Hybrid Approach for PEM Fuel Cell Electrode Microstructural Analysis

C. F. Cetinbas, R. K. Ahluwalia, N. Kariuki, D. J. Myers,
V. J. De Andrade
Argonne National Laboratory, Argonne, IL

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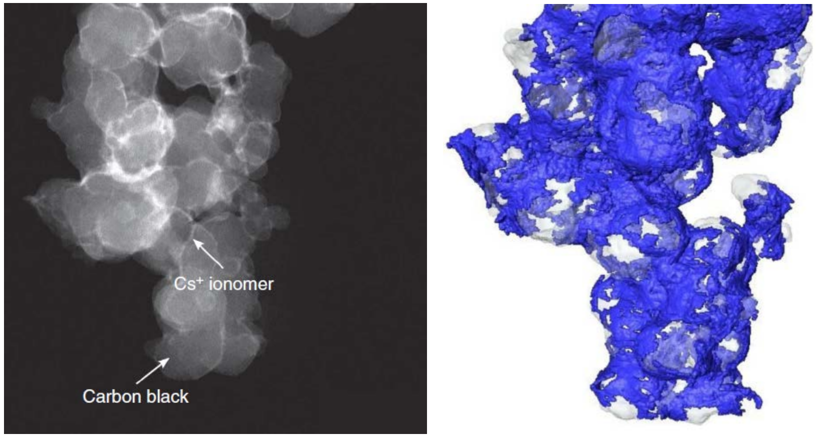
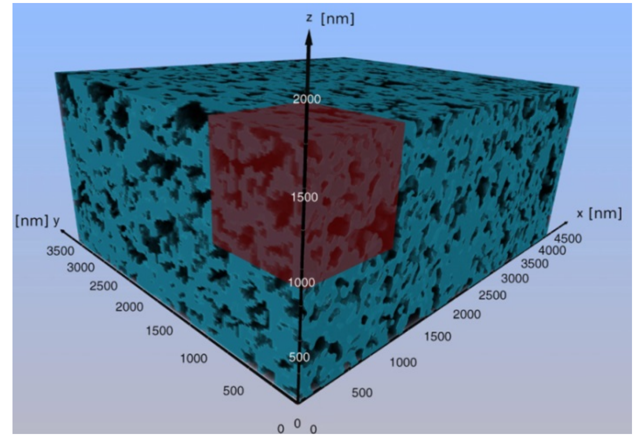
Electrode Microstructure Characterization

Experimental electrode microstructure characterization:

- Porosimetry
- Electron microscopy (SEM, TEM, ET)
- FIB-SEM
- Nano scale X-CT

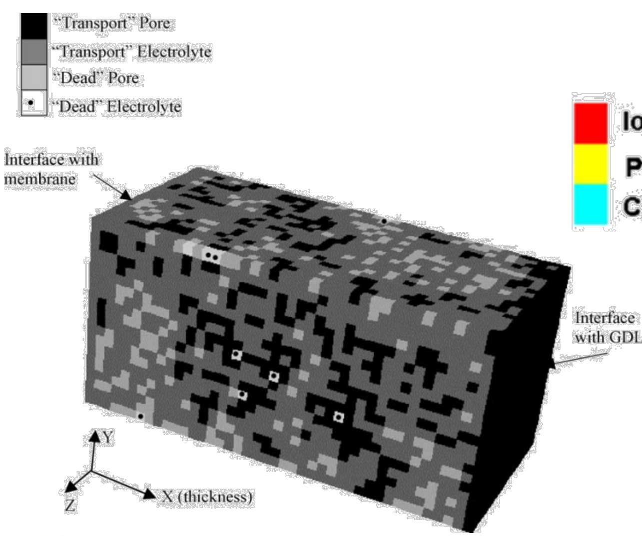


Electron Tomography, ***Lopez-Haro et al. Nature Commun. (2014)***

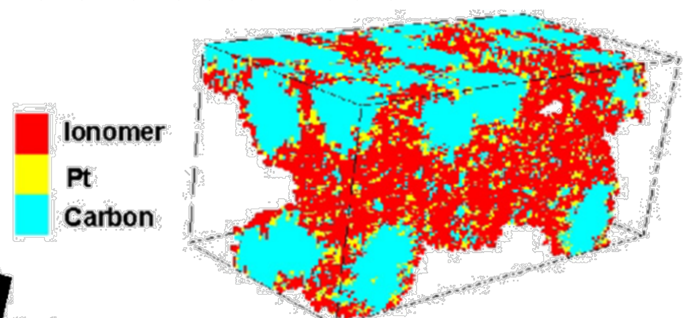


FIB-SEM, ***Ziegler et al. J. Power Sources (2011)***

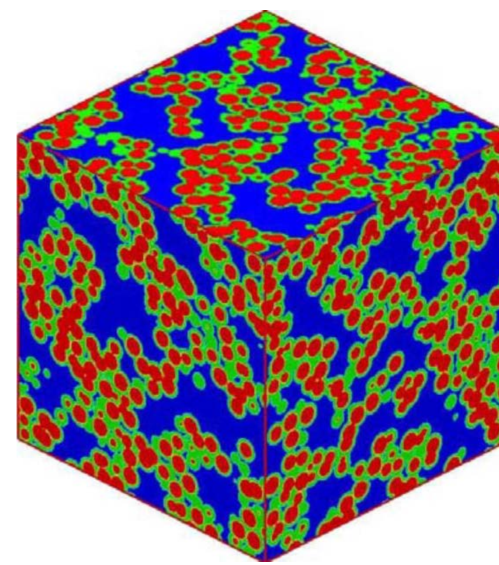
Numerical microstructure characterization:



Mukherjee and Wang J. Electrochem. Soc. 2007

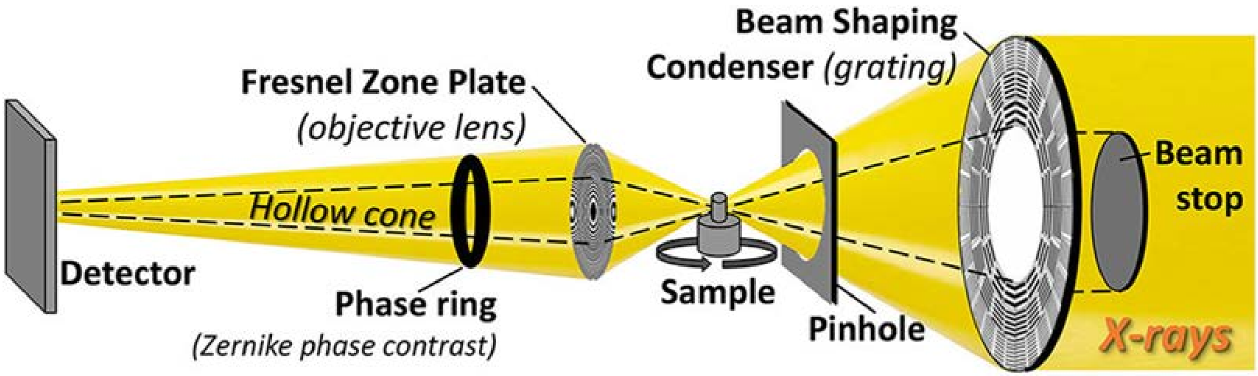


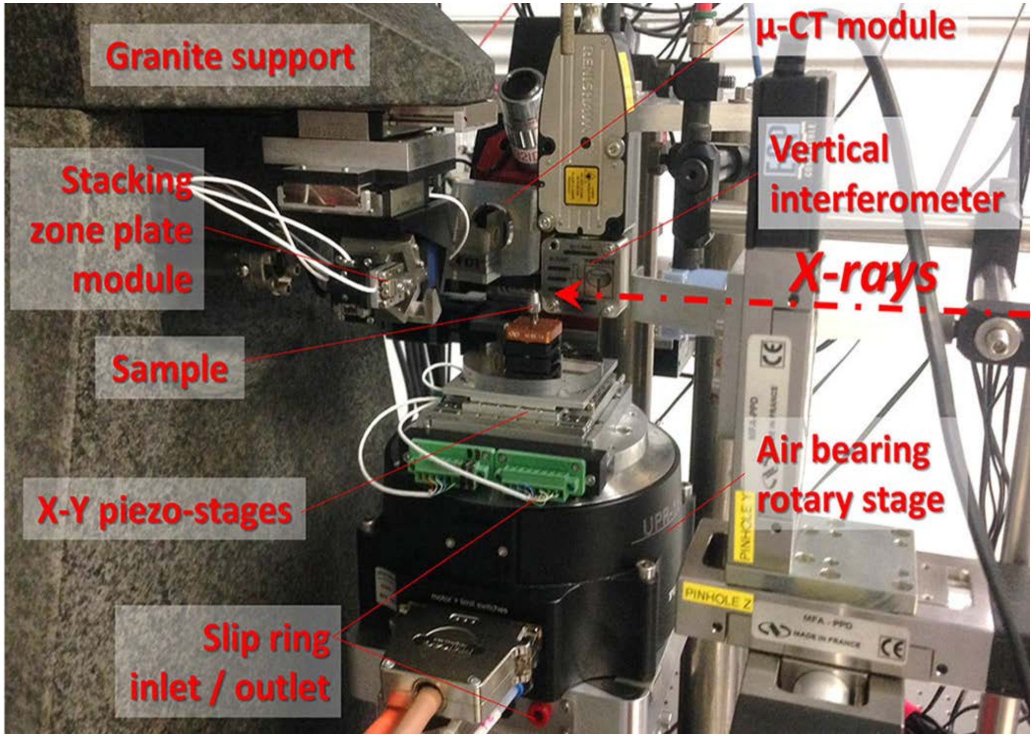
Siddique and Liu Electrochim. Acta (2010)



Kim and Pitsch J. Electrochem. Soc. (2009)

Hard X-ray Nanoprobe Beamline at APS



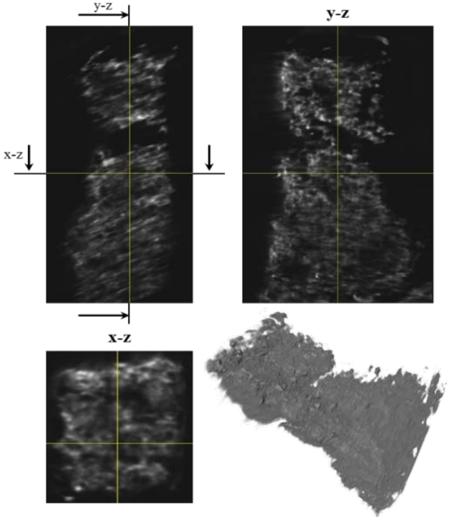


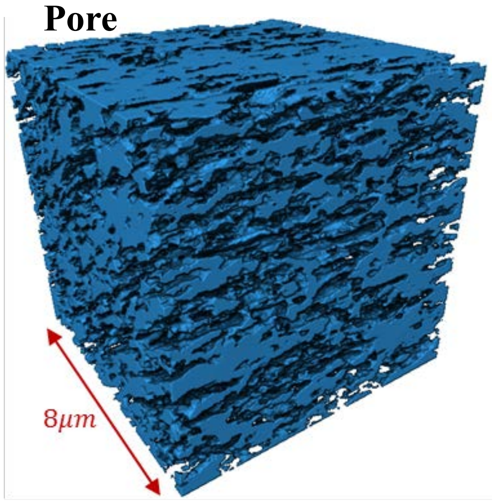
Optical Enclosure for X-ray Nanotomography at APS

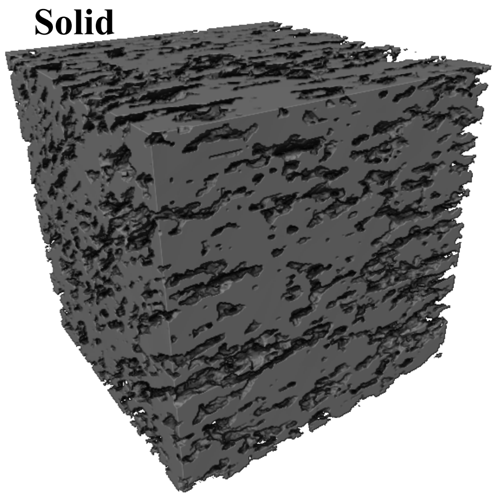
- X-ray energies from 3 to 30 keV
- Sample rotated in X-ray beam, 451 images for 0.4^{o} rotation
- 60 nm Fresnel zone plate with ~20 nm resolution used in initial experiments at 32-ID
- Imaging optics with CCD camera sensitive to absorption contrast and Zernike phase contrast
- Large field of view and flexible sample environment for in situ experiments
- Air bearing stage dampens most of the jittering and helps in aligning projection images

X-ray Tomography of Annealed Pt/C Catalyst at 32-ID

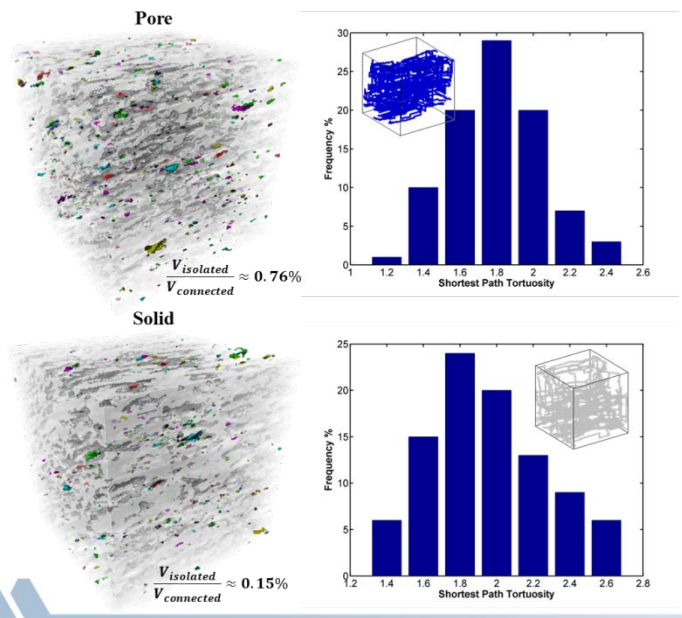
- 451 images over 180^o rotation, 20 nm voxel size



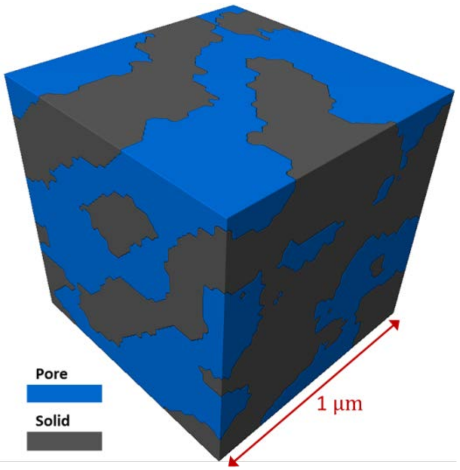


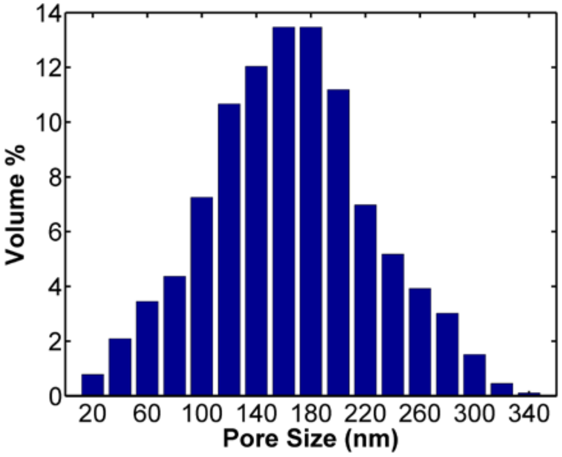


- X-CT can only provide morphology of secondary pores due to 20 nm resolution



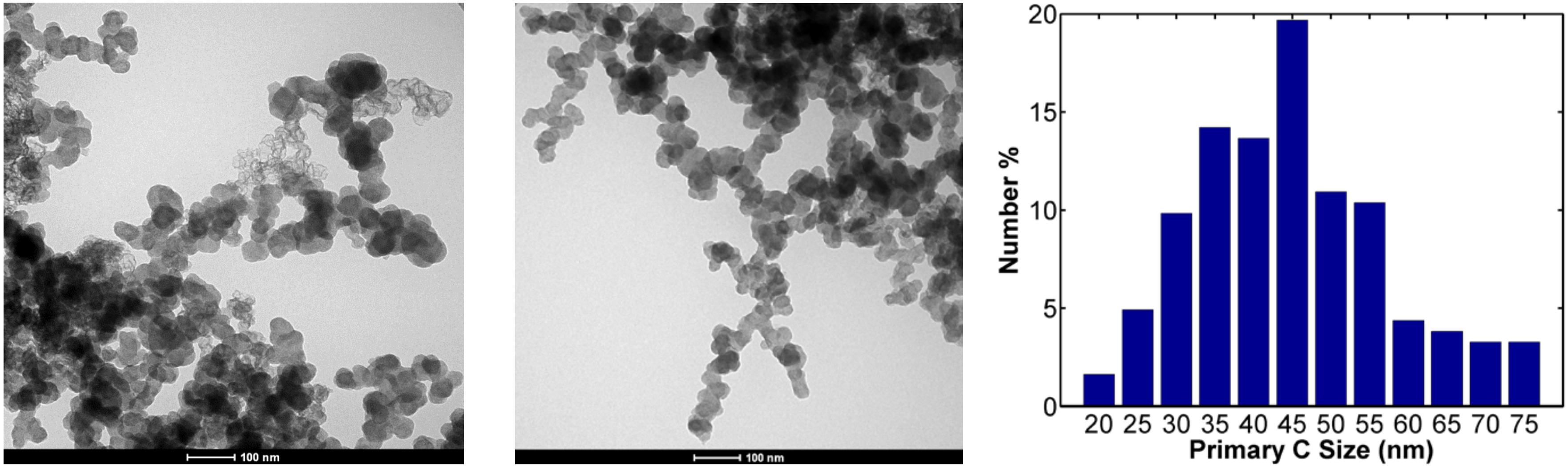
- 1μm sample is extracted to use in hybrid approach



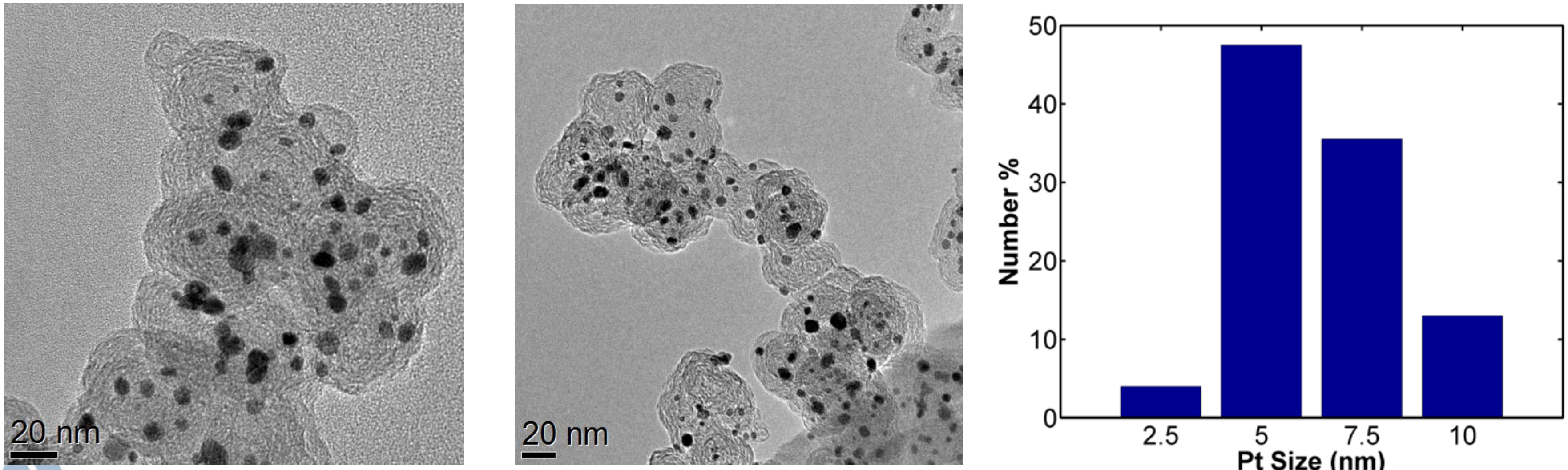


Catalyst and Support Particle Size Distributions

- TEM images taken at UT-Austin to measure the primary C particle size distribution in the Ketjen 300J powder



- Pt particle size distribution in annealed Pt/C catalyst



Hybrid Approach: Volume Fractions of Pt, C, N and Pores

- Microstructure of the electrode strongly depends on the ink composition

$$I/C = f_{IC} = 0.8 \qquad f_{PtC} = 0.297$$

- Volume fraction of primary pores (that are lost in solid X-CT volume) needs to be determined approximately
- Mercury intrusion porosimetry results are used to determine f_{pm}

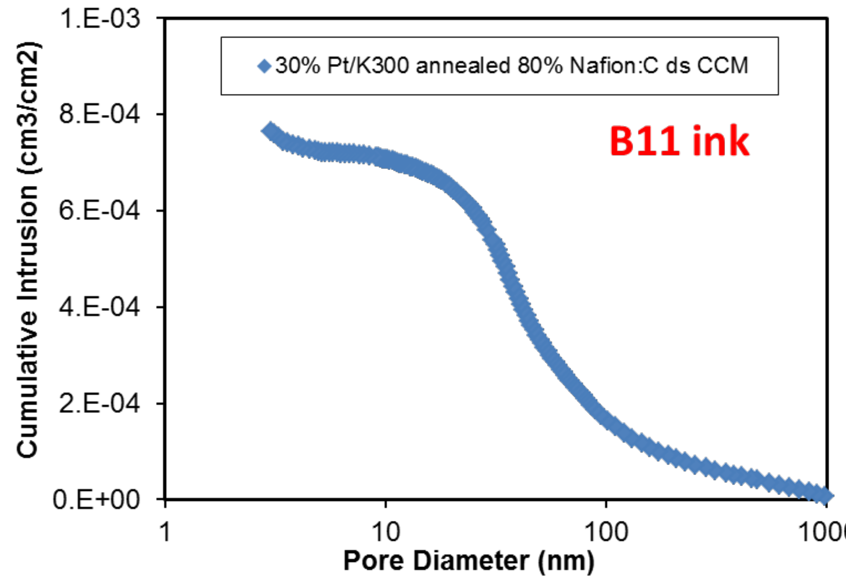
$$f_{pm} = \frac{\text{volume of pores } d_p < 20\ nm}{\text{total volume of pores}}$$

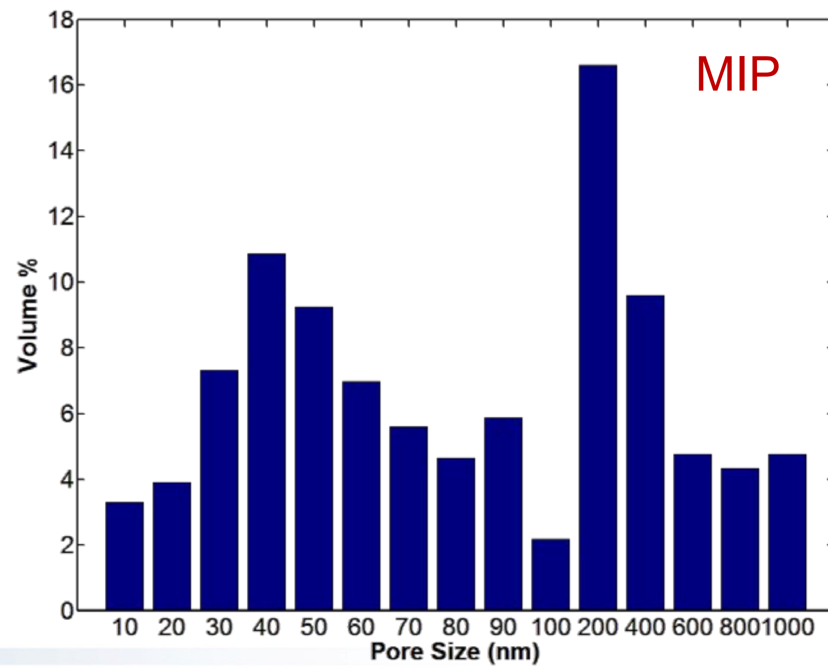
ε_{vs}: *porosity obtained from X − CT*

$$\varepsilon_{vp} = \varepsilon_{vs} \frac{f_{pm}}{1 - f_{pm}} \qquad \varepsilon_v = \varepsilon_{vp} + \varepsilon_{vs}$$

$$\varepsilon_C = \frac{1 - \varepsilon_v}{1 + f \dfrac{\rho_C}{\rho_{Pt}} + f_{IC} \dfrac{\rho_C}{\rho_N}}$$

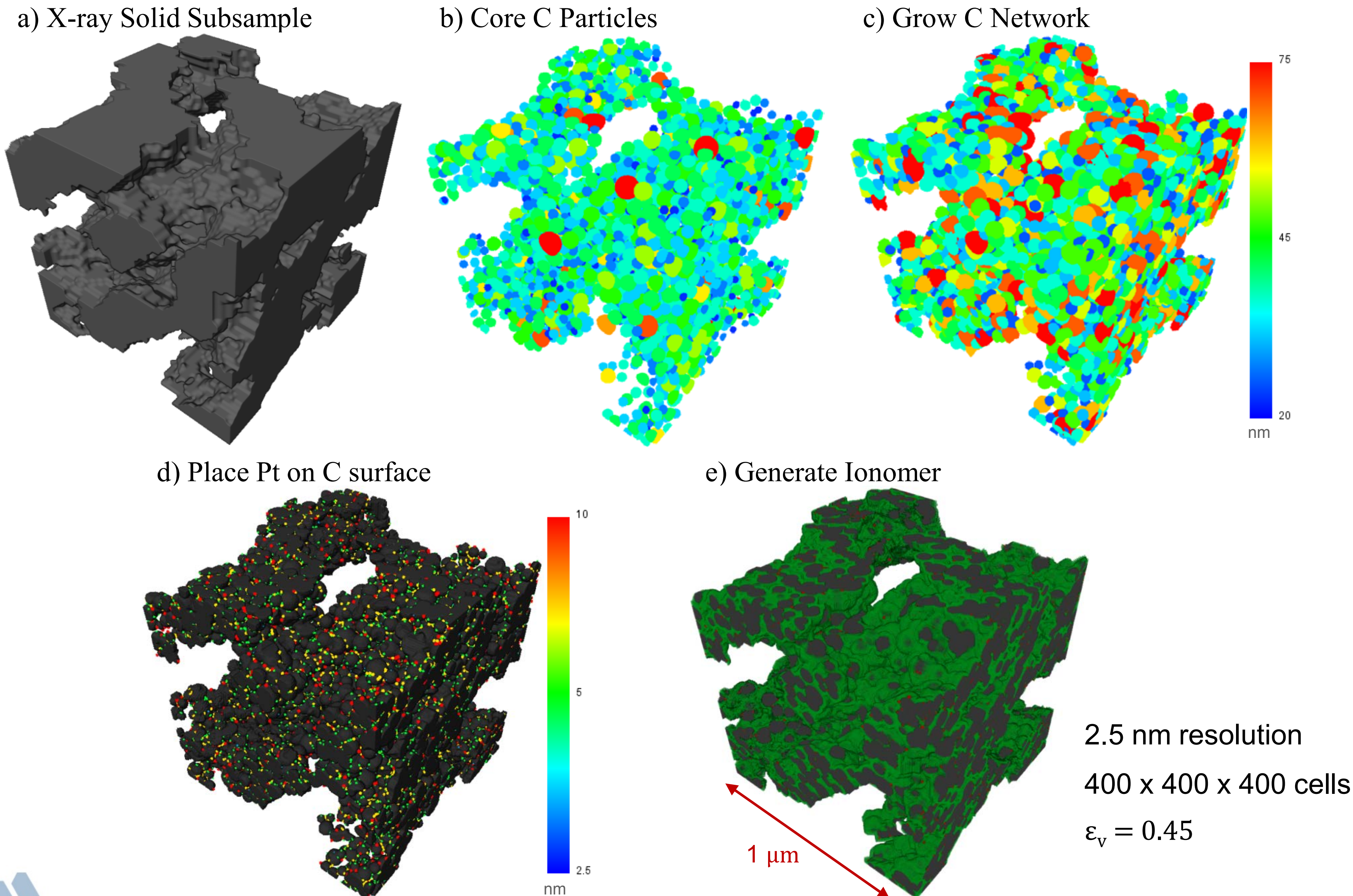
$$\varepsilon_{Pt} = f_{PtC} \frac{\rho_C}{\rho_{Pt}} \varepsilon_C \qquad \varepsilon_N = f_{IC} \frac{\rho_C}{\rho_N} \varepsilon_C$$





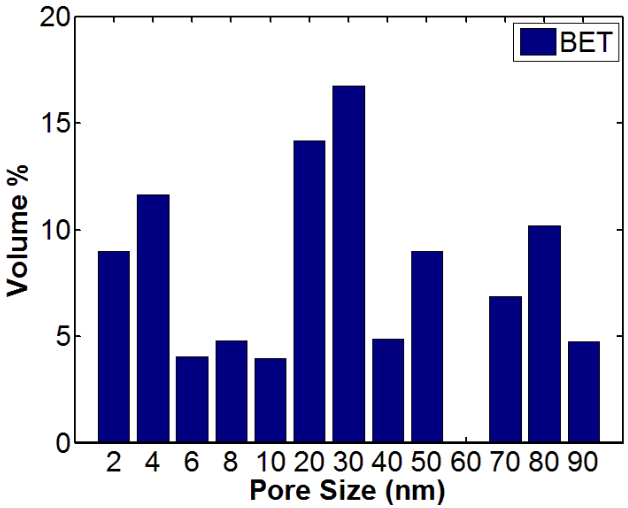
Hybrid Microstructure Algorithm

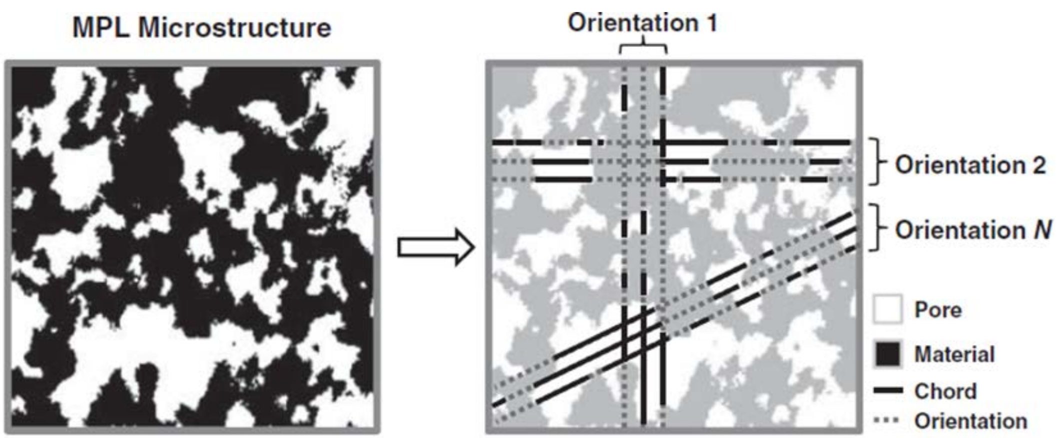
- An algorithm is developed to regenerate microstructure from C, Pt and ionomer



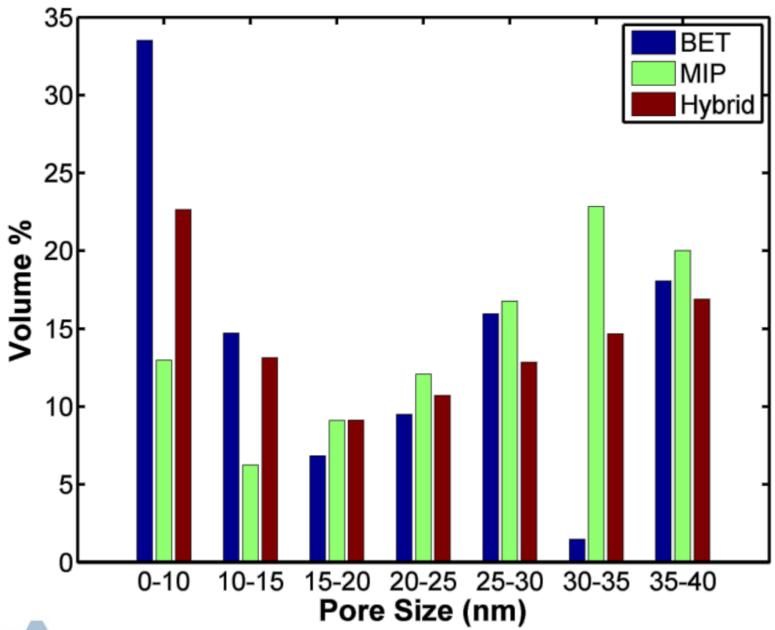
Hybrid Model Validation

- BET porosimetry is performed for validation along with MIP





Cecen et al. J. Electrochem. Soc. (2012)

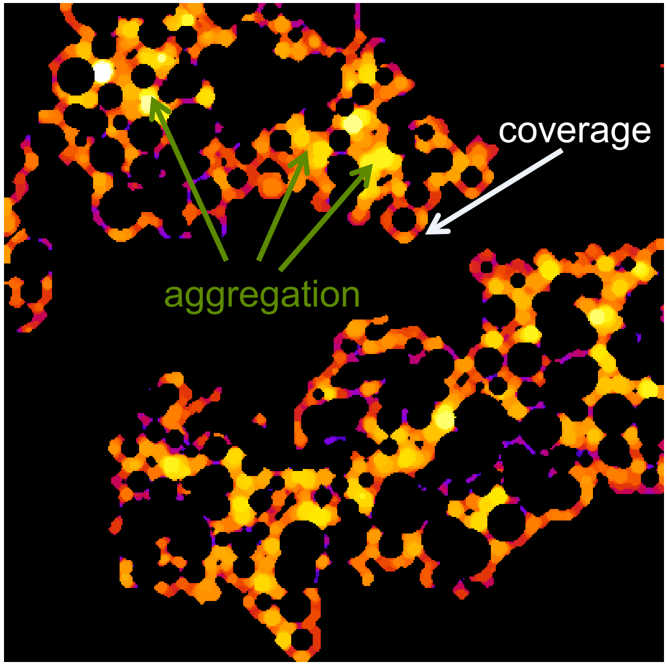


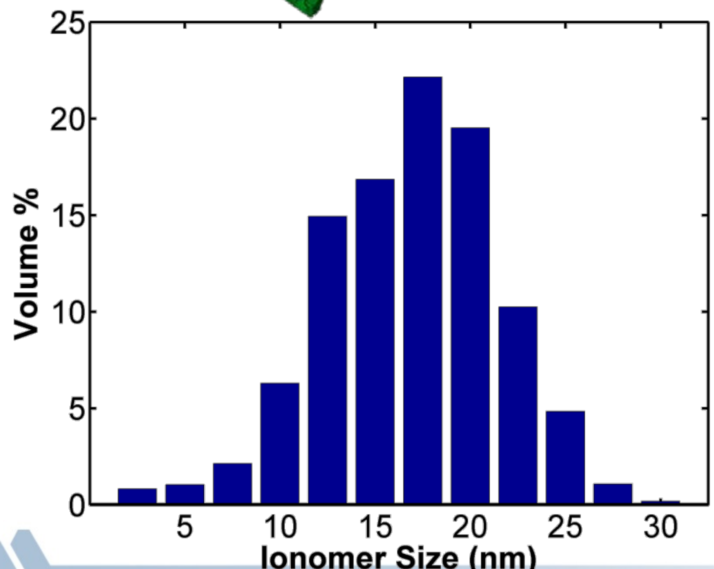
- Pore size distribution is calculated by employing the chord length method
- Pore sizes smaller than 2.5 nm are not modeled in hybrid microstructure
- Smallest pore sizes calculated from BET and MIP data are 1.35 and 3 nm, respectively
- Overall trend obtained by Hybrid approach agrees well with both porosimetry techniques

Hybrid Approach: Ionomer Structure

- Direct imaging of 3D ionomer network still remains a challenge

Thiele et al. Nano Res (2011)





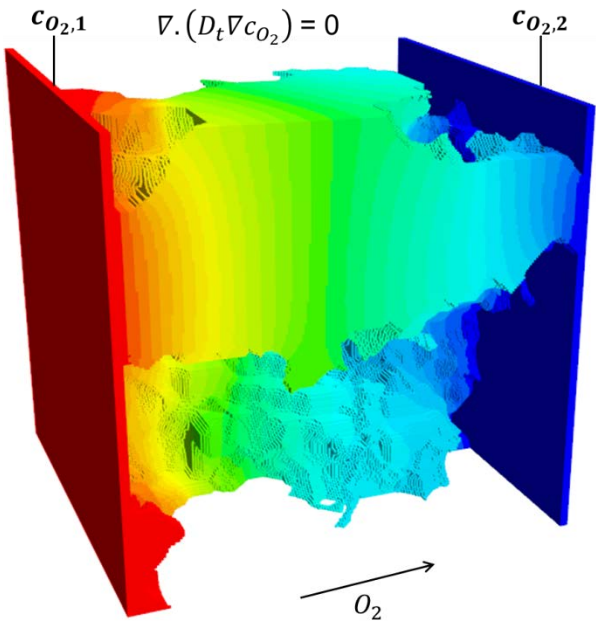
- Ionomer size distribution is characterized by using sphere fitting method
- The size distribution does not directly correspond to ionomer film coverage
- Larger sizes such as 15-30 nm correspond to ionomer agglomerates whereas the film sizes are observed to be in range of 5-12.5 nm

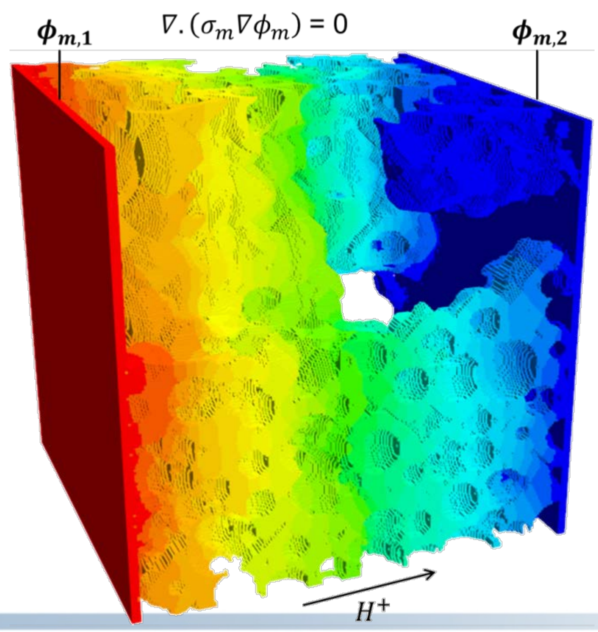
Transport Simulations

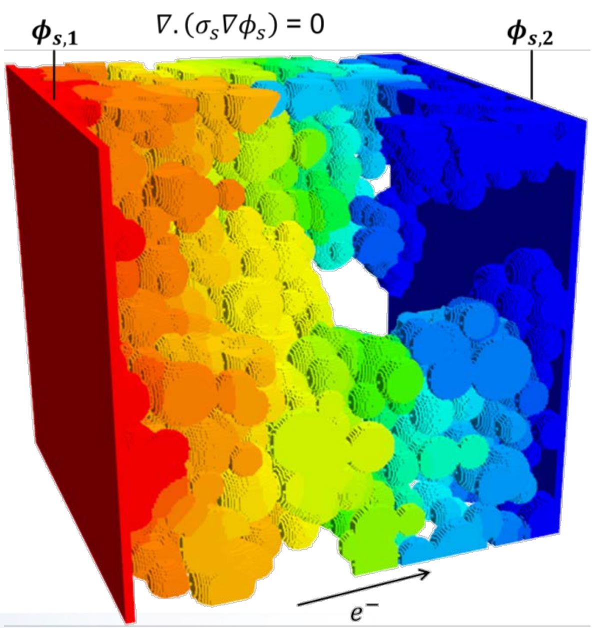
- Transport related characteristic properties are investigated by performing simulations
- σ_m and σ_s are assumed to be constant
- Local diffusivity D_t is calculated by accounting for Knudsen diffusion:

$$\frac{1}{D_t} = \frac{1}{D_b} + \frac{1}{D_k} \qquad \mathrm{D_k} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M_{O_2}}}$$

$$D_{eff} = J\frac{t_{cl}}{\Delta c} \qquad \tau = \varepsilon_i \frac{\langle D_t \rangle}{D_{eff}}$$

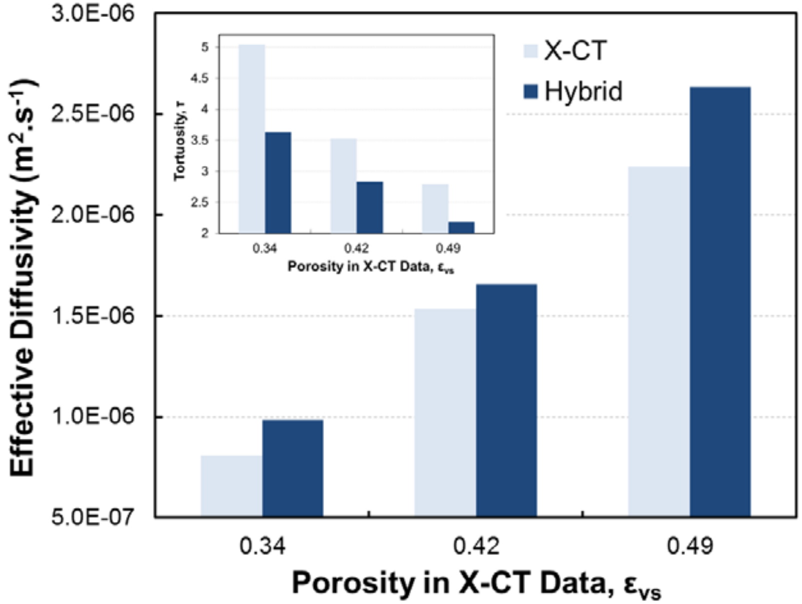


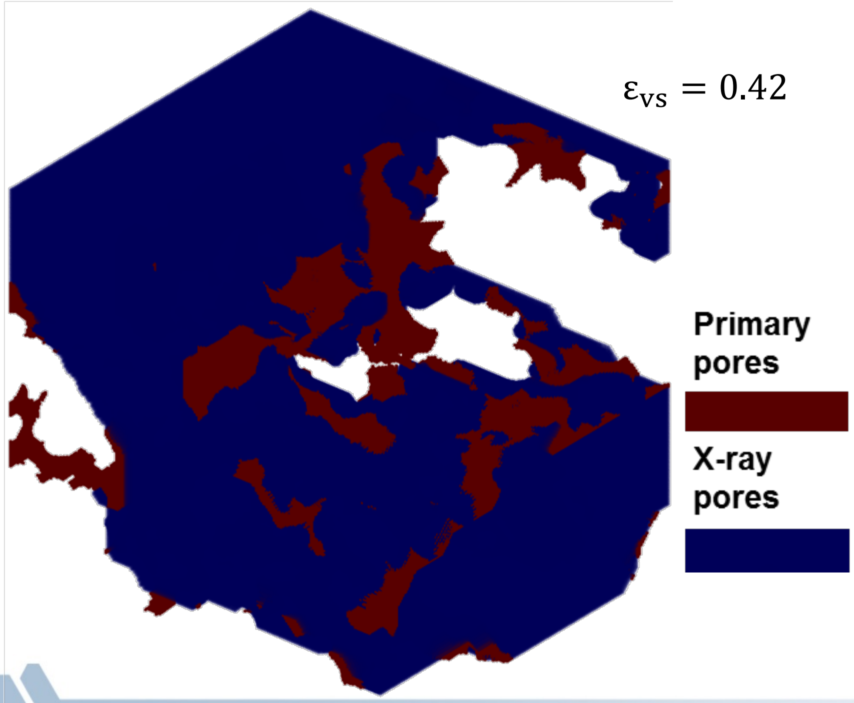


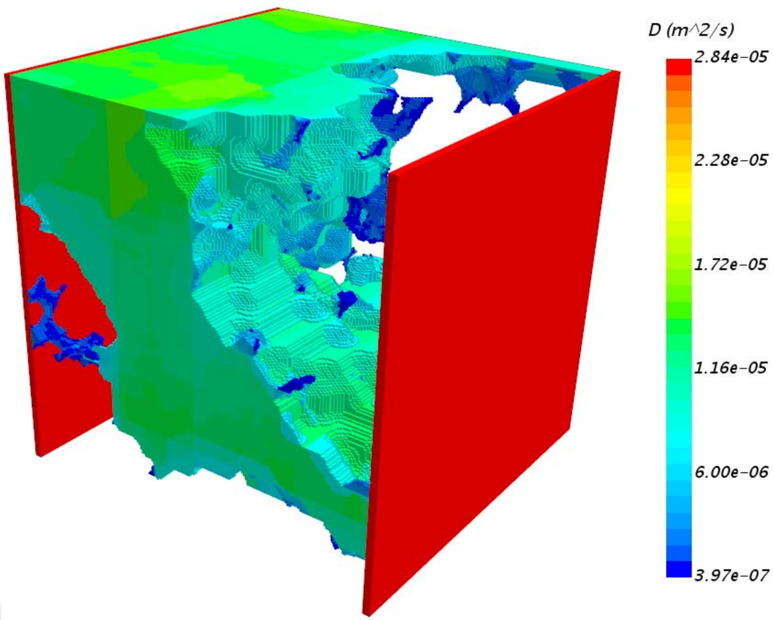


Oxygen Transport

- Effective diffusivities for X-CT data and the corresponding hybrid microstructure are compared
- Even though the primary pores decrease the tortuosity, they have minor effect on computed effective diffusivities because of slower Knudsen diffusion in primary pores

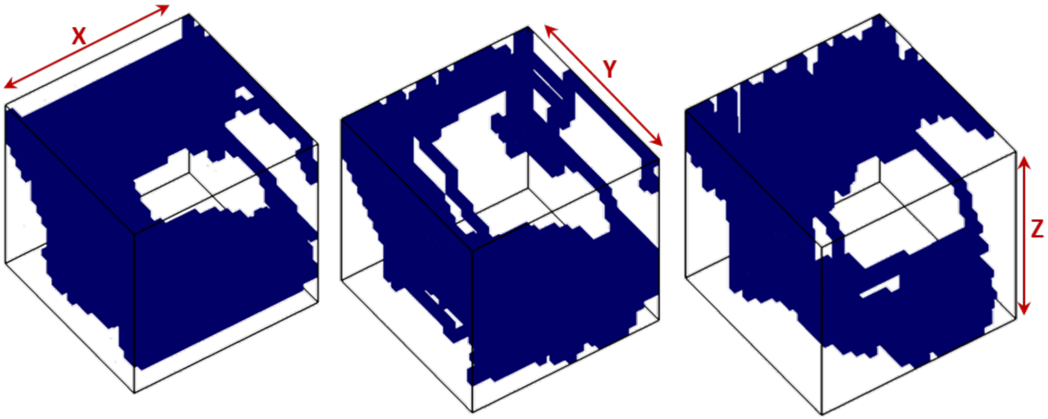


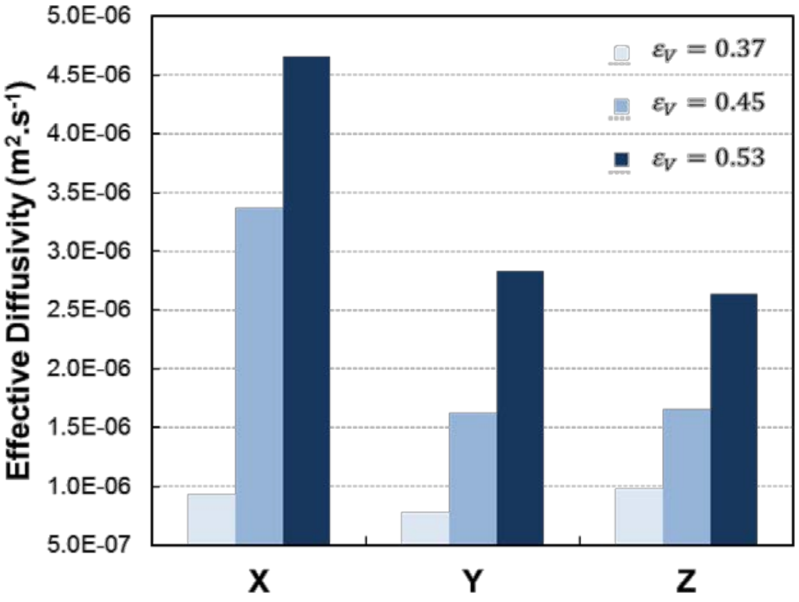


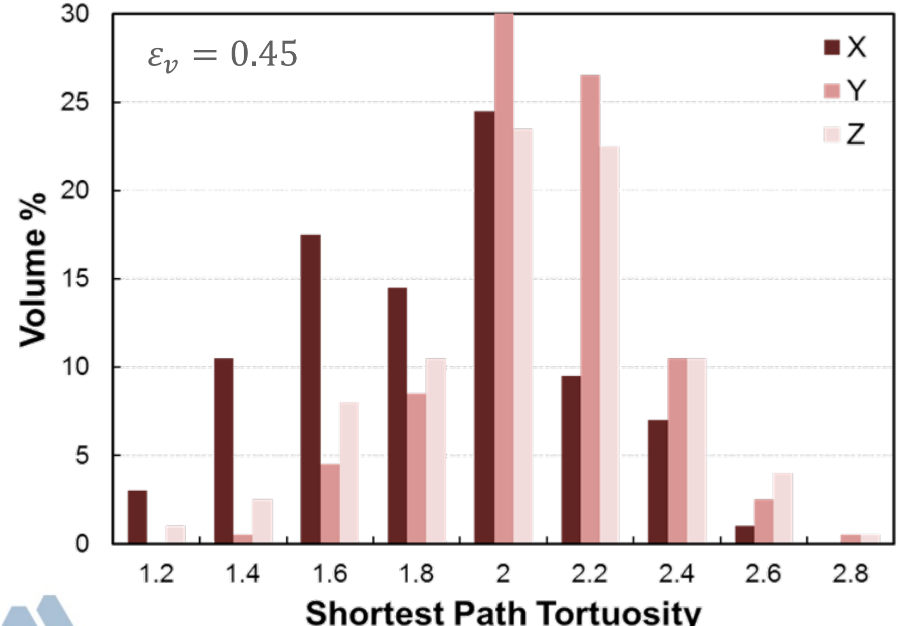


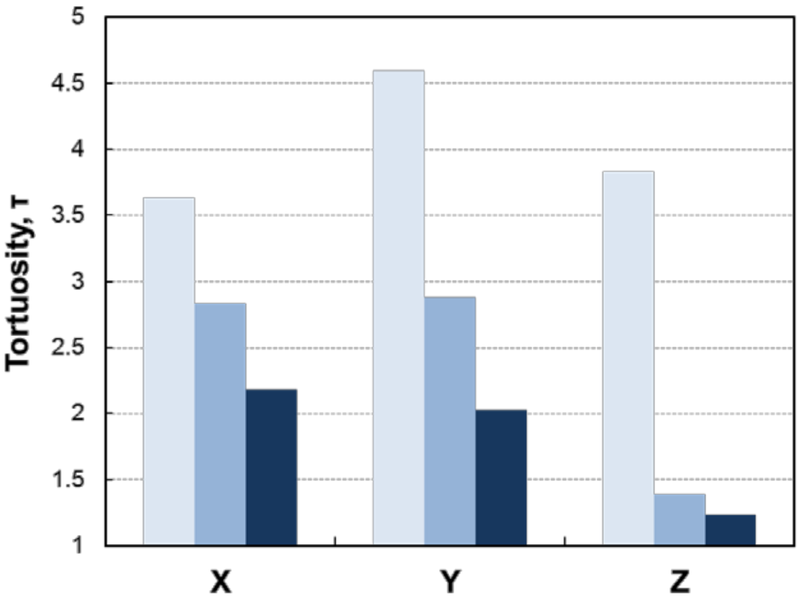
Oxygen Transport: Anisotropy

- The anisotropy of the microstructure is investigated by performing simulations in orthogonal directions



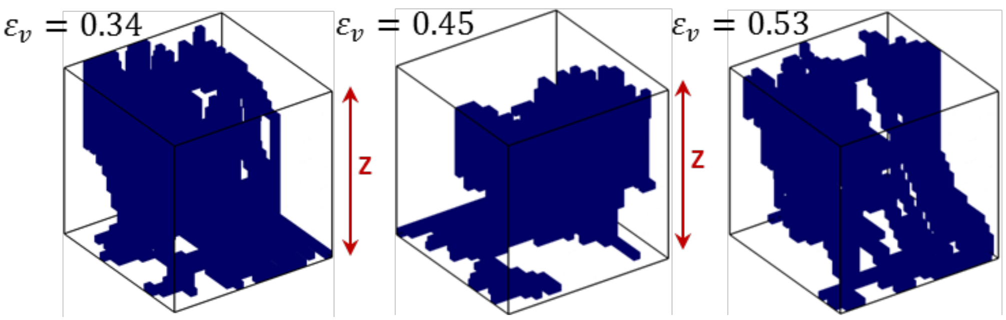


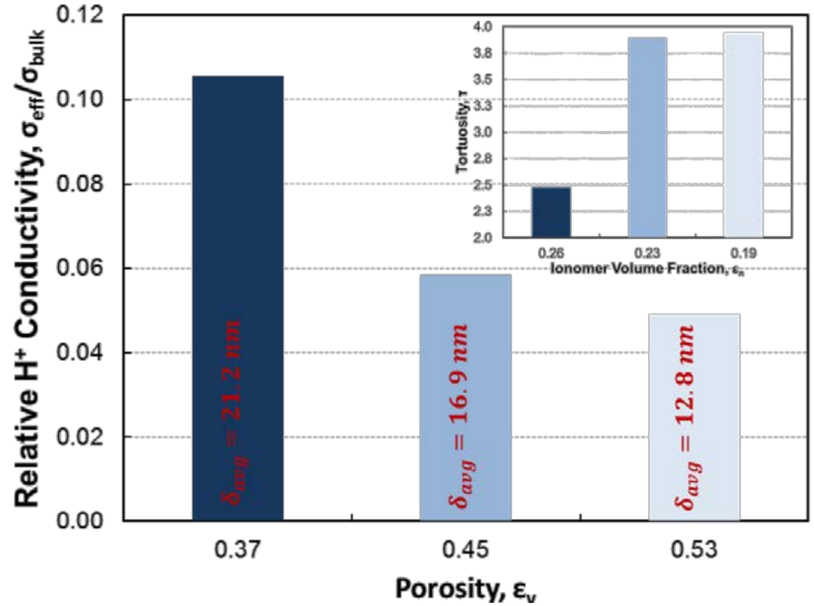


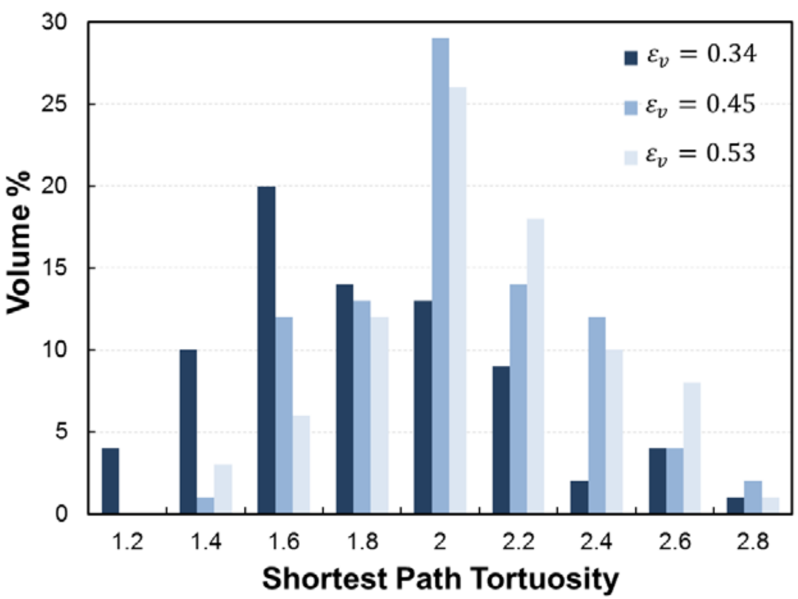


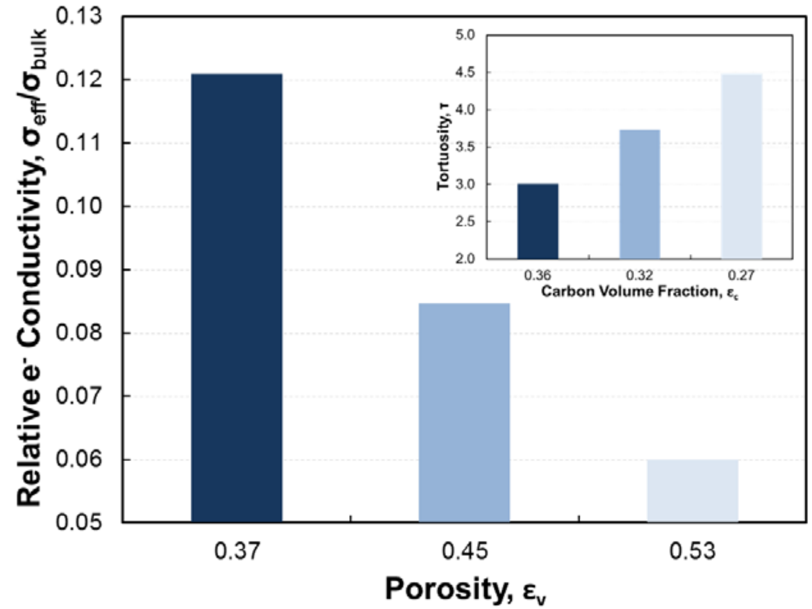
Charge Transport

- Effects of local composition on the charge transport are investigated
- Shortest path tortuosity is used to characterize the transport properties







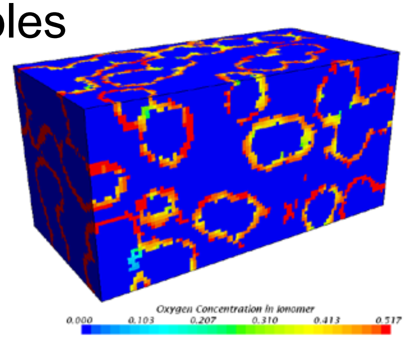


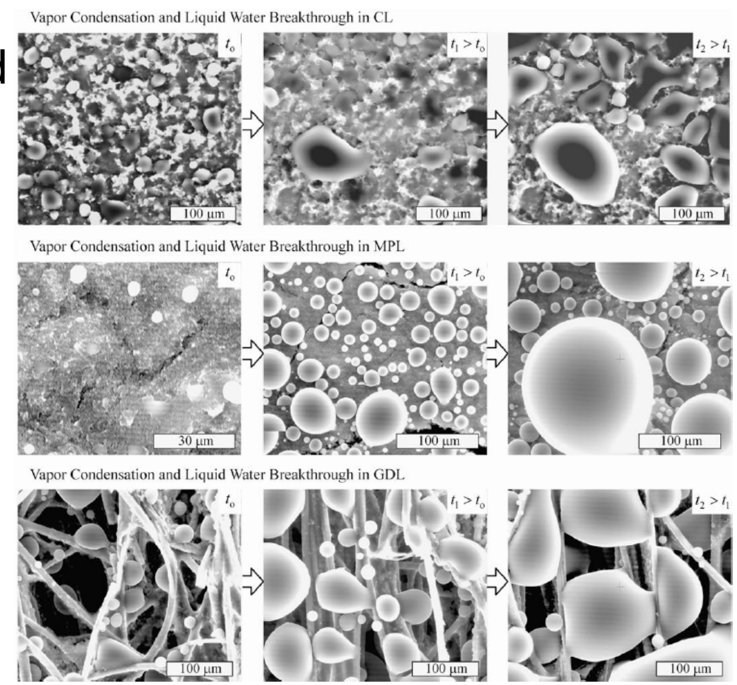
Conclusions and Future Work

- Detailed microstructure (C, Pt, ionomer, primary pores) of PEFC electrodes reconstructed by incorporating data from different experimental techniques
- Ionomer size distribution is calculated by combining X-CT with other techniques
- Although primary pores generate new pathways, they have minor effect on calculated effective diffusivity due to Knudsen diffusion regime
- Transport simulations and the shortest path tortuosity calculations illustrate heterogeneity and anisotropy of the microstructure

Next steps:

- X-CT (with 12.5 nm voxel) of samples doped with Cs to resolve ionomer network
- Electrochemical reactions will be solved and compared with experimental data
- Water transport will be studied by performing X-CT on water logged samples
- Application of methodology to PGM-free electrodes





ESEM micrographs, *Nam et al. Int. J. Heat Mass Tran. (2009)*