

活性炭自吸附单层改性增强锌离子混合超级电容器性能

曲 强^{1,2}; 朱铭强^{1,2}

(1. 西北农林科技大学 机械与电子工程学院, 陕西 杨凌 712100; 2. 农业农村部农村可再生能源开发利用西部观测实验站 陕西 杨凌 712100)

摘 要:【目的】活性炭是目前废水净化方面应用最广泛的材料, 但其使用后自身仍携带有毒污染物。污染物在活性炭中通过自吸附在孔隙通道中单层覆盖, 能够增强其电化学性能, 用于构建高性能锌离子混合超级电容器, 为全面促进农林生物质资源化利用和提升碳基超级电容器储能容量提供一个可行的碳材料制备体系。【方法】以杜仲木粉为原料, 采用微波辐照技术结合物化协同活化方法制备多孔碳, 将其用于吸附废水中 Cr(VI)、亚甲基蓝、Cu(II)、Co(II)和 Ag(I), 采用不同温度吸附等温线确定多孔碳在不同初始浓度下对各种污染物的吸附能力, 经离心、冻干后回收。采用 BET、XRD、FTIR、XPS 等技术对多孔碳材料进行理化特性表征, 在三电极水系超级电容器体系中测试回收活性炭的电化学性能, 并构建高性能锌离子混合超级电容器检测其储锌性能, 利用非原位 XRD、Raman 和 XPS 技术对充放电状态下的活性炭电极进行理化特性表征, 揭示废水污染物对储锌性能的增强机制。【结果】采用物化协同活化方法制备的多孔碳 (PC) 比表面积达到 1489.86 m²/g, 介孔比为 58%, 经吸附污染物后的活性炭比表面积和孔径减小, 吸附等温线符合 Langmuir 等温线模型, SEM 和 TEM-EDX 图像结果也说明污染物在活性炭中成功改性, 孔隙内部通道实现均匀单层覆盖。三电极水系超级电容器体系中 GCD 法测试结果表明, 相比于 PC, 吸附 Cr(VI)、亚甲基蓝、Cu(II)、Co(II)和 Ag(I)后的活性炭电化学比容量分别提高 115%、123%、146%、84%和 242%, 并且电化学传输内阻明显减小。将 PC 和吸附 Cr(VI)、亚甲基蓝、Cu(II)、Co(II)和 Ag(I)后的活性炭制备成电极片, 储锌比容量分别达到 35 mAh g⁻¹、396.35 mAh g⁻¹、38 mAh g⁻¹、249 mAh g⁻¹、45 mAh g⁻¹ 和 564 mAh g⁻¹。通过分析赝电容贡献率结果发现, Cr(VI)污染物在不同扫描速率下能够明显促进赝电容产生, Ag(I)污染物则能够提高导电性和离子传输动力学特性, 进一步促进扩散控制电容产生行为。【结果】回收净化废水后的活性炭能够用于构建高性能锌离子混合超级电容器, 并具有优异的经济可行性, 这将为生物质资源高值化利用和“双碳”背景下储能系统高效运行提供理论和技术支撑。

关键词: 杜仲; 多孔碳; 废水净化; 自吸附单层改性; 锌离子混合超级电容器

基金项目: 国家林业和草原局科技创新青年拔尖人才项目 (2019132616)、国家自然科学基金 (21908181)、国家重点研发计划 (2018YFE0127000) 和陕西省重点研发计划 (2024NC-YBXM232)。

Enhanced performance of zinc-ion hybrid supercapacitors by activated carbon self-adsorption monolayer modification

Qiang Qu^{1,2}, Mingqiang Zhu^{1,2}

(1. Northwest A&F University, College of Mechanical and Electronic Engineering, Yangling 712100, Shaanxi, China; 2. Northwest Research Center of Rural Renewable Energy Exploitation and Utilization of M.O.A, Yangling 712100, Shaanxi, China)

Abstract: 【Objective】 Activated carbon is currently the most widely used material in wastewater purification, but it still carries toxic pollutants on its own after use. The pollutants are covered by a monolayer in activated carbon

through self-adsorption in pore channels, which can enhance its electrochemical performance for constructing high-performance zinc-ion hybrid supercapacitors, providing a feasible carbon material preparation system for comprehensively promoting the resourceful use of agricultural and forestry biomass and enhancing the energy storage capacity of carbon-based supercapacitors. **【Method】** Porous carbon was prepared from *Eucommia ulmoides* Oliver wood powder using microwave irradiation technology combined with physical-chemical synergistic activation method, which was used for the adsorption of Cr(VI), methylene blue, Cu(II), Co(II), and Ag(I) in wastewater, and adsorption isotherms with different temperatures were used to determine the adsorption capacity of the porous carbon for various pollutants at different initial concentrations, which was recovered by centrifugation and lyophilisation. The physicochemical properties of the porous carbon materials were characterised using BET, XRD, FTIR and XPS techniques, the electrochemical properties of the recovered activated carbon were tested in a three-electrode aqueous supercapacitor system, and a high-performance zinc-ion hybrid supercapacitor was constructed to test the zinc storage performance, and the physicochemical properties of activated carbon electrodes in the charging and discharging state were characterized using non-in-situ XRD, Raman and XPS techniques, to The physicochemical characterisation of the activated carbon electrodes in the charged and discharged state using non-in-situ XRD and XPS techniques was carried out to reveal the enhancement mechanism of wastewater pollutants on the zinc storage performance. **【Result】** The specific surface area of the porous carbon (PC) prepared by the physical-chemical co-activation method reached 1489.86 m²/g with a mesopore ratio of 58%, the specific surface area and pore size of the activated carbon after adsorption of the pollutants decreased, and the adsorption isotherms were in accordance with the Langmuir isotherm model, and the results of the SEM and TEM-EDX images also indicated that the pollutants were successfully modified in the activated carbon, and the pore internal channels achieved a homogeneous monolayer coverage. The results of the GCD method in the three-electrode aqueous supercapacitor system showed that the electrochemical specific capacities of the activated carbon adsorbed with Cr(VI), methylene blue, Cu(II), Co(II), and Ag(I) were increased by 115, 123, 146, 84, and 242%, respectively, and the internal resistance of electrochemical transport was significantly reduced compared with that of PC. The activated carbon after PC and adsorption of Cr(VI), methylene blue, Cu(II), Co(II) and Ag(I) were prepared into electrode sheets with zinc storage specific capacities of 35 mAh g⁻¹, 396.35 mAh g⁻¹, 38 mAh g⁻¹, 249 mAh g⁻¹, 45 mAh g⁻¹, and 564 mAh g⁻¹, respectively. By analysing the results of the pseudo capacitance contribution It was found that Cr(VI) pollutant was able to significantly promote the pseudocapacitance generation at different scanning rates, while Ag(I) pollutant was able to improve the electrical conductivity and ion transport kinetic properties, which further contributed to the diffusion-controlled capacitance generation behaviour. **【Conclusion】** Finally, the recycled activated carbon can be used to construct high-performance zinc-ion hybrid supercapacitors with excellent economic feasibility, which will provide theoretical and technological support for the high-value utilisation of biomass resources and the efficient operation of the energy storage system under the background of "dual-carbon".

Key words: *Eucommia ulmoides* Oliver; porous carbon; wastewater purifying; self-adsorption single-layer modification, zinc ion hybrid supercapacitor