
Probing the Mechanism of Improved Performance for Sodium-ion Batteries by Utilizing Three-electrode Cells: Effects of Sodium-ion Concentration in Ionic Liquid Electrolytes

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ABSTRACT
We investigated the full-cell performance of sodium-ion batteries composed of a hard carbon (HC) negative electrode, a NaCrO2 positive electrode, and an ionic liquid electrolyte Na[FSA]–[C3C1pyrr][FSA] (FSA = bis(fluorosulfonyl)amide, C3C1pyrr = N-methyl-N-propylpyrroldinium) at 333 K. Before the full-cell tests, charge–discharge tests of the Na/HC and Na/NaCrO2 half cells were conducted, from which the practical capacities were determined to be ca. 250 mAh (g-HC)–1 and ca. 115 mAh (g-NaCrO2)–1, respectively. Using these capacities, the performance of HC/NaCrO2 full cells with practical loading masses was evaluated by three-electrode cells with a sodium metal reference electrode, and the energy density was calculated to be 177 Wh (kg-(NaCrO2 + HC))–1. In particular, we focused on the effect of the sodium-ion concentration on the performance by varying the molar fraction of Na[FSA] (x(Na[FSA])) from 0.20 to 0.50. The best rate capability was obtained at a composition of x(Na[FSA]) = 0.50. The effect of the sodium-ion concentration was discussed in terms of the potential profiles of the positive and negative electrodes. The results were explained by the sodium-ion supplying capability of the electrolyte inside the electrode, where the sodium insertion reaction occurs.

Keywords : Sodium-ion Battery, Ionic Liquid, High Concentration, Full-cell Performance

1. Introduction
Lithium-ion batteries (Li-ion batteries; LIBs) have become widespread in small electronic devices such as mobile phones and PC laptops due to their high energy densities. Recently, many researchers and companies have struggled to develop large-scale LIBs, especially for electric vehicles and stationary storage batteries.1,2 Two issues have emerged as the main concerns with the adoption of such large-scale electrical energy storage systems. One issue is safety, due to the utilization of flammable organic solvent-based electrolytes. In general, the specific surface area per volume decreases with increasing size, and thus large batteries inherently face difficulties in releasing heat to the environment, which can lead to thermal runaway and result in ignition accidents. Based on the backgrounds, ionic liquids are promising electrolytes, owing to their high safety in terms of non-flammability and negligible volatility. In recent decades, intensive studies on the development of ionic liquid electrolytes for LIBs have been conducted.1–3

Another problem is the scarcity of lithium and cobalt resources, which are used in the main components of current LIBs; it will not be possible to meet the demand for these resources in the production of large-scale power storage devices in the future.4–8 Thus, new batteries utilizing more abundant resources that represent feasible alternatives to LIBs must be developed. Sodium-ion batteries (Na-ion batteries; NIBs) are promising candidates for large-scale applications because sodium resources are abundant in the earth’s crust and sea water.9–10 Moreover, although copper current collectors are needed for the negative electrodes in LIBs, inexpensive aluminum current collectors can be used for both the negative and positive electrodes in NIBs.

Recently, several groups have reported the full-cell performance of organic solvent-based NIBs,11–15 some of which have shown energy densities higher than 200 Wh kg–1 based on the total mass of active materials in the positive and negative electrodes. However, most of these NIBs utilized a loading mass lower than 10 (mg-active materials) cm–2, and almost no intensive studies on practical-scale NIBs have been conducted.

Many researchers have reported a variety of active materials and electrolytes for NIBs, and several groups, including ours, have focused on developing ionic liquid electrolytes that fulfill both safety and performance requirements.14–30 Our group has developed the ionic liquid Na[FSA]–[C3C1pyrr][FSA] (FSA = bis(fluorosulfonyl)amide, C3C1pyrr = N-methyl-N-propylpyrroldinium, and found that the composition of x(Na[FSA]) = 0.20 (x(Na[FSA]) = molar fraction of Na[FSA]) exhibited a reasonably high ionic conductivity of 3.6 mS cm–1 and a wide electrochemical window of ca. 5 V at 298 K.34 The standard redox potential of Na+/Na in water is higher than that of Li+/Li by 0.3 V, which decreases the energy densities of NIBs. However, the potential differences between these redox couples depend on the electrolyte. For example, in the case of the ionic liquid electrolyte M[FSA]–[C3C1pyrr][FSA] (M = Li, Na; x(M[FSA]) = 0.20), the potential difference is reduced to ca. 0.1 V (E(Na+/Na) = E(Li+/Li) + 0.1).31 Thus, the utilization of ionic liquid electrolytes can eliminate the drawback of reduced energy density for NIBs. In addition, one of the most unique characteristics for ionic liquid batteries is the wide operating temperature range, which realizes superior performance at intermediate temperature range (333–363 K) compared with room temperature, due to their higher ion conductivities as well as higher reactivity of the electrode materials.
We have shown that a variety of active materials can be used in the ionic liquid Na[FSAl]–[C3C1pyrr][FSAl],25-27. Very recently, we realized a practical sodium-ion full cell consisting of a hard carbon (HC) negative electrode and a NaCrO2 positive electrode, which reached energy densities of 125 Wh L−1 and 75 Wh kg−1 at an operating temperature range of 298–363 K.28 However, the sodium-ion concentration of the ionic liquid electrolyte was as low as 1 mol dm−3, and there is room to improve the performance by increasing the composition of Na[FSAl]. In fact, the NaCrO2 positive electrode shows better rate capability at a composition of x(Na[FSAl]) = 0.40 or 0.50.29

In the present study, we investigated the performance of HC/Na[FSAl]–[C3C1pyrr][FSAl]/NaCrO2 full cells utilizing practical loading masses of 4.8–6.9 (mg-HC) cm−2 and 12.3–15.4 (mg-NaCrO2) cm−2. We adopted the three-electrode cell configuration with a sodium metal reference electrode in order to evaluate the charge–discharge behaviors of both the positive and negative electrodes separately, and discussed the effect of the sodium-ion concentration on the rate capability of the sodium-ion full cells in the ionic liquids Na[FSAl]–[C3C1pyrr][FSAl] (x(Na[FSAl]) = 0.20–0.50) at 333 K.

2. Experimental

2.1 Reagents and their handling

Na[FSAl] (>99.5%; Mitsubishi Materials Electronic Chemicals Co., Ltd.) and [C3C1pyrr][FSAl] (>99.9%; Kanto Chemical Co., Inc.) were dried under vacuum prior to use. The drying temperature and time were respectively 353 K and 48 h for Na[FSAl], and 333 K and 24 h for [C3C1pyrr][FSAl]. The Na[FSAl]–[C3C1pyrr][FSAl] ionic liquids (x(Na[FSAl]) = 0.20, 0.30, 0.40, and 0.50) were prepared by mixing Na[FSAl] and [C3C1pyrr][FSAl] in an argon-filled glove box. The sodium-ion concentrations for all the compositions are summarized in Table S1.

The preparation procedures for the hard carbon (HC) and NaCrO2 electrodes were as follows. An aqueous slurry was prepared by mixing HC powder (CARBOTRON P, Kureha Battery Materials Japan Co., Ltd.), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) in a weight ratio of HC/CMC/SBR = 97/2/1. Similarly, NaCrO2 powder, acetylene black (AB), and polyvinylidene difluoride (PVdF) were mixed in N-methyl-2-pyrrolidone (NMP) with a weight ratio of NaCrO2:PVdF = 92/5/3 to make a slurry. NaCrO2 was synthesized by the solid-state reaction method which was reported previously.26 Both slurries were coated onto aluminum foils, and were dried at 363 K in air to remove the solvents. Finally, these electrodes were dried under vacuum at 423 K for 24 h. The loading masses of HC and NaCrO2 were within the ranges of 4.8–6.9 mg cm−2 and 12.3–15.4 mg cm−2, respectively.

2.2 Charge–discharge tests and analysis

2.2.1 Two-electrode half cells

Charge–discharge tests were conducted using electrochemical measurement apparatuses (VSP, Bio-Logic Co., or 580-type battery cycler, Toyo Co.). The charge–discharge behaviors of a HC electrode and a NaCrO2 electrode were investigated respectively using 2032-type coin cells under an argon atmosphere. The working electrode was a HC or NaCrO2 electrode, and the counter electrode was sodium metal. The Na[FSAl]–[C3C1pyrr][FSAl] ionic liquids (x(Na[FSAl]) = 0.20, 0.30, 0.40, and 0.50) were used as the electrolyte. Both the HC and NaCrO2 electrodes were impregnated with the electrolytes under vacuum before assembling the cells. The operating voltage ranges were 0.005–1.4 V for the Na/HC half cell, and 2.5–3.5 V for the Na/NaCrO2 half cell. The operating temperatures were set to 313 or 353 K. The charge–discharge rates are provided in the section of Results and discussion.

2.2.2 Three-electrode full cell

A sodium-ion full cell was constructed using an air-tight three-electrode cell (Hohsen Corp.; see Fig. S1) in the argon-filled glovebox. A two-ply polyolefin filter (50 µm thickness per sheet) was used as a separator. The HC negative electrodes, NaCrO2 positive electrodes, and polyolefin filters were vacuum-impregnated with the electrolyte prior to the test. Sodium metal was used as a reference electrode. The temperature of the three-electrode cell was controlled using a temperature-controlled bath. Based on the results of the half-cell tests, the practical capacities of HC and NaCrO2 were assumed to be 250 and 115 mAh g−1, respectively. In the sodium-ion full cells, the ratio of the practical capacities of HC and NaCrO2 (N/P ratio; N/H = QHC/QNaCrO2; Q is the quantity of electricity (C)) were controlled to be within the range of 0.85–1.00. The loading masses and N/P ratios of HC/NaCrO2 full cells for discharge and charge rate capability tests are summarized in Tables S2 and S3, respectively. For the current densities, in this study, a rate of 100 mA g−1 (g-NaCrO2)−1 was regarded as 1C rate. The cut-off potentials were set at 0.002 and 1.5 V (vs. Na+/Na) for the HC negative electrodes, and 2.5 and 3.5 V (vs. Na+/Na) for the NaCrO2 positive electrodes. The cut-off voltages were 1.5 and 3.4 V for the full cells. When the potentials and voltages reached at least one of these limits, the system was switched from charging to discharging or vice versa.

The operating procedures were as follows. First, to stabilize the performance of the sodium-ion cells, all the full cells were operated at 0.2C rate for 3 cycles with the charge capacity limited to 85 mAh (g-NaCrO2)−1, and then operated at 0.2C rate without the capacity limitation for an additional 5 cycles. This stabilization step was conducted at 313 K (x(Na[FSAl]) = 0.20, 0.30, 0.40) or 333 K (x(Na[FSAl]) = 0.50). For all the full cells, the subsequent rate capability tests were performed at 333 K. In the discharge rate capability test, the charge rate was fixed at 0.5C, and various discharge rates were tested from the lowest (0.5C) to the highest (8C). A similar procedure was adopted for the charge rate capability test.

2.2.3 Instrumental analysis

The surface morphologies and the elemental distributions of a HC electrode and a NaCrO2 electrode were observed using a field emission scanning electron microscope (FE-SEM; SU-8020, Hitachi) and with an energy dispersive X-ray spectrometer (EDX; X-max, Horiba, or X-max80, Oxford Instruments).

3. Results and Discussion

3.1 Charge–discharge behavior of the Na/HC and Na/NaCrO2 half cells

Figure 1 shows selected surface SEM images of the HC and NaCrO2 electrodes. The size distributions of the HC and NaCrO2 particles were confirmed to be 2–10 µm and 1–2 µm, respectively. In addition, selected results of the SEM observations and EDX mapping analysis for both electrodes are summarized in Fig. S2. For the HC electrode (Fig. S2a–S2c), carbon and sodium are detected by EDX mapping. The carbon-rich areas correspond to the HC particles according to the SEM results, and sodium is detected over the whole electrode surface. Since CMC is the only source of sodium in the HC electrode, this result indicates that the CMC binder is homogeneously dispersed in the HC electrode. On the other hand, for the NaCrO2 electrode (Fig. S2d–S2h), the carbon component is attributed to the conductive agent (acetylene black), and the sodium and chromium are ascribed to the NaCrO2 particles. Fluorine is detected on the whole area of the electrode surface. Since the PVdF binder is the only the fluorine source, this indicates that the binder is almost uniformly distributed in both the electrode composite.

Figure 2 shows the typical charge–discharge performance of the HC and NaCrO2 electrodes using two-electrode half cells with
sodium metal counter electrodes. As shown in Fig. 2a, the discharge capacities obtained for the HC electrode at 313 and 353 K are 230 and 256 mAh (g-HC)$^{-1}$, respectively. The first three cycles were measured at 313 K, while the subsequent three cycles are conducted at 353 K, as shown in Fig. 2b. Higher capacities are observed at 353 K due to the extension of the plateau region at around 0.1 V. This mainly originates from the lower resistance for sodium-ion diffusion in the surface layer of the sodium metal counter electrode at higher temperatures. Based on the above results, a capacity of 250 mAh (g-HC)$^{-1}$ is adopted as the standard practical capacity of the electrode. The calculation of the N/P ratios in the HC/NaCrO₂ full cells. As shown in Fig. 2c and 2d, the NaCrO₂ electrode shows a stable reversible capacity of approximately 115 mAh (g-NaCrO₂)$^{-1}$ at both 313 and 353 K. Thus, the standard practical capacity of NaCrO₂ is determined to be 115 mAh (g-NaCrO₂)$^{-1}$.

3.2 Charge–discharge behavior of the HC/NaCrO₂ full cell

Figure 3 shows typical charge–discharge curves of the HC/NaCrO₂ three-electrode full cell with an electrolyte composition of α(NaFSI) = 0.20. The solid line, the broken line, and the dotted line correspond to the cell voltage, the potential of the NaCrO₂ positive electrode, and the potential of the HC negative electrode, respectively. The charge–discharge profiles of HC and NaCrO₂ are consistent with the above results from the two-electrode half cells, which indicates that the sodium-ion full cell functions properly.

A reversible capacity of 92 mAh (g-NaCrO₂)$^{-1}$ is obtained at a rate of 0.5C. Since the N/P ratio, Rₙ/p, of this cell is 0.88, the ideal practical capacity of the cell is calculated to be 101 mAh (g-NaCrO₂)$^{-1}$ using Eq. (1).

$$C_{\text{NaCrO}_2}^{\text{Full-cell}} = C_{\text{NaCrO}_2}^{\text{Std}} \times R_{\text{n/p}} \quad (R_{\text{n/p}} \leq 1)$$ (1)

where $C_{\text{NaCrO}_2}^{\text{Std}}$ is the ideal practical capacity of the full cell and $C_{\text{NaCrO}_2}^{\text{Std}}$ is the standard practical capacity of NaCrO₂ (115 mAh (g-NaCrO₂)$^{-1}$). Thus, the full cell has achieved almost 90% of the ideal practical capacity. The deviation between the ideal and obtained full-cell capacities can be explained by the irreversible capacity of the hard carbon negative electrode (ca. 40 mAh (g-HC)$^{-1}$). The average operating voltage during discharge ($V_{\text{Average}}$) of this full cell is calculated by the following Eq. (2).

$$V_{\text{Average}} = \left( \int_{Q_{\text{d}}}^{Q_{\text{i}}} V \, dQ \right) / Q_{\text{d}}$$ (2)

where $V$ is the cell voltage and $Q_{\text{d}}$ (C) is the total quantity of charge during discharge process. In this case, $V_{\text{Average}}$ is calculated to be 2.72 V. The gravimetric energy density of the full cell, $W_{\text{Full-cell}}$ (mWh g$^{-1}$ = Wh kg$^{-1}$), is defined as:

$$W_{\text{Full-cell}} = V_{\text{Average}} \times \left( \frac{Q_{\text{i}}}{3.6} \right) / \left( m_{\text{NaCrO}_2} + m_{\text{HC}} \right)$$ (3)

where $m_{\text{NaCrO}_2}$ (g) and $m_{\text{HC}}$ (g) are the weight of NaCrO₂ and HC, respectively. It should be noted that 1 mAh = 3.6 C. Here, $W_{\text{Full-cell}}$ can also be calculated from specific capacities of NaCrO₂ and HC as follows.

The specific capacities of NaCrO₂ and HC, $C_{\text{NaCrO}_2}$ (mAh (g-NaCrO₂)$^{-1}$) and $C_{\text{HC}}$ (mAh (g-HC)$^{-1}$), are expressed as

$$C_{\text{NaCrO}_2} = \frac{Q_{\text{i}}}{3.6} / m_{\text{NaCrO}_2}$$ (4)

$$C_{\text{HC}} = \frac{Q_{\text{i}}}{3.6} / m_{\text{HC}}$$ (5)

Then, from Eqs. (3), (4) and (5), the gravimetric energy density, $W_{\text{Full-cell}}$ (Wh (kg-(NaCrO₂ + HC))$^{-1}$), is obtained by the following equation:

$$W_{\text{Full-cell}} = V_{\text{Average}} \times C_{\text{NaCrO}_2} / C_{\text{HC}}$$ (6)

In the case of the discharge curve in Fig. 3, since $V_{\text{Average}} = 2.72$ V, $C_{\text{NaCrO}_2} = 91.5$ mAh (g-NaCrO₂)$^{-1}$ and $C_{\text{HC}} = 226$ mAh (g-HC)$^{-1}$, the gravimetric energy density, $W_{\text{Full-cell}}$, is calculated to be 177 Wh (kg-(NaCrO₂ + HC))$^{-1}$.

Table S4 compares the energy density obtained in this study with those of previously reported sodium-ion full cells. It should be noted that the reported energy densities are calculated based on the weight of the active materials, and that these calculations disregard the contribution of other components such as the conductive agent, binder, current collector, separator, electrolyte, and outer battery case. Moreover, the loading mass of the active material is one of the most important factors to determine the energy density of batteries. There are many full-cell studies of NIBs; some reports have used lower loading mass than that for practical batteries. Some groups have assembled full cells after eliminating the irreversible capacities of hard carbon negative electrode chemically or electrochemically. Dugas et al. constructed sodium-ion full cell by a similar way to the present study, and reported the energy density of a Na₃V₂(PO₄)₂F₃ full cell in an organic solvent-based electrolyte to be 237 Wh (kg-(Na₁₇V₁₉F₂₆PO₄)F₂ + HC))$^{-1}$. Although this value is larger than the value obtained in the present study, the difference is mainly originated from the average operating potential of positive electrodes. The average operating potentials of NaCrO₂ and Na₃V₂(PO₄)₂F₃ are 3.0 V and 3.9 V (vs. Na+/Na), respectively. Assuming that NaCrO₂ and Na₃V₂(PO₄)₂F₃ positive electrodes show the same capacity in the ionic liquid electrolyte and the operating potential of HC negative electrode is 0.30 V (vs. Na+/Na), the estimated energy density of the full cell is calculated to be 234 Wh (kg-(Na₁₇V₁₉F₂₆PO₄)F₂ + HC))$^{-1}$. Thus, by selecting superior active materials, there is much room to enhance the energy density of the full cell utilizing ionic liquid electrolyte. In our previous NIB full-cell study, loading masses of 5.2 (mg-HC) cm$^{-2}$ and 13.5 (mg-NaCrO₂) cm$^{-2}$ realized a gravimetric energy density of 75 Wh kg$^{-1}$ for a 27 Ah-class battery;
Discharge rate: 25 mA (g-HC) and the potential of the NaCrO₂ positive electrode and the potential of the HC negative electrode, respectively.

Figure 2. Typical charge–discharge performance of the HC and NaCrO₂ electrodes in Na[FSA]–[C₃C₁pyrr][FSA] ionic liquid electrolytes. (a) Charge–discharge curves of a Na/[FSA]–[C₃C₁pyrr][FSA]/HC half cell (x[Na[FSA]] = 0.20). Charge rate: 25 mA (g-HC)^{-1}. Discharge rate: 25 mA (g-HC)^{-1} (1st–3rd cycle) and 125 mA (g-HC)^{-1} (4th–6th cycle). Operating temperature: 313 K (1st–3rd cycle) and 353 K (6th cycle). Operating temperature: 313 K (1st–3rd cycle) and 353 K (4th–6th cycle). (b) Cycling properties of specific capacity and coulombic efficiency of the Na/HC half cell. (c) Charge–discharge curves of a Na/[FSA]–[C₃C₁pyrr][FSA]/NaCrO₂ half cell (x[Na[FSA]] = 0.20). Charge rate: 10 mA (g-NaCrO₂)^{-1}. Discharge rate: 10 mA (g-NaCrO₂)^{-1} (1st–3rd cycle) and 50 mA (g-NaCrO₂)^{-1} (4th–6th cycle). Operating temperature: 313 K (1st–3rd cycle) and 353 K (4th–6th cycle). (d) Cycling properties of specific capacity and coulombic efficiency of the Na/NaCrO₂ half cell.

Figure 3. Charge–discharge curves of a HC/Na[FSA]–[C₃C₁pyrr][FSA]/NaCrO₂ full cell (x[Na[FSA]] = 0.20). Operating temperature: 333 K. Charge–discharge rate: 0.5C (1C = 100 mA (g-NaCrO₂)^{-1}). The legends, V_{Cdl}, E_{PE}, and E_{NE} are the cell voltage, the potential of the NaCrO₂ positive electrode and the potential of the HC negative electrode, respectively.

which corresponds to that of LIBs in the early 2000s.²⁸ Thus, the results of previous full-cell studies with lower loading masses do not necessarily reflect the performance of practical batteries. Since we utilized high loading masses of 4.8–6.9 (mg-HC) cm⁻² and 12.3–15.4 (mg-NaCrO₂) cm⁻², the performance of our full cells is representative of practical batteries. In addition, the cycleability of HC/NaCrO₂ full cell is confirmed using the same electrolyte composition. As shown in Fig S3, the discharge capacity and coulombic efficiency in the 1st cycle were 88 mAh (g-NaCrO₂)^{-1} and 95.6%, respectively. The coulombic efficiency after the 2nd cycle is over 99.5%, and the discharge capacity at the 100th cycle is 79 mAh (g-NaCrO₂)^{-1}, which corresponds to 90% capacity retention.

3.3 Rate capabilities of the HC/NaCrO₂ full cells with different sodium-ion concentrations

Figure 4 shows the discharge curves of HC/NaCrO₂ full cells with x[Na[FSA]] = 0.20 and 0.40 at different discharge rates. The charge rate is fixed at 0.5C, and the discharge rates are varied from 0.5C to 8C. For x[Na[FSA]] = 0.20 (Fig. 4a), a discharge capacity of 89 mAh (g-NaCrO₂)^{-1} is obtained at 1C rate, which corresponds to 97% of the capacity at 0.5C rate. However, the capacity falls to...
The discharge rate capabilities for the compositions of \( \text{NaCrO}_2 \) are compared to determine the effectiveness of different electrolytes. Higher capacity retention is observed with increasing sodium-ion concentrations in the electrolyte. The capacity of the NaCrO2 positive electrode is compared, and it is observed that the capacity at 0.5C rate, except for the composition \( x = 0.40 \), is higher than 90 mAh (g-NaCrO2)^−1. For electrolytes with sodium-ion concentrations higher than \( x = 0.30 \), the capacities are maintained at around 80 mAh (g-NaCrO2)^−1 at 2C rate. The concentration dependence becomes distinct at discharge rates higher than 4C. Larger discharge capacities are observed for highly concentrated electrolytes, especially for the composition of \( x = 0.50 \), in which 84% of the capacity is retained even at 4C rate.

Figure 5 shows the rate dependence of the discharge capacity at \( x = 0.20–0.50 \). Discharge capacities of approximately 90 mAh (g-NaCrO2)^−1 are obtained at 0.5C rate. For electrolytes with sodium-ion concentrations higher than \( x = 0.30 \), the capacities are maintained at around 80 mAh (g-NaCrO2)^−1 at 2C rate. The concentration dependence becomes distinct at discharge rates higher than 4C. Larger discharge capacities are observed for highly concentrated electrolytes, especially for the composition of \( x = 0.50 \), in which 84% of the capacity is retained even at 4C rate.

52 mAh (g-NaCrO2)^−1 at 2C rate, and further decreases to less than 20 mAh (g-NaCrO2)^−1 at 4C and 8C rates. On the other hand, when the sodium salt composition is increased to \( x = 0.40 \) (Fig. 4b), improved rate performance is observed. A discharge capacity of 79 mAh (g-NaCrO2)^−1 is maintained at 2C rate, which is 1.5 times as great as the capacity in the case of \( x = 0.20 \). When the discharge curves at 2C rate are compared, almost no differences are observed in the potential profiles of the HC negative electrodes (dotted lines). On the other hand, when the potential profiles of the NaCrO2 positive electrodes (broken lines) are different, i.e., the potential rapidly drops at a capacity of 50 mAh (g-NaCrO2)^−1 for \( x = 0.20 \). Since the sodium insertion reaction occurs at the positive electrode during the charge process, the sodium-ion concentration decreases in the electrolyte inside the NaCrO2 composite electrode. The potential drop is therefore explained by the depletion of sodium ions in the electrode. In the case of \( x = 0.40 \), such sodium-ion depletion is less likely to occur than the case of \( x = 0.20 \), which results in a higher discharge capacity. In other words, electrolytes with higher sodium-ion concentrations have a superior sodium-ion supplying capability. In fact, we reported a similar improvement in the discharge rate capability of a NaCrO2 electrode using Na/NaCrO2 half cells at 363K. The discharge rate capabilities for the compositions of \( x = 0.30 \) and 0.50 are also evaluated, as shown in Fig. S4.
Figure 6. Charge curves of the HC/[Na][FSA]–[C3C1pyrr][FSA]/NaCrO2 full cells at 333 K. Charge rate: 0.5–8C. Discharge rates: 0.5C (1C = 100 mA (g-NaCrO2)−1). (a) Charge curves for x[Na[FSA]] = 0.20. (b) Charge curves for x[Na[FSA]] = 0.40.

Figure 7. Rate dependence of charge capacity for the HC/[Na][FSA]–[C3C1pyrr][FSA]/NaCrO2 full cells (x[Na[FSA]] = 0.20–0.50) at 333 K. Charge rates: 0.5–8C. Discharge rate: 0.5C (1C = 100 mA (g-NaCrO2)−1).

4. Conclusions

We investigated the performance of HC/NaCrO2 full cells in Na[FSA]–[C3C1pyrr][FSA] ionic liquid electrolytes with various sodium-ion concentrations (x[Na[FSA]] = 0.20–0.50) at 333 K. In particular, to evaluate the performance of practical sodium-ion batteries, we utilized electrodes with high loading masses of 4.8–6.9 (mg-HC) cm−2 and 12.3–15.4 (mg-NaCrO2) cm−2. First, via half-cell tests, we determined the practical capacities of HC and NaCrO2 to be 250 mAh (g-HC)−1 and 115 mAh (g-NaCrO2)−1, respectively. The NaCrO2 full cell exhibited a reversible capacity of 92 mAh (g-NaCrO2)−1, resulting in an energy density of 177 Wh (kg-NaCrO2 + HC)−1. We evaluated the effect of the sodium-ion concentration on the rate capability of the HC/NaCrO2 full cells by utilizing three-electrode cells, and discussed its mechanism based on the potential profiles of the positive and negative electrodes. In the discharge process, better rate capability was obtained using electrolytes with higher sodium-ion concentrations at discharge rates over 2C. Since the potential profiles of the NaCrO2 positive electrodes were different during the discharge process, the sodium-ion supplying capability of the electrolyte inside the composite electrodes determines the full-cell capacity. Similar behavior was observed for the charge rate capability tests, i.e., a steep decrease in the potential of the HC negative electrodes reduced the full-cell capacity for lower sodium electrolyte compositions. This phenomenon was also interpreted in terms of sodium-ion depletion in the electrolyte inside the composite electrode during the sodium insertion reaction. In conclusion, ionic liquid with concentrated sodium ion will realize high-power sodium-ion batteries.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.18-00098.

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