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High rechargeable sodium metal-conducting polymer batteries

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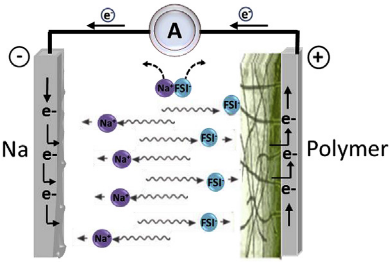
HIGHLIGHTS

- Battery is constructed using PAni Emeraldine-base as cathode and Na as anode.
- The Na-fluoro-based salt in propylene carbonate was used as the electrolyte.
- The PAni/Na battery has a comparable cycling life to lithium cell.
- Na plating and dissolution occur during the charge and compete with each other.

GRAPHICAL ABSTRACT



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ABSTRACT

Rechargeable lithium batteries accelerated the wireless revolution over the last two decades, and they are now a mature technology for transportation applications in electric vehicles (EV). However, numerous studies have concluded that the proven lithium reserves can hardly absorb the growth in demand. Therefore, sustainable sodium batteries are being considered to overcome the lithium resource shortages that may arise from large-scale application in EVs and stationary energy storage. It is difficult to find a suitable host material for reversible Na-ion storage due to the size of the Na^+ ion (0.102 nm) compared to the Li^+ ion (0.076 nm). Here we report a low cost and simple sodium technology that is based on a metal-free cathode material. Sodium metal was used as the anode with a conducting polymer cathode and electrochemically tested in a liquid electrolyte. With this technology, a host material for Na intercalation is not required, and because a polymer conductor is used, the size of the Na ion is not an issue.

1. Introduction

Within the last two decades, the applications of rechargeable batteries have become an indispensable tool for modern society; in particular lithium-ion batteries have dominated the portable electronics market and making strong inroads for EV applications. However, the availability and cost of these batteries are challenges that will be encountered to meet the emerging needs of larger scale energy storage, for e.g. electromobility and load-levelling [1]. Therefore, new strategies are required to replace lithium-ion batteries with more Earth-abundant elements [2]. One sustainable and low cost alternative is sodium-ion batteries. Sodium is inexpensive and significantly more abundant than lithium; it is found in numerous minerals as well as in rather high concentrations in the oceans [3,4]. However, it is difficult to find a suitable host material for reversible Na-ion storage due to the size of the Na^+ ion (0.102 nm) compared to the Li^+ ion (0.076 nm), about 40% larger in radius [5]. Hence, finding and optimizing suitable electrode materials are crucial for the development of Na-ion batteries. A large variety of host materials, such as layered oxides [6,7], phosphates [8], polyanion fluorophosphates [9], hexacyanoferrate [10,11], has

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recently been demonstrated as sodium-ion insertion cathodes, with certain redox capacity and cycling life. In the case of the lithium-ion battery, there is growing concern about cost, as well as the safety and reliability problem [12] and limited lithium reserves [13] for large-scale electrical energy storage applications. In the anode, a number of host compounds showed greatly improved electrochemical performance as a host for Na^+ storage. Among these materials, hard carbons [12,14] and Na-alloy materials (Sn, Sb) [5,15–17] have shown similar electrochemical properties to the anodes of lithium-ion batteries. However, the cathodic Na-storage materials are much inferior to those of their lithium counterparts [18,19]. Therefore, it is of critical importance to further improve the Na-storage capability and cycling stability of the cathodic materials. The redox-active polymers [20–22] seem to be a good choice of electrode-active materials for Na-ion batteries because of their structural diversity and materials sustainability. In fact, the flexibility of their framework can reversibly accommodate the larger Na ions without much spatial hindrance, thus facilitating fast kinetics for Na^+ insertion and extraction reactions [23–25]. Organic cathode and anode materials could be used in a Na-ion battery, but, the disadvantage of this technology is the lower cell voltage of organic electrodes [26]. Therefore, using metallic Li or Na as anode will yield higher voltage and higher energy than in the Li/Na-ion batteries [27].

In this paper, we report the results of a rechargeable battery with a Na-metal anode combined with a polyaniline cathode in an organic electrolyte containing Na-based salts (NaTFSI, $NaPF_6$ and NaFSI). These findings are compared to lithium-metal cells.

2. Experimental

The polyaniline cathode (PAni) was prepared from polyaniline Emeraldine base (Alfa Aeser, US), carbon nanotubes (CNT) (Nanogram China) and polyvinyl difluoride (PVDF). We have selected the polyaniline Emeraldine base (EB) due its high conductivity when it is doped with anions [28,29]. Fifteen percent PVDF was dissolved in NMP, and then polyaniline and CNT were added to the solution in the ratio of 80% and 5% by weight, respectively. After mixing, the slurry was coated on a carbon-treated aluminum collector. The cathode was dried at 60 °C for 12 h under vacuum. The loading of these cathodes was in the range 0.6–0.7 mg/cm^2. For the anode material, a 200 μm thick Na foil from a Na ingot (Sigma-Aldrich) was used. To improve our understanding of Na-battery performance, Li-cells containing comparable materials were investigated. The electrolyte solutions for the Li-battery were prepared by dissolving 1.0 M $LiPF_6$ (UB Japan), 1.0 M $LiN(CF_3SO_2)_2$ (Lithium trifluoromethanesulfonimide) LiTFSI (3 M) or 1.0 M $LiN(SO_2F_3)_2$ (Lithium bis(fluorosulfonyl)imide (LiFSI)) (Nippon Shokubai, Japan) in a mixture of ethylene carbonate: diethyl carbonate (EC:DEC). The corresponding salts investigated in the Na-battery were $NaPF_6$, NaTFSI or NaFSI. The coin cells used in the studies were assembled in a glove box. The electrochemical characterization was carried out at room temperature using a Biologic VMP3 multi-channel battery tester equipped with the Electrochemical Impedance Spectroscopy (EIS) board. The *in-situ* impedance measurements of the cells were conducted to determine the interface resistance as a function of cycle life and discharge rates. Typical EIS experiments were performed at open circuit voltage (OCV) in the frequency range from 0.2 MHz to 10 MHz under a DC stimulus of 5 mV after attaining the equilibrium conditions. The electrochemical studies were performed with a VMP cycler.

A protocol based on different constant current rates was used for the formation cycles; and for studies of cycle life, a constant current at 1C rate was used. The cut-off voltage was maintained between 2.0 V and 3.9 V. The power performance of the cell was evaluated by using a cycling protocol with different rates from 0.1C to 10C. The C-rates were calculated based on the theoretical capacity of the polyaniline-EB which involving 0.5e in the doping and de-doping steps.

3. Results and discussion

We used the semi-oxidized type of PAni called Emeraldine base that consists of two forms -one is completely reduced and the other is completely oxidized. Then only 0.5 electron by formula will be involved in the electrochemical process. The oxidized form of this polymer requires the presence of an anion, A^-, to maintain charge neutrality [27]. This is not present in the neutral polymer, therefore anion mobility (linked with solvent dynamics) is a key factor in the performance of these polymer materials.

During the charging process, Na^+ ions are deposited on a sodium-plate anode in the electrolyte solution, and the PAni cathode is oxidized by anion (A^-: PF_6^-, $TFSI^-$ or FSI^-) doping. During discharge, Na is dissolved in the electrolyte and the PAni particles are reduced with the release of an anion (A^-). The storage mechanism in the system is based on the egress and ingress (doping and de-doping) of the anion (A^-) from the electrolyte in the PAni matrix (1).

During the charge process, the Na^+ cations are plated on the Na-metal anode and accept electrons from an external circuit with Na^+ association, while the PAni cathode is p-doped to donate its electrons to an external circuit with (A^-) anions association for charge counterbalance. During discharge, Na^+ cations and A^- anions are disassociated from the anodic Na-metal and cathodic PAni chains, respectively, while the electrons flow from the anode to the cathode through the external circuit. Therefore, the reactions at the electrodes and the overall cell reaction are described by equations:

$$\text{Cathode } PAni_{red} + x(A^-) - xe^- \leftrightarrow (PAni_{oxy})^{(x+)}(A^-)_x \tag{1}$$

$$\text{Anode } xNa^+ + xe^- \leftrightarrow xNa \tag{2}$$

$$\text{Cell } PAni_{red} + xNaA \leftrightarrow (PAni_{oxy})^{(x+)}(A^-)_x + xNa \tag{3}$$

These reactions explain the mechanism occurs during charge/discharge of the Na/PAni battery. By using the emeraldine base structure where half of the structure is oxidized. For this case, H^+ must be present in the electrolyte by ion exchange with sodium. This is very unlikely, considering the difference in donor numbers between the PAni nitrogens (DN > 25) and that of the carbonate solvents (DN ≈ 15). There is thus no favourable solvation for the protons, and they mainly stay on the PAni chains.

In the long term, however, it is possible the reaction products of the Na° electrode on the solvent (alkoxides, hemicarbonates …) migrate to the positive electrode and deprotonate the PAni, but replacement of this lost proton (with the anion) does not imply substitution on the PAni chains by Na.

In this technology, the polymer cathode PAni is the limiting electrode, while the Na anode is in excess, and its thickness is adjusted to provide only the required capacity in the cell.

During cell evaluation, we noticed that the first charge cannot reach the 4.0 V cut-off voltage due to the instability of the sodium surface. From this observation, we concluded that cycle formation is required to stabilize the electrodes surfaces and increase the coulombic efficiency.

3.1. Formation

The voltage profile of the first few galvanostatic cycles in an organic electrolyte EC-DEC with $NaPF_6$ and $LiPF_6$ cells at a C/24 rate