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An Analytical Study of the Galvanostatic Discharge in Secondary Lithium Cells

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In this work, the material balance equation governing the lithium ion concentration in the electrolyte/solution phase of a lithium cell is considered. This equation is solved by the method of Laplace transform to give an analytical solution for the concentration profile of lithium ions based on the relevant initial and boundary conditions. The solution has been obtained as

$$c_2(x,t) = c_0 + \frac{I(1-t_+^0)L_s}{FD\varepsilon^{3/2}L_+}\left[\frac{1}{2}(L_s + L_+ - x)^2 - \frac{L_+^{\ 2}}{6L_s}\right]$$

$$- \frac{2I(1-t_+^0)L_+}{\pi^2 FD\varepsilon^{3/2}}\cos\left[\frac{\pi}{L_+}(L_s + L_+ - x)\right]\exp\left(-\frac{\pi^2\varepsilon^{1/2}Dt}{L_+^{\ 2}}\right)$$

Using t-test, the profiles of lithium ion concentration calculated using this equation were proven to be in good agreement with the published numerical results within the 95% confidence interval. By defining the cell potential, V, as the difference in the solid-phase potential, Φ_1, at the two current collectors and substituting the solid-phase current density, i_1, with the solution phase current density, $i_2 = I - i_1$, the potential equation was expressed in terms of the solution-phase concentration only. The analytical expression for the voltage of the cell has been obtained as

$$V = U_\theta - I\left[\frac{L_s + L_+}{\sigma} + \frac{L_+ - L_s}{2\kappa} + \frac{L_s}{\kappa_{sep}}\right] - \frac{RT}{F}(1-t_+)\ln\left[\frac{c_2(x = L_s + L_+)}{c_2(x=0)}\right]$$

The cell discharge profile as predicted by the voltage equation was compared with the experimentally determined discharge curves from cells with configuration $Li//LiMn_2O_4$, $Li//TiS_2$, $Li//CoO_2$ and $Li//SOCl_2$. These cells were chosen because of the availability of parameter values needed for calculation of voltage using the equations derived. The t-tests conducted show that the sets of data from the published experimental curves and that predicted from the voltage obtained in this work are in reasonable agreement within a 95% confidence limit.

For cells with parameter values not available from the literature, the experimental discharge characteristics were compared with the Nernst, one-parameter and two-parameter Margules equation. To ensure better fitting between the experimental and the theoretical discharge curves, the one-parameter Margules activity coefficient was modified. The modified one-parameter Margules equation is given by

$$U = U^0 + \frac{RT}{nF}\left[\ln\left(\frac{1-X}{X}\right)\right] + \frac{RT}{nF}[(2X-1)(2.3397 - 0.181T + 3x10^{-5}T^2)]$$

and gives the plot of voltage against state of discharge. The experimental and theoretical voltage distribution showed no significant difference within the 95% confidence limit.