Valorisation of almond residues via deep eutectic solvent-assisted activation for aqueous zinc-ion hybrid supercapacitors

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Abstract

Almond residues were converted into activated carbons via impregnation in K_2CO_3–ethylene glycol deep eutectic solvent for zinc-ion hybrid supercapacitors. This study demonstrates effective biomass valorisation, highlighting precursor hydrothermal pretreatment and DES-assisted activation, with excellent rate capability of 181 and 75 mAh g^{-1} at 0.1 and 10 A g^{-1} respectively.

Introduction

Zinc-ion hybrid supercapacitors (ZHSCs), combining high power density and high energy density, show strong potential for energy storage applications such as hybrid electric vehicles and renewable energy storage [1]. However, their practical performance is still limited by the relatively low capacity and cycling stability of carbon-based cathodes. These challenges can be addressed through strategies such as increasing specific surface area, engineering suitable pore structures, and heteroatom doping.

Agricultural residues provide diverse carbon-rich architectures that can be engineered for electrochemical applications. Biomass-derived carbons have gained significant attention as sustainable electrode materials. However, conventional activation approaches often rely on harsh chemical agents and offer limited control over pore development, restricting performance optimisation. To address these limitations, greener activation strategies such as deep eutectic solvents (DESs), which are eutectic mixtures of hydrogen bond donors and acceptors, have emerged as promising route for carbon structuring [2].

In this work, almond tree pruning (AT) and almond shell (AS), were explored as precursors. These materials underwent DES-assisted swelling in a K_2CO_3–ethylene glycol (EG) system prior to carbonisation, enabling enhanced porosity development and improved electrochemical properties.

Experimental

The precursors (AT and AS) were grounded and immersed in K_2CO_3-EG DES at different molar ratios (1:6, 1:8, and 1:10), using either biomass or their derived hydrochars. The resulting mixtures were filtered, dried, and carbonised under Ar at 800 °C for 2h (5°C min^{-1}). For comparison, wet K_2CO_3-impregnated carbons were also prepared using K_2CO_3–H_2O (1:8 molar ratio) solution under identical processing conditions.

The obtained carbons were washed and used to prepare electrode slurries containing 90 wt% active material, 5 wt% sodium carboxymethyl cellulose (Na-CMC) binder, and 5 wt% acetylene black. The slurry was coated onto stainless steel foil (1.7 mg cm^{-2}). Electrochemical performance was evaluated in a two-electrode configuration using zinc metal as the anode, 1 mol dm^{-3} Zn $(CF_3SO_3)_2$ electrolyte, and a glass fibre separator. Galvanostatic charge–discharge tests were conducted between 0.1–1.7 V at current densities ranging from 0.1 to 20 A g^{-1}.

Results and discussions

Influence of DES-assisted activation

The K_2CO_3–EG DES with the 1:8 molar ratio showed better performance due to an appropriate balance of alkalinity and potassium availability that promotes controlled activation and hierarchical porosity. At lower EG content (1:6), excessive alkalinity likely causes over-etching and inaccessible ultramicropores, while at higher dilution (1:10), reduced active species might limit potassium-driven pore development (see Figure 1).

Carbons prepared via wet K_2CO_3 impregnation (AT-HW8 and AS-HW8) exhibited inferior performance, highlighting the role of the DES medium in precursor swelling and activation control. This improved activation environment facilitates more uniform pore development and enhanced electrochemical behavior in DES-assisted samples.

Influence of precusor type and pretreatment

The electrochemical performance strongly depended on precursor type (AT vs AS) and pretreatment route (biomass vs hydrochar). Overall, AT-derived carbons exhibited higher specific capacities than AS-derived materials (Fig. 1). For AT samples, the directly activated biomass (AT-BD8) showed the highest capacity at low current density (181.11 mAh g^{-1} at 0.1 A g^{-1}), while the hydrochar-derived sample (AT-HD8) delivered superior high-rate performance (72 vs. 52 mAh g^{-1} at 20 A g^{-1}) and better cycling stability (97.7 % vs. 91.1 % over 2000 cycles).

In contrast, AS-derived carbons benefited significantly from hydrothermal pretreatment (116 vs. 65.41 mAh g^{-1} at 0.1 A g^{-1} for AS-HD8 and AS-BD8). This behaviour can be rationalised based on the structure-selective interaction of K_2CO_3–EG DES with lignocellulosic components [2]. The softer and more open AT structure enables effective DES activation in its native form, resulting in higher initial capacity, while the hydrothermal pretreatment improved final stability and rate performance. In contrast, the more lignified AS structure required the hydrothermal treatment in order to open the biomass structure to facilitate DES accessibility and activation efficiency.

Conclusions

DES-assisted activation enables effective biomass processing with improved control over pore architecture, while significantly enhancing rate capability and cycling stability without the use of harsh conventional chemical activating agents. This approach offers a sustainable and efficient route for designing high-performance biomass-derived carbon cathodes.

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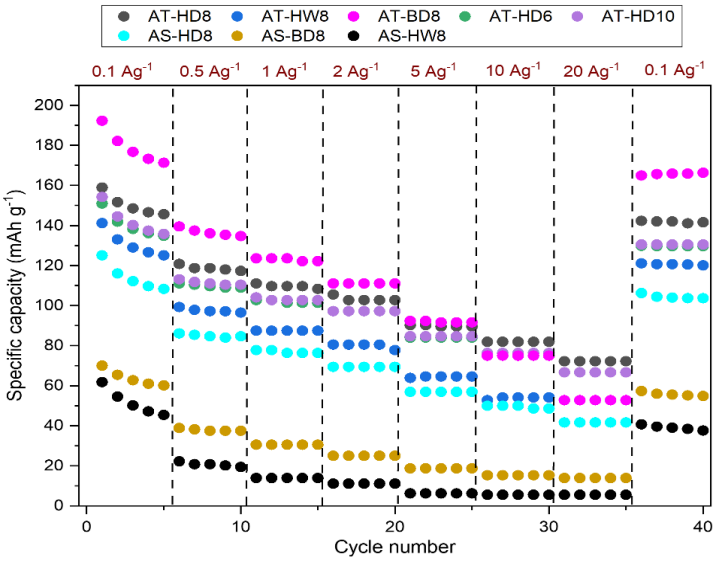

Figure1. Specific capacity versus cycle number at different current densities for samples X–YZN [*X*: AT/AS, *Y*: biomass /hydrochar, *Z*: DES (D)/H_2O (W), *N*: K_2CO_3-to-solvent ratio (6/8/10)] .