

Rechargeable Sodium Batteries
with Mixed Amide Ionic Liquids

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Recently, the development of large-scale secondary batteries has been attracting much attention because they are crucial for realizing load leveling of renewables, electric vehicles (EVs), and smart grid. As high performance secondary batteries, lithium-ion batteries (LIBs) have much popularity not only for mobile applications but also for EV and household uses. Concerning the LIBs, however, we may experience a resource problem in the near future because they employ rare metals like cobalt and nickel. Even for lithium itself, there is a concern about stable supply because lithium raw materials of high quality are unevenly distributed on the earth. On the other hand, sodium can be easily supplied from seawater or earth's crust, and its standard redox potential, -2.714 V vs. SHE, is reasonably negative. Consequently, sodium secondary batteries have emerged as possible alternatives to LIBs.

Previous and current studies on sodium secondary batteries fall into two classifications according to the operation temperature. The first includes those operating at high temperatures (~573 K) such as Na/S and Na/NiCl₂ batteries. There is, however, a potential risk posed by electrical short circuit if the mechanically fragile β"-alumina breaks during operation due to the high reactivity of liquid sodium metal at high temperature. The second class of sodium secondary batteries includes those operating at room temperature using organic solvents as electrolytes. For this type, there are also safety issues due to the flammability and volatility of the organic solvents when the batteries are scaled up.

To circumvent these issues, we have been exploring a new class of ionic liquids (ILs) or molten salts that have wide electrochemical windows and possess the capacity for reversible electrodeposition of metallic sodium. We have previously investigated the thermal and electrochemical properties of single salts, binary and ternary mixtures of MTFSA (M = Li, Na, K, Rb, Cs; TFSA = bis(trifluoromethylsulfonyl)amide) [1-3], and MFSA (M = Li, Na, K, Rb, Cs; FSA = bis(fluorosulfonyl)amide) [4-6]. In the case of the TFSA salts, we have demonstrated that a Na/NaCrO₂ battery utilizing the NaTFSA-CsTFSA melt exhibits excellent cycle and rate performance at 423 K [7]. Depending on the application conditions, however, lower operation temperatures are generally preferable. MFSA salts have melting points in the range of 370 to 410 K, and binary or ternary mixtures of MFSA exhibit lower melting temperatures than those of the single salts. For instance, the binary NaFSA-KFSA (56:44 in mol%) system becomes liquid at 334 K [5]; the melt exhibits a wide electrochemical window of approximately 5 V as well as the capacity for sodium metal deposition/dissolution [4,8]. It should be noted that both NaFSA and KFSA are completely inorganic compounds and as such are expected to be synthesized with a reasonably low cost because they do not contain expensive organic cations. Moreover, FSA anions can be synthesized without using the expensive electrofluorination process. The viscosity, ionic conductivity and density of this IL are 435 cP, 3.3

mS cm⁻¹ and 2.14 g cm⁻³, respectively, at 363 K [8].

By using this new IL, we have confirmed the actual operations of Na/NaFSA-KFSA/NaCrO₂ cell at 353-363 K [8,9]. The cell exhibited a stable capacity of 113 mAh (g-NaCrO₂)⁻¹ at a current density of 125 mA g⁻¹ [9]. The coulombic efficiency and the capacity retention at the 100th cycle were as high as 99.6% and 98.5%, respectively. Even at the high current density of 2000 mA g⁻¹, the discharge capacity was maintained at 63 mAh g⁻¹.

In the above studies, sodium metal was used as a negative electrode. The operation at elevated temperature (353-363 K) close to the melting point of sodium (371 K) fairly suppresses the dendrite formation sodium. However, the dendritic deposition is difficult to be perfectly prevented and especially not avoidable at lower operation temperatures. Thus, we have investigated the Sn-Na alloy negative electrode [10]. Although it showed a very high capacity of more than 700 mAh (g-Sn)⁻¹, its cycleability was limited because of the volume change during alloying and dealloying. As an alternative negative electrode, we have also investigated hard carbon (HC) [11]. Although HC showed poor reversibility with NaFSA-KFSA IL, high reversibility and excellent rate capability have been achieved with NaFSA-C₁C₃pyrFSA (C₁C₃pyr: *N*-methyl-*N*-propylpyrrolidinium) IL at 363 K.

To increase the operation temperature range, we had already developed the above-mentioned NaFSA-C₁C₃pyrFSA IL [12] before applying it to HC electrode. The viscosity and ionic conductivity of NaFSA-C₁C₃pyrFSA (20:80 in mol%) are 16.7 cP and 15.6 mS cm⁻¹, respectively, at 353 K. The electrochemical window of this IL is 5.2 V at 353 K with sodium metal deposition determining the cathode limit. A Na/NaFSA-C₁C₃pyrFSA/NaCrO₂ cell exhibited stable charge-discharge behaviors at both 298 and 353 K with discharge capacities of 92 and 106 mAh (g-NaCrO₂)⁻¹, respectively, at 20 mA g⁻¹ [12]. Very recent study has revealed that this cell is operable even at very low temperature of 253 K.

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