Flowerlike Co$_3$O$_4$ microspheres loaded with copper nanoparticle as an efficient bifunctional catalyst for lithium–air batteries

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ABSTRACT

Porous flowerlike Co$_3$O$_4$ microspheres/Cu nanoparticles composite has been synthesized via a combined solvothermal method, subsequent thermal treatment and polyol process. Due to the 3D mesoporous structure, the resulting Co$_3$O$_4$ microspheres/Cu catalyst shows an efficient and stable bifunctional catalytic activity. The cobalt oxide-based catalysts show better performance during the discharging and charging processes at a current density of 0.05 mA cm^{-2} compared with that of the Vulcan XC-72. The cell with this novel catalyst can be reversibly charged/discharged and has a good cycle performance. The preliminary results indicate that the Porous flowerlike Co$_3$O$_4$ microspheres/Cu nanoparticles composite is a promising material for a metal/air battery or a PEM fuel cell as an efficient and stable bifunctional catalyst.

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1. Introduction

The high cost of energy storage and conversion devices such as the proton-exchange-membrane (PEM) fuel cells and metal/air batteries restrains their practical use [1,2]. Among various metal/air batteries, lithium–air batteries possess the highest theoretical gravimetric energy density. However, for rechargeable lithium–air battery, another issue that has to be addressed in the current technology is the limitations of oxygen reduction reaction (ORR) during discharging process and oxygen evolution reaction (OER) during charging process. The sluggish kinetics of ORR and OER in lithium–air batteries are ascribed to the low efficiency of catalysts [3]. The performance of Li–air batteries can be drastically improved by incorporating an efficient catalyst to achieve higher discharge voltage, lower charge voltage and rate performance [4]. Therefore, the design of a low-cost and stable bifunctional electrocatalyst is a major challenge to the construction of efficient Li–air batteries.

Many spinel cobaltite oxides have been investigated as electrocatalysts for the oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) [5,6]. Molecular mechanisms involving O$_2$/H$_2$O cycles at cobalt centers suggest the involvement of Co^{2+}, Co^{3+}, and

likely Co^{4+} oxidation states during catalysis [7]. In an oxygen-atom ligand field, Co^{2+} (t$_{2g}^5$e$_g^2$) is a high spin ion and substitutionally labile, whereas Co^{3+} (t$_{2g}^6$e$_g^0$) with a higher oxidation state is low spin and substitutionally inert [8]. In general, the ORR is postulated to take place at active sites associated with the cations at the oxide surface in a higher oxidation state [6].

Bruce et al. reported a screening of many catalysts that could be used in facilitating the electrochemical properties of the O$_2$ electrode in a non-aqueous Li/O$_2$ cell [2]. Among the oxide catalysts studied, Co$_3$O$_4$ gives the best compromise between initial capacity and capacity retention as well as the lowest charging voltage of 4 V. Dai et al. reported a hybrid material consisting of Co$_3$O$_4$ nanocrystals grown on reduced graphene oxide as a high-performance bi-functional catalyst for the ORR and OER [9]. Recently, we demonstrated perovskite Sr$_{0.95}$Ce$_{0.05}$CoO$_{3-\delta}$ loaded with copper nanoparticles on their surface are shown to be excellent, low-cost, and stable bifunctional catalysts for oxygen-reduction and oxygen-evolution reactions in aqueous solution [10]. Very recently, Xu et al. demonstrated that the ORR catalytic activity of the prepared Co$_3$O$_4$-based catalysts are sensitive to the number and activity of surface-exposed Co^{3+} ions that can be tailored by the morphology of cobalt oxides [6]. Porous Co$_3$O$_4$ microspheres with an open mesoporous structure have more exposed Co^{3+} species and can increase dispersion of another active component [11]. In this work, we examine and compare the ORR and OER activities of porous Co$_3$O$_4$ microspheres and compare with the Vulcan XC-72 and the 50% Pt/carbon-black catalysts. To further improve the catalytic

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performance, copper nanoparticles were deposited on the surface of the porous Co_3O_4 microspheres. The preliminary results show that a round-trip electric-energy storage efficiency of 75.7% with excellent long-term stability and high rate performance was obtained in an aqueous Li/air cell with the Co_3O_4 microspheres–Cu catalyst.

2. Experimental

The flowerlike Co_3O_4 microspheres were synthesized by a hydrothermal method as reported elsewhere [11]. Copper nanoparticles were loaded on the surface of the porous Co_3O_4 microspheres by a polyol method [10].

Scanning electron microscopy (SEM) was performed on a Quanta 650 scanning electron microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out at a working voltage of 200 kV (FEI Tecnai-F20). The copper loading was analyzed by induced coupled plasma (ICP, Thermo Electron Corporation).

The aqueous Li–air battery was assembled as that previously described [10]. The assembled Li–air battery was exposed to ambient air and connected to the testing station. A Solartron 1470 cell tester was employed to perform the charge and discharge tests at a current density of 0.05 mA cm^{-2}.

3. Results and discussion

The size and morphology of the Co_3O_4 were examined by a field-emission scanning electron microscope (FESEM). Fig. 1a shows that most of the sample displays monodispersed spherical particles with flowerlike texture. The diameter of the microspheres is in the range of 2–5 μm. It can be clearly seen that these flowerlike

microspheres are composed of many nanoplate petals with an average thickness of about 50 nm; these nanoplates interweave together forming an open porous structure (Fig. 1b). A HRTEM image (Fig. 1c) taken on an individual nanoplate of porous Co_3O_4 microspheres displays crystallized Cu nanoparticles lay on the Co_3O_4 nanopalate. The copper loading was about 20 wt.% analyzed by induced coupled plasma (ICP).

Fig. 2a shows an anular dark-field (ADF) scanning transmission electron microscopy (STEM) image of the flowerlike Co_3O_4/Cu composite. To further clarify the chemical composition of the final nanoarchitectures, Fig. 2b presents the corresponding energy dispersive X-ray spectrometry (EDX) elemental mappings of Co and Cu, respectively. It should be noted that the smaller black spots in the Cu mapping are originated from the instability of EDX.

In order to examine the possible application of the porous Co_3O_4 microspheres/Cu catalyst in Li–air batteries, the catalyst was tested in a cell with hybrid electrolytes as previously described in Ref. [10], similar to that reported by Zhou et al. [12,13]. The first discharge and charge curves of cells with Co_3O_4 and Co_3O_4 loaded with Cu nanoparticles were compared with those of cells with Vulcan XC-72 and state-of-the-art 50% Pt/carbon-black catalyst as shown in Fig. 3a. The discharge voltages of the cells with Co_3O_4 and Co_3O_4 loaded with Cu nanoparticles are all lower than that of the 50% Pt/carbon-black catalyst, but slightly higher than that of the Vulcan XC-72 at the rate of 0.05 mA cm^{-2}. It is obvious that the charge voltages of cells with Co_3O_4 and Co_3O_4 loaded with Cu nanoparticles are lower than that of the Vulcan XC-72, especially for porous Co_3O_4 microspheres/Cu catalyst. It means that Co_3O_4–Cu catalysts are more effective for OER.

The difference between discharge and charge voltages (ΔV) as marked in Fig. 3a for the Vulcan XC-72, the commercial Co_3O_4 powder, Co_3O_4 microspheres, Co_3O_4 microspheres–Cu, and 50%Pt/C catalysts is
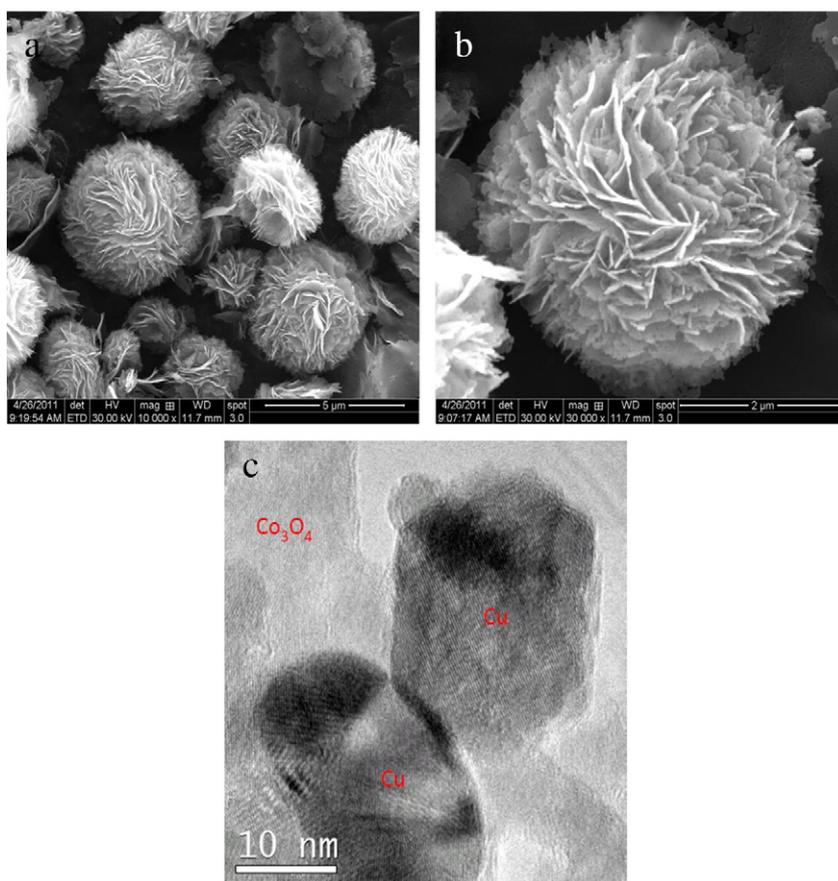
Fig. 1. (a) Overall morphology of the Co_3O_4 products, (b) high-magnification SEM image of an individual Co_3O_4 microsphere revealing the constituent details of the microspheres, and (c) HRTEM images of the Co_3O_4 nanoplate/Cu nanoparticles.
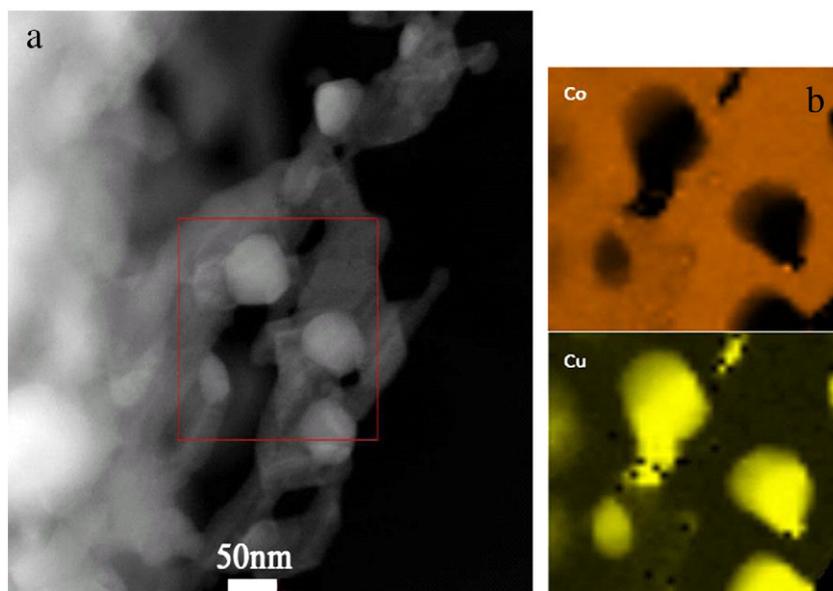
Fig. 2. (a) ADF STEM image of the flowerlike Co_3O_4/Cu, and (b) the corresponding elemental mappings of Co and Cu taken from the area marked.

1.43 V, 1.65 V, 1.19 V, 1.00 V and 0.68 V, respectively, at the current rate of 0.05 mA cm^{-2}. The round-trip efficiency (the ratio of discharge to charge voltages) of the cells with the porous Co_3O_4 microspheres and Co_3O_4 microspheres loaded with Cu nanoparticles as catalysts are 72.1% and 75.7%, respectively. These values are lower than that of the 50% Pt/carbon-black catalyst (83.0%), but higher than those of the Vulcan XC-72 (67.6%) and the commercial Co_3O_4 powder (63.8%). The discharge voltage of the commercial Co_3O_4 powder in micro meter (Aldrich) is lower than that of the pristine flowerlike Co_3O_4 microspheres, and the charge voltage is higher (Fig. 3a). The porous Co_3O_4
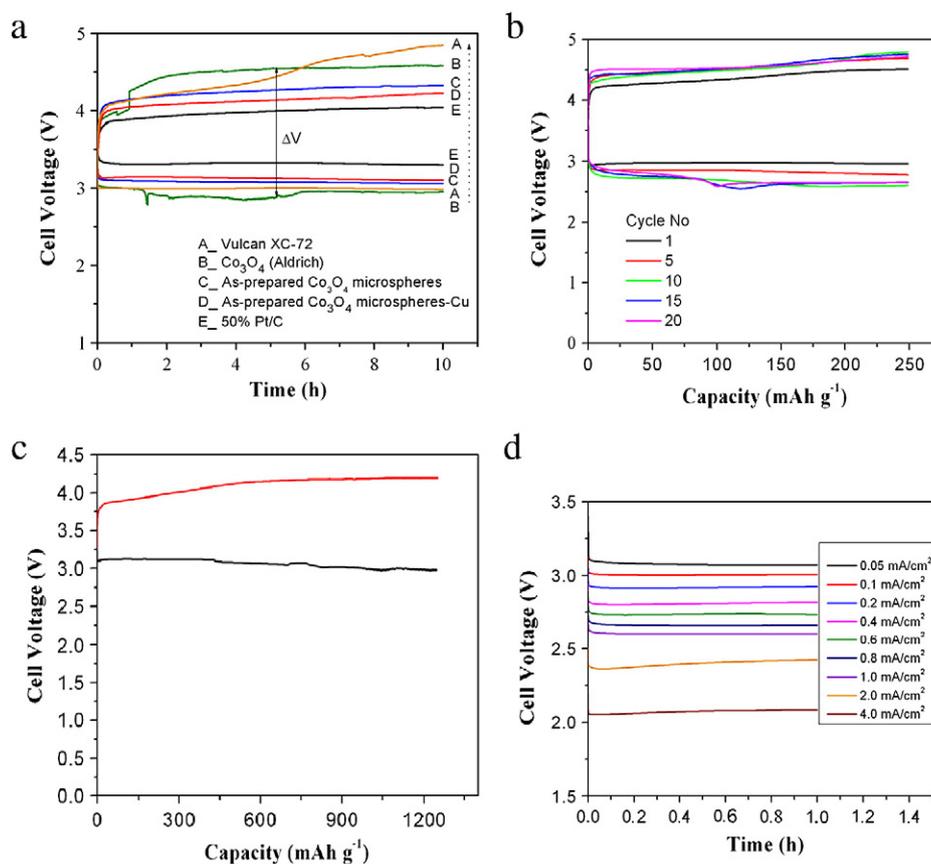
Fig. 3. (a) Comparison of the first charge and discharge curves of the prepared lithium–air batteries with various catalysts at a current density of 0.05 mA cm^{-2}, (b) the discharge–charge curves for the 20 cycles of the prepared lithium–air batteries with the Co_3O_4 microspheres–Cu catalyst at a current density of 0.2 mA cm^{-2}, (c) voltage versus discharge/charge capacity for the lithium–air batteries with the Co_3O_4 microspheres–Cu catalyst at a current density of 0.05 mA cm^{-2} with the active catalyst (Co_3O_4–Cu) mass loading of 0.5 mg cm^{-2}, and (d) the discharge voltage profiles at different current densities of the rechargeable lithium–air batteries with the porous Co_3O_4 microspheres/Cu nanoparticles catalyst.

microspheres loaded with Cu nanoparticle catalyst shows slightly improved performance compared to the one without Cu. We believe that copper nanoparticles may play a dual role in this case. On the one hand, the copper nanoparticles improve the conductivity of the Co_3O_4 catalyst. On the other hand, the metallic copper could catalyze the electrochemical reduction of O_2 at its surface, starting from the copper corrosion in aqueous solution [10,14].

Fig. 3b shows the 20 cycles charge/discharge curves at a current density of 0.2 mA cm^{-2}. It clearly indicates that the cell can be reversibly charged/discharged and the Co_3O_4 microspheres–Cu catalyst has a good cycle performance. It should be noted that most of the results reported so far concerning good cycle performance of cells with a non-aqueous electrolyte are tested with oxygen. Compared with the Li–O_2 battery with a non-aqueous electrode, the cycle performance of its counterpart Li–air battery usually shows quite bad, which might be due to complex reactions arised from CO_2 and H_2O in air as well as the clog effect of the discharged product Li_2O_2 in the porous electrode. All these factors may lead the cell performance to degrade quickly. In contrast, the discharge product of the Li–air cell with hybrid electrolytes is a dissolvable LiOH in the cathode side. Therefore, the cyclability of the hybrid electrolyte cell studied in this work is improved greatly. Fig. 3c shows the long-term discharge/charge curves of the prepared lithium–air batteries with the Co_3O_4 microspheres–Cu catalyst at a current density of 0.05 mA cm^{-2}. The test shows stable performance over 110 h, which corresponds to 1250 mAh g^{-1}. It is worth to point out that there is a limitation arising from the solid electrolyte plate in the cell. The commercial solid electrolyte that is commonly used in an aqueous Li–air battery is $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ (OHARA Inc., Japan). This solid electrolyte has been known to be unstable in alkali liquid electrolytes for a long period of time (>100 h), which will eventually affect the cell voltage and cycle life [15,16]. Fig. 3d shows the discharge voltage profiles at different current densities of the rechargeable lithium–air batteries with the porous Co_3O_4 microspheres/Cu nanoparticles catalyst. It can be seen that the cell works well even at higher current rates. As mentioned above, the ORR and OER are assumed to take place at active sites associated with cations in the higher oxidation state (Co^{3+}) at the Co_3O_4 surface. The open porous morphology of Co_3O_4 is more beneficial for the reactions to take place. Considering the higher round-trip efficiency and excellent long-term stability as well as lower cost compared with noble metal catalysts, the flowerlike Co_3O_4 microspheres/Cu nanoparticles material is a promising bifunctional catalyst for the Li–air battery.

In summary, we have successfully prepared porous Co_3O_4 microspheres/Cu nanoparticles hybrid via a combined solvothermal method, subsequent thermal treatment and polyol process. Due to the 3D mesoporous structure, the resulting Co_3O_4 microspheres/Cu catalyst shows an efficient and stable bifunctional catalytic activity. The cell with this novel catalyst can be reversibly charged/discharged and has an excellent cycle performance. The improved performance of Co_3O_4 microspheres/Cu nanoparticles catalyst can be ascribed to the synergetic effect of Co_3O_4 and copper. We believe that the present synthetic strategy can be extended to develop other 3D oxide/metal materials for various applications, such as batteries, supercapacitors and sensors.

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