$\text{Na}_2\text{MnSiO}_4$ as a positive electrode material
for sodium secondary batteries using an ionic liquid electrolyte

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Abstract

Sodium manganese orthosilicate, $\text{Na}_2\text{MnSiO}_4$, was synthesized by a sol–gel method and investigated for use as a positive electrode material for Na secondary batteries using $\text{Na}[\text{FSA}]\text{--}[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ (FSA = bis(fluorosulfonyl)amide anion and $\text{C}_3\text{C}_1\text{pyrr}$ = *N*-methyl-*N*-propylpyrrolidinium cation) ionic liquid electrolyte in the temperature range 298–363 K. Carbon coating and elevation of operational temperatures significantly improved the electrode performance. A reversible capacity of 125 mAh g^{-1} (90% of the theoretical value based on a one-electron transfer process) was found at a rate of C/10 (13.9 mA g^{-1}) within 2.0–4.0 V at 363 K, with an acceptably high rate capability. $\text{Na}_2\text{MnSiO}_4$ became amorphous upon the electrochemical removal of sodium, exhibiting a similar behavior as its lithium equivalent. Both $\text{Na}_2\text{MnSiO}_4$ and its desodiated form ($\text{Na}_{0.8} \text{MnSiO}_4$) possess remarkable thermal stability, suggesting their safety characteristic.

Keywords: Sodium secondary battery; $\text{Na}_2\text{MnSiO}_4$; Positive electrode; Ionic liquid; Bis(fluorosulfonyl)amide

1. Introduction

Sodium secondary batteries have attracted widespread attention as a next-generation energy storage technology, owing to the low cost and ubiquitous availability of Na resources [1]. The chemical similarities between Na and Li imply that the extensively studied electrode materials for Li batteries provide a superior reference library for research on Na batteries [1,2]. Owing to the open structure and large interstitial space, layered oxides (AMO_2 ; A = Li, Na; M = transition metal) [3,4], NASICON (Na-superionic conductors, $\text{A}_3\text{M}_2(\text{PO}_4)_3$) [5,6] compounds, and pyrophosphates ($\text{A}_2\text{MP}_2\text{O}_7$) [7,8] are generally able to accommodate both Na and Li alkali ions. However, most of these require an improved reversible capacity and/or rate capability. Recently, orthosilicates (A_2MSiO_4) have been proposed as promising Li storage materials owing to low cost, environmental benignity, and excellent safety characteristics [9-13]. Most importantly, they offer the possibility of realizing a two-electron exchange per formula, leading to a high theoretical capacity of ca. 330 mAh g⁻¹. To our knowledge, however, orthosilicates remain as an unexplored Na host matrix.

For Li batteries, orthosilicates of satisfactory electrochemical performance generally necessitate nanosizing and carbon coating to improve their ionic and electronic transport properties [11]. Intermediate-temperature operation (ca. 333 K) is also being pursued to enhance the electrode kinetics [9, 12]. However, safety issues and poor cyclability, owing to the volatility and flammability of conventional organic electrolytes, have been inevitable obstacles [14]. Ionic liquids (ILs) are characterized as task-specific media owing to their nonflammability and good thermal and electrochemical stability [15], which make ILs an ideal electrolyte to investigate electrode performance at both ambient and

elevated temperatures. For Na battery applications, we have developed a series of ILs based on the bis(fluorosulfonyl)amide (FSA) anion [16,17]. Among these, the Na[FSA]–[C₃C₁pyrr][FSA] (20:80 molar ratio; C₃C₁pyrr = *N*-methyl-*N*-propylpyrrolidinium) IL possesses a wide electrochemical window of 5.2 V and a high ionic conductivity of 15.6 mS cm^{−1} at 353 K [17]. Moreover, this IL has been successfully applied to Na batteries in a wide temperature range of 253–363 K [18, 19].

In this study, orthosilicate Na₂MnSiO₄ (theoretical capacity of 278 mAh g^{−1} based on a two-electron reaction) was evaluated for its use as a Na storage material for the first time. Na[FSA]–[C₃C₁pyrr][FSA] IL electrolyte was utilized to exploit its electrochemical behavior from ambient (298 K) to elevated temperatures (363 K). The structural variation upon electrochemical cycling and thermal stability were also investigated.

2. Experimental

Na₂MnSiO₄ and Na₂MnSiO₄/C were synthesized by a sol-gel method as reported in [20]. The carbon content in the Na₂MnSiO₄/C composite is 13.5 wt%, according to elemental analysis. Powder X-ray diffraction (XRD, Rigaku SmartLab; Cu Kα = 1.5418 Å) was used to identify the crystalline phase of the samples. The Na₂MnSiO₄/C sample was also observed by transmission electron microscope (TEM, Hitachi H-9000UHR). The desodiated form, Na_{0.8}MnSiO₄, was prepared by chemical oxidation with NO₂BF₄ oxidizer in acetonitrile at 333 K for 24 h. The resultant compound was washed several times with fresh acetonitrile and vacuum-dried at 333 K. The content of Na in the desodiated compound was determined by X-ray fluorescence analysis (XRF, Rigaku EDXL 300). The

thermal stability of the pristine $\text{Na}_2\text{MnSiO}_4$ and $\text{Na}_{0.8}\text{MnSiO}_4$ was evaluated using thermogravimetric analysis (TGA, Rigaku, TG 8120).

The electrochemical properties of the orthosilicates were assessed using 2032 type coin cells with a Bio-Logic VSP potentiostat, as described in our previous reports [17-19]. The positive electrode was prepared by mixing $\text{Na}_2\text{MnSiO}_4/\text{C}$, acetylene black, and polytetrafluoroethylene in a weight ratio of 75:20:5. A metallic sodium disc pressed onto an aluminum current collector was used as the negative electrode. The $\text{Na}[\text{FSA}]-[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ (20:80 molar ratio) IL was dried according to our previous report [17-19].

3. Results and discussion

In the previous study by Duncan *et al.* [20], $\text{Na}_2\text{MnSiO}_4$ was used as the starting material to obtain a metastable polymorph of $\text{Li}_2\text{MnSiO}_4$ via ion exchange because the latter compound cannot be directly synthesized, but no electrochemical data on Na cell were reported. We have adopted the same synthetic method of $\text{Na}_2\text{MnSiO}_4$. Fig. 1a shows the XRD pattern of the obtained sample; the as-prepared material matches the previously known monoclinic phase with the space group Pn (PDF No. 00-055-0638), which is consistent with that obtained by Duncan *et al.* Some impurities, namely MnO and a trace amount of Na_2SiO_3 , were unavoidably present. The unidentified diffraction peaks may be assigned to another $\text{Na}_2\text{MnSiO}_4$ phase that crystallized into a different crystal structure because lithium orthosilicates are known to provide polymorphs [21]. Similar kinds of impurity phases were also noticed by other researchers during the synthesis of A_2MnSiO_4 by a variety of approaches [10,20,22]. A TEM micrograph

of the $\text{Na}_2\text{MnSiO}_4/\text{C}$ sample is shown as the inset of Fig. 1a, which confirms the formation of a thin layer of amorphous carbon on $\text{Na}_2\text{MnSiO}_4$ particle.

The charge–discharge profiles of the $\text{Na}_2\text{MnSiO}_4/\text{C}$ electrode at a rate of C/10 (13.9 mA g^{-1}) at 298–363 K are shown in Fig. 2a–c. The first charge curve with a short voltage plateau region around 3.0 V is distinct from those of the succeeding cycles, wherein only monotonically sloping curves are observed. Reversible capacities of 70, 94 and 125 mAh g^{-1} are obtained for the cell that was tested at 298, 323 and 363 K, respectively. Approximately 0.9 Na ions per unit formula can be reversibly extracted/inserted from the $\text{Na}_2\text{MnSiO}_4$ crystal at 363 K (Fig. 2c). Obviously, the decrease of polarization and increase of capacity is observed with temperature elevation, which can be attributed to the enhanced kinetics [12]. The capacity retention is about 80% at the 10th cycle for all temperatures investigated, which will require further improvement for practical application. Nevertheless, considering that lithium orthosilicates generally suffer from a very low rate capability [13,21], an acceptably high rate capability is observed for the $\text{Na}_2\text{MnSiO}_4/\text{C}$ electrode at 363 K. As shown in Fig. 2d, the electrode delivers capacities of 115, 76 and 34 mAh g^{-1} at 1 C (139 mA g^{-1}), 3 C and 10 C, respectively.

The structural evolution of $\text{Na}_2\text{MnSiO}_4$ upon electrochemical cycling was investigated by an ex-situ XRD analysis. As shown in Fig. 1b, crystalline $\text{Na}_2\text{MnSiO}_4$ collapses upon charging (Na removal), leaving behind an amorphous phase; furthermore, the diffraction peaks are not recovered during the consecutive discharge (Na insertion). This irreversible structural transformation accounts for the change in the charge–discharge profiles. Although the structural change is significant, the transformed phase can still reversibly accommodate Na ions, as

can be seen in Fig. 2. Duncan *et al.* reported that the electrochemical behavior of different $\text{Li}_2\text{MnSiO}_4$ polymorphs only slightly differed during the first cycle [20]; after the first charge, $\text{Li}_2\text{MnSiO}_4$ become amorphous and no more apparent difference of electrochemical properties was observed [13, 20]. Also, M.E. Arroyo-deDompablo *et al.* concluded that the use of mixed or single $\text{Li}_2\text{MnSiO}_4$ polymorphs is a minor issue from a viewpoint of practical applications [23]. In the present work, $\text{Na}_2\text{MnSiO}_4$ underwent a similar amorphization upon charge–discharge, so we assume that having polymorphs is not a major issue. Meanwhile, a detailed study on the composition and microstructure of $\text{Na}_2\text{MnSiO}_4$ after electrochemical cycling is currently underway.

Safety is an essential concern for large-scale battery applications; in particular, good thermal stability of the positive electrode material in the charged (desodiated) state is crucial to realize an intrinsically safe battery. Fig. 3 shows the thermogravimetric/differential thermal analytic (TG–DTA) profiles for $\text{Na}_2\text{MnSiO}_4$ and its desodiated state ($\text{Na}_{0.8}\text{MnSiO}_4$) at a heating rate of 5 K min^{-1} under the flow of Ar. Pristine $\text{Na}_2\text{MnSiO}_4$ shows negligible weight variation during heating up to 773 K, while the desodiated phase shows a weight loss of 7%. The DTA profiles for both states do not show any noticeable endothermic/exothermic peaks in the same temperature range. Such excellent thermal stability of $\text{Na}_2\text{MnSiO}_4$ is comparable to those of other safe positive electrode materials for lithium batteries. When comparing in the charged state, the thermal stability of $\text{Na}_{0.8}\text{MnSiO}_4$ is substantially better than that of MnPO_4 (423–473 K) [24] and is comparable to that of FePO_4 (773 K) [25]. The superior thermal properties of the orthosilicate will render a safe battery with high tolerance to extreme temperatures. For electrode materials of low electronic

conductivity, though improved electrochemical properties may be achieved by simply increasing the carbon content in electrodes, the volumetric energy density suffers greatly from the excess amount of carbon additive. The present study demonstrates that ILs can be advantageous electrolytes for intermediate-temperature evaluation of the electrochemical properties of new electrode materials that may otherwise be overlooked, without the need of altering electrode formulation.

4. Conclusions

Carbon coated $\text{Na}_2\text{MnSiO}_4$ was successfully synthesized by a so-gel method and evaluated for use as a positive electrode material for Na secondary batteries using $\text{Na}[\text{FSA}]-[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ IL in the temperature range 298–363 K. A reversible capacity of 125 mAh g^{-1} with an acceptably high rate capability was achieved at 363 K. Although issues that include increasing the sample purity or improving the cyclability should be addressed prior to practical applications, this is the first practical demonstration of an orthosilicate electrode material for Na batteries. The low cost, high theoretical capacity, and remarkable thermal stability allow $\text{Na}_2\text{MnSiO}_4$ to potentially serve as a positive electrode material. Further exploration of Na_2MSiO_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Ti}$) materials may offer new opportunities to make substantial improvements in capacity, voltage, and cyclability of positive electrodes for Na secondary batteries.

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Fig. 1 (a) XRD patterns of pristine $\text{Na}_2\text{MnSiO}_4$. Bragg diffraction positions for the parent phase (green ticks for $\text{Na}_2\text{MnSiO}_4$) and impurities (blue ticks for MnO and orange ticks for Na_2SiO_3) are shown. Indices are shown for only selected strong peaks. Triangles represent unidentified peaks. (Inset) A TEM image of $\text{Na}_2\text{MnSiO}_4/\text{C}$. (b) XRD patterns of $\text{Na}_2\text{MnSiO}_4/\text{C}$, first charged, and first discharged electrodes. Peaks marked by asterisks (*) are assigned to the aluminum current collector including K β peaks (**).

Fig. 2 Charge–discharge curves of the Na/Na[FSA]–[C₃C₁pyrr][FSA]/Na₂MnSiO₄/C cell at C/10 (13.9 mA g⁻¹) in the voltage range of 2.0–4.0 V at (a) 298 K, (b) 323 K, and (c) 363 K. (d) Discharge curves of the Na₂MnSiO₄/C positive electrode at various current densities at 363 K. The cells were charged to 4.0 V at a constant rate of C/10 and were kept for 2 h before discharging at different rates to 2.0 V.

Fig. 3 Thermal analysis (TG–DTA) curves at a heating rate of 5 K min⁻¹ under Ar flow for (a) pristine Na₂MnSiO₄ and (b) desodiated Na_{0.8}MnSiO₄.

Graphical Abstract

Positive electrode
 $\text{Na}_2\text{MnSiO}_4$

Ionic liquid
 $[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]\text{-Na}[\text{FSA}]$

**Elevated
Temp.**