Characterization of Water Management in PEM Fuel Cells with Microporous Layer Using Electrochemical Impedance Spectroscopy

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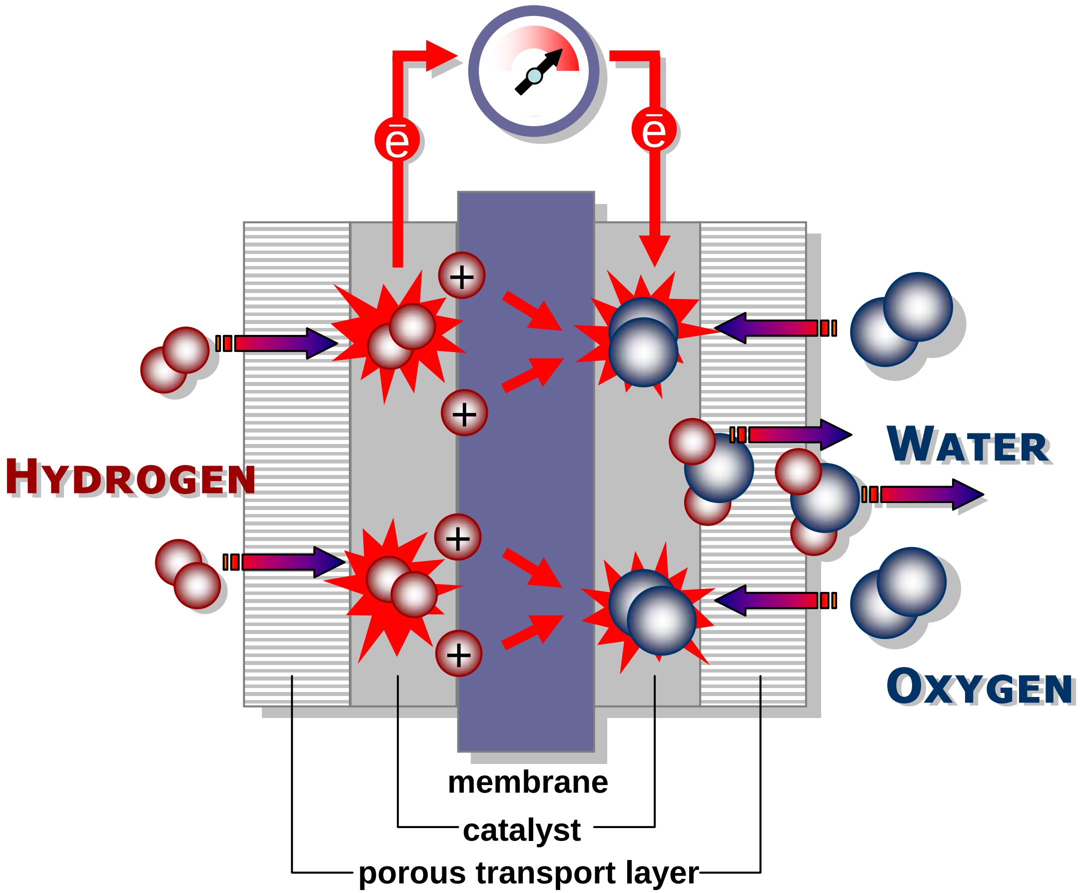
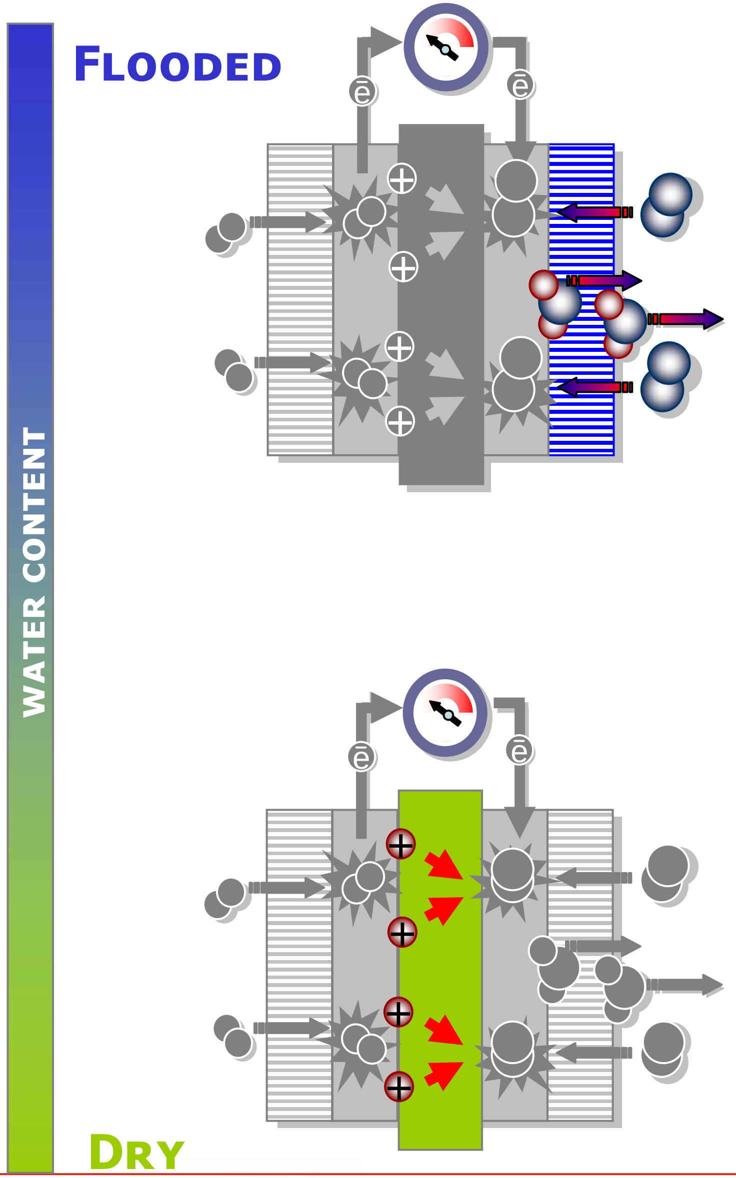
Water management in PEM fuel cell





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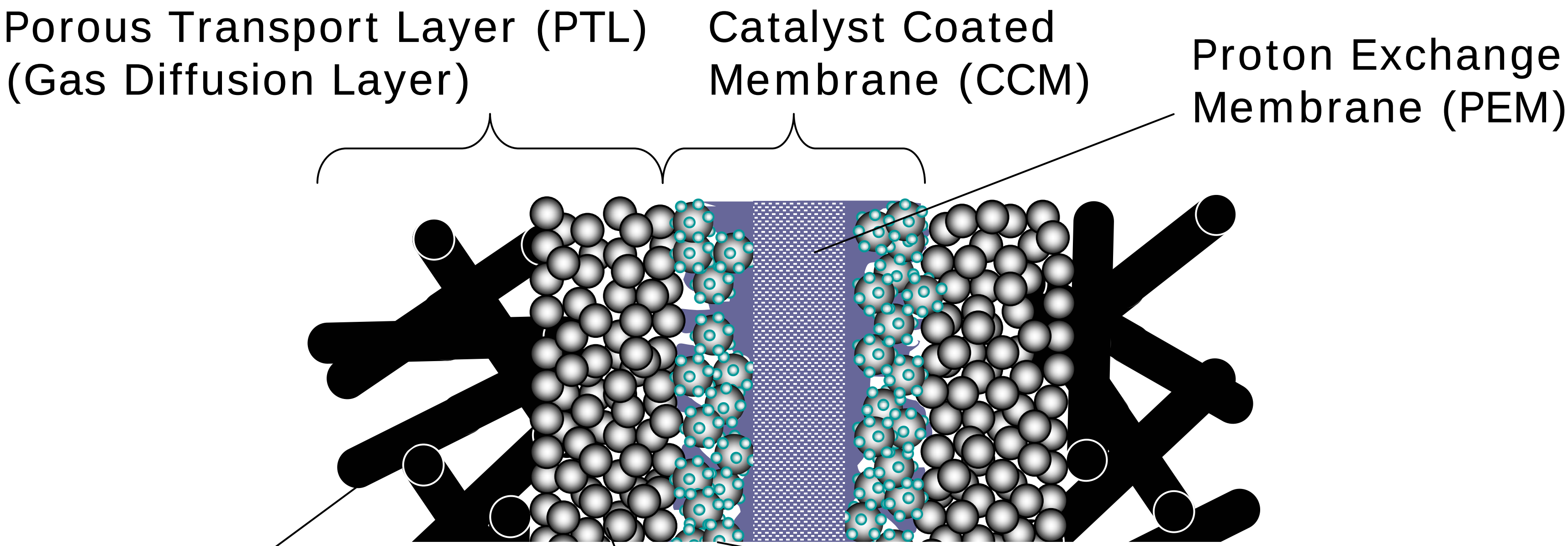
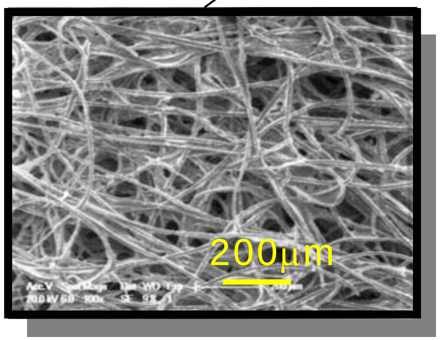
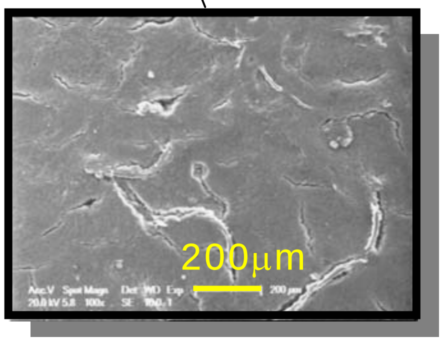
Microporous Layer (MPL)

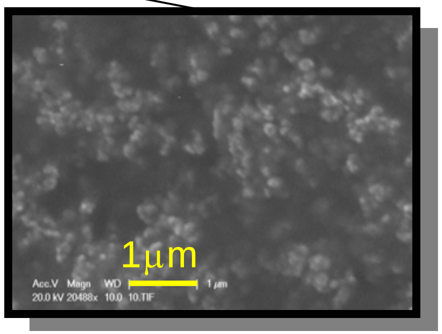




porous carbon backing

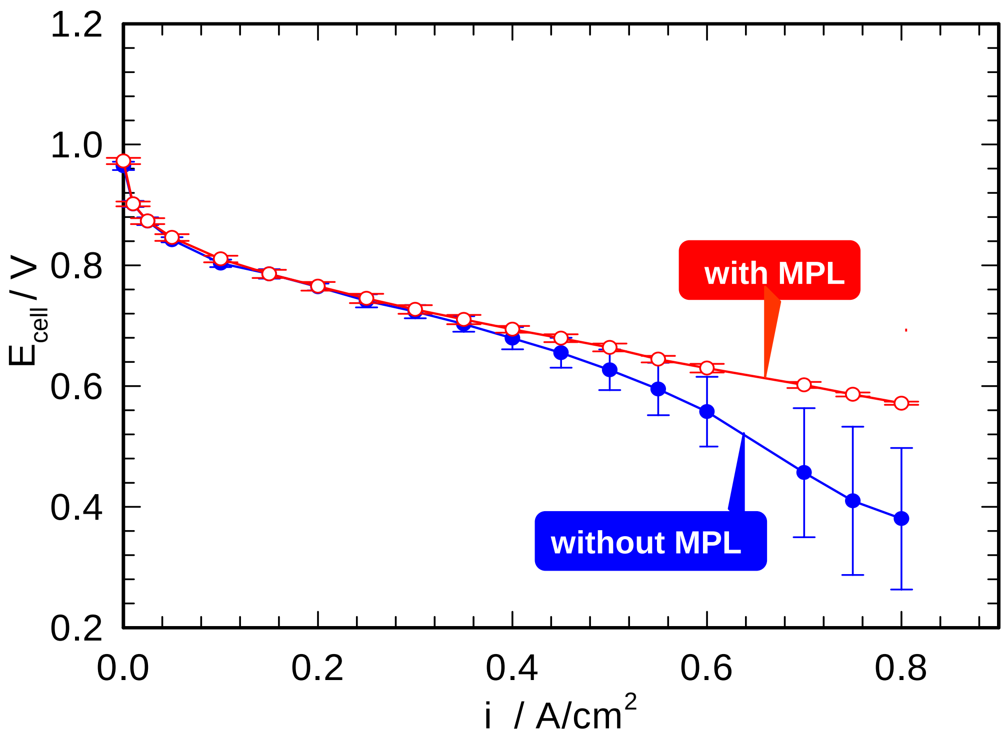


microporous layer



catalyst layer

Effect of MPL on PEMFC performance



Polarization curves for PEMFCs without MPL and with MPL on anode and cathode sides. Error bars represent standard deviation within batch of identically built cells.

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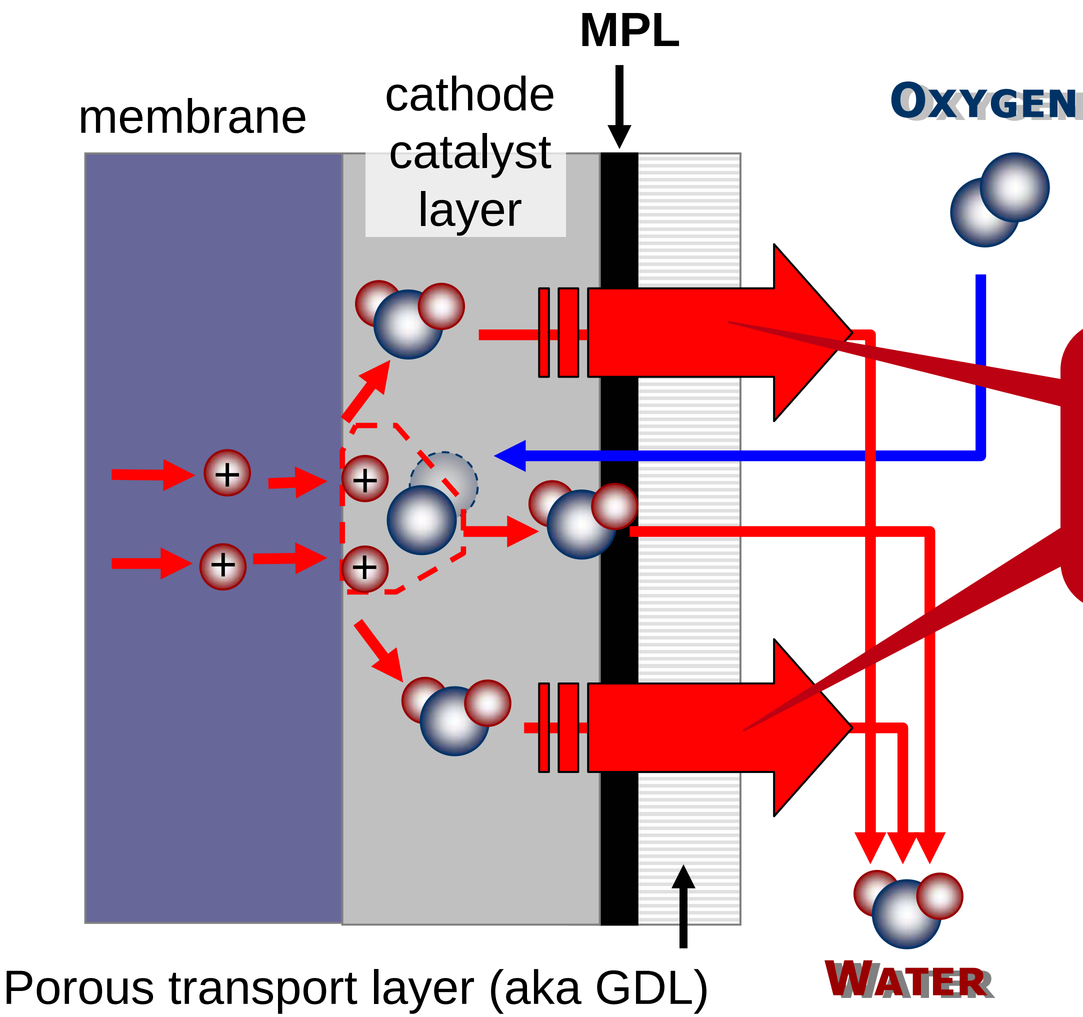
Positive effects of MPL:

- **reduces cathode flooding**
  - U. Pasaogullari, C.-Y. Wang, *Electrochim. Acta* **49** (2004) 4359
  - L. R. Jordan, A. K. Shukla, T. Behrsing, N. R. Avery, B. C. Muddle, M.Forsyth, *J. Power Sources* **86** (2000) 250
- **improves catalyst utilization**
  - Z. Qi, A. Kaufman, *J. Power Sources*, **109** (2002) 38
- **Reduces variability in cell performance**
  - Z. Qi, A. Kaufman, *J. Power Sources*, **109** (2002) 38

Theories explaining MPL effect

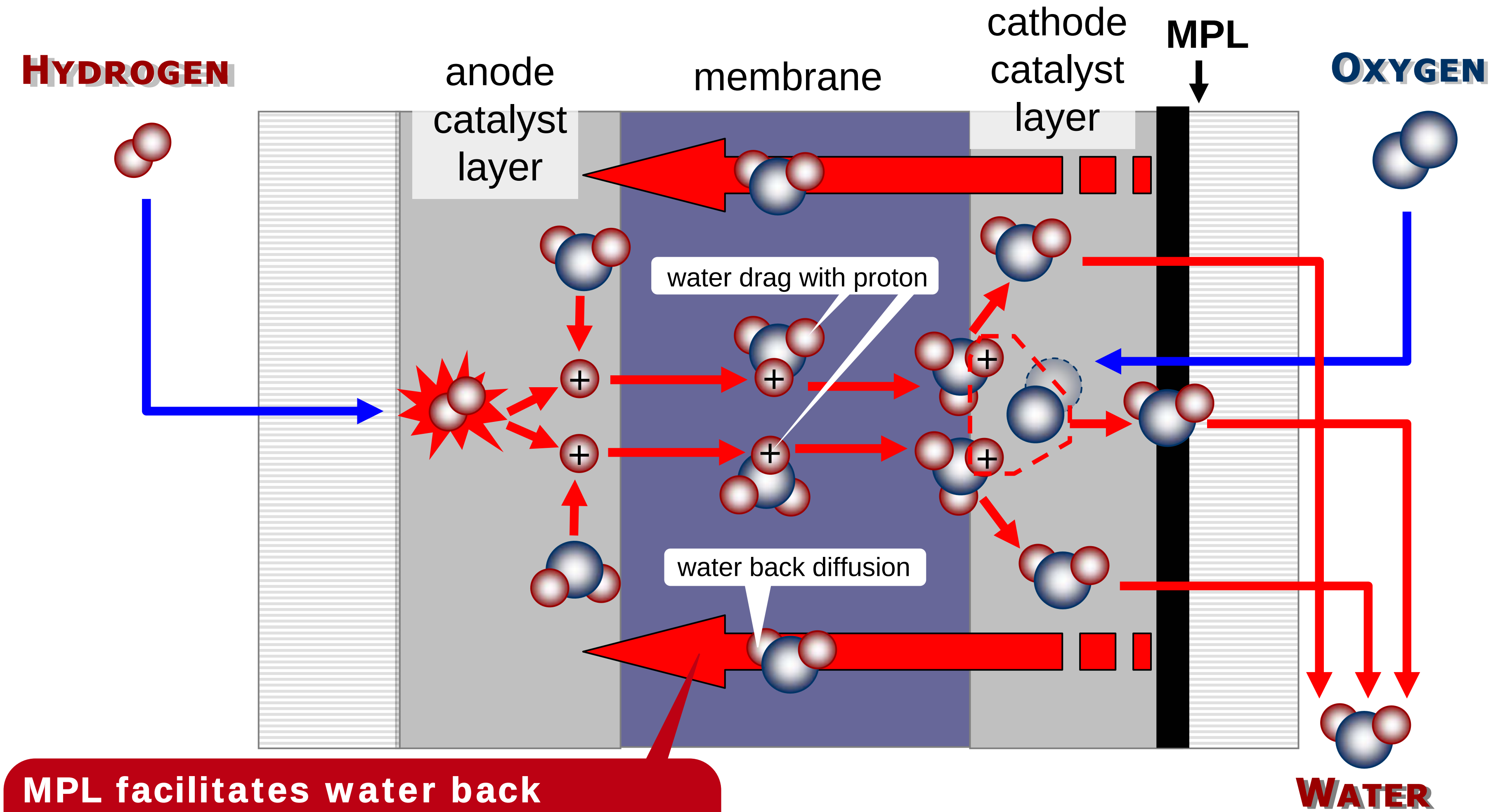


Hydrophobic characteristic of the MPL forces water from cathode towards FFP reducing flooding

Proposed in:

A. Z. Weber and J. Newman, *J. Electrochem. Soc.*, **152**, A677 (2005)

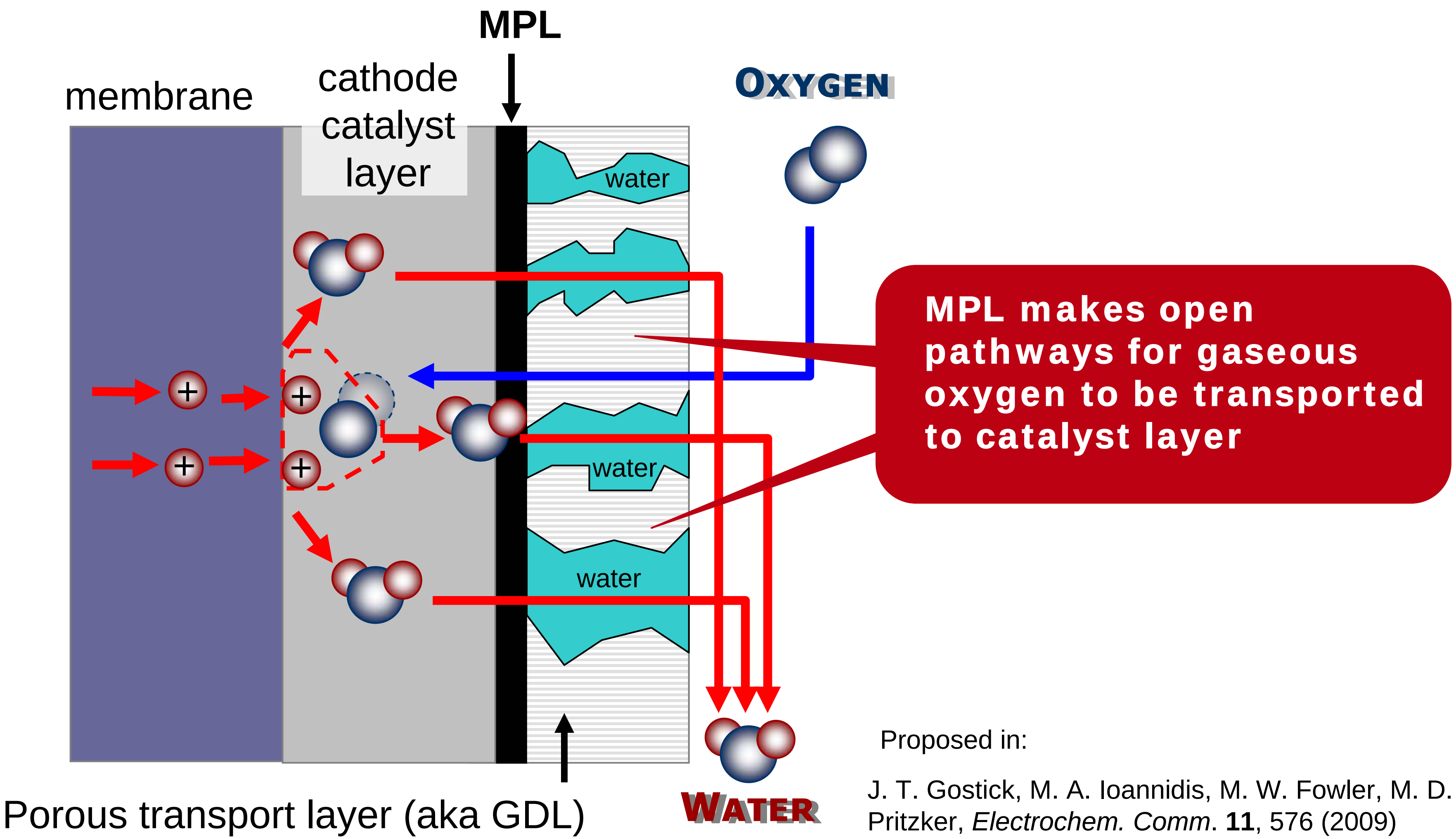
Theories explaining MPL effect



MPL facilitates water back diffusion providing better humidification of membrane and catalyst layers

Proposed in:
G. Lin and T. V. Nguyen, *J. Electrochem. Soc.*, **152**, A1942 (2005).

Theories explaining MPL effect

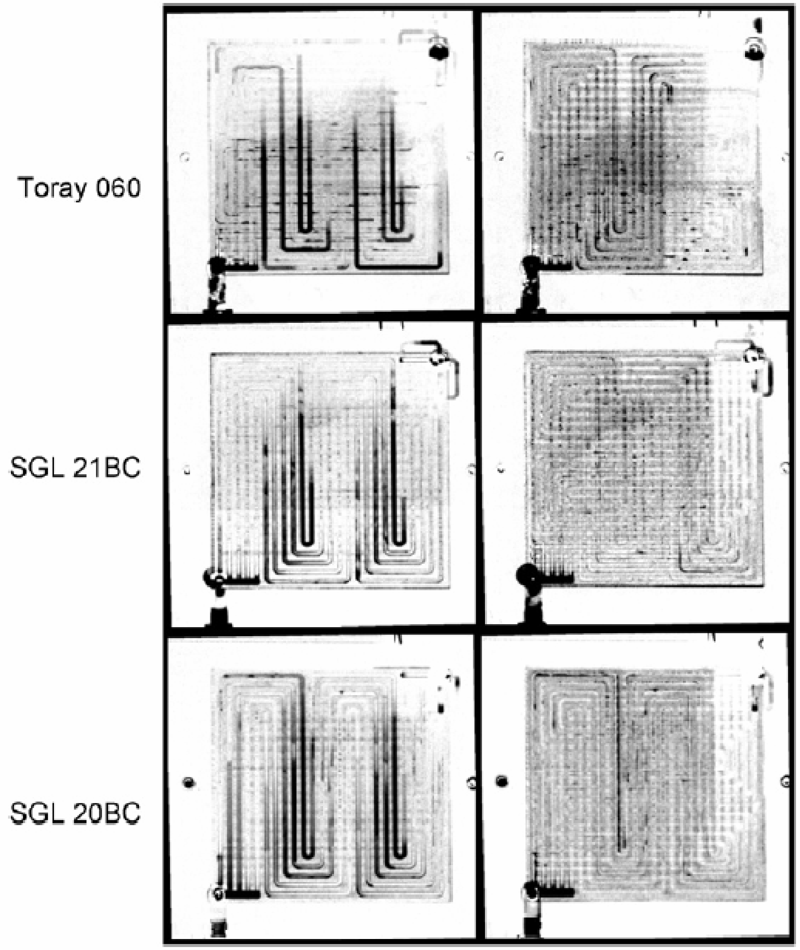


Proposed in:

J. T. Gostick, M. A. Ioannidis, M. W. Fowler, M. D. Pritzker, *Electrochem. Comm*. **11**, 576 (2009)

Approaches to examine proposed mechanisms

Flow visualization

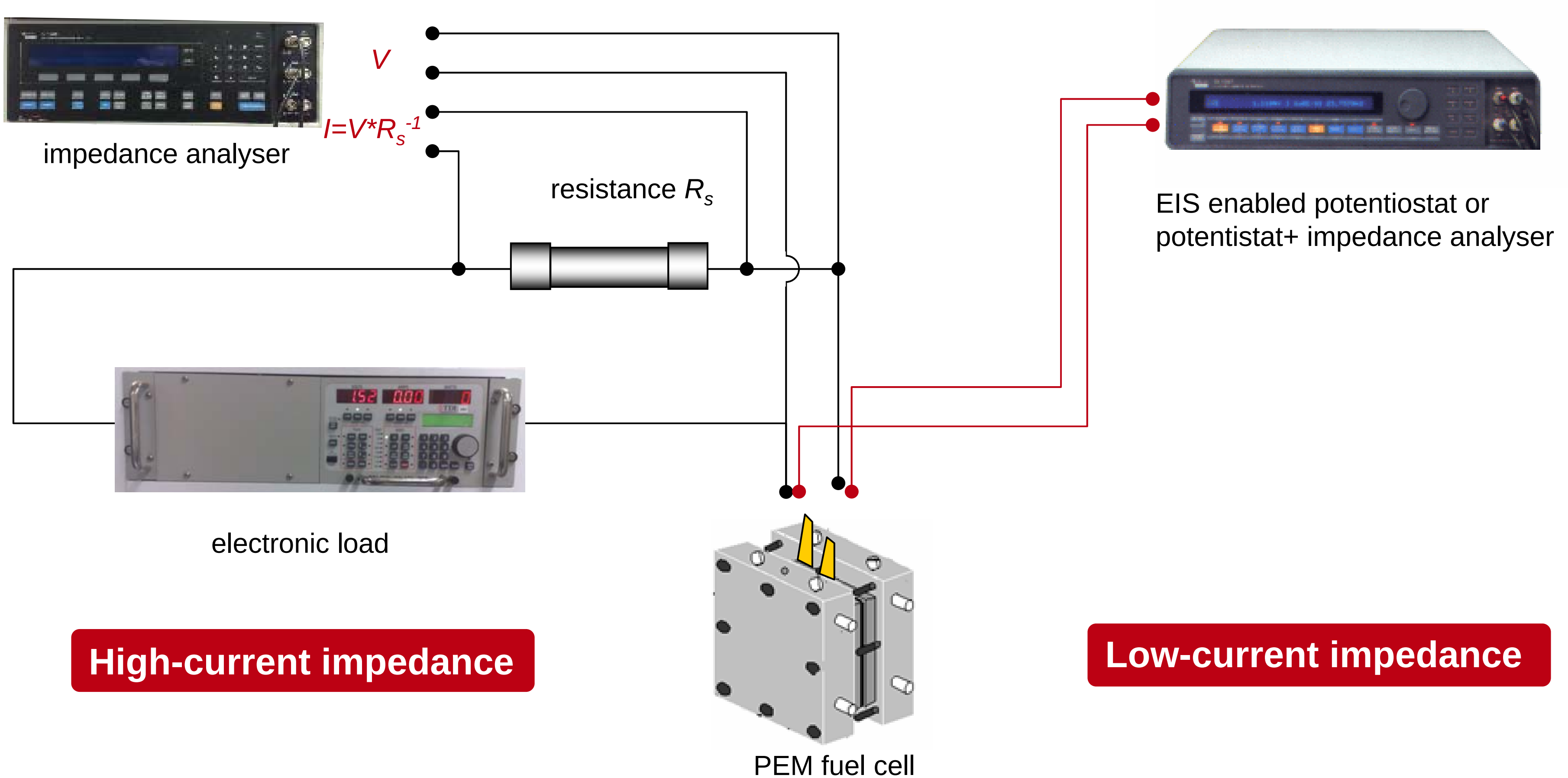


Neutron radiographs of water distribution in flow field channels – effect of PTL (J.P. Owejan, T.A. Trabold, D.L. Jacobson, M. Arif, S.G. Kandlikar, *Int. J. Hydrogen Energy*, **32**, 4489 (2007)

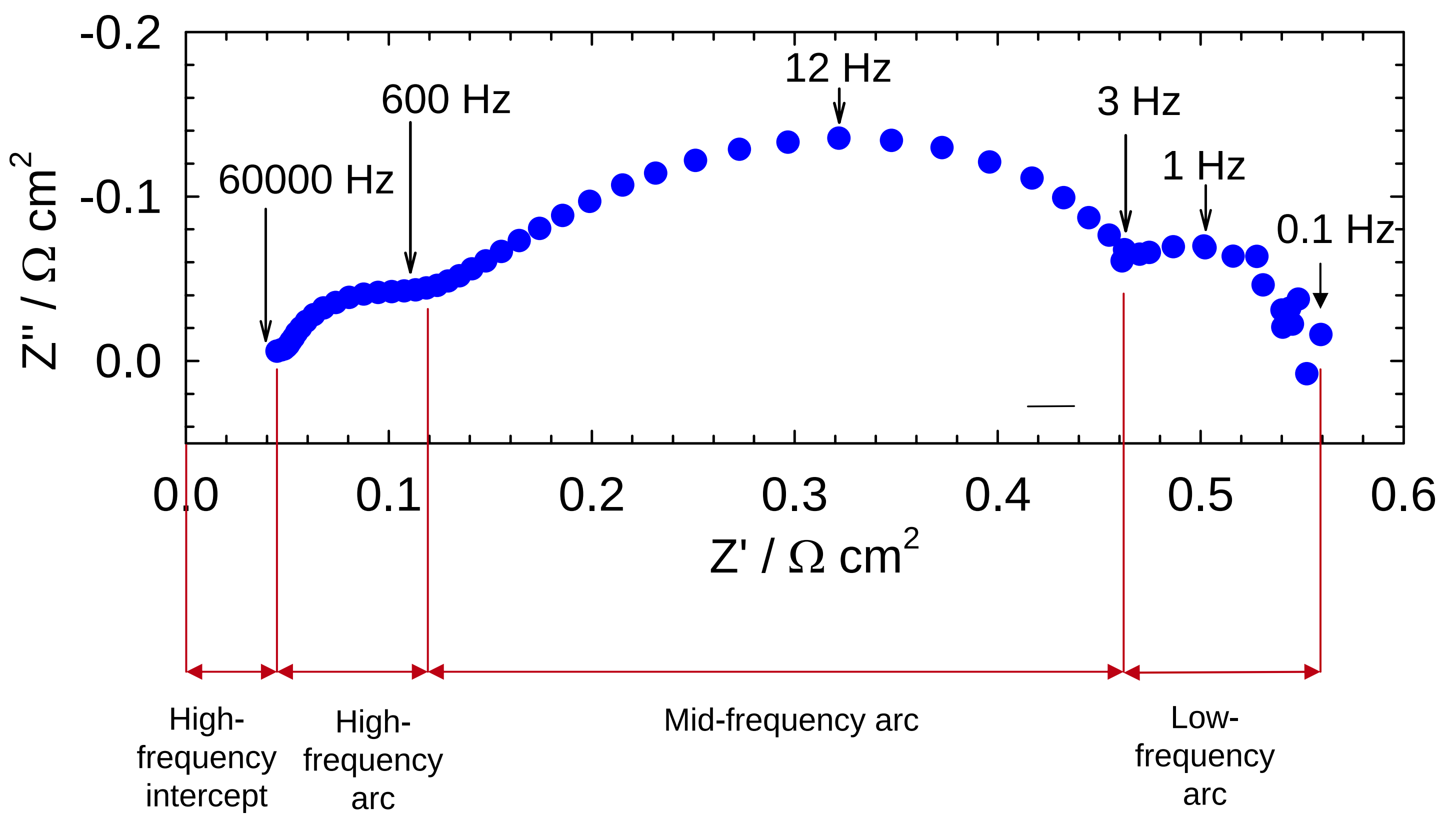
Approaches to examine proposed mechanisms

Electrochemical Impedance Spectroscopy (EIS)

Setup 1 **or** **Setup 2**



EIS response of PEM fuel cell



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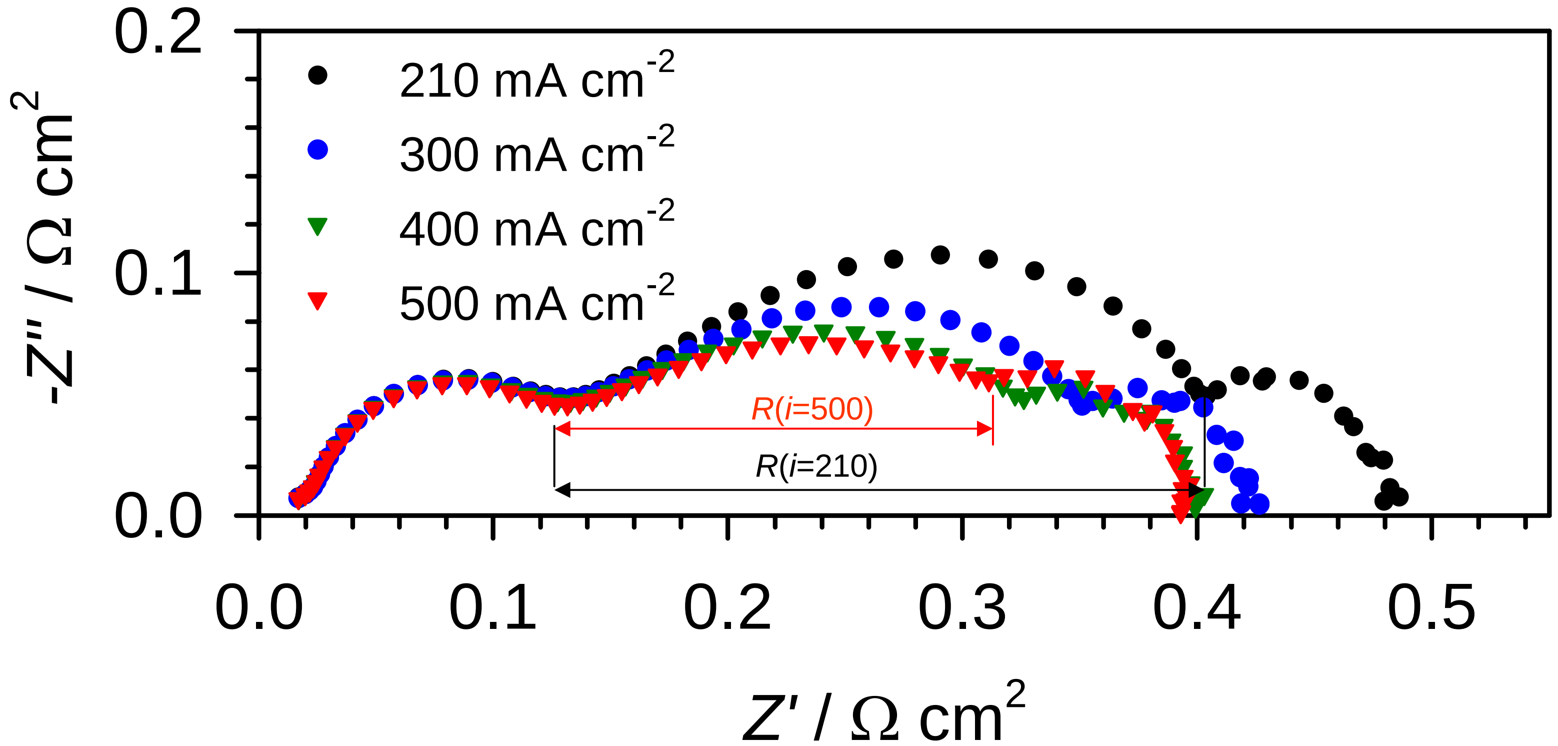
Mid-frequency arc: charge transfer resistance

effect of current density on EIS response



$$R_{ct} = \left(\frac{\partial \eta}{\partial i}\right)_T = -\frac{2.303RT}{\alpha F}\frac{1}{i}$$

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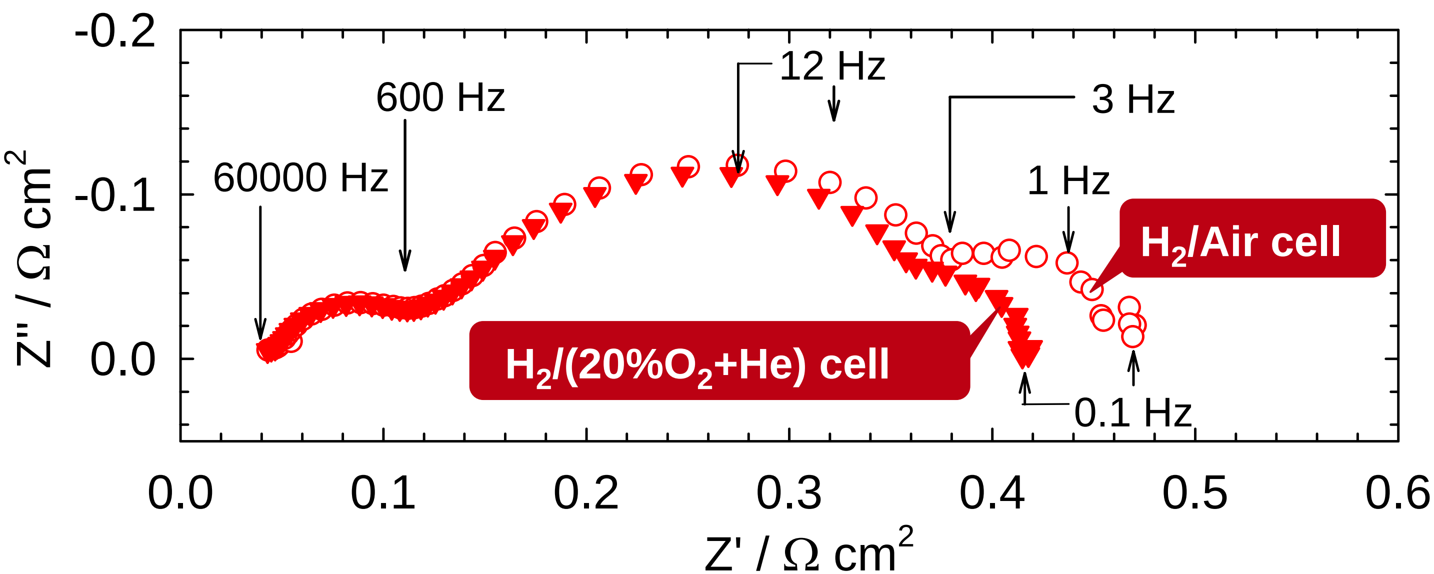
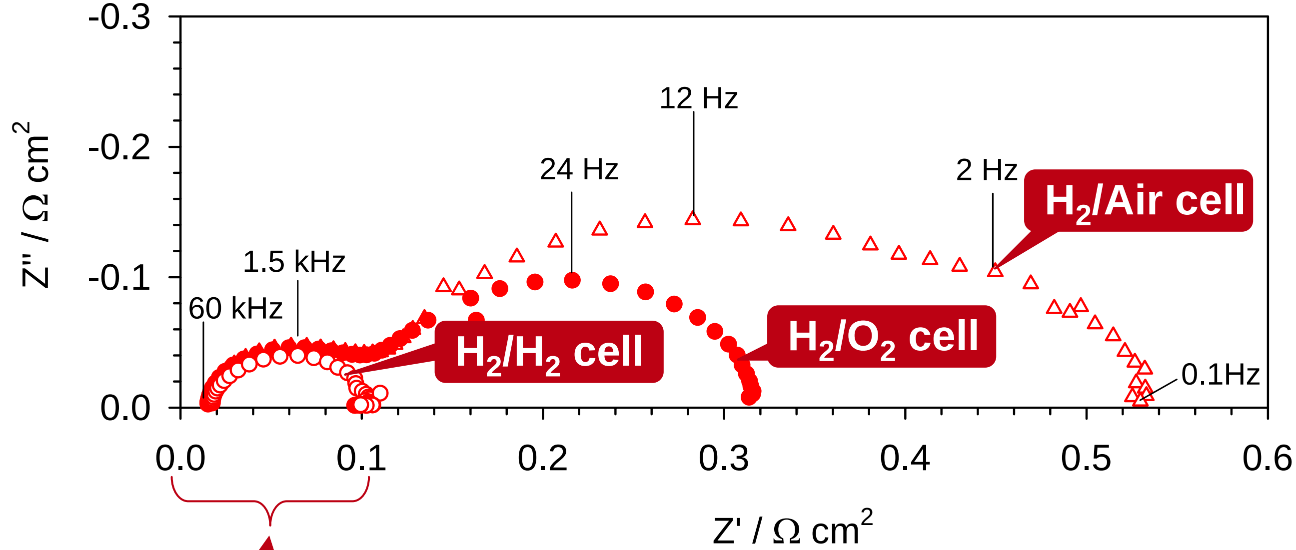
Low-frequency arc: mass-transport resistance

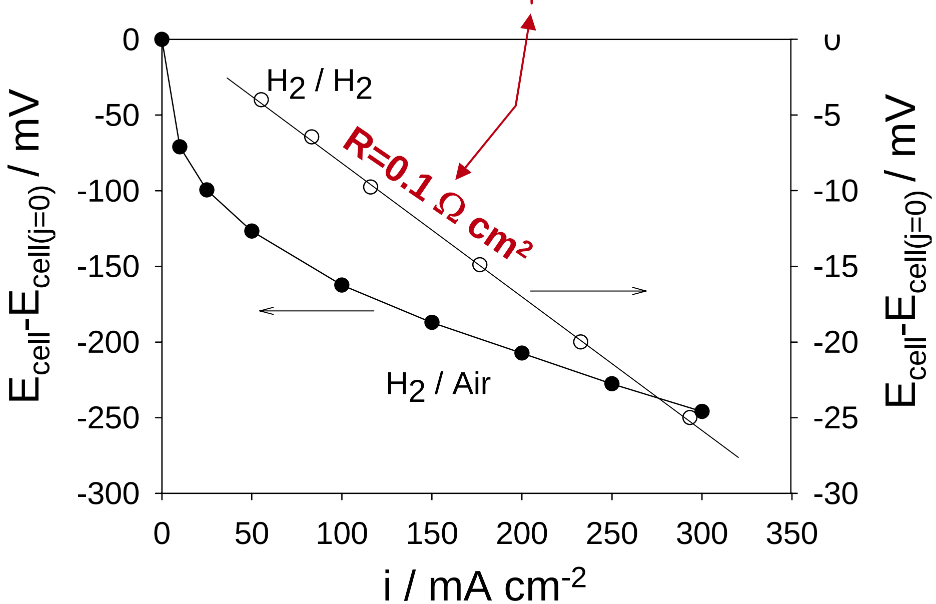
effect of cathode gas on EIS response



D. Malevich, E. Halliop, B. Peppley, J. Pharoah, K. Karan,
J. Electrochem. Soc., **156**, B216 (2009)

High-frequency arc: membrane resistance



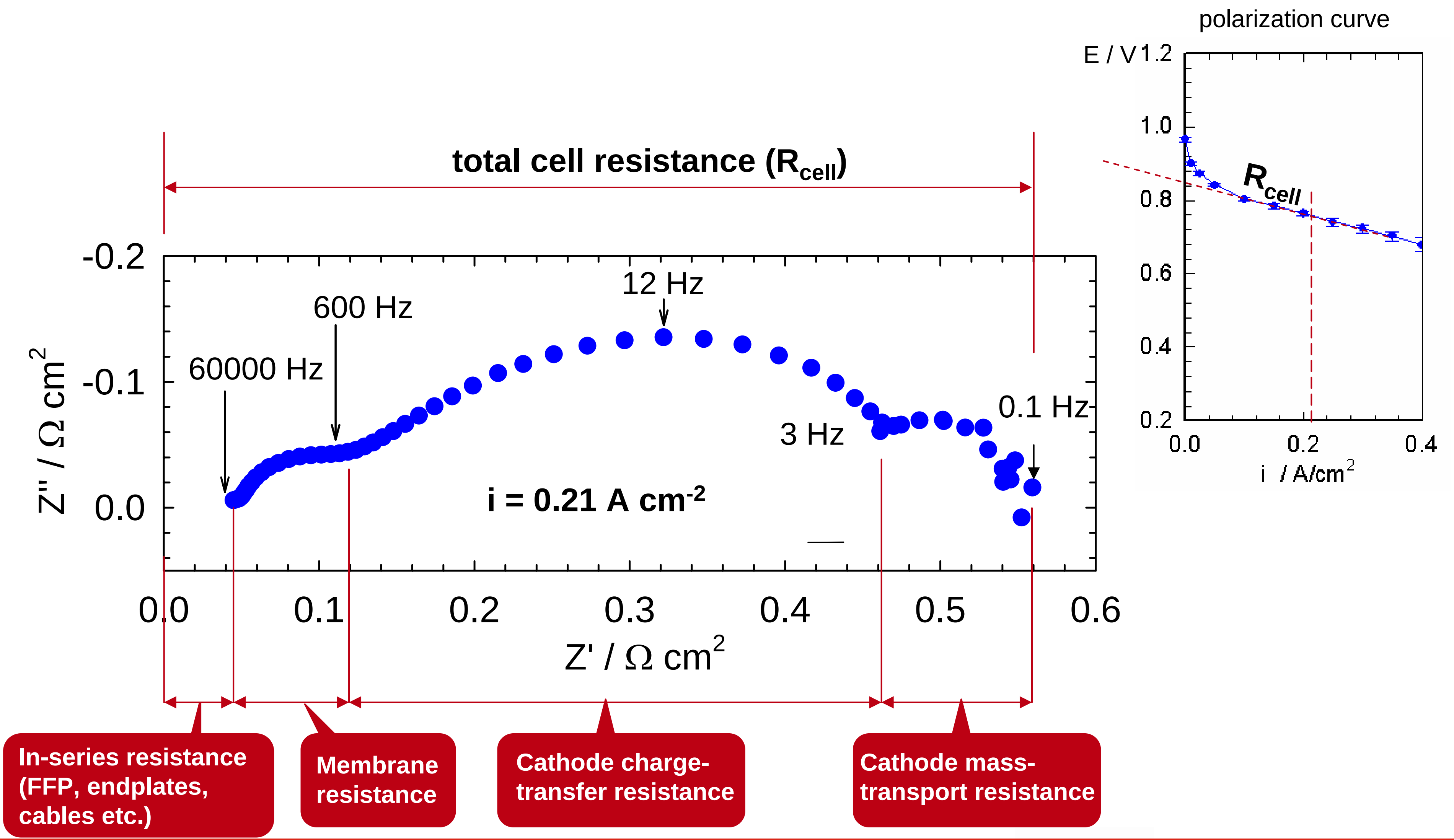


D. Malevich, E. Halliop, B. Peppley, J. Pharoah, K. Karan, *ECS Transactions* **156**, 1763 (2008)

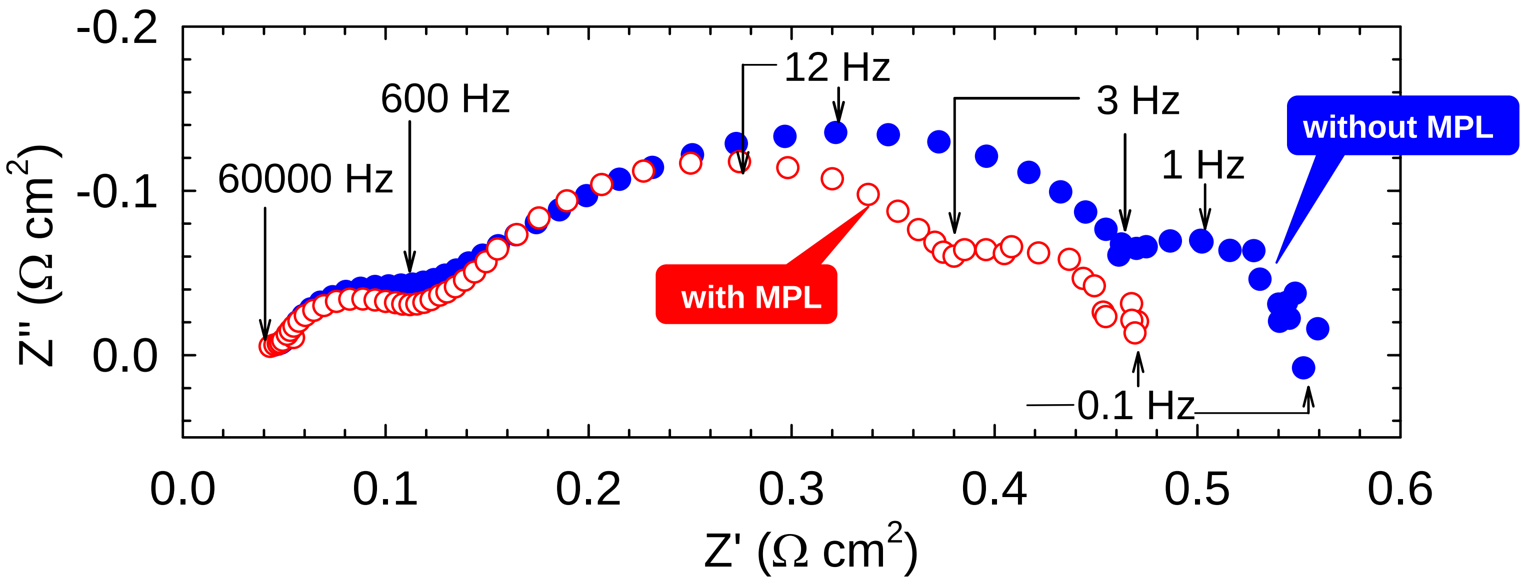
Diameter of high-frequency arc found to be consistent with the resistance calculated from the known geometry and conductivity of the Nafion membrane

J. M. Le Canut, R. Latham, W. Mérida, D. A. Harrington, *J. Power Sources*, **192**, 457 (2009)

EIS response of PEM fuel cell: arc assignment



Effect of MPL on PEMFC EIS response



Impedance diagrams for PEMFC with (2,3) and without (1) MPL fed with H_2/Air. Current density – 0.21 A cm^{-2}.

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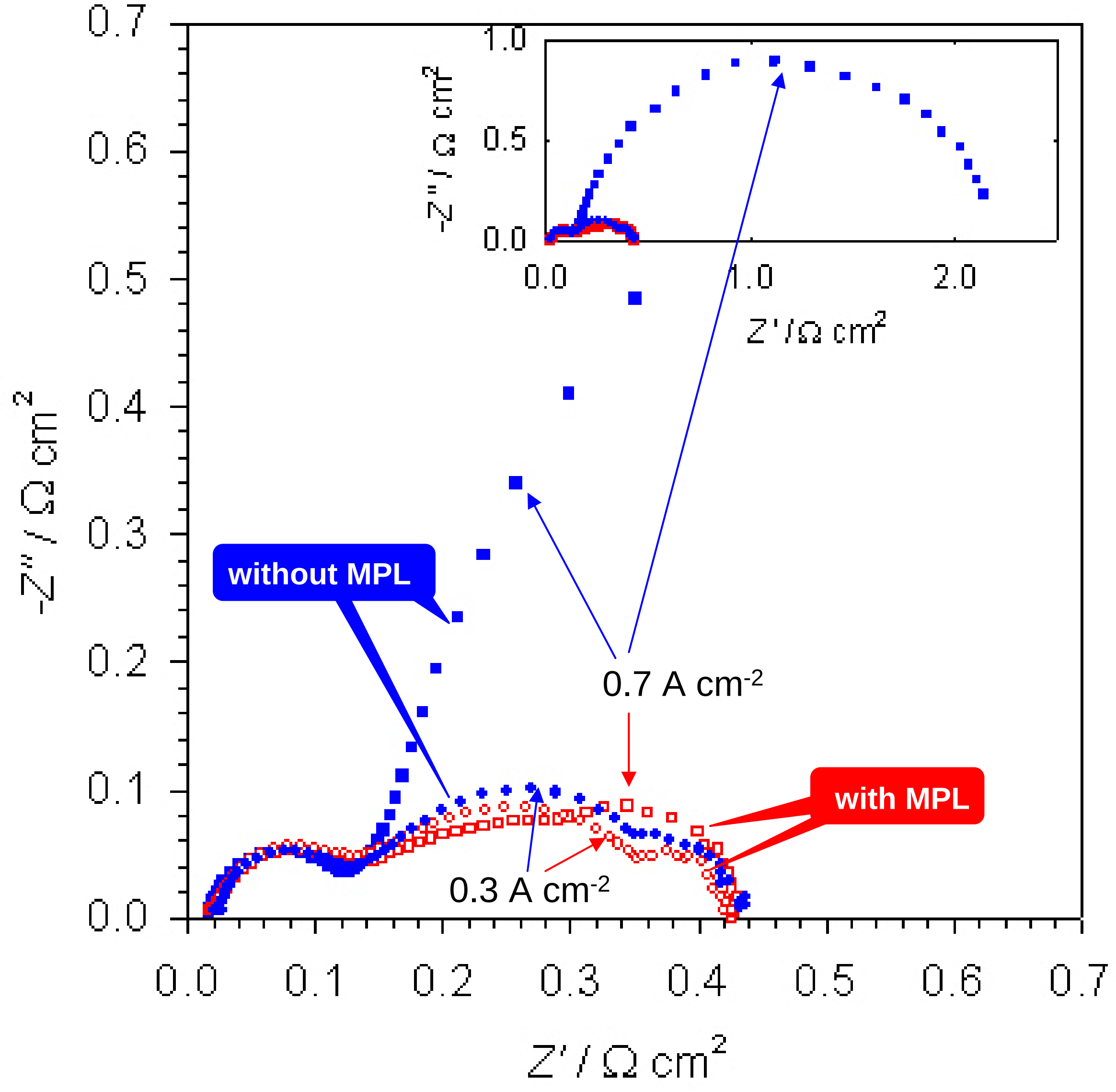
Effect of MPL: influence of current density



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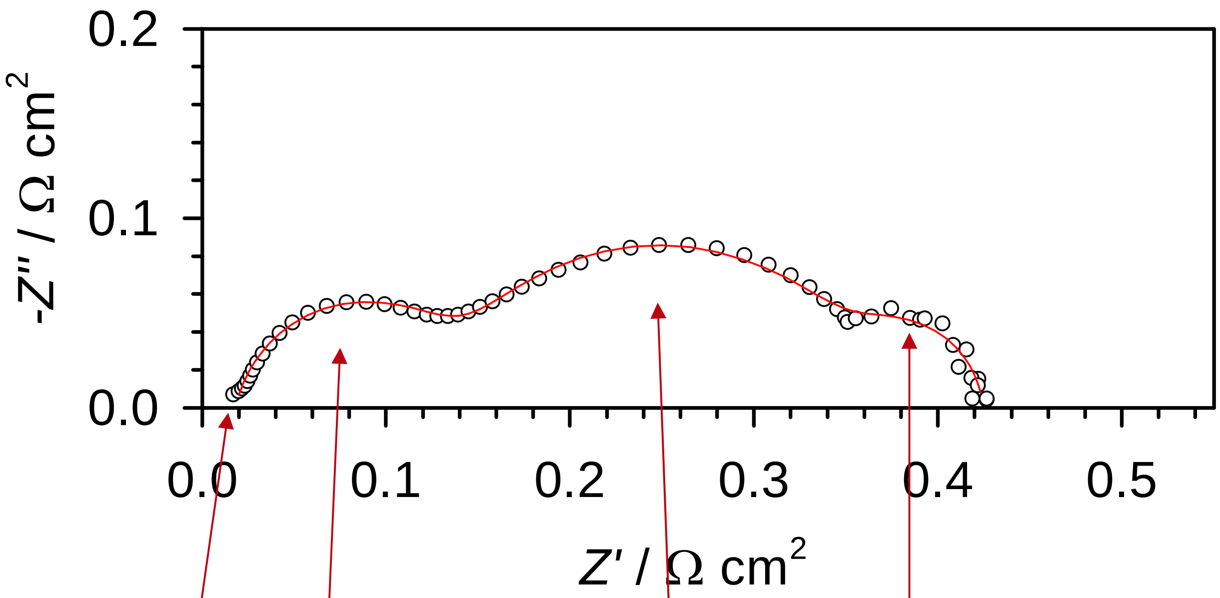
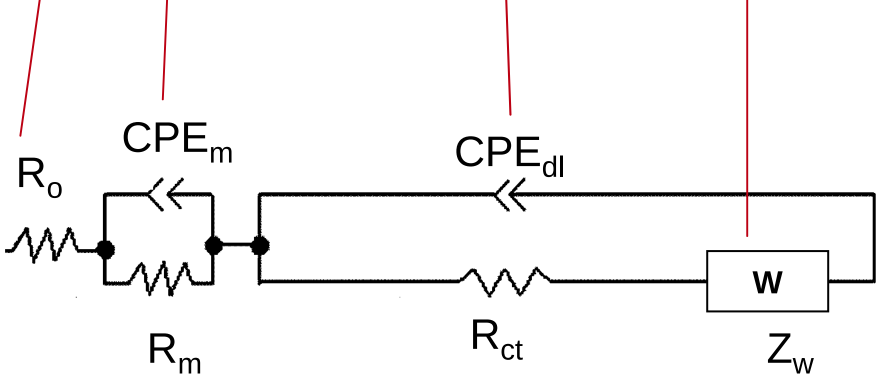
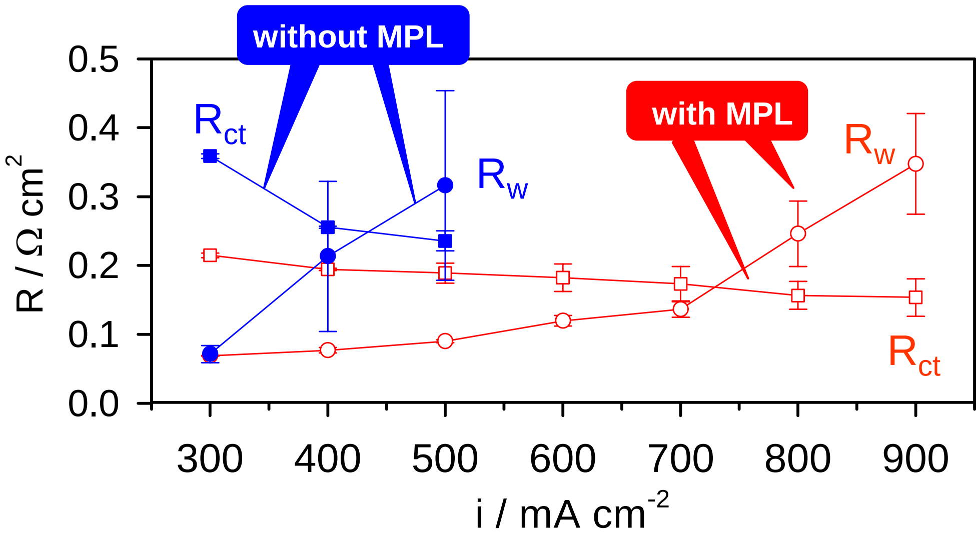
Equivalent circuit fitting

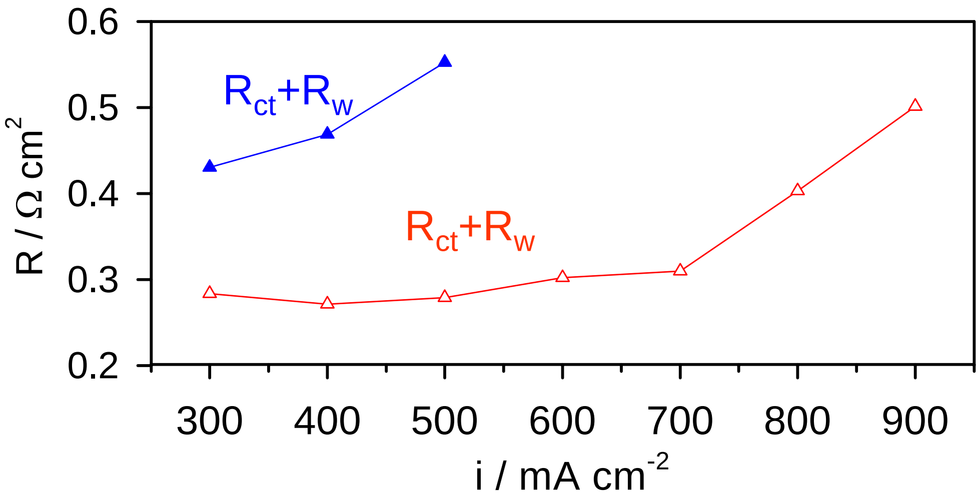


Randles circuit:



Effect of current density on cathode charge-transfer and Warburg resistances





Time constants for oxygen transport process

Experimentally determined:

Table I. Summary of EIS-determined parameters for cells with and without an MPL (average values of the parameters are reported).

	Cell with MPL				Cell without MPL			
i mA/cm^2	R_Ω Ω cm^2	R_{ct} Ω cm^2	R_{mt} Ω cm^2	L^2/D s	R_Ω Ω cm^2	R_{ct} Ω cm^2	R_{mt} Ω cm^2	L^2/D s
300	0.017	0.215	0.069	0.329	0.015	0.359	0.071	0.2461
400	0.017	0.194	0.077	0.239	0.015	0.255	0.213	0.0833
500	0.017	0.189	0.090	0.172	0.015	0.236	0.316	0.0689
600	0.017	0.182	0.120	0.136	0.015	NA[a]	NA	NA
700	0.017	0.173	0.136	0.110	0.015	NA	NA	NA
800	0.017	0.157	0.246	0.098	0.016	NA	NA	NA
900	0.017	0.153	0.347	0.096	0.016	NA	NA	NA

[a] NA = not analyzed.

Theoretically predicted:

Table II. Estimated time constants for various oxygen-transport processes.

	PTL (g)	MPL (g)	Cathode layer (g)	Cathode layer (w)	Cathode layer (agg)
Transporting phase	Gas-filled pore	Gas-filled pore	Gas-filled pore	Water film in cathode layer	Ionomer in cathode layer
L (m)	300×10^{-6}	30×10^{-6}	35×10^{-6}	50×10^{-9}	200×10^{-9}
D (m^2/s)	3×10^{-5}	3×10^{-5}	3×10^{-6}	2×10^{-9}	8×10^{-10}
Volume fraction of transporting phase	0.56	0.2	0.2	1	0.5
D^{eff} (m^2/s)[a]	1.26×10^{-6}	4.93×10^{-6}	2.68×10^{-8}	2.00×10^{-9}	2.83×10^{-10}
L^2/D^{eff} (s)	1.15×10^{-2}	1.83×10^{-4}	4.57×10^{-4}	1.25×10^{-6}	1.41×10^{-4}

[a] $D^{eff} = D \times$ (volume fraction of transporting phase$^{1.5}$).

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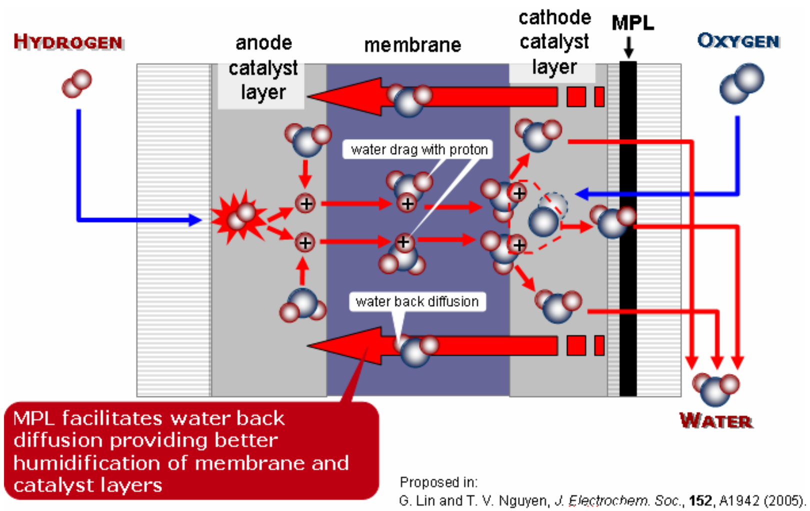
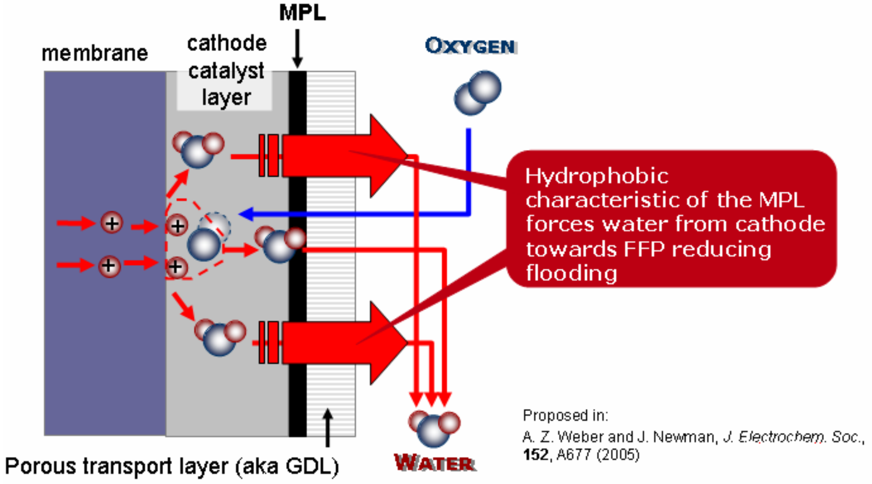
MPL effect models

Model A: MPL promotes water back diffusion



Model B: MPL forces water to FFP



Expected effects:
- Increased amount of water in cathode catalyst layer
- Reduced membrane resistance
- Reduced water content in cathode PTL

observed

Expected effects:
- Reduced amount of water in cathode catalyst layer
- Increased water content in cathode PTL

not observed