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Electrolyte dependence of the performance of a $Na_2FeP_2O_7$// $NaTi_2(PO_4)_3$ rechargeable aqueous sodium-ion battery

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HIGHLIGHTS

- $Na_2FeP_2O_7$ with aqueous electrolytes has higher rate capability than non-aqueous.
- $Na_2FeP_2O_7$ with concentrated electrolytes has larger capacity than diluted.
- $NaTi_2(PO_4)_3$ with $NaNO_3$ aq. shows irreversiblility with corrosive side reactions.

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ABSTRACT

Aqueous sodium-ion battery is attractive, because of the low cost and the high safety. However, since the electrochemical window of the aqueous electrolyte is narrow, there have been few reports concerning the optimum cathode materials for use in aqueous sodium-ion batteries up to now. This work focused on $Na_2FeP_2O_7$ as a cathode material for a novel aqueous sodium-ion battery, and investigated the electrolyte dependence of the performances of a $Na_2FeP_2O_7$//$NaTi_2(PO_4)_3$ full-cell. The battery performances such as the rate capability and cyclability of $Na_2FeP_2O_7$//$NaTi_2(PO_4)_3$ full-cell with 2 M Na_2SO_4 or 4 M $NaClO_4$ aqueous electrolyte were better than that with the non-aqueous electrolyte. However, a $Na_2FeP_2O_7$// $NaTi_2(PO_4)_3$ full-cell with 4 M $NaNO_3$ aqueous electrolyte exhibited a large irreversible capacity due to the corrosive side reaction.

1. Introduction

To achieve the efficient utilization of the renewable energies, such as solar and wind power, the large-scale grid energy storage for load leveling system is an indispensable device. At present, there are Ni-Cd battery, Ni-metal hydride (MH) battery, Li-ion battery and sodium-sulfur battery as the commercially available rechargeable batteries. Among them, the Li-ion battery has certain advantages, such as high voltage and high energy density. However, the performance needs to be improved with regard to battery cycle life, production costs and safety. In particular, high-quality lithium provided by the sun drying of the salt lake is relatively costly, and the annual production in the world is insufficient. Na-ion batteries, which have a working mechanism similar to that of Li-ion batteries, have attracted much interest as a power source for large-scale grid energy storage, because of the low cost and abundance of sodium. However, both Li- and Na-ion batteries have an associated safety issue: at elevated temperatures, charged oxide cathodes such as Li_xCoO_2 readily release oxygen gas, which can cause the exothermic reaction with the organic electrolytes [1,2]. In addition, conventional organic electrolytes are low conductive and fairly expensive. To overcome these drawbacks, aqueous Na-ion batteries with noninflammable, high conductive and inexpensive aqueous electrolytes rather than organic electrolytes have been proposed. Recently, Aquion Energy Ltd. released a commercially-available energy storage system composed of a $Na_4Mn_9O_{18}$ ($Na_{0.44}MnO_2$) cathode, activated carbon (AC) anode and Na_2SO_4 aqueous electrolyte [3,4]. This $Na_{0.44}MnO_2$//AC system is not a rocking-chair type cell, but a hybrid capacitor. That is, the cathode reaction involves the intercalation/deintercalation of Na^+ ions into/from the $Na_{0.44}MnO_2$ bronze matrix, while the anode reaction consists of the adsorption/desorption of SO_4^{2-} on the surface of AC. Since the rechargeable capacity of this hybrid capacitor is restricted by the concentration of SO_4^{2-} anion in the electrolyte, the rechargeable capacity per weight or volume is smaller than that of a rocking-

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chair type cell.

Although several cathode active materials for the aqueous Na-ion battery have been proposed in recent years [5–16], reports of the anode active materials are still limited. Among them, minor-metal free NASICON-type $NaTi_2(PO_4)_3$ (NTP) is a rare and valuable anode example for the aqueous Na-ion battery [5,6]. The flat charge/discharge profile, corresponding to Ti^{3+}/Ti^{4+} redox reaction, locates within the electrochemical window of water. As the most inexpensive 3*d* transition metal, iron-based cathode active materials have also been proposed. In particular, olivine-type $NaFePO_4$, as the Na counterpart of $LiFePO_4$ is promising. However, it cannot be obtained by the direct synthesis method, because electrochemically inactive maricite-type $NaFePO_4$ is more stable than olivine-type $NaFePO_4$. Therefore, the only synthetic route to olivine-type $NaFePO_4$ is ion exchange between Na^+ and Li^+ in $LiFePO_4$ [17,18]. Because the ion-exchange process is relatively costly, concerted efforts are being devoted to finding new low-cost materials and manufacturing processes.

Our own group has focused on $Na_2FeP_2O_7$ as a promising cathode material for aqueous Na-ion batteries, because $Na_2FeP_2O_7$ can be obtained by simple, conventional solid state processes [19–23]. This compound exhibits a reversible specific capacity of approximately 57 mAh g^{-1} with an average voltage of −0.05 V vs. SCE, and therefore has a redox potential within the electrochemical window of water [22]. In the present work, we evaluated the electrochemical performance of $Na_2FeP_2O_7$ as a cathode for aqueous Na-ion batteries, in conjunction with typical Na-salt electrolytes, such as 0.5–4 M Na_2SO_4, $NaNO_3$ and $NaClO_4$ solutions. In addition, we investigated the electrochemical performance of an aqueous $Na_2FeP_2O_7$//$NaTi_2(PO_4)_3$ full-cell with various Na salt concentrations.

2. Experimental

2.1. Materials synthesis

As cathode active material, $Na_2FeP_2O_7$ was synthesized according to a previously reported procedure [19]. Briefly, stoichiometric amounts of NaH_2PO_4 and $Fe(COO)_2{\cdot}2H_2O$ (Wako Pure Chemical Industries, Ltd.) were placed in an alumina container along with 3 mmϕ zirconia balls. The precursor was subsequently prepared by wet ball-milling in acetone at 400 rpm for 2 h. After evaporating the acetone to obtain a dry mass, the precursor was ground in an agate mortar and pressed into cylindrical pellets. These pellets were sintered at 600 °C for 10 h under Ar containing 5% H_2. After cooling to ambient temperature, the desired $Na_2FeP_2O_7$ powder (as-prepared $Na_2FeP_2O_7$) was obtained.

On the other hand, anode active material, $NaTi_2(PO_4)_3$ was prepared from a stoichiometric mixture of Na_2CO_3 (Kishida Chemical Co., Ltd.), titanium (IV) butoxide (Sigma-Aldrich Co. LLC.) and $NH_4H_2PO_4$ (Nacalai Tesque, INC.) using the Pechini method [5,24]. This precursor mixture was decomposed at 350 °C for 3 h in air to eliminate the ammonia and organic components. The resulting powder was ground, pressed into cylindrical pellets and calcined at 800 °C for 12 h in air. The products were characterized by X-ray powder diffraction (XRD, 50 kV and 300 mA, Cu-Kα, RINT 2100HLR/PC, Rigaku Corporation) while the chemical composition of the $Na_2FeP_2O_7$ was ascertained using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; PerkinElmer Optima 8300). In ICP measurement, the powder was dissolved in a mixture of 30 wt% H_2O_2 and conc. aqueous HCl.

2.2. Electrochemical properties

To improve the electronic conductivity, 25 wt% acetylene black (AB) was subsequently added to 70 wt% $Na_2FeP_2O_7$ powder and the mixtures were dry ball-milled at 300 rpm for 10 h. In addition to the carbon coating, the carbothermal annealing for the obtained $Na_2FeP_2O_7$/C composite was performed at 600 °C for 10 h under Ar containing 5% H_2 [21]. Hereinafter, the $Na_2FeP_2O_7$/C carbon composites after carbon coating and carbothermal annealing are referred to as CC and CT samples, respectively. In combination with 5 wt% polytetrafluoroethylene binder (Polyflon PTFE F-104, Daikin Industries, Ltd.), the cathode pellets were fabricated from the CC and CT carbon composites (95 wt%), respectively.

On the other hand, 70 wt% $NaTi_2(PO_4)_3$ anode powder was combined with 25 wt% AB and ball-milled at 400 rpm for 1 h. Then, for the obtained $NaTi_2(PO_4)_3$/C composite, the carbothermal treatment was done at 800 °C for 1 h under N_2 [5]. To fabricate the anode pellet, 95 wt% $NaTi_2(PO_4)_3$/C carbon composite was fabricated from with 5 wt% PTFE binder.

They were subsequently punched into discs (10 mmϕ). These discs were sandwiched between sheets of nickel mesh (Thank Metal Co., LTD.). A three-electrode electrochemical cells incorporating various aqueous electrolytes were used in cyclic voltammetry and galvanostatic discharge/charge tests. An Ag-AgCl electrode with saturated KCl (RE-6, BAS Inc.) and pure zinc (99.9%, Nilaco Corp.) were used as the reference and counter electrodes, respectively. The electrochemical performances of the $Na_2FeP_2O_7$//$NaTi_2(PO_4)_3$ full-cell with various aqueous electrolytes were evaluated by a 2032 coin-type cell setup. The cathode/anode mass balance in this full-cell was 2:3 and the cathode/anode capacity balance was approximately 1:3. Employed aqueous electrolytes consisted of 0.5 M Na_2SO_4, 2 M Na_2SO_4, 1 M $NaNO_3$, 4 M $NaNO_3$, 1 M $NaClO_4$ and 4 M $NaClO_4$, respectively. Dissolved oxygen was purged from each aqueous electrolyte by bubbling Ar, since the $Na_3Ti_2(PO_4)_3$ generated on charging process is readily oxidized by dissolved oxygen in an aqueous solution [25]. The electrochemical performance of the $Na_2FeP_2O_7$ was also confirmed in a 2032 coin-type cell with non-aqueous electrolyte (1 M $NaClO_4$ in propylene carbonate (PC), Tomiyama Pure Chemical Industries, LTD.) and a polypropylene separator and Na metal (Sigma-Aldrich Co. LLC.). The cell incorporating the non-aqueous electrolyte and Na metal was assembled in an Ar-filled glove box (dew point < −80 °C). Cyclic voltammetry was performed with a Versastat 3 (AMETEK, Inc.). Galvanostatic charge/discharge tests were carried out using a cycler (NAGANO & Co., Ltd.) at a constant current density.

3. Result and discussion

3.1. Structural characterization of $Na_2FeP_2O_7$

The obtained samples were characterized by XRD, generating the patterns presented in Fig. 1. The $Na_2FeP_2O_7$ powder was identified as triclinic with *P*-1 diffraction pattern consistent with $Na_{1.56}Fe_{1.22}P_2O_7$ (ICDD # 83–0255), with no impurity phases detectable.

The XRD profile of the CC sample (Fig. 1 (b)) contained peaks that were broader than those of the as-prepared $Na_2FeP_2O_7$, indicating the lower crystallinity. In contrast, the XRD peaks of the CT sample became sharper following the carbothermal treatment, suggesting that the crystallinity of the $Na_2FeP_2O_7$ was improved by annealing at 600 °C.

3.2. Electrochemical performances of a $Na_2FeP_2O_7$ cathode against Zn counter electrode

Fig. 2 compares the initial and second charge-discharge profiles of CC and CT cathodes in 2 M Na_2SO_4 aqueous electrolyte. These electrochemical measurements were carried out within a potential