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Nitrogen-doped Carbon Nanoweb as Metal-free Catalysts for Hybrid Li-air Batteries

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Introduction

Growing environmental concerns and an increasing demand for energy have stimulated extensive interest in battery research. Lithium-ion batteries have revolutionized our everyday life with portable electronics. However, the energy density of lithium-ion batteries is not able to meet the demands of electric vehicles and grid energy storage. Metal-air batteries are appealing in this regard as they offer high energy density.[1] However, the practical energy density of Li-air batteries is limited by the insoluble discharge products (Li_2O_2 and Li_2O) formed in the aprotic electrolyte. To solve this problem, hybrid Li-air batteries (or dual-electrolyte cells) in which a solid electrolyte separates the lithium metal anode in an aprotic electrolyte from the air electrode in an aqueous catholyte have become appealing.

Platinum and its alloys are still the mostly utilized catalysts for oxygen reduction reaction (ORR) due to their high catalytic activity. However, the high cost and scarcity of Pt will impede large-scale commercialization of fuel cells or metal-air batteries.[2] Moreover, Pt catalysts suffer from time-dependent drift and CO deactivation. The practical catalysts for metal-air batteries should ideally be based on environmentally abundant elements that could facilitate high catalytic activity.

Nitrogen-doped carbon materials have been proposed as an effective ORR catalyst. For example, nitrogen doping has been shown to greatly enhance the ORR activity of carbon nanotube and graphene. We present here the nitrogen-doped carbon nanoweb (NCNW) obtained by the carbonization of a polypyrrole precursor as a potential metal-free catalyst for ORR for hybrid lithium-air cells. The polypyrrole precursor has a high nitrogen content of about 16 wt. %. After carbonization, a high nitrogen-doping content of 10 wt. % is still retained in NCNW. The ORR activity of NCNW is further improved by grafting oxygen-containing functional groups by a KOH activation process.

Experimental

The nitrogen-doped carbon nanoweb (NCNW) was obtained by a two-step carbonization and activation process of polypyrrole nanoweb, which was synthesized by an oxidative template assembly method. The activation process was realized by chemically activating the carbonized polypyrrole nanoweb with KOH at 600 ºC in N_2 atmosphere.

A home-made PTFE layered battery mould was used to carry out the full cell test. The anode side consisted of a nickel foam current collector, a lithium metal foil, and the organic carbonate electrolyte. The cathode side consisted of 0.5 M LiOH + 1 M $LiNO_3$ as the catholyte, an air electrode (0.76 × 0.76 cm) containing 1.0 mg cm^{-2} NCNW as the catalyst, and a platinum mesh current collector.[3] The anode and cathode were separated by a LISICON solid Li^+-ion conducting electrolyte.

Results and Discussion

Fig. 1 shows the typical SEM images of the synthesized NCNW. NCNW consists of interconnected nitrogen-doped carbon nanofibers with an average diameter of ~ 70 nm. This three-dimensional nanoweb structure provides fast electron transport and efficient oxygen diffusion path, which is beneficial for the oxygen reduction reaction. Moreover, the oxygen-containing functional groups grafted through the activation process helps increase the electron transfer number per oxygen by helping HO_2^- disproportionation to OH^- and O_2.

The NCNW was made into air electrodes with a net mass loading of 1.0 mg/cm^2 and tested in hybrid Li-air batteries with an alkaline catholyte (0.5 M LiOH + 1 M $LiNO_3$). Discharge and charge curves with a constant current density of 0.5 mA cm^{-2} are shown in Figure 2. The observed capacity of 1000 mA g^{-1} is based on the mass of the NCNW catalyst in the air electrode. A high discharge voltage plateau of about 3.0 V vs. Li^+/Li is obtained in the first cycle, indicating the good ORR catalytic activity of the NCNW. As the cycle number increases, the discharge plateau drops slightly and becomes stable after five cycles, revealing the stable ORR performance of NCNW. The cell shows a round-trip overpotential of 0.8 V in the first cycle contributing to an energy efficiency of ~ 79 %. After twenty cycles, the round-trip overpotential increased to 1.2 V and the energy efficiency dropped to 70 %, which is attributed to the degradation of the active sites for oxygen evolution reaction (OER) upon cycling.

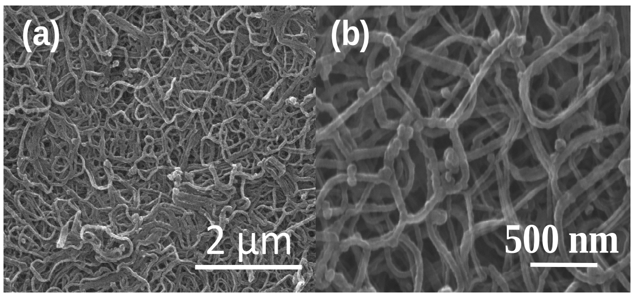

Fig. 1. SEM images of synthesized NCNW: (a) low magnification and (b) high magnification.

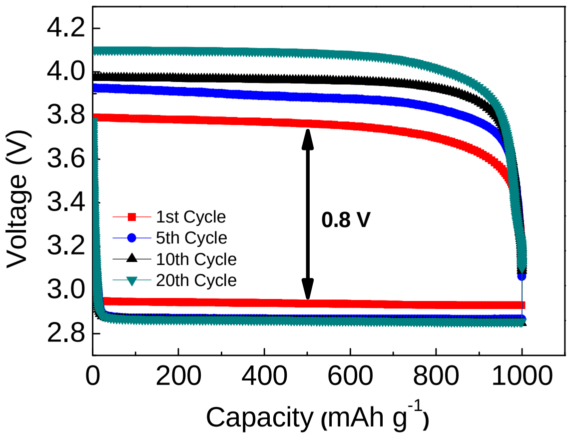

Fig. 2. Cycling performance of the hybrid Li-air cell with the NCNW catalyst and the LISICON solid electrolyte at 0.5 mA cm^{-2}.

References

1. G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson and W. Wilcke, *J. Phys. Chem. Lett.*, **1**, 2193 (2010).
2. K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, *Science*, **323**, 760 (2009).
3. L. Li, X. Zhao and A. Manthiram, *Electrochem. Commun.*, **14,** 1 (2012).