

**Physicochemical and Electrochemical Properties of the
(Fluorosulfonyl)(trifluoromethylsulfonyl)amide Ionic Liquid for
Na Secondary Batteries**

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Abstract

In this study, thermal, physical, and electrochemical properties of the ionic liquid electrolyte system, Na[FTA]-[C₃C₁pyrr][FTA], (FTA⁻ = (fluorosulfonyl)(trifluoromethylsulfonyl)amide and C₃C₁pyrr⁺ = *N*-methyl-*N*-propylpyrrolidinium) have been investigated for Na secondary batteries. The asymmetric FTA⁻ structure provides a wide liquid-phase temperature range, especially at low $x(\text{Na[FTA]})$ ($x(\text{Na[FTA]})$ = molar fraction of Na[FTA]) and low temperature range. Glass transition at 170 – 209 K is the only observed thermal behavior in the $x(\text{Na[FTA]})$ of 0.0–0.4. Temperature dependence of viscosity and ionic conductivity obey the Vogel–Tammann–Fulcher equation, and the correlation between molar conductivity and viscosity follows the fractional Walden rule. The anodic potential limits are above 5 V vs. Na⁺/Na at 298 and 363 K. The noticeable effects of $x(\text{Na[FTA]})$ are observed in the electrochemical performance of Na metal and hard carbon electrodes. In both cases, a moderate concentration, $x(\text{Na[FTA]})$ of 0.2–0.3, enables favorable charge-discharge behavior. At 363 K, the discharge capacities of the hard carbon electrode at $x(\text{Na[FTA]})$ of 0.3 are 260 and 236 mAh g⁻¹ at the current densities of 20 and 200 mA g⁻¹, respectively. The optimum cycling performance occurs at $x(\text{Na[FTA]})$ = 0.3, providing satisfactory capacity retention and high average coulombic efficiency.

Keywords: Na secondary batteries, ionic liquids, (fluorosulfonyl)(trifluoromethylsulfonyl)amide,

hard carbon

1. Introduction

Grid-scale energy storage devices are critical towards the application of power leveling for renewable energy, such as solar and wind power [1]. For such a large-scale system, Na secondary battery is one of the possible candidates because of the high abundance of Na resource and relatively high energy density owing to the low Na^+/Na redox potential (-2.71 V vs. SHE) [2, 3]. However, a more cautious design, including high safety and long-term durability, is a current challenge for this purpose. Among all battery components, properties of electrolytes, such as volatility, flammability, and compatibility with cell components, can dominate this issue, and lead to optimal cell performance.

Ionic liquids (ILs) are exclusively composed of ionic species [4] and considered as good electrolytes to improve safety and durability issues owing to their low volatility, low flammability, and wide electrochemical window [5, 6]. For the application on Na secondary batteries, amide-based ILs, such as FSA^- (bis(fluorosulfonyl)amide) and TFSA^- (bis(trifluoromethylsulfonyl)amide), have been examined because of their relatively high ionic conductivity and superior electrochemical compatibility with battery components (e.g. Al substrate and various electrode materials) [7-9]. Advantages of the FSA-based ILs to form stable solid electrolyte interphase (SEI) have been widely recognized in both lithium and Na systems, which is in contrast to the TFSA-based ILs [10, 11]. Among this research field, extending the liquid temperature range of ILs, which is derived from high stability at elevated temperature and reduction of a melting point (or disappearance of a melting point), is one of the targets to widen application areas. A number of recent studies highlight the desire to use in wide

temperatures within mobile applications and further electric vehicle (EV) market [12-14]. The use of asymmetric cation or anion is one of the feasible methods to extend a temperature range to the lower side because asymmetric molecules hinder ordered packing of ions to generate a crystalline phase [15, 16]. Among various organic cations, asymmetric pyrrolidinium-based and imidazolium-based cations showed high potentials as electrolytes in Na secondary battery studies [3, 17]. On the other hand, compared to symmetric FSA^- and TFSA^- , the asymmetric (fluorosulfonyl)(trifluoromethylsulfonyl)amide (FTA) anion has a potential to reduce melting point or prevent crystallization without losing advantages observed for FSA and TFSA ILs [18, 19].

Clarifying the intrinsic thermal, physical, and electrochemical properties of ILs is crucial to select proper ILs for particular applications. In previous studies, several FSA^- -based ILs were investigated for Na secondary batteries, including inorganic and inorganic-organic hybrid systems such as $\text{Na}[\text{FSA}]\text{-K}[\text{FSA}]$ [20], $\text{Na}[\text{FSA}]\text{-[C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ [21, 22], and $\text{Na}[\text{FSA}]\text{-[C}_2\text{C}_1\text{im}][\text{FSA}]$ [7] [23]. The TFSA-based ILs, $\text{Na}[\text{TFSA}]\text{-[C}_2\text{C}_1\text{im}][\text{TFSA}]$ [24], $\text{Na}[\text{TFSA}]\text{-[C}_4\text{C}_1\text{im}][\text{TFSA}]$ [24], and $\text{Na}[\text{TFSA}]\text{-[C}_4\text{C}_1\text{pyrr}][\text{TFSA}]$ [25], were also studied as Na secondary battery electrolytes, but their use is limited because of the instability against reduction as mentioned above. Concerning the FTA-based IL electrolytes for energy storage devices, their performance in Li-ion batteries and supercapacitors were demonstrated in previous works [26, 27], which suggested large temperature range and high stability against Al corrosion. However, there is no systematic study on the physicochemical and electrochemical properties of FTA-based ILs available for Na secondary batteries.

The aim of the present study is to investigate thermal, physical, and electrochemical characterization of the Na[FTA]-[C₃C₁pyrr][FTA] system. This includes their application as electrolytes for intermediate-temperature operated Na secondary batteries as proposed in previous works [28, 29] because intermediate operation using waste heat and hot environment is energetically efficient and enhance battery performance but requires safe electrolytes such as ILs. Battery performance of the FTA-based ILs will be discussed with the hard carbon (HC) electrode which is one of the most studied and promising negative electrode materials. Its performance in ILs was investigated in previous works, exhibiting a reasonably high discharge capacity and long cycle life, especially at intermediate temperatures [30, 31].

2. Experimental procedure

2.1. General experimental procedure and synthesis

All the volatile materials used were handled using a vacuum line constructed of SUS-316 stainless steel and tetrafluoroethylene–perfluoroalkylvinylether copolymer. Nonvolatile materials were handled under a dry Ar atmosphere in a glove box ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$). Neat $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ was synthesized by ion exchange between aqueous solutions of $[\text{C}_3\text{C}_1\text{pyrr}]\text{Br}$ (IoLiTec, purity $> 99\%$) and $\text{Na}[\text{FTA}]$ (Provisco CS Ltd. purity $> 98\%$) in the molar ratio of $[\text{C}_3\text{C}_1\text{pyrr}]\text{Br}:\text{Na}[\text{FTA}] = 1:1.2$. After 24 h stirring, a water non-miscible phase of $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ formed. Subsequently, the obtained $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ was purified with deionized water for several times to remove water-soluble byproduct (NaBr) until the Br content in the aqueous solution became below the detectable level by an AgNO_3 test using 1 mol dm^{-3} AgNO_3 aqueous solution. Finally, $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ was extracted from the aqueous solution with dichloromethane (Wako Pure Chemical Industries, purity 99%) and dried under vacuum at 353 K. The Br content in the final product was below its detectable limit ($\text{Br}^- < 1 \text{ ppm}$) according to X-ray fluorescence spectroscopy (Rigaku, EDXL-300). The $\text{Na}[\text{FTA}]-[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ ILs were prepared by mixing $\text{Na}[\text{FTA}]$ in the range of molar fraction of $\text{Na}[\text{FTA}]$ ($x(\text{Na}[\text{FTA}])$) of 0–0.9 with $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$.

2.2. Physicochemical analysis

Thermal transition temperatures were determined by a differential scanning calorimetry (DSC) system (DSC-8230, Rigaku Thermo Plus EVO II Series) under a scan rate of 5 K min^{-1} from 150 K to

375 K. Each DSC sample was sealed in an airtight Al pan under an atmosphere of dry Ar. The thermal stability was measured by thermogravimetric (TG) analysis (STA2500 Regulus, NETZSCH) at a scan rate of 5 K min⁻¹ from 303 K to 773 K under a dry Ar atmosphere. Viscosities of ILs were obtained using an electromagnetically spinning viscometer EMS-100 (Kyoto Electronics Manufacturing Co., Ltd.). Ionic conductivities were measured using the ac impedance technique by an impedance analyzer (3532-80, Hioki E.E. Corp.). The ILs were sealed into an airtight T-shaped cell equipped with two stainless steel electrodes under dry Ar atmosphere. Densities were measured using an oscillating U-tube density meter (DMA 4500 M, Anton Paar GmbH).

2.3. Electrochemical characterization

Electrochemical properties of anodic stability, Al dissolution, and Na metal deposition/dissolution were analyzed using a VSP-300 system (BioLogic) in 2032 type coin-cells with the target working and Na metal counter electrodes. The anodic stability was tested by linear sweep voltammetry with a Pt working electrode. The stability of the Al electrode was also tested by cyclic voltammetry. The Na metal deposition/dissolution was evaluated by voltage profiles and electrochemical impedance spectroscopy (EIS) of Na symmetric cells. In addition, an Al working electrode with 13 mm in diameter and 0.2 mm of thickness were used to test the cycle efficiency of Na metal deposition/dissolution process performed at a current density of 0.1 mA cm⁻² in the Na[FTA]-[C₃C₁pyrr][FTA] IL electrolytes with $x(\text{Na[FSA]}) = 0.1\text{--}0.4$ at 363 K.

Hard carbon (Carbotron P, Kureha Battery Materials Japan Co., Ltd) was used as an active

material. HC electrodes were prepared in the following manner. The HC (96 wt%) powder and PAI binder (4 wt%) were uniformly mixed in NMP by a solid/liquid ratio of 0.52, and the obtained slurry was coated onto Al foil. The HC electrodes were dried in vacuum at 473 K for 12 h before being transferred into an Ar-filled glove box. Electrochemical characterization of the HC electrodes using the Na[FTA]-[C₃C₁pyrr][FTA] ILs was carried out using a 2032-type coin cell, fabricated with the HC working electrode and Na counter electrode. A glass fiber filter (Whatman, GF-A, 260 mm) was used as a separator. The specific capacity of the charge-discharge process was calculated based on the mass of active material. Rate capability was tested at constant current rates of 20–2000 mA (g-HC)⁻¹ within a voltage range of 0.005–1.5 V. The cycle tests were performed at a constant current rate of 200 mA (g-HC)⁻¹ in the same voltage range with the rate capability test.

3. Results and discussion

3.1. Thermal Behavior.

Fig. 1 shows DSC curves at $x(\text{Na[FTA]}) = 0.0, 0.5$, and 0.7 (see Fig. S1 for DSC curves at other $x(\text{Na[FTA]})$), and the corresponding phase diagram of the $\text{Na[FTA]}\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ system. As shown in Fig. S2, the decomposition temperature (T_{dec}) of the neat $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ (the temperature at which the weight loss exceeds 1 wt%) is 500 K, which is slightly lower than the previous report (558 K) [18]. Table 1 summarizes thermal transition temperatures based on the DSC results. In the $x(\text{Na[FTA]})$ range of 0.0–0.4, only the glass transition is observed in the DSC curves. The glass transition temperature is 170 K for the neat $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$, which well-agrees with the previous report (166 K) [18] and monotonously increases to reach 209 K at $x(\text{Na[FTA]}) = 0.5$ which is kept almost constant above. Such a trend of glass transition temperature increase with an increasing fraction of alkali metal ion was also observed in a lithium system ($\text{Li[FTA]}\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$) [32]. Crystallization does not occur in this region including the neat $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ because of the asymmetric structure of FTA^- which hinders efficient packing from generating periodic structures [15]. Thus, a wide liquid temperature range is observed from $x(\text{Na[FTA]}) = 0.0$ to 0.4. The absence of crystallization behavior at such a low Na salt fraction was not observed in the previously studied FSA systems [21] [23]. At $x(\text{Na[FTA]}) = 0.5$ and 0.6, a weak and broad peak appears around 310–320 K, but it disappears in the second DSC cycle. According to visual observation, the samples at $x(\text{Na[FTA]}) = 0.0$ to 0.4 are clear liquid at room temperature, whereas the samples become cloudy and highly

viscous above $x(\text{Na[FTA]}) = 0.5$, implying that Na[FTA] is already saturated in $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ at $x(\text{Na[FTA]})$ of 0.5. During the first heating of DSC at $x(\text{Na[FTA]})$ of 0.5 and 0.6, the residual solid Na[FTA] dissolves into the liquid phase, resulting in the weak endothermic peaks at 312 and 333 K, respectively. However, there is no corresponding exothermic peak of precipitation in the second cooling because of supercooling. For $x(\text{Na[FTA]})$ of 0.7–0.9, the solid phase become a major component according to visual observation and a pair of exothermic and endothermic peaks, resulting from the melting of the solid phase and solidification of the melt, are observed in DSC curves. In summary,

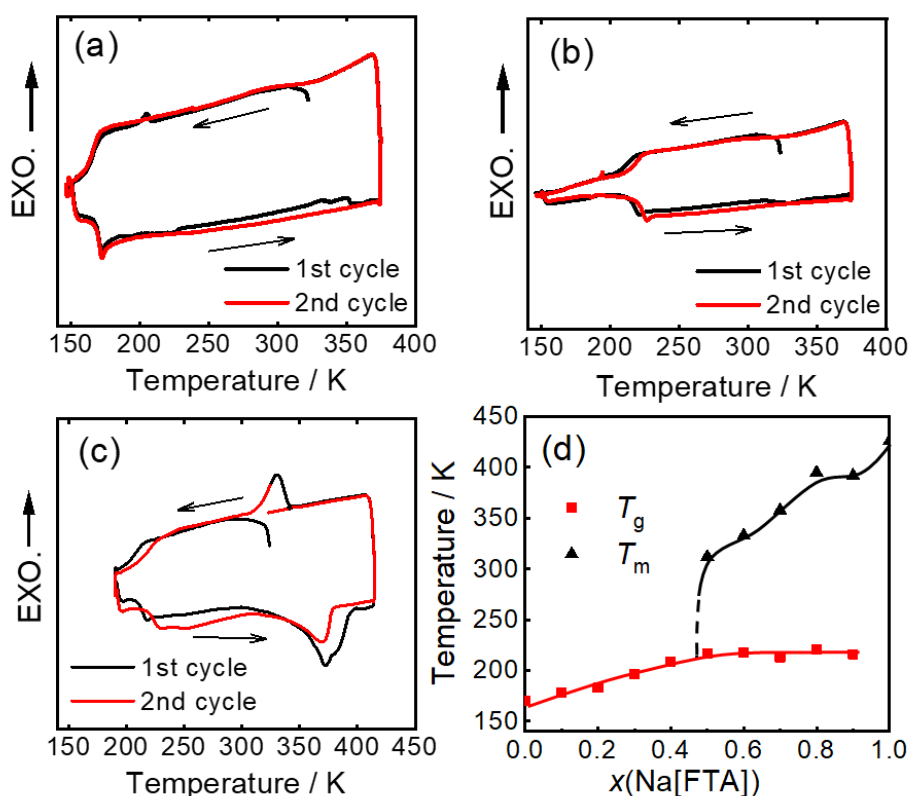


Fig. 1. DSC curves at $x(\text{Na[FTA]}) =$ (a) 0.0, (b) 0.5, (c) 0.7, and (d) the resultant phase diagram for the Na[FTA]- $[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ system (see SI for the DSC curves at other $x(\text{Na[FTA]})$). T_g : glass transition temperature, and T_m : melting point. T_g and T_m were determined from the first cycle.

as shown in Fig. 1 (d) the phase diagram of the Na[FTA]-[C₃C₁pyrr][FTA] system is composed of glass transition and solid/liquid transition without showing any intermediate compound. The $x(\text{Na[FTA]})$ range of 0.0–0.4 that has a wide liquid-phase temperature range is selected for further transport and electrochemical investigations.

Table 1. DSC transition temperatures for the Na[FTA]-[C₃C₁pyrr][FTA] system.^a

$x(\text{Na[FSA]})$	T_g / K	T_m / K
0	170	--.
0.1	178	--
0.2	183	--
0.3	196	--
0.4	209	--
0.5	217	312
0.6	218	333
0.7	213	358
0.8	221	395
0.9	217	392
^a T_g : glass transition temperature and T_m : melting point.		

3.2. Physical properties

Figures 2 show the temperature-dependence of density, viscosity, and ionic conductivity for the Na[FTA]-[C₃C₁pyrr][FTA] system, respectively. The density values and fitting parameters are listed in Table S1. For the $x(\text{Na[FTA]})$ range of 0.0–0.4, a linear relation was obtained; densities increase with increasing $x(\text{Na[FTA]})$ and decreasing temperature. The temperature dependence of density can be fitted by the following equation (Eq. 1):

$$\rho = AT + B \quad (1)$$

where ρ and T are density and temperature, respectively, and A and B are the fitting parameters.

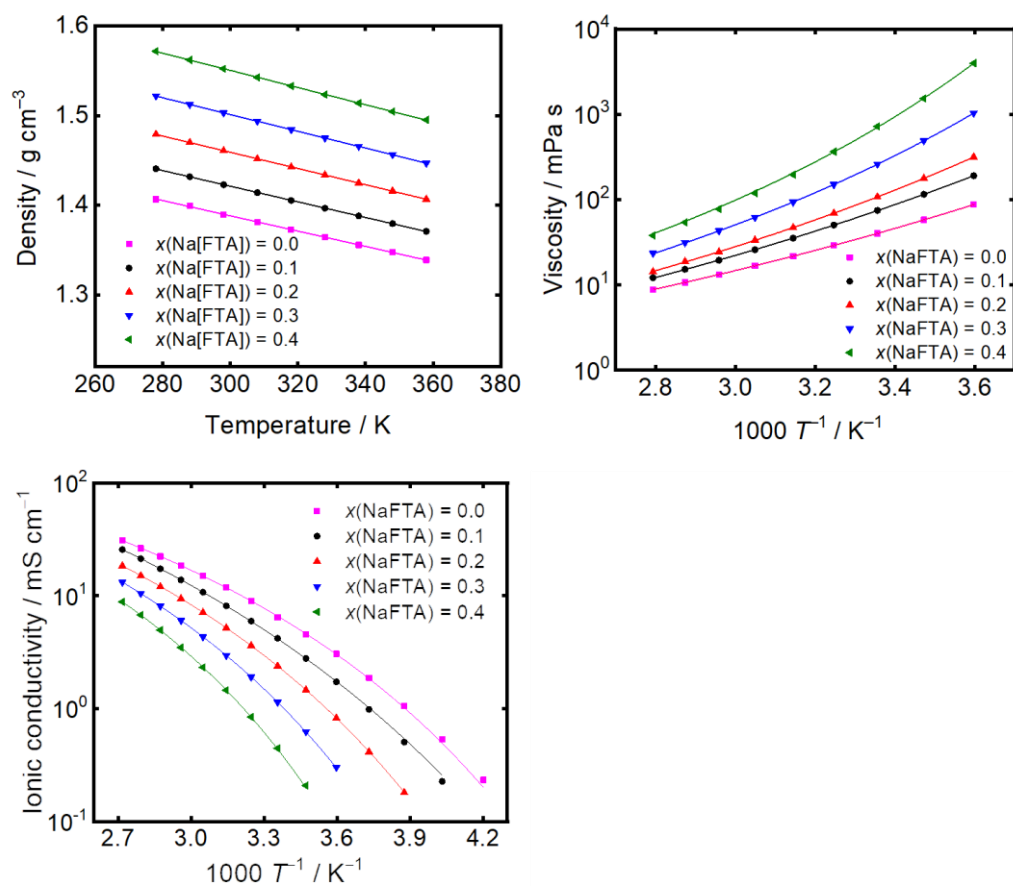


Fig. 2. Temperature dependence of (a) density, (b) viscosities, and (c) ionic conductivities of the Na[FTA]-[C₃C₁pyrr][FTA] ILs in the $x(\text{Na[FTA]})$ range of 0.0–0.4

Table 2 lists the molar concentration of Na[FTA] (mol dm^{-3}) in the Na[FTA]-[C₃C₁pyrr][FTA] system calculated from the density results and formula weight data. The $x(\text{Na[FTA]})$ at 0.1, 0.2, 0.3, and 0.4 correspond to 0.4, 0.9, 1.4, and 2.0 mol dm^{-3} at 298 K respectively, which complies with the requirement for practical cells.

Table 2. Molar concentrations (mol dm^{-3}) of the Na[FTA]-[C₃C₁pyrr][FTA] system.

T / K	$x(\text{Na[FSA]})$				
	0	0.1	0.2	0.3	0.4
278	0	0.414	0.877	1.397	1.988
288	0	0.412	0.872	1.388	1.975
298	0	0.409	0.866	1.380	1.963
308	0	0.407	0.861	1.371	1.951
318	0	0.404	0.855	1.363	1.939
328	0	0.402	0.850	1.354	1.927
338	0	0.399	0.845	1.345	1.915
348	0	0.397	0.839	1.337	1.903
358	0	0.394	0.834	1.328	1.891

Viscosities and ionic conductivities of the investigated ILs are listed in Tables S2 and S3, respectively. At 298 K, ionic conductivity decreases with increasing $x(\text{Na[FTA]})$ from 6.5 mS cm^{-1} at $x(\text{Na[FTA]}) = 0$ to 0.45 mS cm^{-1} at $x(\text{Na[FTA]}) = 0.4$. Comparison of the Na and lithium IL systems shows that the Na system has a slightly higher or equivalent ionic conductivities compared to the lithium system (at 298K, 4.2 mS cm^{-1} for Na[FTA]-[C₃C₁pyrr][FTA] at $x(\text{Na[FTA]}) = 0.1$ and 3.7 mS cm^{-1} at $x(\text{Na[FTA]}) = 0.4$).

cm⁻¹ for Li[FTA]-[C₃C₁pyrr][FTA] at $x(\text{Li[FTA]}) = 0.1$). The ionic conductivities of the Na[FTA]-[C₃C₁pyrr][FTA] system show slightly lower values than those of the Na[FSA]-[C₃C₁pyrr][FSA] system [21] because of the substitution of fluorine atom by a bulky trifluoromethyl group. This disadvantage can be compensated by intermediate-temperature operation, as ionic conductivity rapidly increases with increasing temperature (for instance, 2.4 mS cm⁻¹ at 298 K, 9.4 mS cm⁻¹ at 338 K, and 18.4 mS cm⁻¹ at 368 K for $x(\text{Na[FTA]})$ of 0.2). Temperature dependence of viscosity and ionic conductivity obey the Vogel-Tammann-Fulcher(VTF) equation [33-35], which can be fitted by Eqs. 2 and 3 with the fitting parameters A_η , B_η , $T_{0\eta}$, A_σ , B_σ , and $T_{0\sigma}$ ($R^2 > 0.999$; refer to Tables S4 and S5).

$$\eta(T) = A_\eta \sqrt{T} \exp\left(\frac{B_\eta}{T - T_{0\eta}}\right) \quad (2)$$

$$\sigma(T) = A_\sigma \sqrt{T}^{-1} \exp\left(\frac{B_\sigma}{T - T_{0\sigma}}\right) \quad (3)$$

Deviation from the linear Arrhenius behavior in Fig. 2 (concave for viscosity and convex for ionic conductivity) was widely observed for pure ILs and metal ion containing ILs in previous works [36-39]. This behavior is interpreted by including the effects of glass transition with the concept of fragility which refers to the rate at which the transport properties change with temperature near the glass transition; the liquids with high and low fragilities are called fragile and strong, respectively. Although physical interpretation of fragility is not completely clear yet, the rapid change in transport properties of ions near glass transition is considered to cause the VTF behavior. The $T_{0\eta}$ and $T_{0\sigma}$ parameters are

the ideal glass-transition temperature and usually lower than the glass-transition temperature observed by DSC analysis. $T_{0\eta}$ and $T_{0\sigma}$ show the same trends against $x(\text{Na[FTA]})$ with the T_g observed in Fig. S1. Concerning the ion transport properties of electrolytes, Fig. S3 shows the correlation between molar ionic conductivity (λ) and viscosity (η) connected by the fractional Walden rule (see Supporting Information for additional discussion on the Walden plot).

3.3. Electrochemical stability

The anodic stability of the Na[FTA]-[C₃C₁pyrr][FTA] ILs was identified by linear sweep voltammetry (LSV) using a coin-cell with Pt working and Na counter electrodes. Fig. S4 (a, b) shows the LSV results at 298 and 363 K. When the current flowing through the cell reached 0.1 mA cm⁻², the corresponding potential is recognized as an anodic limit [15]. The anodic potential limit of 5.4–5.5 V vs. Na⁺/Na is observed at 298 K at any $x(\text{Na[FTA]})$. In this case, decomposition of component ions causes oxidation currents at the anodic limit, and Na ion concentration seems to have a minor influence on it, agreeing with other IL systems [40]. However, the Na[FTA]-[C₃C₁pyrr][FTA] ILs become less stable against anodic decomposition at elevated temperature; the anodic limit is 5.1–5.3 V vs. Na⁺/Na at 363 K, reflecting the lower kinetic barrier to oxidize the ILs. The wide anodic limit over 5 V vs. Na⁺/Na still fits the requirement for a practical positive electrode material in Na secondary batteries.

Compatibility of Al electrodes as current collectors for positive electrodes was investigated by cyclic voltammetry in the Na[FTA]-[C₃C₁pyrr][FTA] IL at different $x(\text{Na[FTA]})$. As shown in Fig. S5, the IL with the $x(\text{Na[FTA]})$ range of 0.1–0.4 shows similar anodic behavior. The anodic current of 3–

$4 \mu\text{A cm}^{-2}$ in the first anodic scan is attributed to the formation of the passivation layer. During this anodic reaction, Al surface is oxidized and forms sulfonyl-amide containing species. Different from organic solutions, the solubility of this species into ILs is small, and further anodic reaction is limited [9, 27]. The negligible currents (less than $1 \mu\text{A cm}^{-2}$ at 5.5 V vs. Na^+/Na) in the subsequent cycles prove the high compatibility of Al current collector to the $\text{Na}[\text{FTA}]\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ ILs.

Sodium metal deposition-dissolution test of Na/Na symmetric cells is a facile method to identify the electrochemical performance in terms of overpotential for different electrolytes. The performance of various electrolyte compositions is exclusively evaluated at the Na electrodes, independent of any positive electrode [41, 42]. Besides, among the battery community, metal electrodes are widely used as counter electrodes in two-electrode type cells for mostly laboratory-scaled researches. Therefore, clarifying the contribution of Na counter electrodes on electrochemical performance in a given electrolyte is also inevitable. The deposition-dissolution was cycled in the $x(\text{Na}[\text{FTA}])$ range of 0.1–0.4 with a sequence of constant currents of 10, 50, 100, 500, 1000, and $3000 \mu\text{A cm}^{-2}$ for 10 cycles at each value. For each cycle, 8-min deposition (or dissolution) and 2-min rest were applied (20 min per cycle). The obtained voltage profiles at 298 and 363 K are shown in Fig. 3. The recorded overpotential of the Na/Na cells is attributed to several factors, including bulk resistance of Na-ion transport, resistance of surface film on Na electrodes, and charge transfer resistance [42, 43]. At 298 K, the polarization significantly decreases and is stabilized with increasing $x(\text{Na}[\text{FTA}])$ in spite of the lower ionic conductivity at high $x(\text{Na}[\text{FTA}])$. The major reason for this trend is the lower interfacial

resistance at high $x(\text{Na[FTA]})$, agreeing with previous reports [42-44]. The polarization of the Na/Na symmetric cells decreases dramatically at 363 K (note the difference in the range of the horizontal axis in Fig. 3). Only the overpotential of 0.04–0.09 V was observed even at $1000 \mu\text{A cm}^{-2}$. Although the ion mobility in the IL electrolyte is increased at elevated temperature (see temperature dependence of ionic

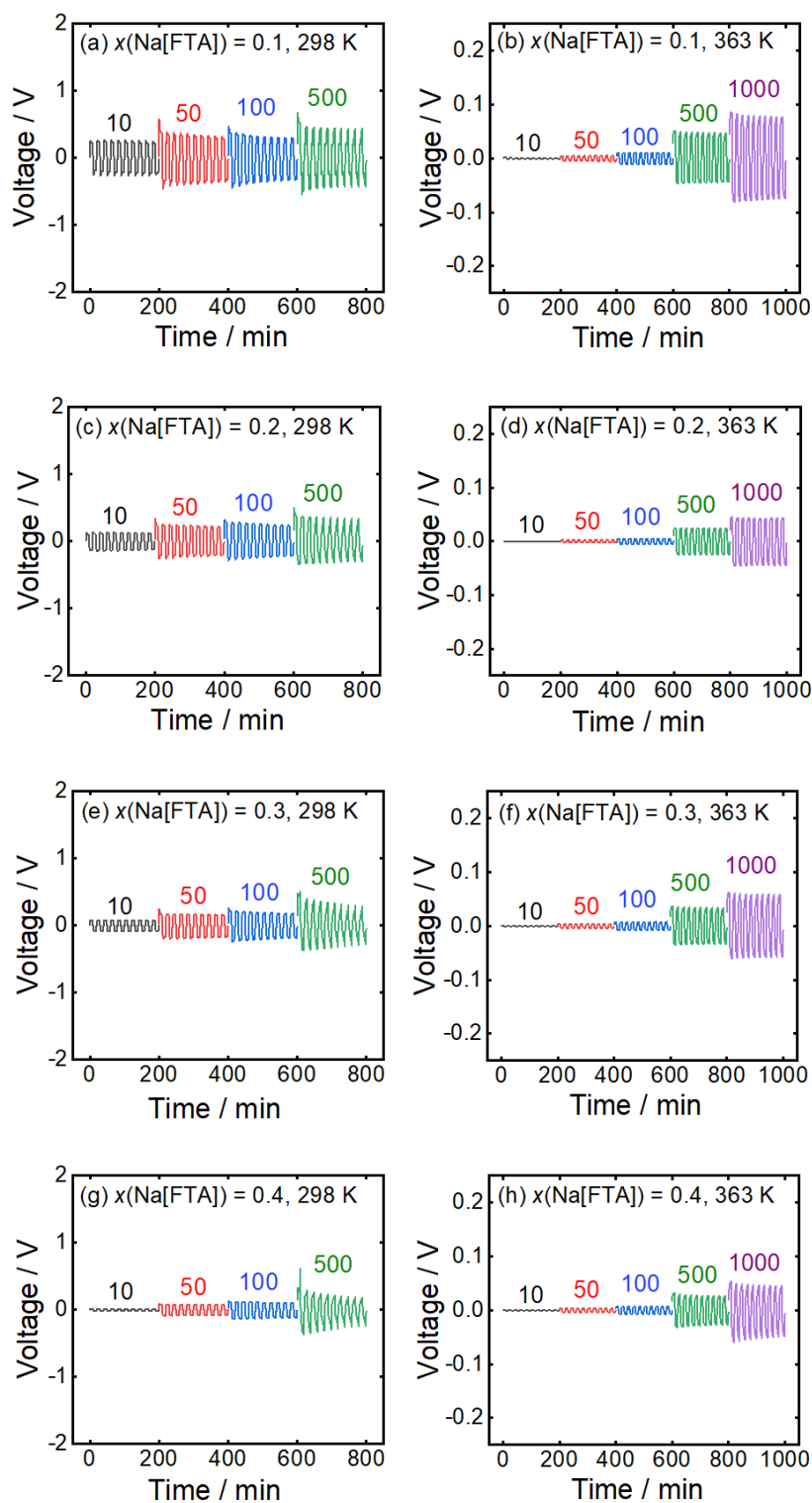


Fig. 3. Na/Na symmetrical cell polarization voltage profiles at 298 and 363 K with the Na[FTA]-[C₃C₁pyrr][FTA] ILs ($x(\text{Na[FTA]})$) = (a, b) 0.1, (c, d) 0.2, (e, f) 0.3, and (g, h) 0.4). The unit of current density is $\mu\text{A}\cdot\text{cm}^{-2}$.

conductivity above), enhanced interfacial properties, including ion migration in SEI films and charge transfer, mainly contribute to this behavior [31, 45]. The concentration dependence is not obvious at 363 K, and similar polarization values, which are lower than that at $x(\text{Na[FTA]}) = 0.1$, were obtained for $x(\text{Na[FTA]})$ of 0.2–0.4. In brief summary, elevated temperature promotes the Na metal deposition-dissolution behavior, whereas $x(\text{Na[FTA]})$ also has an impact on the degree of polarization. Further discussions will be done with EIS results in the next section.

3.5. EIS of Na/Na symmetric cells.

Fig. 4 shows the EIS results of Na symmetric cells in the Na[FTA]-[C₃C₁pyrr][FTA] ILs in the temperature range of 298–363 K. These Nyquist plots are recorded after three charge/discharge cycles at a current density of 10 $\mu\text{A cm}^{-2}$ for 8 min during each charge and discharge period in order to form a stable SEI layer. A slightly depressed semicircle was obtained at all $x(\text{Na[FTA]})$ values and temperatures. This may indicate that multiple factors contribute to resistances at electrolyte/Na interface, including naturally formed passivation layer, SEI film, and charge transfer. However, it is hard to distinguish them clearly in the case of Na electrodes. Fig. 4 (d) shows the simplified equivalent circuit used for fitting. The R_{bulk} and R_{int} parameters are the electrolyte and interfacial resistances (including resistance of surface films and charge transfer), respectively.

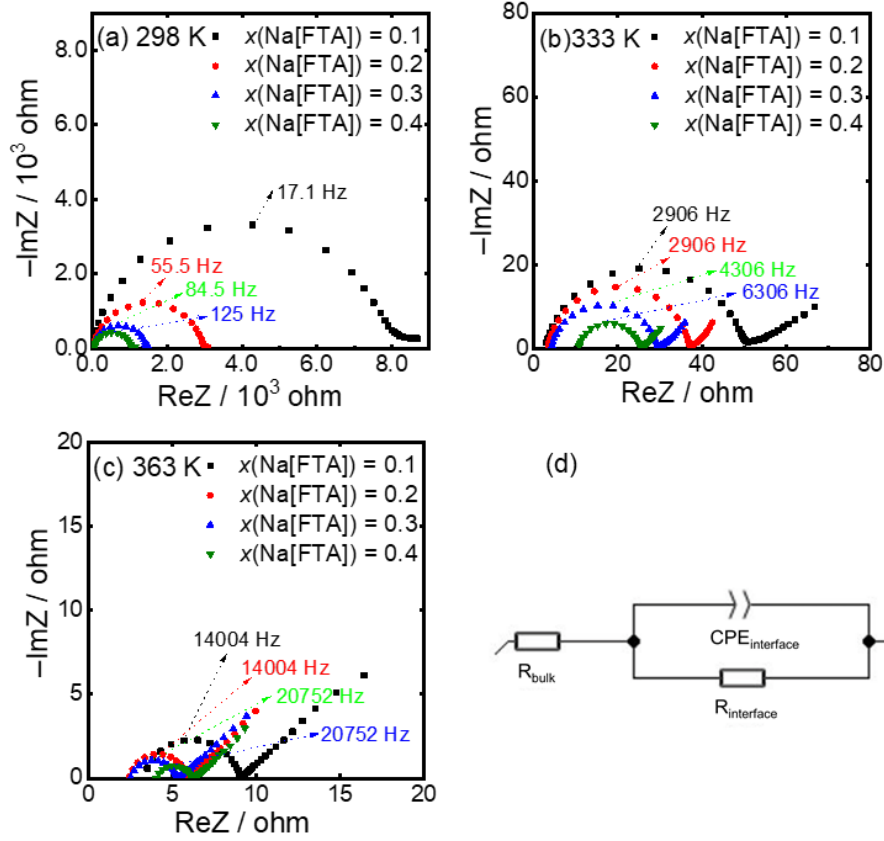


Fig. 4. Nyquist plots of the Na/Na symmetric cells with the Na[FTA]-[C₃C₁pyrr][FTA] ILs ($x(\text{Na[FTA]}) = 0.1\text{--}0.4$) at (a) 298 K (characteristic frequencies are 17.1 Hz for $x(\text{Na[FTA]}) = 0.1$, 55.5 Hz for $x(\text{Na[FTA]}) = 0.2$, 84.5 Hz for $x(\text{Na[FTA]}) = 0.3$, 125 Hz for $x(\text{Na[FTA]}) = 0.4$), (b) 333 K (characteristic frequencies are 2906 Hz for $x(\text{Na[FTA]}) = 0.1$, 2906 Hz for $x(\text{Na[FTA]}) = 0.2$, 4306 Hz for $x(\text{Na[FTA]}) = 0.3$, 6306 Hz for $x(\text{Na[FTA]}) = 0.4$), and (c) 363 K (characteristic frequencies are 14004 Hz for $x(\text{Na[FTA]}) = 0.1$, 14004 Hz for $x(\text{Na[FTA]}) = 0.2$, 20752 Hz for $x(\text{Na[FTA]}) = 0.3$, 20752 Hz for $x(\text{Na[FTA]}) = 0.4$), in the frequency range of 100 kHz–10 mHz. (d) Equivalent circuit. AC amplitude = 10 mV.

The fitting results are listed in Table 3. The diffusion components were not fitted here as it made the fitting unstable. The large R_{int} with the characteristic frequencies of 150–10 Hz suggests that charge transfer dominates the interfacial behavior at 298 K [43] and explains the huge polarization of the Na symmetric cells at 298 K (see Fig. 3). Regarding the effect of Na ion concentration, a negative correlation was observed for R_{int} ; R_{int} decreases as $x(\text{Na[FTA]})$ increases. Furthermore, the characteristic frequency shifts from 17.1 Hz ($x(\text{Na[FTA]}) = 0.1$) to 125 Hz ($x(\text{Na[FTA]}) = 0.4$) at 298

Table 3. Fitting results of the EIS for the Na/Na symmetric cells with the Na[FTA]-[C₃C₁pyrr][FTA] system (Fig. 4).^a

$x(\text{Na[FTA]})$		0.1	0.2	0.3	0.4
298 K	R_{bulk} / Ω	7.2	12	23	40
	R_{int} / Ω	7758	2938	1432	996
	$C.F. / \text{Hz}$	17.1	55.5	84.5	125
	$Q / \text{F s}^{\alpha-1}$	1.46×10^{-6}	2.03×10^{-6}	2.62×10^{-6}	2.65×10^{-6}
	α	0.93	0.89	0.91	0.90
333 K	R_{bulk} / Ω	2.7	3.5	4.2	11
	R_{int} / Ω	48	33	25	15
	$C.F. / \text{Hz}$	2906	2906	4306	6306
	$Q / \text{F s}^{\alpha-1}$	3.84×10^{-6}	3.19×10^{-6}	4.26×10^{-6}	7.02×10^{-6}
	α	0.89	0.94	0.91	0.88
363 K	R_{bulk} / Ω	3.43	2.58	2.62	4.22
	R_{int} / Ω	5.63	3.17	2.66	2.18
	$C.F. / \text{Hz}$	1.4×10^4	1.4×10^4	2.1×10^4	2.1×10^4
	$Q / \text{F s}^{\alpha-1}$	4.44×10^{-6}	3.36×10^{-6}	7.91×10^{-6}	42.2×10^{-6}
	α	0.93	1	0.94	0.82

^a $C.F.$, Q , and α denote characteristic frequency, CPE parameter, and CPE exponent, respectively.

K. This phenomenon reveals that R_{int} gradually decreases with increasing $x(\text{Na[FTA]})$, coinciding with the voltage profiles of Na symmetric cells at current densities of $10\text{--}500 \mu\text{A cm}^{-2}$ at 298 K.

The temperature dependence of EIS results was also investigated. At 333 K and 363 K, Na symmetric cells with $x(\text{Na[FTA]}) = 0.1\text{--}0.4$ exhibit a remarkable decrease in R_{int} and R_{bulk} with increasing temperature. Elevated temperatures can activate the interfacial electrochemical process, which agrees with the low polarization of the Na/Na symmetric cells at 363 K (Fig. 3). In addition, the

characteristic frequencies of the semicircles shift to 3000–20000 Hz at elevated temperature. Because the surface film is observed at a higher frequency than that of charge transfer, this change indicates that the semicircle in the present Nyquist plots has two contributions, charge transfer and surface film, and the surface film becomes the major contribution at elevated temperatures [43]. Concerning transport properties of the investigated ILs, R_{bulk} is relatively smaller than R_{int} at 298 K and 333 K, however, the $R_{\text{bulk}}/R_{\text{int}}$ ratio in the total resistance is relatively large at 363 K. When considering the total resistance of $R_{\text{bulk}} + R_{\text{int}}$, the values of 9.06, 5.75, 5.28, and 6.40 ohm were obtained for $x(\text{Na}[\text{FTA}])$ of 0.1–0.4 at 363 K, respectively. Na symmetric cells at $x(\text{Na}[\text{FTA}]) = 0.1$ shows the largest resistance among all the tested $x(\text{Na}[\text{FTA}])$. Similar values of total resistance were obtained in $x(\text{Na}[\text{FTA}])$ of 0.2–0.4, which coincides with the similar polarization results during deposition/dissolution tests of Na/Na symmetric cells at 363 K (Fig. 3 (d, f, h)).

3.6. Na Metal Deposition/Dissolution on Al electrode.

Since the results of Na metal deposition/dissolution and EIS based on Na/Na symmetric cells have difficulties to estimate Na metal deposition/dissolution efficiency, Na metal deposition/dissolution test on Al electrode was also examined. Fig. 5 shows the voltage profiles during Na metal deposition/dissolution test in $\text{Na}[\text{FTA}]\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{FTA}]$ with $x(\text{Na}[\text{FTA}]) = 0.1\text{--}0.4$ at 363 K. For comparison, $\text{Na}[\text{FSA}]\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ ($x(\text{Na}[\text{FSA}]) = 0.1$) and $\text{Na}[\text{TFSA}]\text{-}[\text{C}_3\text{C}_1\text{pyrr}][\text{TFSA}]$ ($x(\text{Na}[\text{TFSA}]) = 0.1$) were also tested in the same condition (the Na salt fraction of 0.1 was selected

because of the limited solubility of Na[TFSA] into [C₃C₁pyrr][TFSA]). The cycle efficiency of Na deposition/dissolution (ϵ_{cycle}) was evaluated by Eq. (4):

$$\epsilon_{\text{cycle}} = N_{\text{eff}} \cdot Q_{\text{cycle}} / (Q_{\text{ex}} + N_{\text{eff}} \cdot Q_{\text{cycle}}) \quad (4)$$

where N_{eff} is the number of cycles until the electrode potential reaches 0.5 V vs. Na⁺/Na, Q_{cycle} is the electric charge for each cycle of Na deposition/dissolution (0.02 C cm⁻²), and Q_{ex} is the extra amount of electricity deposited just before starting cycling (0.08 C cm⁻²).

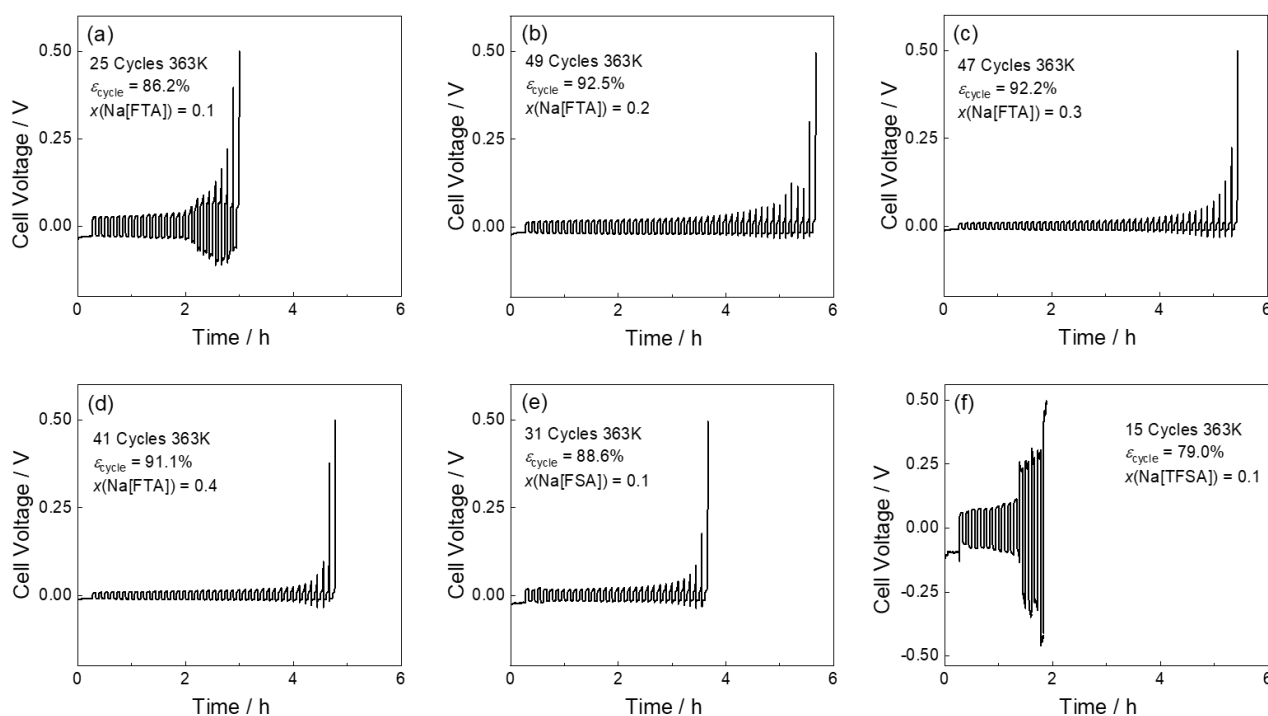


Fig. 5. Voltage profiles during Na deposition/dissolution at 363 K in (a–d) Na[FTA]-[C₃C₁pyrr][FTA] at $x(\text{Na[FTA]}) = 0.1$ – 0.4 , (e) Na[FSA]-[C₃C₁pyrr][FSA] at $x(\text{Na[FSA]}) = 0.1$, and (f) Na[TFSA]-[C₃C₁pyrr][TFSA] at $x(\text{Na[TFSA]}) = 0.1$. The working and counter electrodes were Al and Na plates, respectively. Na metal of 0.08 C cm⁻² was deposited on the Al substrate, and 0.02 C cm⁻² Na deposition and dissolution was repeated until the electrode potential reached 0.5 V vs. Na⁺/Na during dissolution (see Experimental Section). The current density was ± 0.1 mA cm⁻² for all tests.

An increase in $x(\text{Na[FTA]})$ from 0.1 to 0.3 improves ϵ_{cycle} and alleviate the overpotential of each Na metal deposition/dissolution cycle from 0.03 to 0.01 V. The maximum ϵ_{cycle} is achieved at

$x(\text{Na}[\text{FTA}]) = 0.2$ (92.5%) and 0.3 (92.2%), in contrast to 86.2% at $x(\text{Na}[\text{FTA}]) = 0.1$. The benefit of SEI formation by a high fraction of Na^+ in the electrolyte deriving from a stable supply of Na^+ at the electrode. Consequently, high $x(\text{Na}[\text{FTA}])$ facilitates SEI-layer stabilization and suppresses dendrite formation giving a high ϵ_{cycle} as result. The ϵ_{cycle} at $x(\text{Na}[\text{FTA}]) = 0.4$ slightly decreases to 91.1%, but the overpotential of Na metal deposition/dissolution cycles could still be held around 0.01 V. The Na[FSA]-[C₃C₁pyrr][FSA] electrolyte at $x(\text{Na}[\text{FSA}]) = 0.1$ exhibits a similar ϵ_{cycle} value to that of the Na[FTA]-[C₃C₁pyrr][FTA] electrolyte at $x(\text{Na}[\text{FTA}]) = 0.1$ with a smaller overpotential. On the other hand, the Na[TFSA]-[C₃C₁pyrr][TFSA] ($x(\text{Na}[\text{TFSA}]) = 0.1$) apparently shows an inferior ϵ_{cycle} with large overpotential. Instability of the TFSA system against reduction was suggested in previous works [10], which was interpreted by the formation of unstable radical anion according to an electron paramagnetic resonance analysis [11]. Comparison of the present three cases with FTA⁻, FSA⁻, and TFSA⁻ indicates that even substitution of one trifluoromethyl group with F atom [10] results in formation of stable SEI [46] on Na metal.

3.7. Electrochemical behavior of hard carbon.

Performance of the Na[FTA]-[C₃C₁pyrr][FTA] system was further studied in terms of the reversibility of HC negative electrode. Fig. 6 shows the charge-discharge curves of Na/HC cells with the IL at $x(\text{Na}[\text{FTA}])$ of 0.1–0.4 at 363 K (charge-discharge rate: 20 mA g⁻¹) and the corresponding dQ/dV plot. The first charge-discharge curves can be classified into several parts. A short plateau is

observed at 1.3–1.0 V during the initial charge (sodiation), which is attributed to the reductive decomposition of the electrolyte and SEI film formation [31]. The following sloping region

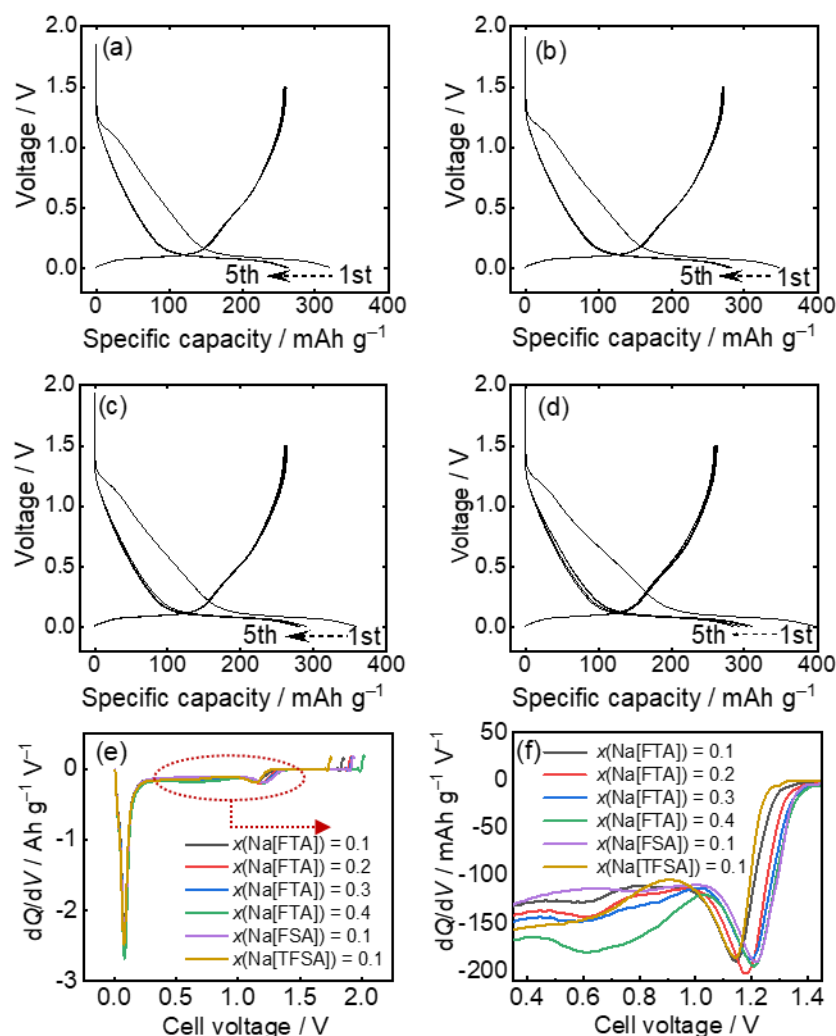


Fig. 6. Charge-discharge curves of the Na/HC cells with the Na[FTA]-[C₃C₁pyrr][FTA] ILs at 363 K. Charge-discharge rate: 20 mA g⁻¹. $x(\text{Na[FTA]}) =$ (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4. The corresponding differential capacity vs. voltage (dQ/dV) plots (e, f) show the first charge cycle behavior with those observed for Na[FSA]-[C₃C₁pyrr][FSA] at $x(\text{Na[FSA]}) = 0.1$ and Na[TFSA]-[C₃C₁pyrr][TFSA] at $x(\text{Na[TFSA]}) = 0.1$. (see Fig. S6 for the corresponding (dQ/dV) plots of the 5th charge-discharge cycle).

from 1.2 to 0.1 V and the plateau below 0.1 V is assigned to Na⁺ insertion/extraction between graphene layers and nanopore within HC, respectively, according to the previous work [47]. The subsequent

initial discharge curve has the corresponding electrochemical behavior. The Na/HC cells show similar discharge capacities of 260–270 mAh g⁻¹ regardless of $x(\text{Na[FTA]})$, whereas the charge capacities are significantly different. The discharge capacities obtained in this study are similar to that obtained with the same HC material in a previous work [31].

Table 4. Coulombic efficiencies (%) of the Na/HC cells with $x(\text{Na[FTA]}) = 0.1\text{--}0.4$ at the charge-discharge rate of 20 mA g⁻¹ from the initial to fifth cycles.

$x(\text{Na[FTA]})$	0.1	0.2	0.3	0.4
1st.	81.3	78.3	73.8	65.4
2nd	98.4	96.1	90.9	83.3
3rd	98.7	96.8	92.9	86.0
4th	98.9	97.2	93.3	89.4
5th	99.1	97.3	93.7	92.4

The Coulombic efficiencies of the initial five cycles at $x(\text{Na[FTA]})$ of 0.1–0.4 are listed in Table 4. The Na/HC cell at $x(\text{Na[FTA]}) = 0.1$ exhibits a high Coulombic efficiency of 81.3% in the first cycle and quickly reaches a stable state in the subsequent cycles (Coulombic efficiency > 99%). The Coulombic efficiency decreases with increasing $x(\text{Na[FTA]})$, giving the initial Coulombic efficiency of 65.4% at $x(\text{Na[FTA]}) = 0.4$. Even in the fifth cycle, the Coulombic efficiency does not efficiently improve at $x(\text{Na[FTA]}) = 0.4$ (92.4%), indicating the unstable SEI formation at high $x(\text{Na[FTA]})$. In an organic electrolyte (Na[FSA]-succinonitrile), a different behavior was observed; an increase of

Na[FSA] concentration stabilizes the Na/HC cell and leads to the higher Coulombic efficiency [48].

These results imply that particular irreversible reactions, triggered by increasing $x(\text{Na[FTA]})$, occur during the charging process on HC. The corresponding dQ/dV plots of the first and fifth cycles in Fig. 6 and Fig. S6 were used to confirm the voltage location of this particular irreversible reaction. As shown in Fig. 6 (f), during the first charge, the peak of SEI formation located around 1.2 V monotonously move to high voltage value with increasing $x(\text{Na[FTA]})$, indicating the increasing $x(\text{Na[FTA]})$ is preferable for the SEI film formation with lower reaction barrier. However, a broad peak around 0.6 V becomes more and more obvious with increasing $x(\text{Na[FTA]})$ and disappears in the following cycles (see Fig. S6 for the fifth cycle), which confirms additional irreversible reactions including severe decomposition of ILs occurs especially at $x(\text{Na[FTA]}) = 0.4$. Electrolyte decomposition was also observed during the initial charging for the HC electrode in an organic electrolyte, resulting in the constant deterioration of cycle performance from the early cycles [47].

Such a decomposition peak does not appear with FSA^- but does with TFSA^- (see Fig. 6 (f)), indicating that the CF_3 group on the sulfonylamide causes this decomposition reaction in this voltage range.

Further research is needed for clarifying the reduction mechanism of FTA^- -based ILs.

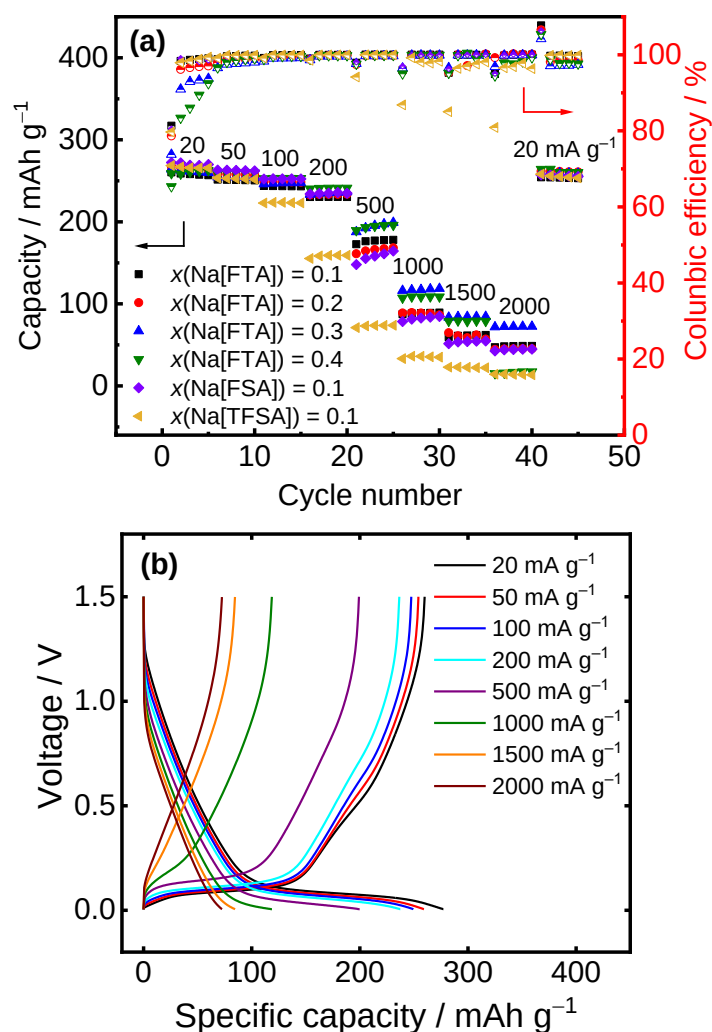


Fig. 7. (a) Rate capability of the Na/HC cells with Na[FTA]-[C₃C₁pyrr][FTA] at $x(\text{Na[FTA]}) = 0.1\text{--}0.4$, Na[FSA]-[C₃C₁pyrr][FSA] at $x(\text{Na[FSA]}) = 0.1$ and Na[TFSA]-[C₃C₁pyrr][TFSA] at $x(\text{Na[TFSA]}) = 0.1$ at 363 K. (b) Charge-discharge curves of the Na/HC cell (5th cycle at each rate) in the Na[FTA]-[C₃C₁pyrr][FTA] IL at $x(\text{Na[FTA]}) = 0.3$ in charge-discharge rate from 20 to 2000 mA g⁻¹ at 363 K. Cut-off voltages: 0.005–1.5 V. Coulombic efficiency is plotted with half-filled marks. See Fig. S7 for charge-discharge curves of $x(\text{Na[FTA]}) = 0.1, 0.2$, and 0.4 , Na[FSA]-[C₃C₁pyrr][FSA] at $x(\text{Na[FSA]}) = 0.1$ and Na[TFSA]-[C₃C₁pyrr][TFSA] at $x(\text{Na[TFSA]}) = 0.1$. See Fig. S8 for the corresponding differential capacity vs. voltage (dQ/dV) plots of each charge-discharge rate at $x(\text{Na[FTA]}) = 0.3$.

Figure 7 shows the rate capability of the Na/HC cells at $x(\text{Na[FTA]}) = 0.1\text{--}0.4$ at 363 K. The data with Na[FSA] and Na[TFSA] are also shown for comparison ($x(\text{Na[FSA]}) = 0.1$ and $x(\text{Na[TFSA]}) =$

0.1). As shown in Fig. 7 (a), the capacity gradually decreases with an increasing rate up to 200 mA g^{-1} . A capacity of $230\text{--}270 \text{ mA g}^{-1}$ was obtained within this range of charge-discharge rates. In contrast, at high charge-discharge rates, $x(\text{Na[FTA]})$ considerably influences the discharge capacities of the Na/HC cells; with increasing rate, the Na/HC cell at $x(\text{Na[FTA]})$ of 0.3 provides the highest discharge capacities among all the investigated $x(\text{Na[FTA]})$ values. Fig. 7 (b) shows charge-discharge curves of the Na/HC cell with the Na[FTA]-[C₃C₁pyrr][FTA] IL ($x(\text{Na[FTA]}) = 0.3$) during rate test at 363 K (see Fig. S7 for the curves at other $x(\text{Na[FTA]})$ and those with FSA[−] and TFSA[−] ILs), giving the discharge capacity of 238 mAh g^{-1} at 200 mA g^{-1} (Coulombic efficiency > 99%) with about 91% capacity retention based on the initial capacity at 20 mA g^{-1} . The general charge-discharge curves of HC remain similar within a rate range of $20\text{--}500 \text{ mA g}^{-1}$. At high rates, the capacity of the plateau region around 0.1 V is gradually decreased, and polarization becomes more and more severe with increasing rate (Fig. S7), whereas capacity acquired during the sloping region is less sensitive to rate. The capacity decay at high rates is governed by the polarization based on interfacial reactions (Na metal and HC electrodes) and ion transport in the electrolyte. As was observed in the results of the Na/Na symmetric cell tests, the polarization at the Na metal electrode does not notably differ above $x(\text{Na[FTA]})$ of 0.3. Thus, the rate performance is dependent on the interfacial reaction at the HC electrode and ion transport. Because the high R_{bulk} at high $x(\text{Na[FTA]})$ (corresponding to the low ionic conductivity at high $x(\text{Na[FTA]})$ in Table S3) works against the rate performance, the appearance of the maximum rate performance at $x(\text{Na[FTA]}) = 0.3$ suggests the improved interfacial reaction at the

HC electrode at high $x(\text{Na[FTA]})$. Although rate performance for the FTA and FSA IL, $x(\text{Na[FTA]}) = 0.1$ and $x(\text{Na[FSA]}) = 0.1$, are similar to each other, the rate performance of the TFSA IL ($x(\text{Na[TFSA]}) = 0.1$) is obviously worse. True evaluation for the TFSA system requires a trustable counter electrode because high polarization and low $\varepsilon_{\text{cycle}}$ mentioned for the Na metal electrode (Fig. 5).

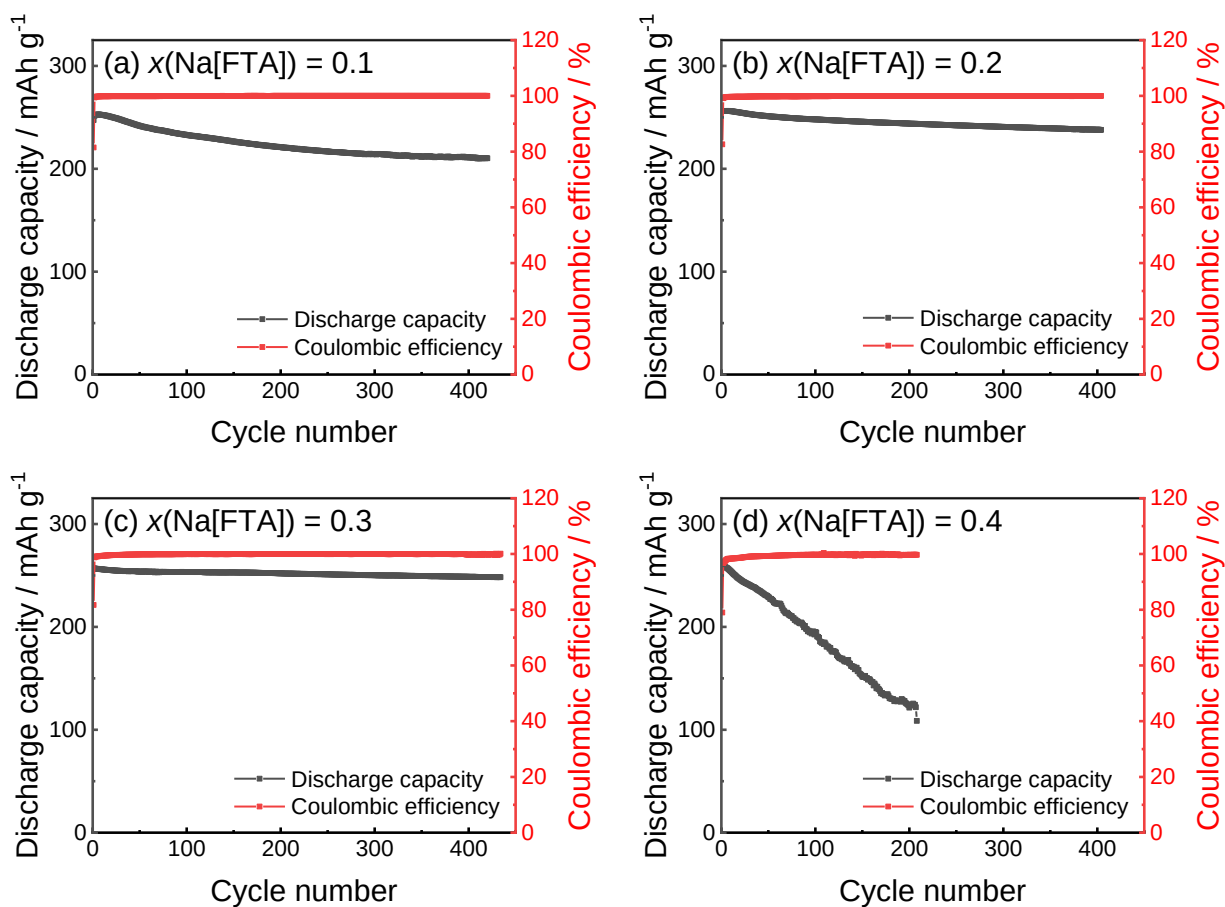


Fig. 8. Cycling performance of the HC electrode at 363 K. Electrolyte: $\text{Na[FTA]}-\text{[C}_3\text{C}_1\text{pyrr] [FTA]}$ with $x(\text{Na[FSA]}) =$ (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4. Current rate: 200 mA g^{-1} . Cut-off voltages: 0.005–1.5 V. See Fig. S9 for charge-discharge curves and corresponding differential capacity vs. voltage (dQ/dV) plots at 200th cycle for $x(\text{Na[FTA]}) = 0.1\text{--}0.4$.

Figure 8 shows the cycling performance of the Na/HC cell with the IL at $x(\text{Na[FTA]}) = 0.1\text{--}0.4$ at 200 mA g^{-1} . Capacity retentions of 84.2, 93.1, and 97.0% are achieved at 363 K after 400 cycles for

$x(\text{Na[FTA]}) = 0.1, 0.2$ and 0.3 , respectively, providing 99.9% average Coulombic efficiency. The discharge capacity at $x(\text{Na[FTA]}) = 0.4$ is constantly deteriorated from the early cycles with the capacity retentions of 48.2% at the 200th cycle. The capacity retention increases with increasing $x(\text{Na[FTA]}) = 0.1\text{--}0.3$, however, decreases at $x(\text{Na[FTA]}) = 0.4$. Fig. S9 shows the charge-discharge curves and corresponding dQ/dV plots of the 200th cycle, which can be compared with the 5th cycle (see Fig. S6 for dQ/dV plots of the 5th cycle), illustrating the influence of $x(\text{Na[FTA]})$ on cycle capability. For $x(\text{Na[FTA]}) = 0.1\text{--}0.3$, a clear and long plateau was observed around 0.1 V at the 200th cycle in Fig. S9 (a, b, and c). Combining the corresponding dQ/dV plots at the 200th cycle in Fig. S9 (e), the polarization of $x(\text{Na[FTA]}) = 0.2\text{--}0.3$ is alleviated comparing with $x(\text{Na[FTA]}) = 0.1$ indicating high concentration of Na[FTA] have a positive impact on cycle performance. In contrast, the capacity obtained in the plateau region of $x(\text{Na[FTA]}) = 0.4$ is considerably reduced at the 200th cycle, while the capacity in the sloping region based on Na^+ insertion is similar at any $x(\text{Na[FTA]})$. The capacity achieved at the plateau is attributed to the reversible Na insertion into the nanopores, in which the plateau features are affected on $x(\text{Na[FTA]})$ in the present IL system. High $x(\text{Na[FTA]})$ of 0.4 has difficulties in the Na insertion into the nanopores, which could be related to the unfavorable decomposition of ILs during the formation of SEI film in the first cycle as shown in Fig. 6 (f). Details on the decomposition process is not clear in the current stage, but the decomposition products slowly deposit during cycling may block the nanopores of HC. Since the insertion into the nanopores is essential to capacity in the Na system, high $x(\text{Na[FTA]})$ out of a certain range should be avoided for

long term stability.

4. Conclusion

This study demonstrates the thermal, transport, and electrochemical properties of the Na[FTA]-[C₃C₁pyrr][FTA] ILs in view of their applications as electrolytes in Na secondary batteries. Intermediate temperature operation is one of the targets of this work and thus electrochemical behavior was investigated at 298 and 363 K. According to DSC results, a wide liquid temperature range that holds the pure liquid phase even at 170–209 K is observed in $x(\text{Na[FTA]}) = 0.0\text{--}0.4$. Absence of crystallization behavior in such a low Na salt fraction was not observed for the previously known FSA[−] systems and is attributed to the asymmetric structure of FTA[−]. Characterization of fundamental physical properties of this system, including density, viscosity, and ionic conductivity, were conducted. Neat [C₃C₁pyrr][FTA] exhibits an ionic conductivity of 6.46 and 30.9 mS cm^{−1} at 298 K and 368 K, respectively. The viscosity and ionic conductivity obeys fractional Walden rule for $x(\text{Na[FTA]}) = 0.0\text{--}0.4$. The high anodic limit above 5 V vs. Na⁺/Na and high compatibility with an Al electrode were confirmed. Furthermore, the effect of $x(\text{Na[FTA]})$ on Na metal deposition/dissolution behavior was investigated. Na symmetric cells show better performance with the increase of $x(\text{Na[FTA]})$ and temperature. The Na metal deposition/dissolution test with Al electrode reveals the inferior SEI formation ability and less electrochemical stability of C–F bond of FTA anion. The electrochemical tests of HC electrodes showed that discharge capacities around 260–270 mAh g^{−1} are delivered at a

low rate of 20 mA g⁻¹ at 363 K with Coulombic efficiency decreasing with the increasing $x(\text{Na}[\text{FTA}])$.

A higher rate capability and stable cycle performance maintaining 97.0% capacity retention at the 400th cycle were confirmed at $x(\text{Na}[\text{FTA}]) = 0.3$, which is considered to result from the balance of the interfacial reaction and ion transport. The wide liquid temperature range derived from FTA^- is a remarkable characteristic as IL electrolytes for Na secondary batteries, and incorporation of different cationic frames is an interesting future study. The physicochemical properties of FTA-based ILs are somewhat between those of FSA- and TFSA-based ILs, whereas the electrochemical stability against reduction related to stable SEI formation was observed as for FSA-based ILs. Further studies fully making use of these advantages are required to design practical batteries.

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