Magnesium-mediated synthesis of mesoporous FeNC fuel cell catalysts enabled by a zinc adeninate framework

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Iron single atoms coordinated in nitrogen doped carbon materials (Fe-NC) represent the most promising alternative to scarce and expensive Platinum-group-metal catalysts in the cathode of proton-exchange membrane fuel cells, where the oxygen reduction reaction (ORR) takes place.[1] However, their controlled synthesis and stability for practical applications remains challenging due to the stochastic processes happening simultaneously during the synthetic thermal treatments of organic/inorganic mixtures, such as precursor decomposition, formation of a conductive support, metal migration and metal aggregation, which doesn't enable control over active site density and structure.[2]

Decoupling the high-temperature pyrolysis from the metal coordination can circumvent the disadvantages of the high temperature pyrolysis.[3] This approach leverages Lewis acids salts that interact efficiently with nitrogen based molecules to retain a square-planar M-N_x coordination, and the subsequent cation exchange at low temperatures, overcoming metal aggregation and carbothermal reduction.[4] This approach has been explored with organic building blocks,[5] metal-organic frameworks,[6] microporous polymers,[7] or resins.[8] However, the field still faces the trade-off between active site number, and active site utilization. The zeolitic-imidazole framework 8 (ZIF-8), built from of Zn^{2+} coordinated to methylimidazole (Mim) ligands,[9,10] enables a high density of active sites, yet their microporous nature results in poor active site accessibility of <10%,[11] while Mg^{2+} templating agents enable a high mesopore volume and high active site utilizations of >50%, yet relatively low metal loadings (~ 1 wt%).[12] Furthermore, the Mg^{2+} mediated pyrolysis of ZIF-8 results in the early loss of Zn^{2+}-N coordination of the parent ZIF due to the release of HCl from $MgCl_2.6H_2O$, which protonates MIm ligands, resulting still in highly mesoporous materials with low active site density and moderate performance.[13]

In this work, we address this dilemma by employing a zinc adeninate hydrogen-bonded framework (ZAF) containing Zn^{2+}-MIm moieties as precursor for the Mg^{2+} mediated high temperature pyrolysis. The presence of adenine in the framework with basic nitrogen sites preserves more efficiently the Zn^{2+}-MIm coordination during pyrolysis, leading to a higher Zn-N_x and Mg-N_x active site density in a mesoporous framework with specific surface area >2600 m^2g^{-1}. Therefore, the low temperature cation exchange results in highly efficient Fe-NC ORR catalysts in acidic media that display a kinetic mass activity of 22.6 A g^{-1} at 0.8V_{RHE} in 0.1M $HClO_4$, and state-of-the-art performance in a proton-exchange membrane fuel cell.

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