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Publication Date

2011-10-09

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Water Uptake in PEMFC Catalyst Layers

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Water uptake profiles of proton-exchange-membrane fuel-cell catalyst layers are characterized in the form of capillary-pressure saturation (Pc-S) curves. The curves indicate that the catalyst layers tested are highly hydrophilic and require capillary pressures as low as -80 kPa to eject imbibed water. Comparison of materials made with and without Pt indicates a difference in water ejection and uptake phenomena due to the presence of Pt. The addition of Pt increases the tendency of the catalyst layer to retain water. Dynamic vapor sorption (DVS) is used to characterize the water-vapor sorption onto Nafion, Pt/C, and C surfaces. The DVS results align with the trends found from the Pc-S curves and show an increased propensity for water uptake in the presence of Pt. The effect of the ion in Nafion, sodium or protonated form, is also compared and demonstrates that although the protonation of the Nafion in the catalyst layer also increases hydrophilicity, the effect is not as great as that caused by Pt.

Introduction

Achieving proper water management in proton-exchange-membrane fuel cells (PEMFC) is rife with challenges. Cathode-catalyst-layer (cCL) flooding is of one concern due to the already slow kinetics of oxygen reduction. Characterization of CL water-uptake profiles enables a fundamental understanding of the driving forces behind flooding and facilitates targeted improvement. However, to date, there has not been data on the wettability and water-uptake behavior of CLs. In this paper, we present results from characterization techniques including capillary pressure vs saturation (Pc-S) curves [1] and ionomer water content measurements taken from DVS.

Materials

20 wt% Pt/C (5:2 Pt/C:Nafion) CLs were made in-house using an ink painting process and applied directly onto polytetrafluoroethylene (PTFE) membranes from Sartorius Stedim with 0.2 μm pores. Successive layers of catalyst ink were added to the PTFE membranes and dried at 140 °C between coatings. Coats were added until the catalyst layer began to show signs of cracking which occurred typically around 20~40 μm . The samples were made to be as thick as possible given this limitation to facilitate accurate measurement. Samples without Pt were also made to compare the effect of Pt on wettability resulting in a 2:1 C:Nafion layer.

Assembly

The wettability characteristics were measured via a setup and methodology developed by Gostick et al. [2]. The sample is sandwiched between hydrophilic and hydrophobic membranes to create an isolated two-phase region. Air may be injected or withdrawn

from the sample region to alter P_c where $P_c = P_L - P_G$. Capillary pressure is thus varied and the weight of a connected water reservoir is measured to determine the saturation.

A Millipore polyvinylidene fluoride (PVDF) membrane with 0.22 μm pores was used for the hydrophilic membrane with a Sartorius Stedim PTFE 0.22 μm pore membrane used as the hydrophobic barrier above the sample. To prepare the sample before introduction to the rig, the catalyst layer is brought to full saturation so that the initial saturation level may be known. This is in contrast to the traditional method of starting with a dry sample, typically gas-diffusion layer, because due to the water wicking property of Nafion, a catalyst-layer measurement cannot be started from an initial saturation of zero. Once the catalyst layer comes into contact with the hydrophilic membrane and water reservoir, it uptakes water. Instead, we aim for full saturation by preparing it in a similar fashion to the preparation of the hydrophilic membrane by placing the catalyst layer in a flask partially filled with water. The flask is evacuated by vacuum pump. Next, the water is tilted into contact with the catalyst layer so that water may wick into the sample and displace the air without entrapment. The sample is kept submerged in water as the vacuum is released and the sample is loaded onto the P_c -S measurement rig. Capillary pressure is kept at zero or above to maintain saturation.

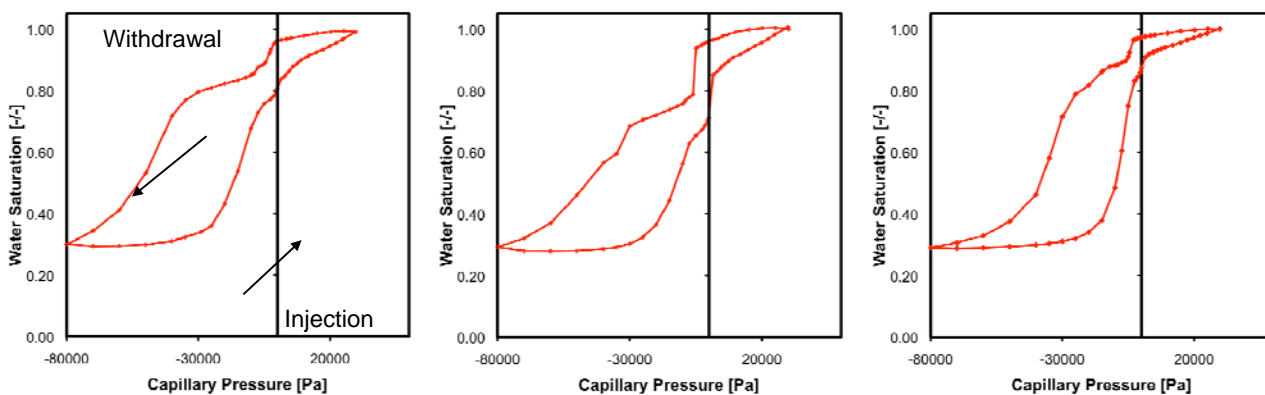
Results

A P_c -S curve for a sodium-form Pt/C catalyst layer sample is shown in Figure 1a. Much of the curve lies in the negative P_c region and shows the highly hydrophilic nature of the CL. The withdrawal portion of the curve is observed by starting at the right and tracing the top curve toward the left. The withdrawal curve demonstrates little loss of saturation until $P_G > P_L$ and shows forced ejection of water thus signifying that water must

be actively forced or drawn out of the CL. The curve shows a noticeable knee along the withdrawal curve that is a unique feature of the CL. The knee suggests an abundance of a type of pore, to be discussed, that leads to water ejection around -5 kPa. The trailing tail of the curve moving left shows that even at -80 kPa, all water is not removed from the catalyst layer. Subsequent injection of water shows a hysteretic effect and spontaneous imbibition occurring at capillary pressures as low as -30 kPa, which attests to the hydrophilicity of the catalyst layer. The path of the curves was also found to be reproducible when letting the system rest between cycles and restarting from high P_c .

Figure 1b shows a similar measurement for a sample made without Pt. The carbon-only sample shows more punctuated ejection and uptake phenomena near $P_c = 0$ as may be expected given the neutral wetting behavior of carbon. We see by comparing Figures 1a and 1b that water movement in the -5 kPa to 0 range constitutes a larger proportion of the total water cycling profile for the carbon-only sample vs the Pt/C catalyst layer. The presence of Pt leads to a slower release of water on ejection and a more gradual uptake upon imbibition.

Comparison of Figure 1a and 1c demonstrates the effect of the counterion in Nafion. The protonated CL shown in 1c exhibits very similar characteristics to the nonprotonated form again with a small knee in the -5 kPa range and gradual uptake from -20 kPa through 0. In the case of the protonated sample, the enclosed area of the curve in the positive-capillary-pressure range appears to be smaller which would suggest that more water movement occurs in the negative-capillary-pressure range which corresponds to increased hydrophilicity due to protonation. Nonetheless, the composition of the catalyst powder, Pt/C vs C only, is seen to impose a greater effect on the shape of the P_c -S curve than does the composition of the polymer.



1 a

1 b

1 c

Figure 1. Pc-S curves of catalyst-layer samples with 3 variations. a) sample with 20 wt% Pt/C and 5:2 Pt/C:Nafion ratio in sodium form. b) sample with carbon only, 2:1 C:Nafion ratio in sodium form. c) Pt/C sample with Nafion in protonated form.

Dynamic-Vapor-Sorption characterization

Dynamic vapor sorption (DVS) was used to characterize the water-vapor sorption of the CLs as shown in Figure 2. Water content is calculated based on the fraction of ionomer present in the test sample. A comparison of a traditional Pt/C catalyst sample with one without Pt shows a higher water sorption curve in the presence of Pt. Differences in lambda increase as relative humidity increases thereby suggesting a compounding effect of Pt on water attraction; once a surface is wet, additional wetting is facilitated. Whether with or without Pt, the water content of the ionomer when mixed

with catalyst powder is less than that of bulk ionomer in Nafion 117 across the entire humidity range. The increased propensity for water sorption by the Pt-containing sample is in agreement with the Pc-S curves discussed previously.

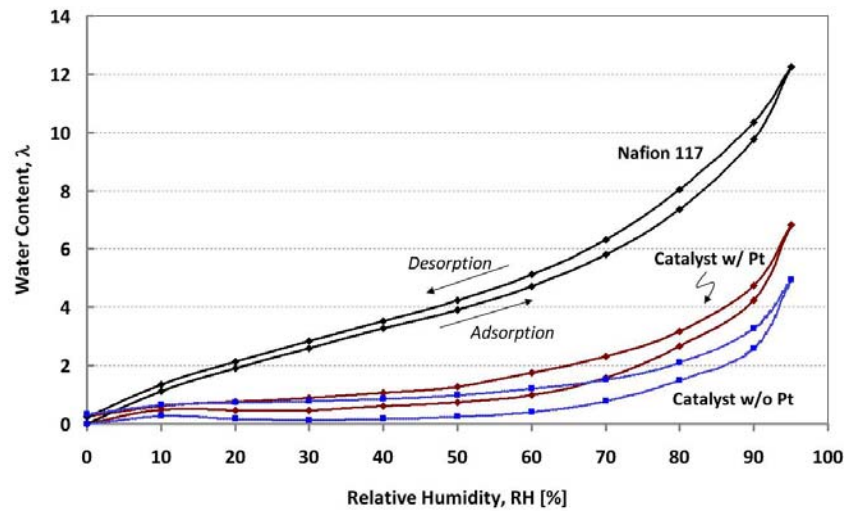


Figure 2. Water content as a function of humidity for bulk Nafion 117, catalyst-layer with 20wt% Pt/C and 5:2 Pt/C:Nafion, and catalyst layer with 2:1 C:Nafion.

Conclusions

Water-uptake curves were measured for isolated catalyst layers made by standard ink painting protocol with 20 wt% Pt/C in a 5:2 particle-to-Nafion mixture and with samples not containing Pt. The findings demonstrate the highly wetting nature of catalyst layers that can retain over 50% saturation at capillary pressures near -40 kPa. The results indicate that the Pt has a distinct wetting effect that leads to more gradual Pc-S profiles without distinct ejection or uptake events when compared to a carbon-only sample. The effect of the presence of Pt on water profiles is greater than the effect of protonating the Nafion. Therefore the precious metal used in catalysts may play a dominant role in influencing Pc-S relations as opposed to other components of the catalyst layer such as the ionomer.

Acknowledgments

This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Fuel Cell Technologies, of the U. S. Department of Energy under contract number DE-AC02-05CH11231.

We also thank the Los Alamos National Laboratory Fuel Cell Team.

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