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Modeling Diffusivity in Catalyst Layer of a PEMFC Based on a Unit Cell Approach

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Importance of gas diffusion in CL

- CL is a porous layer with ~30-60% porosity
- Oxygen reduces in vicinity of Pt particles embedded in CCL
- Oxygen and product water vapor transport through diffusion into and out of the CCL respectively

CL diffusivity affects

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

Challenges to model diffusivity of CCL

- CL has a random, to some extend, unpredictable structure
- Structure of CL is affected by many factors from composition to manufacturing process of producing CL
- Different diffusion mechanisms are happening within CL
- Generally working condition is a humid one which affects gas diffusion in several ways (interaction of water vapor with gas, ionomer swelling, etc.)

Existing models for gas diffusivity within CL

Model	ref	Note
Medium theory percolation theory	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	Compact relationships but low accuracy
Pore network	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	Moderately demanding

Existing models for gas diffusivity within CL

Model	ref	Note
Reconstructing the geometry	N.A. Siddique, F. Liu, Electrochim Acta, 55, 5357–5366 (2010). 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).	Accurate, but highly demanding and expensive

Objective of this study

Develop a diffusivity model for CL to be integrated in PEMFC toolbox developed at AFCC which is:

- ✓ Accurate enough for performance prediction
- ✓ Considers the most important parameters affecting gas diffusion: porosity, PSD, and connectivity
- ✓ Low demanding and not expensive
- ✓ Easy to implement

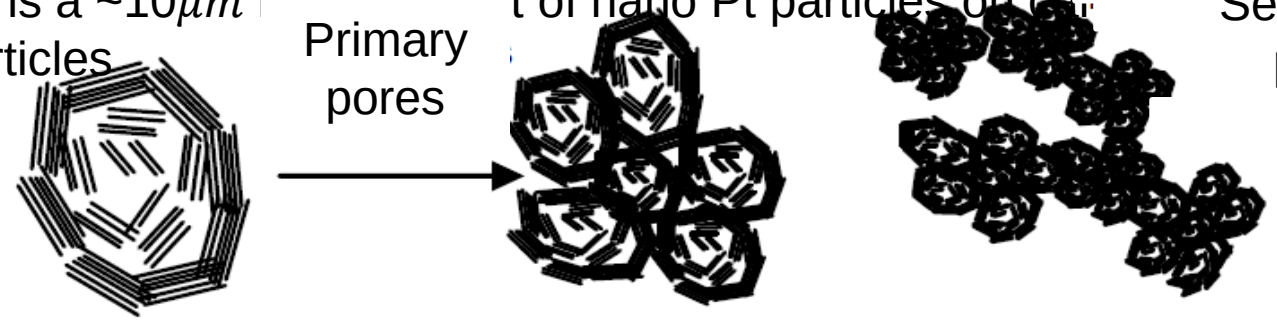
Unit Cell approach:

- ✓ Could be Accurate enough for performance prediction [1-3]
- ✓ Considers porosity, PSD, and a connectivity to some extend close to CL connectivity
- ✓ Low demanding and not expensive
- ✓ Easy to implement

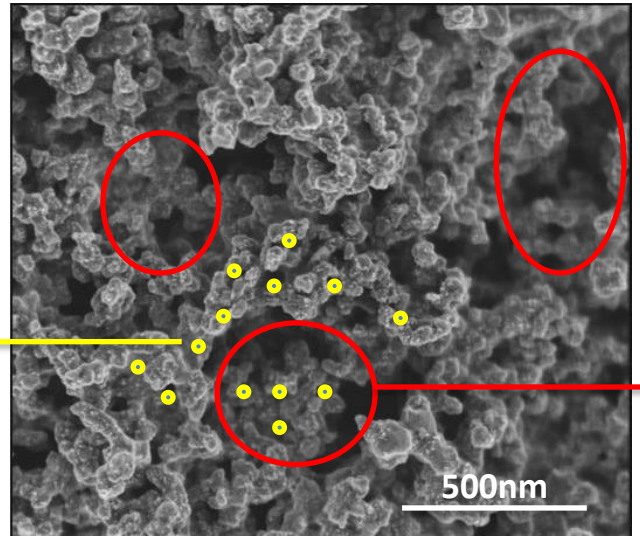
[1] H. Sadeghifar, N. Djilali, and M. Bahrami, (2014) *J. Power Sources*, Vol. 266, pp. 51-59
[2] V. Norouzifard and M. Bahrami, (2014) *J. Power Sources*, Vol. 264, pp. 92-99
[3] H. Sadeghifar, N. Djilali, and M. Bahrami, (2014) *J. Power Sources*, Vol. 248, pp. 632-641.

Microstructure of catalyst layer

CL is a ~10μm layer consist of nano Pt particles on co... particles

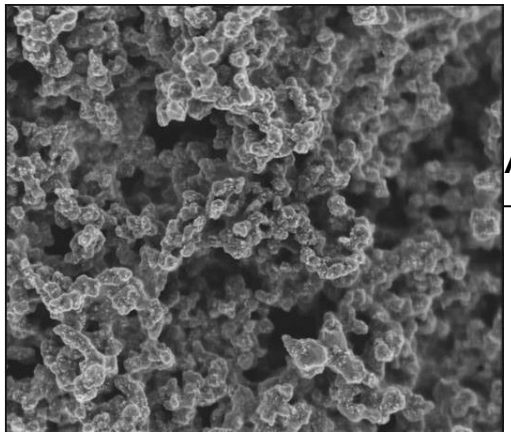


[1]



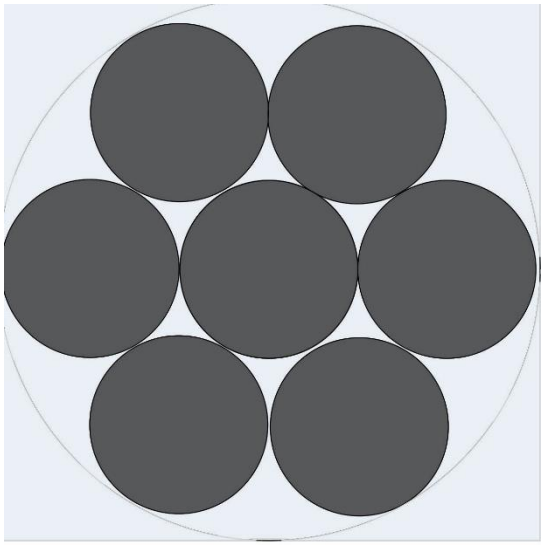
[1] T. Sobolyeva"On the Microstructure of PEM Fuel Cell Catalyst Layer " (2010) Simon Fraser University, PhD Thesis.

Simplified structure of catalyst layer

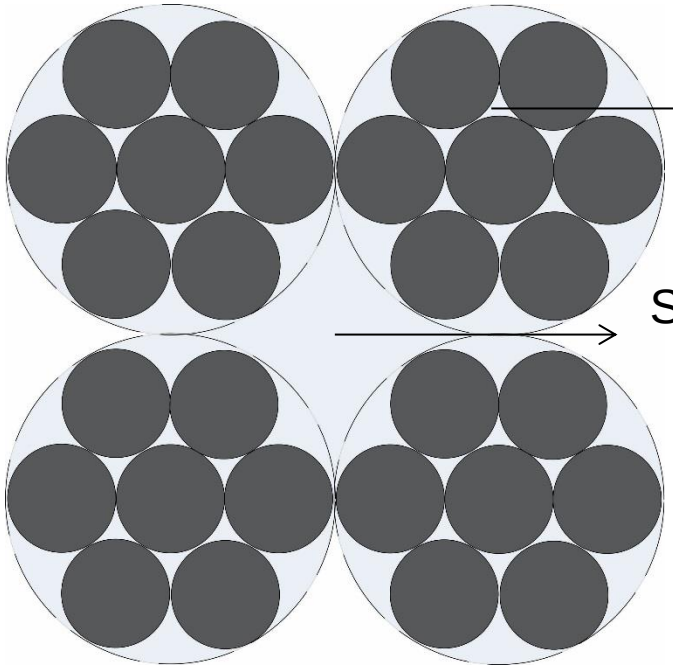


Assumption

1. There is no difference between ionomer and carbon or Pt particles
2. All primary particles are spheres with the same diameter
3. All agglomerates are spheres with the same diameter
4. There are known arrangements for primary particles and agglomerates

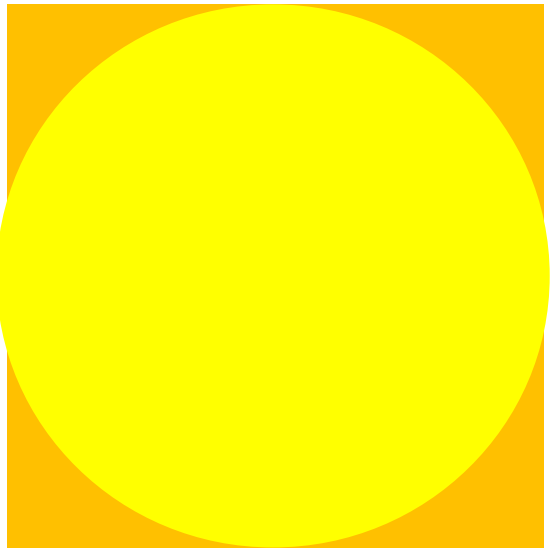


Unit Cell for CL



Modeling Diffusivity for simplified CL

1. Finding the geometry parameters of the unit cell e.g. dimensions
2. Calculating diffusivity within agglomerates (primary pores)
3. Calculating diffusivity of secondary pores
4. Calculating effective diffusivity of unit cell based on geometry and diffusivities of the secondary pores and primary pores

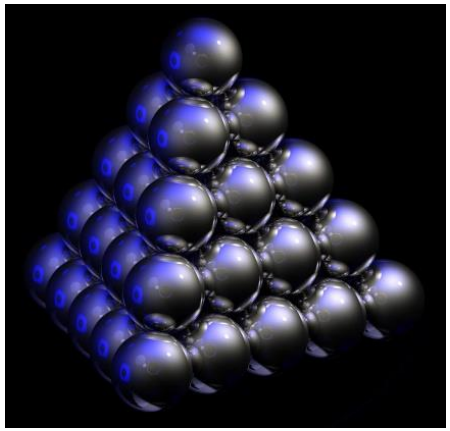


Unit Cell for CL

Arrangement for primary particles within agglomerates

Close-packing of spheres (FCC):

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



Pore dimeter for FCC arrangement:

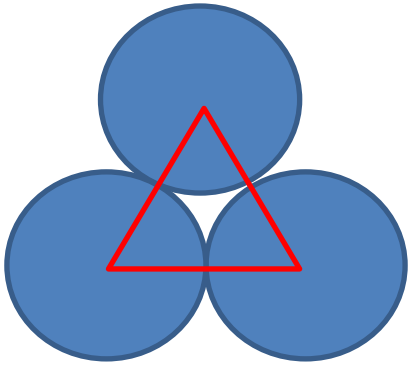
$$A_{tri} = \frac{d^2\sqrt{3}}{4}$$

$$A_{pore} = A_{tri} - \left(3 \times \frac{\pi}{3} \times \frac{d^2}{8}\right) = \frac{d^2\sqrt{3}}{4} - \frac{\pi d^2}{8}$$

$$= 0.04d^2$$

$$P_{pore} = 3 \times \frac{\pi}{3} \times \frac{d}{2} = \frac{\pi d}{2}$$

$$d_{pore} = \frac{4A_{pore}}{P_{pore}} = \frac{0.16d}{\pi/2} = 0.1d$$



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

Effective diffusivity of primary pores agglomerates

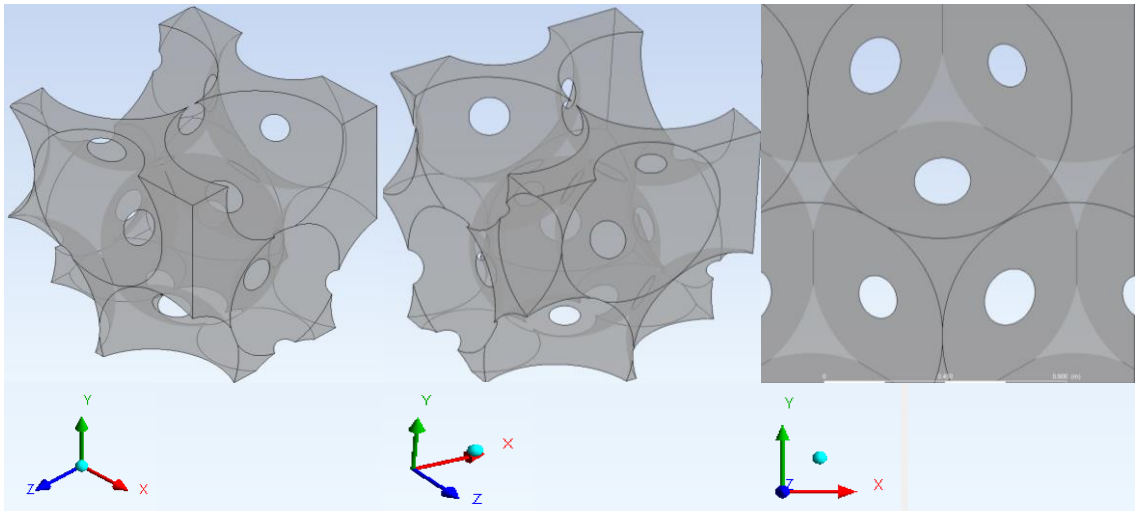
Effective diffusivity:

$D_{solid} = 0$ (for primary particles)

$$D_{Kn} = \frac{4}{3} d_{pore} \sqrt{\frac{RT}{2\pi M}}$$ [1]

$$D_b = 0.2 D_{binary}$$

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

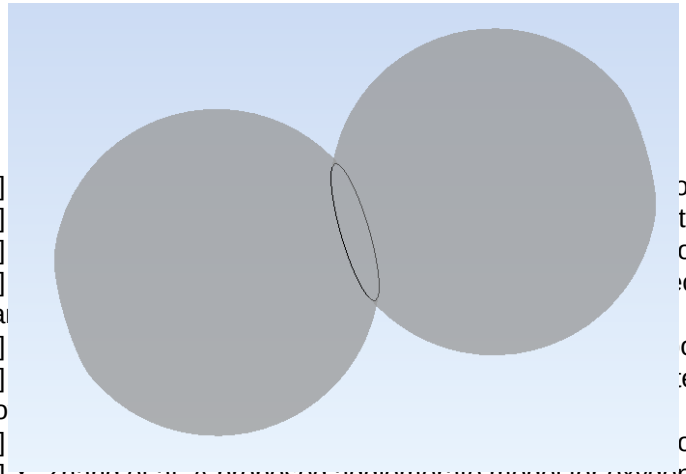


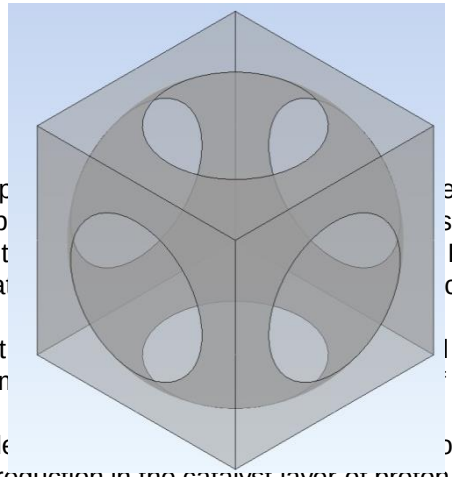
[1] Kast W, C-R Hohenthanner. Mass transfer within the gas-phase of porous media, International Journal of Heat and Mass Transfer

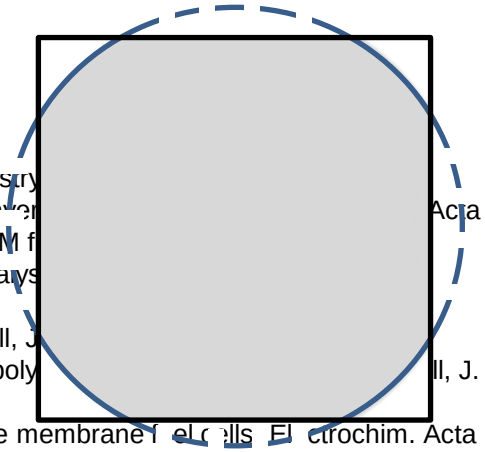
Modeling agglomerates

- Spherical agglomerates touching each other have been used widely by researchers[1-6]
- Such agglomerates have higher surface area than the real agglomerates [7-8]
- Such agglomerates results in high porosity for CL

✓ Overlapped spheres with simple cubic arrangement: less porosity, and less active surface area than spherical agglomerates







[1]
[2]
[3]
[4]
[5]
[6]
[7]
[8] X. Zhang et al, A proposed agglomerate model for oxygen reduction in the catalyst layer of proton exchange membrane fuel cells , Electrochim. Acta

Pore diameter and porosity of overlapped agglomerates

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

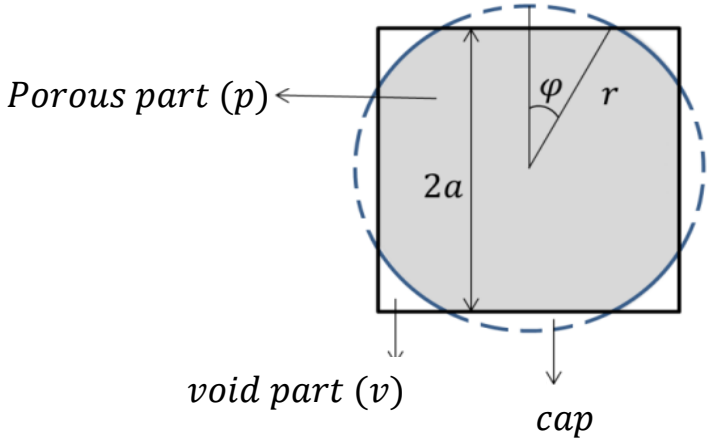
$$\varphi = cos^{-1}\left(\frac{1}{\xi}\right)$$

$$A_p = \pi r^2 - 4A_{cap}$$

$$A_v = 4a^2 - A_p$$

$$d_{pore} = \frac{4A_v}{P_p}$$

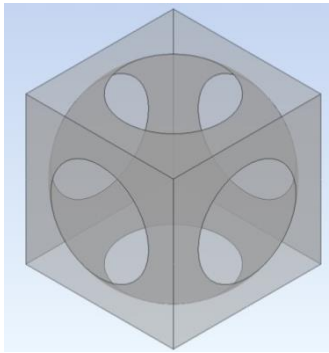
$$\boldsymbol{d_{pore} = a\frac{4(1 - tan(\varphi)) - (\pi - 4\varphi)\xi^2}{\xi\left(\frac{\pi}{2} - 2\varphi\right)}}$$



$$\varepsilon = 1 - \frac{V_p\left(1 - \varepsilon_{porous}\right)}{8a^3}$$

$$\varepsilon_p = 0.26$$

$$\boldsymbol{\varepsilon = 1 - 0.387\left(3\xi^2 - \xi^3 - 1\right)}$$



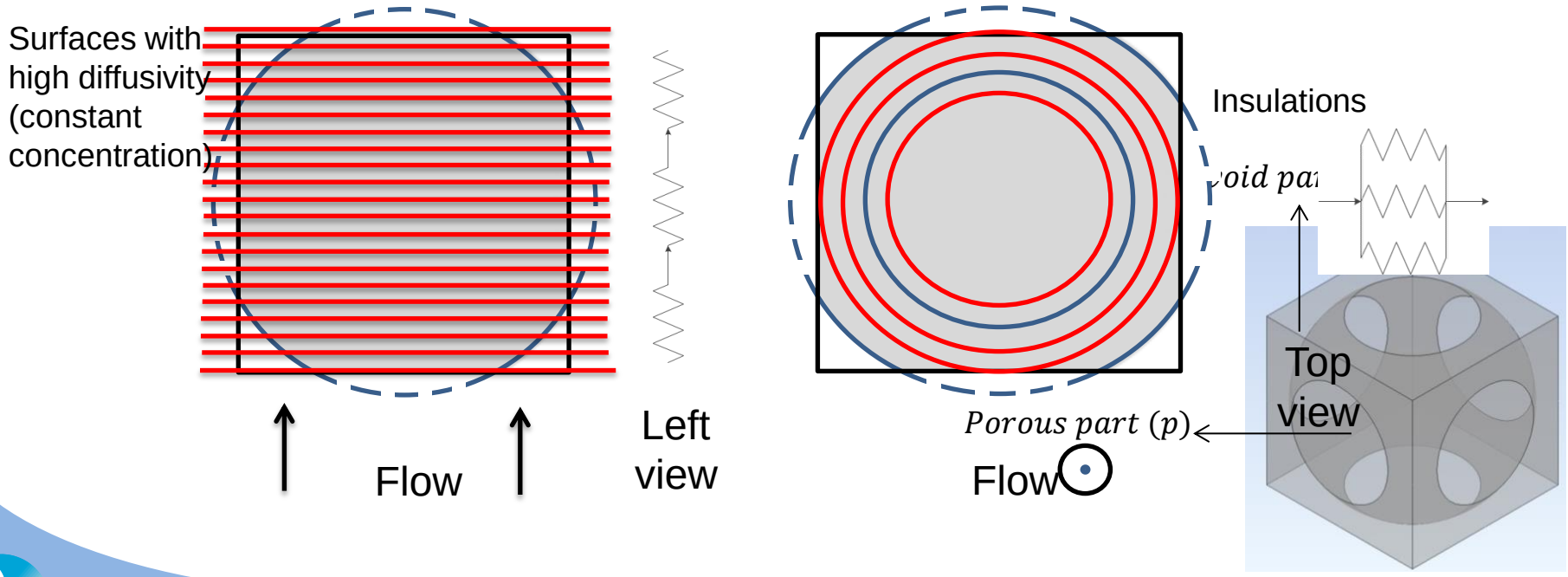
Diffusivity of overlapped agglomerates

$$D_{eff} = f(D_v, D_p)$$

$$D_v = \left(\frac{1}{D_{kn}} + \frac{1}{D_{binary}}\right)^{-1}$$

$$D_p = D_{eff}\ of\ primary\ pores$$

To find *f* the lower and upper bound of the unit cell resistance are introduced:



Effective diffusivity of lower bound

Lower bound for resistance

$$R_1 = \frac{2}{aD_v}\int_0^{\cos^{-1}\left(\frac{1}{\xi}\right)} \frac{\xi\cos\theta\, d\theta}{\left[\left(\pi - 4\cos^{-1}\left(\frac{1}{\xi\cos\theta}\right)\right)(\xi\cos\theta)^2 + 4\sqrt{(\xi\cos\theta)^2 - 1}\right](D-1)+4}$$

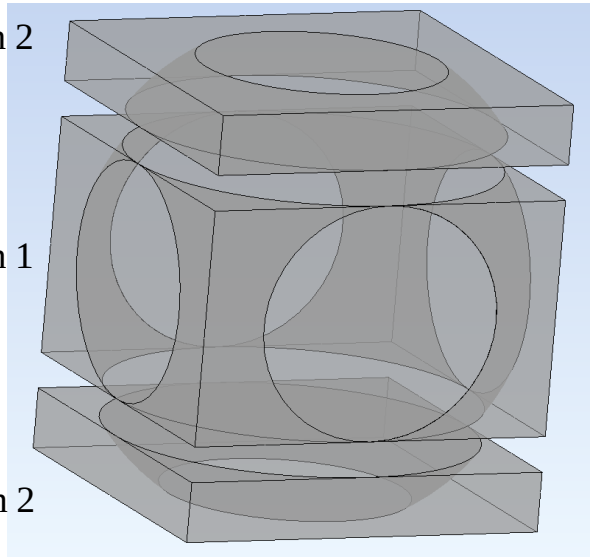
$$R_2 = \frac{2}{aD_v}\left[\frac{\sqrt{\frac{\pi\xi^2 D}{4+\pi\xi^2 D}}}{\pi D\xi}\tan^{-1}\left(s\sqrt{\frac{\pi\xi^2 D}{4+\pi\xi^2 D}}\right)\right]_{s=\sqrt{\frac{\xi^2-1}{\xi^2}}}^{s=\frac{1}{\xi}}$$

$$R_l = R_1 + R_2$$

ξ=overlap parameter

$$D = \frac{D_p}{D_v}$$

a=cell dimension



Effective diffusivity of upper bound

Upper bound for resistance

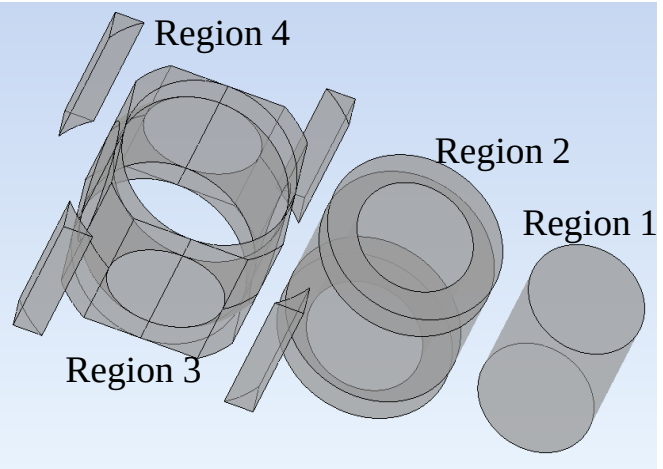
$$R_1 = \frac{1}{aD_v} \times \frac{2}{\pi D(\xi^2 - 1)}$$

$$R_2 = \frac{1}{D_v a} \times \frac{1}{\pi \xi^2} \left[\frac{D}{\xi(1-D)} \left(s - \frac{\ln\left(1 + \frac{\xi(1-D)}{D} s\right)}{\xi(1-D)/D} \right)^{\frac{1}{\xi}} \Bigg/ \sqrt{\frac{\xi^2 - 1}{\xi^2}} \right]^{-1}$$

$$R_3 = \frac{1}{aD_v} \left[\int_0^{\cos^{-1}\left(\frac{1}{\xi}\right)} - \frac{D}{\xi sin\varphi + D(1 - \xi sin\varphi)} \left(\pi \xi cos\varphi - 4\xi cos\varphi cos^{-1}\left(\frac{1}{\xi cos\varphi}\right) \right) \xi sin\varphi d\varphi \right]^{-1}$$

$$R_4 = \frac{1}{D_v a} \times \frac{2}{\left[4 - \pi\xi^2 + 4\left(\xi^2 cos^{-1}\left(\frac{1}{\xi}\right) - \sqrt{\xi^2 - 1} \right) \right]}$$

$$R_u = \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \frac{1}{R_4} \right)^{-1}$$



Resistance semi-analytical results vs numerical one

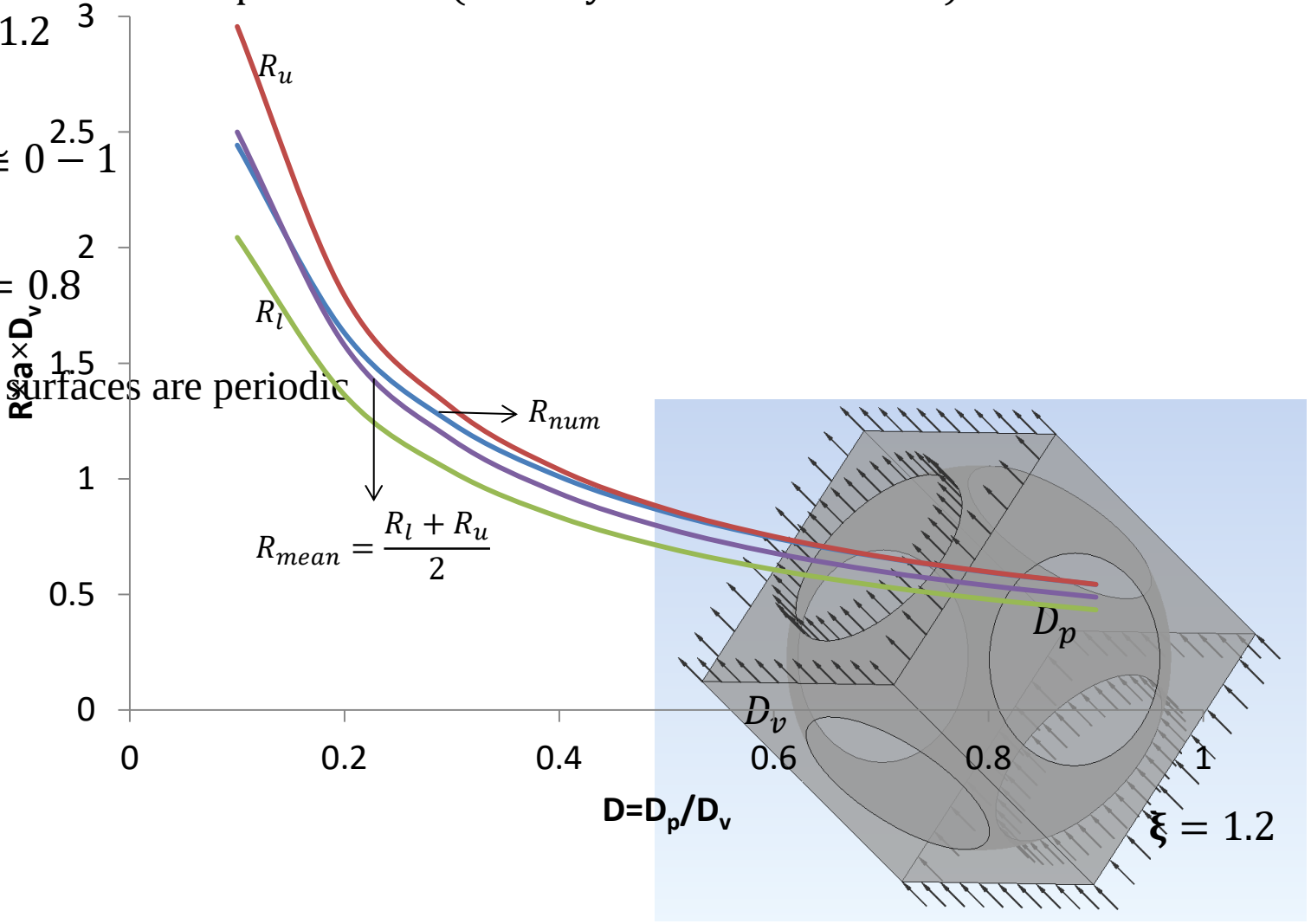
Numerical model parameters (done by ANSYS Fluent 14.5)

$\xi = 1.2$

$\frac{D_p}{D_v} \cong 0 - 1$

$\Delta C = 0.8$

Side surfaces are periodic



Modeling diffusivity for simplified CL

Simplified CL has porosity=ε, a primary pore size d_p and a secondary pore size d_s:

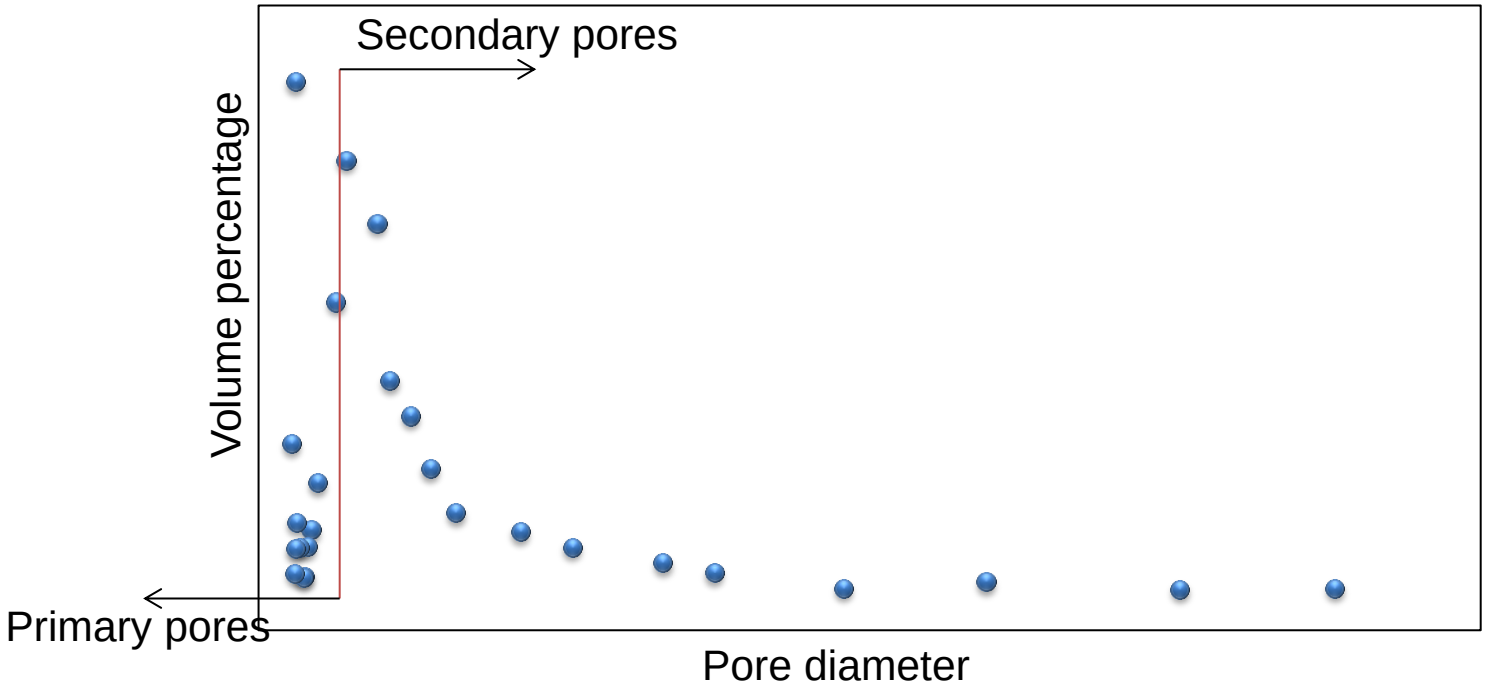
$d_p$is the pore size for FCC arrangement then D_p could be calculated.

$$D_p = \mathrm{g}(d_p)\ for\ FCC\ arrangement$$

Geometry parameters of unit cell: $(\mathrm{a}, \xi) = h(\varepsilon, d_s)$

$$D_{eff} = f(\mathrm{a}, \xi, D_p, D_{binary})$$

Considering different pore sizes

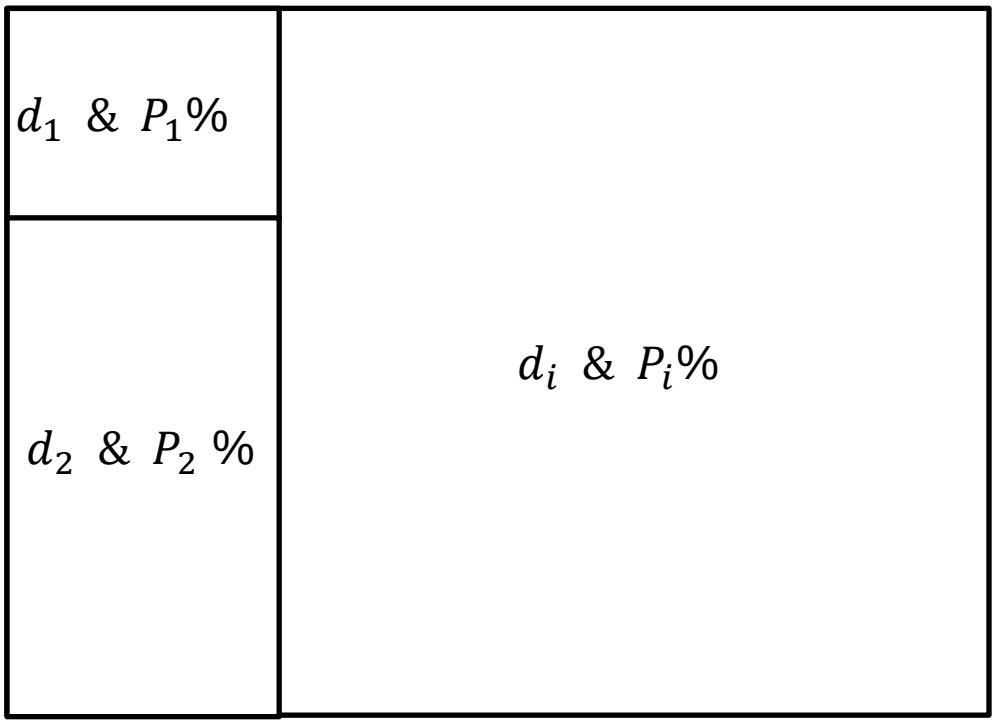


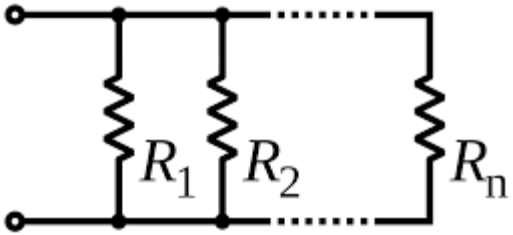
For primary pores Kn diffusivity is dominant which is a linear function of diameter

- d_p =volume average of all primary pore diameters
- For each secondary pore there would be a unit cell with dimension compatible with the considered diameter and porosity of CL

Connection of unit cells with different pore diameters

Thickness of CL is negligible in compare with its width and length, then we assume parallel unit cells



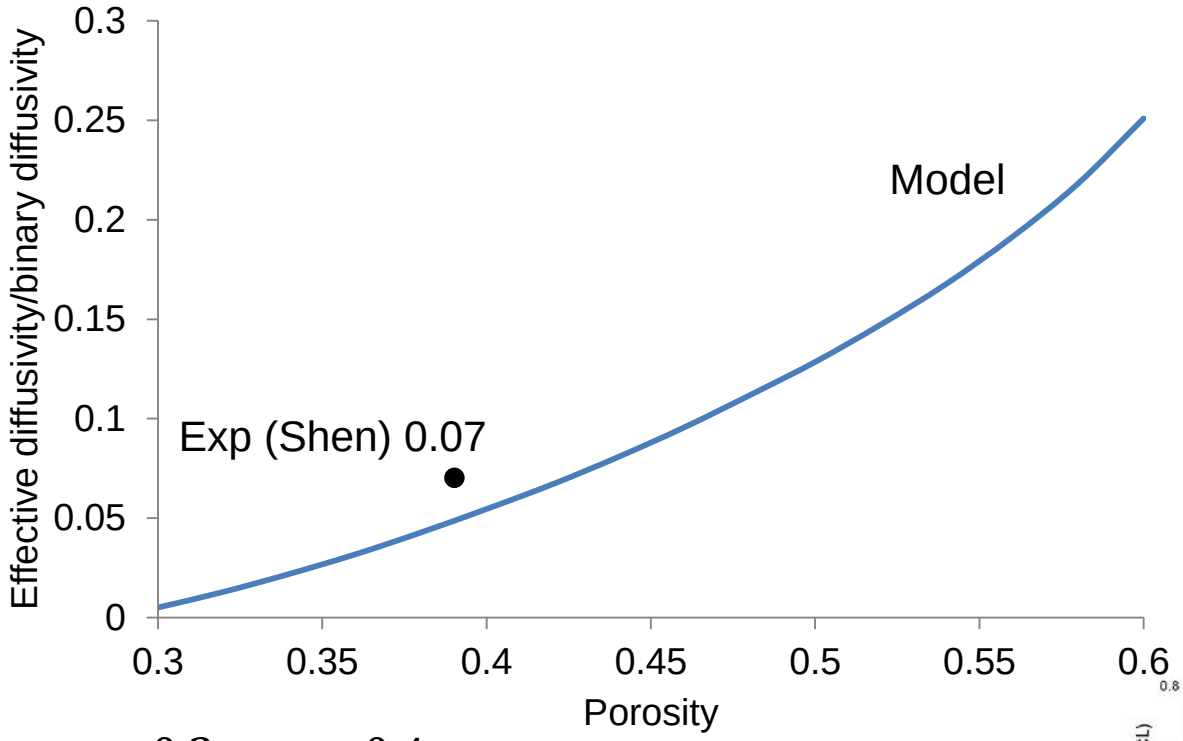


The model features

The model considers the followings:

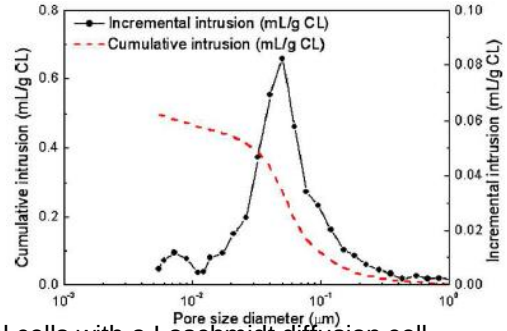
1. Porosity (each unit cell has a porosity same as CL porosity)
2. Pore size distribution (through introducing different unit cell sizes)
3. Connectivity of the structure in the model is different than one in CL but tried to be as close as possible
4. Knudsen and classical diffusion mechanisms are both considered
5. There in no difference between ionomer, carbon, and Pt particles yet
6. Model works for dry condition, and still no humidity effects

Diffusivity vs Porosity (input data from Shen study)



$0.2 < \varepsilon < 0.4$

Diffusivity measured ex-situ by modified Loschmidt cell for CL coated by spraying on Alumina with different CL thickness: 6 to 29 μm



[1] Shen J, et al. Measurement of effective gas diffusion coefficients of catalyst layers of PEM fuel cells with a Loschmidt diffusion cell, Journal of Power Source, 196 (2011) 674–678.

Next steps

1. Changing the unit cell distribution to make the CL homogeneous
2. Defining the pore diameter in the structure based on the one applied by the input PSD measurement method
3. Introducing ionomer effect
4. Introducing water content effect
5. Introducing cracks effect
6. Introducing a proper PSD measurement method

ACKNOWLEDGEMENT

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Automotive Fuel Cell Cooperation Crop

Laboratory for Alternative Energy Conversion

Thanks for your attention!
Any questions?