

# The Storage of Marine Hydrokinetic Power through Hydrogen Production

June 2021

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Prepared for  
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## Project Summary

Marine hydrokinetic (MHK) power is likely to play a crucial role in future energy diversification and remote energy supply efforts. Providing a means of direct energy storage for MHK power would provide additional benefits to applications in ship microgrids and remote communities. Hydrogen (H<sub>2</sub>) has long been pursued as a means of green energy storage and can be generated through electrolysis of water in an electrolyzer. However, electrolyzer technology for H<sub>2</sub> production is currently only possible on the commercial scale using fresh water, a precious resource in our society. The direct electrolysis of seawater would alleviate the freshwater constraints for a new H<sub>2</sub> feedstock and a seawater-fed electrolyzer could be powered locally at an MHK platform. Several technical challenges exist before efficient direct seawater electrolysis can be realized. This project was designed as a demonstration of efficient direct seawater electrolysis that limits chlorine evolution, avoids use of platinum (Pt) group metals, and overcomes cathode fouling over long service times.

## Introduction and Project Description

Renewable H<sub>2</sub> is becoming widely viewed as a necessity in our evolving energy sector as its expanded use in fuel cells can cut total US CO<sub>2</sub> emissions in half by 2050, based on analysis by the Energy Information Agency, National Academies using Argonne National Laboratory's *Greenhouse gases, Regulated Emissions and Energy use in Transportation* (GREET) model. The use of H<sub>2</sub> fuel cells can have direct applicability in ship microgrids and remote communities. Three primary methods are currently used for H<sub>2</sub> production: steam-methane reforming, chloro-alkali processing, and electrolysis, with all methods incurring a large energy and cost penalty up front. Steam-methane reforming uses hydrocarbons (natural gas) as a feed stock and fuel source for combustion to supply the necessary energy (i.e.,  $\Delta H = 206.2$  kJ/mol CH<sub>4</sub>) for the reforming reactions to proceed. Steam methane reforming is not a long-term viable solution due to the consumption of fossil fuels and the generation of greenhouse gases. The chloro-alkali process can utilize seawater but requires the use of carbon-based materials and long-term stability issues are a concern.

By comparison, electrolysis is considered a "greener" H<sub>2</sub> production pathway but may also contribute to greenhouse emissions if energy requirements are sourced from processes that generate CO<sub>2</sub> (e.g., coal and natural gas).

Current electrolysis systems require >50 kWh/kg of H<sub>2</sub> produced at ~70% efficiency using freshwater.

Demand for fresh water across the globe is expected to grow by 55% by 2050 [1] and assigning a portion of this to hydrogen production would further tax demand. Thus, moving to direct seawater electrolysis would remove the need for a freshwater feed for electrolysis and produce renewable hydrogen without taxing valuable freshwater reserves. The cost associated with H<sub>2</sub> generation from a seawater-fed electrolyzer can be decreased, moving toward the DOE target of \$2/kg H<sub>2</sub> [2], by powering the electrolyzer from excess energy at an MHK platform or use of a dedicated MHK system. The electrolytically generated H<sub>2</sub> can be

stored or cost-effectively transferred through non-metal pipelines [3]. The implementation of electrolytically generated  $H_2$  from seawater has been limited due to lower efficiency in seawater (e.g., due to chemical fouling of the electrodes and system biofouling), harmful anode product generation during electrolysis [e.g. chlorine ( $Cl_2$ ) competition during oxygen ( $O_2$ ) evolution], the high cost of Pt-group metal electrodes and infeasibility of off-shore deployment.

To address these technical challenges, several goals were set out at the start of the project:

- 1) Identify non-Pt group anode electrode materials that can sustain efficient electrolysis while minimizing  $Cl_2$  evolution in chloride containing environments,
- 2) Assess cathode fouling in raw seawater and methods of *in-situ* cleaning,
- 3) Perform longer-term testing of candidate electrode materials in a continuous seawater feed at the Marine Sciences Laboratory.

## Results and Accomplishments

Candidate anode materials were based on manganese (Mn) – molybdenum (Mo) (1.5 mol%) catalysts, which would provide stability in neutral to acidic conditions that would be expected in the anodic chamber of a seawater-fed electrolyzer. When mounted on a metallic substrate, the Mn-Mo catalysts have limited catalytic activity on their own. Thus, the candidate anode materials were mounted onto a titanium (Ti) electrode with an iridium oxide ( $IrO_2$ ) conductive layer between the substrate and the Mn-Mo catalyst. The  $IrO_2$  layer was deposited onto an etched Ti substrate using thermal decomposition and it was determined that electrodeposition of the Mn-Mo catalyst onto the  $IrO_2$  produced a stable and uniform catalyst. The Mn-Mo anodes had a cracked mud structure with minimal exposure of the underlying  $IrO_2$  layer as shown in Figure 1.

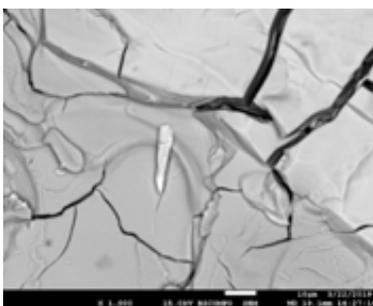


Figure 1 - Representative Mn-Mo anode surface showing a cracked-mud structure. Multiple depositions were used to limit exposure of the underlying  $IrO_2$  layer.

Electrochemical testing of the anodes were performed in both Hoffman apparatuses and H-cells in a three-electrode configuration using a Pt-counter electrode and a silver (Ag)/AgCl reference electrode using both simple chloride salts and raw seawater as electrolytes.  $Cl_2$  generation (and conversion to  $OCl^-$ ) was measured using the iodometric titration method. Baseline performance of Pt and  $IrO_2$  measured  $O_2$  conversion efficiencies of ~70 % with  $Cl_2$  evolution. Mn-Mo anodes measured an improvement to 85-90% efficiency.

To further improve anode performance, a series of transition metal dopants were added to the Mn-Mo (up to 5 mol%) to assess enhancements to overall efficiency and Cl<sub>2</sub> suppression. The dopants included Fe, Sn, W, Co, and Ru. Through testing in both simple chloride salts and raw seawater, the Mn-Mo-Ru catalysts were observed to have ~1.5× improvement in anodic activity over the second-best anodes (Fe and W) while sustaining > 94% O<sub>2</sub> efficiency (see Figures 2 and 3). The Ru generates a more active anode for O<sub>2</sub> evolution which facilitates increased H<sub>2</sub> generation at the cathode while minimizing Cl<sub>2</sub> evolution. Work was done to optimize the Mn-Mo-Ru catalyst through adjusting the deposition pH and duration of electrodeposition.

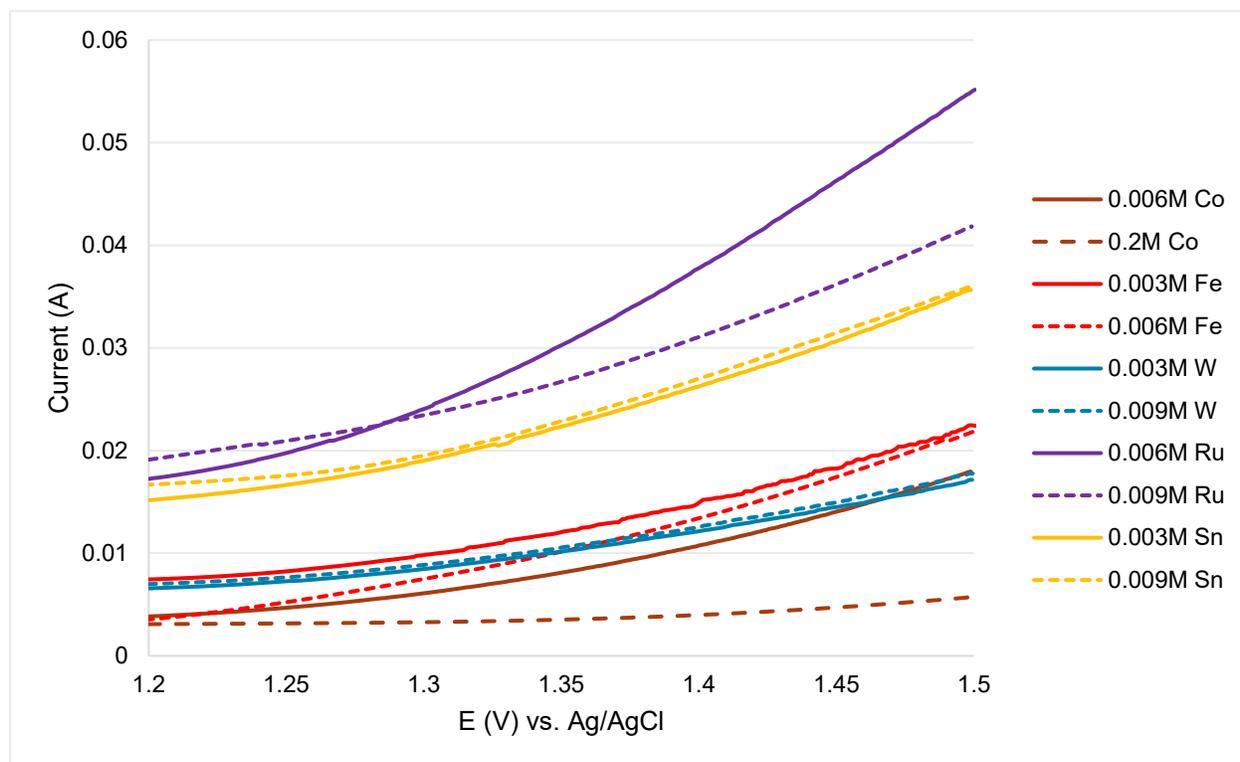


Figure 2 - Linear sweep voltammogram of the best performing catalysts in raw seawater at a scan rate of 0.5 mV/s.

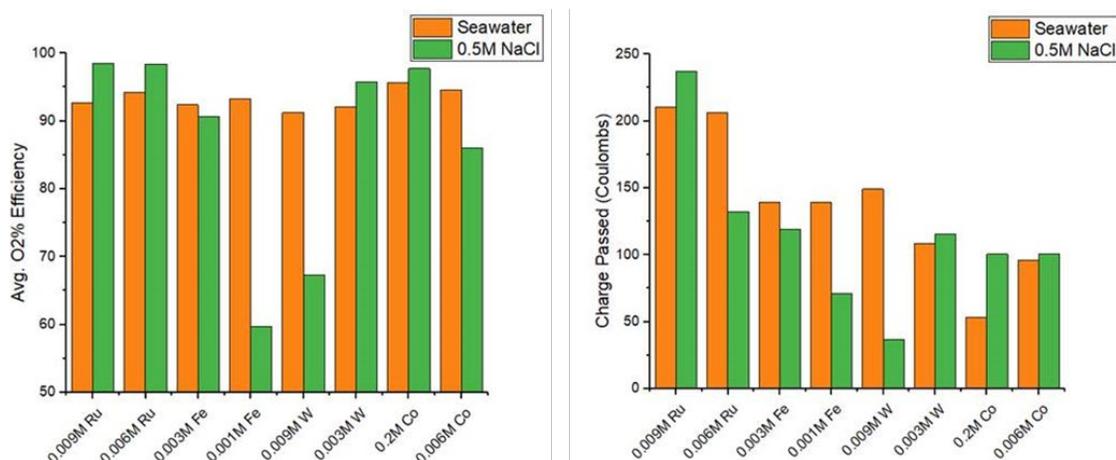


Figure 3 - Summary of best performing catalysts for a) avg O<sub>2</sub> efficiency and b) charge passed in seawater and 0.5 NaCl at E = 1.5 V.

During seawater electrolysis, deposits were observed on the cathode. Analysis of the deposits found them to contain ~93 wt% Mg, ~6 wt% Ca, 1 wt% Na and other minor components. This deposition would be problematic with in-service conditions. Two means of cleaning the cathode were found to be successful: 1) pH control by adding the acidic anode solution into the cathode compartment and 2) electrochemical removal using an anodic current applied to the cathode electrode. Both approaches could be applied within an electrolyzer. Due to the ease of removal, the collected material can be valuable in a co-generation scenario as a source of Mg, or other minor species present in the deposit.

Long-term electrolysis measurements were made in a continuous seawater feed to assess electrode stability. MnMo, IrO<sub>2</sub>, and Mn-Mo-Ru electrodes were tested for up to 7 days of electrolysis in the continuous flow seawater flumes at the Marine Sciences Laboratory, Figure 4. Minor fluctuations in performance were observed; < 10 mA transients in chronoamperometric measurements and < 5 mV transients in chronopotentiometric measurements, confirming stable performance. Some flaking was observed from the electrodes in the tests and a cathodic Mg deposit was observed (Figure 5), but preliminary laboratory studies have shown a Nafion coating to stabilize the catalysts.

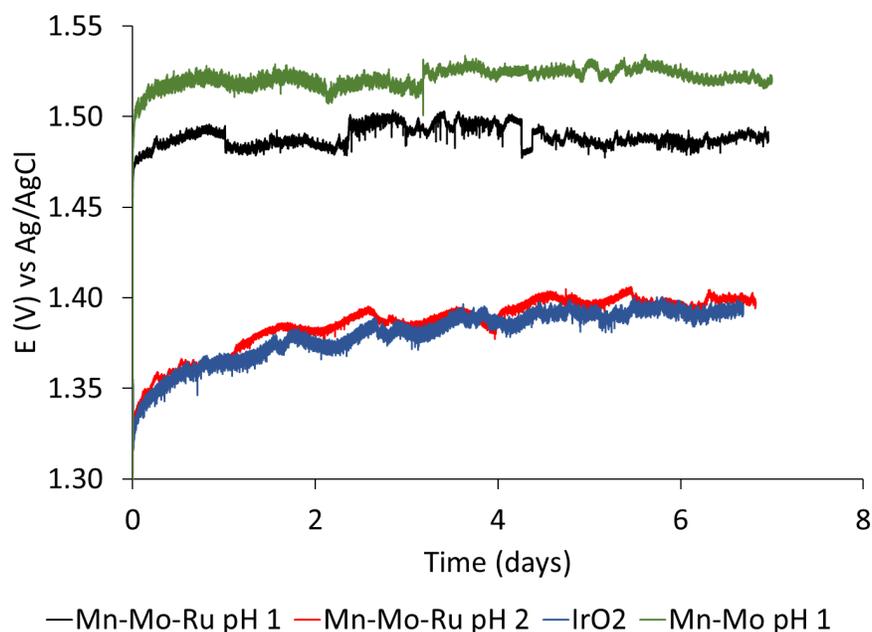


Figure 4 - Chronopotentiometric behavior of Mn-Mo-based electrodes in a flowing seawater flume at 10 A/cm<sup>2</sup> applied current



Figure 5 - Photo of the Mg-rich cathode deposit observed in seawater testing.

In summary, the project addressed several pertinent issues related to raw seawater electrolysis. A Mn-Mo- Ru catalyst has been shown to have high catalytical activity with low  $\text{Cl}_2$  evolution and stability in bulk seawater. This catalyst can be further optimized through co-doping or introduction of a hierarchal surface structure. In-service cathode fouling can be overcome through pH or electrochemical control, and the removed deposit may contain valuable elements. The full summary of this work is expected to be published in a special issue of *Applied Sciences* in FY21. Follow on funding has been supplied through the DOE Water Power Technology Office's Seedling Program with continued growth in FY20 and FY21. Future work should focus on coupling the anode material with earth abundant cathode materials, methods for catalyst deposition onto porous polymer membranes used in commercial electrolyzers, and performance under simulated MHK power sources.

## References:

- [1] UNESCO, WWAP (United Nations World Water Assessment Programme). 2015. The United Nations World Water Development Report 2015: Water for a Sustainable World. Paris, UNESCO.
- [2] [www.energy.gov/eere/fuelcells/doe-technical-targets-hydrogen-production-electrolysis](http://www.energy.gov/eere/fuelcells/doe-technical-targets-hydrogen-production-electrolysis)
- [3] D. DeSantis, B. D. James, C. Houchins, G. Saur, and M. Lyubovsky, "Relative Cost of Long-Distance Energy Transmission by Electricity vs. Gaseous and Liquid Fuels", submitted.

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