Crack Mitigation in PEMFC Electrode Layers

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The durability of polymer exchange membrane fuel cell (*PEMFC*) stacks is a current limitation for its widespread use in the automotive industry. Electrode layer cracks develop during ink drying after wet application and directly impact the durability of the fabricated membrane-electrode assembly (*MEA*) during fuel cell operation[1]. As an example, Figure 1 shows the polymer flow and resulting thickness reduction that occurs in a 25 μm thick Nafion® membrane at an electrode crack after humidity cycling.
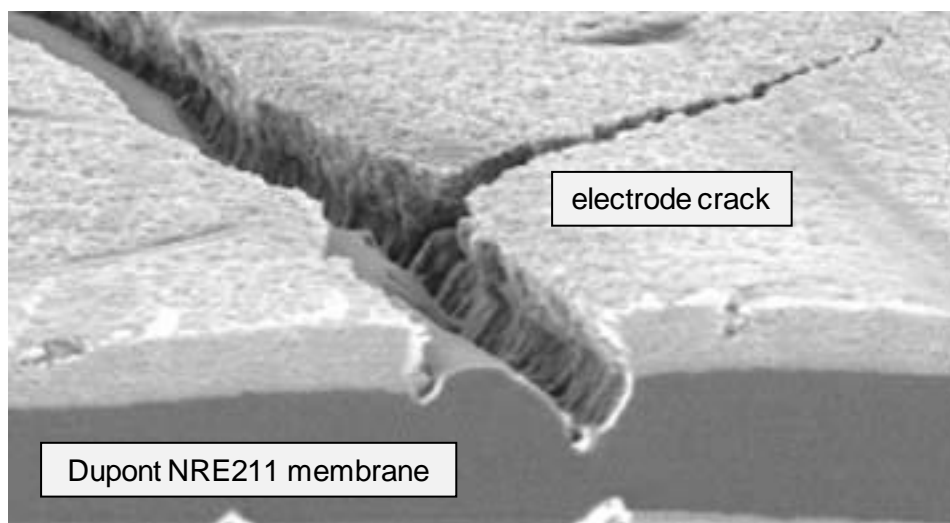

Figure 1. MEA x-sectional micrograph after humidity cycling.

In other prior work[2-7], the stress development during drying of nanoporous alumina and silica layers has been systematically measured at varying organic binder loading using the curvature or deflection of the coated elastic substrate. The organic binder is typically added at low loading to mitigate crack formation by increasing the layer modulus, while the binder is assumed to be evenly distributed throughout the particle network.

In this work, we manipulate the agglomerate size of a Pt-alloy electrocatalyst ink prior to coating which in turn dramatically impacts the crack yield of the resulting electrode layer; we assign the

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higher crack yield observed for the coating ink with a monodisperse large catalyst agglomerate to a likely μm-scale non-uniform distribution of the perfluorosulfonic acid (PFSA) polymer within the porous electrode structure.

The electrode inks are formulated and coated as follows:
a) Pt-alloy nanoparticle catalyst on HSC (*high surface carbon*) support from TKK (*Tanaka Kikinzoku Kogyo K.K.*) at 3.0% carbon/ink w/w.
b) Dupont D2020 Nafion® polymer (*measured equivalent weight at 950 g/mol sulfonic acid by titration*) at 4.2% polymer/ink w/w.
c) dispersant addition at 0.00 vs. 0.30% w/w ink.
d) n-propanol:water :: 3:1 w/w solvent.
e) ball milling with 5 mm ZrO_2 beads for 1 day at bead:ink :: 3:1 w/w with 63% head space v/v.
f) rod-coated with a gravimetrically-measured dry laydown of 0.200 +- 0.008 mg Pt/cm^2 and 0.472 +- 0.019 mg $carbon/cm^2$ on a gas diffusion layer which is comprised of a 200 μm thick carbon fiber paper overcoated with a 25 μm micro-porous carbon black layer.
g) dry thickness of the electrode layers is measured separately on ETFE (*ethylene-tetrafluoroethylene alternating co-polymer*) decal support at 12.7 +-1.4 μm for 0.47 mg $carbon/cm^2$ laydown which implies a 18.5% carbon volume fraction that is independent of dispersant addition to the coating ink.

Figure 2 gives the ink rheology in an up-down shear rate profile to assess PtCoHSC colloidal stability. A high yield stress is detected for the electrode ink without dispersant, while Newtownian flow and a much lower viscosity is measured for the electrode ink with dispersant.
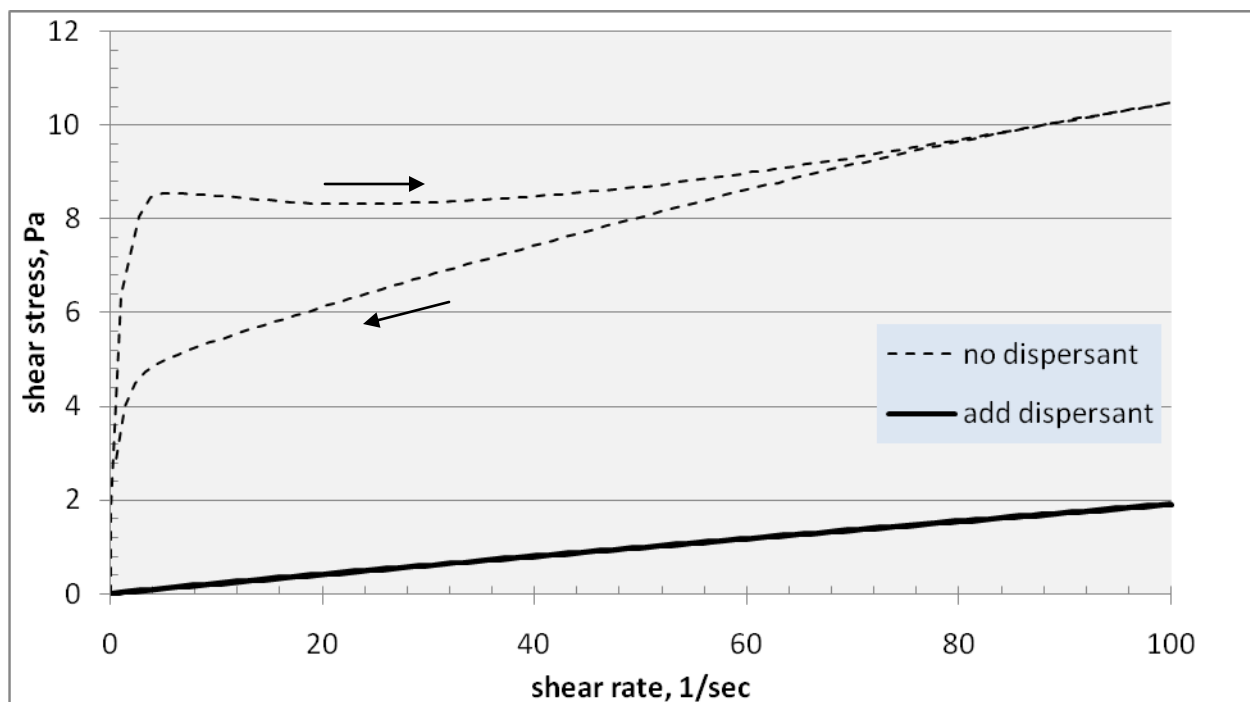

Figure 2. Pt-alloy electrocatalyst ink rheology.

After ball milling (*"1-day mill"),* both electrode inks are transferred to another polyethylene bottle without ZrO_2 beads to mix for 1 more day *("1-day mill + 1-day hold").* The inks are coated immediately after each time step, while a quench dilution to 0.10% carbon with ethanol:water ::1:3 w/w solvent is also prepared immediately with a small ink sample for particle size measurement (*low angle laser light scattering*) by the following day. After this quench dilution, we find that the resulting particle size distribution remains stable over the course of the following day.

Figure 3 shows the resulting ink particle size distributions (*without instrument sonication*) for both inks with hold time. The ink with dispersant addition shows a low diameter distribution which is also stable with ink aging. However, the ink without dispersant yields a monodisperse secondary agglomerate at 10 μm diameter after a 1-day ink age which also approximates the dry electrode thickness.
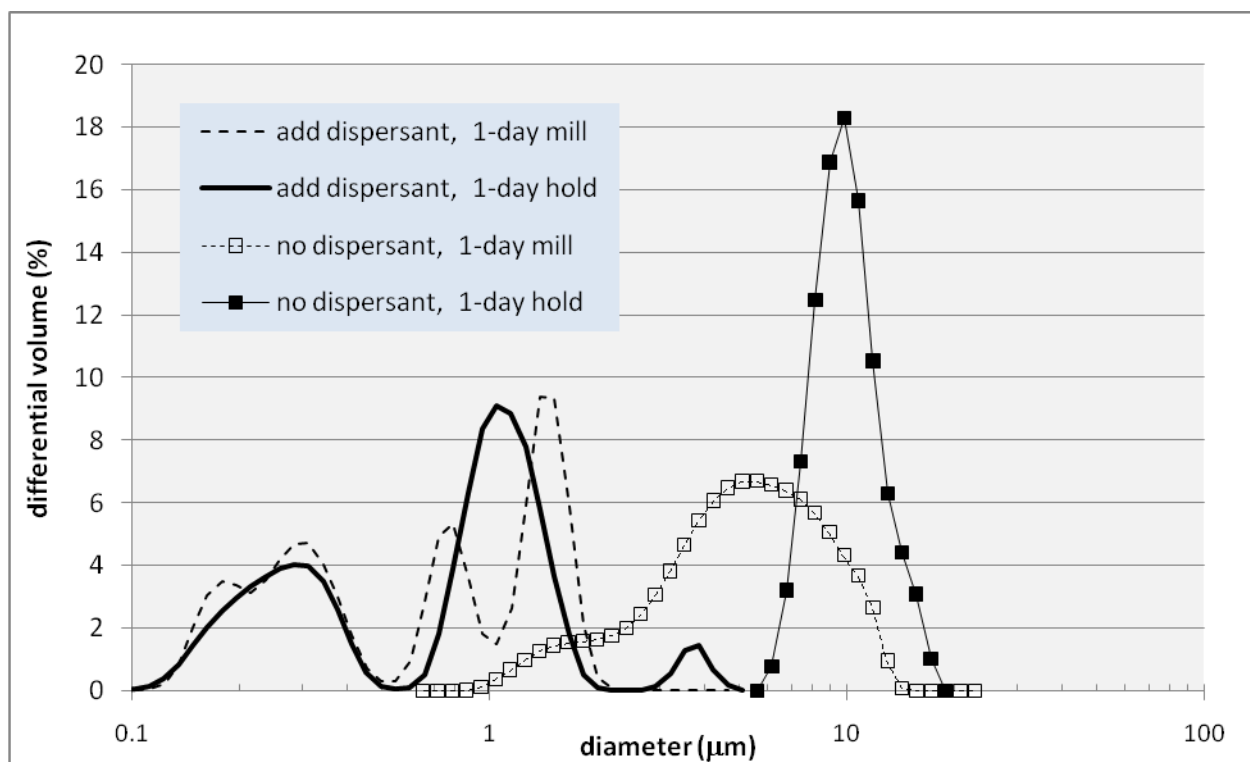

Figure 3. ink particle size distribution using Low-Angle Laser Light Scattering (LALLS).

As the catalyst secondary agglomerate size increases in the electrode ink prior to coating, the layer crack yield shown in Figures 4-5 increases as well. We assign this higher crack yield to a non-uniform polymer location distribution. The layer porosity and carbon volume loading did not change within the precision of our dry thickness measurement on the sacrificial ETFE decal support. The polymer in the surrounding ink solution is expected to preferentially deposit near its geometric (*or external*) surface rather than permeate and evenly deposit throughout the catalyst secondary agglomerate volume. Since the PFSA polymer location distribution within the electrode layer can also affect the proton and oxygen mass transport resistance, the PEMFC cell voltage performance will be presented and discussed as well.
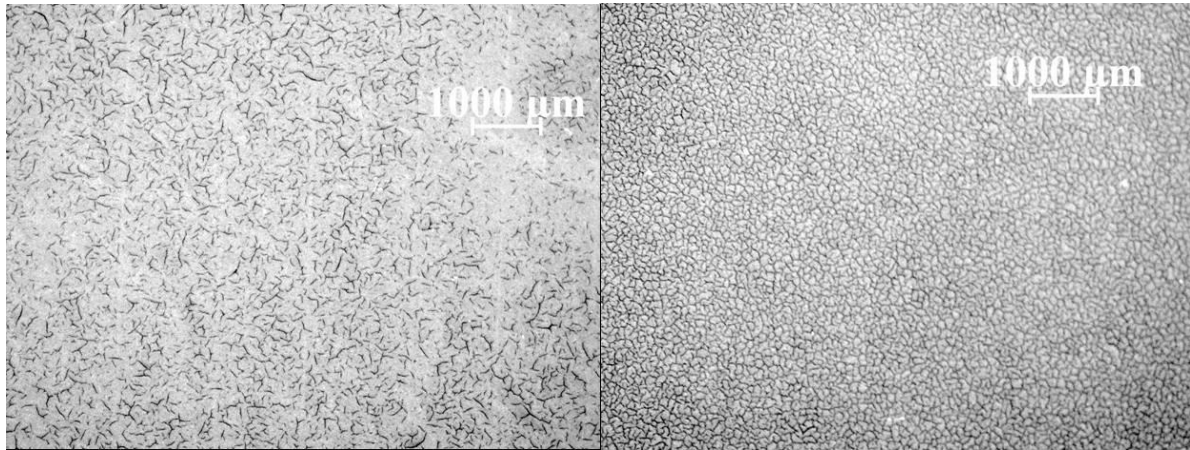
Figure 4. normally reflected light micrographs of electrode cracking for the "no dispersant" ink before (*left*) and after (*right*) ink aging.
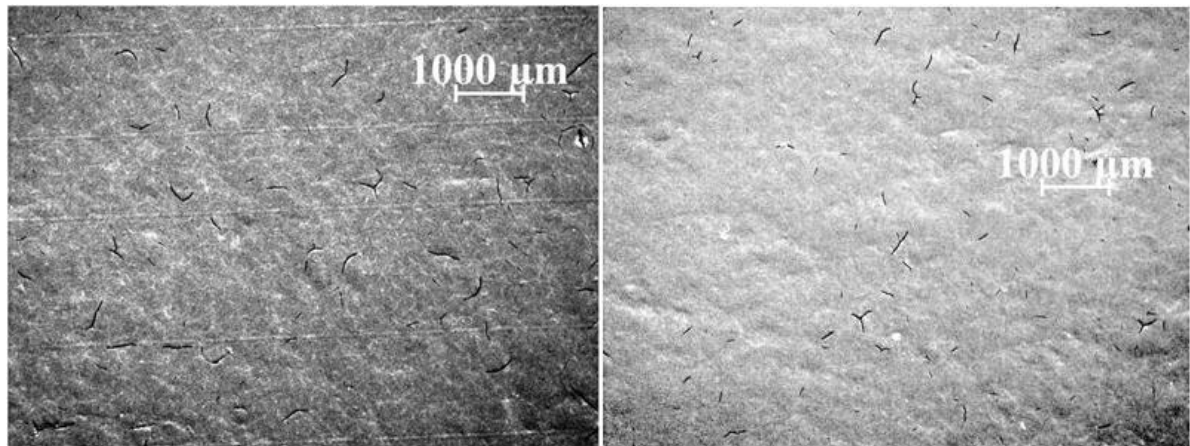

Figure 5. normally reflected light micrographs of electrode cracking for the "dispersant add" ink before (*left*) and after (*right*) ink aging.

References

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