Abstract

Oxygen reduction reaction (ORR) is considered as one of the essential reactions widely involved in energy storage and chemical production, such as fuel cells (FCs), metal–air batteries (MAB) and H_2O_2 production. The ORR plays a crucial role in numerous energy conversion technologies. Still, the intrinsically sluggish nature, due to the high overpotential of ORR limits the energy-conversion devices' overall efficiency. Therefore, an appropriate electrocatalyst is required that can effectively influence the kinetics of reactions and direct ORR towards more efficient pathways. Platinum (Pt) is the best catalyst among its contemporary pure metals, possessing all requisite properties conducive to efficient ORR. However, the sluggish kinetics of ORR demands higher loading of the Pt catalyst, and being a noble metal itself, the meager availability of Pt, CO poisoning, durability issues and consequently, its high cost emerge as additional barriers. Most current ORR electrocatalytic research investigations are focused on ways to lower the costs by reducing cathode Pt loadings or replacing Pt with other non-Pt metals while maintaining the high performance.

Palladium (Pd)-based electrocatalysts have attracted much attention due to their analogous physical structures, including an *fcc* crystal structure and a similar atomic radius, comparable performance, and lower price than Pt. Therefore, developing high-efficiency and cost-effective Pd-based electrocatalysts are highly desirable and necessary to significantly improve the ORR performance. While ORR electrocatalysts are projected to have the qualities of low cost, high activity, and high stability synchronously, they still do not meet all the requirements for implementation in FCs. Several alternatives have been developed to further enhance the electrocatalytic performance of Pd-based electrocatalysts to achieve this. Incorporating non-noble transition metals in the Pd lattice reduces the Pd usage and modifies the electronic structure and induces lattice strain. The modulated electronic structure causes a downward shift of the *d*-band center, reducing the binding strength of adsorbed intermediates and significantly enhancing ORR activity. This approach not only enhances catalytic performance but also reduces the cost of Pd-based nanoparticles (NPs). According to the perspectives above, the present study focuses on developing and assessing durable, highly active, and economical Pd-based electrocatalysts for ORR.

Chapter 1 is the introductory chapter that deals with a general aspect, a brief overview of FCs, and the importance of ORR and the mechanisms of ORR. The need for cathode catalysts and their synthesis methods for catalytic application are described. The present chapter includes an overview of the history, background and use of catalysts in ORR. A systematic review of Pt-free metal NPs, Pd-based NPs and their alloys for electrocatalytic ORR are discussed. Additionally, the role of carbon support for instance Vulcan XC-72R and graphene and their advantages as support materials are also explored with a literature review. At the end of this chapter, the final objectives of the thesis are highlighted. **Chapter 2** summarizes the details of the materials used in the work. All the experimental methods for the synthesis of hybrid NPs and the analysis procedures to evaluate the electrocatalytic activities are described herein. Furthermore, the present chapter also contains the details of the different analytical techniques and tools used to characterize the synthesized hybrid system. In **Chapter 3**, we have discussed the synthesis of $Pd_3Ag_{0.5}Cu_{0.5}/C$, via a typical solvothermal route. Different analytical and spectroscopic techniques characterized the synthesized hybrid electrocatalysts. The catalytic activities were evaluated towards ORR in alkaline media by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) analysis. The synthesis and characterization of Pd_2CuCo/C and their ORR activities are presented in **Chapter 4**. In this section, Pd_2CuCo/C electrocatalysts were synthesized via a facile one step solvothermal process and studied their electrocatalytic activity for ORR in 0.1M KOH. Introducing Cu and Co into the Pd lattice creates ligand and strain effects and tunes the electronic structure. **Chapter 5** deals with the synthesis of the PdFeCu electrocatalyst on Vulcan carbon support. The NPs were efficient electrocatalysts for ORR and had excellent stability and durability. The PdFeCu NPs are uniformly embedded on the carbon support and resulting in a strong metallic support interaction (SMSI). This SMSI prevents agglomeration of the PdFeCu NPs, providing more active sites and enhancing the intrinsic activity of the PdFeCu/C hybrid electrocatalysts. **Chapter 6** covers the synthesis of $PdCuO_x$ NPs with a small amount of Pd loading and supported on graphene support. The ORR activity was significantly enhanced for $PdCuO_x/C$ compared to CuO_x/C, $PdCuO_x$ and CuO_x. The inclusion of graphene support has excellent electrical conductivity and facilitates relatively uniform dispersion of metal components on the surfaces. Finally, **Chapter 7** describes the overall conclusions and summary of the major findings of the experiments with the significance of the work. The future avenues of the present investigation are also highlighted in this chapter.