Improved rate performance of Prussian blue cathode materials for sodium ion batteries induced by ion-conductive solid-electrolyte interphase layer

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HIGHLIGHTS

- PB cathode materials with different amounts of zeolite water were synthesized.
- A high rate performance of 84 mAh g^{-1} at 1000 mA g^{-1} was achieved.
- Improved cycling stability (1.2% capacity loss after 100 cycles) was demonstrated.
- Zeolite water in PB led to the formation of Na_2CO_3 in SEI layer.

GRAPHICAL ABSTRACT
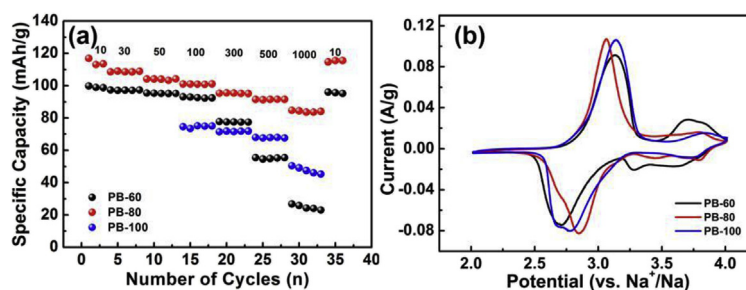
ARTICLE INFO

ABSTRACT

Prussian blue (PB) and its analogues (PBAs) are promising cathode materials for sodium ion batteries (SIBs) because of their wide diffusion tunnels for sodium ions. However, water molecules typically contained within PB structures have been hypothesized to undermine their stability and rate performance. Here we report that zeolite water molecules in PB structures may induce the formation of Na_2CO_3 as one of the main components in SEI layer on the surface of PB materials. From PB samples containing zeolite water synthesized *via* a solvothermal method at different temperatures, a specific capacity of 113 mAh g^{-1} is demonstrated at 10 mA g^{-1}, with a capacity retention of 75% at 1000 mA g^{-1}. Cycling tests reveal a capacity loss of only 1.2% after 100 cycles at 200 mA g^{-1}. It is suggested that Na_2CO_3 contained in the SEI layer not only protects the electrode materials from side reactions with the electrolyte, but also facilitates quick charge transfer at the interfaces, leading to improved electrochemical performances.

1. Introduction

Among a variety of energy storage systems, particularly for large-scale applications, sodium ion batteries (SIBs) are competitive candidates because of the natural abundance and cost-effectiveness of sodium [1–5]. Current SIB electrode materials are mostly analogues derived from lithium ion batteries (LIBs). However, the relatively high redox potential of Na$^+$/Na (-2.71 V *vs.* NHE compared with -3.04 V

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vs. NHE for Li^+/Li) and the large ionic radius of Na^+ ions (1.02 Å) are challenges for SIBs to achieve similar energy and power densities as that of LIBs. In addition, the storage mechanisms for sodium ions in these materials are different from lithium ions [6–9]. Despite that some materials (e.g., $Na_3V_2(PO_4)_3$) have shown improved capacity retention and cycling stability for SIBs compared to LIBs [10–12], further understanding on the fundamentals and practical issues of sodium ion storage materials is necessary to advance the SIB technology.

Prussian blue (PB) and its analogues (PBAs) as promising SIB cathode materials are a series of metal-organic-frameworks (MOFs) with a cubic crystalline structure in which metallic ion centers are 6-fold coordinated to cyanide ligands (-C≡N-). The metallic ions, through experiencing different crystal fields from coordinated C or N, take two distinguished electron configurations at their valence shells, namely, low-spin and high-spin states [13,14]. Therefore, most PBAs are featured with a two-stage redox reaction by accommodating two sodium ions within their loose open-framework during charge/discharge process. With a theoretical capacity of 170 mA h/g [15,16], plus their low toxicity and low cost, PB materials have shown great perspective for practical application in SIBs. PBAs can provide wide diffusion tunnels (approx. 3 Å) for intercalated alkaline ions. Therefore, excellent high rate capacity retention is expected. However, quite a few studies have suggested that the existence of $[Fe(CN)_6]^{x-}$ vacancies and correspondingly induced coordinated water molecules in PBAs compromise their electrochemical activity and ionic diffusion. In addition, the repeating cubic-rhombohedral phase transfers during electrochemical reactions also cause structural collapse at the defected sites, leading to capacity decline during cycling process [17–22]. Hence, reducing the content of vacancies is considered an effective way to enhance the cycling stability of PB-type materials. It has been reported that PBAs synthesized with chemical inhibition method exhibit less defects due to the slower growth rate of PB crystals [23–25]. These PB materials did show improved stability but experienced substantial capacity drop at high charge/discharge rates. The unsatisfying rate performance of PBAs has been attributed to their low electric conductivity, which causes severe electrode polarization at high rates. This issue may be alleviated by combining PBAs with conductive carbon materials to form composites [26–28]. However, the suppressed capacity contribution from C-coordinated Fe ions is still a problem and its origin is yet to be revealed [29,30].

Apart from the electronic conductivity of active materials, solid electrolyte interphase (SEI) layer also plays an important role in the rate performance of electrodes because of its influence on the charge transfer resistance at electrode/electrolyte interface [31–35]. Typical SEI layers consist of a variety of components with diverse influence on the charge transfer process. For example, SEIs of Li anodes with Li_2CO_3 as the major component are thin and tend to show lowered interfacial resistance [36]. But when components such as Li_2O, Li_3N, and LiOH accumulate in the SEI, the passivating effect of the SEI layer drops [37]. As for PBA materials, it has been believed that side reactions occurred at ~4.0 V (*vs.* Na^+/Na) have detrimental effect on the cycling stability of the electrodes [38]. On the other hand, however, it has also been reported that an SEI layer of PBA materials could form around 4.0 V (*vs.* Na^+/Na) as a result of the side reactions with electrolyte and the SEI may improve charge transfer performance at the surface of the PBA materials once it fully covers the surface the active materials [28]. However, the evolution of the components with in the SEI layer of PBAs has not been elucidated.

In this report, a solvothermal method was applied to synthesize Prussian blue cathode material at different temperatures. It was found that different synthesis temperatures tend to affect the stoichiometry of the as-prepared PB materials and the content of zeolite water molecules within the PB lattices. Electrochemical measurements indicated that samples containing zeolite water molecules showed better rate performance and cycling stability. Among them, Prussian blue produced at 80 °C demonstrated the best electrochemical performance of 113 mA h/

g at 10 mA/g with 75% of the capacity retained at 1000 mA/g. Based on Fourier transform infrared (FTIR) and electrochemical impedance (EIS) spectroscopy results, it was proposed that zeolite water molecules were essential to the formation of a stable SEI layer of low interfacial resistance for PB materials with enhanced rate and cycling performances.

2. Experimental

2.1. Material synthesis

3 mmol Na_4Fe $[Fe(CN)_6]\cdot10H_2O$ and 1 mmol ascorbic acid were dissolved in 150 mL distilled water. Then 3 mL hydrochloric acid (HCl) was added into the mixed solution. The as-prepared solution was heated to 60 °C, 80 °C or 100 °C in oil bath and maintained at the temperature for 4 h under vigorous magnetic stirring. The synthesized light blue powder was collected through centrifugation and washed by distilled water and ethanol several times before dried at 120 °C for 12 h. The as-prepared PB materials were denoted as PB-60, PB-80 and PB-100 according to the synthesis temperatures.

2.2. Material characterization

The crystalline structure of the as-prepared materials was identified by an X'Pert 3 diffractometer (PANalytical, Netherlands) with a Cu Kα radiation source (λ = 1.54056 Å) and the crystalline sizes were calculated according to Debye-Scherer formula. Thermogravimetric analyses of the samples were conducted on a Mettler Toledo TGA/DSC 1 STARe system under argon flow between 50 and 350 °C at a scan rate of 10 °C/min. The morphology and nanostructure of the samples were examined by field emission scanning electron microscope (FESEM, FEI Nova NanoSEM 450) and field emission transition electron microscope (FETEM, FEI Tecnai G2 F20S-TWIN TMP). FTIR (IRTracer-100) was employed to examine the chemical environment of the transition metallic ions.

2.3. Electrochemical tests

Electrochemical tests of the samples were conducted in 2032 coin cells. The working electrodes consisted of 70 wt% of the as-prepared material, 20 wt% carbon black, and 10 wt% poly-(vinyldifluoride) (PVDF). The mass loadings of the electrodes were 2.7–3.0 mg/cm². VWR glass fibers were used as the separators and the counter electrodes were sodium metal. The capacities of the electrode materials were calculated based on the mass of the active material.

All electrochemical tests were conducted at room temperature. Galvanostatic tests were performed on a LAND CT2001A (Wuhan, China) at various current densities. The voltage window was 2.0–4.0 V (*vs.* Na^+/Na). Cyclic voltammetry (CV) tests were conducted at various scan rates ranging from 0.1 to 0.5 mV/s within a potential window of 2.0–4.0 V (*vs.* Na^+/Na) using a Solartron SI 1287 electrochemical workstation. The cycling stabilities of the materials were tested at a current density of 200 mA/g for 100 cycles after activated at 10 mA/g. Half-cell EIS tests were conducted before and after the cycling tests using the Solartron SI 1287 electrochemical workstation in conjunction with a Solartron 1260 A impedance analyzer over a frequency range from 100 kHz to 0.01 Hz with an AC amplitude of 10 mV. In order to investigate the SEI formation on the surface of the electrode materials, aged batteries without electrochemical tests and batteries subjected to 100 cycling tests were dissembled in glovebox. The corresponding working electrodes were washed thoroughly with dimethyl carbonate (DMC) solution and dried in an inert atmosphere for 12 h before FTIR measurements. Fresh electrode materials with no contact with electrolyte were also subjected to FTIR tests.