

Theoretical prediction of state of charge of lithium ion cells

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Abstract

The prediction of the state of charge of batteries is a classic topic of considerable interest. The present work aims to predict the state of charge of lithium ion cells using a simple diffusion model. The extent of lithium ion diffusion into the cathode is given as a measure of the state of charge. Similarly an attempt has been made to correlate the impedance response of the cell to its state of charge. Coin cells were assembled. Charge–discharge studies and impedance measurements at various states of charge were carried out and the results are compared with the values predicted theoretically.

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1. Introduction

Lithium ion batteries with insertion type positive electrodes have received considerable attention for the past two decades [1]. As the development of electrode and electrolyte materials proceeds at a rapid rate, and the market for the cell widens, it becomes pertinent to obtain a better understanding of the underlying processes in this type of battery and to predict the performance of the cell. This would facilitate the evaluation as to whether the cell assembled would meet the requirements corresponding to the application for which it is intended.

The process of intercalation/de-intercalation is essentially a diffusion-controlled topotactic phenomenon [2] and in depth studies from various angles have been carried out to investigate this subject. The amount of lithium present inside the electrode is a direct measure of the state of charge of the battery [3]. The present work aims to develop a mathematical correlation between

the lithium content of the positive electrode and the state of charge of the battery.

2. Modeling of the cathode

A simple diffusion model is developed to characterize the intercalation/de-intercalation of the lithium ion into (or out of) the cathode. There is no major convection component while the migration effects due to the movement of a charged species in an electric field is found to be negligible.

3. Assumptions

The following assumptions are made in developing the model:

- (i) The cation and electronic fluxes are uniformly distributed over the entire electrode surface. This assumption requires that the particles of the electrode have very high conductivity and form adequate contacts with the metallic current collector.

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- (ii) A constant diffusion co-efficient is used as described by Subramanian et al. [4] as this is reasonably applicable for low rate of discharges.
- (iii) The particles of the cathode material are assumed to be an infinite plane sheet of unit thickness.
- (iv) The anisotropy arising out of the ion transport in the layered structures used for the solid solution cathodes is assumed to have little effect on the diffusion of the cation.

The mathematical formulation of the problem and the solution are discussed in detail in Appendix A. With the above assumptions, the model becomes semi-quantitative; nevertheless, it gives a good overview of the process.

4. Experimental

Lithium ion coin cells (Type 2016) were fabricated adopting the standard routine. Lithium foil (Footé Corporation, France) cut to appropriate dimensions was used as the anode material while LiCoO_2 (E. Merck) coated over aluminum foil was used as the cathode. The entire process of assembling the cell was carried out inside an MBraun (from -5 to $+5$ mbar) glove box, under an argon atmosphere. The assembled cells were allowed a settling time of 24 h before subjecting them to further studies.

The open circuit potential was measured after the settling time. It was found to be 3.15 V. The cell was then subjected to charging and discharging under constant current mode at the rate of $100 \mu\text{A/h}$ in a potential window of 3–4.2 V. Cycling experiments were carried out using a Bitrode 0–3 mA automated life cycle tester, USA.

Electrochemical impedance spectroscopy (EIS) studies were carried out using an Autolab PGSTAT 20, Netherlands, at various states of charge. The measurements were carried out at the OCP after the electrode had been discharged with a constant current at 1 h intervals. The frequency was varied between 10 mHz and 10^5 Hz and the ac amplitude was set to 5 mV.

5. Results and discussion

5.1. State of charge

The state of charge (SOC) is an important parameter used to assess the useful life of the battery. The state of charge of the cell is obtained from experimental values at various intervals of time and compared with the actual values generated by the use the diffusion model. The experimental values of cell discharge are given in Table 1. The assembled cell is discharged to estimate

Table 1
Experimental discharge data

Time/h	Capacity (normalized)	Cell voltage/V
0.03	1.00	4.10
0.5	0.97	4.09
1.0	0.93	4.07
2.0	0.87	4.03
3.0	0.70	3.99
4.0	0.62	3.95
5.0	0.54	3.92
6.0	0.40	3.89
7.0	0.35	3.83
8.0	0.18	3.59
8.04	0.11	3.01

the capacity of the cell (Fig. 1). The estimated capacity is taken as the stoichiometric energy content (S) for the model. Further the concentration X , is derived from the discharge curve as the function of the change in potential. Thus, the factor $(1 - X^*)$ is calculated from the experimental part. The capacity is normalized to facilitate the plot in Fig. 2.

The input parameters for the model are the stoichiometric energy content (S), the diffusion coefficient of Li^+ ion into the cathode (D) and the thickness (d) of the electrode (which is assumed to be planar). These are shown in Table 2.

Based on Eq. (A.28), as shown in Appendix A, the concentration of the Li^+ ion at the electrode surface (X^*) is evaluated for various time periods. A plot of $(1 - X^*)$ vs. dimensionless time (τ) is shown in Fig. 2. As discussed earlier, the stoichiometric content of Li^+ ion in the cathode is an indirect measure of the SOC of the battery. Hence, the plot signifies the variation of SOC with time. In addition the figure shows a superimposition of the theoretical and the experimental values of SOC and their variation with respect to time. The good correlation between the two is an indication that the model fits very well.

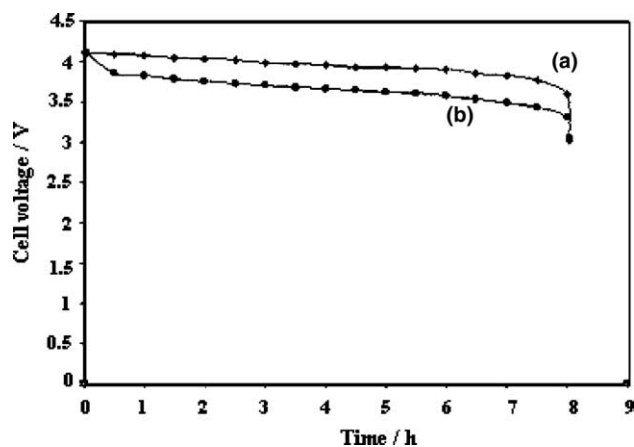


Fig. 1. Discharge curve for Li/LiCoO_2 : (a) first cycle; (b) fifth cycle.

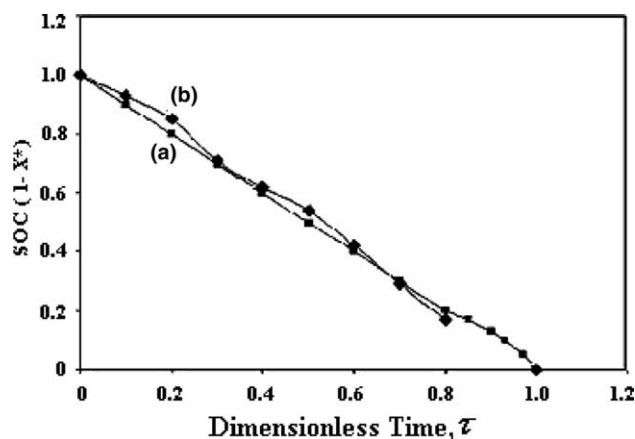


Fig. 2. Plot of SOC ($1 - X^*$) vs. τ : (a) theoretical; (b) experimental.

Table 2
Model parameters

Parameter	Value
Stoichiometric energy content (S)/mA h g ⁻¹	125
Diffusion coefficient of lithium ion (D)/m ² s ⁻¹	8.2×10^{-12}
Electrode thickness (d)/ μ m	100

To validate the method described above, another attempt was made to measure the SOC of the battery using impedance measurement made at various states of charge. The double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) are calculated using the impedance data collected at various depths of discharge. Table 3 summarizes the results obtained from the impedance plots. It is clear from Table 3 that the R_{ct} values increase with the drop in SOC. This can be attributed to the semiconductor to metal transition, i.e., when the cell is charged, lithium is removed from the cathode and metallic behaviour is regained. On the other hand, the double layer capacitance C_{dl} shows an increase with the decrease in the depth of discharge. The above results can be used empirically to predict the value of the SOC from the impedance response

Table 3
Interfacial parameters from impedance plots after various times of discharge

Time/h	$R_{ct}/m\Omega^a$	C_{dl}/F^b
1	171.9	5.179
2	259.9	3.828
3	290.4	3.458
4	344.7	3.019
5	409.0	2.445
6	483.1	2.170
7	511.2	2.040
8	547.4	1.727
Drained	572.7	1.654

^a Charge transfer resistance at the cathode|electrolyte interface.

^b Double layer capacitance at the cathode|electrolyte interface.

Table 4
Interfacial parameters from simulated plots

Time/h	$R_{ct}/m\Omega$	C_{dl}/F
1	180.0	5.515
3	294.5	3.190
5	413.1	2.615
7	520.0	2.050

at any given instant. This is a very powerful tool of practical significance, since it does not perturb the system from its equilibrium state. All other conventional methods involve discharging the battery to estimate the residual capacity. To prove the viability of this procedure, the SOC after 7 h was evaluated from a typical impedance measurement. The value of R_{ct} was found from impedance measurements to be 511.2 m Ω . Using the R_{ct} values obtained for different SOC's, the SOC of the battery after 7 h could be interpolated. The value of SOC calculated thus was 32.3%, which agrees reasonably well with the actual SOC value reported from experimental results (35%) and calculated using the diffusion model.

The battery was modeled based on an equivalent circuit analysis, which has been dealt with in detail in the literature [5]. The impedance parameters such as R_{ct} and C_{dl} were simulated using EG&G PAR – Version 4.3 Equivalent Circuit Analyzer software and the fit was compared with the results obtained experimentally. The simulated values of R_{ct} and C_{dl} at the cathode|electrolyte interface for various SOC's are given in Table 4. The SOC obtained using impedance measurements was compared with the SOC predicted theoretically from the diffusion model. From Fig. 2, it is clear that both the values obtained experimentally from the impedance results of SOC and the theoretical estimates of the SOC obtained from the concentration of Li agree to an appreciable extent.

6. Conclusions

A theoretical model to investigate the charge/discharge process was built. Results of the model were compared with the actual experimental values. This model, though simple, provides an eloquent simulation of the intercalation kinetics of Li⁺ ion into the transition metal oxide matrix. A good degree of concurrence between the two is a positive step towards an understanding of the battery kinetics. EIS measurements were used to estimate the state of charge of battery system. The double layer parameters were estimated and their variation with the state of charge was studied. Attempts have been made to correlate the charge/discharge and impedance responses of the battery mathematically to validate the model proposed.

Appendix A

A.1. Statement of the problem

The process of diffusion is essentially governed by the phenomenological equations from Fick's laws

$$\frac{\partial}{\partial t} c(x, t) = D \left(\frac{\partial^2}{\partial x^2} c(x, t) \right), \quad (\text{A.1})$$

$$J = -D \left(\frac{\partial}{\partial x} \right) c(x, t), \quad (\text{A.2})$$

where $c(x, t)$ signifies the concentration of the diffusing species, D is the diffusion coefficient of the diffusing species, and J is the flux.

The initial condition is given by

$$c(x, 0) = 0, \quad (\text{A.3})$$

which signifies that the concentration of the diffusing species at the cathode is zero with respect to the reference level (it can as well be assumed to be at some constant value c_0).

The boundary conditions are as follows:

- (1) At the cathode|current collector interface, the flux is given by

$$\frac{\partial}{\partial x} c(0, t) = 0, \quad (\text{A.4})$$

since no lithium ions diffuse through that boundary.

- (2) At the cathode|electrolyte interface, the flux is given by

$$\frac{\partial}{\partial x} c(1, t) = \frac{j}{nFD}, \quad (\text{A.5})$$

where j is the current density, F is the Faraday constant and n is the number of electrons.

A.2. Solution

Similar situations are encountered in heat transfer problems involving conduction of heat through solids. Several numerical methods of solution have been attempted to solve this problem, e.g., Laplace transforms [6] and separation of variables method [4]. The latter method reported by Subramanian et al. [4] proves to be simple and elegant in that it avoids the approximations in inverting the Laplace functions and other additional complications, which the other methods require. Hence, this method is adopted in this discussion.

We introduce a variable transformation for $c(x, t)$ as follows

$$c(x, t) = u(x, t) + P(x) + Q(t). \quad (\text{A.6})$$

In the above equation, $u(x, t)$ stands for concentration equivalent of $c(x, t)$ under zero flux boundary conditions. $P(x)$ and $Q(t)$ stand for the non-homogeneity due to the flux at the boundary $x = 1$. Subsequently, the boundary conditions (A.4) and (A.5) are transformed as follows:

$$\frac{\partial}{\partial x} u(0, t) = 0, \quad (\text{A.7})$$

$$\frac{\partial}{\partial x} u(1, t) = 0, \quad (\text{A.8})$$

$$\left(\frac{dP}{dx} \right)_{x=0} = 0, \quad (\text{A.9})$$

$$\left(\frac{dP}{dx} \right)_{x=1} = \frac{j}{nFD} = \delta(\text{say}). \quad (\text{A.10})$$

The variable $Q(t)$ satisfies

$$Q(0) = 0. \quad (\text{A.11})$$

All three variables together satisfy the initial condition

$$u(x, 0) + P(x) + Q(0) = 0. \quad (\text{A.12})$$

Now, the original equation is transformed as follows:

$$\frac{\partial u(x, t)}{\partial t} + \frac{dQ(t)}{dt} = D \left(\frac{\partial^2 u}{\partial x^2} + \frac{d^2 P}{dx^2} \right). \quad (\text{A.13})$$

Separating the homogeneous and non-homogeneous terms

$$\frac{\partial u(x, t)}{\partial t} = D \frac{\partial^2 u(x, t)}{\partial x^2}, \quad (\text{A.14})$$

$$\frac{dQ}{dt} = D \frac{d^2 P}{dx^2}. \quad (\text{A.15})$$

Now, we solve Eq. (A.15) first

$$\frac{dQ}{dt} = D \frac{d^2 P}{dx^2} = k(\text{say}), \quad (\text{A.16})$$

which implies

$$\frac{d^2 P}{dx^2} = k_1, \quad (\text{A.17})$$

where $k_1 = k/D$. Solving (A.17) and applying boundary conditions (A.9) and (A.10), we have

$$P(x) = \delta \frac{x^2}{2} + C_1, \quad (\text{A.18})$$

where C_1 is a constant.

Solving for Q similarly, using (A.16) and (A.11), we have

$$Q(t) = D\delta t. \quad (\text{A.19})$$

Therefore

$$c(x, t) = u(x, t) + \delta \frac{x^2}{2} + C_1 + D\delta t. \quad (\text{A.20})$$

The solution for $u(x, t)$ is readily obtainable by a routine procedure. Thus, using Eqs. (A.14), (A.7) and (A.8) we have

$$u(x, t) = \sum_{n=1-\infty} A_n \exp(-n^2 \pi^2 D t) \cos(n \pi x). \quad (\text{A.21})$$

Therefore, we have

$$c(x, t) = \delta \frac{x^2}{2} + C_1 + D\delta t + \sum_{n=1-\infty} A_n \exp(-n^2 \pi^2 D t) \cos(n \pi x), \quad (\text{A.22})$$

A_n and C_1 in (A.22) can be evaluated using the initial condition (A.12)

$$c(x, 0) = 0 = \delta \frac{x^2}{2} + \sum_{n=1-\infty} A_n \cos(n \pi x). \quad (\text{A.23})$$

From Eq. (A.23), A_n is obtained by integrating between 0 and 1 after pre-multiplying both sides by $\cos(n \pi x)$. C_1 is obtained by integrating both sides of (A.23) between 0 and 1 or by choosing some arbitrary value for x and evaluating the series for a large number of terms.

Finally, we have

$$c(x, t) = \delta \left\{ \frac{x^2}{2} - \frac{1}{6} + D t - 2 \sum_{n=1-\infty} \frac{\exp(-n^2 \pi^2 D t)}{n^2 \pi^2} \frac{\cos(n \pi x)}{\cos(n \pi)} \right\}. \quad (\text{A.24})$$

Now, $c(x, t)$ is a measure of the concentration of the diffusing ionic species. If this is multiplied by the average molar volume (V_m) and divided by the number of moles of the ion, one obtains the number of ions inserted per mole of the host material, which is in turn the degree

of discharge. We denote this term $V_m \frac{c(x, t)}{n}$ by X . Similarly, other parameters are made dimensionless by the following notations:

$$Q = T \times D, \quad (\text{A.25})$$

where T is the theoretical discharge period of the battery, given by

$$T = \frac{\text{Stoichiometric energy content } (S)}{\text{Average power drawn } (P)}. \quad (\text{A.26})$$

The time ' t ' is transformed into the dimensionless form τ

$$\tau = \frac{t}{T}. \quad (\text{A.27})$$

Introducing these transformations in (A.24), and evaluating the dimensionless surface concentration X^* (which equals X at $x = 1$), we obtain

$$X^* = \tau + \frac{1}{Q} \left\{ \frac{1}{3} - 2 \sum_{n=1-\infty} \frac{\exp(-n^2 \pi^2 Q \tau)}{n^2 \pi^2} \right\}. \quad (\text{A.28})$$

When X^* attains a value of 1, the battery is considered totally discharged. When X^* equals 0, the battery is in the fully charged condition. Thus, the state of charge at any instant of time is given by $(1 - X^*)$.

References

- [1] J.P. Pereira-Ramos, N. Baffier, G. Pistoia, *Lithium Batteries: New Materials Development and Perspectives*, Elsevier, Amsterdam, 1994.
- [2] T. Ozhuku, *J. Electrochem. Soc.* 144 (1997) 988.
- [3] M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries – Fundamentals and Performance*, Wiley-VCH, Weinheim, 1998.
- [4] V.R. Subramanian, R.E. White, *J. Power Sources* 96 (2001) 385.
- [5] B.A. Boukamp, *Solid State Ionics* 20 (1986) 31.
- [6] H.S. Carslaw, J.C. Jaeger, *Conduction of Heat in Solids*, second ed., Oxford University Press, Oxford, 1976 (Chapter XII).