VI.9 High-Speed, Low-Cost Fabrication of Gas Diffusion Electrodes for Membrane Electrode Assemblies

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Objectives

- Reduce cost in fabricating gas diffusion electrodes through the introduction of high-speed coating technology, with a focus on materials used for combined heat and power generation (CHP).
- Relate manufacturing variations to actual fuel cell performance in order to establish a cost-effective product specification.
- Develop advanced quality control methods to guide realization of these two objectives.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Section 3.5):

(A) Lack of High Volume Membrane Electrode Assembly (MEA) Processes

(F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing R&D Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (Section 3.5.7):

- Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

This project addresses coating speed and uniformity of gas diffusion electrodes (GDE), a critical component for MEA fabrication. One sub-task is to develop a continuous X-ray fluorescence (XRF) analyzer that directly measures catalyst deposition level and distribution on rolled goods, ultimately guiding improvements in through-put and uniformity. This sub-task directly contributes to the forth quarter 2012 goal for in-line measurement. Another sub-task is to develop models that predict the effect of manufacturing variations in catalyst distribution and porosity in GDEs, and relate these variations as six-sigma limits for a component specification. The establishment of a model that predicts MEA performance based on manufacturing variations in GDEs contributes to improving the quality of the component as well as achieving the forth quarter 2013 DOE milestone above.

Accomplishments

- Developed an innovative on-line analyzer ahead of plan. For the first time have a complete “map” of precious metal catalyst level and distribution throughout the roll during coating.
- Team has established a framework for understanding ink stability issues:
  - For cathode, identified an additive that significantly improved key quality indicator by reducing the incidence of surface agglomerates on the GDE by ~80%.
- Established first critical task milestone: full length coating on carbon cloth whereby coating length increased by double.
- Identified a path to higher speed coating through reduction of coating steps by ~30%.

Introduction

The basis of this project is to create GDEs at a far lower cost than those currently available. GDEs are critical components of MEAs and represent the highest cost subcomponent of the MEA. Cost reduction will be accomplished through development of a higher throughput coating process, modeling the impact of defects due to the higher speed process, and overcoming these limitations and providing a six-sigma manufacturing specification that relates performance to defects. The main focus of the effort is creating next-generation inks through advanced additives and processing methodologies. As part of our approach, we will also develop on-line quality control methods such as determination of platinum concentration and distribution during the coating process. We will also develop correlations between manufacturing parameters and performance as well as establish models to predict the effect of manufacturing variations in MEA performance.

For this reporting period we designed, built, and validated an on-line analyzer for determination of loading and distribution of precious metal catalyst during coating. This accomplishment directly contributes to DOE's goal of improving quality control instrumentation throughout the manufacturing process. We also developed improved ink formulations that led to lower defects during longer coating runs – a first step towards reduction in cost.

Approach

GDEs are comprised of a gas diffusion layer coated with catalyst. The gas diffusion layer is simply carbon cloth or a non-woven carbon paper that has been coated with carbon black and serves as a current collector for the catalyst. For both the carbon black and catalyst, a hydrophobic binder is added to achieve critical porosity and hydrophobicity in the final structure. Of the carbon black, catalyst, or hydrophobic binder none are highly soluble in aqueous solutions. Aqueous solutions must be used as solvents since the use of organic solvents with a highly active catalyst is too dangerous in a production environment. Also, the hydrophobic binder is shear-sensitive, meaning it becomes less stable when pumped or subjected to shear forces in the coating applicator. Thus, the challenge in this project is overcoming the inherent physical limitations in these materials through advanced formulations and processing.

Our approach to solving this challenge begins with identifying key quality GDE metrics that relate directly to ink performance, develop an understanding of the forces behind ink stability, and introduce solution measurement methods that relate ink performance to the quality metrics. With more stable ink formulations, we anticipate being able to coat longer and wider webs at higher speeds or lower numbers of application passes. This process is supplemented by two other activities that ultimately lead to lower cost GDEs. We will develop a model that will predict the impact of manufacturing variations on MEA performance, and use this model to determine the level of coating quality needed to maintain consistent current and voltage. Also, we will create on-line instruments to lead more precise coating processes.

Results

Our first objective was to develop the in-line analytical method to follow improvements in coating. For developing continuous in-line analysis of catalyst deposition, we selected a custom XRF engine designed by X-Ray Optical Systems in New York. The key to their technology is the use of micro-capillary tube optics that amplifies the fluorescence signal and thus allows a greater signal with low powered X-ray tubes. Traditional commercial XRF units need a long time to obtain a signal – roughly 60-90 seconds and would not be able to provide an accurate measurement on webs moving 8-10 cm/s. We exploited the high signal gain of the micro-capillary tube in order to facilitate very short acquisition times and thus obtain detailed distribution maps of catalyst being coated on rolls of gas diffusion layers. The following are design targets and achievements to date, and a photo of the device is shown in Figure 1.

- Safely used by production staff. Employed extensive guards and auto-shut-off switches.
- Date acquisition rate 25 ms: 10 ms achieved.
- Rail scan 10 m/s: 20 m/s achieved.
- Instrument variation +/-2.5%: <+/-1% preliminary achieved.

FIGURE 1. Picture of Custom-Designed In-Line Analyzer for Precious Metal on Gas Diffusion Electrodes

- Minimum level <1 g/m^2 Pt: initially achieved 1.7 g/m^2 but believe can exceed minimum with parameter optimization.

We identified a key quality parameter for coating that relates directly to ink performance – agglomerates. Agglomerates are precipitations of catalyst, binder, or catalyst and binder that form protrusions on the gas diffusion electrode surface, interrupting the smooth coating. In the extreme case, these protrusions can pierce the membrane in the MEA. See Figure 2 for examples. As part of investigating the forces that destabilize our ink formulations, we found that the measurement of the zeta-potential of our solutions provided a measurable characteristic that is related to ink stability. For aqueous formulations, one typically needs charge to stabilize the particles and zeta-potential values between 15 and 25 mV are typically desired. For our base formulations, we obtained zeta potentials between 5 and 10 mV and when attempting to apply this ink to longer rolls of GDL developed significant agglomerations.

Using a combination of the zeta potential and developmental scale coating runs, we identified an additive that stabilized the cathode catalyst. A key to selection of this additive was to find a material that met the following selection rules: 1. stabilize ink components, 2. can be removed through higher processing temperature so no residuals remain that could interfere with catalyst performance, and 3. no significant change in porosity or hydrophobicity introduced through the use of the additive. Through this process we identified an additive that reduced cathode agglomerates by 77% over baseline formulations when scaled to the full production coating machine.

FIGURE 2. Example of Agglomerates Found on Gas Diffusion Electrodes

Lastly, we identified a new high energy process that facilitates creating more concentrated inks. By increasing the concentration of the catalyst and binder in the ink, we can reduce the number of application passes needed to achieve a final catalyst loading, and thus effectively "increasing speed" by actually reducing the number of coats. Although preliminary as of this writing, by using this new formulation we have reduced the number of application coats by 30% when using developmental scale coating machines.

Conclusions and Future Directions

We have developed a methodology to create more stable ink formulations, and have applied this to reduce a key quality feature – agglomerates on the electrode surface while increasing the length of GDL coated. A new instrument has been introduced for following our catalyst coating distribution and uniformity, and providing critical feedback on improvements in formulation and ink processing. A new high energy process for ink making has been identified with encouraging preliminary results. Thus, by being able to produce greater amounts of GDEs over shorter times, we can create a path to the higher volumes of MEAs targeted by the Department of Energy objectives.

Upcoming Focus:

1. Further improve additives combined with the high energy process.
2. Leverage these improvements towards either higher speed coating and/or reduction in number of passes as well as full-width coating.
3. Continue modeling and validation of the impact of manufacturing defects on performance.
4. Using the approach developed for carbon cloth gas diffusion electrodes, develop ink formulations appropriate for non-woven carbon paper gas diffusion electrodes.