

Department of Chemistry, IIT Madras
Ph.D. Seminar II

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Venue: CB310
Time: 3:00 pm

Nickel and Copper Based Electrocatalysts and Nitrogen-Doped Carbon Support for Oxygen Reduction Reaction in the Energy Conversion Systems

Oxygen reduction reaction (ORR) occur at the cathode of fuel cells and metal-air batteries but it is sluggish in comparison to the reaction occurring at the anode. Hence ORR contributes to large overpotential during operation of the fuel cells and meal-air batteries.^{1,2} Therefore, efforts are underway to develop the efficient electrocatalyst for the facile kinetics of ORR. Although platinum (Pt) and Pt-based materials are the most efficient ORR catalysts, the high cost, poor durability, and scarcity of Pt have been shown as the primary issues to large-scale commercial applications. Considerable efforts have been devoted to find the alternative catalysts and reducing the platinum loading.^{3,4} Transition metal-based macrocycles compounds containing MN₄ structure is explored for ORR, where M is a central metal atom, which is coordinated to four nitrogen atoms that are part of a stable cyclic aromatic structure. In addition, heteroatom doped carbon supports were developed to counter the corrosion of supports and to decrease the platinum loading in PEMFCs.

Inspired by the MN₄ type active site in metal macrocycles, we have synthesized the copper (II)-based 1D coordination polymer (Cu-1D-CP). The crystal structure of Cu-1D-CP consists of two independent di- μ -hydroxido-bis(2,2'-bipyridine) Copper(II) binuclear moieties, which are connected to the central copper(Cu) unit via two carbonate bridges with different bridging modes, resulting to a pentanuclear unit. This Cu-1D-CP, supported on ketjenblack carbon (KBC), was used as an oxygen reduction catalyst in alkaline medium. The density functional theory (DFT) was employed to study the oxygen adsorption properties on mononuclear and binuclear moieties in Cu-1D-CP.⁵

In chapter 2, a Cu-based metal-organic framework (MOF) with 4, 4'-bipyridine ligand has been synthesized on activated KBC support and demonstrated for ORR in alkaline medium. The catalyst was synthesized via both in-situ and ex-situ route to compare the electrochemical activity and found that in-situ immobilization of Cu-MOF on carbon surface to exhibit best ORR activity. Further, the MOF was pyrolyzed at 800° C and ORR behavior has been studied for both pyrolyzed and unpyrolysed catalysts. As pyrolysis embeds the active site on the KBC surface, the overpotential towards ORR decreases significantly.

Further, in chapter 3, various N-heterocyclic ligands coordinated Ni-complexes were synthesized using 1, 10 phenanthroline, 2, 2'-bipyridine, and benzimidazole ligands. Their crystal structure was analyzed by single-crystal XRD. These complexes were covalently connected to the activated KBC to improve the ORR activity. Since active site structure is clearly known in this case, oxygen adsorption energy was calculated for each of the complexes using the DFT to understand the reason behind the ORR activity shown by these complexes.


In the process of developing an excellent active and stable Pt/C electrocatalyst for ORR in fuel cells, metals are supported on heteroatom doped mesoporous carbon derived from natural resources. In this context, tamarind seeds are utilized to derive high surface area porous carbon for N heteroatom doping and followed by Pt deposition for oxygen reduction reaction (ORR) catalyst. The synthesized catalyst, i.e., Pt/N-TC-1000, exhibits a peak power density of 800 mW cm⁻² in a H₂-O₂ fuel cell, at 70 °C and ambient pressure, whereas commercial Pt/C exhibited 490 mW cm⁻². This enhancement in the power density is attributed to the highly porous and corrosion resistive nature of carbon support in addition to effective anchoring of the Pt nanoparticles on the N functional groups present on the carbon.⁶

References

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Guide


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