Journal of Power Sources 340 (2017) 14–21

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

The mechanism of the sodiation and desodiation in Super P carbon electrode for sodium-ion battery

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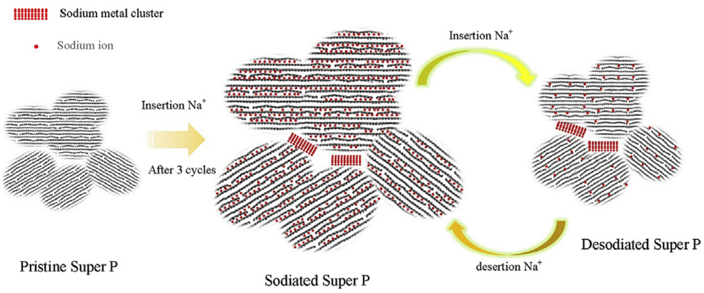
HIGHLIGHTS

- Super P (SP) consists of few-layer-thick graphite, interlayer distance ca. 0.357 nm.
- The graphitic layer distance increases on sodiation to ~3.84 and 4.41 Å.
- Metallic Na plating were observed at the micro-pores between the carbon particles.
- Pathways of Na^+ into graphite layers and micro-pores were proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 September 2016
Received in revised form
28 October 2016
Accepted 11 November 2016

Keywords:
Sodium-ion battery
Anode
Super P carbon
Neutron powder diffraction

ABSTRACT

The sodiation and desodiation of sodium (Na) into the Super-P carbon anode material were investigated using electrochemical analyses, high-resolution transmission electron microscopy (HRTEM), and neutron powder diffraction (NPD). In the sodiated Super-P carbon, sodium is stored both in the graphite interlayer space of carbon nano-particles and pores between the particles. Sodium metal clusters found in micro-pores between the carbon particles are responsible for the large irreversible capacity of the Super-P electrode. The graphite interlayer distance increases on sodiation from 3.57 Å to two distinct values of ~3.84 and 4.41 Å. The mechanism of the process is discussed.

1. Introduction

The unstable sources of renewable energy generation, such as solar and wind power, are challenging to be integrated with a power grid. Combining the renewable energy generation with an inexpensive and sufficiently large-scale local electricity energy storage (EES) system is a potential solution for micro-grid integration [1]. To meet the requirements of a sustainable battery technology, the electrode materials for EES devices need to be environmentally friendly and with low cost and good electrochemical properties, e.g., durable cycling life, high rate capability,

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http://dx.doi.org/10.1016/j.jpowsour.2016.11.048

and high energy density [2]. Sodium (Na) is abundant in the Earth crust, so sodium-ion battery (SIB) with Na as the active material can notably reduce the cost of raw materials for large-scale EESs compared with lithium-ion batteries (LIBs).

Graphite, the most commonly used negative electrode for LIBs, has a theoretical specific capacity of 372 mAh g^{-1} for lithium (Li) in LIB; however, it performs poorly in SIBs for intercalation of the bigger Na ions (Na^+) because of the small interlayer distance [3–5]. Various alternative carbonaceous materials have been proposed as negative electrodes for SIB [6,7], e.g. graphene materials [4,8,9], carbon nanoparticles [2,10,11], templated carbons [5,12,13], petroleum cokes [14–19], and pitch-based carbon-fibers [20,21]. The electrochemical characteristics of these carbonaceous materials vary in a very wide range due to their great differences in morphologies, surface areas, surface compositions, and pore size.

In order to improve electrochemical properties of carbonaceous materials for SIB, extensive research effort has been devoted to understanding the reaction mechanisms for Na insertion into the disordered carbon materials. The Na capacity of 300 mAh g^{-1} (with plating) was achieved for hard carbons derived from sugar carbon sources, as reported by Stevens and Dahn [7]. The hard-carbon materials consist of few-layer-stacked graphite nanocrystallites with large interlayer distances in the range of 0.37–0.40 nm [22]. The few-layer-stacked graphite nanocrystallites are widely distributed over amorphous carbon with disordered nanovoids in the hard carbon materials [7,9,11,12,22–24]. It is believed that the Na^+ ions can be inserted into both the graphite nanocrystallites and the nanovoids in hard carbon. The voltage-capacity curves show a sloping region and a plateau region indicating that – Na^+ is inserted into the nanocrystallite in the sloping region at the voltage ranging from 1.5 to 0.15 V (versus Na/Na^+)), and fills into the nanovoids in the plateau region at the voltage of 0.15–0.0 V (versus Na/Na^+), which is close to the equilibrium voltage of Na plating [9,11,12,18,22–24]. The filling of Na^+ into the nanovoids was confirmed with small angle neutron and X-ray scattering analyses [25–28]. Between the two mechanisms, the interlayer insertion behavior is the preferable, while the pore filling involves large irreversibility and results in trapped Na and capacity loss. However, in contrast to the metallic clusters of Li reported based on ^7Li nuclear magnetic resonance spectroscopy (NMR) [29–31], the formation of metallic Na clusters in nanovoids of hard carbon was not confirmed using ^{23}Na NMR, which is likely influenced by the products of electrolyte decomposition [2,32]. The mechanism of Na^+ insertion into disordered carbon remains controversial.

The process of Na^+ intercalation into carbon-based anode is quite complex. Limited capability for Na was detected by experimental techniques such as NMR or high-energy synchrotron X-ray powder diffraction. However, there is no direct observation of Na^+ insertion in carbonaceous matrixes in literature. In this paper, Na^+ insertion in the spherical carbon (Super P carbon black material) was investigated using the neutron powder diffraction (NPD) and high-resolution transmission electron microscopy (HR-TEM). The Na^+ insertion into nanovoids and graphite layers in the Super P electrode in sodium-ion battery is identified and the mechanism is proposed.

2. Experimental

2.1. Electrode preparation

Spherical carbon (Super P, nanosphere carbon material) was supplied by MMM Carbon (Belgium) as a negative electrode. The Super P electrode was made of 80 wt% Super P, a 20 wt% polyvinylidene difluoride (PVdF KF#1700, Kureha Battery Materials Japan Co., Ltd) binder dissolved in N-methyl-2-pyrrolidinone (NMP, International Specialty Products Inc.). The resulting slurry was cast on copper foil (10 μm, Nippon Foil Co., Japan) and dried at 100 °C in vacuum for 2 h. The dried electrodes were roller-compressed at room temperature to make a smooth and compact structure, and then inspected for uniform surface. Electrodes of similar thickness and weight were selected for further testing. Finally, to remove residual water and standardize the level of hydration, the selected electrodes were stored in a glove box with oxygen and water level maintained below 1 ppm for more than 24 h before electrochemical characterization.

2.2. Coin cell fabrication and electrochemical measurements

The charge/discharge characteristics were tested in a coin-type cell (CR2032) with a Na foil counter electrode at 25 °C. Na foil (Sigma-Aldrich Fine Chemicals, 99.99% pure) pressed to a foil was placed on the lower casing and covered with Celgard 2325 trilayer separator (polypropylene/polyethylene/polypropylene) separator. Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and $NaPF_6$ were obtained from Sigma-Aldrich Co. LLC. The composition of electrolyte was 0.78 mol kg^{-1} $NaPF_6$ added in the carbonate solvents. All coin cells were assembled under controlled argon atmosphere in a glove box with oxygen and water content below 1 ppm. All cells were charged and discharged galvanostatically for 3 cycles at a C/10 current rate (~0.13 mA cm^{-2}) in the voltage range of 0.002–2 V for conditioning the cell properties. For further studies, the half cells were charged to 0.002 V (as the sodiated state) and then discharged to 2.0 V (as the desodiated state). Cyclic voltammetry (CV) measurements were carried out on an Autolab electrochemical analyzer with a current sensitivity of 1 nA (Autolab PGSTAT30, Eco. Chemie). A single-compartment and triple-electrode polypropylene cell was used, and the entire apparatus was placed in a glove box. A three-electrode cell was used for cyclic voltammetry measurements, with the Super P electrode as the working electrode and sodium foils as counter and reference electrodes.

2.3. Material characterization

High-resolution transmission electron microscopy (HRTEM) characterization was carried out on a JEOL JEM-2100F transmission electron microscope. The cycled Super P samples were handled carefully to avoid exposure to air. The samples were cleaned in DMC solution and transported in Teflon-sealed glass vials filled with Ar. The sodiated Super P particles were dissolved in NMP by sonication and then several drops of the solution were dropped onto the TEM copper grids. The TEM copper grids were dried under $3*10^{-3}$ torr vacuum for 48 h thoroughly and then delivered to TEM in sealed vials. The neutron powder diffraction (NPD) measurements were carried out on the high-resolution powder diffractometer Echidna at the Australian Nuclear Science and Technology Organisation OPAL facility. The data were recorded by loading the samples in vanadium can using $\lambda = 2.44$ Å over the 2θ range of 10–163° at a step size 0.125°. To reduce background from hydrogen-containing cell components, the Super P electrode samples were separated from other cell components and sealed in vanadium cans in a glove box.

3. Results and discussion

3.1. Cyclic voltammetry and coin cell test

The electrochemical behavior of sodium ion insertion–extraction in Super P electrode was investigated using cyclic voltammetric (CV) and galvanostatic charge–discharge cycling