Preface

The increasing global energy demand, the vulnerability of the fossil fuel supply, and associated environmental concerns have all spurred the requirement for alternative green energy solutions. Electrocatalytic Oxygen evolution reaction (OER) is one of the key technologies for the large-scale storage of electricity produced from renewable sources in Metal-air batteries and in the form of Hydrogen fuel from water splitting. For the large-scale application of these technologies, highly efficient, low cost and stable electrocatalysts are required. Due to high earth abundance and cost-effectiveness, transition metal-based layered $LiMO_2$ cathode materials have garnered significant attention as potential electrocatalysts for OER.

This thesis entitled **"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"** explores the layered lithium chromium oxide ($LiCrO_2$) for the first time as efficient OER electrocatalyst. The thesis explores the fundamental understanding of defect formation, electronic structure, and the relative ionic strength of a chemical bond to elucidate the electrocatalytic activity of $LiCrO_2$ by introducing different metal ion dopants and lithium vacancy for the pining of $Cr^{3+/6+}$-3*d* energy with O-2*p* band, which is required for good OER activity. The thesis involves the study of reaction kinetics, charge transfer resistance, surface redox reactions, electrochemically active surface area, and long-term stability of all the synthesized catalysts in 1M aqueous KOH electrolyte. The following chapters comprise the structure of my thesis:

- The **first chapter** includes the general introduction, literature review, and objective of this work. The chapter begins with a brief introduction to the need for alternative energy storage and conversion technologies and describes the importance and limitations of oxygen evolution reactions. 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. The highlighting part of this chapter concludes the significant objective of this research, which offers a unifying idea between electronic structures and electrochemical properties.

- The **second chapter** provides basic information about the experimental methodology, which includes the synthesis techniques for producing materials with controlled structure and composition as well as a comprehensive theoretical framework for their physical characterizations along with electrochemical techniques to measure the electrocatalytic OER performances of the synthesized catalysts.
- The **third chapter** 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 for OER electrocatalysis. The formation of stable structural dumbbell defects in the lattice occurs due to the incorporation of Cr^{6+} ions at interstitial sites. This study suggests the mixing of Cr/Fe ion in the Li-layer due to the formation of O3-type layered rhombohedral structure and the formation of Cr^{6+} ion interstitials in the Li-layer, which can further participate in the tunning of $Cr^{3+/6+}$ redox couple that results in a better OER activity of the catalysts.
- In the **fourth chapter,** I discussed the electrocatalytic 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. Upon Ni-substitution, a decrease in layered ordering and creation of cation (Cr/Ni) mixing in the Li-layer along with the formation of partial Li-vacancy in the structure can substantially induce the Cr^{6+} ion to be partially occupied at the Li-interstitial site creating dumbbell defect in

layered $Li_yCr_{1-x}Ni_xO_2$ lattice. This study further suggests that the substitution of more electronegative Ni^{3+} ion in $LiCrO_2$ lattice can significantly increase the ionicity of counterpart Cr-O bond through the inductive effect and increase the effective charge on Cr ion and shifting the redox potential more positively, which would lead to greater overlap between the $Cr^{3+}/^{6+}$ (3*d*) energy and O^{2-}(2*p*) band and resulting the superior OER activity of the catalysts.

- The **fifth chapter** discussed 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. 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. This study further suggests that 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) has a higher affinity to electrons than the Cr^{3+} ion, which induces the formation of more covalent Al-O bond in $Li_{1-x}Cr_{1-x}Al_xO_2$ and increases the ionicity of neighbouring/counterpart Cr-O and Li-O bonds and shift the redox potential to a more positive side leading to greater overlap between the $Cr^{3+}/^{6+}$ (3*d*) and O^{2-}(2*p*) orbitals and superior electrocatalytic OER of the catalysts.
- The concluding **sixth chapter** briefly summarizes the research findings of this thesis for the layered lithium chromium oxide as a potential electrocatalyst for oxygen evolution reaction. The superior OER activity of the catalysts was 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.