

# High Entropy Metal Oxides as Catalyst for Water Splitting

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## Motivation For Research

The Colorado School of Mines is a great place for a budding scientist or engineer to do research. The school has a lot of resources and a plethora of projects to become a part of. However, there is one crucial aspect I think Mines is missing, or at the very least, doesn't have enough focus on. What drives us to do research? I'm not talking about how research looks good on your resume and helps build your network but why is it important to do research in the broader sense of societal contribution? I think this is the ideal time in our lives to develop our personal philosophy and figure out

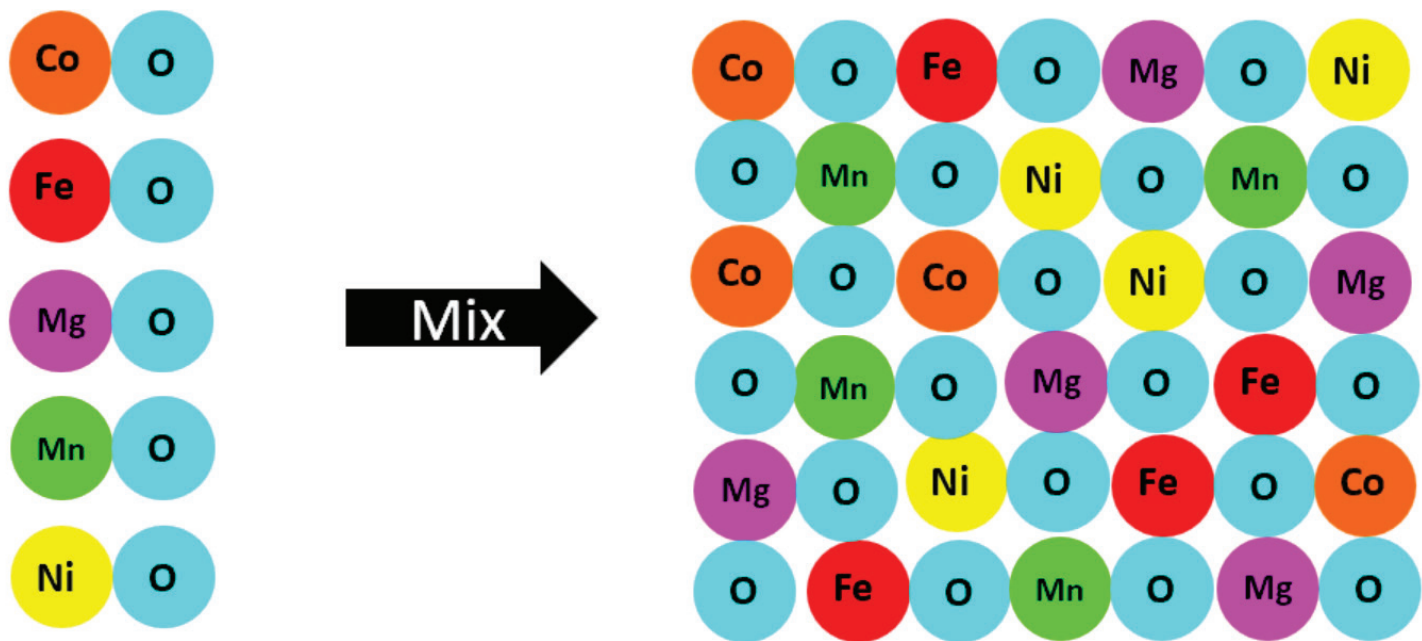
what drives us to do research. All my life I have loved the outdoors and being in nature. I grew up with strong Native American influences and a large part of the culture is respecting and revering nature. It pains me to see trash on a hiking trail and smog on an otherwise clear sky. I grew up in Pueblo, Colorado. I have seen raging disparities in quality of life from Pueblo to here in Golden. Both cities are in a 1st world country with access to clean water, energy, and food. There are billions of people who don't have these things. The majority of people alive on the planet live in worse conditions than most Americans can imagine. These are

the types of things that motivate me to do research. It is my personal philosophy that research should be focused on sustainability and bettering the human condition.

## The Big Picture

In 2021 President Joe Biden implemented the Bipartisan Infrastructure Law. This law put an unprecedented amount of money into clean hydrogen research, totalling over \$7 billion in funds [1].

Currently, the best-known way to make clean hydrogen is with a process called water splitting. Water



**Figure 1** A cartoon of a high entropy metal oxide.

splitting is an inherently inefficient process and needs a catalyst. Once water splitting is catalyzed, it produces hydrogen fuel, which in turn can be used to generate electricity.

**“The best-known way to make clean hydrogen is with a process called water splitting.”**

## Background

Water splitting is a chemical reaction that takes water ( $H_2O$ ) and breaks it down into its elemental components. Hydrogen gas ( $H_2$ ) and oxygen gas ( $O_2$ ). This reaction is one of the “holy grails” of science because, in theory, it is a reaction who’s only products are clean fuel and breathable air.

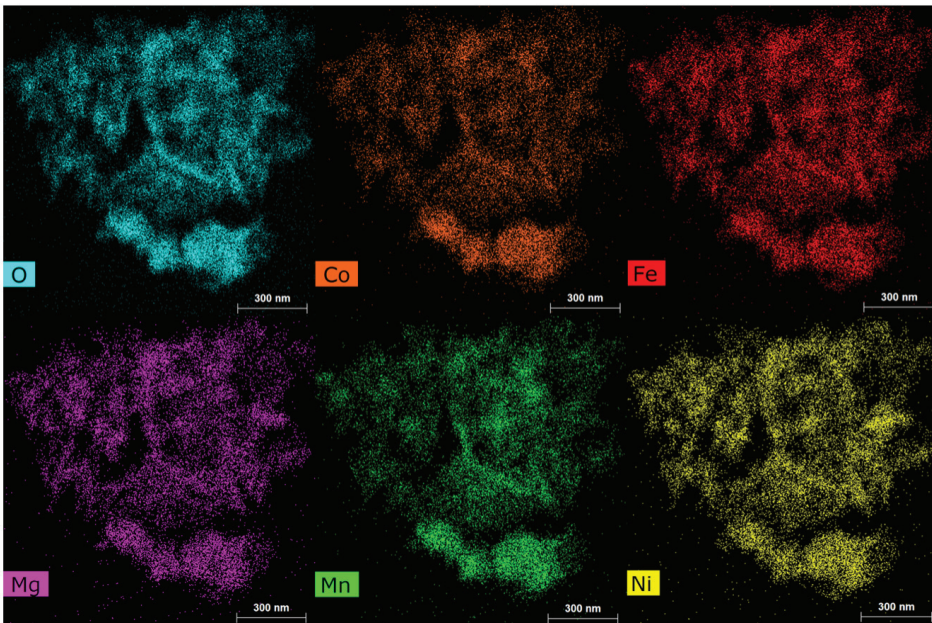
**“Water splitting is a chemical reaction that takes water and breaks it down into its elemental components.”**

You might find yourself saying “That sounds fantastic, why isn’t it being used everywhere?” The best water-splitting catalysts are ruthenium oxide ( $RuO$ ) and iridium oxide ( $IrO$ ) [2]. Ruthenium cost \$475 per ounce and iridium cost \$4,800 per ounce. For perspective gold cost \$1,800 per ounce [3]. The reason why these metals are so expensive is because of how rare they are, so the prices of these metals would likely go up, assuming the supply doesn’t run dry. Thus, cheap and earth-abundant water-splitting catalysts are needed.

## What the Research is About

There is a relatively new class of materials called high entropy metal oxides (HEOs). Normally in a crystal structure enthalpy is the driving force of formation but in the case of these materials, it is entropy that is the driving force of formation. The first HEO was made in 2016 [4]. HEOs are composed of multiple metal cations in equal molar proportions (figure 1). Past works have shown that HEOs are promising candidates for water-splitting catalysts. Which is contributed to their unique complex surfaces and stability [4].

Most of the time these materials are made with a top-down approach, which is like trying to build a brick by blowing up a building. The aim of this work is to make HEOs from a bottom-up approach, which is like trying to make a brick with mold and clay. This in theory allows for greater manipulation of the size and shape



**Figure 2** A TEM-EDX image of the sample which shows a uniform distribution of elements.

of the individual HEO crystals. Past work has shown that shape (faceting) can drastically affect catalytic activity [5].

Our group is really good at manipulating metal oxides that are in a rock-salt crystal structure (which is just a name for the orientation of metal cations and oxygen anions). What we would like to see is if the toolbox we have developed to manipulate regular metal oxides in a rock-salt crystal structure works on HEOs.

## Research Goals

The goals of this project are as follows. To make an HEO from earth-abundant metals. To make this HEO into a rock-salt crystal structure. To manipulate the faceting (the shape) of the rock salt crystal structure (using the toolbox we have developed on other similar structures) to increase the catalytic activity of the HEO. To use this material as a catalyst for water splitting.

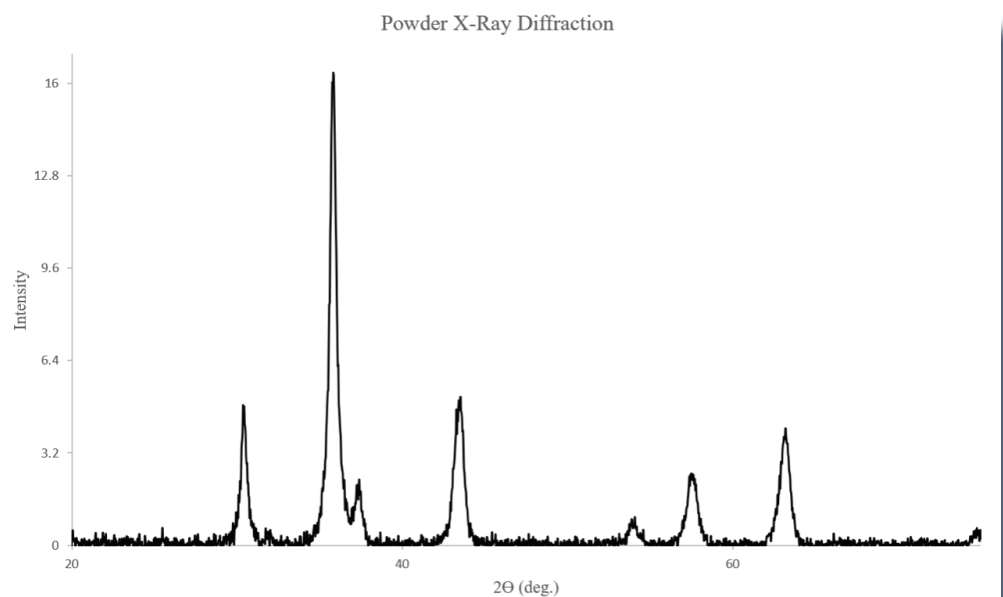
## Results So Far

In an HEO, it would be expected that the elements take on a formation that maximizes entropy, which we can interpret as meaning that the elements will be homogeneously distributed in the sample. To determine if this is the case we used a TEM-EDX, which

is a powerful electron microscope technique that is capable of elemental mapping on the nanometer range.

**“In an HEO it would be expected that the elements take on a formation that maximizes entropy.”**

Our TEM-EDX result is as exactly as we expected (figure 2). This is great news but it is still too early to celebrate. TEM-EDX is a little like an X-ray scan in the sense that it is a 2D representation of a 3D object, inherently losing some information. In theory, each metal could have formed individual oxides and stacked themselves like a layer cake. If the system was truly an HEO we would expect there to be only one phase and we need a way to determine how many phases (layers in the layer cake) there are in the sample. For this, we used powdered X-ray diffraction (PXRD), which is a technique that works by shining



**Figure 3** Powder X-ray diffraction, suggests formation of a single phase.

an X-ray source through a sample. If the sample had one phase, we would expect one set of peaks which describes that phase. If it was multiple phases (like a layer cake) we would expect multiple sets of peaks. The PXRD diffractogram we took (Figure 3) indicates a single phase.

I started this project last fall and I have successfully finished the first goal of this project, making an HEO from earth-abundant metals. I used iron, magnesium, nickel, manganese, and cobalt, which are some of the most earth-abundant transition metals on the planet, and most of which can be found naturally at the beach and in your home.

## Future Work

Only the first goal was achieved, naturally, we are working on the rest

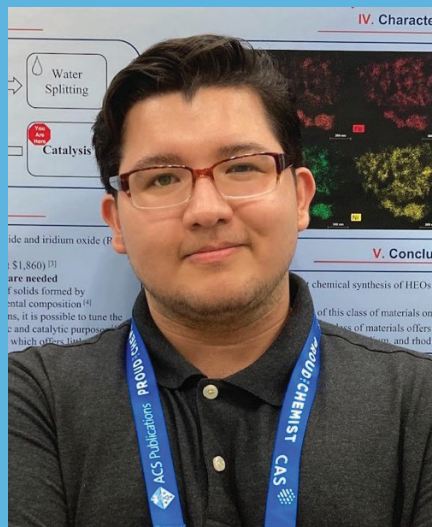
of them. Specifically, the main focus has been trying to make an HEO form earth-abundant materials in a rock-salt crystal structure.

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Zek Kelly graduated from Colorado School of Mines with a B.S. in Chemistry. Zek has done research in both the Chemical & Biological Engineering and Chemistry & Geochemistry departments. He is a proud Achievement Rewards for College Scientists (ARCS) and Endowed American Chemical Society (ACS) Scholar. He had the pleasure of presenting at the Fall 2020 Undergraduate Research Symposium, at the State Capitol for STEM

Poster Day, and the Spring 2023 National ACS Conference. He has been awarded the E-days Engineer Award and the Outstanding Chemistry and Service Award for Superior Performance in Academics and Service. This year he has worked with Dr. Ryan Richards in the Chemistry department making high-entropy oxide nanomaterials. Zek will attend Northwestern University for a Ph.D.