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Nanocomposites CoPt-x/Diatomite-C as oxygen reversible electrocatalysts for zinc-air batteries: Diatomite boosted the catalytic activity and durability

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ABSTRACT

The exploration of oxygen reversible electrocatalysts to boost oxygen reduction reaction and oxygen evolution reaction is critical for the development of high-performance aqueous Zn-air batteries. Since diatomite with porous structure can adsorb metal ions in aqueous solution, herein, we prepare the nanocomposite CoPt-x/Diatomite-C for both oxygen reduction and evolution reactions, and diatomite is found significantly promotes the electrocatalytic activity and durability. With the presence of diatomite, CoPt-1/Diatomite-C shows a lower Tafel slope (63 mV dec^{-1} at high potential range), larger diffusion-limited current density (4.94 mA cm^{-2}) and superior durability for ORR. Particularly, the specific and mass activities of CoPt-1/Diatomite-C for ORR are 0.74 mA cm^{-2} and 286 mA mg^{-1}, respectively, which are 2.5 and 3.0 times higher than that of CoPt-1/C without diatomite; For OER, the overpotential of CoPt-9/Diatomite-C decreases nearly 30 mV at 10 mA cm^{-2}, while the Tafel slope also reduces 16 mV dec^{-1} versus CoPt-9/C catalyst. Moreover, a rechargeable Zn-air battery with these composites as air-cathode is self-assembled, and diatomite boosts the battery performance with desirable properties. CoPt-9/Diatomite-C displays the optimal performance, with a power density of 140 mW cm^{-2}, a specific capacity of 616 mA h g^{-1} at 10 mA cm^{-2} and an exceedingly robust cycling life. This work provides a viable and cost-effective strategy for fabricating oxygen reversible electrocatalysts for metal-air battery applications.

1. Introduction

Rechargeable zinc-air batteries are gaining increasing attentions in energy storage and conversion thanks to their high theoretical energy density, low cost and safety [1–3]. However, the large-scale commercialization of rechargeable zinc-air batteries has been significantly hindered by the sluggish reaction kinetics of both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) occurring at the cathode [4–8]. Therefore, developing more efficient and durable oxygen reversible electrocatalysts as air-cathode for zinc-air batteries are highly desirable [9,10].

Currently, Pt-based materials have been considered as the benchmark ORR catalysts while Ru/Ir based materials possess the best OER activities [11–13]. However, all these noble-metal-based

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materials are suffering from limited availability resulted high costs as well as poor stability for practical applications. To reduce the cost and acquire enhanced activity and stability, one effective strategy is to alloy the noble metals with 3d transitional metals [14]. For instance, a variety of Pt-M (M = Fe [15,16], Co [17,18], Ni [19,20] and other transition metals) alloys with different structures and various morphologies have demonstrated superior catalytic activity toward ORR than Pt. On the other hand, transition metal oxides, hydroxides and complexes have demonstrated great potentials in catalyzing OER to serve as alternatives for Ir or Ru based materials [21–25]. To realize real-world applications of the catalyst for rechargeable zinc-air battery, it is essential to integrate both ORR and OER catalytic activity into one sample [26]. The so-called "Two-in-one" strategy requires the rational design, which not only can achieve optimized performance in both reactions, but also be able to develop a facile and cost-effective approach for fabrication [27]. Coupling PtM alloys with transitional metal oxides or complexes to fabricate hybrid materials can be a viable strategy and have shown great promises for catalyzing both ORR and OER and/or for further zinc-air battery applications. Through a laser ablation synthesis, PtCo nanoalloys embedded in CoO_x matrices have been prepared as bifunctional electrocatalysts for ORR and OER by Mukherjee group, and a combined overpotential of 756 mV vs. RHE for the sample of PtCo-3 NC was achieved [28]. Goodenough group developed a robust Fe_3Mo_3C supported IrMn clusters as bifunctional air-electrode, which could enable Zn–air batteries to achieve long-term cycling performance over 200 h with high efficiency [29]. In addition, porous metallic nickel-iron nitride (Ni_3FeN) supporting ordered Fe_3Pt intermetallic nanoalloy was also prepared by this group as advanced bifunctional electrocatalysts for zinc-air battery, and a long-term cycling performance of over 480 h at 10 mA cm^{-2} was recorded [30].

Despite these progresses on bi-functional electrocatalysts for ORR and OER, the activity and durability for the two reactions are far from satisfaction. Furthermore, the preparation of these hybrid materials was also tedious, sophisticated and time-consuming hence not cost-effective. Herein, we developed a new strategy for preparing highly efficient electrocatalysts toward both ORR and OER for zinc-air batteries. As PtM alloys have already demonstrated excellent activity toward ORR, and metal oxides showed good OER performance, instead of simply combining PtM alloys with transitional metal oxides, we developed a strategy to integrate CoPt nanoparticles with SiO_2 as dual functional electrocatalysts for both ORR and OER, where SiO_2 are from widely accessible natural diatomite (DTM). Note that, diatomite (DTM) is a near pure sedimentary deposit consisting almost entirely of silica (SiO_2). Known as diatomaceous earth, DTM is the naturally occurring fossilized remains of diatoms, which are ubiquitous in nature hence extremely cheap [31,32]. Furthermore, DTM possesses porous structure which not only can adsorb metal ions, but also is favourable for electrocatalytic reaction.

In this study, we prepared the composite CoPt-x/DTM-C via reducing the Pt^{4+} and Co^{2+} ions that were co-adsorbed into the DTM in ethylene glycol solution. TEM analysis demonstrated that CoPt nanoparticles were well-dispersed on the surface of the DTM. The nanocomposite catalyst exhibited excellent performance for both ORR and OER, and we found that DTM significantly promoted the electrocatalytic activity and long-term durability. With the presence of the DTM, the catalysts showed lower Tafel slope, higher diffusion-limited current and significantly enhanced durability. The specific and mass activities of CoPt-1/DTM-C for ORR are 0.74 mA cm^{-2} and 286 mA mg^{-1} (at 0.9 V vs. RHE), which are 2.5 and 3.0 times higher than that of CoPt-1/C catalyst; the overpotential of CoPt-9/DTM-C for OER decreased nearly 30 mV versus CoPt-9/C catalyst. In the rechargeable Zn-air battery applications, CoPt-9/DTM-C displayed superior performance than the sample without DTM and the other samples, with a power density of 140 mW cm^{-2}, a specific capacity of 616 mAh g^{-1} at the current density of 10 mA cm^{-2} and an exceedingly robust cycling life.

2. Experimental section

2.1. Materials

Diatomite was received from the Guangzhou Institute of Geochemistry, Chinese Academy of Science, ethylene glycol (EG, 99.9%, Tianjin Fuchen Chemical Regents), hydrochloric acid (HCl, 37%, Tianjin Damao Chemical Regents), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 97%, Tianjin Fuchen Chemical Regents), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99.9%, Energy Chemicals, Shanghai, China), commercial Pt/C (20 wt%, Alfa Aesar). Water was supplied by a Barnstead Nanopure Water System (18.3 MΩ cm). All the chemicals were used as received without further purification.

2.2. Preparation of nanocomposite electrocatalysts

All the CoPt-x/DTM-C (x equaling to the molar ratio of Co-to-Pt) samples were prepared via a conventional ethylene glycol (EG) reduction method. Take CoPt-1/DTM-C as an example, and the detailed procedure is described below: DTM was first immersed into the HCl solution (3 M, 40 mL) under stirring overnight, then washed with de-ionized water until the pH of the filtrate reached ~7. The filter cake was dried at 40 °C under vacuum overnight. Subsequently, $H_2PtCl_6 \cdot 6H_2O$ (0.15 mmol) and $CoCl_2 \cdot 6H_2O$ (0.15 mmol) were dissolved in EG (20 mL) with sonication for 15 min, the above obtained solid (76 mg) was added to the above solution under vigorous stirring at room temperature for 4 h to ensure the Pt^{4+} and Co^{2+} ions were completely adsorbed. The mixture was then heated to 160 °C for 6 h. After that, it was cooled down to 40 °C, and XC-72 (76 mg) was added. The solution was kept 40 °C for 4 h under magnetic stirring. The whole process was under protection of nitrogen atmosphere. Afterward, the sample was separated by centrifugation, washed with de-ionized water several times, and dried at 40 °C under vacuum for 12 h. The synthesis of CoPt-3/DTM-C, CoPt-9/DTM-C was in the same manner with that of CoPt-1/DTM-C, except the amount of $CoCl_2 \cdot 6H_2O$ was changed into 0.45 mmol and 1.35 mmol, respectively, whereas for Co/DTM-C, 1.85 mmol $CoCl_2 \cdot 6H_2O$ and no $H_2PtCl_6 \cdot 6H_2O$ were added. Other than that, the samples of CoPt-x/C and Co-x/C were synthesized by following the procedure of CoPt-x/DTM-C and Co/DTM-C but without the addition of DTM. The weight percentage of platinum in the CoPt-x/DTM-C series and CoPt-x/C series are compiled in Table S1.

2.3. Characterizations

X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo Escalab 250Xi instrument. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-Advance diffractometer using Cu K_α radiation. Transmission electron microscopic (TEM) measurements were carried out on high-resolution transmission electron microscope (JEOL-JEM-2010) with an acceleration voltage of 200 kV. Barrett-Emmett-Teller (BET) surface areas of the catalysts were measured by a Quantachrome Autosorb-iQ2 instrument with N_2 adsorption at 77 K using the Barret-Joyner-Halenda (BJH) method.

2.4. Electrochemical measurements

The electrochemical experiments were performed using a CHI