

Macroscopic modelling of degradation phenomena in fuel cells

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Outline

- Introduction
- Poisoning wave along the feed channel
- Carbon corrosion in PEM fuel cells
- Ruthenium corrosion in DMFCs
- Poisoning wave in the catalyst layer: Cr deposition in SOFC
- Conclusions





What is wrong with our cells?



Key aging problems are in catalyst layers (agglomeration, dissolution, corrosion etc)



General aging models?

Can we develop general models of cell aging, not specifying microscopic mechanisms?

Yes, we can!

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Quasi-2D cell modeling



In the MEA, the dominant transport is through-plane; in the channels, it is along the channel.

Quasi-2D models.



Quasi-2D equations

$$\begin{split} &\frac{\eta}{b} = \ln \left(\frac{j}{j_* c \ / \ c_{ref}} \right) - \ln \left(1 - \frac{j}{j_{\lim}^0 c \ / \ c_{ref}} \right) & \text{Voltage loss on the cathode side} \\ &V_{cell} = V_{oc} - \eta - RJ & \text{Cell voltage} \end{split}$$

$$v^0 \frac{\partial c}{\partial z} = -\frac{j}{nFh}$$

Mass conservation in the channel (plug flow)



Solutions:



The lower stoich, the larger local current at the inlet



Model and experiment of Kućernak's group



$$rac{j_0}{J} = -\lambda \ln \Big(1 - rac{1}{\lambda} \Big) \Big(1 - rac{1}{\lambda} \Big)^{z \, / \, L}$$

Model (lines) and experiment



A.A.Kulikovsky, A.Kucernak and A.A.Kornyshev *Electrochim. Acta* **50** (2005) 1323.



Suppose that there exists a critical current density



$$\begin{split} \frac{j}{J} &= \left(\frac{L}{L-z_w}\right) f_{\lambda} \cdot \left(1 - \frac{1}{\lambda}\right)^{\frac{z-z_w}{L-z_w}} \\ \frac{j}{J} &= \left(\frac{1}{1-z_w}\right) f_{\lambda} \cdot \left(1 - \frac{1}{\lambda}\right)^{\frac{z-z_w}{1-z_w}} \end{split}$$

The length of the domain subject to degradation is obtained from

$$j(z_w + l_w) = j_{crit}$$



Equation of wave motion

$$l_{w} = \frac{\left(1 - z_{w}\right) \ln\left(j_{crit}(1 - z_{w}) / (f_{\lambda}J)\right)}{\ln\left(1 - \left(1 / \lambda\right)\right)}$$

Just a simple algebra...



This is an equation of degradation wave motion. Tau_d is the characteristic time of degradation, determined by the microscopic nature of the degradation.



The law of wave motion



Wavefront position vs. time

$$z_w = 1 - a \exp \left[-\ln(a) \exp t \right]$$

where

$$a = j(0) / j_{crit}$$

It seems that typically $a \simeq 1$ Time is scaled according to

$$t = \frac{t}{\tau_d \ln\left(1 - 1/\lambda\right)}$$



Degradation wave: overpotential



Cathode overpotential vs. time

A.A.Kulikovsky, H. Scharmann and K.Wippermann *Electrochem. Comm* **6** (2004) 75.

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PEFC lifetime experiment from PSI



Figure 2: Single cell durability experiment, using a 35 μm FEP25 based radiation-grafted membrane, and carbon cloth based electrodes (from E-TEK) with a Pt loading of 0.6 mg/cm².



PEFC flooding (ZSW and Fraunhofer ISE)





Some lessons

It seems that fuel cell never dies uniformly: some areas are more stressed and they die first. Then, the "stressing spot" shifts to a new position and it starts killing a new domain. In the stack, the process is facilitated by the fixed total current.

Stressing factors: (i) high local current, (ii) high local temperature, (iii) high local overpotential. These factors induce numerous microscopic aging processes.

We could imagine radial waves propagating from the circular spot, or 2D waves. However, the mechanism of propagation remains the same.





C.A.Reiser, L.Bregoli, T.W.Patterson, J.S.Yi, J.D.Yang, M.L.Perry, T.D.Jarvi. ESSL 8 (2005) A273

Cell "reversal"



Anode inlet

$$\eta = \varphi_c - \Phi - E^{eq}$$

metal electrolyte OCV



Carbon corrosion in PEM fuel cells





Model





ł

Membrane potential

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$$

$$\int_{x} \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$$

$$\int_{x} \frac{\partial^2 \Phi}{\partial y^2} = \frac{1}{\sigma_m} \frac{\partial}{\partial y} \left(\sigma_m \frac{\partial \Phi}{\partial y} \right) \approx \frac{\sigma_m \frac{\partial \Phi}{\partial y} \Big|^a - \sigma_m \frac{\partial \Phi}{\partial y} \Big|^c}{\sigma_m l_m} = \frac{j^c - j^a}{\sigma_m l_m}$$

Where we have used Ohm's law: $\,j=-\sigma_{_{m}}\,\frac{\partial\Phi}{\partial y}\,$

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Membrane potential

Ok, instead of

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$$

we get

$$\frac{\partial^2 \Phi}{\partial x^2} = \frac{j^a - j^c}{\sigma_m l_m}$$

Introducing dimensionless vars

$$x = \frac{x}{L}, \ \Phi = \frac{\Phi}{b}, \ j = \frac{jl_m}{\sigma_m b_c}$$

we obtain

$$\varepsilon^2 \frac{\partial^2 \Phi}{\partial x^2} = j^a - j^c$$

where

$$\varepsilon = \frac{l_m}{L}$$

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What is epsilon?

$$\varepsilon^2 = \left(\frac{l_m}{L}\right)^2 = \left(\frac{2.5 \cdot 10^{-3}}{10}\right)^2 \simeq 10^{-7}$$

Thus, at leading order we can set epsilon = 0 and the Poisson equation

$$\varepsilon^2 \frac{\partial^2 \Phi}{\partial x^2} = j^a - j^c$$

simplifies to

$$j^a = j^c$$

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$$
$$\int j^a = j^c$$

2D Laplace equation is reduced to a much simpler algebraic equation!

For j^a and j^c we can write Butler-Volmer-like equations. For concentrations we take a step function.



Currents



$$\left(j_{hy}^{a} - j_{ox}^{a}\right) - \left(j_{ox}^{c} - j_{cr}^{c}\right) = 0$$

No current in the external circuit

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An example: HOR current

$$\frac{f_n}{j_{hy}^a} = \frac{1}{j_{hy}^{BV}} + \frac{1}{j_{hy}^{\lim}}$$
$$j_{hy}^{BV} = 2j_{hy}^* \sinh\left(\frac{\eta_{hy}}{b_{hy}}\right)$$

(Crude approximation for HOR...)

$$j_{hy}^{\lim} = rac{2FD_{hy}c_{hy}^{ref}}{l_b j_{ref}}$$

$$f_{n} = \frac{1}{2} \left(1 - \tanh\left(\frac{x - x_{0}}{s}\right) \right)$$



Concentrations and currents

Anode concentrations and Phi

"Cathode" currents



Prescribed step functions for hydrogen and oxygen concentrations and the solution for Phi. Our approximation fails in a narrow yellow zone. ORR and CCR current densities on the cathode side.



 $\partial \Phi$

 ∂x

8

7

9

10

large

More currents



HOR and ORR currents on the anode side. Note the peak of HOR, something is happening there.

These differences are expected to be zero; however, they are not. Peak manifests an **in—plane current** at the interface.

5

Distance

6

4

In-plane current

2

1.5

0.5

0

0

j_x membrane / A cm⁻²

 $\begin{array}{l} j^a_{hy} \, - \, j^c_{ox} \\ j^a_{ox} \, - \, j^c_{cr} \end{array}$

2

3



Oxygen on the anode due to crossover



The interface is much wider now, as the currents are much lower. Note large shift of Phi gradient position with respect to concentration gradient.

Very similar to the previous case; however, the gradients are smaller.



Currents



Peak of **in—plane current** at the interface gets wider.



Experiment: T.W.Patterson, R.M.Darling, ESSL 9 (2006) A183





Experiment 2 Location #1 Location # 2 anode Fuel Inlet cath #1 Kynar Impregnation 2#2 Location # 3 Location #4 **3**#3 Air Exit Air Inlet **4**#4 **5**#5 「「「「「「「「」」」「「「」」」」」」「「」」」」」」」 100 ^{#6} 6 Location # 5 Location # 6 Fuel Exit



N/R interface: Virtual fuel cell



A.A.Kulikovsky J. Electrochem. Soc. (2011)

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N/R interface: proton trajectory





How could we block reversal?



- Simple solution is to apply external potential to the cell; this is what companies are doing.
- More exotic solution is the membrane with anisotropic conductivity. If proton conductivity along the y—axis is small, the virtual fuel cell cannot form and no reversal could happen.



DMFC with methanol starvation





Methanol starvation: Environment for Ru corrosion



The same model leads to balance of currents produced on the anode and the cathode sides. From this balance we get the shape of Phi, currents and overpotentials for all reactions.

The shaded domain suffers from carbon corrosion and Ru dissolution on the anode side.

$$\mathrm{Ru} \to \mathrm{Ru}^{2+} + 2\mathrm{e}^{-}$$



The effect of depleted domain length



Fraction of methanol-depleted domain



Degradation wave in the catalyst layer







Current conversion with transport loss





Polarization curves







Cr poisoning of the CCL in SOFC

$$\operatorname{Cr}_2O_3(s) + \frac{3}{2}O_2(g) + 2H_2O \rightarrow 2\operatorname{Cr}O_2(OH)_2(g)$$

On the BP surface

$$CrO_2(OH)_2(g) + 6e^- \rightarrow 3O^{2-} + Cr_2O_3(s) + 2H_2O(g)$$

In the FL, electrochemical process!





Model of CL aging



$$\eta = \varphi_c - \Phi - E^{eq}$$

The shape of overpotential for the parasitic reaction is simply a shifted ORR overpotential.

The rate of CL aging has peak in the conversion domain, which dies first.



Degradation wave



When the conversion domain is dead, the ORR/poisoning peak shifts toward the GDL and a new domain is subject to aging.



Auxiliary problem: Performance of partially degraded CL





Note a small residual conversion activity of the poisoned domain (inset).

Polarization curves for the indicated poisoned fraction of the CL.

A.A.Kulikovsky, Electrochem. Comm.12 (2010) 1780



DW in the CL: Cr poisoning of SOFC cathode





Cathode polarization voltage vs. time for different cell currents, **model**

A.A.Kulikovsky, J. Electrochem. Soc. 158 (2011) B253.



DW in the CL: Cr poisoning of SOFC cathode



Experiment (Konysheva et al. JES, **154** (2007) B1252)

A.A.Kulikovsky, J. Electrochem. Soc. 158 (2011) B253.



Why?



Conversion runs in a fresh domain.

At 40% poisoned fraction, conversion runs in a poisoned domain, i.e., 40%-poisoned CL works almost as bad as fully poisoned.

A.A.Kulikovsky, J. Electrochem. Soc. 158 (2011) B253.



Cr distribution in the FL



J.A.Schuler, P.Tanasini, A.Hessler-Wyser, C.Comninellis, J. Van herle EleComm, **12** (2010) 1682–1685

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Experimental cell voltage vs. time (A.Schuler and J. van Herle, Lausanne Univ.)





Polarization curves



To prevent fast Cr deposition, the ionic conductivity of the FL should be large.

A.A.Kulikovsky, Electrochim. Acta 55 (2010) 6391.

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Conclusions

• Macroscopic equations suggest the general scenarios of cell performance degradation

• Fuel cell never die uniformly. Some domains of the cell are stressed more and they die first. This simple idea leads to various aging waves in cells.

• In a stack environment, more degradation waves are possible...

