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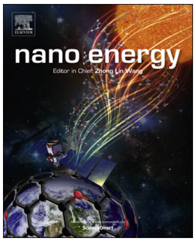

RAPID COMMUNICATION

Nanoconfinement of low-conductivity products in rechargeable sodium-air batteries

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Abstract

To alleviate the high polarization and short cycle lifetime of rechargeable Na-air batteries, ordered mesoporous carbon (OMC) was synthesized and evaluated as a nanostructured conductive matrix to host low-conductivity products generated during the discharge of Na-air batteries. The OMC had high specific surface area (1544 m^2/g) and a narrow pore size (2.7 nm), with the voltage polarization of 1.5 V, lower than that of the commonly used Super P carbon black (~1.8 V). Although the carbonate-based electrolyte was decomposed to produce Na_2CO_3, the OMC cathode allowed reversible formation and decomposition of Na_2CO_3 and exhibited stable cycling behavior with low polarization for 20 cycles with a delivered capacity of 500 mAh/g at the current density of 100 mA/g.

Introduction

Recent interest in developing eco-friendly renewable energy sources has been largely stemmed from the uncontrolled use of fossil fuels, which has sharply raised awareness of environmental problems around the world and has inevitably led to rapid exhaustion of natural reservoirs of fossil fuels. Development of renewable energy resources requires high-efficiency energy conversion and large-scale, low-cost, high-density energy storage devices. The energy density of traditional Li ion batteries is inadequate to meet the increased requirements, especially for electric or hybrid electric vehicles. Li- [1-4], Fe- [5], Si- [6], Zn- [7], Al- [8], and Na-air [9-12] batteries have attracted a

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great deal of attention mainly because of the extremely high energy density of the metal-air battery system, which is close to the energy density of fossil fuels. One advantage of Na-air batteries over Li-ion or Li-air batteries is its low material cost and its natural abundance, as sodium is 30 times cheaper than lithium. Moreover, the energy density of an Na-air battery is similar to the maximum practical energy density of a Li-air battery (1600 Wh/kg) [9]. As a common challenge to be addressed for all air-based battery technologies, excessive discharge products can accumulate on the cathode surface; most of these have very low electrical conductivity, and thus tend to inactivate surface reaction sites and block oxygen diffusion channels. Hence, the over-accumulation of discharge products can lead to the increase in polarization during charging of the Na-air battery and eventual termination of the oxygen evolution reaction [13]. To reduce the accumulation of discharge products for decreased charge potential and improved cycling performance, morphological properties of the cathode (e.g. surface area, pore volume, and pore size) need to be tailored while employing different catalysts. Recently, Liu et al. demonstrated that the graphene nanosheets (GNSs) can be used as cathode materials in Na-air batteries, delivering a high discharge capacity and maintained stable cycling behavior up to 10 cycles [14]. However, the batteries' charge potential increased gradually during cycling due to the accumulation of discharge products. Li et al. employed nitrogen-doped GNSs as a cathode material in Na-air batteries and confirmed the excellent electrocatalytic activity of this material for the oxygen reduction reaction, delivering a discharge capacity double that of undoped GNSs; however, the charge potential also increased during cycling [15]. Jian et al. demonstrated that the use of 3D interpenetrating carbon nanotube paper as a binder-free cathode material in Na-air batteries yielded high discharge capacity and low overpotential; however, these batteries' charge potential increased drastically during charging [16]. Clearly, it is necessary to limit the accumulation of discharge products; however, to the best of our knowledge, there have been no reports of research efforts to confine the size or arrangement of discharge products in the vicinity of the cathode to decrease the charge potential and improve the cycling behavior of Na-air batteries. In the present work, OMC having 2.7 nm size pore [17] (OMC-2.7) was employed as a cathode material to control the formation and subsequent decomposition of discharge products, and thus to reduce polarization and improve cycling behavior.

Experimental

Synthesis of ordered mesoporous carbons (OMCs)

For synthesis of OMC-2.7, triblock copolymer Pluronic® F127, resols synthesized according to a previously reported method [18], and tetraethyl orthosilicate were prepared as a template, carbon source, and silica source, respectively. With slight modification and scale-up from a previously reported OMC preparation method [19], large amounts of OMC-2.7 powder could be synthesized. Typically, 24.0 g of block copolymer F127 was dissolved in a solution of 120 g of ethanol and 7.5 g of 0.2 M hydrochloric acid, and stirred for at least 1 h at 40 °C to make a clear solution. Next, 38.65 g of a 20 wt% ethanolic resol solution and 15.6 g of tetraethyl orthosilicate were added in sequence. The mixture was stirred for 5 h and then transferred into flat and wide dishes. Ethanol in solution was evaporated by heating the samples for 24 h at 40 °C, and then the samples were thermopolymerized for 24 h at 100 °C. The temperature transition from 40 to 100 °C was carried out slowly to avoid boiling of remaining ethanol, which could destroy the desired mesoporous structure. The solidified transparent product was scraped from the dishes and ground into fine powders, which were then calcined to yield a carbon-silica nanocomposite. This calcination was carried out in a tubular furnace for 2 h at 900 °C under argon flow, the heating rates used to reach this temperature were 1 °C min^{-1} below 600 °C and 5 °C min^{-1} above 600 °C. To remove the silica from the carbon-silica nanocomposites, they were immersed in a 10 wt% solution of HF in deionized water; the samples were then washed with distilled water and ethanol before finally dried for 12 h at 100 °C under vacuum.

The OMC-17 was synthesized using poly(ethylene oxide)-b-polystyrene block copolymer (PEO-b-PS) as a structure-directing agent [20]. The molecular weight of PEO-b-PS was 30,200 g mol^{-1} (16.5 wt% PEO) and its polydispersity index was 1.34. In a typical synthesis, 0.4 g of PEO-b-PS was dissolved in 10 mL of tetrahydrofuran (THF). Then, 0.19 g of 0.2 M HCl was added. After 10 min, 0.78 g of TEOS and 3.87 g of resols' ethanolic solution were added and the solution was stirred for 1 h. The solution was poured into a Petri dish for THF evaporation. After 8 h, the composite film was thermopolymerized at 100 °C in an oven for one day. The as-synthesized film was carbonized in N_2 atmosphere at 450 °C for 3 h and 900 °C for 2 h in a tube furnace (heating rate, 1 °C min^{-1}). Finally, the C-SiO_2 nanocomposite was treated with a 10 wt% HF solution to remove SiO_2.

Electrode preparation and measurement

The carbon material (OMC-2.7, OMC-17, and Super P) and polyvinylidene fluoride binder were mixed in a mass ratio of 9:1 in N-methyl-2-pyrrolidone, and the resulting slurry was coated on the gas diffusion layer (GDL; SGL-35BC carbon paper, SGL Carbon) in a dry room. The coated electrode was dried for 12 h at 100 °C under vacuum to remove residual solvent. Circular electrodes 1.8 cm in diameter were cut from the coated GDL material; the loading of carbon materials on the GDL was about 0.5 mg. R2032 coin-type cells were assembled in an argon-filled glove box with water and oxygen content both less than 0.1 ppm. The cell consisted of a metallic Na foil anode (thickness 400 μm) and the prepared carbon electrodes, separated by glass fiber paper (GF/A microfiber filter paper, Whatman; thickness 0.26 mm, pore size 1.6 μm), and filled with a solution of 0.5 M sodium triflate ($NaCF_3SO_3$) in propylene carbonate (PC) as the electrolyte. For comparison, we also used 0.5 M solutions of $NaCF_3SO_3$ in DEGDME, TEGDME, and DME as ether-based electrolytes. Cells were placed in an oxygen-filled chamber with pressure slightly higher than 1 atm at room temperature and electrochemically tested under galvanostatic cycling applied using a potentiostat (VMP3, Biologic Instruments). Full discharge and charge testing was performed over the voltage range of 1.8–4.3 V with a current density of 100 mA/g. To test the cells' cycling performance, charge–discharge cycling tests were carried out in the time-controlled mode at a current density of 100 mA/g for 5 h, or 200 mA/g for 10 h. Specific capacities were calculated based on the carbon weight