影响锂离子电池实际容量的材料因素

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2018-08-04 收稿, 2018-09-27 修回, 2018-10-14 接受, 2018-11-14 网络版发表

工业和信息化部重点专项(2016YFB0700503-7)资助

摘要 正极材料的实际比容量一般都低于理论比容量, 实际容量是直接影响电池能量密度的关键因素之一, 不同电极活性材料的实际比容量/理论比容量的差别很大, 差距主要来自充电前后的实际脱锂系数大小. 通过大数据的整理, 本文收集了层状 LiMO_2 ($M=\text{Ni}$ 和 Co), 尖晶石 LiMn_2O_4 和 LiMPO_4 ($M=\text{Fe}$, Mn 和 Ni)等20种典型正极材料的晶体结构和实际容量实验参数. 利用第一性原理计算方法, 得到了这些典型体系母体的价带和导带之间的能隙值. 通过比较脱锂前后两种结构的能隙, 确定了能隙比值与实际脱锂系数的关系, 结果表明, 脱锂前后结构的能隙越接近, 正极材料的实际脱锂系数就越大, 相对的实际容量也就越大. 因此, 通过比较能隙大小, 可以了解影响锂离子电池活性材料的实际容量的本质因素.

关键词 锂离子电池, 正极材料, 实际容量, 能隙

锂离子电池是一种电能储备转换的新能源技术, 它利用了锂离子在正负电极材料中的可逆循环脱嵌过程. 正负电极活性材料的能量密度、循环稳定性和输出效率都是决定整个电池性能的关键因素. 正极材料的理论容量可以直接利用化学式估算得到. 例如, LiCoO_2 摩尔质量 $M=97.8698\text{ g/mol}$, 如果锂离子全部脱嵌, 其理论容量 $=F/M=985.8535\text{ C/g}$, 单位换算后为 273.848 mAh/g . 但是, 这个值只是理论的克容量, 实际容量则是指在一定的放电制度下(一定温度, 一定的电流密度和终止电压)电池所能给出的电量, 为保证其结构可逆, 正极材料并不是所有的锂离子都从正极材料结构中脱出. 对于不同材料来讲, 实际容量有很大差异^[1], 一般 LiCoO_2 的实际脱锂系数只有0.6左右. 脱锂系数是影响实际容量中的关键因素之一, 实际脱锂系数越大, 实际容量越大.

目前实验研究表明, 正极材料在首次充放电过程中会产生固体电解质界面(SEI)膜, 将造成一定的

锂损耗, 但事先可以添加富裕锂来弥补损失, 脱嵌系数在此后的过程中相对变化不大. 研究发现, 影响锂离子脱嵌系数的因素有很多, 除了测量条件影响外, 本身材料的影响因素也很重要, 本身因素中还包括本征结构、表面形貌和微结构等. 但是, 后两者可以通过制备过程的优化和微结构设计的调整实现一部分改善, 而关键的本征影响因素则是由材料本身成分和结构特征决定的, 无法后天来弥补, 因此, 正极材料的成分和结构对实际脱锂系数的影响更为关键, 成为锂离子电池技术重点研究的问题^[2,3].

本文为了确定影响锂离子电池正极材料实际容量的本征因素, 系统地研究了目前主要的20种典型正极材料体系, 计算了脱锂前后2种模型的能带结构, 确定了能隙变化与实际脱锂系数的一个定量关系, 此规律表明, 正极材料的实际脱锂系数本质上是与脱锂前后能隙比值有关联, 利用这一规律可以评估活性材料的实际容量, 这些结果对于正极材料的改性优化和

引用格式: 陈宁, 王博, 刘洋, 等. 影响锂离子电池实际容量的材料因素. 科学通报, 2018, 63: 3484–3493

Chen N, Wang B, Liu Y, et al. The material influence factors on the actual capacity of lithium ion battery (in Chinese). Chin Sci Bull, 2018, 63: 3484–3493, doi: 10.1360/N972018-00790

新的正极材料开发有着一定的理论指导意义。

1 研究思路

目前为止,研究实际容量的手段还主要是实验方法,通过系统的实际样品测量比较,可得到实际容量密度参数.在该研究中,需要排除材料表面形貌和微结构等外界影响因素,实验测试过程比较复杂.虽然可以根据材料的化学方程式给出一个理论容量密度,但理论上无法评估它的实际容量,我们还不清楚有哪些材料因素能够影响实际容量,特别是与成分和结构关系密切的那些本征影响因素.

正极材料的实际脱锂系数(actual delithiation coefficient, %)=实际比容量/理论比容量,从理论上来看往往由材料的综合稳定性决定,要得到一个较高的实际容量,要求充放电前后,也就是脱锂前后结构的整体稳定性都要高^[4,5](本文只讨论脱嵌型正极材料热力学,不讨论转化型正极以及可能涉及到的动力学问题).但是,整体稳定性只是一个理论概念,还需要找到一个比较实用的,可计算甚至可测量的方法获得,所以我们需要寻找到一个能够评价实际脱锂系数的分析参数.

由于脱锂前后,晶体结构类型可能会发生变化,晶体结构既有二维层状晶型也有三维立体晶型,不同结构之间的差异很难直接比较.此外,虽然化学键的变化对于结构稳定性也很重要,但是,正极材料化学键类型很多,脱锂前后化学键的类型和数量都在变化,很难利用化学键来评价实际容量的影响^[6].所以,如果要定量了解影响实际脱锂系数的本质因素,需要挖掘更深层次的结构特征参数.

材料能带结构中,价带与导带之间的禁带宽度叫作能隙,如图1所示.对于正极材料,多数为半导体晶体材料,能隙是这类材料重要的电子结构特征参数^[7].从能带理论上,能隙似乎只与电子跃迁(激发)相关.但是,实际上,能隙与相结构稳定性也有关系,特别是与二级相变(磁性相变)的转变温度相关,甚至与催化活性等性质也有一定的联系^[8].由于脱嵌过程很多性质问题主要是与结构稳定性变化相关,因此通过能隙比较可以讨论脱锂前后性能的变化.所以,这里尝试利用脱锂前后结构带来的能隙变化,讨论脱嵌过程中的实际脱锂系数问题.

正极材料本质上属于晶体材料,实际中还包括小于微米的微晶以及部分非晶态,以下只讨论晶态

图1 (网络版彩色) LiCoO₂的第一性原理DFT方法计算得到的电子态密度图,其中显示脱锂前后能隙分别为2.51 eV(脱锂前)和1.16 eV(脱锂后).计算结果显示,对于大多数正极材料脱锂前后两相都有一定的并且相近的能隙值. DOS图展宽因子为0.1 eV,费米能级设为0

Figure 1 (Color online) Density of states (DOS) diagram of LiCoO₂, calculated by first-principle DFT methods, with the energy gaps (E_g) of LiCoO₂ (before delithiation) and CoO₂ (after delithiation). It shows that the E_g values of two phase structures before and after delithiation are similar and finite for most of cathode materials (also seeing Table 1). DOS is calculated by smearing width 0.1 eV. 0 is set to be Fermi level

结构的相关本征影响因素,根据晶体结构模型的能带结构计算可以得到体系总能量^[9],通过脱锂前后的总能量差,可以直接得到不同正极材料的脱锂电压^[10],这说明这种计算方法对于锂离子材料研究是相对成熟的.此外,通过能带结构(图1)确定能隙也相对简单.我们首先需要建立相关正极体系纯母体的计算模型,然后再选择合理的计算参数,通过理论计算,最终得到电子结构能隙参数.但是,要正确得到一个相对准确的能带参数还是有一定困难的,特别是对于含有过渡族金属元素的正极材料,过渡族金属离子与O离子的相互作用比较复杂,因此,计算参数对能隙的计算结果有一定的影响(见后面讨论).作为原子尺度上的计算,第一性原理可以给出热力学平衡下的性质,如晶体结构和相变,可以对储能材料设计中的容量、循环稳定性和热稳定性等电化学特性进行了深入研究,可用于材料性能的提升以及新材料设计^[11,12].本研究使用基于第一性原理的密度泛函理论(DFT)方法,采用了Materials Studio中的CASTEP模块^[13],交互关联函数采用PBE的广义梯度近似^[14](generalized gradient approximations, GGA)方法来描述,离子势采用超软(ultrasoft)赝势.为了减少晶体结构参数的相对误差,本研究对于脱嵌锂离子

子的2个模型都根据初始晶胞参数(表1), 采用了相同的几何优化(geometry optimization), 其中利用了程序中的BFGS算法拟合算法, 残留应力(residual force)< 0.02 eV/Å. 在倒易的k空间中, 计算选取平面波动能截止能量为480 eV. 电子和离子弛豫运动的阈值为 2×10^{-6} eV, 相关计算k网格点均设置为Medium. 模型均采用反铁磁模型(与实验结果基本一致^[76]), U势均取为4.5 eV.

2 研究结果和规律

为了确定实际容量与脱锂前后结构能隙之间的关系, 需要比较足够多具有代表性的材料体系. 锂离子电池体系的正极材料选择有很多, 收集最典型的体系会更客观地了解实际容量的客观规律. 本文所用的大数据主要来源已发表的各种锂电池相关文献(Web of Science), 近十几年有两万多篇, 实际容量测

量数据的占比不大, 但也有接近1000篇, 我们从总结中总结出目前最常见的20多种典型的纯母体体系(可参照材料基因工程专用数据库<https://www.mgdata.cn>能源材料分类), 它们可占有体系总数的91%以上, 实际还有很多体系都是以这些母体为主演变出来, 目前常用的LiMO₂, 尖晶石LiM₂O₄和LiFePO₄(磷酸铁锂)等3种正极材料体系, 三者之和接近70%, 这些体系占据比例如图2所示.

除了确定典型体系外, 还要收集这些体系实际容量的实验数据. 收集数据时, 首先需要剔除晶体微结构和表面形貌差异造成的影响, 也要排除测量条件的差异, 才能合理地分析出体系对性能影响的本征因素. 本文选择了测试条件和材料非本征结构因素尽可能一致的数据, 这些数据能反映出材料更本征的性能特征, 其性能数据如表1所示, 同时也列出了相关体系脱锂前后的能隙的计算值. 将实际脱锂

表1 20种典型锂离子电池正极材料的理论比容量和实际比容量(平均值)、脱锂前后能隙以及晶格参数

Table 1 Theoretical and practical capacities (average value), band-gaps before and after delithiation, and lattice constants for 20 typical cathode materials

体系	化学式	比容量(mAh/g)			能隙 E_g (eV)		晶格参数(Å)			
		理论	实际 ^{a)}	文献	脱锂前	脱锂后	<i>a</i>	<i>b</i>	<i>c</i>	文献
层状化合物	LiCoO ₂	274	159.1	[15~17]	2.507	1.160	2.816	2.816	14.0542	[28]
	LiNiO ₂	275	169.9	[18~22]	0	1.357	2.878	2.878	14.19	[29]
	LiMnO ₂	285	171.3	[23,24]	1.347	0	2.804	5.758	4.576	[30]
	LiV ₃ O ₈	372	239.5	[25~27]	0.01	1.752	6.68	3.60	12.03	[31]
橄榄石	LiFePO ₄	170	134.3	[32~36]	3.71	2.396	10.3009	5.9925	4.6942	[45]
	LiCoPO ₄	167	111.4	[37~40]	3.57	1.383	5.037	6.793	10.199	[46]
	LiNiPO ₄	167	72.7	[41,42]	3.117	0.782	10.0317	5.8539	4.6768	[47]
	LiMnPO ₄	171	112	[43,44]	3.54	1.188	6.10	10.46	4.744	[48]
尖晶石	LiMn ₂ O ₄	148	117.6	[50~51]	0	1.241	8.245	8.245	8.245	[52]
硅酸盐	Li ₂ FeSiO ₄	331	143	[53,54]	3.384	0	8.325	5.114	10.804	[46]
	Li ₂ MnSiO ₄	333	121.6	[55,56]	3.318	0.122	5.058	5.454	6.374	[46]
	Li ₂ NiSiO ₄	326	151	[53]	1.723	0.404	4.99	6.345	10.736	[46]
硼酸盐	LiFeBO ₃	220	119	[57]	3.347	1.049	5.197	9.081	10.338	[46]
	LiMnBO ₃	222	65.5	[58,59]	3.002	0	8.27	8.27	3.195	[46]
	LiCoBO ₃	215	37	[60]	3.217	0.827	5.283	8.387	6.686	[46]
其他	Li ₃ V ₂ (PO ₄) ₃	197	143.3	[61~64]	2.157	1.169	8.6056	8.5917	12.037	[75]
	Li ₂ FeP ₂ O ₇	220	97	[65]	3.768	0.507	15.555	5.067	8.952	[46]
	LiVOPO ₄	159	117.3	[66~69]	2.11	1.78	6.937	7.154	7.964	[46]
	LiVPO ₄ F	156	117.7	[70,71]	2.308	1.169	5.235	5.39	7.43	[46]
	LiFeSO ₄ F	151	61	[72~74]	4.023	1.491	5.199	5.588	7.354	[46]

a) 数据筛选条件. 测试所用负极: 锂金属; 电解质: LiPF₆/DMC/EC; 电流密度: 0.1 C; 测试温度: 25℃; 不同的正极材料取其对应的充放电平台

图2 基于锂离子电池数据库的正极材料比例分布图, 其中Li₂MSiO₄(M=Fe, Mn, Ni)和LiMBO₃(M=Fe, Mn, Co)含多个体系, 以上显示的分类占所有正极材料的90%以上

Figure 2 The cartogram for most cathode materials based on lithium ion battery database, in which Li₂MSiO₄ (M=Fe, Mn and Ni) and LiMBO₃(M=Fe, Mn and Co) are composed of several similar systems. The above materials account for more than 90% of all cathode materials

系数(实际比容量/理论比容量)与能隙计算参数进行分析后, 最终总结了两者之间的关系, 如图3(a)所示, 这个规律反映了实际脱锂系数与脱锂前后的能隙比之间的定量关系, 其中的修正参数 C_0 为常数, 物理意义见后面详细讨论. 从这个规律可以看出, 脱锂前后的能隙相对比值是决定实际容量的重要因素, 两者修正后的比值非常关键, 脱锂前后能隙越接近, 实际容量相对越大.

这个规律反映了正极材料脱嵌锂离子循环过程中能隙变化的特点. 对于脱锂后的能隙相对大的体系, 如图3(b)(上)所示, 这相当于脱锂前(后)的瓶子比较大, 脱锂后(前)的瓶子比较小, 从一个小瓶子倒“水”(锂离子)到另一个大瓶子的时候, 所有“水”都被有效地转移到后面的过程中, 虽然整个脱嵌过程基本没有损耗, 但瓶子的利用效率比较小(Bad%). 另一方面, 如果脱锂前后的能隙相差不大的情况, 如图3(b)(下)所示, 前面的瓶子与后面的瓶子基本一样, 从一个瓶子倒“水”到另一个瓶子的时候, 所有“水”都被有效地转换到后面的循环过程中, 因此, 实际脱锂系数就会保持一定的效率(Good%). 因此, 脱锂前后

的能隙差别越大, 实际脱锂系数就越小, 实际容量也就相对于理论容量也越小.

在研究过程中我们还发现, 典型体系计算得到的能隙理论值与它们实际测量值有一定差距, 能隙值一般都偏小, 因此, 在前后能隙比较前, 两边都加上一个常数 C_0 , 其中有部分原因就是因为在DFT理论计算得到能隙会有一定的偏小, 多数与文献报道的实验值偏小大约1 eV. 此外, 增加常数 C_0 还有一个重要的物理意义: 作为一个锂离子电池正极材料, 其脱锂前后必须有一定的稳定性. 实验也证实, 首次充放电后材料的表面都会增加一些稳定SEI膜. 由于SEI膜包裹在正负极材料外层, 隔绝电解液, 相当于形成了一个稳定框架结构, 所以正极材料(包括负极)在脱嵌过程都会有一些稳定性增加, 正极材料本身都有一个基础的“能隙值”, 这里最终取了 $C_0 \sim 1.5$ eV, 可以得到一个相对好的规律(其他 $C_0 = 2.0 \sim 0.5$ 的规律也比较好), 如图3(a)所示.

此外, 我们知道对于所有的负极活性材料(如石墨), 基本上是导电率比较好的材料, 因此, 无论是理论还是实际测量, 负极材料的能隙都很小, 脱锂前

图3 实际容量与能隙变化规律及示意图. (a) 脱锂前后的能隙比较与实际脱锂系数的关系; (b) 好的(Good%)和坏的(Bad%)两种情况下的实际脱锂系数示意图

Figure 3 The rule and schematic diagram of actual capacity and the change of energy gap. (a) Comparison plots between energy band-gaps of before and after delithiation and actual delithiation coefficient (%); (b) the sketch diagram for “Good%” and “Bad%” two conditions of actual delithiation coefficient

后比值基本都接近于1, 而这类材料的实际脱嵌锂离子效应都很高, 一般在锂离子电池设计中都不太考虑这些材料的实际容量问题. 所以, 所有负极材料的位置都应该在规律图3中的右上角(图3(a)中负极材料). 再者, 对于锂离子电池中所有的电解质材料, 其母体的能隙非常大, 基本在4 eV以上, 而且, 材料中没有含可变价元素, 所以只要有锂离子脱出, 该结构晶体马上就变成没有能隙的体系, 脱锂前后的能隙比值基本上是接近于0的; 而且按实际情况, 脱锂的效率也为0, 电解质材料的位置正好处于整个图3(a)的左下角(图3(a)中电解质材料). 图3(a)的趋势实际上已经包含了锂离子电池所有材料的规律, 不仅是正极负极活性材料, 也包括固体电解质材料, 可以作为未来选择锂离子电池材料和优化锂离子电池材料的理论指导的本征因素规律.

3 讨论

从得到的规律可以看出(图3(a)), 对于大多数正极材料, 脱锂前后都存在一定的能隙, 前后相当的能隙能够很好地改善实际容量/理论容量的数值, 这是该规律能够比较好地反映实际容量本质的根本原因. 但是, 究竟是什么原因导致了脱锂前后都保留有一定能隙, 而且好的正极材料脱锂前后能隙还能基本不变呢? 让我们仔细分析一下LiCoO₂的脱锂前后的电子结构键价的特点, 如图4所示.

图4 LiCoO₂的脱锂前后的化学键变化过程示意图. 对于脱锂前锂离子(右侧黄色小球)提供正电荷, Co-O层提供负电荷, 因此结构整体为纯的离子键. 脱嵌锂离子之后, 只留下Co离子(左侧深色大球)与O离子(左侧绿色小球)构成的Co-O层, 层间为范德化键, 层内为超交换作用, 因此, 同时包括超交换作用和范德化键. 这种化学键的变化能够很好地解释LiCoO₂在脱嵌锂离子过程中能保持相对一致能隙的原因

Figure 4 The sketch diagram of chemical bonding change in delithiation progress of the LiCoO₂ structure. For the lithiation process of LiCoO₂ structure, there is an ionic bond (red rod) in the Co-O layer and the Li-ion (right small yellow ball). Meanwhile, for the delithiation process of LiCoO₂ layer, only Co-ions (left large dark ball) and O-ions (left small green ball) layer is left, which presents a super-exchange interaction as well as the Van del Waals bond between each CoO₂ layer. This gives a good explanation on these two similar energy gaps of LiCoO₂ before and after the extraction of Li-ions

我们发现, 正极材料体系之所以多数脱锂前后都有能隙, 与过渡族金属元素(例如Co等)具有变价特征是分不开的, Co离子与O离子可以在脱锂前后发生相互作用的变化, 可以在离子库伦作用(脱锂前)与超交

换作用和范德化作用(Van del Walls)(脱锂后)——2个“平台”之间不断的切换,如图4所示,存在左右两个不同化学键平台。

从图4可以看出,脱锂前,当 Li^+ 在体系中时, CoO_2 层没有显示出反铁磁的排布特征(理论计算可以给出脱嵌 Li^+ 结构的反铁磁的自旋分布图),此时由于 Li^+ 存在, CoO_2 层得到部分锂离子电荷,整个层显示出一定的负电荷,因此 CoO_2 层与 Li^+ 之间存在一定的离子库伦相互作用,这是 LiCoO_2 脱锂前具有一个较大能隙的主要原因。另一方面,当 Li^+ 脱出之后,虽然层间的库伦作用消失了,但 CoO_2 层内部出现反铁磁的排列,也表明脱 Li^+ 结构中出现了超交换作用(图4左边Co-O之间的杂化共价键,红色棒),是脱出 Li^+ 后的体系能隙的主要来源。总之,脱锂之前会有一个较弱离子键对应产生的能隙。脱锂之后,层间的离子键消失,层间的范德化键出现,这导致能隙会有所下降或消失。最关键的是,此时反铁磁的超交换作用的出现,能隙有一定的恢复,最终导致脱锂前后能隙变化不大。因此,能隙前后变化较小的体系,对于 Li^+ 保持前后的容量非常有利。很显然,从材料本质原因看,正是由于以上化学键变化的存在,因此用能隙对比来分析脱锂前后稳定性是比较合理的,适合用它来讨论正极材料的有效脱锂系数的本征影响因素,

这个化学键的变化规律其实最早是由锂离子电池之父Goodenough^[77]提出,他也由此开发出了 LiCoO_2 和 LiFePO_4 等几种关键的锂离子正极材料。

当然,实际研究中容量非常复杂,影响因素非常多,不仅要考虑这里讨论的材料本征因素,还要考虑材料表面形貌和微结构等影响因素,甚至还考虑影响充放电制度等外部环境因素,有时候这些附加影响因素甚至能够完全超过我们这里讨论的本征因素,但毕竟本征因素是材料最基础的不可替代因素,其他因素都可以后天弥补。

4 结论

从目前理论计算的能隙值和实验测量得到的数据看,多数正极材料中,在脱锂前后往往都存在着一一定的能隙。通过20种典型体系的性能数据与能隙计算值的比较,我们确定了正极材料的能隙与实际脱锂系数的关系,这个规律反映了正极材料中结构本征因素对实际容量的直接影响。新得到的规律表明,影响实际容量的本征结构因素是与能隙有密切关系,正极材料的脱锂前后的能隙比可以作为分析影响锂电池实际脱锂系数的材料本征参数,两者越接近,体系的实际容量/理论容量就越大。此外,该规律也适合负极和电解质材料的能隙变化特征。

参考文献

- 1 Lei W, He Y, Yu J. Preliminary study of structural stability of cathode material LiMn_2O_4 for lithium batteries. *Mater Rev*, 2001, 15: 62–64
- 2 Yadav G G, David A, Zhu H, et al. Microemulsion-based synthesis and electrochemical evaluation of different nanostructures of LiCoO_2 prepared through sacrificial nanowire templates. *Nanoscale*, 2014, 6: 860–866
- 3 Wang H, Tan T A, Yang P, et al. High-rate performances of the Ru-doped spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$: Effects of doping and particle size. *J Phys Chem C*, 2011, 115: 6102–6110
- 4 Wang W, Zhang J, Jia Z, et al. Enhancement of the cycling performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ by stabilizing the crystal structure through Zn^{2+} doping. *Phys Chem Chem Phys*, 2014, 16: 13858–13865
- 5 Kitamura N, Korechika Y, Saruwatari H, et al. Effect of supersonic-wave treatment in Zn aqueous solution on property, crystal structure and cycle performance of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as a cathode material for 5 V class Li ion battery. *Solid State Ionics*, 2011, 183: 54–59
- 6 Song J W, Nguyen C C, Choi H, et al. Impacts of surface Mn valence on cycling performance and surface chemistry of Li- and Al-substituted spinel battery cathodes. *J Electrochem Soc*, 2011, 158: A458–A464
- 7 Canivez Y. Quick and easy measurement of the band gap in semiconductors. *Eur J Phys*, 1983, 4: 42
- 8 Chang X W, Chen N, Wang L J, et al. Optimization rule of anode materials for solid oxide fuel cells. *J Inorg Mater*, 2015, 30: 1043–1048
- 9 Ren Y M, Chen N, Zhao H L, et al. Theoretical research on optimization dopant regulation of La_2BO_4 (B:B-site element) series mixed conductor materials. *J Inorg Mater*, 2013, 28: 841–846
- 10 Zhu X H, Chen N, Lian F, et al. First principle calculation of lithiation/delithiation voltage in Li-ion battery materials. *Chin Sci Bull*, 2011, 56: 3229–3232
- 11 Shi S, Gao J, Liu Y, et al. Multi-scale computation methods: Their applications in lithium-ion battery research and development. *Chin Phys B*, 2016, 25: 178–201

- 12 Liu Y, Zhao T, Ju W, et al. Materials discovery and design using machine learning. *J Materiomics*, 2017, 3: 159–177
- 13 Clark S J, Segall M D, Pickard C J, et al. First principles methods using CASTEP. *Z Kristallogr*, 2005, 220: 567–570
- 14 Perdew J P, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*, 1996, 77: 3865–3868
- 15 Chen G, Geng H, Wang Z, et al. On electrochemistry of Al_2O_3 -coated LiCoO_2 composite cathode with improved cycle stability. *Ionics*, 2016, 22: 629–636
- 16 Zhang W, Chi Z X, Mao W X, et al. One-nanometer-precision control of Al_2O_3 nanoshells through a solution-based synthesis route. *Angew Chem Int Ed*, 2014, 53: 12776–12780
- 17 Cao H, Xia B J, Zhang Y, et al. LiAlO_2 -coated LiCoO_2 as cathode material for lithium ion batteries. *Solid State Ionics*, 2005, 176: 911–914
- 18 Ke D U. Research on synthesis and performance of composite cathode material $\text{Li}[\text{Ni}_{0.92}\text{Co}_{0.04}\text{Mn}_{0.04}]\text{O}_2$ with gradient-coating layer as lithium ion battery. *Chin J Inorg Chem*, 2013, 29: 1031–1036
- 19 Kwon S N, Song M Y, Park H R. Electrochemical properties of LiNiO_2 substituted by Al or Ti for Ni via the combustion method. *Ceram Int*, 2014, 40: 14141–14147
- 20 Song M, Kwon I, Shim S, et al. Electrochemical characterizations of Fe-substituted LiNiO_2 synthesized in air by the combustion method. *Ceram Int*, 2010, 36: 1225–1231
- 21 Kwon S N, Song J, Mumm D R. Effects of cathode fabrication conditions and cycling on the electrochemical performance of LiNiO_2 synthesized by combustion and calcination. *Ceram Int*, 2011, 37: 1543–1548
- 22 Park H R. Electrochemical properties of LiNiO_2 and LiNiO_2 substituted with Ga, Al and/or Ti. *J Ind Eng Chem*, 2010, 16: 698–702
- 23 Yoshida R, Kodera T, Myoujin K, et al. Synthesis and electrochemical properties of layered type LiMnO_2 powders by spray pyrolysis. *Trans Mat Res Soc Jpn*, 2009, 34: 129–132
- 24 Ji H, Miao X, Wang L, et al. Effects of microwave-hydrothermal conditions on the purity and electrochemical performance of orthorhombic LiMnO_2 . *ACS Sustain Chem Eng*, 2014, 2: 359–366
- 25 He C X, Hu S M, Ren X Z, et al. Synthesis conditions optimization of lithium vanadium as cathode materials for lithium-ion battery by sol-gel method. *Rare Metal Mat Eng*, 2012, 41: 663–667
- 26 Ren X, Hu S, Shi C, et al. Preparation and electrochemical properties of Zr-doped LiV_3O_8 cathode materials for lithium-ion batteries. *J Solid State Electrochem*, 2012, 16: 2135–2141
- 27 Ren X, Hu S, Shi C, et al. Preparation of Ga-doped lithium trivanadates as cathode materials for lithium-ion batteries. *Electrochim Acta*, 2012, 63: 232–237
- 28 Takahashi Y, Kijima N, Dokko K, et al. Structure and electron density analysis of electrochemically and chemically delithiated LiCoO_2 single crystals. *J Solid State Chem*, 2007, 180: 313–321
- 29 Dyer L D, Jr B S B, Smith G P. Alkali metal-nickel oxides of the type MNiO_2 . *J Am Chem Soc*, 1954, 76: 1499–1503
- 30 Dittrich G, Hoppe R. Zur Kristallstruktur von LiMnO_2 . *Z Anorg Allg Chem*, 1969, 368: 262–270
- 31 Wadsley A D. Crystal chemistry of non-stoichiometric pentavalent vanadium oxides: crystal structure of $\text{Li}_{1+x}\text{V}_3\text{O}_8$. *Acta Crystallogr*, 1957, 10: 261–267
- 32 Wang L, Tang Z Y, Ruan Y L, et al. Improvement of electrochemical performance of LiFePO_4 as a novel cathode material. *Chin J Power Sources*, 2006, 30: 549–548
- 33 Zhang X D, Zhang X G, He W, et al. High-performance mesoporous LiFePO_4 from Baker's yeast. *Colloid Surf B Biointerfaces*, 2013, 103: 114–120
- 34 Dai Y, Ma L, Zhang H, et al. Hydrothermal synthesis of spindle-like nanostructured LiFePO_4 powders mediated by organic acid. *Int J Electrochem Sci*, 2016, 11: 1730–1737
- 35 Guo H, Zhang X, He W, et al. Fabricating three-dimensional mesoporous carbon network-coated $\text{LiFePO}_4/\text{Fe}$ nanospheres using thermal conversion of alginate-biomass. *RSC Adv*, 2016, 6: 16933–16940
- 36 Xu F, Wang R, Zhang R, et al. Structure and electrochemical performance of LiFePO_4 modified with mononuclear and binuclear phthalocyanines as cathode materials. *J Mater Res*, 2017, 32: 1168–1176
- 37 Eftekhari A. Surface modification of thin-film based LiCoPO_4 5 V cathode with metal oxide. *J Electrochem Soc*, 2004, 151: A1456–A1460
- 38 Maeyoshi Y, Miyamoto S, Noda Y, et al. Effect of organic additives on characteristics of carbon-coated LiCoPO_4 synthesized by hydrothermal method. *J Power Sources*, 2017, 337: 92–99
- 39 Chen H, Chen M, Du C, et al. Synthesis and electrochemical performance of hierarchical nanocomposite of carbon coated LiCoPO_4 crosslinked by graphene. *Mater Chem Phys*, 2016, 171: 6–10
- 40 Wang F, Yang J, NuLi Y, et al. Highly promoted electrochemical performance of 5 V LiCoPO_4 cathode material by addition of vanadium. *J Power Sources*, 2010, 195: 6884–6887

- 41 Örnek A. The synthesis of novel LiNiPO_4 core and $\text{Co}_3\text{O}_4/\text{CoO}$ shell materials by combining them with hard-template and solvothermal routes. *J Colloid Interface Sci*, 2017, 504: 468–478
- 42 Örnek A, Kazancioglu M Z. A novel and effective strategy for producing core-shell LiNiPO_4/C cathode material for excellent electrochemical stability using a long-time and low-level microwave approach. *Scr Mater*, 2016, 122: 45–49
- 43 Kim J K, Shin C R, Ahn J H, et al. Highly porous LiMnPO_4 in combination with an ionic liquid-based polymer gel electrolyte for lithium batteries. *Electrochem Commun*, 2011, 13: 1105–1108
- 44 Rajammal K, Sivakumar D, Duraisamy N, et al. Structural and electrochemical characterizations of $\text{LiMn}_{1-x}\text{Al}_{0.5x}\text{Cu}_{0.5x}\text{PO}_4$ ($x=0.0, 0.1, 0.2$) cathode materials for lithium ion batteries. *Mater Lett*, 2016, 173: 131–135
- 45 Sanchez M A E, Brito G E S, Fantini M C A, et al. Synthesis and characterization of LiFePO_4 prepared by sol-gel technique. *Solid State Ionics*, 2006, 177: 497–500
- 46 Jain A, Ong S P, Hautier G, et al. Commentary: The materials project: A materials genome approach to accelerating materials innovation. *APL Mater*, 2013, 1: 1049
- 47 Abrahams I, Easson K S. Structure of lithium nickel phosphate. *Acta Crystallogr*, 1993, 49: 925–926
- 48 Geller S, Durand J L. Refinement of the structure of LiMnPO_4 . *Acta Crystallogr*, 1960, 13: 325–331
- 49 Wang L B, Tang W J, Su L W, et al. Preparation and lithium storage performance of LiMn_2O_4 nanomaterials by dynamic hydrothermal synthesis. *J Zhejiang Univ Technol (China)*, 2014, 42: 473–477
- 50 Cui Y L, Xu K, Yuan Z, et al. Synthesis and electrochemical performance of graphene modified nano-spinel LiMn_2O_4 cathode materials. *Chin J Inorg Chem*, 2013, 29: 50–56
- 51 Zou X, Wu P, Xie H C. Effect of high levels of impurity calcium on the electrochemical performance of Spinel LiMn_2O_4 . In: *Proceedings of the 2016 International Conference on Material Science and Engineering*. Paris: Atlantis Press, 2016. 503–509
- 52 Mosbah A, Verbaere A, Tournoux M. Phases $\text{Li}_x\text{MnO}_{2x}$ rattachees au type spinelle. *Mater Res Bull*, 1983, 18: 1375–1381
- 53 Shenouda A Y, Sanad M M S. Electrochemical performance optimization of $\text{Li}_2\text{Ni}_x\text{Fe}_{1-x}\text{SiO}_4$ cathode materials for lithium-ion batteries. *J Electrochem Energy Convers Storage*, 2017, 14: 5
- 54 Liu L, Wang P, Li J, et al. Hydrothermal preparation and intrinsic transport properties of nanoscale $\text{Li}_2\text{FeSiO}_4$. *Solid State Ionics*, 2018, 320: 353–359
- 55 Tan G, Gui D, Xiong W, et al. Sol-gel synthesis of $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite with improved electrochemical performance for lithium-ion batteries. In: *Proceedings of the 16th International Conference on Electronic Packaging Technology*, 2015
- 56 Wu T T, Liu J Y, Li Y H, et al. Effects of B doping on electrochemical performance of $\text{Li}_2\text{MnSiO}_4$. *Chin J Power Sources*, 2018, 42: 321–323, 332
- 57 Dong Y Z, Zhao Y M, Shi Z D, et al. The structure and electrochemical performance of LiFeBO_3 as a novel Li-battery cathode material. *Electrochim Acta*, 2008, 53: 2339–2345
- 58 Ragupathi V, Srimathi K, Panigrahi P, et al. Electrochemical performance of sol-gel derived hexagonal LiMnBO_3 cathode material for lithium-ion batteries. *Nano Hybrids Compos*, 2017, 17: 106–112
- 59 Hou X M, Zhao Y M, Dong Y Z. Preparation and characterization of new cathode material LiMnBO_3 for lithium ion battery. *Chin J Power Sources*, 2008, 32: 611–613
- 60 Chen W, Liu J, Zhang X, et al. Synthesis and electrochemical performance of carbon-coated LiCoBO_3 as cathode materials for lithium-ion batteries. *Ionics*, 2017, 24: 1571–1577
- 61 Zhang L, Wang X L, Xiang J Y, et al. Synthesis and electrochemical performances of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/(\text{Ag}+\text{C})$ composite cathode. *J Power Sources*, 2010, 195: 5057–5061
- 62 Lee S N, Kim H S, An J Y, et al. Preparation and characterization of chlorine doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as high rate cathode active material for lithium secondary batteries. *J Nanosci Nanotechnol*, 2014, 14: 7516–7520
- 63 Li W L, Li Y J, Cao M L, et al. Synthesis and electrochemical performance of alginate acid-based carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite by rheological phase method. *Acta Phys Chim Sin*, 2017, 33: 2261–2267
- 64 Lai C, Wei J, Wang Z, et al. $\text{Li}_3\text{V}_2(\text{PO}_4)_3/(\text{SiO}_2+\text{C})$ composite with better stability and electrochemical properties for lithium-ion batteries. *Solid State Ionics*, 2015, 272: 121–126
- 65 Xu J, Chou S L, Gu Q F, et al. Study on vanadium substitution to iron in $\text{Li}_2\text{FeP}_2\text{O}_7$ as cathode material for lithium-ion batteries. *Electrochim Acta*, 2014, 141: 195–202
- 66 Kerr T A, Gaubicher J, Nazar L F. Highly reversible Li insertion at 4 V in $\text{e-VOPO}_4/\text{a-LiVOPO}_4$ cathodes. *Electrochem Solid-State Lett*, 2000, 3: 460–462
- 67 Shen C, Zheng J, Zhang B, et al. Composite cathode material $\beta\text{-LiVOPO}_4/\text{LaPO}_4$ with enhanced electrochemical properties for lithium ion batteries. *RSC Adv*, 2014, 4: 40912–40916

- 68 Hameed A S, Nagarathinam M, Reddy M V, et al. Synthesis and electrochemical studies of layer-structured metastable α - LiVOPO_4 . *J Mater Chem*, 2012, 22: 7206–7213
- 69 Xiong L Z, He Z Q. A new rheological phase route to synthesize nano- LiVOPO_4 cathode material for lithium-ion batteries. *Acta Phys-Chim Sin*, 2010, 26: 573–577
- 70 Yang B, Yang L. Silver-coated LiVPO_4F composite with improved electrochemical performance as cathode material for lithium-ion batteries. *J Phys Chem Solids*, 2015, 87: 228–232
- 71 Li Y Z, Ren J X, Zhou Z, et al. Preparation and electrochemical performance of rechargeable lithium battery LiVPO_4F cathode material. *Chin J Inorg Chem*, 2005, 21: 1597–1600
- 72 Guo W, Yin Y X, Zhang Y L, et al. Synthesis and electrochemical properties of LiFeSO_4F /graphene composite as cathode material for lithium-ion batteries. *J Electrochem*, 2012, 44: 201–206
- 73 Guo Z, Zhang D, Qiu H, et al. Improved electrochemical properties of tavorite LiFeSO_4F by surface coating with hydrophilic poly-dopamine via a self-polymerization process. *RSC Adv*, 2016, 6: 6523–6527
- 74 Guo Z, Zhang D, Qiu H, et al. Improved cycle stability and rate capability of graphene oxide wrapped tavorite LiFeSO_4F as cathode material for lithium-ion batteries. *ACS Appl Mater Interfaces*, 2015, 7: 13972–13979
- 75 Yin S C, Grondy H, Strobel P, et al. Electrochemical property: Structure relationships in monoclinic $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$. *J Am Chem Soc*, 2003, 125: 10402–10411
- 76 Feng R, Jin G. *Condensed State Physics. Volume 1*. Beijing: Higher Education Press, 2003. 290
- 77 Goodenough J B. Theory of the role of covalence in the perovskite-type manganites $[\text{La}, \text{M(II)}]\text{MnO}_3$. *Phys Rev*, 1955, 100: 564–573

Summary for “影响锂离子电池实际容量的材料因素”

The material influence factors on the actual capacity of lithium ion battery

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The actual specific capacity of the cathode materials, as one of the key factors affecting the energy density of the lithium ion battery, is lower than its theoretical specific capacity. The ratio of actual capacity to theoretical capacity is various for different cathode active materials for lithium ion battery (LIB), which mainly due to the difference in delithiation coefficient caused by the difference in the actual delithiation mechanism during charging. The previous experimental results show that there are many factors influencing the actual delithiation coefficient. In addition to the effects of measurement and preparation conditions, material intrinsic factors are also critical. Although the crystal structure factor, including surface morphology and microstructure, can be improved by process optimization during the preparation process to improve battery capacity, it has not been well understood why the material causing low battery capacity is intrinsic. Therefore, improving the intrinsic structural factors of the cathode materials is more critical to the actual delithiation coefficient, which becomes a key issue in lithium ion battery technology.

Since the experimental value of actual capacity are influenced by many macro factors, in order to find material-dependency parameters that affect the actual capacity and get a big data properties including as much parent cathode material systems for LIB as possible, a unified data collection standard designed by the author of this article is used to eliminate the influence of macro factors. In this paper, under the unified standard, the crystal structures and actual capacity experimental parameters of 20 typical cathode materials were collected through the big data, such as layered LiMO_2 ($\text{M}=\text{Ni}$ and Co), spinel LiMn_2O_4 , LiMPO_4 ($\text{M}=\text{Fe}$, Mn and Ni) and LiMBO_3 ($\text{M}=\text{Fe}$, Mn and Co), etc. Then, the energy gaps between the valence bands and the conduction bands of these typical matrices were calculated by means of the first-principles calculation.

The correlation between the energy gap change and the actuality delithiation coefficient was obtained by comparing the energy gap values between these two structure models before and after deintercalation of lithium ion. It shows that the cathode material possesses larger actual delithiation coefficient as well as the actual capacity when two energy gaps are comparable before and after delithiation. These results reveal that the energy gap comparison is suitable to understanding the essential material factors affecting the actual capacity of the cathode material of the lithium ion battery. The detailed analysis of electronic structure shows that the parameter of energy gap can represent the stability before and after delithiation for cathode materials. In the process of lithium removal from stable lithiation phase, the stability of the cathode material rises with the decrease of the difference between the energy gap before and after delithiation, which ultimately pushes the actual capacity closer to the theoretical capacity of the material in essence.

Based on the big data analysis of material genome, this paper gives an explanation to why and how the actual capacity is less than the theoretical capacity one. This study also shows the necessity of studying the energy band structure of cathode material, which can provide an important parameter to estimate the actual capacity of lithium ion battery material, and a basic theoretical method for the exploration of new lithium ion battery materials in the future.

lithium ion battery, cathode material, actual capacity, band-gap

doi: 10.1360/N972018-00790