

Short communication

## Fabrication of high precision PEFC membrane electrode assemblies

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### Abstract

Membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells (PEFCs) are commonly prepared in the research laboratory by hand painting liquid catalyst material onto Teflon supports, then transferring the dried catalyst to a membrane separator by hot pressing. This hand application of the catalyst is a time consuming process of modest precision with respect to catalyst loading, producing samples not ideally suited for controlled experimentation. We report the results of a method for preparing MEA catalyst layers in a faster and highly reproducible fashion. This method relies on catalyst inks that have been modified to increase their coating reproducibility, and the use of a support material that improves the hot press transfer of the catalyst to the membrane separator. The result is a process which is not only significantly more precise and faster than hand painting, but which produces cells with nearly 25% higher current density in the critical voltage operating region.

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### 1. Introduction

Modern polymer electrolyte fuel cells (PEFCs) show great promise for industrial application owing to their high power density and low precious metal loadings. Several companies are presently offering PEFCs for commercial use. However, depending on the methods used, preparation of PEFCs in the research laboratory can suffer from two limitations: first, the time needed to accurately prepare coatings of the electrode catalyst materials that are ultimately bonded to the membrane separator; second, the relatively modest reproducibility of platinum loadings resulting after hot press transfer of the catalyst material to the separator. One common method of preparing the catalyst layers involves painstaking application by hand of thin coats of the liquid catalyst suspension to a hot press transfer decal, with drying and careful weighing of the decal between coats to determine when the appropriate platinum loading has been reached. This process can take 6 h to several days depending on the degree of precision required, though even the most painstaking preparation does not result in standard deviations of platinum loading

of less than 12 or 13%. While it is clearly advantageous in a basic research setting to have a rapid means of membrane electrode assembly (MEA) production in order to efficiently generate large numbers of test samples, it is likewise necessary that these samples achieve the highest precision possible for important characterizations such as platinum loading.

There are faster means of catalyst coating than hand painting, many of which have been reported in the literature. Screen printing [1,2], rolling techniques [3–5], and spraying methods [6,7] have been the most prevalent, and can all be adopted for use in the research lab. However, there have been no reports on the potential impact of these methods on the precision of the resulting MEA catalyst loading. Further, nothing has been reported regarding the effect of changes in material parameters, such as ink composition and type of coating substrate, on loading precision. In the present work, we discuss the results of using a motor driven doctor blade spreader (essentially, a screen printer) to coat transfer decals for MEA production in the research and development laboratory. We show that, while expectedly faster than hand painting, the machine spreader requires the use of an ink of appropriate composition and a properly selected transfer decal material in order to achieve superior MEA platinum loading reproducibility. Further, MEAs made by this method show a surprising 25% increase in the kinetic region current density over MEAs made with hand painting.

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## 2. Fabrication methodology

The spreading apparatus, originally described in a previous publication [8], consists of a doctor blade device, from the Paul N. Gardner Company, driven by the time base of a Soltec X–Y plotter. The plotter time base is a highly accurate mechanical drive with a broad range of selectable speeds (20–0.05 cm/s), which is useful when compensating for liquids of varying viscosity. Machined aluminum slabs are used as the substrate support, and sit on the table of the X–Y plotter.

Fuel cell catalyst ink was prepared as previously described [9]. Several experimental inks were also prepared, wherein alcohols were evaporated from 10 wt.% Nafion<sup>TM</sup> solution as received from Solution Technologies, Inc. until the sample mass was approximately 50% of its initial value. Glycerol, diglyme, or water was then added to achieve a final sample concentration of about 5 wt.% Nafion. These Nafion solutions were then used in the preparation of inks as given in [9].

The coating procedure entailed positioning the doctor blade apparatus above the hot press transfer substrate (usually fiberglass reinforced Teflon), micropipetting an appropriate amount of material on the substrate in front of the blade, and activating the time base to drive the spreader through the liquid until the coat has covered a sufficient area. Pipetted volume of liquid catalyst, blade height, and drive speed were all adjusted for a given ink composition until maximum reproducibility of a certain platinum loading was achieved, as determined by weighing of the dried coats. These parameters were then used for all subsequent coatings of that particular ink formulation. Once coated, the transfer substrates were oven dried overnight and then prepared into MEAs by hot pressing onto Nafion 1135 ionomeric membrane, as described. For polarization measurements, 5 cm<sup>2</sup> MEAs were run as cells in a humidified hydrogen/air configuration, at a cell temperature of 80 °C and anode and cathode gas pressures of 30 psig.

Table 1 compares the results of hand painting of the original catalyst formulation onto 10 fiberglass reinforced Teflon transfer decals (each 5 cm × 1.6 cm) with doctor blade application of the same ink onto 10 additional substrates. The values of coating and loading precision reported are expressed as standard deviations from the respective averages. In order to achieve the reported deviations for hand application, the catalyst layers were painstakingly built up from succes-

sive ink coats, which were extensively dried and carefully weighed until the desired platinum loading was achieved. This process typically required for 10 samples total painting and weighing times of 6 h, and about 3 days of drying time. In contrast, the machine coating method required only 45 min for application of coatings to 10 substrates, and a single overnight drying. Although there was a considerable time saving seen with the machine coater, there was no evident improvement in the platinum loading reproducibility (Table 1). This was determined to originate from time dependent viscosity changes in the ink. As stated above, this mechanized doctor blade technique was developed in order to form highly uniform catalyst layers needed for accurate resistivity measurements [8]. Fig. 1 presents profilometry results of a hand painted sample, and one prepared for resistivity measurement with the machine spreader. These samples were not hot press transferred, rather coated onto polycarbonate substrates and dried. As the figure shows, the geometric uniformity of a sample prepared by this method is high; however, it was observed that the mass reproducibility between samples coated from the same ink lot varied by about 6–8%, indicating variable spreading characteristics of the ink. This was attributed to rapid evaporation of the alcohol solvent from the applied drop of catalyst ink and possibly component settling, causing ink viscosity and therefore spreading rate changes over time. Such changes were observed to take place on a time scale of a few seconds, meaning that a volume of ink added to the substrate and allowed to sit for a short time before coating would show different spreading behavior than the same volume coated immediately. Since the hand painting method requires even longer times than the machine coater, it is certain that it too suffers from material irregularities due to solvent evaporation.

To compensate for this behavior, a variety of polar, lower vapor pressure solvents, including diglyme, glycerol, and water, were substituted for the alcohols as described above. The diglyme and glycerol inks coated Teflon well, but showed poor release characteristics during hot pressing, requiring many attempts to obtain usable MEAs. In contrast, the extreme hydrophilicity of the water ink caused poor wetting behavior on Teflon. Thus, transfer decals made of 10 mil Kapton film were substituted for the usual Teflon decal for the application of water-containing catalyst ink. Kapton was chosen since it is more hydrophilic than Teflon, yet still highly chemically inert, with a glass transition temperature (>300 °C) that ensures little interaction between

Table 1  
Reproducibility results for hand painting and machine spreader application of a conventional catalyst ink

MEA type	Total application/drying time for 10 samples	Average coat mass (mg/cm <sup>2</sup> )	Coat mass S.D.	Average Pt loading after transfer (mg/cm <sup>2</sup> )	Pt loading S.D.
Standard ink, hand painted, Teflon decal	6 h/3 days	10.78	0.45	0.20	0.027
Standard ink, doctor blade applied, Teflon decal	0.75 h/1 day	10.11	0.32	0.18	0.026
Water ink, doctor blade applied, Kapton decal	0.75 h/1 day	11.02	0.51	0.20	0.009

Reported coating masses and platinum loadings are the average of 10 samples.

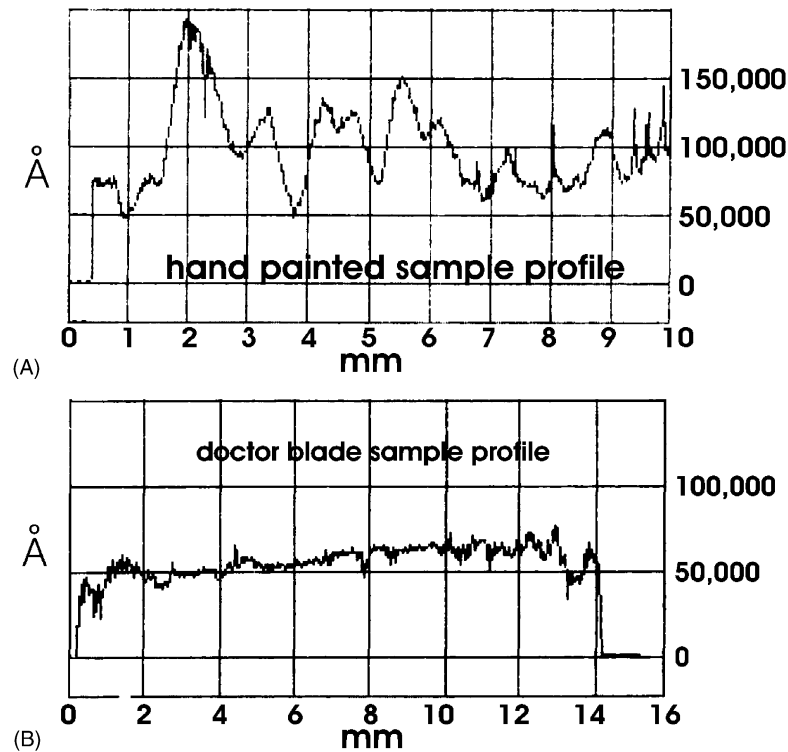


Fig. 1. Profilometry measurements of hand painted and machine spreader applied catalyst layers. These samples were unpressed, and were typical of those used in [8].

Table 2

Example calibration data for platinum loading achieved by machine spreading

Sample	Blade height (mil)	Ink volume ( $\mu\text{l}$ )	Final Pt loading ( $\text{mg}/\text{cm}^2$ )
1	6	150	0.1278
2	8	150	0.1876
3	10	150	0.2328
4	12	150	0.2414
5	16	150	0.2584
6	6	250	0.1278
7	8	250	0.2016
8	10	250	0.2925
9	12	250	0.3266
10	14	250	0.3152

These particular data are for standard ink on Teflon substrates.

itself and the Nafion while hot pressing. As mentioned earlier it was necessary to calibrate the platinum loading for a given solvent composition, substrate material, applied ink volume and height of the machine spreader blade. Table 2 shows the results of this calibration for the water-based ink on Kapton. The resulting precision of the platinum loading (Table 1) was about  $\pm 5\%$ , as compared to  $\pm 14\%$  for the conventional ink when coated onto Teflon, indicating the extreme transfer efficiency of the Kapton decal for the water ink formulation.

Clearly, this method suffers from the drawback of not being able to quickly assess new ink compositions. The

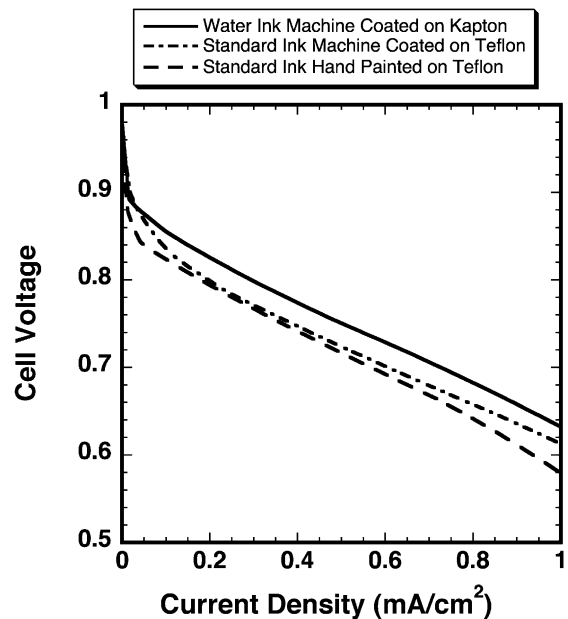


Fig. 2. Cathodic polarization curves for MEAs prepared using various methods and ink compositions. The operating conditions for these  $5\text{ cm}^2$  cells were: anode—inlet flow rate 160 sccm hydrogen, back pressure 30 psig, humidifier temperature  $105^\circ\text{C}$ ; cathode—inlet flow rate 550 sccm air, back pressure 30 psig, humidifier temperature  $90^\circ\text{C}$ , cell temperature  $80^\circ\text{C}$ . Each curve represents the average of the polarization of two MEAs.

time involved in testing new ink formulations and substrates for coating and transfer characteristics can be considerable. However, since much MEA research relies upon studying a large number of samples of a given composition, once discovered an optimized system such as the water ink/Kapton described herein becomes valuable for work in the laboratory. The present system in particular should be immediately useful since it represents the most commonly used catalyst to Nafion mass ratio of 5:2.

The performance characteristics of the MEAs prepared by either hand painting or doctor blade application and consisting of standard catalyst ink or water-based catalyst ink are presented in Fig. 2. The polarization data was collected for 5 cm<sup>2</sup> samples prepared as noted. Clearly, among the MEAs made from modified solvent inks, the one based on water-containing ink demonstrates the best performance. Comparison of the polarization curves of MEAs based on machine coated water-containing ink to the curves of those MEAs made with hand painted typical inks shows an increase in current density of 25–50% in between 0.6 and 0.8 V. This performance enhancement is likely due to greater catalyst utilization arising from structural changes in the electrode, which are in turn a consequence of the Kapton substrates, water solvent, or an interplay between the two. A detailed study of this phenomenon for future publication is underway [10].

### 3. Summary

In summation, we have demonstrated that by use of a water-based catalyst ink along with Kapton as a hot press transfer material, high precision fuel cell MEAs for research can be rapidly fabricated with using a simple machine-driven coater. We also show that careful calibration of the ink/substrate combination can allow a predictable catalyst loading, with precision nearly three times better

than that achievable under the best circumstances with the conventional ink formulation transferred from a Teflon decal. This indicates the superior release characteristics of the water ink/Kapton system. Surprisingly, for the case of water-based inks hot press transferred from Kapton substrates, cell performance seems to increase, a phenomenon we are presently investigating. While this method may have no commercial implications, it should be of value to the scientist wishing to produce high quality MEAs for careful study.

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