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Title: Intermetallic PtCo Catalysts with Enhanced Performance and Stability

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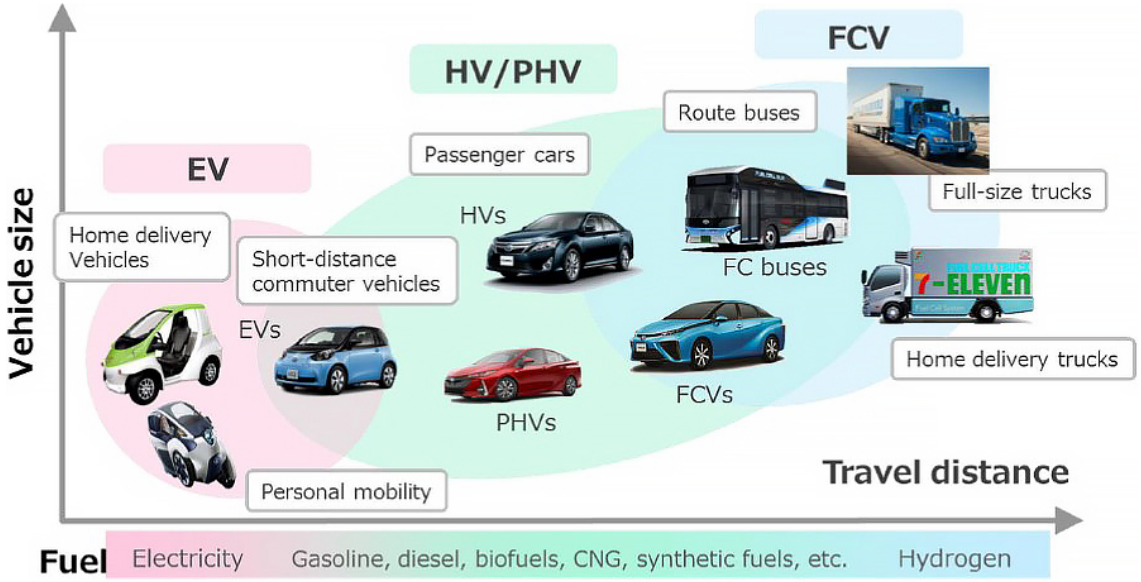
Intermetallic PtCo Catalysts with Enhanced Performance and Stability

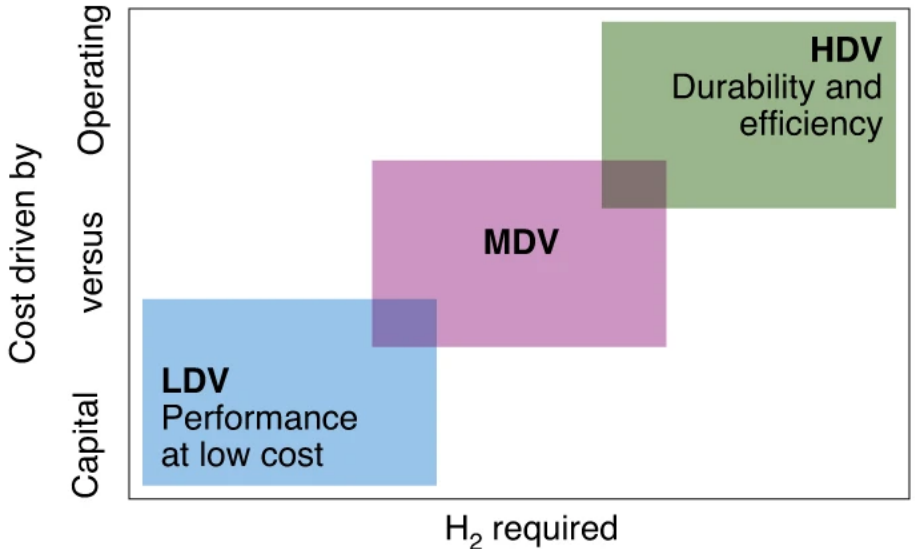
Chenyu Wang
Los Alamos National Laboratory

April 16, 2021

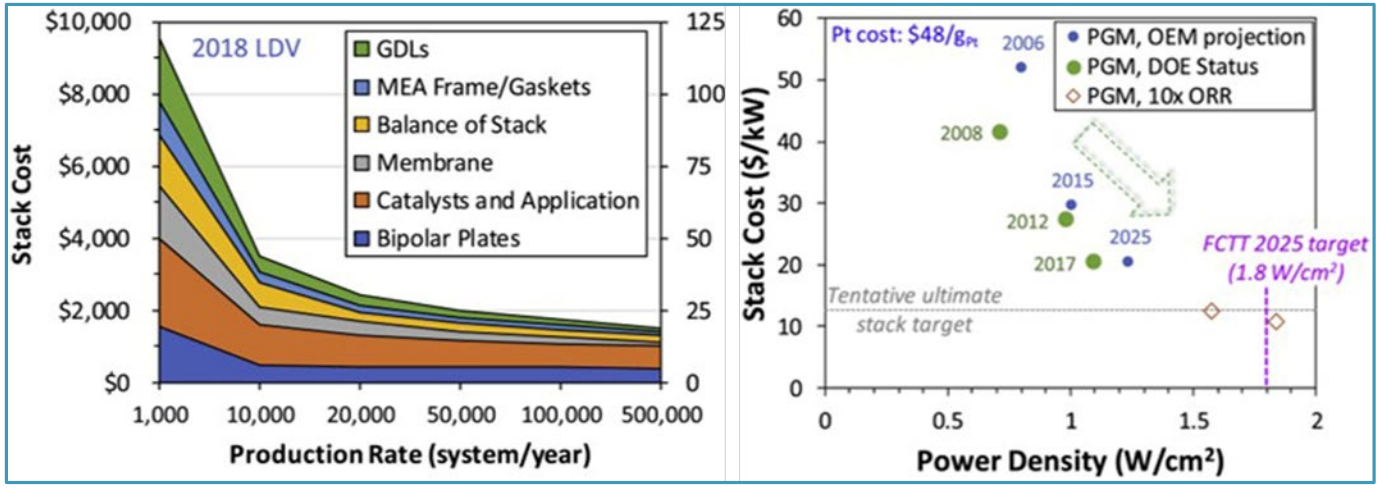
Markets for Polymer Electrolyte Membrane Fuel Cells (PEMFCs)



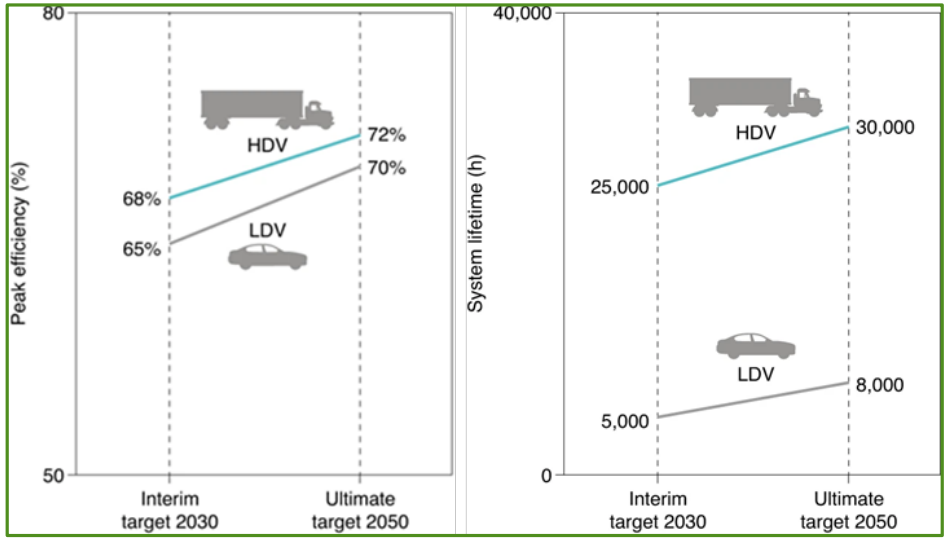
https://insideevs.com/news/327627/toyota-to-sell-30000-hydrogen-fuel-cell-cars-annually-by-2020/



Cullen, D. A., *et al.*, **2021**, *Nature Energy*, 1-13.

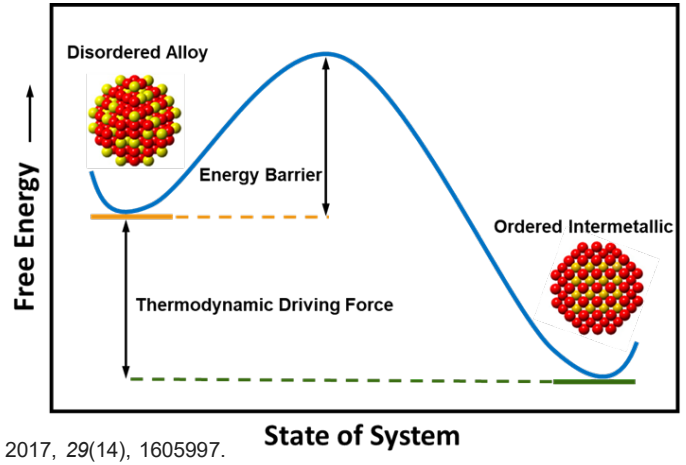


Gittleman, C. S., *et al.*, *Current Opinion in Electrochemistry*, **2020**, *18*, 81-89.



Adapting Pt-based Catalysts Based on the Demand (HDV or LDV)

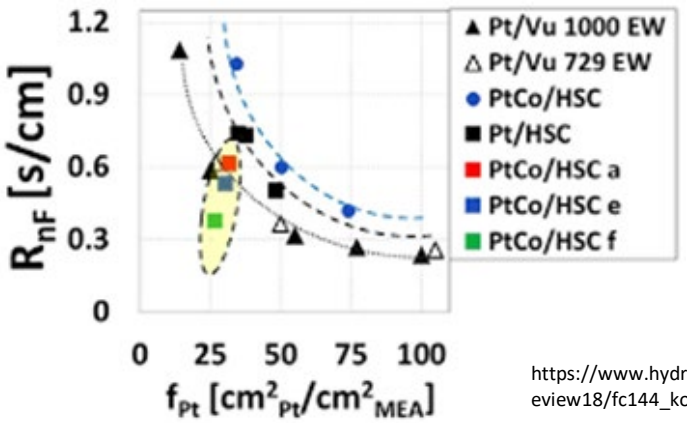
Ordered Structure



Yan, Y., *et al.*, *Adv. Mater.*, 2017, *29*(14), 1605997.

- Highly Strained Pt surfaces (High Efficiency)
- Robust Intermetallic Core (High Stability)

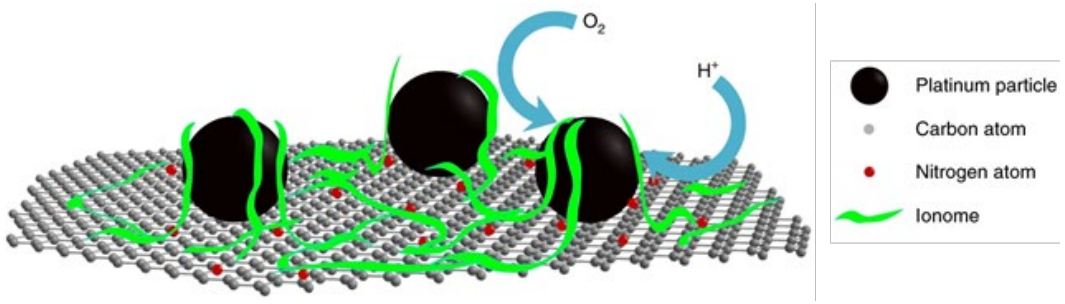
Controlled Particle-Size



https://www.hydrogen.energy.gov/pdfs/review18/fc144_kongkanand_2018_o.pdf

- High Pt Particle Dispersion (High Power)
- Large Interparticle Distance (High Stability)

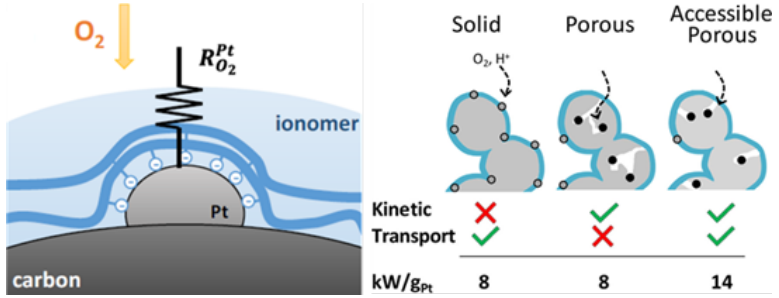
Heteroatom Doping



Ott, S., et al., *Nature materials*, 2020, *19*(1), 77-85.

- Uniform Ionomer Distribution (High Efficiency and Power)
- Strong Particle-Support Interaction (High Stability)

Suitable Pore Size/Depth



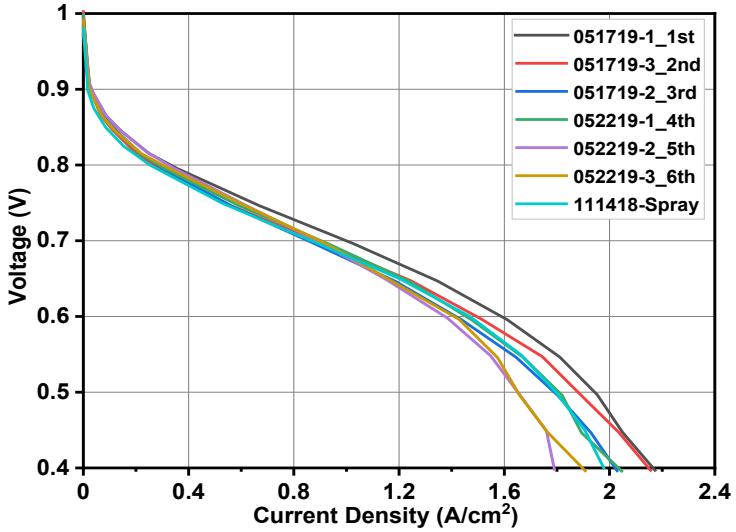
Kongkanand, A., et al. *J. Phys. Chem. Lett.*, 2016, *7*(7), 1127-1137. Yarlagadda, V., *et al. ACS Energy Lett.*, 2018, *3*(3), 618-621.

- Mitigate Ionomer Poisoning (High Efficiency)
- Desirable Mass Transport (High Power)
- Inhibit Particle Migration (High Stability)

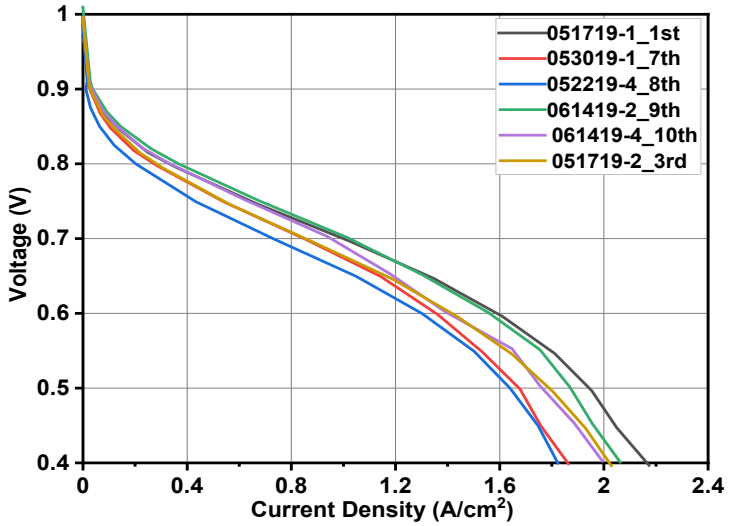
Simplified Taguchi method for Screening and Studying Catalysts

Full factorial is more suitable to a crew, while an individual relies more on the Taguchi method

- Above-mentioned factors entangled with each other
- Too much noise data could appear due to the adjustment of MEA preparation methods



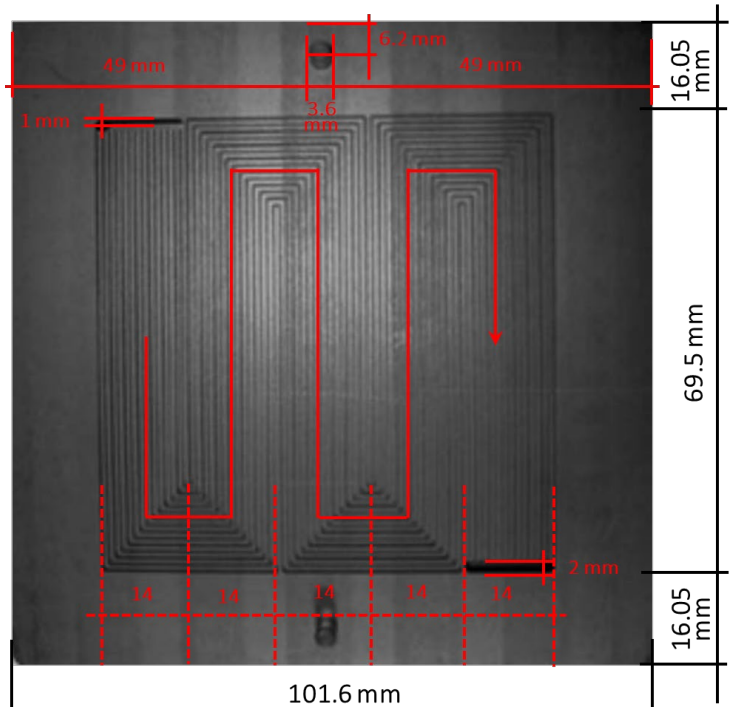
	ECSA (m^2/g)	MA (A/mg)	Note
051719-1_1st	81.25	0.614	Kapton 3mil mask
051719-3_2nd	78.07	0.508	Decal
051719-2_3rd	76.79	0.597	Kapton 3mil mask
052219-1_4th	80.96	0.617	Kapton 1mil mask
052219-2_5th	82.01	0.735	PTFE 6mil & 7mil
052219-3_6th	90.11	0.625	PTFE 6mil for both
111418-Spray	78.30	0.557	Spray Coating



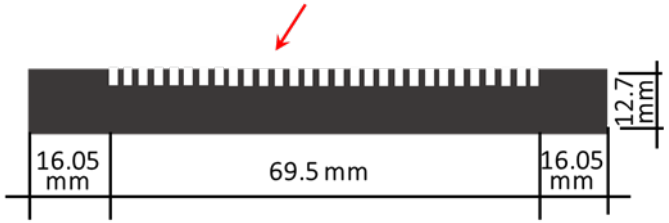
	ECSA (m^2/g)	MA (A/mg)	Note
051719-1_1st	81.25	0.614	1200μl-IPA; 100μl-H_2O
053019-1_7th	87.24	0.550	1800μl-IPA; 100μl-H_2O
052219-4_8th	64.22	0.445	2120μl-IPA; 100μl-H_2O
061419-2_9th	N/A	0.540	1750μl-IPA; 145μl-H_2O
061419-4_10th	N/A	0.611	1750μl-IPA; 145μl-H_2O
051719-2_3rd	76.79	0.597	1200μl-IPA; 100μl-H_2O

I only focus on one or two factors, while neglecting the others to better balance my time and output

MEA Preparation, Cell Assembly, and Single-Cell Testing



70 channels were 0.5 mm wide by 0.8mm deep and spaced 0.5 mm apart.

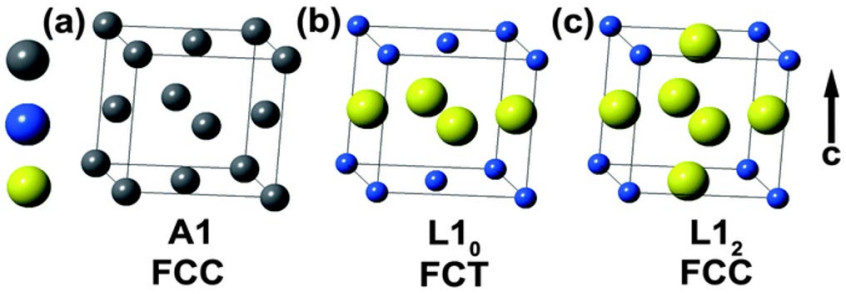


Cell Type	Differential Cell 5cm^2
Cathode Coating	Spray Coating, 0.1 mg$_{Pt}$/cm^2
Anode Coating	Spray Coating, 0.1 mg$_{Pt}$/cm^2
Cell Compression	60 in-lbs
GDL	SGL Carbon 29BC
Ink Solvent	H_2O/NPA, 4/3 vol.
Membrane	Nafion 211
Cathode Ionomer	EW1100, 0.9 I/C for porous carbon, 0.5 I/C for solid carbon
Anode Ionomer	EW1100, 0.9 I/C for porous carbon, 0.5 I/C for solid carbon
Cell Temp	80°C(150 kPa), 80°C or 94°C(250 kPa)
MA Measurement	H_2/O_2; 100%RH; 150 kPa
POL Curve	H_2/Air; 100%RH; 150 kPa, 250 kPa H_2/Air; 75%RH; 150 kPa, 250 kPa H_2/Air; 65%RH; 250 kPa
AST	0.6-0.95V, 30,000 cycles
Diagnostics	RO_2 Measurement, RH% dependent CO stripping and sheet resistance measurement

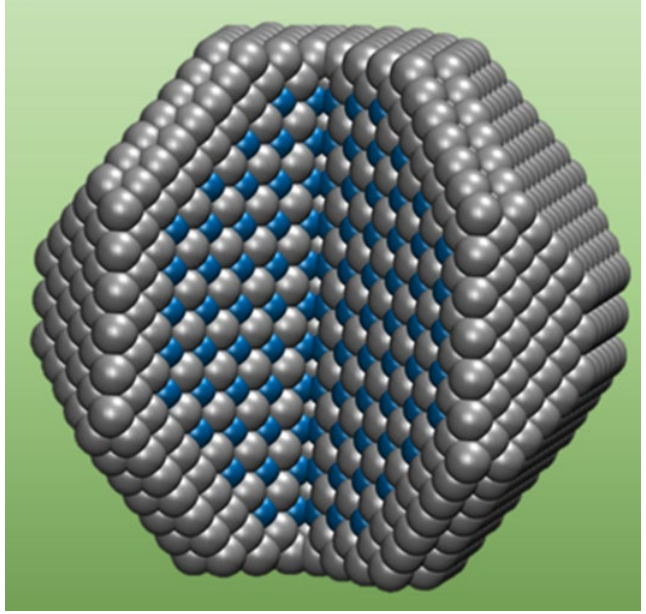
Tailoring the Crystal Structure of Pt-based Catalysts

Use atomic-level ordering to increase performance and durability of Pt-based catalysts

- Synthesize intermetallic nanoparticles (MPt)
  - Prepare ordered cores to stabilize M
  - Further protect core with Pt skin
- Integrate supported nanoparticles into MEAs, test initial performance and durability
- Perform MEA diagnostics to characterize loss mechanisms and guide electrode design
- Perform initial and post-mortem characterization (XRD, XAS, XRF, SEM-EDS, TEM, STEM-HAADF, STEM-EDS) to guide synthetic work and determine effect of structure and composition on performance and durability

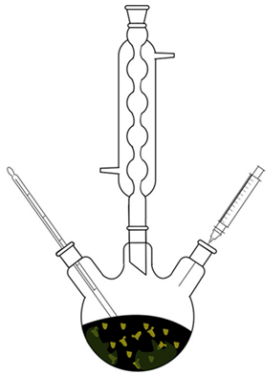


Adapted from Johnston-Peck *et al.*, *Nanoscale*, **2011**, *3*, 4142

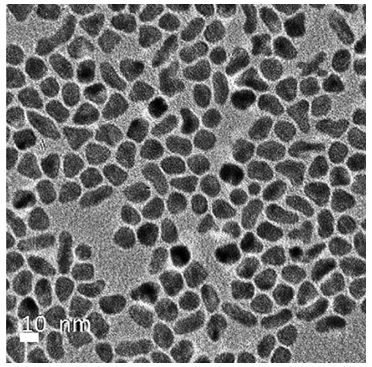


Johnston-Peck et al., *Nanoscale*, 2011, **3**, 4142

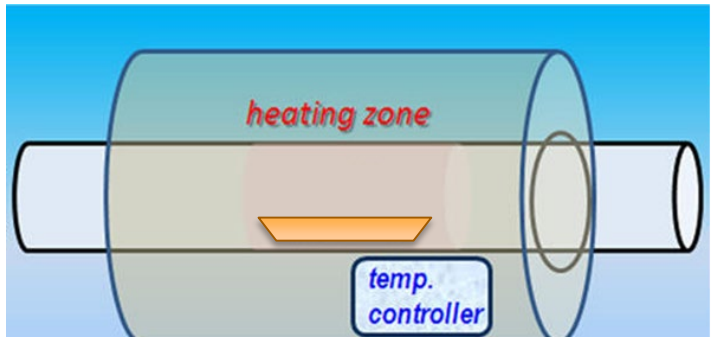
Approach: Colloidal Synthesis and Thermal Annealing



A1-CoPt

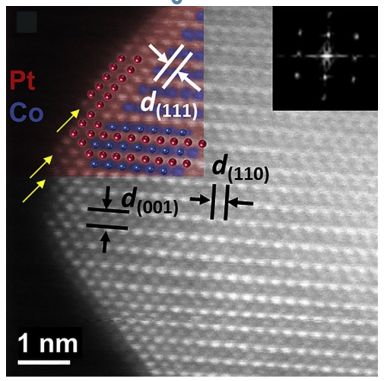


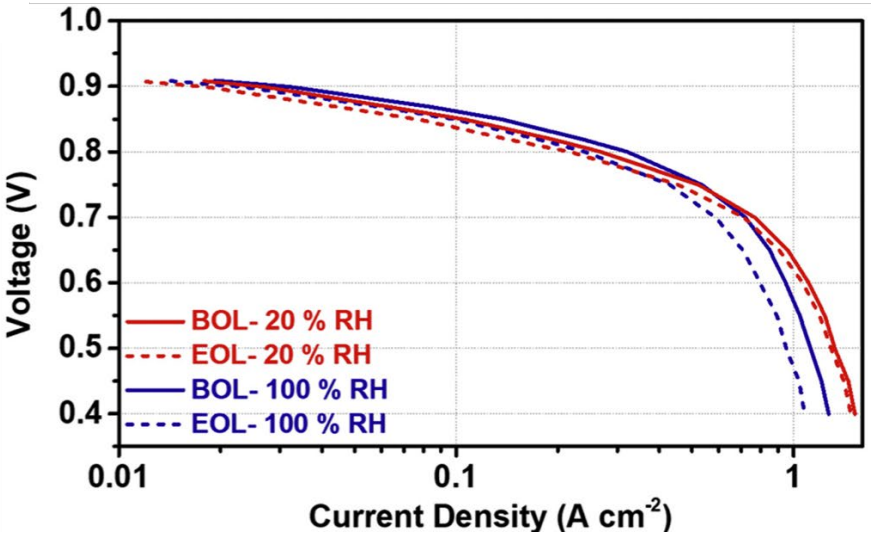
Carbon Loading

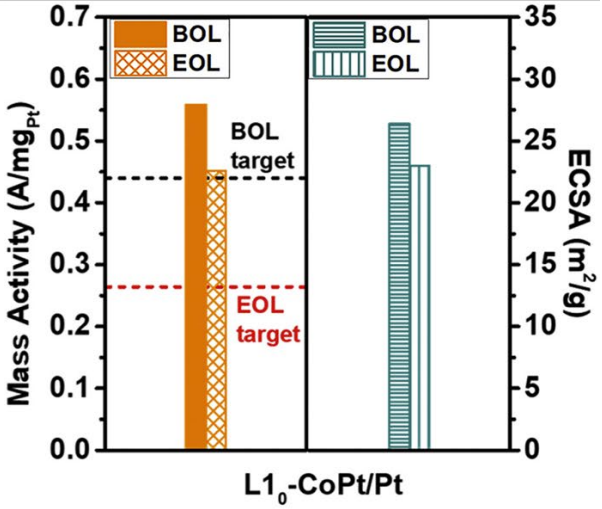


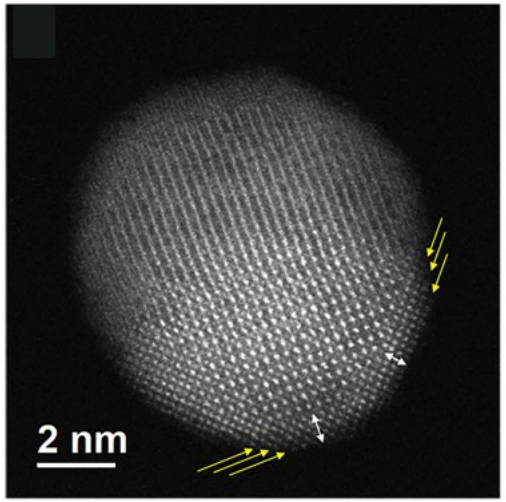
Ordering

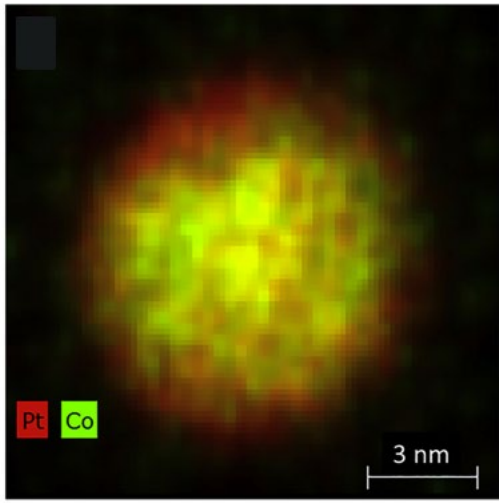
$L1_0$-CoPt









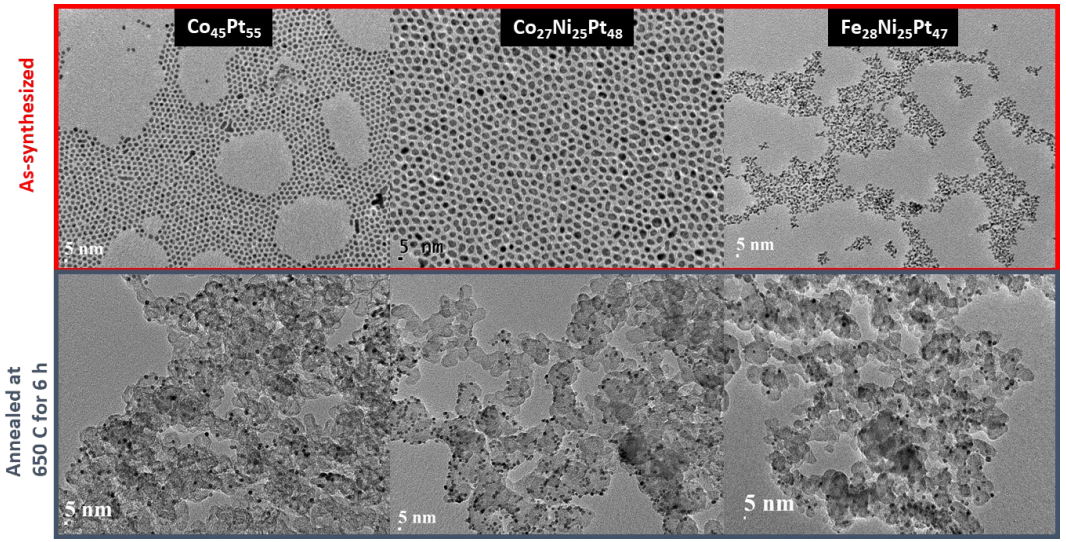


- The biaxial surface strain renders the catalyst superior intrinsic activity, exceeding the DOE target
- The catalyst displays excellent stability, owing to ordered intermetallic cores mitigate the Co dissolution
- Poor high-current performance could stem from the large particle size and low Pt loading

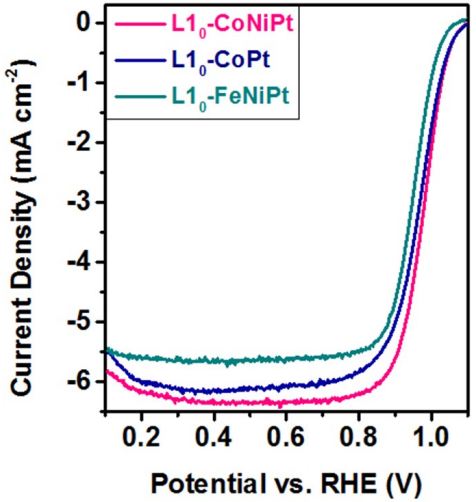
BROWN

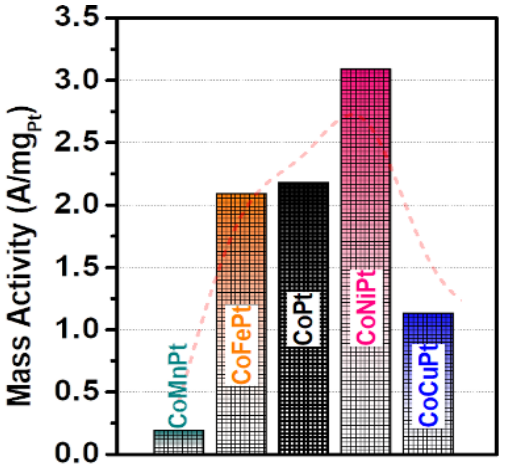
Approach: Colloidal Synthesis and Thermal Annealing

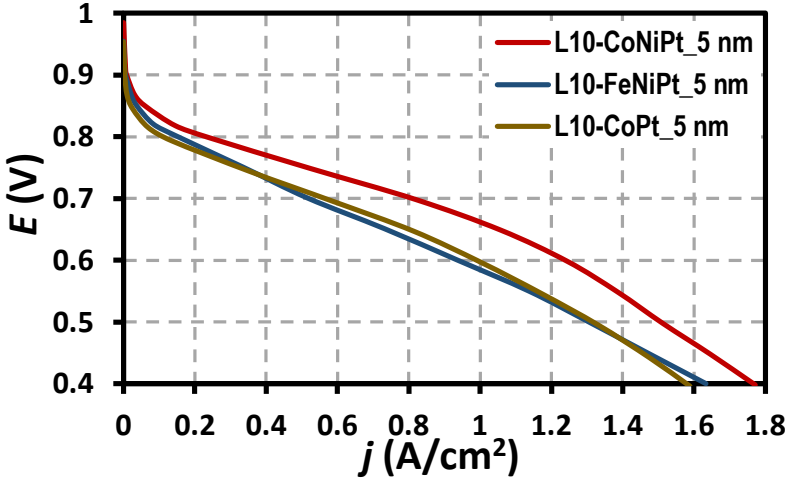
Synthesis of $L1_0$ intermetallic catalysts of 5 nm

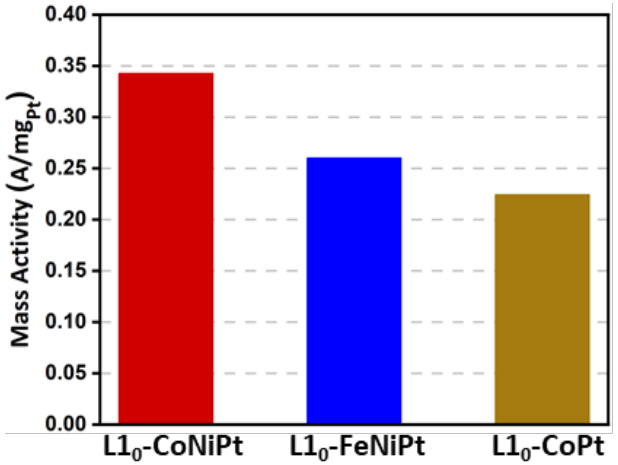


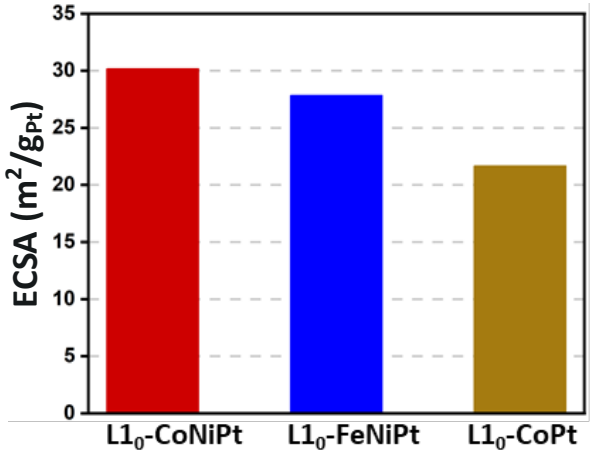
RDE mass activity of 5 nm particles





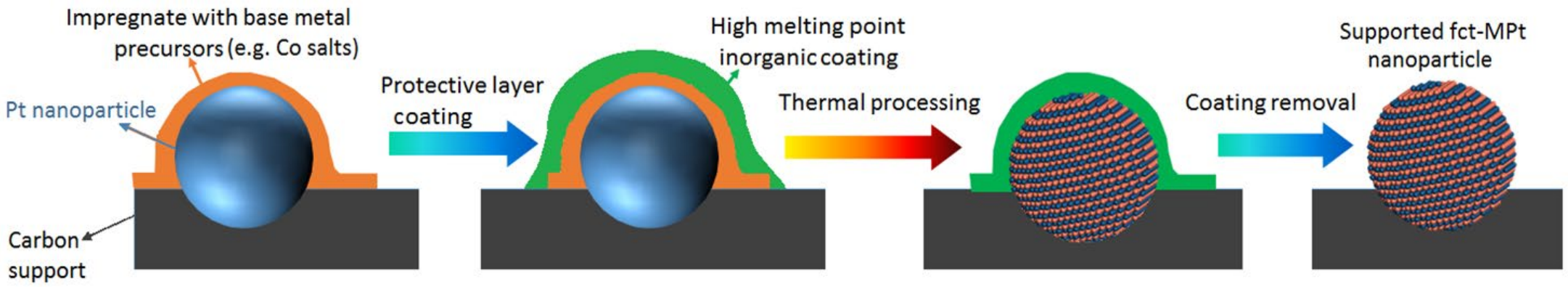


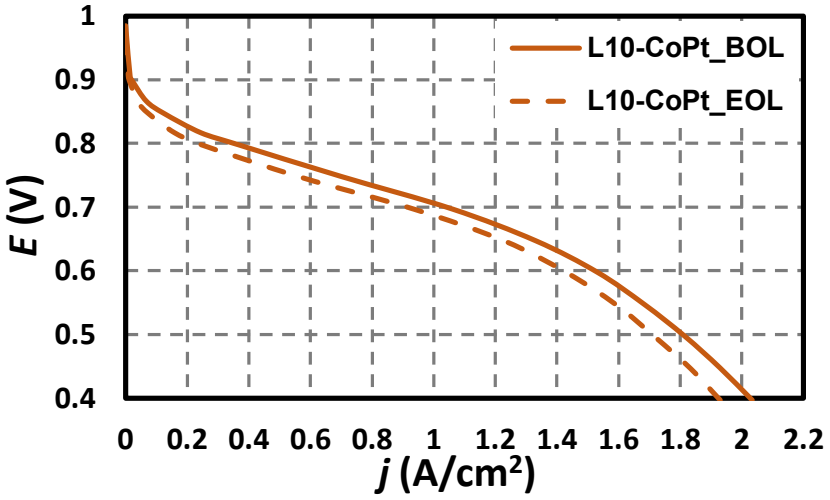




Poor MEA-RDE agreement could be a result of the residual surfactants on nanoparticles

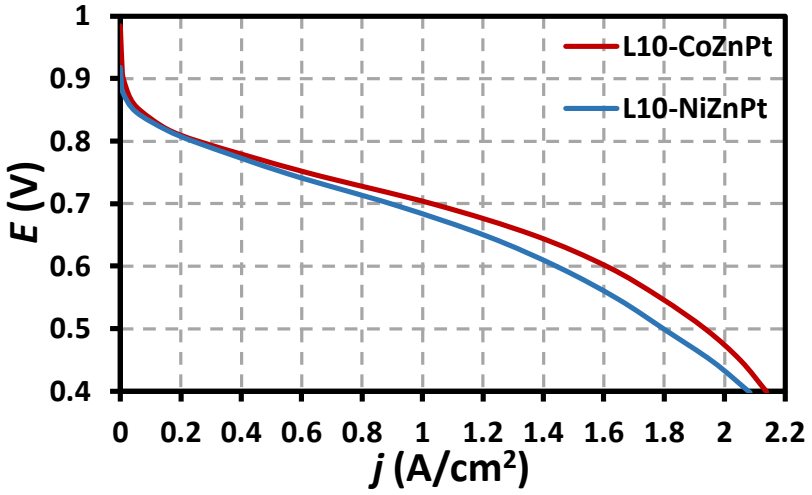
Approach: Cobalt Impregnation on Pt/C





	Units	Measured	Target
Mass Activity	A/mgPGM	0.72	0.44
Mass Activity Loss [1]	%	40	40
Degradation at 0.8 A/cm^2 [1]	mV	19	30
Current Density at 0.8 V	A/cm^2	0.34	0.3
Power at 0.67 V, 150 kPa$_{abs}$	W/cm^2	0.81	1
ECSA	m^2/g	48	N/A
ECSA Loss	%	33	N/A
PGM Loading [2]	mg/cm^2	0.095	0.125

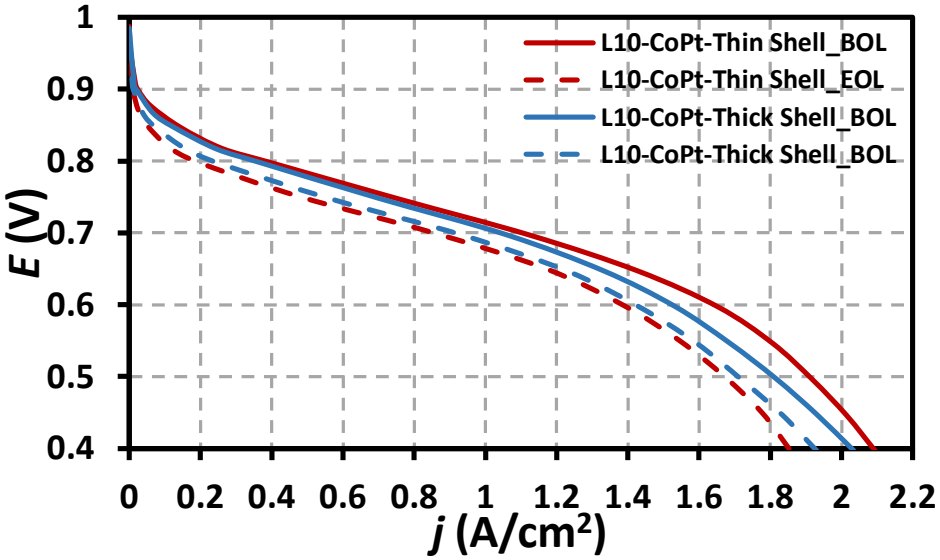
[1] 30K square wave cycles, 0.6-0.95 V [2] Cathode

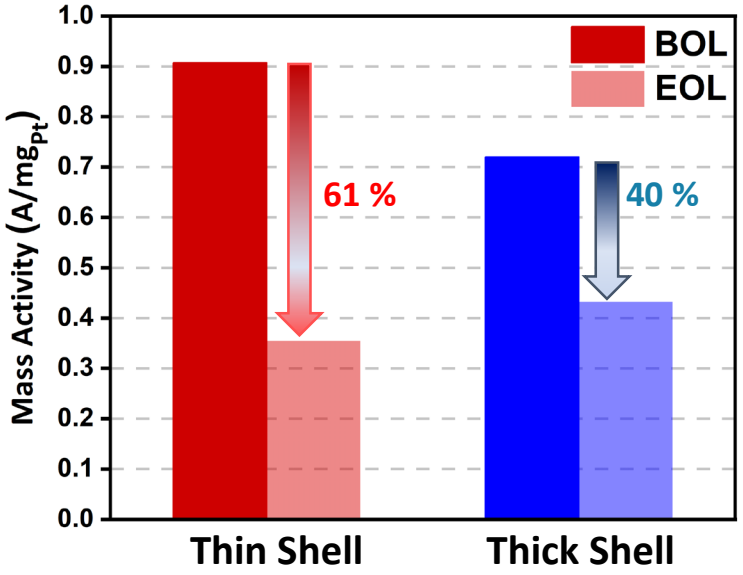


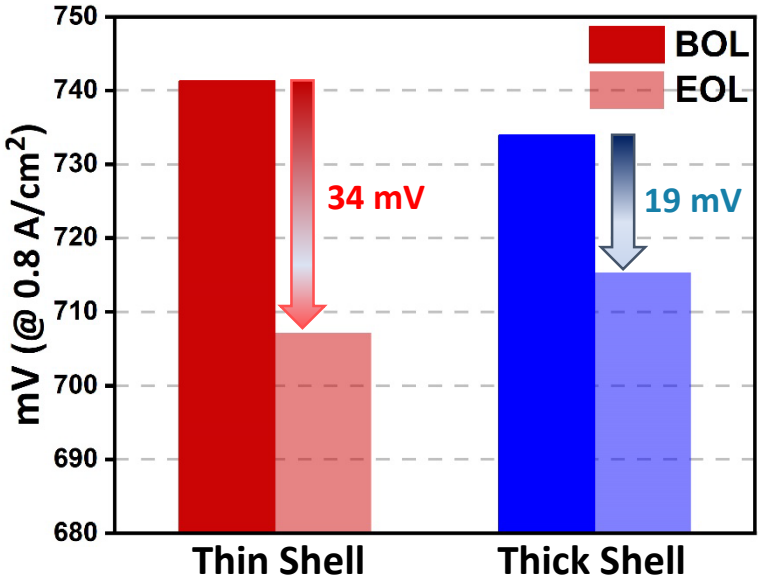
$L1_0$-CoPt intermetallic catalyst with relatively small particle size exhibited desirable intrinsic activity, stability, and power density, which is an ideal cathode catalyst for the LDV application

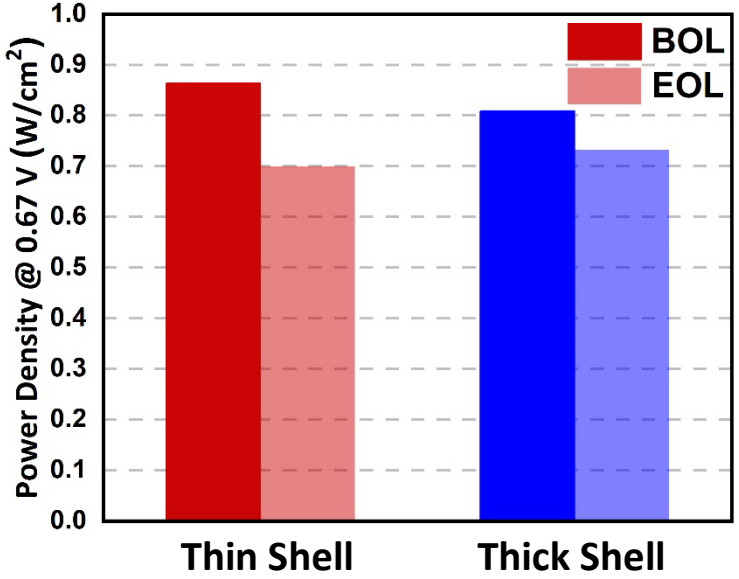
Approach: Cobalt Impregnation on Pt/C

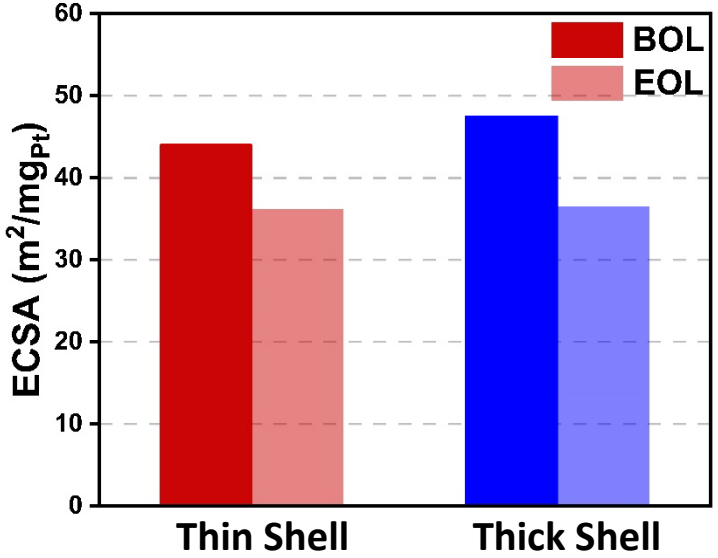
Acid leaching/heating plays a key role in the formation of a thick Pt shell











The loss of Co content for thin shell catalysts is as high as 41.5 %, whereas that for thick shell counterpart is 27.9 %, which demonstrates effect of shell thickness in inhibiting the Co leaching.

Tailoring both the Crystal Structure and Particle Size

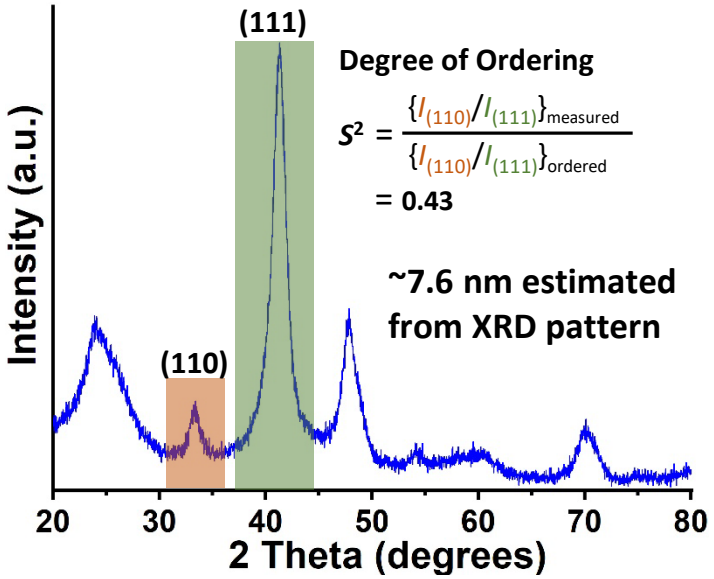
$L1_0$-CoPt #A

- Large Particle Size
- High Ordering Degree

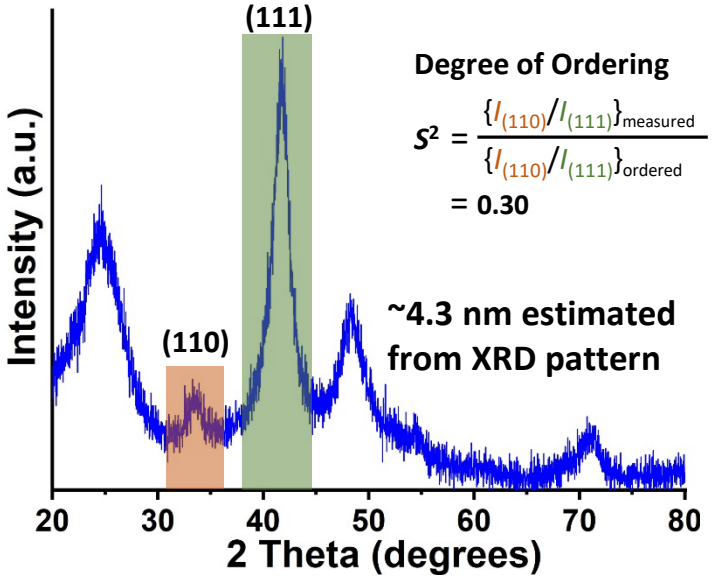
$L1_0$-CoPt #B

- Small Particle Size
- Low Ordering Degree

$L1_0$-CoPt #A: 10% $Pt_{67}Co_{33}$ on Vulcan

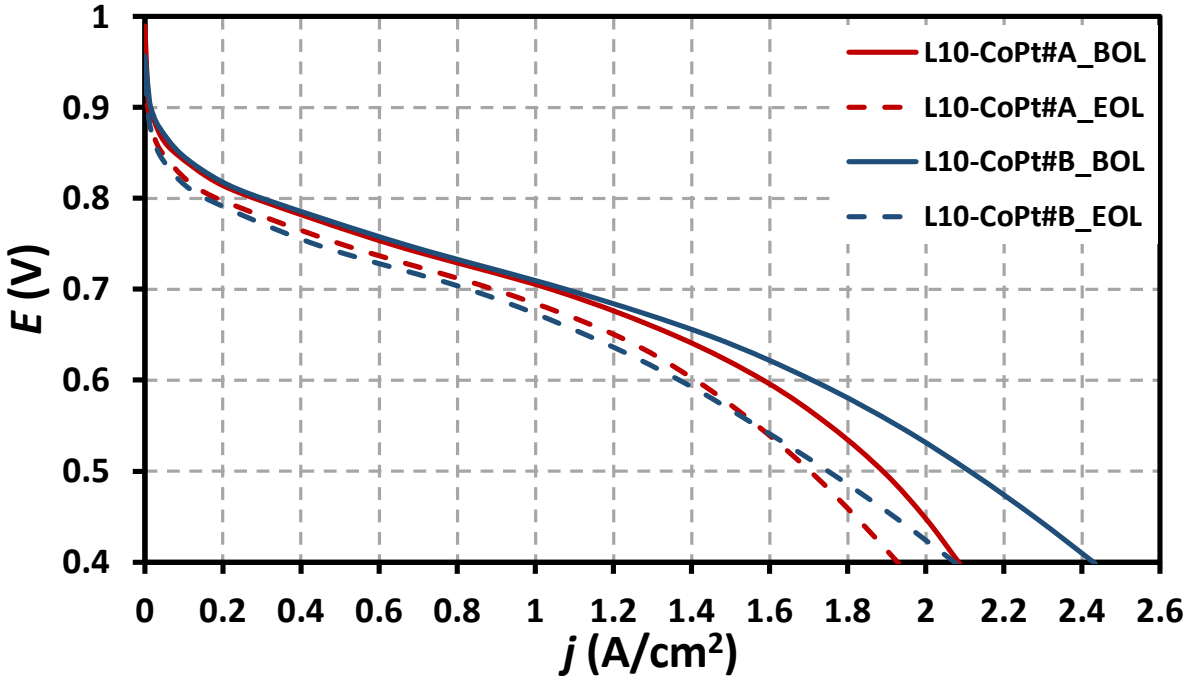


$L1_0$-CoPt #B: 10% $Pt_{72}Co_{28}$ on Vulcan



$L1_0$-CoPt #A with a large particle size also displays a higher ordering degree

Tailoring both the Crystal Structure and Particle Size



	MA (A/mg_{Pt})	ECSA (m^2/g_{Pt})	Power Density (W/cm^2)	@0.8 A/cm^2 (mV)
$L1_0$-CoPt#A_BOL	0.500	39.3	0.823	729
$L1_0$-CoPt#A_EOL	0.323	30.0	0.723	712
$L1_0$-CoPt#A_Loss	35.4%	23.7%	12.1%	17
$L1_0$-CoPt#B_BOL	0.633	62.5	0.867	733
$L1_0$-CoPt#B_EOL	0.277	31.9	0.677	705
$L1_0$-CoPt#B_Loss	56.2%	49.0%	21.8%	28

Cobalt Loss: $L1_0$-CoPt #A: 30.7% $L1_0$-CoPt #B: 57.3%

- Catalyst with a large particle size displayed better stability, while catalyst with a small particle size exhibited a better BOL performance.
- Both catalysts showed a similar EOL ECSA, suggesting the better EOL performance of $L1_0$-CoPt#A catalyst should stem from the mitigated Co loss owing to more ordered core.
- This study demonstrates controllably increasing the particle size is viable route to improve the catalyst stability without sacrificing the performance too much.

Tailoring both the Crystal Structure and Particle Size

We also extend this study to $L1_0$-CoPt catalysts supported by the high-surface area carbon

$L1_0$-CoPt #A

- Small Particle Size
- Low Ordering Degree

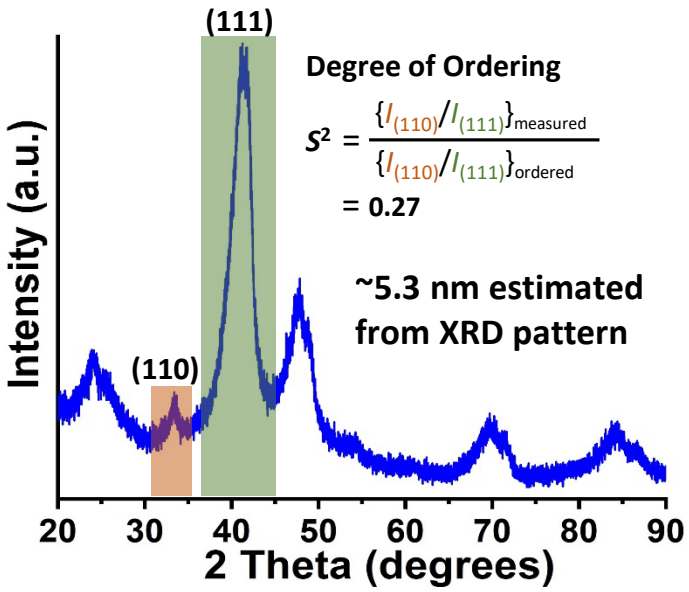
$L1_0$-CoPt #B

- Large Particle Size
- High Ordering Degree

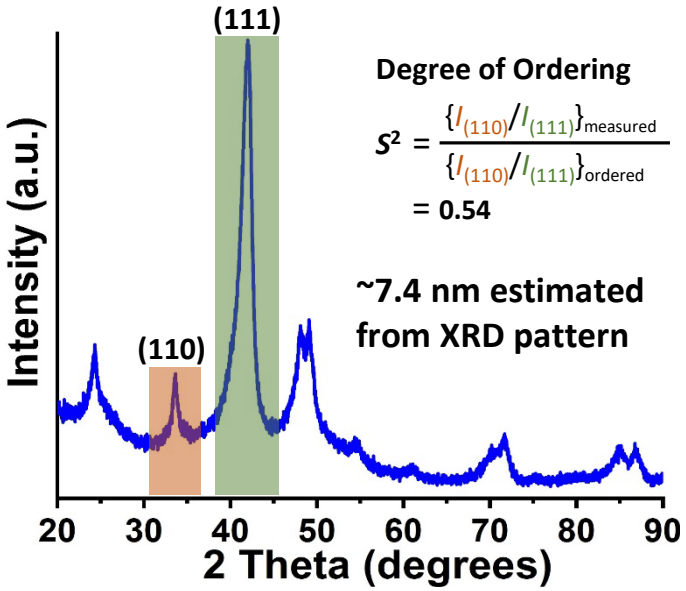
$L1_0$-CoPt #C

- Large Particle Size
- Medium Ordering Degree

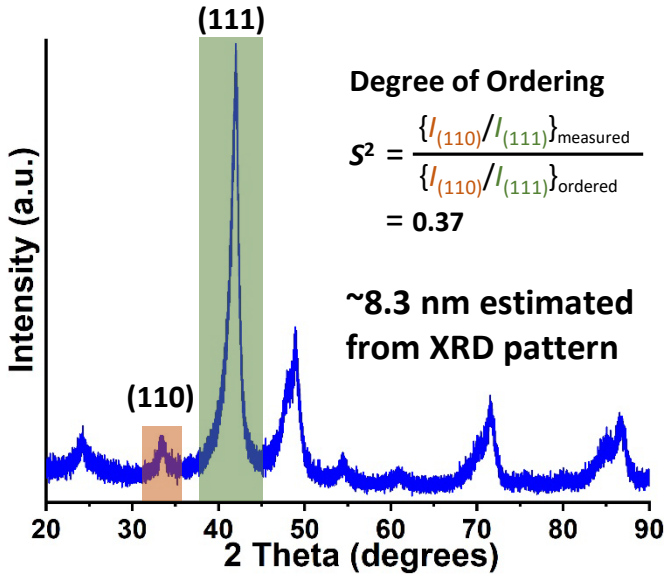
$L1_0$-CoPt #A: $Pt_{61}Co_{39}$



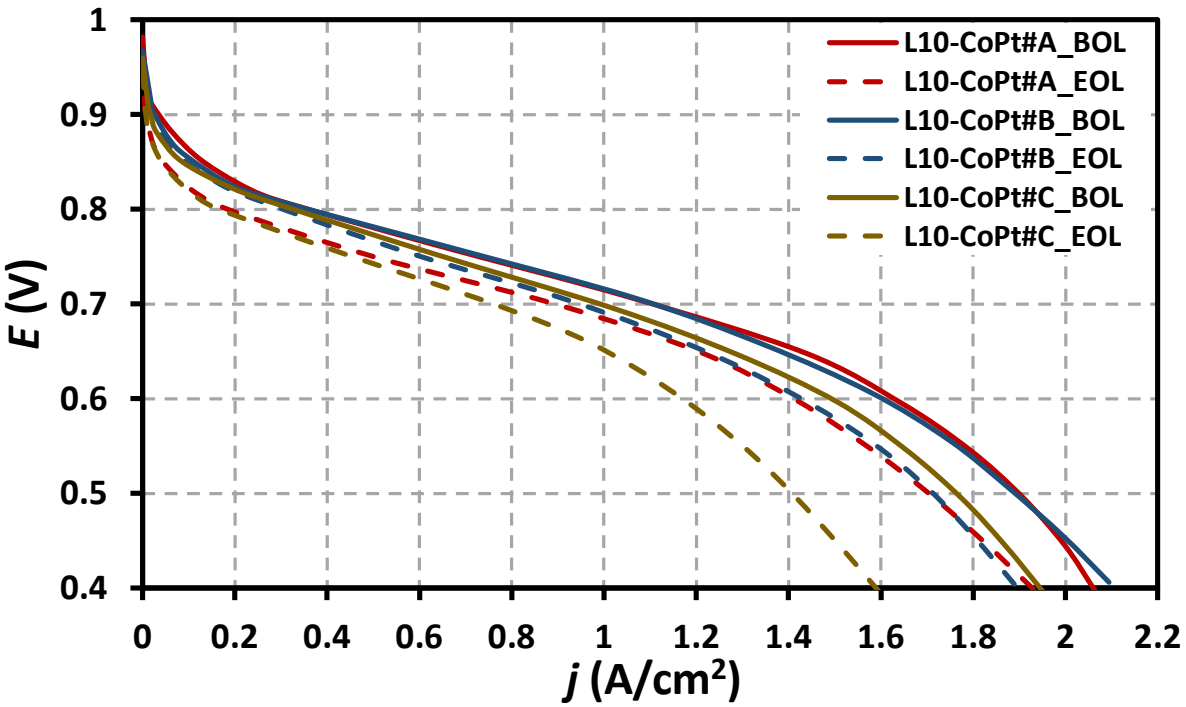
$L1_0$-CoPt #B: $Pt_{65}Co_{35}$



$L1_0$-CoPt #C: $Pt_{65}Co_{35}$



Tailoring both the Crystal Structure and Particle Size



Cobalt Loss: $L1_0$-CoPt #A: 51.7% $L1_0$-CoPt #B: 35.0% $L1_0$-CoPt #C: 45.4%

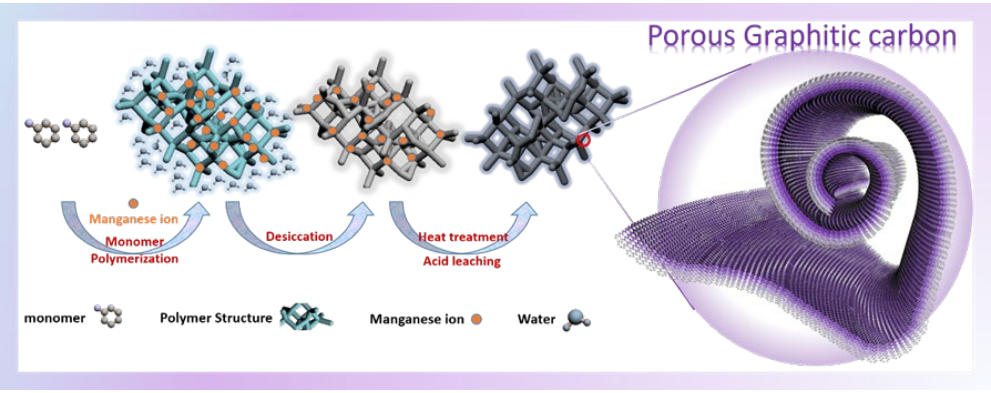
	MA (A/mg_{Pt})	ECSA (m^2/g_{Pt})	Power Density (W/cm^2)	@0.8 A/cm^2 (mV)
$L1_0$-CoPt#A_BOL	0.688	55.4	0.868	740
$L1_0$-CoPt#A_EOL	0.224	16.4	0.599	687
$L1_0$-CoPt#A_Loss	67.4%	70.5%	31.0%	53
$L1_0$-CoPt#B_BOL	0.616	39.4	0.853	742
$L1_0$-CoPt#B_EOL	0.369	25.0	0.745	722
$L1_0$-CoPt#B_Loss	40.0%	36.4%	12.7%	20
$L1_0$-CoPt#C_BOL	0.480	33.5	0.777	728
$L1_0$-CoPt#C_EOL	0.220	20.5	0.612	692
$L1_0$-CoPt#C_Loss	54.1%	38.8%	21.3%	36

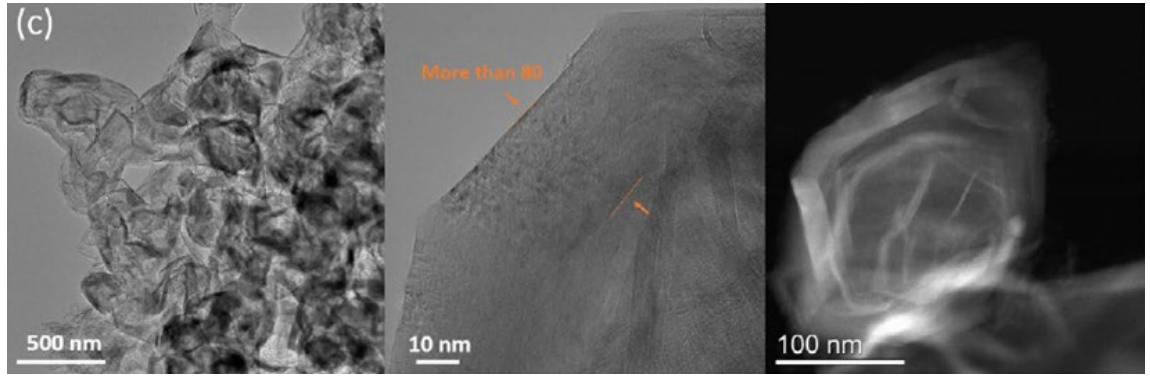
RO_2, local: $L1_0$-CoPt #A: BOL:0.206 s/cm EOL: 0.363 s/cm
$L1_0$-CoPt #B: BOL: 0.257 s/cm EOL: 0.293 s/cm
$L1_0$-CoPt #C: BOL: 0.266 s/cm EOL: N/A

- Catalyst with a large particle size displayed better stability, while catalyst with a small particle size exhibited a better BOL performance, which agrees well with the results from RO_2 measurement.
- $L1_0$-CoPt #C catalyst showed the largest transport resistance because its ECSA is too small. $L1_0$-CoPt #B catalyst of a large particle size and a high ordering degree showed the highest stability and the least Co loss.
- This study demonstrates controllably increasing both the **particle size and the ordering degree** is key to improving the catalyst stability without sacrificing the initial performance too much.

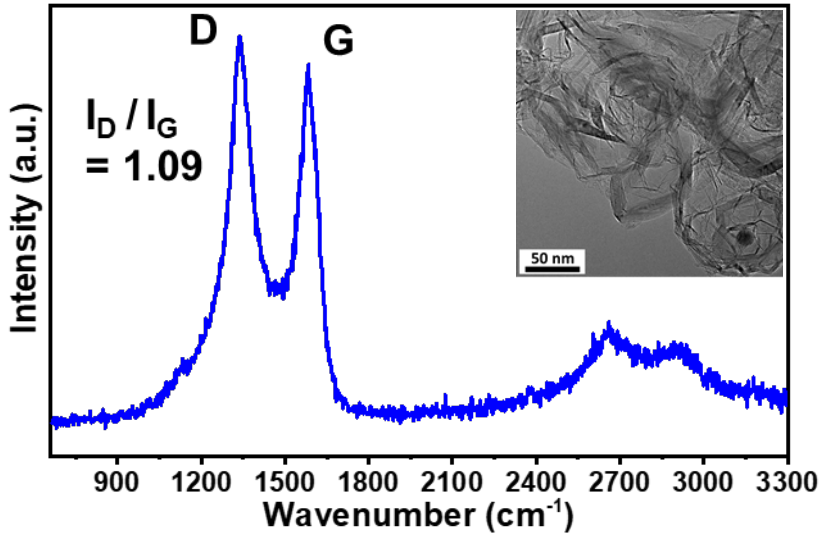
Tailoring the Structure for both the Particle and Carbon Support

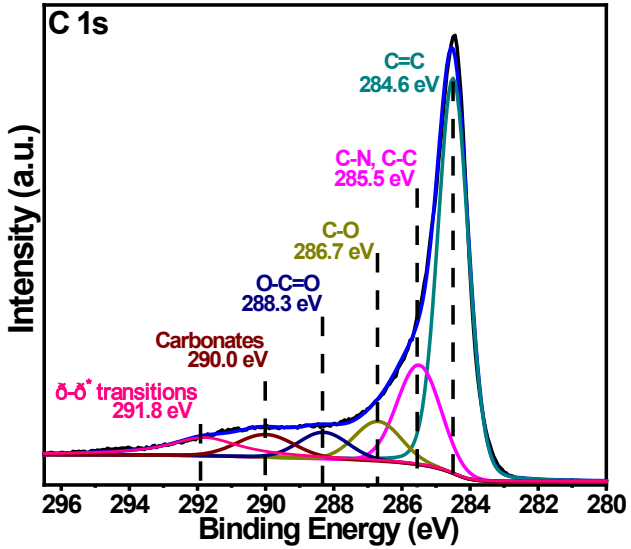
- Mn was demonstrated to be an effective catalyst for graphitization of polymer-derived carbon, which significantly decreases the required temperature from above 3000 to around 1100 °C.
- Addition of polypyrrole can further improve the graphitization and porosity.

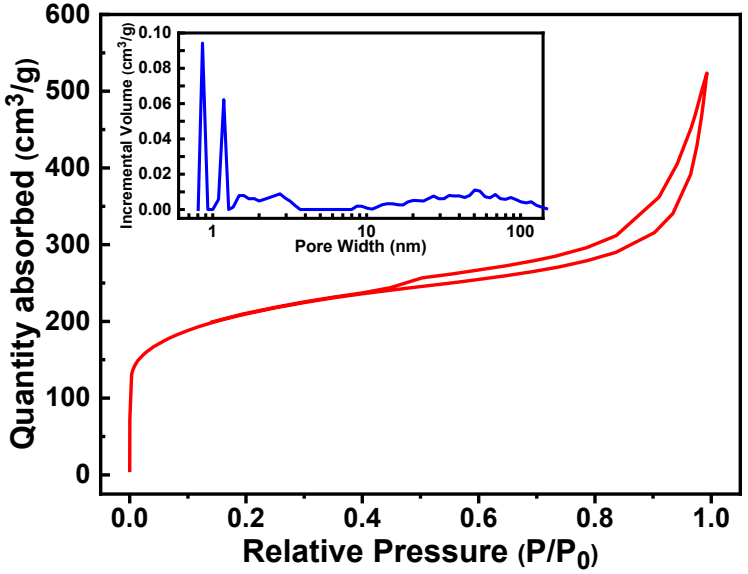




Qiao, Z., *et al.* Energy & Environmental Science, **2019**, *12*(9), 2830-2841.

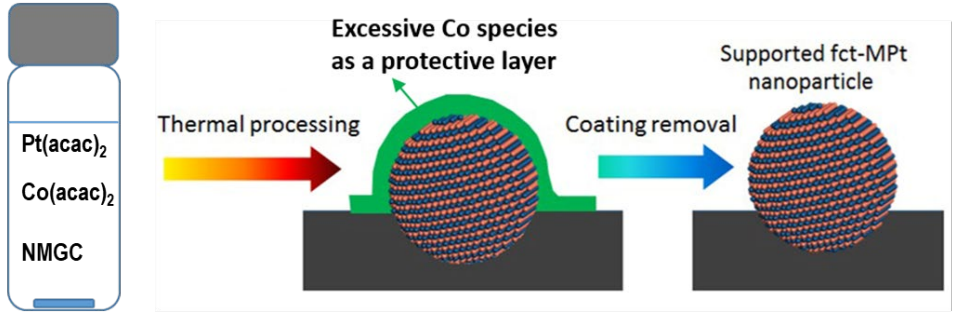






Tailoring the Structure for both the Particle and Carbon Support

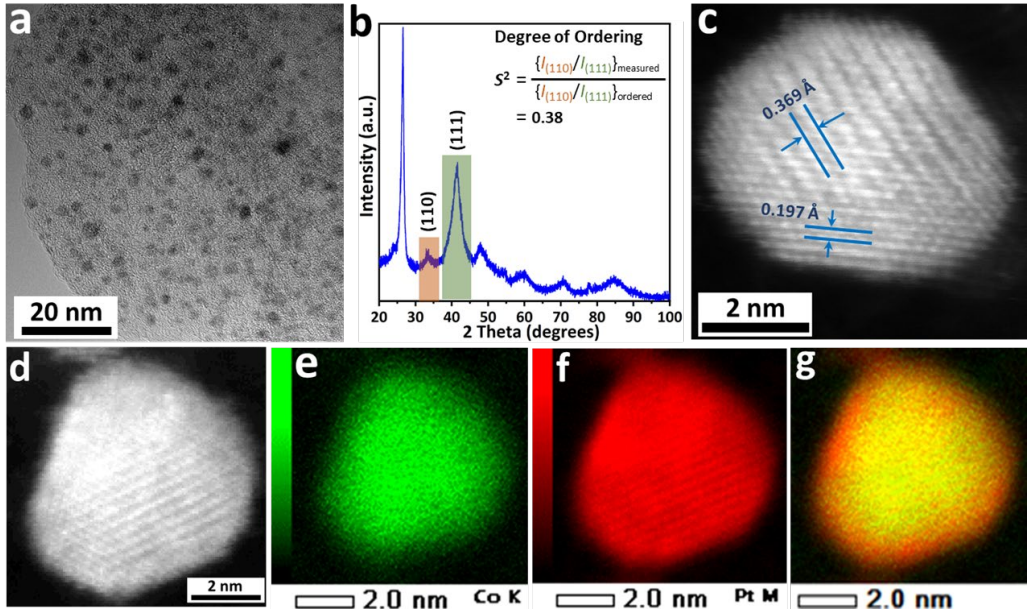
Impregnation Synthesis of $L1_0$-CoPt on NMGC



After mixing, the slurry was dried to powder

Heat treatment under H_2/Ar (6%) atmosphere

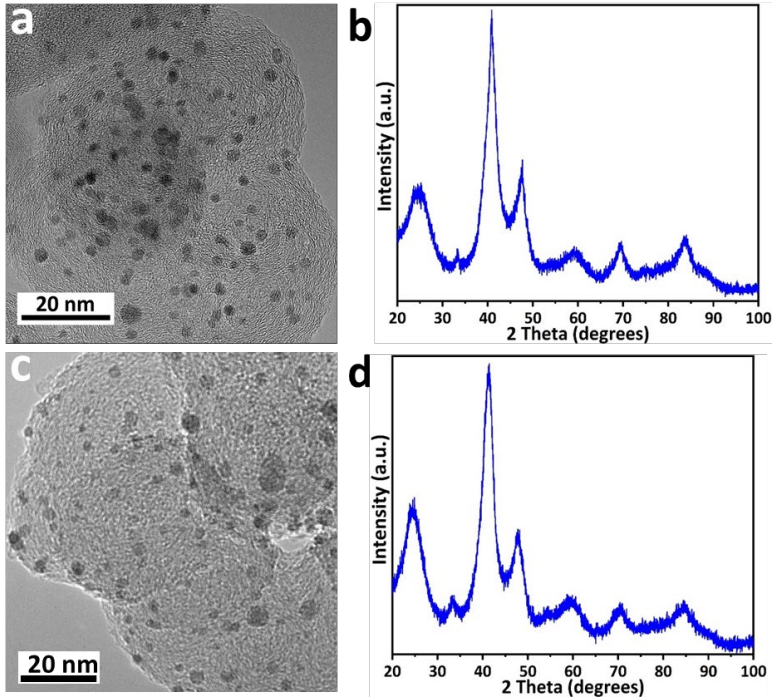
Acid cleaning and leaching out surface Co



Reference Catalysts

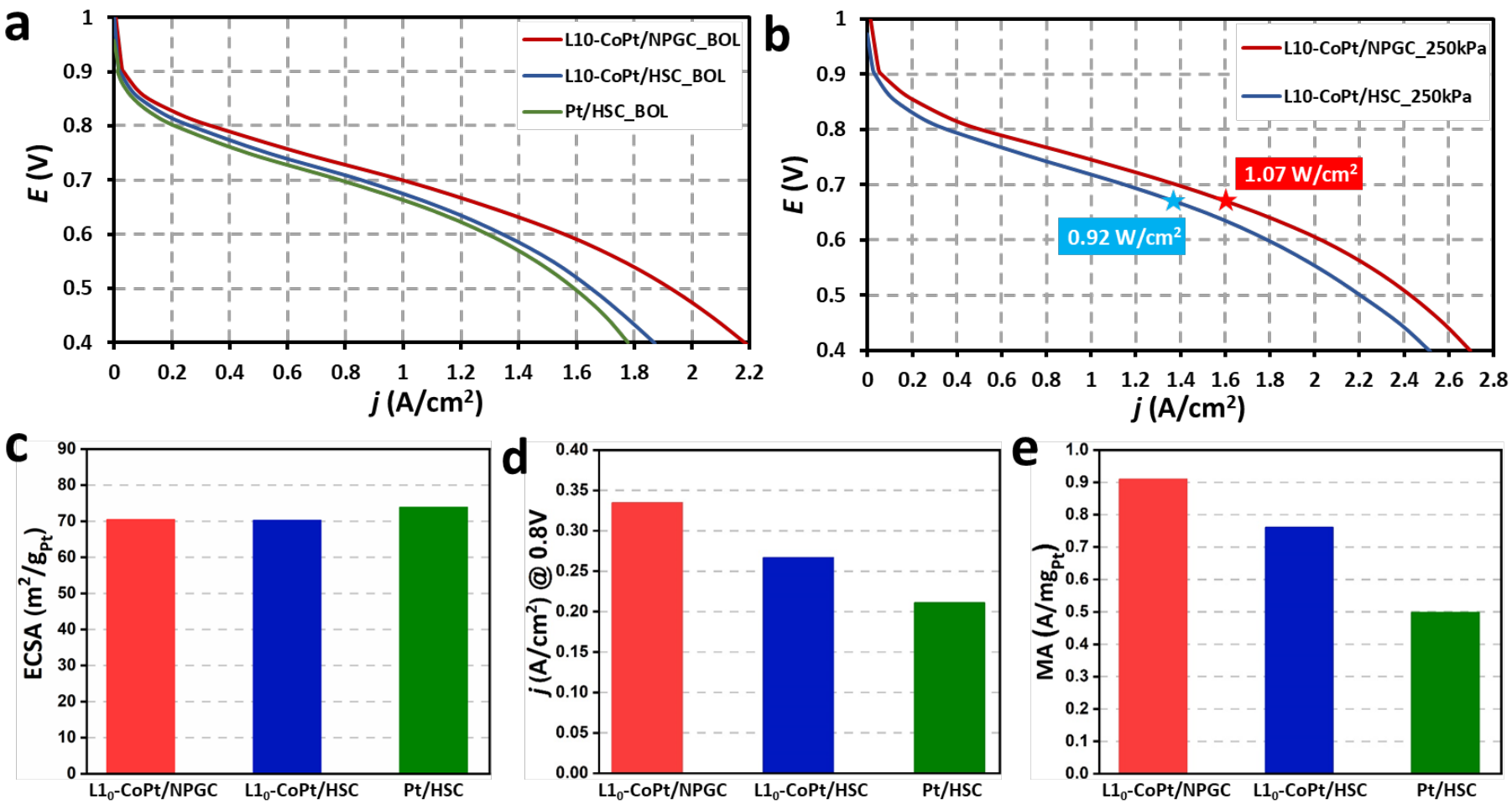
10% $L1_0$-CoPt/HSC

10% $L1_0$-CoPt/Vulcan



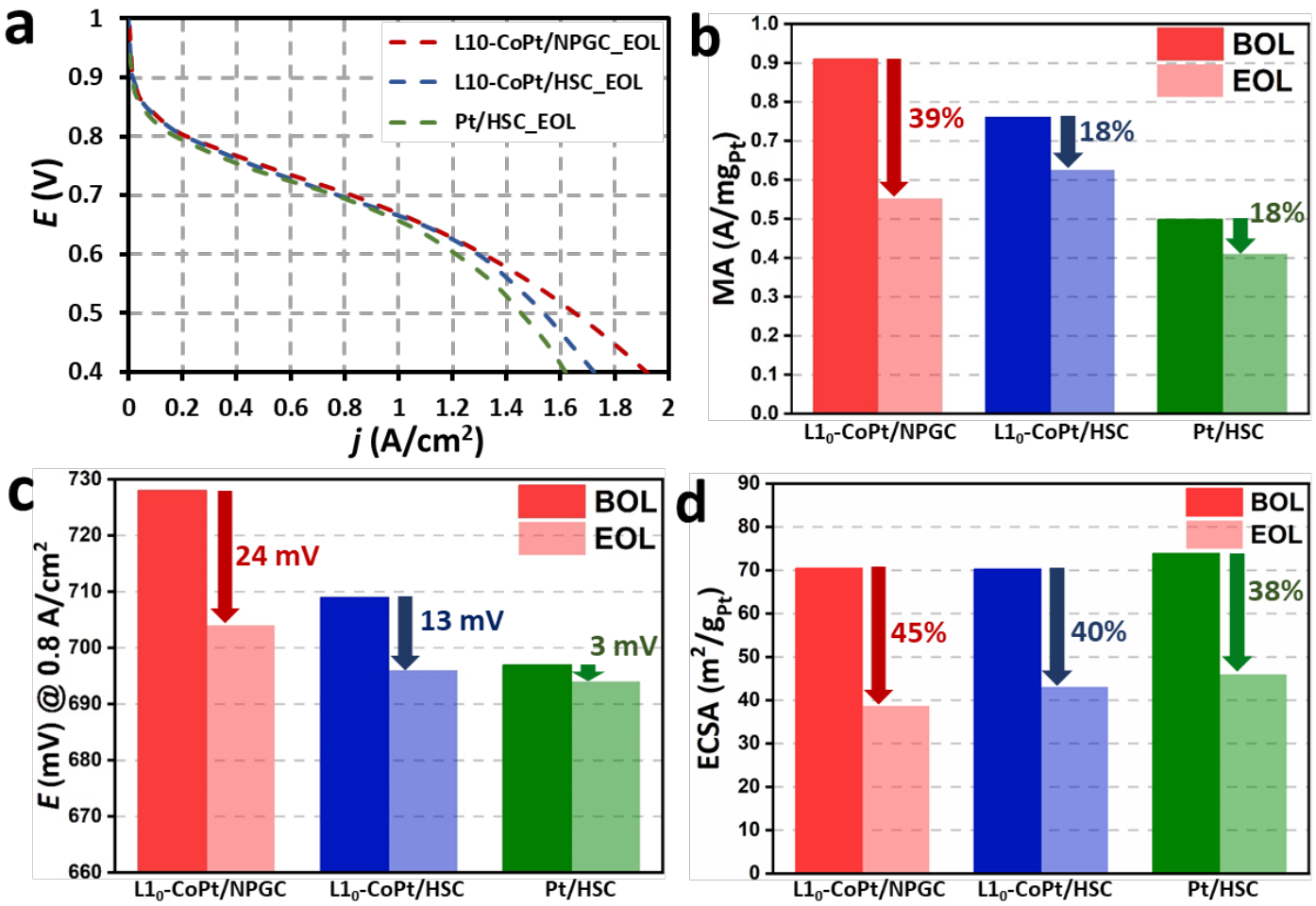
- Porous network inhibits the particle migration, which benefits the generation of small particles during the annealing treatment
- The XRD pattern reveals the ordered intermetallic identity of the catalyst
- STEM characterizations confirm the Pt on $L1_0$-CoPt core-shell structure
- We also synthesized the reference catalysts for studying the role of carbon supports in fuel cell testing

Tailoring the Structure for both the Particle and Carbon Support



- $L1_0$-CoPt/NPGC exhibited much higher current densities in the low-voltage region because of that NPGC possesses relatively lower porosity, which reduces the voltage loss, despite three catalysts showed similar ECSA
- The rated power density for $L1_0$-CoPt/NPGC surpassed 1 W/cm^2, demonstrating the applicability of this catalyst in the real PEMFC
- $L1_0$-CoPt/NPGC also showed better performance in the kinetic region and an outstanding mass activity

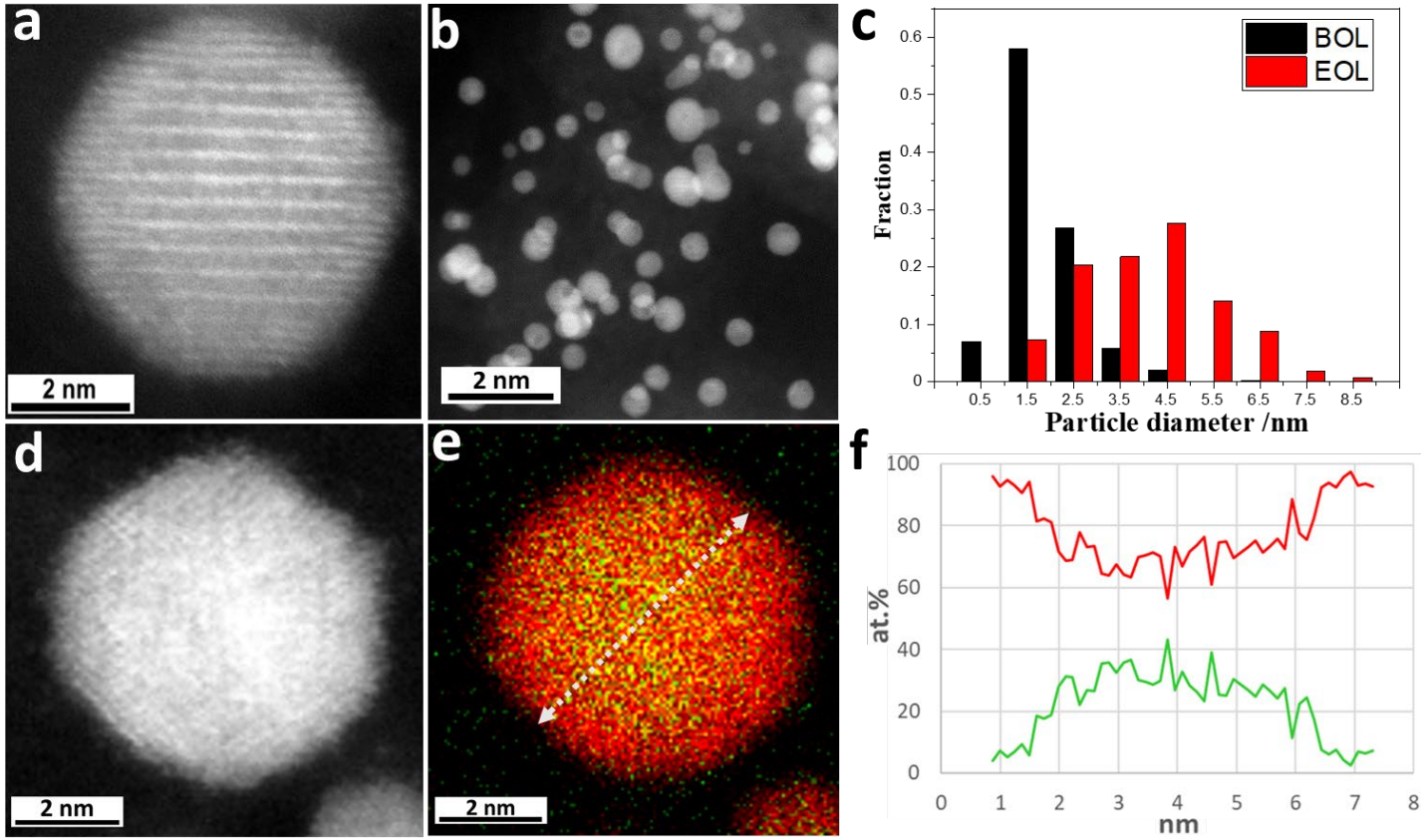
Tailoring the Structure for both the Particle and Carbon Support



- The stabilities of all three catalysts meet the DOE target
- Compared the HSC, NPGC has a relatively lower porosity, which could not afford strong protection of particles
- Considering the higher BOL performance, it is more advantageous to apply $L1_0$-CoPt/NPGC catalyst in real fuel cells

Tailoring the Structure for both the Particle and Carbon Support

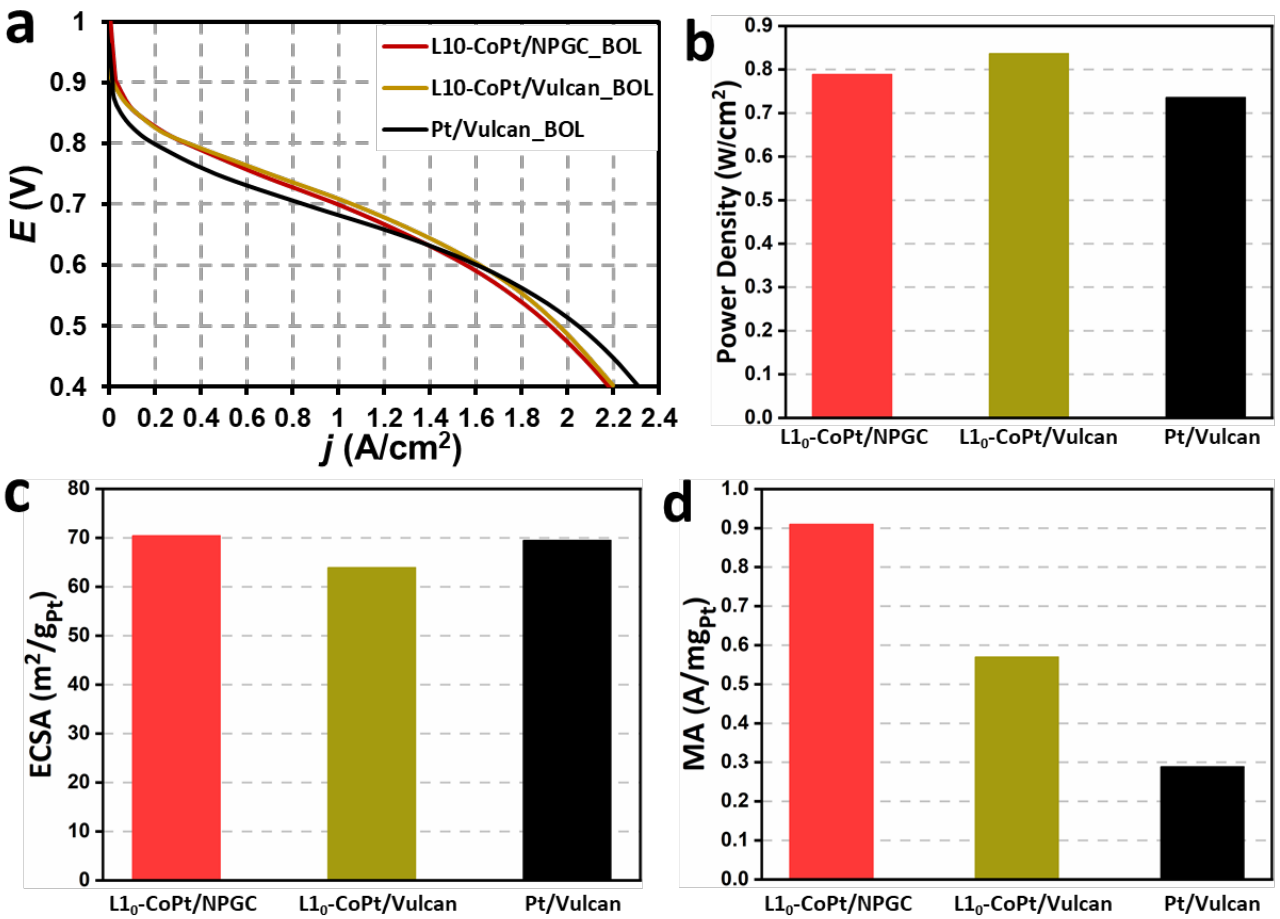
Structural Characterizations for EOL $L1_0$-CoPt/NPGC



	Pt (at.%)	Co(at.%)	Co Loss
$L1_0$-CoPt/NPGC_Powder	78.7	21.3	
$L1_0$-CoPt/NPGC_EOL	87.8	12.2	51.3%
$L1_0$-CoPt/HSC_Powder	78.0	22.0	
$L1_0$-CoPt/HSC_EOL	88.5	11.5	53.9%

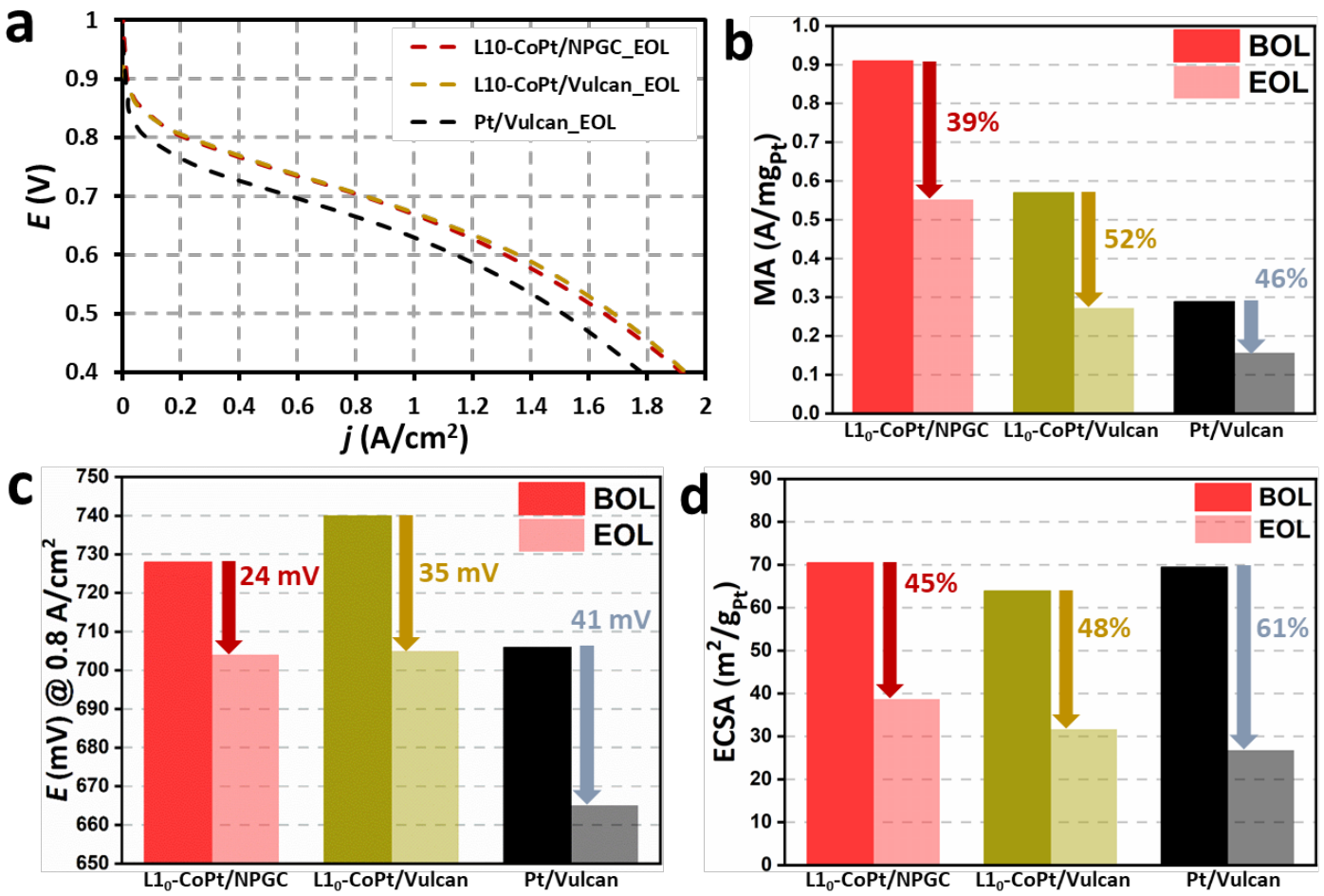
- The ordered intermetallic identity of $L1_0$-CoPt/NPGC was preserved after 30K cycles of AST
- The average particle size for $L1_0$-CoPt/NPGC increased from 2.6 nm to 4.0 nm
- Further study needs to be carried out to understand the effect of porosity on the transition metal dissolution

Tailoring the Structure for both the Particle and Carbon Support



- The gap in power density between $L1_0$-CoPt/NPGC and $L1_0$-CoPt/Vulcan is not remarkable, as the voltage penalty caused by the porous structure of NPGC could be compensated by high ECSA and high mass activity
- $L1_0$-CoPt/Vulcan showed a relatively low ECSA as particles on solid carbons usually undergo a higher degree of sintering and agglomeration during thermal annealing

Tailoring the Structure for both the Particle and Carbon Support



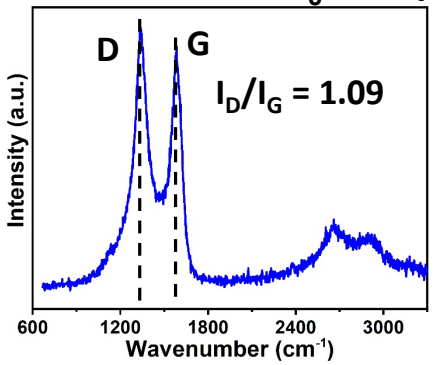
Owing to the robust intermetallic crystal structure and the porous structure/nitrogen dopants of NPGC, $L1_0$-CoPt on NPGC catalyst exhibited significantly improved stability compared with the other two reference catalysts

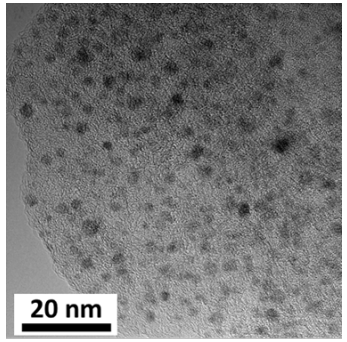
Tailoring the Structure for both the Particle and Carbon Support

Porosity Increase

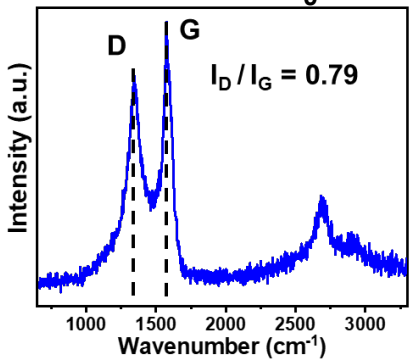
Graphitization Increase

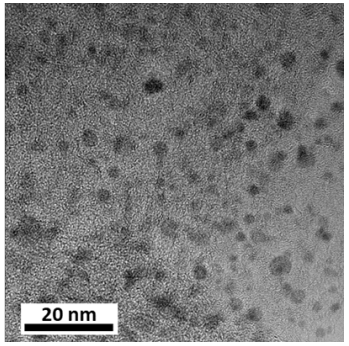
$L1_0$-CoPt/NPGC-1



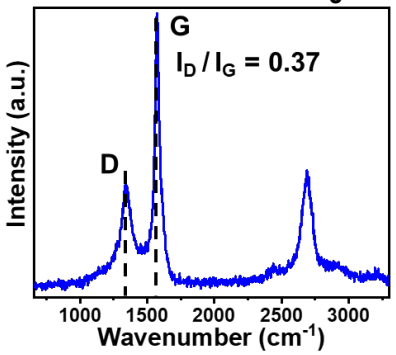


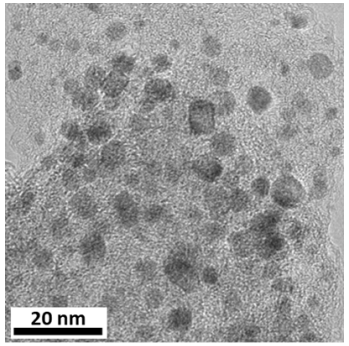
$L1_0$-CoPt/NPGC-2

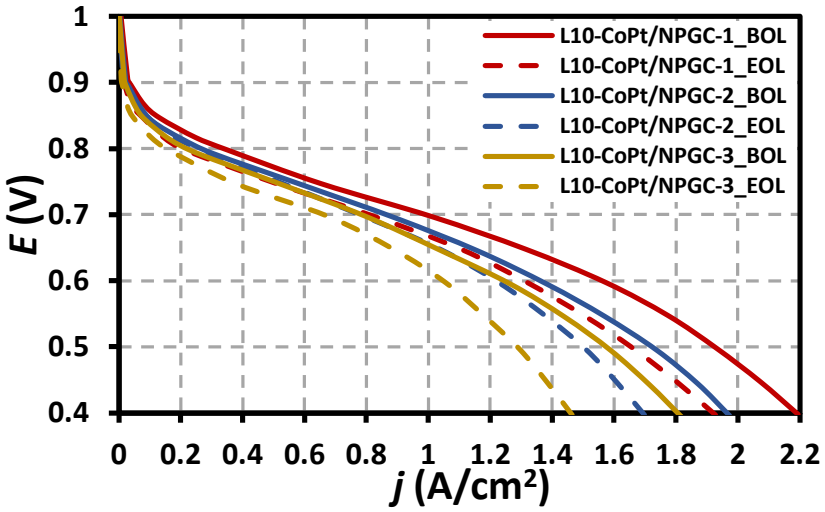


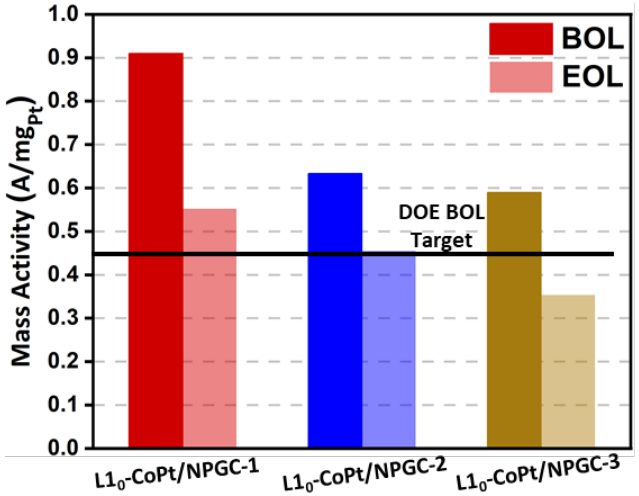


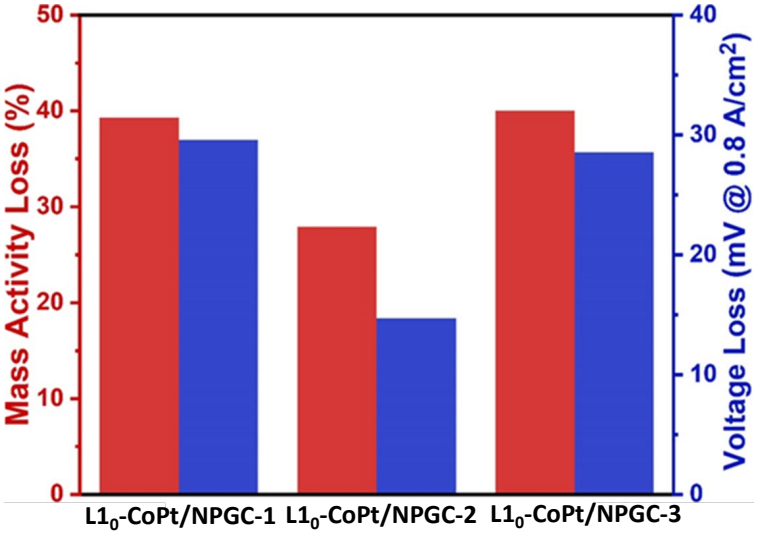
$L1_0$-CoPt/NPGC-3











- Altering the graphitization of supports leads to the change of carbon particle size and thus the electrode structure
- NPGC of balanced porosity and graphitization afforded the catalyst optimum stability

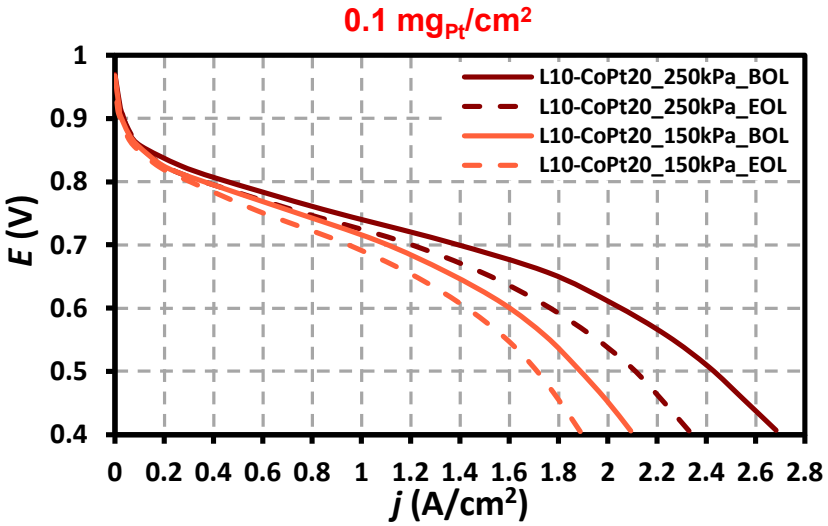
Advancing from Low-Loading to High-Loading Testing

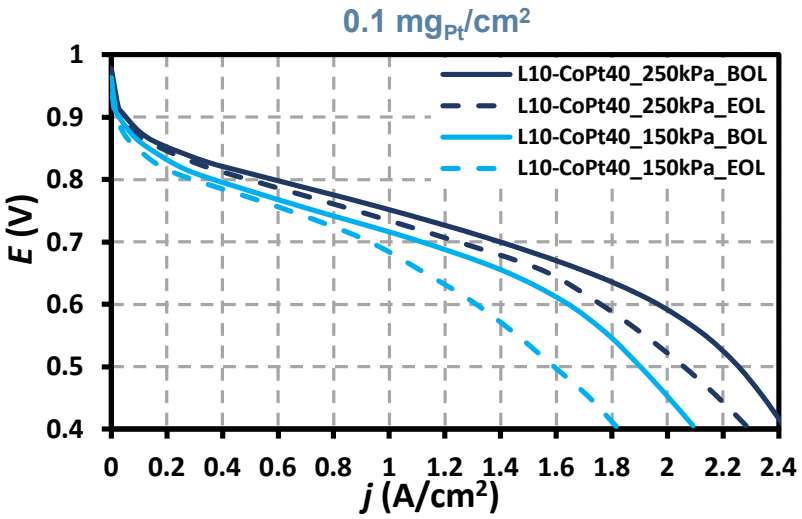
Goals

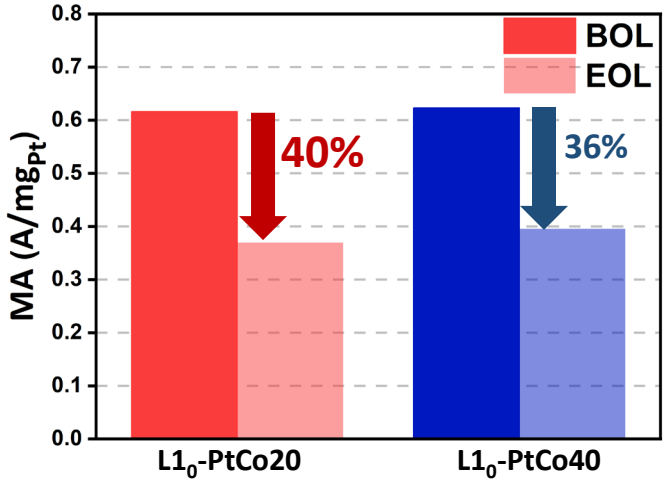
- Catalysts with large particle sizes and more stable structures are promising candidates for the HDV application
- Investigating the fuel-cell behaviors of large-sized $L1_0$-CoPt catalysts with high loading is beneficial to adapting our MEA preparation/assembly method to the requirements of high-loading testing

Results

$L1_0$-CoPt20 (Pt 20wt%) and $L1_0$-CoPt40 (Pt 40wt%) catalysts have shown promising activity and stability in low-loading (0.1 mg_{Pt}/cm^2) testing

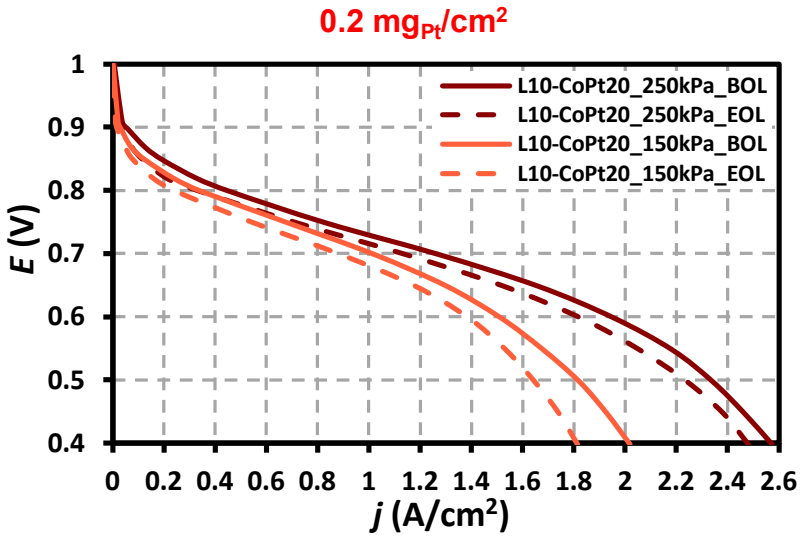


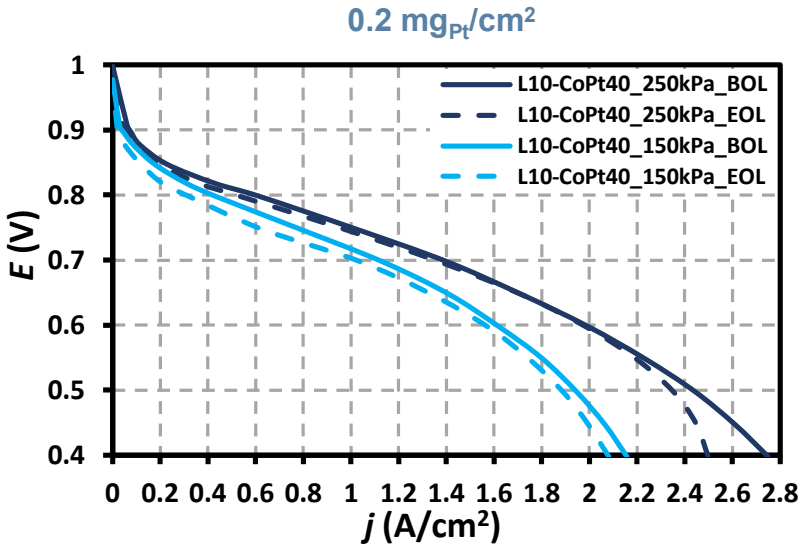


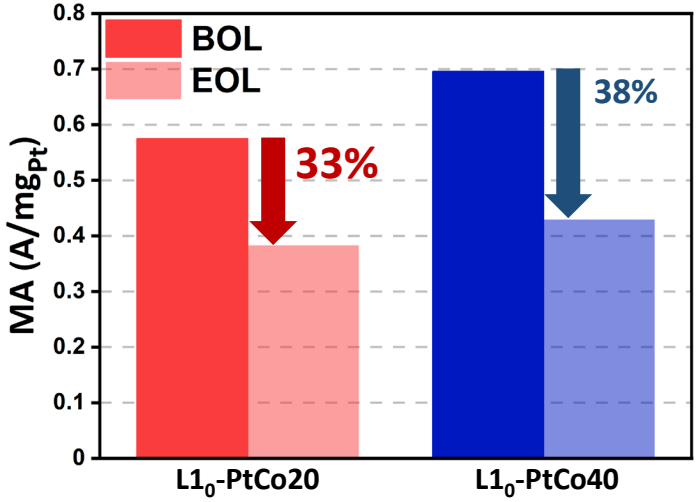


	Rated Power at 0.67V 150 kPa (W/cm^2)	Rated Power at 0.67V 250 kPa (W/cm^2)	Voltage Loss at 0.8 A/cm^2 150 kPa (mV)	Voltage Loss at 0.8 A/cm^2 250 kPa (mV)	ECSA (m^2/g_{Pt})	ECSA Loss (%)
$L1_0$-PtCo20	0.85	1.10	20	14	39.4	36.4
$L1_0$-PtCo40	0.87	1.07	18	15	41.7	40.6

Advancing from Low-Loading to High-Loading Testing







	Rated Power at 0.67V 150 kPa (W/cm^2)	Rated Power at 0.67V 250 kPa (W/cm^2)	Voltage Loss at 0.8 A/cm^2 150 kPa (mV)	Voltage Loss at 0.8 A/cm^2 250 kPa (mV)	ECSA (m^2/g$_{Pt}$)	ECSA Loss (%)
L1$_0$-PtCo20	0.79	1.00	20	14	43.1	25.6
L1$_0$-PtCo40	0.86	1.06	8	8	42.6	24.4

- MEAs with a high loading exhibited slightly improved stability, possibly due to the presence of more deposition sites for dissolved Pt and the better preservation of the ECSA
- The differences for the mass activity and ECSA between high-loading and low-loading MEAs are minimal, indicative of no loss of Pt utilization due to increased electrode thickness
- No improvement in rated power is observed, suggesting diagnostics for the transport losses should be carried out and the electrode structure needs to be further optimized

Take-Aways

1. Pt-based catalysts need systematic modifications to be adapted to different applications (LDV or HDV)

2. $L1_0$-CoPt particles have been demonstrated as highly active and durable cathode materials for fuel cells

3. Colloidal synthesis can generate catalysts with highly uniform particles size but the removal of surfactants is challenging

4. Acid leaching warrants a Pt shell with certain thickness, which mitigates the Co leaching

5. Controlling the size of $L1_0$-CoPt particles is a robust method to alter their catalytic behaviours and tailor the function of catalysts

6. Modifying the carbon features (*e.g.* porosity and graphitization) is an effective method to regulate the performance and stability of catalysts to adapt the catalysts to different applications.

Future Work

1. Extend gram-scale synthesis to multi-gram batches that match performance of small batches using the "fluidized-bed reactor"

2. Optimizing the electrode structure to allow catalysts maximally exhibit their intrinsic catalytic properties

3. Further narrowing the particle size distribution and improve the batch-to-batch consistency through adopting the strong electrostatic adsorption (SEA) method

4. Scale up MEA testing from 5 cm^2 to 50 cm^2

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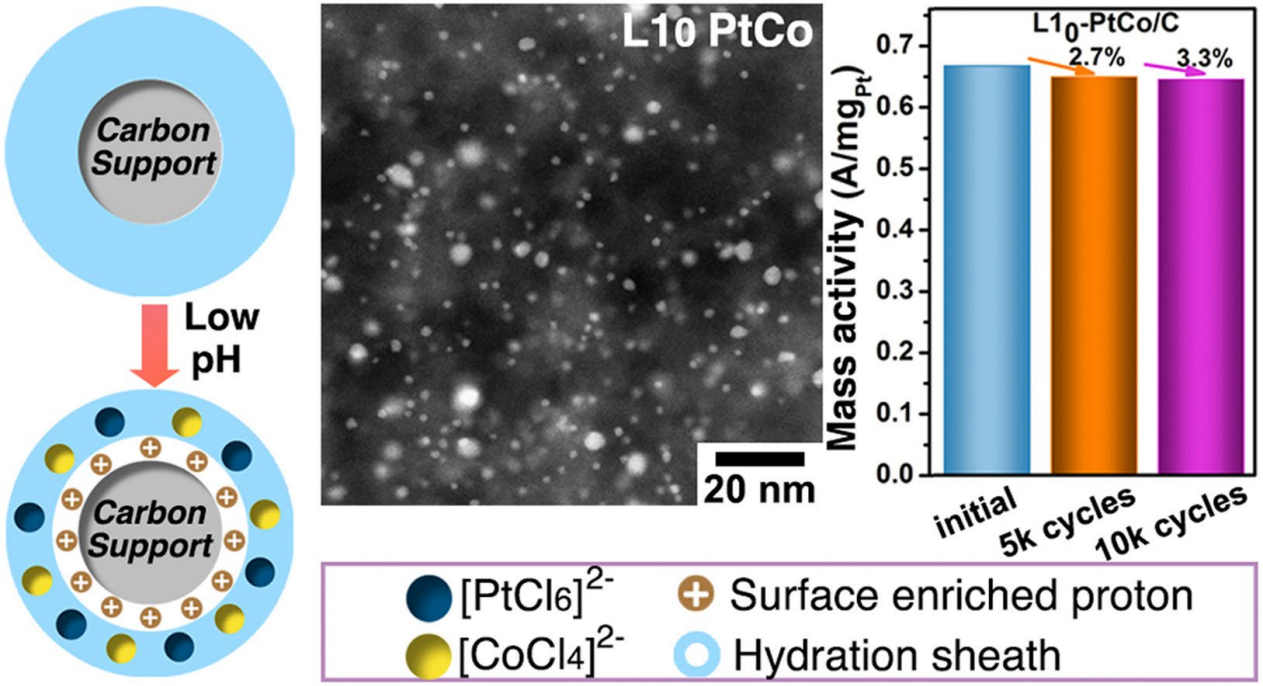
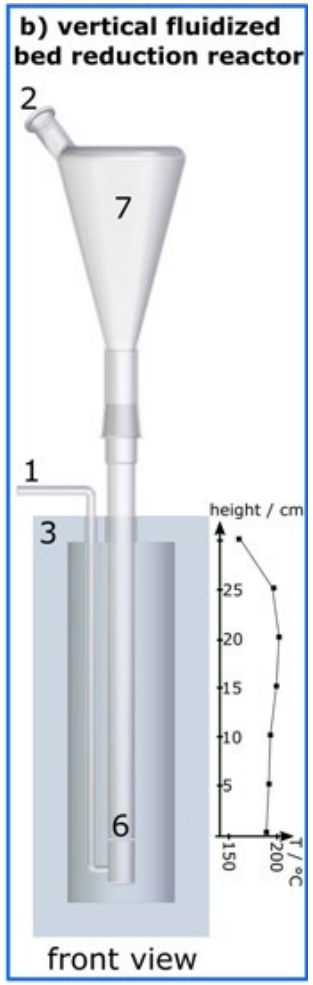
M^2FCT seeks to advance efficiency, performance, and durability of fuel cells and is lead by 5 national laboratories with significant outreach and support to industry and academia. For more information, visit https://millionmilefuelcelltruck.org/

Strong Electrostatic Adsorption



Ma, Y., *et al.*, *Nano Energy*, 2021, *79*, 105465.

Fluidized Bed Reactor



Hornberger, E., *et al.*, *Journal of The Electrochemical Society*, 2020, *167*(11), 114509.