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Effect of Pore Size on Pseudo-Capacitive Performance of NiO in the Mixed Electrolyte of KOH and Hexacyanoferrate

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KOH 和 $K_3[Fe(CN)_6]$ 混合液中颗粒孔径对 NiO 电极电容器性能的影响

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摘要: 合成 5 种孔径大小分布的 NiO 样品, 测定各 NiO 电极在 3 mol/L KOH 或其添加 $K_3[Fe(CN)_6]$ 的电解液中的电化学电容性能. 结果表明, NiO 电极孔径分布在 15 nm 左右, 可有效减慢铁氰酸根离子向液相的扩散, 从而提高 N_4 (NiO) 电极的充放电效率.

关键词: 超级电容器; NiO; 多孔材料; $K_3[Fe(CN)_6]$

中图分类号: O646

文献标识码: A

电化学电容器是介于传统电容器和化学电源之间的储能器件, 它在混合动力汽车, 航空航天, 便携式电子设备, 轨道车辆能量存储等方面有着非常广泛的应用. 超级电容器按储能机理区分大致有 2 类: 以双电层存储电荷的双电层电容和以表面氧化还原反应存储电荷的法拉第准电容^[1-2]. 双电层电容器通常以碳作电极材料^[3-4], 而法拉第准电容器则大多采用过渡金属氧化物(如 RuO_2 ^[5], NiO_x ^[6-9], CoO_x ^[10], MnO_2 ^[11-13]) 或导电聚合物等作电极材料^[14-17].

毫无疑问, RuO_2 是当前最佳的准电容材料, 但资源稀缺价格昂贵限制它的应用. Zhang 报道了将 $K_3[Fe(CN)_6]$ 加入到 1 mol/L KOH 电解液中参与氧化还原反应, 从而提高了 CoAl 双氢氧层状化合物电容器的比电容, 但该电容器在充放过程中充放电效率衰减快. 这是由于放电过程电极表面和电解液产生离子浓度差, 造成 $[Fe(CN)_6]^{3-}$ 不断向溶液相扩散, 致使电容器自放电现象加重. 针对这些问题, 本文选用 NiO 作为电极材料, 改善、优化 NiO 孔径, 以抑制 $[Fe(CN)_6]^{3-}$ 的扩散, 有望提高电容器的充放电效率.

1 实验部分

1.1 NiO 的合成

采用不同方法, 分别制备 5 种 NiO 样品($N_1 \sim$

N_5): N_1 , 硝酸镍直接煅烧(550 °C); N_2 , 水热法合成^[16]; N_3 , 有序介孔 NiO 由 SBA-15 模板法制得^[17]; N_4 , 多级孔径氧化镍^[18]; N_5 , 大孔 NiO^[19-20].

1.2 表征及测试

使用 X 射线衍射分析仪(XRD, Brucker D8)表征样品结构; 透射电子显微镜(TEM, Jeol JEM-2010)和扫描电子显微镜(SEM, Philip XL30)观测样品形貌; 自动物理吸附仪(Micromeritics Tristar 3000)测定样品比表面积和孔结构参数(液氮为吸附质), BET 测定样品的比表面积, B. J. H. 法计算孔径分布.

将 NiO、乙炔黑和聚四氟乙烯(PTFE)按 85:10:5 (by mass) 混合, 辊压成膜, 120 °C 烘干(24 h, 面积 1 cm² 膜), 压在泡沫镍网上制成电极. 由 NiO 电极、铂辅助电极、Hg/HgO 参比电极, 电解液 3 mol/L KOH 或 3 mol/L KOH + 0.1 mol/L $K_3[Fe(CN)_6]$ 组成三电极体系. 电化学工作站(Solartron Instrument Model 1287 and Electrochemical Interface1255B Frequency Response Analyzer)测定样品电极的循环伏安曲线、充放电曲线以及交流阻抗谱.

2 结果与讨论

2.1 NiO 形貌和结构特征

图1为不同NiO样品的XRD衍射图谱. 可以看

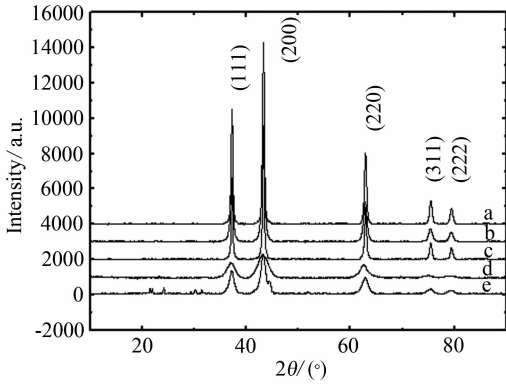


图1 5种NiO样品的XRD图谱

Fig. 1 XRD patterns of five NiO samples
a ~ e: N1; N2; N3; N4; N5

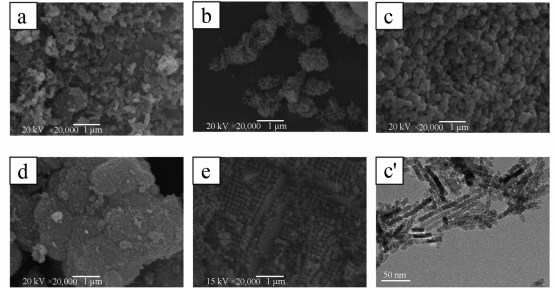
出,5种NiO样品均在 37.2° , 43.3° , 62.9° , 75.4° 和 79.4° 处呈现衍射峰,与标准NiO特征峰(ICDD-JCPDS Card No. 14-0117)一致.其中,N1~N3 NiO样品因合成过程处理温度较高,故对应的XRD峰更高,即结晶度更好.而N4和N5 NiO样品的XRD特征峰明显宽化,说明该2种样品颗粒尺寸较小.

图2示出上述5种NiO样品(N1~N5)扫描电镜照片.由图看出,N1样品呈现出小颗粒团聚,平均粒径250 nm左右,且聚成团块状.N2样品呈海胆状形貌,每个“海胆”分别由许多片状团聚成(直径 $0.5 \sim 1 \mu\text{m}$).N3样品呈无规则状,大部分颗粒尺寸300~500 nm,但从TEM照片(c')可以清晰看出由SBA-15为母体合成的NiO纳米线,孔径分布在3~4 nm之间.N4样品具有蠕虫状的结构,似乎在局部范围内形成了堆积孔结构.N5样品存在三维有序的大孔(130 nm)阵列结构.

图3示出5种NiO样品的孔径分布.从图看出N1(a) N2(b)样品没有出现明显的分布峰,比表面较小,即不具有明显的多孔特性.N3(c)样品在4 nm处有一尖峰,这是由SBA-15产生的典型介孔结构.N4(d)样品的孔径主要分布在15 nm左右.N5(e)样品在30~60 nm有一宽峰,该峰由100 nm以下颗粒堆积而成,其大孔尺寸处于100~200 nm之间.

2.2 NiO 电极电化学性能

N4(NiO)电极分别在3 mol/L KOH和加入0.1 mol/L $\text{K}_3[\text{Fe}(\text{CN})_6]$ 的3 mol/L KOH电解液中的循环伏安曲线如图4所示.据图,在KOH

图2 5种NiO样品的SEM及N3(c')样品的TEM照片
Fig. 2 SEM images of the N1 (a), N2 (b), N3 (c), N4 (d), N5 (e) samples and TEM image of N3 (c')

溶液中,曲线(a)于0.25 V和0.45 V处清溶液中,曲线(a)于0.25 V和0.45 V处清晰出现的一对氧化还原峰,对应于NiO的氧化还原:



电解液添加 $\text{K}_3[\text{Fe}(\text{CN})_6]$ 后,在0.25~0.45 V电位区,呈现了两对氧化还原峰(b),峰宽明显增加.这是由于加入了活性的 $\text{K}_3[\text{Fe}(\text{CN})_6]$ 参与了另一电极反应:

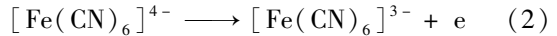


图5示出N4电极恒流(1 A/g)电容器充放电曲线.从图看出,KOH电解液中加入 $0.1 \text{ mol} \cdot \text{L}^{-1} \text{K}_3[\text{Fe}(\text{CN})_6]$ 后,电容器容量显著增加.实验同时表明,本文制备的5种NiO电极均能有效地提高电极比容量.但 $[\text{Fe}(\text{CN})_6]^{3-}$ 无法被约束在NiO电极表面,充放电过程中会不断地向溶液相扩散.多次循环后,电极容量不断下降,充放电效率降低.因此,本研究关注焦点即在尝试控制电极孔径及表面状况,以期有效地降低 $[\text{Fe}(\text{CN})_6]^{3-}$ 扩散速率及电极容量衰减.

图6示出NiO电极(恒电位0.54 V)N1和N4交流阻抗图谱.图中,高频区两条曲线的半圆弧与实轴的交点均在 0.2Ω 左右,表明二者的电极、溶液电阻相差不大.在 $10^6 \sim 316.2 \text{ Hz}$ 频区,两种电极的阻抗曲线都呈现出一个半圆弧,此乃NiO电极法拉第电容.而在低频区,N4电极谱出现了第2个半圆弧,对应于电极上 $[\text{Fe}(\text{CN})_6]^{3-}$ 的电荷转移过程,但N1的电极谱线无此过程.由此,可说明N4电极对 $[\text{Fe}(\text{CN})_6]^{3-}$ 有更好的约束能力,使该离子可在电极上进行充放电反应.此外,在 $<1 \text{ Hz}$ 的低频区,N4电极谱线的斜率也大于N1电极的,而且趋近于垂直,可见其电容性能更好.

图7示出5种(NiO)电极在不同充放条件下

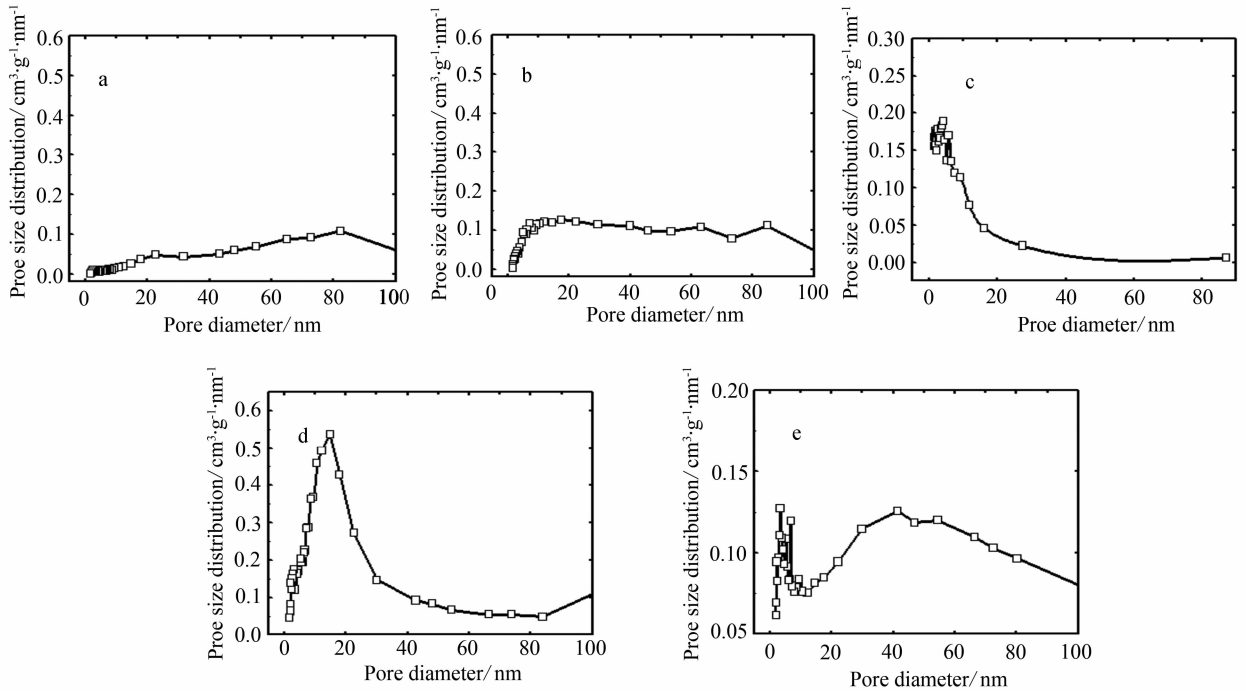


图3 5种NiO样品的孔径分布

Fig. 3 Pore size distributions of five NiO samples N1 (a), N2 (b), N3 (c), N4 (d), N5 (e)

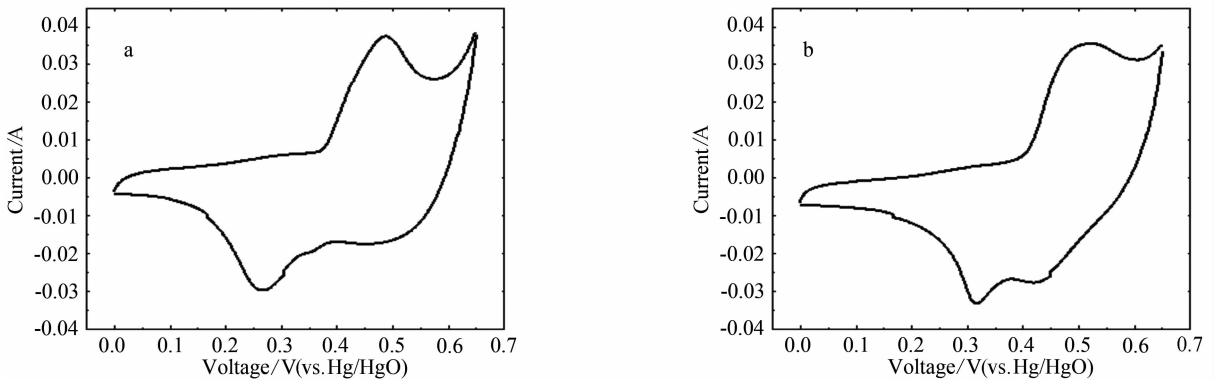


图4 N4(NiO)电极的循环伏安曲线(扫速5 mV/s)

电解液 3 mol/L KOH(a), 3 mol/L KOH + 0.1 mol/L $K_3[Fe(CN)_6]$ (b)

Fig. 4 Cyclic voltammograms of the N4 electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH(a), and $3 \text{ mol} \cdot \text{L}^{-1}$ KOH + $0.1 \text{ mol} \cdot \text{L}^{-1}$ $K_3[Fe(CN)_6]$ (b) electrolytes at a scan rate of 5 mV/s

的库仑效率曲线. 从图中看出, 在 KOH 电解液中, 各电极库仑效率都接近 100%. 而当电解液含有 $K_3[Fe(CN)_6]$, 则其库仑效率相差逐渐明显. 5 A/g 大电流密度下, N1 ~ N5 电极都呈现出较好的库仑效率, 此时 $[Fe(CN)_6]^{3-}$ 的扩散速率还赶不上充放电电流速率. 而在较小电流密度下, 情况就不同. 此时 $[Fe(CN)_6]^{4-}$ 被不断地氧化为 $[Fe(CN)_6]^{3-}$, 且新生成的 $[Fe(CN)_6]^{3-}$ 会从电极表面向电解液体相扩散. 况且, 由于被还原的

$[Fe(CN)_6]^{3-}$ 的量逐渐减少, 随着充放电电流密度之下调, 电极电流效率差别越明显. 但在 1 A/g 电流密度下, N4 (NiO) 电极的库仑效率仍达 90% 以上(见表 1). 相比之下, 该电极能更好的抑制 $[Fe(CN)_6]^{3-}$ 的扩散和转移.

表 1 示出 N1 ~ N5 (NiO) 电极孔径、比表面及其比容量和库仑效率(电解液 3 mol/L KOH + 0.1 mol/L $K_3[Fe(CN)_6]$, 电流密度 1 A/g). 如表, 样品比表面直接影响着电极比容量. 总体来讲, 样品

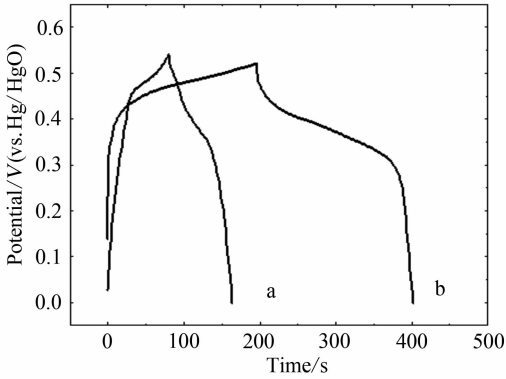


图 5 N4(NiO) 电极恒流充放电曲线
a. 3 mol/L KOH, b. 3 mol/L KOH + 0.1 mol/L $K_3[Fe(CN)_6]$, 电流密度 1 A/g

Fig. 5 The charge-discharge curves of N4 electrode in different electrolytes a. $3 \text{ mol} \cdot \text{L}^{-1} \text{KOH}$, b. $3 \text{ mol} \cdot \text{L}^{-1} \text{KOH} + 0.1 \text{ mol} \cdot \text{L}^{-1} K_3[Fe(CN)_6]$ at current density of 1 A/g

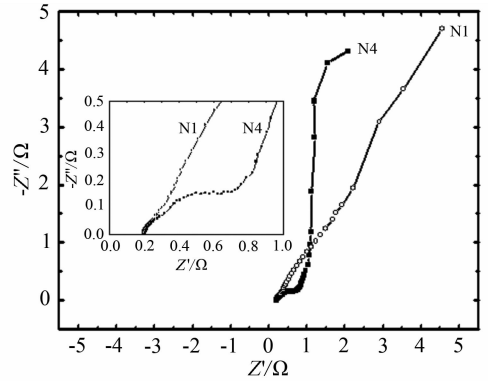


图 6 N1(NiO) 和 N4(NiO) 电极的电化学阻抗谱
恒电位 0.54V, 频率范围 $10^6 \sim 0.01 \text{ Hz}$

Fig. 6 Impedance spectra of the N1 and N4 electrodes at applied potential 0.54V, frequency ranges: $10^6 \sim 0.01 \text{ Hz}$

比表面增大, 电极比容量随之增大. 大比表面使电极能够更好地吸收与接触电解液, 从而提高 NiO

的比容量; 另外, 高比表面样品可为 $[Fe(CN)_6]^{3-}$ 提供更多反应的空间, 使参与电极反应的 $[Fe(CN)_6]^{3-}$ 的量增加. 电极比电容 (C_s): $C_s = (I\Delta t) / (m\Delta V)$. 式中 I 电流, Δt 充放电时间, m 活性物质

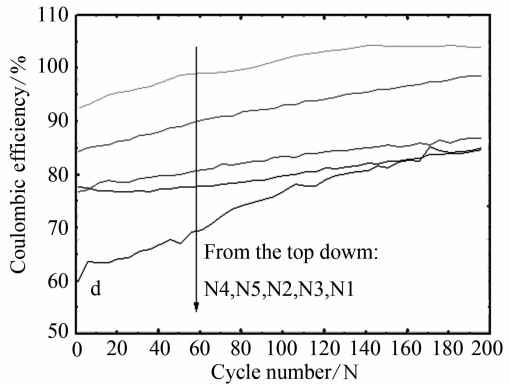
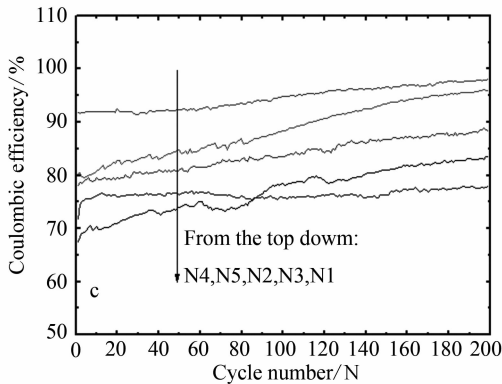
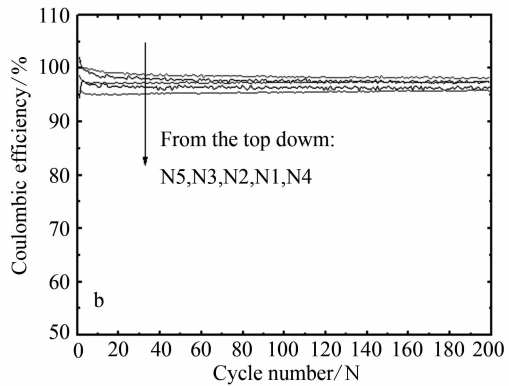
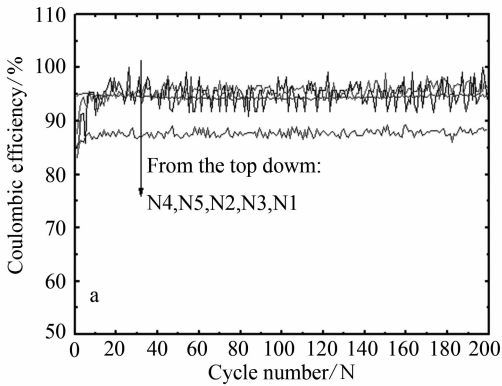


图 7 5 种 NiO 电极的库仑效率

Fig. 7 Coulombic efficiency of the five kinds of NiO electrodes
a. without hexacyanoferrate and 1 A/g current density; b. with hexacyanoferrate and 5 A/g current density; c. with hexacyanoferrate and 2 A/g current density; d. with hexacyanoferrate and 1 A/g current density

表1 5种NiO电极BET测试参数及其比容量

Tab.1 Specific capacitance and BET test results for the five kinds of NiO electrodes

	Pore size/nm	BET surface area/ $m^2 \cdot g^{-1}$	C_s (discharge) / $F \cdot g^{-1}$	Coulombic efficiency/%	Cycle
	N1	10.7	243	63.2	1
	N1	10.7	156	84.2	200
	N2	45.8	290	77.2	1
	N2	45.8	167	85.8	200
	N3 3~4	96.6	123	78.3	1
	N3 3~4	96.6	92	84.7	200
	N4 15	158.4	470	90.0	1
	N4 15	158.4	418	100	200
	N5 30~60	76.6	411	83.4	1
	N5 30~60	76.6	318	92.2	200

质量, ΔV 充放电的电位区间. N4 (NiO) 电极比表面 $158.4 \text{ m}^2/\text{g}$, 比电容达 470 F/g . 样品孔径对电极性能的影响不可忽略, 也直接影响电极衰减速率. 可以从表1看出, 虽然 N3 样品比表面 $96.6 \text{ m}^2/\text{g}$, 该比表面大于 N1, N2 和 N5 样品, 但 N3 电极比电容并没有明显提高. 原因在于其孔径 (3~4 nm) 不利于 $[Fe(CN)_6]^{3-}$ 的迁移并有效地参与到电极反应. 可以认为, 只有选取合适孔径 (15 nm) 的样品, 该电极才能有效约束活性 $K_3[Fe(CN)_6]$, 使其发生氧化还原反应, 进而提高由此制备的超级电容器的电化学性能.

3 结论

在 KOH 电解液中添加 $K_3[Fe(CN)_6]$ 活性物, (NiO) 电极上还可发生 $[Fe(CN)_6]^{3-}$ 与 $[Fe(CN)_6]^{4-}$ 之间的氧化还原反应, 使该电极的比电容显著提高. 但因该活性离子从电极向液相的扩散, 导致电极不可避免产生自放电, 使电极比容量衰减. 但由本文制备的 N4 (NiO) 电极却具有合适的孔径 (15 nm), 利于约束 $K_3[Fe(CN)_6]$ 活性物性能, 从而明显提高了该电极比容量, 达 418 F/g .

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Effect of Pore Size on Pseudo-Capacitive Performance of NiO in the Mixed Electrolyte of KOH and Hexacyanoferrate

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Abstract: In this paper, five kinds of NiO samples with different pore size distributions were synthesized. The electrochemical capacitance of the samples were characterized in 3 mol/L KOH solution with and without hexacyanoferrate addition. Electrochemical test results indicated that the NiO sample with an optimum pore size of about 15 nm shows high Coulombic efficiency of the N4(NiO) electrode as the redox reaction of hexacyanoferrate ions would be limited in the pore, thus prevent ion diffusion into the bulk electrolyte solution.

Key words: supercapacitors; nickel oxides; porous materials; hexacyanoferrate