

New synthetic strategies for obtaining atomically dispersed Fe-N-C electrocatalysts for oxygen reduction reaction

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Abstract

Single-atom electrocatalysts owing to their exceptional aptitude for bridging the homogenous and heterogeneous electrocatalysis together are glossing in the paradigm of oxygen reduction reaction (ORR) which is the key bottleneck in the commercial realization of fuel cell technology. Fe-N-C holding atomically distributed active moieties (Fe-N_x and nitrogen-based sites) within the porous framework of carbon is emerging as a potential candidate to replace platinum group metals (PGMs). However, the fine control of the iron coordination and distribution is a critical issue to mitigate performance restrictions. In this frame, a novel strategy to engineer the Fe-N-C electrocatalyst is herein reported, with well-dispersed porosity, essential to uplift the mass transportation, and homogeneously distributed active moieties at the atomic level. Differently from the previously published methods where nitrogen-rich organic molecules, metal salts, as well as silica sacrificial template to induce micro-meso porosity, were mixed through impregnation or mechanochemical methods [1]–[4], here, silica nanoparticles (NPs) were exploited as functional support to distribute iron single centers through suitable nitrogen-based ligands. The experimental design first involved the growth of silica NPs through the Stöber process (diameter = 70 ± 7 nm) which were then surface functionalized with two amino-based ligands, namely 3-aminopropyltriethoxysilane (APTES) and N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (EDTMS). The exposed amino groups were further used to coordinate iron(III) centers on the silica surface (SiO₂-APTES-Fe and SiO₂-EDTMS-Fe). The electrocatalysts were later prepared by mixing the materials with nicarbazine (used as nitrogen and carbon precursor) and pyrolyzing (P1) under Ar flux at 900 °C. The obtained black powder was then washed with hydrofluoric acid (P1A) to remove the silica NPs leaving the porous architecture behind. As a final step, the acid-washed samples were again given a pyrolysis treatment at 900 °C under a slightly reducing environment of N₂/H₂ (P1AP2). The electrocatalytic activity of the samples achieved at each step was elucidated in both acidic and alkaline media. The performance tends to improve after each preparation step, where the samples at the finalized stage, i.e. SiO₂-APTES-Fe_P1AP2 and SiO₂-EDTMS-Fe_P1AP2 demonstrated the exceptional tetra-electronic electro-reduction of oxygen in both electrolytic conditions. Besides, SiO₂-APTES-Fe_P1AP2 realized the exceptional onset potential (E_{onset}) of 0.85 V and 0.99 V vs RHE in 0.5 M H₂SO₄ and 0.1 M KOH, respectively, while the E_{onset} of SiO₂-EDTMS-Fe_P1AP2 delivered of 0.87 V and 0.98 V vs RHE in 0.5 M H₂SO₄ and 0.1 M KOH, respectively. Alkaline medium exhibited relatively higher electrokinetics as the half-wave potential (E_{1/2}) for SiO₂-APTES-Fe_P1AP2 and SiO₂-EDTMS-Fe_P1AP2 came out to be 0.91 V and 0.89 V vs RHE, respectively, in 0.1 M KOH whereas, in the acidic medium, the values of E_{1/2} endured at 0.76 V and 0.75 V vs RHE, respectively, for the aforementioned electrocatalysts. The adopted synthesis pathway confirmed the remarkable performance of the derived electrocatalysts owing to atomically dispersed active sites within the porous carbon platform, making them a viable alternative to PGMs for sustainable energy applications.

References:

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