Influence of Coating Method on the Performance of Roll-to-Roll Coated PEM Fuel Cell Catalyst Layers

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Proton Exchange Membrane Fuel Cells

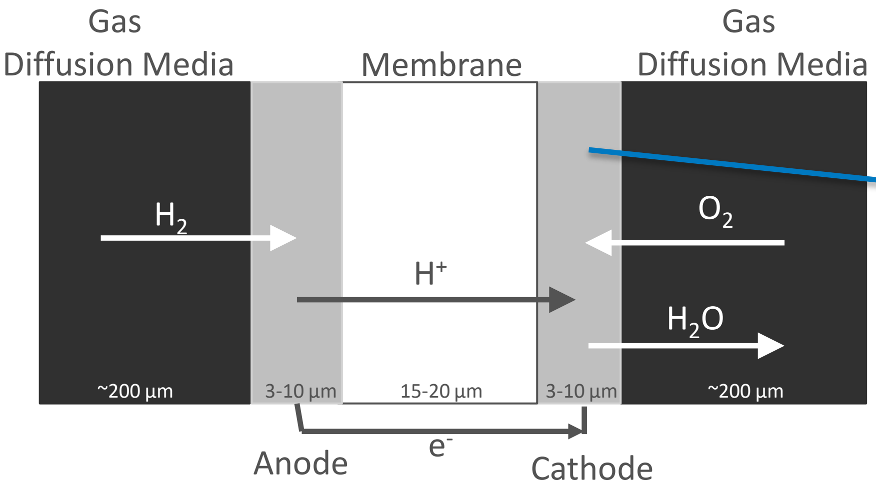
- Light duty vehicles (LDV), heavy duty trucking, trains, marine transportation, stationary power
- High efficiency (>2x internal combustion)
- Zero GHG emissions
- Long-range EV (LDV - 300+ miles/tank)
- Short refueling time (LDV - 5 min)

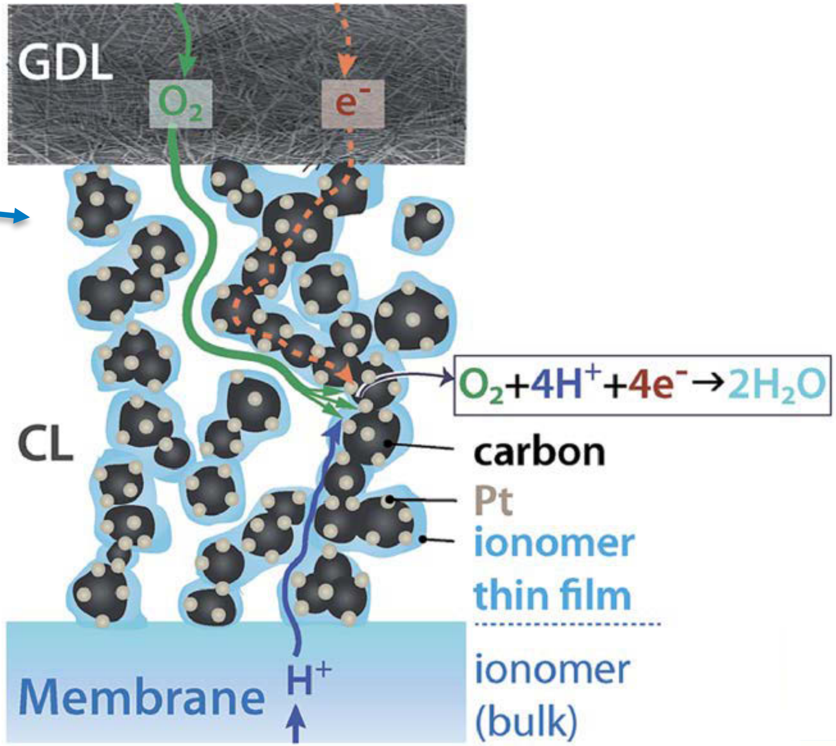
https://www.nrel.gov/hydrogen/

https://nikolamotor.com/one

https://www.alstom.com/press-releases-news/2020/3/alstoms-hydrogen-train-coradia-ilint-completes-successful-tests

Fuel Cell Structure



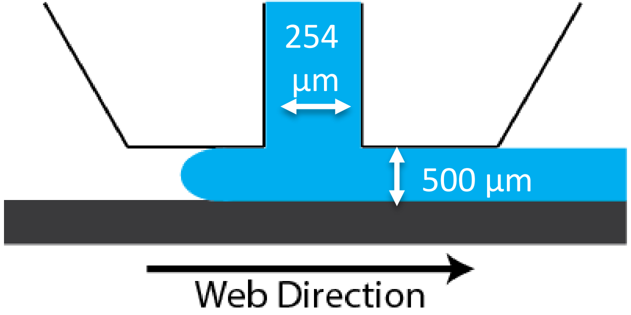


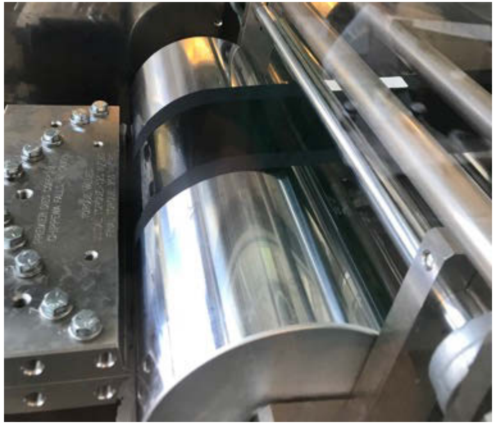
Weber and Kusoglu, *J. Mater. Chem. A* 2014, **2**, 17207–17211

- Catalyst layer microstructure impacts fuel cell performance
- Unknown how R2R coating methods impact catalyst layer structure

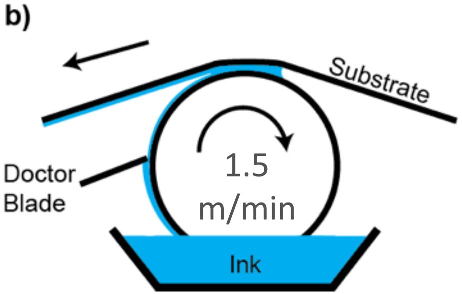
Experimental

Slot Die Coating

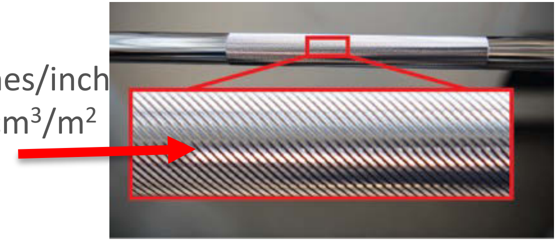




Gravure Coating

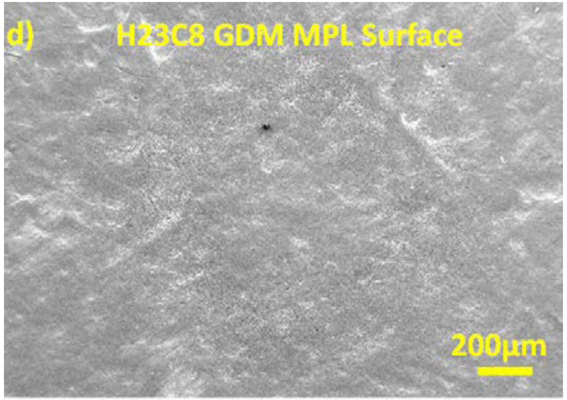


25 lines/inch
170 cm^3/m^2



Mauger, S. A.; et al.; *J Electrochem Soc* **2018**, *165* (11), F1012–F1018. https://doi.org/10.1149/2.0091813jes.

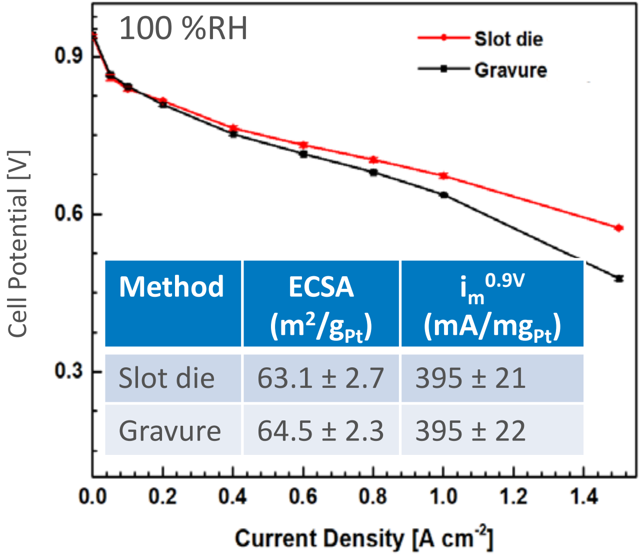
Web Speed: 1 m/min
Oven Temp: 80 ˚C
Substrate: diffusion media



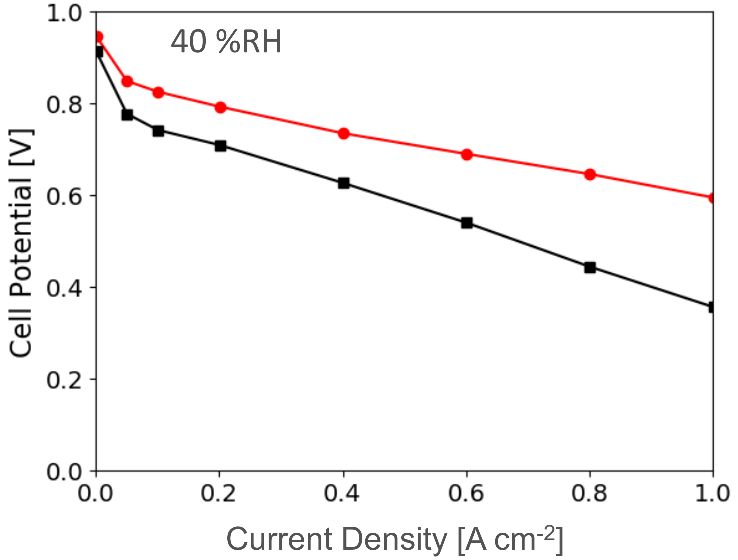
Wang, M.;. *ACS Appl. Energy Mater.* **2019**, *2* (11), 7757–7761. https://doi.org/10.1021/acsaem.9b01871.

Fuel Cell Performance

0.12 mg_{Pt}/cm^2
80 ˚C
150 kPa_{abs}
H_2/Air
50 cm^2



Method	ECSA (m^2/g_{Pt})	$i_m^{0.9V}$ (mA/mg_{Pt})
Slot die	63.1 ± 2.7	395 ± 21
Gravure	64.5 ± 2.3	395 ± 22



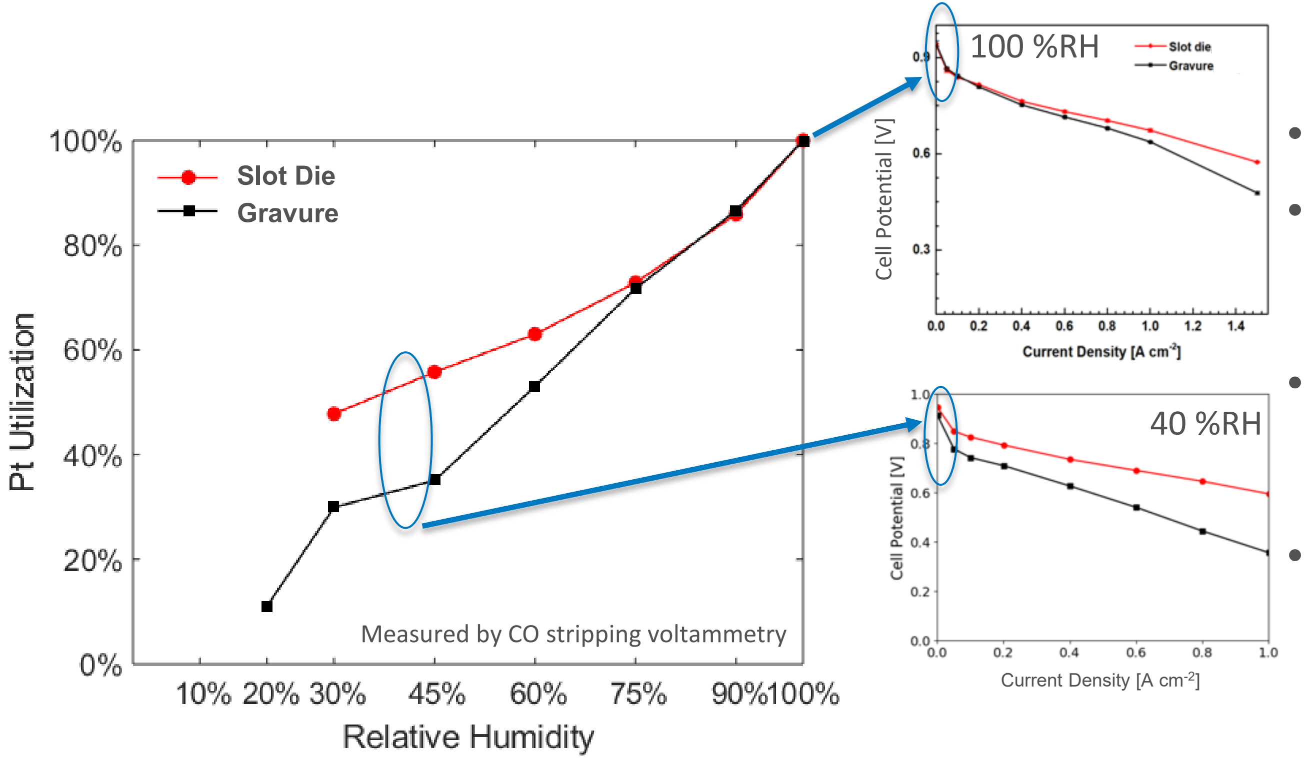
At 100% RH

- No differences in kinetics
- Slot die better at high current densities

At 40% RH

- Large difference in kinetics
- Slot die better at all current densities

Electrochemical Surface Area

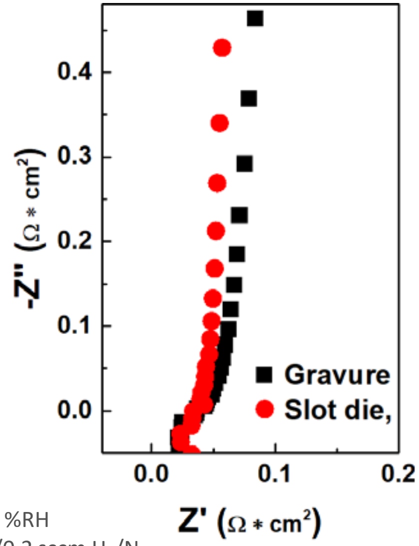


- $Pt\ Util. = \frac{ECSA(X\ \%RH)}{ECSA\ (100\%RH)}$
- At high RH, little effect of coating method on Pt utilization
- At lower RH, gravure coated CL losses more surface area
- Less ionomer-Pt contact

H_2/N_2 Electrochemical Impedance Spectroscopy

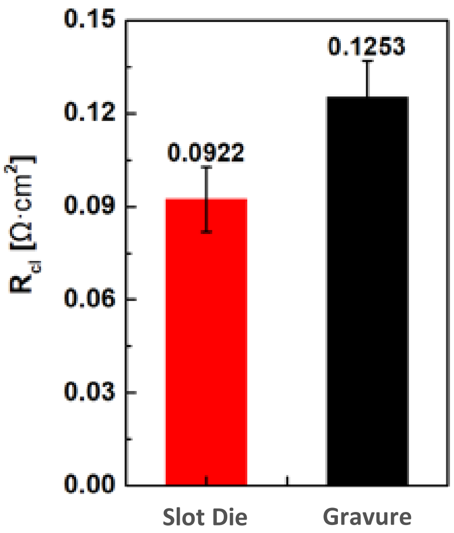
$$Z(\omega)_{model} = j\omega L_{wire} + R_{\Omega} + \sqrt{\frac{R_{CL}}{Q_{DL}(j\omega)^{\phi}}}\coth\left(\sqrt{R_{CL}Q_{DL}(j\omega)^{\phi}}\right)$$

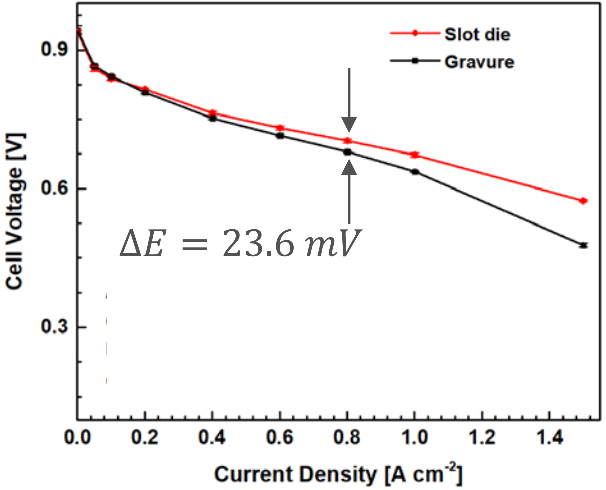
Setzler & Fuller, *JES,* **162** (6) F519-F530 (2015)
https://github.com/NREL/OSIF



100 %RH
0.2/0.2 sccm H_2/N_2
80 ˚C
V_{DC} = 200 mV
V_{AC} = 1 mV
1 – 10k Hz

Model Fit





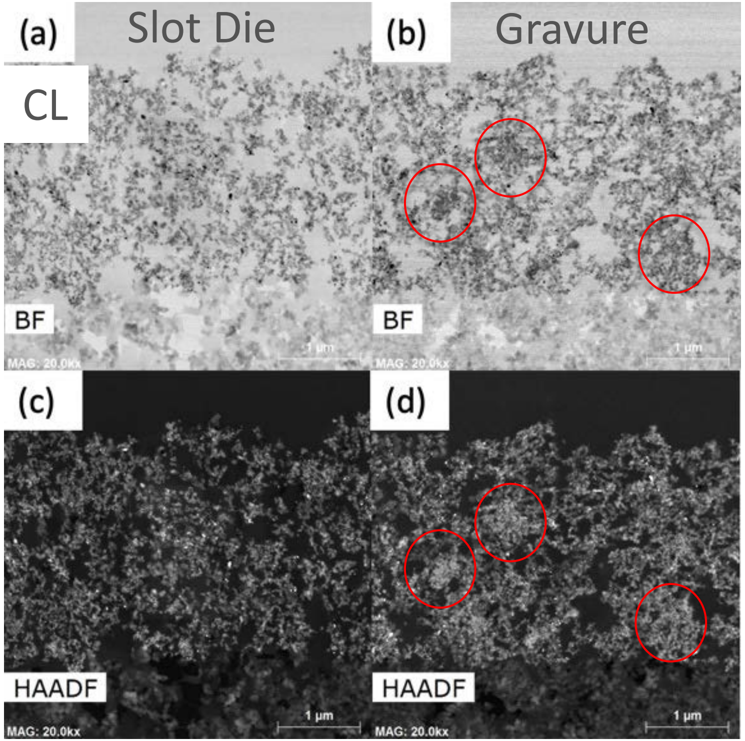
$$\Delta R_{CL} = 33.1\ m\Omega \cdot cm^2$$
$$\Delta E = i\Delta R_{CL}$$
$$\Delta E\left(0.8\frac{A}{cm^2}\right) = 26.5\ mV$$

Why does Gravure have higher resistance

- Higher tortuosity/fewer conduction pathways
- Lower surface ionomer content

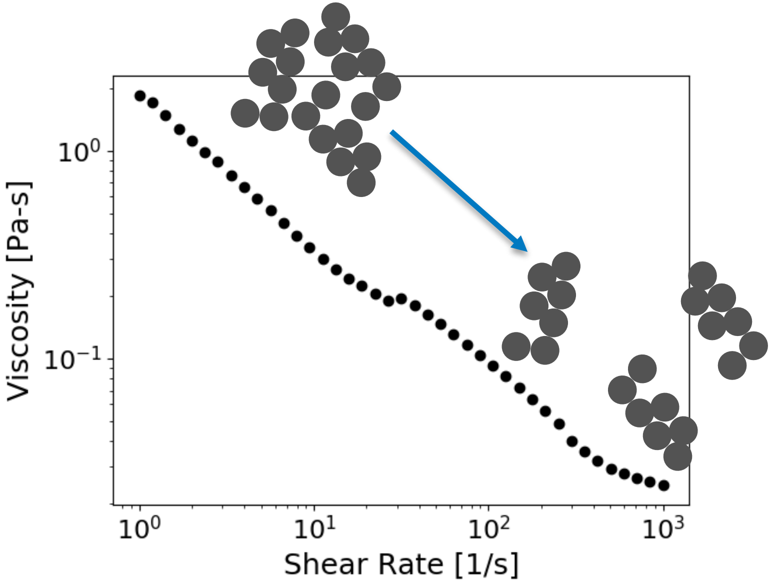
Catalyst Layer Microscopy

Scanning Transmission Electron Microscopy



- Gravure results in more clustered, denser catalyst layer
- Dense clusters lead to lower ionomer accessibility to catalyst – lower ECSA at low RH
- If ionomer is less dispersed it could lead to fewer proton conduction pathways

Catalyst Ink Rheology



- Catalyst inks are weakly agglomerated
- Shear thinning due to agglomerate break up
- Could the different shear rates of coating processes impact catalyst layer microstructure

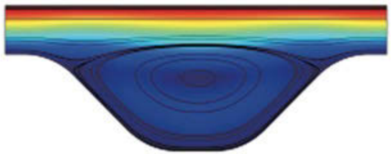
How does coating method effect microstructure

Slot Die

- In Die Body – Plane Poiseuille
  - $\dot{\gamma} = \frac{6Q}{W^2}\left(1 - \frac{y}{W}\right)$
  - Avg $\dot{\gamma} \approx 4\ s^{-1}$
- In coating gap – Poiseuille/Couette
  - $\dot{\gamma} = \frac{6Q}{LH^2}\left(1 - \frac{2y}{H}\right) + \frac{V}{H}\left(\frac{6y}{H} - 4\right)$
  - Avg $\dot{\gamma} \approx 50\ s^{-1}$
- In tubing to die – Pipe Poiseuille
  - $\dot{\gamma} = \frac{-4Qr}{\pi R^4}$
  - Avg $\dot{\gamma} \approx 110\ s^{-1}$
  - Avg residence time in tube ≈ 12 s

Gravure

- Shear profile not analytically solvable
- Low shear in gravure cell



Kapur, N. et al.; A Review of Gravure Coating Systems. *Convertech & e-Print* **2011**.

- If we assume Couette flow between web and gravure lands and gap equals 2x liquid film thickness
  - Avg $\dot{\gamma} \approx 300\ s^{-1}$

Suggests time at high shear is most important

Conclusions

- Slot die leads to better dispersed catalyst particles which leads to more homogenous distribution of catalyst and ionomer
- This results in more ionomer in contact with catalyst, leading to better performance
- Indicates time at high shear, not just shear rate is important for high performance catalyst layers

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Thank You

www.nrel.gov

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Materials and Methods

- Catalyst: Pt on high surface area carbon (TKK TEC10E50E)
- Ionomer: Nafion, 1000 EW (Ion Power D2020)
- Membrane: Nafion, 1000 EW, 25 µm (Nafion NR211)
- Diffusion Media: Freudenberg H23C8
- Catalyst ink – 3.2 wt% PtHSC
- Ink Dispersion: High shear mixer (Ika Ultra Turrax)
- Gravure Coating
  - 1 m/min
  - Air floatation oven: 80 ˚C