure 5.3b, when charging to x = 0.5, the lattice parameter a of the fluorination product LaNiO<sub>2</sub>F<sub>x</sub> obtained from Le bail refinement was 3.931(5) Å, which was close to the lattice parameter a of the LaNiO<sub>2</sub> in cathode composite (3.955(8) Å). This suggested that the fluoride ions might have inserted into the anion deficiency sites along the caxis in the infinite layer structure (Figure 5.3c). However, at the fully charged state, the patterns of  $LaNiO_2F_x$  were weakened, almost no diffraction pattern other than the 101 peak can be observed, indicating that the fluorination product at the fully charged state might also have a perovskite structure, but the excessive fluoride-ion insertion led to a decrease in the crystallinity of the active material. After discharging, the crystal structure of the LaNiO<sub>2</sub> $F_x$  didn't return to the pristine one with the space group of P4/mmm, but remained a broad 101 peak of the space group  $Pm\overline{3}m$ . This irreversible structural evolution was similar to that of our previous study on SrFeO<sub>2</sub>,<sup>25</sup> except that the structural transformation of LaNiO<sub>2</sub> was accompanied by a decrease in crystallinity and a larger volume expansion.

## 5.3.2 Charge compensation mechanism of LaNiO<sub>2</sub> during the 1st cycle

Although the expected amount of inserted fluoride ion based on Ni<sup>+</sup> to Ni<sup>+3</sup> (exists in perovskite compounds such as LaNiO<sub>3</sub>) redox in LaNiO<sub>2</sub> didn't exceed 2 F<sup>-</sup>, the experimental result showed the electrochemical insertion of  $3.2 \text{ F}^-$  during the 1st cycle. We attempted to demonstrate that LaNiO<sub>2</sub> can accommodate anomalous amounts of fluoride ions by mixed cation and anion redox. To investigate the electronic structure during fluorination and defluorination processes in LaNiO<sub>2</sub>, a series of electrodes were prepared for X-ray absorption spectroscopy (XAS) analyzation during the 1st cycle (activation process). **Figure 5.5a** shows the Ni *L*<sub>3</sub>-edge XAS results. The La *M*-edge peaks at approximately 850 eV were regarded as calibrant, because the Lanthanum in both electrode and solid electrolyte didn't participate in charge compensation. Since the Ni<sup>+</sup> has the ionic configuration 3d<sup>9</sup>, only one absorption peak associated with the  $2p^63d^9-2p^53d^{10}$  transition occurred at 852.5 eV (*L*<sub>3</sub>-edge) in pristine LaNiO<sub>2</sub>.<sup>27, 28</sup> During the 1st charge process, a new peak associated with Ni 3d-hole emerged at 854.5 eV (*L*<sub>3</sub>-edge) and shifted toward higher energy, indicating that the valence state of Ni increased upon charging. We have discussed in **Chapter 4** that the oxidation-state changes for Ni can be qualitatively evaluated by Ni *L*-edge, where the ratio *L*<sub>3</sub> (high energy)/*L*<sub>3</sub> (low energy) is in a positive relationship with the Ni valence state.<sup>29–31</sup> As shown in Figure 5.5b, the valence state of Ni continuously increased upon charging.

Furthermore, in O *K*-edge spectra (Figure 5.5c), since the oxygen ligands showed a weak effective mixing with Ni<sup>+</sup> cations, a weak pre-edge peak corresponded to O 2p–Ni 3d hybridization was observed in LaNiO<sub>2</sub> pristine at 529.8 eV.<sup>27, 28</sup> During the 1st charge process, a pre-edge peak emerged at around 528 eV. This absorption peak, which was commonly found in the 3d transition metal-based perovskite compounds,<sup>32</sup> represented the strong O 2p–Ni 3d hybridization, and its appearance indicated the formation of Ni<sup>3+</sup>, which was consistent with the Ni *L*-edge XAS results. The variation tendency of F *K*-edge XAS during the 1st cycle is shown in Figure 5.5d. All the samples showed similar absorption edge features ( $\geq 687$  eV) because of the abundance of fluorine in LBF solid electrolyte. Upon charging, a pre-edge peak emerged at 685.5 eV and gradually increased upon charging, which was related to the formation of Ni–F bond as observed in the NiF<sub>2</sub> reference.<sup>33</sup>

It is worth noting that the excessive fluoride ions insertion ( $x \ge 1$ ) resulted in a new appearance at 530.8 eV in O *K*-edge spectra (Figure 5.5c), which gradually increased until the fully charged state. This feature was commonly considered as O–O bond originated from oxygen oxidation and has been intensively discussed in the LIBs and SIBs studies, which further proved that oxygen redox was involved into the charge compensation process.<sup>34, 35</sup> In our recent research on La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub> cathode material, 2 F<sup>-</sup> can be inserted into the rock-salt interstitial layers, and the excessive F<sup>-</sup> ions can also be inserted into the perovskite layers to bond with Mn, leading to the formation of molecular  $O_2$  in the lattice, which is very similar to the reaction mechanism of oxygen in this study.<sup>12</sup> The formation of molecular  $O_2$  will be discussed in the subsequent section. After discharging, the Ni *L*-edge and O *K*-edge XAS spectra didn't fully recover to the same shape as the pristine LaNiO<sub>2</sub>. Combining with the XRD results we can know that the structure of the active material changed irreversibly after discharging. Although the valence state of Ni showed a reversible change, the local structure change led to distinct variations in the absorption spectra, and the pronounced differences observed in the shape of the charge/discharge curves between the 1st and the 2nd cycles can be attributed to these irreversible changes.

Comprehensively considering the abovementioned characterization results, the electrochemical fluorination mechanism during the 1st cycle can be concluded in **Figure 5.6**. The fluoride-ion insertion into the LaNiO<sub>2</sub> lattice generated LaNiO<sub>2</sub>F with a perovskite structure (space group:  $Pm\bar{3}m$ ). As the excessive amount of fluoride ions was inserted into the lattice, the O–O bonds were formed in the lattice and the crystallinity of LaNiO<sub>2</sub>F<sub>x</sub> decreased. Then after fully discharging, the crystal structure of LaNiO<sub>2</sub> changed irreversibly from the infinite layer structure (space group: P4/mmm) to a perovskite structure (space group:  $Pm\bar{3}m$ ), which was similar to the behaviors we observed in our previous study on SrFeO<sub>2</sub>.<sup>25</sup>

## 5.3.3 Fluoride ion (de)intercalation behavior of LaNiO<sub>2</sub> after activation

After activation process, LaNiO<sub>2</sub> cathode showed remarkable electrochemical performances. As shown in **Figure 5.7b**, it maintained a reversible capacity of 330 mAh  $g^{-1}$  upon 20 cycles, and the coulombic efficiency for each cycle is close to 100 %. Moreover, it exhibited an excellent rate capability with a capacity of 283 mAh  $g^{-1}$  maintained at a current density of 200 mA  $g^{-1}$ , which was far beyond that of the infinite-layered SrFeO<sub>2</sub> (retention of 74 vs. 41 %),<sup>25</sup> suggesting rapid diffusion of fluoride ions in the bulk. As shown in Figure. 5.7d, LaNiO<sub>2</sub> exhibited both high energy density and outstanding power density in volumetric scale, which not only exceeded our previous

studied SrFeO<sub>2</sub>, but also surpassed the commercial LIB cathodes, and stood out from the post-LIB battery systems.<sup>36–40</sup>

Furthermore, we also used La/LaF<sub>3</sub> (-2.41 V vs. Pb/PbF<sub>2</sub>) as anode material to verify the feasibility of high energy density, a full cell consisted of LaNiO<sub>2</sub>|LBF|La foil as cathode, solid electrolyte and anode was tested for electrochemical performance, as shown in **Figure 5.8**. Due to the lack of optimization of the fabrication conditions of La foil anode, we used a lower current density of 5 mA g<sup>-1</sup> for charge/discharge measurement, and the full cell exhibited similar charge/discharge curves shape to those of the LaNiO<sub>2</sub>|LBF|Pb/PbF<sub>2</sub> cell (Figure 3.8b). A preliminary evaluation of LaNiO<sub>2</sub>|LaF<sub>3</sub> cell compared with LiCoO<sub>2</sub>|graphite cell was given in **Table 5.2**. Based on the LaNiO<sub>2</sub> in the cathode, an excellent volumetric energy density (4202 Wh L<sup>-1</sup>) can be achieved that was 2.7-fold of the LiCoO<sub>2</sub>|graphite cell (1552 Wh L<sup>-1</sup>), in addition to a high gravimetric energy density of up to 627 Wh kg<sup>-1</sup>, which made it more significant for practical applications in the future.

The structural evolution after activation was different, since it was difficult to obtain cathode powder after activation, the XRD results of the pellet samples after activation were conducted at BL19B2 beamline in SPring-8. As shown in **Figure 5.9**, the activated LaNiO<sub>2</sub> cathode material showed a broad diffraction pattern at around  $2\theta = 26^{\circ}$  at the 1st discharged state, which was consistent with the result in Figure 5.3a. This peak implied that the structure of the active material transformed to a perovskite-related structure after the first cycle with a reduction in crystallinity. During the subsequent charging process, the intensity of this peak gradually diminished and almost disappeared in the fully charged state, indicating that the insertion of excess fluoride ions led to the amorphous transformation. The reappearance of this broad peak after discharge process indicated a reversible transformation of the crystal structure. Similar phase transition mechanism has been found in our recent study on CuLaO<sub>2</sub> cathode material for FIBs.<sup>41</sup>

#### 5.3.4 Charge compensation mechanism of LaNiO<sub>2</sub> after activation

The charge compensation mechanisms of LaNiO<sub>2</sub> after activation were examined by XAS, as shown in **Figure 5.10**. The absorption peak at 855 eV in Ni  $L_3$ -edge gradually increased and shifted towards higher energy upon charging (Figure 5.10a). The continuously increased peak intensity ratio  $L_3 \text{ high}/L_3 \text{ low}$  during the whole charge process indicated the oxidation of Ni (Figure 5.10b). Moreover, the broad pre-edge peak which corresponded to the transitions from O 1s to the hybridized states of the Ni 3d and O 2p orbitals was observed at 528.5 eV at early stage of fluoride ion insertion (x =1 in Figure 5.10c). This result showed the oxidation of Ni upon charging, which was in consistent with the Ni XAS results.<sup>42</sup> Similar to the 1st cycle, further fluoride ion insertion ( $x \ge 2$ ) resulted in the emergence of the new O *K*-edge peak at 530.8 eV, which strongly proved the O–O bond formation. In the F *K*-edge XAS (Figure 5.10d), a small pre-edge peak attributed to metal-fluoride bonds can be observed upon fluoride ion insertion, suggesting the Ni–F bonds in the LaNiO<sub>2</sub> structure. After discharging, the shape of the Ni, O, and F XAS results recovered to the state before charging, indicating a high reversibility of the LaNiO<sub>2</sub> cathode material after activation.

#### 5.3.5 O<sub>2</sub> molecule formation in LaNiO<sub>2</sub>F<sub>x</sub> cathode

To further examine the electronic structure of oxidized oxygen species in detail, we also carried out RIXS measurement on the pristine LaNiO<sub>2</sub>, fully charged state and discharged state in the 1st cycle and after activation, as shown in **Figure 5.11b**. The excitation energy of RIXS measurement for the 1st fully charged state was confirmed to be 530.8 eV as the O *K*-edge soft XAS was proceeded in advance (Figure 5.11a). It was clearly observed that a zero-loss elastic peak and progressive vibrational features at energy loss -2.0 to 0 eV (ground state  $3\Sigma_g^-$ ), and the vibrational frequency was  $\sim 1600$  cm<sup>-1</sup>.<sup>13, 43</sup> The observed scattering behavior closely resembled that of molecular O<sub>2</sub>, a phenomenon previously noted in charged LIB intercalation cathode materials,<sup>13, 15, 44</sup> providing strong evidence for the formation of molecular O<sub>2</sub> in the 1st fully charged

state of LaNiO<sub>2</sub>. Furthermore, in the RIXS results of the fully charged sample after activation (Figure 5.11c), we also detected the same progressive vibrational feature as that in the 1st fully charged state, which was the fingerprint signal of the molecular O<sub>2</sub>. This vibration disappeared after discharging, indicating the reversible formation and breaking of molecular O<sub>2</sub> in the LaNiO<sub>2</sub>F<sub>x</sub> after activation process.

The electrochemical fluorination mechanism after activation was slightly different from the 1st cycle. After the activation process, the crystallinity of  $LaNiO_2F_x$  was significantly reduced and the diffraction patterns of the activated  $LaNiO_2F_x$  were weakened, as observed in Figure 5.9. It can be observed from the XAS results that both Ni and O redox reactions were involved in charge compensation after activation. Since the pristine LaNiO<sub>2</sub> structure can accommodate only 1 F<sup>-</sup>, additional anion sites were required for LaNiO<sub>2</sub> to accept more than 1 F<sup>-</sup>. The molecular O<sub>2</sub> observed in RIXS results which was formed upon charging not only served as a charge compensator, but also created additional vacancies to accept the excessive fluoride ions. Although it was not clear that how the molecular O<sub>2</sub> and excessive fluoride ions existed in the charged LaNiO<sub>2</sub> $F_x$ , the abovementioned characterization results revealed that the molecular O<sub>2</sub> and excessive fluoride ions may exist in some cavities in the structure, as the presence of H<sub>2</sub> molecule was found in SrTiO<sub>3</sub> structure,<sup>45</sup> and the formation of molecular O<sub>2</sub> can create the irregular sites for inserted fluoride ions, as found in the Li-rich cathode material for LIBs.<sup>44</sup> In our previous research on SrFeO<sub>2</sub> cathode material and in some disordered rock-salt Li-excess (DRX) materials in LIBs, such isotropic ion conduction (F<sup>-</sup> or Li<sup>+</sup>) can achieve zero-strain of the cathode upon cycling.<sup>25, 46, 47</sup> In this work, the excessive fluoride ion insertion led to structural deformation and reduction in crystallinity of the material, which was one of the reasons for the gradual capacity fading upon cycling. Nevertheless, further analyses such as the quantification of the fluoride ions and first-principal calculation are needed to determine the precise structure after fluorination/defluorination.

#### 5.3.6 Kinetic properties of LaNiO<sub>2</sub> after activation

In order to investigate the reason for the excellent rate capability of LaNiO<sub>2</sub>, GITT measurement was performed after activation. As shown in **Figure 5.12a**, the polarization of OCV at high state of charge was significantly larger than those in low state of charge. According to the abovementioned results, the excessive fluoride ion insertion triggered the formation of molecular O<sub>2</sub> at high state of charge region, leading to structural distortion and reduction in crystallinity. This might be one of the reasons for large hysteresis near fully charged state.<sup>13,44</sup> However, comparing the overpotential obtained from GITT measurements (which responded to the magnitude of polarization) of LaNiO<sub>2</sub> and SrFeO<sub>2</sub> upon the charging process, LaNiO<sub>2</sub> exhibited much lower overpotential than that of SrFeO<sub>2</sub> especially near fully charged state (Figure 5.12b). Compared to SrFeO<sub>2</sub>, which also has an infinite-layer structure, LaNiO<sub>2</sub> exhibited a much higher diffusion coefficient when charged to x > 2 (Figure 5.12c). This indicated that LaNiO<sub>2</sub> possessed superior bulk diffusion properties.

## **5.4 Conclusion**

We demonstrated the electrochemical intercalation of fluoride ions into the infinite layered LaNiO<sub>2</sub> host lattice. LaNiO<sub>2</sub> showed excellent capacity and rate capability. Compared to the infinite layer SrFeO<sub>2</sub> cathode, LaNiO<sub>2</sub> exhibited higher power density due to its high electronic conductivity resulting from the strong hybridization of Ni 3d and O 2p orbitals. We also achieved high energy density cells by using La metal anode. The XAS analysis confirmed the reversible redox of Ni<sup>+</sup>/Ni<sup>3+</sup> throughout the whole voltage range and the oxygen redox at the high voltage stage (after the insertion of 1 F<sup>-</sup>). Moreover, the RIXS analysis proved that the formation of molecular oxygen and the anion sites in the structure allow the insertion of excess fluoride ions. It is not clear how the molecular O<sub>2</sub> and excess fluoride ions exist in the LaNiO<sub>2</sub>F<sub>x</sub> structure, which requires further analysis in future studies. We believe that this study is important for the development of high-performance mixed-anion cathode materials with a perovskite-

related structure.



Figure 5.1 (a) Sample preparation for electrochemical measurement. (a) Structural characterization of LaNiO<sub>2</sub> by Rietveld refinement. Wavelength = 0.4133Å,  $R_f$ = 3.99 %,  $R_{wp}$ = 9.24 %. The green lines are the position of Bragg reflections. The difference between the measured and calculated profiles is plotted in blue solid line. (b) Crystal structure and the sites that can accommodate fluoride ions. (c) STEM image and EDS mapping of as-prepared LaNiO<sub>2</sub>.

 Table 5.1 Structural parameters of as-prepared LaNiO2 determined from the Rietveld refinement.

Atom	Wyckoff Position	x	у	Z	B <sub>iso</sub> / Å <sup>2</sup>	Occupancy
Lal	1d	0.5	0.5	0.5	0.51(3)	1
Ni1	1a	0	0	0	0.28(1)	1
01	2f	0	0.5	0	0.098(9)	1

Space group: P4/mmm;  $R_p = 6.79$  %,  $R_{wp} = 9.24$  %,  $R_f = 3.99$  %;

a = 3.9578(7) Å, c = 3.3895(5) Å.



**Figure 5.2** (a) Charge/discharge profiles during the initial 3 cycles at a current density of 10 mA g<sup>-1</sup> at 140 °C, the voltage range is –1.5~2.5 V. (b) Average voltage of LaNiO<sub>2</sub> cathode during the initial 3 cycles.



Figure 5.3 (a) XRD patterns of LaNiO<sub>2</sub> during the 1st cycle. The cathode composite contains solid electrolyte LBF, and the diffraction patterns of LBF can be regarded as the calibrant. (b) The changes of lattice parameters *a* and *c* for the pristine phase LaNiO<sub>2</sub> (space group: *P4/mmm*) and the fluorinated phase LaNiO<sub>2</sub>F<sub>x</sub> (space group:  $Pm\bar{3}m$ ) during the 1st cycle. (c) Lattice parameters and volume changes of LaNiO<sub>2</sub> and LaNiO<sub>2</sub>F<sub>x</sub> during the 1st cycle.



**Figure 5.4** (a) XRD patterns of the chemical fluorination products at different temperatures. (b) Rietveld refinement of the fluorination product LaNiO<sub>2</sub>F at 210 °C, 48 h, wavelength = 0.4133 Å.


Figure 5.5 (a) Ni L<sub>3</sub>-edge XAS results of LaNiO<sub>2</sub> at various fluorination states upon the 1st cycle.
Ni, LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4</sub>, and LaNiO<sub>3</sub> are provided as references. (b) The relative intensity ratio between Ni L<sub>3</sub> high energy peak to low energy peak (Ni L<sub>3 high</sub>/L<sub>3 low</sub>) at different fluorination states. (c) O *K*-edge XAS results collected at different fluorination states during the 1st cycle.
La<sub>2</sub>NiO<sub>4</sub> and LaNiO<sub>3</sub> are provided as references. (d) F *K*-edge XAS spectra, solid electrolyte LBF and NiF<sub>2</sub> are provided as references.



**Figure 5.6** Schematic illustration of the phase transition model during the 1st cycle for LaNiO<sub>2</sub>. At early state of charge, the lattice structure of LaNiO<sub>2</sub> can accept 1 F<sup>-</sup>, and the infinite layer structure (P4/mmm) transformed to perovskite structure ( $Pm\overline{3}m$ ) during charging. The excessive fluoride-ion insertion resulted in fluorinated composition LaNiO<sub>2</sub>F<sub>x</sub>, and O–O bonds generated at high state of charge.



Figure 5.7 Electrochemical properties of LaNiO<sub>2</sub> using LaNiO<sub>2</sub>|LBF|Pb/PbF<sub>2</sub> all-solid FIB cell.
(a) Charge/discharge profiles after activation at a current density of 10 mA g<sup>-1</sup> at 140 °C. (b) Cycle performance at 10 mA g<sup>-1</sup>. (c) Comparison on rate capability with infinite layer SrFeO<sub>2</sub> cathode between 10 and 200 mA g<sup>-1</sup>.(d) Ragone plots of different battery systems at cathode level. 1. LaNiO<sub>2</sub>, 2. SrFeO<sub>2</sub>,<sup>25</sup> 3. LiFePO<sub>4</sub>,<sup>36</sup> 4. LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>,<sup>37</sup> 5. Sulfur in all-solid-state Li-S battery,<sup>38</sup> 6. Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> in Sodium-ion battery,<sup>39</sup> 7. CuS in Mg-ion battery.<sup>40</sup>



Figure 5.8 (a) Charge/discharge profiles of LaNiO<sub>2</sub>|LBF|La full cell at a rate of 5 mA g<sup>-1</sup> at 140 °C. The anode reaction is the fluorination and defluorination of La metal. (b) A comparison of full cell data with the half-cell data as shown in Figure 5.7a, in which the data for the half-cell voltage are shown with an offset of 2.41 V since the La deposition/dissolution potential is -2.41 V vs. Pb/PbF<sub>2</sub>.

Battery	LIB	FIB
Cathode	LiCoO <sub>2</sub>	LaNiO <sub>2</sub>
Capacity / mAh g <sup>-1</sup>	170	400
Density / g cm <sup>-3</sup>	5.05	7.13
		_
Anode	Graphite	La
Capacity / mAh g <sup>-1</sup>	372	579
Density / g cm <sup>-3</sup>	2.20	6.16
Utilization ratio / %	100	100
Capacity ratio of anode/cathode	1	1
Weight ratio of anode/cathode	0.457	0.691
Volume ratio of anode/cathode	1.05	0.799
Average Voltage	3.7	2.65
Gravimetric energy density / Wh kg <sup>-1</sup>	432	627
Volumetric energy density / Wh L <sup>-1</sup>	1550	4202

Table 5.2 Comparison of energy density based on active materials between LIB and FIB.

The extra part such as current collector, electrolyte, battery shell, separator, conductive additives, binder, etc. are not involved in the calculation.



Figure 5.9 XRD patterns of LaNiO<sub>2</sub> after activation (wavelength = 1.23981 Å). The cathode composite contains solid electrolyte LBF, and the diffraction patterns of LBF can be regarded as the calibrant. The broad diffraction pattern at around  $2\theta = 26^{\circ}$  may be related to the perovskite-

related structure.



Figure 5.10 (a) Ni L<sub>3</sub>-edge XAS results of LaNiO<sub>2</sub> at various fluorination states after activation.
Ni, LaNiO<sub>2</sub>, La<sub>2</sub>NiO<sub>4</sub>, and LaNiO<sub>3</sub> are provided as references. (b) The relative intensity ratio between Ni L<sub>3</sub> high energy peak to low energy peak (Ni L<sub>3 high</sub>/L<sub>3 low</sub>) at different fluorination states. (c) O *K*-edge XAS results collected at different fluorination states after activation. La<sub>2</sub>NiO<sub>4</sub> and LaNiO<sub>3</sub> are provided as references. (d) F *K*-edge XAS spectra, solid electrolyte LBF and NiF<sub>2</sub> are provided as references.



Figure 5.11 (a) O K-edge XAS of the LaNiO<sub>2</sub> pristine and the 1st fully charged sample. (b) O K-edge RIXS patterns of LaNiO<sub>2</sub> at pristine and 1st fully charged state. The excitation energy is calibrated as 530.8 eV for RIXS measurements. The inset figure shows the elastic peaks and corresponding scattering behaviors. (c) RIXS results of LaNiO<sub>2</sub> pristine, fully charged and discharged states of LaNiO<sub>2</sub>F<sub>x</sub> after activation process. The inset figures show the related XAS results, the elastic peaks and the scattering behaviors.



Figure 5.12 (a) GITT measurement conducted after activation process at a current density of 10 mA g<sup>-1</sup>, with a 12-hour relaxation period after each current pulse. (b) Comparison of the overpotential during each GITT charge step between LaNiO<sub>2</sub> and SrFeO<sub>2</sub>.<sup>25</sup> (c) Comparison of the apparent F<sup>-</sup> diffusion coefficients (*D*<sub>F</sub>-) of LaNiO<sub>2</sub> and SrFeO<sub>2</sub> during the charging process after activation process.<sup>25</sup>

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# Reference

- Mizushima, K.; Jones, P.; Wiseman, P.; Goodenough, J. B. Li<sub>x</sub>CoO<sub>2</sub> (0 < x ≤1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* 1980, 15 (6), 783–789.
- Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vezin, H.; Sougrati, M. T.; Doublet, M. L.; Foix, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine, M.; Dupont, L.; Tarascon, J. M. Reversible anionic redox chemistry in highcapacity layered-oxide electrodes. *Nat. Mater.* 2013, *12* (9), 827–35.
- Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y. S.; Edstrom, K.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Chargecompensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* 2016, 8 (7), 684–91.
- Anji Reddy, M.; Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem.
   2011, 21 (43), 17059–17062.
- Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Reddy, M. A.; Clemens, O. Fluoride ion batteries-past, present, and future. *J. Mater. Chem. A* 2021, 9 (10), 5980–6012.
- Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Amezawa K.; Uchimoto, Y. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, 9 (1), 406–412.
- Thieu, D. T.; Fawey, M. H.; Bhatia, H.; Diemant, T.; Chakravadhanula, V. S. K.; Behm, R. J.; Kübel, C.; Fichtner, M. CuF<sub>2</sub> as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* 2017, *27* (31), 1701051.
- 8. Rongeat, C.; Reddy, M. A.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chem. A*

**2014**, *2* (48), 20861–20872.

- Clemens, O.; Rongeat, C.; Reddy, M. A.; Giehr, A.; Fichtner, M.; Hahn, H. Electrochemical fluorination of perovskite type BaFeO<sub>2.5</sub>. *Dalton Trans.* 2014, 43 (42), 15771–8.
- Wang, Y.; Yamamoto, K.; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; Cao, Z.; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion Substitution at Apical Sites of Ruddlesden-Popper-type Cathodes toward High Power Density for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2022, *34* (2), 609–616.
- Wang, Y.; Takami, T.; Li, Z.; Yamamoto, K.; Matsunaga, T.; Uchiyama, T.; Watanabe, T.; Miki, H.; Inoue, T.; Iba, H.; Mizutani, U.; Sato, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Oxyfluoride Cathode for All-Solid-State Fluoride-Ion Batteries with Small Volume Change Using Three-Dimensional Diffusion Paths. *Chem. Mater.* 2022, *34* (23), 10631–10638.
- Miki, H.; Yamamoto, K.; Nakaki, H.; Yoshinari, T.; Nakanishi, K.; Nakanishi, S.; Iba, H.; Miyawaki, J.; Harada, Y.; Kuwabara, A.; Wang, Y.; Watanabe, T.; Matsunaga, T.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Double-Layered Perovskite Oxyfluoride Cathodes with High Capacity Involving O–O Bond Formation for Fluoride-Ion Batteries. J. Am. Chem. Soc. 2024, 146 (6), 3844–3853.
- House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K. J.; Roberts, M. R.; Bruce, P. G. Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes. *Nature* 2020, *577* (7791), 502–508.
- Li, Z.; Kong, W.; Yu, Y.; Zhang, J.; Wong, D.; Xu, Z.; Chen, Z.; Schulz, C.; Bartkowiak, M.; Liu, X. Tuning Bulk O<sub>2</sub> and Nonbonding Oxygen State for Reversible Anionic Redox Chemistry in P2-Layered Cathodes. *Angew. Chem.* 2022, 134 (16), e202115552.

- House, R. A.; Marie, J. J.; Pérez-Osorio, M. A.; Rees, G. J.; Boivin, E.; Bruce,
  P. G. The role of O<sub>2</sub> in O-redox cathodes for Li-ion batteries. *Nat. Energy* 2021,
  6 (8), 781–789.
- Takamatsu, T.; Kato, M.; Noji, T.; Koike, Y. Low-Temperature Synthesis of the Infinite-Layer Compound LaNiO<sub>2</sub> by Soft-Chemical Techniques. *Jpn. J. Appl. Phys.* 2010, 49 (9), 093101.
- Petříček, V.; Dusěk, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. Z. Kristallogr.-Cryst. Mater. 2014, 229 (5), 345–352.
- Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537–541.
- Harada, Y.; Kobayashi, M.; Niwa, H.; Senba, Y.; Ohashi, H.; Tokushima, T.;
   Horikawa, Y.; Shin, S.; Oshima, M. Ultrahigh resolution soft x-ray emission spectrometer at BL07LSU in SPring-8. *Rev. Sci. Instrum.* 2012, *83* (1), 013116.
- Haruyama, J.; Okazaki, K.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji, T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. ACS Appl. Mater. Interfaces 2020, 12 (1), 428–435.
- Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Reversible and Fast (De)fluorination of High-Capacity Cu<sub>2</sub>O Cathode: One Step Toward Practically Applicable All-Solid-State Fluoride-Ion Battery. *Adv. Energy Mater*:2021, *11* (45), 2102285.
- House, R. A.; Maitra, U.; Jin, L.; Lozano, J. G.; Somerville, J. W.; Rees, N. H.; Naylor, A. J.; Duda, L. C.; Massel, F.; Chadwick, A. V.; Ramos, S.; Pickup, D. M.; McNally, D. E.; Lu, X.; Schmitt, T.; Roberts, M. R.; Bruce, P. G. What Triggers Oxygen Loss in Oxygen Redox Cathode Materials? *Chem. Mater.* 2019,

31 (9), 3293-3300.

- Xiao, R.; Li, H.; Chen, L. Density Functional Investigation on Li<sub>2</sub>MnO<sub>3</sub>. *Chem. Mater.* 2012, 24 (21), 4242–4251.
- Blakely, C. K.; Davis, J. D.; Bruno, S. R.; Kraemer, S. K.; Zhu, M.; Ke, X.; Bi, W.; Alp, E. E.; Poltavets, V. V. Multistep synthesis of the SrFeO<sub>2</sub>F perovskite oxyfluoride via the SrFeO<sub>2</sub> infinite-layer intermediate. *J. Fluorine Chem.* 2014, *159*, 8–14.
- Wang, Y. Development of Iron-based Oxyfluoride Cathodes for High Energy Density All-Solid-State Fluoride-ion Batteries. 2023.
- Orikasa, Y.; Maeda, T.; Koyama, Y.; Murayama, H.; Fukuda, K.; Tanida, H.; Arai, H.; Matsubara, E.; Uchimoto, Y.; Ogumi, Z. Transient phase change in two phase reaction between LiFePO<sub>4</sub> and FePO<sub>4</sub> under battery operation. *Chem. Mater.* 2013, 25 (7), 1032–1039.
- Hepting, M.; Li, D.; Jia, C. J.; Lu, H.; Paris, E.; Tseng, Y.; Feng, X.; Osada, M.; Been, E.; Hikita, Y.; Chuang, Y. D.; Hussain, Z.; Zhou, K. J.; Nag, A.; Garcia-Fernandez, M.; Rossi, M.; Huang, H. Y.; Huang, D. J.; Shen, Z. X.; Schmitt, T.; Hwang, H. Y.; Moritz, B.; Zaanen, J.; Devereaux, T. P.; Lee, W. S. Electronic structure of the parent compound of superconducting infinite-layer nickelates. *Nat. Mater.* 2020, *19* (4), 381–385.
- Lee, K. W.; Pickett, W. E. Infinite-layer LaNiO<sub>2</sub>: Ni<sup>1+</sup> is not Cu<sup>2+</sup>. *Phys. Rev. B* 2004, 70 (16), 165109.
- 29. Tian, C.; Nordlund, D.; Xin, H.; Xu, Y.; Liu, Y.; Sokaras, D.; Lin, F.; Doeff, M. M. Depth-Dependent Redox Behavior of LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub>. *J. Electrochem. Soc.* 2018, *165* (3), A696–A704.
- Lin, F.; Markus, I. M.; Nordlund, D.; Weng, T. C.; Asta, M. D.; Xin, H. L.; Doeff, M. M. Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries. *Nat. Commun.* 2014, *5*, 3529.
- 31. Xu, J.; Hu, E.; Nordlund, D.; Mehta, A.; Ehrlich, S. N.; Yang, X.; Tong, W.

Understanding the Degradation Mechanism of Lithium Nickel Oxide Cathodes for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8* (46), 31677-31683.

- 32. Frati, F.; Hunault, M. O. J. Y.; De Groot, F. M. F. Oxygen *K*-edge X-ray Absorption Spectra. *Chem. Rev.* **2020**, *120* (9), 4056–4110.
- Olalde-Velasco, P.; Jimenez-Mier, J.; Denlinger, J. D.; Hussain, Z.; Yang, W. L.
   Direct probe of Mott-Hubbard to charge-transfer insulator transition and electronic structure evolution in transition-metal systems. *Phys. Rev. B* 2011, *83* (24), 241102.
- 34. Zhuo, Z.; Dai, K.; Wu, J.; Zhang, L.; Tamura, N.; Chuang, Y.; Feng, J.; Guo, J.;
  Shen, Z.; Liu, G.; Pan, F.; Yang, W. Distinct Oxygen Redox Activities in Li<sub>2</sub>MO<sub>3</sub>
  (M = Mn, Ru, Ir). ACS Energy Lett. 2021, 6 (10), 3417–3424.
- Rahman, M. M.; Lin, F. Oxygen Redox Chemistry in Rechargeable Li-Ion and Na-Ion Batteries. *Matter* 2021, 4 (2), 490–527.
- Huang, C. Y.; Kuo, T. R.; Yougbare, S.; Lin, L. Y. Design of LiFePO<sub>4</sub> and porous carbon composites with excellent High-Rate charging performance for Lithium-Ion secondary battery. *J. Colloid Interface Sci.* 2022, 607, 1457–1465.
- Xia, Y.; Zheng, J.; Wang, C.; Gu, M. Designing principle for Ni-rich cathode materials with high energy density for practical applications. *Nano Energy* 2018, 49, 434–452.
- Zhang, Y.; Liu, T.; Zhang, Q.; Zhang, X.; Wang, S.; Wang, X.; Li, L.; Fan, L.-Z.; Nan, C.-W.; Shen, Y. High-performance all-solid-state lithium-sulfur batteries with sulfur/carbon nano-hybrids in a composite cathode. *J. Mater. Chem. A* 2018, 6 (46), 23345–23356.
- Li, S.; Dong, Y.; Xu, L.; Xu, X.; He, L.; Mai, L. Effect of carbon matrix dimensions on the electrochemical properties of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> nanograins for high-performance symmetric sodium-ion batteries. *Adv. Mater.* 2014, *26* (21), 3545–3553.
- 40. Du, C.; Zhu, Y.; Wang, Z.; Wang, L.; Younas, W.; Ma, X.; Cao, C. Cuprous self-

doping regulated mesoporous CuS nanotube cathode materials for rechargeable magnesium batteries. *ACS Appl. Mater. Interfaces* **2020**, *12* (31), 35035–35042.

- Cao, Z.; Yamamoto, K.; Matsunaga, T.; Kumar, M.; Thakur, N.; Watanabe, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Kageyama, H.; Uchimoto, Y. Reversible Fluoride-Ion (De)Intercalation of CuLaO<sub>2</sub> Cathodes with Crystalline/Amorphous Phase Transition Involving Multi-Electron Reaction. *ACS Appl. Energy Mater.* 2024, 7 (15), 6640–6648.
- 42. Kuiper, P.; Kruizinga, G.; Ghijsen, J.; Sawatzky, G. A.; Verweij, H. Character of holes in Li<sub>x</sub>Ni<sub>1-x</sub>O and their magnetic behavior. *Phys. Rev. Lett.* 1989, *62* (2), 221–224.
- Hennies, F.; Pietzsch, A.; Berglund, M.; Fohlisch, A.; Schmitt, T.; Strocov, V.; Karlsson, H. O.; Andersson, J.; Rubensson, J. E. Resonant inelastic scattering spectra of free molecules with vibrational resolution. *Phys. Rev. Lett.* 2010, *104* (19), 193002.
- House, R. A.; Rees, G. J.; Pérez-Osorio, M. A.; Marie, J.-J.; Boivin, E.; Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3*d* cathodes associated with molecular O<sub>2</sub> trapped in the bulk. *Nat. Energy* 2020, 5 (10), 777–785.
- Li, H. B.; Lou, F.; Wang, Y.; Zhang, Y.; Zhang, Q.; Wu, D.; Li, Z.; Wang, M.; Huang, T.; Lyu, Y.; Guo, J.; Chen, T.; Wu, Y.; Arenholz, E.; Lu, N.; Wang, N.; He, Q.; Gu, L.; Zhu, J.; Nan, C. W.; Zhong, X.; Xiang, H.; Yu, P. Electric Field-Controlled Multistep Proton Evolution in H<sub>x</sub>SrCoO<sub>2.5</sub> with Formation of H-H Dimer. *Adv. Sci.* 2019, *6* (20), 1901432.
- 46. Zhao, X.; Tian, Y.; Lun, Z.; Cai, Z.; Chen, T.; Ouyang, B.; Ceder, G. Design principles for zero-strain Li-ion cathodes. *Joule* **2022**, *6* (7), 1654–1671.
- 47. Nakajima, M.; Yabuuchi, N. Lithium-Excess Cation-Disordered Rocksalt-Type Oxide with Nanoscale Phase Segregation: Li<sub>1.25</sub>Nb<sub>0.25</sub>V<sub>0.5</sub>O<sub>2</sub>. *Chem. Mater.*2017, 29 (16), 6927–6935.

# Chapter 6 Revealing the Unusual Mechanism of Mixed Cationic and Anionic Redox in Oxyfluorosulfide Cathode



All-solid-state fluoride-ion batteries (FIBs) have been considered nextgeneration energy storage devices because of their high theoretical energy density. However, previously reported metal/metal fluoride active materials suffer from severe degradation due to

large volume expansion; consequentially, fluoride-ion-intercalating active materials fail to deliver a high capacity. Here, oxyfluorosulfide  $Sr_2F_2Fe_2OS_2$  (SFFOS) with layer structure is reported as a topotactic fluoride-ion (de)intercalation host. This material delivers a high reversible capacity of more than 340 mAh g<sup>-1</sup>, which remains well maintained after 20 cycles. The intercalation reaction mechanism for this high and stable capacity is elucidated via X-ray diffraction and fine structure analysis. Wherein both  $Fe^{2+}/Fe^{3+}$  redox and sulfide ion redox are involved in charge compensation during charge/discharge processes, where the sulfide ion redox contributes to the whole voltage range of -1.5 to 1.5 V and  $Fe^{2+}/Fe^{3+}$  redox only contributes from the middle state of charge. Fluoride ions can not only insert into the Sr–S interstitial sites but also combine with Fe cations. Meanwhile, excessive fluoride-ion intercalation leads to the formation of S–S bonds in the SFFOS lattice. These results highlight the oxyfluorosulfides with layer structure as a new class of active materials for constructing high-performance FIBs.

# 6.1 Introduction

Lithium-ion batteries (LIBs) have dominated the consumer electronics market over the past decades, and their graceful merits have extended their application to electric vehicles. However, the rocketing prices of raw materials, limited energy density, and safety concerns associated with its flammable organic electrolyte serve as a bottleneck for its future applications, where safety and high energy density are two governing parameters.<sup>1-3</sup> Therefore, developing safe and high-energy-density batteries other than LIBs is one of the biggest challenges of the 21st century. Consequentially, batteries using different types of charge carriers (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, etc.) have been proposed.<sup>4-11</sup> Among all these alternatives, all-solid-state fluoride-ion batteries (FIBs), which are based on the shuttling of fluoride ions, have been considered one of the promising future energy storage systems because of their high theoretical energy density and safety.<sup>12-14</sup> Benefiting from the multivalent fluorination process, metal/metal fluorides  $(M/MF_x)$  were first utilized as electrode materials for FIBs due to their high theoretical energy densities.<sup>15–20</sup> However,  $M/MF_x$  systems suffer from exceptionable volume expansion upon fluorination process due to the close-packed metal atoms, which would cause blockage of the fluoride ion (F<sup>-</sup>) diffusion pathway, thus resulting in devastating damage to the electrode-electrolyte interfaces.<sup>16, 21, 22</sup>

Besides M/MF<sub>x</sub> electrodes, intercalation-type cathode materials (LaSrMnO<sub>4</sub>, La<sub>2</sub>CoO<sub>4</sub>, Sr<sub>2</sub>MnO<sub>3</sub>F) that obey topotactic fluorination behavior have also been investigated recently.<sup>23–25</sup> The robust (de)fluorination process of these materials is due to a layered lattice structure with intercalation sites or channels, where  $F^-$  can be inserted or extracted into/from the host lattice reversibly with much lower volume change than the M/MF<sub>x</sub> systems. However, these intercalation-type materials usually contain heavy elements to hold the framework, which are redox-inactive and do not contribute to charge–discharge capacity. For instance, LaSrMnO<sub>4</sub> only provides a capacity of 77.5 mAh g<sup>-1</sup> of one F<sup>-</sup> intercalation, because the La/Sr components are

redox-inactive but take 65.6 % of formula weight. The heavy formula weight will decrease the overall gravimetric energy density due to the lower theoretical capacity, requiring the discovery of an alternative reaction principle that can improve the capacity and energy density.

Various strategies have been reported to improve the practical capacity of LIBs and sodium-ion batteries (SIBs), among which the anionic redox reactions are receiving significant research attention.<sup>26–29</sup> The combined redox of both anionic redox and transition metal (TM) redox in charge compensation allows the electrode to host an excess amount of charge carriers, which results in a higher capacity far beyond that solely based on TM redox. Rigorous research has been carried out to understand the electrochemical properties and structural evolution of anionic redox, which were documented in the studies of LIB and SIB cathodes.<sup>30–32</sup> As the congener of oxygen, sulfur shows less electronegativity, which can improve the ligand p band penetration into the metal d band to form a stronger hybridization with TM ions. Therefore, the chalcogen cathodes possess advanced structural reversibility and accelerated electronic transfer, and such materials utilizing sulfur redox have exhibited fascinating electrochemical properties as LIB or SIB cathode materials.<sup>33–35</sup> Unfortunately, the electrode potential of sulfur redox is typically much lower in LIBs and SIBs, which does not contribute to improving practical energy density.<sup>36</sup>

Extending the redox chemistry of sulfur reported in the cation intercalation host to fluoride ions will lead to novel, high-capacity FIB electrode-active materials. Herein, we have developed a  $Sr_2F_2Fe_2OS_2$  (SFFOS) compound with layered structure and intrinsic F sites within the crystal structure as a novel cathode material for all-solid-state FIBs, where the sulfur redox has been confirmed for the first time to contribute to the charge compensation for the fluoride-ion insertion and deinsertion. Our developed cathode demonstrates a surprisingly high capacity of ~400 mAh g<sup>-1</sup> (corresponding to ~6.1 F<sup>-</sup> insertion). The mechanism of unusually high capacity has been analyzed by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The observed high

capacity is attributed to the intercalation mechanism in SFFOS lattices, where  $F^-$  not only bond with Fe but also occupy the interstitial sites surrounding Sr atoms. Through this mechanism,  $Fe^{2+}/Fe^{3+}$  redox occurs, and the sulfur forms S<sub>2</sub> units retained in the structure (S<sub>2</sub>)<sup>*n*-</sup> (0 ≤ *n* < 2) to provide sufficient charge compensation. This work is expected to deepen our understanding of the development of new series of cathode materials for all-solid-state FIBs and bring new considerations toward the applicationrelated bottlenecks facing anionic redox.

## 6.2 Experimantal

#### 6.2.1 Material preparation

 $Sr_2F_2Fe_2OS_2$  was synthesized by a solid-state reaction under vacuum environment.<sup>37</sup>  $SrF_2$  (99.5 %, FUJIFILM Wako), SrO (99.9 %, Sigma-Aldrich), Fe (99.9 %, FUJIFILM Wako), and S (98 %+, FUJIFILM Wako) were mixed in stoichiometric ratio and then pelletized in an argon-filled glovebox. The pellet was then sealed in an evacuated silica tube with vacuum condition and heated at 800 °C for 36 h. Solid electrolyte  $La_{0.9}Ba_{0.1}F_{2.9}$  (LBF) was synthesized by the mechanochemical method, as described in Section 2.2.1.

The cathode composite was obtained by mixing  $Sr_2F_2Fe_2OS_2$  with solid electrolyte LBF and vapor-grown carbon fiber (VGCF; Showa Denko, Japan) in a weight ratio of 3: 6: 1 by ball-milling for 10 h at 100 rpm using  $ZrO_2$  pot and  $ZrO_2$  balls. For the XRD measurement, the cathode composite with a weight ratio of SFFOS/LBF/VGCF = 40: 51: 9 and a ball-milling speed of 300 rpm was also prepared. The anode composite was obtained by mixing PbF<sub>2</sub> (99.9 %, Kojundo) and Acetylene Black (AB; Showa Denko, Japan) by ball-milling for 6 h at 600 rpm. The mass ratio of the anode composite was PbF<sub>2</sub>/AB = 95: 5.

The synthesis of the oxyfluoride  $Sr_3Fe_2O_5F_2$ , as well as the preparation of the cathode/anode composites, were carried out according to our previous work.<sup>38</sup>

## 6.2.2 Electrochemical measurements

Electrochemical tests were carried out on bulk-type cells. 200 mg LBF powder was put into a poly(ether-ether-ketone) (PEEK) insulator (10 mm diameter) and pressed under a pressure of 100 MPa for 5 min. Then, 10 mg of cathode composite, and 50 mg of anode composite were placed on the opposite sides of the LBF pellet, and an Au foil and a Pb foil were set on the cathode and anode, respectively. Finally, the cell was compressed under a pressure of 360 MPa for 5 min. All the assembling processes were

carried out in an argon-filled glove box with oxygen and moisture contents of less than 0.2 ppm.

The galvanostatic charging–discharging tests, as well as the galvanostatic intermittent titration technique (GITT), were evaluated by HJ1020mSD8 battery testing systems (Hokuto Denko, Japan) with a potential range of -1.5 to 1.5 V vs. Pb/PbF<sub>2</sub> at 140°C without exposure to air. For GITT, each galvanostatic step was carried out at a current density of 10 mA g<sup>-1</sup>, followed by a relaxation step at the open circuit voltage (OCV) for 12 h to allow it to reach a quasi-equilibrium state. The galvanostatic charging–discharging measurement of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub> was carried out with a lower cutoff voltage of -1.5 V (vs. Pb/PbF<sub>2</sub>) and a limited charge capacity of 118 mAh g<sup>-1.38</sup>

## 6.2.3 Characterization

Synchrotron XRD data were collected at room temperature in the Ar atmosphere, at the BL02B2 beamline at SPring-8 (Hyogo, Japan). The pristine powder samples were characterized at BL02B2 beamline with an X-ray energy of 20 keV. The diffractometer was equipped with six MYTHEN silicon micro-strip photon-counting detectors (Dectris Ltd., Baden, Switzerland), and the measurements were performed in Debye-Scherrer transmission geometry. Rietveld refinement was performed by using Jana software.<sup>39</sup> The crystallographic information was supported by VESTA.<sup>40</sup> Laboratory XRD patterns were collected by using an X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å, Rigaku Ultima IV, Japan). The morphology of the as-synthesized material and energy-dispersive spectroscopy spectra (EDS) were characterized using a SU6600 scanning electron microscope (Hitachi, Japan).

Fe *K*-edge, Fe  $L_{2,3}$ -edge, F *K*-edge as well as O *K*-edge XAS measurements were conducted at the BL14B2 and BL27SU beamlines at SPring-8, respectively. S *K*-edge XAS measurement was carried out at the BL6N1 beamline at Aichi-SR (Aichi, Japan) and the BL13 beamline at Ritsumeikan SR center (Shiga, Japan). To prepare the samples during the first and the second cycle for the measurements, all the cells were charged and discharged at a current density of 10 mA  $g^{-1}$  and then transferred from an argon-filled glovebox. The measurements were carried out under vacuum conditions. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using the ATHENA software package.<sup>41</sup>

Resonant inelastic X-ray scattering (RIXS) measurements were performed at BL07LSU in SPring-8 using a grazing flat-field type high-resolution soft X-ray emission spectrometer.<sup>42</sup> O *K*-edge soft XAS was proceeded in advance to determine the proper excitation energy of RIXS. The pellet samples were supported on the holders by carbon tape in an argon-filled glovebox and then were transferred to the measurement chamber without any exposure to air and moisture. The sample positions were slowly changed with a speed of 2.4  $\mu$ m s<sup>-1</sup> during the RIXS measurements to avoid radiation damage.

## 6.3 Results and discussion

## 6.3.1 Structure and compositions

SFFOS was synthesized by a single-step solid-state reaction detailed in Section 6.2.1.<sup>37</sup> The X-ray Rietveld refinement of the prepared SFFOS shown in **Figure 6.1a** and **Table 6.1** demonstrated a layered structure (space group *I4/mmm*) with lattice parameters of a = 4.0468(4) Å and c = 18.0491(1) Å. In this structure, the Fe-centered octahedra share one face with the first neighbor octahedra and one corner with the second neighbor octahedra along the 2D layers. In FeS4O<sub>2</sub> octahedrons, the S atoms occupy the equatorial planes and the O atoms form a Fe<sub>2</sub>O plane with the Fe atoms. Furthermore, F atoms were located in the interstitial sites between Sr layers, and the [Sr<sub>2</sub>F<sub>2</sub>] and [Fe<sub>2</sub>OS<sub>2</sub>] were stacked to form the layer structure, as shown in Figure 6.1b.<sup>37, 43</sup> The particle morphology with elemental mapping of the as-prepared SFFOS is provided in **Figure 6.2**. The Scanning electron microscope (SEM) images of SFFOS revealed a particle size of less than 10  $\mu$ m, and the EDS mapping results (Figure 6.2 and **Table 6.2**) indicated that Sr, F, Fe, O, and S elements were distributed

homogeneously in the particles over the scanned area, and the elemental composition was close to the theoretical value.

#### 6.3.2 Electrochemical performance

The electrochemical performance of SFFOS with fluoride solid electrolytes were measured over the voltage range of -1.5 V and 1.5 V against Pb/PbF<sub>2</sub> anode by bulk-type all-solid battery cells. To improve the ionic and electronic conductivities, the cathode was mixed with a LBF solid electrolyte and VGCF, and the anode was mixed with AB. In this study, although the solid electrolyte LBF would not be oxidized in the voltage range we used,<sup>44</sup> a slight capacity attributed to the side reaction of VGCF in the cathode composite was confirmed by galvanostatic measurement, as shown in **Figure 6.3**. It is noteworthy to mention that we utilized an excessive amount of Pb/PbF<sub>2</sub> as anode material for fabricating a "fluoride-ion half-cell" in reference to our previous study, not only because of the smooth fluorination of PbF<sub>2</sub> but also the gaseous nature and the highest standard electrode potential of F<sub>2</sub> made it not suitable as the other electrode.<sup>22, 45</sup>

As shown in **Figure 6.4a**, a charge capacity of 340 mAh  $g^{-1}$  and an initial coulombic efficiency of 100.2 % were obtained during the 1st cycle. Assuming that the total charge capacity is derived from the F<sup>-</sup> insertion reaction, about 5.1 F<sup>-</sup> insertion into the pristine SFFOS was achieved by the electrochemical fluorination process as follows:

$$Sr_2F_2Fe_2OS_2 + xF^- \to Sr_2F_{2+x}Fe_2OS_2 + xe^-$$
 (6 - 1)

The 1st cycle was regarded to be an activation process since a differently shaped charging curve and an obvious capacity increase were observed in the 2nd cycle. As a result of activation, a higher charge capacity of 403 mAh  $g^{-1}$  and a Coulombic efficiency of 96.8 % were achieved, which corresponded to 6.1 F<sup>-</sup> insertion. Considering the charge compensation in this material, even if the 2 Fe<sup>2+</sup> ions in the

structure were oxidized to  $Fe^{3+}$  (contributed to 132.3 mAh g<sup>-1</sup>), they could not meet the demand of charge compensation during the charge/discharge process. Therefore, we speculated that reversible anionic redox also participated in charge compensation. Figure 6.4b illustrates the cycle performance of SFFOS at 10 mA  $g^{-1}$  between -1.5 V and 1.5 V. Although the discharge capacity decreased from 390 mAh g<sup>-1</sup> during the initial 8 cycles, it maintained a reversible capacity of 346 mAh  $g^{-1}$  (5.1 F<sup>-</sup> insertion) after 20 cycles. The rate capability of SFFOS is shown in Figure 6.4c, where the specific discharge capacities were 313, 271, 217, 172, and 128 mAh g<sup>-1</sup> at the current densities of 10, 20, 50, 100, and 200 mA g<sup>-1</sup>, respectively. These results proved the reversibility and reasonable rate capability of SFFOS in a wide voltage range. In addition, the comparison in gravimetric capacity and volumetric capacity of SFFOS cathode with those previously reported LIB and FIB cathodes are shown in Figure 6.4d.<sup>23, 33, 38, 45-54</sup> SFFOS exhibited a gravimetric capacity of 346 mAh g<sup>-1</sup> and a volumetric capacity of 1522 mAh L<sup>-1</sup>, which surpassed the commercial LIB cathode materials, the Li-excess sulfide and oxide cathode materials, as well as the FIB cathode materials in previous researches. In terms of practical applications, we estimated the energy density by using La/LaF<sub>3</sub> anode with lower potentials (-2.41 V vs. Pb/PbF<sub>2</sub>), which has been utilized in many previous researches.<sup>15, 16, 19, 20, 44, 45</sup> A preliminary evaluation of SFFOS|LaF<sub>3</sub> cell compared with LiCoO<sub>2</sub>|graphite cell is given in Table 6.3. In particular, the volumetric energy density (2304 Wh  $L^{-1}$ ) was twice that of the LiCoO<sub>2</sub>|graphite cell (1552 Wh  $L^{-1}$ ), in addition to the high gravimetric energy density of up to 466 Wh kg<sup>-1</sup>, which was more meaningful for practical applications.

#### 6.3.3 Structural evolution

Further, for an in-depth understanding of the reaction mechanism and the crystal structure evolution of SFFOS upon the fluoride-ion insertion and extraction, XRD (Cu  $K\alpha$ ,  $\lambda = 1.54056$  Å) was recorded during the 1st and the 2nd cycles, as shown in **Figure 6.5**. Since a large ratio of active material in the cathode composite would cause a

significant capacity decrease, while a low ratio would lead to weak intensity of XRD patterns, we have optimized a ratio of active materials for cathode composite to achieve a balance between capacity and XRD pattern intensity, as described in Section 6.2.1. We have calculated the lattice parameters of solid electrolyte LBF, and the crystallite sizes of LBF and SFFOS in the cathode composites under different ball-milling rotation speeds, and the results are shown in **Table 6.4** and **6.5**. It was observed that the lattice parameters of LBF did not change significantly after ball-milling process. However, the crystallite sizes of both LBF and SFFOS calculated by Scherrer equation were significantly reduced after ball-milling process (Table 6.5). The above-mentioned results indicated that the active material SFFOS and solid electrolyte LBF did not react with each other, and that only a decrease in crystallinity occurred during ball-milling process.

By comparing the XRD patterns, as shown in Figure 6.6, it was observed that no other fluoride or oxyfluoride diffraction patterns (e.g., SrF<sub>2</sub>, FeF<sub>3</sub>, FeOF) were detected in the 1st fully charged state, except for the diffraction peaks of the solid electrolyte LBF and the active material. A closer examination of Figure 6.5a,b, revealed that it was highly possible for 5.1 F<sup>-</sup> to be inserted into the SFFOS host lattice at the fully charged state during the 1st cycle. Based upon these observations, we speculated that the F<sup>-</sup> were inserted into the interstitial layers between Sr and S atoms, which could expand the lattice volume. As shown in Figure 6.5a, although the strongest diffraction peaks of the active material (26.5° and 29.9°) were only slightly shifted, some new small peaks such as the peak around 35.4° and some shoulders from the broadened peaks, were observed after charging. The F<sup>-</sup> insertion might have caused some symmetry reduction; therefore, we attempted to refine the charged samples with a subspace group of I4/mmm. Because the XRD patterns of SFFOS were broadened and weakened during ball-milling process, they were largely hidden by those of LBF, making the Rietveld refinement impossible. The lattice parameters (a and c) and the lattice volume assessed via Le bail refinement based on the P4/mmm space group are shown in Figure 6.5b, Figure 6.7,

**Table 6.6**, and **6.7**. There was a significant expansion of the lattice volume at early state of charge (x = 0-2), which was related to the topotactic intercalation of fluoride ions into the lattice. Similar fluoride ion insertion behavior was found in the Ruddlesden–Popper-type La<sub>2</sub>NiO<sub>4</sub> lattice, but the magnitude of volume expansion in this study was much smaller than that of La<sub>2</sub>NiO<sub>4</sub> (4.7 vs. 14.6 %).<sup>55</sup> The fluoride ion insertion sites as well as the local structure, will be discussed in the following section. After discharging, the volume change was about 2 % compared to SFFOS pristine, and the XRD diffraction patterns could be fitted with the *P*4/*mmm* space group with higher accuracy. This indicated that although F<sup>-</sup> could be topotactical inserted into the SFFOS lattice, the structure underwent an irreversible structural change after the 1st cycle.

The main diffraction peaks at 26.5° and 29.9° exhibited a similar trend as the 1st cycle during the 2nd charge/discharge cycle (Figure 6.5c). On the other hand, the overall peak intensity gradually diminished at the end of charging (x > 5), which was similar to what we found in our recently published research on the Ruddlesden–Popper-type La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode material.<sup>44</sup> The insertion of the excessive F<sup>-</sup> into the lattice led to a decrease in the crystallinity of the active material, while the diffraction peaks could recover after discharging. The XRD results demonstrated the reversible insertion/extraction behaviors of fluoride ions in the SFFOS lattice which did not significantly affect the integrity of layer structure, similar to the previous findings in Ruddlesden–Popper structured cathode materials.<sup>23, 44, 55</sup> It is worth pointing out that the expansion during the 2nd charging process was about 4.8 %, which remains 0.5 % after discharging compared to the beginning of the 2nd charge. The volume expansion of SFFOS was lower than that of La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode with 5 F<sup>-</sup> insertion (6 %) and was even comparable to that of LiCoO<sub>2</sub> (~3 %),<sup>44, 56</sup> which was the reason for its outstanding cycle performance.

The experimental result showed that the superior capacity of SFFOS was due to the electrochemical insertion of 6.1 F<sup>-</sup>, which was quite strange and surpassed the expected amount of 2 F<sup>-</sup> insertion based on  $Fe^{2+}/Fe^{3+}$  redox in SFFOS. Through the

analysis of this unusual redox reaction mechanism, we attempted to demonstrate that SFFOS can accept anomalous amounts of fluoride ions by mixed cation and anion redox. To investigate the electronic and local structures of both cation and anions during fluoride ion insertion/extraction processes in SFFOS, a series of electrodes were examined by XAS. After clarifying the mechanism by which the redox reaction of iron ions occurred, the anion redox of oxide and sulfide ions were examined.

#### 6.3.4 Charge compensation mechanisms

Figure 6.8a shows the XANES at Fe K-edge during the 1st charge/discharge cycle (activation process). To identify the spectrum of the pristine SFFOS, the spectrum of SFFOS was further compared with the referenced samples such as FeO, FeS, and FeS<sub>2</sub> (Figure 6.9), which revealed that the features appeared at the energy of 7128.1 eV and 7135.3 eV were ascribed to the multiple scattering contributions of O and S around the Fe atoms respectively,<sup>57–59</sup> and Fe existed in +2 oxidation state in this structure, as was proved in previous research.<sup>37</sup> The Fe K-edge absorption of SFFOS gradually shifted to higher energy upon charging, which was related to the oxidation from  $Fe^{2+}$  to  $Fe^{3+}$ . Although the absorption edge returned to lower energy after discharge process, the shape and intensity differed significantly from the pristine state. The energy of the absorption edge ( $E_0$ ) increased drastically at the end of the charging process (x > 4 in  $Sr_2F_{2+x}Fe_2OS_2$ ), and it reached the  $Fe^{3+}$  level (using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with 6-fold  $Fe^{3+}$ coordination as reference) at full-charged state (x = 5.1) (Figure 6.8b). This oxidation change was further supported by the Fe L-edge XAS, as shown in Figure 6.10. A new peak of Fe  $L_3$ -edge around 710 eV associated with Fe 3d-hole emerged at the end of the charging process, suggesting a valence state of  $Fe^{3+}$  (3d<sup>5</sup> state) in the full-charged sample. The variation tendency of F K-edge XANES results during the initial cycle is shown in Figure 6.8c. All the samples showed similar absorption edge features ( $\geq 687$ eV) because of the fluorine abundance in LBF solid electrolyte. Upon charging, a doublet pre-edge peak emerged at approximately 684 eV and increased drastically at

the end of the 1st charging process, corresponding to F 2p–Fe 3d hybridization as observed in the FeF<sub>3</sub> reference.<sup>60</sup> It was observed that the Fe *K*-edge XANES spectra of the 1st fully charged sample was quite different from the FeF<sub>3</sub> reference (**Figure 6.11**) and the spectra of FeOF in the literature,<sup>61</sup> indicating that the charging product of SFFOS was not simply iron (III) fluoride or oxyfluoride, but with a high possibility of forming an intercalated fluoride. The abovementioned Fe *K*-edge, *L*-edge, and F *K*-edge XANES all showed a significant change at x > 4, indicating that the charge compensation of Fe, with the accompanying change in Fe–F hybridization, was dominant in the later stage of the first charging process.

In previous studies, many works in LIB systems have proved that anions such as oxide and sulfide ions can contribute to the charge compensation in cathode materials.<sup>31-33, 62</sup> Therefore, the extra capacity beyond 2 electrons for the SFFOS cathode during the charging process may arise due to the contribution of anionic redox. To explore the origin of the excess fluoride-ion intercalation capacity beyond Fe redox and the electronic structure changes of anions in SFFOS during charge and discharge, S K-edge, as well as O K-edge soft XAS at a series of charged states, were measured in partial fluorescence yield (PFY) mode. The results of S K-edge XANES during the initial cycle are shown in Figure 6.8d. The shoulder peak at 2470 eV in the pristine SFFOS was attributed to the transition of the unoccupied S 3p-Fe 3d hybridization state, and the broad feature at 2477 eV represented S 3p-Fe 4sp hybridization.<sup>60, 63</sup> During the 1st charging process, the intensity of the pre-edge increased at a very early state of charge (x = 1), corresponding to the strong Fe 3d–S 3p hybridization state as observed in FeS reference.<sup>63</sup> A new peak emerged at 2471.8 eV at x = 2, implying the formation of a new electronic state associated with oxidized sulfide ion. A feature with a similar shape and energy was found in the pyrite-FeS<sub>2</sub> reference, assigned to the transition from S 1s to the antibonding S 3p band to form dumbbell-shaped  $S_2^{2-.35, 60, 64}$  With the F<sup>-</sup> insertion, the intensity of the pre-edge peak decreased while the peak at 2471.8 eV increased, indicating the gradual breakage of Fe-S bonds and the continuous formation

of S–S bonds. At fully charged state, the broad feature at 2482 eV can be ascribed to S–Fe scattering resonance, which can be observed in FeS and FeS<sub>2</sub> standards but not in elemental sulfur.<sup>65</sup> The S *K*-edge XANES results demonstrated that S and Fe remained bonded in the fully charged state, implying that the final product of sulfur was likely to be the neutral S<sub>2</sub> units retained in the structure rather than the elemental sulfur. After discharging, the peak at 2471.8 eV disappeared and the pre-edge peak recovered, which proved the cleavage of S–S bonds and the reformation of Fe–S interaction, indicating the reversibility of the sulfide ion redox.

The O *K*-edge XANES of the initial cycle is provided in Figure **6.12a**, where the pre-edge peaks at 529.4 eV and 530.7 eV corresponded to the transition of O 1s to unoccupied hybridized orbitals.<sup>37</sup> Previous studies in LIBs cathodes have proved that the integrated area of the pre-edge peak in O *K*-edge XANES represents the density and vibration of the unoccupied states and can provide crucial information on the distribution of hole states.<sup>29, 66</sup> However, the F<sup>-</sup> intercalated in SFFOS looked different from the conventional oxide-ion contribution mechanism. Therefore, in order to examine the electronic structure of oxide-ion in detail, we also carried out the RIXS measurement on the fully charged state in the 2nd cycle (Figure 6.12c). There was no progressive peak representing oxygen vibration on the RIXS spectrum with an excitation energy of 530.9 eV,<sup>67</sup> indicating no oxidation products such as O<sup>-</sup>, O<sub>2</sub><sup>2-</sup> were generated upon fluorination process. Therefore, the O *K*-edge pre-edge change was probably due to the formation of the S 3p hole state, which changed the 3d orbital of the neighboring Fe and, thus, the O 2p orbital adjacent to Fe.

The Fourier transforms (FTs) of Fe *K*-edge, S *K*-edge, and Sr *K*-edge EXAFS at various charge/discharge states during the 1st cycle are shown in **Figure 6.13**. The *R*-space and *k*-space of the pristine SFFOS, fully charged, and fully discharged samples were fitted by using FEFF, and the parameters refined during fit were Debye-Waller factor ( $\sigma^2$ ) and atomic distance/bond length (*R*), as shown in **Figure 6.14**, **15**, **16**, and **Table 6.8**, respectively.<sup>68, 69</sup> As shown in Figure 6.13a, during the 1st charge process,

only one main peak for Fe-O/F was observed in the Fe K-edge EXAFS, which suggested that the intercalated fluoride ions around Fe cations might have a similar coordination environment to the O sites.<sup>45</sup> The initial change of the first shell peak was related to the formation of Fe-F bonds due to F<sup>-</sup> insertion and its intensity significantly increased in the fully charged state, accompanied by a shift to a smaller radial distance. This was because the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  at the end of the charge process resulted in a decrease in the ionic radius. Figure 6.17 revealed that there were no peaks related to Fe-Fe interactions in the EXAFS FT of the fully charged state. This observation suggested that there was no formation of FeF<sub>3</sub> or FeOF upon charging, which was in consistent with the XRD and XANES results. After discharging process, the FT was quite different from the pristine state, indicating a phase transformation during the 1st cycle. A new peak emerged at 1.9 Å, and the real interatomic distance obtained from the EXAFS fitting was 2.23 Å (Table 6.8), suggesting the shortening of the Fe–S bonds. In the case of S K-edge EXAFS, the peak around 2.2 Å represented the S-Fe coordination shell (corresponding to a real interatomic distance of 2.66 Å) in pristine SFFOS (Figure 6.13b).<sup>66</sup> This peak disappeared upon charging while a new peak at a shorter radial distance of 1.67 Å (the fitted interatomic distance was 2.08 Å vs. 2.66 Å of S-Fe bond in pristine) appeared (Figure 6.15 and Table 6.8),<sup>71, 72</sup> which indicated the formation of S-S interaction. The peak that appeared at approximately 1.9 Å (corresponding to a real interatomic distance of 2.31 Å) was ascribed to the shortened S-Fe interaction after the discharging process, which was consistent with the results of the Fe K-edge EXAFS.

Based upon the above analysis, we confirmed the formation of the Fe–F bonds as well as S–S bonds, and the fluoride ions occupied around Fe at the end of the charging process. It has been proved in the XRD results that the lattice gradually expanded upon charging. Therefore, it was highly possible that the fluoride ions can achieve reversible insertion/extraction in the Sr–S interstitial layers, as was found in Ruddlesden–Popper type cathode materials.<sup>25, 44, 55</sup> On the other hand, in the FTs of Sr *K*-edge EXAFS, the

first and second shells represented Sr-F and Sr-S coordinations for the pristine SFFOS, respectively (Figure 6.13c). During the 1st charging process (Figure 6.13c), the F<sup>-</sup> insertion led to an increased Sr-F interaction from x = 1 and remained almost unchanged until the fully charged state, and the weakened Sr-S interaction from x=1 to the fully charged state also suggested the continuous insertion of fluoride ions to the Sr-S interstitial layer. Similarly to the EXAFS of Fe, no peaks corresponding to Sr-Sr interaction were found in the Sr K-edge EXAFS of the fully charged state (Figure 6.18), indicating no SrF<sub>2</sub> production. These proved that fluoride ions occupied the interstitial sites around Sr atoms at very early charging stage. To explore the fluoride-ion insertion behavior, we assumed a model for the insertion of F<sup>-</sup> ions into the SFFOS lattice, as shown in Figure 6.19. In the pristine structure, the F atoms (F1) occupied 4d sites, located in the Sr-Sr interstitial layers, and the atomic parameters are shown in Table **6.9.** The ionic radius of  $S^{2-}$  was approximately 1.8 Å.<sup>74</sup> and there was no space in the structure for the  $F^-$  to be inserted (Figure 6.19a). However, we have observed the sulfur redox continued throughout the charging process in the XAS results (Figure 6.8d), and the valence state of sulfur increased to approximately 0 in the fully charged state according to the charge compensation. As the valence state increased, the ionic radius of sulfur underwent a strong contraction, with approximately 1.0 Å for S<sup>0,74</sup> and some void would be created in the Sr-S interstitial layers, as shown in Figure 6.19b. Assuming that the *c*-axis of the material lattice remained unchanged after the  $F^-$  ion insertion, the inserted  $F^-$  (F2) occupied 8g sites (0, 0.5, z), and it was found that there was enough space in the structure to accommodate at least 4  $F^-$  ions (Figure 6.19c), the atomic parameters are shown in Table 6.10.

It was observed in the La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode material that excessive F<sup>-</sup> ions (> 2) can be inserted into the perovskite units to form Mn–F bonds, leading to the formation of molecular O<sub>2</sub> in the lattice.<sup>44</sup> Since S is the congener of O, and the S<sub>2</sub> and O<sub>2</sub> are isoelectronic species. Combing with our XAS results, we believed that there was a high possibility that the SFFOS followed a similar reaction mechanism: The excessive

 $F^-(x > 4)$  were inserted into the Fe-anion layer and bond with Fe, and a part of Fe–S bonds was broken with the formation of S–S bonds. As we mentioned in the structural evolution section, the XRD patterns of SFFOS were hidden by those of LBF, making Rietveld refinement impossible. Consequently, we proposed several possible configurations based on the presences of S–S bonds in the existing compounds, as shown in Figure 6.13d (i, ii). Figure 6.13d (i) represents a folded Fe–S–S–Fe configuration, which is similar to the local configuration in FeS<sub>2</sub> (Space group: *Pa*-3).<sup>64</sup> Figure 5d (ii) represents a triangular Fe–S–S configuration, which can be found in the polysulfide cluster  $[Mo_2S_{12}]^{2-.71, 72}$  Nevertheless, these configurations have not been demonstrated to be thermodynamically stable, and this calls for further theoretical calculations in future study.

According to the abovementioned XRD and XAS results, the reaction mechanism during the 1st cycle is summarized in **Figure 6.20**. The fluorination process may cause a decrease in symmetry (I4/mmm to P4/mmm), the ionic radius of sulfur decreased significantly with the increasing valence state, creating enough space in the Sr–S interstitial layers to accommodate F<sup>-</sup> ions. Moreover, the excessive F<sup>-</sup> ions could bind with Fe, leading to the formation of S–S bonds within the Fe-anion stocks. After discharging, both Sr–F and Sr–S interactions were partially recovered, indicating that the inserted fluoride ions were not completely extracted. The XRD, XANES, and EXAFS during the 1st cycle exhibited consistent results. Although SFFOS can access reversible fluoride ion insertion/extraction, it underwent some irreversible local strutural changes during the 1st cycle (i.e., the shortened S–Fe bonds shown in Figure 6.13a, b), which might be the reason for the capacity fading during the initial few cycles.

Interestingly the Fe *K*-edge spectra during the 2nd cycle (**Figure 6.21a**) showed a similar charge compensation mechanism to the 1st cycle, however during the 2nd cycle,  $Fe^{2+/3+}$  redox occurred from x = 3 to the fully charged state. Besides, the intensity of the pre-edge peak in F *K*-edge XANES spectra gradually strengthened upon charging, indicating the increased Fe–F bonds (Figure 6.21c). Since Fe in SFFOS can provide

only  $2e^{-}$  for charge compensation, the remaining charge was contributed by sulfide ions, as evidenced by the varied S *K*-edge spectra during the charging process (Figure 6.21d). The peak at approximately 2472 eV related to the S–S bond, appeared from x = 3 and gradually increased until the fully-charged state, finally forming the electronic structure of S<sub>2</sub><sup>0</sup>, and the S–Fe scattering resonance feature around 2482 eV can also be observed at fully charged state.

According to the EXAFS results of the 2nd cycle, the FTs of Fe *K*-edge EXAFS drastically changed from x = 3 due to the binding with fluoride ions (**Figure 6.22a**). The main peak in the FTs of S *K*-edge EXAFS gradually moved to a shorter radial distance from x = 3, suggesting that with the increase of the sulfur valence state (Figure 6.22b), the electrostatic repulsion, and the ionic radius of Sulfur became smaller; thus, the S–S bond became shorter.<sup>34</sup> The S–S bond length in the 2nd fully charged state was 2.09 Å, similar to the 1st fully charged state, confirming the reproducibility of the S–S bond formation (Table 6.8). Moreover, the FT intensity of the first shell on Sr *K*-edge EXAFS gradually increased at the early charging state ( $x = 1 \sim 2$ ), and it remained almost unchanged from x = 2 to the fully charged state. This indicated that the fluoride ions preferentially occupied the interstitial sites around Sr in the early charging stage. After discharging, the FTs' shapes on Fe and S *K*-edge EXAFS did not show noticeable change from the 1st discharged one, proving the 2nd cycle exhibited better local structural reversibility.

Based upon the electrochemical and XAS studies, it was quite evident that SFFOS exhibited quite an interesting reaction mechanism wherein the fluoride ions can locate in both Fe-anion stocks and Sr–S interstitial layers, which has never been reported before. The reaction mechaism during the 2nd cycle was slight different from that of the 1st cycle, as shown in **Figure 6.23**. After the 1st cycle, the SFFOS underwent some irreversible structural changes, such as the shortening of the Fe–S bonds, and the incomplete extraction of the  $F^-$  in the Sr–S interstitial layers. Upon the 2nd charging process, the oxidation of sulfur could produce some space for accepting the inserted  $F^-$ 

in the host lattice. Sulfur at the fully-charged state existed as neutral  $S_2^0$ , which was similar to the "trapped-O<sub>2</sub> molecule" in the La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7- $\delta$ </sub>F<sub>2</sub> cathode and in Li-rich cathode materials for LIBs.<sup>44, 75</sup> The excessive F<sup>-</sup> insertion led to a decrease in the crystallinity of the material, but this process exhibited a good reversibility.

Regarding the precise structure of SFFOS after charging, previous studies have successfully prepared fluorinated products using chemical fluorination method, which is an important tool for probing the reaction mechanism.<sup>76, 77</sup> In this experiment, we attempted to chemically fluorinate SFFOS with poly(vinylidene fluoride) (PVdF) and NH<sub>4</sub>F as fluorination agents. However, SFFOS decomposed into SrF<sub>2</sub> and no intercalated fluorination product was obtained. In addition, the quantitative analysis about the fluorine in the charging products is also significant for clarifing the reaction mechanism. Previous research has used <sup>19</sup>F magic angle spinning nuclear magnetic resonance (MAS NMR) to analyze the ionic conduction of F<sup>-</sup> in different chemical environments in the Sm<sub>1-x</sub>Ca<sub>x</sub>F<sub>3-x</sub> solid solution system.<sup>78</sup> In this study, since the amount of the active material was very small, the solid electrolyte and the side reaction product of VGCF might interfere with the characterization result. Therefore, chemical fluorination and quantitative analysis of fluorine are the main issues to be addressed in future study.

In our proposed reaction mechanism model, the Sr–S interstitial layers in the pristine structure could accommodate about 4 F<sup>-</sup>, and the excessive fluoride ions were considered to be inserted into the Fe-anion stocks. In order to investigate the kinetic properties upon fluoride ion insertion and S–S bond formation, the GITT measurement was carried out during the 2nd cycle (**Figure 6.24**). The obtained results indicated that the polarization of open circuit voltage for x > 5 was significantly larger than those in low state of charge, which might be caused by the formation of S–S bonds that could involve local distortions, as we have found similar phenomenon in the La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7–8</sub>F<sub>2</sub> cathode, in which the formation of oxygen-oxygen bond that could involve local distortions.<sup>44</sup> According to our previous studies on 3d transition

metal/metal fluoride conversion-type cathodes,<sup>16</sup> the OCVs during the conversion reaction remained almost constant. However, as shown in Figure 6.24b, the GITT results we obtained in this study showed that the OCV continuously changed during the charging process, which resembled a characteristic of an intercalation reaction. Although it was not clear how the S–S bonds and excessive fluoride ions existed in the charged  $Sr_2F_{2+x}Fe_2OS_2$ , the abovementioned characterization results revealed that the S–S bonds (or neutral  $S_2$ ) and excessive fluoride ions might exist in some cavities in the structure, as the presence of H<sub>2</sub> molecule was found in SrTiO<sub>3</sub> structure,<sup>79</sup> and the formation of S–S bonds could create the irregular sites for inserted fluoride ions.

## 6.3.5 Discussion on the performance of oxyfluoride and oxyfluorosulfide

Concerning the high capacity of this oxyfluorosulfide, we discussed a comparison of Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub> with layered oxyfluoride Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>.<sup>38</sup> The comparison of the charge/discharge profiles and the open circuit voltage obtained from GITT measurements during the 2nd cycle is shown in Figure 6.25. It was observed that SFFOS exhibited much higher capacity than that of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>, while its average voltage throughout the charging process was slightly lower by 0.05 V. For Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>, we have demonstrated in our previous research that the  $Fe^{2+}/Fe^{3+}$  redox was the main contributor for the charge compensation.<sup>38</sup> On the other hand, it was clear from the XAS results of  $Sr_2F_2Fe_2OS_2$  that  $Fe^{2+}/Fe^{3+}$  redox contributed to the charge compensation from the middle state of charge (x > 3 in Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub>). In LIBs, the average charge voltage of the commercial LiCoO<sub>2</sub> cathode material is about 3.7 V, while the average charge voltage of  $LiMS_2$  (M = Ti, Fe) is considered to be about 2.8 V, according to the previous study.<sup>33</sup> The sulfide generally shows much lower voltage than oxide, mainly because the difference between S 3p bands and the electrochemical potential of Li is much smaller than that of O 2p bands.<sup>36</sup> It is worth noting that, benefiting from the increase in the energy level of the oxygen, the oxyfluorosulfide SFFOS not only exhibited about 3-fold the capacity of the oxyfluoride Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub> but also the potential penalty was significantly reduced compared to that in LIBs (Figure 6.25a, 0.397 vs. 0.449 V).

# 6.4 Conclusion

In summary, we have demonstrated high-performance  $Sr_2F_2Fe_2OS_2$  involving iron and sulfide ion redox as cathode material for all-solid-state FIBs. The charge compensation mechanism was disclosed for SFFOS, where sulfide ion redox contributed to the whole voltage range from -1.5 V to 1.5 V against Pb/PbF<sub>2</sub>, and Fe<sup>+2</sup>/Fe<sup>+3</sup> redox contributed from the middle state of charge. The ionic radius of sulfur decreased with the increasing oxidation state, which created space in the Sr-S interstitial layers to accommodate F<sup>-</sup>. The excessive F<sup>-</sup> could also be inserted into the Fe-anion stocks to form Fe-F bonds to achieve a high capacity of 403 mAh  $g^{-1}$  (~6.1  $F^{-}$ ). The S-S bonds were formed upon charging to extend the intercalated fluoride ion sites, although the specific location and precise lattice structure still needed to be further investigated. Although the sulfide ion redox reaction might suffer from the sluggish kinetics at high state of charge, and the structure underwent irreversible local structural change, which resulted in the capacity fading during the initial several cycles, the high capacity of more than 340 mAh g<sup>-1</sup> through fluoride ion intercalation in SFFOS could be maintained for up to 20 cycles. Compared to the Fe-based layered oxyfluoride Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>, the Fe-based oxyfluorosulfide SFFOS reduced the energy density penalty and exhibited a much higher capacity and a reasonable volumetric energy density. We believe that this study could provide a new understanding of sulfur-based charge compensation and electrochemical fluorination reactions.


Figure 6.1 Crystal structural information of SFFOS. (a) Rietveld refinement of the SFFOS sample, wavelength = 0.41491 Å,  $R_{\rm f}$ = 4.08 %,  $R_{\rm wp}$ = 8.17 %. (b) Crystal structure of SFFOS expressed in terms of ionic radii.

Table 6.1	Structural	parameters	of as-prepare	ed Sr <sub>2</sub> F <sub>2</sub> Fe <sub>2</sub> OS	S <sub>2</sub> determined	l from 1	the
		R	ietveld refine	ement.			

Atom	Wyckoff Position	x	у	Z	$B_{ m iso}$ / ${ m \AA}^2$	Occupancy
Sr1	4e	0.5	0.5	0.1708(3)	0.79(0)	1
Fe1	4c	0.5	0	0	0.79(4)	1
<b>S</b> 1	4e	0	0	0.09365(0)	0.83(6)	1
O1	2b	0.5	0.5	0	0.83(0)	1
F1	4d	0.5	0	0.25	0.83(0)	1

Space group: I4/mmm;  $R_{wp} = 8.17$  %,  $R_f = 4.08$  %; a = 4.0468(4) Å, c = 18.0491(1) Å.



Figure 6.2 Morphology and elemental distribution of as-prepared SFFOS by SEM and EDS mapping analysis. The yellow squared area 1 and 2 represents the test areas for elemental composition.

Areas	Atomic ratio / %					
111045	Sr	F	Fe	0	S	
Spectra1	48	50	54	24	44	
Spectra2	49	50	51	27	46	

**Table 6.2** Elemental composition obtained from the SEM-EDS mapping results.



Figure 6.3 Charge/discharge curves of a composite consisting only of VGCF and LBF solid electrolyte in a weight ratio of 60: 10, at a current density of 10 mA  $g^{-1}$  at 140 °C.



Figure 6.4 Electrochemical properties of SFFOS using SFFOS|LBF|Pb/PbF<sub>2</sub> all-solid FIB cell. (a) Charge/discharge profiles for the 1st and 2nd cycle at a current density of 10 mA g<sup>-1</sup> at 140 °C. (b) Cycle performance at 10 mA g<sup>-1</sup>. (c) Rate capability between 10 and 200 mA g<sup>-1</sup>.(d) Comparison of gravimetric capacity and volumetric capacity for SFFOS and cathode materials reported in LIBs and FIBs: 1. LiCoO<sub>2</sub>,<sup>46</sup> 2. LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>,<sup>47</sup> 3. LiFePO<sub>4</sub>,<sup>48</sup> 4. Li<sub>1.13</sub>Ti<sub>0.57</sub>Fe<sub>0.3</sub>S<sub>2</sub>,<sup>33</sup> 5. Li<sub>1.25</sub>Nb<sub>0.25</sub>Mn<sub>0.5</sub>O<sub>2</sub>,<sup>49</sup> 6. Li<sub>1.2</sub>Ni<sub>0.333</sub>Ti<sub>0.333</sub>Mo<sub>0.133</sub>O<sub>2</sub>,<sup>50</sup> 7. Li<sub>1.2</sub>Mn<sub>0.2</sub>Ti<sub>0.4</sub>Cr<sub>0.2</sub>O<sub>2</sub>,<sup>51</sup> 8. Li<sub>1.25</sub>Nb<sub>0.25</sub>V<sub>0.5</sub>O<sub>2</sub>,<sup>52</sup> 9. Li<sub>1.25</sub>V<sub>0.55</sub>Nb<sub>0.2</sub>O<sub>1.9</sub>F<sub>0.1</sub>,<sup>53</sup> 10. Li<sub>8/7</sub>Ti<sub>2/7</sub>V<sub>4/7</sub>O<sub>2</sub>,<sup>54</sup> 11. Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>,<sup>38</sup> 12. Sr<sub>2</sub>MnO<sub>3</sub>F<sub>2</sub>,<sup>23</sup> 13. LaSrMnO<sub>4</sub>F,<sup>23</sup> 14. La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7-8</sub>F<sub>2</sub>.<sup>44</sup>

Battery	LIB	FIB
Cathode	LiCoO <sub>2</sub>	$Sr_2F_2Fe_2OS_2$
Capacity / mAh g <sup>-1</sup>	170	350
Density / g cm <sup>-3</sup>	5.05	4.4
Anode	Graphite	La
Capacity / mAh g <sup>-1</sup>	372	579
Density / g cm <sup>-3</sup>	2.20	6.16
Utilization ratio / %	100	100
Capacity ratio of anode/cathode	1	1
Weight ratio of anode/cathode	0.456	0.604
Volume ratio of anode/cathode	1.047	0.432
Average Voltage / V	3.7	2.14
Gravimetric energy density / Wh kg <sup>-1</sup>	432	466
Volumetric energy density / Wh L <sup>-1</sup>	1552	2304

 Table 6.3 Comparison of gravimetric/volumetric energy densities based on active

materials between LIB and FIB.

The extra part such as current collector, electrolyte, battery shell, separator, conductive additives, binder, etc. are not involved in the calculation.



Figure 6.5 (a) XRD patterns of Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub> during the 1st cycle. An enlarged view of 2θ = 25-28° is shown on the right side. The cathode composite contains solid electrolyte LBF, and the diffraction patterns of LBF can also be regarded as the calibrant. (b) The changes of lattice parameters *a* and *c*, and volume expansion during the 1st cycle. (c) XRD patterns of Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub> during the 2nd cycle. An enlarged view of 2θ = 25-28° is shown on the right side.
(d) The changes of lattice parameters *a* and *c*, as well as volume expansion during the 2nd cycle.

Samples	La <sub>0.9</sub> Ba <sub>0.1</sub> F <sub>2.9</sub> P3c1				
	<i>a/b</i> / Å	<i>c</i> / Å	$V/ \mathrm{\AA^3}$		
as-prepared La <sub>0.9</sub> Ba <sub>0.1</sub> F <sub>2.9</sub>	7.224(2)	7.388(2)	333.947(0)		
30% cathode composite	7.229(3)	7.394(5)	334.681(6)		
40% cathode composite	7.239(1)	7.405(2)	336.135(8)		

**Table 6.4** The lattice parameters of the as-prepared solid electrolyte  $La_{0.9}Ba_{0.1}F_{2.9}$ , and the solid electrolyte in the cathode composites after ball-milling process.

Table 6.5 The fitted Full Width at Half Maximum (FWHM) of LBF 002 diffraction

peak and SFFOS 103 diffraction peak, and the calculated crystallite size.

Sample	FWHM / LBF002	2 <i>θ</i> / °	Crystallite / nm	FWHM / SFFOS103	2 <i>θ</i> / °	Crystallite / nm
as-prepared LBF	0.1922	24.071	41.8	-	-	-
30% cathode composite	0.2817	24.048	28.5	0.4889	26.611	16.5
40% cathode composite	0.3219	24.014	24.9	1.177	26.499	6.8



Figure 6.6 XRD pattern of the fully charged state during the 1st cycle, wavelength = 1.54056 Å.

SrF<sub>2</sub>, FeF<sub>3</sub>, and FeOF are provided as references.



**Figure 6.7** Respective XRD patterns and their Le bail refinement results of cathode in different states of charge, wavelength = 1.54056 Å. (a) the 1st cycle. (b) the 2nd cycle.

Samples	Sr <sub>2</sub> F <sub>2+x</sub> Fe <sub>2</sub> OS <sub>2</sub> P4/mmm			Sr <sub>2</sub> F <sub>2</sub> Fe <sub>2</sub> OS <sub>2</sub> I4/mmm		
	a/b / Å	<i>c</i> / Å	$V/\text{\AA}^3$	<i>a/b</i> / Å	<i>c</i> / Å	V / Å <sup>3</sup>
SFFOS	-	-	-	4.049(7)	17.999(0)	295.177(8)
<i>x</i> =1	4.112(6)	17.822(0)	301.431(2)	-	-	-
<i>x</i> =2	4.141(4)	17.885(1)	306.805(6)	-	-	-
<i>x</i> =3	4.148(2)	17.902(9)	308.079(4)	-	-	-
<i>x</i> =4	4.151(3)	17.904(5)	308.538(8)	-	-	-
Fullchg (x=4.9)	4.153(2)	17.917(7)	309.056(5)	-	-	-
Dischg (x=0.18)	4.118(8)	17.777(7)	301.573(5)	-	-	-

**Table 6.6** Refined lattice parameters and space group for  $Sr_2F_{2+x}Fe_2OS_2$  during the 1stcycle.

Samples	Sr <sub>2</sub> ]	mm	
	<i>a/b</i> / Å	<i>c</i> / Å	$V/  m \AA^3$
1st-Dischg	4.118(8)	17.777(7)	301.573(5)
<i>x</i> =1	4.131(9)	17.794(1)	303.794(1)
<i>x</i> =2	4.141(1)	17.833(3)	305.876(2)
<i>x</i> =3	4.161(5)	17.911(8)	310.217(5)
<i>x</i> =4	4.180(5)	17.919(6)	313.130(9)
<i>x</i> =5	4.189(9)	17.900(6)	314.124(3)
Fullchg ( $x=5.4$ )	4.193(2)	17.973(9)	316.131(0)
Dischg ( <i>x</i> =0.11)	4.128(2)	17.785(5)	303.088(0)

**Table 6.7** Refined lattice parameters and space group for  $Sr_2F_{2+x}Fe_2OS_2$  during the2nd cycle.



Figure 6.8 Changes in electronic structures for Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub> during the 1st cycle. (a) Fe *K*-edge XANES at various fluorination states for Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub> in the 1st cycle, the inset figure shows the pre-edge variation. (b) The changes of *E*<sub>0</sub> summarized from the Fe *K*-edge XANES of Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub>. As-prepared SFFOS and α-Fe<sub>2</sub>O<sub>3</sub> are provided as Fe<sup>2+</sup>/Fe<sup>3+</sup> references. (c) F *K*-edge XANES spectra. La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> and FeF<sub>3</sub> are provided as references. (d) S *K*-edge XANES spectra. FeS, FeS<sub>2</sub>, and sulfur are provided as references.



Figure 6.9 Fe K-edge XANES for the pristine  $Sr_2F_2Fe_2OS_2$ . FeS, FeS<sub>2</sub>, and FeO are provided as references for different  $Fe^{2+}$  electronic structures.



Figure 6.10 Fe *L*-edge XAS spectra of  $Sr_2F_2Fe_2OS_2$  at various fluorination states upon the 1st cycle. LiFePO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> are provided as Fe<sup>2+</sup>/Fe<sup>3+</sup> references.



Figure 6.11 Fe K-edge XANES for the fully charged states. FeF<sub>3</sub> is provided as the reference.



Figure 6.12 O K-edge XAS spectra collected at different fluorination states during (a) the 1st cycle and (b) the 2nd cycle. (c) RIXS results of Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub> at fully charged states in the 2nd cycle. The inset figure (1) shows the XAS results recorded at BL07LSU in SPring-8 beforehand RIXS measurement and the accurate incident energy for RIXS was calibrated to be 530.9 eV. The inset figure (2) shows the elastic peaks and corresponding scattering behaviors which are calibrated to energy loss.



Figure 6.13 k<sup>3</sup>-Weighted Fourier transform magnitudes of (a) Fe K-edge, (b) S K-edge, and (c) Sr K-edge EXAFS at various fluorination states during the 1st cycle. (d) Schematic illustration for different fluorination states upon the 1st charging process, (i) and (ii) represent probable ball-and-stick S–Fe local configurations.



**Figure 6.14** (a) *R*-space and (b) *k*-space of Fe *K*-edge EXAFS fitting results for SFFOS pristine, 1st-fully charged, 1st-discharged, 2nd-fully charged, and 2nd-discharged samples.



Figure 6.15 (a) *R*-space and (b) *k*-space of S *K*-edge EXAFS fitting results for SFFOS pristine, 1st-fully charged, 1st-discharged, 2nd-fully charged, and 2nd-discharged samples.



**Figure 6.16** (a) *R*-space and (b) *k*-space of Sr *K*-edge EXAFS fitting results for SFFOS pristine, 1st-fully charged, 1st-discharged, 2nd-fully charged, and 2nd-discharged samples.

Sample	Path	N	$S_0^2$	$\sigma^2$ / ×10 <sup>-3</sup> Å <sup>2</sup>	<i>R</i> / Å	R factor	
	S–Fe	4(f)	0.718	15.65(2)	2.66(3)	0.02185	
	S–Sr	4(f)	0.718	8.96(3)	3.16(4)	0.02185	
Pristine	Fe–O	2(f)	1(f)	10.20(7)	1.99(6)	0.02407	
11150000	Fe–S	4(f)	1(f)	2.23(7)	2.70(2)	0.02407	
	Sr–F	4(f)	1(f)	10.40(1)	2.47(2)	0.01860	
	Sr–S	4(f)	1(f)	12.92(9)	3.12(5)		
	S–S	1(f)	1(f)	1.00(7)	2.08(8)	0.02329	
1st-Fullcharge	Fe-O/F	1(f)	3.8(3)	4.43(9)	1.93(1)	0.03512	
	Sr-F	1(f)	8.1(2)	19.06(4)	2.49(1)	0.03419	
	S–Fe	1(f)	1(f)	3.91(1)	2.31(1)	0.02892	
1st-Discharge	Fe–S	1(f)	1(f)	11.68(2)	2.23(4)	0.02302	
	Sr–F	1(f)	4.2(5)	12.49(4)	2.43(4)	0.04348	
	S–S	1(f)	1(f)	2.36(2)	2.09(8)	0.02039	
2nd-Fullcharge	Fe–O/F	1(f)	3.2(6)	4.77(5)	1.94(7)	0.00668	
	Sr–F	1(f)	7.7(3)	15.37(8)	2.50(2)	0.00992	
	S–Fe	1(f)	1(f)	1.00(7)	2.33(3)	0.02657	
2nd-Discharge	Fe–S	1(f)	1(f)	3.67(5)	2.23(8)	0.01385	
	Sr-F	1(f)	4.7(2)	13.10(2)	2.48(0)	0.01940	

 Table S8. EXAFS fitting parameters for various samples.

The parameters N,  $S_0^2$ ,  $\sigma^2$ , and R represent coordination number, amplitude reduction factor, Debye-Waller factor, and atomic distance/bond length, respectively. f = fixed.



**Figure 6.17** Normalized Fourier transform magnitudes of Fe *K*-edge for the 1st fully chagred state and the 2nd fully charged state. FeF<sub>3</sub> and FeOF are provided as references. The FTs of FeOF are calculated from the structure model provided by *the materials project*.<sup>73</sup>



Figure 6.18 Normalized Fourier transform magnitudes of Sr *K*-edge for the 1st fully chagred state and the 2nd fully charged state.  $SrF_2$  is provided as the reference. The FTs of  $SrF_2$  are calculated from the structure model provided by *the materials project*.<sup>73</sup>



Figure 6.19 Space filling model of SFFOS. (a) Pristine state. (b) Hypothetical intermediate structure model, in which sulfur is oxidized to a zero-valence state, resulting in a contraction of the ionic radius. (c) Assuming that 4 F<sup>-</sup> ions are inserted into the 8g sites of the *I*4/*mmm* space group, and the *c*-axis remains unchanged.



**Figure 6.20** Schematic of reaction mechanism of SFFOS during the 1st cycle. Probable space filling models and ball-and-stick local configurations for different fluorination states are set surrounding the central figure. At early state of charge, sulfide ion redox starts, accompanied by a decrease in ionic radius, and fluoride ions predominantly insert into Sr–S interstitial layers. The symmetry of the lattice structure is reduced after fluorination, and it is possible to classify it as a

P4/mmm space group. At near fully charged state, fluoride ions start bonding with Fe. Sulfur forms S<sub>2</sub> units and gets further oxidized at this stage and the final valence state could be S<sub>2</sub><sup>0</sup>. The possible configurations in the Fe-anion stocks are shown in the blue frame. It has not been clear

where S-S bond and excess fluoride ions are in the charged SFFOS.



Figure 6.21 Changes in electronic structures for Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub> in the 2nd cycle. (a) Fe *K*-edge XANES patterns at various fluorination states, the inset figure shows the pre-edge variation. (b) The changes of E<sub>0</sub> summarized from the Fe *K*-edge XANES of Sr<sub>2</sub>F<sub>2+x</sub>Fe<sub>2</sub>OS<sub>2</sub>. As-prepared SFFOS and α-Fe<sub>2</sub>O<sub>3</sub> are provided as Fe<sup>2+</sup>/Fe<sup>3+</sup> references. (c) F *K*-edge XANES spectra.
La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> and FeF<sub>3</sub> are provided as references. (d) S *K*-edge XANES spectra. FeS, FeS<sub>2</sub>, and sulfur are provided as references.

Atom	Wyckoff Position	x	у	Ζ	Oxidation state
Sr1	4e	0.5	0.5	0.1708(3)	+2
Fe1	4c	0.5	0	0	+2
S1	4e	0	0	0.09365(0)	-2
01	2b	0.5	0.5	0	-2
F1	4d	0.5	0	0.25	-1

 Table 6.9 Atomic parameters of the pristine SFFOS.

Table 6.10 Atomic parameters of the hypothetical Sr<sub>2</sub>F<sub>6</sub>Fe<sub>2</sub>OS<sub>2</sub>.

Atom	Wyckoff Position	x	у	Z	Oxidation state
Sr1	4e	0.5	0.5	0.1708	+2
Fe1	4c	0.5	0	0	+2
<b>S</b> 1	4e	0	0	0.048	0
01	2b	0.5	0.5	0	-2
F1	4d	0.5	0	0.25	-1
F2	8g	0	0.5	0.11	-1



Figure 6.22 k<sup>3</sup>-Weighted Fourier transform magnitudes of (a) Fe K-edge, (b) S K-edge, and (c) Sr K-edge EXAFS at various fluorination states during the 2nd cycle.

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**Figure 6.23** Charge/discharge scheme of SFFOS during the 2nd cycle. In the 1st discharged state, the Fe–S bond length is shorter compared to the pristine state. Not all F<sup>-</sup> ions in the Sr–S interstitial layers are extracted. The S–S bonds form near the fully charged state, and the crystallinity is recuced due to the excessive F<sup>-</sup> ion insertion. It has not been clear where S–S bond and excess fluoride ions are in the charged SFFOS.



Figure 6.24 (a) Galvanostatic Intermittent Titration Technique (GITT) measurement conducted on the 2nd cycle at a current density of 10 mA g<sup>-1</sup>, with a 12-hour relaxation period after every current pulse. (b) The open circuit voltage obtained from GITT measurement during the 2nd charging process.



**Figure 6.25** (a) Comparison of charge/discharge profiles between Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub> and Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub> during the 2nd cycle, the average charging voltages are marked in the figure. (b) Comparison of the open circuit voltage between Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub> and Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub> during the 2nd charging process. For Sr<sub>3</sub>Fe<sub>2</sub>O<sub>5</sub>F<sub>2</sub>, it was proved in our previous research that the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox contributed to the charge compensation. And for Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub>, Fe<sup>2+</sup>/Fe<sup>3+</sup> redox starts from the middle state of charge

 $(x > 3 \text{ in } Sr_2F_{2+x}Fe_2OS_2).$ 

## Reference

- Armand, M.; Tarascon, J.-M. Building better batteries. *Nature* 2008, 451 (7179), 652–657.
- 2. Grey, C.; Tarascon, J.-M. Sustainability and in situ monitoring in battery development., *Nat. Mater.* **2017**, *16* (1), 45–56.
- Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* 2017, 16 (1), 16–22.
- Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen,
   Y.; Moshkovich, M.; Levi, E. Prototype systems for rechargeable magnesium
   batteries. *Nature* 2000, 407 (6805), 724–727.
- Delmas, C.; Braconnier, J.-J.; Fouassier, C.; Hagenmuller, P. Electrochemical intercalation of sodium in Na<sub>x</sub>CoO<sub>2</sub> bronzes. *Solid State Ionics* 1981, *3*, 165–169.
- Jian, Z.; Luo, W.; Ji, X. Carbon electrodes for K-ion batteries. J. Am. Chem. Soc.
   2015, 137 (36), 11566–11569.
- Lin, M.-C.; Gong, M.; Lu, B.; Wu, Y.; Wang, D.-Y.; Guan, M.; Angell, M.; Chen, C.; Yang, J.; Hwang, B.-J. An ultrafast rechargeable aluminium-ion battery. *Nature* 2015, 520 (7547), 324–328.
- 8. Xu, C.; Li, B.; Du, H.; Kang, F. Energetic zinc ion chemistry: the rechargeable zinc ion battery. *Angew. Chem.* **2012**, *124* (4), 957–959.
- Zhao, X.; Zhao-Karger, Z.; Fichtner, M.; Shen, X. Halide-Based Materials and Chemistry for Rechargeable Batteries. *Angew. Chem. Int. Ed. Engl.* 2020, 59 (15), 5902–5949.
- Masese, T.; Yoshii, K.; Yamaguchi, Y.; Okumura, T.; Huang, Z. D.; Kato, M.; Kubota, K.; Furutani, J.; Orikasa, Y.; Senoh, H.; Sakaebe, H.; Shikano, M. Rechargeable potassium-ion batteries with honeycomb-layered tellurates as high voltage cathodes and fast potassium-ion conductors. *Nat. Commun.* 2018, 9 (1), 3823.

- Orikasa, Y.; Masese, T.; Koyama, Y.; Mori, T.; Hattori, M.; Yamamoto, K.;
   Okado, T.; Huang, Z. D.; Minato, T.; Tassel, C.; Kim, J.; Kobayashi, Y.; Abe, T.;
   Kageyama, H.; Uchimoto, Y. High energy density rechargeable magnesium
   battery using earth-abundant and non-toxic elements. *Sci. Rep.* 2014, *4*, 5622.
- Anji Reddy, M.; Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem.
   2011, 21 (43), 17059–17062.
- Xiao, A. W.; Galatolo, G.; Pasta, M. The case for fluoride-ion batteries. *Joule* 2021, 5 (11), 2823–2844.
- Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Munnangi, A. R.; Clemens, O. Fluoride ion batteries-past, present, and future. *J. Mater. Chem. A* 2021, 9 (10), 5980–6012.
- Thieu, D. T.; Fawey, M. H.; Bhatia, H.; Diemant, T.; Chakravadhanula, V. S. K.;
   Behm, R. J.; Kübel, C.; Fichtner, M. CuF<sub>2</sub> as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* 2017, *27* (31), 1701051.
- Zhang, D.; Yamamoto, K.; Ochi, A.; Wang, Y.; Yoshinari, T.; Nakanishi, K.; Nakano, H.; Miki, H.; Nakanishi, S.; Iba, H. Uchiyama, T.; Watanabe, T.; Amezawa, K.; Uchimoto, Y. Understanding the reaction mechanism and performances of 3*d* transition metal cathodes for all-solid-state fluoride ion batteries. *J. Mater. Chem. A* 2021, 9 (1), 406–412.
- Mohammad, I.; Witter, R. Testing Mg as an anode against BiF<sub>3</sub> and SnF<sub>2</sub> cathodes for room temperature rechargeable fluoride ion batteries. *Mater. Lett.*2019, 244, 159–162.
- Rongeat, C.; Anji Reddy, M.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chem. A* 2014, 2 (48), 20861–20872.
- Zhang, D.; Yoshinari, T.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.;
   Miki, H.; Nakanishi, S.; Iba, H.; Watanabe, T.; Uchiyama, T.; Orikasa, Y.;
   Amezawa, K.; Uchimoto, Y. Cu–Pb Nanocomposite Cathode Material toward

Room-Temperature Cycling for All-Solid-State Fluoride-Ion Batteries. ACS Appl. Energy Mater. 2021, 4 (4), 3352–3357.

- Nakano, H.; Matsunaga, T.; Mori, T.; Nakanishi, K.; Morita, Y.; Ide, K.; Okazaki, K.-i.; Orikasa, Y.; Minato, T.; Yamamoto, K.; Ogumi, Z.; Uchimoto, Y. Fluoride-Ion Shuttle Battery with High Volumetric Energy Density. *Chem. Mater.* 2020, *33* (1), 459–466.
- Yoshinari, T.; Zhang, D.; Yamamoto, K.; Kitaguchi, Y.; Ochi, A.; Nakanishi, K.; Miki, H.; Nakanishi, S.; Iba, H.; Uchiyama, T.; Watanabe, T.; Matsunaga, T.; Amezawa, K.; Uchimoto, Y. Kinetic analysis and alloy designs for metal/metal fluorides toward high rate capability for all-solid-state fluoride-ion batteries. *J. Mater. Chem. A* 2021, 9 (11), 7018–7024.
- Haruyama, J.; Okazaki, K. I.; Morita, Y.; Nakamoto, H.; Matsubara, E.; Ikeshoji, T.; Otani, M. Two-Phase Reaction Mechanism for Fluorination and Defluorination in Fluoride-Shuttle Batteries: A First-Principles Study. *ACS Appl. Mater. Interfaces* 2020, *12* (1), 428–435.
- Wang, Y.; Yamamoto, K.; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; Cao, Z.; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion Substitution at Apical Sites of Ruddlesden-Popper-type Cathodes toward High Power Density for All-Solid-State Fluoride-Ion Batteries. *Chem. Mater.* 2022, *34* (2), 609–616.
- Nowroozi, M. A.; Ivlev, S.; Rohrer, J.; Clemens, O. La<sub>2</sub>CoO<sub>4</sub>: a new intercalation based cathode material for fluoride ion batteries with improved cycling stability. *J. Mater. Chem. A* 2018, 6 (11), 4658–4669.
- Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O. LaSrMnO<sub>4</sub>: reversible electrochemical intercalation of fluoride ions in the context of fluoride ion batteries. *Chem. Mater.* 2017, 29 (8), 3441–3453.
- Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C. P.; Vezin, H.; Sougrati, M. T.;
   Doublet, M. L.; Foix, D.; Gonbeau, D.; Walker, W.; Prakash, A. S.; Ben Hassine,

M.; Dupont, L.; Tarascon, J. M. Reversible anionic redox chemistry in highcapacity layered-oxide electrodes. *Nat. Mater.* **2013**, *12* (9), 827–35.

- Maitra, U.; House, R. A.; Somerville, J. W.; Tapia-Ruiz, N.; Lozano, J. G.; Guerrini, N.; Hao, R.; Luo, K.; Jin, L.; Perez-Osorio, M. A.; Massel, F.; Pickup, D. M.; Ramos, S.; Lu, X.; McNally, D. E.; Chadwick, A. V.; Giustino, F.; Schmitt, T.; Duda, L. C.; Roberts, M. R.; Bruce, P. G. Oxygen redox chemistry without excess alkali-metal ions in Na<sub>2/3</sub>[Mg<sub>0.28</sub>Mn<sub>0.72</sub>]O<sub>2</sub>. *Nat. Chem.* 2018, *10* (3), 288–295.
- Seo, D. H.; Lee, J.; Urban, A.; Malik, R.; Kang, S.; Ceder, G. The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials., *Nat. Chem.* 2016, 8 (7), 692–697.
- Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y. S.; Edstrom, K.; Guo, J.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Chargecompensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* 2016, 8 (7), 684–691.
- Li, X.; Wang, T.; Yuan, Y.; Yue, X.; Wang, Q.; Wang, J.; Zhong, J.; Lin, R.; Yao,
   Y.; Wu, X.; Yu, X.; Fu, Z.; Xia, Y.; Yang, X.; Liu, T.; Amine, K.; Shadike, Z.;
   Zhou, Y.; Lu, J. Whole-Voltage-Range Oxygen Redox in P2-Layered Cathode
   Materials for Sodium-Ion Batteries. *Adv. Mater.* 2021, *33* (13), e2008194.
- Zhang, K.; Qi, J.; Song, J.; Zuo, Y.; Yang, Y.; Yang, T.; Chen, T.; Liu, X.; Chen,
   L.; Xia, D. Sulfuration of Li-Rich Mn-Based Cathode Materials for
   Multianionic Redox and Stabilized Coordination Environment. *Adv. Mater.* 2022, 34 (11), 2109564.
- House, R. A.; Marie, J.-J.; Pérez-Osorio, M. A.; Rees, G. J.; Boivin, E.; Bruce,
  P. G. The role of O<sub>2</sub> in O-redox cathodes for Li-ion batteries. *Nat. Energy* 2021,
  6 (8), 781–789.
- 33. Saha, S.; Assat, G.; Sougrati, M. T.; Foix, D.; Li, H.; Vergnet, J.; Turi, S.; Ha,

Y.; Yang, W.; Cabana, J.; Rousse, G.; Abakumov, A. M.; Tarascon, J.-M. Exploring the bottlenecks of anionic redox in Li-rich layered sulfides. *Nat. Energy* **2019**, *4* (11), 977–987.

- Wang, T.; Ren, G.; Shadike, Z.; Yue, J.; Cao, M.; Zhang, J.; Chen, M.; Yang, X.; Bak, S. M.; Northrup, P.; Liu, P.; Liu, X.; Fu, Z. Anionic redox reaction in layered NaCr<sub>2/3</sub>Ti<sub>1/3</sub>S<sub>2</sub> through electron holes formation and dimerization of S-S. *Nat. Commun.* 2019, *10* (1), 4458.
- Hansen, C. J.; Zak, J. J.; Martinolich, A. J.; Ko, J. S.; Bashian, N. H.; Kaboudvand, F.; Van der Ven, A.; Melot, B. C.; Nelson Weker, J.; See, K. A. Multielectron, Cation and Anion Redox in Lithium-Rich Iron Sulfide Cathodes. *J. Am. Chem. Soc.* 2020, *142* (14), 6737–6749.
- Goodenough, J. B.; Park, K. S. The Li-ion rechargeable battery: a perspective.
   J. Am. Chem. Soc. 2013, 135 (4), 1167–1176.
- 37. Kabbour,H.; Janod, E; Corraze, B.; Danot, M.; Lee, C.; Whangbo, M.-H. W.;
  Cario, L. Structure and Magnetic Properties of Oxychalcogenides A<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OQ<sub>2</sub>
  (A = Sr, Ba; Q = S, Se) with Fe<sub>2</sub>O Square Planar Layers Representing an Antiferromagnetic Checkerboard Spin Lattice. *J. Am. Chem. Soc.* 2008, *130*, 8261–8270.
- Wang, Y.; Takami, T.; Li, Z.; Yamamoto, K.; Matsunaga, T.; Uchiyama, T.; Watanabe, T.; Miki, H.; Inoue, T.; Iba, H.; Mizutani, U.; Sato, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Oxyfluoride Cathode for All-Solid-State Fluoride-Ion Batteries with Small Volume Change Using Three-Dimensional Diffusion Paths. *Chem. Mater.* 2022, *34* (23), 10631–10638.
- 39. Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. Z. Krist. Cryst. Mater. 2014, 229 (5), 345–352.
- 40. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276.
- 41. Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis

for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537–541.

- Harada, Y.; Kobayashi, M.; Niwa, H.; Senba, Y.; Ohashi, H.; Tokushima, T.; Horikawa, Y.; Shin, S.; Oshima, M. Ultrahigh resolution soft x-ray emission spectrometer at BL07LSU in SPring-8. *Rev. Sci. Instrum.* 2012, *83* (1), 013116.
- Zhao, L.; Wu, S.; Wang, J.; Hodges, J. P.; Broholm, C.; Morosan, E. Quasi-twodimensional noncollinear magnetism in the Mott insulator Sr<sub>2</sub>F<sub>2</sub>Fe<sub>2</sub>OS<sub>2</sub>. *Phys. Rev. B* 2013, 87 (2), 020406.
- Miki, H.; Yamamoto, K.; Nakaki, H.; Yoshinari, T.; Nakanishi, K.; Nakanishi, S.; Iba, H.; Miyawaki, J.; Harada, Y.; Kuwabara, A.; Wang, Y.; Watanabe, T.; Matsunaga, T.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Double-Layered Perovskite Oxyfluoride Cathodes with High Capacity Involving O–O Bond Formation for Fluoride-Ion Batteries. J. Am. Chem. Soc. 2024, 146 (6), 3844–3853.
- 45. Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Reversible and Fast (De)fluorination of High-Capacity Cu<sub>2</sub>O Cathode: One Step Toward Practically Applicable All-Solid-State Fluoride-Ion Battery. *Adv. Energy Mater.* **2021**, *11* (45), 2102285.
- Lyu, Y.; Wu, X.; Wang, K.; Feng, Z.; Cheng, T.; Liu, Y.; Wang, M.; Chen, R.;
   Xu, L.; Zhou, J.; Lu, Y.; Guo, B. An Overview on the Advances of LiCoO<sub>2</sub>
   Cathodes for Lithium-Ion Batteries. *Adv. Energy Mater.* 2021, *11* (2), 2000982.
- 47. Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y. K. Comparison of the structural and electrochemical properties of layered Li[Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> (*x*=1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries. *J. Power Sources* 2013, 233, 121–130.
- 48. Huang, C. Y.; Kuo, T. R.; Yougbare, S.; Lin, L. Y. Design of LiFePO<sub>4</sub> and porous carbon composites with excellent High-Rate charging performance for Lithium-

Ion secondary battery. J. Colloid Interface Sci. 2022, 607, 1457–1465.

- 49. Wang, R.; Liu, X.; Liu, L.; Lee, J.; Seo, D. H.; Bo, S. H.; Urban, A.; Ceder, G. A disordered rock-salt Li-excess cathode material with high capacity and substantial oxygen redox activity: Li<sub>1.25</sub>Nb<sub>0.25</sub>Mn<sub>0.5</sub>O<sub>2</sub>. *Electrochem. Commun.* 2015, 60, 70–73.
- Lee, J.; Papp, J. K.; Clement, R. J.; Sallis, S.; Kwon, D. H.; Shi, T.; Yang, W.; McCloskey, B. D.; Ceder, G. Mitigating oxygen loss to improve the cycling performance of high capacity cation-disordered cathode materials. *Nat. Commun.* 2017, 8 (1), 981.
- Huang, J.; Zhong, P.; Ha, Y.; Kwon, D.-H.; Crafton, M. J.; Tian, Y.; Balasubramanian, M.; McCloskey, B. D.; Yang, W.; Ceder, G. Non-topotactic reactions enable high rate capability in Li-rich cathode materials. *Nat. Energy* 2021, 6 (7), 706–714.
- 52. Nakajima, M.; Yabuuchi, N. Lithium-Excess Cation-Disordered Rocksalt-Type Oxide with Nanoscale Phase Segregation: Li<sub>1.25</sub>Nb<sub>0.25</sub>V<sub>0.5</sub>O<sub>2</sub>. *Chem. Mater.*2017, 29 (16), 6927–6935.
- 53. Zhao, X.; Tian, Y.; Lun, Z.; Cai, Z.; Chen, T.; Ouyang, B.; Ceder, G. Design principles for zero-strain Li-ion cathodes. *Joule* **2022**, *6* (7), 1654–1671.
- 54. Konuma, I.; Goonetilleke, D.; Sharma, N.; Miyuki, T.; Hiroi, S.; Ohara, K.; Yamakawa, Y.; Morino, Y.; Rajendra, H. B.; Ishigaki, T.; Yabuuchi, N. A near dimensionally invariable high-capacity positive electrode material. *Nat. Mater.* 2023, *22* (2), 225–234.
- 55. Nowroozi, M. A.; Wissel, K.; Donzelli, M.; Hosseinpourkahvaz, N.; Plana-Ruiz, S.; Kolb, U.; Schoch, R.; Bauer, M.; Malik, A. M.; Rohrer, J.; Ivlev, S.; Kraus, F.; Clemens, O. High cycle life all-solid-state fluoride ion battery with La<sub>2</sub>NiO<sub>4+d</sub> high voltage cathode. *Commun. Mater.* 2020, *1* (1), 27.
- Reimers, J. N.; Dahn, J. R. Electrochemical and In Situ X-Ray Diffraction Studies of Lithium Intercalation in Li<sub>x</sub>CoO<sub>2</sub>. *J. Electrochem. Soc.* 1992, *139* (8),

2091.

- Paris, E.; Tyson. T. A. Iron Site Geometry in Orthopyroxene: Multiple Scattering Calculations and XANES Study. *Phys. Chem. Miner.* 1994, *21*, 299–308.
- Prince, A. A. M.; Mylswamy, S.; Chan, T. S.; Liu, R. S.; Hannoyer, B.; Jean, M.; Shen, C. H.; Huang, S. M.; Lee, J. F.; Wang, G. X. Investigation of Fe valence in LiFePO<sub>4</sub> by Mössbauer and XANES spectroscopic techniques. *Solid State Commun.* 2004, *132* (7), 455–458.
- Womes, M.; Karnatak, R. C.; Esteva, J. M.; Lefebvre, I.; Allan, G.; Olivier-Fourcades, J.; Jumas, J. C. ELECTRONIC STRUCTURES OF FeS AND FeS<sub>2</sub>: X-RAY ABSORPTION SPECTROSCOPY AND BAND STRUCTURE CALCULATIONS. J. Phys. Chem. Solid 1996, 58, 345–352.
- Krasnikov, S. A.; Vinogradov, A. S.; Preobrajenski, A. B.; Gridneva, L. K.; Molodtsov, S. L.; Laubschat C.; Szargan, R. Electronic structure of FeF<sub>2</sub> and FeF<sub>3</sub> studied by x-ray absorption and fluorescence spectroscopy. *Phys. Scr.* 2005, *T115*, 1074.
- Kitajou, A.; Komatsu, H.; Nagano, R.; Okada, S. Synthesis of FeOF using rollquenching method and the cathode properties for lithium-ion battery. *J. Power Sources.* 2013, 243, 494–498.
- Yue, Y.; Ha, Y.; Huang, T.-Y.; Li, N.; Li, L.; Li, Q.; Feng, J.; Wang, C.; McCloskey, B. D.; Yang, W.; Tong, W. Interplay between Cation and Anion Redox in Ni-Based Disordered Rocksalt Cathodes. *ACS Nano* 2021, *15* (8), 13360–13369.
- 63. Fleet, M. E. XANES spectroscopy of sulfur in earth materials. *Can. Mineral.*2005, 43 (6), 1811–1838.
- Mori, T.; Orikasa, Y.; Nakanishi, K.; Chen, K.; Hattori, M.; Ohta, T.; Uchimoto,
  Y. Discharge/charge reaction mechanisms of FeS<sub>2</sub> cathode material for aluminum rechargeable batteries at 55°C. *J. Power Sources* 2016, *313*, 9–14.

- 65. Farrell, S. P.; Fleet, M. E.; Stekhin, I. E.; Kravtsova, A.; Soldatov, A. V.; Liu, X. Evolution of local electronic structure in alabandite and niningerite solid solutions [(Mn,Fe)S, (Mg,Mn)S, (Mg,Fe)S] using sulfur *K* and *L*-edge XANES spectroscopy. *Am. Mineral.* 2002, *87* (10), 1321–1332.
- Luo, K.; Roberts, M. R.; Guerrini, N.; Tapia-Ruiz, N.; Hao, R.; Massel, F.;
  Pickup, D. M.; Ramos, S.; Liu, Y. S.; Guo, J.; Chadwick, A. V.; Duda, L. C.;
  Bruce, P. G. Anion Redox Chemistry in the Cobalt Free 3d Transition Metal
  Oxide Intercalation Electrode Li[Li<sub>0.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>]O<sub>2</sub>. J. Am. Chem. Soc. 2016, 138 (35), 11211–11218.
- 67. House, R. A.; Maitra, U.; Perez-Osorio, M. A.; Lozano, J. G.; Jin, L.; Somerville, J. W.; Duda, L. C.; Nag, A.; Walters, A.; Zhou, K. J.; Roberts, M. R.; Bruce, P. G. Superstructure control of first-cycle voltage hysteresis in oxygen-redox cathodes. *Nature* 2020, *577* (7791), 502–508.
- 68. Rehr, J. J.; Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **2000**, *72* (3), 621.
- 69. Rehr, J. J.; Kas, J. J.; Prange, M. P.; Sorini, A. P.; Takimoto, Y.; Vila, F. Ab initio theory and calculations of X-ray spectra. *C. R. Phys.* **2009**, *10* (6), 548–559.
- 70. Takeuchi, T.; Kageyama, H.; Nakanishi, K.; Ogawa, M.; Ohta, T.; Sakuda, A.; Sakaebe, H.; Kobayashi, H.; Ogumi, Z. Preparation of Li<sub>2</sub>S-FeS<sub>x</sub> composite positive electrode materials and their electrochemical properties with pre-cycling treatments. *J. Electrochem. Soc.* **2015**, *162* (9), A1745.
- Ma, Z.; Liu, W.; Jiang, X.; Liu, Y.; Yang, G.; Wu, Z.; Zhou, Q.; Chen, M.; Xie, J.; Ni, L.; Diao, G. Wide-Temperature-Range Li-S Batteries Enabled by Thiodimolybdate [Mo<sub>2</sub>S<sub>12</sub>]<sup>2-</sup> as a Dual-Function Molecular Catalyst for Polysulfide Redox and Lithium Intercalation. ACS Nano 2022, 16 (9), 14569–14581.
- 72. Huang, Z.; Luo, W.; Ma, L.; Yu, M.; Ren, X.; He, M.; Polen, S.; Click, K.; Garrett, B.; Lu, J.; Amine, K.; Hadad, C.; Chen, W.; Asthagiri, A.; Wu, Y.

Dimeric [Mo<sub>2</sub>S<sub>12</sub>]<sup>2-</sup> Cluster: A Molecular Analogue of MoS<sub>2</sub> Edges for Superior Hydrogen-Evolution Electrocatalysis. *Angew. Chem. Int. Ed. Engl.* **2015**, *54* (50), 15181–15185.

- Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater*. 2013, *1* (1), 011002.
- 74. Emsley, J. The Elements 3rd Edition. *Clarenden Press*, 1998.
- 75. House, R. A.; Rees, G. J.; Pérez-Osorio, M. A.; Marie, J.-J.; Boivin, E.; Robertson, A. W.; Nag, A.; Garcia-Fernandez, M.; Zhou, K.-J.; Bruce, P. G. First-cycle voltage hysteresis in Li-rich 3*d* cathodes associated with molecular O<sub>2</sub> trapped in the bulk. *Nat. Energy* 2020, 5 (10), 777–785.
- Sivakumar, T.; Wiley, J. B. Topotactic route for new layered perovskite oxides containing fluorine: Ln<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>F<sub>2</sub> (Ln=Pr, Nd, Sm, Eu, and Gd). *Mater. Res. Bull.* 2009, 44, 74–77.
- Adachi, S.; Wu, X. -J.; Tamura, T.; Tatsuki, T.; Tokiwa-Yamamoto, A.; Tanabe,
  K. Synthesis and superconducting properties of fluorinated La<sub>2</sub>CuO<sub>4</sub> using NH<sub>4</sub>F. *Phys. C* 1997, *291* (1-2), 59–66.
- 78. Dieudonné, B.; Chable J.; Mauvy, F.; Fourcade, S.; Durand, E.; Lebraud, E.; Leblanc, M.; Legein, C.; Body, M.; Maisonneuve, V. Exploring the Sm<sub>1-x</sub>Ca<sub>x</sub>F<sub>3-x</sub> Tysonite Solid Solution as a Solid-State Electrolyte: Relationships between Structural Features and F–Ionic Conductivity. *J. Phys. Chem. C* 2015, *119* (45), 25170–25179.
- Li, H. B.; Lou, F.; Wang, Y.; Zhang, Y.; Zhang, Q.; Wu, D.; Li, Z.; Wang, M.; Huang, T.; Lyu, Y.; Guo, J.; Chen, T.; Wu, Y.; Arenholz, E.; Lu, N.; Wang, N.; He, Q.; Gu, L.; Zhu, J.; Nan, C. W.; Zhong, X.; Xiang, H.; Yu, P. Electric Field-Controlled Multistep Proton Evolution in H<sub>x</sub>SrCoO<sub>2.5</sub> with Formation of H-H Dimer. *Adv. Sci.* 2019, *6* (20), 1901432.
## **Chapter 7** General Conclusion

All-solid-state fluoride ion batteries (FIBs), recognized for their extraordinary theoretical energy density and high safety, are considered as a potential next-generation energy storage device alternative to lithium-ion batteries (LIBs). Currently, the research on FIBs is in its nascent stage, necessitating continuous iterations and development of the high-performance electrode materials comparable to the LiCoO<sub>2</sub>|Graphite LIBs. Pioneers in this field have provided invaluable insights, including elucidating the conversion reaction mechanisms of the metal/metal fluoride electrodes, and developing a class of intercalation-type electrodes that follow a topotactic (de)fluorination mechanism similar to that of LiCoO<sub>2</sub>. In this study, we initiate our discussion with the objectives of achieving a zero-carbon society and the development of electric vehicles, tracing the history of LIBs and shifting our focus to the future of FIBs. We have modified a kind of the conversion-type cathode material, the composite material prepared by a facile method has exhibited excellent practical performance. Subsequently, we have developed several types of intercalation cathode materials with different reaction mechanisms, including the use of multi-electron reactions of transition metals or transition metal/anion redox reactions for charge compensation, achieving high capacity, high energy density, and high rate capability. Using synchrotron radiation X-ray absorption spectroscopy (XAS) techniques, we have attained a more comprehensive and integrated understanding of these reaction mechanisms.

In Chapter 1, we discuss the history and working principles of LIBs, based on which we introduce the concept of fluoride ion batteries, research progress, current challenges, and the motivation of this study. In Chapter 2, we employ a facile ball milling method to synthesize Cu/Cu<sub>2</sub>O nanocomposite cathode materials, achieving superior cycle and rate performance compared to metal copper cathodes. The Chapter

3 details the electrochemical performance of CuLaO<sub>2</sub> intercalation-type cathode material and the elucidation of the multielectron reaction mechanism using XAS. The 2D diffusion pathway allows for rapid F<sup>-</sup> diffusion in the lattice structure. Chapter 4 to 6 extensively utilize anion redox reactions for charge compensation, leading to the development of high-capacity FIB cathode materials. Chapter 4 demonstrates that fluoride ions can insert not only into both the two interstitial layers of the Ruddlesden–Popper La<sub>2</sub>NiO<sub>4+d</sub> structure but also into the perovskite slabs, achieving high capacity through the charge transfer from Ni and O redox reactions. Chapter 5 presents infinite-layer LaNiO<sub>2</sub> cathode material, exhibiting high capacity and excellent rate performance. This chapter also proves the relatively high reversibility of  $O_2$ molecule formation/deformation mechanisms by RIXS measurement. In Chapter 6, we utilize sulfur redox for the first time in all-solid-state FIBs. This compound features a unique structure and interesting reaction mechanism, with the observation of stable S-S dimers in the charged state. Its stable structure allows for excess fluoride ion (de)intercalation, achieving high reversible capacity. These studies demonstrate that utilizing anion redox reactions can enable intercalation-type cathode materials to achieve high capacity, high energy density, and good cycle stability in solid-state systems, undoubtedly filling us with hope for the future of fluoride ion batteries.

## List of publications

- <u>Cao, Z.;</u> Yamamoto, K.\*; Zhang, D.; Matsunaga, T.; Kumar, M.; Thakur, N.; Watanabe, T.; Miki, H.; Iba, H.; Amezawa, K.; Uchimoto, Y. High-performance Copper/Copper Oxide-Based Cathode Prepared by a Facile Ball-Milling Method for All-Solid-State Fluoride-Ion Batteries. *ACS Appl. Energy Mater.* 2023, 6 (23), 11906–11914. DOI: 10.1021/acsaem.3c02003. (Chapter 2)
- <u>Cao, Z.;</u> Yamamoto, K.\*; Matsunaga, T.; Kumar, M.; Thakur, N.; Watanabe, T.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Kageyama, H.; Uchimoto, Y. Reversible Fluoride-Ion (De)Intercalation of CuLaO<sub>2</sub> Cathodes with Crystalline/Amorphous Phase Transition Involving Multi-Electron Reaction. *ACS Appl. Energy Mater.* 2024, 7 (15), 6640–6648. DOI: 10.1021/acsaem.4c01271. (Chapter 3)
- <u>Cao, Z.;</u> Yamamoto, K.\*; Matsunaga, T.; Watanabe, T.; Wang, Y.; Kumar, M.; Thakur, N.; Nakanishi, K.; Miki, H.; Iba, H.; Amezawa, K.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Extending Exploration on Fluoride-Ion (De)Insertion Behaviors of the Ruddlesden–Popper-Type Cathode Material La<sub>2</sub>NiO<sub>4+d</sub> for All-Solid-State Fluoride-Ion Batteries. *J. Mater. Chem. A* In revision. (Chapter 4)
- <u>Cao, Z.;</u> Yamamoto, K.\*; Matsunaga, T.; Wang, Y.; Kiuchi, H.; Nakanishi, K.; Watanabe, T.; Kumar, M.; Thakur, N.; Miki, H.; Iba, H.; Maeda, K.; Harada, Y.; Amezawa, K.; Kageyama, H.; Uchimoto, Y. Infinite Layer Oxide Cathode Material LaNiO<sub>2</sub> for All-Solid-State Fluoride-Ion Batteries toward High Energy Density and Power Density. *J. Mater. Chem. A* In revision. (Chapter 5)
- <u>Cao, Z.</u>; Yamamoto, K.; Matsunaga, T.; Watanabe, T.; Kumar, M.; Thakur, N.; Ohashi, R.; Tachibana, S.; Miki, H.; Ide, K.; Iba, H.; Kiuchi, H.; Harada, Y.; Orikasa, Y.\*; Uchimoto, Y. Revealing the Unusual Mechanism of Mixed Cationic and Anionic Redox in Oxyfluorosulfide Cathode for All-Solid-State

Fluoride-Ion Batteries. *Chem. Mater.* **2024**, *36* (4), 1928–1940. DOI: 10.1021/acs.chemmater.3c02650. (Chapter 6)

- Wang, Y.; Yamamoto, K.\*; Tsujimoto, Y.; Matsunaga, T.; Zhang, D.; <u>Cao, Z.</u>; Nakanishi, K.; Uchiyama, T.; Watanabe, T.; Takami, T.; Miki, H.; Iba, H.; Maeda, K.; Kageyama, H.; Uchimoto, Y. Anion substitution at apical sites of Ruddlesden-Popper-type cathodes toward high power density for all-solid-state fluoride ion battery. *Chem. Mater.* **2022**, *34* (2), 609–616. DOI: 10.1021/acs.chemmater.1c03189.
- Miki, H.; Matsunaga, T.; Li, Z.; <u>Cao, Z.;</u> Yamamoto, K.; Kumar, M.; Thakur, N.; Watanabe, T.; Iba, H.; Kobayashi, S.; Kawaguchi, S.; Ikeda, K.; Hagihara, M.; Kamiyama, T.; Kuwabara, A.; Kageyama, H.; Maeda, K.; Uchimoto, Y. Fluoride ion storage and conduction mechanism in fluoride ion battery cathode, Ruddlesden-Popper-type layered perovskite La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> crystal. *Inorg. Chem.* 2024, submitted.

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High-Performance Copper/Copper Oxide-Based Cathode Prepared by a Facile Ball-Milling Method for All-Solid-State Fluoride-Ion Batteries.

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Revealing the Unusual Mechanism of Mixed Cationic and Anionic Redox in Oxyfluorosulfide Cathode for All-Solid-State Fluoride-Ion Batteries.

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