Chapter 7

Conclusions and Future Scopes

7.1 Conclusions

This chapter comprises of the major findings and key takeaways from the thesis work. It contains chapter-wise conclusions and provides a comprehensive understanding from the investigations. The primary outline of the thesis work is synthesis, physical characterization, and electrochemical investigation of four non-PGM (hydr)oxides, viz. $Ni(OH)_2$, Co_3O_4, CeO_2, $CoO_x(OH)_y$. In all the chapters, graphene nanoplatelet is used as the conductive support. The influence of heterogeneous interfaces between the component (hydr)oxides towards ORR and OER is studied in detail. Towards the end of the research tenure, some aspects have been identified that could have given more insights into the field. These have been listed as the future scopes towards the end of the chapter. The chapter-wise conclusions are presented in the following bullet points.

Chapter 1: This chapter discusses the importance of clean energy and the role of ORR and OER in fuel cells and water electrolyzers. A detailed survey of literature on the recent advancements and challenges in the application of metal-based electrocatalysts has been presented. Some crucial research gaps in this field were identified and a list of objectives were set to achieve insightful knowledge on these gaps.

Chapter 2: This chapter provides the list of all chemicals and equipment used throughout the thesis work. It also provides detailed descriptions of the experimental setup, methodologies employed to conduct the experiments. It contains brief descriptions of the theories employed to analyze the obtained data.

Chapter 3: This chapter is a systematic study of three non-PGM catalysts of cobalt (Co), nickel (Ni) and cerium (Ce). This study has been sub-divided into two sections, Section 3A and 3B. Section 3A studies the electrochemical affinity of Co_3O_4, $Ni(OH)_2$ and CeO_2 towards ORR and OER while Section 3B studies the electrochemical affinity of Co_3O_4/ CeO_2, $Ni(OH)_2/CeO_2$ and $Co_3O_4/Ni(OH)_2/CeO_2$. The major findings of this chapter are:

- Co_3O_4 exhibits earliest $E_{1/2}$ and n~4. Cobalt-based mixed electrocatalysts to be studied.
- CeO_2 has a very high C_{DL}. It can be employed as catalytic activity booster with Co_3O_4 and $Ni(OH)_2$.

- CeO_2 -based hybrids of the type $MO_x(OH)_y$ where M=Co, Ni can be studied for subsequent chapters.
- Co_3O_4/CeO_2 hybrid is superior in mass specific activity, onset potential for ORR, half-wave potential, stability surpasses that of Pt/C, overpotential for OER, n ~ $4e^-$.
- In-depth study of Co_3O_4/CeO_2/GNP is required to uncover the factors affecting above phenomena.
- CeO_2-based mixed (hydro)oxides of the type $MO/(OH)_x$ where M=Co could be explored for ORR and OER.

Chapter 4: This chapter studies the influence of the oxide-oxide interfaces between Co_3O_4 and CeO_2 in their electrocatalytic activities. The idea was conceived from the observations of the previous chapter where the hybrid Co_3O_4/CeO_2 is seen as a potential candidate for ORR and OER. The major findings of this chapter are:

- The enhanced catalysis could be attributed to the close contact of heterogeneous oxide interfaces of Co_3O_4 and CeO_2.
- The generation of large number of oxygen vacancies in Co_3O_4/CeO_2 creates more active sites.
- This work paves the path for more research in CeO_2-based non-PGM electrocatalysts.

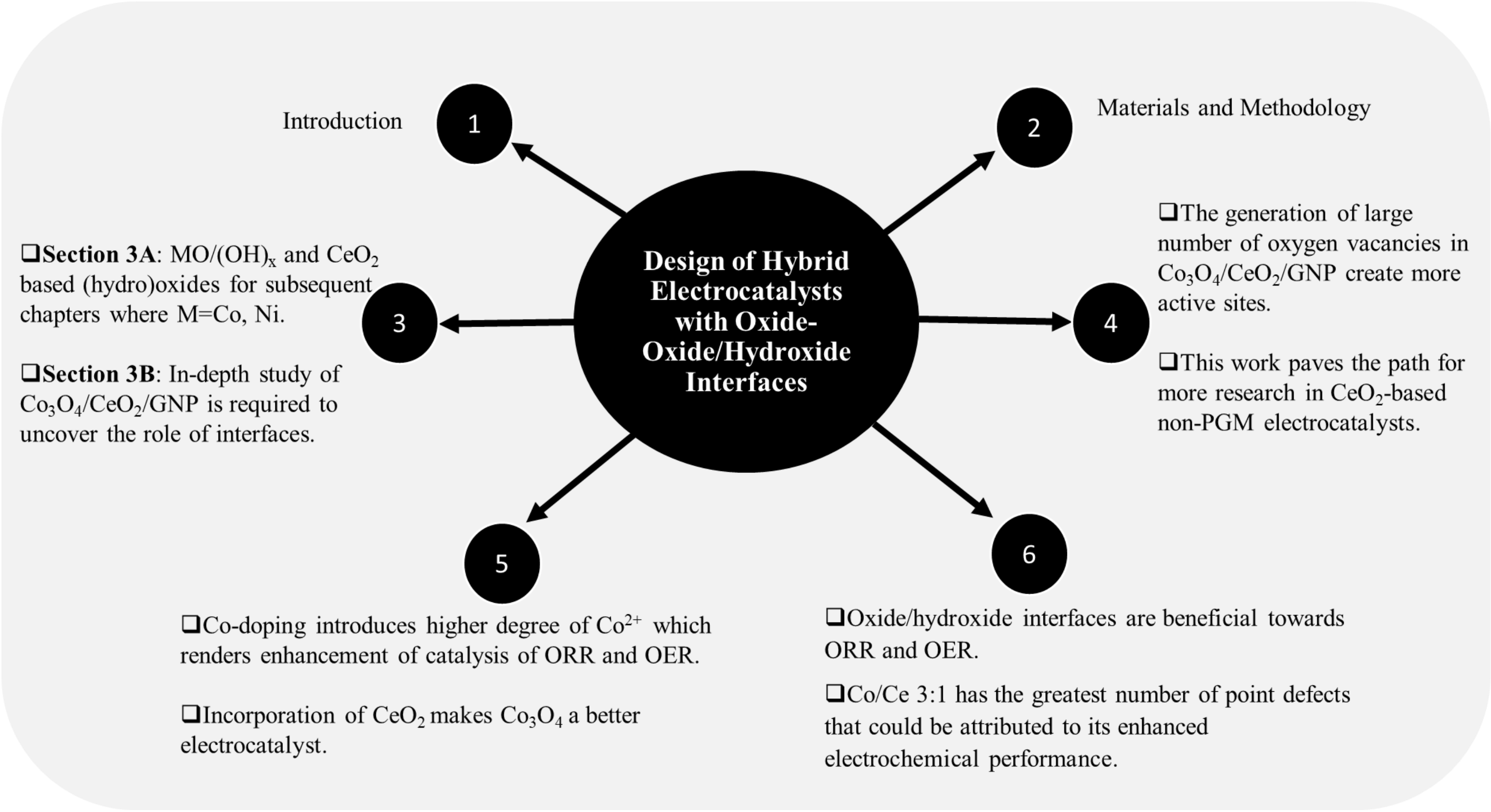
Chapter 5: This chapter studies a slightly modified version of the catalysts studied in the previous chapter. A thermal treatment has been employed to bring about slight changes in the crystallinity and possible doping of cobalt ions into CeO_2 lattice, viz. $Co_3O_4/Co_xCe_{1-x}O_{2-\delta}$. These catalysts were studied for their electrocatalytic affinity towards ORR and OER. The major findings of this chapter are:

- Doping of cobalt ions introduces a higher degree of Co^{2+} which supposedly renders enhancement of catalysis of ORR and OER.
- Integration of CeO_2 with Co_3O_4 makes it a better electrocatalyst.

Chapter 6: This chapter studies the electrocatalytic ability of the hybrid $CoO_x(OH)_y/CeO_2$ towards ORR and OER. The idea for this chapter is conceived from the findings of the previous chapters where CeO_2 integration resulted in enhanced electrocatalysis. The influence of oxide-hydroxide interfaces between $CoO_x(OH)_y$ and CeO_2 is studied here, in addition to varied ratios of Co:Ce. The major findings of this chapter are:

- The hybrid variant with Co:Ce=3:1 exhibits most favorable electrocatalytic parameters owing to its versatile oxide-hydroxide interfaces.
- The hybrid variants with Co:Ce=3:1 and 9:1 exhibit no prominent morphology change in morphology post electrocatalytic cycles. This could be correlated to the minimal change in their $E_{1/2}$.
- Co/Ce 3:1 has the greatest number of point defects (surface oxygen vacancies) as deduced from higher ratio of Co^{2+}:Co^{3+} and Ce^{3+}:Ce^{4+}. This supposedly enhances its electrochemical performance.

A visual summary of the above findings has been presented in the schematic in Figure 7.1.



☐**Section 3A**: MO/(OH)$_x$ and CeO$_2$ based (hydro)oxides for subsequent chapters where M=Co, Ni.

☐**Section 3B**: In-depth study of Co$_3$O$_4$/CeO$_2$/GNP is required to uncover the role of interfaces.

☐The generation of large number of oxygen vacancies in Co$_3$O$_4$/CeO$_2$/GNP create more active sites.

☐This work paves the path for more research in CeO$_2$-based non-PGM electrocatalysts.

☐Co-doping introduces higher degree of Co^{2+} which renders enhancement of catalysis of ORR and OER.

☐Incorporation of CeO$_2$ makes Co$_3$O$_4$ a better electrocatalyst.

☐Oxide/hydroxide interfaces are beneficial towards ORR and OER.

☐Co/Ce 3:1 has the greatest number of point defects that could be attributed to its enhanced electrochemical performance.

Figure 7.1. Schematic summary of chapter-wise experimental findings.

Table 7.1: A summary of all the catalysts synthesized in the thesis work and their catalytic performance indicators like onset potential for ORR ($onset_{ORR}$), half-wave potentials ($E_{1/2}$), limiting current density (j_{lim}), number of electrons transferred for ORR (n) and overpotential for OER (η10).

Chapter	**Catalysts**		**$onset_{ORR}$/V**	**$E_{1/2}$**	**j_{lim} / $mAcm^{-2}$**	**n**	**η10/V**
3A	Co_3O_4/GNP	best	0.85	0.733	3.36	3.91	0.6
	$Ni(OH)_2$/GNP		0.80	0.669	2.79	2.56	0.54
	CeO_2/GNP		0.83	0.648	3.84	4.49	-
3B	Co_3O_4/ CeO_2/GNP	best	0.86	0.73	3.6	3.9	0.57
	$Ni(OH)_2$/ CeO_2/GNP		0.82	0.66	2.4	2.7	0.67
	CoNiCe/GNP		0.83	0.66	3.1	3.0	-
4	Co_3O_4/GNP		0.87	0.74	4.33	3.0	0.71
	CeO_2/GNP		0.85	0.74	3.34	3.1	-
	Co_3O_4/ CeO_2/GNP	best	0.85	0.70	5.14	3.5	0.44
5	Co_3O_4/C		0.85	0.72	3.80	3.8	0.71
	$Co_3O_4/Co_xCe_{1-x}O_{2-\delta}$/C	best	0.85	0.67	4.26	4.1	0.5
	CeO_2/C		0.77	0.61	2.40	2.3	0.87
6	$CoO_x(OH)_y$/C		0.87	0.72	3.55	4.6	0.6
	Co/Ce/C-1:1		0.82	0.65	2.76	2.0	0.53
	Co/Ce/C-3:1	best	0.85	0.68	3.75	4.25	0.6
	Co/Ce/C-9:1		0.80	0.66	2.5	2.4	0.55
	CeO_2/C		0.84	0.68	3.08	3.5	-

Table 7.1 provides a chapter-wise summary of all the synthesized catalysts of the thesis work and their catalytic parameters. The best catalyst from Chapter 3 have been taken studied in depth from different angles (like the influence of mixed oxides over individual oxides and oxygen vacancies) in Chapter 4. A slightly modified version of the best catalyst from Chapter 4 has been studied in Chapter 5 to give clearer understanding of the correlation between oxygen vacancies and oxidation states of Co in the hybrid system. In Chapter 6, a series of oxide/hydroxides were studied to understand the influence of compositional variations of CeO_2 in the hybrid systems towards ORR/OER. Figure 7.1 presents a bar diagram of the best catalysts from each chapter with their performance indicators. Hence, we can say that we have successfully synthesized electrocatalysts with some desired properties like early onset for ORR, operating through ~4e^- transfer and good current densities for ORR. Although a direct comparison of all the catalysts from each

chapter might be complex, some fundamental understandings have been put forward that are believed to contribute towards better understanding of hybrid electrocatalysts with oxide-oxide/hydroxide interfaces towards ORR/OER.

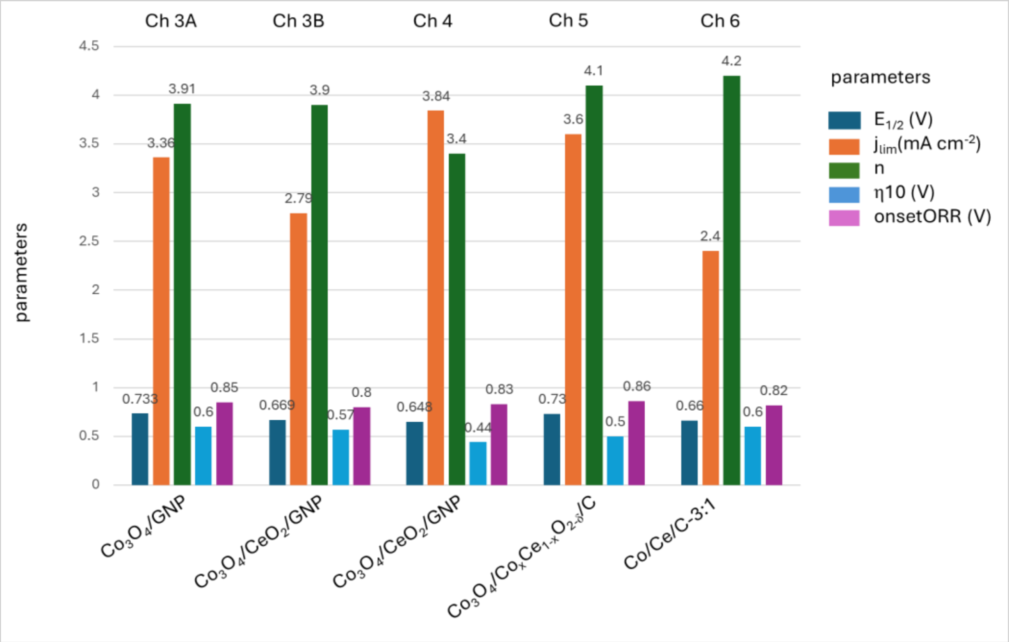


Figure 7.2: A bar diagram comprising of the best catalyst from each chapter and their catalytic performance indicators.

The fundamental findings and key takeaways from the thesis work as as follows:

- ☑ The study presents successful synthesis of Co-, Ni and Ce-based bimetallic and trimetallic mixed (hydr)oxides.
- ☑ The synthesized (hydr)oxides display versatile oxide-oxide and oxide-hydroxide interfaces.
- ☑ The interfacial composites exhibit good electrocatalytic activity for ORR and OER.
- ☑ The synthesized catalysts display superior stability and durability compared to commercial benchmark catalyst for ORR.
- ☑ Tuning of catalytic activity by modification with CeO_2 is one of the most important observations in the study. This observation has been reconfirmed in all the experiments in the study.
- ☑ The factors behind this phenomenon– defects, oxygen vacancies, divalent and trivalent cobalt ions, etc. have been decoded and explained in detail.

- ☑ Insights on changes in crystal structure of some of the synthesized catalysts have been presented.
- ☑ Cobalt-based oxides and hydroxides backed up by ceria could be a potential replacement of Pt/C.
- ☑ The study paves way for more research into the ‘cobalt-ceria’ combination for ORR and OER.

7.2 Future scopes

As the synthesized catalysts exhibit enhanced stability towards prolonged ORR tests, these are believed to hold potential scope for commercialization. Although detailed physical characterizations and analysis have been done on the fabricated electrode materials, the mechanistic insights can only be decoded via in-situ and operando characterizations. *in-situ* Raman, *in-situ* PXRD, *operando* XAS are expected to give important mechanistic insights and real-time reaction dynamics on the influence of CeO_2 on cobalt-based interfaces. Although XPS and EPR gives us a fair comparison of the oxygen vacancies, a more insightful information can be gained by more sophisticated techniques like positron annihilation spectroscopy (PALS) and temperature dependent EPR. Fine tuning of oxide-oxide and oxide-hydroxide interfaces via optimal composition of CeO_2 is also another branch of extension that has can provide more information on the effect of content of ceria on the interfaces and ultimately how it affects the electrochemistry of the materials. Gass diffusion electrodes (GDE) can be fabricated with the studied materials and employed in more realistic reaction conditions like flow cells. This can give a more viable picture of the scope of commercialization. Physical and spectral characterization of exhausted electrodes post-electrocatalysis can provide information on changes in morphological changes as well as crystal structure changes. Advanced computational studies can be employed to see interaction between specific Miller planes and their interfacial interactions towards influencing ORR and OER.

****