



Moderate oxophilic CoFe in carbon nanofiber for the oxygen evolution reaction in anion exchange membrane water electrolysis

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ABSTRACT

We propose corrosion-resistant carbon-coated $\text{Co}_{0.9}\text{Fe}_{0.1}$ alloy nanoparticles as highly active and durable electrocatalysts for the oxygen evolution reaction (OER) in anion exchange membrane water electrolysis (AEMWE). In the presence of 10% Fe atoms, the oxophilicity of Co metal is modulated in a direction to facilitate OH^- adsorption on Co^{3+} ; thus, $\text{Co}_{0.9}\text{Fe}_{0.1}$ -carbon nanofiber (CNF) can exhibit smaller overpotentials than other metal ratios in $\text{Co}_{1-x}\text{Fe}_x$ -CNF. Additionally, we confirm catalytic degradation from the oxidation of the carbon layer, which is triggered by defects in the carbon originating from Fe during the pyrolysis step. The $\text{Co}_{0.9}\text{Fe}_{0.1}$ metal is further optimized by increasing graphitization to simultaneously achieve superior activity and durability for application on AEMWE. This work not only demonstrates the role of Fe in Co metal for controlling the proper oxophilicity but also shows the importance of graphitized carbon as a catalyst support for stable water oxidation.

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1. Introduction

The development of active, cost-effective, and long-lasting catalysts for water electrolyzers is a challenging task for H_2 production from renewable energy [1,2]. The first bottleneck in commercializing electrolyzers is the sluggish oxygen evolution reaction (OER), where the expensive noble metal catalyst is needed to produce a meaningful current density [3,4]. Considering both performance and economic efficiency, earth-abundant first row (3d) transition metals are urgently required to substitute for the noble metal. In particular, Co-based materials have received considerable attention due to their promising activity and stability in alkaline media as well as their relatively inexpensive price [5–7]. Previous computational studies show that the OER activity is dependent on the binding energy of the OER intermediates (M-OH_{ads} , M-O_{ads} , and $\text{M-OOH}_{\text{ads}}$) [8,9]. The combination of Fe, Co and Ni has been investigated with respect to the tunable adsorption energies of their

intermediates with modulated electronic properties [10–13]. However, experimental evidence of their tunable nature is still lacking due to insufficient advanced spectroscopic tools. The second bottleneck for electrocatalytic water splitting is the instability of electrode materials [3]. Although carbon is widely used as a support material in electrochemistry due to its large surface area, high electrical conductivity, tunable graphitization and pore structure [14–16], it is still vulnerable under corrosive conditions, especially in alkaline media [17,18]. The reported mechanistic origin of carbon corrosion suggests that oxygenated functional groups are formed on the carbon surface above $0.207 \text{ V}_{\text{RHE}}$, then mostly converted into carbon dioxide (CO_2) [19–22]. Unstable support induces agglomeration or detachment of active metal particles, resulting in an activity drop [23–25]. To solve this problem, a number of groups have focused on graphitized carbon to be free from carbon corrosion [26,27]. However, these materials still cannot prevent irreversible carbon oxidation at high potentials since the susceptible site of carbon oxidation is not fully understood.

Herein, Fe incorporated Co nanoparticles embedded in carbon nanofibers ($\text{Co}_{1-x}\text{Fe}_x$ -CNFs) are synthesized via electrospinning [28–38] and compared in terms of their OER activity, durability along the Fe content. The combination of classical electrochemical methods (Tafel slopes) with advanced spectroscopy (*in situ* XANES) demonstrates the role of Fe in modulating the oxophilicity of Co.

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