

原位硒化法制备 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极材料及其在超级电容器中的应用

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摘 要: 开发高性能、高效的电极材料对提高混合超级电容器的能量密度具有重要意义。以泡沫镍为基底, 制备了 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 复合材料, 系统地研究了不同镍钼摩尔比例对其电化学性能的影响。当 $n(\text{Ni}):n(\text{Mo})=2:1$ (摩比) 时, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 复合材料的电化学性能最优, 在 1 A/g 电流密度下, 样品比电容为 940.9 F/g 。此外, 该电极材料具有良好的倍率性能和循环稳定性。由 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 和活性炭(AC)制成的 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ 混合型超级电容器(ASC)表现出较高的能量($46.5\text{ W}\cdot\text{h/kg}$)和功率密度(800 W/kg), 表明 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 复合材料在未来储能器件研究领域具有潜在的应用价值。

关键词: 过渡金属硒化物; 超级电容器; 电化学性能

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由于化石燃料的快速消耗和环境污染的加剧, 迫切需要探索高效、环保的储能设备, 以满足来自可再生能源的日益增长的储能需求^[1]。在各种储能设备中, 超级电容器具有功率密度高、充放电时间短、循环稳定性好、安全可靠等优点, 在便携式电子设备、电网、混合动力汽车等领域具有很大的应用潜力^[2]。而超级电容器的比电容、功率密度、能量密度和循环稳定性都受到电极材料的显著影响^[3]。电导率高、能量密度高、性能稳定的电极材料被认为是理想的电极材料^[4]。因此, 为了提高超级电容器的储能性能, 使其适合实际应用, 寻找可靠的电极材料已成为研究的重点领域^[5]。

得益于自然界丰富的资源, 过渡金属硫化物是超级电容器电极材料的主要成员^[6]。同时, 大量的相关研究主要集中在过渡金属氧化物和硫化物方面。然而, 因为它们的导电性和循环稳定性非常差, 严重阻碍了它们在超级电容器中的广泛应用^[7]。因此, 定制和构建倍率好、导电性相对较高的电极材料非常重要。一般来说, 硒与氧和硫在元素周期表中处于同一主族, 理论上具有相似的化学性质,

但实际上硒的电负性低于氧和硫, 并且具有更好的导电性和增强的电化学活性。因此, 与过渡金属氧化物和硫化物相比, 过渡金属硒化物作为一种先进的多功能材料, 凭借其理论容量高、导电性好、循环稳定性好等优势, 在储能和转换领域牢牢占据主导地位^[8]。例如, Chang 等^[9]在等离子体辅助干燥剥离下制备了二维 NiSe_2 纳米片, 在 1 A/g 下具有 466 F/g 的高比电容, 并且在 1000 次循环后具有良好的循环稳定性, 保留率为 81.3%。

另外, 相比于单金属硒化合物, 引入其他金属组分制备的双金属硒化物的电化学性质有显著提高。由于具有多个价态跃迁的不同金属阳离子的共存可以实现多个氧化还原反应并丰富结构缺陷, 且双金属之间的耦合可以更好地调节电子结构和提高导电性, 从而比单金属硒化合物具有更好的电化学活性^[10]。例如, Liu 等^[11]通过引入具有大比表面积 of 金属有机骨架制备了空心 $(\text{Ni}, \text{Co})\text{Se}_2$ 纳米立方体@rGO, 在 1 A/g 时表现出了优异的电化学性能, 创建了不对称 $(\text{Ni}, \text{Co})\text{Se}_2/\text{rGO}/\text{AC}$ 超级电容器, 其能量密度高达 $52.6\text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$, 功率为 803.4 W/kg 。

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在众多的金属元素中,镍因其良好的导电性、可变的价态和理想的氧化还原活性而被广泛应用于构建器件的正极。此外,钼元素也因其突出的优点而在电极制备方面引起了极大的关注,包括丰富的价态和无毒等。例如,Manuraj 等^[12]通过简单的水热法成功合成了用于超级电容器的多孔 MoSe₂ 纳米花。基于 MoSe₂ 电极的对称超级电容器在 1 A/g 的恒定电流密度下表现出 95 F/g 的比电容、4.75 W·h·kg⁻¹ 的能量密度和 619.6 W/kg 的功率密度。

用于电化学研究的过渡金属硒化物电极通常是用聚合物粘结剂通过传统的浆料涂层方法制备的,这增加了活性过渡金属硒化物表面的死体积,与电解液的接触降低^[13]。电极材料的导电性能也因粘合剂而明显下降,这使得它在工业储能应用中的作用降低。在导电衬底上开发电活性材料是进一步优化其性能的方法。泡沫镍作为廉价的通用基底,具有高的比表面积、优良的导电性和优异的集流、供流能力。为了获得更好的电荷存储性能,可以在具有理想多孔网络的导电衬底上设计和制备过渡金属硒化物。例如,Mariappan 等^[14]采用简易电化学沉积法直接在泡沫镍上制备了 MoSe₂ 片,极大地改善和优化了其电化学性能。

本工作首先通过水热法在泡沫镍基底上合成了 NiMo 前驱体,然后将该前驱体与 Se 粉进行原位硒化反应,制备了 NiSe/Mo₁₅Se₁₉ 电极材料。系统地研究了不同镍钼比例对其电化学性能的影响。

1 实验

1.1 样品制备

根据已有的报道^[15]合成了浅绿色的 NiMo 前驱体。首先对泡沫镍(NF)基底进行预处理:用 2 mol/L 的 HCl、丙酮、无水乙醇和去离子水把 2 cm×4 cm 的 NF 超声处理,然后真空干燥过夜以去除杂质和表面氧化物。再称出 6 mmol Ni(NO₃)₂·6H₂O 和 3 mmol Na₂MoO₄·2H₂O,随后依次溶解在 60 mL 去离子水中。在 1 个 100 mL 的聚四氟乙烯内衬的反应釜中,加入溶解的混合物和 1 块预先处理过的 NF,150 °C 水热反应 5 h。冷却至室温后洗涤,然后在真空干燥箱中 60 °C 干燥过夜。为了考察不同 Ni、Mo 摩尔比对电化学性能的影响,还选择了其它 Ni:Mo 摩尔比 ($n(\text{Ni}):n(\text{Mo})=1:1$ 、 $3:1$) 的 Ni(O₃)₂·6H₂O 和 Na₂MoO₄·2H₂O 相结合。

NiSe/Mo₁₅Se₁₉ 的合成是通过将前驱体一步硒化制成的。具体为将前驱体与 0.13 g Se 粉分别置于

石英舟的两端(Se 粉置于上流)。随后,将石英舟放入管式炉,350 °C 保温 2 h,Ar 气作为保护气体。待自然冷却后,即获得 NiSe/Mo₁₅Se₁₉。

1.2 样品表征

采用 X 射线衍射仪(XRD, Bruker D8AA25)确定样品的晶体结构。使用扫描电子显微镜(SEM, 日本日立 S-4800)观察样品的微观结构。利用透射电子显微镜(TEM, Tecnai F30G2)分析样品的形貌、晶格以及晶格间距,在原子尺度上观察样品的晶格缺陷。用 X 射线光电子能谱(XPS, ESCALAB Xi+)分析分子结构、元素价态及化学键等信息。

1.3 电化学测试

三电极体系和两电极体系下样品的电化学性能通过电化学工作站(CHI660E, 上海辰华)测试。所有测试使用的电解液均为 6 mol/L KOH。用 Pt 作对电极,饱和甘汞作参比电极进行三电极测量。双电极体系中以 NiSe/Mo₁₅Se₁₉ 为正极,活性碳(AC)做负极制成 ASC 器件。分别根据式(1)、式(2)、式(3)来计算电极材料的比电容(C)、功率密度(E)和能量密度(P):

$$C = \frac{I \times \Delta t}{M \times \Delta V} \quad (1)$$

式中: C 为比电容,单位为 F/g; I 为放电电流,单位为 A; Δt 为放电时间,单位为 s; M 为活性物质的质量,单位为 g; ΔV 为放电的电位范围,单位为 V。

$$E = \frac{C \times \Delta V^2}{7.2} \quad (2)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (3)$$

2 结果与讨论

2.1 晶体结构分析

对不同 Ni、Mo 摩尔比下得到的样品进行 XRD 分析,如图 1 所示。3 个样品中都可以观察到 $2\theta=44.4^\circ$ 、 51.6° 和 76.2° 的特征峰,是来自于 NF 衬底的特征峰^[16],此外,3 个样品中都存在 27.2° 处的特征峰,对应于 Mo₁₅Se₁₉ 相(JCPDS 80-1179)的(006)晶面。3 个样品在 43.4° 处出现的衍射峰可归属于 NiSe 的(102)晶面(JCPDS 02-0892)^[17]。XRD 结果所合成的样品为 NiSe/Mo₁₅Se₁₉,样品的结晶性较低。

2.2 微观形貌分析

图 2 为不同 Ni、Mo 摩尔比样品的 NiSe/Mo₁₅Se₁₉

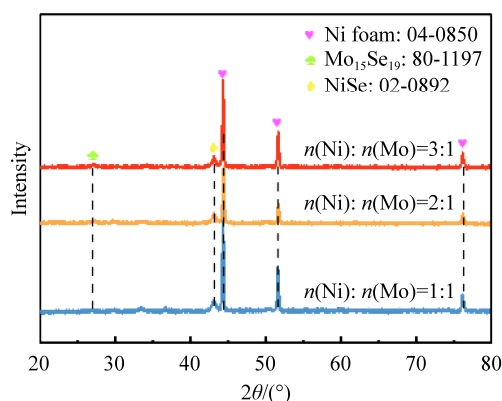


图 1 不同样品的 XRD 谱

Fig. 1 XRD patterns of different samples

SEM 照片。由图 2 可见, 不同的 Ni、Mo 摩尔样品的形貌不同。图 2a 和图 2b 中 $n(\text{Ni}):n(\text{Mo})=1:1$, 图 2c 和图 2d 中 $n(\text{Ni}):n(\text{Mo})=2:1$, 图 2e 和图 2f 中 $n(\text{Ni}):n(\text{Mo})=3:1$, 表明 Ni、Mo 摩尔比对样品的形貌有较大的影响。由图 2a 和图 2b 可见, 当 Ni、Mo 摩尔比为 1:1 时, 样品形貌为纳米棒和纳米片组成的花状微米球共存, 杂乱的分子孔道排列方式, 不利于电解质离子的流通^[18]。纳米片组成的微球的直径约为 $1\ \mu\text{m}$ (图 2a 插图), 纳米片的厚度为 $30\sim 40\ \text{nm}$, 纳米棒的直径为 $150\sim 200\ \text{nm}$ (如图 2b 插图所示), 纳米棒的长度约为 $2\ \mu\text{m}$ 。从图 2c 和图 2d 可以看出, 当 Ni、Mo 摩尔比为 2:1 时, 样品的形

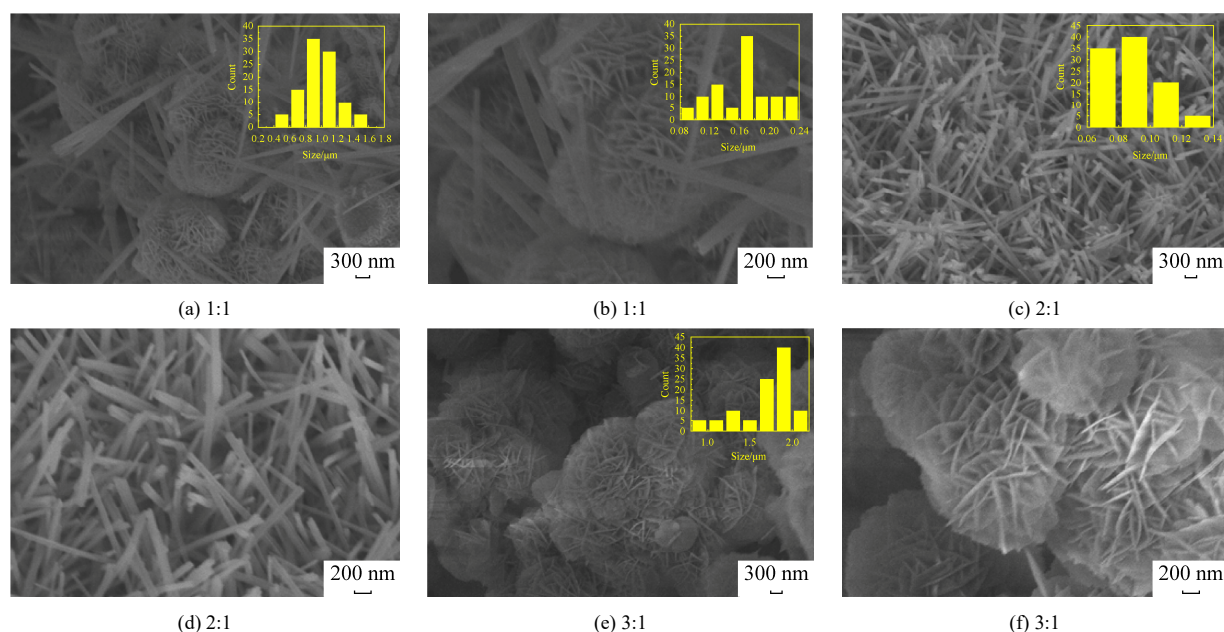


图 2 不同 Ni、Mo 摩尔比样品的 SEM 照片

Fig. 2 SEM images of samples with different Ni and Mo mole ratios

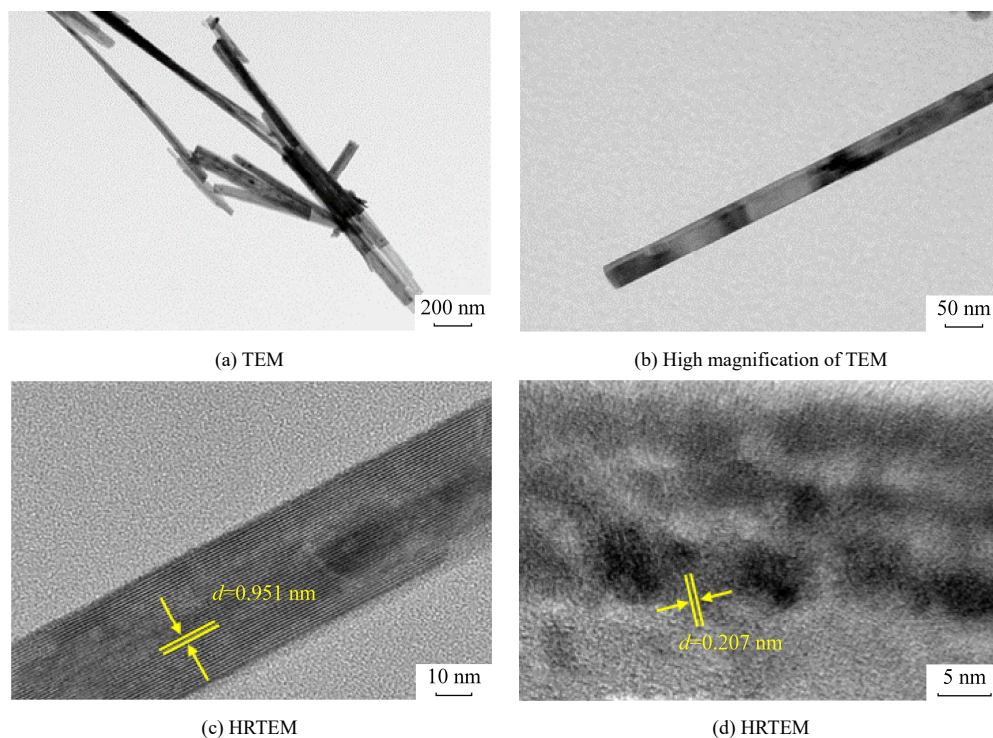
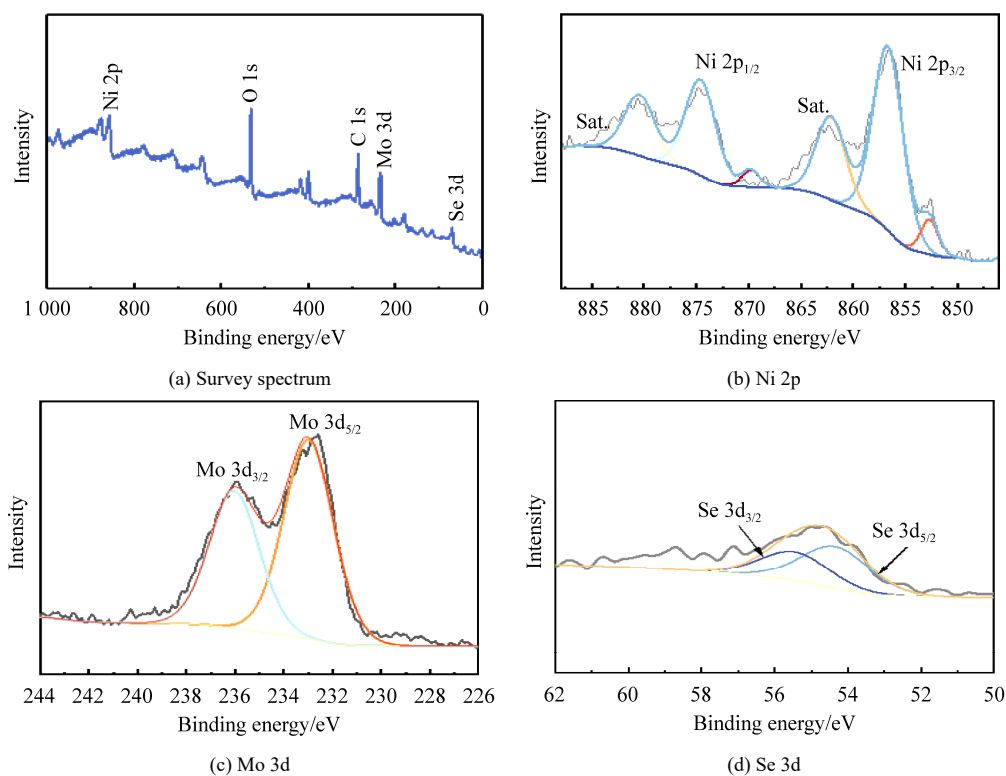
貌为纳米棒, 且垂直取向生长在 NF 基底上, 纳米棒长度为 $1.0\sim 1.5\ \mu\text{m}$, 直径为 $50\sim 120\ \text{nm}$ (如图 2c 插图所示)。由图 2e 和图 2f 可见, 当 Ni、Mo 摩尔比为 3:1 时, 样品的形貌是由纳米片组成的花状微米球, 微米球直径为 $1.5\sim 2.0\ \mu\text{m}$ (图 2e 插图), 纳米片的厚度为 $20\sim 30\ \text{nm}$ 。结合后续电化学测试可知 Ni、Mo 摩尔比为 2:1 时, 样品具有最佳的电化学性能, 这是由于棒状纳米结构拥有较大的比表面积, 可以为电化学反应提供更多的活性位点, 有利于储能器件^[19]。

通过 TEM 进一步研究了当 $n(\text{Ni}):n(\text{Mo})=2:1$ 时 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 纳米棒的微观形貌。图 3 是当 $n(\text{Ni}):n(\text{Mo})=2:1$ 的样品的 TEM 照片。由图 3a 和图 3b 可见, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 纳米棒具有多孔结构, 这归

因于煅烧过程中气体的释放^[20]。这种独特的多孔结构将为电解质离子提供较多的传输通道, 并在 Faraday 反应中提供大量活性位点^[21]。图 3c 和图 3d 为 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 的 HRTEM 照片。由图 3c 可见, 晶面间距为 $0.951\ \text{nm}$, 与 $\text{Mo}_{15}\text{Se}_{19}$ (JCPDS 80-1179) 的 (002) 晶面相吻合。由图 3d 可见, 晶面间距为 $0.207\ \text{nm}$, 与 NiSe (JCPDS 02-0892) 的 (102) 面相匹配^[17]。HRTEM 的结果与 XRD 结果相一致。

2.3 XPS 分析

图 4 为样品的 XPS 能谱。图 4a 为样品的 XPS 全谱, 表明 Ni、Mo、Se、O 和 C 5 种元素共存。C 元素的峰归因于 XPS 测试采用污染碳成分校正的原因, 显著的 O 元素归因于空气中氧气和水分污染

图 3 $n(\text{Ni}): n(\text{Mo})=2:1$ 时 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 的 TEM 照片Fig. 3 TEM images of $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ at $n(\text{Ni}): n(\text{Mo})=2:1$ 图 4 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 的 XPS 谱Fig. 4 XPS spectra of $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$

的结果^[22]。图 4b 为 Ni 2p 的高分辨 XPS 能谱，结合能位于 856.7 eV 和 874.6 eV 的特征峰，归因于 Ni^{2+} 的 Ni 2p_{3/2} 和 Ni 2p_{1/2}，结合能位于 852.7 eV 和

869.8 eV 的特征峰对应于 0 价的 Ni 2p_{3/2} 和 Ni 2p_{1/2}，这来自 NF 衬底^[23]。此外，结合能位于 862.1 eV 和 880.4 eV 处的特征峰对应 2 个卫星峰(标注为 Sat.)

分别与 Ni 2p_{3/2} 和 Ni 2p_{1/2} 的自旋双峰很好地吻合^[23]。图 4c 为 Mo 3d 的高分辨 XPS 能谱, 由图 4c 可见, 结合能位于 236.0 eV 和 232.9 eV 的特征峰归属于 Mo 3d_{3/2} 和 Mo 3d_{5/2}^[24]。图 4d 为 Se 3d 高分辨 XPS 能谱, 结合能位于 54.3 eV 和 55.5 eV 的特征峰, 分别对应于 Se 3d_{5/2} 和 Se 3d_{3/2}^[25]。

2.4 电化学性能分析

图 5a 为 1 A/g 时不同 Ni、Mo 摩尔比电极的 GCD 曲线。从图 5a 可以看出, GCD 曲线呈扭曲的三角形, 这是赝电容的典型特征^[26]。结合 GCD 曲线和式(1)计算了 3 个电极的比电容。当电流密度为 1 A/g

时, $n(\text{Ni}):n(\text{Mo})=1:1$ 、 $n(\text{Ni}):n(\text{Mo})=2:1$ 和 $n(\text{Ni}):n(\text{Mo})=3:1$ 的样品的比电容分别为 347.1、940.9 F/g 和 630.8 F/g。当 $n(\text{Ni}):n(\text{Mo})=2:1$ 时, 电极的放电时间最长, 曲线对称, 可逆性较好, 比电容较高。这是因为当 $n(\text{Ni}):n(\text{Mo})=2:1$ 时, 复合材料的纳米棒结构具有良好的表面积和多孔结构, 可使氧化还原反应充分进行, 活化整个材料, 并使电解液离子易于扩散, 从而获得优异的电化学性能^[19]。

图 5b 为 $n(\text{Ni}):n(\text{Mo})=2:1$ 样品在不同扫速下的 CV 曲线。由图 5b 可见, CV 曲线的峰电流随着扫描速率的增加而增大, 表明 NiSe/Mo₁₅Se₁₉ 电极

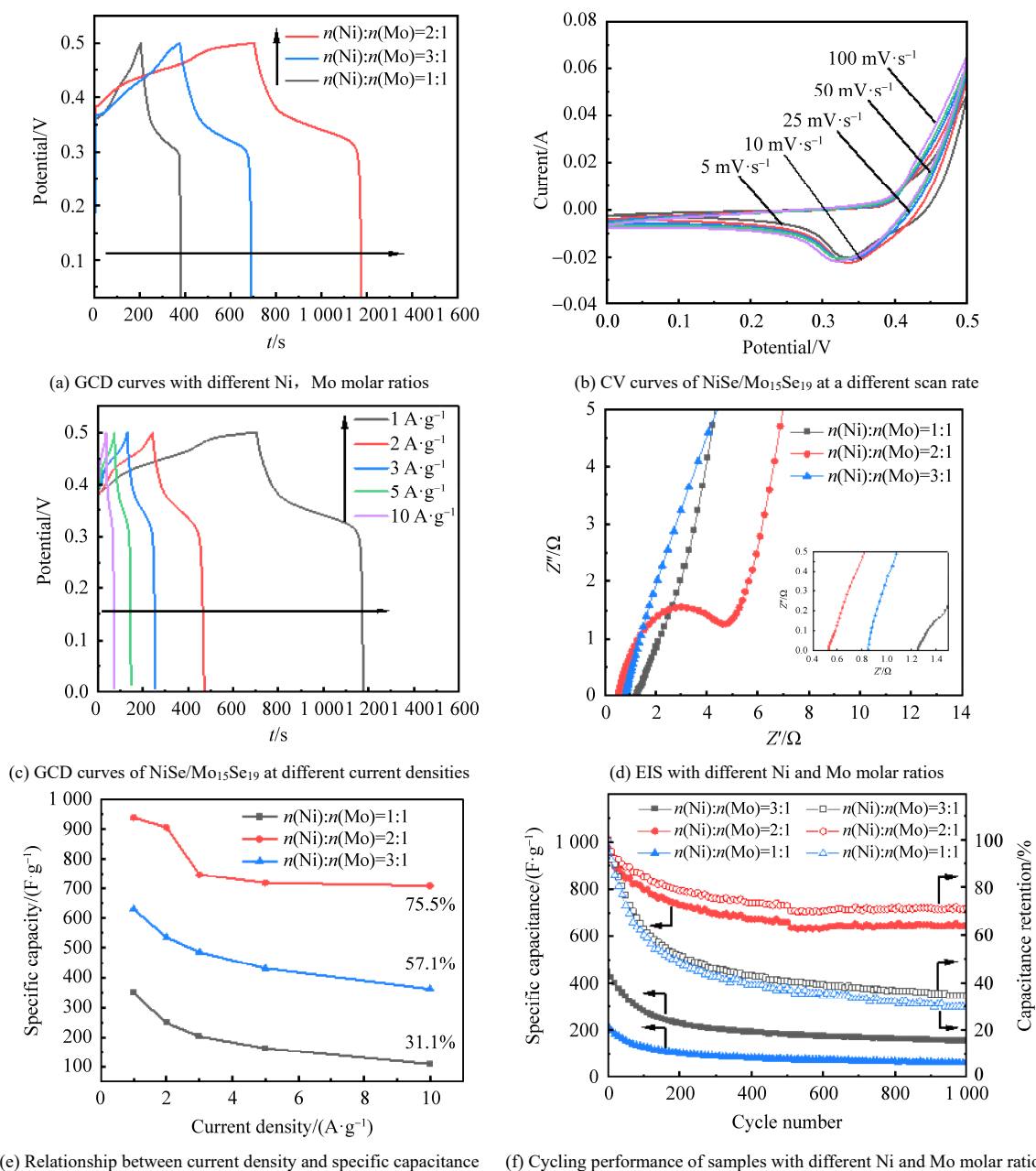


图 5 NiSe/Mo₁₅Se₁₉ 电极材料的电化学性能

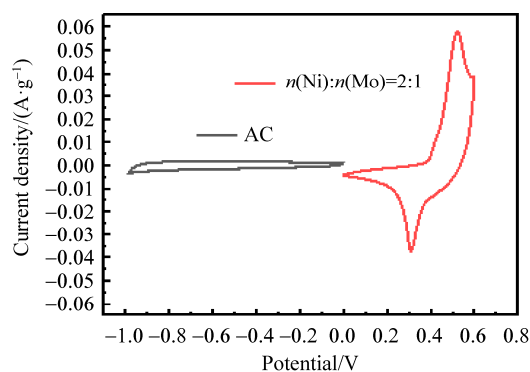
Fig. 5 Electrochemical properties of NiSe/Mo₁₅Se₁₉ electrode materials

具有快速可逆的 Faraday 行为和高倍率能力^[27–28]。图 5c 为不同电流密度下, $n(\text{Ni}): n(\text{Mo})=2:1$ 样品的 GCD 曲线。由图 5c 可见, 充电曲线与放电曲线基本对称, 具有一对充放电平台, 分别对应于氧化和还原过程, 表明材料发生了典型的氧化还原反应, 这些结果与 CV 曲线中的电化学行为一致。根据式 (1) 计算电极在 1、2、3、5、10 A/g 时的比电容分别为 940.9、906.6、748.8、720.0、710.0 F/g。

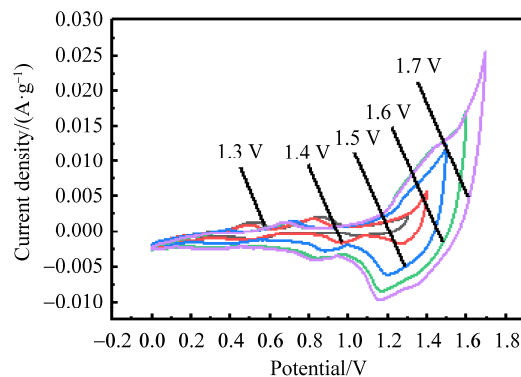
电化学阻抗光谱(EIS)被用来探索电极和电解质界面上的 Faraday 反应^[29]。Nyquist 曲线如图 5d 所示。EIS 曲线由 1 个半圆和 1 条直线组成, 高频下与 X 轴的交点表示等效串联电阻(R_s), 从图 5d 可以看出, $n(\text{Ni}): n(\text{Mo})=1:1$ 、 $n(\text{Ni}): n(\text{Mo})=2:1$ 和 $n(\text{Ni}): n(\text{Mo})=3:1$ 的 R_s 分别为 1.3、0.5 Ω 和 0.9 Ω , 这表明 $n(\text{Ni}): n(\text{Mo})=2:1$ 的样品电子传输过程较快。当 $n(\text{Ni}): n(\text{Mo})=2:1$ 时, 相比于其他实验组有较大的 1 个界面电阻与该组电极的形貌有关^[30]。低频区域内的线的斜率与扩散过程中的离子传输阻抗相对应。 $n(\text{Ni}): n(\text{Mo})=2:1$ 的样品显示出比其它 2 个样品更陡峭的斜率, 这表明该样品的电子传输更快。这进一步证明了 $n(\text{Ni}): n(\text{Mo})=2:1$ 时, 样品的电化学性能最好。

不同 Ni、Mo 摩尔比电极的倍率性能如图 5e 所示。从图 5e 可以看出, 随着电流密度的增大, 比电容减小, 这是电极材料的电荷存储容量在较高电流密度下减小所致^[31]。当电流密度从 1 A/g 增加到 10 A/g 时, $n(\text{Ni}): n(\text{Mo})=2:1$ 的电极仍能保持 710.0 F/g 的比电容, 比电容保持率约为 75.5%, 高于 $n(\text{Ni}): n(\text{Mo})=1:1$ (31.1%) 和 $n(\text{Ni}): n(\text{Mo})=3:1$ (57.1%), 因此, $n(\text{Ni}): n(\text{Mo})=2:1$ 的样品具有最优的倍率性能。图 5f 为不同 Ni、Mo 摩尔比电极的循环稳定性图。在 1 000 次循环后, $n(\text{Ni}): n(\text{Mo})=2:1$ 的电极保持了 71.5% 的初始比电容, 表明该电极具有良好的循环稳定性。此外, $n(\text{Ni}): n(\text{Mo})=3:1$ 和 $n(\text{Ni}): n(\text{Mo})=1:1$ 的容量保持率仅能保持 34.9% 和 29.9%, 这是由于材料在充放电过程中体积发生了变化^[25]。

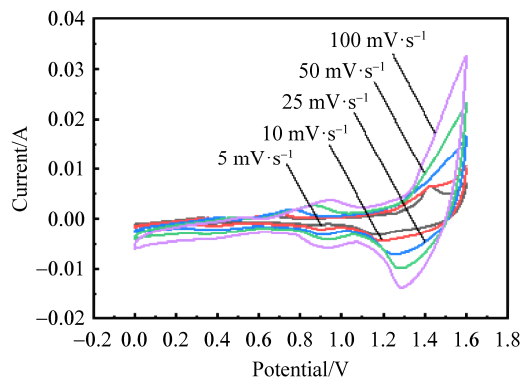
为了进一步研究 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极在实际生产中的应用潜力, 以 $n(\text{Ni}): n(\text{Mo})=2:1$ 制备的 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极为正极, 以 AC 为负极, 制备了 ASC。图 6a 为 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 和 AC 电极在 5 mV/s 时的 CV 曲线。为了进一步确定 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ 的电位窗口, 双电极体系选用扫描速率为 25 mV/s, 测试了一系列电压窗口下的 CV 曲线如图 6b 所示。



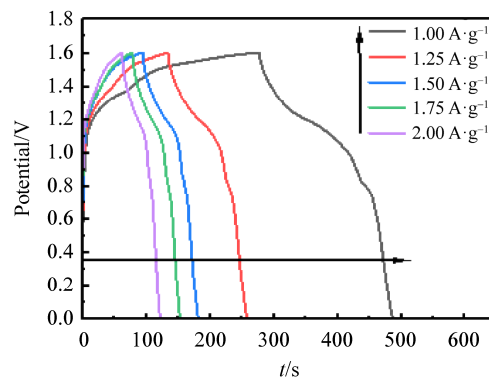
(a) CV curves of three-electrode system
 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ and AC at 5 mV·s⁻¹



(b) CV curves of ASC under different
voltage windows at 25 mV·s⁻¹



(c) CV curves of ASC at different scanning rates



(d) GCD curves of ASC at different current densities

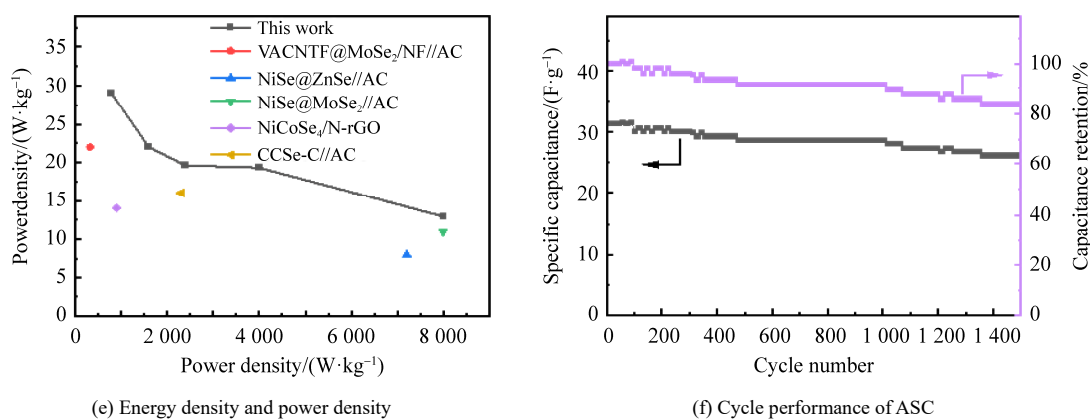


图 6 混合型超级电容器装置 ASC 的电化学性能
Fig. 6 Electrochemical performance diagrams of ASC

当工作电压从 1.3 V 扩大到 1.6 V 时, ASC 的 CV 曲线具有相似的形状。当工作电压大于 1.6 V 时, CV 曲线出现了极化。因此, 选择最佳的电压窗口为 0~1.6 V。在 0.0~1.6 V 的电压窗口内, 5、10、25、50 mV/s 和 100 mV/s 的扫描速率下, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ ASC 的 CV 曲线如图 6c 所示。从图 6c 可以看出, CV 曲线的大致形状相似, 显示了双电层电容器和电池行为的结合^[12]。图 6d 为电流密度在 1.00、1.25、1.50、1.75 A/g 和 2.00 A/g 时, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ ASC 的 GCD 曲线, 对称的形状表明了当前 ASC 的高度可逆性^[32]。

图 6e 将 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ 的能量密度和功率密度与文献中描述的其他类似材料进行了比较。在 800 W/kg 的功率密度下, 可获得 46.5 $\text{W} \cdot \text{h}/\text{kg}$ 的能量密度, 性能优于以往报道的类似材料, 如 VACNTF@MoSe₂/NF//AC^[33]、NiSe@ZnSe//AC^[34]、NiSe@MoSe₂//AC^[35]、NiCoSe₄/N-rGO//AC^[36] 和 CCSe-C//AC^[37]。此外, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}/\text{AC}$ ASC 的循环稳定性是在 5 A/g 时进行测试的(图 6f)。结果表明, 该器件在 1500 次循环后仍能保持 83.6% 的初始比电容, 表现出良好的稳定性。

3 结论

采用原位硒化法合成了用于超级电容器的 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 复合材料。该复合材料具有明显的多孔纳米棒状形貌, 能够为电荷的高速传输提供快速通道。此外, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极在 1 A/g 电流密度时的比电容为 940.9 F/g, 在 10 A/g 电流密度时的比电容 710.0 F/g, 比电容保持率为 75.5%。循环稳定实验表明 1000 次循环后的比电容保持率为 71.5%。因此, $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极具有较好的倍率性能和循环稳定性。由 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 和 AC 组成的 ASC

器件在 800 W/kg 的功率密度下的能量密度为 46.5 $\text{W} \cdot \text{h} \cdot \text{kg}^{-1}$, 1500 次充放电循环后的比电容保持率为 83.6%, 因此 $\text{NiSe}/\text{Mo}_{15}\text{Se}_{19}$ 电极材料在储能方面具有广阔的应用前景。

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Preparation of NiSe/Mo₁₅Se₁₉ Electrode Materials by *in-situ* Selenization and Their Application in Supercapacitors

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Extended Abstract

Introduction It is necessary to explore efficient and environmentally friendly energy storage devices due to the rapid consumption of fossil fuels and increasing environmental pollution. Among various energy storage devices, supercapacitors have some advantages of high power density, short charging and discharging time, good cycle stability, safety and reliability. The related studies focused on transition metal oxides and sulfides. However, their conductivity and cycle stability are rather poor. Compared with transition metal oxides and sulfides, transition metal selenides as an advanced multifunctional material dominate the field of energy storage and conversion by virtue of their high theoretical capacity, good electrical conductivity, and good cycling stability. Also, the coexistence of different metal cations with multiple valence leaps enables multiple redox reactions and enriches structural defects, and the coupling between the bimetals favors the regulation of the electronic structure and improved electrical conductivity, resulting in better electrochemical activity than monometallic selenides. Transition metal selenide electrodes for electrochemical studies are usually prepared with polymer binders by conventional slurry coating methods, which increases the dead volume of the active transition metal selenide surface and decreases the contact with the electrolyte. Therefore, transition metal selenides can be designed and prepared on a conductive substrate with an ideal porous network to obtain better charge storage performance. In this paper, NiMo precursor was firstly synthesized on a nickel foam substrate by a hydrothermal method, and then NiSe/Mo₁₅Se₁₉ electrode materials were prepared *via in-situ* selenation reaction of this precursor with Se powder. In addition, the effect of NiMo ratio on their electrochemical properties was also investigated.

Methods A 2 cm × 4 cm nickel foam (NF) substrate was firstly pretreated with 2 mol/L HCl, acetone, anhydrous ethanol and deionized water, and then 6 mmol of Ni(NO₃)₂·6H₂O and 3 mmol of Na₂MoO₄·2H₂O were dissolved in 60 mL of deionized water. The dissolved mixture and 1 block of pre-treated NF were added into a PTFE-lined reactor, and the hydrothermal reaction was carried out at 150 °C for 5 h. The effect of nickel and molybdenum molar ratio (*i.e.*, 1:1 and 3:1) on the electrochemical performance was investigated. Finally, the precursor and 0.13 g of Se powder were placed at the two ends of a quartz boat into a tube furnace in Ar gas as a protective gas at 350 °C for 2 h. After natural cooling, NiSe/Mo₁₅Se₁₉ was obtained. The crystal structure of the samples was determined by a model D8AA25 X-ray diffractometer (XRD, Bruker). The microstructure of the samples was observed using a model S-4800 scanning electron microscope (SEM, Hitachi Co., Japan). The morphology, lattice, and lattice spacing of the samples were analyzed by a model F30G2 transmission electron microscope (TEM, Tecnai). The molecular structure, elemental valence states and chemical bonding were analyzed by a model Xi+ X-ray photoelectron spectroscopy (XPS, ESCALAB). The electrochemical properties of the samples in the three-electrode system and the two-electrode system were tested by a model CHI660E electrochemical workstation (Chenhua Co., China) under an electrolyte of 6 mol/L KOH. Three-electrode measurements were carried out using Pt as a counter electrode and saturated calomel as a reference electrode. The ASC devices were made with NiSe/Mo₁₅Se₁₉ as a positive electrode and activated carbon (AC) as a negative electrode in the two-electrode system.

Results and discussion The SEM images show that the Ni:Mo molar ratio has an effect on the morphology of the samples. When the Ni:Mo molar ratio is 1:1, the sample morphology is the coexistence of flower-like microspheres composed of nanorods and nanosheets, and the disorganized molecular pore arrangement is not conducive to the flow of electrolyte ions. The diameter of the microspheres composed of nanosheets is approximately 1 μm, the thicknesses of the nanosheets are 30–40 nm, the diameters of the nanorods are 150–200 nm, and the length of the nanorods is approximately 2 μm. When the Ni:Mo molar ratio is 2:1, the morphology of the sample is nanorods, and they are grown vertically oriented on the NF substrate, with the lengths of the nanorods of 1.0–1.5 μm, and the diameters of the nanorods of 50–120 nm. At the Ni: Mo molar ratio of 3:1, the morphology of the sample is flower-like

microspheres composed of nanosheets, the diameters of the microspheres are 1.5–2.0 μm , and the thicknesses of the nanosheets are 20–30 nm. The electrochemical test shows that the sample has the optimum electrochemical performance when the molar ratio of Ni:Mo is 2:1. The specific capacitance of the sample is 940.9 F/g at the current density of 1 A/g, and the specific capacitance of the sample is 940.9 F/g when the current density increases from 1 A/g to 10 A/g. The electrode with n(Ni): n(Mo) of 2:1 still maintains a specific capacitance of 75.5% when the current density increases from 1 A/g to 10 A/g. This is since the rod-like nanostructure possesses a large specific surface area, thus providing more active sites for the electrochemical reaction and being beneficial to the energy storage device. From the TEM images, NiSe/Mo₁₅Se₁₉ nanorods have a porous structure due to the release of gases during the calcination process. This unique porous structure can provide more transport channels for electrolyte ions and a large number of active sites in the Faraday reaction.

Conclusions NiSe/Mo₁₅Se₁₉ composites had an optimum electrochemical performance at a Ni:Mo molar ratio of 2:1. The sample-specific capacitance was 940.9 F·g⁻¹ at a current density of 1 A·g⁻¹. In addition, this electrode material exhibited good multiplication properties and cycling stability. The NiSe/Mo₁₅Se₁₉//AC hybrid supercapacitor (ASC) made from NiSe/Mo₁₅Se₁₉ and activated carbon (AC) had a high energy (*i.e.*, 46.5 Wh·kg⁻¹) and a power density (*i.e.*, 800 W·kg⁻¹), indicating that NiSe/Mo₁₅Se₁₉ composites have a promising application potential in energy storage devices.

Keywords transition metal selenide; supercapacitor; electrochemical performance