SFU

THROUGH PLANE GAS DIFFUSION OF CATALYST LAYER OF PEMFC: BIMODAL UNIT CELL MODELING

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The 27th International Symposium on Transport Phenomena
Honolulu– September 20-23, 2016

SFU Mechatronic Systems Engineering
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LAEC Laboratory for Alternative Energy Conversion

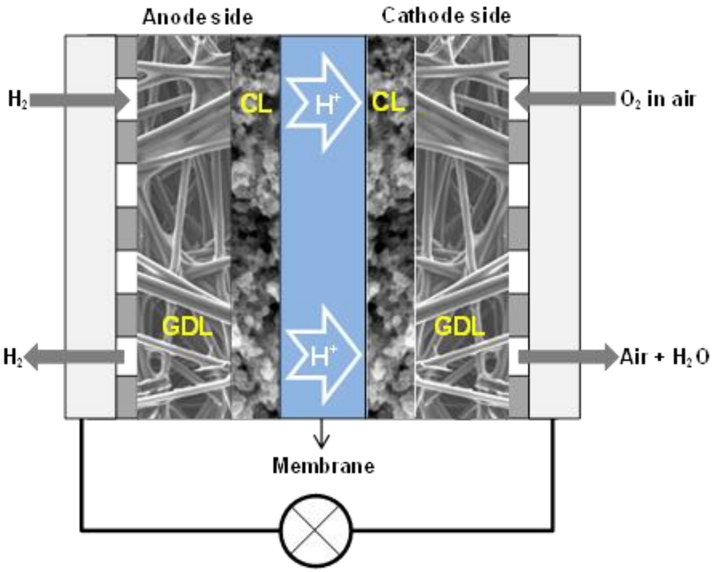
Introduction of LAEC group

- HVA[illegible]nd refr[illegible]eration systems
- The[illegible]ment of emerging bat[illegible]
- Ele[illegible]nic and power electronics cooling
- Ads[illegible]tion cooling system (ACS)
- Tra[illegible]phe[illegible]omena

A view of the LAEC lab near the SFU surrey campus

A view of the SFU Surrey campus

Importance of gas diffusion in catalyst layer of PEM fuel cell



- Oxygen transport through diffusion into catalyst layer (CL) and reduces in vicinity of embedded Pt particles

CL diffusivity affects

- ✓ Uniformity of oxygen reduction through the whole CL
- ✓ The CL lifetime
- ✓ The power density of PEMFC

Existing models for gas diffusivity within CL

Model	Note	ref
Medium theory	Compact relationship but low accuracy	DAG. Bruggeman, Annalen Der Physik (Leipzig). 24, 636–664 (1935). GH. Neale, WK. Nader., AIChE J. 19, 112–119 (1973). P.K. Das, X. Li, Z.S. Liu Appl. Energy, 87 (2010), p. 2785 M.M. Tomadakis, S.V. Sotirchos AIChE J., 39 (2004), p. 397 J.H. Nam, M. Kaviany Int. J. Heat Mass Transfer, 46 (2003), p. 4595
Pore network	Low-moderate computational cost Low accuracy	G.M. Laudonea, G.P. Matthewsa, P.A.C. Gane, Chem Eng Sci, 63, 1987 – 1996 (2008). M. Piri, M.J. Blunt, Physcs Review, 71, 26301 (2005). M. Prat, Chem Eng J., 86, 153–164 (2002). P.K. Sinha, C.Y. Wang, Electrochimica Acta 52 (2007) 7936–7945 J.T. Gostick, M.A. Ioannidis, M.W. Fowler , M.D. Pritzker, Journal of Power Sources 173 (2007) 277–290
Mimicking fabrication process	Accurate but computationally demanding	N.A. Siddique, F. Liu, Electrochim Acta, 55, 5357–5366 G. Inoue, M. Kawase, J. Power Sources. 327 (2016) 1–10 T. Rosen, J. Eller, J. Kang, N.I. Prasianakis, J. Mantzaras, F.N. Buchi,, J. Electrochem. Soc. 159 (2012) F536–F544
Reconstructing the geometry	Very accurate, but highly demanding and expensive	S. Zils, M. Timpel, T. Arlt, A. Wolz, I. Manke, C. Roth, Fuel Cells, 6, 966–972 (2010). H. Ostadia, P. Rama, Y. Liu, R. Chen, X.X. Zhang, K. Jiang, J. Membrane Sci, 351, 69–74 (2010). A. Berson, H.-W. Choi, J.G. Pharoah, Physic Rev, 83, 026310 (2011). A. Bertei, B. Nucci, C. Nicolella, Chem Eng Sci, 101, 175–190 (2013). A. Bertei, C. Nicolella, J. Power Sources, 196, 9429–9436 (2011). F. Jinang, A.C.M. Sousa, Transp Porous Medium, 75, 17–23 (2008). N. Zamel, X. Li, J. Shen, Energ Fuel. 23, 6070–6078 (2009).

Objective of this study

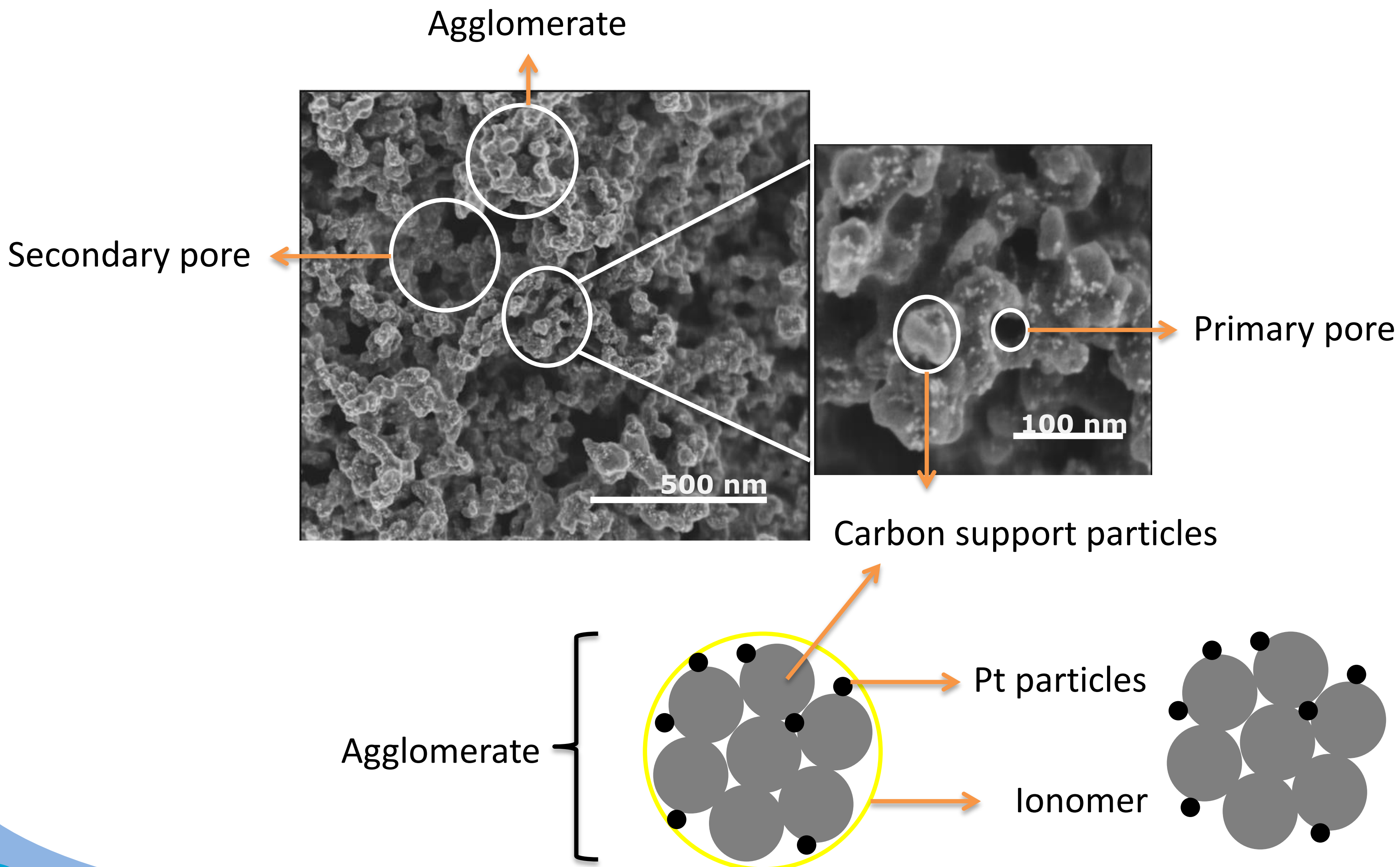
Develop a diffusivity model for CL which is:

- ✓ Accurate enough for performance prediction
- ✓ Considers porosity, and pore size distribution (PSD)
- ✓ Easy to implement

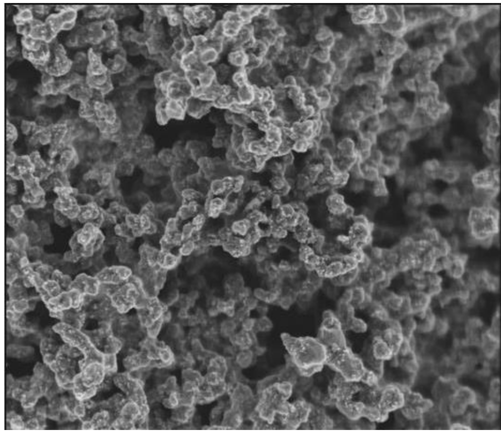
Unit Cell approach [1-3]
Considering a small unit as a representative for the whole problem

[1] H. Sadeghifar, N. Djilali, and M. Bahrami, (2014) *J. Power Sources*, Vol. 266, pp. 51-59
[2] V. Norouzifard and M. Bahrami, (2014) *J. Power Sources*, Vol. 264, pp. 92-99
[3] H. Sadeghifar, N. Djilali, and M. Bahrami, (2014) *J. Power Sources*, Vol. 248, pp. 632-641.

Microstructure of catalyst layer



The geometrical model for catalyst layer



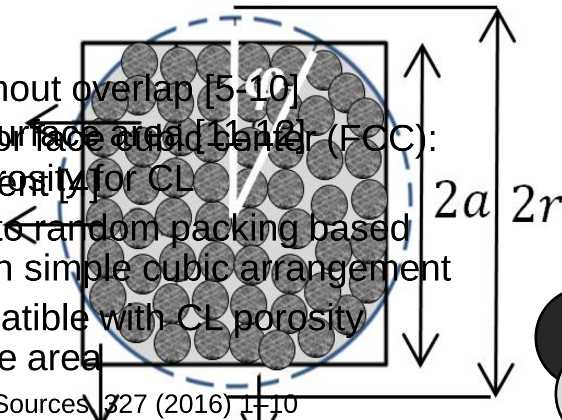
Assumption

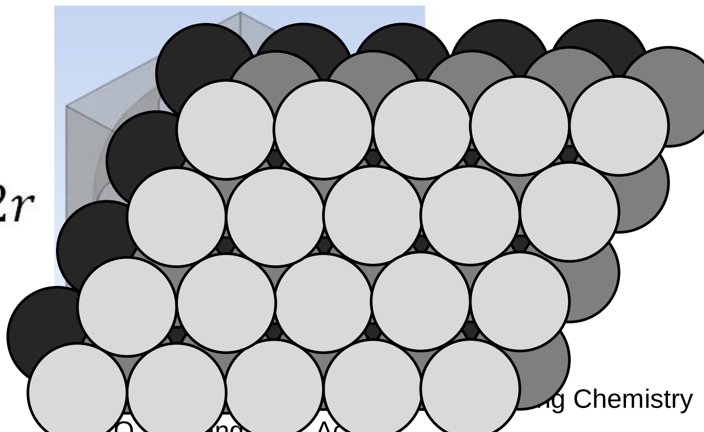
1. Carbon support particles has zero diffusivity
2. Ionomer has zero diffusivity
3. Carbon particles have spherical shape [1-3]
4. There are known arrangements for primary particles and agglomerates
5. Agglomerates are spheres with overlap

Spherical agglomerates without overlap [5-10]
- have high active surface area [11-12]
- Results in high porosity for CL

Close-packing of spheres or face cubic center (FCC):
- Is a stable arrangement [4]
- Have close porosity to random packing based on [4]
- ✓ Less porosity
- ✓ $\varepsilon = 0.26$

✓ Overlapped spheres with simple cubic arrangement
- ✓ The porosity is compatible with CL porosity
- ✓ Less active surface area



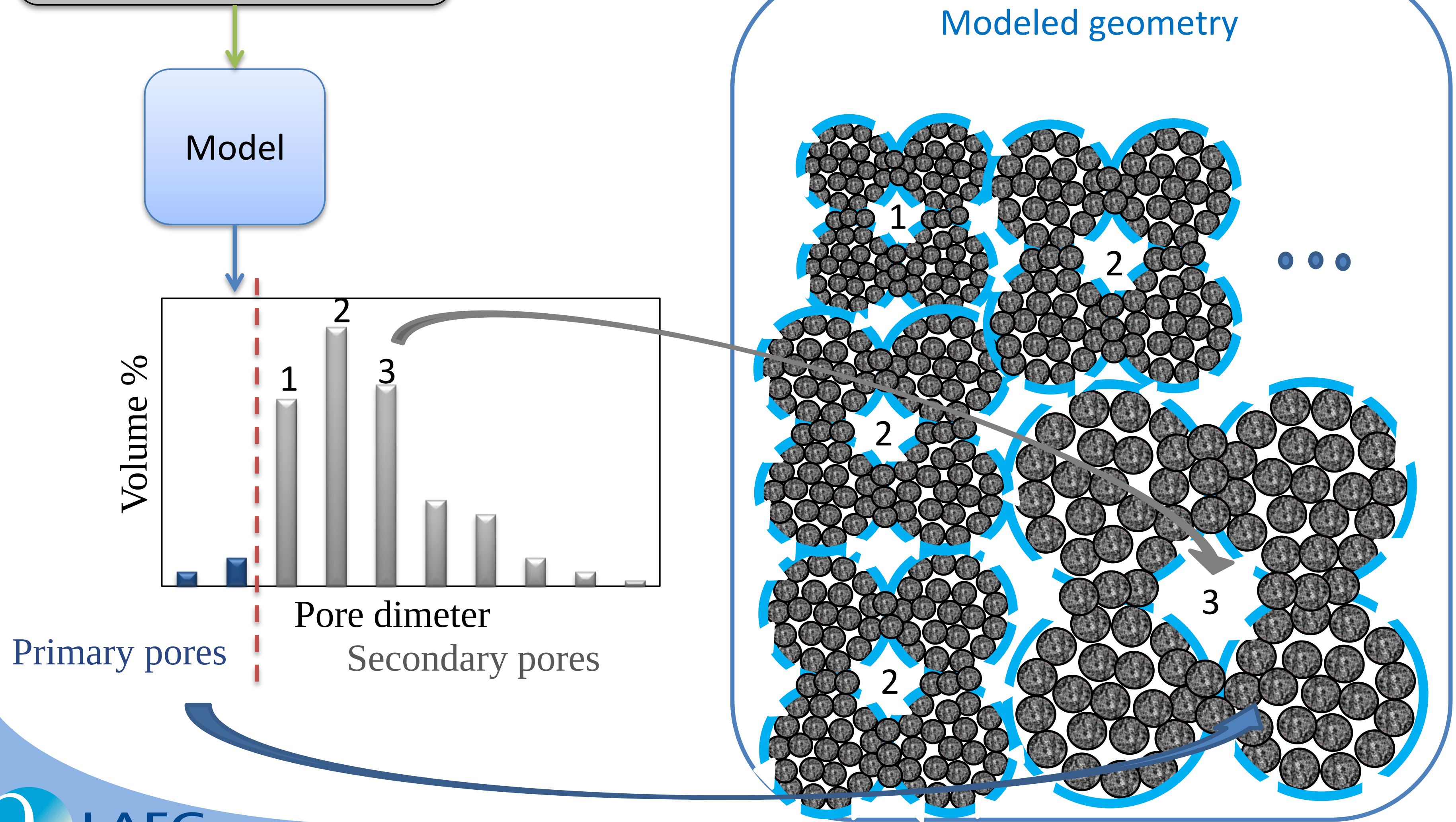


[1] G. Inoue, M. Kawase, J. Power Sources, 327 (2016) 1–10
[2] N.A. Siddique, F. Liu, Electrochim Acta, 55, 5357–5366
[3] K. Lange, P. Sui, N. Djilali, J Electrochem Soc, 157, B14334
[4] T.C. Hales(1998). "An overview of the Kepler conjecture".arXiv:math/9811071v2

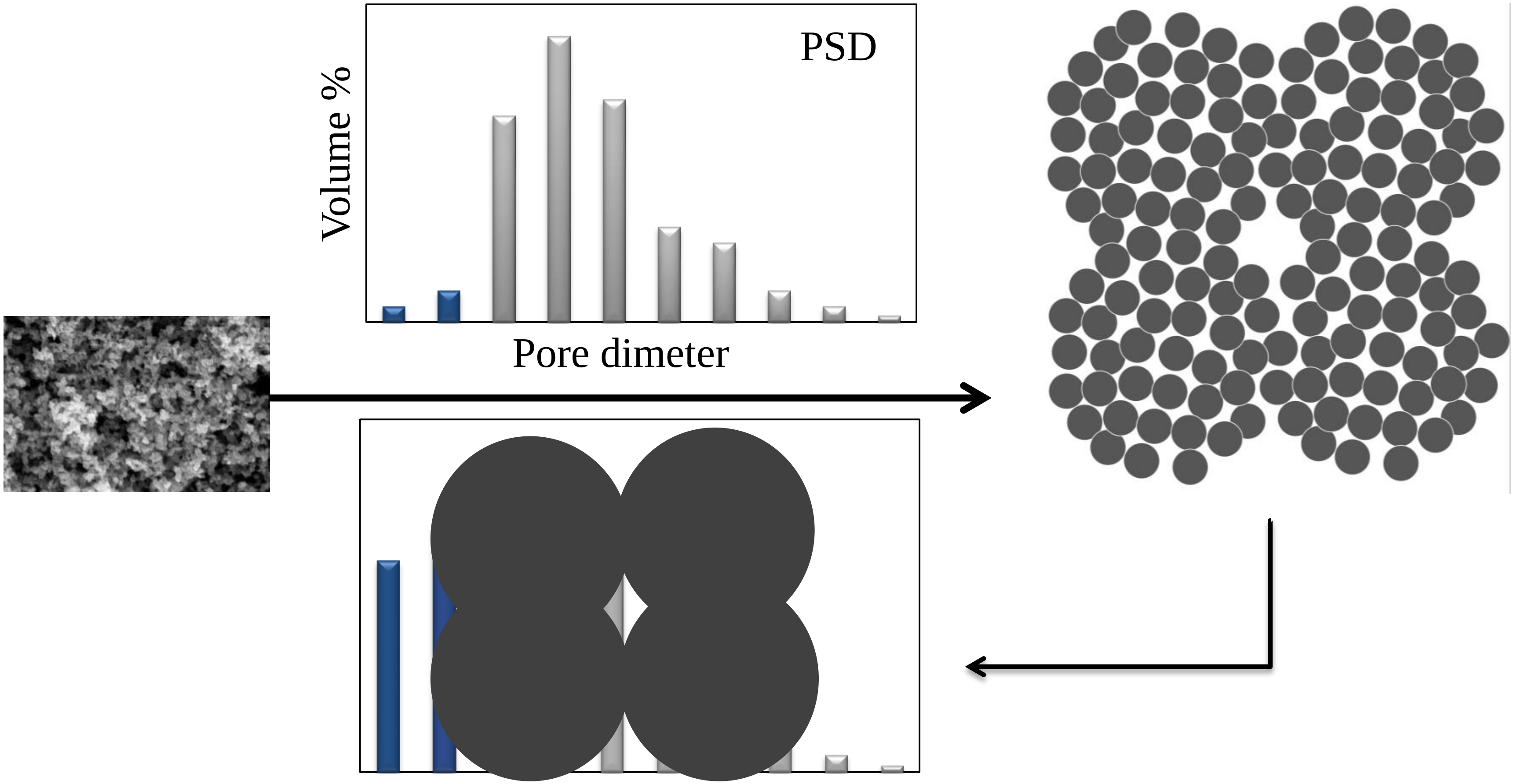
...ng Chemistry
[6] Q.P. Wang et al. Acta
[7] Q.P. Wang et al, Elec-trochim. Acta
[8] W. Sun, et al,Electrochim. Acta
[9] T. Suzuki, et al, J. Power Sources.
[10] S. Kamarajugadda et al, J. PowerSources
[11] X. Zhang et al, Electrochim. Acta
[12] X. Zhang et al, Electrochim. Acta

The geometrical model for catalyst layer

1. Pore size distribution
2. Porosity



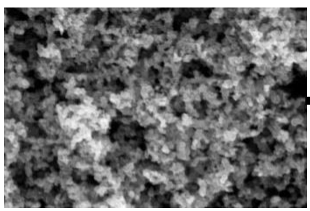
Open and covered agglomerates

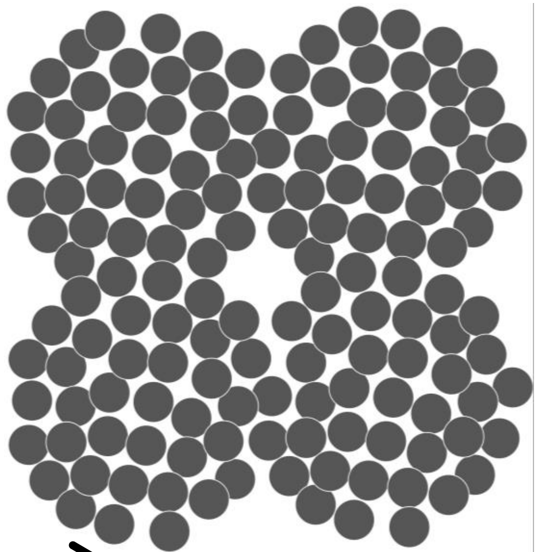


There has to be some units without open primary pores, larger than carbon support particles which secondary pores lay between them

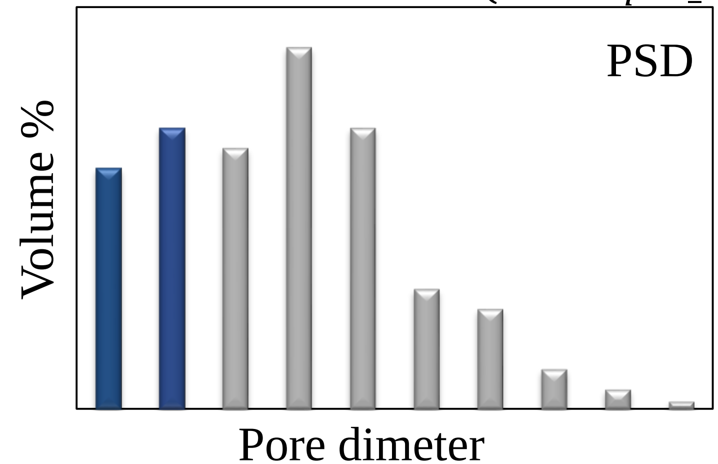
Open and covered agglomerates

Open agglomerates

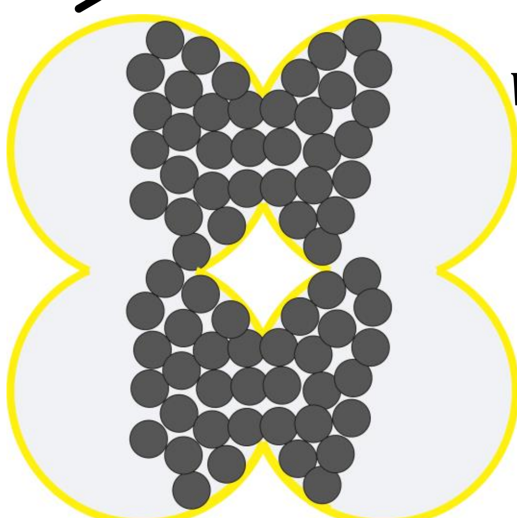




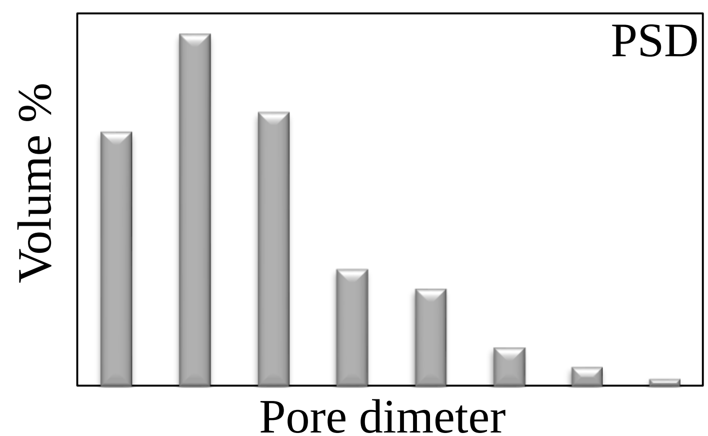
$$Volume = V_{\text{Primary pores}} \frac{\varepsilon_{open\_agg}(1-\varepsilon)}{\varepsilon(1-\varepsilon_{open\_agg})}$$



Covered agglomerates with ionomer/Blind pores



$$Volume = V_{\text{pores}} - V_{\text{Primary pores}} \frac{\varepsilon_{open\_agg}(1-\varepsilon)}{\varepsilon(1-\varepsilon_{open\_agg})}$$

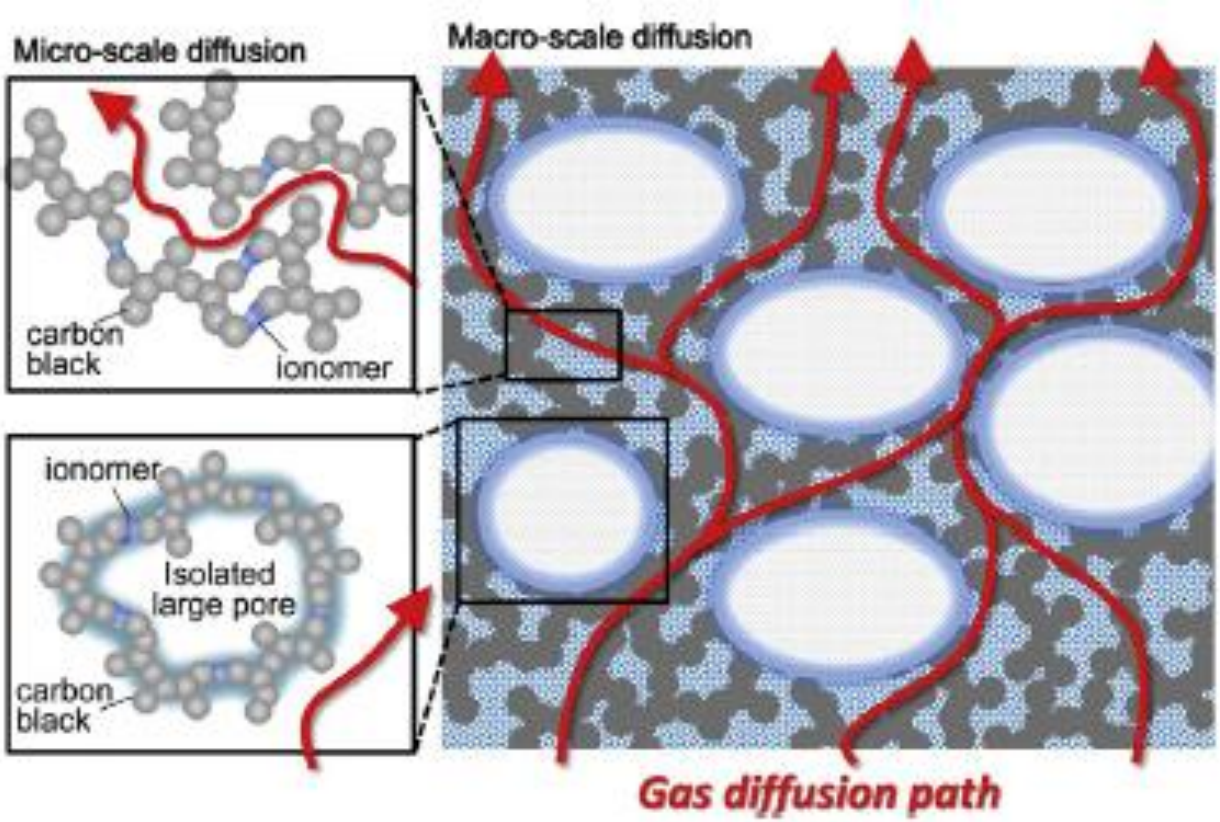


Large units with zero diffusivity

Effect of porous structure of catalyst layer on effective oxygen diffusion coefficient in polymer electrolyte fuel cell

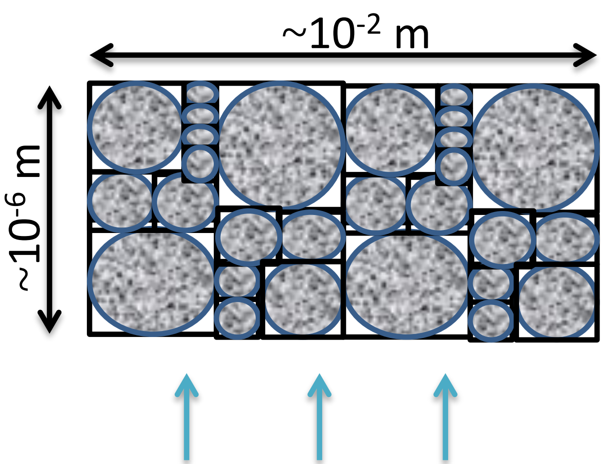
Gen Inoue*, Motoaki Kawase

Journal of Power Sources 327 (2016) 1–10

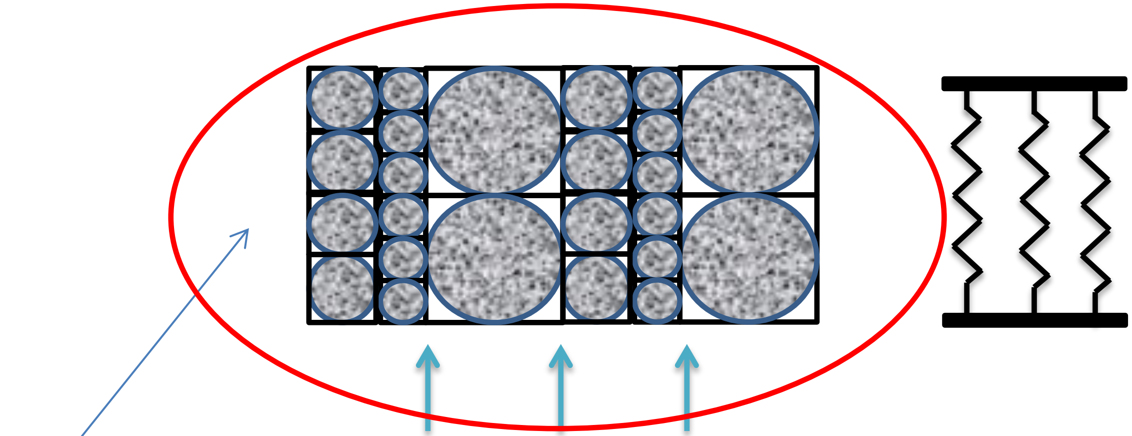


Asymptotic approach

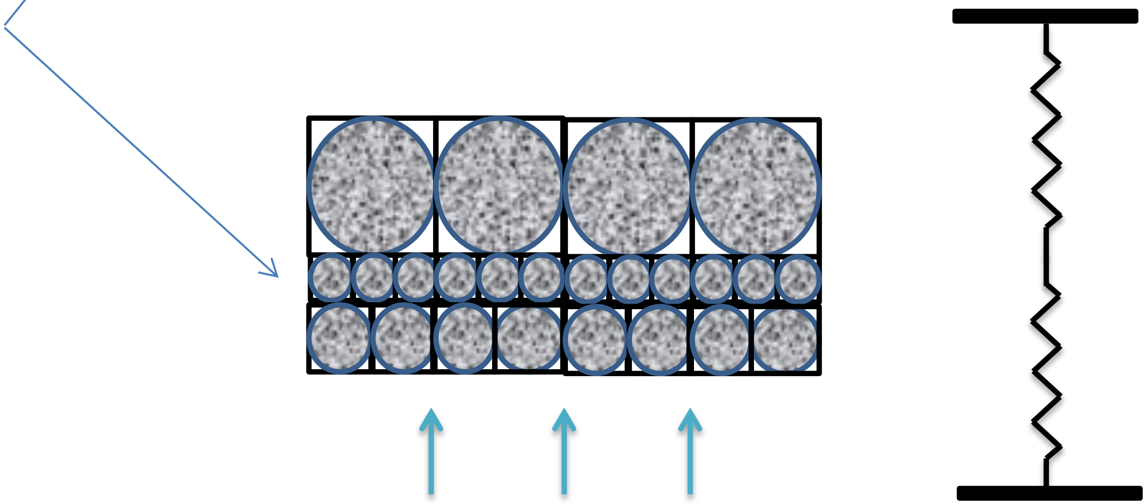
Randomly distributed unit cells



Diffusivity direction



Parallel asymptote



Series asymptote

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The geometrical model for catalyst layer

$$D^* = 0.5\left[\int_0^{\cos^{-1}\left(\frac{1}{\xi}\right)} \frac{\xi\cos\theta d\theta}{\left[\left(\pi - 4\cos^{-1}\left(\frac{1}{\xi\cos\theta}\right)\right)(\xi\cos\theta)^2 + 4\sqrt{(\xi\cos\theta)^2 - 1}\right](D^*_{\text{micro}} - 1) + 4}\right.$$

$$+\left[\frac{\sqrt{\frac{\pi\xi^2 D^*_{\text{micro}}}{4+\pi\xi^2 D^*_{\text{micro}}}}}{\pi D^*_{\text{micro}}\xi}\tan^{-1}\left(s\sqrt{\frac{\pi\xi^2 D^*_{\text{micro}}}{4+\pi D^*_{\text{micro}}}}\right)\right]_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}\Bigg]^{-1} + \frac{\pi D^*_{\text{micro}}(\xi^2-1)}{4}$$

$$+ 0.5\left[\frac{D^*_{\text{micro}}\pi\xi}{(1-D^*_{\text{micro}})}\left(s - \frac{\ln\left(1+\frac{\xi(1-D^*_{\text{micro}})}{D^*_{\text{micro}}}s\right)}{\xi(1-D^*_{\text{micro}})/D^*_{\text{micro}}}\right)_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}\right]$$

$$+ 0.5\int_0^{\cos^{-1}\left(\frac{1}{\xi}\right)} \frac{D^*_{\text{micro}}\left(4\xi\cos\varphi\cos^{-1}\left(\frac{1}{\xi\cos\varphi}\right) - \pi\xi\cos\varphi\right)\xi\sin\varphi d\varphi}{\xi\sin\varphi + D^*_{\text{micro}}(1-\xi\sin\varphi)}$$

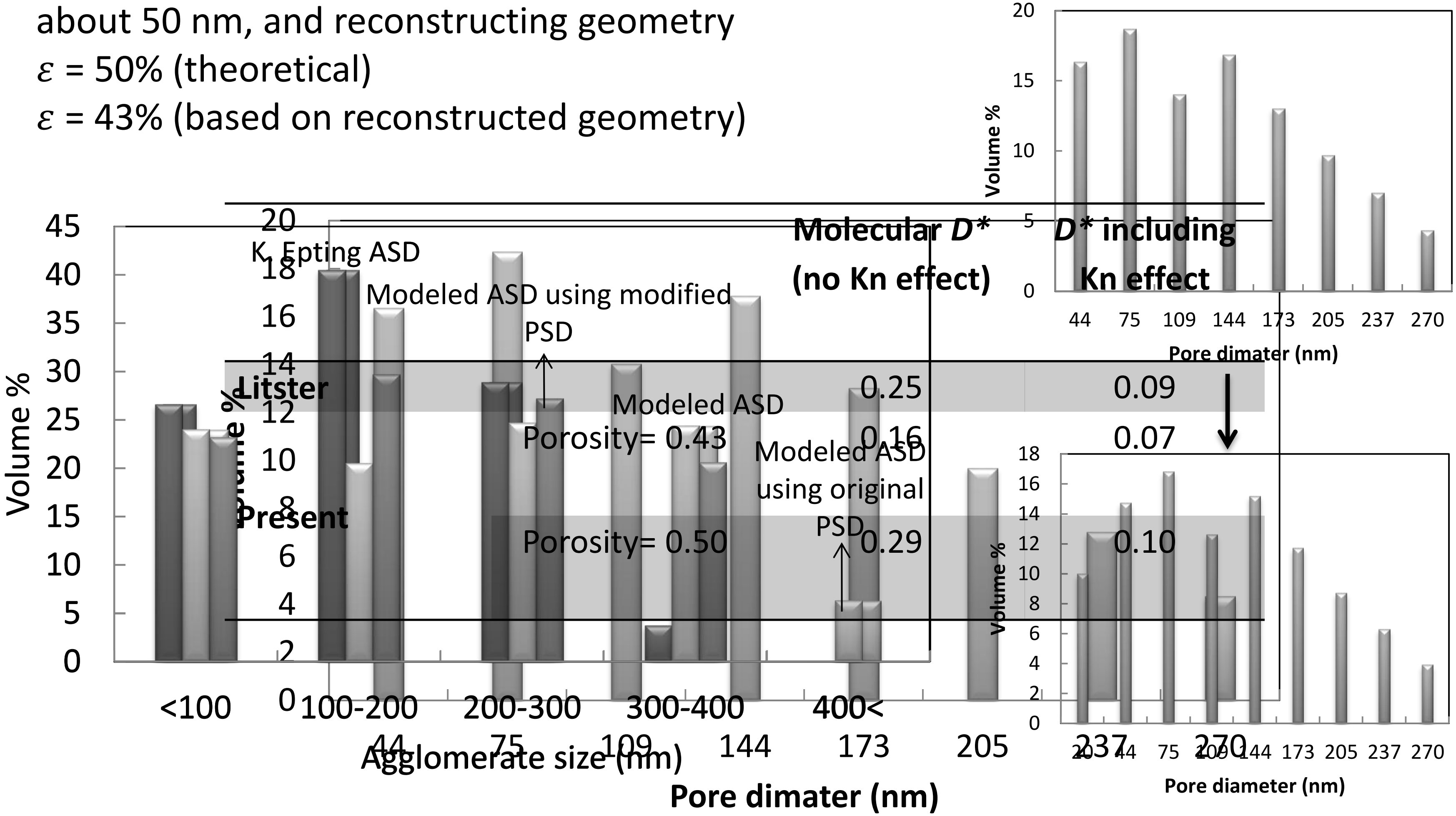
$$+\frac{\left[4 - \pi\xi^2 + 4\left(\xi^2\cos^{-1}\left(\frac{1}{\xi}\right) - \sqrt{\xi^2-1}\right)\right]}{4}$$

Model validation with Epting and Litster study

Nano-CT XRay tomography with resolution about 50 nm, and reconstructing geometry

ε = 50% (theoretical)

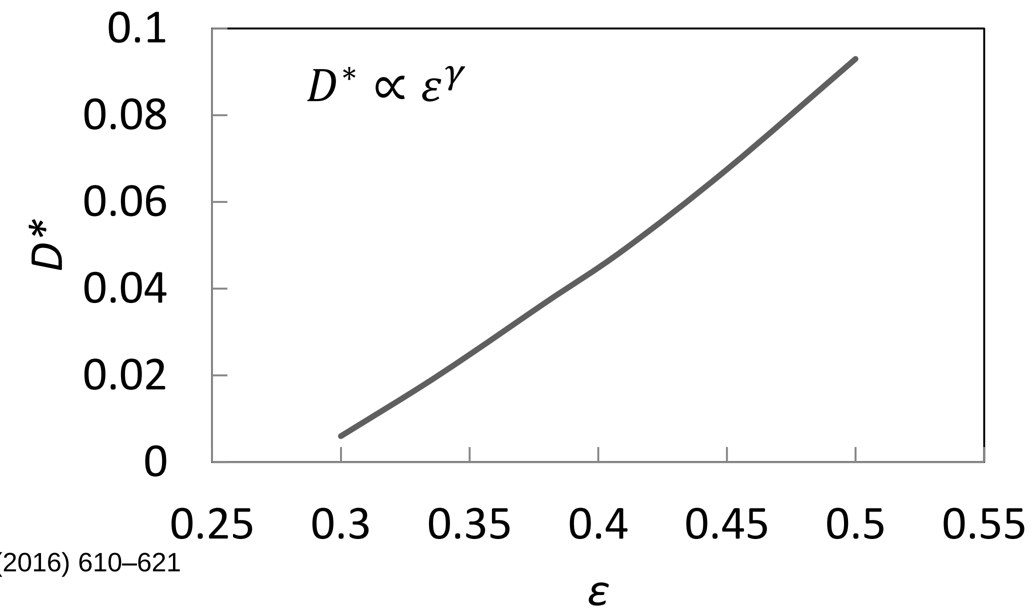
ε = 43% (based on reconstructed geometry)



W.K. Epting, J. Gelb, S. Litster, Resolving the three-dimensional microstructure of polymer electrolyte fuel cell electrodes using nanometer-scale X-ray computed tomography, Adv. Funct. Mater. 22 (2012) 555–560

Diffusivity versus porosity considering Knudsen effect

	γ with Knudsen effect	γ without Knudsen effect
Present study	5	4
Mimicking fabrication [1]	5	4
Reconstructing geometry (FIB-SEM) [2]	5	4
Experimentally [2]	6	-



[1] G. Inoue, M. Kawase, J. Power Sources. 327 (2016) 1–10
[2] G. Inoue, K. Yokoyama, T. Ooyama, T. Junpei Terao, T. Takeshi, K. Tomomi, M. Kawase, J. Power Sources. 327 (2016) 610–621

Conclusion

An analytical model is developed for catalyst layer of PEM fuel cell

- Inputs:
  - ✓ Porosity
  - ✓ Pore size distribution
- Outputs:
  - ✓ Agglomerate size distribution
  - ✓ Ionomer coverage
  - ✓ Diffusivity within agglomerates
  - ✓ Diffusivity of catalyst layer

The model is validated in compare with Epting and litster study for

- ✓ Agglomerate size distribution range
- ✓ Catalyst layer diffusivity with Knudsen effect
- ✓ Catalyst layer diffusivity without Knudsen effect

ACKNOWLEDGEMENT

Natural Sciences and Engineering Research Council of Canada (NSERC)

Automotive Fuel Cell Cooperation Crop

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Thanks for your attention!

Any questions?

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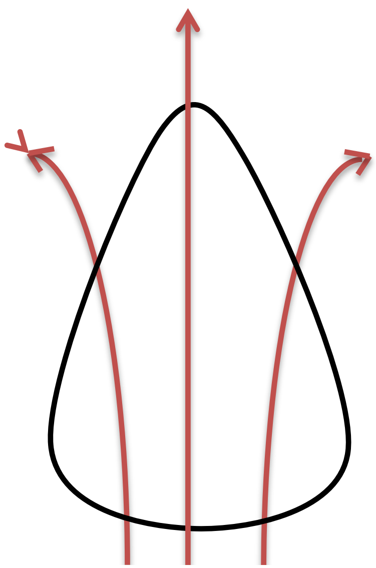
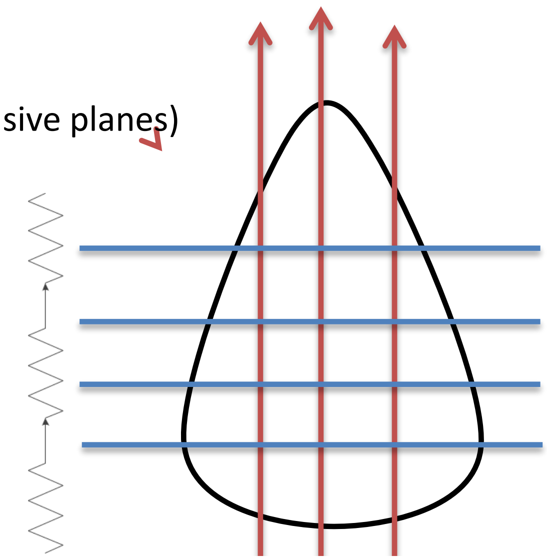
Estimation of Unit cell diffusivity

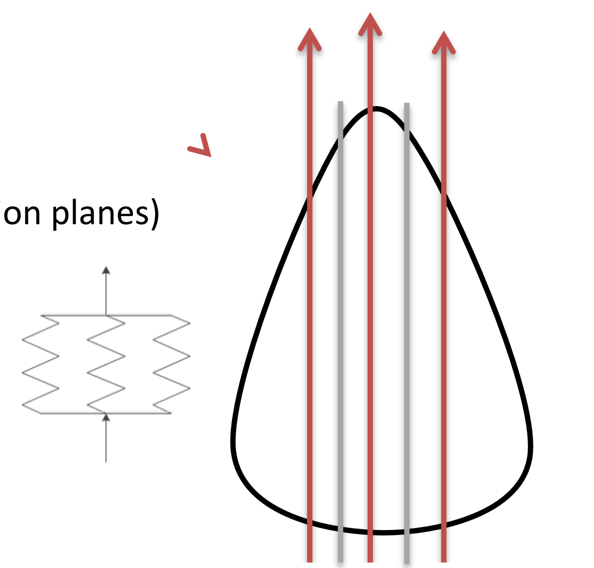


C=Const.
(super diffusive planes)



Introducing super diffusive planes into the geometry:
Higher diffusivity (***Upper bound***)

N=0
(insolation planes)



Introducing insolation planes into the geometry:
lower diffusivity (***Lower bound***)

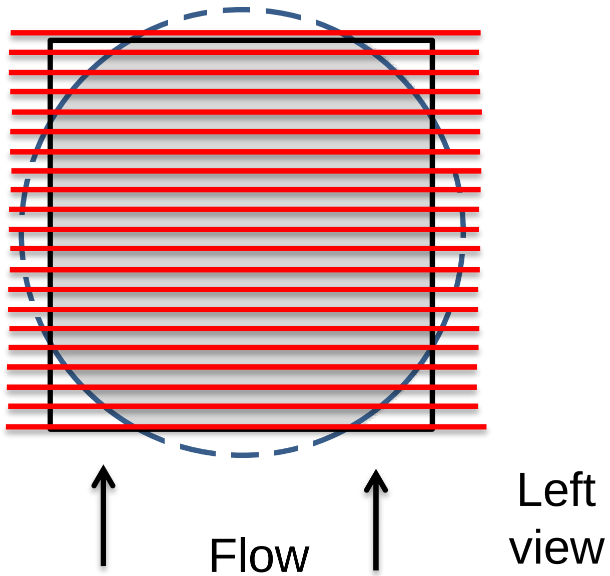
Effective diffusivity of upper bound

Lower bound for resistance

$$D^{*-1} = \int_0^{cos^{-1}\left(\frac{1}{\xi}\right)} \frac{\xi cos\theta d\theta}{\left[\left(\pi - 4cos^{-1}\left(\frac{1}{\xi cos\theta}\right)\right)(\xi cos\theta)^2 + 4\sqrt{(\xi cos\theta)^2 - 1}\right](D^*_{agg/pore} - 1) + 4}$$

$$+ \left[\frac{\sqrt{\frac{\pi\xi^2 D^*_{agg/pore}}{4 + \pi\xi^2 D^*_{agg/pore}}}}{\pi D^*_{agg/pore}\xi} tan^{-1}\left(s\sqrt{\frac{\pi\xi^2 D^*_{agg/pore}}{4 + \pi D^*_{agg/pore}}}\right)\right]_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}$$

$$D^*_{agg/pore} = \frac{D_{\text{agglomerate}}}{D_{\text{binary}}}$$

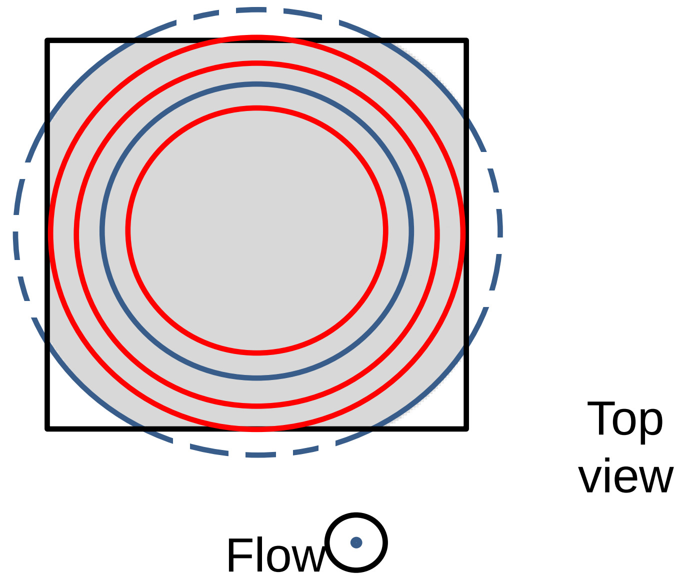


Effective diffusivity of lower bound

$$D^* = \frac{\pi D^*{}_{agg/pore}(\xi^2 - 1)}{2} + \left[\frac{D\pi\xi}{\left(1 - D^*{}_{agg/pore}\right)} \left(s - \frac{\ln\left(1 + \frac{\xi\left(1 - D^*{}_{agg/pore}\right)}{D^*{}_{agg/pore}} s\right)}{\xi\left(1 - D^*{}_{agg/pore}\right)/D^*{}_{agg/pore}} \right)_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}} \right]$$

$$+ \int_0^{cos^{-1}\left(\frac{1}{\xi}\right)} \frac{D^*{}_{agg/pore}\left(4\xi cos\varphi cos^{-1}\left(\frac{1}{\xi cos\varphi}\right) - \pi\xi cos\varphi\right)\xi sin\varphi d\varphi}{\xi sin\varphi + D^*{}_{agg/pore}(1 - \xi sin\varphi)}$$

$$+ \frac{\left[4 - \pi\xi^2 + 4\left(\xi^2 cos^{-1}\left(\frac{1}{\xi}\right) - \sqrt{\xi^2 - 1}\right)\right]}{2}$$



Unit cell parameters and diffusivity

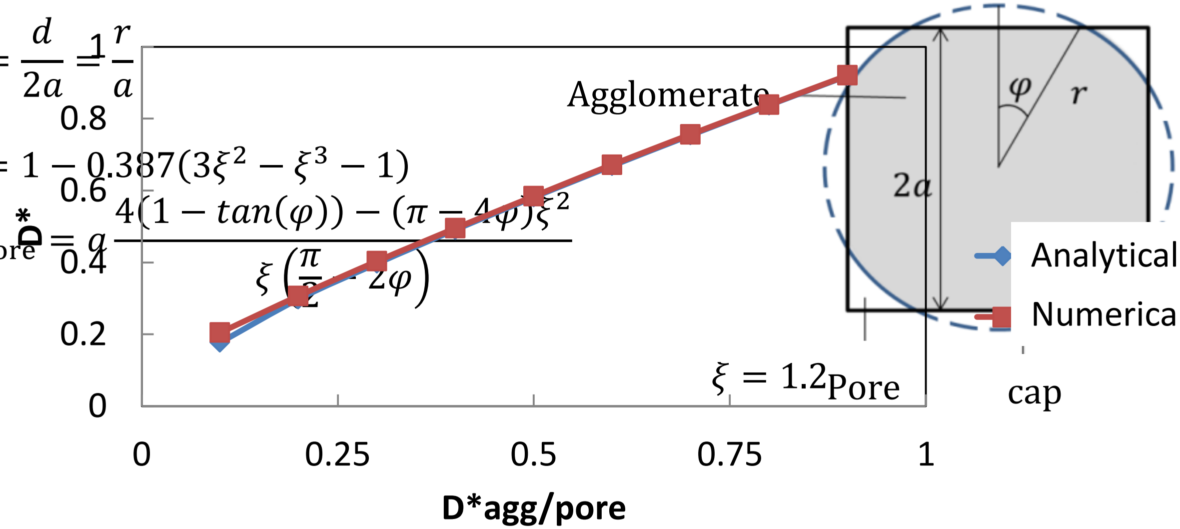
$\varepsilon \rightarrow$ Agglomerate overlap

$d_{\text{pore}} \rightarrow$ Cell dimension

$$\xi = \frac{d}{2a} = \frac{r}{a}$$

$$\varepsilon = 1 - 0.387(3\xi^2 - \xi^3 - 1)$$

$$d_{\text{pore}} = a\,\frac{4(1 - tan(\varphi)) - (\pi - 4\varphi)\xi^2}{\xi\left(\frac{\pi}{2} - 2\varphi\right)}$$



$$D^* = 0.5\left[\int_0^{cos^{-1}\left(\frac{1}{\xi}\right)} \frac{\xi cos\theta d\theta}{\left[\left(\pi - 4cos^{-1}\left(\frac{1}{\xi cos\theta}\right)\right)(\xi cos\theta)^2 + 4\sqrt{(\xi cos\theta)^2 - 1}\right](D^*_{\text{micro}} - 1) + 4} + \left[\frac{\sqrt{\frac{\pi\xi^2 D^*_{\text{micro}}}{4 + \pi\xi^2 D^*_{\text{micro}}}}}{\pi D^*_{\text{micro}}\xi} tan^{-1}\left(s\sqrt{\frac{\pi\xi^2 D^*_{\text{micro}}}{4 + \pi D^*_{\text{micro}}}}\right)\right]_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}\right.$$

$$+ \frac{\pi D^*_{\text{micro}}(\xi^2 - 1)}{4} + 0.5\left[\frac{D^*_{\text{micro}}\pi\xi}{(1 - D^*_{\text{micro}})}\left(s - \frac{\ln\left(1 + \frac{\xi(1 - D^*_{\text{micro}})}{D^*_{\text{micro}}}s\right)}{\xi(1 - D^*_{\text{micro}})/D^*_{\text{micro}}}\right)\right]_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}$$

$$\left. + 0.5\int_0^{cos^{-1}\left(\frac{1}{\xi}\right)} \frac{D^*_{\text{micro}}\left(4\xi cos\varphi cos^{-1}\left(\frac{1}{\xi cos\varphi}\right) - \pi\xi cos\varphi\right)\xi sin\varphi d\varphi}{\xi sin\varphi + D^*_{\text{micro}}(1 - \xi sin\varphi)} + \frac{\left[4 - \pi\xi^2 + 4\left(\xi^2 cos^{-1}\left(\frac{1}{\xi}\right) - \sqrt{\xi^2 - 1}\right)\right]}{4}\right]^{-1}$$

Diffusivity Model

Close-packing of spheres or face cubic center (FCC):

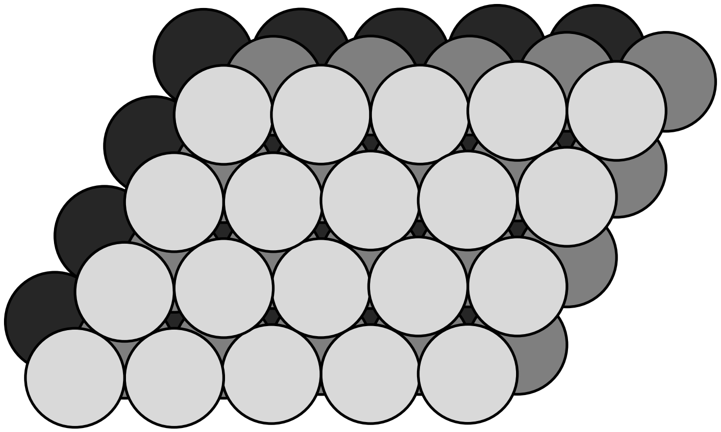
- Is a stable arrangement [1]
- Have close porosity to random packing based on [1]
- The porosity is compatible with CL porosity
- $\varepsilon = 0.26$

$$D_{eff} = \left(\frac{1}{D_{\text{bulk}}} + \frac{1}{D_{Kn}}\right)^{-1}$$

$$D_{Kn} = \frac{8}{3} r_{\text{pore}} \sqrt{\frac{RT}{2\pi M}}$$

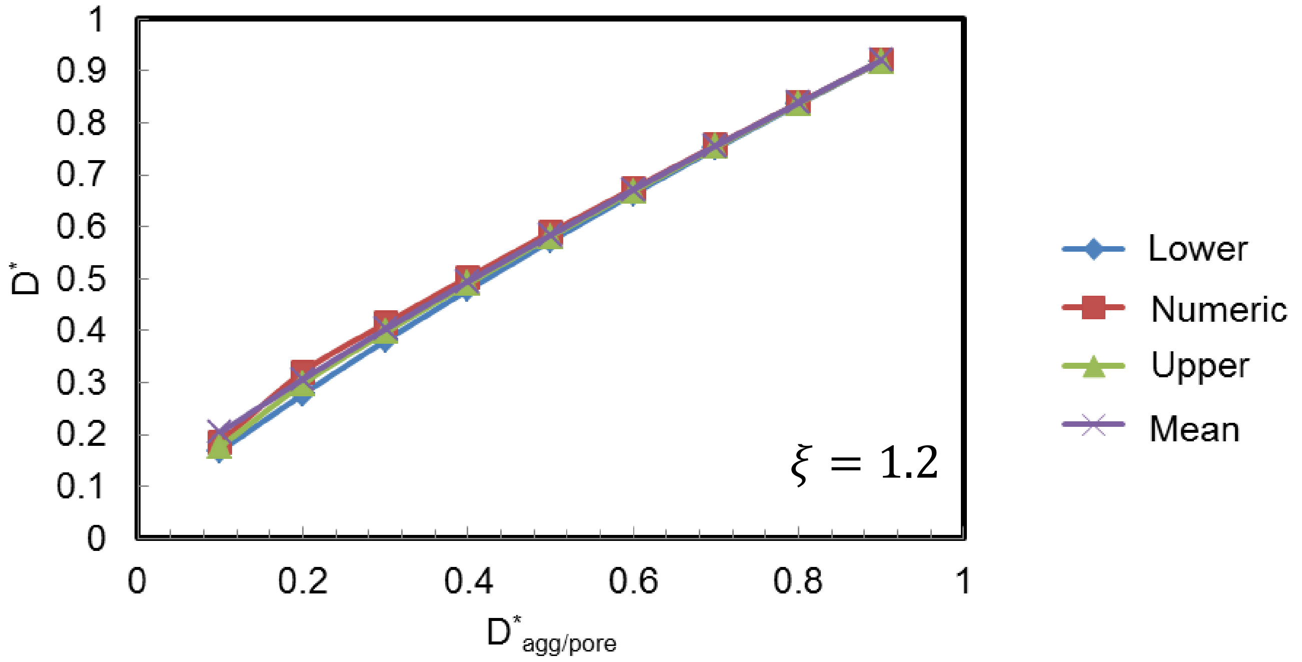
$$\text{Relative diffusivity} = D^* = \frac{D_{\text{bulk}}}{D_{\text{binary}}}$$

$$D^* = \frac{NL}{D_{\text{binary}} A \Delta C} \xrightarrow{\text{Numerical model}} D^* = 0.11$$



[1] T.C. Hales(1998). "An overview of the Kepler conjecture".arXiv:math/9811071v2.

Resistance semi-analytical results vs numerical one

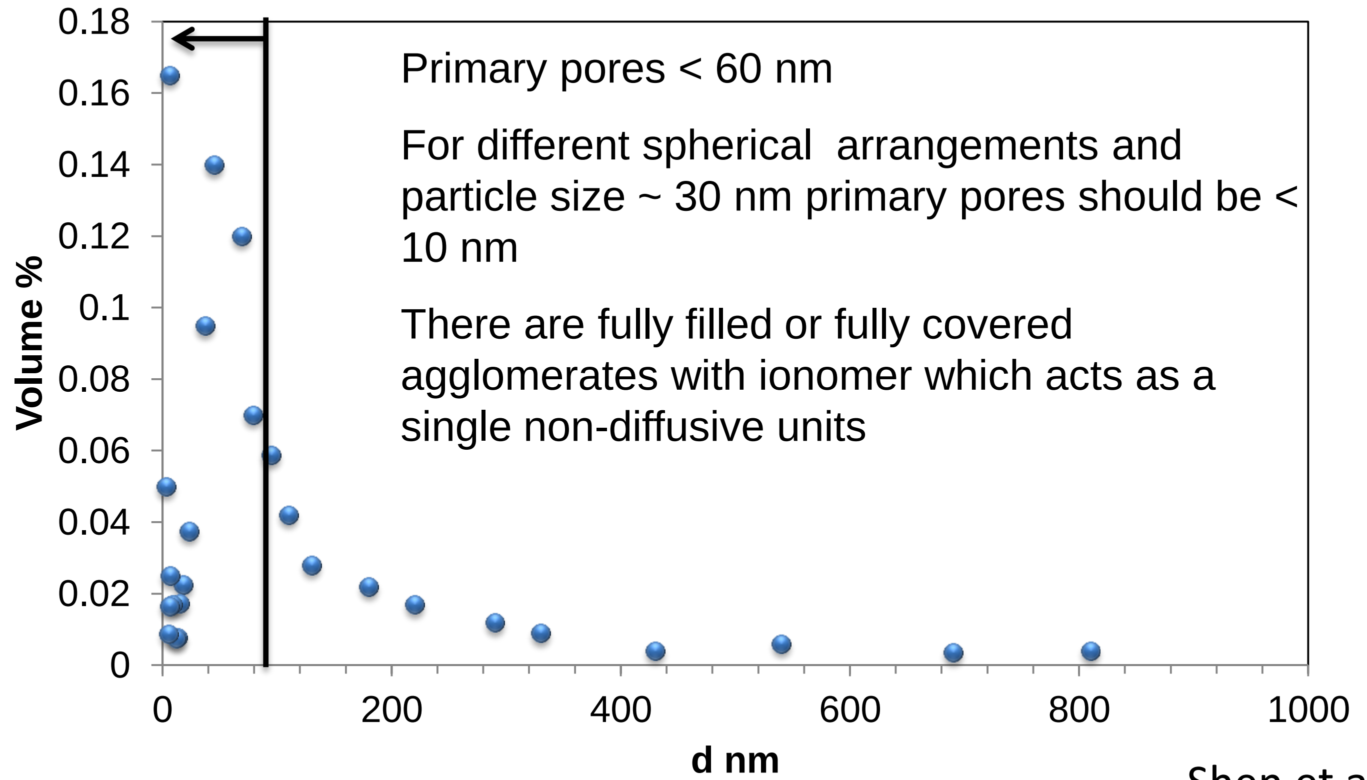


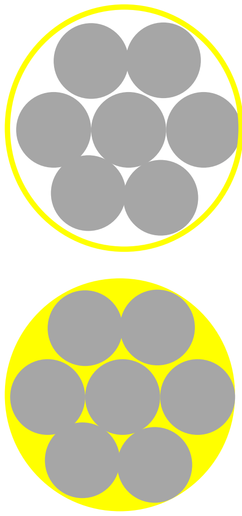
Ratio of primary pores to total pore volume

Based on the model:

$$\frac{V_{\text{Primary pores}}}{V_{\text{Total pores}}} = \frac{\varepsilon_{bp}(1-\varepsilon)}{\varepsilon(1-\varepsilon_{bp})} = 0.53\ (for\ Shen\ study)$$

ε_{bp} is porosity within agglomerates





Shen et al. PSD

Portion of covered agglomerates with ionomer

- Pores with less than 10 nm diameter are considered as primary pores [1-5]
- Primary pores in PSD belong to open agglomerates (not covered with ionomer)
- $V_{\text{Primary pores}}(in\ PSD) \times \frac{V_{\text{Total pores}}}{V_{\text{Primary pores}}}$ =Volume of pores of open agglomerates
- Total pore volume in PSD –volume of pores of open agglomerates

[1] B. Andreaus, M. Eikerling, Catalyst Layer Operation in PEM Fuel Cells: From Structural Pictures to Tractable Models, 2009.
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[3] K. Malek, M. Eikerling, Q. Wang, T. Navessin, Z. Liu, Self-Organization in Catalyst Layers of Polymer Electrolyte Fuel Cells, J. Phys. Chem. C. 111 (2007) 13627–13634..
[4] M. Eikerling, A.A. Kornyshev, Modelling the performance of the cathode catalyst layer of polymer electrolyte fuel cells, J. Electroanal. Chem. 453 (1998) 89–106..
[5] M. Eikerling, A.S. Ioselevich, A.A. Kornyshev, How good are the electrodes we use in PEFC? (Understanding structure vs. performance of membrane-electrode assemblies), Fuel Cells. 4 (2004) 131–140.