
Stationary Direct Methanol Fuel Cells Using Pure Methanol

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- Kansas State University (KSU), Manhattan, KS
- University at Buffalo (UB), Buffalo, NY
- Carnegie Mellon University (CMU), Pittsburgh, PA

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Project End Date: December 31, 2021

Overall Objectives

The goal of this project is to develop stationary direct methanol fuel cells (DMFCs) using *pure methanol* as the fuel. This collaborative research will resolve three critical challenges from material to electrode and system levels:

1. Decrease methanol crossover
2. Enhance cathode tolerance of methanol poisoning
3. Reduce noble catalyst loading and cost.

Fiscal Year (FY) 2019 Objectives

- Establish correlation of rotating disk electrode activity of prescreened platinum-group-metal-free (PGM-free) catalysts and membrane electrode assembly (MEA) performance for DMFC.
- Synthesize cathode PGM-free catalysts with $E_{1/2} > 0.80$ V using dilute methanol solution.

- Synthesize PtRu catalyst on vertically aligned carbon nanofibers (VACNFs) and evaluate its anodic methanol oxidation reaction activity in dilute methanol solution.
- Incorporate customized anode and cathode catalysts into electrodes and generate nanoscale resolution X-ray computed tomography images of electrodes.
- Develop MEAs to achieve a peak power of ≥ 250 mW/cm² with ≤ 4 mg_{PGM}/cm² using > 3.0 M methanol solution.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Cost: high-performance catalysts with ultra-low-PGM or PGM-free loading
- Performance: higher power densities
- Performance: fuel and water management.

Technical Targets

This project will integrate complementary institutional expertise on PGM-free cathode catalyst (UB), supported anode catalysts (KSU), electrode fabrication, characterization, and optimization (CMU), and multi-phase mass transfer (KU) to meet the following DOE targets for DMFC:

- PGM catalyst loading: 3 mg/cm²
- Peak power density: 300 mW/cm².

FY 2019 Accomplishments

- Developed a testing platform to control fuel cell temperature, fuel and cathode flow rates, and relative humidity.
- Developed a system to sputter PtRu onto VACNFs and evaluate catalytic activities using cyclic voltammetry (CV).

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Developed a microwave-assisted system to synthesize PtRu on carbon nanofibers (CNFs) as the anode fuel cell catalyst.
- Developed a system to synthesize PGM-free cathode catalysts and evaluate catalytic activities using rotating disk electrode (RDE).
- Set up the sample preparation system, Micro-CT facility, and data processing platform.
- The MEAs (25 cm²) made from the best-performing commercial electrodes achieved 124.3 mW/cm² peak power density with 1.0 M methanol solution and 82.3 mW/cm² with 3.0 M methanol solution.
- The MEAs made from PGM-free cathode catalyst obtained the peak power density of 170 mW/cm² with 3.0 M methanol solution.
- Obtained nano-tomography of commercial electrodes (both anode and cathode) with 3 nm voxel resolution.
- Established correlation of RDE activity of prescreened catalysts and MEA performance for DMFCs.

INTRODUCTION

DMFCs that can be directly supplied with pure methanol, rather than methanol solutions, have higher fuel density and are more desirable for all applications including stationary applications. Using high-concentration methanol solutions or pure methanol, however, causes high methanol crossover rates, decreases the fuel efficiency, and severely deteriorates the fuel cell performance. In addition, the state-of-the-art cost of DMFCs needs to be significantly decreased in order to compete with conventional stationary power systems. This project will develop stationary DMFCs using pure methanol and resolve three critical challenges in DMFCs: (1) decreasing methanol crossover, (2) enhancing cathode tolerance of methanol poisoning, and (3) reducing noble catalyst loading and cost.

The research team has developed a system to sputter PtRu on VACNF to reduce the anode catalyst loading and synthesized high-performance PGM-free cathode catalyst to reduce the overall noble catalyst loading and cost. The development of liquid-vapor two-phase fuel cell models and nano-tomography measurements of commercial and customized fuel cell electrodes will facilitate the design of high-performing electrode architectures to reduce methanol crossover and improve fuel cell performance.

APPROACH

This project will integrate complementary institutional expertise on PGM-free cathode catalyst (UB), supported anode catalysts (KSU), electrode fabrication, characterization, and optimization (CMU), and multi-phase mass transfer (KU) to achieve the project goal through the following technical innovations:

- Pt-free methanol-tolerant cathode catalysts that outperform Pt-based catalysts (led by UB)
- Anode catalyst support provided by VACNFs with conically stacked graphitic structure to enable ultralow PGM catalyst loading (led by KSU)
- Electrode fabrication and characterization to improve catalyst utilization (led by CMU)
- Passive fuel and water management to enable DMFCs using pure methanol (led by KU).

RESULTS

Cathode PGM-Free Catalyst (led by University at Buffalo)

The UB team has chemically doped Fe into zeolitic imidazolate frameworks (ZIFs) with tunable Fe content to synthesize Fe–metal organic framework catalysts with controllable particle sizes (Figure 1a). By adjusting the ratios between the large and small particles, it was verified that the oxygen reduction reaction (ORR) catalytic activity of the composite Fe-N-C catalysts derived from pyrolysis of the in situ growth of 60 nm particles on surface of 200 nm shows the best performance. The team has optimized the RDE activity of customized Fe-N-C catalysts via adjusting the integration ratios between particles with different sizes as displayed in Figure 1b. The best $E_{1/2}$ was about 0.88 V and the H₂O₂ yield less than 1% when the content of 200 nm particle reached to 55 at %. The Fe-N-C catalyst shows negligible activity change when methanol concentration is less than 2 M.

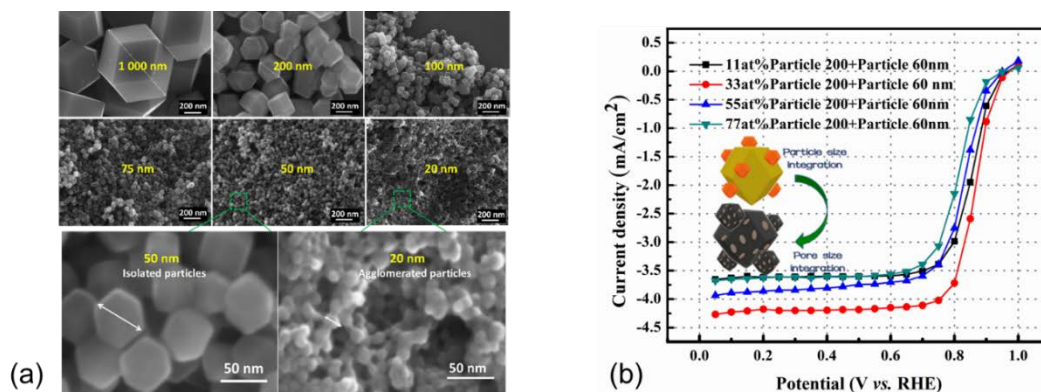


Figure 1. (a) Synthetic chemistry to control Fe–metal organic framework particle sizes and (b) synthesis of composite catalyst with 60-nm particle grown on the surface of 200-nm particles.

When the catalyst is tested in 0.5 M H_2SO_4 electrolyte containing 4 M and 8 M methanol solutions, the $E_{1/2}$ could be partially recovered after it is transferred back to methanol-free electrolyte. The team has also tested SCV of the catalyst before and after being immersed in pure methanol and water. The results suggested that the methanol adsorption and poisoning of catalyst is mainly caused by the electrochemistry process instead of physical adsorption, and physical adsorption of pure methanol couldn't cause any damage to the catalysts. The degradation of the activity may originate from the change of electrolyte properties and the blocking effect of adsorbed methanol. The underlining factors that affect methanol adsorption on Fe-N-C catalysts, such as the electrolyte pH, H^+ concentration, and applied potentials, as well as the selectivity of MN_x ($\text{M}=\text{Fe}, \text{Co}$ and Mn) active sites toward methanol adsorption, are still under investigation.

Anode Catalyst (led by Kansas State University)

The goal of this task is to prepare new PtRu catalysts for methanol oxidation reactions (MOR) that surpass the performance of commercial PtRu/C catalyst. The focus is on using CNFs consisting of conically stacked graphitic structure as the novel catalyst support as well as the microporous layer (MPL). The graphitic edge sites at the sidewall of CNFs are expected to have much stronger interaction with the PGM catalyst particles than the commercial PtRu/C system, leading to enhanced catalyst activity and durability. Furthermore, the 3-D architecture would facilitate better electron and mass transport, which are more critical for DMFCs than hydrogen proton exchange membrane fuel cells. Three research approaches are taken to reach the goal step by step (Figure 2), including: (1) preparing ultralow-PGM-loading catalyst ($10\text{--}100 \mu\text{g}/\text{cm}^2$) by ion-beam sputtering PtRu alloy onto VACNFs grown on gas diffusion layers (GDLs); (2) preparing medium-level-PGM-loading catalyst ($100\text{--}1,000 \mu\text{g}/\text{cm}^2$) by airbrush spraying commercial PtRu nanoparticles onto VACNFs grown on GDL; and (3) preparing high-PGM-loading catalyst ($1\text{--}4 \text{mg}/\text{cm}^2$) using microwave-assisted wet chemical synthesis of PtRu nanoparticles on dispersed CNFs and then airbrush spraying them onto GDLs.

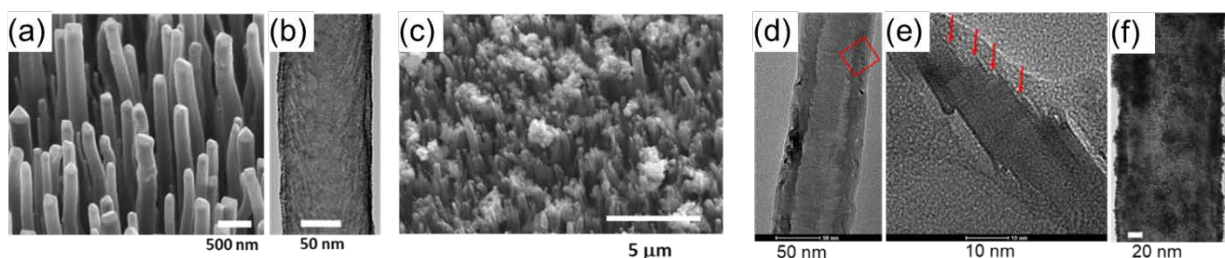


Figure 2. *Approach 1:* (a) scanning electron microscopy (SEM) and (b) transmission electron microscopy (TEM) images of PtRu (1:1 atomic ratio) sputtered onto the VACNFs grown on a graphite paper substrate. *Approach 2:* (c) a SEM image of commercial PtRu nanoparticles (1:1 atomic ratio, ~2:1 weight ratio) airbrush spray-coated on a VACNF array grown on a graphite paper substrate. *Approach 3:* TEM images of (d) a bare CNF at low magnification, (e) the high-resolution structure of the part highlighted by the red box showing the conically stacked graphitic CNF sidewall (indicated by red arrows) at high magnification, and (f) PtRu nanoparticles deposited on a CNF by the microwave process.

In Approach 1, the KSU team has grown VACNFs on several different types of commercial carbon paper and GDLs and sputtered Pt and Pt-Ru (1:1 atomic ratio) nanoparticles on VACNFs with controlled catalyst loading (of 10–100 $\mu\text{g}/\text{cm}^2$), Figure 2a and 2b. The MOR of commercial Pt-Ru catalyst and Pt-Ru/VACNF have been tested with 3.0 M methanol in 0.50 M H_2SO_4 solutions using CV.

The results show that the MOR reaction represented by the forward scan peak current density (I_f) for PtRu/VACNF (28/15 $\mu\text{g}/\text{cm}^2$ Pt/Ru loading) is nearly twice that of commercial PtRu/C at the similar PGM loading (32/16 $\mu\text{g}/\text{cm}^2$ Pt/Ru) (i.e., 20.3 vs. 11.0 mA/cm^2). As the PGM loading is increased to 43/22 $\mu\text{g}/\text{cm}^2$ Pt/Ru in the PtRu/VACNF system, the MOR capability, I_f , increases to 27.1 mA/cm^2 . The I_f of 43 $\mu\text{g}/\text{cm}^2$ Pt/VACNF is clearly smaller than the PtRu/VACNF catalyst at the same total PGM loading (28/15 $\mu\text{g}/\text{cm}^2$ Pt/Ru). Clearly PtRu catalyst provides higher MOR activity than Pt alone. Furthermore, besides the MOR peak in the forward scan denoted as I_f , all catalysts show a peak I_b in the backward scan, which corresponds to the removal of carbonaceous intermediates produced during MOR. The magnitude of I_b needs to be small in order to suppress the poison to the catalyst by the intermediates. In addition, the PGM loading and VACNF length are coupled to affect the MOR capability. Higher PGM loading gives higher I_f but shifts the peak potential to more positive and also requires the use of longer VACNFs so that the PGM nanoparticles can remain the 3–5 nm diameter without aggregation. These studies at low PGM loading on VACNFs are consistent with the literature and validate catalytic properties of the prepared catalysts for MOR. The KSU team has provided various low-loading Pt/VACNF and PtRu/VACNF anode electrode samples to KU for H_2/air and methanol/air tests. Investigation results will be included in future reports. It is noteworthy that the low PGM loading is below DOE's 2025 targets for hydrogen proton exchange membrane fuel cells (100 $\mu\text{g}/\text{cm}^2$ for cathode and 25 $\mu\text{g}/\text{cm}^2$ for anode).

In Approach 2, the commercial PtRu nanoparticles (~3 nm in diameter) are spray-coated on VACNFs grown on GDL by airbrush. The PGM loading can be controlled from ~100 $\mu\text{g}/\text{cm}^2$ to 1,000 $\mu\text{g}/\text{cm}^2$. As shown in Figure 2c, the PtRu nanoparticles are able to penetrate into the VACNF array through the inter-fiber space while the VACNF array retain the initial vertical aligned structure. Different parameters such as the solvent, substrate temperature, and spray pressure have been optimized. It has been found that PtRu nanoparticles suspended in a mixture of water and ethanol give the best results. The PtRu nanoparticles are able to remain well dispersed during spraying. CV measurements in 0.50 M H_2SO_4 solution with 3.0 M methanol solution exhibit a large stable MOR current. Interestingly, the MOR current increases vs. the potential, but most of the CVs do not show clear peaks in either forward or backward scans with a few exceptions. Incorporating Nafion in the PtRu suspension has been found to boost the MOR current. In fact, at such high MOR current (~160 mA/cm^2), a large amount of gas bubbles has been generated during the CV measurements and thus makes the measurement unstable. It is more proper to characterize these electrodes in DMFCs. The KSU team has prepared samples with various PGM loadings (up to 380 $\mu\text{g}/\text{cm}^2$) and provided them to KU or CMU for such tests.

In Approach 3, a microwave-assisted process is used to synthesize PtRu nanoparticles on dispersed CNFs, which will then be spray-coated onto GDLs using airbrush. The goal is to fabricate PtRu/CNF catalyst/MPL at high PGM loading (1–3 mg/cm^2) on GDL for MOR. The CNFs have diameter distributed in the range of 30–150 nm and length from 2–15 μm . They can be suspended in solution during catalyst deposition and then drop-cast on a glassy carbon electrode or airbrush sprayed onto a GDL. In both cases, it forms an interconnected thin film with a high porosity. The pore sizes are quite large, varying from 50 nm to 2 μm . In contrast to the VACNFs, the CNFs are randomly stacked in such films. Nevertheless, they also serve well as a 3-D nanostructured catalyst support and MPL. More importantly, the internal microstructure of the CNFs is similar to that of VACNFs (i.e., consisting of conically stacked graphitic structure leading to abundant graphitic edge sites at the fiber sidewall). Figure 2d and 2e show the low-mag image of the CNF and the high-mag image of the sidewall, respectively. Clearly, the sidewall of tube-like CNF structure actually consists of stacked graphitic layers tilted by 15 to 30 degrees from the fiber axis. The graphitic edges are clearly seen (highlighted by the red arrows). The graphitic edge sites are known to have stronger interaction with PGM nanoparticles and are highly electrochemically active. This unique microstructure is one of the factors enabling uniform deposition of PtRu nanoparticles from molecular precursors during microwave-assisted synthesis (as shown in Figure 2f). The initial results by the KSU team show that the MOR current density of PtRu/CNF at the low

PGM loading of $55 \mu\text{g}/\text{cm}^2$ is slightly lower than the $48 \mu\text{g}/\text{cm}^2$ commercial PtRu/C. A relatively high I_b is observed. As the PGM loading is increased to $137 \mu\text{g}/\text{cm}^2$, much higher MOR current density is obtained. Increasing PGM loading to $\sim 694 \mu\text{g}/\text{cm}^2$ gives a large MOR current, but again the generation of a large amount of gas bubbles limits the measurement using CV. The preliminary results are very encouraging. The KSU team is working to characterize and optimize the PtRu composition as well as spray deposition technique. Anodes with thus prepared PtRu/CNF MPL on GDL will be prepared and sent to KU and CMU for DMFC testing.

Electrode Tomography (led by Carnegie Mellon University)

The CMU team has measured pore-scale geometries of commercial anode and cathode electrodes using plasma-focused ion beam–scanning electron microscopy (pFIB-SEM). The voxel size of the pFIB images is 3 nm and 1,000 slices of 1770×2015 voxel images (Figure 3a) have been captured to reconstruct the 3-D nanotomography of each electrode. The total size of the reconstructed sample is $5.5 \times 6 \times 3 \mu\text{m}^3$ (Figure 3b). The high-resolution tomography data of commercial electrodes can estimate statistical properties of electrodes (pore-size distribution, surface area, etc.). A similar approach has also been used to reconstruct and compare tomography of electrodes made from customized catalysts.

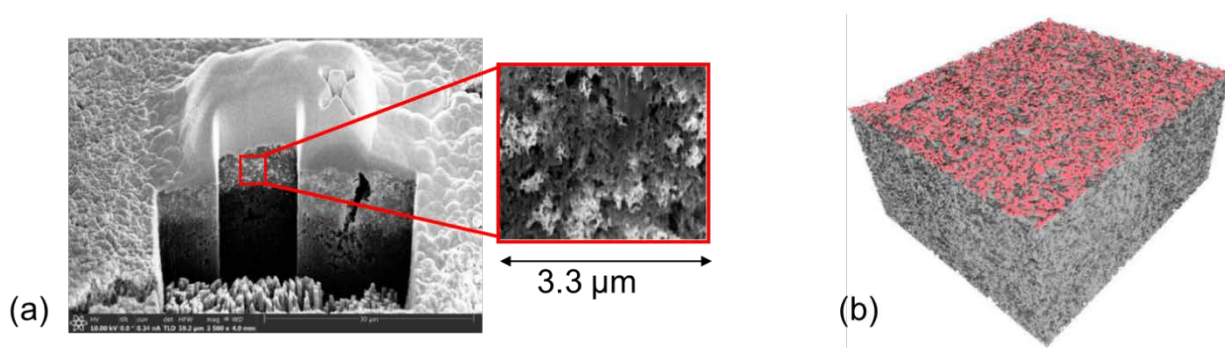


Figure 3. (a) The area of cut after imaging and one slice of anode electrode and (b) reconstructed tomography of commercial cathode electrode ($5.5 \times 6 \times 3 \mu\text{m}^3$).

Liquid-Vapor Two-Phase Model (led by University of Kansas)

The KU team has developed a two-dimensional liquid-vapor two-phase DMFC model to simulate the heat and mass transfer within fuel cell components as well as the electrochemical performance the fuel cell. The model includes all major components of the MEA: GDL, MPL, catalyst layer, and proton exchange membrane. The model can also consider the deformation, and the resulted property change, of the GDL caused by pressure from the flow channel ribs. The model can simulate concentrations of liquid and vapor methanol and water as well as saturation distributions. Polarization curves simulated by the current model match pretty well with 0.25, 0.5, and 1.0 M methanol solutions as the fuel.

Fuel Cell Performance

The project team has collaborated to test MEAs made from commercially available electrodes as well as MEAs integrating customized anode and cathode catalysts designed and developed in this project. The MEAs made from commercial electrodes showed peak power density of $124.3 \text{ mW}/\text{cm}^2$ using 1 M methanol and the peak power density of the MEA decreased to $73.4 \text{ mW}/\text{cm}^2$ with 3 M methanol solution and air (Figure 4a). The MEA using $4.5 \text{ mg}/\text{cm}^2$ Fe-N-C catalysts in the cathode and $4.2 \text{ mg}/\text{cm}^2$ commercial Pt₂Ru/C catalyst in the anode was tested with 3 M methanol solutions with methanol flowrate 0.5 mL/min and 2 bar air flowrate of 1 L/min. The peak power density reached $170 \text{ mW}/\text{cm}^2$ (Figure 4b), much higher than for electrodes made from commercial catalyst and almost reaching the milestone for Q3. Figure 4c shows a comparative plot of power density versus PGM loading for DMFCs with PGM-free cathodes reported in the literature. This project has demonstrated the highest power density to date and is matching the best for power density normalized by PGM loading.

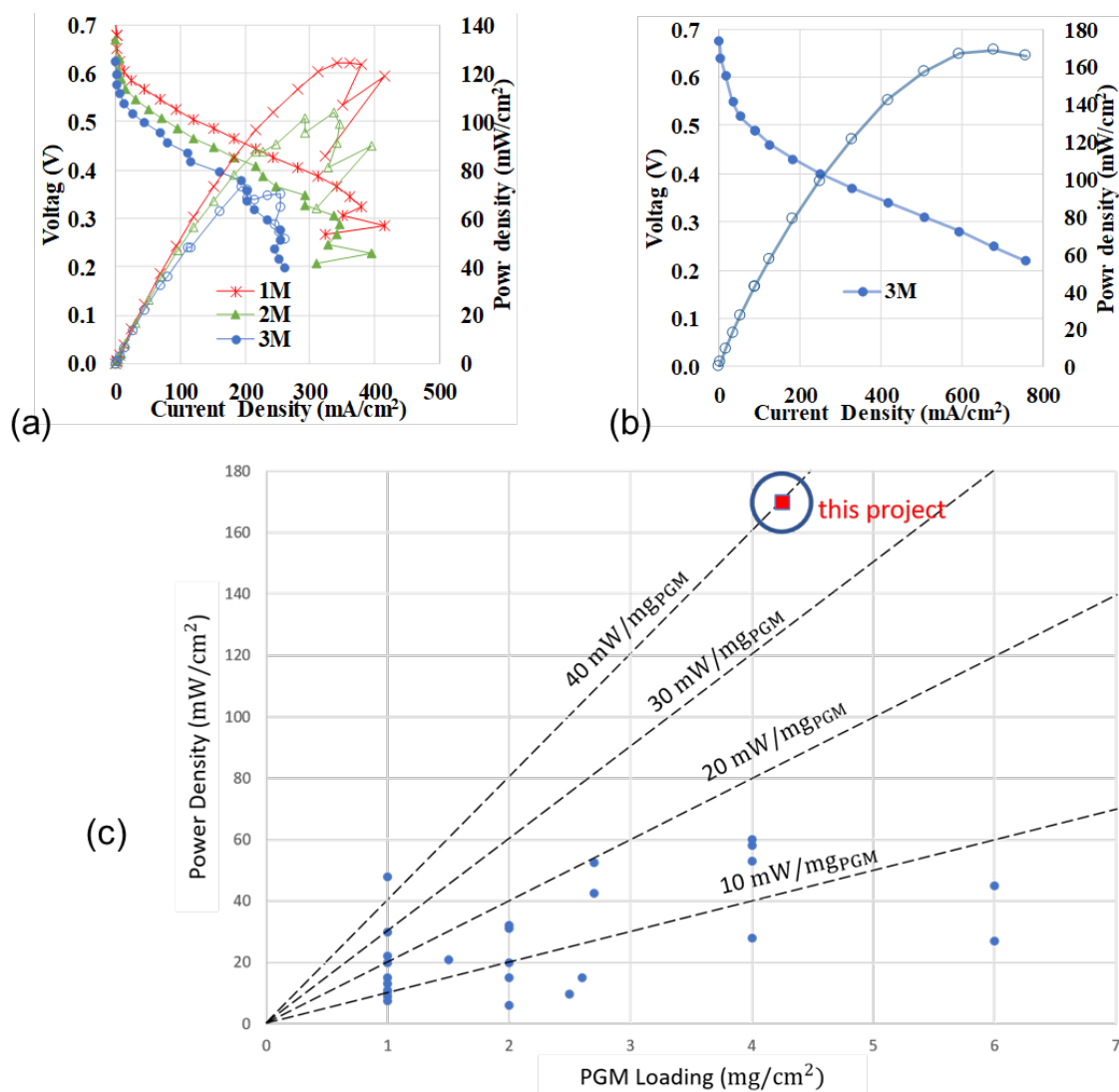


Figure 4. MEA performance of methanol-air cells (a) made from commercially available PGM catalysts: 4.5 mg/cm² Pt₂Ru as anode and 1.25 mg/cm² Pt as cathode. Flowrates of methanol solutions are 1 mL/min and flowrate of air is 0.1 L/min at 80 °C; and (b) employing 4.2 mg/cm² commercial Pt₂Ru/C as anode and 4.5 mg/cm² Fe-N-C catalysts as cathode with 3 M methanol flowrate of 0.5 mL/min and 2 bar air flowrate of 1 L/min at 80 °C. (c) Power density versus anode PGM loading for DMFCs with PGM-free cathodes reported in the literature.

Comparative experiments have been done to show the ability to operate on high molarity fuels with PGM-free cathode catalysts. The fuel molarity has negligible effect in PGM-free cathode catalyst performance and PGM-free catalysts performance significantly better than commercial catalyst with >2 M fuels. To identify the contributions of the individual electrode overpotentials to the overall cell voltage loss, CMU has integrated reference electrodes into their DMFC hardware. The reference electrode provides a method to optimize the cell based on the dominant overpotentials and identify the source (fuel vs. air) of mass transport limitations. Results show that leading overpotential is from the cathode with a 3 M fuel.

Meanwhile, the MEA with customized 2.6 mg/cm² Pt₂Ru on CNF as anode and commercial 1.25 mg/cm² Pt as cathode was tested with 1 M and 3 M methanol solutions with methanol flowrate of 1 mL/min and air flowrate of 0.2 L/min. The peak power density (91.87 mW/cm²) is comparable to MEAs made from commercial catalyst tested with 1 M and 3 M methanol solutions. It should be noted that the PtRu loading on the customized anode catalyst was only half that of the commercial electrodes. Increasing the PtRu loading has

great potential to significantly improve the fuel cell performance. The research team is also testing anode catalysts synthesized using new approaches to substantially increase the catalyst and electrode performance.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project team has made critical progress to improve the peak power density of DMFCs. MEAs fabricated from customized catalysts showed higher peak power density (170 mW/cm^2) than MEAs fabricated from best-performing commercial catalysts (124.3 mW/cm^2). We will keep collaborative efforts to optimize the catalysts and electrode designs and further increase the power density to meet DOE's performance target. In specific, the team will carry out the following research plans:

- Optimize and characterize wet chemical deposition by microwave-assisted synthesis (Pt to Ru ratio, PGM vs. CNF ratio, moderate loading, possibly better uniformity, DMFC tests).
- Further improve ORR activity of the PGM-free catalyst and study methanol tolerance of several transition metal (Fe, Co, Mn)-based catalysts.
- Optimize electrode structures of MEAs with PGM-free ORR catalysts and customized anode catalysts.
- Apply the liquid-vapor two-phase model to instruct MEA designs with improved mass transfer and electrochemical performance.
- Continue the case study to compare the initial costs as well as the operating costs of forklifts driven by internal combustion engine, batteries, and DMFCs.