

A model for DMFC cathode impedance: The effect of virtual anode inside the cathode

A.A.Kulikovsky
Research Centre Juelich, IEK-3
Juelich 52425, Germany

One of the largest problems in DMFC technology is fuel crossover. Methanol readily permeates through the membrane to the cathode, where it is oxidized. The effect of crossover on the DMFC cathode impedance spectra is not fully understood.

We report a model for the DMFC cathode catalyst layer (CCL) impedance. The model is based on charge and mass balance equations:

$$C_{dl} \frac{\partial \eta_{ox}}{\partial t} + \frac{\partial j}{\partial x} = R_{MOR} - R_{ORR} \quad (1)$$

$$\frac{\partial c_{ox}}{\partial t} - D_{ox} \frac{\partial^2 c_{ox}}{\partial x^2} = -\frac{1}{4F} R_{ORR} \quad (2)$$

$$\frac{\partial c_{mt}}{\partial t} - D_{mt} \frac{\partial^2 c_{mt}}{\partial x^2} = -\frac{1}{6F} R_{MOR} \quad (3)$$

$$j = -\sigma_t \frac{\partial \eta_{ox}}{\partial x} \quad (4)$$

$$\eta_{ox} + \eta_{mt} = E_{ox}^{eq} - E_{mt}^{eq} \quad (5)$$

Here η_{ox} and η_{mt} are the positive ORR and MOR

overpotentials, respectively, E_{ox}^{eq} , E_{mt}^{eq} are the respective

equilibrium potentials, R_{ORR} , R_{MOR} are the ORR and

MOR reaction rates, c_{ox} and c_{mt} are the oxygen and

methanol molar concentrations, D_{ox} , D_{mt} are oxygen and

methanol diffusion coefficients, C_{dl} is the double layer volumetric capacitance, j is the proton current density, x is the distance from the membrane.

The ORR rate was calculated using the Butler–Volmer equation, while for the MOR rate we used [1,2]

$$R_{MOR} = \frac{2i_{mt} \sinh(\eta_{mt}/b_{mt})}{1 + \sinh(\eta_{mt}/b_{mt}) / (ac_{mt}/c_{mt}^{ref})} \quad (6)$$

which takes into account finite rate of methanol adsorption on the catalyst surface and zero–order dependence on the methanol concentration c_{mt} at low overpotentials.

Here a is a model parameter, i_{mt} is the MOR exchange current density. Eqs.(1)–(6) were non–dimensionalized, linearized, converted to a frequency domain and solved numerically using Maple® software (for details see [3]).

Fig.1 shows the CCL impedance spectra corresponding to the methanol concentrations of 1M, 1.25M and 1.5M on the anode side. The respective steady–state shapes of the ORR and MOR rate through the CCL thickness, and of the proton current density are shown in Fig.2.

With 1M methanol feed, the rates of MOR and ORR are nearly “parallel”, and the proton current decays monotonically toward the GDL (Fig.2a). The respective impedance spectrum does not show any features in the high–frequency domain (Fig.1a). With 1.25M feed, close to the membrane, the rate of MOR exceeds the rate of ORR and the proton current first increases and then decreases along x (Fig.2b). This peak manifests formation of a virtual anode (VA) near the membrane, a

domain where the MOR rate exceeds the ORR rate.

However, as η_{mt} is large, the rate of MOR in the VA is independent of potential (see Eq.(6)) and the VA simply increases the length of the straight 45° high–frequency line, which determines the CCL ionic resistivity (Fig.1b).

With 1.5M feed, the VA is fully developed: Close to the membrane, the rate of ORR vanishes and only MOR runs in this domain (Fig.2c). At 1.5M feed, η_{mt} drops and the rate of MOR becomes dependent on potential, Eq.(6). This dependence shows up as the spectrum overshoot in the high–frequency domain (Fig.1c).

With the Butler–Volmer conversion function, the rate of MOR always depends on η_{mt} and the virtual anode manifests itself as a second high–frequency arc in the CCL spectrum [3]. Eq.(6) is a more realistic approximation for the MOR rate and hence in an experiment, the overshoot similar to those in Fig.1c could be expected.

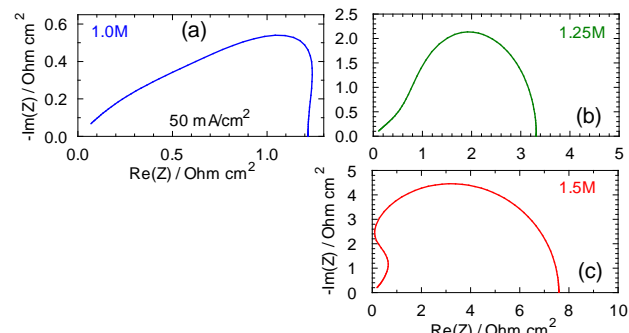


Figure 1. Calculated CCL impedance spectra for the indicated molar concentrations of methanol feed.

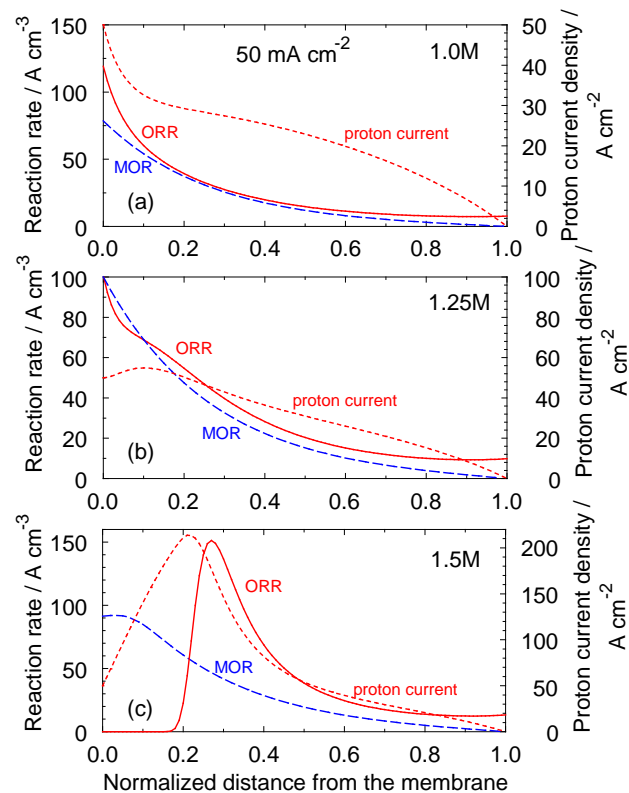


Figure 2. The shapes of MOR and ORR and of the proton current density through the CCL thickness for the same as in Fig.1 methanol molar concentrations on the anode side.

[1]. J.Meyers, J.Newman. JES, **149**, A718 (2002).

[2]. J.Nordlund, G.Lindbergh. JES, **151**, A1357 (2004).

[3]. A.A.Kulikovsky. Electrochem. Comm. **24**, 65 (2012).