Vine shoot-derived hard carbons as promising anodes for sodium-ion batteries: valorization of pig manure as HTC solvent.

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Abstract

Sodium-ion batteries (SIBs) are one of the most promising candidates to replace lithium-ion batteries (LIBs) in grid-scale energy storage applications. The design of high-performance anodes and the fully understanding of the sodium storage mechanisms are the main bottleneck to overcome. Herein, a vine shoot-based hard carbon anode was synthesized via hydrothermal carbonization followed by a pyrolysis step (800 to 1200 °C). In addition to water, pig manure and diluted hydrochloric acid were tested as reaction media.

Introduction

Sodium-ion batteries (SIBs) are one of the most promising candidates to lead the next generation of large-scale electrochemical energy storage systems required to support the grid integration of intermittent renewable sources. However, the implementation of this technology is contingent upon the development of new high-performance anodes. HCs derived from biomass tissues can retain the plant raw microstructure, resulting in a 3D structure composed of pores and channels that allows for electrolyte penetration and serves as sodium pathways and ion buffering reservoirs. Furthermore, the biomass provides a large number of defects and some remaining heteroatoms, together with randomly oriented pseudographitic domains [1].

Hydrothermal carbonization (HTC) mimics the natural coal process and involve several reactions mechanisms (e.g., hydrolysis, dehydration, decarboxylation, aromatization, and condensation polymerization). Compared with the direct pyrolysis strategy, HTC can promote the enlargement of the HC pores and the creation of surface nanospheres to improve the reversible capacity of the electrode [2]. In addition, the HTC treatment allows the addition of other chemicals to the aqueous solution in order to promote certain decomposition or doping reactions. In this regard, we checked the role of HCl as catalyst, since it is supposed to promote hydrolysis, deoxygenation and the formation of spherical structures [3]. We also conducted the hydrothermal process using pig manure as a solvent with the aim at valorizing this livestock waste, whose use as fertilizer has severe environmental impacts related to eutrophication and release of pathogens, antibiotics, and heavy metals.

Methods

15 g of VS and 50 g of distilled water were hydrothermally treated for 12 h at 180 °C. The material was then collected through vacuum filtration and dried at 100 °C for 12 h. The obtained hydrochar was heated at higher temperature (800, 1000 or 1200 °C) at a heating rate of 5 °C min−1 and kept at the peak temperature for 2 h under Ar. The resulting carbonaceous material was washed with HCl, grounded, and sieved to obtain particle sizes lower than 90 mm. The final product was denoted as HTC-*x*, where *x* refers to the highest carbonization temperature. When pig manure was used as solvent, same procedure was followed by using 50 g of the slurry instead of 50 g of water. The final product was denoted as HTCman-*x*. Finally, both HTC-1000 and HTCman-1000 were synthesized under a HCl-catalyzed (0.5 mol dm^{-3}) hydrothermal treatment and named as HTC-1000ac and HTCman-1000ac, respectively.

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 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 3-electrode 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

Hard carbons produced by hydrothermal carbonization also maintained the 3D structure of the raw biomass, although the walls of the honeycomb-like structures appear to have undergone some morphological changes, likely due to degradation (hydrolysis) and condensation polymerization of lignocellulosic components. The HR-TEM image of the HTC-1000 carbon also indicates a high degree of ordering, highlighting the appearance of abundant pseudographitic domains and closed microporosity. The use of pig manure as hydrothermal medium led to the formation of new aggregates attached to the surface of the VS-derived carbon. The EDX analysis of these new structures confirmed the presence of N (ca. 13%) and, to a lesser extent, K, Ca, Mg, and S. This suggests that the pig manure can be used as a green pathway for the heteroatom doping of lignocellulosic carbons, valorizing a potentially harmful waste for agronomic soils. Regarding the use of HCl as catalyst, its influence on the morphology of HTC-1000ac was limited to the appearance of some isolated microspheres. However, in the case of the HTCman-1000ac carbon, it led to the formation of bigger sphere clusters, given the higher proportion of soluble and easily accessible molecules for hydrolysis (such as proteins, carbohydrates, and fats) available in pig manure.

Among the HTC-x carbons, HTC-1000 exhibited the best reversible capacity, as annealing at 800 and 1200 ˚C generated insufficient and excessive ordering, respectively (see Figure 1). Unfortunately, the addition of HCl (HTC-1000ac) has not resulted in any improvement, but rather a loss of ICE from 71 to 58% due to the increase in open micro and meso-porosity. When HTC in pig manure was employed, HTCman-1000 achieved a capacity of 244 mAh g^{-1} at 0.1 A g^{-1} (ICE of 72%), as shown in Figure 3b. Moreover, the use of acid hydrolysis in conjunction with pig manure has indeed led to synergistic improvements in rate capability, delivering 86 mAh g^{-1} at 1 A g^{-1} and 64 mAh g^{-1} at 2 A g^{-1}.

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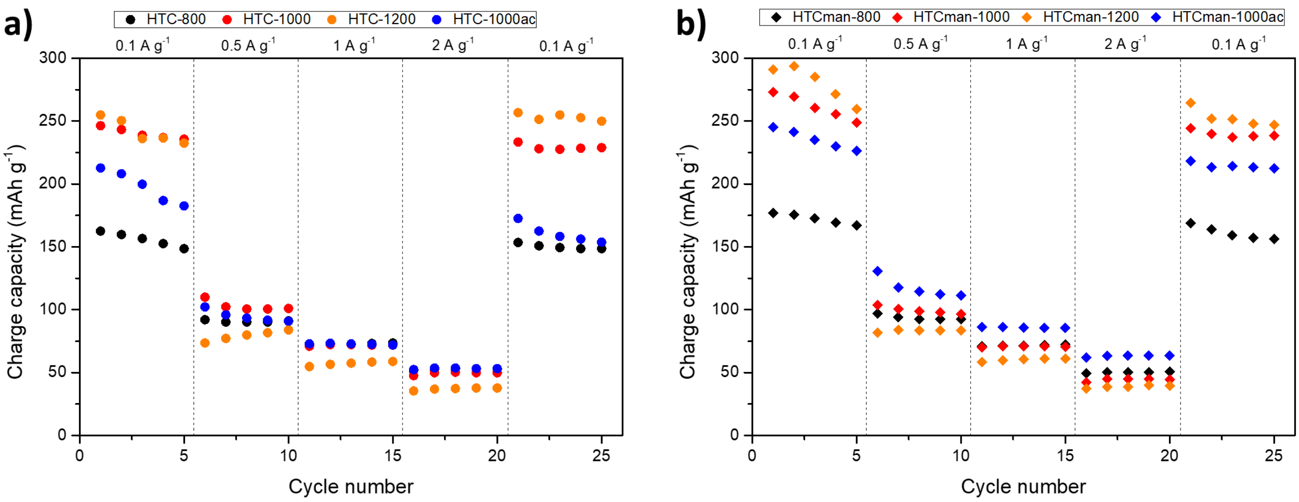

Figure 1. Rate performance of HTC-*x* (a) and HTCman-*x* (b) carbons.