基于多酸制备的新型氮化钼基复合材料作为锂离子电池负极材料

王晓丽[†], 张阿曼[†], 李顺利^{*}, 兰亚乾^{*}

南京师范大学化学与材料科学学院, 江苏省生物功能材料重点实验室, 南京 210023

[†] 同等贡献

^{*} 联系人, E-mail: slli@njnu.edu.cn; yqlan@njnu.edu.cn

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摘要 锂离子电池作为新一代储能装置, 已经在生产和生活中得到了广泛应用. 多酸有着多电子转移、化学结构稳定、氧化还原性可逆等诸多优点, 具有作为电池电极材料的良好潜力. 但易溶于电解液、导电性差且易发生团聚等问题阻碍了多酸用于电池电极材料的应用研究. 本工作为解决上述问题, 充分利用磷钼酸良好的水溶性、优异的氧化还原性和独特的酸性, 通过简单的一锅法, 在温和的条件下制备了磷钼酸/聚吡咯/石墨烯前驱体($\text{PMo}_{12}/\text{PPy}/\text{RGO}$, 简称PCG), 并通过高温氮化处理制备了新型氮化钼基复合材料($\text{NPC@Mo}_2\text{N/NPRGO}$), 磷钼酸、聚吡咯在提供金属源和碳源的同时也提供了P, N杂原子掺杂到多孔碳和石墨烯中, 该材料作为锂离子电池负极材料表现出较好的循环性能和倍率性能. 在电流密度为100 mA/g时, $\text{NPC@Mo}_2\text{N/NPRGO}$ 的首周放电比容量可以达到1446 mAh/g, 循环200周后仍然可以达到771 mAh/g. 在电流密度为100, 200, 500, 1000, 2000 mA/g时, 循环比容量分别为797, 725, 630, 545, 460 mAh/g. 尤其是在大电流密度(1000 mA/g)循环300周后容量仍能达到554 mAh/g.

关键词 磷钼酸, 聚吡咯, 石墨烯, 锂离子电池, 负极

随着工业、经济的不断发展, 人类对能源的需求日趋增长. 锂离子电池作为新一代储能器材, 已经在便携式电子产品和电动汽车领域取得了巨大进展^[1-4]. 然而, 这些领域的持续发展需要高功率、高容量、高稳定性的锂离子电池, 这激发了人们对新型电极材料的探索. 对于锂离子电池负极材料, 已经商业化的石墨存在比容量低、产生枝晶等问题, 因此, 开发新的锂离子电池负极材料用于取代传统石墨至关重要^[5-8].

金属氮化物作为锂离子电池电极材料最早开始于20世纪90年代, 当时采用层状锂化过渡金属氮化

物作为锂离子嵌入的主体基质, 但由于其电化学活性差、稳定性差, 并没有得到蓬勃发展^[9,10]. 随着转换机制的发现^[11]以及氮化物作为负极材料表现出的优点: (1) 由于M-X键极性降低, 使得材料的极性损失减少; (2) 与金属氧化物相比, 氮化物所得终产物 LiX_n 具有更好的电子电导率, 过渡金属氮化物又引起了锂电研究者的关注^[12].

多酸是具有阴离子骨架的金属氧簇分子, 具备良好的物理化学性质, 如多电子转移、化学结构稳定以及多阳离子调变等, 这使得多酸在作为电极材料方面表现出良好的潜力. Wang等人^[13]曾对Keggin

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型 $[\text{N}(\text{C}_4\text{H}_9)_4]_3[\text{PMo}_{12}\text{O}_{40}]$ 的多电子转移氧化还原反应作了探索. 结果表明, 在进行氧化还原反应时, 12个Mo原子的化合价会在+6价和+4价之间转换, 同时进行24电子的转移. Sonoyama等人^[14-16]也对多酸作为锂离子电池电极材料做了细致的工作, 这些研究均表明多酸有望作为电极材料应用到锂离子电池的研究中. 然而, 多酸溶于各种溶剂使其作为锂电电极材料的循环性能较差, 虽然首周容量很高, 但容量衰减较快, 循环寿命不佳. 而且多酸作为无机大分子在研究及应用过程中易发生团聚结晶, 使得本身的优异性质不能得到充分的发挥. 为此, 科学家分别对多酸进行有机阳离子的调变和有机官能团修饰, 使易团聚的问题有了进一步的改善, 但仍不尽如意. 为了有效而彻底地解决这个问题, 将多酸分散固定在基底上是当前的研究重点.

磷钼酸($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, PMo_{12})是一种典型的Keggin型多酸, 含有大量的钼源, 并且具有优异的可逆氧化还原性能和内存储电子能力, 有望用于氮化钼基材料的制备并应用于锂离子电池领域^[17-19]. 为改善材料的导电性, 具有良好化学稳定性和导电性的氧化石墨烯(GO)是理想的导电基底^[20,21]. 然而, GO的表面官能团带负电荷, 与 PMo_{12} 的阴离子骨架间存在静电排斥, 使得 PMo_{12} 在GO上的固载变得困难^[22], 因此, 需要合适的桥梁用来连接 PMo_{12} 和GO. 导电聚吡咯(PPy)既具有金属和无机半导体的电学和光学性能, 又具有电化学氧化还原活性^[23], 是吡咯单体(Py)在酸性且存在氧化剂的条件下氧化聚合形成的. 这样的聚合条件恰好是 PMo_{12} 水溶液同时兼具的. 因此, 结合 PMo_{12} 的酸性和强氧化还原性、PPy的形成条件以及GO的优异导电性, 便可同时解决 PMo_{12} 在GO上的固载以及材料的导电性问题.

基于上述思路, 本文采用简单的一锅法首先制备了磷钼酸/导电聚吡咯/氧化石墨烯(PMo_{12} -PPy/RGO, PCG)前驱体. 磷钼酸水溶液的酸性和强氧化性能能够将Py原位聚合形成PPy, PPy包覆 PMo_{12} 实现了 PMo_{12} 在GO上的均匀固载, GO作为良好的碳导电基底提高了材料的导电性, PMo_{12} 和PPy中所含的P、N元素能够在高温处理过程中为材料提供了杂原子, 有助于调节材料的电子结构从而改善材料性能. 将 PMo_{12} -PPy/RGO前驱体进一步氮化制备的氮化钼基纳米复合材料NPC@ Mo_2N /NPRGO用作锂离子电池负极材料, 表现出较好的循环性能和倍率性能.

1 实验

(i) 材料的制备. 氧化石墨烯(GO)的制备参考已报道的文献[24], 采用改进的Hummers方法预先制备. PMo_{12} -PPy/RGO的制备: 称取25 mg GO超声分散在25 mL蒸馏水中, 使形成浓度为1 mg/mL的GO分散液. 称取0.7301 g PMo_{12} 于250 mL圆底烧瓶中, 加入100 mL蒸馏水. 将上述两溶液混合, 在超声的条件下用恒压滴液漏斗缓慢滴加入622 μL Py和25 mL蒸馏水的混合溶液. 随着Py的加入, 反应体系逐渐由黄棕色变成了深蓝色, 并产生了黑色沉淀. Py滴加完毕后, 将圆底烧瓶转移到油浴中, 在60℃下搅拌反应24 h. 温度降至室温后, 减压抽滤, 并用蒸馏水洗涤多次至滤液变为无色, 所得黑色固体即为 PMo_{12} -PPy/RGO前驱体, 在60℃真空烘箱烘干, 研成粉末.

NPC@ Mo_2N /NPRGO的制备: 取适量 PMo_{12} -PPy/RGO粉末于磁舟中, 放入管式炉, 在气流量为150 sccm的氨气气氛中以5°/min升温至650℃, 保持4 h, 待管式炉在氨气气氛中冷却到室温后, 以150 sccm的气流量通氮气, 使排出管式炉中残留的氨气(尾气吸收溶液为稀硫酸), 最后所得产物为NPC@ Mo_2N /NPRGO.

NRGO的制备: 称取25 mg GO超声分散在25 mL蒸馏水中, 使形成浓度为1 mg/mL的GO溶液. 称取0.018 mol FeCl_3 于250 mL圆底烧瓶中, 加入100 mL蒸馏水. 将上述两溶液混合, 在超声的条件下缓慢滴加入622 μL Py和25 mL蒸馏水的混合溶液. Py滴加完毕后, 将圆底烧瓶转移到油浴中, 在60℃下搅拌反应24 h. 温度降至室温后, 减压抽滤洗涤多次, 所得黑色固体为PPy/RGO, 在60℃真空烘箱烘干后, 用同于NPC@ Mo_2N /NRGO的方法进行氮化处理, 终产物为NRGO.

NPC@ Mo_2N 的制备: 称取0.2190 g PMo_{12} 溶解在30 mL蒸馏水中, 向其中加入125 μL Py单体. 将混合后的溶液转移到50 mL的高压反应釜中, 在180℃持续加热12 h. 反应釜降温后, 减压抽滤反应釜中所得黑色产物, 并用蒸馏水洗涤多次至滤液变为无色, 所得黑色固体即为 PMo_{12} -PPy, 在60℃真空烘箱烘干, 研成粉末, 用同于NPC@ Mo_2N /NPRGO的方法进行氮化处理, 终产物为NPC@ Mo_2N .

(ii) 电极的制备. 工作电极采用涂膜法制备, 分别以制备的样品为活性物质, 导电炭黑(super P carbon)为导电剂, 聚偏氟乙烯(PVDF)为黏结剂, N-甲

基吡咯烷酮(NMP)为溶剂. 将活性材料、导电剂、黏结剂按质量比7:2:1准确称量于玛瑙研钵中, 研磨混合均匀后滴加适量NMP黏结剂, 继续研磨至呈均匀浆状物. 取大小合适且干净的铜箔, 将浆状物转移至其上并涂抹均匀, 90℃真空干燥12 h除去溶剂. 将干燥好的铜箔切成直径14 mm的圆片后继续干燥12 h, 降至室温后取出称重, 用以确定活性质量($\sim 1 \text{ mg/cm}^2$). 纽扣式半电池在充有氩气的手套箱中组装, 其水分和氧气浓度严格限制在1 ppm(1 ppm=1 mg/L)以下. 半电池组装中, 电极片作负极, 锂片作正极, Celgard 2400膜作隔膜, 电解液是 LiPF_6 溶于碳酸乙烯酯(EC)/碳酸二甲酯(DMC)/碳酸甲乙酯(EMC)(v:v:v=1:1:1)的混合溶剂中.

(iii) 电化学测试. 恒电流充放电测试在蓝电测试系统上(Land, CT2001A, 中国)以不同的电流密度(100~2000 mA/g)进行, 电位范围为0.01~3 V vs. Li^+/Li . 电化学阻抗谱(EIS)和循环伏安测试(CV)均在上海辰华CHI 660e型电化学工作站上进行, EIS的振幅为5 mV, 频率范围为100 kHz~0.01 Hz, CV的电位范围为0.01~3 V, 扫描速率为0.2 mV/s.

2 结果与讨论

2.1 材料表征

以 PMo_{12} , Py, GO为原料, 通过简单的一锅法, 本文首先得到了PCG前驱体, 并在进一步高温氮化处理后得到了材料NPC@ Mo_2N /NPRGO. 为了了解PCG前驱体和终产物NPC@ Mo_2N /NPRGO的形貌特征, 利用扫描电子显微镜(SEM, JEOL-2100F)和透射电子显微镜(TEM, JEM-200CX)对材料进行了微观表征. 从前驱体的SEM(图1(a))和TEM(图1(b))中均可以看出, PMo_{12} -PPy纳米粒子在石墨烯上均匀分布, 这得益于磷钼酸良好的水溶性, 使磷钼酸在溶解的过程中可以均一地扩散在石墨烯的分散液中. 同时, 磷钼酸水溶液的酸性和强氧化性保证了Py单体能够原位聚合形成聚合物PPy, 从而包覆 PMo_{12} , 实现磷钼酸在石墨烯上的均匀固载. 由图1(c)可知, NPC@ Mo_2N /NPRGO是具有褶皱边缘的片层结构, 将SEM倍数放大时, 可以看到 Mo_2N 纳米粒子均匀分布在石墨烯上(图1(d)), 图1(e)的TEM图也进一步说明 Mo_2N 纳米粒子在石墨烯上均匀分布. 在NPC@ Mo_2N /NPRGO的HRTEM图(图1(f))中可以明确找到两种晶格条纹, 其

图1 PMo_{12} -PPy/RGO和NPC@ Mo_2N /NPRGO的形貌表征图. PMo_{12} -PPy/RGO的SEM(a)和TEM(b)图. NPC@ Mo_2N /NPRGO的SEM(c, d), TEM(e), HRTEM(f)和元素分布图(g)

Figure 1 Morphology characterization of PMo_{12} -PPy/RGO precursor and NPC@ Mo_2N /NPRGO. SEM (a) and TEM (b) images of PMo_{12} -PPy/RGO precursor. SEM (c, d), TEM (e) and HRTEM (f) images of NPC@ Mo_2N /NPRGO. (g) STEM image of NPC@ Mo_2N /NPRGO and the corresponding mapping of C, N, O, Mo and P

中, 0.15 nm对应 Mo_2N 的220晶面, 0.34 nm对应无定形碳的002晶面, 说明 Mo_2N 纳米粒子被PPy分解产生的无定形碳包覆. 图1(g)的元素分布图说明NPC@ Mo_2N /

NPRGO中含有C, N, O, P, Mo元素, 并且这些元素在NPC@Mo₂N/NPRGO中均匀分布.

为了探索PMo₁₂和GO对材料的形貌和性能影响, 在PMo₁₂和GO各不参与反应体系的条件下分别制备了对比样, 并对材料进行了结构表征. 多晶粉末X射线衍射(PXRD)表征提供了材料的组分信息, 如图2(a)所示, 在约25°处出现的衍射峰对应石墨碳的002晶面, 该组分来源于还原石墨烯和PPy分解得到的无定形碳^[25], 其他衍射峰均对应物相Mo₂N(JCPDS No. 3-907). Raman光谱进一步提供了材料的结构信息, 在1351 cm⁻¹处出现的峰归属于石墨碳的D带; 在1595 cm⁻¹处出现的峰归属于石墨碳的G带(图2(b)), D带和G带的强度比可以反映材料的石墨化程度和缺陷程度. 由图2(b)可知, NPC@Mo₂N/NPRGO, NRGO, NPC@Mo₂N的D带, G带强度比(I_D/I_G)分别为1.11, 0.99, 0.89, 表明NPC@Mo₂N/NPRGO具有较高的缺陷程度^[26], 说明在PMo₁₂, GO, PPy同时存在于反应体系时, 所制备的材料有更多的缺陷位点, 有助于提供更多的活性位点与锂离子相互作用, 从而改善材料

的性能. 氮气吸附-脱附曲线的表征可以用来说明材料的比表面积和孔结构. 由图2(c)可知, NPC@Mo₂N/NPRGO, NRGO, NPC@Mo₂N相应的比表面积分别为356, 68, 37 m²/g. BJH孔径分布表明这几种材料均为介孔结构(图2(d)). NPC@Mo₂N/NPRGO的介孔结构和较高的比表面积有助于锂离子和电子的快速传递和电解液在电极材料上的渗透.

XPS总谱分析(图3(a))说明NPC@Mo₂N/NPRGO中含有C, N, O, P, Mo元素, 各元素的高分辨谱可以具体说明该材料中各元素的电子状态. 图3(b)中, C 1s在284.3 eV处出现1个强峰, 对应于C-C/C=C键, 源于sp²杂化的石墨碳, 说明材料中的GO被还原成了RGO^[18]. 其他2个峰分别对应C-N键(285.1 eV)和C-O键(286.4 eV), 说明PPy分解产生的杂原子N掺杂入了石墨烯和无定形碳. N 1s(图3(c))可以分为4个峰, 分别对应吡咯氮(399.0 eV)、石墨氮(401.67 eV)、吡啶氮(399.1 eV)和Mo-N键(397.8 eV), 根据峰面积可知, N元素中Mo-N键为主要成分, 说明材料中生成了Mo₂N. 图3(d)中, O 1s中的峰出现在530.5, 531.1,

图2 NPC@Mo₂N/NPRGO, NRGO和NPC@Mo₂N结构表征. (a) PXRD图; (b) Raman图; (c) 氮气吸附-脱附曲线图; (d) BJH孔径分布图

Figure 2 Structural characterization of the materials. (a) PXRD patterns, (b) Raman spectra, (c) nitrogen adsorption-desorption isotherms, and (d) the corresponding pore size distribution of NPC@Mo₂N/NPRGO, NRGO and NPC@Mo₂N

图3 NPC@Mo₂N/NPRGO的XPS总谱(a)和各元素的高分辨谱(b)~(f). (b) C 1s; (c) N 1s; (d) O 1s; (e) P 2p; (f) Mo 3d

Figure 3 Compositional characterization of NPC@Mo₂N/NPRGO. (a) XPS survey spectrum of NPC@Mo₂N/NPRGO and the corresponding high-resolution spectra of (b) C 1s, (c) N 1s, (d) O 1s, (e) P 2p, and (f) Mo 3d

531.9 eV处, 分别归属于C-O/O=C键、N-C-O键、C-OH键^[27]. P 2p分出的2个峰(图3(e))分别对应P-O键(132.9 eV)和P-C键(133.8 eV), 说明PMo₁₂提供的P源掺杂到了石墨烯和无定形碳中^[17]. Mo 3d(图3(f))在232.7 eV处有1个强峰, 对应Mo⁴⁺; 229.6 eV处的峰对应Mo-N键; 235.9 eV处的峰对应Mo⁶⁺, 可能是材料

暴露在空气中表面生成了氧化物^[28].

2.2 锂离子电池性能

对于材料NPC@Mo₂N/NPRGO, 首先组装了复合电极材料的纽扣半电池, 在电位范围0.01~3 V, 扫速0.2 mV/s的条件下, 通过循环伏安测试(CV)探究了

NPC@Mo₂N/NPRGO对锂离子的电化学反应行为。如图4(a)所示,首周CV在约1.1 V处出现1个还原峰,并在随后几周的CV测试中消失,而且首周CV曲线的形状与第2和第3周存在区别,说明在首周CV测试中,NPC@Mo₂N/NPRGO在电极界面发生了不可逆的副反应,形成了稳定的固体电解质界面膜(SEI膜)^[29]。第2和第3周的CV曲线在1.2 V出现1个还原峰、在1.5 V左右出现1个还原峰,说明元素 NPC@Mo₂N/

NPRGO中的Mo元素在充放电过程中发生了可逆的氧化还原反应^[30]。此外,第2和第3周的CV曲线能够很好地重合,进一步说明NPC@Mo₂N/NPRGO在锂离子嵌入脱出过程中有着良好的稳定性和可逆性。

NPC@Mo₂N/NPRGO的充放电曲线如图4(b)所示,首周放电曲线与第2、5、10、50、100周的放电曲线存在明显不同,说明NPC@Mo₂N/NPRGO在首周放电过程中形成了稳定的SEI膜。此外,第2、5、10、50、

图4 NPC@Mo₂N/NPRGO的锂电性能图。(a) NPC@Mo₂N/NPRGO的CV曲线和(b)充放电曲线; (c) NPC@Mo₂N/NPRGO, NRGO, NPC@Mo₂N在电流密度为 100 mA/g时的循环性能图; (d) NPC@Mo₂N/NPRGO的倍率性能图; (e) NPC@Mo₂N/NPRGO在电流密度为 1000 mA/g时的循环性能图; (f) NPC@Mo₂N/NPRGO充放电前后的阻抗图

Figure 4 Electrochemical performance of NPC@Mo₂N/NPRGO. (a) CV profiles of NPC@Mo₂N/NPRGO at a scan rate of 0.2 mV/s; (b) charge/discharge profiles of NPC@Mo₂N/NPRGO for different cycles constantly at 100 mA/g; (c) cycling performance of NPC@Mo₂N/NPRGO, NRGO and NPC@Mo₂N at a current density of 100 mA/g; (d) rate capability performance of NPC@Mo₂N/NPRGO at various current densities; (e) stability test of NPC@Mo₂N/NPRGO for 300 cycles at 1000 mA/g; (f) Nyquist plots of NPC@Mo₂N/NPRGO before and after Li-ion battery cycling

100周的充放电曲线几乎重合,也说明NPC@Mo₂N/NPRGO具有良好的电化学稳定性. NPC@Mo₂N/NPRGO, NRGO, NPC@Mo₂N在电流密度为100 mA/g时的循环性能如图4(c)所示, NPC@Mo₂N/NPRGO的首周放电比容量为1449 mAh/g,首周充电比容量为806 mAh/g,库伦效率(CE)为55.60%,在循环200周后放电比容量仍可以达到771 mAh/g. 与最近报道的氮化钼基材料的性能对比可以看出,磷钼酸、导电聚合物、石墨烯的综合作用对于改善氮化钼的电池性能具有一定的优势(表1).

图4(d)是NPC@Mo₂N/NPRGO的倍率性能,可知,在电流密度为100, 200, 500, 1000, 2000 mA/g时, NPC@Mo₂N/NPRGO的循环比容量分别为797, 725,

630, 545, 460 mAh/g. 当电流密度从2000 mA/g重新回到100 mA/g时,容量还可以达到773 mAh/g,说明 NPC@Mo₂N/NPRGO具有良好的循环稳定性. 而且 NPC@Mo₂N/NPRGO在大电流密度(1000 mA/g)循环300周后容量仍可以达到554 mAh/g(图4(e)). 此外,在充放电10周后, NPC@Mo₂N/NPRGO的电荷转移电阻明显减小(图4(f)),这是因为在电池充放电过程中,活性材料被活化,电解液不断扩散,增加了活性材料与电解液的接触面积. 对于对比材料NRGO和 NPC@Mo₂N,由充放电曲线可知(图5(a), (c)), NRGO和NPC@Mo₂N的首周放电比容量均低于NPC@Mo₂N/NPRGO. 在电流密度为100, 200, 500, 1000, 2000 mA/g时, NRGO的循环比容量分别为678, 567, 464,

表1 氮化钼基材料作为锂离子电池负极材料的性能对比

Table 1 Comparison of molybdenum nitride based composites for Li-ion batteries

活性材料	电流密度(mA/g)	首周放电比容量(mAh/g)	循环周数	参考文献
NPC@Mo ₂ N/NPRGO	100	1449	200	本工作
Mo ₂ N包覆MoO ₂	100	706	100	[5]
meso-Mo ₂ N-NBs	100	862	20	[31]
MoN在Ti箔上	—	720	—	[32]

图5 NRGO和NPC@Mo₂N的锂电性能图. NRGO的充放电曲线(a)和倍率性能图(b); NPC@Mo₂N的充放电曲线(c)和倍率性能图(d)

Figure 5 Electrochemical performance of NRGO and NPC@Mo₂N. (a) Charge/discharge profiles of NRGO for different cycles constantly at 100 mA/g. (b) Rate capability performance of NRGO at various current densities. (c) Charge/discharge profiles of NPC@Mo₂N for different cycles constantly at 100 mA/g. (d) Rate capability performance of NPC@Mo₂N at various current densities

395, 317 mAh/g(图5(b)), NPC@Mo₂N的循环比容量分别为557, 512, 442, 367, 287 mAh/g(图5(d)). 由此可见, 与NRGO和NPC@Mo₂N相比, NPC@Mo₂N/NPRGO具有较高的比容量、较好的循环稳定性和倍率性能, 说明PMo₁₂和PPy的存在有助于提高材料的电化学性能.

3 结论

本工作充分利用磷钼酸良好的溶解性、水溶液的酸性和强氧化性, 通过简单的一锅法制备了磷钼酸/

导电聚吡咯/石墨烯(PMo₁₂-PPy/RGO, PCG)前驱体, 实现了Py的原位聚合和PMo₁₂在GO上的均匀固载. 前驱体进一步氨化制备的氮化钼基纳米复合材料(NPC@Mo₂N/NPRGO)用作锂离子电池负极材料表现出较好的循环性能和倍率性能. PMo₁₂良好的水溶性保证了纳米粒子在石墨烯表面的均匀分布, 使材料在充放电过程中不发生聚集与粉碎, 在提高材料电化学性能的同时也改善了材料的稳定性. 该工作为多酸在锂离子电池方面的应用研究以及氮化钼基复合材料的制备提供了思路.

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Summary for “基于多酸制备的新型氮化钼基复合材料作为锂离子电池负极材料”

A novel molybdenum nitride composite based on polyoxometalates as anode for Li-ion batteries

Xiao-Li Wang[†], A-Man Zhang[†], Shun-Li Li^{*} & Ya-Qian Lan^{*}

Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

^{*} Corresponding authors, E-mail: slli@njnu.edu.cn; yqlan@njnu.edu.cn

With the increasing energy crisis and environmental pollution, the development of energy storage devices has attracted widespread attention. Lithium-ion batteries (LIBs), as new energy storage devices, have made great progress in the field of portable electronic products and electric vehicles. However, traditional batteries electrode materials are difficult to meet people's increasing demand for energy density and power density. Therefore, it is essential to find higher performance electrode materials for LIBs. Polyoxometalates (POMs) have already demonstrated great promise for LIBs owing to their electron storage, chemical structure and reversible redox. However, the application of POMs in LIBs is hindered for the poor electronic conductivity and its dissolution in electrolyte. Consequently, taking full advantage of POMs and solving the immobilization of POMs is of great significance for the research of POMs in the application of LIBs. Phosphomolybdate ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, PMo_{12}) is a typical Keggin-type POMs, containing abundant molybdenum source, and has excellent reversible redox. To improve the conductivity of the materials, graphene oxide (GO) with good chemical stability and electrical conductivity is an ideal substrate. However, both GO and PMo_{12} are negatively charged, the electrostatic between them makes it difficult to conjugate preferably. Considering the polymerization conditions of conductive polymer, pyrrole (Py) can be chosen to bridge PMo_{12} and GO, then realizing the anchor of PMo_{12} on GO. Inspired by these, in the present work, by taking full advantage of good solubility, unique acidity and reversible redox of PMo_{12} , the polyoxometalate/conductive polymer/graphene oxide ($\text{PMo}_{12}/\text{PPy}/\text{RGO}$, PCG) precursor was prepared via a simple one-pot method under milder condition, which realizes the *in-situ* polymerization of Py and uniform loading of PMo_{12} on GO. Then a novel molybdenum nitride composite ($\text{NPC@Mo}_2\text{N}/\text{NPRGO}$) was obtained by direct ammoniation of $\text{PMo}_{12}/\text{PPy}/\text{RGO}$ precursors. As anode materials for LIBs, $\text{NPC@Mo}_2\text{N}/\text{NPRGO}$ exhibits a good cycling reversibility and achieves a high capacity, which can deliver a discharge capacity of 1446 mAh/g at 100 mA/g at the first cycle. And a reversible capacity of 771 mAh/g is maintained after 200 cycles. In addition, at the current density of 100, 200, 500, 1000, 2000 mA/g, the reversible capacities are about 797, 725, 630, 545, 460 mAh/g, respectively. With the decrease of current density back to 100 mA/g, the capacity can almost resume to the original values, demonstrating the good reversibility and excellent rate capability of the composite. The excellent performance of $\text{NPC@Mo}_2\text{N}/\text{NPRGO}$ toward LIBs could be attributed to the synergistic effects of each component in the composite. The good solubility of PMo_{12} ensures the uniform distribution of molybdenum nitride on the surface of graphene substrate, so that the material does not aggregate and pulverize during the process of charging and discharging, which improves the electrochemical performance and stability of the composite. This work prepared a novel two-dimensional nanocomposite by simple method, which is not only cheap in raw materials, simple in preparation, but also has high yield. It is convenient both for materials characterization and performance research. The design could provide ideas for the application of POMs in LIBs and the preparation of molybdenum nitride-based composites for other energy storage technology.

phosphomolybdate acid, polypyrrole, graphene, lithium-ion batteries, anode materials

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