

## Surendra B. Karki

### Dissertation Defense

When: April 20, 2022

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## Structural, Charge Transport, Gas Sensing, Magnetic, Pseudocapacitive, and Electrocatalytic Properties of Perovskite Oxides

### Abstract

Perovskites are functional materials with the general formula  $ABO_3$  (A = alkali, alkaline earth or lanthanoid cations and B = transition metal or main group cations). These materials are marked by a variety of crystal structures and interesting properties such as colossal magnetoresistance, ferroelectricity, multiferroicity, superconductivity, pseudocapacitance, gas sensing, charge transport, and electrocatalytic properties.<sup>1</sup> The formula of perovskite can be written as  $AA'BB'O_6$ , when there is ordering between two cations over A and B-sites. Such compounds are called double perovskite oxides. Some amount of oxygen could be lost from crystal structure without decomposition of the phase. Such class of materials are termed oxygen deficient perovskites (ODPs). In this study, several double perovskite oxides and ODPs are utilized for systematic study of magnetic, charge transport, pseudocapacitive, and electrocatalytic properties. The magnetic and electrical properties of  $BaSrMMoO_6$  (M = Mn, Fe, Co, Ni) double perovskite oxides show an interesting property trend.<sup>2</sup>  $BaSrFeMoO_6$  shows a ferrimagnetic ordering of moments of Fe along with metallic behavior in variable temperature conductivity studies. However, Mn, Co, and Ni containing materials show an antiferromagnetic ordering of moments and semiconducting features from 25 – 800 °C.

Another focus of our research is to solve problems and issues of energy conversion process that is involved with an electrochemical water splitting to generate hydrogen gas for fuel. Water splitting has two half reactions namely oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).<sup>3-7</sup> Both reactions have significant amounts of overpotential and require catalysts to lower the overpotential and enhance the reaction kinetics. Overpotential has been reduced by catalyzing both OER and HER using commercial  $RuO_2$ ,  $IrO_2$ , and Pt/C. However, such catalysts are expensive, use precious metals, and some of them have stability issues in acidic condition. Our approach involves development of economic perovskite oxide-based catalysts that contain earth abundant metals.

The main tools for the problem-solving approach of our research involved both A and B-sites modification, conductivity enhancement, structural transformation, and control of the oxygen content in perovskite structure. For example, A-site substitution strategy is adopted by substituting Sr with Ca in  $Sr_2FeCoO_{6-\delta}$  and  $LaSr_2Fe_3O_8$ . This leads to significant enhancement of OER/HER activity in structurally ordered compounds namely  $Ca_2FeCoO_{6-\delta}$  and  $LaCa_2Fe_3O_8$ . The B-site modification, on the other hand, is also utilized by systematically varying the Mn content in the series  $CaSrFe_{1-x}Co_{1-x}Mn_{2x}O_{6-\delta}$  ( $x = 0-1$ ). This helped to identify a material with formula  $CaSrFe_{0.75}Co_{0.75}Mn_{0.5}O_{6-\delta}$  (CSFCM), that has an  $e_g$  occupancy of near unity, as required for optimized activity. Additionally, upon using both experimental and computation methods, we have studied the electronic structure of several materials, including CSFCM. This has led to the discovery of a new descriptor, namely free  $e_g$  carrier. This could be a universal descriptor for both OER and HER for bifunctional catalysts. Similarly, we have discovered several other oxide catalysts such as  $CaSrFeMnO_{6-\delta}$ ,  $BaSrCoMoO_6$ ,  $Sr_3FeMnO_6$ ,  $Ca_2Sr_2Mn_2CoO_{10-\delta}$ , and  $La_3Co_3O_8$ , which have remarkably low overpotentials, as low as 0.25 V in both acidic and basic media. In most of these oxides, electrocatalytic properties arise from the combination of structure, enhanced electrical conductivity, and higher amount of oxygen vacancies.

### References

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