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Short Communication

Nanoporous Carbon Sponge as the Anode Materials for Lithium Ion Batteries

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Abstract: *Lithium ion battery is the choice for future generations of portable electronics and hybrid and electric vehicles due to its high energy density, power density and long cycle life compared to other battery technologies. However, current graphite anode limits its application due to the low energy density derived from layered graphitic structure and low rate capability due to the slow diffusion of Li ion in graphite. In this study, a simple and versatile approach was developed to generate nanoporous carbon sponge using the combination of hard templating and etching reaction. The electrochemical properties have been tested with these novel anode materials, which showed remarkable electrochemical performance and cycling stability. Therefore, the nanoporous carbon sponge is promising to be used as the anode materials for next generation lithium ion batteries requiring high energy density and power density.*

Keywords: Lithium ion batteries, Nanoporous carbon sponge, Charging and discharging

1. INTRODUCTION

The present graphite-based lithium-ion battery limits its application due to the low energy density derived from layered graphitic structure and low rate capability due to the slow diffusion of Li ion in graphite [1]. Therefore, the next generation of anode material in lithium-ion batteries should possess higher energy storage density and high rate capability [2,3]. Among them, nanostructured carbon materials, such as carbon nanotubes, pyrolytic and mesoporous carbons, have already been tested as anode materials in lithium-ion batteries [4-6]. Porous carbon materials have received a great deal of attention due to their many applications, for example, natural gas storage and capacitor electrodes [7]. These applications require porous carbons to have a tailored mesoporous structure. To meet the requirement, many novel approaches to control pore structure have been proposed. Among them, great attention has been paid to the templating carbonization method. So far, many researchers have prepared mesoporous carbons (pore sizes between 2 and 50 nm) with this technique using a variety of inorganic rigid and designed porous templates [8,9].

Mesoporous carbon materials are very promising for their applications involving large molecules, catalyst supports and electrodes for biosensors [10,11]. Since its emergence, these materials have also attracted much attention in electrochemical and energy-related applications. This kind of carbon is formed by using porous silica as the template, the removal of which leaves a partially ordered graphitic framework. The carbon skeleton is resulted from the carbonization of polymerized furfuryl alcohol, which has shown a very high capacity for lithium insertion. Nanoporous carbon sponge (NCS) is a novel nano-carbon that makes a highly porous and strong absorbing media with significant internal surface area. In this study, we report the application of nanoporous carbon sponge as the anode materials and the electrochemical characteristics of rechargeable lithium ion batteries. The nanoporous structure (pore size <2 nm) adds more complexity and possibilities for lithium storage.

2. EXPERIMENTAL

2.1. Materials synthesis

Mesoporous silica structures are versatile platforms to achieve ordered nanoscale porous carbon materials because of their tendency to self-assemble in periodic structures of tens of nanometers [12-14]. To direct porous-controlled synthesis of the silica template, in this work we used triblock copolymer Pluronic P123 (EO20PO70EO20, Mav= 5800) and tetraethoxylsilicon (TEOS) as a surfactant and silica source, respectively. The mesostructured silica was formed by mixing P123, HCl and deionized water and followed by calcinations at 823 K. The resulted silica template was

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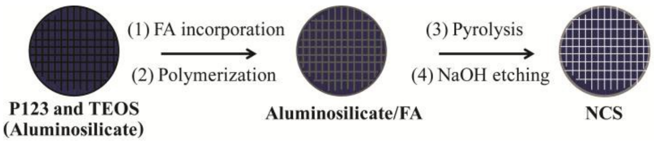

Figure 1. Schematic illustration of nanoporous carbon sponge synthesis using the hard templating and etching reaction.

converted to an aluminosilicate form with a Si/Al ratio of 40:1, following the post-synthesis incorporative procedure. Furfuryl alcohol (FA, $C_5H_6O_2$) as the carbon precursor was filled with the aluminosilicate template and heated at 95 °C for 5 h, which resulted in a layer of polymerized carbon inside the template pores. The NCS structure was obtained by pyrolysis at 1000 °C for 4 h under vacuum. The porous carbon was obtained after subsequent dissolution of the silica framework in 10 wt% NaOH solution at room temperature (Figure 1).

2.2. Electrochemical testing

The electrode was made by mixing nanoporous carbon sponge (80 wt%), conductive carbon (super C65, 10 wt%) and polymer binder (polyethylenetetrafluoride (PTFE), 10 wt%) and the mixture was coated on copper foil. Swagelok type cells used Li metal foil as the counter electrode (also as the reference electrode), two layers of microporous polymer (Celgard 2500) as the separator and liquid electrolyte mixtures containing 1:1:1 by mole ethylene carbonate: dimethyl carbonate: diethyl carbonate (EC: DMC: DEC), and 1 M $LiPF_6$ as the conductive salt. For the electrochemical tests, VMP3 from Biological Instrument was used. Cyclic voltammetry (CV) was conducted in the potential range of 0V~3.5V at 1mV/s for 5 cycles. Electrochemical cells were charged at constant current (C/15) constant voltage (CCCV) and discharged at constant current (CC) with different rates in -1.5V~0V voltage range at room temperature. The same low charging (lithiation) rate was adopted since discharging capability was important in the commercial applications and discharging (delithiation) performance was mainly evaluated here. After finishing the rate capability tests, the cell was charged and discharged at 5C for cycle life tests. Electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential with uncharged, charged and discharged states and the perturbation amplitude was 10mV.

3. RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) and Plan-view transmission electron microscopy (TEM) images of the NCS obtained under the optimum synthesis condition were shown in Figure 2. The analysis of SEM presents the nanoporous carbon sponge with two-dimensional (2D) layered hierarchical structures (Figure 2a and 2b). According to TEM characterization, the as-prepared carbon sponge shows porous structure (Figure 2c), which is highlighted by the bright area. The enlarged magnification TEM image (Figure 2d) reveals that these materials comprise of open-pore structure domains with 1.2+/-0.2 nm spacing after the activation treatment by NaOH solution, probably due to the removal of silica framework. The Brunauer-Emmett-Teller (BET) specific surface area of the nanoporous carbon sponge is 721 m2 g^{-1}.

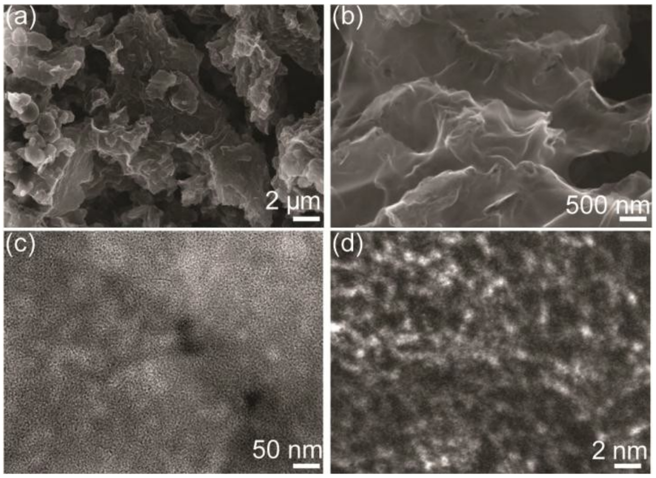

Figure 2. (a-b) SEM images (upper row) of nanoporous carbon sponge synthesis using alumonosilicate template and carbon polymerized reaction. (c-d) The HRTEM images of the same sample show the uniform porous structures.

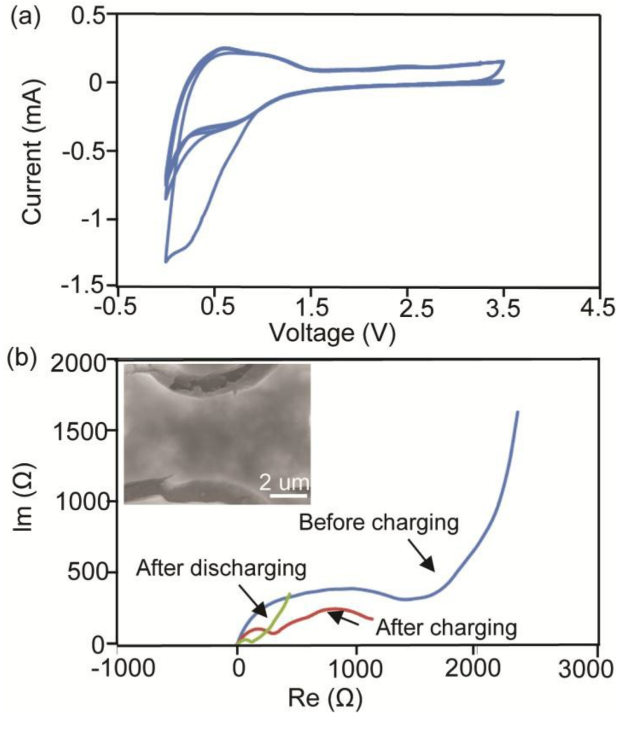

Figure 3. (a) Cyclic voltammetry tests for nanoporous carbon sponge electrode, (b) Electrochemical impedance spectroscopy of nanoporous carbon sponge before and after charging (lithiation) and discharging (delithiation).

The CV curves for the NCS at a scan rate of 1mV/s in the voltage range of 0 ~ 3.5V are shown in Figure 3a. In the cathodic scan, a pronounced reduction peak is located at 0.2V (peak 1), mainly during the first cycle and less pronounced in the following cycles, which is mostly the result of the electrolyte decomposition and formation of a solid electrolyte interphase (SEI) layer [15]. Also we can see that there is a peak at about 0.5V (peak 2), from the lithiation of the nanoporous carbon sponge. In the anodic scan, one peak is also shown at about 0.5V (peak 3), which is the delithiation of nanoporous carbon sponge. The anodic and cathodic peaks at 0.5V show good consistence with 5 cycles, which suggests that nanoporous carbon sponge should have good cyclability. Also compared to the 5 cycles, a large irreversible capacity existed in the first cycle because of forming SEI layer, which is common for graphite and carbon electrodes [16-19].

EIS results are shown in Figure 3b before and after charging and discharging. The solution resistance keeps constant with charging and discharging. The impedance before charging includes two depressed semicircles and an inclined line. The first semicircle is because of the interfacial resistance, the second semicircle is because of the charge transfer resistance and the inclined line is because of mass transfer resistance. The impedance after charging includes three semicircles and we believe that a SEI layer was formed after charging in the first cycle and contributes a semicircle. We do not see the inclined line because the frequency is not low enough to see the mass transfer effects. After discharging, we can only see one semicircle and inclined line and the possible reason is that the resistances decrease significantly after discharging and combine together. Comparing to the three curves, the resistance reduces after charging and discharging and the possible reason is that forming a SEI layer reduces the charge transfer resistance and/or interfacial resistance.

Discharge profiles and capacity at different C rates are shown in Figures 4a and 4b. At C/10, the discharge capacity is about 500 mAh/g, which is 30% more than the theoretical capacity of commercial graphite anode (372 mAh/g). Although this number is lower than previous reported [15], here we only charge carbon electrode to -1.5V. Surprisingly, at 5C charge and discharge rate, the specific capacity is still around 300mAh/g, which is similar with the previous results with addition of carbon nanotube [15]. Even at 20C, it still has about 80mAh/g. The excellent rate performance is mainly contributed to the nanosize pores, which reduce the solid diffusion length of the carbon electrode.

Long term cycle test results are shown in Figure 4c. The electrode had completed the rate capability tests, and two cycles for each C rate were conducted. Therefore, the cell had been cycled for 102 times in total and the capacity still shows very good stability. Although the capacity decreases a little in the first 50 cycles, we believe that it is mainly from two reasons. The first one is the increase of impedance of the lithium metal anode [19]. The second one is caused by the decrease of lithium storage in the defect sites, especially on the carbon surfaces [15, 20-22]. After 50 cycles (68 cycles including the rate tests) in Figure 4c, the capacity recovered after we changed a fresh lithium metal. Then the capacity shows very good stability, which is very impressive for the porous carbon.

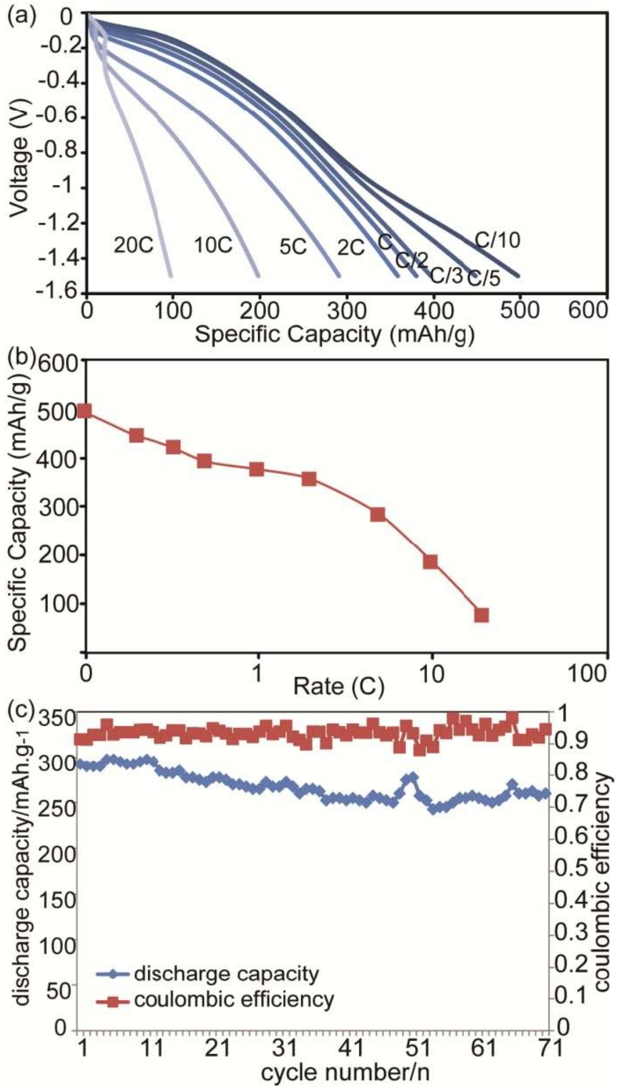

Figure 4. (a) Discharge profiles at different C rates, (b) Calculated specific discharge capacity, (c) Cycle life test for nanoporous carbon sponge electrode. Note: we reverse the anode and cathode during assembling the cells for charging and discharging tests. Therefore, the potential is negative in Fig.4(a), which is opposite with Fig.3(a).

4. CONCLUSIONS

In summary, with the development of portable electronics, hybrid and electrical vehicles, lithium ion batteries with high power and energy densities are needed. However, in current lithium ion batteries, the energy and power of graphite anode is limited due to the layered graphitic structure and the sluggish lithium diffusion. In this study, a simple and versatile approach was developed to generate nanoporous carbon sponge using the combination of hard templating and etching reaction. Both high capacity and high power with good cycle life have been proved for nanoporous carbon sponge electrode, which can be a promising candidate for next generation lithium ion batteries.

5. ACKNOWLEDGEMENTS

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