Introduction and Motivation

- Fuel cells are a rapidly developing alternative energy technology that address the emerging issues of current fossil fuels
- Reverse hydrogen fuel cells can be used to address issues of energy storage of intermittent source (solar, wind, etc.) and provide clean burning hydrogen gas fuels
- The oxygen evolution reaction or OER (the pair reaction of the hydrogen evolution reactions) suffers from an overpotential, which is related to energy lost in the conversion process from a source to fuel
- Perovskite replacements for the cathode of the fuel cell, typically made of rare, expensive elements, can reduce the cost and reduce the overpotential of the OER
- SrTiO$_3$ is a promising candidate for this application and can be engineered to further reduce the overpotential

Results and Conclusions

- A lower overpotential for the OER than SrTiO$_3$ alone was achieved via substitutional doping with cobalt a spectator site
- Changes in surface hydration were also observed due to the effect of surface dopants

Future Work

- Analysis of effect of changing hydration states on overpotential
- Study other transition metal dopants to determine potential trend of overpotential reduction
- Experimental testing of designed materials

Methods

- Density Functional Theory (DFT) calculations of SrTiO$_3$ structures were carried out for the four step OER mechanism using the Quantum Espresso software package
- Surfaces of SrTiO$_3$ were substitutionally doped at spectator sites (see figure 4)

The undoped surface

- The change in Gibbs free energy of each step of the OER mechanism was calculated according to the following formulas:
  \[ \Delta G \downarrow ox = \Delta E \downarrow DFT - T \Delta S + \Delta ZPE \]
  \[ \Delta G \downarrow ox = \Delta G^\circ \downarrow SHE + \Delta G^\circ \downarrow ox - n \cdot e \cdot U - n \cdot 0.0592 \cdot p^\circ \]

  Where $\Delta E_{DFT}$ is the change in energy of the structures and species involved, $\Delta S$ is the change in entropy, and $\Delta ZPE$ is the change in zero point energy. The applied potential and pH of OER conditions are applied by the second equation.

- The overpotential of the steps were analyzed for the original SrTiO$_3$ structure and the Ni and Co doped structures.
- Due to the differing oxidation states of nickel and cobalt, different hydration states were determined and calculated
- Gibbs free energy analysis of altered hydration of doped sites determined the most stable forms of the doped structures
- Structures doped at spectator site 1 are most stable for transition metals without hydrated species for both cobalt and nickel
- Structures doped at spectator site 2 are most stable with an OH species for nickel and O for cobalt

Methods

- Experimental testing of designed materials

Figure 1: Intermittent nature of solar power, the power generation varies through the day, necessitating energy storage solutions (from Martinez-Anido et al.)

Figure 2: Volcano plot of perovskite material overpotentials for the OER, the overpotential is related to the descriptor on the x-axis (from Man et al.)

Figure 3: Surface Reconstruction of SrTiO$_3$ under OER conditions; Spectator and Participant sites denoted in yellow and orange, respectively

Figure 4: R1 structure of cobalt (blue) doped surface at (a) spectator site 1 and (b) spectator site 2

Figure 5: Doped structures were tested for potential changes in oxidation and hydration states due to different metals

Figure 6: Doped SrTiO$_3$ surfaces for catalysis of hydrogen fuel production

Doped SrTiO$_3$ Surfaces for Catalysis of Hydrogen Fuel Production

Vignesh C. Bhethanabotla¹, Robert B. Wexler¹, Andrew M. Rappe¹
University of Pennsylvania, Department of Chemistry

References