

Preparation and performance of hierarchically porous carbons as oxygen electrodes for lithium oxygen batteries

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Abstract: The hierarchically porous carbons (HPCs) were prepared by sol–gel self-assembly technology in different surfactant concentrations and were used as the potential electrode for lithium oxygen batteries. The physical and electrochemical properties of the as-prepared HPCs were investigated by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption isotherm and galvanostatic charge/discharge. The results indicate that all of the HPCs mainly possess mesoporous structure with nearly similar pore size distribution. Using the HPCs as the electrode, a high discharge capacity for lithium oxygen battery can be achieved, and the discharge capacity increases with the specific surface area. Especially, the HPCs-3 oxygen electrode with CTAB concentration of 0.27 mol/L exhibits good capacity retention through controlling discharge depth to 800 mA·h/g and the highest discharge capacity of 2050 mA·h/g at a rate of 0.1 mA/cm².

Key words: lithium oxygen battery; hierarchically porous carbon; oxygen electrode; oxygen reduction

1 Introduction

Metal oxygen batteries have much higher specific energy than most available primary and rechargeable batteries in which their active cathode materials, and oxygen can be accessed from the environment. Lithium air (oxygen) batteries have the highest theoretical specific energy among all metal oxygen batteries because of the high specific energy of lithium metal. The theoretical specific energy of lithium air (oxygen) batteries is 11140 W·h/kg, excluding O₂ (5200 W·h/kg including O₂). The present lithium air (oxygen) cell appears to be rechargeable due to the use of nonaqueous electrolyte [1–3]. The first lithium oxygen battery with nonaqueous polymer electrolyte was reported in 1996 by ABRAHAM and JIANG [4]. Prototype lithium oxygen batteries typically consist of a lithium-metal anode, organic electrolyte and a porous carbon-based cathode exposed to gaseous O₂ during cell operation [5]. In an organic system, the discharge mechanism was determined to be primarily the deposition of Li₂O₂ in the

porous structure of the oxygen electrode, and discharge ceases when the porous cathode is completely filled with these reaction precipitates.

There is an urgent need to design and synthesize a highly effective carbon cathode for high-performance lithium oxygen batteries. Recently, intensive research effort has been devoted to improve the performance of lithium oxygen batteries by tuning the morphology and structure of the carbon cathode. KUBOKI et al [6] compared the effect of the specific surface area and pore volume of porous carbon on discharge performance of lithium oxygen battery. It has been found that the pore volume has a more marked effect on specific capacity than the surface area. Another study carried out by YANG et al [7] showed that the porous carbon material with a significantly lower surface area but a much larger pore size displayed much better electrochemical performance than one with higher surface area but smaller pore size. And different kinds of carbon, including high-surface area carbons [8–12], mesocellular carbons, carbon nanotube [13–16], carbon fiber or carbon paper [17], and graphene [18–20], have been

used as O₂ electrodes in lithium oxygen battery. However, different kinds of porous carbon materials represent apparently different characteristics when they are used as oxygen electrode. Among all porous carbon materials, the mesoporous carbon materials lead the electrolyte ions to transport into the bulk of material quickly and also provide larger space for formation of discharge products, thus the mesoporous carbon materials are often used to improve discharge performance of the lithium oxygen batteries [21]. In contrast, the porous carbon materials with micropore size are not be suitable in lithium oxygen batteries because small pores could be easily choked by discharge product [22].

Hierarchical porous carbons (HPCs) with a multimodal pore size distribution of micro-, meso- and/or macro-pores show high electrochemically accessible surface area, short diffusion distance, and high mass transfer rate when used as electrode materials in energy storage devices [23–25]. If the size of pore is further controlled, it will reveal some excellent electrochemical performance, so it will be an interesting work for using the hierarchical porous carbons with mesoporous structure as the oxygen electrode of lithium oxygen battery. Recently, our group has carried out a lot of researches on hierarchical porous carbon materials and their supercapacitive behaviors [26–30]. In this work, the hierarchically porous carbons (HPCs) with meso-porous structure are prepared by sol-gel self-assembly process with nickel oxides and surfactant as the templates and are used as oxygen electrode of lithium oxygen batteries. The discharge behavior and battery characteristics of lithium oxygen battery are investigated in detail.

2 Experimental

Hierarchically porous carbons [26] were prepared by carbonization and corrosion of the dual template precursor. A solution of phenolic resin (PF) in ethanol as the source of carbon was added into the mixture of cetyltrimethyl ammonium bromide (CTAB), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and sodium hydroxide (NaOH) with sufficiently stirring. The mixture was left with a blending-layered-settlement program and dried in air at 60 °C for 12 h. The sample was heated to 200 °C (5 °C/min) and maintained for 2 h in pure argon, then heated to 600 °C (5 °C/min) and maintained for 5 h, and finally cooled down naturally to room temperature. The resultant product was etched with 3 mol/L HCl thoroughly to remove Ni(OH)₂/NiO, then filtered and washed several times with deionized water and dried in an oven at 100 °C, finally treated with 2 mol/L HNO₃. During preparation process, the molar ratios of Ni(NO₃)₂ and CTAB were 4:0, 4:2, 4:4, and 4:6, and the corresponding CTAB template concentrations were 0,

0.14, 0.27, and 0.41 mol/L, respectively. The as-prepared samples were denoted as HPCs-1, HPCs-2, HPCs-3, and HPCs-4, respectively.

The porous properties of HPCs were characterized by adsorption experiments of nitrogen, and adsorption/desorption isotherms of nitrogen were measured at 77 K on a Quantachrome autosorb automated gas sorption system. The estimation of the Brunauer–Emmett–Teller (BET) specific surface area (SSA), pore volume and pore size distribution (PSD) were carried out according to the Barrett–Joyner–Halenda (BJH). Field emission scanning electron microscope (FE-SEM) (Sirion 200, FEI) and transmission electron microscope (TEM) (JEM–2100F, JEOL) were used to study the morphology and size of HPCs.

The oxygen electrode was fabricated by compressing a mixture of carbon material (HPCs) and poly (vinylidene fluoride) binder with a mass ratio of 9:1 onto a nickel foam current collector. The geometric surface area of the oxygen electrode disks was kept to be 0.785 cm² and the typical loading of the oxygen electrode was 5 mg/cm².

The electrochemical characterizations were carried out using Swagelok type cell with components consisting of a nickel foam as the cathode current collector and a lithium metal foil as anode. A commercial electrolyte solution of 1 mol/L LiPF₆ in a mixture of mass fraction of ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1 was impregnated into membrane as separator and sandwiched between a lithium metal anode and oxygen cathode.

The cells were tested in a sealed oxygen chamber under oxygen flow, and the oxygen pressure was maintained at normal pressure. The cell was cycled in Neware battery test system BTS-XWJ-6.44S-00052 (Newell, Shenzhen, China) with a voltage range of 2.0–4.5 V (vs Li⁺/Li) at different current densities, which can control the test conditions such as the voltage, current, capacity and time of the charge and discharge.

3 Results and discussion

The nitrogen adsorption/desorption isotherms at 77 K for HPCs marked with HPCs-1, HPCs-2, HPCs-3, HPCs-4, respectively, are shown in Fig. 1(a). As shown in Fig. 1(a), all isotherms are type IV isotherm according to the IUPAC classification [31]. High adsorption of nitrogen occurs in the low relative pressure (p/p_0) range, and obvious hysteresis is detected, suggesting the existence of micro-pores and meso-pores in HPCs [31]. A hysteresis between adsorption and desorption branches can be observed at medium relative pressure (0.4–1.0), which demonstrates the presence of a large number of

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