



Short communication

Properties of an intermediate temperature ionic liquid NaTFSA–CsTFSA and charge–discharge properties of NaCrO₂ positive electrode at 423 K for a sodium secondary battery

Toshiyuki Nohira*, Tatsuya Ishibashi, Rika Hagiwara*

Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

ARTICLE INFO

Article history:

Received 14 November 2011

Received in revised form

29 November 2011

Accepted 30 November 2011

Available online 8 December 2011

Keywords:

Sodium secondary battery

Intermediate temperature

Ionic liquid

Bis(trifluoromethylsulfonyl)amide

TFSA

NaCrO₂

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⁻¹, 2.29 g cm⁻³ 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 NaCrO₂ positive electrode in this ITIL at 423 K were investigated. The discharge capacities at constant current rates of 10 mA g⁻¹ (after 10 cycles) and 100 mA g⁻¹ (after 50 cycles) were 83.0 and 66.4 mAh g⁻¹, 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/NaCrO₂ cell is promising as a new type of sodium secondary battery operating at intermediate temperatures.

© 2011 Elsevier B.V. All rights reserved.

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/NiCl₂ 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 NaClO₄/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

* Corresponding authors. Tel.: +81 75 753 5822; fax: +81 75 753 5906.

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

promising as an electrolyte for lithium metal secondary batteries from the good cycle performance of a Li/LiFePO₄ 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/Na₂S_x 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 NaCrO₂ positive electrode with this electrolyte were also investigated at 423 K. NaCrO₂ 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%), Na₂CO₃ (Wako Pure Chemical Industries, purity >99.9%) and Cs₂CO₃ (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 M₂CO₃ 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 NaCrO₂

Cr₂O₃ (Wako Pure Chemical Industries, purity >98%) was mixed well with an equimolar amount of Na₂CO₃ 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 α radiation.

2.4. Electrochemical measurements

Electrochemical measurements were performed with a three-electrode system constructed in a Pyrex[®] 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 ⁻¹)	Density (g cm ⁻³)
42.5	12.1	2.29

this study; therefore, liquid sodium was immobilized in a Pyrex[®] 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 NaCrO₂ positive electrode by the galvanostatic method using a three-electrode cell with liquid sodium was used as counter and reference electrodes. The prepared NaCrO₂ 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⁻¹ NaCrO₂ between potentials of 2.3 and 3.1 V vs. Na⁺/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⁻¹ 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⁺/Na, which possibly corresponds to the deposition and dissolution of sodium metal. To confirm this,

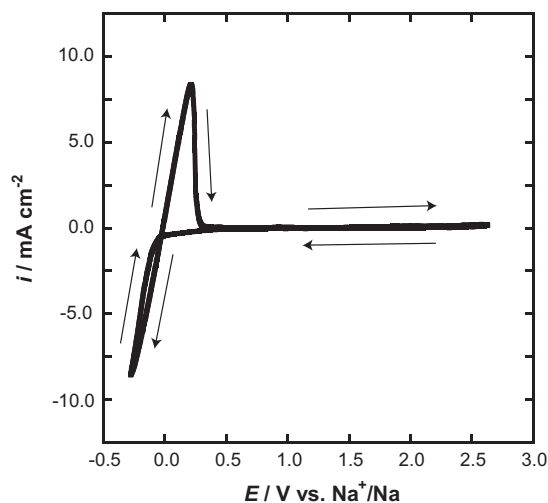


Fig. 1. Cyclic voltammogram of a Ni plate electrode in (Na10, Cs90)TFSA at 423 K, measured at a scan rate of 10 mV s⁻¹.

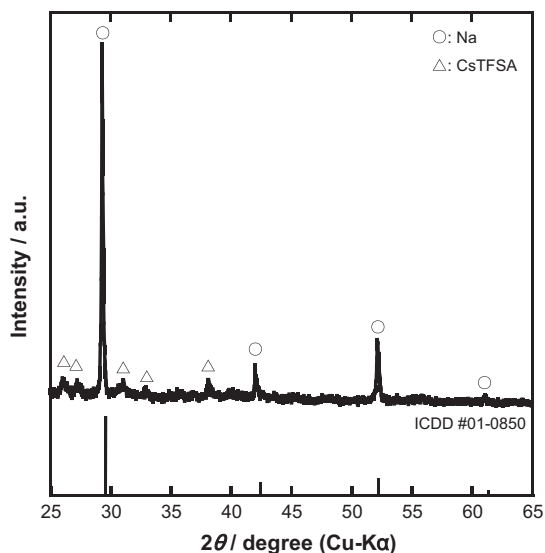


Fig. 2. XRD pattern of the deposit prepared by galvanostatic electrolysis at -2.3 mA for 10 h in (Na10, Cs90)TFSA at 423 K. A pattern of Na (ICDD #01-0850) is also shown as a reference.

galvanostatic electrolysis was conducted using a nickel plate electrode at -2.3 mA for 10 h. Fig. 2 shows an XRD pattern of the deposit, where except for the peaks of CsTFSA remaining, only peaks ascribed to sodium metal are evident, which confirmed that the reaction at the cathodic limit results in the deposition of sodium metal.

The anodic limit of (Na10, Cs90)TFSA was investigated using cyclic voltammetry with a glassy carbon rod electrode. The voltammogram shown in Fig. 3 indicates a sharp increase of anodic current from 4.9 V vs. Na^+/Na . The anodic current is believed to correspond to the irreversible oxidation of TFSA anions [20]. From the results in Figs. 2 and 3, the electrochemical window of (Na10, Cs90)TFSA is determined to be 4.9 V at 423 K.

These results indicate that this binary ITIL exhibits excellent properties as an electrolyte for sodium secondary batteries at intermediate temperatures.

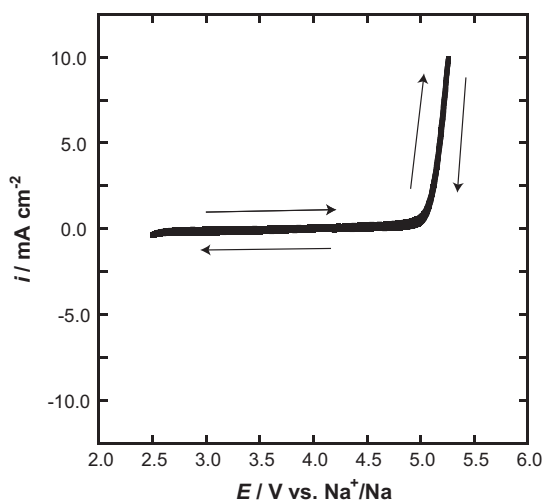


Fig. 3. Cyclic voltammogram of a glassy carbon rod electrode in (Na10, Cs90)TFSA at 423 K, measured at a scan rate of 10 mV s^{-1} .

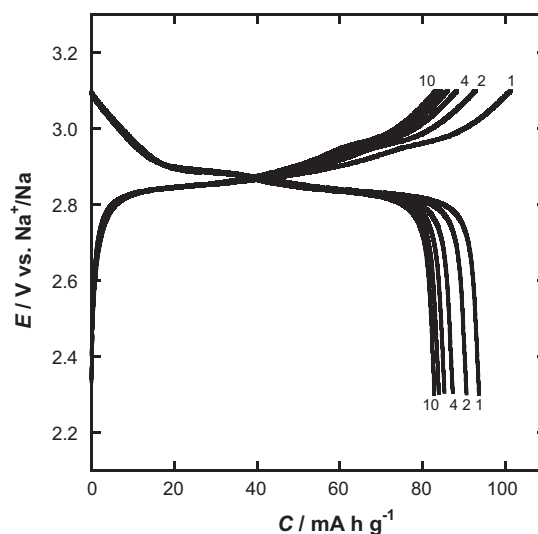


Fig. 4. Charge–discharge curves for the NaCrO_2 positive electrode in (Na10, Cs90)TFSA at 423 K. Charge–discharge rate: $10 \text{ mA (g-NaCrO}_2\text{)}^{-1}$. Cut-off potentials: 2.3 and 3.1 V vs. Na^+/Na . Cycle number: 1, 2, 4, 6, 8 and 10.

3.2. Charge–discharge tests of NaCrO_2 positive electrode

The charge–discharge properties of the NaCrO_2 positive electrode were investigated at 423 K using (Na10, Cs90)TFSA as an electrolyte. Fig. 4 shows the charge–discharge curves at a constant current of $10 \text{ mA (g-NaCrO}_2\text{)}^{-1}$. Potential plateaus are observed at 2.80–2.85 V vs. Na^+/Na in both the charge and discharge curves, in addition to other potential plateaus at 2.90–3.00 V. The features of these charge–discharge curves are similar to the previous results reported by Komaba et al. for NaCrO_2 measured in a NaClO_4/PC electrolyte at 298 K [12,13]. With reference to one report [12], the first plateau is considered to correspond to the two phase state of hexagonal O3 and monoclinic O3 structures, and the second plateau to that of monoclinic O3 and monoclinic P3 structures. Fig. 5 shows a plot of the variations of charge capacity, discharge capacity and coulombic efficiency during the cycles. In the first cycle, charge capacity and discharge capacity were 101.4 mAh g^{-1} and 93.8 mAh g^{-1} , respectively, which gives coulombic efficiency of 92.5%. It has been reported that TFSA anions decompose on the

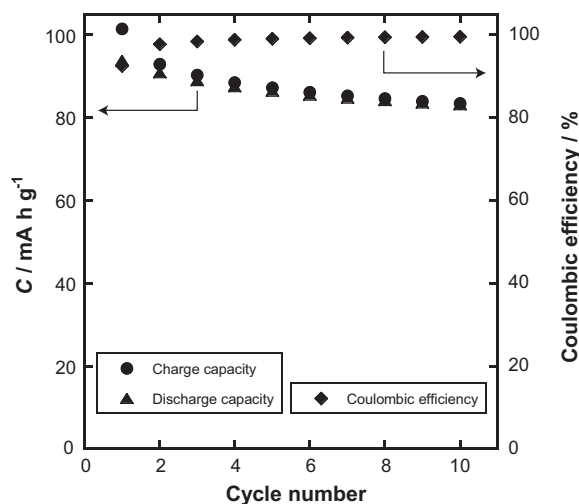


Fig. 5. Charge capacity, discharge capacity, and coulombic efficiency for the NaCrO_2 positive electrode in (Na10, Cs90)TFSA at 423 K. Charge–discharge rate: $10 \text{ mA (g-NaCrO}_2\text{)}^{-1}$. Cut-off potentials: 2.3 and 3.1 V vs. Na^+/Na .

Table 2

Summary of charge–discharge tests at various rates. The capacities and coulombic efficiencies presented were obtained in the last cycles.

Rate (mA g^{-1})	Cycle number	Charge capacity (mAh g^{-1})	Discharge capacity (mAh g^{-1})	Coulombic efficiency (%)
10	10	83.4	83.0	99.5
20	10	80.2	80.2	100.0
50	20	75.6	75.6	100.0
100	50	66.3	66.4	100.2

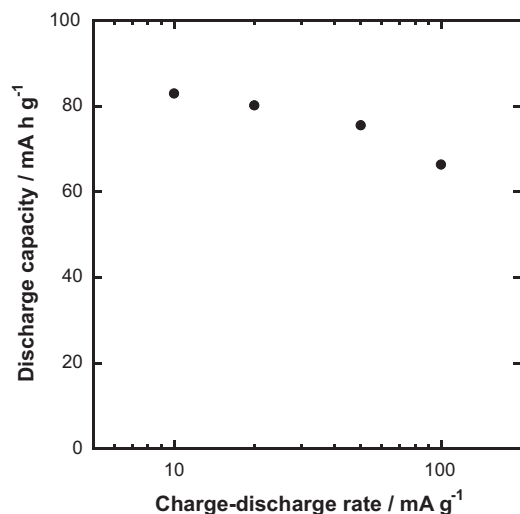


Fig. 6. Rate dependence of the discharge capacity for the last cycles of the NaCrO_2 positive electrode in $(\text{Na}_{10}, \text{Cs}_{90})\text{TFSA}$ at 423 K.

LiCoO_2 positive electrode to form a solid electrolyte interface containing LiF in a room-temperature ionic liquid LiTFSA-PMPyrTFSA (PMPyr ; 1-methyl-1-propylpyrrolidinium) at 298 K [23]. Thus, the irreversible capacity might be due to the formation of surface film on the NaCrO_2 electrode by the oxidative decomposition of TFSA anion. However, the electrode surface must be analyzed by XPS and/or SEM for decisive evidence, which is planned in our laboratory. On the other hand, stable capacities and high coulombic efficiency were observed after the initial few cycles. In the 10th cycle, the charge capacity, discharge capacity and coulombic efficiency were 83.0 mAh g^{-1} , 83.4 mAh g^{-1} and 99.5%, respectively. These results indicate that the reversibility of NaCrO_2 positive electrode is excellent, even at an elevated temperature of 423 K.

Charge–discharge tests were then conducted at higher rates using the same cell, and the results are summarized in Table 2. The capacities gradually decreased as the rate increased. However, the coulombic efficiencies were almost 100% at all rates except for the first cycles at each rate. Even at a high rate of 100 mA g^{-1} , a discharge capacity of 66.4 mAh g^{-1} was obtained after 50 cycles, which corresponds to 79.9% of the discharge capacity in the 10th cycle at 10 mA g^{-1} . Fig. 6 plots the rate dependence of the discharge capacity, which indicates a good rate capability, probably due to the high operation temperature.

From these results, it is concluded that the $(\text{Na}_{10}, \text{Cs}_{90})\text{TFSA}/\text{NaCrO}_2$ cell is promising as a new sodium secondary battery for intermediate temperature operation.

4. Conclusion

The viscosity, conductivity and density of $(\text{Na}_{10}, \text{Cs}_{90})\text{TFSA}$ were measured at 423 K. The electrochemical window of this ITIL is 4.9 V with the cathodic limit being the deposition of sodium metal. The NaCrO_2 positive electrode exhibited good cycle and rate performance at 423 K. The discharge capacities at 10 and 100 mA g^{-1} were 83.0 and 66.4 mAh g^{-1} , respectively. Except for the initial few cycles, excellent coulombic efficiency higher than 99.5% was obtained during the charge–discharge tests. It is concluded that $(\text{Na}_{10}, \text{Cs}_{90})\text{TFSA}$ is a promising electrolyte for sodium secondary batteries operated at intermediate temperature and that NaCrO_2 is a good candidate for a high performance positive electrode material.

Acknowledgement

This work was financially supported by a Grant in Aid for Scientific Research (A) from the Japan Society for the Promotion of Science (JSPS).

References

- [1] J.L. Sudworth, *J. Power Sources* 11 (1984) 143–154.
- [2] T. Oshima, M. Kajita, A. Okuno, *Int. J. Appl. Ceram. Technol.* 1 (3) (2004) 269–276.
- [3] J. Coetzer, *J. Power Sources* 18 (1986) 377–380.
- [4] C.-H. Dustmann, *J. Power Sources* 127 (2004) 85–92.
- [5] S. Bach, M. Millet, J.P. Periera-Ramos, L. Sanchez, P. Lavela, J.L. Tiradob, *Electrochem. Solid-State Lett.* 2 (11) (1999) 545–546.
- [6] D.A. Stevens, J.R. Dahn, *J. Electrochem. Soc.* 147 (4) (2000) 1271–1273.
- [7] J. Barker, M.Y. Saidi, J.L. Swoyer, *Electrochem. Solid-State Lett.* 6 (1) (2003) A1–A4.
- [8] F. Sauvage, L. Laffont, J.M. Tarascon, E. Baudrin, *Inorg. Chem.* 46 (2007) 3289–3294.
- [9] B.L. Ellis, W.R.M. Mskahnouk, Y. Makimura, K. Toghill, L.F. Nazar, *Nat. Mater.* 6 (2007) 749.
- [10] I.D. Gocheva, M. Nishijima, T. Doi, S. Okada, J. Yamaki, T. Nishida, *J. Power Sources* 187 (2009) 247–252.
- [11] N. Recham, J.N. Chotard, L. Dupont, K. Djellab, M. Armand, J.M. Tarascon, *J. Electrochem. Soc.* 156 (2009) A993.
- [12] S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takeda, A. Hokura, N. Nakai, *ECS Trans.* 16 (42) (2009) 43.
- [13] S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, *Electrochem. Commun.* 12 (2010) 355.
- [14] Y. Yamada, T. Doi, I. Tanaka, S. Okada, J. Yamaki, *J. Power Sources* 196 (2011) 4837.
- [15] Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai, S. Komaba, *Electrochem. Commun.* 13 (2011) 1225.
- [16] J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 1, Plenum Press, 1970 (Chapter 6).
- [17] K. Ui, M. Ueda, R. Hagiwara, Y. Mizuhata, *Yoyuen Oyobi Koon Kagaku* 47 (2004) 114.
- [18] R. Hagiwara, K. Tamaki, K. Kubota, T. Goto, T. Nohira, *J. Chem. Eng. Data* 53 (2008) 355–358.
- [19] K. Kubota, T. Nohira, T. Goto, R. Hagiwara, *J. Chem. Eng. Data* 53 (2008) 2144.
- [20] K. Kubota, K. Tamaki, T. Nohira, T. Goto, R. Hagiwara, *Electrochim. Acta* 55 (2010) 1113.
- [21] A. Watarai, K. Kubota, M. Yamagata, T. Goto, T. Nohira, R. Hagiwara, K. Ui, N. Kumagai, *J. Power Sources* 183 (2008) 724–729.
- [22] T. Nohira, T. Goto, R. Hagiwara, *Yoyuen Oyobi Koon Kagaku* 50 (2008) 148.
- [23] J. Mun, S. Kim, T. Yim, J.H. Ryu, Y.G. Kim, S.M. Oh, *J. Electrochem. Soc.* 157 (2010) A136–A141.