Activated carbon derived from coconut shell chars for use as a cathode material in aluminium-ion batteries

P Thanwisai\textsuperscript{1}, P Phuenhinlad\textsuperscript{2}, N Chaiyapo\textsuperscript{2}, Y Kanaphan\textsuperscript{2}, J Nash\textsuperscript{3}, C Chotsuwan\textsuperscript{4}, T Rattana-amron\textsuperscript{4}, A Klamchuen\textsuperscript{4} and N Meethong\textsuperscript{1,5,*}

\textsuperscript{1}Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand.
\textsuperscript{2}Materials Science and Nanotechnology Program, Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand
\textsuperscript{3}The Graduate School, Udon Thani Rajabhat University, Udon Thani, 41000, Thailand
\textsuperscript{4}National Nanotechnology Centre (NANOTEC), National Science and Technology Development Agency, Pathumthani, 12120, Thailand
\textsuperscript{5}Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), NANOTEC-KKU RNN on Nanomaterials Research and Innovation for Energy, Khon Kaen University, Khon Kaen, 40002, Thailand

\textsuperscript{*}E-mail: nonmee@kku.ac.th

Abstract. Aluminium-ion batteries (AIBs) are a promising energy storage system due to their significant advantages of low cost, high anode capacity and safety. Nevertheless, the critical challenge limiting AIB performance is an inadequate cathode capacity that diminishes their cell energy density. To overcome this limitation, it is important to develop novel cathode materials with high cathode capacity for AIBs. Herein, we report an activated carbon derived from coconut shell chars for use as a cathode material in AIBs. The activated carbon was synthesized via KOH activation and carbonization. The prepared cathode material exhibits a high specific capacity of 38 mAh g\textsuperscript{-1} at a high current density of 1 A g\textsuperscript{-1} due to its high specific surface area of 2686 m\textsuperscript{2} g\textsuperscript{-1}, which is beneficial for chloroaluminate-ion accommodation. This result indicates that the activated carbon derived from coconut shell chars with its high surface area is electrochemically active and is likely to be a promising cathode material for AIBs.

1. Introduction
In recent years, aluminium-ion batteries (AIBs) have been regarded as a possible alternative energy storage system owing to the natural abundance and nonflammability of aluminium metal. Additionally, aluminium metal possesses relatively high volumetric capacity and comparable gravimetric capacity to lithium metal. These intriguing advantages endow AIBs with low cost, high safety, and potentially high energy density \cite{1,2}. Despite the excellent merits of aluminium anodes, a vital issue limiting the AIB cell energy density and cycle-life is the lack of suitable cathode materials \cite{3}. Hence, finding cathodes with high capacity, high operating voltage and good cycling stability is a great challenge in AIB research. Several cathode materials such as carbon-based materials, metal oxides metal sulphides, as well as composite materials have been widely studied \cite{1–8}. Among them, graphitic carbon materials have received much attention due to their high electrical conductivity, long cycle-life, and availability in commercially needed quantities \cite{1,2,4}. However, AIBs using graphitic cathodes have
poor specific capacity leading to low energy density [5, 6]. This is apparently because the interlayer space of graphite (~0.335 nm) is too narrow to accommodate the larger sized chloroaluminate anions (~0.6 nm), hindering the charge-storage process. Additionally, the intercalation of such large ions can cause volume expansion after a few cycles, damaging the host structure and resulting in poor cycle-life of batteries [5, 6]. Using porous carbon materials such as activated carbon as cathodes is a very appealing strategy. Their porous structures can promote charge-storage reactions due to adsorption/desorption of chloroaluminate anions on their surfaces. This surface-based mechanism normally provides long cycle-life. Furthermore, porous carbon materials can provide large surface areas that can accommodate chloroaluminate anions, leading to high gravimetric capacity [5, 6].

In this work, we introduce an activated carbon with a high specific surface area (SSA) for use as a cathode material in AIBs. Coconut shell chars were utilized as a precursor to produce activated carbon via KOH activation and carbonization processes. The carbon source provides the important benefits of high abundance, low cost, and high carbon content. The activated carbon is expected to have a porous structure and a high SSA leading to a high specific capacity and good cycling stability due to the non-intercalation mechanism.

2. Experiments

2.1. Preparation of activated carbon from coconut shell chars

Coconut shell chars, collected from Ratchaburi Province, Thailand, were cleaned with tap water to remove soil and impurities. Then, the cleaned chars were ground, and ball milled to produce fine grains that passed through a 325-mesh screen. In the chemical activation process, the milled chars were soaked with KOH at a KOH:C ratio of 5:1 (mass basis) for 24 h. This was followed by carbonization at 850 °C for 1 h under an Ar atmosphere. After carbonization, the resulting sample was thoroughly washed with 1 M HCl acid, subsequently adjusted to neutral pH (~7) with distilled water washing, followed by vacuum drying at 80 °C for 24 h. The prepared activated carbon is referenced as the AC-5:1 sample.

2.2. Material characterizations

X-ray diffraction spectroscopy (XRD) (EMPYREAN, PANalytical) using Cu-Kα radiation at 40kV and scanning electron microscopy (SEM) (Zeiss, LEO-1450VP) were employed to respectively analyse the crystal structure and surface morphology of the activated carbon. Moreover, the SSA was measured using the Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption method (Micromeritics).

2.3. Cathode preparation and cell assembly

The obtained activated carbon (90 %wt) was mixed with polyvinylidene fluoride (PVDF Kynar 2801, Arkema) (10 %wt) dissolved in N-methyl pyrrolidone (NMP, anhydrous, 99.5%, Sigma-Aldrich) acting as a binder to prepare an initial slurry. The mixture was stirred until the slurry became homogeneous. It was applied to a molybdenum foil using a doctor blade and subsequently vacuum dried at 80 °C for 12 h. A Swagelok-type cell was utilized to assemble a full-cell AIB. In the cell configuration, aluminium foil with a thickness of 0.25 mm (purity 99.99%, Alfa Aesar) was served as an anode, whereas the active material coated on molybdenum foil and glass microfiber paper (Grade GF/D, Whatman) were used as a cathode and a separator, respectively. These two electrodes were separated by two layers of the separators soaked in an ionic liquid electrolyte prepared by mixing AlCl₃ (Sigma-Aldrich) and EMImCl (97%, Sigma-Aldrich) in a molar ratio of 1.3:1. Cell assembly was done in a glovebox under an Ar flow to prevent moisture and air contacts.
2.4. Electrochemistry measurements
The electrochemical properties of the activated carbon derived from coconut shell chars were investigated using a galvanostatic charge/discharge test (GCD) (BST8-MA, MTI) and cyclic voltammetry (CV) (Wuhan CorrTest) with a potential window of 0.01-2.25 V at various current densities and scan rates.

3. Results and discussion

3.1. Characterizations of the activated carbon derived from coconut shell chars
Activated carbon derived from coconut shell chars with a high SSA was successfully synthesized via KOH activation method with a KOH:C ratio of 5:1 followed by carbonization at 850 °C. After synthesizing the material, its crystalline structure and surface morphology were characterized using XRD, SEM and BET techniques and the results were shown in figure 1. The XRD pattern of the activated carbon in figure 1(a) indicates two broad peaks positioned at 2θ = 26° and 44° corresponding to a highly disordered crystalline structure of amorphous carbon. A peak shift from 26° of graphite to 20° at the (002) reflecting plane can be attributed to an expansion of the interlayer spacing of graphite. The SEM image in figure 1(b) reveals that the resulting activated carbon consists of large particles with irregular surfaces, implying porosity. Additionally, the porous characteristic of the activated carbon is revealed in figure 1(c). As can be seen, this activated carbon shows a Type I isotherm, according to the IUPAC classification. This can be attributed to the presence of micropores and small-mesopores. In a relatively low-pressure range, the amount of N₂ uptake increases steeply, implying the presence of microporous structures. When increasing the relative pressure, a moderate increase in adsorbed N₂ and a plateau can be observed, which is consistent with the presence of mesoporous structures [9]. In addition, the BET surface area of 2686 m² g⁻¹ is obtained for this sample.

![Figure 1](image1.png)

Figure 1. (a) X-ray diffraction pattern, (b) SEM image of the activated carbon derived from coconut shell chars at a magnification of 10K and (c) N₂ adsorption/desorption isotherm.

3.2. Electrochemical properties of the activated carbon derived from coconut shell chars
The electrochemical properties of the prepared activated carbon were investigated using the GCD and CV methods. The results were displayed in figure 2. Figure 2(a) shows charge/discharge curves at various current densities. It can be observed that the charge/discharge capacities depend on the applied current densities. At a low current density of 0.025 A g⁻¹, the specific discharge capacity is as high as 140 mAh g⁻¹. However, it is decreased to 38 mAh g⁻¹ when applying a high current density of 1 A g⁻¹. The charge/discharge curves also show capacitive behavior with no intercalation. No voltage plateaus were observed in any of the charge/discharge curves. This means that the redox reaction in this material does not involve a charge-storage mechanism. The GCD results are consistent with the CV curves shown in figure 2(b). The CV curves at all scan rates illustrate a rectangular shape with no oxidation and reduction peaks. These GCD and CV results indicate that the charge-storage mechanism of the activated carbon cathode is based on the surface adsorption/desorption of chloroaluminate.
anions, which mimics the typical behavior of capacitors [6], yet with a much higher capacitance. Furthermore, cycling stability of the cathode was examined over 500 charge/discharge cycles. It is clearly seen in figure 2(c) that the charge/discharge specific capacities remain stable throughout 500 cycles at a current density of 1 A g\(^{-1}\), with a high Coulombic efficiency, approaching 100%. The porous structures of the activated carbon cathode with a high surface area lead to high specific capacity and stable cycling performance by providing large surface areas for storing the active ions without intercalations.

**Figure 2.** (a) Galvanostatic charge/discharge profiles at different current densities, (b) cyclic voltammetry curves at various scan rates, and (c) capacity retention and Coulombic efficiency over 500 cycles of the cathode.

4. Conclusions

We successfully synthesized highly porous activated carbon with a high SSA of 2686 m\(^2\) g\(^{-1}\) from coconut shell chars employing KOH activation and carbonization. The porous structures and large surface areas play a vital role in the charge-storage mechanism where the chloroaluminate anions are stored on the surfaces of the porous activated carbon. The capacitor-like mechanism is different from the intercalation process reported in graphite-based AIBs. This surface-based behavior endows the activated carbon cathode with a discharge capacity of 38 mAh g\(^{-1}\) at a current density of 1 A g\(^{-1}\) and excellent capacity retention over 500 charge/discharge cycles. This work illustrates that the activated carbon is a very promising cathode material for AIBs.

Acknowledgements

We appreciate the financial support from the Development and Promotion of Science and Technology Project (DPST) and the Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), Khon Kaen University.

References

[1] Lin M-C et al 2015 Nature **520** 324–8
[2] Hu H et al 2020 Chem. Commun., **56** 1593–6
[3] Wu C et al 2019 Nat. Commun. **10** 73
[4] Hu Y, Debnath S, Hu H, Luo B, Zhu X, Wang S, Hankel M, Searles D J and Wang L 2019 J. Mater. Chem. A **7** 15123–30
[5] Zhang C, He R, Zhang J, Hu Y, Wang Z and Jin X 2018 ACS Appl. Mater. Interfaces **10** 26510–6
[6] Stadie N P, Wang S, Kravchyk K V and Kovalenko M V 2017 ACS Nano **11** 1911–9
[7] Vanitha M, Joni I M, Wibawa B M and Panatarani C 2019 IOP Conf. Ser.: Mater. Sci. Eng. **550** 012003
[8] Canever N and Nann T 2020 Nano Express **1** 010016
[9] Phiri J, Dou J, Vuorinen T, Gane P A C and Maloney T C 2019 ACS Omega **4** 18108–17