University of Louisville
Department of Chemistry
Kinithi Wickramaratne

Research Seminar

When: April 20, 2023
Time: 1:15 p.m.
Location: CBLL-16

Investigation of Oxygen-Deficient Perovskite Oxides: Their Electrocatalytic Activity and Pseudocapacitive Properties

Abstract:

The development of efficient and stable electrocatalysts is crucial in the production of hydrogen through electrochemical water splitting, as it can help to mitigate both the energy crisis and environmental pollution.[1] Due to distinctive structural and compositional flexibility, perovskite oxides and their derivatives have been investigated as promising candidates for Hydrogen Evolution Reaction (HER).[2, 3] Herein, we synthesized La-Fe-Ga-O oxides to optimize HER activity by introducing oxygen vacancies into parent perovskite material $La_3Fe_2GaO_9$ (ABO_3).[4] Modifying the A-site of ABO_3 changes the structural features of the material, which gives a highly ordered $LaCa_2Fe_2GaO_8$ ($ABO_{2.67}$) oxygen-vacant perovskite oxide. Especially remarkable is that the highly ordered $ABO_{2.67}$ oxide exhibits outstanding HER activity with faster reaction kinetics and higher electrical conductivity in a wide range of temperatures, markedly greater than that of the parent perovskite. The distinctive stacking of octahedral and tetrahedral layers, due to the ordered oxygen vacancies in $ABO_{2.67}$, facilitates desired interactions between the catalyst surface and the HER intermediates. Next, we studied a series of Ca-Fe-Mn-O oxygen-deficient perovskite oxides (ODPs) to examine the systematic trends in electrocatalytic activity for the hydrogen evolution reaction.[5] The crystal structure of ODPs is transformed by modifying the B-site composition and gradual increase of the Fe/Mn ratio, leading to changes in their electrocatalytic activity for the HER. In this series, the two materials with higher Fe content exhibit an ordered oxygen vacancy pattern with alternating layers of $(Fe)O_4$ and $(FeMn)O_6$ units, whereas oxide the material with lower Fe content has a regular perovskite oxide structure with disordered oxygen vacancies. In this series, the two materials with ordered oxygen vacancies exhibit superior HER activity in acidic conditions compared to disordered oxygen-vacancy oxide. Furthermore, pseudocapacitive properties have been studied for two materials belonging to a family of layered perovskite oxides.[6] These materials show excellent pseudocapacitive energy storage with outstanding stability up to 1000 cycles of charge−discharge. These studies highlight the importance of tuning the A and B sites in perovskite oxides to modify the structural order to enhance electrochemical properties and electrical charge transport.

References:

1. Wang, S.; Lu, A.; Zhong, C.-J., Hydrogen production from water electrolysis: role of catalysts. *Nano Converg.* **2021,** *8*, 1-23.

2. Cheng, X.; Fabbri, E.; Nachtegaal, M.; Castelli, I. E.; El Kazzi, M.; Haumont, R.; Marzari, N.; Schmidt, T. J., Oxygen evolution reaction on $La_{1-x}Sr_xCoO_3$ perovskites: a combined experimental and theoretical study of their structural, electronic, and electrochemical properties. *Chem. Mater.* **2015,** *27* (22), 7662-7672.

3. Karki, S. B.; Hona, R. K.; Yu, M.; Ramezanipour, F., Enhancement of Electrocatalytic Activity as a Function of Structural Order in Perovskite Oxides. *ACS Catal.* **2022,** *12*, 10333-10337.

4. Wickramaratne, K. M. K., Ramezanipour F., Impact of Oxygen-Vacancies on Electrocatalytic Activity of $La_{3-x}Ca_xFe_2GaO_{9-\delta}$ (x = 0, 2; δ = 0, 1) for Hydrogen Evolution Reaction. *Solid State Sci.* **2023**, (Revisions submitted)

5. Wickramaratne, K. M. K., Ramezanipour F., Karki S. B., Cooperative Effect of the Transition Metal Type and Structural Order on Electrcatalytic Activity for Hydrogen Evolution Reaction. **2023**, (Manuscript in final preparations)

6. Lang, X.; Mo, H.; Hu, X.; Tian, H., Supercapacitor performance of perovskite $La_{1-x}Sr_xMnO_3$. *Dalton Trans.* **2017,** *46* (40), 13720-13730.