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Porous anode of lithium–oxygen battery based on double-gas-path structure

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ABSTRACT

A lithium–oxygen battery of double-gas-path structure and porous anode is presented in this work. Different from traditional structure battery, porous anode and the gas channel of anode side are used to provide argon gas for the battery. In order to protect the anode from corrosion of oxygen which penetrates from the cathode to the anode by dynamic gas-phase equilibrium. The improvement of the battery performance is attributed to the novel structure that can protect lithium metal from the corrosion of oxygen and it also reduces the growth of dendrite. The lithium–oxygen battery based on double-gas-path structure shows long cycle life (38 cycles), high discharge specific capacity (2510 mAh g⁻¹) and specific energy density (7200 W h kg⁻¹). More importantly, this work will also provide new ideas and methods for the research of other metal–air battery.

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Introduction

With the trend of gradually replacing fossil fuels with renewable, environment-friendly, and safe energy sources, the demand for energy conversion lead to the development of efficient energy storage devices and renewable but unsteady energy sources [1–3]. Lithium–oxygen battery is promising energy storage devices owing to their high theoretical specific energy. It is because the lithium–metal anodes have low atomic mass and the oxygen of their cathodes can be directly

obtained from air without being stored in the internal battery [4]. Furthermore, lithium–oxygen battery has advantages such as low cost, convenient to use and non-pollution [5].

Indeed, lithium–oxygen battery demonstrates attractive prospects [6–9]. However, numerous academic and practical challenges must be overcome at first before the potential of this novel battery can be realized [10]. Such challenges include anode corrosion, low mass transfer rate, dendrite formation and so on, which restrict the practical application of lithium–oxygen battery [11]. Existing research results show that these problems may be solved by improving the performance

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of the electrolyte and the diaphragm [12–16]. In addition, changes from the composition and structure of the anode can also solve these problems. Up to now, a lot of work focuses on cathode structure and electrolyte for lithium–oxygen battery [17–19]. The lithium anode is the key component of the battery but has not attention enough [20–23]. In the current study, we try to change the battery structure of the anode side to solve above problems. And this work will provide new ideas and methods for other researchers.

In this work, we present double-gas-path structure for lithium–oxygen battery with porous anode. The influences of the porous anode on the performance of battery are investigated. The surface morphologies of the electrodes are observed by scanning electron microscopy (SEM) and the structure of corrosion products is studied by Raman spectrum (RS). The performances of the battery are characterized by constant current charge/discharge curves.

Experimental

Preparation of electrode materials

Lithium (16 mm in diameter, 0.2 mm thick, China Energy Lithium Co., Ltd.) was processed by using a special mold in order to achieve its porous structure. Twenty-four pores (0.1 mm in diameter) were evenly distributed on the lithium metal.

Electrolytic manganese dioxide (homemade) combined with Pt/C (homemade) was used as a catalyst and was sprayed along with conductive carbon black (SCM Industrial Chemical Co., Ltd.) and Teflon binder onto a gas diffusion layer (GDL35BC carbon paper, Germany SGL Company). The conductive carbon black/catalyst/binder ratio was 70/20/10, and the spraying step was performed at a temperature of 100 °C and a gas pressure of 2 atm. The active layer loading of the oxygen electrode was 0.85 mg cm⁻².

The commercial electrolyte solution was prepared by adding 1 mol LiPF₆ to a mixture of 1:1:1 (w/w/w) ethylene

carbonate/ethyl methyl carbonate/dimethyl carbonate (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.). The composite electrolyte with 2.0 mol L⁻¹ C (Li⁺) was prepared as follows: equal volumes of the commercial electrolyte and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄) were mixed and then added to LiBF₄ such that the mole ratio of the commercial electrolyte to LiBF₄ was 1:3. The electrolyte was continuously oscillated to facilitate the complete mixing of the solute and the solution until the solution becomes clear. The composite electrolyte is transferred to a reagent bottle and aged for 24 h before use.

Fabrication of battery

Lithium sheets after porous processing were used as the anode. Disks (10 mm diameter) cut from oxygen electrodes were used as the cathode. In this study, 2.0 mol L⁻¹ composite electrolytes acted as the electrolyte. Disks (16.0 mm diameter) cut from a polypropylene microporous membrane (Celgard 2400) was used as the separators.

The battery structure is illustrated in Fig. 1. The batteries were constructed in a glove box in an argon atmosphere. Foam nickel was used as the filler to ensure good contact with the inside of the battery. Two pieces of separators were sandwiched between the lithium metal and oxygen electrodes. The stainless steel shells and electrodes were connected by stainless steel springs. Pure argon gas and oxygen gas were supplied to the anode side and cathode side at the same flow rate of 50 mL min⁻¹ to achieve dynamic gas-phase equilibrium in the internal battery. The batteries were left for 3 h before testing.

Physical characterization

The surface morphologies and structure of the electrodes were observed through scanning electron microscopy (SEM, Hitachi S-4800) to further analyze the relationship between the electrode structure and performance of the electrode.

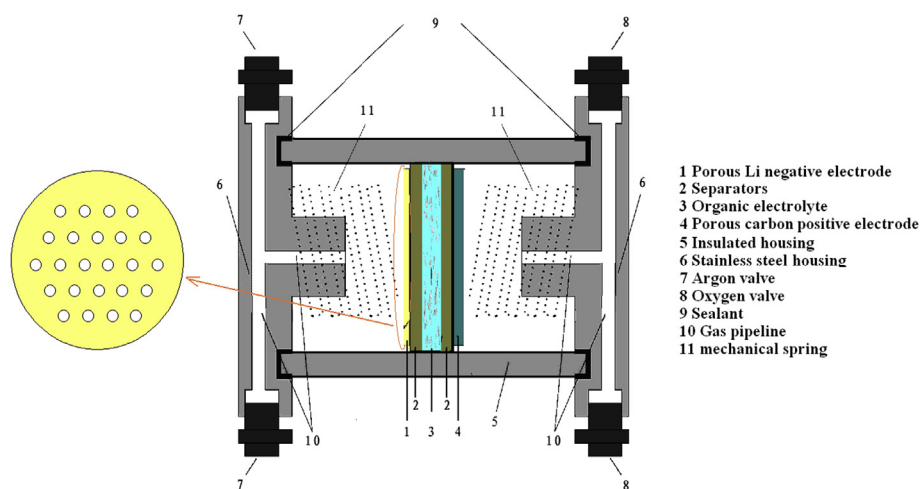


Fig. 1 – Double-gas-path structure of lithium–oxygen batteries with porous anode.

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