

## Improved PEMFC Cathode Performance with Controlled Ionomer Aggregation

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The heart of the proton exchange membrane fuel cell (*PEMFC*) comprises a gas separator membrane laminated to porous electrodes (*membrane electrode assembly, MEA*) where the dispersed Pt catalyzes the H<sub>2</sub> oxidation (*anode*) and O<sub>2</sub> reduction (*cathode*) electrochemical reactions. A perfluorosulfonic acid (*PFSA*) polymer such as Nafion<sup>®</sup> is typically used in the membrane and electrode layers to provide a proton conduction path to the Pt catalyst sites.

The CCDM electrode fabrication method involves direct application and subsequent solvent drying of the catalyst ink on porous diffusion media (*catalyst-coating-on-diffusion-media*), while the CCD method involves application of the electrode ink to a solvent-impermeable decal substrate (*catalyst-coating-on-decal*) with subsequent transfer to the PFSA membrane layer. The electrode ink typically carries a Pt/C catalyst and PFSA polymer in an alcohol-water solvent that can wet the porous coating substrate in the CCDM method.

The gas diffusion media (*GDM for reactant gas concentration uniformity and water management*) typically comprises a 200 μm thick carbon paper with a proprietary 25 μm thick microporous layer (*MPL, carbon black with polytetrafluoroethylene beads*) that is located adjacent to both anode and cathode. To minimize the drying stress and cracking<sup>2,3</sup> in the CCDM electrode layer, the alcohol-water composition in the electrode ink is frequently formulated at a low static surface tension which then readily wets the porous GDM substrate. Figure 1 shows that the nPrOH:H<sub>2</sub>O::3:1 w/w solvent mixture (*24.2 mN/m static surface tension*) has a low contact angle (*14.4° after 1 sec*) and is easily absorbed into the MPL layer (*~100 nm pore*) of the porous GDM substrate.

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<sup>1</sup> Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

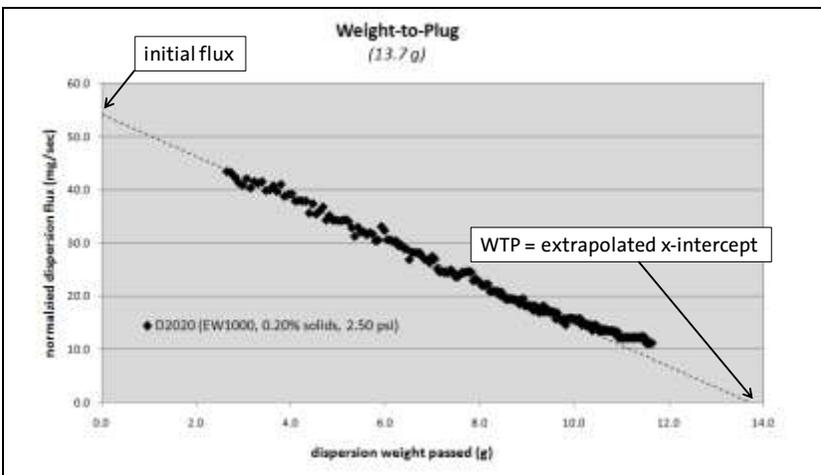
<sup>2</sup> R. C. Chiu and M. J. Cima, J.Am.Ceram. Soc. 76 (1993) 2769.

<sup>3</sup> R.Koestner, "Crack Mitigation in PEMFC Electrode Layers", extended abstract presented at the 15th International Coating Science and Technology Symposium, September 13-15, 2010, St. Paul, MN



**Figure 1.** Solvent contact angle and absorption on the MPL layer of a GDM substrate. (left) EtOH:H<sub>2</sub>O::3:2 w/w, 26.2 mN/m, 93.4° after 1sec; (center) nPrOH:H<sub>2</sub>O::3:1 w/w, 24.2 mN/m, 14.4° after 1sec; (right) nPrOH:H<sub>2</sub>O::3:1 w/w, 7.1° after 5sec.

However, the PFSA permeation into the diffusion media during CCDM electrode fabrication must be controlled to maintain an adequate polymer loading in the electrode layer for optimal cell performance. Since the PFSA polymer class is susceptible to chain aggregation in alcohol-water solvent dispersions<sup>4,5</sup>, its microgel fraction in the electrode ink can then be used to limit ionomer entrainment with the solvent flow into the GDM substrate by hydrodynamic size exclusion.



**Figure2.** Microgel assay via WTP method of a Nafion<sup>®</sup> polymer dispersion.

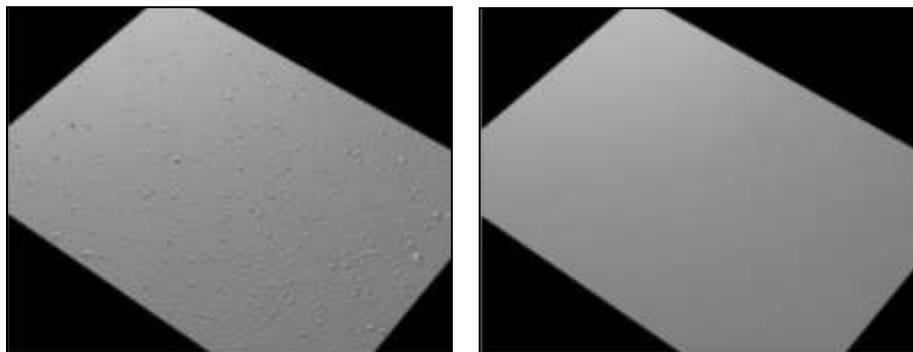
A weight-to-plug (WTP) method is used to assay the microgel fraction in the ionomer dispersion for an electrode ink by measuring the dispersion weight (in grams at 0.20% solids) needed to plug a model IsoPore<sup>™</sup> membrane filter (47 mm disk and 0.40 μm pore diameters). A regulated backpressure at 2.50 psi is applied to the dispersion column, while the resulting flow is then measured with a digital scale and normalized to correct for the change in column head pressure. Figure 2 shows the measured WTP for a commercial Nafion<sup>®</sup> dispersion (Dupont D2020). The dispersion flow is measured at 2 sec intervals and then plotted

<sup>4</sup> R.D. Lousenberg, J. Polym. Sci.: Part B: Polym. Phys. 43 (2005) 421.

<sup>5</sup> T.H. Mourey, L.A. Slater, R.C. Galipo and R.J. Koestner, J Chromatography A. 1218 [34] (2011) 5801.

after smoothing using a 10-point moving average. The dispersion flow decreases linearly with the dispersion weight that passes through the membrane filter which gives a WTP of 13.7 g in this case using the extrapolated x-intercept. In contrast, the solvent-only control sample (*without pre-filtration*) has a much higher WTP in the 400-800 g range with replicate measurements.

The microgel content for this Nafion<sup>®</sup> dispersion lot is also visualized directly in Figure 3 where a 400 nm dry film is cast on the atomically flat Si(001) wafer surface. A minimal rms roughness of 0.6-0.7 nm is measured at three locations (*each at 180 x 240 μm<sup>2</sup>*) on the bare Si substrate surface, while a large topography contrast is found on the Nafion<sup>®</sup> film surface with vs without the 0.2 μm pre-filtration step at 2.67% solids that is assigned to entrained ionomer microgels in the applied wet film.



**Figure 3.** Microgel visualization (Veeco NT 8000 Optical profiler) for a 400 nm Nafion<sup>®</sup> film on Si(001) over 180 x 240 μm<sup>2</sup>. (left) no pre-filtration; (right) 0.2 μm pre-filtration of the 2.67% solids coating dispersion.

Nafion <sup>®</sup> Dispersion Weight-to-Plug		WTP (g)
<b>D2020 (EW965)</b>		(average +- range error)
	no prefiltration	3.3 +- 0.2
	0.2 μm pre-filtration	48 +- 2.1
<b>D2020 (EW1000)</b>		
	control	13.6 +- 0.7
	HNO <sub>3</sub> addition	13.8 +- 0.3
	sonic/heat treatment	13.4 +- 0.4
	HNO <sub>3</sub> /sonic/heat	22.3 +- 0.9

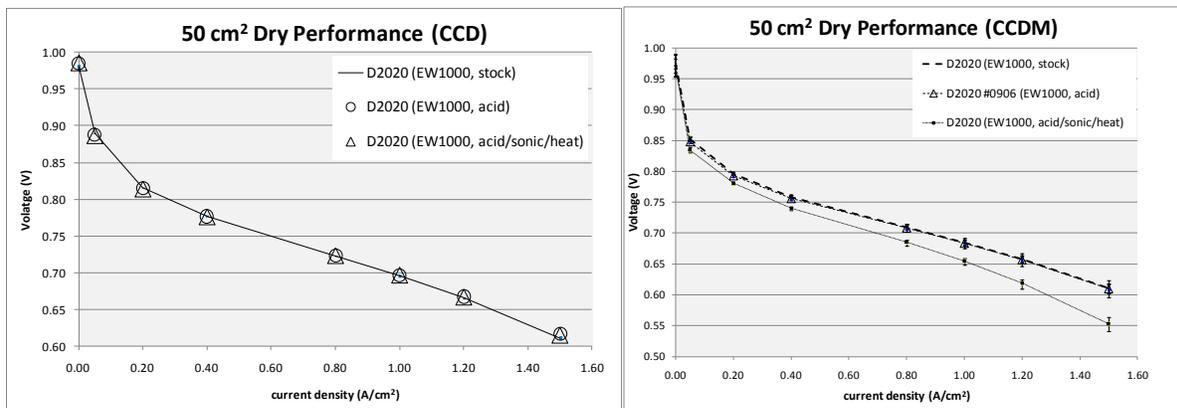
**Table 1.** WTP summary for Dupont D2020 Nafion<sup>®</sup> dispersions.

Table 1 summarizes the measured WTP for two Nafion<sup>®</sup> dispersion lots after varying treatments. The 965 g/mol equivalent weight (EW) dispersion lot is used to coat the 400 nm Nafion<sup>®</sup> films in Figure 3 with a corresponding WTP increase from 3.3 to 48 g after the 0.2 μm pre-filtration step which is consistent with the observed contrast in film surface topography. The EW1000 dispersion lot is used to fabricate CCD and CCDM cathode layers where the ionomer dispersion for each cathode ink is treated by a combination of HNO<sub>3</sub> acid addition (10 mmol/kg solution) and sonication/heat (1 hr at 60 °C in a water bath). The measured

WTP remains constant at 13.4–13.8 g except for the last treatment variation with acid/sonic/heat which gives a WTP at 22.3 g.

Figure 4 shows the dry voltage performance for the CCD vs CCDM cathode layers after 1 hr voltage recovery for varying treatments of the ionomer dispersion in the cathode ink. Each cathode part variation is tested in 4 PEMFC replicates using 2 test stands x 2 flow fields and is plotted as the average voltage with range error bars. The cell is held at 80 °C with H<sub>2</sub>/air at the anode/cathode for 1.5/2.0 stoic. The inlet RH is maintained at 32% at both electrodes, which is calculated to give 87% RH at the cathode for the 1.5 A/cm<sup>2</sup> current density.

The MEA's are constructed with 50 cm<sup>2</sup> active area and use an 18µm reinforced PFSA membrane (EW830) laminated to CCD vs CCDM electrodes at 145°C and 1,500 kPa for 2 min. The CCD vs CCDM anode design uses 20% Pt (*by weight*) dispersed on Vulcan<sup>®</sup> (*amorphous vs corrosion-resistant*) carbon black at 0.050 mgPt/cm<sup>2</sup> with a Nafion<sup>®</sup>/carbon (I/C) ratio of 0.61 vs 1.20 w/w. The CCD vs CCDM cathode design uses 30% Pt-alloy dispersed on Ketjen carbon black (*also TKK, Tanaka Kikinzoku Kogyo K.K.*) at a platinum loading at 0.20 mgPt/cm<sup>2</sup> with an I/C ratio of 0.95 vs 1.40 w/w. The CCD cathode variations in Figure 4 result in the same dry voltage performance; but the CCDM cathode variations show a dry performance loss for the electrode ink whose Nafion<sup>®</sup> dispersion has a lower measured microgel content by the WTP method in Table 1.



**Figure 4.** Dry voltage performance for CCD vs CCDM cathodes with varying treatments of the ink ionomer dispersion.

In conclusion, these results are consistent with Nafion<sup>®</sup> loading and dry performance loss in the CCDM cathode layer if the polymer permeation into the GDM substrate is not controlled by hydrodynamic size exclusion. The acid/sonic/heat treatment of the Nafion<sup>®</sup> polymer dispersion in the cathode ink led to a higher permeation flow into the porous GDM substrate for the CCDM electrode fabrication process, while the same treatment for the CCD cathode ink did not show any dry performance loss.