Electrochemical Reformation of Methane to High Purity Hydrogen
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1. Motivation and Project Goals

The continued rise in domestic production of natural gas (methane) has initiated a growth in research centered about the efficient conversion of methane to useful precursors and commodity chemicals and fuels. Industrial scale processes for generating hydrogen, both a valuable fuel a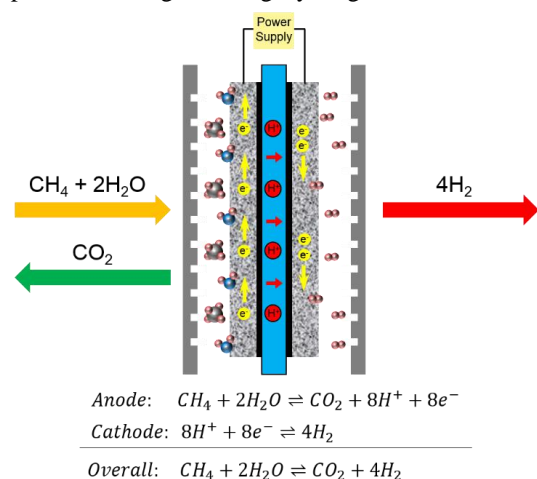nd chemical precursor, from methane are characterized by high capital and operational costs and are neither amenable to variability of scale nor on-site operation. Here we propose the production of electrolytically pure hydrogen from methane through an electrochemical reformation process in which methane is oxidized at the anode of a proton exchange membrane (PEM) electrolyzer and the abstracted protons are recombined on the cathode evolving hydrogen as shown in the device schematic in Figure 1. The complete electrooxidation of methane to carbon dioxide will be driven by a unique composite electrocatalyst architecture where the interface of a metallic catalyst will be modified by a functionalized metal organic framework (MOF) thin film. Metal centered molecular catalyst functionalities imbedded within the MOF in addition to the high methane sorption capability will act to destabilize the C-H bond and drive insertion of -O- with water as the source of oxygen, forming a CH_3O* intermediate which will be readily oxidized to CO_2 on the metallic electrocatalyst surface. The key advantage of the proposed composite electrocatalyst architecture lies in the vast library of organic and molecular catalytic species that can be incorporated into the MOF thin film, facilitating the manipulation of catalyst functionality, activity, selectivity, and stability. Use of a PEM electrolysis device will allow on-site production of high purity, high pressure hydrogen from methane at a broad range of scales with on-demand rate variability.

Anode: $\quad CH_4 + 2H_2O \rightleftharpoons CO_2 + 8H^+ + 8e^-$
Cathode: $\quad 8H^+ + 8e^- \rightleftharpoons 4H_2$
Overall: $\quad CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$

Figure 1: *Schematic of methane electrochemical reformation in a PEM electrolyzer including half-cell and overall reactions.*

2. Results

The first phase of this project has focused on the formation of MOF thin films on metal electrodes. The goal here has been to develop techniques to seed the surface of a metal electrode or catalyst to initiate targeted growth of the MOF, creating a thin and conformal coating. Efforts were focused to optimize coverage to ensure no metal was exposed and to minimize MOF film thickness. The MOF will impose a diffusional barrier for the methane and carbon dioxide, so minimization of thickness is critical to limit mass transport resistances in the electrolyzer. We tested two methodologies for the directed growth of MOF thin films: (1) in-situ reduction of $Cu(OH)_2$ thin films, and (2) in-situ galvanic displacement of Cu initiated by Ag^+ ions. Figure 2 contains an SEM of a Cu(BDC) MOF thin film grown on a Cu electrode through methodology (1). Here the in-situ electrochemical reduction of a thermally grown $Cu(OH)_2$ thin film provides the source of Cu^{2+} ions that act as nodes of the MOF. An excess of BDC linker is placed in the growth electrolyte. By limiting the concentration of Cu^{2+} ions and confining them to the interface of the electrode and electrolyte, we both slow the growth of the MOF, limiting its thickness, and confine the growth to the surface of the electrode. The second methodology was not as successful. In this technique, Cu^{2+} ions are evolved into solution at the electrode surface by the galvanic displacement with Ag^+. Small patches of large Cu(BDC) MOF crystals resulted rather than the desired thin film, Figure 3.
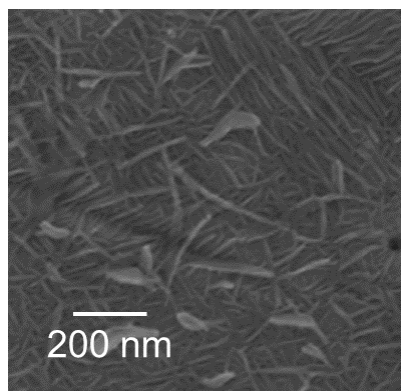

Figure 2: *SEM of Cu(BDC) MOF on Cu electrode induced by method (1): reduction of $Cu(OH)_2$.*

As a risk mitigation strategy for the MOF thin films, we have also successfully synthesized catalyst nanoparticles, specifically Pd nanoparticles, within MOF particles, Figure 4. Due to the demonstrated electrical
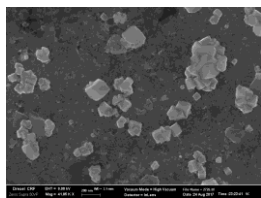
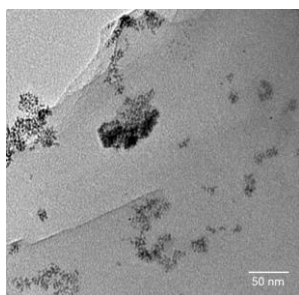**Figure 3:** *SEM of Cu(BDC) MOF on Cu electrode induced by method (2): Ag galvanic displacement.*

conductivity of the MOFs selected, see following paragraph, the particles located within the MOF particles are electrochemically active. The advantages of this technique are the control of loading, the high interfacial area between catalyst particles and MOFs, and the ability to readily scale-up the synthesis.

Key to the fulfillment of the proposed catalyst design is an electrochemical participation of either the metal ion nodes of the MOF or metal centered porphyrins that have been substituted into the framework. For this participation, the MOFs must be sufficiently electrically conductive. We have conducted some preliminary tests to show that the metal ion nodes are redox active and can participate in electrochemical reactions. In Figure 5 we show the redox peaks for a Cu(BDC) thin film grown on a Au electrode through the sacrificial oxidation of a few monolayers of $Cu(OH)_2$. The only redox active species present is the Cu ions in the MOF as all of the $Cu(OH)_2$ was consumed during synthesis of the thin film, confirmed by EDS. Additionally, the redox peak locations can be associated with higher valent Cu species as indicated by the Pourbaix diagram for Cu. We find the redox signal to be stable over multiple cycles which

Figure 4: *TEM of Pd particles grown into Cu(BDC) MOF particles.*

is critical for the use of these thin films as part of a composite electrocatalyst. Initial assessment of the viability of the proposed operation of the composite electrocatalyst material was completed with formate ($HCOO^-$) oxidation as a test case, Figure 6. Briefly, it was hypothesized that the metal ion nodes of the MOF or metal centered catalysts exchanged into the MOF post-synthesis, would act to "sensitize" or initiate the breaking of one of the C-H bonds in methane, making its further oxidation more facile on the neighboring metallic electrocatalyst. In Figure 6, we demonstrate that this hypothesized mechanism is possible. As a test case we have chosen $HCOO^-$ oxidation on Cu(BDC) MOF coated Pd nanoparticles (grown through method 1). The rate limiting step for the oxidation of $HCOO^-$ is the deprotonation of the molecule. Therefore, if this step can be accelerated, the peak current for oxidation should increase. In Figure 6, we see a significant increase in peak current density for $HCOO^-$ oxidation in the presence of the Cu(BDC) thin film as compared to a bare Pd nanoparticle catalyst. We argue that this evidence points to the viability of the proposed cascade catalysis mechanism.

Figure 5: *CV of Cu(BDC) thin film on Au electrode in Ar purged 0.1 M $HClO_4$.*

3. Impact

The research that has been conducted under this project has opened a new area of study for the PI's group. Cascade catalysis is readily applied in the heterogeneous or homogeneous synthesis of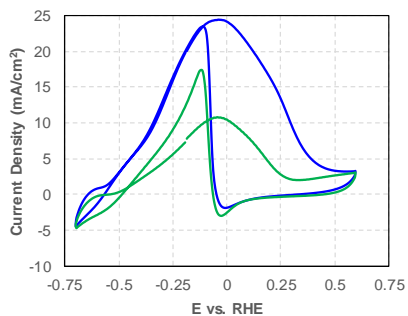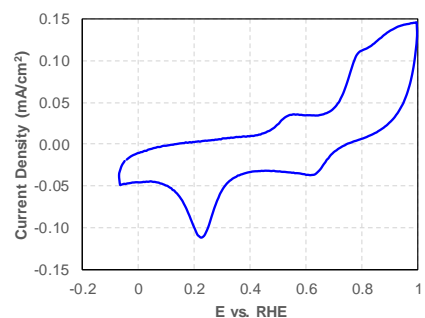 organic chemical compounds. However, electrochemical cascade catalysis is a completely novel area of research with the potential to address many of the limitations associated with the redox transformations of stable molecules. It also has the potential to address scaling behavior and selectivity limitations associated with multi-electron/proton transfer reactions. The graduate student participating in this work has been exposed to new synthesis techniques, been given a deeper understanding of the fundamentals of electrochemistry and electrocatalysis, and been exposed to a new and exciting field of catalysis research.

Figure 6: *$HCOO^-$ oxidation in 0.1 M $KHCO_3$ on Pd/C (green) and Pd/C+Cu(BDC) (blue).*

4. Future Work

Future work for this project will include testing of the Pd/C+Cu(BDC) catalyst for methane oxidation, identifying the formed products. In addiction to the metal nodes, selective linker exchange will be used to dope the MOF thin films with additional redox active species. Systematic assessment of the activity of a range of metal centered linkers will be used to identify the best performing combinations. An analysis of the stability of the MOF thin films will be assessed in the half-cell through accelerated durability testing. Finally, the best-of-class materials will be tested in a full-cell electrolyzer, quantifying and qualifying the performance of the materials for both the oxidation of methane and the production of high purity hydrogen.