

LiFePO₄电极放电曲线的阻抗模拟

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摘要: 建立了磷酸铁锂(LiFePO₄)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: LiFePO₄; 阻抗模型; 模拟

中图分类号: O646

文献标识码: A

磷酸铁锂(LiFePO₄)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 $10^{-2} \text{ S} \cdot \text{cm}^{-1}$ 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, LiFePO₄与FePO₄两相共存, 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LiFePO₄(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·L⁻¹ LiPF₆/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:

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

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° 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].

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

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

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.

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

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

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]:

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

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]:

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

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]:

$$D(x) = \frac{D_{\text{j}}(x)}{k_{\text{B}} T} x \frac{\text{d}\mu}{\text{d}x} \tag{8}$$

式中, D_{j} 为动力系数^[11]:

$$D_{\text{j}}(X) = \frac{M_0}{x} \exp \left(-\frac{E_{\text{a}}}{RT} \right) P(0;0) \tag{9}$$

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:

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

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:

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

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, 其平阶电位可视作为电极平衡电位 ($E^0 = 3.4 \text{ V}$).

表 1 上述各式中参数与物理意义

Tab. 1 Parameters used in the aforementioned equations

Para-meters	Description	Values
R	Gas constant	$8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$
T	Temperature	298.15 K
F	Faraday constant	$96.5 \text{ kC} \cdot \text{mol}^{-1}$
α	Transfer coefficient	0.5
e	Elementary charge	$1.6 \times 10^{-19} \text{ C}$
k_{B}	Boltzmann constant	$1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
i_0	Exchange current density	
M_0	Ion mobility coefficient	
V	Active material volume	
L	Characteristic length	
E_{a}	Activation energy	

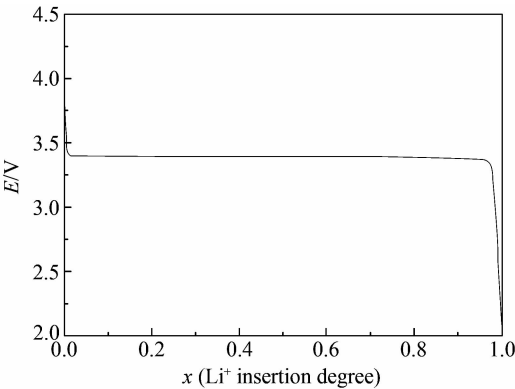


图 1 微弱电流下 (0.02C) 磷酸铁锂电极放电曲线
Fig. 1 The discharge curve of LiFePO_4 at very low rate (0.02C)

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 $1.5 \, \Omega$ 与 $15 \, \Omega$.

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:

$$E(x) = E^0 - i \cdot R_{\text{ohm}} - \frac{RT}{nF\alpha} \cdot \ln\left(\frac{i}{i_0}\right) - i \cdot \left(\frac{A}{(1-x)^B} + C \right) \quad (12)$$

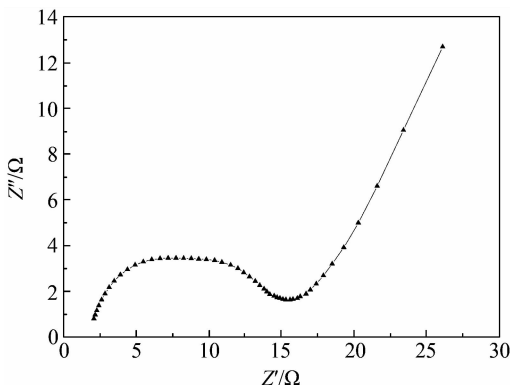


图2 磷酸铁锂电极的交流阻抗谱图(锂离子嵌入度 $x = 0.375$)

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

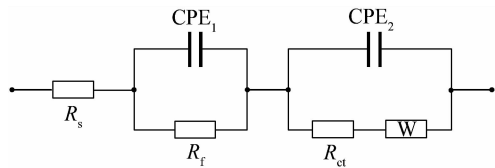


图3 磷酸铁锂电极交流阻抗谱等效电路

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

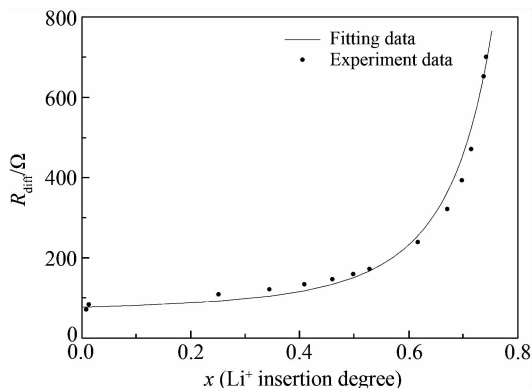


图4 磷酸铁锂电极扩散阻抗拟合曲线

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.

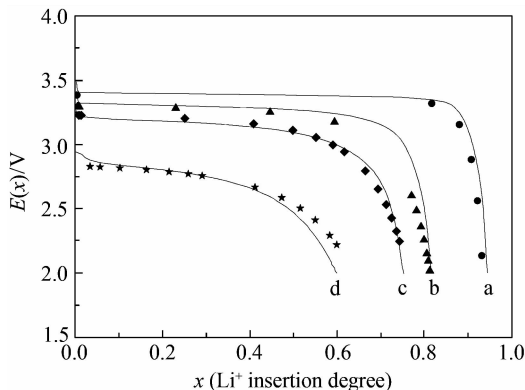


图5 不同放电倍率磷酸铁锂电极 $E(x)$ - x 曲线(散点为拟合值,实线为实验值)

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.

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Discharge Curve Fitting of LiFePO₄ Based on Impedance Model

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Abstract: In this paper, an impedance model is developed for simulating the discharge curve of LiFePO₄ 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: LiFePO₄; impedance model; fitting