Highly Concentrated NaN(SO2F)2/3-Methylsulfolane Electrolyte Solution Showing High Na-ion Transference Number under Anion-Blocking Conditions

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Abstract Graphic
Highly Concentrated NaN(SO$_2$F)$_2$/3-Methylsulfolane Electrolyte Solution Showing High Na-Ion Transference Number under Anion-Blocking Conditions

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ABSTRACT

The performance of a Na battery is significantly influenced by its electrolyte characteristics. In particular, the transport properties of the electrolyte have considerable effects on the discharge rate capability. During discharging of a Na battery at high current densities, a concentration gradient of Na salt develops because both cations and anions are mobile in the liquid electrolyte. Concentration polarization can be suppressed by increasing the Na$^+$ transference number ($t_{\text{Na}^+}$) of the electrolyte. This study demonstrates that highly concentrated NaN(SO$_2$F)$_2$ dissolved in 3-methylsulfolane (MSL) exhibits a high $t_{\text{Na}^+}$ value of $>0.6$ under anion-blocking conditions. Raman spectroscopy revealed that Na$^+$ ions formed complexes with MSL and anions in the electrolyte. Na$^+$ ions exchange ligands dynamically and move faster than the ligands, resulting in a high $t_{\text{Na}^+}$. The high $t_{\text{Na}^+}$ enables a high-rate discharge of the Na battery, despite the low ionic conductivity of the highly concentrated electrolyte.

Keywords: Sodium batteries, Ligand exchange, Transference number, Concentration polarization
1. Introduction

Na is an earth-abundant element compared to Li, and many research groups are attempting to develop high performance Na-ion batteries with the aim of replacing Li-ion batteries. The energy density of a battery is largely governed by the cathode and anode materials, and various electrode materials for Na-ion batteries have been proposed. The operating voltage of a Na-ion battery with a carbonaceous anode and a transition-metal-oxide cathode is typically in the range of 2−4 V. Therefore, in the field of Na-ion battery research, nonaqueous electrolytes containing Na salts are often used to deliver high voltages. The electrolyte also significantly influences the performance of Na-ion batteries. The ionic conductivity of the electrolyte affects the power density of a battery, and a high ionic conductivity is favorable for minimizing the internal resistance of a cell. The ionic conductivity of Na salt solutions is typically highest at a salt concentration of ~1 M (= mol dm$^{-3}$); therefore, 1 M Na salts dissolved in aprotic solvents, such as propylene carbonate (PC) and ethylene carbonate (EC), have been widely used as electrolytes. In nonaqueous solutions, Na salts dissociate into Na$^+$ and anions, and Na$^+$ complexes with the solvent to generate a solvated cation [Na(solvent)]$^+$. Weak Lewis basic anions, such as PF$_6^-$ and N(SO$_2$F)$_2^-$, are generally selected as the counter anions for Na$^+$ to enhance the dissociation of the salt in solution. With increasing salt concentration, the number of charge carriers in the electrolyte increases; however, the viscosity of the electrolyte decreases and the charge carrier mobility decreases. This trade-off relationship between the number and mobility of charge carriers results in maximum ionic conductivity being attained at a salt concentration of approximately 1 M.

Recently, highly concentrated (> 3 M) electrolytes containing alkali metal salts have been extensively investigated, despite the reduced ionic conductivity resulting from high salt concentrations. This is because highly concentrated electrolytes are reported to be thermally stable and have wide...
electrochemical windows. Wide electrochemical windows are advantageous for suppressing electrolyte side reactions and prolonging the charge-discharge life of a battery. In addition to these attractive properties, certain highly concentrated electrolytes have been reported to exhibit high cation transference numbers (> 0.5). In liquid electrolytes, both cations and anions can migrate. Conventional electrolyte solutions containing 1 M alkali metal salts are known to have low cation-transference numbers (< 0.5) because the hydrodynamic radius of a solvated cation \([M(\text{solv})]^{+}\) (M: alkali metal) is larger than that of the anion in solution. We have reported that highly concentrated solutions of alkali metal salts dissolved in sulfolane (SL) exhibit unique transport properties with cation-transference numbers of > 0.5. In these solutions, solvent-bridged \(M^{+} - \text{SL} - M^{+}\) and anion-bridged \(M^{+} - \text{anion} - M^{+}\) structures are formed, and the \(M^{+}\) ion exchanges SL and anions dynamically, moving faster than them. High cation-transference numbers result in suppressed concentration polarization in a battery during discharge at high current densities.

In this study, we report the physicochemical properties of highly concentrated Na salt solutions in 3-methylsulfolane (MSL), an asymmetric homologue of SL (Fig. 1). The properties of the binary mixtures of Na salts and SL have been previously investigated. The mixtures are prone to form crystalline solvates at a molar ratio of \([\text{Na salt}]/[\text{SL}] = 1/3\) and maintain a liquid state only within a limited composition range at room temperature. The asymmetric structure of MSL hinders solvate crystallization and widens the liquid-state composition range of the mixture. In this study, we primarily focused on the properties of sodium bis(fluorosulfonyl)amide (NaFSA) solutions in MSL because highly concentrated solutions of NaFSA can form an effective passivation layer on the negative electrode in a Na battery, while NaPF6 and sodium bis(trifluoromethanesulfonyl)amide (NaTFSA) cannot form effective passivation layers and the electrolytes gradually decompose on Na metal. The highly
concentrated NaFSA/MSL electrolyte gives rise to a high Na\(^+\) transference number \(t_{Na^+}\) and enhances the rate capability of the Na battery.

2. Experimental Section

2.1. Materials. Purified MSL (battery grade, > 98 %, [H\(_2\)O] < 30ppm), PC (battery grade, > 99.5 %, [H\(_2\)O] < 30ppm), FEC (> 99.5%, [H\(_2\)O] < 50ppm), NaFSA (battery grade, > 99 %), and NaPF\(_6\) (battery grade, > 99 %, [H\(_2\)O] <50 ppm) were purchased from Kishida Chemical and used as received. NaTFSA was synthesized by neutralization of bis(trifluoromethanesulfonyl)amide acid (HNSO\(_2\)CF\(_3\)\(_2\), Kanto Chemical, > 99.0 %) with Na\(_2\)CO\(_3\) (Wako Chemicals, >99.8 %) and dried overnight at 120 °C under vacuum.\(^{27,28}\) Electrolyte solutions were prepared by mixing salts and solvents followed by stirring at 60 °C for 24 h in an Ar-filled glovebox with [H\(_2\)O] < 1 ppm and [O\(_2\)] < 1 ppm (Nexus glove box system, Vacuum Atmospheres Company).

\(\text{Na}_{0.44}\text{MnO}_2\) was synthesized via a solid-state reaction following a previously reported procedure.\(^{28-30}\) Na\(_2\)CO\(_3\) and MnCO\(_3\) (Aldrich, > 99.9%) were mixed in a molar ratio of 0.48:2 and pressed into pellets. The obtained pellets were calcined at 300 °C for 8 h in air, followed by grinding. The resulting powder was pelletized and heat-treated again at 800 °C for 9 h in air. The synthesized \(\text{Na}_{0.44}\text{MnO}_2\) pellets were crushed into a powder and dried at 120 °C overnight.

2.2. Measurements. The thermal properties of the Na salts/MSL mixtures were investigated employing differential scanning calorimetry (DSC) using a DSC6220 or DSC7020 instrument (Hitachi High-Tech Science). DSC samples were sealed in aluminum pans in an Ar-filled glovebox. The samples were first heated to appropriate temperatures to remove the thermal hysteresis, followed by cooling to −150 °C, and finally heating to 90–120 °C at a rate of 10 °C min\(^{-1}\). The thermograms were recorded during the
final heating process. Thermogravimetric (TG) measurements were performed on a TG/DTA 7200 instrument (Hitachi High-Tech Science) to evaluate the thermal stability of the electrolyte solutions. TG measurements were performed under a N₂ atmosphere. Al₂O₃ pans were used for the FSA-containing samples to avoid corrosion of the pan during heating. Al pans were used for the other samples.

Raman spectra of the electrolytes were measured using a Raman spectrometer equipped with a 785 nm laser (NRS–4100, JASCO). The instrument was calibrated using a polypropylene standard. The electrolyte samples were sealed in a capillary glass tube, and the sample temperature was maintained at 30 °C using a TS62 Peltier microscope stage (Instec) with a temperature controller (mK1000, Instec). Raman spectra were normalized using the integrated intensity of the SO₂ scissoring vibration peak of the MSL molecule in the range of 550–600 cm⁻¹.

The density and viscosity of the electrolytes were determined using a Stabinger viscometer (SVM 3000, Anton Paar). The ionic conductivities of the electrolyte solutions were determined employing the AC impedance method using an impedance analyzer (VMP3, Biologic) in the frequency range of 500 kHz–1 Hz with an amplitude of 10 mV. A probe cell equipped with two platinized platinum electrodes (CG-511B, TOA Electronics) was used to measure the conductivity. The cell constant was determined using a 0.01 M KCl aqueous solution at 25 °C before each measurement.

The Na⁺ ion transference numbers (fNa⁺) of the electrolytes were evaluated using symmetric Na/Na cells. Na metal (Kanto Chemical, >99.0%, in kerosene) was pressed into a plate shape, cut into a circle (16 mm diameter), and washed with hexane (Wako Chemical, [H₂O] <10ppm). The disk-shaped Na-metal plates and a glass fiber filter (200 µm thick, GA-55, Advantec), which was used as the separator between the two Na-metal plates, and an electrolyte were encapsulated into a 2032-type coin cell. Chronoamperometry and AC impedance measurements were performed for the cell using an electrochemical analyzer (VMP3, Biologic).
Battery tests were conducted using 2032-type coin cells. A Na metal plate (16 mm diameter) and Na\textsubscript{0.44}MnO\textsubscript{2} were used as the negative and positive electrodes, respectively. The cells were fabricated in an Ar-filled glovebox. The Na\textsubscript{0.44}MnO\textsubscript{2} electrode was prepared as follows. Na\textsubscript{0.44}MnO\textsubscript{2}, acetylene black (Denka black, Denka Company), and poly(vinylidene fluoride) (PVdF #1100, Kishida Chemical) were mixed in a weight ratio of 80:10:10. An appropriate amount of N\textendash methyl\textendash 2\textendash pyrrolidinone (Kanto Chemical) was added for further mixing using a planetary mixer (AR-250, THINKY) to obtain a homogeneous slurry. The slurry was pasted onto an Al foil current collector using an automatic coater (K Control Coater, RK Print Coat Instruments) and dried overnight at 80 °C. The obtained Na\textsubscript{0.44}MnO\textsubscript{2} composite sheet was cut into a disk (15.95 mm diameter), uniaxially pressed at 50 MPa, and used as the positive electrode. The thickness of the composite electrode on Al foil was \~ 11 μm, and the mass loading of Na\textsubscript{0.44}MnO\textsubscript{2} was 3.3–3.5 mg cm\textsuperscript{−2}. The Na\textsubscript{0.44}MnO\textsubscript{2} sheet electrode was further dried under vacuum at 120 °C for 12 h before use. A single piece of glass fiber filter (GA−55) was used as a separator, and an electrolyte was injected before crimping the coin cell. The charge\textendash discharge tests of the Na/Na\textsubscript{0.44}MnO\textsubscript{2} cells were conducted using a battery cycler (HJ1001SD, Hokuto Denko).

3. Results and Discussion

3.1. Thermal Properties.

The phase behaviors of the binary mixtures of NaFSA and MSL are shown in Fig. 2. The melting points (\(T_m\)) and glass transition temperatures (\(T_g\)) of the mixtures were estimated from the maxima of the endothermic peaks and the onset of heat capacity changes in the differential scanning calorimetric curves (Fig. S1), respectively. As shown in Fig. 2, the \(T_m\) of NaFSA/MSL mixtures decreased with increasing NaFSA mole fraction (\(X_{\text{NaFSA}}\)) up to 0.091 ([NaFSA]/[MSL] = 1/10). The mixtures in the range of 1/7 \(\leq \)}
[NaFSA]/[MSL] ≤ 1/1 did not show a $T_m$, and only $T_g$ was observed. The $T_m$ of the [NaFSA]/[MSL] = 1/0.5 ($X_{NaFSA} = 0.667$) mixture was relatively high (107 °C), implying that a stable solvate was formed at this composition. The mixture remained in a liquid state in the composition range of $1/7 \leq [\text{NaFSA}]/[\text{MSL}] \leq 1/1$ over a wide temperature range, which is wider than the liquidus range of the NaFSA/SL mixture. NaTFSA/MSL and NaPF$_6$/MSL mixtures showed phase behavior similar to that of NaFSA/MSL (Fig. S2). According to a previous study, Na salts are prone to form stable crystalline solvates with SL at a molar ratio of [Na salt]/[SL] = 1/3; however, the Na salts (NaFSA, NaTFSA, and NaPF$_6$) investigated in this study do not form crystalline solvates with a composition of [Na salt]/[MSL] = 1/3, despite the structural similarity between the two solvents. This difference possibly originates from the asymmetric structure of MSL and the steric effect of its methyl group, which hinder the growth of an ordered packing structure and crystallization of the solvates. However, precipitation was observed in the [NaFSA]/[MSL] = 1/1 liquid after storage at room temperature. The solid-state solvate of [NaFSA]/[MSL] = 1/0.5 possibly precipitated in the liquid, but the crystal structure of the precipitate could not be analyzed due to its low crystallinity.

It is worth mentioning that highly concentrated electrolytes exhibit high thermal stabilities. The thermogravimetric (TG) analyses for the electrolytes are shown in Fig. 3. Weight loss from the [NaFSA]/[MSL] =1/2 electrolyte did not occur until ~150 °C, whereas the [NaFSA]/[MSL] =1/10 electrolyte and pure MSL lost weight at lower temperatures. For comparison, the TG curve of a conventional PC-based electrolyte (1 M NaPF$_6$/PC + 0.5 vol% fluoroethylene carbonate (FEC)) is also shown in Fig. 3. The PC-based electrolyte started to lose weight at approximately 100 °C owing to the evaporation of PC. The isothermal TG curve of [NaFSA]/[MSL] =1/2 measured at 100 °C showed < 5% weight loss over 60 min (Fig. S3). With increasing Na salt concentration in the electrolyte, the fraction of MSL bound to Na$^+$ increases, and the amount of uncoordinated (free) MSL decreases. The strong ion-
dipole interaction between Na$^+$ and MSL retards MSL evaporation; thus, the thermal stability of the electrolyte can be improved by increasing the salt concentration.

### 3.2. Liquid structure of NaFSA/MSL.

Raman spectroscopy was performed to study Na$^+$ coordination in the liquid-state mixtures of NaFSA/MSL. Figure 4 shows the Raman spectra of the liquid-state NaFSA/MSL mixtures. The peak observed at 572 cm$^{-1}$ for pure MSL is assignable to the SO$_2$ scissoring vibration of MSL (Fig. 4a).$^{16,31}$ This peak shifted to a higher wavenumber and became broader with increasing NaFSA molar ratio, indicating complex formation between Na$^+$ and MSL.$^{16}$ The fraction of MSL bound to Na$^+$ increased with increasing molar ratio of NaFSA in the liquid, and the SO$_2$ peaks of bound and free MSL molecules overlapped, resulting in peak broadening. The coordination number of Na$^+$ in liquid electrolytes is typically 5−7,$^{20,32-34}$ and Na$^+$ is solvated by solvent molecules in electrolytes containing excess solvent. According to our previous study on NaFSA/SL electrolytes, SL molecules are coordinated to Na$^+$ in the monodentate form in electrolytes containing excess amounts of SL.$^{22}$ However, in highly concentrated electrolytes, the solvent-bridged structure (Na$^+$−SL−Na$^+$) is also formed, wherein the two oxygen atoms of the SO$_2$ group of SL are coordinated to two different Na$^+$ ions. The crystalline solvate of [NaFSA]/[SL] = 1/3 gave rise to Raman peaks at 574.2 and 577.5 cm$^{-1}$, attributed to monodentate and bridging-type SL molecules, respectively.$^{22}$ As can be seen in Fig. 4a, the [NaFSA]/[MSL] = 1/10 mixture showed a peak at 574.7 cm$^{-1}$, indicating that free and monodentate coordinated MSL coexist due to MSL being in excess in the liquid. As the NaFSA concentration increased, the amount of free MSL decreased. The broad peak arising from the [NaFSA]/[MSL] = 1/2 electrolyte showed a relatively large shift (577.1 cm$^{-1}$), tailing at ~590 cm$^{-1}$. This observation suggests that the [NaFSA]/[MSL] = 1/2 electrolyte contains bridging-type MSL in addition to the monodentate-type MSL species owing to the low MSL content.
Raman spectra for the liquid-state NaFSA/MSL mixtures in the wavenumber range of 700–820 cm\(^{-1}\) are shown in Fig. 4b. The peak arising from the symmetric S-N-S stretching vibration mode of the FSA anion appears in the range of 720–750 cm\(^{-1}\). The [NaFSA]/[MSL] = 1/10 electrolyte showed a peak of S-N-S stretching vibration at 721 cm\(^{-1}\). The intensity of this peak increased, and the peak shifted to a higher wavenumber with increasing mole fraction of NaFSA, indicating that the interaction between FSA\(^{-}\) and Na\(^{+}\) became stronger.\(^{36,37}\) The symmetric S=O stretching vibration mode of the FSA anion (\(~1220\) cm\(^{-1}\)) also shifted to a higher wavenumber at a higher mole fraction of NaFSA (Fig. 4c).\(^{22}\) The shifts of the S-N-S and the S=O vibrations to higher wavenumbers suggest that contact ion pairs (CIPs) and ionic aggregates (AGGs) are formed in the electrolytes.\(^{20}\) In the [NaFSA]/[MSL] = 1/2 electrolyte, the coordination number (5–7) of Na\(^{+}\) cannot be satisfied solely by the MSL molecules; therefore, the FSA anions are also involved in Na\(^{+}\) coordination. An FSA anion has two sulfonyl groups and can serve both as a bidentate and bridging-type ligand for Na\(^{+}\).\(^{22}\) Hence, in the solvent-deficient [NaFSA]/[MSL] = 1/2 electrolyte, CIPs (Na(MSL)_nFSA) and AGGs ([Na_x(MSL)_y(FSA)_z]^{(y+z)}, x \geq 1, y \geq 1, x + y \geq 3) are likely to be formed.

### 3.3. Na\(^{+}\) transport properties.

The ionic conductivities and viscosities of the NaFSA/MSL electrolytes were measured to study their transport properties (Table S1). For comparison, the ionic conductivity of a 1 M NaPF\(_6\)/PC + 0.5 vol% FEC solution was also measured (Table S2). Figure 5 shows the Arrhenius plots of the conductivities and viscosities. The ionic conductivities of the MSL-based electrolytes were considerably lower than those of 1M NaPF\(_6\)/PC + 0.5 vol% FEC. This is primarily because the viscosity of the MSL solvent (11 mPa s) is higher than that of the PC solvent (2.53 mPa s), resulting in a lower ion mobility in the MSL-based electrolytes. As the NaFSA concentration increased, the ionic conductivity decreased. This
is possibly due to an increase in viscosity. While the number of charge carriers increases with increasing NaFSA concentration, increasing the salt concentration leads to lower diffusion coefficients of ionic species associated with increased viscosity.

To further study Na\textsuperscript{+} transport in the electrolytes, the $t_{\text{Na}^+}$ was estimated using a symmetric Na/Na cell under anion-blocking conditions. The $t_{\text{Na}^+}$ of the [NaFSA]/[MSL] = 1/10 electrolyte could not be evaluated because this electrolyte was not stable against Na metal. We have previously reported the reductive stability of NaFSA/SL electrolytes and found that SL-based electrolytes containing excess solvent continuously decomposed during the electrochemical deposition of Na metal.\textsuperscript{22} In contrast, the solvent-deficient [NaFSA]/[SL] = 1/1 electrolyte was stable against Na metal. The suppression of reductive decomposition was attributed to the formation of an effective solid electrolyte interphase (SEI) on the Na metal. According to Yamada et al., FSA anions involved in CIPs and AGGs in highly concentrated electrolytes decompose slightly on Na metal, and the decomposition products form an effective SEI on the Na metal to prevent the subsequent decomposition of the electrolytes.\textsuperscript{25,26} In fact, Na metal deposition and dissolution was possible in the [NaFSA]/[MSL] = 1/2 electrolyte (Fig. S4).

**Figure 6a** shows the chronoamperogram of the symmetric Na/Na cell with the [NaFSA]/[MSL] = 1/2 electrolyte measured at a constant voltage of 10 mV. The ionic conductivity of the electrolyte was relatively low at 30 °C; therefore, the electrochemical measurements were performed at an elevated temperature of 60 °C to increase the conductivity and reduce the internal resistance of the cell. Once a constant voltage $\Delta V$ of 10 mV was being applied to the cell, a virtually constant current was observed from ca. 1000 s. This steady-state current ($I_{\text{ss}}$) is solely carried by Na\textsuperscript{+} ions in the electrolyte because of the anion-blocking conditions in the Na/Na cell. To assess the interfacial resistance arising from the electrochemical reactions in the Na/Na cell, AC impedance measurements were performed. **Figure 6b** shows the Nyquist plots of the Na/Na cell before and after chronoamperometry measurements. The
impedance of the cell changed negligibly during the chronoamperometry measurements, suggesting that the Na electrodes were stable in the electrolyte and that the decomposition of the electrolyte was minimal. The intercept of the real axis at the highest frequency (Fig. 6b) corresponds to the resistance for migration of ions (Na\(^{+}\) and FSA\(^{-}\)) in the bulk electrolyte \((R_b)\), and the diameter of the semicircle observed in the intermediate frequency region is attributed to the interfacial resistance \((R_{int})\) for the electrochemical reactions at the Na metal electrodes. The \(t_{Na^{+}}\) was estimated from the \(I_{ss}, R_b\), and \(R_{int}\) as follows: \(t_{Na^{+}} = I_{ss}/I_{\Omega,ss}\), where \(I_{\Omega,ss}\) is the ohmic current calculated from \(R_b\) and the potential drop across the electrolyte at the steady-state, \(I_{\Omega,ss} = (\Delta V - I_{ss}R_{int})/R_b\). Note that the values of \(I_{\Omega,ss}\) were calculated assuming that both Na\(^{+}\) and FSA\(^{-}\) were not blocked at the electrode. Detailed theoretical rationales regarding the measurement and its reliability have been reported elsewhere.\(^{19,38}\) The \(t_{Na^{+}}\) in the [NaFSA]/[MSL] = 1/2 electrolyte under anion-blocking conditions was estimated to be 0.66. The \(t_{Na^{+}}\) in 1 M NaPF\(_6\)/PC + 0.5 vol\% FEC was also evaluated for comparison. 1 M NaPF\(_6\)/PC + 0.5 vol\% FEC solution was reported to be stable against Na metal owing to the SEI derived from FEC.\(^{4}\) The chronoamperogram and Nyquist plots of the Na/Na cell with 1 M NaPF\(_6\)/PC + 0.5 vol\% FEC are shown in Fig. S5. The \(t_{Na^{+}}\) in the PC-based electrolyte was estimated to be 0.18. The \(t_{Na^{+}}\) in the [NaFSA]/[MSL] = 1/2 electrolyte was significantly higher than that in the PC-based electrolyte. In the PC-based electrolyte containing excess solvent, Na\(^{+}\) is predominantly solvated by PC molecules, and the solvated [Na(PC)\(_x\)]\(^{+}\) cation migrates in the electrolyte.\(^{9,11}\) The hydrodynamic radius of solvated Na\(^{+}\) is larger than that of PF\(_6^{-}\), and cation mobility is lower than anion mobility according to Stokes’ law,\(^{39}\) leading to a low \(t_{Na^{+}}\) in the PC-based electrolyte. In contrast, Na\(^{+}\) ions form CIPs and AGGs in the [NaFSA]/[MSL] = 1/2 electrolyte (vide supra), and the CIPs and AGGs are in close proximity to each other. Therefore, the Na\(^{+}\) transport mechanism in the [NaFSA]/[MSL] = 1/2 electrolyte differs from that in the PC-based electrolyte. The high \(t_{Na^{+}}\) in the [NaFSA]/[MSL] = 1/2 electrolyte likely originated from the dynamic ligand exchange of
Na⁺. We have previously reported that highly concentrated Li salt/SL electrolytes exhibit high Li⁺ transference numbers of > 0.6. In highly concentrated electrolytes, solvent-bridged Li⁺-SL-Li⁺ and anion-bridged Li⁺-anion-Li⁺ structures (i.e., AGGs) are formed, and Li⁺ ions exchange the ligands (solvents and anions) dynamically and move faster than the ligands, resulting in a high Li⁺ transference number. Cyclic sulfone structure facilitates the ligand exchange of Li ions, and the introduction of a bulky functional group to the solvent molecule decreases the exchange rate due to its steric hindrance. Other high salt-concentration electrolytes have also been reported to show high cation transference numbers.

3.4. Performance of the Na/Na₀.₄₄MnO₂ cell

To study the effect of the Na⁺ transference number on the battery performance, Na/Na₀.₄₄MnO₂ (NMO) cells were prepared and charge-discharge measurements were conducted. Na⁺ is extracted from Na₀.₄₄MnO₂ during the first charging of the cell as following (Fig. S6): Na₀.₄₄MnO₂ → Na₀.₁₈MnO₂ + 0.26Na⁺ + 0.26e⁻. In the subsequent discharge-charge cycles, the following reversible reaction occurs: Na₀.₁₈MnO₂ + 0.₄₆Na⁺ + 0.₄₆e⁻ ↔ Na₀.₆₄MnO₂, where the theoretical capacity is 127 mAh g⁻¹ based on the mass of NMO. Figure 7 shows the discharge curves of the cells with [NaFSA]/[MSL] = 1/2 and 1 M NaPF₆/PC + 0.5 vol% FEC electrolytes, measured at various current densities. Discharge capacities of > 100 mAh g⁻¹ were observed for both cells at current densities < 0.1 mA cm⁻². This result is in good agreement with the previously reported ones. With increasing current density, the operating voltage of the cell is lowered. The discharge capacities of the cells decrease rapidly at current densities > 0.5 mA cm⁻² because the cell voltage reaches the cut-off voltage before full discharge capacity is attained. Although the ionic conductivity (σ) of the [NaFSA]/[MSL] = 1/2 electrolyte is lower than that of 1 M
NaPF$_6$/PC + 0.5 vol% FEC (Table 1), the cell with [NaFSA]/[MSL] = 1/2 shows a slightly better rate performance.

The voltage drop of a cell due to Na$^+$ migration resistance in the bulk electrolyte is proportional to $1/(\sigma \times t_{\text{Na}^+})$ under anion-blocking conditions.$^{42,43}$ The Na$^+$ ion conductivity ($\sigma \times t_{\text{Na}^+}$) of the [NaFSA]/[MSL] = 1/2 electrolyte is lower than that of 1 M NaPF$_6$/PC + 0.5 vol% FEC (Table 1); therefore, the $iR$ drop in the electrolyte layer is not the origin of the difference in the rate capability of the cells. There is a possibility that the charge transfer resistances for the electrochemical reactions at Na metal/electrolyte and NMO/electrolyte interfaces affect the rate capability of the cell. The interfacial resistances of Na/electrolyte in [NaFSA]/[MSL] = 1/2 and 1 M NaPF$_6$/PC + 0.5 vol% FEC were roughly estimated to be 15 $\Omega$ and 20 $\Omega$, respectively, from the Nyquist plots of the Na/Na cells (Fig. 6b and Fig. S5). The 5 $\Omega$ difference does not provide a large polarization even at 4 mA cm$^{-2}$ (4 mA cm$^{-2}$ $\times$ 5 $\Omega$ $\times$ 2 cm$^2$ = 40 mV). The interfacial resistance at the NMO composite electrode is reported to be lower than that at the Na metal electrode.$^{22}$ Therefore, the charge transfer resistances of the electrochemical reactions likely do not give rise to the difference in the rate capability of the cells.

We postulated that the superior rate capability of the cell with the [NaFSA]/[MSL] = 1/2 electrolyte resulted from the suppression of concentration polarization. During the discharge of a Na/NMO cell, Na$^+$ ions are consumed at the NMO cathode and released from the Na metal anode, and a concentration gradient of Na salt is formed in the electrolyte. The reduced Na salt concentration in the vicinity of the cathode lowers the electrode potential of NMO, and the increased concentration at the anode surface raises the electrode potential of Na metal, resulting in a cell voltage drop. The concentration gradient of the Na salt becomes steeper with increasing current density. The slope of the discharge curve of the Na/NMO cell with 1 M NaPF$_6$/PC + 0.5 vol% FEC becomes steeper with increasing current density (Fig. 7), indicating that concentration polarization occurred in the cell. The
concentration polarization can be suppressed using an electrolyte having a high $t_{Na^+}$.\textsuperscript{23,24} The $t_{Na^+}$ value of the [NaFSA]/[MSL] = 1/2 is significantly higher than that of 1 M NaPF$_6$/PC + 0.5 vol% FEC (Table 1), and concentration polarization could be reduced even at a high current density. In fact, the slope of the discharge curve of the cell with the [NaFSA]/[MSL] = 1/2 electrolyte measured at a high current density of ≥ 2 mA cm$^{-2}$ is less steep than that of the cell with 1 M NaPF$_6$/PC + 0.5 vol% FEC (Fig. 7). In addition to the high $t_{Na^+}$ value, the high concentration of NaFSA in the electrolyte may be beneficial for preventing the depletion of Na$^+$ in the porous NMO cathode during high-rate discharging.

The rate capabilities of the Na/NMO cells were also evaluated at 30 °C (Fig. S7). The rate capability of the [NaFSA]/[MSL] = 1/2 cell was comparable to that of the 1 M NaPF$_6$/PC + 0.5 vol% FEC cell. The reduced rate capability of the former is attributed to increased interfacial resistance and/or decreased ionic conductivity of the electrolyte as a result of lowering the temperature. However, it is surprising that the cell with the [NaFSA]/[MSL] = 1/2 electrolyte ($\sigma = 0.30$ mS cm$^{-1}$ at 30 °C) shows a rate capability similar to that of the 1 M NaPF$_6$/PC + 0.5 vol% FEC cell ($\sigma = 8.51$ mS cm$^{-1}$ at 30 °C), despite the ionic conductivity of the latter electrolyte being 28-fold higher than that of the former. This observation implies that mitigating concentration polarization using a high-salt-concentration electrolyte with a high $t_{Na^+}$ is a feasible strategy for obtaining Na-ion cells with enhanced rate capabilities.

4. Conclusions

Binary mixtures of Na salt/MSL remain in the liquid state at room temperature over a wide range of compositions. The thermal stability of the NaFSA/MSL electrolyte improved with increasing salt concentration. Na$^+$ is predominantly solvated by MSL in the [NaFSA]/[MSL] = 1/10 electrolyte containing excess solvent. In contrast, the FSA anion is involved in Na$^+$ coordination in solvent-deficient
[NaFSA]/[MSL] = 1/2 electrolyte, wherein solvent-bridged Na\(^+\)-MSL-Na\(^+\) and anion-bridged Na\(^+\)-FSA-Na\(^+\) structures were formed. Although the ionic conductivity of the [NaFSA]/[MSL] = 1/2 electrolyte is lower compared to that of [NaFSA]/[MSL] = 1/10 and 1 M NaPF\(_6\)/PC + 0.5 vol% FEC, the [NaFSA]/[MSL] = 1/2 electrolyte exhibits a greater \(t_{Na^+}\) under anion-blocking conditions. Thus, despite its lower ionic conductivity, the Na/Na\(_{0.44}\)MnO\(_2\) cell with the [NaFSA]/[MSL] = 1/2 electrolyte displayed a superior rate performance compared to that of the 1 M NaPF\(_6\)/PC + 0.5 vol% FEC cell. The superior rate capability of the [NaFSA]/[MSL] = 1/2 cell is attributed to the suppression of concentration polarization during high-rate discharge, owing to its higher \(t_{Na^+}\).

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Conflict of Interest

The authors declare no conflict of interest.
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Figure Captions

Figure 1. Structures of MSL and NaFSA.

Figure 2. Melting points ($T_m$) and glass transition temperatures ($T_g$) of the binary mixtures of NaFSA/MSL. $X_{NaFSA}$ is the mole fraction of the Na salt; $X_{NaFSA} = 1/(1+x)$, where $x$ in the molar ratio of [NaFSA]/[MSL] = 1/x.

Figure 3. TG curves of the electrolytes measured at a heating rate of 10 °C min$^{-1}$.

Figure 4. Raman spectra of liquid-state NaFSA/MSL mixtures showing regions corresponding to (a) SO$_2$ scissoring of MSL, (b) S-N stretching of FSA$^-$, and (c) S=O stretching of FSA$^-$ measured at 30 °C. The peaks at marked *, **, *** in (b) are derived from MSL.

Figure 5. Arrhenius plots of (a) ionic conductivities and (b) viscosities of NaFSA/MSL mixtures and 1 M NaPF$_6$/PC + 0.5 vol% FEC.

Figure 6. (a) Chronoamperogram of a symmetric Na/Na cell with [NaFSA]/[MSL] = 1/2 electrolyte measured at a constant voltage of 10 mV at 60 °C. (b) Nyquist plots of the cell before and after chronoamperometry measurements.

Figure 7. Discharge curves of Na/Na$_{0.44}$MnO$_2$ cells with (a) [NaFSA]/[MSL] = 1/2 and (b) 1 M NaPF$_6$/PC + 0.5 vol% FEC electrolytes at 60 °C. (c) Discharge capacities of the cells measured at various current densities. Prior to each discharge, the cells were charged to 3.8 V at a constant current density of 0.1 C (12.7 mA g$^{-1}$).

Table 1. Na$^+$ transference numbers ($t_{Na^+}$), NaFSA concentration ($c$), viscosities ($\eta$), ionic conductivities ($\sigma$), and Na$^+$ ion conductivities ($\sigma \times t_{Na^+}$) of the electrolytes measured at 60 °C.
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Table 1. Na\(^+\) transference numbers \((t_{\text{Na}^+})\), NaFSA concentration \((c)\), viscosities \((\eta)\), ionic conductivities \((\sigma)\), and Na\(^+\) ion conductivities \((\sigma \times t_{\text{Na}^+})\) of the electrolytes measured at 60 °C.

|                | \(c / \text{mol dm}^{-3}\) | \(\eta / \text{mPa s}\) | \(\sigma / \text{mS cm}^{-1}\) | \(t_{\text{Na}^+} / -\) | \(\sigma \times t_{\text{Na}^+} / \text{mS cm}^{-1}\) |
|----------------|-----------------------------|--------------------------|-----------------------------|--------------------------|----------------------------------|
| [NaFSA]/[MSL]=1/2 | 3.08                        | 124.6                    | 2.03                        | 0.66                     | 1.34                             |
| 1 M NaPF\(_6\)/PC + 0.5 vol% FEC | -                           | 3.14                     | 13.2                        | 0.18                     | 2.38                             |