V.D.8 Molecular-Scale, Three-Dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions

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Fiscal Year (FY) 2012 Objectives

1) Demonstrate that non-platinum group metal (non-PGM) catalysts can be used for oxygen reduction reactions (ORRs) in polymer-coated electrode structures based on polyelectrolyte membranes. (Year 1)
2) Incorporate catalysts into polymer binders of composite electrodes for the construction of membrane electrode assemblies (MEAs) to demonstrate that this is an effective matrix for testing of new catalysts. (Year 2)
3) Demonstrate that the three-dimensional (3-D) structure of polymer-coated electrocatalyst layers can offset slower kinetics of the catalyst centers when compared with two-dimensional platinum or non-platinum catalysts. (Year 3)
4) Demonstrate that significant stability of the matrix is possible. (Year 3)

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(C) Performance (better electrode efficiency)
(B) Cost
(A) Durability

Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst: 300 A/cm^3
- Cost: <$3/kW
- Durability: >5,000 hours (>120°C)
- Electrochemical support loss: <30 mV after 100 hrs @ 1.2 V

FY 2012 Accomplishments

- Completed Objective #1) to demonstrate that non-PGM catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes.
- Completed Objective #2). Non-PGM catalysts have been incorporated into the polymer binders of composite electrodes used in MEAs and have been shown to support high current densities (up to 1.2 A/cm^2).
- Completed Objective #3). Achievement and maintenance of high current densities (>250 A/cm^3) has demonstrated that the 3-D matrix is capable of supporting high current densities. However, calculation of turnover frequencies (TOFs) based on the catalyst loading indicates that the catalysts possess activity at least as great as platinum and that the assumption of low activity for these catalysts does not hold. The 3-D matrix is able to make up for low loading of the catalysts due to the larger size of the catalyst centers. Use of redox mediators within the catalyst layers has been shown to be an effective method to reduce the overpotential of the ORR and to increase electron conduction within the catalyst layers. It has been demonstrated by theoretical calculation and by experimental results that the morphology of the 3-D matrix polymer array is particularly important in the promotion of the mediation effect.
- Completed Objective #4). MEAs containing the catalysts and mediators have been operated under high current conditions and appear to be stable after initial break-in for up to 50 hours of operation. The MEAs underwent temperature, humidity and voltage cycling. Impedance measurements were taken at a variety of current densities (up to 250 mA/cm^2, 125 A/cm^3) prior to and after steady state operation which showed very little change in the various impedances within the cell. The

results confirmed that the 3-D matrix is stable enough in an MEA to warrant further investigation of such matrices as catalyst supports.

- The project achieved all the goals and milestones set out in the original proposal save one, which is to achieve a current density of 100 A/cm^3 of catalyst layer volume for greater than 10 hours at a voltage of 800 $mV_{ir\text{-}free}$. Both the current density and lifetime criteria were met but the voltage was not met. Since this was a Go/No-Go criterion, the project is now in close-out due to failure to meet this milestone. However, the results have provided a clear, science-based path to how the voltage criterion may be achieved:
  - Methods for mechanistic determination have been developed that provide intrinsic catalyst activity. Combination of these methods with molecular modeling and targeted catalyst synthesis provides well defined pathways to lower overpotentials and achieve higher TOFs. The use of electron transfer mediators with high TOF catalysts mimics the action of enzyme catalysts known to outperform platinum and provides a route to achieve The DOE long-term goals for non-PGM catalysts.
  - Modeling procedures have been developed and validated for prediction of MEA performance using non-PGM catalyst layers. The model predicts that the catalyst layer morphology is critical for achievement of the electron mediation and this has been experimentally confirmed.

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Introduction

Proton exchange membrane (PEM) fuel cells are not particularly efficient energy conversion devices (~50% fuel efficiency) and there is considerable interest in improving the performance while reducing the cost. One approach is to develop alternative catalysts that are more efficient than the traditional PGM catalysts and which also might be less expensive. Gasteiger and co-workers [1] have provided a very thorough review of the benchmark activities required for Pt, Pt-alloy and non-Pt catalysts for oxygen reduction and which describes in detail different approaches to catalysis of this important reaction. Methods have been reported to prepare non-PGM catalysts that involve a curious procedure whereby a rather complicated molecule such as a metal porphyrin or a complex such as iron phenanthroline is adsorbed on carbon and then heated to over 800°C to form the catalyst [2-5]. In some cases the carbon support is treated with nitrogenous compounds at high temperature followed by addition of metal ions such as Fe or Co. The pyrolysis process introduces considerable uncertainty as to the actual identity of the catalytic center but the reported results imply that new physics of considerable complexity must be occurring. By contrast, the approach taken in this project involves electrode structures which can allow incorporation of catalytic species of known structure into MEAs, which increase the density of the electrocatalysts in the catalyst layer and which allow the known homogeneous activity of the catalyst to be retained. No "new physics" is required.

Approach

Homogeneous redox catalysis has been the center of considerable academic attention for several decades and a review by Saveant [6] provides an extensive overview of the topic and includes methods of tethering catalysts close to the electrode surface. These methods suggest ways to incorporate into fuel cell MEAs electrocatalysts that mimic very efficient enzyme catalyst centers and may lead to better performance at reduced cost. The principles, advantages and drawbacks behind the approach were explained at greater length in the FY 2010 and 2011 annual reports. The most important advantage of the approach is that the catalyst functions essentially as a homogeneous catalyst that can be thoroughly characterized in solution. This makes design and synthesis of the catalysts straight forward since they can be studied without resort to surface analysis techniques and to the invocation of surface effects that are poorly understood. The catalysts are then incorporated into polymers for coating on electrode surfaces and again the behavior can be characterized by simple electrochemical methods prior to incorporation of the polymer-bound catalysts into composite electrodes for MEAs. This last step is critical for the project and represented the Go/No-Go decision point that allows the flow of more efficient catalysts into the PEM fuel cell platform for practical use. This report outlines the experiments that have been carried out that demonstrate the validity of the approach. Although the project failed to achieve the required voltage it demonstrated that the catalyst matrix can achieve high current densities for extended periods of operation and also provided clear indications of how to achieve the voltage through appropriate catalyst design and control of the electrode layer structure.

Results

Figure 1 illustrates the concept of the 3-D electrode structure and the dynamics of the transport processes that deliver electrons and substrate to the catalytic centers. Examples of a catalyst and an electron mediator are shown. Since the objective is to keep the catalyst and mediator off the surface of the carbon to achieve the 3-D effect they both contain solubilizing groups (hydroxymethyl for the ferrocene and quaternized pyridines for the catalysts). The flow of the electrons is shown in Figure 1(c) where one can observe that the process is precisely the same as in a homogeneous system. Figure 1(d) shows the progress that has been

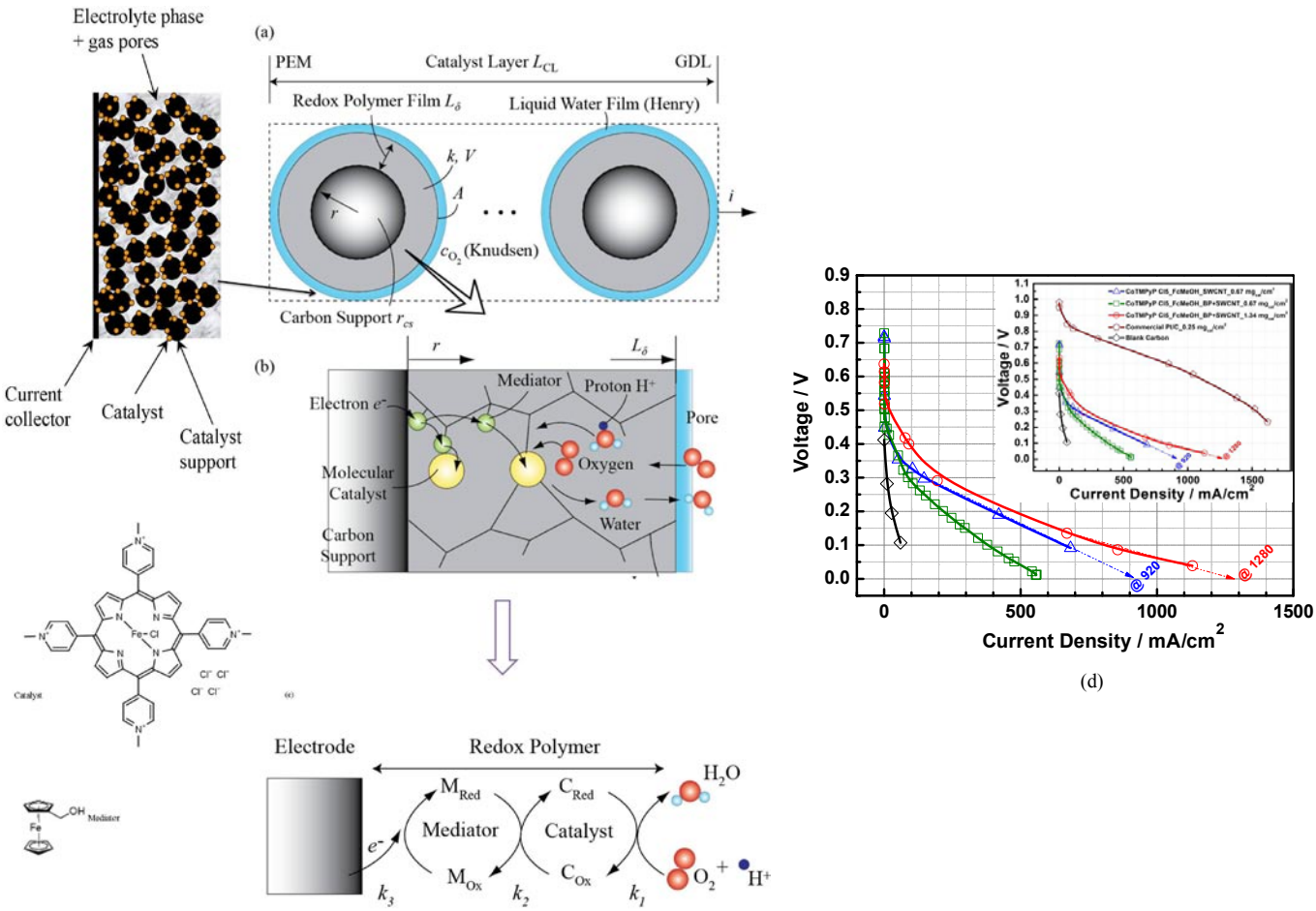


FIGURE 1. Schematic representation of the incorporation of catalysts and electron mediators into the binder polymers of a normal MEA (a) where the carbon support is represented as the spheres of readius r and which are coated with polymer layers of thickness L_δ. The polymer layer shown in (b) contains the molecular catalyst and electron mediator into which diffuses the reactant oxygen. (c) shows the floe of electrons from the electrode surface to the substrate oxygen. Examples of a catalyst and a mediator are shown. (d) shows the polarization curves achieved by incorporating such mediators and catalysts into MEA electrode layers. The inset graph shows compares the MEAs with Pt/C electrodes.

achieved by the introduction of mediators and optimization of the catalyst layer. The results clearly demonstrate that the matrix can support high current densities. The inset shows a comparison with a standard Pt/C electrode, which demonstrates that considerable improvement is still required to achieve the voltage goals. However, one may observe that the slope of the improved MEA polarization curve parallels the slope of the Pt/c electrode which indicates that the electrode structure functions well with respect to the transport properties. The lower voltage derives from the intrinsic potential of the catalysts some of which are given in Figure 2(c).

Figure 2 illustrates the route to achieve the voltage. The scheme in Figure 2(a) is a postulated mechanism for the reaction of the catalysts with the oxygen. It was shown in FY 2011 that the measured rate constants were too high to be consistent with an outer-sphere electron transfer process and that some kind of intermediate complex must be formed to provide a low energy pathway. In this case a dimer of two catalyst molecules with one oxygen is postulated. The catalyst molecules are activated by reduction by the ferrocene which returns to the electrode to pick up more electrons. The ferrocenes have a very rapide electron transfer rate and can also pass electrons rapidly from one mediator molecule to another thereby providing a pathway for electron hopping from the electrode surface to the catalyst which is not at the surface. Since the catalyst can be approached from all directions by both mediators and oxygen the rate of reaction is increased by the geometric effect. Such effects are enhanced by providing a high concentration of catalyst within the polymer layer which may provide a means to increase the rate of reaction with oxygen thereby allowing the voltage to be driven to the right in Figure 2(c) without loss of rate. If such were to be the case, then the reaction could be mediated at higher voltages by mediators such as those shown in Figure 2(b), some of which possess voltages which are

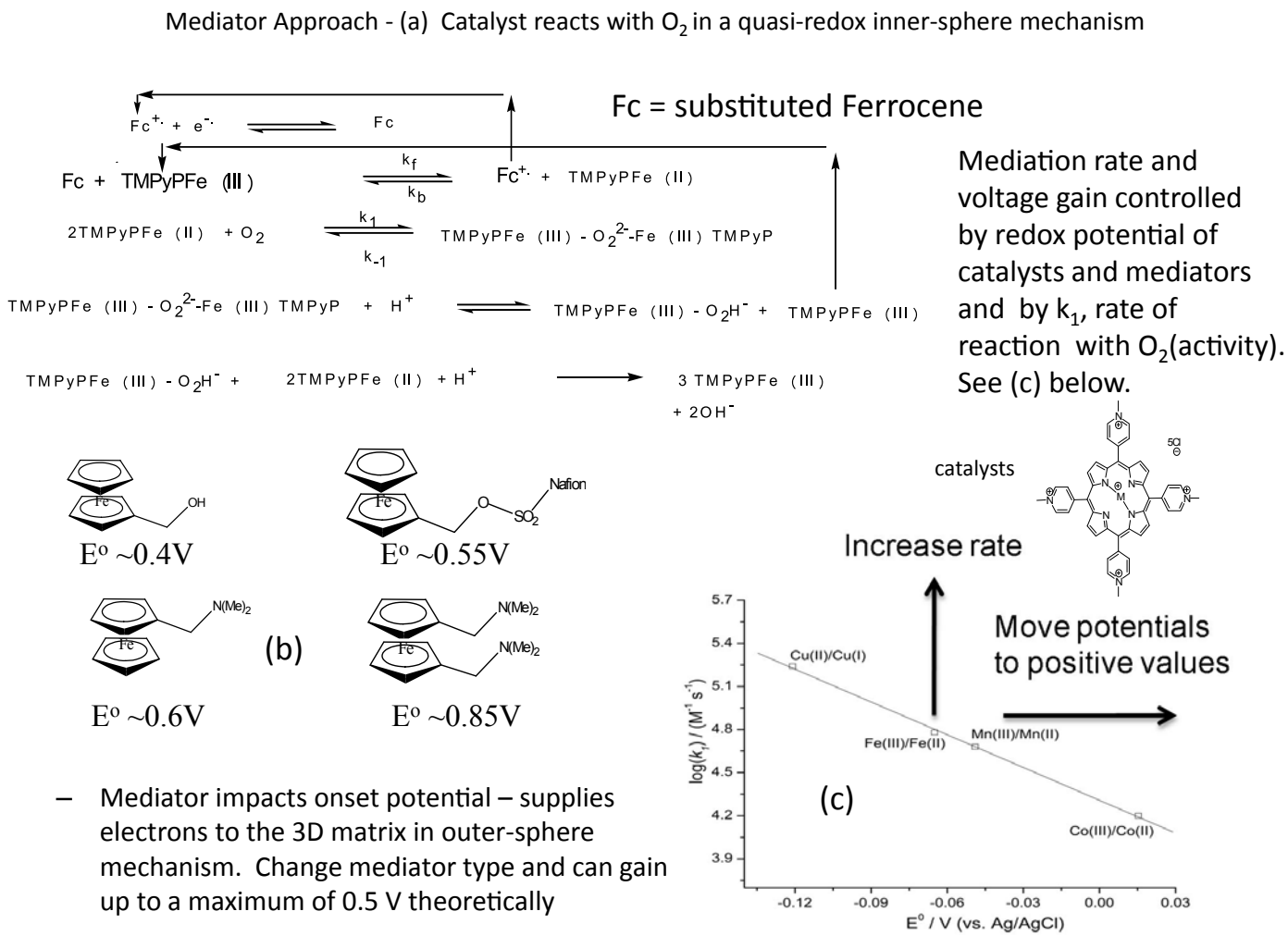


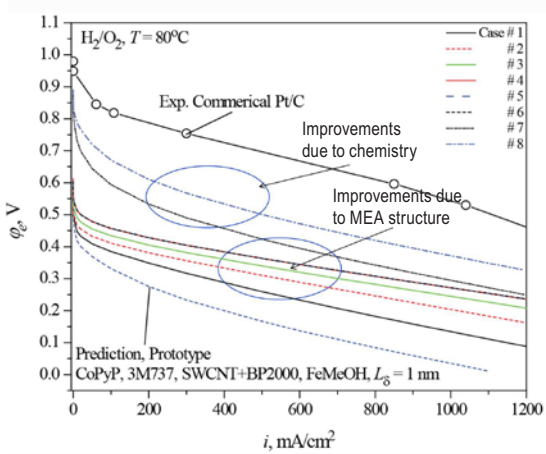
FIGURE 2. (a) Postulated mechanism of the reaction of the catalyst with oxygen through an inner-sphere route where the catalyst is activated by reduction by the ferrocene mediator. (b) shows the structures and potentials of candidate mediators that progress towards the desired potential. (c) is a plot of the measured rate constant of reaction of metal catalysts with oxygen as a function of potential, add 0.2 V to convert from the Ag/AgCl reference to the normal hydrogen electrode.

close to the target voltage of 0.9 V. These mediators will only function if the voltage of the catalyst is sufficiently positive and still with a high rate of reaction with oxygen as is shown in Figure 2(c).

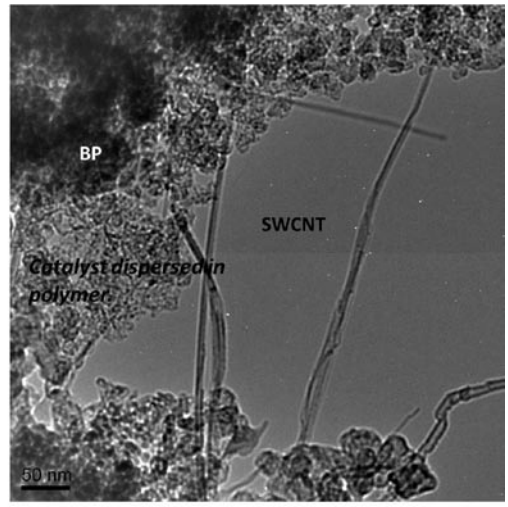
Modification of the catalyst structure is one approach to provide higher voltage. This may be accomplished by means of electron withdrawing substituents on the pyridine rings or by direct substitution of the porphyrin rings with electron withdrawing groups such as fluoride, chloride, CF_3 or amino groups. These groups alter the electron density on the metal which leads to a shift in potential. The change in the metal electron density also leads to a difference in the rate of the reaction with oxygen which is equally important. Unfortunately as shown in Figure 2(c) a shift in the potential to more positive values tends to lead to lower activity. To approach this problem a combination of molecular modeling, synthesis and measurement has been undertaken to provide data on how substituents may affect the potentials and the rate constants. The former are relatively easy to obtain for substituents on the porphyrin ring but more difficult for the pyridines due to the greater complexity of the molecules. Even more difficult is calculation of the rates of reaction with oxygen but both are necessary to provide complete understanding of the chemistry. As was mentioned in the FY 2011 report, deformed rings such as corrin or coorole rings can lead to faster rates due to extra strain in the moleucles. This work is ongoing and will be pursued under alternative funding to support such fundamental research.

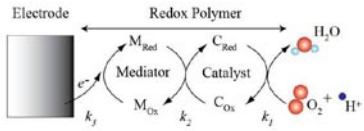
Figure 3(a) shows the results on modeling of the transport properties within the electrode layer. The prototype prediction has been validated by experiment and a number of parameters have been varied such as the loading of catalyst/mediator, nature of the carbon support, the equivalent weight of the ionomer used and the solvent used for the electrode inks. Variation of these properties leads to variations in the polymer thickness, the surface area/volume ratio, for

(a) Eight design improvements towards commercial Pt/C catalyst performance.



Prototype 20μm CL thickness.
#1: 10 x L thickness
#2 :10 x σ_{H^+}
#3: 10 x k_1
#4: 100 x k_1
#5: 100 x k_1; 10 x D_{O2}
#6: 100 x k_1; 10 x D_e
#7: 10 X k_1; E_m^o = 0.8V
#8: 100 X k_1; E_m^o = 0.8V





(b) TEM picture of MEA electrode showing black pearl (BP) carbon and Single wall carbon nanotube (SWCNT) support and PFSA polymer with catalyst.

FIGURE 3. (a) Results of modeling of the catalyst layer using the schematic in Figure 1 where various parameters are modified to observe the predicted effect on the performance. (b) TEM picture of an MEA electrode showing the carbon support and the polymer morphology. This electrode had not been hot-pressed.

example, which allows the overall rate to be increased as well as the transport of electrons and oxygen to be varied. Curves 1-6 show the effects of modification of the layer structure which represent optimization strategies. Curves 7 and 8 show the effects of using mediators with better voltages and catalysts with better kinetics although the intrinsic potential of the catalyst is not changed. The intrinsic potential of the catalyst is thought to be the cause of the low open circuit voltage, which can be improved with catalysts with more positive voltages and higher activity. Thus two regimes are identified where optimization of the structure can achieve some improvement but major improvements are realized by changes in the chemistry of the mediator and the catalyst structures. It is important to realize that the improvements that accrue from the chemistry changes are only effective if the electrode structure changes are also made. This can be illustrated by Figure 3(b) which is a transmission electron microscope (TEM) picture of an MEA electrode prepared with the mediators and catalysts. It can be immediately seen that the polymer possesses a morphology that is derived from the shapes of the dispersed particles in the electrode inks. Such morphologies clearly affect the transport pathways of the electrons and oxygen and also the dispersion of the catalyst through the layer. The morphology observed here indicates that the catalysts are distributed on the outside of the polymer particles and that this limits the catalyst loading that can be achieved. It is anticipated that changing the morphology by use of different solvents to disperse the polymer will lead to better catalyst and mediator distribution. Clearly there remains much work to do to understand the effect of morphology and to optimize the electrode structures. One striking feature of the TEM picture is that the polymer thickness is quite small, of the order of 50 nm. This is consistent with the modeling which also indicated that the film thicknesses were rather small and that under these circumstances the efficiency of the mediation would be impaired.

Figure 4(a) shows polarization curves for some of the catalysts whose potentials and kinetics are shown in Figure 2(c), as well as cobalamin (vitamin B_{12}). The cobalamin is an example of the use of a catalyst obtained from nature. It is quite striking that the performances in the MEAs track the behavior in the voltammetry experiments almost exactly. This was one of the goals of the project and is very gratifying that the correlation is so strong. Figure 4(b) shows the performance of MEAs with catalyst that includes some that are not water soluble. The excellent performance in the kinetic region of the CoTPP shows that it is not necessary to provide solubilizing groups and that smaller catalyst can be used that will allow for higher loadings. It appears that these water insoluble catalysts are partitioned into some of the hydrophobic phases of the ionomer and hence held off the electrode surface but are still available to mediators, protons and oxygen. The DiCop catalyst did not perform well in this set of experiments but since its structure is rather different some optimization needed. This material was obtained from Professor Love at the University of Edinburgh, Scotland

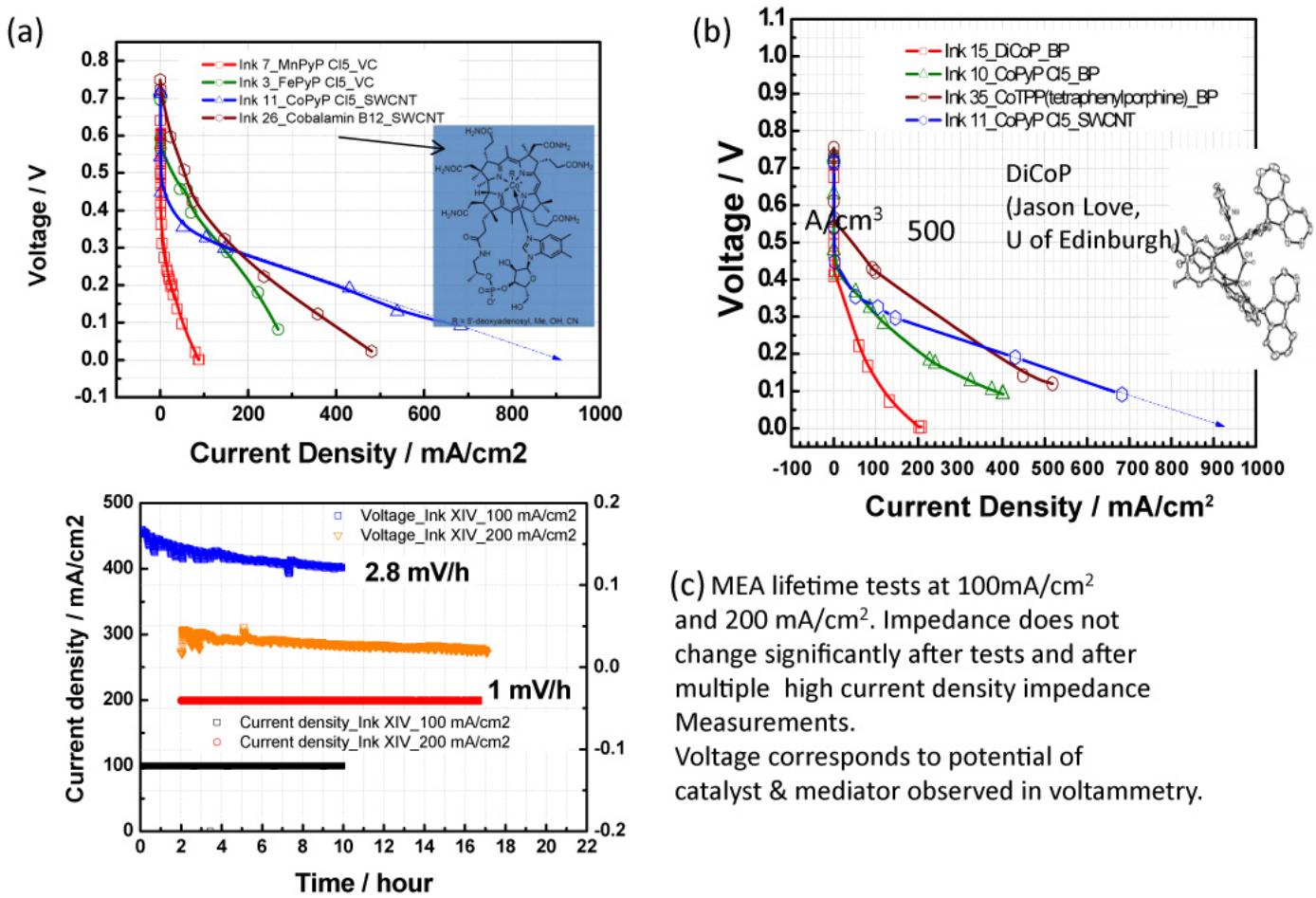


FIGURE 4. (a) Polarization curves of MEAs with different catlsysts including cobalamin (vitamin B12). (b) Polarization curves of MEAs with different catalysts including two which are not soluble in water (CoTPP and DiCoP), (b) hadut which are apparently supported by the polymermatrix. (c) Steady-state potentials for an MEA under two different current densities.

and this provides an excellent example of the how this MEA system can be used to evaluate catalysts from many different sources.

Finally Figure 4(c) shows the evolution of potential of an MEA under steady-state current conditions that clearly demonstrate stable performance. Although the delivered potential is very low it is stable and quite reproducible after the initial break-in. Similar behavior was observed for many MEAs which were run at various current densities to obtain impedance values. The impedance measurements showed no significant changes after multiple voltage, temperature and humidity cycles. These observations lead to the conclusion that the electrodes are surprisingly stable as are the catalysts under these conditions. This therefore refutes a frequent criticism of this approach that the catalyst will not be stable under "real" fuel cell conditions.

Conclusions and Future Directions

Conclusions

- The results from the MEA experiments reported here represent a proof-of-principle of the concept of polymer supported 3-D catalyst arrays for MEA. The correspondence of the modeling with the experimental results indicates that the correct parameters are being considered.
- The correspondence of the MEA results with the electroanalytical results indicates that a practical method catalyst screening exists that is rapid, inexpensive and relevant to MEA operation. Quantitative electroanalytical results are applicable to MEA operation through the electrode modeling.
- Better catalysts can be obtained through fundamental understanding of the factors that influence redox potential and rate of reaction with oxygen. Molecular modeling can address these problems.

- Somewhat surprisingly, the MEAs exhibit stable performance after break-in that indicate the catalysts and the supporting electrode matrix are stable for extended periods and are able to support high current densities.

Future Directions

- Optimization of MEA fabrication to improve performance through modification of electrode inks, coating procedures and initial break-in treatments.
- Use of electrochemical techniques including impedance to determine rate limiting phenomena in the MEAs and correlation with electroanalytical measurements made using conventional cell systems.
- Development of a coordinated molecular modeling/ synthesis/ electrochemical screening process that will provide understanding of the catalyst structural features that yield better performance. Better performance requires more positive intrinsic potentials and higher activities.

FY 2012 Publications/Presentations

1. "Molecular-scale, Three-dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions," John Kerr, DOE Fuel CellsTechnologies Program Review Meeting, May 15, 2012, Arlington, VA, poster presentation FC 11.

2. Ward, A.L., Elbaz, L., Kerr, J.B. & Arnold, J. Nonprecious Metal Catalysts for Fuel Cell Applications: Electrochemical Dioxygen Activation by a Series of First Row Transition Metal Tris(2-pyridylmethyl)amine Complexes. Inorg Chem 51, 4694-4706, (2012).

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4. Zhu, X. et al. Bridge to Fuel Cell Molecular Catalysis: 3D Non-Platinum Group Metal Catalyst in MEAs. ECS Transactions 45, 143-152 (2012).

5. Electroreduction of Molecular Oxygen by Water-Soluble Metal Porphyrins in Trifluoromethane Sulfonic Acid Solution, Qinggang He, Gi Suk Hwang, Adam Z. Weber, Robert Kostecki and John B. Kerr, Abstract 1154 ECS Fall Meeting, Boston MA, October 13, 2011.

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