ADVANCED ELECTRODE DEVELOPMENT AT W. L. GORE & ASSOCIATES, INC.
VACUUM COATED CATALYZED / INKING HYBRID ELECTRODES

Carlos Cavalca, Mahesh Murthy and Daniel Frydrych
W. L. Gore & Associates, Inc. - Fuel Cell Technologies
201 Airport Road, Elkton MD 21922

James Arps and Kevin Walter*
Southwest Research Institute - Materials Engineering Department
6220 Culebra Road, San Antonio TX 78238
*Current address: Technology 2146 Michelson Drive, Suite B, Irvine CA 92612

ABSTRACT

One aspect of advanced electrode development at Gore Fuel Cell Technologies is presented and discussed: Membrane Electrode Assemblies (MEAs) with improved power output by concentration of a vacuum-deposited catalyst metal at the electrode/membrane interface.

These MEAs have electrodes exhibiting a gradient in the concentration of catalyst metal at the catalyzed electrode/membrane interface. The gradient can be formed by various vacuum-deposition techniques including electron-beam physical vapor deposition, EB-PVD, and dc sputtering. The process can be performed on the outer surface of a catalyzed electrode, on the surface on the PEM membrane or onto appropriate backings, which can be used to transfer the metal deposit to the membrane surface or electrode surface. The purpose of this structure is to enhance the performance of the electrode by concentrating the metal catalyst at the electrode/membrane interface, where the highest level of electrochemical activity takes place.

INTRODUCTION

Fuel cells show great commercial promise throughout the world as an alternative high efficiency energy source. Despite improvements in fuel cell technology key challenges still remain in the development of PEM fuel cells that need to be addressed. Improvements in power output, reduction of noble metal catalyst loading, improvements in water management, and lengthening of operational lifetimes are key technological challenges being addressed by numerous industrial and academic fuel cell developers.

Electrochemical Society Proceedings Volume 2002-31 25
The electrode technology development presented in this paper addresses the first two needs: improvement in power density and decrease in electrode Pt loading by modification of composite cathode electrodes. Good reviews on the state of the art in PEMFC science and technology have been published by Srinivasan and coworkers [1, 2], Appleby [3] and by Gottesfeld and Zawodzinski [4].

It is widely recognized that the cathode overpotential loss (activation, ohmic, and concentration) is mainly responsible for the polarization behavior in a H₂/air PEMFC. This controlling polarization is mainly due to the electrocatalytic sluggishness of the oxygen reduction reaction (ORR). It then follows that electrode design variables such as catalyst crystallite size and catalyst intrinsic loading, electrode loading, and electrode structure/architecture will have a significant impact on the electrode activity. Electrode formulation variables, such as type of process, ionomer and PTFE levels, solvent nature, etc. will also play a key role in overall electrode performance. Examples of development addressing the latter group of variables are the interesting work of Uchida [5] and Oh [6].

Addressing the first group of electrode design variables, one general approach to optimize electrode activity and minimize loading of expensive catalytic metal has been to use smaller catalyst particles. However, long operational lifetimes may be particularly difficult to achieve with low catalyst loadings. Also, catalyst particle size may be unstable and increase by agglomeration or sintering [7]. From another electrode design strategy, the pioneering work of LANL [8] is a nice example of cathode performance optimization by modifying electrode architecture. In this work the performance of MEAs with cathodes with catalyst layers of variable thickness (but same loading) are compared. This work demonstrated that thinner catalyst layers (using higher intrinsic loading electrocatalyst) of comparable electrode Pt loading are relatively more active than thicker ones (when one takes in consideration the difference in crystallite size between low and high intrinsic loading catalysts).

An alternative strategy to improve electrode performance by changing its architecture has also been to selectively elevate electrode Pt loading at its surface by concentration of relatively large amounts of metal catalyst at the gas diffusion electrode surface [8, 9]. Typically 500 Å (ca. 0.1 mg Pt cm⁻² equivalent loading range) dense layers of metal catalyst have been sputtered onto gas diffusion electrodes. Improved electrode performance was reported for all three regions of the polarization curve (activation, ohmic and mass transport).
EXPERIMENTAL

For this study, ink-based composite ionomer/carbon-supported Pt catalyst electrodes compatible with PRIMEA® membrane electrode assembly technology were used. All the reference and modified MEAs were prepared with 20 μm GORE-SELECT® membranes. The MEAs used double-sided ELAT® as gas diffusion media for their fuel cell characterization.

The vacuum catalyst deposition was carried out using two techniques: electron-beam physical vapor deposition (EB-PVD) and magnetron sputtering. These deposition processes take place in-vacuum at pressures below $10^{-4}$ torr. The catalyzed substrates (15.24 cm x 15.24 cm swatches) were coated in batch mode using a double-rotation 4 point-holder carousel to assure uniformity of the coating. For the EB-PVD process, the evaporator consisted of a 5.08cm x 5.08 cm crucible loaded with high purity Pt slugs (99.95%). The Pt source was first re-melted and then evaporated using an electron beam source. For the sputtering deposition runs, a 15.24 cm diameter DC magnetron unit was used, which was loaded with a Pt foil target (0.127 mm thickness, 99.9%, Alfa). Typical deposition rates for both processes were kept comparable and ranged from 1 – 0.1 A/sec.

All the testing was done using a standard 25 cm² single cell fixture (Fuel Cell Technologies) with triple-channel serpentine flow field using appropriate gasketing and cell compression. The assembled cells were loaded in Globetech fuel cell testing plants interfaced with Scribner & Assoc. electronic load units (500 W, 10 A Model 890B). The testing plant allowed for reactant flowrate (stoichiometric control), reactant saturation, cell temperature, and backpressure control. Polarization curves were obtained potentiostatically after ca. 1-day cell break-in. The polarization curves were taken using stability criteria, i.e., steady-state current per selected (controlled) voltage level. Current-interrupt techniques built in the Scribner load allowed the measurement of cell resistance and extraction of IR-compensated cell voltage.

To measure the cathode electrochemical active area and cell H₂ crossover, a galvanostat-potentiostat and function generator setup (Amel high-power galvanostat/potentiostat, Model 2055 interfaced with an AMEL function generator, Model 568) was used in conjunction with the gas unit during cell diagnostics.

RESULTS AND DISCUSSION

Part I - Vacuum Catalyzation process characterization: EB-PVD vs. sputtering

Although there are many well known vacuum deposition technologies, for this work two general deposition technologies were selected and compared as catalyzation strategies: thermal evaporation and sputter deposition.
In thermal evaporation or physical vapor deposition (PVD), a vaporized catalyst phase is obtained by direct heating and concomitant evaporation (sublimation) of a metal source. The choice of heating is dependent of several factors, including melting point, thermal resistance, etc. Examples include the use of ovens, resistance heater and electron-beam (EB). For the case of evaporation (sublimation) of noble metals (Pt, Pd, Ir, etc.), their high melting point forces the use of EB heating. Figure 1 depicts the EB-PVD process. An electron beam heats a Pt source and the resulting evaporated flux of catalyst physically condenses on MEA components, which are used as substrates, forming electrochemically active catalyst deposits. Fuel cell MEA components used as substrates include the exposed surface of electrodes, the exposed surface of proton-conducting membranes and the exposed surface of decal layers, such as skived PTFE.

Sputter deposition of metals is also a well-known technique in the art of metallization. Sputtering deposition can typically be done by direct ion bombardment or magnetron sputtering. Figure 2 depicts the sputtering process using a magnetron for a bimetallic system using a dual target array (i.e., two targets: Pt and Ru).

There are some key distinctions between these two processes that may direct their selection as catalyzation processes. First, the vaporized atom or cluster energy is higher for magnetron sputtering than thermal (typically 100 eV for magnetron vs. 10 eV for thermal). Second, alloys can be sputtered but not thermally evaporated. And third, one can typically expect more substrate heating from thermal evaporation.

In order to characterize the morphological and electrochemical behavior of EB-PVD and sputtered electrocatalysts, vacuum-coated catalyzed gas diffusion electrodes were prepared. Swatches of ELAT® gas diffusion media were catalyzed to a loading of 0.1 mg Pt cm$^{-2}$ (ca. 500 Å equivalent thickness) via EB-PVD and magnetron sputtering. Figures 3a and 3b show field emission SEM conducted on the samples to achieve a deposition morphology characterization. Although the macro-morphology is mainly controlled by the GDM substrate roughness (vacuum deposition is a line-of-sight process that forms conformational coatings on a substrate), the micro-morphology between samples (which is of interest in catalysis) is clearly different and dependent on the vacuum catalyzation process used.

Analysis of the micrographs indicates that relatively uniform zones of the vaporized metal phase are formed. Electron-beam evaporated catalyzed samples exhibit a greater degree of surface micro-texture, characterized by high dispersion spherical nodules or clusters approximately 25 nm to about 100 nm in diameter, as well as the presence of rod-shaped structures. On the other hand, sputter deposition provided more dense catalyst layers with larger clusters. One possible explanation for this difference in micro-morphology could be attributed to the difference in energy between vaporized samples. Sputtered Pt atoms are more energetic than evaporated ones, thus it is possible that upon deposition, sputtered atoms or clusters relax (i.e., thermalize) the excess energy via surface migration, exhibiting cluster-to-cluster collision and concomitant sintering.
Electrochemical characterization of the above vacuum catalyzed GDEs was conducted next. MEAs were prepared bonding these catalyzed GDEs to 20 μm GORE-SELECT® membranes. Prior to bonding, the electrodes were impregnated with perfluorinated ionomer solution via brushing at a level of ca. 0.05 mg dry ionomer cm$^{-2}$. The cells were conditioned in H$_2$/air at $T_{cell} = 65$ °C with saturated reactants, and their polarization performance was then measured. Figure 4 shows a Tafel analysis for both prototype cathodes. The Tafel performance indicates that the EB-PVD catalyzed electrode offers superior electrocatalytic performance in comparison with the sputtered sample. Curve fitting of the data to the semi-empirical relation:

$$E_c = E(i) + iR = E_o - b \log i$$  \[1\]  

suggests that the evaporation process yields electrodes with improved exchange current density $i_o$, i.e., less polarizability of catalyst/electrolyte interface with overall improvement in ORR electrocatalytic activity.

The above finding clearly depicts a structure-performance relationship: EB-PVD catalyzed GDEs, which show more dispersed and abundant catalyst micro-structure yields superior electroc performance when compared to the more agglomerated and denser Pt sputtered active phase formed by magnetron sputtering.

**Part II - Pt EB-PVD Pt/C-ionomer composite hybrid electrode**

This section describes how EB-PVD is used to modify standard inking-based Pt/C-ionomer composite electrodes to obtain higher performance hybrid structures.

Figure 5 depicts the concept: Pt EB-PVD is used to place a gradient in the concentration of catalyst metal at the electrode/membrane interface using very low levels of vaporized catalyst. The equivalent loading of vaporized Pt is very low, typically ranging from 0.001 mg Pt cm$^{-2}$ (5 Å) up to 0.03 mg Pt cm$^{-2}$ (150 Å). It should be noted that at the Pt loading levels used for the evaporated phase, it is expected that its effect on electrode activity due to increased metal loading in itself should be very small or negligible (depending upon the Pt loading of the base composite electrode).

This gradient in the concentration of Pt at the electrode/membrane interface can be implemented using diverse strategies, each one more or less appropriate to the electrode technology used: Pt EB-PVD of exposed surface of Gas Diffusion Electrodes (GDEs), Pt EB-PVD of the exposed surface of proton-conducting membranes and Pt EB-PVD of the exposed surface of decal layers, like skived PTFE.

MEAs containing modified cathodes and reference MEAs were electrochemically characterized by polarization performance, Tafel analysis and cyclic voltammetry. Figure 6 shows a Tafel analysis comparing the specific activity (as cathode mass activity) for the MEA containing the hybrid cathode versus a reference MEA. The MEA with the hybrid air electrode contained a total loading of 0.11 mg Pt cm$^{-2}$, formed by 0.1 mg Pt cm$^{-2}$ at the electrode and 0.01 mg Pt cm$^{-2}$ (ca. 50 Å) EB-PVD at the membrane electrode.
interface. The reference MEA had a cathode loading of 0.1 mg cm$^{-2}$. The data clearly shows that the hybrid cathode exhibits superior specific activity than the reference cathode at the overall same Pt loading.

Cathode Electrochemical Active area (ECA) titration was done on the hybrid cathodes consisting of 0.1 mg Pt cm$^{-2}$ at the composite electrode and 0.03 (150 Å) and 0.01 (50 Å) mg Pt cm$^{-2}$ EB-PVD at the interface. The ECA was then compared to the one of a reference 0.1 mg Pt cm$^{-2}$ composite electrode. The cyclic voltammetry analysis showed that adding 0.01-0.03 (i.e., 50 - 150 Å) mg Pt cm$^{-2}$ PVD at the interface results in a significant (non linear) increase in cathode specific ECA (cm$^2$/mg Pt). This increase in number of electrochemically-active sites is possibly due to the combined effect of the highly dispersed evaporated Pt deposition and the concomitant increase in electrode Pt utilization (Figure 7).

The effect of Pt vaporized phase loading at the membrane/electrode interface on the hybrid electrode performance can be seen in Figures 8a and b. This data demonstrates that the addition of more Pt at the interface does not guarantee an increase in performance. It may instead cause an adverse effect on electrode activity, as it can be seen for "larger" PVD loadings of 0.03 (150 Å) and 0.1 (500 Å) using a 0.3 mg Pt cm$^{-2}$ composite cathode. This adverse effect on performance with high PVD loadings could be due to the formation of blocking electrode structures that reduce the proton ionic continuity between electrode and membrane.

It is interesting to note that the vaporized catalyst phase, at the loading levels applied of ca. 0.01 mg Pt cm$^{-2}$, displays very little activity in itself when tested as the only source of Pt in the electrode (Figure 8c). The poor activity level is due to the catalyst-intensive nature of ORR and the low loading magnitude for this electrode. On the other hand, when the ultra-low loading PVD phase is used in conjunction with a composite catalyzed structure, it forms a hybrid structure, and the effect is synergetic, thereby improving the activity of the base composite electrode. It will be seen in the coming section that this improvement is beyond the performance gain that may be obtained just by increasing the electrode loading (using conventional methods) by an amount comparable to the PVD deposition. The intrinsic activity Tafel analysis presented in Figure 6 and mass activity polarization curves presented in Figures 11 and 13 are in agreement with the above explanation.

**Hybrid cathode performance – medium Pt loading range**

Figure 9 shows data for a MEA using a hybrid cathode: 0.3 mg Pt cm$^{-2}$ loading composite base electrode and 0.01 mg Pt cm$^{-2}$ (50 Å) EB-PVD at the electrode/membrane interface. The performance is compared to the one of a reference MEA using a standard composite electrode (0.3 mg Pt cm$^{-2}$ loading). Polarization analysis shows that the MEA using the hybrid cathode offers superior performance compared to a reference MEA with standard electrocatalyst layers at the same loading. For example, at 0/0 psig and 65°C cell temperature the hybrid electrode containing MEA yields ca. 1200 mA cm$^{-2}$ versus ca. 820 for the reference.
Figure 10 shows data for the same system, but at 15 psig and higher cell temperature (75°C). The same improvement can again be observed. The improvement in performance extends throughout the entire region of the polarization curve, showing at 0.6 V 1600 mA cm\(^{-2}\) versus 1200 mA cm\(^{-2}\) for the reference MEA. In the right axis, power density is also plotted. The system displays an improvement in power density with a displacement of the peak power to larger current densities.

Figure 11 shows an electrocatalyst mass activity analysis for the same system. For practicality reasons, and to get an idea of overall MEA Pt utilization economy, mass activity is here defined as current density (or power density) normalized by the overall MEA electrocatalyst loading (Pt at anode, Pt at cathode and vaporized Pt at the interface). The figure shows the improvement in electrocatalyst mass activity obtained when using hybrid cathodes, observing an improvement in mass activity almost proportional to the improvement in power density.

**Hybrid cathode performance – low Pt loading range**

Figure 12 depicts performance for a low loading MEA comprising a 0.1 mg Pt cm\(^{-2}\) composite cathode and 0.001 mg Pt cm\(^{-2}\) (5Å) EB-PVD Pt at the cathode/membrane interface. The anode was a standard composite electrode, 0.05 mg Pt cm\(^{-2}\). The performance of this MEA using a hybrid low loading cathode is again compared against the one of a reference MEA having a standard composite cathode with 0.1 mg Pt cm\(^{-2}\) (same anode). Performance was evaluated at 15 psig cell backpressure and 65°C cell temperature. The data indicates that the low loading MEA using the hybrid cathode achieves an increase in current density of a factor of 2 at 0.6 V (from 440 mA cm\(^{-2}\) up to 860 mA cm\(^{-2}\)) with a substantial increase in peak power density.

The same graph also shows iR-free polarization performance (compensated potential), that, for the conditions of our test, mostly reflects cathode overpotential losses. All the tests are conducted with pure H\(_2\) in the anode, thus it is expected that activation polarization losses at the anode, at the loading level of 0.05 mg Pt cm\(^{-2}\), if any, may show up as linear overpotential contributions which are extractable by the current interrupt technique. It is observed that the compensated potential polarization curve perfectly tracks with the polarization curve expressed as a function of total cell potential. This behavior indicates that the enhancement in performance is solely due to the cathode, i.e. due the evaporated gradient at the cathode/membrane interface.

The mass activity behavior for the above MEA is showed in Figure 13. It is again observed that the enhancement in electrocatalyst utilization is mostly proportional to the measured enhancement in current/power density.

**Part III - Spectroscopic characterization of electrode Pt distribution: RBS characterization**

In order to characterize the Pt distribution on the hybrid inking/EB-PVD electrode, Rutherford Backscattering Spectrometry (RBS) was used. RBS has been successfully...
used in the past for post-mortem analysis and confirmation of Pt migration in PAFC gas diffusion electrode assemblies [10].

During RBS, an energetic ion beam (typically 2 MeV alpha particles) is directed onto the sample to be characterized. Some of the ions elastically scatter from the atoms on the sample surface and from atoms beneath the sample surface. These ions are said to backscatter from the sample. The ions that pass by the surface lose energy inelastically while traversing the sample, thus showing a shift in their energy. The energy and number of backscattered ions is measured by a detector and displayed as a plot of intensity versus channel (energy). This RBS spectrum can then be qualitatively and quantitatively interpreted to determine the concentration and depth distribution of an element (or elements) in a material. The backscattered ion energy is proportional to the mass of the atom from which the ion scattered and the amount of an element can be determined quantitatively by measuring the area under the part of the RBS spectrum that is due to the presence of that element. The profile is extracted by analysis of RBS signal with energy. The analysis depth is proportional to ion energy, that is, higher energy ions allow analysis to greater depths, but depth resolution is inversely proportional to ion energy. A more in-depth explanation of backscattering spectrometry can be found in reference [11].

Cells containing the hybrid cathode technology (0.1 mg Pt cm\(^{-2}\) composite electrode and ca. 0.01 mg Pt cm\(^{-2}\) (50 Å) at the electrode/membrane interface) and reference cells containing only 0.1 mg Pt cm\(^{-2}\) composite electrodes were characterized using RBS. Experiments were performed at the ion beam analysis (IBA) facility at Los Alamos National Laboratory. Two energies were used to perform the analysis (2 and 5.6 MeV). The RBS spectra were analyzed using RUMP computer program.

The RBS spectra presented in Figure 14 compare a hybrid electrode to a reference electrode. The data indicates that RBS can be successfully used to measure and quantify Pt distribution in a MEA half-cell. The Pt EB-PBD gradient at the electrode/membrane interface of the hybrid electrode technology is clearly visible: the Pt-portion of the RBS spectrum shows a very pronounced, highly localized distribution, mostly “spike” or delta-function in shape.

Simulation of the spectra was also done to confirm the loading of the PVD-applied phase. The quantitative analysis shows very good agreement with the targeted loading measured during the evaporation/catalyzation process using catalyst evaporation rates, dosing time and a vibrating micro-crystal balance placed in-situ the vacuum chamber.

CONCLUSIONS

Advanced high power density PEMFC MEA architectures from W. L. Gore & Associates, Inc. that have hybrid inking/vacuum deposited catalyzed electrodes have been characterized electrochemically and spectroscopically. These electrodes are compatible with PRIMEA\(^{\circledR}\) membrane electrode assembly technology.
These hybrid electrodes exhibit a gradient in the concentration of catalyst metal at the catalyzed composite electrode/membrane interface, where the highest level of electrochemical activity takes place. This interfacial gradient in catalyst concentration is formed by vacuum deposition using electron-beam physical vapor deposition (EB-PVD), and/or dc magnetron sputtering. The amount of vacuum-deposited catalyst metal that forms such gradient is very low (ca. 0.001 – 0.03 mg Pt cm$^{-2}$), thus not affecting, nor effectively increasing, the overall Pt loading of the cathode. This hybrid electrode architecture improves the current density distribution and overall electrode Pt utilization, yielding improved electrode performance and a concomitant increase in electrode Pt mass activity. It is found that EB-PVD yields catalytically more active microstructures both when tested as GDEs (i.e., vaporized layer as only catalytic metal) and as hybrid structures.

MEAs containing hybrid cathodes show improved single-cell polarization performance both at medium (ca. 0.3 mg Pt cm$^{-2}$) and low cathode loadings (ca. 0.1 mg Pt cm$^{-2}$) when compared to standard composite cathode. Concomitant almost-proportional enhancements in catalyst mass activity are also found, thus suggesting overall improvement in cathode electrocatalytic activity. Cell diagnostics indicates that the concentration of this ultra-low loading Pt evaporated gradient at the Pt/C-ionomer composite electrode/membrane interface improves both the cathode specific electrochemical active area (i.e., cm$^{2}$/mg Pt) and specific activity (mA/mg Pt).

Rutherford Backscattering Spectroscopy (RBS) was successfully used to characterize the Pt distribution on the hybrid electrode. The Pt portion of the RBS spectra clearly shows a very pronounced gradient of catalyst at the electrode/membrane interface for the hybrid cathode due to the vacuum catalyzation step. Quantification of the interfacial PVD-gradient was successfully done via modeling of the spectra.

**ACKNOWLEDGMENTS**

The authors would like to thank the following associates on the Gore Fuel Cell Technologies team for their contribution during this work: Connie Gibson (MEA prototype preparation), Will Johnson (intellectual property), Nick Sisofo and Dave Everson (fuel cell station set-up and qualification), Judy Rudolph and Tsueychen Long (SEM characterization), Carole Baczkowski (fuel cell testing), and Bonnie Sue Heist (manuscript preparation).

The following personnel at SwRI also deserve special recognition: Dr. Richard Page, Steve Clay, and Jim Riggs.

PRIMEA, CARBEL, GORE-SELECT, GORE and designs are trademarks of W.L. Gore & Associates, Inc.

ELAT is a registered trademark of E-TEK, Inc.
REFERENCES

1. P. Costamagna and S. Srinivasan J. Power Sources 102 242-252 (2001)
2. P. Costamagna and S. Srinivasan J. Power Sources 102 253-269 (2001)
3. S. Gamburzev and A. Appleby J. Power Sources 107 5-12 (2002)
4. S. Gottesfeld and T. Zawodzinski Adv. Electrochem. Sci. Eng. 5 195-301 (1997)
5. M. Uchida, Y. Aoyama, N. Eda and A. Ohta J. Electrochem. Soc. 142 No. 12 (1995)
6. S. Shin, J. Lee, H. Ha, S. Hong, H. Chun and I. Oh J. Power Sources 106 146-152 (2002)
7. M. Wilson, F. Garzon, K. Sickafus and S. Gottesfeld J. Electrochem. Soc. 140 No. 10 (1993)
8. E. A. Ticianelli, C. R. Derouin, A. Redondo and S. Srinivasan J. Electroanal. Chem. 251, 257 (1988)
9. S. Mukerjee, S. Srinivasan and A. Appleby Electrochimica Acta 38, No.12 (1993)
10. L. Borodovsky, J. Beery and M. Paffett Nuclear Instruments and Methods in Physics Research B24/25 568 (1987)
11. W. Chu, J. Mayer and M. Nicolet in “Backscattering Spectrometry”, Academic Press
Figure 1: Electron-Beam Physical Vapor Deposition (EB-PVD) vacuum deposition / catalyzation process.

Figure 2: Dual-target magnetron sputtering deposition.
Figures 3 a & b: Field emission SEM micrographs (x 25k magnification) of a: (top) Pt EB-PVD catalyzed ELAT® gas diffusion media and b: (bottom) Magnetron sputtering catalyzed ELAT® gas diffusion media showing difference in electrocatalyst microstructure. Electrode loading is 0.1 mg Pt cm⁻² (500 Å equivalent PVD thickness). Micrographs are of electrodes prior to ionomer impregnation.
Figure 4: Tafel analysis for Pt EB-PVD and sputtering catalyzed ELAT® GDEs. The vaporized phase is the only source of cathode electrocatalyst.

Figure 5: Vacuum coated catalyzed / composite (inking) hybrid electrode concept. The vaporized catalyst phase is of ultra-low loading in nature (ca. 0.001 – 0.03 mg cm⁻²), and forms a highly localized gradient of catalyst at the composite electrode/membrane interface.
Figure 6: Specific activity (as electrocatalyst mass activity) for the hybrid cathode versus a composite reference electrode. The hybrid cathode structure shows superior specific activity (i.e., activity per catalyst mass) than the reference.

Figure 7: Cathode specific electrochemical active area titration. Hybrid electrodes are shown versus a reference. Both modified structures yield improved number of active sites per gram of catalyst.
Figures 8 a & b: Effect of Pt vaporized phase loading at the membrane/electrode interface on the hybrid electrode performance. a: (top) Effect of incremental PVD loadings using a medium loading composite cathode. b: (bottom) Effect of decreasing PVD loadings using a low loading composite cathode.
Figure 8c: Electrodic activity of Pt vaporized phase (i.e., Pt PVD phase at 0.01 mg cm$^{-2}$ loading level as the only source of electrode catalyst) versus activity of the hybrid electrode counterpart (0.1 mg Pt cm$^{-2}$ base composite electrode / 0.01 mg cm$^{-2}$ Pt EB-PVD at interface).

Figure 9: Performance of MEA using a hybrid cathode: 0.3 mg Pt cm$^{-2}$ loading composite base electrode and 0.01 mg Pt cm$^{-2}$ (50 Å) EB-PVD at the electrode/membrane interface. Performance compared to reference MEA using standard composite cathode of same loading. $T_{cell} = 60$ °C, $P_{cell} = 0$ psig.
**Figure 10:** Performance of MEA using a hybrid cathode: 0.3 mg Pt cm\(^{-2}\) loading composite base electrode and 0.01 mg Pt cm\(^{-2}\) (50 Å) EB-PVD at the electrode/membrane interface. Performance compared to reference MEA using standard composite cathode of same loading. \(T_{\text{cell}} = 75\, {^{\circ}\text{C}}, \ P_{\text{cell}} = 15\) psig.

**Figure 11:** Electrocatalyst mass activity for MEA using a hybrid cathode: 0.3 mg Pt cm\(^{-2}\) loading composite base electrode and 0.01 mg Pt cm\(^{-2}\) (50 Å) EB-PVD at the electrode/membrane interface. Performance compared to reference MEA using standard composite cathode of same loading. \(T_{\text{cell}} = 75\, {^{\circ}\text{C}}, \ P_{\text{cell}} = 15\) psig.
Figure 12: Performance of low loading MEA using a hybrid cathode: 0.1 mg Pt cm\(^{-2}\) loading composite base electrode and 0.001 mg Pt cm\(^{-2}\) (5 Å) EB-PVD at the electrode/membrane interface. Performance compared to reference MEA using standard composite cathode of same loading. All anodes contain 0.05 mg Pt cm\(^{-2}\) \(T_{\text{cell}} = 65^\circ\text{C}, P_{\text{cell}} = 15\) psig. Solid lines correspond to total cell potential and dashed lines to iR-free (compensated) potential.

Figure 13: Electrocatalyst mass activity of low loading MEA using a hybrid cathode: 0.1 mg Pt cm\(^{-2}\) loading composite base electrode and 0.001 mg Pt cm\(^{-2}\) (5 Å) EB-PVD at the electrode/membrane interface. Performance compared to reference MEA using standard composite cathode of same loading. All anodes contain 0.05 mg Pt cm\(^{-2}\) \(T_{\text{cell}} = 65^\circ\text{C}, P_{\text{cell}} = 15\) psig.
Figure 14: Rutherford Backscattering Spectroscopy (RBS) characterization of hybrid half cell structure consisting of 0.1 mg Pt cm\(^{-2}\) composite base electrode and 0.01 mg Pt cm\(^{-2}\) (50 Å) EB-PVD at the electrode/membrane interface (versus a reference cell). Along the spectral Pt edge, the electrode Pt distribution for the hybrid structure clearly shows the steep highly localized gradient in Pt due to the PVD catalyzation.