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Comparisons of heat treatment on the electrochemical performance of different carbons for lithium-oxygen cells

Peng Guan [a], Guixin Wang [a,*], Chunhui Luo [a], Kangping Yan [a], Elton J. Cairns [b,c], Xueshan Hu [d]

[a] College of Chemical Engineering, Sichuan University, Chengdu 610065, China
[b] Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA, USA
[c] Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
[d] Novolyte Technologies Co. Ltd., Suzhou Industrial Park, Suzhou 215123, Jiangsu, China

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ABSTRACT

Lithium-oxygen (Li-O_2) cells are a promising power source, and carbons are an attractive non-metal catalyst for air electrodes. To improve the electrochemical performance, various carbons are heated in an inert atmosphere. It is found that heat treatment at 900 °C can differently improve the electrochemical performance of multiwalled carbon nanotubes (CNTs), acetylene carbon black (AB) and activated carbon (AC), but the improvement of CNTs is the most obvious. After heat treatment, the peak current density of the oxygen reduction reaction (ORR) and the 1st discharge capacity of CNTs increase ~30% and ~125%, respectively, while the charge transfer reaction resistance and the Warburg diffusion resistance decrease ~7.0% and ~11.1%, respectively. AC has the highest charge capacities and capacity retention ratio in spite of little influence by heat treatment. The possible mechanism and reasons are analyzed using different techniques. Microstructure is superior to conductivity for enhancing the rechargeability and the cyclability, and heat treatment is effective for some carbon materials in improving the electrochemical performance of Li-O_2 cells.

1. Introduction

Lithium-air (Li-air) cells have received considerable attention ranging from fundamental studies to applications as promising power supplies for electric vehicles (EVs) or mobile devices with high specific energy. These cells have significant advantages over conventional electrochemical energy storage and conversion devices for their high theoretical energy density because they use oxygen from the air instead of storing an oxidizer internally, comparable to traditional gasoline engine systems. Because they work using the reduction of oxygen at the cathode, Li-air cells are also called Li-oxygen (Li-O_2) cells. According to the Faradic law, a Li-O_2 cell can deliver $\sim 5.2 \times 10^3$ Wh kg^{-1} (including the weight of oxygen) and 1.1×10^4 Wh kg^{-1} (excluding the weight of oxygen), 5 ~ 10 times more energy than that of state-of-the-art lithium-ion cells [1–9]. However, the development of practical Li-air cells for use in an ambient environment faces many challenges such as the air electrode, the current collector, the electrolyte, the separator and the lithium anode. Air electrodes, where oxygen reduction and evolution reactions take place, are at the heart of the technologies required for rechargeable Li-air cells. Several major obstacles, such as the deposition of discharge products in the pores of air electrodes, passivation by deposits of insulating discharge products, oxygen diffusion transport and reaction kinetic limitations, have to be overcome to achieve higher capacity and longer-life cells [2–12]. Currently, many materials, including Pt and its alloys [2–9,13,14], Au and its alloys [2–9,14], MnO_y [2–9,15–17], FeO_y [2–9,16], CoO_y [2–9,16], $LaMn_{0.6}Fe_{0.4}O_3$ [18], $La_{0.5}Sr_{0.5}CoO_{2.91}$ [19], conducting PEDOT polymers [2–9,20], carbon black [2–9,12], carbon nanotubes and their composites [2–9,21,22], activated carbons [2–11], graphene oxides [2–10], graphenes and their composites [2–9,23,24], have been explored as possible air electrodes.

The microstructure of the air electrode notably affects the electrochemical performance of Li–air cells because pores must supply plenty of microchannels for oxygen diffusion to the three-phase reaction interface and rooms for the storage of product deposition during the discharge process. Carbon materials are interesting as emerging and conceptually new advanced catalysts [25]. Therefore, porous carbons are attractive non-metal materials of choice as air electrodes due to their excellent properties such as highly

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* Corresponding author. Tel.: +86 28 85406192.
E-mail addresses: guixinwang1@gmail.com, guixin68@yahoo.com (G. Wang).

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accessible surface area, unique gas diffusion microchannels, chemical stability, electrical and thermal conductivity, mechanical strength, low weight, plentiful raw materials like waste biomaterials, various allotropes, and environmental compatibility. However, the deposition of reaction products makes it possible to block some pores, hindering gas transport during the discharge process [26]. On the other hand, carbon itself generally exhibits a poor ORR activity in Li-O_2 cells using non-aqueous electrolytes [27]. In order to improve the electrocatalytic activities, different approaches, such as the use of heteroatom doping [24,25,28–31], graphitization [32], and MnO_2 nanoflake coatings [33], have been extensively investigated. Considering the requirements of porous structure and oxygen reduction reaction activity, much research has been conducted on the surface activation treatment of carbons [34,35]. Heat treatment is one of the effective ways to improve the graphitization degree, and modify the microstructure and surface chemistry of carbons [36–38], but its influence on the electrocatalytic activities of different carbons in a Li-O_2 cell is still not clear.

In this study, comparisons of heat treatment on the electrocatalytic performance of various carbon materials have been carried out using different methods, and the possible mechanisms and reasons have been analyzed using a combination of techniques.

2. Experimental Section

2.1. Heat treatment of different carbons

High surface area is one of the important properties of a material with a well-developed pore structure that benefits gas diffusion and supply of reaction sites. According to the references [34,38], heat treatment at 900 °C significantly increases the surface area of carbon, so 900 °C was chosen as the heat treatment temperature in this work. Three kinds of carbon materials, i.e. multiwalled CNTs produced from methane, commercial AC from coconut shells and AB from acetylene [39], were heat treated in a quartz tube furnace where nitrogen gas was passed through at a flow rate of 100 sccm. With a temperature increase rate of 10 °C min^{-1}, the samples were heated to 900 °C and kept at this temperature for 1.5 h, and then naturally cooled to room temperature in the furnace. These samples were ground in an agate mortar for characterization. The as-obtained heat treated CNTs, AC and AB at high temperature were denoted as HT-CNTs, HT-AC and HT-AB, respectively.

2.2. Materials characterization

The crystalline structure of the carbons was verified by X-ray diffraction (XRD, Philips X'Pert pro MPD) using Cu-Kα radiation in the range from 10 to 70° at a scan rate of 0.04° s^{-1}. The surface functional groups on the carbons were evaluated by Fourier transform infrared spectroscopy (FTIR) on a thermo Nicolet Magna IR 560 spectrometer in the range of 900 ~ 3800 cm^{-1} using the KBr pellet method, and all spectra were obtained using 0.05 cm^{-1} resolution. Nitrogen adsorption-desorption isotherms were determined at 77 K on an Autosorb SI surface area & pore size analyzer (Quantachrome instruments, USA). Samples were pretreated under vacuum at 300 °C for 3 h to degas prior to adsorption measurements. The specific surface areas of the samples were calculated with the Brunauer-Emmett-Teller (BET) equation in a relative pressure range from 0.06 to 0.35, whereas the pore size distribution (PSD) was obtained by the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume (V_t) was estimated from the adsorbed amount at a relative pressure (P/P_0) of 0.99. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos XSAM800 photoelectron spectrometer with Al-Mg X-ray radiation at 12 kV × 15 mA under vacuum. All the binding energies were corrected based on the internal standard of the C1s peak position at 284.8 eV.

2.3. Electrochemical evaluation

To increase the cell operating voltage and thus the energy density, the electrocatalytic performance of the carbons were evaluated in an organic electrolyte with a wide electrochemical potential window using self-made two-electrode Li-air cells with gas channels. The working electrode was prepared by coating a carbon slurry onto a clean nickel foam using a doctor blade, and being dried at 100 °C in a vacuum oven before being cut into wafers of 1.9 cm diameter. The carbon slurry with a composition of 90 wt.% carbon and 10 wt.% polytetrafluoroethylene (PTFE) was prepared by stirring and grinding the mixture of carbon powder and PTFE emulsion (solid content = 60 wt.%, Shanghai 3F New Material Co.) diluted with an appropriate amount of deionized water. In order to test the performance of each carbon by itself, no conductive carbon was added to make the slurry. Porous nickel foam was used as not only the support for the active materials, but also the storage for the discharge products, current collector, and gas channels for oxygen transfer. These wafers with a loading density of ~0.57 mg (carbon materials)/cm^{-2} (apparent surface area of nickel disk) were further dried at 100 °C for 12 hours in a vacuum drying oven for use as working electrodes. Pure lithium foil was used as the counter and reference electrodes. 1.0 M $LiPF_6$ dissolved in tetraethylene glycol dimethyl ether (Novolyte Technologies Co. Ltd., China) solution was used as the non-aqueous electrolyte, and its amount in each electrode was controlled at around 0.08 ml using a precision graduated syringe. The cells were assembled by sandwiching a Celgard 2300 microporous separator between the working electrode and the metal lithium in an argon-filled glove box. One side of the cell with open vent holes is adjacent to the carbon cathode to allow for oxygen transfer, while the other side is adjacent to the lithium foil with air tightness to prevent lithium corrosion. The electrochemical performance of the cells was evaluated in a dry oxygen atmosphere at room temperature using different techniques, including the galvanostatic discharge/charge method, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The discharge/charge tests were conducted on a battery testing instrument (Neware Technologies Co. Ltd., China) with a constant current density of 70 mA (g carbon)$^{-1}$ in a potential window of 2.0 ~ 4.2 V *vs.* Li^+/Li. CV measurements of the Li-O_2 cells were carried out at a scan rate of 0.2 mV s^{-1} between 2.0 and 4.2 V *vs.* Li^+/Li on a PAR 273A potentiostat/galvanostat (Princeton Applied Research, USA). EIS measurements of the fresh Li-O_2 cells were performed over a frequency range of 10 mHz ~ 100 kHz with a sinusoidal excitation voltage amplitude of 10 mV on an electrochemical workstation consisting of the PAR273A and a signal recovery model 5210 lock-in-amplifier controlled by Powersuite software. The impedance curves were fitted using Zsimpwin and Zview software [40,41].

3. Results and discussion

In order to understand the influence of heat treatment on the electrochemical performance of carbon materials and to improve the energy density of Li-O_2 cells beyond that available with aqueous electrolytes, these carbons were evaluated using an organic electrolyte with a wide electrochemical window. Fig. 1 shows the galvanostatic discharge/charge curves of the Li-O_2 cells prepared with different carbon materials, and the key values are summarized in Table 1. From the testing results, it can be seen that the heat treatment differently improves the discharge/charge capacities and capacity retention of all carbons in the organic electrolyte.