Thermal efficiency of electrochemical systems
Thermal self-destruction of highly energy-intensive lithium power sources

Ye. V. Kuz'minskii and A. A. Andriiko
Scientific Engineering Centre 'Teknoelektrokhim' of the Ukrainian Academy of Sciences, 32-34 Prospect Palladium, Kiev 142 252680 (Ukraine)

Abstract

A theoretical analysis of the spontaneous self-destruction of chemical power sources (CPS) was carried out. A mathematical model of the process in the form of a nonlinear differential equation system was elaborated explaining the origin of the inner local heat source which can initiate the self-destruction process during storage.

Introduction

Highly energy-intensive chemical power sources (CPSs), such as lithium thionylchloride systems, are known to be subject to thermal destruction during storage [1]. Thermodynamic causes of this phenomenon have been analysed in refs. 1–3. In ref. 4, it has been shown that the self-destruction can be initiated by a local heat source. Some cases are known, however, in which the self-destruction proceeds without any external action, i.e., only due to internal causes. These causes are considered in the present work.

A model of chemical power source (CPS) self-discharge

It is assumed that CPS self-discharge during storage is not uniform in the whole cell, but proceeds at local regions, where the film of lithium has defects which provide access for an oxidizer. Such a region, together with a volume of electrolyte — limited within the pores of the separator, and in the corresponding regions of the cathode, anode and current collectors — can be represented as a local cell, connected in the circuit by its internal resistance in parallel to the main source (Fig. 1).

At the point of the electrolyte contact a chemical reaction proceeds with the rate:

$$V\left(\frac{dC}{dt}\right)_{chem} = -kS_dC \tag{1}$$

where C (mol/cm^3) is the concentration of the oxidizer in the defect region, V (cm^3) the volume of electrolyte in the pore, S_d (cm^2) the area of contact of the electrolyte with lithium in the defect region, and k (cm s^{-1}) the heterogeneous rate constant.
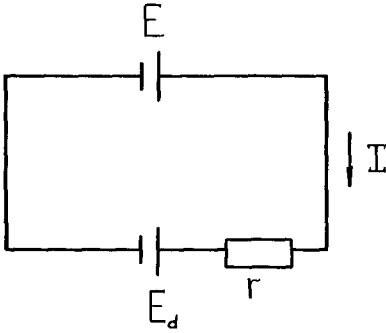
Fig. 1. A circuit with a local cell.

The rate constant is exponentially dependent on the temperature:

$$k = k_0 e^{-E_c/RT} \tag{2}$$

where E_c (~ 100 kJ/mol) is the activation energy of the chemical reaction. The case is possible, when the reaction rate depends on the diffusion of oxidizer. Then $k_0 = D_0/l_d$ is the diffusion constant, where D_0 and l_d are the coefficient and length of diffusion path, respectively. As to the activation energy, it is smaller by a factor of 3 to 4.

Due to this reaction, the local cell in the defect region becomes more discharged in comparison with the main one. A current, I, arises charging the defect region:

$$I = \frac{\Delta E}{r} = \Delta E \kappa_n S \tag{3}$$

where $\Delta E = E_c - E_d$; κ (Ω^{-1} cm^{-2}) is the conductivity, and S is the area of the defect section which approximates to the section of the separator pore.

E.m.f. decreases due to a decrease in the oxidizer concentration in the pore:

$$\Delta E = \frac{RT}{nF} \ln \frac{C_o}{C} \tag{4}$$

where C_o is the concentration of oxidizer in the initial charged cell.

The rate of charge of the defect region:

$$V\left(\frac{dC}{dt}\right)_{el} = \frac{I}{nF} = \Delta E \kappa S = \frac{RT\kappa S}{nF} \ln \frac{C_o}{C} \tag{5}$$

The sum of eqns. (1) and (5) is a differential eqn. of the oxidizer mass balance with two variables — concentration and temperature. The conductivity of the cell, κ, is also, in general, temperature-dependent, and this dependence should be similar to eqn. (2) if the migration of ions through the film at lithium determines the cell resistance.

The second differential eqn. presents the heat balance of the local cell:

$$W_H = -W_{HT} + W_\Pi + W_J + W_C \tag{6}$$

where W_H is the heat for heating the local region, W_Π the latent heat of reaction (the Peltier heat); W_J is the Joule heat, W_C is the chemical reaction heat, and W_{HT} is the heat transferred from the defect region.

The heat for heating the region:

$$W_H = VC_H\rho \frac{dT}{dt} \tag{7}$$

where C_H is the average heat capacity and ρ the cell density.

The heat transfer from the defect region is assumed, as usual, to be proportional to the difference in temperature:

$$W_{HT} = \alpha S_i(T - T_0) \tag{8}$$

where α is the effective coefficient of heat transfer, and S_i the area of heat transfer.

The latent heat of the reaction may be conveniently written as:

$$W_\Pi = T\Pi = \Delta E \kappa S \Pi \tag{9}$$

where,

$$\Pi = T\frac{\partial E}{\partial T} \tag{10}$$

is the Peltier coefficient (V), and $\partial E/\partial t$ the temperature coefficient of e.m.f. of the cell. We assume $\Pi > 0$, if the heat is evolved during charge, which corresponds to cells with $\partial E/\partial T > 0$; the Joule heat:

$$W_J = (\Delta E)^2 \kappa S \tag{11}$$

and the heat of the chemical reaction in the form:

$$W_C = \Delta HV \left(\frac{dC}{dt}\right)_{chem} \tag{12}$$

Substituting eqns. (7)–(12) into eqn. (6) and introducing dimensionless variables — concentration (the degree of charge):

$$\xi = \frac{C}{C_o} \tag{13}$$

and temperature:

$$\Theta = \frac{T - T_0}{T} \approx \frac{T - T_0}{T_0} \tag{14}$$

we obtain the final model of CPS self-discharge through the defects in the form of a set of nonlinear differential equations:

$$\begin{cases} \tau_\xi \dot{\xi} = -\xi e^{\epsilon\theta} - e^{\epsilon\theta}k \ln \xi = P(\xi, \theta) \\ \tau_\theta \dot{\theta} = -\theta - (p - d \ln \xi)e^{\epsilon\theta} \ln \xi + H\xi e^{\epsilon\theta} = Q(\xi, \theta) \end{cases} \tag{15}$$

where,

$$\tau_\xi = \frac{V}{k_0 S_d} \tag{16}$$

and,

$$\tau_\theta = \frac{VC_H\rho}{\alpha S_i} \tag{17}$$

are constants with the dimensions of time;

$$\epsilon = \frac{E_c}{RT_0} \text{ and } \epsilon_r = \frac{E_r}{RT_0} \tag{18}$$

are the dimensionless activation energies of chemical reaction and conductivities (or internal resistance) of the cell, respectively:

$$K = \frac{RT_0 S \kappa_0}{n^2 F^2 S_d C_o k_0} \tag{19}$$

$$p = \frac{RS\Pi\kappa_0}{\alpha S_i n F} \tag{20}$$

$$d = \frac{R^2 T_0 S \kappa}{n^2 F^2 \alpha S_i} \tag{21}$$

$$H = \frac{\Delta H k_0 C_o S_d}{\alpha S_t T_0} \tag{22}$$

are the dimensionless parameters, depending on the system properties.

Conditions of CPS stability during storage

Estimation of possible variation limits of the parameters from eqn. (15) using data on the properties of the Li/SO$_2$Cl$_2$ system cells available in the literature [3, 5, 6, 7–15], gives the following orders of magnitudes: $\tau_\xi \sim 10^2$–10^5 s; $\tau_\theta \sim 0.01$–1 s; $k \sim 0.1$–100; $p \sim d \sim 10^{-2}$–10^{-5}; $H \sim 10^{-2}$–10^{-4}. Hence, $\tau_\xi \gg \tau_\theta$, i.e., the time constant for variation of oxidizer concentration is much less than that for temperature variation. This allows the concentration to be considered as a 'slow' variable, and each of eqns. (15) can be analysed separately. Thus, analysing the equation of heat balance we can consider ξ_r to be constant at any moment of time, whereas the heat exchange proceed under almost stationary conditions.

$$Q(\xi_r, \theta) = -\theta - (p - d \ln \xi_r) e^{\epsilon_r \theta} \ln \xi_r + H \xi e^{\epsilon \theta} = 0 \tag{23}$$

In this case, the analysis of the thermal stability of the local cell is similar to that used in the theory of heat explosion [5, 15–18], Fig. 2. The stationary condition at any moment of time, according to eqn. (23), follows from the condition of equality of the rate of heat transfer, presented in Fig. 2 by the line $W_1 = \theta$, and heat evolution W_2 which, in the model accepted, is equal to the sum of the two last terms from eqn. (23). In the general case, the system has three stationary states, of which only two are considered within the model accepted (due to the simplification in determining the dimensionless temperature, eqn. (14), the third — high-temperature stationary state disappears). The 'low-temperature' equilibrium state 1 (Fig. 2) is a stationary one, and, if it exists, the local 'defect' cell will be stable for unlimitedly long period of time, provided that the degree of charge remains constant. In the model accepted, the presence of such stable local cells is the cause of the usual low self-discharge of a CPS during storage.

Combinations of parameters are possible, however, at which, during storage, curve W_2 will gradually shift upwards. The stationary states 1 and 2 will converge and, at some critical value of ξ_r will disappear. This bifurcation will lead to the development
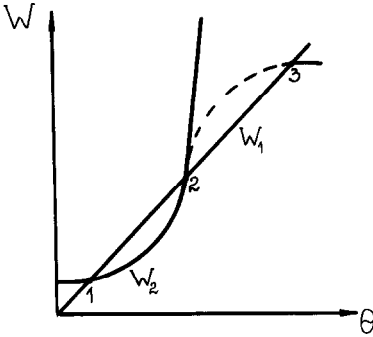
Fig. 2. Graphical representation of the critical situation under uncontrolled self-acceleration of an exothermal reaction.

of local heat source and to catastrophic destruction of the cell. The condition of this is:

$$Q(\xi_r, \theta_k) > 0 \tag{24}$$

where θ_k is determined from the equation:

$$\left. \frac{\partial Q}{\partial \theta} \right|_{\theta = \theta_k} = 0 \tag{25}$$

The appearance of nonstability has been analysed for two limiting cases of eqn. (15):

(i) the internal resistance of the cell decreases with increasing temperature in accordance with the same regularity as an increase in the rate of chemical interaction, i.e. $\epsilon = \epsilon_r$, and

(ii) the internal resistance of the cell is temperature-independent, $\epsilon_r = 0$. From eqns. (24) and (25) functions are found, whose sign determines the cell stability for these two limiting cases:

$$F_1 = e\epsilon[H\xi - (p - d \ln \xi) \ln \xi] - 1 \tag{26}$$

$$F_2 = \ln e\epsilon H\xi - \epsilon(p - d \ln \xi) \ln \xi \tag{27}$$

At $F < 0$ the local defect is stable, whereas at $F < 0$ unstable.

It is obvious that in a 'fresh' charged cell ($\xi = 1$) the defect should be stable, because otherwise it fails immediately after its production. This is possible under the following condition:

$$e\epsilon H < 1 \tag{28}$$

But even if eqn. (28) is satisfied, this does not guarantee stability of the cell during a long storage.

The combination of parameters, at which the defect is stable (at some unchanged stationary ξ_C value) are determined from the inequality $F(\xi_C) < 0$, where the value of ξ_C is determined from the set of equations $p(\xi_C, \theta_k) = 0$ (see eqns. (15) and (25)). For case (i), this inequality cannot be written in the explicit form, because ξ_C should be found numerically from the transient equation $\xi_C + k \ln \xi_C = 0$. For case (ii) it has the form:

$$kH \ln \epsilon H + 1 - \frac{1}{\epsilon} + p + \frac{d}{\epsilon kH} < 0 \tag{29}$$

As analysis shows, the two parameters K and H exert the greatest effect on the local cell stability. This can be represented by a rough diagram (Fig. 3), where the line represents the lefthand side of eqn. (29), when the last three terms are much less than 1 and, therefore, can be neglected. The form of the curve (Fig. 3) as well as the position and height of maximum depend, to a certain extent, on the value of p and d which display the contribution of the latent heat of reaction and the Joule heat, but the qualitative form of the diagram remains unchanged. The region of stationary stability is limited by the curve and the x-axis, whereas the shaded part of this region corresponds to an absolutely stable defect, where the condition of initial stability eqn. (28) holds true. With all other combinations of parameters the defect is unstable and, with time, can become a local heat source, capable of initiating thermal destruction of the cell as has been described in refs. 4 and 5. A possible development of the process is presented by Fig. 4, where numerical solutions of a set of differential eqn. (15) are given at a combination of parameters which does not fall in the stability
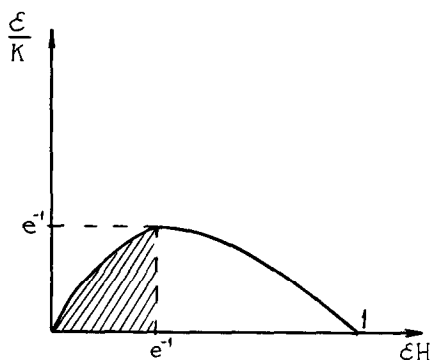

Fig. 3. A diagram of mutual influence of K and H on the stability of the local cell.
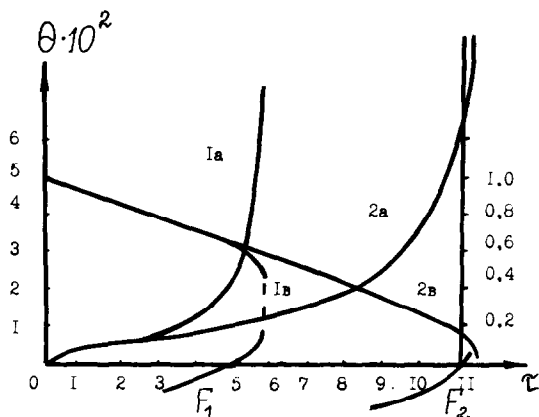

Fig. 4. Variation of local temperature (curve a) and the degree of charge (curve b) of the defect in the approximation of exponential decrease in the internal resistance with temperature (curves 1) and without dependence on temperature (curves 2) as well as variation of stability eqns. (26) and (27) in the critical region. The values of parameters: $\epsilon = 40$; $H = 0.003$; $D = 0.02$; $K = 0.4$; the ratio of time constants $\tau_\xi/\tau_\theta = 100$; dimensionless time $\tau = t/\sqrt{\tau_\xi\tau_\theta}$.

region (Fig. 3). Calculations are presented for two limiting cases, corresponding to stability eqns. (26) and (27).

In both cases, the system behaviour has pronounced 'catastrophic' character. After a fairly long induction period (the unit of dimensionless time in Fig. 4 corresponds to hours or tens of hours of real time) an abrupt increase in the temperature of the local cell proceeds. The 'catastrophe' occurs firstly for case (i), when the internal resistance decreases rapidly with increasing temperature.

The theoretical study carried out allows some practical conclusions to be drawn. Firstly, to produce a stable source the condition of initial stability of eqn. (28) must be achieved. Consequently, the parameter, determined from eqn. (22), should be as small as possible. All parameters in eqn. (22), except for S_d, are rigidly prescribed either by physicochemical properties of the system or by standards for production and operation conditions. As to the area of the defect, where the contact of the oxidizer with lithium occurs (S_d), it depends, in the first place, on the presence of impurities in lithium, including mechanical ones. Therefore, the more pure the anode material is, the lesser is the probability of formation of the local source. Secondly, if the condition of eqn. (28) is satisfied, then, to get in the stationary stability region, Fig. 3, the K constant, determined from eqn. (19) should be as large as possible. An increase in purity and the absence of mechanical impurities in lithium (a decrease in S_d) also promote this. Besides, the conductivity of local elements, determined as the product of κ and the area of the separator pore section, should be maximum. The probability of formation of the local heat source greatly increases if the distribution of pore sizes in the material of the separator is highly nonuniform and the local defect of the film at lithium falls in an anomalously narrow pore (small S). This probability also highly increases in the case of nonuniform electrolyte and the defect falls in a pore, where the concentration of the ionic compound is decreased (small κ).

Thus, the appearance of local heat sources, capable of initiating CPS destruction during storage, is less probable, the smaller the content of impurities (including mechanical ones) in lithium, the more uniform the pore sizes in the separator material and the more uniform the distribution of concentration of ionic compound (fluoroborate, lithium preparation, etc.) in the bulk separator.

References

1 T. R. Crompton, *Small Batteries*, Vol. 2, *Primary Cells*, MacMillan, London, 1982, p. 328.
2 N. A. Godshall and J. R. Driscoll, *J. Electrochem. Soc.*, *131* (1984) 2221–2226.
3 N. A. Godshall and J. R. Driscoll, *Proc. Symp. Lithium Batteries, Washington, DC, USA, Oct. 9–14, 1983*, The Electrochemical Society, Pennington, NJ, 1984, pp. 171–183.
4 L. A. Parnell and S. Szpak, *Electrochim. Acta*, *30* (1985) 913–922.
5 S. Szpak, C. J. Gabriel and J. R. Driscoll, *Electrochim. Acta*, *32* (1987) 239–246.
6 C. A. Vincent, B. Scrosati, M. Lazzari and F. Bonino, *Modern Batteries*, Edward Arnold, London, 1984, p. 264.
7 J. I. Cho, *J. Electrochem. Soc.*, *134* (1987) 771–779.
8 T. Iwamaru and J. Vetani, *J. Power Sources*, *20* (1987) 47–52.
9 N. Marincic and J. Epstein, *Prog. Batteries Solar Cells*, *4* (1982) 37–39.
10 J. R. Driscoll, R. Pollard, J. J. Smith and S. Szpak, *Proc. 20th Intersoc. Energy Convers. Eng. Conf., 1985, Energy 21st Century*, Vol. 2, Warrendale, PA, USA, 1985, pp. 55–62.
11 K. M. Abraham and L. Pitts, *J. Electrochem. Soc.*, *132* (1985) 2301–2308.
12 J. J. Ciesta, *J. Power Sources*, *18* (1986) 101–107.
13 S. Subbarao, F. Deligiannis, D. H. Shen and S. Dawson, *J. Electrochem. Soc.*, *134* (1987) 404.

14 J. Ocamara and M. Midzutani, *Tech. Rept. GS News, 46* (1987) 26–30.

15 N. N. Semenov, *Zh. Russk. Fiz.-Khim, O-va, 60* (1928) 241–250.

16 N. N. Semenov, *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaksionnoi Sposobnosti* (About some problems of chemical kinetics and reaction ability), Akademiya Nauka SSSR, Moscow, 1958, p. 486.

17 D. A. Frank-Kamenetskii, *Diffuziya i Teploperedacha v Khimiches-koi Kinetike* (Diffusion and heat transfer in chemical kinetics), Nauka, Moscow, 1967, p. 491.

18 N. N. Semenov, *Tsepnye Reaktsii* (Chain reactions), Nauka, Moscow, 1986, p. 535.