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Reduced Graphene Oxide Supported CoO/MnO_2 Electrocatalysts from Layered Double Hydroxides for Oxygen Reduction Reaction

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ABSTRACT

It is of great interest to explore non-precious metal electrocatalysts with high catalytic activity, complete tolerance, and long durability for oxygen reduction reaction (ORR) and then to move the alkaline fuel cell technology closer to commercialization. Here, we fabricated reduced graphene oxide (RGO) supported CoO/MnO_2 nanocomposites from Co, Mn-containing layered double hydroxides (Co_3Mn-CO_3-LDH) by calcination at 550 °C under nitrogen atmosphere. Also, we systemically investigated the electrocatalytic performance of CoO/MnO_2/RGO composite for ORR in 0.1 M KOH. Because of synergistic effect between CoO and MnO_2, the CoO/MnO_2/RGO nanocomposite exhibits excellent ORR catalytic activity with a 4-electron transfer pathway, an onset potential of 0.95 V *vs.* RHE, a half-wave potential of 0.76 V *vs.* RHE, and cathodic current density of 4.2 $mA\,cm^{-2}$ at 0.5 V *vs.* RHE at a rotating speed of 1600 rpm, which are comparable with the commercial Pt/C catalyst. Furthermore, the catalyst has complete tolerance to methanol and longer durability compared to the Pt/C catalyst under the investigated conditions. The CoO/MnO_2/RGO nanocomposite is one of promising non-precious metal electrocatalysts for alkaline membrane/membraneless fuel cells.

1. Introduction

It is of great interest and importance to develop non-precious metal electrocatalysts with high activity and long durability for oxygen reduction reaction (ORR) in fuel cells and metal-air batteries [1–3]. The ORR performance mainly depends on electrode materials and electrolytes [4,5]. Pt-based materials have been considered as the best ones for the ORR with four-electron reaction pathway and relatively low overpotential. Yet high cost, low tolerance to methanol and CO, and limited stability seriously hinder the commercialization of fuel cells. Recently, some multicomponent non-precious metal electrocatalysts have been fabricated, e.g. Mn_3O_4-CoO/CNT [6], Co_3O_4/Co_2MnO_4 [7], and N-doped graphene/CNT/Co_3O_4 [8], which have exhibited far higher ORR catalytic performance compared to the corresponding single electrocatalytic active component because of synergistic effects between electrocatalytic active components. Mixed transition-metal oxides (MTMOs) as one kind of multicomponent catalysts have shown promising catalytic performance for ORR with desirable activity, low cost, and environmental friendliness [9,10]. Yet it is still a big challenge to reasonably design and controllably synthesize MTMOs with higher ORR catalytic performance.

Layered double hydroxides (LDH) is one kind of anionic clays with a general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\bullet yH_2O$ (abbreviated as $M^{2+}{}_{1-x/x}M^{3+}$-A-LDH), where M^{2+} and M^{3+} represent di- and trivalent metal cations in the brucite-like host sheets with atomic level dispersion, A^{n-} anions located in the interlayer region between the host sheets further improve dispersion of metal cations in the adjacent sheets [11]. LDHs are desired precursors to prepare the MTMOs by calcination of the LDHs at certain temperature because of tuneable chemical compositions in the host sheets, adjustable charge density and exchangeable anions in the interlayer regions [12,13]. Therefore, it is possible to obtain MTMOs with high catalytic performance towards ORR based on the LDH precursors.

In this work, we developed a reduced graphene oxide (RGO) supported MTMOs (CoO/MnO_2/RGO) electrocatalyst by calcination of Co_3Mn-CO_3-LDH/RGO under nitrogen atmosphere and investigated the electrocatalytic performance (activity, selectivity, and durability) towards ORR in alkaline medium. Here are three considerations: (1) CoO and MnO_2 are separately one kind of non-precious-metal electrocatalysts with highly electrocatalytic

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performance towards ORR in alkaline media [6,14,15]; (2) Co_3Mn-CO_3-LDH precursor can be easily produced by one-step coprecipitation method and be thermally decomposed to MTMOs [7,16]; (3) RGO is a favourable electrocatalysts-support with high electrical conductivity [17,18]. Based on the synergistic effects, therefore, it is possible to prepare CoO/MnO_2/RGO electrocatalyst from Co_3Mn-CO_3-LDH with enhanced catalytic performance compared to each active component.

2. Experimental

2.1. Chemicals

All the chemicals were A.R. grade and used as received without further purification.

2.2. Synthesis of CoO/MnO_2/RGO electrocatalyst

Firstly, Co_3Mn-CO_3-LDH/RGO precursor was prepared by one-step coprecipitation method. Typically, 4.3655 g $Co(NO_3)_2 \cdot 6H_2O$ (15 mmol), 1.7895 g 50 wt% $Mn(NO_3)_2 \cdot 4H_2O$ solution (5 mmol) and extra 50 mL water were added into the suspension resulting from dispersion of 0.7000 g exfoliated graphite oxide in 100 mL water by ultrasound for 200 min. Here graphite oxide was prepared by a modified Hummers method as reported in ref. [19]. Then the resulting suspension was vigorously stirred for 1 h. Subsequently, an alkaline solution containing of 0.21 mol/L NaOH and 0.066 mol/L Na_2CO_3 was added to the above suspension at a slow addition rate of 200 mL/h under vigorous stirring until pH = 9 at 25 °C and then the suspension was aged at 40 °C under vigorous stirring for another 24 h. The Co_3Mn-CO_3-LDH/RGO precursor was collected after washing with water five times and dried at 60 °C overnight. Finally, CoO/MnO_2/RGO electrocatalyst was obtained after calcination of the LDH precursor at 550 °C under nitrogen at a ramp rate of 5 °C/min for 4 h.

In comparison, RGO, CoO/RGO, and MnO_2/RGO were prepared following the similar way as described for CoO/MnO_2/RGO: without addition of salts for RGO and without addition of Mn$(NO_3)_2$ or $Co(NO_3)_2$ for CoO/RGO or MnO_2/RGO, respectively. Details of the synthesis are seen in Supplementary Information.

2.3. Characterizations

Powder X-ray diffraction (PXRD) patterns were collected on a Shimadzu XRD-6000 X-ray diffractometer with a scanning rate of 10°/2θ min^{-1} using Cu-Kα (λ = 0.15046 nm) radiation at 40 kV and 30 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, a resolution of 0.19 nm) were carried out on a JEOL JEM-2010 electron microscope at 200 kV. Species for TEM and HRTEM were covered with an additional coating to reduce magnetism. X-ray photoelectron spectroscopy (XPS) was measured on VG ESCALAB 2201 XL spectrometer.

2.4. Electrochemical test

All the electrochemical measurements were carried out on a potentiostat (ChenHua Instruments Co.) in a standard three-electrode cell with a glassy carbon disc (GC, 0.07 cm^2), a Pt wire and a saturated calomel electrode (0.99 V *vs.* RHE in 0.1 M KOH at 25 °C) as the working electrode, the counter electrode, and the reference electrode, respectively. All the potential values in this work are present with the reversible hydrogen electrode (RHE). Prior to catalyst deposition, the working electrode was polished with γ-alumina powder (5A) and then washed ultrasonically in water and ethanol for a few minutes, respectively. The catalyst ink was prepared by dispersing 5.3 mg catalyst powder (for example, CoO/MnO_2/RGO) in 1500 μL ethanol solution containing 250 μL Nafion (5 wt% in mixture of lower aliphatic alcohols and water, DuPont) in a ultrasound bath for 30 min. 4 μL of the catalyst ink was deposited on the pre-treated GC electrode surface. An aqueous solution of 0.1 M KOH (pH = 12.97) was used as an electrolyte. Before the electrochemical measurements, Ar or O_2 was bubbled for 30 min to ensure saturation. 50 scans of cyclic voltammetry under Ar and 20 scans under O_2 were recorded to clean the electrode surface and detect the onset potential. A linear-sweep voltammetry was recorded by scanning the disc potential *vs.* RHE at 5 mV s^{-1} at six rotating speeds (625, 900, 1225, 1600, 2025, and 2500 rpm).

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows PXRD patterns of Co_3Mn-CO_3-LDH/RGO (the precursor) and CoO/MnO_2/RGO (the calcinated product). For Co_3Mn-LDH/RGO, one observes a series of the characteristic *hkl* Bragg reflections of Co_3Mn-CO_3-LDH structure (marked in the graph) with a typical basal spacing of 0.76 nm [7,16]. Interestingly, no characteristic peak of RGO located at 24.5°/2θ [20] is observed, possibly because of the growth of Co_3Mn-CO_3-LDH on the graphene effectively preventing from the stacked sheets of graphene [21]. Here, it is worthy to noting that the exfoliated GO is reduced to RGO under the experimental conditions [20]. For CoO/MnO_2/RGO, the three diffraction peaks at 2θ = 36.53°, 42.60° and 61.47° correspond to (1 1 1), (2 0 0) and (2 2 0) reflections of

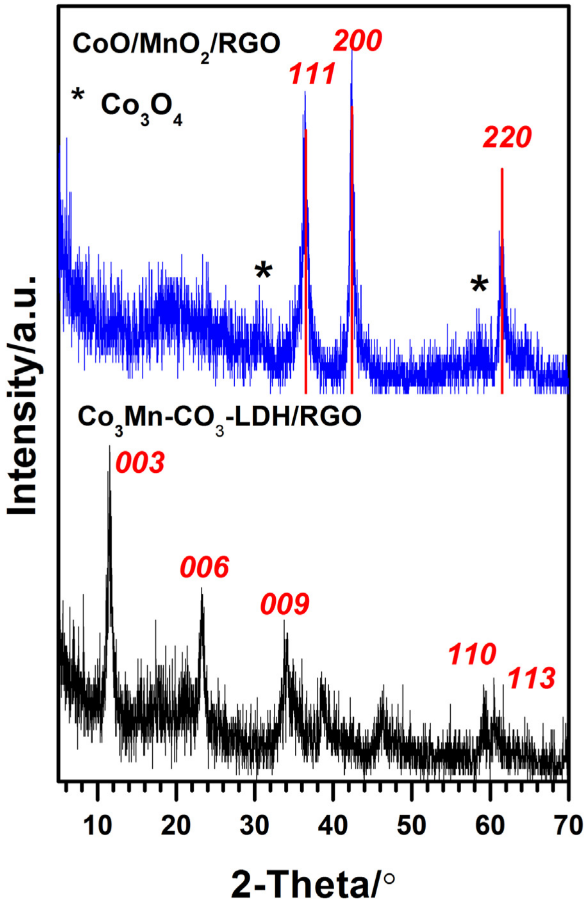

Fig. 1. Powder XRD patterns of the prepared samples: Co_3Mn-CO_3-LDH/RGO and CoO/MnO_2/RGO.