Chinese Chemical Letters Vol. 16, No. 8, pp 1077-1080, 2005
http://www.imm.ac.cn/journal/ccl.html

Capacity Titration Technique for Determining the Solid Diffusion Coefficient of Intercalary Species within Insertion-host Materials

Xin Cun TANG[1]*, Tian Duo LI[2]

[1] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083
[2] Shandong Institute of Light Industry, Jinan 250100

Abstract: In this paper, the capacity titration technique (CT technique) was developed on basis of the RPG (ratio of potentio-charge capacity to galvano-charge capacity) method to continuously determine the solid diffusion coefficient *D* of the intercalary species within insertion-host materials with a small voltage region. The linear equations of *D vs. q* (value of ratio of the potentio-charge capacity to the galvano-charge capacity) were given in different range of *q*. By the CT technique, the Li^+ solid diffusion coefficients *D* within $LiMn_2O_4$ at different voltages were determined. The results showed that the values of *D* varied from 3.447×10^{-9} cm^2/s to $7.60\times10^{-11}cm^2/s$ in the voltage range of charge from 3.3V to 4.3V as a function of voltage with "W" shape.

Keywords: Capacity titration technique, Li^+ solid diffusion coefficient, $LiMn_2O_4$.

Investigation on the solid diffusion process of intercalary species within insertion-host materials plays an important role in the energy storage and output of secondary batteries[1]. To determine the solid diffusion coefficient, several electrochemical techniques have been developed such as galvanostatic intermittent titration (GITT)[2,3], electrochemical impedance spectroscopy (EIS)[4,5], potential intermittent titration technique (PITT)[6], and potential step chronoamperometry (PSCA)[7], potential relaxation technique[8], *etc*. These techniques usually need to determine many complementary parameters, which would influence the measured values of the diffusion coefficient due to experimental difficulties[4]. In our previous works[9,10], a simple method was developed by introducing the ratio of the potentio-charge capacity to the galvano-charge capacity (*q*), in which only one complementary parameter (the radius of insertion-host particle *R*) was needed. In this paper, we further develop the RPG method to the capacity titration technique (CT technique). Relative to the RPG method, the main advantage of CT technique is that it allows to continuously determining the diffusion coefficient at different SOC (state of charge) with a small voltage region.

Sample of the spinel $LiMn_2O_4$ was prepared by the low-heating solid-state method according to the literature[11,12]. The particle size distribution was determined by Mastersizer 2000 laser-size analyzer, from which the average particle radius *R* can be obtained as 14.8 μm. The galvano-potentio-charge tests were performed by Land

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* E-mail: tangxincun@163.com

CT2001A Batteries Test Instrument at 28℃ in a lab cells, which were assembled as the literature[10]. The difference of the galvano-potentio-charge testing procedure of CT from that of the RPG method (see literature [10]) only was that the galvano-potentio-charge repeats many times by dividing the whole charge voltage range into different small voltage regions.

In the theory, the value of q can be expressed as follows[10]:

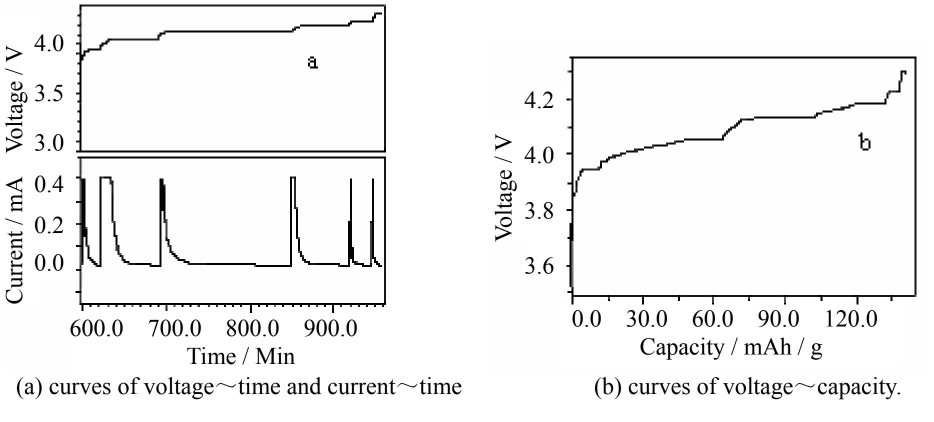
$$q = \frac{\xi}{15} - \frac{2\xi}{3}\sum_{j=1}^{\infty}\frac{1}{\alpha_j^2}\exp\left(-\frac{a_j^{2}}{\xi}\right), \qquad \xi = \frac{R^2}{Dt_G}$$

D is diffusion coefficient, cm^2/s; t_G is the galvano-charge time, s; a_j is constant. Equation above can be linearly fitted by the linear least-square fitting in different range of the values of q or ξ as shown in **Table 1**.

Table 1 The linear equations fitted by the linear least-square in different range of the values of q or ξ

ξ	$q = f(\xi)$	q	$D = g(q)$	Interrelation coefficient (%)
0-8	$q = 6.51\times10^{-2}\xi$	0.00-0.51	$D = \dfrac{R^2}{15.36qt_G}$	99.98
8-16	$q = (10.38 + 5.15\xi)\times10^{-2}$	0.51-0.82	$D = \dfrac{5.15\times10^{-2}R^2}{(q - 10.38\times10^{-2})t_G}$	99.96
16-32	$q = (32.71 + 3.73\xi)\times10^{-2}$	0.82-1.51	$D = \dfrac{3.73\times10^{-2}R^2}{(q - 32.71\times10^{-2})t_G}$	99.91
32-60	$q = (64.86 + 2.75\xi)\times10^{-2}$	1.51-2.28	$D = \dfrac{2.75\times10^{-2}R^2}{(q - 64.86\times10^{-2})t_G}$	99.91
60-400	$q = (164.10 + 1.37\xi)\times10^{-2}$	2.28-6.90	$D = \dfrac{1.37\times10^{-2}R^2}{(q - 164.10\times10^{-2})t_G}$	99.53
≥400	$q = (495.55 + 0.69\xi)\times10^{-2}$	≥6.90	$D = \dfrac{0.69\times10^{-2}R^2}{(q - 495.55\times10^{-2})t_G}$	99.99

Figure 1 The CT curves of $LiMn_2O_4$ with a galvano-charge current of 0.4 mA.



(a) curves of voltage～time and current～time

(b) curves of voltage～capacity.

The typical CT curves for spinel $LiMn_2O_4$ with a galvano-charge current of 0.4 mA are shown in **Figure 1**. **Figure 1a** showed that the voltage increases gradually in galvano-charge steps and the current decreases gradually in the potentio-charge steps. The galvano-charge time t_G can be obtained from the curve of current *vs.* time or from the curve of voltage *vs.* time. **Figure 1b** showed the corresponding dependence of the charge capacity on the voltage (*vs.* Li/Li^+) steps, from which both of the galvano-charge capacities and potentio-charge capacities can be obtained and the values of q can be calculated. Thus the solid diffusion coefficients of the all galvano-potentio-charge steps can be obtained from the equations in **Table 1**. The detailed data are given in **Table 2**.

Table 2 showed that the values of Li^+ solid diffusion coefficients within $LiMn_2O_4$ varied from 3.44×10^{-9} cm^2/s to $7.60\times10^{-11}cm^2/s$ in the voltage range of charge from 3.3V to 4.3V. A. K. Hjelm and G. Lindbergh reported the values of Li^+ solid diffusion coefficients within $LiMn_2O_4$ by electrochemical impedance spectroscopy (EIS) which varied from 10^{-10} cm^2/s to 10^{-12} cm^2/s with the state-of-discharge (SOD) range from about 0.25 to 0.9[13]. F. Cao and J. Prakash reported the values of Li^+ solid diffusion coefficients within $LiMn_2O_4$ by PITT measurement which varied from 10^{-10} cm^2/s to$10^{-11}cm^2/s$ in the voltage range of charge from 4.05V to 4.2V[14]. These results are matched with the D values that shown in **Table 2**.

Table 2 Data of CT test and the values of the D at different voltages

Voltage (V)	Charge capacity (mAh/g) Galvano-charge	Potentio-charge	$q\times10^2$	t_G (s)	D (cm^2/s)
3.30	16.7	4.0	23.95	378	1.57×10^{-9}
3.60	0.3	1.8	600.00	7	9.83×10^{-10}
3.85	1.3	1.9	146.15	29	3.44×10^{-9}
3.95	4.0	8.1	202.50	90	4.86×10^{-10}
4.05	43.6	16.5	37.84	985	3.83×10^{-10}
4.13	13.0	38.8	298.46	294	7.60×10^{-11}
4.18	15.4	9.3	60.39	349	6.46×10^{-10}
4.23	1.7	2.5	147.06	39	1.83×10^{-9}
4.30	0.8	2.1	262.50	17	1.79×10^{-9}

Figure 2 The Li^+ solid diffusion coefficient in $LiMn_2O_4$ as a function of voltage

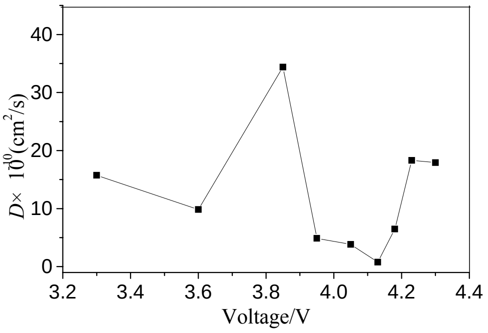


Figure 3 The curves of C～V and (dC/dV)～V

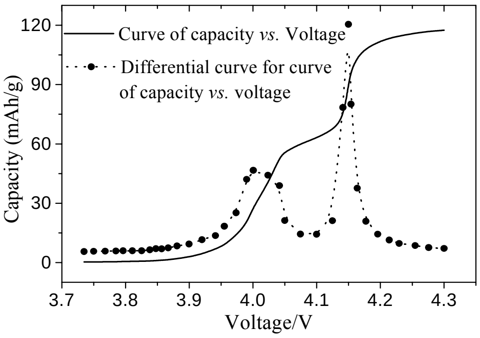


Figure 2 shows the Li^+ solid diffusion coefficients within $LiMn_2O_4$ as a function of voltage with "W" shape. R. Darling and J. Newman had simulated the diffusion of Li^+ in $Li_yMn_2O_4$ by Monte Carlo technique, the Li^+-Li^+ interactions on the activation energy led to the diffusion coefficient depending on the concentration of Li^+ with "W" shape[15]. **Figure 3** showed the curve of charge capacity *vs.* voltage and its differential curve of $LiMn_2O_4$. The differential curve shows a "M" shape with the top peaks at 3.98V and 4.16V, which are well-matched with the bottom peaks of the curve of *D*～*V* as shown in **Figure 2**. This result suggests that *D* is in inverse proportion to dC/dV.

Acknowledgments

The authors thank prof. Dian-Zeng JIA (Xinjiang University) for his assistance in performing the experiments. This work was supported by NNSF of China (No.20406024) and the Postdoctoral Science Foundation of Central South University (No.76600).

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Received 10 September, 2004