

Hardcarbon Synthesis From Nipah Palm (*Nypa Fruticans*) Shell Waste

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Abstract. Lithium-ion batteries are among the most widely used energy storage systems. The negative electrode (anode) material plays a crucial role in determining their electrochemical performance. However, graphite anodes face several drawbacks, including high cost. Hard carbon has emerged as a promising alternative due to its high storage capacity and cycling stability. This study aims to synthesize and characterize hard carbon derived from nipah palm shell waste as a sustainable anode material. Nipah biomass was selected as the precursor because of its high cellulose (36.5%) and lignin (27.3%) content, which are essential for forming a robust hard carbon structure. The conversion process was carried out through a one-stage pyrolysis method consisting of three steps: pre-treatment, pyrolysis, and activation. The nipah shells were washed, dried, and pyrolyzed at 800 °C under a nitrogen atmosphere. The resulting hard carbon was activated using acidic and basic solutions (HCl, KOH, and NaOH), rinsed with deionized water until neutral pH, and subsequently dried. SEM–EDX analysis revealed that HCl activation produced a morphology most like commercial hard carbon. XRD analysis showed a strong peak near $2\theta = 23^\circ$ and a weaker peak at $2\theta = 41^\circ$. FTIR spectra confirmed the presence of oxygen-containing functional groups (C–O and C=O), with absorption peaks around 1050 cm^{-1} (C–O stretching) and 1600 cm^{-1} (C=C/C=O stretching), typical of biomass-derived hard carbon. The HCl-activated sample exhibited weaker oxygen-related bands compared to NaOH- and KOH-activated samples, indicating a cleaner carbon surface and supporting its closer similarity to commercial hard carbon. Electrochemical evaluation demonstrated that HCl-activated hard carbon delivered a specific capacity of $\sim 28\text{ mAh g}^{-1}$ at 0.5C, maintained stable capacity up to 3C, and achieved 78.79% retention after 20 cycles. These findings confirm the successful conversion of nipah palm shell waste into hard carbon and highlight its potential as a sustainable anode material for lithium-ion batteries.

1 Introduction

Nypa palm is an underutilized biomass resource covering approximately 700,000 hectares [5]. Each tree generates about 3 kg of biomass waste, primarily consisting of shells and fibers. Although the fibers are often discarded, they contain up to 87.1% lignocellulosic components

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[6], indicating that Nypa shells have strong potential as carbon precursors. However, Nypa palm biomass has rarely been investigated for hard carbon production. Therefore, this study aims to synthesize hard carbon from Nypa palm shell waste and evaluate its electrochemical performance as a sustainable anode material for lithium-ion batteries.

Biomass-derived hard carbon has attracted increasing attention due to its low cost, environmental sustainability, and wide availability. Nevertheless, many biomass-based carbons still suffer from inconsistent morphology and unstable electrochemical performance, whereas commercial graphite remains dominant because of its reliability and reproducibility [3]. These limitations are strongly influenced by synthesis parameters, particularly pyrolysis temperature. Previous studies have reported various approaches to hard carbon synthesis, and in this research, a pyrolysis temperature of 800 °C was selected. Literature indicates that the temperature range of 800–1000 °C is optimal for producing hard carbon suitable for lithium-ion batteries, as it promotes amorphous carbon structures with high porosity and stable electrochemical behavior, while avoiding incomplete carbonization at lower temperatures and excessive graphitization at higher temperatures [7].

In addition to pyrolysis temperature, chemical activation plays a crucial role in tailoring pore structure and surface chemistry. In this study, NaOH, KOH, and HCl were employed as activating agents to systematically examine their effects on the physicochemical properties of the resulting hard carbon. Strong alkaline activators such as KOH and NaOH interact differently with carbon precursors: KOH generally promotes the formation of high microporosity and large surface area, while NaOH produces distinct pore characteristics. In contrast, HCl activation typically results in lower porosity but can lead to a cleaner carbon surface with different functional group distributions and adsorption behavior. This comparative approach enables a clearer understanding of how acidic and alkaline activation influence pore morphology, surface chemistry, and textural properties relevant to adsorption and electrochemical applications [8].

Nypa palm shell waste has not yet been systematically explored as a precursor for hard carbon in lithium-ion batteries. This research therefore provides a novel contribution by synthesizing Nypa-derived hard carbon and directly comparing acidic (HCl) and alkaline (NaOH, KOH) activation routes. By elucidating the relationship between pore morphology, surface chemistry, and electrochemical performance, our work highlights the potential of Nypa palm biomass as a sustainable and underutilized resource for next-generation anode materials.

2 Material and Methods

2.1 Material

The main material used in the production of hardcarbon is nipa shell waste. The additional materials include NaOH, HCl, KOH, H₂O (distilled water), Acetylene Black (AB), Polyvinylidene Fluoride (PvDF), Mesocarbon Microbeads (MCMB), N-Methyl-2-Pyrrolidone (NMP), and LiPF₆.

2.2 Methods

To prepare the solid biochar, the nipa palm shells (*Nypa fruticans*) were first chopped into smaller sizes. They were then thoroughly washed with distilled water to remove surface contaminants, after which the washed pieces were thermally dried at 110 °C in an oven for 24 hours to remove any residual moisture and consequently lower the humidity. The next operation carried out with the dried biomass was that of pyrolysis, whereby this was achieved

thermally in a muffle furnace maintained at 800 °C for a period of about 2 hours, with a heating rate maintained at 5 °C per minute, the pyrolysis being carried under an inert atmosphere of nitrogen, the gas being constantly fed during the pyrolysis at a rate of 3 L/min. At the completion of the carbonisation of the biomass a solid product was obtained being subsequently crushed in a mortar and pestle pulverised to a fine powder. The grinding was done to ensure uniformity of the particle size before treatment thereafter.

The powdered carbon was chemically activated by immersing it in separate solutions of 1 M sodium hydroxide (NaOH), potassium hydroxide (KOH), and hydrochloric acid (HCl) for 24 hours. After the activation, the samples were thoroughly washed with distilled water. The neutralized materials were subsequently dried again at 100 °C to eliminate any remaining moisture content.

To assess the physicochemical properties of the final hard-carbon material different analytical techniques were employed. The identification of the functional groups was performed using Fourier Transform Infrared Spectroscopy (FTIR). For the structural analyses including crystallinity and the degree of carbonisation used in X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a 2θ distribution. The surface morphology and the elemental composition were analysed using Energy Dispersive X-ray Spectroscopy (EDX) and a JEOL JSM-6510LA (Tokyo, Japan).

After following testing on hard carbon samples that had been activated with HCL, KOH, and NaOH. Hard carbon is crushed using an aluminum mortar to ensure consistent particle size and filtered through a 200-mesh screen. A mortar is used to create a homogenous combination of hard carbon, acetylene black (AB), mesocarbon microbeads (MCMB), polyvinylidene fluoride (PvDF), and N-Methyl-2-pyrrolidone (NMP). An anode film is then created by applying this homogenous slurry to copper foil that is 25 mm thick using a doctor blade. The resulting film was dried in a vacuum oven at 100°C for 1 hour. After drying, the anode film was cut with a slitting machine and pressed with a hot rolling machine. Mass of the anode film was measured, and a nickel plate was affixed to the end. The anode film was rolled together with the cathode film and separator before being fitted into the battery housing. The lithium-ion battery was tested using 1M LiPF₆ [1].

Battery performance testing was performed to get charge-discharge and efficiency statistics. The testing was carried out in cycles by monitoring the current from full voltage to zero voltage, within a current range of 20 mAh/g to 70 mAh/g. The discharge cut-off voltage was 2.5 V, and the charge cut-off voltage was set to 4.3 V.

3 Results and Discussion

Hardcarbon based on nipah shell waste was produced using three different activating agents. Samples were characterized using XRD, SEM-EDX, and FTIR. Figure 1 shows the x-ray diffraction pattern of Nipa Shell Waste and Commerical Hardcarbon. The characteristic of the amorphous character of that material exhibiting the broad diffractions bands at about $2\theta = 23^\circ$ and 41° , which correspond to the typical structural features of hardcarbon materials [2]. Activation was performed employing NaOH, KOH, and HCl as the activating agents. In the samples treated with NaOH and KOH, the amorphous backbone is preserved, yet an additional sharp peak appears at about 31° . According to the JCPDS card reference No. 26-1077, this peak corresponds to crystalline sodium carbonate (Na₂CO₃), indicating that alkaline activation leaves residual carbonate phases embedded in the carbon matrix.

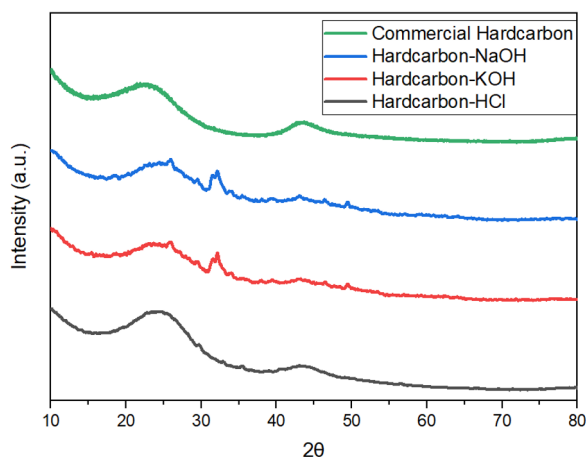


Fig. 1. XRD Patterns of Hardcarbon with Various Activating Agents

Furthermore, literature reports have also assigned the peak near 31° to crystalline potassium carbonate (K_2CO_3), which may form in KOH-activated samples [3]. In contrast, the HCl-treated sample shows no such peak from the outset, and its diffraction pattern remains purely amorphous. This demonstrates that while alkaline activation introduces carbonate residues, acid treatment yields a cleaner hard carbon phase. The obtained results further suggest that the observed impurities are not completely removed during carbonisation and activation, but are converted into various compounds due to interactions with the activating agents at high temperature[4].

Table 1. EDX Analysis of Hardcarbon with Various Activating Agents

Element	Hard Carbon			
	HCL	NaOH	KOH	Commercial
	Mass%	Mass%	Mass%	Mass%
C	92.42 ± 0.43	82.54 ± 0.34	88.68 ± 0.34	92.64 ± 1.04
O	5.87 ± 0.32	10.83 ± 0.33	8.08 ± 0.30	7.36 ± 1.21
Na	-	0.91 ± 0.05	0.95 ± 0.05	-
Mg	-	0.9 ± 0.04	0.44 ± 0.03	-
Si	0.94 ± 0.05	0.61 ± 0.02	0.19 ± 0.02	-
Cl	0.57 ± 0.04	0.39 ± 0.03	0.44 ± 0.03	-
Ca	0.20 ± 0.03	2.51 ± 0.08	0.71 ± 0.05	-
K	-	0.53 ± 0.03	0.52 ± 0.04	-
P	-	0.63 ± 0.03	-	-
Al	-	0.16 ± 0.03	-	-

According to the EDX examination, the hard carbon samples treated with HCl showed a carbon fraction of 92.42%, which falls within the typical range reported for biomass-derived hard carbon materials. This suggests that acid activation reduces inorganic residues more effectively than alkaline treatments. However, it should be noted that EDX is a semi-quantitative, surface-sensitive technique, and therefore the values obtained primarily reflect the near-surface composition rather than the bulk purity of the material[5]. It is also

noteworthy that hard carbon derived from other biomass precursors generally exhibits carbon contents in the range of 92–95% [6]. In contrast, NaOH- and KOH-activated samples exhibited lower carbon fractions and higher oxygen and alkalis contents, consistent with the presence of residual oxides or carbonate species. These compositional differences are reflected in the electrochemical tests, where the HCl-activated sample achieved the highest specific discharge capacity compared to the NaOH- and KOH-treated samples. It is also important to mention that washing induces an increase in the percentage of carbon, which is favorable for storage [7].

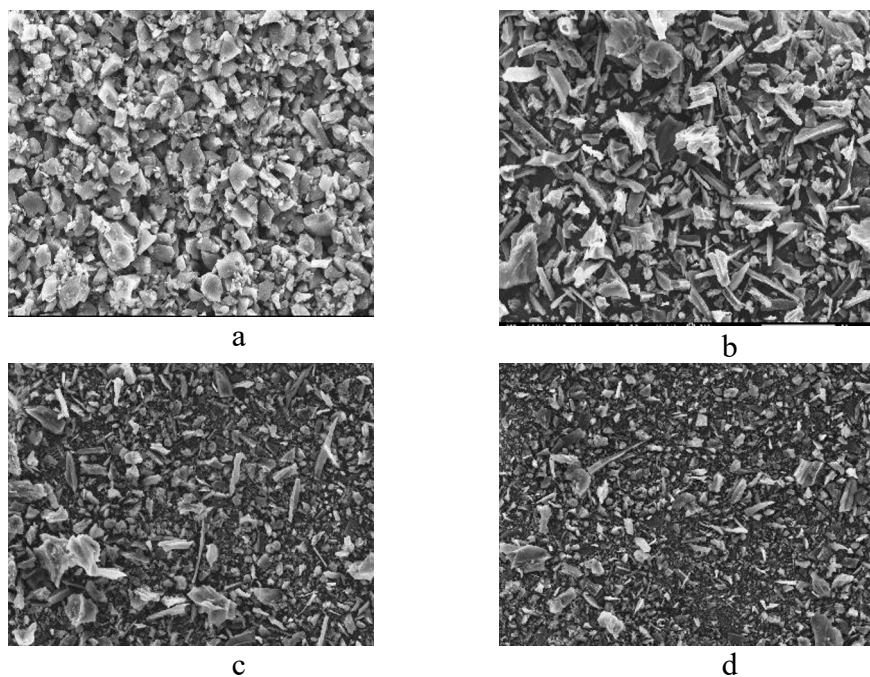


Fig. 2. SEM Morphology Of The Hardcarbon (a) Commercial Hard Carbon, (b) HCl (c) KOH, and (d) NaOH

The SEM analysis shows that commercial hard carbon exhibits compact particles with smooth surfaces, serving as the benchmark morphology. The HCl-treated sample displays irregularly shaped particles with smoother surfaces, while KOH- and NaOH-treated samples present highly porous and heterogeneous structures. These morphologies resemble a characteristic hard carbon structure, characterized by the presence of small lumps with irregular shapes and uneven sizes, which have been widely reported in biomass-derived carbons. The presence of such irregular lumps and porous features already indicates that the synthesized material belongs to the category of hard carbon, consistent with related findings in biomass-derived carbon studies. Such irregularity and porosity are known to enhance ion transport and adsorption capacity, though excessive disorder may reduce cycling stability and efficiency. Among the treatments, HCl activation produces morphology closest to commercial hard carbon and literature, confirming its superiority compared to alkaline activation methods [8]. The FTIR spectra of commercial hard carbon and chemically activated samples using NaOH, KOH, and HCl show similar functional group attributes indicating that the activation method does not significantly affect the chemical character of the carbon surface. Two bands of absorbing light are clearly apparent in all samples, one near 1600 cm^{-1} to the left, due to C=C stretching of aromatic spaces or C=O stretching of a carbonyl group, and a second about 1050 cm^{-1} to the left, due to C–O stretching vibrations and chemical

groupings of ethers, alcohols or esters. The FTIR spectra confirmed the presence of oxygen-containing functional groups (C–O, C=O), with stronger signals in the NaOH- and KOH-activated samples compared to the HCl-treated material. These bands indicate that these samples are rich in oxygenated groups and graphitic patterns, which would be expected in hard carbon products wherein the raw materials arise from biomass [9]. The O atoms in C=O and COOH possess extra electron pairs and are susceptible to Lewis acid–base interactions with Li^+ , enabling rapid and reversible Li^+ storage. In contrast, C–O groups with different oxygen configurations show weak Li^+ adsorption and generally act as irreversible sites, contributing to initial capacity loss [10]. The stronger C–O signals in NaOH- and KOH-treated samples suggest higher oxygen content, which promotes side reactions during the first cycles, leading to irreversible lithium consumption and unstable solid electrolyte interphase (SEI) formation. Conversely, the HCl-treated sample, with weaker oxygen-related bands and lower oxygen content, presents a cleaner carbon surface and more stable electrochemical behavior. This explains the lower initial discharge capacities observed for the NaOH- and KOH-treated samples. Thus, the differences in oxygen group content directly correlate with the electrochemical behavior of the samples, highlighting the importance of controlled surface chemistry in optimizing hard carbon anodes for lithium-ion

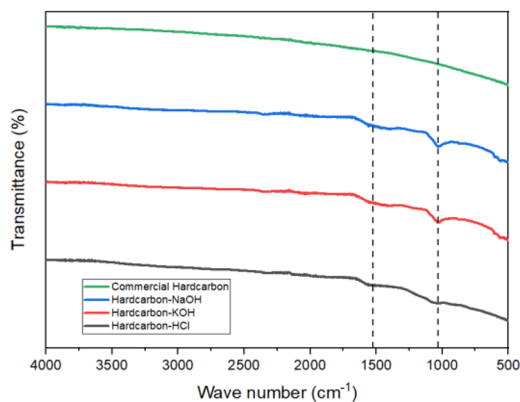


Fig. 3. FTIR Patterns of Hardcarbon with Various Activating Agents

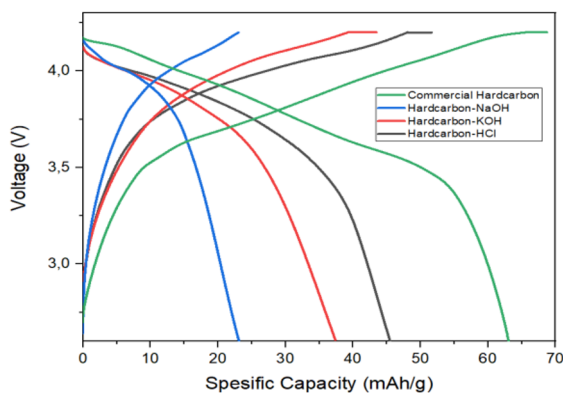


Fig. 4. Specific Initial Discharge Capacity Test Results of Hardcarbon with Various Activating Agents

As shown in the voltage–capacity profiles, the commercial hard carbon delivered the highest initial specific discharge capacity of approximately 63.06 mAh/g, serving as the benchmark. Among the activated samples, HCl-treated hard carbon exhibited the closest

performance, reaching 45,52 mAh/g. In comparison, NaOH-activated and KOH-activated hard carbon samples showed lower initial capacities of 37,38 mAh/g and 23,12 mAh/g. The electrochemical evaluation of the synthesized hard carbon revealed specific discharge capacities in the range of 23–63 mAh g⁻¹, which are considerably lower than the values typically reported for biomass-derived hard carbon anodes (>200 mAh g⁻¹) in the literature [8]. This discrepancy may be attributed to residual inorganic impurities detected by EDX and FTIR in the NaOH- and KOH-activated samples. In contrast, the HCl-treated sample exhibited the highest discharge capacity among the tested variants and retained 78.79% of its initial capacity after 20 cycles, reflecting moderate short-term stability. However, the cycling data are limited to 20 cycles and therefore cannot substantiate long-term durability claims. These results indicate that acid activation produces morphology and composition closest to commercial hard carbon, yet further optimization of synthesis conditions and extended cycling studies are required to achieve performance comparable to benchmark values reported in the literature.

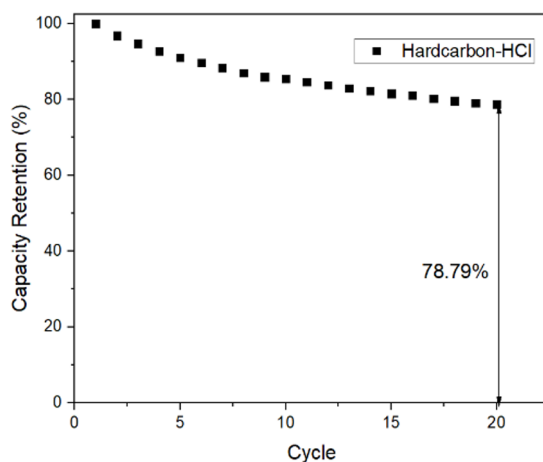


Fig. 5. Cycling ability test results at 0.1C charging current and 1C discharging current of HCl Treated Hardcarbon for 20 cycles

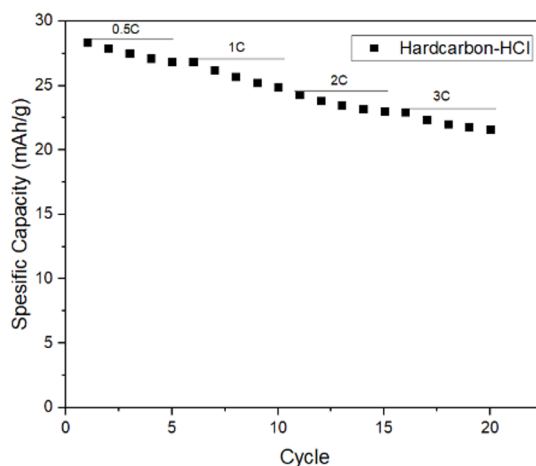


Fig. 6. Rate capability test results of HCl Treated Hardcarbon

The battery results from the Hardcarbon–HCl material rate capability test are shown in Fig. 5. The battery cell was first tested at different discharge currents between 0.5C and 3C to discover the ability of the electrode material to sustain capacity at an appropriate discharge rate. The specific capacity of the battery cell diminishes slightly to lower at increased discharge currents. Initially, when working at a discharge current of 0.5C, the specific cell capacity is about 28 mAh/g, but this figure continuously lowers to about 27 mAh/g at 1C, 24 mAh/g at 2C and 23 mAh/g at 3C.

4 Conclusion

In this study, hard carbon was successfully synthesized from *Nypa fruticans* shell waste using different activating agents. Among the treatments, HCl activation produced morphology and composition closest to commercial hard carbon, while NaOH and KOH activation resulted in higher oxygen content and residual inorganic impurities. Electrochemical testing demonstrated that the HCl-treated sample achieved the highest discharge capacity ($\sim 45 \text{ mAh g}^{-1}$) and retained 78.79% of its capacity after 20 cycles, although these values remain below benchmark capacities typically reported for biomass-derived hard carbon anodes. These findings highlight the potential of nipah palm shell waste as a sustainable precursor for hard carbon, but further optimization of synthesis conditions and extended cycling studies are required to enhance performance and approach commercial standards.

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References

- [1] D. Feng, Y. Li, X. Qin, L. Zheng, B. Guo, and W. Dai, "International Journal of Electrochemical Science Biomass derived porous carbon anode materials for lithium-ion batteries with high electrochemical performance," *Int. J. Electrochem. Sci.*, vol. 19, no. 3, p. 100488, (2024), doi: 10.1016/j.ijoes.2024.100488.
- [2] K. Hong *et al.*, "Biomass derived hard carbon used as a high performance anode material for sodium ion," pp. 12733–12738, (2014), doi: 10.1039/C4TA02068E.
- [3] M. Saavedra, L. Simonin, A. De Geyer, C. M. Ghimbeu, and C. Dupont, "Unraveling the Properties of Biomass-Derived Hard Carbons upon Thermal Treatment for a Practical Application in Na-Ion Batteries," *Energies*, (2020).
- [4] J. Serafin *et al.*, "Functional Activated Biocarbons Based on Biomass Waste for CO₂ Capture and Heavy Metal Sorption," *Am. Chem. Soc.*, (2023), doi: 10.1021/acsomega.3c07120.
- [5] T. E. Connors and S. Banerjee, *Surface Analysis of Paper*, 1st ed. CRC Press, (1995). doi: <https://doi.org/10.1201/9780429279997>.
- [6] C. Nita, B. Zhang, J. Dentzer, and C. Matei, "Hard carbon derived from coconut shells, walnut shells, and corn silk biomass waste exhibiting high capacity for Na-ion batteries," *J. Energy Chem.*, vol. 33, no. 0, pp. 1–36.
- [7] A. Beda, J. Le Meins, P. Taberna, and C. M. Ghimbeu, "Impact of biomass inorganic

- impurities on hard carbon properties and performance in Na-ion batteries,” *Sustain. Mater. Technol.*, p. e00227, (2020), doi: 10.1016/j.susmat.2020.e00227.
- [8] Y. Chen, J. Cui, S. Wang, W. Xu, and R. Guo, “Biomass-Derived Hard Carbon Materials for High-Performance Sodium-Ion Battery,” *Coatings*, 2025.
- [9] J. Coates, “Interpretation of Infrared Spectra , A Practical Approach,” *Encycl. Anal. Chem.*, pp. 10815–10837, (2000).
- [10] C. Zhao *et al.*, “Correlation between oxygen-containing functional groups and lithium storage of hard carbon materials,” *J. Power Sources*, vol. 658, no. January, p. 238299, (2025), doi: 10.1016/j.jpowsour.2025.238299.