

Link Foundation Energy Fellowship Report

Understanding and Improving the Activity of Oxygen Evolution Reaction Catalysts in Alkaline and Chloride-Containing Electrolytes

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1. Introduction

Hydrogen is a feedstock in many chemical processes and can also be used as an energy carrier to store, move, and deliver energy produced from other sources. Recently, hydrogen is of interest for storing renewable electricity and helping address the intermittent nature of electricity generation from renewable sources.¹ Water electrolysis plays a pivotal role in achieving a green hydrogen economy by sourcing electricity from intermittent renewable sources. However, the efficiency of the electrolysis process is limited by the sluggish oxygen evolution reaction (OER) kinetics,²⁻⁵ whereas the kinetics of the hydrogen evolution reaction (HER) are more facile. My work focused on tailoring oxide electrodes by controlling their composition, strain and crystallographic orientation to enhance the intrinsic activity of the OER. Furthermore, the stability of these electrodes driving the OER and availability of low-cost earth-abundant materials has been focused on to eventually develop active, stable and relatively inexpensive OER electrocatalysts.

With limited fresh water resources, seawater offers an infinite source of hydrogen.⁶ However, chloride salts compete with the OER at the anode, where generation of toxic chlorine gas (chlorine evolution reaction, CER) poses selectivity issues.^{6,7} Here, we also performed experimental investigation on epitaxial films to utilize surface strain to tune the selectivity towards OER and tested the OER performance and selectivity of transition metal dopants in mixed manganese oxides in raw seawater electrolysis.

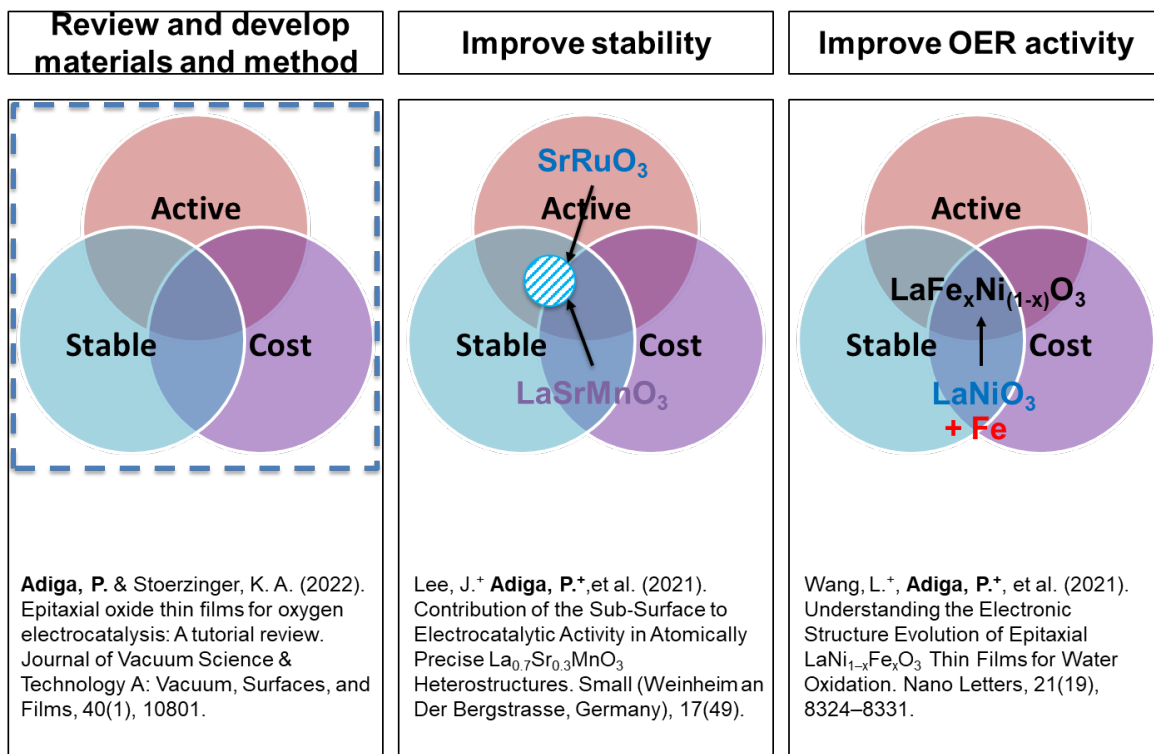
2. Objectives

The objectives for my thesis work can be split into four parts: (a) enhanced OER activity, (b) improved stability of OER electrocatalysts, (c) utilization of low-cost earth-abundant

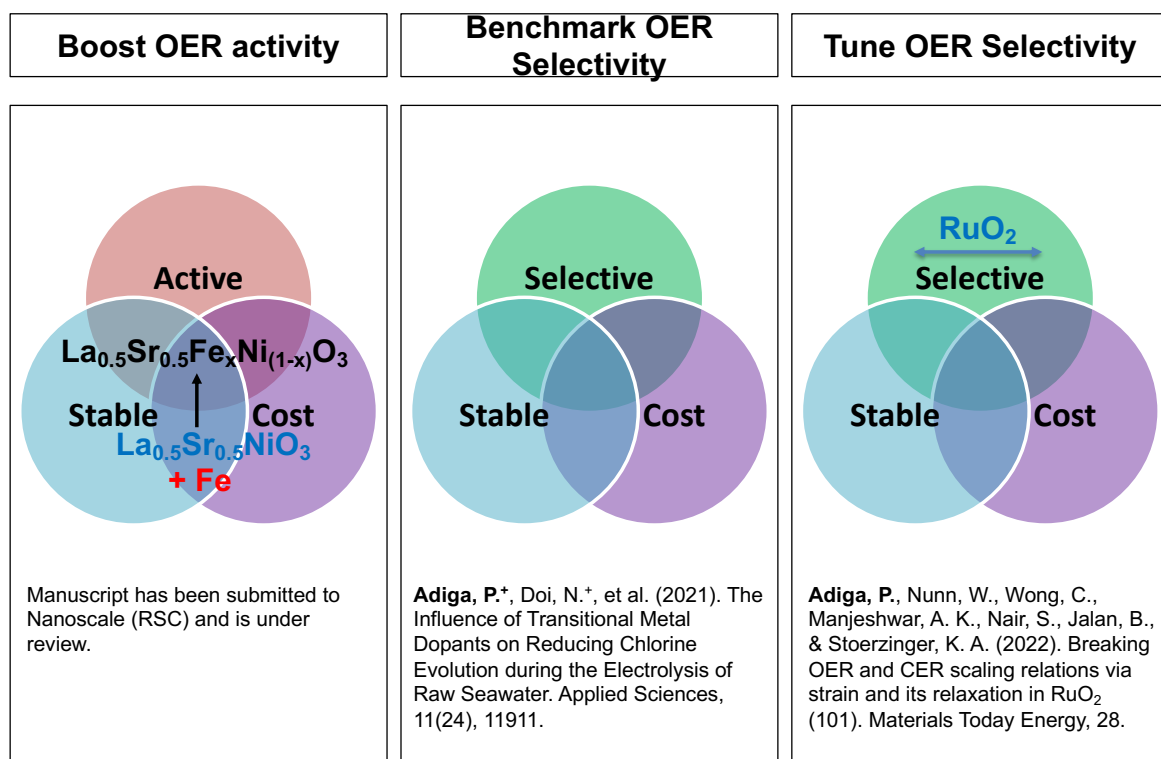
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electrodes, (d) better control over OER/CER selectivity (in chloride-containing electrolytes).

These objectives were achieved in five separate projects which are summarized below: We first summarized the materials and methods essential testing OER electrodes configured as epitaxial films, enabling unprecedented insight into catalyst characterization and its relation to catalysis.⁸ We then looked to understand the enhancement of alkaline OER activity in Ni-Fe based perovskite oxides by relating electronic structure and performance.⁹ We then built the understanding of the link between alkaline OER catalyst activity and stability in Ru-Mn perovskite heterostructures by varying the outer layer thickness.¹⁰ We next considered the alkaline OER activity and effect of cycling on the surface restructuring of a Sr-substituted Ni-Fe perovskite oxide. [Manuscript under preparation] We then investigated strategies to break the scaling relationship between OER and OER/CER reaction intermediates by strain and its relaxation on a benchmark catalyst like RuO₂ (101).[Manuscript submitted to Materials Today Energy] Finally, we performed experimental investigations to understand the role that transition metal dopants play in a Mn-Mo electrode with an undercoating of IrO₂ in sea water.¹¹



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3. Significance and Impact

In this collection of work, we addressed three of the most important aspects of electrocatalysis: activity, stability and selectivity in favor of oxygen evolution reaction (OER) using experimental and spectroscopic approaches. We have shown that rational design of earth-abundant OER electrocatalysts using electronic structure, composition and strain relaxation can enhance the intrinsic OER activity and improve the selectivity towards OER in presence of chloride salts.

We also provided mechanistic understandings for observed changes in OER activity and potential sweep-driven surface changes and utilized electrochemistry and spectroscopic techniques to report the changes in electronic structure and performance with compositional tuning. The epitaxial films studied here enabled us to understand structure-property relationships with greater detail compared to rough, porous surfaces grown using electrodeposition, ink casting or electroflocculation. Thus, our studies have investigated the role of strain, active site availability and electronic structure changes on catalyst selectivity and activity for the OER. Thus, the collection of work presented here adds a wealth of information to the current knowledge of OER electrocatalyst tuning for improved

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activity, stability and selectivity and aiding in making green hydrogen-based economy more feasible.

4. List of Scholarly Outcomes

Link Foundation Energy Fellowship has been acknowledged in the following list of scholarly outcomes authored/co-authored by P. Adiga.

- [1] **P. Adiga**, W. Nunn, C. Wong, A. K. Manjeshwar, S. Nair, B. Jalan, K. A. Stoerzinger, Breaking OER and CER scaling relations via strain and its relaxation in RuO₂ (101). *Materials Today Energy*, 28 (2022), 101087.
- [2] **P. Adiga**, and K. A. Stoerzinger, Epitaxial oxide thin films for oxygen electrocatalysis: A tutorial review, *Journal of Vacuum Science & Technology A* 40 (1) (2022), 010801.
- [3] L. Wang, **P. Adiga**, J. Zhao, W. S. Samarakoon, K. A. Stoerzinger, S. R. Spurgeon, B. E. Matthews, M. E. Bowden, P. V. Sushko, T. C. Kaspar, G. E. Sterbinsky, S. M. Heald, H. Wang, L. W. Wangoh, J. Wu, E.-J. Guo, H. Qian, J. Wang, T. Varga, S. Thevuthasan, Z. Feng, W. Yang, Y. Du, S. A. Chambers, Understanding the Electronic Structure Evolution of Epitaxial LaNi_{1-x}Fe_xO₃ Thin Films for Water Oxidation, *Nano Letters* 21 (19) (2021), 8324-8331.
- [4] J. Lee, **P. Adiga**, S. A. Lee, S. H. Nam, H.-A. Ju, M.-H. Jung, H. Y. Jeong, Y.-M. Kim, C. Wong, R. Elzein, R. Addou, K. A. Stoerzinger, W. S. Choi, Contribution of the Sub-Surface to Electrocatalytic Activity in Atomically Precise La_{0.7}Sr_{0.3}MnO₃ Heterostructures, *Small* 17 (49) (2021), 2103632.
- [5] **P. Adiga**, N. Doi, C. Wong, D. M. Santosa, L.-J. Kuo, G. A. Gill, J. A. Silverstein, N. M. Avalos, J. V. Crum, M. H. Engelhard, K. A. Stoerzinger, R. M. Asmussen, The Influence of Transitional Metal Dopants on Reducing Chlorine Evolution during the Electrolysis of Raw Seawater, *Applied Sciences* 11 (24) (2021), 11911.
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- [8] **P. Adiga**, L. Wang, C. Wong, B. Matthews, M. Bowden, S. Spurgeon, G. Sterbinsky, M. Blum, M. Choi, J. Tao, T. Kaspar, S. Chambers, K. A. Stoerzinger, Y. Du,

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Correlation between oxygen evolution reaction activity and surface compositional evolution in epitaxial $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ni}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ thin films (*Manuscript under review at NanoScale, The Royal Society of Chemistry.*)

5. Statement of how discretionary funds were spent

The funds were primarily used to cover living and personal travel expenses. It also supported me in covering the school administrative and health insurance expenses.

6. How did the fellowship make a difference? Describe any ways that the direction of the Fellow's thesis, or the Fellow's professional development, was changed or impacted by virtue of receiving a Link Foundation Fellowship.

The Link Foundation Energy Fellowship was crucial in liberating me from my Teaching Assistant (TA) duties which was my primary source of stipend. This allowed me to work on multiple projects in the Stoerzinger lab and solely focus on research which expedited my graduation. Furthermore, the fellowship paid a stipend that was above par relative to the stipend paid as a TA which certainly helped me in improving my standard of life as a graduate student. This prestigious and highly competitive award was also recognized in my job interviews as it gave me a noticeable edge over other job applicants. I sincerely thank Link Foundation to have offered me this fellowship and help expedite my growth as a researcher and a professional.

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