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Dissertation Defense

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Synthesis, Electrical Conductivity, Electrocatalytic Activity for Water Splitting, and Pseudocapacitive Properties of Perovskite Oxide Derivatives

ABSTRACT:

Developing green and sustainable energy solutions is crucial to addressing the energy and environmental challenges. Hydrogen is an attractive candidate given its high energy density and low carbon emission compared to gasoline and coal. Electrochemical water splitting through a water electrolyzer is recognized as a green method for generating hydrogen and oxygen gases. Developing cost-effective electrocatalysts to reduce overpotential in hydrogen and oxygen generation is essential for the overall process. The growing interest in perovskite oxides as versatile and sustainable catalysts is driven by their compositional flexibility, tunable electronic structure, earth abundance, and inherent catalytic performance. In our research, we synthesized diverse perovskite structures and perovskite derivatives to explore their electrocatalytic potential. First, we investigated the impact of oxygen vacancies on functional properties by examining the oxygen-deficient perovskite (ODP) structure $LaCa_2Fe_2GaO_8$, showcasing enhanced HER electrocatalysis compared to $La_3Fe_2GaO_9$ with the same Fe/Ga composition but lacking oxygen vacancies.[1] Furthermore, we identified a systematic trend in HER electrocatalytic activity influenced by transition metal type and structural order. By synthesizing ODPs $Ca_3Fe_{3-x}Mn_xO_8$ (with x = 1, 1.5, 2), we demonstrated a gradual increase in oxygen vacancy ordering with varying Fe/Mn content, with oxygen vacancy ordered oxides displaying superior HER activity.[2] Moreover, we expanded our exploration to a series of layered quasi-2D oxides, (K_2NiF_4-type oxides), incorporating different transition metals (Co, Ni, Cu, Zn). In this series, materials with improved charge transport exhibited superior electrocatalytic performance for both HER and OER.[3]

Additionally, perovskite-derived oxides are gaining attention as electrodes for anion intercalation-type pseudocapacitors, addressing the need for advanced energy storage solutions in the context of renewable energy technologies. Our study demonstrated pseudocapacitive charge storage properties for a library of isostructural layered quasi-2D oxides by changing the B site from Co, Ni, Cu, and Zn. The spaces between layers are occupied by La and Sr ions, and the remaining empty spaces are available for oxide ion intercalation, resulting in pseudocapacitive charge storage.[4] Next, we demonstrated that the anion intercalation mechanism is affected by variations in the structure and the ordered arrangement of oxygen vacancies, achieved by adjusting the stoichiometric ratio on the B-site.[5]

REFERENCES:

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3. Wickramaratne, K. M.; Ramezanipour, F., Enhancing Electrocatalytic Properties of Quasi-2D Oxides $LaSrMn_{0.5}M_{0.5}O_4$ (M = Co, Ni, Cu, and Zn) for Hydrogen and Oxygen Evolution Reactions. **2024**, *(Prepared for submission).*
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5. Wickramaratne, K. M.; Ramezanipour, F., Structural Effect of $Ca_3Fe_{3-x}Mn_xO_8$ (x = 0, 1, 2) Oxygen-Deficient Perovskites for Intercalation Pseudocapacitance. 2**024**, *Manuscript in final preparation)*.