Exploration of $LiCrO_2$ Based Superior OER Catalysts: Understanding the Role of Structural Defects and Relative Ionicity of M-O Bonds in Doped Layered Oxides

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by

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Chapter 6

Summary and Future Scope

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6.1 Summary

The forthcoming insecurity of fossil fuel supply, rising global energy demand as well as critical environmental and climate issues resulted in a momentum shift toward alternative green energy technologies. Exploring earth-abundant and relatively inexpensive transition metal–based materials as potential OER electrocatalysts used for highly developing electrochemical processes based on renewable energy technologies like water splitting, rechargeable next-generation metal-air batteries, and fuel cells, have emerged as promising alternatives for overcoming the kinetic limitations and energy conversion efficiency of these renewable energy technologies. Layered $LiMO_2$ cathode materials exhibit a variety of tunable properties in an aqueous electrolyte solution (such as lithium-ion de-intercalation, surface reconstruction, change of metal oxidation state and lattice oxygen activation) that make them highly desirable and potentially active electrocatalysts for the use of OER applications.

- This thesis aimed to explore layered lithium chromium oxide ($LiCrO_2$) for first time as efficient OER electrocatalyst, which is an inactive cathode material in Li-ion battery resulting in the formation of the stable dumbbell defect structure due to the Cr^{6+} ion at interstitial sites during charging that block Li^+-ion conduction pathways.
- The thesis explores the fundamental electrochemical processes to elucidate the electrocatalytic activity of $LiCrO_2$ (LCO) by introducing different metal ion dopants and lithium vacancy for the pining of $Cr^{3+/6+}$-3d energy with O-2p band, which is required for good OER activity. This research work further involves the study of reaction kinetics, charge transfer resistance, surface redox reactions, electrochemically active surface area, long-term durability of LCO catalysts in 1M aqueous KOH electrolyte.

- This thesis utilizes the inductive effect concept for the tuning of redox potential of transition metal ion ($Cr^{3+/6+}$) in $LiCrO_2$ by introducing metal ion substituents (X^{n+} = Fe, Ni, Al) with higher electronegativity or stronger Lewis' acidity in the structure that makes the counterpart Cr-O and Li-O bonds more ionic resulting in a smaller energy separation between bonding and antibonding orbitals (ΔE_{M-O}), i.e., the greater overlap between the M (3*d*) and O (2*p*) orbital, giving loosely bounded O atom to the active metal ion surface and making O_2 evolution more feasible.
- **Chapter 1** briefly illustrates the general introduction, literature review and objective of this work. The chapter 1 incudes the need for alternative energy storage and conversion technologies to produce highly pure hydrogen (a future fuel) from renewable energy sources, and describes the importance and limitations of oxygen evolution reaction in these energy storage and conversion systems. The chapter further discussed the OER mechanism, activity parameters, and the development history of various OER catalysts for alkaline water splitting. There is a detailed explanation of Layered $LiMO_2$ cathode materials as potential OER catalysts.
- **Chapter 2** provides basic overview of the experimental methodology, which includes the synthesis techniques for producing materials with controlled structure and composition as well as comprehensive theoretical framework for their physical characterizations along with electrochemical techniques to measure the electrocatalytic OER performances of the synthesized catalysts.
- **Chapter 3** describes the systematic study of dumbbell defects containing chromium-rich lithium-vacant layered $Li_yCr_{1-x}Fe_xO_2$ ($y \leq 1$, $0 \leq x \leq 0.2$) structure with Fe doping concentration and lithium vacancies synthesized via conventional solid-state ceramic synthesis route in oxygen environments. The presence of Cr^{6+} ions at the Li-interstitial sites creating a dumbbell defect in the hexagonal close-packed $LiCrO_2$ lattice which was

confirmed by XPS and FTIR studies. The crystal structure, morphology, and composition of the materials were confirmed by XRD, SEM, HR-TEM, and ICP-MS analysis. This study suggests the mixing of Cr/Fe ion in the Li-layer due to formation of O3-type layered rhombohedral structure and formation of Cr^{6+} ion interstitials in the Li-layer increases by varying Li and Fe content in $Li_yCr_{1-x}Fe_xO_2$ ($y \leq 1, 0 \leq x \leq 0.2$) structure, which can further participate in the tunning of $Cr^{3+/6+}$ redox couple that results in a better OER activity. Among the synthesized catalysts, LCFO-10 with the ICP composition of $Li_{0.6}Cr_{0.9}Fe_{0.1}O_2$ exhibit superior OER activity with a Tafel slope of 50 mV dec^{-1} and an overpotential of 311 mV at a current density of 10 mA cm^{-2}, better than that of the RuO_2 benchmark catalyst, measured in similar experimental conditions.

- **Chapter 4** describes a systematic OER study of layered $Li_yCr_{1-x}Ni_xO_2$ ($y \leq 1, 0 \leq x \leq 0.2$) with different Ni doping amounts and Li-vacancies synthesized via a conventional solid-state reaction as well as solution combustion method. The crystal structure, morphology, and composition of the materials were confirmed by XRD, SEM, HR-TEM, and ICP-MS analysis. Decrease in layered ordering and creation of cations (Cr/Ni) mixing along with the formation of Li-vacancy in the structure confirms with the XRD and refinements results. The XPS and FT-IR studies confirm the successful formation of layered $Li_yCr_{1-x}Ni_xO_2$ structure and, also reveal the presence of Cr^{6+} ion in Li- interstitial sites creating dumbbell defect in the $Li_yCr_{1-x}Ni_xO_2$ lattice. The binding energies of Ni(2*p*) and Cr(2*p*), obtained from XPS studies confirm that the presence of more electronegative Ni^{3+} ion as major component in $LiCrO_2$ lattice, which can significantly increase the effective charge on Cr ions resulting in a more ionic Cr-O bond through the inductive effect of highly covalent of Ni-O bond (also supported by the Rietveld refinement results). The electrochemical results shows that the combustion synthesized LCNO-10(c) sample with the nominal composition of $Li_{0.7}Cr_{0.9}Ni_{0.1}O_2$ exhibits highest activity with a Tafel slope of

65 mV dec^{-1} and an overpotential of 277 mV at a current density of 10 mA cm^{-2}. The activity of solution combustion synthesized $Li_{0.7}Cr_{0.9}Ni_{0.1}O_2$ (LCNO-10(c)) remarkably competes with the performance of RuO_2 (336 mV at 10 mA cm^{-2}) and showed superior or comparable OER activity to the other best-known OER catalysts such as α-MnO_2, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and $LaNiO_3$.

- **Chapter 5** illustrates a systematic investigation of OER activity of layered $Li_{1-x}Cr_{1-x}Al_xO_2$ ($x = 0, 0.17, 0.20, 0.25, 0.33$), synthesized via conventional solid-state method. The crystal structure, morphology, and composition of the materials were confirmed by XRD, XPS, SEM, HR-TEM, and ICP-MS analysis. The doping of Al can substantially induce the Cr^{6+} ions to be partially occupied at the Li interstitial site creating a dumbbell defect in the hexagonal lattice of $Li_{1-x}Cr_{1-x}Al_xO_2$ and thereby stabilizing the layered structure of the system with partial Li-deficiency and cation mixing. Al^{3+} substitution in the lattice increases the ionicity of the Cr-O and Li-O bonds in general as well as results in the high concentration of Cr^{6+} ions in the lattice. The more polarizing Al^{3+} ion (with stronger Lewis acidity) have a higher affinity to electrons than the Cr^{3+} ion, that induces the formation of more covalent Al-O bond in $Li_{1-x}Cr_{1-x}Al_xO_2$ and increasing the ionicity of neighbouring/counterpart Cr-O and Li-O bonds (by increasing the effective charge of Cr) which would lead to lowering the redox energy of filled antibonding states, and shift the redox potential to a more positive side to result in superior electrocatalytic OER of the catalyst. Among the $Li_{1-x}Cr_{1-x}Al_xO_2$ (LCAO) samples, the activity of $Li_{0.25}Cr_{0.75}Al_{0.25}O_2$ (LCAO-25) with overpotential of 327 mV at 10 mA cm^{-2} and Tafel slope of 59 mV dec^{-1}, remarkably approaches the performance of benchmark oxide catalyst RuO_2 (336 mV at 10 mA cm^{-2}) and showed superior or comparable OER activity to the best known OER catalyst such as α-MnO_2, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and $LaNiO_3$.

- **Chapter 6** briefly summarizes the research findings of this thesis for the layered lithium chromium oxide as potential electrocatalyst for oxygen evolution reaction. The superior OER activity of the catalysts were obtained due to the interplay of layered crystal structure and mixing of O(2*p*) band in Cr(3*d*) levels via the tuning of oxidation state of $Cr^{3+}/^{6+}$ by varying the Li-content and doping of different metal substituents (Fe, Ni, Al) in the layered $LiCrO_2$ structure. Further, **Figure 6.1** compares the electrocatalytic activity of all best performing synthesized catalysts along with the benchmark catalysts such as commercial RuO_2, α-MnO_2, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and $LaNiO_3$ measured in similar experimental condition. The overpotentials at a current density of 10 mA cm^{-2} and Tafel slope values of catalysts are listed in **Table 6.1**.

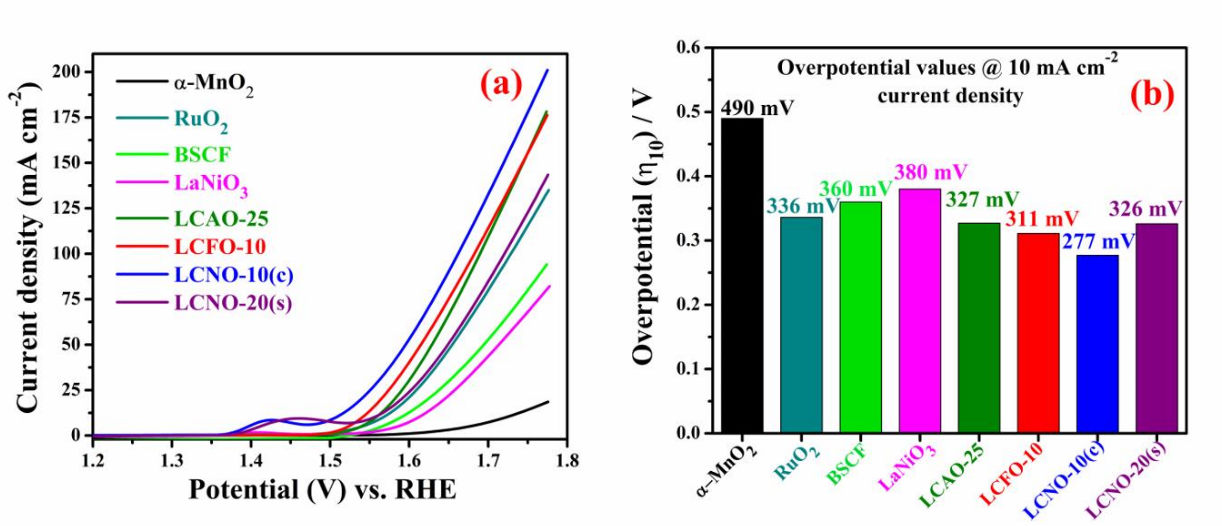

Figure 6.1 OER performance of all the best performing catalysts synthesized in the present study along with the benchmark catalysts such as commercial RuO_2, α-MnO_2, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and $LaNiO_3$ measured in similar experimental condition which shows activity similar to the previous reports [1-5].

Table 6.1 listed the overpotential and Tafel slope values of all synthesized catalysts.

Catalysts	**Overpotential at 10 mA cm^{-2} current density (η_{10})/ mV**	**Tafel slope (mV dec^{-1})**
LCFO-10 ($Li_{0.6}Cr_{0.9}Fe_{0.1}O_2$)	311 mV	50
LCNO-10(c) ($Li_{0.7}Cr_{0.9}Ni_{0.1}O_2$)	277 mV	65
LCNO-20(s) ($Li_{0.7}Cr_{0.8}Ni_{0.2}O_2$)	326 mV	90
LCAO-25 ($Li_{0.75}Cr_{0.75}Al_{0.25}O_2$)	327 mV	59
Commercial RuO_2	336 mV	87
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	360 mV	90
$LaNiO_3$	380 mV	93
α-MnO_2	490 mV	132

6.2 Future scope

Though there have been significant advancements in the field of OER, there are still certain obstacles that researchers need to address. Some perspectives and future directions in this field are provided as follows.

- Testing of material as bifunctional catalyst or overall water splitting (HER and OER).
- Nano-engineering in the synthesis of catalyst materials to improve its surface and electronic properties
- Search of framework and hybrid structured materials to enhance the activity and stability of catalysts.
- An alkaline electrolyte medium is used for the majority of electrocatalytic OER investigations. The development of an electrocatalyst that functions at all pH values is therefore difficult.
- The practical application of OER electrocatalysts in real devices is possible only by increasing the intrinsic activity and exposing a greater number of electrochemically active sites. The electronic structure plays a major role in determining intrinsic activity. To attain

the maximum intrinsic activity, future research should more concentrate on tuning the electronic structure of the catalyst.

- Commercialization of OER catalysts into practical devices (water electrolyzer, metal-air batteries, fuel cell) at low cost, with outstanding OER activity, and stability remains a great challenge for researchers.
- A superior electrocatalyst must be developed by understanding the mechanism of the oxygen evolution reaction. While the mechanisms of some materials have currently been found, most compounds still require more investigation.
- The advancement of in-situ characterization is crucial in obtaining additional insights into the active sites and intermediates that direct the logical design of an effective electrocatalyst for green energy production.

6.3 References

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List of Publications

1. **Vaishali Soni**, Abhay Narayan Singh, Preetam Singh and Asha Gupta, *Photocatalytic dye-degradation activity of nano-crystalline* $Ti_{1-x}M_xO_{2-\delta}$ *(M =Ag, Pd, Fe, Ni and* $x = 0, 0.01$*) for water pollution abatement.* **RSC Advances**. 2022, 12, 18794-18805 (https://doi.org/10.1039/D2RA02847F).
2. **Vaishali Soni**, Rakesh Mondal, Abhay Narayan Singh, Preetam Singh, and Asha Gupta, *Dumbbell Defect Containing Chromium-Rich Lithium-Vacant Layered* $Li_yCr_{1-x}Fe_xO_2$ *(*$y \leq 1$*,* $0 \leq x \leq 0.2$*): An Unexplored and Highly Efficient Electrocatalyst for the Oxygen Evolution Reaction.* **ACS Applied Energy Materials**. 2023, 6, 1308−1320 (https://doi.org/10.1021/acsaem.2c03056).
3. **Vaishali Soni**, Shraddha Jaiswal, Preetam Singh, & Asha Gupta, *Aluminium doped Lithium-vacant Layered* $Li_{1-x}Cr_{1-x}Al_xO_2$*: A Potentially Active Electrocatalyst for Oxygen Evolution Reaction.* **ACS Applied Energy Materials.** 2024, 7, 8, 3175–3186 (https://doi.org/10.1021/acsaem.3c03160).
4. **Vaishali Soni**, Shraddha Jaiswal, Krishna Gopal Nigam, Preetam Singh, & Asha Gupta, *Nickel doped Lithium-vacant Layered* $Li_yCr_{1-x}Ni_xO_2$*: A Potentially Active Electrocatalyst for Oxygen Evolution Reaction*. **Journal of Material Chemistry A,** 2024 (https://doi.org/10.1039/d4ta02717e).
5. Shraddha Jaiswal, **Vaishali Soni**, Preetam Singh, & Asha Gupta, *Role of cation deficiency and inductive effect in Ti-doped NiO for developing superior electrocatalysts for Oxygen Evolution Reaction.* **ACS Applied Energy Materials** (Revision submitted), Manuscript ID: ae-2024-01774z.

International/National Conferences Attended

1. The international conference on "**ChemCatCon 2.0: Mechanistic investigation on heterogeneous processes"** IIT Gandhinagar, India, 14-16 May 2022.
2. The International conference on **Beyond Fossil Fuels: The Future of Alternative Energy Technologies (B: FAT-2020)**, IIT (BHU) Varanasi, India, 23-25, July 2022.