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Advanced sodium-ion batteries using superior low cost pyrolyzed anthracite anode: towards practical applications

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ABSTRACT

Energy storage technologies are the core technology for smooth integration of renewable energy into the grid. Among which sodium-ion batteries show great promise due to the potential low cost originated from the abundant resources and wide distribution of sodium. However, the anode still remains great challenge for the commercialization of sodium-ion batteries. Here we report a pyrolyzed anthracite (PA) anode material with superior low cost and high safety through one simple carbonization process. The PA anode material shows promising sodium storage performance demonstrated by prototype pouch cells with a practical energy density of 100 Wh kg^{-1}, good rate and cycling performance. Furthermore, the high safety of pouch cells with PA anode was also proved by a series of safety experiments. These desirable properties of the PA anode can meet the requirements for practical applications and pave the way for the industrial production of low-cost and high-safety sodium-ion batteries for large-scale electrical energy storage.

1. Introduction

Recently, air pollution, climate change and the depletion of fossil fuels become overwhelming challenges for mankind, so the utilization of renewable energy such as solar energy and wind energy becomes more and more important for sustainable long-term development. A near challenge is to find a safe, cheap and long-life energy storage system to smoothly integrate renewable energy into the grid. Although lithium-ion batteries (LIBs) are good alternatives, the recent estimation shows that lithium resources could become insufficient if the electric vehicles and overall energy storage market grow as anticipated [1–4]. Sodium-ion batteries (SIBs) are promising options due to low cost, abundant resources and wide distribution of sodium [5–11]. The design and development of high-performance electrode materials including both cathodes and anodes is the most crucial step for the future commercialization of SIBs. Thankfully, several developed cathode materials including oxides and polyanionic compounds make it possible for the manufacture of practical SIBs with high voltage, high energy and power density [12–18]. Particularly, we recently discovered air-stable Cu based layered oxide of O3-$Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$ with a capacity of 100 mAh g^{-1} and an average storage voltage of 3.2 V and excellent cycling performance. However, the anode still remains a grand challenge for the commercialization of SIBs.

Carbon materials have long been of particular interest since the early 1980s as an important class of anode materials for rechargeable batteries and supercapacitors due to their huge abundance, excellent corrosion resistance and high conductivity [4–10,19–26]. The most typical representative is graphite that is the widely used as anode material in LIBs with high reversible capacity, low lithium storage potential and long cycle life for portable electronic devices and electric vehicles. However, the graphite shows electrochemical inactivity in SIBs due to the thermodynamic reason [27]. In recent years, a variety of carbon materials with different structures (soft carbons [27,28], hard carbons [29–33] and hybrid carbons [34,35]), different compositions (N-doped carbons [36] and sulfur-doped carbon [37]) and different morphologies (carbon nanotubes [38], porous carbons [39] and expanded graphite [40]) have been investigated as anodes for SIBs. It is noteworthy that the soft carbon also delivers very low sodium storage capacity (*ca.* 100 mAh g^{-1}) with a sloping voltage profiles

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(Fig. S1). In contrast, the hard carbon with highly disordered structure which allows significant sodium insertion at potential below 0.1 V attracts more and more attention due to the high capacity, low sodium storage potential and good cycling stability since first reported by Dahn's group [28]. However, the high cost caused by relatively high price and/or low carbon yield of precursors limits its industrialization (Table S1). Therefore, the development of new precursors and preparation technologies to improve the carbon yield and reduce the cost has become an important research direction to satisfy the requirement for practical application.

Coal is one of the most important energy sources accounting for 25% of energy consumption around the world with features of abundant resources, wide geographic distribution and superior low cost (Table S2), and it is a kind of precursor for producing soft carbon. Among all coals, the anthracite shows the highest carbon content and lowest impurity content. Here we reported a novel pyrolyzed anthracite (PA) anode for SIBs through one simple carbonization process. Surprisingly, it delivers a high sodium storage capacity of 222 mAh g^{-1} with good rate performance and long cycle life. When coupled with air-stable $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$, prototype pouch cells exhibit a practical energy density of 100 Wh kg^{-1}, good cycle performance and high safety. In particular, the carbon anode material is very suitable for industrial production because of easy preparation, low cost, high carbon yield (> 90%) and little pollution.

2. Experimental

2.1. Materials synthesis

PA was prepared by the direct pyrolysis of anthracite. The anthracite was carbonized for 2 h in a tube furnace under Argon flow. The carbonization temperatures were 1000 °C, 1200 °C and 1400 °C, respectively. The fabricated pyrolysed anthracite denoted as PA1000, PA1200 and PA1400 were prepared as summarized in Table S3.

2.2. Materials characterizations

Thermogravimetric analysis (TGA) data were obtained using a NETZSCH STA 409 PC Luxx simultaneous thermal analyser (Germany) from room temperature to 1000 °C at a heating rate of 5 °C min^{-1} under a nitrogen gas atmosphere. The structure was characterized by an X'Pert Pro MPD X-ray diffraction (XRD) (Philips, Netherlands) using Cu-Kα radiation (1.5405 Å) and Raman spectra (JY-HR 800). For *in situ* XRD experiment during electrochemical cycling, a special cell was used with a Be window for X-ray penetration. The in situ cell was discharged and charged at a current rate of 0.05 C. The L_c was obtained based on the Scherrer equation: $L_c = K\lambda/\beta_{002}\cos\theta$, where K is shape factor, λ is wave length of X-ray and β_{002} is the half width of (002) peak in X-ray diffraction. The La was calculated based on the following simplified equation: $L_a(nm) = 4.4I_G/I_D$, I_G and I_D are the intensity of G-band peak and D-band peak in Raman spectra, respectively. The morphologies of the samples were investigated with scanning electron microscope (SEM) (Hitachi S-4800). High-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) patterns were recorded on a FEI Tecnai F20 transmission electron microscope. Nitrogen adsorption and desorption isotherms were determined by nitrogen physisorption on a Micrometritics ASAP 2020 analyzer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with a spectrometer having Mg/Al Kα radiation (ESCALAB 250 Xi, ThermoFisher). All binding energies reported were corrected using the signal of the carbon at 284.8 eV as an internal standard. For the *ex situ* XPS measurements, the coin cells were disassembled in an argon-filled glove box with different condition and the electrodes were washed in dimethyl carbonate (DMC) for three times to remove the $NaPF_6$, then the drying samples were obtained and moved to the machine with Argon-filled sealing tube as transferred box. In this process, all samples were exposed to air within 3–4 s.

2.3. Electrochemical measurements

The working electrodes were prepared by spreading the mixed slurry of active material and sodium alginate binder in water solvent with a weight ratio of 9.5:0.5 onto Al foil, and then dried at 100 °C in vacuum for 10 h. The electrolyte was a solution of 0.8 M $NaPF_6$ in ethylene (EC) and dimethyl carbonate (DMC) (1:1 in volume). A sodium foil was used as the counter electrode and glass fiber was used as the separator. All the operations were performed in the Argon-filled glove box. The discharge and charge tests were carried out on a Land BT2000 battery test system (Wuhan, China) in a voltage range of 0–2 V at various C-rates under room temperature. For the galvanostatic intermittent titration technique (GITT) tests, the cell was discharged/charged at 0.1C with current pulse duration of 0.5 h and interval time of 2 h. According to Fick's second law of diffusion, the diffusivity coefficient of Na^+ ions (D_{Na+}) can be estimated based on the following simplified equation:

$$D = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2$$

where τ is the pulse duration, m_B and M_B are the active mass and molar mass of carbon, V_M is the molar volume, and S is the active surface area of the PA1200 electrode. ΔE_S and ΔE_τ can be obtained from the GITT curves. Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were measured using Autolab PGSTAT302N (Metrohm, Switzerland). The sodium-ion full cells were constructed using PA1200 as the anode and $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$ as the cathode. Synthesis method of the $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$ material was a conventional solid state reaction. The coin type full cells were charged and discharged in a voltage range of 1–4.05 V at various current rates with a 1:2.4 weight ratio of the two electrodes (anode/cathode). The prototype pouch cells were charged and discharged in a voltage range of 1.5–4 V at various current rates with an anode capacity in excess of 10 percent.

3. Results and discussion

The thermal weight loss of precursors determines not only the carbon yield but also the emission of pollution gas, so it is a key issue for the fabrication of carbon materials. As presented in Fig. 1a, the anthracite shows an extremely high carbon yield of above 90%, which is the highest carbon yield among all precursors for production amorphous carbon materials as reported so far. The low weight loss also demonstrates a small amount of gas emission, indicating a more environmentally-friendly precursor and preparation process. The scanning electron microscopy (SEM) image of PA (Fig. 1b) reveals the granular morphology and a particle size distribution in the range of 1 to 10 μm.

The microstructure of PA was first determined by X-ray diffraction (XRD) and Raman spectra as shown in Fig. 1c and d. All the Bragg diffractions exhibit the broad peaks at 24° and 43°, which correspond to the diffraction of (002) and (100) planes in the disordered carbon structure. Raman spectra present two separate characteristic bands of D-band peak at ~1343 cm^{-1} (the defect-