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Discharge Curve Fitting of $LiFePO_4$ Based on Impedance Model

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$LiFePO_4$电极放电曲线的阻抗模拟

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摘要: 建立了磷酸铁锂($LiFePO_4$)电极材料放电曲线的阻抗模型. 将不同倍率放电的电位分为欧姆电位降、电荷转移电位降与扩散阻抗电位降三部分,以电极交流阻抗谱图结合理论分析,推导出不同倍率电极电位的表达式. 模拟结果显示,拟合值与实验值吻合较好.

关键词: $LiFePO_4$; 阻抗模型; 模拟

中图分类号: O646　　**文献标识码:** A

磷酸铁锂($LiFePO_4$)已被视为动力电池最理想的正极材料之一[1-2]. 然而,磷酸铁锂的离子和电子电导率均很低,不能高倍率放电. 通过碳包覆与离子掺杂,磷酸铁锂电子电导率已提高至约 10^{-2} $S \cdot cm^{-1}$数量级[3-4],但其离子电导率仍是制约其倍率性能的主要因素.

磷酸铁锂充放电过程会发生相变,$LiFePO_4$ 与 $FePO_4$ 两相共存,电位曲线相对平坦,荷电状态(State of Charge,SOC)难以估算. Newman 等提出缩核模型(Shrinking-core Model),并结合多孔电极模型,建立了磷酸铁锂电极的模型[5-7]. 该模型将电极内部传质、电场以及电化学反应相耦合,能够较准确地模拟磷酸铁锂电极放电的电化学性能,但其表达式相当复杂,计算量大,且需要测定多个电极参数,无法实时监测电极放电情况.

作者提出了模拟磷酸铁锂放电电位曲线的新思路,设定磷酸铁锂的放电过程主要受制于其离子电导率,扩散阻抗是磷酸铁锂电极倍率性能的主要影响因素. 通过理论推导与实验拟合,导出磷酸铁锂电极电位、电流与锂离子嵌入度的关系式,与实验值比较,可较好地吻合. 为磷酸铁锂电极荷电状态的实时估算提供了一种可能的新方法.

1　实　验

1.1　模拟电池

将 $LiFePO_4$(Aleees, 台湾), Super-P 及 KS6 (Timcal)导电剂,聚偏氟乙烯(PVDF6020)粘结剂,按 89:2.5:2.5:6(by mass)比例混匀,用乳化剂调浆,刮涂于铜箔集流体(12 μm 厚)上构成正极,与金属锂片负极,1 $mol \cdot L^{-1}$ $LiPF_6$/EC + DMC + EMC(1:1:1,by volume)电解液,在充满氩气的手套箱中组装模拟电池.

1.2　电池测试

使用蓝电电池测试仪,测试模拟电池 0.02C、0.2C、1C、2C 和 5C 倍率下电极的放电曲线. 采用电化学工作站(ZAHNER-IM6EX 型,德国)测试电极交流阻抗谱(两电极体系,锂片对电极与参比电极). 残余电流 < 0.5 μA, 开路正弦波振幅为 2 mV,频率范围 100 kHz ~ 0.1 Hz.

2　结果与讨论

2.1　理论推导

电极电位表达式如下:

$$E(x) = E^{o} - \Delta E_{ohm} - \Delta E_{ct} - \Delta E_{diff} \quad (1)$$

式中 $E(x)$为电池的电极电位,x 为放电过程中锂离子的嵌入度(Li^+ Insertion Degree),E^{o} 为平衡电位,ΔE_{ohm}、ΔE_{ct}和 ΔE_{diff}分别为欧姆阻抗、电荷转移阻抗以及扩散阻抗引起的电位降[9-10].

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$$\Delta E_{ohm} = i \cdot R_{ohm} \tag{2}$$

$$\Delta E_{ct} = \frac{RT}{nF\alpha}\ln\left(\frac{i}{i_0}\right) \tag{3}$$

式中 R 为气体常数,T 为绝对温度,n 为参与电化学反应的电子数,F 为法拉第常数,α 为传递系数,i 为外电流密度,i_0 为交换电流密度.

$$i_0 = \frac{RT}{nFR_{ct}} \text{[11]} \tag{4}$$

$$\Delta E_{diff} = i \cdot R_{diff} \tag{5}$$

对于不同的锂离子嵌入度,扩散阻抗值各不相同.

充放电过程中,Li_xFePO_4 化学势是锂离子嵌入度 x 的函数[11]:

$$\mu(x) = E_0 + k_B T \ln\left(\frac{x}{1-x}\right) \tag{6}$$

式中,E_0 为晶格位的能量,k_B 为波尔兹曼常数.

由此,扩散阻抗表达式如下[11]:

$$R_{diff}(x) = \frac{L^2}{D \cdot \bar{V}e^2 N \frac{dx}{d\mu}} \tag{7}$$

式中,D 为固相扩散系数,根据准平衡近似(Quasi-Equilibrium Approximation),其扩散系数为[11-12]:

$$D(x) = \frac{D_J(x)}{k_B T} x \frac{d\mu}{dx} \tag{8}$$

式中,D_J 为动力系数[11]:

$$D_J(X) = \frac{M_0}{x}\exp\left(-\frac{E_a}{RT}\right)P(0;0) \tag{9}$$

式中,$P(0;0)$ 表示两个相邻晶格点阵位未被填满的概率,对无相互作用的晶格,$P(0;0) = (1-x)^2$,E_a 为活化能.

综合以上各式,可以得到扩散电阻的表达式:

$$R_{diff}(x) = \frac{L^2 k_B T}{\bar{V}e^2 N M_0 \exp\left(\frac{E_a}{RT}\right)(1-x)^2} \tag{10}$$

上述各式中参数及其物理意义列于表 1.

将式中常数合并,扩散阻抗拟合式如下:

$$R_{diff}(x) = \frac{A}{(1-x)^B} + C \tag{11}$$

2.2　数据拟合

图 1 给出微弱电流(0.02C)下磷酸铁锂电极的放电电位曲线. 从图 1 中看出,其平阶电位可视为电极平衡电位($E^o = 3.4$ V).

表 1　上述各式中参数与物理意义

Tab. 1　Parameters used in the aforementioned equations

Parameters	Description	Values
R	Gas constant	8.314 J·(mol·K)$^{-1}$
T	Temperature	298.15 K
F	Faraday constant	96.5 kC·moL^{-1}
α	Transfer coefficient	0.5
e	Elementary charge	1.6×10^{-19}C
k_B	Boltzmann constant	1.38×10^{-23} J·K^{-1}
i_0	Exchange current density	
M_0	Ion mobility coefficient	
V	Active material volume	
L	Characteristic length	
E_a	Activation energy	

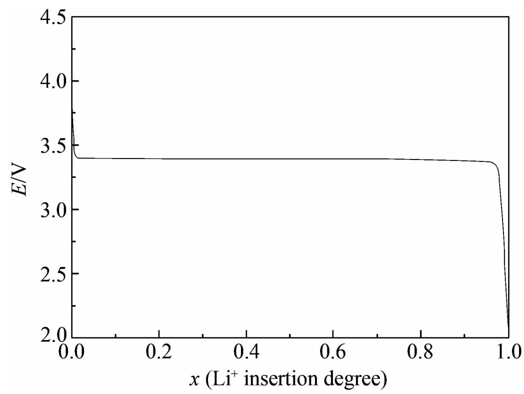

图 1　微弱电流下(0.02C)磷酸铁锂电极放电曲线

Fig. 1　The discharge curve of $LiFePO_4$ at very low rate (0.02C)

图 2、图 3 是磷酸铁锂电极交流阻抗谱图及其等效电路. 拟合测得欧姆阻抗(R_{ohm})与电荷转移阻抗(R_{ct})分别为 1.5 Ω 与 15 Ω.

电极扩散阻抗由 1C 倍率的数据拟合,扣除欧姆阻抗与电荷转移阻抗的影响,可得扩散阻抗与锂离子嵌入度的关系. 根据式(11)进行曲线非线性拟合,如图 4 所示. 拟合可得式(11)中的常数:$A = 10.61$,$B = 3$,$C = 66.46$.

因此,磷酸铁锂电极电位、放电电流和锂离子嵌入度 x 的拟合表达式如下:

$$E(x)=E^{\circ}-i\cdot R_{ohm}-\frac{RT}{nF\alpha}\cdot\ln\left(\frac{i}{i_0}\right)-i\cdot\left(\frac{A}{(1-x)^{B}}+C\right) \quad (12)$$

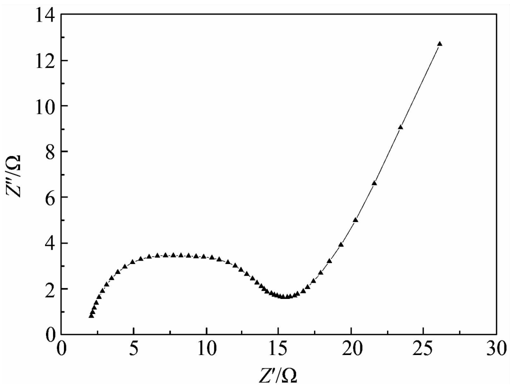

图 2 磷酸铁锂电极的交流阻抗谱图(锂离子嵌入度 $x=0.375$)

Fig. 2 EIS plot of $LiFePO_4$ cell at x(Li^+ insertion degree) = 0.375

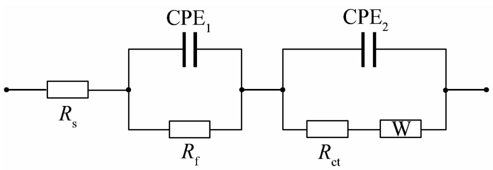

图 3 磷酸铁锂电极交流阻抗谱等效电路

Fig. 3 The equivalent circuit used for fitting the EIS data

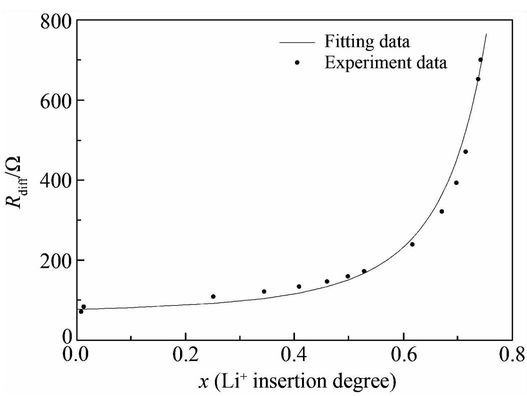

图 4 磷酸铁锂电极扩散阻抗拟合曲线

Fig. 4 The fitting result of the diffusion resistance for $LiFePO_4$ electrode

据表达式可计算不同放电倍率电极电位,为简化拟合,忽略放电初期突降电位. 图 5 示出 0.2C、1C、2C 和 5C 倍率下电极放电曲线及 $E(x)$-x 模拟结果.

从图 5 中可以看出,式(12)的拟合值与实验曲线相吻合,故此模拟可准确预测不同倍率电位平台,但放电末期拟合值与实验曲线则稍有偏差.

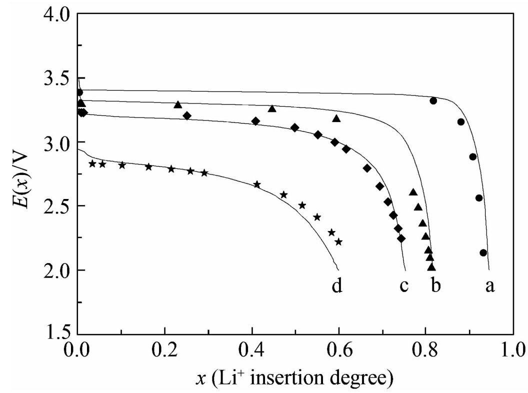

图 5 不同放电倍率磷酸铁锂电极 $E(x)$-x 曲线(散点为拟合值,实线为实验值)

放电倍率:a. 0.2C; b. 1C; c. 2C; d. 5C

Fig. 5 The $E(x)$-x curves at different rates for $LiFePO_4$ electrode

Symbols indicate the fitting data, while solid lines indicate the experiment data, discharge rate: a. 0.2C; b. 1C; c. 2C; d. 5C

3 结 论

建立了磷酸铁锂放电曲线的阻抗模型. 通电流条件下,该电极电位由平衡电位、欧姆电位、降电荷转移阻抗电位降与扩散电位阻抗电位降构成,并分别导出了各部分电位降的表达式. 通过拟合,可得磷酸铁锂电极电位、电流及锂离子嵌入度的半经验关系式. 据此估算不同放电倍率的 $E(x)$-x 放电曲线,模拟值与实验值基本符合. 为磷酸铁锂电极的荷电状态估算提供了一条新途径.

参考文献(References):

[1] Padhi A K, Nanjundaswamy K S, Goodenough J B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries [J]. Journal of the Electrochemical Society, 1997, 144(4): 1188-1194.

[2] Yamada A, Chung S C, Hinokuma K. Optimized $LiFePO_4$ for lithium battery cathodes [J]. Journal of the Electrochemical Society, 2001, 148(3): A224-A229.

[3] Chung S Y, Bloking J T, Chiang Y M. Electronically

conductive phospho-olivines as lithium storage electrodes [J]. Nature Materials, 2002, 1(2): 123-128.

[4] Huang H, Yin S C, Nazar L F. Approaching theoretical capacity of $LiFePO_4$ at room temperature at high rates [J]. Electrochemical and Solid-State Letters, 2001, 4(10): A170-A172.

[5] Doyle M, Fuller T F, Newman J. Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell [J]. Journal of the Electrochemical Society, 1993, 140(6): 1526-1533.

[6] Doyle M, Newman J, Gozdz A S, et al. Comparison of modeling predictions with experimental data from plastic lithium ion cells [J]. Journal of the Electrochemical Society, 1996, 143(6): 1890-1903.

[7] Srinivasan V, Newman J. Discharge model for the lithium iron-phosphate electrode [J]. Journal of the Electrochemical Society, 2004, 151(10): A1517-A1529.

[8] Prosini P P. Modeling the voltage profile for $LiFePO_4$ [J]. Journal of the Electrochemical Society, 2005, 152(10): A1925-A1929.

[9] Pasquali M, Dell, Era A, Prosini P P. Fitting of the voltage-Li^+ insertion curve of $LiFePO_4$ [J]. Journal of Solid State Electrochemistry, 2009, 13(12): 1859-1865.

[10] Ho C, Raistrick I D, Huggins R A. Application of A-C techniques to the study of lithium diffusion in tungsten trioxide thin films [J]. Journal of the Electrochemical Society, 1980, 127(2): 343-350.

[11] Bisquert J, Vikhrenko V S. Analysis of the kinetics of ion intercalation. Two state model describing the coupling of solid state ion diffusion and ion binding processes [J]. Electrochimica Acta, 2002, 47(24): 3977-3988.

[12] Zhdanov V P. General equations for description of surface diffusion in the framework of the lattice-gas model [J]. Surface Science, 1985, 149(1): L13-L17.

Discharge Curve Fitting of $LiFePO_4$ Based on Impedance Model

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Abstract: In this paper, an impedance model is developed for simulating the discharge curve of $LiFePO_4$ cathode material. The voltage drop is divided into three parts: the Ohm voltage drop, the charge transfer voltage drop and the diffusion voltage drop. A theoretical expression has been derived to predict the discharge curves at various discharge rates. The parameters of the equation have been obtained by fitting the results of EIS measurement, and a good agreement between the fitting and the experimental data has been found at all discharge rates.

Key words: $LiFePO_4$; impedance model; fitting