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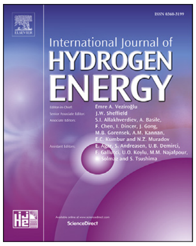

Molybdenum-containing amorphous metal oxide catalysts for oxygen evolution reaction

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ABSTRACT

Amorphous mixed metal oxide oxygen evolution reaction catalysts containing Mo, Co, and Fe were synthesized by a low energy required photochemical metal-organic deposition (PMOD) process. The composition of the ternary amorphous metal oxide catalyst film can be precisely controlled as to its precursor solution, and there was no phase segregation observed. The electrocatalytic activity of this ternary catalyst system was carefully mapped out as contour plots to illustrate the kinetics parameters such as onset potential, Tafel slope as well as the overall performance, i.e. the potential required to reach the benchmark current density. In this study, adding higher valence state material, Mo, into catalytic active metal oxides, such as CoO_x and FeO_x, to form $Co_{50}Mo_{50}O_x$ and $Fe_{50}Mo_{50}O_x$ could highly increase the catalyst stability. More importantly, the ternary metal oxide $Fe_{10}Co_{25}Mo_{65}O_x$ showed the advantage of the relatively low onset potential (1.52 V), low Tafel slope (~31 mV/dec), lowest potential to reach the benchmark 1 mA/cm^2 and a better stability for the oxygen evolution reaction in Mo/Co/Fe system.

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Introduction

In the water splitting reaction, the major overpotential comes from the oxygen evolution reaction, OER. As a result, many studies have been focused on the new catalyst material development. The criteria for a suitable catalyst material that can be used in large scale are: (1) cheap and abundant on earth, (2) generate high current at low overpotential, and (3) stable for a long period of time [1]. Among the highly active OER catalysts, metal oxide is generally more stable, such as IrO_2 [2], RuO_2 [3] and spinel solids [4], as well as some amorphous metal oxides which are getting much more attention these days [1,5–7]. For example, the amorphous iron oxide (a-Fe_2O_3) has been demonstrated as a better OER catalyst comparing to the crystalline α-Fe_2O_3 [1]. Other earth abundant amorphous metal oxides, such as a-CoO_x, a-NiO_x, and a-FeO_x [1] also showed their catalytic ability towards OER. However, some of the most active metal oxide OER catalysts still suffer from the stability issue by nature [8]. Luckily, mixing the catalytic active metal oxide with other material to form a multi-component OER catalyst might relieve this situation.

In the previous studies, researchers found that mixing different redox-active metal oxides, such as the mid-to-late first-row transition metals, $Ni_{50}Co_{50}O_x$ [5], $Fe_{40}Ni_{60}O_x$ [5], $Ni_{50}Co_{50}O_x$ [9], $NiCo_2O_4$ [10], $Ni_xFe_{3-x}O_x$ [11], and $NiFeO_x$ [12,13], could play synergistic roles in buffering the multi-electron processes for achieving the efficient water oxidation reaction. Furthermore, when there was a higher oxidation state metal ion, such as iron (Fe), in the active CoO_x and NiO_x catalysts, the overall catalytic ability can be enhanced because iron might stabilize higher oxidation levels, lower the amount

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of hydroxyl groups at the surface, and even lower the Tafel slopes [5,9,12]. More recently, the introduction of the redox-inert Lewis acidic metal ions, such as Al^{3+}, Mg^{2+}, and Ca^{2+} also showed an enhanced OER performance, and this was possibly by facilitating deprotonation of a reactive water molecule [14]. In the Ni–, Fe–, Co – mixed oxide catalysts, it was found that Al^{3+} can serve as an effective promoter for catalytic activity of the mixed-metal oxides by resembling the role of Ca^{2+} in biological oxygen evolution process, i.e. photosystem II [14–17]. Lately, the high-valence metal tungsten (W) incorporated with alloyed oxide also demonstrated an outstanding OER performance because the electronic structure of 3 d metals can be modulated by W^{6+} to form the optimized adsorption energy for OER [18]. Similar for the high-valence Mo^{6+} hosted ternary metal (oxy)hydroxide, it was reported that it could produce 10 mA/cm^2 at ~1.51 V and could maintain a current density of 10 mA/cm^2 for ~40 h without obvious degradation [19].

From these studies, it hints that a better OER performance could be expected when we formulate the catalyst with (1) catalytic active component such as Ni or Co and (2) high valence redox-inert Lewis acidic metal such as Fe or Mo. Based on this formulation concept, several crystalline OER catalysts such as $CoMoO_4$, $FeMoO_4$, $NiMoO_4$, $CoFe_2O_4$ were studied and demonstrated the relatively high catalytic activity [13,20–24]. However, the possible composition of crystalline material was limited by the lattice structures and some studies have shown that the mix amorphous metal oxides could have a better performance than the crystalline ones [5,25].

As a result, in order to search the best material composition, the low temperature photochemical metal-organic deposition (PMOD) process was selected. By this method, several highly active OER catalysts such as FeO_x, Fe/Co/Ni oxides, and Al/Fe/Ni oxides have been demonstrated [5,26]. In this study, based on the formulating concept, the high valence Lewis acidic metal Mo was introduced to the catalytic active amorphous Co–Fe oxide, forming Mo–Co–Fe ternary oxide system in the ambient environment. The introducing of Mo highly increased the stability of binary and ternary metal oxides. The ternary $Fe_{10}Co_{25}Mo_{65}O_x$ demonstrated a low onset potential, Tafel slope, and an outstanding stability.

Materials and method

Electrocatalysts preparation

The amorphous OER catalyst preparation flow chart is illustrated in Fig. 1. Molybdenum (IV) 2-ethylhexanoate, cobalt (II) 2-ethylhexanoate, and iron (III) 2-ethylhexanoate serving as the metal organic sources were purchased from Strem chemicals, Aldrich chemistry, and Alfa Aeser, respectively, and used without further purification. The precursors were prepared by dissolving these metal organic compounds in n-hexane resulting in 15 wt% metal 2-ehtylhexanoate solutions. The solution was well-mixed by sonication for 3 min and spin-coated at 3000 rpm for 1 min on ITO substrates. A 6 W UV lamp (UVGL-58, UVP, USA) with 254 nm wavelength was used to irradiate the precursor film for 36 h. After the photochemical process, the samples were then heated at 100 °C for 1 h to remove the final trace organic parts and form as the amorphous metal oxides. Fourier transform infrared spectroscopy (FTS-3500, Bio-Rad) was used to confirm the elimination of the carboxylate ligand, i.e. the organic parts from the precursor, in the thin film.

Electrochemical measurement

The electrochemical measurements were conducted by a potentiostat (PGSTAT302 N, Autolab) coupling with a standard three-electrode cell. The Ag/AgCl in 3 M KCl was used as the reference electrode while a 2.5 cm × 2.5 cm Pt mesh (100 mesh) served as the counter electrode. The PMOD prepared amorphous metal oxides on ITO glass was the working electrode. Oxygen evolution reaction was carried under 0.1 M NaOH solution with pH 12.9. In this study, all the potentials were converted into the reversible hydrogen electrode (RHE) with considering the solution ohmic resistance compensation, iR_s, as shown in Eq. (1). The R_s was obtained from the electrochemical impedance spectroscopy (EIS) with scanning frequency from 0.1 Hz to 100 kHz and amplitude of 0.01 V at 0.7 V vs. Ag/AgCl. Cyclic voltammetry (CV) was run between 0 V and 1 V vs. Ag/AgCl with scan rate at 10 mV/s and linear sweep voltammetry (LSV) was conducted from 0.3 V to 1 V vs. Ag/AgCl at the scan rate of 5 mV/s. The chronopotentiometry was performed to demonstrate the long-term stability of the mixed amorphous metal oxide electrodes at a constant current density of 1 mA/cm^2.

$$E_{RHE} = E + 0.21 + 0.059 \times pH - iR_s \qquad (1)$$

Characterizations

Dual beam focused ion beam microscopy (DB-FIB) (FEI Quanta 3D FEG, USA) was used for the characterization of the morphology and the energy dispersive spectrometer (EDS) was used for the element composition analysis. The amorphous property of the samples was further confirmed by the

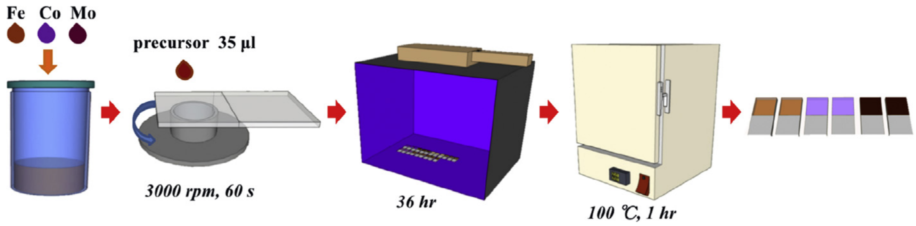

Fig. 1 – The illustration of the PMOD process for preparing amorphous metal oxide OER catalysts.

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