

Aluminum Corrosion and Interface Stability for High-Voltage Positive Electrodes in Secondary Batteries

Huazhen Liu

2025

Table of Contents

Chapter 1 General Introduction	1
1.1 Electrochemical energy storage systems.....	1
1.2 Lithium and sodium secondary batteries	2
1.3 Aluminum current collector	4
1.4 High-voltage positive electrode materials	13
1.5 Aims of this study	19
References.....	30
 Chapter 2 Experimental	 41
2.1 Apparatus and material handing	41
2.2 Electrode and cell preparation	43
2.3 Material characterization	44
2.3.1 X-ray diffraction (XRD)	44
2.3.2 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).....	44
2.3.3 X-ray photoelectron spectroscopy (XPS)	44
2.3.4 X-ray fluorescence spectroscopy (XRF).....	45
2.3.5 Raman spectroscopy	45

2.3.6	Specific surface area measurement with Brunauer–Emmett–Teller (BET) method.....	45
2.3.7	Analysis of particle size distribution.....	45
2.4	Electrochemical measurements.....	45
2.4.1	Galvanostatic charge-discharge test.....	45
2.4.2	Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)	46
	References.....	51

Chapter 3 Systematic Study of Aluminum Corrosion in Ionic Liquid Electrolytes for Sodium-Ion Batteries: Impact of Temperature and Concentration53

3.1	Introduction.....	53
3.2	Experimental	56
3.3	Results and discussion	58
3.4	Conclusions.....	69
	References.....	100

Chapter 4 Enhanced Cycle Stability of LiNiO₂ in Highly Concentrated Ionic Liquid Electrolyte 107

4.1	Introduction.....	107
4.2	Experimental	109

4.3	Results and discussion	111
4.4	Conclusions.....	121
	References.....	151
Chapter 5 Failure Mechanisms of Aluminum Passivation in Preventing Corrosion in Bis(fluorosulfonyl)amide-based Electrolytes		
		157
5.1	Introduction.....	157
5.2	Experimental	159
5.3	Results and discussion	160
5.4	Conclusions.....	167
	References.....	190
Chapter 6 Investigation of Conditions for Realizing One-Pot Synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$		
		195
6.1	Introduction.....	195
6.2	Experimental	198
6.3	Results and discussion	200
6.4	Conclusions.....	210
	References.....	233
Chapter 7 General Conclusions		
		239

List of Publications	243
----------------------------	-----

Acknowledgement	245
-----------------------	-----

Chapter 1

General Introduction

1.1 Electrochemical energy storage systems

Over the past decade, electricity consumption has grown at double the rate of overall energy consumption [1]. It is projected to accelerate further in the coming years, driven by industrial consumption, electric vehicles (EV), and other emerging technologies. Fossil fuels are still the primary energy source globally, while power stations using these energy sources generate significant amounts of carbon dioxide. To mitigate global warming, greenhouse gas emissions must be reduced by at least 43% by 2030 relative to 2019 levels [2]. Environmental concerns and the energy crisis have spurred great interest in developing sustainable and low-carbon energy sources (e.g., solar and wind) for power generation. By 2025, renewable energy will supply over a third of global electricity, surpassing coal as the dominant power source [3]. However, the intermittent and variable nature of solar and wind power presents challenges to the stability of electric power grids.

To balance energy generation with demand, energy storage systems (ESSs) are an effective solution for improving the efficient use of energy. ESSs are categorized by the form of stored energy, such as thermal, mechanical, chemical, electrochemical, and hybrid energy [4]. Among them, electrochemical ESSs are promising technologies that offer advantages such as high energy density, high energy conversion efficiency, and

environmentally benign [5]. In addition, electrochemical ESSs have drawn considerable interest because of their widespread applications in portable electronics and potential in emerging EV markets. Regarding electrochemical ESSs, various devices have been developed over the past decades, including supercapacitors, lead-acid batteries, metal-ion batteries, and metal-air batteries [6, 7]. To meet evolving energy demands and environmental standards, advancements in stability, efficiency, safety, and sustainability for energy storage devices are desired.

1.2 Lithium and sodium secondary batteries

Since their commercialization in the 1990s, lithium-ion batteries (LIBs) have become one of the dominant devices for electrochemical energy storage, due to their high energy density, long cycling stability, and high safety [8, 9]. LIB applications range from portable electronic devices to electric transportation and grid-level ESSs. **Figure 1-1** shows the configuration of a typical LIB, consisting of a positive electrode, a negative electrode, an electrolyte, and two current collectors [10]. The working principle of LIBs relies on the reversible movement of Li^+ between the positive electrode and negative electrodes through the separator and electrolyte during the charging and discharging, converting chemical energy into electrical energy. In order to realize a decarbonized society, demand for LIBs has risen substantially, primarily driven by the rapid expansion of EV markets and the integration of renewable energy sources [11]. The EV sales could reach 17 million in 2024, representing more than 20% of all passenger

vehicles worldwide [12]. Although the EV sector dominates the total demand (>80%), the demand for LIBs in ESSs has continued to grow, reaching a share of 10% in 2023 [13]. In view of the rapid growth of the LIBs market (**Table 1-1**) [14], the target of LIBs development is not only for higher energy/power density but also for enhanced safety and lower production costs, especially in the EV sector [15]. However, these requirements are increasingly challenging to meet due to the high costs and limited availability of lithium resources [16]. While LIBs remain the dominant choice, researchers have focused on exploring alternative technologies that offer cost-effective solutions for large-scale applications.

Sodium-ion batteries (SIBs) have been revived as potential candidates over the last decade for several reasons. First, sodium resources are far more abundant than lithium resources, with widespread distribution both in the Earth's crust and ocean, mitigating concerns about supply and costs [17]. As depicted in **Figure 1-2**, the price of sodium carbonate is considerably less than the raw materials used for LIBs [18]. Second, sodium and lithium, both alkali metals in group 1, share similar electrochemical characteristics, readily losing one electron to form Na^+ and Li^+ . **Table 1-2** compares these physical properties as charge carriers for rechargeable batteries [19]. Their standard electrode potentials are comparable, with sodium at -2.71 V versus the standard hydrogen electrode (SHE) being only 0.3 V higher than lithium. The material structures and working principles of SIBs closely resemble those of LIBs, facilitating SIB development and scaling based on the established LIB technology. Third, SIBs

have a broader selection of positive electrodes, as many transition metals (e.g., Fe, Mn, Ni, Co, Cr, Ti, V) exhibit electrochemical activity in Na-based layered oxides, whereas only Mn, Co, and Ni are effective in their Li analogues [20, 21]. Fourth, Na^+ possesses a smaller Stokes radius, and de-solvation energy in the solution than Li^+ , indicating the higher ionic conductivities of Na^+ -based electrolytes [22]. Thus, low-concentration Na^+ -based electrolytes can maintain ionic conductivity comparable to Li^+ -based electrolytes, further reducing electrolyte costs. Fifth, unlike lithium, sodium does not react with Al to form an alloy, allowing the replacement of Cu with lighter, cheaper Al as the current collector for negative electrodes in SIBs. Although SIBs and LIBs share similar properties, the distinct electrochemical behaviors of SIBs necessitate improvements in material performance and interface stability for practical applications.

1.3 Aluminum current collector

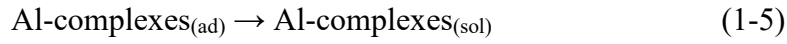
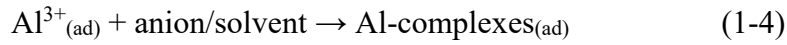
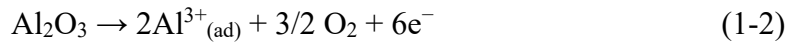
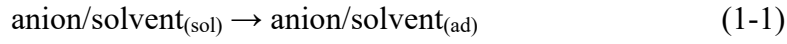
The current collector is a critical component in battery systems, providing mechanical support for electrode materials and ensuring efficient collection and transport of electrons [23]. Thus, current collectors significantly impact the battery performance, including energy density, cycle life, and safety [24]. While significant advancements have been made in electrode and electrolyte materials for secondary batteries over the past decades, current collectors have not received equivalent attention despite their essential function. As current collectors contribute to the overall weight of batteries, their design must balance multiple factors, including high electrical conductivity, low

density, mechanical robustness, and electrochemical stability, all while maintaining cost-effectiveness and sustainability [25]. Among various current collector materials, aluminum (Al) foil is widely employed as the positive electrode current collector due to its high electrical conductivity, low density (2.70 g cm^{-3}), ductility, good chemical stability, and low cost [26].

In the development of secondary batteries, enhancing electrochemical performance while maintaining the stability of battery components is critical. However, with the pursuit of higher energy density and wide operation temperatures, the stability of the Al current collector has emerged as a significant challenge. In the organic electrolytes used in LIBs, which consist of lithium salts, solvents, and additives, the standard electrode potential of Al (1.38 V vs. Li^+/Li) is significantly lower than the operating voltage of positive electrode materials ($> 3.5 \text{ V vs. Li}^+/\text{Li}$) [27]. As a result, Al serves thermodynamically as the anode in a galvanic cell, undergoing oxidation while reduction reactions occur in the electrolyte [23, 28]. The native Al_2O_3 layer ($\sim 5\text{--}20 \text{ nm}$) formed on the surface of Al foil protects against corrosion to an extent. However, as the operating voltage increases (around $3.8 \text{ V vs. Li}^+/\text{Li}$), this passivation layer deteriorates and the bared Al metal is exposed to the electrolyte, resulting in Al corrosion [29, 30]. Elevated operating voltages and harsh environmental conditions exacerbate Al corrosion, leading to the detachment of active materials, increased contact resistance, and the accumulation of corrosion products that hinder ion mobility and electronic conductivity [31, 32]. Over time, these effects result in capacity loss,

decreased power output, and, in severe cases, short circuits that pose serious safety hazards [33].

The corrosion mechanism of Al current collectors in LIBs has been explored and is currently recognized as a process governed by the interaction between the native Al_2O_3 layer and organic electrolytes. This corrosion process is composed of a series of consecutive steps as follows: [34-37]



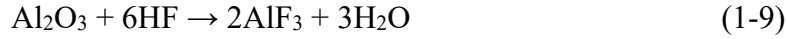
The process begins with the diffusion of anions or solvent molecules from the bulk electrolyte to the Al electrode (1-1). Under the influence of electrochemical forces, the protective Al_2O_3 layer degrades, leading to the formation of Al^{3+} ions adsorbed on the surface of the current collector (1-2). If the underlying Al metal is exposed, further anodic polarization results in the direct oxidation of the underlying Al metal to generate additional Al^{3+} ions (1-3). As a strong Lewis acid, the unstable Al^{3+} ions tend to react with ligands such as solvent molecules or anions from lithium salts to form Al-complexes adsorbed on the Al surface (1-4). The solubility of these complexes in the

electrolyte determines the subsequent corrosion behavior. Insoluble complexes, such as AlF_3 , serve as a passivation layer to stabilize the Al surface. However, if the complexes are soluble, such as $\text{Al}[\text{TFSA}]_3$, they desorb and diffuse into the bulk electrolyte (1-5), thereby accelerating the corrosion process.

The corrosion of Al current collectors is governed by multiple interdependent factors. These include the applied anodic voltage, the composition and concentration of the electrolyte, the uniformity and thickness of the native Al_2O_3 layer, the mechanical stability of the Al substrate, and temperature [27, 38-40]. Additionally, interactions with the active material and the presence of impurities or contaminants in the electrolyte can exacerbate Al corrosion [30, 41]. In particular, although the Al_2O_3 layer provides the kinetic stability of Al foil, the protective effects of the Al_2O_3 layer on Al foils are subtle, depending on the electrolyte composition [42].

Lithium hexafluorophosphate (LiPF_6)-based carbonate electrolytes are the prevailing commercial formulations. Regarding the compatibility with Al current collector, a widely accepted explanation is that the decomposition of LiPF_6 in the presence of trace water generates HF, which reacts with the native Al_2O_3 layer to form AlF_3 to stabilize the Al interface and prevent further corrosion (**Figure 1-3a**). The relevant reactions are suggested as follows: [43-45]





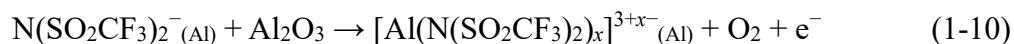
Recent studies, however, suggest that the corrosion mechanism in LiPF₆-based electrolytes is more complex than previously understood. Specifically, the electrochemical stability of the electrolyte components plays a significant role [46, 47]. At potentials exceeding 3.9 V, the oxidation of solvent molecules—likely ethylene carbonate—near the Al surface produces H⁺. These protons dissolve the Al₂O₃ layer, exposing the Al surface to the electrolyte. The increasing active sites not only accelerate solvent oxidation but also facilitate further HF formation through reactions between H⁺ and PF₆[−] anions. The HF then reacts with Al₂O₃ to form AlF₃ as a passivation layer.

However, the stability of the AlF₃ passivation layer is less robust than anticipated. Its limited thickness (approximately 1 nm) and susceptibility to local inhomogeneities in current density render it vulnerable to accidental breakdown during long-term operation [48-50]. High temperatures and elevated cutoff voltages can also compromise its protective effects, leading to accelerated Al corrosion [24]. Yoon et al. investigated the evolution of the passivation layer formed on the Al surface in LiPF₆-containing electrolyte at 55 °C and found that ion diffusion under high-temperature conditions significantly compromises the protective film [51]. The outward diffusion of Al³⁺ leads to voids at the Al metal/passivation layer interface, which eventually grow into pits.

Concurrently, inward diffusion of F^- facilitates the fluorination of Al_2O_3 into AlF_3 , leading to a large tensile stress on the passivation layer due the smaller density of AlF_3 , finally forming cracks on the Al surface when this stress exceeds the fracture toughness. Additionally, ion diffusion tends to concentrate at specific sites, such as grain boundaries, where localized accumulation of erosive particles further degrades the passivation layer [52].

Amide-based electrolytes, such as lithium bis(trifluoromethylsulfonyl)amide (Li[TFSA]) and lithium bis(fluorosulfonyl)amide (Li[FSA]), have gained attention due to their superior thermal and chemical stability, and high hydrolysis resistance compared to $LiPF_6$ [53, 54]. However, these salts are significantly more corrosive to Al current collectors at the potential above 3.5 V vs. Li^+/Li [55-57]. The primary reason for Al corrosion in Li[TFSA]-based electrolytes lies in the solubility of the corrosion products. Similar to the mechanism described earlier, the anions in Li[TFSA] electrolytes migrate to the Al surface and react with the native Al_2O_3 layer, forming soluble $Al[TFSA]_3$ complexes (1-10). Unlike in $LiPF_6$ systems, these soluble products cannot re-passivate the Al surface (**Figure 1-3b**). Instead, the dissolution of Al^{3+} continues, exposing fresh Al to further reactions. This perpetual depletion of Al^{3+} prevents the formation of a stable protective layer, leading to ongoing corrosion. The corrosion mechanism of Li[FSA] is analogous, following the same pattern of Al_2O_3 dissolution, soluble complex formation, and the failure to re-passivate the Al surface [37]. Na[FSA] and Na[TFSA] also face challenges regarding Al current collector

corrosion, following mechanisms similar to those observed in lithium amide-based electrolytes [58-60].



Regardless of the electrolyte system, the corrosion of Al foil as a current collector continues to hinder the long-term performance and reduce the cycle life of rechargeable batteries. For the development of next-generation LIBs and SIBs possessing high-energy-density, particularly those operating at 5 V, the problem is even more pronounced. Thus, advanced strategies are needed to address Al corrosion without sacrificing energy density. Broadly, effective corrosion mitigation strategies fall into two categories: (1) optimizing the electrolyte composition (functional additives, solvent regulation, highly concentrated electrolyte, etc.) to facilitate the formation of a stable passivation layer, and (2) modifying the Al current collector (structured Al surfaces, surface coating, effective inhibitors, etc.) to enhance its electrochemical stability [61, 62].

Lithium salt additives, such as LiPF_6 , lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB), are effective in forming a secondary passivation layer after the initial period of corrosion to inhibit Al corrosion. For example, Park et al. [63] added LiDFOB as an Al corrosion inhibitor and the mixture of 0.8 M $\text{Li}[\text{FSA}]$ + 0.2 M LiDFOB shows comparable Al corrosion behavior to 1 M LiPF_6 -based electrolyte (**Figure 1-4a**). This approach is also applicable to SIBs.

Hatchard et al. found that the significant corrosion caused by 1M Na[TFSA] solutions could be suppressed by additions of 0.3 M NaPF₆ [64].

The dielectric constant of the solvent plays a critical role in determining its oxidative stability with Al. Solvents with low dielectric constants tend to produce insoluble corrosion products, which can form a protective passivation layer on Al [65]. Yamada et al. [66] modified ethylene carbonate (EC) by incorporating the non-flammability of the phosphate group and introducing a fluorinated moiety, synthesized a fluorinated cyclic phosphate solvent, 2-(2,2,2-trifluoroethoxy)-1,3,2-dioxaphospholane 2-oxide (TFEP) (**Figure 1-4b**). The electrolytes consisting of 0.95 M Li[FSA], TFEP, and 2,2-trifluoroethyl methyl carbonate (FEMC) facilitated the formation of AlF₃ and Al₂O₃ passivation layers, achieving stability at 4.9 V. Similarly, monofluoride bis(2-fluoroethyl) ethers (BFE) is designed based on the chemical structure of 1,2-Dimethoxyethane (DME) [67]. The electrolyte combining Li[FSA] and BFE solvent promotes a passivation layer rich in LiF and AlF₃ on Al surfaces, effectively enhancing corrosion resistance.

Increasing the salt concentration to prepare highly concentrated electrolytes is an effective strategy to suppress Al corrosion by reducing free solvent molecules and manipulating the interfacial chemistry. Yamada et al. [37] demonstrated that a highly concentrated electrolyte of Li[FSA]/acetonitrile electrolyte effectively suppressed Al corrosion up to 4.5 V vs. Li⁺/Li. Compared to dilute electrolytes, the formation of solvated Al³⁺ is sluggish (1-4) in concentrated Li[FSA] electrolytes because they have

no free solvent molecules that can readily solvate cations (**Figure 1-4c**). Building upon this concept, further investigations have extended to SIBs. For instance, highly concentrated Na[TFSA] in propylene carbonate (PC) has demonstrated the ability to passivate the Al surface, thereby mitigating Al corrosion [68]. Although Al[TFSA]₃ is soluble in carbonated-based electrolytes, it can precipitate onto the Al surface and reduce Al dissolution in highly concentrated electrolytes [39].

Structured Al current collectors (e.g., acicular or porous) through chemical or electrochemical modifications can enhance adhesion and contact area [69, 70]. For instance, Jeong et al. [71] successfully fabricated an embossed Al current collector with highly ordered concave patterns using anodization followed by chromate-phosphate treatments. This modified Al foil demonstrated excellent electrochemical stability during charge-discharge due to improved electrical contact between the active material and the current collector. Additionally, while 3D current collectors show promise in anode applications as they reduce ion/electron diffusion distances, further exploration is needed to assess their potential in Al corrosion fields [72, 73].

To prevent the corrosion of Al current collectors, forming a passivation layer on the Al surface to isolate it from electrolytes has proven to be an effective approach. For example, Meister et al. [65] prepared a thicker Al-O film by treating Al with high-purity water at 100 °C, which provided better protection for the Al surface (**Figure 1-4d**). Similarly, Han et al. [47] developed an AlPO₄ passivation layer on Al, which suppresses electrolyte oxidation and increases corrosion resistivity, thereby enhancing the cycling

stability of the positive electrodes.

The protective capability of the passivation layer on Al becomes insufficient when the working voltage exceeds 4.3 V. Effective inhibitors, such as graphene-based materials [74], inorganic materials [75], and conductive polymer layers [76], are promising solutions to address Al corrosion issues. For example, graphene oxide (GO) adheres strongly to Al through a spin-coating method, suppressing Al oxidation by acting as a charge transport barrier (**Figure 1-4e**) [77]. Chromate conversion coating (CCC) provides a dense barrier against corrosive media and releases chromate to self-repair corrosion areas, making it suitable for use with Li[TFSA]-based electrolytes [78].

1.4 High-voltage positive electrode materials

Despite the rapid growth in the global production of LIBs over the last decade, the practical energy density of state-of-the-art LIBs, ranging between 150–250 Wh kg⁻¹ (cell-level), still falls short of market demands for applications like EV requiring over 350 Wh kg⁻¹ [79, 80]. To address this gap, researchers have been focusing on designing positive electrode materials with higher specific capacity and/or higher working voltages to enhance the energy density of LIBs while enabling smaller and lighter battery systems [81-83].

High-voltage positive electrode materials, operating above 4 V vs. Li⁺/Li, are broadly categorized into four types: (1) nickel-rich layered oxides (e.g., LiNiO₂, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂) [84, 85], (2) lithium-rich layered oxides (Li_{1+x}M_{1-x}O₂, where M =

Ni, Co, Mn, etc.) [86, 87], (3) high-voltage spinel oxides ($\text{LiMn}_{2-x}\text{MO}_4$, M = transition metal) [88, 89], and (4) high-voltage polyanionic compounds (e.g., phosphates, sulfates, silicates) [90]. **Figure 1-5** presents the estimation of the material- and cell-level gravimetric energy densities for both conventional and high-voltage LIBs. At the cell level, high-voltage batteries can achieve up to 350 Wh kg^{-1} , and substituting graphite with a Li-metal anode could further boost this value to around 400 Wh kg^{-1} . Nickel-rich layered oxides are known for their high energy densities, but their widespread application is hindered by inherent chemical and physical limitations, such as poor storage stability, initial capacity degradation, limited cycle life, and inferior thermal stability [91]. Lithium-rich layered oxides exhibit a high reversibility capacity exceeding 250 mAh g^{-1} but suffer from voltage decay due to a layered-to-spinel phase transition [92]. High-voltage spinel oxides have attracted attention for their low cost and environmental benefits but have moderate energy densities and rate performance limitations at elevated temperatures owing to inferior structure stability [93]. Polyanionic compounds are limited by lower reversible capacities, poor electronic conductivity, and rate performance [94].

The overall performance of these high-voltage positive electrode materials remains inadequate to meet the demands for practical application. This limitation is primarily attributed to poor interfacial stability between the high-voltage positive electrode and the electrolyte, resulting in their relatively short lifespan compared to traditional positive electrode materials. **Figure 1-6** summarizes the failure mechanisms

of high-voltage positive electrode materials, including lattice oxygen evolution, intragranular and intergranular crack formation, and transition metal (TM) dissolution from active materials.

Oxygen release from oxides-based positive electrode materials is a major cause of structural degradation, leading to rapid capacity and voltage fading, as well as increasing the risk of thermal runaway [95]. The remarkable capacity of Ni-rich materials primarily arises from the redox reactions of Ni/Co cations and oxygen anions ($\text{O}^{2-} \rightarrow \text{O}^{\alpha-}$, $\alpha < 2$) under high cut-off voltage (≥ 4.5 V) [96]. However, at such voltages, the oxidation of O^{2-} to $\text{O}^{\alpha-}$ ($\alpha < 2$) promotes lattice oxygen loss, undermining structural stability and leading to capacity degradation [97]. In Li-rich materials, the conversion of Li–O–M bonds into Li–O–Li bonds generates labile electrons around oxygen atoms, which readily hybridize to form O–O dimers with a low kinetic barrier, ultimately leading to the release of molecular oxygen [98]. Additionally, irreversible oxygen release intensifies interfacial side reactions due to electrolyte decomposition [99].

Cracking in high-voltage positive electrode materials is a critical issue that contributes to capacity fading and voltage decay. Mechanical cracking arises from multiple factors, including multiphase transition, electrochemical creep, large lattice parameter changes and internal fatigue [100]. Intragranular cracks, initiated within individual grains during high-voltage cycling, are an electrochemically driven and diffusion-controlled process [101]. Volume changes during lithiation and delithiation generate mechanical stress, leading to particle pulverization and loss of electrical

contact among electrode components [102]. Furthermore, anisotropic volume changes cause separation of primary particles, forming pathways along grain boundaries that allow electrolyte penetration into secondary particles [103]. This exposure renders interior grains susceptible to parasitic reactions, while the reactivity of surface oxide ions and the oxidative stability of the electrolyte influence surface reconstruction at the exposed grain boundaries of positive electrode materials. It is imperative to understand the crystal structure variation and secondary particle behavior during cycling.

Dissolution of TM cations from active positive materials is a major contributor to capacity fade and limited cycle life. This phenomenon is aggravated by the decomposition and hydrolysis of LiPF_6 , the most widely used lithium salt, which generates acidic species such as HF. Although HF enables passivation of the Al current collector, it can also attack high-voltage positive electrode materials, triggering TM dissolution and leading to interfacial instability [104]. In addition, Mn-based materials like LiMn_2O_4 are highly susceptible to dissolution due to disproportionation reactions (e.g., $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) [105]. Furthermore, oxygen release during high-voltage operation accelerates TM dissolution by widening the TM–O band and reducing the coordination number of surface metal ions, promoting further reduction and dissolution of TM [106]. Dissolved TM cations migrate to the anode, promoting the growth of solid electrolyte interphase (SEI) layers and increasing interfacial impedance [107]. Additionally, the accumulation of TM side products in separator pores obstructs Li^+ transport across the interface, resulting in larger internal impedance and capacity loss

during cycling [108].

To enhance the energy density of SIBs, efforts must focus on increasing output voltage or capacity. Since the positive electrode typically limits energy output, significant research has been devoted to developing advanced high-voltage positive electrode materials. Promising candidates include layered Na_xMO_2 ($0 < x \leq 1$, M = transition metal), Na-rich materials like $\text{Na}_2\text{M}'\text{O}_3$ ($\text{M}' = \text{Ir, Ru, Sn, etc.}$), and polyanionic compounds (phosphates, fluorophosphates, and pyrophosphates, etc.) [109, 110]. However, the Na^+ insertion/extraction process in the lattice of Na_xMO_2 undergoes complicated phase transitions, especially at high cut-off voltage, leading to irreversible structural changes, large volume changes, and rapid capacity degradation [111, 112]. Compared to layered oxides, polyanionic compounds offer higher operating potential due to the inductive effect of polyanion groups [113]. Their robust 3D frameworks minimize structural changes during sodium-ion insertion/extraction, and strong X–O ($\text{X} = \text{S, P, Si, etc.}$) covalent bonds effectively suppress oxygen evolution, contributing to enhanced cycle stability and safety [114]. Among them, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) has emerged as a promising positive electrode material for high-voltage SIBs due to its high theoretical capacity of 128 mAh g^{-1} , high operating voltage, and fast Na-ion diffusion rate [115, 116]. However, the inherently low electronic conductivity of NVPF ($2.4 \times 10^{-12} \text{ S cm}^{-1}$) remains a major challenge, limiting its rate capability and cycling stability [117, 118]. Several strategies have been investigated to improve the electrochemical performance of NVPF, such as the regulation of crystal structure, carbon coating, and

element doping [119].

However, fluorine loss during the synthesis of NVPF should not be overlooked, which causes the emergence of a low-voltage plateau in the charge/discharge curves of NVPF, especially in modified NVPF materials [120, 121]. To eliminate the low-voltage plateau, Deng et al. [122] proposed a fluorine stabilization strategy by carefully adjusting the pH of the precursor solution and optimizing calcination conditions (**Figure 1-7a**), which effectively suppressed fluorine volatilization and maintained its chemical integrity. This approach preserved the $[\text{VO}_4\text{F}_2]$ octahedral structure, preventing its transformation into $[\text{VO}_6]$, which was identified as the root cause of the low-voltage plateau. The optimized NVPF demonstrated a 100 mV increase in operating voltage, superior rate capability, and remarkable cycling performance. Researchers have investigated some fluorine supplements, such as polytetrafluoroethylene (PTFE) [123], polyvinylidene fluoride (PVDF) [124], fluorinated ionic liquid (IL) [125], and ammonium fluoride (NH_4F) [126], which compensate for the fluorine loss during NVPF synthesis. For example, Yan et al. [125] proposed a low-surface-energy strategy utilizing a fluorinated IL as both a fluorine supplement and a structural-directing agent (**Figure 1-7b**). This approach promoted crystal growth along the (002) plane, reduced particle size, and effectively compensated for fluorine loss during high-temperature synthesis.

1.5 Aims of this study

LIBs and SIBs have garnered immense attention as essential energy storage technologies for electric vehicles and grid applications. Achieving the high energy density required for these applications necessitates the development of high-voltage positive electrodes. However, electrode components of secondary batteries present serious challenges under high-voltage operation, such as the corrosion of the Al current collector, structural degradation, and transition metal dissolution of electrode materials. Moreover, optimizing the synthetic parameters of positive electrodes is critical to ensure product purity and performance. This research focuses on addressing these challenges by investigating the corrosion behavior of Al and the interfacial stability of high-voltage positive electrode material.

Chapter 2 provides the experimental methodologies, characterization techniques, and testing conditions that form the foundation of the investigations conducted in Chapters 3 to 6.

Chapter 3 examines the effects of temperature and Na salt concentration on Al corrosion behavior in sulfonylamide-based IL electrolytes. Cyclic voltammetry and morphological characterization reveal that severe corrosion occurs at high temperatures and low salt concentrations. Further investigations confirm that Al corrosion behavior differences in varying electrolytes are linked to the free $[\text{FSA}]^-$ to Na^+ -coordinated $[\text{FSA}]^-$ ratio and passivation layer stability. This work enhances the understanding of Al corrosion in IL electrolytes for advanced battery systems.

Chapter 4 investigates Li[FSA]-based IL electrolytes for their compatibility with LiNiO₂ positive electrodes. High Li salt concentrations improve cycling performance, achieving 73.1% capacity retention in Li/LiNiO₂ cells after 500 cycles. Further analyses show that the cathode electrolyte interphase is stable in highly concentrated electrolytes to suppress Ni dissolution and side reactions, while also alleviating Al corrosion at high potentials. This study highlights the role of electrolytes in stabilizing high-voltage electrodes.

Chapter 5 explores the detailed failure mechanism of Al corrosion behavior in Li[FSA]-based carbonate electrolytes. Contrary to expectations, cyclic voltammetry and surface characterization reveal that HF-treated Al does not effectively suppress corrosion. Through a series of experiments related to the reaction between AlF₃ and Li[FSA]-based electrolytes, the failure mechanism of the passivation layer is elucidated, offering insights into the limitations of this approach and guiding future corrosion mitigation strategies.

Chapter 6 systematically investigates the synthetic conditions of NVPF using a one-pot sol-gel method. The effects of NH₄F as a fluorine supplement and synthesis parameters such as pH, carbon content, and temperature on the crystal structure and morphology of NVPF are analyzed. Selected samples are evaluated by electrochemical tests to identify critical factors for pure-phase NVPF formation.

Chapter 7 summarizes the thesis and discusses prospects related to this work.

Table 1-1. LIBs market in GWh/y, past development and future perspectives [14].

Applications	2010	2015	2020	2025	2030
Portable electronics	21	31	45	66	100
Road-transports	0	13	76	137	245
Storage in power supplies	0	0	2	10	30
Others	1	1	2	7	15
Total	22	45	125	220	390

Table 1-2. Physical properties for “lithium”, and “sodium” as charge carriers for rechargeable batteries [19].

	Li ⁺	Na ⁺
Relative atomic mass	6.94	23.00
Mass-to-electron ratio	6.94	23.00
Shannon's ionic radii/Å	0.76	1.02
E ⁰ (A ⁺ _{aq} /A)/V vs. SHE	−3.04	−2.71
Melting point/°C	180.5	97.7
Desolvation energy in PC/kJ mol ^{−1}	215.8	158.2
Coordination preference of A ⁺ in AMO ₂ (M = transition metal)	Octahedral and tetrahedral	Octahedral and prismatic

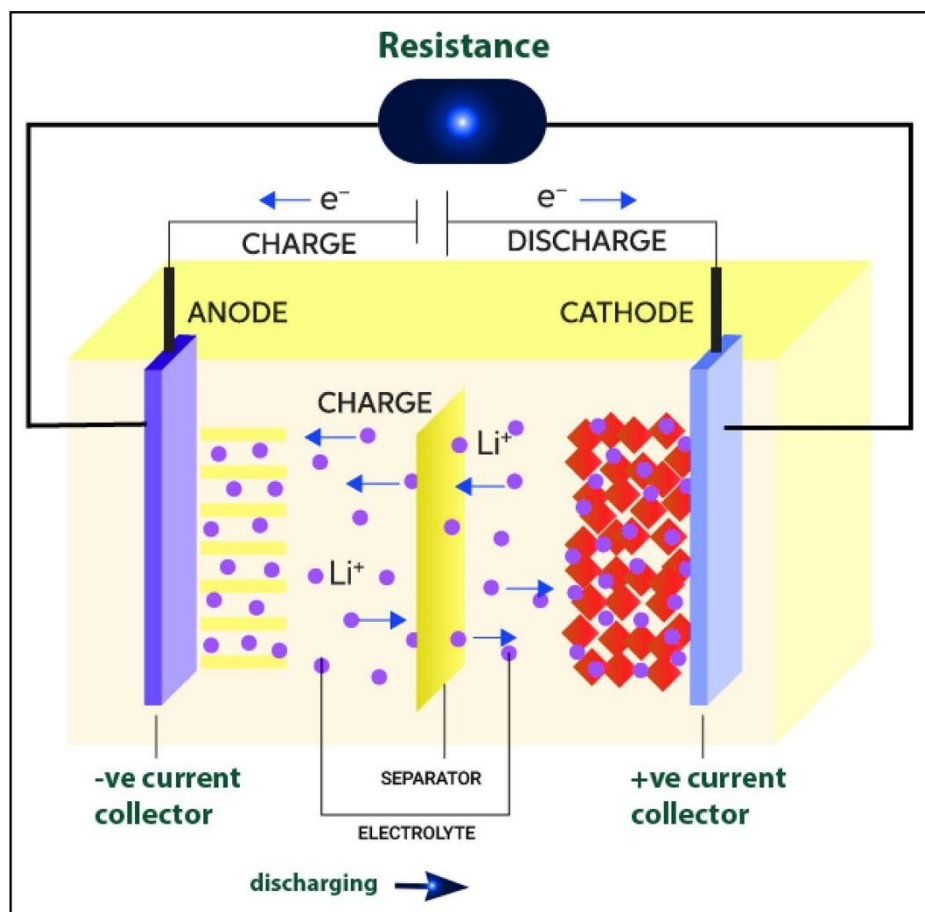


Figure 1-1. A schematic diagram of LIBs showing the lithium intercalation–deintercalation reaction mechanism. Reproduced with permission [10]. Copyright 2023, Elsevier.

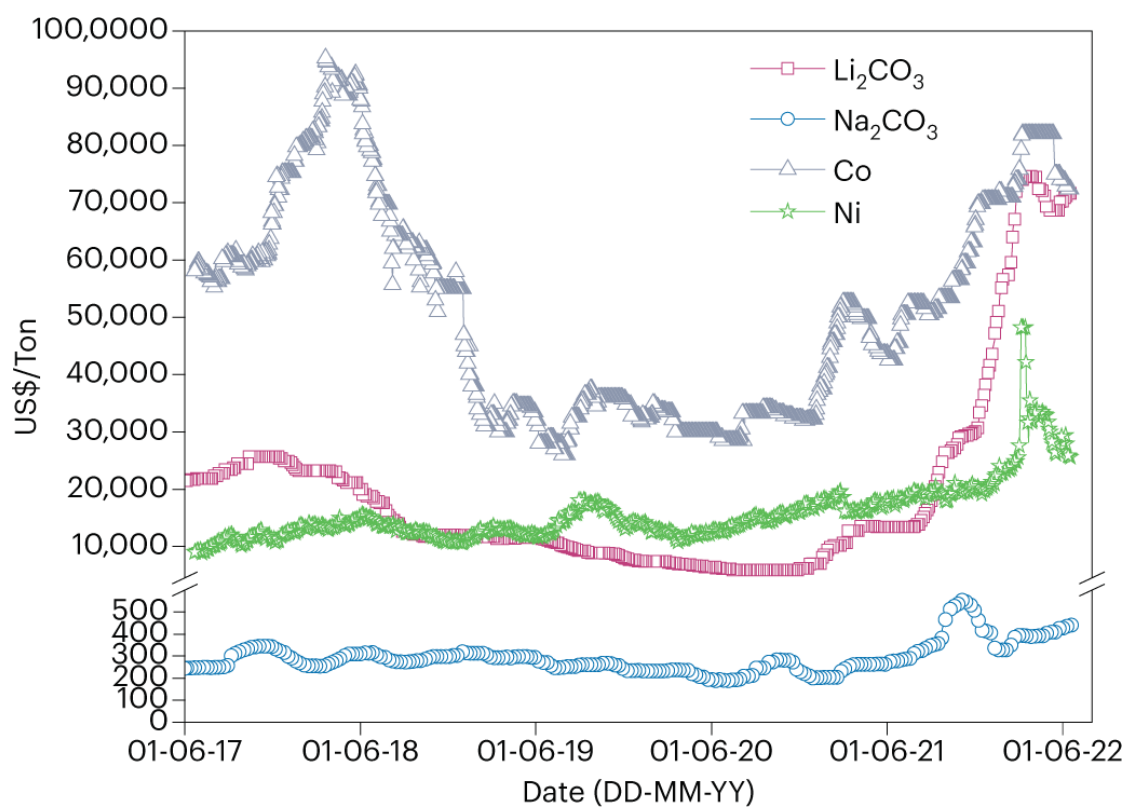


Figure 1-2. The closing price of lithium carbonate, sodium carbonate, cobalt, and nickel from 2017 to 2022. Reproduced with permission [18]. Copyright 2023, Springer Nature.

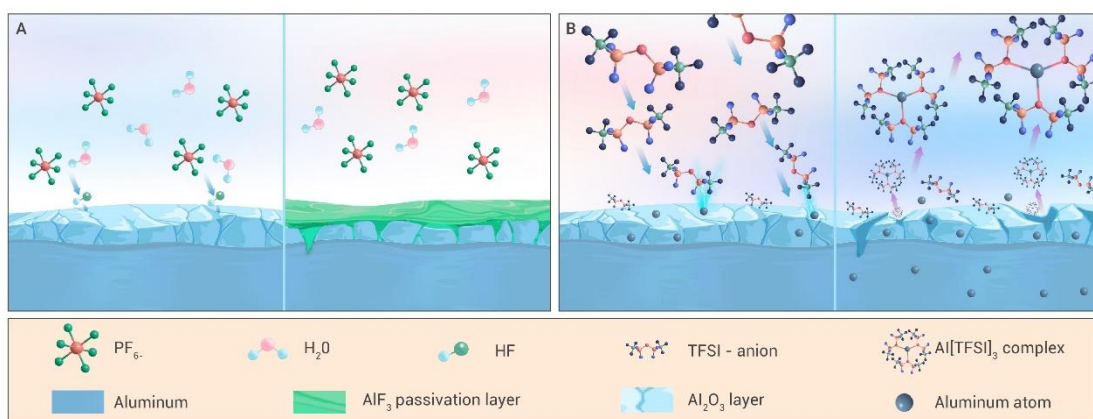


Figure 1-3. Corrosion mechanism for LiPF_6 and $\text{Li}[\text{TFSA}]$ -based electrolytes in LIBs. (a) The Al current collector (left) and Al with passivation layer (right) in LiPF_6 -based electrolyte. (b) The Al current collector (left) and Al current collector and solution production (right) in $\text{Li}[\text{TFSA}]$ -based electrolytes. Reproduced from Ref. [127] with a Creative Commons (CC) BY license.

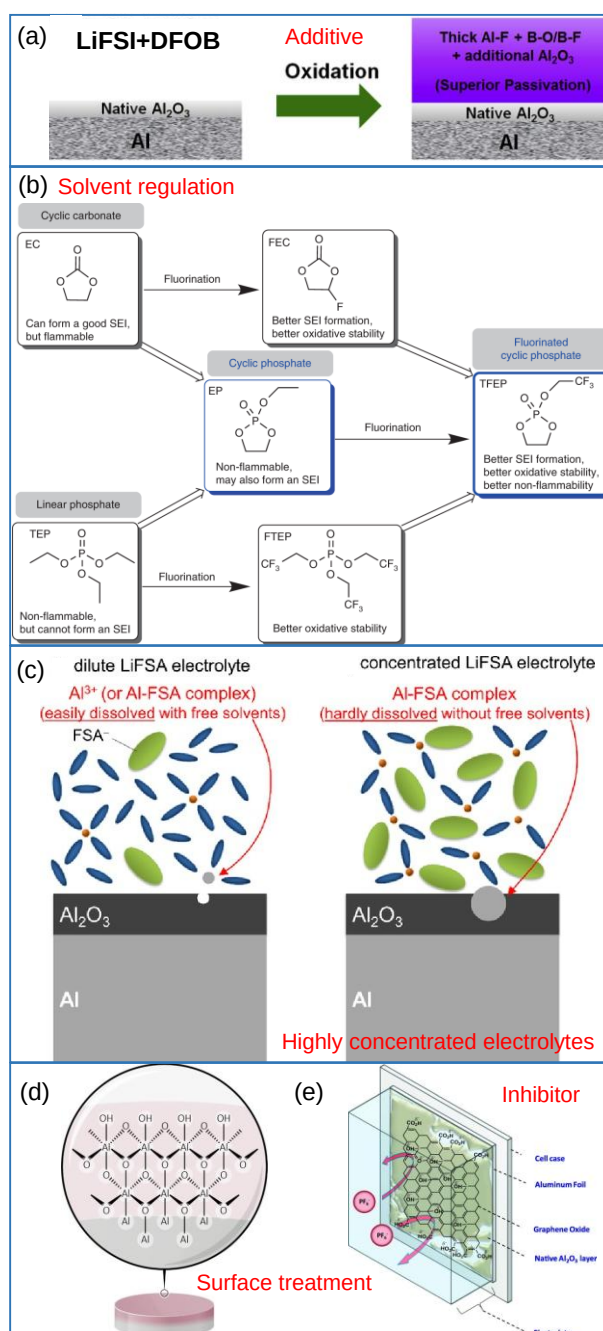


Figure 1-4. (a) A schematic diagram of passive layer formation on an Al electrode cycled in Li[FSA] + DFOB. Reproduced from Ref. [63] with permission. Copyright 2015 Elsevier Ltd. (b) A schematic illustration for designing of TFEF solvent. Reproduced from Ref. [66] with permission. Copyright 2020 Springer Nature. (c) Schematic illustrations of the behavior of Al electrodes in dilute Li[FSA]/AN electrolyte and highly concentrated Li[FSA]/AN electrolyte. Reproduced from Ref. [37] with permission. Copyright 2015 John Wiley and Sons. (d) A schematic illustration of the Al–O surface layer after treatment with KOH and water. Reproduced from Ref. [65] with permission. Copyright 2017 John Wiley and Sons. (e) A schematic illustration representation of the corrosion inhibition properties of GO when used on an aluminum current collector. Reproduced from Ref. [77] with permission. Copyright 2013 Elsevier Ltd.

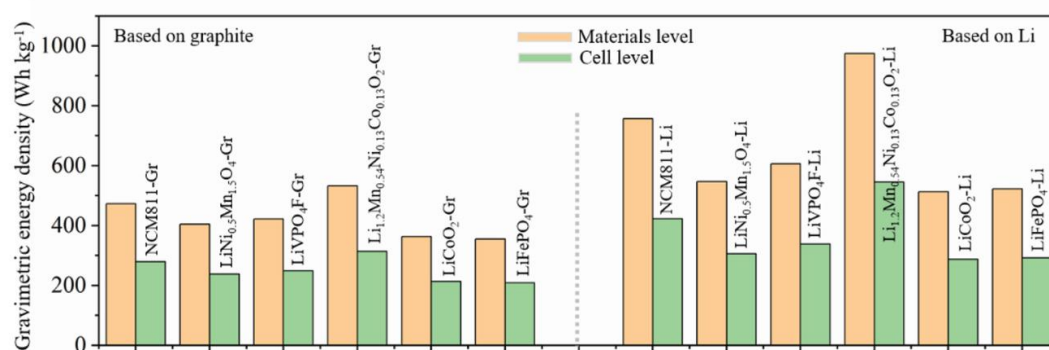


Figure 1-5. Estimation of the gravimetric energy densities of high-voltage and conventional rechargeable LIBs. Reproduced from Ref. [128] with permission. Copyright 2022 John Wiley and Sons.

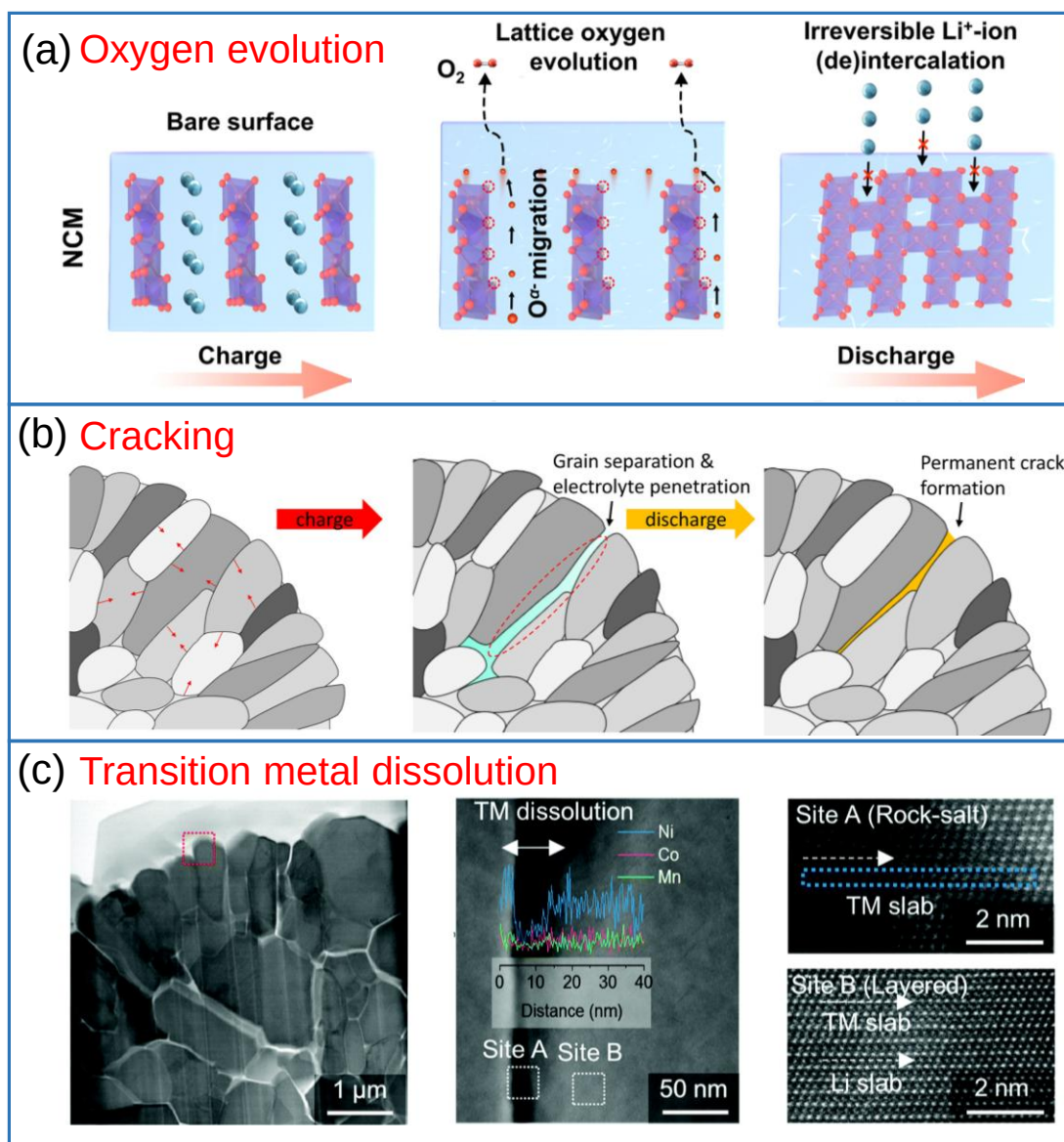


Figure 1-6. Degradation mechanisms of high-voltage positive electrode materials. (a) The mechanism schematic diagram for the interface evolution of pristine $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ during the charge/discharge process. Reproduced from Ref. [129] with permission. Copyright 2024 Elsevier Ltd. (b) A proposed microcrack formation mechanism in nickel-rich layered oxides. Reproduced from Ref. [103] with permission. Copyright 2023 Elsevier Ltd. (c) Surface microstructure of the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ after 500 cycles at 45 °C, where significant amounts of transition metal ions were extracted from the surface. Reproduced from Ref. [130] with permission. Copyright 2018 RSC Publishing.

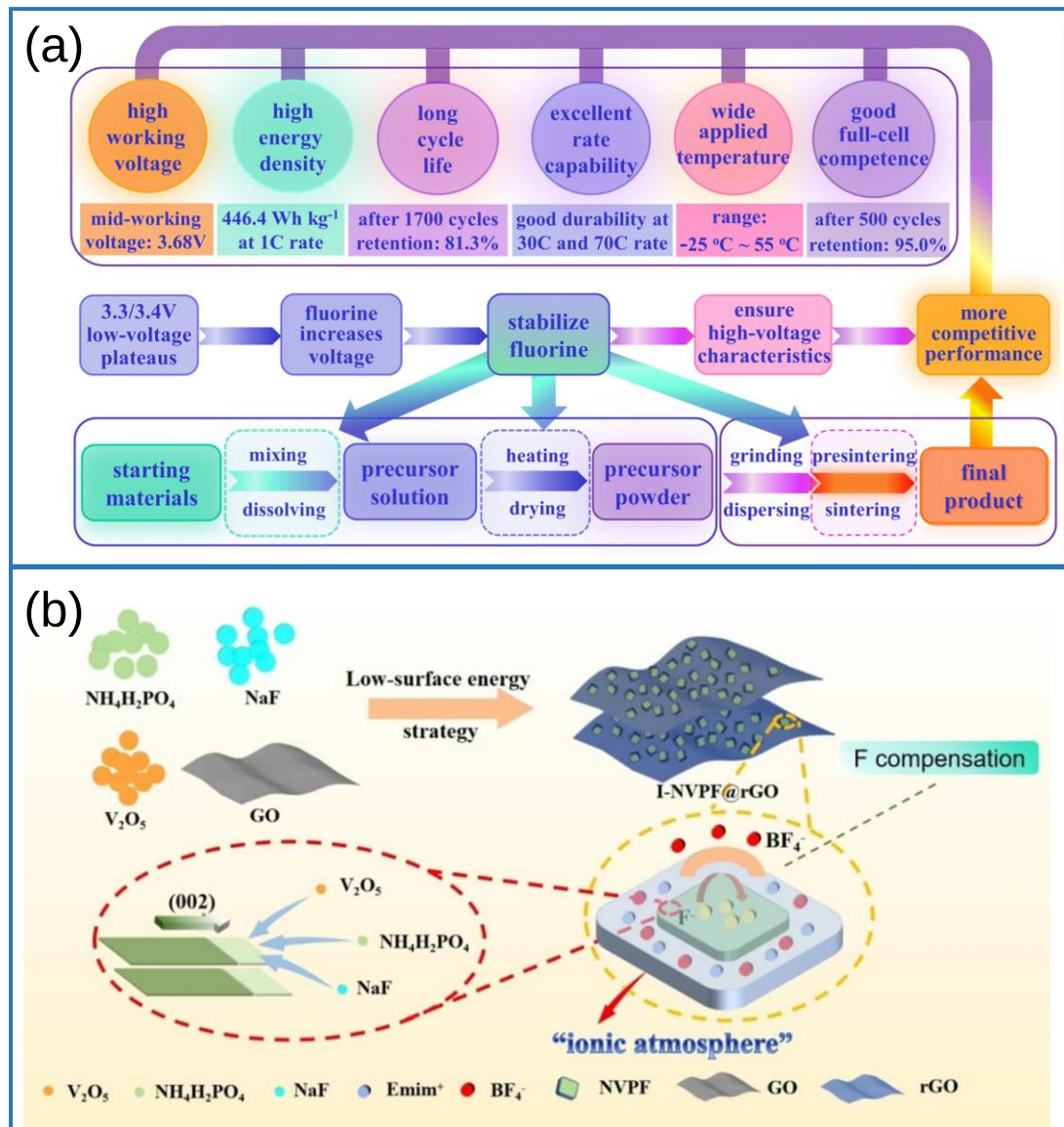


Figure 1-7. (a) A schematic diagram showing the synthesis route of NVPF, the strategy of stabilizing fluorine, and the advantages of the final NVPF product. Reproduced from Ref. [122] with permission. Copyright 2024 Elsevier Ltd. (b) A schematic illustration of low-surface-energy strategy to prepare the I-NVPF@rGO. Reproduced from Ref. [125] with permission. Copyright 2024 Elsevier Ltd.

References

- [1] World Energy Outlook 2024, International Energy Agency (IEA), Paris, (2024).
- [2] H. Lee and J. Romero, Climate Change 2023: Synthesis Report, Intergovernmental Panel on Climate Change (IPCC), Geneva, Switzerland, (2023).
- [3] Electricity 2024, International Energy Agency (IEA), Paris, (2024).
- [4] J. Mitali, S. Dhinakaran and A.A. Mohamad, *Energy Storage and Saving*, **1** (2022) 166-216.
- [5] M. De Rosa, O. Afanaseva, A.V. Fedyukhin and V. Bianco, *J. Energy Storage*, **44** (2021) 103443.
- [6] V. Fernão Pires, E. Romero-Cadaval, D. Vinnikov, I. Roasto and J.F. Martins, *Energy Convers. Manage.*, **86** (2014) 453-475.
- [7] T. Kopac, Electrochemical Energy Conversion and Storage Strategies, in: A. Kumar, R.K. Gupta (Eds.) *Atomically Precise Electrocatalysts for Electrochemical Energy Applications*, Springer Cham, (2024).
- [8] F.M.N.U. Khan, M.G. Rasul, A.S.M. Sayem and N.K. Mandal, *J. Energy Storage*, **71** (2023) 108033.
- [9] R. Monsef and M. Salavati-Niasari, *J. Energy Storage*, **74** (2023) 109395.
- [10] R. Sharma, H. Kumar, G. Kumar, S. Sharma, R. Aneja, A.K. Sharma, R. Kumar and P. Kumar, *Chem. Eng. J.*, **468** (2023) 143706.
- [11] F. Aguilar Lopez, D. Lauinger, F. Vuille and D.B. Müller, *Nat. Commun.*, **15** (2024) 4179.

- [12] Global EV Outlook 2024, International Energy Agency (IEA), Paris, (2024).
- [13] C. Nichols, Batteries for Stationary Energy Storage 2025-2035, (2024).
- [14] G. Zubi, R. Dufo-López, M. Carvalho and G. Pasaoglu, *Renew. Sustain. Energy Rev.*, **89** (2018) 292-308.
- [15] M. Li, J. Lu, Z. Chen and K. Amine, *Adv. Mater.*, **30** (2018) 1800561.
- [16] N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, *Chem. Rev.*, **114** (2014) 11636-11682.
- [17] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-González and T. Rojo, *Energy Environ. Sci.*, **5** (2012) 5884-5901.
- [18] A. Rudola, R. Sayers, C.J. Wright and J. Barker, *Nat. Energy*, **8** (2023) 215-218.
- [19] K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura and S. Komaba, *Chem. Rec.*, **18** (2018) 459-479.
- [20] Q. Liu, Z. Hu, M. Chen, C. Zou, H. Jin, S. Wang, S.-L. Chou and S.-X. Dou, *Small*, **15** (2019) 1805381.
- [21] A. Manthiram, *Nat. Commun.*, **11** (2020) 1550.
- [22] Z. Tian, Y. Zou, G. Liu, Y. Wang, J. Yin, J. Ming and H.N. Alshareef, *Adv. Sci.*, **9** (2022) 2201207.
- [23] Z. Wang, C. Wei, H. Jiang, Y. Zhang, K. Tian, Y. Li, X. Zhang, S. Xiong, C. Zhang and J. Feng, *Adv. Mater.*, **36** (2024) e2306015.
- [24] H. Li, L. Wang, Y. Song, Z. Zhang, H. Zhang, A. Du and X. He, *Adv. Funct. Mater.*, **33** (2023) 2305515.

- [25] P. Zhu, D. Gastol, J. Marshall, R. Sommerville, V. Goodship and E. Kendrick, *J. Power Sources*, **485** (2021) 229321.
- [26] J. Chen, Z. Bai, X. Li, Q. Wang, J. Du, R. Lu and X. Liu, *Appl. Surf. Sci.*, **606** (2022) 155002.
- [27] M. Wang, M. Tang, S. Chen, H. Ci, K. Wang, L. Shi, L. Lin, H. Ren, J. Shan, P. Gao, Z. Liu and H. Peng, *Adv. Mater.*, **29** (2017) 1703882.
- [28] Z. Ahmad, Principles of corrosion engineering and corrosion control, Elsevier, 2006.
- [29] K. Kanamura, T. Umegaki, S. Shiraishi, M. Ohashi and Z.-i. Takehara, *J. Electrochem. Soc.*, **149** (2002) A185.
- [30] A. Gabryelczyk, S. Ivanov, A. Bund and G. Lota, *J. Energy Storage*, **43** (2021) 103226.
- [31] S.S. Zhang and T.R. Jow, *J. Power Sources*, **109** (2002) 458-464.
- [32] E. Krämer, S. Passerini and M. Winter, *ECS Electrochem. Lett.*, **1** (2012) C9.
- [33] G. Zhang, K. Lin, X. Qin, L. Zhang, T. Li, F. Lv, Y. Xia, W. Han, F. Kang and B. Li, *ACS Appl. Mater. Interfaces*, **12** (2020) 37034-37046.
- [34] K. Kanamura, *J. Power Sources*, **81-82** (1999) 123-129.
- [35] X. Wang, E. Yasukawa and S. Mori, *Electrochim. Acta*, **45** (2000) 2677-2684.
- [36] K. Xu, *Chem. Rev.*, **104** (2004) 4303-4418.
- [37] Y. Yamada, C.H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama and A. Yamada, *ChemElectroChem*, **2** (2015) 1687-1694.

- [38] X. Zhang, B. Winget, M. Doeff, J. W. Evans and T.M. Devine, *J. Electrochem. Soc.*, **152** (2005) B448.
- [39] D.W. McOwen, D.M. Seo, O. Borodin, J. Vatamanu, P.D. Boyle and W.A. Henderson, *Energy Environ. Sci.*, **7** (2014) 416-426.
- [40] F.N. Sayed, M.-T.F. Rodrigues, K. Kalaga, H. Gullapalli and P.M. Ajayan, *ACS Appl. Mater. Interfaces*, **9** (2017) 43623-43631.
- [41] H.-B. Han, S.-S. Zhou, D.-J. Zhang, S.-W. Feng, L.-F. Li, K. Liu, W.-F. Feng, J. Nie, H. Li, X.-J. Huang, M. Armand and Z.-B. Zhou, *J. Power Sources*, **196** (2011) 3623-3632.
- [42] X. Zhang and T.M. Devine, *J. Electrochem. Soc.*, **153** (2006) B344.
- [43] M.S. Whittingham, *Chem. Rev.*, **104** (2004) 4271-4302.
- [44] R. Wagner, M. Korth, B. Streipert, J. Kasnatscheew, D.R. Gallus, S. Brox, M. Amereller, I. Cekic-Laskovic and M. Winter, *ACS Appl. Mater. Interfaces.*, **8** (2016) 30871-30878.
- [45] J. Lan, Q. Zheng, H. Zhou, J. Li, L. Xing, K. Xu, W. Fan, L. Yu and W. Li, *ACS Appl. Mater. Interfaces.*, **11** (2019) 28841-28850.
- [46] T. Ma, G.L. Xu, Y. Li, L. Wang, X. He, J. Zheng, J. Liu, M.H. Engelhard, P. Zapol, L.A. Curtiss, J. Jorne, K. Amine and Z. Chen, *J Phys Chem Lett*, **8** (2017) 1072-1077.
- [47] H. Gao, T. Ma, T. Duong, L. Wang, X. He, I. Lyubinetzky, Z. Feng, F. Maglia, P. Lamp, K. Amine and Z. Chen, *Mater. Today Energy*, **7** (2018) 18-26.
- [48] Y. Chen, T.M. Devine, J. W. Evans, O.R. Monteiro and I.G. Brown, *J. Electrochem.*

Soc., **146** (1999) 1310.

[49] B.C. Bunker, G.C. Nelson, K.R. Zavadil, J.C. Barbour, F.D. Wall, J.P. Sullivan, C.F. Windisch, M.H. Engelhardt and D.R. Baer, *J. Phys. Chem. B*, **106** (2002) 4705-4713.

[50] X. Zhang and T.M. Devine, *J. Electrochem. Soc.*, **153** (2006) B375.

[51] E. Yoon, J. Lee, S. Byun, D. Kim and T. Yoon, *Adv. Funct. Mater.*, **32** (2022) 2200026.

[52] Y. Li, X.-W. Zhang, S.A. Khan and P.S. Fedkiw, *Electrochem. Solid-State Lett.*, **7** (2004) A228.

[53] R. Younesi, G.M. Veith, P. Johansson, K. Edström and T. Vegge, *Energy Environ. Sci.*, **8** (2015) 1905-1922.

[54] J. Kalhoff, G.G. Eshetu, D. Bresser and S. Passerini, *ChemSusChem*, **8** (2015) 2154-2175.

[55] J. Kalhoff, D. Bresser, M. Bolloli, F. Alloin, J.-Y. Sanchez and S. Passerini, *ChemSusChem*, **7** (2014) 2939-2946.

[56] C. Peng, L. Yang, Z. Zhang, K. Tachibana, Y. Yang and S. Zhao, *Electrochim. Acta*, **53** (2008) 4764-4772.

[57] E. Cho, J. Mun, O.B. Chae, O.M. Kwon, H.-T. Kim, J.H. Ryu, Y.G. Kim and S.M. Oh, *Electrochem. Commun.*, **22** (2012) 1-3.

[58] Y. Huang, L. Zhao, L. Li, M. Xie, F. Wu and R. Chen, *Adv. Mater.*, **31** (2019) e1808393.

- [59] K. Matsumoto, J. Hwang, S. Kaushik, C.-Y. Chen and R. Hagiwara, *Energy Environ. Sci.*, **12** (2019) 3247-3287.
- [60] Y. Sun, P. Shi, H. Xiang, X. Liang and Y. Yu, *Small*, **15** (2019) 1805479.
- [61] C. Han, G. Chen, Y. Ma, J. Ma, X. Shui, S. Dong, G. Xu, X. Zhou, Z. Cui, L. Qiao and G. Cui, *Energy Mater.*, **3** (2023) 300052.
- [62] S. Yang, J. Zhong, S. Li and B. Li, *J. Energy Chem.*, **89** (2024) 610-634.
- [63] K. Park, S. Yu, C. Lee and H. Lee, *J. Power Sources*, **296** (2015) 197-203.
- [64] T.D. Hatchard and M.N. Obrovac, *J. Electrochem. Soc.*, **161** (2014) A1748-A1752.
- [65] P. Meister, X. Qi, R. Kloepsch, E. Kramer, B. Streipert, M. Winter and T. Placke, *ChemSusChem*, **10** (2017) 804-814.
- [66] Q. Zheng, Y. Yamada, R. Shang, S. Ko, Y.-Y. Lee, K. Kim, E. Nakamura and A. Yamada, *Nat. Energy*, **5** (2020) 291-298.
- [67] G. Zhang, J. Chang, L. Wang, J. Li, C. Wang, R. Wang, G. Shi, K. Yu, W. Huang, H. Zheng, T. Wu, Y. Deng and J. Lu, *Nat. Commun.*, **14** (2023) 1081.
- [68] C. Geng, D. Buchholz, G.T. Kim, D.V. Carvalho, H. Zhang, L.G. Chagas and S. Passerini, *Small Methods*, **3** (2018) 1800208.
- [69] C. Lecoœur, J.-M. Tarascon and C. Guery, *J. Electrochem. Soc.*, **157** (2010) A641.
- [70] H.-C. Wu, H.-C. Wu, E. Lee and N.-L. Wu, *Electrochem. Commun.*, **12** (2010) 488-491.
- [71] C.U. Jeong, S.-Y. Lee, J. Kim, K.Y. Cho and S. Yoon, *J. Power Sources*, **398** (2018) 193-200.

- [72] S.K. Cheah, E. Perre, M. Rooth, M. Fondell, A. Hårsta, L. Nyholm, M. Boman, T. Gustafsson, J. Lu, P. Simon and K. Edström, *Nano Lett.*, **9** (2009) 3230-3233.
- [73] Y. Yue and H. Liang, *Small Methods*, **2** (2018) 1800056.
- [74] S.Y. Kim, Y.I. Song, J.-H. Wee, C.H. Kim, B.W. Ahn, J.W. Lee, S.J. Shu, M. Terrones, Y.A. Kim and C.-M. Yang, *Carbon*, **153** (2019) 495-503.
- [75] A. Heckmann, M. Krott, B. Streipert, S. Uhlenbruck, M. Winter and T. Placke, *ChemPhysChem*, **18** (2017) 156-163.
- [76] D. Lepage, L. Savignac, M. Saulnier, S. Gervais and S.B. Schougaard, *Electrochem. Commun.*, **102** (2019) 1-4.
- [77] S.J. Richard Prabakar, Y.-H. Hwang, E.G. Bae, D.K. Lee and M. Pyo, *Carbon*, **52** (2013) 128-136.
- [78] N. Piao, L. Wang, T. Anwar, X. Feng, S.e. Sheng, G. Tian, J. Wang, Y. Tang and X. He, *Corros. Sci.*, **158** (2019) 108100.
- [79] J. Deng, C. Bae, A. Denlinger and T. Miller, *Joule*, **4** (2020) 511-515.
- [80] J.T. Frith, M.J. Lacey and U. Ulissi, *Nat. Commun.*, **14** (2023) 420.
- [81] B.L. Ellis, K.T. Lee and L.F. Nazar, *Chem. Mater.*, **22** (2010) 691-714.
- [82] M. Hu, X. Pang and Z. Zhou, *J. Power Sources*, **237** (2013) 229-242.
- [83] L. Croguennec and M.R. Palacin, *J. Am. Chem. Soc.*, **137** (2015) 3140-3156.
- [84] Y.-K. Sun, D.-J. Lee, Y.J. Lee, Z. Chen and S.-T. Myung, *ACS Appl. Mater. Interfaces*, **5** (2013) 11434-11440.
- [85] Y. Lv, S. Huang, Y. Zhao, S. Roy, X. Lu, Y. Hou and J. Zhang, *Applied Energy*, **305**

(2022) 117849.

[86] S. Liu, Z. Liu, X. Shen, W. Li, Y. Gao, M.N. Banis, M. Li, K. Chen, L. Zhu, R. Yu, Z. Wang, X. Sun, G. Lu, Q. Kong, X. Bai and L. Chen, *Adv. Energy Mater.*, **8** (2018) 1802105.

[87] H.-Y. Jang, D. Eum, J. Cho, J. Lim, Y. Lee, J.-H. Song, H. Park, B. Kim, D.-H. Kim, S.-P. Cho, S. Jo, J.H. Heo, S. Lee, J. Lim and K. Kang, *Nat. Commun.*, **15** (2024) 1288.

[88] L. Miara, A. Windmüller, C.-L. Tsai, W.D. Richards, Q. Ma, S. Uhlenbruck, O. Guillon and G. Ceder, *ACS Appl. Mater. Interfaces*, **8** (2016) 26842-26850.

[89] Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li and J. Li, *Adv. Energy Mater.*, **11** (2021) 2000997.

[90] J. Ling, C. Karuppiyah, S.G. Krishnan, M.V. Reddy, I.I. Misnon, M.H. Ab Rahim, C.-C. Yang and R. Jose, *Energy Fuels*, **35** (2021) 10428-10450.

[91] Y. Ding, D. Mu, B. Wu, R. Wang, Z. Zhao and F. Wu, *Applied Energy*, **195** (2017) 586-599.

[92] F. Zheng, C. Yang, X. Xiong, J. Xiong, R. Hu, Y. Chen and M. Liu, *Angew. Chem. Int. Ed.*, **54** (2015) 13058-13062.

[93] T.-F. Yi, J. Mei and Y.-R. Zhu, *J. Power Sources*, **316** (2016) 85-105.

[94] D. Guo, S. Chu, B. Zhang and Z. Li, *Small Methods*, **8** (2024) 2400587.

[95] S. Sharifi-Asl, J. Lu, K. Amine and R. Shahbazian-Yassar, *Adv. Energy Mater.*, **9** (2019) 1900551.

- [96] L. Wang, G. Liu, R. Xu, X. Wang, L. Wang, Z. Yao, C. Zhan and J. Lu, *Adv. Energy Mater.*, **13** (2023) 2203999.
- [97] Z. Zhu, H. Wang, Y. Li, R. Gao, X. Xiao, Q. Yu, C. Wang, I. Waluyo, J. Ding and A. Hunt, *Adv. Mater.*, **32** (2020) 2005182.
- [98] D.-H. Seo, J. Lee, A. Urban, R. Malik, S. Kang and G. Ceder, *Nat. Chem.*, **8** (2016) 692-697.
- [99] J. Yang, P. Li, F. Zhong, X. Feng, W. Chen, X. Ai, H. Yang, D. Xia and Y. Cao, *Adv. Energy Mater.*, **10** (2020) 1904264.
- [100] K.-Y. Park, Y. Zhu, C.G. Torres-Castanedo, H.J. Jung, N.S. Luu, O. Kahvecioglu, Y. Yoo, J.-W.T. Seo, J.R. Downing, H.-D. Lim, M.J. Bedzyk, C. Wolverton and M.C. Hersam, *Adv. Mater.*, **34** (2022) 2106402.
- [101] P. Yan, J. Zheng, M. Gu, J. Xiao, J.-G. Zhang and C.-M. Wang, *Nat. Commun.*, **8** (2017) 14101.
- [102] M. Ebner, F. Marone, M. Stampanoni and V. Wood, *Science*, **342** (2013) 716-720.
- [103] S. Lee, L. Su, A. Mesnier, Z. Cui and A. Manthiram, *Joule*, **7** (2023) 2430-2444.
- [104] M. Liu, J. Vatamanu, X. Chen, L. Xing, K. Xu and W. Li, *ACS Energy Lett.*, **6** (2021) 2096-2102.
- [105] C. Zhan, T. Wu, J. Lu and K. Amine, *Energy Environ. Sci.*, **11** (2018) 243-257.
- [106] J. Wandt, A.T.S. Freiberg, A. Ogrodnik and H.A. Gasteiger, *Mater. Today*, **21** (2018) 825-833.
- [107] J. Wandt, A. Freiberg, R. Thomas, Y. Gorlin, A. Siebel, R. Jung, H.A. Gasteiger

- and M. Tromp, *J. Mater. Chem. A*, **4** (2016) 18300-18305.
- [108] W. Li, B. Song and A. Manthiram, *Chem. Soc. Rev.*, **46** (2017) 3006-3059.
- [109] Y. You and A. Manthiram, *Adv. Energy Mater.*, **8** (2018) 1701785.
- [110] A. Liu, S. Lu and X. Wu, *Batteries Supercaps*, **7** (2024) e202400290.
- [111] S. Komaba, C. Takei, T. Nakayama, A. Ogata and N. Yabuuchi, *Electrochem. Commun.*, **12** (2010) 355-358.
- [112] C. Fang, Y. Huang, W. Zhang, J. Han, Z. Deng, Y. Cao and H. Yang, *Adv. Energy Mater.*, **6** (2016) 1501727.
- [113] C. Xu, J. Zhao, C. Yang and Y.-S. Hu, *ACS Central Science*, **9** (2023) 1721-1736.
- [114] T. Jin, H. Li, K. Zhu, P.-F. Wang, P. Liu and L. Jiao, *Chem. Soc. Rev.*, **49** (2020) 2342-2377.
- [115] J. Zhao, X. Yang, Y. Yao, Y. Gao, Y. Sui, B. Zou, H. Ehrenberg, G. Chen and F. Du, *Adv. Sci.*, **5** (2018) 1700768.
- [116] Y. Pi, Z. Gan, M. Yan, C. Pei, H. Yu, Y. Ge, Q. An and L. Mai, *Chem. Eng. J.*, **413** (2021) 127565.
- [117] Q. Zhou, Y. Wang, R. Ou, X. Ding, Y. Xin, F. Wu and H. Gao, *Small*, **20** (2024) 2310699.
- [118] Q. Wu, Y. Ma, S. Zhang, X. Chen, J. Bai, H. Wang and X. Liu, *Small*, **20** (2024) 2404660.
- [119] K. Liang, D. Wu, Y. Ren, X. Huang and J. Ma, *Chin. Chem. Lett.*, **34** (2023) 107978.

- [120] Z. Yang, G. Li, J. Sun, L. Xie, Y. Jiang, Y. Huang and S. Chen, *Energy Storage Mater.*, **25** (2020) 724-730.
- [121] W.x. Zhan, C.l. Fan, W.h. Zhang, G.d. Yi, H. Chen, S.c. Han and J.s. Liu, *Int. J. Energy Res.*, **44** (2020) 6608-6622.
- [122] L. Deng, F.-D. Yu, Y. Xia, Y.-S. Jiang, X.-L. Sui, L. Zhao, X.-H. Meng, L.-F. Que and Z.-B. Wang, *Nano Energy*, **82** (2021) 105659.
- [123] C. Sun, L.L. Zhang, Z.R. Deng, H.B. Sun and X.L. Yang, *ACS Appl. Mater. Interfaces*, **16** (2024) 35179-35189.
- [124] Y. Subramanian, W. Oh, W. Choi, H. Lee, M. Jeong, R. Thangavel and W.-S. Yoon, *Chem. Eng. J.*, **403** (2021) 126291.
- [125] Y. Yan, J.-Q. Xu, J.-M. Cao, H.-W. Huang, S.-S. Xue, G.-L. Li, A.-M. Liu, C.-J. Li, D. Dai, B. Li and X.-L. Wu, *Chem. Eng. J.*, **498** (2024) 155640.
- [126] K. Liang, H. Zhao, J. Li, X. Huang and Y. Ren, *Appl. Surf. Sci.*, **615** (2023) 156412.
- [127] X. Shi, H. Zhang, Y. Zhang, J. Liu, J. Zhang and L. Li, *Innov. Mater.*, **1** (2023) 100030.
- [128] J. Xiang, Y. Wei, Y. Zhong, Y. Yang, H. Cheng, L. Yuan, H. Xu and Y. Huang, *Adv. Mater.*, **34** (2022) e2200912.
- [129] Y. Huang, D. Su, L. Zheng, G. Yang, K. Li, J. Jiang, Q. Pan, S. Hu, Y. Li, Q. Li, H. Wang, F. Zheng and X. Ou, *Energy Storage Mater.*, **71** (2024) 103678.
- [130] J. Kim, H. Ma, H. Cha, H. Lee, J. Sung, M. Seo, P. Oh, M. Park and J. Cho, *Energy Environ. Sci.*, **11** (2018) 1449-1459.

Chapter 2

Experimental

2.1 Apparatus and material handing

Experimental tools, such as tweezers, scissors, beakers, cutting knives, medicine spoons, and measuring cylinders, were cleaned sequentially with ion-exchanged water and ethanol, then dried in an oven at 60 °C for at least 2 h before use.

All handling of air-sensitive reagents and active materials, including the assembly and disassembly of coin cells, was conducted in an argon-filled glove box (Miwa Manufacturing Co., Ltd., DBO-2LKH-HNBR) with a gas purification system (Miwa Manufacturing Co., Ltd., MS3-P60S-N). The argon atmosphere, with a purity of 99.995%, was carefully maintained at a dew point below −90 °C and an oxygen concentration under 1 ppm, continuously monitored by a dew point meter (GE Panametrics Ltd., MTS5-311-10) and an oxygen analyzer (GE Sensing & Inspection Technologies Co., Ltd., DF-150ε). An analytical balance (Sartorius Mechatronics Japan K.K., CPA225D) was installed in the glove box to measure chemical weights precisely.

Chemicals and ionic liquid (IL) electrolytes were dried in a drying vessel (**Figure 2-1**) connected to a vacuum line (**Figure 2-2**). This vacuum line was composed of stainless-steel (SUS316, 1/2 inch OD) and PFA (1/2 inch OD) tubing, connected through stainless steel joints and Kel-F-tipped (polychlorotrifluoroethylene) valves

(Swagelok). The vacuum line was connected to a rotary vacuum pump (ULVAC KIKO, Inc., GLD-136C) through a Pyrex glass cold trap cooled with liquid nitrogen to capture volatiles. The pressure within the system, monitored by Pirani gauges, achieved a final vacuum level of approximately 1 Pa. The temperature of the drying vessel was maintained by silicone oil heated in an oil bath with a magnetic stirrer. Heating devices, a hot plate (AS ONE REXIM RSH-1DN), a muffle furnace (AS ONE 1-5925-02HPM-1G), and a tube furnace (KTF045N1, Koyo), were used for the synthesis process of electrode materials. The temperature control procedure of the tube furnace involves a heating rate of 5 °C min⁻¹ and a cooling rate of 2 °C min⁻¹. **Figure 2-3** presents the schematic diagram of the tube furnace. Detailed preparation methods will be described in Chapter 6.

Li[FSA] (Mitsubishi Materials Electronic Chemicals, purity > 99%), Na[FSA] (Mitsubishi Materials Electronic Chemicals, purity > 99%), Na[TFSA] (Kishida Chemical, purity > 99%), and organic salts, [C₂C₁im][FSA], [C₃C₁pyrr][FSA], [C₂C₁im][TFSA], and [C₃C₁pyrr][TFSA] (Kanto Chemical Co., Inc., purity > 99.9%), were purchased and dried under vacuum at 80 °C for 24 h before use. Propylene carbonate (PC, Fujifilm Wako Pure Chemicals), ethylene carbonate/dimethyl carbonate (EC/DMC = 1:1 v/v, Kishida Chemical, battery grade), fluoroethylene carbonate (FEC, Fujifilm Wako Pure Chemicals), 1 mol dm⁻³ LiPF₆-EC/DMC (1:1 v/v, Kishida Chemical, battery grade), and 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v, Kishida Chemical, battery grade) were used without further purification.

2.2 Electrode and cell preparation

The LiNiO_2 electrodes were prepared by mixing LiNiO_2 (Toshiba MFG), Super C65 (Timcal Ltd.), and PVDF binder (poly(vinylidene fluoride), Kureha Corp.) in a weight ratio of 80:10:10 with NMP (*N*-methyl-2-pyrrolidone, Fujifilm Wako Pure Chemicals) solvent. The resulting slurry was mixed by a planetary mixer (AR-100, Thinky, Tokyo, Japan) and cast onto an Al foil (20 μm) using a coating machine (Hosen). After drying at 60 °C overnight, the electrodes were punched (10 mm in diameter) and vacuum-dried at 60 °C for 4 h. The $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) electrodes were prepared by mixing the active material (see Chapter 6), Super C65, and PVDF binder in a weight ratio of 80:15:5 with NMP solvent. The subsequent process was the same as the preparation of LiNiO_2 electrodes.

Coin cells (2032-type), illustrated in **Figure 2-4**, were assembled in an Ar-filled glove box for electrochemical measurements. Al foil was punched into discs (diameter: 10 mm) and used as the working electrode when investigating the corrosion of the Al current collector. A glass fiber filter (Whatman, GF-A, diameter: 16 mm, and thickness: 260 μm) was used as a separator after being immersed in electrolytes. Lithium (Sigma-Aldrich, purity 99.95%) or sodium (Sigma-Aldrich, purity 99.95%) metal was used as counter electrodes by spreading, punching into 13 mm disks, and pressing onto Al foil before using them in cell assembly.

2.3 Material characterization

2.3.1 X-ray diffraction (XRD)

The crystal structures of NVPF samples with different synthetic conditions were characterized by XRD using a Rigaku Smart-Lab diffractometer equipped with a D/teX Ultra 250 silicon strip high-speed detector. Measurements were conducted in the Bragg–Brentano geometry with Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 30 mA).

2.3.2 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The field-emission scanning electron microscopic (FE-SEM, Hitachi SU-8020) and EDX (Horiba EMAXEvolution X-max) analyses were employed to investigate the morphology and elemental distribution of samples.

2.3.3 X-ray photoelectron spectroscopy (XPS)

The chemical states and elemental compositions were analyzed by an XPS (JEOL, JPS-9030) instrument using Mg K α radiation ($\lambda = 9.89 \text{ \AA}$, 10 kV–10 mA). Depth profiles were obtained by etching samples for different times with an Ar beam at an accelerating voltage of 400 V. The obtained spectra were processed with SpecSurf software (JEOL, Ltd). Samples were rinsed with ethanol before XPS measurements.

2.3.4 X-ray fluorescence spectroscopy (XRF)

The contents of specific elements in samples were analyzed by XRF spectroscopy (EDXL 300, Rigaku Corp.) under a He atmosphere.

2.3.5 Raman spectroscopy

Raman spectra of the IL electrolytes were recorded by Raman spectroscopy (DXR3, Thermo Fisher Scientific) using a laser with an excitation wavelength of 785 nm.

2.3.6 Specific surface area measurement with Brunauer–Emmett–Teller (BET) method

The BET surface area of powder samples was evaluated through nitrogen adsorption analysis conducted by a Tristar II 3020 system (Shimadzu Corp.).

2.3.7 Analysis of particle size distribution

The particle size distribution of powder samples was determined using a laser diffraction particle size distribution analyzer (Microtrac MT3000 II, Nikkiso, Japan).

2.4 Electrochemical measurements

2.4.1 Galvanostatic charge-discharge test

The electrochemical performance of the cells, including specific capacity, rate capability, and cycling stability, was evaluated using a charge-discharge system

(Hokuto Denko, HJ1001SD8). The operating temperature was controlled through an environmental test chamber (ESPEC SU221). Before testing, the assembled coin cells were kept at an open circuit voltage for at least 3 h. Galvanostatic charge-discharge tests at specified current densities were conducted to evaluate charge-discharge curves and cycling stability.

2.4.2 Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)

Cyclic voltammetry and EIS tests were performed using a VSP potentiostat (Bio-Logic) equipped with a thermostatic chamber (ESPEC SU-242). The CV curves of Li/Al and Na/Al half cells were collected over a voltage range of 2 to 6 V at a scan rate of 0.5 mV s⁻¹ at 25, 60, and 90 °C. The EIS data was recorded in a frequency range of 10⁵-10⁻¹ Hz with an AC amplitude of 10 mV at 25 °C.

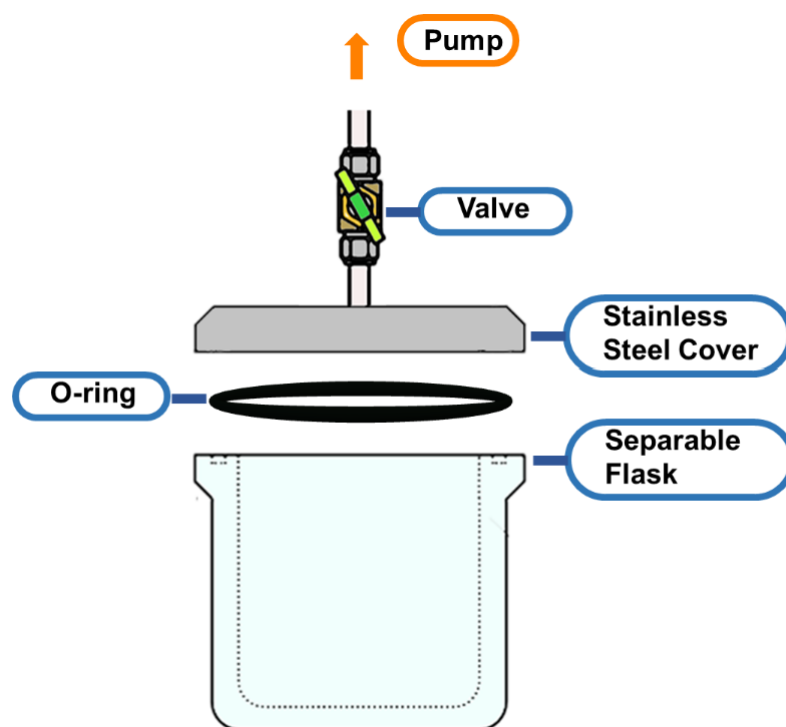


Figure 2-1. A schematic diagram of the drying vessel [1].

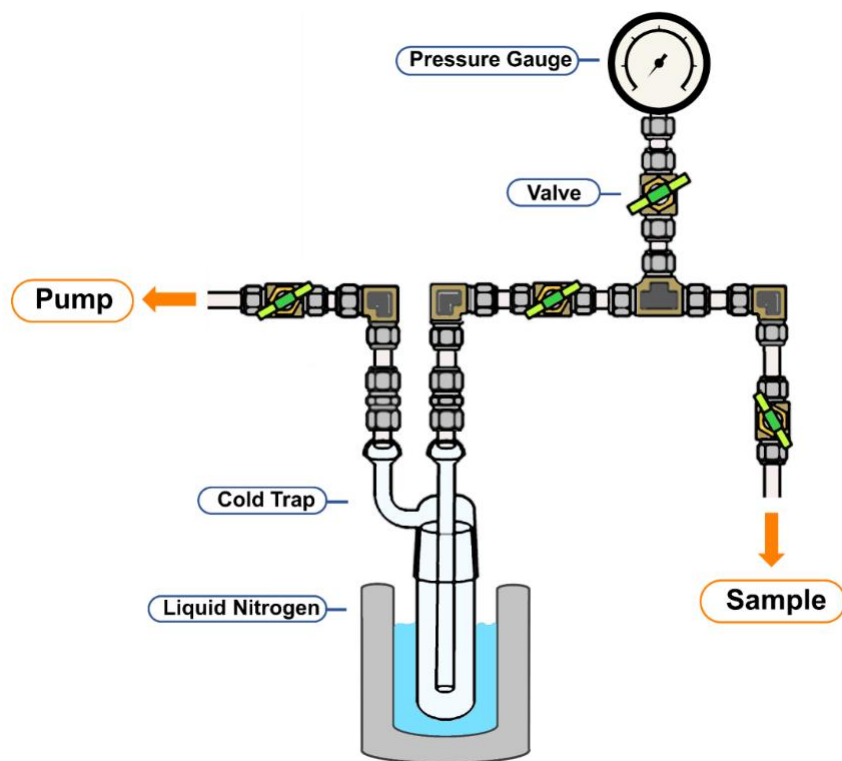


Figure 2-2. A schematic diagram of the vacuum line [1].

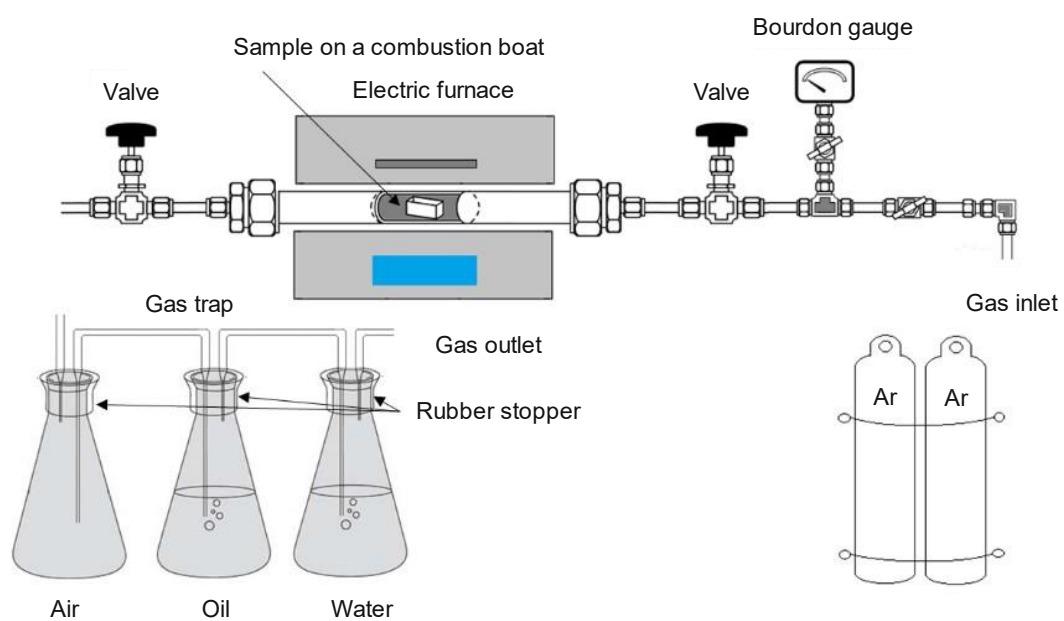


Figure 2-3. A schematic diagram of a tube furnace with Ar cylinders and gas trap [1].

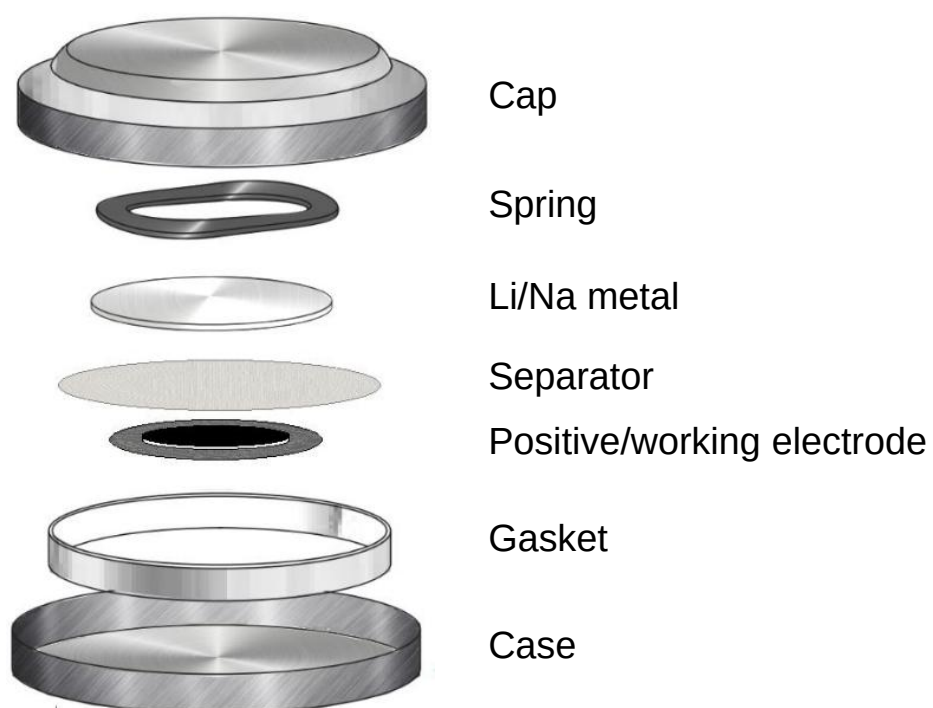


Figure 2-4. A schematic diagram of 2032-type coin cell [2].

References

- [1] J. Hwang, PhD Thesis, Graduate School of Energy Science, Kyoto University (2019).
- [2] S. Kaushik, PhD Thesis, Graduate School of Energy Science, Kyoto University (2020).

Chapter 3

Systematic Study of Aluminum Corrosion in Ionic Liquid Electrolytes for Sodium-Ion Batteries: Impact of Temperature and Concentration

3.1 Introduction

Lithium-ion batteries (LIBs), accredited as the contemporary secondary batteries of choice, have gained dominant utility in portable electronic devices, electric vehicles, and energy storage systems (ESS) [1]. Despite this widespread success, the increasing costs of lithium resources and the scarcity of critical elements such as Co and Ni present significant hurdles to the deployment of LIBs in large-scale ESS applications [2, 3]. These limitations have expedited the development of alternative battery technologies that utilize low-cost and earth-abundant materials. Among the secondary batteries fronted so far, sodium-ion batteries (SIBs) have emerged as promising candidates for grid-scale applications due to the environmental benignity and affordability of sodium resources [4, 5]. Besides the promise for improved feasibility, the progress of SIB development is further bolstered by the similarities in SIB and LIB intercalation chemistries which allow the appropriation of Na analogs of established LIB technologies [6].

The success of SIBs as next-generation secondary batteries is highly contingent on the adoption of cheap, environmentally friendly, and compatible battery components [7-9]. By this token, the lack of reactivity between Na metal and Al metal enables the utilization of Al foil as current collectors for both the negative and positive SIB electrodes, which presents significant cost benefits for these energy storage devices [10-12]. Besides economic viability, Al foil shows high electronic conductivity and mechanical durability [13, 14]. It is worth noting that even though the native Al_2O_3 passivation layer is formed on Al foil, Al current collectors are prone to attack and corrosion by sulfonylamide-based electrolytes during cycling at high potentials, leading to increased electrical resistance, electrolyte depletion, and capacity loss as well as poor cycling performance [15-17]. As such, comprehending Al corrosion behavior and exploring possible suppression measures is considered an essential requirement for next-generation SIBs.

Contemporary SIBs extensively utilize electrolytes containing organic carbonate solvents in combination with NaPF_6 or NaClO_4 salts due to their low viscosities and high ionic conductivities [18, 19]. Although Al current correctors are smoothly passivated in NaPF_6 -based electrolytes, NaPF_6 is highly hygroscopic, which makes it prone to hydrolysis [20-22]. On the other hand, the explosive nature of NaClO_4 heavily hinders its application in electrolytes for safety reasons. In this light, sodium salts based on sulfonylamide anions, such as $\text{Na}[\text{FSA}]$ ($[\text{FSA}]^-$ = bis(fluorosulfonyl)amide) and $\text{Na}[\text{TFSA}]$ ($[\text{TFSA}]^-$ = bis(trifluoromethylsulfonyl)amide) are considered attractive

options on the merits of their high stabilities, low toxicities, and safety [23, 24]. Compared to NaPF_6 and NaClO_4 , sulfonamide salts facilitate the formation of solid electrolyte interphase (SEI) with more inorganic species on the negative electrodes, enhancing the transport of Na ions and providing a more stable SEI layer [25, 26]. However, carbonate-based electrolytes employing Na[FSA] or Na[TFSA] salts tend to be corrosive towards the Al current collector at potentials above 4 V, thus deteriorating battery performance [27-31].

Taking practical viability into account, organic electrolytes are considered unsuitable for high-temperature batteries because of their flammability and volatility [32-34]. In this context, ionic liquids (ILs) have attracted interest as alternative electrolytes on the grounds of their high thermal and electrochemical stability, negligible vapor pressure, low flammability, wide liquidus temperature range, and broad electrochemical window [35-37]. In fact, studies have shown that replacing organic electrolytes with ILs can be an effective strategy for accelerating the passivation of the Al surface [38-47]. Otaegui et al. compared the stability of the Al current collector in the propylene carbonate solution of Na[FSA] and ILs and revealed that the latter prevents Al corrosion at 55 °C up to 5 V (the former is 3.5 V) [48]. Nevertheless, a recent study by our team revealed the occurrence of Al corrosion and severe capacity loss at elevated temperatures even after the adoption of [FSA]-based IL electrolytes in SIBs [49]. In any case, the current understanding of the Al corrosion behavior in IL electrolytes containing Na[FSA] or Na[TFSA] remains relatively limited, providing the

impetus for our inquest into the effects of these electrolytes on the Al current collector: specifically the influence of temperature and Na salt concentration. In particular, the effect of temperature on Al corrosion is an important point of interest, considering the possibilities of accidental heating [50, 51] or even the prospects of intermediate-temperature batteries exploiting the significant performance improvements embodied by IL electrolytes after temperature elevation [36, 52, 53].

In this chapter, the effects of operating temperature and Na salt concentration on the corrosion behavior of the Al current collector are examined using [FSA]- and [TFSA]-based IL electrolytes formulated with two different ammonium cations: $[\text{C}_2\text{C}_1\text{im}]^+$ = 1-ethyl-3-methylimidazolium) and $[\text{C}_3\text{C}_1\text{pyrr}]^+$ = *N*-methyl-*N*-propylpyrrolidinium). These two cationic species are typical for the use in Li and Na ion batteries, according to previous works [36]. Herein, aluminum corrosion behavior is analyzed through a series of analyses based on cyclic voltammetry (CV), field-emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, X-ray fluorescence spectroscopy (XRF), and X-ray photoelectron spectroscopy (XPS).

3.2 Experimental

The Na salts, Na[FSA] and Na[TFSA], and organic salts, $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$, $[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$, $[\text{C}_2\text{C}_1\text{im}][\text{TFSA}]$, and $[\text{C}_3\text{C}_1\text{pyrr}][\text{TFSA}]$, were dried under vacuum at 80 °C for 24 h before use. A series of IL electrolytes with different Na^+ concentrations,

as summarized in **Table 3-1**, were prepared by mixing the Na and organic salts in the target molar ratios in an argon-filled glove box (H_2O and $\text{O}_2 < 1$ ppm). The [TFSA] salt, $\text{Al}[\text{TFSA}]_3$, was synthesized using Al metal and bis(trifluoromethylsulfonyl)imide acid following procedures prescribed in previous reports [54-56]. EC/DMC = 1:1 v/v was used without further purification. The organic electrolyte of 1 mol dm^{-3} $\text{Na}[\text{TFSA}]$ -EC/DMC and 1 mol dm^{-3} $\text{Na}[\text{FSA}]$ -EC/DMC were prepared by dissolving $\text{Na}[\text{FSA}]$ or $\text{Na}[\text{TFSA}]$ into EC/DMC.

Coin cells used for CV measurements were assembled in the argon-filled glove box. Aluminum foil and metallic Na were used as the working and the counter electrodes, respectively. A glass fiber separator was used after immersion in the as-prepared electrolyte. Cyclic voltammetry measurements were performed using a VSP potentiostat equipped with a thermostatic chamber (SU-242, ESPEC) at 25, 60, and 90 °C, using the coin cells between 2 and 6 V (vs. Na^+/Na) at a scan rate of 0.5 mV s^{-1} (the first cycle started from the rest potential).

After the CV tests, coin cells were disassembled, and the Al electrodes were rinsed with ethanol. The surface of Al electrodes (after ten cycles) was subjected to FE-SEM and EDX analysis. The elemental composition of the surface of Al electrodes was analyzed by XPS. Depth profiles were obtained from the XPS data by etching Al electrodes using an Ar beam with an accelerating voltage of 400 V. Raman spectra of the IL electrolytes were recorded using a laser with a wavelength of 785 nm. For solubility tests of $\text{Al}[\text{TFSA}]_3$ in different electrolytes, the sample was added to 1 mol

dm^{-3} $\text{Na}[\text{TFSA}]\text{-EC/DMC}$, $\text{Na}_{0.1}[\text{C}_2\text{C}_1\text{im}]_{0.9}[\text{TFSA}]$, $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{TFSA}]$, and $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{TFSA}]$ electrolytes. After these samples were stirred at 600 rpm at room temperature for one day, the content of Al species was determined by XRF spectroscopy under a He atmosphere.

3.3 Results and discussion

In this study, the corrosion behavior of the Al current collector was analyzed by CV measurements on Al electrodes in different sulfonylamide-based IL electrolytes at varied temperatures. **Figure 3-1** shows the CV curves of Al electrodes in a representative electrolyte: $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ IL measured at 25, 60, and 90 °C. Here, the anodic current is seen to gradually increase during the anodic scan and continues to rise even during the cathodic scan, achieving prominent peaks in the 4.4 to 6 V range. This anodic current is ascribed to electrolyte decomposition and Al corrosion during the electrochemical process [13, 57]. Markedly, the anodic current during the cathodic scan is larger than during the anodic scan, indicative of the exacerbated corrosion due to the increased electrode surface area after the removal of the native Al_2O_3 passivation film on the pristine Al foil and the dissolution of Al^{3+} species [58, 59]. The peak current density, approximately 0.02 mA cm^{-2} at 25 °C during the first cycle (**Figure 3-1a**), was observed to increase with temperature elevation and reached roughly six times higher at 90 °C (**Figure 3-1b, c**). The high current density evinces intensified Al electrode corrosion and severe electrolyte decomposition at elevated

temperatures [16]. By carefully comparing the positive and negative scan curves, one can notice the inconstant behavior; for example, the first and second positive scan curves roughly overlap at 25 °C, but the first and second negative scans do not at 60 °C. This also depends on the kind of IL as discussed below. Even so, the anodic current was generally observed to decrease with continued cycling, signaling the formation of a passivation layer. However, more CV scans are needed to passivate Al at elevated temperatures in contrast to 25 °C. Furthermore, it should be noted that if the passivation layer formed during the electrochemical measurement is not robust enough, the exposed part of the Al electrode will undergo further corrosion [17]. The stability of the passivation layer highly depends on the electrolyte composition and operation conditions, which will be also discussed below by combining with the CV results and XPS data.

For insight into their impact on Al corrosion, two sulfonylamide anion species ($[\text{FSA}]^-$ and $[\text{TFSA}]^-$) were employed in combination with two cation species ($[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{C}_3\text{C}_1\text{pyrr}]^+$) to prepare different IL electrolyte formulations with varied Na salt concentrations (see **Table 3-1** for the ILs used in this study and **Figures 3-2 – 3-8** for CV curves in different concentrations and other IL electrolytes). For the $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ electrolytes, the anodic current was noted to decrease with increasing Na^+ fraction, providing negligible anodic current for the $\text{Na}_{0.5}[\text{C}_2\text{C}_1\text{im}]_{0.5}[\text{FSA}]$ electrolyte at 25 °C (**Figures 3-3** and **3-4**). The CV curves obtained from the $\text{Na}_x[\text{C}_3\text{C}_1\text{pyrr}]_{1-x}[\text{FSA}]$ electrolytes exhibited similar effects of

temperature and Na^+ concentration on the anodic current, although their current densities were generally lower than the $\text{Na}_x[\text{C}_2\text{C}_{1\text{im}}]_{1-x}[\text{FSA}]$ electrolytes (**Figures 3-6 – 3-8**). In addition, the CV curves obtained from the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte reveal that temperature elevation engendered significant increases in the anodic current, as shown in **Figure 3-2**. The highest anodic current of $\text{Na}_{0.2}[\text{C}_3\text{C}_{1\text{pyrr}}]_{0.8}[\text{TFSA}]$ electrolyte was observed at 60 °C. Notably, the anodic current for $\text{Na}_{0.2}[\text{C}_3\text{C}_{1\text{pyrr}}]_{0.8}[\text{TFSA}]$ electrolyte at 90 °C was observed to be an order of magnitude lower than that of the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte at the same temperature (**Figure 3-5**). The effect of cations on different CV curves will be discussed below.

Figures 3-9 and 3-10 summarize the total charge calculated by integrating the total anodic peak area of the cyclic voltammogram of each cycle (**Figure 3-9** for the $[\text{C}_2\text{C}_{1\text{im}}]$ -based ILs and **Figure 3-10** for the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based ILs). The total charge exhibits a clear correlation to the Na^+ concentration in the $\text{Na}_x[\text{C}_2\text{C}_{1\text{im}}]_{1-x}[\text{FSA}]$ IL electrolyte and the operating temperatures (**Figure 3-9**). When the temperature is kept constant, increasing the Na^+ fraction of the electrolyte results in a continuous decrease in the total charge. On the other hand, temperature elevation is noted to engender an increase in the total charge during the initial few cycles. Notably, the total charge of the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte is less than the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{FSA}]$ electrolyte at 25 °C. However, these trends are inversed at elevated temperatures; the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte exhibits larger total charge values, which do not significantly decrease even with repeated CV scans. These results suggest that the

passivation process in the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte fails at 60 and 90 °C, resulting in severe Al corrosion.

The total charge data obtained from the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based IL electrolytes betoken similar trends as illustrated in **Figure 3-10**. However, the total charge values derived from the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based electrolytes are found to be significantly lower than those from the $[\text{C}_2\text{C}_{1\text{im}}]$ -based electrolytes. Further, temperature elevation of the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based electrolytes is seen to have less effect on the resultant total charge than in the case of the $[\text{C}_2\text{C}_{1\text{im}}]$ -based electrolytes. Here, the total charge values for the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based electrolytes at 60 °C are higher than at 90 °C, which may be attributed to the dissolution and reconstruction of the unstable passivation layer formed at 60 °C. These observations indicate that the Al corrosion behavior in the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based electrolytes is intrinsically different from the one in the $[\text{C}_2\text{C}_{1\text{im}}]$ -based electrolytes. The passivation layer based on the $[\text{C}_3\text{C}_{1\text{pyrr}}]$ -based electrolytes might contain beneficial components to kinetically slow down the side reaction and facilitate Al passivation compared to the $[\text{C}_2\text{C}_{1\text{im}}]$ -based electrolytes. Another possible reason for such differences is the higher anodic stability of the $[\text{C}_3\text{C}_{1\text{pyrr}}]^+$ compared to that of the $[\text{C}_2\text{C}_{1\text{im}}]^+$ cations [60]. Besides, differences in Al corrosion behavior could also be rationalized by the differences in the ratios of the free $[\text{FSA}]^-$ (non-coordinating to Na^+ , abbreviated as FR) to coordinating $[\text{FSA}]^-$ (coordinating to Na^+ , abbreviated as CDN) in the ILs. The coordination states of $[\text{FSA}]^-$ in ILs can easily be determined through Raman spectrometry, where the S-N-S bending mode shifts, depending on the

coordination state to Na^+ ($\sim 730\text{ cm}^{-1}$ for FR $[\text{FSA}]^-$ and above 740 cm^{-1} for CDN $[\text{FSA}]^-$) [61]. When the two states of $[\text{FSA}]^-$, CDN and FR, are assumed, the ratio of CDN/FR is higher for the $[\text{C}_3\text{C}_1\text{pyrr}]$ -based electrolyte (50/50) than for the $[\text{C}_2\text{C}_1\text{im}]$ -based electrolyte (36/64) (**Figure 3-11**). Consequently, $[\text{FSA}]^-$ is more electron deficient and more resistive to oxidation in the $[\text{C}_3\text{C}_1\text{pyrr}]$ -based electrolyte (see the discussion of the Raman spectroscopy below for details).

For the aim of understanding the corrosion process of Al foil, further discussion will be made for the $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ electrolytes that exhibit the representative characteristics in the following. Additional results from the other ILs are included in Supporting Information.

The surface morphology and elemental composition of the Al electrode surface after CV measurements were subsequently evaluated using FE-SEM and EDX techniques to visually confirm Al corrosion behavior. **Figure 3-12** shows the FE-SEM and EDX mapping images of Al electrodes cycled in the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte under different operating temperatures. **Figure 3-13** shows the corresponding electrodes cycled in varied Na^+ concentrations using a series of $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ electrolytes, respectively (see **Figure 3-14 – 3-20** for FE-SEM and EDX mapping images related to other conditions and electrolytes). As illustrated, the surfaces of the Al electrodes cycled in $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ reveal typical pitting corrosion in the range of temperatures investigated. At $25\text{ }^\circ\text{C}$, corrosion pits with diameters of $< 50\text{ }\mu\text{m}$ are observed on the entire electrode surfaces (**Figure 3-12**).

Additionally, the corrosion pits are noted to become larger with increasing temperature, eventually becoming interconnected at 90 °C due to severe corrosion. The EDX mapping images show the presence of Al, F, S, O, N, and Na elements on the electrode surfaces. The images also show an even distribution of F, S, and O elements in the corrosion pits, suggesting that $[\text{FSA}]^-$ is deeply involved in the corrosion process. On an interesting note, Al was hardly detected in the corrosion pits. These results evince that $[\text{FSA}]^-$ reacts with the native oxide on the Al current collector, and the Al^{3+} reacts with the amide anions to form complexes that are dissolved into the electrolyte as has been previously proposed in studies on organic solvent electrolytes [18, 27].

The correlation between the Na^+ concentration and Al corrosion behavior at 25 °C is demonstrated in **Figure 3-13**. Here, the FE-SEM images illustrate numerous pits on the surface of the Al electrode cycled in the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte. In contrast, only a few pits are observed on the Al electrode cycled in the $\text{Na}_{0.3}[\text{C}_2\text{C}_1\text{im}]_{0.7}[\text{FSA}]$ electrolyte. The diameters of the corrosion pits are found to decrease with increasing Na^+ fractions: an affirmation that increasing the Na^+ concentration can suppress corrosion of the Al electrode. Furthermore, the pitting corrosion is not seen on the electrodes obtained from the $\text{Na}_{0.5}[\text{C}_2\text{C}_1\text{im}]_{0.5}[\text{FSA}]$ electrolyte at 25 °C, in congruence with the negligible anodic current visualized in the CV curves (**Figure 3-4a**). These observations are consistent with the CV results wherein the anodic current significantly decreases when the Na salt fraction is increased (**Figures 3-3 and 3-4**). Likewise, the $[\text{C}_3\text{C}_1\text{pyrr}]$ -based electrolytes exhibited similar Al

corrosion behavior when subjected to analogous operating temperatures and Na salt concentrations (**Figures 3-17 – 3-20**).

It is worth noting that hemispherical deposits appeared on the surface of the Al electrode when the Na salt concentration was increased. These deposits are presumed to be a new passivation layer formed by the decomposition of the IL electrolytes (**Figures 3-13b and c**). These hemispherical deposits were also found on the Al electrode after CV measurements were performed in the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{TFSA}]$ and $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{TFSA}]$ IL electrolytes (**Figures 3-14 and 3-17**, respectively). The results suggest that the degree of Al corrosion is highly contingent on the properties of the passivation layer formed during the electrochemical process. Notably, the [TFSA]-based ILs manifested slightly better passivation capabilities at 25 °C than [FSA]-based ILs. However, these capabilities were seen to drastically diminish at elevated temperatures in the case of the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{TFSA}]$ IL electrolyte.

In previous studies by Kühnel et al. and Garcia et al., the Al complex formed during the corrosion process was found to have considerably lower solubility in IL electrolytes than the ones in organic carbonate-based electrolytes, and thus ILs facilitate the formation of a more effective passivation layer that resists Al corrosion [40, 62]. Since Al corrosion is not so severe in the IL electrolytes at high Na^+ fractions in this work, it is reasonable to tentatively postulate that the solubility of Al complexes into electrolytes is a major reason for the different corrosion behaviors observed. As such, $\text{Al}[\text{TFSA}]_3$, whose synthesis route has been established in previous works, was

subjected to solubility measurements involving the various electrolytes in the present work (preparation of $\text{Al}[\text{FSA}]_n^{(3-n)+}$ complex is not well-established). According to XRF analysis (**Table 3-2**), the solubility of $\text{Al}[\text{TFSA}]_3$ into 1 mol dm^{-3} $\text{Na}[\text{TFSA}]\text{-EC/DMC}$ is noted to be approximately two times higher than in the ILs. Even so, the difference between the organic electrolyte and the IL is insignificant, considering their vastly different Al corrosion behaviors (**Figure 3-21**). Moreover, the differences in the Al concentrations of the ILs are subtle which demonstrates that the solubility of the Al complexes is not the main reason for the different Al corrosion behaviors.

The factors influencing the Al corrosion behavior can also be postulated to involve both the operating temperatures and Na salt concentrations. In this conjecture, the passivation layers formed on Al electrodes cycled at lower temperatures and high concentration conditions are considered more robust or better stabilized than those formed at higher temperatures and low Na^+ concentration conditions. As such, the passivation layer formed during cycling was subjected to stability tests through further CV analysis to verify this hypothesis. First, ten consecutive CV cycles were performed without intervals to sufficiently form a passivation layer. Subsequently, five CV cycles were performed with an interval (12-hour rest) after each cycle (**Figure 3-22**). This interval was set to determine the stability of the newly-formed passivation layer. Specifically, if the passivation layer dissolves during an interval, extra capacity is required to reform the passivation layer during the next cycle. **Figures 3-23a and 3-23b** summarize the total charge during the 10th, 12th, and 14th anodic scans of CV in

the $\text{Na}_x[\text{C}_2\text{C}_{1\text{im}}]_{1-x}[\text{FSA}]$ electrolytes ($x = 0.2$ and 0.5) at $25\text{ }^\circ\text{C}$ (**Figure 3-23a**) and $90\text{ }^\circ\text{C}$ (**Figure 3-23b**). When $x = 0.2$, the total charge at $90\text{ }^\circ\text{C}$ increases at the subsequent 14th cycle, whereas it remains relatively stable at $25\text{ }^\circ\text{C}$. Correspondingly, the current density decreases at the 12th cycle but increases at the 14th cycle (**Figure 3-22c**), suggesting that the passivation layer dissolves and Al corrosion and electrolyte decomposition occur again if intervals are taken after each cycle. In the case of $x = 0.5$, the total charge was lower than that of $x = 0.2$ during measurements performed at $25\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$. This observation suggests that less charge participates in the repetitive passivation process, and the passivation layer remains stable during the cycles with intervals.

The chemical composition of the passivation layer formed on the Al electrode was analyzed by XPS after the first cycle of the CV measurements under different temperature and concentration conditions. As shown in **Figure 3-23c**, the F 1s XPS spectra for Al electrodes were deconvoluted into three different contributions [44, 63, 64]. The peak at 686.6 eV is assigned to the F atom involved in an ionic bond such as Al–F. The presence of $-\text{SO}_x\text{F}$ is identified by the peaks at 688.0 and 689.4 eV . Comparing the passivation layers formed by each electrolyte at different temperatures shows the ratio of $-\text{SO}_x\text{F}$ to Al–F at $90\text{ }^\circ\text{C}$ is higher than that of $25\text{ }^\circ\text{C}$, evincing that the passivation layer formed at $90\text{ }^\circ\text{C}$ has more components derived from $[\text{FSA}]^-$ decomposition. XPS depth profiles (**Figure 3-23d**) were also obtained to illustrate the relative thickness of the passivation layer on the surface of the Al current collectors.

Here, the F 1s peak intensities of the electrodes cycled at 90 °C exhibit a more gradual decrease with increasing etching time compared to those measured for the electrodes cycled at 25 °C: an indicator that cycling at 90 °C forms a thicker passivation layer. This observation is in accord with the XPS results of Al 2p (**Figure 3-24**), where the peak intensity of Al metal on electrodes cycled at 90 °C increases more gently with increasing etching time than those cycled at 25 °C: evidence that the thicker passivation layer covers the Al substrate at 90 °C.

The difference in ion-ion interactions in the electrolytes with respect to Na salt concentration was studied by Raman spectroscopy to clarify the effects of the electrolyte structure on the Al corrosion behavior. **Figure 3-25** presents the Raman spectra of the FSA-based IL electrolytes at various Na[FSA] concentrations (see **Figure 3-26** for [TFSA]-based ILs). The peaks in the region between 700 and 800 cm^{-1} are assigned to the S-N-S bending mode, which can be deconvoluted to those of free $[\text{FSA}]^-$ and Na^+ -coordinating $[\text{FSA}]^-$ as mentioned in the discussion above (FR and CDN, respectively) [65]. The peak in this region exhibits a blue shift with increasing Na salt concentration regardless of the cationic species, suggesting an increase of the CDN $[\text{FSA}]^-$ and a decrease of the FR $[\text{FSA}]^-$. This phenomenon may affect the Al corrosion behavior in two distinct ways: the formation of passivation layers with different thicknesses and the reaction for the dissolution of the native Al_2O_3 passivation layer. The increase of CDN $[\text{FSA}]^-$ can lead to the formation of a thinner passivation layer because CDN $[\text{FSA}]^-$ is more electron deficient and oxidatively robust than FR $[\text{FSA}]^-$.

[66]. Consequently, the thinner passivation layer sufficiently prevents further reactions caused by the contact between the electrode surface and the electrolyte with oxidatively robust anions. On the other hand, FR [FSA]⁻ is more reactive to Al₂O₃ because it has more coordinating ability than CDN [FSA]⁻ [67-70].

Based on the results above, the possible mechanism of Al corrosion behavior is illustrated in **Figure 3-27**. Here two of the most severe and the mildest conditions of high Na⁺ concentration and low temperature (**Figure 3-27a**) and low Na⁺ concentration and high temperature (**Figure 3-27b**) are selected to visualize and simplified the mechanism. As shown in the schematic, free [FSA]⁻ are adsorbed on the native Al₂O₃ passivation film, which decays the film at high potentials along with O₂ generation and Al³⁺ dissolution in the form of Al[anion]_n⁽³⁻ⁿ⁾⁺. As Raman spectra clearly indicate a blue shift of peaks with increasing Na salt concentration, which explains the severe corrosion degree of the native Al₂O₃ passivation film by free [FSA]⁻ in the initial cycle at low Na⁺ concentration and high temperature conditions. This phenomenon is explained by the fact that the electrolytes with low Na⁺ concentrations have more free [FSA]⁻ that vigorously abrades the native Al₂O₃ passivation layer and accelerates the corrosion process. Markedly, the passivation layer is seen to dissolve progressively at elevated temperatures, especially with electrolytes of lower Na salt concentrations. Accordingly, a thicker passivation layer formed by the decomposition of the electrolyte is required to comprehensively cover the Al electrode surface. Otherwise, Al corrosion occurred again after the breakdown of the passivation layer. Whereas under high Na⁺

concentration and low temperature conditions, the ratio of free $[\text{FSA}]^-$ to Na^+ -coordinating $[\text{FSA}]^-$ is low, forming a new passivation layer with very low solubility in the electrolytes. As discussed in **Figure 3-23a**, this passivation layer keeps robust to protect the Al electrode. Veritably, increasing the Na salt concentration of the electrolytes suppresses the Al corrosion process to a certain extent but does not alleviate severe Al corrosion when temperatures are elevated.

3.4 Conclusions

In summary, this chapter explored the effects of temperature and salt concentration variations on the corrosion behavior of the Al current collector in IL electrolytes. The CV results showed that the anodic current increases with increasing temperature and decreasing Na^+ concentrations. The SEM images after CV measurements revealed that Al corrosion was exacerbated in electrolytes with low Na^+ concentration and suppressed for electrolytes with high Na^+ concentration at room temperature. Even so, the electrolytes with high Na^+ concentration were still ineffective in suppressing Al corrosion at elevated temperatures. The EDX mapping further revealed the involvement of $[\text{FSA}]^-$ in the Al corrosion, and XRF measurements confirmed that the solubility of Al complexes in the electrolytes investigated is not the primary cause of the different corrosion degrees observed. The results from the present analyses suggest that the differences in Al corrosion behavior are caused by the variegated stabilities of the newly-formed passivation layers on the surfaces. The Al corrosion process in

electrolytes with high Na^+ concentrations is possibly alleviated by the more robust passivation layer formed with Na^+ -coordinating $[\text{FSA}]^-$. However, this robust passivation layer becomes unstable when the temperature is elevated, consuming extra capacity to form a new passivation layer at every cycle. The results presented herein promise to augment the present understanding of the corrosion behavior of Al current collectors in a range of ILs electrolytes. Accordingly, future inquests into the surface modification of Al current collectors can be expected to be a propitious strategy for enhancing the performance of SIBs using IL electrolytes.

Table 3-1. Summary of selected ionic liquid electrolytes used in this study.

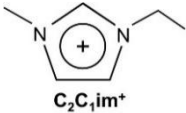
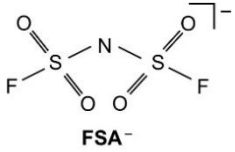
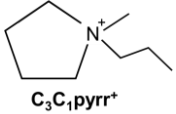
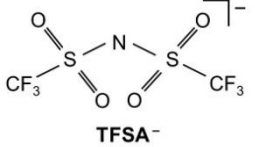
Sodium salts	Organic salts	Molar ratio (Na salt : organic salt)	Abbreviations
Na[FSA]	[C ₂ C ₁ im][FSA]	2:8	Na _{0.2} [C ₂ C ₁ im] _{0.8} [FSA]
	 C ₂ C ₁ im ⁺	3:7	Na _{0.3} [C ₂ C ₁ im] _{0.7} [FSA]
	 FSA ⁻	5:5	Na _{0.5} [C ₂ C ₁ im] _{0.5} [FSA]
Na[TFSA]	[C ₃ C ₁ pyrr][FSA]	2:8	Na _{0.2} [C ₃ C ₁ pyrr] _{0.8} [FSA]
	 C ₃ C ₁ pyrr ⁺	3:7	Na _{0.3} [C ₃ C ₁ pyrr] _{0.7} [FSA]
		5:5	Na _{0.5} [C ₃ C ₁ pyrr] _{0.5} [FSA]
	[C ₂ C ₁ im][TFSA]	2:8	Na _{0.2} [C ₂ C ₁ im] _{0.8} [TFSA]
	[C ₃ C ₁ pyrr][TFSA]	2:8	Na _{0.2} [C ₃ C ₁ pyrr] _{0.8} [TFSA]
	[C ₃ C ₁ pyrr][TFSA]	1:9	Na _{0.1} [C ₃ C ₁ pyrr] _{0.9} [TFSA]
	 TFSA ⁻		

Table 3-2. Results of the XRF analysis on the electrolytes.

Electrolytes	Al (ppm)	S (ppm)
1 mol dm ⁻³ Na[TFSA]-EC/DMC (1:1 v/v)	4.1×10 ³	4.2×10 ⁴
Na _{0.1} [C ₃ C ₁ pyrr] _{0.9} [TFSA]	2.1×10 ³	1.3×10 ⁵
Na _{0.2} [C ₃ C ₁ pyrr] _{0.8} [TFSA]	2.1×10 ³	1.2×10 ⁵
Na _{0.2} [C ₂ C ₁ im] _{0.8} [TFSA]	2.2×10 ³	1.3×10 ⁵

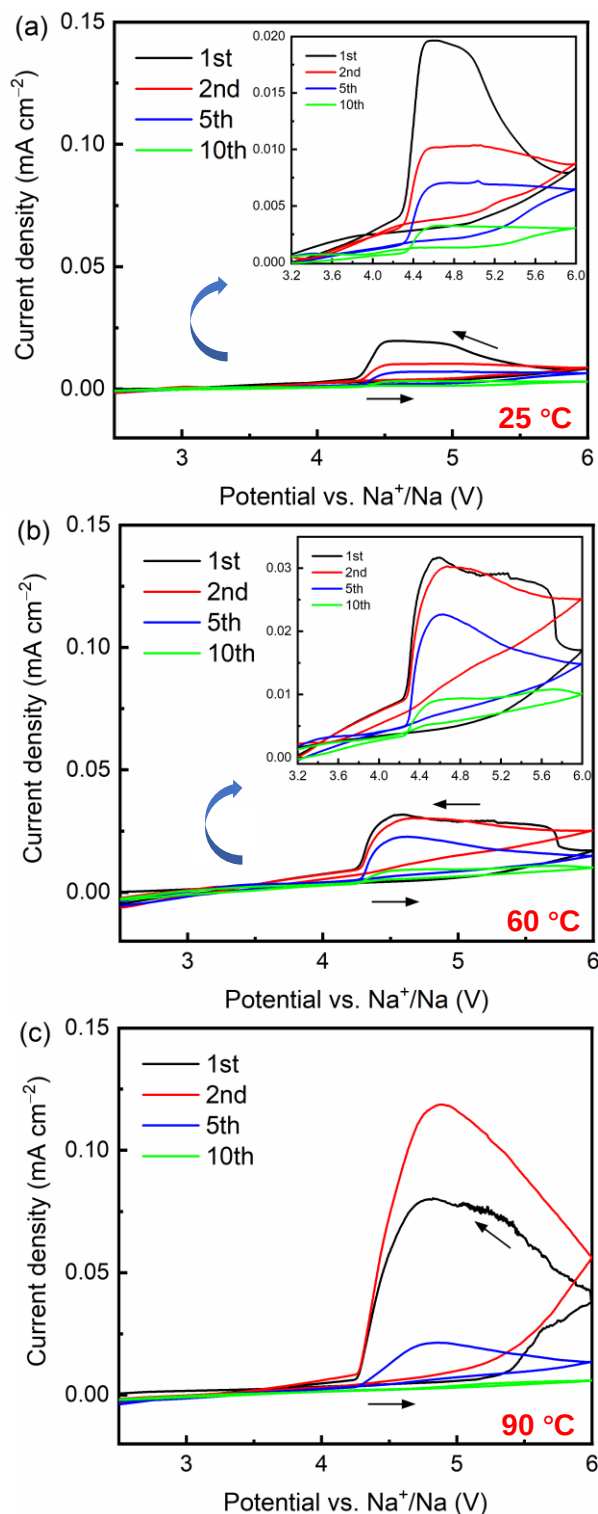


Figure 3-1. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ IL electrolyte at (a) 25, (b) 60, and (c) 90 °C from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The black arrows indicate the scan direction. The insets show the enlarged part of the cyclic voltammograms (see **Figures 3-2–3-8** for cyclic voltammograms in other concentrations and other IL electrolytes and see **Figure 3-9** for the summary of total charges during anodic scans of CV results for the Al electrodes in different electrolytes.)

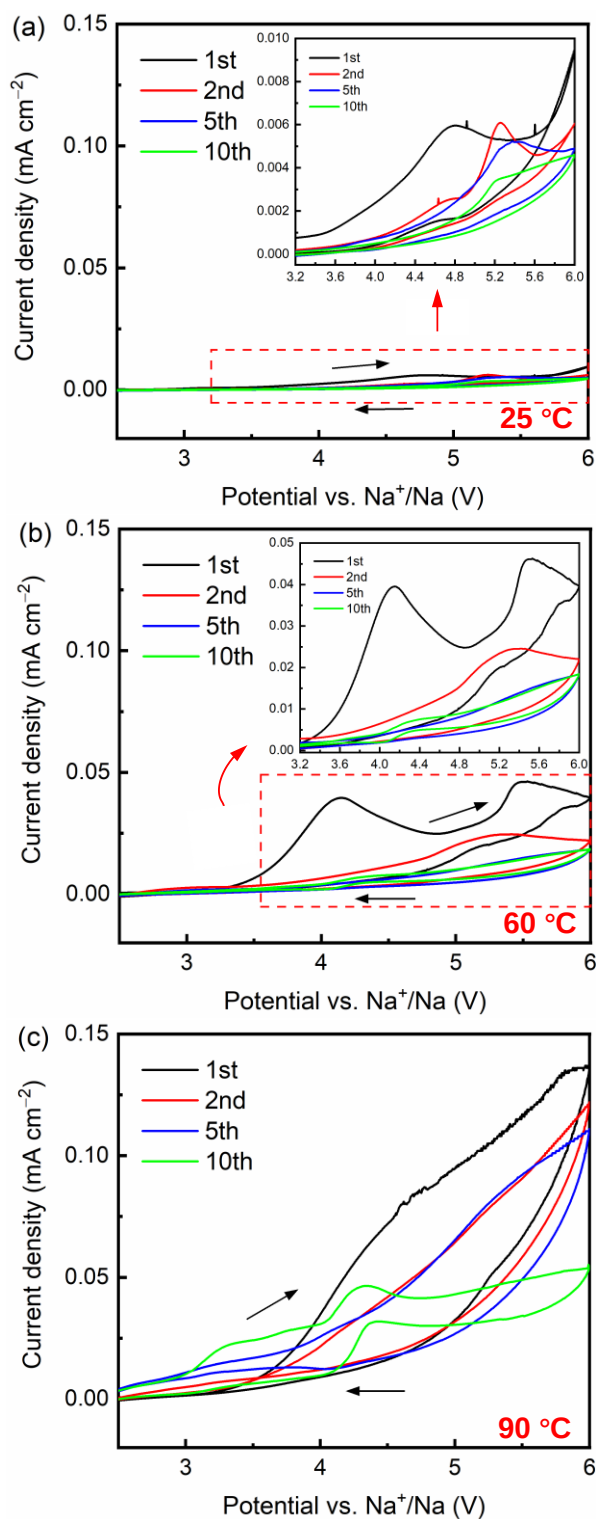


Figure 3-2. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{TFSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

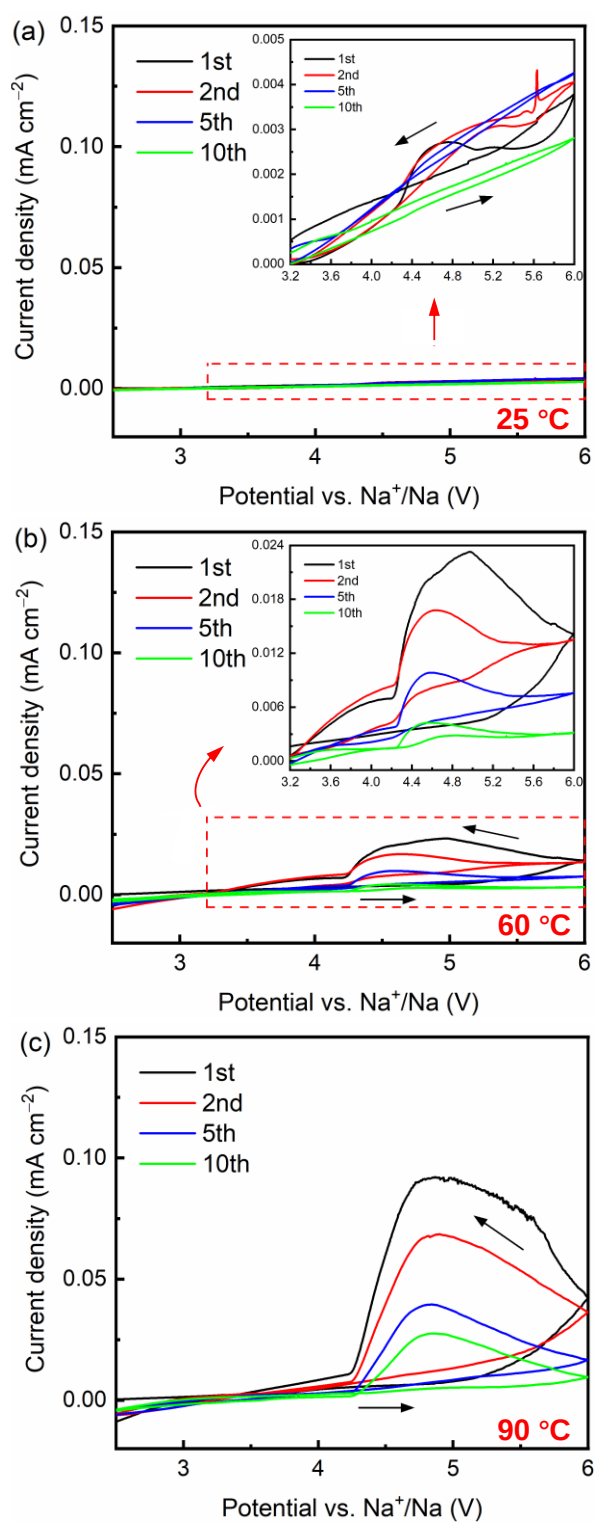


Figure 3-3. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.3}[\text{C}_2\text{C}_1\text{im}]_{0.7}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

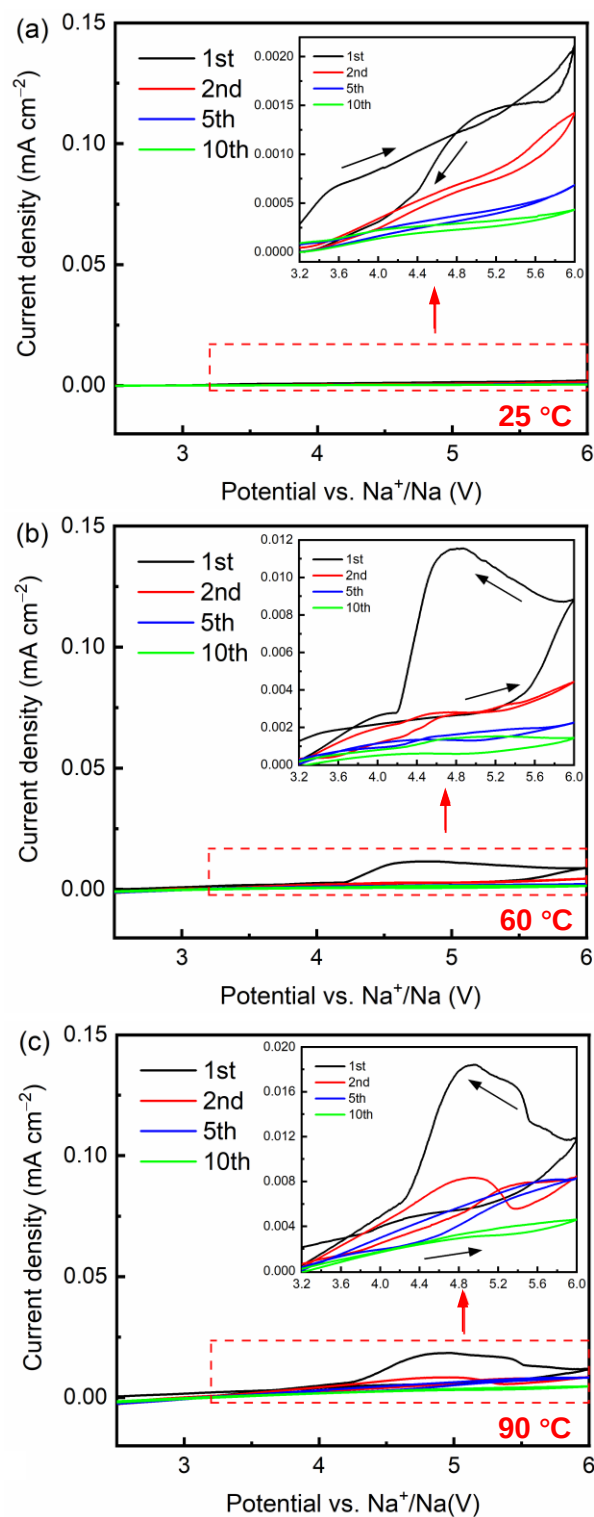


Figure 3-4. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.5}[\text{C}_2\text{C}_1\text{im}]_{0.5}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

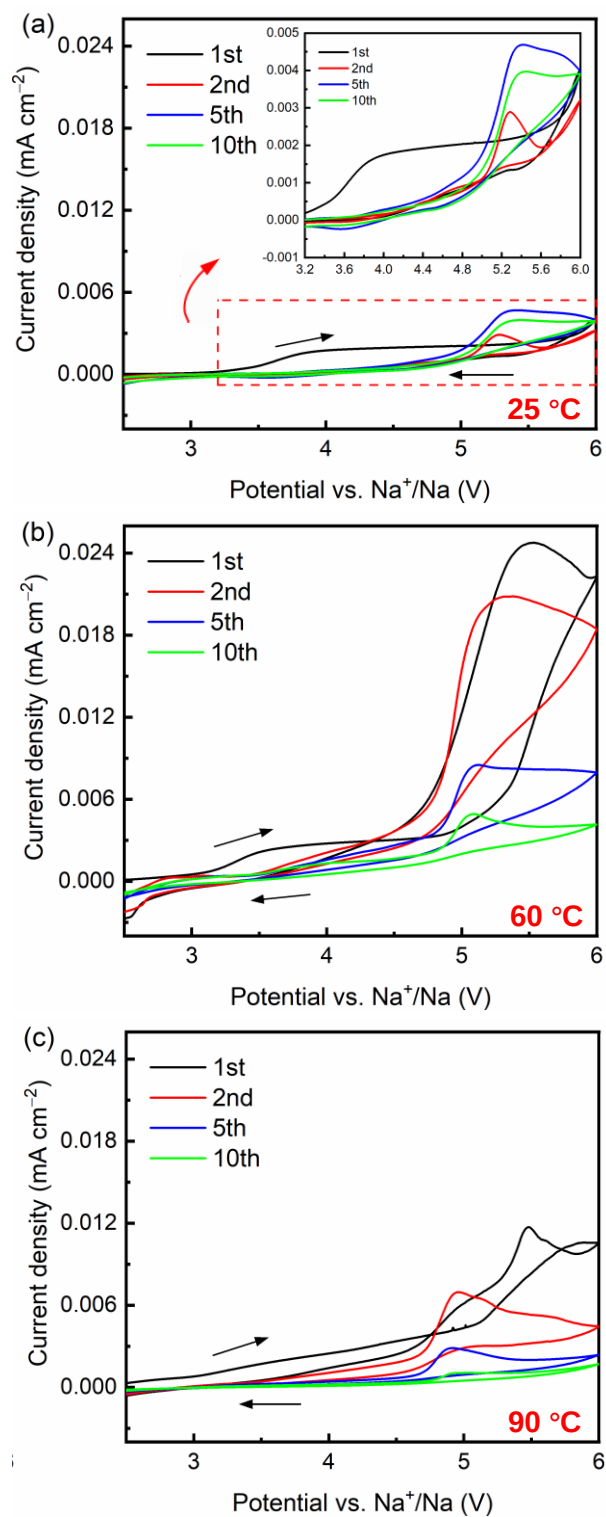


Figure 3-5. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{TFSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

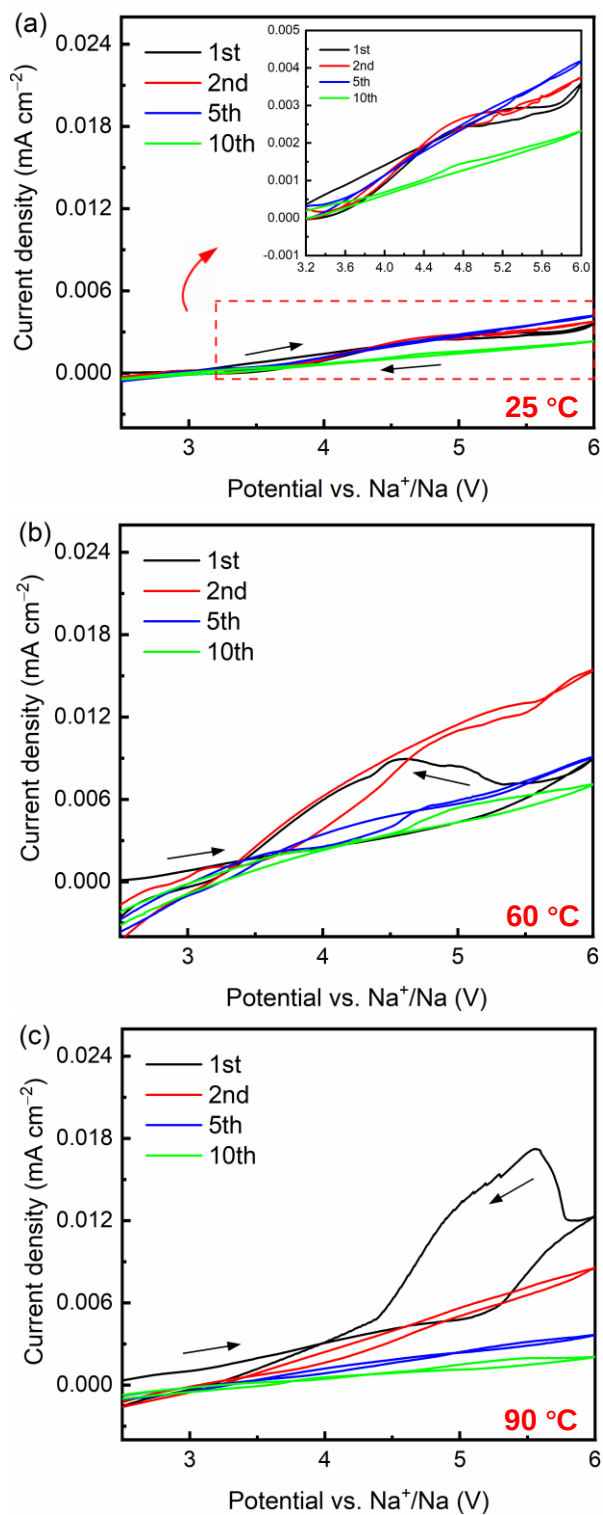


Figure 3-6. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

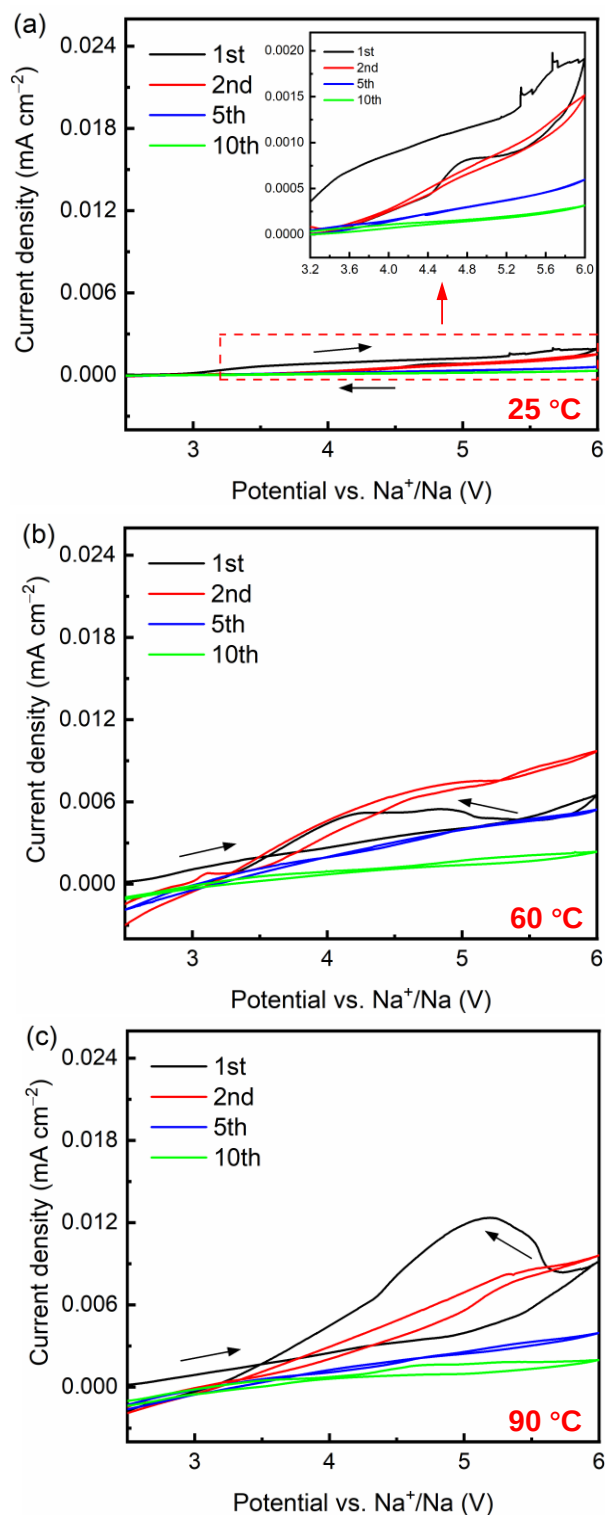


Figure 3-7. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.3}[\text{C}_3\text{C}_1\text{pyrr}]_{0.7}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

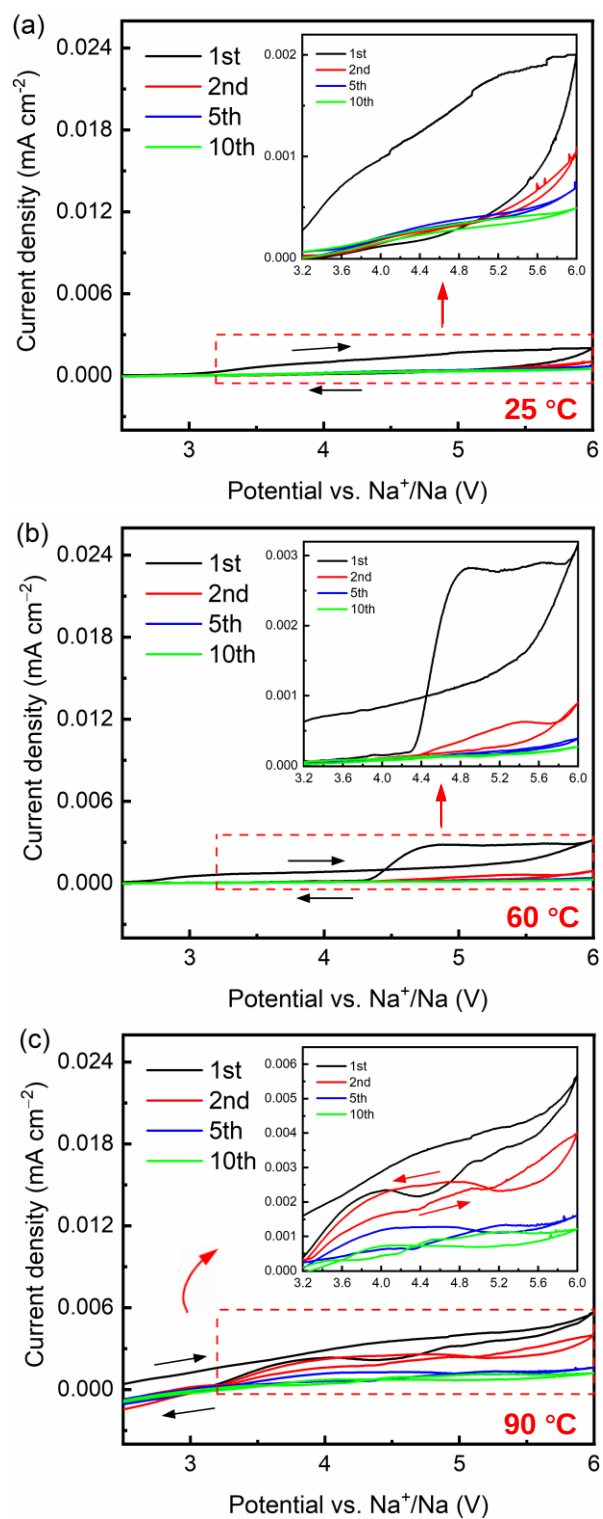


Figure 3-8. Cyclic voltammograms of an Al electrode in the $\text{Na}_{0.5}[\text{C}_3\text{C}_1\text{pyrr}]_{0.5}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s^{-1} . The region with red dashed line is enlarged as an inset.

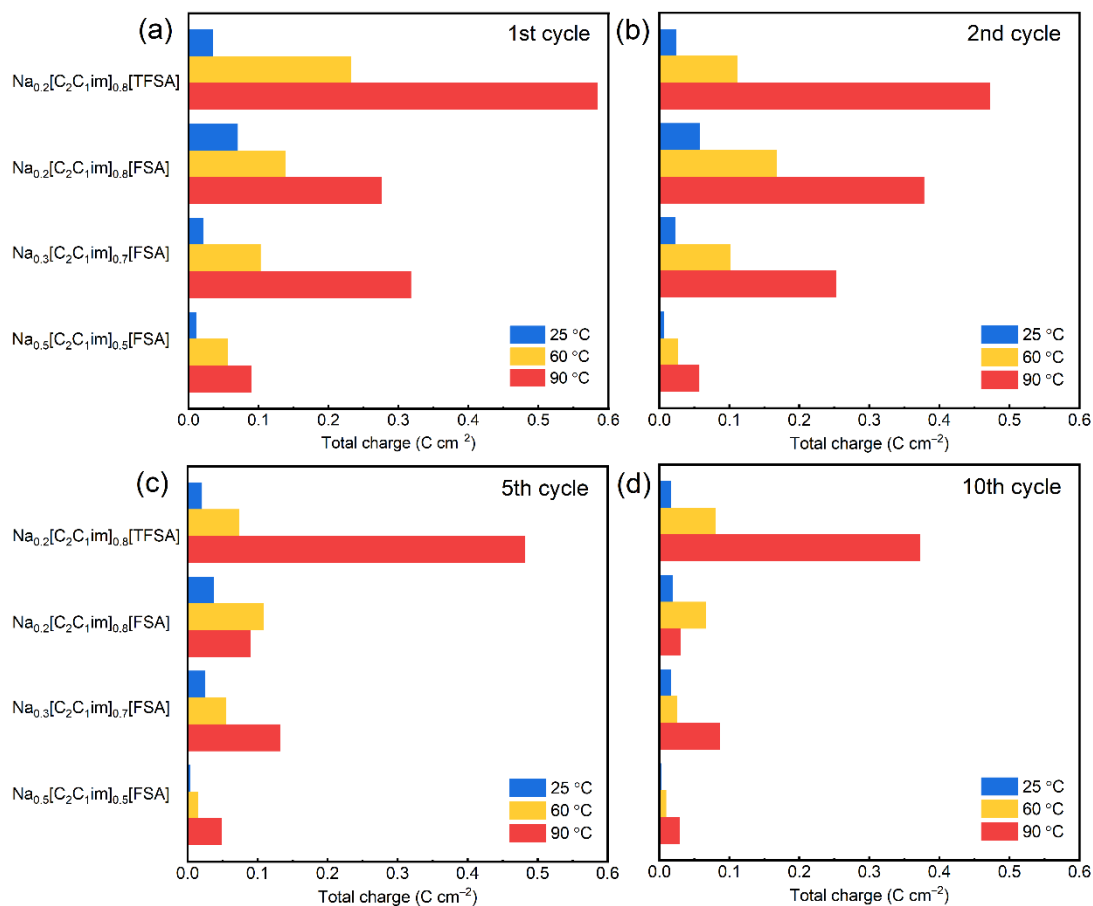


Figure 3-9. Summary of total charges during anodic scans in the CV measurements in the [C₂C₁im]-based IL electrolytes at the (a) 1st, (b) 2nd, (c) 5th, and (d) 10th cycles (see **Figures 3-1 – 3-4** for the corresponding cyclic voltammograms). Temperature: 25, 60, and 90 °C. The total charges were calculated by integrating the anodic current.

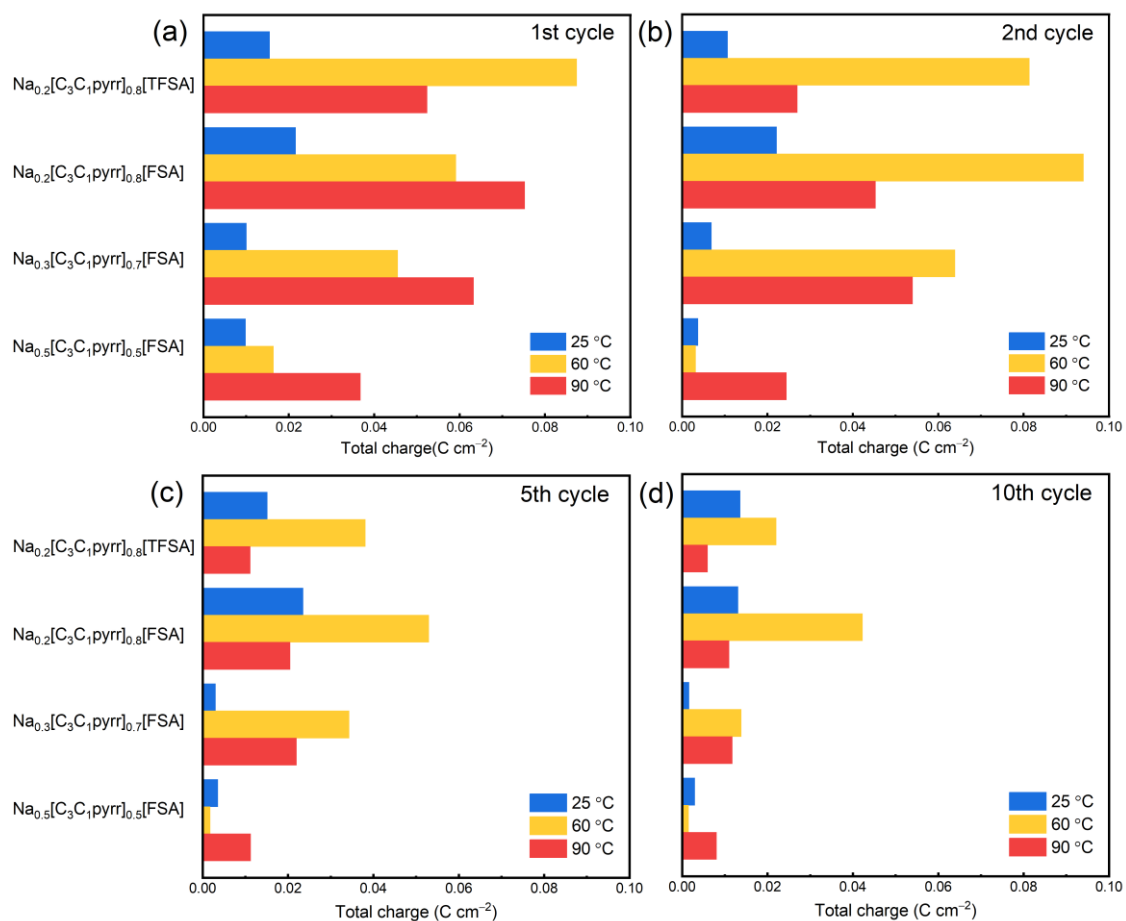


Figure 3-10. Summary of total charges during anodic scans in the CV measurements in the [C₃C₁pyrr]-based electrolytes at the (a) 1st, (b) 2nd, (c) 5th, and (d) 10th cycles (see **Figures 3-5 – 3-8** for the corresponding cyclic voltammograms). Temperature: 25, 60, and 90 °C. The total charges are calculated by integrating the anodic currents.

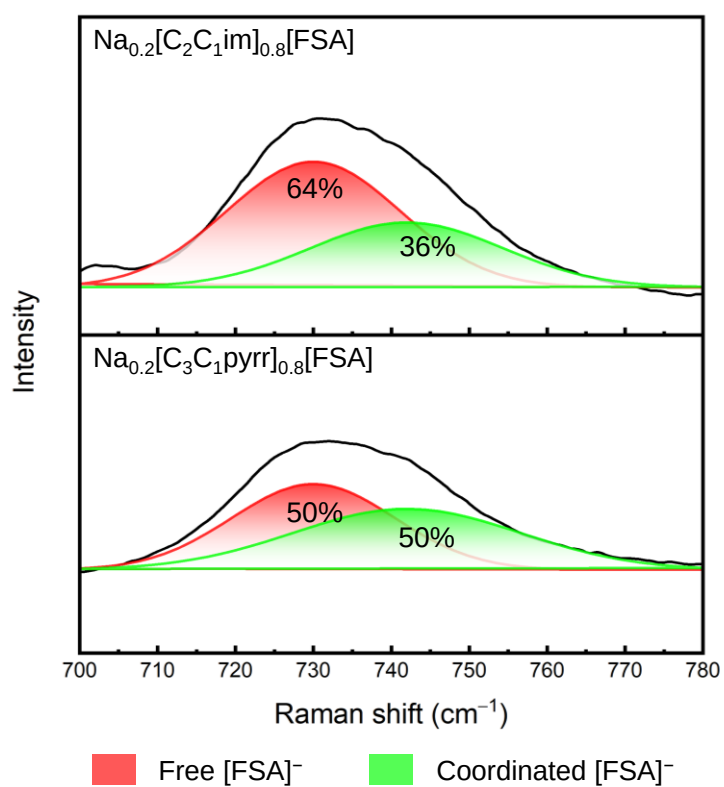


Figure 3-11. Raman spectra and peak fitting of the $\text{Na}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ and $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ IL electrolytes in the range of 700–780 cm^{-1} . The two peaks represent free (FR, red) and Na^+ -coordinated (CDN, green) $[\text{FSA}]^-$ anions.

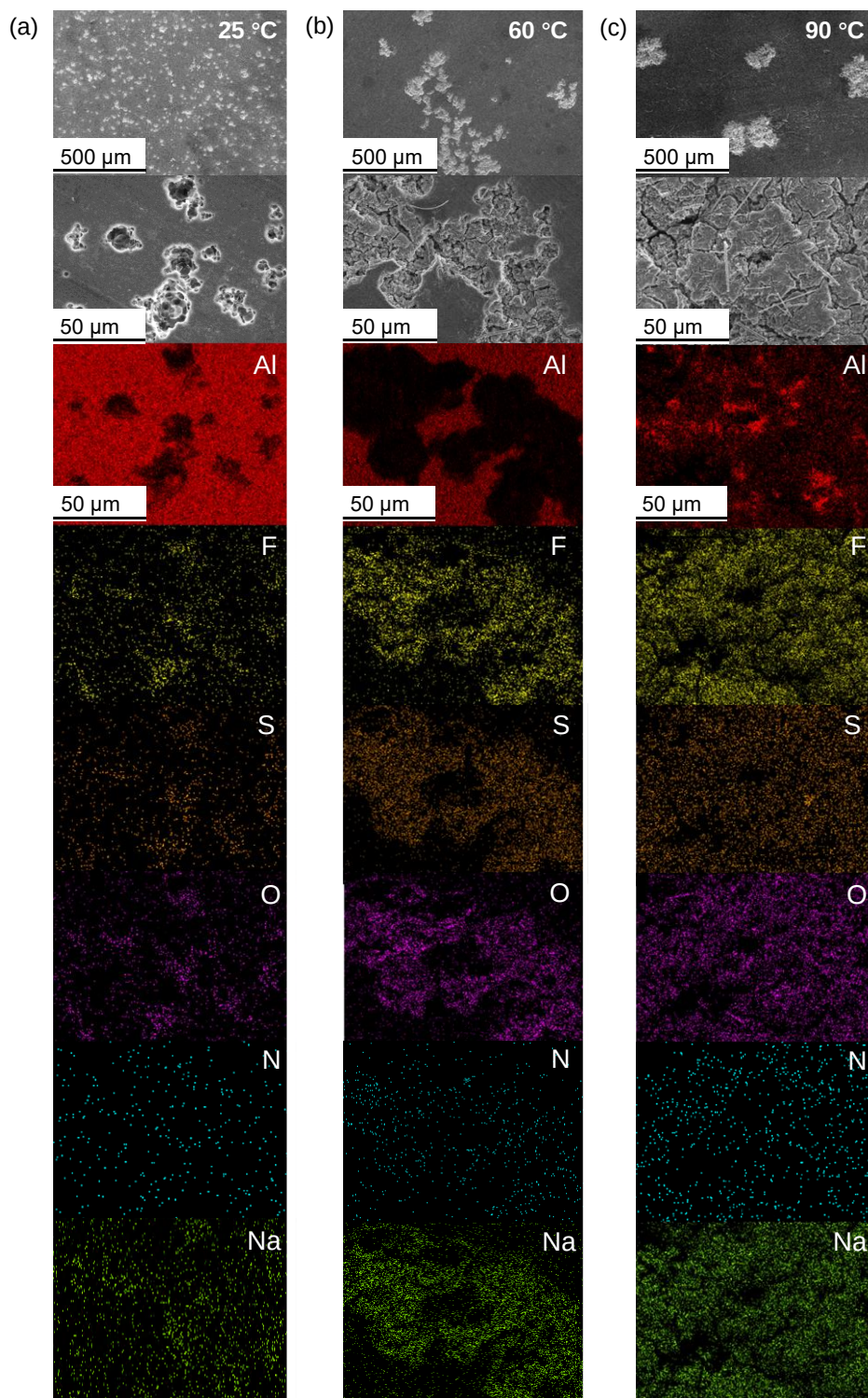


Figure 3-12. Temperature dependence of FE-SEM and EDX mapping images for the Al electrode after the 10 cycles of CV measurements in the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

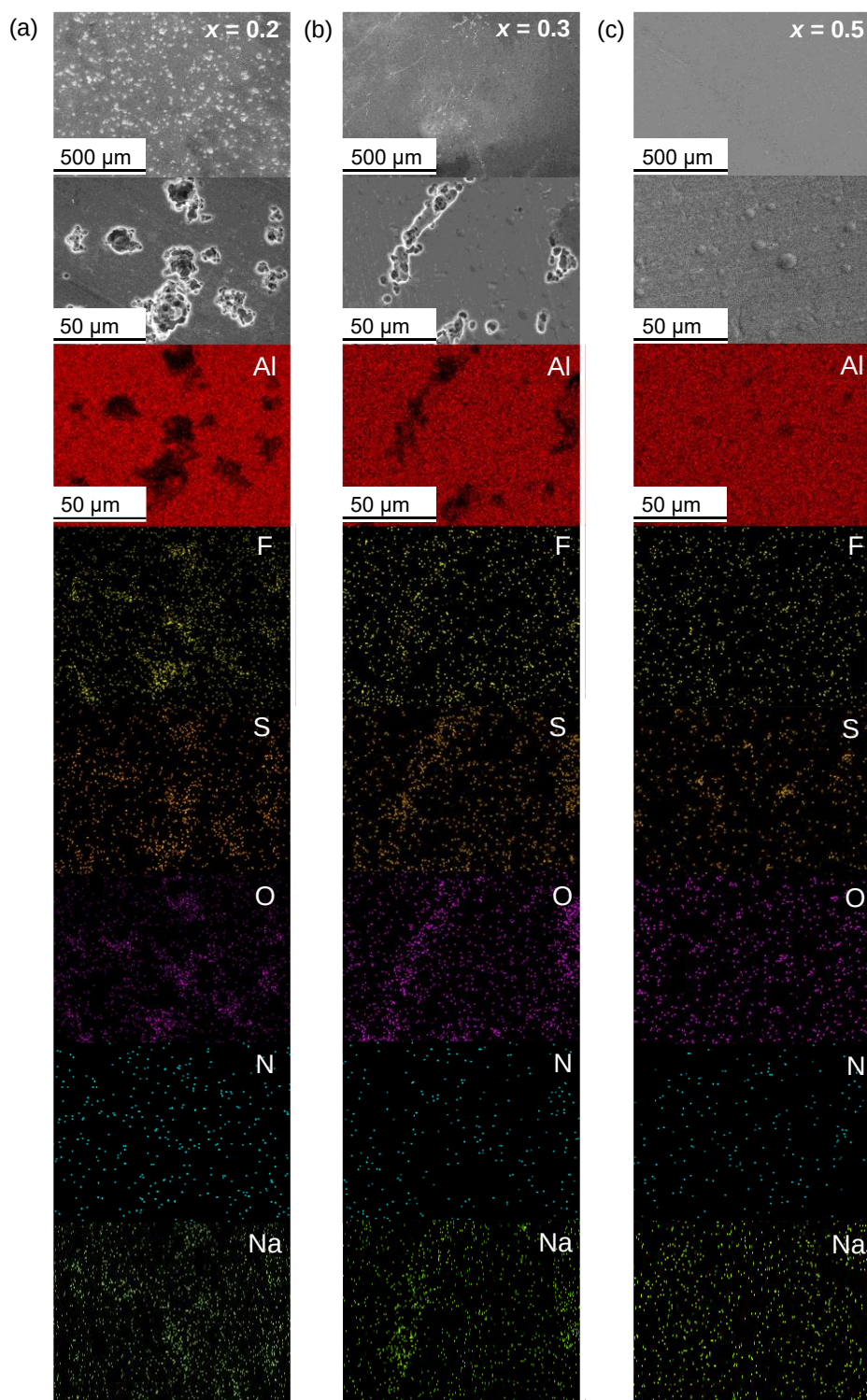


Figure 3-13. Na salt fraction dependence of FE-SEM and EDX mapping images for the Al electrode after the 10 cycles of CV measurements at 25 °C in the $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ electrolyte, (a) $x = 0.2$, (b) $x = 0.3$, and (c) $x = 0.5$, respectively. (Figure 3-13a is the same as Figure 3-12a), added once again here for comparison.)

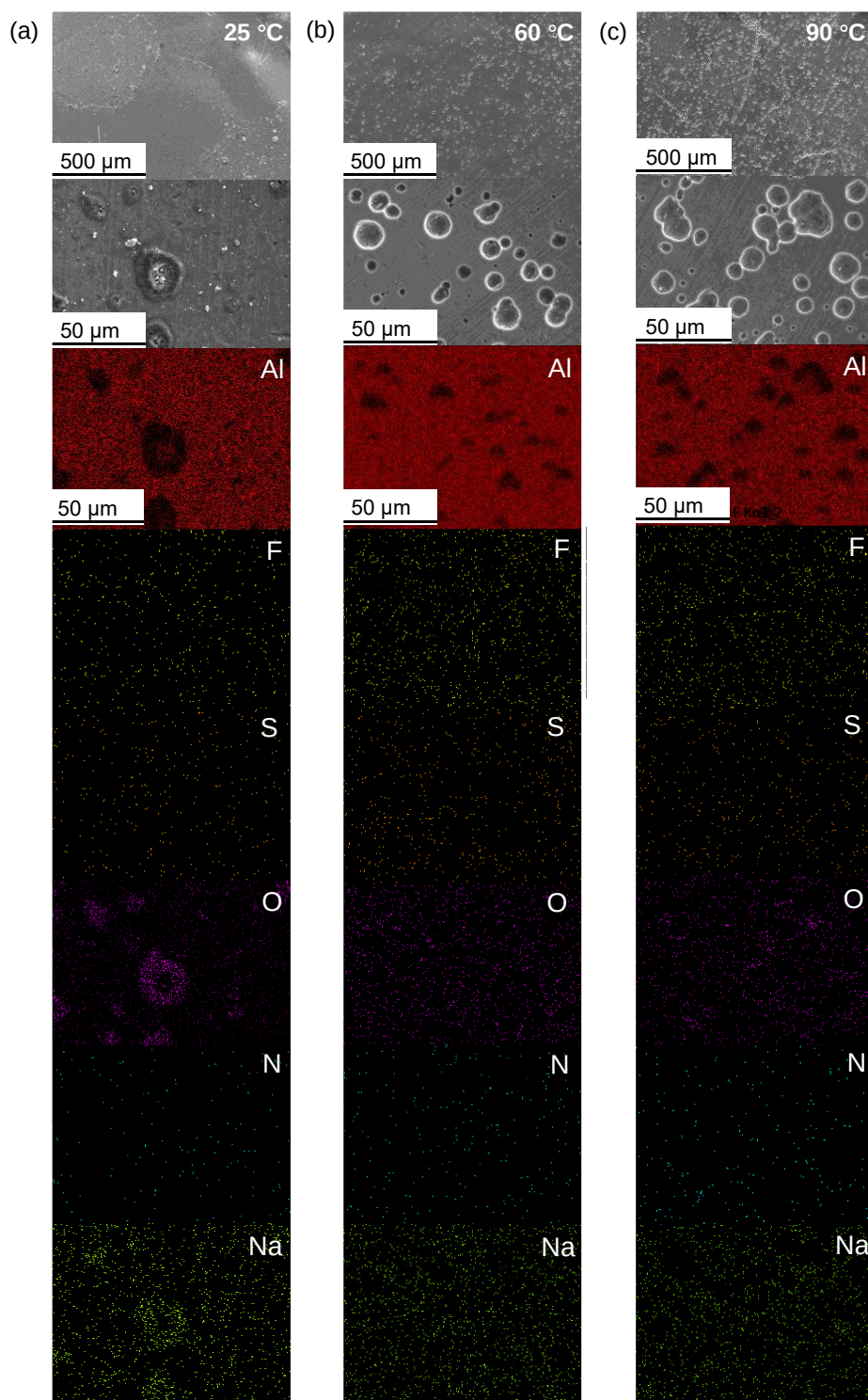


Figure 3-14. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{TFSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

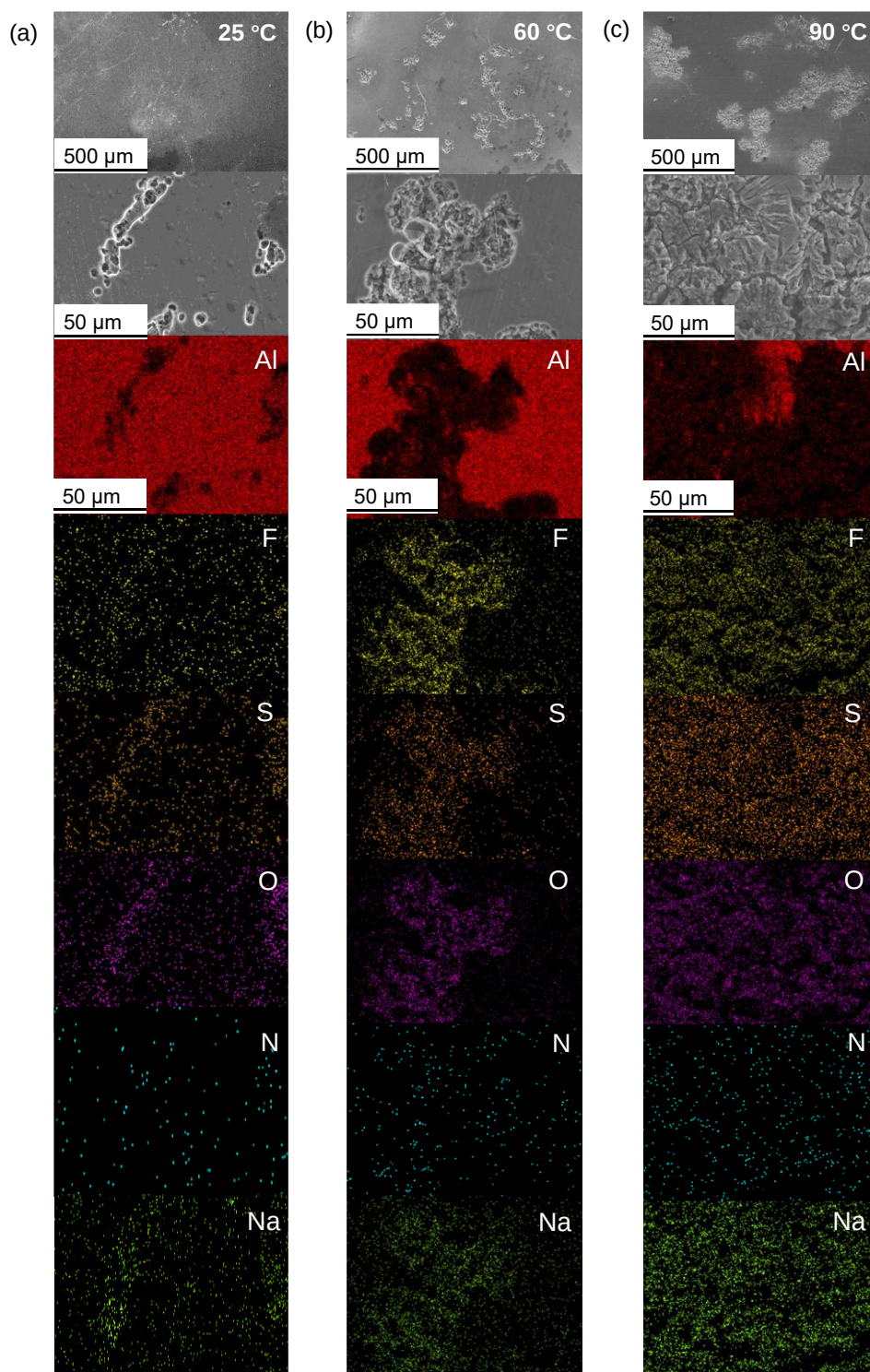


Figure 3-15. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.3}[\text{C}_2\text{C}_{11}\text{im}]_{0.7}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

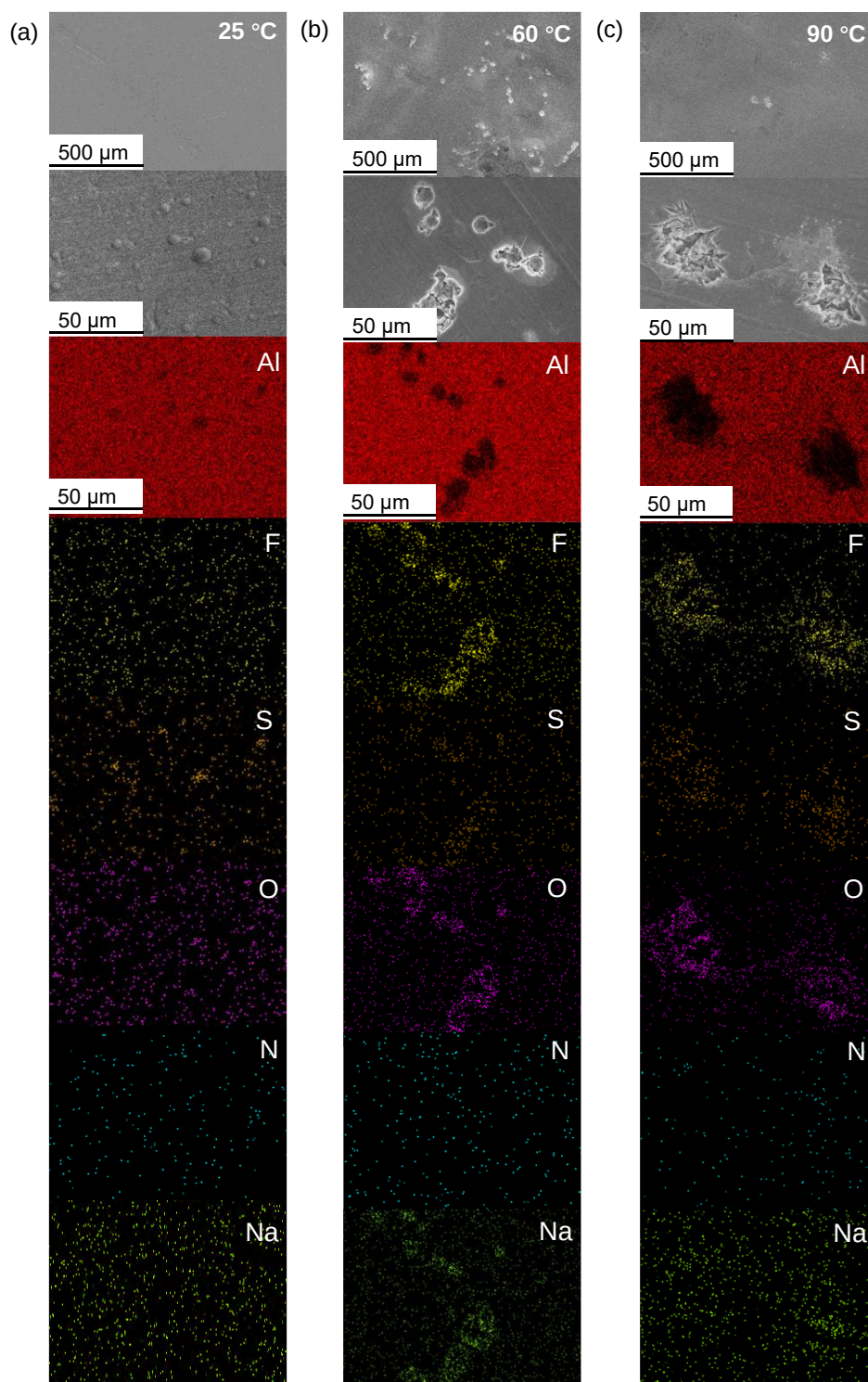


Figure 3-16. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.5}[\text{C}_2\text{C}_{1}\text{im}]_{0.5}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

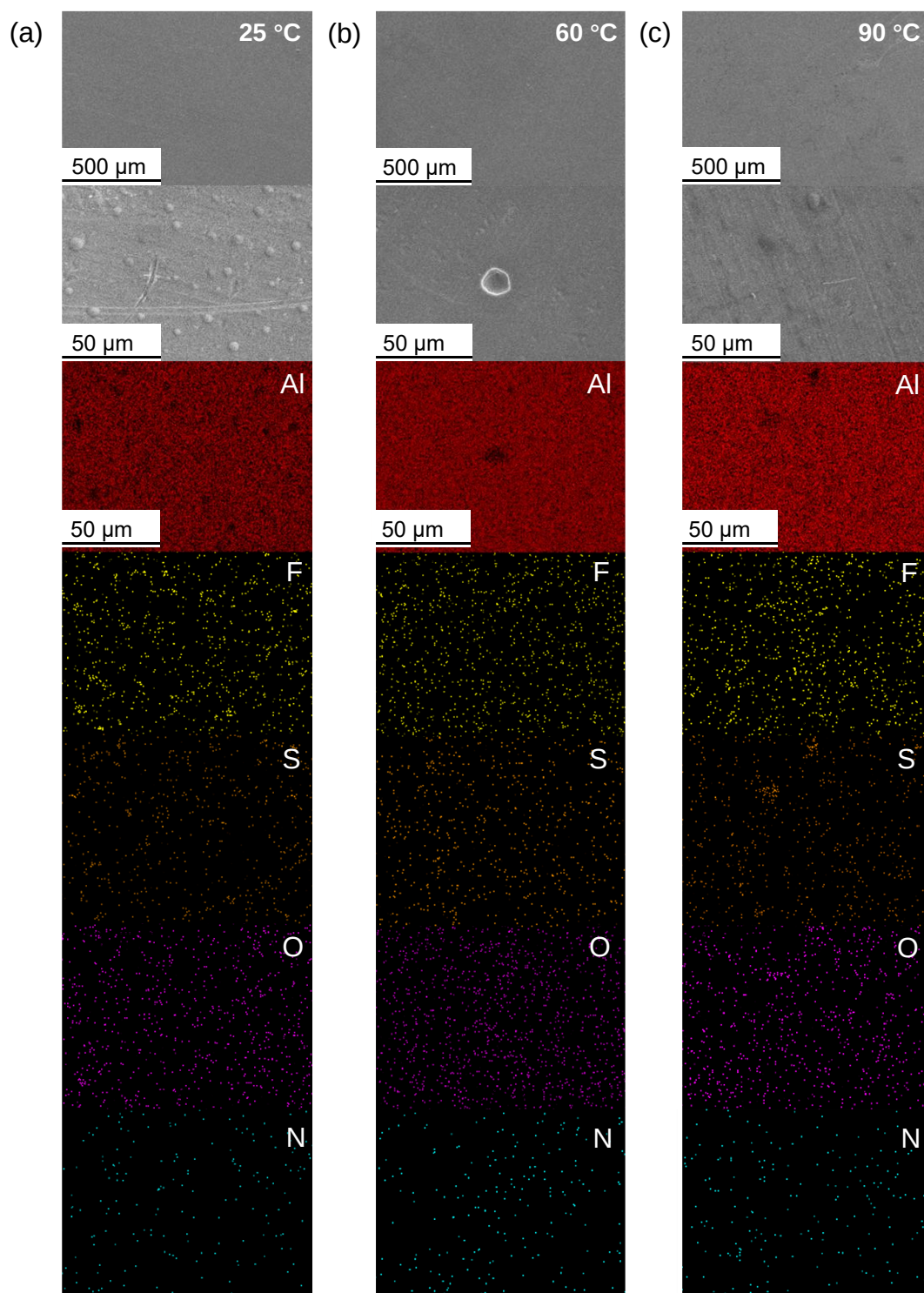


Figure 3-17. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV test in the $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{TFSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

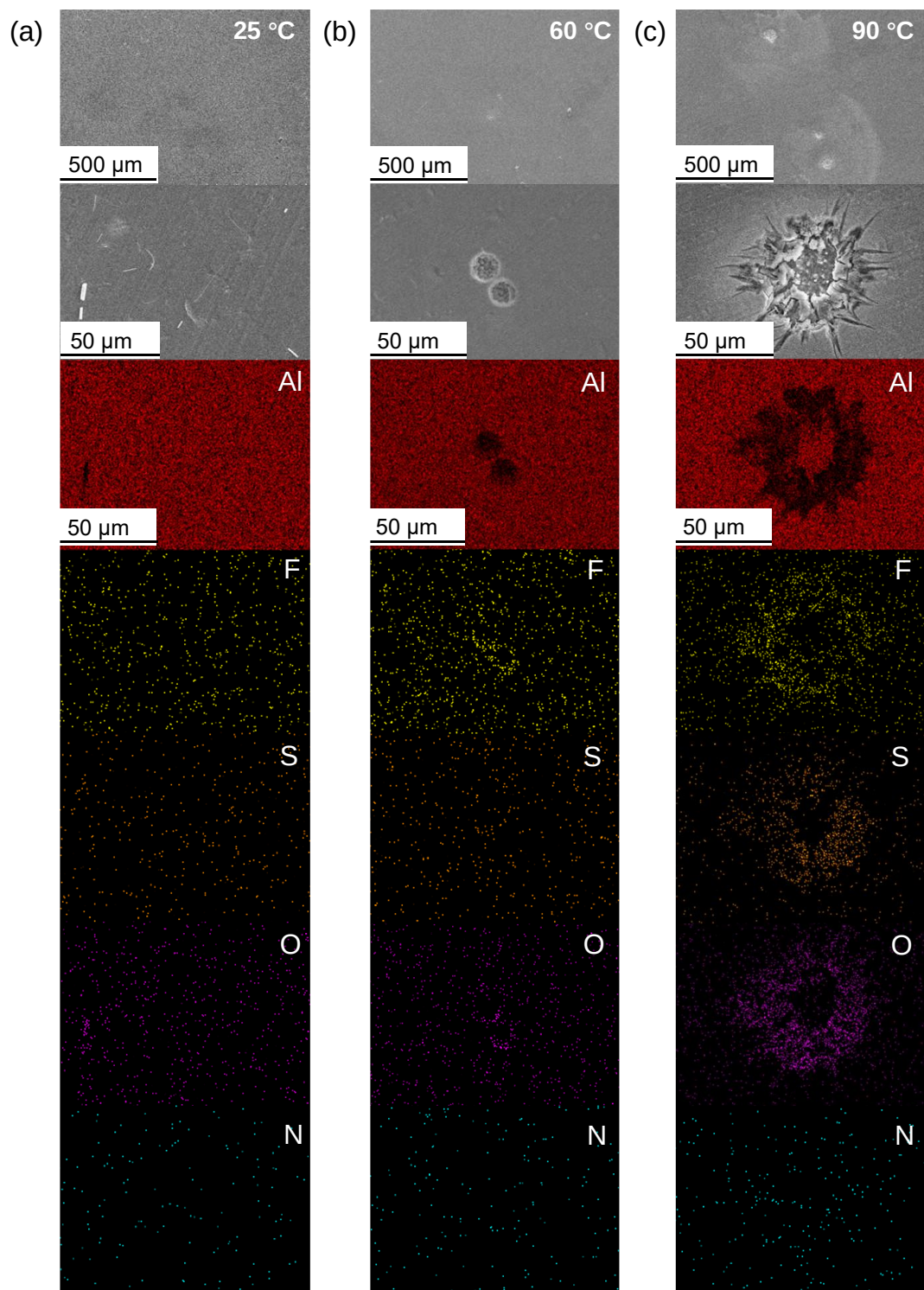


Figure 3-18. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

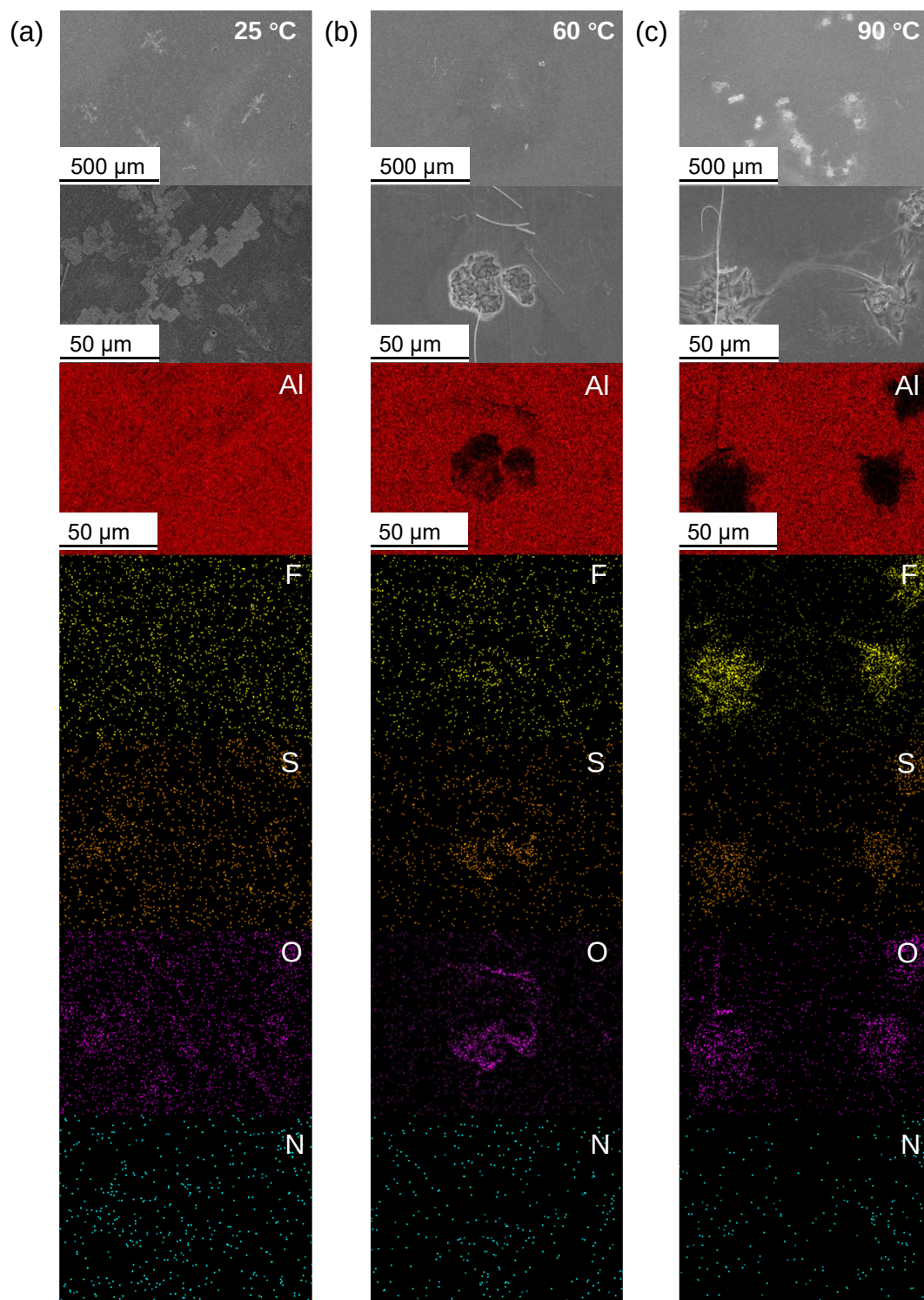


Figure 3-19. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.3}[\text{C}_3\text{C}_1\text{pyrr}]_{0.7}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

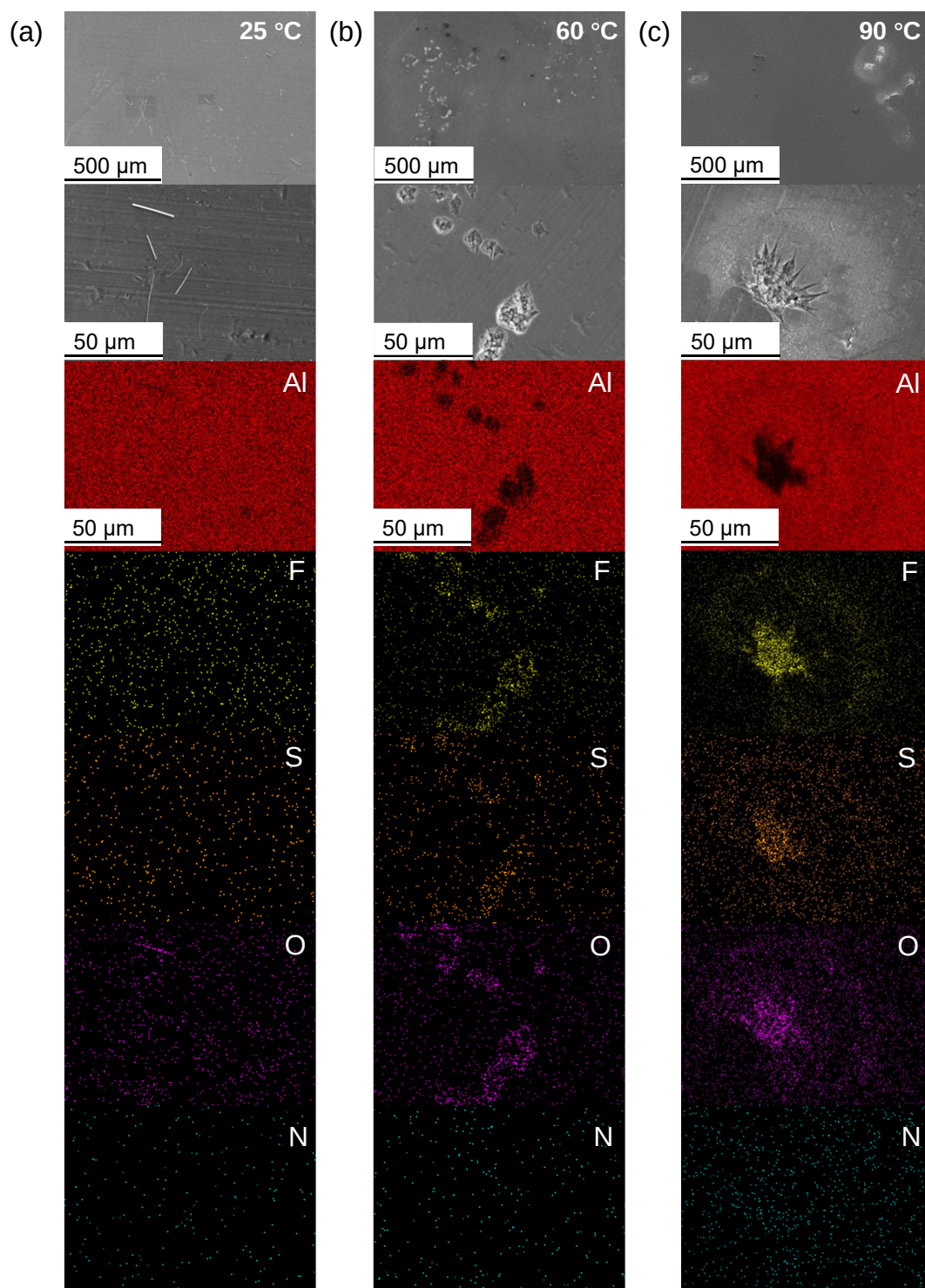


Figure 3-20. Temperature dependence of FE-SEM and EDX mapping images of the Al electrode after the CV measurements in the $\text{Na}_{0.5}[\text{C}_3\text{C}_1\text{pyrr}]_{0.5}[\text{FSA}]$ electrolyte at (a) 25, (b) 60, and (c) 90 °C.

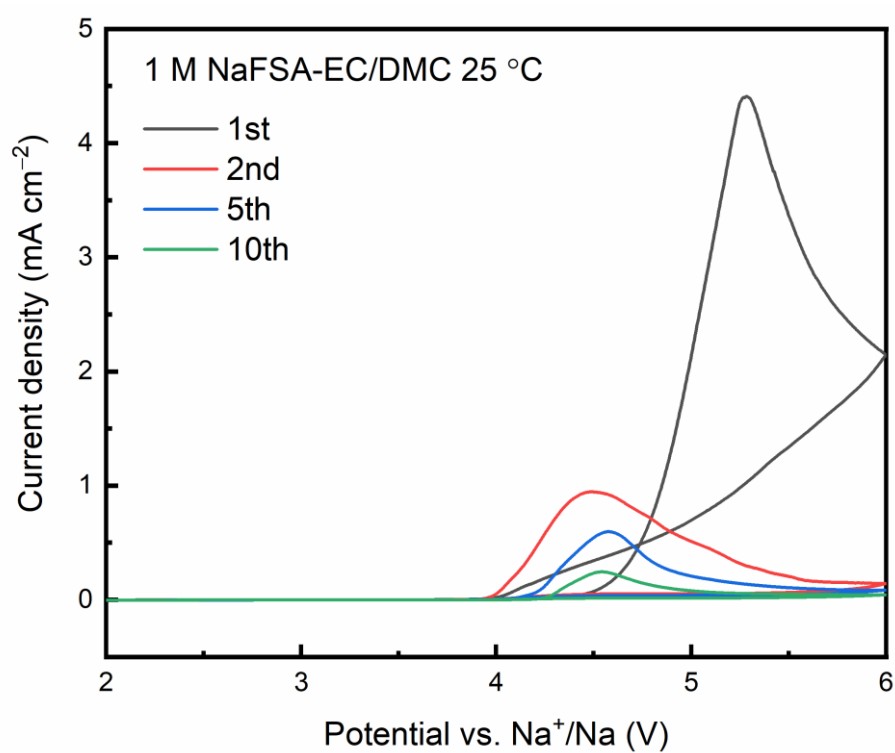


Figure 3-21. Cyclic voltammograms of an Al electrode in the 1 mol dm⁻³ Na[FSA]-EC/DMC electrolyte at 25 °C. Scanned from the rest potential to 6 V. Scan rate: 0.5 mV s⁻¹.

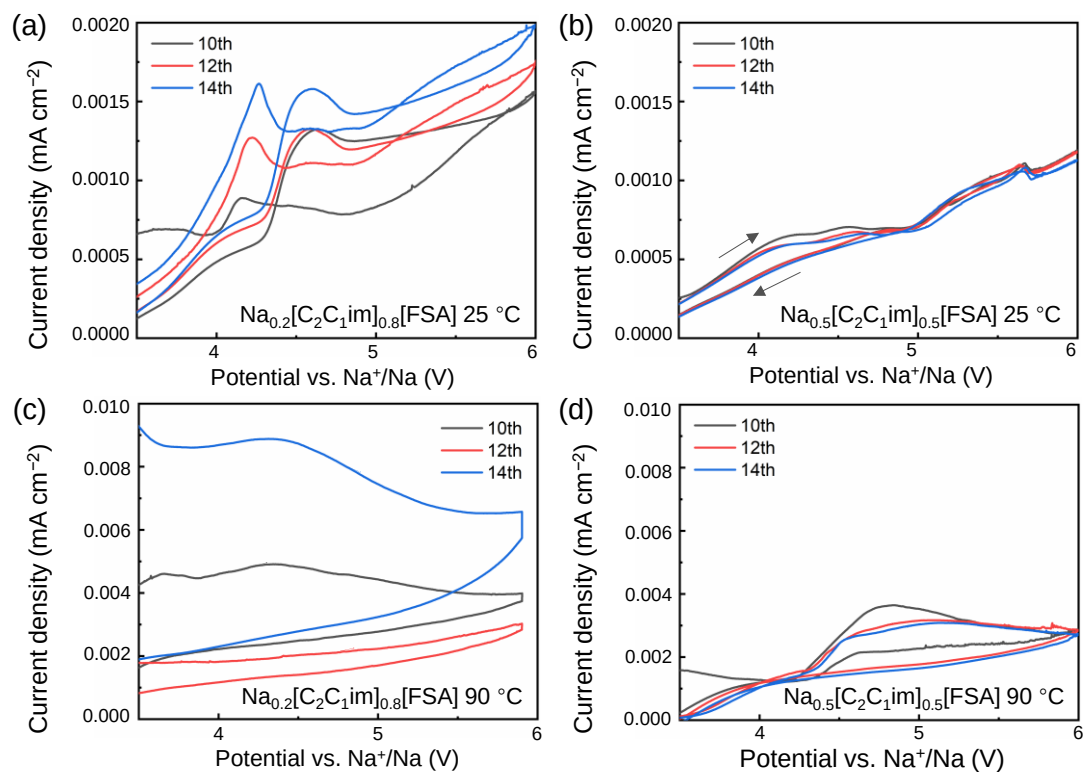


Figure 3-22. Cyclic voltammograms of an Al electrode at the 10th, 12th, and 14th cycles in the $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ IL electrolyte ($x =$ (a, c) 0.2 and (b, d) 0.5). Temperature: (a, b) 25 and (c, d) 90 °C. Scan rate: 0.5 mV s^{-1} . Ten consecutive CV cycles without intervals were performed to form the passivation layer sufficiently, and the subsequent five CV cycles were performed with an interval (12-hour rest per cycle) after each cycle.

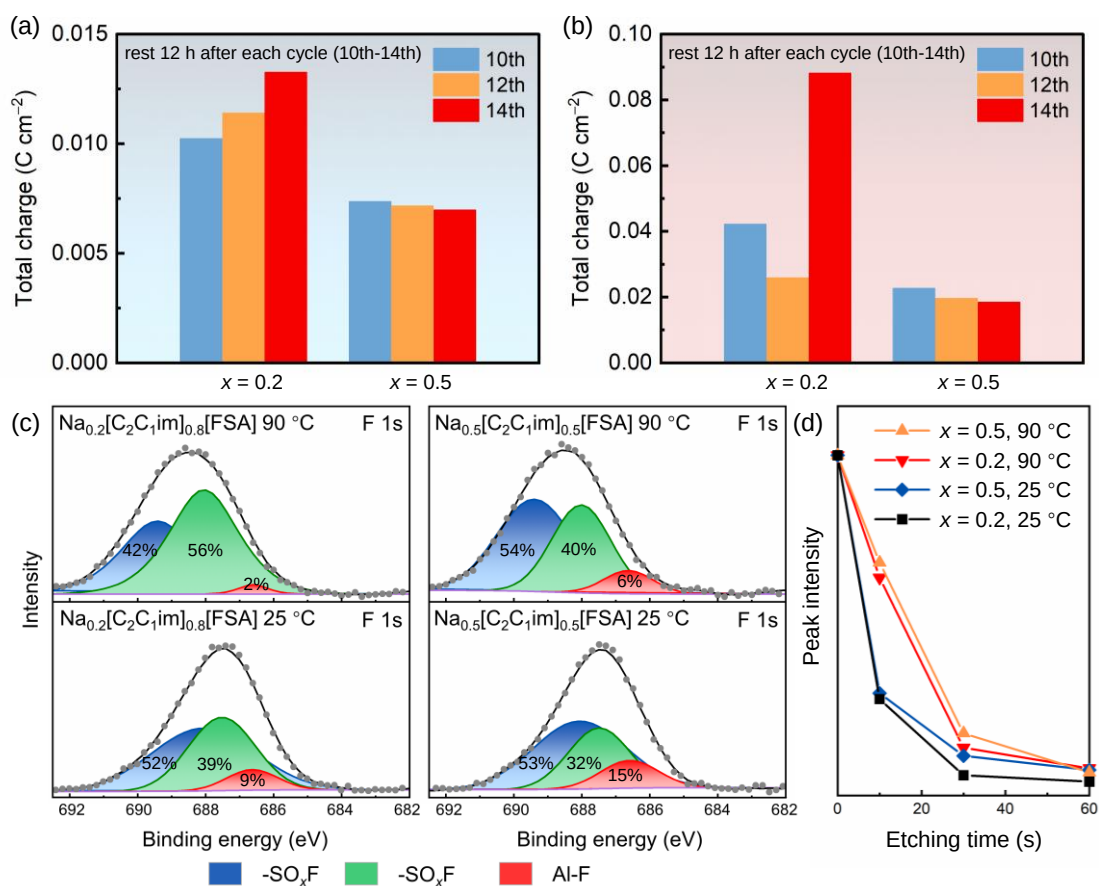


Figure 3-23. (a, b) Comparison of total charges during anodic scans of the CV measurements at (a) 25 °C and (b) 90 °C. (c) F 1s XPS spectra of the Al electrodes after the first cycle of the CV measurements at 25 °C and 90 °C. Electrolyte: Na_x[C₂C₁im]_{1-x}[FSA] ILs (x = 0.2 and 0.5). (d) Depth profile of F atom on the Al electrode before and after the first cycle of the CV measurements at 25 °C and 90 °C based on the F 1s XPS peak intensity against etching time.

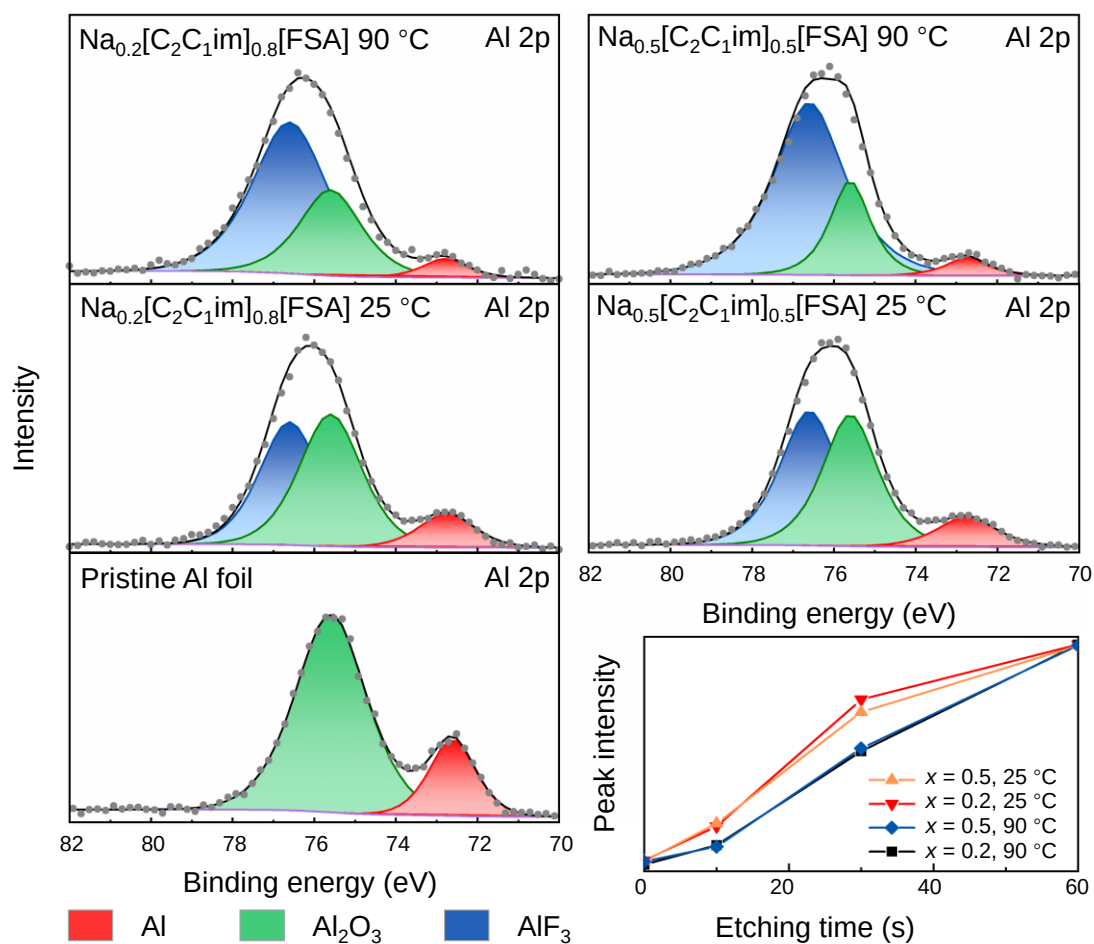


Figure 3-24. The Al 2p XPS spectra of the Al electrodes after one cycle CV measurement in different ionic liquids with the depth profile based on the peak intensity of Al metal against etching time.

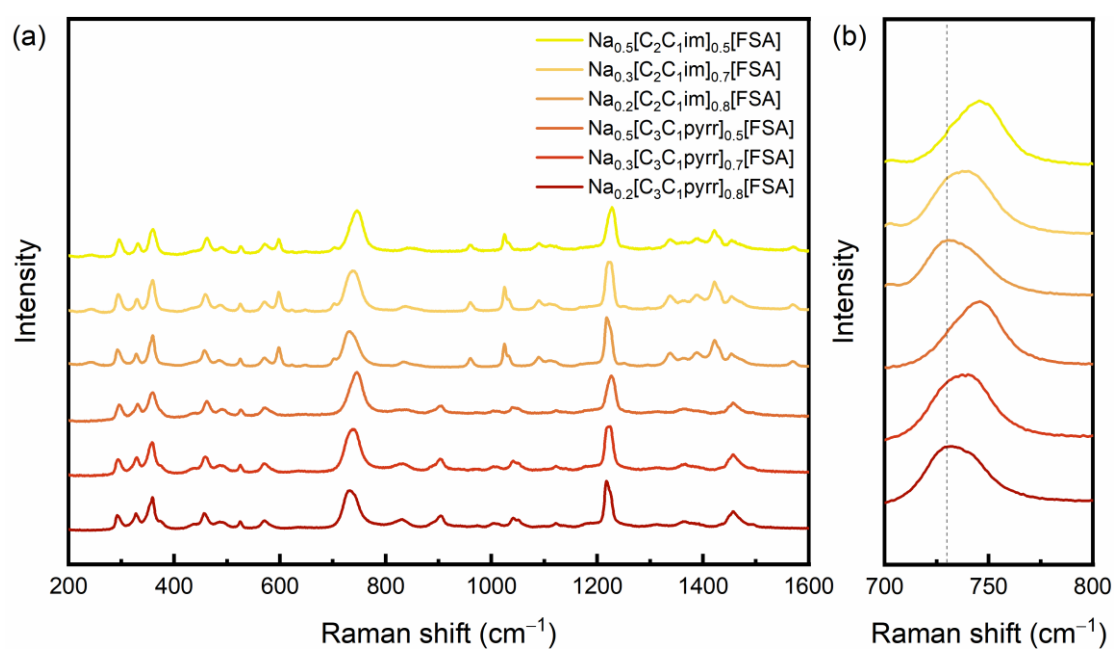


Figure 3-25. Raman spectra of the $\text{Na}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ and $\text{Na}_x[\text{C}_3\text{C}_1\text{pyrr}]_{1-x}[\text{FSA}]$ IL electrolytes in the range of (a) 200-1600 cm^{-1} and (b) 700-800 cm^{-1} . The dashed line in (b) represents the peak position of free $[\text{FSA}]^-$ anions.

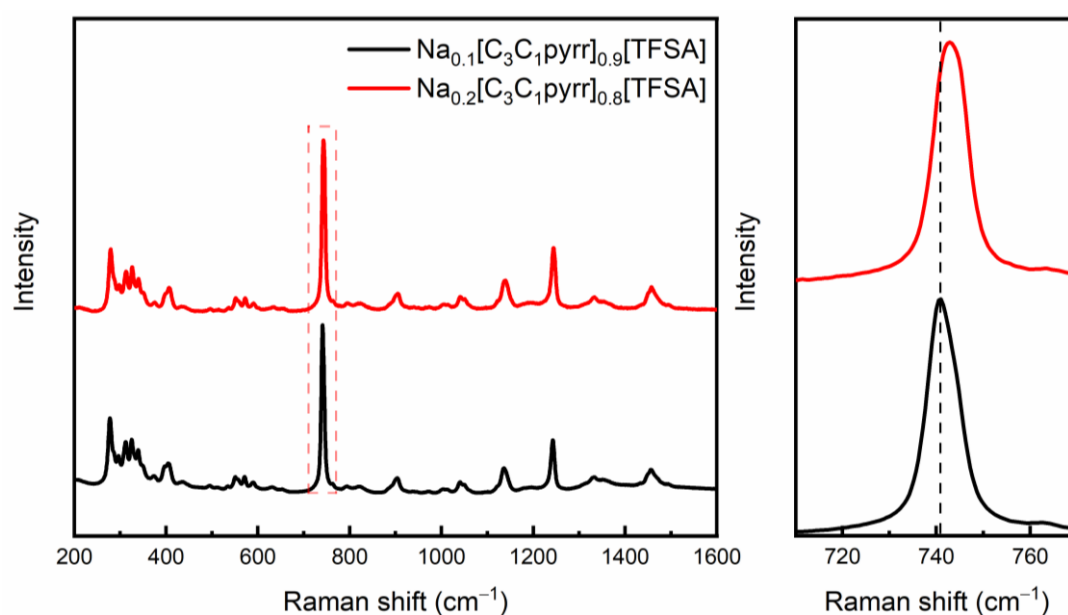


Figure 3-26. Raman spectra of $\text{Na}_{0.1}[\text{C}_3\text{C}_1\text{pyrr}]_{0.9}[\text{TFSA}]$ and $\text{Na}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{TFSA}]$ in the range of (a) 200-1600 cm^{-1} and (b) 710-770 cm^{-1} . The dashed line in (b) represents the peak position of free $[\text{TFSA}]^-$ anions.

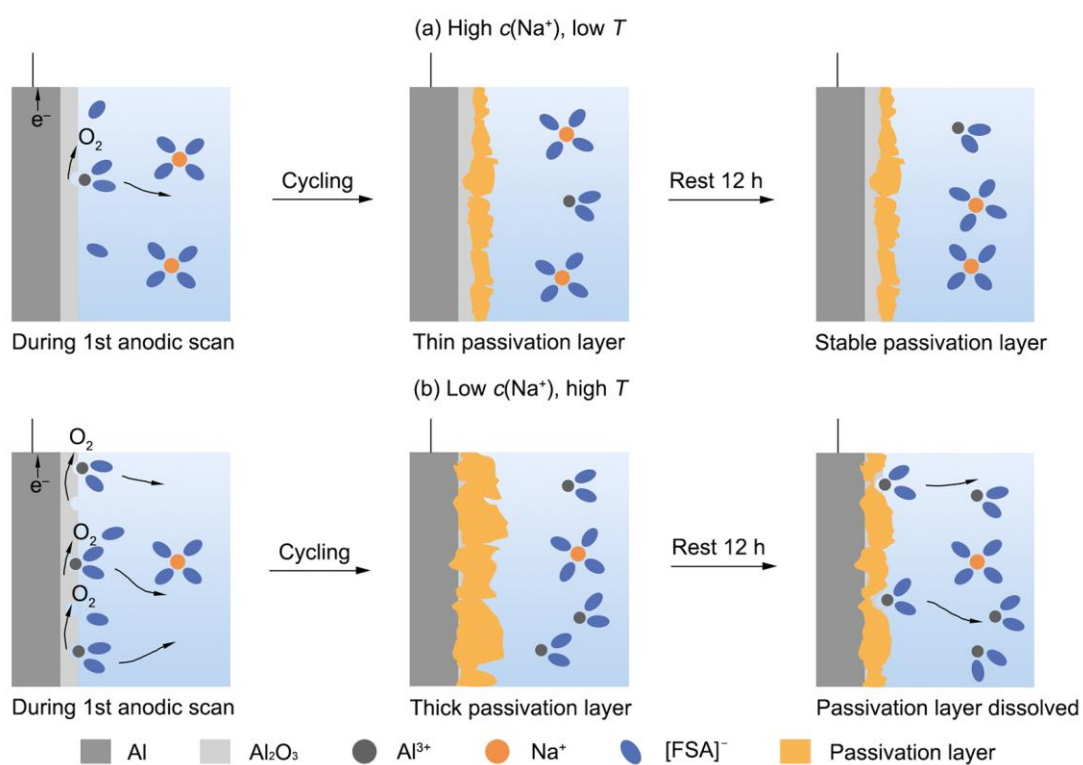


Figure 3-27. Schematic illustration of the formation and dissolution processes for the passivation layer on the Al electrodes in the investigated IL electrolytes (a) under high Na^+ concentration and low temperature conditions and (b) under low Na^+ concentration and high temperature conditions.

References

- [1] M.A. Hannan, M.H. Lipu, A. Hussain and A. Mohamed, *Renew. Sust. Energ. Rev.*, **78** (2017) 834-854.
- [2] N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, *Chem. Rev.*, **114** (2014) 11636-11682.
- [3] H.S. Hirsh, Y. Li, D.H.S. Tan, M. Zhang, E. Zhao and Y.S. Meng, *Adv. Energy Mater.*, **10** (2020) 2001274.
- [4] B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, **334** (2011) 928-935.
- [5] Y. Niu, Y. Zhao and M. Xu, *Carbon Neutralization*, **2** (2023) 150-168.
- [6] P. Du, L. Cao, B. Zhang, C. Wang, Z. Xiao, J. Zhang, D. Wang and X. Ou, *Renew. Sust. Energ. Rev.*, **151** (2021) 111640.
- [7] D. Larcher and J.M. Tarascon, *Nat. Chem.*, **7** (2015) 19-29.
- [8] K. Wang, C. Wang, H. Yang, X. Wang, F. Cao, Q. Wu and H. Peng, *Nano Res.*, **13** (2020) 1948-1954.
- [9] X. Casas, M. Niederberger and E. Lizundia, *ACS Appl. Mater. Interfaces*, **12** (2020) 29264-29274.
- [10] J.L. Murray, *Bull. Alloy Phase Diagr.*, **4** (1983) 407-410.
- [11] D. Kundu, E. Talaie, V. Duffort and L.F. Nazar, *Angew. Chem. Int. Ed.*, **54** (2015) 3431-3448.
- [12] C. Vaalma, D. Buchholz, M. Weil and S. Passerini, *Nat. Rev. Mater.*, **3** (2018) 18013.

- [13] S.S. Zhang and T.R. Jow, *J. Power Sources*, **109** (2002) 458-464.
- [14] Y. Huang, L. Zhao, L. Li, M. Xie, F. Wu and R. Chen, *Adv. Mater.*, **31** (2019) 1808393.
- [15] J.W. Braithwaite, A. Gonzales, G. Nagasubramanian, S.J. Lucero, D.E. Peebles, J.A. Ohlhausen and W.R. Cieslak, *J. Electrochem. Soc.*, **146** (1999) 448-456.
- [16] X. Li, S. Deng, M.N. Banis, K. Doyle-Davis, D. Zhang, T. Zhang, J. Yang, R. Divigalpitiya, F. Brandys, R. Li and X. Sun, *ACS Appl. Mater. Interfaces*, **11** (2019) 32826-32832.
- [17] J. Chen, Z. Bai, X. Li, Q. Wang, J. Du, R. Lu and X. Liu, *Appl. Surf. Sci.*, **606** (2022) 155002.
- [18] G.G. Eshetu, S. Grugeon, H. Kim, S. Jeong, L. Wu, G. Gachot, S. Laruelle, M. Armand and S. Passerini, *ChemSusChem*, **9** (2016) 462-471.
- [19] X. Zheng, Z. Gu, X. Liu, Z. Wang, J. Wen, X. Wu, W. Luo and Y. Huang, *Energy Environ. Sci.*, **13** (2020) 1788-1798.
- [20] A. Ponrouch, E. Marchante, M. Courty, J.-M. Tarascon and M.R. Palacin, *Energy Environ. Sci.*, **5** (2012) 8572-8583.
- [21] M. Dahbi, T. Nakano, N. Yabuuchi, S. Fujimura, K. Chihara, K. Kubota, J.-Y. Son, Y.-T. Cui, H. Oji and S. Komaba, *ChemElectroChem*, **3** (2016) 1856-1867.
- [22] P. Barnes, K. Smith, R. Parrish, C. Jones, P. Skinner, E. Storch, Q. White, C. Deng, D. Karsann, M.L. Lau, J.J. Dumais, E.J. Dufek and H. Xiong, *J. Power Sources*, **447** (2020) 227363.

- [23] L. Zhao, J. Zhao, Y.-S. Hu, H. Li, Z. Zhou, M. Armand and L. Chen, *Adv. Energy Mater.*, **2** (2012) 962-965.
- [24] D.M. Ould, S. Menkin, H.E. Smith, V. Riesgo-Gonzalez, E. Jónsson, C.A. O'Keefe, F. Coowar, J. Barker, A.D. Bond, C.P. Grey and D.S. Wright, *Angew. Chem. Int. Ed.*, **61** (2022) e202202133.
- [25] G.G. Eshetu, T. Diemant, M. Hekmatfar, S. Grugeon, R.J. Behm, S. Laruelle, M. Armand and S. Passerini, *Nano Energy*, **55** (2019) 327-340.
- [26] Y. Ding, X. Guo, Y. Qian, H. Gao, D.H. Weber, L. Zhang, J.B. Goodenough and G. Yu, *Angew. Chem. Int. Ed.*, **59** (2020) 12170-12177.
- [27] H. Yang, K. Kwon, T.M. Devine and J. W. Evans, *J. Electrochem. Soc.*, **147** (2000) 4399.
- [28] T. Hatchard and M. Obrovac, *J. Electrochem. Soc.*, **161** (2014) A1748.
- [29] K. Park, S. Yu, C. Lee and H. Lee, *J. Power Sources*, **296** (2015) 197-203.
- [30] J. Lee, Y. Lee, J. Lee, S.-M. Lee, J.-H. Choi, H. Kim, M.-S. Kwon, K. Kang, K.T. Lee and N.-S. Choi, *ACS Appl. Mater. Interfaces*, **9** (2017) 3723-3732.
- [31] C. Geng, D. Buchholz, G.-T. Kim, D.V. Carvalho, H. Zhang, L.G. Chagas and S. Passerini, *Small Methods*, **3** (2019) 1800208.
- [32] Z. Zeng, X. Jiang, R. Li, D. Yuan, X. Ai, H. Yang and Y. Cao, *Adv. Sci.*, **3** (2016) 1600066.
- [33] H. Che, S. Chen, Y. Xie, H. Wang, K. Amine, X.-Z. Liao and Z.-F. Ma, *Energy Environ. Sci.*, **10** (2017) 1075-1101.

- [34] Y. Sun, P. Shi, H. Xiang, X. Liang and Y. Yu, *Small*, **15** (2019) 1805479.
- [35] P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, **39** (2000) 3772-3789.
- [36] K. Matsumoto, J. Hwang, S. Kaushik, C.-Y. Chen and R. Hagiwara, *Energy Environ. Sci.*, **12** (2019) 3247-3287.
- [37] H. Yin, C. Han, Q. Liu, F. Wu, F. Zhang and Y. Tang, *Small*, **17** (2021) 2006627.
- [38] J. Mun, T. Yim, C.Y. Choi, J.H. Ryu, Y.G. Kim and S.M. Oh, *Electrochem. Solid-State Lett.*, **13** (2010) A109-A111.
- [39] E. Cho, J. Mun, O.B. Chae, O.M. Kwon, H.-T. Kim, J.H. Ryu, Y.G. Kim and S.M. Oh, *Electrochem. Commun.*, **22** (2012) 1-3.
- [40] R.-S. Kühnel, M. Lübke, M. Winter, S. Passerini and A. Balducci, *J. Power Sources*, **214** (2012) 178-184.
- [41] J.L. Allen, D.W. McOwen, S.A. Delp, E.T. Fox, J.S. Dickmann, S.-D. Han, Z.-B. Zhou, T.R. Jow and W.A. Henderson, *J. Power Sources*, **237** (2013) 104-111.
- [42] C. Liu, X. Ma, F. Xu, L. Zheng, H. Zhang, W. Feng, X. Huang, M. Armand, J. Nie, H. Chen and Z. Zhou, *Electrochim. Acta*, **149** (2014) 370-385.
- [43] T. Vogl, S. Menne and A. Balducci, *Phys. Chem. Chem. Phys.*, **16** (2014) 25014-25023.
- [44] S. Theivaprakasam, G. Girard, P. Howlett, M. Forsyth, S. Mitra and D. MacFarlane, *npj Mater. Degrad.*, **2** (2018) 13.
- [45] Q. Liu, T.L. Dzwiniel, K.Z. Pupek and Z. Zhang, *J. Electrochem. Soc.*, **166** (2019) A3959-A3964.

- [46] J. Hwang, K. Matsumoto and R. Hagiwara, *Adv. Energy Mater.*, **10** (2020) 2001880.
- [47] H. Onuma, K. Kubota, S. Muratsubaki, T. Hosaka, R. Tatara, T. Yamamoto, K. Matsumoto, T. Nohira, R. Hagiwara, H. Oji, S. Yasuno and S. Komaba, *ACS Energy Lett.*, **5** (2020) 2849-2857.
- [48] L. Otaegui, E. Goikolea, F. Aguesse, M. Armand, T. Rojo and G. Singh, *J. Power Sources*, **297** (2015) 168-173.
- [49] J. Hwang, I. Aoyagi, M. Takiyama, K. Matsumoto and R. Hagiwara, *J. Electrochem. Soc.*, **169** (2022) 080522.
- [50] D.H. Doughty and E.P. Roth, *Electrochem. Soc. Interface*, **21** (2012) 37.
- [51] Y. Chen, Y. Kang, Y. Zhao, L. Wang, J. Liu, Y. Li, Z. Liang, X. He, X. Li, N. Tavajohi and B. Li, *J. Energy Chem.*, **59** (2021) 83-99.
- [52] X. Lin, M. Salari, L.M.R. Arava, P.M. Ajayan and M.W. Grinstaff, *Chem. Soc. Rev.*, **45** (2016) 5848-5887.
- [53] Y. Feng, L. Zhou, H. Ma, Z. Wu, Q. Zhao, H. Li, K. Zhang and J. Chen, *Energy Environ. Sci.*, **15** (2022) 1711-1759.
- [54] M.J. Earle, B.J. Mcauley, A. Ramani, K.R. Seddon and J.M. Thomson, in, United States 2006.
- [55] J. Krummacher and A. Balducci, *Chem. Mater.*, **30** (2018) 4857-4863.
- [56] J. Krummacher, L. Hess and A. Balducci, *J. Electrochem. Soc.*, **166** (2019) A1763.

- [57] T. Ma, G.-L. Xu, Y. Li, L. Wang, X. He, J. Zheng, J. Liu, M.H. Engelhard, P. Zapol, L.A. Curtiss, J. Jorne, K. Amine and Z. Chen, *J. Phys. Chem. Lett.*, **8** (2017) 1072-1077.
- [58] M. Morita, T. Shibata, N. Yoshimoto and M. Ishikawa, *Electrochim. Acta*, **47** (2002) 2787-2793.
- [59] C. Peng, L. Yang, Z. Zhang, K. Tachibana, Y. Yang and S. Zhao, *Electrochim. Acta*, **53** (2008) 4764-4772.
- [60] M.P. Mousavi, B.E. Wilson, S. Kashefolgheta, E.L. Anderson, S. He, P. Buhlmann and A. Stein, *ACS Appl. Mater. Interfaces*, **8** (2016) 3396-3406.
- [61] M. Kunze, S. Jeong, E. Paillard, M. Schönhoff, M. Winter and S. Passerini, *Adv. Energy Mater.*, **1** (2011) 274-281.
- [62] B. Garcia and M. Armand, *J. Power Sources*, **132** (2004) 206-208.
- [63] A. Kotronia, H.D. Asfaw, C.-W. Tai, M. Hahlin, D. Brandell and K. Edström, *ACS Appl. Mater. Interfaces*, **13** (2021) 3867-3880.
- [64] W. Xue, Z. Shi, M. Huang, S. Feng, C. Wang, F. Wang, J. Lopez, B. Qiao, G. Xu and W. Zhang, *Energy Environ. Sci.*, **13** (2020) 212-220.
- [65] M. Kerner, N. Plylahan, J. Scheers and P. Johansson, *Phys. Chem. Chem. Phys.*, **17** (2015) 19569-19581.
- [66] T.D. Pham, A. Bin Faheem, J. Kim, H.M. Oh and K.-K. Lee, *Small*, **18** (2022) 2107492.

- [67] Y. Yamada, C.H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama and A. Yamada, *ChemElectroChem*, **2** (2015) 1687-1694.
- [68] R. Wang, W. Li, L. Liu, Y. Qian, F. Liu, M. Chen, Y. Guo and L. Liu, *J. Electroanal. Chem.*, **833** (2019) 63-69.
- [69] T. Hosaka, T. Matsuyama, K. Kubota, R. Tatara and S. Komaba, *J. Mater. Chem. A*, **8** (2020) 23766-23771.
- [70] P.C. Rath, Y.-W. Wang, J. Patra, B. Umesh, T.-J. Yeh, S. Okada, J. Li and J.-K. Chang, *Chem. Eng. J.*, **415** (2021) 128904.

Chapter 4

Enhanced Cycle Stability of LiNiO_2 in Highly Concentrated Ionic Liquid Electrolyte

4.1 Introduction

Lithium-ion batteries (LIBs) have emerged as the predominant choice for powering electric vehicles (EVs) due to their impressive energy density [1, 2]. With the concern for global warming and the need for an eco-friendly environment, the global EV market is exploding to replace traditional fuel vehicles [3, 4]. However, the full transition to EVs is plagued by their high cost, limited driving range, and safety concerns, which are primarily dictated by the components and performance of LIBs [5-7]. The most commonly used positive material in LIBs is LiCoO_2 due to its high energy density and long cycle life [8]. Given the high cost and limited resources of Co, increasing Ni and reducing Co contents has been an attractive strategy to explore positive materials with enhanced energy density [9, 10].

LiNiO_2 (LNO), with a theoretical capacity of 275 mA h g^{-1} , resurges as an appealing positive material for next-generation EVs [11, 12]. However, its commercialization has not been realized due to the rapid capacity fading, limited Coulombic efficiency (CE), and safety problems [13, 14]. These impediments are derived from its instability during charge and discharge, related to Ni dissolution, mechanical and thermal degradation, and the high reactivity of Ni^{4+} ions formed in

delithiated states [15-18]. A lot of effort has been made to address these issues, resulting in several strategies, such as doping and surface modification [19-21]. Although the composition and morphology of LNO play a vital role in its stability, equally crucial is the electrolyte that contacts LNO.

Hydrogen fluoride (HF), the hydrolysis product of LiPF_6 , is known to facilitate the formation of AlF_3 passivation film for suppressing the corrosion of the Al current collector [22]. However, it also expedites Ni dissolution from the active electrode material, especially at high voltages, causing material deterioration and severe capacity decay [23, 24]. Thus, LiPF_6 -based carbonate electrolytes exhibit limited cycle performance with LNO positive electrodes [25-27]. Li[FSA] salt possesses higher chemical stability than LiPF_6 , and is well dissociated in carbonate solvents [28, 29]. Unfortunately, Li[FSA] -based organic solvent electrolytes would corrode the Al current collector at high potentials, leading to the loss of electric contact between active materials and Al current collectors, undermining the structural stability of positive electrodes, and ultimately damaging the overall battery performance [30-32].

Ionic liquids (ILs), which entirely comprise ions, possess low flammability and volatility, and high thermal and electrochemical stability, making them promising substitutes for current organic electrolytes in LIBs [33-35]. Some reports demonstrated that the utilization of ILs is an effective strategy to inhibit the corrosion of the Al current collector [36-38]. Moreover, researchers found that Li[FSA] -based IL electrolytes sometimes prevent parasitic reactions and improve the structural stability of positive

electrode materials [26, 39, 40]. Therefore, it is reasonable to investigate the unique potential of Li[FSA]-based IL electrolytes to stabilize both LNO positive electrodes and Al current collectors for the commercialization of LNO positive electrodes.

This chapter investigates the effects of Li[FSA]-based IL electrolytes in different molar ratios of 2:8 and 4:6 labeled as $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ (1.11 mol dm^{-3}), $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ ($2.529 \text{ mol dm}^{-3}$), $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ (1.13 mol dm^{-3}), and $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ (2.89 mol dm^{-3}) ($[\text{C}_2\text{C}_1\text{im}]^+ = 1\text{-ethyl-3-methylimidazolium}$ and $[\text{C}_3\text{C}_1\text{pyrr}]^+ = N\text{-methyl-}N\text{-propylpyrrolidinium}$), where on the electrochemical performance of the LNO positive electrode and corrosion behavior of the Al current collector. The cycling stability, rate performance, and CE in the Li/LNO cells are examined to assess the stability of IL electrolytes toward LNO positive electrodes. The differences in morphology, surface chemistry, and Ni dissolution of cells are compared between the cases with IL and conventional organic electrolytes through field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence spectroscopy (XRF). The corrosion behavior of Al foil and solvation structures of IL electrolytes are discussed based on the results of cyclic voltammetry (CV), SEM, XPS, and Raman spectroscopy.

4.2 Experimental

The Li[FSA] salt, $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$, and $[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ were dried under vacuum before use. The IL electrolytes were prepared by dissolving Li[FSA] in the

corresponding IL ([C₂C₁im][FSA] or [C₃C₁pyrr][FSA]). The organic electrolyte, 1 mol dm⁻³ LiPF₆-EC/DMC, was used as the baseline electrolyte (abbreviated as LiPF₆-EC/DMC). The LNO/SuperC65/PVDF (80:10:10wt%) composite electrodes were prepared with the mass loading of active materials of ~2 mg cm⁻² and thickness of ~20 μm. All the sample preparation and cell assembly/disassembly were conducted in an Ar-filled glove box (H₂O and O₂ < 1 ppm).

The Li/LNO cells were prepared using the LNO positive electrode, glass fiber separator, and Li metal disk counter electrode. Cycling tests were performed using an HJ-SD8 charge-discharge system with the thermostatic chamber at 25 °C in the voltage range of 2.7-4.3 V. Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range of 10⁵-10⁻¹ Hz with an AC amplitude of 10 mV using a VSP potentiostat. The Al corrosive behavior of these electrolytes was evaluated by CV tests with the Al foil working electrode and Li disk counter electrode. The CV data of the Li/Al cells was collected using a VSP potentiostat at 25 °C at a scan rate of 0.5 mV s⁻¹.

Raman spectra of the IL electrolytes were recorded by Raman spectroscopy using a laser with an excitation wavelength of 785 nm. The morphologies and surface components of the LNO positive electrode and Al foil were observed by FE-SEM and XPS, respectively. The LNO positive electrode after 10 cycles at a rate of 0.1C (1C = 180 mA g⁻¹ based on the practical capacity of LNO)[41, 42] was washed with EC/DMC (1:1 v/v). The Al electrode was rinsed with ethanol. Etching treatment was carried out using an Ar beam with an accelerating voltage of 400 V. To evaluate the Ni dissolution,

the Li/LNO cell after 100 cycles at a rate of 1C was disassembled and immersed in PC for 2 days. The resulting electrolyte was analyzed by XRF spectroscopy under a He atmosphere.

4.3 Results and discussion

The electrochemical performance of the LNO positive electrode was evaluated in the range of 2.7-4.3 V in four different electrolytes: LiPF₆-EC/DMC and Li[FSA]-IL electrolytes. **Figure 4-1** presents the charge-discharge curves of LNO in Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] at different rates from 0.1C to 5C (the first cycle of each rate is plotted here). Compared to the LNO performance in LiPF₆-EC/DMC (**Figure 4-2**), the cell with Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] shows a smaller polarization of the charge-discharge curves. The discrepancy in polarization can be attributed to the facile kinetic behavior of the cell with Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] at both the negative (lithium metal) and positive electrodes. **Figure 4-3** shows the EIS data for the cells after 200 cycles in LiPF₆-EC/DMC and Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] electrolytes. The cell with Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] electrolyte displays a markedly smaller impedance than that with LiPF₆-EC/DMC electrolyte. **Figure 4-4** compares the rate capabilities of Li/LNO cells with LiPF₆-EC/DMC and Li[FSA]-IL electrolytes. The discharge capacities of all the cells decrease with the increase of the C-rate. LiPF₆-EC/DMC shows the worst rate performance, for which only ~50% of the capacity measured at 0.1C is kept at 2C. Although the cell with Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] electrolyte shows slightly higher

capacity up to 1C compared to the cell with LiPF₆-EC/DMC, their capacities are similar at 2 and 5C. In contrast, cells with the Li[FSA]-IL electrolytes at high concentrations (Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] and Li_{0.4}[C₂C₁im]_{0.6}[FSA]) exhibit improved rate performance, achieving higher capacity retention at 5C. Surprisingly, the capacities of the cells using IL electrolytes recuperate to levels comparable to that at the initial 0.1C when the discharge rate returns to 0.1C, which is in stark contrast to the poor recovery performance of LiPF₆-EC/DMC.

After the rate capability test, the cycling performance of LNO electrodes in these electrolytes is investigated at 25 °C at 1C (**Figure 4-5**). The capacity of the cell cycled with LiPF₆-EC/DMC decreases rapidly and records a capacity retention of 51.5% over 500 cycles, whereas all the cells with Li[FSA]-IL electrolytes demonstrate superior cycling performance compared to those using the baseline electrolyte. The capacity retention of cells follows the order of Li_{0.4}[C₂C₁im]_{0.6}[FSA] (64.5%) < Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] (67.7%) < Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] (73.1%). Interestingly, even at a high concentration of Li salt, Li_{0.4}[C₂C₁im]_{0.6}[FSA] exhibits lower capacity retention compared to Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA]. These trends in cycleability are clearly reflected in the CE during cycle tests. **Figure 4-6** depicts the corresponding CEs of these cells as a function of cycle numbers. The Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] electrolyte exhibits the highest CE during long-term cycling, with an average value of 99.9%; the outstanding cycling performance and higher CE can be ascribed to the minimum electrode-electrolyte reaction and Ni dissolution, which will be elaborated in the

following [43]. The CEs of all the other electrolytes are unstable and extremely fluctuant. The lower CEs in $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ and $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ electrolytes result from corrosion of the Al current collector as shown below, although Ni dissolution also contributes to instability in the CE.

FE-SEM analysis was taken to further investigate the impact of $\text{LiPF}_6\text{-EC/DMC}$ and Li[FSA]-IL electrolytes on capacity fading. **Figure 4-7a** shows the pristine LNO particles before electrochemical tests with an immaculate surface. The LNO positive electrode after 10 cycles in $\text{LiPF}_6\text{-EC/DMC}$ shows significant particle cracking (**Figure 4-7b**). In sharp contrast, the LNO positive electrode cycled in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ remains intact and appears to be covered by a uniform layer (**Figure 4-7c**) (see **Figure 4-8** for FE-SEM images at lower magnifications). Particle cracking is one of the main reasons that cause capacity fade in high-Ni positive electrodes [44]. LNO undergoes several phase transitions during charge-discharge [45]. The most accepted mechanism is the transition including three hexagonal phases (H1, H2, and H3) and one monoclinic phase (M) in the order of H1, M, H2, and H3 during charge. During the H2-H3 phase transition at the high potential, cracks are caused by anisotropic lattice volume change upon cycling, which accelerates the impregnation of electrolytes along the grain separation boundaries [46]. This promotes undesirable reactions between the active material of the electrode component and the electrolyte. In addition, these reactions could be exacerbated due to large amounts of Ni^{3+} ions converting to reactive Ni^{4+} at high voltages [46]. Therefore, it is reasonable that the LNO positive electrode in $\text{LiPF}_6\text{-}$

EC/DMC with severe particle cracking results in poor cycle performance. In $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$, on the other hand, the electrode-electrolyte reaction is not as severe as in $\text{LiPF}_6\text{-EC/DMC}$, and the surface layer protects the LNO electrode.

Figure 4-9 compares the corresponding dQ/dV curves in different electrolytes at 1st and 10th cycles at 0.1C. The H2-H3 phase transition occurs at all the tested Li/LNO cells during the first charge-discharge process. This feature disappears after 10 cycles in the cell with $\text{LiPF}_6\text{-EC/DMC}$ electrolyte due to the phase degradation that makes some certain areas inactive [4]. Accompanied by the shift of potential peaks over cycles, the deterioration situation is consistent with the increasing polarization within charge-discharge curves. In IL electrolytes, the presence of the H2-H3 phase transition after 10 cycles suggests the less degraded electrode compared to the case in $\text{LiPF}_6\text{-EC/DMC}$, which supports the long-term cycling stability and the mitigation of side reactions.

Ni dissolution from the positive electrode is known to cause severe capacity fading over cycles. To assess the Ni dissolution behavior of electrodes cycled in different electrolytes, XRF analyses were conducted after preprocessing cycled cells. **Table 4-1** lists the Ni dissolution amounts of the LNO positive electrodes in different electrolytes after 100 cycles. The amount of the dissolved Ni is the highest in $\text{LiPF}_6\text{-EC/DMC}$ and lowest in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte, exhibiting the same order as the capacity retention in **Figure 4-5**. For $\text{LiPF}_6\text{-EC/DMC}$, the cathode electrolyte interphase (CEI) layer on the LNO surface is unstable, and volume changes derived from the H2-H3 phase transition cause cracks in LNO particles as seen in **Figure 4-7b**. During ongoing

charge-discharge cycles, Ni dissolution has resulted from the intensive reactions between electrode and electrolyte due to the high reactivity of Ni^{4+} ions from LNO and HF from LiPF_6 . [47] On the other hand, when using $\text{Li}_x[\text{C}_3\text{C}_1\text{pyrr}]_{1-x}[\text{FSA}]$ electrolyte, the stable CEI layer on the LNO surface minimizes the reaction between the electrode and electrolyte, thus preventing Ni dissolution and alleviating capacity loss. Moreover, XRF results indicate that increasing the fraction of $\text{Li}[\text{FSA}]$ salt can reduce the Ni dissolved percent. The formation of CEI on LNO electrodes was quantitatively analyzed after 10 cycles in $\text{LiPF}_6\text{-EC/DMC}$ and $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ by XPS. As shown in **Figure 4-10**, the intensity of Ni 2p XPS spectra as a function of etching time further supports the XRF results; the peak intensity of Ni 2p significantly increases with etching time in $\text{LiPF}_6\text{-EC/DMC}$, indicating the severe Ni dissolution of the LNO electrode. On the contrary, obvious growth of Ni 2p peak for $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ is not observed, indicating the CEI layer is protecting the LNO from Ni dissolution.

The Ni dissolution mechanisms of LNO in $\text{LiPF}_6\text{-EC/DMC}$ and $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ are illustrated in **Figure 4-11**. The LNO positive electrode undergoes a severe parasitic reaction with $\text{LiPF}_6\text{-EC/DMC}$, along with the reduction of Ni^{4+} and gas evolution [48]. The particle cracking caused by volume expansion and shrinkage further intensifies this reaction during long-term cycling. Thus, the CEI layer formed on the LNO electrode surface becomes fragmented, leading to continuous Ni dissolution in the $\text{LiPF}_6\text{-EC/DMC}$ electrolyte. On the other hand, the minimal Ni dissolution can be attributed to the stable CEI layer formed on the LNO electrode

surface when using $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte, thereby contributing to the excellent capacity retention of Li/LNO cells.

In view of the presence of $[\text{FSA}]^-$, the corrosion of the Al current collector should be considered a factor in the capacity fading of Li/LNO cells. Here, the corrosion behavior of the Al current collector was analyzed in the $\text{Li}_x[\text{C}_3\text{C}_1\text{pyrr}]_{1-x}[\text{FSA}]$ and $\text{Li}_x[\text{C}_2\text{C}_1\text{im}]_{1-x}[\text{FSA}]$ IL electrolytes ($x = 0.2$ and 0.4). **Figure 4-12** shows the CV curves of an Al electrode in the $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ electrolyte at selected cycles. The anodic current is likely to arise from the electrolyte decomposition and Al corrosion at high potentials. For the initial cycle, the anodic current during the reverse scan is higher than that of the forward scan, indicating that the corrosion of the Al electrode occurs along with the removal of the native Al_2O_3 layer, triggered by the chemical reaction with $[\text{FSA}]^-$. This is further confirmed by the SEM image of the Al electrode after 10 cycles (**Figure 4-13**), which shows corrosion pits on the surface of the Al electrode. As cycles proceed, the decrease in anodic current suggests the passivation process. The CV curves for Al electrodes in other three electrolytes are shown in **Figure 4-14–4-16**. For $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte, the peak intensity of the anodic current is higher with respect to $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$, corresponding to the more severe corrosion of Al electrode as seen in **Figure 4-17**. Besides, the comparison of CV and SEM results between $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ and $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ reveals that increasing the fraction of Li[FSA] salt is helpful for inhibiting Al corrosion (**Figure 4-18**). Notably, the anodic current increases during the forward scan but declines rapidly during the

reverse scan in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ at the first cycle (**Figure 4-15**), which implies the effective passivation ability [49, 50]. This is consistent with the SEM image: very little pitting corrosion is observed on the Al electrode in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ (**Figure 4-19**).

To visualize CV results in varying electrolytes, **Figure 4-20** displays the summary of total charges, calculated as the integral of the anodic peak area of selected cycles. Generally, total charges present a decreasing trend with increasing cycles, meaning the passivation layer forms and less charge is involved in the corrosion process. Total charges of the electrolyte with a low Li[FSA] fraction are always higher than those with a high Li[FSA] fraction. Moreover, total charges for $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ are not as low as those for $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte. Combined with the results from SEM images, this phenomenon reveals that the Al corrosion in $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ is not negligible. This provides strong evidence that the fluctuating CE for $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ electrolyte in **Figure 4-6** is caused by the corrosion of the Al current collector. The impact of different cations and Li[FSA] fractions on the Al corrosion behavior is further discussed in the following.

According to the previous report on Al corrosion behavior in IL electrolytes, the stability of the passivation layer formed on the Al electrode is considered an important factor.[35] If the passivation layer is not robust, Al corrosion aggravates and leads to the deterioration of the passivation layer and the exposure of unprotected Al surface. A series of CV analyses were conducted to evaluate the stability of the passivation layer,

following the procedure shown in **Figure 4-21**. Initially, 10 cycles of CV measurements were performed without intervals to passivate the Al electrode. Then, a rest step of 12 h was set before each cycle until the end of 15th cycle. If the passivation layer cannot be maintained well during the interval, additional reactions occur to reconstruct the passivation layer. **Figure 4-22** compares the changes of total charges for stability tests in these four electrolytes from 10th to 15th cycle. An increase of total charges is observed for electrolytes with a low Li[FSA] fraction, especially in the [C₂C₁im]-based electrolyte. Moreover, a marked increase in total charge can be found in Li_{0.4}[C₂C₁im]_{0.6}[FSA] electrolyte at 13th cycle, meaning the partial detachment of the passivation layer, which likely occurs during the previous interval. The total charges for Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] electrolyte remain constantly low without an obvious increase, indicating minimal charges participate in the repetitive CV scans and the stable passivation layer forms. The passivation ability toward the Al electrode for the [C₃C₁pyrr]-based IL is superior to that of the [C₂C₁im]-based IL, which also supports the high CE for the Li/LNO cells with Li_{0.4}[C₂C₁im]_{0.6}[FSA] electrolyte.

XPS with Ar⁺ sputtering was performed on the Al electrode to investigate the characteristics of the passivation layer formed in these electrolytes. **Figure 4-23** shows the Al 2p XPS spectra of the Al electrode with different etching times (0, 10, 20, 30, and 60 s) after the first cycle of the CV test. All electrodes exhibit the peak of metallic Al at ~72.8 eV. The changes in peak intensity of metallic Al can provide insights into the thickness of the passivation layer; a shorter etching time to detect metallic Al

indicates a thinner passivation layer, as the underlying Al is exposed more quickly due to the loss of the native Al_2O_3 as discussed above (**Figure 4-12**), and the newly formed passivation layer. For $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte, metallic Al is detected when the etching time is 60 s, suggesting a thicker passivation layer. Although less etching time is needed for $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ electrolyte, the passivation layer remains thicker compared to that formed in $[\text{C}_3\text{C}_1\text{pyrr}]$ -based electrolyte.

Raman spectra were collected to analyze coordination structures of investigated electrolytes. **Figure 4-24** shows the S-N-S bending mode of $[\text{FSA}]^-$ in $[\text{C}_3\text{C}_1\text{pyrr}]$ -based electrolytes in the region of $680\text{-}800\text{ cm}^{-1}$ (see **Figure 4-25** for the selected region of $[\text{C}_2\text{C}_1\text{im}]$ -based electrolyte and **Figure 4-26** for overall Raman spectra of four electrolytes). The peaks appearing in this region are assigned to free $[\text{FSA}]^-$ and coordinated $[\text{FSA}]^-$. The blue shift of $[\text{FSA}]^-$ band observed at the high fraction of $\text{Li}[\text{FSA}]$ matches the literature [51, 52]. The proportion of free $[\text{FSA}]^-$ to coordinated $[\text{FSA}]^-$ can be calculated according to peak areas. The ratio of coordinated $[\text{FSA}]^-$ increases with increasing $\text{Li}[\text{FSA}]$ fraction from 62% to 93%. The free $[\text{FSA}]^-$ has a stronger Lewis basicity than the coordinated $[\text{FSA}]^-$ and a higher reactivity to Al^{3+} , accelerating Al corrosion. A high ratio of coordinated $[\text{FSA}]^-$ (the low ratio of free $[\text{FSA}]^-$) indicates a lower probability of corrosion [53]. Therefore, the suppression of Al corrosion in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte can be attributed to the low ratio of free $[\text{FSA}]^-$ to coordinated $[\text{FSA}]^-$. Besides, with a higher proportion of free $[\text{FSA}]^-$, the Al corrosion in $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ is more severe compared to

Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] electrolyte. However, the variation ratio of free [FSA][−] to coordinated [FSA][−] is not sufficient to explain the difference in the Al corrosion behavior between [C₃C₁pyrr]-based electrolyte and [C₂C₁im]-based electrolyte, because obvious pitting corrosion is observed on the surface of Al electrode in Li_{0.4}[C₂C₁im]_{0.6}[FSA] electrolyte with less free [FSA][−]. One possible reason is the lower anodic stability of [C₂C₁im]⁺ compared to [C₃C₁pyrr]⁺, which results in decomposition species that may impede the passivation process of the Al electrode. Another is the passivation layer formed in [C₃C₁pyrr]-based electrolyte may contain advantageous components that effectively retard side reactions and promote Al passivation, contrasting with [C₂C₁im]-based electrolyte. Therefore, the thin passivation layer formed in Li_{0.4}[C₃C₁pyrr]_{0.6}[FSA] electrolyte can mitigate Al corrosion to an extent. It is worth exploring the impact of different cations in Al corrosion from exhaustive perspectives for future studies.

Figure 4-27 illustrates the corrosion mechanism of the Al current collector focusing on [C₃C₁pyrr]-based electrolyte. Free [FSA][−] diffuses from the bulk electrolyte to the Al electrode, attacking the native Al₂O₃ layer as the active anion. This interaction causes Al₂O₃ to generate O₂ and Al³⁺, with Al³⁺ subsequently participating in continuous reactions to form Al[anion]_n^{(3−n)+} or Al[solvent] complexes [54]. In Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] electrolyte, more free [FSA][−] attack the Al electrode causing more severe Al corrosion. Besides, the progress of the passivation layer formation depends on the fraction of Li[FSA]. For Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] electrolyte, it takes

several cycles to form a passivation layer. In contrast, with a higher fraction of Li[FSA], the formation of the passivation layer starts from the first cycle in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte. Furthermore, the passivation layer formed in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte is more stable to resist Al corrosion.

4.4 Conclusions

In summary, this chapter demonstrated an electrolyte manipulation method to significantly improve the electrochemical properties and stability of the LNO positive electrode as well as the Al current collector. The adoption of Li[FSA]-based IL electrolytes overcomes the challenge faced by the unstable LiPF_6 -based electrolytes (unavoidable transitional metal dissolution for positive electrodes). The highly concentrated IL electrolyte, $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$, enables the prolonged cycling of Li/LNO cells, demonstrating an excellent capacity retention of 73.1% over 500 cycles and a superior average CE exceeding 99.9%. Further SEM, XRF, and XPS results indicate that the outstanding performance is attributed to the mitigated Ni dissolution and stable CEI layer formed in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$. The $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte also shows good compatibility with the Al current collector even in the presence of aggressive $[\text{FSA}]^-$. Owing to its peculiar solvation structures, less free $[\text{FSA}]^-$ attacks and corrode Al surface. Different from the electrolyte with a low fraction of Li[FSA] and $[\text{C}_2\text{C}_1\text{im}]$ -based electrolytes, this electrolyte shows an effective passivation process and facilitates the formation of a robust passivation layer.

Furthermore, the good thermal stability and low flammability of highly concentrated IL electrolytes mitigate the safety risk for high-voltage batteries compared to conventional electrolytes. Although the costs of IL and Li salt, particularly at high concentrations, are a remaining issue, recent industrial efforts have been addressing this issue. Therefore, these findings might guide the exploration and development of [FSA]-based IL electrolytes, contributing to the advancement of stable and safe high-voltage batteries.

Table 4-1. Quantitative analysis of Ni dissolved in Li/LNO cells with different electrolytes after 100 cycles at 1C. Voltage range: 2.7-4.3 V.

	Li _{0.4} [C ₃ C ₁ pyrr] _{0.6} [FSA]	Li _{0.2} [C ₃ C ₁ pyrr] _{0.8} [FSA]	LiPF ₆ - EC/DMC
Mass of LNO (mg)	1.4080	1.4144	1.4208
Ni content in LNO (mg)	0.8464	0.8503	0.8541
Dissolved Ni (mg)	0.0043	0.0161	0.0429
Dissolved percent (%)	0.50	1.89	5.02

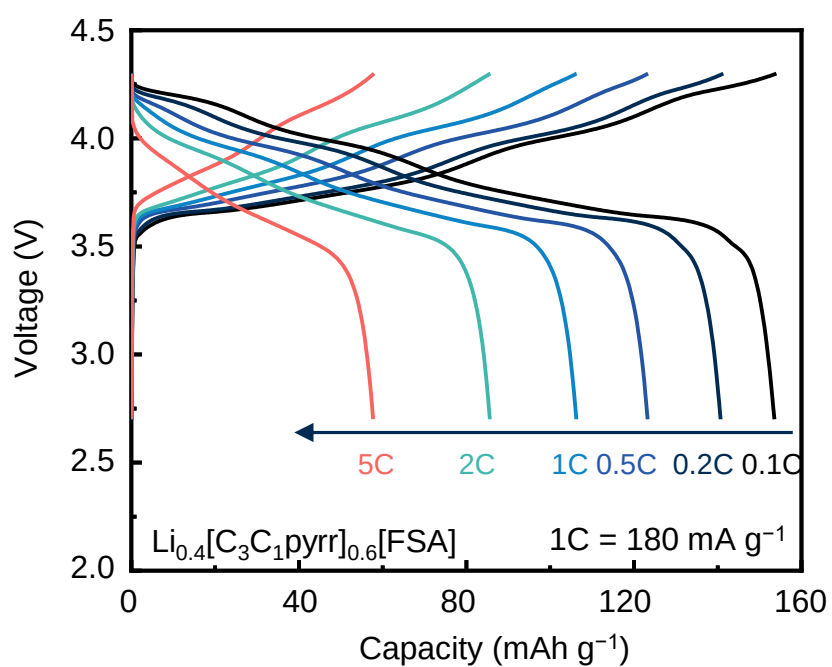


Figure 4-1. Charge-discharge curves of the Li/LNO cell with $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ at different C rates, increasing from 0.1C to 5C ($1\text{C} = 180 \text{ mA g}^{-1}$).

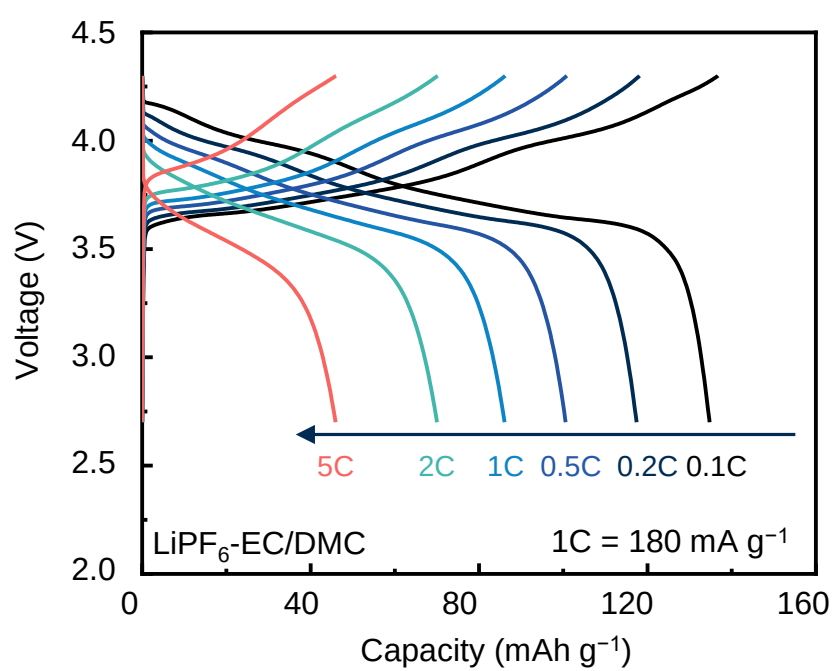


Figure 4-2. Charge-discharge curves of the Li/LNO cell with LiPF₆-EC/DMC at different C rates from 0.1C to 5C (1C = 180 mA g⁻¹).

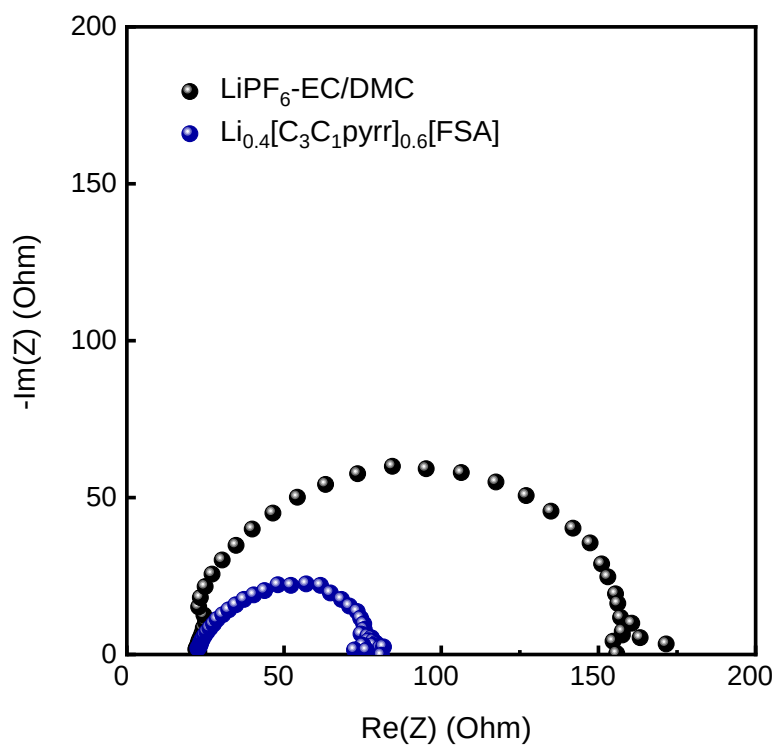


Figure 4-3. EIS spectra of the Li/LNO cells with $\text{LiPF}_6\text{-EC/DMC}$ and $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ after 200 cycles tested at 1C.

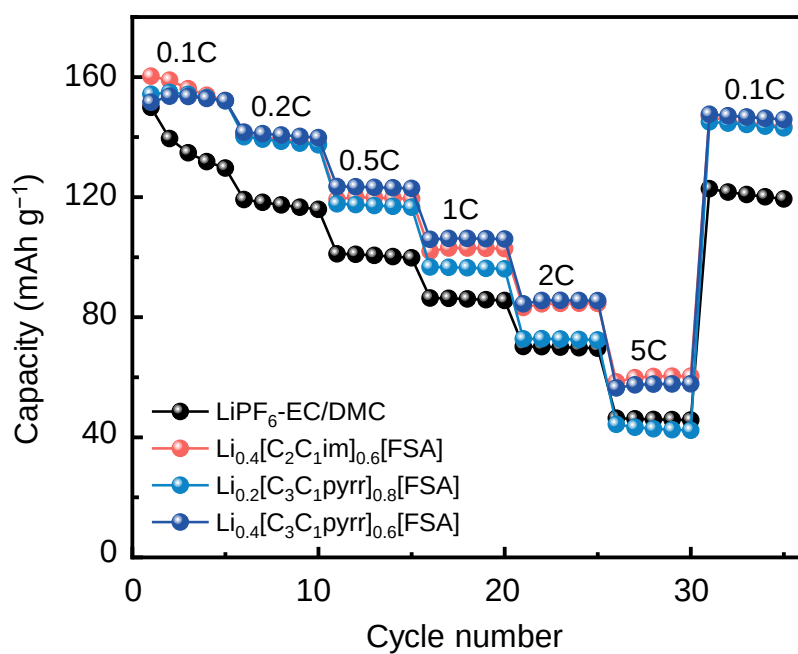


Figure 4-4. Rate capability of the Li/LNO cells with different electrolytes.

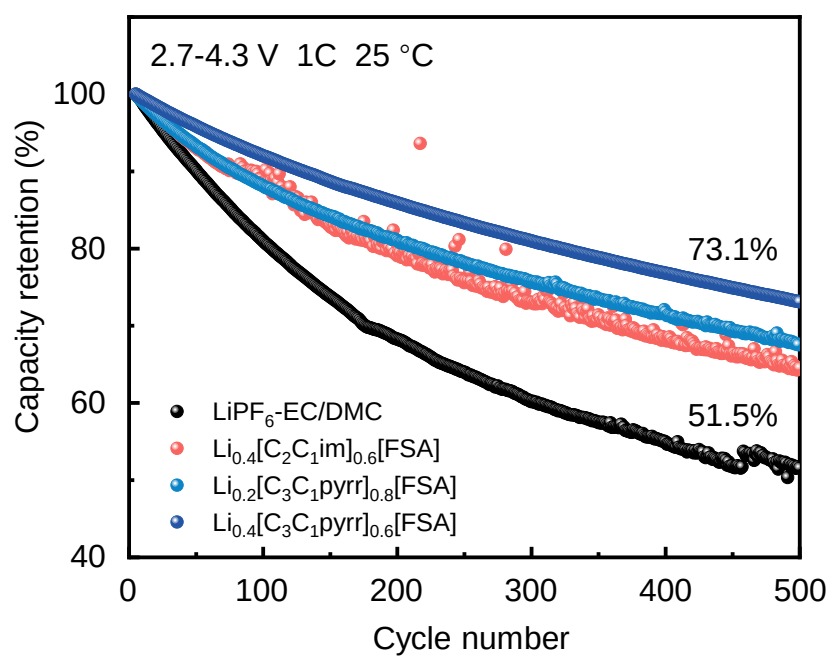


Figure 4-5. Capacity retention of the Li/LNO cell during cycling with four electrolytes.

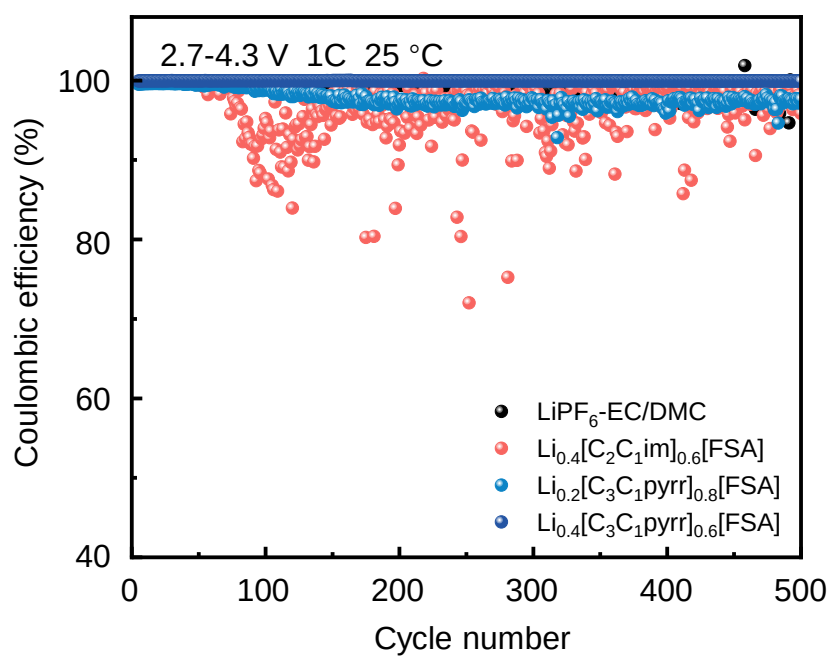


Figure 4-6. Coulombic efficiencies of the Li/LNO cell during cycling with four electrolytes.

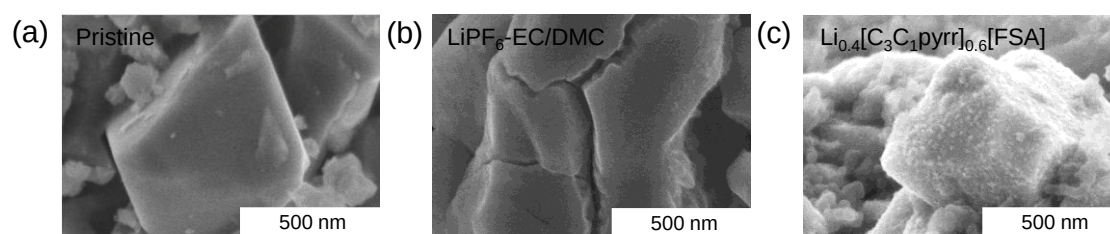


Figure 4-7. (a) An FE-SEM image of the pristine LNO particles. FE-SEM images of the LNO positive electrode after 10 cycles in (b) $\text{LiPF}_6\text{-EC/DMC}$ and (c) $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$.

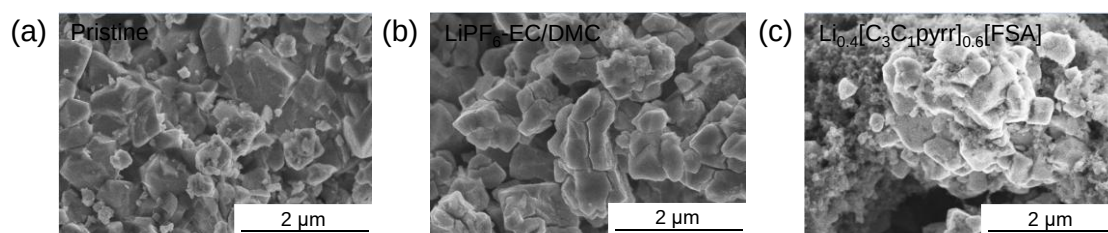


Figure 4-8. FE-SEM images of (a) pristine LNO particles, LNO positive electrode after 10 cycles in (b) $\text{LiPF}_6\text{-EC/DMC}$ electrolyte, and (c) $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte at lower magnifications.

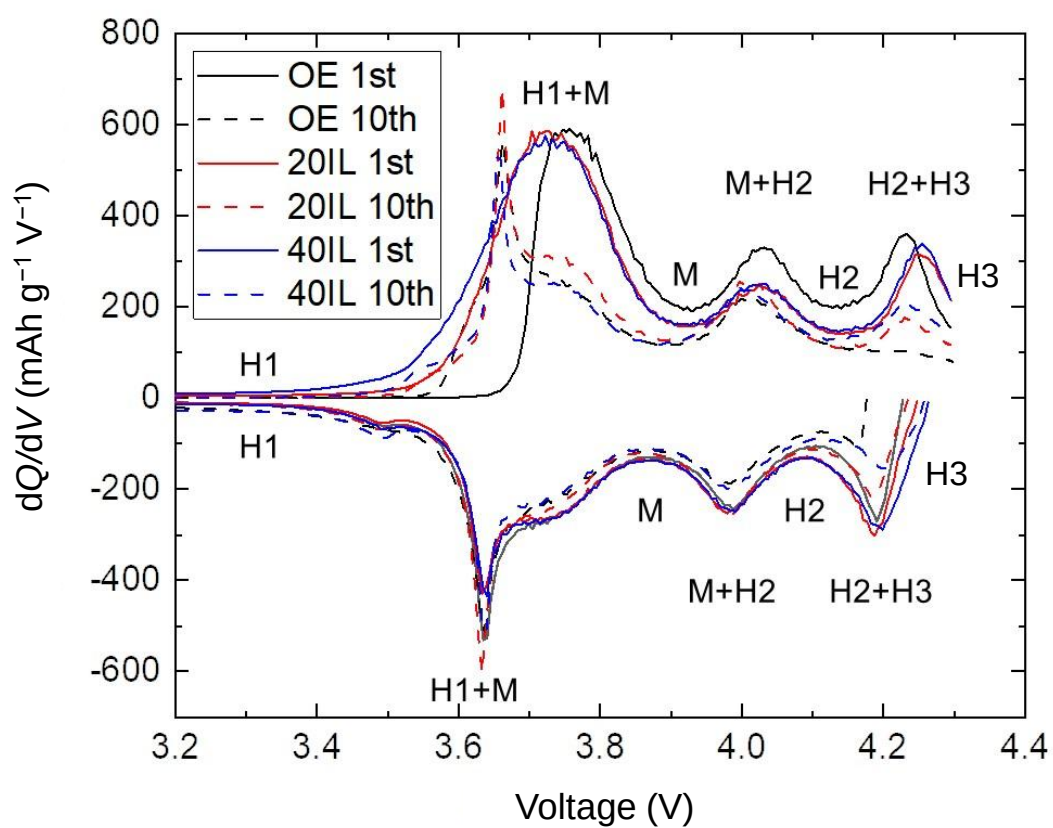


Figure 4-9. Differential capacity analysis of cycled Li | LNO cells in different electrolytes. OE: $\text{LiPF}_6\text{-EC/DMC}$, 20 IL: $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$, and 40 IL: $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte. C-rate: 0.1C.

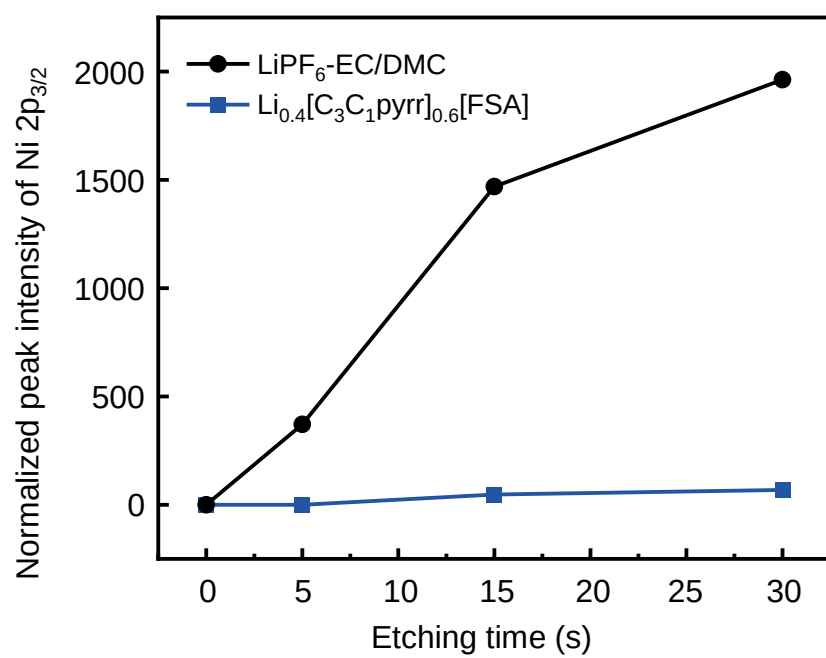


Figure 4-10. Etching time dependency of the Ni 2p_{3/2} XPS peak intensity for the LNO electrode after 10 cycles.

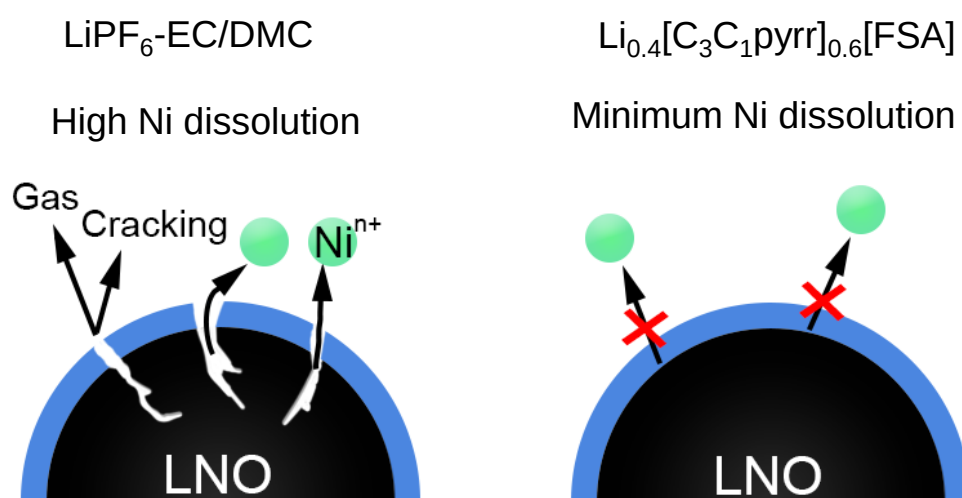


Figure 4-11. Schematic illustrations of Ni dissolution from LNO electrode in $\text{LiPF}_6\text{-EC/DMC}$ and $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$.

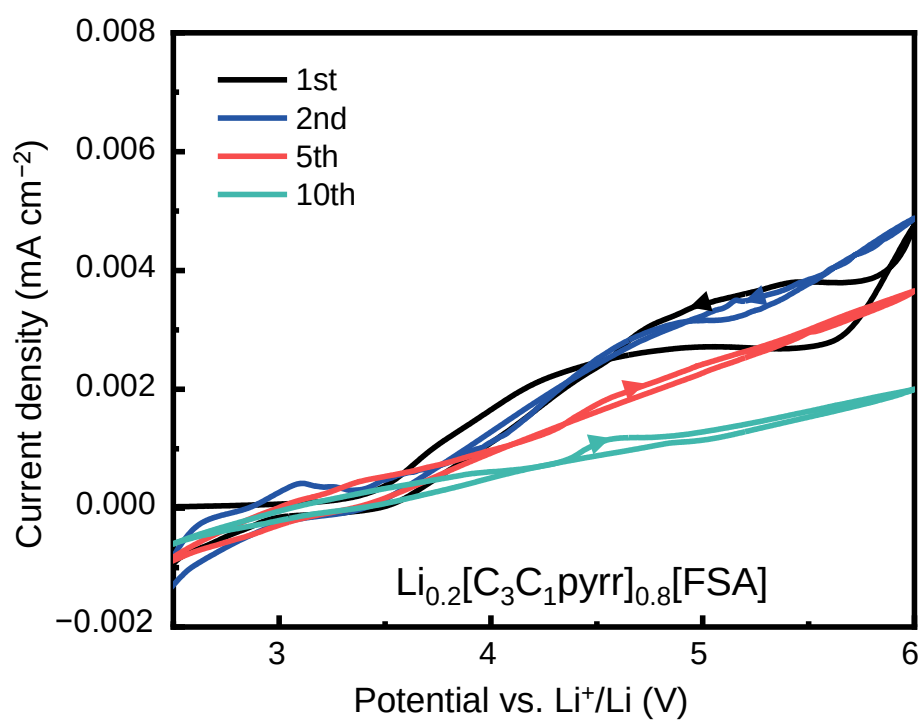


Figure 4-12. CV curves of an Al electrode in Li_{0.2}[C₃C₁pyrr]_{0.8}[FSA] electrolyte. Scan rate: 0.5 mV s⁻¹.

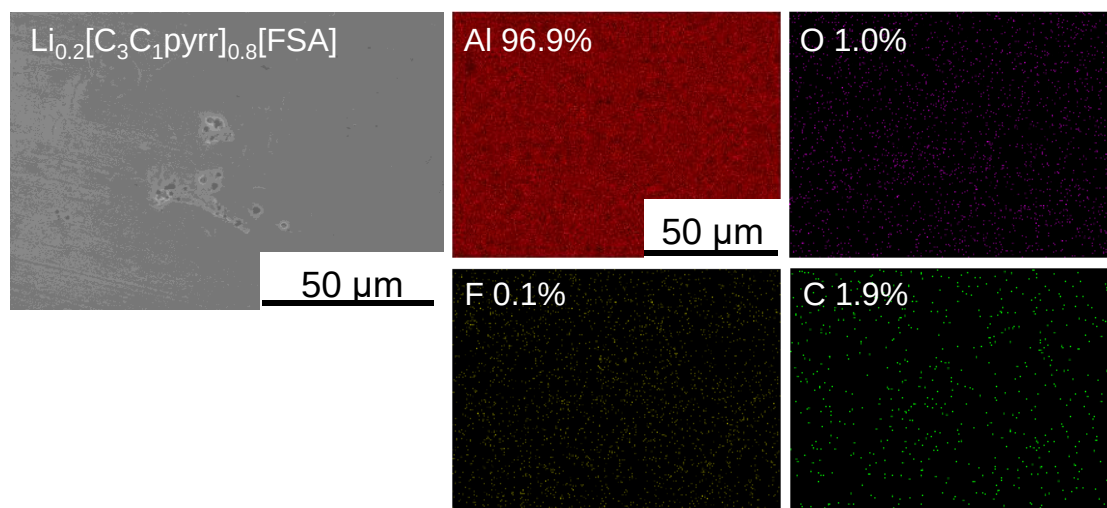


Figure 4-13. FE-SEM and EDX mapping images for the Al electrode after 10 cycles of CV measurements in the $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$ electrolyte.

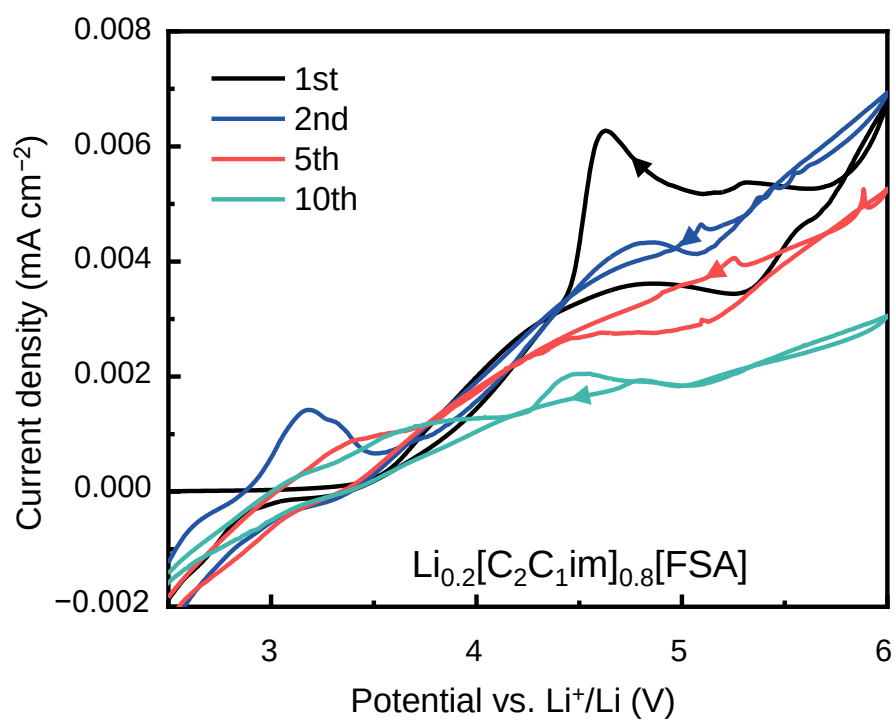


Figure 4-14. CV curves of an Al electrode in $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte. Scan rate: 0.5 mV s^{-1} .

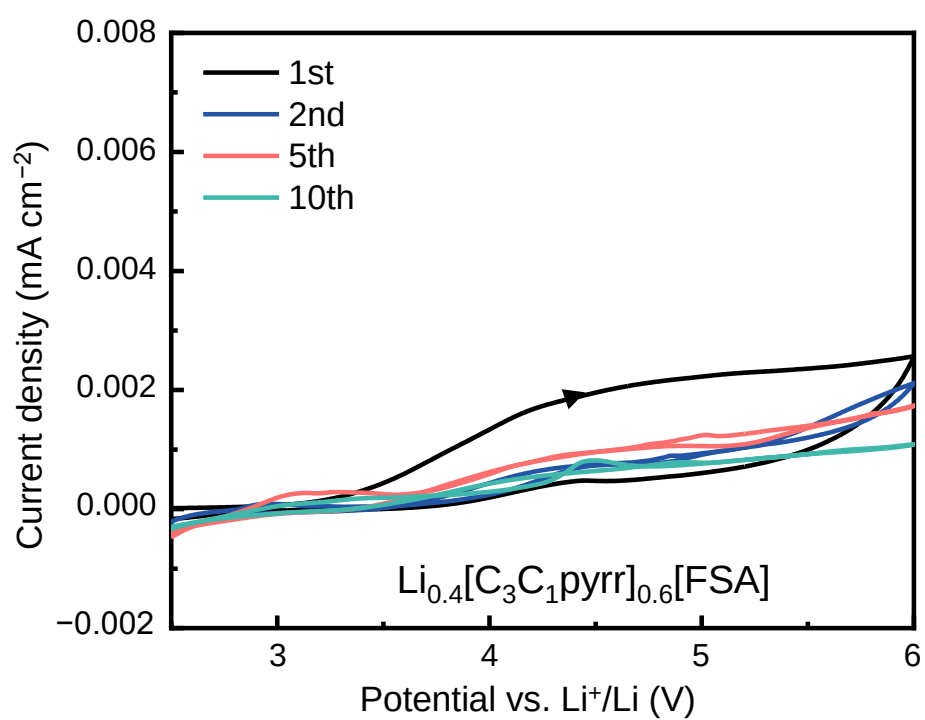


Figure 4-15. CV curves of an Al electrode in $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte. Scan rate: 0.5 mV s^{-1} .

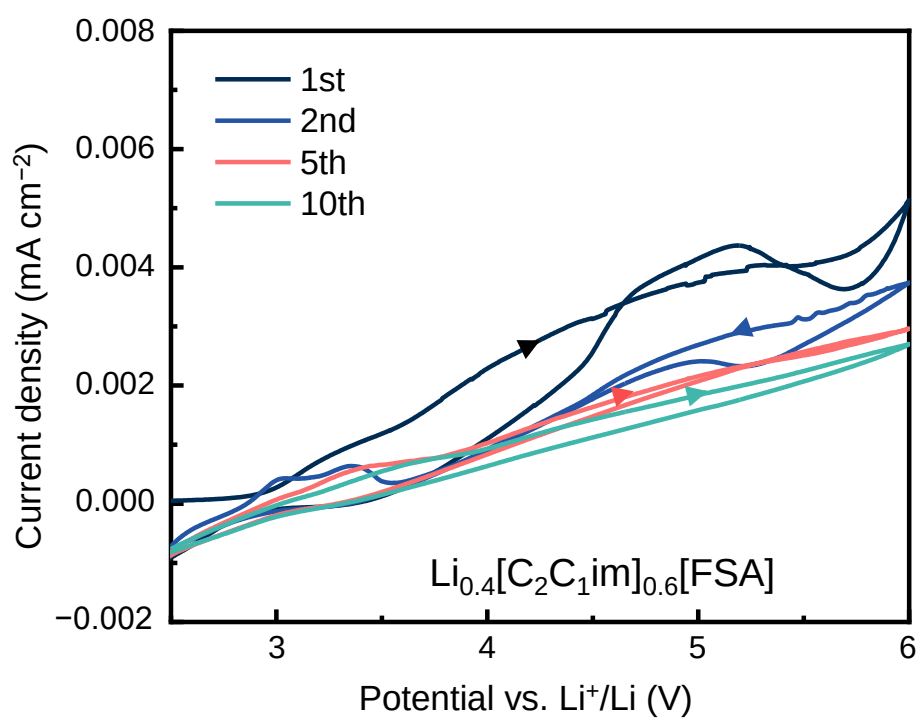


Figure 4-16. CV curves of an Al electrode in $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$ electrolyte. Scan rate: 0.5 mV s^{-1} .

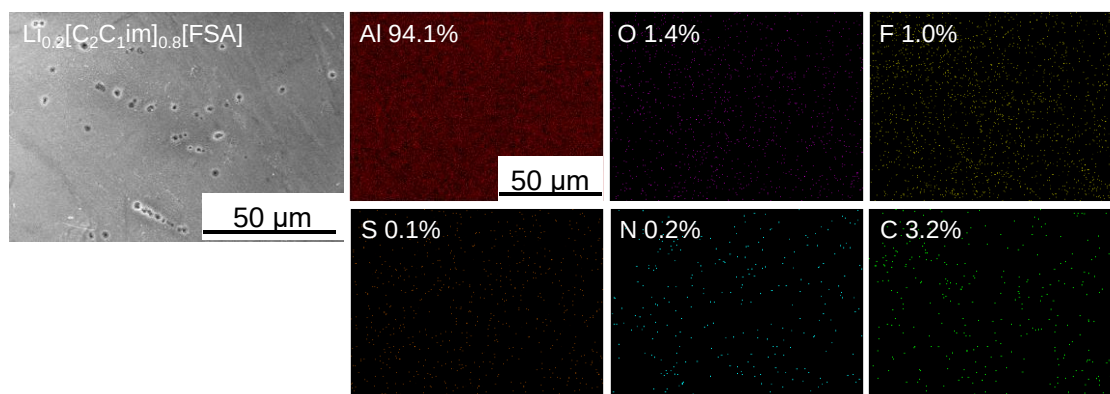


Figure 4-17. FE-SEM and EDX mapping images for the Al electrode after 10 cycles of CV measurements in the $\text{Li}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{FSA}]$ electrolyte.

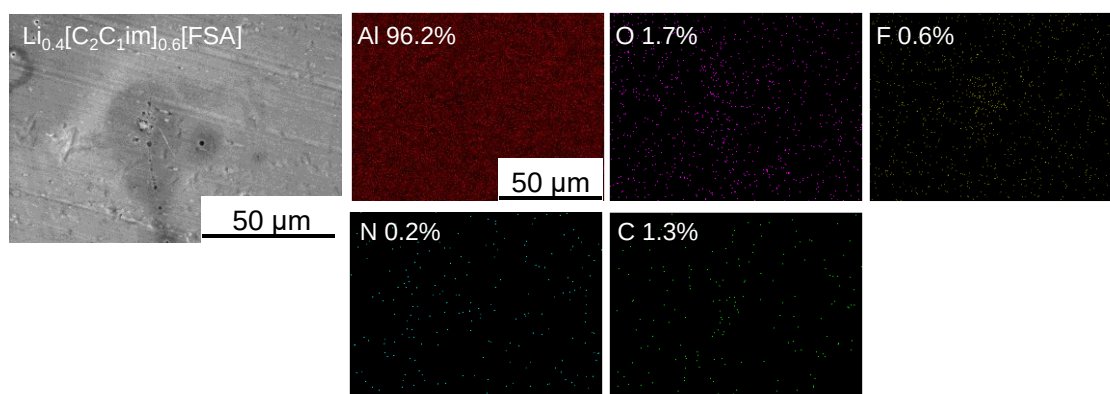


Figure 4-18. FE-SEM and EDX mapping images for the Al electrode after 10 cycles of CV measurements in the Li_{0.4}[C₂C₁im]_{0.6}[FSA] electrolyte.

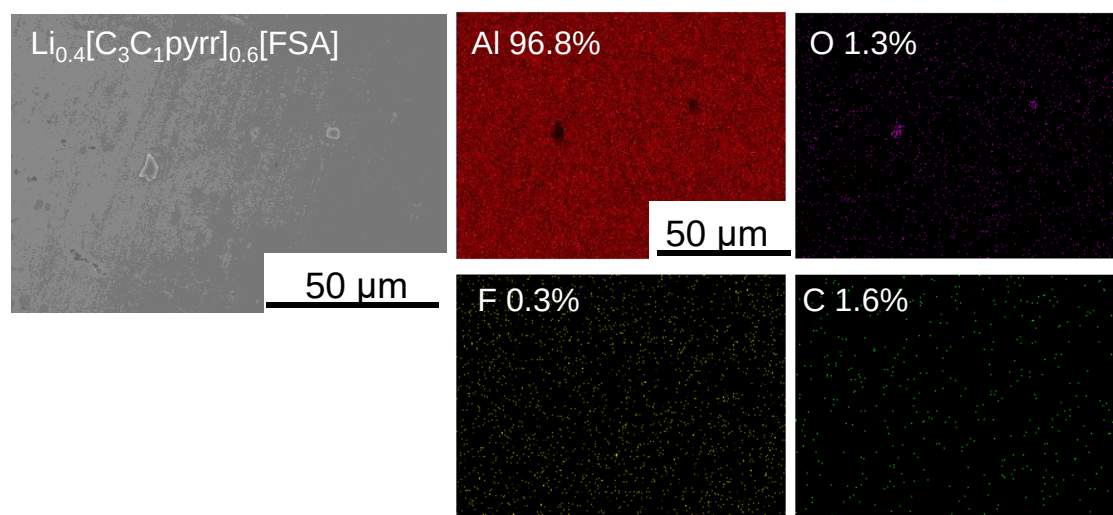


Figure 4-19. FE-SEM and EDX mapping images for the Al electrode after 10 cycles of CV measurements in the $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$ electrolyte.

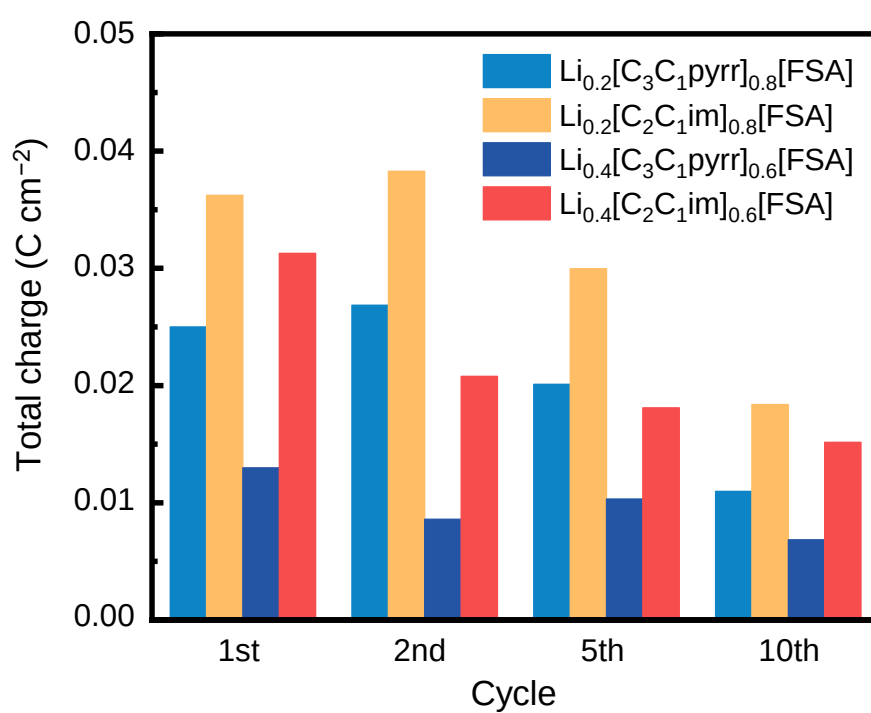


Figure 4-20. Summary of total charges during the anodic scans from the CV data in different electrolytes.

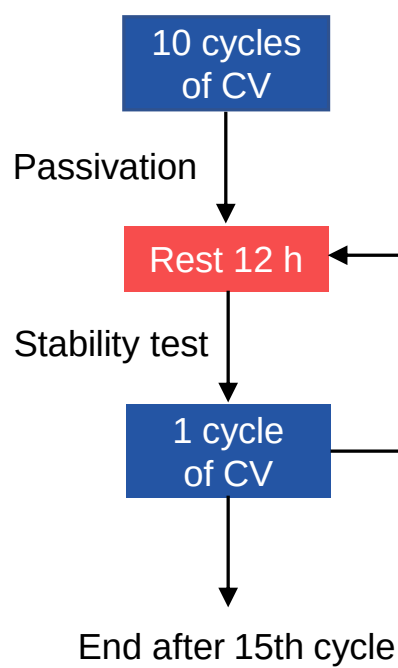


Figure 4-21. The procedure of the passivation layer stability test.

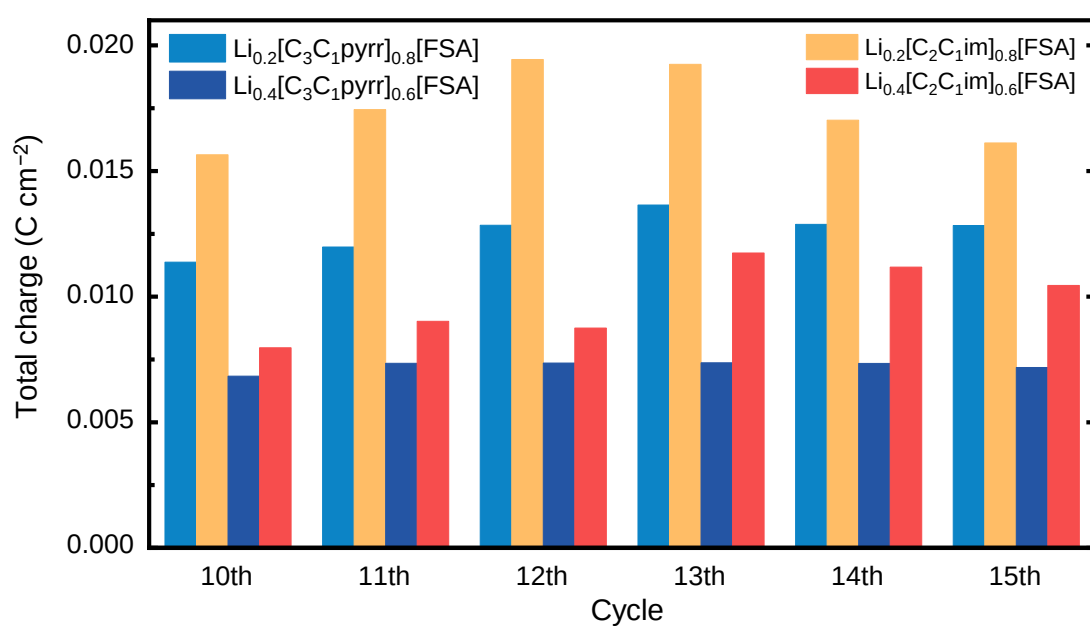


Figure 4-22. Comparison of total charges during the anodic scans from the CV data for the stability tests in different electrolytes.

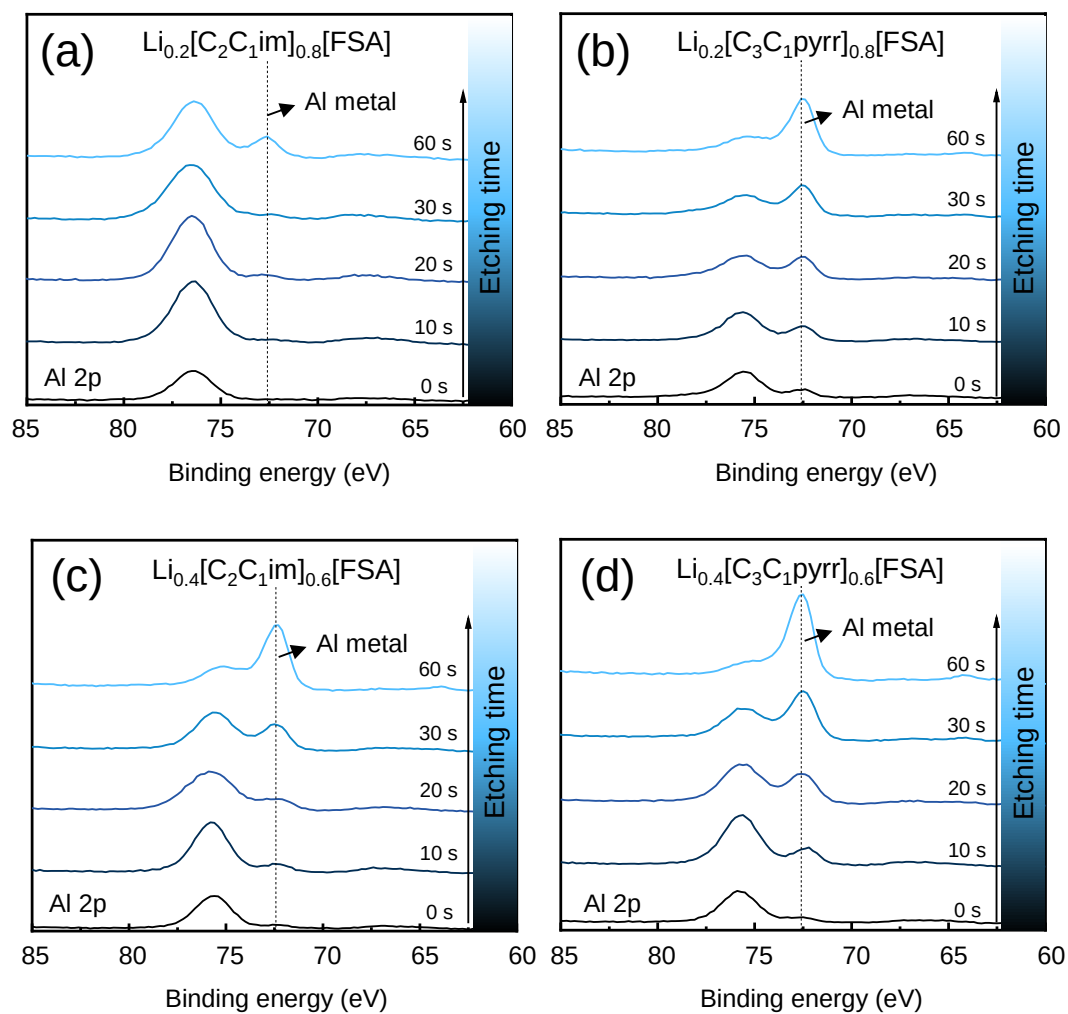


Figure 4-23. Al 2p XPS depth profiles of an Al electrode after the first cycle of CV measurements in (a) $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$, (b) $\text{Li}_{0.2}[\text{C}_3\text{C}_1\text{pyrr}]_{0.8}[\text{FSA}]$, (c) $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{FSA}]$, and (d) $\text{Li}_{0.4}[\text{C}_3\text{C}_1\text{pyrr}]_{0.6}[\text{FSA}]$.

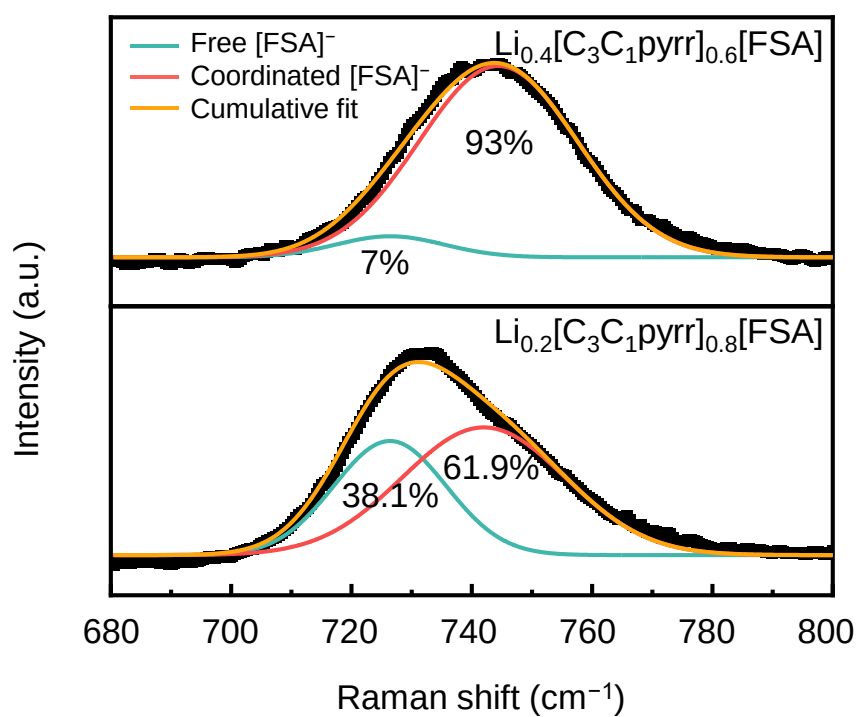


Figure 4-24. Raman spectra of $[\text{C}_3\text{C}_1\text{pyrr}]$ -based IL electrolytes from 680 to 800 cm^{-1} .

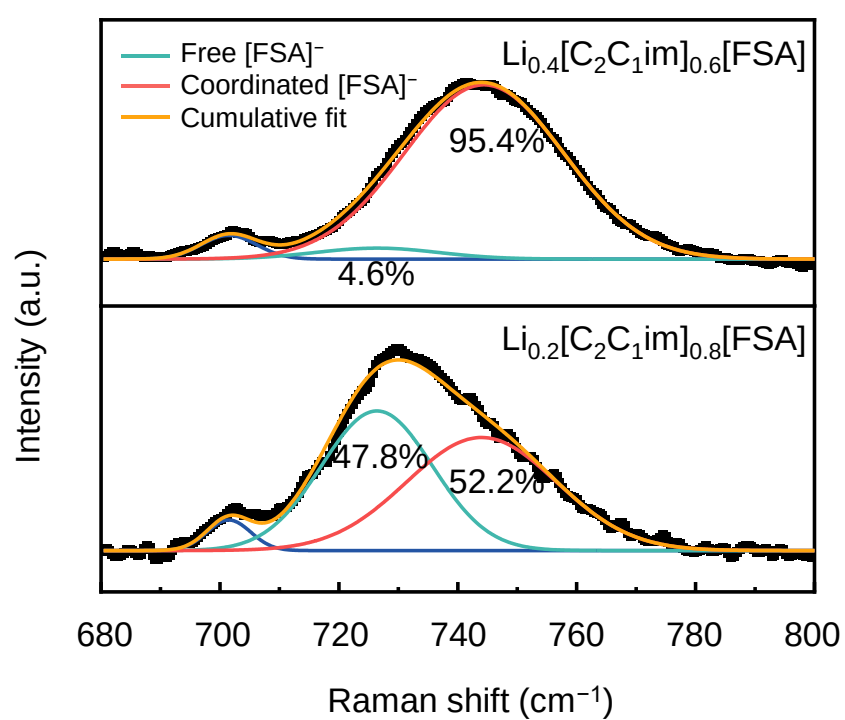


Figure 4-25. Raman spectra of [C₂C₁im]-based IL electrolytes from 680 to 800 cm⁻¹.

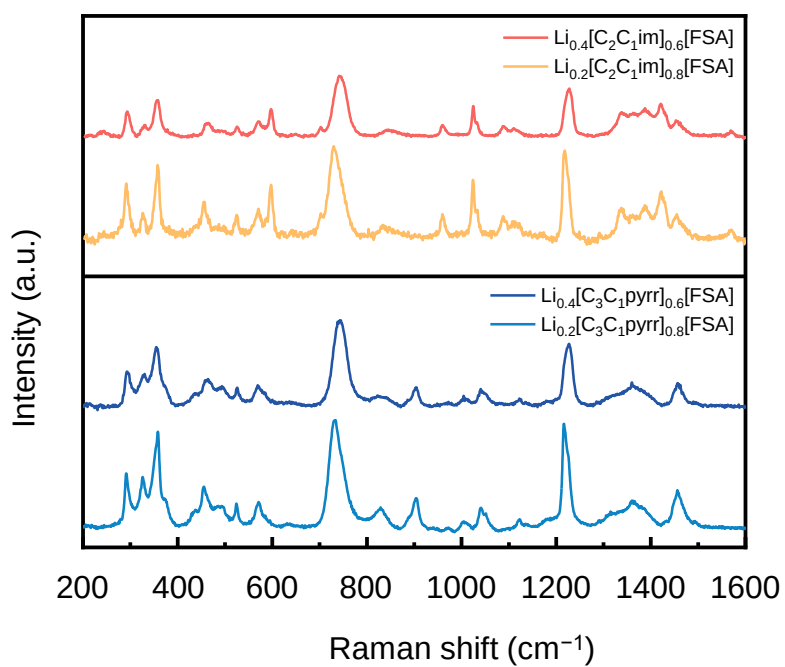


Figure 4-26. Raman spectra of four electrolytes in the range of 200-1600 cm^{-1} .

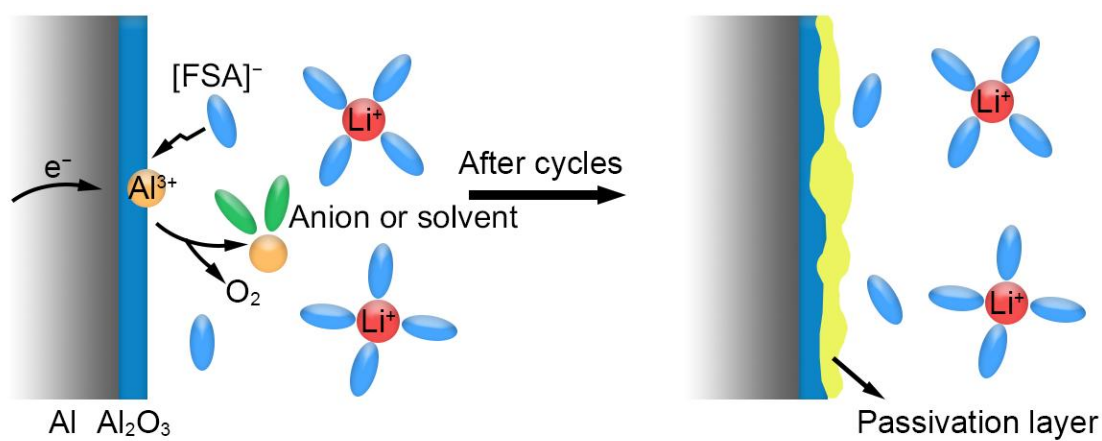


Figure 4-27. Schematic representation of Al corrosion mechanism. Since the dissolved Al^{3+} species are not defined with $[\text{FSA}]^-$, the coordinating species are shown with green color. We call this $\text{Al}[\text{anion}]_n^{(3-n)+}$ or $\text{Al}[\text{solvent}]$ complexes in this study.

References

- [1] J. Duan, X. Tang, H. Dai, Y. Yang, W. Wu, X. Wei and Y. Huang, *Electrochem. Energy Rev.*, **3** (2020) 1-42.
- [2] X. Chen, Y. Meng, D. Xiao and L. Qin, *ACS Appl. Mater. Interfaces*, **16** (2024) 24464-24472.
- [3] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines and P. Anderson, *Nature*, **575** (2019) 75-86.
- [4] Y. Zhang, H. Li, J. Liu, J. Liu, H. Ma and F. Cheng, *J. Energy Chem.*, **63** (2021) 312-319.
- [5] J. Neubauer, A. Pesaran, C. Bae, R. Elder and B. Cunningham, *J. Power Sources*, **271** (2014) 614-621.
- [6] J.W. Choi and D. Aurbach, *Nat. Rev. Mater.*, **1** (2016) 16013.
- [7] U.-H. Kim, G.-T. Park, B.-K. Son, G.W. Nam, J. Liu, L.-Y. Kuo, P. Kaghazchi, C.S. Yoon and Y.-K. Sun, *Nat. Energy*, **5** (2020) 860-869.
- [8] J. Liu, J. Wang, Y. Ni, J. Liu, Y. Zhang, Y. Lu, Z. Yan, K. Zhang, Q. Zhao, F. Cheng and J. Chen, *Angew. Chem. Int. Ed.*, **61** (2022) e202207000.
- [9] F. Kong, C. Liang, L. Wang, Y. Zheng, S. Peranathan, R.C. Longo, J.P. Ferraris, M. Kim and K. Cho, *Adv. Energy Mater.*, **9** (2019) 1802586.
- [10] H. Li, W. Hua, X. Liu-Théato, Q. Fu, M. Desmau, A. Missyul, M. Knapp, H. Ehrenberg and S. Indris, *Chem. Mater.*, **33** (2021) 9546-9559.

- [11] C.S. Yoon, M.-J. Choi, D.-W. Jun, Q. Zhang, P. Kaghazchi, K.-H. Kim and Y.-K. Sun, *Chem. Mater.*, **30** (2018) 1808-1814.
- [12] W.-C. Zheng, J.-X. Lin, H. Chen, S.-S. Liu, C.-G. Shi, L. Huang and S.-G. Sun, *Chem. Eng. J.*, **472** (2023) 144890.
- [13] W. Liu, P. Oh, X. Liu, M.-J. Lee, W. Cho, S. Chae, Y. Kim and J. Cho, *Angew. Chem. Int. Ed.*, **54** (2015) 4440-4457.
- [14] C.S. Yoon, D.-W. Jun, S.-T. Myung and Y.-K. Sun, *ACS Energy Lett.*, **2** (2017) 1150-1155.
- [15] S.-T. Myung, K. Amine and Y.-K. Sun, *J. Mater. Chem.*, **20** (2010) 7074-7095.
- [16] M. Bianchini, M. Roca-Ayats, P. Hartmann, T. Brezesinski and J. Janek, *Angew. Chem. Int. Ed.*, **58** (2019) 10434-10458.
- [17] J. Liu, J. Wang, Y. Ni, K. Zhang, F. Cheng and J. Chen, *Mater. Today*, **43** (2021) 132-165.
- [18] J. Li and A. Manthiram, *Adv. Energy Mater.*, **9** (2019) 1902731.
- [19] D.-W. Jun, C.S. Yoon, U.-H. Kim and Y.-K. Sun, *Chem. Mater.*, **29** (2017) 5048-5052.
- [20] X. Zeng, C. Zhan, J. Lu and K. Amine, *Chem*, **4** (2018) 690-704.
- [21] L. Mu, R. Zhang, W.H. Kan, Y. Zhang, L. Li, C. Kuai, B. Zydlewski, M.M. Rahman, C.-J. Sun, S. Sainio, M. Avdeev, D. Nordlund, H.L. Xin and F. Lin, *Chem. Mater.*, **31** (2019) 9769-9776.

- [22] H. Gao, T. Ma, T. Duong, L. Wang, X. He, I. Lyubinetzky, Z. Feng, F. Maglia, P. Lamp, K. Amine and Z. Chen, *Mater. Today Energy*, **7** (2018) 18-26.
- [23] Y. Yamada, J. Wang, S. Ko, E. Watanabe and A. Yamada, *Nat. Energy*, **4** (2019) 269-280.
- [24] L. Su, K. Jarvis, H. Charalambous, A. Dolocan and A. Manthiram, *Adv. Funct. Mater.*, **33** (2023) 2213675.
- [25] S.S. Zhang, *Energy Storage Mater.*, **24** (2020) 247-254.
- [26] M. Hasanpoor, D. Saurel, R.C. Barreno, K. Fraysse, M. Echeverría, M. Jáuregui, F. Bonilla, G.W. Greene, R. Kerr, M. Forsyth and P.C. Howlett, *ACS Appl. Mater. Interfaces*, **14** (2022) 13196-13205.
- [27] R. Pan, E. Jo, Z. Cui and A. Manthiram, *Adv. Funct. Mater.*, **33** (2023) 2211461.
- [28] H.-B. Han, S.-S. Zhou, D.-J. Zhang, S.-W. Feng, L.-F. Li, K. Liu, W.-F. Feng, J. Nie, H. Li, X.-J. Huang, M. Armand and Z.-B. Zhou, *J. Power Sources*, **196** (2011) 3623-3632.
- [29] L. Qiao, U. Oteo, M. Martinez-Ibañez, A. Santiago, R. Cid, E. Sanchez-Diez, E. Lobato, L. Meabe, M. Armand and H. Zhang, *Nat. Mater.*, **21** (2022) 455-462.
- [30] Y.-Y. Wang, X.-Q. Zhang, M.-Y. Zhou and J.-Q. Huang, *Nano Res. Energy*, **2** (2023) e9120046.
- [31] P. Du, D. Liu, X. Chen, H. Xie, X. Qu, D. Wang and H. Yin, *Energy Storage Mater.*, **57** (2023) 371-399.

- [32] X. Chen, Y. Meng, D. Xiao, Y. Wu and L. Qin, *Energy Storage Mater.*, **61** (2023) 102923.
- [33] M. Kunze, S. Jeong, E. Paillard, M. Schönhoff, M. Winter and S. Passerini, *Adv. Energy Mater.*, **1** (2011) 274-281.
- [34] Y. Zheng, D. Wang, S. Kaushik, S. Zhang, T. Wada, J. Hwang, K. Matsumoto and R. Hagiwara, *EnergyChem*, **4** (2022) 100075.
- [35] H. Liu, J. Hwang, K. Matsumoto and R. Hagiwara, *ACS Appl. Mater. Interfaces*, **15** (2023) 35062-35071.
- [36] J.L. Allen, D.W. McOwen, S.A. Delp, E.T. Fox, J.S. Dickmann, S.-D. Han, Z.-B. Zhou, T.R. Jow and W.A. Henderson, *J. Power Sources*, **237** (2013) 104-111.
- [37] S. Theivaprakasam, G. Girard, P. Howlett, M. Forsyth, S. Mitra and D. MacFarlane, *npj Mater. Degrad.*, **2** (2018) 13.
- [38] Q. Liu, T.L. Dzwiniel, K.Z. Pupek and Z. Zhang, *J. Electrochem. Soc.*, **166** (2019) A3959.
- [39] J. Li, S. Jeong, R. Kloepsch, M. Winter and S. Passerini, *J. Power Sources*, **239** (2013) 490-495.
- [40] F. Wu, G.-T. Kim, T. Diemant, M. Kuenzel, A.R. Schür, X. Gao, B. Qin, D. Alwast, Z. Jusys, R.J. Behm, D. Geiger, U. Kaiser and S. Passerini, *Adv. Energy Mater.*, **10** (2020) 2001830.
- [41] Y. Chu, J. Zhou, W. Liu, F. Chu, J. Li and F. Wu, *Small Sci.*, **3** (2023) 2300023.
- [42] P. Vanaphuti, Z. Cui and A. Manthiram, *Adv. Funct. Mater.*, **34** (2024) 2308619.

- [43] T. Deng, X. Fan, L. Cao, J. Chen, S. Hou, X. Ji, L. Chen, S. Li, X. Zhou and E. Hu, *Joule*, **3** (2019) 2550-2564.
- [44] Q. Xie, Z. Cui and A. Manthiram, *Adv. Mater.*, **33** (2021) 2100804.
- [45] C. Xu, P.J. Reeves, Q. Jacquet and C.P. Grey, *Adv. Energy Mater.*, **11** (2021) 2003404.
- [46] U.-H. Kim, E.-J. Lee, C.S. Yoon, S.-T. Myung and Y.-K. Sun, *Adv. Energy Mater.*, **6** (2016) 1601417.
- [47] Z. Guo, Z. Cui, R. Sim and A. Manthiram, *Small*, **19** (2023) 2305055.
- [48] F. Schipper, E.M. Erickson, C. Erk, J.-Y. Shin, F.F. Chesneau and D. Aurbach, *J. Electrochem. Soc.*, **164** (2016) A6220.
- [49] E. Cho, J. Mun, O.B. Chae, O.M. Kwon, H.-T. Kim, J.H. Ryu, Y.G. Kim and S.M. Oh, *Electrochem. Commun.*, **22** (2012) 1-3.
- [50] A. Celik-Kucuk and T. Abe, *J. Power Sources*, **556** (2023) 232520.
- [51] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama and A. Yamada, *J. Am. Chem. Soc.*, **136** (2014) 5039-5046.
- [52] A.K. Chan, R. Tatara, S. Feng, P. Karayaylali, J. Lopez, I.E. Stephens and Y. Shao-Horn, *J. Electrochem. Soc.*, **166** (2019) A1867.
- [53] J. Wang, Y. Yamada, K. Sodeyama, C.H. Chiang, Y. Tateyama and A. Yamada, *Nat. Commun.*, **7** (2016) 12032.
- [54] S. Yang, J. Zhong, S. Li and B. Li, *J. Energy Chem.*, **89** (2024) 610-634.

Chapter 5

Failure Mechanisms of Aluminum Passivation in Preventing Corrosion in Bis(fluorosulfonyl)amide-based Electrolytes

5.1 Introduction

Lithium-ion batteries (LIBs) have revolutionized energy storage systems with their high energy density, long lifespan, and widespread application in portable electronics and electric vehicles (EVs) [1, 2]. As global demand for high-performance energy storage increases, especially for EVs, the development of LIBs with higher energy densities and high operating voltage has become a key focus to meet these growing requirements [3, 4]. While extensive research has been conducted to enhance the performance of electrode materials and electrolytes, the role of the Al current collector, an essential yet often overlooked component, warrants more attention [5-8]. Corrosion of Al current collectors under high-voltage cycling compromises the stability of battery components, leading to increased interfacial resistance, capacity loss, and safety risks, ultimately impairing their long-term performance [9, 10].

The Al current collector is widely used for positive electrodes in LIBs due to its high electronic conductivity and low cost. However, its low standard reduction potential (1.364 V vs. Li^+/Li), much lower than the operating potential of commercial positive electrode materials, makes it susceptible to anodic dissolution (often called corrosion in this context) [11, 12]. Although a naturally formed Al_2O_3 layer provides some degree of protection, it is insufficient to resist corrosion, particularly at high potentials and elevated temperatures [13]. Commercial LiPF_6 -containing electrolytes are recognized

for their ability to resist Al corrosion through the formation of AlF_3 passivation film [14-16]. The mechanism underlying this corrosion resistance is multifaceted. The hydrolysis of LiPF_6 in the presence of trace moisture generates HF, which reacts with the native Al_2O_3 layer to form an AlF_3 layer that stabilizes the Al surface [17, 18]. Recent findings further suggest that the formation of this passivation layer is driven by a coupled electrochemical–chemical reaction, where the potential above 3.9 V triggers proton generation from the electrochemical oxidation of solvent [13]. These protons dissolve the Al_2O_3 layer and concurrently react with PF_6^- to produce HF, which converts Al_2O_3 into AlF_3 . However, the HF accelerates the dissolution of transition metal ions for the positive electrode and reacts with solid electrolyte interphase (SEI) for the negative electrode, leading to adverse effects on battery performance [19, 20]. Furthermore, LiPF_6 presents inherent drawbacks, including thermal and hydrolytic instability, and safety risks [21, 22]. These issues limited its application scenarios in next-generation high-energy-density LIBs, necessitating the exploration of alternative lithium salts to address these challenges.

The $\text{Li}[\text{FSA}]$ ($[\text{FSA}]^-$ = bis(fluorosulfonyl)amide) salt is considered an alternative to LiPF_6 due to its high thermal and chemical stabilities and ionic conductivity [23, 24]. However, $\text{Li}[\text{FSA}]$ -based carbonate electrolytes are known to cause severe corrosion of Al current collectors at high potentials, a chronic issue associated with such amide-based salts [25, 26]. The prevailing explanation attributes Al corrosion to the formation of soluble $\text{Al}[\text{FSA}]_3$ complexes: when the working potential exceeds 3.5 V, the Al_2O_3 layer is broken down and the underlying Al metal is electrochemically oxidized to form Al^{3+} , which subsequently forms soluble complexes with anions and diffuses into the bulk electrolyte, leading to Al corrosion [27-30]. However, the existence of $\text{Al}[\text{FSA}]_3$ has yet to be confirmed experimentally, and research into the corrosion mechanism has

entertained a period of stagnation. Various strategies have been proposed to mitigate Al corrosion, including the addition of LiPF_6 as an electrolyte additive, the adjustment of solvents, the adoption of superconcentrated electrolytes, and the surface modification of Al current collector [31-34]. Moreover, some studies suggested that the incorporation of fluorinated solvent would induce the formation of an F-rich passivation layer, such as AlF_3 , to protect the Al current collector from corrosion [35-37]. However, a deeper understanding of the Al corrosion mechanism remains essential for guiding the rational design of electrolyte formulations to improve the long-term performance of LIBs.

In this chapter, inspired by the role of HF in forming a protective AlF_3 passivation layer in LiPF_6 -based electrolytes, Al current collectors were pretreated with HF to create an AlF_3 -coated surface. This modified Al current collector was then evaluated in $\text{Li}[\text{FSA}]$ -based carbonate electrolytes for its anti-corrosion performance. Contrary to expectations, cyclic voltammetry (CV) and field-emission scanning electron microscopy (FE-SEM) revealed that the HF-treated Al foil failed to suppress corrosion effectively. This discrepancy was investigated by a series of analyses, including X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Based on the results from these analyses, a mechanism for the failure passivation of the Al current collector was proposed.

5.2 Experimental

The $\text{Li}[\text{FSA}]$ and $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$ ($[\text{C}_2\text{C}_{1\text{im}}]^+ = 1\text{-ethyl-3-methylimidazolium}$) salts were dried under vacuum before at $60\text{ }^\circ\text{C}$ use. The 1 mol dm^{-3} $\text{Li}[\text{FSA}]\text{-EC/DMC}$ (1:1 v/v) electrolyte was chosen as the representative $\text{Li}[\text{FSA}]$ -based carbonate electrolyte. 1 mol dm^{-3} $\text{Na}[\text{FSA}]\text{-EC/DMC}$ (1:1 v/v) was used in the Na system. The $\text{Li}[\text{FSA}]$ -based ionic liquid (IL) electrolyte was prepared by mixing $\text{Li}[\text{FSA}]$ and $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$

in a molar ratio of 2:8, labeled as $\text{Li}_{0.2}[\text{C}_2\text{C}_{1\text{im}}]_{0.8}[\text{FSA}]$. Aluminum foil was immersed in a 1 wt% HF aqueous solution for 5 min, followed by rinsing with deionized water and ethanol to remove the HF solution on the surface. The resulting HF-treated Al is labeled as HF-Al. Electrolyte preparation and cell assembly/disassembly were performed in an Ar-filled glove box (H_2O and $\text{O}_2 < 1$ ppm).

For electrochemical measurements, 2032-coin cells were assembled with untreated Al or HF-Al working electrode, Li metal or Na metal counter electrode, and a polypropylene separator. Cyclic voltammetry tests were conducted using a VSP potentiostat at 25 °C in the voltage range of 2–5 V at a scan rate of 0.5 mV s^{-1} . After CV tests, the morphologies of Al electrodes recovered from coin cells were observed by FE-SEM.

To evaluate the stability of HF-Al in Li[FSA]-based electrolytes, HF-Al foils were immersed in 1 mol dm^{-3} Li[FSA]-EC/DMC for two days. The resulting foils were rinsed with ethanol and dried, labeled as HF-Al-Li[FSA]-EC/DMC. Finally, to explore the possible reaction pathway of AlF_3 and Li[FSA]-based electrolytes, excess AlF_3 was added to 1 mol dm^{-3} Li[FSA]-EC/DMC and stirred at 50 °C for one day. The upper solution was carefully collected, cooled gradually from 50 °C to 20 °C over 24 hours, and left to stand for 20 days. The resulting solution was dried and the obtained powder was analyzed using XRD, SEM, and XPS to study changes in composition.

5.3 Results and discussion

To investigate the feasibility of replicating the passivation mechanism observed in LiPF_6 -based electrolytes, Al foils were pretreated with HF to form an AlF_3 passivation layer. The surface morphologies of untreated Al and HF-Al were first examined using FE-SEM to visualize the changes induced by the treatment process. As shown in **Figure**

5-1, the untreated Al foil surface exhibits machining streaks, with a relatively smooth texture and no noticeable particulate features [38]. In contrast, FE-SEM images of HF-Al (**Figure 5-2**) reveal the formation of distinct surface particles distributed across the foil, indicating morphological changes caused by the fluorination process. Furthermore, EDX mapping of the HF-Al surface (**Figure 5-2**) confirms the presence of F atoms alongside Al and O, suggesting the successful incorporation of fluorine into the surface structure. To further characterize the elemental composition and chemical states of the Al foils, XPS analysis was conducted (**Figure 5-3**). The Al 2p XPS spectra of untreated Al show peaks corresponding to Al—O (75.6 eV) and metallic Al (72.6 eV), indicating the presence of a thin native oxide layer. For HF-Al, the Al—O peak diminished, while a Al—F peak at ~76.6 eV emerges, demonstrating the replacement of Al—O bonds with Al—F bonds during the fluorination process. The Al metal peak also weakens in HF-Al compared to untreated Al, indicating that the passivation layer formed after HF treatment is thicker than the native Al₂O₃ layer. In addition, F 1s XPS spectra confirm the formation of Al—F bonds. These results suggest that the HF treatment successfully produced an AlF₃-coated Al foil surface.

The corrosion behaviors of untreated Al and HF-Al were evaluated in Li[FSA]-based and Na[FSA]-based carbonate electrolytes using CV measurements. **Figure 5-4** shows the first-cycle CV curves of untreated Al and HF-Al electrodes in 1 M Li[FSA]-EC/DMC electrolyte. Both electrodes exhibit higher current density during the reverse scan compared to the forward scan. This hysteresis loops are ascribed to Al passivation and corrosion and electrolyte oxidation [39, 40]. The anodic peak current density and total charge of HF-Al are comparable to those of untreated Al. Considering the identical electrolyte and voltage range, this current difference suggests that the AlF₃ layer on HF-Al could not effectively inhibit Al corrosion in the 1 M Li[FSA]-EC/DMC electrolyte.

To further examine the discrepancy of Al corrosion behaviors between untreated Al and HF-Al, Na[FSA]-based carbonate electrolytes were employed, due to their known high corrosive effect toward Al electrodes (see Chapter 3). **Figure 5-5** displays the first-cycle CV curves of untreated Al and HF-Al in the 1 M Na[FSA]-EC/DMC electrolyte. The anodic current of HF-Al appears at 4.1 V, earlier than the untreated Al at 4.3 V, indicating a more severe corrosion process for HF-Al. The peak anodic current density and total charge for HF-Al is higher than that for untreated Al. The surface morphologies of the Al electrodes after CV tests were examined using SEM (**Figure 5-6** and see **Figure 5-7** for higher magnification). Corrosion pits with diameters of approximately 40 μm are observed on both untreated Al and HF-Al. All the above results demonstrate the inefficacy of the AlF_3 passivation layer in mitigating Al corrosion in [FSA]-based carbonated electrolytes. This passivation failure seems to contradict previous literature that the formation of AlF_3 is helpful to resist the Al corrosion in amide-based electrolytes [41-44].

To further explore the passivation effectiveness of AlF_3 in [FSA]-based electrolytes, sequential CV tests with alternating electrolytes, 1 M LiPF_6 -EC/DMC and 1 M Li[FSA]-EC/DMC, were conducted. These experiments aimed to evaluate whether the passivation layer generated during cycling in LiPF_6 -EC/DMC could suppress Al corrosion in Li[FSA]-EC/DMC. **Figure 5-8** shows the CV curves for untreated Al, where the first cycle was performed in LiPF_6 -EC/DMC, followed by the second cycle in Li[FSA]-EC/DMC (the coin cell was reassembled after disassembling, rinsing with EC/DMC, and drying). During the first cycle in LiPF_6 -EC/DMC, the anodic current density was low, and the forward scan exhibited higher current density than the reverse scan, indicating the formation of an effective passivation layer. However, upon altering to Li[FSA]-EC/DMC for the second cycle, the anodic current density increased

significantly, suggesting that the passivation layer formed in $\text{LiPF}_6\text{-EC/DMC}$ could not effectively suppress Al corrosion in Li[FSA]-EC/DMC . Conversely, **Figure 5-9** shows the CV results for untreated Al, where the first cycle was conducted in Li[FSA]-EC/DMC , followed by a second cycle in $\text{LiPF}_6\text{-EC/DMC}$. The first cycle exhibited the high anodic current density in Li[FSA]-EC/DMC as expected. However, in the second cycle, after changing the electrolyte to $\text{LiPF}_6\text{-EC/DMC}$, the current density dropped considerably, demonstrating that a passivation layer formed by LiPF_6 effectively inhibits Al corrosion even after the prior exposure to Li[FSA]-EC/DMC . Comparing the second cycle in **Figure 5-8** (Li[FSA] after LiPF_6) with the first cycle in **Figure 5-9** (Li[FSA] directly) reveals that the passivation layer generated in $\text{LiPF}_6\text{-EC/DMC}$ slightly mitigates Al corrosion in Li[FSA]-EC/DMC , though its effectiveness is limited. These results highlight the aggressive corrosive effects of $[\text{FSA}]^-$ on both Al electrodes and potential passivation layers formed on Al surface. This finding aligns with the previous study, where Al corrosion was observed even with as little as 0.01 M Li[FSA] added to 1 M $\text{LiPF}_6\text{-EC/DMC}$ [45].

The surface morphology and chemical composition of HF-Al after immersion in 1 M Li[FSA]-EC/DMC for two days were examined using SEM, EDX, and XPS. To ensure meaningful comparison, the same HF-Al sample characterized in **Figure 5-2** (before immersion) was used, with the surface analyzed after ethanol washing. **Figure 5-10** shows the SEM and EDX mapping images of HF-Al after immersion. Compared to the sample without immersion (**Figure 5-2**), the surface of HF-Al after immersion exhibits a more pronounced granular texture, indicating morphological changes due to interaction with the electrolyte. The EDX mapping images further reveal an increase in the F content (from 0.2 wt% to 0.7 wt%) and the emergence of S, which are derived from $[\text{FSA}]^-$. These observations may suggest that AlF_3 on the HF-Al surface reacted

with Li[FSA]. To further investigate the surface chemistry of HF-Al, XPS analysis was conducted on the samples before and after immersion (**Figure 5-11**) (see **Figure 5-3** for the data of HF-Al before immersion)). The Al 2p spectra for both samples display three peaks corresponding to metallic Al, Al—O, and Al—F species. However, after immersion, the Al—F peak intensity significantly decreases, indicating partial degradation of the AlF₃ layer. Similarly, the F 1s spectra show a reduction in the Al—F signal and the emergence of a distinct SO_xF peak. The appearance of S in the S 2p spectra further confirms the incorporation of S-containing species onto the HF-Al surface. These results provide the evidence that AlF₃ on HF-Al undergoes reactions with Li[FSA], leading to changes in surface morphology and chemical composition.

To investigate the interactions between Al³⁺ and anions ([FSA][−] or [TFSA][−]), Raman spectroscopy was conducted on 1 M Li[FSA]-EC/DMC and 1 M Li[TFSA]-EC/DMC electrolytes with added Al[OTf]₃ at selected time intervals. This experiment simulates the chemical environment of Al corrosion, where Al³⁺ ions participate in the reaction to form Al-complexes. **Figure 5-12** presents the evolution of Raman spectra for 1 M Li[FSA]-EC/DMC with added Al[OTf]₃. The spectrum of the pure 1 M Li[FSA]-EC/DMC shows two characteristic peaks in the 700–750 cm^{−1} region; the first one at ~715 cm^{−1} corresponds to the ring-bending vibrational mode of EC [46, 47], while the broad peak at ~726 cm^{−1} is attributed to the S—N—S bending mode of [FSA][−] [48, 49]. Upon the addition of Al[OTf]₃, both peaks exhibited a blue shift, which intensifies over time, implying the interaction of Al³⁺ with [FSA][−]. The gradual evolution indicates a dynamic interaction, potentially reflecting the instability of the Al-FSA complexes. In contrast, **Figure 5-13** illustrates the Raman spectra for 1 M Li[TFSA]-EC/DMC with added Al[OTf]₃. The pure 1 M Li[TFSA]-EC/DMC shows a peak at ~715 cm^{−1} (ring-bending vibration of EC) and a symmetric stretching vibration

of the S—N—S bond at $\sim 740\text{ cm}^{-1}$ corresponding to $[\text{TFSA}]^-$ [50]. Unlike in the $\text{Li}[\text{FSA}]\text{-EC/DMC}$ system, no significant peak shifts were observed after adding $\text{Al}[\text{OTf}]_3$, meaning that Al^{3+} and $[\text{TFSA}]^-$ coexist stably in the electrolyte without forming complexes. These spectroscopic data indicate a fundamental difference between the behaviors of $[\text{FSA}]^-$ and $[\text{TFSA}]^-$ toward Al^{3+} . The interactions between Al^{3+} and $[\text{FSA}]^-$ in the presence of AlF_3 were further explored. 0.02 g $\text{Al}[\text{OTf}]_3$ and 0.1 g AlF_3 were simultaneously added to 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$ (2.0 g), and the Raman spectra were monitored at selected time intervals (**Figure 5-14**). Compared to pure 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$, the characteristic $[\text{FSA}]^-$ peak ($\sim 726\text{ cm}^{-1}$) diminishes gradually and nearly disappears, indicating that $[\text{FSA}]^-$ is depleted due to continuous chemical reactions. The visual observations of the final solutions after Raman experiments (**Figure 5-15**) provided additional evidence. The solution of $\text{Al}[\text{OTf}]_3$ in 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$ turned pale yellow, while the solution containing both $\text{Al}[\text{OTf}]_3$ and AlF_3 in 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$ exhibited a deeper yellow color. In contrast, $\text{Al}[\text{OTf}]_3$ in 1 M $\text{Li}[\text{TFSA}]\text{-EC/DMC}$ remained clear and colorless. The color change in $\text{Li}[\text{FSA}]\text{-EC/DMC}$ electrolytes aligns with the Raman results, suggesting chemical transformations involving $[\text{FSA}]^-$. These findings suggest that the distinct reactivity of $[\text{FSA}]^-$ in the presence of Al^{3+} and AlF_3 likely contributed to the failure of AlF_3 passivation layers in $\text{Li}[\text{FSA}]\text{-EC/DMC}$.

To further explore this hypothesis, subsequent experiments focused on the direct interaction between AlF_3 and $\text{Li}[\text{FSA}]\text{-EC/DMC}$. 2.5 g AlF_3 was added to 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$ (20 mL) and stored for 20 days (see Experimental Section for details). The solution turned pale yellow (**Figure 5-16**), indicating chemical reactions between AlF_3 and $\text{Li}[\text{FSA}]$. Some crystals (or sediments) were observed in the separated upper solution, but attempts to identify their composition and structure via

single-crystal XRD were unsuccessful. The dried product from the upper solution was further analyzed using XRD (**Figure 5-17**). The primary characteristic peaks are assigned to Li[FSA]. However, three unidentified broad peaks are also observed, which do not match the known XRD patterns of AlF_3 or LiF. These unknown peaks suggest the formation of new products, although their exact nature remains elusive. EDX analysis (**Figure 5-18**) of the dried product detected Al in addition to S, O, F, and N, confirming that AlF_3 reacted with Li[FSA]. The pressed pellet of the dried product was further examined using XPS (**Figure 5-19**). The F 1s, S 2p, N 1s, and Li 1s spectra revealed features corresponding to Li[FSA] as well as additional signals, indicating the presence of new chemical species. In particular, the Al 2p spectrum (**Figure 5-20**) showed a weak Al signal, consistent with the EDX results, confirming the incorporation of Al species into the reaction. These findings suggest that AlF_3 may undergo anion exchange reactions with $[\text{FSA}]^-$, potentially forming compounds such as $\text{AlF}_x[\text{FSA}]_{3-x}$ or the Al with FSA-decomposed species. However, the exact identification of these products and reaction pathways was not considered in this study, and further investigation is required to elucidate the underlying mechanisms of Al corrosion in [FSA]-based electrolytes.

The reactivity of $[\text{FSA}]^-$ may be influenced by the presence of solvents. To evaluate the stability of HF-Al in a solvent-free system, CV measurements were conducted using untreated Al and HF-Al electrodes in a $\text{Li}_{0.2}[\text{C}_2\text{C}_{11}\text{im}]_{0.8}[\text{FSA}]$ IL electrolyte (**Figure 5-21**). Although both the electrodes exhibited low current densities at 25 °C the difference becomes more pronounced at 90 °C with the peak anodic current density of HF-Al (0.014 mA cm^{-2}) significantly lower compared to untreated Al (0.031 mA cm^{-2}). These results indicate that the AlF_3 layer on the HF-Al demonstrates improved anti-corrosion performance in IL electrolytes, where the absence of solvent

may reduce the reactivity of $[\text{FSA}]^-$ (or IL environment provides the absence of free $[\text{FSA}]^-$).

The findings in this study demonstrate that $[\text{FSA}]^-$ is reactive toward F-containing passivation layers, such as AlF_3 , undermining their effectiveness in suppressing Al corrosion. These results underscore the necessity of developing alternative passivation layers that are either free of fluorine or incorporate components capable of resisting $[\text{FSA}]^-$ attack. Salt or solvent regulation is essential to improve the long-term stability and anti-corrosion performance of Al electrodes in $[\text{FSA}]$ -based electrolytes.

5.4 Conclusions

In summary, this study systematically investigated the corrosion behavior of Al electrodes in $[\text{FSA}]$ -based carbonate electrolytes, with a particular focus on understanding the interactions between $[\text{FSA}]^-$ and F-containing passivation layers. Inspired by the anti-corrosion mechanism for the LiPF_6 -based electrolyte, we compared the performance of untreated Al and HF-Al in 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$ and 1 M $\text{Na}[\text{FSA}]\text{-EC/DMC}$ electrolytes through electrochemical and surface analyses. Despite the formation of an AlF_3 passivation layer, HF-Al did not exhibit improvement in suppression of Al corrosion, highlighting the failure of conventional passivation strategies in $[\text{FSA}]$ -based systems. To further probe the mechanisms of passivation failure, we investigated the reactivity of $[\text{FSA}]^-$ with AlF_3 and Al^{3+} using Raman spectroscopy, XRD, EDX, and XPS. These analyses revealed that $[\text{FSA}]^-$ actively reacts with AlF_3 , leading to the depletion of $[\text{FSA}]^-$ and the formation of unidentified reaction products. In addition, CV measurements in a solvent-free ionic liquid electrolyte demonstrated that the absence of solvent improved the stability of HF-Al, emphasizing the role of the solvent in exacerbating $[\text{FSA}]^-$ reactivity. These findings

suggest that the reactivity of $[\text{FSA}]^-$ poses a fundamental challenge for the F-containing passivation layer to protect Al electrodes in $[\text{FSA}]$ -based systems. Elucidating the detailed reaction mechanisms between $[\text{FSA}]^-$ and AlF_3 will be critical for advancing the design of corrosion-resistant Al electrodes.

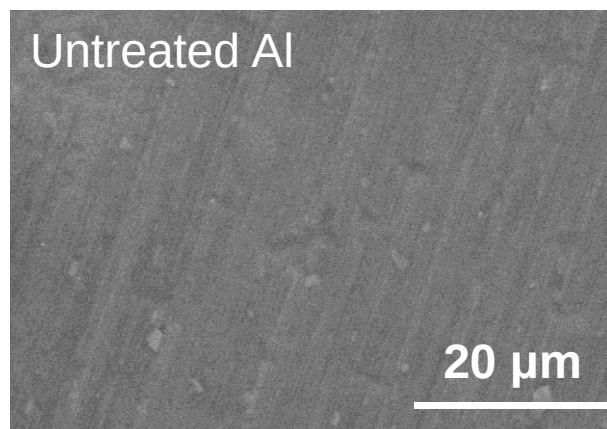


Figure 5-1. An SEM image of the untreated Al foil.

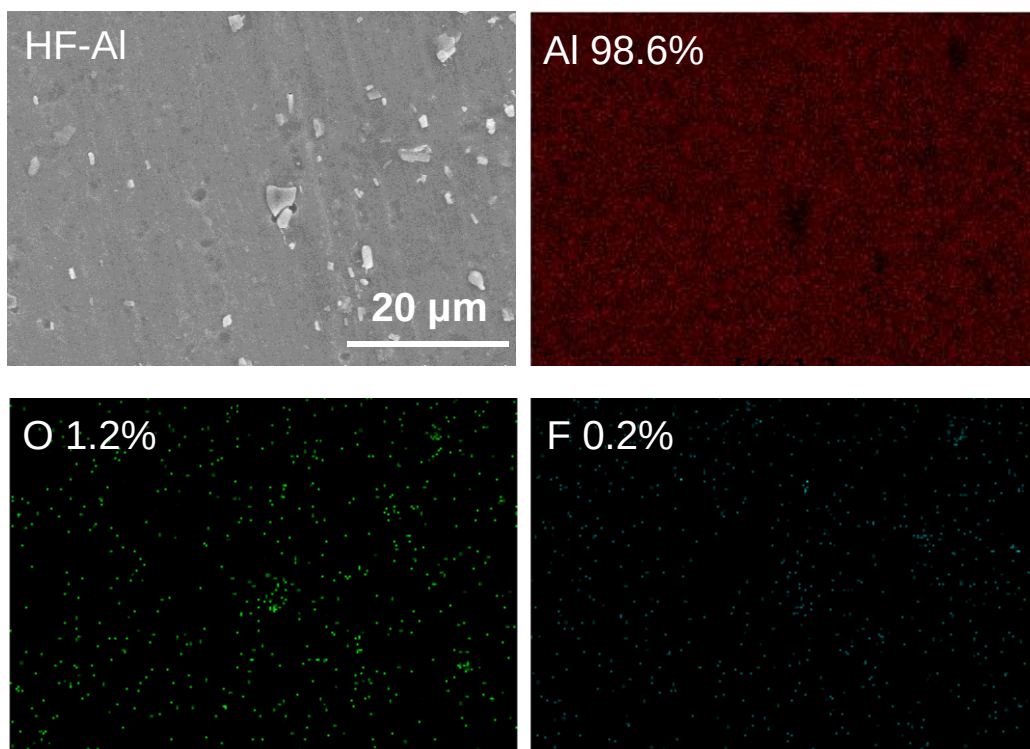


Figure 5-2. SEM and EDX mapping images of HF-Al.

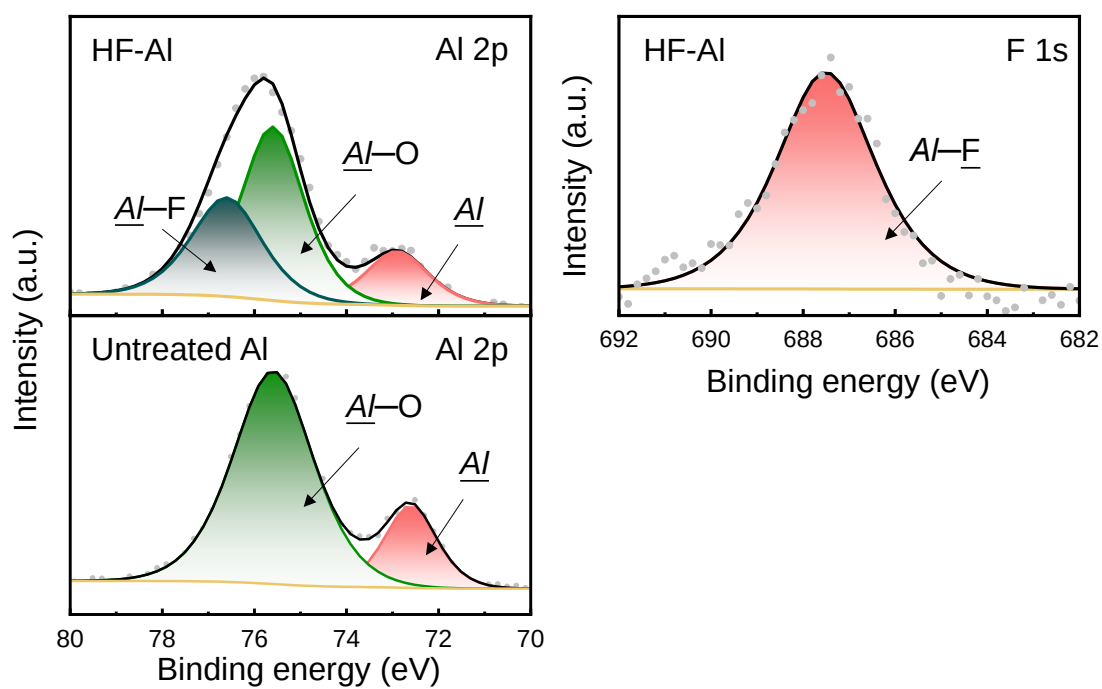


Figure 5-3. XPS spectra of the untreated Al and HF-Al. (The Al 2p XPS spectrum of untreated Al is from **Figure 3-24**)

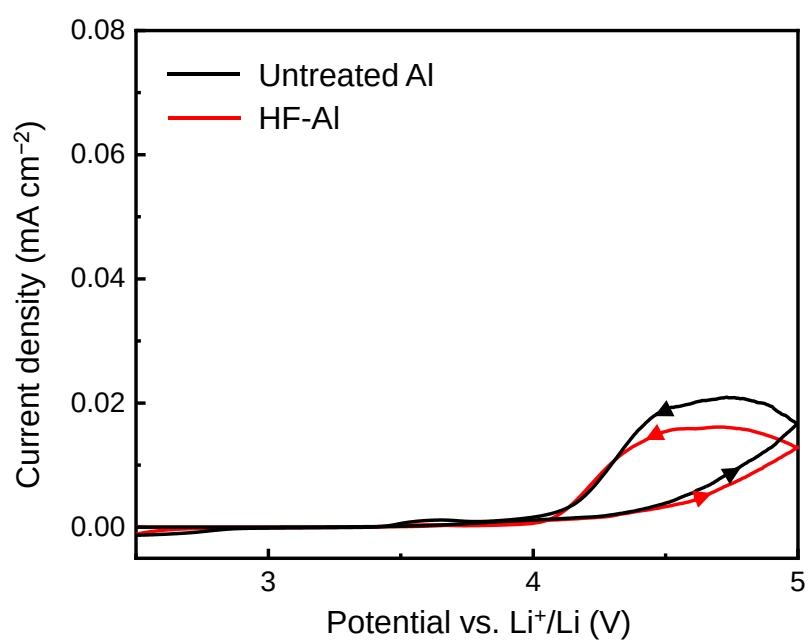


Figure 5-4. Cyclic voltammograms of the untreated Al and HF-Al electrodes in the 1 M Li[FSA]-EC/DMC electrolyte at 25 °C. Scan rate: 0.5 mV s⁻¹.

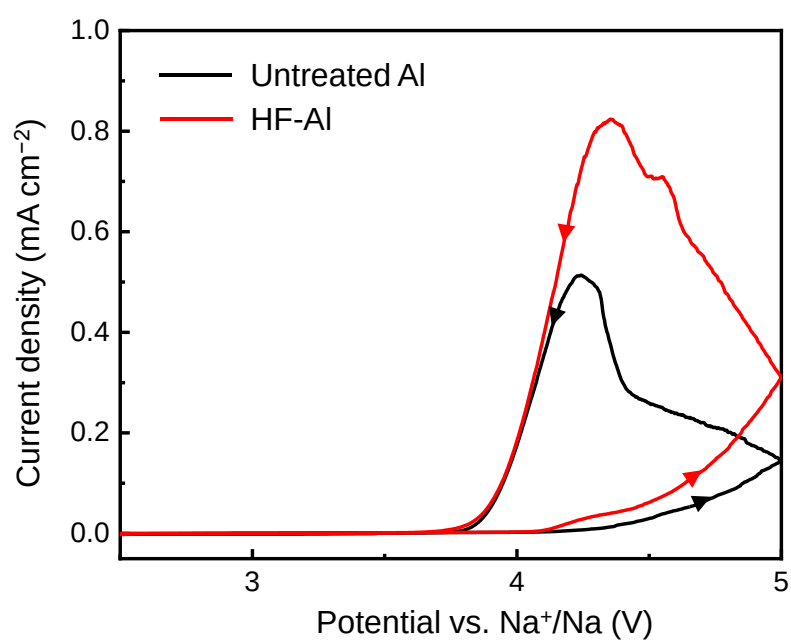


Figure 5-5. Cyclic voltammograms of the untreated Al and HF-Al electrodes in the 1 M Na[FSA]-EC/DMC electrolyte at 25 °C. Scan rate: 0.5 mV s⁻¹.

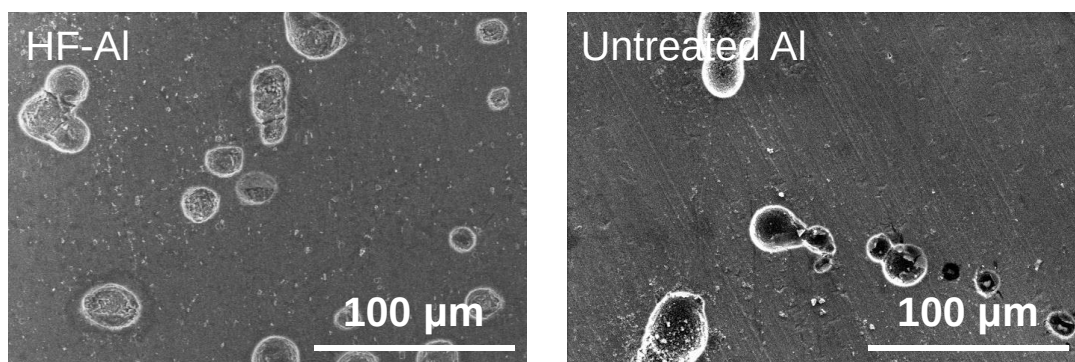


Figure 5-6. SEM images for the untreated Al and HF-Al electrodes after CV measurements in 1 M Na[FSA]-EC/DMC electrolyte at 25 °C.

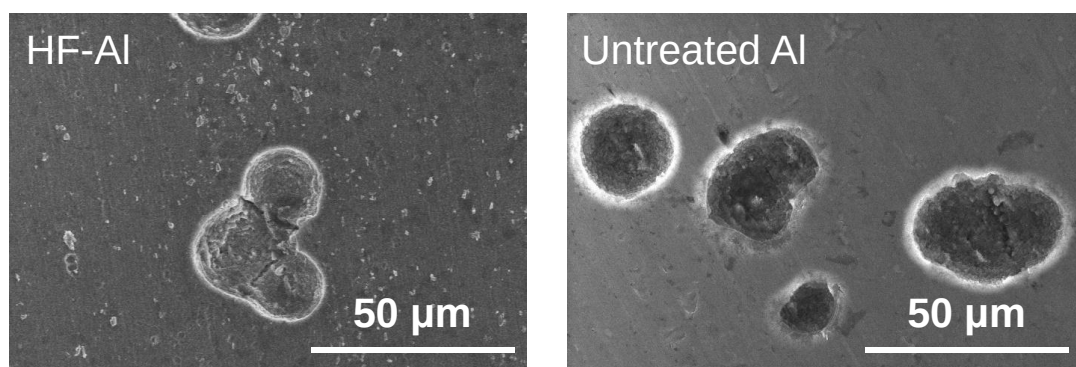


Figure 5-7. SEM images for the untreated Al/HF-Al electrode at higher magnifications after CV measurements in 1 M Na[FSA]-EC/DMC electrolyte at 25 °C.

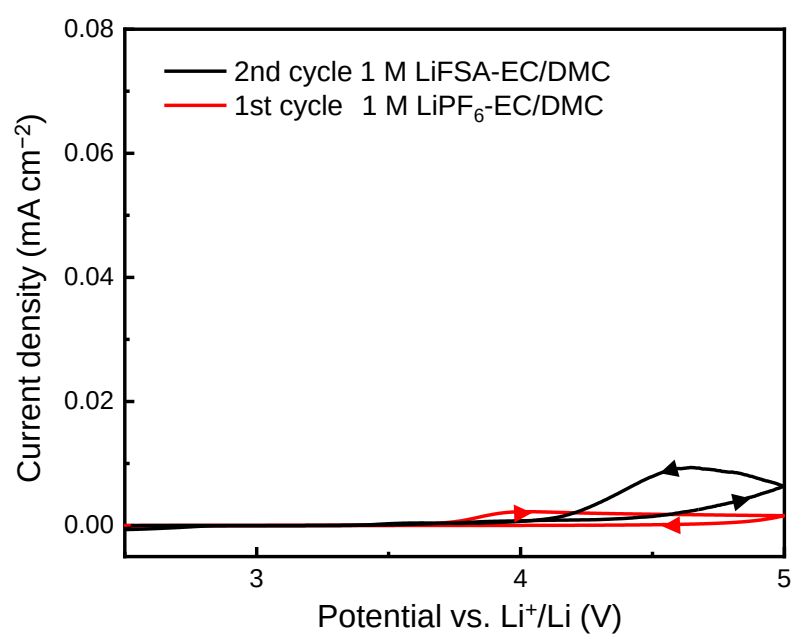


Figure 5-8. Cyclic voltammograms of the untreated Al electrode using 1 M LiPF₆-EC/DMC electrolyte in the first cycle and 1 M Li[FSA]-EC/DMC electrolyte in the second cycle at 25 °C. Scan rate: 0.5 mV s⁻¹.

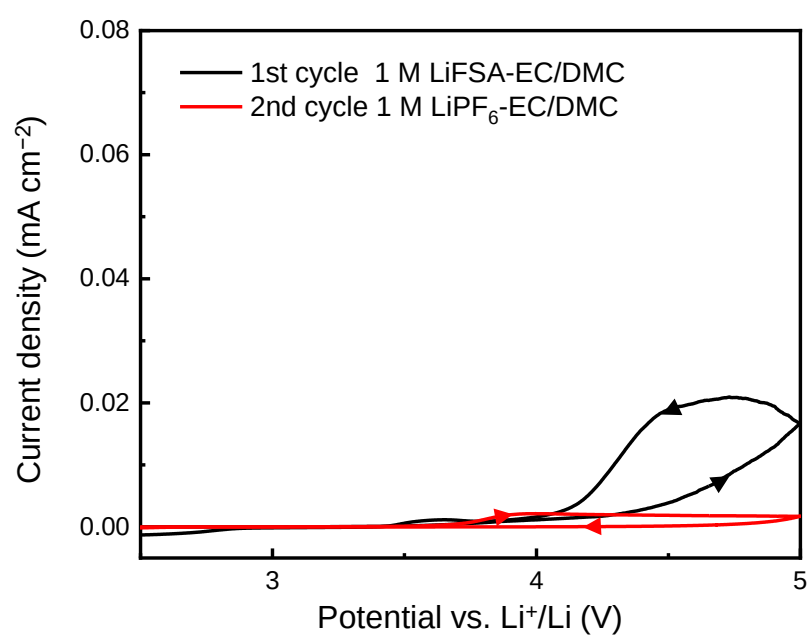


Figure 5-9. Cyclic voltammograms of the untreated Al electrode using 1 M Li[FSA]-EC/DMC electrolyte in the first cycle and 1 M LiPF₆-EC/DMC electrolyte in the second cycle at 25 °C. Scan rate: 0.5 mV s⁻¹.

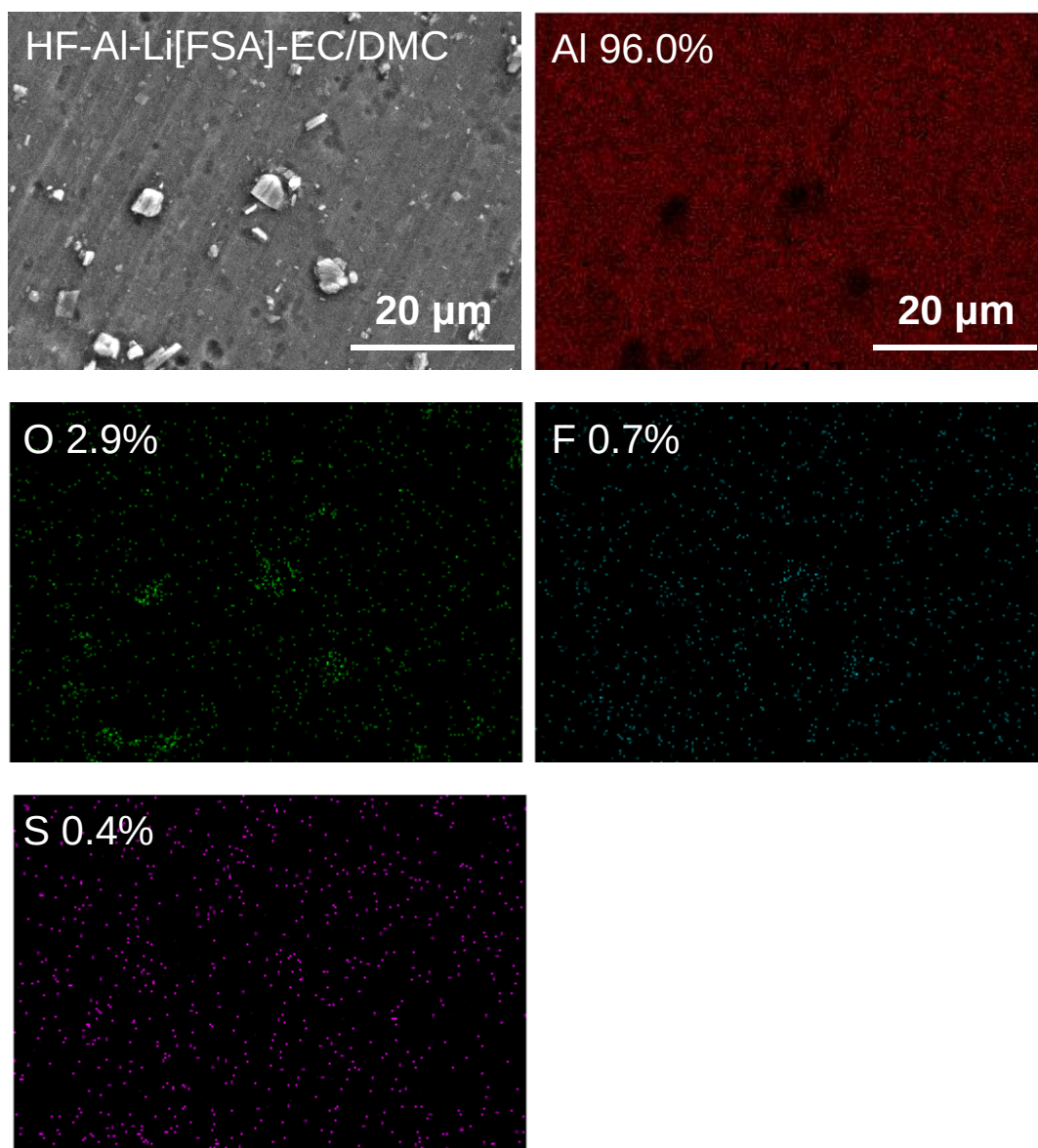


Figure 5-10. SEM and EDX mapping images of HF-Al (previously characterized in **Figure 5-2**) after immersion in 1 M Li[FSA]-EC/DMC electrolyte for two days.

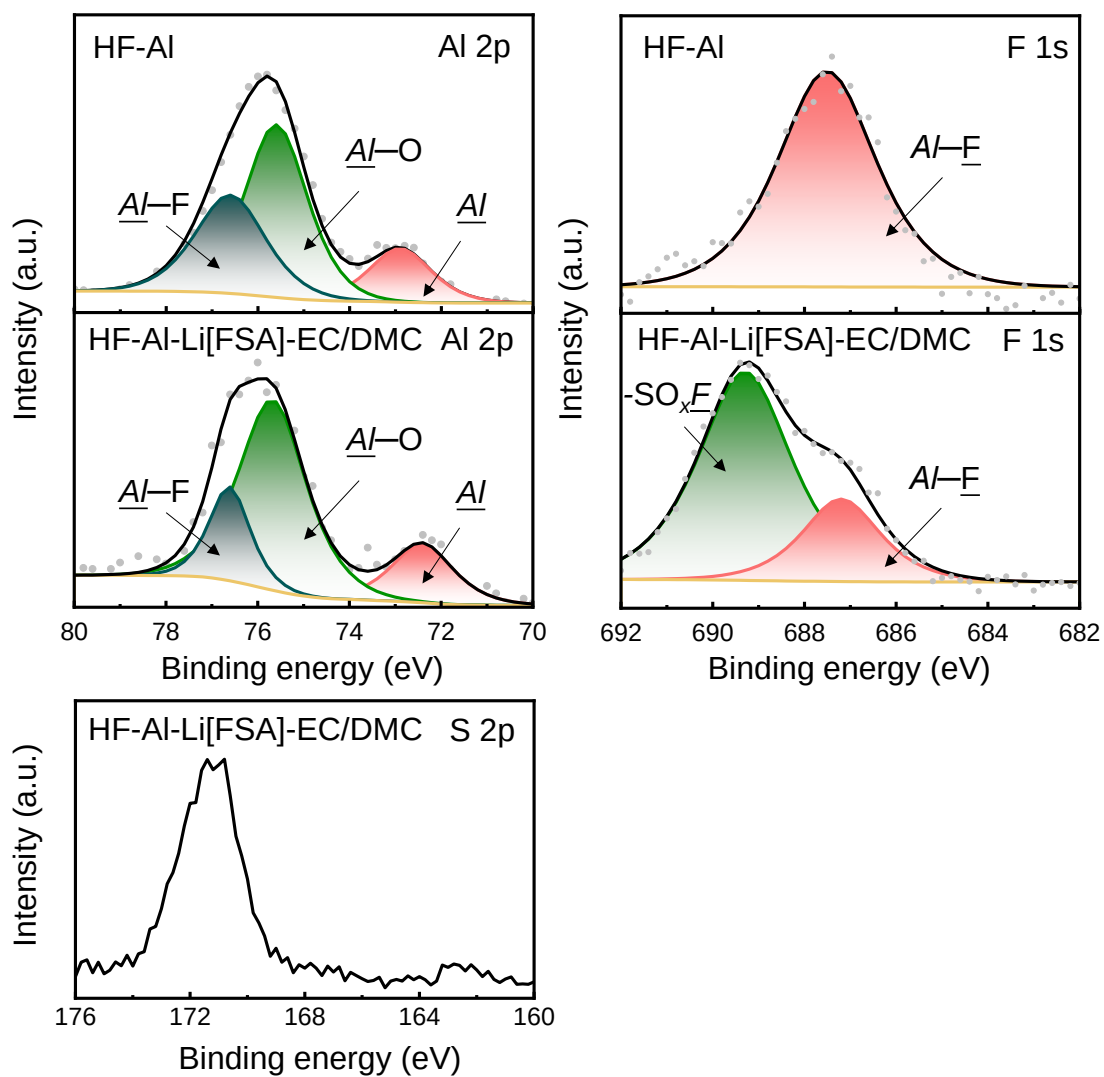


Figure 5-11. XPS spectra of HF-Al, and HF-Al-Li[FSA]-EC/DMC. (XPS spectra of HF-Al are the same as **Figure 5-3**, added once again here for comparison.)

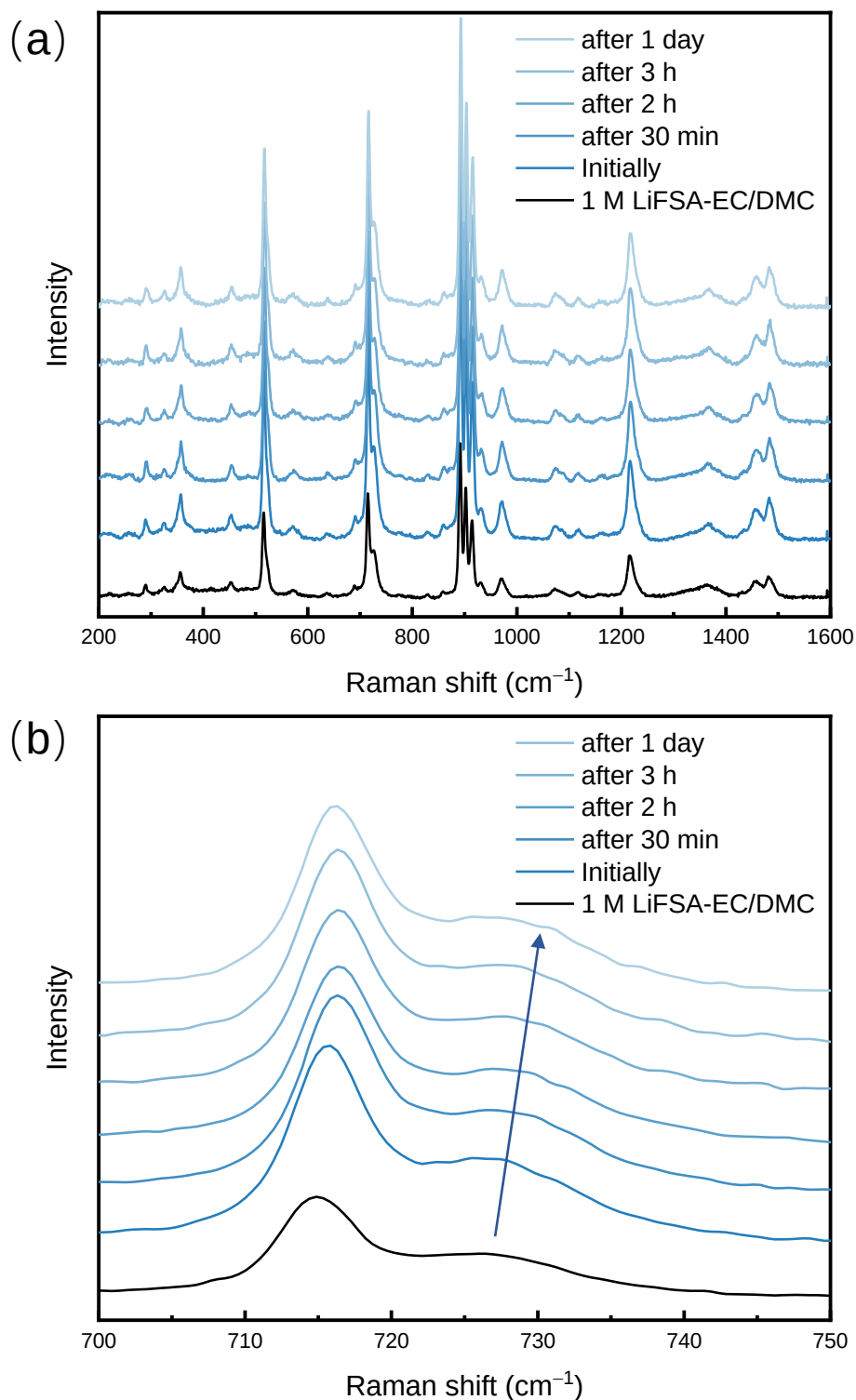


Figure 5-12. Evolution of Raman spectra for 1 M Li[FSA]-EC/DMC electrolyte with Al[OTf]₃ at selected time intervals in the range of (a) 200-1600 cm⁻¹ and (b) 700-750 cm⁻¹.

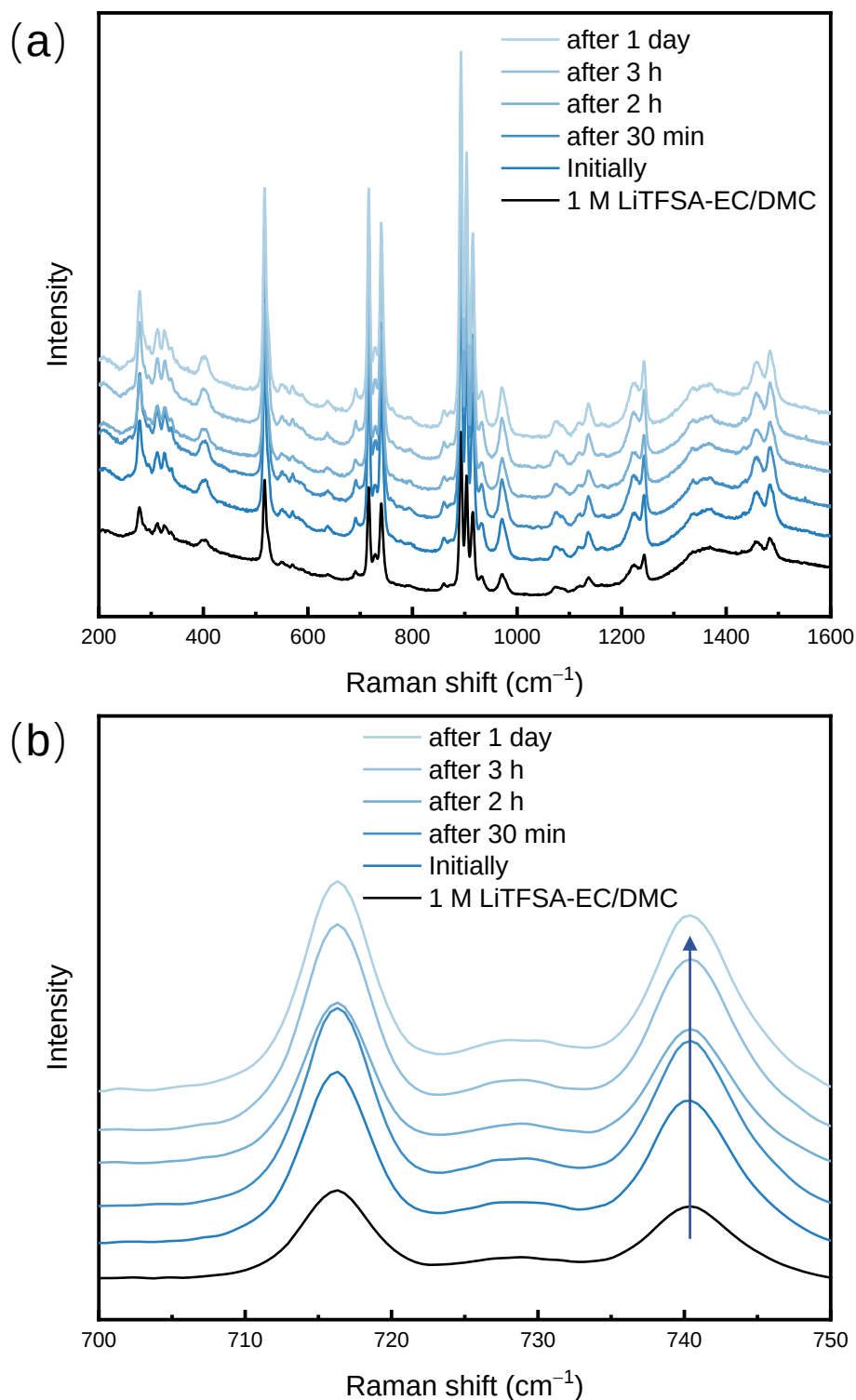


Figure 5-13. Evolution of Raman spectra of 1 M Li[TFSA]-EC/DMC electrolyte with $\text{Al}[\text{OTf}]_3$ at selected time intervals in the range of (a) 200-1600 cm^{-1} and (b) 700-750 cm^{-1} .

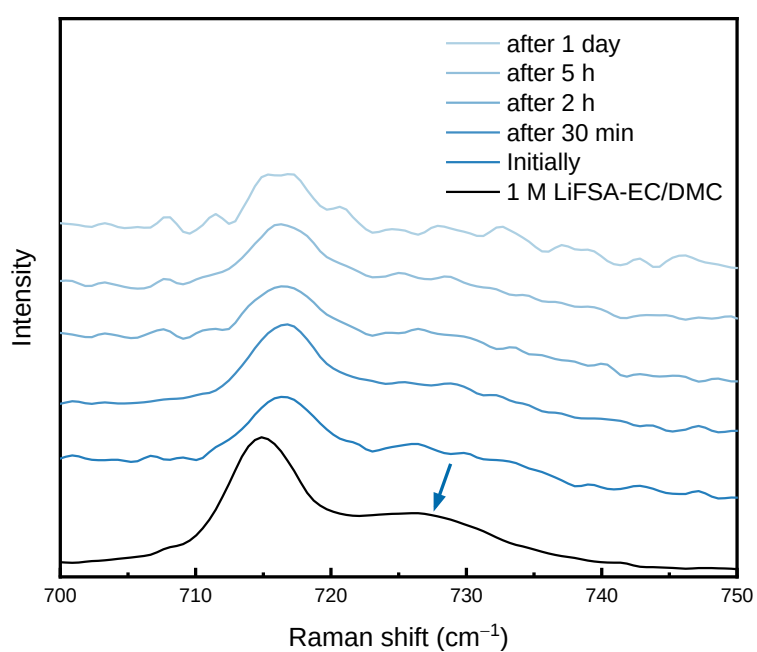


Figure 5-14. Raman spectra evolution of 1 M Li[FSA]-EC/DMC electrolyte with added Al[OTf]₃ and AlF₃ at selected time intervals in the range of 700-750 cm⁻¹.

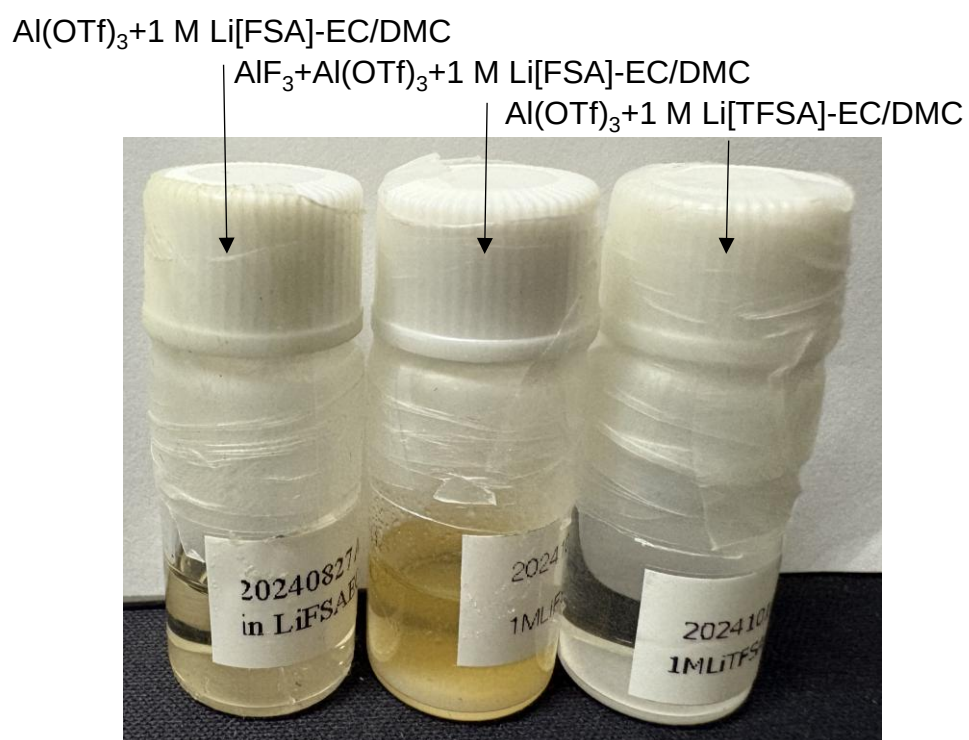
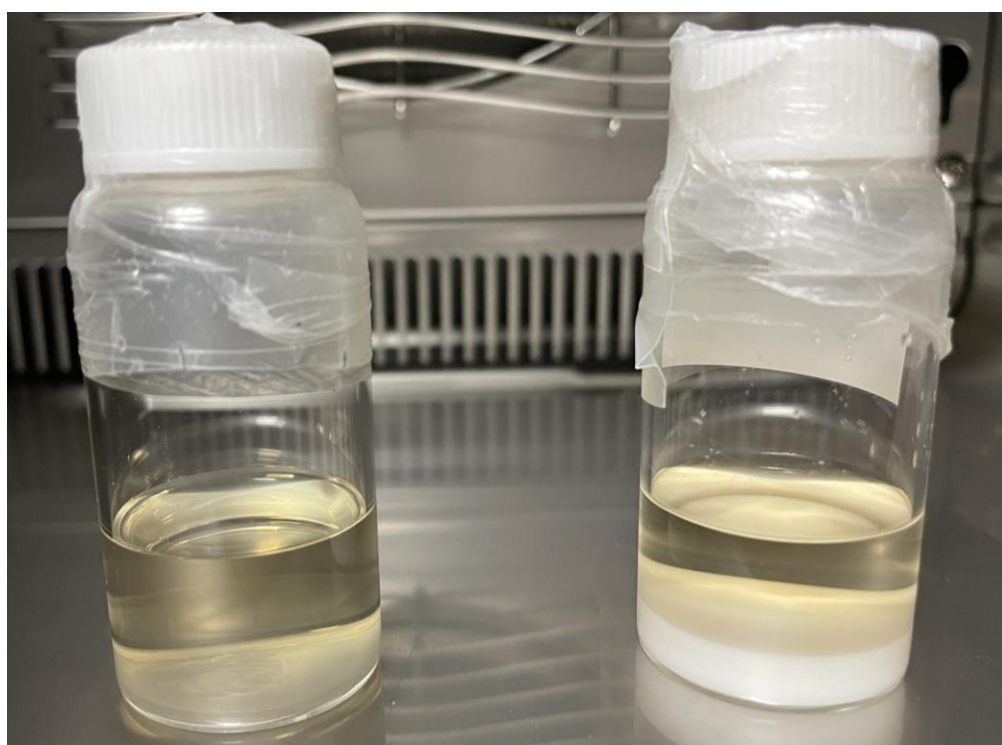


Figure 5-15. Visual observations of $\text{Al}(\text{OTf})_3 + 1 \text{ M Li[FSA]}\text{-EC/DMC}$, $\text{Al}(\text{OTf})_3 + \text{AlF}_3 + 1 \text{ M Li[FSA]}\text{-EC/DMC}$, and $\text{Al}(\text{OTf})_3 + 1 \text{ M Li[TFSA]}\text{-EC/DMC}$.



Upper half

Bottom half

Figure 5-16. Visual observations of separated upper and bottom layers obtained from 1 M Li[FSA]-EC/DMC with excess AlF_3 .

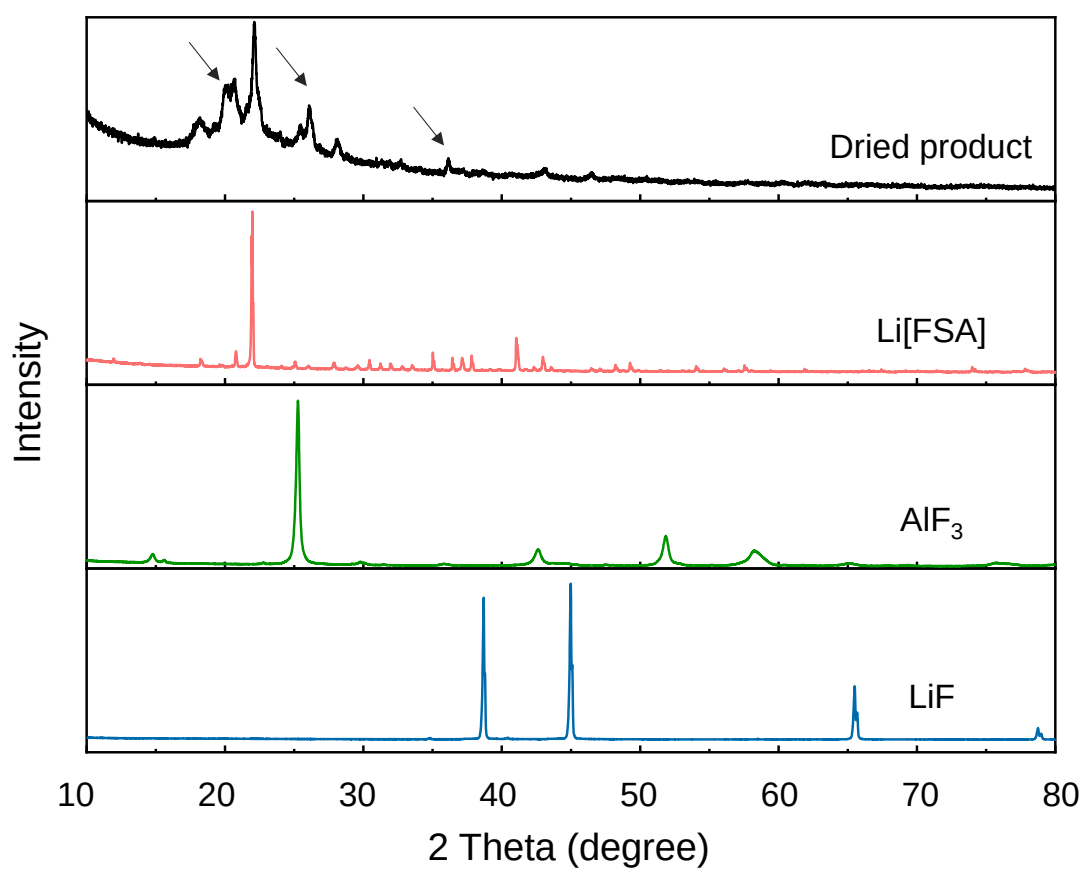


Figure 5-17. The XRD patterns of the dried product, Li[FSA], AlF₃, and LiF. The dried product is obtained from the upper solution of AlF₃ added in 1 M Li[FSA]-EC/DMC.

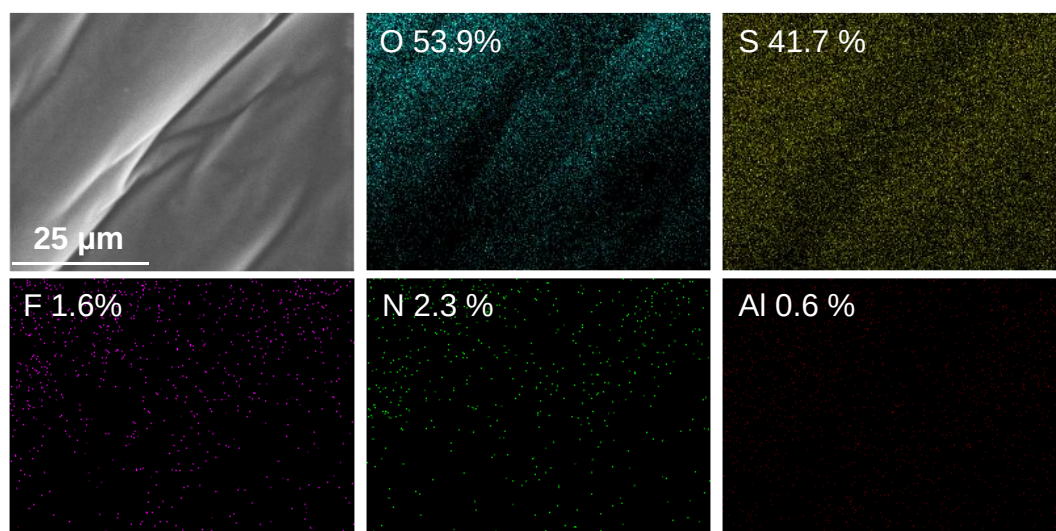


Figure 5-18. SEM and EDX mapping images of the dried product. The dried product is obtained from the upper solution of AlF_3 added in 1 M $\text{Li}[\text{FSA}]\text{-EC/DMC}$.

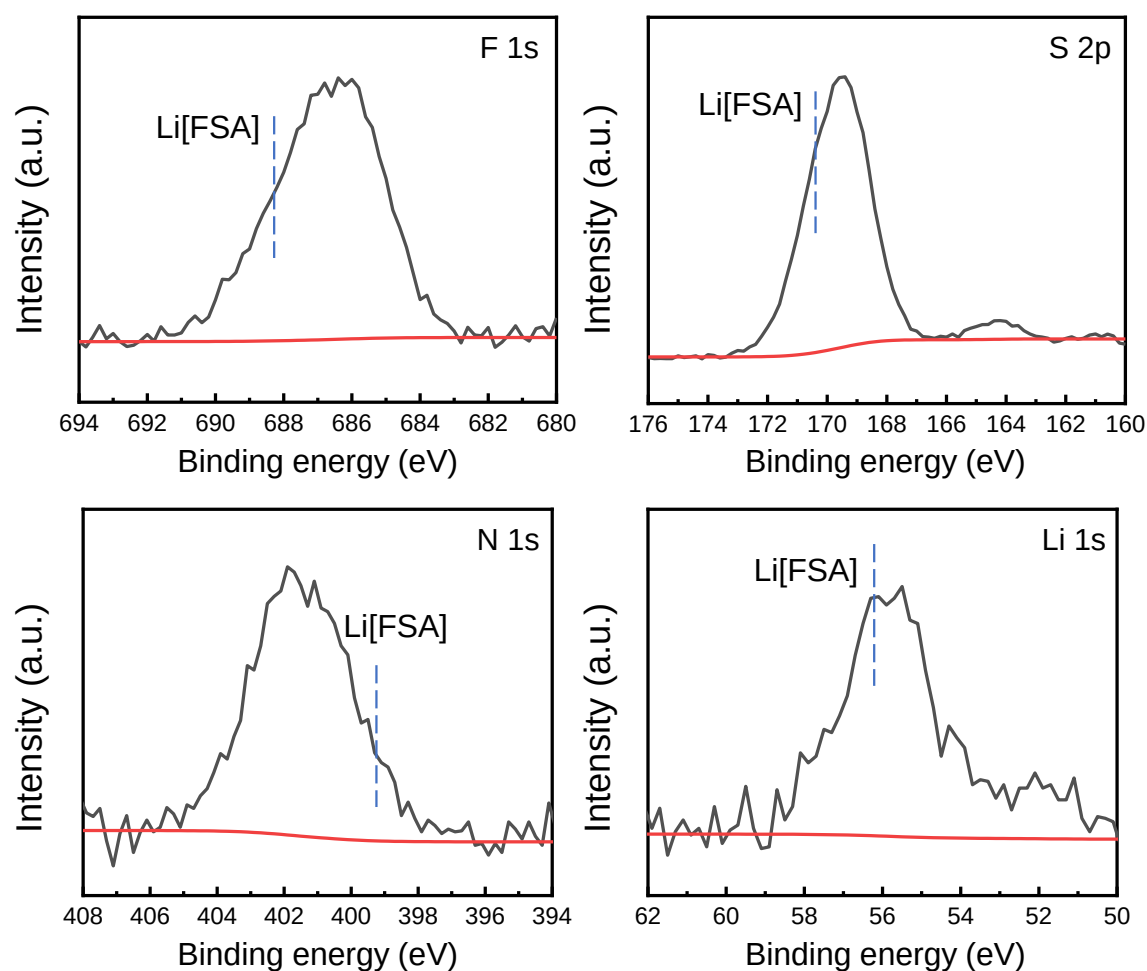


Figure 5-19. F 1s, S 2p, N 1s, and Li 1s XPS spectra of the dried product (pressed into pellet). The dried product is obtained from the upper solution of AlF_3 added in 1 M Li[FSA]-EC/DMC.

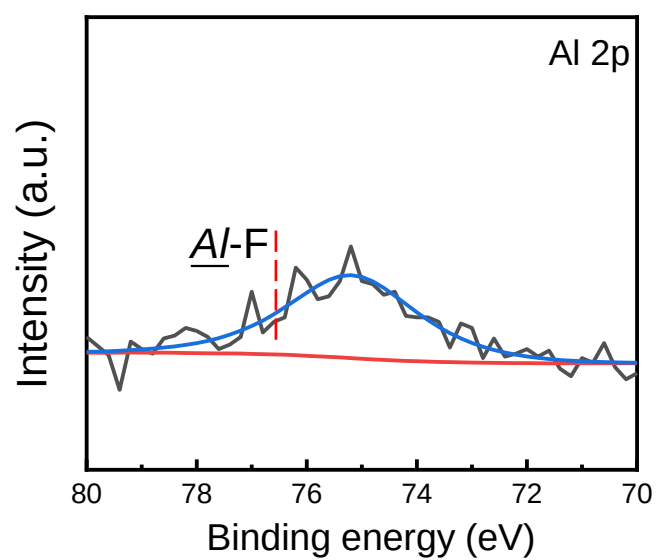


Figure 5-20. Al 2p XPS spectrum of the dried product (pressed into pellet). The dried product is obtained from the upper solution of AlF_3 added in 1 M Li[FSA]-EC/DMC.

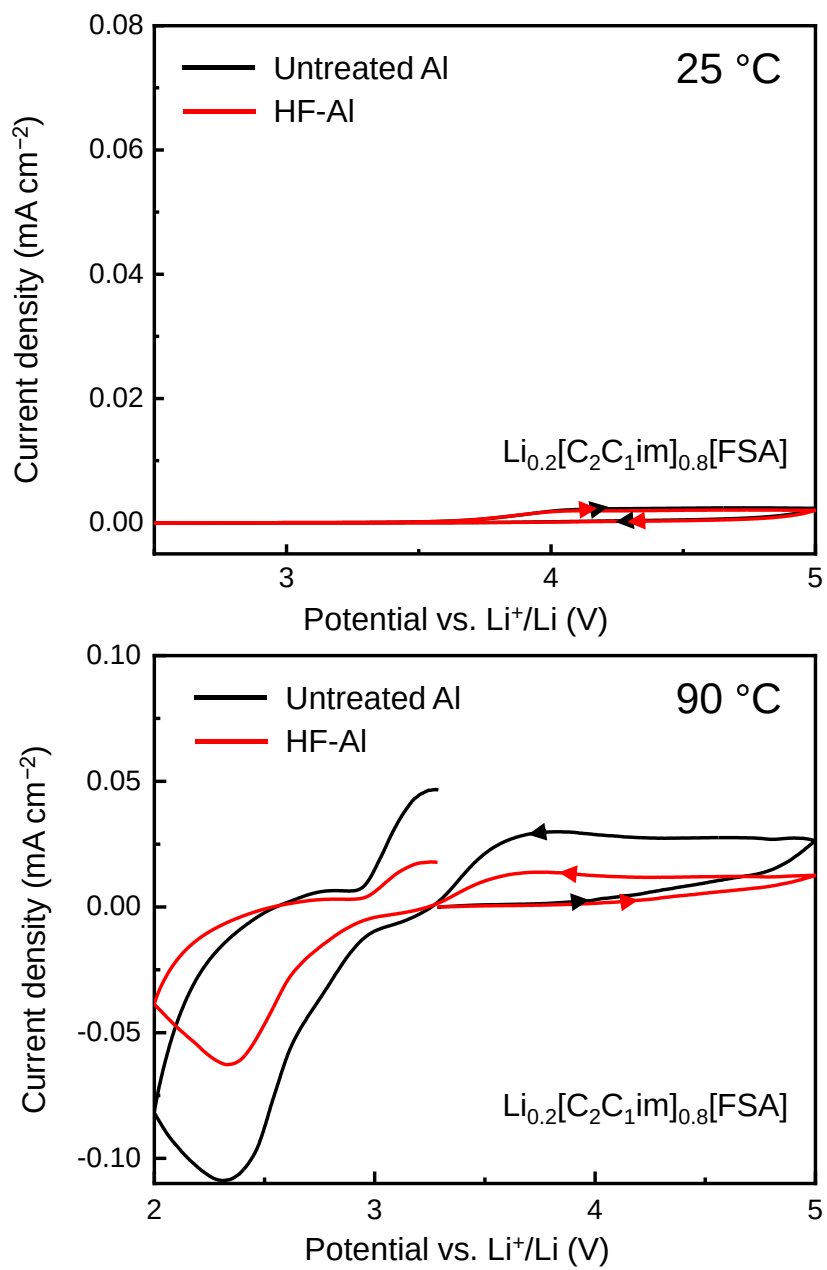


Figure 5-21. Cyclic voltammograms of the untreated Al and HF-Al electrodes in the $\text{Li}_{0.2}[\text{C}_2\text{C}_1\text{im}]_{0.8}[\text{FSA}]$ electrolyte at (a) 25 °C, and (b) 90 °C. Scan rate: 0.5 mV s^{-1} .

References

- [1] X. Shen, H. Liu, X.-B. Cheng, C. Yan and J.-Q. Huang, *Energy Storage Mater.*, **12** (2018) 161-175.
- [2] J. Duan, X. Tang, H. Dai, Y. Yang, W. Wu, X. Wei and Y. Huang, *Electrochem. Energy Rev.*, **3** (2020) 1-42.
- [3] J. Deng, C. Bae, A. Denlinger and T. Miller, *Joule*, **4** (2020) 511-515.
- [4] W. Li, X. Liu, Q. Xie, Y. You, M. Chi and A. Manthiram, *Chem. Mater.*, **32** (2020) 7796-7804.
- [5] L. Zhou, K. Zhang, Z. Hu, Z. Tao, L. Mai, Y.-M. Kang, S.-L. Chou and J. Chen, *Adv. Energy Mater.*, **8** (2018) 1701415.
- [6] J. Xiang, Y. Wei, Y. Zhong, Y. Yang, H. Cheng, L. Yuan, H. Xu and Y. Huang, *Adv. Mater.*, **34** (2022) 2200912.
- [7] Y.-K. Liu, C.-Z. Zhao, J. Du, X.-Q. Zhang, A.-B. Chen and Q. Zhang, *Small*, **19** (2023) 2205315.
- [8] C. Lamiel, I. Hussain, X. Ma and K. Zhang, *Mater. Today Chem.*, **26** (2022) 101152.
- [9] J. Chen, Z. Bai, X. Li, Q. Wang, J. Du, R. Lu and X. Liu, *Appl. Surf. Sci.*, **606** (2022) 155002.
- [10] S. Yang, S. Li, J. Du, C. Han, J. Zhong, M. Yu and B. Li, *Corros. Sci.*, **237** (2024) 112359.
- [11] S. Yang, S. Li, Z. Du, J. Du, C. Han and B. Li, *Adv. Mater. Interfaces*, **9** (2022) 2200856.

- [12] M. Li, C. Wang, K. Davey, J. Li, G. Li, S. Zhang, J. Mao and Z. Guo, *SmartMat*, **4** (2023) e1185.
- [13] T. Ma, G.-L. Xu, Y. Li, L. Wang, X. He, J. Zheng, J. Liu, M.H. Engelhard, P. Zapol, L.A. Curtiss, J. Jorne, K. Amine and Z. Chen, *J. Phys. Chem. Lett.*, **8** (2017) 1072-1077.
- [14] X. Zhang and T.M. Devine, *J. Electrochem. Soc.*, **153** (2006) B375.
- [15] X. Zhang and T.M. Devine, *J. Electrochem. Soc.*, **153** (2006) B344.
- [16] S.-T. Myung, Y. Sasaki, S. Sakurada, Y.-K. Sun and H. Yashiro, *Electrochim. Acta*, **55** (2009) 288-297.
- [17] M. Morita, T. Shibata, N. Yoshimoto and M. Ishikawa, *Electrochim. Acta*, **47** (2002) 2787-2793.
- [18] A. Gabryelczyk, S. Ivanov, A. Bund and G. Lota, *J. Energy Storage*, **43** (2021) 103226.
- [19] M.-T.F. Rodrigues, G. Babu, H. Gullapalli, K. Kalaga, F.N. Sayed, K. Kato, J. Joyner and P.M. Ajayan, *Nat. Energy*, **2** (2017) 17108.
- [20] M. Liu, J. Vatamanu, X. Chen, L. Xing, K. Xu and W. Li, *ACS Energy Lett.*, **6** (2021) 2096-2102.
- [21] H. Yang, G.V. Zhuang and P.N. Ross, *J. Power Sources*, **161** (2006) 573-579.
- [22] L. Sheng, D. Zhu, K. Yang, Y. Wu, L. Wang, J. Wang, H. Xu and X. He, *Nano Lett.*, **24** (2024) 533-540.

- [23] R. Younesi, G.M. Veith, P. Johansson, K. Edström and T. Vegge, *Energy Environ. Sci.*, **8** (2015) 1905-1922.
- [24] J. Chen, F. Wang, X. Fan, J. Zhang, Y. Zhao, W. Xia, Y. Yan, Y. Song, F. Rao and L. Kong, *Energy Fuels*, **38** (2024) 14696-14703.
- [25] A. Abouimrane, J. Ding and I.J. Davidson, *J. Power Sources*, **189** (2009) 693-696.
- [26] H.-B. Han, S.-S. Zhou, D.-J. Zhang, S.-W. Feng, L.-F. Li, K. Liu, W.-F. Feng, J. Nie, H. Li, X.-J. Huang, M. Armand and Z.-B. Zhou, *J. Power Sources*, **196** (2011) 3623-3632.
- [27] E. Cho, J. Mun, O.B. Chae, O.M. Kwon, H.-T. Kim, J.H. Ryu, Y.G. Kim and S.M. Oh, *Electrochem. Commun.*, **22** (2012) 1-3.
- [28] Y. Yamada, C.H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama and A. Yamada, *ChemElectroChem*, **2** (2015) 1687-1694.
- [29] G. Yan, X. Li, Z. Wang, H. Guo, W. Peng and Q. Hu, *J. Solid State Electrochem.*, **20** (2016) 507-516.
- [30] Y.-Y. Wang, X.-Q. Zhang, M.-Y. Zhou and J.-Q. Huang, *Nano Res. Energy*, **2** (2023).
- [31] C.J. Wu, P.C. Rath, J. Patra, D. Bresser, S. Passerini, B. Umesh, Q.F. Dong, T.C. Lee and J.K. Chang, *ACS Appl. Mater. Interfaces*, **11** (2019) 42049-42056.
- [32] G. Zhang, J. Chang, L. Wang, J. Li, C. Wang, R. Wang, G. Shi, K. Yu, W. Huang, H. Zheng, T. Wu, Y. Deng and J. Lu, *Nat. Commun.*, **14** (2023) 1081.

- [33] Y. Chen, Z. Yu, P. Rudnicki, H. Gong, Z. Huang, S.C. Kim, J.-C. Lai, X. Kong, J. Qin, Y. Cui and Z. Bao, *J. Am. Chem. Soc.*, **143** (2021) 18703-18713.
- [34] X. Shi, Y. Zhang, H. Zhang, Z. Zhao, B. Liu, J. Liu, X. Liu and L. Li, *Nano Lett.*, **24** (2024) 12398-12405.
- [35] T. Kawamura, T. Tanaka, M. Egashira, I. Watanabe, S. Okada and J.-i. Yamaki, *Electrochem. Solid-State Lett.*, **8** (2005) A459.
- [36] M. Bolloli, J. Kalhoff, F. Alloin, D. Bresser, M.L. Phung Le, B. Langlois, S. Passerini and J.-Y. Sanchez, *J. Phys. Chem. C*, **119** (2015) 22404-22414.
- [37] Q. Zheng, Y. Yamada, R. Shang, S. Ko, Y.-Y. Lee, K. Kim, E. Nakamura and A. Yamada, *Nat. Energy*, **5** (2020) 291-298.
- [38] N. Piao, L. Wang, T. Anwar, X. Feng, S.e. Sheng, G. Tian, J. Wang, Y. Tang and X. He, *Corros. Sci.*, **158** (2019) 108100.
- [39] K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, T. Noguchi and K. Utsugi, *J. Power Sources*, **231** (2013) 234-238.
- [40] G.G. Eshetu, S. Grugeon, H. Kim, S. Jeong, L. Wu, G. Gachot, S. Laruelle, M. Armand and S. Passerini, *ChemSusChem*, **9** (2016) 462-471.
- [41] A. Hofmann, M. Schulz, V. Winkler and T. Hanemann, *J. Electrochem. Soc.*, **161** (2014) A431.
- [42] X. Shangguan, G. Jia, F. Li, Q. Wang and B. Bai, *J. Electrochem. Soc.*, **163** (2016) A2797-A2802.

- [43] S. Theivaprakasam, G. Girard, P. Howlett, M. Forsyth, S. Mitra and D. MacFarlane, *npj Mater. Degrad.*, **2** (2018) 13.
- [44] C. Luo, Y. Li, W. Sun, P. Xiao, S. Liu, D. Wang and C. Zheng, *Electrochim. Acta*, **419** (2022) 140353.
- [45] J.W. Kim, M.J. Seong, D.W. Park, G. Jeong and T. Yim, *Corros. Sci.*, **198** (2022) 110117.
- [46] K. Mukai, T. Inoue, Y. Kato and S. Shirai, *ACS Omega*, **2** (2017) 864-872.
- [47] Y. Peng, K. Nishikawa and K. Kanamura, *J. Electrochem. Soc.*, **169** (2022) 060548.
- [48] S. Wu, Y. Nishigaki, R. Hagiwara, J. Hwang and K. Matsumoto, *Small*, **20** (2024) 2405007.
- [49] M. Zhang, F. Makhlooghiazad, U. Pal, M. Maleki, S. Kondou, G.A. Elia, C. Gerbaldi and M. Forsyth, *ACS Appl. Polym. Mater.*, **6** (2024) 14469-14476.
- [50] T.D. Pham, A. Bin Faheem, J. Kim, S.-H. Ma, K. Kwak and K.-K. Lee, *Small*, **20** (2024) 2307951.

Chapter 6

Investigation of Conditions for Realizing One-Pot Synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$

6.1 Introduction

As a dominant technology for energy storage systems, lithium-ion batteries (LIBs) have been widely used in portable electronics, electric vehicles, and grid-level energy storage due to their high energy density, durability, and low environmental impact. However, the scarcity, high costs of lithium resources, and safety concerns associated with LIBs have compelled efforts to explore alternative technologies to meet the growing energy demands [1]. Recently, sodium-ion batteries (SIBs) have received intensive attention as a promising candidate for energy storage owing to their abundant and low-cost sodium resources [2]. Despite these advantages, practical applications for SIBs still face challenges including relatively low energy density and poor cycle life, primarily due to the large radius and mass of Na^+ [3, 4].

Positive electrode materials are crucial components of SIBs, having an important impact on electrochemical performance regarding specific energy, cycle life, and specific power [5, 6]. Given that the output voltage of a battery depends on the potential difference between positive and negative electrodes, it is imperative to develop positive electrode materials with high output voltage and capacity to break through the energy density bottleneck [7, 8]. Common positive electrode materials for SIBs include layered

transition metal oxides (LTMOs), polyanionic compounds, and Prussian blue analogs (PBAs). However, both LTMOs and PBAs encounter challenges in cycling stability, which currently falls short of industry standards [9, 10]. In contrast, polyanionic compounds with good structural integrity and open crystal framework are promising electrode materials because of their long-term cycling and thermal stability [11, 12].

Among polyanionic compounds, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) stands out due to its high average working voltage (~ 3.95 V), and large theoretical capacity (~ 128 mAh g^{-1}), delivering a superior energy density in theory comparable to commercial positive electrodes for LIBs [13, 14]. NVPF has an open three-dimensional framework consisting of interconnected $[\text{V}_2\text{O}_8\text{F}_3]$ bi-octahedron and $[\text{PO}_4]$ tetrahedra, providing large channels that facilitate rapid Na^+ diffusion and minimize volume changes during Na^+ insertion/extraction [15, 16]. Nevertheless, its further application is constrained by the low intrinsic electronic conductivity (2.4×10^{-12} S cm^{-1}), which leads to low discharge capacity and poor rate performance [17, 18]. Carbon coating is an effective strategy to overcome this issue. Besides enabling fast electron/ion transport, the carbon layer also buffers volume changes of NVPF and suppresses side reactions with the electrolyte [19, 20].

However, introducing carbon materials results in more F loss during high-temperature synthesis, leading to the formation of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) impurity [21, 22]. This issue is evidenced by a plateau around 3.4 V in reports on carbon-coated NVPF, which affects the structural stability and sodiation kinetics [23-25]. The

formation of NVP can be attributed to two reactions: the formation of VF_3 during high-temperature sintering and the hydrolysis of NaF to HF under acidic conditions [26, 27]. Thus, it is imperative to optimize the synthesis process to obtain pure phase NVPF. For instance, Deng et al. [28] demonstrated that adjusting the pH of precursor solution through ammonia water addition could successfully synthesize pure phase NVPF, while Li et al. [24] synthesized pure phase NVPF by controlling heating temperatures below 600 °C. Excessive NaF has been added to mitigate F loss, but this approach introduces inert sodium salt that compromises the electrochemical performance [27, 29-31]. Some fluorine supplements have also been explored to compensate for F loss during the synthesis, such as polytetrafluoroethylene (PTFE) [32, 33], polyvinylidene fluoride (PVDF) [34, 35], fluorinated ionic liquid [25], and NH_4F [36, 37]. Therefore, it is of paramount importance to understand how preparation conditions and fluorine supplements affect the chemical composition and electrochemical performance of NVPF.

In this chapter, synthetic conditions of NVPF are systematically investigated using a facile one-pot sol-gel method, focusing on the effects of NH_4F as a fluorine supplement and synthesis parameters (pH, carbon content, temperature) on its crystal structure, morphology, and electrochemical performance. Through a comprehensive analysis in terms of preparation conditions, the critical factors controlling the formation of pure phase NVPF are identified. The synthesized NVPF/C is characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) to

examine its crystal structure and morphology, respectively. Several representative samples are selected to evaluate the electrochemical performance.

6.2 Experimental

Electrolytes and materials, 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) (Kishida Chemical, battery grade), FEC (Fujifilm Wako Pure Chemicals), V₂O₅ (Sigma-Aldrich Chemistry, purity ≥ 99.6%), H₂C₂O₄·2H₂O (Fujifilm Wako Pure Chemicals, 99.5–100.2% purity), NH₄H₂PO₄ (Fujifilm Wako Pure Chemicals, purity > 99%), NaF (Sigma-Aldrich Chemistry, purity ≥ 99%), 40 wt% NH₄F solution (Hayashi Pure Chemical Ind., Ltd), glucose (Fujifilm Wako Pure Chemicals, purity ≥ 99.5%), sucrose (Sigma-Aldrich Chemistry, purity ≥ 99.5%), and 25 wt% ammonia solution (Fujifilm Wako Pure Chemicals) were used without any purification. The FSA salts, Na[FSA] ([FSA]⁻ = bis(fluorosulfonyl)amide) and [C₃C₁pyrr][FSA] ([C₃C₁pyrr]⁺ = *N*-methyl-*N*-propylpyrrolidinium), were dried under vacuum before use.

The organic electrolyte, 1 mol dm⁻³ Na[PF₆]-EC/DMC with 3 wt% FEC, was prepared by mixing FEC with 1 mol dm⁻³ Na[PF₆]-EC/DMC, labeled as OE. The Na[FSA]-[C₃C₁pyrr][FSA] IL electrolyte was prepared by dissolving Na[FSA] into [C₃C₁pyrr][FSA] in the molar ratio of 3:7, labeled as 30IL. All the air-sensitive materials and cell assembly were handled in an Ar-filled glove box (H₂O and O₂ < 1 ppm).

The NVPF/C composites were synthesized by the one-pot sol-gel method. First, stoichiometric V_2O_5 and $H_2C_2O_4 \cdot 2H_2O$ were dissolved in deionized water and stirred at 75 °C for 1 h to form a blue homogeneous solution. Then, stoichiometric $NH_4H_2PO_4$ and NaF were added to it, followed by the addition of NH_4F and sucrose in varying amounts, depending on the target sample. When considering the pH effect, 25 wt% ammonia solution was additionally mixed with the solution. The resulting solution was continuously stirred at 80 °C for approximately 10 h and then transferred to an oven and maintained at 120 °C overnight to obtain the precursor. The precursor was subsequently transferred to a tube furnace and preheated at 350 °C for 4 h under an argon atmosphere. After grinding, the preheated sample was further heated at 600 °C (two samples were heated at 550 °C and 650 °C to investigate the effect of heating temperature on NVPF synthesis) for 8 h under an argon atmosphere to obtain the final NVPF/C composites. The samples with different experimental parameters were listed with their abbreviations in **Table 6-1**.

The crystallinity and purity of the synthesized materials were characterized through XRD using a Rigaku Smart Lab diffractometer with Cu-K α radiation (40 kV and 30 mA). Morphological and compositional analyses of these materials were performed by FE-SEM (Hitachi SU-8020) equipped with an energy-dispersive X-ray spectroscopy (EDX) analyzer (Horiba EMAXEvolution X-max). The surface area of the samples was evaluated through nitrogen adsorption analysis based on the Brunauer–Emmett–Teller (BET) theory, conducted with a Tristar II 3020 system (Shimadzu

Corp.). The particle size distribution of powder samples was determined using a laser diffraction particle size distribution analyzer (Microtrac MT3000 II, Nikkiso, Japan).

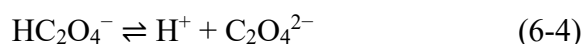
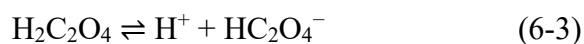
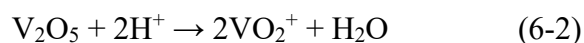
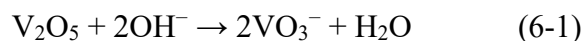
The positive electrodes were prepared by mixing the NVPF/C composite, Super C65 (Timcal Ltd.), and PVDF binder (poly(vinylidene fluoride), Kureha Corp.) in a weight ratio of 80:15:5 with NMP (*N*-methyl-2-pyrrolidone, FUJIFILM Wako Pure Chemical Corp.) solvent. The resulting slurry was mixed by a planetary mixer (AR-100, Thinky, Tokyo, Japan) and cast onto an Al foil (20 μm). After drying at 60 $^{\circ}\text{C}$ for 4 h, the electrodes were punched (10 mm in diameter) and vacuum-dried overnight at 60 $^{\circ}\text{C}$. The mass loading of the active materials in the electrodes was approximately 2 mg cm^{-2} . Sodium metal (Aldrich, 99.95 purity) was cut into a disk and fixed on an Al plate current collector as the counter electrode. One glass fiber separator and two polypropylene (PP) separators were used in 2032-coin cells for short-term and long-term charge/discharge tests. The charge-discharge, rate, and cycling performance were measured with HJ-SD8 charge-discharge system (Hokuto Denko) using the thermostatic chamber (SU-242, ESPEC) in the voltage range of 2.0-4.3 V.

6.3 Results and discussion

The preparation procedure of NVPF/C composites is illustrated in **Figure 6-1**. The purity of NVPF/C is affected by experimental conditions. To investigate the impact of heating temperature on the structure evolution of NVPF/C composites, samples were synthesized at 550 $^{\circ}\text{C}$, 600 $^{\circ}\text{C}$, and 650 $^{\circ}\text{C}$. **Figure 6-2** presents XRD patterns of these

samples, revealing the coexistence of NVPF (PDF#89-8485) and NVP (PDF#53-0018) phases across all samples [38]. The main diffraction peaks of samples align well with the tetragonal NVPF structure indexed to a primitive tetragonal cell, in agreement with the previous report (the $P4_2/mnm$ space group) [39]. For C7.5-F1"-pH7-550 and C7.5-F1"-pH7, the appearance of peaks at $\sim 20.05^\circ$, 20.33° , 23.75° , 31.59° , and 31.99° indicates the presence of the NVP impurity phase. With increasing temperature to 650°C , the peak intensities of NVP impurity increase significantly, suggesting an increase in the proportion of the NVP impurity phase. In addition, the emergence of new peaks at $\sim 14.22^\circ$, 35.63° , and 48.64° further confirms the NVP phase formation. These results suggest that achieving phase-pure NVPF is challenging while incorporating the carbon source. The formation of NVP impurity is attributed to F loss, which can be explained by two side reactions [24, 27, 28, 34]: (1) the hydrolysis of NaF to produce HF ($\text{H}^+ + \text{F}^- \rightarrow \text{HF}$) in an acidic condition, where volatile HF is eliminated under constant stirring and heating conditions and (2) the decomposition of NVPF to form VF_3 at high temperature ($\text{Na}_3\text{V}_2(\text{PO}_4)_3\text{F}_3 + \text{VPO}_4 \rightarrow \text{Na}_3\text{V}_2(\text{PO}_4)_3 + \text{VF}_3 \uparrow$). Reaction (2) can be prevented by lowering heating temperatures. However, reaction (1) is endothermic, and high temperature promotes the generation of HF, driving the reaction forward. In addition, the HF volatilization causes the formation of F vacancies, inducing structural defects in NVPF, which then decomposes above 600°C . In consideration of the XRD results, the temperature was fixed at 600°C for further study to optimize other parameters in the preparation of the pure NVPF phase.

For the preparation of the precursor solution, the reactions involving V_2O_5 and $H_2C_2O_4$ are distinct across varying pH conditions. Detailed reactions include: [28]



The complexation reaction between $H_2C_2O_4$ and vanadium species may alter under different pH conditions, consequently influencing the structural evolution of NVPF and the quality of the final product. To evaluate the influence of pH, NVPF/C composites were synthesized at varying pH values (unaltered, 5.5, 7, and 9). For these samples, NH_4F was used to compensate for F loss during the synthesis process. This approach allowed pH to be maintained as the primary variable under investigation, providing clearer insights into its effect on product quality. The specific role of NH_4F in NVPF synthesis and properties will be discussed in detail in a subsequent section. The XRD patterns for NVPF/C composites synthesized with varying pH are displayed in **Figure 6-3**. For C2.5-F1'-UpH, the predominant diffraction peaks are well-indexed to the primitive tetragonal cell of NVPF, suggesting the product is primarily composed of NVPF. However, several minor peaks corresponding to NVP are observed at $\sim 19.97^\circ$, 20.29° , 23.72° , 31.57° , and 31.94° , indicating a little NVP impurity in the as-prepared sample. After pH adjustment, the number and intensity of characteristic peaks associated with the NVP phase increase, suggesting a higher level of NVP impurity in

the samples. In addition, other minor peaks can be attributed to Na_3PO_4 and V_2O_3 impurities, as well as unidentified phases in trace amounts. Among the adjusted samples, the composite synthesized at $\text{pH} = 7$ exhibits comparatively weaker impurity peaks, suggesting that it contains less impurities than those prepared at $\text{pH} = 5.5$ and 9 . The formation of these impurities can be attributed to the decomposition of unstable phosphate species or NVPF itself during the high-temperature sintering process [40, 41].

To evaluate the sodium storage performance of as-prepared materials, half cells using OE were tested in the cutoff voltage of $2.0\text{--}4.3\text{ V}$. **Figure 6-4** compares the initial charge and discharge profiles of C2.5-F1' synthesized at different pH at a rate of 0.1C ($1\text{C} = 128\text{ mA g}^{-1}$). For C2.5-F1'-UpH, two main voltage plateaus at $\sim 3.7/3.6\text{ V}$ and $\sim 4.2/4.1\text{ V}$ (vs. Na^+/Na) are observed, corresponding to two Na^+ extraction/insertion reactions characteristic of the NVPF phase. After adjusting the pH, an additional plateau appears at $\sim 3.4/3.3\text{ V}$ (vs. Na^+/Na) in all the samples, being ascribed to the presence of NVP impurity [24, 42]. The capacity of this low-voltage plateau reflects the relative content of the NVP phase [28]. Notably, the longer low-voltage plateau observed for C2.5-F1'-pH5.5 and -pH9 compared to C2.5-F1'-pH7 indicates a higher NVP impurity content, which aligns with the XRD results. Furthermore, the large potential gaps between the charge and discharge curves for C2.5-F1'-pH5.5 and -pH9 may stem from the worse structural stability caused by their higher impurity levels. For C2.5-F1'-UpH, a slight plateau is observed at $\sim 3.4\text{ V}$ in the charge/discharge profiles, consistent with

the trace amount of NVP impurity detected in its XRD pattern. Although the primary goal of this study is to investigate the synthesis of pure NVPF phase, an interesting observation is that a controlled amount of NVP impurity might be beneficial for improving sodium storage performance. For example, C2.5-F1'-pH7 achieves the highest discharge capacity of 114.1 mAh g⁻¹, compared to 97.4 mAh g⁻¹ for C2.5-F1'-UpH. Considering that C2.5-F1'-pH7 exhibits relatively lower impurity content with the highest discharge capacity, pH = 7 was selected as the optimal pH condition for further investigation into the effects of NH₄F addition on the production of pure phase NVPF.

Introducing an appropriate amount of fluorine source is expected to suppress the formation of the NVP impurity phase during the synthesis process [43]. As previously discussed, NH₄F serves as a critical fluorine source to compensate for F loss during synthesis. However, in the previous pH study, even with NH₄F addition, pure phase NVPF could not be obtained, suggesting the involvement of other influential factors. One such factor is the carbon source content, which plays a pivotal role in the preparation process by affecting the crystallinity and electrical conductivity of NVPF, consequently influencing its electrochemical performance [23, 44]. To further investigate the role of NH₄F in achieving the pure NVPF phase, the influence of NH₄F addition was systematically examined under modified conditions with an increased carbon content (double compared to previous pH experiments). **Figure 6-5** shows the XRD patterns of NVPF/C composites synthesized with varying NH₄F addition. For C5-

F1-pH7 and C5-F2-pH7, the major diffraction peaks correspond to NVPF while minor peaks at $\sim 14.41^\circ$, 20.21° , 20.50° , 23.91° , 31.75° , and 32.18° indicate the presence of NVP impurities. In contrast, the XRD patterns of C5-F3-pH7 are well-indexed to NVPF, revealing the isostructural tetragonal phase without any impurity peaks detected. These findings suggest that the combination of increased carbon and NH_4F addition could effectively suppress impurity formation and promote the production of pure phase NVPF. This conclusion is further substantiated by comparative experiments under varying synthetic conditions (**Figures 6-2, 6-3, 6-5, and 6-6**). Notably, for C5-F1''-UpH, with less NH_4F and unadjusted pH (**Figure 6-6**), the unsuccessful preparation of pure phase NVPF confirms that pH adjustment plays a less critical role compared to the synergistic effects of fluorine supplementation and carbon source content in achieving phase-pure NVPF.

To further explore the influence of impurities on electrochemical performance, the electrochemical behavior of C5-F1-pH7 was tested by galvanostatic charge-discharge measurements. The typical galvanostatic charge/discharge curves exhibit two prominent plateaus at $\sim 3.7/3.6$ V and $\sim 4.2/4.1$ V (vs. Na^+/Na) corresponding to the extraction/insertion of Na^+ from the NVPF crystal structure (**Figure 6-7**). In addition, a shorter plateau at $\sim 3.4/3.3$ V (vs. Na^+/Na) is observed, which is attributed to the NVP phase. Despite the presence of this minor impurity, the sample demonstrates high sodium storage performance, achieving a discharge capacity of 119.7 mAh g^{-1} at 0.1C . This observation aligns with the earlier pH study, where a controlled amount of NVP

impurity was found to potentially enhance sodium storage properties.

In addition to carbon content, the choice of carbon source also plays a significant role in the synthesis of NVPF by determining the uniformity of the carbon coating and the reduction behavior of vanadium precursors [38, 40]. To investigate this, glucose was used as an alternative to sucrose under identical carbon content (C5) and NH_4F addition (F1') conditions. However, as shown in **Figure 6-8**, the XRD pattern of the resulting sample reveals the presence of NVP impurity alongside the NVPF phase, indicating that glucose was less effective than sucrose in facilitating the formation of phase-pure NVPF. The exact reasons for this difference remain unclear but may be attributed to variations in the decomposition pathways of glucose and sucrose during the sol-gel synthesis process. These differences could influence the distribution of carbon species, the gelation kinetics, or the uniformity of the precursor mixture, ultimately affecting the crystallization of NVPF. It is necessary to elucidate the underlying mechanisms and optimize carbon sources in future studies.

Based on the systematic exploration of synthesis conditions, the optimal parameters for obtaining phase-pure NVPF were identified as carbon content (C5), NH_4F addition (F1'), and sucrose as the carbon source. **Figure 6-9** shows the XRD patterns of C5-F1'-pH7 and C5-F1'-UpH samples. Notably, all diffraction peaks can be indexed to the tetragonal NVPF phase, confirming the successful synthesis of pure-phase NVPF in both the cases. This finding further substantiates that pH adjustment is not critical for achieving phase-pure NVPF under optimized synthetic conditions. The

morphology and microstructure of the as-prepared NVPF/C composites were investigated by SEM, as shown in **Figures 6-10** and **6-11** at different magnifications. Both the samples exhibit micro-sized clusters of approximately 5-10 μm . The negligible morphological differences between the two samples reveal that pH adjustment does not significantly influence the morphologies of the synthesized materials. The elemental composition and distribution of samples were examined by EDX analyses. The resulting EDX elemental mapping demonstrates that Na, V, P, O, and F are uniformly distributed (see **Figure 6-12** for C5-F1'-pH7 and **Figure 6-13** for C5-F1'-UpH). The quantitative elemental analysis further indicates that the weight percent of the F element closely aligns with its theoretical value, suggesting that F loss during synthesis is effectively mitigated. These observations are consistent with the XRD results.

To provide further insights into the material characteristics, the specific surface area and particle size distribution of the C5-F1'-pH7 sample were evaluated. **Figure 6-14** depicts the BET surface area measured by nitrogen absorption-desorption isotherms. The specific surface area of C5-F1'-pH7 is $19 \text{ m}^2 \text{ g}^{-1}$. **Figure 6-15** presents the particle size distribution measured by laser diffraction analysis in water, revealing a median diameter of 18.2 μm for C5-F1'-pH7 without sonication. In addition, the actual C content of C5-F1'-pH7 was 3.4 wt%, obtained by the elemental analytical instrument.

C5-F1'-pH7 was selected as the representative sample to evaluate the electrochemical performance in the voltage range between 2 and 4.3 V. **Figure 6-16** illustrates the galvanostatic charge and discharge curves of C5-F1'-pH7 in OE

electrolyte at various C-rates from 0.1C to 5C, with the first cycle at each rate shown. Two distinct and stable voltage plateaus, located at $\sim 3.7/3.6$ V and $\sim 4.2/4.1$ V (vs. Na^+/Na), correspond to the $\text{V}^{3+}/\text{V}^{4+}$ redox pair associated with the extraction and insertion of Na^+ in NVPF. As the current density increases, a gradual decrease in the voltage plateau is observed due to the internal ohmic drop and the increasing electrode overpotential. Compared to previous samples, such as C2.5-F1'-pH7 (**Figure 6-4**) and C5-F1-pH7 (**Figure 6-7**), the charge-discharge curves of C5-F1'-pH7 hardly show the plateau around 3.4 V, indicating a significant reduction in NVP impurity. **Figure 6-17** depicts the favorable rate capability of the C5-F1'-pH7 electrode, with average discharge capacities of 119.5, 118.0, 113.2, 107.5, 99.8, and 84.9 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2, and 5C. Remarkably, when the current density is reduced back to 0.5C after 30 cycles, the discharge capacity recovers to 116.3 mAh g^{-1} , which is comparable to its initial value, suggesting the outstanding rate performance. This result suggests that the insertion and extraction of Na^+ in the NVPF structure are highly reversible, even under high current densities. **Figures 6-18** and **6-19** demonstrate the cycle performance of C5-F1'-pH7 in OE with two PP separators at a rate of 5C and 1C, respectively. At 5C, the electrode retains 92.2% of its initial capacity after 200 cycles. The lower capacity retention (84.5%) observed at 1C may be attributed to prolonged interfacial reactions between the electrolyte and the positive electrode material, which deteriorates the electrode structure stability. Additionally, the coulombic efficiency (CE) remains close to 100% throughout the entire cycling process, further demonstrating the remarkable

electrochemical reversibility of C5-F1'-pH7. The material based on the optimized synthesis parameters exhibits enhanced specific capacities (compared to C2.5-F1'-UpH), high rate capability, and satisfactory cycling stability. These results indicate that appropriate adjustments to synthesis parameters can not only regulate the purity of NVPF but also improve its sodium storage performance.

The cycle stability of C5-F1'-pH7 was further evaluated in 30IL electrolyte, as shown in **Figure 6-20**. Although the capacity notably decreases during the initial 100 cycles, it stabilizes over prolonged cycling. Specifically, C5-F1'-pH7 shows a high capacity retention of 82.4% after 1500 cycles at 2C, with an average CE of 99.9%. Moreover, the long-term cycling performance of C5-F1'-pH7 at 5C is presented in **Figure 6-21**. While the discharge capacity is lower in 30IL compared to OE electrolyte, C5-F1'-pH7 shows higher long-term cycling stability with a capacity retention of 96.2% after 5000 cycles and an average CE of 98.9%. The lower capacity observed in 30IL electrolyte may be attributed to its relatively high viscosity and low ionic conductivity compared to OE, which can limit ion transport [45]. The exceptional cycling stability in 30IL electrolyte could be ascribed to the high durability of ionic liquid against redox reactions, including oxidative decomposition and Al corrosion, as well as the formation of a robust cathode-electrolyte interface layer from the oxidation of FSA⁻ [46, 47]. These factors effectively minimize side reactions and preserve electrode integrity during prolonged cycling.

6.4 Conclusions

In summary, the synthesis of phase-pure NVPF was systematically explored using a one-pot sol-gel method, focusing on the key synthesis parameters, including temperature, pH, NH_4F , carbon content, and carbon source. The optimal conditions were identified as sucrose as the carbon source, excess NH_4F addition, and controlled carbon content, which successfully enabled the formation of pure NVPF phase. Moreover, pH is not as significant as expected for the suppression of impurity formation when adequate NH_4F and carbon were added. SEM and EDX analysis identified microsized clusters ($\sim 5\text{--}10\text{ }\mu\text{m}$) with uniformly distributed elements and alleviated F loss. Electrochemical measurements demonstrated that the optimized C5-F1'-pH7 sample exhibited excellent rate capability, satisfactory cycling stability, and a high discharge capacity of 119.5 mAh g^{-1} at 0.1C in OE electrolyte. Notably, when tested in 30IL electrolyte, the material achieved superior long-term cycling stability, retaining 96.2% of its capacity after 5000 cycles at 5C . While achieving pure NVPF phase is ideal for structural consistency, the presence of minor NVP impurity under controlled conditions could offer unexpected advantages for performance enhancement. This comprehensive study revealed the relationship between various synthesis parameters and phase-pure NVPF preparation, paving the way for the efficient and scalable production of NVPF with high performance.

Table 6-1. Synthetic conditions and abbreviations for NVPF in this work.

Abbreviation	NH ₄ F/V ₂ O ₅ (molar ratio)	Carbon content theoretically (wt%)	pH	Temperature (°C)
C5-F1-pH7	1/1*	5	7	600
C5-F2-pH7	2/1*	5	7	600
C5-F3-pH7	3/1*	5	7	600
C7.5-F1''-pH7-550	1''/1	7.5	7	550
C7.5-F1''-pH7	1''/1	7.5	7	600
C7.5-F1''-pH7-650	1''/1	7.5	7	650
C2.5-F1'-UpH	1'/1	2.5	Unadjusted	600
C2.5-F1'-pH5.5	1'/1	2.5	5.5	600
C2.5-F1'-pH7	1'/1	2.5	7	600
C2.5-F1'-pH9	1'/1	2.5	9	600
C5-F1''-UpH	1''/1	5	Unadjusted	600
C5-F1'-UpH	1'/1	5	Unadjusted	600
C5-F1'-pH7	1'/1	5	7	600

The two symbols ' and '' indicate two different NH₄F sources. For the symbol ('), the powdery NH₄F as purchased was used in the synthesis, which guaranteed the molar ratio of NH₄F added. For the symbol (''), the powdery NH₄F was stored for a prolonged period and may have absorbed moisture, potentially altering the actual ratio of NH₄F added. *To examine the effect of fluorine sources on the purity of NVPF, 40 wt% solution is selected to avoid the moisture effect. Therefore, two NH₄F sources (powder and 40 wt% solution) were used in this work.

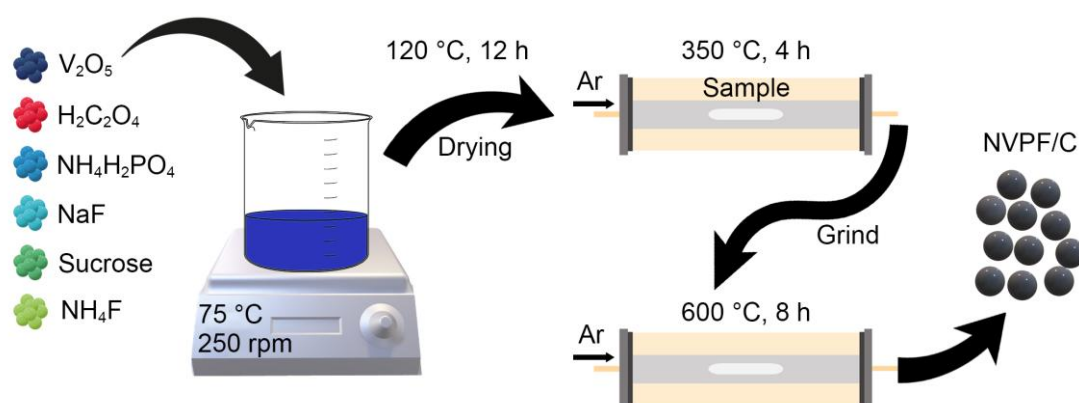


Figure 6-1. Preparation procedure of NVPF/C composites.

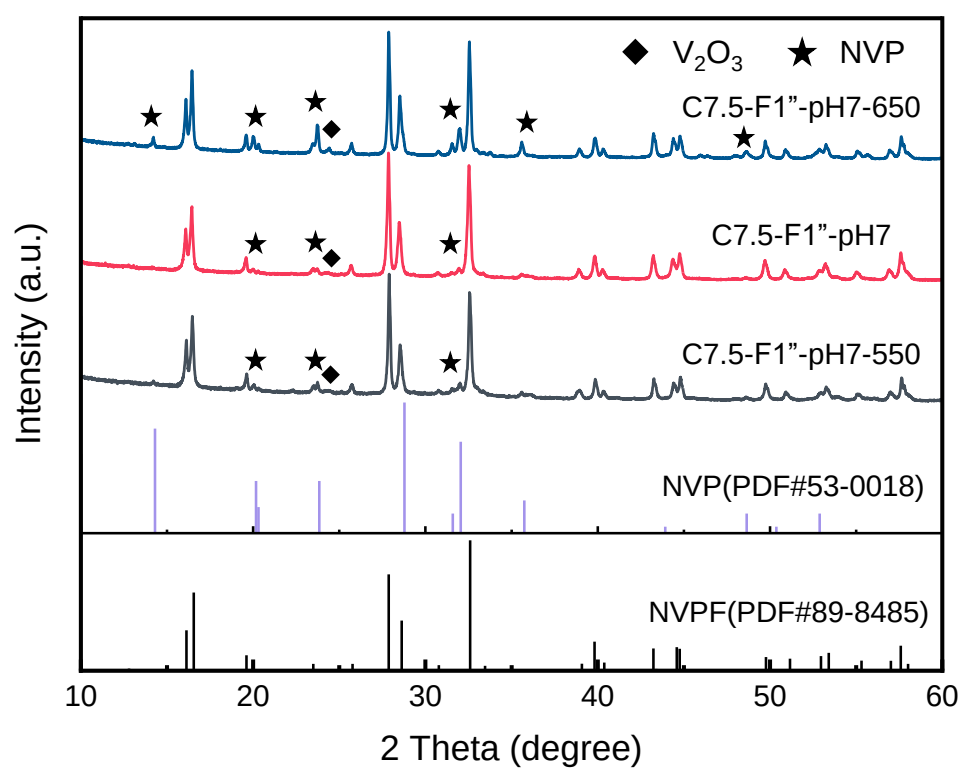


Figure 6-2. XRD patterns of NVPF/C composites synthesized with varying heating temperatures.

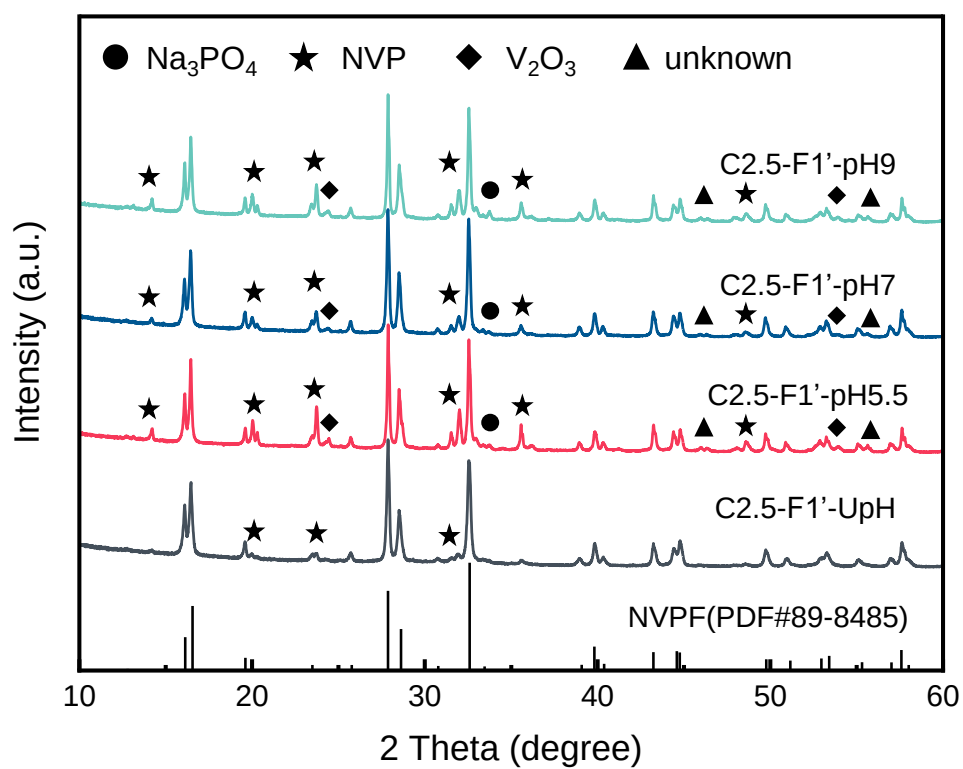


Figure 6-3. XRD patterns of NVPF/C composites synthesized with varying pH.

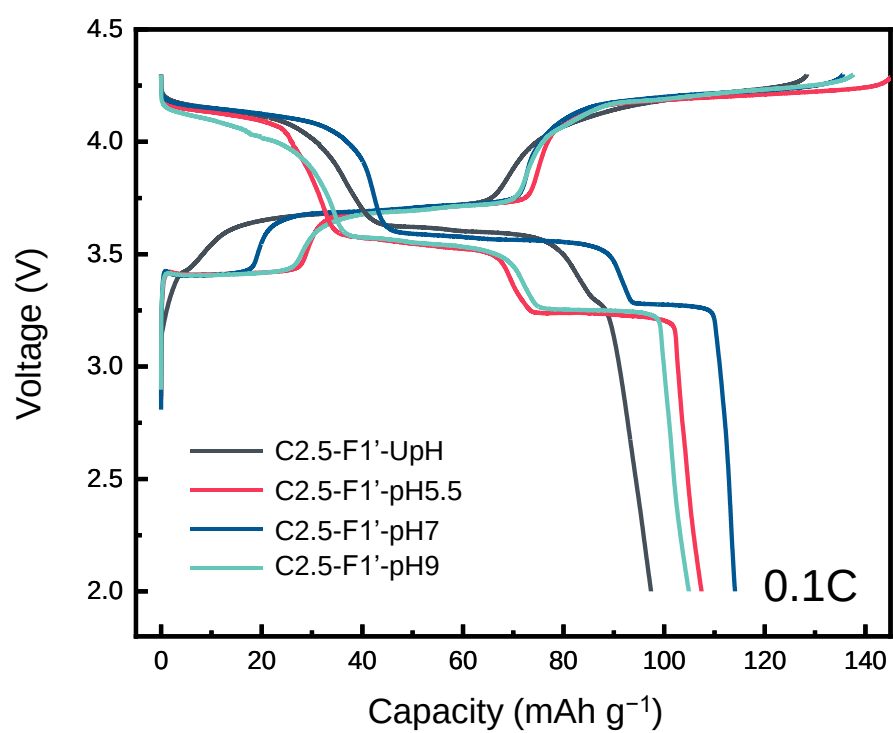


Figure 6-4. Initial charge and discharge profiles of C2.5-F1' samples at 0.1 C.

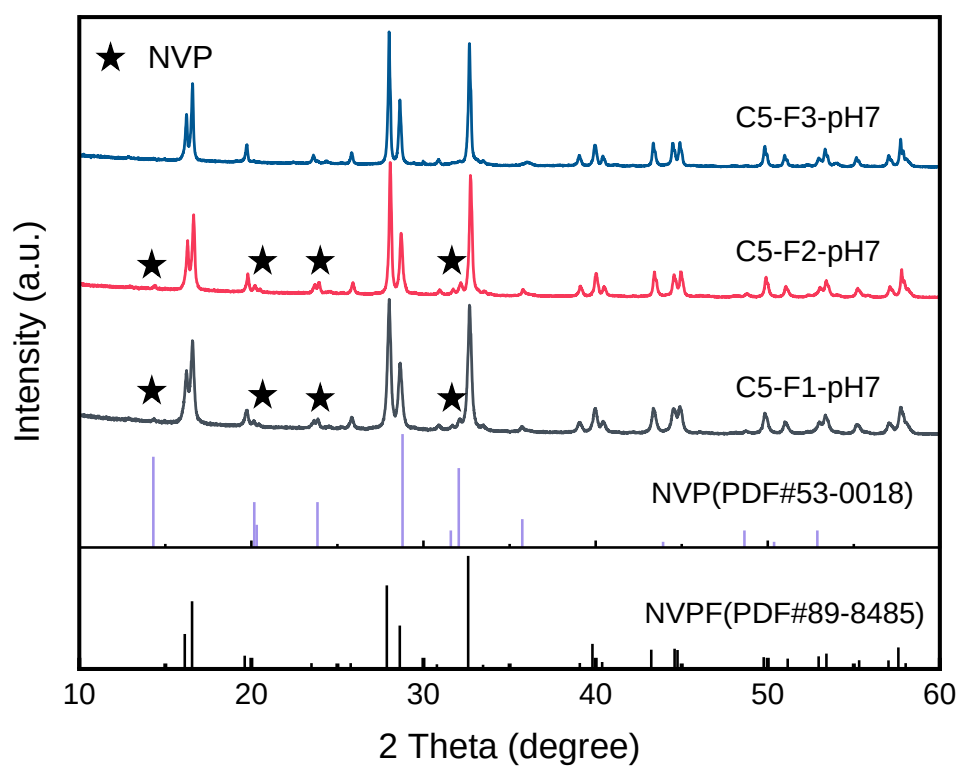


Figure 6-5. XRD patterns of NVPF/C composites synthesized with varying NH_4F addition.

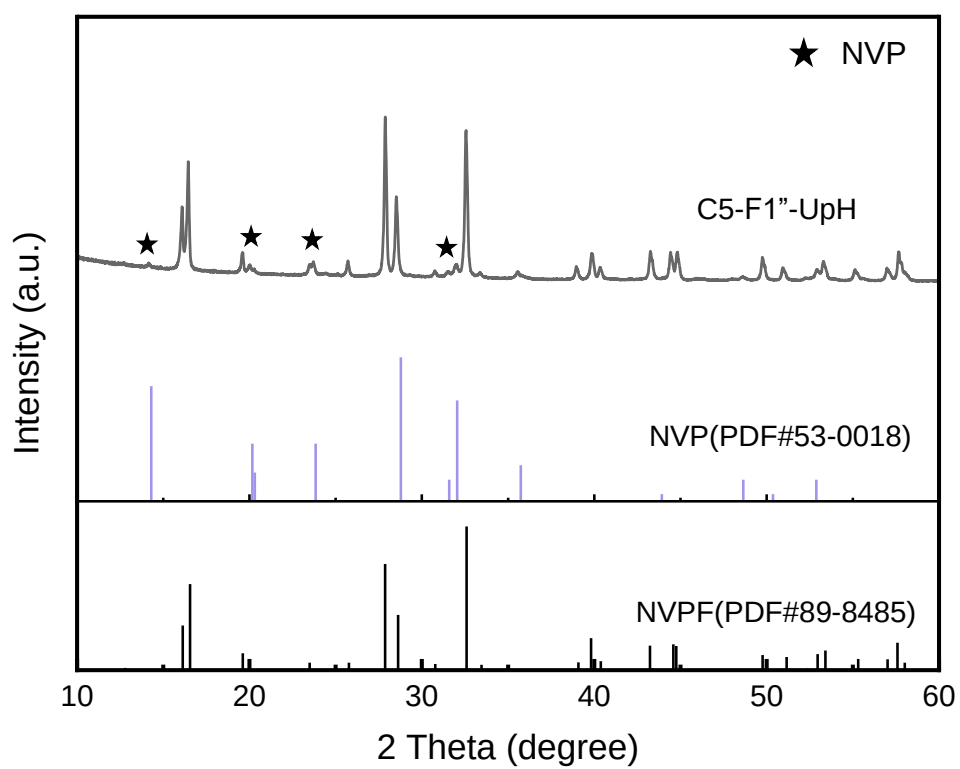


Figure 6-6. XRD pattern of C5-F1''-UpH sample.

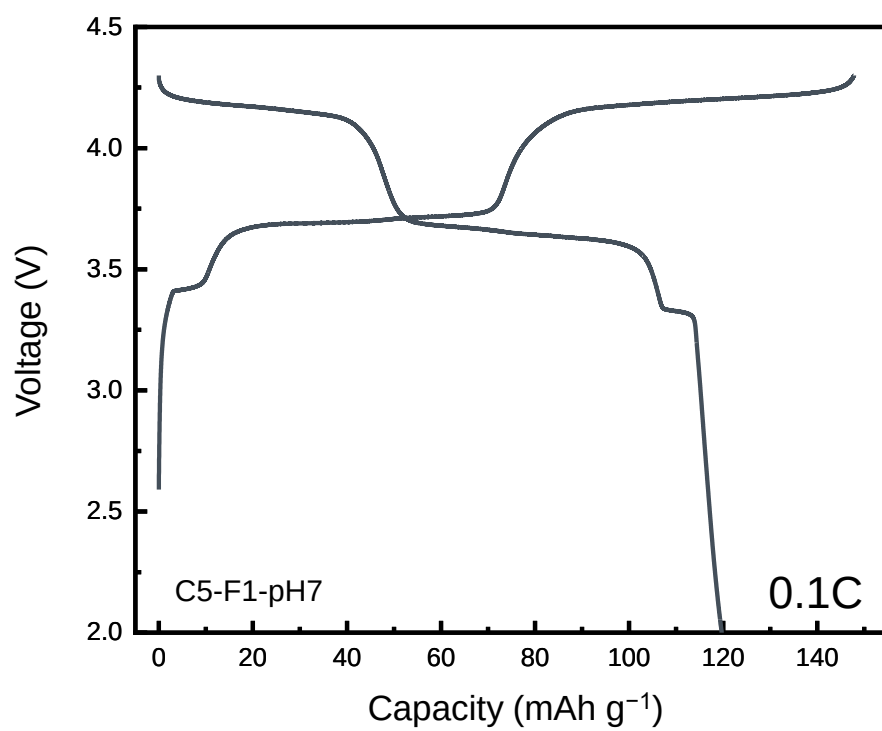


Figure 6-7. Initial charge and discharge profiles of the C5-F1-pH7 electrode at a rate of 0.1C.

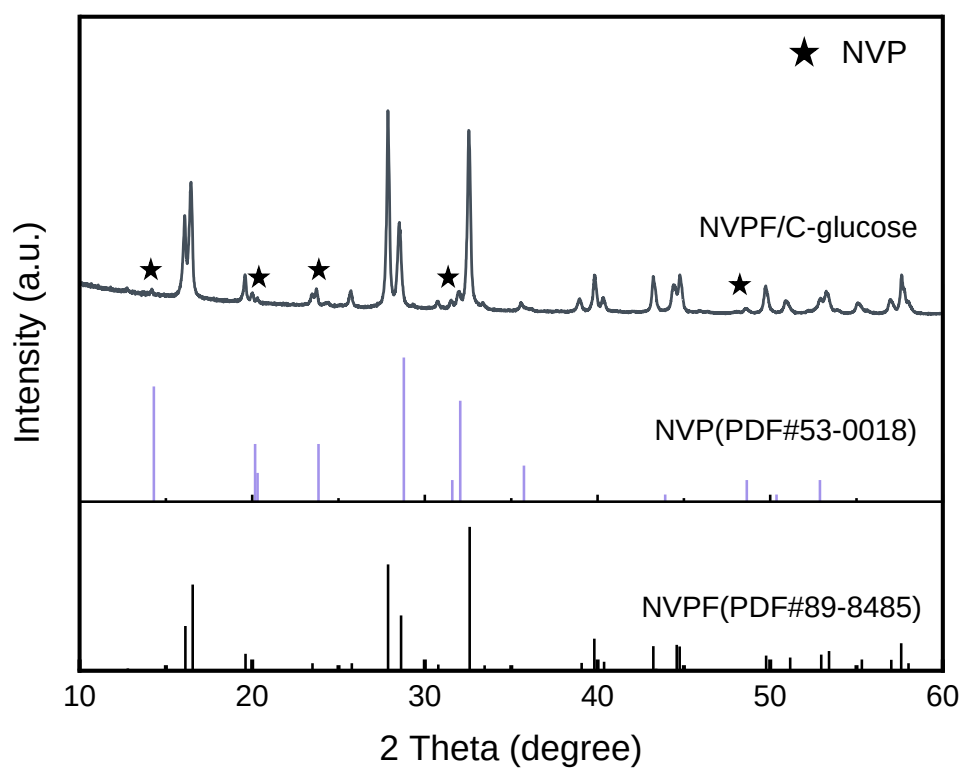


Figure 6-8. XRD patterns of NVPF/C composites using glucose as a carbon source. (600 °C, NH_4F addition is F1', the theoretical carbon content is same as C5)

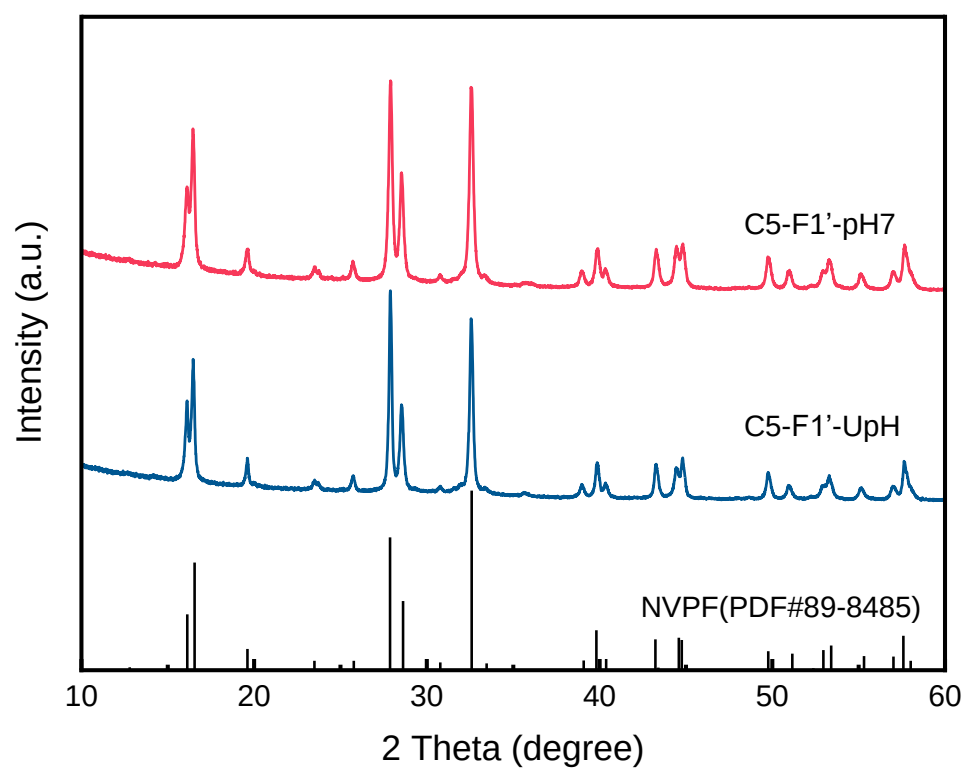


Figure 6-9. XRD patterns of C5-F1'-pH7 and C5-F1'-UpH samples.

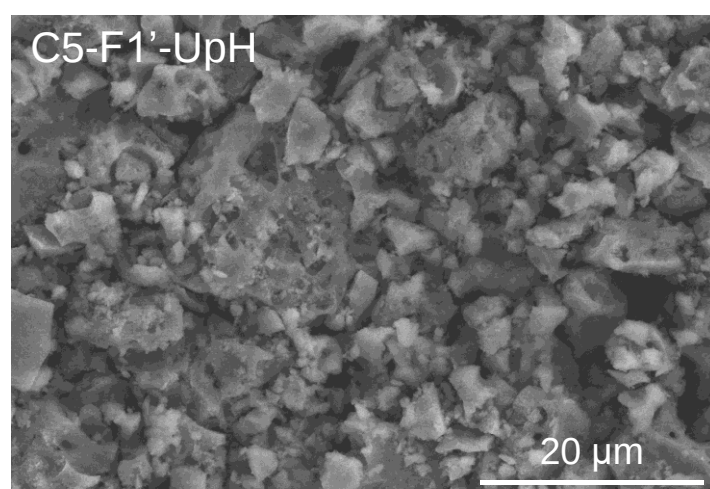
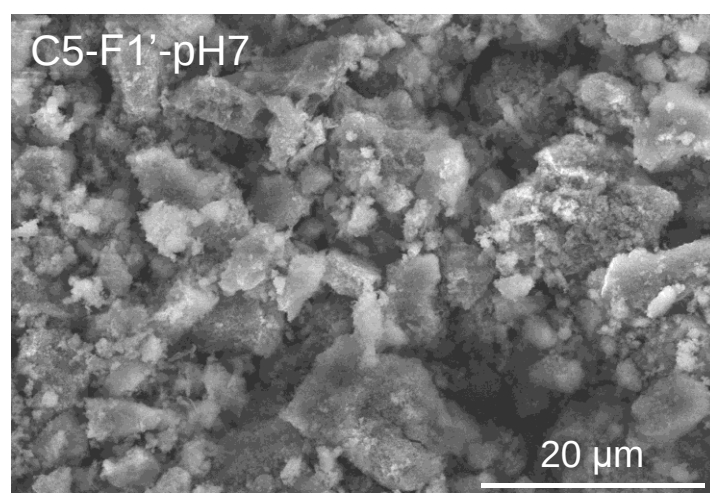


Figure 6-10. FE-SEM images of C5-F1'-pH7 and C5-F1'-UpH samples.

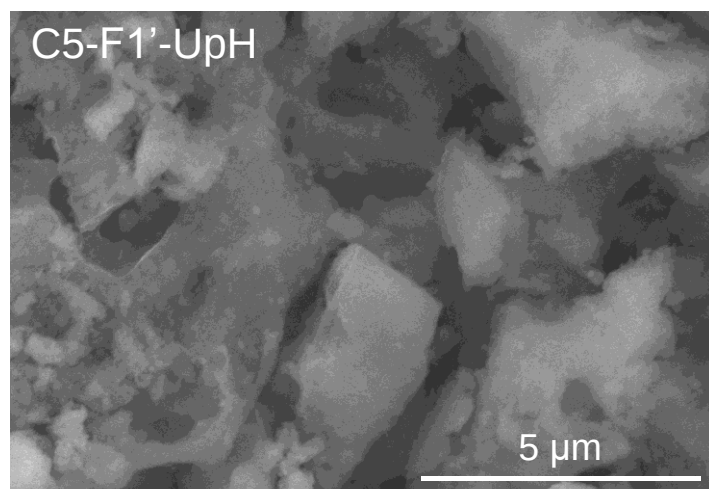
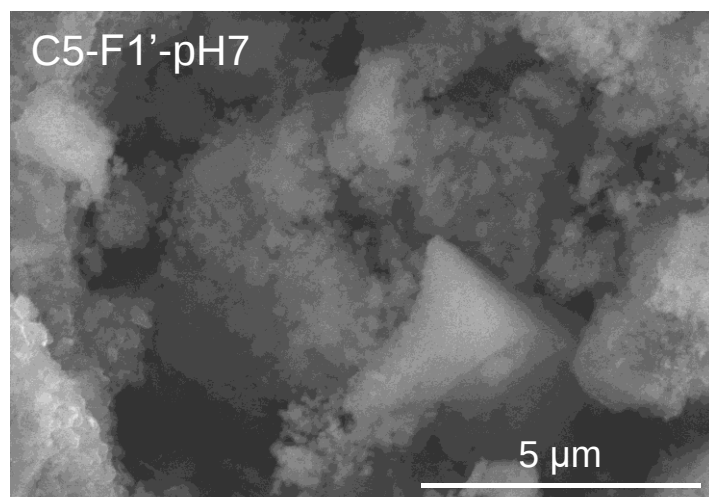


Figure 6-11. FE-SEM images of C5-F1'-pH7 and C5-F1'-UpH samples.

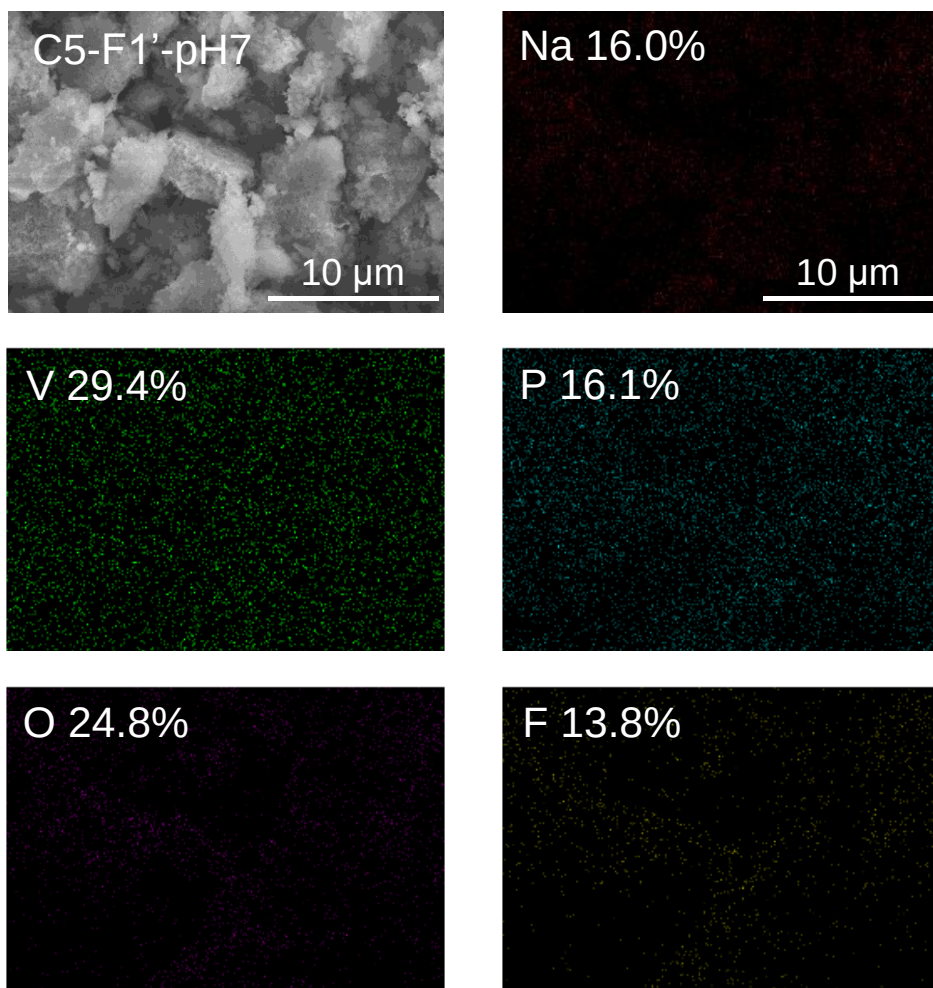


Figure 6-12. FE-SEM and EDX mapping images for C5-F1'-pH7.

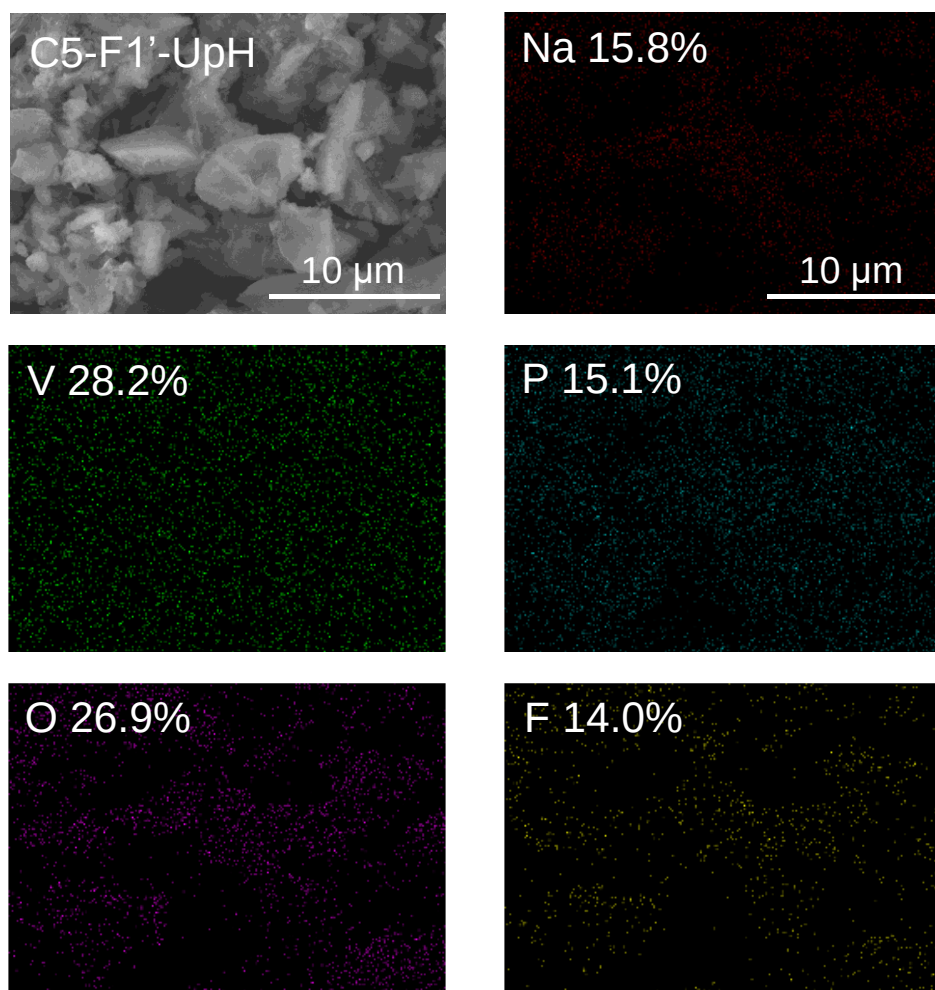


Figure 6-13. FE-SEM and EDX mapping images for C5-F1'-UpH.

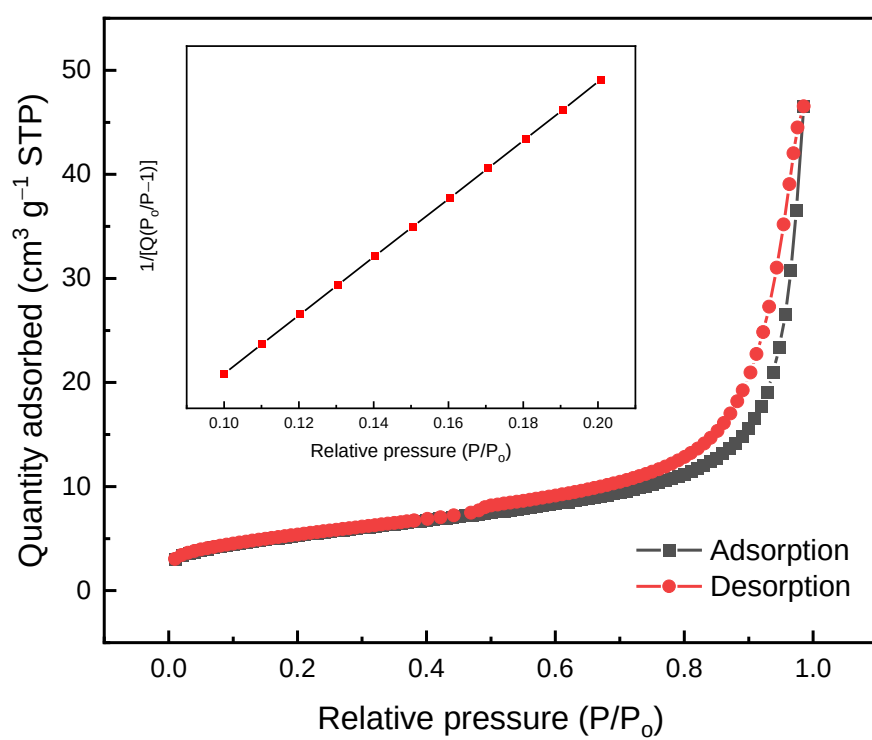


Figure 6-14. Nitrogen adsorption-desorption isotherms and BET surface area plot (inset) for C5-F1'-pH7.

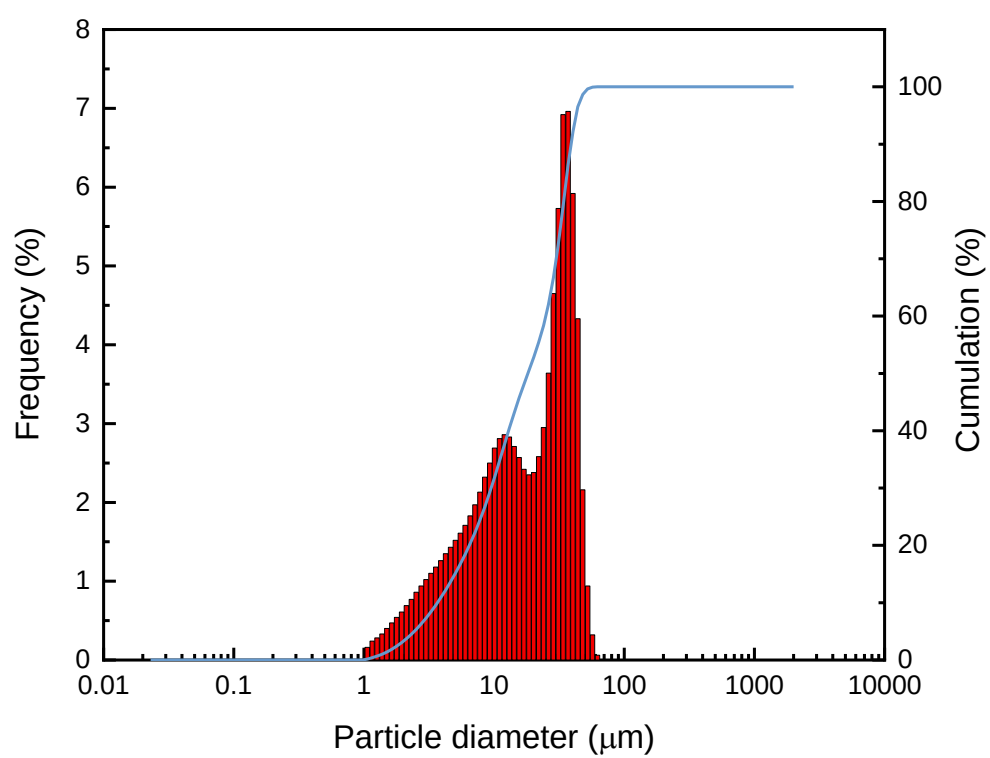


Figure 6-15. Particle size distribution of C5-F1'-pH7.

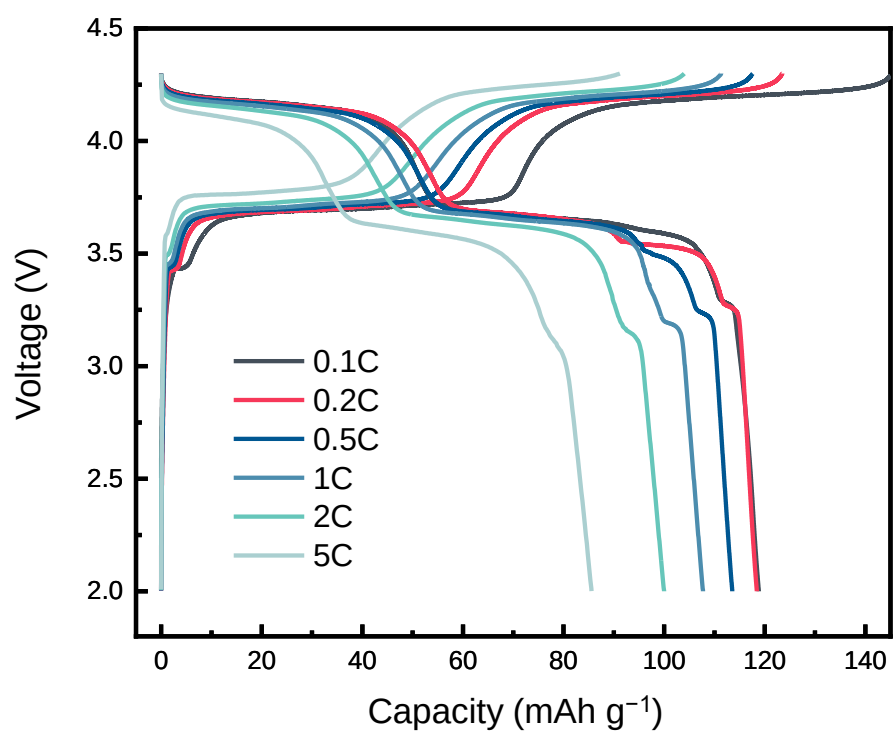


Figure 6-16. Charge and discharge curves of C5-F1'-pH7 from 0.1C to 5C.

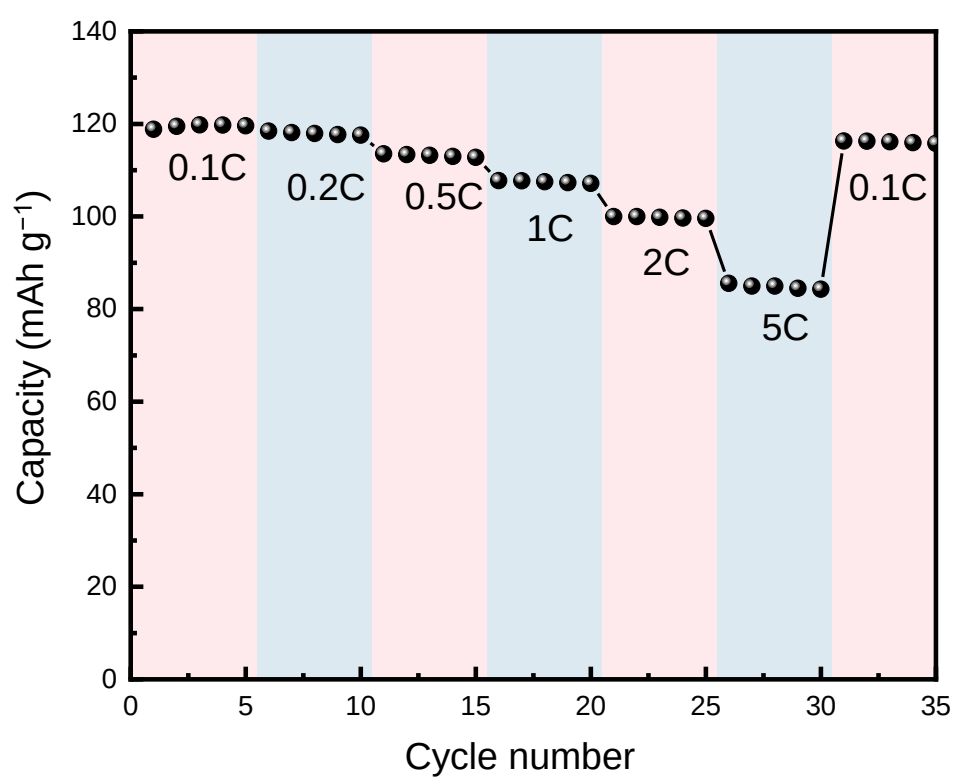


Figure 6-17. Rate capability of C5-F1'-pH7.

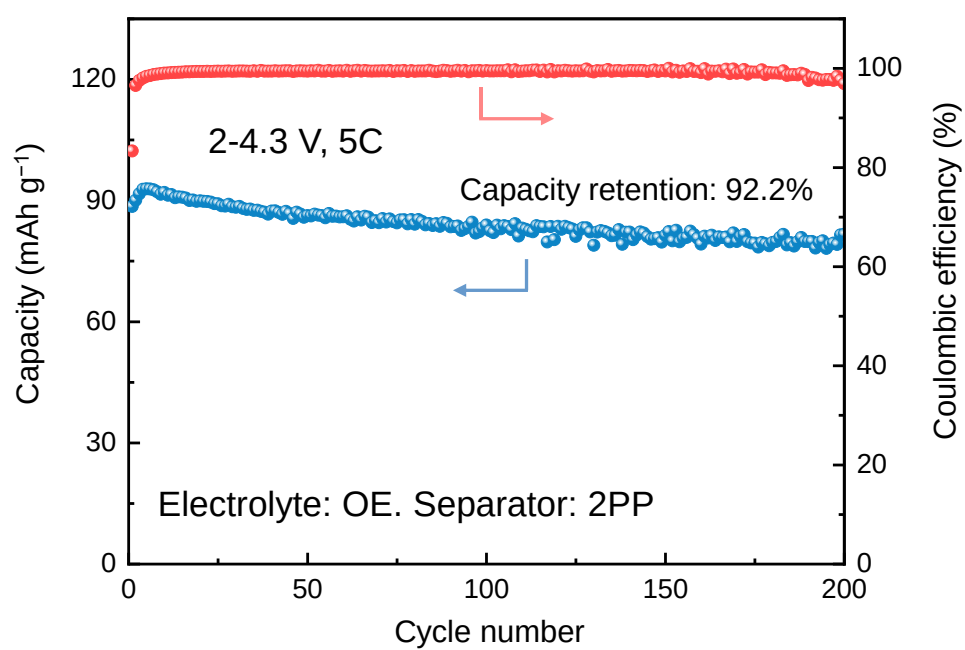


Figure 6-18. Cycle stability of C5-F1'-pH7 at a rate of 5C using OE electrolyte.

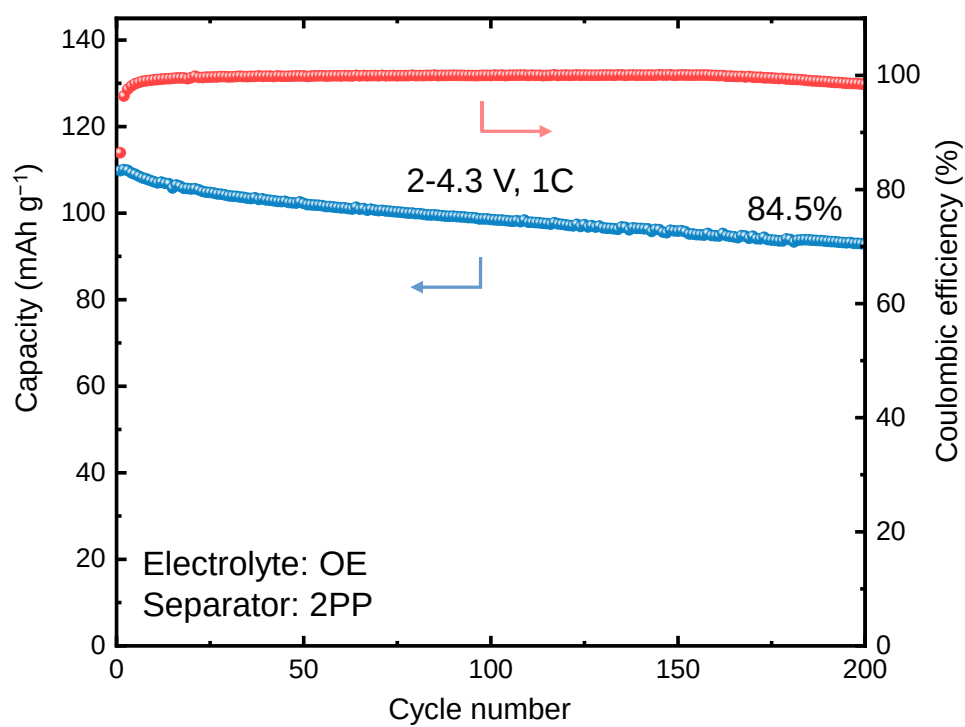


Figure 6-19. Cycle stability of C5-F1'-pH7 at a rate of 1C using OE electrolyte.

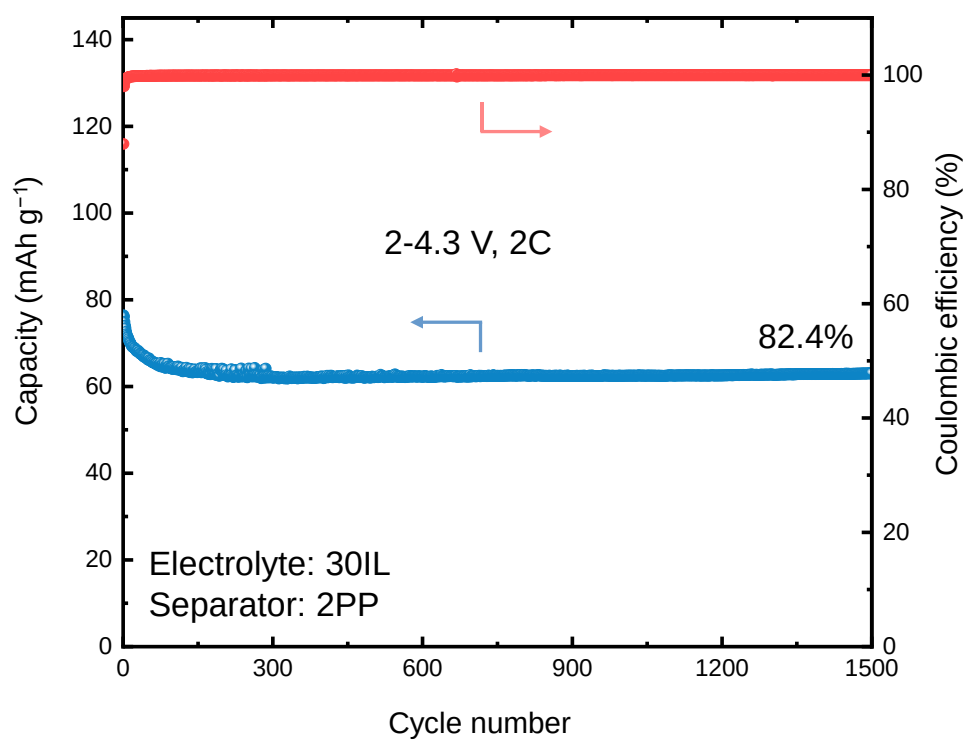


Figure 6-20. Long-term cycling performance of C5-F1'-pH7 at a rate of 2C using 30IL electrolyte.

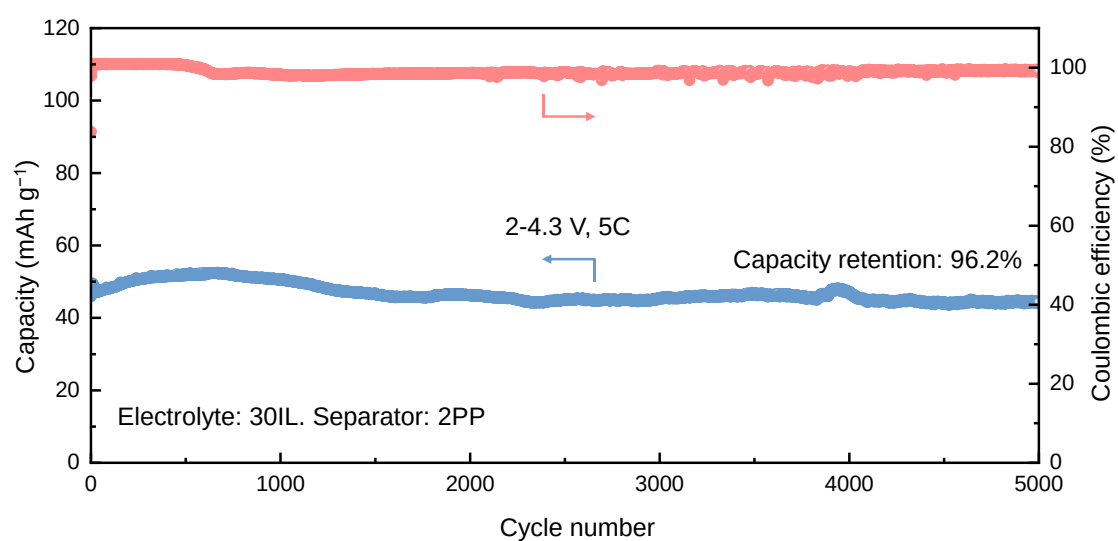


Figure 6-21. Long-term cycling performance of C5-F1'-pH7 at a rate of 5C using 30IL electrolyte.

References

- [1] D. Kundu, E. Talaie, V. Duffort and L.F. Nazar, *Angew. Chem. Int. Ed.*, **54** (2015) 3431-3448.
- [2] S. Yang, K. Cheng and Z. Cao, *J. Mater. Chem. A*, **12** (2024) 13059-13080.
- [3] X. Xiang, K. Zhang and J. Chen, *Adv. Mater.*, **27** (2015) 5343-5364.
- [4] H. Bai, X. Zhu, H. Ao, G. He, H. Xiao and Y. Chen, *J. Energy Chem.*, **90** (2024) 518-539.
- [5] S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder and K. Kang, *Adv. Energy Mater.*, **2** (2012) 710-721.
- [6] H. Yang, D. Wang, Y. Liu, Y. Liu, B. Zhong, Y. Song, Q. Kong, Z. Wu and X. Guo, *Energy Environ. Sci.*, **17** (2024) 1756-1780.
- [7] X.-H. Zhang, W.-L. Pang, F. Wan, J.-Z. Guo, H.-Y. Lü, J.-Y. Li, Y.-M. Xing, J.-P. Zhang and X.-L. Wu, *ACS Appl. Mater. Interfaces*, **8** (2016) 20650-20659.
- [8] J.W. Choi and D. Aurbach, *Nat. Rev. Mater.*, **1** (2016) 16013.
- [9] J. Peng, W. Zhang, Q. Liu, J. Wang, S. Chou, H. Liu and S. Dou, *Adv. Mater.*, **34** (2022) 2108384.
- [10] H. Rostami, J. Valio, P. Suominen, P. Tynjälä and U. Lassi, *Chem. Eng. J.*, **495** (2024) 153471.
- [11] Y. Niu, Y. Zhang and M. Xu, *J. Mater. Chem. A*, **7** (2019) 15006-15025.
- [12] J.-Z. Guo, H.-X. Zhang, Z.-Y. Gu, M. Du, H.-Y. Lü, X.-X. Zhao, J.-L. Yang, W.-H. Li, S. Kang, W. Zou and X.-L. Wu, *Adv. Funct. Mater.*, **32** (2022) 2209482.

- [13] M. Bianchini, F. Fauth, N. Brisset, F. Weill, E. Suard, C. Masquelier and L. Croguennec, *Chem. Mater.*, **27** (2015) 3009-3020.
- [14] C. Shi, J. Xu, T. Tao, X. Lu, G. Liu, F. Xie, S. Wu, Y. Wu and Z. Sun, *Small Methods*, **8** (2024) 2301277.
- [15] Y.-U. Park, D.-H. Seo, H. Kim, J. Kim, S. Lee, B. Kim and K. Kang, *Adv. Funct. Mater.*, **24** (2014) 4603-4614.
- [16] H. Xiong, Y. Liu, H. Shao and Y. Yang, *Electrochim. Acta*, **292** (2018) 234-246.
- [17] Q. Wu, Y. Ma, S. Zhang, X. Chen, J. Bai, H. Wang and X. Liu, *Small*, **20** (2024) 2404660.
- [18] Y. Hu, P. Chen, F. Liu, X. Cheng, Y. Shao, P. Lu, H. Zhang, S. Li, F. Huang and Y. Jiang, *J. Power Sources*, **602** (2024) 234405.
- [19] D. Ma, L.-L. Zhang, T. Li, C. Liu, G. Liang, Y.-X. Zhou and X.-L. Yang, *Electrochim. Acta*, **283** (2018) 1441-1449.
- [20] L. Zhu, H. Wang, D. Sun, Y. Tang and H. Wang, *J. Mater. Chem. A*, **8** (2020) 21387-21407.
- [21] Q. Liu, D. Wang, X. Yang, N. Chen, C. Wang, X. Bie, Y. Wei, G. Chen and F. Du, *J. Mater. Chem. A*, **3** (2015) 21478-21485.
- [22] Z. Yang, G. Li, J. Sun, L. Xie, Y. Jiang, Y. Huang and S. Chen, *Energy Storage Mater.*, **25** (2020) 724-730.
- [23] L. Deng, G. Sun, K. Goh, L. Zheng, F. Yu, X. Sui, L. Zhao and Z. Wang, *Electrochim. Acta*, **298** (2019) 459-467.

- [24] L. Li, J. Zhao, H. Zhao, Y. Qin, X. Zhu, H. Wu, Z. Song and S. Ding, *J. Mater. Chem. A*, **10** (2022) 8877-8886.
- [25] Y. Yan, J. Xu, J. Cao, H. Huang, S. Xue, G. Li, A. Liu, C. Li, D. Dai, B. Li and X. Wu, *Chem. Eng. J.*, **498** (2024) 155640.
- [26] L. Li, Y. Xu, X. Sun, R. Chang, Y. Zhang, X. Zhang and J. Li, *Adv. Energy Mater.*, **8** (2018) 1801064.
- [27] Z. Hu, R. Zhang, C. Fan, X. Liu, P. Gao, W. Zhang, Z. Liu, S. Han, J. Liu and J. Liu, *Small*, **18** (2022) 2201719.
- [28] L. Deng, F. Yu, Y. Xia, Y. Jiang, X. Sui, L. Zhao, X. Meng, L. Que and Z. Wang, *Nano Energy*, **82** (2021) 105659.
- [29] N. Eshraghi, S. Caes, A. Mahmoud, R. Cloots, B. Vertruyen and F. Boschini, *Electrochim. Acta*, **228** (2017) 319-324.
- [30] C. Shen, H. Long, G. Wang, W. Lu, L. Shao and K. Xie, *J. Mater. Chem. A*, **6** (2018) 6007-6014.
- [31] A. Criado, P. Lavela, C. Pérez-Vicente, G.F. Ortiz and J.L. Tirado, *J. Electroanal. Chem.*, **856** (2020) 113694.
- [32] C. Sun, L. Zhang, Z. Deng, B. Yan, L. Gao and X. Yang, *Electrochim. Acta*, **432** (2022) 141187.
- [33] C. Sun, L. Zhang, Z. Deng, H. Sun and X. Yang, *ACS Appl. Mater. Interfaces*, **16** (2024) 35179-35189.

- [34] W. Zhan, C. Fan, W. Zhang, G. Yi, H. Chen, S. Han and J. Liu, *Int. J. Energy Res.*, **44** (2020) 6608-6622.
- [35] G. Yi, C. Fan, Z. Hu, W. Zhang, S. Han and J. Liu, *Electrochim. Acta*, **383** (2021) 138370.
- [36] K. Liang, H. Zhao, J. Li, X. Huang and Y. Ren, *Appl. Surf. Sci.*, **615** (2023) 156412.
- [37] Z. Gu, J. Guo, J. Cao, X. Wang, X. Zhao, X. Zheng, W. Li, Z. Sun, H. Liang and X. Wu, *Adv. Mater.*, **34** (2022) 2110108.
- [38] C. Guo, J. Yang, Z. Cui, S. Qi, Q. Peng, W. Sun, L. Lv, Y. Xu, Y. Wang and S. Chen, *J. Energy Chem.*, **65** (2022) 514-523.
- [39] K. Liang, H. Zhao, J. Li, X. Huang, S. Jia, W. Chen and Y. Ren, *Small*, **19** (2023) 2207562.
- [40] P. Zhu, W. Peng, H. Guo, X. Li, Z. Wang, D. Wang, J. Duan, J. Wang and G. Yan, *J. Power Sources*, **546** (2022) 231986.
- [41] Z. Song, Y. Liu, Z. Guo, Z. Liu, Z. Li, J. Zhou, W. Liu, R. Liu, J. Zhang, J. Luo, H. Jiang, J. Ding, W. Hu and Y. Chen, *Adv. Funct. Mater.*, **34** (2024) 2313998.
- [42] J. Li, X. Cao, A. Pan, Y. Zhao, H. Yang, G. Cao and S. Liang, *Chem. Eng. J.*, **335** (2018) 301-308.
- [43] Y. Chen, Y. Zhao, S. Tian, P. Wang, F. Qiu and T. Yi, *Compos. Part B: Eng.*, **266** (2023) 111030.
- [44] S. Liu, X. Cao, Y. Zhang, K. Wang, Q. Su, J. Chen, Q. He, S. Liang, G. Cao and A. Pan, *J. Mater. Chem. A*, **8** (2020) 18872-18879.

- [45] Y. Zheng, D. Wang, S. Kaushik, S. Zhang, T. Wada, J. Hwang, K. Matsumoto and R. Hagiwara, *EnergyChem*, **4** (2022) 100075.
- [46] R. Hagiwara, K. Matsumoto, J. Hwang and T. Nohira, *Chem. Rec.*, **19** (2019) 758-770.
- [47] J. Hwang, K. Matsumoto and R. Hagiwara, *Adv. Energy Mater.*, **10** (2020) 2001880.

Chapter 7

General Conclusions

As the renewable energy transition accelerates and electric vehicles become more prevalent, advanced energy storage systems have taken on new importance. Lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) are among the key solutions for meeting these emerging demands. Nevertheless, achieving higher energy densities necessitates elevated cell voltages, which introduces complex challenges such as Al current collector corrosion and interfacial instability between electrode and electrolyte. This doctoral dissertation addresses these challenges by focusing on the corrosion behavior of Al and the interfacial stability of high-voltage positive electrode materials, offering insights into strategies for improving the electrochemical performance and durability of positive electrode materials.

Chapter 3 elucidated the influences of temperature and Na salt concentration on Al corrosion in sulfonamide-based IL electrolytes. Cyclic voltammetry revealed a marked increase in anodic currents under elevated temperatures and low Na^+ concentrations. Morphological examinations of the Al surface indicated that lower- Na^+ conditions accelerated corrosion at room temperature, whereas higher- Na^+ conditions partially prevented it. Nevertheless, this protective effect diminished at elevated temperatures. Subsequent analyses showed that Al complexes solubility was not the key factor in corrosion behaviors; instead, the stability of passivation layers played a

crucial role. These findings expand the current understanding of Al corrosion in IL electrolytes and highlight the importance of robust passivation layer formation for optimizing SIB performance using IL electrolytes.

Chapter 4 demonstrated an electrolyte optimization strategy to enhance the stability of LiNiO_2 positive electrode and Al current collector for LIBs. Highly concentrated $\text{Li}[\text{FSA}]$ -based IL electrolytes significantly reduced Ni dissolution and stabilized the cathode-electrolyte interface. The Li/LiNiO_2 cells achieved a high capacity retention of 73.1% after 500 cycles, with an average Coulombic efficiency exceeding 99.9%. Moreover, the highly concentrated electrolyte facilitated the formation of a robust passivation layer on the Al surface, mitigating corrosion caused by $[\text{FSA}]^-$. The good thermal stability and low flammability of this electrolyte also addressed safety concerns for high-voltage operations. Although IL cost remains a challenge, this work underscores the potential of highly concentrated IL electrolytes for developing stable, high-voltage batteries.

Chapter 5 systematically examined the corrosion behavior of Al current collectors in $[\text{FSA}]$ -based carbonate electrolytes, with special attention to F-containing passivation layers. Contrary to expectations, electrochemical and surface analyses showed that HF-treated Al failed to suppress Al corrosion effectively. Further characterization demonstrated that $[\text{FSA}]^-$ actively reacts with AlF_3 , undermining its protective properties and yielding unidentified reaction products. In addition, the solvent environment intensified the reactivity of $[\text{FSA}]^-$, leading to passivation failure.

These findings emphasize the limited understanding of $[\text{FSA}]^-$ and AlF_3 interactions and highlight the need for novel passivation strategies to address the fundamental challenges posed by $[\text{FSA}]^-$ -based carbonated electrolytes.

Chapter 6 investigated the one-pot sol-gel synthesis of pure $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) phase, focusing on the roles of NH_4F addition, carbon source content, pH, and temperature. By integrating sucrose as a carbon source, carefully controlling the temperature, and optimizing NH_4F content, an almost pure NVPF phase was achieved with minimal impurities. The resulting material demonstrated a high discharge capacity of 119.5 mAh g^{-1} at 0.1C and superior cycling stability, retaining 96.2% capacity after 5000 cycles at 5C in a $\text{Na}[\text{FSA}]$ -based IL electrolyte. Structural and morphological analyses confirmed that controlled synthesis conditions minimized impurity formation and alleviated fluorine loss, enhancing electrochemical performance. This study provides valuable insights into the scalable production of high-performance NVPF, bridging the gap between material synthesis and practical application in SIBs.

The findings in this dissertation deepen our understanding of corrosion/passivation mechanisms of Al current collectors, stabilizing strategies for positive electrodes, and synthesis optimization of positive electrode materials in advanced battery systems. Such knowledge lays a foundation for improving the stability, safety, and performance of lithium- and sodium-based positive electrodes. Future endeavors should focus on fully elucidating the passivation chemistries of $[\text{FSA}]^-$ and refining electrolyte

formulations, thereby further enhancing interface stability during high-voltage operation.

List of Publications

Chapter 3

Huazhen Liu, Jinkwang Hwang, Kazuhiko Matsumoto, Rika Hagiwara

ACS Applied Materials & Interfaces, 15 (2023) 35062–35071.

“Systematic Study of Aluminum Corrosion in Ionic Liquid Electrolytes for Sodium-Ion Batteries: Impact of Temperature and Concentration”

Chapter 4

Huazhen Liu, Hiroki Maeda, Jinkwang Hwang, Kazuhiko Matsumoto

ACS Applied Materials & Interfaces, 16 (2024) 53963–53971.

“Enhanced Cycle Stability of LiNiO₂ in a Highly Concentrated Ionic Liquid Electrolyte”

Chapter 5

Huazhen Liu, Jinkwang Hwang, Kazuhiko Matsumoto

To be submitted.

“Failure Mechanisms of Aluminum Passivation in Preventing Corrosion in Bis(fluorosulfonyl)amide-based Electrolytes”

Chapter 6

Huazhen Liu, Jinkwang Hwang, Kazuhiko Matsumoto

ACS Applied Energy Materials, submitted.

“Preparation Conditions of Precursor Solution for Carbon-Coated $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ”

Related work not described in this thesis

Huazhen Liu,[#] Fumiyasu Nozaki,[#] Jinkwang Hwang, Kazuhiko Matsumoto

Journal of Power Sources, 630 (2025) 236172.

“Journey of Olivine Materials from Classic to State-of-the-art Technologies for Next-generation Batteries”

[#]Equally contributed

Acknowledgement

As I complete my doctoral dissertation, I would like to express my deepest gratitude to my supervisor, Professor Kazuhiko Matsumoto. From the inception of my research topic to the completion of this dissertation, Professor Kazuhiko Matsumoto has provided meticulous guidance, unwavering support, and invaluable encouragement. His profound knowledge, broad vision, and keen insights have laid a solid foundation for my academic growth and significantly enhanced my research capabilities.

I am also deeply grateful to Assistant Professor Jinkwang Hwang. Not only has he been an exceptional academic mentor, but also a reliable friend. His relentless pursuit of excellence and dedication to research have set a high standard that has continuously motivated me. His academic expertise, critical feedback, and constructive suggestions have been instrumental in shaping the direction and outcomes of my work. Moreover, his personal support during challenging times has helped me persevere with confidence and determination.

My heartfelt appreciation goes to Professor Emeritus Rika Hagiwara. His high academic standards, perceptive insights, and invaluable critiques have greatly refined the quality of my research. Professor Hagiwara's enthusiasm for scholarship and his meticulous attention to detail inspired me to delve deeper into my studies and broaden my intellectual horizons. The time spent under his guidance has been an enriching and transformative academic experience, for which I am immensely thankful.

I would like to express my sincere gratitude to Professor Takashi Sagawa and Professor Toshiyuki Nohira for their careful review of my dissertation. Their insightful comments and constructive suggestions have greatly improved the clarity and depth of my work.

I would like to extend my sincere gratitude to all the current and former members of our research group. Your collaborative spirit, intellectual discussions, and unwavering support have created a warm and stimulating environment that propelled my research forward. The camaraderie and encouragement I have received from all of you made my doctoral journey enjoyable and fulfilling.

My sincere thanks are also due to the Japan Science and Technology Agency (JST) and the Graduate School of Energy Science for providing essential financial support for my research. This funding allowed me to fully dedicate myself to my academic pursuits, a privilege I deeply appreciate. JST's recognition of my work and trust in my potential have been both motivating and instrumental in my scholarly journey.

Lastly, I owe my deepest gratitude to my parents and parents-in-law. Their unconditional love, unwavering support, and belief in my abilities have been my greatest sources of strength. To my husband, Chiaan Fan, I am profoundly thankful for his patience, understanding, and steadfast encouragement throughout this challenging journey. His care and companionship have provided me with balance and resilience, enabling me to focus on my research and overcome countless hurdles.

This dissertation represents not only my individual efforts but also the collective support, guidance, and encouragement I have received from so many remarkable individuals. It is a testament to their generosity, wisdom, and belief in me. To everyone who has contributed to this journey, I extend my heartfelt thanks—this achievement is as much yours as it is mine.

March 2025

劉 樺珍