

Electrochemical Engineering with Thin Film Polymer Electrolytes

Christopher G. Arges, PhD
April 29th, 2021

500 nm



LOUISIANA STATE UNIVERSITY

Presentation overview

High-temperature polymer electrolyte membranes (HT-PEMs) and binders for fuel cells

Studying the electrochemical properties of electrode ionomer binders as thin films

~~**Activity coefficients of ions in thin film polymer electrolytes**~~

M. Ramos-Garcés, R. Kumar, [C.G. Arges](#), *RSC Adv.* **2021**

Q. Lei, R. Kumar, [C.G. Arges.](#), *J. Mater. Chem. A.* **2020**

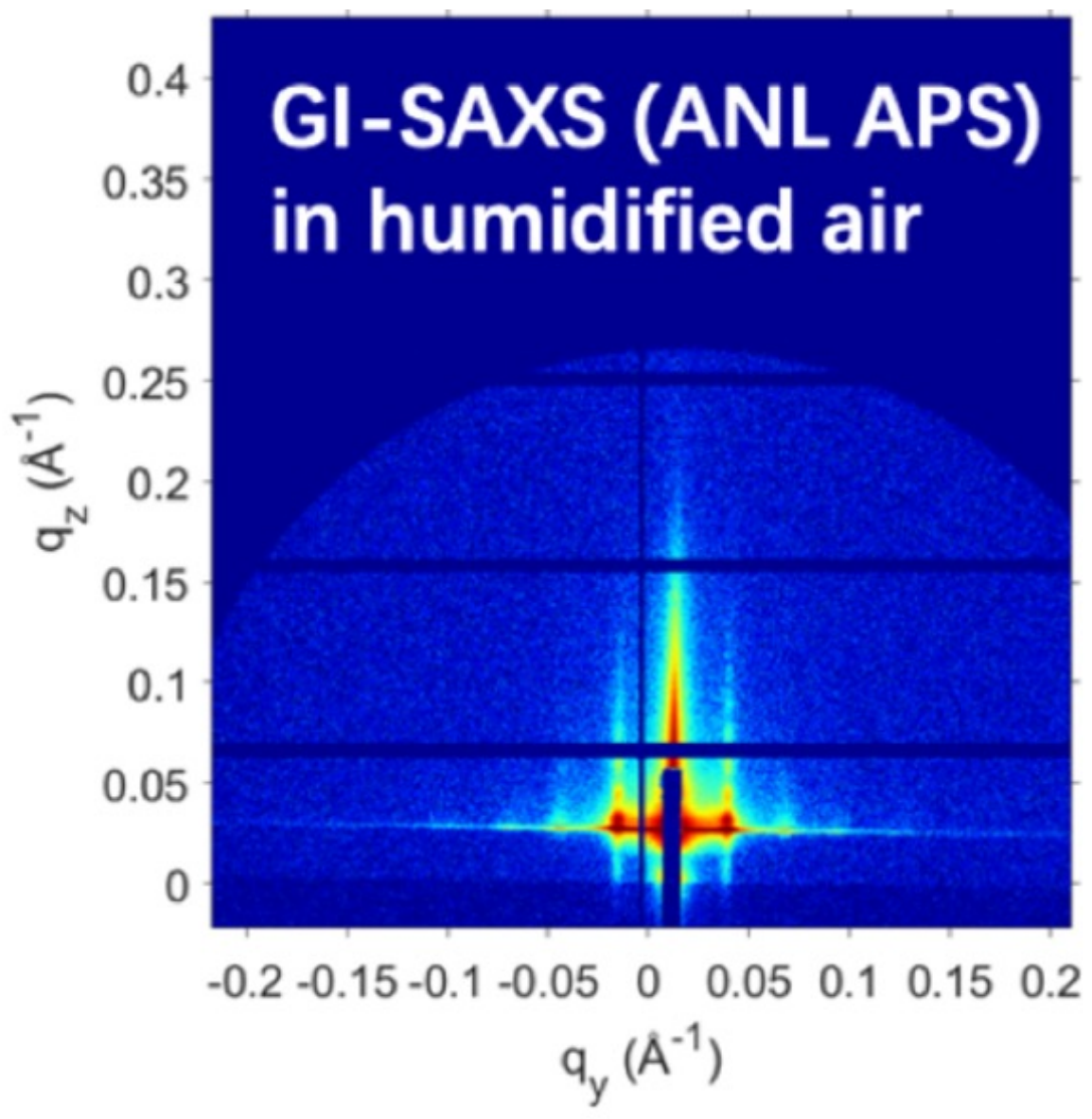
Louisiana State University in Baton Rouge



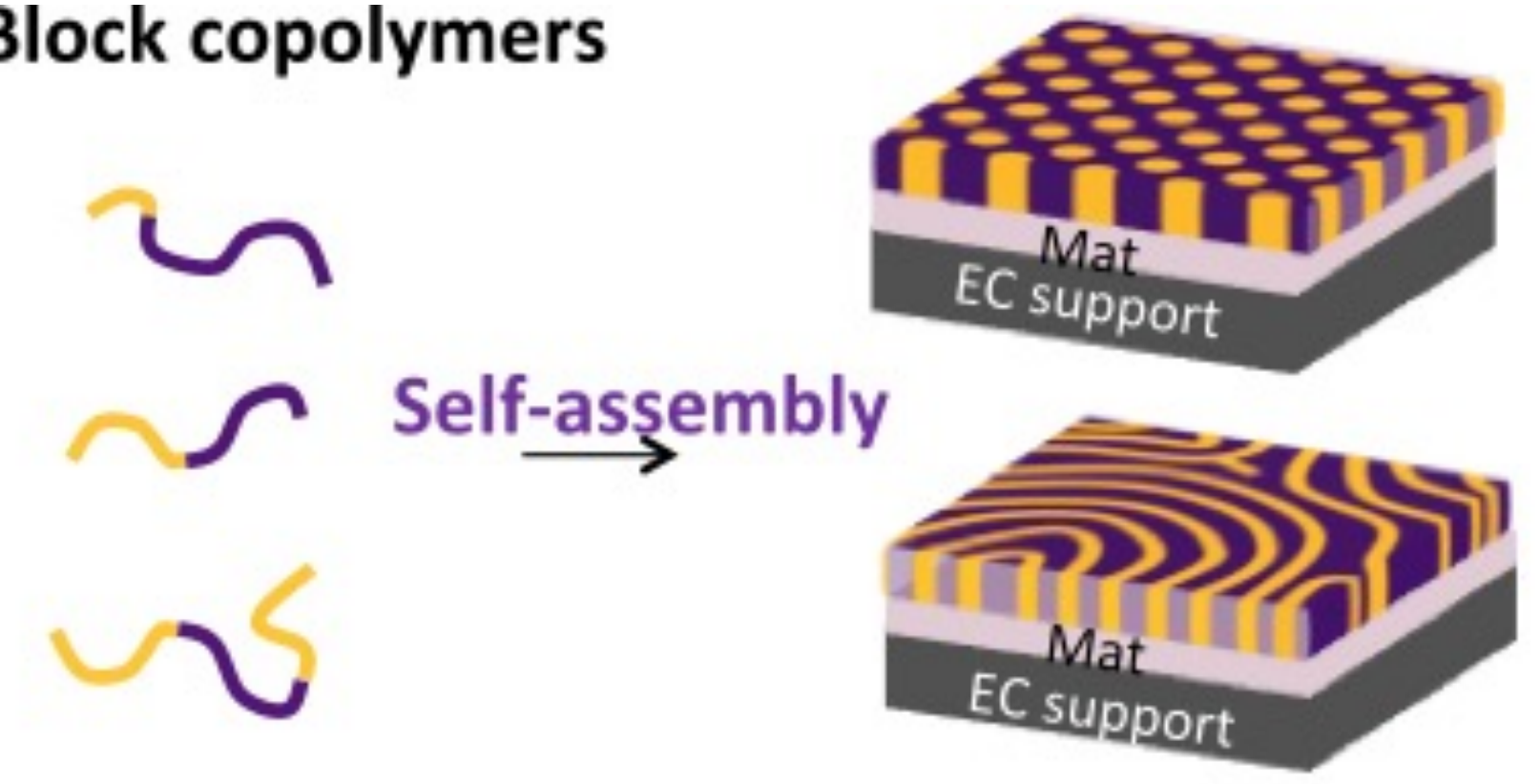
LSU has 34,000 students and 1200 endowed oak trees

Louisiana ranks 2nd in the US for chemical manufacturing

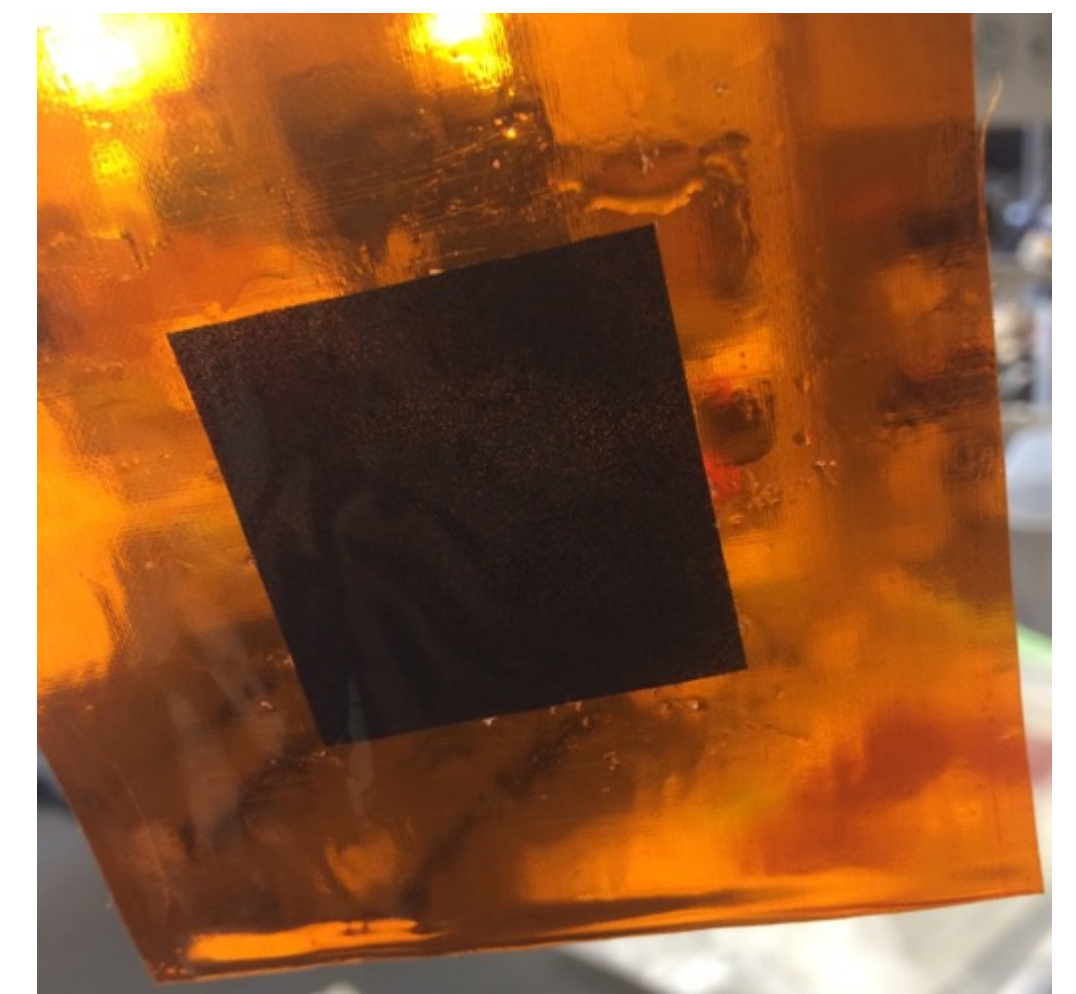
About my lab: polymeric materials engineered with precision over 6 orders of magnitude in length scale



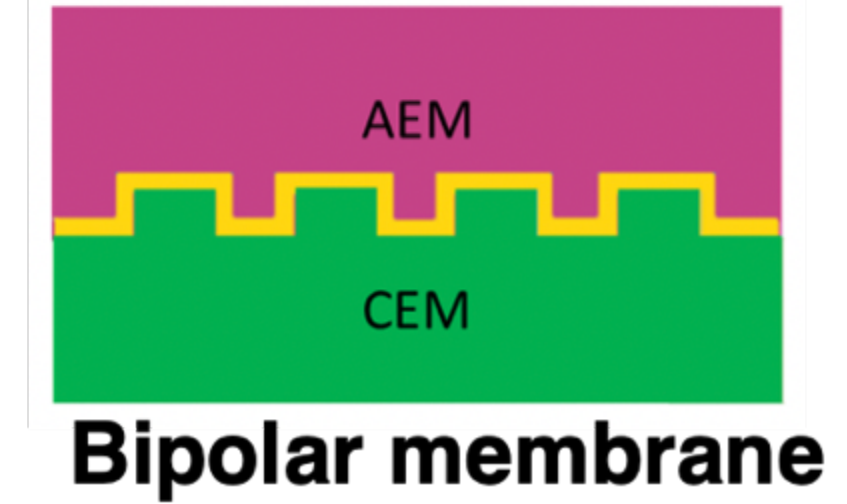
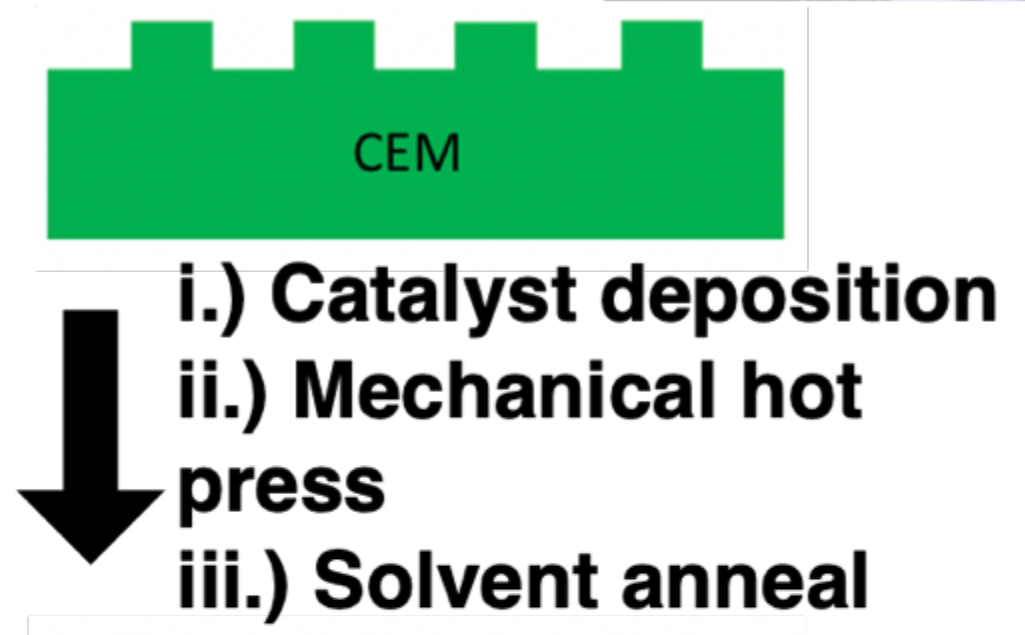
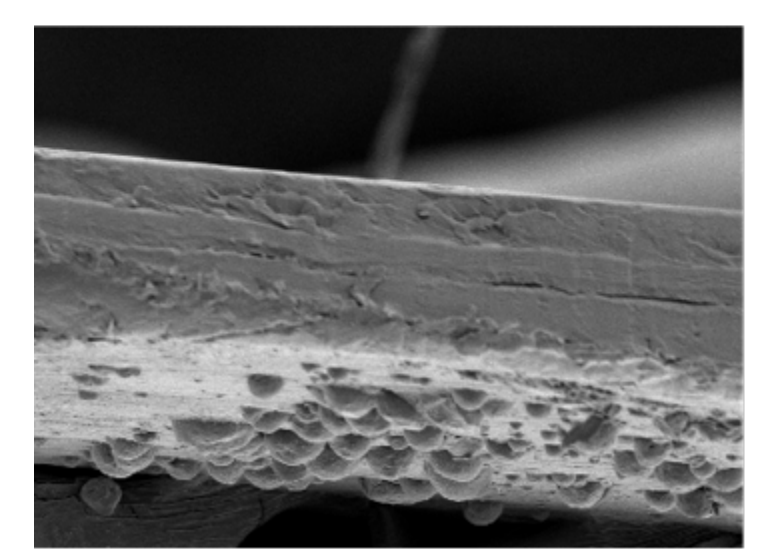
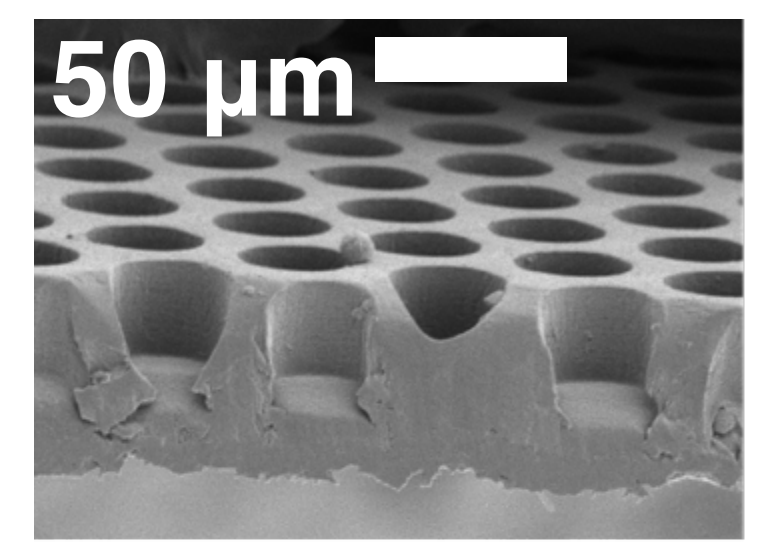
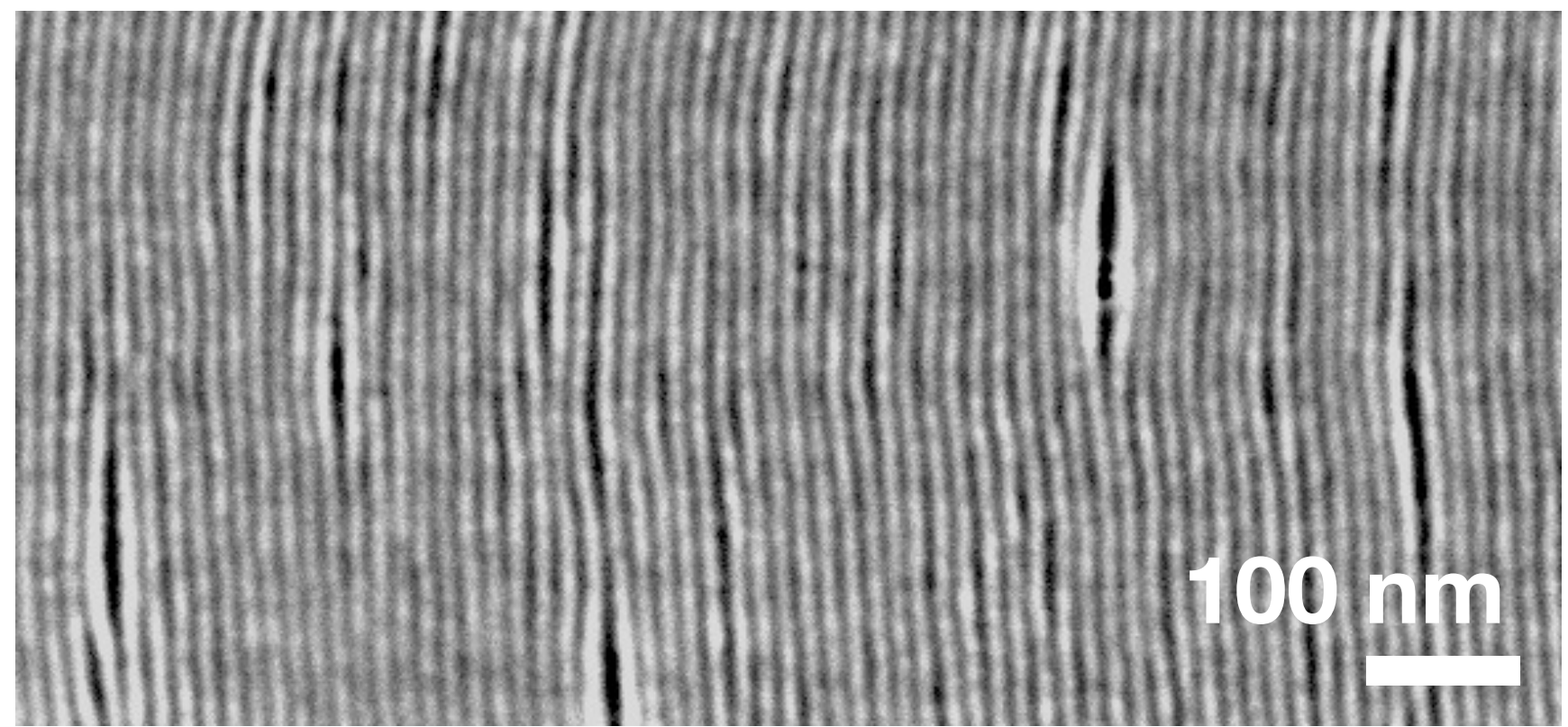
Block copolymers



V.M. Palakkal, C.G. Arges
et al. npj Clean Water 2020



S.Kole, C.G. Arges *et al.*
J. Mater. Chem. A. 2021

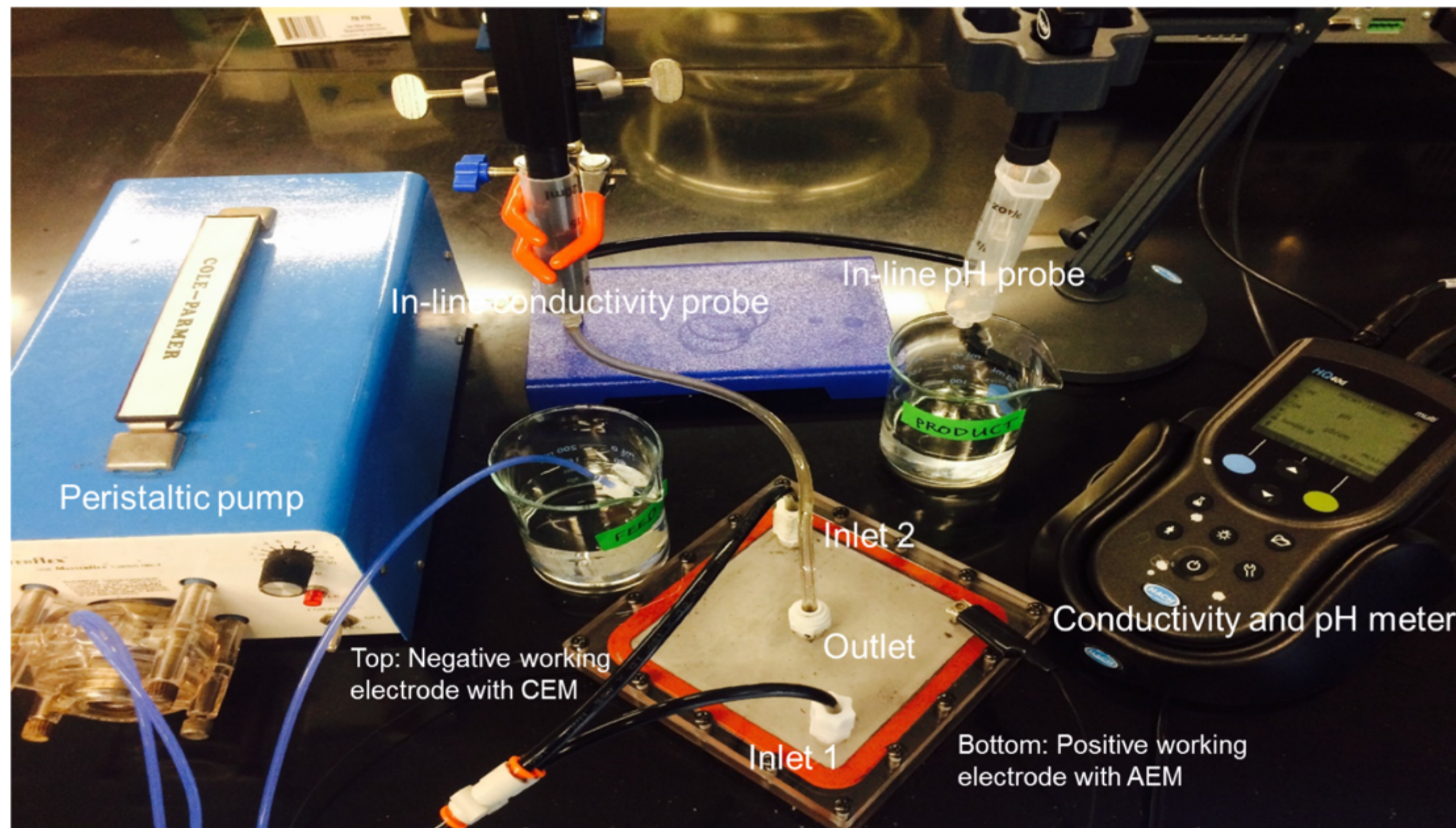


Model systems with long-range order and high fidelity nanostructures

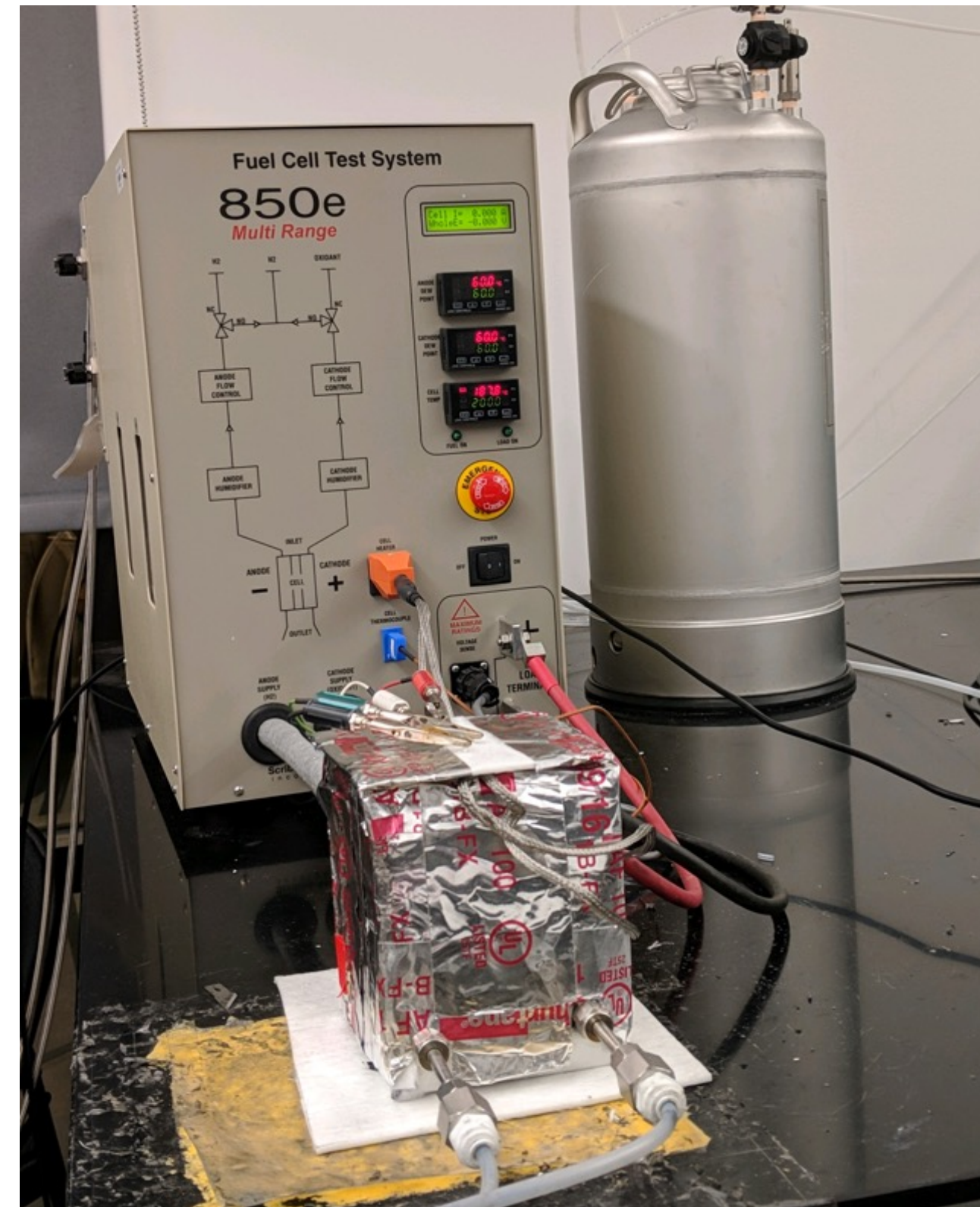
Inform fundamental transport, kinetic, and thermodynamic properties at the molecular level



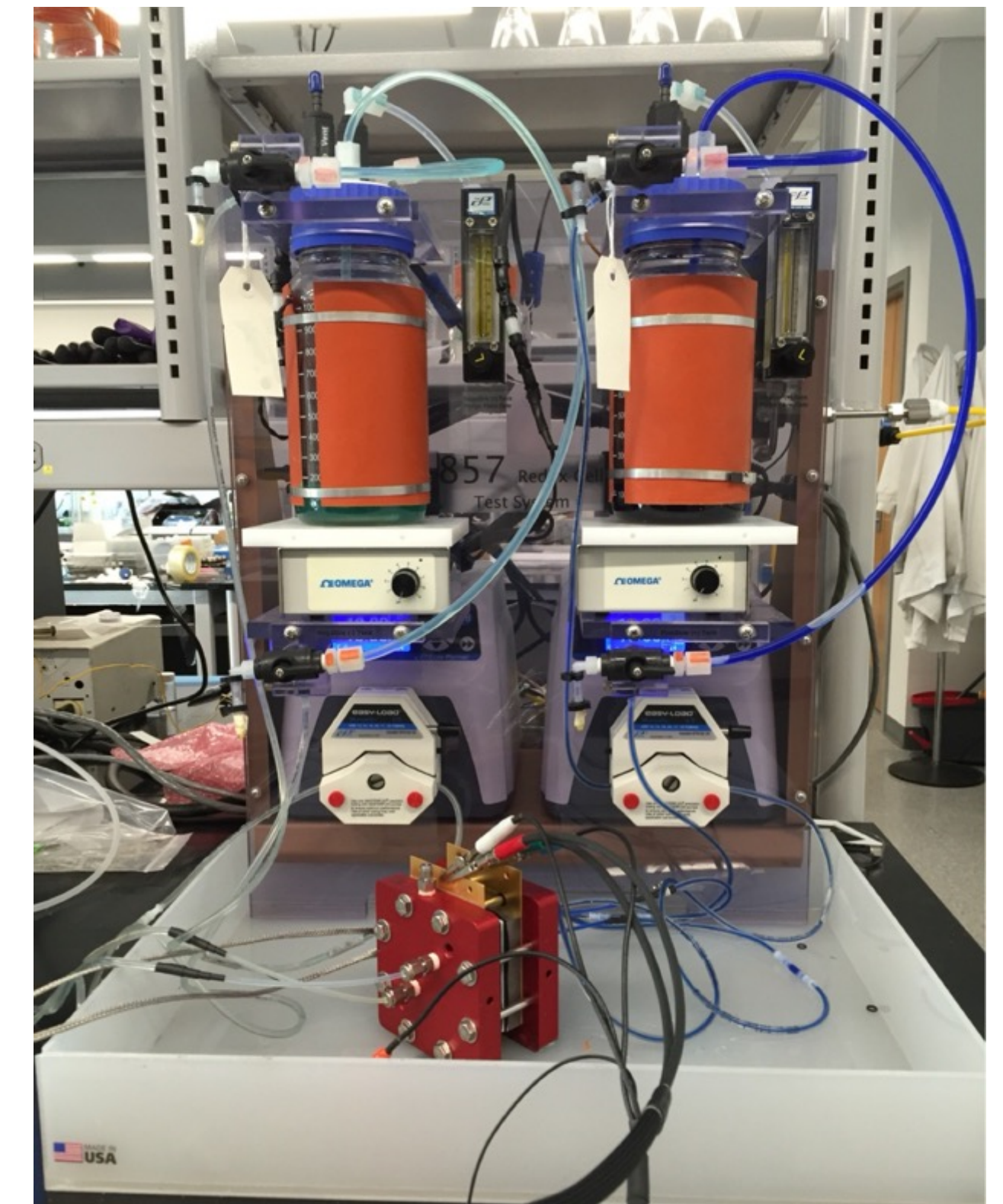
Cell level studies in Arges Lab



Membrane capacitive deionization unit for electrochemical separations



Gas handling test station - fuel cell and electrolysis



Liquid handling test station - flow battery and electrolysis

Presentation overview

High-temperature polymer electrolyte membranes (HT-PEMs) and binders for fuel cells

Studying the electrochemical properties of electrode ionomer binders as thin films

Future directions and concluding remarks

I see an electric vehicle in your future



All of GM's vehicles will be electric by 2035



Tesla - the most valuable car company

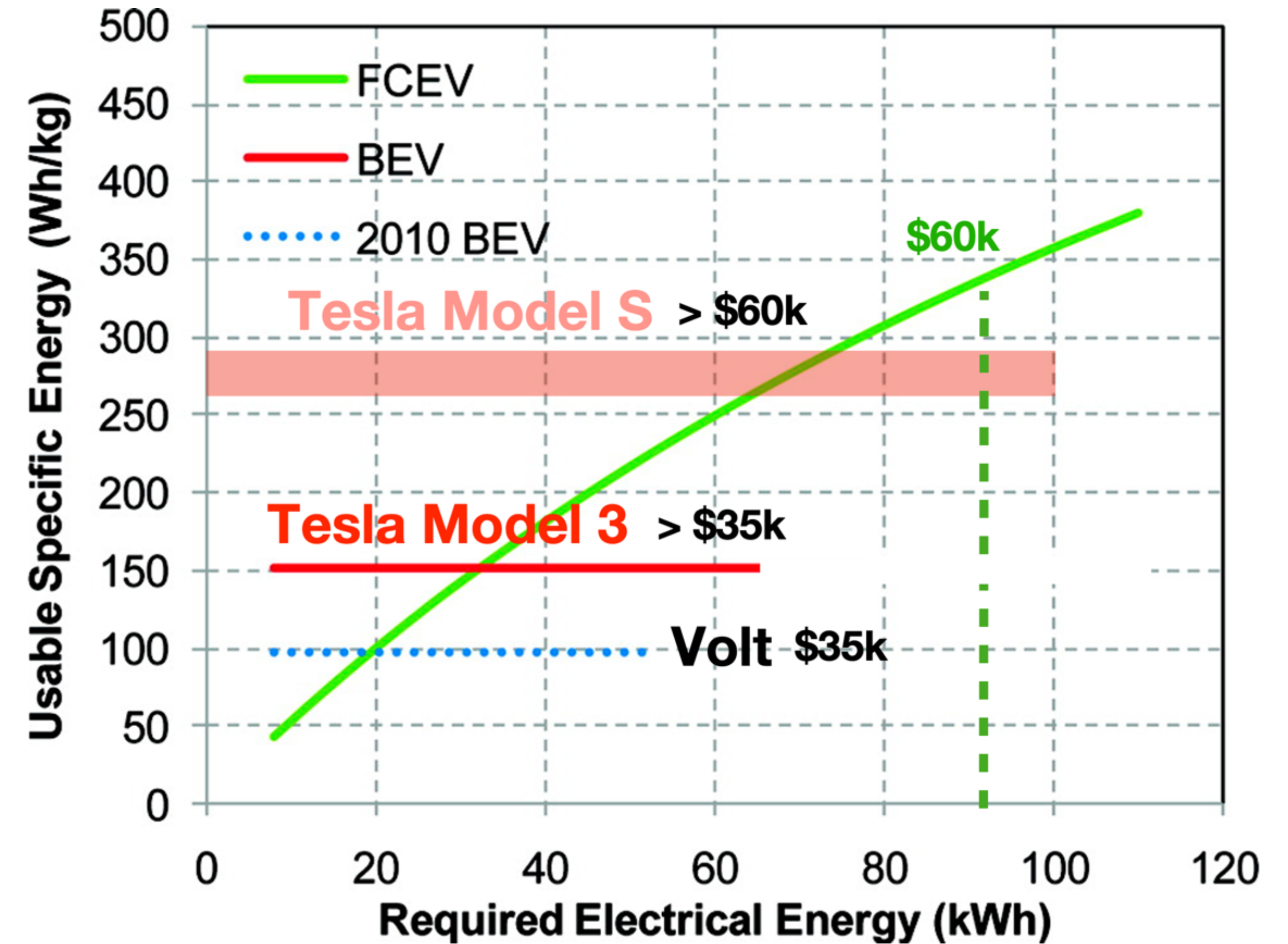
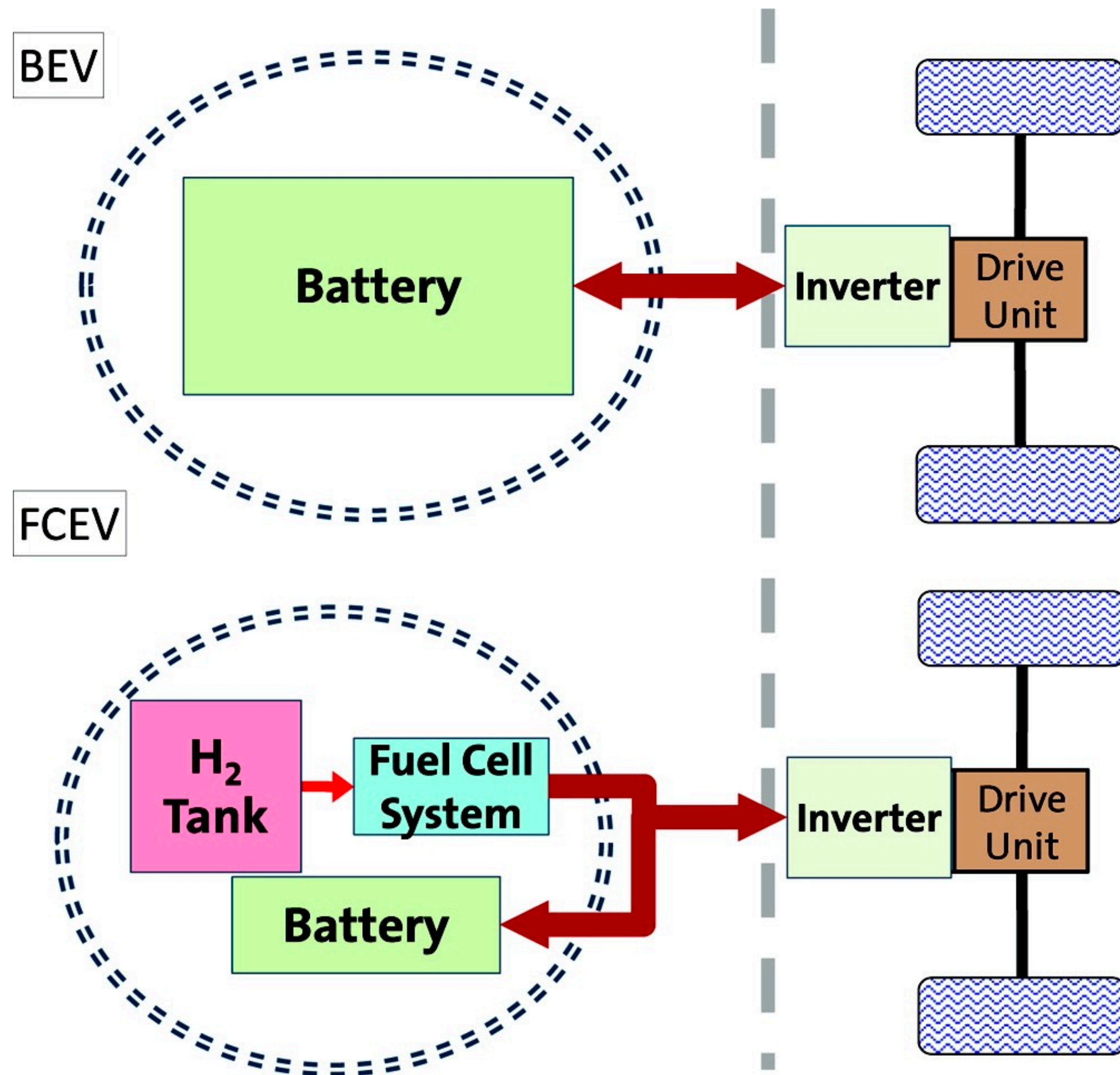


**2021 Toyota Mirai Fuel Cell Electric Vehicle
(~ 400 mile range)**

**Vehicle electrification is critical
to the 50% GHG reduction goal
by 2030**



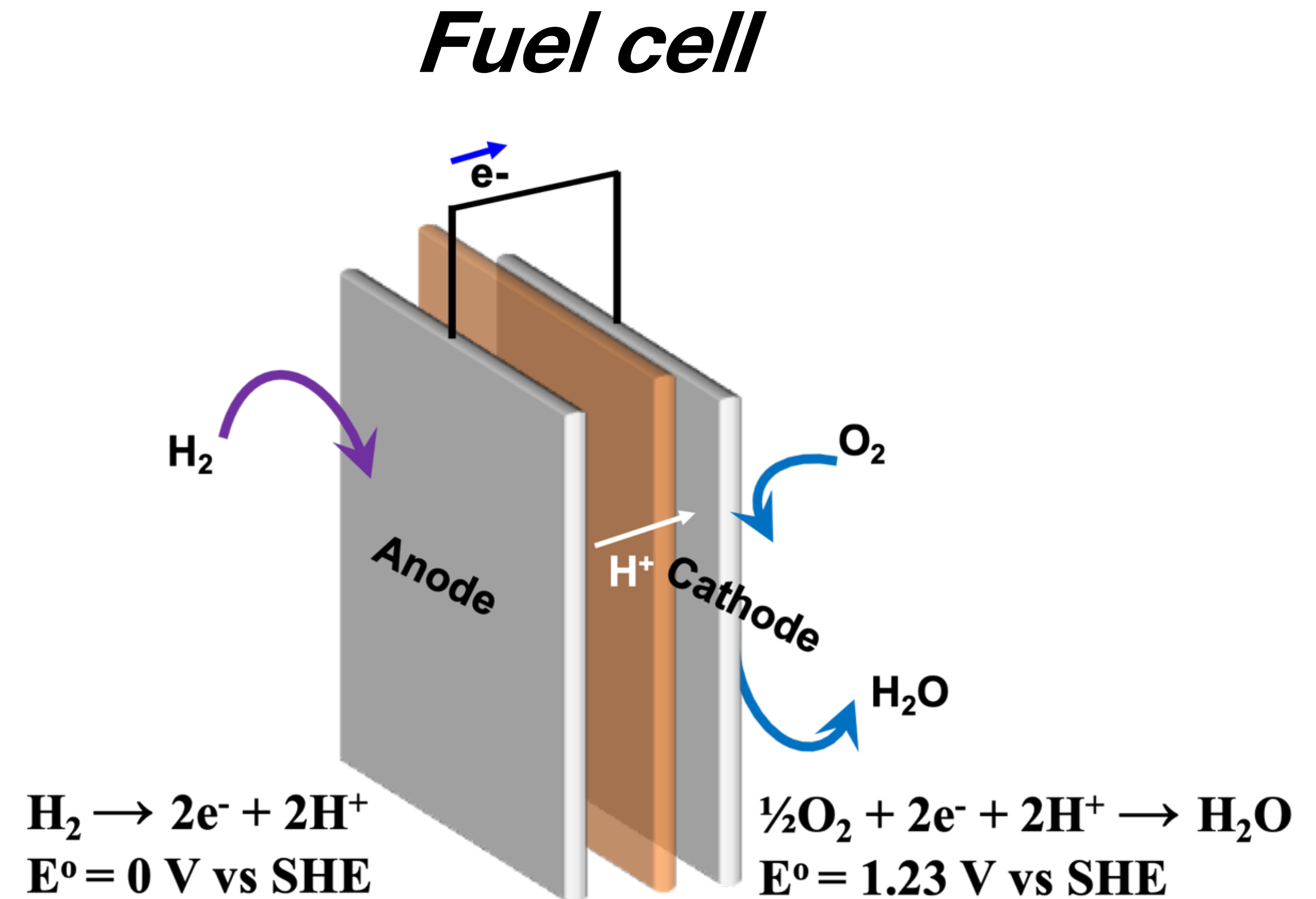
Fuel cell electric vehicles (FCEVs) v. battery electric vehicles (BEVs)



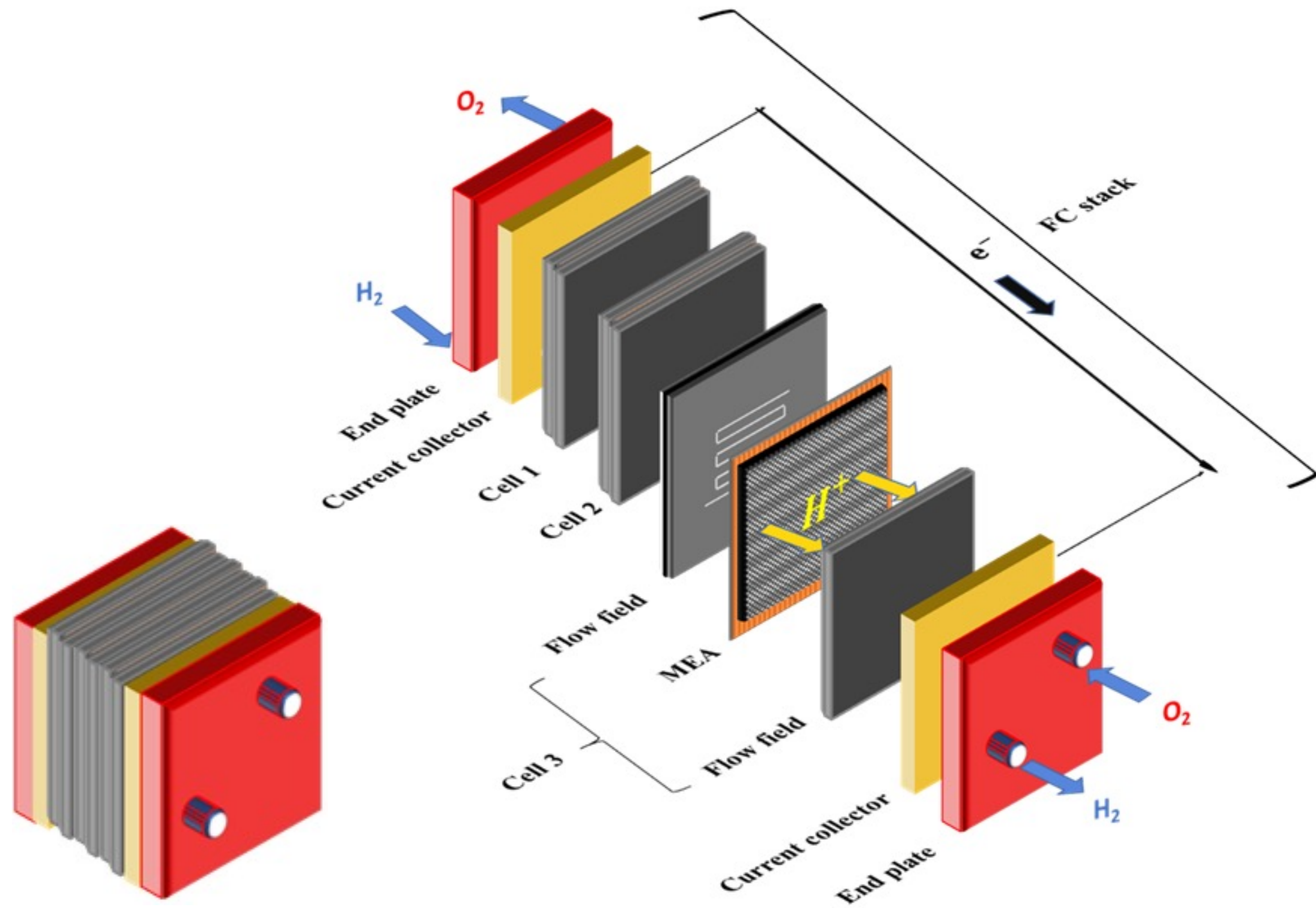
Vehicle Range and Weight

Both battery electric vehicles (BEVs) and fuel cell electric vehicles (FCEVs) warrant continued strong development investment, given the strong societal need for full vehicle electrification

One plausible scenario is that both technologies will have a place in the automotive future, with batteries finding theirs in smaller cars for short trips, while *fuel cells find application in larger vehicles used regularly for longer trips.* ~ *General Motors (2010)*



Fuel cell stacks - modular systems



$$Power = I \times V$$

The stack requires coolant delivered by a radiator because the redox reactions in each cell generates heat

New roads and challenges for fuel cells in heavy-duty transportation

1 horsepower = 0.75 kW

Size (weight in tons)

100

10

1

Average mileage (miles per day)

10

50

100

200

500

1,000

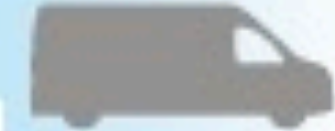
Material handling
Forklifts



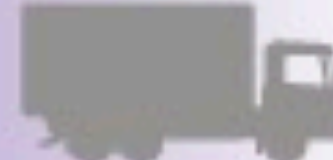
Passenger cars
80–200 kW



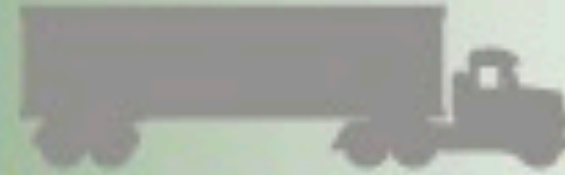
LDVs
100–200 kW




MDVs
Delivery trucks, city buses
100–200 kW




HDVs
Long-haul trucks, coaches
150–400 kW



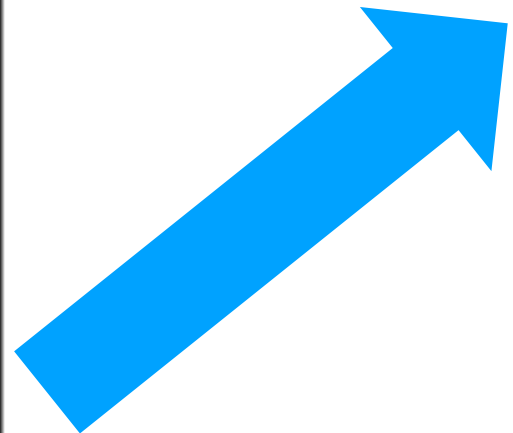
Trains
1.5–3 MW



Aircraft
0.1–8 MW



Ships
4–60 MW



Vehicle Range and Weight

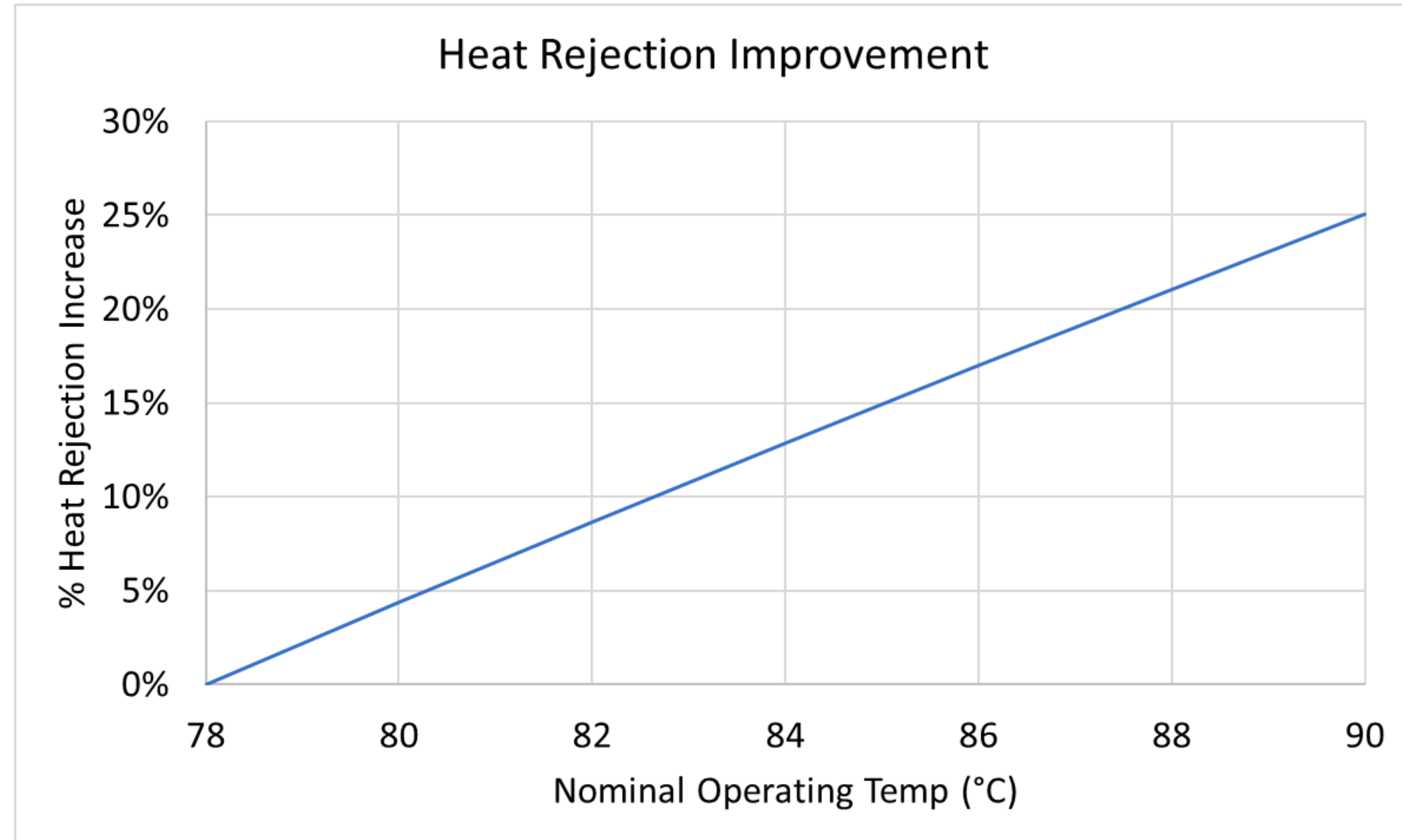
HDVs and fuel cell stack heat management

Heavy duty vehicles (HDVs)



HDV (class 8 tractor trailers) - US DOE

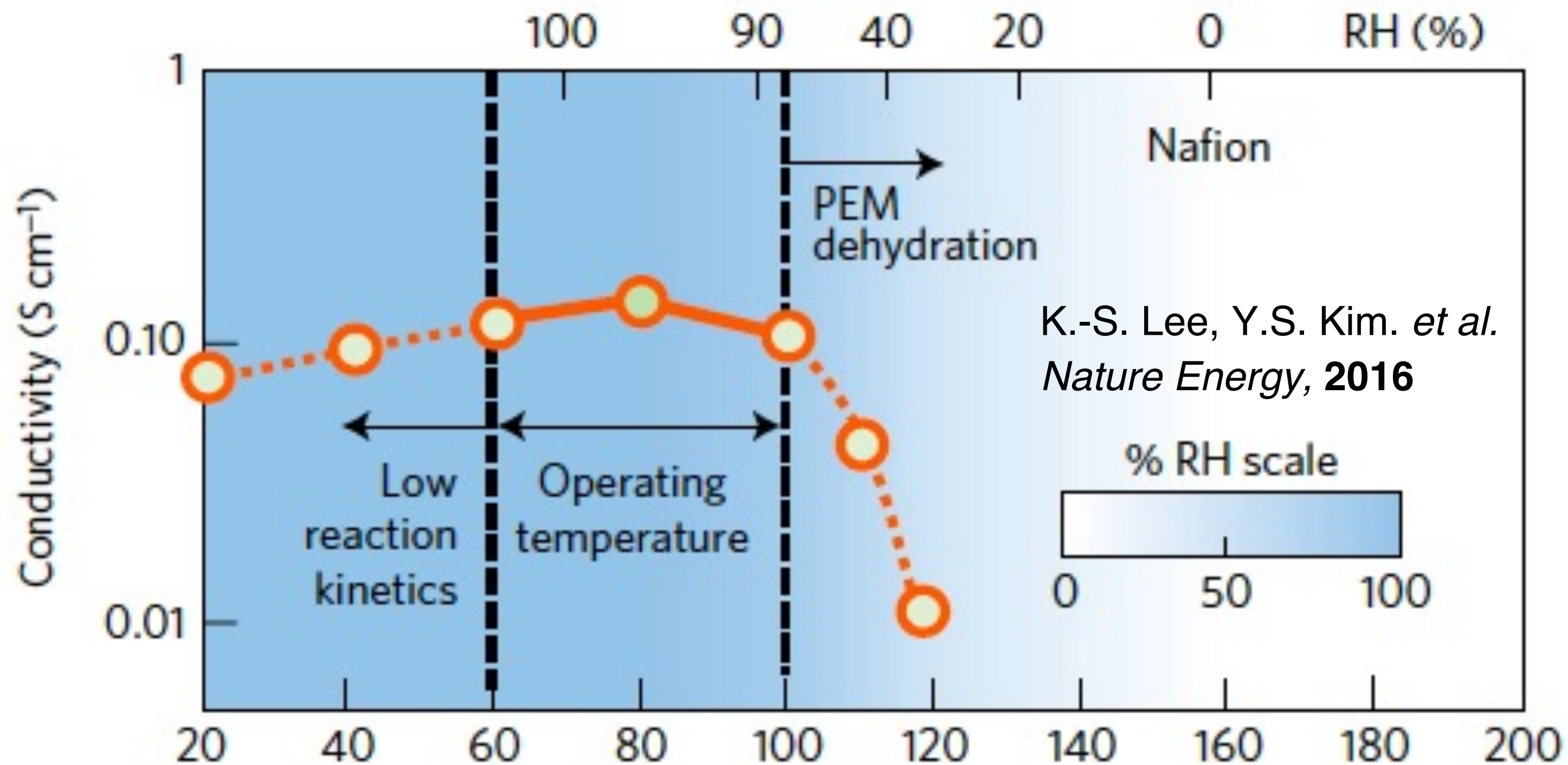
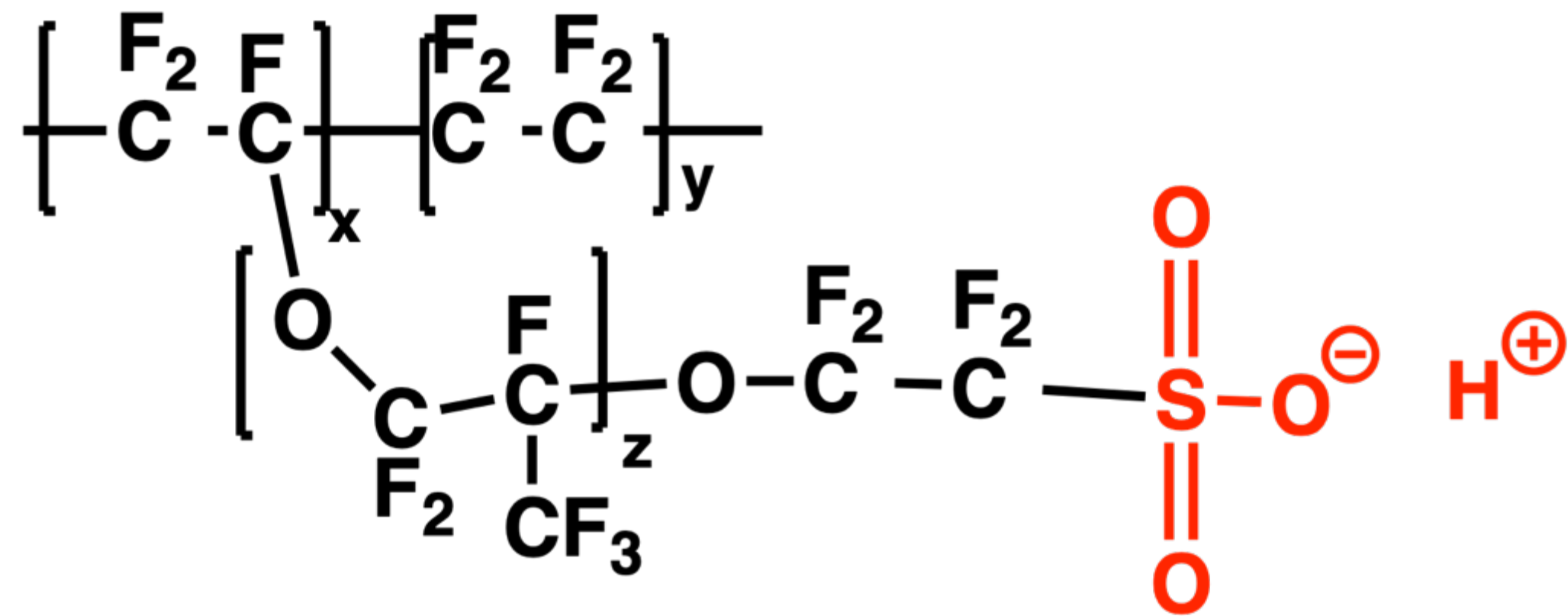
- up to 400 kW stacks
- 25,000 hours of stability
- \$80 kW⁻¹
- 68% efficiency



$$Q = UA(T_{stack} - T_{environment})$$

Operating the cell at higher temperatures yields better heat rejection

Limitations of Nafion[®] at elevated temperatures



$$\eta_{ohmic} = iR = i \frac{\delta}{\kappa}$$

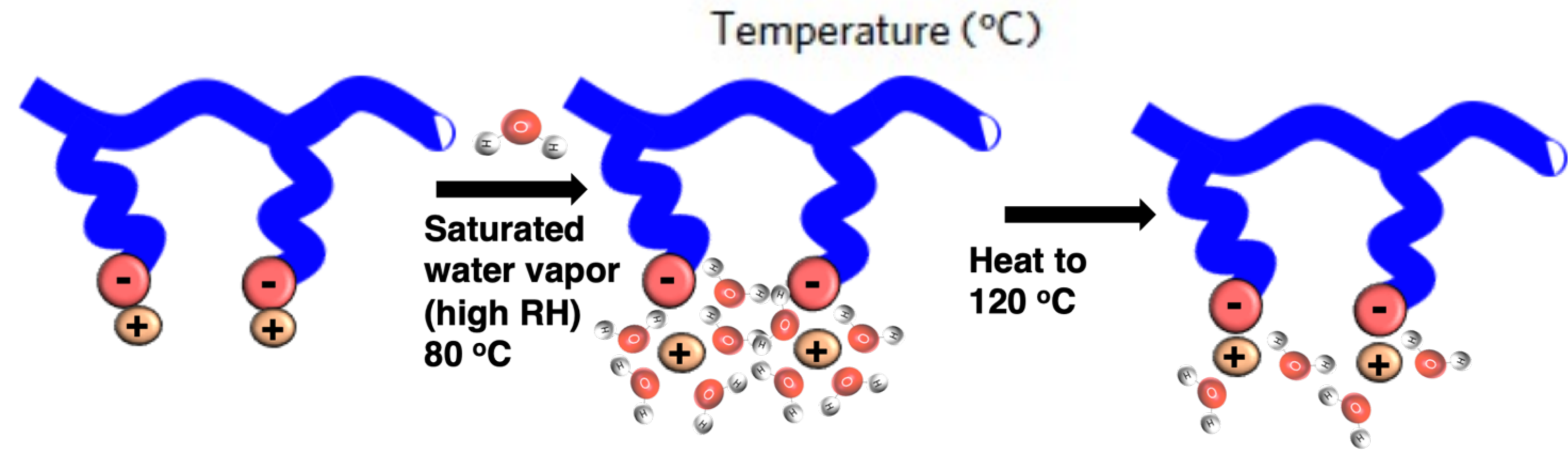
η_{ohmic} = ohmic overpotential (V)

κ = ionic conductivity

R = area specific resistance ($\Omega\text{-cm}^2$)

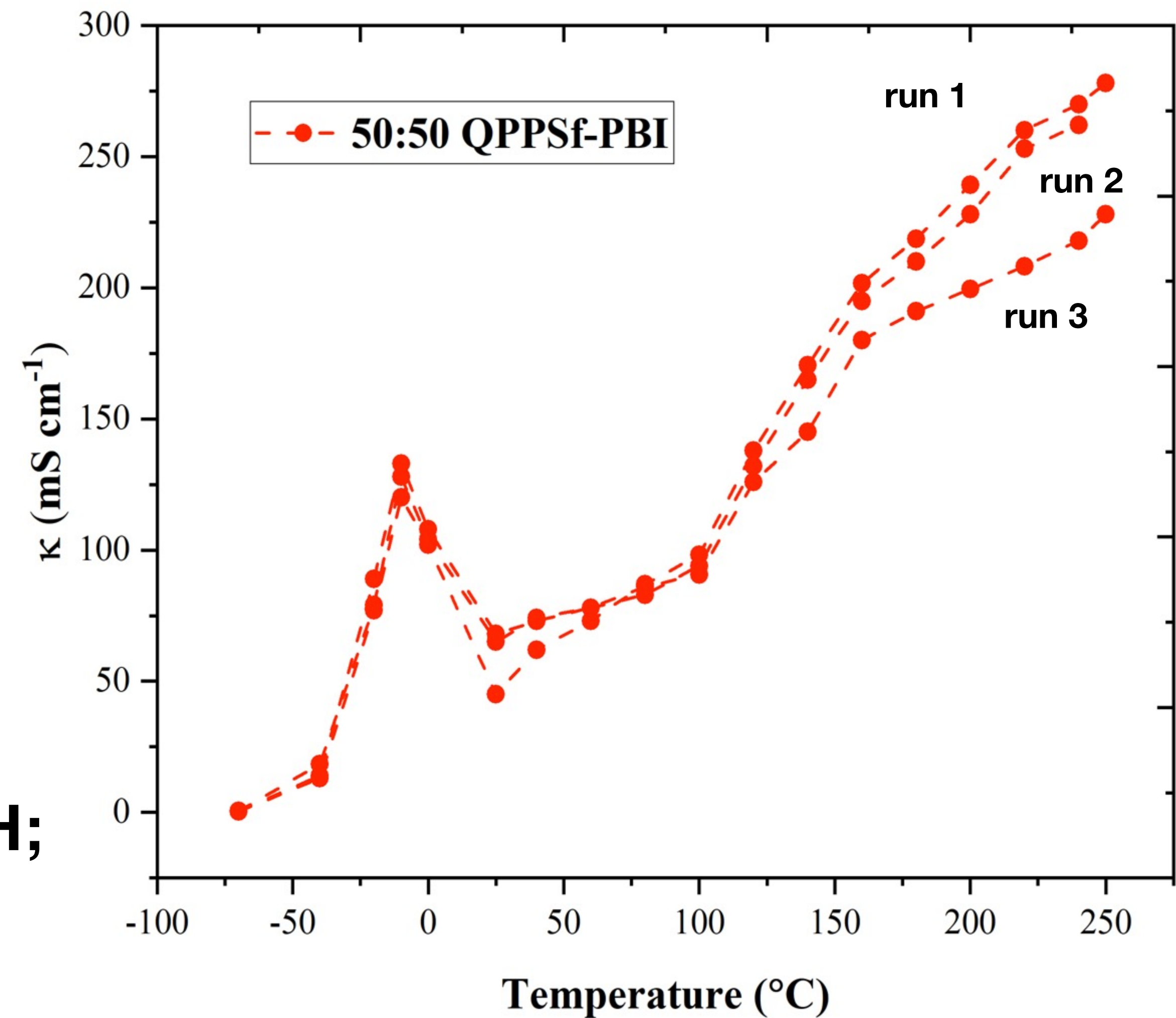
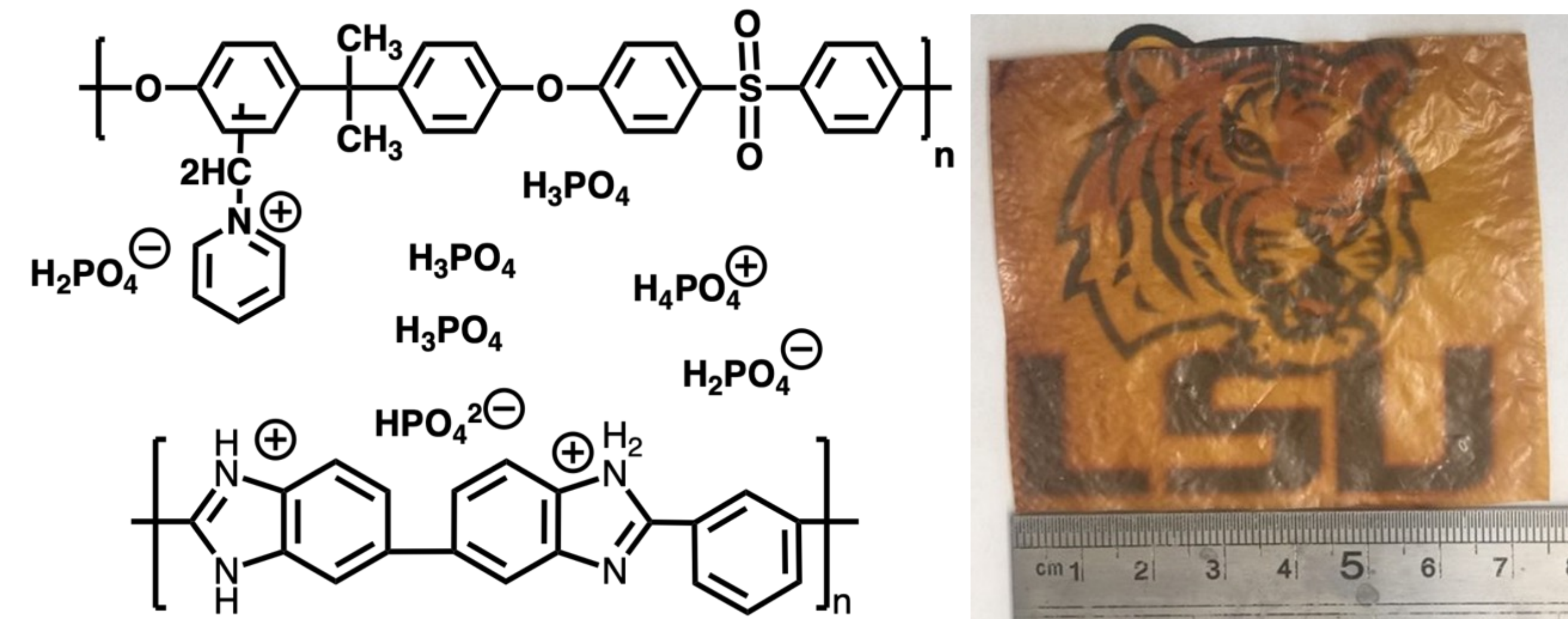
δ = membrane thickness

i = current density (A cm^{-2})



Condensed water within the PFSA dissociates ionic charge pairs & mediates conductivity

New HT-PEM based on phosphate ion-pairs



Stable membrane across a wide range of conditions: 220 $^{\circ}C$ /0% RH and 80 $^{\circ}C$ /40% RH; >100 hours in fuel cell at 200 $^{\circ}C$

A. Chaichi, G. Venugopalan, C.G. Arges, M.R. Gartia, *ACS Applied Energy Materials*, 2020

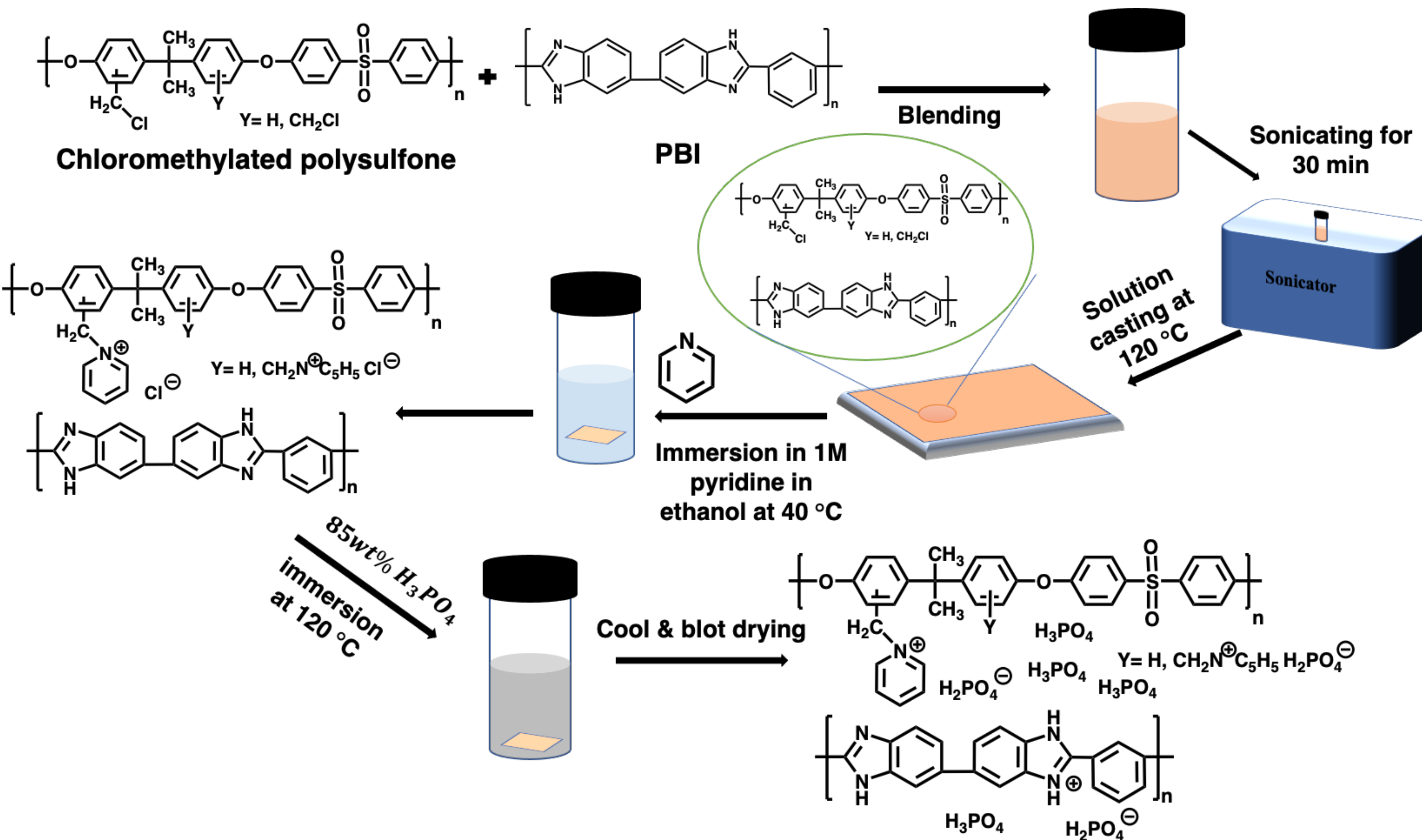
G. Venugopalan, C.G. Arges *et al.*, *ACS Applied Energy Materials*, 2020

C.G. Arges, *U.S. Patent Application #62,656,538* 2018

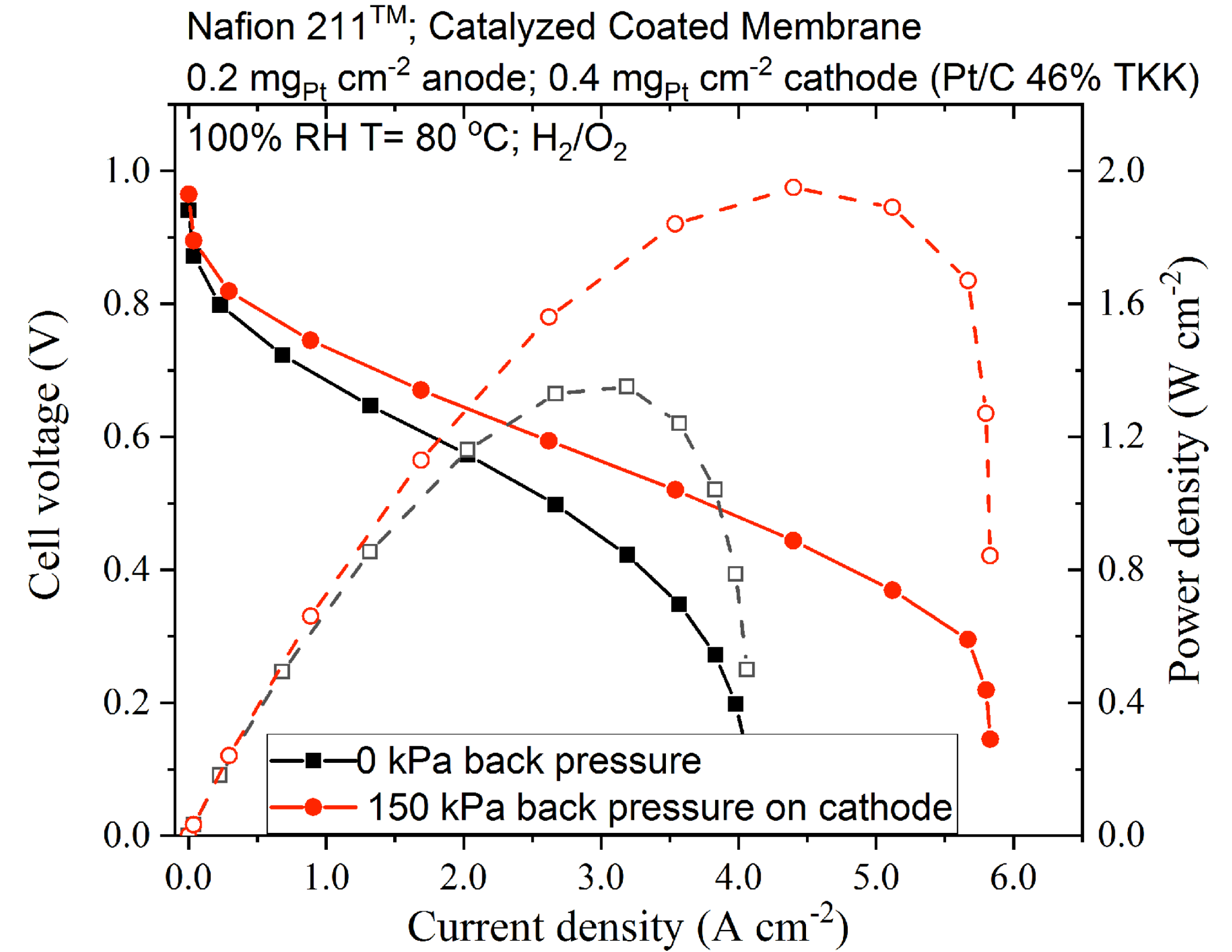
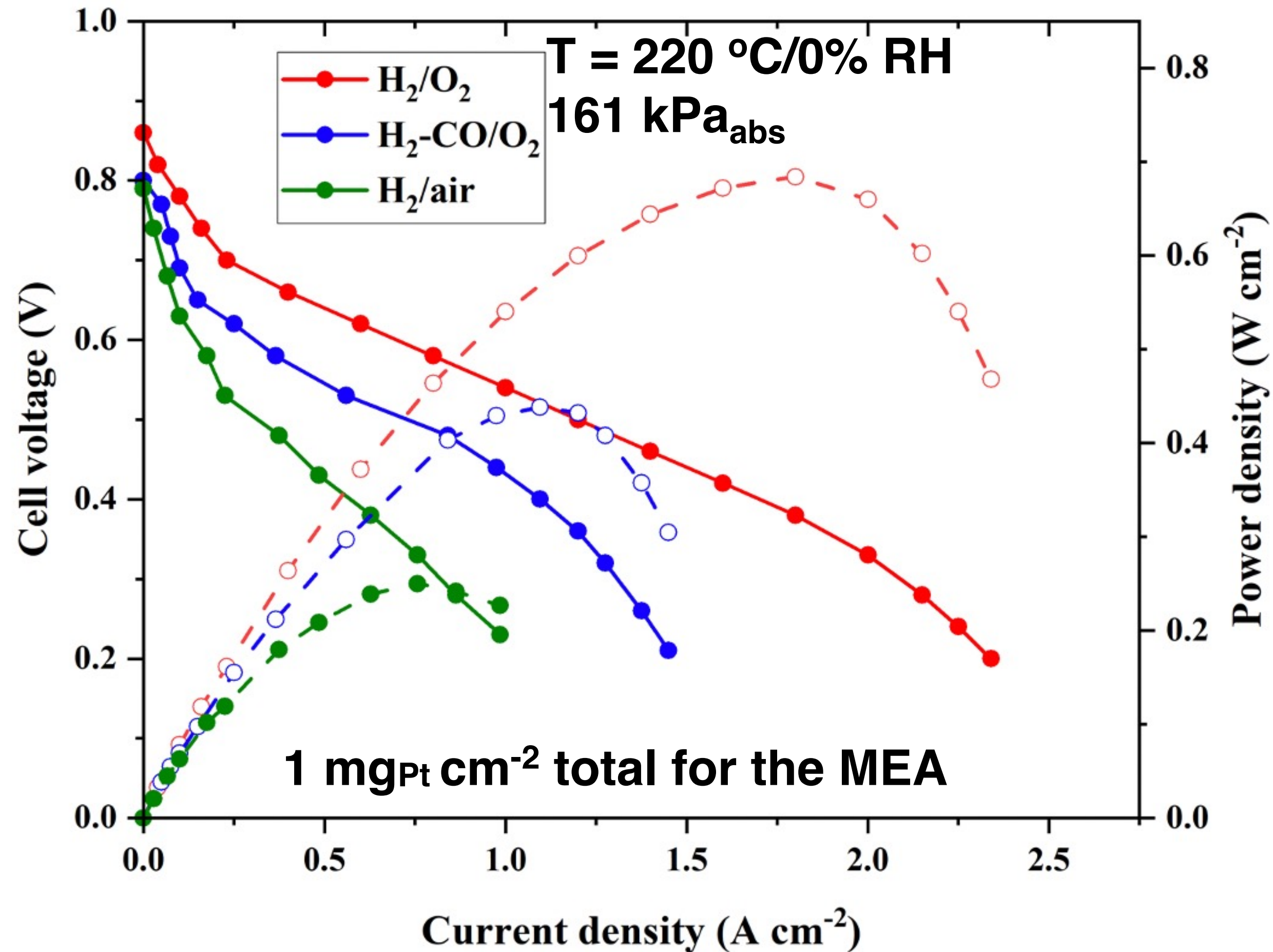
Preparation of polycation-PBI blends for use as HT-PEMs



Dr. Gokul Venugopalan
PhD 2021



Fuel cell performance with new HT-PEMs

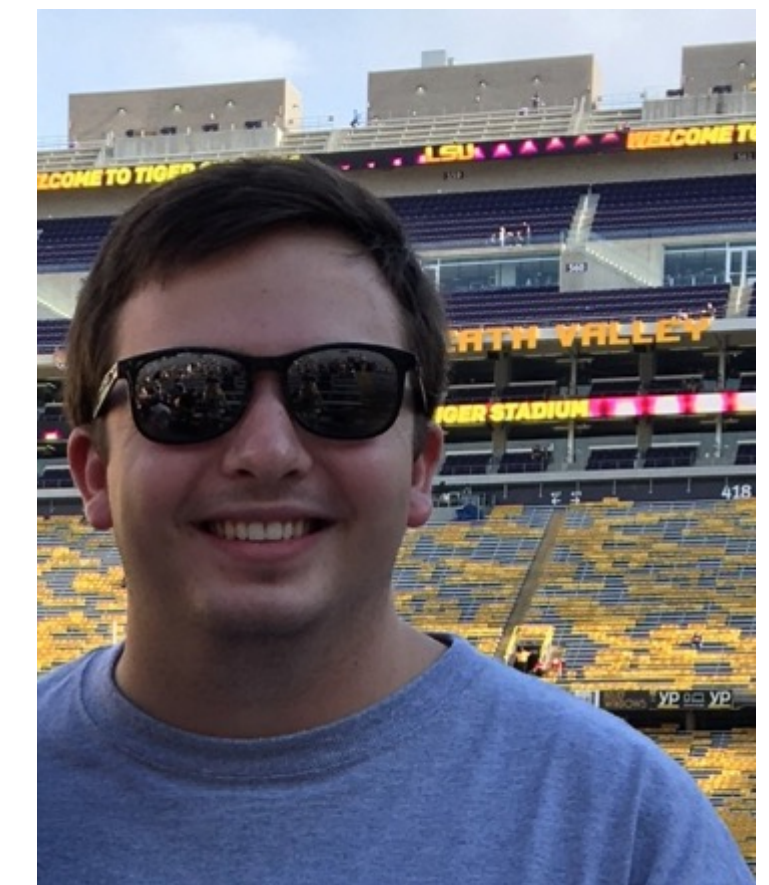


Reasonable power density was attained

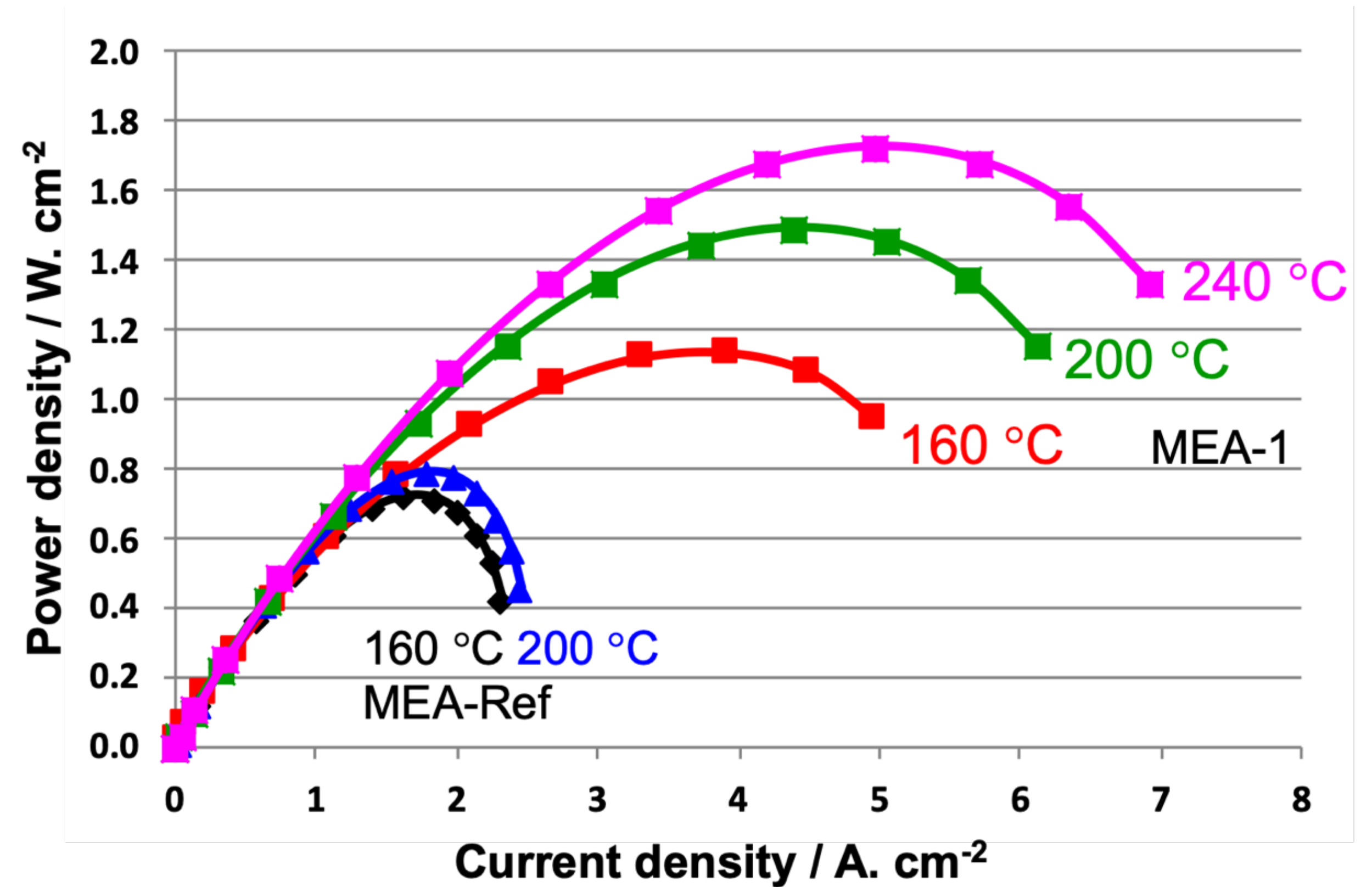
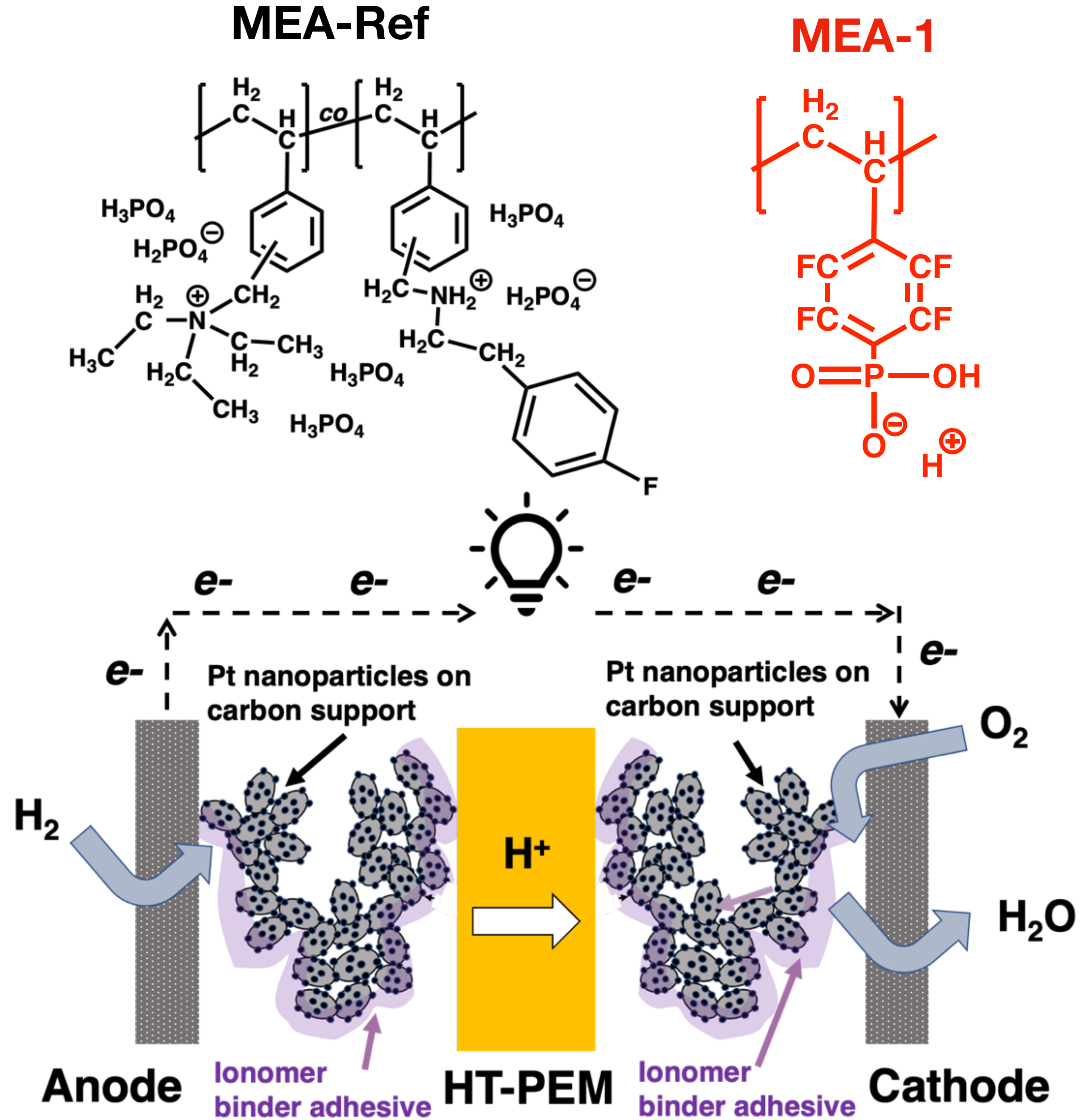
Cell could be operated with 25% CO in the fuel stream

G. Venugopalan, C.G. Arges *et al.*, *ACS Applied Energy Materials*, 2020

Troy Porter
LSU BS ChE 2018
now at Jacobs
Engineering

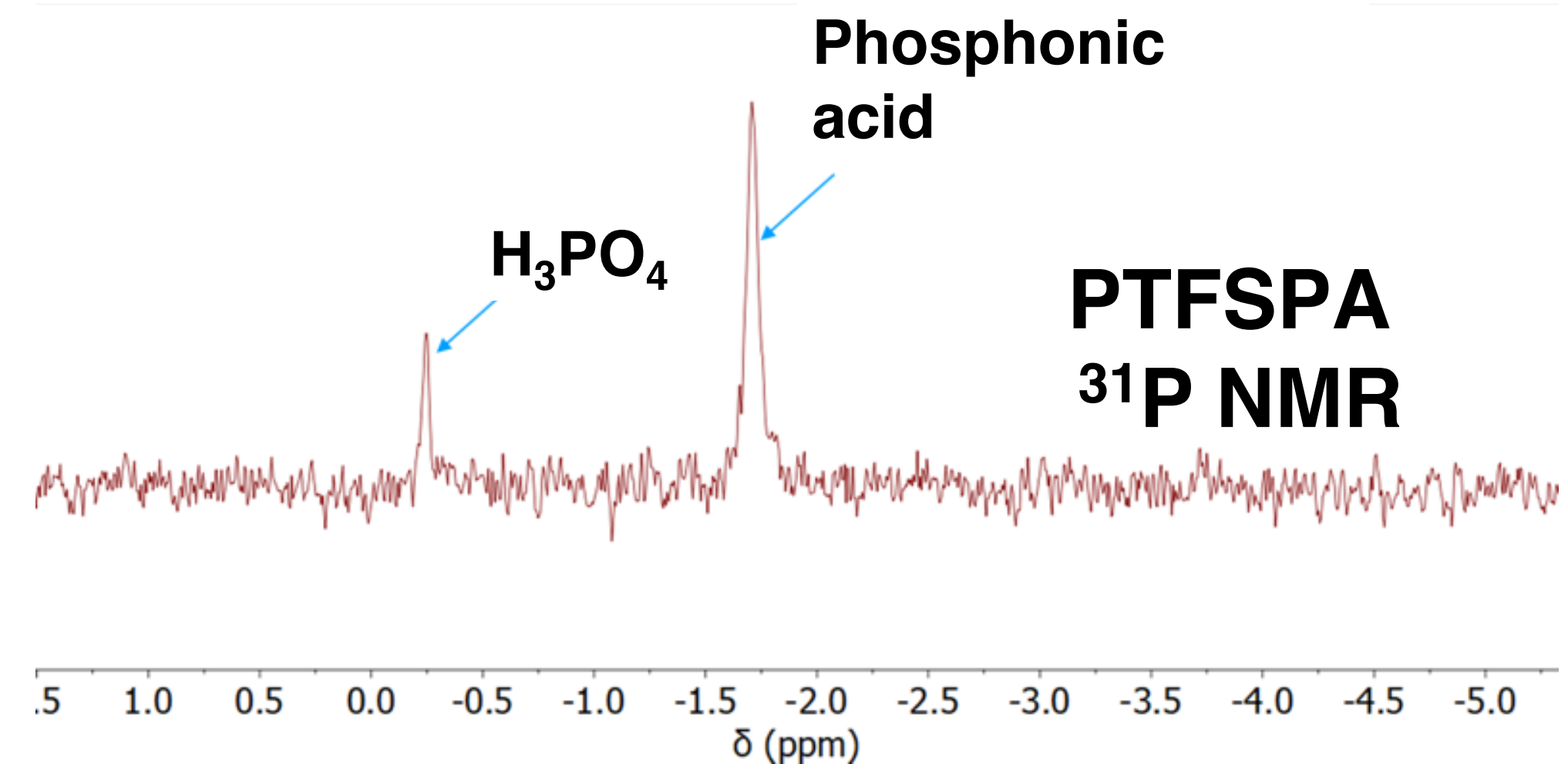
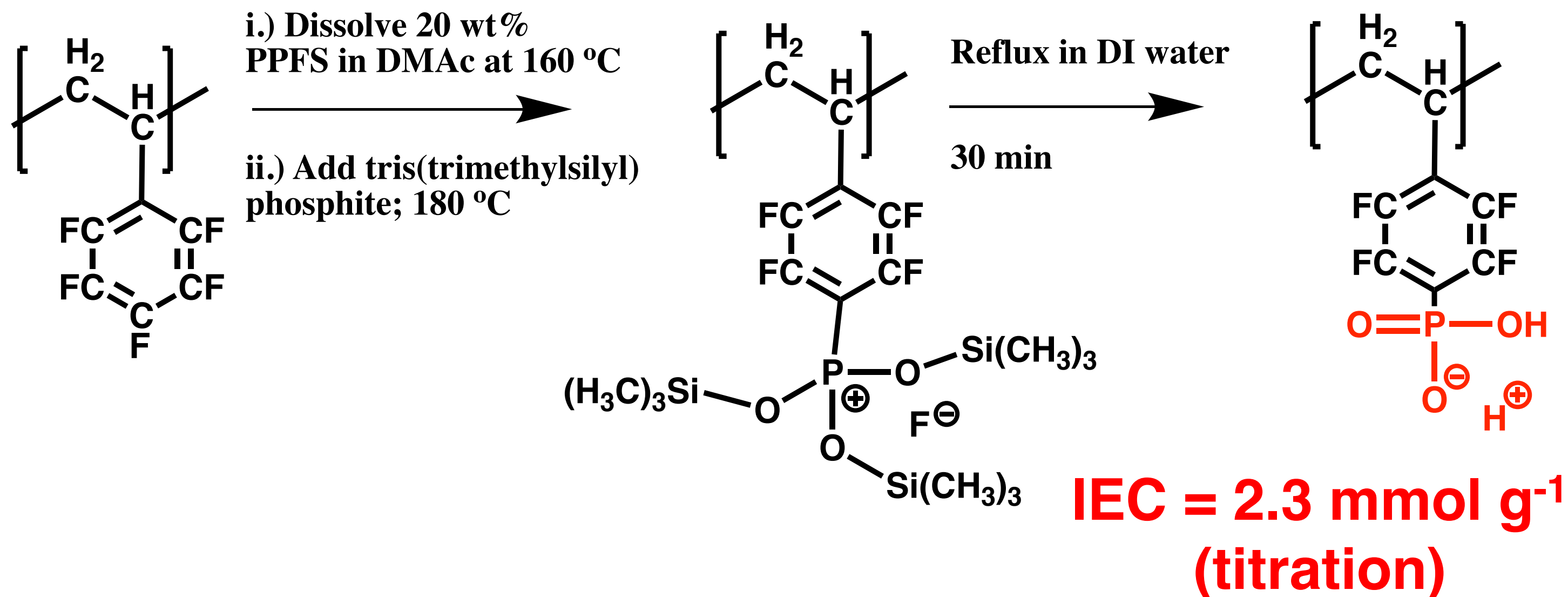
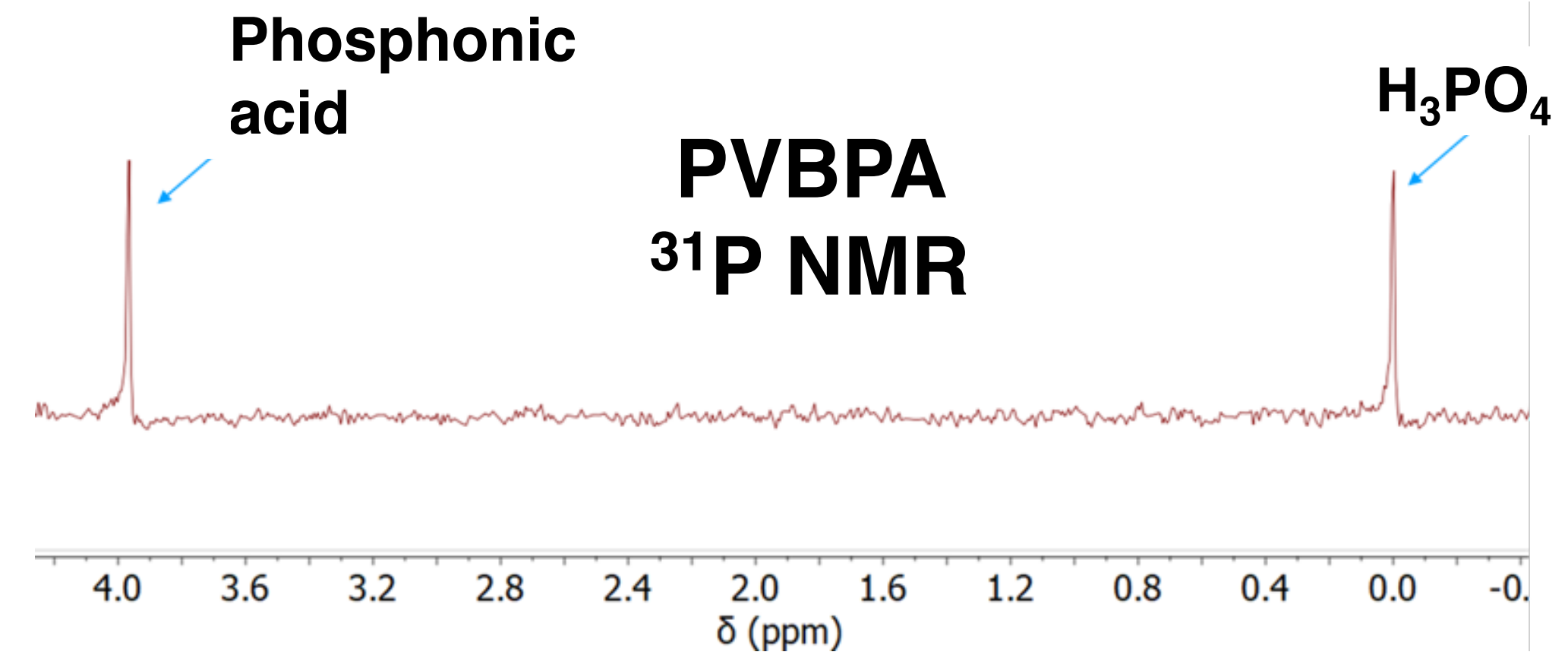
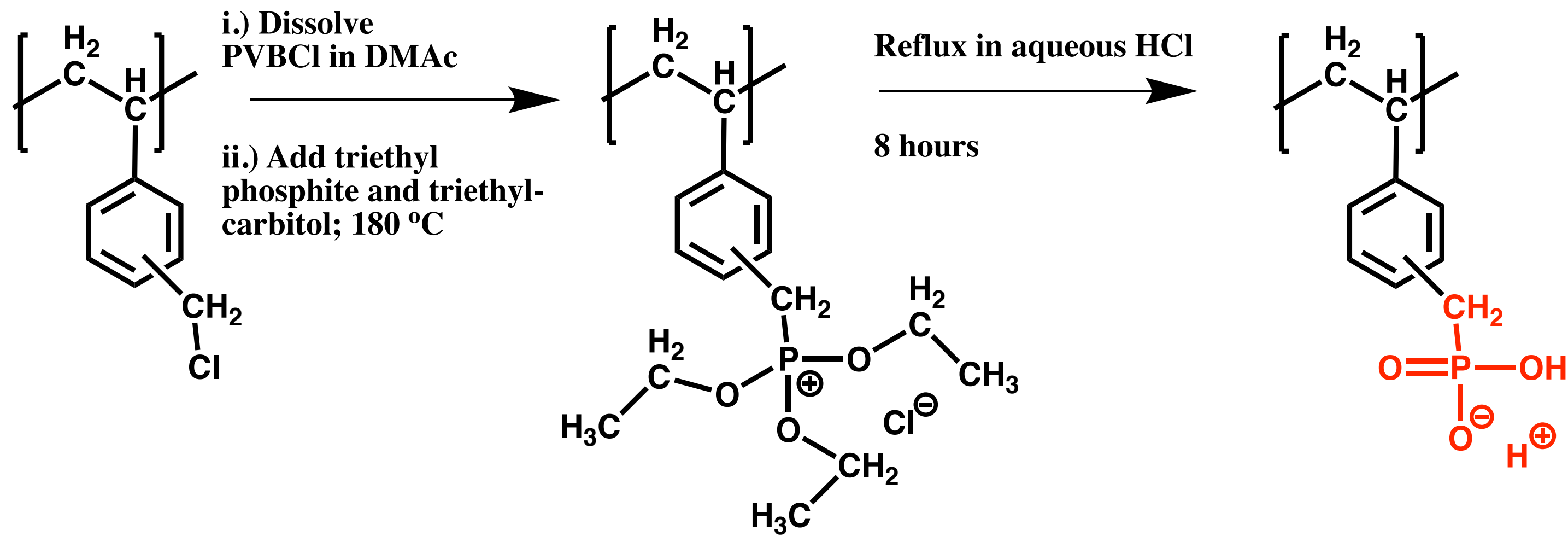


Electrode ionomer has a profound impact on performance



By switching the electrode binder, Los Alamos doubled its power density

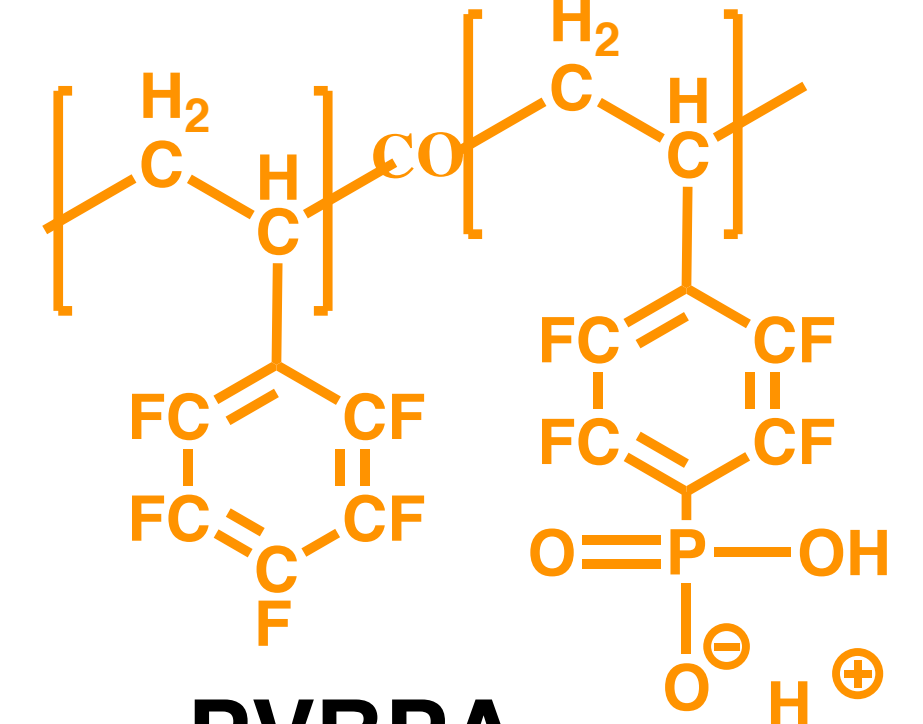
Synthesis of phosphonic acid ionomers



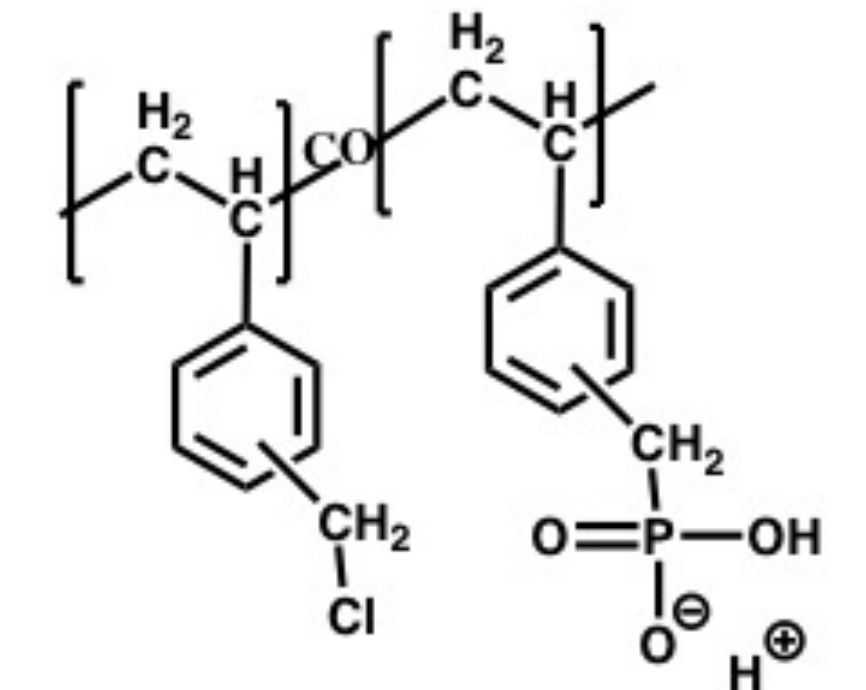
Properties of phosphonic acid ionomers

Type of binder

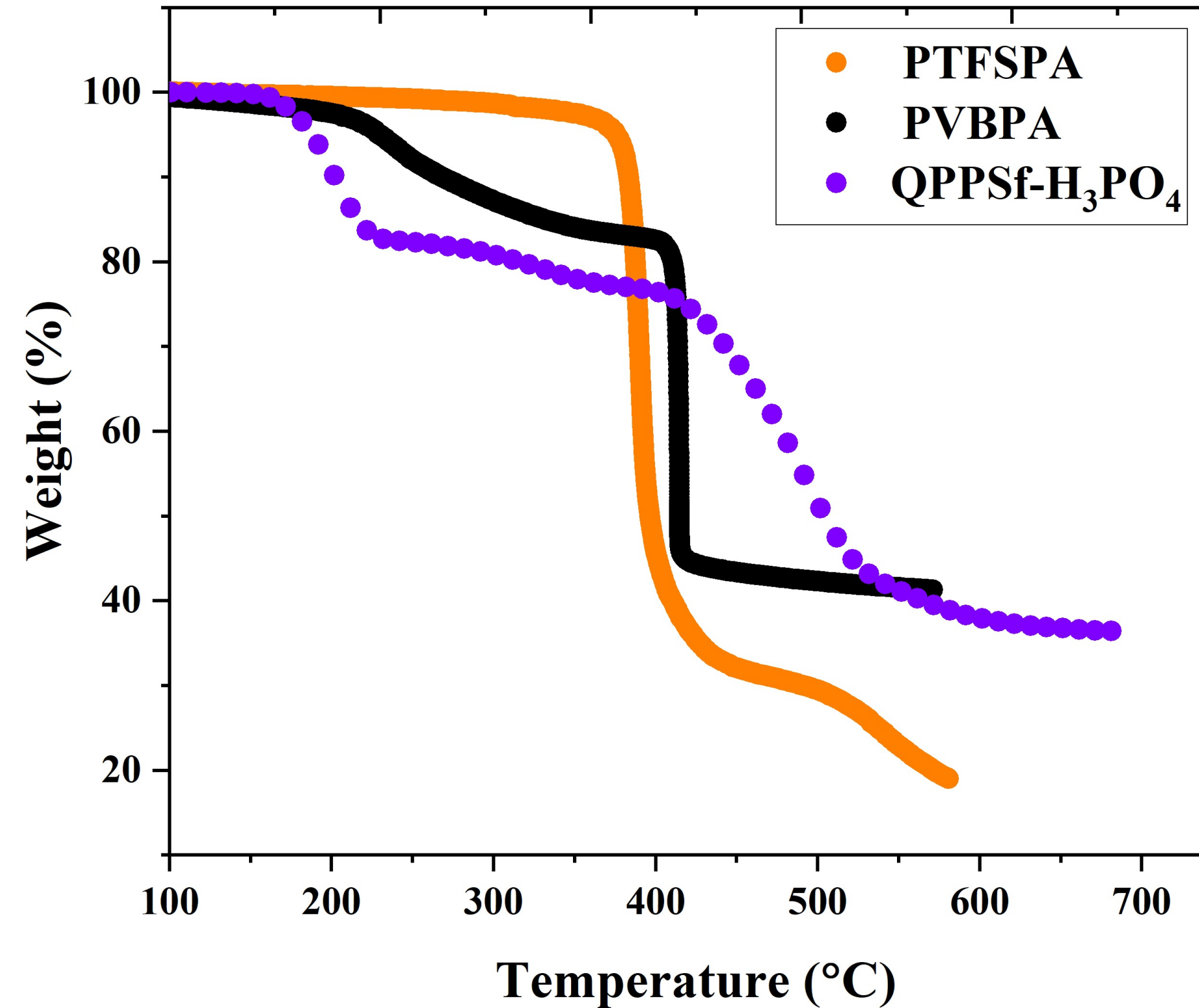
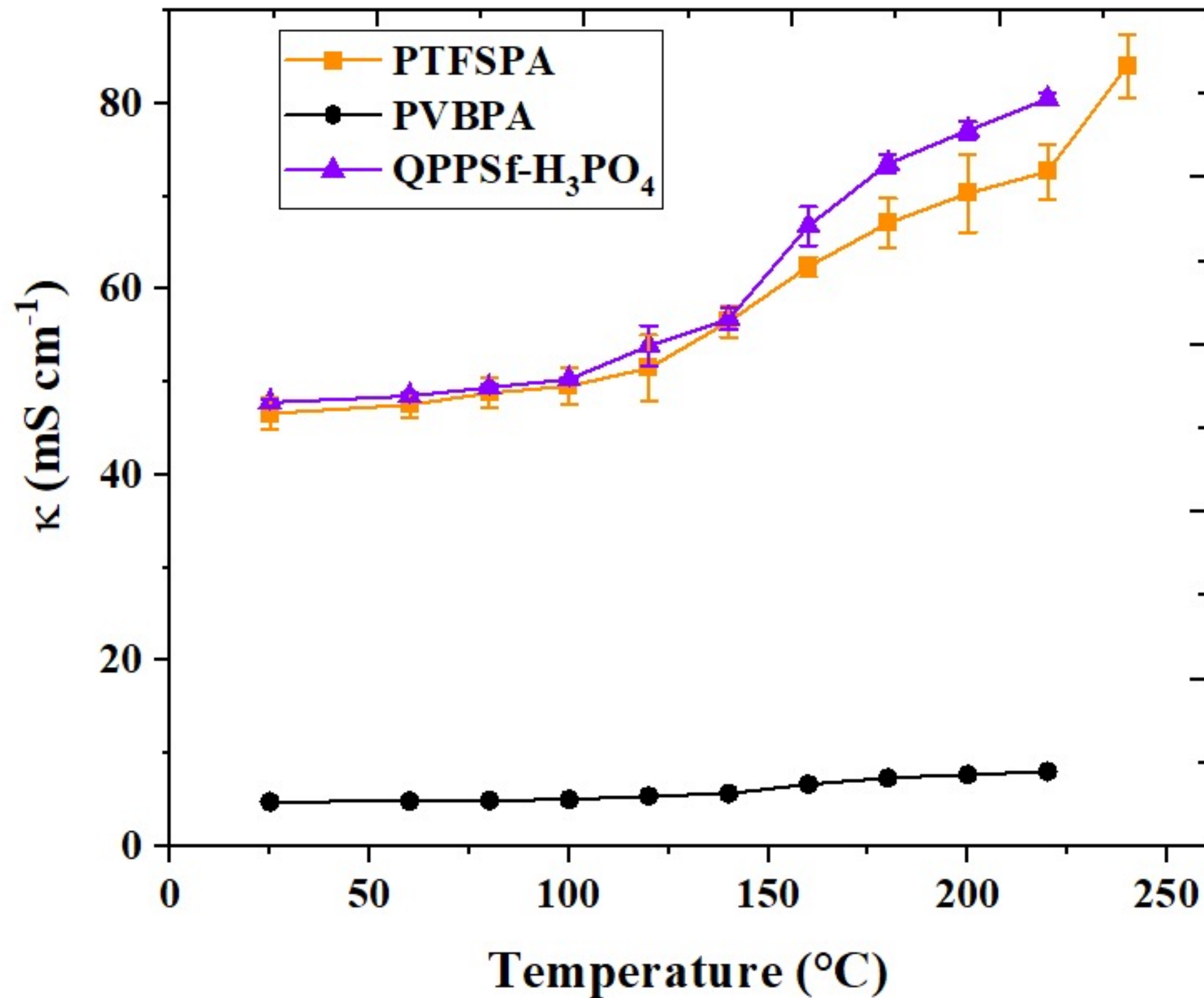
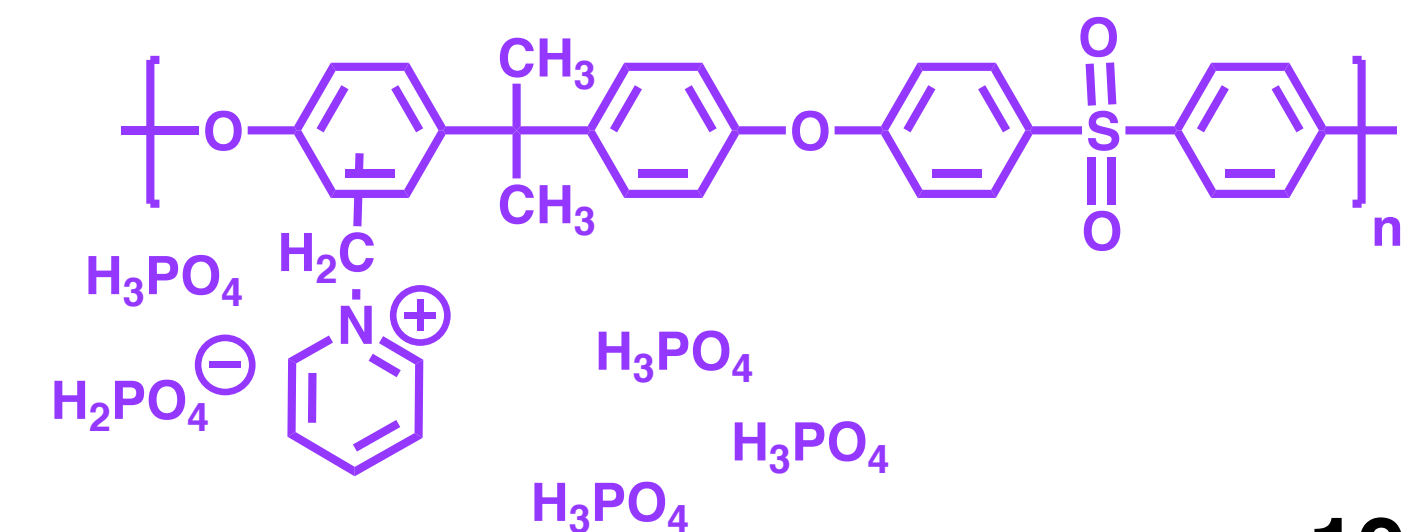
PTFSPA



PVBPA



QPPSf- H₃PO₄

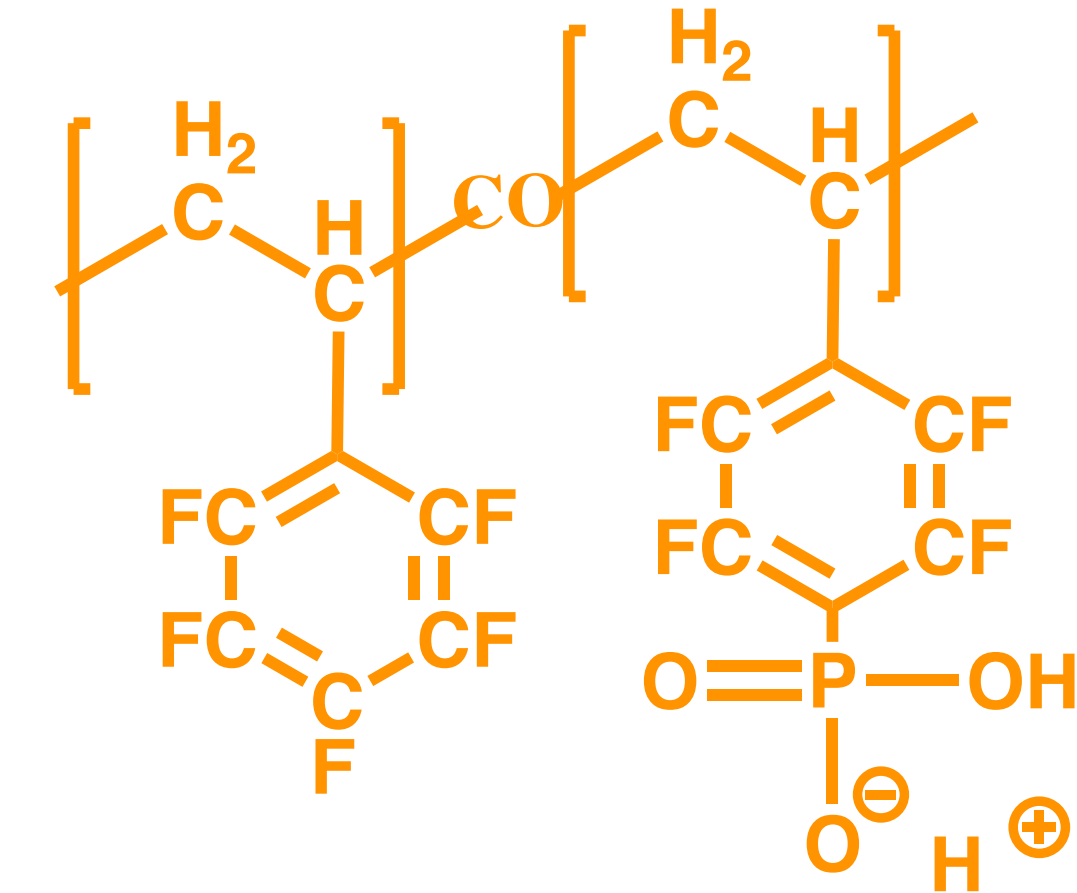


PTFSPA shows the same thin film conductivity as QPPSf-H₃PO₄ and has excellent thermal stability

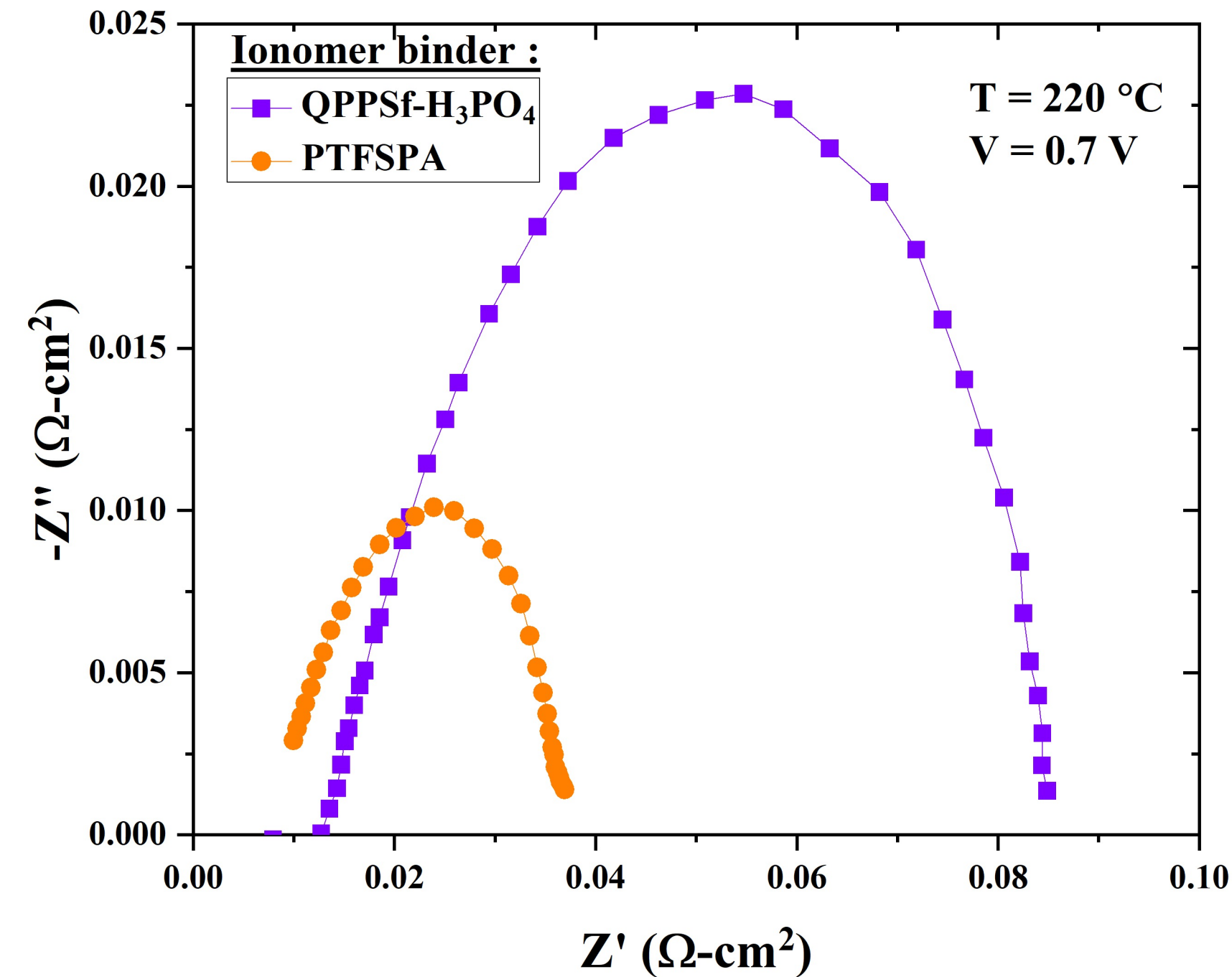
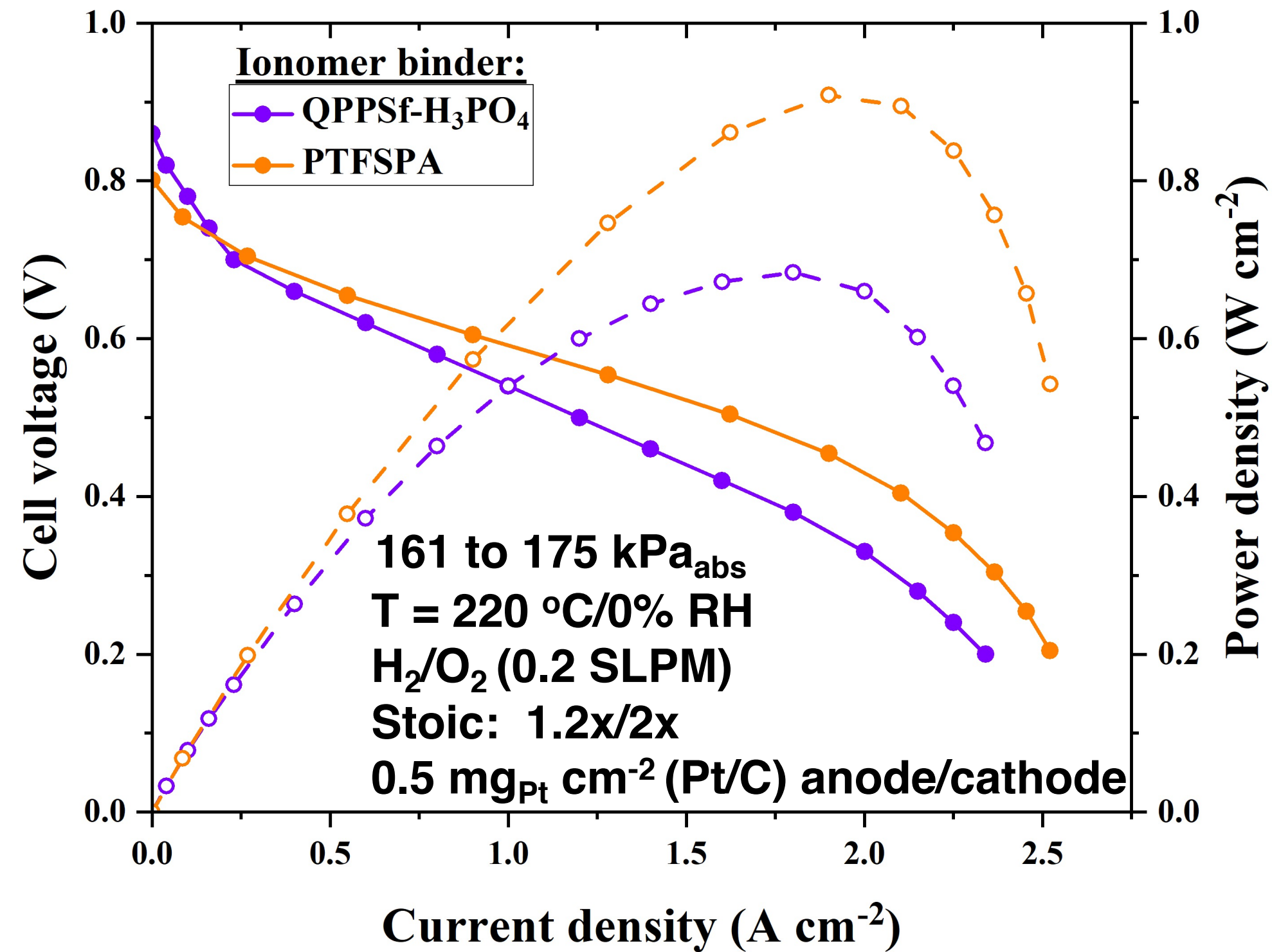
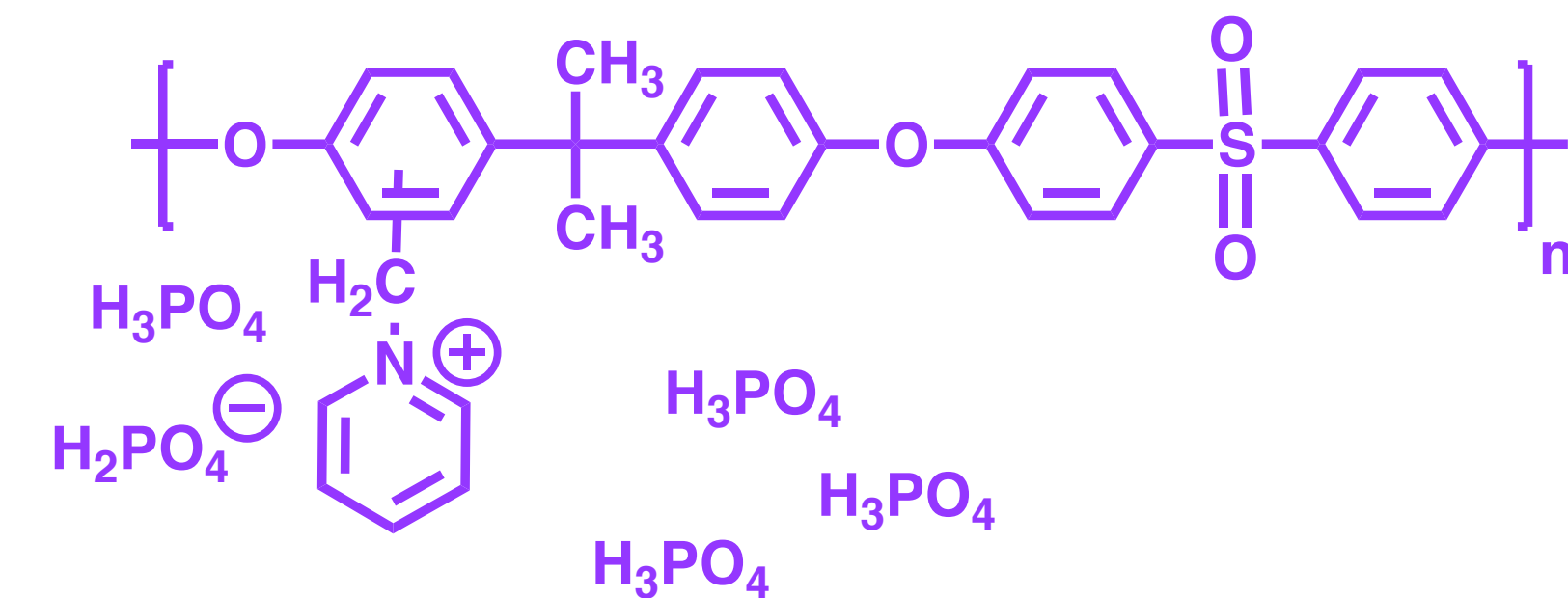
Our fuel cell data with phosphonic acid ionomer binders

Type of binder

PTFSPA



QPPSf- H₃PO₄



By switching the electrode binder only, fuel cell performance improved because of improved electrode kinetics

Presentation overview

High-temperature polymer electrolyte membranes (HT-PEMs) and binders for fuel cells

Studying the electrochemical properties of electrode ionomer binders as thin films

Future directions and concluding remarks

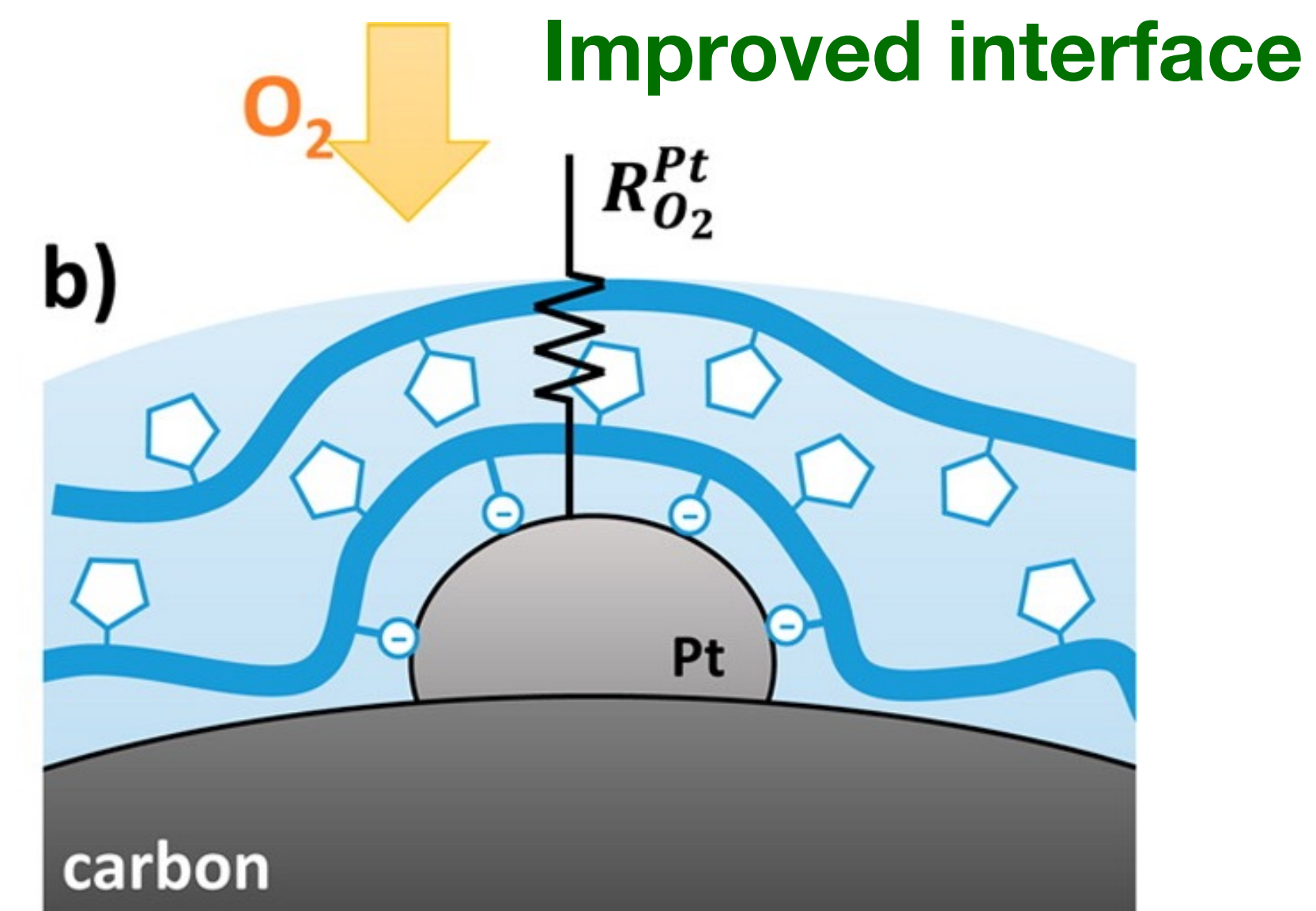
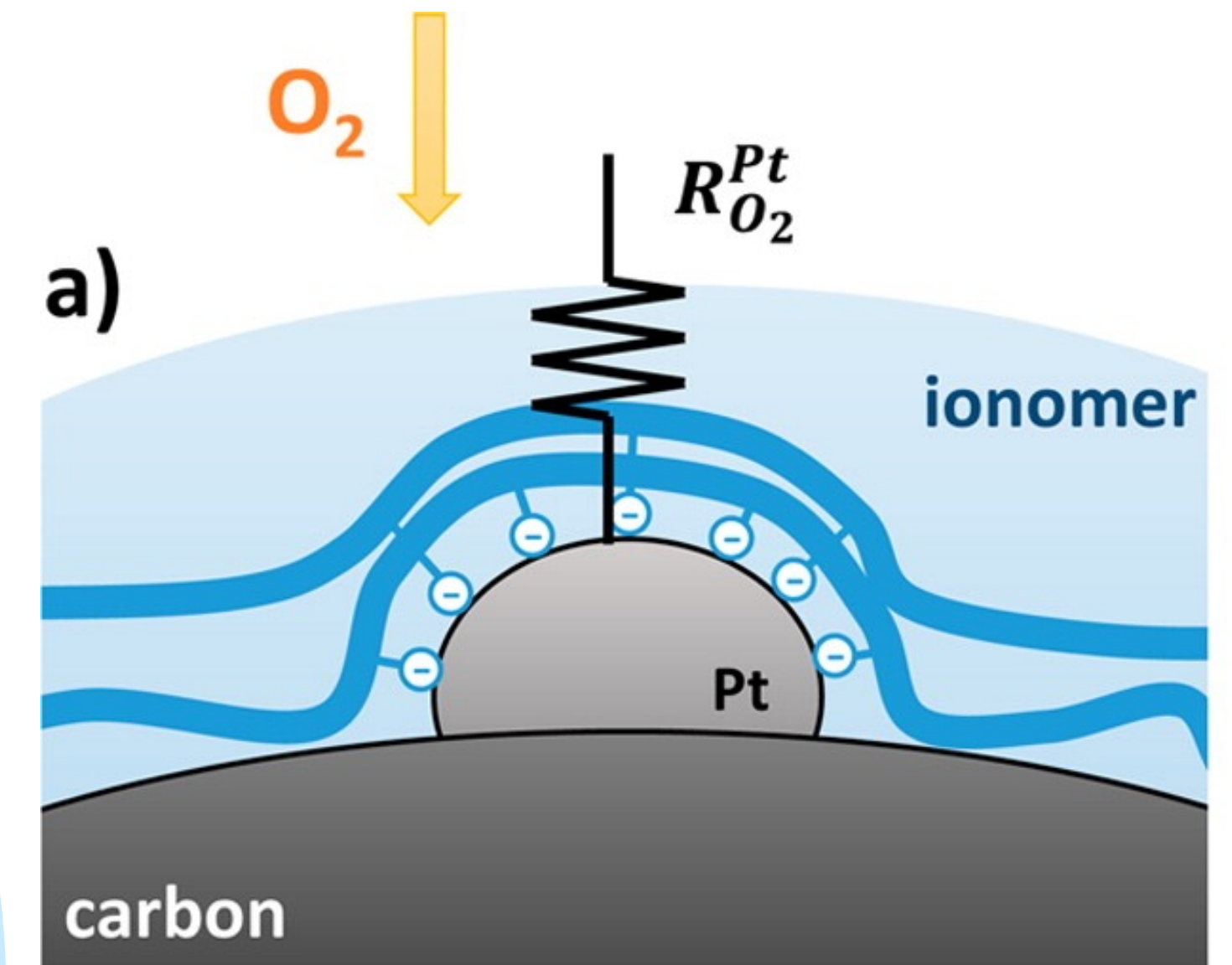
Property requirement differences: binders vs. membranes

Membrane

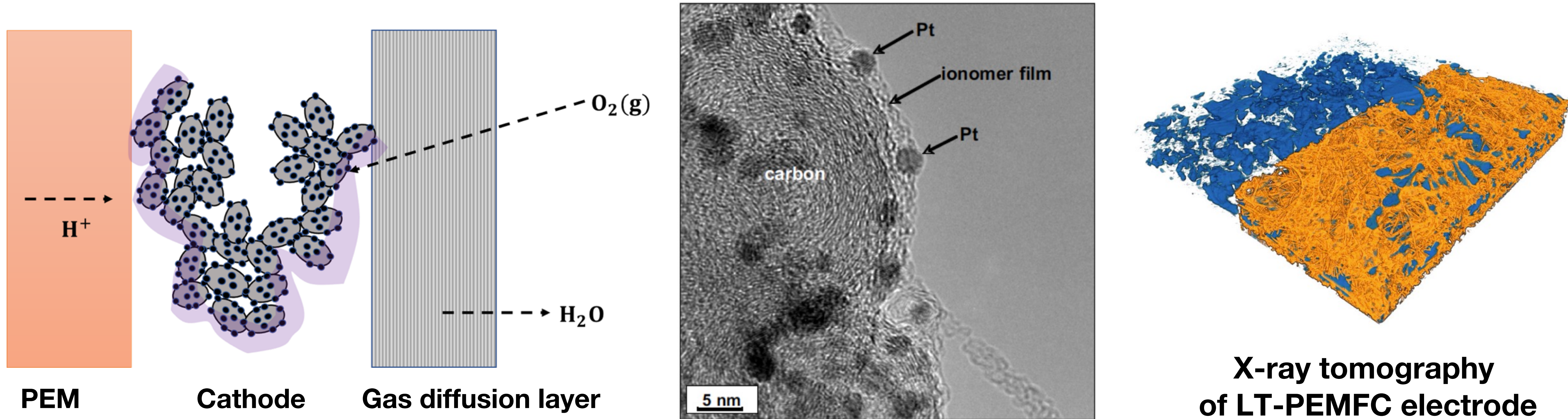
- Low gas (H_2 & O_2) permeability
- Mechanically robust
- Electron insulating

Binder

- High ionic conductivity
- Chemically & thermally stable
- No excessive swelling
- Good gas (H_2 & O_2) permeability
- Solution processable (low boiling point & non-toxic solvents preferred)
- Small to negligible interaction with catalyst surface
- Electrically conductive is a plus

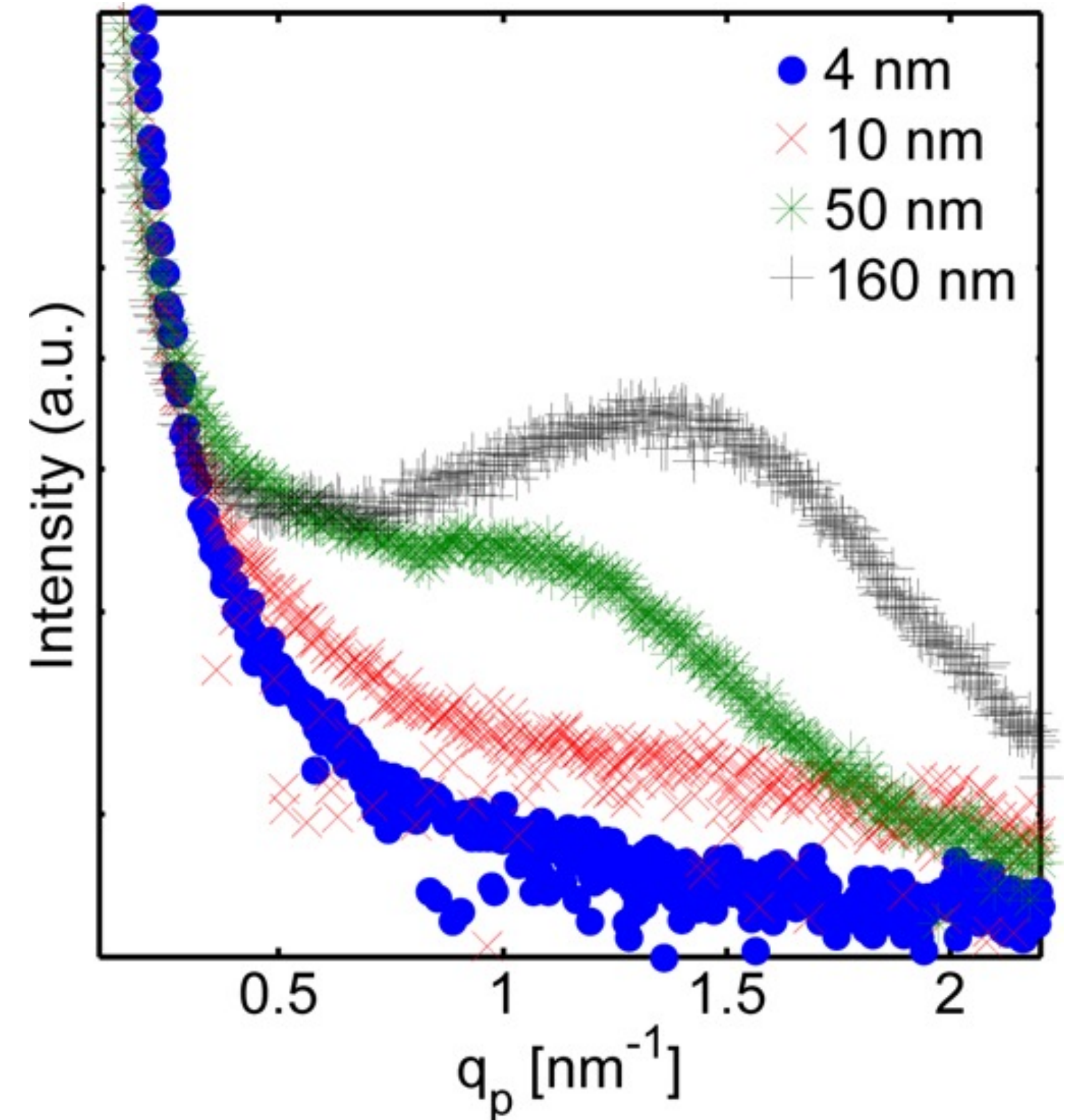
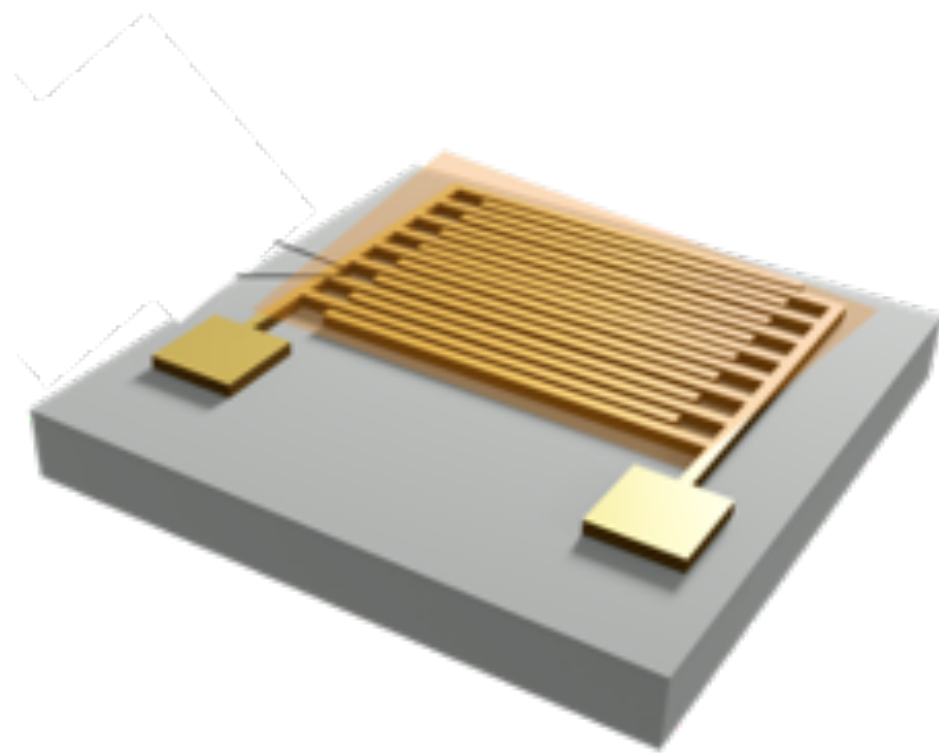
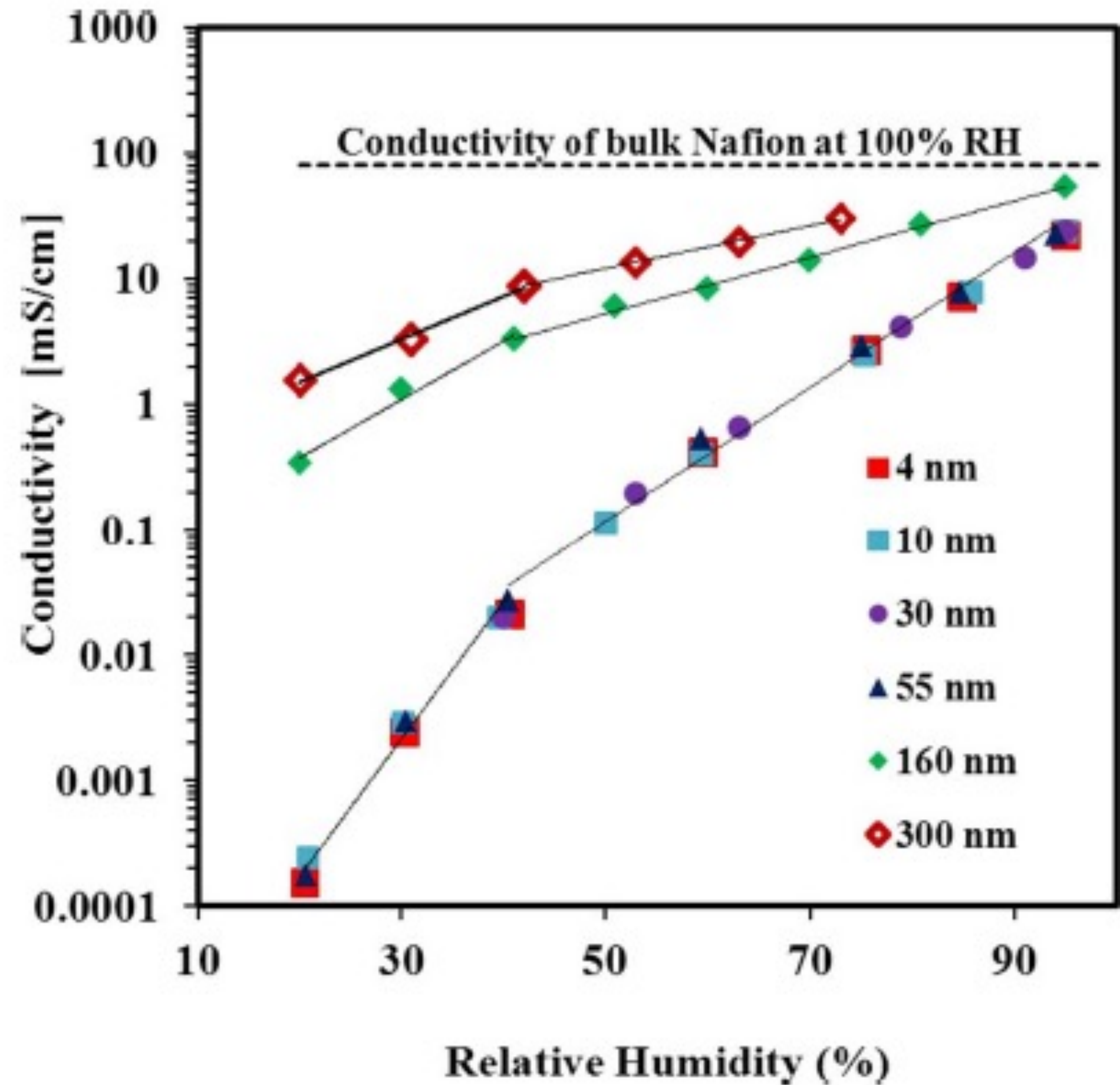


Motivation for studying thin film polymer electrolyte properties



Porous electrodes have a complex structure. They are required to deliver electrons, reactants, and protons to the electrocatalyst surface for the redox reactions

Electrochemical properties of thin film Nafion[®]



Nafion[®], when confined as a thin film, cannot self-assemble into percolated pathways compromising conductivity

Can we measure how the polymer electrolyte binder affects reaction kinetics and gas permeability?

Can we do it without using liquid supporting liquid electrolyte and fabricating membrane electrode assemblies?

Ionic conductivity often has a relatively small impact on fuel cell performance

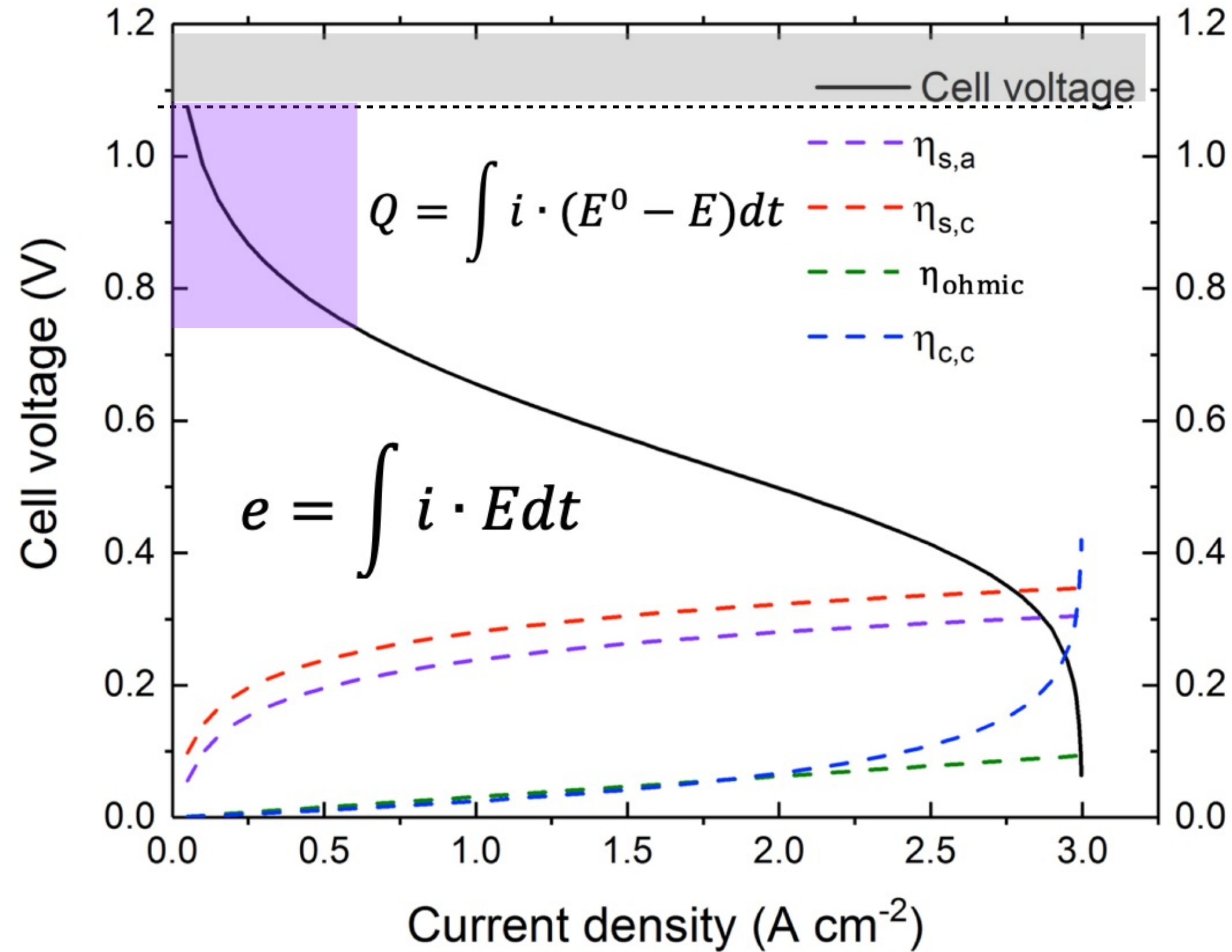


Luis Briceno-Mena
PhD candidate



Prof. José
Romagnoli

Current distribution analysis for fuel cells



$$i = -\frac{n}{S_i} F N_i \quad \text{Faraday's Law}$$

Cell polarization relationship between voltage & current

$$E(i) = E_{oc} - \eta_{act} - \eta_{con} - \eta_{ohm}$$

$$\Delta G^0 = -nFE^0$$

Cell voltage is informed from thermodynamics

$$E_{oc} = 1.23 - 0.9 \times 10^{-3}(T - 298.15) + \frac{RT}{2F} \ln(P_{H_2} \sqrt{P_{O_2}})$$

H₃PO₄ uptake in electrodes $m_{io} = 0.0902IEC_{io} + 0.0352$

$$\eta_{act} = \frac{RT}{\alpha_{an}F} \ln\left(\frac{i}{i_0^{an}(1-\theta_{CO})^2}\right) + \frac{RT}{\alpha_{cat}F} \ln\left(\frac{i}{i_0^{cat}}\right)$$

Reaction kinetics for the electrodes (Butler-Volmer)

Exchange current density (i_0) ~ rxn rate coeff.

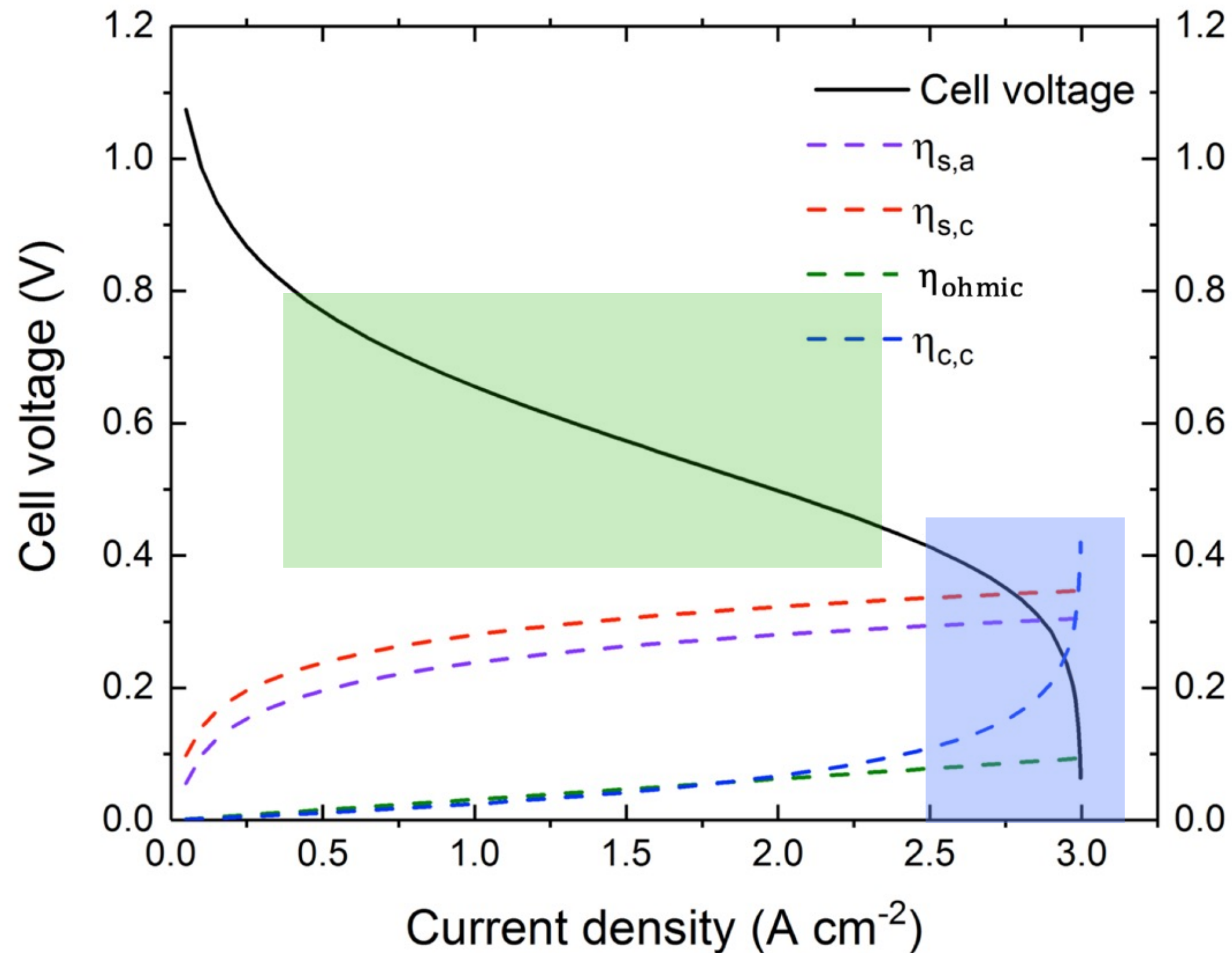
$$i_0^{an} = a_c L_c \left(\frac{P_{H_2} H_{H_2}^{CL}}{C_{H_2}^0}\right)^{0.5} \exp\left(-\frac{E_C^{H_2}}{R} \left(\frac{1}{T_{an}} - \frac{1}{T_{ref}^0}\right)\right) i_{0-ref}^{an} \exp(-\eta(1 - m_{io}))$$

$$i_0^{cat} = a_c L_c \left(\frac{P_{O_2} H_{O_2}^{CL}}{C_{O_2}^0}\right) \exp\left(-\frac{E_C^{O_2}}{R} \left(\frac{1}{T_{cat}} - \frac{1}{T_{ref}^0}\right)\right) i_{0-ref}^{cat} \exp(-\eta(1 - m_{io}))$$

CO coverage on catalyst

$$\theta_{CO} = 19.9 \exp(-7.69 \times 10^{-3} T_{an}) + 0.085 \ln\left(\frac{y_{CO}}{y_{H_2}}\right)$$

Current distribution analysis for fuel cells



$$i = -\frac{n}{s_i} F \frac{m_i}{A \cdot M W_i \cdot t} = -\frac{n}{s_i} F N_i \quad \text{Current is measure of chemical species flux}$$

$$E(i) = E_{oc} - \eta_{act} - \eta_{con} - \eta_{ohm}$$

$$\eta_{ohm} = i \left(\frac{\delta_{mem}}{\kappa_{mem}} + \frac{\delta_{io}}{\kappa_{io}} \right)$$

Ohmic drop arises from ion transport mass transfer resistance

Concentration polarization
(mass-transfer controlled behavior)

$$\eta_{con} = -B \left(\ln \left(1 - \frac{i}{i_{lim}^{an}} \right) + \ln \left(1 - \frac{i}{i_{lim}^{cat}} \right) \right)$$

$$i_{lim}^{cat} = \frac{K_{an} D_{H_2}^{CL} P_{H_2}}{T \delta_{CL}} (1 - \theta_{CO})^2 \quad i_{lim}^{an} = \frac{K_{cat} D_{O_2}^{CL} P_{O_2}}{T \delta_{CL}}$$

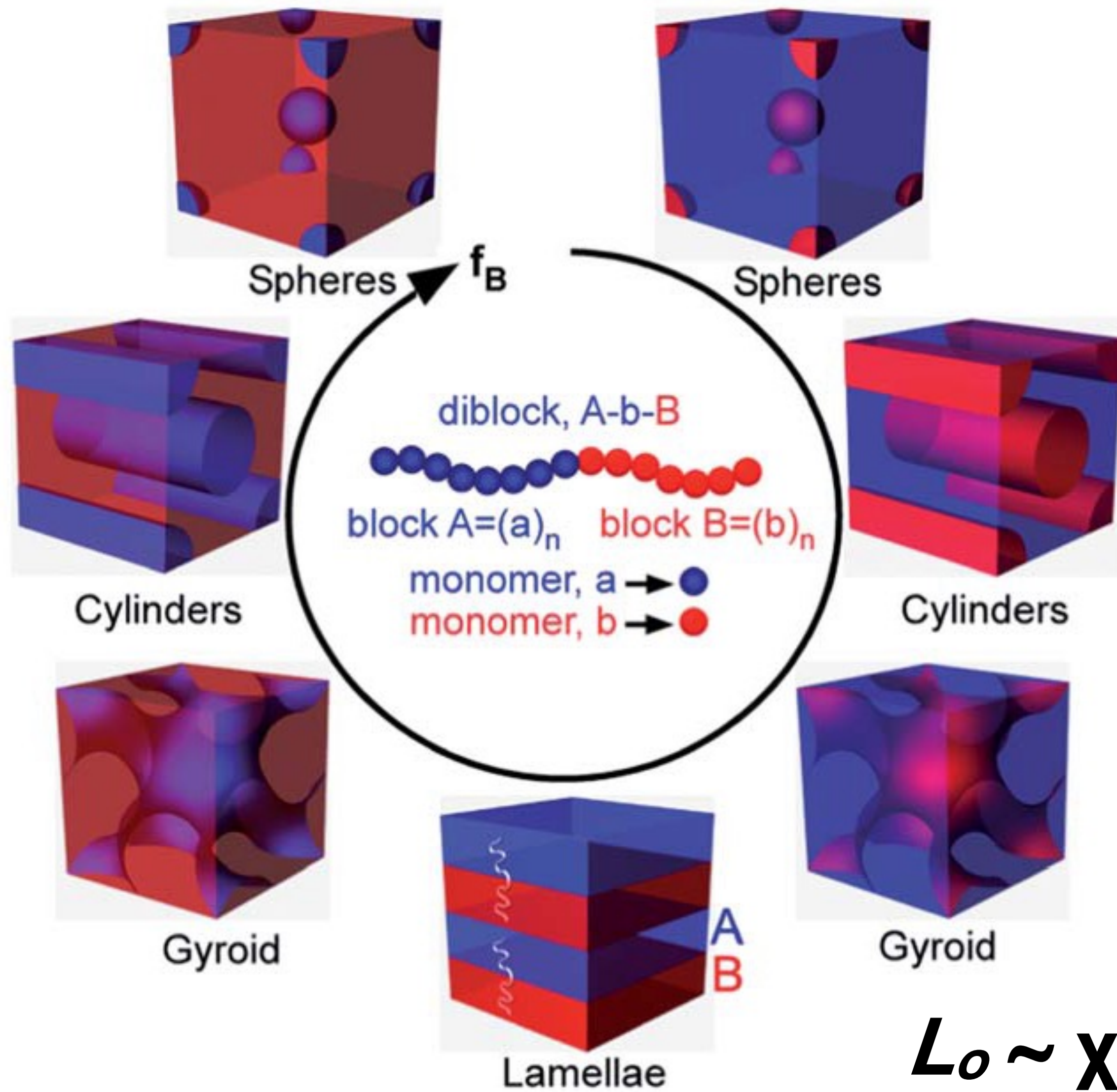
$$D_{H_2}^{CL} = 2 D_{O_2}^{CL}$$

$$K_{an} = 0.5 K_{cat}$$

Diffusion coefficient

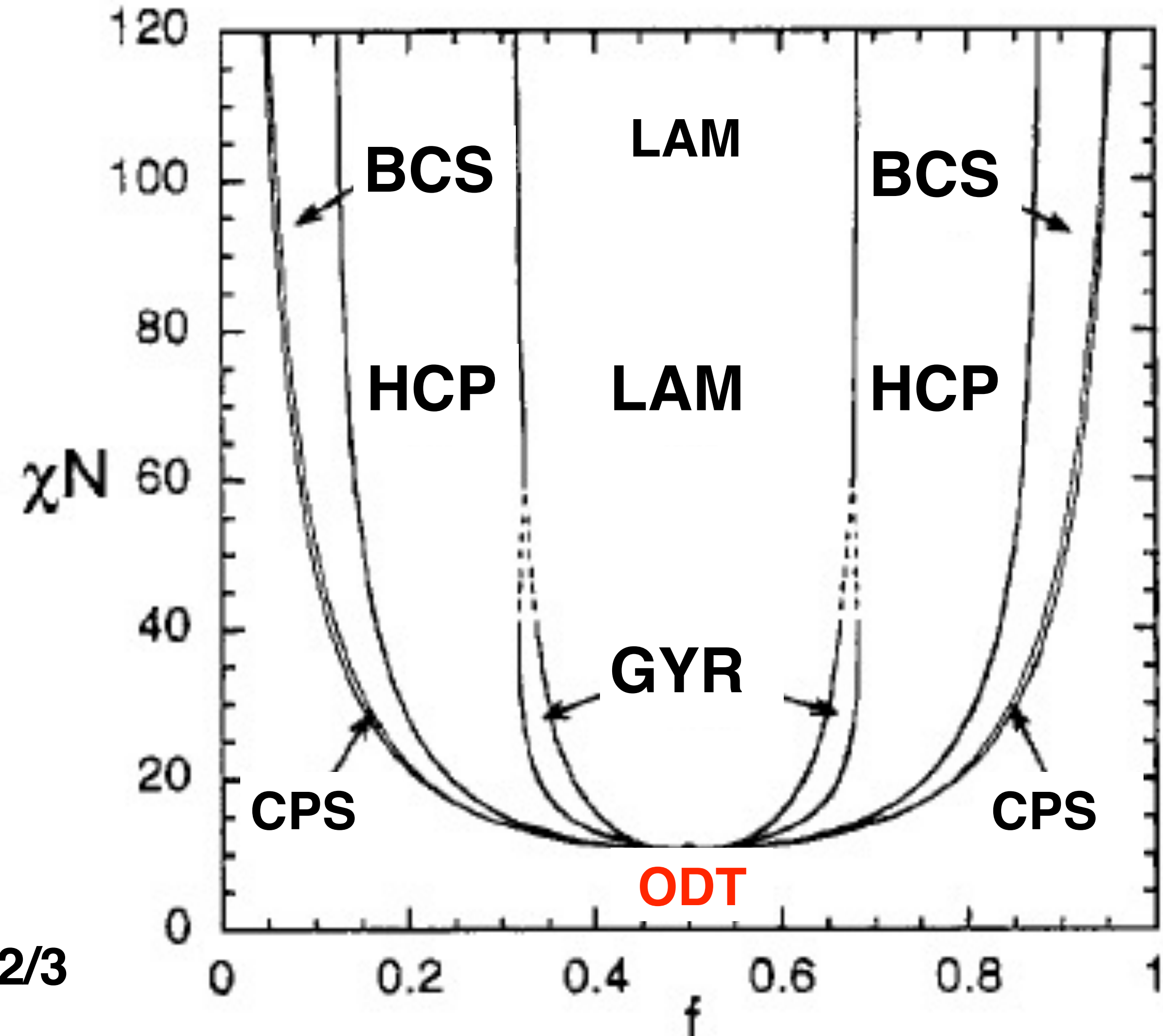
$$D_{O_2}^{CL} = (1.0 \times 10^{-6}) \exp \left(-\frac{4500 m_{io}^2 - 10000 m_{io} + 4010}{T} \right)$$

Versatile materials for nanostructure templating - BCP self-assembly

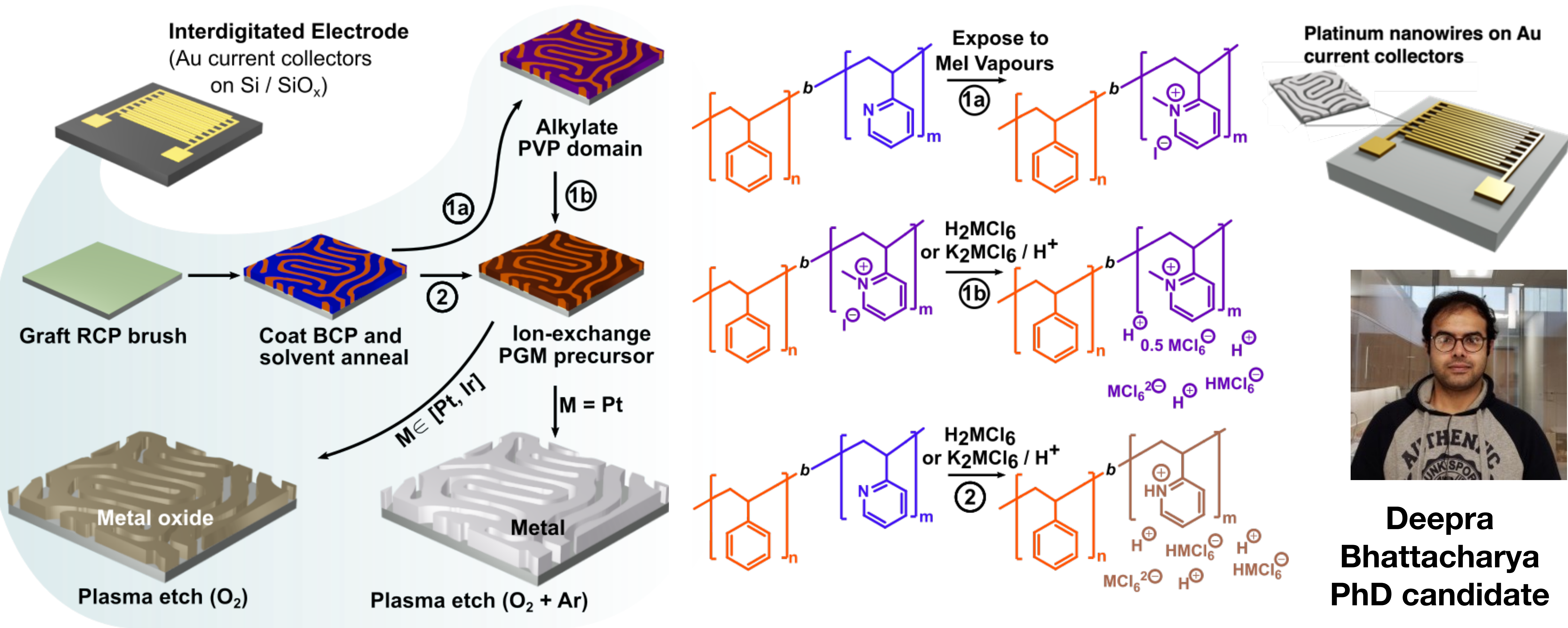


$$L_o \sim \chi^{1/6} N^{2/3}$$

Self-consistent field theory phase diagram

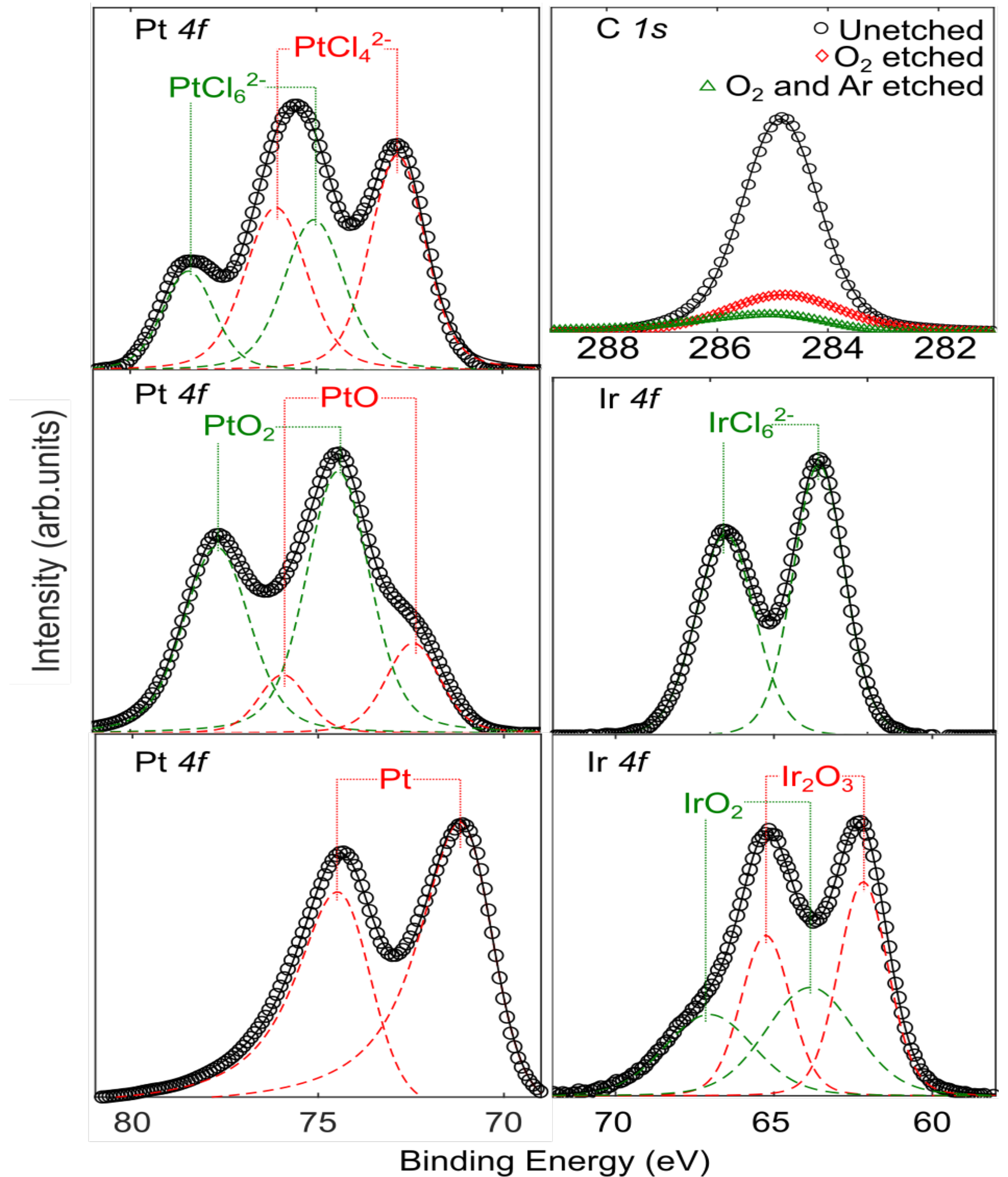
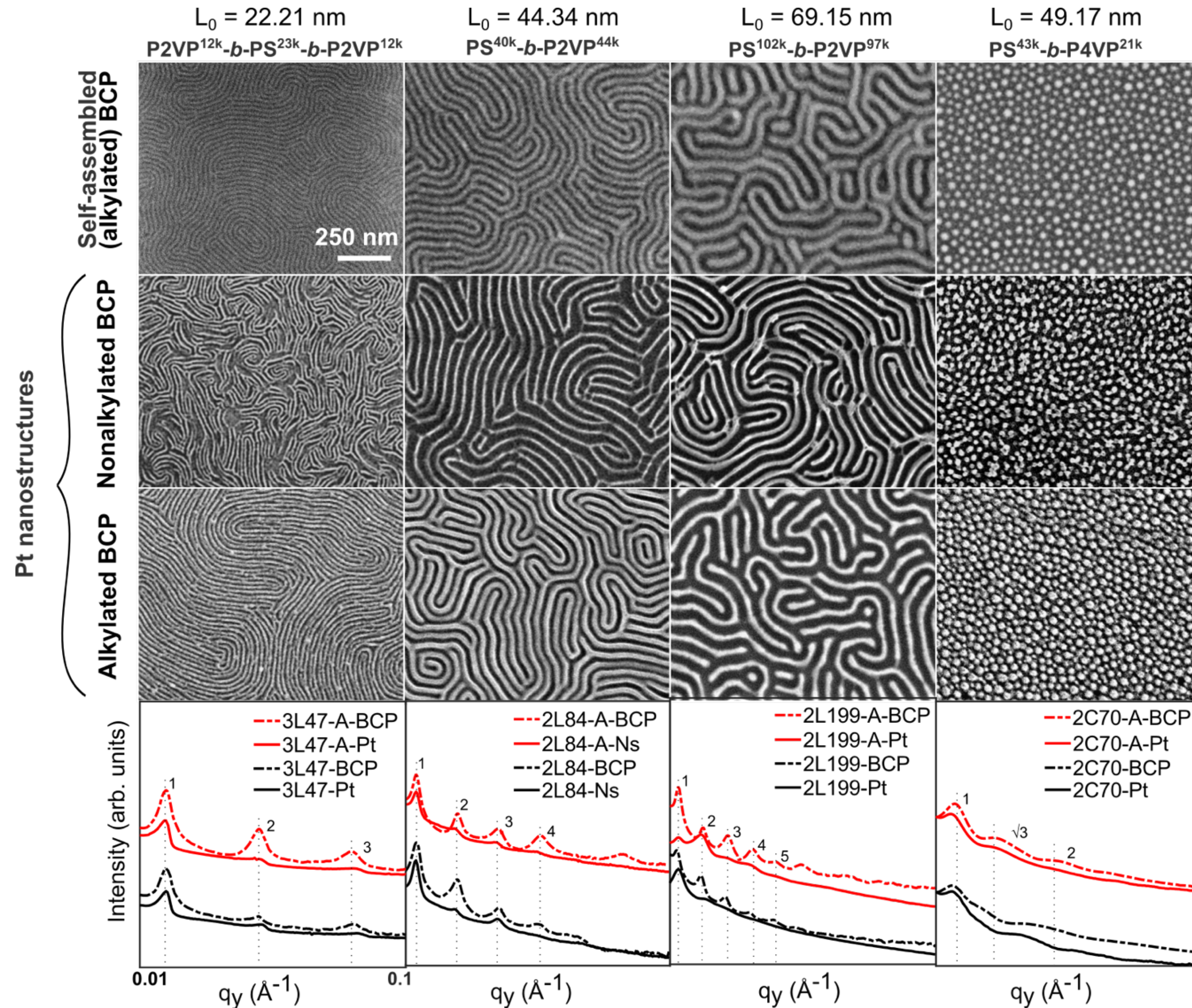


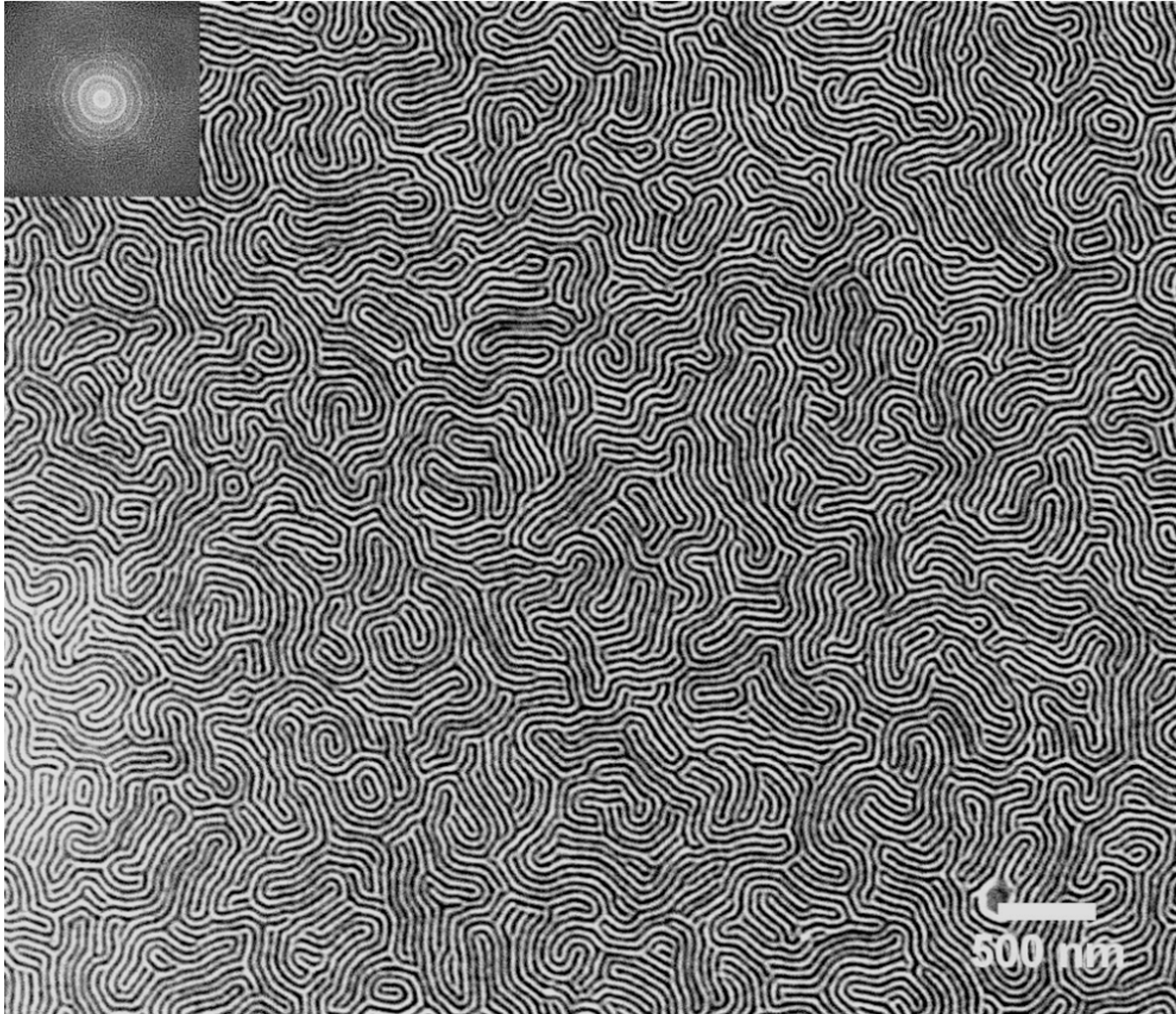
Probing reaction kinetics and gas transport at electrocatalyst-thin film ionomer interfaces



Deepra Bhattacharya
PhD candidate

PGM nanostructures from self-assembled BCP templates





**High density platinum
nanowires
(22 nm diameter)**

6 μm x 6 μm micrograph

PGM nanostructures – surface area

Height (h) from AFM topography images

P2VP^{12k}-*b*-PS^{23k}-*b*-P2VP^{12k}

PS^{40k}-*b*-P2VP^{44k}

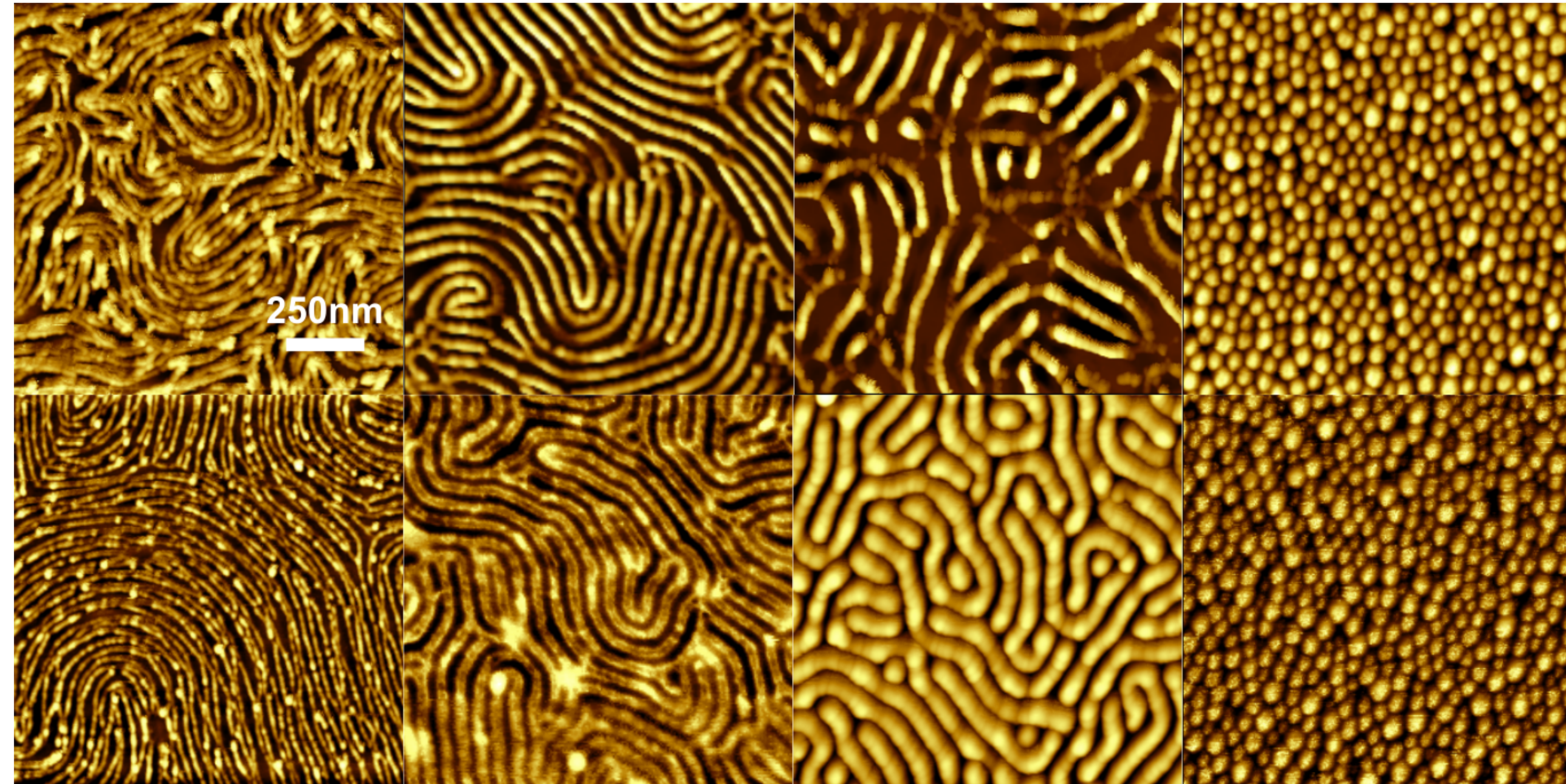
PS^{102k}-*b*-P2VP^{97k}

PS^{40k}-*b*-P4VP^{44k}



Filter and
binarize

Analyze
2D area
of the
structures

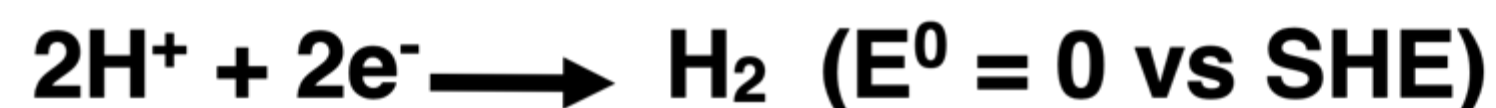
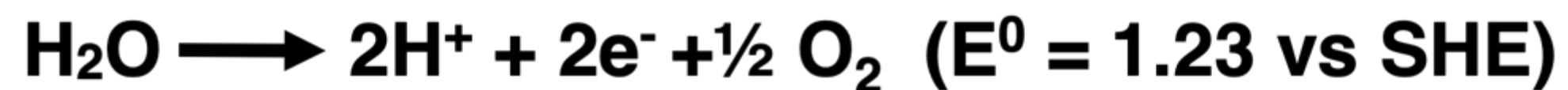
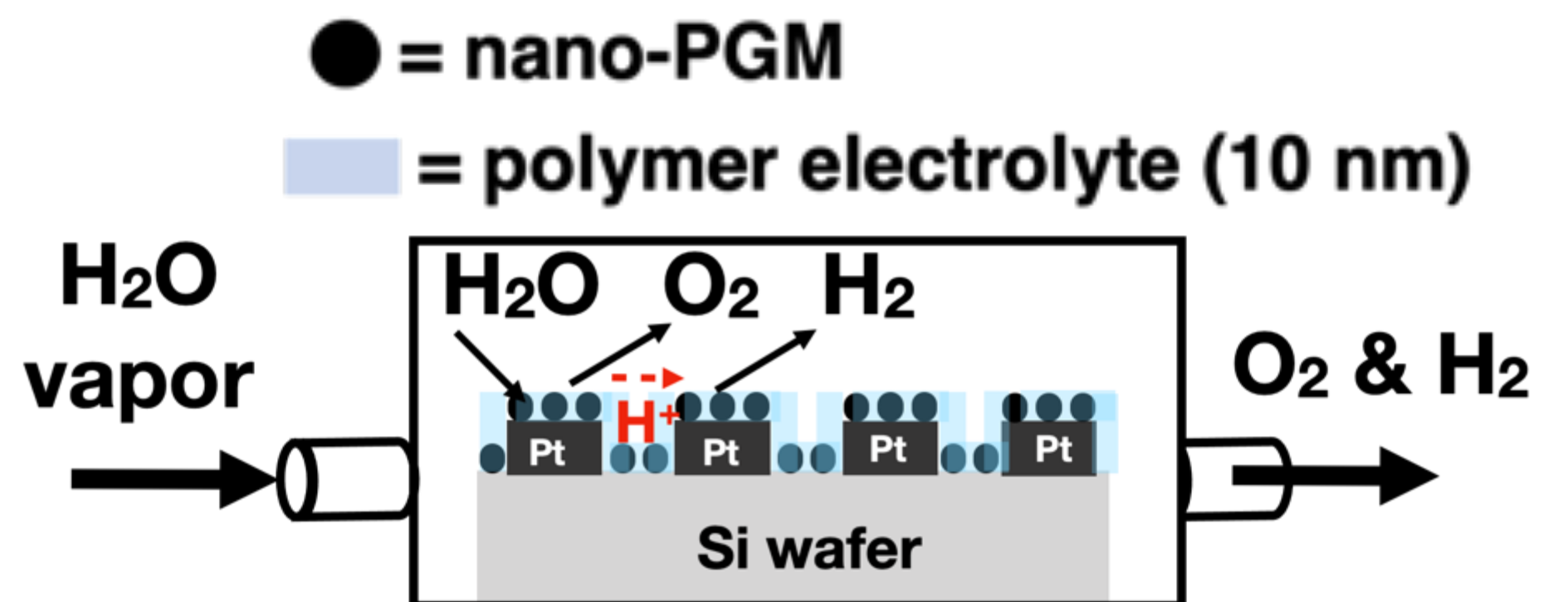
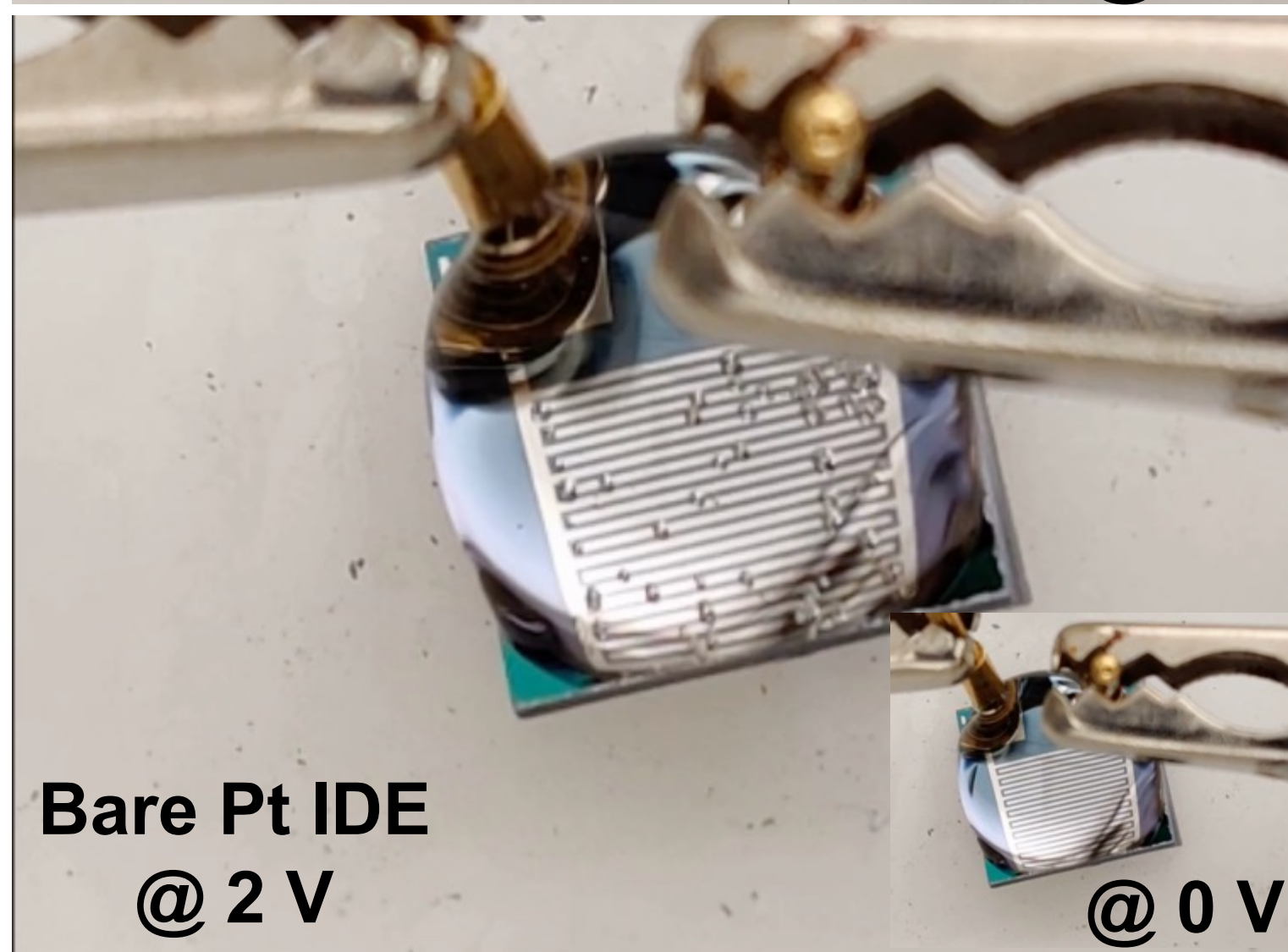
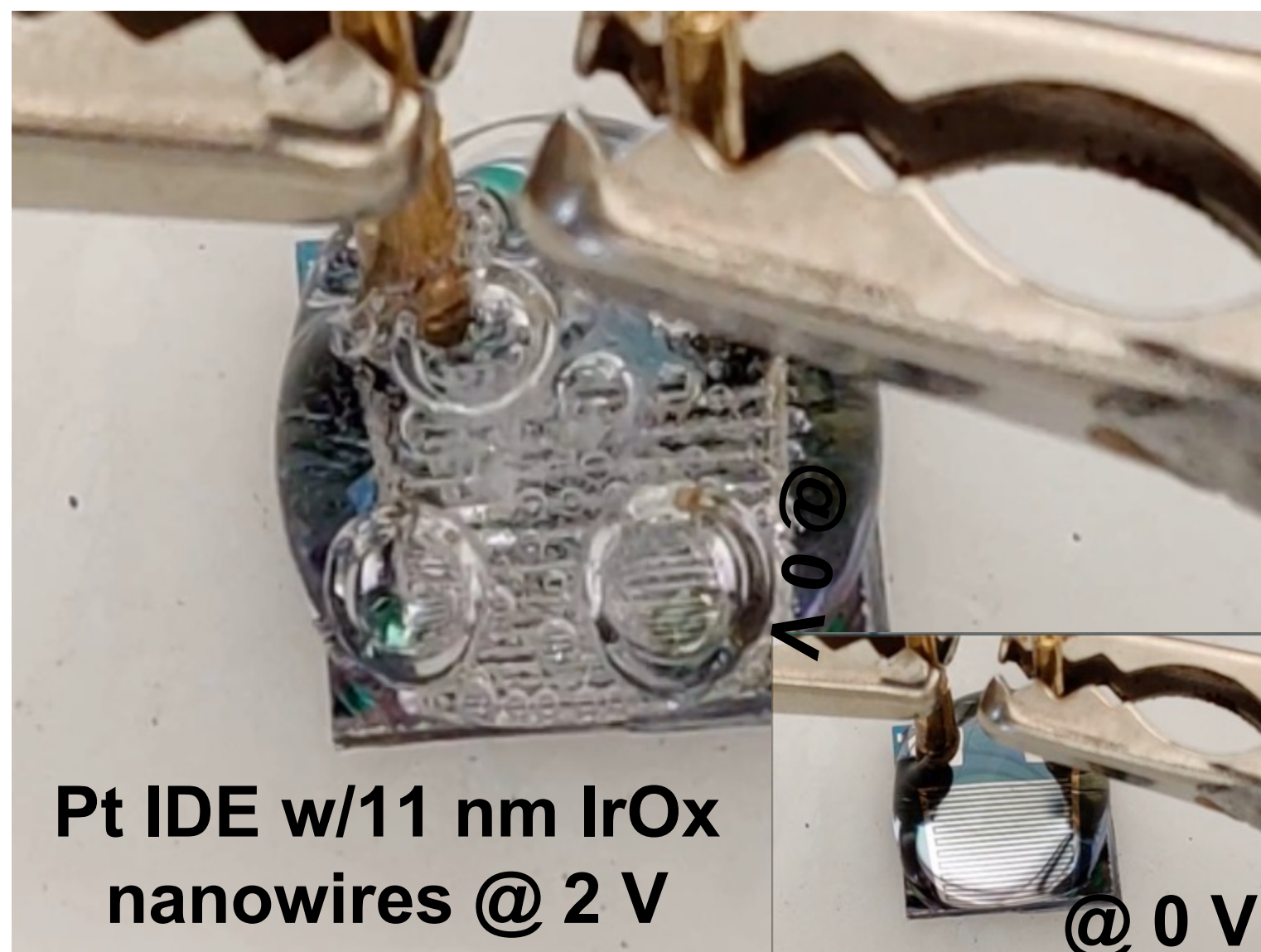


Surface coverage (φ), area covered by the nanowires (A),
perimeter (p) from image analysis

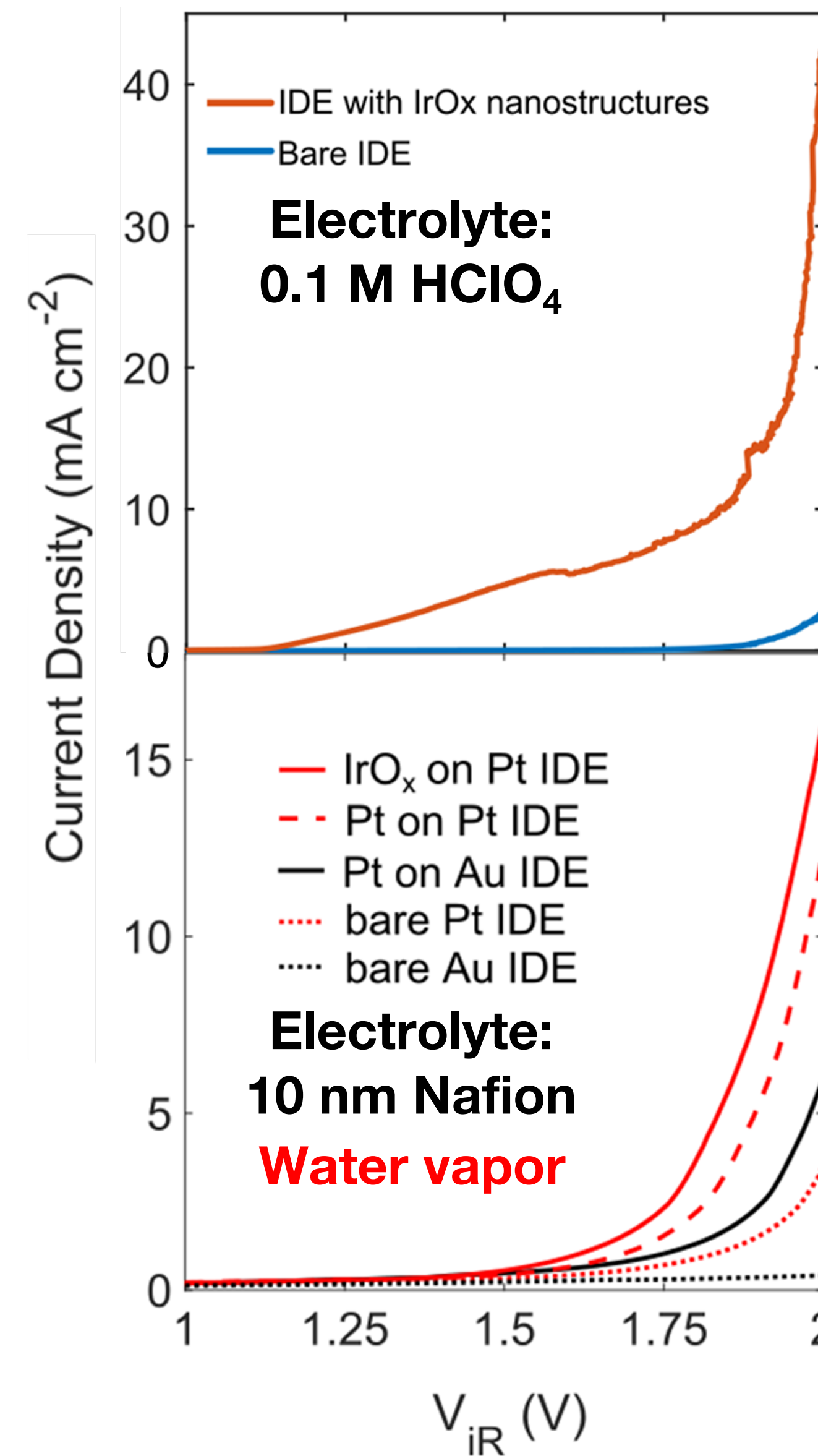
$$S = ph + \varphi A$$

Water electrolysis on IDEs

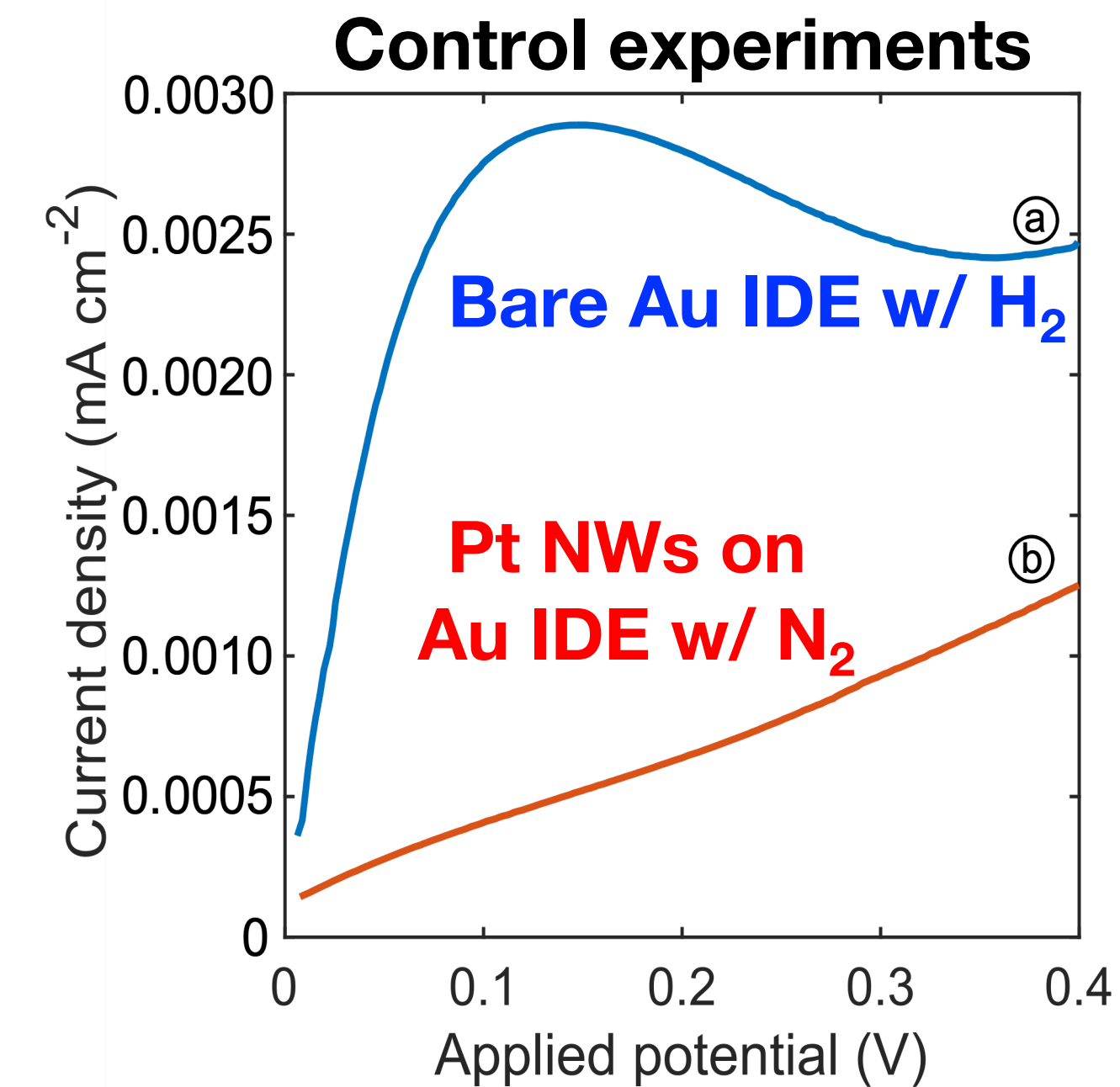
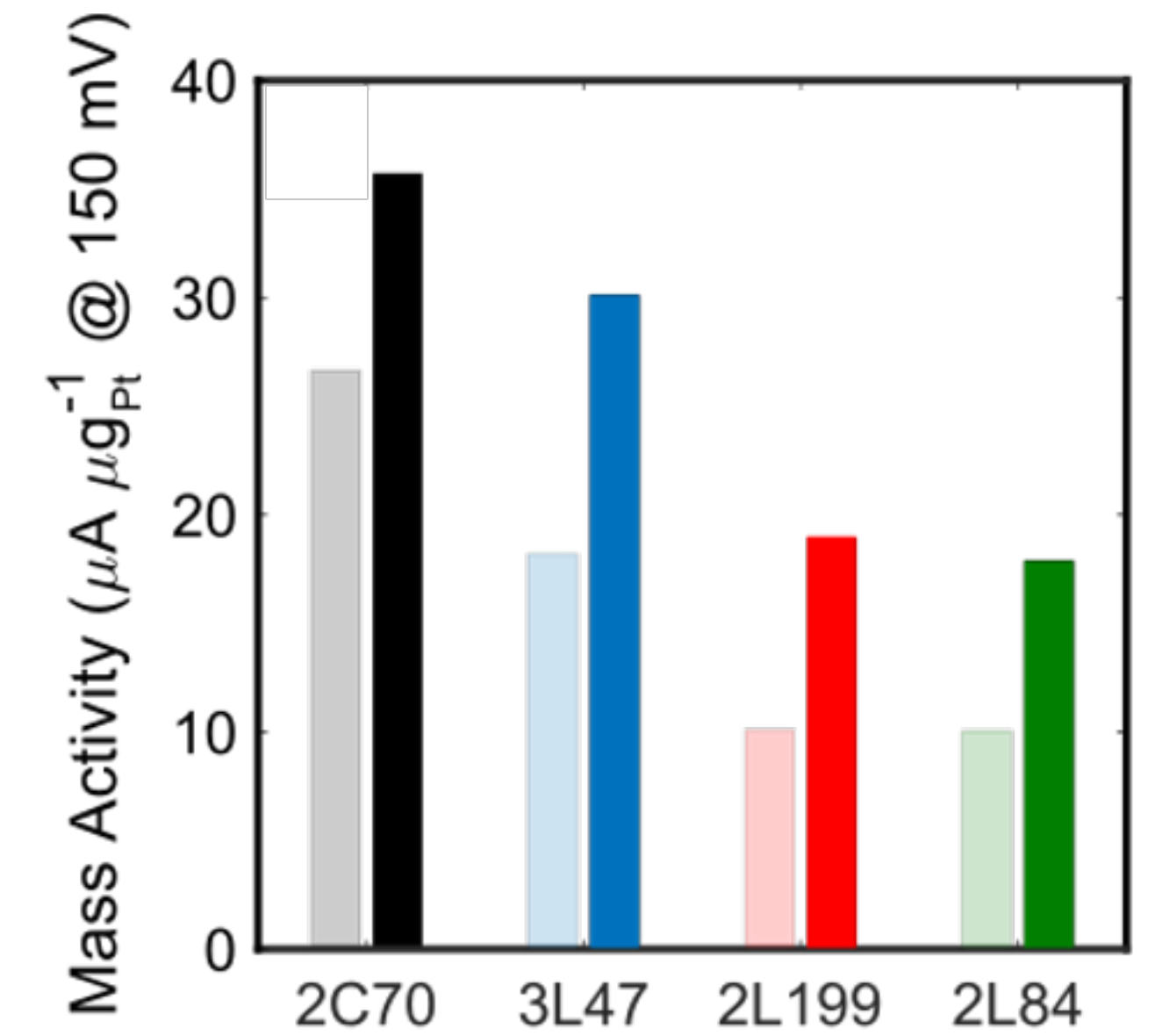
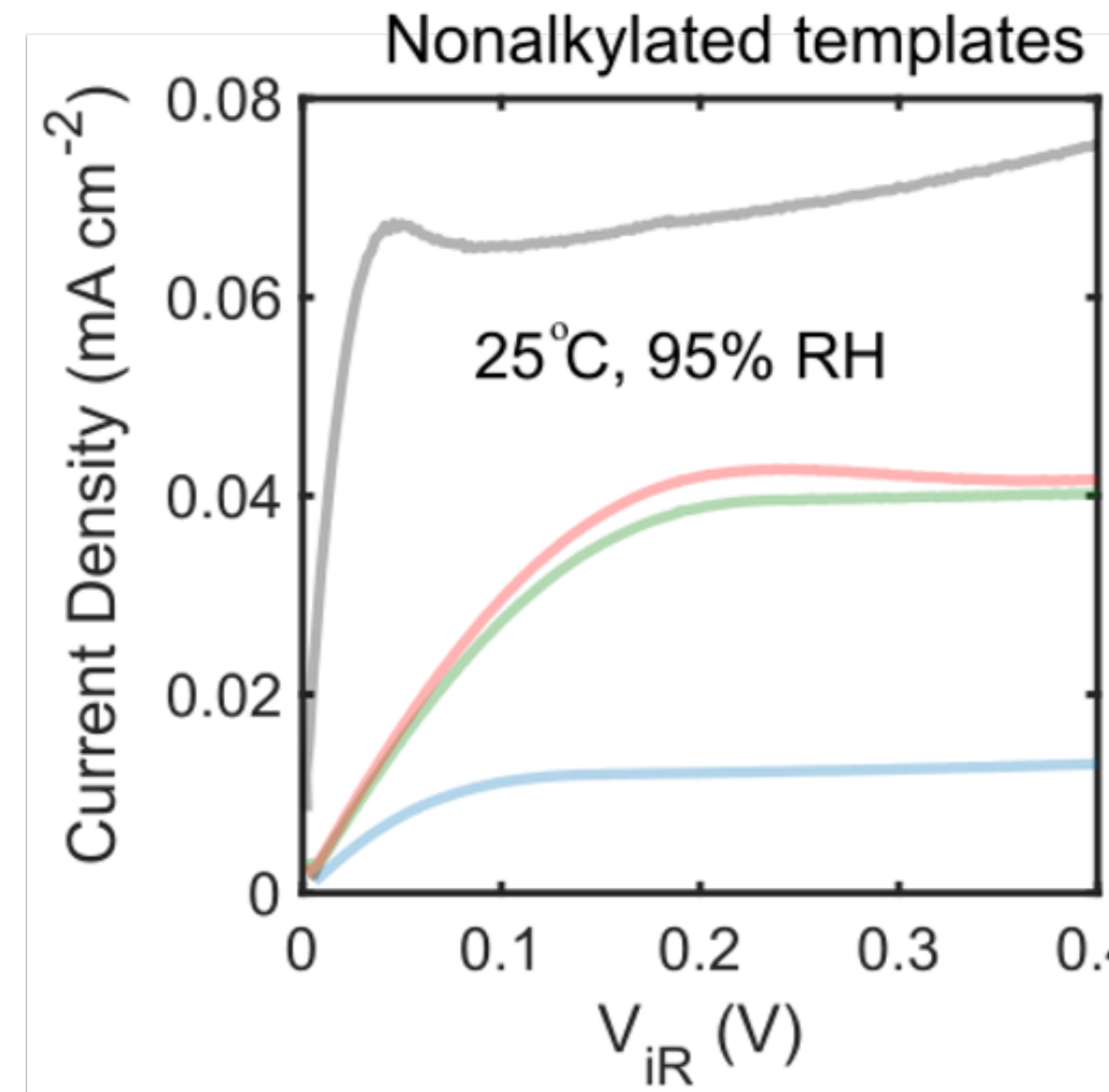
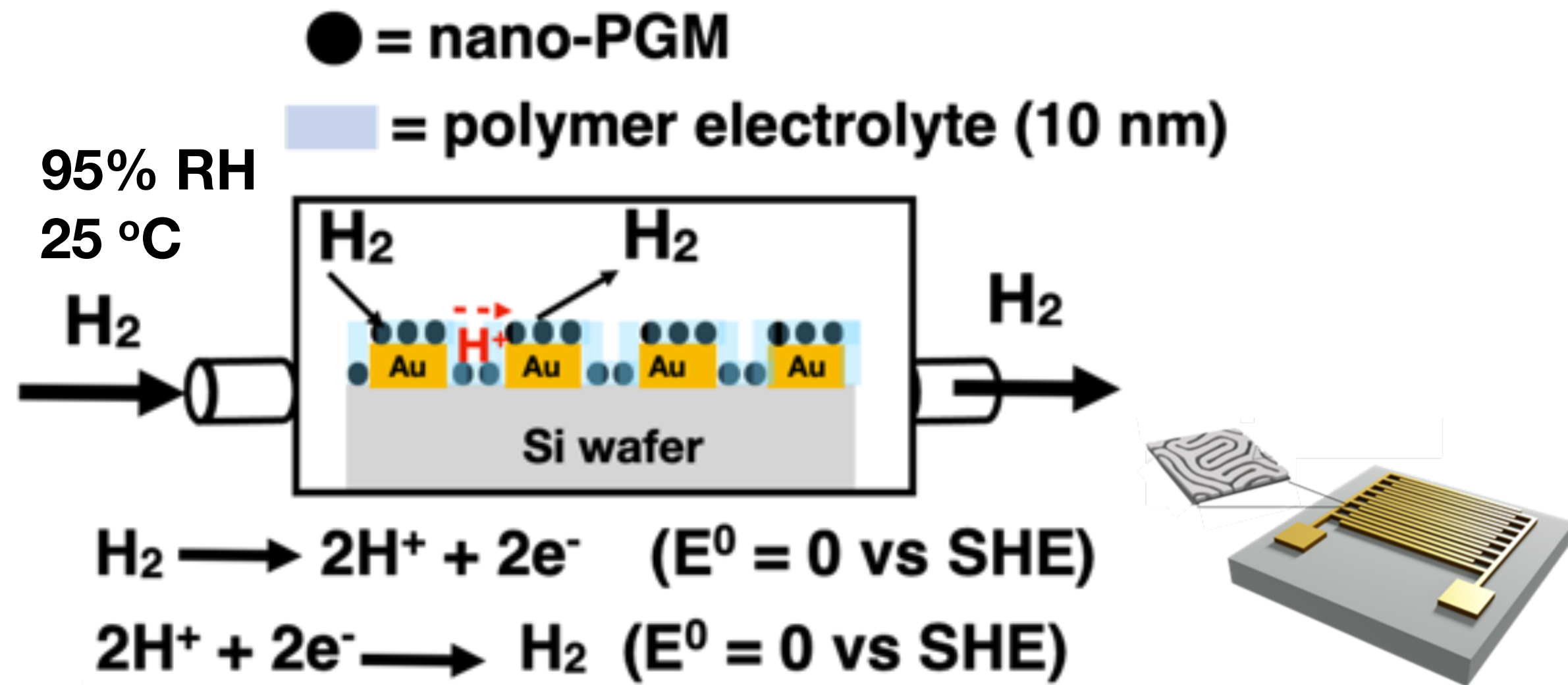
Droplet of 0.1 M HClO₄



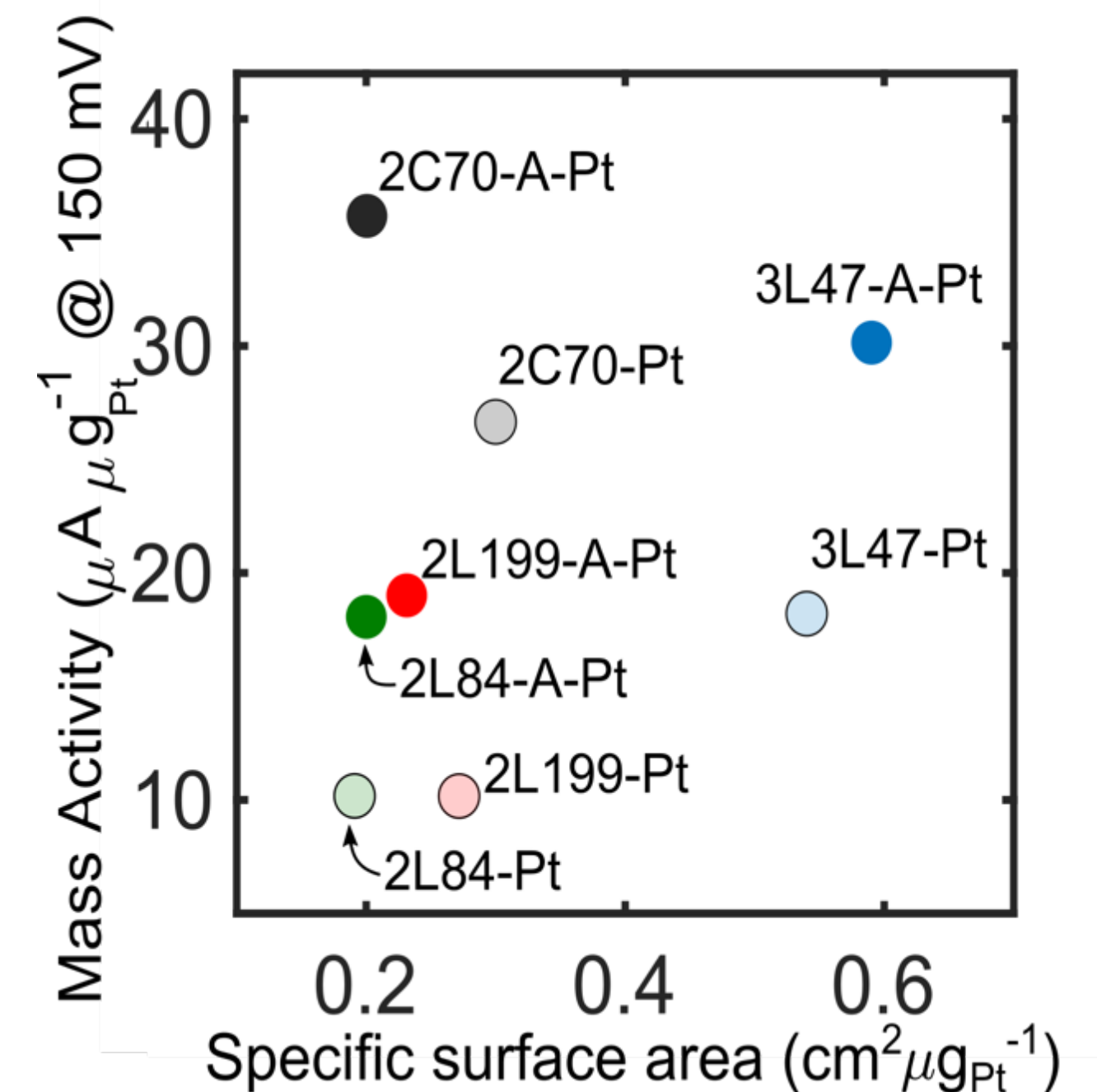
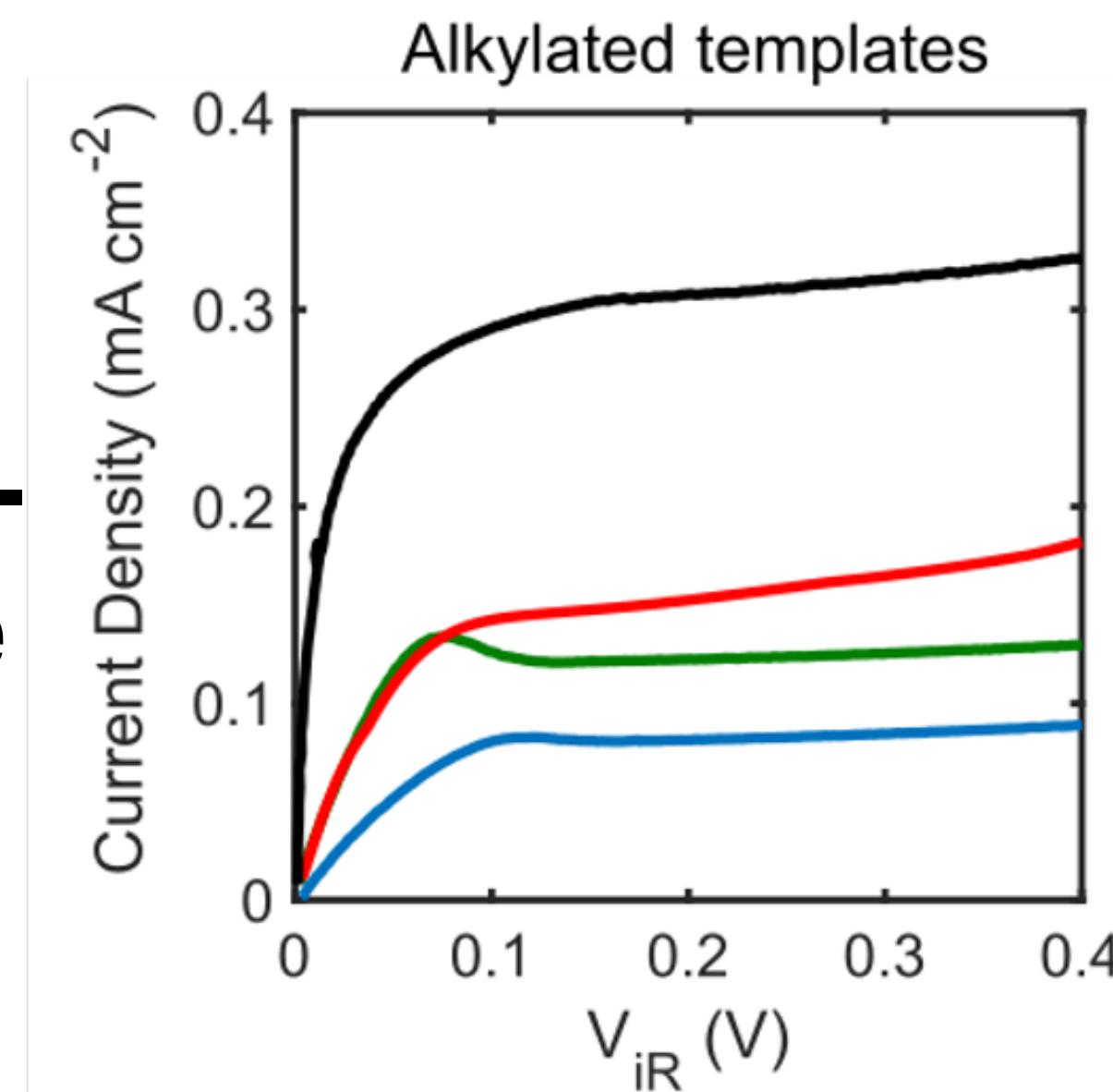
Differences in reactivity were observed depending on the PGM type



Hydrogen pump on IDEs with Nafion[®] thin films

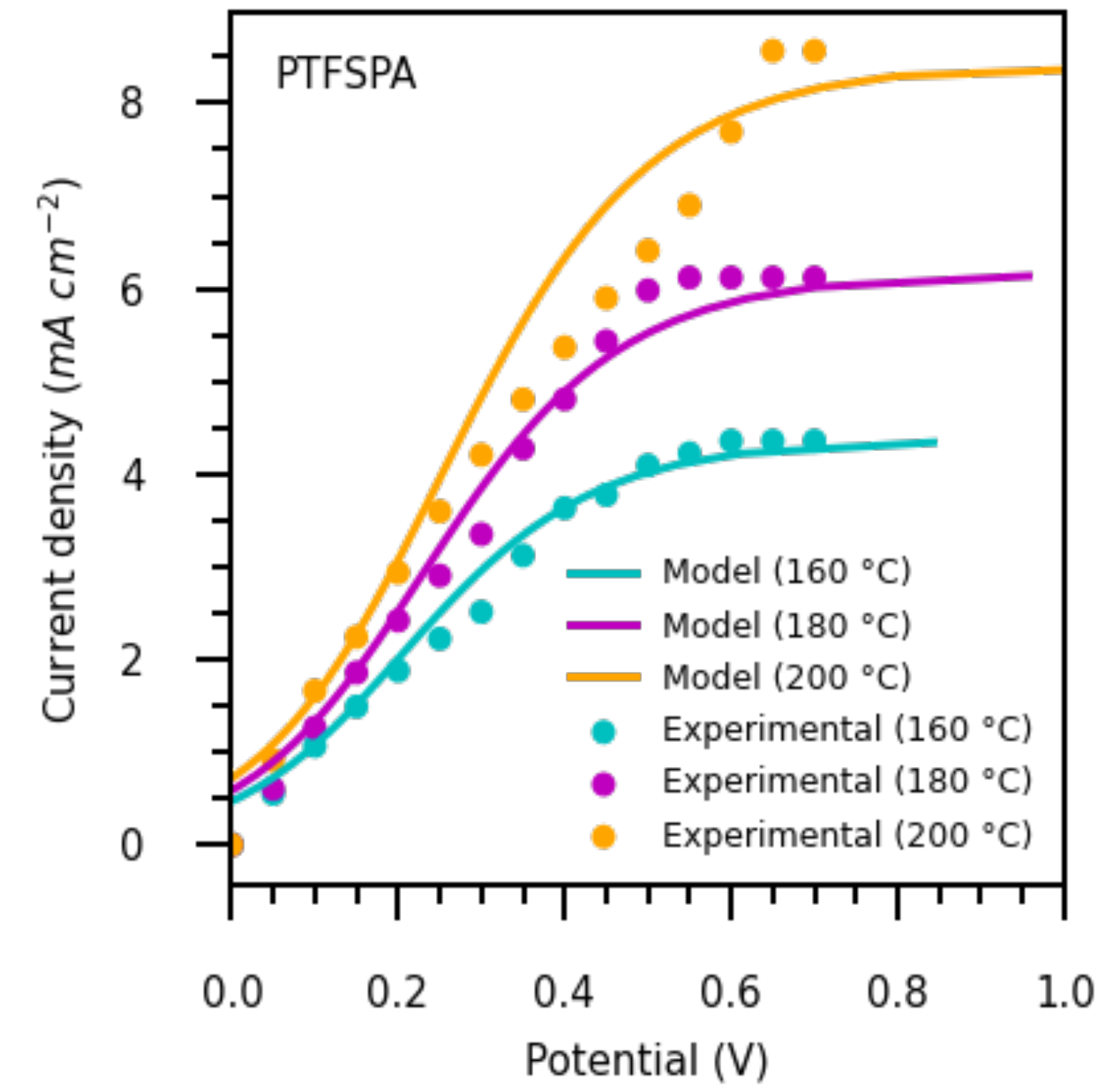
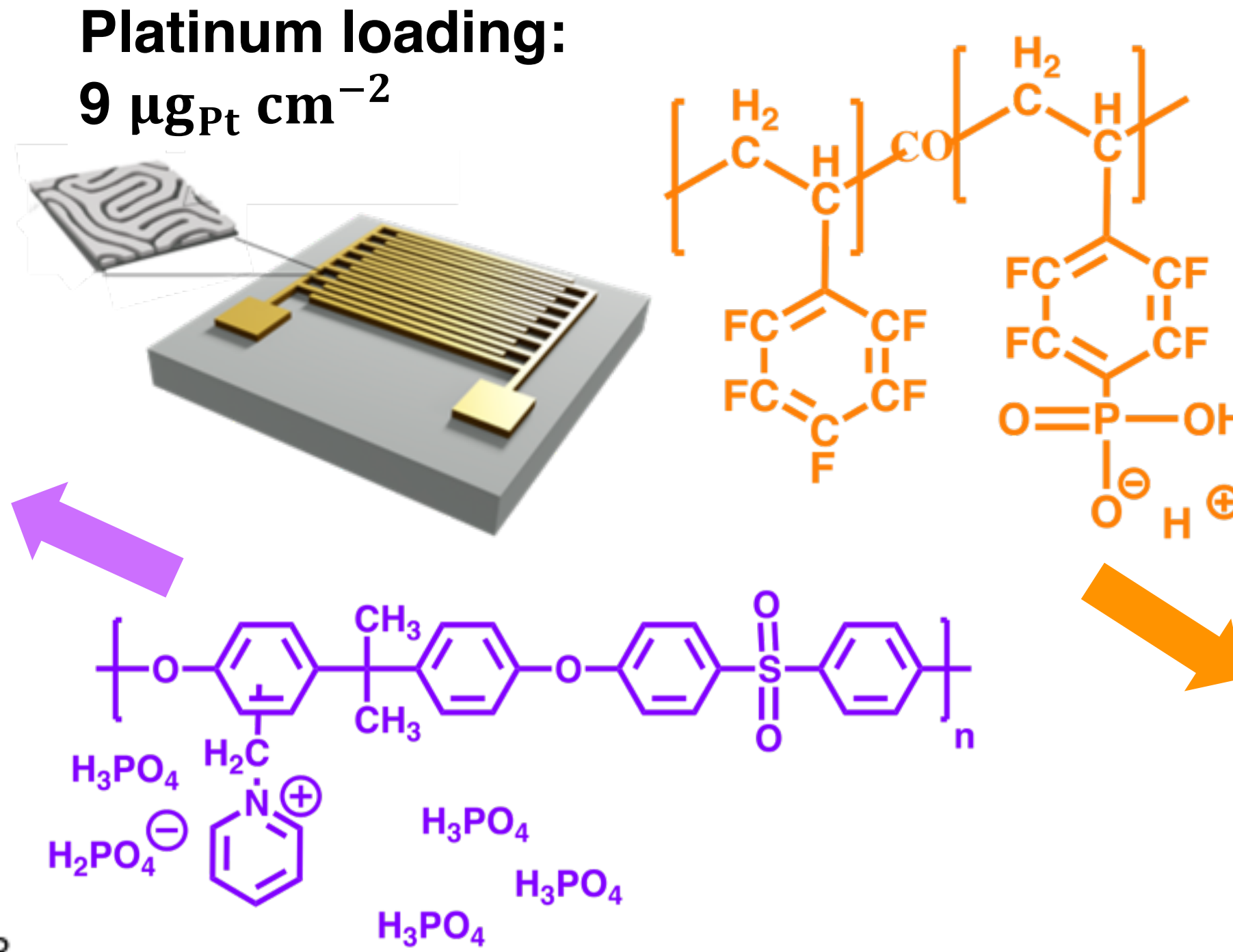
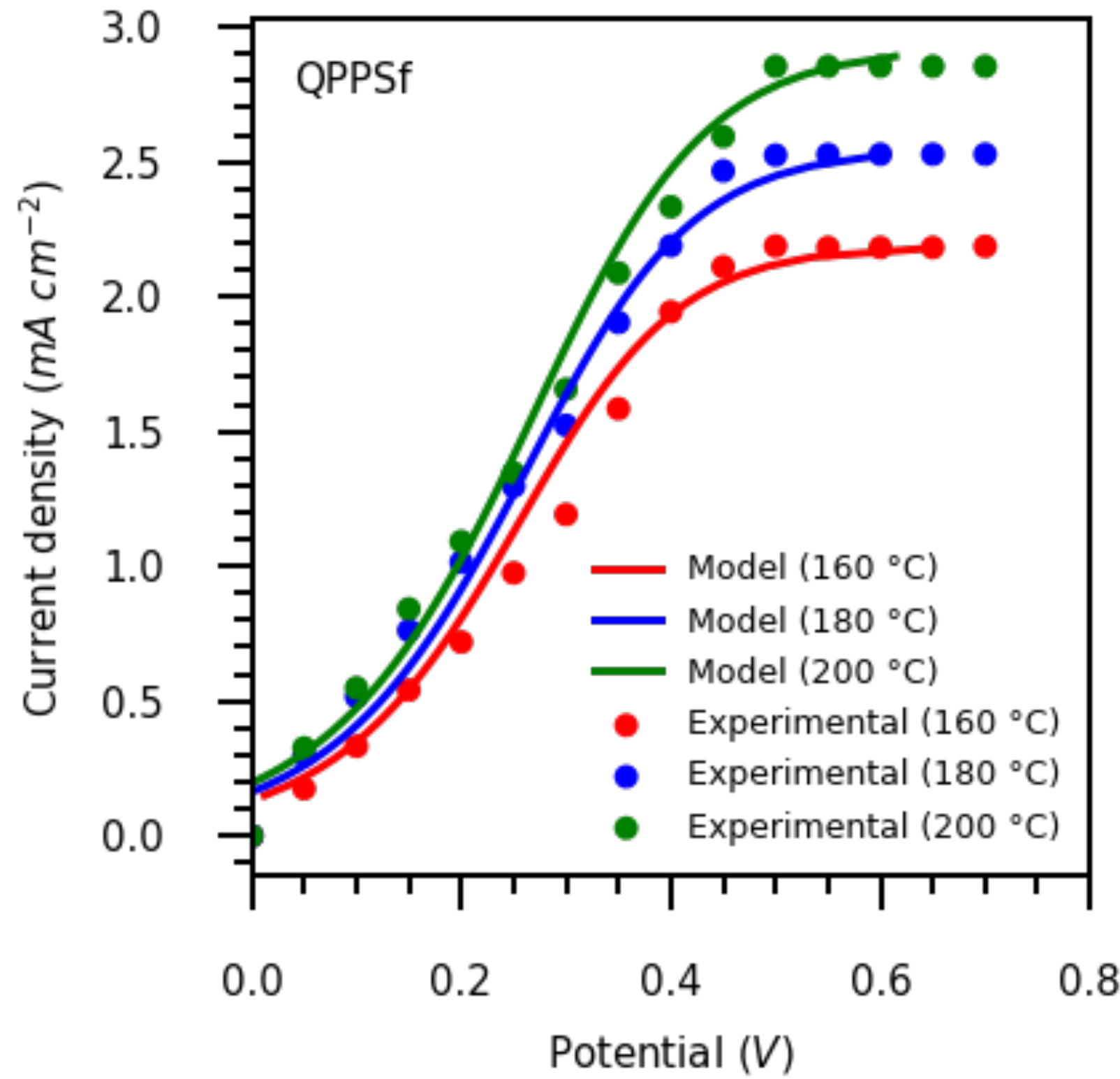


Reactivity differences between Pt meso-structures can be discerned



Using the IDE platform to assess how thin film polymer electrolytes affect reactant transport and HOR/HER kinetics

H₂ pump w/ high-temperature thin film polymer electrolytes on IDEs



$$E(i) = E_o + \frac{RT}{(\alpha_{an} + \alpha_{ca})F} \ln\left(\frac{i}{i_0}\right) + i \left(\frac{\delta_{io}}{\kappa_{io}^+} \right) - B \left(\ln\left(1 - \frac{i}{i_{lim}}\right) \right)$$

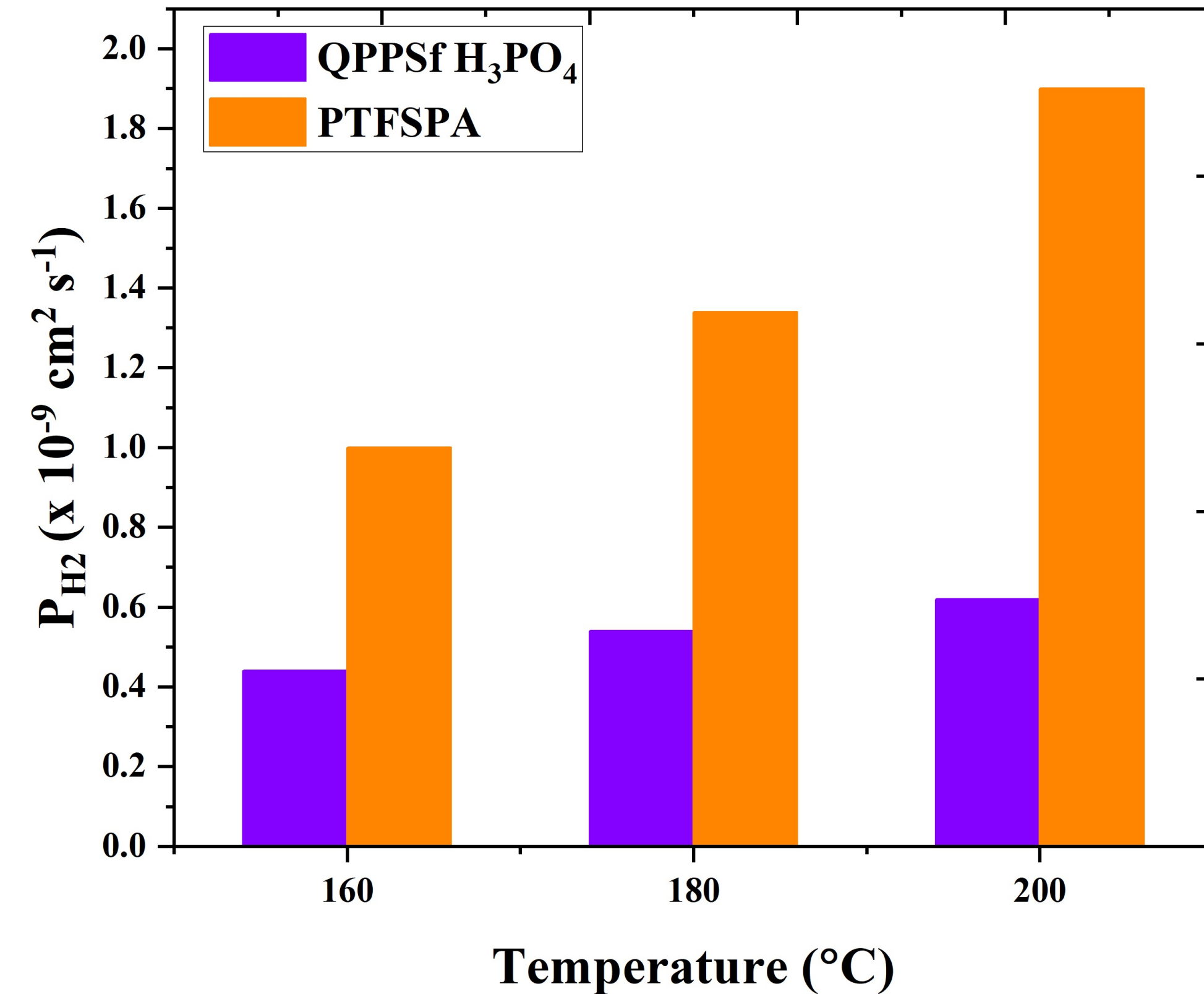
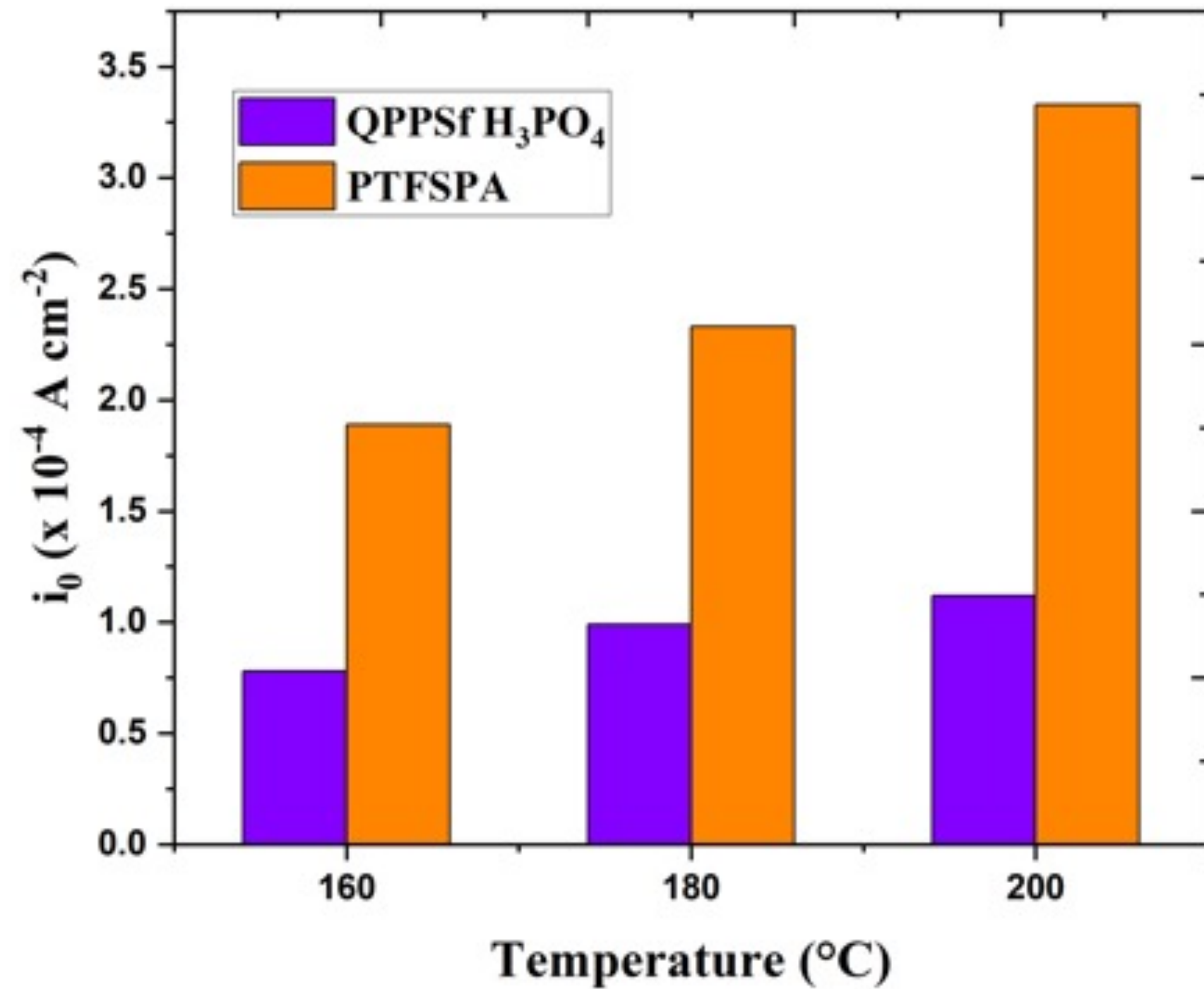
Thermo Rxn kinetics Ohmic Mass transfer

$$i_{lim} = nFP_{H_2} \frac{C_{H_2}}{\delta} \quad P_{H_2} = D_{H_2} H_{H_2}$$

Adjustable parameters
 γ , B , and i_{0-ref}

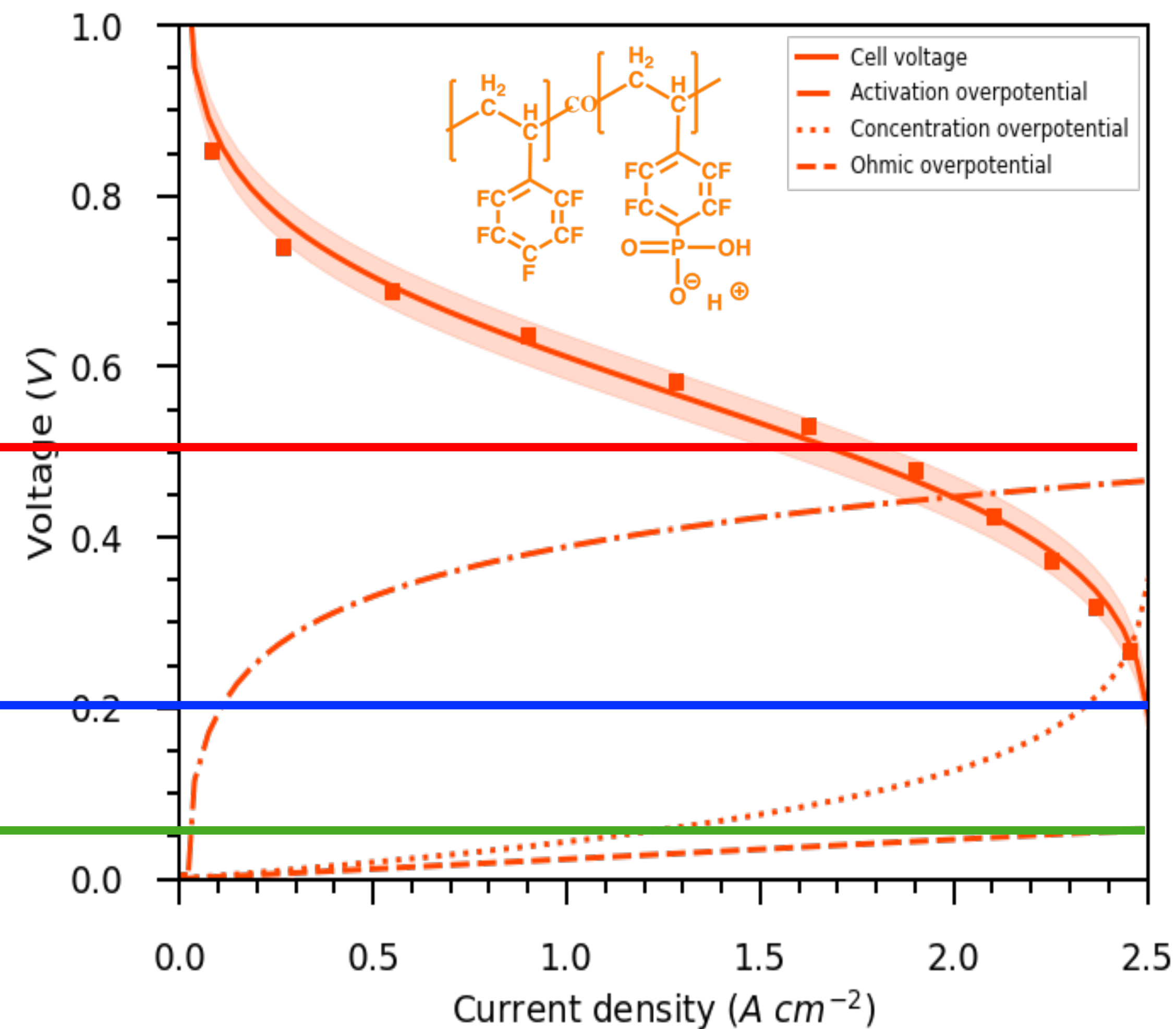
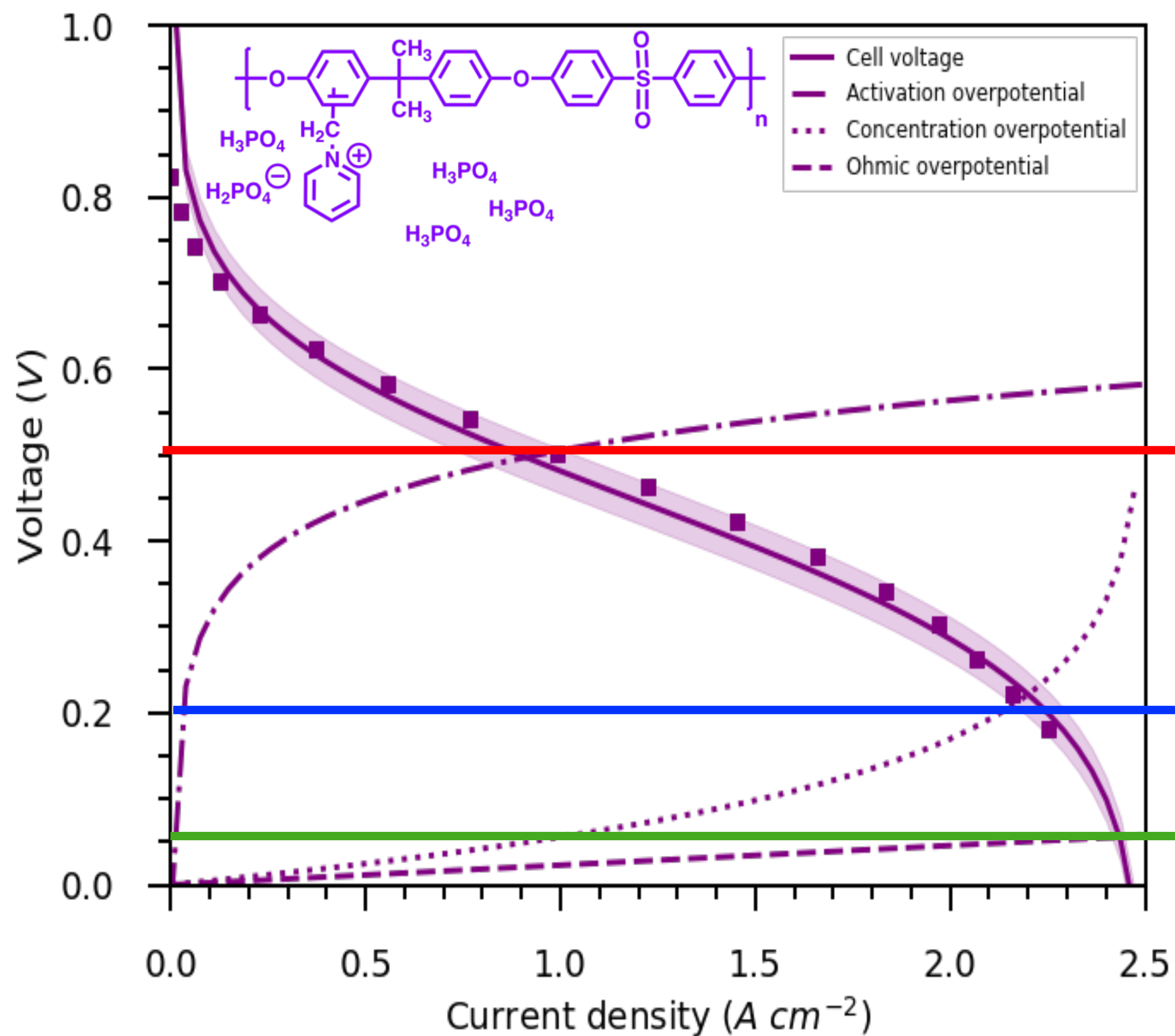
$$i_0 = a_c L_c \left(\frac{C_{H_2} H_{H_2}}{C_{H_2}^0} \right)^{0.5} \exp\left(-\frac{E_C^{H_2}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}^0} \right) \right) i_{0-ref} \exp(-\gamma(1 - m_{io}))$$

H₂ pump with HT-ionomer thin films on IDEs



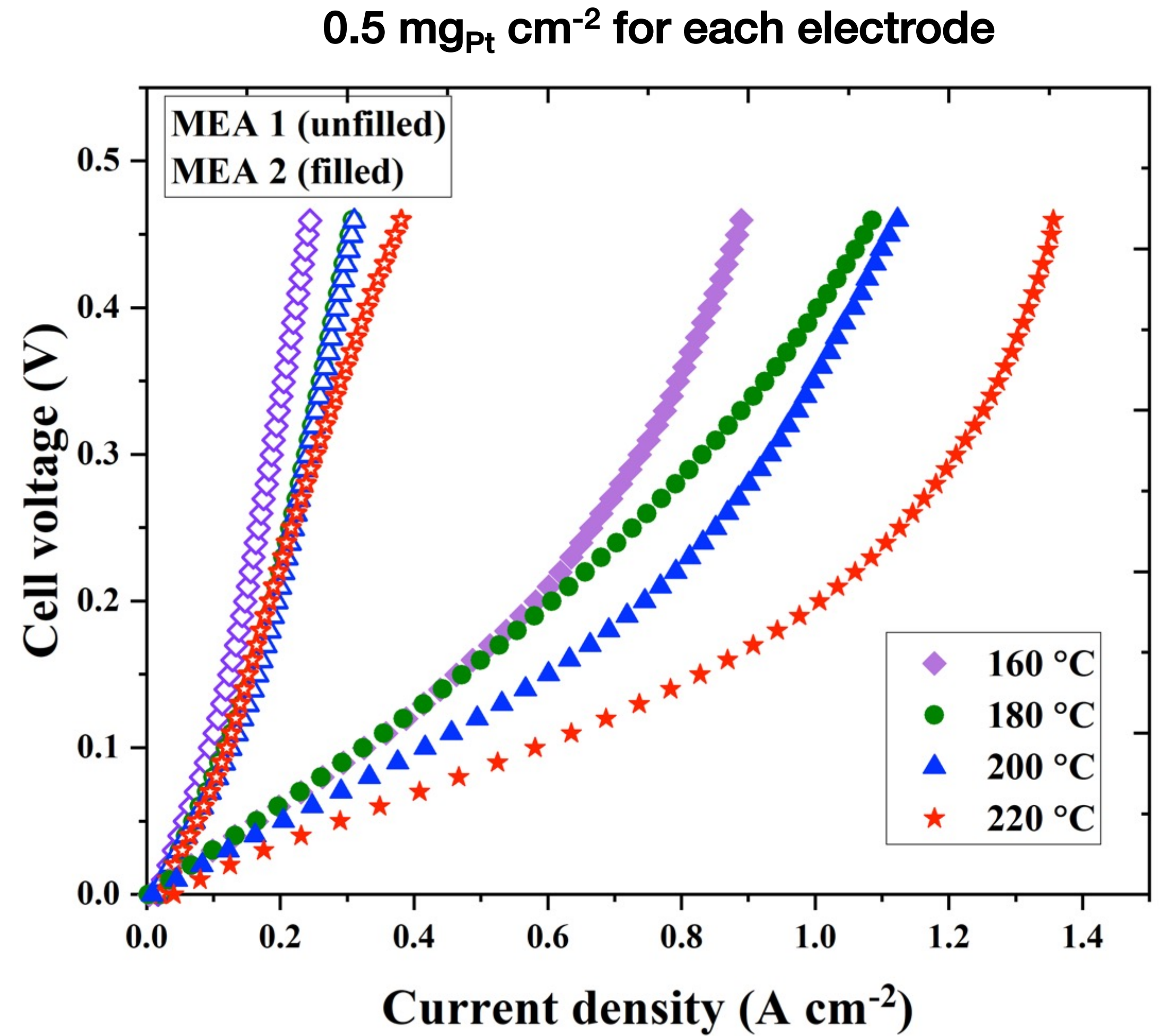
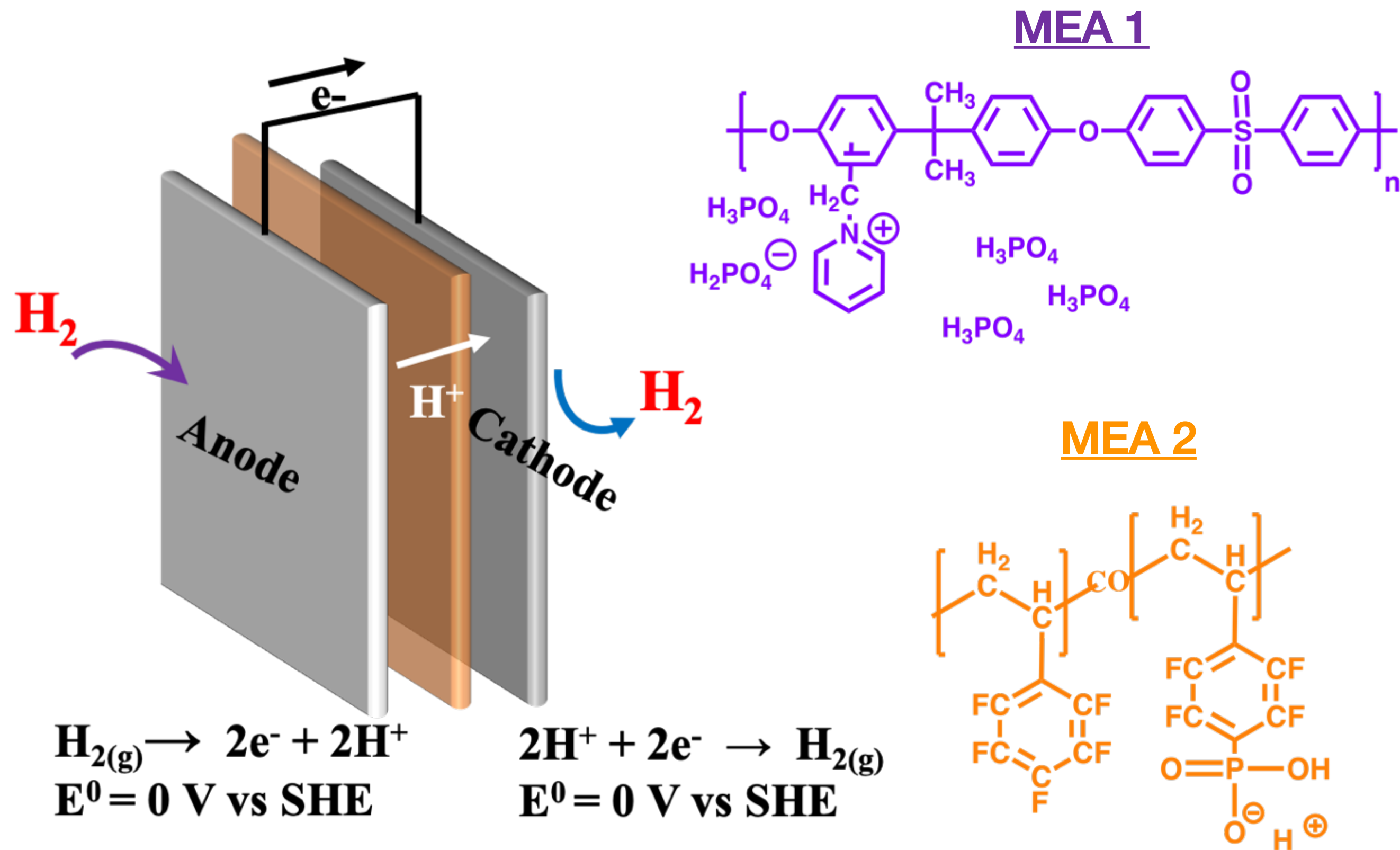
Removal of H₃PO₄ enhances reaction kinetics and gas permeability

IDE data for informing fuel cell polarization

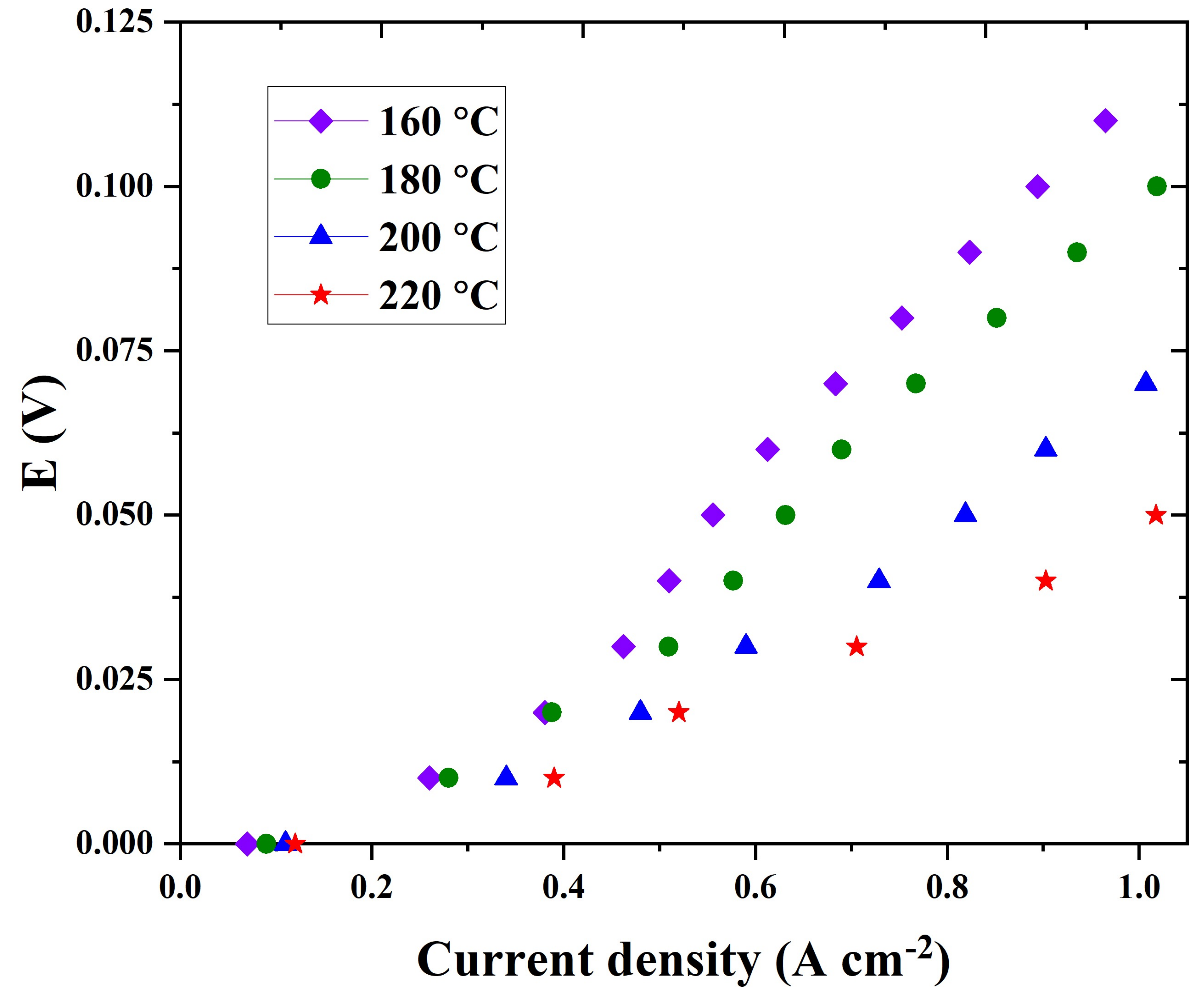
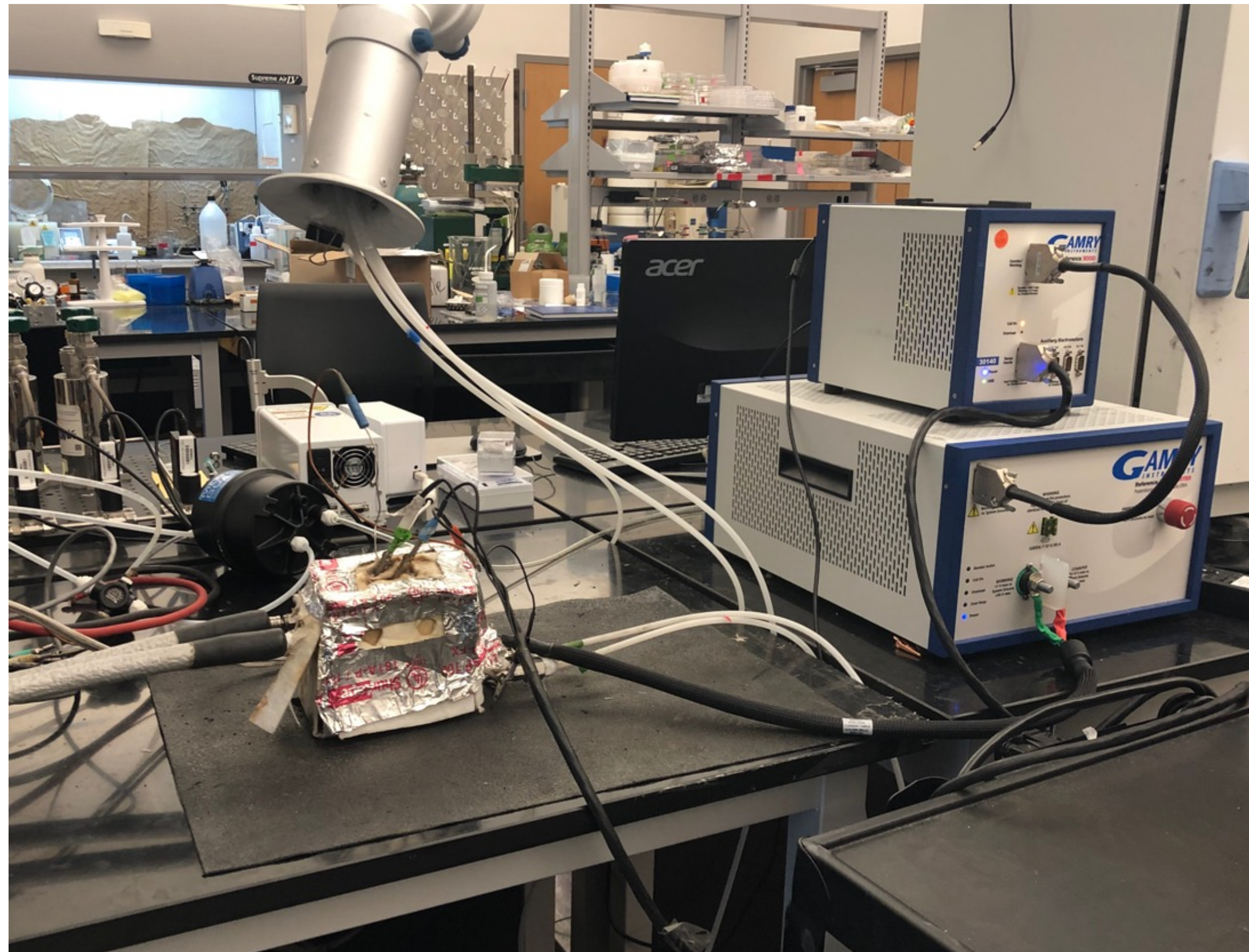


Adjustable parameters γ and B

Membrane electrode assembly (MEA) H₂ pump data with different binders

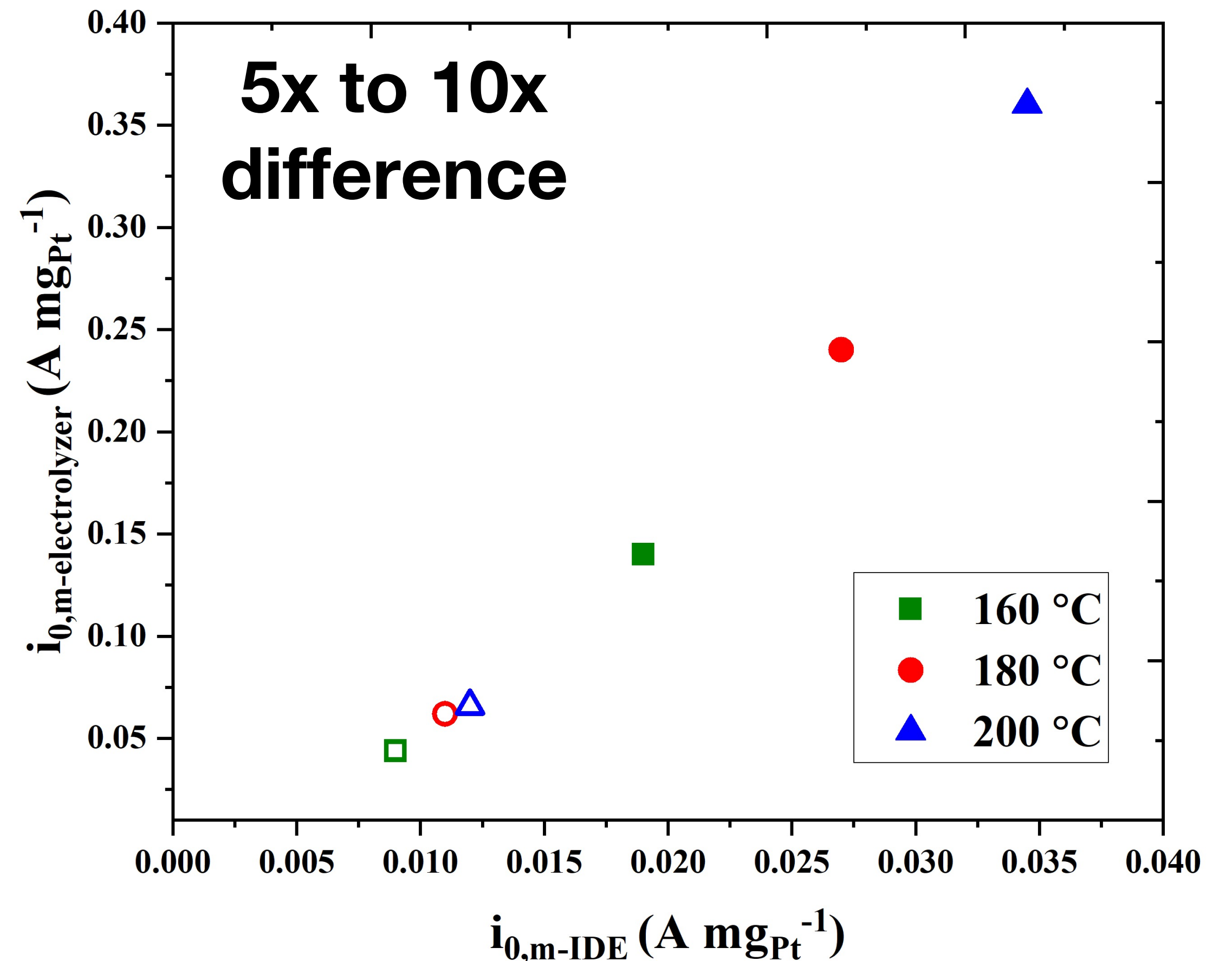
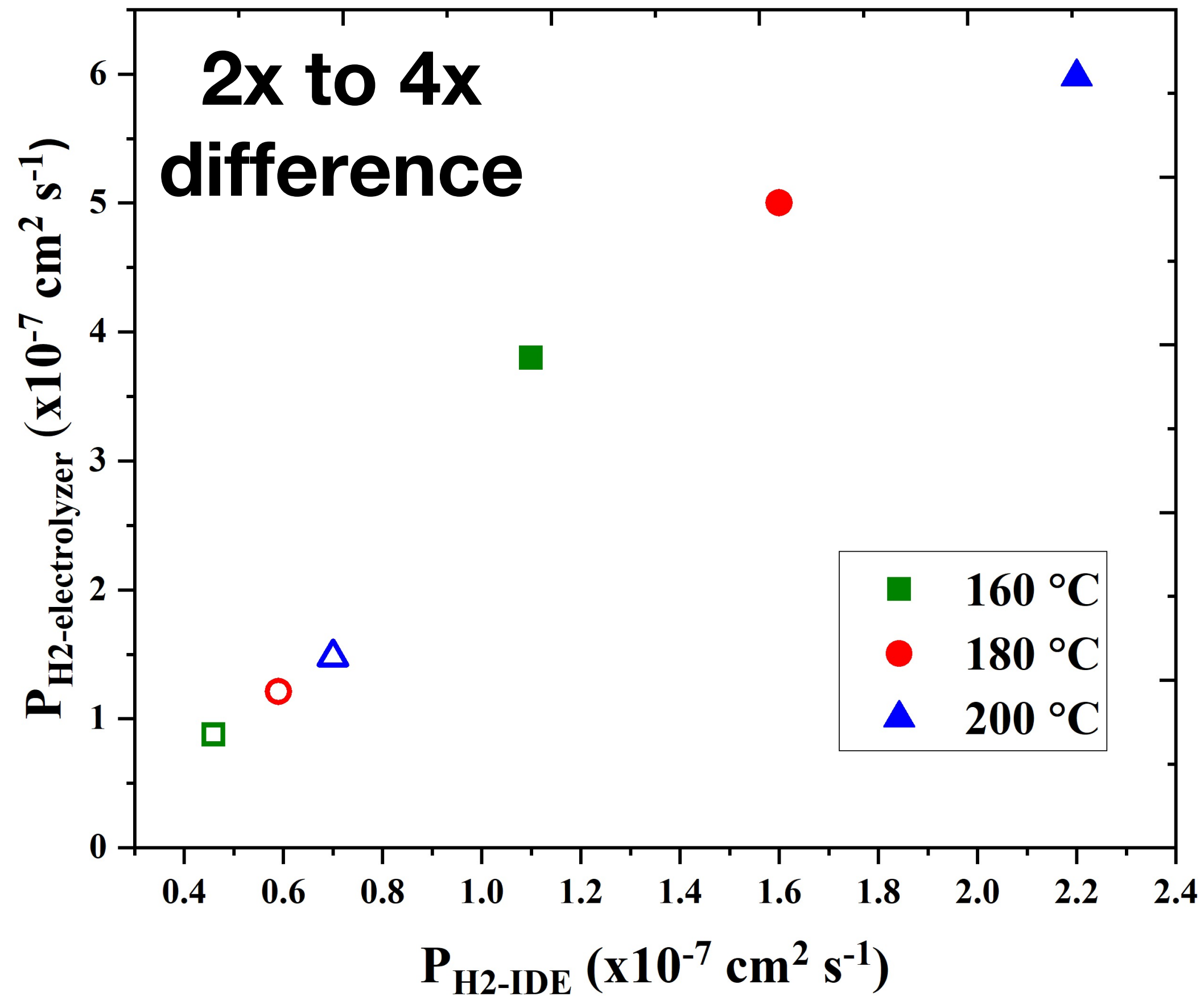


Best HT-PEM H₂ pump data



1 A cm⁻² at 50 mV

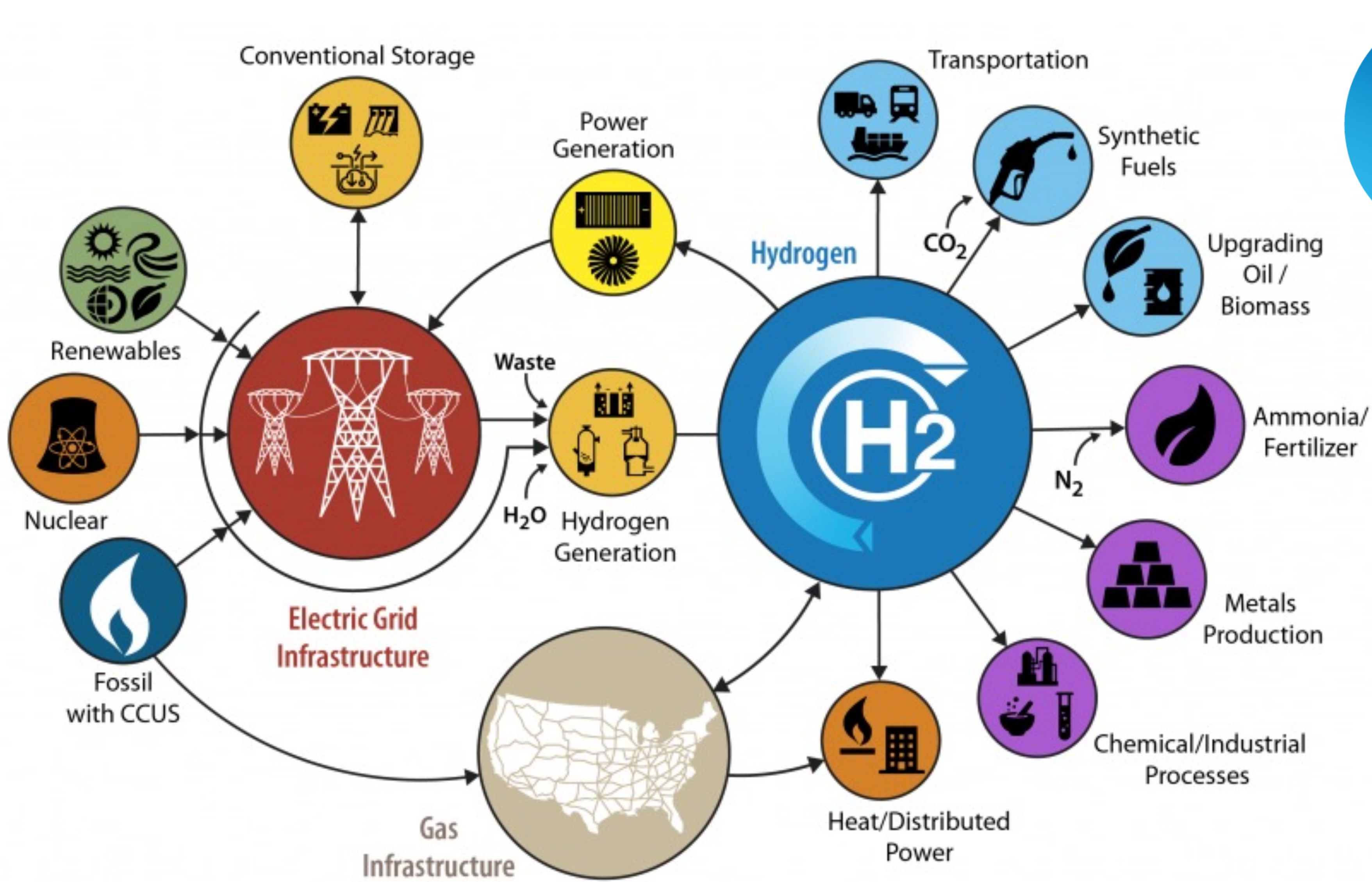
Correlating IDE data to MEA H₂ pump data



IDEs are a high-throughput, cost-effective platform for downselecting electrode ionomer binders for MEAs.

They use 100x less PGM, a small amount of binder, and do not require a bulk membrane and cell testing hardware.

Broader use of hydrogen in the U.S. economy: H₂@Scale



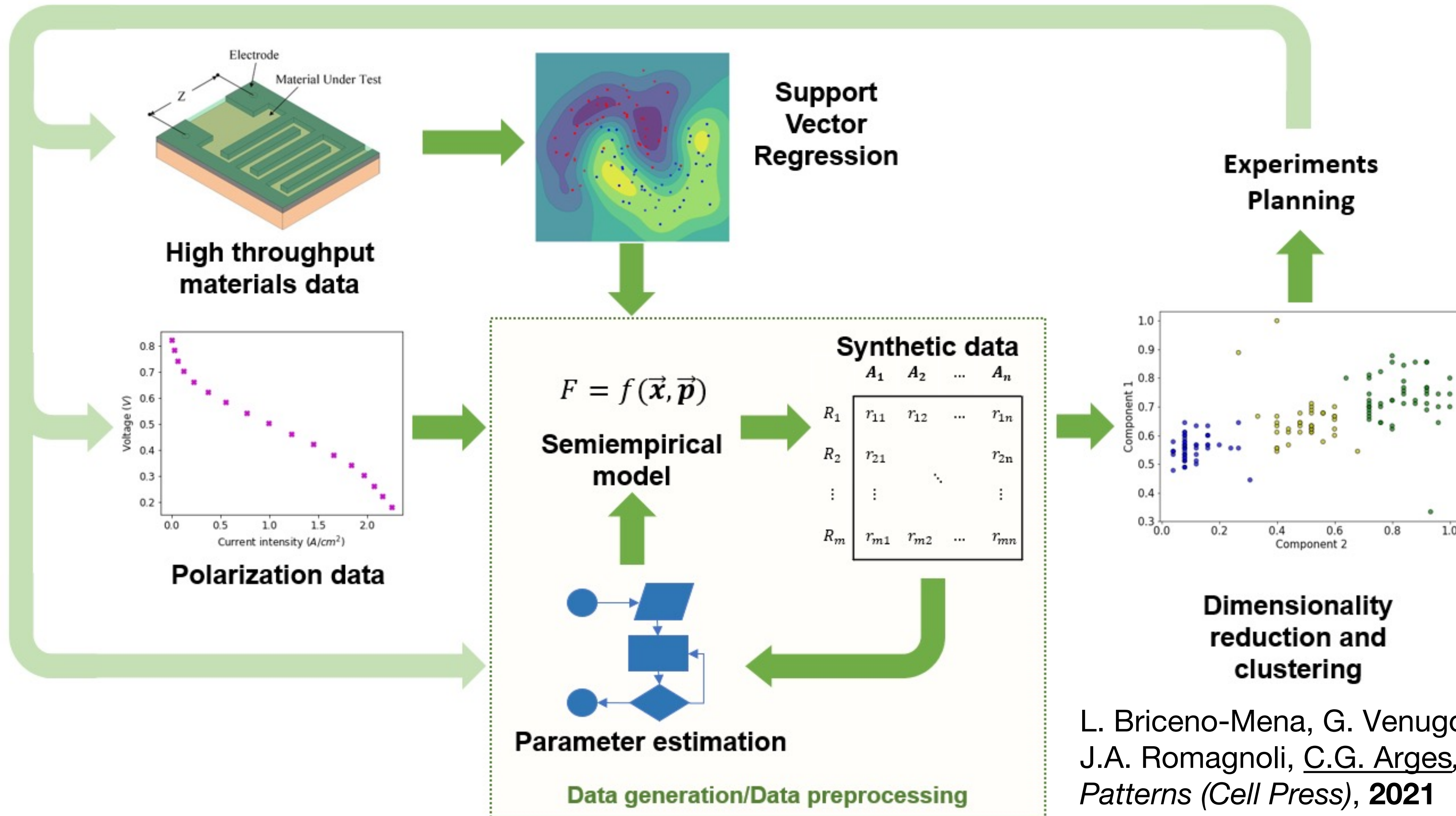
Presentation overview

High-temperature polymer electrolyte membranes (HT-PEMs) and binders for fuel cells

Studying the electrochemical properties of electrode ionomer binders as thin films

Future directions and concluding remarks

Machine Learning (ML) & data framework analysis approach



Luis Briceno-Mena
PhD candidate



Prof. José Romagnoli

L. Briceno-Mena, G. Venugopalan, J.A. Romagnoli, C.G. Arges, *Patterns (Cell Press)*, 2021

Goal: Use ML to identify material properties and cell operating parameters for optimizing power constrained to 68% fuel efficiency and $0.3 \text{ mg}_{\text{PGM}} \text{ cm}^{-2}$ in the MEA

Concluding remarks

Model thin films of electrocatalysts and polymer electrolytes are useful for establishing structure-property relationships and generating a large library of materials data.

This is important for the rationale design of electrodes that enable high performing fuel cell and electrolysis units as well as the development of Machine Learning (ML) tools that bridge materials properties to cell level performance.

Acknowledgements



Postdocs and Graduate students

Mario Ramos-Garcés (Postdoc)
Matthew Jordan
Gokul Venugopalan
Varada Palakkal (PhD 2020)
Le Zhang (MS 2018)

Subarna Kole
Deepra Bhattacharya
Qi Lei (MS 2020)
Luis Briceno-Mena
(advised by Prof. José Romagnoli)



U.S. DEPARTMENT OF
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Renewable Energy
ADVANCED MANUFACTURING OFFICE

Award # DE-EE0009101



Yu Seung Kim



Hongfei Jia

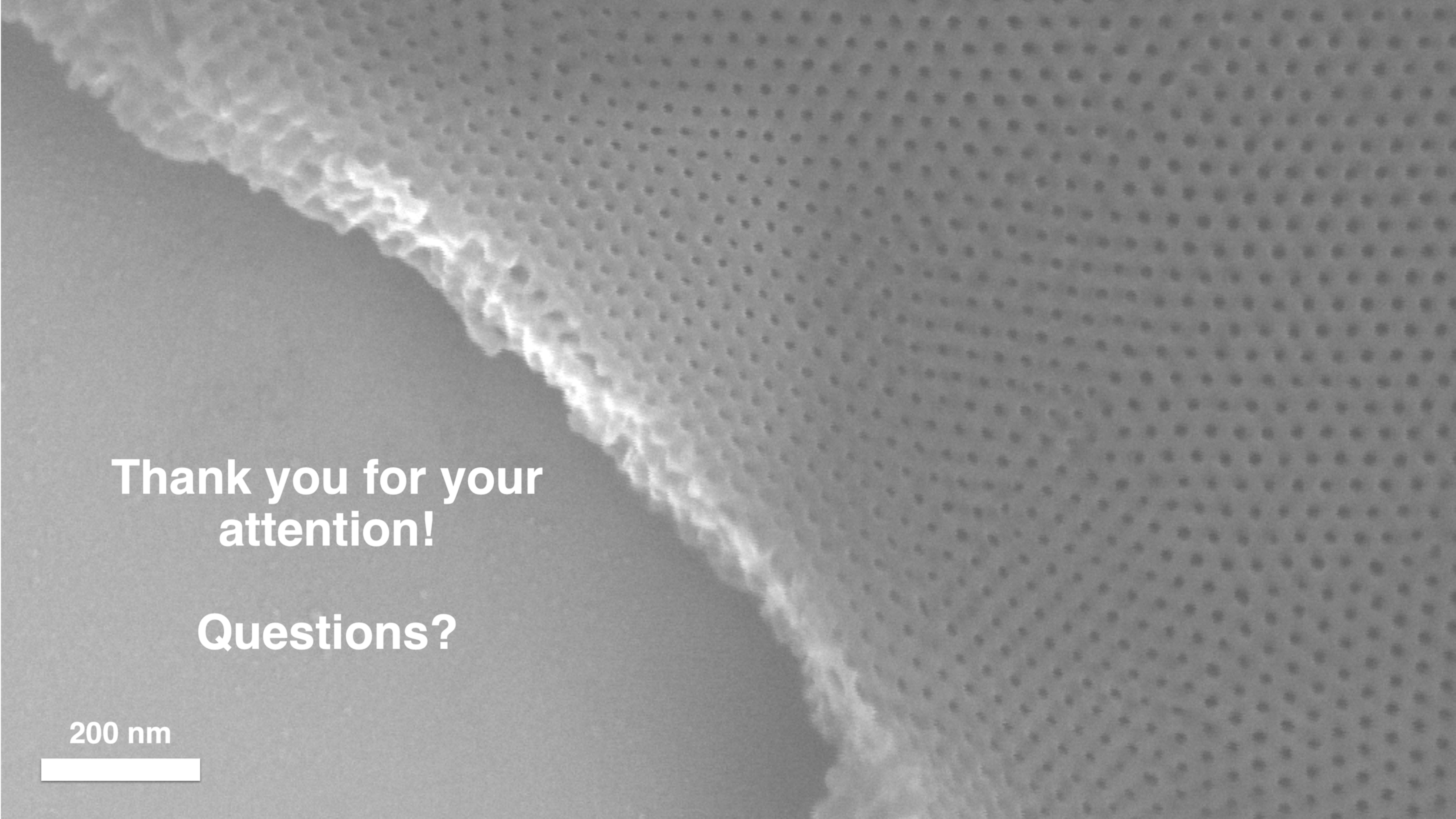


Bamdad Bahar



**Advanced
Photon
Source**

Joe Strzalka (ANL)



**Thank you for your
attention!**

Questions?

200 nm



H₃PO₄ doped PBI is commercial and mature

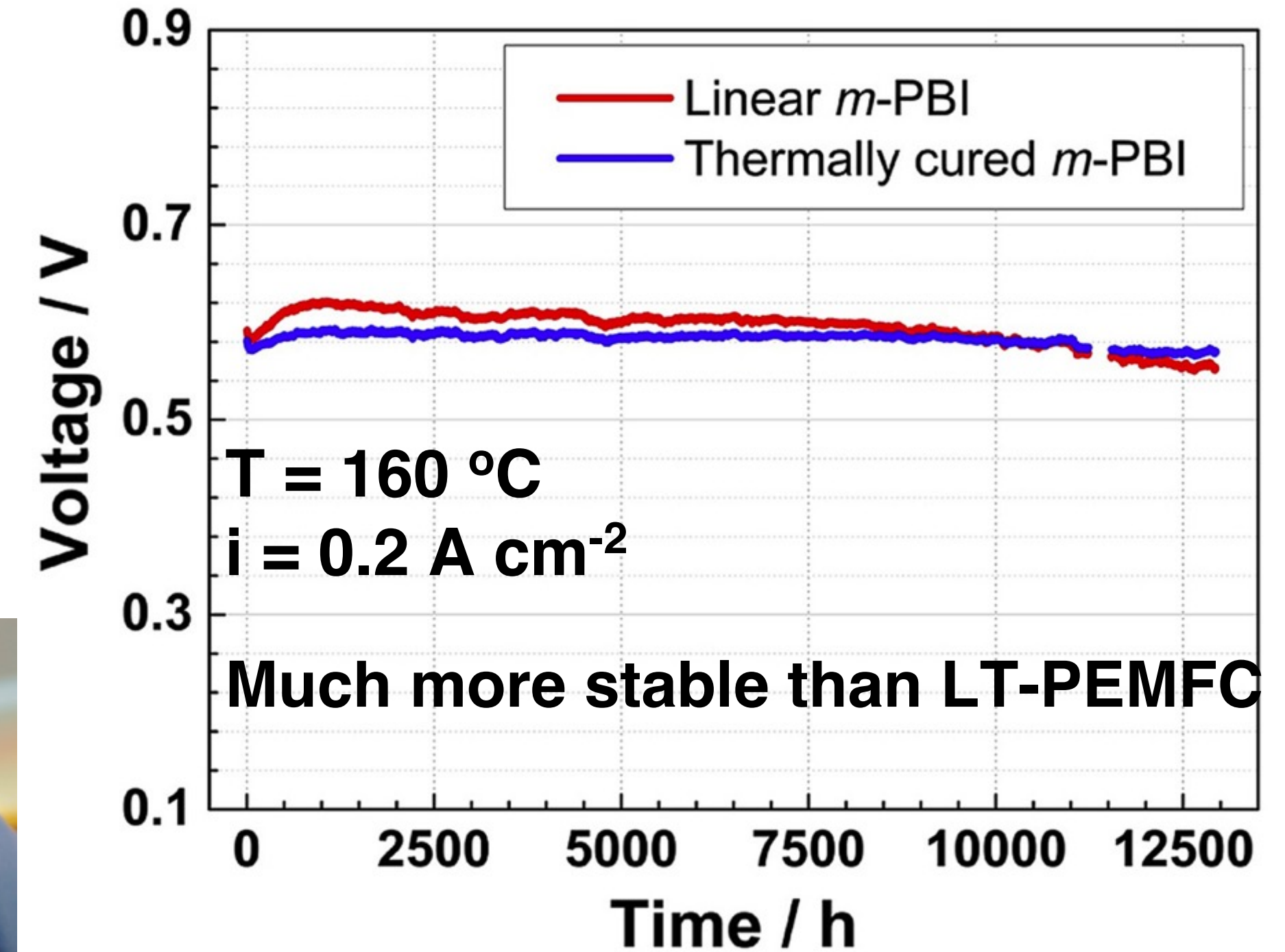
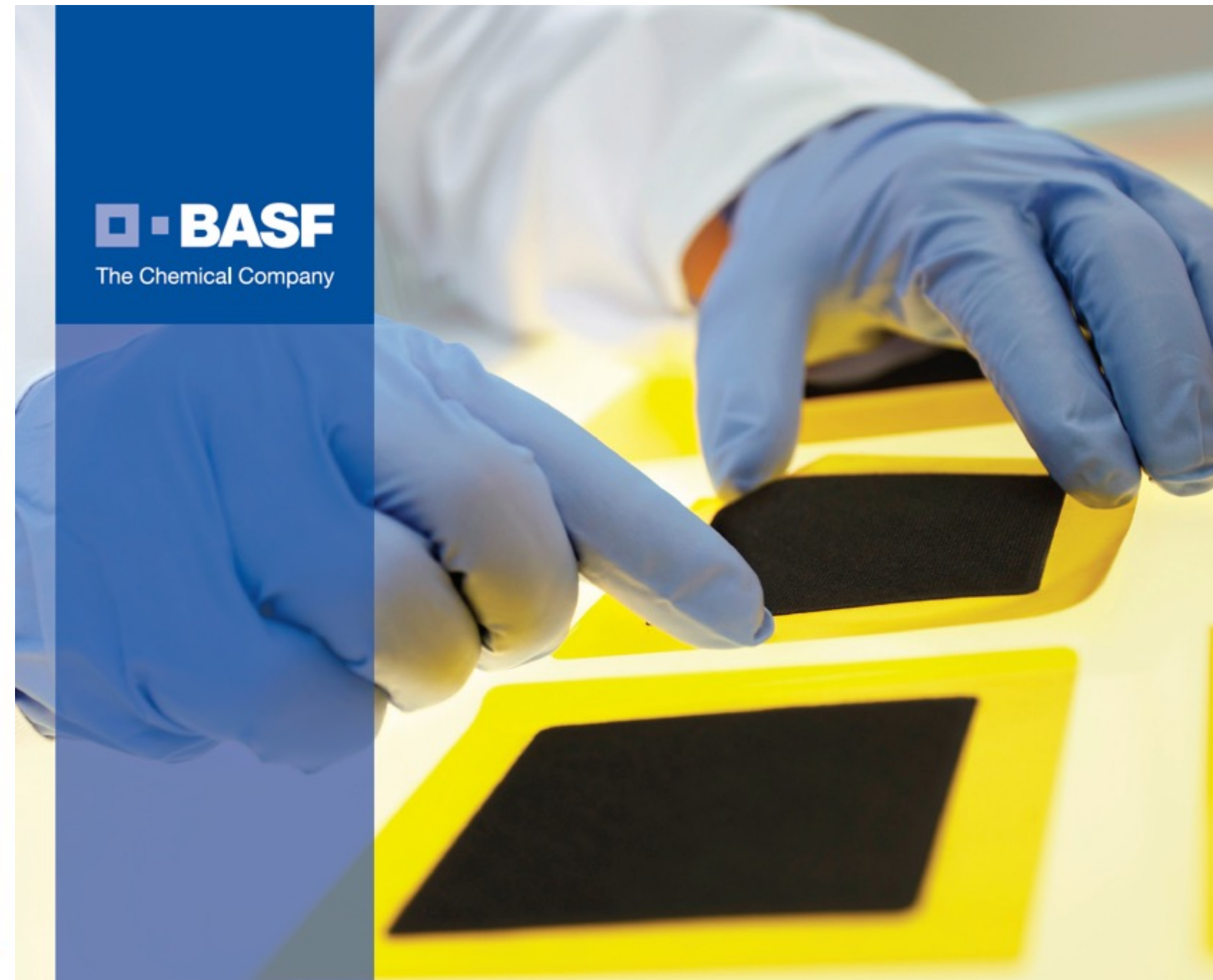
Acid-Doped Polybenzimidazoles: A New Polymer Electrolyte

J. S. Wainright,^{*,a} J-T. Wang,^a D. Weng,^a R. F. Savinell,^{*,a} and M. Litt^b

^a Department of Chemical Engineering and ^b Department of Macromolecular Science and Engineering,
E. B. Yeager Center for Electrochemical Sciences, Case Western Reserve University, Cleveland, Ohio 44106-7217, USA

J. Electrochem. Soc. 1995

BASF Celtec®

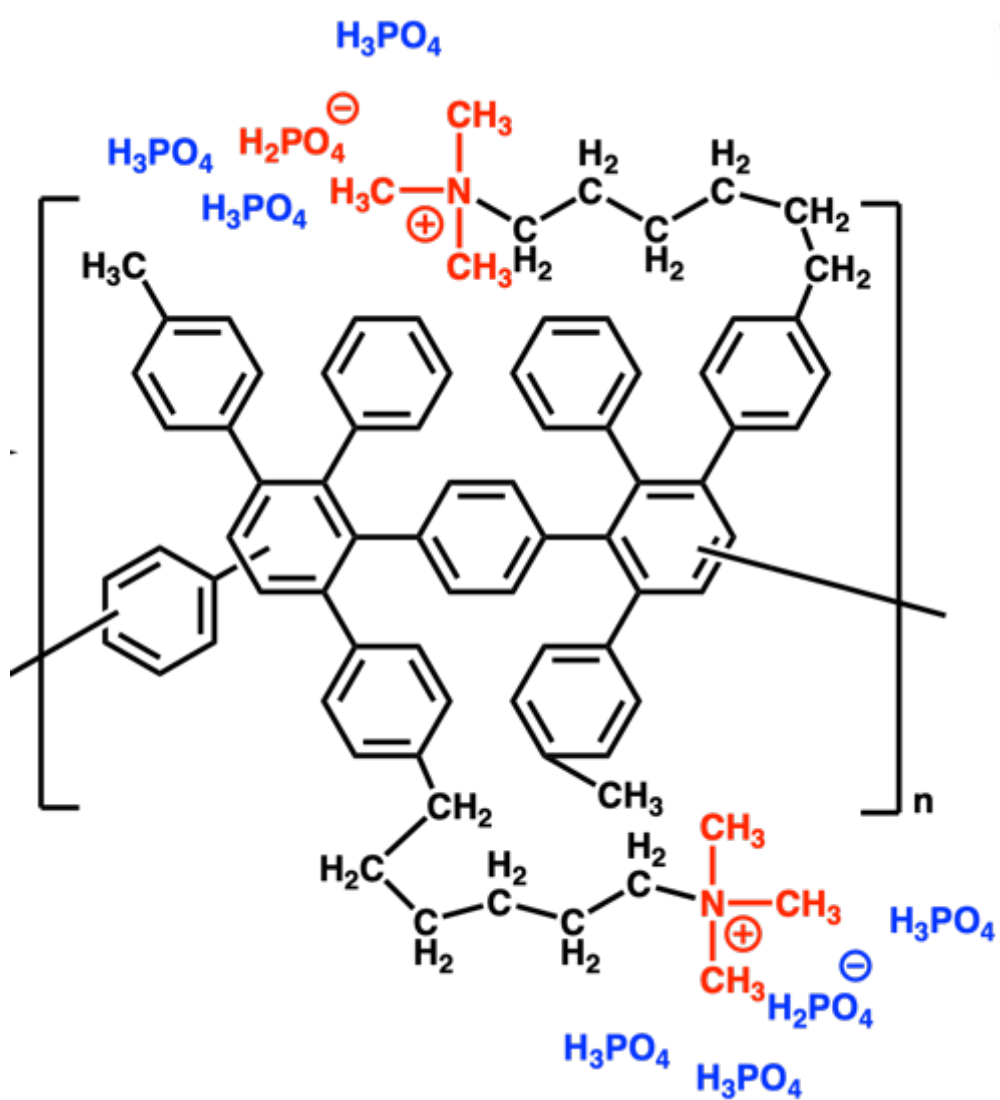
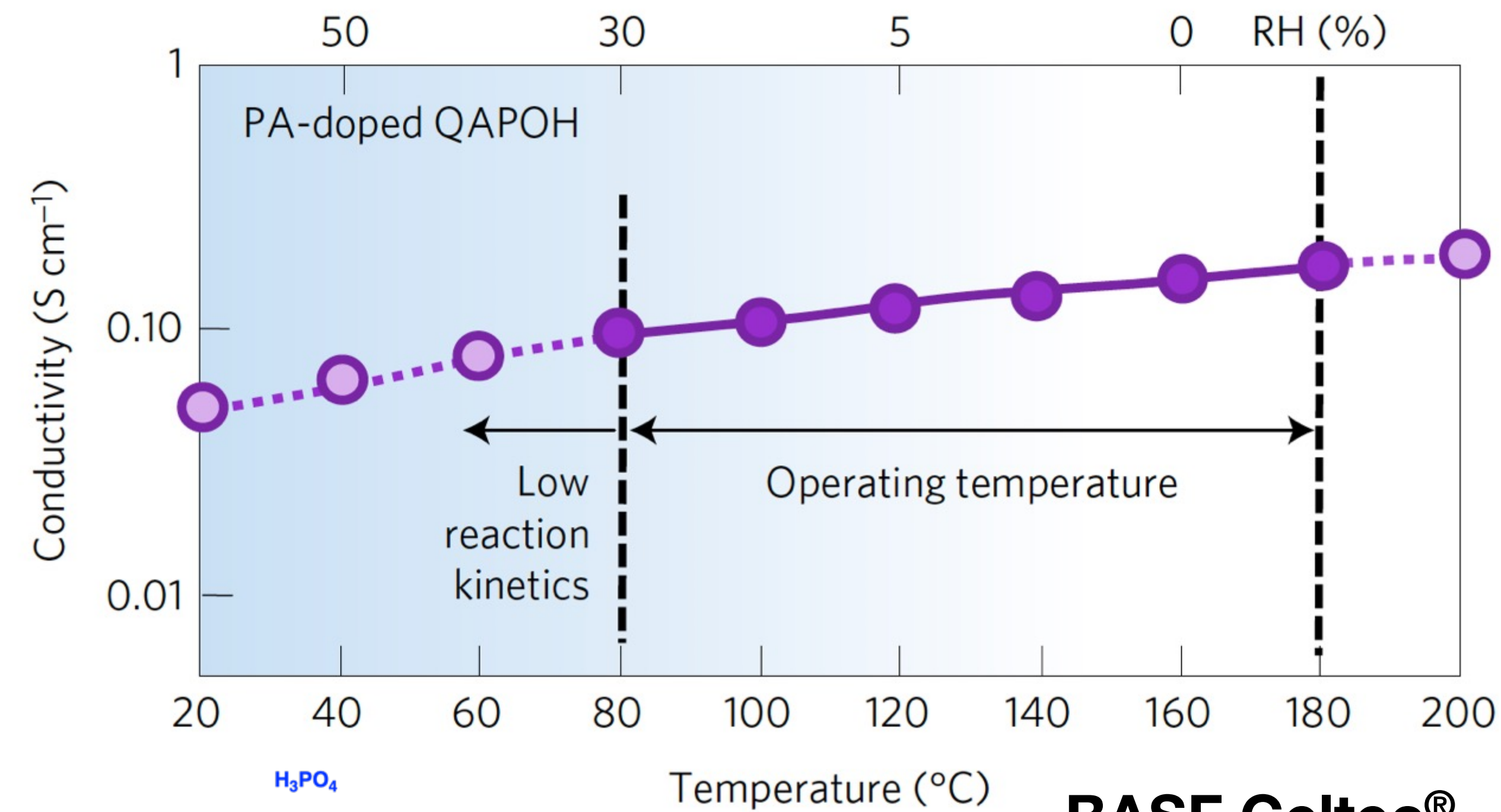


Other limitations of PBI

- Cells use +1 mg_{Pt} cm⁻² (large Pt loadings)
- Low power (400 mW cm⁻² w/ H₂ & air)

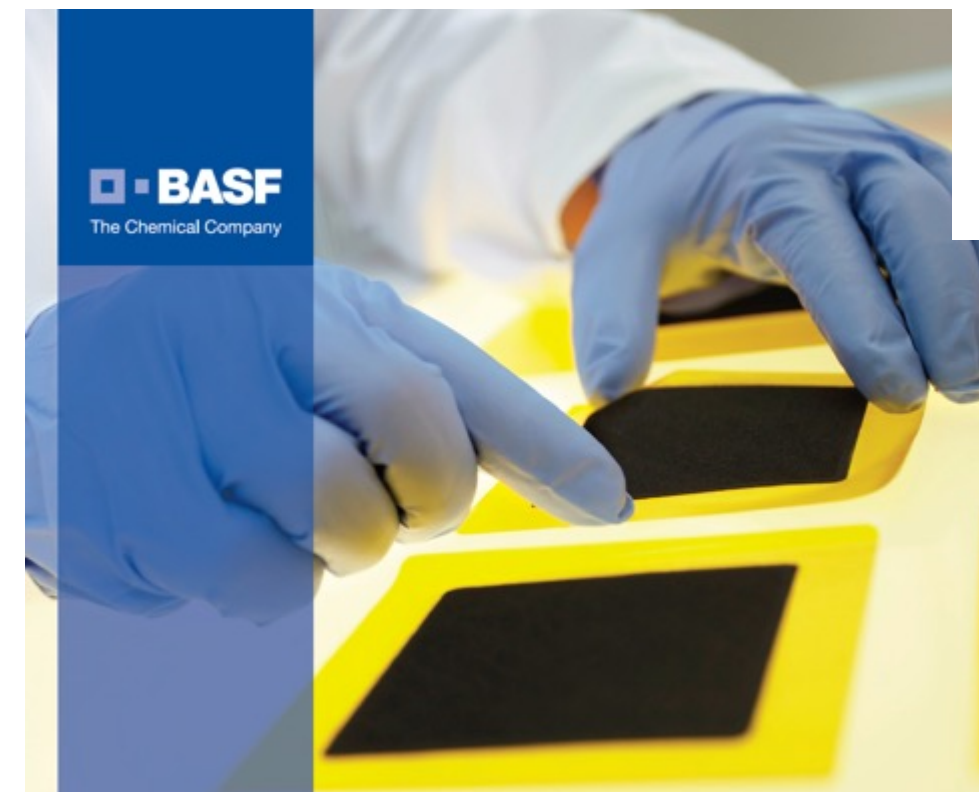
These properties limit it to niche applications (e.g., stationary power)

Ion-pair HT-PEMs as superior alternatives to PBI

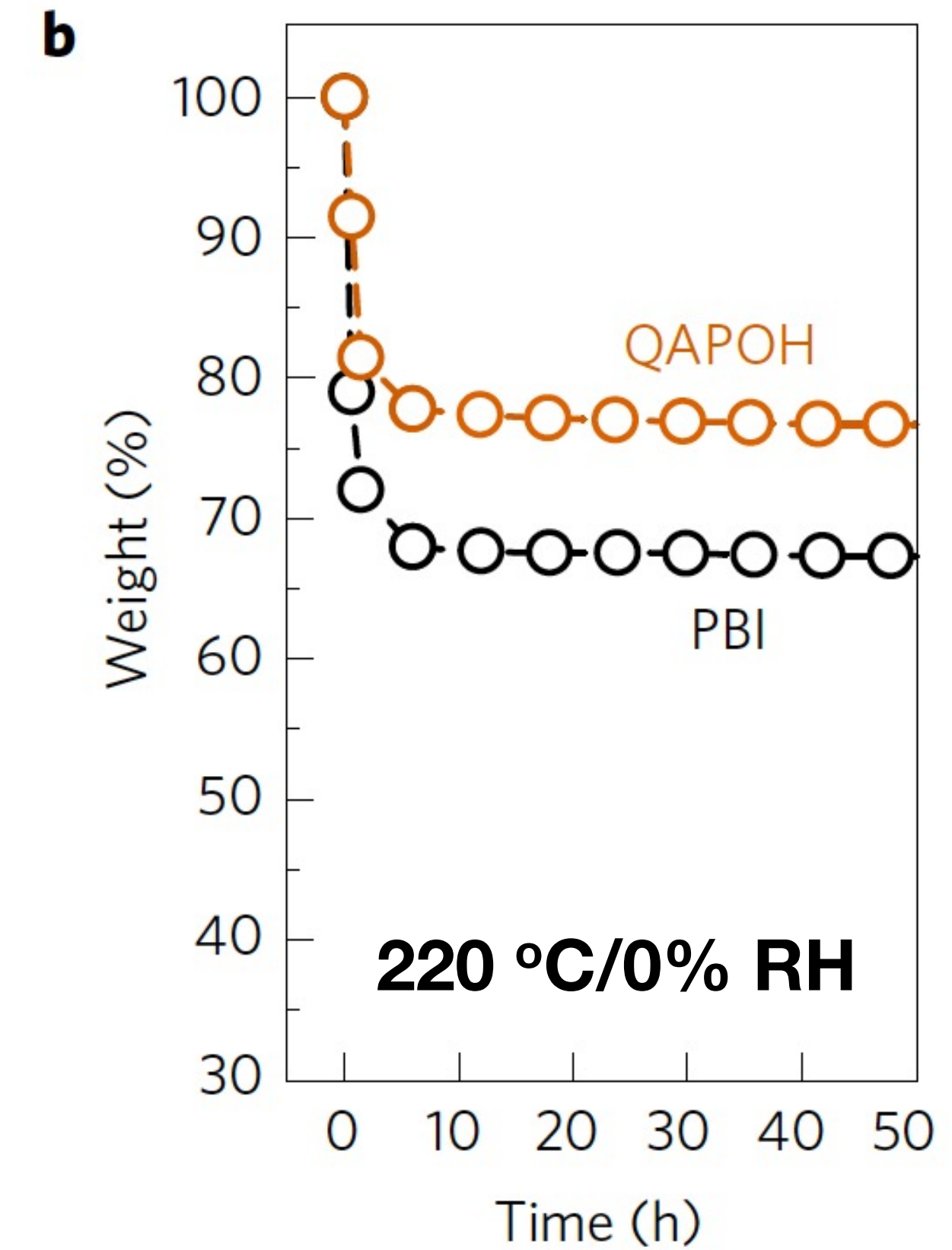
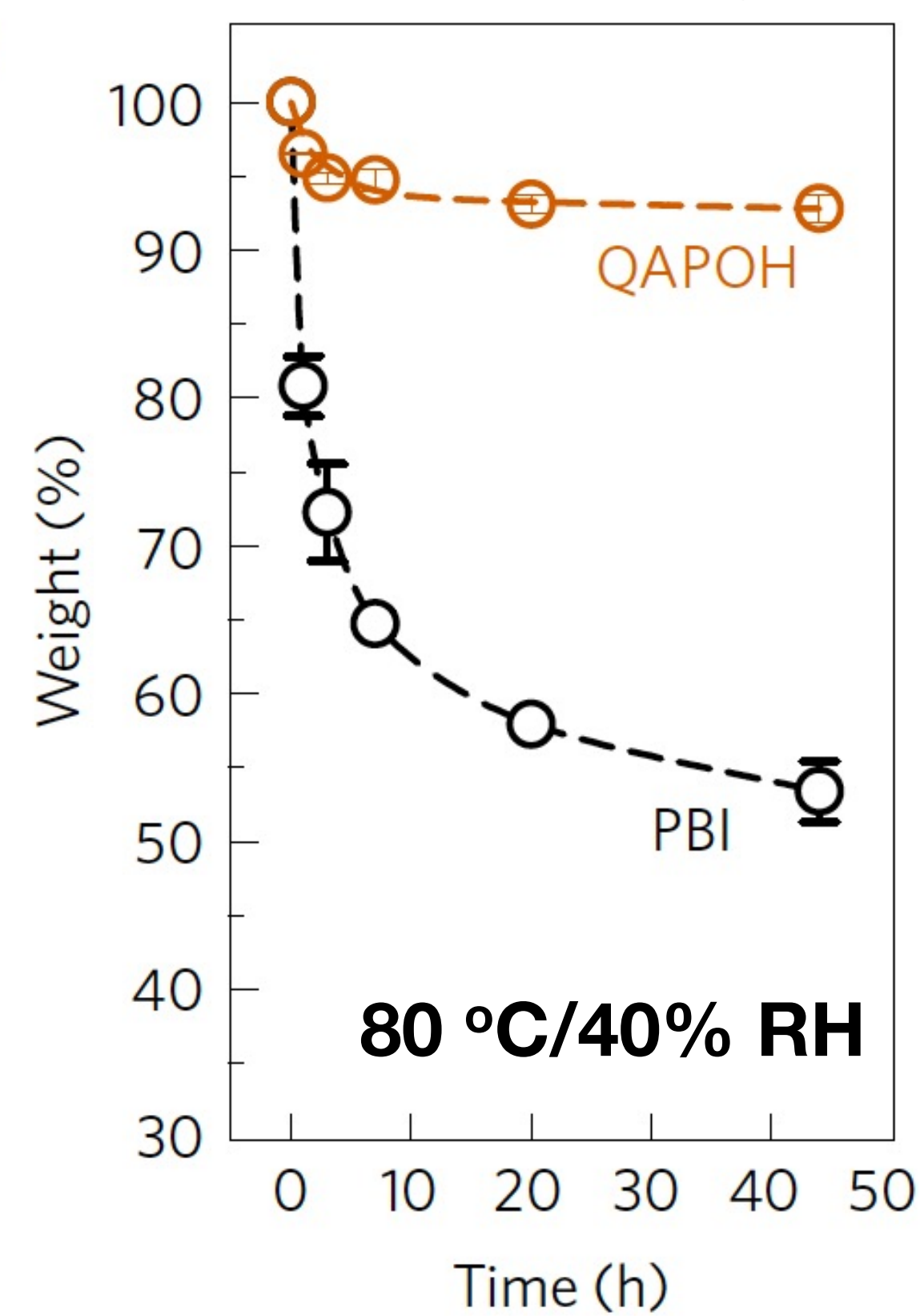


**BASF Celtec®
(PBI-H₃PO₄)**

VS

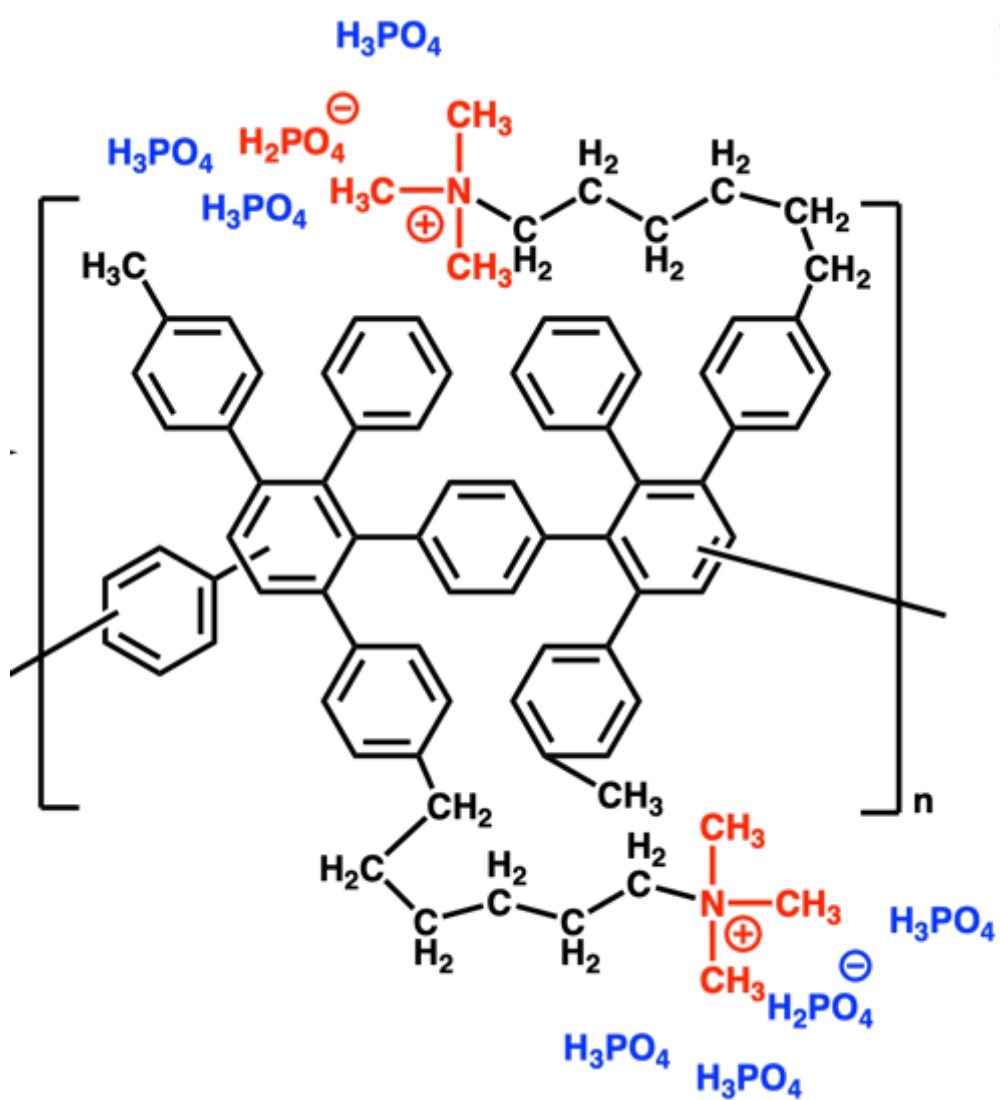
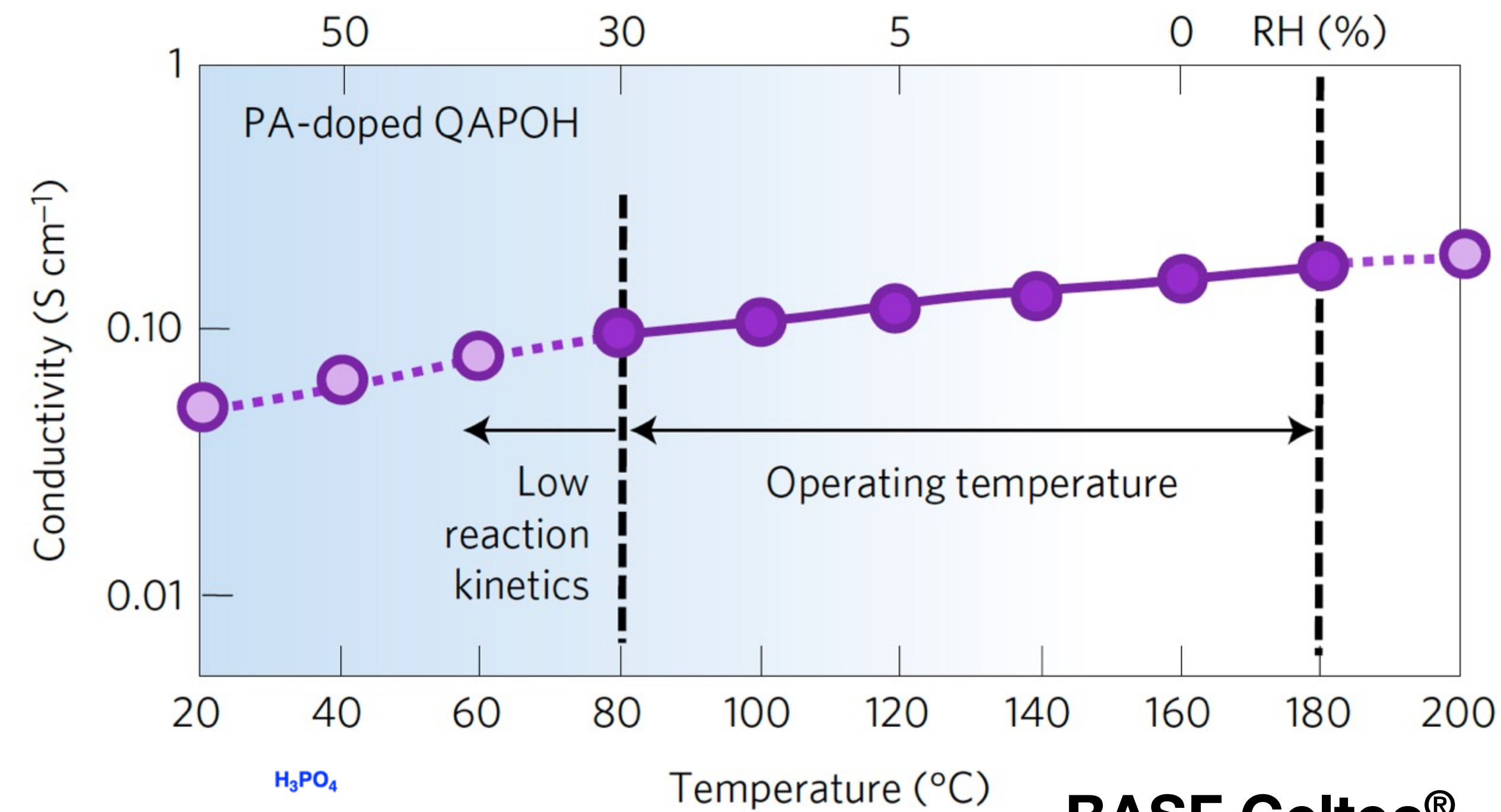


H₃PO₄ weight loss from the polymer



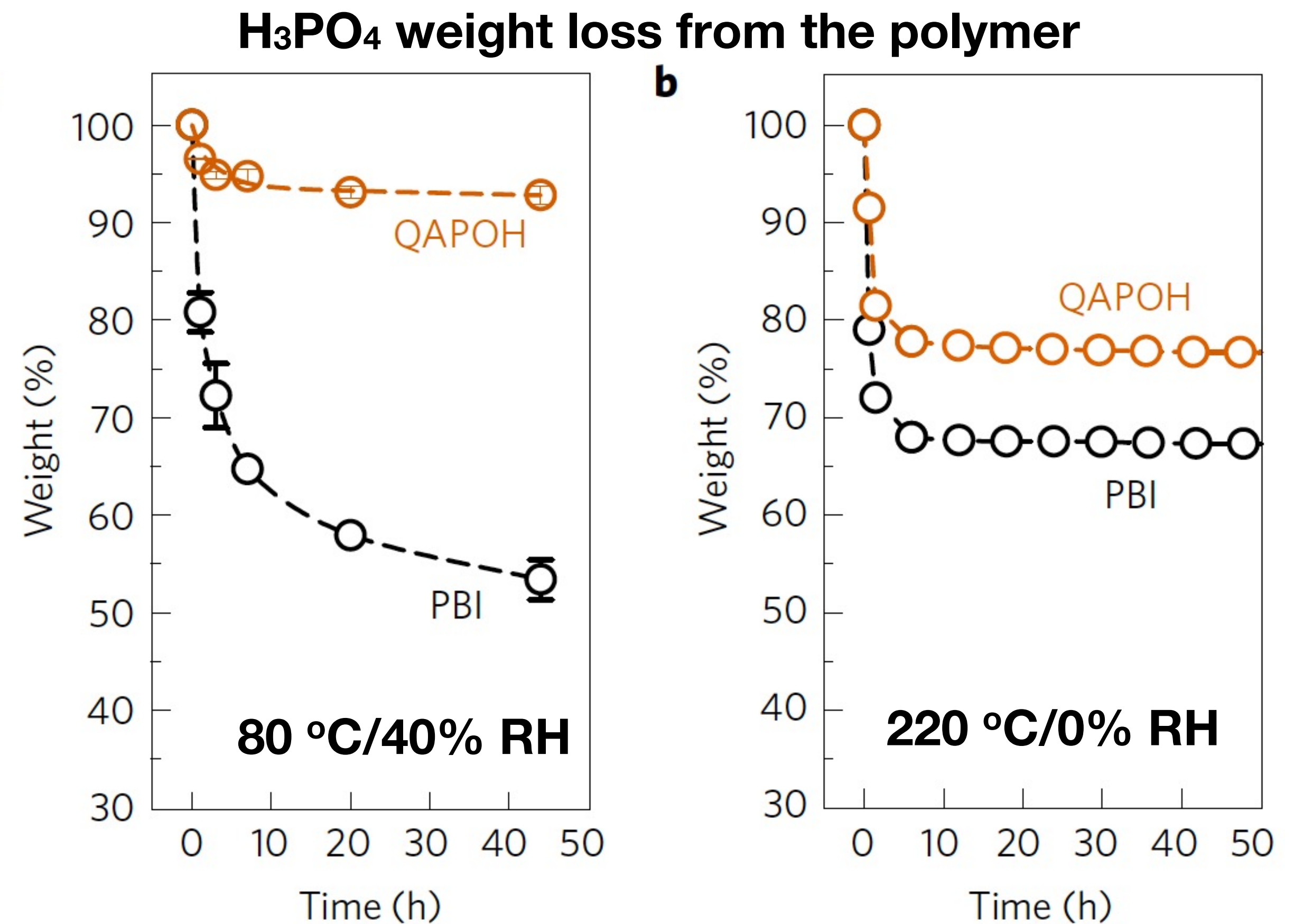
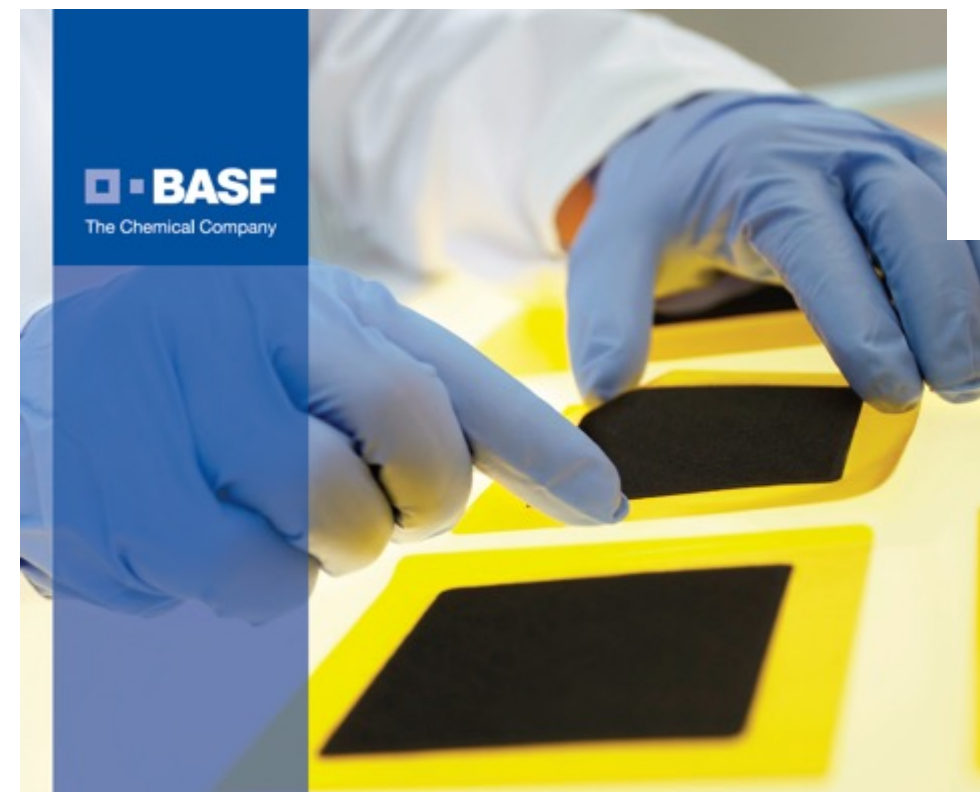
Quaternary ammonium group provides a strong ion pair interaction for stability

Ion-pair HT-PEMs as superior alternatives to PBI



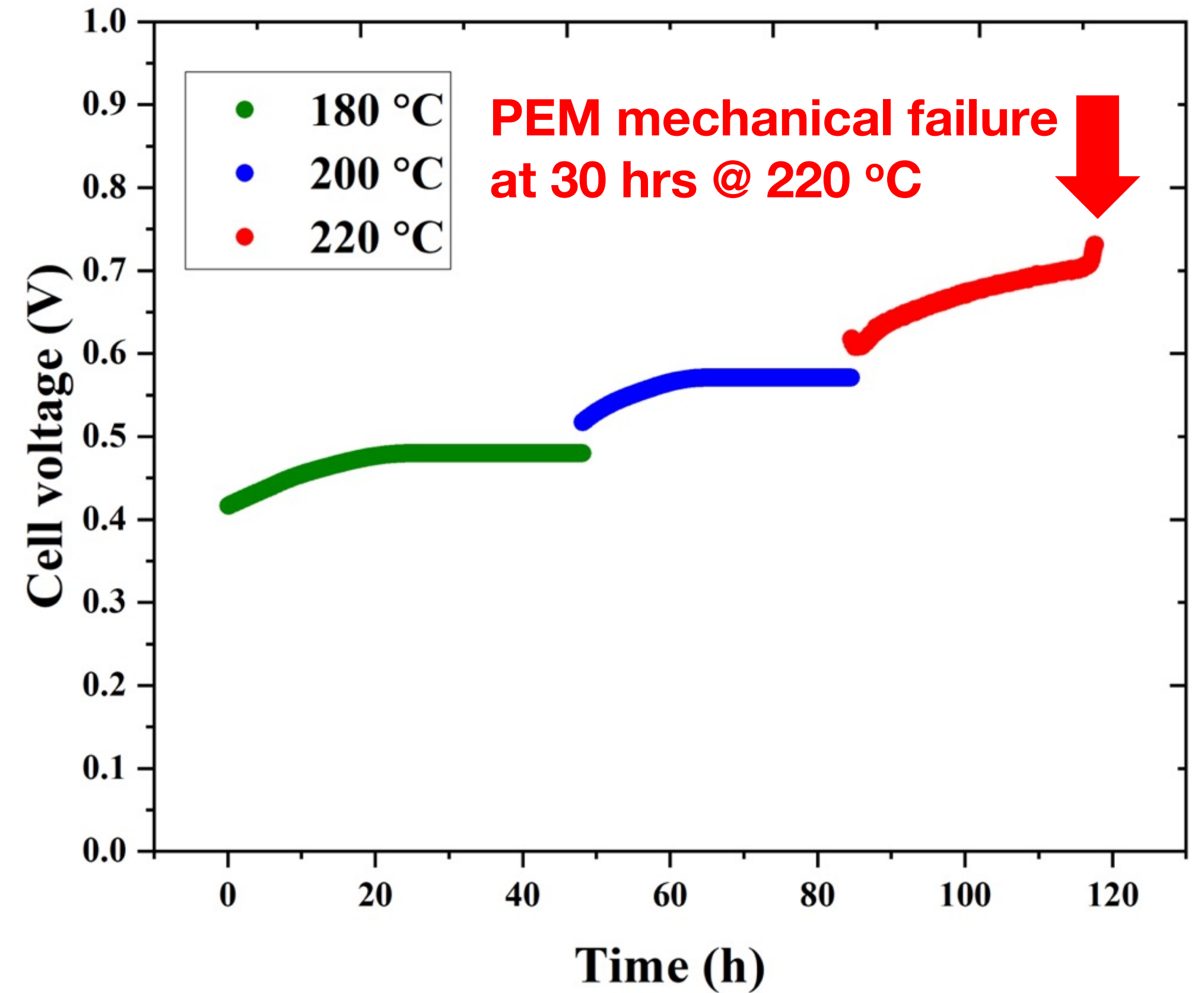
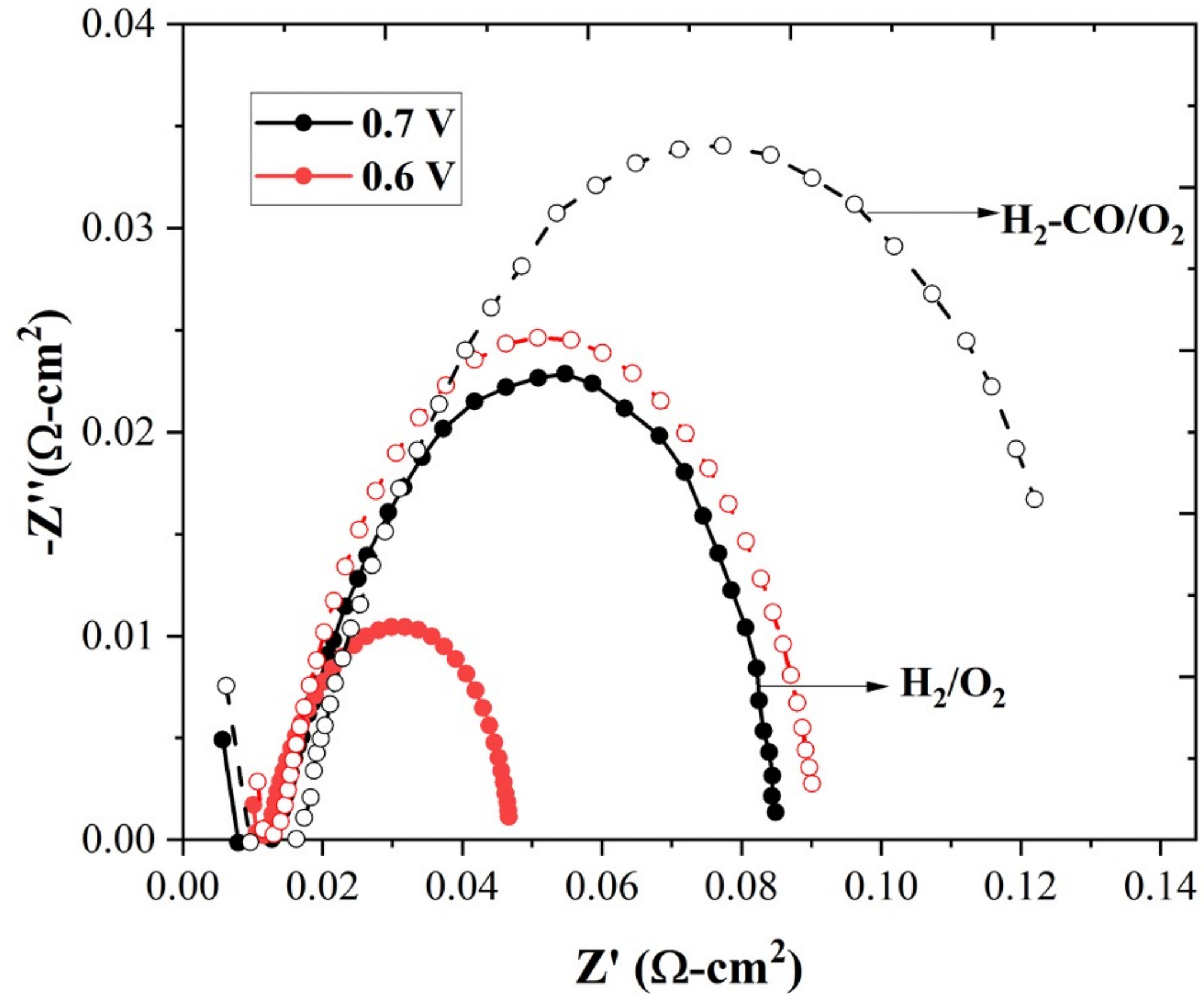
BASF Celtec[®]
(PBI-H₃PO₄)

VS



Ion-coordinated HT-PEMs have better stability when compared to Celtec[®] and comparable proton conductivity

Sources of resistances in the fuel cell and cell stability



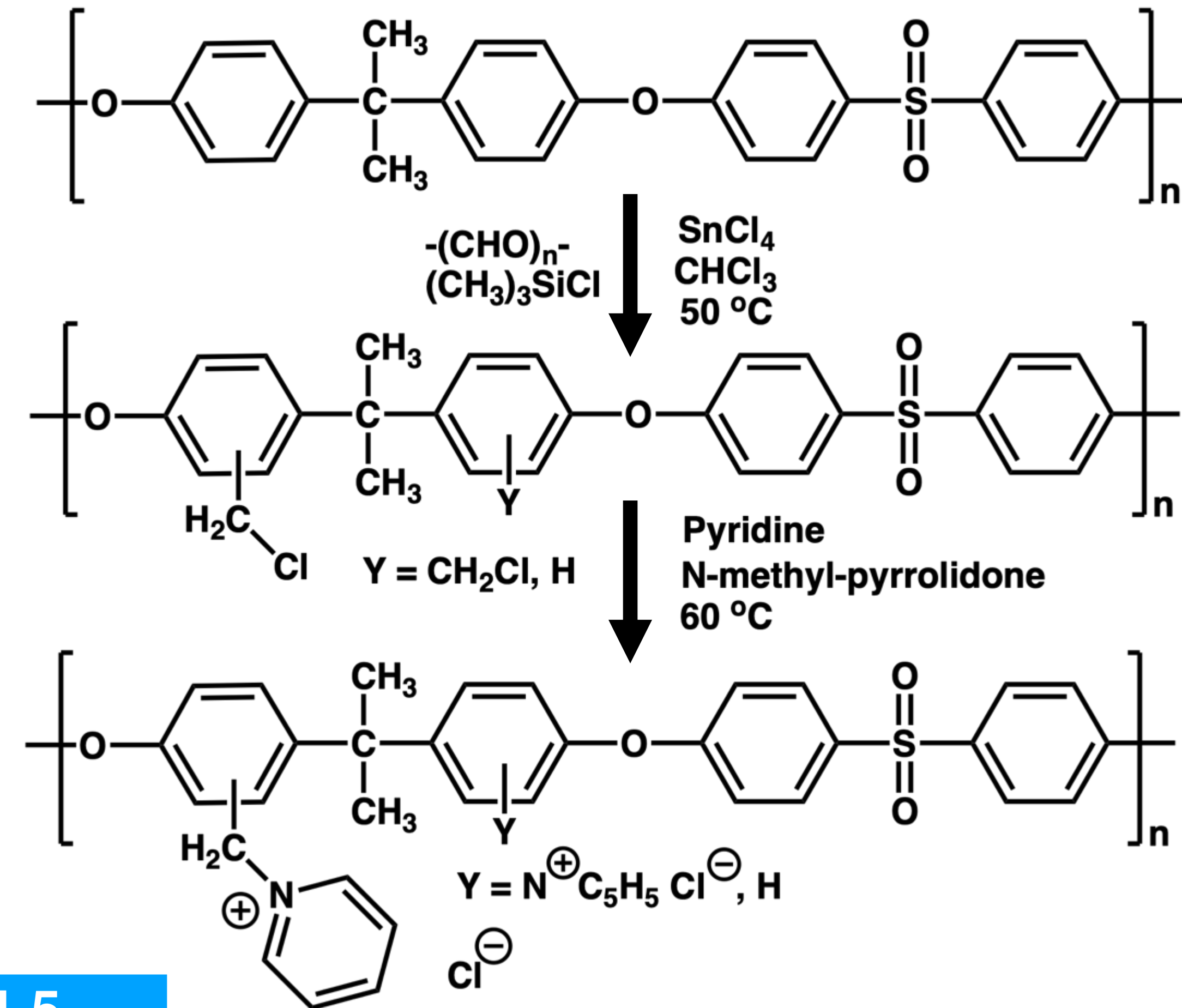
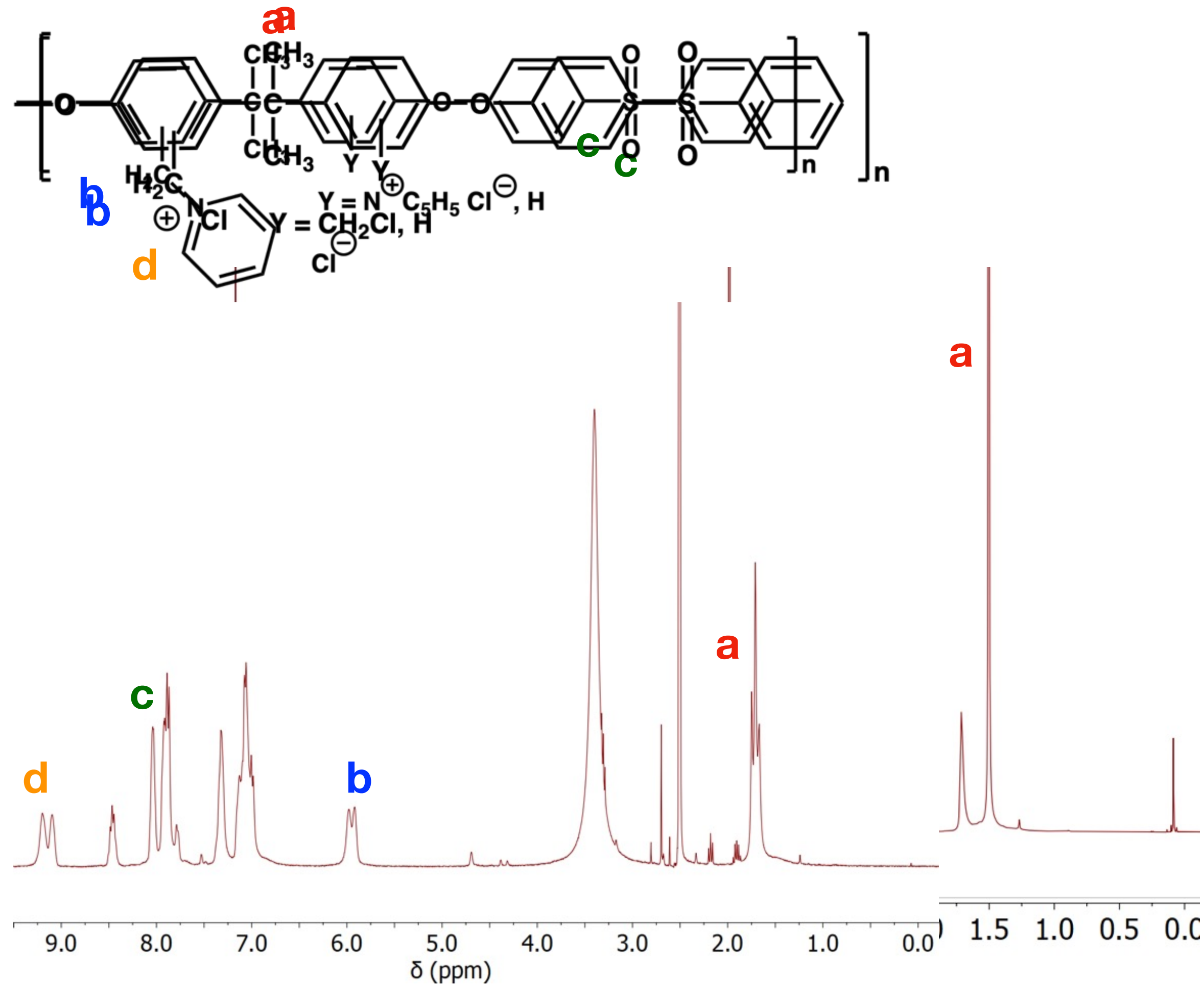
HFR: 15 m $\Omega\text{-cm}^2$

Kinetic/charge-transfer resistances dominate

We also suspect mass transfer limitations

Stable 90+ hours in 180 to 200 °C

QPPSf with different IEC values



CMPSf (DF)

0.7

0.9

1.1

1.26

1.5

**QPPSf IEC
(mmol g⁻¹)**

0.9

1.24

1.45

1.76

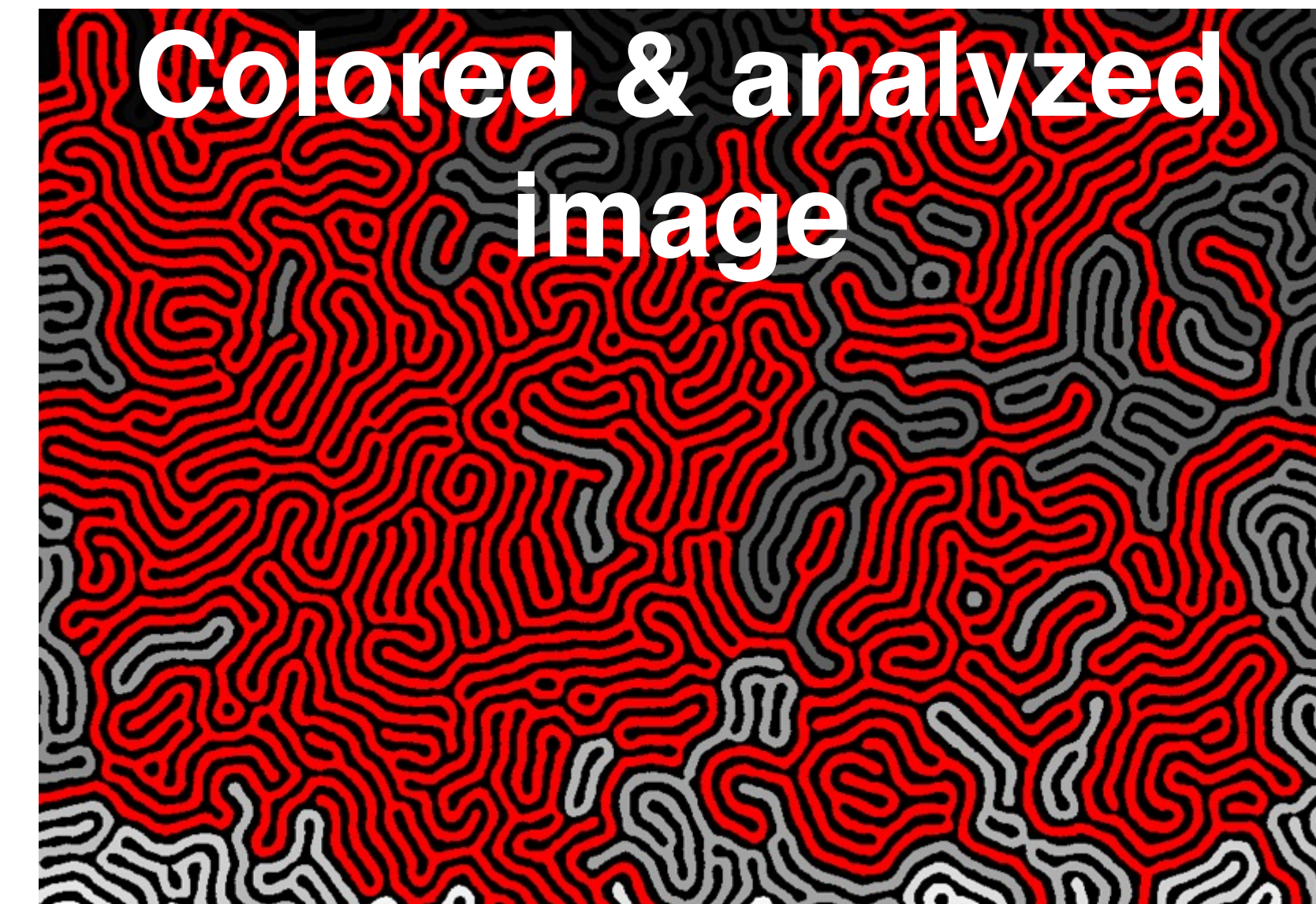
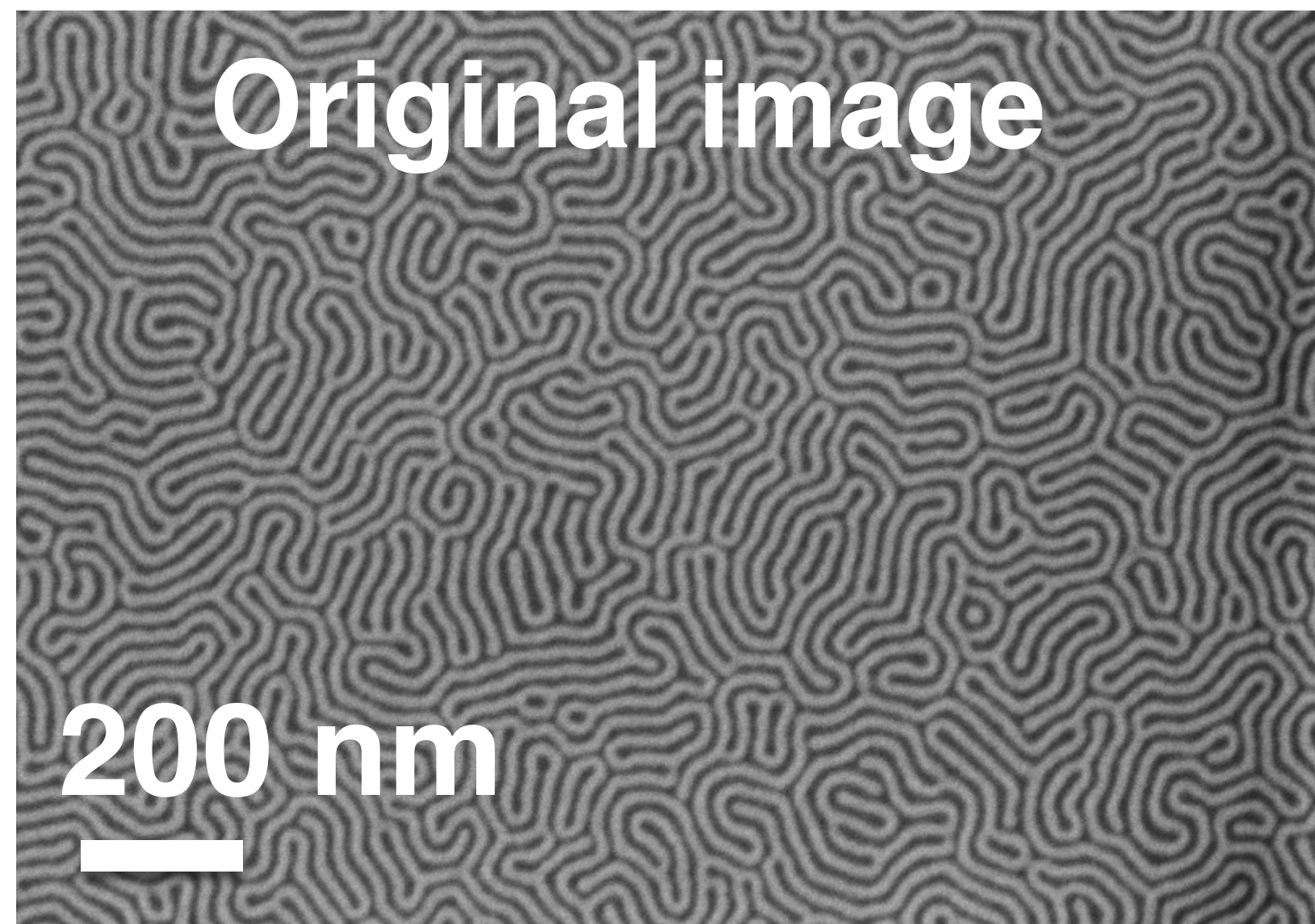
1.96

PGM nanostructures – loading & surface area

Sample ID	Mass loading ($\mu\text{g}_{\text{PGM}} \text{cm}^{-2}_{\text{geo}}$)	Thickness (nm)	Specific Surface Area ($\text{cm}^2_{\text{PGM}} \text{cm}^{-2}_{\text{geo}}$)
PS^{40k}-<i>b</i>-P2VP^{44k} (Pt)	4.95	11.9	0.94
PS^{40k}-<i>b</i>-P2VP^{44k} (Pt, alkylated)	9.68	28.0	1.91
PS^{102k}-<i>b</i>-P2VP^{97k} (Pt)	5.85	34.1	1.53
PS^{102k}-<i>b</i>-P2VP^{97k} (Pt, alkylated)	11.25	56.6	2.55
P2VP^{12k}-<i>b</i>-PS^{23k}-<i>b</i>-P2VP^{12k} (Pt)	1.58	8.5	0.85
P2VP^{12k}-<i>b</i>-PS^{23k}-<i>b</i>-P2VP^{12k} (Pt, alkylated)	3.83	17.4	2.27
P2VP^{12k}-<i>b</i>-PS^{23k}-<i>b</i>-P2VP^{12k} (IrOx, alkylated)	2.67 (Ir only)	17.7	2.31
PS^{48k}-<i>b</i>-P4VP^{21k} (Pt)	3.60	13.3	1.09
PS^{48k}-<i>b</i>-P4VP^{21k} (Pt, alkylated)	11.72	22.3	2.34

The alkylated block copolymer templates give larger PGM loadings and surface area values.

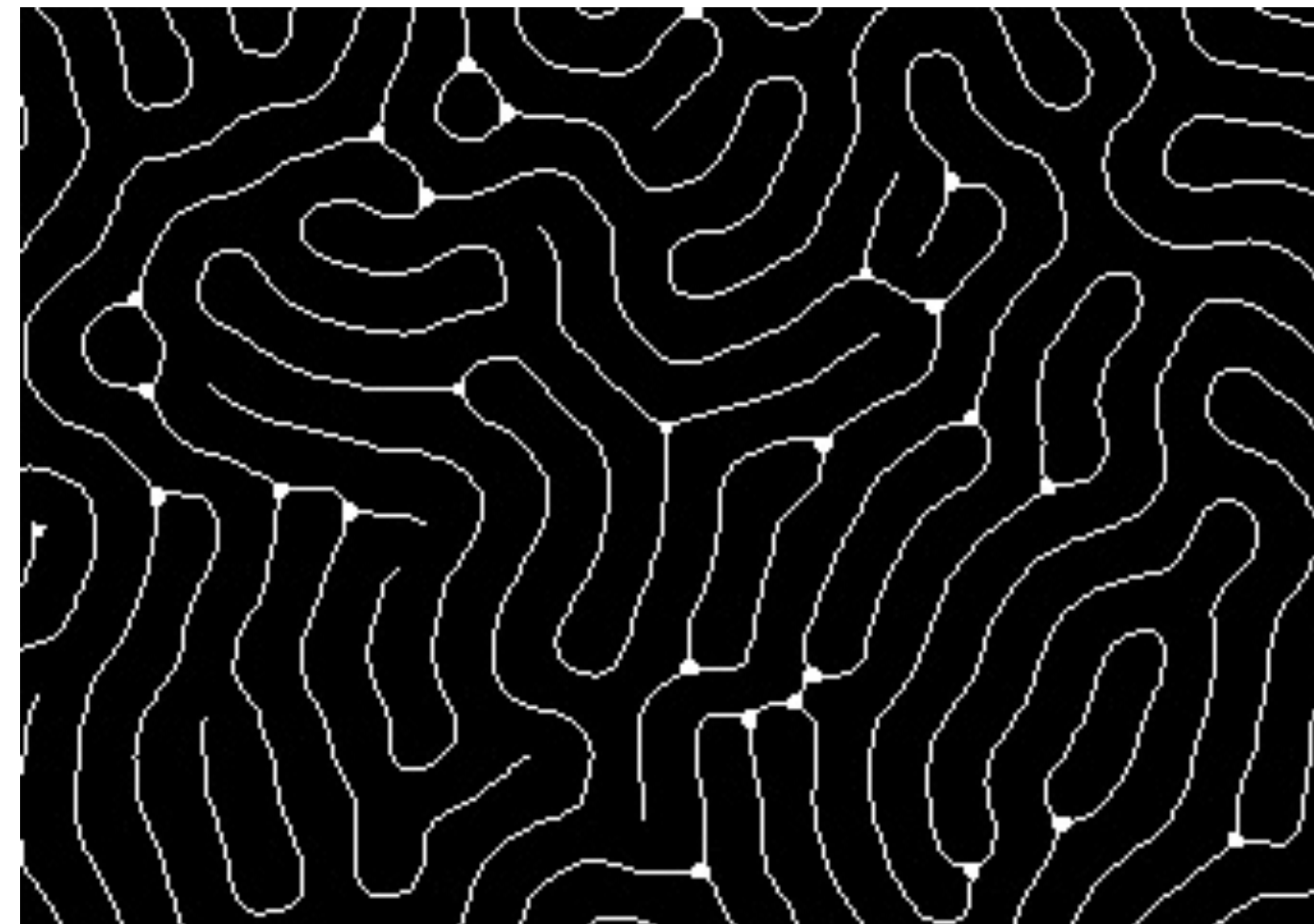
Processing SEM images for structural data



Branched point defects

Terminal point defects

Skeleton images



Poor connectivity of the nanowire electrocatalysts prevents shorting the IDE

