



Ionic liquid electrolytes with high sodium ion fraction for high-rate and long-life sodium secondary batteries



Chih-Yao Chen ^a, Tomohiro Kiko ^a, Takafumi Hosokawa ^a, Kazuhiko Matsumoto ^{a,*},
Toshiyuki Nohira ^{b,**}, Rika Hagiwara ^a

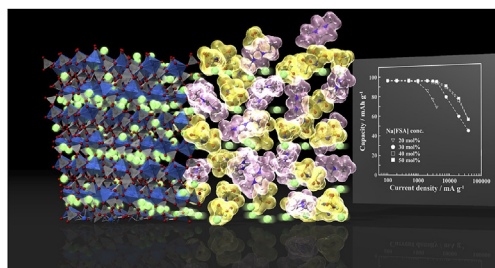
^a Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^b Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

HIGHLIGHTS

- Ionic liquids at high Na⁺ fraction derive high performance of Na₂FeP₂O₇ at 363 K.
- High rate capability of 40000 mA g⁻¹ at 363 K is attained.
- The structure of ionic liquids plays a dominant role in the high rate capability.
- A long cycle life over 1500 cycles at 1000 mA g⁻¹ at 363 K is confirmed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 July 2016

Received in revised form

3 September 2016

Accepted 18 September 2016

Keywords:

Sodium secondary batteries

Ionic liquids

Pyrophosphates

bis(fluorosulfonyl)amide

ABSTRACT

Sodium secondary batteries are attracting considerably renewed interest as new battery systems owing to the high and uniform abundance and cost advantages of Na. However, their performance is still far from optimal as compared to the well-developed Li-ion technology. Herein, Na secondary batteries with unprecedented rate capability and a long life has been achieved by using a highly concentrated bis(fluorosulfonyl)amide anion (FSA⁻)-based ionic liquid electrolyte (3.3 mol dm⁻³ Na[FSA]) and a Na₂FeP₂O₇ positive electrode, in a targeted operating temperature range from room to intermediate. Nearly full discharge capacity is obtained at 4000 mA g⁻¹, and 79% of the capacity is retained at a discharge rate as high as 20000 mA g⁻¹ at 363 K. Stable cycling (>300 cycles) with satisfactory coulombic efficiency (>99.5%) is found at an intermediate rate (100 mA g⁻¹) over 298–363 K. A high-rate cycling test (1000 mA g⁻¹) at 363 K reveals that the cell could retain 93% of its initial capacity after 1500 cycles.

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1. Introduction

Driven by the exponentially growing demand for large-scale stationary and vehicular energy storage devices, Na secondary

batteries have received renewed research interest owing to the high and uniform abundance, cost advantages, and environmental benignity of Na [1–4]. Sodium and lithium secondary batteries share many similarities: for example, the Na⁺-conducting electrolytes that have been investigated are mainly based on nonaqueous organic solvents (typically, propylene carbonate), which parallel the well-developed Li-ion technology [4–6]. However, the diverse applications expected for Na secondary batteries pose requirements different from those for portable electronics, including

* Corresponding author.

** Corresponding author.

E-mail addresses: k-matsumoto@energy.kyoto-u.ac.jp (K. Matsumoto), nohira.toshiyuki.8r@kyoto-u.ac.jp (T. Nohira).

a high level of safety, long cycle life, and wide working-temperature span, as well as fast charging/discharging capabilities. The further development of possible electrolyte materials is therefore essential [7].

Ionic liquids (ILs) are potentially ideal candidates for this pursuit, owing to their unique suite of properties, including low flammability, negligible vapor pressure, wide liquidus temperature, and high electrochemical/thermal stability [8,9]. Despite these advantages, only a few publications have detailed IL electrolytes for use in Na secondary batteries [10–13], for several reasons. First, a larger interfacial impedance is generally observed for Na cells than for the Li equivalents [14,15], primarily caused by the unstable solid electrolyte interphase (SEI) film that forms on Na metal [4]. Second, ILs typically exhibit high viscosity and inferior ionic conductivity compared to conventional organic electrolytes [5]. Consequently, Na batteries applying ILs have been tested at very low rates (e.g., 10–20 mA g⁻¹) and show a strong trade-off between accessible capacity and charge/discharge rates in most cases [11–13]. In our previous studies, the physical properties of a series of purely inorganic [16] and inorganic-organic hybrid [17–20] IL electrolytes based on the bis(fluorosulfonyl)amide anion (FSA⁻) were evaluated for Na secondary battery applications. Electrochemical performance as a function of temperature (between 253 and 363 K) was tested for a range of positive and negative electrode materials utilizing Na[FSA]–[C₃C₁pyrr][FSA] (C₃C₁pyrr: *N*-propyl-*N*-methylpyrrolidinium) in both half and full cells [21–25]. The results indicate that elevation of the operating temperature effectively facilitates ion transport in the electrolyte and electrode, permitting the cells to be cycled at a current density of 2360 mA g⁻¹ and discharged at a current density higher than 4000 mA g⁻¹ when combined with a suitable electrode material [22–24]. Although temperatures above 323 K may be considered too high for battery operation, they are practicable and even preferable with the aid of thermally and chemically stable ionic liquid electrolytes. Such environments are not particularly rare, if one considers the engine compartments of automobiles or the constant waste heat generated from devices or machines that operate in our daily lives or industrially. Alternatively, if the environment is not at an elevated temperature, batteries working at high rates are easily self-heated under appropriate insulating conditions.

Recently, superconcentrated electrolytes composed of aprotic solvents with high Li salt concentrations (i.e., >3 mol dm⁻³) have received intense attention in the Li battery research community [26–33]. This new class of electrolytes offers unusual functionality including the facilitated formation of passivation films [26], inhibited dendritic Li deposition [27,28], suppressed corrosion of Al current collectors [29], and enhanced reductive or oxidative stability [30,31]. Most importantly, ultrafast electrode kinetics was found for particular systems utilizing Li[FSA], in spite of their high viscosities [28,30,32]. These phenomena were attributed to entirely different solution structures between the highly concentrated electrolyte and the corresponding dilute electrolyte [33]. Our prior work using Na[FSA]–[C₃C₁pyrr][FSA] showed that the rate capability of the NaCrO₂ positive electrode could be improved by adjusting the Na[FSA] content [18]. Layered-structured sodium transition metal oxides (such as NaCrO₂) are attractive intercalation hosts; however, they are prone to undergo successive phase transformations induced by oxygen layer glides at specific Na contents [2–4]. The kinetic energy barrier for the phase transition is a complex interplay of multiple experimental factors, making a comprehensive understanding of the electrochemical results challenging.

To clarify the role of the electrolyte in improved electrode kinetics, an electrode material that has been thoroughly studied is preferable. Further, it must be a good Na host material, allowing the

reversible and facile insertion and extraction of Na⁺. The Na₂FeP₂O₇ positive electrode was first reported by Yamada et al., in 2012 [34]. Atomistic simulation studies revealed that Na₂FeP₂O₇ supports favorable three-dimensional Na ion diffusion paths with acceptably low activation energies, and hence, high Na⁺ mobility [35]. This assertion was experimentally verified in a number of publications [36–38], including ours involving ILs [24,39]. In this work, the electrode characteristics of Na₂FeP₂O₇ positive electrodes in the Na [FSA]–[C₂C₁im][FSA] (C₂C₁im: 1-ethyl-3-methylimidazolium) IL electrolytes were investigated as a function of both Na salt fraction and working temperature. This imidazolium-based IL exhibits higher ionic conductivity and lower viscosity than the corresponding pyrrolidinium-based IL [19,20]. Transport and structural properties are described in the first part of the paper. The electrochemical behavior discussed in the following part focuses on the differences between the Na[FSA]–[C₂C₁im][FSA] and Na[FSA]–[C₃C₁pyrr][FSA] systems, as well as the rate capability and cyclability.

2. Experimental

2.1. Materials

The FSA salts, Na[FSA] (Mitsubishi Materials Electronic Chemicals, water content < 72 ppm), [C₂C₁im][FSA] (Kanto Chemical, water content < 28 ppm), and [C₃C₁pyrr][FSA] (Kanto Chemical, water content < 30 ppm) were dried under vacuum at 363 K for 24 h prior to use. To compare the effects of the imidazolium- and pyrrolidinium-based ILs, Na[FSA]–[C₂C₁im][FSA] and Na[FSA]–[C₃C₁pyrr][FSA] were prepared at the same Na[FSA] fraction of 30 mol%. To investigate the effects of Na salt content on the physical and electrochemical properties, Na[FSA]–[C₂C₁im][FSA] ILs at Na [FSA] fractions of 0, 10, 20, 30, 40, and 50 mol% were also prepared. The apparent transport number was measured for a symmetric Na/Na 2032 type coin cell at 363 K using an ac-dc method [40,41], as described in our previous study (see Ref. 19 for a discussion of the apparent transport number concept). Measurements at each concentration were performed at least three times to ensure reproducibility. Raman spectra were recorded at 298 and 363 K using a Nanofinder 30 (Tokyo Instruments Inc.) microfocus Raman spectrometer with a 532 nm He-Ne laser. Peak deconvolution of the Raman spectra was performed using the Voigt function. Table 1 lists the IL electrolytes used in this work with their ionic conductivities ($\sigma(\text{IL})$), apparent transport numbers of Na⁺ ($t'(\text{Na}^+)$), and Na⁺ ion conductivities ($\sigma(\text{Na}^+)$). Sodium iron pyrophosphate, Na₂FeP₂O₇, was synthesized by a conventional solid-state method, as reported previously [39]. The starting materials Na₂CO₃, FeC₂O₄·2H₂O, and (NH₄)₂HPO₄ were stoichiometrically mixed by wet planetary ball-milling (Fritsch Pulverisette 7 Premium Line) in acetone at 600 rpm for 8 h. After evaporating the acetone, the mixture was ground and then initially heated at 573 K for 6 h. The calcined sample was reground and heated again at 873 K for 12 h. The heat treatment was carried out under a steady flow of either Ar or Ar/H₂ (95:5). Pulverization of the obtained sample was conducted using an agate mortar in either an Ar-filled glovebox or ambient air. Crystal structures of the prepared Na₂FeP₂O₇ samples were analyzed by X-ray diffraction (XRD), using a Rigaku SmartLab diffractometer equipped with a one-dimensional high-speed Si strip detector (D/teX Ultra) and utilizing Cu K α radiation (40 kV and 30 mA). Structural refinements were carried out by the Rietveld method with an iterative procedure using the software package PDXL-2 (Rigaku).

2.2. Electrochemical measurements

The charge–discharge tests were performed with a Bio-Logic VSP potentiostat or a charge–discharge unit (HJ1001SD8, Hokuto

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