



Silver decorated beta-manganese oxide nanorods as an effective cathode electrocatalyst for rechargeable lithium–oxygen battery



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ABSTRACT

In this paper, Ag nanoparticles decorated β -MnO₂ nanorods are studied as cathode catalyst for rechargeable lithium–oxygen battery (LOB). β -MnO₂ nanorods are prepared using a simple hydrothermal method based on MnO₄⁻ and the decoration of Ag nanoparticles is performed by in-situ composite technique in the presence of polymeric additives. The as-prepared materials are characterized by XRD, TEM, XPS, BET and Raman spectrum. Electrochemical charging and discharging capacity of β -MnO₂ and Ag/ β -MnO₂ electrodes are investigated at the current density of 0.02 mA cm⁻² in the voltage window of 2.0–4.0 V. LOB with Ag/ β -MnO₂ electrode shows an initial discharge capacity of 873 mA hg_(electrode)⁻¹, with reversible charge capacity of 811 mA hg_(electrode)⁻¹ while battery with only β -MnO₂ has discharge capacity of 541 mA hg_(electrode)⁻¹ and charge capacity of 445 mA hg_(electrode)⁻¹. Ag/ β -MnO₂ nanocomposite electrode shows good rate capability and cycle stability. After 10 cycles, the capacity of 742 mA hg_(electrode)⁻¹ is still retained at the current density of 0.02 mA cm⁻² while only 219 mA hg_(electrode)⁻¹ is retained at 0.5 mA cm⁻². The capacity retention rate is 84.9% and 70.2% at 0.02 and 0.5 mA cm⁻², respectively. During discharging, Li₂O is the main discharge product and no Li₂CO₃ is formed. The results show that the electrochemical performance of β -MnO₂ is greatly enhanced when Ag nanoparticles are introduced. And it is highly effective for decreasing the charging potential close to the theoretical value. Ag nanoparticles can enhance the electronic conductivity of the network. The study confirms that Ag/ β -MnO₂ catalyst is a promising effective catalyst for LOB.

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1. Introduction

Compared with the sustainable resources as wind and solar powers, chemical energy storage using batteries can contribute to a potential solution. There are growing interests in hybrid electric vehicles requiring smaller and lighter weight batteries to meet today's energy and environmental challenges. The remarkable high energy density of metal air batteries has attracted the focus of all battery researchers. The development of metal air batteries becomes attractive since they use metal anode and oxygen in the air as cathode. Theoretically, with an environmentally abundant oxygen cathode, the metal air battery could be lighter, cheaper and long lasting (regenerative) with high energy density [1–4]. Among the various metal-air battery systems, LOB is the most attractive one because it has the highest energy density per unit

weight [5–9]. The battery discharge reaction occurs between Li and O₂ to yield Li₂O or Li₂O₂, with a theoretical specific energy density up to 5200 W h kg⁻¹ (including oxygen). In practice, the storage of oxygen in the battery is unnecessary since air can be directly used. Therefore, the theoretical specific energy (excluding oxygen) can reach 11,140 W h kg⁻¹, which is much higher than those of the advanced batteries and fuel cells proposed to date, even rivaling that of gasoline [10–13].

For LOBs, one of the biggest obstacles is the large over potential during charge and discharge, even at very low current density (0.01–0.05 mA cm⁻²), which results in very low round-trip efficiency and low power capability [14–16]. This performance is strongly believed to depend on the nature of catalysts and their loading onto a high surface area cathode. In previous works by other researchers [17–21], metal complexes and metal oxides have been examined as the cathode catalysts for oxygen reduction reaction (ORR), showing large differences in discharge capacity among different catalysts. This effect probably indicates that the ORR

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kinetics in a LOB cathode is either not catalytically sensitive or limited by the oxygen mass transport resistance toward the catalyst. The oxygen oxidation plateau can be significantly lowered when catalysts are introduced to the cathode [22–26]. Therefore, it is important to develop highly efficient catalysts for ORR and OER in air cathode to realize the commercial LOBs.

Manganese oxides (MnO_x) have been widely studied as an alternative to noble metal based catalysts because of their advantages, such as abundance, low cost, environmental friendliness, and favorable ORR and OER activity [27–30]. Recently, Wei et al. [29] reported that the Mn ion oxidation state in MnO_x significantly influenced the catalytic activity for oxygen reduction and oxidation catalysis by using a combination of computational modeling and behavioral experiments. Mn changes oxidation states from +2 to +3 to +4 near the equilibrium potential for ORR and OER, suggesting that Mn can exchange oxygen atoms with the electrolyte at relevant potentials property which could potentially facilitate ORR and OER chemistry. The presence of the intrinsic tunnels in $\beta\text{-MnO}_2$ crystalline lattice and its electrical conductivity were attributed to facilitate the accommodation and transportation of Li ions when used in LOBs [27,31]. However, MnO_2 prepared by the traditional route shows limited electrocatalytic activity because of its large particle size and low specific surface area. In addition, the decomposition of electrolytes containing propylene carbonate (PC) during charge and discharge may lead to the formation of Li_2CO_3 , which is the main reason for the high charge potential [32,33]. Furthermore, for metal–metal oxide composites, Ag is a promising candidate to combine with MnO_x as it is active for oxygen reduction, and it is also less expensive than Pd or Pt.

The entire gas diffusion oxygen electrode structure must have high electronic conductivity to ensure effective collection of the current and reduce ohmic resistance [34]. Without this, an undesirable voltage-drop will occur. In addition to ohmic voltage drop, kinetic (reaction rate dependent) and mass transfer polarization can also reduce the battery voltage. Therefore, it is a goal of air electrode design to increase oxygen reduction and reduce polarization from all sources. In order to reduce the polarization of the air electrode, the effective route is to utilize the dual functional catalysts. Because of the excellent electronic conductivity of silver, it would be an ideal conductor to form electron-transferring channels during manganese dioxide discharging. Recent investigations show that the battery performance of manganese dioxide electrode can be significantly improved by addition Ag [35]. It was reported that silver nanoparticles can form electron transfer channels during manganese dioxide discharging due to their excellent electronic conductivity, and the conductivity of MnO_2 can be significantly improved by loading Ag nanoparticles on it. Ag can facilitate the direct reduction of O_2 to O^{2-} . This is important because MnO_2 cannot participate in the oxygen reduction. Those oxygen atoms that are not reduced to O^{2-} in the $4e^-$ process may be reduced to O_2^{2-} in a two electrons process [36]. Rapid elimination of this peroxide will enable a higher running voltage for the cathode. Both Ag and MnO_2 are effective peroxide elimination catalysts. A further advantage is that Ag improves the conductivity of the electrode. So, combination of those two catalysts can significantly enhance the performance of the air electrode.

In the current study, we studied the preparation and the performance of Ag nanoparticles decorated $\beta\text{-MnO}_2$ nanorods as a cathode catalyst for LOB. $\beta\text{-MnO}_2$ nanorods were synthesized through a simple hydrothermal process using only potassium permanganate (KMnO_4) and polyvinylpyrrolidone (PVP). And the decoration of Ag nanoparticles was performed by in-situ composite technique in the presence of polymeric additives. The results confirm that Ag decorated $\beta\text{-MnO}_2$ nanorods are effective catalysts for ORR in LOB and can improve the discharge capacity as well as the cycle life of the battery. And it is also effective for increasing discharge and

decreasing charge potentials. During discharging, Li_2O is the main discharge product other than Li_2CO_3 .

2. Experimental

2.1. Synthesis

In brief, 0.01 mol KMnO_4 and 1.5 g PVP ($M_w = 40,000$, Aldrich) were dissolved in 30 mL of deionized water. After stirring for 1 h, the solution was transferred into a 100 mL Teflon-line stainless steel autoclave and heated at 140 °C for 24 h. The products ($\beta\text{-MnO}_2$) were collected by centrifugation, washed with deionized water and dried under vacuum at 80 °C.

For preparation of Ag decorated $\beta\text{-MnO}_2$, Ag nanoparticles were prepared by the reduction of AgNO_3 solution in glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution in the presence of polyvinylpyrrolidone (PVP). 3.5 g AgNO_3 was dissolved in 60 mL deionized water, then 0.1 M $\text{NH}_3\cdot\text{H}_2\text{O}$ (28 wt%) was added until the solution became transparent again to form $[\text{Ag}(\text{NH}_3)_2]^+$ solution. Reducing solution was prepared by mixing 45 g $\text{C}_6\text{H}_{12}\text{O}_6$, 1.5 g PVP, 100 mL ethanol and 1 L deionized water together. 0.5 g $\beta\text{-MnO}_2$ was dispersed in 50 mL of 1 wt% sodium dodecyl sulfonate (SDS) of $[\text{Ag}(\text{NH}_3)_2]^+$ solution for 30 min. Then $\beta\text{-MnO}_2$ with Ag nanoparticles can be obtained by mixing $[\text{Ag}(\text{NH}_3)_2]^+$ solution and reducing solution with a ratio of 1/1 (v/v) dropwise under magnetic stirring for 6 h. The final products were collected by centrifugation, washed with ethanol and dried under vacuum at 80 °C.

2.2. Air electrode preparation

For air electrode preparation, the catalytic layers of air electrodes were composed of Ketjen black EC-600JD (KB) (Fuhua Industry (shanghai) Ltd.), the as-prepared Ag/ $\beta\text{-MnO}_2$ nanostructured catalysts, and polyvinylidene fluoride (PVdF) (Sigma Aldrich, MW 534,000, 99.9%) in a mass ratio of 70:20:10, using N-methyl-2-pyrrolidinone (NMP) (Aladdin Reagent, AR) as solvent. For comparison, the air electrode composed of the as-prepared $\beta\text{-MnO}_2$ catalysts and PVdF with the same composition was also prepared. Nickel foam disk (15.6 mm diameter, 1.7 mm thickness, 420 g cm^{-2}) was submerged in the NMP/PVdF/carbon slurry. The disks were ultra-sonicated for 20 min to encourage slurry penetration into the foam structure. After sonication, disks were heated at 120 °C overnight to remove the NMP. The loading of the catalyst in air electrode is about 5–8 mgcm⁻².

2.3. Battery assembly

Lithium ribbon (15.6 mm diameter, 0.4 mm thickness, China Energy Lithium Co., Ltd.) was used as the negative electrode. The as-prepared air electrode was used as the positive electrode. A commercial electrolyte solution of 1 M lithium trifluoromethanesulfonate (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) was acted as the electrolyte. Polypropylene microporous membrane Celgard 2400 (16.0 mm diameter) was used as the separator. The electrochemical characterizations were carried out using R2032 coin-type battery. The batteries were assembled in an argon-filled glove box with both water and oxygen concentrations less than 0.1 ppm.

2.4. Measurement and characterization

Powder X-ray diffraction (XRD) was carried out by using an X'Pert PRO X-ray diffractometer with Cu K α radiation. The morphology and composition were investigated using a transmission electron microscope (TEM, Philips TF-F20), a field emission scanning electron microscope (FE-SEM, FEI, Sirion 200) and X-ray photoelectron spectroscopy (XPS, ESCA-LAB 250 photoelectron spectrometer). Nitrogen adsorption-desorption isotherms were measured using a Bell Japan (BellMini) instrument and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Raman spectra were measured and collected using a 633 nm laser by a Lab RAM HR800 (Horiba JobinYvon Co., Ltd.).

Discharge-charge (DC) performance was carried out in a Hantest cyler (Wuhan Hantest Technology Co., Ltd.) with a lower voltage limit of 2.0 V and an upper limit of 4.0 V vs Li⁺/Li under different current densities. The observed capacity was normalized by the total weight of the air electrode, but not with the weight of carbon for capacity comparison in this study. Before test, the batteries were rested for 4 h to reach equilibrium of the oxygen concentrations and moisture of the electrolyte. Electrochemical impedance spectra (EIS) of the batteries were measured by AC impedance on a Zennium IM6 station over the frequency range of 0.1–10⁵ Hz with amplitude of 5 mV.

3. Results and discussion

The phase purity and crystal structure of as-synthesized MnO_2 with and without Ag nanoparticles decorating were investigated by XRD, as shown in Fig. 1. It can be seen that the undecorated MnO_2 shows sharp peaks at corresponding diffraction 2θ angles

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