On charge conditions for Li-ion and other secondary lithium batteries with solid intercalation electrodes

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Abstract

The simple model of continuous non-porous electrode was found to provide a reasonable theoretical description for the electrochemical process of lithium insertion into a convenient solid electrode, consisting of active material, fine carbon and binder, of the rechargeable lithium batteries with common liquid organic electrolytes. The model uses only one experimental fit parameter–effective diffusion coefficient of inserted Li that can easily be obtained from galvanostatic charge–discharge data. Approximate simple equations were derived to calculate the charge conditions for secondary lithium batteries. It was shown that charging with linearly descending current results in more than 2.5-fold reduction of charging time as compared to the constant current charging at the same charge depth. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In view of the growing market of Li-ion and other rechargeable lithium batteries [1], the problem of its efficient charging becomes of significant importance for researchers and developers and users of such power sources.

Eventually, this problem roots in correct formulation and description of the mechanism of the reversible electrochemical intercalation of lithium into solid electroactive materials used as the cathodes as well as the anodes in Li-ion batteries. Following features for the reliable model of the process are envisaged: (1) as simple as possible mathematics, allowing for formulation of practical equations for the calculations of charge efficiency factors (depth of charge, time) from the conditions applied (current, electrode thickness etc.); (2) minimal number of the model parameters that should be determined from independent experimental measurements and that are never known precisely (pore dimensions and distribution, electric conductivities, diffusion coefficients, and so on); and, of course, (3) adequacy, that is, reasonable consistency with the main traits of the real process.

Most if not all of the researches on the theory of electrochemical lithium insertion into the solid electrode used the models of porous electrode that were reviewed in many details back in 1960s [2]. The papers of West et al. [3] and Atlung et al. [4] seemed to pioneer these studies having considered the coupled charge transport across the interpenetrating phases of the active material and electrolyte. Later on, this model was persistently refined by including electrochemical kinetics [5,6], transport across a separator [7], theory of non-ideal concentrated solutions [8], thermal effects [9,10], pore sizes and distribution [11].

In spite of a number of simplifications usually adopted, these models still remain too complicated for practical engineering usage. The results of the modelling commonly permit for only the computer simulations employing a set of poorly determined physico-chemical parameters. Thus, an essential practical value of these calculations is doubtful for practical purposes.

Meanwhile, another possible way of a simplified analysis was pointed to by the early work of Atlung et al. [4]. It was found that, at certain conditions, the operation of the porous electrode could be represented in terms of the model of a compact solid electrode with some effective diffusion coefficient of lithium in the bulk. Recently, it was shown that such simple model accounts well for the

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operation of solid rechargeable electrode consisted commonly of electroactive substance, binder and conductive admixture [12]. The present paper considers the potentialities of this model in more details. The main purposes of the analysis presented were to derive the practical formulas for the calculations of the charge conditions. The equations obtained were checked experimentally, with 2325 button type cells based on rechargeable manganese oxide [13] as the positive electrode material.

2. Experimental

In order to verify the theoretical equations below, the experimental button cells of 2325 size were manufactured.

The cathodes of the cells were prepared from the rechargeable Li_2O–MnO_2 oxides [13] in the following way. The paste contained 25 mass% of graphite powder, 25 mass% of acetylene black and 50 mass% of Teflon binder was rolled into 0.5 mm thick ribbon that was then dried at 150°C for 2 h. Round tablets of 3.2 cm^2 area were cut from this band, and 50 mg of active mass contained 85% oxide, 5% graphite powder, 5% acetylene black and 5% of the binder were evenly distributed on the surface of each tablet.

After that, the tablets were pressed, dried for 2 h at 200°C and then pressed into the cases of the standard 2325 button cells. The active layer thickness thus obtained was $3.8 * 10^{-3}$ cm with accuracy limits being $\pm 10\%$.

The negative electrode was prepared from Li–Al alloy; 1 M solution of $LiClO_4$ in propylene carbonate (70 vol.%)–dimetoxyethane (30 vol.%) was used as the electrolyte.

Charge–discharge experiments were performed with potentiostat PI-50-1, the temperature was maintained at $25 \pm 0.2°C$ with thermostat.

3. Model formulation

Similar to the notation of Ref. [14] for lithium electrochemical insertion from the anode into a polymer matrix, the charge–discharge process is represented as filling or emptying the 'vacancies', that is, the sites in the bulk that can be occupied by Li:

$$Li^+ + e + V \rightarrow (Li)_v, \tag{1}$$

The process (1) may occur either at outer, electrode/electrolyte interface in case of large electronic and small ionic conductivity, or at inner, electrode/current collector, plane in the opposite case. Presumably, the first case holds true in real systems where the addition of fine carbon particles ensures the electronic conductivity. Thus, here we assume the electrochemical process (1) to occur at the plane

separator/electrode, the electrons being supplied by conductive matrix formed with carbon additives.

The model accounts for the process (1) governed by diffusion of Li in the layer of a thickness l. Then, the concentration of lithium (or free vacancies) varies in time and space in accordance with 2nd Fick's law in the form of the differential equation:

$$\frac{\partial C}{\partial X} = D \cdot \frac{\partial^2 C}{\partial X^2}, \tag{2}$$

with initial condition

$$t = 0; \quad C = C_0. \tag{3}$$

The boundary condition at the plane $x = 0$ (electrode/electrolyte) is

$$D \cdot \left.\frac{\partial C}{\partial X}\right|_{x=0} = \frac{i(t)}{F}, \tag{4}$$

where $i(t)$ is the current density that can vary with time in a general case and F is the Faraday constant.

The employment of the differential Eq. (2) with the conditions (3) and (4) assumes that the diffusion coefficient is independent of lithium insertion degree, and that ionic conductivity is much less than the electronic one.

The second boundary condition, at the plane $x = l$:

$$D \cdot \left.\frac{\partial C}{\partial X}\right|_{x=l} = 0, \tag{5}$$

takes into account the absence of Li flux across the electrolyte/current collector boundary.

Eq. (2) with the conditions (3–5) represents the simplest mathematical model of the lithium insertion (and deinsertion) process into a solid electrode, with only one fit parameter, effective diffusion coefficient D.

4. Results and discussion

The analysis of the model (2–5) has been performed for constant current charge condition

$$i = i_0 = \text{const} \tag{6}$$

and for the current diminishing by linear law

$$i = i_i - kt. \tag{7}$$

The solution of Eqs. (2)–(5) should be represented in the form of the dependency of the achieved capacity on the current density:

$$Q_\tau = \int_0^\tau i(t)\,dt = f(i) \tag{8}$$

where τ is the time when the process is finished. We determine it as the time when zero concentration of free

vacancies (discharge) or $(Li)_v$ (charge) is achieved at the plane $x = 0$:

$$C(\tau)|_{x=0} = 0 \qquad (9)$$

It was obtained for two limiting cases (see Appendix A). (I) Thick layers, large currents,

$$\frac{D \cdot t}{l^2} \ll 1 \qquad (10)$$

This case corresponds to a 'semi-infinite' behaviour when $l \rightarrow \infty$, and the system does not 'feel' the restriction imposed by the condition (5). In particular, when $k = 0$ (galvanostatic conditions), we obtain the familiar Sand's equation for transition time in chronopotentiometry:

$$i \cdot \sqrt{\tau} = \frac{1}{2} \cdot \sqrt{\pi \cdot D} \cdot F \cdot C_0. \qquad (11)$$

(II) Thin layers, small currents, large times:

$$\frac{D \cdot \tau}{l^2} \gg 1 \qquad (12)$$

The solution in dimensionless variables are given by Eq. (22a) (constant current) and Eq. (21a) (linearly lowering current).

The achieved capacity vs. constant current density takes the form

$$i_0 \cdot \tau_0 = Q_m - (l^2 l3 \cdot D) \cdot i, \qquad (13)$$

where Q_m is the maximal (theoretical) capacity per unit volume of the material determined by the number of active sites in the bulk [12].

Fig. 1 shows the experimental data for the button cell of 2325 size representing the galvanostatic discharge capacity at different discharge current values (the charge current was equal to 0.7 mA for every test, the final times were determined from inflection points as in Ref. [12]). One can see that the larger part of this plot is linear in accordance with Eq. (13). The diffusion coefficient calculated from the

slope of this line, for the particular oxide of $Li_{0.25}Mn_2O_{4+\delta}$ composition being equal to $6.7 * 10^{-9} \ cm^2/s$, is in good agreement with the values reported for rechargeable oxides of Ni, Co, and Mn [14–16].

The results above show the capability of this simple model to analyze the operation of the porous rechargeable solid cathodes prepared from active substance (lithiated Mn oxide [13]), conductive carbon additive and binder by convenient technology in a secondary lithium battery with liquid organic electrolyte. It would be reasonable to suggest that this approach should be valid to some extent for any real solid porous electrodes of lithium batteries containing conductive carbon additives and binder. The following considerations maintain this opinion.

(i) The recently developed packed theory for the mixture of two different size particles [11,17], like grains of active material and carbon in the electrodes, predicts the porosity of such systems to be 0.2–0.35 with minimum at 0.75–0.8 volume fraction of large component. That is enough to form continuous pore system for the access of the liquid electrolyte. Such conclusion is confirmed by direct measurements with mercury porosimeter. For example, the porosity of $-MnO_2$-based electrode (80%) with carbon and binder was found to be 20% [18]. The porosity of our electrode estimated from the apparent density of pressed tablet is about 22–25%. Thus, the investigated system can be thought of as a typical porous one with interpenetrating continuum of pores filled with liquid electrolyte.

(ii) The above value of diffusion coefficient is in good agreement with the data reported for rechargeable oxide of Ni, Co and Mn in similar electrodes with carbon and binder [14–16]. However, thin film cathodes of $LiCoO_2$ and $LiMn_2O_4$ produced with pulsed laser deposition show significantly lower values, $1 * 10^{-10}$ and $2.5 * 10^{-11} \ cm^2/s$ accordingly [19]. Since these films are much closer in structure to the bulk oxides, one may conclude that the transport in the electrodes is assisted by the electrolyte in pores resulting in the increased value of the apparent diffusion coefficient, the simple description based on the compact electrode theory remaining valid.

The only fit parameter of the model considered, effective diffusion coefficient, can easily be obtained from charge–discharge constant current experiments. Provided this parameter is known, one can predict the capacity (or the depth of charge) from the charge current density and electrode thickness. On the other hand, prescribing the desired charge efficiency (charge depth) η, one can calculate the charge current and time required. These useful relationships are given below:
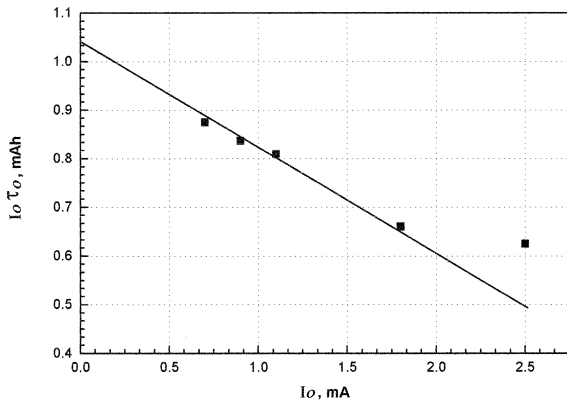

Fig. 1. Dependence of discharge capacity on current value for the galvanostatic charge–discharge of the experimental button-type cell with the rechargeable Li_2O–MnO_2 cathode material [13]. The charge current was kept constant and equal to 0.7 mA for every cycle.

$$i_c = (3D/l)Q_m(1 - \eta), \qquad (14)$$

$$\tau_c = \frac{\eta l Q_m}{i_c} = \frac{l^2}{3D} \cdot \frac{\eta}{1 - \eta}, \qquad (15)$$

Table 1
Charging of 2325 size button-type cells with linearly programmed current: charge conditions, experimental data, results of approximate (Eq. (17)) and numerical calculations

#	Current I, mA (time is given in hours)	I_i/I_0	Charge depth, η			Factor of time reduction, τ_0/τ_i		
			Experimental	Anticip.	Numerical calculations	Experimental	Eq. (17)	Numerical calculations
1	0.7	1.000	0.875	0.875	0.875	1	1	1
2	1.06–0.36t	1.514	0.832	0.875	0.863	1.452	1.257	1.309
3	1.33–0.72t	1.900	0.842	0.875	0.849	1.541	1.450	1.580
4	1.93–1.80t	2.757	0.848	0.875	0.787	2.446	1.879	2.415
5	2.63–3.60t	3.757	0.692	0.875	0.660	3.634	2.379	4.176

where the maximal capacity Q_m (mAh/cm^3) should be determined by the extrapolation of the linear dependencies similar to that in Fig. 1, to zero current.

As follows from Eqs. (14) and (15), unlike the primary cells, a thin-film design is preferable for the rechargeable electrodes of secondary lithium batteries. Otherwise, the charge time would exceed reasonable limits at sufficiently deep charges. For example, if the desired efficiency for 0.5 mm thick rechargeable cathode with theoretical capacity ~ 400 mA h/cm^3 is $\eta = 0.8$, we obtain charge current $i_c = 0.032$ mA/cm^2 and time $\tau_c = 138$ h at the above mentioned value of the diffusion coefficient. Reducing the electrode thickness to, e.g., 0.1 mm, we could increase the charge current to $i_c = 0.17$ mA/cm^2 and decrease the time to a reasonable value of $\tau_c = 5.5$ h.

The efficiency of charge process could be improved considerably by applying the charge conditions other then constant current ones. Several methods of charging with varying current are known for practical secondary batteries [1] (Chap. 24.7)—constant current, multiple decreasing current steps, modified constant current, constant potential, modified constant potential with constant initial current and some others. All of them are based on the principle of current decrease to the end of discharge. The analysis is
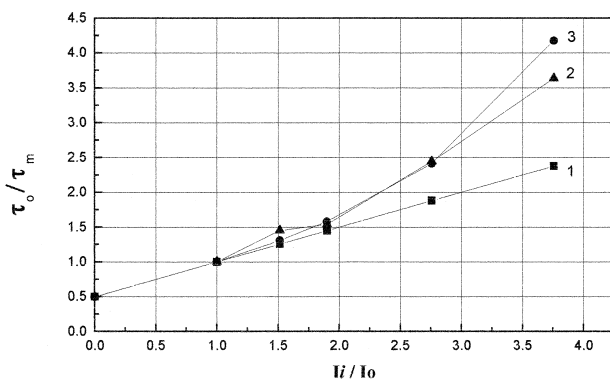

Fig. 2. Reduction of the charge time when applying the programmed charge current instead of constant current: 1—approximate formula (17); 2—experiment; 3—numerical calculations. The depth of charge was preset at $\eta = 0.875$; the experimentally obtained values are given in the Table 1. The parameters of the current program (column 2 of the Table 1) were determined from Eq. (16).

given below for charge current continuously decreasing with linear law.

Eqs. (25a) and (26a) show that, if a specified depth of charge is η (that would be attained galvanostatically at the charge current i_0 and time τ_0 given by Eqs. (14) and (15)), and if the coefficient k in Eq. (7) satisfies the relationship

$$k = \frac{i_i^2 - i_0^2}{2Q_m l \eta}, \tag{16}$$

then the charge time τ_m should be at minimum determined by the equation

$$\frac{\tau_0}{\tau_m} = \frac{1}{2} \cdot \left(\frac{i_i}{i_0} + 1 \right), \tag{17}$$

where i_i is the initial current of Eq. (7).

Once Eqs. (16) and (17) are valid, one may expect significant reduction of the charge time (at the same charge depth) applying linearly lowering charge current instead of constant current.

To check this assumption, a series of experiments on charge–discharge of the experimental button cells with linearly programmed charge current was performed. The time coefficients were calculated by formula (16). Table 1 gives the conditions and the results of these experiments, along with the data of more precise numerical computer calculations directly from basic equation system (2–5).

Fig. 2 plots the time reduction factor against the initial current in terms of Eq. (17), the time coefficient k being determined from Eq. (16). These data shows that the experimental reductions of charge time are even larger then prescribed by approximate formula (17) and correspond with good precision to the results of numerical calculations. The charge depths obtained were kept practically constant and, only after 2.5-fold reduction, some decrease occurred.

5. Conclusions

In spite of its relative simplicity, the model of electrochemical lithium intercalation into a compact continuous

solid is in good consistency with the behaviour of a real porous solid electrodes with rechargeable Li_2O–MnO_2 prepared by common technology (electroactive material + conductive admixture + binder) in rechargeable lithium batteries with liquid organic electrolytes.

The model uses only one empirical parameter, effective diffusion coefficient of lithium, that can easily be determined from constant current charge–discharge data in form of the dependency of achieved capacity on charge or discharge current value.

The model allows deriving practically useful approximate formulas for the calculation of optimal charge condition for secondary lithium batteries. Such formulas have been obtained for constant current charge conditions as well as for charging with programmed linearly diminishing current. As follows from the theory and validations by the experiments, the latter charge conditions make possible to reduce the charge time at least by a factor 2.5 at the same charge depths in comparison with constant current charging.

Appendix A

It is convenient to rewrite Eqs. (2)–(5) in the dimensionless form:

$$\frac{\partial Y}{\partial T} = \frac{\partial^2 Y}{\partial X^2};\tag{1a}$$

$$T = 0; \qquad Y = 1;\tag{2a}$$

$$\left.\frac{\partial Y}{\partial X}\right|_{x=0} = J(T);\tag{3a}$$

$$\left.\frac{\partial Y}{\partial X}\right|_{x=l} = 0.\tag{4a}$$

The dimensionless variables X, Y, T and parameter J (dimensionless current) are defined here as:

$$X = \frac{x}{l};\tag{5a}$$

$$Y = \frac{C}{C_0};\tag{6a}$$

$$T = \frac{D \cdot t}{l^2}\tag{7a}$$

and

$$J = \frac{i \cdot l^2}{F \cdot D \cdot C_0}\tag{8a}$$

We shall consider the solutions of the equation under the conditions of the current varying with linear law and, as a particular case, under the constant current conditions. Eq. (7) for the current can then be rewritten in the dimensionless form:

$$J = J_i - \alpha T\tag{9a}$$

where

$$\alpha = kl^3 / FD^2 C_0\tag{10a}$$

is the dimensionless parameter.

After Laplace's transform, we obtain the ordinary differential equation

$$\frac{d^2 F(S, X)}{dX^2} = S \cdot F(S, X) - 1\tag{11a}$$

with transformed boundary conditions

$$\left.\frac{dF}{dX}\right|_{x=0} = \frac{J}{S} - \frac{\alpha}{S^2},\tag{12a}$$

and

$$\left.\frac{dF}{dX}\right|_{x=1} = 0.\tag{13a}$$

We are interested in the solution at $x = 0$. It is as follows:

$$F_0 = \frac{1}{S} - \frac{J - \alpha/S}{S\sqrt{S}}\,\text{cth}\,\sqrt{S},\tag{14a}$$

where

$$\text{cth}\,\sqrt{S} = \frac{e^{\sqrt{S}} + e^{-\sqrt{S}}}{e^{\sqrt{S}} - e^{-\sqrt{S}}}\tag{15a}$$

is a hyperbolic cotangent.

The exact reverse transform of Eq. (14a) has a form of an infinite series that is rather cumbersome for practical purposes. Therefore, we shall derive approximate solutions for the two limit cases denoted in the main text above.

(a) Under condition (10), the approximation $\text{cth}\sqrt{S} \cong 1$ should be approximately correct. Then

$$F_0 = \frac{1}{S} - \frac{J}{S \cdot \sqrt{S}} + \frac{\alpha}{S^2\sqrt{S}}.\tag{16a}$$

The reverse transform of Eq. (16a) results in the dependencies similar to those obtained in the theory of chronopotentiometric electrochemical method. In particular, if $\alpha = 0$ (galvanostatic conditions), we obtain

$$Y_0 = 1 - \frac{2}{\sqrt{\pi}} \cdot J \cdot \sqrt{T}.\tag{17a}$$

The surface layer becomes depleted of vacancies or lithium and the electrochemical process is completed at the time $T = \tau$ when $Y_0 = 0$. Then, for galvanostatic conditions, Eq. (17a) gives the relation

$$J \cdot \sqrt{\tau} = \frac{1}{2} \cdot \sqrt{\pi} \qquad (18a)$$

corresponding to the dimensionless form of Sand equation (11). This case, when the electrode system behaves as a semi-infinite, is not very important for the operation of a real battery electrode.

(b) In case of small S (or large T), where condition (12) is valid, we can apply the approximate formula for hyperbolic cotangents:

$$\text{cth } z \approx \frac{1}{Z} + \frac{Z}{3}. \qquad (19a)$$

Then

$$F_0 = \frac{1}{S}(1 - J/3) - \frac{1}{S^2}(\alpha/3 - J) - \frac{\alpha}{S^3}, \qquad (20a)$$

and the reverse transform is

$$Y_0 = 1 - \frac{J}{3} + (\alpha/3 - J)T + \frac{\alpha T^2}{2}. \qquad (21a)$$

For galvanostatic conditions ($\alpha = 0$):

$$Y_0 = 1 - \frac{J}{3} - J \cdot T, \qquad (22a)$$

and final time ($Y_0 = 0$) is determined by the equation

$$\eta = J\tau = 1 - J/3. \qquad (23a)$$

In the general case of linearly varying current, the charge–discharge parameters (J_0, α), and charge time are bound by Eq. (21a) at $Y_0 = 0$, and by definition,

$$\eta = \int_0^\tau J(T)\,\mathrm{d}T = J_0\tau - \frac{1}{2}\alpha\tau^2. \qquad (24a)$$

These equations can be transformed into a more compact relation between the galvanostatic and the programmed current charge parameters

$$\frac{\tau_0}{\tau_\mathrm{m}} = \frac{1}{2} \cdot \left(\frac{J_i}{J_0} + 1 \right), \qquad (25a)$$

that is valid if the value of α coefficient in Eq. (9a) meets the condition

$$\alpha = \frac{J_i^2 - J_0^2}{2(1 - J_0/3)}, \qquad (26a)$$

Going over the natural variables (Eqs. (5a), (6a), (7a), (8a) and (10a)), we obtain the main formulas (13), (16) and (17) from the dimensionless Eqs. (23a), (25a) and (26a).

A.1. List of symbols

C	concentration, mol/cm^3
D	diffusion coefficient, cm^2/s
e	electron
F	Faraday's constant, C/mol; function of complex variable (Laplace transform)
f	sign of a function
i	current density, A/cm^2
J	dimensionless current
k	rate of change of charge current, A/cm^2 s
l	thickness of the electrode, cm
Q	capacity, C/cm^2
s	complex variable (Laplace transform)
T	time variable, dimensionless
t	time, s
V	notation for vacancies
X	space coordinate, dimensionless
x	coordinate, cm
Y	dimensionless concentration

Greek

α	rate of current change, dimensionless
η	efficiency (depth of charge), dimensionless
τ	time corresponding to the end of charge/discharge, s

Subscripts

c	charge
i	initial
m	maximum
0	refers to zero time or space coordinate

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