

# MAKING FUEL FROM WATER AND CO<sub>2</sub> : THE IMPORTANCE OF STABILIZING HIGHLY REACTIVE NICKEL CATALYSTS IN NEUTRAL pH SOLUTION

## KEYWORDS

computational modeling; Earth-abundant catalysts; soft X-ray absorption spectroscopy; water oxidation; CO<sub>2</sub> electrolyzer

## FOCUS OF STUDY

This study compared computational predictions with experimental measurements to demonstrate the importance of generating highly reactive nickel species (Ni<sup>4+</sup>) for the catalytic conversion of water into oxygen in neutral pH solution.

## BACKGROUND

The conversion of CO<sub>2</sub> into carbon-based fuels and products (such as methane, carbon monoxide, methanol, ethylene, etc.) could help reduce our dependence on fossil fuels while simultaneously mitigating net CO<sub>2</sub> emissions through a CO<sub>2</sub> recycling process. To do this, water must first be converted into oxygen, which releases the electrons and protons needed to turn CO<sub>2</sub> into artificial fuels. However, an ongoing problem is the lack of catalysts for water oxidation that operate efficiently under neutral-pH conditions – the ideal conditions for CO<sub>2</sub> conversion – resulting in the need for large energy inputs to run the overall process with any reasonable rate of production.

To reduce this energy requirement and improve efficiency and turnover at neutral pH, Professor Ted Sargent (CIFAR Program Director, Bio-inspired Solar Energy; University of Toronto) and colleagues recently took an atomistic approach to this problem.<sup>1</sup> The researchers posited that the

key is the generation of highly reactive metal sites (specifically highly charged nickel species (Ni<sup>4+</sup>)) created with minimal electrical energy input to drive electrochemical water oxidation in neutral pH with high efficiency. Previous studies have reported high conversion rates in neutral pH for metal catalysts that contain phosphorus,<sup>2</sup> which Sargent and co-workers reasoned could help promote the formation of highly reactive metal species in their own catalysts. Adding other metals (such as iron (Fe) and cobalt (Co)) can also increase the activity and efficiency for water oxidation,<sup>3,4</sup> suggesting another key to optimizing these materials.

To that end, the researchers ran a series of computational simulations to understand the effect of the presence of phosphorus and other metals on the stability of nickel structures and specifically on the presence of Ni<sup>4+</sup>. They then compared the results of these computational studies with real experimental measurements using an advanced

technique called *in situ* soft X-ray absorption spectroscopy (sXAS) to look for these important, highly reactive nickel centres in their materials under operational conditions. By combining their optimized nickel-containing water oxidation catalyst with a known, highly active CO<sub>2</sub> reduction catalyst,

the research team was able to demonstrate a fully-functioning CO<sub>2</sub> electrolyzer operating in neutral pH electrolyte with high efficiency, low electrical energy input and long-term stability for the production of artificial fuels.

## STUDY DESIGN AND METHODS

The computational simulations were performed using a technique known as density functional theory (DFT), modified with additional corrections (DFT + U) to improve accuracy. Various model structures - Ni(OH)<sub>2</sub>, β-NiOOH and NiO<sub>2</sub> - were simulated both in their pure state and with varying amounts of impurities (or dopants) added (including other metals (Fe and Co) as well as phosphorus) to determine the effect of these other elements on the stability of nickel sites in these structures.

The actual nickel catalysts tested experimentally were created using a modified version of a procedure known as a “sol-gel” technique, which allowed the researchers to quickly and easily add in different amounts of metals (Fe and Co) as well as phosphorus in order to mix and match different compositions for testing. The catalysts were then subjected to X-ray

measurements *in situ* using a flow cell to look for the presence of highly reactive Ni<sup>4+</sup> centres, in order to understand how the presence of these various impurities affect the stability of Ni<sup>4+</sup> species during actual operation and to compare the results to the theoretical models.

Electrochemical tests were used to determine the overall activity and efficiency of these catalysts in promoting the water oxidation reaction in neutral pH, and the results were compared to the leading precious metal oxide water oxidation catalyst, iridium(IV) oxide (IrO<sub>2</sub>). The highest performing catalyst was then combined with recently reported<sup>5</sup> gold nanoneedles (used as a CO<sub>2</sub> reduction catalyst) to create a fully-functioning CO<sub>2</sub> electrolyzer that converts water into oxygen and CO<sub>2</sub> into carbon monoxide.

## FIGURE



Image from one of the authors showing the electrochemical cell used to test the nickel containing catalysts for the conversion of CO<sub>2</sub> and water into carbon monoxide and oxygen.

## KEY FINDINGS

- Computational modeling (DFT + U) and theoretical calculations demonstrated that highly reactive Ni<sup>4+</sup> sites are stabilized and favoured in materials that also contain impurities (Fe, Co and phosphorus).
- Calculations also suggested that both Fe<sup>4+</sup> and Ni<sup>4+</sup> could act as active sites for water oxidation due to preferential alignment of their electronic states.
- Soft X-ray absorption spectroscopy (sXAS) measurements performed under operating conditions revealed the presence of Ni<sup>4+</sup> for the synthetic catalysts containing metal dopants (NiCoFe sample), with significantly more Ni<sup>4+</sup> observed when phosphorus is also present (NiCoFeP oxyhydroxide sample). The results are consistent with the computational modeling.
- Electrochemical testing revealed that the NiCoFeP oxyhydroxide sample outperformed all other samples in converting water into oxygen (including the standard high-performing commercial IrO<sub>2</sub> catalyst). Long term tests revealed stable activity of this catalyst over 100 hours of operation with essentially no loss in efficiency (>97% throughout).
- The high-performing NiCoFeP oxyhydroxide catalyst was combined with gold nanoneedles that convert CO<sub>2</sub> into carbon monoxide, in order to create a CO<sub>2</sub> electrolyzer that efficiently transforms water and CO<sub>2</sub> in neutral pH electrolyte. The system required a low operating potential of 1.99 V to maintain a high current density of 10 mA/cm<sup>2</sup> for approximately 2 hours with essentially no loss in activity.

## CONCLUSION AND IMPLICATIONS

This study confirmed the importance of metal and phosphorus dopants in stabilizing highly reactive nickel sites in mixed metal catalysts for the conversion of water into oxygen. Theoretical calculations using DFT and experimental measurements using sXAS both confirmed the expected presence and stability of Ni<sup>4+</sup> under operating conditions, which is the key to achieving high activity in these materials. The NiCoFeP oxyhydroxide catalyst beat out all other tested catalysts, including the best commercially-available IrO<sub>2</sub> catalyst, demonstrating the first Earth-abundant catalyst to consistently outperform a precious-metal oxide catalyst for water oxidation in a pH-neutral medium. This catalyst was found to perform consistently for almost 100 hours with essentially no loss in efficiency, and combined with a state-of-the-art CO<sub>2</sub> reduction catalyst could convert water and CO<sub>2</sub> into oxygen and carbon monoxide at an overall

efficiency of 63% with essentially no loss in activity over long periods of testing.

This study has important implications for the commercial development of CO<sub>2</sub> electrolyzers. In particular, the optimization of a water oxidation catalyst in neutral pH electrolyte is an important step towards decreasing the energy required to operate these electrolyzers, which traditionally require two different electrolytes separated by a membrane that can create unwanted resistance across the system. In addition, the long-term stability demonstrated by these cheap, Earth-abundant and efficient catalysts is key to developing an industrially reliable electrolyzer system. Such systems in their fully developed form could see applications across the industrial landscape, from refineries and manufacturing plants to refueling stations and even one day in private residences.

## REFERENCES

**Ted Sargent** is Professor of Electrical and Computer Engineering at the University of Toronto, and Director of the CIFAR Program in Bio-Inspired Solar Energy. He is the lead principal investigator on this study. This work was supported by CIFAR catalyst funding.

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## RESEARCH BRIEF AUTHORSHIP

Jonathon Moir, PhD

Research Analyst

Canadian Institute for Advanced Research (CIFAR)

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MaRS Centre, West Tower  
661 University Ave. Suite 505  
Toronto, ON M5G 1M1

[www.cifar.ca](http://www.cifar.ca)