Materials Research Bulletin 48 (2013) 4979–4983

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Conducting polymer-doped polyprrrole as an effective cathode catalyst for Li-O_2 batteries

Jinqiang Zhang [a], Bing Sun [a], Hyo-Jun Ahn [b], Chengyin Wang [c], Guoxiu Wang [a,*]

[a] Centre for Clean Energy Technology, School of Chemistry and Forensic Science, University of Technology Sydney, Broadway, Sydney, NSW 2007, Australia
[b] School of Materials Science and Engineering, Gyeongsang National University, Jinju, South Korea
[c] College of Chemistry and Chemical Engineering, Yangzhou University, 180 Si-Wang-Ting Road, Yangzhou 225002, China

ARTICLE INFO

Article history:
Received 22 January 2013
Received in revised form 22 April 2013
Accepted 22 April 2013
Available online 29 April 2013

Keywords:
A. Polymers
B. Chemical synthesis
D. Catalytic properties

ABSTRACT

Polypyrrole conducting polymers with different dopants have been synthesized and applied as the cathode catalyst in Li-O_2 batteries. Polypyrrole polymers exhibited an effective catalytic activity towards oxygen reduction in lithium oxygen batteries. It was discovered that dopant significantly influenced the electrochemical performance of polypyrrole. The polypyrrole doped with Cl^- demonstrated higher capacity and more stable cyclability than that doped with ClO_4^-. Polypyrrole conducting polymers also exhibited higher capacity and better cycling performance than that of carbon black catalysts.

1. Introduction

In the last few years, Li-O_2 batteries have attracted extensive investigations, owing to their high energy density [1,2]. Since Abraham and Jiang first reported the use of organic electrolyte in Li-O_2 battery [3], many efforts have been devoted to develop high performance Li-O_2 batteries. A Li-O_2 battery consists of a lithium anode, a porous cathode that allows oxygen to diffuse, and electrolyte to provide ionic conduction for lithium ions. During the discharge reaction, the oxygen is drawn from the outside atmosphere and form Li_2O_2 with lithium ions from the electrolyte, while the lithium ion could be replenished by the anode. The reaction can be reversed during the charge process [4–6].

Li-O_2 batteries face many challenges for use in practical applications, such as poor cyclability, large over-potential, and low practical specific capacity [1,2,7]. In order to solve these problems, many catalyst materials have been developed. Carbon materials such as carbon nanotube [8] and graphene [9,10] are applied as catalysts for oxygen reduction reaction (ORR). Furthermore, transition metals oxides such as PdO, Co_3O_4, α-MnO_2 nanowires and precious metals such as Pt, Au, Pd, have also been reported as cathode catalysts [11–16].

Owing to the intrinsic reversible redox property, doped conducting polymers could be potentially used as catalysts for Li-O_2 batteries. The electrode reaction is considered as below:

$$CP^+A^- + e^- \leftrightarrow CP + A^- \qquad (1)$$

where CP stands for conducting polymer, and A^- is the dopant ion [17–19]. Recently, Cui et al. reported the replacement of carbon with tubular polypyrrole (PPy) as catalyst for Li-O_2 batteries and achieved a very good cycling performance [20]. However, the influence of different dopants on electrochemistry performance of conducting polymers as catalysts in Li-O_2 battery has not yet been reported. In this paper, we report the use of polypyrrole, one of the most commonly used conducting polymers, with different dopants as catalysts in non-aqueous Li-O_2 batteries for the first time. Polypyrrole doped with Cl^- and ClO_4^- were synthesized and applied as the cathode catalyst in Li-O_2 batteries.

2. Experiment

2.1. Synthesis of materials

Polypyrrole polymers with different dopants were synthesized by an *in situ* chemical polymerization method. In a typical synthesis process, 10 mmol pyrrole monomers were added into 40 mL aqueous solution consisting of 1 M dopant acid under stirring. The dopant acids are HCl and $HClO_4$, respectively. After

---

* Corresponding author. Tel.: +61 295141741; fax: +61 295141460.
E-mail address: Guoxiu.Wang@uts.edu.au (G. Wang).

0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.04.050

stirring for 30 min, 20 mL aqueous solution consisting of 5 mmol $(NH_4)_2S_2O_8$ and 1 M dopant acid was added into the previous solution. The mixture was kept stirring at room temperature for 6 h. The black precipitate was filtered and washed with distilled water and ethanol for several times and then dried in a vacuum oven at 60 °C for 12 h.

2.2. *Characterization of samples*

Field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) was used to investigate the morphology of the as-prepared PPy polymers. Infrared spectra were measured using a Nicolet Magna 6700 FT-IR spectrometer. All spectra were obtained using 4 cm^{-1} resolution and 64 scans at room temperature.

2.3. *Electrochemical measurements*

Cathode slurry was prepared by mixing the as-prepared PPy, poly(tetrafluoroethylene) (PTFE) with Super-P carbon black together in isopropanol with the weight ratio of 60:10:30. The mixture was coated on a stainless steel mesh substrate and then cut into discs with a diameter of 14 mm. The electrodes were dried at 80 °C under vacuum for 12 h. The loading of the cathode materials is about 2 mg cm^{-2}. For comparison, pure carbon black electrodes were fabricated by mixing PTFE and Super-P carbon black in isopropanol with the weight ratio of 10:90. Some carbon black electrodes were chosen to soak into 0.5 M LiCl ethanol solution under vacuum for 3 h and dried under vacuum at 150 °C for 6 h. A Swagelok type cell with an air hole (0.785 cm^2) on the cathode side was used to test the electrochemical performance. The cell was assembled in argon filled glove box (Mbraun, Germany) with water and oxygen level less than 0.1 ppm. A lithium foil was used as the anode and was separated from cathode by a glass microfiber filter (Whatman) soaked in electrolyte (1 M $LiClO_4$ in propylene carbonate). The cell was gas tight except for the cathode side window that exposed the cathode film to the oxygen atmosphere. All measurements were conducted at 1 atm in dry oxygen atmosphere to avoid any negative effects of humidity and CO_2.

3. Results and discussion

Fig. 1(a) and (b) shows the SEM images of the as-prepared PPy-Cl and PPy-ClO_4 polymers. Both of them showed similar morphology, which consists of nanoparticles with a diameter about 200–400 nm. The FT-IR spectra of the as-prepared PPy are shown in Fig. 1(c). The vibrations of pyrrole ring can be observed at 1544 and 1456 cm^{-1} and =C–H vibrations appeared at 1298 and 1042 cm^{-1} in the PPy spectra. The vibration at 1175 cm^{-1} can be assigned to the stretching of C–N group.

The electrocatalytic activity of the as-prepared PPy was examined in Li-O_2 battery and compared with carbon black at room temperature. The charge–discharge voltage range was set between 2.0 and 4.5 V for all the measurements. The voltage profiles of the electrodes in the first cycle are shown in Fig. 2(a). The discharge capacities of PPy-Cl and PPy-ClO_4 electrodes are 6208 mAh g^{-1} and 5164 mAh g^{-1}, respectively. The carbon black electrode delivered a lower capacity of 1365 mAh g^{-1}. The discharge plateaus of both conducting polymer electrodes were higher than that of carbon black electrode, indicating that PPy had better catalytic activity towards ORR than carbon black. The charge potential plateaus of conducting polymer electrodes were also lower comparing to carbon black electrode, demonstrating that PPy had better catalytic activity towards oxygen evolution reaction (OER) than carbon black. The cycling performances of both PPy and carbon black electrodes are shown in Fig. 2(b). PPy-Cl and PPy-ClO_4 electrodes exhibited much better cycling stability than carbon black electrodes in the first five cycles. Furthermore, PPy doped with Cl^- showed better cycling stability than the PPy-ClO_4 electrode.

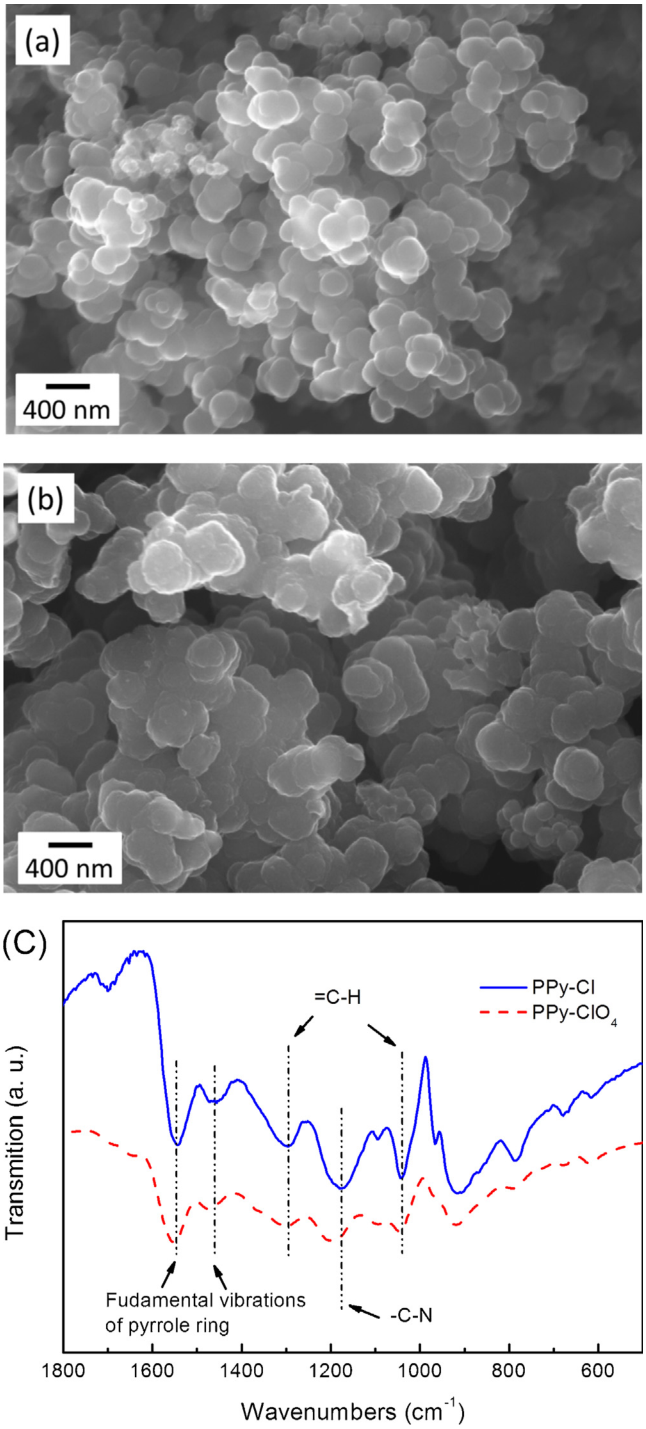

Fig. 1. SEM images of the as-prepared (a) PPy-Cl and (b) PPy-ClO_4 and (c) FT-IR spectra of both PPy polymers. (For interpretation of the references to spectra in figure legend, the reader is referred to the web version of the article.)

The ORR reaction with the presence of PPy on cathode in Li-O_2 batteries could involve in two steps:

$$PPy^+A^- + e^- \rightarrow PPy + A^- \quad (2)$$

$$PPy + O_2 + A^- \rightarrow PPy + A^- + O_2{}^- \quad (3)$$