

Numerical Model of Platinum Dissolution in Polymer Exchange Membrane Fuel Cells with Slow Proton Transfer

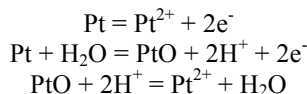
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Platinum dissolution in the catalyst layer of proton exchange membrane fuel cells is one of the critical issues for practical application. Darling et al. has presented mathematical models to reproduce the platinum dissolution and ion movement in the catalyst layers and proton exchange membrane [1,2]. The simulation results show good agreement with experimental results under potential cycling condition, except the maximum potential at which platinum dissolution begins to occur. The maximum potential produced by the numerical simulation is approximately 0.2 V higher than that by the experiments [3,4].

In this study, the slow proton transfer in the proton exchange membrane that causes a delay of membrane-phase potential changing against solid-phase one is taken into the numerical model and the difference between the experimental and simulation results is elucidated.

The numerical model includes three electrochemical reactions, namely platinum dissolution, platinum oxide film formation, and chemical dissolution of platinum oxide:



Rate equations are described as follows:

$$\begin{aligned} r_1 &= k_1 \theta \left[\exp\left(\frac{\alpha_{a,1} n_1 F}{RT} (\Phi_1 - \Phi_2 - U_1)\right) \right. \\ &\quad \left. - \left(\frac{c_{\text{Pt}^{2+}}}{c_{\text{Pt}^{2+,ref}}}\right) \exp\left(-\frac{\alpha_{c,1} n_1 F}{RT} (\Phi_1 - \Phi_2 - U_1)\right) \right] \\ r_2 &= k_1 \theta \left[\exp\left(-\frac{\omega \theta}{RT}\right) \exp\left(\frac{\alpha_{a,2} n_2 F}{RT} (\Phi_1 - \Phi_2 - U_2)\right) \right. \\ &\quad \left. - \theta \left(\frac{c_{\text{H}^+}}{c_{\text{H}^+,ref}}\right)^2 \exp\left(-\frac{\alpha_{c,2} n_2 F}{RT} (\Phi_1 - \Phi_2 - U_2)\right) \right] \\ r_3 &= k_3 \left[\frac{F}{RT} (n_1 U_1 - n_2 U_2) \right] \end{aligned}$$

Hydrogen oxidation reaction and oxygen reduction reaction is described as Butler-Volmer expression. Fick's law and material balances are applied to movement of hydrogen, oxygen, proton, and platinum ions. The cathode potential is changed from 0.5 V to 0.9 V in 1 s.

Figure 1 shows time changing of solid-phase and membrane-phase potential profiles where the cathode potential is changed at 0 s. When the cathode potential is 0.5 V, the membrane phase has potential gradient (-1 s) because of proton transfer. Right after changing potential to 0.9 V (0-1 s), the solid-phase potential rapidly is raised, while the potential profile of the membrane phase remains. That causes potential difference between the solid-phase and the membrane phase to be higher than the cell voltage, which may results in platinum dissolution.

Figure 2 shows time variations of concentration of platinum ions and voltage. After changing potential, the platinum ion concentration has high value for about 15 s, in spite of the cell voltage of 0.9 V, which is lower than equilibrium potential of platinum dissolution.

1. R. M. Darling and J. P. Meyers, *J. Electrochem. Soc.*, **150**, A1523–A1527 (2003).
2. R. M. Darling and J. P. Meyers, *J. Electrochem. Soc.*, **152**, A242–A247 (2005).
3. M. Uno and K. Tanaka, *Journal of Power Sources*, **196**, 9884–9889 (2011).
4. K. Kinoshita, J. T. Lundquist, and P. Stonehart, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **48**, 157–166 (1973).

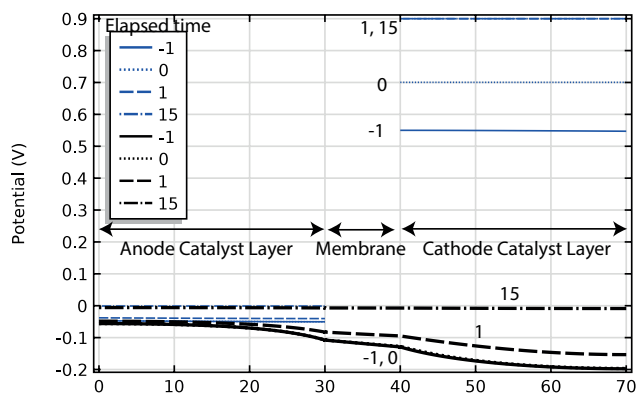


Figure 1. Potential profiles of solid phase (blue) and membrane phase (black).

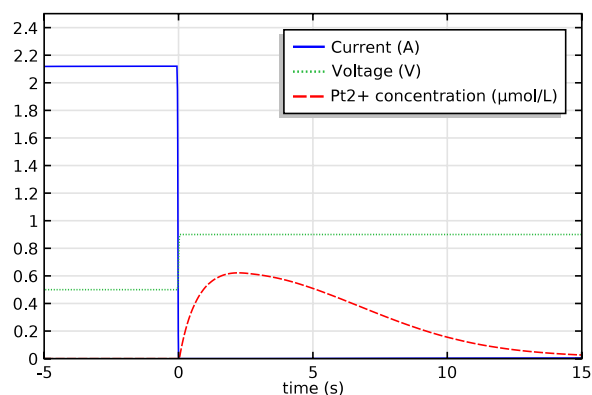


Figure 2. Time variations of current, cell voltage and platinum ion concentration.