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YF₃ 包覆 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 正极材料的性能

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摘要: 富锂层状氧化物作为锂离子电池正极材料具有高比容量优势. 采用草酸盐共沉淀法制备 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂, 并用 YF₃ 包覆电极. 采用 X 射线衍射(XRD)、扫描电子显微镜(SEM)和 X 射线能谱分析(EDS)表征材料结构、观察材料形貌. 结果表明, 材料颗粒尺寸在 100~200 nm 范围, YF₃ 包覆不会改变材料结构和形貌. 电化学恒流充放电测试表明, YF₃ 包覆 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 电极的比容量, 尤其倍率比容量明显提高. 60 mA·g⁻¹ 电流密度下包覆电极材料 30 周循环后其比容量保持在 220 mAh·g⁻¹ 以上, 1500 mA·g⁻¹ 电流密度下其比容量仍可达 150 mAh·g⁻¹. 电化学阻抗谱(EIS)测试结果表明, YF₃ 包覆电极电荷转移电阻和扩散阻抗均明显降低, 有利于电化学性能改善.

关键词: 锂离子电池; 正极材料; 富锂层状氧化物; YF₃ 包覆; 高倍率性能

中图分类号: O646

文献标识码: A

富锂层状氧化物 Li[Li_{(1-2x)/3}Ni_xMn_{(2-x)/3}]O₂ 是层状 Li₂MnO₃ 与层状 LiNi_{0.5}Mn_{0.5}O₂ 互嵌形成的固溶体^[1]. 与现有商业化的锂离子电池正极材料 LiCoO₂、LiMn₂O₄ 和 LiFePO₄ 相比, 富锂层状氧化物正极具有更加明显的性能优势^[2,4]. 近年来富锂层状氧化物的制备和电化学性能研究受到了广泛关注.

然而, 富锂层状氧化物电极存在首周期不可逆容量较大和倍率性能较差等缺点, 已报道的改性方法主要有材料表面弱酸处理、掺杂、预循环处理和表面包覆^[5]. 其中, 表面包覆不仅提高了电极的循环性能, 而且不同程度地改善了其倍率性能, 尤为引人注目. 应用 Al₂O₃^[6], AlF₃^[7] 和 MnO₂^[8] 等包覆后, 富锂层状氧化物电极的电化学容量、倍率性能和循环寿命均能相应提高. 应用 SrF₂^[9] 和 YF₃^[10] 等氟化物包覆, 其包覆层还可有效地阻止电解液中 HF 对活性材料的腐蚀. 本文应用草酸盐共沉淀法制备了富锂层状氧化物 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 材料, 经 YF₃ 包覆并研究该材料结构和电极电化学性能.

1 实验

1.1 材料制备

按照文献^[11]的制备方法, 以 LiCH₃COO·

2H₂O、Ni(CH₃COO)₂·4H₂O 和 Mn(CH₃COO)₂·4H₂O 按分子式计量比(12.2:1.7:6.1)加入过量草酸, 配制成 100 mL 水溶液. 在反应釜中再加入 2 mL 冰醋酸, 搅拌均匀. 反应釜置于烘箱加热反应(160 °C, 10 h)后自然冷却. 将该反应物转移至烧杯, 加热搅拌使溶剂挥发. 将固体产物研磨, 并置于坩埚中焙烧(450 °C, 5 h). 冷却后, 再研磨、压片. 该极片置于马弗炉高温烧结, 升温程序为 500 °C(4 h) → 750 °C(4 h) → 900 °C(12 h), 即可得 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂. 该正极浸渍于 Y(NO₃)₃·6H₂O 溶液, 然后缓慢滴入 NH₄F 溶液(Y:F = 1:3, by mole), 而 YF₃ 与 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 质量比为 2%. 该材料溶液水浴加热搅拌(80 °C, 5 h), 然后 60 °C 真空恒温箱干燥. 最后置于氩气保护下焙烧(400 °C, 5 h), 即可得 YF₃ 包覆 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂.

1.2 材料表征

采用 X 射线衍射(XRD, 日本理学 Rigaku MiniFlex II 型)测试材料结构. CuK_α 射线, 管电压 30 kV, 管电流 15 mA, 扫描范围 10°~80°, 扫描速率为 5°·min⁻¹. 用配备 X 射线能谱仪的扫描电镜(SEM, 日本 HITACHI S-4800)观察材料形貌及分

析材料组分.

1.3 电池组装与测试

正极材料、乙炔黑和 PTFE 按质量比 80:12:8 混匀,加少量乙醇(分散剂)搅拌成浆状,并压制成膜,制成直径 8 mm 的极片,该极片放于烘箱 50 °C 烘干即可. 由工作电极、金属锂负极、多孔聚丙烯膜(Celgard 2400)隔膜和 1 mol·L⁻¹ 的 LiPF₆(碳酸乙烯酯(EC):碳酸二甲酯(DMC) = 3:7, by volume)混合电解液在充满氩气的干燥手套箱中组装成模拟电池. 使用 LAND CT-2001A 测试系统测量电池充放电曲线,电位区间 2.0 ~ 4.8 V (vs. Li⁺/Li). 使用 Zahner IM6ex 电化学工作站测试电极交流阻抗,频率范围 100 kHz ~ 10 mHz,振幅 5 mV.

2 结果与讨论

2.1 材料表征

图 1 是 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 和 2% (by mass,下同) YF₃ 包覆的 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ 材料的 XRD 谱图. 由图 1 可知,两种材料于 2θ = 23° 处有强度较弱的峰,该峰源于 Li、Ni 和 Mn 原子在过渡层中的有序排列所形成的超晶格结构^[3,12]. 而其它衍射峰都可归属于 α-NaFeO₂ 型层状结构的特

征峰,属于 R₃m 空间群. 谱图中(006)、(012)和(018)、(110)两组峰能清晰地分开,表明材料有明显层状结构特征^[13-14]. 包覆后材料的衍射峰没有明显变化,表明材料的晶型结构不因包覆而变化. 因 YF₃ 包覆量很少,谱图上没有发现 YF₃ 的衍射峰.

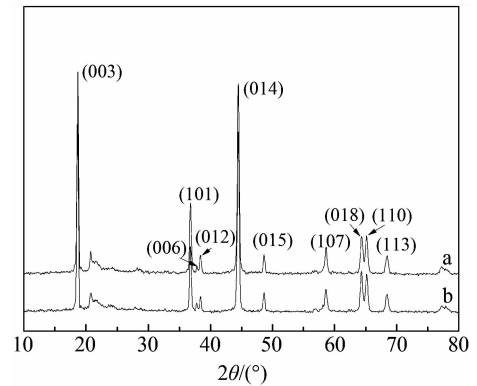


图 1 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (a) 和 YF₃ 包覆 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (b) 的 XRD 谱图

Fig. 1 XRD patterns of Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (a) and YF₃-coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (b)

图 2 示出两种材料 SEM 照片和 X 射线能谱

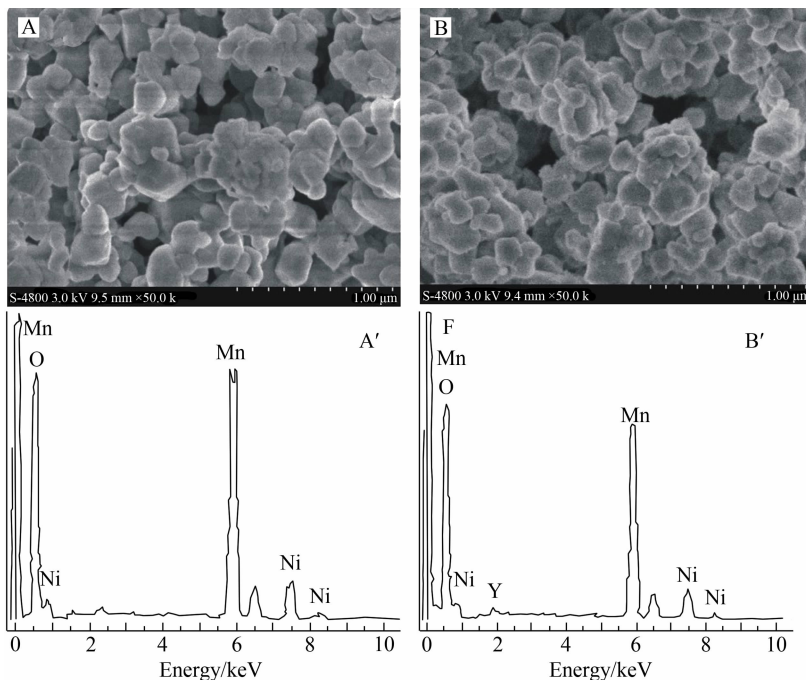


图 2 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (A, A') 材料和 YF₃ 包覆的 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (B, B') 材料的 SEM 照片和 EDS 谱图

Fig. 2 SEM images and EDS results of the as-prepared (A, A') and YF₃-coated (B, B') Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂

图. 如图 2 所示, $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 材料由 100 ~ 200 nm 大小的不规则颗粒组成(A), YF_3 包覆对材料的形貌无明显变化(B). $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 材料 Ni、Mn 和 O 的原子个数比为 1:3.8:9.7, 接近分子式的元素配比(A'). YF_3 包覆材料的 EDS 谱图(B') 出现明显的 Y 和 F 的特征峰, 且 Y、Ni 和 Mn 摩尔比为 1:14.9:57.8, 与 2% YF_3 包覆量基本相符.

2.2 电极电化学性能

图 3 是 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极和 YF_3 包覆的 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极 0.2C (60 $\text{mA} \cdot \text{g}^{-1}$) 倍率循环寿命曲线 (电位范围为 2.0 ~ 4.8 V). $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极的首周放电比容量为 230 $\text{mAh} \cdot \text{g}^{-1}$, 30 周循环后其放电比容量仍保持在 204.8 $\text{mAh} \cdot \text{g}^{-1}$, 其容量保持率高达 89%. 而 YF_3 包覆的 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极首周放电比容量为 210.7 $\text{mAh} \cdot \text{g}^{-1}$, 经前 2 周循环活化, 其放电比容量升至 243.7 $\text{mAh} \cdot \text{g}^{-1}$, 30 周循环后其放电比容量仍保持在 221.7 $\text{mAh} \cdot \text{g}^{-1}$, 电极的放电比容量优于 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$.

图 4 为 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极 YF_3 包覆前后在不同倍率下的充放电曲线. 如图所示, 两电极首周 (0.2C, 1st) 充电曲线中在 3.7 ~ 4.5 V 区间有一缓慢上升的电位区, 而 4.5 V 有一较长的电位平台. 3.7 ~ 4.5 V 区间相应于 Ni^{2+} 氧化, 4.5 V 处的长电位平台相应于 Li_2O 脱出. 因 Li_2O 脱出是不可逆的, 第 2 周期 (0.2C, 2nd) 充电过程 4.5 V

处电位平台消失^[3]. $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极首周库仑效率为 73.4%, YF_3 包覆电极首周库仑效率为 76.9%, 表明 YF_3 包覆可减小电极首周不可逆容量损失. 5C 倍率 (1500 $\text{mA} \cdot \text{g}^{-1}$, 6th) $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极的放电比容量为 137.1 $\text{mAh} \cdot \text{g}^{-1}$ (图 4A), 而 YF_3 包覆电极放电比容量达到 150 $\text{mAh} \cdot \text{g}^{-1}$ (图 4B), 电极倍率性能也提高. 曾有报道^[15], 电解液的 LiPF_6 与微量水作用可生成极强腐蚀性的 HF, 破坏活性材料结构, 降低其电化学性能. 类似于 AlF_3 对富锂材料的表面包覆^[16], YF_3 包覆层也可阻止 HF 对材料表面的腐

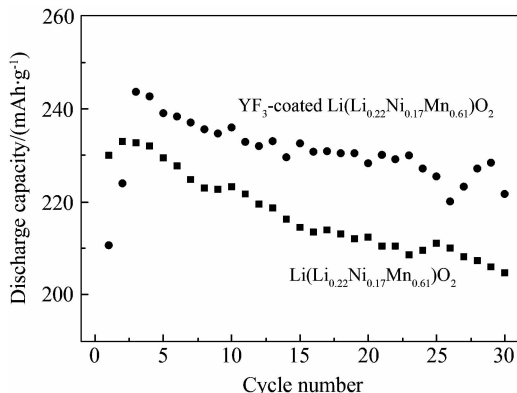


图 3 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极和 YF_3 包覆 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极 0.2C 倍率的循环寿命曲线 (电位范围为 2.0 ~ 4.8 V)

Fig. 3 The cycling curves of $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ and YF_3 -coated $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ at 0.2C rate in a potential range of 2.0 ~ 4.8 V (vs. Li^+/Li)

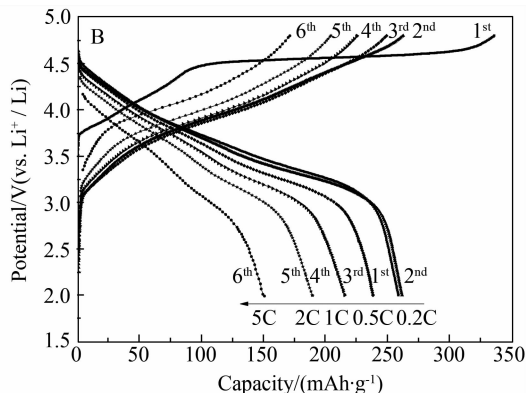
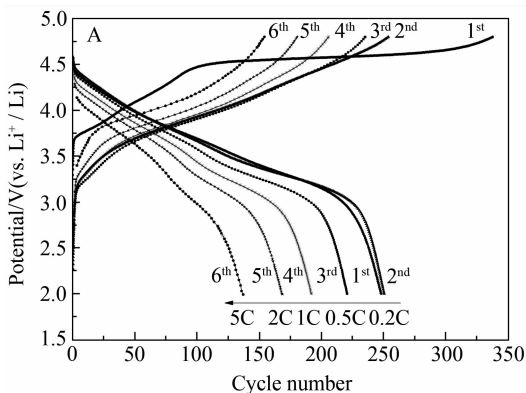


图 4 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极(A)和 YF_3 包覆 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极(B)不同倍率的充放电曲线 0.2C (1st, 2nd), 0.5C (3rd), 1.0C (4th), 2.0C (5th), 5.0C (6th)

Fig. 4 The charge-discharge curves of the as-prepared (A) and the YF_3 -coated $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ (B) at different rates 0.2C (1st, 2nd), 0.5C (3rd), 1.0C (4th), 2.0C (5th), 5.0C (6th)

蚀,从而有利于改善电极的电化学性能^[9].

图5示出Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极(A)和YF₃包覆Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极(B)在充放

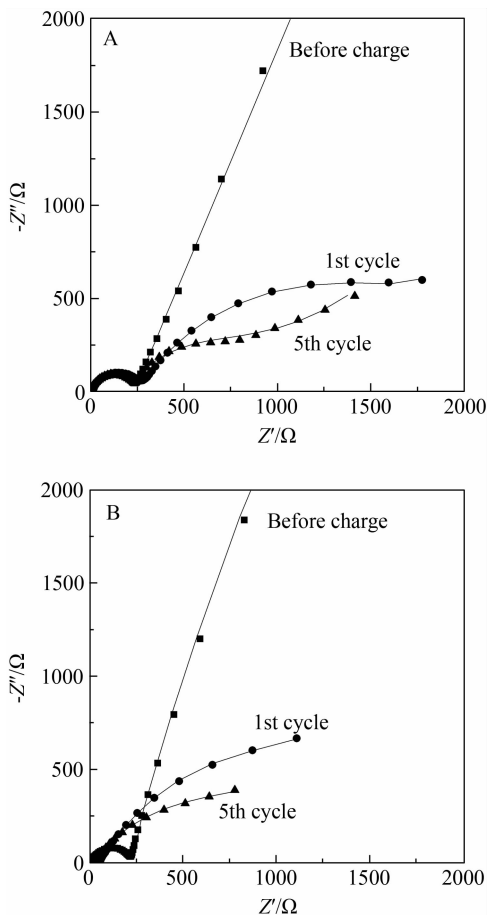


图5 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极(A)和YF₃包覆Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极(B)不同周期循环放电后的交流阻抗谱图

Fig. 5 EIS plots of the as-prepared (A) and YF₃-coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ (B) at different cycles

电前、1周循环和5周循环放电后的电极电化学阻抗谱图. 由图可见, Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极在充电前, EIS图由一个高频区的半圆和一条低频区的直线组成. 高频区的半圆相应于电极界面电荷转移过程, 低频区的直线相应于电极半无限扩散过程^[17]. 第1周期放电后, 电极高频区的半圆直径无明显变化, 而其低频区由直线改变为一条弧线, 在充放电过程电极表面形成活性层, 导致离子由半无限扩散转为有限扩散. 此外, 第5周期循环放电后, 其低频区的末端(100 mHz ~ 10 mHz)呈现了一明显的短线, 这意味着电极半无限扩散过程仍然存在, 且归因于离子穿越表面活性层后在体相扩散^[17]. 因此可以判断, 富锂电极在充放电过程中同时存在半无限扩散和有限扩散. 对其它富锂层状氧化物电极的研究, 也证实了类似表面活性层的存在^[7-18]. YF₃包覆Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极的EIS谱图与Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极的类似, 但高频区半圆直径明显减小, 低频区圆弧占主导地位. 这表明YF₃包覆后电极界面电荷转移电阻明显减小, 表面活性层的影响更加明显.

图6示出两电极模拟等效电路图, 其中R_s为溶液电阻, R_{ct}为电荷转移电阻, CPE和CPE1为常

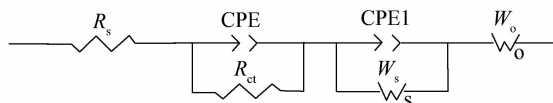


图6 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极和YF₃包覆Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂电极相应的拟合等效电路图

Fig. 6 The equivalent circuit used to fit the impedance spectra of the as-prepared and YF₃ coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂

表1 Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂和YF₃包覆Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂依据图6的EIS谱图拟合结果
Tab. 1 The simulated data from EIS spectra using the equivalent circuit shown in Fig. 6

Sample	Cycle number	R _s /Ω	R _{ct} /Ω	W _s /Ω	W _o /Ω
Li(Li _{0.22} Ni _{0.17} Mn _{0.61})O ₂	0	6.3	229		47797
	1st	6.7	255	2442	2047
	5th	8.0	224	2193	1906
YF ₃ -coated Li(Li _{0.22} Ni _{0.17} Mn _{0.61})O ₂	0	3.4	214	4405	38794
	1st	3.4	48	1264	1264
	5th	4.5	27	1033	702

相位元件, W_s 为 Nernst 扩散阻抗, W_0 为半无限的 Warburg 扩散阻抗. 相应的拟合结果列于表 1. $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极在充电前、第 1 和 5 周期循环放电后, 其电荷转移电阻变化不甚明显, 总扩散阻抗呈下降趋势. YF_3 包覆 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极的电荷转移电阻随周期循环明显减小, 由 214 Ω 减为 48 Ω , 直至 27 Ω , 该值仅相当于未包覆电极的 12%. YF_3 包覆有利于富锂层状氧化物中活性位的形成, 电极扩散阻抗随充放循环而急速降低, 增强电化学反应能力.

3 结 论

应用草酸盐共沉淀法制备了锂离子电池富锂层状氧化物正极材料 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$, 该材料具有 $\alpha\text{-NaFeO}_2$ 型层状结构, 经 YF_3 包覆其材料的晶型结构和形貌均无变化. 在充放电过程中, $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极同时存在半无限扩散和有限扩散过程, 经 YF_3 包覆界面电荷转移电阻和扩散阻抗都明显减小. YF_3 包覆 $\text{Li}(\text{Li}_{0.22}\text{Ni}_{0.17}\text{Mn}_{0.61})\text{O}_2$ 电极, 60 $\text{mA} \cdot \text{g}^{-1}$ 电流密度下其放电比容量可达 240 $\text{mAh} \cdot \text{g}^{-1}$, 30 周循环后其容量保持率 92% 以上, 5C (1500 $\text{mA} \cdot \text{g}^{-1}$) 倍率其放电比容量仍维持 150 $\text{mAh} \cdot \text{g}^{-1}$.

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Electrochemical Performance of YF₃-Coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ Cathode Material for Li-Ion Batteries

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Abstract: The Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ was prepared with oxalic co-precipitation and coated with an YF₃ layer by a chemical deposition method. The as-prepared and YF₃-coated Li-rich materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The results demonstrate that the as-prepared and YF₃-coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ materials have a typical layered structure and are composed of sphere-like particles with a diameter of 100 ~ 200 nm. Galvanostatic charge-discharge tests show that the discharge capacity of the YF₃-coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ is obviously improved. At the low current density of 60 mA·g⁻¹, the discharge capacity reaches 240 mAh·g⁻¹, and remains 220 mAh·g⁻¹ after 30 cycles. At the high current density of 1500 mA·g⁻¹, the discharge capacity still keeps 150 mAh·g⁻¹, showing an excellent high-rate capability. Electrochemical impedance spectra (EIS) reveal that the YF₃-coated Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂ shows lower charge-transfer resistance and diffusion impedance as compared with the as-prepared Li(Li_{0.22}Ni_{0.17}Mn_{0.61})O₂.

Key words: Li-ion batteries; cathode material; Li-rich layered oxides; YF₃-coating; high-rate capability