

Engineering Atomically Dispersed and Accessible Active Moieties in Fe-N-Cs

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Abstract

Fe-N-C electrocatalysts composed of atomically dispersed Fe atom coordinated with nitrogen (FeN_x) and embedded in the porous carbon framework are emerging as a reliable alternative to noble metal electrocatalysts for oxygen reduction reaction (ORR). This substitution is pivotal in overcoming the main obstacle in the commercial implementation of fuel cells. However, the selective activity of Fe-N-Cs can be ensured by meticulous engineering of the active-site structure where the key focus lies in populating and making the active moieties accessible while maintaining a single-atom configuration. In this context, a novel strategy has been adopted to construct Fe-N-Cs with atomically dispersed active centers i.e. FeN_x and nitrogen-based moieties in the micro-mesoporous environment that facilitates mass transportation. Different from the traditional route of hard templating [1]–[4], this time, silica nanoparticles of ca. 70 nm were inhouse grown via the typical Stöber process and then functionalized with Fe through amino-based ligands namely 3-aminopropyltriethoxysilane (APTES) and N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (EDTMS). Hence the achieved materials i.e. SAFe (silica functionalized with Fe via APTES) and SEFe (silica functionalized with Fe via EDTMS) simultaneously acted as the template to induce porosity and Fe source that can concurrently restrict the undesired coalesce of Fe into metallic nanoparticles. Subsequently, SEFe and SAFe were mixed with an organic precursor of carbon and nitrogen (methylimidazole) using the wet impregnation method. The obtained dried sludge was then subjected to atmosphere-control pyrolysis for 1 h at 900 °C to launch the basic architecture of Fe-N-C (SEFe_M_P1 and SAFe_M_P1) followed by etching with an acidic solution to get rid of the silica template leaving behind the tri-modal porous structure (SEFe_M_P1A and SAFe_M_P1A). Finally, another pyrolysis treatment similar to the previous one was given in a slightly reducing atmosphere to atomically disperse the active moieties in the defect-rich graphitic matrix of carbon (SEFe_M_P1AP2 and SAFe_M_P1AP2). Using a rotating ring disk electrode (RRDE) technique ORR the electrocatalytic performance of the samples achieved at each step was elucidated under acidic and alkaline conditions and it was observed that performance markedly boosted as the synthesis design proceeded. The samples achieved at the final stages SEFe_P1AP2 and SAFe_P1AP2 demonstrated the best performance due to the highest surface area and well-dispersed porosity as confirmed through Brunauer-Emmett-Teller (BET) analysis. X-ray diffraction (XRD) and High-resolution transmission electron microscopy (HR-TEM) indicated a high defects-rich structure with the absence of Fe nanoparticles, giving an impression of atomically dispersed FeN_x moieties. Moreover, X-ray photoelectron spectroscopy (XPS) confirmed the presence of surface active species of interest in a suitable combination to carry out tetra-electronic and 2X2 ORR. Owing such remarkable attributes, the samples SEFe_M_P1AP2 and SAFe_M_P1AP2 outperformed the other counterparts by delivering the highest onset potentials of 950 mV and 965 mV, respectively in alkaline media while 772 and 808 mV, respectively in acidic media with a clear tetra-electronic ORR pathway. Given their best ORR activities in the half-cell measurements, full device tests were carried out after configuring the alkaline exchange membrane fuel cells (AEMFC). The recorded open circuit voltage (OCV) in the AEMFC was 0.825 V for SAFe_M_P1AP2 and 0.845 V for SEFe_M_P1AP2 while the peak power densities came out to be 219 mW cm⁻² (at 500 mA cm⁻²) and 103 mW cm⁻² (at 230 mA cm⁻²) for the aforementioned electrocatalysts, respectively.

References:

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