An Experimental Investigation of Multilayer Flow in a Slide Die Coating Process

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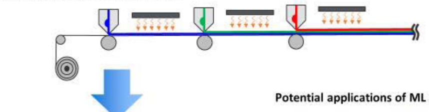
Introduction

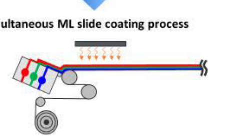
- Roll-to-roll (R2R) coating technology has been actively applied not only for conventional film production but also for emerging energy devices such as organic solar cells, organic light emitting diodes, batteries, smart windows, and fuel cells.
- The devices are multilayer (ML) structures requiring several coating and drying steps when implemented in a serial fashion, which increases capital costs and energy consumption.
- Simultaneous ML coating technologies present an opportunity for cost reductions and improved process efficiency by reducing equipment footprint and the number of process steps.
- In this study, we present a statistical study of fuel cell catalyst inks which to be used in ML slide coating process for the manufacturing of fuel cell membrane electrode assemblies (MEAs).

Why Multi-Layer Slide Coating?

Multi-layer (ML) coating process



Simultaneous ML slide coating process



- Simultaneous ML coating has the advantage of high-throughput, simplify equipment (cost-effective), and stable web handling.

Potential applications of ML coating


© Imprint Energy

Thin film batteries


© FuelCellsWorks

PEM fuel cells and electrolyzers


© InfinityPV

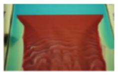
Thin film solar cells


© UniteGlass

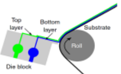
Smart windows

Literature Survey and Project Target

Perturbations in a multilayer flow

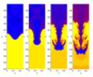


Miscible liquids



Two-layer slide coating

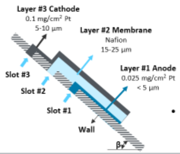
Interfacial tension



Rayleigh–Taylor instability

Buerkin, Cornelia K., et al. *Journal of Coatings Technology and Research* 14.5 (2017)
Li, Shengtai, and Hui Li. *Los Alamos National Laboratory* (2006).

Suggested structure for "three-layer" coating



Guidelines from the literature

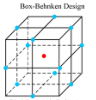
Parameters	Guidelines
Surface tension	$\sigma_3 < \sigma_2 < \sigma_1,\ \frac{\sigma_n}{\sigma_k} \approx 1$
Density	$\rho_1 < \rho_2 > \rho_3$
Viscosity	$\mu_1 < \mu_2 > \mu_3,\ \frac{\mu_n}{\mu_k} \approx 1$
Thickness	$t_1 < t_3 < t_2$

- To realize three-layer coating, selection of appropriate solvents, carbons, and ionomers; and optimization between them are essential.

Detailed Ink Formulation Strategy

	Viscosity	Density	Surface tension	Thickness
Bottom layer (Anode, Pt/Vulcan)	Lowest μ • Dilute • Low surface area carbon	Lower ρ • Favors more alcohol • More dilute	Highest σ • Favors more water	Lowest t • More concentrated • High Pt% on C
Middle layer (Membrane, Nafion)	Highest μ • More concentrated	Highest ρ • More water • More concentrated	Moderate σ • Function of other layer	Highest t • More dilute
Top layer (Cathode, Pt/HSC)	Lower μ than the membrane • More dilute • Higher Pt%	Lower ρ than the membrane • More dilute • Alcohol	Lowest σ • More alcohol • More Nafion (I/C_{opt}~0.9, explore I/C>1)	Lower t • More concentrated • Higher Pt%

Design of Experiment (D.O.E)



Box-Behnken Design

Lian, Binbin, et al. *Robotics and Computer-Integrated Manufacturing* 46 (2017): 1-14.

- Box-Behnken Design (BBD) can reduce the number of experiments than other DOE methodologies and can produce non-linear fitting by deriving quadric models.
- To understand the effect of each ink formulation variable on the ink properties, analysis of variance (ANOVA) is performed and the relationship is investigated through quadratic regression analysis.

Box-Behnken Design

Three screening factors

Parameters	Unit	High (+1)	Low (-1)
Catalyst	%	3	7.5
nPA percents	%	10	50
I/C ratio	-	0.9	1.2

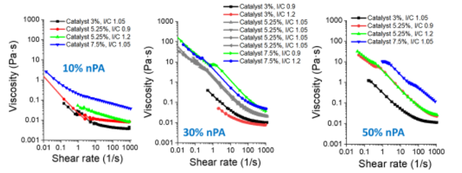
The number of experiments (N) for BBD

$$N = 2k(k-1) + C_0$$

The non-linear computer-generated quadratic model

$$Y = \beta_0 + \sum_{i=0}^{3}\beta_i X_i + \sum_{j=0}^{3}\beta_{ii} X_i^2 + \sum_{i=0}^{3}\sum_{j=0}^{3}\beta_{ij} X_i X_j$$

Measured shear viscosities of the inks



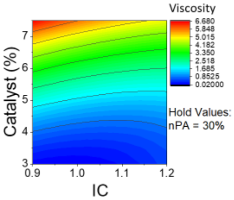
- The BBD method was used to investigate the impact of different variables on ink properties – response of the system – such as density, viscosity and surface tension.

ANOVA Result for Viscosity at Low Shear

Viscosity @ 1/s

	DF	Sum of squares	Mean square	F value	P value
Catalyst	1	59.83797	59.83797	900.0383	8.13E-05
nPA	1	41.13245	41.13245	618.6837	1.42E-04
IC	1	0.89292	0.89292	13.43057	0.03513
Catalyst*Catalyst	1	4.3467	4.3467	65.37988	0.00395
nPA*nPA	1	0.01572	0.01572	0.23643	0.6601
IC*IC	1	0.19658	0.19658	2.95683	0.18401
Catalyst*nPA	1	24.78297	24.78297	372.767	3.03E-04
Catalyst*IC	1	1.23921	1.23921	18.63934	0.02289
nPA*IC	1	0.009	0.009	0.13532	0.7374
Error	6	2.22075	0.37012		
Lack of fit	3	2.0213	0.67377	10.13429	0.04444
Pure Error	3	0.19945	0.06648		
Total	21	136.895			

R-square=98.3%



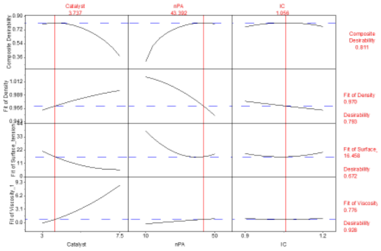
Hold Values:
nPA = 30%

Regression model (*A*: catalyst, *B*: nPA, *C*: I/C ratio)
Viscosity @ 1/s (Pa·s) = $2.73491A+2.2675B-0.33409C+1.04244A^2-0.06269B^2+0.22169C^2+2.48912AB-0.5566AC-0.04742BC+1.77403$

- Catalyst contents have the greatest effect on viscosity
- The I/C ratio has a very small effect on the viscosity

Ink Optimization Process

Optimization result



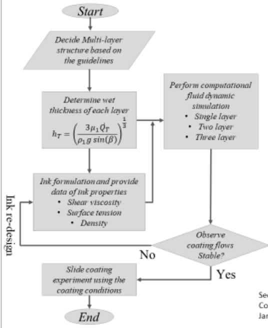
Optimization goal

Pt/HSC ink for top layer → **lowest surface tension, lowest density and lowest viscosity**
Viscosity (1/s): minimize (importance → 3, most important)
Surface tension: minimize (importance → 2)
Density: minimize (importance → 1)

Catalyst *3.737%*
nPA *43.392%*
I:C *1.056*

- Based on the regression model, it is possible to derive optimal mixing conditions to obtain desired ink characteristics for each layer

Project Workflow



Start

Decide Multi-layer structure based on the guidelines

Determine wet thickness of each layer

$$h_T = \left(\frac{3\mu_1 Q_T}{\rho_1 g \sin(\beta)}\right)^{\frac{1}{3}}$$

Perform computational fluid dynamic simulation
- *Single layer*
- *Two layer*
- *Three layer*

Ink formulation and provide data of ink properties
- *Shear viscosity*
- *Surface tension*
- *Density*

Observe coating flows Stable?

No

Ink re-design

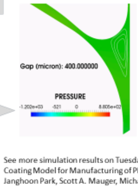
Yes

Slide coating experiment using the coating conditions

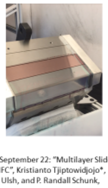
End

- Measured ink properties according to the mixing conditions were provided to Sandia National Labs for their simulation, and the layer will be designed and optimized by using this database in the experiment

Simulation example



Coating verification



See more simulation results on Tuesday, September 22: "Multilayer Slide Coating Model for Manufacturing of PEMFC", Kristianto Tjiptowidjojo*, Janghoon Park, Scott A. Mauger, Michael Ulsh, and P. Randall Schunk,

Conclusion and Future Work

- A statistical approach was introduced to analyze the effect of the ink formulation parameters on ink properties of the fuel cell catalyst inks.
- Based on the regression analysis, it is possible to derive optimal mixing conditions to obtain desired ink characteristics for each layer of fuel cell membrane electrode assemblies/
- Experimental verification will be performed on a ML slide die and the degree of miscibility was observed for various ink formulation conditions.

Acknowledgments

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