

Chapter 7: Conclusions and Future Scopes

This chapter provides a comprehensive synopsis of the significant findings made during the investigation. This study aimed to synthesize, perform physicochemical characterization and perform electrocatalytic analyses of carbon supported Pd-based electrocatalysts towards ORR in alkaline media. This chapter also includes future perspectives that could be investigated with current research to comprehend the underlying molecular mechanisms and theoretical understanding of ORR of the synthesized catalysts and their relevance to additional fuel cell (FC) related reactions and the commercial applications that were not addressed in this work.

7.1. Conclusions

Chapters 1 and 2 highlighted a general introduction to the thesis work along with objectives and experimental conditions/methodologies employed in the thesis work, respectively.

Chapter 3: This chapter covers the synthesis, physicochemical characterization and electrocatalytic performance of carbon-supported PdM¹M² (M¹/M²= Ag, Cu) NPs of different compositions towards ORR. Among them, the Pd₃Ag_{0.5}Cu_{0.5}/C hybrid was highly active and more stable toward ORR than the other reported counterparts. Introducing Cu and Ag in Pd lattice modifies its electronic environment, imparts lattice strain and eventually improves the active sites for ORR. It is observed that generating a new environment while introducing Ag and Cu in the Pd lattice can enhance the ORR process. The enhanced ORR catalytic activities and durability of the developed materials could result from the robust anchoring of Pd₃Ag_{0.5}Cu_{0.5} to the carbon substrate and reduce the electrochemical degradation of carbon. It is expected that this work held great promise for developing high-performance and non-Pt catalysts in practical applications of FCs. The following are some of the most important conclusions identified in Chapter 3.

- Pd₃Ag_{0.5}Cu_{0.5}/C displays superior performance in terms of its high current density (-5.84 mAcm⁻²), early onset potential ($E_{\text{onset}} = 0.94\text{V vs. RHE}$) and half-wave potential ($E_{1/2} = 0.80\text{V vs. RHE}$) than the other synthesized electrocatalysts.
- The Pd₃Ag_{0.5}Cu_{0.5}/C exhibits excellent long-term stability and durability than commercial Pt/C.

- The presence of Ag and Cu metals tune the electronic structure of Pd due to the synergetic effect among them and thus promoting the ORR process.
- The morphology of the Pd₃Ag_{0.5}Cu_{0.5}/C after a long hour CA remains intact, indicating the robustness of the catalysts.

Chapter 4: In this chapter, we focused on synthesizing Pd₂CuCo/C, PdCu/C and PdCo/C and carried out their physicochemical characterizations and electrochemical analysis on ORR activity. The evaluation of the electrocatalytic activity of these catalysts infers that Pd₂CuCo/C displays remarkable performance among them. The excellent electrocatalytic performances of the Pd₂CuCo/C hybrid were assumed owing to the homogeneous dispersion over the carbon support that provided a large surface area and enhanced active sites. Some significant findings elucidated from this chapter are listed below:

- Pd₂CuCo/C showed a current retention of 96% after 6 h stability test, while the Pt/C exhibited a current retention of 72.5%.
- The ORR Tafel plot demonstrated the faster kinetics of Pd₂CuCo/C compared to Pt/C.
- It also demonstrated excellent methanol tolerance compared to the benchmark Pt/C.

Chapter 5: This chapter discusses the synthesis, characterizations and electrochemical evaluation of ORR activity of PdFeCu/C, PdFe/C and PdCu/C. The study found that introducing Cu and Fe into the Pd lattice effectively tunes the electronic structure of the nanomaterial. Additionally, the uniform dispersion of these nanoparticles on the carbon matrix results 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 electrocatalysts. Some of the major conclusions drawn from this chapter are highlighted below:

- The PdFeCu/C exhibits superior ORR activity than PdFe/C and PdCu/C in alkaline electrolytes.

- The PdFeCu/C delivered excellent stability with only 5 mV degradation in $E_{1/2}$, whereas PdFe/C and PdCu/C were 110 mV and 56 mV, respectively, after 10000 redox cycles.
- After 10000 redox cycles, a slight shift in the binding energy in XPS indicates that catalyst degradation was insignificant.

Chapter 6: In this chapter, we have investigated the effect of Pd in boosting the activity of CuO_x/C towards ORR in alkaline electrolytes. PdCuO_x/C electrocatalyst is superior towards ORR compared to its CuO_x/C , PdCuO_x and CuO_x counterparts and it exclusively proceeds through the $4e^-$ reduction pathway, indicating the formation of OH^- as the ORR product. The remarkable activity and durability of the PdCuO_x/C are attributed to the synergistic interaction between PdCuO_x and carbon support. Also, CuO_x tunes the electronic structure of Pd simultaneously to reduce the Pd loading. Following are some key conclusions drawn from this chapter:

- PdCuO_x/C demonstrated enhanced ORR performance with an E_{onset} of 0.86 V vs. RHE and $E_{1/2}$ of 0.72 V vs. RHE compared to the other electrocatalysts.
- It exhibits excellent methanol tolerance, remarkable durability and rapid ORR kinetics.
- Incorporation of Pd in CuO_x/C significantly increases the number of electrochemically active sites and results in higher ECSA than CuO_x/C , PdCuO_x and CuO_x .

7.2. Future Scopes

This thesis represents a comprehensive investigation of Pd-based catalysts supported over carbon for electrocatalytic ORR in alkaline electrolytes. The as-synthesized materials were highly active towards ORR and displayed excellent stability and durability; hence, they would be expected to perform well in energy-conversion-related devices. However, the in-depth mechanism underlying the intrinsic and improved electrocatalytic activity toward ORR on the surface of the catalysts needs further study. The following listed points can be addressed as future perspectives of the current study:

- In depth mechanistic studies of the synthesized electrocatalysts to better understand the ORR mechanism by theoretical studies.
- Detailed analysis of changes in the local structure of Pd/C by incorporating foreign metals by XAS and study the structural changes and switchover of the oxidation states in atomic sites during the ORR process via operando XAS.
- The influence of various modified carbonaceous materials like functionalized carbon can be studied towards ORR.
- The synthesized electrocatalyst can be explored for real life applications of PEMFCs, DMFCs and direct formic acid FCs (DFAFCs).