



Short communication

# Properties of an intermediate temperature ionic liquid NaTFSA–CsTFSA and charge–discharge properties of NaCrO<sub>2</sub> positive electrode at 423 K for a sodium secondary battery

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## ABSTRACT

The physicochemical properties of an intermediate temperature ionic liquid (ITIL), NaTFSA (10 mol%)-CsTFSA (90 mol%) (TFSA = bis(trifluoromethylsulfonyl)amide), were investigated as a new electrolyte for a sodium secondary battery operating at elevated temperatures (around 423 K). The viscosity, ionic conductivity, density and electrochemical window of this ITIL measured at 423 K were 42.5 cP, 12.1 mS cm<sup>-1</sup>, 2.29 g cm<sup>-3</sup> and 4.9 V, respectively. The electrodeposition of metallic sodium at the cathode limit was confirmed by X-ray diffraction. The charge–discharge properties of a NaCrO<sub>2</sub> positive electrode in this ITIL at 423 K were investigated. The discharge capacities at constant current rates of 10 mA g<sup>-1</sup> (after 10 cycles) and 100 mA g<sup>-1</sup> (after 50 cycles) were 83.0 and 66.4 mAh g<sup>-1</sup>, respectively. Except for the initial few cycles, the coulombic efficiencies were higher than 99.5% during the charge–discharge tests, which indicates that the Na/NaTFSA–CsTFSA/NaCrO<sub>2</sub> cell is promising as a new type of sodium secondary battery operating at intermediate temperatures.

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## 1. Introduction

Sodium secondary batteries have been studied for a long time, due to the favorable features of sodium, such as low cost, abundance, low toxicity and reasonably high energy density [1–15]. Among the many types of sodium secondary batteries, the Na/S [1,2] and Na/NiCl<sub>2</sub> batteries [3,4] have already been applied in practice. However, high operation temperatures (523–573 K) are required, because the solid β'-alumina electrolyte only exhibits high ionic conductivity at high temperatures. Moreover, the handling of these batteries can be difficult due to the brittleness of β'-alumina, especially during the heating and cooling operations. On the other hand, sodium secondary batteries operating at room temperature have also been reported [5–15]. In the last few years, the number of reports has rapidly increased [10–15] due to the possibility of a room temperature sodium battery as a post-lithium ion battery that is low-cost, scalable and exhibits high performance. However, the cyclability and charge–discharge rates of the reported room temperature sodium batteries are still low compared with the current lithium ion batteries. The slower rate is considered to be caused by the slower mass transport of sodium ions in the solid

state, due to the larger ionic radius of sodium than that of lithium. A simple and effective approach to solving this problem is to elevate the operation temperature. However, elevation of the temperature is very difficult for conventional room temperature sodium batteries from a safety aspect, because flammable organic electrolytes combined with strong oxidizing salts such as NaClO<sub>4</sub>/propylene carbonate (PC) are typically employed. As for lithium ion batteries, the volatility and flammability of such organic electrolytes are highly disadvantageous for the construction of a safe battery. If a new nonvolatile and nonflammable electrolyte that can operate at intermediate temperatures (e.g. 373–473 K) is developed, then the slow kinetics and low safety problems are expected to be solved without causing much difficulty in the handling.

Molten salts (or ionic liquids in original definition [16,17]) generally provide negligibly low volatility, nonflammability, and high thermal and electrochemical stability, and have therefore been studied and used as electrolytes in many electrochemical fields. We have reported that salts consisting of alkali metal cations and the bis(trifluoromethylsulfonyl)amide (TFSA) anion, MTFSA (M = Li, Na, K, Rb, Cs), have melting points in the range of 400–540 K and their melting points are significantly lowered by mixing two or three of these salts in prescribed compositions [18,19]. MTFSA mixed salts also have wide electrochemical windows of approximately 5 V, due to the high electrochemical stability of the TFSA anion [20]. Among the ternary MTFSA systems, we have reported that the LiTFSA–KTFSA–CsTFSA system is highly

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promising as an electrolyte for lithium metal secondary batteries from the good cycle performance of a Li/LiFePO<sub>4</sub> cell at 423 K [21]. Thus, the MTFSA system is also attractive as an electrolyte for sodium secondary batteries operated at intermediate temperatures. Although the melting point of NaTFSA (530 K) is rather high, binary NaTFSA–CsTFSA systems have reasonably low melting points [18]. For example, the mixture of NaTFSA (10 mol%)–CsTFSA (90 mol%), denoted as (Na10, Cs90)TFSA, has a liquidus temperature at 390 K. The successful operation of a Na/S battery was confirmed using a test cell of Na/(Na10, Cs90)TFSA/Na<sub>2</sub>S<sub>x</sub> at 423–493 K [22].

In the present study, the viscosity, conductivity, density and electrochemical window of the (Na10, Cs90)TFSA intermediate temperature ionic liquid (ITIL) were measured at 423 K for evaluation as a new electrolyte for sodium secondary batteries. The charge–discharge properties of a NaCrO<sub>2</sub> positive electrode with this electrolyte were also investigated at 423 K. NaCrO<sub>2</sub> was selected as a positive active material due to its relatively good performance at room temperature [12,13] and thermal stability.

## 2. Experimental

### 2.1. Preparation of MTFSAs

Bis(trifluoromethylsulfonyl)imide (HTFSA; Morita Chemical Industries, purity >99%), Na<sub>2</sub>CO<sub>3</sub> (Wako Pure Chemical Industries, purity >99.9%) and Cs<sub>2</sub>CO<sub>3</sub> (Sigma–Aldrich, purity >99.9%) were used for preparation of the MTFSA salts. MTFSAs (M = Na, Cs) were synthesized by the neutralization of HTFSA and M<sub>2</sub>CO<sub>3</sub> in ethanol at room temperature and then dried under vacuum for 72 h at the temperatures lower than the melting points of each MTFSA [18].

### 2.2. Viscosity, conductivity and density measurements

The viscosity of the (Na10, Cs90)TFSA ITIL was measured using a viscometer (Brookfield Engineering Laboratories, DV-II+ pro). The temperature of the melt was controlled using an electric furnace equipped with a temperature controller (Brookfield Engineering Laboratories, Thermosel). Conductivity was measured by electrochemical impedance spectroscopy using a calibrated cell with two platinum plate electrodes and a potentiostat/galvanostat/frequency response analyzer (Ivium Technologies, IviumStat). The cell constant was determined with a standard KCl aqueous solution. Density was measured using the Archimedes method by measuring weight change of a volume-known nickel ball immersed in the salt. The cell temperatures during the conductivity and density measurements were controlled using a heater with a temperature controller.

### 2.3. Preparation of NaCrO<sub>2</sub>

Cr<sub>2</sub>O<sub>3</sub> (Wako Pure Chemical Industries, purity >98%) was mixed well with an equimolar amount of Na<sub>2</sub>CO<sub>3</sub> using a mortar and pestle, and then pelletized to the size of 10 mm in diameter at 100 MPa. The pellet was heated at 1123 K for 5 h under argon flow and was then ground using a mortar and pestle. Identification of the product was performed by X-ray diffraction (XRD; Rigaku, MultiFlex-KB) analysis using Cu K $\alpha$  radiation.

### 2.4. Electrochemical measurements

Electrochemical measurements were performed with a three-electrode system constructed in a Pyrex<sup>®</sup> beaker cell using a potentiostat/galvanostat (Hokuto Denko, HZ-3000). The electrochemical window of the melt was measured by cyclic voltammetry. Sodium metal was used as counter and reference electrodes. Sodium (m.p. 371 K) fuses at the operation temperature used in

**Table 1**

Viscosity, conductivity and density of (Na10, Cs90)TFSA at 423 K.

Viscosity (cP)	Conductivity (mS cm <sup>-1</sup> )	Density (g cm <sup>-3</sup> )
42.5	12.1	2.29

this study; therefore, liquid sodium was immobilized in a Pyrex<sup>®</sup> tube and a nickel plate was used as a current collector. A nickel plate disk ( $\varnothing$ 6 mm,  $t$ =0.1 mm) and a glassy carbon rod ( $\varnothing$ 3 mm) were used as working electrodes to investigate the cathodic and anodic limits of the (Na10, Cs90)TFSA ITIL, respectively. Identification of the deposit at the cathodic limit was performed by XRD analysis. The deposited sample was first washed with tetrahydrofuran, scraped from the nickel plate, and then placed on a glass holder in a glove box. The holder was wrapped with a transparent flexible film (Pechiney Plastic Packaging, Parafilm) to protect the sample from oxidation.

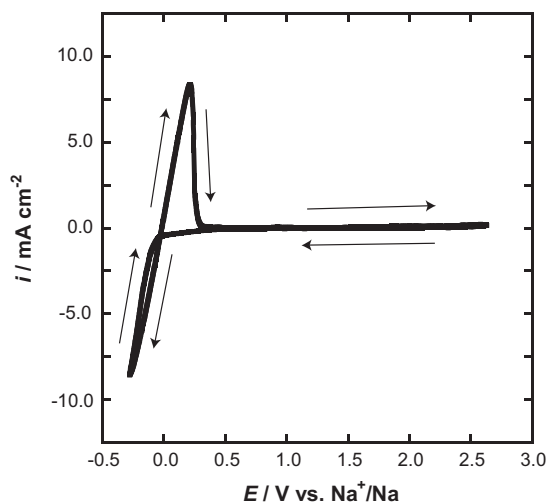
A charge–discharge test was conducted for the NaCrO<sub>2</sub> positive electrode by the galvanostatic method using a three-electrode cell with liquid sodium was used as counter and reference electrodes. The prepared NaCrO<sub>2</sub> was mixed well with acetylene black (Wako Pure Chemical Industries, purity >99.99%) and polytetrafluoroethylene (PTFE; Sigma–Aldrich) at a weight ratio of 80:15:5 using a mortar and pestle. The mixture of weight, ca. 10 mg, was stretched in the disk shape ( $\varnothing$ 12 mm) then pressed onto an aluminum mesh current collector at 300 MPa. The charge–discharge performance was evaluated at constant current rates of 10, 20, 50 and 100 mAh g<sup>-1</sup> NaCrO<sub>2</sub> between potentials of 2.3 and 3.1 V vs. Na<sup>+</sup>/Na. All measurements were conducted in an argon glove box equipped with a gas-refining instrument.

## 3. Results and discussion

### 3.1. Physicochemical and electrochemical properties of (Na10, Cs90)TFSA at 423 K

The viscosity, conductivity and density of (Na10, Cs90)TFSA at 423 K are shown in Table 1. The conductivity of 12.1 mS cm<sup>-1</sup> is sufficient for electrochemical applications such as sodium secondary batteries.

A cyclic voltammogram of a nickel plate electrode in (Na10, Cs90)TFSA at 423 K is shown in Fig. 1. A pair of cathodic and anodic waves is evident around 0 V vs. Na<sup>+</sup>/Na, which possibly corresponds to the deposition and dissolution of sodium metal. To confirm this,



**Fig. 1.** Cyclic voltammogram of a Ni plate electrode in (Na10, Cs90)TFSA at 423 K, measured at a scan rate of 10 mV s<sup>-1</sup>.

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