# Catalyst Renewal Electroplating: Design, Investigation, and Testing (CREDIT)

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## INTRODUCTION

Oxygen recovery from carbon dioxide is necessary to ensure full recovery of metabolic resources during human spaceflight. Doing so enables greater mission distances and extends our range out into the stars. One way to recover oxygen from carbon dioxide is through the Bosch process, where carbon dioxide and hydrogen are converted into water and carbon. The Bosh process offers theoretically 100% metabolic oxygen and feedstock hydrogen recovery, well above the long-duration mission goal of >75% $O_2$ recovery.

However, the Bosch process is complicated by significant carbon fouling on the catalyst (Figure 1), which causes issues from clogs to quenching the reaction by no longer allowing the gas to interact with the catalyst underneath.

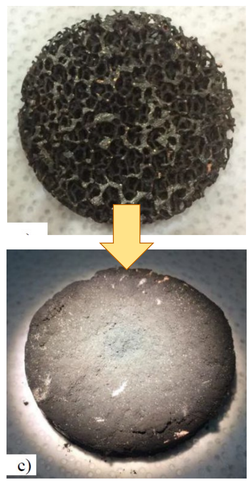


**Figure 1:** Catalyst fouling

A variety of methods have been tested to remove the carbon build up, but it tends to form bricks in the reactor that must be forcefully broken up to be removed and clings to the surface of the catalyst. The technique employed for catalyst renewal in this project is reclaiming the catalyst from the carbon with digestion and electroplating utilizing an Ionic Liquid (IL). Iron, the typical Bosch catalyst, readily dissolves in some ILs (Figure 2) and then electroplates out of it onto a substrate– earlier work has shown that [EMIM][HSO4], 1-Ethyl-3-methylimidazolium hydrogen sulfate, can eat the iron out from under the Bosch carbon layer. After the carbon and iron are redissolved into the IL solution, the carbon be filtered out, leaving the iron to be re-plated onto internal reactor substrates. This creates a closed-loop catalyst renewal process (Figure 3) to enable the Bosch process.

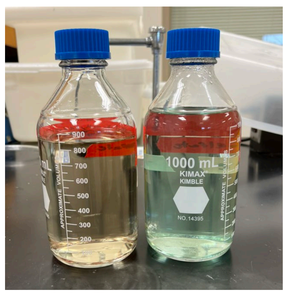



**Figure 2:** Yellow stock 1-M Aqueous [EMIM]HSO4] next to the same stock solution after Fe digestion, turning it green.

## OBJECTIVES

CREDIT seeks to further develop the electroplating aspects of the ionic-liquids-based carbon formation reactor. To do so, this project will achieve four major objectives:

- *Improve the test setup from prior work.*
- *Perform a material selection study for the electrodes.*
- *Perform a cell configuration study.*
- *Conduct plating-digestion cycle testing.*

**Work is ongoing at the time of this event, so this poster focuses on the test material selection study.**

## EXPERIMENTAL METHODS

A key electroplating study is cyclic voltammetry (CV), which is an electrochemical method that enables the examination of how electrocell current changes with an applied potential. In CV, the applied potential is swept from the open-cell potential (OCP) to a potential defined by the operator, and current is measured. The current indicates the reactions taking place inside of the cell, including parasitic reactions such as hydrogen evolution.

To assess materials for use in a Bosch reactor, an electrochemical cell was designed and built, shown in Figure 4, for performing CV on several cathode materials to best gauge material suitability for IL-Fe electroplating. All materials selected for the study were compatible with the 550-700 °C temperatures used for the Bosch reactions; key to this is creating an anode able to withstand these temperatures, as COTS options are not available.

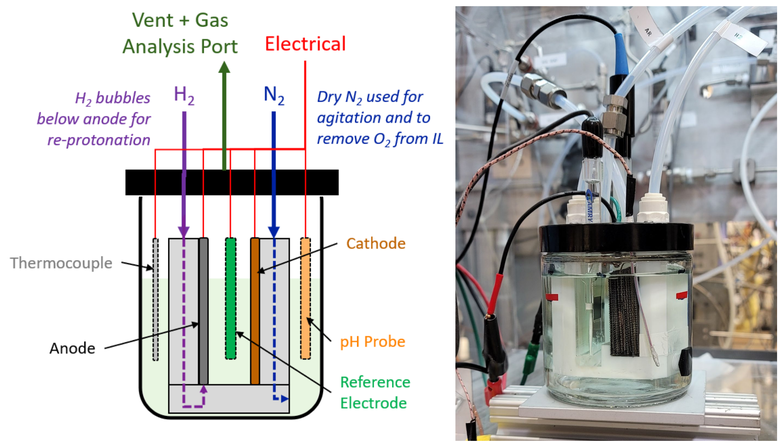



**Figure 4:** (Left) A diagram of the electrochemical cell. (Right) The electro-chemical cell setup fully installed. To mitigate hazards associated with the hydrogen, the cell was operated in a nitrogen-purged enclosure.

## ANODE FABRICATION

Platinum is the material of choice for anodes in many electrocells, including this one, due to its electrochemical properties and non-reactivity. For electroplating, an anode's design is geared towards enabling the surface of the platinum to interact with hydrogen and the solution in order to efficiently re-pronate the solution and avoid degradation. Typical electroplating setups use commercially-available High-Load Gas Diffusion Electrodes (HLDGEs), which use Platinum black, but they are built on a plastic substrate incompatible with Bosch temperatures. Thus, a novel anode had to be fabricated.

Since platinum is a high-cost material, cost reduction was a high priority. Rather than using a solid platinum substrate, an ink containing platinum was painted and baked onto several pieces of a 304 stainless steel mesh. Individual mesh squares were stacked and tied together, resulting in platinized mesh block with high surface area, shown in Figure 4. The resulting anode, costing roughly a hundred dollars in materials, met performance expectations in the electrocell, replacing an HLDGE and pure platinum foam or mesh that, of equal material, would cost a couple thousand dollars.

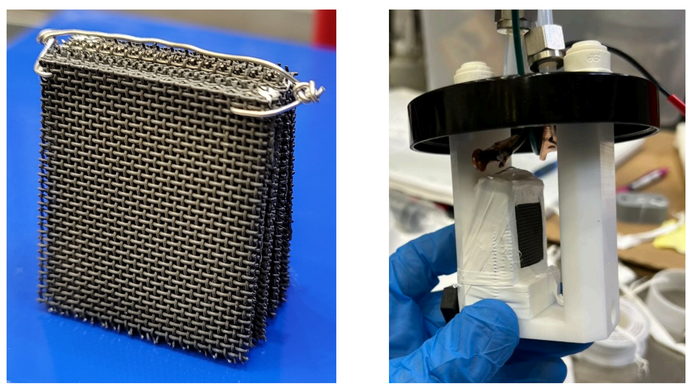


**Figure 5:** (Left) The anode mesh stack. (Right) The anode masked and installed in the electrochemical cell.

## CATHODE MATERIALS

**Table 1: Cathode Materials Investigated**

| Material | Selection Rationale |
|---|---|
| ***Round 1 Testing*** | |
| Copper | Excellent cathode for electroplating; good history of use in prior project efforts |
| Tungsten | Potentially IL compatible and easily available |
| 304 Stainless Steel | Compatible with IL and potentially easy Fe plating due to material similarity |
| Low-Carbon Steel (A36) | Potential for exceptionally easy plating of Fe that offsets IL digestion (known incompatibility) |
| ***Round 2 Testing (Additions)*** | |
| Amorphous (Glassy) Carbon | Slow hydrogen evolution kinetics; good history of use in other electroplating experiments |
| Microporous carbon | More readily available than amorphous carbon while potentially holding the same strengths |

## DATA & DISCUSSION

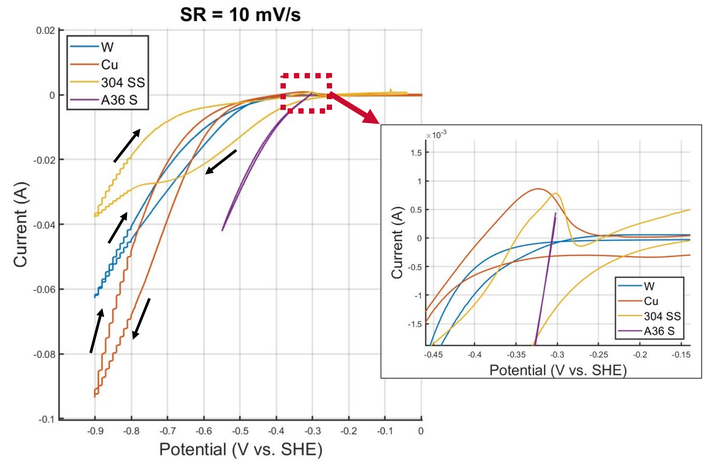



**Figure 6:** CV results for Round 1 testing with Tungsten (W), Copper (Cu), 304 Stainless Steel (304 SS), and low-carbon steel (A36 S). (Inset) A close-up of the plots near the open-circuit potential for each setup. A high slope or the presence of a "hump" in the curve represents a successful plating run.

Several CV experiments were run using the electrocell test setup and newly fabricated anode. The cathode material was varied, per Table 1. Figure 6 shows the results from the first round of tests, where Tungsten (W), Copper (Cu), 304 Stainless Steel (304 SS), and low-carbon steel (A36 S) were tested. The CV curve begins at the electrocell OCP, which is measured at the start of each experiment, and swept negatively to -0.9 V vs. SHE (standard hydrogen electrode), where iron electroplating theoretically should occur. After reaching -0.9 V, the potential sweeps back to the OCP, which was roughly -0.2 to -0.3 V for each configuration. Arrows on the plot in Figure 6 indicate the forward and backward sweeps.

The shape of the CV curve indicates several factors; "dips" or "humps" in the curve indicate ongoing reactions, and depending on the potential at which this occurs, this can indicate if this is a plating reaction or another parasitic reaction, such as hydrogen evolution evident in the 304 SS curve by the dip near the bottom of the plot.

The surest sign of quality electro-plating is on the return sweep, where a hump will appear as the iron is electropolished back into solution *if* it was electroplated during the run; if it was not, then no hump will be present.

The inset in Figure 6 shows that tungsten did not electroplate, and thus it was eliminated. The A36 S behaved in a difficult-to-characterize manner, so it was also eliminated. Copper later showed long-term IL in-compatibility, and so 304 SS was the best candidate tested.

A second run was conducted with 304 SS and carbon electrodes to study the hydrogen evolution reaction; carbon electrodes have slow hydrogen kinetics and thus rarely suffer from that parasitic reaction. This run confirmed that 304 SS, despite the parasitic hydrogen reaction, remains the best choice for the cathode, as it showed a stronger polishing peak than the carbon electrodes (Figure 7).

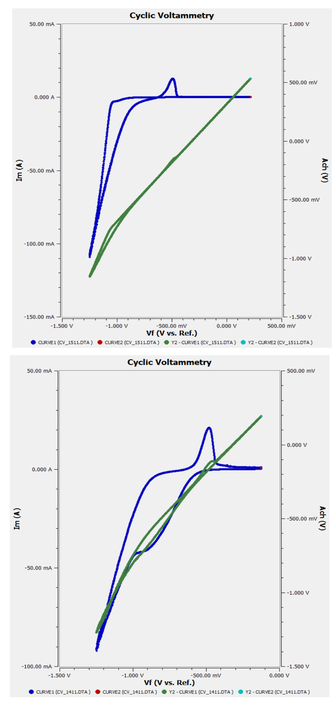



**Figure 7:** (Left) CV using Glassy Carbon. (Right) CV using 304 SS. Note different y-axes on the plots.

## FUTURE WORK

The stainless steel electrode offers the best combination of factors, with IL compatibility and clear success of electroplating. Future work will address configuration and scaling questions, building towards application in a Bosch reactor capable of the full renewal cycle.

*ACKNOWLEDGEMENTS: This work was possible thanks to TIP24 funding and support from the NSTGRO program.*