

## Supplementary Information

### Sulfur: An intermediary template for advanced silicon anode architectures

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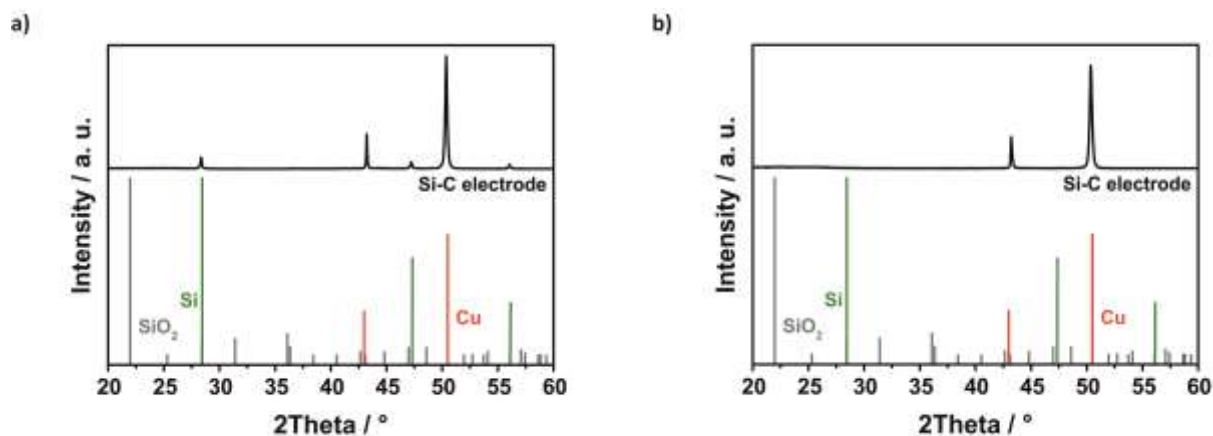


Fig. S1 XRD pattern of the Si-C electrode which is templated via a sulfur shell (a) and of the Si-C electrode where no sulfur template is used and the SiNPs are dissolved during the alkaline polymerisation of sucrose (b). For a directly carbon coating of SiNPs, sucrose is polymerized in an acidic medium.

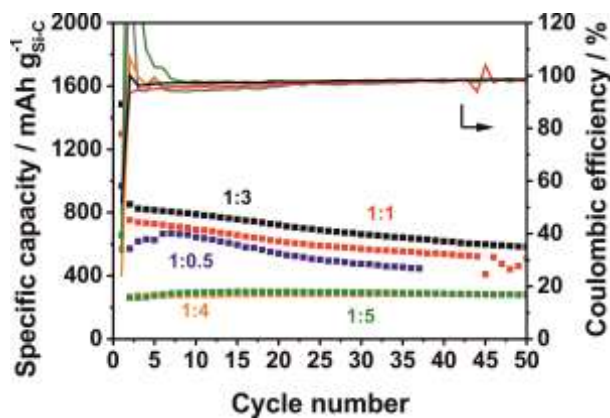


Fig. S2 Results of the half cell testing of Si@Void@C electrodes with different silicon:sulfur ratios vs.  $\text{Li}/\text{Li}^+$ . The molar ratio Si:S of 1:3 shows the highest specific capacity and stability. Introducing large voids by a thicker sulfur shell (Si:S 1:4 and Si:S 1:5) led to a poor electronic contact of the silicon cores.

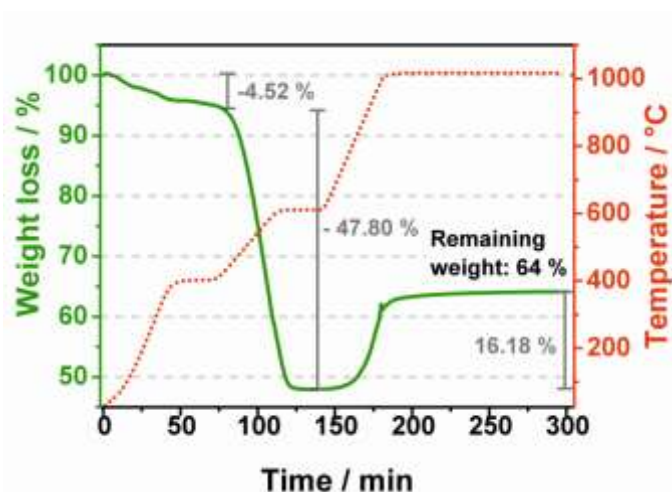


Fig. S3 TGA profile of the determination of the silicon content under atmosphere. The Si@Void@C composite contains about 30 % silicon.

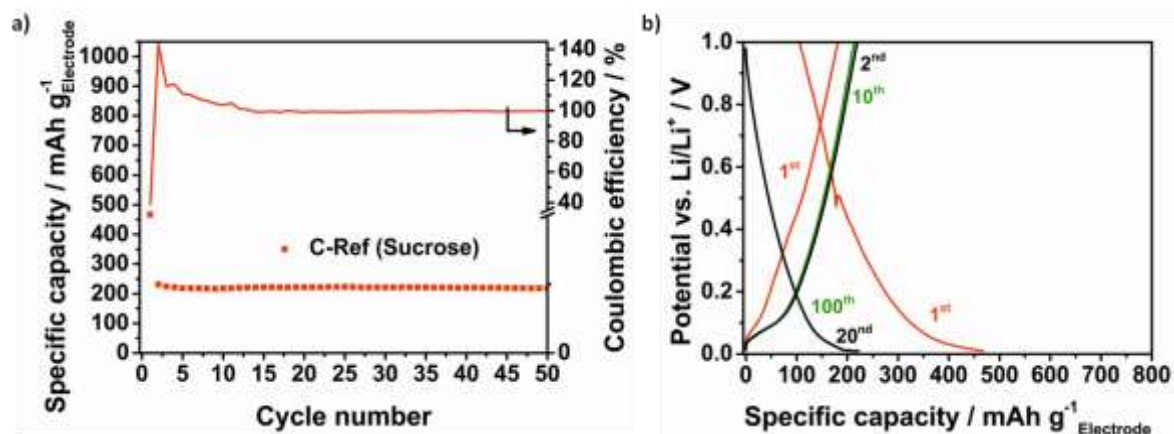


Fig. S4 Results of the half cell testing of the sucrose based C-Ref electrode vs. Li/Li<sup>+</sup>: Specific capacity based on the C-Ref electrode, the corresponding CE (a) and selected voltage profiles (b). The C-Ref electrode has a stable capacity of about 220 mAh g<sup>-1</sup>.

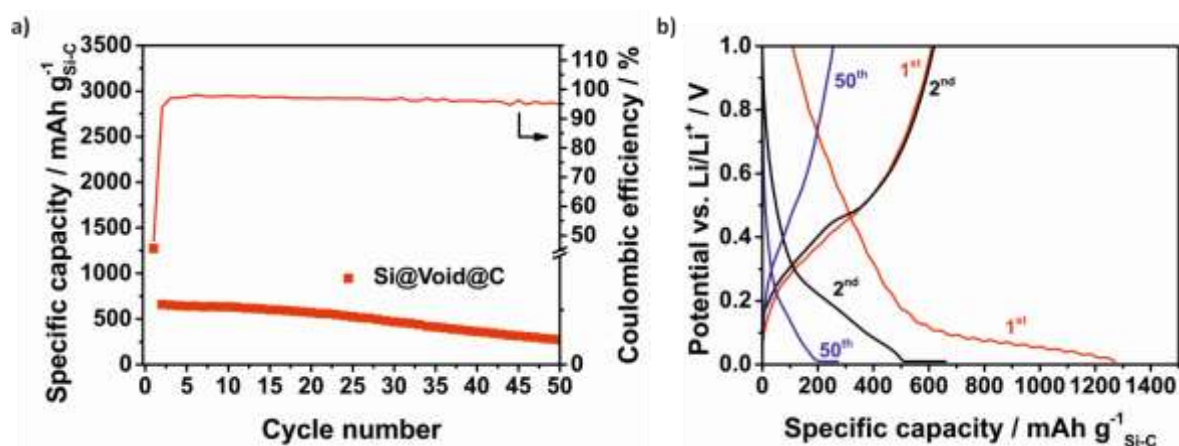


Fig. S5 Results of the half cell testing of the Si@Void@C electrode vs. Li/Li<sup>+</sup> in LP30 (1 M LiPF<sub>6</sub> in 1:1 (m/m) ethylene carbonate/dimethyl carbonate): Specific capacity based on the silicon carbon composite, the corresponding CE (a) and selected voltage profiles (b). The electrolyte consumption in LP30 is reduced compared to the DME/DOL electrolyte which could be seen from to stable CE around 97 % for 50 cycles.

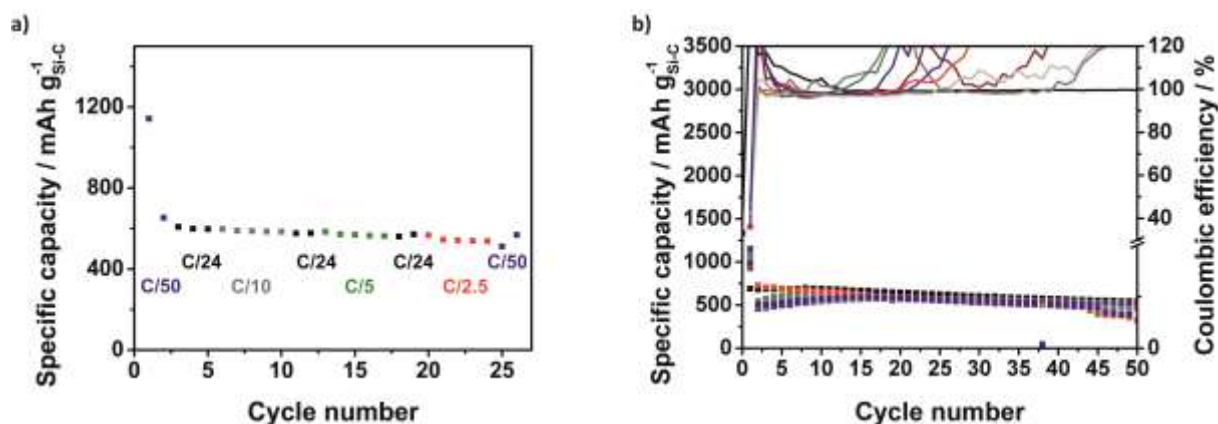


Fig. S6 Electrochemical performance of the Si@Void@C electrode vs. Li/Li<sup>+</sup> at various rates from C/50 to C/2.5 (a) and in different batches during the up-scale of the synthesis (b).

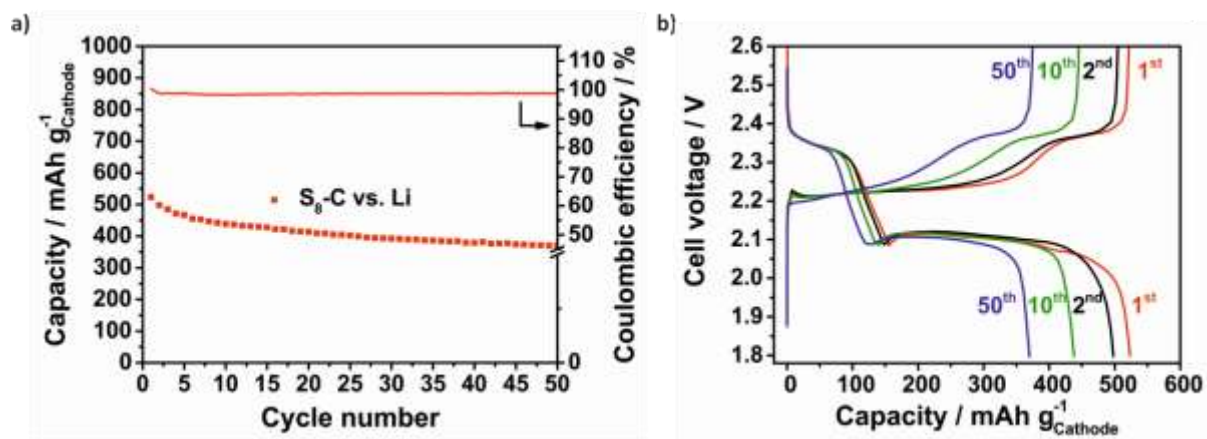


Fig. S7. Results of the Li-S cell (Coin cell): Specific capacity, corresponding CE (a) and voltage profiles for selected cycles (b).