HYDROGEN
JURNAL KEPENDIDIKAN KIMIA
https://e-journal.undikma.ac.id/index.php/hydrogen/index

June 2025. 13(3)
e-ISSN: 2656-3061
p-ISSN: 2338-6487
pp. 492-500

Synthesis of Silicon/Silica/Carbon Composite from Rice Husk via Mechanical Milling Method as Anode Lithium-Ion Batteries

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Article History
Received: 25-05-2025
Revised: 28-06-2025
Published: 30-06-2025

Keywords:
aluminothermic reduction; lithium-ion battery; mechanical milling; rice husk; Si/Sio₂/C Composite

Abstract

Silicon (Si) and silicon dioxide (SiO_2), with high theoretical capacities of 4200 mAh g^{-1} and 1965 mAh g^{-1} respectively, have attracted considerable interest as potential anode materials for lithium-ion batteries (LIBs), especially when derived from abundant and renewable sources like rice husk (RH). However, their practical applications are hindered by major challenges, such as significant volume expansion (100%–300%) during charge/discharge cycles and inherently low electrical conductivity (~10^{-1} S m^{-1}). This study aims to develop a low-cost, sustainable, and high-performance Si/SiO_2/C composite anode material from rice husk using a combination of mechanical milling and $AlCl_3$/NaCl-activated aluminothermic reduction. The work specifically explores the effects of single-step versus two-step milling processes on the structural integrity and electrochemical performance of the resulting composites. The two-step milling method, a relatively new and more controlled approach, effectively eliminated unwanted metal oxide by-products, as confirmed by X-ray diffraction (XRD) analysis. In contrast, the single-step process resulted in residual impurities. Electrochemical tests revealed that the two-step Si/SiO_2/C composite delivered a significantly higher specific capacity of 280.01 mAh g^{-1} after 50 cycles, compared to 146.15 mAh g^{-1} from the single-step method. These results highlight the potential of rice husk-derived Si/SiO_2/C composites as eco-friendly and efficient anode materials for next-generation LIBs.

How to Cite: Ramdhan, M., & Muliawati, N. (2025). Synthesis of Silicon/Silica/Carbon Composite from Rice Husk via Mechanical Milling Method as Anode Lithium-Ion Batteries. Hydrogen: Jurnal Kependidikan Kimia, 13(3), 492-500. doi:https://doi.org/10.33394/hjkk.v13i3.16618

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INTRODUCTION

Silicon dioxide (SiO_2) and silicon (Si) are widely used in the electronics industry due to their excellent physical and chemical properties, such as thermal stability, oxidation resistance, and compatibility with various microfabrication processes. One of the most promising applications of these materials is as anodes in lithium-ion batteries (LIBs), owing to their high theoretical specific capacities—1965 mAh g^{-1} for SiO_2 and 4200 mAh g^{-1} for Si (Zheng et al., 2021). Furthermore, their natural abundance (~28% of the Earth's crust) and suitability for low-voltage operation (~0.01 V vs. Li^+/Li) (Majeed et al., 2020) make them attractive candidates for the development of high-capacity energy storage technologies.

However, despite their significant potential, the practical application of Si and SiO_2 as anode materials remains hindered by several fundamental issues. The primary challenges include large volume expansion (100–300%) during lithiation and delithiation, which leads to structural degradation and progressive capacity loss. Additionally, the unstable formation of the solid electrolyte interphase (SEI) layer (L. Wang et al., 2015) and the inherently low electrical conductivity (~10^{-1} S m^{-1}) (Al Ja'farawy et al., 2021) further limit the long-term performance and stability of Si- and SiO_2-based anodes.

To address these challenges, numerous strategies have been proposed. These include nanostructuring approaches—such as the fabrication of nanoparticles, nanowires, nanotubes, and porous silica—which can effectively buffer mechanical stress caused by volume changes. In addition, the formation of composites with conductive matrices, such as carbon-based or metallic materials (Shen et al., 2017), has been shown to enhance both electronic and ionic transport within the anode material. While these approaches are promising, many still rely on synthetic silicon precursors and complex manufacturing processes, which are often costly and environmentally unsustainable at scale.

In the context of sustainability and cost-efficiency, the use of agricultural biomass—particularly rice husk (RH)—emerges as an attractive alternative. RH is a rich source of silica (15–20%) (Hou et al., 2021), making it a potential precursor for producing Si and SiO_2. Previous studies have demonstrated the conversion of RH into active materials such as Si/C and $Si/SiO_2/C$ composites (Majeed et al., 2020; Z. Wang et al., 2021; Zheng et al., 2021). However, most of these studies employed partial synthesis routes or required additional complex reagents, and few have explored a fully RH-based synthesis pathway using aluminothermic reduction activated by molten salts.

Therefore, this study aims to bridge this research gap by developing a biomass-based synthesis method that is efficient, low-cost, and environmentally friendly. The primary objective of this research is to synthesize $Si/SiO_2/C$ composites from rice husk via a two-step mechanical milling process followed by aluminothermic reduction using an $AlCl_3/NaCl$ molten salt mixture. Aluminum (Al) was selected as the reducing agent due to its lower cost and greater abundance compared to magnesium. This study specifically evaluates the impact of single-step and two-step milling procedures on the structural and electrochemical performance of the resulting composites. Through this approach, we aim to produce rice husk-derived anode materials that are not only competitive in performance but also contribute to waste reduction and the advancement of sustainable battery technologies.

METHOD

Research Type

This study employed an experimental research design with a quantitative approach to evaluate the structural and electrochemical performance of $Si/SiO_2/C$ composites derived from rice husk. The research involved a comparative analysis between materials synthesized using a single-step and two-step mechanical milling method.

Variables

Independent Variable: Milling method (single-step vs. two-step). Dependent Variables: Structural characteristics (phase composition, morphology, elemental composition) and electrochemical performance (specific capacity, cycling stability). Controlled Variables: Precursor material (rice husk), reduction agents, temperature, milling speed, electrolyte composition, and testing voltage window.

Materials

Raw rice husk (RH) was obtained from a local rice milling facility in Ciwaringin, West Java, Indonesia. The chemicals used were of analytical grade and supplied by Merck: ethanol (99.5%), sulfuric acid (97%), hydrochloric acid (37%), sodium hydroxide, aluminum powder, anhydrous aluminum chloride, sodium chloride, and deionized water.

Preparation of Silica and Carbon

The RH was washed, oven-dried at 100 °C for 12 h, and ground. For hydrolysis, 70% ethanol (RH:ethanol = 1:8 w/v) was added and heated in an autoclave at 180 °C for 4 h. The precipitate was washed, oven-dried at 80 °C for 12 h, then treated with 5% sulfuric acid for 12 h. After neutralization and washing, the solid was treated with 8% NaOH (1:7 w/v), refluxed for 4 h, and filtered. The filtrate was acidified to pH 5 using 1 M H_2SO_4 to precipitate silica. The solid residue (SP2) was carbonized at 800 °C for 2 h in a furnace.

Synthesis of $Si/SiO_2/C$ Composites

Single-Step Milling: A mixture of SP2, SiO_2, Al, NaCl, and $AlCl_3$ (ratio: 1:1:0.5976:2.6594:6.6484 g) was ball-milled at 350 rpm for 2 h under an argon atmosphere, followed by heat treatment at 250 °C for 8 h. The resulting mixture was sequentially washed with 1 M HCl, ethanol, and deionized water, then dried under vacuum at 70 °C. Samples were labeled SSC1-200 and SSC1-250, based on heat treatment temperature.

Two-Step Milling: A mixture of SiO_2, Al, NaCl, and $AlCl_3$ (1:0.5976:2.6594:6.6484 g) was ball-milled at 350 rpm for 2 h under argon, then heat-treated at 250 °C for 8 h. After washing, the solids were ball-milled again with carbon (1:1 w/w) at 400 rpm for 12 h. The resulting sample was labeled SSC2-250.

Data Collection Techniques

Structural Characterization:

X-ray Diffraction (XRD): Performed using a Rigaku Miniflex 600 diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å) to analyze crystalline phases.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS): Conducted using a Hitachi SU3500 to examine surface morphology and determine elemental distribution.

Electrochemical Testing

- Anode slurries were prepared by mixing $Si/SiO_2/C$, acetylene black, and sodium alginate in a 7:1.5:1.5 weight ratio, dispersed in N-methyl-2-pyrrolidone (NMP), and coated onto copper foil. After vacuum drying at 80 °C for 12 h, the electrodes were punched into 16 mm discs.
- Half-cell Assembly: Coin cells (CR2032) were assembled in an Ar-filled glovebox using Li metal as counter/reference electrodes, Celgard 2400 separators, and 1 M $LiPF_6$ in EC/DMC (1:1 v/v) as electrolyte.
- Galvanostatic Charge-Discharge (GCD): Performed using a Neware battery tester within 0.01–3 V vs. Li/Li^+ at a constant current density to assess capacity and cycling performance.

Data Analysis Techniques

- Qualitative analysis was conducted through comparison of XRD patterns and SEM-EDS images to evaluate phase purity, morphology, and elemental uniformity.
- Quantitative analysis of electrochemical data (specific capacity, coulombic efficiency, and capacity retention) was performed using Microsoft Excel and OriginPro software. The performance of each composite was compared statistically based on average values from at least three repeated measurements per sample.
- The impact of milling method on the final properties was interpreted critically to determine the most effective synthesis route.

The process scheme for the synthesis of Si/SiO2/C composites is presented in Figure 1.

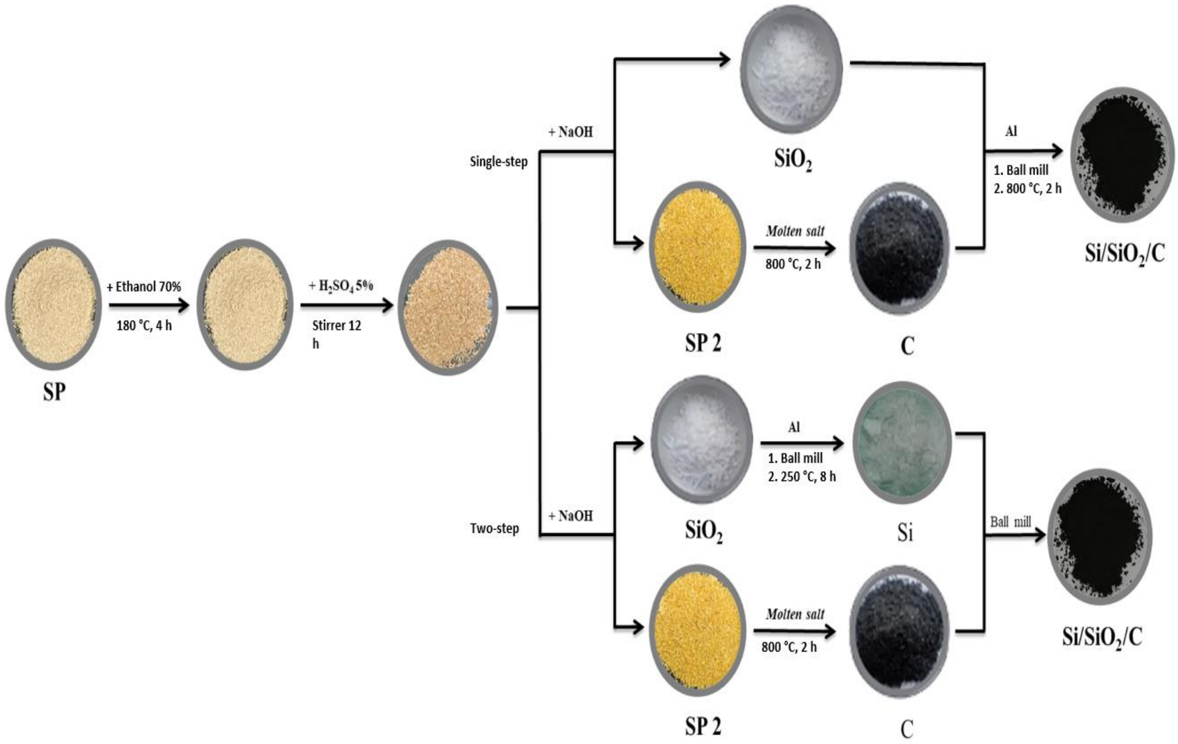


Figure 1. Schematic of Si/SiO_2/C composite synthesis process

RESULTS AND DISCUSSION

Structural and Phase Analysis

The four-step process for Si/SiO_2/C production included: (i) cellulose purification, (ii) SiO_2–C separation, (iii) SiO_2 reduction, and (iv) composite formation. Successful separation was confirmed by XRD (Figure 2a): amorphous SiO_2 showed a broad peak at 2θ ≈ 22°, while carbon displayed peaks at 2θ ≈ 23° and 43°, consistent with previous reports(Z. Wang et al., 2021). In the synthesis process of the Si/SiO_2/C composite, aluminum (Al) metal is used as a reducing agent for SiO_2, while aluminum chloride ($AlCl_3$) functions as a molten salt, and sodium chloride (NaCl) acts as a heat scavenger. This enables the reduction of silica to occur at a lower temperature range (200 °C – 500 °C). The reaction mechanisms involved in the SiO_2 reduction process have been described by Huang et al., (2019) as follows:

$$3SiO_{2(aq)} + 4Al_{(s)} + 3AlCl_{3\,(s)} + NaCl \rightarrow 3Si_{(s)} + 6AlOCl_{(s)} + NaAlCl_{4\,(s)}$$

In the final composites, SSC1-250 and SSC2-250 showed clear Si peaks (2θ ≈ 28.3°, 47.18°, 56°, 68.96°, 76.22°) matching the reference (RRUFF ID: R050145.1) (Tian et al., 2015), alongside broad peaks of amorphous C and SiO_2 (Figure 2b). In contrast, SSC1-200 lacked Si peaks, indicating incomplete reduction. Thus, 250 °C was identified as the optimal reaction temperature for $AlCl_3$/NaCl-activated reduction.

X-ray diffraction (XRD) analysis confirmed the successful reduction of SiO_2 into elemental silicon (Si) through an aluminothermic process activated by a molten salt mixture of $AlCl_3$/NaCl. This was evidenced by the appearance of characteristic crystalline Si peaks at 2θ ≈ 28.3°, 47.18°, 56°, 68.96°, and 76.22° in both SSC1-250 and SSC2-250 samples. These peak positions are consistent with the crystallographic reference (RRUFF ID: R050145.1), indicating that the reduction reaction effectively produced crystalline Si (Tian et al., 2015). In contrast, no such peaks were observed in the SSC1-200 sample, suggesting that the reduction process did not proceed efficiently at 200 °C.

These findings highlight that 250 °C serves as a critical minimum temperature required to initiate the reduction of SiO_2 by Al effectively within the molten salt system. This observation aligns with the report by Huang et al. (2019), which demonstrated that molten salt activation can lower the activation energy and reaction temperature compared to conventional aluminothermic methods. As a result, silicon formation can occur at lower temperatures, offering energy efficiency and suitability for sustainable processing.

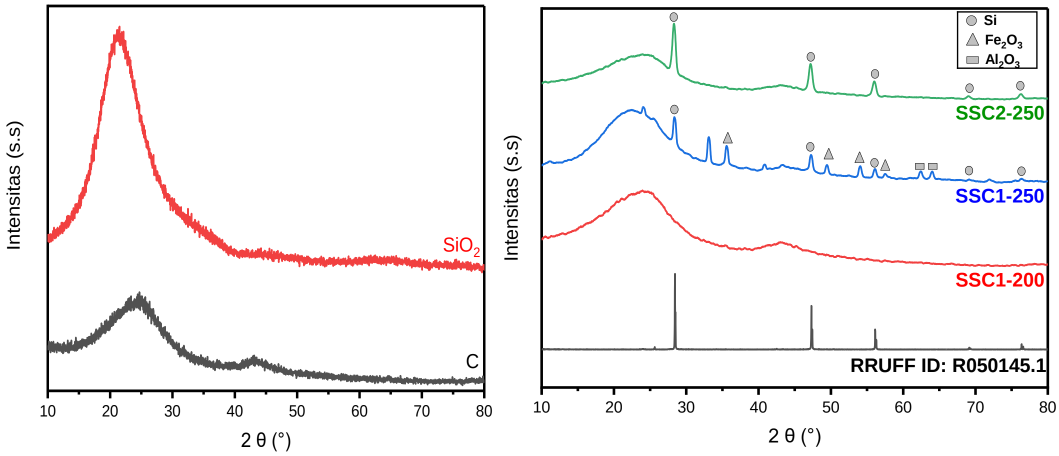
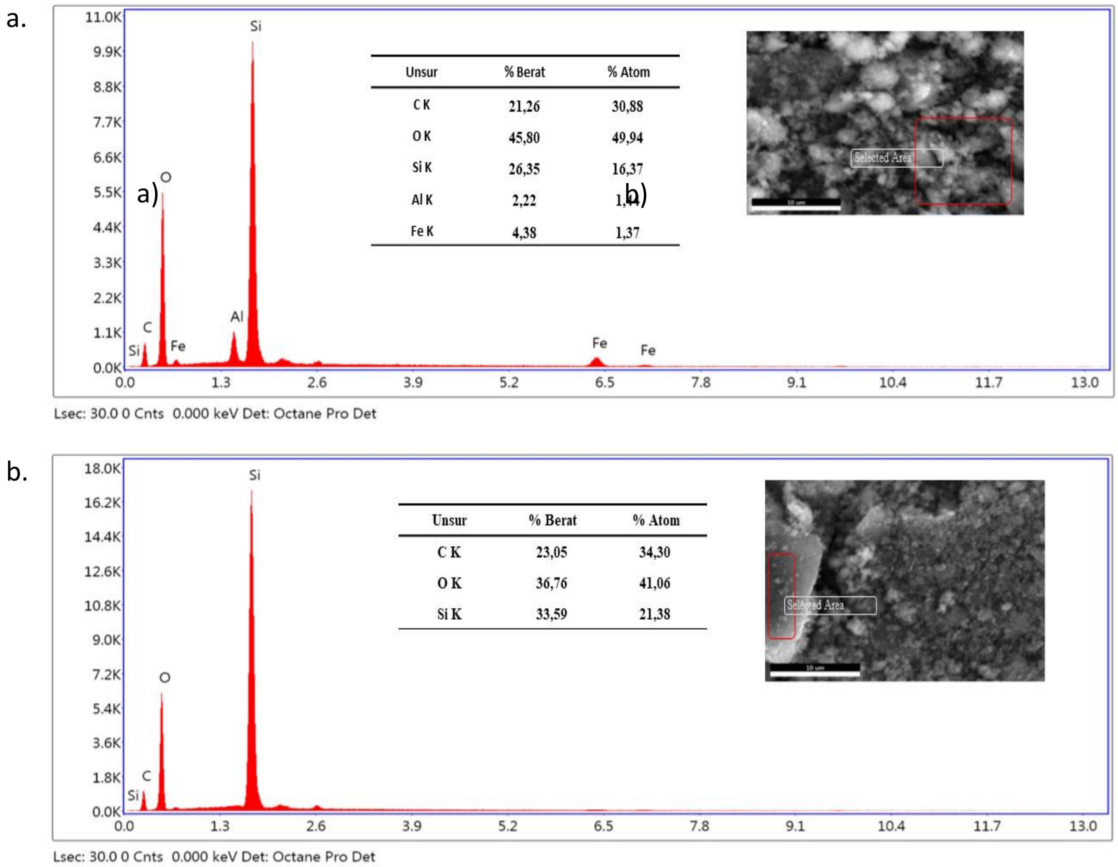


Figure 2. Diffractogram of a) SiO_2 and C, b) $Si/SiO_2/C$ Composite



Unsur	% Berat	% Atom
C K	21,26	30,88
O K	45,80	49,94
Si K	26,35	16,37
Al K	2,22	1,44
Fe K	4,38	1,37

Unsur	% Berat	% Atom
C K	23,05	34,30
O K	36,76	41,06
Si K	33,59	21,38

Figure 3. EDS mapping results of the samples after the washing process for the composites: a. SSC1-250 and b. SSC2-250.

However, further characterization via energy-dispersive X-ray spectroscopy (EDS) on SSC1-250 revealed the presence of Al_2O_3 and Fe_2O_3, with respective concentrations of 2.22 wt% and 4.38 wt%. These contaminants likely resulted from cross-oxidation caused by oxygen infiltration during the heating stage. The presence of such metal oxides may compromise structural integrity and hinder the electrochemical performance of the composite. In contrast, SSC2-250, synthesized via the two-step process, exhibited higher purity without detectable metal oxide contamination, indicating that the two-step method effectively limits oxidation and enhances the chemical stability of the composite.

Nevertheless, it is important to note that this study did not provide a quantitative analysis of the ratio between crystalline Si and amorphous SiO_2 and C. Such data would be crucial for correlating structural composition with electrochemical performance. Additionally, transmission electron microscopy (TEM) is recommended to further investigate the nanoscale morphology and carbon dispersion within the matrix, as demonstrated in the study by Shen et al. (2017). Contaminants like Al_2O_3 and Fe_2O_3 were observed in SSC1-250, likely from oxygen infiltration during heating. EDS mapping (Figure 3a,b) confirmed the presence of 2.22 wt% Al and 4.38 wt% Fe in SSC1-250, while SSC2-250 showed no such impurities, corroborating the XRD findings.

Electrochemical Performance

Figure 4a presents rate capability results of SSC1-250 and SSC2-250 samples over 30 cycles under various current densities (50–1000 mA/g). Initial charge capacities of SSC1-250 ranged from 658.63 to 13.01 mAh g^{-1}, and SSC2-250 from 663.09 to 69.04 mAh g^{-1}. Both samples exhibited high initial charging capacities, which may be attributed to electrolyte consumption during the initial cycles. This is supported by the low initial coulombic efficiency (ICE) values observed in both samples—42.35% for SSC1-250 and 46.83% for SSC2-250. The low ICE is likely due to the predominance of SiO_2 over Si in the synthesized composites. According to Kim et al., (2021), during the discharge process, lithium (Li) reacts with SiO_2 as shown in the following reaction.

$$SiO_2 + 2Li + \frac{3{,}75}{2}\,Li \rightarrow \frac{1}{2}Li_4SiO_4 + \frac{1}{2}Li_{3{,}75}Si$$

The SiO_2 present in the SSC composites reacts with lithium (Li) to form Li_4SiO_4, which is electrochemically inactive and thus cannot revert to its original state. This reaction contributes to the formation of the solid electrolyte interphase (SEI) layer on the anode surface, resulting in a low initial coulombic efficiency (ICE) and a high irreversible capacity. However, the formation of Li_4SiO_4 offers an advantage, as it can act as a buffer layer that mitigates the volume expansion of the active Si and SiO_2 materials, thereby enhancing the long-term cycling stability of the anode.

The galvanostatic charge-discharge (GCD) analysis at various current densities showed that the SSC2-250 sample exhibited superior capacity compared to SSC1-250. The lower capacity observed in SSC1-250 may be attributed to the presence of metal oxides on the anode surface, which behave as part of the SEI and hinder Li^+ ion transfer within the battery cell. The curves also indicate that, upon returning the current density to 200 mA/g, the specific charging capacities of SSC1-250 and SSC2-250 were 90.46 and 128.93 mAh/g, respectively. These results demonstrate high capacity retention for both composites—94.66% for SSC1-250 and 98.21% for SSC2-250.

Electrochemical performance evaluation revealed that the SSC2-250 composite exhibited superior behavior compared to SSC1-250. After 30 cycles at a constant current of 100 mA/g, SSC2-250 recorded a specific capacity of 280.01 mAh g^{-1}, while SSC1-250 only reached

146.15 mAh g^{-1}. This significant difference reflects the effectiveness of the two-step process in producing a cleaner and more electrochemically active structure. The enhanced performance of SSC2-250 can be attributed to the absence of metal oxides such as Al_2O_3 and Fe_2O_3, which were detected in SSC1-250 and are believed to hinder lithium-ion (Li^+) transport within the electrode matrix (Al Ja'farawy et al., 2021).

Both samples exhibited relatively low initial coulombic efficiency (ICE), with 42.35% for SSC1-250 and 46.83% for SSC2-250. Such low ICE values indicate a substantial capacity loss during the first cycle, primarily due to irreversible reactions between SiO_2 and lithium that result in the formation of electrochemically inactive Li_4SiO_4 (Kim et al., 2021). This reaction consumes a significant amount of Li^+ and leads to the development of a thick solid electrolyte interphase (SEI) layer, thereby reducing the initial efficiency.

Interestingly, although Li_4SiO_4 is inactive from an electrochemical standpoint, it serves as a mechanical buffer that helps stabilize the anode structure against extreme volume expansion during lithiation and delithiation processes (Majeed et al., 2020). This explains the high capacity retention observed after 30 cycles at a restored current density of 200 mA/g—98.21% for SSC2-250 and 94.66% for SSC1-250.

Despite these promising results, the final capacities remain below 300 mAh g^{-1}, suggesting that the material's full potential has yet to be realized. Several strategies can be adopted to further enhance performance, optimization of the $Si:SiO_2:C$ ratio, to increase the proportion of active silicon without compromising structural stability. Surface coating with conductive materials such as graphene or conductive polymers (e.g., polypyrrole) to improve both electrical conductivity and SEI stability (Hamedani, 2021). Utilization of flexible binders, such as a blend of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR), which can better accommodate structural deformation due to volume changes during cycling (Zheng et al., 2021). Through these optimization strategies, the electrochemical performance of rice husk-derived $Si/SiO_2/C$ composites can be further improved, making them more competitive and viable for practical applications in next-generation lithium-ion batteries.

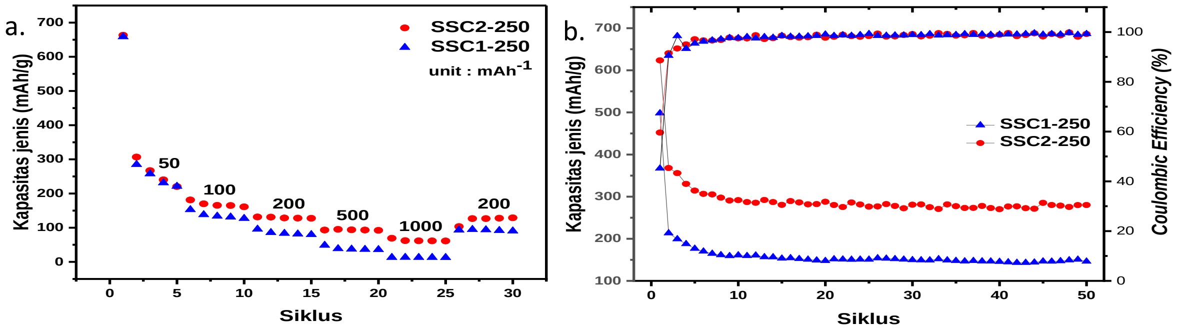


Figure 4. GCD Curve of SSC Composite a. various current densities, b. after 50 cycles

Subsequently, the cycling performance and coulombic efficiency (CE) of both samples were evaluated using GCD analysis over 50 cycles at a current density of 100 mA/g, as shown in Figure 4b. From the curve, it can be observed that after 5 cycles, the capacities of SSC1-250 and SSC2-250 were 176.65 and 314.32 mAh/g, respectively. After 50 cycles, SSC2-250 maintained a capacity of 280.01 mAh/g, significantly higher than SSC1-250, which retained only 146.15 mAh/g. These results indicate that the SSC composites derived from rice husk have strong potential as low-cost and environmentally friendly anode materials for lithium-ion batteries. However, further optimization of the SSC samples is necessary to improve their electrochemical performance for practical application.

CONCLUSION

$Si/SiO_2/C$ composites were successfully synthesized from rice husk using mechanical milling and $AlCl_3/NaCl$-activated aluminothermic reduction. XRD analysis confirmed that 250 °C is the optimal reduction temperature, yielding high-purity Si and minimizing metal oxide formation. The two-step milling process produced a cleaner composite (SSC2-250) with superior electrochemical performance, achieving a reversible capacity of 280.01 mAh g^{-1} after 50 cycles. These results demonstrate the feasibility of utilizing rice husk as a sustainable source for high-performance LIB anodes. Further optimization is recommended to improve initial coulombic efficiency and long-term cycling stability

RECOMMENDATIONS

Further optimization is recommended to improve initial coulombic efficiency and long-term cycling stability such as finding the optimal material composition.

BIBLIOGRAPHY

Al Ja'farawy, M. S., Hikmah, D. N., Riyadi, U., Purwanto, A., & Widiyandari, H. (2021). A Review: The Development of SiO2/C Anode Materials for Lithium-Ion Batteries. *Journal of Electronic Materials, 50*(12), 6667–6687. https://doi.org/10.1007/s11664-021-09187-x

Hamedani, A. A. (2021). *Development of Silicon/Carbon Nanocomposite Anodes From Simple Precursors for Lithium-Ion Batteries*. Sabanci University.

Hou, J., Mao, X., Wang, J., Liang, C., & Liang, J. (2021). Preparation of rice husk-derived porous hard carbon: A self-template method for biomass anode material used for high-performance lithium-ion battery. *Chemical Physics, 551*(June), 111352. https://doi.org/10.1016/j.chemphys.2021.111352

Huang, X., Cen, D., Wei, R., Fan, H., & Bao, Z. (2019). Synthesis of Porous Si/C Composite Nanosheets from Vermiculite with a Hierarchical Structure as a High-Performance Anode for Lithium-Ion Battery. *ACS Applied Materials and Interfaces, 11*(30), 26854–26862. https://doi.org/10.1021/acsami.9b06976

Kim, M., Yang, Z., & Bloom, I. (n.d.). The lithiation/delithiation behavior of Si-based electrodes: A connection between electrochemistry and mechanics. *Journal of The Electrochemical Society*.

Majeed, M. K., Saleem, A., Wang, C., Song, C., & Yang, J. (2020). Simplified Synthesis of Biomass-Derived Si/C Composites as Stable Anode Materials for Lithium-Ion Batteries. *Chemistry - A European Journal*, *26*(46), 10544–10549. https://doi.org/10.1002/chem.202000953

Shen, T., Xie, D., Tang, W., Wang, D., Zhang, X., Xia, X., Wang, X., & Tu, J. (2017). Biomass-derived carbon/silicon three-dimensional hierarchical nanostructure as anode material for lithium ion batteries. *Materials Research Bulletin, 96*, 340–346. https://doi.org/10.1016/j.materresbull.2017.04.014

Tian, H., Tan, X., Xin, F., Wang, C., & Han, W. (2015). Micro-sized nano-porous Si/C anodes for lithium ion batteries. *Nano Energy*, *11*, 490–499. https://doi.org/10.1016/j.nanoen.2014.11.031

Wang, L., Gao, B., Peng, C., Peng, X., Fu, J., Chu, P. K., & Huo, K. (2015). Bamboo Leaves

Derived Ultrafine Si Nanoparticles and Si/C Nanocomposites. *Nanoscale*. https://doi.org/10.1039/x0xx00000x

Wang, Z., Zheng, B., Liu, H., Zhang, C., Wu, F., Luo, H., & Yu, P. (2021). One-step synthesis of nanoporous silicon @ graphitized carbon composite and its superior lithium storage properties. *Journal of Alloys and Compounds*, *861*(xxxx), 157955. https://doi.org/10.1016/j.jallcom.2020.157955

Zheng, C. H., Zhang, G. P., Wang, S. S., Mao, A. Q., & Fang, D. L. (2021). Efficient transformation of rice husk to a high-performance Si@SiO2@C anode material by a mechanical milling and molten salt coactivated magnesiothermic reduction. *Journal of Alloys and Compounds*, *875*, 159974. https://doi.org/10.1016/j.jallcom.2021.159974