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Characterization of Prussian blue as positive electrode materials for sodium-ion batteries

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ABSTRACT

Prussian blue, $K_xFe_y[Fe(CN)_6]_z/nH_2O$, was investigated as a positive electrode material for sodium-ion batteries. A Na cell with a Prussian blue positive electrode exhibited a first discharge capacity of 57 mAh/g. However, the discharge capacity rapidly decreased. It appears that the lattice parameter of Prussian blue changes and electron conductivity is gradually lost. Then, we attempted to improve the cycle performance of the cell with a positive electrode using high conductivity carbon, ketjen black EC600JD. As a result, a positive electrode of Prussian blue and ketjen black exhibited a first discharge capacity of 67 mAh/g and exhibited a retention of more than 80% at the 40th cycle. Moreover, the positive electrode was improved owing to dehydration caused by the thermal treatment of the Prussian blue. Prussian blue showed a reversible Na^+ intercalation potential around 2.5 V vs. Na, which corresponds to the redox of Fe^{2+}/Fe^{3+}.

1. Introduction

We can expect an extraordinarily large number of lithium-ion batteries to be used for electric vehicles and electricity energy storage. However, due to the depletion of lithium sources, the supply of lithium-ion batteries may become unstable. As a result, the sodium-ion battery has been focused on as a high-energy-density battery to replace the lithium ion battery, and many researchers have reported various component materials for sodium-ion batteries [1–9] because sodium is a widely available material. As the positive electrode material for a sodium-ion battery, we have concentrated on Prussian blue ($Fe_4[Fe(CN)_6]_3$) as a rare metal free material. The theoretical capacity is 126 mAh/g when 4 mol sodium ions react with one Prussian blue molecule. Prussian blue has Fm3m symmetry and the lattice parameter ($a = b = c$) is large (>10 Å). It has been reported that lithium ions can be intercalated into Prussian blue [10]. Then, positive electrode materials which have a similar crystal structure to Prussian blue have been studied for use in sodium-ion batteries [4,5].

In this study, we evaluated the electrochemical characteristics of a Prussian blue electrode and attempted to improve Na cell performances.

2. Experimental

Prussian blue was purchased from Acros Organics (Thermo Fisher Scientific Inc.). The positive electrodes were prepared by the following procedure. A mixture of Prussian blue powder, carbon powder and PTFE (polytetrafluoroethylene) powder (weight ratio of 70: 25: 5) was rolled into a 0.5 mm thick sheet and cut into 16 mm diameter pellets, which were then pressed on a Ti mesh. In this study, two carbon materials, acetylene black (DENKI KAGAKU KOGYO) and ketjen black EC600JD (Lion Corp.), were used. The electrodes were fabricated in dry air with a dew point of less than −50 °C. The crystalline structures of the samples were confirmed by using an X-ray diffractometer (Rigaku Co., RINT2500, X-ray radiation: CuK_α). The dehydration behavior of the Prussian blue was confirmed by using thermogravimetry (TG)-differential thermal analysis (DTA) (Rigaku Co., Thermo Plus TG 8120). The conductivities of the electrodes were measured with FLUKE 87 multimeter (TFF Fluke Corp.)

The Na cell (beaker type cell) was composed of a Prussian blue electrode, a sodium metal sheet (0.8 mm thick) and 1 mol/l $NaClO_4$/PC as a positive electrode, a negative electrode and an electrolyte solution, respectively. The cells and were constructed the electrochemical tests were carried out in glove box with a dew point of less than −75 °C in Ar.

Discharge–charge measurements were carried out under a galvanostatic condition in a 2.0 – 3.5 V range at room temperature. The current density was 0.5 mA/cm^2. The discharge and charge capacities were normalized by the weight of the Prussian blue in the positive electrode.

3. Results and discussion

3.1. Electrochemical performance of Prussian blue mixed with acetylene black

Fig. 1 shows the discharge and charge curves and cycle properties of Na cell incorporating Prussian blue mixed with acetylene black as a

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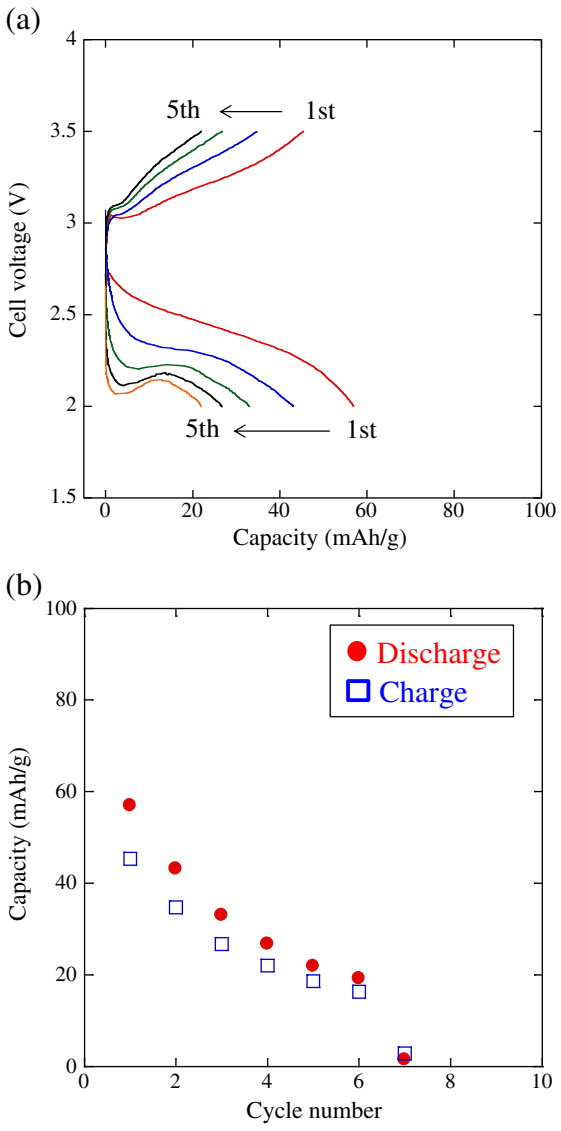

Fig. 1. (a) Discharge–charge curves and (b) cycle properties of Na cell incorporating Prussian blue mixed with acetylene black.

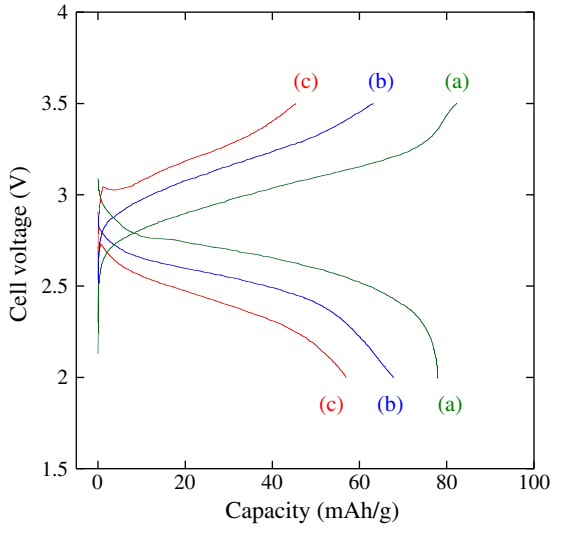

Fig. 2. XRD patterns of a positive electrode incorporating Prussian blue mixed with acetylene black before and after discharge–charge test, (1) pristine, (2) after 1st discharge, (3) after 1st charge, (4) after 2nd discharge, (5) after 50th discharge.

conductive material. The first discharge and charge capacities were 57 and 45 mAh/g, respectively and the capacity was irreversible. The capacities decreased and the overvoltage became higher with every cycle. Fig. 2 shows the rate performance of Na cells incorporating Prussian blue mixed with acetylene black. The largest discharge capacity was 78 mAh/g at a current density of 0.125 mA/cm^2 and irreversible capacity was not observed. On the other hand, at a higher current density of 0.5 mA/cm^2, the overvoltage became higher and irreversible capacity appeared.

Fig. 3 shows XRD patterns of a positive electrode incorporating Prussian blue mixed with acetylene black before and after a discharge–charge test. The pristine electrode was identified as $Fe_4[Fe(CN)_6]_3$ (PDF No.00-052-1907) and PTFE (PDF No.00-047-2217), respectively. After the discharge–charge test, a new peak of $Na_4Fe(CN)_6$ (PDF No.00-001-1026) other than $Fe_4[Fe(CN)_6]_3$ and PTFE was observed in the XRD patterns of the other electrodes. As a result, it is likely that $Na_4Fe(CN)_6$ was generated in the positive electrode and this caused resistance and irreversible capacity.

3.2. Electrochemical performance of Prussian blue mixed with ketjen black

We attempted to improve the conductivity of the positive electrode by employing ketjen black. Fig. 4 shows the discharge and charge curves and cycle properties of a Na cell incorporating Prussian blue mixed with ketjen black. The first discharge and charge capacities were 67 and 76 mAh/g, respectively. After the 2nd cycle, the capacities exceeded 70 mAh/g and the cycle performance was better. K-ion in Prussian blue may be extracted in the first charge process. This is the reason why the first discharge capacity is smaller than the first charge capacity. The actual conductivities of pristine positive electrodes with acetylene black and ketjen black were 0.96 and 9.62 mScm^2, respectively. The conductivity of the positive electrode with ketjen black was 10 times that with acetylene black. It appears that a reversible discharge–charge cycle became possible because the resistance of the positive electrode was improved and the overvoltage became smaller than with acetylene black.

We attempted to achieve further improvement by removing the water content from the Prussian blue because Prussian blue tends to adsorb water. Prussian blue has a three-dimensional network of $[Fe^{2+}(CN)_6]^{4-}$ and Fe^{3+}, and an open structure of the large asymmetric CN^- [11]. These open spaces connect together to construct a tunnel structure in the lattice. Prussian blue can easily contain water molecules inside this tunnel. To understand the hydration behavior of Prussian blue, TG-DTA was performed from room temperature to 300 °C at a heating speed of 5 °C/min. A TG-DTA curve recorded in air is shown in

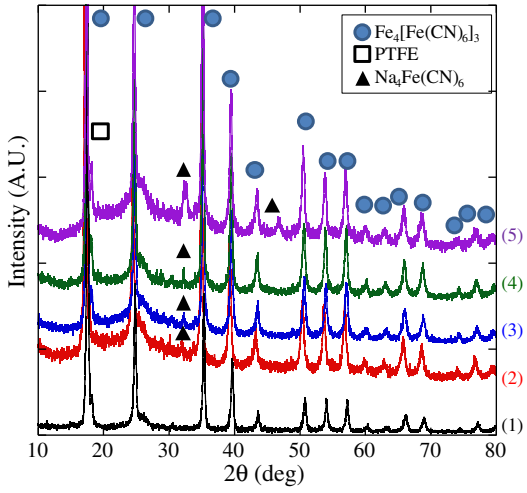

Fig. 3. Rate performance of Na cell incorporating Prussian blue mixed with acetylene black, (a) 0.125 mA/cm^2, (b) 0.25 mA/cm^2, (c) 0.5 mA/cm^2.

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