

Dynamic First-Principles Molecular-Scale Model for Solid Oxide Fuel Cells

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This model for the voltage-current density (V - i) characteristics predicts behavior in both the fuel cell and steam electrolyzer modes. It uses the Stefan-Maxwell equations to find concentrations at the electrode-electrolyte interfaces of hydrogen, oxygen, and steam as functions of i . These concentrations and parameters such as electrode pore characteristics and temperature T are used to calculate "attempt current density" magnitudes a , b , c , d . Here, a and b are the forward and reverse values at the anode, and c and d at the cathode, interfaces with the electrolyte. Multiplying each value by the corresponding "success probability" yields forward and reverse current density magnitudes $i(\text{fa})$ and $i(\text{ra})$ at the anode and $i(\text{fc})$ and $i(\text{rc})$ at the cathode interfaces. The differences at either interface yield

$$i = i(\text{fa}) - i(\text{ra}) = (a-b)/2 + [(a+b)/2] \tanh\{[-H(a) - 2FV(a)]/2RT\}, \quad (H = \text{enthalpy change})$$

$$i = i(\text{fc}) - i(\text{rc}) = (c-d)/2 + [(c+d)/2] \tanh\{[-H(c) - 2FV(c)]/RT\}. \quad [H = H(a) + H(c)]$$

For infinite $V = V(a) + V(c)$ in the electrolyzer mode, i remains finite whereas the Butler-Volmer equation predicts infinite negative i , because the success probabilities are Boltzmann factors modified to keep them < 1 . Combining the above two equations yields

$$V = -H/2F - (RT/2F) \ln[(b+i)\sqrt{d+i}/(a-i)\sqrt{c-i}]. \quad (F = \text{Far. const.}, R = \text{gas const.})$$

The first term in V contains the enthalpy change and not the change in Gibbs free energy, so the second term plays the role of change in $-TS$ for the $i=0$ case for which V is the open-circuit emf. Because a , b , and c are determined by hydrogen, steam, and oxygen inflow rates respectively, whereas d is much larger and depends on the model for oxygen ion deionization and association to form oxygen gas molecules, any deviation of the second term for $i=0$ from the known change in $-TS$ implies an incorrect value for the d term. This model for the case described below comes close to predicting the correct open-circuit emf. The large value of d compared to possible i values results in activation polarization $V(\text{act})$ and concentration polarization $V(\text{con})$ being insensitive to d . Whereas $V(\text{act}) = V(i=0) - V(i)$ for a , b , c , d fixed at their $i=0$ values, $V(\text{con})$ is the additional change due to the actual changes in a , b , c , d due to nonzero i .

This model has been tested so far for experiments by Jiang and Virkar(1) for their 50/50 hydrogen/steam anode input gas mixture. Model predictions fit their results shown in their Fig. 5 quite well, without adjusting any parameters. The model predicts maximum negative current density $-2.30 \text{ A}/(\text{sq cm})$ in the electrolyzer mode, for which no experimental results were reported. This model shows promise for predicting results for new solid oxide fuel cell designs, including those with graded electrode structures and 3D corrugated electrode configurations.

(1) Y. Jiang and A. V. Virkar, *J. Electrochem. Soc.* 150, A942-A951 (2003).