

Short communication

## Modeling self-discharge of Li/SOCl<sub>2</sub> 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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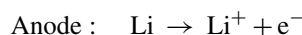
**Keywords:** Thionyl chloride; Battery; Fade; Lithium corrosion; Safety

### 1. Introduction

Self-discharge in Li/SOCl<sub>2</sub> 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<sub>2</sub> 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.

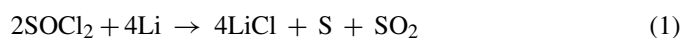
The design and general behavior of Li/SOCl<sub>2</sub> batteries is described by Linden and Reddy [1]. The desired electrochemical

reactions are,



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<sub>2</sub> cells [2–5], the problem of cathode expansion has not been addressed. Others have considered the thermal [6–8] behavior of Li/SOCl<sub>2</sub> batteries. However, the problem of self-discharge has received little attention.

The self-discharge reaction,



is known to form a lithium chloride film at the lithium anode. Roth [9] characterized the self-discharge of Li/SOCl<sub>2</sub> 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 ( $\Delta H = -3.65\text{E}5 \text{ J mol}^{-1}$ ) 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	$\frac{\partial \phi_2}{\partial x} = -\frac{i_{2,x}\tau}{\kappa\varepsilon} - \frac{2RT}{cF} \left( -t_- - \frac{cV_0}{2(1-c\hat{V})} \right) \frac{\partial c}{\partial x}$	
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	$i_y = i_{0,1,\text{ref}} \left[ \exp \left( \frac{\alpha_{a,1} F}{RT} \eta_1 \right) - \left( \frac{c}{c_{\text{ref}}} \right) \exp \left( \frac{-\alpha_{c,1} F}{RT} \eta_1 \right) \right], \quad \eta_1 = \phi_1 - \phi_2 - U_{1,\text{ref}}; \quad i_{0,1,\text{ref}} = 1.157 \times 10^3 \exp \left( \frac{-4641}{T} \right)$	
Positive electrode kinetic	$j_y = i_{0,2,\text{ref}} a_s \left[ \exp \left( \frac{\alpha_{a,2} F}{RT} \eta_2 \right) - \left( \frac{c}{c_{\text{ref}}} \right) \left( \frac{c_0}{c_{0,\text{ref}}} \right)^2 \exp \left( \frac{-\alpha_{c,2} F}{RT} \eta_2 \right) \right], \quad \eta_2 = \phi_1 - \phi_2$	
Volume balance	$\frac{\partial \varepsilon}{\partial x} = V_{\text{LiCl}} j_y$	
Darcy's law	$v = \left[ (1-t_+) \hat{V} + \frac{(V_0 - 2V_{\text{LiCl}})}{2} \right] \frac{i_{2,x}}{F}$	
Li metal mass balance	$\frac{\partial n_{\text{Li}}}{\partial t} = -\frac{i_{2,x}}{F} - R_f$	
LiCl mass balance	$\frac{\partial n_{\text{LiCl}}}{\partial t} = R_f - R_b, \quad R_f = \frac{1/k_{f1}}{1/k_{f1}k_{f0} + t}, \quad R_b = k_{b0}(1 - e^{-k_{b1}n_{\text{LiCl}}})i_y$	
Energy balance	$m c_p \frac{dT}{dt} = A i_{\text{set}} (E_{\text{tn}} - E) - A_{\text{HT}} h (T - T_{\text{amb}}) + Q$	
Parameter	Units	Description
(b) Symbols		
$A$	$\text{m}^2$	Separator area (one side)
$A_{\text{HT}}$	$\text{m}^2$	Heat-transfer area of cell
$D$	$\text{m}^2 \text{s}^{-1}$	Diffusion coefficient of $\text{LiAlCl}_4$
$c$	Equivalents $\text{m}^{-3}$	$\text{LiAlCl}_4$ concentration
$c_p$	$\text{J kg}^{-1} \text{K}^{-1}$	Heat capacity of cell
$E$	V	Cell potential
$E_{\text{tn}}$	V	Thermo-neutral potential for $\text{Li}/\text{SOCl}_2$
$F$	$\text{C eq}^{-1}$	Faraday's constant
$h$	$\text{W m}^{-2} \text{K}^{-1}$	Faraday's constant
$i_{\text{set}}$	$\text{A m}^{-2}$	Applied current per unit area of separator
$i_{2,x}$	$\text{A m}^{-2}$	Liquid-phase current density
$j_y$	Equivalents $\text{m}^{-3}$	$\text{SOCl}_2$ reduction rate per volume of cathode
$m$	Kg	Mass of cell
$n_{\text{Li}}$	$\text{mol m}^{-2}$	Amount of lithium metal per area of separator
$n_{\text{LiCl}}$	$\text{mol m}^{-2}$	Amount of $\text{LiCl}$ 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
$T_{\text{amb}}$	K	Ambient temperature
$V_0$	$\text{m}^3 \text{mol}^{-1}$	Partial molar volume of $\text{SOCl}_2$
$V_{\text{LiCl}}$	$\text{m}^3 \text{mol}^{-1}$	Partial molar volume of $\text{LiCl}$
$\hat{V}$	$\text{m}^3 \text{mol}^{-1}$	Partial molar volume of $\text{LiAlCl}_4$
$x$	m	Distance from negative electrode surface
$\alpha$	None	Transfer coefficient
$\varepsilon$	None	Porosity
$\phi_1$	V	Solid-phase potential
$\phi_2$	V	Liquid-phase potential
$\kappa$	$\Omega^{-1} \text{cm}^{-1}$	Liquid-phase ionic conductivity
$v$	$\text{m-s}^{-1}$	Volume average velocity of electrolyte
$\sigma_{\text{eff}}$	$\Omega^{-1} \text{cm}^{-1}$	Effective electronic conductivity of cathode
$\tau$	None	Tortuosity

ately after a discharge, the self-discharge was significant but decreased rapidly over time; on storage the self-discharge reaction decreased to a very low-rate, but could be reinvigorated by a pulse discharge. Nainville et al. [10] presented a percolation cluster model to describe passivation of a lithium anode that could predict the effect of additives on the thickness and porosity of the passive film. Here, a simpler model is presented for estimating the effect of the film on the discharge behavior with the goal of estimating lithium consumption over long periods of time.

## 2. Model development

Several authors have all presented very similar electrochemical models for the discharge of a thionyl chloride cell [2–4]. These models consist of equations describing mass balances on reactants, charge-transfer kinetics, porosity change in the cathode, electrolyte flow, temperature changes, and ohmic drops in the liquid and solid phases (see Table 1). These equations are explained in detail by Jain et al. [4] and their formulation was used in this work. This work extends previous models by accounting for direct reaction of the lithium electrode with thionyl chloride; that is, the self-discharge reaction.

In the work mentioned above, Roth [9] found that the rate of heat generation from self-discharge,  $Q$ , had the functional form

$$Q = \frac{a_0}{(t + a_1)^x} \quad (2)$$

where  $t$  is time,  $a_0$  and  $a_1$  are constants, and  $x$  ranged from 1.17 to 1.34. For consistency with Roth's experimental results, the rate of formation of LiCl layer,  $R_f$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) was posited to decrease exponentially with the amount of LiCl,  $n_{\text{LiCl}}$  ( $\text{mol m}^{-2}$ )

$$R_f = \frac{dn_{\text{LiCl}}}{dt} = k_{f0} e^{-k_{f1} n_{\text{LiCl}}} \quad (3)$$

where  $k_{f0}$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) is a rate constant and  $k_{f1}$  ( $\text{m}^2 \text{mol}^{-1}$ ) is a constant. Integrating this equation and taking the time derivative gives

$$R_f = \frac{1/k_{f1}}{(1/k_{f1} k_{f0}) + t} \quad (4)$$

Since the rate of heat generation due to self-discharge,  $Q$  (W) can be calculated as

$$Q = A \times \Delta H \times R_f = \frac{A \times \Delta H / k_{f1}}{(1/k_{f1} k_{f0}) + t} \quad (5)$$

where  $A$  is active area ( $\text{m}^2$ ) of the lithium electrode. Eq. (5) is consistent with Roth's Eq. (2) with  $x=1$ .

Eq. (4) describes the formation of a LiCl film at the negative electrode. To account for Roth's finding that pulse discharge accelerated the reaction between lithium and thionyl chloride, the following equation is posited to describe the destruction of the LiCl film.

$$R_b = k_{b0} (1 - e^{-k_{b1} n_{\text{LiCl}}}) i_y \quad (6)$$

Table 2  
LR D-cell properties at build time

Battery Property	Value	
(a) Battery		
Voltage (V)	3.723	
Weight (g)	120.4	
Volume ( $\text{cm}^3$ )	57.9	
Active area ( $\text{cm}^2$ )	122.0	
Jellyroll property		
(b) Jellyroll		
Weight (g)	13.89	
Diameter (mm)	30.94	
Volume ( $\text{cm}^3$ )	19.43	
Coating property	Positive	Negative
(c) Active layers		
Thickness <sup>a</sup> (w/collector), ( $\mu\text{m}$ )	1803.4	1295.4
Porosity (%)	83.5	0
Total length (cm)	19.8	15.49

<sup>a</sup> Overall thickness, since two-sided, thickness per active area is half.

where  $R_b$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) is the rate of film destruction,  $i_y$  ( $\text{A m}^{-2}$ ) the current density,  $k_{b0}$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) a rate constant, and  $k_{b1}$  ( $\text{m}^2 \text{mol}^{-1}$ ) is a constant. This equation accounts for the destruction of the LiCl layer by application of a current and the requirement that LiCl must be present in order to be destroyed.

Eqs. (4) and (6) constitute a kinetic model for LiCl film formation and destruction at the lithium electrode. This kinetic model was incorporated into the electrochemical model described in detail by Jain et al. [4]. The equations constituting the electrochemical model have been presented many times [2–5] and are summarized for reference here in Table 1. There is a slight difference between the electrochemical model here and that used by Jain et al. [4] in that Jain used a complex empirical expression to represent the temperature dependence of the salt diffusion coefficient while in this work a simple Arrhenius equation was used. The partial differential equations defining the electrochemical model were solved using a pentadiagonal band solver.

The code implementing the model was incorporated into Battery Design Studio<sup>®</sup> (see [www.batdesign.com](http://www.batdesign.com)) in order to provide a user-friendly interface as well as provide capabilities for regression to experimental data and visualization of results.

Table 3  
Discharge model parameters

Parameter	Values
Positive thickness (single side) ( $\mu\text{m}$ )	1220.59
$D_0$ , salt diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )	1.24e-02
$E_a$ , diffusion coefficient ( $\text{J mol}^{-1}$ )	-3008.73
$i_0$ , positive exchange current density ( $\text{mA cm}^{-2}$ )	2.19e+06
$E_a$ , positive activation energy ( $\text{J mol}^{-1}$ )	5611.32
$i_0$ , negative exchange current density ( $\text{mA cm}^{-2}$ )	2.65e+05
$E_a$ , negative activation energy ( $\text{J mol}^{-1}$ )	4434.75
Positive Bruggeman coefficient	2.26e-01
Morphology factor	5.63e-02

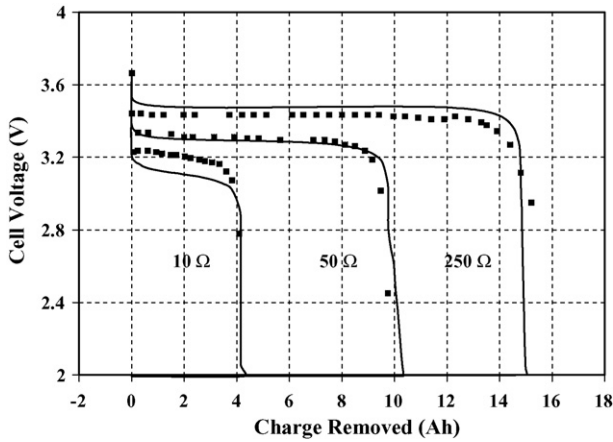


Fig. 1. Comparison of experimental [4] and simulated discharge curves at  $-18\text{ }^{\circ}\text{C}$  for loads 10, 50, and  $250\text{ }\Omega$ .

### 3. Results and discussion

Table 2 lists the properties of the low-rate (LR) D-size cell. To verify the implementation of the model used here, the results presented by Jain et al. [4] were reproduced. Then the parameters determining the discharge behavior were refitted to the experimental data reported by Jain et al. [4] using the model described above (that is, simple Arrhenius expression for salt diffusion and self-discharge kinetics). In this work, a smaller value of the active electrode area was used ( $122\text{ cm}^2$  versus  $180\text{ cm}^2$ ) because a careful analysis of the cell construction revealed that only a fraction of the cathode area in the D-cell was actually facing lithium foil. Use of the smaller value necessitated refitting the parameters listed in Table 3.

Table 3 summarizes the model parameters that best fit the experimental data. Note that the positive electrode thickness used to simulate discharge performance is significantly higher than the build value listed in Table 2. Although the electrochemical model does not account for the expansion of the cathode during discharge, the cathode is known to swell during dis-

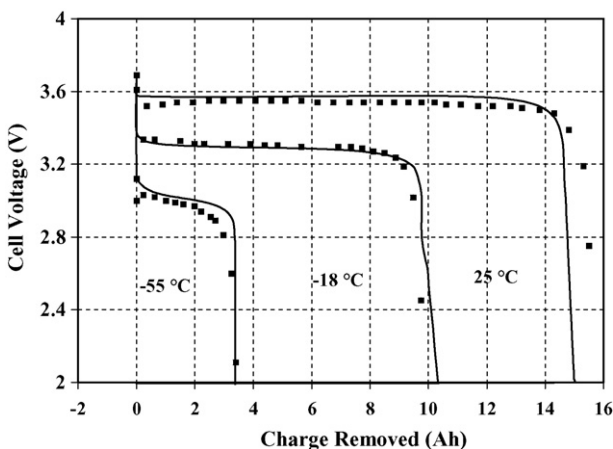


Fig. 2. Comparison of experimental [4] and simulated discharge curves for a  $50\text{ }\Omega$  load at  $-55$ ,  $-18$ , and  $25\text{ }^{\circ}\text{C}$ .

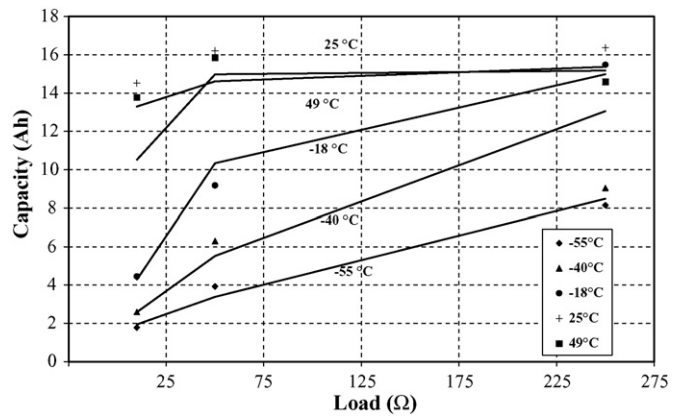


Fig. 3. Comparison of experimental [4] and simulated discharge capacity as a function of the load over a temperature range of  $-55$  to  $49\text{ }^{\circ}\text{C}$ .

Table 4

Comparison of simulated mid-discharge voltages to experimental

Discharge conditions		Mid V	Mid V	Difference (%)
Resistance ( $\Omega$ )	$T$ ( $^{\circ}\text{C}$ )	(simulation)	(experimental)	
50	25	3.57	3.54	0.99
50	$-18$	3.29	3.30	0.39
50	$-55$	3.01	2.97	1.10
10	$-18$	3.10	3.20	3.12
250	$-18$	3.47	3.43	1.26

Table 5

Comparison of simulated discharge capacities to experimental

Discharge simulation		Simulation	Experimental	Difference (%)
Resistance ( $\Omega$ )	$T$ ( $^{\circ}\text{C}$ )	(Ah)	(Ah)	
50	25	14.98	15.6	3.92
50	$-18$	10.33	9.97	3.69
50	$-55$	3.38	3.52	3.84
10	$-18$	4.27	4.44	3.63
250	$-18$	14.99	15.4	2.64

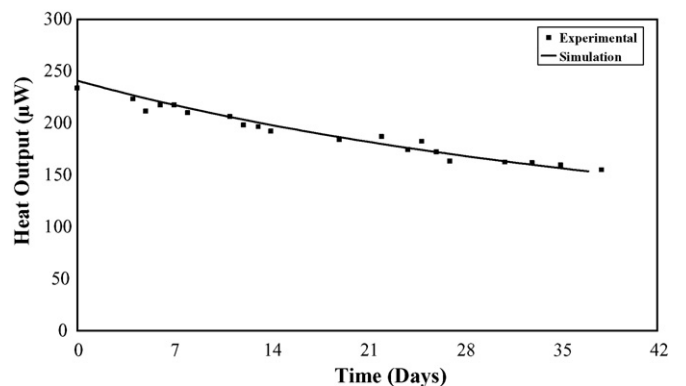


Fig. 4. Comparison of simulated and experimental results [9] for results for self-discharge heat output for LR D-cell under open circuit conditions.

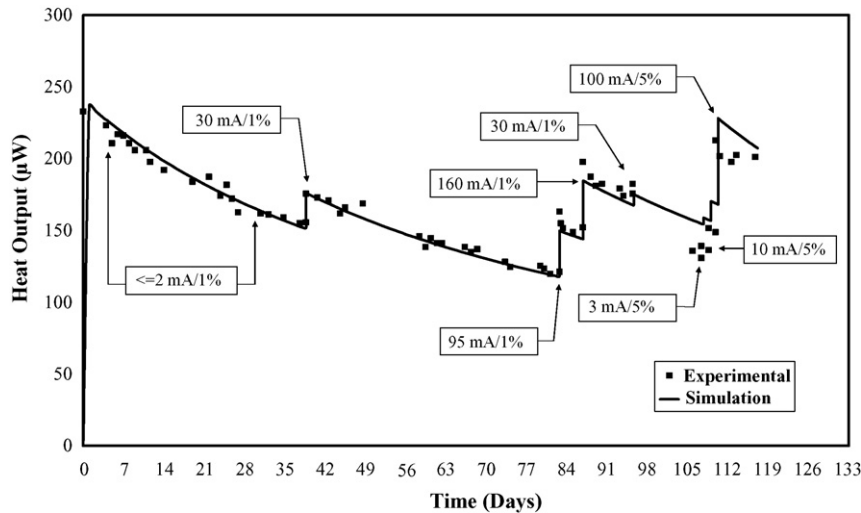


Fig. 5. Comparison of simulated and experimental results [9] for self-discharge heat output for LR D-cell after current pulses.

charge [2,3,11]. Unfortunately, no data on the degree of swelling seems to be available to validate use of the fitted value. However, swelling of the cathode is necessary since the cathode pore volume of the as-built cathode would limit cell capacity to 13.8 Ah (based on volume of solid LiCl formed) while experiments produce >15 Ah discharge capacity.

Figs. 1–3 compare simulation results to experimental data; Tables 4 and 5 give a quantitative comparison. The fit is comparable to that obtained by Jain et al. [4] and provides confidence that the model was correctly implemented. This model was then used to fit the calorimetric data of Roth [9].

For no-load, self-discharge conditions, parameters  $k_{b0}$  and  $k_{b1}$  are set to zero, and  $k_{f0}$  and  $k_{f1}$  are adjusted; Fig. 4 compares experimental and simulation results. For pulse-load conditions that involve a series of single and continuous pulses of 1-s duration, with duty cycles of 1%, 5%, and dc (100%),  $k_{b0}$  and  $k_{b1}$  are adjusted; Fig. 5 compares experimental and simulation results. Parameter values giving the best fit are listed in Table 6. The simulation model gives a very reasonable fit to the behavior. This model was used to predict the effect of long-term (10 year) use of the cell.

To assess the importance of lithium corrosion, an intermittent discharge was simulated where the rest period varied from 1 day to 30 days. A pulse current of 0.3 A of 5 s duration was applied and a rest current of 20  $\mu\text{A}$  was used. Fig. 6 shows the consumption of lithium (in ampere hour) versus discharge capacity over a 10 year period. For the three cases considered, pulses every 1, 5, or 30 days, the total amount of lithium consumed by

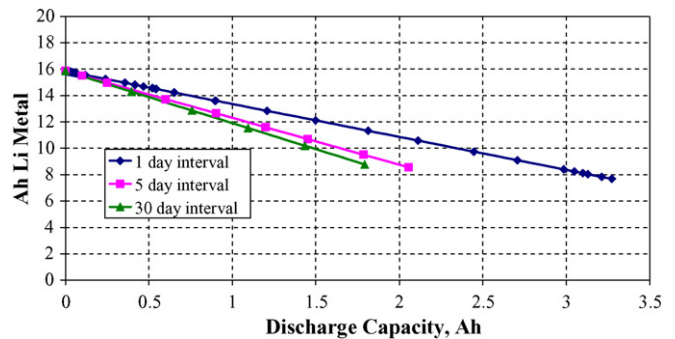


Fig. 6. Simulation 10 year intermittent discharge. Each line ends at 10 years.

both self-discharge and discharge after 10 years is approximately 8 Ah. So, there is no danger of depleting the lithium and thereby introducing a safety hazard. However, since the cathode-limited capacity is  $\sim 15$  Ah, the lithium might be depleted if, at the end of 10 years, the cell were completely discharged.

The simulation model presented here enables estimates of the discharge behavior of Li/SOCl<sub>2</sub> cells over a wide range of temperatures and discharge rates, as well as the self-discharge rate. This capability provides a rational basis for the design of battery-powered devices. However, the model is of limited use for design of batteries because it relies heavily on adjustable parameters (see Tables 3 and 6) to obtain good fidelity with experimental data.

Table 6  
Kinetic parameters for Li/SOCl<sub>2</sub> self-discharge (see Eqs. (3) and (5))

Parameter	Value
$k_{f0}$	5.21e-008
$k_{f1}$	2.8
$k_{b0}$	2.95
$k_{b1}$	3.6

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