

An Alternative Dispense Process for Application of Catalyst Films on MEA's

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Abstract

Traditional methods of applying fluid on surfaces in particular, catalyst films on Membrane Electrode Assembly (MEA) including, manual and semi-automatic brushing, acoustic spraying, printing, silk screening are commonly used in fuel cell manufacturing today. Several issues have been identified during the manufacturing implementation of these methods. Product quality, film consistency film cracking is amongst some of the major problem during MEA film dispensing. An alternative catalyst film applicator, jetting technology can circumvent most of these issues. This paper proposes an integrated system for film application process than consists of closed loop mass calibration to assure film thickness, a noncontact fast jetting process with high edge definition capable of applying films for highly selective areas and patterns. A system to obtain homogeneity of the solid-fluid mix is described and results are shared.

Keywords: agitation system, atomization, conformal coating, fuel cells, jetting, mass calibration, MEA, nafion, particle settlement.

Introduction

Fluid dispensing onto surfaces is an integral part of many manufacturing processes namely, semiconductors, solar and fuel cells. In the latter process, fluid doped with solid conductive and insulator particles, is to be dispensed in a form of a uniform and homogeneous thin film as part of the MEA catalyst for the chemical reaction occurring in the cell. Atomization of the fluid-solid substance prior to film application can be accomplished by way of mixing air and the catalyst, and then delivering this mixture onto the MEA surface. In this work the air-fluid mixing is carried out by means of impinging turbulent coaxial flow of air as the fluid exits a high pressure chamber through an orifice. This mixture is then directed in a conformal manner onto the surface topography. The momentum imparted to this mixture by the jetting action

taking place results in contactless deposition process, hence, the actual breakup of the substance deposited occurs at some distance from the orifice and prior to the surface being coated. As mentioned above, the film needs to be homogeneous; the positive buoyancy nature of the particles i.e., platinum, in the fluid, has the tendency to separate the fluid mixture in a form of particle settling. This issue mandates for an integrated system that keeps the particles suspended in addition to the fluid delivery system. In addition to the requirements of homogeneity the amount of material coated must be consistent from part-to-part. A way of assuring such consistency is accomplished by including an in-situ process that monitors the amount of material jetted and is integrated with the rest of the coater/jetter hardware. The authors propose an integrated mass calibration fluid delivery

system that assures uniformity and yields improvements for the entire fluid dispensing process.

Background

The fuel cell process that includes the manufacturing of MEA is still in a development process and far from being mature and well established. An important and costly component of the fuel is the membrane which contains the platinum catalyst. Fuel cells are becoming a more attractive form of alternative energy as the efficiency of this membrane is increased, defined by watts per given mass of platinum, and the manufacturing costs are lowered. Less precise coating methods such as silk screening, spraying, dip and squeeze, air knife do not address all issues in the MEA fabrication. Some of the above methods result in waste of material that often poses complicated processes for reclaiming the precious platinum from the adds-on to the various manufacturing processes. Numerous approaches are being sought to robustly obtain a uniform and homogeneous catalyst film on fuel cell membranes.

Jetting Process Fundamentals

The jetting process proposed in this work consists on a dispensing valve that can operate in a tri-modal way: pressure differential and momentum transfer with and without atomizing simultaneously. The pressure differential mode consists of a fluid chamber that is kept at high pressure relative to that of the medium in which the fluid is jetted (generally this pressure is atmospheric). In this mode, the jetting occurs as the high pressure chamber and the lower pressure outside media are put in

contact by way of opening the orifice; the fluid will soon move to that region of lower pressure and is ejected from the valve. The fluid stream ejected is ceased by closing the exit and establishing again the pressure differential. The time during which the orifice exit is open and other parameters including pressure differential dictates the amount of material jetted. The opening and closing times must be much shorter than that of the open-valve -time. The proposed method has a positive shutoff system free from leakage and dripping. Figure 1 depicts the pressure differential jetting mode. This mode is often used for low viscosity fluids and spraying. A second jetting mode, momentum transfer mode, consists of imparting momentum to the fluid by a sudden stopping of a moving mass.

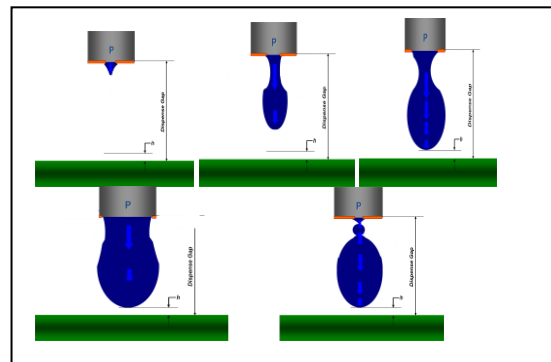


Figure1. Pressure differential jetting mode

During this mode the material is ejected as the impact of the moving mass comes to a full stop and a compressive wave travels through the fluid towards the surface at the orifice exit point. This mode is used for high viscosity fluid and may have some degree of atomization as well. Figure 2 depicts the momentum transfer jetting mode. The jetting dispensing process is contactless and hence it is not damaging prom to wire bonds

and to the LED package. The fact that no z-motion (no retraction) is required to break up the material make the jetting a much faster process compared to that of the traditional needle dispensing.

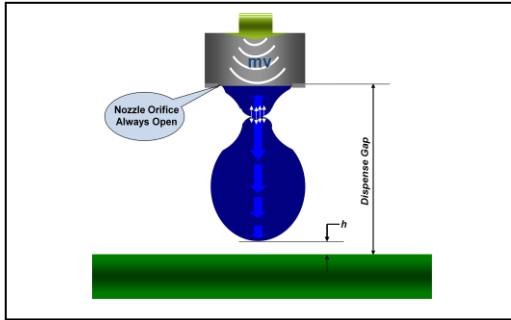


Figure2. Momentum transfer jet mode

The atomization of the fuel cell fluid is often required for coating MEA membranes, edge definition possess a challenge for any type of spraying. This work includes a bimodal jetting process where one mode is may be used to obtain high edge definition by jetting and decreasing the air supply for atomization, this mode results in a very well defined fluid stream that van be as small as one hundred micrometers. Figure 3 shows the unassisted air jetting of low viscosity fluid for pressure differential jetting mode.

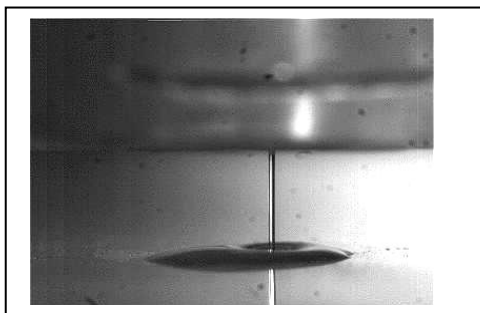


Figure3. Fluid stream from unassisted air jetting differential pressure mode

For this mode the fluid flow which is controlled by the pressure differential along the fluid path we can determine the flow rate by simply looking at its velocity as expressed in the following expression:

$$Q = -\frac{\Delta P \pi R^4}{8 \mu L}$$

Where ΔP is the pressure differential, R and L are the radius and length of the nozzle and μ is the viscosity of the fluid.

From above expression one can derive the average velocity of the fluid, Q/A , an important parameter in the jetting as well as in the agitation system proposed here.

$$v = -\frac{\Delta P R^2}{8 \mu L}$$

Where v is the average velocity of the fluid and A is the area; note that the average velocity is half the velocity of the fluid at the center of the duct for fully developed laminar flow.

For the case of momentum transfer jetting mode the droplet is formed in midair and moves towards the substrate surface with low energy (< 10 dynes), typical velocities of the droplet range between 2m/s to 20 m/s, typical speed is about 8 m/s. Figure 4 shows a sequence of the drop moving through air after ejection from orifice in jetting. As seen there, the mass ejected is metered by the momentum imparted and other parameters during the ejection time including fluid pressure and valve-on-time ^[1]. It should be pointed out that similar drops are obtainable for the pressure differential jetting mode by making the valve-on-time shorter.

Thin film coating is usually accomplished by atomization of the fluid with some gas (generally air is used), in addition to either fluid jetting mode.

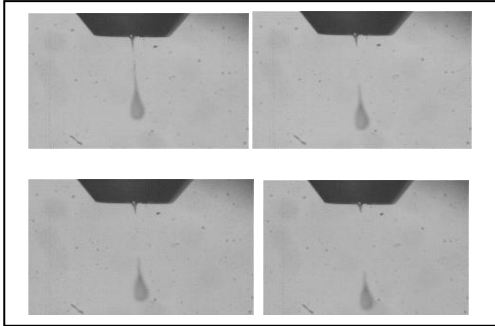


Figure4. Droplet ejected from momentum transfer jetting mode

For the case of low viscosity fluid as in the MEA catalyst dispensing, this method is the preferred process. Figure 5 shows a picture frame of the atomization occurring for a low viscosity fluid during MEA dispensing.

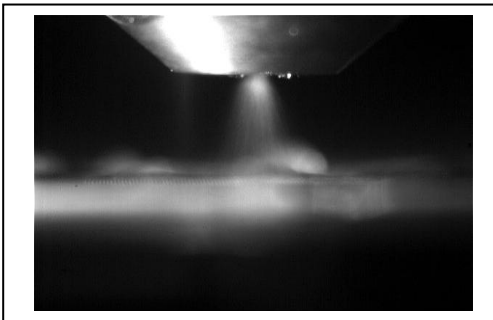


Figure5. Jet air-assist for spraying catalyst on MEA membrane

This spraying mode may result in a film thickness of ten micrometers or more. The jetting process is not a positive displacement process, hence the viscosity of the material influences the amount jetted; process control for this dispensing method must include pressure regulation, accurate temperature control and consistent valve-on-time with repeatable open and shut off profiles.

MEA Film Coating

Coating fuel cell membranes poses numerous challenges. The catalyst materials consist of a fluid matrix with doping of solid particulates with negative buoyancy that need to be kept in constant suspension and bonding material that can be highly reactive with some metals. Evaporation occurring even at room conditions, i.e., atmospheric pressure and 22 degrees Celsius poses a challenge for recirculation or agitation system that promotes particles suspension. Many catalysts are inks that contain high percent of water and some binding fluids such as ionomers i.e., nafion made from cationic conductor materials, and adding catalyst such as platinum particulates ^[2]. We propose in this work: a) A method to precisely jet the catalyst, which reduces manufacturing costs while giving a more homogenous coating, a method of closing the loop by weighing the dispensed material. b) A method of keeping the catalyst in suspension with the solvent. c) A method of reducing the probability of a clog. d) A method to obtain high edge definition and capable of dispensing different patterns and geometries with small dimension geometries.

Mass Fluid Control

The dispensed material weight can be periodically checked by dispensing into a precision balance. The system will then automatically adjust the fluid pressure to compensate for changes in the material and or fluid path. Alarms can be set to detect out of limit conditions ^[3].

Material Suspension

Material suspension is achieved via an agitation system. The fluid reservoir consists of two syringes. During machine idling,

material is automatically transferred through the entire fluid path (back and forth) from one syringe to the other. The fluid flow rate used in the agitation system was about 1.5cc/s; this resulted in a maximum fluid velocity in the feed tubes of 200 mm/s. The maximum Reynolds number for the agitation systems is about 100. When dispensing is required the material is divided equally between the two syringes and the required dispense pressure is applied. The system can also detect low fluid conditions, and has the ability to roughly predict the amount of material used. Figure 6 shows the settling tendency in the syringe.

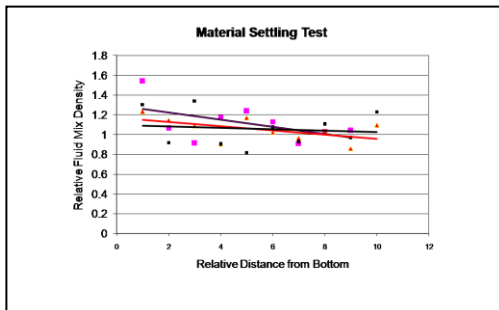


Figure6. Settling trends in syringe

This process can accelerate evaporation inside of the syringes, which causes the material to dry on the walls of the syringe. For this reason closed loop agitation systems are sought.

Reducing System Clogging

Empirically it has been found that the process of atomization can cause the material to dry onto surfaces causing clogs. This problem has been mitigated by atomizing at the proper height with respect to the exit point of the nozzle, and when the system is idle parking the nozzle in a cleaning system. Material volume and area covered are related to nozzle size, fluid pressure, dispensing speed and height. The minimum nozzle size is to be determined

accordingly to the maximum particle size and the length of nozzle; the nozzle diameter should be several times larger than that of the maximum particle size of the mixture. Since the flow rate of the material is a function of the diameter to the fourth power (as shown above) and linear with fluid pressure, the fluid pressure is typically very low and must be precisely controlled.

Edge Definition and Small Geometries

For coating requiring high edge definition, jetting with some atomization can be successfully performed. Figure 7 depicts a picture of jet with air assist dispensing various geometries with high edge definition.



Figure7. Jet sprayed geometries with high edge definition.

Conclusions

Jetting fluid is a viable fluid dispensing method for conformal coating, with high flexibility and adaptability to uneven surfaces. The high edge definition obtained from jetting with coaxial air assist allows for dispensing in small areas with minimum over spraying and facilitates pattern dispensing with small geometries.

Agitation systems allow for consistent and homogeneous fluid dispensing over long periods of time (as it is the case in a production environment.) Fluid velocities less than 1m/s seem appropriate for particle suspension. Vapor free systems are

necessary for MEA inks. Jet dispensing while agitation is occurring may be possible, however fluid pressures must be controlled adequately to obtain consistent fluid dispensing and needs to be explored further. The film thickness consistency requires volumetric accuracy of the jetted homogeneous mixture. Closed-loop mass calibration assures the consistency of fluid dispensed as function of time and other possible changes.

The root cause of clogging issues, although were mitigated in the experiments, are still not well understood. Plausible causes may include the particulate settling, a dried material resulting from fluid air interfacing. Further work still needs to be performed to better understand this issue.

Acknowledgment

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