Influence of Ink Formulation and Drying Conditions on Ionomer Distribution in High-Performance Roll-to-Roll-Coated Gas-Diffusion Electrodes

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PRiME/236th ECS Meeting, I01B-2218

October 6, 2020

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Funding – D.O.E. Advanced Manufacturing Office, Roll-to-Roll Advanced Materials Manufacturing Lab Collaboration

Roll-to-Roll Manufacturing

REVIEW

doi:10.1038/nature11115

Electrocatalyst approaches and challenges for automotive fuel cells

Mark K. Debe[1]

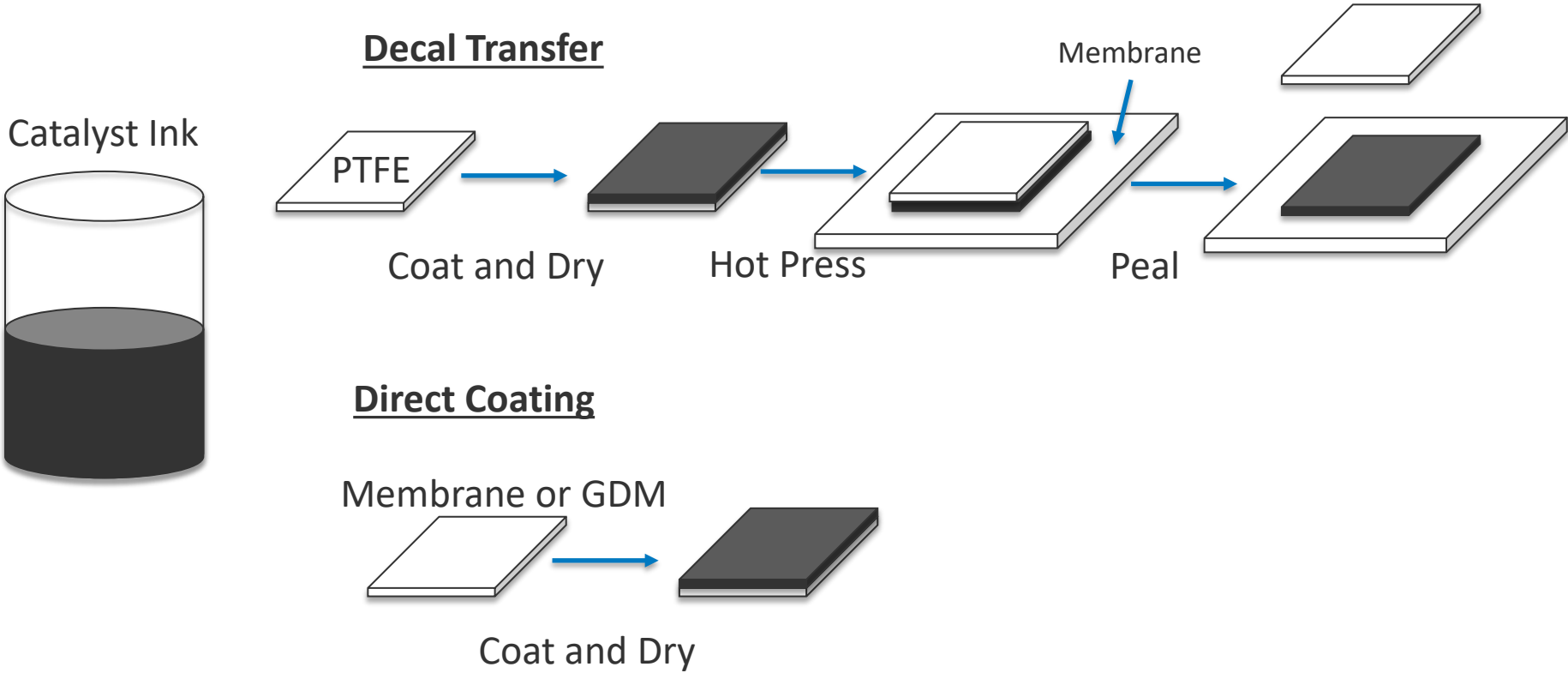
10% of 2030 market = 15M vehicles/year

= 4.5B MEAs/year

- 20 production lines – 585 MEAs/min
  - Coating – 1 m wide x 20 m/min

High-performance R2R-manufactrured MEAs needed to meet cost and volume targets

Direct Coating vs Decal Transfer



Motivation for Direct Coating

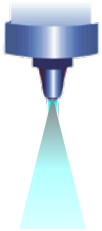
Production Volume (sys/yr)	1000	10,000	20,000	50,000	100,000	500,000
m^2 active area/yr	7,470	74,702	149,404	373,511	747,022	3,735,111
Slot die coating process ($/$m^2$)	$52.59	$9.14	$4.92	$4.00	$2.93	$1.30

- Direct coating offers significant savings over decal coating
- Gas diffusion media easier to coat on than membrane

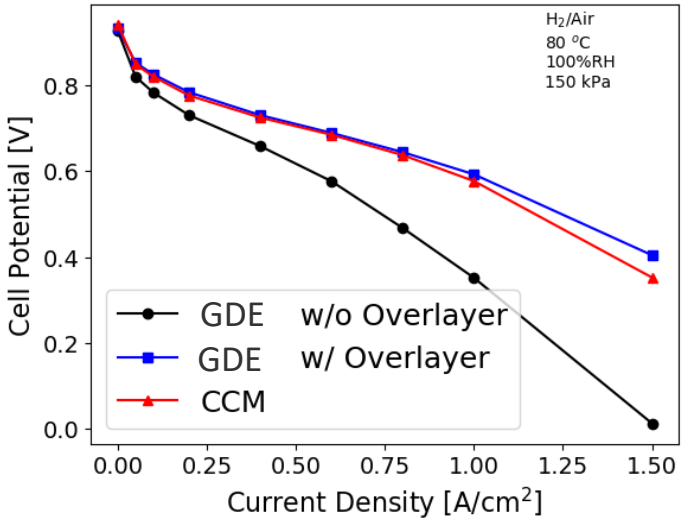
Data courtesy of Strategic Analysis, Inc.

The GDE Challenge

- Spray-coated GDEs often don't perform as well as CCMs
- Need an ionomer overlayer to form good GDE-membrane interface



Ionomer Overlayer
Cathode Layer: Catalyst & Ionomer
Microporous Layer
Gas Diffusion Layer

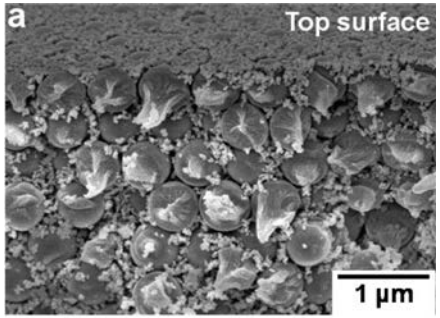


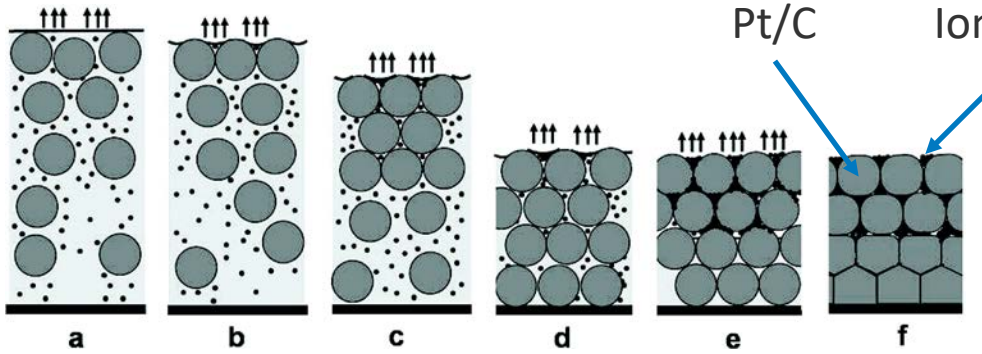
Two coating steps (CL + overlayer) does not have an advantage over decal process

Mauger, et al., *J Power Sources* **2020**, *450* (29), 227581. https://doi.org/10.1016/j.jpowsour.2019.227581.
Wang, et al., *ACS Appl. Energy Mater.* **2019**, *2* (11), 7757–7761. https://doi.org/10.1021/acsaem.9b01871.

The Roll-to-Roll Advantage

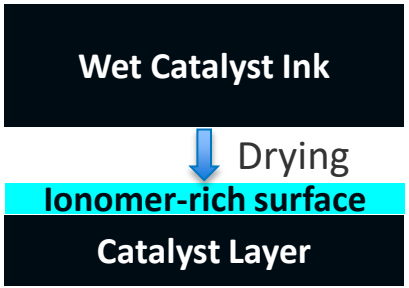
- In colloidal mixtures materials can phase separate form enriched surfaces



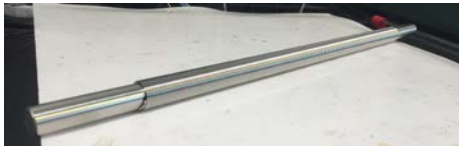


Luo, H., et al., *Langmuir* **2008**, *24* (10), 5552–5561. https://doi.org/10.1021/la800050u.

- Separation is favorable when:
  - Evaporation >> Diffusion, Sedimentation
  - Large difference in particle size
  - Higher concentration of small particles
- *Goal– can we design **an ink and single coating step** that leads a GDE with an ionomer rich surface*



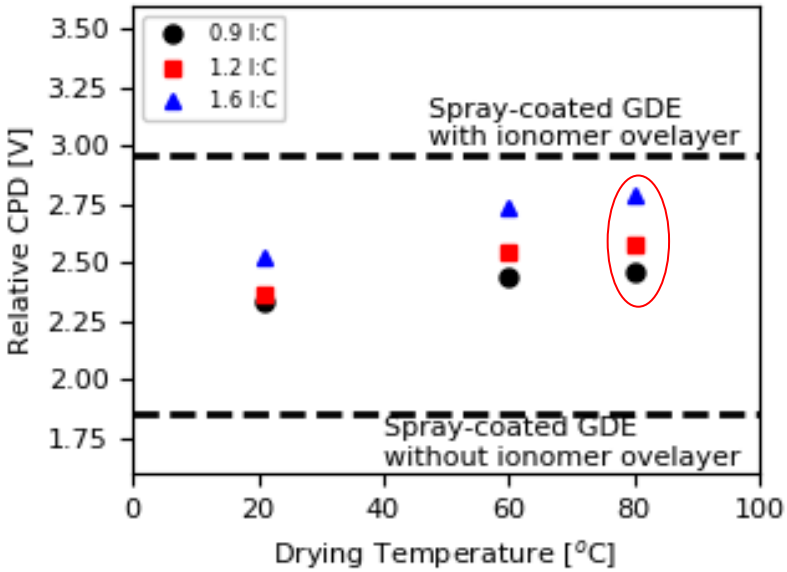
Small Scale Coating Trials



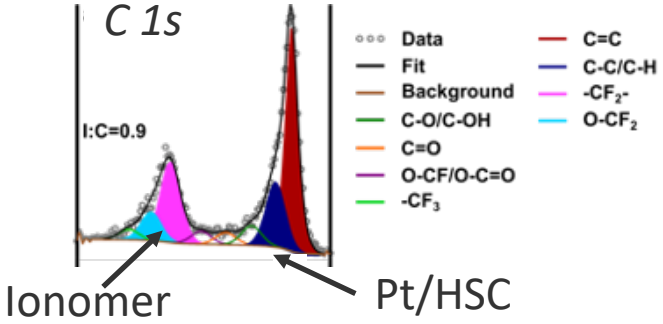
- Mayer Rod coating on SGL 29BC diffusion media to simulate R2R coating
- Increase drying temperature to increase evaporation rate
  - 25, 60, and 80 ˚C
- Increase ionomer:carbon ratio to increase volume of ionomer available to move to surface
  - 0.9, 1.2, 1.6 I/C
- Ink
  - Pt/HSC (TKK TEC10E50E): 3.2 wt%
  - Dispersion Media: water/1-propanol (75/25 w/w)
  - Nafion, 1000 EW

Measurement of Surface Ionomer

Kelvin Probe Method



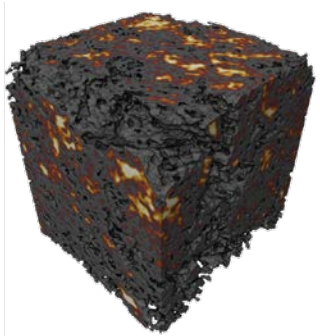
X-ray Photoelectron Spectroscopy



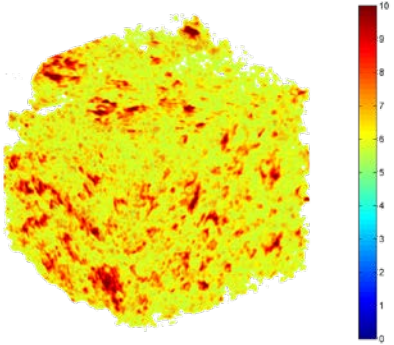
Coating Method	I/C	C_I/C_C	ΔCPD [mV]
Spray-coated without overlayer	0.9	0.21	-
Spray-coated with overlayer	0.9	0.38	1104
Mayer Rod	0.9	0.49	605
	1.2	0.58	726
	1.6	0.86	933

Increasing I/C and drying temp increase surface ionomer content

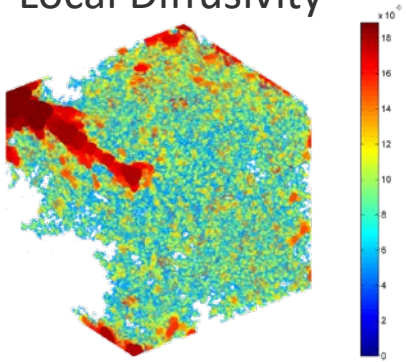
X-ray Computed Tomography



Local Ion Conductivity

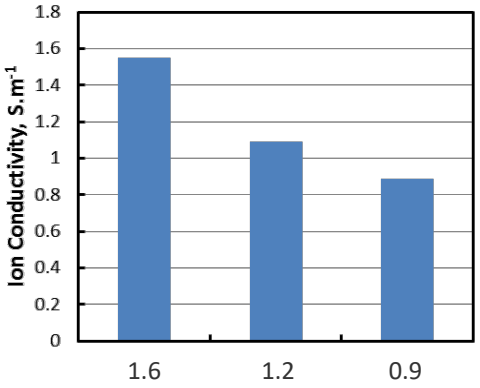


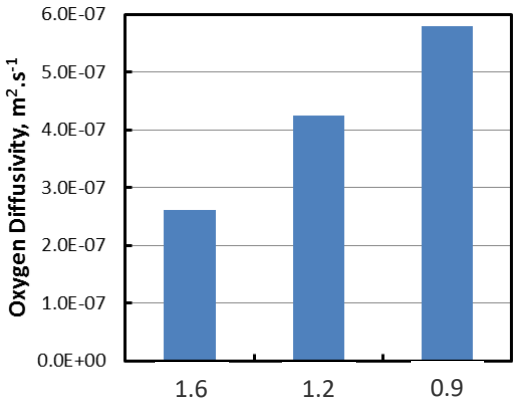
Local Diffusivity



Increasing I/C:

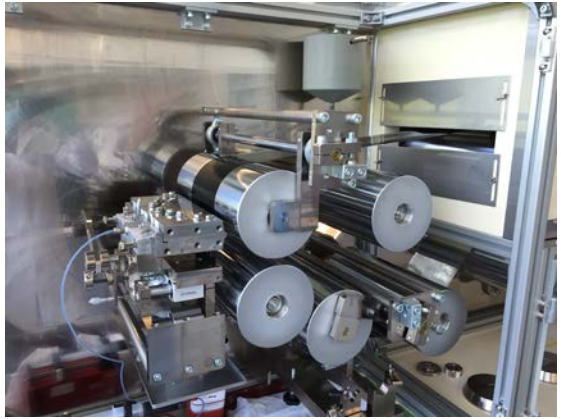
- Increases conductivity
- Decrease diffusivity





Slot-Die-Coated GDEs

- Same ink as rod coating
- Coating speed - 1 m/min
- Dry at 80 ˚C
- Freudenberg H23C8 diffusion media

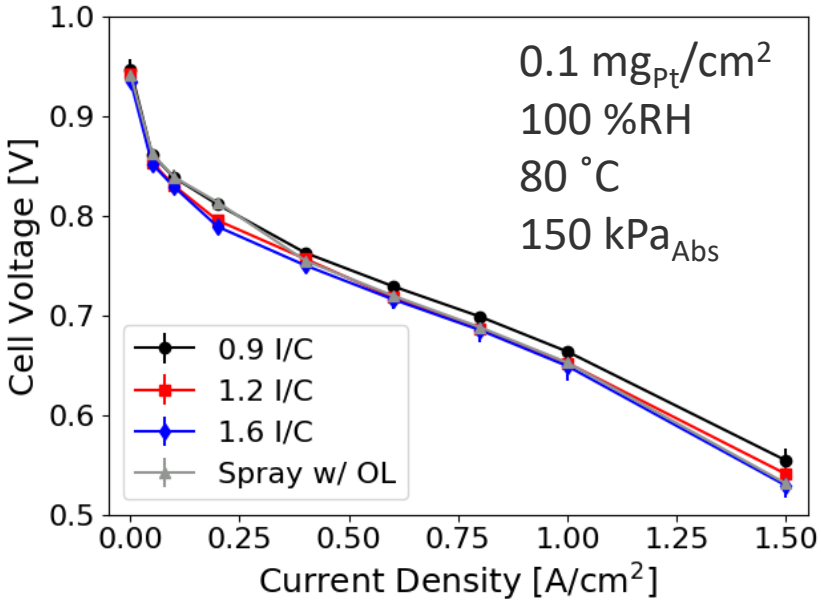


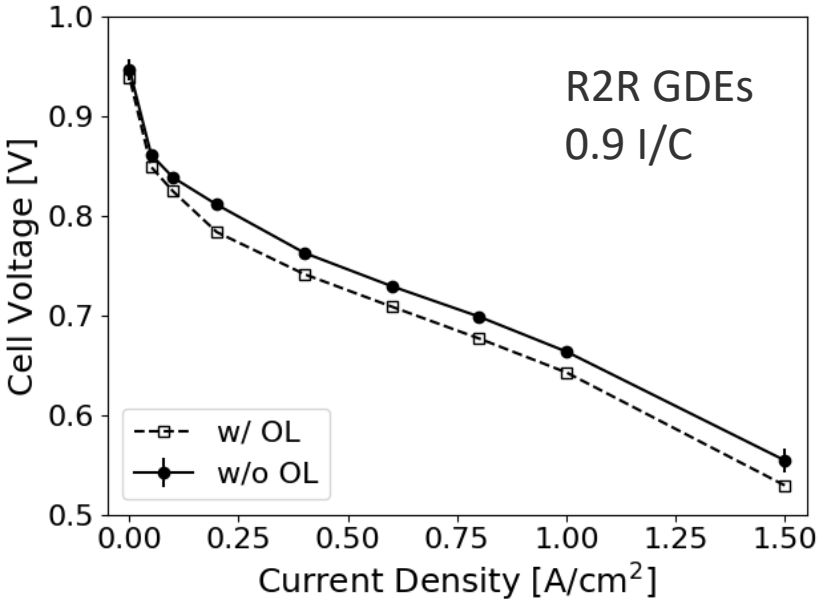
X-ray Photoelectron Spectroscopy

Coating Method	I/C	C_I/C_S
Spray – no overlayer	0.9	0.21
Spray – overlayer	0.9	0.38
R2R slot die	0.9	0.63
	1.2	1.4
	1.6	3.6

R2R GDEs show same trends as rod coated

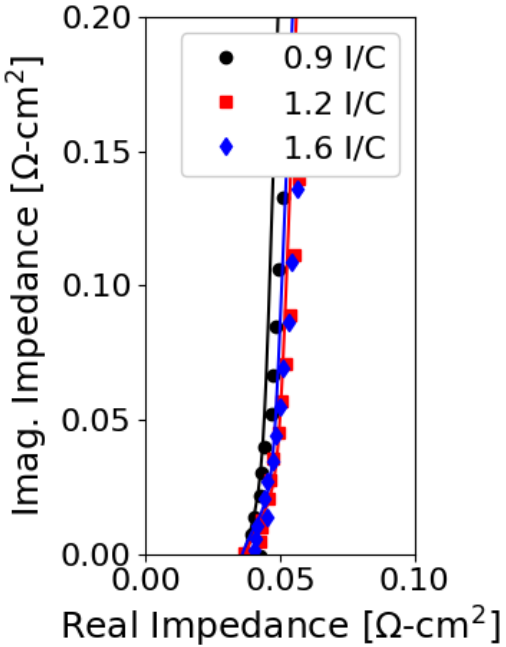
Fuel Cell Performance





- ***1-step R2R GDEs perform as well as 2-step spray-coated GDEs***
- High performance also shown with PtCo-based R2R GDEs

H_2/N_2 Impedance Spectroscopy



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

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

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

Coating Method	I/C	R_{CL} [mΩ-cm²]
Roll-to-Roll Slot Die	0.9	92 ± 10
	1.2	88 ± 10
	1.6	81 ± 10
Spray – without ionomer overlayer	0.9	222 ± 10
Spray – with ionomer overlayer	0.9	108 ± 10

0.9 I/C has sufficient ionomer to form good interface with membrane

Conclusions

- Increasing drying temperature leads to ionomer enrichment at GDE surface
- Ionomer rich surface forms low resistance interface with membrane
- 1-coating step R2R GDEs have same performance as 2-step spray coated GDEs
- GDEs are viable for industrial manufacturing

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PRiME/236th ECS Meeting
I01B-2218
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Thank You

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NREL/PR-5900-76952

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. The submitted manuscript was created, in part, by U Chicago Argonne, LLC, Operator of Argonne National Laboratory, Argonne, U.S. Department of Energy Office of Science laboratory, operated under Contract No. DE-AC02-06CH11357. This research used the resources of the Advanced Photon Source (APS), a U.S. Department of Energy (DOE) Office of Science User Facility, operated for the DOE Office of Science by Argonne National Laboratory, also under Contract No. DE-AC02 06CH11357. Funding provided by U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. This work was conducted as part of the Roll-to-Roll Advanced Materials Manufacturing Laboratory Collaboration, and strongly leveraged work supported by the Hydrogen and Fuel Cell Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

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