



Fabrication of iron-doped cobalt oxide nanocomposite films by electrodeposition and application as electrocatalyst for oxygen reduction reaction



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ABSTRACT

In this work, Fe-doped Co₃O₄ nanofilms were fabricated by electrodeposition on FTO glass substrates for the first time. The structures of the as-prepared nanofilms were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Characterization results demonstrate that Fe was doped homogeneously in the nanofilms. As the different concentration ratios of Fe²⁺/Co²⁺ were explored, nanofilm with the ratio of 1:5 exhibits the optimal performance in electrochemical properties assessments. It is considered that the difference in the catalytic activities for the ORR of the samples may be due to the fact that the joining of iron changed the catalyst surface's electric state and enhanced the acidity of cobalt centers, on the other hand, the doping process probably modified the absorption property of the nanofilms. The experimental results suggest that the Fe-doped Co₃O₄ nanofilms in this work exhibit favorable electrocatalytic activity toward ORR and appear to be promising cathodic electrocatalyst in alkaline fuel cells.

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1. Introduction

With an urgent need to look for alternative energy sources to reduce the dependency on fossil fuels for energy and transportation purposes, as well as reducing environmental contamination, fuel cells become significant in the field of renewable resources and more considerable attention has received due to its high efficiency, cleanliness, and other several key advantages, such as reusability of exhaust heat, fuel diversity and modularity [1]. Oxygen reduction reaction (ORR) plays a significant role in fuel cells especially proton exchange of membrane fuel cells (PEMFC), since ORR dominates the overall performance of these energy storage and conversion systems. Common oxygen reduction electrocatalysts include nanoparticles [2], macrocycles and cleavage products [3], carbon and sulfur compounds [4–6], enzyme and the corresponding complexes [7,8]. For fuel cells, the performance depends largely on the oxygen reduction reaction, which is substantially affected by the activity of the cathode catalyst. Pt and Pt-alloy

catalyst has always been the principal metallic based element used for ORR which is carried out on the cathodic side of a proton exchange membrane fuel cell (PEMFC). Nonetheless, in order to meet large-scale production, several technical and economic issues such as electrocatalytic activity, stability, durability, etc., should be previously resolved. In practical applications, Pt and Pt-alloy catalysts were needed to promote hydrogen oxidation reaction at the anode and oxygen reduction reaction at the cathode [9–11], but because of it being too expensive and lack of resources, it was subjected to considerable limitations in practical applications [12–15]. Consequently, to become commercially viable and overcome the barrier of high catalyst cost caused by the exclusive use of Pt-based catalysts, as well as the slow reaction of the oxygen reduction reaction (ORR) leads to a higher overpotential at the cathode, the greatest challenge for the current research and development of fuel cells is to develop low cost and high activity non-platinum electrocatalysts [16,17]. In this respect, a series of alternative catalysts, which based on non-precious metals (Fe, Co, and Mn, etc.) or metal oxides (Fe₃O₄, CoO, Co₃O₄, and MnOx, etc.) as well as nitrogen-coordinated metal on carbon and metal-free doped carbon materials, have attracted intense attention because they exhibit satisfied catalytic activity, long-term durability and excellent tolerance to poisoning toward the ORR [18,19].

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Previous studies have shown that oxygen in alkaline medium reduced following by two different pathways. One is the $4e^-$ pathway with OH^- being the final product, the other is a lone pair of electrons which HO_2^- being the products. The $2e^-$ pathway with HO_2^- as the final product is unexpected because of the reduction of oxygen is incomplete, resulting in not only the loss of the cathode potential, but also the corrosion of the catalyst [20]. To solve these problems, the best way is to prevent the formation or accelerate its decomposition. As we all know, it is widely reported that transition metals support the ORR for the PEFC cathode [21–25]. The preparation of coatings of transition metals such as Co, Fe, Ni, Cu, etc. has attracted considerable attention in view of their potential applications in scientific and technological fields [26–28]. As an important transition metal oxide, Co_3O_4 has been applied in various fields such as lithium-ion batteries, electrochemical capacitors [29], electrochromic devices [30], magnetic materials [31], gas sensors [32] and catalysts [24,33]. Cobalt oxides (Co_3O_4) are known to act as non-precious ORR catalysts in alkaline media. It belongs to the normal spinel crystal structure based on a close-packed face centered cubic configuration of O_2^- ions, in which Co^{2+} ions occupy the one-eighth of the tetrahedral A sites while Co^{3+} ions occupy one half of the octahedral B sites [34,35]. Meanwhile, iron oxides not only have good magnetic properties, but also exhibit some catalytic activity. To the best of our knowledge, there are a handful of literatures reported about the Fe–Co nanocomposite materials and of which very few have been applied in electrochemical catalysis [31]. On the basis of the concept, we fabricated iron-doped cobalt oxide nanofilms by electrodeposition method for the first time and further explored its electrocatalytic performance in the oxygen reduction reaction.

In this work, we demonstrate a facile and low cost way to synthesize Fe-doped Co_3O_4 nanofilms by electrodeposition because (i) it can be uniformly deposited on the complex substrate with a variety of morphologies and (ii) the deposition thickness and the chemical composition structure of the materials can be significantly affected by controlling the processing conditions. Compared with other methods, electrodeposition is an economical method, for its simple equipment, easy to operate, and friendly to the environment. It is well known that the properties of Fe–Co composites are seriously affected by their compositions and structures [36], therefore, the doping amount of iron is a crucial impact factor in designing the electrocatalytic activity of these materials [31,37,38]. The work presented in this paper is focused on the investigation of materials based on Fe and Co as catalysts for ORR. The electrocatalytic properties of electrodeposited Fe–Co films were studied as a variable factor of the concentration ratio of $\text{Fe}^{2+}/\text{Co}^{2+}$ in electrolyte. It was clearly observed that the electrocatalytic properties of the iron-doped cobalt oxide nanofilms have been influenced by the different concentration ratio of $\text{Fe}^{2+}/\text{Co}^{2+}$ in electrolyte. Meanwhile, some other properties have been studied to further illustrate the advantages of the nanofilms.

2. Experimental

2.1. Chemicals

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, KCl, KOH were purchased from Tianjin Kaitong Chemical Reagent Corp. Fluorine-doped tin oxide conducting glasses were purchased from Zhuhai KaiVo Electronic Components Ltd. All chemicals were used as received without any further purification. Ultrapure water was used in all experiments. High purity nitrogen (Purity: 99.999%) and oxygen (Purity: 99.999%) was purchased from Lanzhou Institute of Chemical Physics.

2.2. Catalysts preparation

The electrodeposition was performed in a conventional three-electrode cell. FTO conductive glass with a size of $1.5\text{ cm} \times 1.0\text{ cm}$ was used as the working electrode. Before the electrodeposition, the glasses were first prepared from a consecutive ultrasonication in aqua detergente, ethanol, and ultrapure water. Pt and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The precursor films were synthesized by a one-step potentiostatic electrodeposition at -0.8 V for 600 s from aqueous solution containing $0.05\text{ M Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $x\text{ M FeCl}_2 \cdot 4\text{H}_2\text{O}$ ($x = 0.005, 0.00625, 0.01, 0.025, 0.05$) dissolved in 0.1 M KCl . Thereafter, the FTO conductive glasses modified with the precursor nanofilms were washed in ultrapure water three times, allowed to dry in air, and then annealing at the target temperatures of 400°C for 4 h.

2.3. Characterization

The morphology and microstructure of the as-prepared Fe-doped Co_3O_4 thin films were characterized by Scanning electron microscopy (SEM) on a Zeiss Ultra plus field emission scanning electron microscope (Germany). Transmission Electron Microscope (TEM) image was taken with a JEM-3010 transmission electron microscope (JEOL Co., Ltd., Japan). X-Ray Diffraction (XRD) study was conducted by D/max2400 ($\lambda = 1.54056\text{ \AA}$). X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 X-ray photoelectron spectrometer.

2.4. Electrochemical measurements

All electrochemical experiments were conducted on a CHI 660C electrochemical workstation which included cyclic voltammetry (CV), chronoamperometry response, differential pulse voltammetry (DPV) and Tafel plots. The electrochemical workstation in conjunction with a three electrode system was used to carry out the electrochemical tests, with an Ag/AgCl reference electrode, a platinum counter electrode, while the FTO conductive glass modified by iron-doped cobalt oxide nanofilm was used as the working electrode. Unless otherwise specified, all potentials reported in this paper are referred to the Ag/AgCl (saturated KCl) reference electrode. The ORR activity of the doped-graphene was characterized by cyclic voltammetry with a potential from 0 to -1.0 V at a scan rate of 100 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) experiments were performed on Multi-potentiostat (VMP2, Princeton Applied Research, USA), which were made with a superimposed 5 mV sinusoidal voltage in the frequency range of $100\text{ mHz} - 100\text{ kHz}$. All the electrochemical measurements were carried out in the O_2 purged 0.1 M KOH electrolyte solution at room temperature.

3. Results and discussion

3.1. Fabrication of the iron-doped cobalt oxide nanofilms

The LSVs of Fe, Co and Co/Fe deposition on FTO conductive glass in the aqueous solution of 0.01 M FeCl_2 , $0.05\text{ M Co}(\text{NO}_3)_2$, as well as a mixed solution of 0.01 M FeCl_2 and $0.05\text{ M Co}(\text{NO}_3)_2$ are measured to determine the deposition potential interval of each metal. Reference to the co-deposition of Co and other transition metal such as Ni which has been studied previously [39,40], the co-deposition of Co and Fe started at about $-0.8\text{ V vs. Ag/AgCl}$, while the Fe deposition started in more positive potential than about $-0.4\text{ V vs. Ag/AgCl}$ and Co deposition started in more negative position than about $-1.0\text{ V vs. Ag/AgCl}$. According to the linear sweep voltammetry curves, the deposition potential of -0.8 V vs.

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