Supplementary Information

Experimental and One-Dimensional Mathematical Modeling of Different Operating Parameters in Direct Formic Acid Fuel Cells

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The assumptions for this model are described as follows:

(i) The full cell is under isothermal conditions.
(ii) The reference condition is taken as ambient temperature and 1 atmospheric pressure
(iii) The formic acid concentration in the anode catalyst layer is constant.
(iv) The Tafel equation was used to determine the electrode kinetic reactions.
(v) Formic acid crossover is caused by diffusion in the electrolytic membrane.
(vi) The electro-osmosis effect on the formic acid transport rate through the membrane is negligible.
(vii) The formic acid concentration gradient is linear with respect to the trans-membrane direction inside the membrane.
(viii) Electrolytic membrane resistance directs the ohmic voltage drop in the cell.
(ix) The oxygen pressure in the cathode catalyst layer is constant.
(x) The gas hold-up volume due to carbon dioxide progress is negligible; the produced gas is immediately removed by the anode feed flow.
(xi) The reactions at the cathode and anode are first order.
(xii) The concentration distributions are one-dimensional and only differ with respect to the trans-membrane direction.

Oxygen Diffusion Coefficient into the Cathode (D_{bc})

The simplified Boltzmann equation was used to estimate the oxygen diffusion coefficient in air at the cathode [1]:

$$D_{OA} = \frac{0.00266T^{1.5}}{pM_{OA}^{0.5}\sigma_{OA}^{2}\Omega_{D}} \tag{25}$$

where p is oxygen pressure, T is temperature, M_{OA} is equivalent molar mass (defined in Eq. (27)), Ω_D is the dimensionless diffusion collision integral as shown in Eq. (28), and σ_{OA} is the Lennard-Jones length (Å) and the equation is

$$\sigma_{OA} = \left(\frac{\sigma_O + \sigma_A}{2} \right) \tag{26}$$

where σ_O and σ_A data were attained from the literature [2]. M_{OA} is equivalent molar mass, defined as [1]:

$$M_{OA} = 2\left[(\frac{1}{M_O}) + (\frac{1}{M_A}) \right]^{-1} \tag{27}$$

where M_A and M_O are the molar masses of air and oxygen, respectively. The diffusion collision integral (Ω_D) is calculated as [3]:

$$\Omega_D = \frac{1.06036}{(T^*)^{0.1561}} + \frac{0.193}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)} \tag{28}$$

where T^* (reduced temperature) equals $\kappa T/\varepsilon_{OA}$, κ is Boltzmann's constant and ε_{OA} is the characteristic Lennard-Jones energy shown in the following equation:

$$\varepsilon_{OA} = (\varepsilon_O \varepsilon_A)^{1/2} \tag{29}$$

where ε_O and ε_A are the Lennard-Jones energies of oxygen and air, respectively.

The effective oxygen diffusion coefficient (D_{OA}^{eff}) in the porous gas diffusion layer was calculated as [4]:

$$D_{OA}^{eff} = (1 - (\frac{3(1-\theta_c)}{3-\theta_c}))D_{OA} \tag{30}$$

where θ_c is the porosity of the cathode gas diffusion layer. The experimental effective diffusion coefficient of oxidant at the cathode at 90°C has been reported to be 0.9×10^{-3} cm^2 s^{-1} [5] when L_{bc} is 0.3 mm. This value was used to calculate the apparent porosity θ_c (0.406). If the apparent porosity is recognized, the effective gas diffusion coefficient in the porous electrode can be established and used to estimate the cathode overpotential (as explained in Section 2.4).

References

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