World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:17, No:08, 2023

Single Cu–N_4 Sites Enable Atomic Fe Clusters with High-Performance Oxygen Reduction Reaction

Authors : Shuwen Wu, Zhi LI

Abstract : Atomically dispersed Fe–N_4 catalysts are proven as promising alternatives to commercial Pt/C for the oxygen reduction reaction. Most reported Fe–N_4 catalysts suffer from inferior O–O bond-breaking capability due to superoxo-like O_2 adsorption, though the isolated dual-atomic metal sites strategy is extensively adopted. Atomic Fe clusters hold greater promise for promoting O–O bond cleavage by forming peroxo-like O_2 adsorption. However, the excessively strong binding strength between Fe clusters and oxygenated intermediates sacrifices the activity. Here, we first report a Fex/Cu–N@CF catalyst with atomic Fe clusters functionalized by adjacent single Cu–N_4 sites anchoring on a porous carbon nanofiber membrane. The theoretical calculation indicates that the single Cu–N_4 sites can modulate the electronic configuration of Fe clusters to reduce O_2* protonation reaction free energy, which ultimately enhances the electrocatalytic performance. Particularly, the Cu–N_4 sites can increase the overlaps between the d orbitals of Fe and p orbitals of O to accelerate O–O cleavage in OOH*. As a result, this unique atomic catalyst exhibits a half potential (E1/2) of 0.944 V in an alkaline medium exceeding that of commercial Pt/C, whereas acidic performance E1/2 = 0.815 V is comparable to Pt/C. This work shows the great potential of single atoms for improvements in atomic cluster catalysts.

Keywords : Hierarchical porous fibers, atomic Fe clusters, Cu single atoms, oxygen reduction reaction; O-O bond cleavage
Conference Title : ICRAHC 2023 : International Conference on Recent Advances in Homogeneous Catalysis
Conference Location : Montreal, Canada
Conference Dates : August 03-04, 2023