Sputter-Deposited Pt PEM Fuel Cell Electrodes: Particles vs Layers


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Platinum catalyst layers with Pt loadings \( w = 0.05-0.40 \text{ mg/cm}^2 \) were deposited by magnetron sputtering from a variable deposition angle \( \alpha \) onto a gas diffusion layer (GDL) substrates and tested as cathode electrodes in proton exchange membrane (PEM) fuel cells using Nafion 1135 membranes and Teflon-bonded Pt-black electrodes (TBPBE) anodes. Layers deposited at normal incidence \( (\alpha = 0^\circ) \) are continuous and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with \( \alpha = 87^\circ \) and continuous substrate rotation yields highly porous layers consisting of vertically oriented Pt particles, 100-500 nm high and 100-300 nm wide, that are separated by 20-100 nm. The particle electrodes exhibit a higher (lower) mass-specific performance than the continuous-layer electrodes for a high (low) current density \( i \). This is attributed to a higher porosity but lower overall electrochemically active surface area for the particles compared to the continuous layer. Increasing \( w \) in particle cells from 0.05 to 0.10 to 0.18 mg/cm\(^2\) yields increasing potentials, but \( w = 0.40 \text{ mg/cm}^2 \) causes a voltage drop at \( i > 0.4 \text{ A/cm}^2 \), associated with the reduced pore density at large \( w \). Comparison cells with a TBPBE cathode exhibit comparatively low Tafel slopes but a lower Pt mass specific performance than the sputtered catalysts. Quantitative analyses of kinetic and mass-transport losses in the polarization curves suggest a competing microstructural effect, favoring mass-transport efficiency and an efficient oxygen reduction reaction for particle and continuous layer electrodes, respectively. The overall results suggest that in addition to the well-known promise of sputter-deposited Pt catalysts as an approach to increase Pt utilization at low loading, GLAD provides the unique ability to control Pt porosity and to achieve efficient reactant flow for high-current-density operation.

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Polymer electrolyte membrane or proton exchange membrane (PEM) fuel cells are energy conversion devices that show promise for future use in portable, stationary, and transportation applications. A key hurdle for mass-market adoption of fuel cell technology is overall system cost, driven in large part by materials and materials processing costs in the stack. Therefore, a considerable effort in fuel cell research is directed toward minimizing Pt loadings for a given target efficiency. A Pt catalyst loading \( w \) of 4.0 mg/cm\(^2\) is typical for Teflon-bonded Pt-black electrodes (TBPBE), TBPBEs consist of a hydrophobic, porous structure of micrometer-sized Pt agglomerates and were used in early space applications due to their high efficiency and long lifetime.

Further optimization and the addition of ionomer to the electrode surface resulted in the reduction of TBPBE loading to below \( w = 1 \text{ mg/cm}^2 \) without significant performance loss. Current fuel cell technology mostly employs ionomer-bonded thin-film electrodes with 2-5 nm wide Pt nanoparticles supported on carbon (designated Pt/C), with typical \( w = 0.4 \text{ mg/cm}^2 \). However, the carbon support also introduces some challenges, including reduced operating lifetimes due to carbon corrosion, peroxide attack of the membrane, and sintering and growth of the Pt particles over time. Further reduction of \( w \) below 0.4 mg/cm\(^2\) typically results in voltage losses consistent with the fundamental kinetic losses associated with the oxygen reduction reaction (ORR).

Sputter deposition of Pt has been explored by various researchers as a potential path for manufacturing ultralow Pt loading electrodes in a controlled process. Pt has been sputtered onto the gas diffusion layer (GDL) to the membrane, or deposited onto poly(tetrafluoroethylene) (PTFE) sheets or similar support substrates and subsequently transferred to the membrane. Most researchers found that the sputtered Pt morphology strongly affects fuel cell performance and have reported increases in catalyst utilization through roughening the membrane, patterning the catalyst, depositing on polymer nanowhiskers, or selecting appropriately rough GDL substrates. Depositing additional conductive layers such as Cr, carbon, Au, or Nafion-carbon ink also affects performance by enhancing the gas transport or electron conduction within the electrode. Work is already in progress to characterize the angular distribution of the sputtered Pt flux for the possible application of such methods to commercial manufacturing. Rabat and Braun deposited carbon layers at 45° with respect to the substrate, creating the resulting columnar morphology with Pt, and found a higher open-circuit voltage of the assembled fuel cell as compared to a commercial electrode. Sputtering Pt onto carbon nanofibers grown directly on the GDL results in higher Pt utilization as compared to a commercial cathode.

In this paper, we present an alternative approach to engineer the nanoscale structure of fuel cell electrodes by varying the deposition angle during sputtering of Pt onto the GDL. Normal-incidence deposition results in a conformal, nearly continuous layer that covers the porous surface of the GDL. In contrast, deposition from a highly oblique angle of \( \alpha = 87^\circ \) causes Pt to nucleate preferentially on raised areas of the GDL surface and form a porous coating consisting of vertically oriented Pt particles. This approach is based on the glancing-angle deposition (GLAD) technique which exploits atomic shadowing effects during line-of-sight physical vapor deposition to engineer nanorods into various shapes such as nanopillars, zigzags, nanospirals, nanotubes, two-component rods, and branched nanocolumns with such potential applications as photonic crystals, sensors, catalyst supports, magnetic storage media, radiation-resistant coatings, and field emitters.

We evaluate the deposited Pt layer and particle electrodes as cathodes in PEM fuel cells in order to understand the effect of GLAD on the Pt utilization. At high power, particle cells have higher Pt utilization than cells with “normally deposited” continuous layers of Pt. The superior mass-transport performance of the Pt-particle layers is due to the porous, columnar morphology. High-porosity Pt layers formed by GLAD offer a potential path to high-performance sputtered fuel cell electrodes.

Experimental

All electrodes were deposited onto the microporous layer (MPL) of as-received, commercially available GDLs (Sigracet 35DC supplied by SGL Technologies, GmbH). The MPL is a Teflon-

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bonded layer of carbon particles that provides mechanical support for the electrode. The MPL substrates were introduced into a magnetron sputter deposition system with a base pressure of $<8 \times 10^{-7}$ Torr, placed 15 cm from a 7.6 cm diam Pt target (Plasmatronics, 99.99% pure), tilted by $\alpha = 0$ and $87^\circ$ for continuous layer and particle depositions, respectively, and rotated about the surface normal at 0.5 Hz (30 rpm) in order to achieve particle orientation normal to the surface. It is important to clearly define our geometry by noting that $\alpha$ is the angle between the substrate normal and a line drawn through the centers of the target and the substrate as in Ref. 27. Ar (99.999% pure) was introduced into the system to reach a constant pressure of 2.3 mTorr. No external heating was applied to the substrate during the deposition process. A constant dc power of 200 W yielded deposition rates of 2 and 0.3 nm min$^{-1}$ for the Pt layer and particles, respectively. This corresponds to Pt loading rates of 0.05 and 0.007 mg cm$^{-2}$ min$^{-1}$, as determined using differential weighting of 0.2 and 1.5 mg samples in an electronic semi-microbalance (Sartorius 2024 MP6, standard deviation $\pm 0.02$ mg).

The sputter-deposited electrodes were integrated as cathodes into fuel cells with an active area of 10 cm$^2$. Nafion 1135 polymer electrolyte membranes (Ion Power), 1100 equivalent weight and 89 $\mu$m thick, were activated by boiling in 0.5 M H$_2$SO$_4$ for 30 min, followed by three separate 30 min boiling steps in distilled water, and stored in distilled water until being assembled into a membrane-electrode assembly (MEA). Anode (counter) electrodes were TB-PBE with 1 mg/cm$^2$ Pt and were prepared following the procedure described in Ref. 5. To facilitate electrode/electrolyte interfacial contact, a 15 wt % dispersion of Nafion in water, isopropanol, and methanol (Ion Power Liquion LQ-1115) was applied to the surface of the electrodes before bonding to the membrane. After this coating dried, the electrodes contained 5--10 wt % Nafion. Finally, electrodes were bonded to the membrane at a pressure and temperature of 350 psi (2.4 MPa) and 126°C for 5 min.

Fuel cells were operated at 70°C with atmospheric pressure H$_2$ and air reactants that were humidified to a dew point of 70°C (100% relative humidity). Prior to performance testing, all cells were “incubated” by applying a constant voltage of 0.4 V and allowing the output current to stabilize for 24 h. H$_2$ and air flow rates were set to stoichiometric ratios of 1.2 and 2.0, respectively, for 1.0 A/cm$^2$, corresponding to 84 and 333 sccm. The raw polarization curves were corrected for shorting, crossover, and internal ohmic resistance (IR) in order to isolate the performance of the cathode electrode from confounding effects, as discussed in the Results section. Typical values for the current correction due to shorting and crossover were 5--6 mA/cm$^2$, as determined by applying H$_2$ and N$_2$ to the anode and cathode, respectively, and measuring the steady-state H$_2$ crossover current at high cathode potential. The IR correction for the voltage, ranging from 0.15 to 0.30 $\Omega \text{cm}^2$, was obtained from the slope of the linear polarization curve of the cell in hydrogen pumping mode, as described in Ref. 5. Electrochemical surface area (ECSA) measurements were performed via cyclic voltammetry (CV) with a Parstat 2273 (Princeton Applied Research) under humidified N$_2$ at 70°C and a scan rate of 20 mV/s. ECSA was calculated from the raw CV curve by integration under the H-underpotential deposition region after subtracting the double-layer charging current as described in Ref. 45. After fuel cell testing, MEAs were prepared for scanning electron microscopy (SEM) analysis by freeze-fracturing after immersion for 15 min in liquid N$_2$. SEM micrographs were collected on a Carl Zeiss Supra SEM in secondary electron mode at 2.5 kV.

### Results and Discussion

The schematics in Fig. 1 illustrate the geometry for (a) normal and (b) glancing-angle deposition of the Pt catalyst onto the MPL. In the case of normal deposition, where the angle between the substrate surface normal and the deposition flux $\alpha = 0^\circ$, the Pt forms a continuous layer that approximately replicates the rough surface morphology of the underlying MPL, as shown on the left side in Fig. 1a. The corresponding cross-sectional scanning electron micrograph on the right is from an electrode with $\alpha = 87^\circ$. It shows at the bottom the 30--50 nm wide carbon nanoparticles from the uppermost part of the MPL and at the top the membrane electrolyte, which exhibits little contrast. The catalyst layer at the interface between MPL and membrane appears bright, because the high-Z Pt exhibits a higher secondary electron yield during SEM imaging. Its measured thickness is 50 nm, which is slightly less than the nominal thickness of 70 nm. We attribute this difference to the roughness of the layer which conforms to the rough MPL surface, resulting in an effective Pt layer area that is larger than the nominal (flat) area. This observation shows that the morphology of the catalyst is strongly affected by the MPL surface, which may explain previous reports indicating a strong impact of substrate morphology on fuel cell performance.

Figure 1b illustrates the case for an oblique deposition angle $\alpha = 87^\circ$. The incoming Pt atoms preferentially deposit on substrate features that protrude out of the surface, as the flux to the lowering GDL is blocked as a result of a line-of-sight deposition process. During continued deposition, this atomic shadowing effect leads to the formation of well-separated particles which grow vertically due to a circular symmetry achieved by continuous substrate rotation about the surface normal. Statistical fluctuations in the substrate roughness and the deposition process cause differences in the growth rates of individual particles and lead to a competitive growth process. The taller particles capture a larger fraction of the incident light.
particle flux while their smaller neighbors are shadowed and terminate their growth prematurely, as previously reported for GLAD nanorods. Consequently, the particles exhibit a relatively large distribution in both height and width, as also observed in the corresponding SEM micrograph on the right of Fig. 1b from a cell with a 0.40 mg/cm² Pt loading. This cross-sectional micrograph shows Pt particles, 100–500 nm high and 100–300 nm wide, that have nucleated on the MPL surface and are embedded in the membrane. The gaps between the particles exhibit widths ranging from 20 to over 100 nm. These pores become partially filled with electrolyte during the drying of the Nafion dispersion and the membrane bonding process, as described above.

Figure 2 shows polarization curves for three fuel cells that were assembled using a Pt layer, a Pt particle, and a conventional TBPBE cathode electrode with loadings of 0.25, 0.18, and 0.88 mg/cm², respectively. The plot shows the iR-corrected potential E vs the mass activity iₐ, which is the current density normalized to the amount of Pt. Therefore, the graph shows a direct comparison of the catalyst utilization efficiency. The potential for the continuous Pt layer decreases with increasing current density for iₐ < 0.6 A/mg. Such a decrease is typical for PEM fuel cells and is consistent with activation polarization. However, E exhibits a distinct drop from 0.67 to 0.37 V as iₐ increases from 0.6 to 1.0 A/mg. This drop is caused by a significant concentration overpotential that dominates the performance of the continuous layer at high current density, indicating poor electrode porosity, as discussed below. The fuel cell with the Pt-particle electrode shows a slightly steeper increase in E at low current in comparison to the Pt-layer electrode, with E = 0.65 and 0.69 V at iₐ = 0.45 A/mg for Pt particles and the Pt layer, respectively. However, the particle cell shows negligible concentration overpotential, leading to a mass activity of 2.7 A/mg at E = 0.5 V, which is more than a factor of 3 larger than 0.86 A/mg, the value for the continuous layer. Figure 2 also contains a plot of the mass activity from a cell with a TBPBE cathode, which serves in this study as comparison data. This cell with w = 0.88 mg/cm² exhibits the highest mass activity output of a set of TBPBE cathodes with different values of w. Higher w values result in lower mass activity, because a smaller fraction of Pt/PTFE agglomerates is in ionic contact with the bulk electrolyte, while lower w (w < 0.88 mg/cm²) TBPBE loadings also result in a reduced mass activity, associated with an increasing fraction of the Pt/PTFE agglomerates that seep into the MPL during the application and drying process. This effect results in the smallest possible TBPBE loading within our processing approach of w = 0.5 mg/cm², which is considerably higher than what is achieved by both types of sputtered Pt. The absolute (non-normalized current) performance of the TBPBE cell is higher than for any sputter-deposited electrode cell of this study. However, in a mass-specific comparison as shown in Fig. 2, the layer electrode (iₐ/m = 0.068) outperforms the TBPBE (iₐ/m = 0.033) at a high potential of 0.8 V, while the particle electrode (iₐ/m = 2.7) outperforms the TBPBE (iₐ/m = 0.77) at a low potential E = 0.5 V. We attribute the high performance at low iₐ/m of the layer electrode to a high Pt fraction that is in direct contact with the electrolyte, facilitated by the relative thinness of this electrode. In contrast, the relatively high voltage of the particle electrode at high current is associated with the excellent electrode porosity, which facilitates oxygen transport from the bulk GDL pores to catalyst sites throughout the electrode.

Figure 3 shows plots of the cell potential E vs the current density i for Pt-particle fuel cells with increasing catalyst loadings w = 0.05, 0.10, 0.18, and 0.40 mg/cm², obtained by increasing the GLAD time from 7.5 to 60 min. All cells show a characteristic decrease in E with increasing i. However, the slope of the E(i) curves is less steep for higher Pt loadings, corresponding to a higher current density at a given potential. This indicates that increasing the particle size leads to larger catalytically active surface areas. Adding a given amount of Pt has the greatest effect at low loadings. For example, i at 0.60 V doubles from 0.04 to 0.08 A/cm² for an increase in w from 0.05 to 0.10 mg/cm², but only increases by 23%, from 0.17 to 0.21 A/cm², for an increase in w from 0.18 to 0.40 mg/cm². The trend of increasing i with increasing w is eventually reversed for the two highest Pt loadings at high current. The voltage of the 0.40 mg/cm² cell drops below the 0.18 mg/cm² cell for i > 0.38 A/cm². This indicates a mass-transport limitation for w = 0.40 mg/cm², which we attribute to limited oxygen transport through the pores of the catalyst layer. Increasing w leads to longer and wider particles and, in turn, reduced pore density and longer diffusion paths, resulting in inefficient oxygen transport from the GDL to the active Pt-membrane interface. This causes a drop in E for i ≈ 0.35 A/cm² and w = 0.40 mg/cm². Nevertheless, this drop is much less pronounced than for the electrode with the continuous Pt layer shown in Fig. 2.

Figure 4 shows comparative plots of the mass activity vs Pt loading for both particle and layer cells in the low and high current density regimes defined by E = 0.80 and 0.50 V, respectively.
cells with $w \approx 0.18 \text{mg/cm}^2$ exhibit higher $i_{\text{mV}}^{0.8}$-values than that of the TBPBE cell, which are loadings that are too low to achieve with the TBPBE architecture, as discussed above.

The plot of the low-potential (high current) mass activity, shown in Fig. 4b for the same cells as in (a), reveals different trends. The particle electrodes exhibit a maximum in $i_{\text{mV}}^{0.8}$ of 2.7 A/mg at an intermediate loading of $w = 0.18 \text{mg/cm}^2$. The mass activity decreases slightly with decreasing $w$, indicating that flooding by product water of the smaller pores (at smaller $w$) is more likely. As $w$ is increased to 0.40 mg/cm$^2$, $i_{\text{mV}}^{0.8}$ decreases to 1.1 A/mg. This is attributed to the decreased pore density and increased pore length with increasing $w$, because longer pores result in decreased oxygen flux, and lower pore density combined with wider particles increases the oxygen diffusion path through the electrolyte to access active sites on the particle tips that are embedded in the membrane. The low-potential mass activity of the continuous layers, also shown in Fig. 4b, is by more than a factor of 2 lower than that for the particle cells with comparable $w$. This dramatic difference is attributed to mass-transport-limiting effects of the continuous layers. The low porosity of the layer inhibits efficient reactant (oxygen) distribution or product (water) rejection. The TBPBE comparison cell has a mass activity of 0.76 A/mg at 0.5 V, which is lower than $i_{\text{mV}}^{0.8}$ for all particle electrodes but within the range of the continuous layer electrodes.

The polarization curves for all fuel cells shown in Fig. 2-4 were analyzed using a semiempirical model which provides insight into kinetic and mass-transport losses as described in greater detail in Ref. 49. The fuel cell voltage $E$ at the current density $i$ is described by

$$E = E_0 - (R - b \log i - m \exp(m))$$

where $E_0$ is given by

$$E_0 = E_0 + b \log i_0$$

$E_0$ is the reversible open-circuit voltage which is 1.17 V at 70°C.\textsuperscript{50} $R$ is the ohmic resistance which was measured independently and is controlled by proton transport in the membrane as well as electron transport within the cell components, $i_0$ is the exchange current density, i.e., the equilibrium rate of reaction at the electrode/electrolyte interface, and $b$ is the characteristic slope associated with the Tafel relationship of current and overpotential.\textsuperscript{51} The last term in Eq. 1 is an empirical quantity that describes the high current density overpotential which is associated with mass transport. A nonlinear curve fit routine was used to determine the values of the unknown parameters $E_0$, $b$, $m$, and $n$ in Eq. 1 for each polarization curve, as summarized in Table I and plotted with the measured data on a logarithmic scale in Fig. 5. The Tafel slope $b$ is lowest for the cell with a continuous $w = 0.25 \text{mg/cm}^2$ Pt layer and for the TBPBE comparison cell, with $b = 97$ and 101 mV/dec, respectively. The particle electrodes have considerably higher slopes, ranging from 142 to 171 mV/dec. We attribute the higher Tafel slope for the particles to losses within the electrode,\textsuperscript{52} because the slope is expected to double when the ORR rate is determined by reaction kinetics plus either (i)

Table I. Kinetic and mass-transport parameters given by Eq. 1. $R$ is the slope extracted from the hydrogen pumping polarization curve as discussed in the text, and $E_0$, $b$, $m$, and $n$ are obtained from a nonlinear curve fit.

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<th>Electrode</th>
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<th>$R$ (Ω cm$^2$)</th>
<th>$E_0$ (mV)</th>
<th>$b$ (mV/dec)</th>
<th>$m$ (mV)</th>
<th>$n$ (cm$^2$/mA)</th>
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<td>869</td>
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Conclusion

Cathode electrodes consisting of Pt layers and particles were deposited onto GDL substrates by sputtering from deposition angles of 0 and 87°, respectively, and integrated into PEM fuel cells. A comparison of polarization curves from cells with Pt layers and particles shows that the mass-specific activity is higher for Pt layers at low current densities but higher for Pt particles at high current densities. These trends are attributed to a higher catalytically active surface area for the Pt layer but a more efficient mass transport (oxygen or water) for the particles. These results illustrate the performance tradeoff associated with the Pt surface area and porosity and demonstrate that the GLAD technique is a promising method to control the catalyst nanostructure in that regard.

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