Bifunctional electrocatalysts based on Fe-Co oxide nanoparticles supported on multiwalled carbon nanotubes for ORR/OER reactions in alkaline media

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Abstract:

Herein, we present a facile strategy of synthesis of Fe-Co mixed metal oxide nanoparticles supported on multiwalled carbon nanotubes (MWCNTs) as an effective bifunctional catalyst able to drive the oxygen evolution reaction and oxygen reduction reaction. The mixed oxide 13.5 wt.% $Fe_{0.5}Co_{0.5}$/MWCNT shows highest bifunctional activity and a substantial long-term stability in alkaline electrolyte. For comparison, Co and Fe oxides supported on multiwalled carbon nanotubes (Co_3O_4/MWCNT and Fe_3O_4/MWCNT) with different metal oxide loading are also investigated. Moreover, the investigations of the electrocatalytic performance of samples with different metal ratios as well as their phase composition changes are presented in detail.

Keywords: electrocatalysts, Fe-Co catalyst, multiwalled carbon nanotubes.

1. Introduction

The fabrication of highly active and low cost bifunctional oxygen electrodes is a bottleneck in wide-spread commercialization of renewable energy technologies such as unitized regenerative fuel cells, metal-air batteries and electrolyzers. The main challenge is to achieve high performance and selectivity of both the oxygen evolution (OER) and oxygen reduction (ORR) reactions. Numerous approaches have tried to create bifunctional oxygen electrocatalysts including *in situ* formation of systems able to catalyze both reactions [1,2] as well as combination of precious metal- (like Pt and IrO_2) [3] or non-precious metal compounds (like perovskite and Fe-N doped carbon) [4]. The combination of ORR and OER catalysts into a composite aims at producing materials that can retain their individual properties or even slightly alter their activity due to a synergetic effect. However, to date most bifunctional catalytic systems suffer from lack of activity of one of the reactions leading to a wide gap between overpotentials for the OER and ORR, along with low stability or high cost. Here, we present a comparatively simple strategy to produce Fe-Co mixed metal oxide nanoparticles supported on multi-walled carbon nanotubes as an effective bifunctional catalyst for both the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). For comparison, monometallic Co and Fe oxides supported on multiwalled carbon nanotubes (CoO/MWCNT and Fe_3O_4/MWCNT) with different metal oxide loading have shown lower bifunctional activity in OER and ORR reactions as compared with the mixed Fe-Co oxide catalyst.

2. Experimental

MWCNTs were synthesized by CVD technique based on ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. The tubes were oxidized by boiling in concentrated nitric acid (denoted as MWCNT-Ox-NA) [5]. Co, Fe and Co-Fe-containing samples were prepared by impregnation of MWCNTs with the aqueous solutions of Co(II) Fe(III) salts followed by calcination under inert atmosphere. The samples with various concentrations of Co, Fe and Fe-Co of different ratios were investigated.

3. Results and discussion

The structure of monometallic Fe and Co as well as bimetallic Fe-Co- containing MWCNTs was investigated by TEM as presented in Figure 1.

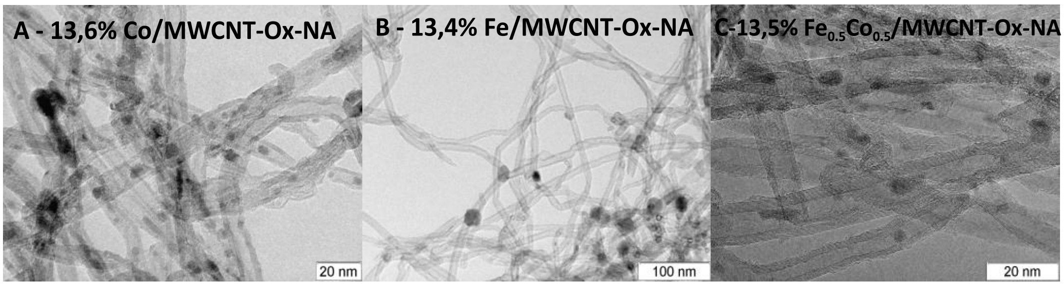

Figure 1. TEM images of of A - 13.6 wt. % Co/MWCNT-Ox-NA; B - 13.4 wt. % Fe/MWCNT-Ox-NA; C - 13.5 wt. % $Fe_{0.5}Co_{0.5}$/MWCNT-Ox-NA.

Samples with 13.6% of Co and 13.5% of Fe-Co (1:1) mainly contain small metal-oxide particles (3-5 nm) within the channels of MWCNTs. The sample with 13.4% Fe contains the metal oxide nanoparticles inside the channels of MWCNTs with an average diameter of 5 nm, as well as particles located on the surface of tubes of average diameters 20-30 nm.

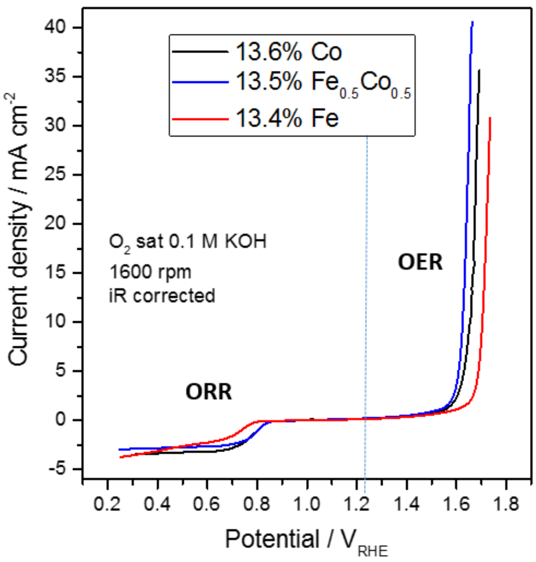

Figure 2. Polarization curves (iR compensated) of 13.6 wt. % Co/MWCNT-Ox-NA; 13.4 wt. % Fe/MWCNT-Ox-NA and 13.5 wt. % $Fe_{0.5}Co_{0.5}$/MWCNT-Ox-NA recorded in O_2 - saturated 0.1M KOH at a scan rate of 5 mV s^{-1} and 1600 rpm electrode rotation.

The bifunctional activity of the electrocatalysts was evaluated in a standard 3-electrode electrochemical cell in 0.1 M KOH solution. The mixed oxide sample with 13.5 wt.% of FeCo (1:1) has shown the best electrocatalytic performance in both ORR and OER (Fig. 2). The difference between potentials (the bifunctional parameter) measured at current densities of -1 mA cm^{-2} for ORR and 10 mA cm^{-2} for OER in oxygen-saturated 0.1 M KOH solution under rotation at 1600 rpm did not exceed 820 mV, a value which is smaller than for many other non-precious bifunctional catalyst known in literature. Mono-metallic oxide catalysts (Fe or Co) have shown lower activity in both OER and ORR in contrast to the bimetallic (Fe-Co) oxide catalysts. Increase of metal concentration did not get the activity improvement. Moreover, the most active samples possessed good bifunctional long-term stability that was measured chronopotentiometrically using a gas diffusion working electrode.

4. Conclusions

A comparatively simple procedure is introduced for designing bifunctional electrocatalysts for the oxygen evolution reaction and the oxygen reduction reaction in alkaline electrolytes. The low overpotential difference between ORR and OER as well as long-term durability show great promise of bimetallic samples as developed in this work to be applied in the real bifunctional oxygen electrodes used in regenerative fuel cells and Zn-air batteries.

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