

Co-based nanospinels as earth-abundant catalysts for ORR and OER in alkaline medium

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One of the challenges to overcome for the large-scale development of regenerative fuel cells concerns the development of highly stable reversible air electrodes which are able to catalyze efficiently both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Recently, numerous studies were dedicated to the activation of ORR and/or OER in alkaline medium on heteroatom-doped graphene supported transition metal oxides (TMO) [1-4]. Identification of the active sites, understanding of reaction mechanisms, and that of the interaction between oxide nanoparticles and carbon-based substrate in this type of catalyst are of upmost interest in improving catalysts design. The development of such electrode materials, free from precious group metals and capable of decreasing overpotentials in fuel cells and water electrolyzer, requires stable supporting and conducting substrates in order to deposit low metal oxide loadings (ca. 30 wt.%). This challenging approach led us to prepare Co3O4materials on graphene-based composites more stable than the commonly used electrode support (Vulcan carbon). Co3O4 particles synthesized from a solvothermal method were thereby deposited onto reduced graphene oxide (RGO) and N-doped reduced graphene oxide (NRGO) prepared from the Hummers method (Figure 1A). The structural properties and surface composition of the different materials characterized by X-ray induced photoelectron spectroscopy measurements were combined to cyclic voltammetry experiments for revealing the charge transfer from cobalt to nitrogen, which greatly affects the charge acceptance of the surface Co atoms. Changes in electron density on surface Co atoms are responsible for enhancing catalytic performances of the composite catalysts towards the ORR and OER. For the first time, a work focused on the investigation of oxide-carbon heterointerface, allows highlighting the importance of nitrogen doping in the graphene substrate. With only 30 wt. % of metal oxide, the difference between the charge and discharge voltages (ΔE) due to the ORR and OER is 810 mV, as shown in Figure 1B.



Figure 1: A) Facile two-step synthesis of $Co_3O_4/NRGO$ material B) Polarization curves obtained with $Co_3O_4/NRGO$ electrode in an O_2 -saturated electrolyte (0.1 mol $L^{-1}KOH$) at 1600 rpm.

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