



## Short communication

# A safe and high-rate negative electrode for sodium-ion batteries: Hard carbon in NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid at 363 K



Atsushi Fukunaga<sup>a,b</sup>, Toshiyuki Nohira<sup>a,\*</sup>, Rika Hagiwara<sup>a,\*</sup>, Koma Numata<sup>b</sup>, Eiko Itani<sup>b</sup>, Shoichiro Sakai<sup>b</sup>, Koji Nitta<sup>b</sup>, Shinji Inazawa<sup>b</sup>

<sup>a</sup> Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

<sup>b</sup> Sumitomo Electric Industries Ltd., 1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan

## HIGHLIGHTS

- Hard carbon (HC) negative electrodes were examined in several ionic liquids.
- A Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell exhibited good cycle performance at 363 K.
- The discharge capacity was 260 mAh (g-HC)<sup>-1</sup> at 50 mA (g-HC)<sup>-1</sup>.
- The cell showed high rate capability up to 1000 mA (g-HC)<sup>-1</sup>.
- The coulombic efficiency was higher than 99.9% for 40 cycles.

## ARTICLE INFO

## Article history:

Received 22 May 2013

Received in revised form

25 July 2013

Accepted 29 July 2013

Available online 6 August 2013

## Keywords:

Hard carbon

Sodium secondary battery

Ionic liquid

Bis(fluorosulfonyl)amide

N-Methyl-N-propylpyrrolidinium

## ABSTRACT

Charge–discharge properties of hard carbon (HC) for sodium secondary batteries using NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (FSA: bis(fluorosulfonyl)amide, C<sub>1</sub>C<sub>3</sub>pyr: N-methyl-N-propylpyrrolidinium) ionic liquids were investigated. A Na/NaFSA-C<sub>1</sub>C<sub>3</sub>FSA/HC cell showed reversible capacity of 260 mAh (g-HC)<sup>-1</sup> at a constant rate of 50 mA (g-HC)<sup>-1</sup> at 363 K, maintaining cell capacities of approximately 95.5% of the initial capacity after 50 cycles. Coulombic efficiency was higher than 99.5% except for the initial few cycles, reaching 99.9% after 40 cycles. The Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell also exhibited a high rate capability of 211 mAh (g-HC)<sup>-1</sup> at a rate of 1000 mA (g-HC)<sup>-1</sup>, which corresponds to a charge rate of approximately 4C.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The demand for secondary batteries for energy-storage devices has recently experienced significant growth for use in important applications such as load leveling, emergency power supply devices, and smart grids. As high-performance secondary batteries, lithium-ion batteries (LIB) are highly popular not only for mobile applications but also for electric vehicle and household uses. However, difficulties in locating and extracting material resources for LIBs are anticipated in the near future, because such devices

employ minor metals like cobalt and nickel. Even for lithium, it is difficult to maintain a stable supply because high-quality lithium resources are unevenly distributed, which occur mainly in China and South America. Thus, the research and development of secondary batteries using only easily available raw materials such as sodium has become an active field of investigation in recent times. In particular, the number of reports on sodium secondary batteries has risen rapidly in the past 2–3 years [1–8]. Sodium, which can be easily obtained from seawater or the earth's crust, possesses a reasonably negative standard redox potential of –2.714 V vs. SHE. Furthermore, many advanced technologies designed for use in LIBs are expected to be applicable for sodium secondary batteries.

The development of sodium secondary batteries has a long history; batteries using a β"-alumina electrolyte have been studied for many years [9–12], and Na/S and Na/NiCl<sub>2</sub> batteries are

\* Corresponding authors. Tel.: +81 75 753 5827; fax: +81 75 753 5906.

E-mail addresses: [nohira@energy.kyoto-u.ac.jp](mailto:nohira@energy.kyoto-u.ac.jp) (T. Nohira), [hagiwara@energy.kyoto-u.ac.jp](mailto:hagiwara@energy.kyoto-u.ac.jp) (R. Hagiwara).

currently in practical usage as large-scale energy-storage devices for mega solar power plants and wind farms. However, these batteries have less-than-ideal operating conditions for practical industrial applications. The  $\beta''$ -alumina electrolyte needs high operation temperatures of approximately 573 K to raise its conductivity. Furthermore, Na/S and Na/NiCl<sub>2</sub> batteries require liquid sodium metal, which is an extremely hazardous material. Thus, storage and installation of Na/S and Na/NiCl<sub>2</sub> batteries have been restricted because of their large sizes and regulations placed on the use of sodium metal.

At the same time, reports on sodium secondary batteries using organic electrolytes have recently increased [1–8]. These reports highlight promising advantages of the electrolyte, such as energy density, cost, and material abundance. However, the use of organic solvents in batteries, similar to conventional LIBs, requires considerations for safety apparatus, because manufacturing hazards can prove destructive (and potentially lethal) for production of large-scale batteries. Moreover, the required organic solvents cannot be used at intermediate or high temperatures because of their high volatilities. Accordingly, large-scale and assembled sodium secondary batteries using organic solvents have to be equipped with cooling systems similar to LIBs in order to assure the safety.

To address the drawbacks listed above, the development of safe and high-performance electrolytes is strongly needed. We have developed several ionic liquids [13] that have high thermal stabilities, high ionic conductivities, and wide electrochemical windows as electrolytes for sodium secondary batteries and demonstrated their actual operation: Na/NaTFSA-CsTFSA/NaCrO<sub>2</sub> (TFSA: bis(trifluoromethylsulfonyl)amide; operating temperature: 423 K) [14], and Na/NaFSA-KFSA/NaCrO<sub>2</sub> (FSA: bis(fluorosulfonyl)amide; operating temperature: 353 K) [15,16]. We have confirmed excellent cycle performances, rate capabilities, and wide operating temperatures for the batteries using these ionic liquids as the electrolyte medium. In these studies, sodium metal was used as a negative electrode. Dendrite formation as a result of the deposition of sodium metal can be suppressed by operations at elevated temperatures, close to the melting point of sodium. However, the dendritic deposition of sodium metal is difficult to prevent completely and is unavoidable, especially at lower operation temperatures. To avoid the use of Na metal, we also investigated negative electrodes composed of Sn–Na alloys [17,18]. Although the electrode showed a very high capacity of more than 700 mAh (g-Sn)<sup>-1</sup>, its cyclability was limited because of the volume change during alloying and dealloying processes.

Concerning the studies on negative electrodes in organic electrolytes, Komaba et al. [19] and Ponrouch et al. [20] have reported that hard carbon (HC) shows a stable charge–discharge behavior with 250–300 mAh (g-HC)<sup>-1</sup> at 298 K. However, HC shows poor rate capability at room temperature; the capacity at a discharge rate of 2C shows only 40% of the capacity at rate of C/10 [20]. Because high rate capability is one of the more important properties for the practical use of HC (e.g. batteries for EVs), the improvement of rate capability is necessary for the Na/HC system.

It is reasonably expected that rate capability is largely improved by the elevation of operation temperature. We have already reported an excellent rate capability of 2000 mA (g-NaCrO<sub>2</sub>)<sup>-1</sup> (approximately 18C) for the NaCrO<sub>2</sub> positive electrode in a NaFSA-KFSA ionic liquid at 353 K [16]. Thus, we first tried applying the HC negative electrode to NaFSA-KFSA ionic liquid at 363 K. As described in Section 3, however, a Na/NaFSA-KFSA/HC cell showed a small discharge capacity and poor cyclability. Because the presence of K<sup>+</sup> ions was presumed to be the cause of the poor properties obtained, we selected NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (C<sub>1</sub>C<sub>3</sub>pyr: *N*-methyl-*N*-propylpyrrolidinium, Fig. 1) as a second ionic liquid for

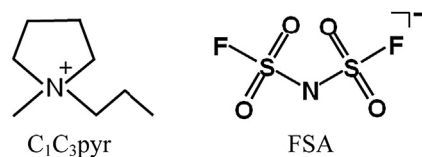


Fig. 1. Structure formula of C<sub>1</sub>C<sub>3</sub>pyrFSA.

investigation. In our previous study, fundamental properties such as ionic conductivity and viscosity were measured for this ionic liquid; a Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (20:80 mol%)/NaCrO<sub>2</sub> cell was successfully operated at 298–353 K [21]. In the present study, we report the charge–discharge behavior of Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA (10:90 mol%)/HC cells at 363 K. To study the influence of the K<sup>+</sup> ion, the behavior of the HC negative electrode was also investigated by using different compositions of ionic liquids (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 8:2:90, 5:5:90, 0:10:90 mol%). Finally, to demonstrate high rate capability at 363 K, the Na/NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA/HC cell was tested in the range 25–1000 mA (g-HC)<sup>-1</sup>.

## 2. Experimental

NaFSA, KFSA (Mitsubishi Materials Electronic Chemicals Co., Ltd., Japan, >99.0%) and C<sub>1</sub>C<sub>3</sub>pyrFSA (Kanto Chemical Co., Inc. Japan, >99.0%) were dried under vacuum at 333 K for 24 h. The eutectic NaFSA-KFSA ionic liquid (NaFSA:KFSA = 56:44 mol% [15]) was prepared by grinding the two salts with a mortar and pestle. NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquid (NaFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 10:90 mol%) and NaFSA-KFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA ionic liquids (NaFSA:KFSA:C<sub>1</sub>C<sub>3</sub>pyrFSA = 8:2:90, 5:5:90 and 0:10:90 mol%) were prepared by mixing each salt under magnetic stirring. Contents of impurities in the electrolytes such as metallic cations or halide anions were determined to be less than 10 ppm by ICP-AES and ion chromatography analysis. Electrochemical windows of NaFSA-KFSA [15] and NaFSA-C<sub>1</sub>C<sub>3</sub>pyrFSA [21] systems have been previously measured as 5.2 V at 353 K. Water content of all electrolytes was determined to be less than 50 ppm by the Karl Fischer titration method.

HC (Carbotron P, Kureha Battery Materials Japan Co., Ltd.) and polyamide-imide binder were mixed in *N*-methyl-2-pyrrolidone (Kishida Chemical Co., Ltd., >99.5%) at a weight ratio of 96:4 using a dispersion mixer. The obtained slurry was coated onto an aluminum foil current collector and pressed by roller press. Loading density of HC was 4.7 (mg-HC) cm<sup>-2</sup>. Thickness of the obtained HC electrode was ca. 50 μm.

Charge–discharge properties of the Na/HC cell were measured with a 2032 type two-electrode cell using a perfluoroalkoxy polymer gasket. The HC electrode was used as a positive (working) electrode. Sodium foil (Aldrich, >99.9%) was used for the negative (reference and counter) electrode. A microporous membrane (NPS050, Nippon Sheet Glass Co., Ltd., thickness: 50 μm) was used as a separator. Charge–discharge tests were conducted at a constant charge current rate of 25 mA (g-HC)<sup>-1</sup> and discharge current rates of 25–1000 mA (g-HC)<sup>-1</sup> in the voltage region 0.005–1.200 V. Temperature of the cell was maintained at 363 K by a thermostatic oven during the charge–discharge tests.

## 3. Results and discussion

Fig. 2 indicates the charge–discharge curves of first, second, and third cycles for a Na/NaFSA-KFSA/HC cell at 363 K. Unfortunately, the cell showed poor charge–discharge properties; the capacity at first charge was 147 mAh (g-HC)<sup>-1</sup>, which is much smaller than the reported value of 250 mAh (g-HC)<sup>-1</sup> for NaClO<sub>4</sub>/PC at 298 K [19]. An even smaller capacity of 72 mAh (g-HC)<sup>-1</sup> was observed for the first

Download English Version:

<https://daneshyari.com/en/article/1284325>

Download Persian Version:

<https://daneshyari.com/article/1284325>

[Daneshyari.com](https://daneshyari.com)