

Abstract

The deployment of safe, green, and sustainable energy sources is an imminent technological challenge in the 21st century. Among the various energy sources the polymer electrolyte membrane fuel cells (PEMFCs), unitized regenerative fuel cells (URFCs) and metal-air batteries (MABs) are the most promising alternatives for future energy due to its zero carbon tracks, high conversion efficiency and high energy density. However, the sluggish oxygen reduction reaction (ORR) as well as oxygen evolution reaction (OER) and the use of the precious Pt-group metals as electrode catalysts restrict the commercialization of PEMFCs and MABs. Additionally, the lower stability and durability of such electrocatalysts (ECs) in acidic or alkaline media triggers considerable limitations. Consequently, the development of advanced, abundant and cost-effective ECs for ORR and OER is one of the key areas of research in the field of renewable energies. In place of Pt-group metals, designing ECs with transition metal oxides (TMOs) supported on carbonaceous material have emerged as a promising strategy in recent years because of the low cost and high abundance on the earth's crust. Benefitting from the multivalent states, characteristics redox properties, interfacial effect and vacancy defects, TMO-based ECs attain significantly high intrinsic electrocatalytic activity toward ORR and OER in an alkaline medium. Currently, structural engineering of TMOs such as oxygen vacancy, defects and interface modulation, morphology controlled, doping etc. has become the potential and futuristic strategy to tailor the active sites for ORR and OER.

In line with the aforementioned scenario, I focused on the design of non-Pt-group metal oxide-based ECs by enjoying facile and easily scalable approaches for ORR and OER in alkaline medium. The accomplished work that is presented in the thesis is categorically illustrated in seven chapters. A brief overview of the content of the chapters is highlighted below:

Chapter 1 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 URFCs, MABs, etc. along with the different types of 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. Especial 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** includes the detailed specifications of the chemicals used during the experiments. All the experimental procedures, synthetic methods, and physico-chemical and electrochemical characterization techniques adopted during the study are explained elaborately in this section. **In Chapter 3**, we investigated the electrocatalytic properties of morphology-controlled Co_3O_4 (nanooctahedron and sponge-like) nanoparticles (NPs) anchored on carbon towards ORR and OER in an alkaline media. For comparison, the electrocatalytic activity of carbon (C), polycrystalline $\text{Co}_3\text{O}_4/\text{C}$ (synthesized via hydrothermal method), standard Pt/C (20 wt.%) and RuO_2 was also studied. This chapter is divided into two sections (**Section 3A** and **Section 3B**) depending on the morphology of Co_3O_4 , *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 a morphology-controlled 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 electrocatalytic activity of the resultant ECs was explored towards ORR and OER in alkaline media. **Section 3B** describes the synthesis of sponge-like Co_3O_4 NPs supported on Vulcan XC-72R (Sp- $\text{Co}_3\text{O}_4/\text{C}$). The electrochemical activity was studied using the as-synthesized EC which exhibited enhanced and stable bifunctional performance towards ORR and OER in alkaline solution as compared to that of carbon (C), polycrystalline $\text{Co}_3\text{O}_4/\text{C}$, standard Pt/C (20 wt.%) and RuO_2 . **In Chapter 4**, we studied the effect of CeO_2 in boosting the activity of CuO/C towards ORR in an alkaline media. The $\text{CuO}/\text{CeO}_2/\text{C}$ NPs were synthesized using a solvothermal method and are characterized by various analytical tools. CeO_2/C and CuO/C NPs were also synthesized via the same method for comparison of their electrocatalytic activity with $\text{CuO}/\text{CeO}_2/\text{C}$ NPs. **In Chapter 5**, we have discussed the synthesis of a robust nanostructured $\text{Fe}_2\text{O}_3/\text{CeO}_2$ 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 Fe_2O_3 and CeO_2 on the resultant EC, $\text{Fe}_2\text{O}_3/\text{C}$ and CeO_2/C were also synthesized for comparison of electrocatalytic activities. The experimental results and various electrochemical parameters proved that the $\text{Fe}_2\text{O}_3/\text{CeO}_2/\text{C}$ acts as high-performance and oxygen EC toward ORR in an alkaline media. **Chapter 6** describes the synthesis of a

non-precious transition and a post-transition MO comprising nanostructured α -MnO₂/Mn₃O₄ and CeO₂ supported on carbon (α -MnO₂/Mn₃O₄/CeO₂/C). The resultant EC was evaluated for ORR and OER in an alkaline medium. The remarkable activity and durability of the α -MnO₂/Mn₃O₄/CeO₂/C hybrid represent a promising route to replace noble metals and develop low-cost bifunctional electrodes for energy devices. Finally, **Chapter 7** summarizes the major findings of the experiments carried out in due course along with the importance of the work. The future scopes related to the current research topic are also highlighted in this chapter.