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Readily fabricated NiCo alloy-metal oxide-carbon black hybrid catalysts for the oxygen reduction reactions in the alkaline media

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ABSTRACT

Highly efficient, cost-effective and environmental-friendly electrocatalysts play a crucial role in oxygen reduction reaction (ORR) for fuel cells and metal-air batteries. Herein, a series of hybrids comprising of NiCo alloy, metal oxides and carbon black were readily prepared by a one-pot pyrolysis approach and employed as efficient ORR electrocatalysts in the alkaline media. Different amounts of Ketjen Black EC 300J (EC) with a large mesoporous area and exceptional electrical conductivity were directly added to synthesize the hybrids. Among the hybrids tested, the NC-MMO-EC-3 (where NC stands for NiCo alloy and MMO for mixed metal oxides) with an appropriate amount of EC displayed the best ORR electrochemical activity. The enhanced activity of the NC-MMO-EC-3 could be attributed to the conductivity improved by EC, the high dispersion of MMO and NC on EC support, and the beneficial interaction among those three components.

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Introduction

In recent years, the harvest of renewable energy has driven increasing demands on energy storage and conversion (e.g., fuel cells, metal-air batteries, and water splitting) owing to the exhaustion of fossil fuels and associated environmental pollution and global warming [1,2]. The oxygen reduction reaction (ORR) is currently regarded as a crucial but sluggish process for the above technologies, so that development of effective electrocatalysts to accelerate the ORR process has been attracting worldwide attention and interest [3–7]. To date, satisfactory ORR performance could be achieved over the state-of-the-art precious-metal catalysts such as Pt and

its alloys [8–11], but the high cost, scarce availability and poor stability will inevitably hamper their applications on large scale. Therefore, substantial and ever-increasing efforts have been devoted to fabricating highly efficient, cost-effective and environment-friendly catalysts for the ORR process. For instance, various kinds of non-precious electrocatalysts for ORR have been constructed and utilized in the alkaline media, such as transition metal oxides [5,12–14], carbonaceous materials [15–18] and inorganic-organic composites [19–22].

Among the above-mentioned promising alternatives to noble-metal-based ORR catalysts, perovskite oxides with a general formula of ABO_3 have drawn particular interest due to the merits of low cost, rich abundance, attractive

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electrochemical performance and exceptional stability in the alkaline environment [14,23–28]. Moreover, the excellent intrinsic reactivity of perovskite oxides in ORR which is strongly correlated to the σ^* -antibonding (e_g) orbital occupancy close to unity and the extent of B-site transition-metal–oxygen covalency was demonstrated [29,30]. Recently, A-site ordered Mn-containing double perovskite oxides have shown outstanding catalytic activities towards ORR. Chen et al. [13] found that the layered $\text{PrBaMn}_2\text{O}_{5+\delta}$ (H-PBM) obtained by annealing pristine $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ in H_2 remarkably enhanced the ORR activity, ascribing to the introduction of additional oxygen vacancies, and the facile incorporation of oxygen into layered H-PBM. Luo et al. [31] reported that the cation-ordered $\text{PrBa}_{0.85}\text{Ca}_{0.15}\text{MnFeO}_{5+\delta}$ double perovskite oxide exhibited the best electrocatalytic activity and excellent stability for ORR among the Ca, Fe–co-doped double perovskite oxides. They also prepared an Ag-(Pr, Ba) $_{0.95}\text{Mn}_2\text{O}_{5+\delta}$ composite catalyst with favorable ORR activity and durability in the alkaline solution, which should be attributed to the rationally designed nano-architectures, surface oxygen vacancies, A-site deficiency, and dual phase catalyst systems [12]. Nevertheless, these materials usually required an additional hydrogen reduction process to transfer the simple perovskite oxides to the A-site ordered layered perovskite oxides and the combination of carbonaceous materials to overcome the limitation of the low electrical conductivity and limited surface area of perovskite oxides for ORR.

Alternatively, in this work, we report the synthesis of NiCo alloy–metal oxide–carbon black hybrid catalysts by a one-pot pyrolysis route using praseodymium nitrate, barium nitrate, manganese acetate, nickel nitrate, cobalt nitrate and carbon black as precursors under Ar atmosphere. In the initial planning, we were targeting for the metal-layered perovskite oxide-carbon nanohybrids, using the carbon black as a reducing agent to transfer the simple Ni/Co-doped perovskite oxide into the metal-layered double perovskite oxide composite by simultaneous in-situ exsolution of NiCo alloy in one step, and as an electron-conducting carrier to support the exsolved metal (i.e. NiCo alloy) and metal oxides (i.e. layered perovskite oxide). Compared with the two-step method (including synthesis of simple perovskite oxide (Step 1) and the reduction of simple perovskite oxide to the layered double perovskite oxide by hydrogen (Step 2), this one-pot method could avoid use of hydrogen, and complex and energy consumption step, while obtain the metal-layered perovskite oxide–carbon nanohybrid more easily. Unfortunately, the direct contact of higher amounts of carbon with perovskite oxide in one-pot pyrolysis process damaged the crystal phase to result in the oxide composite. Nevertheless, it did not affect the electrocatalytic performance for ORR. Therefore, the effects of the amount of carbon black on the physicochemical and structural properties of the NiCo alloy–metal oxide–carbon black hybrid catalysts, ORR activities and durability in the alkaline solution were further investigated in details. This work demonstrates a facile one-pot fabrication of the NiCo alloy–metal oxide–carbon black hybrid catalysts, and also provides an insight into the contributing aspects of the ORR process behind such hybrid catalysts.

Experimental

Preparation of catalysts

The NiCo alloy–metal oxide–carbon black hybrid electrocatalysts containing different amounts of Ketjen Black EC 300J (abbreviated as EC) were prepared by a one-pot pyrolysis route. Typically, stoichiometric amounts of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($n(\text{Pr}^{3+}): n(\text{Ba}^{2+}): n(\text{Mn}^{2+}): n(\text{Ni}^{2+}): n(\text{Co}^{2+}) = 9.5: 9.5: 18: 1: 1$) were firstly dissolved in 150 mL distilled water to form an aqueous solution. Subsequently, glycine as a complexing agent was added into the above aqueous solution at the molar ratio of glycine to the total metal ions of 2:1. After vigorous stirring for 1 h, EC was added into the above-formed nitrate & acetate–glycine complex. The weight ratio of the EC to the total obtained NiCo alloy (denoted as NC) and metal oxides was theoretically varied as 1:1, 2:1, 3:1 and 4:1, respectively. The suspension was mixed and continuously stirred for 1 h, water evaporated at 100 °C, dried at 120 °C, and then solidified at 300 °C for 1 h in ambient air. The obtained black solid precursors were finally calcined at 1050 °C for 5 h under Ar atmosphere with a heating rate of 5 °C min^{-1} . For clarity, the obtained hybrid containing the least amount of EC (where the weight ratio of the EC to the total obtained NC and metal oxide (i.e. the layered perovskite oxide $\text{Pr}_{0.95}\text{Ba}_{0.95}\text{Mn}_{1.8}\text{O}_{5+\delta}$, abbreviated as LPBMO) was theoretically equal to 1) was denoted as NC-LPBMO-EC-1. Compared with the NC-LPBMO-EC-1 hybrid, the rest hybrids containing different compositions of metal oxides (where the weight ratio of the EC to the total obtained NC and the metal oxides (mostly made of mixture of Pr_2O_3 , BaO and MnO, abbreviated as MMO) was theoretically equal to 2, 3 and 4) were denoted as NC-MMO-EC-X (X = 2, 3 and 4), respectively.

Characterization of catalysts

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Brunauer-Emmett-Teller (BET) surface area and porous structure were measured using an ASAP 2460 apparatus from the nitrogen adsorption and desorption isotherms at liquid nitrogen temperature (77 K). Raman measurements were conducted on a Renishaw inVia Reflex Raman Microscope and Spectrometer. The morphologies were observed with a field emission scanning electron microscope (FESEM, JSM-7800F & TEAM Octane Plus with an accelerating voltage of 5 kV), a transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2100 & X-Max80 with an accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed under an ultrahigh vacuum using an ESCALAB 250Xi spectrometer with Al $K\alpha$ radiation (1486.6 eV) and a multichannel detector. All the collected binding energies were calibrated by using the C1s peak at 284.6 eV as the reference with an uncertainty of $\pm 0.2 \text{ eV}$.

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