

Hard carbons from waste hemp via hydrothermal carbonization with mild chemical activation for sodium-ion batteries

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Abstract

Owing to its wide availability and low cost, sodium-ion batteries (SIBs) appear as a very promising option for post-lithium energy storage systems. However, commercial graphite anodes used in lithium-ion batteries are not suitable for SIBs, due to a difficult insertion of sodium ions into the graphitic layers. Possible anode candidates focus on hard carbons (HCs). Here, HCs were synthesized from waste hemp hurd (WHH) via hydrothermal pretreatment (with either heteroatom doping or K_2CO_3 activation) and subsequent carbonization under Ar at 800 or 1000 °C. Regarding mild chemically activated HCs, the best material (exhibiting a 76% ICE and impressive reversible charge capacities of 354 and 77 mA h g⁻¹ at 0.1 and 2 A g⁻¹, respectively) was the carbon produced via hydrothermal pretreatment in HCl aqueous solution and subsequently heated up to 1000 °C. However, poor cycling stability was observed for the last material, suggesting that some irreversible sodiation processes can take place.

Introduction

The need to explore new rechargeable battery systems on a large scale has become imperative due to the high cost and limited accessibility of lithium reserves. Sodium-ion batteries (SIBs) have emerged as a very promising option, owing to the wide availability and low cost of sodium [1]. However, the commercial graphite anode used in lithium-ion batteries (LIBs) is not suitable for SIBs due to the difficult insertion of sodium ions into the graphite layers. Therefore, possible anode candidates are focused on hard carbons, which are capable of storing Na⁺ ions due to their larger spacing between pseudographitic layers, as well as reversible adsorption of ions in their pores, defects, and functional groups on the surface [2]. In this study, hemp hurd waste (WHH) was used as a raw material for the production of hard carbon (HC).

Hydrothermal carbonization (HTC) is an attractive process due to its low cost and mild synthesis conditions [3]. It involves heating biomass in an aqueous suspension under saturated pressure and low temperatures (below 250 °C). To enhance the energy storage capacity and electrical conductivity of materials mild chemical activation has been employed. A reactant is impregnated and subjected to thermal treatment under an inert atmosphere. Potassium carbonate can be utilized as a chemical agent to develop moderate porosity [4]. In this study, the effect of hydrothermal pretreatment with simultaneous K_2CO_3 activation on the electrochemical performance of the resulting HC-based electrodes has been explored.

Experimental

WHH-derived hard carbons were synthesized via mild chemical-activation: 1 g of K_2CO_3 was dissolved into 60 mL of distilled water to create a homogeneous solution, which was then hydrothermally treated with 5 g of WHH at 180 °C for 12 h. For comparison purposes, a HCl-catalyzed hydrothermal pretreatment was also performed using a 2M HCl solution as aqueous medium. The resulting hydrochars were then heated under Ar atmosphere at highest temperatures of 800 °C and 1000 °C for 2 h (HCl-hydrochars were just heated up to 1000 °C). The resulting carbonaceous material was washed in a 2M HCl solution and subsequently with distilled water until a neutral pH value was reached. It was then dried at 120 °C for 12 h in a vacuum oven, ground, and sieved to particle sizes below 90 μm. Final HCs were denoted as KHC800 and KHC1000 (for HTC pretreatment in water) and KHC1000HCL (for HCl-catalyzed HTC).

The working electrodes were fabricated by mixing in aqueous solution the synthesized HCs with acetylene black (as a conductive agent), styrene-butadiene rubber (SBR) and carboxymethyl

cellulose (CMC) —as binders— in an 80:10:5:5 mass ratio. The resulting homogeneous slurry was coated on a high-purity aluminum sheet (current collector) using a baker applicator. The composite electrode (100 μm thickness) was then punched (12 mm diameter) and dried under vacuum at 120 °C overnight. The final mass loading of the electrodes was approximately 2 mg cm^{-2} . The cells were assembled inside an argon-filled glovebox, with O_2 and H_2O contents below 0.5 ppm. The electrolyte used was 1M NaTFSI in DMC:EC 1:1 (vol.), with a volume of 120 μL . The half-cell was arranged in a Swagelok T-type cell configuration, using sodium foil as counter and reference electrodes, and high-density polyethylene and glass fiber separators as internal cover and separators, respectively. To evaluate the electrochemical performance of the batteries, galvanostatic charge-discharge (GCD) tests were carried out using a potentiostat (Bio-Logic SP-200) in the potential range of 0.01 to 2.50 V vs. Na/Na⁺.

Results and conclusions

Concerning the chemically activated HCs, it is well known that K_2CO_3 can promote graphitization of HC and also increase their porosity, thereby enhancing their energy storage capacity and electrochemical performance [5]. Figure 1a shows a HRTEM image obtained for a WHH-derived HC, which was synthesized via pyrolysis at 500 °C, impregnation with K_2CO_3 and further heating up to 800 °C under Ar. As can be seen, highly ordered microdomains appeared surrounding the pores. This could be explained by the deposition of recondensed/repolymerized volatiles and/or higher degree of catalytic graphitization by locally-available metallic potassium. On the other hand, Figures 1b and 1c display the SEM images of KHC1000 and KHC1000HCL materials. For KHC1000HCL, relatively small carbon microspheres were abundant, suggesting that this material could have an appropriate morphology to enhance sodiation/desodiation processes thanks to the high number of active sites easily achievable for Na ions [6].

In terms of electrochemical performance, the overall best results were obtained for the KHC1000HCL material, with an ICE of 76% and impressive charge capacities of 354 and 77 mA h g^{-1} at 0.1 and 2 A g^{-1}

¹, respectively, thanks to the synergistic effects induced by K_2CO_3 and HCl-catalyzed HTC. However, and as can be seen in Figure 1d, the KHC1000HCL-based electrode did not exhibit the best cycling stability, suggesting that some irreversible processes can take place during cycling. Further research is needed to clarify this point.

References

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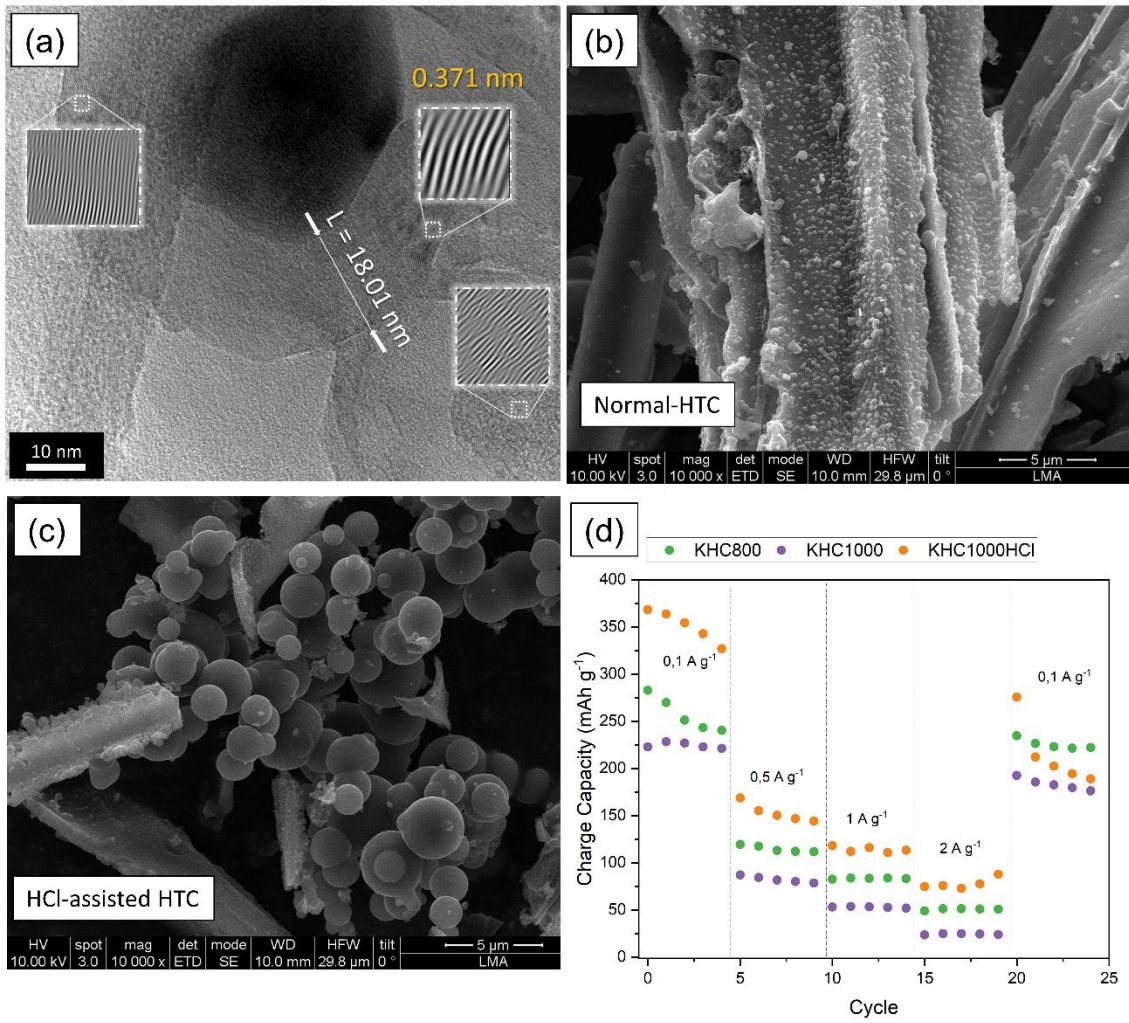


Figure 1. HRTEM image showing the effect of K₂CO₃ activation in WHH-derived hard carbons (a), SEM images of KHC1000 (b) and KHC1000HCl (c), and charge specific capacities at various current densities ranging from 0.1 to 2 A g⁻¹ obtained for mild chemically activated HCs(d).