

Fe 基普鲁士蓝@纳米多孔碳复合材料的制备及其电容性能

陈秋爽^{1,2}, 赵春霞^{1,2}, 陈业凯², 陈 文²

(1. 湖北隆中实验室, 湖北 襄阳 441000; 2. 武汉理工大学材料科学与工程学院, 武汉 430070)

摘 要: Fe 基普鲁士蓝(PB)具有开放的框架结构和高理论容量, 但是导电性不佳, 这限制了其倍率性能和循环性能。利用溶液共沉淀法成功将 PB 负载于纳米多孔碳(NPC)上, 制备出普鲁士蓝@纳米多孔碳复合材料(PB@NPC)。PB@NPC 比表面积高达 $2122\text{ m}^2/\text{g}$, 充分发挥出双电层电容和赝电容的协同作用, 具有高容量和良好的导电性。在扫速为 5 mV/s 时的比电容为 483.45 F/g , 在 0.2 A/g 下的比电容为 309.35 F/g 。将 PB@NPC 电极组装成对称式电容器, 循环 1 000 圈后的容量保持率为 91%, 具有优异的循环稳定性。

关键词: Fe 基普鲁士蓝; 纳米多孔碳; 溶液共沉淀法; 协同作用; 对称电容器

中图分类号: TB332/O646 文献标志码: A 文章编号: 0454-5648(2024)09-3055-08

网络出版时间: 2024-08-21



超级电容器具有高功率密度、高能量密度和优异的循环稳定性, 被认为是最有前途的储能器件之一^[1]。根据电荷储存机制, 超级电容器一般可分为 2 种类型: 双电层电容器和赝电容器。双电层电容器储能原理是在电极-电解质界面处通过静电吸附/解吸来存储电荷^[2], 电极材料以碳材料为主, 包括活性炭(AC)^[3]、碳气凝胶^[4]、碳纳米管^[5]、石墨烯^[6]、三维多孔碳^[7]等。赝电容器则依据电极材料表面发生的快速法拉第反应来储存电能^[2], 研究最广泛的赝电容材料主要包括导电聚合物^[8]、过渡金属氧化物^[9]和金属有机骨架材料^[10]。

在金属有机骨架材料中, 普鲁士蓝类似物(PBA)具有开放的框架结构和较宽的离子通道, 有利于离子的高速迁移, 具有较高的理论容量^[11]。但是 PBA 的导电性能较差, 实际容量不高, 循环寿命不佳^[12]。Lee 等^[13]制备了普鲁士蓝/氧化石墨烯复合材料(PB/GO), PB 的开放框架结构与 GO 网络的结合促进了钠离子和电子的快速转移。PB/GO||AC 混合电容器在 1.0 A/g 下循环 10 000 圈后容量保持率为 79%。Wu 等^[14]制备出聚吡咯(PPy)包覆六氰铁酸镍钴(Ni_2CoHCF)的核壳结构材料, 提升了材料的导

电性, 将其与活性炭耦合构建的非对称超级电容器, 在功率密度为 888 W/kg 时显示出 $21.7\text{ W}\cdot\text{h/kg}$ 的能量密度, 5 000 次循环后容量保持率为 85%。虽然将 PBA 与导电材料复合会明显改善材料的电容性能, 但容量和稳定性与理论预期仍有差距, 研发新型复合材料并低成本制备对产业推广尤为重要。

褐煤价格低廉且含碳量高, 可用于制备高比表面积和孔结构丰富的纳米多孔碳(NPC)^[15-16], 具有较高的功率密度。本工作通过溶液共沉淀法成功将 Fe 基普鲁士蓝负载于 NPC 上得到 Fe 基普鲁士蓝@纳米多孔碳复合材料(PB@NPC), 比表面积高达 $2122\text{ m}^2/\text{g}$, 并研究复合材料的电化学性能和储能机理。

1 实验

1.1 纳米多孔碳的制备

将褐煤粉碎后 100 目过筛得到褐煤粉末。将 4 g 褐煤粉加入到 100 mL 4 mol/L HNO_3 中, 在室温下搅拌 8~10 h, 然后用去离子水抽滤洗涤至滤液呈中性。将烘干的样品置于 5 mol/L NaOH 的溶液中, 在水浴温度 $50\text{ }^\circ\text{C}$ 搅拌 8~10 h, 用去离子水抽滤清洗至滤液呈中性, 将产物烘干。将褐煤与 KOH 混合

收稿日期: 2023-10-27。 修订日期: 2023-12-09。

基金项目: 湖北隆中实验室自主创新研究项目(2022ZZ-35)。

第一作者: 陈秋爽(2000), 女, 硕士研究生。

通信作者: 赵春霞(1977), 女, 博士, 教授。

Received date: 2023-10-27. Revised date: 2023-12-09.

First author: CHEN Qiushuang (2000-), female, Master candidate.

E-mail: chenqsdejv@163.com

Correspondent author: ZHAO Chunxia (1977-), female, Ph.D., Professor.

E-mail: zhaochunxia@whut.edu.cn

(质量比为 1:3)后在 Ar 气氛下 800 °C 热处理 1 h, 再次清洗后干燥, 得到纳米多孔碳(NPC)。

1.2 PB@NPC 的制备

称取 0.32 g 六水合三氯化铁($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)溶于 100 mL 去离子水中, 记为 A 液; 称取 0.5 g NPC 和 0.37 g 三水合亚铁氰化钾($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$)溶于 100 mL 去离子水中, 超声分散得到黑色悬浊液, 记为 B 液。在搅拌条件下, 将 A 液以恒定流速泵入到 B 液中, 继续搅拌 4 h 后静置 2 h, 抽滤洗涤后烘干, 得到蓝黑色粉末(PB@NPC)。PB 的制备方法与 PB@NPC 类似, 但在制备过程中不加入 NPC。

1.3 样品表征

采用荷兰 PANalytical 生产的 Empyrean 型 X 射线衍射仪(XRD)和法国 LabRAM Odyssey 型 Raman 光谱仪分析样品的物相结构和组成。采用美国 Micromeritics 公司生产的 ASAP 2020M 型比表面积及孔隙度分析仪对样品进行 N_2 吸脱附测试, 分析样品的比表面积和孔径分布。采用美国 Thermo Fisher 公司生产的 ESCALAB 250Xi 型 X 射线光电子能谱仪(XPS)分析样品的元素种类、价态以及成键方式。

1.4 电化学性能测试

将活性物质、乙炔黑以及 10%(质量分数)的聚四氟乙烯(PTFE)乳液按照 8:1:1 的质量比混合, 并加入 3 mL 异丙醇于玛瑙研钵中充分研磨至泥团状, 使用对辊机将样品均匀压覆成片状, 真空干燥后将其压覆在 1 cm×1 cm 的泡沫镍上, 得到测试所需的电极。

采用美国 AMETEK 公司的 Solartron Analytical 1470E 电化学工作站进行循环伏安测试(CV)、恒电流充放电测试(GCD)及电化学阻抗谱测试(EIS)。三电极系统采用 Ag/AgCl 电极为参比电极, 铂片为对电极, 所制备材料电极作为工作电极。以 1 mol/L KNO_3 水溶液为电解液, 玻璃纤维膜作为隔膜, 组装成 2032 型对称式电容器。

基于 CV 测试数据, 利用式(1)计算出电极材料的比电容:

$$C_s = \frac{\int_{V_1}^{V_2} I_s dV}{m \Delta V} \quad (1)$$

式中: C_s 为电极的比电容(F/g); I_s 表示响应电流(A); v 为扫描速率(V/s); m 为活性物质的质量(g); ΔV 是 $V_2 - V_1$ 测试电位差(V); V_1 、 V_2 分别为循环过程中的低位和高位电压(V); V 是循环过程中的瞬时电压。

基于 GCD 测试数据, 采用式(2)可计算电极材料的比电容:

$$C = \frac{I \Delta t}{m \Delta V} \quad (2)$$

式中: C 为放电比电容(F/g); I 为放电电流(A); Δt 为放电时间(s)。

电容器的能量密度 E (W·h/kg)和功率密度 P (W/kg)分别根据式(3)和式(4)计算:

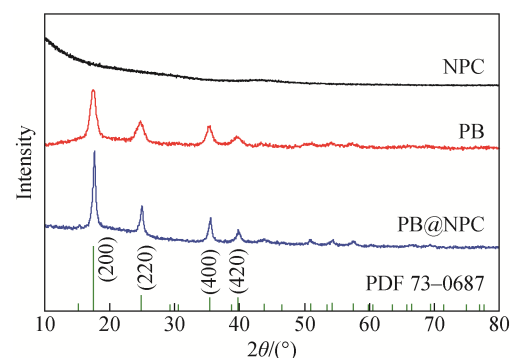
$$E = \frac{C \Delta V^2}{2} \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

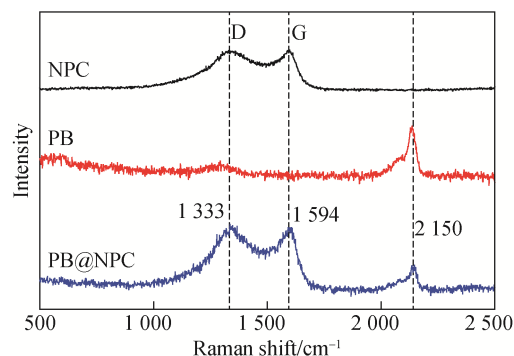
2 结果与讨论

2.1 晶体结构及成分分析

对所制备的 PB@NPC 及其对照样进行 XRD 测试, 结果如图 1a 所示, 在 17.5°、24.8°、35.4°、39.8° 的衍射峰对应于立方相 PB 的(200)、(220)、(400)、(420)晶面^[17]。在 PB@NPC 复合样品的 XRD 谱中, PB 特征峰的峰位没有明显改变, 但峰强增大, 说明复合后 PB 结晶性较好。图 1b 是对应的 Raman 光谱, PB@NPC 在 1 333 cm^{-1} 和 1 594 cm^{-1} 处的 2 个峰分别对应于复合材料中碳的 D 峰和 G 峰, 在 2 150 cm^{-1} 附近的峰对应于 PB 中—CN 的伸缩振动^[18]。



(a) XRD patterns of NPC, PB and PB@NPC



(b) Raman spectra of NPC, PB and PB@NPC

Note: NPC is nanoporous carbon; PB is Prussian blue; PB@NPC is Prussian blue@ nanoporous carbon composite.

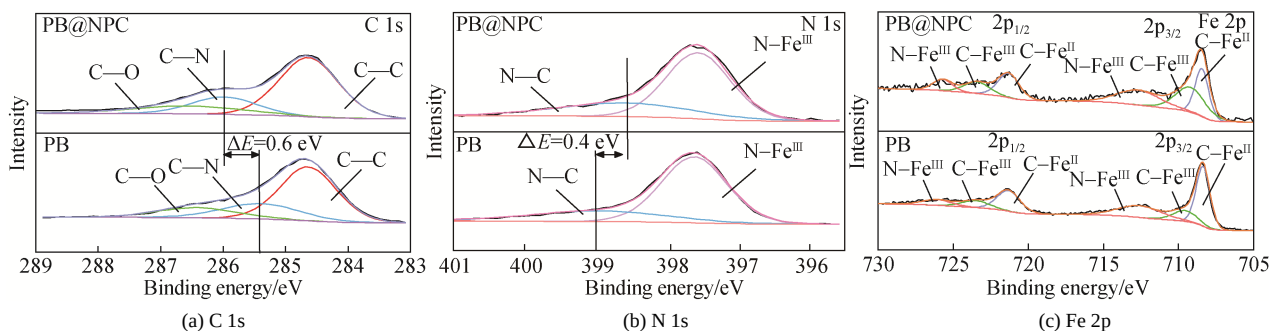
图 1 样品的 XRD 谱和 Raman 光谱

Fig. 1 XRD patterns and Raman spectra of samples

对样品进行 XPS 测试, 其中 C 1s 的 XPS 谱解卷积可得图 2a, 分别对应为 C—C 键(284.6 eV)、C—O 键(286.4 eV)和 C—N 键^[19]。与 PB 相比, PB@NPC 中 C—N 向高结合能位置偏移了 0.6 eV; 图 2b 为 N 1s 的高分辨能谱, PB 与 PB@NPC 中 N—C 的结合能分别为 399.0 eV 和 398.6 eV, 后者中 N—C 向低结合能位置偏移了 0.4 eV。分析认为, 复合材料中 C 与 N 结合能的变化与其电负性改变有关, 是由 PB 和 NPC 之间的界面结合影响

所致。

图 2c 是 Fe 2p 的高分辨能谱, 均呈现为 3 对特征峰, 结合能没有发生明显化学位移。位于 708.4 eV 和 721.3 eV 的峰归属于 $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ 中的 $\text{Fe}^{\text{II}} 2p_{3/2}$ 和 $\text{Fe}^{\text{II}} 2p_{1/2}$, 位于 709.5 eV 和 723.5 eV 的峰为 $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ 中的 $\text{Fe}^{\text{III}} 2p_{3/2}$ 和 $\text{Fe}^{\text{III}} 2p_{1/2}$ 。此外, 在 712.6 eV 和 726.1 eV 观察到与 N 配位的 $\text{Fe}^{\text{II}} 2p_{3/2}$ 和 $\text{Fe}^{\text{III}} 2p_{1/2}$ 对应的峰^[17, 20], 分析认为, 所制备的 PB 中部分 $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ 中的 Fe^{2+} 被氧化为 Fe^{3+} 。



Note: ΔE is the shift of the binding energy between PB and PB@NPC.

图 2 PB 与 PB@NPC 的 XPS 高分辨能谱

Fig. 2 XPS spectra of PB and PB@NPC

2.2 孔径分布与比表面积分析

基于 N_2 吸脱附测试分析获得材料的孔结构信息列于表 1。PB 的 N_2 吸脱附曲线(图 3a)存在明显的滞后环, 属于 IV 型曲线, 孔径分布集中在 1~4 nm, 最可几孔径为 3.5 nm(图 3b)。而 PB@NPC 的 N_2 吸脱附曲线为 I 型线(图 3c), 比表面积高达 2 122 m^2/g , 最可几孔径为 2.3 nm(图 3d), 具有大量的微孔和介孔, 主要源自 NPC 的多孔结构。

2.3 电化学性能研究

图 4a 是样品在三电极体系中的 CV 曲线对比图。NPC 的 CV 曲线近似矩形, 反映出典型的双电层电容行为。PB 的 CV 曲线在 0.5 V 附近可以观察到 1 个较宽的氧化峰, 对应于 Fe^{2+} 向 Fe^{3+} 转化, 同时 K^+ 脱出^[21]。PB@NPC 的 CV 曲线有 1 对清晰的氧化还原峰, 为典型的赝电容行为; 在高电位和低电位附近的曲线近似矩形, 说明其也具有双电层电容特性。PB 的电压区间为 0.9 V, 而 PB@NPC 的电压区间拓宽到了 1.1 V, 这是由于复合材料中 NPC

的三维多孔结构对 PB 颗粒的稳定作用延缓了晶格畸变^[22], 拓宽了电压窗口。

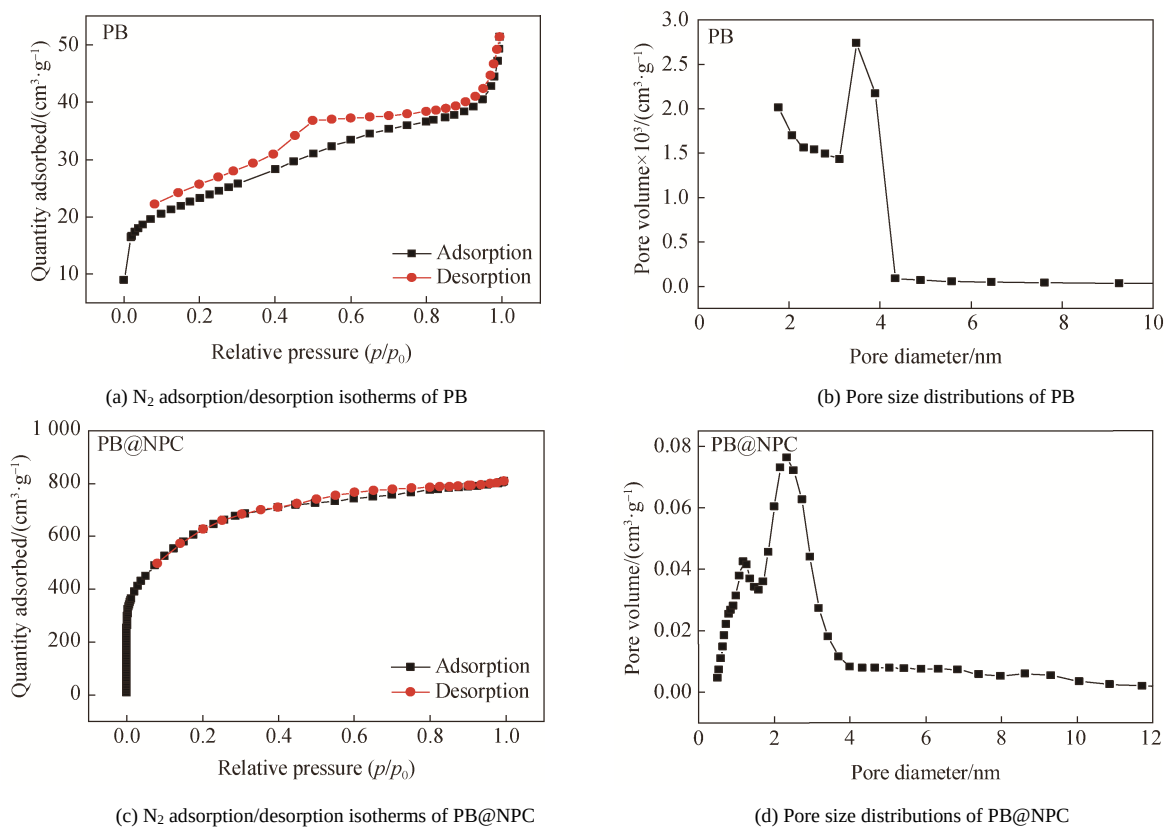
根据式(1)计算可知, 在 5 mV/s 的扫速下 NPC、PB 和 PB@NPC 的比电容分别为 181.02、184.38 F/g 和 483.45 F/g, PB@NPC 材料的比电容最高。图 4b 中显示 PB@NPC 的放电时间最长, 其比电容高于目前报道的空心普鲁士蓝/碳纳米管复合材料^[19]和普鲁士蓝/三维氮掺杂碳复合材料^[22]。分析认为, NPC 的多孔结构能加速材料对于离子的吸附速率, 且能提供更多的电化学反应位点, 更有利于电化学反应的进行。结合图 4c 的 EIS 曲线和表 1 的拟合数据可知, 对于系统电阻 R_s , $R_s(\text{PB}) > R_s(\text{PB@NPC}) > R_s(\text{NPC})$, 说明加入 NPC 可以改善 PB 的导电性; PB@NPC 在低频区直线的斜率大于 PB, 说明其扩散电阻小于 PB。因此, PB 负载于 NPC 上后 R_s 和扩散电阻均减小, 呈现出较好的导电性和离子扩散速率。分析认为 NPC 的多孔结构为 PB 提供了更多的离子传输通道, 加速了离子转移。

表 1 样品的孔结构数据、比电容和 EIS 拟合数据

Table 1 Parameters of pore structure, specific capacitance and EIS fitting data of samples

Samples	BET specific surface area/($\text{m}^2 \cdot \text{g}^{-1}$)	Average pore diameter/nm	Specific capacitance/($\text{F} \cdot \text{g}^{-1}$)	R_s/Ω	R_{ct}/Ω
NPC	2 700	2.3	181.02	1.88	0.62
PB	80	3.5	184.38	2.85	0.45
PB@NPC	2 122	2.3	483.45	2.04	0.58

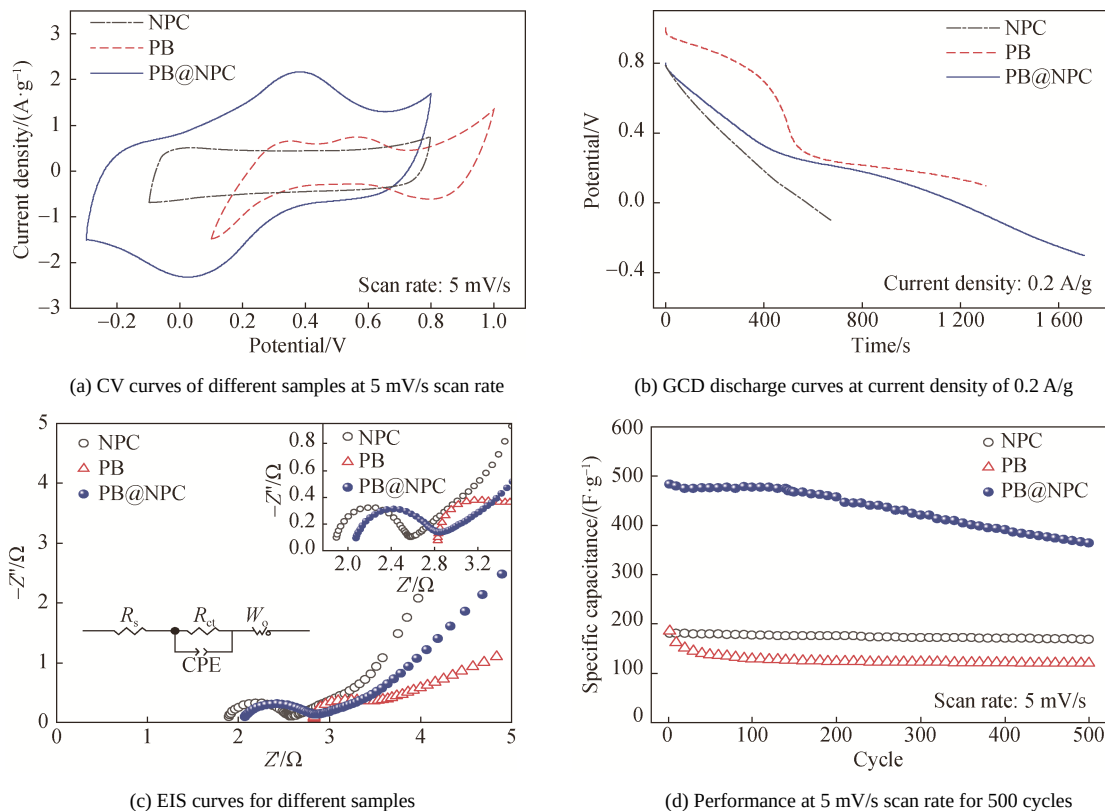
Note: R_s is internal resistance; R_{ct} is charge transfer resistance.



Note: p is pressure of the adsorbed gas at equilibrium at 77 K; p_0 is saturated pressure of adsorbate gas.

图3 PB与PB@NPC的N₂吸脱附等温曲线和孔径分布曲线

Fig. 3 N₂ adsorption/desorption isotherms and pore size distributions of PB and PB@NPC



Note: Z' is real part of resistance while Z'' indicates the imaginary part of the impedance Z ; W_o is warburg impedance; CPE is constant phase element.

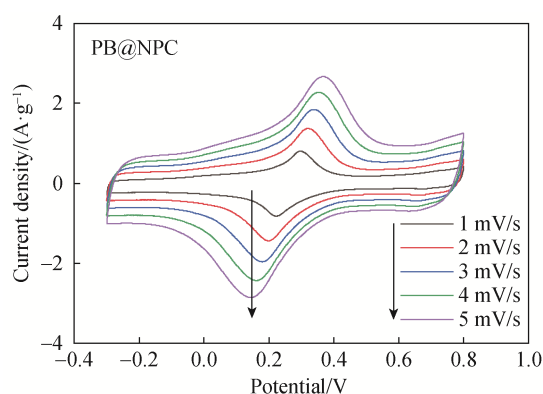
图4 样品的CV曲线、GCD放电曲线、EIS曲线和循环性能图

Fig. 4 CV curves, GCD discharge curves, EIS curves and cycle performance of samples

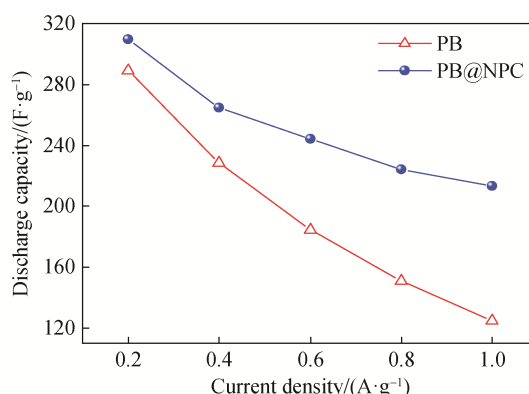
图 4d 为各样品在 5 mV/s 扫速下循环 500 圈后的比电容变化图, 其中 NPC 的容量保持率为 93%, 体现出碳材料双电层储能的循环稳定性优点。而 PB 在循环 500 圈后的容量保持率仅为 65%, 这与法拉第反应造成晶格畸变有关。而 PB@NPC 在循环 500 圈后仍具有 364.14 F/g 的比电容, 容量保持率为 75%, 相较 PB 有了明显提升。这是由于部分 PB 被限制在 NPC 孔结构中, NPC 的三维框架延缓了 PB 的晶格畸变, 同时 PB@NPC 的扩散电阻降低, 减弱了材料在多次循环后的电化学极化现象, 获得了

较好的循环稳定性^[22]。

图 5a 是 PB@NPC 在不同扫速下的 CV 曲线, 随着扫速的增加, 氧化还原峰发生偏移, 这是电极极化和氧化还原反应不完全造成的^[23]。根据式(2)计算得出不同电流密度下的比电容(图 5b)。PB@NPC 在 0.2 A/g 下容量为 309.35 F/g, 在 1.0 A/g 下仍有 213.09 F/g 的容量, 明显高于 PB(124.67 F/g), 显示了优良的倍率性能。综上, 所构筑的复合材料发挥赝电容与双电层电容的协同作用, 拓宽了电化学电压区间, 加速了离子转移, 提升了储能容量。



(a) CV curves of PB@NPC at different scan rates



(b) Change in discharge capacity with respect to current densities

图 5 PB@NPC 的 CV 曲线和比电容随电流密度的变化关系图

Fig. 5 CV curves of PB@NPC and specific capacitance at different current densities

2.4 电容器的性能和机理分析

将材料制作电极并组装成对称式电容器后, PB 电容器的电压区间选定为 0.2~1.2 V, PB@NPC 电容器的电压区间选定为 -0.8~0.8 V。图 6a 所示为在不同电流密度下的倍率性能, 结果显示: PB 的容量衰减严重, 而 PB@NPC 在不同电流密度下都有着更高的容量, 在 0.05 A/g 时的容量为 72.19 F/g, 在 1.0 A/g 时容量保持率仍有 87%, 且经过大电流密度的充放电之后仍能回到初始容量值, 反映出复合材料的结构稳定性良好。

图 6b 为电容器循环 1 000 圈的容量变化图, PB 电容器和 PB@NPC 电容器在反应前期都有一定的容量衰减, 对应于电极材料与电解液之间的副反应以及 SEI 膜的形成。但在随后的循环中, PB@NPC 电容器的容量衰减变缓, 循环 1 000 圈后的容量保持率为 91%, 显著优于 PB 电容器 (34%)。结合 EIS 分析结果可知(图 6c 和表 2), 循环 1 000 圈后 PB 的电荷转移电阻(R_{ct})增加, 这与 PB 中空位缺陷有关, 会破坏电子转移路径^[24], 同时 PB 与电解液的副反应加剧, 进而破坏材料的结构, 电阻增大。而 PB@NPC 的 R_{ct} (0.86 Ω)

明显减小(初始值为 3.81 Ω), 分析认为, NPC 在反应过程中有助于 SEI 膜的形成及改善, SEI 膜可以形成一个钝化层, 有效防止电极材料的脱落, 并阻止材料与电解液之间的副反应^[25], 进而有利于材料的结构稳定, 使之在长循环中仍具有高效的电子传导。此外, PB@NPC 循环 1 000 圈后的扩散电阻也小于初始扩散电阻值, 这是由于 NPC 材料在循环过程逐渐活化, 多孔结构使得金属阳离子的扩散速度逐渐提升。

计算电容器的功率密度和能量密度并绘制成 Ragone 曲线(图 6d)。所制备的 PB@NPC 对称电容器在功率密度为 800 W/kg 时仍提供 22.4 W·h/kg 的能量密度, 与已报道的 PBA 电容器相比, 在相当的功率密度下具有更高的能量密度^[14, 26]。分析认为, PB@NPC 复合材料中 NPC 的多孔结构可以延缓 PB 的晶格畸变, 为可能引起的结构坍塌起到了缓冲作用, 还可以促进电解液的渗透与扩散, 提供更多的电化学反应位点。同时, NPC 的三维结构改善了材料的导电性, 所以二者复合之后电极材料的容量、导电性、倍率性能和循环性能都得到了显著提升。

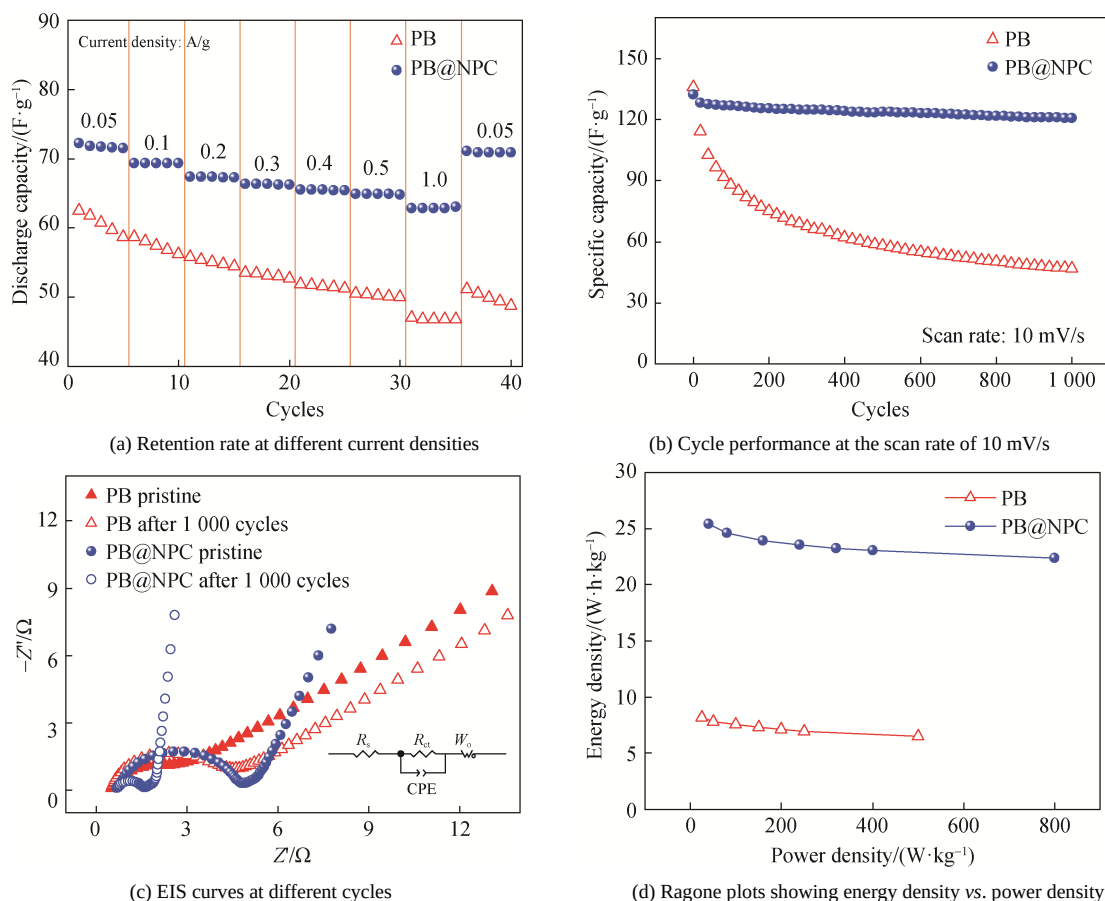


图6 PB电容器和PB@NPC电容器的电化学性能对比

Fig. 6 Comparison of electrochemical performance of PB and PB@NPC capacitors

表2 PB和PB@NPC对称式电容器的EIS拟合数据

Table 2 EIS fitting data of PB and PB@NPC capacitors

Samples	R_s/Ω	R_{ct}/Ω
PB pristine	0.66	1.39
PB after 1000 cycles	0.51	3.50
PB@NPC pristine	0.77	3.81
PB@NPC after 1000 cycles	0.67	0.86

3 结论

采用溶液共沉淀法一步制备了PB@NPC复合材料,不仅具有高比表面积和优良的导电性,并且多孔结构提供了丰富的离子传输路径,促进电解液的渗透和扩散,双电层电容和赝电容协同作用,极大地提高了电化学性能。在三电极体系下,PB@NPC的比电容为483.45 F/g (5 mV/s),在0.2 A/g下的比电容为309.35 F/g,并且倍率性能良好。组装的水系钾离子对称电容器具有循环寿命长(1 000圈,91%)、倍率性能佳和功率密度大等优点,是一类性能优良、具有应用潜力的新型超级电容器电极材料。

参考文献:

[1] DENG X L, ZOU K Y, CAI P, et al. Advanced battery-type anode

materials for high-performance sodium-ion capacitors[J]. Small Meth, 2020, 4(10): 2000401.

- [2] BUENO P R. Nanoscale origins of super-capacitance phenomena[J]. J Power Sources, 2019, 414: 420–434.
- [3] LEE K S, SEO Y J, JEONG H T. Capacitive behavior of functionalized activated carbon-based all-solid-state supercapacitor[J]. Carbon Lett, 2021, 31(5): 1041–1049.
- [4] CHEN R W, LI X S, HUANG Q B, et al. Self-assembled porous biomass carbon/RGO/nanocellulose hybrid aerogels for self-supporting supercapacitor electrodes[J]. Chem Eng J, 2021, 412: 128755.
- [5] ARKHIPOVA E A, VIKTOROVA A S, IVANOV A S, et al. Nitrogen- and oxygen-doped multi-walled carbon nanotubes for supercapacitor with ionic liquid-based electrolyte[J]. Funct Mater Lett, 2020, 13(4): 2040002.
- [6] WORSLEY E A, MARGADONNA S, BERTONCELLO P. Application of graphene nanoplatelets in supercapacitor devices: A review of recent developments[J]. Nanomaterials (Basel), 2022, 12(20): 3600.
- [7] ZHANG X H, HAN R Y, LIU Y Z, et al. Porous and graphitic structure optimization of biomass-based carbon materials from 0D to 3D for supercapacitors: A review[J]. Chem Eng J, 2023, 460: 141607.
- [8] ETMAN A E S, IBRAHIM A M, DARWISH F A Z M, et al. A 10years-developmental study on conducting polymers composites for supercapacitors electrodes: A review for extensive data interpretation[J]. J Ind Eng Chem, 2023, 122: 27–45.
- [9] DAI M Z, ZHAO D P, WU X. Research progress on transition metal oxide based electrode materials for asymmetric hybrid capacitors[J].

- Chin Chemical Lett, 2020, 31(9): 2177–2188.
- [10] DĚDEK I, KUPKA V, JAKUBEC P, et al. Metal-organic framework/conductive polymer hybrid materials for supercapacitors[J]. Appl Mater Today, 2022, 26: 101387.
- [11] XIE B X, SUN B Y, GAO T Y, et al. Recent progress of Prussian blue analogues as cathode materials for nonaqueous sodium-ion batteries[J]. Coord Chem Rev, 2022, 460: 214478.
- [12] 魏程, 江宁波, 张露露, 等. 普鲁士蓝类化合物作为钠离子电池正极材料的研究进展[J]. 硅酸盐学报, 2021, 49(6): 1078–1090. WEI Cheng, JIANG Ningbo, ZHANG Lulu, et al. J Chin Ceram Soc, 2021, 49(6): 1078–1090.
- [13] LEE S Y, PARK J Y, KIM H J, et al. Prussian blue-graphene oxide composite cathode for a sodium-ion capacitor with improved cyclic stability and energy density[J]. J Alloys Compd, 2022, 898: 162952.
- [14] WU S, FENG Q L, ZHOU S, et al. Core-shell shaped $\text{Ni}_2\text{CoHCF}@PPy$ microspheres from Prussian blue analogues for high performance asymmetric supercapacitors[J]. Nanotechnology, 2021, 32(44): 445402.
- [15] ZHAO J, JIANG Y F, FAN H, et al. Porous 3D few-layer graphene-like carbon for ultrahigh-power supercapacitors with well-defined structure-performance relationship[J]. Adv Mater, 2017, 29(11): 1604569.
- [16] ZHAO C X, YU Z G, CHEN Q S, et al. Molten salt-assisted fabrication of hierarchical porous carbon derived from lignite for Zn-ion hybrid supercapacitors[J]. Mater Lett, 2024, 362: 136180.
- [17] SHI W H, LIU X Y, DENG T Q, et al. Enabling superior sodium capture for efficient water desalination by a tubular polyaniline decorated with Prussian blue nanocrystals[J]. Adv Mater, 2020, 32(33): e1907404.
- [18] MAŽEIKIENĖ R, NIAURA G, MALINAUSKAS A. Electrocatalytic reduction of hydrogen peroxide at Prussian blue modified electrode: An *in situ* Raman spectroelectrochemical study[J]. J Electroanal Chem, 2011, 660(1): 140–146.
- [19] GONG A, ZHAO Y B, LIANG B L, et al. Stepwise hollow Prussian blue/carbon nanotubes composite as a novel electrode material for high-performance desalination[J]. J Colloid Interface Sci, 2022, 605: 432–440.
- [20] WU X Y, SHAO M M, WU C H, et al. Low defect $\text{FeFe}(\text{CN})_6$ framework as stable host material for high performance Li-ion batteries[J]. ACS Appl Mater Interfaces, 2016, 8(36): 23706–23712.
- [21] ZHANG X J, TAO L, HE P, et al. A novel cobalt hexacyanoferrate/multi-walled carbon nanotubes nanocomposite: Spontaneous assembly synthesis and application as electrode materials with significantly improved capacitance for supercapacitors[J]. Electrochim Acta, 2018, 259: 793–802.
- [22] GONG A, ZHAO Y B, HE M M, et al. High-performance desalination of three-dimensional nitrogen-doped carbon framework reinforced Prussian blue in capacitive deionization[J]. Desalination, 2021, 505: 114997.
- [23] ZHANG D P, ZHANG J S, YANG Z X, et al. Nickel hexacyanoferrate/carbon composite as a high-rate and long-life cathode material for aqueous hybrid energy storage[J]. Chem Commun, 2017, 53(76): 10556–10559.
- [24] LUO J H, SUN S X, PENG J, et al. Graphene-roll-wrapped Prussian blue nanospheres as a high-performance binder-free cathode for sodium-ion batteries[J]. ACS Appl Mater Interfaces, 2017, 9(30): 25317–25322.
- [25] SHAO H, WU Y C, LIN Z F, et al. Nanoporous carbon for electrochemical capacitive energy storage[J]. Chem Soc Rev, 2020, 49(10): 3005–3039.
- [26] NASKAR P, DEBNATH S, MAITI A, et al. Low-cost and scalable Ni-prussian blue analogue// functionalized carbon based Na-ion systems for all climate operations[J]. Chemphyschem, 2023, 24(4): e202200588.

Preparation and Supercapacitive Properties of Fe-based Prussian Blue@Nanoporous Carbon Composites

CHEN Qiushuang^{1,2}, ZHAO Chunxia^{1,2}, CHEN Yekai², CHEN Wen²

(1. Hubei Longzhong Laboratory, Xiangyang 441000, Hubei, China;

2. School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, China)

Extended Abstract

Introduction Supercapacitors (SCs) are known as one of the most promising energy storage devices due to their high-power density and excellent cycle stability. The performance of SCs is closely related to the electrochemical performance of electrode materials. The widely-used electrodes are carbon-based materials and their derivatives. Carbon materials contribute energy storage based on double layer capacitance associated with ion adsorption and desorption, achieving excellent power density and cycle stability. However, they lack in high capacitance because of limitation of surface area. Instead, Fe-based Prussian blue (PB) is a promising pseudocapacitive material with open frame structure and high theoretical capacitance, but the poor electrical conductivity limits its rate performance and cycle stability. Combining PB with carbon materials is considered as an effective solution to develop advanced electrode composites. Herein, nanoporous carbon (NPC) derived from lignite has been prepared with high specific surface area and good electrical conductivity. Then, Fe-Prussian blue was successfully loaded on NPC via co-precipitation method to obtain Fe-Prussian blue@ nanoporous carbon composite (PB@NPC). The fabricated PB@NPC composite possesses high specific surface area, high specific capacitance and excellent cycle stability.

Methods The lignite powder was obtained by crushing the lignite with 100 mesh and sifting, and then mixed in 4 mol/L HNO_3 and

stirred for 8–10 h. After washing and drying, the collection was dispersed in 5 mol/L NaOH for 8–10 h with stirring, following by washing with deionized water and drying to obtained pre-treated lignite. Then, the pre-treated lignite was mixed with KOH at a mass ratio of 1:3 and heat treated at 800 °C in Ar atmosphere for 1 h, and then washed and dried to obtain nanoporous carbon (NPC).

0.32 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL deionized water. 0.5 g NPC and 0.37 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ were mixed with 100 mL deionized water and ultrasonicated to obtain a black suspension. Then, ferric chloride solution was added into the suspension under stirring for 4 h and aging for 2 h. The precipitate formed was collected by centrifugation and then dried at 80 °C for 12 h. The as-prepared sample was labeled as PB@NPC. The preparation method of PB was similar to that of PB@NPC but without NPC addition in the preparation process.

The phase structure, valence state, bonding mode, specific surface area and pore size distribution of NPC, PB and PB@NPC were investigated. The mechanism of improved properties of PB@NPC was discussed. The electrochemical performance of both PB and PB@NPC symmetrical capacitor were conducted.

Results and discussion From XRD and Raman tests, the characteristic peaks of PB and NPC can be observed, which proves the successful synthesis of PB@NPC. The XPS spectra show that C-N bond binding energy in PB@NPC is significantly shifted compared with PB. It is concluded that the shift of binding energy of C and N in the composite is related to the change of electronegativity, which is the result of the interface binding effects between PB and NPC. The specific surface area of PB@NPC reached to 2122 m^2/g with a large number of micropores and mesopores by N_2 adsorption/desorption analysis.

The electrochemical performance was tested in a three-electrode system. The CV curves of PB@NPC have clear redox peaks, revealing typical pseudocapacitive behavior. The curve near the high potential and low potential is approximately rectangular, also indicating the characteristics of double layer capacitance. The specific capacitance of PB@NPC is 309.35 F/g at a current density of 0.2 A/g and even maintains 213.09 F/g at 1.0 A/g, which is much higher than PB (112.20 F/g), showing remarkable rate performance of PB@NPC. The EIS results demonstrate that the internal resistance R_s and diffusion resistance R_{ct} of PB@NPC are both lower than that of PB, showing better electrical conductivity and ions diffusion rate. It is proposed that the porous structure of NPC provides more ion transportation channels for PB and accelerates ion transfer. At a sweep speed of 5 mV/s, PB@NPC yields a specific capacitance of 364.14 F/g after 500 cycles. The capacitance retention rate is 75%, which is higher than that of PB (65%).

Compared with PB capacitors, PB@NPC capacitors have higher capacitance under different current density and can still return to the initial capacitance after high current density, reflecting the good structural stability. As shown in Ragone plot, PB@NPC capacitor has much better performance than PB capacitor, providing 22.4 Wh/kg energy density at the power density of 800 W/kg. Moreover, the capacitance retention of the capacitor after 1000 cycles is 91%, much higher than that of PB capacitor (34%). It is proposed that the porous structure of NPC in the composite can delay the lattice distortion of PB and promote the penetration and diffusion of electrolyte.

Conclusions The PB@NPC composite was prepared *via* co-precipitation method. It possesses high specific surface area and excellent electrical conductivity. The fabricated porous structure provides abundant ion transport paths to promote the penetration and diffusion of electrolyte. PB@NPC demonstrates high capacitance due to synergistic effect of double-layer capacitance and pseudo-capacitance. The specific capacitance of PB@NPC electrode is 483.45 F/g at a scan rate of 5 mV/s. The specific capacitance is 309.35 F/g at a current density of 0.2 A/g. The symmetrical capacitor assembled with PB@NPC electrodes exhibits capacitance retention of 91% after 1 000 cycles, revealing excellent cycle stability. PB@NPC is a new type of supercapacitor electrode material with excellent performance and a potential electrode material to be commercialized.

Keywords Fe-based Prussian blue; nanoporous carbon; solution co-precipitation method; synergistic effect; symmetrical capacitor