

NON-PRECIOUS HYBRID METAL OXIDE-BASED ELECTROCATALYSTS FOR ENERGY APPLICATIONS

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Bhugendra Chutia

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Department of Chemical Sciences

School of Sciences

Tezpur University

Napaam, Tezpur - 784028

Assam, India

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Conclusions and Future Prospects

The key findings of the investigated work are precisely summarized in this chapter. The projection of this study involved the synthesis, characterization and electrocatalytic activity analysis of non-noble metal oxides including oxides of Co, Cu, Fe, Mn and Ce towards ORR and OER in alkaline electrolyte. In addition, this chapter comprises the future prospects that may be explored with the present investigations to understand the root-level molecular mechanism of ORR and OER electrocatalysis on the synthesized ECs and their applicability toward the other energy-related reactions and applications, which are not covered in this work.

7.1. Conclusions

The overall study and works illustrated in the thesis stand out as an intensive effort to surpass some of the significant issues allied with the prevailing precious metal-based ECs which are being employed for numerous energy-related technologies such as MABs, PEMFCs, water splitting, etc. MOs and MMOs as EC for ORR/OER demonstrate potential alternatives to the precious metal-based EC and these materials have attracted enormous attention in recent times. In this thesis work, we have designed non-noble metal oxide-based EC for ORR and OER using facile solvothermal and hydrothermal approaches. We studied single MO (Oct- $\text{Co}_3\text{O}_4/\text{C}$ and Sp- $\text{Co}_3\text{O}_4/\text{C}$) as EC for ORR/OER emphasizing on morphological effect on its performance and MMO of the type $\text{M}_x\text{O}_y/\text{CeO}_2/\text{C}$ (M= Fe, Cu, and Mn) highlighting the oxide-oxide interfacial phenomenon on ORR/OER processes. Various analytical techniques such as XRD, Raman spectroscopy, TGA, SEM, STEM, HRTEM, EDX, BET, XPS, etc. have been employed to establish the physicochemical properties and CV, LSV, CA, EIS, ADT, etc. are used to evaluate the electrocatalytic characterization. The key outcome of the inclusive study reveals that all the investigated ECs (Oct- $\text{Co}_3\text{O}_4/\text{C}$, Sp- $\text{Co}_3\text{O}_4/\text{C}$, $\text{CuO}/\text{CeO}_2/\text{C}$, $\text{Fe}_2\text{O}_3/\text{CeO}_2/\text{C}$ and $\alpha\text{-MnO}_2/\text{Mn}_3\text{O}_4/\text{CeO}_2/\text{C}$) have shown outstanding electrocatalytic activity in terms of its specific electrochemical parameters which are comparable to the benchmark Pt/C (for ORR) and RuO_2 (for OER). It is noteworthy that morphology-controlled $\text{Co}_3\text{O}_4/\text{C}$ shows far better ORR/OER electrocatalytic activity than MMO ($\text{CuO}/\text{CeO}_2/\text{C}$, $\text{Fe}_2\text{O}_3/\text{CeO}_2/\text{C}$, and $\alpha\text{-MnO}_2/\text{Mn}_3\text{O}_4/\text{CeO}_2/\text{C}$) being single MO suggesting its enhanced and inherent ORR/OER active properties. Moreover, it exhibited high ECSA and BET surface area availing larger active sites for the reaction processes. Conversely, the

species CuO/C, Fe₂O₃/C and α -MnO₂/Mn₃O₄/C portray less ORR/OER active properties and hence CeO₂ has been incorporated as the promoter to enhance their inherent catalytic properties. The CeO₂-promoted CuO/CeO₂/C, Fe₂O₃/CeO₂/C, and α -MnO₂/Mn₃O₄/CeO₂/C hybrid structures show enhanced ORR/OER demonstrating the oxygen vacancy assisted synergistic effect, random and overlapping structures of the oxide-oxide interface, high ECSA and BET surface area as the root-cause for the catalytic actions. However, Sp-Co₃O₄/C among all other ECs exhibited superior electrocatalytic activity as an ORR/OER bifunctional EC with reference to the electrochemical parameters such as current density, mass activity, reversibility index, half wave potential, kinetics, onset potential, stability, durability etc. The key points of all the chapters are briefly presented as follows-

Chapter 1: The introductory chapter commences with basic insights about the limited reserve and climatical impact of fossil fuel, the importance of alternatives to fossil fuels energy sources, energy converting and storage devices, especially regenerative fuel cells, metal-air batteries etc. along with the different types and the reactions involved in it, focusing mainly on the ORR and OER. Recent trends in the development of Pt-free ECs over a period of time will also be discussed in this chapter. Special emphasis has been given to the TMO-based ECs for ORR and OER. This chapter also includes an extensive literature survey related to the research area based on which the final objectives for the present investigation are established.

Chapter 2: This chapter includes the detailed specifications of the chemicals and reagents used during the experiments. All the experimental procedures, electrocatalysts synthesis methods, principles of the physicochemical characterization techniques, catalysts fabrication and electrochemical characterization procedures were implemented during the entire study.

Chapter 3: In this chapter, we have investigated the electrocatalytic properties of morphology-controlled Co₃O₄ (nanooctahedron and sponge-like) NPs anchored on carbon towards ORR and OER in an alkaline media. For comparison, the electrocatalytic activity of carbon, polycrystalline Co₃O₄/C (synthesized via hydrothermal method), standard Pt/C (20 wt.%) and RuO₂ was also studied. This chapter is divided into two sections depending on the morphology of Co₃O₄, *i.e.*;

carbon supported Co_3O_4 nanooctahedron (Oct- $\text{Co}_3\text{O}_4/\text{C}$) and sponge-like Co_3O_4 (Sp- $\text{Co}_3\text{O}_4/\text{C}$).

In section 3A, we have studied the synthesis of Co_3O_4 nanooctahedron and polycrystalline Co_3O_4 supported on Vulcan XC-72R (Oct- $\text{Co}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$, respectively) via a modified solvothermal method followed by thermal annealing. The major findings pertaining to the work are highlighted below:

- The solvothermal and hydrothermal methodology as illustrated in Chapter 3A encompasses with an effective two step one-pot synthesis approach for designing morphology controlled Co_3O_4 anchored on carbon.
- Oct- $\text{Co}_3\text{O}_4/\text{C}$ exhibited an enhanced bifunctional ORR and OER electrocatalytic performance compared to that of $\text{Co}_3\text{O}_4/\text{C}$, Pt/C and RuO_2 in alkaline medium.
- Oct- $\text{Co}_3\text{O}_4/\text{C}$ exhibited direct “4e⁻” reduction pathway without forming H_2O_2 as intermediate product.
- The Oct- $\text{Co}_3\text{O}_4/\text{C}$ EC exhibits remarkable ORR/OER activity with higher ORR onset potential ($E_{\text{onset}} = 0.89$ V), half-wave potential ($E_{1/2} = 0.68$ V), large limiting current density ($j = -6.38$ mA cm⁻²) and significantly lower overpotential for 10% energy conversion ($\eta_{10} = 0.45$ V).
- The chronoamperometric and accelerated durability test demonstrated superior stability and durability for the catalytic process.
- The superior bifunctional activity can be attributed to the synergistic contribution of high specific surface area (131.3 m² g⁻¹), high ECSA (35.83 m² g⁻¹) and rich oxygen vacancies in the well-defined octahedral crystal symmetry.

In section 3B the synthesis of sponge-like Co_3O_4 NPs supported on Vulcan XC-72R (Sp- $\text{Co}_3\text{O}_4/\text{C}$) was performed with their bifunctional performance towards ORR and OER in alkaline solution. Some significant findings of this chapter are listed as follows:

- The solvothermal method was very successful in designing highly dispersed sponge-like Co_3O_4 NPs over carbon support.
- Sp- $\text{Co}_3\text{O}_4/\text{C}$ proceed via direct “4e⁻” reduction pathway during ORR like that of benchmark Pt/C.

- The Sp-Co₃O₄/C exhibits promising bifunctional ORR/OER activity with ORR onset potential ($E_{\text{onset}} = 0.88$ V vs. RHE), half-wave potential ($E_{1/2} = 0.75$ V), limiting current density ($j = -6.60$ mA cm⁻²), OER onset potential ($E_{\text{onset}} = 1.26$ V), and OER overpotential for 10% energy conversion ($\eta_{10} = 0.38$ V) in 0.1 M KOH.
- It demonstrates a significantly lower reversibility index ($\Delta E = E_{j_{10}} - E_{1/2} = 0.86$ V), comparable to benchmarks Pt/C and RuO₂ ECs.
- The Sp-Co₃O₄/C is efficiently stable up to 6 h and durable up to 10,000 redox cycles towards ORR in alkaline medium which is comparable to the benchmark Pt/C.
- The superior ORR/OER performances of Sp-Co₃O₄/C EC are ascribed to the synergistic contribution of high ECSA (48.33 m² g⁻¹), BET surface area (131.5 m² g⁻¹), the rich interfacial structure of the crystal facets (111), (220) and (311), and the abundant oxygen vacancies in the sponge-like morphology.

Chapter 4: In this chapter, we have studied the effect of CeO₂ in boosting the activity of CuO/C towards ORR in an alkaline media. The CuO/CeO₂/C NPs were synthesized using a solvothermal method and are characterized by various analytical tools. CeO₂/C and CuO/C NPs were also synthesized via the same method for comparison of their electrocatalytic activity with CuO/CeO₂/C NPs. Some of the major findings earmarked in this work are highlighted below:

- CuO/CeO₂/C nanostructure exhibits higher electrocatalytic activity toward ORR compared to that of CeO₂/C CuO/C and the benchmark Pt/C.
- Both CuO/C, and CuO/CeO₂/C proceed via direct “4e⁻” reduction pathway during the ORR process.
- CuO/CeO₂/C possesses a more positive E_{onset} (0.78 V) and $E_{1/2}$ (0.68 V), high limiting current density (-6.14 mA cm⁻² at 1600 rpm) and high mass activity toward ORR.
- It also delivered enhanced ORR stability with 78.7% retention of its initial current after the 6 h of chronoamperometric operation which is superior to that of Pt/C (72.5%).
- The enhanced electrocatalytic activities mainly originate from the boosted electrical conductivity, the adequate O₂ incorporation and transport abilities,

high specific surface area and high ECSA and the synergistic effect between CuO, CeO₂ and carbon in the CuO/CeO₂/C nanostructure.

Chapter 5: In this chapter, we have discussed the synthesis of a robust nanostructured Fe₂O₃/CeO₂ via a solvothermal method, followed by thermal annealing and carbonization. The resultant EC was found to contain abundant surface oxygen vacancies and distinguished oxide-oxide/carbon interfaces, as evident from XPS and TEM results. To explore the promotional and synergistic effects of Fe₂O₃ and CeO₂ on the resultant EC, Fe₂O₃/C and CeO₂/C were also synthesized for comparison of electrocatalytic activities. The major findings derived from this chapter are highlighted below:

- The experimental results and various electrochemical parameters demonstrates that the Fe₂O₃/CeO₂/C acts as a high-performance and stable ORR EC in an alkaline media.
- Taking the advantage of its unique redox property it shows an appreciable positive onset potential (0.81 V), half-wave potential (0.57 V vs. RHE), smaller Tafel slope (68 mV dec⁻¹) as compared to Fe₂O₃/C and higher limiting current density (– 6.05 mA cm⁻²) compared to that of 20 wt.% Pt/C.
- Fe₂O₃/CeO₂/C possesses a faster ORR kinetics than that of Fe₂O₃/C with a lower Tafel slope of 68 mV dec⁻¹.
- It exhibited remarkable stability with 87.5% of current retention during the chronoamperometric test establishing it as a promising EC.
- The higher ORR activity of Fe₂O₃-CeO₂/C is attributed to the efficient charge transport and synergistic properties of the EC resulting in a favourable reduction of O₂ and the adequate diffusion of molecular O₂ into the activated surface of the EC.

Chapter 6: This chapter describes the synthesis of nanohybrids of α-MnO₂/Mn₃O₄ and CeO₂ on carbon (α-MnO₂/Mn₃O₄/CeO₂/C). The resultant EC exhibits remarkable activity and durability for ORR and OER in an alkaline medium. Some of the significant achievement of this work are listed as follows:

- α-MnO₂/Mn₃O₄/CeO₂/C hybrid shows enhanced bifunctional activity toward ORR and OER, superior to that of the benchmark 20 wt.% Pt/C and Pd/C catalysts.

- It displays ORR onset potential of -0.13 V (vs. Ag/AgCl), limiting current density of -6.63 mA cm⁻² (at 1600 rpm), mass-specific current of 47.6 mA mg_{MO}⁻¹ with a lower Tafel slope (921.9 mV dec⁻¹) and an inclusive $4e^-$ transfer involved in ORR. The OER onset potential and current density are 0.58 V (vs. Ag/AgCl) and 8.45 mA cm⁻² (at 0.8 V).
- The unique hybrid structure with oxide-oxide interface in α -MnO₂/Mn₃O₄/CeO₂ is correlated to explain the mechanistic pathway. Multi-state Mn(II/III/IV) and Ce(III/IV) synergistically influence tendering superior activity with enhanced stability.

7.2. Future Prospects

This set of work encompasses a methodical study on noble-metal free metal oxides anchored on carbon for oxygen electrocatalysis in an alkaline medium. The investigated as-synthesized materials were observed to be efficiently active towards oxygen electrocatalysis. However, in-depth molecular mechanism which is responsible for the inherent and enhanced electrocatalytic response toward oxygen electrocatalysis on the ECs surface need further works. The following points may be contemplated as future perspectives of the current study:

- In-depth study and understanding of the ORR and OER mechanism by computational studies.
- The morphology controlled Co₃O₄/C and CeO₂ promoted CuO/C, Fe₂O₃/C and α -MnO₂/Mn₃O₄/C may be explored in neutral medium for microbial fuel cell applications.
- The influence of various carbonaceous materials like graphene, rGO, CNTs, KB *etc.* may be studied towards ORR, and OER.
- The designed ECs may be studied for electrochemical CO₂ reduction reaction.