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D1.2	**Structural and electrochemical properties of silicon/graphite anode with increasing silicon content binders**	WP1	IICh SAS	Report	N	Experimental results	M12

D1.2 Structural and electrochemical properties of silicon/graphite anode with increasing silicon content (IICh SAS), M12

Introduction

Despite the ultra-high capacity of silicon (around 3000 mAh/g) the industrial application of Si/graphite anodes is limited to 15 wt% of Si due to substantial volume expansion (300 %) of Si during lithiation. Therefore, increasing the silicon content in graphite matrix necessitates deliberate modifications in silicon morphology as higher Si loading amplify the challenges associated with volume expansion, particle cracking, and SEI instability. To address these issues, we systematically varied the milling conditions and mixing procedures for silicon to tune particle size, surface area, and structural homogeneity.

Objectives

- Modification of silicon particles to mitigate key challenges such as particle cracking, excessive volume expansion and SEI instability.
- Optimization of mixing protocol and systematic increase in silicon content (≤ 50%) to enhance the electrochemical performance while maintaining balanced structural and interfacial stability.
- Comprehensive structural evaluation of the silicon particle and Si/Gr composite anodes to assess the influence of varied milling parameters on particle morphology, dispersion and composite integrity.
- Electrochemical characterisation of Si/Gr||Na half cells to quantify the impact of reduced silicon particle size and increased Si loading on capacity, rate capability and long-term cycling stability.

1) The influence of milling conditions on silicon particles:

- **Planetary ball milling:** Planetary ball milling was carried out on 4D-grade silicon powder (SicoMill, Vesta Ceramics, Sweden) at rotational speeds between 250 and 450 rpm for a fixed duration of 12 h. Among the tested conditions, milling at 400 rpm for 12 h yielded the most favorable balance between particle refinement and powder handling. Under these conditions, the average particle size was reduced from approximately 7 μm to 3 μm.

Although this represents a measurable reduction, the extent of the size decrease remains insufficient for fast-charging battery applications that require rapid lithium transport. The characteristic lithium penetration time into a silicon particle scales with the square of the diffusion distance, meaning that even a 3 μm particle can retain a lithium-poor core for an extended period during fast-charging operation. Furthermore, a 3 μm particle will still expand by 300% during lithiation. This substantial expansion poses a significant challenge, as conventional binders often struggle to effectively bridge the gaps generated by the movement of particles of this magnitude. Consequently, further particle size reduction or alternative processing strategies were necessary to ensure homogeneous lithiation under high-rate conditions as well as to mitigate mechanical degradation arising from repeated expansion-contraction cycles.

- **High energy milling:** To reduce the particle size beyond 3μm plateau, the high-energy planetary ball milling of silicon was optimized across a range of rotational speeds from 500 to 1500 rpm. This shift to high-impact fragmentation dramatically reduced the primary particle size from 7 μm to 0.7 μm within just one hour at 1000 rpm. Figure 1 visualizes the reduction in particle size *via* SEM images of the as-received and high-energy milled Silicon powder. The resulting sub-micron refinement significantly increased the specific surface area from 2 m^2/g to 30 m^2/g, enhancing the electrochemical performance of the anode. This balance allows for a higher number of active sites for lithium-ion flux while minimising the risks associated with both pulverisation and handling issues, achieving an optimal combination of gravimetric capacity and industrial practicality. The strategic benefit of maintaining these modified micro-sized particles lies in their ability to integrate seamlessly into a silicon-graphite (Si/Gr) composite architecture. At 0.7 μm, the silicon particles are small enough to lodge within the natural crevices and interlayer voids of the much larger graphite flakes. This proximity ensures a robust electronic percolation network where the graphite acts as both a conductive "highway" and a mechanical buffer. Unlike 3 μm particles that act as isolated, high-stress islands, these sub-micron particles distribute the 300% volumetric strain across a much larger contact area with the sulphonated alginate (S-Alg) binder. This prevents the binder chains from reaching their breaking point, thereby

preserving the structural integrity of the electrode throughout the repeated "breathing" cycles of charge and discharge.

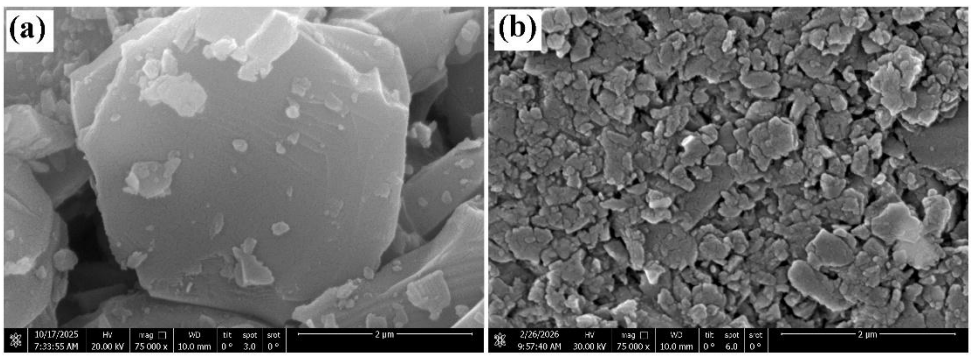


Figure 1. *SEM images of (a) as-received silicon and (b) high-energy-milled silicon showing the transition from large angular particles to a finer, fragmented morphology (bar 2 mm).*

2. Effects of surface area and particle morphology.

- Particle size analysis was performed using a laser diffraction particle size analyzer to evaluate the morphological changes in the as-received and high-energy milled Silicon powder. The particle size decreased substantially from approximately 7 µm in the as-received material to about 0.7 µm in the processed samples.
- To evaluate the impact of high energy milling on the silicon particles, nitrogen adsorption-desorption measurements were performed. The BET specific surface area (BET) of the as-received silicon was found to be 2 m^2/g. Following high-energy milling, the surface area increased significantly to 30 m^2/g.

3. Electrochemical performance comparison

- **Electrode preparation and cell assembly:**

  Si (planetary milled or SiHEM) and graphite powders (with a ratio of 20:80 wt% and 50:50 wt%) were ball-milled in ethanol using a planetary mill (Retsch PM100) with tungsten carbide media to achieve an average particle size of ~3 µm. A slurry comprising 75 wt% active material, 10 wt% carbon black, and 15 wt% s-alginate binder in deionised water was prepared. This slurry was cast onto Cu foil (with a speed of 10 mm s^{-1}), air-dried, and vacuum-dried at 70 °C for 24 h. Finally, 18-mm-diameter disks were punched with an active material loading of 1.0–1.3 mg cm^{-2}. Electrochemical testing was performed using two-electrode PAT-cell test cells (EL-CELL GmbH). Cells were assembled in an argon-filled glovebox with moisture and oxygen levels maintained below 1 ppm. Half-cells

were constructed using the Si/Gr composite electrodes as the working electrodes and lithium metal as the counter/reference electrode.

Prior to cell assembly, the Si/Gr electrodes, glass-fiber separators, and poly (ether ether ketone) components from the PAT-cell kit were dried at 120 °C for 24 h. The separators were then wetted with 100 µL of electrolyte consisting of 1.0 M $LiPF_6$ dissolved in a 50/50 (v/v) mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). Electrochemical measurements were conducted using an 8X-PAT channel system controlled by EL-CELL software, or by Biologic BCS 905 2*8 channels, within a voltage window of 0.01–1.5 V vs. Li/Li^+

- **Effects of initial milling conditions on electrochemical performance**

Figure 2 compares the rate performance of the high-energy milled Si (SiHEM)/Gr composite anode with a planetary-milled Si (SiPBM)/Gr composite with the ratio of 50:50 at different C-rates. The SiHEM/Gr anode delivers more than double the specific discharge capacity at low rates and maintains superior capacity retention as the current increases, indicating significantly improved charge kinetics. The strong recovery upon reducing the rate back to 0.2C highlights the robustness of the modified silicon structure and its improved compatibility with graphite**.** These results demonstrate that the high-energy milling of silicon significantly enhances both the intrinsic capacity and the rate performance of Si-based composite anodes.

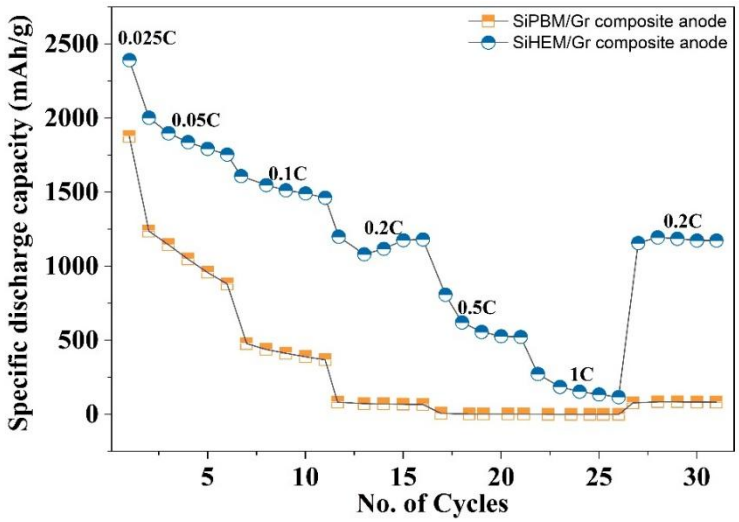


Figure 2. Rate-capability performance of (high energy milled) SiHEM/Gr and (planetary milled) SiPBM/Gr composite anodes measured across sequential C-rates.

- **Effects of increased Si content**

  Electrochemical measurements on SiHEM/Gr composite anodes with increased Si content were performed at different C-rates to evaluate variations in specific discharge capacity, rate performance, coulombic efficiency, and capacity recovery (Figure 3). As expected, increasing Si content from 20 % to 50 % in composite anodes has led to a drastic increase in initial discharge capacity from ~950 mAh/g to ~2400 mAh/g, owing to the ultrahigh theoretical capacity of Si.

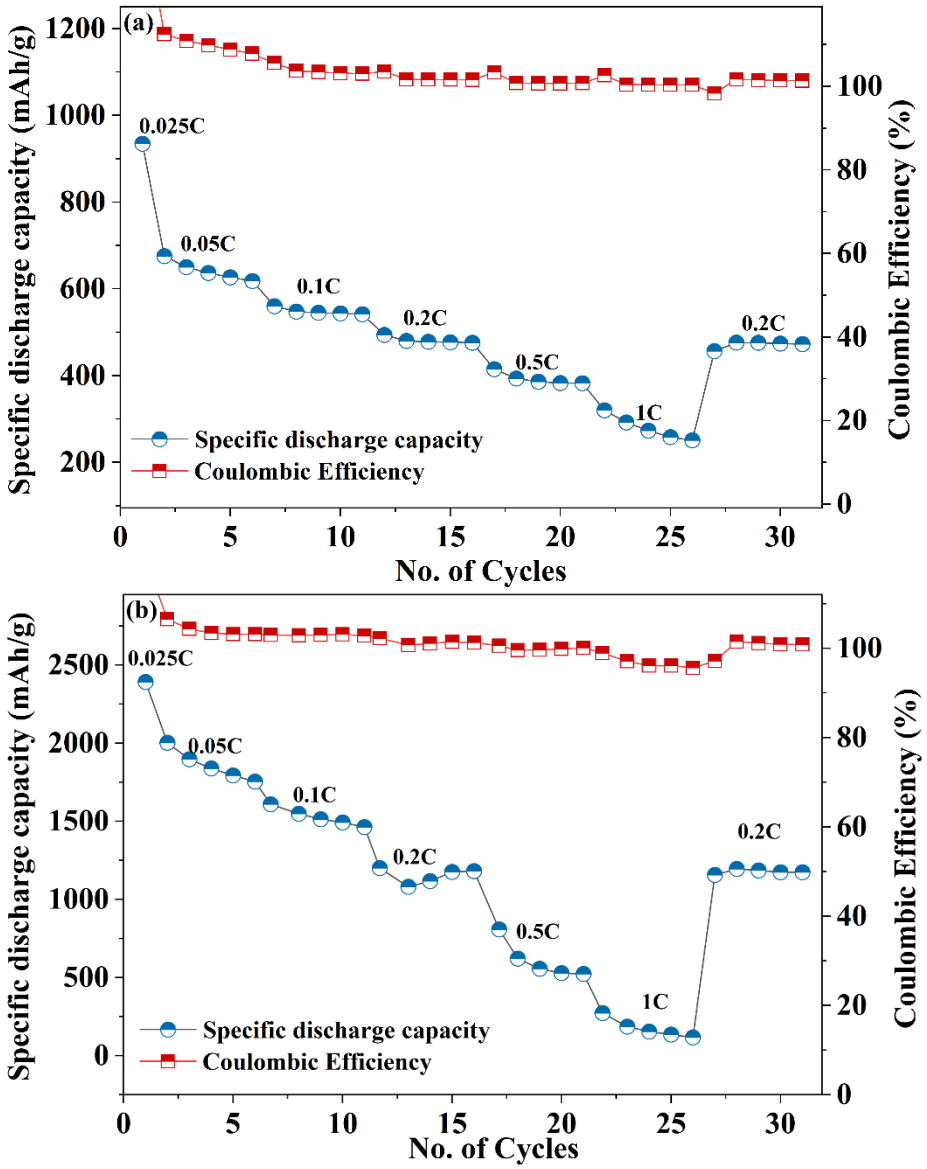


Figure 3. Cycling performance and Coulombic efficiency of the Si/Gr composite anode containing 20% Si (a) and 50% Si (b) measured at various C-rates.

However, the rate capability analysis indicates that a 20% Si anode has robust structural stability compared to a high-Si-content anode. At 1C, the 20% Si electrode retained ~300 mAh g^{-1}, slightly outperforming the 50% Si electrode (~250 mAh g^{-1}), indicating that the higher graphite content provides a more stable, conductive framework, mitigating the effects of Si volume expansion during fast charging/discharging.

Both electrodes demonstrated excellent capacity recovery when the current rate was returned to 0.2C after high-rate testing and maintained a high Coulombic Efficiency (CE) of nearly 100% after initial formation cycles, suggesting stable solid electrolyte interface (SEI) layer formation. This indicates that, despite the large volume expansion of Si at high C-rates, no irreversible structural degradation occurred.

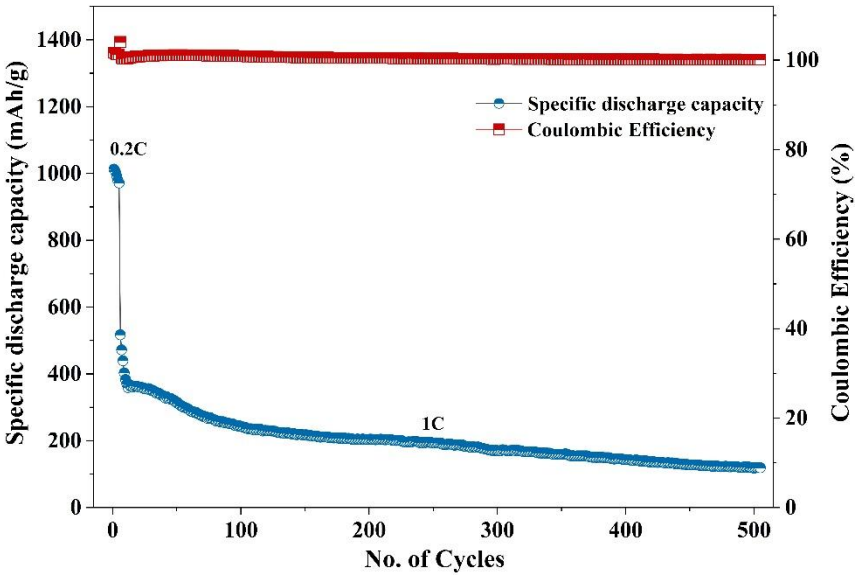


Figure 4. Long-term cycling stability and Coulombic efficiency of the SiHEM/Gr 50:50 composite anode at 1C discharge rates for 500 cycles.

Fig. 4 illustrates the long-term cycling stability of the SiHEM/Gr anode at a 1C rate over 500 cycles. The composite demonstrates robust structural integrity, exhibiting a controlled, gradual capacity decay rather than catastrophic failure over extended cycling. The coulombic efficiency remains ~100% even during long-term cycling, indicating the formation of a stable SEI and suggesting that high-energy milling effectively mitigates particle cracking and pulverization. In commercial Si/Gr systems, the silicon content is typically limited to <10–15 wt% due to severe volume expansion. Achieving 500 cycles with a 50:50 Si/Gr blend without abrupt capacity collapse therefore represents a significant advancement. Although the ~70% capacity retention is not ideal for EV-grade requirements, it provides a strong baseline for a high-loading, lab-scale

composite anode and highlights the potential of high-energy-milled silicon for further optimization.

Summary

This deliverable presents a detailed investigation report on the effects of increasing silicon content on the structural and electrochemical behavior of silicon/graphite composite anodes. It emphasizes the critical need for modification of silicon particles to mitigate cracking, pulverization, and interfacial instability. Planetary ball milling at 400 rpm for 12 hours reduced particle size from 7 μm to 3 μm, but the resulting morphology remained insufficient for fast-charging applications due to the relatively low specific surface area providing fewer active sites for lithium interactions and significant volumetric expansion of Si during lithiation. Whereas high-energy milling at 1000 rpm reduced the particle size to 0.7 μm within one hour, increasing the specific surface area from 2 $m^2 g^{-1}$ to 30 $m^2 g^{-1}$. These finer particles provide more active sites for lithium-ion transport, enhance electronic connectivity within the Si/Gr composite, and distribute volumetric strain more effectively, thereby minimizing mechanical degradation. As a result, the optimized silicon morphology delivers improved capacity, rate capability, and long-term cycling stability. This highlights the essential role of particle-size engineering in developing high-performance silicon/graphite anodes with high Si loading for future battery applications.