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Reduced graphene oxide supported chromium oxide hybrid as high efficient catalyst for oxygen reduction reaction

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ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form

8 May 2016

Accepted 8 May 2016

Available online 28 May 2016

Keywords:

Oxygen reduction reaction

Electrocatalysis

Reduced graphene oxide

Chromium oxides

ABSTRACT

Reduced graphene oxide (rGO) supported nano-chromium oxide ($\text{Cr}_2\text{O}_3/\text{rGO}$) catalyst for oxygen reduction reaction (ORR) has been successfully synthesized by the pyrolysis of chromium-urea coordination compound. The structure and morphology of the hybrid are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) tests. XRD tests reveal that the Cr_2O_3 with hexagonal structure is obtained. SEM and TEM tests show that the nano- Cr_2O_3 is supported by rGO sheet. The cyclic voltammetry, tafel, linear scanning voltammetry and current-time chronoamperometric tests prove that the obtained $\text{Cr}_2\text{O}_3/\text{rGO}$ hybrid has a remarkable catalytic activity and good stability for oxygen reduction. Both the rotating disc electrode and rotating ring disc electrode tests approve that the ORR major happens through 4-electron reaction style. The $\text{Cr}_2\text{O}_3/\text{rGO}$ hybrid is a promising low cost and high performances catalyst for ORR of alkaline electrolyte.

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Introduction

Catalysts for oxygen reduction and evolution reactions are key factors to novel-energy technologies, such as fuel cells, water splitting and etc. Despite tremendous efforts have been made, developing oxygen reduction catalysts with high activity and low cost still remains a great challenge for scientists.

Traditionally, Pt-based catalysts are regarded as the most promising catalysts for oxygen reduction reaction (ORR). Unfortunately, rare resources, high cost, and sluggish oxygen reduction catalytic activity limited the large scale applications of Pt-based catalysts [1–3]. To eliminate the dependence on the Pt-based catalysts for oxygen reduction, great efforts are being taken to develop precious metal free catalysts with high

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<http://dx.doi.org/10.1016/j.ijhydene.2016.05.051>

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cost effectiveness and comparable or even better catalytic performances [4,5]. Metal oxide is one of the most promising alternatives for Pt-based catalysts among all the being investigated catalysts. The catalytic performances of Mn_2O_3 , CoO and spinel-type LiCoO_2 for ORR have been investigated [6–8]. The benefits of abundant in sources, low cost, high chemical and electrochemical stability make the metal oxide based catalysts to be hopeful alternatives for Pt-based precious metal catalysts for ORR [9–11]. Investigations on transitional metal oxides for ORR have been conducted. Results showed that the non-precious transitional-metal oxides, including binary and mixed oxides, had great potential to be alternative catalysts with high activity and stability for ORR [12,13]. Liang et al. reported that the rGO supported Co_3O_4 nano-crystals was a high-performance catalyst for both ORR and oxygen evolution reaction (OER) [14]. Similarly, the $\text{Cu}_2\text{O}/\text{rGO}$ composite also exhibited remarkable electrocatalytic activity for ORR in alkaline fuel cells [15]. It is believed that the metal oxides, such as titanium oxide, tungsten oxide, molybdenum oxide, etc., could be adopted as independent electro-catalysts for ORR [16]. But, in fact, each kind of metal oxide has some drawbacks for practical applications. More efforts are being taken to develop high efficiency non-precious transitional metal oxide based catalysts for ORR.

Chromium oxides, Cr_2O_3 , a trivalent chromium (Cr(III)) oxide, is an important industrial material that has been adopted as abrading agents and pigments [17]. Cr_2O_3 is chemically stable and insoluble in both acidic and alkaline medium [18]. But the conductivity of Cr_2O_3 is rather weak, which inhibits its application in electrochemical research fields. Graphene, an ultra thin two-dimensional carbonaceous material, has attracted tremendous attention in the scientific community due to its excellent electronic conductivity and mechanical properties [19]. Graphene supported non-precious metal oxides based catalysts have showed great promise for ORR [20–22]. Reduced graphene oxide (rGO) supported metal oxide for fuel cells had been investigated [23–25]. The rGO based materials also adopted in sensors with the aim of enhancing conductivity [26–29]. But the structure and catalytic characteristics of graphene supported Cr_2O_3 have never been reported. In this work, we synthesized the rGO supported nano- Cr_2O_3 ($\text{Cr}_2\text{O}_3/\text{rGO}$) catalysts for ORR by the pyrolysis of the graphene oxide supported chromium-urea coordination compound. The obtained $\text{Cr}_2\text{O}_3/\text{rGO}$ showed surprisingly high catalytic activity and electrochemical stability for ORR in alkaline electrolyte. The peak current intensity was above three times higher than that of Pt/C catalyst. To the best of our knowledge, this is the first report on the rGO supported chromium oxide as catalyst for ORR. This research explores a new kind of high-performance, low-cost, and rich sources catalyst for ORR.

Experimental

Preparation of $\text{Cr}_2\text{O}_3/\text{rGO}$ catalyst

The graphene oxide was prepared from graphite by using improved Hummer's method that had been reported

previously [30]. All the other chemicals are analytical reagents and used as received without any further treatment.

1 g $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 50 ml absolute ethanol and 16.0 ml graphene oxide (GO) (3 mg/ml in DI water). And the mixture was ultra-sonicated 30 min. Then saturated urea/ethanol solution was added dropwise into the solution at 75–80 °C with violent stirring until the final mole ratio of Cr^{3+} to urea reached 1:6 [31]. Finally we got the mixture of GO and green precipitation of Cr-urea coordination compound. The mixture was filtered and the solid was dried at 80 °C. The obtained metal coordination had also been adopted as catalysts for ORR [32]. The coordination compound was moved into a quartz boat and heated in nitrogen atmosphere with the flowing rate of 0.5 L/min at 600 °C for 2 h with a quartz tube furnace. The hybrid of $\text{Cr}_2\text{O}_3/\text{rGO}$ was obtained. And the loading content of Cr_2O_3 was 3.9 mg per 1 mg rGO. The heating temperature was determined according to the thermal gravimetric and differential scanning calorimetry (TG-DSC) tests using Perkin Elmer STA6000. The TG-DSC test results are shown in Fig. 1. It was clearly observed that there were no peaks appeared anymore when the temperature above 500 °C, which meant that the structure of the obtained material reached a stable state. To ensure the material's structure, 600 °C was adopted to prepare the catalyst.

Structure and electrochemical tests

The morphology of the as-prepared catalyst, the selected area electron diffraction (SAED) pattern, the energy-dispersive X-ray spectroscopy (EDS), and the elemental mapping were obtained by using a Tecnai 20 U-TWIN transmission electron microscope (TEM) and a Hitachi (S-4800) scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy analyzer. Powder X-ray diffraction (XRD) test was performed on a Bruker D8-advance diffractometer using Cu-K α 1 radiation. The data were collected between the diffraction angles (2 theta) of 10° and 80°. Based on the XRD test results, the corresponding cell parameters of Cr_2O_3 were calculated by using the Jade software. X-ray photoelectron spectroscopy (XPS) tests were conducted using a Perkin Elmer PHI5300 spectrometer with a Mg K α source.

The electro-chemical performances tests were conducted by using a CHI 760D electrochemical workstation (CHI Inc.,

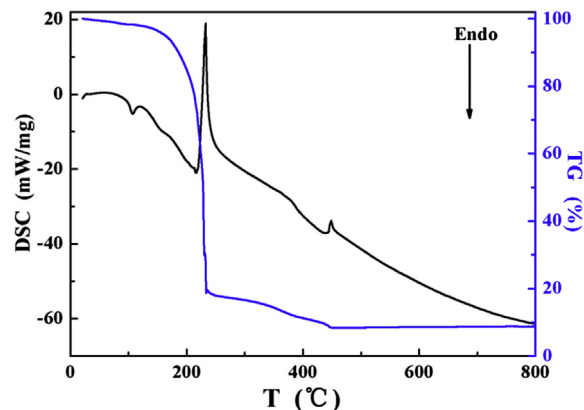


Fig. 1 – TG-DSC tests of Cr-urea coordination compound.

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