Effect of Electrode Kinetic Parameters on Performances of PEMFCs and DMFCs- Theoretical and Experimental Aspects

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1. Theoretical Aspects- In general proton exchange membrane fuel cells (PEMFCs) and Direct Methanol Fuel Cells (DMFCs), exhibit all forms of rate control (activation, ohmic and mass transport) over the entire cell potential (E) vs. current density (i) plot. Though extensive modeling studies have been carried out to analyze the E vs. i behavior, the basic second order differential equations have not yielded analytic solutions of the E vs. i behavior and have thus been subjected only to numerical analysis. On the contrary, the following semi-empirical equation has been found to excellently fit the experimental data in PEMFCs:

$E=E_0$-b log i-iR-m exp (ni) (1)

where $E_0= E_r+b \log i_0$ (2)

E_r is the reversible potential of the cell; b and i_0 are the Tafel parameters for oxygen reduction; R is predominantly the ohmic overpotential in the cell, but has a small contribution from the charge-transfer resistance of the reaction-the electrooxidation; and m and n are semi empirical parameters, representing the mass transport region.

For the case of the DMFC, equations (1) and (2) can be modified with

$b=b_a+b_c$ (3)

and $\log i_0=\log i_{0,a}+\log i_{0,c}$ (4)

where b_a and b_c are the anodic and cathodic Tafel slope and $i_{0,a}$ and $i_{0,c}$ are the anodic and cathodes exchange current densities. The expressions for the other performance parameters for the single cell are

$\varepsilon=E/E_r$ (5)

$P=Ei$ (6)

$Q=(E_t-E)i$ (7)

where $E_t=-\Delta H/nF$ (8)

The symbols ε, P, Q represent the voltage efficiency, power density and heat generation rate of the single cell; E_t is the thermo-neutral potential, corresponding to the enthalpy exchange of the fuel cell reaction.

The results of the theoretical analysis to determine the effects of the electrode kinetic parameters on the performances of PEMFCs and DMFCs are summarized as follows:

(i) Exchange Current Density: In the case of PEMFCs, there are parallel displacements of the E vs.i plot with variation of exchange current density for oxygen reduction but the effects are not so large because of the semi-logarithmic dependence of E on i_0. The effect is considerably higher in the case of DMFCs, because the Tafel slope (b_a) for the electrooxidation of methanol is twice that for oxygen reduction (b_c). Corresponding effects are observed for the plots of ε, P and Q on current density

(ii) Tafel Slope: The Tafel slope has a significant effect on the plots of E, ε,P and Q on current density because of the linear dependence of E on b. This applies to both PEMFCs and DMFCs.

(iii) Ohmic Resistance: Here again, there is a marked effect of the value of R on the performance parameters for PEMFCs and DMFCs because of the linear dependence of E on i. The effect is more so in the linear region of the E vs. i plot.

(iv) Mass Transport Parameters: The effect of the mass transport parameters on performance characteristics are considerably higher for PEMFCs rather than for DMFCs. This is because mass transport limitations are obtained at relatively high current densities that PEMFCs can attain because of the reversibility of the hydrogen electrode and DMFCs cannot deliver higher current densities because of the irreversibility of the electrooxidation of methanol.

2. Experimental Aspects- The theoretical predictions, as stated above, are better illustrated in the plots of the performance characteristics of PEMFCs and DMFCs (Figs. 1 and 2), as derived from experimental data. Fig.1 shows the effects of pressure of reactant gases on the performance of the PEMFC, with a Nafion/SiO_x composite membrane at 130^0 C, while Fig.2 shows the effect of the cathode gas pressure on the performance of a DMFC, also with a composite membrane. The excellent fit of the semi-empirical equation for E vs. i is demonstrated as reported earlier. Some problems were encountered with obtaining electrode kinetic data for electrooxidation of methanol using the semi empirical equation and experimental data for DMFCs because of the crossover of methanol