

Interfacial Behavior of Negative Electrode and Electrolyte Materials for Li-Ion Batteries

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2025

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Chapter 1

General Introduction

1.1 Electrochemical energy storage systems

With rapid development in science and technology, it is universally acknowledged that the production and storage of energy are among the most crucial factors for a sustainable society. However, the current energy supply is highly driven by non-renewable resources such as fossil fuels, which are proven to be the main cause of global climate change and the severe threat of the greenhouse effect [1, 2]. The utilization of renewable energy resources, such as solar energy, wind energy, and hydro energy, has attracted attention as a feasible solution for the above issues, while their practical applications highly rely on geographical and climate circumstances. Consequently, electrochemical energy storage systems (EESs) have drawn great interest because they have the potential to make a major contribution to the implementation of these renewable energies with high versatility and stable power supply. Besides, EESs are getting widespread attention from large-scale to portable devices, such as from electric vehicles (EV) to smartphones and laptops, respectively, with the clear trend of the global mobility revolution.

1.2 Lithium-ion batteries

Lithium-ion batteries (LIBs) are the most widely used secondary batteries in EESs [3, 4]. The schematic in Figure 1-1 illustrates the movement of Li ions during the charging process of a conventional “rocking-chair” type LIB. This process can be divided into several steps: (1) Li^+ is deintercalated from the structure of positive electrode (i.e. delithiation processes) and passes through the positive electrode (cathode) electrolyte

interphase (CEI) and enters the bulk electrolyte; (2)–(4) Li^+ undergoes diffuses toward the negative electrode in the solvated form through the separator (coordinated form); (5)–(6) desolvated Li^+ passes through the solid electrolyte interphase (SEI) and is intercalated into the negative electrode (lithiation processes). As such, conventional battery-type materials, such as graphite negative electrodes, can store and release ions by reversible electrochemical reactions involving an insertion/extraction of Li^+ into/from active host materials (Figure 1-2a). Figure 1-2b shows the apparent plateaus during galvanostatic charge-discharge profiles in the typical topotactic electrode materials for batteries. Cyclic voltammetric (CV) profiles exhibit clear oxidative and reductive peaks typically observed in the battery-type charge storage processes (Figure 1-2c). Among secondary batteries, LIBs reach a position of prominence in the rechargeable batteries owing to their remarkably high gravimetric energy ($\sim 250 \text{ Wh kg}^{-1}$) and volumetric energy ($\sim 700 \text{ Wh L}_{\text{cell}}^{-1}$) densities [3-6]. With the mass adoption of EV, lithium-ion batteries account for over 95% of battery systems in the EV market, making them the dominant energy storage technology across all vehicle segments [5, 6]. To provide a recharging experience comparable to that of gasoline vehicles, the U.S. Department of Energy (DOE) has set a fast-charging goal of under 15 min for batteries of EV. However, the slow diffusion of ions in the electrodes limits the kinetics of current lithium-ion batteries (LIBs), resulting in long charging times that can take several hours. These issues drive research interest in advanced electrode materials for higher power densities.

1.3 Negative electrode materials

As described in Section 1.2, at the peak of the vibrant rechargeable battery market, LIBs have become ubiquitous in a wide swath of applications owing to their remarkable

energy densities [7-9]. Despite these successes, the growing demand for large-scale applications, such as EVs, has raised concerns about the viability of current secondary batteries for modern energy storage. In addition to higher energy density and improved safety, fast-charging capability and superior power output are increasingly required, pushing lithium-ion batteries closer to their theoretical performance limits. Thus, the advancement of electrode materials in LIBs is of paramount importance to future mobility systems and energy applications.

Against this backdrop, the negative electrode of LIBs is expected to meet the requirement of high reversible capacity, along with good rate performance and cycling performance. However, it is evident that current graphite-based negative electrode materials, which are mostly employed in the commercialized LIBs, cannot fulfil future energy needs in delivering high powder density due to their limited ion kinetics and resultant inferior rate capabilities [10-13]. Moreover, it is reported that metallic lithium deposition may occur on the surface of the graphite negative electrode, especially under a high current density condition ($> 6\text{C}$), which leads to reducing the interfacial reaction, triggering dendrite formation and propagation, and short-circuit of the battery [13, 14]. On the other hand, silicon-based compounds have been proposed as possible replacements on the grounds of their high Li-ion storage capacities over 3000 mAh g^{-1} (graphite: $\sim 360\text{ mAh g}^{-1}$). However, electrodes derived from silicon-based materials have been found to undergo large volume changes ($\sim 300\%$) during (de)lithiation processes, causing SEI and electrode bulk degradation and safety concerns during cycling [15-17]. These issues have led to the exploration of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrode as a candidate for commercialization, exhibiting not only minimal volume changes during the charge-discharge processes but also excellent rate performance compared with graphite-based electrodes [18]. However, its severe gas evolution has

hindered its utilization, particularly at elevated temperatures [19, 20]. The gas evolution from LTO is closely linked to the (111) facet of the material, due to the heightened reactivity of the oxygen atoms at the (111) plane during lithiation [21]. Inspiringly, highly oriented LTO improves its long-term cycling stability, achieving 500 cycles with a capacity retention of 83.6% at 60 °C [22]. Even so, the practical utility of this insertion-type negative electrode is heavily hampered by its limited capacity of 175 mAh g⁻¹ and high working potential of 1.5 V (Li⁺/Li), making it hard to meet the requirement of high energy density.

Given this situation, an exquisite class of negative electrode materials has come into the spotlight, exhibiting unique pseudocapacitive kinetics that engender superior power and energy densities for advanced electrical energy storage devices. Different from the typical electrical double-layer capacitor (EDLC) which store charges through a non-faradic electrostatic charge absorption (Figure 1-2d-f), materials exhibit pseudocapacitive effect, define as pseudocapacitive materials therefore, store charge through reversible redox reaction on or near the surface of electrodes (Figure 1-2g), presenting a similar electrochemical response to an EDLC in GCD tests (Figure 1-2h), but showing redox peaks in CV (Figure 1-2i). Pseudocapacitive materials often allow them to surpass the capacity limitations of EDLCs and mass-transfer limitations of batteries, which bridge the gap of energy and power densities between batteries and EDLCs [23]. The tremendous growth in the understanding of pseudocapacitive materials has been seen in recent years, such as MnO₂, MoS₂, TiO₂, V₂O₅, MXenes (two-dimensional transition metal carbides and nitrides), and conducting polymers (such as polyaniline, polypyrrole, and polythiophene) [24-31]. Pseudocapacitive materials can be categorized into two groups. Materials that only exhibit pseudocapacitive behavior on a nanometer scale and large surface area are termed extrinsic pseudocapacitive

materials, while other materials that show capacitive responses regardless of particle size are termed intrinsically pseudocapacitive materials [23, 32].

Niobium pentoxide (Nb_2O_5), a representative intrinsic pseudocapacitive materials, has attracted considerable attention owing to its structural merits of the fast Li^+ diffusion, high theoretical capacity (201.7 mAh g^{-1} based on $\text{Nb}^{\text{V}}/\text{Nb}^{\text{IV}}$ two-electron reaction), and relatively low working potential ($1.0\text{--}1.5 \text{ V vs. Li}^+/\text{Li}$) [33-35]. Nb_2O_5 presents several polymorphs including pseudo-hexagonal Nb_2O_5 , orthorhombic Nb_2O_5 , tetragonal Nb_2O_5 , monoclinic Nb_2O_5 , and amorphous Nb_2O_5 , depending on synthetic conditions [36-38]. The crystal structure and the crystallinity of Nb_2O_5 greatly affect their electrochemical performance [36, 39-42]. Griffith *et al.* confirmed the electrochemical properties of bulk Nb_2O_5 polymorphs. Tetragonal Nb_2O_5 showed limited charge-discharge performance among the polymorphs. Monoclinic Nb_2O_5 showed the highest reversible capacity but exhibited inferior rate capability to pseudo-hexagonal Nb_2O_5 and orthorhombic Nb_2O_5 ($\sim 140 \text{ mAh g}^{-1}$ at 2000 mA g^{-1}) in micrometer-sized particles. Within this family, orthorhombic Nb_2O_5 has attracted attention owing to its unique properties based on fast Li^+ diffusivity through bulk to nanometer particles, so-called intrinsic intercalation pseudocapacitance [43-45]. Intercalation pseudocapacitance involves the rapid diffusion of ions in and out of the ion-conduction channel or layers within the host material. The theoretical work suggested that the fast Li diffusion is demonstrated in orthorhombic Nb_2O_5 benefits from the energetically favorable Li^+ diffusion pathway along loosely packed (001) planes (Figure 1-3) [46]. These intrinsic structural features of orthorhombic Nb_2O_5 give rise to pseudocapacitive Li^+ storage at charging time up to about 60 s, demonstrating much better rate performance, especially under high current densities (Figure 1-4) [45]. In this point of view, Nb_2O_5 shows the intrinsic properties of overcoming the limitation

of solid-state diffusion for a rapid pseudocapacitive response, which is expected to further contribute to the true realization of the practical application, simultaneously achieving high energy and power densities. However, the further utilization of Nb₂O₅, as well as other transition metal oxide-based pseudocapacitive materials, is still hindered by inherent challenges. For example, compared to graphite electrodes, their low capacity and high working potential render these materials to achieve high energy density. With this regard, a deeper understanding of the electrochemical behavior of Nb₂O₅, especially within the lower voltage range, is urgently needed. This may reveal pathways to enhance its capacity while maintaining its intrinsic pseudocapacitive advantages, such as rapid ion diffusion and excellent rate performance.

At the same time, Li metal negative electrodes have attracted increasing attention due to its high theoretical capacity of 3860 mAh g⁻¹. During discharge, the lithium metal electrode accepts electrons and undergoes a lithium plating process (Li deposition, $\text{Li}^+ + \text{e}^- = \text{Li}$), while during charging, it experiences lithium stripping (Li dissolution, $\text{Li} + \text{e}^- = \text{Li}^+$). Therefore, stable and reversible lithium deposition and dissolution with high efficiency are essential for this type of electrode to achieve high performance while maintaining long-term cycling stability [47-49]. In this context, considerable efforts have been devoted to realizing the stable operation of lithium metal electrodes, including the development of metal host structures [50, 51], interfacial engineering [52-54], and electrolyte formulation [55-58], paving the way toward high-energy-density batteries. However, the practical application of such negative electrodes is still largely hindered by issues such as dendrite formation, safety risks, poor rate performance, and limited cycle life.

1.4 Electrolyte and interfacial properties

The electrolyte, serving as a bridge between the negative and positive electrodes, is considered a key factor influencing battery performance. As illustrated in Figure 1-1, several steps, (2) Li^+ undergoes solvation; (3)/(4) Li^+ diffuses toward the negative electrode in the solvated form (coordinated form) and (5) Li^+ undergoes desolvation (decoordination) (6) Li^+ passes through the SEI into the negative electrode, are significantly influenced by both bulk and interfacial properties, including thermodynamic and kinetic behavior. All of these ultimately determine the efficiency, energy density, and cycling durability of batteries.

For conventional organic electrolytes, organic solvents, such as linear and cyclic carbonate (EC: ethylene carbonate; EMC: ethyl methyl carbonate; PC: propylene carbonate; DEC: diethyl carbonate and DMC: dimethyl carbonate) and ether-based (DME: 1,2-dimethoxyethane and diglyme: diethylene glycol dimethyl ether), couple with the Li salts (such as $\text{Li}[\text{PF}_6]$ and $\text{Li}[\text{FSA}]$ ($[\text{FSA}]^-$: bis(fluorosulfonyl)amide anion)) emerged as electrolytes for LIB. A high value of ionic conductivity of $\sim 10 \text{ mS cm}^{-1}$ is observed in these organic electrolytes at room temperature. However, these organic solvent electrolytes have been challenged by their safety risks above 60°C , generating volatile gases that cause swelling of batteries. Several physicochemical parameters of organic solvents used in secondary batteries are summarized as shown in Figure 1-5a [59]. Among these, the flash point of the organic solvent has been deemed to be the primary factor of the thermal stability of the electrolyte since it is the lowest temperature at which sustained combustion can be continued. Low flashing points of less than 30°C are shown in the group of common linear carbonate esters such as DMC and EMC, widely employed as a co-solvent in organic electrolyte systems due to their low viscosity, posing a significant safety risk even at room temperature. Considerable

efforts for electrolyte development have been devoted to achieving stable and safe operability of organic electrolytes. Representative examples are the utilization of fluorinated and/or phosphate ester solvent and ionic liquid (IL) electrolytes. As shown in Figure 1-5b, a fluorinated phosphate ester is developed combined with non-flammable phosphate esters ($-(\text{RO})_3\text{-P=O}$) and salts soluble ethers ($-\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CF}_3$), achieving better compatibility at elevated temperature of 90 °C and high-voltage operation [60].

With regard to that, unique features such as non-flammability and negligible volatility of IL electrolytes have attracted attention [32, 61, 62]. In a thermogravimetric measurement, minimal weight loss is observed below 277 °C using an IL electrolyte, whereas a significant weight loss is noted to commence at 60 °C due to the evaporation of the PC organic solvent [63]. Furthermore, constructed from differential scanning calorimetric (DSC) measurements, a phase diagram of $\text{Li[FSA]}\text{-[C}_2\text{C}_1\text{im][FSA]}$ IL electrolyte indicate that a wide liquid-phase temperature range exists around room temperature between $x(\text{Li[FSA]}) = 0.0\text{--}0.4$, allowing their adaptability across from intermediate to below room temperature with high thermostability [64]. As such, IL electrolytes enable stable operation of batteries with high safety even at an intermediate temperature. At intermediate temperature, these IL electrolytes exhibit a wide electrochemical window and high ionic conductivity: 36.9 mS cm^{-1} at 85 °C for 1.1 mol dm^{-3} $\text{Li[FSA]}\text{-[C}_2\text{C}_1\text{im][FSA]}$ [64]. Therefore, improved electrochemical performance of batteries is observed owing to their enhanced ion transport and kinetic properties within the electrolyte and electrode facilitate the electrode reaction [65-72].

The interfacial properties of electrode–electrolyte systems are of critical importance for ensuring stable ion transport, minimizing parasitic reactions, and enhancing the long-term cycling performance of batteries. During battery operation, a

SEI spontaneously forms on the surface of the negative electrode. This process is initiated by the reductive decomposition of electrolyte components at the electrode surface, resulting in the formation of a passivating layer. SEI layers play a vital role in preventing continuous electrolyte degradation and maintaining electrode integrity over prolonged cycling.

Within this framework, the characteristics and durability of the SEI are significantly influenced by a variety of parameters, including factors intrinsic to the electrolyte, such as its formulation and coordination environment, as well as external operating conditions, such as the applied current density and temperature of the system [73]. Specifically, as shown in Figure 1-6b, inorganic components such as LiF, Li₂O, and Li₃N, which typically originate from the anions of lithium salts, are recognized as mechanically robust and ionically conductive constituents of the SEI [59, 74]. In contrast, organic species in the conventional electrolytes, such as carbonates (e.g., C=O–O and C–O–C moieties) derived from the decomposition of organic solvents, tend to be less stable, leading to the gradual deterioration of the formed SEI layer [74].

Considering the above, increasing the concentration of Li salts in electrolytes (nonaqueous and aqueous) has been intensively pursued as a strategy for enhancing and differentiating the electrochemical properties of electrolytes [75-77]. These highly concentrated electrolytes (HCE) have been found to offer electrochemical advantages by reducing the amount of solvating molecules (Figure 1-6a). For instance, the first solvation of the Li⁺ ion sheath in highly concentrated electrolytes harbors more anions than their diluted counterparts, forming abundant ion pairs such as contact ion pairs and aggregates (commonly referred to as CIP and AGG, respectively) [78]. This distinct solvation environment primarily leads to the reduction of anions: a factor that plays a significant role in the creation of a durable, anion-rich SEI with advantageous properties

such as superior passivation capabilities for both the negative and positive electrodes, ultimately resulting in improved electrochemical performance [75, 78-84]. To overcome the disadvantages of the high viscosity of HCE, an inert solvent is introduced to the HCE to dilute the concentrated electrolyte, defined as localized high-concentrated electrolyte (LHCE, Figure 1-6a) [76, 85-87]. Generally, the existence of diluent decreases the viscosity of HCE while it does not form a solvation structure with Li^+ , preventing the unique local coordination environment of Li^+ in HCE. Therefore, the formation of anion-derived SEI can be reserved in LHCE. Various diluents, including hydrofluoroether (HFEs) as a class of fluorinated ethers [57], as well as specific compounds such as bis(2,2,2-trifluoroethyl) ether (BTFE) [85], and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) [56], have successfully emerged for these LHCE, and features including expansion electrochemical window, formation of LiF-rich SEI contribute to enhancing the cyclability under harsh conditions like high-voltage and/or high-temperature operation [88].

In line with this trend, highly Li-concentrated IL (HCIL) electrolytes using sulfonylamide anions ($[\text{FSA}]^-$ and bis(trifluoromethylsulfonyl)amide ($[\text{TFSA}]^-$)) have been reported to demonstrate advantageous characteristics such as, expanded electrochemical stability windows [89], high transference numbers of Li and Na ions [90, 91], high rate capability [92], enhanced cycling performance in high-voltage cells and the formation of a stable electrolyte/electrode interphase in Li and Na metal-based batteries [93-95]. Extensive efforts have been undertaken to understand the enhanced Li^+ transport in the HCIL electrolyte. The clustering behaviors of Li-anion pairs have been well investigated through experimental, theoretical, and computational methodologies [96-100]. Furthermore, a number of HCIL electrolytes employing $[\text{FSA}]^-$ and $[\text{TFSA}]^-$ anions have been noted to effectively suppress the side reactions

between the electrolyte and the Al current collector. This benefit is attributed to the reduced presence of free $[\text{FSA}]^-$ anions, which tend to corrode the Al current collector when the fraction of Li^+ ions is increased [101-104].

On the other hand, the temperature effects on the variation of the coordination environment of ions in the electrolyte have sparked curiosity. The coordination environment of alkali ions within the electrolyte evolves significantly with temperature (Figure 1-6c,d), it is revealed that a higher ratio of $(\text{Li}[\text{FSA}]_x)^{1-x}$ or $(\text{Na}[\text{FSA}]_x)^{1-x}$ complexes is obtained in total ion clusters at elevated temperature than that at room temperature, leading to the formation of $[\text{FSA}]^-$ -driven SEI layer [92, 105]. The formation of these inorganic-rich, sturdy SEI layers originating from ILs electrolytes is considered to act as a major contributor to their stable electrochemical performance across a wide temperature range. Furthermore, the temperature-dependent solvating electrolyte is designed and applied to Li metal batteries to enable their wide-temperature operation. A eutectic electrolyte system composed 2.1 mol dm^{-3} LiDFOB-NMTFA ($[\text{DFOB}]^- = [\text{BF}_2(\text{C}_2\text{O}_4)]^-$, NMTFSA = *N*-methyl-2,2,2-trifluoroacetamide) triggers a temperature-dependent solvation structure (Figure 1-6e), showing a decreased role of NMTFA and increased proportion of anions in the Li^+ solvation structure by increasing temperature, contributing to a long-cycling performance with a capacity retention of 82.79% after 1000 cycles in a rate of 3400 mA g^{-1} at 100°C [106]. In addition, it is also found that the effect of temperature on the other physical properties, such as dielectric constant, pronouncedly changes due to accelerated molecular motions with the rise of temperature, which also highly affects the solvation structure of the alkali ion.

1.5 Aims of this study

As stated above, lithium-ion batteries (LIB) must offer improved rate capability and

durability to meet the demands of future consumer electronics in diverse environmental conditions [45]. In this context, a class of pseudocapacitive materials has attracted attention as negative electrode candidates offering a pathway to simultaneously achieve high energy and power densities. It is therefore essential to investigate their electrochemical behavior across broad temperature and voltage ranges, and to enhance their interfacial charge transfer processes, in order to develop high-performance negative electrode materials. Furthermore, understanding the coordination environment of electrolytes is critical for gaining insight into SEI formation mechanisms and improving their compatibility with electrode surfaces, thereby enhancing overall electrochemical performance. This research aims to investigate the interfacial properties of negative electrodes and electrolytes, with a focus on electrode reactions and SEI formation, to advance the design of high-performance lithium-ion batteries.

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

Chapter 3 explores the effect of temperature on pseudocapacitive behavior of submicron-sized Nb_2O_5 within a wide voltage window (0.01–2.3 V). Material characterizations reveal Nb_2O_5 amorphization and NbO formation via a conversion reaction in the initial cycle, followed by reversible $\text{Nb}^{\text{V}}/\text{Nb}^{\text{III,II}}$ redox reaction in amorphous $\text{Li}_x\text{Nb}_2\text{O}_5$. Elevated-temperature operations are found to enhance pseudocapacitive ion storage behavior. Further analysis confirms that long-term cycling stability is associated with the formation of a robust $[\text{FSA}]^-$ -derived solid electrolyte interphase. This work provides insights into the temperature-dependent charge storage mechanisms in pseudocapacitive transition-metal oxide electrodes.

Chapter 4 investigates a surface-modified Nb_2O_5 negative electrode material by

introducing conductive NbO_x ($1 \leq x \leq 2$) layer via a methodology of short-time Argon-ion bombardment. Materials characterization confirms the surface reduction and the formation of the NbO_x layer on Nb_2O_5 electrode, which effectively reduces the charge-transfer resistance and enhances the electrical conductivity of the electrode. The modified Nb_2O_5 electrodes are found to exhibit improved discharge capacity and better rate capability. This work underscores the critical role of interfacial charge transfer in enhancing pseudocapacitive ion storage.

Chapter 5 investigates how the reduction behavior of ILs changes due to alterations in the coordination environment of their organic cations as the concentration of Li salt increases. Physicochemical characterizations reveal that the weakened cation–anion interactions cause organic cation decomposition during initial charging, leading to poor initial efficiency and high irreversible capacity. Strategies for mixing anions to adjust the coordination environment of organic cations are proposed, which improve electrolyte stability and Coulombic efficiency, highlighting the importance of ionic coordination focusing on organic cations.

Chapter 6 investigates how Ar^+ sputtering affects X-ray photoelectron spectroscopy (XPS) analysis of electrode materials by altering surface composition and oxidation states, potentially leading to misinterpretation of redox mechanisms. It further proposes strategies to minimize sputtering-induced artifacts, enabling more accurate surface characterization in battery research.

Chapter 7 concludes the thesis and explores potential avenues for future investigation.

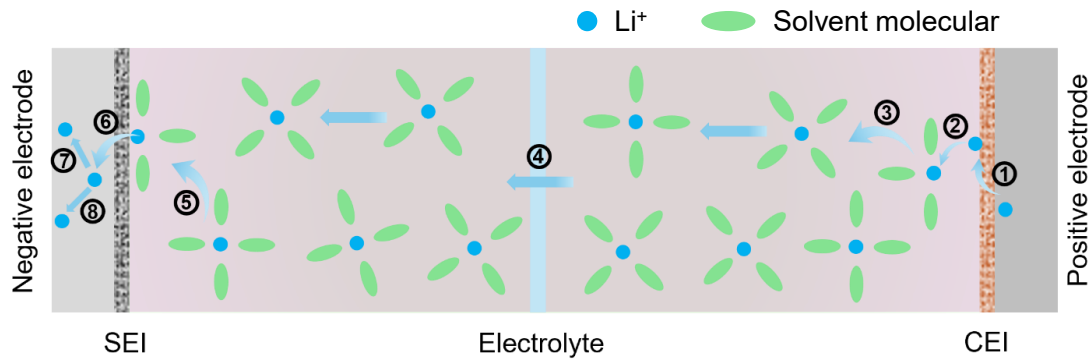


Figure 1-1. Schematic illustration of the working principle of LIBs during charge, showing lithium-ion transport and interfacial processes. Lithium ions are extracted from the positive electrode, pass through the CEI, diffuse through the electrolyte, and cross the SEI to be inserted into the negative electrode.

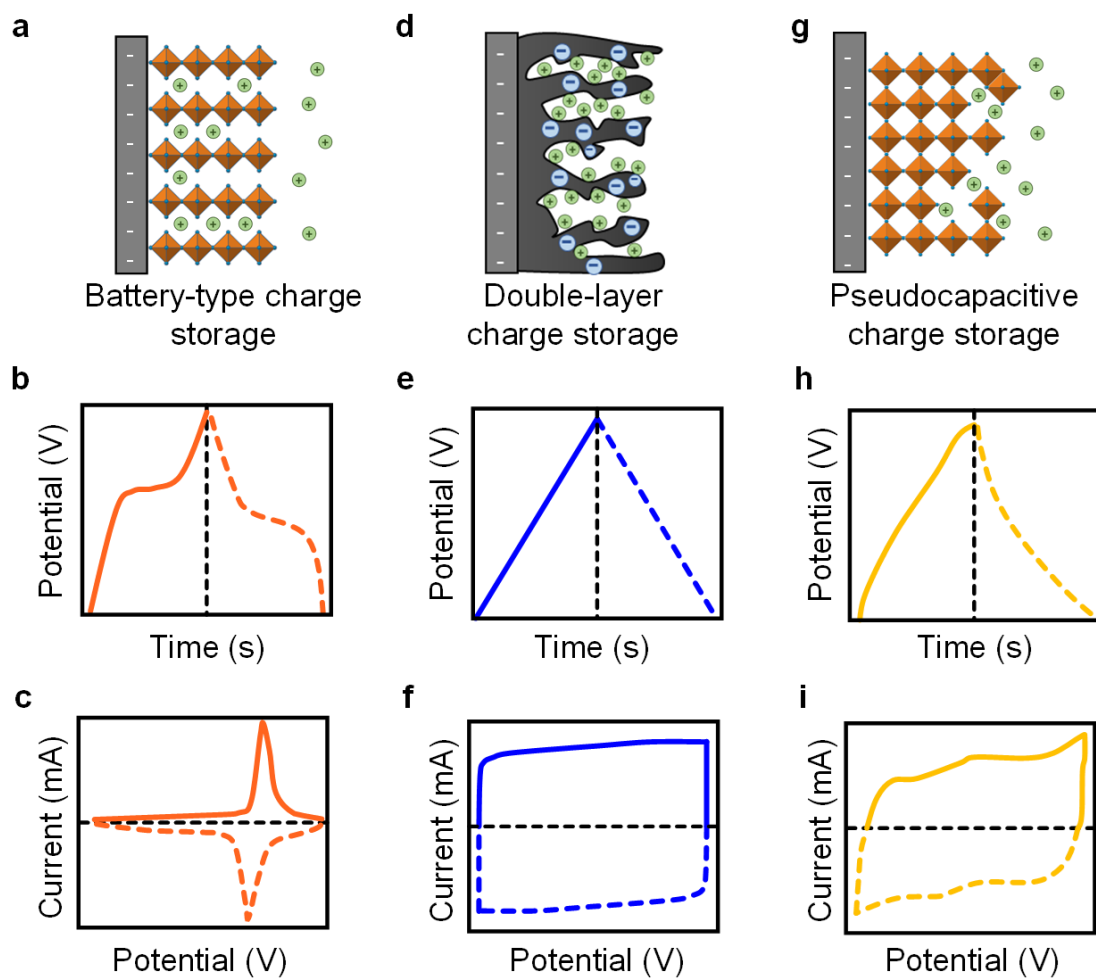


Figure 1-2. Schematic drawing of several main electrochemical energy storage mechanisms in the case of (a) battery-type, (d) electrical double-layer capacitive, and (g) pseudocapacitive charge storage. (b,e,h) galvanostatic charge-discharge profiles and (c,f,i) cyclic voltammograms corresponding to (a,d,g).

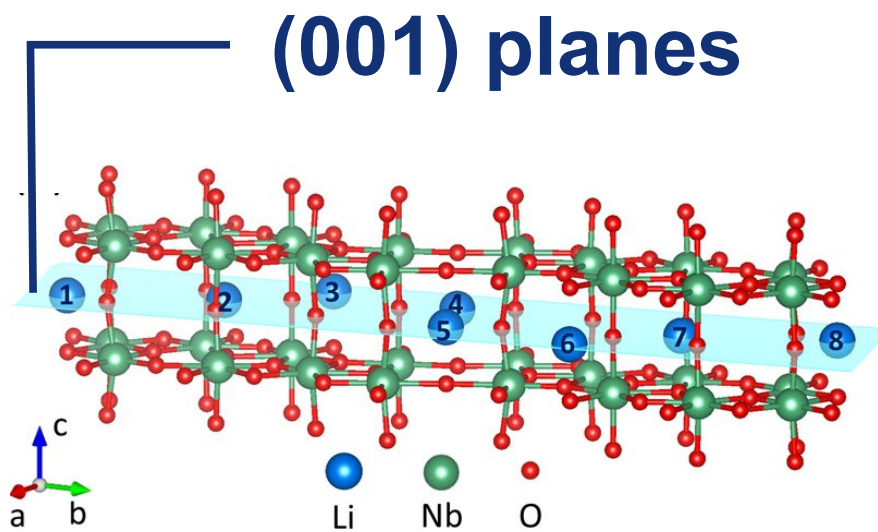


Figure 1-3. Structure of lithiated orthorhombic Nb_2O_5 after geometry optimization [46].

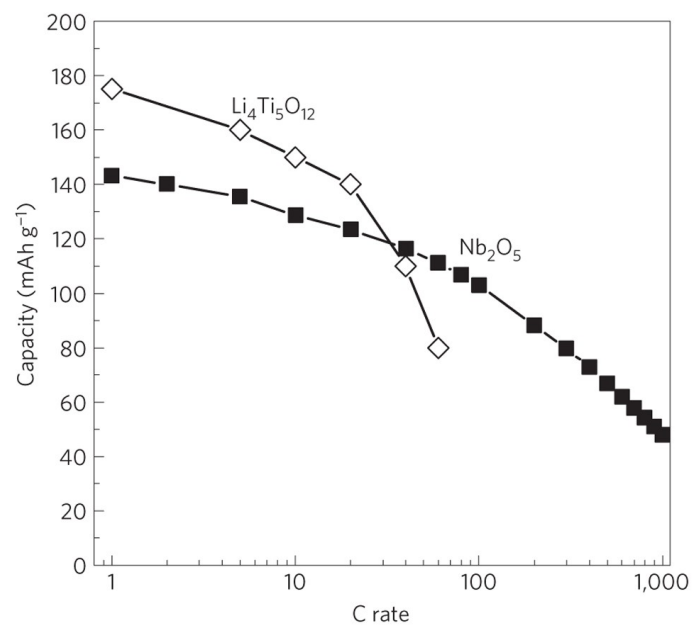


Figure 1-4. Fast pseudocapacitive Li ion storage properties of orthorhombic Nb_2O_5 [45].

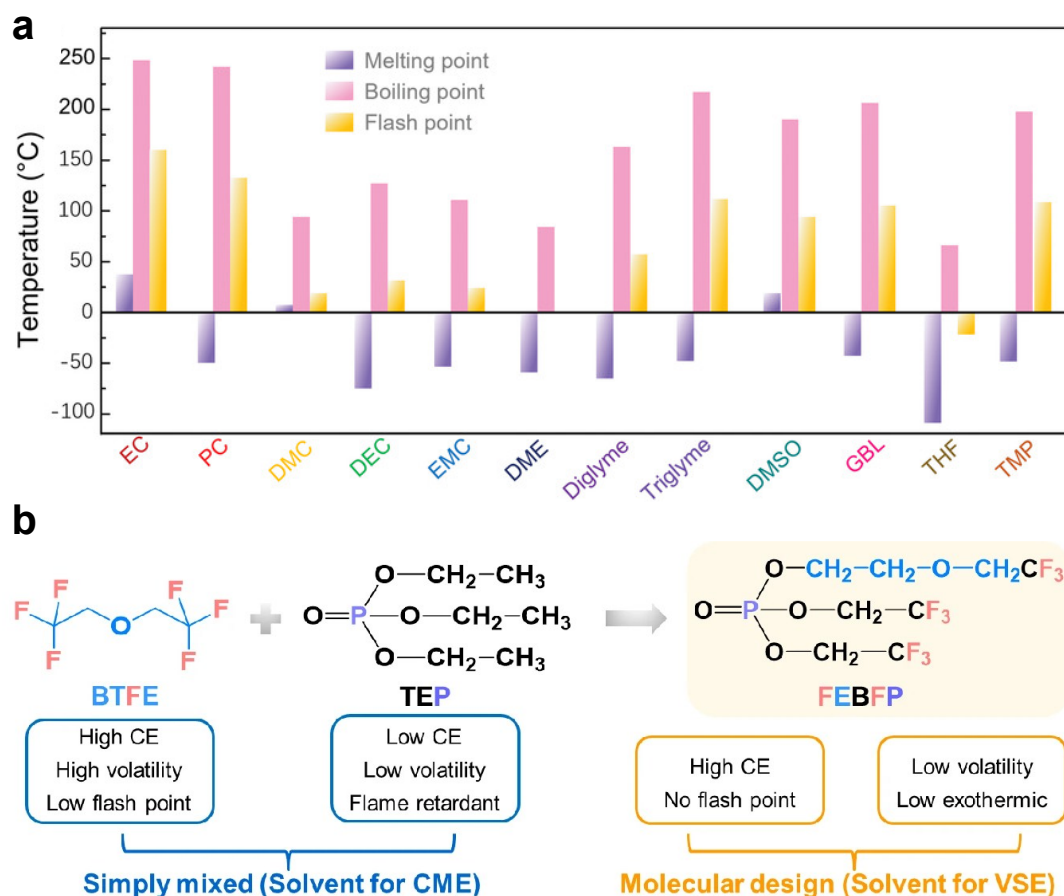


Figure 1-5. (a) Comparison of several physicochemical properties, including melting point, boiling point, and flash point of various organic solvents in organic electrolytes. Reproduced with permission [59]. Copyright 2022 Wiley-VCH under a Creative Commons Attribution 4.0. (b) Design scheme and molecular structures of fluorinated phosphate ester (FEBFP). Reproduced with permission [60]. Copyright 2024 Springer Nature under a Creative Commons Attribution 4.0.

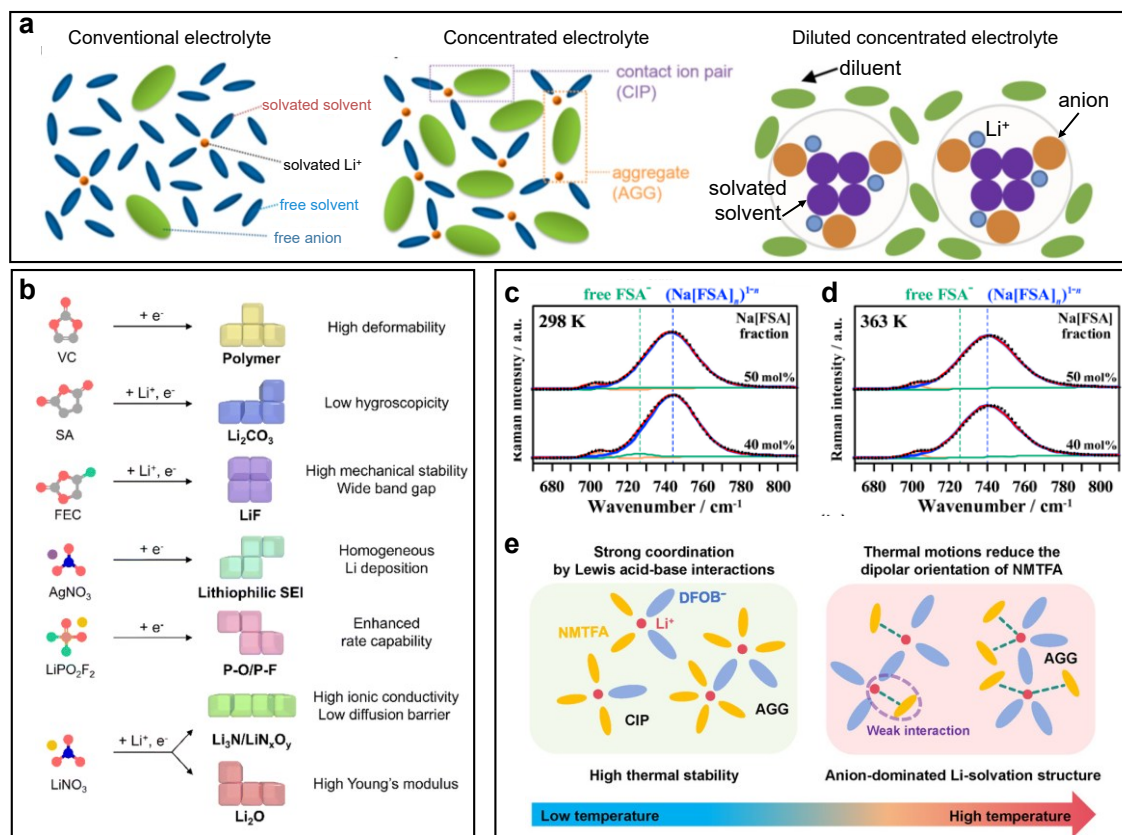


Figure 1-6. Coordination environment of electrolyte and SEI properties. (a) Schematics of coordination structures of the three electrolytes: conventional electrolyte, concentrated electrolyte, and diluted (locally) high-concentration electrolyte. Reproduced with permission [78]. Copyright 2014 American Chemical Society. Reproduced with permission [85]. Copyright 2018 Elsevier. (b) Schematic illustration of individual component properties of SEI. Reproduced with permission [74]. Copyright 2023 the Royal Society of Chemistry under a CC BY-NC 3.0. The temperature-dependent coordination structure in electrolytes. Raman spectra of the $\text{Na}[\text{FSA}]\text{--}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ at $\text{Na}[\text{FSA}]$ fractions of 40 and 50 mol% electrolytes at (c) 25 °C and (d) 90 °C, increased ratios on coordinated $[\text{FSA}]^-$ ($(\text{Na}[\text{FSA}])_n^{1-n}$) indicating the temperature-induced change in coordination structure. Reproduced with permission from ref [92]. Copyright 2016 Elsevier. (e) Schematic diagram of temperature-dependent solvation structures in a LiDFOB - NMTFA eutectic electrolyte as a function of temperature. Reproduced with permission from ref [106]. Copyright 2024 Elsevier under a Creative Commons Attribution 4.0.

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Chapter 2

Experimental

2.1 Apparatus and material handling

The tools used in the experiments, including cutting knives, tweezers, scissors, spatulas, and beakers, were cleaned with ion-exchanged water, acetone, and ethanol in turn. All of the aforementioned tools were dried in an oven at 60 °C for 2 h.

All of the samples and air-sensitive chemicals were handled under a dry Ar atmosphere in a glove box (Miwa Manufacturing, DBO-2LKH-HNBR) of a dried and deoxygenated argon atmosphere with a gas-refining instrument ($\text{H}_2\text{O} < 1$ ppm and $\text{O}_2 < 1$ ppm). Oxygen concentration was continuously monitored by Panametrics Oxygen Meters, OXY.IQ-011-00. An electronic balance (Shimadzu UX balances, UX420H) was installed in the glove box, which was used for measuring the weights of electrodes and chemicals to prepare electrolytes.

Figures 2-1 and 2-2 show the schematic diagram of the drying vessel and vacuum line, respectively, used for drying moisture-sensitive chemicals and impregnating electrolytes. As shown in Figure 2-2, the system was made of stainless steel and PFA tubes and connected with stainless steel joints and valves (Swagelok Co.). The vacuum atmosphere was created by a rotary vacuum pump and monitored by a pressure gauge

to confirm that the pressure was 1 Pa before use. The cold trap was cooled with liquid nitrogen to prevent the volatiles from entering the pump.

All the samples in this study were handled under a dry Ar atmosphere in a glove box ($\text{H}_2\text{O} < 1$ ppm and $\text{O}_2 < 1$ ppm). Nb_2O_5 (Wako Pure Chemical Industries, purity: 99.9%), $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811, MTI Corp.), and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO, TOSHIMA Manufacturing) were used to prepare electrode materials without further purification. The electronic scale balance (Shimadzu ATY Balances, ATY224) was utilized to weigh the chemical to prepare electrode in the open-air atmosphere. A commercial LiFePO_4 electrode sheet was purchased from MTI Corporation. The $\text{Li}[\text{FSA}]$ ($[\text{FSA}]^- = \text{bis}(\text{fluorosulfonyl})\text{amide}$, Mitsubishi Materials Electronic Chemicals, purity > 99%) salts, and $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($[\text{C}_2\text{C}_1\text{im}]^+ = 1\text{-ethyl-3-methylimidazolium}$, Kanto Chemical, purity > 99.9%; water content < 20 ppm) ionic liquid were purchased and dried under vacuum for 24 h at 80 °C prior to use. The organic electrolytes, 1 mol dm^{-3} LiPF_6 -EC/DMC (1:1 v/v; battery grade, Kishida Chemical), was used as purchased.

2.2 Electrode and cell preparation

The Nb_2O_5 electrodes were prepared by well-mixing the commercial Nb_2O_5 with Super C65 (Timcal Ltd.) and PAI (Polyamide-imide) binder in NMP (*N*-methyl-2-pyrrolidone, Fujifilm Wako Pure Chemicals) using a planetary mixer (AR-100, Thinky, Tokyo, Japan). The resulting slurry was pasted on Cu foil and was dried under vacuum at 120 °C for 12 h. The electrodes were punched into 10 mm diameter discs. The graphite

electrodes were prepared by well-mixing the graphite powder with Super C65 (Timical Ltd.) and PVDF (poly(vinylidene fluoride), Kureha Corp.) binder in the ratio of 85:10:5 wt% with NMP using a Thinky mixer. The subsequent process was the same as the preparation of Nb₂O₅ electrodes. For positive electrodes, a slurry was prepared by mixing the NMC811 powder with conductive carbon and PVDF binder in the ratio of 85:6:9 wt% and pasted on an Al foil and shaped to 10 mm diameter discs. The NCM811 positive electrodes used in the three-electrode tests were prepared by well-mixing NCM811 powder, Super C65, and PVDF binder in the ratio of 90:5:5 wt%, and the resulting slurry was pasted on an Al foil and shaped to 10 mm diameter discs. All positive electrodes prepared were dried under vacuum at 60 °C for 12 h before cell assembly.

Coin cells (2032-type), illustrated in Figure 2-3, were assembled in an Ar-filled glove box for electrochemical measurements. A glass fiber filter (Whatman, GF-A, diameter: 16 mm, and thickness: 260 μm) was used as a separator after being immersed in the electrolytes. The Li/NCM811, LFP, LTO, graphite, and Nb₂O₅ half cells were assembled with the prepared organic and IL electrolytes, a working electrode, and a 13 mm diameter lithium metal counter electrode (Sigma-Aldrich Chemistry, 99.95% purity) fixed on a stainless steel (SUS316L) plate.

2.3 Material characterization

2.3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were collected in the Bragg-Brentano geometry using a Rigaku SmartLab diffractometer with Ni-filtered Cu-K α radiation (40 kV and 30 mA) and a silicon strip high-speed detector (Rigaku D/teX Ultra 250). The crystal structures were visualized using the VESTA program [1].

2.3.2 Scanning electron microscopy (SEM)

The morphologies of active material were observed by field emission scanning electron microscopy (FE-SEM) (Hitachi SU-8020).

2.3.3 X-ray photoelectron spectroscopy (XPS)

The oxidation state and solid-electrolyte interphase (SEI) layer components were analyzed by X-ray photoelectron spectroscopy (XPS) (JEOL, JPS-9030, Mg K α source). All samples for XRD and XPS after electrochemical tests were washed with THF (tetrahydrofuran) and dried under vacuum at room temperature. Surface etching treatment was conducted with a monatomic Ar ion-beam sputtering for different energy and time durations.

2.3.4 Raman spectroscopy

Raman spectra were recorded on the Raman spectrometer (DXR3, Thermo Scientific) using the diode-pumped solid-state laser with an excitation wavelength of 785 nm.

2.3.5 Fourier transform infrared spectroscopy (FT-IR)

Infrared (IR) spectroscopy was recorded on a Bruker Alpha II spectrometer equipped with an attenuated total reflection (ATR) setup in a dry chamber (Daikin Industries, LTD.) under a dry air (dew point below $-60\text{ }^{\circ}\text{C}$) at $25\text{ }^{\circ}\text{C}$.

2.3.6 Nuclear magnetic resonance (NMR) spectroscopy

The chemical structures of the ILs were analyzed by ^1H NMR on a JNM-ECA600 NMR spectrometer (14.09637 T , 600.1723 MHz for ^1H , JEOL Ltd.) equipped with a TH5AT/FG2 probe at $25\text{ }^{\circ}\text{C}$. The NMR experiment was employed using a coaxial NMR tube with the ILs sample situated in the outer tube and deuterated solvent (specifically deuterated dimethyl sulfoxide, $(\text{CD}_3)_2\text{SO}$) positioned in the inner tube to avoid the solvent interaction.

2.3.7 Specific surface area measurement with

Brunauer–Emmett–Teller (BET) method

The surface area of electrode materials was evaluated by the Brunauer-Emmett-Teller (BET) method based on nitrogen adsorption analysis using a Tristar II 3020 equipment (Shimadzu Corp.).

2.4 Electrochemical measurements

The electrochemical measurement data, including rate capability and cycling performance, were recorded by an HJ-SD8 charge-discharge system (Hokuto Denko) using the thermostatic chamber SU-242 (ESPEC). A cyclic voltammetry (CV) was performed by a VSP potentiostat (Bio-Logic). The symmetric cell electrochemical impedance spectroscopy (SCEIS) was conducted using the electrodes after adjusting their voltage in a half-cell setup. EIS data were obtained by a VSP potentiostat (Bio-Logic) in a frequency range from 0.1 Hz to 100 kHz. All the electrochemical measurements were performed with the relevant temperature adjustment of at least 2 h.

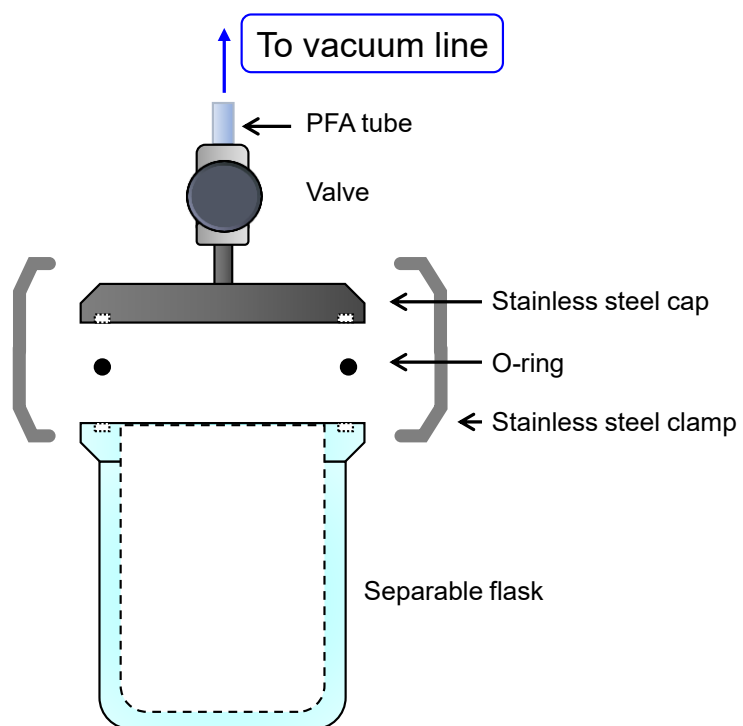


Figure 2-1. A schematic diagram of the drying vessel.

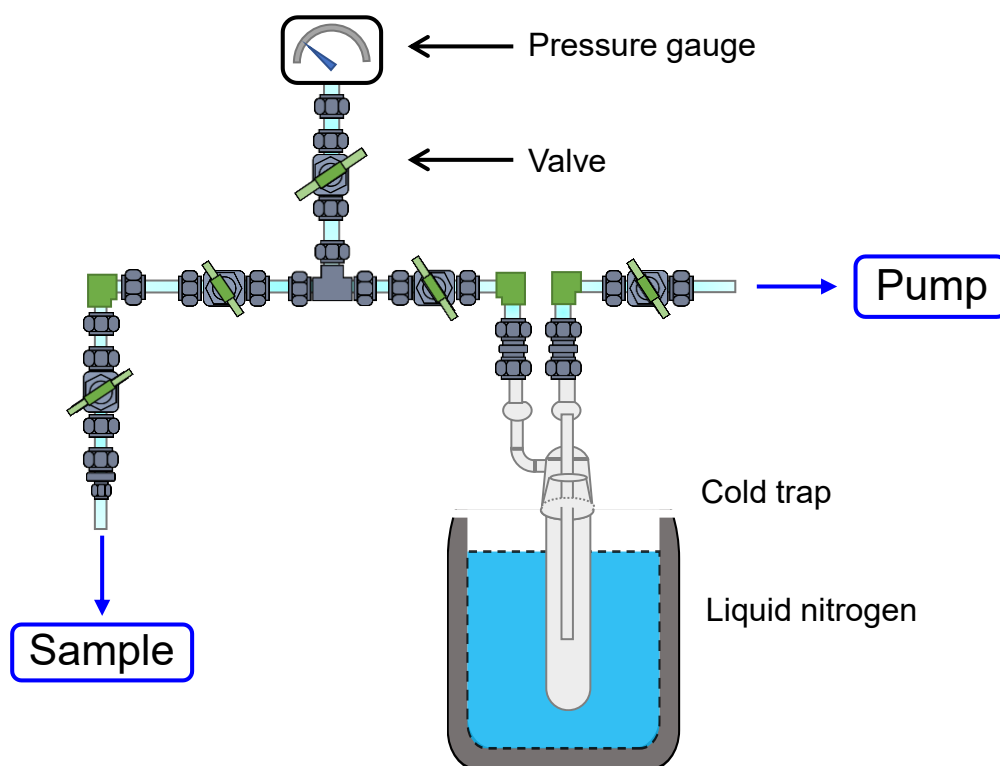


Figure 2-2. A schematic diagram of a vacuum line.

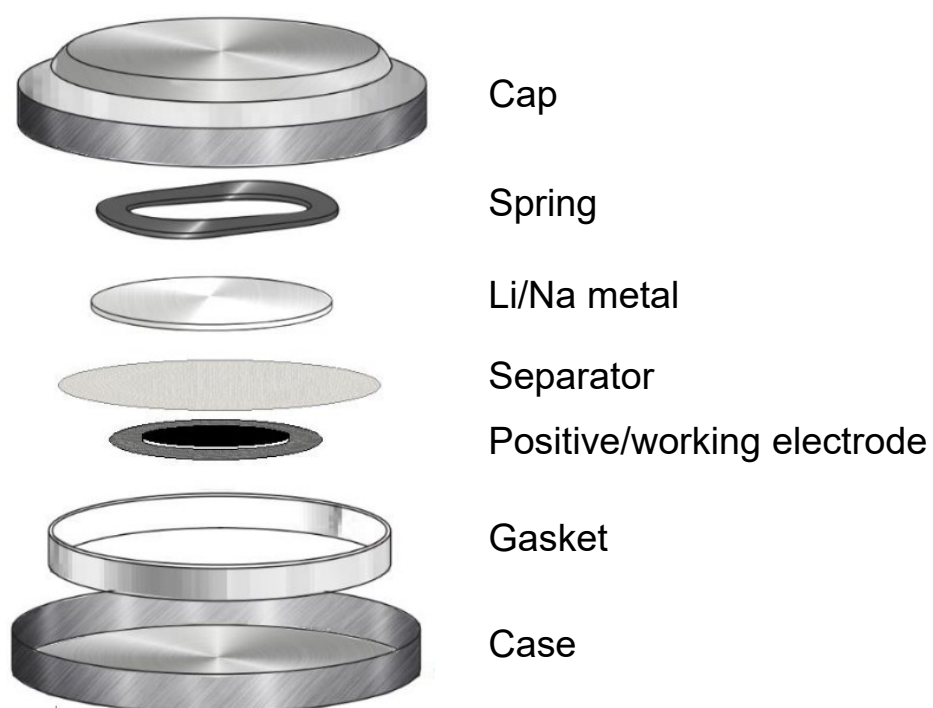


Figure 2-3. A schematic diagram of 2032-type coin cell [2].

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Chapter 3

In Situ Orthorhombic to Amorphous Phase Transition of Nb₂O₅ and Its Temperature Effect on Pseudocapacitive Behavior

3.1 Introduction

As stated in Section 1.3, the pseudocapacitive effect as well as materials that exhibit this phenomenon, has attracted a considerable interest as a strategy to reach simultaneous high energy and power densities. With the recent progress in understanding and improving synthetic routes of nanostructured materials, as to RuO₂, V₂O₅, MnO₂, MoS₂, and SnO₂, many of these materials in the characteristic forms such as nonporous [1, 2], nanosheet [3, 4], nanobelt [5, 6], nanocrystals [7-10], and nanocomposite [11-13] exhibit the pseudocapacitive responses in their electrochemical performance, taking the advantage of their reduced particle size to shorten the diffusion length and increase surface area. However, disadvantages of nanoarchitectures for electrode materials are also well-known as high surface area results in increased electrode dissolution, low packing density, enhanced electrolyte decomposition, and often synthetic complexity [14, 15]. Therefore, the intrinsic pseudocapacitive materials, which exhibit pseudocapacitive behavior even with a state of bulk, is expected to further contribution to the realization of practical applications.

Moreover, portable devices and electric vehicles are required to stably operate at intermediate temperatures (above room temperature operation) to ensure their safe function under uncertain temperature fluctuations [16]. So far, elevated temperatures

have been a hindrance to further commercialize LIBs utilizing carbonate-based organic electrolytes owing to its potentials of fatal fire hazards [17-21]. The concern of safety can be mitigated by introducing ionic liquid (IL) electrolytes owing to their non-flammability and low volatility [16, 22-25]. In another aspect, intermediate-temperature operation with IL electrolytes can achieve high performance energy storage devices by effectively utilizing ubiquitous waste heat because many factors limiting battery performance are improved at elevated temperature [16, 26-28].

Beyond a normally applied cutoff voltage range of 1.0–3.0 V in a half-cell setting, recent electrochemical studies of Nb₂O₅ in the extended range of 0.0–3.0 V showed impressive cycle stability and rate capability [29-32]. However, the charge storage mechanisms in the wider cutoff voltage is still not fully understood, especially in LIB systems [29, 33, 34]. Herein, electrochemical properties of non-modified (commercial powder of orthorhombic Nb₂O₅) are investigated in a cutoff voltage of 0.01–2.3 V vs. Li⁺/Li using a thermally stable Li[FSA]-[C₂C₁im][FSA] ([FSA][−] = bis(fluorosulfonyl)amide and [C₂C₁im]⁺ = 1-ethyl-3-methylimidazolium) IL electrolyte to gain comprehensive insights on temperature effect of pseudocapacitive behavior and charge-discharge mechanisms of the orthorhombic Nb₂O₅. Structural evolution accompanied by charge-discharge behavior in the extended cutoff voltage is discussed based on the results of *ex-situ* XRD (X-ray diffraction) and X-ray photoelectron (XPS) analysis. Capacitive contribution to charge-discharge capacities is evaluated by cyclic voltammetry (CV) tests and symmetric cell electrochemical impedance spectroscopy (SCEIS).

3.2 Experimental

The Li[FSA]-[C₂C₁im][FSA] IL electrolyte was prepared by mixing Li[FSA] and

[C₂C₁im][FSA] in the 20:80 mol% (1.1 mol dm⁻³) [35]. The typical water contents of the prepared Li[FSA]-[C₂C₁im][FSA] IL were below 20 ppm according to Karl-Fischer titration (899 Coulometer, Metrohm). The IL electrolyte immersed in a glass microfiber (Whatman GF/A) was used as a separator. The Nb₂O₅ electrodes were prepared in the method stated in Section 2.4 by mixing pristine Nb₂O₅ with Super C65 and PAI binder in a certain weight ratio of 70 : 20 : 10. The loading mass of the electrode was approximately 0.7 mg cm⁻². Coin cells of type-2032 (half-cell: Li/IL/Nb₂O₅) were assembled with the prepared IL electrolyte, Nb₂O₅ electrode, and lithium metal (Sigma-Aldrich Chemistry, 99.95% purity) with cell configuration shown in Figure 2-3.

The electrochemical data were controlled by an HJ-SD8 charge-discharge system (Hokuto Denko) at both 25 and 90 °C. A current density of 200 mA g⁻¹ was applied to understand basic charge-discharge behavior. Discharge rate performance was performed at various current rates from 200 mA g⁻¹ to 20000 mA g⁻¹ while the charge current rate was maintained to be 200 mA g⁻¹. Cyclic voltammetry was performed at a scan rate from 0.5 to 50 mV s⁻¹ with the aid of a VSP potentiostat (Bio-Logic) at 25 and 90 °C. The cells were first fully charged to 0.01 V and discharge to 1.0 V to conduct SCEIS tests with a symmetric cell configuration (Nb₂O₅/IL/Nb₂O₅). EIS data were obtained by a VSP potentiostat (Bio-Logic) at 25, 70, and 90 °C in a frequency range from 0.1 Hz to 100 kHz.

3.3 Results and discussion

Characterization of the Nb₂O₅ electrode. According to previous studies, elevation of operating temperature using IL electrolytes can enhance ion diffusion both in the electrode and electrolyte and interfacial processes, resulting in the activation of materials that are even nearly inert at room temperature [36-38]. Figure 3-1a

schematically shows the temperature effect on the pseudocapacitive contribution of Nb₂O₅ with temperature dependence of ionic conductivity and viscosity of the Li[FSA]-[C₂C₁im][FSA] IL electrolyte (ionic conductivity and viscosity are plotted based on the previous study [35]). Highly enhanced pseudocapacitive energy storage is expected at elevated temperatures, and thus, the temperature-dependence of the pseudocapacitive behavior of Nb₂O₅ is an interesting subject to be examined.

In this study, the non-nanoarchitecture (or non-fabricated) Nb₂O₅ with an average diameter of ~300 nm (see Figure 3-2) was selected. The present Nb₂O₅ belongs to the orthorhombic space group *Pbam* according to XRD analysis (see Figure 3-3). The surface areas of the Nb₂O₅, Nb₂O₅-Super C65, and Super C65 were evaluated by the N₂ adsorption/desorption isotherm using the BET method (Figure 3-4). The results indicate the non-fabricated Nb₂O₅ has a small surface area of 5.5 m² g⁻¹, compared to the surface area of nanoarchitecture of Nb₂O₅ electrode materials, such as T-Nb₂O₅ nanoparticle (59.0 m² g⁻¹) [7], TT-Nb₂O₅ (57.5 m² g⁻¹) [39], and Nb₂O₅ nanoparticle (57.5 m² g⁻¹) [40], and the conventional activated carbon (2000 m² g⁻¹) [41].

Investigation on the charge–discharge mechanism and amorphization. The Li storage mechanisms in the Nb₂O₅ electrode was investigated by XPS and *ex-situ* XRD measurements at several different SOC's in the first charge-discharge profiles as shown in Figure 3-5a-c (XRD patterns are Patterns a-i and XPS spectra are Spectra a-e, h, and i). To avoid the reduction of niobium oxides caused by ion-beam bombardment, the least Ar beam was applied to get rid of the surface layer for all XPS samples (Ar⁺ beam could reduce Nb₂O₅) [42, 43]. During the charge-discharge at 25 °C, the peak of Nb 3d_{5/2} at 206.9 eV, which is ascribed to orthorhombic Nb₂O₅ according to the XPS spectrum of pristine sample (Spectrum a) [44]. After charging (lithiation) to 1.0 V

(Spectrum b), appearance of the $3d_{5/2}$ and $3d_{3/2}$ peaks at 205.7 and 208.5 eV, respectively, indicates reduction from Nb^V to Nb^{IV} [45]. After discharging (delithiation) from 1.0 V to 2.3 V (Spectrum c), the XPS peaks return to the original position of the pristine state, suggesting the reversible Nb^V/Nb^{IV} redox reaction. The *ex-situ* XRD patterns of the charge-discharge process in a cutoff voltage from 1.0 to 2.3 V confirms the reversible 2θ shift (Patterns a-c), maintaining in the crystalline orthorhombic Nb_2O_5 framework [46]. On the other hand, when Nb_2O_5 is further charged to 0.01 V at 25 °C (Spectrum d), the $3d_{5/2}$ peaks assigned to the oxidation states of Nb(III) and Nb(II) appear in the range from 203 to 205 eV [47]. At the same time, the XRD peaks further shift to the lower angle as charged to 0.01 V, demonstrating further lithiation of the orthorhombic Nb_2O_5 (Pattern d). After discharge from 0.01 to 2.3 V, the XPS peak almost returns to the original position, indicating a reversible $Nb^{V,IV}/Nb^{III}$ reaction (Spectrum e). Nonetheless, the XRD patterns suggest phase transition of the orthorhombic Nb_2O_5 to an amorphous phase ($a-Li_xNb_2O_5$) during the 1st cycle (Pattern e). Furthermore, the XRD patterns after the charge to 0.01 V (Patterns d and h) confirm the existence of the cubic phase of NbO with the diffraction peaks at $2\theta = 29.99^\circ$ (110 line), 36.95° (111 line) and 42.93° (200 line) [48, 49]. The formation of NbO occurs in the conversion reaction during the first charge to 0.01 V and these peaks remain after the discharge to 2.3 V (Patterns e), suggesting that NbO is not involved in the charge-discharge reaction. The XPS peak at 203.8 eV for Nb $3d_{5/2}$ in Spectrum e also suggest the Nb^{II} state even in the charge state. Meanwhile, at the elevated temperature of 90 °C, Nb_2O_5 exhibits a similar charge-discharge mechanism, including the amorphization and the formation of NbO due to conversion reaction during the initial charge to 0.01 V. It is noticeable that the intensities of the XPS peaks assigned to Nb^{IV} , Nb^{III} , and Nb^{II} for the sample at 0.01 V (Spectrum h) is stronger than those at 25 °C (Spectrum d). This

observation suggests that a higher level of activated Nb_2O_5 is involved in the redox reaction leading to more Li^+ storage combined with its deeper charge-discharge and more production of NbO , finally resulting in higher capacities at 90 °C.

The charge-discharge mechanism of the Nb_2O_5 electrode is summarized and illustrated in Figure 3-6. Li^+ ions are stored by a reversible redox reaction of $\text{Nb}^{\text{V}}/\text{Nb}^{\text{IV}}$ in the orthorhombic Nb_2O_5 in the cutoff voltage range of 1.0–2.3 V. $\text{Li}_x\text{Nb}_2\text{O}_5$ then transforms to the a- $\text{Li}_x\text{Nb}_2\text{O}_5$ amorphous phase during charging to 0.01 V, along with partial conversion to NbO and Li_2O . The consecutive lithiation-delithiation process occurs in the completely amorphous phase of a- $\text{Li}_x\text{Nb}_2\text{O}_5$ with a reversible $\text{Nb}^{\text{V,IV}}/\text{Nb}^{\text{III}}$ reaction with cutoff voltage of 0.01-2.3 V. The NbO phase remains inactive during the following cycles (XRD pattern obtained after 300 cycles is shown in Figure 3-7). Referring to other oxide negative electrode materials, such as amorphous V_2O_5 [50, 51] and amorphous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [52], the origin of their enhanced electrochemical performance was explained by fast Li-ion diffusion through enhanced diffusion pathways in the amorphous phase. In the same manner, the amorphization of Nb_2O_5 observed in the study can be expected to have a contribution to the quick (de)lithiation processes and result in the high-rate capabilities of a- $\text{Li}_x\text{Nb}_2\text{O}_5$ within the extended cut-off voltage.

Electrochemical performance of amorphous $\text{Li}_x\text{Nb}_2\text{O}_5$ and its temperature effect.

Figure 3-8 shows the galvanostatic charge-discharge profiles, comparative rate capability and cycle performance of the $\text{Li}/\text{IL}/\text{Nb}_2\text{O}_5$ cell at (a) 25 and (b) 90 °C at 200 mA g^{-1} . The first charge curve at 25 °C exhibits a large irreversible capacity of 520 mAh g^{-1} , which indicates the SEI formation with the electrolyte decomposition (Figure 3-8a). After the 1st charge, all the subsequent charge-discharge curves essentially

overlap each other, demonstrating reversible electrochemical properties (210.0 mAh g⁻¹ at the 5th cycle). The charge-discharge curves at 90 °C exhibit the initial capacity of 1200 mAh g⁻¹ (Figure 3-8b), which indicates more electrolyte decomposition occurs to form the SEI layer at elevated temperature (see the later section for the detailed interpretation on the SEI components). The discharge capacities at 90 °C are higher than those at 25 °C (408.9 mAh g⁻¹ at the 5th cycle), benefiting from elevated temperature. The rate capability was tested to further demonstrate the performance enhancement at intermediate temperature. The polarization increases and decreases with increasing current and temperature, respectively. Notably, the curves can be distinguished from the two regions of 0.01–1.5 V and 1.5–2.3 V (Figure 3-9a,b), and the lower voltage region clearly shows less polarization than the higher voltage region. This observation suggests that the two voltage regions possess different electrochemical processes (Figure 3-9c,d). As shown in Figure 3-8c and Table 3-1, a high-rate capability of 119.8 mAh g⁻¹ at 4000 mA g⁻¹, 98.5 mAh g⁻¹ at 10000 mA g⁻¹ and 86.0 mAh g⁻¹ at 20000 mA g⁻¹ is obtained at 25 °C. The discharge curves at 90 °C exhibit less polarization than the curves at 25 °C, and further improved rate capability with higher discharge capacities is shown by delivering 234.8 mAh g⁻¹ at 4000 mA g⁻¹, 183.0 mAh g⁻¹ at 10000 mA g⁻¹, and 130.6 mAh g⁻¹ at 20000 mA g⁻¹.

Figure 3-8d shows the cycle performance of the Li/IL/Nb₂O₅ cells at 2000 mA g⁻¹. Prior to the cycle measurement, an aging process of 5 cycles at 400 mA g⁻¹ and 5 cycles at 1000 mA g⁻¹ was applied. Consequently, stable cycle performance is obtained at 25 °C, delivering a reversible capacity of 89.2 mAh g⁻¹ in the initial cycle and capacity retentions of 102.6, 94.5, and 96.1% at the 100th, 1000th, and 2000th cycles, respectively (Table 3-2). The reversible capacity at 2000 mA g⁻¹ is 279.2 mAh g⁻¹ in the initial cycle at an elevated temperature of 90 °C, followed by a gradual capacity

fade to 167.4 mAh g⁻¹ at the 2000th cycle (see Figure 3-10 for charge-discharge profiles). Even though an unfavorable decay is observed in starting cycles, there is no distinct capacity fade with an average Coulombic efficiency of 99.4% over 2000 cycles, demonstrating the excellent and temperature-resistive Li⁺ storage of the Li/IL/Nb₂O₅ cells. Overall, the a-Li_xNb₂O₅ electrode exhibits fast and stable electrochemical charge storage properties, and there is a clear trend of enhanced performance benefiting from elevated temperature. For a long time, the intrinsic pseudocapacitive behavior of Nb₂O₅ has been thought to be highly dependent on its crystalline structure. However, the current study clearly demonstrates that a-Li_xNb₂O₅ can also exhibit rapid pseudocapacitive responses, especially at elevated temperatures.

Kinetic analysis of amorphous Li_xNb₂O₅. To investigate the high charge-discharge kinetics of Nb₂O₅, the CV tests were carried out at 25 and 90 °C at different scan rates from 0.5 to 50 mV s⁻¹ using a two-electrode cell with the Li metal counter electrode. The charge-discharge processes can be generally divided into diffusion-controlled and capacitive processes. The contribution of the capacitive process is determined by investigating, according to Equations 1 and 2 [53], the relationship between the scan rate (ν) and observed current (i) (so-called b -value analysis).

$$i = a\nu^b \quad (1)$$

$$\log(i) = b \log(\nu) + \log a \quad (2)$$

Here, a and b are adjustable parameters, and b can be determined as a slope of the $\log(i)$ vs. $\log(\nu)$ plot, where $b = 0.5$ and 1.0 correspond to the diffusion-controlled and capacitive processes, respectively. This analysis is also applicable to distinguish the

capacitive process from the diffusion-controlled process in the mixed control system [53].

Figure 3-11a-d shows the CV curves of the Nb₂O₅ electrode and the resulting $\log(i)$ vs. $\log(v)$ plot for the anodic and cathodic peaks at 25 and 90 °C. The CV curves are characterized by two representative cathodic and anodic peaks at both temperatures. The relatively higher b -value of each redox peak of the measurements at 90 °C suggests that capacitive behavior is more dominant than that at 25 °C. Meanwhile, the increase in measurement temperature increases current density in the whole range, especially prominent at high potential (Figure 3-11a,c). According to the plots in Figure 3-11b and d, the b -values calculated from Equation 2 are higher in low potential regions (anodic/cathodic 1 and 3) than those in the high potential regions (anodic/cathodic 2 and 4) at both 25 and 90 °C. The evaluation indicates that the high potential region is more diffusion-controlled, whereas the low potential region is more capacitive-controlled at 25 °C. Nevertheless, the capacitive process dominates the lithium storage process across all the potential regions at 90 °C.

The contribution ratio of capacitive behavior at various scan rates are determined by Equations 3 and 4 [54]. Different from the linear relationship between capacitive current (i_{cap}) and v , the current (i_{diff}) varies with the square root of v in a diffusion-controlled process.

$$\begin{aligned} i &= i_{cap} + i_{diff} \\ &= k_1 v + k_2 v^{1/2} \end{aligned} \quad (3)$$

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \quad (4)$$

Here, k_1 and k_2 are constants at each applied potential. Determination of k_1 and k_2

provide the capacitive contribution to charge storage for the Nb₂O₅ electrodes as shown in Figure 3-11e,f. For instance, the CV profile for capacitive behavior (orangish region in Figure 3-11e) can be compared to the experimentally obtained CV at a scan rate of 5 mV s⁻¹, which exhibited a capacitive contribution ratio of 37% at 25 °C and 71% at 90 °C. The deconvoluted capacitive contribution ($= i_{\text{cap}} / (i_{\text{cap}} + i_{\text{diff}})$) at 25 and 90 °C are obtained at various scan rates and summarized in Figure 3-11f. There is a clear trend that the capacitive contribution increases with increasing scan rates. Another trend observed is that the capacitive contribution at 90 °C is larger than that at 25 °C, demonstrating the dominance of capacitive response at elevated temperature owing to the enhanced ion diffusion. All capacitive contribution analysis based on the experimentally obtained CV data were restricted to scan rates from 0.5 to 10 mV s⁻¹ to avoid ohmic polarization which is often observed in profiles at high rates [55]. These CV-based analyses on the capacitive behavior well-explain the different trend in rate capability at 25 and 90 °C. Accordingly, the contribution of the diffusion-controlled process to the overall capacity was seen to decrease at high rates and with increasing operating temperature, in proportion to the increases in the capacitive process.

Interfacial properties of amorphous Li_xNb₂O₅ and the solid electrolyte interphase (SEI) formation. For insight into the effect of temperature on the interfacial behavior of the Nb₂O₅ electrode, analysis using EIS was carried out to investigate the temperature effect on the electrochemical behavior of the Nb₂O₅ electrode. As illustrated in the schematic drawing of Figure 3-12a, SCEIS with two identical electrodes at the same state of charge (SOC) is an efficient way to directly provide data of the corresponding electrodes without being affected by the behavior of the Li metal counter electrode unlike EIS using a half-cell configuration [56-58]. Here, the SOC was adjusted to 40%.

The experimentally obtained EIS data were interpreted with the equivalent circuit (Figure 3-12a), where R_h , R_{ct} , C_{dl} , and CPE_{pseudo} represent the resistance in the high-frequency range, the charge transfer resistance in a faradaic process, a capacitance element for double-layer capacitance and a constant phase element (CPE) for pseudocapacitance, respectively. The locations of R_{ct} are designated by the characteristic frequency (see Table 3-3 for the EIS fitting results). Figure 3-12b shows the Nyquist plots of the $Nb_2O_5/IL/Nb_2O_5$ cells over a frequency range between 0.1 Hz to 100 kHz. The result of R_{ct} is shown in Figure 3-12c. A dramatic decrease of R_{ct} was observed in the $Nb_2O_5/IL/Nb_2O_5$ cells at elevated temperature, implying facilitation of charge transfer in the faradic redox reaction and enhancement in rate performance test.

The R_{ct} connects with the CPE_{pseudo} in series due to its redox-involved properties, while the C_{dl} , a non-faradaic process, contribute in parallel with the charge transfer component. Thus, the equivalent circuit and EIS model can separate the pseudocapacitive process from the double-layer capacitance process [59]. Moreover, the impedance (Z) of the CPE_{pseudo} is given by Equation 5 [60-62].

$$Z_{CPE} = [B(j\omega)^n]^{-1} \quad (5)$$

Here, B and n are frequency-independent adjustable constants, where j is the imaginary unit and ω is the angular frequency. The values of $n = 0, 0.5$, and 1 correspond to the pure resistance, Warburg diffusion, and ideal capacitance, respectively [63]. The values of n in CPE_{pseudo} are obtained to be $0.6-0.7$ in the present fitting. As shown in Figure 3-12d, pseudocapacitance is temperature-dependence and dominantly contributes to total capacitance at $90\text{ }^{\circ}\text{C}$, whereas no significant changes along with temperature variation

are observed for the contribution of double-layer capacitance. This result provides that Nb₂O₅ exhibits the fast kinetic behavior with a larger ratio of charge storage from the pseudocapacitive mechanism at a higher temperature which matches well with the results of CV measurement discussed in Section 3.3.4.

To further understand the excellent cycle performance of the amorphous Nb₂O₅, the characteristics of the SEI layer formed in the IL electrolyte is investigated by XPS at 25 and 90 °C. The scanning transmission electron microscopy images show morphological evidence of SEI formation after cycling with a cut-off voltage of 0.01–2.3 V (Figure 3-13). Figure 3-14 shows the F 1s, C 1s, N 1s, and S 2p_{3/2} XPS spectra of the Nb₂O₅ electrodes after the 2nd charge (see Table 3-4 for peak assignments of the XPS). The presence of S and N is considered to be one key difference between those in organic (*e.g.* Li[PF₆]-EC/DMC) and Li[FSA]-[C₂C₁im][FSA] ionic liquid electrolytes. It is noticeable that regardless of operating temperature, [FSA][−]-based SEI components (LiF: 684.5 eV and S-F: 687.6 eV in the F 1s spectrum, SO_x: 166 eV in the S 2p_{3/2} spectrum, and N-S 400.9 eV in the N1s spectrum) are richly formed on the surface of the Nb₂O₅ electrode. In the previous studies of NIBs and LIBs utilizing [FSA][−]-based electrolytes, the sulfur-contained component in the SEI layer was identified as a main factor to improve electrochemical performance [64, 65].

3.4 Conclusions

In this chapter, the temperature effect of the pseudocapacitive behavior of non-modified Nb₂O₅ was investigated in a wide cutoff voltage range of 0.01–2.3 V by a comparative study at 25 and 90 °C with the thermally stable Li[FSA]-[C₂C₁im][FSA] IL electrolyte. Charge-discharge with low cutoff voltage to 0.01 V resulted in the amorphization of Nb₂O₅ in the first cycle accompanied with formation of inactive NbO due to conversion

reaction. *Ex-situ* XPS and XRD revealed that the deeper Nb^{V,IV}/Nb^{III} redox reactions are involved into charge-discharge in cutoff voltage of 0.01–2.3 V in amorphized a-Li_xNb₂O₅ phase. The amorphous Li_xNb₂O₅ exhibited a very fast Li-storage process during charge-discharge based on reversible Nb^{V,IV}/Nb^{III} redox reaction, demonstrating an exciting result of discharge time around 30 s (20000 mA g⁻¹) at an intermediate temperature of 90 °C. The CV and SCEIS results quantitatively identified that the capacitive contribution of amorphized Li_xNb₂O₅ in Li⁺ storage increased with the elevation of operating temperature.

Table 3-1. Discharge capacity and capacity retention of the Li/IL/Nb₂O₅ cell in the rate capability test at 25 and 90 °C.^{a)}

Current density (mA g ⁻¹)	Geometric current density (mA cm ⁻²)	25 °C		90 °C	
		Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 1C (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 1C (%)
200	0.18	228.4	100.0	369.5	100.0
400	0.36	205.8	90.1	336.6	91.1
1000	0.89	172.0	75.3	293.4	79.4
2000	1.8	143.0	62.6	265.3	71.8
4000	3.6	119.8	52.5	234.8	63.5
10000	8.9	98.5	43.1	183.0	49.5
20000	17.8	86.0	37.6	130.6	35.3

^{a)} Charge rate: 200 mA g⁻¹, discharge rate: 200 to 20000 mA g⁻¹, cutoff voltage: 0.01–2.3 V. IL: Li[FSA]-[C₂C₁im][FSA] (20 : 80 in mol). See Figure 3-8 for the results of the rate capability test.

Table 3-2. Discharge capacities and capacity retentions of the Li/IL/Nb₂O₅ cell in the cycle test at 25 and 90 °C for 2000 cycles.^{a)}

Cycle number	25 °C		90 °C	
	Capacity (mAh g ⁻¹)	Capacity retention vs. 1st (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. 1st (%)
1	89.6	100.0	279.2	100
5	100.0	111.6	269.4	96.5
10	98.5	110.0	262.1	93.9
50	93.3	104.1	235	84.2
100	91.9	102.6	224.3	80.3
200	88.4	98.7	212.9	76.3
500	85.8	95.8	199.6	71.5
1000	84.6	94.5	188.8	67.6
2000	86.1	96.1	167.4	60

^{a)} Current density: 2000 mA g⁻¹ for charging and discharging, cutoff voltage: 0.01–2.3 V. IL: Li[FSA]-[C₂C₁im][FSA] (20 : 80 in mol). See Figure 3-8d for the results of the cycle test.

Table 3-3. Fitting parameters of the Nyquist plots for the Nb₂O₅/IL/Nb₂O₅ symmetric cell at 1.0 V at 25, 70 and 90 °C, respectively. See Figure 3-12b for Nyquist plot of EIS.

Temperature (°C)	R_h (Ω)	R_{ct} / SF (Ω , HZ)	C_{dl} (mF)	CPE_{pseudo} (mF s ⁽ⁿ⁻¹⁾)		
				Q_{pseudo}	n_{pseudo}	capacitance (mF)
25	29.8	127 / 3.4	0.28	1.1	0.6	0.30
70	18.3	43.2 / 5.2	0.89	4.0	0.6	1.24
90	12.1	16.4 / 11.9	0.91	1.1	0.7	5.28

Table 3-4. The XPS data for the SEI components formed on the Nb₂O₅ electrode in the Li[FSA]-[C₂C₁im][FSA] IL electrolyte after the 2nd charge at 25 and 90 °C, respectively. See Figure 3-14 for the corresponding spectra.^{a)}

Binding energy (eV)								
	F 1s	ratio (%)	C 1s	ratio (%)	N 1s	ratio (%)	S 2p _{3/2}	ratio (%)
25 °C	687.6	13.0	288.8	3.8	401.9	1.0	169.7	7.4
	684.7	87.0	286.3	35.9	397.9	99.0	168.2	45.3
			284.7	53.8			166.7	47.2
			282.3	6.5				
90 °C	687.6	25.0	288.9	3.1	400.9	18.0	169.6	4.4
	684.4	75.0	286.2	61.0	398.0	82.0	168.2	62.6
			284.5	33.0			166.2	33.0
			282.3	3.0				
SEI layer components								
LiF	684.5 ± .2							
S-F	687.6		169.6 ± .1					
SO _x			166.4 ± .2					
N-C			397.9 ± .1					
N-S			400.9 ± .1					
C-C			284.6 ± .1					
C-O			286.2 ± .1					
C=O			288.8 ± .1					
NbC			282.2					
^{a)} The electrode for this measurement was charged to 0.01 V.								

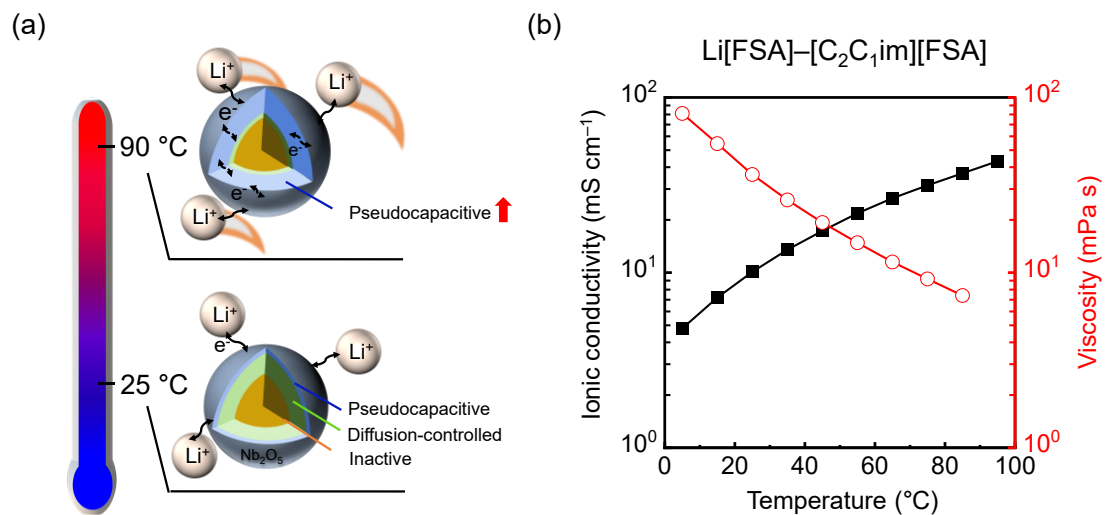


Figure 3-1. (a) Schematic illustration of the temperature effect on pseudocapacitive contribution for micro-sized Nb_2O_5 toward an energy device with ultrahigh rate performance at elevated temperature. (b) The enhanced ionic conductivity and decreased viscosity of the $\text{Li}[\text{FSA}]-[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ (20:80 in mol) IL electrolyte with temperature increasing [35].

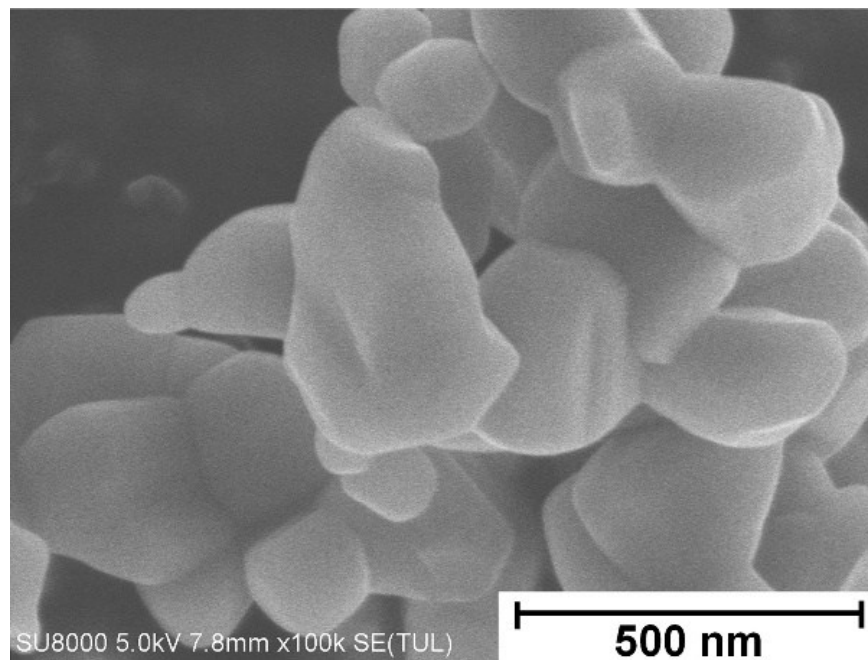


Figure 3-2. A SEM image of the pristine Nb₂O₅.

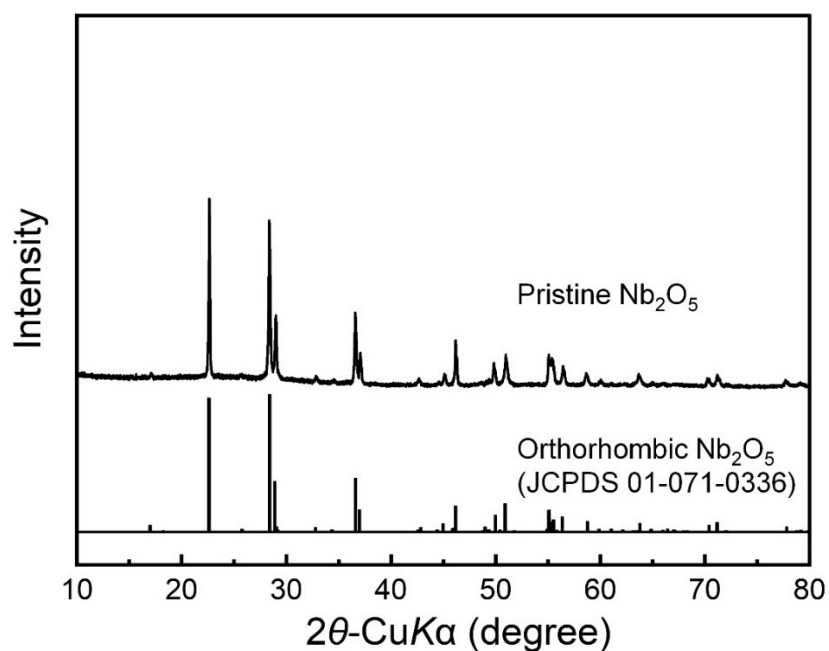
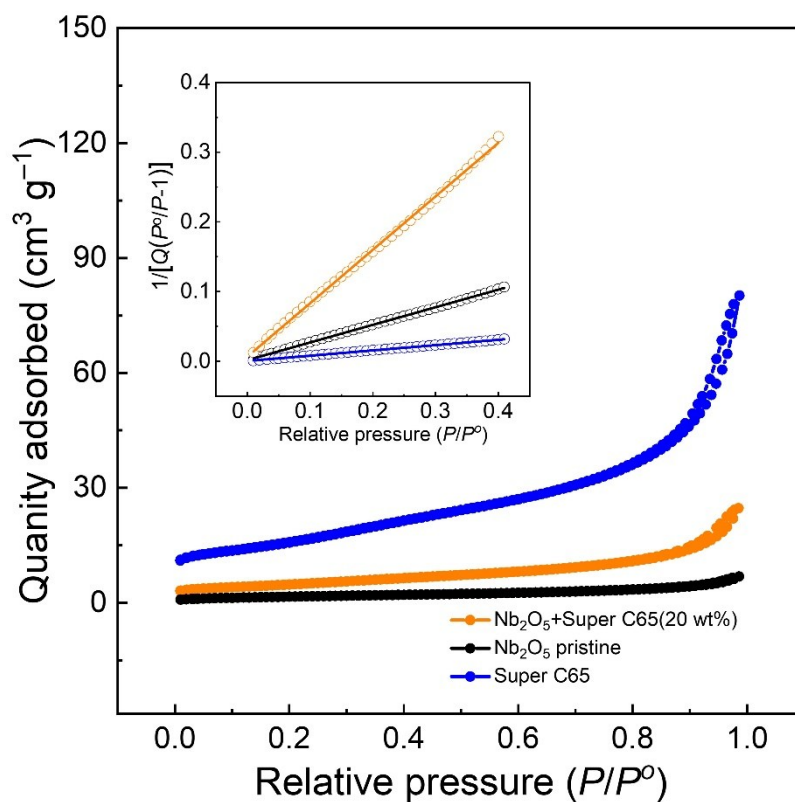


Figure 3-3. The XRD pattern of the pristine Nb₂O₅. Reference peaks of the orthorhombic Nb₂O₅ represented by black bars are reproduced from intensities of the previous data (JCPDS 01-071-0336).



	Nb ₂ O ₅ -Super C65(7:2 in weight)	Nb ₂ O ₅ pristine	Super C65
Specific surface area (m ² g ⁻¹)	17	5.5	56

Figure 3-4. Nitrogen adsorption/desorption isotherms (inset: BET surface area plots) for the electrode material (Nb₂O₅+Super C65), active material (Nb₂O₅ pristine), and conductive material (Super C65).

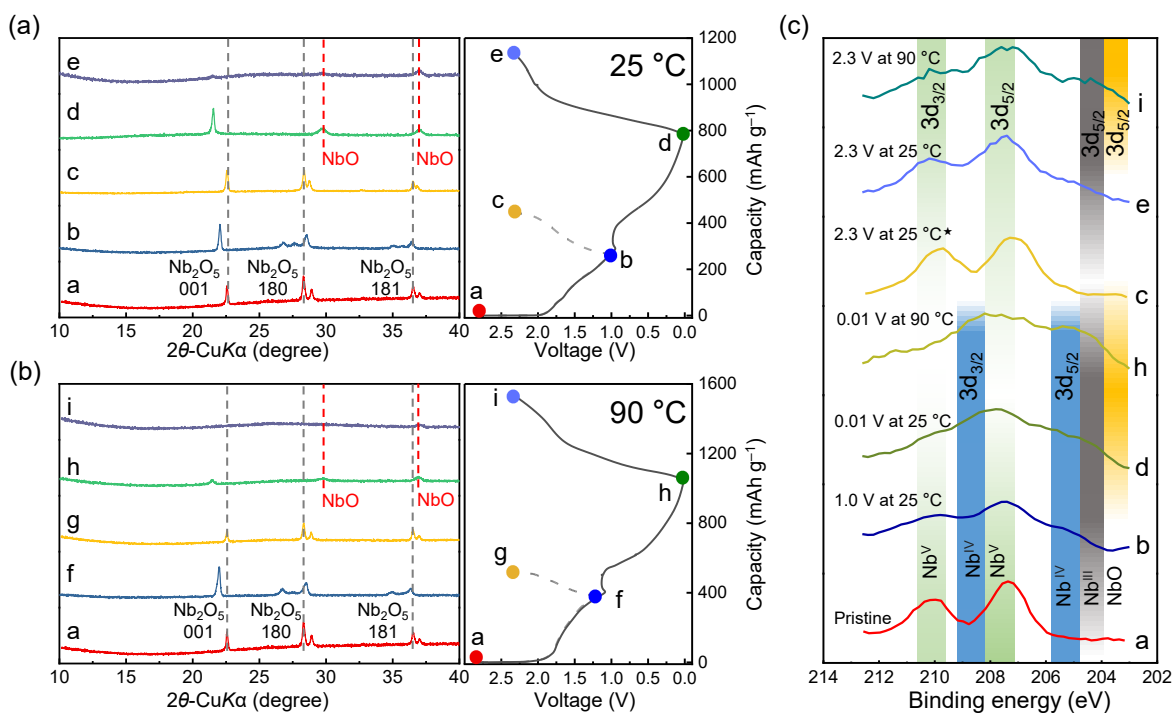


Figure 3-5. (a, b) Ex-situ XRD patterns at various SOC of the Nb_2O_5 in the $\text{Li}[\text{FSA}]\text{-}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ IL at (a) 25 and (b) 90 °C. Dashed lines of the orthorhombic Nb_2O_5 and cubic NbO are drawn from the previous data of JCPDS 01-071-0336 for Nb_2O_5 and JCPDS 01-071-2146 for NbO , respectively [46, 48]. See Figures 3-3 and 3-7 for reference patterns of Nb_2O_5 and NbO , respectively. (c) Ex-situ XPS spectra of the pristine and (d) lithiated Nb_2O_5 in the $\text{Li}[\text{FSA}]\text{-}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ IL at 25 and 90 °C. The star mark is used to denote the discharged sample from 1.0 to 2.3 V (charge-discharge curve point c) at 25 °C.

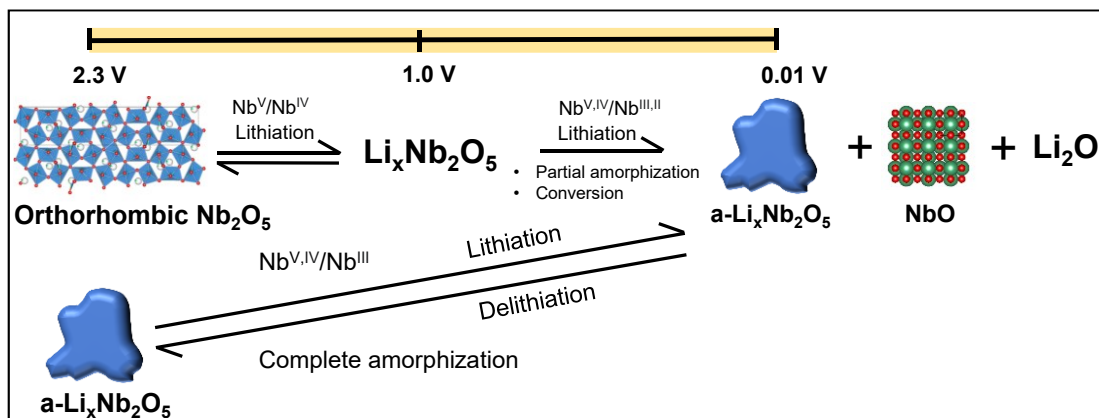


Figure 3-6. Schematic illustration of the charge-discharge mechanism of the orthorhombic- Nb_2O_5 ($\text{a-Li}_x\text{Nb}_2\text{O}_5$ after the initial cycle).

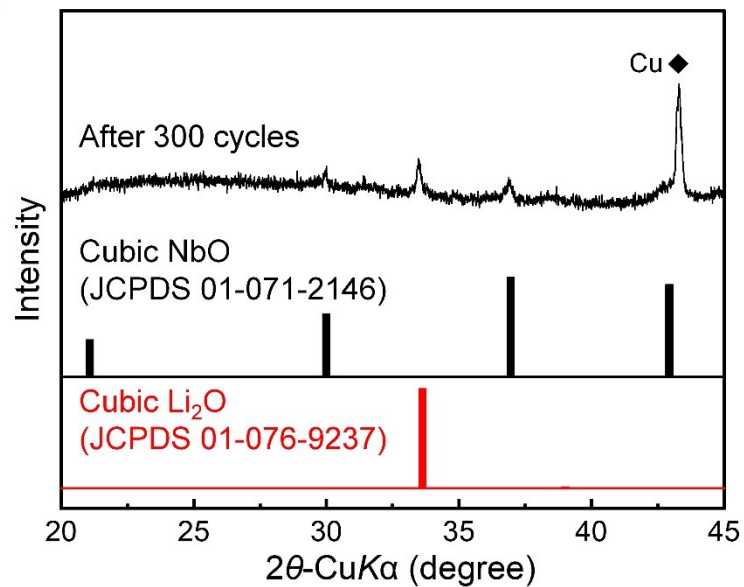


Figure 3-7. The XRD pattern of the Nb₂O₅ electrode after 300 cycles at 90 °C in the Li[FSA]-[C₂C₁im][FSA] IL electrolyte. Reference peaks of cubic NbO and Li₂O represented by black and red bars are reproduced from intensities of the peak data JCPDS 01-071-2146 and 01-076-9237, respectively. See Figure 3-8 for the cycle performance.

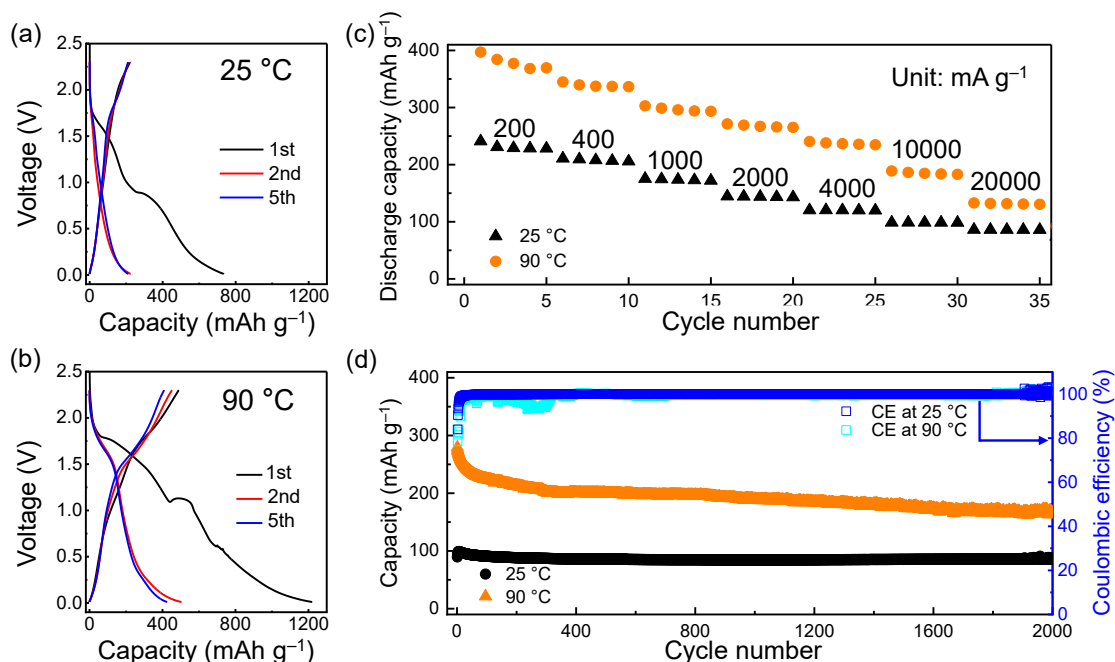


Figure 3-8. Electrochemical performance of the Li/IL/Nb₂O₅ cells (IL = Li[FSA]-[C₂C₁im][FSA] (20:80 in mol)). Charge-discharge curves in the 0.01–2.3 V cutoff voltage range and current density of 200 mA g⁻¹ at (a) 25 and (b) 90 °C. (c) Rate capability at 25 and 90 °C. The current density for charge: 200 mA g⁻¹. The current density for discharge: 200–20000 mA g⁻¹. Cutoff voltage: 0.01–2.3 V. See Figure 3-9 and Table 3-1 for the corresponding discharge curves and details on the capacity, capacity retention, and geometric current density of rate capability, respectively. (d) Cycle performance at 25 and 90 °C. Current densities for both charge and discharge: 2000 mA g⁻¹ and cutoff voltage: 0.01–2.3 V. See Figure 3-10 and Table 3-2 for the corresponding charge-discharge curves and details of capacity and capacity retention during cycle performance, respectively.

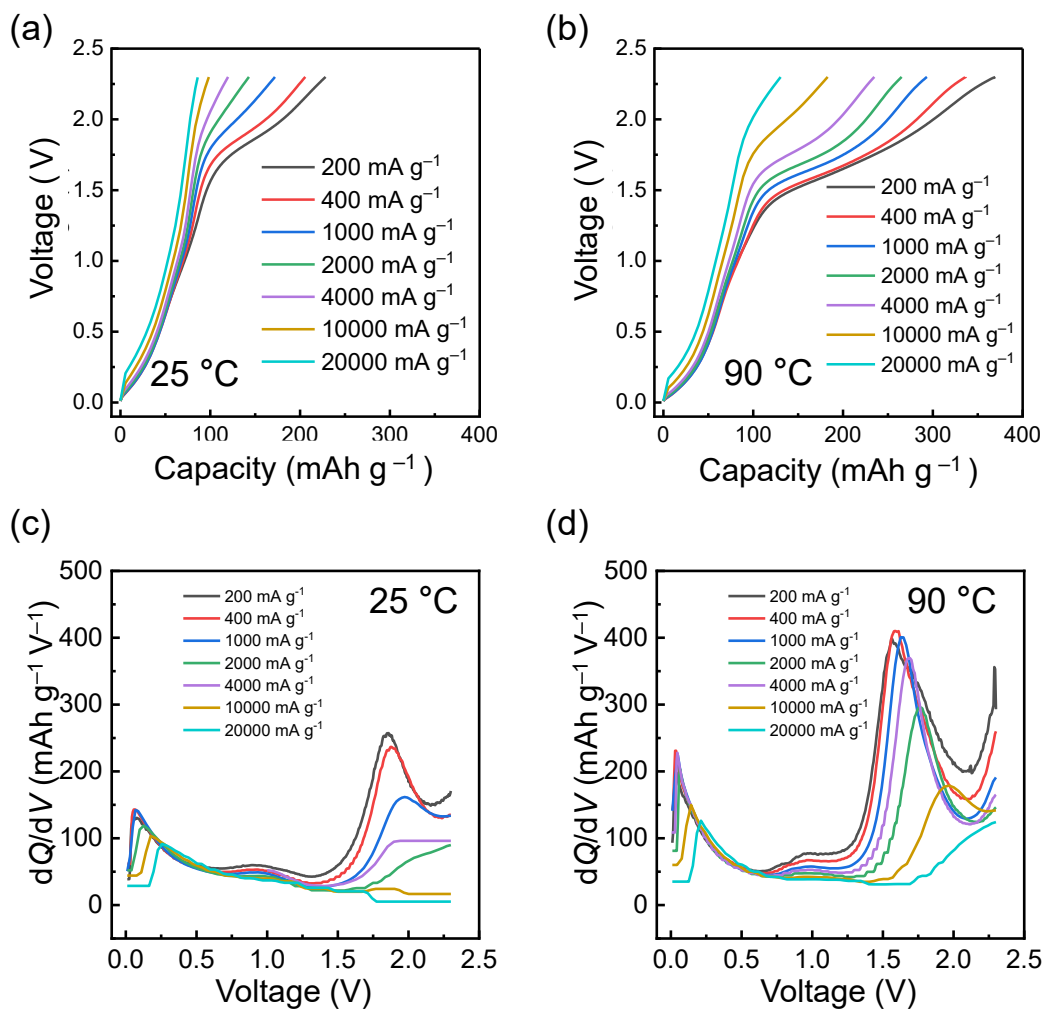


Figure 3-9. Discharge curves and corresponding dQ/dV plots for the rate capability tests of the Li/IL/Nb₂O₅ cell at various current densities at (a,c) 25 and (b,d) 90 °C. Current densities: 200 mA g⁻¹ for charging and 200–20000 mA g⁻¹ for discharging with cutoff voltage of 0.01–2.3 V. The 5th discharge curve of each rate is plotted. See Figure 3-8 for the corresponding rate capability and Table 3-1 for the related data.

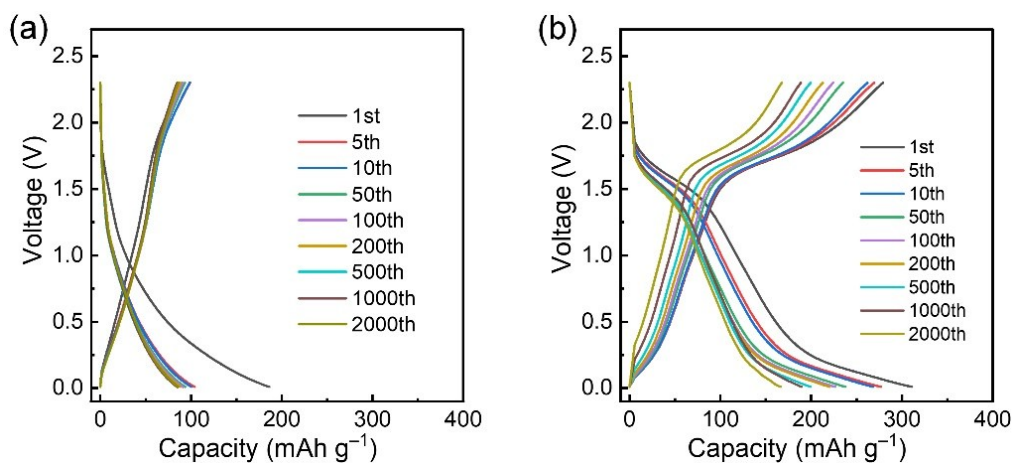


Figure 3-10. Charge-discharge curves of the Li/IL/Nb₂O₅ cell over 2000 cycles at (a) 25 and (b) 90 °C. Current densities: 2000 mA g⁻¹ for charging and discharging with cutoff voltage of 0.01–2.3 V. See Figure 3-8d the corresponding cyclability and Table 3-2 for the related data.

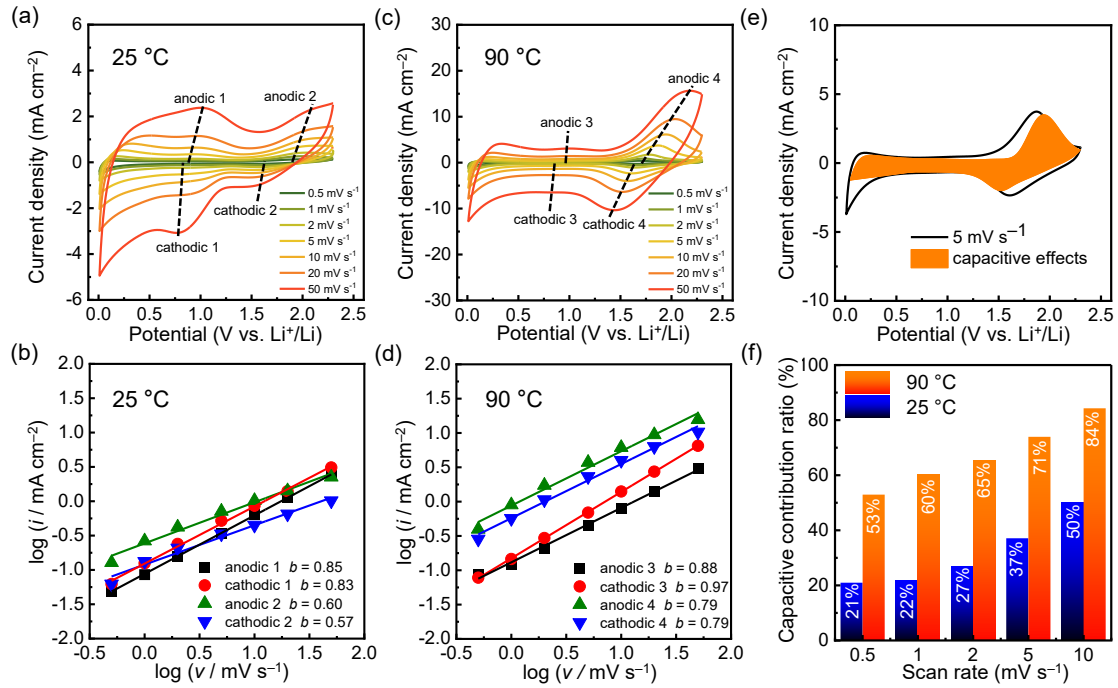


Figure 3-11. Kinetic analysis of the electrochemical performance of Nb₂O₅ electrodes in the Li/IL/Nb₂O₅ cells at 25 and 90 °C (IL = Li[FSA]-[C₂C₁im][FSA] (20:80 in mol). Cyclic voltammograms at scan rates from 0.5 to 50 mV s⁻¹ at (a) 25 and (c) 90 °C (3rd cycle of each scan rate is plotted). (b, d) The log(*i*)-log(*v*) plot for *b*-value determination of cathodic and anodic peaks at (b) 25 and (d) 90 °C. (e) Voltametric responses at a scan rate of 5 mV s⁻¹ at 90 °C. The bright orange region represents the capacitive responses derived from *k*₁ and *k*₂ analysis. (f) Comparison of capacitive contribution of capacitive current at 25 and 90 °C at different scan rates.

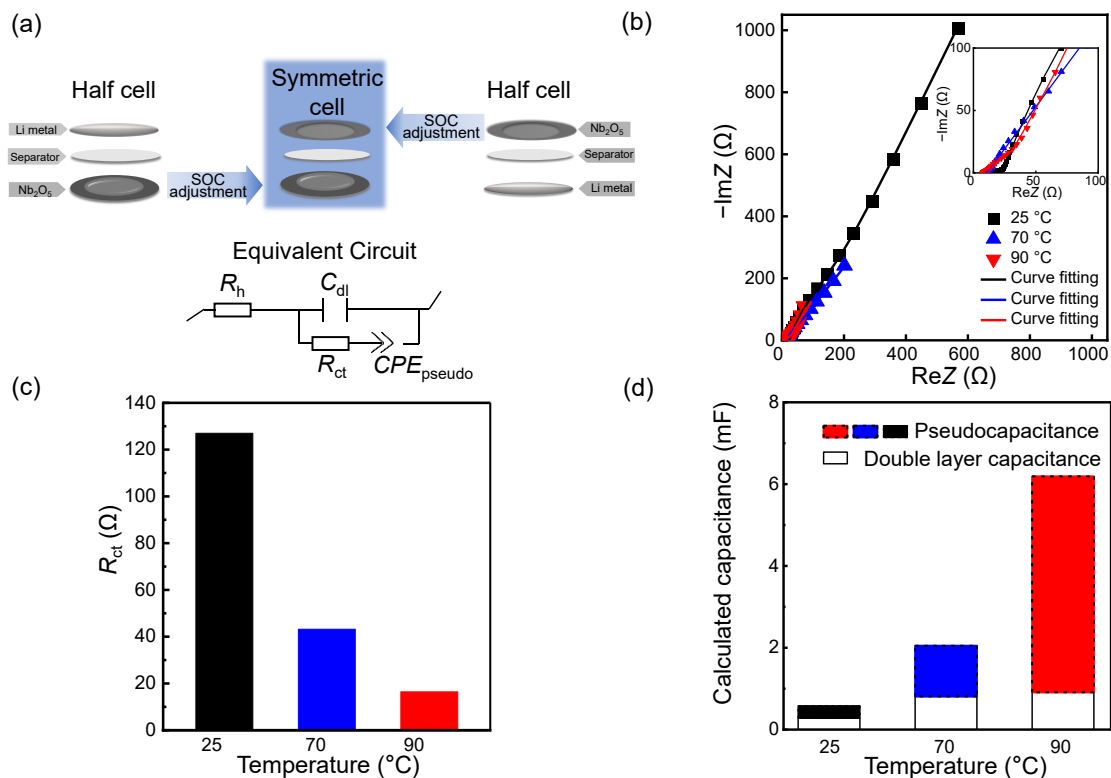


Figure 3-12. Analysis for the effect of temperature on the electrochemical behavior of the Nb_2O_5 through SCEIS on a $\text{Nb}_2\text{O}_5/\text{IL}/\text{Nb}_2\text{O}_5$ symmetric cell. IL = $\text{Li}[\text{FSA}]-[\text{C}_2\text{C}_{1}\text{im}][\text{FSA}]$ (20:80 in mol) IL electrolyte. (a) Schematic illustration of the preparation of symmetric cell using two SOC-adjusted Nb_2O_5 electrodes and an equivalent circuit to fit the Nyquist plots. (b) Nyquist plots of the $\text{Nb}_2\text{O}_5/\text{IL}/\text{Nb}_2\text{O}_5$ symmetric cells at SOC of 1.0 V at 25, 70, and 90 °C. Frequency range: 0.1 Hz–100 kHz. The high-frequency region of (b) is shown in the inset. (c, d) Dependence of (c) R_{ct} and (d) capacitance upon applied temperatures for the Nb_2O_5 electrodes at 25, 70, and 90 °C, respectively. (See Table 3-3 for the EIS fitting results).

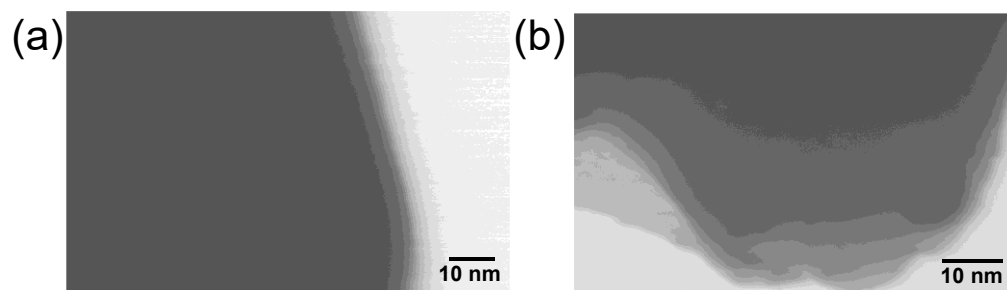


Figure 3-13. Scanning transmission electron microscopy (STEM) images of the Nb₂O₅ electrodes ((a) pristine and (b) after 3000 cycles).

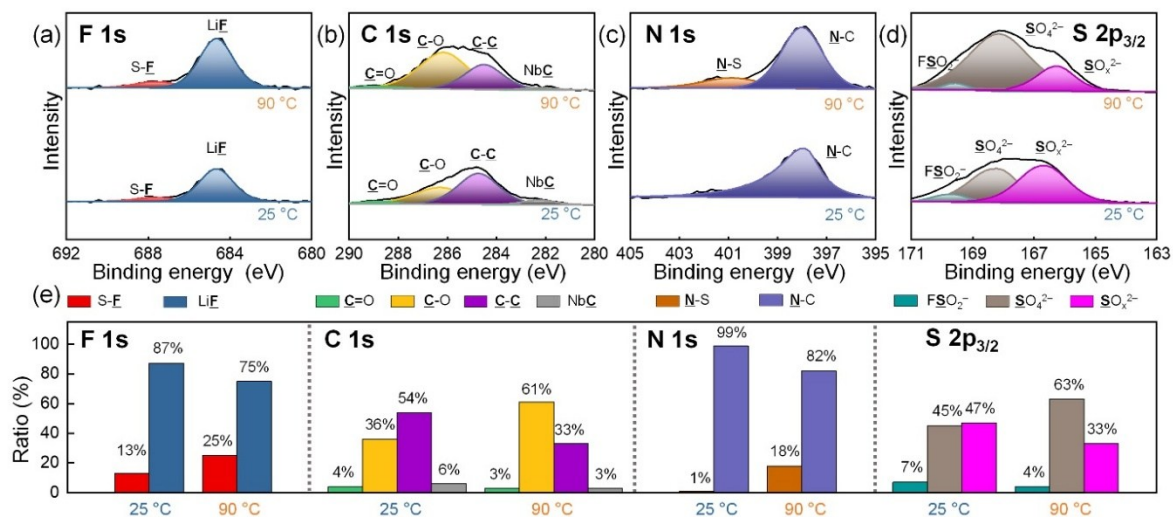


Figure 3-14. XPS spectra of the Nb_2O_5 in the $\text{Li}[\text{FSA}]\text{-}[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$ IL after 2nd charge at 25 and 90 °C. (a) F 1s, (b) C 1s, (c) N 1s and (d) S 2p_{3/2} regions, and (e) SEI component ratios (See Table 3-4 for the fitting results).

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Chapter 4

Inducing a Conductive Surface Layer on Nb₂O₅ via Argon-Ion Bombardment: Enhanced Electrochemical Performance for Li-Ion Batteries

4.1 Introduction

The increasing demand for advanced electrochemical storage devices requires electrode materials which provide high energy and power densities to meet their practical needs [1-3]. Niobium pentoxide, especially the orthorhombic polymorph, has attracted considerable interest as a high-performance negative electrode material for secondary batteries which demonstrate pseudocapacitive Li⁺ insertion mechanism [4, 5]. However, the stoichiometric Nb₂O₅ is an insulator with a wide bandgap between 3.2 and 4.0 eV, thus its intrinsic poor electronic conductivity ($\sigma \sim 3 \times 10^{-6} \text{ S cm}^{-1}$) hinders further application without fabrications; building nanostructures and conductive carbon network are considered to be the strategies to overcome these problems [6]. To overcome the drawback, considerable efforts have been devoted to investigating fabrication techniques such as building special morphology, introducing conductive carbon networks, doping foreign elements for adequate utilization, and nanoarchitecture current collectors (see Table 4-1 for representative modification of the reported Nb₂O₅-based materials) [6-21].

On the other hand, higher electrical conductivity is exhibited by the lower oxidation state of Nb-O systems (NbO_x), such as niobium monoxide (NbO) and niobium dioxide (NbO₂). The monoxide, NbO, shows a characteristic metallic behavior with a low

resistivity at room temperature and NbO₂ is also a semiconductor at room temperature with electronic conductivity higher than that of the orthorhombic Nb₂O₅ by approximately two orders of magnitude ($\sim 10^{-4}$ S cm⁻¹) [22]. The monoclinic Nb₂O₅/NbO₂ composites recently reported demonstrate enhanced electrochemical performance given beneficial effects of the introduction of NbO₂ [23]. This encourages the interest of introducing the lower oxidation states of Nb-O systems serving as an experimental strategy to break the limitations of poor electronic conductivity of Nb₂O₅.

The reduction of metal oxides, such as iron, cobalt, titanium, and niobium by ion-beam bombardment have been investigated in details due to preferential sputtering of oxygen since the 1970s [24-26]. Herein, in this chapter, a one-step approach is utilized to introducing highly conductive NbO_x on the surface of Nb₂O₅ electrode by low-energy Ar-ion bombardment (AIB). As illustrated in Figure 4-1, the Nb₂O₅ electrodes are flashed by AIB for different periods to reduce its surface and expected to enhance the rate performance as a negative electrode material.

4.2 Experimental

All the materials were handled under the same condition as the statement in Section 2.2. The Nb₂O₅ electrode samples were prepared in the same manner with statement in Section 2.4. The Ar-ion beam was flashed to the Nb₂O₅ electrode for 15, 30, 60, 90, 120 and 180 s. Each AIB treatment was applied several times of 15-second duration and 15-second rest to avoid overheating. The Li metal counter electrode was prepared by fixing Li metal (Sigma-Aldrich Co. Ltd., 99.95% purity) on stainless steel (SUS316L) plate. Coin cells of type-2032 were assembled with the 1 M LiPF₆-EC/DMC electrolyte, Nb₂O₅ working electrode, and lithium metal counter electrode (Figure 2-3).

The change of the oxidation state of Nb₂O₅ after AIB was analyzed by XPS (JEOL, JPS-9030) with MgK α line as the exciting radiation. The morphology of the prepared samples was observed by field emission scanning electron microscopy (FE-SEM, Hitachi, SU-8020). The X-ray diffraction (XRD) patterns of the samples were recorded in the Bragg-Brentano geometry using a Rigaku SmartLab diffractometer with Ni-filtered Cu-K α radiation (40 kV and 30 mA) and a silicon strip high-speed detector (Rigaku D/teX Ultra 250). The electrochemical data were obtained by HJ-SD8 charge-discharge system (Hokuto Denko) and VSP potentiostat (Bio-Logic) at 25 °C. A current density of 200 mA g⁻¹ was applied to charge-discharge tests. Discharge rate performance was examined at various discharge current rates from 200 to 40000 mA g⁻¹ while the charge current rate was maintained to be 200 mA g⁻¹. Cyclic voltammetry (CV) was performed at a scan rate from 0.5 to 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was conducted in a frequency range from 0.01 Hz to 100 kHz. The half-cell EIS was conducted using the Nb₂O₅ electrode and Li metal counter electrode. The symmetric-cell EIS (SCEIS) was conducted using the electrodes after adjusting their voltage to 1.5 V in a half-cell setup.

4.3 Result and discussion

Characterization of Nb₂O₅ electrode and AIB treatment. Figures 4-2 and 4-3 show the XPS results carried out for the Nb₂O₅ electrodes treated by AIB for different periods (hereafter, the sample names of AIB-treated Nb₂O₅ electrodes are abbreviated as Nb₂O₅-AIB $_{xx}$, where xx indicates AIB time in the unit of second) and the resulting spectra are shown in Figures 4-2. For the pristine Nb₂O₅ electrode, the Nb 3d_{5/2} and 3d_{3/2} peaks are assigned to Nb^V at binding energies of 206.3 and 209.6 eV, respectively [27], while additional peaks ascribed to the lower oxidation states of Nb^{IV} and Nb^{II} are

evident with the electrode samples after the AIB-treated electrodes [28, 29]. Intensities of the peaks in the low-energy range increase with increasing AIB time, suggesting AIB promote reduction of the Nb₂O₅ electrode surface (Figure 4-3 and Table 4-2). XRD patterns confirmed the Nb₂O₅-AIB electrodes still preserve the crystal lattice of orthorhombic Nb₂O₅ regardless of AIB time, indicating that trace amounts of AIB-induced Nb^{IV} and Nb^{II} species solely exist on the surface of Nb₂O₅ (Figure 4-4).

The surface modification by AIB was manifested by transmission electron microscopy (TEM) and field emission scanning electron microscopic (FE-SEM) images. The high-resolution (HR)-TEM micrographs and the fast Fourier transform (FFT) power suggest that AIB treatment reduces the surface (~5 nm) of Nb₂O₅ to NbO₂, showing lattice fringes at $d = 0.406$ and 0.203 nm which correspond to the diffraction indices of 001 and 002 for Nb₂O₅, respectively, and $d = 0.334$, 0.282 , and 0.221 nm which correspond to 400, 112 and 332 indices for NbO₂, respectively (Figure 4-5). TEM images in Figure 4-6 provide more evidence of the existence of a reduced NbO_x layer, showing distinguished phases with different d -spacing values in regions A and B, near and away from the surface, respectively. On the one hand, the d -spacing value of 0.169 nm is assigned to the diffraction index of 800 for NbO₂ or 211 for NbO observed in the near surface region (region A), which is in agreement with the XPS results of the existence of Nb^{IV} and Nb^{II} species after the AIB treatment. On the other hand, in region B, the d -spacing values of 0.578 , 0.325 , and 0.323 nm correspond to the diffraction indices of 120, 111, and 121 for Nb₂O₅, respectively. The FE-SEM images (Figure 4-7) show morphology changes in the surface, seen particle edges becoming rougher and blurred with protracted AIB exposure due to extended oxygen sputtering from the Nb₂O₅ surface [24, 26].

Electrochemical performance of Nb₂O₅-AIB electrodes. The electrochemical performance of the pristine Nb₂O₅ and Nb₂O₅-AIB electrodes was investigated using Li/Nb₂O₅ half cells with 1M LiPF₆-EC/DMC = 1:1 (v/v) electrolyte at 25 °C. In the cutoff voltage of 1.0–2.3 V, Nb₂O₅ works based on an insertion mechanism. The Nb₂O₅-AIB30 electrode exhibits a capacity of 211 mAh g⁻¹ at 40 mA g⁻¹, which is significantly higher than that delivered by the pristine Nb₂O₅ electrode (138 mAh g⁻¹) (Figure 4-8). Rate capabilities were tested at the current densities from 200 to 40000 mA g⁻¹ during discharging and the fixed current density of 200 mA g⁻¹ during charging (Figure 4-9 and Table 4-3). The Nb₂O₅-AIB30 electrode delivers 132, 76, and 22 mAh g⁻¹ at the discharging rates of 200, 2000, and 10000 mA g⁻¹, respectively. The rate capability does not improve even the AIB time is increased to 120 s (see Figure 4-10 for discharge profiles during rate capability tests for the Nb₂O₅ AIB electrodes with different AIB times). Although longer AIB time increases the amount of NbO_x, too long treatment results in the inferior rate performance as shown for Nb₂O₅-AIB180. Chemical damage of the electrode material, conductive material, and binder may occur due to longer Ar-ion beam exposure (see SEM images in Figure 4-7).

Moreover, the corresponding dQ/dV plots (Figure 4-9b) indicate that voltage polarization was lower in Nb₂O₅-AIB30 than in pristine Nb₂O₅, taking the beneficial influence of NbO_x on the electrical conductivity. Although the direct measurement of electronic conductivity was difficult for the AIB-treated Nb₂O₅, the electrical conductivities of pristine Nb₂O₅ and Nb₂O₅-AIB30 electrodes were evaluated from DC resistances utilizing a two-electrode ion-blocking cell configuration, and the corresponding illustration is shown in Figure 4-11. It was quantitatively proved that the electrical conductivity of the entire increases over an order of magnitude from pristine Nb₂O₅ (2.5×10^{-4} S cm⁻¹) electrode to Nb₂O₅-AIB30 (1.3×10^{-3} S cm⁻¹) electrode. In

addition, cycle performance tests were conducted at the current density of 200 mA g⁻¹ after an aging process entailing 5 cycles at 40 mA g⁻¹ followed by 5 cycles at 100 mA g⁻¹ (Figures 4-12 and 4-13 and Table 4-3e). The results indicate 150% improvement in discharge capacity by 30-second AIB compared to that of the pristine state. Stable cycling continues over 300 cycles.

Electrochemical impedance spectroscopy analysis. To assess the electrode interfacial behavior, EIS was performed on half- and symmetric-cell configurations at the electrode voltage of 1.5 V where the symmetric cell was composed of two identical Nb₂O₅/Nb₂O₅ electrodes to eliminate the influence of the Li metal counter electrode. Nyquist plots by symmetric-cell and half-cell EIS are shown in Figures 4-14 and 4-15, respectively. The resistance corresponding to the semi-circle distinctly decreases by the AIB treatment, confirming introduction of NbO_x facilitates charge transfer at the surface of the electrode.

To gain a more quantitative measure for the kinetics of electrochemical reaction for Nb₂O₅-AIB electrodes, the EIS was conducted in symmetric cell configuration at various temperatures from 10 to 25 °C, and the activation energies (E_a) of the reciprocal of charge transfer resistance (R_{ct}) were calculated by the slope of the linearly fitted line in Figure 4-14 according to the following equation [35-37].

$$\ln\left(\frac{1}{R_{ct}}\right) = -\left(\frac{E_a}{R_g}\right)\left(\frac{1}{T}\right) + \ln(A)$$

Here, A is frequency factor, R_g is gas constant, and T is the absolute temperature. The E_a value for R^{-1} is 86.9 kJ mol⁻¹ of the pristine Nb₂O₅ and decreased to 62.4 kJ mol⁻¹ for the Nb₂O₅-AIB30. The corresponding Arrhenius plot manifested lower activation

energy in Nb₂O₅-AIB30 compared to the pristine electrode for the reciprocal charge transfer resistance, contributing the obtained enhanced electrochemical performance.

4.4 Conclusions

In summary, this chapter revealed a facile one-step AIB treatment effectively introduces electronically conductive NbO_x on the surface of Nb₂O₅, with which the surface modification and enhancement of electrochemical performance have achieved simultaneously. The introduction of NbO_x species with AIB treatment was confirmed by XPS spectra and TEM observation. The electrically conductive NbO_x species contributed to decrease the charge transfer resistance of AIB electrodes. Electrodes exposed to certain AIB durations exhibit enhanced electrochemical performance.

Table 4-1. Modification of the reported Nb₂O₅-based electrochemical energy storage materials and the performance.

Materials	Rate capability (mAh g ⁻¹)	Potentials (V)	Reference
3D ordered microporous (3DOM) T-Nb ₂ O ₅	205 (0.5C), 106 (20C), 77 (50C)	1.0–3.0	[11]
T-Nb ₂ O ₅ nanowires (20–50 nm in diameter) on carbon	182 (1C), 143(5C), 120 (20C)	1.0–3.0	[12]
Hollow and mesoporous Nb ₂ O ₅	195 (1C), 125(50C)	1.0–3.0	[38]
T-Nb ₂ O ₅ nanoparticles on 3D porous carbon nanowebs	118 (1 A g ⁻¹), 107 (2), 95 (5), 82(10)	1.0–3.0	[14]
Popcorn-like Nb ₂ O ₅ with cloned hierarchical architectuere	179 (0.2C), 154 (1C), 126 (5C), 103 (10C), 82 (20C)	1.0–2.5	[39]
Graphene nanoscroll wrapping Nb ₂ O ₅ nanoparticles	281 (1C), 238 (2.5C), 224 (5C), 210(10C)	0–2.5	[17]
Carbon-confined T-Nb ₂ O ₅ @C nanoparticles	205 (0.1 A g ⁻¹), 199 (0.2), 190(1), 185(2), 179(5), 177 (6)	1.1–3.0	[40]
Amorphous N-doped carbon shell on micrometer-sized single crystal H-Nb ₂ O ₅	250 (0.05 A g ⁻¹), 200 (1), 150 (4), 130 (12), 100 (16)	1.0–3.0	[19]
Ag-coated 1D T-Nb ₂ O ₅ fibers	180 (0.5 A g ⁻¹), 104 (5)	1.0–2.6	[16]
Ag nanoparticle coated nitridated Nb ₂ O ₅ electrode	250 (0.05 A g ⁻¹), 190 (0.5), 150(1), 105(3), 80(5)	1.0–2.6	[41]
Oxygen vacancies are implanted into T-Nb ₂ O ₅	256 (1C), 187 (5C), 144 (10C), 107 (25C)	0.4–3.0	[20]
Nb ₂ O ₅ -AIB30	132 (0.2 A g ⁻¹), 96 (1), 54 (4), 22 (10)	1.0–2.3	This work
T-Nb ₂ O ₅ : orthorhombic Nb ₂ O ₅ ; H-Nb ₂ O ₅ : monoclinic Nb ₂ O ₅			

Table 4-2. Peak assignment of XPS spectra for the Nb₂O₅-AIB electrodes. See Figure 4-2 for the corresponding spectra.

Sample	Binding energy (eV)					
	Nb ^V		Nb ^{IV}		Nb ^{II}	
	Nb 3d	ratio (%)	Nb 3d	ratio (%)	Nb 3d	ratio (%)
Pristine	209.3 206.6	100				
AIB15	209.6 206.6	25.1	207.5 204.3	57.3	205.8 203.4	17.7
AIB30	209.6 206.3	23.7	207.6 204.2	55.2	205.5 203.4	21.1
AIB60	210.0 206.4	23.1	207.6 204.1	54.7	205.9 203.4	22.2
AIB90	210.0 206.6	15.4	207.5 204.3	54.3	205.9 203.3	30.2
AIB120	206.3 210.0	10.5	207.3 204.1	54.6	206.0 203.3	34.9
AIB180	210.0 206.3	10.3	207.3 204.1	54.4	206.0 203.3	35.3
Peak assignment						
Oxidation state	Spectral line	Binding energy (eV)		Reference		
Nb ₂ O ₅	3d _{3/2}	209.6 ± .3		[42]		
	3d _{5/2}	206.3 ± .3		[27]		
NbO ₂	3d _{3/2}	207.5 ± .1		[29]		
	3d _{5/2}	204.3 ± .2		[29]		
NbO	3d _{3/2}	205.8 ± .2		[28, 29]		
	3d _{5/2}	203.3 ± .1		[29]		

Table 4-3. Discharge capacity and capacity retention of the Li/Nb₂O₅ cell of the pristine Nb₂O₅, Nb₂O₅-AIB30, 120 and 180 electrodes in the rate capability test at 25 °C. ^{a)}

Current density (mA g ⁻¹)	Geometric current density (mA cm ⁻²)	Nb ₂ O ₅ pristine		Nb ₂ O ₅ -AIB30		Nb ₂ O ₅ -AIB120		Nb ₂ O ₅ -AIB180	
		Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 200 mA g ⁻¹ (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 200 mA g ⁻¹ (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 200 mA g ⁻¹ (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 200 mA g ⁻¹ (%)
200	0.2	77	100	132	100	121	100	31	100
400	0.3	65	84	115	87	105	87	22	71
1000	0.8	48	62	96	73	84	69	11	35
2000	1.5	33	43	76	58	65	54	6	19
4000	3.0	17	22	54	41	45	37	3	10
10000	7.5	2	3	22	17	19	16	2	6
20000	15	1	1	4	3	4	3	1	3
40000	30	0.5	1	1	1	1	1	0.7	2
200	0.2	69	90	120	91	107	88	31	100

^{a)} Charge rate: 200 mA g⁻¹, discharge rate: 200 to 40000 mA g⁻¹, cutoff voltage: 1.0–2.3 V. See Figure 4-9 for comparative rate capabilities and Figure 4-10 for the respective discharge profiles.

Table 4-4. Discharge capacities and capacity retentions of the pristine Nb₂O₅ and Nb₂O₅-AIB30 electrodes during the cycle test at 25 °C for 300 cycles.^{a)}

Cycle number	Pristine Nb ₂ O ₅		Nb ₂ O ₅ -AIB30	
	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 1st cycle (%)	Capacity (mAh g ⁻¹)	Capacity retention vs. Capacity at 1st cycle (%)
1	82	100	122	100
5	80	98	112	92
10	78	95	117	96
50	70	85	98	80
100	63	77	93	76
300	54	66	98	80

^{a)} Current density: 200 mA g⁻¹ for charging and discharging, cutoff voltage: 1.0–2.3 V.

Table 4-5. Fitting parameters of the Nyquist plots for the pristine Nb₂O₅ and Nb₂O₅-AIB30 symmetric cell at 1.5 V at 10, 15, 20 and 25 °C, respectively. See Figures 4-16 and 18 for the corresponding Nyquist plot.

Sample	Temperature (°C)	R_s (Ω)	R_{ct} (Ω)	Q_1 (mF s ⁽ⁿ⁻¹⁾)		
				Q_1	n	C_1 (mF)
pristine	10	5.5	6460	0.22	0.7	0.27
	15	4.2	3500	0.28	0.7	0.31
	20	4.0	2000	0.40	0.7	0.33
	25	3.9	1334	0.45	0.7	0.35
AIB30	10	3.5	1302	0.50	0.8	0.39
	15	3.3	826	0.58	0.8	0.44
	20	3.0	466	0.7	0.8	0.45
	25	2.8	331	0.9	0.8	0.52

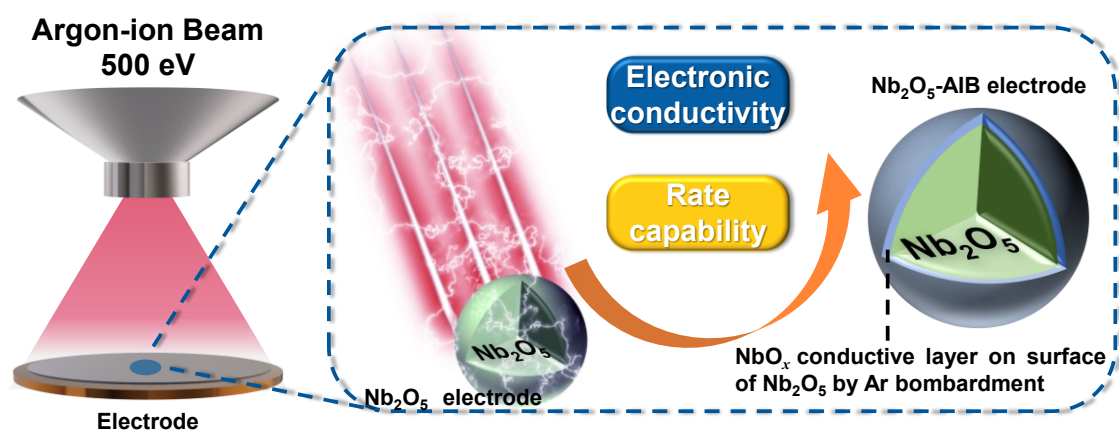


Figure 4-1. Schematic illustration of introducing NbO_x conductive layer on Nb_2O_5 Electrode by AIB treatment.

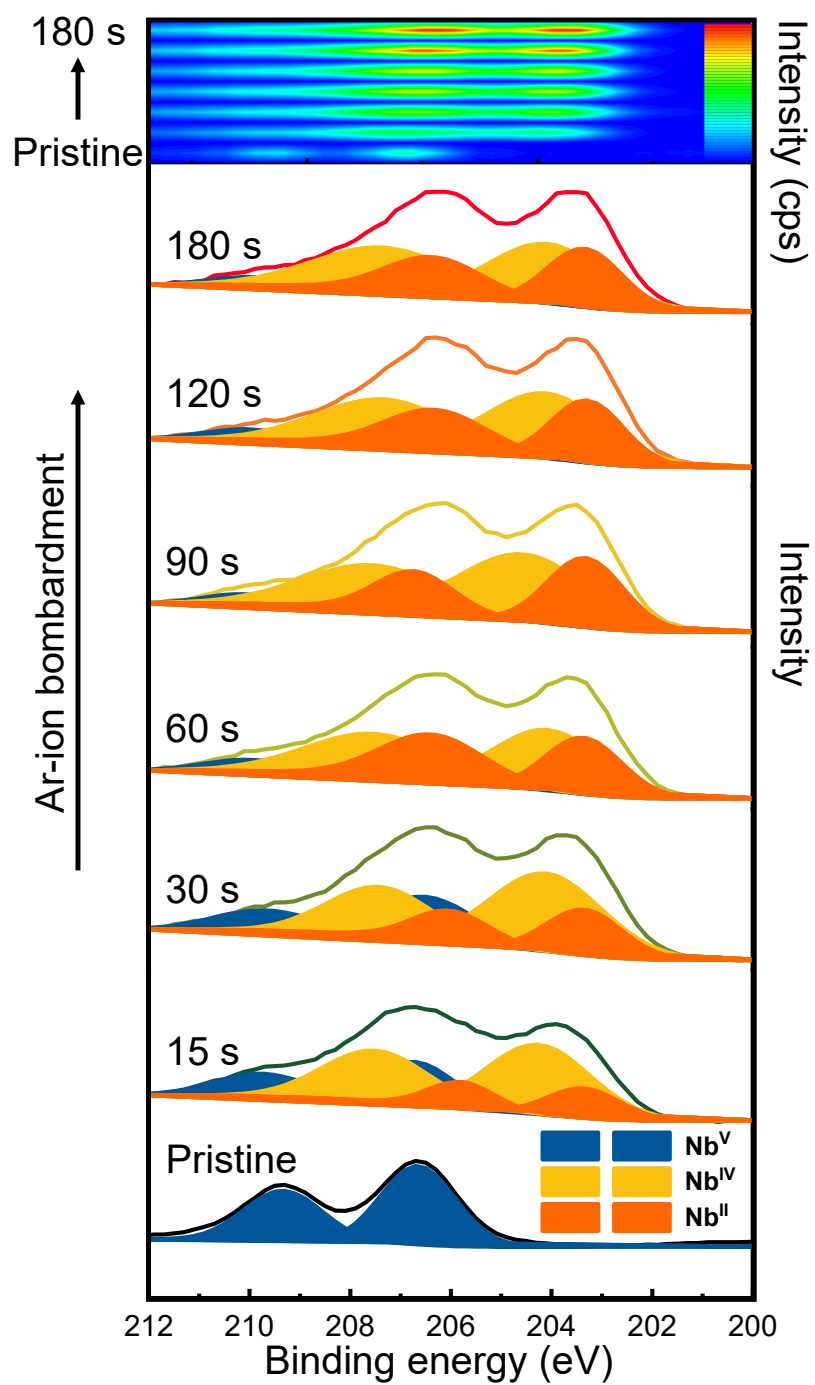


Figure 4-2. Nb 3d XPS spectra of pristine Nb₂O₅ and Nb₂O₅-AIB15, 30, 60, 90, 120, and 180 electrodes to monitor changes in valence state of Nb during AIB duration increasing.

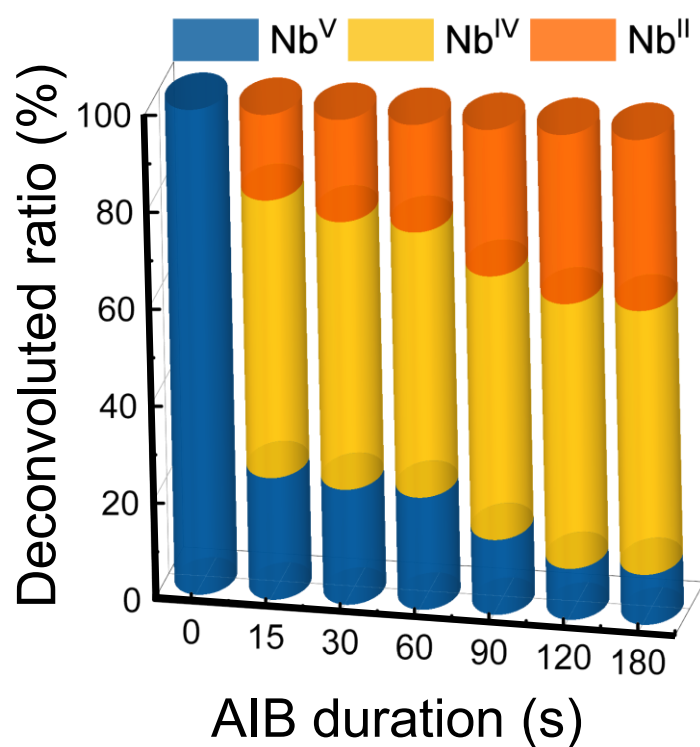


Figure 4-3. Ratio of Nb oxidation states in the surface of pristine Nb₂O₅ and Nb₂O₅-AIB electrodes. See Table 4-2 for peak assignment and deconvoluted ratios for each AIB sample.

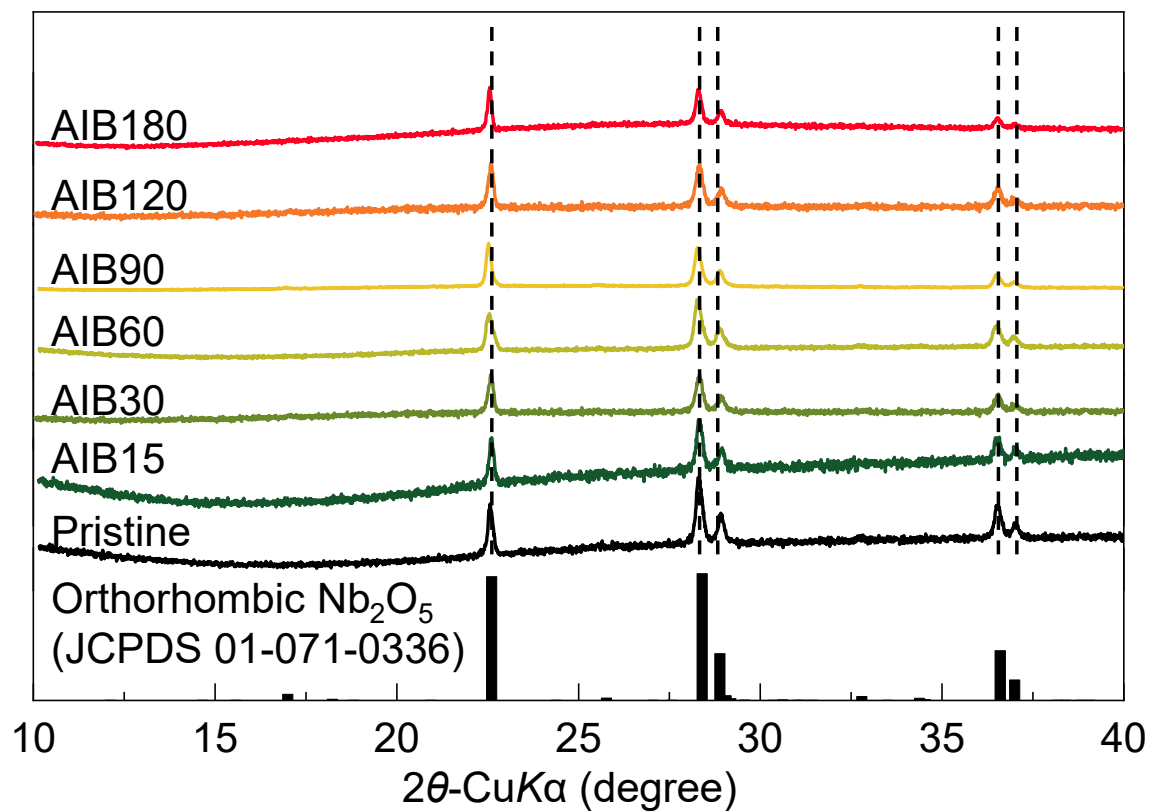


Figure 4-4. XRD patterns for pristine Nb₂O₅ and Nb₂O₅-AIB15, 30, 60, 90, 120, and 180 electrodes. Reference patterns of orthorhombic Nb₂O₅ are reproduced from the intensities of the previous data (JCPDS 01-071-0336) [43].

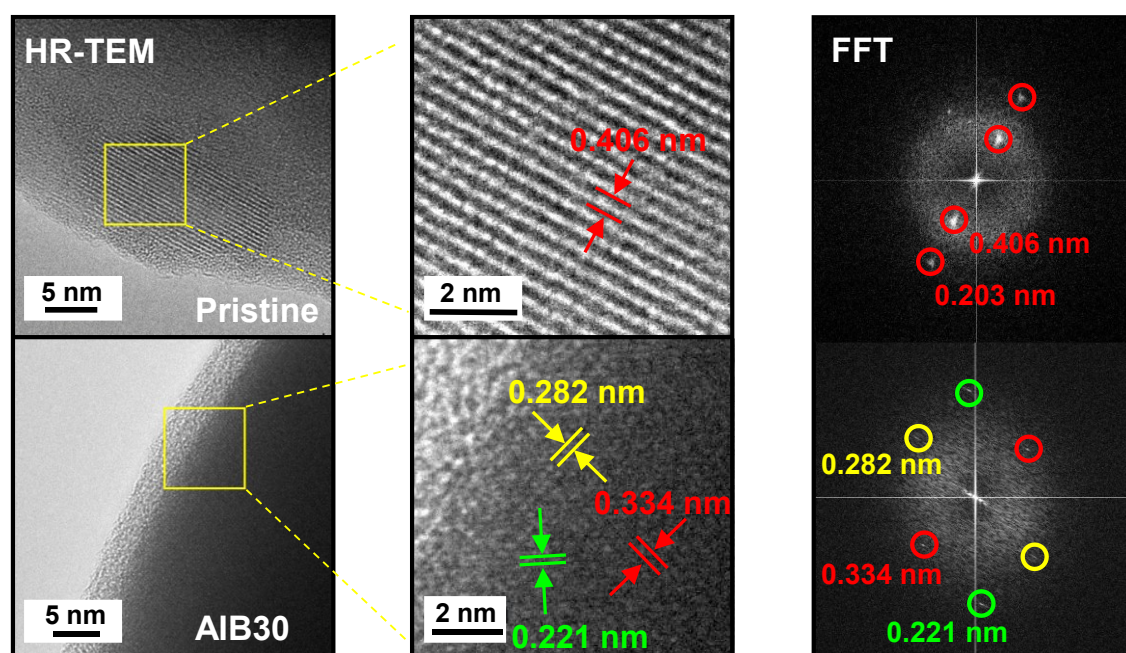


Figure 4-5. HR-TEM images and corresponding FFT of the pristine Nb_2O_5 and Nb_2O_5 -AIB30 electrodes.

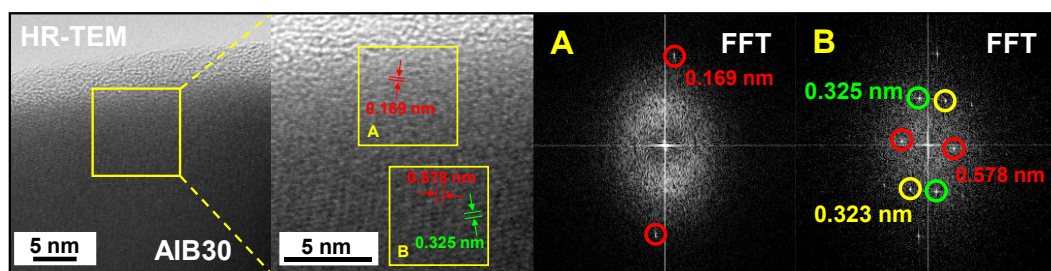


Figure 4-6. Additional HR-TEM images and corresponding FFT of the Nb_2O_5 -AIB30 electrode.

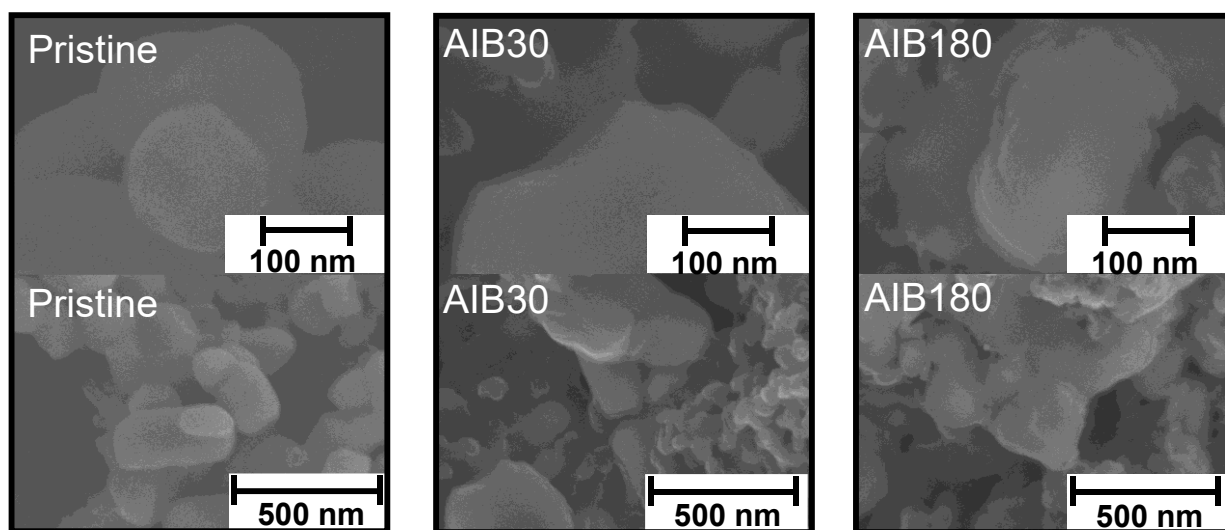


Figure 4-7. FE-SEM images of pristine Nb_2O_5 , $\text{Nb}_2\text{O}_5\text{-AIB30}$, and $\text{Nb}_2\text{O}_5\text{-AIB180}$.

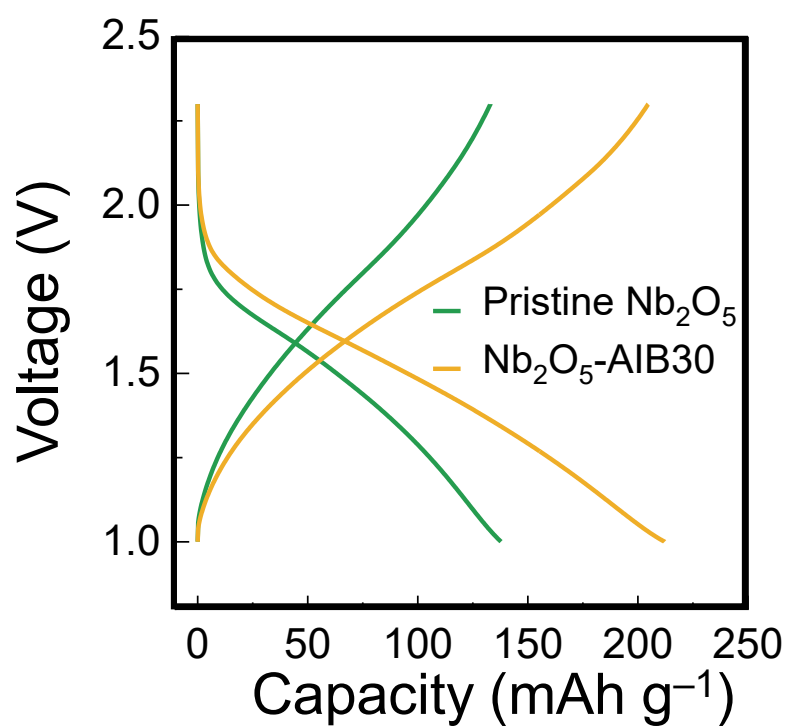


Figure 4-8. Charge-discharge curves in the 1.0–2.3 V cutoff voltage range at the current density of 40 mA g⁻¹.

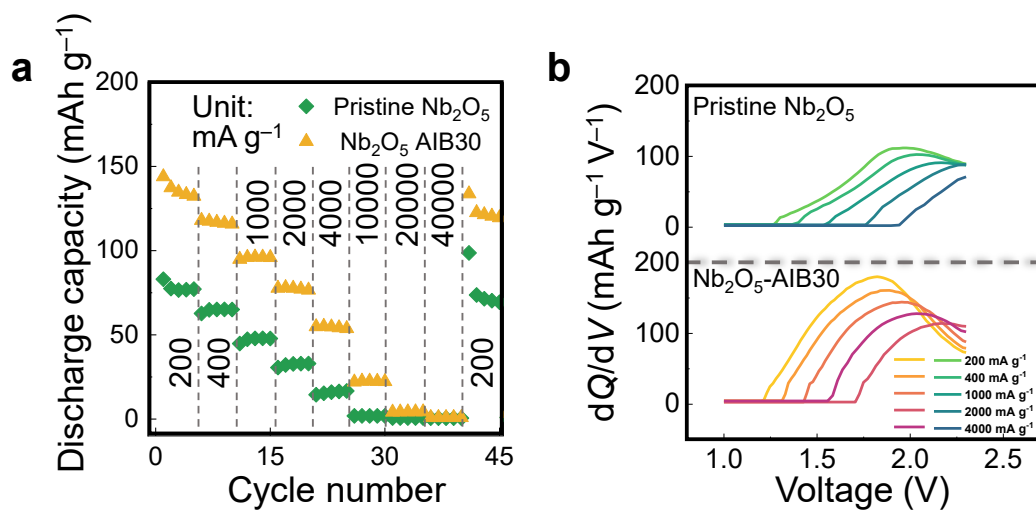


Figure 4-9. (a) Comparative rate capabilities. Current density during charge: 200 mA g⁻¹. Current density during discharge: 200 – 40000 mA g⁻¹ (see Figure 4-10 for the respective discharge profiles and Table 4-3 for capacity and capacity retention). (b) Corresponding dQ/dV plots for the rate capability tests in (a).

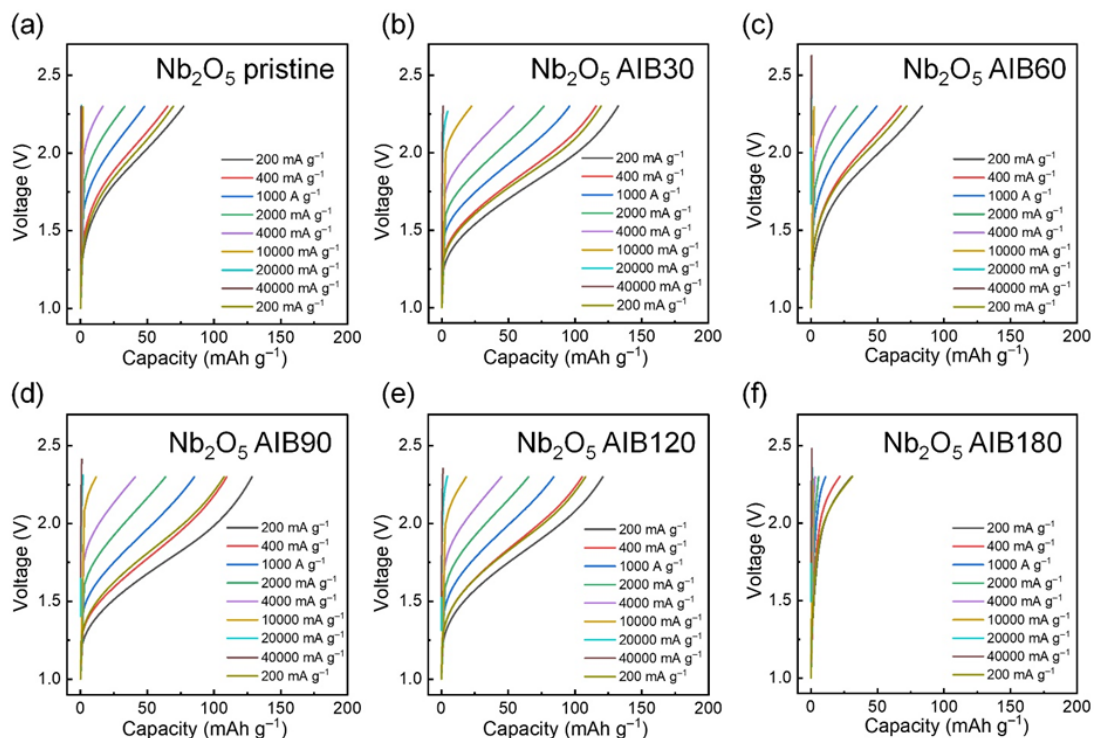


Figure 4-10. Discharge curves of the (a) pristine Nb₂O₅, (b) Nb₂O₅-AIB30, (c) Nb₂O₅-AIB60, (d) Nb₂O₅-AIB90, (e) Nb₂O₅-AIB120 and (f) Nb₂O₅-AIB180 at various current densities. The current density for charging: 200 mA g⁻¹. The current density for discharge: 200 to 40000 mA g⁻¹ and cutoff voltage: 1.0–2.3 V. The cells were charge-discharged for 5 cycles at each rate and the 5th discharge curve is plotted for each rate. See Figure 4-9 for rate capability and Table 4-3 for discharge capacity and capacity retention.

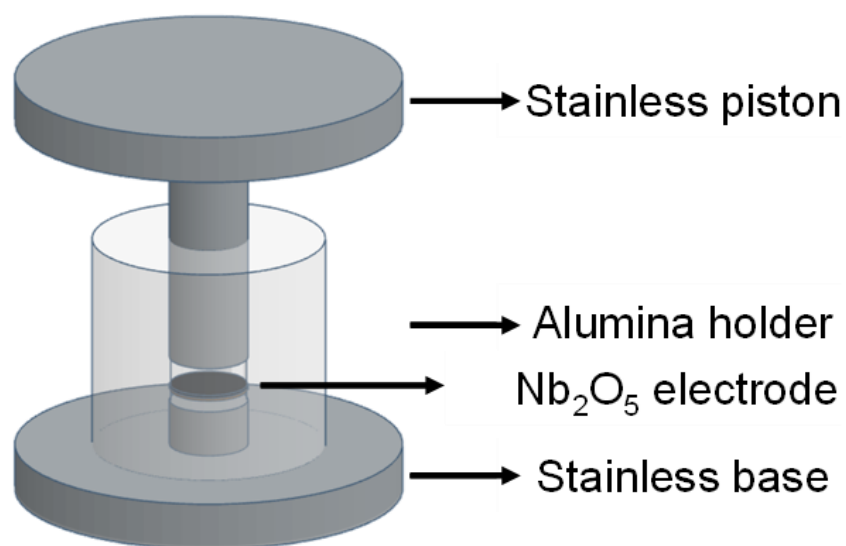


Figure 4-11. Illustration of an ion-blocking cell configuration for the electrical conductivity measurement.

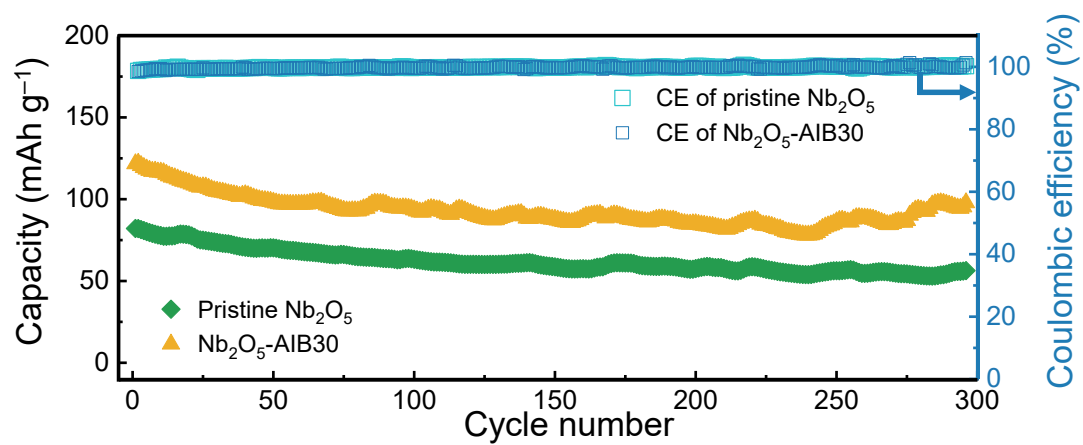


Figure 4-12. Comparative cycle performance. Current densities for both charge and discharge: 200 mA g⁻¹ and cutoff voltage range: 1.0–2.3 V.

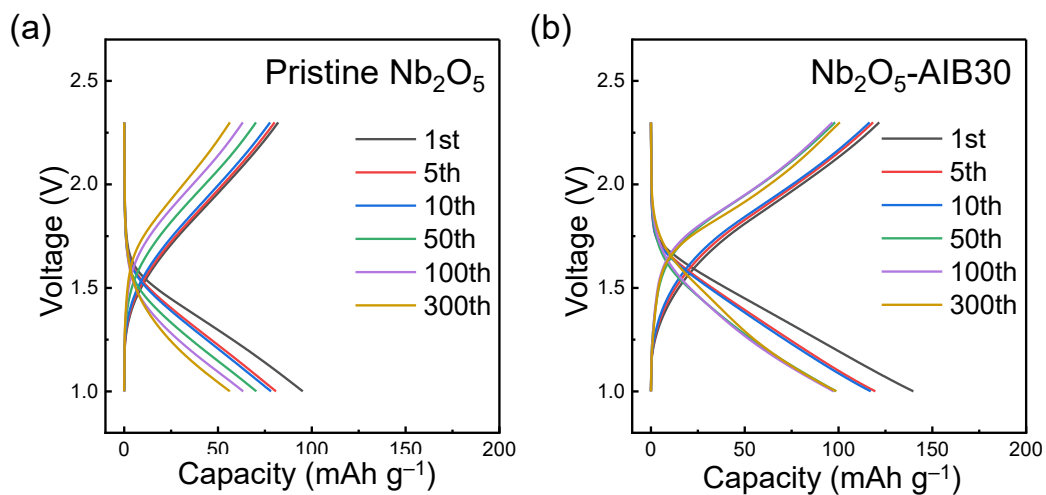


Figure 4-13. Charge-discharge curves of the (a) pristine Nb₂O₅ and (b) Nb₂O₅-AIB30 electrodes over 300 cycles at a current density of 200 mA g⁻¹ with the cutoff voltage of 1.0 – 2.3 V. See Table 4-3 for the related data.

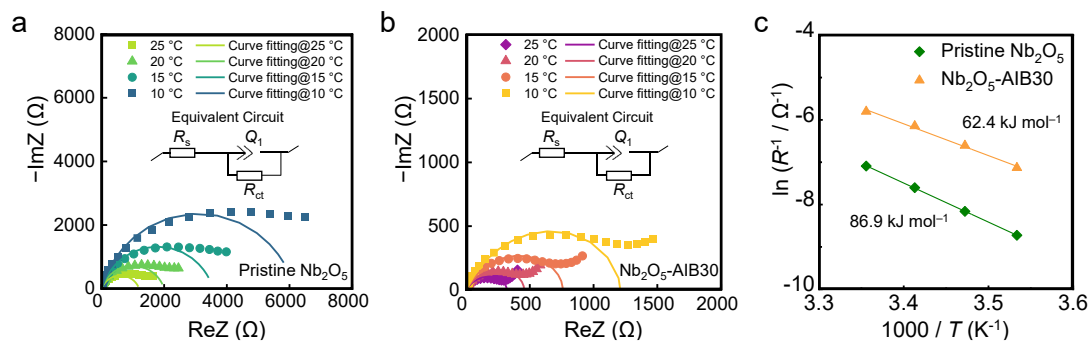


Figure 4-14. Comparative (a, b) Nyquist plots of the pristine Nb_2O_5 and $\text{Nb}_2\text{O}_5\text{-AIB30}$ symmetric cells. The inset shows an equivalent circuit to fit the Nyquist plots. (c) The corresponding Arrhenius plots of symmetric cells. The electrode potential was adjusted to be 1.5 V at each temperature. Frequency range: 0.01 Hz – 100 kHz. AC amplitude: 10 mV. Characteristic frequencies for the semicircle are: 1 – 0.5 Hz. See Table 4-5 for fitting results and utilized equivalent circuit.

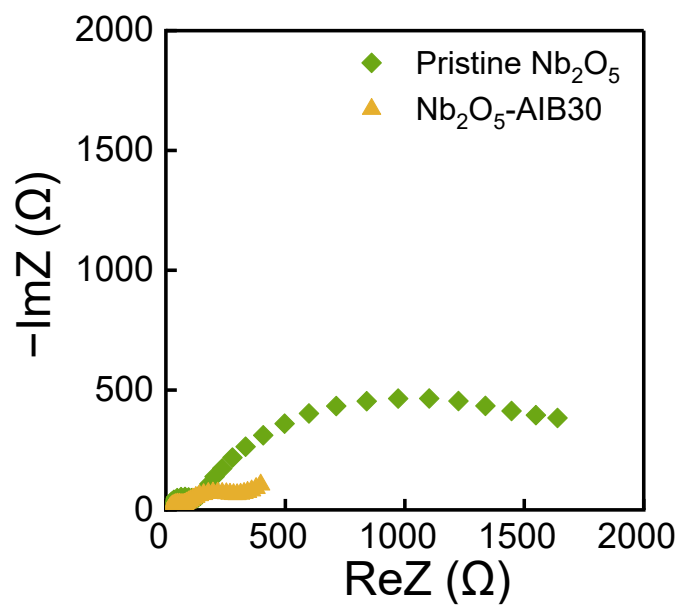


Figure 4-15. Comparative Nyquist plots of half cells at the cell voltage of 1.5 V using the pristine Nb_2O_5 and Nb_2O_5 -AIB30 electrodes. Frequency range: 0.01 Hz – 100 kHz. AC amplitude: 10 mV.

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Chapter 5

Unprotected Organic Cations — The Dilemma of Highly Li-Concentrated Ionic Liquid Electrolytes

5.1 Introduction

Lithium-ion batteries (LIBs) have emerged as the leading technology in secondary batteries, owing to their exceptional electrochemical performance and well-established technologies [1-5]. As a crucial component of electrochemical energy storage devices, the electrolyte selected for LIBs necessitates a stable electrochemical potential window – typically determined by its oxidation and reduction potentials, to enable high operating voltages and consequently, high energy densities [6, 7]. It is worth noting that the performance of LIBs is also closely linked to the different liquid environments established during electrolyte development due to their significant impact on the interfacial properties [8-15].

As stated in Section 1.4, highly Li-concentrated electrolytes have been widely studied to harness their uniquely varying bulk and interface properties that arise from their distinctive physicochemical properties and coordination structures [16-23]. Similar strategies have been applied in the realm of ionic liquid (IL) electrolytes to exploit their improved functionalities. Accordingly, considerable research efforts have been dedicated to exploring the Li-anion coordination structures within the bulk highly concentrated ionic liquid (HCIL) electrolytes and understanding their interfacial behavior and ionic dynamics. These studies are in line with inquests into conventional nonaqueous and aqueous electrolytes where the anions have been found to move in

tandem with the Li^+ ions during the insertion/extraction or deposition/dissolution electrochemical processes. Driven by these insights, the investigations into the irreversible capacities and the consequent SEI formation in IL electrolytes have also been primarily focused on the decomposition behavior of anionic species [24-32], with less attention paid to the behavior of organic cations in these IL electrolytes. Previous studies on organic cations have highlighted the effects of structures such as the alkyl chain length [33, 34], functional group [32, 35], and interfacial nanostructures [36], on the physicochemical properties of IL electrolytes. Nevertheless, only a few studies have investigated their co-intercalation behavior [37, 38], and the impact of cation on the initial formation of the SEI layer needs a more profound understanding.

On another front, the poor electrolyte compatibility with common negative LIB electrode materials, such as graphite, still presents a key challenge to the utilization of IL electrolytes. As schematically depicted in Figure 5-1a, full-cell configurations utilizing IL electrolytes have exhibited significant irreversibility during the initial charge step, resulting in notably low initial Coulombic efficiency (ICE) ($< 50\%$). The irreversible phenomenon has been found to become more pronounced when HCIL electrolytes are employed (see Figures 5-2 and 5-3). It is noticed that the N/P ratios lower than 1 in the full cell configuration indicate the positive electrode is excessive compared to the negative electrode. During the first charge, the extracted Li ions are replenished to the electrolyte to compensate for the loss of the organic cation without being intercalated to the negative electrode. This issue significantly impedes the enhancement of the full-cell energy densities through N/P ratio adjustments, posing challenges to the practical applications of IL electrolytes. The coordination structure of Li^+ cations in IL electrolytes primarily encapsulates bidentate or monodentate $[\text{FSA}]^-$ anions that form a tight $\text{Li}^+ - [\text{FSA}]^-$ coordination network. Considering this structural

framework, the emergence of less-interacted $[\text{C}_2\text{C}_1\text{im}]^+$ cations in the “unprotected” state kinetically can be conjectured to enlarge the irreversible capacity due to the decomposition of $[\text{C}_2\text{C}_1\text{im}]^+$ cations in IL electrolytes. As shown in Figure 5-1b, this phenomenon may result in a narrow electrochemical potential window for the HCIL electrolyte, making it unfavorable for practical utilities. As such, understanding the electrochemical and chemical properties of organic cations in HCIL electrolytes is becoming an increasingly urgent concern, especially when Li^+ concentrations are varied instead of fixating on one specific concentration.

In this chapter, we focus on the behavior of the organic cations in the $\text{Li}[\text{FSA}]-[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($[\text{C}_2\text{C}_1\text{im}]^+ =$ 1-ethyl-3-methylimidazolium and $\text{FSA} =$ bis(fluorosulfonyl)amide)) IL electrolytes, particularly their coordination structures and interfacial behavior on the graphite negative electrodes when varied Li salt concentrations are applied. The origins of the changes in the coordination environment in the IL electrolytes with different salt concentrations are discussed through a comprehensive analysis that includes infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. In addition, computational studies, which encompassed density functional theory (DFT) and molecular dynamics (MD) simulations, were conducted to gain a deeper understanding of the interactions between cations and anions in the liquid environment. X-ray photoelectron spectroscopy (XPS) is employed to investigate the decomposed compound and the interphase chemistry on the surface of the negative electrodes. The strategy of tuning the Lewis basicity of anionic species is applied to the HCIL electrolytes to strengthen ionic interactions to effectively inhibit the decomposition of the organic cation.

5.2 Experimental

Electrolyte and Cell Preparation. All the materials were handled under the same condition with the statement in Section 2.1. The Li[FSA]-[C₂C₁im][FSA] and Li[FSA]-[C₃C₁pyrr][FSA] (C₃C₁pyrr⁺ = *N*-methyl-*N*-propylpyrrolidinium) IL electrolytes were prepared by mixing the corresponding Li[FSA] into [C₂C₁im][FSA] and [C₃C₁pyrr][FSA] in the target molar ratios. The typical water contents of the prepared ILs were below 20 ppm according to Karl-Fischer titration (899 Coulometer, Metrohm). The salts, Li[OTf] ([OTf][−] = trifluoromethanesulfonate, Sigma-Aldrich, purity > 98%), , Li[TFSA] ([TFSA][−] = bis(trifluoromethanesulfonyl)amide, Kishida Chemical, purity > 99.0%), Li[FTA] ([FTA][−] = ((fluorosulfonyl)(trifluoromethanesulfonyl)amide, Wako Pure Chemical Industries), Li[PF₆] (Wako Pure Chemical Industries, battery grade) and the extra IL of [C₂C₁im][FAP] ([FAP][−] = tris(pentafluoroethyl)trifluorophosphate, Sigma-Aldrich, purity ≤ 100%) were added into base ILs as anion sources. The organic electrolyte, 1 mol L^{−1} Li[PF₆]-EC/DMC (1:1 v/v; battery grade), was purchased from Kishida Chemical and used without further purification. The graphite and NCM811 electrodes were prepared in the same manner with statement in section 2.2.

The Li/graphite half cells (2032-type) were assembled with the prepared organic and IL electrolytes, a working electrode, and a 13 mm diameter lithium metal counter electrode (Sigma-Aldrich Chemistry, 99.95% purity) fixed on a stainless steel (SUS316L) plate. A three-electrode cell configuration (EC Frontier Co., Ltd) was assembled using a NCM811 working electrode, a graphite counter electrode, and a lithium metal ring reference electrode. Glass microfiber separator was impregnated with the IL electrolytes at 60 °C under vacuum before cell assembly. The mass loading of the working and counter electrodes was controlled with the areal capacity ratio of negative to positive electrodes (N/P ratio).

Density functional theory (DFT) methods. The LUMO energy levels of the cation and cation-anion complexes were calculated using the Forcite and DMol3 modules of Materials Studio 2021, Accelrys Inc [39]. All the structures were first optimized in the Forcite module using the COMPASS III force field² before subjecting them to further geometric optimization and orbital calculations in the DMol3 module. The exchange-correlation energy employed the Becke three-parameter hybrid functional incorporated with the Lee–Yang–Parr correlation (B3LYP) functional [40, 41]. An all-electron numerical basis set with the Double Numerical plus polarization (DNP basis set) and a basic file of 4.4 were employed during the calculation. Tkatchenko–Scheffler (TS) method was adopted to fulfill the van der Waals correction [42]. The LUMO energy levels were calculated under an implicit environment using the conductor-like screening model (COSMO) method [43]. The dielectric constants of IL electrolytes were all set to 15.0 [44]. The convergence tolerance was set to 1.0×10^{-5} Ha (1 Ha=27.21 eV) for energy, 2.0×10^{-3} Ha Å⁻¹ for maximum force, and 5.0×10^{-3} Å for maximum displacement. The basis set superposition error has a limited effect on the E_{red} (below 6 %) and is not considered here.

Molecular dynamics (MD) simulations. The all-atom classic MD simulations were conducted with GROMACS software package [45]. The Generalized Amber Force Field (GAFF) parameters were employed, and additional essential files were generated using the ACPYPE server for IL electrolytes [46, 47]. The neat IL system consisted of 500 ion pairs of [C₂C₁im][FSA] randomly distributed within a cubic simulation box, a configuration achieved using the Packmol code [48]. The Li-salt containing systems were prepared by replacing 50, 100, 150, 200 and 250 [C₂C₁im]⁺ cations with Li⁺ for

Li salt concentrations of 10, 20, 30, 40, and 50 mol%, respectively. The simulation process was conducted in the following steps: Firstly, an energy minimization process was carried out to reduce the system's energy to an acceptable level, enabling a smooth progress to subsequent steps. Secondly, a fast NPT simulation based on the Parrinello-Rahman method was performed for 1 ns to optimize the size of the simulation box efficiently. Thirdly, to stabilize the temperature at 25 °C, a 10 ns NVT simulation using the V-rescale thermostat was conducted. In the end, a 10-ns NVP-NPT simulation was employed to further equilibrate the system, reaching 25 °C and 1.0 atmospheric pressure. This step ensured the system gained sufficient dynamics for a reasonable initial structure for the subsequent equilibration calculations. Both energy and pressure profiles were monitored to confirm system equilibrium. Finally, a 30 ns production run was executed at 25 °C for structural and dynamic analysis. Trajectory data were saved every 2 ps, and the data analyzed were extracted from the last 10 ns of the simulation. The cluster analysis based on the MD results employed a custom code rooted in the single-linkage clustering algorithm. To initiate the process, the program selects a random unvisited central C2 atom on the $[\text{C}_2\text{C}_{1\text{im}}]^+$ ring as the starting point of a cluster (see Figure 5-12b for schematic numbering of $[\text{C}_2\text{C}_{1\text{im}}]^+$ and $[\text{FSA}]^-$). It then explores neighboring S1 atoms, marking the associated $[\text{FSA}]^-$ anions as visited and marked to the cluster. Subsequently, in a secondary step, unvisited neighboring $[\text{C}_2\text{C}_{1\text{im}}]^+$ ions of the marked $[\text{FSA}]^-$ ions from the primary step are also marked as part of the cluster. These two steps repeat recursively to identify all $[\text{C}_2\text{C}_{1\text{im}}]^+$ and $[\text{FSA}]^-$ ions constituting a common cluster. This search procedure iterates across the entire system to ascertain cluster statistics. The grouping of $[\text{C}_2\text{C}_{1\text{im}}]^+$ and $[\text{FSA}]^-$ ions is performed iteratively based on a threshold distance of 4.5 Å between the C2 atom of $[\text{C}_2\text{C}_{1\text{im}}]^+$ and S1 atom of $[\text{FSA}]^-$, aligning with the radial distribution function (RDF) result.

5.3 Results and discussion

Effects of concentration on the irreversible capacity. The present study focuses on the widely used Li[FSA]-[C₂C₁im][FSA] IL electrolytes as the main subject of discussion. The basic physical properties of the Li[FSA]-[C₂C₁im][FSA] IL, namely, density, viscosity, and ionic conductivity, have been reported in a previous work [49]. To elucidate the influence of Li salt concentration on the irreversible capacity of graphite electrodes, galvanostatic charge-discharge tests were conducted on Li/graphite half cells with the Li[FSA]-[C₂C₁im][FSA] IL electrolytes and 1M Li[FSA]-EC/DMC organic electrolyte. The concentrations of the Li[FSA] salt were systematically adjusted to 20, 30, 40, and 50 mol% for ILs to formulate electrolytes denoted as 20IL, 30IL, 40IL, and 50IL, respectively (see Table S1 for the abbreviation of all the electrolytes utilized in this study). The initial charge curves of the Li/graphite cells comprising the series of IL electrolytes and their corresponding capacities are shown in Figure 5-4a. The electrochemical storage of Li⁺ ions in the graphite electrode occurs at a low potential, slightly above 0 V vs. Li⁺/Li, driven by the Li⁺ intercalation process [50]. The plateaus observed around ~1.0 and ~0.8 V are generally attributed to the SEI formation processes, which are presumed to involve the reductive decomposition of [FSA]⁻ and organic solvents, respectively [37, 51]. It is worth noting that the broad plateau emerging between 1.8 and 1.0 V manifests additional charge capacities that depend on the Li salt concentrations of the IL electrolytes. The inset in Figure 5-4a summarizes the specific capacities calculated in the 1.8 – 1.0 V voltage range.

The additional capacities here are seen to increase when the Li concentrations of the IL electrolytes are increased. Comparatively, the capacity of the 1 M Li[PF₆]-EC/DMC remains significantly smaller than the IL electrolytes in this voltage range.

To further elucidate this behavior, control tests were conducted using an organic electrolyte formulated with the Li[PF₆] salt (1 M Li[PF₆]-EC/DMC) and another with a high Li[FSA] salt concentration (5 M Li[FSA]-EC/DMC). The results depicted in Figure 5-5 indicate that the anionic species and salt concentrations have a negligible impact on the additional capacity of these organic electrolytes in voltage ranges above 1.0 V. In contrast, IL electrolytes exhibit a high additional capacity, and there was an obvious trend that increasing Li concentration (50IL) results in a higher charge capacity of 579 mAh g⁻¹ than 20IL (540 mAh g⁻¹), as demonstrated in Figure 5-4a. The plateau voltages are further ascertained using the corresponding dQ/dV plots in Figure 5-4b. The IL electrolytes with different concentrations provide reduction peaks with significantly different intensities and voltages after the initial charge step. Given these electrochemical results, it can be hypothesized that the irreversible capacities of the IL electrolytes are related to the interfacial behavior of organic cations during their 1) electrochemical decomposition and/or 2) intercalation into the graphite electrode.

Ex-situ X-ray diffraction (XRD) patterns of graphite electrodes charged to 1.0 V demonstrate no significant peak shifts in the graphite when compared to the pristine state, suggesting that the intercalation of [C₂C₁im]⁺ in graphite is negligible (Figure 5-6). This observation eliminates the intercalation process as a contributing factor to the irreversible capacity, suggesting that the irreversible capacity observed around 1.5 V is strongly related to the initial reductive decomposition of the organic cations (the irreversible decomposition capacity will be hereafter denoted as IDC). The increase of IDC ultimately results in lower ICE as the Li salt concentrations increase (Figure 5-4c), evincing that higher Li⁺ concentrations intensify the decomposition of [C₂C₁im]⁺ (ICE: 64% in 50IL and 71% in 20IL). In addition, the increment of operation temperature is noted to aggravate the behavior, indicating the reductive decomposition of [C₂C₁im]⁺

is exacerbated at higher temperatures (Figure 5-7). Pyrrolidinium-based IL electrolytes were also investigated to evaluate their cation decomposition on the graphite negative electrode. Similarly, severer decomposition of the IL electrolytes can be observed in the series of Li[FSA]-[C₃C₁pyrr][FSA] IL electrolytes as Li⁺ concentration increases (Figure 5-8).

Investigation of electrode/electrolyte interphases. To gain quantitative and qualitative insights into the decomposition products, scanning electron microscopic (SEM) and XPS analyses were performed on the graphite negative electrodes after initially charging them to 1.5 V. The morphologic alterations of the graphite surface were examined after operation in the 20IL and 50IL electrolytes (Figure 5-9a-c). The pristine graphite exhibits a well-defined layered structure with a smooth basal plane and sharp edges (Figure 5-9a), whereas electrodes examined after the charging process in the IL electrolytes display particles from the decomposition product. In the case of 20IL, the graphite electrode displays bright and blurred edges and a partially covered basal plane (Figure 5-9b). On the other hand, the electrode charged in 50IL manifests considerable growth of the decomposition product along the edges of the graphite particle and a fully covered basal plane (Figure 5-9c). The atomic composition of the decomposition product was investigated through XPS analyses on the pristine graphite electrode compared to electrodes charged to 1.5 V at a current density of 50 mA g⁻¹ in the 20IL and 50IL electrolytes (Figure 5-9d,e). The C 1s spectrum of the pristine graphite electrode was fitted with three distinct peaks assignable to the C-C bond (284.5 eV), the C=O bond from the graphite electrode (285.7 eV), and the C-F bond from the poly(vinylidene fluoride) (PVDF) binder (291 eV) [52]. After charging to 1.5 V, the C-N bond at 286.9 eV [53, 54], and N-C=N bond at 288.7 eV [55, 56] are visible, revealing

the decomposition of $[\text{C}_2\text{C}_1\text{im}]^+$. In the N 1s spectrum, the peak appearing in the high binding energy range of approximately 402 eV is attributed to the presence of neutral (N^0) and/or positively charged (N^+) nitrogen atoms resulting from the $[\text{C}_2\text{C}_1\text{im}]^+$ [55, 57-59]. The electrode from the 50IL yields higher ratios of $[\text{C}_2\text{C}_1\text{im}]^+$ decomposition products (C-N and N-C=N in the C 1s spectrum and N^0/N^+ in the N 1s spectrum) than the one from 20IL (Figure 5-9f and Table 5-2). These findings confirm that the $[\text{C}_2\text{C}_1\text{im}]^+$ decomposition products appear on the graphite electrode initially charged to 1.5 V in the IL electrolytes. In addition, the decomposition of $[\text{C}_2\text{C}_1\text{im}]^+$ is verified to be more severe at higher concentrations, in line with the electrochemical data.

State of the organic cation. The hypothesized change in decomposition of IL electrolytes mentioned above was examined through IR spectroscopy at different Li-salt concentrations (Figure 5-10a,b). The absorption bands around 740, 830, and 1100 cm^{-1} are attributed to the out-of-plane aromatic C-H bending mode, the in-plane bending of the imidazolium ring, and the in-plane aromatic C-H bending modes, respectively (Figure 5-10a,b) [60, 61]. In the neat IL, $[\text{C}_2\text{C}_1\text{im}]^+$ solely interacts with $[\text{FSA}]^-$ [60, 62]. A blue shift becomes apparent with increasing Li[FSA] concentrations for all three modes: indicative that the interaction between $[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{FSA}]^-$ becomes weaker at high concentrations. This phenomenon can be explained by the strong propensity for $[\text{FSA}]^-$ anions to interact with Li^+ ions to form $[\text{Li}(\text{FSA})_x]^{(x-1)-}$ complexes, supported by the blue shift observed in the S-N-S bending mode of $[\text{FSA}]^-$ in the Raman spectra (see Figure 5-11). Consequently, the fewer $[\text{FSA}]^-$ anions are available to coordinate with the $[\text{C}_2\text{C}_1\text{im}]^+$ cations, leading to the blue shift in the three vibrational modes at higher concentrations [62]. Further, ^1H NMR spectroscopy was employed to provide insights into the chemical environment of the $[\text{C}_2\text{C}_1\text{im}]^+$ (Figure

5-10d,e,f). The introduction of Li[FSA] into the neat IL sample results in an up-field shift for the signals from the C2, C4, and C5 ring protons at 7.87, 6.83, and 6.78 ppm, respectively (see Figure 5-10c for the atom numbering scheme), suggesting more shielded states of these protons emerge from the $[C_2C_1im]^+$ cations at high concentrations. This shielding effect is attributed to the reduced interactions between the $[C_2C_1im]^+$ cations and the $[FSA]^-$ anions, in consonance with the FT-IR and Raman results. The concentration dependency of the ion coordination environments in the IL is summarized by the schematic in Figure 5-10g. As shown, all the $[C_2C_1im]^+$ cations in the neat IL engage in interactions with $[FSA]^-$ anions. Upon the addition of Li[FSA] salt, a portion of the $[FSA]^-$ anions coordinate with Li^+ (coordinated $[FSA]^-$) at low Li^+ concentrations, while the remaining $[FSA]^-$ anions remain weakly bound to the $[C_2C_1im]^+$ cations. As the Li[FSA] concentration increases, more $[FSA]^-$ anions participate in the coordination structures around Li^+ ions during the formation of the $[Li(FSA)_x]^{(x-1)-}$ complexes. Consequently, fewer $[FSA]^-$ anions become available for interactions with the $[C_2C_1im]^+$ cations, resulting in the emergence of $[C_2C_1im]^+$ cations with fewer interactions in the unprotected state. As the concentration rises, the number of these unprotected $[C_2C_1im]^+$ becomes prevalent, causing substantial alterations in the coordination environment of the ions in the IL. Accordingly, the change in the coordination structure and interactions between the $[C_2C_1im]^+$ cations and the $[FSA]^-$ anions with the addition of Li salt may impact their reductive stability and engender the severe decomposition observed in the $[C_2C_1im]^+$ cations on the graphite negative electrode from the 50IL electrolytes during the initial charging process (Figure 5-10h).

To elucidate the relationship between the coordination environments of the cation and their reductive stabilities, theoretical calculations are performed for the neutral and reduced forms of $[C_2C_1im]^+$ and cation-anion complexes with the energy levels of the

lowest unoccupied molecular orbitals (LUMO) using the DFT method (Figures 5-12a and 5-13). Given that most of the anions are coordinated by Li^+ , the models with one $[\text{C}_2\text{C}_1\text{im}]^+$ cation coordinated by one or two $[\text{FSA}]^-$ anions (named as ' $[\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^-$ ' and ' $[\text{C}_2\text{C}_1\text{im}]^+ - 2[\text{FSA}]^-$ ') were selected for consideration. The resulting data revealed that the corresponding LUMO energy level decreases in the order of $[\text{C}_2\text{C}_1\text{im}]^+ - 2[\text{FSA}]^- > [\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^- > [\text{C}_2\text{C}_1\text{im}]^+$, implying that the coordination by $[\text{FSA}]^-$ inhibits the reduction of $[\text{C}_2\text{C}_1\text{im}]^+$. In addition, the reduction potentials (E_{red}) of the three species were calculated from the energy difference between the neutral and reduced forms (see Table 5-3 for the values and refer to calculation details in the Section 5.2). The reduction potential decreases with increasing the number of $[\text{FSA}]^-$ around $[\text{C}_2\text{C}_1\text{im}]^+$. The interactions between $[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{FSA}]^-$ in the IL electrolytes at different concentrations were further probed through MD simulations. Six electrolyte models: neat IL, 10IL, 20IL, 30IL, 40IL, and 50IL (Figure 5-14) were considered for analysis. For comparison, C2 and S1 were selected to represent $[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{FSA}]^-$, respectively (see Figure 5-12b for the atom numbering scheme). The coordination states of the cations are primarily dictated by the Li-salt concentration, which is examined through MD simulations to determine RDF. As depicted in Figure 5-12c, the $[\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^-$ coordination is characterized by three primary peaks appearing at 0.44, 0.64, and 0.85 nm. The intensities of the first two peaks decrease while that of the third peak increases when the Li-salt concentration is increased. In other words, $[\text{C}_2\text{C}_1\text{im}]^+$ tends to transfer to the outer coordination structure of $[\text{FSA}]^-$ at high $\text{Li}[\text{FSA}]$ concentrations, providing a longer distance from the anion. The MD simulations demonstrate that increasing Li-salt concentration weakens the interactions between the $[\text{C}_2\text{C}_1\text{im}]^+$ cation and the $[\text{FSA}]^-$ anion, in agreement with the present electrochemical and spectroscopic data. According to the RDF plot of the $\text{Li}^+ - [\text{FSA}]^-$ coordination structure depicted in

Figure 5-15, the first coordination shell is located at 0.34 nm. When the Li salt concentration increases, the predominant coordination structure evolves to form larger aggregates containing multiple Li^+ ions, yielding smaller intensities at the primary peak. By this token, the intensity of the Li^+ and C2 ($[\text{C}_2\text{C}_1\text{im}]^+$) correlation ranging from 0.64 to 0.73 nm decreases while the one around 1.0 nm increases when the $\text{Li}[\text{FSA}]$ concentration is increased, further validating the discussion above (see Figure 5-16). Taking into account the results discussed so far, it becomes evident that the $[\text{FSA}]^-$ preferentially enters the first coordination shell of Li^+ , while the $[\text{C}_2\text{C}_1\text{im}]^+$ is expelled from the $[\text{FSA}]^-$, gradually becoming less protected in the outer coordination shell. Further analysis on the $[\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^-$ interaction behavior was carried out as previous studies about the cluster behavior of ILs [63]. Figure 5-12d and e present the distribution of the cluster compositions for the $[\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^-$ in the electrolytes of 10IL and 50IL. Within a threshold distance of 4.5 Å between the C2 atom of $[\text{C}_2\text{C}_1\text{im}]^+$ and the S1 atom of $[\text{FSA}]^-$, the higher frequency of 42% of unprotected $[\text{C}_2\text{C}_1\text{im}]^+$ is observed in the highly Li-concentrated 50IL (Figure 5-12e) than that in the diluted 10IL (Figure 5-12d, 32%), indicating that the number of unprotected cations increases with increasing concentration.

Changes of the coordination environment by mixing anions. The graphite negative electrode in the highly concentrated 50IL electrolyte exhibited a significantly higher IDC and a low ICE primarily due to the severe decomposition of $[\text{C}_2\text{C}_1\text{im}]^+$. The present hypothesis proposes tuning the coordination structure as an effective approach to address this issue. In this strategy, anions ($[\text{A}]^-$) with different donor numbers (DN) were introduced into the IL electrolyte to formulate a series of $\text{Li}_{0.4}[\text{C}_2\text{C}_1\text{im}]_{0.6}[\text{A}]_{0.1}[\text{FSA}]_{0.9}$ IL electrolytes (hereafter, denoted as 40IL-A where $\text{A}^- =$

[OTf]⁻, [TFSA]⁻, [FTA]⁻, [PF₆]⁻, and [FAP]⁻: in the descending order of their DN, respectively [64]). The components for each electrolyte are listed in Table 5-1. Here, 40IL was chosen because some cases of Li salt precipitation were noted in the 50IL.

Electrochemical measurements were performed on Li/graphite half cells comprising the mixed-anion IL electrolytes, as depicted in Figure 5-17. Notably, the 40IL-OTf electrolyte, which constitutes the anion with the highest DN among the selected anions [64, 65], exhibited the most beneficial effect signified by its higher ICE (69.5%) compared the 40IL electrolyte (66.2%) (Figure 5-18a). In contrast, the ICE values of the cells with the 40IL-PF₆ (64.3%) and 40IL-FAP (63.6%) were lower than the ones with 40IL because their DNs are lower than that of the [FSA]⁻. The [FTA]⁻ and [TFSA]⁻ anions, which have DNs comparable to [FSA]⁻ yield similar ICE (66.7% and 67.1%, respectively), further supporting the proposed DN trend of the anions.

The effect of mixing anions on the coordination environment of IL electrolytes is outlined and illustrated in Figure 5-18b. The addition of low-DN anions weakens the interaction between [C₂C₁im]⁺ cations and [FSA]⁻ anions, whereas the high-DN anions exhaustively interact with Li⁺ cations. This occurrence releases the [FSA]⁻ from the first coordination shell and avails it for coordination to [C₂C₁im]⁺, thus strengthening its interaction with [C₂C₁im]⁺. These results were further ascertained by NMR spectra obtained from the 40IL-OTf, 40IL-PF₆, and 40IL (Figure 5-19). The addition of [OTf]⁻, a high-DN anion, causes a down-field shift of the C2, C4, and C5 ring proton signals; indicative that the interaction between the [C₂C₁im]⁺ and the [FSA]⁻ is stronger than in the 40IL electrolyte. The opposite is observed when the low-DN [PF₆]⁻ anion is added to the electrolyte. The decline in the number of unprotected [C₂C₁im]⁺ cations contributes to its improved reductive stability as fewer species originating from the [C₂C₁im]⁺ are observed on the graphite electrode during the initial charging step in

40IL-OTf (see Figure 5-20 where lower intensity of peaks assigned to carbon species originated from $[\text{C}_2\text{C}_1\text{im}]^+$ are observed in the C 1s XPS spectra). This underscores the importance of regulating unprotected cations when tuning the SEI components. While the addition of high-DN anions does not result in significant enhancement of the ICE, optimizing the ratio of mixing anions can be anticipated to deliver further improvements. As such, the proposed model represents a valuable attempt to address electrolyte issues while demonstrating the significance of altering the coordination structure of organic cations in the design of in-built SEIs and the development of compatible IL electrolyte systems. In addition, the strategies to improve Li^+ transference, such as introducing chelating agents to decouple the Li-anion interaction [63, 66], and applying new organic cations [67], may contribute to strengthening the organic cation-anion interaction and mitigating the dilemma on the IL electrolyte design.

5.4 Conclusions

This chapter investigated the emergence of “unprotected” organic cations and unfavorable decomposition of $[\text{C}_2\text{C}_1\text{im}]^+$, resulting in a high irreversible capacity and a gradual decrease in ICE of graphite electrodes (from 71% in 20IL to 64% in the 50IL electrolyte). The physicochemical investigation and computational study revealed that this significant decomposition of the $[\text{C}_2\text{C}_1\text{im}]^+$ in HCIL electrolytes was attributed to the weakened ionic interactions between the $[\text{C}_2\text{C}_1\text{im}]^+$ and the $[\text{FSA}]^-$ caused by the increased number of $[\text{FSA}]^-$ anions participating in the coordination shell of Li^+ . As a strategy to mitigate the decomposition of the organic cation, introduction of high-DN anions (such as $[\text{OTf}]^-$) was proposed to modify the coordination structures of $[\text{C}_2\text{C}_1\text{im}]^+$ and strengthen the interactions between the $[\text{C}_2\text{C}_1\text{im}]^+$ and the $[\text{FSA}]^-$, leading to the improved the ICE of the graphite negative electrode. This study has

deepened the understanding of the coordination properties of IL electrolytes and elucidated the decomposition behavior of organic cations in ILs, which underscores a new direction for developing IL electrolytes.

Table 5-1. The abbreviation and compositions of the organic and IL electrolyte systems.

Electrolyte	Abbreviation
1 mol dm ⁻³ Li[PF ₆]-EC/DMC (1:1, v:v)	1 M Li[PF ₆]-EC/DMC
1 mol dm ⁻³ Li[FSA]-EC/DMC (1:1, v:v)	1 M Li[FSA]-EC/DMC
5 mol dm ⁻³ Li[FSA]-EC/DMC (1:1, v:v)	5 M Li[FSA]-EC/DMC
[C ₂ C ₁ im][FSA]	neat IL
Li[C ₂ C ₁ im][FSA] (10:90 in mol%)	10IL
Li[FSA]-[C ₂ C ₁ im][FSA] (20:80 in mol%)	20IL
Li[FSA]-[C ₂ C ₁ im][FSA] (30:70 in mol%)	30IL
Li[FSA]-[C ₂ C ₁ im][FSA] (40:60 in mol%)	40IL
Li[FSA]-[C ₂ C ₁ im][FSA] (50:50 in mol%)	50IL
Li[FSA]-Li[OTf]-[C ₂ C ₁ im][FSA] (30:10:60 in mol%)	40IL-OTf
Li[FSA]-Li[TFSA]-[C ₂ C ₁ im][FSA] (30:10:60 in mol%)	40IL-TFSA
Li[FSA]-Li[FTA]-[C ₂ C ₁ im][FSA] (30:10:60 in mol%)	40IL-FTA
Li[FSA]-Li[PF ₆]-[C ₂ C ₁ im][FSA] (30:10:60 in mol%)	40IL-PF ₆
Li[FSA]-[C ₂ C ₁ im][FAP]-[C ₂ C ₁ im][FSA] (40:10:50 in mol%)	40IL-FAP

Table 5-2. The XPS data for the SEI components formed on the graphite electrode in the Li[FSA]-[C₂C₁im][FSA] IL electrolyte adjusted to 1.5 V in the initial cycle, respectively. See Figure 5-9d,e for the corresponding spectra. ^{a)}

Binding energy (eV)				
	C 1s	ratio (%)	N 1s	ratio (%)
Pristine	284.6	50.9		
	285.6	38.6		
	290.8	10.5		
20IL	284.5	47.2	399.0	68.8
	285.6	29.9	400.6	12.2
	286.9	10.6	402.4	19.0
	288.1	7.5		
	291.1	4.9		
50IL	284.6	37.6	399.1	68.1
	285.6	28.1	400.5	8.9
	286.9	21.2	402.2	23.0
	288.1	11.4		
	291.1	1.7		
Decomposition components				
C-C	284.5 ± .1			
C=O	285.7			
C-N	286.9			
N-C=N	288.5 ± .2			
C-F	290.9 ± .2			
N-C			399.0 ± .1	
N ⁻			400.7 ± .2	
N ⁺ /N ⁰			402.2 ± .2	
^{a)} The electrode for the measurement was initially charged to 1.5 V.				

Table 5-3. The DFT calculation details of different species, including HOMO, LUMO, and energy.

	Neutral form			Reduced form			$E_{\text{red}}^{\text{a)}}$ (V)
	HOMO (eV)	LUMO (eV)	Energy (Ha)	HOMO (eV)	Half- filled HOMO (eV)	Energy (Ha)	
Unprotected [C ₂ C ₁ im] ⁺	-8.03	-1.14	-365.0 53126	-3.00	-0.30	-365.12 1745	0
[C ₂ C ₁ im]- [FSA]	-7.59	-0.93	-1775. 617272	-2.36	0.19	-1775.6 73679	-0.34
[C ₂ C ₁ im]- 2[FSA]	-7.13	-0.41	-3186. 175578	-1.89	0.65	-3186.2 13593	-0.84

^{a)} The values are shown with reference to the E_{red} of unprotected [C₂C₁im]⁺.

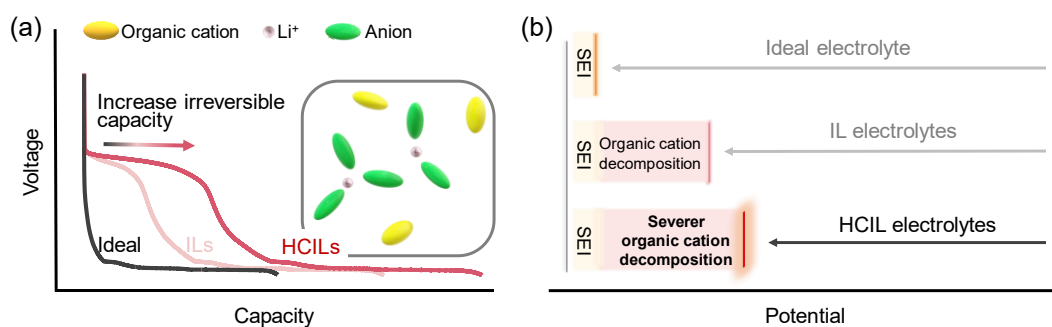


Figure 5-1. Hypothetical illustration of irreversible capacity in IL electrolytes based on the cation decomposition process. (a) Schematic drawing of the phenomena of the increasing irreversible capacity of a graphite negative electrode in IL electrolytes (inset: coordination environment in the HCIL electrolyte). Here, we present a hypothesis that the higher Li-salt concentration induces organic cations weakly interacting with anions. (b) The narrower electrochemical potential windows are suggested in the initial cycle due to the decomposition of organic cations in IL. HCIL electrolytes lead to a severer reductive decomposition of the organic cation.

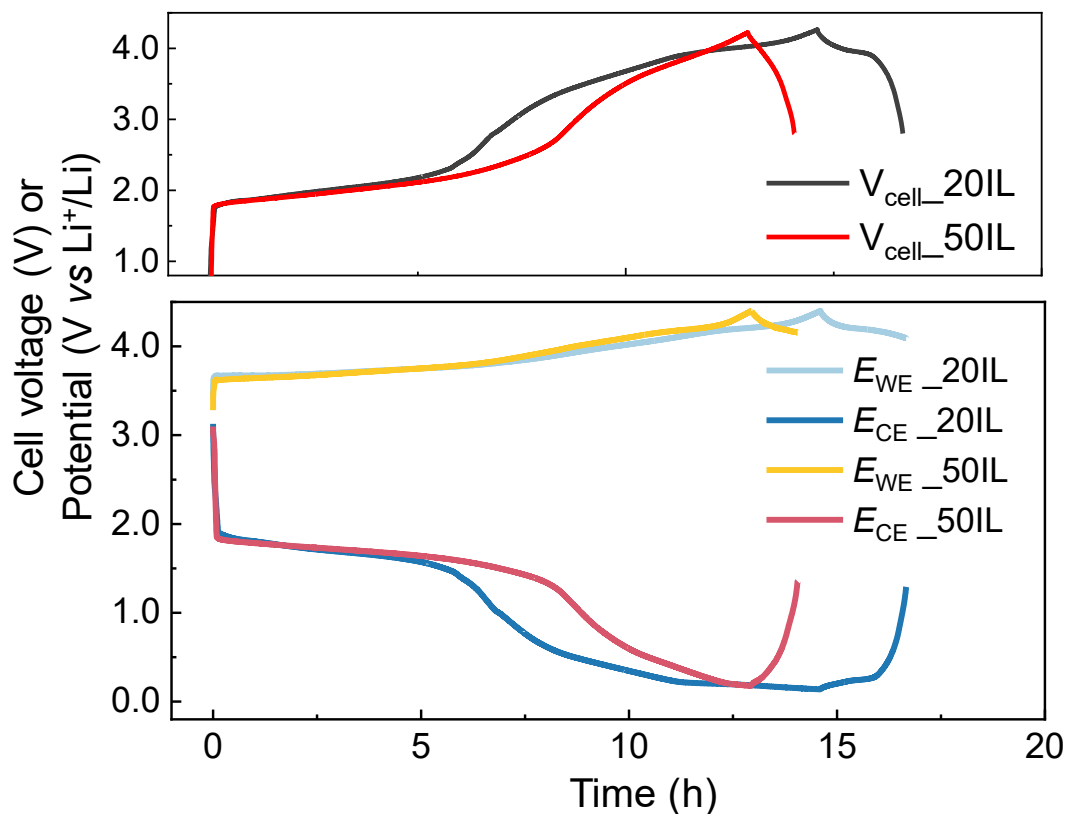


Figure 5-2. The charge-discharge profiles of the initial cycles for the graphite/NCM811 full cell in a three-electrode configuration with the IL electrolytes systems at different Li[FSA] concentrations of 20 and 50 mol% at 60 °C, respectively. Current density: 20 mA g⁻¹, cut-off voltage: 2.8–4.3 V, N/P ratio: 1.15.

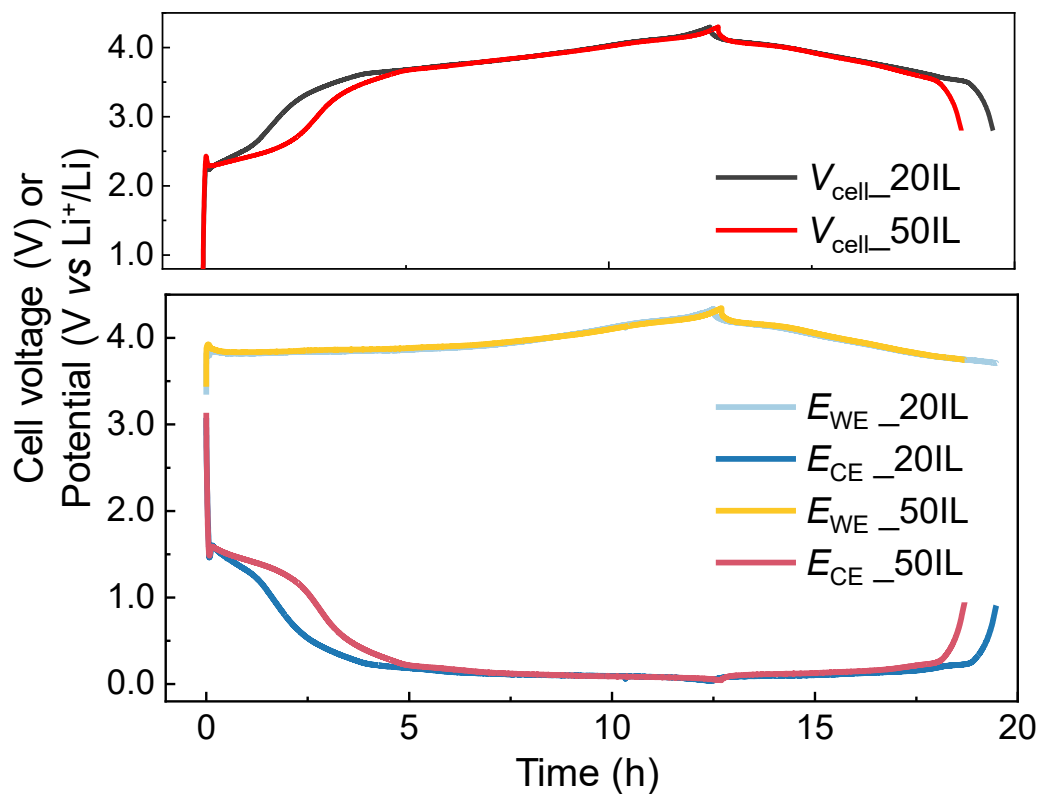


Figure 5-3. The charge-discharge profiles of the initial cycles for the graphite/NCM811 full cell in a three-electrode configuration with the IL electrolytes systems at different Li[FSA] concentrations of 20 and 50 mol% at 25 °C, respectively. Current density: 20 mA g⁻¹, cut-off voltage: 2.8–4.3 V, N/P ratio: 0.86.

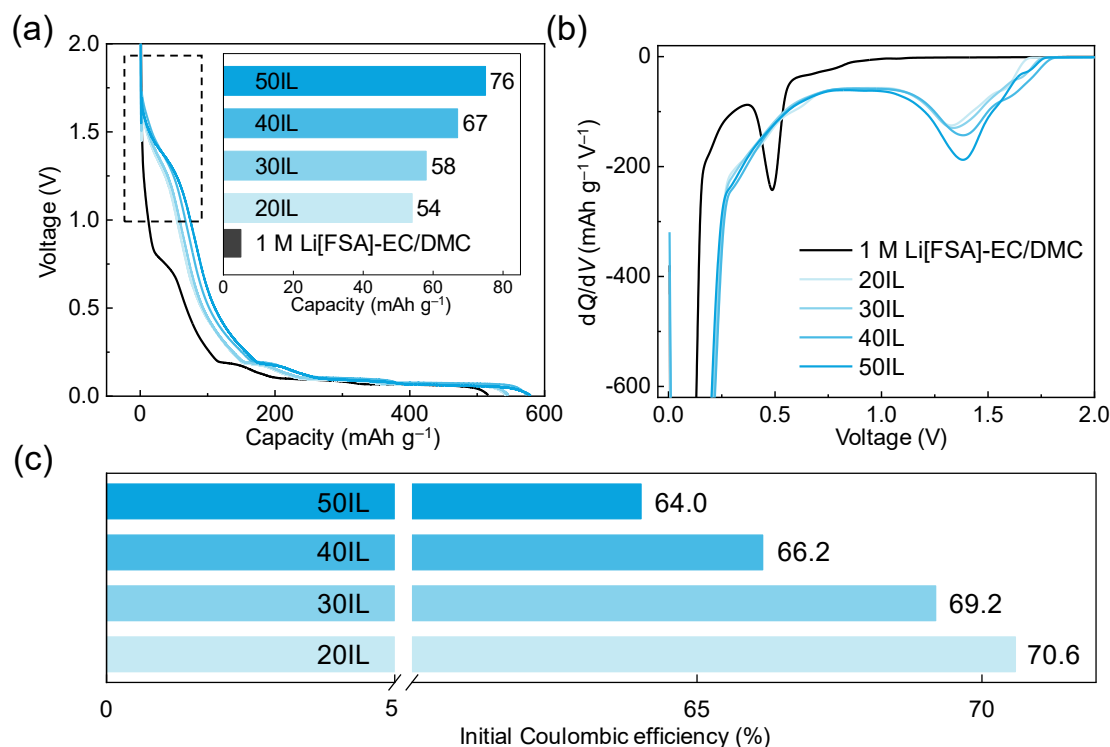


Figure 5-4. Evaluation of the irreversible capacity observed in the initial charge of the graphite electrodes in the Li[FSA]-[C₂C₁im][FSA] IL electrolytes. (a) The initial charge profiles of the Li/graphite half cells utilizing the organic and IL electrolytes at different Li-salt concentrations at 25 °C (current density: 50 mA g⁻¹, cut-off voltage: 0.005–2.0 V). The inset shows the corresponding irreversible capacities delivered by the graphite electrodes above 1.0 V. (b) The corresponding dQ/dV plots of the Li/graphite half cells in (a). (c) The initial Coulombic efficiency of the Li/graphite half cells in (a). The corresponding initial charge-discharge profiles can be found in Figure 5-5. See Figures 5-7 and 5-8 for the electrochemical data of the Li/graphite half cells in [C₂C₁im]-based IL electrolytes at 60 °C and [C₃C₁pyrr]⁺-based IL electrolytes at both 25 and 60 °C, respectively.

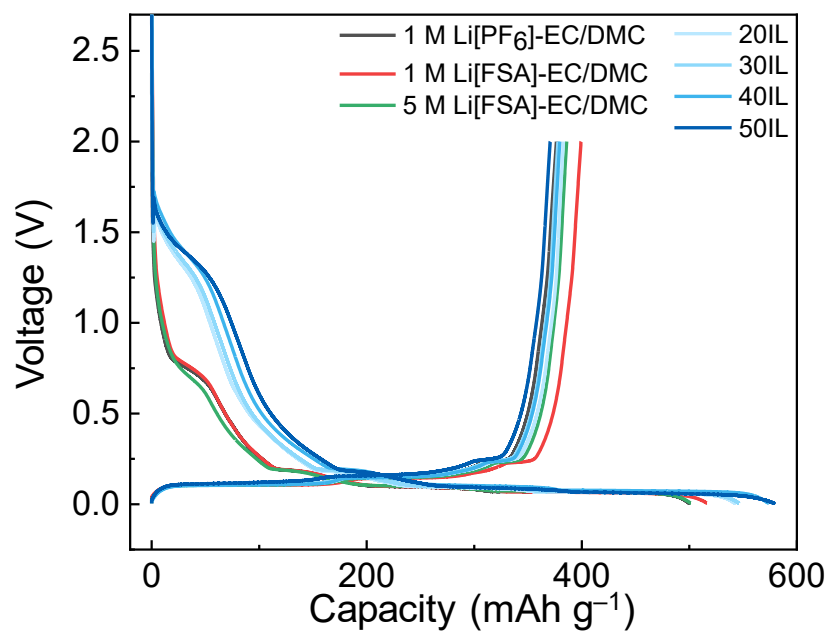


Figure 5-5. The charge-discharge profiles of the initial cycles for the Li/graphite cells with organic electrolytes and the in the Li[FSA]-[C₂C₁im][FSA] IL electrolytes system at different Li[FSA] concentrations from 20 to 50 mol% at 25 °C

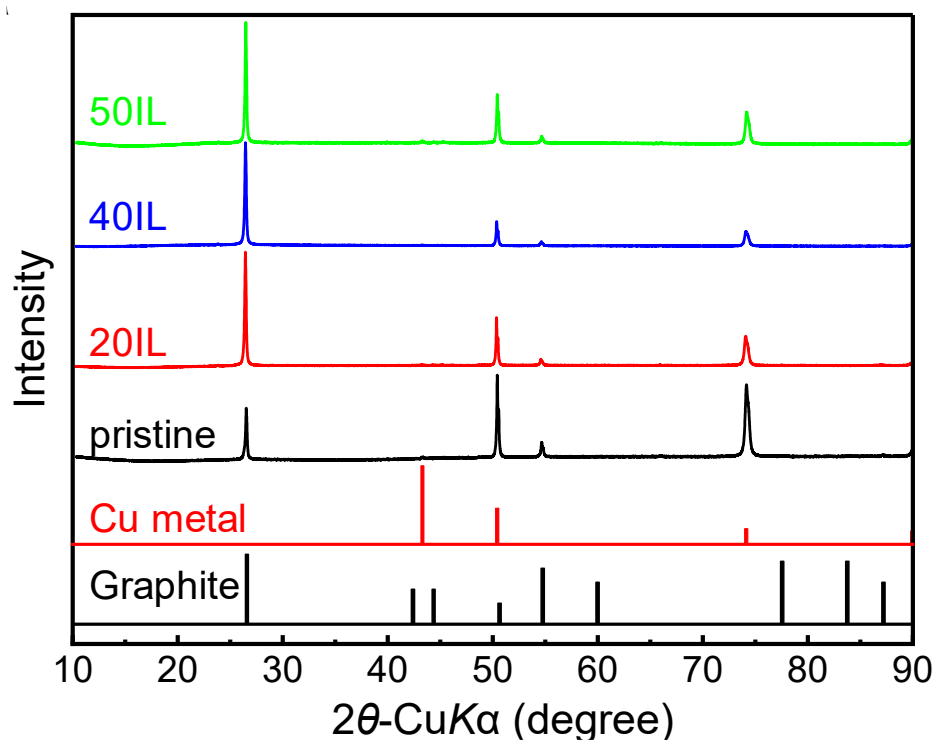


Figure 5-6. XRD patterns of the graphite electrodes initially charged to 1.0 V in the series of ILs to confirm the intercalation of organic cation in the voltage range above 1.0 V. Reference peaks of Cu metal and graphite represented by red and black bars are reproduced from the data JCPDS 00-004-0836 and 00-013-0148, respectively.

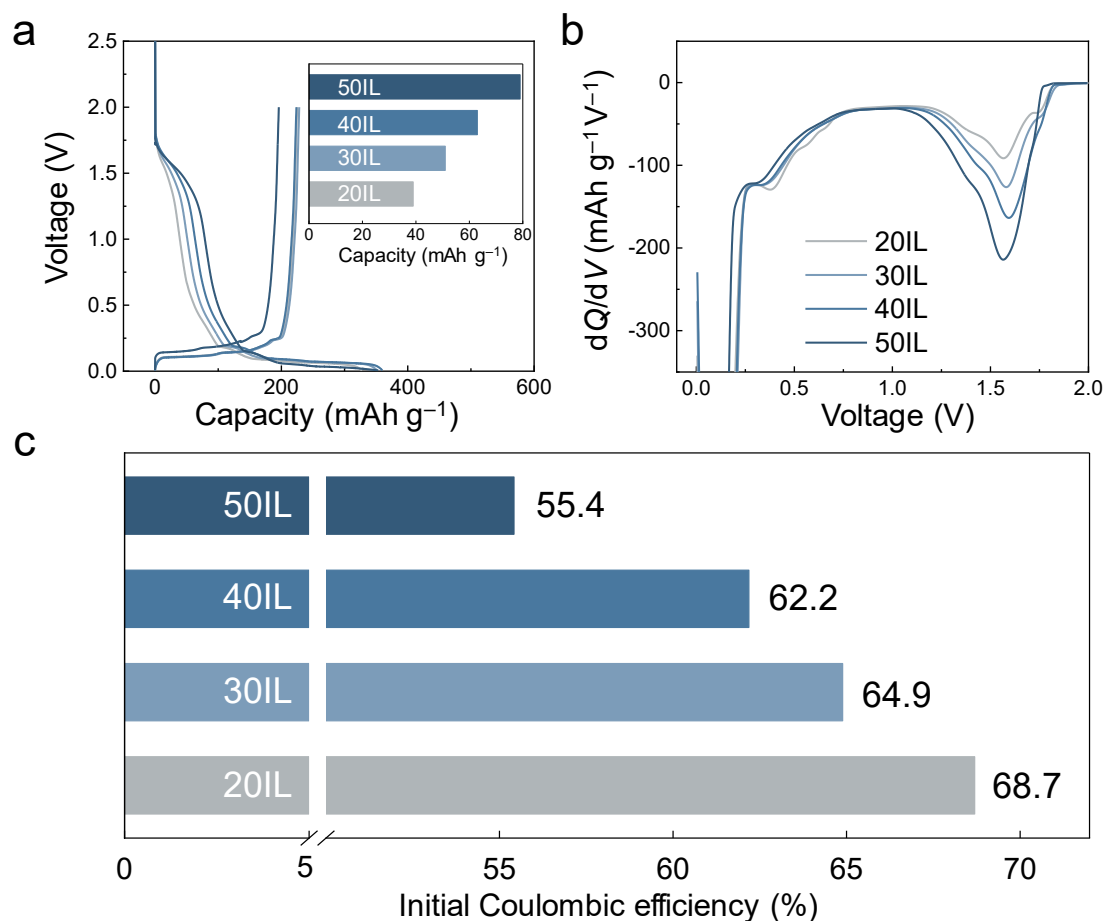


Figure 5-7. (a) The charge-discharge profiles of the initial cycles for the graphite/Li half cells with the Li[FSA]-[C₂C₁im][FSA] IL electrolyte systems at different Li[FSA] concentrations from 20 to 50 mol% at 60 °C. An inset figure in (a) shows the capacity in the voltage of 1.0 V with organic and ILs electrolytes at different concentrations. (b) The corresponding dQ/dV plots for the graphite electrodes for organic and IL electrolytes in (a). See Figure 5-4 for the electrochemical performance of the graphite electrodes at 25 °C. (c) The initial Coulombic efficiency of graphite electrodes at 60 °C using the IL electrolytes utilized in (a).

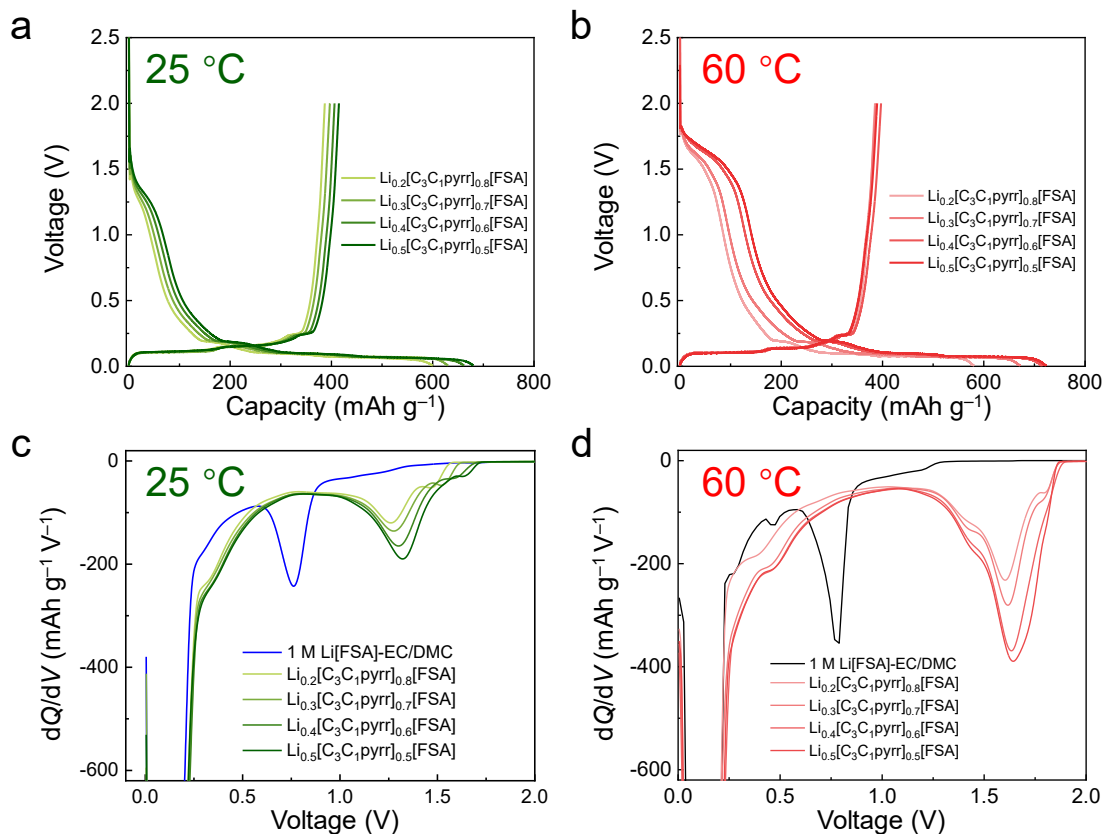


Figure 5-8. (a, b) The initial charge-discharge profiles and (c, d) the corresponding dQ/dV plots of the graphite negative electrodes at 25 and 60 °C utilizing the organic and the Li[FSA]-[C₃C₁pyrr][FSA] IL electrolytes at different Li[FSA] concentrations from 20 to 50 mol%. Current density: 50 mA g⁻¹, cut-off voltage: 0.005–2.0 V.

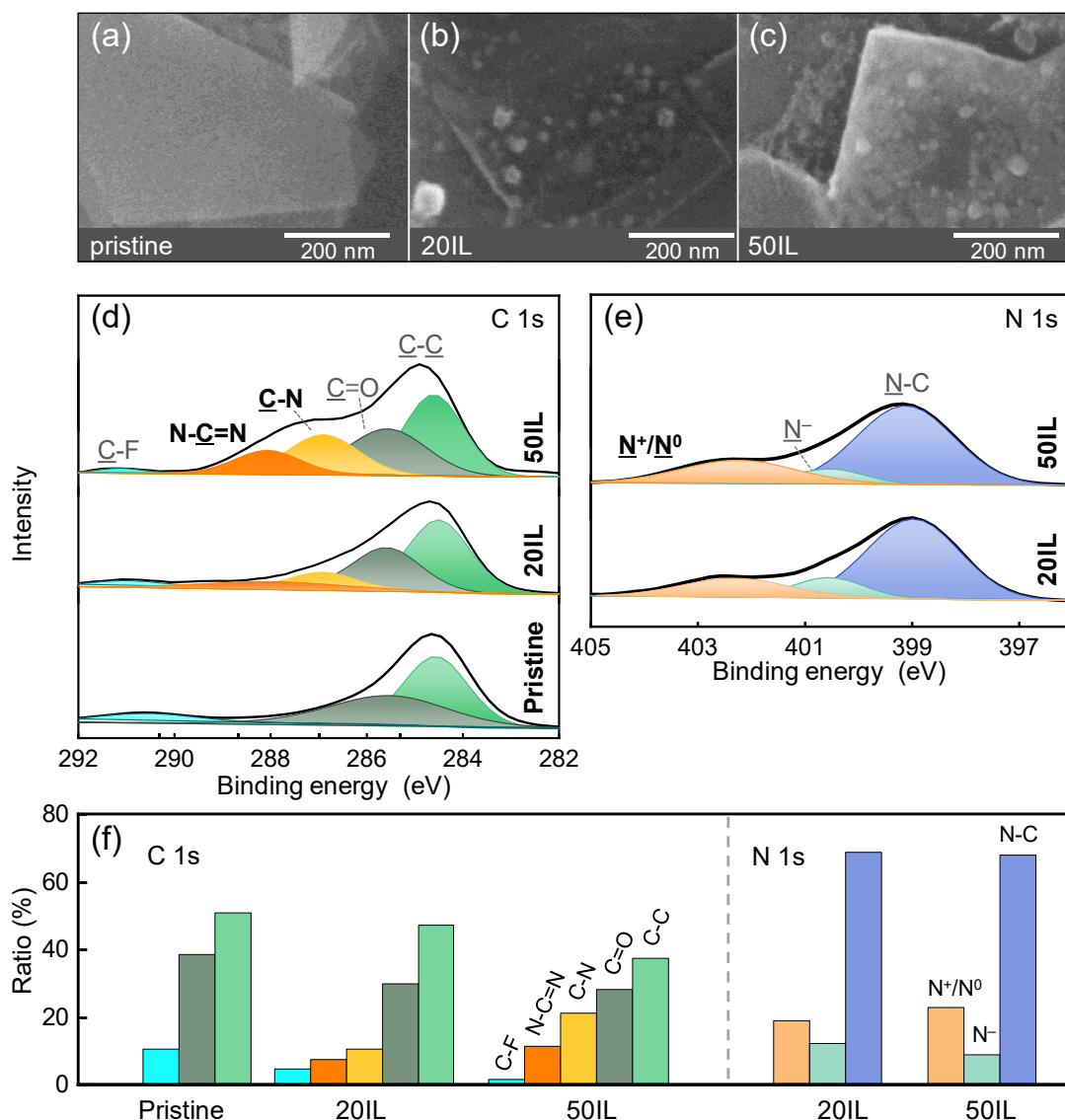


Figure 5-9. Interfacial investigation on the decomposition of the organic cation in the Li[FSA]-[C₂C₁im][FSA] IL electrolytes. SEM images of the (a) pristine graphite electrodes and the graphite electrodes initially charged to 1.5 V in the Li/graphite half cells using (b) 20IL and (c) 50IL electrolytes at a current density of 50 mA g⁻¹. XPS spectra of the (d) C 1s and (e) N 1s regions for the pristine graphite electrode and the electrodes initially charged to 1.5 V at a current density of 50 mA g⁻¹ using 20IL and 50IL electrolytes. (f) The decomposition component ratios in the C 1s and N 1s XPS spectra for the graphite electrodes. The representative decomposition species of [C₂C₁im]⁺ are represented as the legend. Refer Table 5-2 for the peak assignment and fitting results.

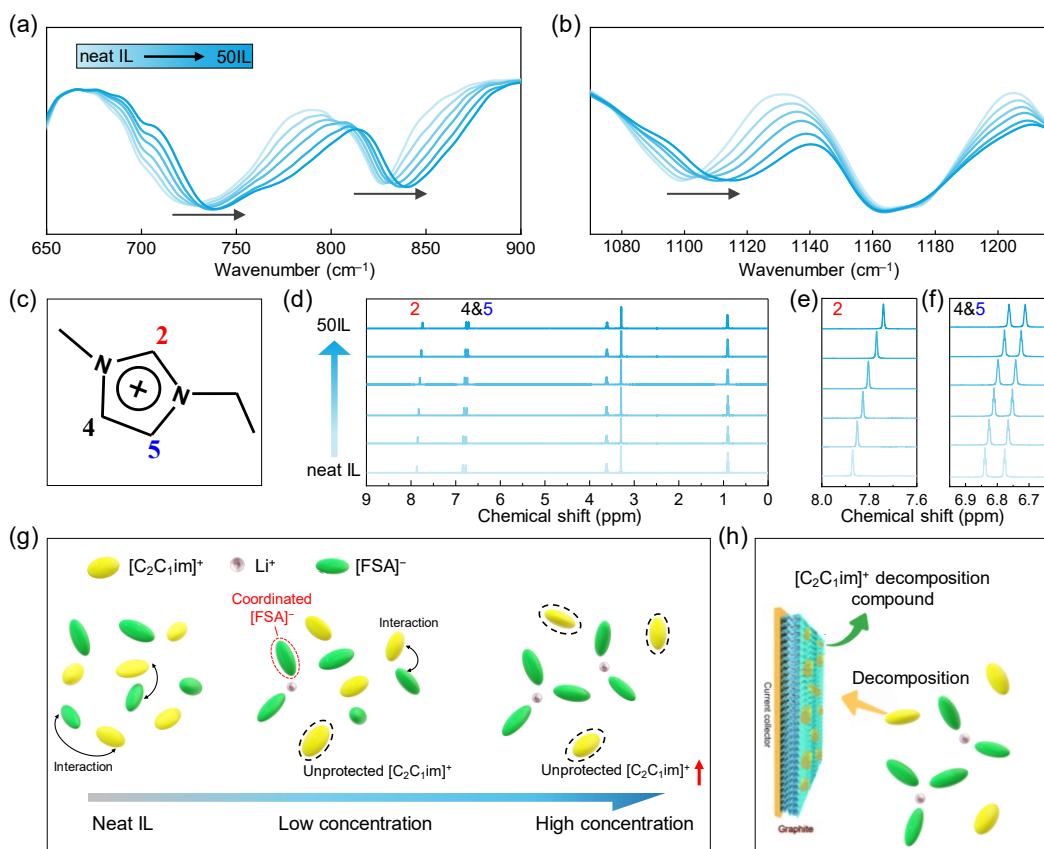


Figure 5-10. Investigation of the coordination structures and ionic interactions in the bulk electrolytes. IR spectra of the IL electrolytes at different Li-salt concentrations in the region (a) from 650 to 900 cm^{-1} and (b) from 1060 to 1220 cm^{-1} . The blue-shift of the vibrational modes regarding the imidazolium ring is marked with black arrows. (c) The structure of $[\text{C}_2\text{C}_1\text{im}]^+$ with the atom numbering scheme. (d) ^1H NMR spectra of the IL electrolytes at different Li[FSA] concentrations. The enlarged spectral range for (e) C2 and (f) C4 and C5 ring protons. (g) Illustration of the interaction model between cation and anion in different Li salt concentration in IL electrolytes. The increasing of Li[FSA] salt concentration encourages the emergence of the “unprotected” $[\text{C}_2\text{C}_1\text{im}]^+$ cations due to their weakened interaction with the $[\text{FSA}]^-$ anions, where the severe reductive decomposition of these unprotected cations result in the growth of the decomposition compound at the surface of a graphite electrode and IL electrolyte, as shown in (h).

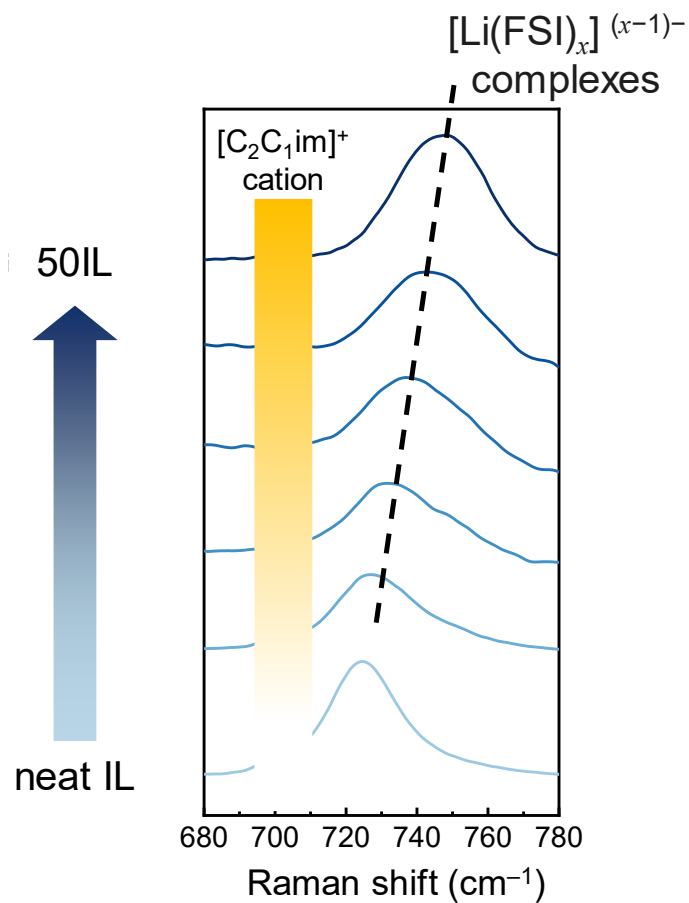


Figure 5-11. Raman spectra of the $\text{Li}[\text{FSA}]\text{-}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ IL with increasing the Li-salt concentrations in the range from 680 to 780 cm^{-1} . The arrow indicates the blue-shift of the S–N–S bending mode of FSA^- by forming the strongly bound $[\text{Li}(\text{FSA})_x]^{(x-1)-}$ complexes with increasing $\text{Li}[\text{FSA}]$ concentration.

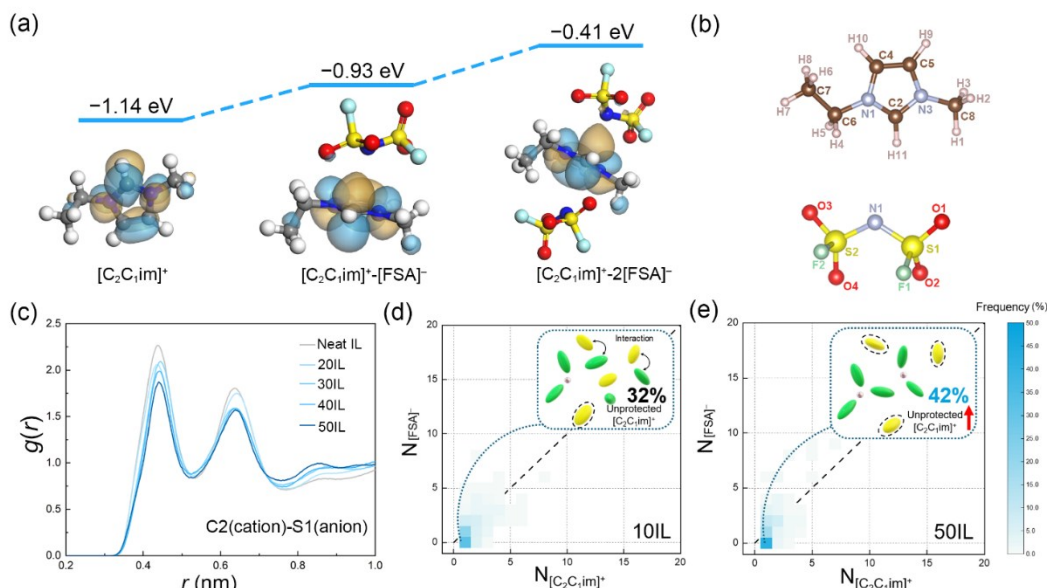


Figure 5-12. Computational investigation of the interactions between the cation and anion in the $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ IL electrolytes. (a) The geometrical structures and the LUMO isosurface and energy levels of $[\text{C}_2\text{C}_1\text{im}]^+$, $[\text{C}_2\text{C}_1\text{im}]^+[\text{FSA}]^-$, and $[\text{C}_2\text{C}_1\text{im}]^+2[\text{FSA}]^-$ neutral complexes. See Figure 5-13 for the geometrical structures and the LUMO isosurface of reduced complexes. (b) Atom numbering scheme of $[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{FSA}]^-$. (c) Radial distribution function (RDF) plots of the neat IL and IL electrolytes at different $\text{Li}[\text{FSA}]$ concentrations. Comparison of the clustering analysis performed on the $[\text{C}_2\text{C}_1\text{im}]^+[\text{FSA}]^-$ in $\text{Li}[\text{FSA}]-[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ system at $x(\text{Li}[\text{FSA}]) =$ (d) 0.1 (10IL) and (e) 0.5 (50IL). The color code indicates the frequency of a given agglomerate. The oblique dashed line marks where the neutral cluster with the equal number of cations and anions would lie.

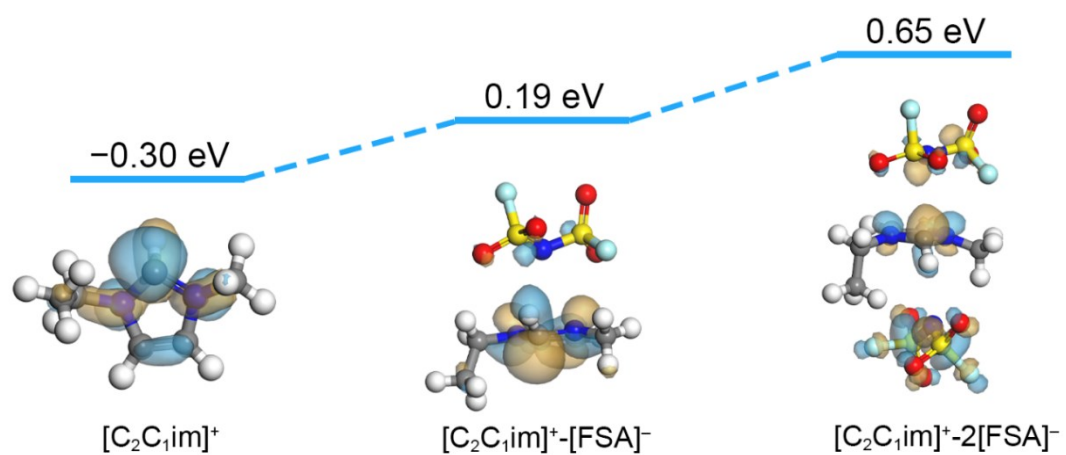


Figure 5-13. The geometrical structures and the LUMO isosurface of $[\text{C}_2\text{C}_1\text{im}]^+$, $[\text{C}_2\text{C}_1\text{im}]^+ - [\text{FSA}]^-$, and $[\text{C}_2\text{C}_1\text{im}]^+ - 2[\text{FSA}]^-$ reduced complexes.

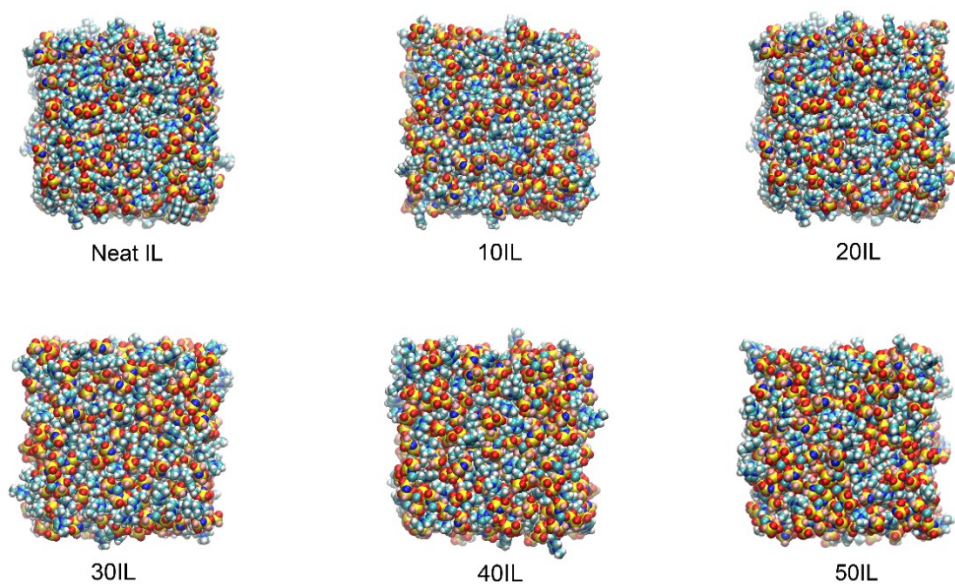


Figure 5-14. Snapshots of the MD simulation cells of the IL electrolytes at different concentrations (Neat IL, 10IL, 20IL, 30IL, 40IL, and 50IL).

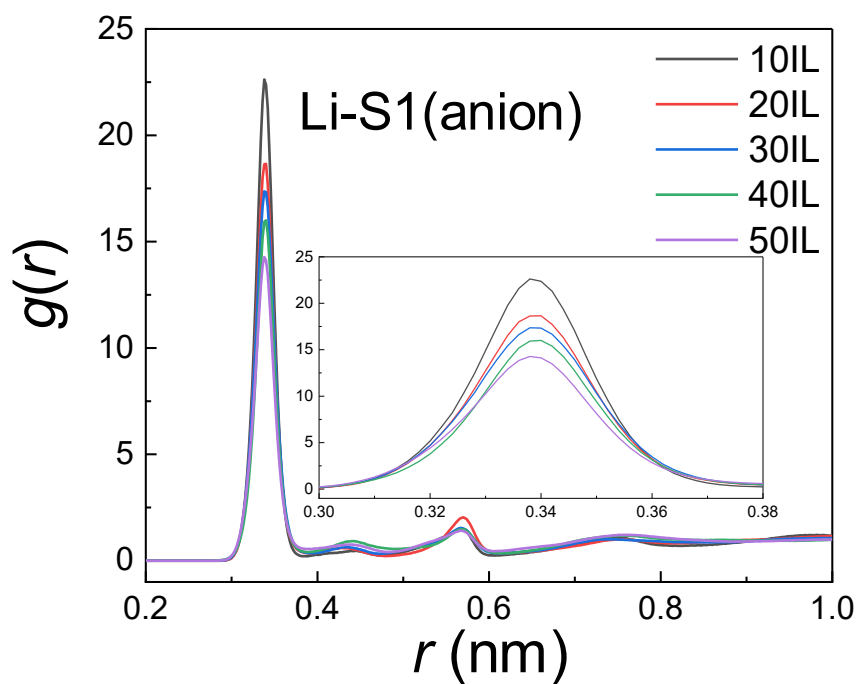


Figure 5-15. RDF plots between the Li and S1 in the Li[FSA]-[C₂C₁im][FSA] IL electrolytes at different Li[FSA] concentrations based on the MD simulation.

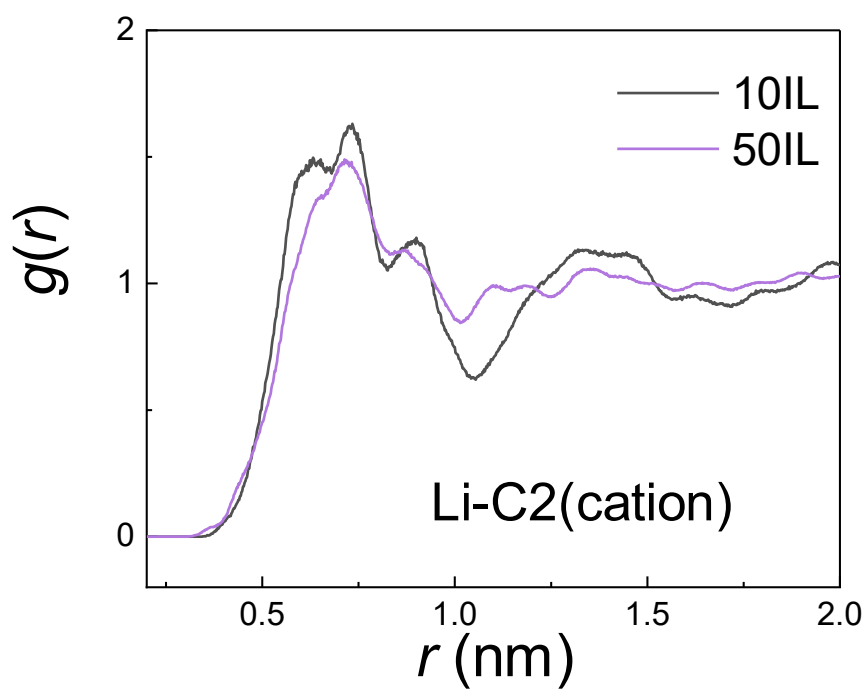


Figure 5-16. RDF plots between Li and C2 in the 10IL and 50IL electrolytes based on the MD simulation.

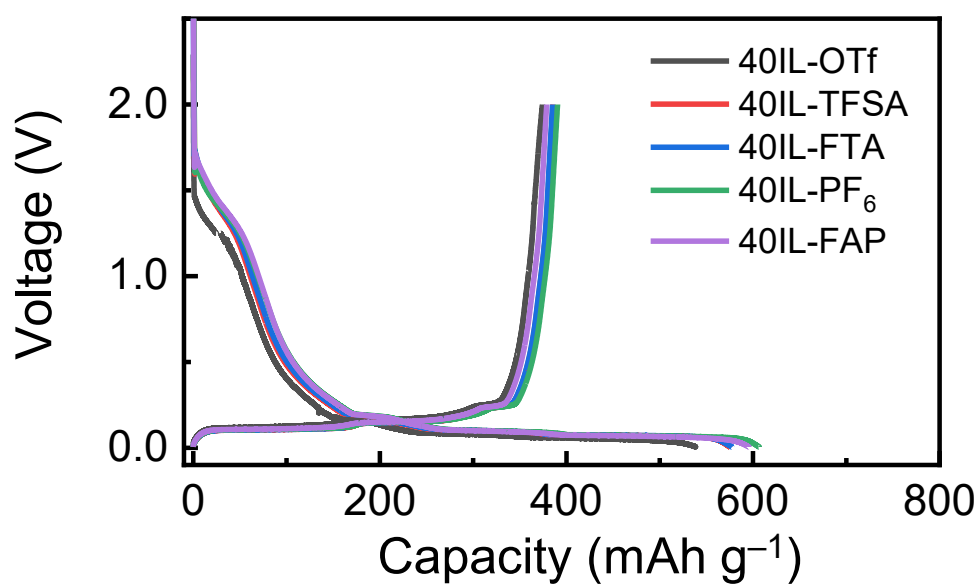


Figure 5-17. The initial charge-discharge curves of the Li/graphite cell with the 40IL-[A] systems mixed with various anionic species. The initial Coulombic efficiencies are summarized in Figure 6a.

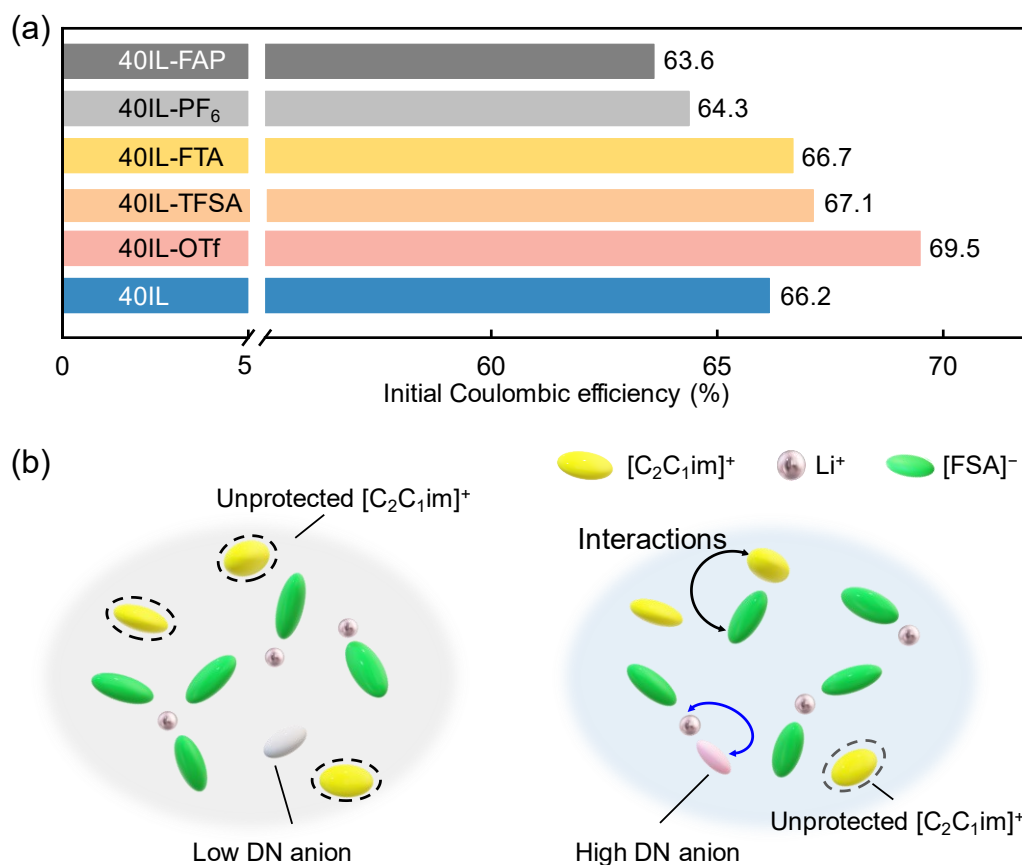


Figure 5-18. Effects of mixing anions with different DN on the decomposition of $[C_2C_1im]^+$ in HCIL. (a) ICE of the Li/graphite half cells using 40IL and 40IL-A. See Table 5-1 for the abbreviation and compositions, where $[A]^- = [OTf]^-$, $[TFSA]^-$, $[FTA]^-$, $[PF_6]^-$, and $[FAP]^-$ anions. See Figure 5-17 for the corresponding initial charge-discharge curves. (b) Schematic illustrations of the mechanism for the strengthened interaction of $[C_2C_1im]^+$ by mixing with high DN anions in the HCIL electrolytes. See Figure 5-19 for the chemical environment of $[C_2C_1im]^+$ in the HCIL electrolytes mixing with anions with different DN.

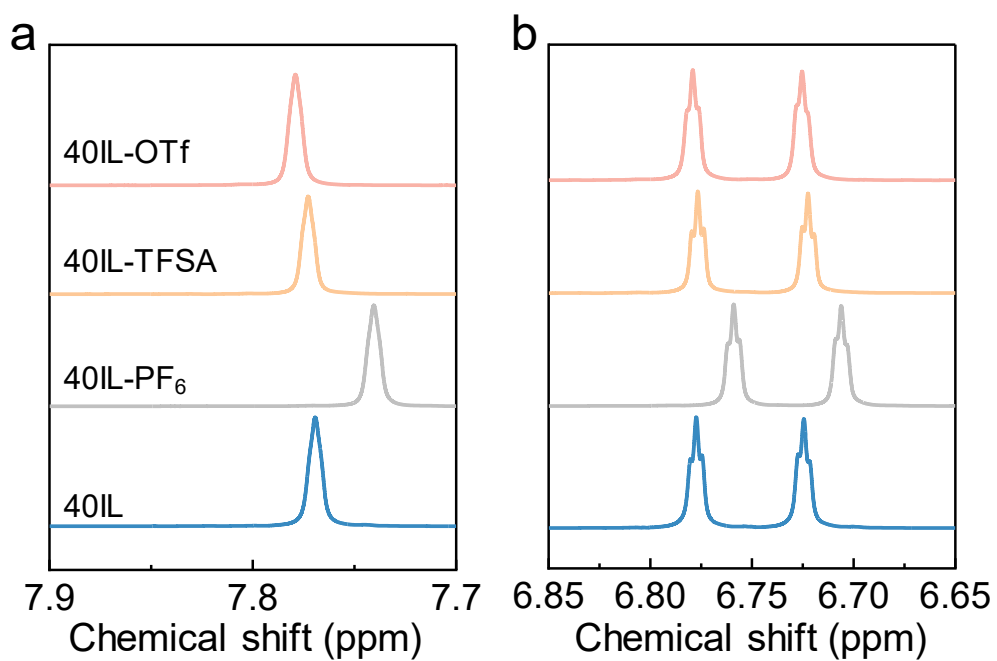


Figure 5-19. ^1H NMR spectra in the chemical shift regions of (a) 7.90–7.70 ppm and (b) 6.85–6.65 ppm of 40IL-[A] and 40IL electrolytes. See Figure 5-17 for the electrochemical performance utilizing these electrolytes.

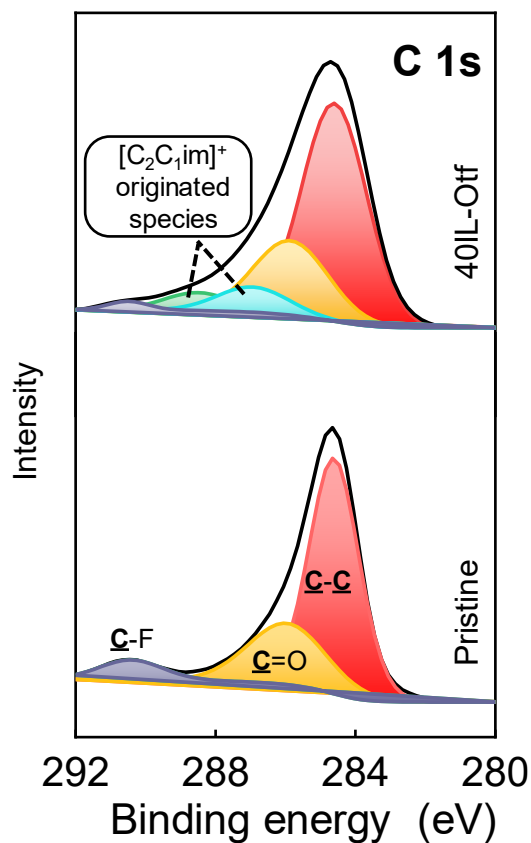


Figure 5-20. C 1s XPS spectra of the SEI formed on the graphite electrode in the 40IL-OTf electrolyte after initially adjusted to 1.5 V in a current density of 50 mA g^{-1} (surface without Ar^+ sputtering). Organic cation-originated species: N-C=N (288.5 eV) and C-N (286.9 eV).

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Chapter 6

Overlooked Issues on Oxidation State Analysis in Electrode Materials by X-ray Photoelectron Spectroscopy

6.1 Introduction

The surging demand for advanced electrochemical storage devices has shifted the focus of development to high energy- and power-density electrode materials to meet current needs for energy devices and applications [1-5]. Secondary batteries, such as lithium-ion and sodium-ion batteries, have garnered considerable interest in both academic and industrial fields. Motivated by the pursuit of higher energy densities, the past decades have witnessed the evolution to chasing high capacity of the negative electrode from the graphite electrodes ($\sim 360 \text{ mAh g}^{-1}$) and transition metal oxides (such as Fe_2O_3 , V_2O_5 , and TiO_2 , $< 1000 \text{ mAh g}^{-1}$) to silicon electrode ($\sim 3579 \text{ mAh g}^{-1}$), alloying metal and Li metal electrodes ($\sim 3860 \text{ mAh g}^{-1}$) [6-8]. On the other hand, insertion-type materials, which contain transition metal elements such as Fe, Co, Ni, and Mn, still occupy a dominant position in positive electrode materials. The lithiation/delithiation process reversibly occurs in the host framework accompanied by the redox reaction involving these transition metal elements. Therefore, the mechanistic underpinning of developing electrode materials requires the understanding of the redox behavior of transition metals such as their redox potential and oxidation state during the charge/discharge processes, which also offers new insights into the further design of

both positive and negative electrode materials [9-11].

Although X-ray absorption spectroscopy is acknowledged as the most proper way to determine the oxidation state of an element in electrode materials, XPS is also utilized as a common technique for this purpose, by providing information on binding energies of core-level electrons changing with different chemical species. It serves to provide valuable, in many cases even the sole information for determining the oxidation state of metal elements and also evaluating the chemical ingredient of solid-electrolyte interphase (SEI). In general, a high-energy ion-beam gun with an ion-sputtering source is usually equipped to apply a depth-profiling analysis or removal of the surface impurity of the materials due to the high surface-sensitivity of XPS. However, this ion bombardment treatment of the surface can damage the examined sample. Recently, a few XPS studies revealed that exposure of a SEI layer to destructive Ar^+ sputtering alters the original SEI chemistry [12, 13]. The SEI derived from three different Li salts is spontaneously detected to form LiF which is proved to be produced by the gradation of residual Li salt under an Ar^+ sputtering during XPS analysis, regardless of battery operation (chemical reduction of electrolytes was proceeded by Ar^+ sputtering). This dramatic finding warns the battery community about the potential pitfall while identifying actual SEI components via XPS analysis.

Similarly, equal concern should also be given to the investigation of the oxidation state of the sample via an XPS analysis accompanied by the Ar^+ sputtering. Chemical damages caused by Ar^+ sputtering treatment such as the preferential elemental sputter

ejection have been reported since the 1970s [14-18]. According to these studies, the thickness of this sputtering-damage layer is comparable to or even deeper than the XPS probing area which is less than several nanometers of the surface of the examined sample, as illustrated in Figure 6-1. Consequently, Ar^+ sputtering is likely to result in the arising concern of the misanalysis of the oxidation state of the bulk electrode sample ($> 70 \mu\text{m}$ in a lab scale) with a certain grain size (normally micrometer order), further causing a misunderstanding of the redox mechanism of the investigated electrodes in an electrochemical process. Several works have observed the chemical reduction of the transition metal in their borides, carbides, and oxides caused by the Ar^+ sputtering during XPS measurement [19, 20], and raised concerns on the potential pitfalls to be made from sample preparation, measurement to data analysis in spite of the frequent adaption of XPS technique in battery researches [21-23]. Among these, the erroneous effects of overuse of Ar^+ sputtering on the accurate evaluation of the electrode materials have still been overlooked in the field of material analyses for battery research.

In this chapter, we present an XPS study aiming to showcase the chemical changes of the surface with different output power and duration of sputtering time during the sample preparation processes in the XPS chamber. Four kinds of representative materials of both positive and negative electrode materials, namely LiFePO_4 (LFP), $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and Nb_2O_5 , are examined for the harm of Ar^+ sputtering abuse and the resulting potential errors in XPS-derived data interpretation. Finally, we suggest some methodologies to help circumvent these issues,

with the intention of ensuring the accurate investigation of the oxidation of bulk electrode material in the battery study.

6.2 Experimental

All the materials were handled under the same conditions with the statement in Section 2.1. The 20 mol% Li[FSA]-[C₂C₁im][FSA] ionic liquid (IL) electrolytes was prepared by well-mixing the Li[FSA] salts and [C₂C₁im][FSA] ionic liquid in the molar ratio of 20:80. The Nb₂O₅, LTO, LFP, and NCM811 electrodes were prepared in the same manner with statement in Section 2.2.

The Li/NCM811, Li/LFP half cells (2032-type) were assembled with the prepared organic and IL electrolytes, a working electrode, and a 13 mm diameter lithium metal counter electrode (Sigma-Aldrich Chemistry, 99.95% purity) fixed on a stainless steel (SUS316L) plate. The charged pristine LFP and NCM811 electrodes were obtained by a galvanostatic charge-discharge test recorded by an HJ-SD8 charge-discharge system (Hokuto Denko) using the thermostatic chamber SU-242 (ESPEC) at a rate of 0.1C in the cut-off voltage of 4.0 – 2.0 V for LFP electrodes and 4.4 – 2.0 V for NCM811 electrodes. Samples for Nb *L*3-edge X-ray absorption near edge structure (XANES) were prepared through a galvanostatic charge/discharge to various state of charge at 90 °C in a current density of 40 mA g⁻¹.

The Ar⁺ sputtering was carried using a Kaufman-type high etching rate ion gun (JEOL, XP-02300HRIS) at a beam energy of 10, 100, 500, and 1000 eV. The Ar-ion

beam was flashed to the electrode samples for 1, 5, 30, 60, 300, and 600 s at each sputtering energy, respectively. The Ar^+ sputtering over 30 s was applied several times for 30 s duration and 30-second rest to avoid overheating. The change of oxidation state of the transition metal element after Ar^+ sputtering was analyzed by XPS (JOEL, JPS-9030) with $\text{MgK}\alpha$ line as the exciting radiation. The morphology of the prepared samples was observed by FE-SEM (Hitachi, SU-8020). The prepared charged samples after electrochemical tests were washed with tetrahydrofuran and dried under vacuum at room temperature. The Nb $L3$ -edge X-ray absorption near edge structure (XANES) spectra measurements were performed in the beamline BL-10 at the SR center, Ritsumeikan University. All prepared samples for Ar^+ sputtering and FE-SEM observation were transferred in an airtight state.

6.3 Results and discussion

Effects of Ar^+ sputtering on the change in the oxidation state. To comprehensively demonstrate the impact of the sputtering effect on transition metal elements, the change of oxidation state was recorded and analyzed via XPS analyses applying Ar^+ sputtering treatment for various energy of ion beam and time duration with the utilization of the aforementioned four model electrode materials. Positive electrode samples (LFP and NCM811) were prepared by galvanostatic oxidizing the electrode to the fully charged state (see Figure 6-2 for charge profile for both electrodes), while negative electrodes (LTO and Nb_2O_5) were utilized in their pristine state (discharged state). The changes in

the oxidation state of the transition metal element in four kinds of electrodes are recorded by XPS spectra with increasing time duration under Ar^+ sputtering exposure at an output energy of 500 eV (Figure 6-3). In the initially charged LFP (Figure 6-3a), the Fe 2p spectra exhibit the weak peak assigned to Fe^{III} located at 712 eV. A distinct peak shift to the lower binding energy regions is observed with even 1 s of Ar^+ sputtering, resulting in the appearance of the new peak assigned to Fe^{II} . The intensity of Fe^{II} gradually increases for both the $2p_{1/2}$ and $2p_{3/2}$ lines with increasing time duration of Ar^+ sputtering, located at 724 and 710 eV, respectively, and the peak assigned to Fe^0 is observed after Ar^+ sputtering of 300 and 600 s [24, 25]. The significant indicating the significant change in the oxidation state caused by long-time Ar^+ sputtering treatment. With a decreased sputtering energy of 100 eV, a similar peak shifting to the lower binding energy region occurs in the Fe 2p spectra, indicating the reduction of the lower oxidation states (Figure 6-4). Figure 6-3b shows the changes in the oxidation state of Ni on the surface of the charged NCM811 electrode. No peak is observed in the Ni 2p spectra before Ar^+ sputtering due to the existence of cathode-electrolyte interphase. The peak located at a binding energy of 853 eV appears after 5-second Ar^+ sputtering, which corresponds to Ni^{II} that is considered to appear by reduction of $\text{Ni}^{\text{IV/III}}$ in the charged state of the NCM811 sample [26, 27]. Figure 6-6 presents the O 1s spectra of lithiated NCM811 subjected to increasing durations of Ar^+ sputtering. A shift toward lower binding energies is observed as the sputtering time increases, indicating alterations in the chemical state of oxygen during surface treatment. This observation raises concerns

about the reliability of using XPS to determine the oxidation state of oxygen, given its high surface sensitivity. Furthermore, the SEI components during cycling on the electrode surface complicate the evaluation of bulk oxygen oxidation states using XPS.

Similar to positive electrodes, the peak shift to the higher oxidation state can be observed in the sample of the LTO and Nb₂O₅ negative electrodes presented in Figure 6-3c,d, respectively. Trends of pronouncedly peak-shifting to lower binding energies are exhibited in both the Ti 2p and Nb 3d spectra, resulting in the peak assignment of their reduced states of Ti^{II} (located at around 461 and 455 eV) and Nb^{II} (located at 206 and 203 eV) eventually (see Table S1 for peak assignments of each elements and oxidation states) [20, 28]. Furthermore, this chemical damage of the electrode sample could not be avoided with a very short time of 1 s and low energy of 100 eV (Figure 6-7a). The field-emission scanning electron microscopic (FE-SEM) observation is conducted to gain insight into the change in morphology of the sputtered electrodes (Figure 6-8 and 6-9). The blurred edge and rougher surface of the particle are observed in the etched LFP and NCM811 samples after Ar⁺ sputtering especially in the high-energy sputtering at 500 and 1000 eV, suggesting the morphology damage during sputtering processes. This systematic investigation on four model electrodes indicates the preferential loss of oxygen within positive and negative electrodes including phosphate and oxide materials, and the consequent introduction of reductive artifacts during the Ar⁺ sputtering with the output energy varying from 10 to 1000 eV.

Misinterpretation of XPS data. As a common methodology to investigate the oxidation state of transition metal elements, XPS measurement combined with Ar^+ sputtering is widely employed to remove adventitious species on the surface especially when the signal of the target element is obscure after charge-discharge, subjecting the data extracted during Ar^+ sputtering to potential error for the mechanistic study. Here, we provide an example of the effect of Ar^+ sputtering combined with XPS-derived data interpretation on the electrochemical processes study. Figure 6-10 shows the charging curves (reduction) of Nb_2O_5 for lithium ion and sodium ion storage. The XPS analyses were conducted to gain insight into their change in the Nb oxidation state during charging processes.

Similar to the above discussion, a peak shift to the low binding energy regions is observed for both the electrode in LIB and SIB configurations after applying Ar^+ sputtering (Figure 6-10b,c), where a low oxidation state of $\text{Nb}^{\text{IV/II}}$ is suggested for peak assignment with a short duration of 30-second Ar^+ -sputtering (Figure 6-11). The XPS results may lead to the interpretation that the charge curves reflect the redox mechanism of $\text{Nb}^{\text{V/IV/II}}$. However, this is a common misinterpretation in mechanistic studies via the investigation of electrode oxidation states. It is important to note that this information pertains specifically to the surface of the electrode, which can be significantly altered by Ar^+ sputtering treatment.

Here to provide information reflecting the oxidation state of electrodes without the confusing effect of Ar^+ sputtering, total electron yield X-ray absorption spectroscopy

(TEY-XAS) is measured and X-ray absorption near-edge structure (XANES) analysis is performed without Ar^+ sputtering (Figure 6-10d). Regarding the charged electrode sample (in green solid line) in the LIB configuration, the Nb $L3$ -edge absorption edge exhibits a low-energy shift toward the edge of Nb metal reference (in blue solid line), suggesting the reduction of Nb along with the lithiation process in the Nb_2O_5 electrodes in this voltage. Surprisingly, the Nb $L3$ -edge absorption edge of the charged Nb_2O_5 electrode in SIB (in purple dash line) overlaps with the pristine $\text{Nb}_2^{\text{V}}\text{O}_5$ reference line (in black solid line), revealing that no sodiation occurs in this voltage in the Nb_2O_5 electrode in the Na system. These different behaviors in SIBs suggest different redox mechanisms from that demonstrated in LIBs [29]. Overall, these results clearly demonstrate that relying on XPS analyses to determine the oxidation state can lead to erroneous conclusions, which significantly hinders the accurate interpretation and analysis of the electrochemical behavior of transition metal-based electrode materials.

An alternative method for investigating the chemical state of electrodes. It is essential to complement surface-sensitive XPS data with additional techniques such as XAS. Hard X-ray photoelectron spectroscopy (HAXPES) targets the information from a deeper region by high-energy excitation X-ray, enabling a more trustable analysis of the oxidation state. Furthermore, it is important to consider changes in the crystallographic parameters of the materials, which can be effectively assessed using X-ray diffraction (XRD), alongside electrochemical measurements. This multi-

technique approach provides a more accurate picture of the material analysis. Moreover, it is crucial to explore advanced methodology to avoid the influence of the interphase and spectral artifacts from Ar^+ sputtering. For instance, Ar gas cluster ion beams (GCIBs) with a tunable cluster size are an alternative to reducing sputter damage of the examined sample, where GCIB could provide a wider range of energy distributions on each atom [30]. With a cluster size greater than 2000 atoms, the energy per atom could even decrease to ~ 10 eV/atom, which is much lower than the energy per atom of monatomic Ar^+ of hundreds eV currently applied. In addition, a recent work introduces a method of in vacuo scratching to electrode material to remove the surface species before XPS measurement, suggesting its beneficial effects on resulting in high signal-to-noise spectra without the influence of Ar^+ sputtering [31]. However, it still requires more investigation in detail for further applying both GCIB and vacuo scratching in combination with practical measurement of XPS.

6.4 Conclusions

In this chapter, we have demonstrated the erroneous effect of Ar^+ sputtering treatment on the accurate investigation of the oxidation state of bulk electrode material due to its preferential sputtering of oxygen during XPS measurement. Four representative electrode materials have shown uncontrollable reduction after an Ar^+ sputtering and it fails to be avoided by easily decreasing the sputtering energy of the monatomic Ar^+ beam or time duration. Furthermore, this inaccurate information on the oxidation state

of electrodes supplied by these reduced artifacts introduced by Ar^+ sputtering prevents researchers from correctly analyzing and deducing electrochemical processes, resulting in a misleading report to the whole battery research community. Herein, it is suggested sufficient awareness and attention to the potential pitfall in XPS measurement to be caused by abuse of Ar^+ sputtering by accompanying XANES spectra study of the sample or utilizing damage-free pre-treatment methods such as GCIBs.

Table 6-1. Peak assignment of XPS spectra for the examined electrode samples. See Figures 6-3, 6-4, 6-5, and 6-7 for the corresponding spectra.

Element	Oxidation state	Spectral line	Binding energy (eV)	Reference	
Fe	Fe ^{III}	2p _{1/2}	726	[24]	
		2p _{3/2}	712		
	Fe ^{II}	2p _{1/2}	724		
		2p _{3/2}	710		
		Fe ⁰	2p _{3/2}	706.8 ± .1	[25]
Ni	Ni ^{IV}	2p _{3/2}	858	[26-28]	
	Ni ^{III}	2p _{1/2}	875		
		2p _{3/2}	855		
	Ni ^{II}	2p _{1/2}	872.5		
		2p _{3/2}	853		
		Ti ^{IV}	2p _{1/2}		464.74
Ti		2p _{3/2}	458.93		
	Ti ^{III}	2p _{1/2}	461.3 ± .1		
		2p _{3/2}	457.5		
	Ti ^{II}	2p _{1/2}	461.0 ± .1		
		2p _{3/2}	455.3		
Nb	Nb ^V	3d _{3/2}	209.6 ± .3	[20]	
		3d _{5/2}	206.3 ± .3		
	Nb ^{IV}	3d _{3/2}	207.5		
		3d _{5/2}	204.3		
	Nb ^{II}	3d _{3/2}	205.8		
		3d _{5/2}	203.3		
	Metallic Nb	3d _{3/2}	205.0 ± .3		[32]
		3d _{5/2}	202.2 ± .3		

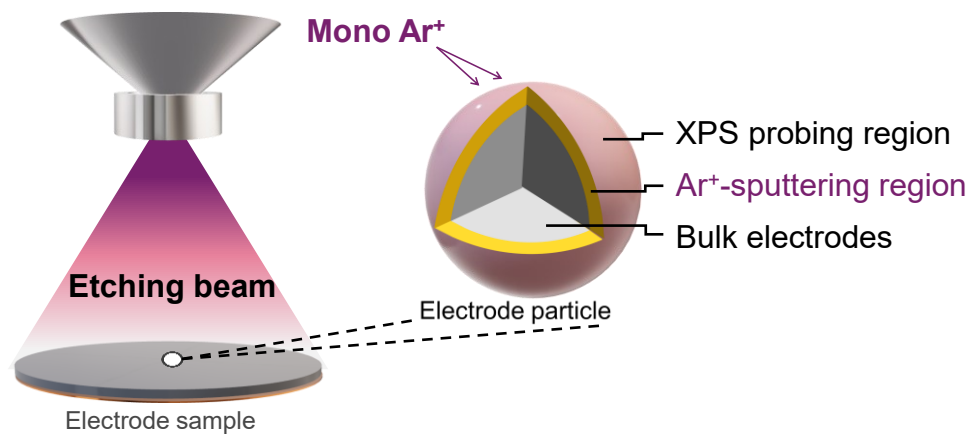


Figure 6-1. Schematic illustration of an Ar^+ sputtering electrode sample during XPS analyses.

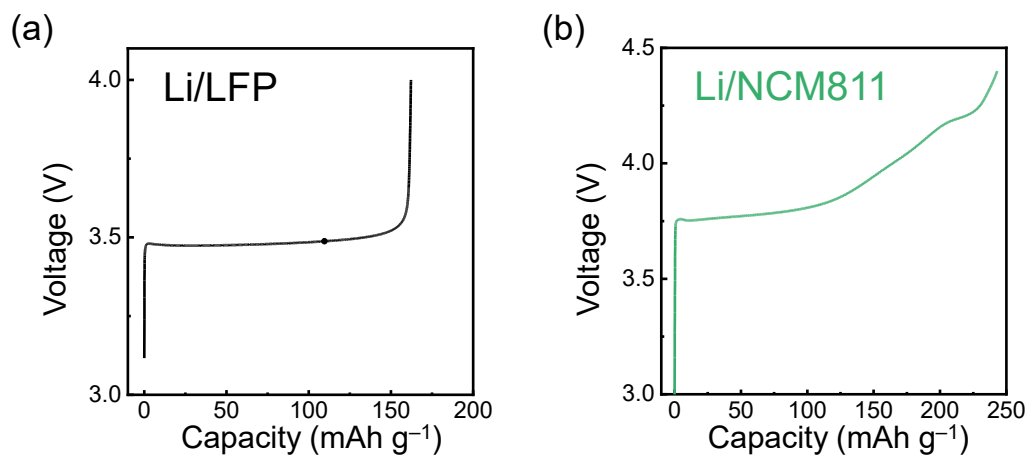


Figure 6-2. Initial charge curve for the positive electrodes of (a) LFP and (b) NCM811 at a current density of 0.1C. Counter electrode: Li metal and electrolyte: 1 mol dm⁻³ LiPF₆ EC/DMC (1:1, v/v).

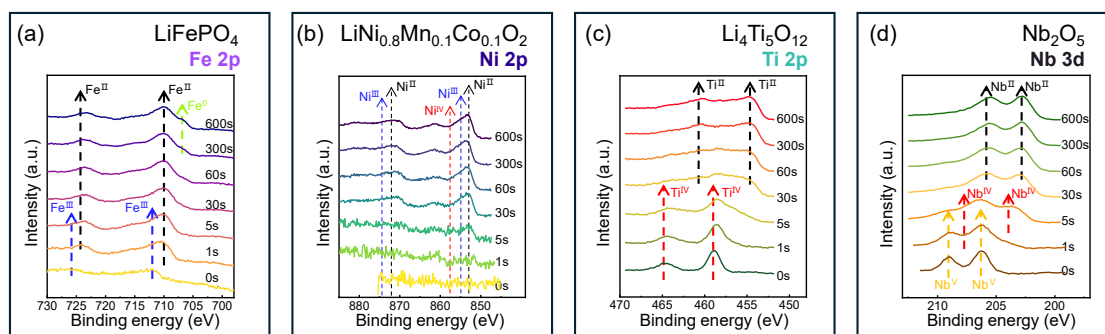


Figure 6-3. XPS spectra with Ar^+ sputtering for four model electrode materials. (a) Fe 2p spectra of the charged LFP, (b) Ni 2p spectra of the charged NCM811, (c) Ti 2p spectra of the pristine LTO, and (d) Nb 3d spectra of the pristine Nb_2O_5 . Ar^+ sputtering duration: 1, 5, 30, 60, 300, and 600 s at an energy of 500 eV, and a duty of 100%. All binding energies of each transition metal are corrected based on the C 1s spectra. See Table 6-1 for the peak assignment of each element. See Figure 6-2 for the charging profile of the LFP and NCM811 electrodes at a current density of 0.1C and Figures 6-4, 6-5, and 6-7 for Fe 2p, Ni 2p, and Ti 2p spectra of the LFP, NCM811, and LTO electrode samples, respectively with the exposure to Ar^+ sputtering of different energies of 100 and 1000 eV.

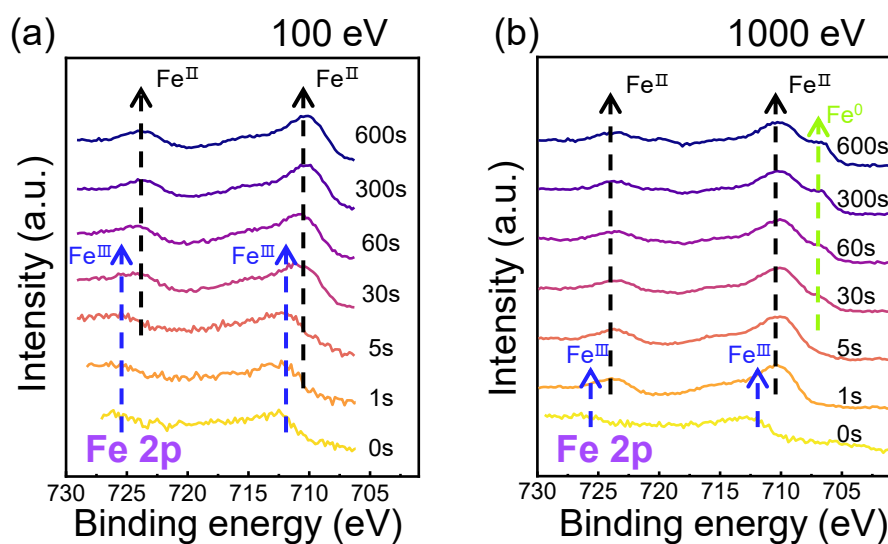


Figure 6-4. Fe 2p XPS spectra of the charged pristine LFP electrode (0 s) and the electrodes under the exposure of Ar^+ ion beam with the energy of (a) 100 eV and (b) 1000 eV, respectively. The Fe 2p peaks show the changes in Fe valence states with increasing time duration. See Figure 6-3 for the changes in Fe 2p spectra under 500 eV Ar^+ sputtering. See Table 6-1 for peak assignment in detail.

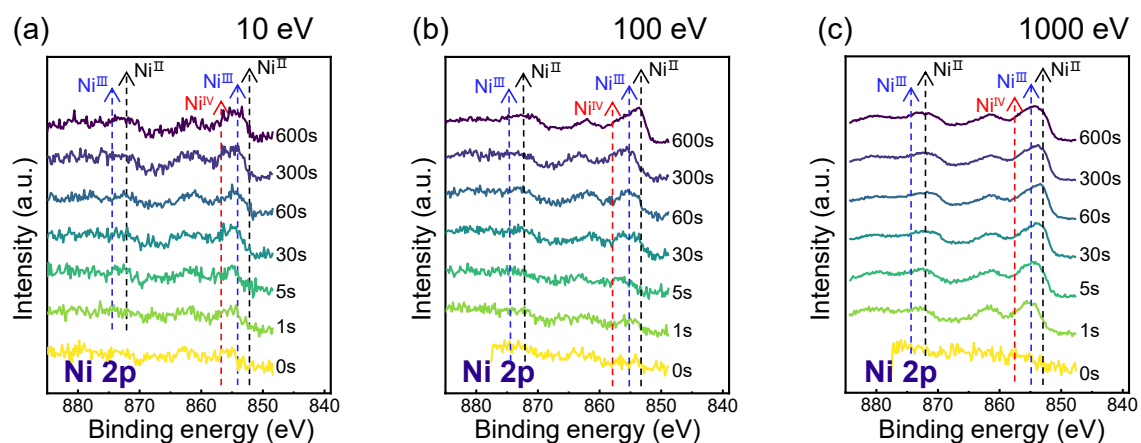


Figure 6-5. Ni 2p XPS spectra of the NCM811 electrode of charged state (0 s) and the electrodes under the exposure of Ar^+ ion beam with the energy of (a) 10, (b) 100 and (c) 1000 eV, respectively. See Figure 6-3b for the changes in Ni 2p spectra under 500 eV Ar^+ sputtering. See Table 6-1 for peak assignment of each oxidation state.

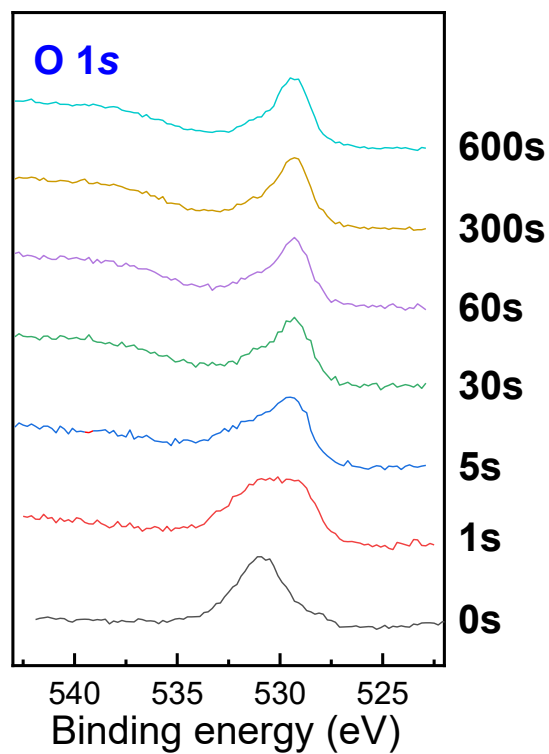


Figure 6-6. O 1s XPS spectra for charged NCM811 positive electrode with Ar⁺ sputtering duration of 0, 1, 5, 30, 60, 300, and 600 s. All binding energies have been calibrated based on the C 1s peak. See Figure 6-3 for the changes in Ni 2p spectra under 500 eV Ar⁺ sputtering.

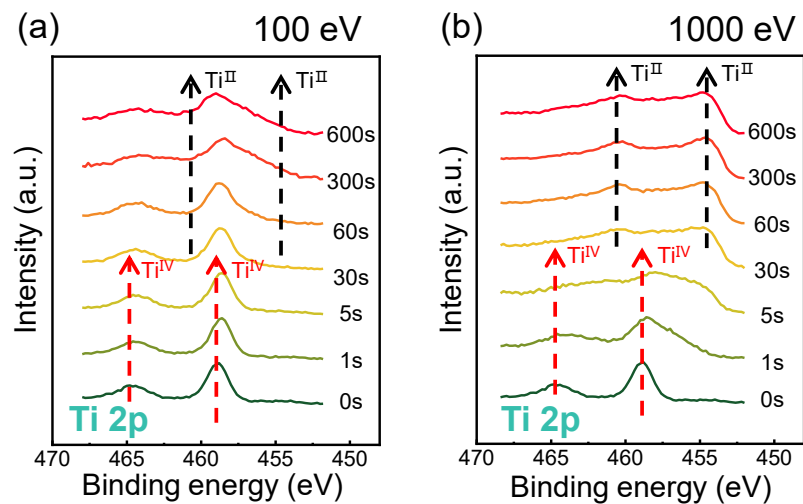


Figure 6-7. Ti 2p XPS spectra of the charged pristine LTO electrode (0 s) and the electrodes under the exposure of Ar^+ ion beam with the energy of (a) 100 eV and (b) 1000 eV, respectively. See Figure 6-3c for the changes in Ti 2p spectra under 500 eV Ar^+ sputtering. See Table 6-1 for peak assignment of each oxidation state.

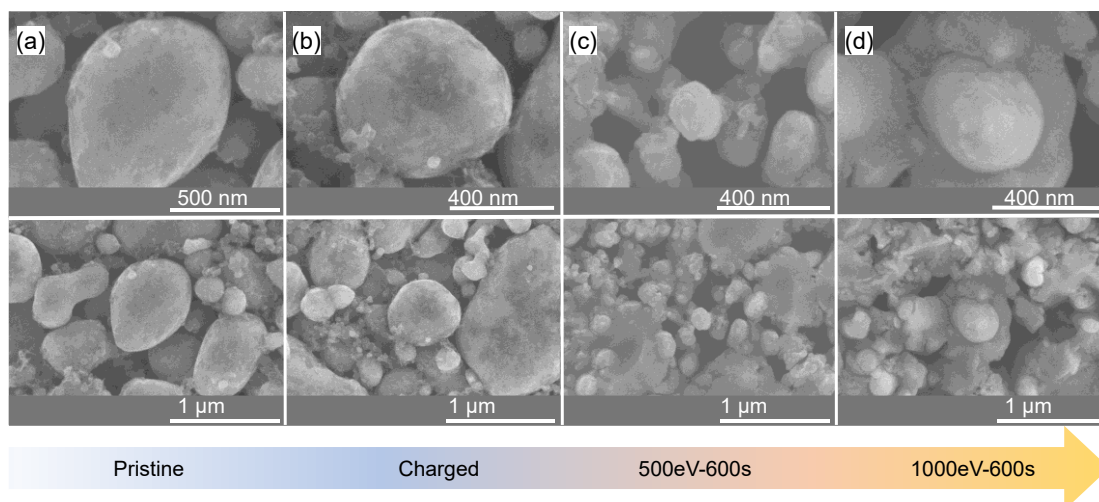


Figure 6-8. FE-SEM images of (a) pristine, (b) initial charged, and (c-f) 600-second sputtered LFP electrode samples with different sputter energy of 500 and 1000 eV. See Figures 6-3a and 6-4 for the XPS spectra.

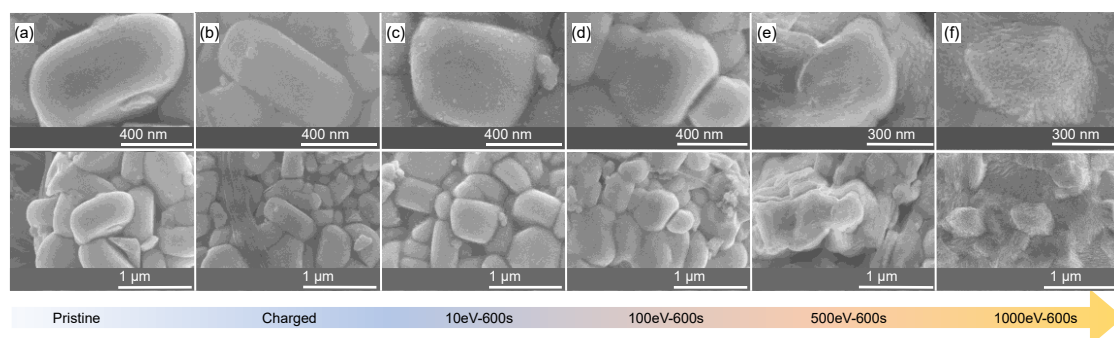


Figure 6-9. FE-SEM images of (a) pristine, (b) initial charged and (c-f) 600-second sputtered NCM811 electrode samples with different sputter energies of 10, 100, 500, and 1000 eV. See Figures 6-3b and 6-5 for the XPS spectra.

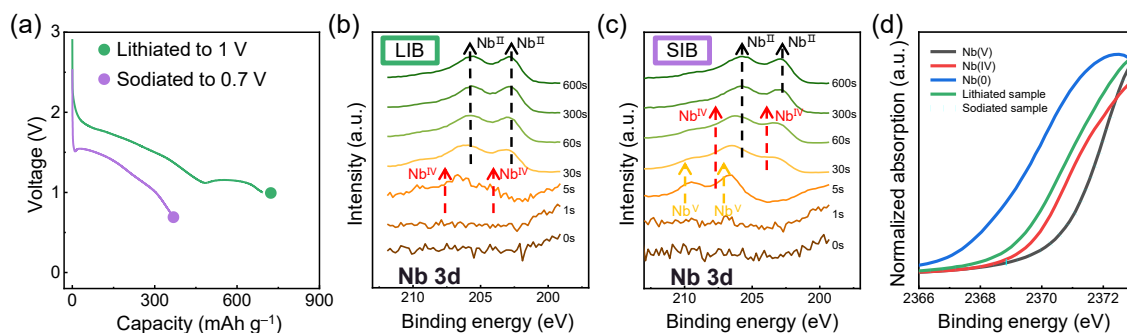


Figure 6-10. The effect of Ar⁺ sputtering on the electrochemical study for ion storage in electrodes. (a) Voltage curves of the initial lithiation and sodiation processes for the Nb₂O₅ electrode in lithium-ion (LIB) and sodium-ion battery (SIB) configuration to 1.0 V (vs. Li⁺/Li) and 0.7 V (vs. Na⁺/Na), respectively. Current density: 200 mA g⁻¹. The XPS analyses are conducted to investigate the oxidation of the Nb₂O₅ electrodes charged in (b) LIB and (c) SIB with different durations of 1, 5, 30, 60, 300, and 600 s at a sputtering energy of 500 eV. See Figure 6-11 and Table 6-1 for peak assignment and fitting details for each oxidation state. (d) Nb L3-edge XANES spectra of charged Nb₂O₅ electrode in LIB and SIB system and standard powders (Nb₂^VO₅, Nb^{IV}O₂, and Nb metal).

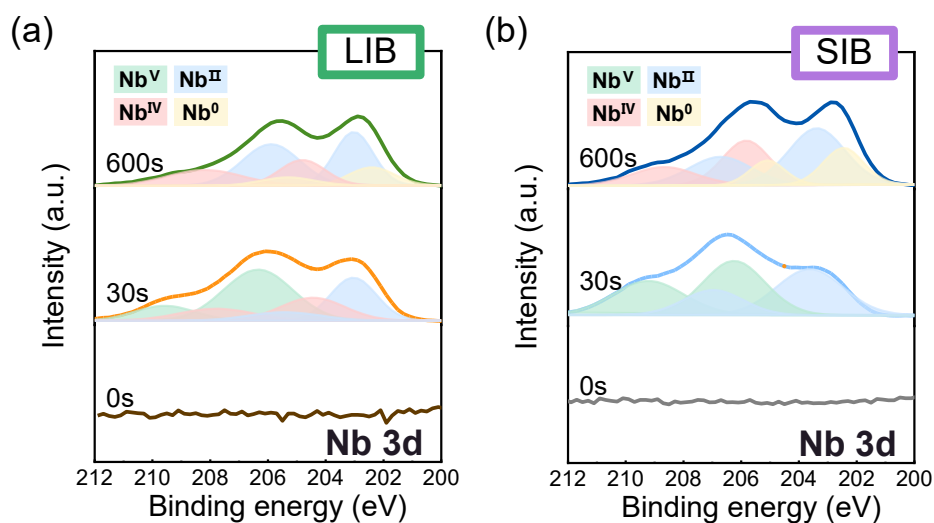


Figure 6-11. Deconvoluted peak fitting and ratios of Nb_2O_5 electrode in (a) lithium-ion (LIB) configuration to 1.0 V (vs. Li^+/Li) and (b) sodium-ion batteries (SIB) configuration and 0.7 V (vs. Na^+/Na), respectively with Ar^+ sputtering of 0, 30, and 600 s under 500 eV Ar^+ sputtering. See Table 6-1 for Nb 3d peak assignment for each oxidation state.

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Chapter 7

General Conclusions

Advanced secondary batteries are essential to meet the growing demands of energy consumption and rapid technological development. Among them, lithium-ion batteries (LIBs) represent one of the most promising secondary battery technologies, offering high energy density and excellent cycle life. With the expanding application of LIBs in increasingly diverse scenarios, such as electric vehicles, the need for fast-charging capability and stable operation under harsh conditions, including high current densities and temperature fluctuations, has become critically important. Given this situation, the electrode materials used in next-generation LIBs must overcome significant challenges, including the sluggish kinetics within electrode materials and electrolytes. This doctoral dissertation addresses these challenges through a multifaceted approach: investigating the pseudocapacitive behavior of negative electrode materials and their interfacial properties from the temperature perspective; examining the decomposition behavior of ionic liquids at the negative electrode; and analyzing electrode surfaces using X-ray photoelectron spectroscopy (XPS).

In Chapter 3, the temperature effect of the pseudocapacitive behavior of orthorhombic Nb_2O_5 was investigated in a wide cutoff voltage range of 0.01–2.3 V at 25 and 90 °C with the thermally stable $\text{Li}[\text{FSA}]\text{-}[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ionic liquid (IL) electrolyte. The orthorhombic Nb_2O_5 phase transformed to the amorphous $\text{Li}_x\text{Nb}_2\text{O}_5$ phase during the initial charge to 0.01 V. Subsequent cycles yield enhanced performance attributed to a series of reversible $\text{Nb}^{\text{V,IV}}/\text{Nb}^{\text{III}}$ redox reactions in the amorphous $\text{Li}_x\text{Nb}_2\text{O}_5$ phase. Through cyclic voltammetry and symmetric cell

electrochemical impedance spectroscopy, temperature elevation is noted to increase the pseudocapacitive contribution of the Nb₂O₅ electrode, resulting in high-rate capability of 131 mAh g⁻¹ at 20000 mA g⁻¹ at 90 °C. The impressive performance demonstrated by the Nb₂O₅ electrode is also attributed by the formation of the [FSA]⁻-based solid-electrolyte interphase (SEI) layer during the initial charge in the IL electrolyte, which enables a long-term cycle life over 2000 cycles at 2000 mA g⁻¹ with an average Coulombic efficiency of 99.4% at 90 °C. This study underscores the operating temperature and pseudocapacitive behavior of Nb₂O₅, consequently offering an efficient way to enhance electrochemical properties and revealing the capacitive processes of Nb₂O₅ in the lithium storage mechanism.

In Chapter 4, argon-ion bombardment (AIB) was utilized as a one-step method for ameliorating the limited electronic conductivity of the Nb₂O₅ negative electrode. The surface chemical reduction is confirmed by XPS spectra and investigation of the deconvoluted peak ratios of Nb^{IV} and Nb^{II} species with increasing AIB duration of time. High-resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM) results show evidence of a surface reduction layer with a depth of around 5 nm. The electrochemical impedance spectroscopy (EIS) and activation energy calculation show the improvement of charge transfer processes in the electrode after AIB treatment, which contributes to enhanced electrochemical performance. Electrodes exposed to AIB exhibit enhanced electrochemical performance, and the modified electrode achieves a higher reversible capacity (211 mAh g⁻¹) compared to the pristine materials (138 mAh g⁻¹). This work provides an efficient method for modifying the electronic conductivity of transition metal oxides negative electrode materials and offers insights into the rational design of materials for high-rate batteries.

In Chapter 5, the impact of organic cation behavior on interfacial processes was

investigated, demonstrating that the weakened interactions between cations and anions engender “unprotected” organic cations in highly Li-concentrated IL electrolytes. These unprotected cations undergo a prior reductive decomposition on the surface of the negative electrode during the initial charge. This behavior is manifested by the substantial irreversible capacities and inferior initial Coulombic efficiencies observed during the initial charging of graphite negative electrodes, resulting in considerable electrolyte consumption and diminished energy densities in full-cell configurations. In addition, anionic species with high Lewis basicity, such as triflate anion ($[\text{OTf}]^-$) were introduced to reinforce the ionic interactions involving organic cations and improve the initial Coulombic efficiency. These results highlight the critical role of organic cations and their coordination environment in enhancing the reductive stability and interfacial properties of ILs, providing a theoretical foundation for designing advanced IL electrolytes.

In Chapter 6, the impact of Ar^+ sputtering conditions in X-ray photoelectron spectroscopy was investigated on the analysis of the oxidation states of various materials used as positive and negative electrodes. Representative electrode materials were shown to undergo uncontrollable reduction when exposed to an Ar^+ sputtering, which fails to be avoided by easily decreasing the sputtering energy of the monatomic Ar^+ beam (less than 100 eV) or time duration ($< 5\text{s}$). These reduced artifacts introduced by Ar^+ sputtering prevent from correct analysis of oxidation states of transition metal elements and a corresponding understanding of their mechanism during Li^+/Na^+ ion storage.

The findings presented in this dissertation advance the understanding of high-rate-capable negative electrodes and their interfacial properties in Li-ion batteries. This research offers valuable insights into the selection and design of electrode materials and

their electrochemical mechanisms, providing a promising pathway toward fast-charging batteries with high energy density and all-climate adaptability. Additionally, it deepens the understanding of ion interactions and coordination environments in ionic liquid electrolytes, contributing to the elucidation of their interphasial chemistry with negative electrodes. These contributions are expected to support the practical development of safe, fast-charging, and durable lithium-ion batteries, complementing the ongoing efforts toward high-energy density battery technologies.

List of Publications

Chapter 3

Shaoning Zhang, Jinkwang Hwang, Kazuhiko Matsumoto, Rika Hagiwara

ACS Applied Materials & Interfaces, 2022, 14, 19426–19436.

“In Situ Orthorhombic to Amorphous Phase Transition of Nb₂O₅ and Its Temperature Effect on Pseudocapacitive Behavior”

Chapter 4

Shaoning Zhang, Jinkwang Hwang, Yuta Sato, Kazuhiko Matsumoto, Rika Hagiwara

ACS Applied Energy Materials, 2024, 16, 53963–53971.

“Inducing a Conductive Surface Layer on Nb₂O₅ via Argon-Ion Bombardment: Enhanced Electrochemical Performance for Li-Ion Batteries”

Chapter 5

Shaoning Zhang[#], Shengan Wu[#], Jinkwang Hwang, Kazuhiko Matsumoto, Rika Hagiwara

Journal of the American Chemical Society, 2024, 146, 8352–8361.

“Unprotected Organic Cations—The Dilemma of Highly Li-Concentrated Ionic Liquid Electrolytes”

[#]Equally contributed

Chapter 6

Shaoning Zhang, Jinkwang Hwang, Keisuke Murakami, Chengchao Zhong, Toyonari Yaji, Yuki Oriksa, Kazuhiko Matsumoto

Journal of Power Sources, 2025, 644, 23709.

“Overlooked Issues on Oxidation State Analysis in Electrode Materials by X-ray Photoelectron Spectroscopy”

Related work not described in this thesis

Yayun Zheng[#], Di Wang[#], Shubham Kaushik[#], Shaoning Zhang, Tomoki Wada, Jinkwang Hwang, Kazuhiko Matsumoto, Rika Hagiwara

EnergyChem, 2022, 4, 100075.

“Ionic Liquid Electrolytes for Next-generation Electrochemical Energy Devices”

[#]Equally contributed

Shaoning Zhang[#], Shengan Wu[#], Keisuke Murakami, Jinkwang Hwang, Kazuhiko Matsumoto

Accounts of Materials Research, 2025, in press.

“Intermediate-Temperature Operable Secondary Batteries”

[#]Equally contributed

Acknowledgement

It is an immense pleasure to express my deep gratitude to Professor Kazuhiko Matsumoto for his enlightening instructions, continuous encouragement, and efficient and fruitful discussion. It is his professional understanding in a wide field that drives the current research smoothly. My sincere gratitude is to Professor Emeritus Rika Hagiwara, who provided me with the invaluable opportunity to have a graduate education under his esteemed supervision. His profound knowledge and thought-provoking advice have motivated the present research. I express my high appreciation to Assistant Professor Jinkwang Hwang, who provides well-informed erudite knowledge and lead to the present research from a fundamental base. Moreover, I am highly motivated by the enthusiasm sprits of Dr. Hwang not only for the scientific study but also for his attitude towards life, in which he supported and encouraged me to explore in the way of academic constantly and strengthen myself in the processes of conducting research activation.

My heartfelt thanks go to Professor Takashi Sagawa and Professor Toshiyuki Nohira for their detailed review and helpful advice, which have substantially refined the clarity and depth of this dissertation. I am also grateful to all of the co-authors for their insightful input and thoughtful guidance during the analysis and discussion phases of this study. My sincere thanks are also due to the Japan Science and Technology Agency (JST) and the Kyoto University Division of graduate Studied for finial support for both my research and daily life.

The warmest thanks to the former and present members of Energy Chemistry Laboratory for their careful and constant support and accompany. I express my indebtedness to Ms. Naoko Sakamoto and Kumiko Matsumoto, who provided their

heedful care. My enthusiastic gratitude goes to Dr. Shuham Kaushik, Dr. Hiroki Yamamoto, Dr. Yayun Zheng, Dr. Di Wang, Dr. Shengan Wu, Dr. Huazhen Liu, Dr. Fumiyasu Nozaki, Mr. Kentaro Kamada and Ms. Nozomi Yoneda, who are always my mentors in the study and real friends in my life. Special thanks are also given to Mr. Keisuke Murakami, Mr. Kosei Ayara, Mr. Hiroki Wada, Ms. Nana Maeda and Ms. Duanfei Han. I would like to give my special mention to Ms. Tingting Liang, Ms. Xuexuan Wang, Ms. Zonghui Zhang, Ms. Yinyin Yu and other dearest friends for their unbounded affection and mental support.

It is my privilege to thank my father Junwei Zhang, my mother Wei Shao, and other beloved family members, who supported my study in Japan. They are the moral power behind the accomplishment of the present study.

Finally, I would like to express my appreciation and thanks to all those related to this study.

Shaoning Zhang

September 2025