Synthesis of affordable activated carbons from almond shell and almond tree pruning waste for aqueous zinc hybrid supercapacitors

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Abstract

To enhance the performance of biomass-derived carbons as cathodes in zinc hybrid supercapacitors, we chemically activated almond shells and almond tree pruning residues through a hydrothermal pretreatment and subsequent carbonisation. We examined the effects of precursor morphology and activating agents on the properties of the resulting carbons. Furthermore, the influence of the type of electrolyte and the use of carbon black as conductive agent on the electrochemical performance was also assessed. The best-performing K_2CO_3-treated sample achieved 142 mA h g^{-1} at 0.1 A g^{-1} with 92 % capacity retention over 2000 cycles at 10 A g^{-1}.

Introduction

Battery technology has advanced steadily from Volta's pioneering cell to modern lithium-ion systems. Still, these longstanding foundations now struggle to meet rising energy demands due to limited power density and safety risks from flammable organic electrolytes [1]. Supercapacitors offer rapid power delivery (10^3–10^5 W kg^{-1}), yet their low energy density limits broader use. To bridge this gap, hybrid supercapacitors (HSCs) combine battery-like faradaic storage with capacitive mechanisms in a single device, overcoming the limitations of each technology alone [2].

Zinc-ion hybrid supercapacitors (ZHSCs) are particularly promising, effectively balancing high energy density with rapid power output. ZHSCs consist of a zinc metal anode (or a Zn^{2+}-intercalating material), a cathode—often carbon-based, such as activated carbon, graphene, or porous carbon—for efficient electrostatic ion adsorption and desorption, and an aqueous zinc salt electrolyte [e.g., $ZnSO_4$, $ZnCl_2$, Zn $(NO_3)_2$, Zn $(CH_3COO)_2$, or Zn $(CF_3SO_3)_2$] tailored for effective Zn^{2+} transport and electrochemical stability [3]. This configuration enables high energy and power densities, long cycle life, and improved safety, making ZHSCs a compelling solution for next-generation energy storage.

Nevertheless, ZHSC technology remains in its early stages, and practical implementation continues to face several challenges, particularly on the cathode side, where limited capacity and sluggish ion kinetics constrain energy density and efficiency [4]. B*iomass-derived hard carbons (BHCs)* have gained attention for their potential use as cathode materials, owing to their inherent porosity, low cost, wide availability, and favourable electrochemical performance, while also contributing to sustainable waste valorisation [5].

In this study, the biomass precursors of choice were almond tree pruning waste (AT) and almond shell (AS) to investigate how their morphological differences influence electrochemical performance. We produced BHCs through hydrothermal carbonisation (HTC) of the biomasses, followed by chemical activation using agents such as KOH or K_2CO_3 to enhance porosity, which is a key factor for improving electrochemical behaviour. We also discuss the influence of carbon black addition and compare the performance in common aqueous electrolytes—$ZnSO_4$ vs. Zn $(CF_3SO_3)_2$—on the electrochemical performance of ZHSCs.

Experimental

Synthesis of biomass-derived hard carbon

The precursors were ground and sieved to obtain particle sizes between 1.4 mm and 4 mm, which were hydrothermally treated at 185 °C for 12 h in water and autogenous pressure. Then the solid fraction was separated through vacuum filtration to obtain the intermediate hydrochar. For chemical activation, the dried hydrochar was mixed with chemical activating agents (KOH or K_2CO_3) using a simple physical dry-mixing method and different hydrochar-to-activating agent mass ratios (from 1:1 to 1:4). These mixtures were then carbonised—in an argon atmosphere at 800 °C for 2 h with a heating rate of 5 °C min^{-1}—in a ceramic tubular reactor. Finally, the carbon was washed with a 2 M HCl solution to extract remaining activating agents and rinsed with distilled water.

Electrode preparation and testing

The resulting BHCs were used to make aqueous electrode slurries with 5 % of sodium carboxymethyl cellulose (Na-CMC) as binder and optionally 10 % of acetylene black as conductive carbon. The slurry was coated onto a stainless-steel foil with active material loading of 1.5 mg cm^{-2}. The electrodes were vacuum dried at 120 °C for 12 h. The electrochemical performance was tested in a 2-electrode cell configuration with zinc metal as the anode, 2 M $ZnSO_4$ or 1 M $Zn(CF_3SO_3)_2$ (ZTFS to abbreviate) as electrolyte, and a glass fibre membrane as the separator. The cell was cycled using a potentiostat/galvanostat (Bio-Logic SP-200) at different current densities ranging from 0.1 A g^{-1} to 20 A g^{-1} in the voltage range 0.1–1.7 V.

Results and discussions

Role of biomass precursor

In this study, AT samples exhibited higher specific capacity and, hence, better electrochemical performance compared to AS samples (see Fig. 1). The best performing sample was AT_K₂CO₃_1:4 with reversible capacities of 138 mAh g^{-1} and 46.5 mAh g^{-1} at 0.1 A g^{-1} and 20 A g^{-1}, respectively. Whereas for AS_K₂CO₃_1:4, the capacity at 0.1 A g^{-1} was 82.9 mAh g^{-1}. Although further characterisation is ongoing, the higher lignin content and structural stability of almond shell appear to limit its activation efficiency and pore formation, in contrast to the more reactive almond tree pruning biomass.

Chemical activating agent

For the activating agent utilised in this chemical activation synthesis procedure, K₂CO₃, with a milder activation process, was better than the commonly used KOH activation. This was beneficial to preserve biomass morphology and to enhance scalability for industrial applications, since KOH is highly corrosive. The K₂CO₃ impregnation ratio was adjusted, and it was observed that the biomass to activating agent ratio of 1:4 and 1:2 for K₂CO₃ was better than the typical 1:1 ratio of KOH (see also Fig. 1). Furthermore, it was found that the hydrothermal pretreatment improved the performance of AT_K₂CO₃_1:4. At 0.1 A g^{-1}, the unpretreated material just delivered 88.3 mAh g^{-1}, 36 % lower than the pretreated one).

Influence of carbon black

The 10 % carbon black (CB) addition to form the sample AT_K₂CO₃_1:4_CB further improved the electrochemical performance, as evidenced in Fig. 1. Although similar capacities were measured for both AT_K₂CO₃_1:4 and AT_K₂CO₃_1:4_CB materials at low current densities (ca. 142 mAh g^{-1} at 0.1 A g^{-1}), the addition of CB led to an improvement in the rate capability (e.g., at 20 A g^{-1}, 55.0 mAh g^{-1} compared to 46.5 mAh g^{-1}). This enhancement is likely attributed to the augmentation of the electrode's electrical conductivity.

Influence of electrolyte

The 2 M $ZnSO_4$ electrolyte, in comparison with the 1 M ZTFS one, exhibited slightly higher specific capacity at low current density (see Fig. 2); however, the ZTFS-based electrolyte performed better at higher current densities (65 vs. 58 mAh g^{-1} at 10 A g^{-1}). In addition, the cycling stability of the best performing electrode (AT_K₂CO₃_1:4_CB) was improved when 1 M ZTFS electrolyte was used, as deduced from Fig. 2. After 2 000 cycles at 10 A g^{-1}, a capacity retention of 92 % and 83 % (with respect to the values measured at 0.1 A g^{-1}) were measured for the ZTFS-based and the ZnSO₄-based electrolytes, respectively.

Conclusions

This study highlights the potential of K₂CO₃ as a superior chemical activating agent for the AT biomass than the commonly used KOH. BHC-derived electrodes could demonstrate their promise for scalable and sustainable energy storage solutions for ZHSCs. Furthermore, carbon black addition elevates the specific capacity at higher current densities. The use of ZTFS electrolyte enhances the stability of the electrochemical system compared to the more widely used ZnSO₄ electrolyte.

Acknowledgement

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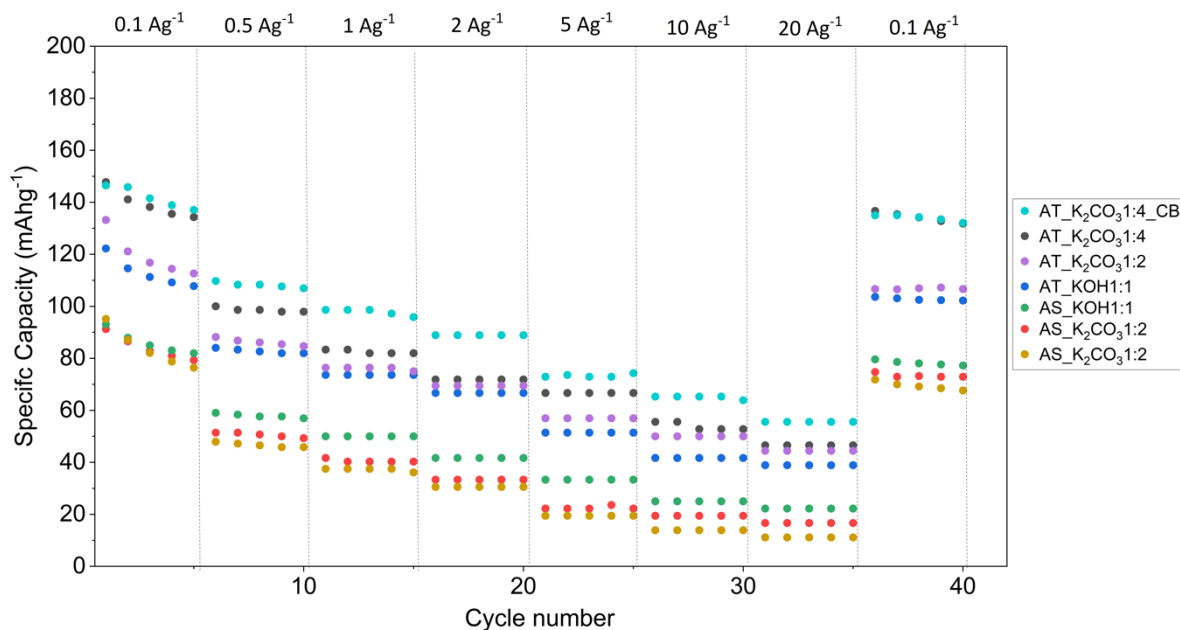
Figure 1. Specific capacity versus cycle number: comparing precursors, activating agent, and influence of CB in ZTFS electrolyte
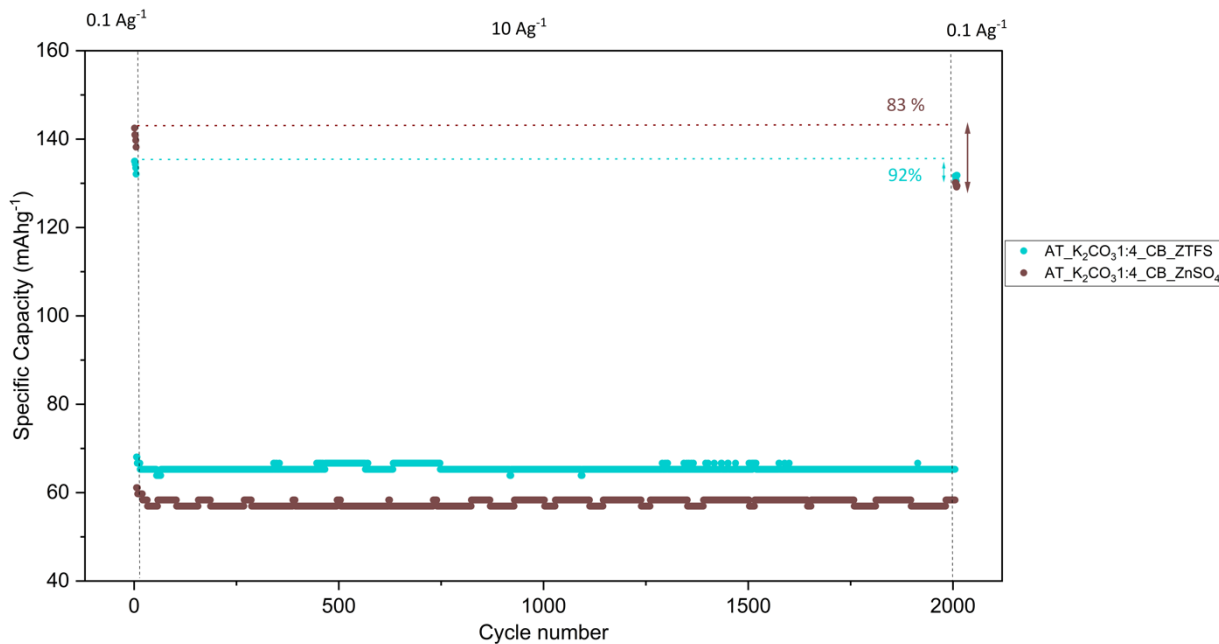

Figure 2. Cycling performance in ZTFS and ZnSO$_4$ based electrolytes