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Carbon Electrode for Nonaqueous Li-O_2 Battery: the Influence of Surface Oxygen Species

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ABSTRACT

Carbon materials are widely used for cathode preparation in Li-O_2 battery. The surface oxygen species is a crucial factor for the application of carbon electrode in nonaqueous Li-O_2 battery. In this work, oxygen species on carbon surface was regulated by heat treatment method, and we found oxygen species make double-edged sword effect. On the one hand, oxygen species will weaken the stability of carbon/electrolyte interface. On the other hand, the surface oxygen species shows promoting effect on oxygen reduction reaction, which is evidenced by cyclic voltammetry, tafel test and electrochemical impedance spectroscopy. In addition to the surface adjustment, the meso-pore and macro-pore volume was enlarged after heat treatment. More importantly, in advantage of more oxygen transport channels and lower affinity to electrolyte, the volume utilization rate of carbon electrode with lower oxygen amount is higher than the untreated carbon electrode. The capacity can reach 9033 mAh g^{-1}, nearly 1.3 times higher than the untreated one.

1. Introduction

Li-O_2 battery, with a theoretical specific energy density of as high as 11, 000 Wh kg^{-1}, has recently attracted extensive interests as one of ideal candidates for electric vehicles[1,2]. One typical nonaqueous Li-O_2 battery consists of a lithium metal anode, an aprotic electrolyte and a porous cathode. As the key component, the porous cathode is employed to provide reaction sites and accumulate insoluble discharge products. Currently, carbon materials with high conductivity and high specific pore volume are always used to fabricate cathode[3–5]. During discharge, O_2 is reduced through electrochemical reaction and combines with Li^+ to form the solid product-Li_2O_2, and the product is decomposed to Li^+ and O_2 directly during charge[6]. In order to improve battery performance, tremendous efforts have been dedicated to control the structure and porosity of cathode to enhance the discharge capacity and cycling stability[4,7–9]. However, as the reaction interface, the surface chemistry property of carbon surface is of great importance to the battery performance.

Recently, numerous researches have focused on surface modifications of carbon materials for Li-O_2 battery, such as heteroatom doping (e.g., nitrogen[10–12] or sulphur[13] doping) and catalyst loading[14–17], aiming to improve the electrochemical activity of electrode. It's well known that surface oxygen is the fundamental heteroatom of carbon materials and the surface chemical nature is dominated by surface oxygen species. For carbon materials preparation, the oxygen atom cannot be completely removed during carbonization process, and the materials can even chemisorb oxygen at low temperature, leaving abundant oxygen species on their surfaces, e.g., O-H, C=O, O=C-O, C-O-C, COOH, etc[18]. As reported, the amount and type of these groups show great effect on material properties, such as adsorption characteristics[19], electrocatalytic activity[20] and lyophilic, thus to improve the performance in fuel cells[21] and supercapacitors[22].

Similarly, for Li-O_2 battery, surface oxygen is one critical factor to battery performance. Although corresponding theoretical calculations have just been carried out[23,24], there has been quite few experimental studies focusing on the role of carbon surface oxygen species. Among these researches, Peter G. Bruce et al. [3] have shown that the stability of carbon materials in nonaqueous Li-O_2 battery depends on the hydrophobicity/hydrophilicity property of carbon surface. Also, Daniil M. Itkis et al. [25] have demonstrated that the intermediate product of discharge process would attack

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carbon containing activated double bonds to form carbonates in solid state Li-O_2 battery.

However, the influence of surface oxygen species on the performance of carbon electrode in nonaqueous Li-O_2 battery is still unclear. In this study, commercial Ketjenblack EC300JD was selected. And a deoxygenation strategy through heat treatment was taken to reduce the surface oxygen amount. As expected, multiple cyclic voltammetry tests indicated that the carbon with less oxygen species showed better stability. Meanwhile, we found that the carbon with higher oxygen species exhibited higher oxygen reduction activity. Furthermore, the pore structure of the carbon material was also modified simultaneously. Attributed to the improved pore utilization, the carbon electrode with lower oxygen amount shows a better discharge capacity.

2. Experimental

2.1. Material Preparation

Commercial Ketjenblack EC300JD (Akzo Nobel Corp.) was heated to 600 °C at 6 °C min^{-1} from room temperature, and then up to 900 °C at 3 °C min^{-1} and held for 5 h in argon atmosphere. The resulting carbon was noted as deoxygenated carbon.

2.2. Physical characterizations

The surface oxygen was detected by a Fourier transform infrared (FT-IR) spectroscope (JASCO FT/IR-4100) and X-ray photoelectron spectroscopy (XPS) which was carried out via a surface analysis system (ESCALAB250) equipped with monochromatic Al-K alpha radiation. The XPS spectra were peak fit and analyzed using XPSPeak4.1 (Photoelectron Spectroscopy Lab, Seoul National University) and the spectra were calibrated according to the C1s (284.6 eV) peak. N_2 adsorption/desorption isotherms were measured at 77 K using an ASAP 2010 system. Surface areas were determined using Brunauer-Emmett-Teller (BET) method. Pore volumes and the pore size distribution (PSD) curves were calculated from the desorption branches using the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM) micrographs were taken on QUANTA 2000FEG operating at an acceleration voltage of 20 kV to get the morphology of carbon electrodes. The contact angle was measured on a JC2000A instrument. During each measurement, 6 μL electrolyte was dropped on the surface of the electrodes with a microsyringe.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) tests were conducted with a three-electrode cell in a glove box. A glass carbon disk (0.1256 cm^{-2}) which was covered by the suspension (50 μL) made with carbon powder (5 mg) and polytetrafluoroethylene (PTFE) solution (5 wt.%, 25 mg) in 2-propanol (5 mL) was used as the working electrode. A lithium metal rod connecting to the main solution through a glass fiber membrane acted as the counter electrode. Another polished lithium metal rod connecting to the main solution through a porous ceramics served as the reference electrode. The electrolyte is 1 M bis(trifluoromethane) sulfonamide lithium (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) solution and the water content was strictly controlled to less than 10 ppm, determined by Karl-Fischer titration. CV curves were recorded from 2 V to 4.3 V *vs.* Li^+/Li by AFCBP1 bipotentiostation (Pine Research Instrumentation) at 25 °C and tafel plots were recorded under the same conditions. The current value was normalized by the glass carbon electrode area.

Single cells were fabricated in a glove box ($H_2O < 1$ ppm, $O_2 < 1$ ppm) to evaluate the discharge performance. The cells were assembled using a porous cathode together with a lithium anode and a polypropylene fiber separator (Novatexx 2471, Freudenberg Filtration Technologies KG). The porous cathode was prepared by mixing carbon power (40 mg) with PTFE solution (5 wt.%, 200 mg) in propylene glycol/water solution (volume ratio: 1/1, 4 mL) and the resulting slurry was coated on the polypropylene fiber separator (16 mm in diameter) with a carbon loading of 1 mg cm^{-2}. The coated electrode was dried for 24 h at 60 °C under vacuum to remove residual solvent. The discharge curves were recorded by Arbin BT-2000 battery station under 1.2 atm of pure O_2 at room temperature. Electrochemical impedance spectroscopy (EIS) of the battery was measured in a frequency range of 100 KHz to 0.1 Hz using a Salarton 1287 test system with perturbation amplitude of 10 mV under open circuit potential conditions.

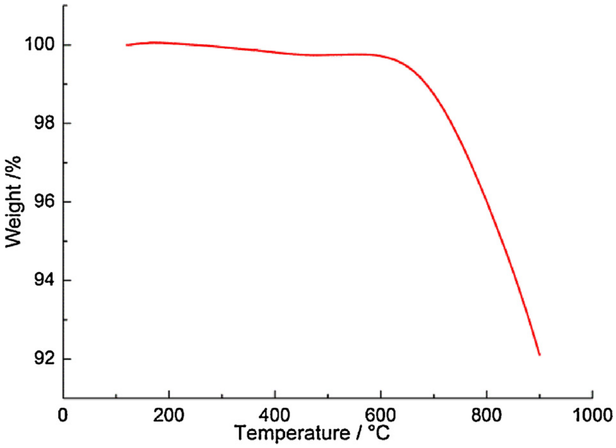

Fig. 1. Thermogravimetric curve of untreated carbon from 120 °C to 900 °C at 5 °C min^{-1} in Ar atmosphere.

3. Results and discussion

Initially, thermogravimetric analysis was carried out to investigate the weight-loss during heat treatment process. As shown in Fig. 1, the slight weight loss between 200 °C and 480 °C is assigned to the decomposition of oxygen species with low decomposition temperature, such as COOH groups[26]. And an abrupt weight-loss is observed between 600 °C and 900 °C. Partial weight-loss is ascribed to the decomposition of oxygen species with high decomposition temperature, such as C-O and C=O groups[26]. Extra weight-loss is caused by the activation effect with carbon matrix of carbon dioxide and water vapour, which generated from the oxygen species decomposition. Because they can react with carbon in this temperature range[27,28]. Hence, heat treatment can effectively reduce the oxygen species amount on carbon surface. On the other hand, it will also cast a great effect on the pore structure of carbon matrix due to the activation effect.

The surface oxygen species on carbon were characterized by FT-IR and XPS. FT-IR analysis was employed to confirm the chemical bond in oxygen species. As shown in Fig. 2a, both of the spectrums display nearly similar absorption peaks: C-H stretching vibrations (2926 cm^{-1} and 2851 cm^{-1}) and blending vibrations (1462 cm^{-1} and 1379 cm^{-1})[29], C=C stretching in aromatic rings (1628 cm^{-1}); the broad and intense peak at 3440 cm^{-1} corresponds to the hydrogen-bonded O-H stretching vibration; the weak shoulder at about 1727 cm^{-1} is related to the C=O stretching vibration[30]; the presence of the peaks at 1122 cm^{-1} and 1088 cm^{-1} is ascribed to C-O stretching vibrations[26]. The similar absorption peaks indicate that the deoxygenation treatment does not change the types of oxygen species. However, the absorption intensity of deoxygenated