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 and 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 CH₂O* intermediate which will be readily oxidized to CO₂ on the metallic electrocatalyst surface.

2. Results

Following the first phase of the project, time in the second year was focused on finalizing the synthesis of the cascade catalyst system and establishing the protocol for testing the designed catalyst for the electrochemical oxidation of methane. The work completed this year was limited due to the loss of the graduate student that was originally working on this project. For this reason, we have asked for and been granted a no cost extension for an additional year.

The desired cascade catalyst architecture is shown in the schematic in Figure 2. Briefly, a metal catalyst is interfaced with a MOF that possesses single active sites that can act to either break or destabilize one of the CH bonds in methane (either chemically or electrochemically), while the neighboring metal electrocatalyst will drive the complete oxidation to CO₂. The metal catalyst of choice is Pd while we have selected bipyridine stabilized PtCl₂ as the methane “sensitizing” catalyst. In the previous year, we developed the methodologies to grow thin films of Cu(BDC) with the goal of replacing the ligands with 4,4′-biphenyldicarboxylic acid and functionalizing with the PtCl₂. We have successfully completed this synthesis through a ligand exchange of the biphenyl ligand for a biphenyl containing PtCl₂ functionality. The process was centered on a hydrothermal displacement and the final ratio of PtCl₂ functionalized biphenyl to unfunctionalized biphenyl of 0.2. Further work is needed to increase that ratio. It is expected that the higher the PtCl₂ loading, the better the catalyst as the site density for driving C-H sensitization is increased. However, it is also possible that the other necessary properties of the MOF are hurt, including conductivity and durability in aqueous electrolyte. Testing that composite catalysts as a function of PtCl₂
loading will identify the optimal content. We have shifted away from thin films to porous MOF particles that are impregnated with Pd nanoparticles. This form factor is more amenable to incorporation into a full-cell electrolyzer. Figure 3 shows an SEM and TEM of the Pd nanoparticle incorporated MOFs with PtCl$_2$ functional groups. MOF particle diameter can be controlled to limit transport resistances of the CH4 reactant into the porous catalyst particle.

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.

4. Future Work

Future work for this project will include testing of the Pd/C+Cu(BDC)/PtCl$_2$ catalyst for methane oxidation, identifying the formed products. Kinetic analysis will be conducted with half-cell testing where PtCl$_2$ loading, Pd loading, and electrolyte pH will be the main variables to be tested. 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 MOFs 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. As mentioned previously, the graduate student that was on this project left abruptly toward the beginning of the year. A no cost extension has been applied for and granted. This next year will focus on testing of the newly synthesized composite catalysts for methane oxidation in both the half-cell and full cell.

Figure 2: (a) Schematic representation of the cascade catalyst architecture and reaction propagation. (b) PtCl$_2$ functionalized biphenyl MOF ligand.

Figure 3: (left) TEM of MOF particles. (right) TEM of Pd nanoparticles loaded into MOF.