Modeling and ex-situ measurement of PEMFC catalyst layer dry diffusivity

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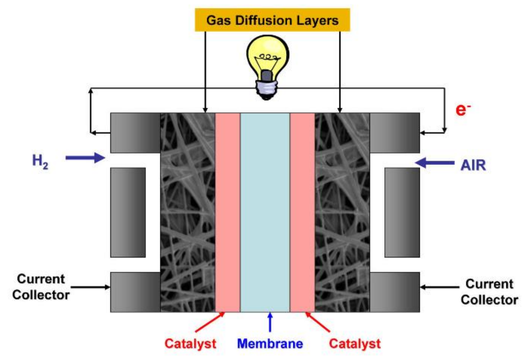
Polymer Electrolyte Membrane Fuel Cells

Introduction:

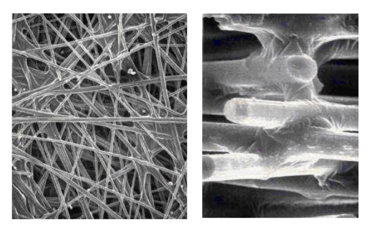
- Polymer electrolyte membrane fuel cells (PEMFC) efficiently convert the reaction energy of hydrogen and oxygen to electricity and heat
- Oxygen reduction occurs in a catalyst layer (CL) formed from platinum nanoparticles supported on a network of carbon support particle agglomerates
- Oxygen diffuses to the reaction site, which makes understanding the diffusion properties of CL vital to proper design and operation of the CL and the PEMFC



Membrane electrode assembly (MEA)

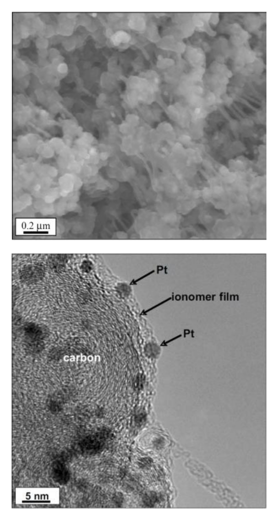
Objectives:

- Measure and model the diffusivity of CL and GDL
- Select a suitable substrate and appropriate coating procedures


GDL surface and cross section

Methods:

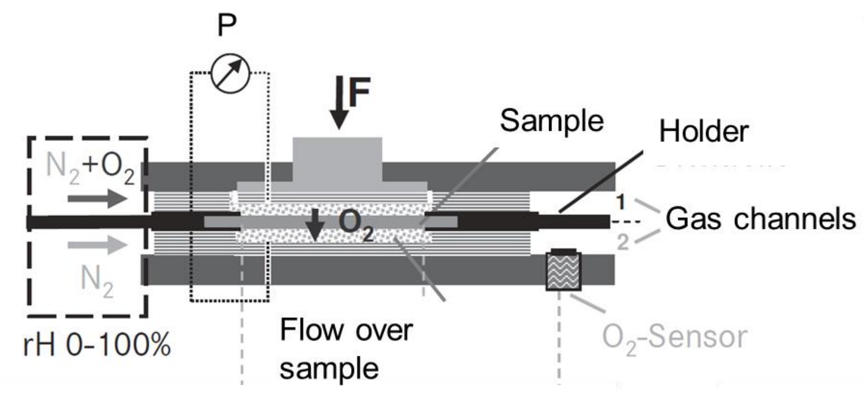
- The diffusivity of gas diffusion layers (GDL) are measured with a dry diffusivity test bed (DDT)
- CL is coated on 70 µm thick hydrophobic porous polymer substrates
- CL thicknesses are measured by SEM
- The diffusivity of the substrate and CL/substrate are measured using DDT
- CL-diffusivity values are determined for different Pt loadings
- To model the CL, its structure is represented by unit cells based on porosimetry and analysis of SEM images
- To calculate effective diffusivity, mass diffusion is analytically solved within the unit cell



SEM and TEM images of the ionomer strands that bind Pt/C agglomerates together

More, K.L., et al., *ECS Transactions*, 3(1), p. 717 (2006)

Dry Diffusivity Testbed (DDT)



Schematic of the Wicke–Kallenbach cell

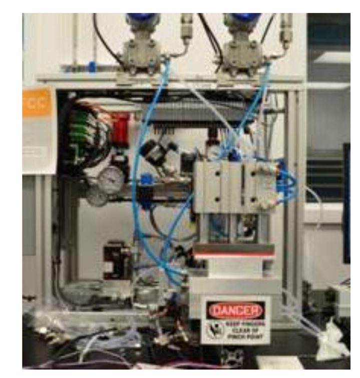
Fick's first law of diffusion:

$$J = -D_{eff}\frac{\partial C}{\partial y}$$

Equation of effective length for DDT:

$$l_{eff} = D_{binary}\left(\frac{89.28A_sRT}{p\dot{V}\ln\left(\frac{C_o^{in}}{C_o^{in}-89.28C_o^{out}}\right)} - \frac{4h}{ShD_g}\right)$$

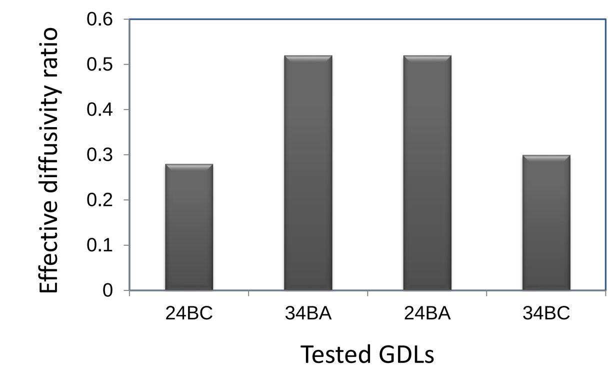
- The dry diffusivity testbed (DDT) is based on a Wicke–Kallenbach cell with two flow channels separated by a porous sample
- Pure nitrogen flows in one channel while air flows in the other
- The oxygen concentration gradient between the two sides of the sample drives oxygen diffusion through the sample
- To avoid any convective flow through the sample, ideally there is no pressure difference between the two channels (actual pressure difference < 20 Pa)
- The resistance to the mass transfer of gas into the sample is measured and subtracted from the total resistance
- Effective length is a representative of resistance and can be related to effective diffusivity


Dry diffusivity test bed

Effective Diffusivity of GDL and CL

GDL Diffusivity Measurement

GDL samples containing MPL (24BC and 34BC) have diffusivity values about 50% less than the ones without MPL (24BA and 34BA)

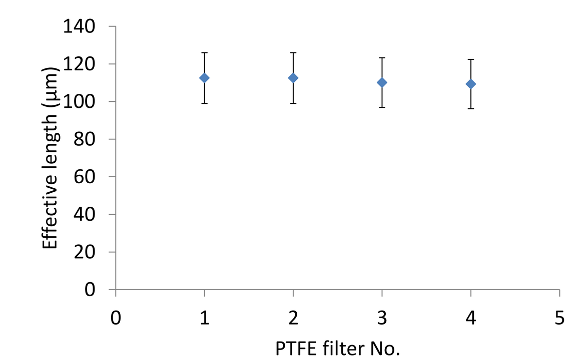


	24BA	34BA	24BC	34BC
GDL thickness μm	190	280	190	280
MPL thickness μm	0	0	45	45

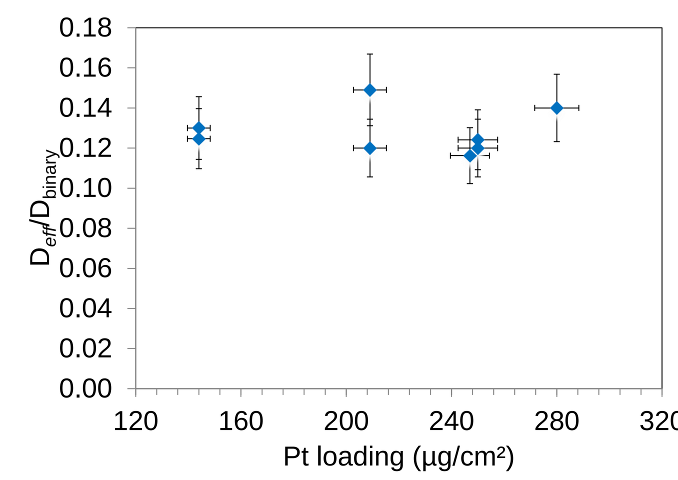
CL Diffusivity Measurement Test Procedure

1. Measure effective length of filter PTFE substrate, $l_{eff\ s}$
2. Measure effective length of catalyst coated filter PTFE substrate $l_{eff\ cs}$
3. $l_{eff\ CL} = l_{eff\ cs} - l_{eff\ s}$
4. $\frac{D_{eff}}{D_{binary}} = \frac{Thickness\ of\ CL}{l_{eff\ CL}}$

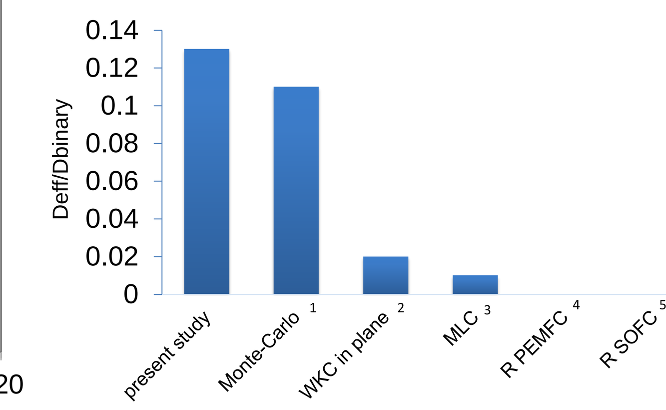
The effective length (diffusion resistance) of filter PTFEs is consistently about 110 µm



Effective length of filter PTFE



Non-dimensional effective diffusivity for CLs with Pt loading from 140 to 290 µg/cm²



Comparison between measured effective diffusivity of CL with literature values

Sample	1	2	3	4	5	6	7	8
Pt loading (µg/cm²)	144	144	209	209	247	250	250	280
Thickness (µm)	5.4	6.5	8.4	9.0	8.6	9.0	9.5	10.4
CCL effective length (µm)	43.0	49.1	72.2	60.1	74	72.5	79.8	74.4
D_{eff}/D_{binary}	0.12	0.13	0.12	0.15	0.12	0.12	0.12	0.14

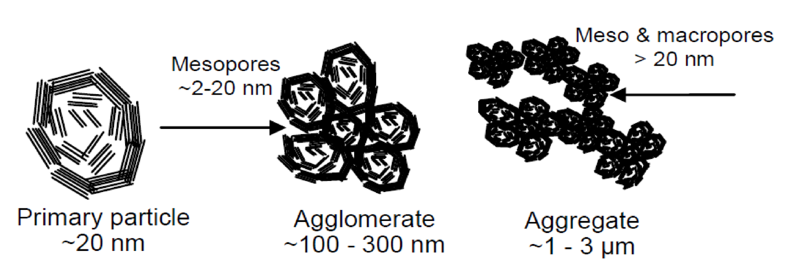
The diffusivity of CCL samples with Pt loadings from 0.14 mg/cm2 to 0.28 mg/cm2 were measured with dry diffusivity test bed. The average non dimensional effective diffusivity of all samples was ~0.12 with 15% uncertainty. To the knowledge of the author, no comparable ex-situ studies of CCL have been reported. The results are in good agreement with models based on geometric reconstructions of CCL. The diffusivities measured in this study are two orders of magnitude higher than diffusivities obtained by in-situ measurement techniques.

[1] A. Berson et al., *Phys Rev*, **83** 026310 (2011).
[2] Z. Yu, R.N. Carter, *J Power Sources*, **195** 1079–1084 (2010).
[3] J. Shen et al., *J Power Sources*, **196** 674–678 (2011).
[4] A.A. Kulikovsky, *J Electroanal Chem*, **720**-721 47–51 (2014).
[5] K. Wippermann, et al., *Electrochimica Acta*, **141** 212–215 (2014).

Diffusivity Model for Catalyst Layer

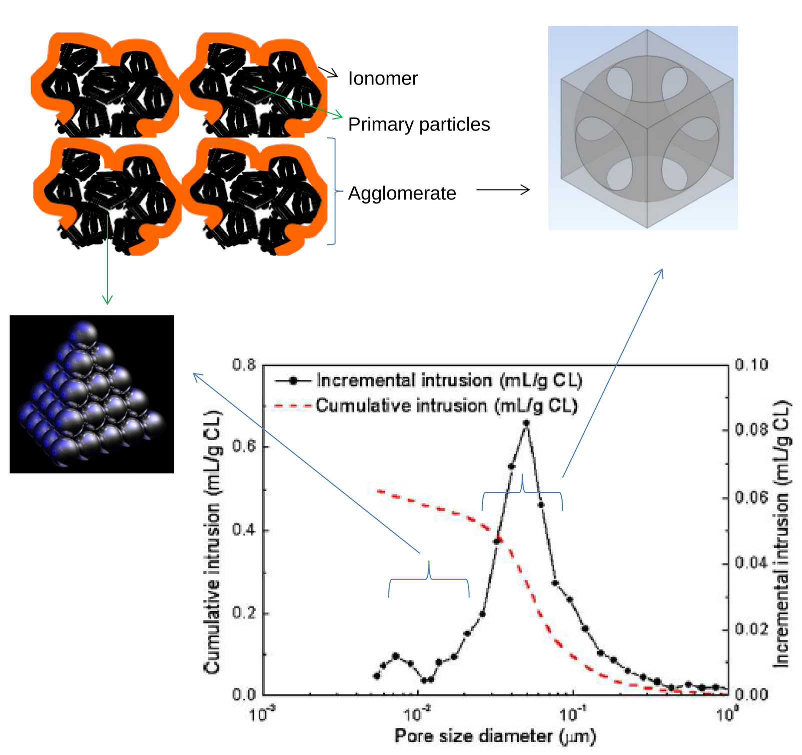
Unit cell approach to modeling diffusivity

- CL is represented by a network of unit cells to model its transport properties
- The unit cell for primary pores consists of a single primary particle in an FCC arrangement with pore space around it
- The unit cell for agglomerates consists of overlapped porous spheres with void space around them



The model considers the followings:

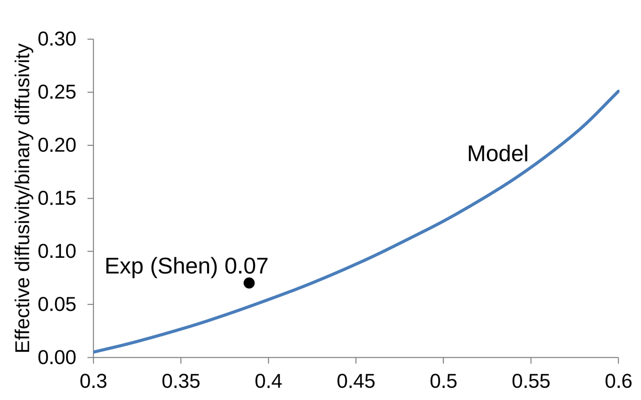
- Porosity (each unit cell has a porosity that is the same as the CL porosity)
- Pore size distribution (through introducing different unit cell sizes)
- Knudsen and classical diffusion mechanisms
- The ionomer, carbon, and Pt particles are all non-diffusive solids



The model has been validated for dry conditions

Future work includes considering the effects of humidity, compression and the diffusivity of ionomer

The modeled effective diffusivity for porosity ~ 0.4 is underestimating the experimental value of Shen study [1] by ~ 5%. According to the modeled values diffusivity is highly function of porosity for the same PSD and to be able to accurately compare the results, porosity should be evaluated precisely. In Shen study porosity is reported about 0.2 – 0.4.



Modeled diffusivity values using Shen study pore size distribution for CL in compare with their diffusivity measured ex-situ by modified Loschmidt cell for CL coated by spraying on alumina with different CL thickness (6 to 29 μm)

[1] J. Shen et al., *J Power Sources*, **196** 674–678 (2011).

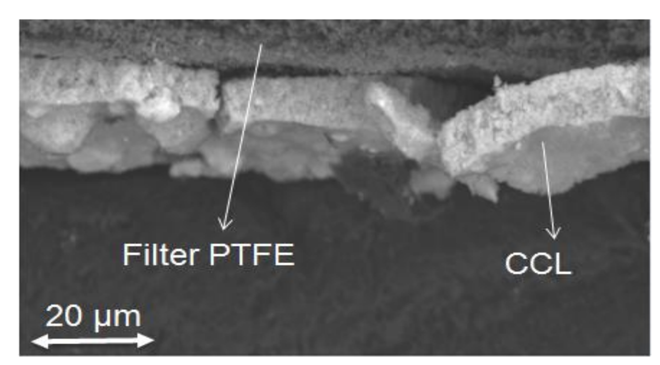
Catalyst Layer and Substrate

For diffusivity testing the catalyst layer must be deposited on a suitable, supportive substrate.

Substrate selection criteria:

- Highly porous with low diffusion resistance
- Low engagement with the CL
- Pore size less than 500 nm
- Highly hydrophobic surface
- Sufficient mechanical strength
- Thickness less than ~100 µm

PTFE membrane filter Fluoropore FHUP04700 meets all the criteria

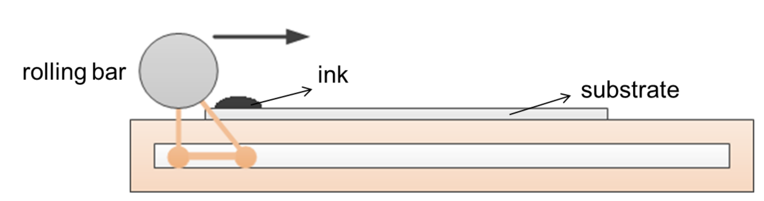


SEM image of freeze and fracture cross section of CL coated by Mayer bar on hydrophobic filter PTFE. The CL does not penetrate the substrate.

Substrate	Pore diam. (µm)	Thickness (µm)	Porosity (%)	Surface property
Filter PTFE	0.45	76	~80	Hydrophobic

Catalyst layer ink preparation:

- Mixing of Pt/C, ionomer and solvents
- Probe sonication of mixture
- Magnetic stirring

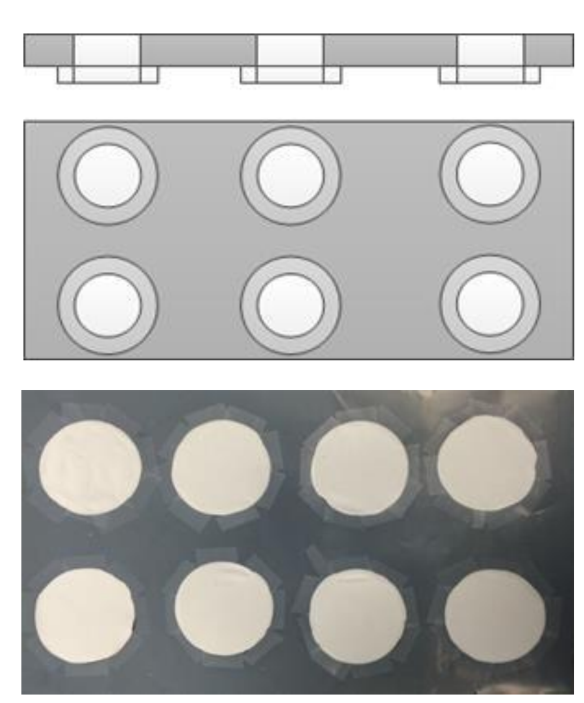


Layer deposition on substrate :

- Mayer bar rolling transfer is effective for mass production and deposition of thick catalyst layers
- The PTFE substrates are mounted on a backing layer of equivalent thickness
- The backing layer is punched with holes and the PTFE is taped into place

Characterization:

- Scanning electron microscopy of cross section obtained by freeze and fracture in liquid nitrogen
- N_2 adsorption porosimetery to evaluate pore size distribution and porosity


Template support for the filter disk substrates to be CL coated by Mayer bar

Conclusions

- Diffusivity of CL for different Pt loadings (different CL thicknesses) is measured and reported to be 0.13 of binary diffusion
- Diffusivity is measured with a WKC based test bed and uncertainty is evaluated to be less than 12%
- The through plane effective resistance of the CL is less than the in plane values reported in literature and several orders lower than the reported values for agglomerate diffusivity
- Effect of operating temperature and humidity, compression and cracks on CL diffusivity should be evaluated
- Interfacial diffusivity resistance between GDL and CL should be measured


In 2008, Ballard, Ford and Daimler formed the Automotive Fuel Cell Cooperation Corporation (AFCC). The LAEC-AFCC collaborative research project on transport phenomena in fuel cell porous layers began in May 2014.

Support

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