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Short communication

Modeling self-discharge of $Li/SOCl_2$ cells

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Abstract

A kinetic expression for the chemical reaction of lithium metal with thionyl chloride is presented that is consistent with calorimetric measurements of the heat generation from a thionyl chloride cell. The kinetics expression is incorporated into a well-established electrochemical model for the discharge behavior, and then used to estimate the life of the battery under an intermittent discharge so as to assess the importance of lithium corrosion. The model predicts that, under the conditions examined, there is no danger of depleting the lithium anode and so introducing a safety hazard.
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Keywords: Thionyl chloride; Battery; Fade; Lithium corrosion; Safety

1. Introduction

Self-discharge in $Li/SOCl_2$ batteries is largely associated with the reaction of the lithium anode with the thionyl chloride electrolyte (see reaction (1) below). Estimation of the self-discharge of $Li/SOCl_2$ batteries is an important problem in the design of safe cells and batteries. If self-discharge leads to a complete loss of lithium anode in one cell in a string of cells, then that cell can go into reversal when the string is discharged and possibly explode. Thus, it is important to estimate the self-discharge rate of the lithium anode. Long-lived (∼10 years) thionyl chloride batteries are of interest for applications, such as utility meters and other applications. Over such long periods of time, the self-discharge reaction should become more significant. Despite its importance, the issue of self-discharge has received little attention compared to the discharge behavior. This paper presents an approach for estimating the self-discharge of the lithium anode under various pulse discharge scenarios.

The design and general of behavior of $Li/SOCl_2$ batteries is described by Linden and Reddy [1]. The desired electrochemical reactions are,

$$\text{Anode}: \quad Li \rightarrow Li^+ + e^-$$

$$\text{Cathode}: \quad 4Li^+ + 4e^- + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$$

A key design requirement is that the cathode must be porous enough to accommodate the solid LiCl formed on discharge. This requirement complicates the design because the cathode can expand during discharge. Although several groups have reported models to simulate discharge of $Li/SOCl_2$ cells [2–5], the problem of cathode expansion has not been addressed. Others have considered the thermal [6–8] behavior of $Li/SOCl_2$ batteries. However, the problem of self-discharge has received little attention.

The self-discharge reaction,

$$2SOCl_2 + 4Li \rightarrow 4LiCl + S + SO_2 \qquad (1)$$

is known to form a lithium chloride film at the lithium anode. Roth [9] characterized the self-discharge of $Li/SOCl_2$ D-size cells using a CSC4400 model microcalorimetry that was calibrated with heaters of similar size and shape to D-cells and corrected the results for background heat leaks. Roth posited that the heat release was attributed to reaction (1) and used the enthalpy change of that reaction ($\Delta H = -3.65\text{E5}\,\text{J mol}^{-1}$) to estimate the lithium loss over time. Roth found that the rate of reaction (1) depended on how the cell was used. Immedi-

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Table 1
Summary of model equations and parameters

Name	Equation
(a) Equations	
Kirchoff's law	$\frac{\partial i_{2,x}}{\partial x} = Fj_y$
Solid-phase Ohm's law	$\frac{\partial \phi_1}{\partial x} = -\frac{i_{\text{set}} - i_{2,x}}{\sigma_{\text{eff}}}$
Liquid-phase Ohm's law	$\frac{\partial \phi_2}{\partial x} = -\frac{i_{2,x}\tau}{\kappa\varepsilon} - \frac{2\text{RT}}{cF}\left(-t_- - \frac{cV_0}{2(1-c\hat{V})}\right)\frac{\partial c}{\partial x}$
Salt mass balance	$\frac{\partial \varepsilon c}{\partial t} = -\frac{\partial}{\partial x}\left[-\frac{\varepsilon D}{\tau}\frac{\partial c}{\partial x} + cv\right] + j_y\left[(1-t_+) - \frac{c^0}{2}(V_0 - 2V_{\text{LiCl}})\right] - \frac{i_{2,x}}{F}\frac{\partial t_+}{\partial x}$
Negative electrode kinetics	$i_y = i_{0,1,\text{ref}}\left[\exp\left(\frac{\alpha_{a,1}F}{\text{RT}}\eta_1\right) - \left(\frac{c}{c_{\text{ref}}}\right)\exp\left(\frac{-\alpha_{c,1}F}{\text{RT}}\eta_1\right)\right], \quad \eta_1 = \phi_1 - \phi_2 - U_{1,\text{ref}};\ i_{0,1,\text{ref}} = 1.157 \times 10^3 \exp\left(\frac{-4641}{T}\right)$
Positve electrode kinetic	$j_y = i_{0,2,\text{ref}}a_{\text{s}}\left[\exp\left(\frac{\alpha_{\text{a},2}F}{\text{RT}}\eta_2\right) - \left(\frac{c}{c_{\text{ref}}}\right)\left(\frac{c_0}{c_{0,\text{ref}}}\right)^2\exp\left(\frac{-\alpha_{c,2}F}{\text{RT}}\eta_2\right)\right], \quad \eta_2 = \phi_1 - \phi_2$
Volume balance	$\frac{\partial \varepsilon}{\partial x} = V_{\text{LiCl}}j_y$
Darcy's law	$v = \left[(1-t_+)\hat{V} + \frac{(V_o - 2V_{\text{LiCl}})}{2}\right]\frac{i_{2,x}}{F}$
Li metal mass balance	$\frac{\partial n_{\text{Li}}}{\partial t} = -\frac{i_{2,x}}{F} - R_{\text{f}}$
LiCl mass balance	$\frac{\partial n_{\text{LiCl}}}{\partial t} = R_{\text{f}} - R_{\text{b}}, \quad R_{\text{f}} = \frac{1/k_{\text{f1}}}{1/k_{\text{f1}}k_{\text{f0}} + t}, \quad R_{\text{b}} = k_{\text{b0}}(1 - \text{e}^{-k_{\text{b1}}n_{\text{LiCl}}})i_y$
Energy balance	$mc_{\text{p}}\frac{\text{d}T}{\text{d}t} = Ai_{\text{set}}(E_{\text{tn}} - E) - A_{\text{HT}}h(T - T_{\text{amb}}) + Q$

Parameter	Units	Description
(b) Symbols		
A	m^2	Separator area (one side)
A_{HT}	m^2	Heat-transfer area of cell
D	$\text{m}^2\ \text{s}^{-1}$	Diffusion coefficient of LiAlCl_4
c	Equivalents m^{-3}	LiAlCl_4 concentration
c_{p}	$\text{J kg}^{-1}\ \text{K}^{-1}$	Heat capacity of cell
E	V	Cell potential
E_{tn}	V	Thermo-neutral potential for Li/SOCl_2
F	C eq^{-1}	Faraday's constant
h	$\text{W m}^{-2}\ \text{K}^{-1}$	Faraday's constant
i_{set}	A m^{-2}	Applied current per unit area of separator
$i_{2,x}$	A m^{-2}	Liquid-phase current density
j_y	Equivalents m^{-3}	SOCl_2 reduction rate per volume of cathode
m	Kg	Mass of cell
n_{Li}	mol m^{-2}	Amount of lithium metal per area of separator
n_{LiCl}	mol m^{-2}	Amount of LiCl at negative per area of separator
Q	W	Heat released by self-discharge reaction
t	s	Time
t_-	None	Anion transport number
t_+	None	Cation transport number
T	K	Temperature
T_{amb}	K	Ambient temperature
V_0	$\text{m}^3\ \text{mol}^{-1}$	Partial molar volume of SOCl_2
V_{LiCl}	$\text{m}^3\ \text{mol}^{-1}$	Partial molar volume of LiCl
$\hat{V}$	$\text{m}^3\ \text{mol}^{-1}$	Partial molar volume of LiAlCl_4
x	m	Distance from negative electrode surface
α	None	Transfer coefficient
ε	None	Porosity
ϕ_1	V	Solid-phase potential
ϕ_2	V	Liquid-phase potential
κ	$\Omega^{-1}\ \text{cm}^{-1}$	Liquid-phase ionic conductivity
ν	m-s^{-1}	Volume average velocity of electrolyte
σ_{eff}	$\Omega^{-1}\ \text{cm}^{-1}$	Effective electronic conductivity of cathode
τ	None	Tortuosity