Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPLEMENTARY INFORMATION

Mechanistic understanding of pore evolution enables high performance mesoporous silicon production for lithium-ion batteries

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<u>Parameter study</u>

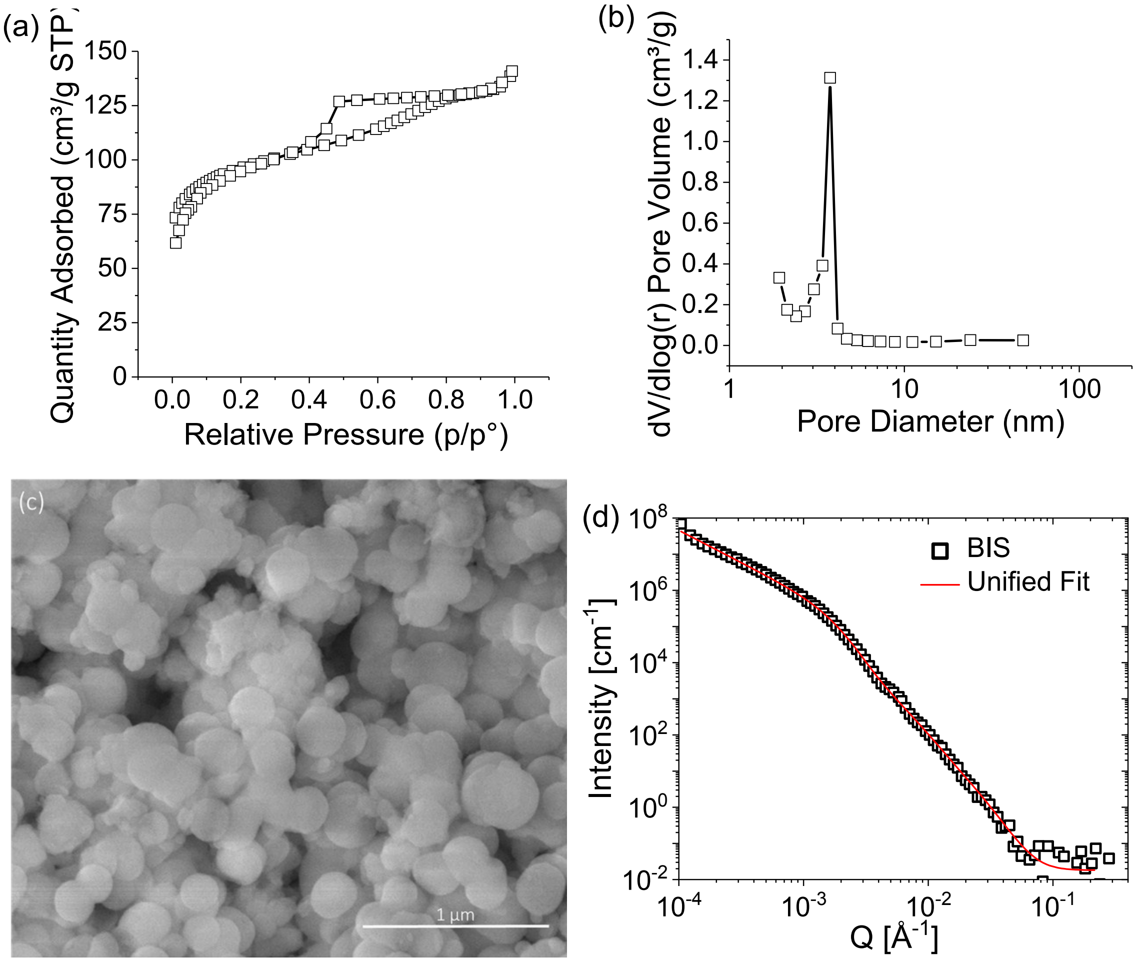
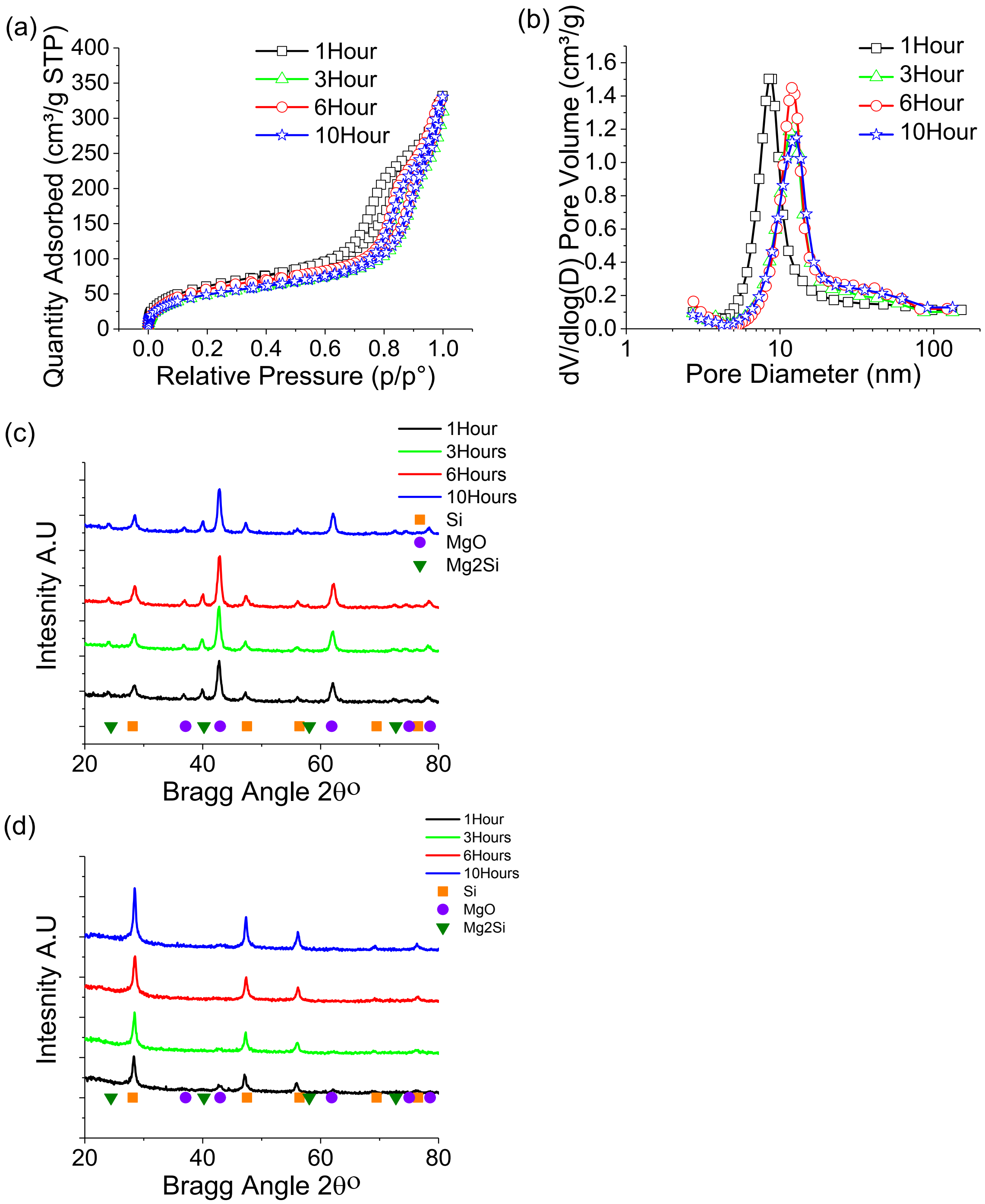


Figure S 1, characterisation of BIS, *(a)* N_2 *absorption Isotherm, (b) BJH pore size distribution, (c) SEM image, (d)USAXS data obtained for BIS along with unified fit.*

Table S 1. Materials properties of BIS

	BET SSA (m^2/g)	BJH PV (cm^3/g)	USAXS Particle Size	
			Level1 (nm)	level 2 (nm)
Bioinspired PEHA	301	0.16	26	370


(a)
Quantity Adsorbed (cm³/g STP)
Relative Pressure (p/p°)
1Hour
3Hour
6Hour
10Hour
(b)
dV/dlog(D) Pore Volume (cm³/g)
Pore Diameter (nm)
1Hour
3Hour
6Hour
10Hour
(c)
Intesnity A.U
Bragg Angle 2θo
1Hour
3Hours
6Hours
10Hours
Si
MgO
Mg2Si
(d)
Intesnity A.U
Bragg Angle 2θo
1Hour
3Hours
6Hours
10Hours
Si
MgO
Mg2Si

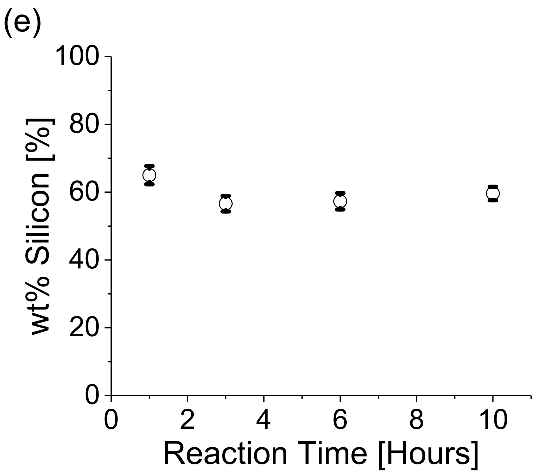
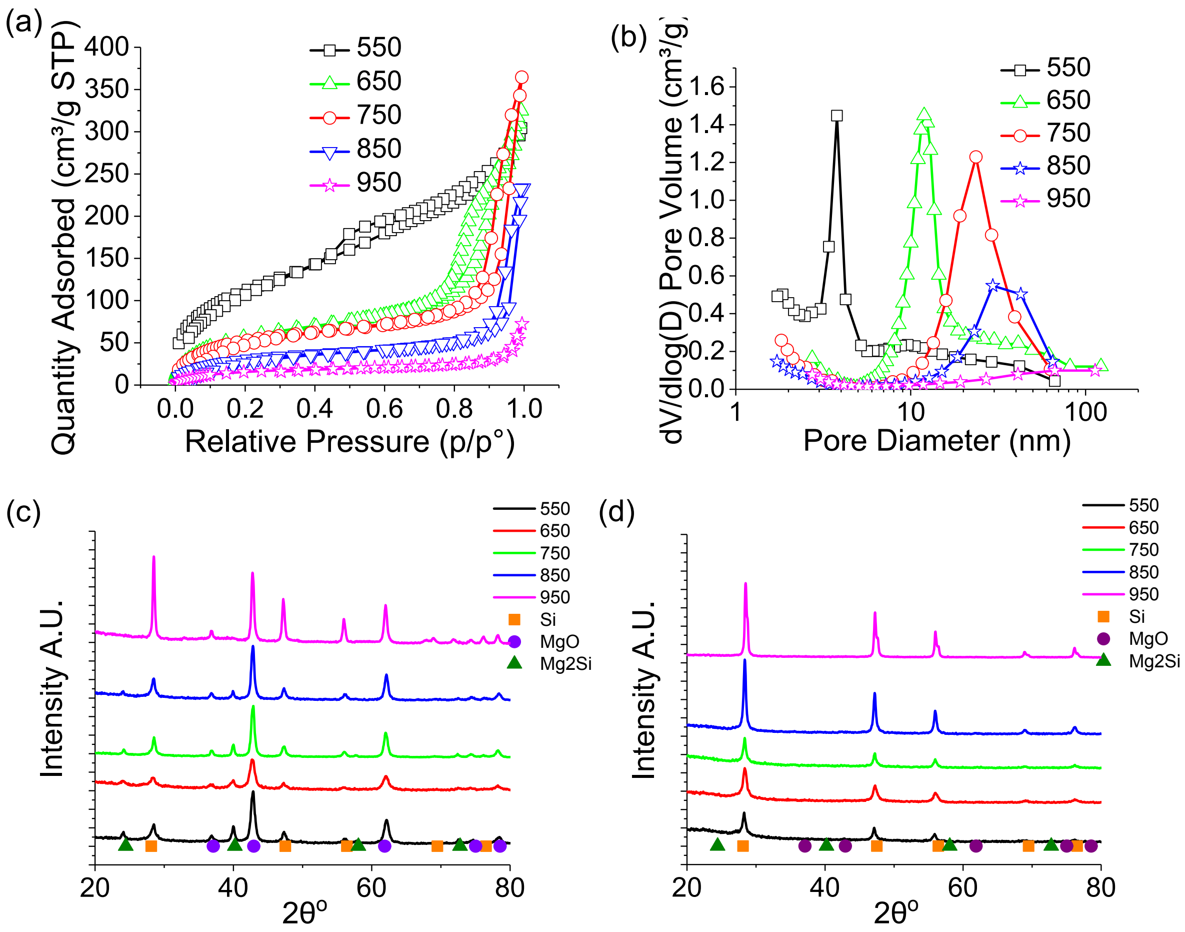


Figure S 2. Characterisation of silicon produced during kinetic study of, 2.5:1 Mg:SiO_2 stochimetry reacted between 1 and 10 hours at 650 °C. (a) N_2 absorption Isotherm, (b) BJH pore size distribution, (c) XRD of reaction products before washing with HCl, (d) XRD of reduction products after washing with HCl, (e) purity of silicon samples.



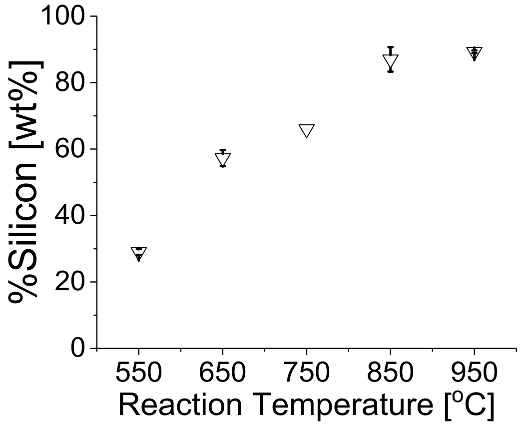
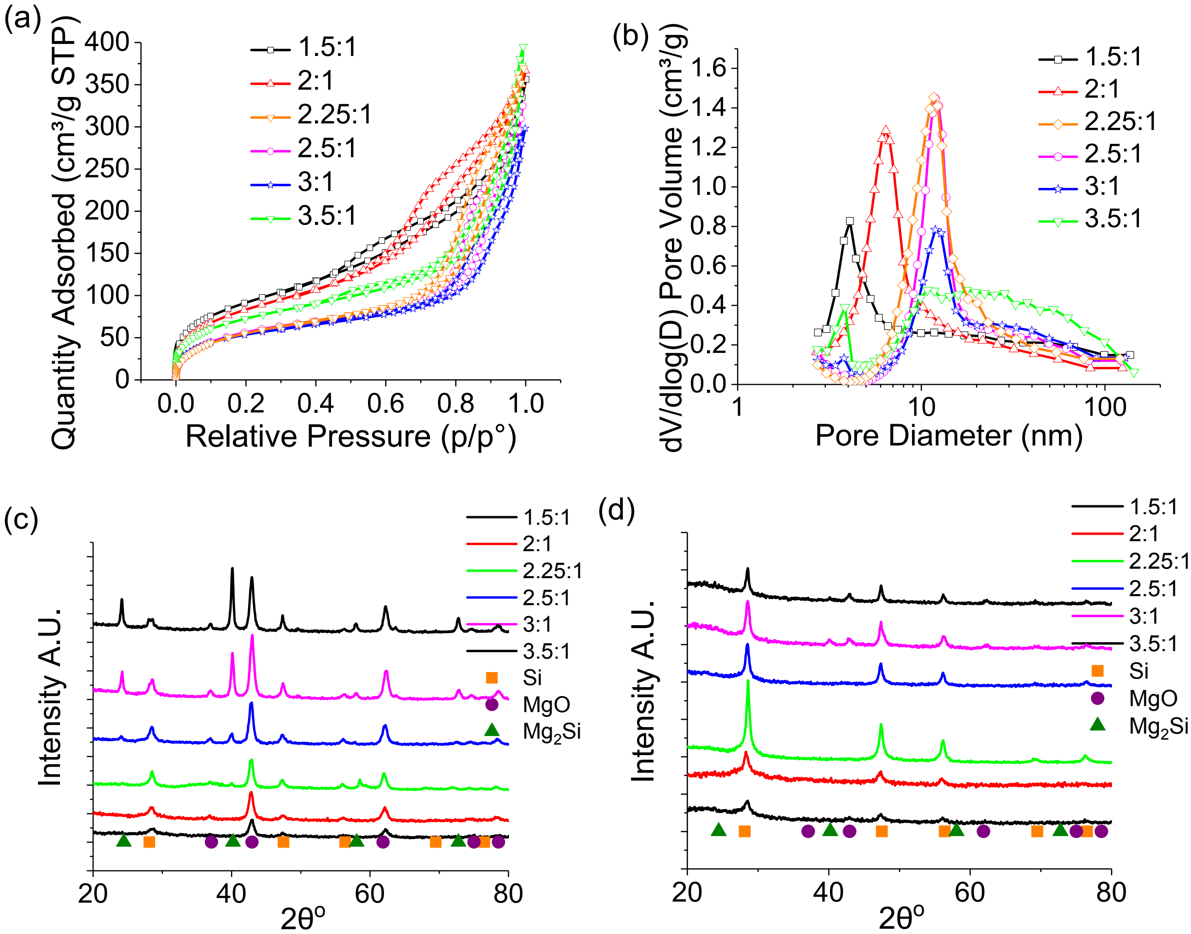


Figure S 3. Characterisation of silicon produced during thermodynamic study of 2.5:1 Mg:SiO2 stoichiometry reacted for 6 hours between temperatures of 550-950 °C. (a) N2 absorption Isotherm, (b) BJH pore size distribution, (c) XRD of reaction products before washing with HCl, (d) XRD of reduction products after washing with HCl, (e) purity of silicon sample.



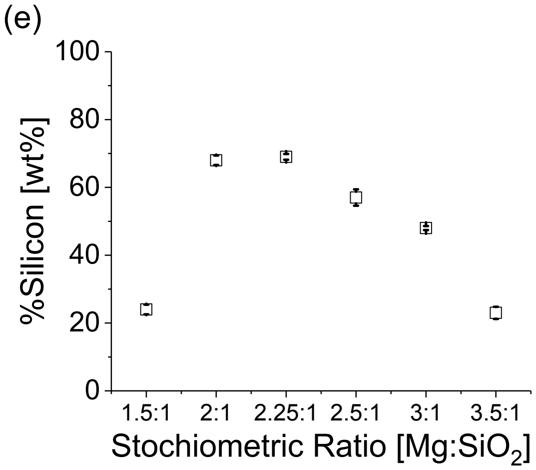


Figure S 4. Characterisation of silicon produced during stoichiometric study for stoichiometries between 1.5-3.5:1 Mg:SiO2 reacted for 6 hours at 650 °C. (a) N2 absorption Isotherms, (b) BJH pore size distributions, (c) XRD of reaction products before washing with HCL, (d) XRD of reduction products after washing with HCl, (e) purity of silicon samples.

Table S 2. Summary of Figure S 2 for the kinetic study of, 2.5:1 Mg:SiO2 stoichiometry reacted between 1 and 10 hours at 650°C

Reaction Time (h)	BET SSA (m^2/g)	BJH PV (cm^3/g)	APD (nm)	wt% Si	Si_{Cry} Size (nm)
1	232	0.50	10	65	12
3	181	0.46	13	57	11
6	221	0.48	13	57	10
10	186	0.49	14	60	12

Table S 3. Summary of Figure S 3 for the thermodynamic study of, 2.5:1 Mg:SiO2 stoichiometry reacted 6 hours at temperatures between 550 and 950°C

Reaction Temp (°C)	BET SSA (m^2/g)	BJH PV (cm^3/g)	APD (nm)	wt% Si	Si_{Cry} Size (nm)	USAXS Particle Size	
						Level 1 (nm)	Level 2 (nm)
550	402	0.48	4	29.0	5	25.84	413
650	230	0.48	12	57.3	10	40.28	208
750	185	0.54	13	66.0	13	49.85	333
850	110	0.35	34	87.0	21	16.94	323

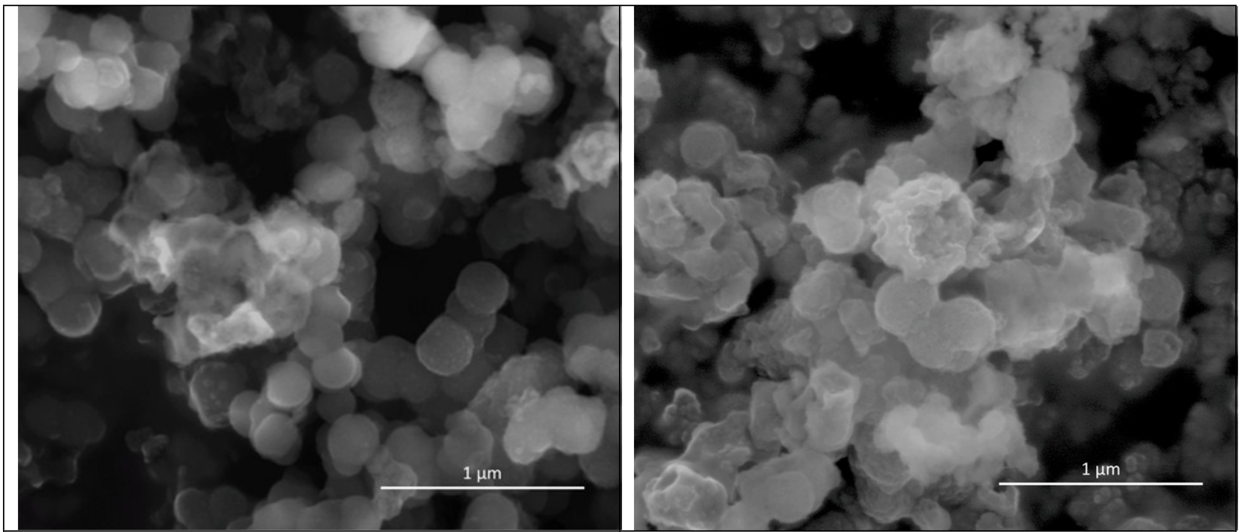
950	65	0.10	-	89.3	48	24.86	645

-outside of BJH model range

Table S 4. summary of Figure S 4 for the stoichiometric study of, Mg:SiO2 stoichiometry between 1.5-3.5:1 Mg:SiO2 reacted 6 hours at 650 °C

Stoichiometric Ratio ($Mg:SiO_2$)	BET SSA (m^2/g)	BJH PV (cm^3/g)	APD (nm)	wt% Si	Si_{Cry} Size (nm)
1.5:1	340	0.50	4	24	11
2.0:1	315	0.55	6	68	6
2.25:1	217	0.56	12	69	10
2.5:1	230	0.48	13	57	10
3.0:1	206	0.43	12*	48	9
3.5:1	271	0.57	28*	23	15

*Bimodal distribution so representative of pore size distribution, see Figure S 4(b)



550°C	650°C

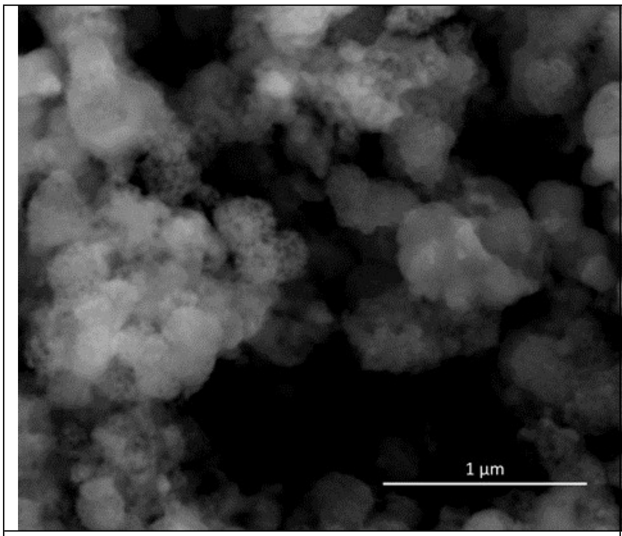
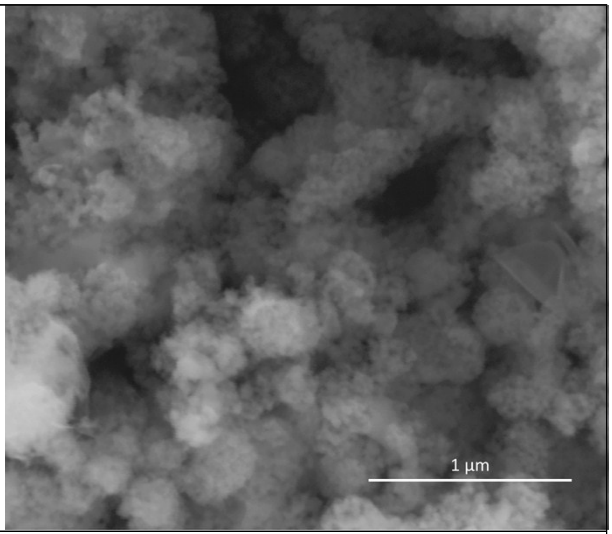
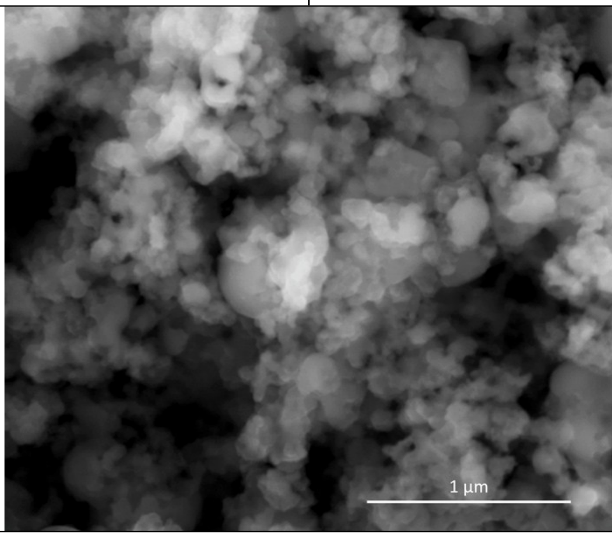
	
750°C	850°C
	
950°C	

Figure S 5, SEM images of BIS *reduced at temperatures 550 – 950°C.*

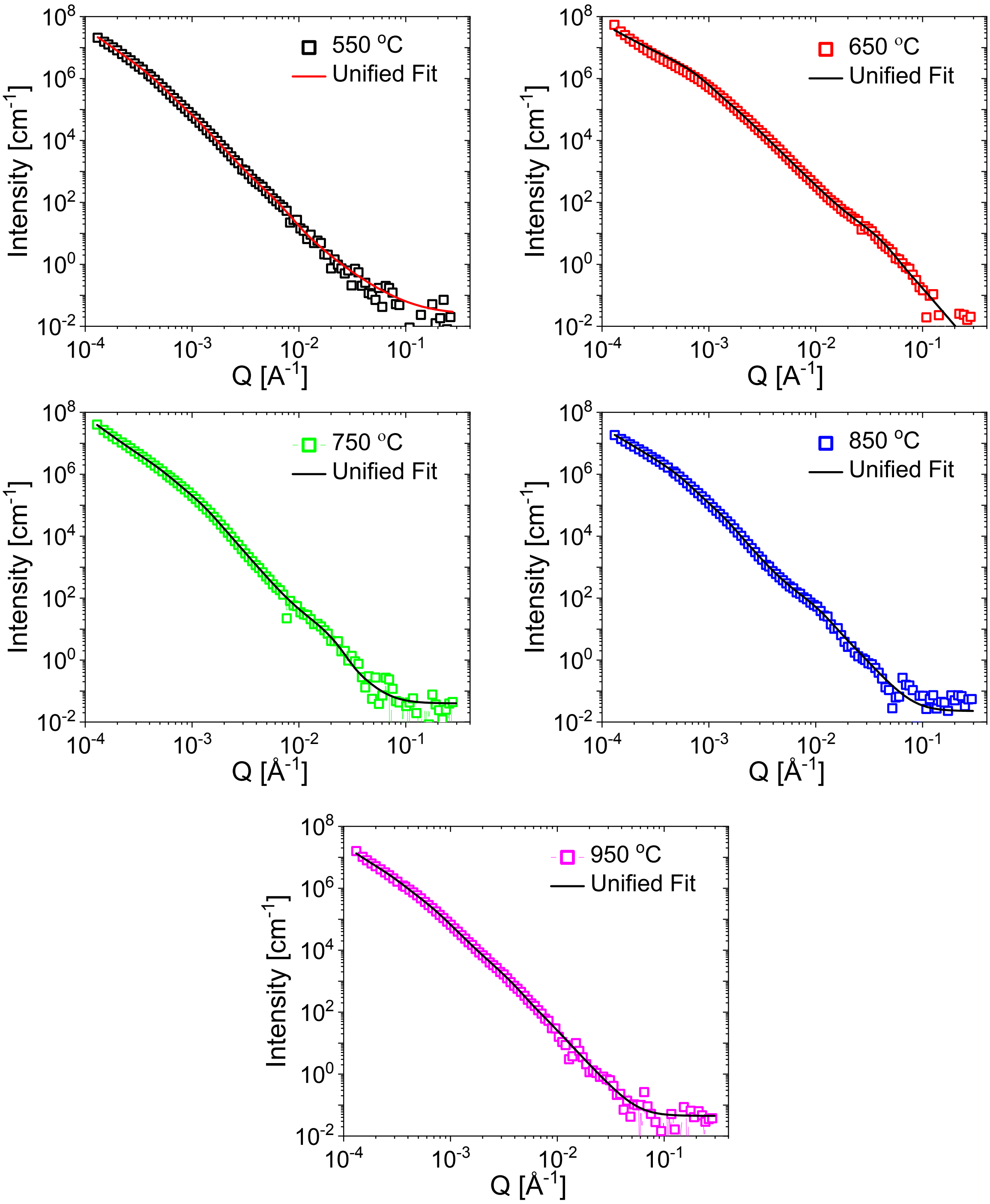


Figure S 6, USAXS data of porous silicon reduced at temperatures between 550-950 °C. Not all data points shown for clarity.

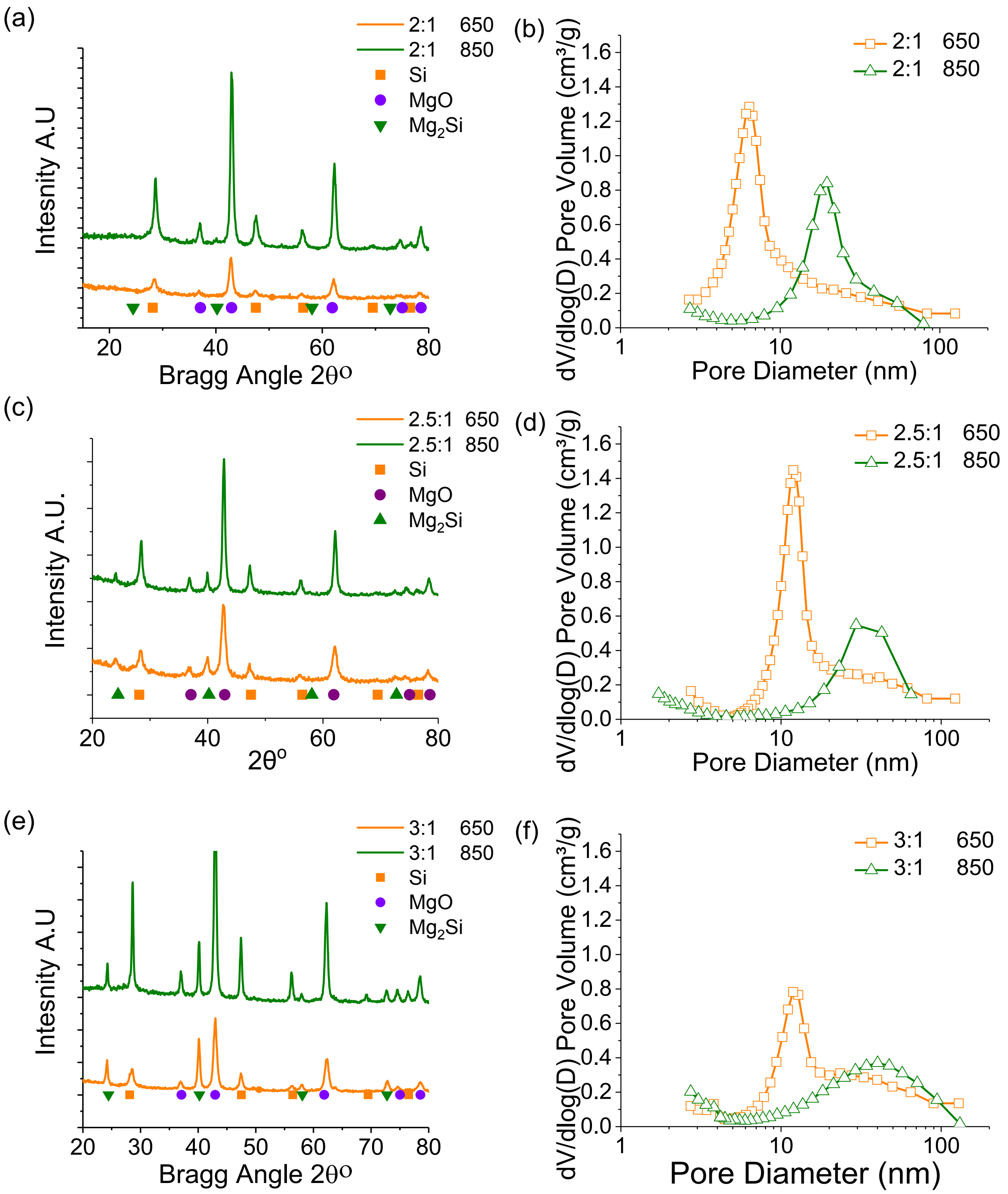
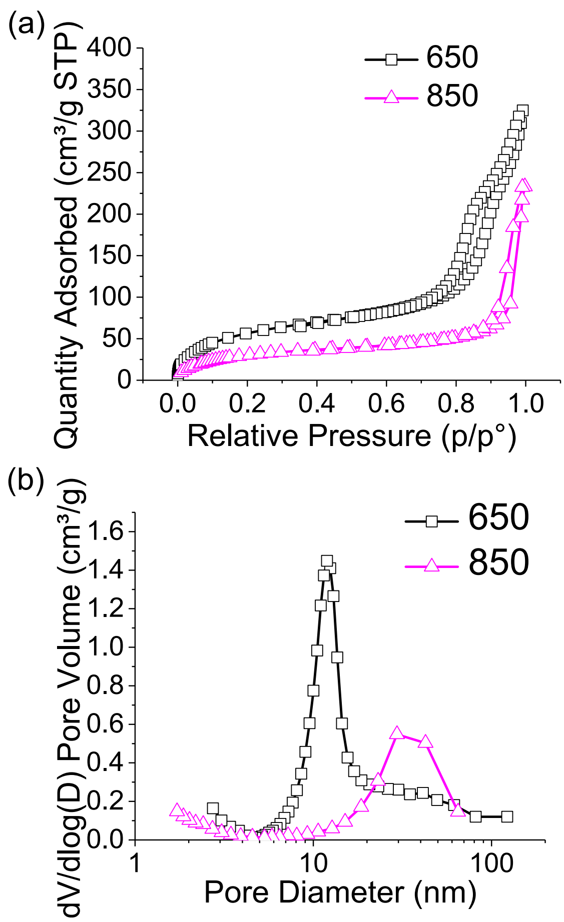


Figure S 7. Silicon/silica composites reduced at 650 and 850 °C with 2:1, 2.5:1 and 3:1 stoichiometric ratios of Mg:SiO2. (a,c,e) Diffraction patterns of after acid washing. (b,d,f) BJH pore size distributions.

Table S 5, summary of Figure S 7 .

Sample	Reduction	BET	BJH	APD	wt%	Si_{Cry}

	Temp (ºC)	SSA (m^2/g)	PV (cm^3/g)	(nm)	Si	Size (nm)
2:1	650	315	0.55	7	68	6
2:1	850	130	0.35	20	83	10
2.5:1	650	230	0.48	12	57	10
2.5:1	850	110	0.35	34	87	21
3:1	650	206	0.48	12	48	9
3:1	850	152	0.32	45	78	30



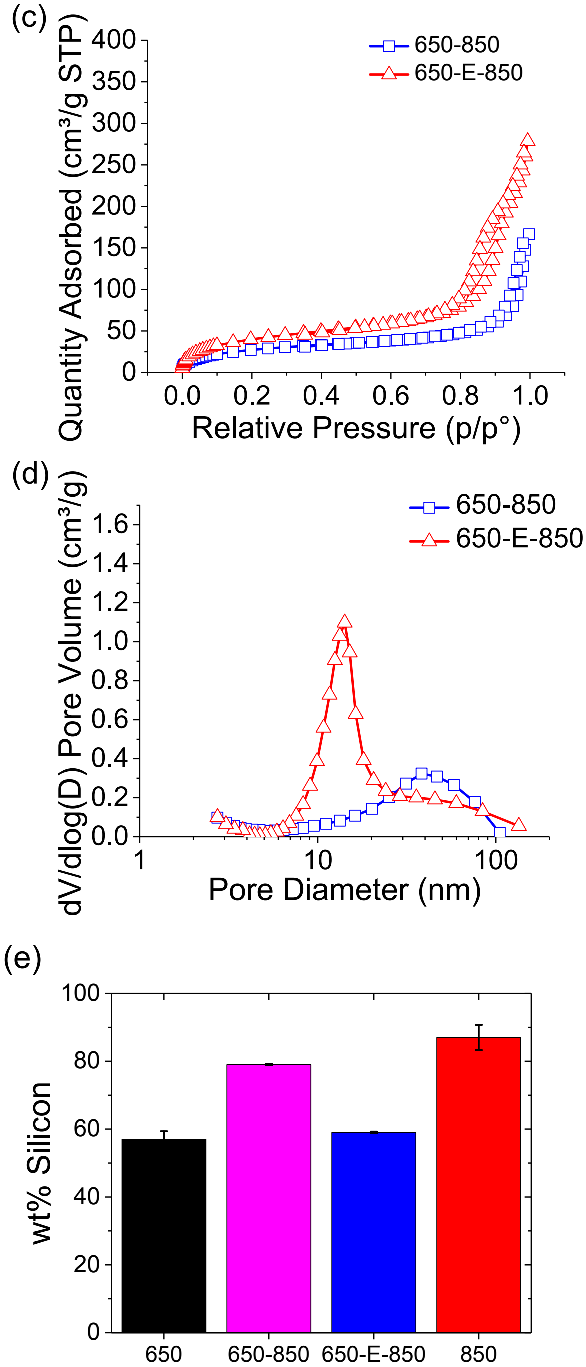
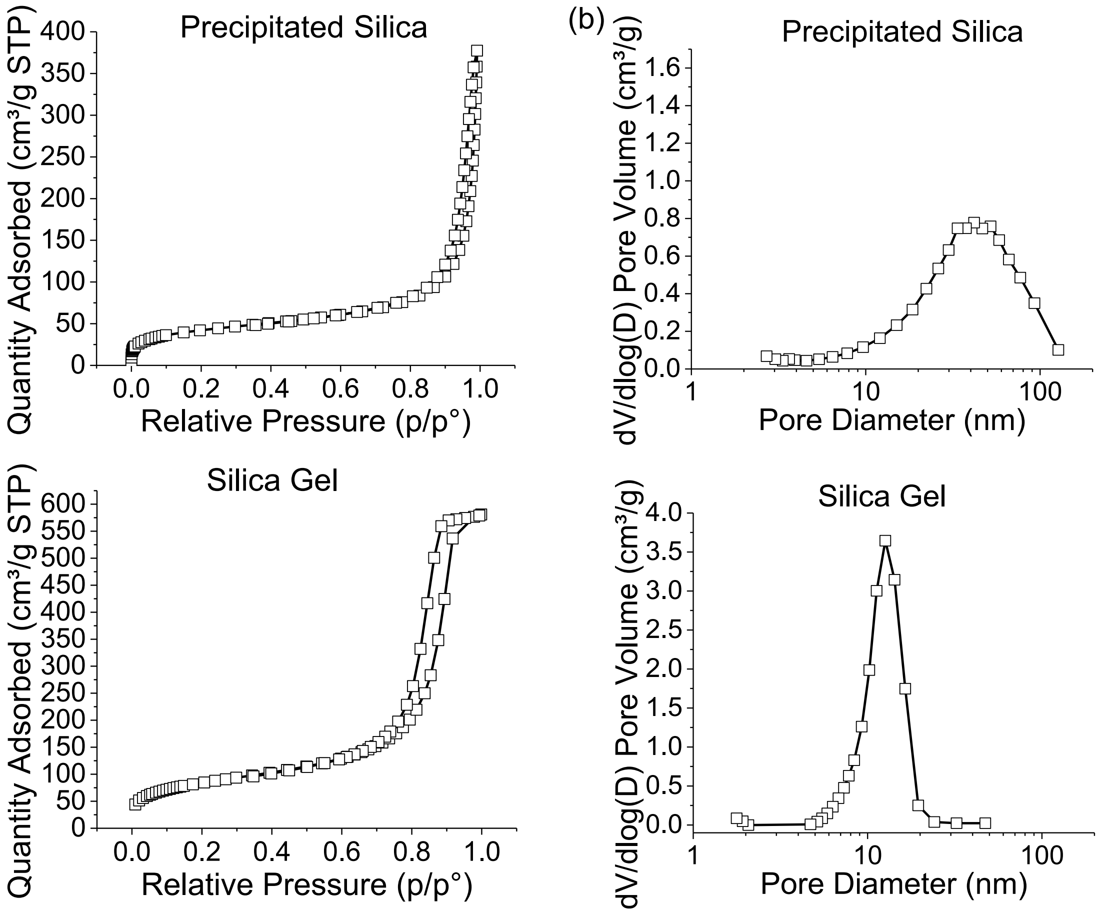


Figure S 8. Characterisation of samples used to understand the thermodynamic evolution of the MgTR *reaction, samples include silicon reduced at 650 and 850°C, Silicon reduced at 650 °C washed in HCl acid then heated to 850 °C under argon (650-E-850), and silicon reduced at 650 °C allowed to cool then reheated to 850°C (650-850). (a)(c) N_2 absorption Isotherms, (b)(d) BJH pore size distributions, (e) purity of silicon samples.*

Silica Precursors



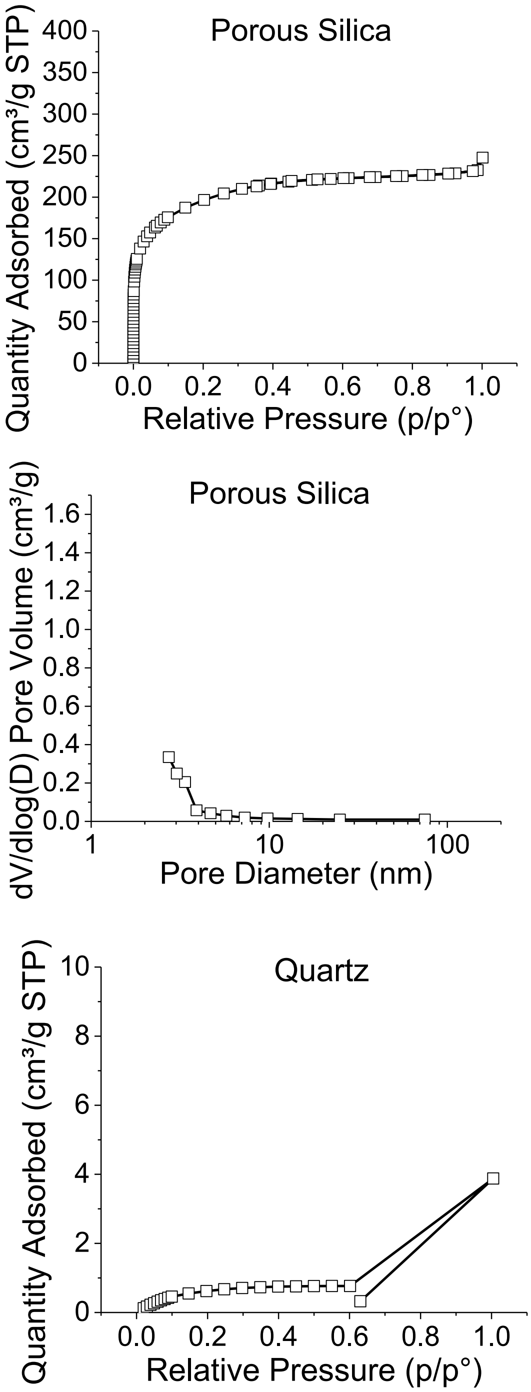


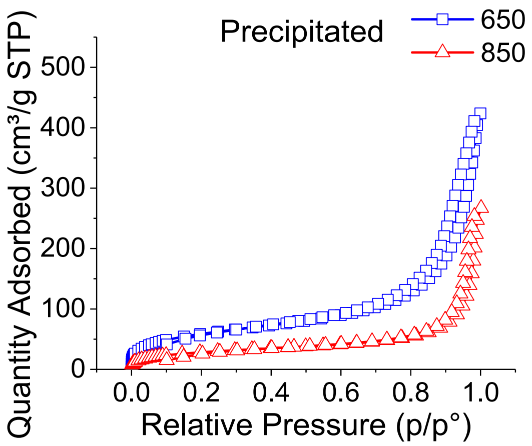
Figure S 9, N_2 absorption Isotherms and BJH pore size distributions of silica sources.

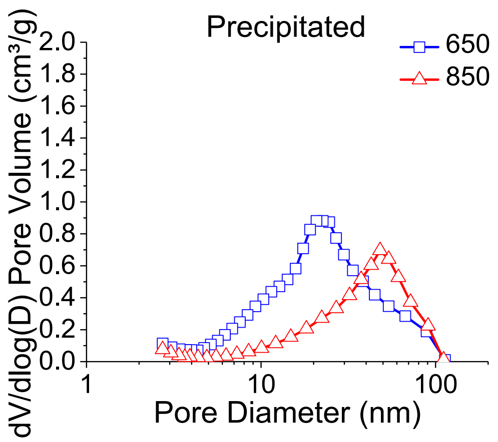
Table S 6.SSA, BJH pore volume, purity and crystallite size of silicon reduced at 650 and 850 °C for different silica precursors.

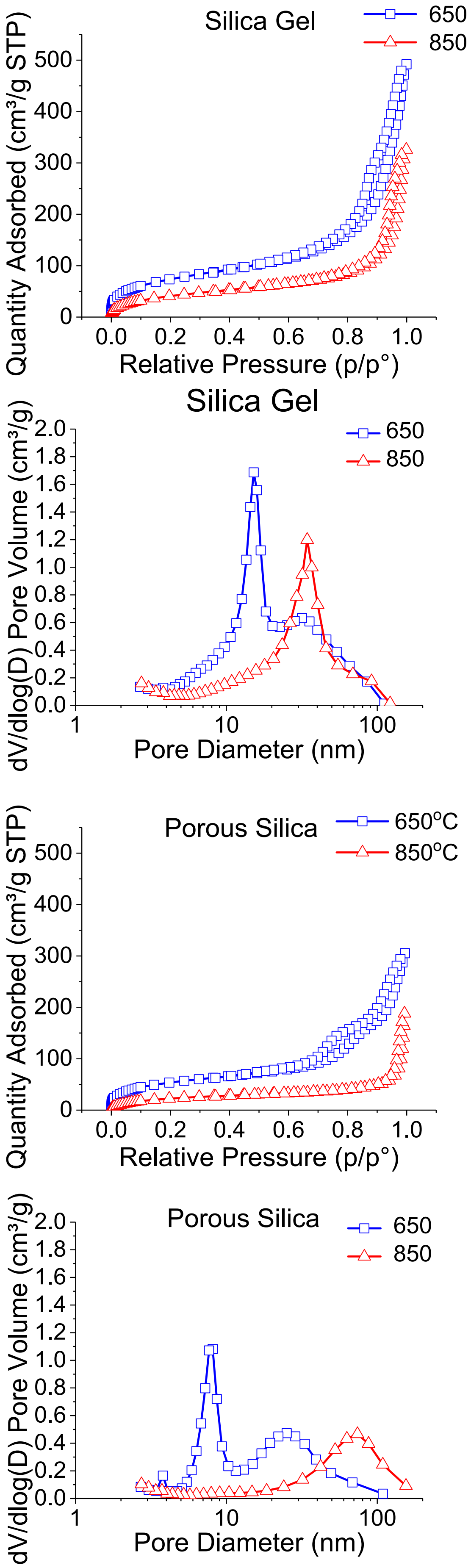
Precursor	Reduction	BET	BJH PV	wt%	Si_{Cry} Size

	Temperature (°C)	SSA (m^2/g)	(cm^3/g)	Si	(nm)
Ppt. silica		156	0.56		
Ppt. silica	650	220	0.63	56.3	9
Ppt. silica	850	108	0.40	60.9	19
Silica Gel		264	0.89		
Silica Gel	650	275	0.73	50.7	6
Silica Gel	850	158	0.48	80.3	13
BIS		301	0.16		
BIS	650	216	0.48	57.3	10
BIS	850	110	0.35	87.0	21
Porous SiO_2		725	0.09		
Porous SiO_2	650	205	0.45	41.9	22
Porous SiO_2	850	90	0.27	79.4	28
Quartz	Non-porous				
Quartz	650	310	0.36	31.1	17
Quartz	850	76	0.30	85.2	26

Reduced Products






Silica Gel
650
850
Quantity Adsorbed (cm³/g STP)
Relative Pressure (p/p°)
Silica Gel
650
850
dV/dlog(D) Pore Volume (cm³/g)
Pore Diameter (nm)
Porous Silica
650°C
850°C
Quantity Adsorbed (cm³/g STP)
Relative Pressure (p/p°)
Porous Silica
650
850
dV/dlog(D) Pore Volume (cm³/g)
Pore Diameter (nm)

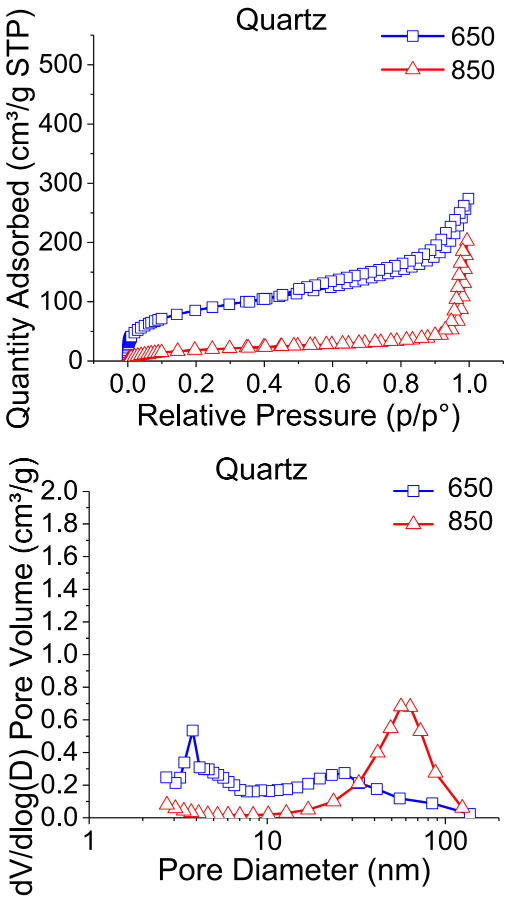


Figure S 10. N_2 absorption Isotherms and BJH pore size distributions of silicon reduced from variety of silica sources at 650 and 850 °C.

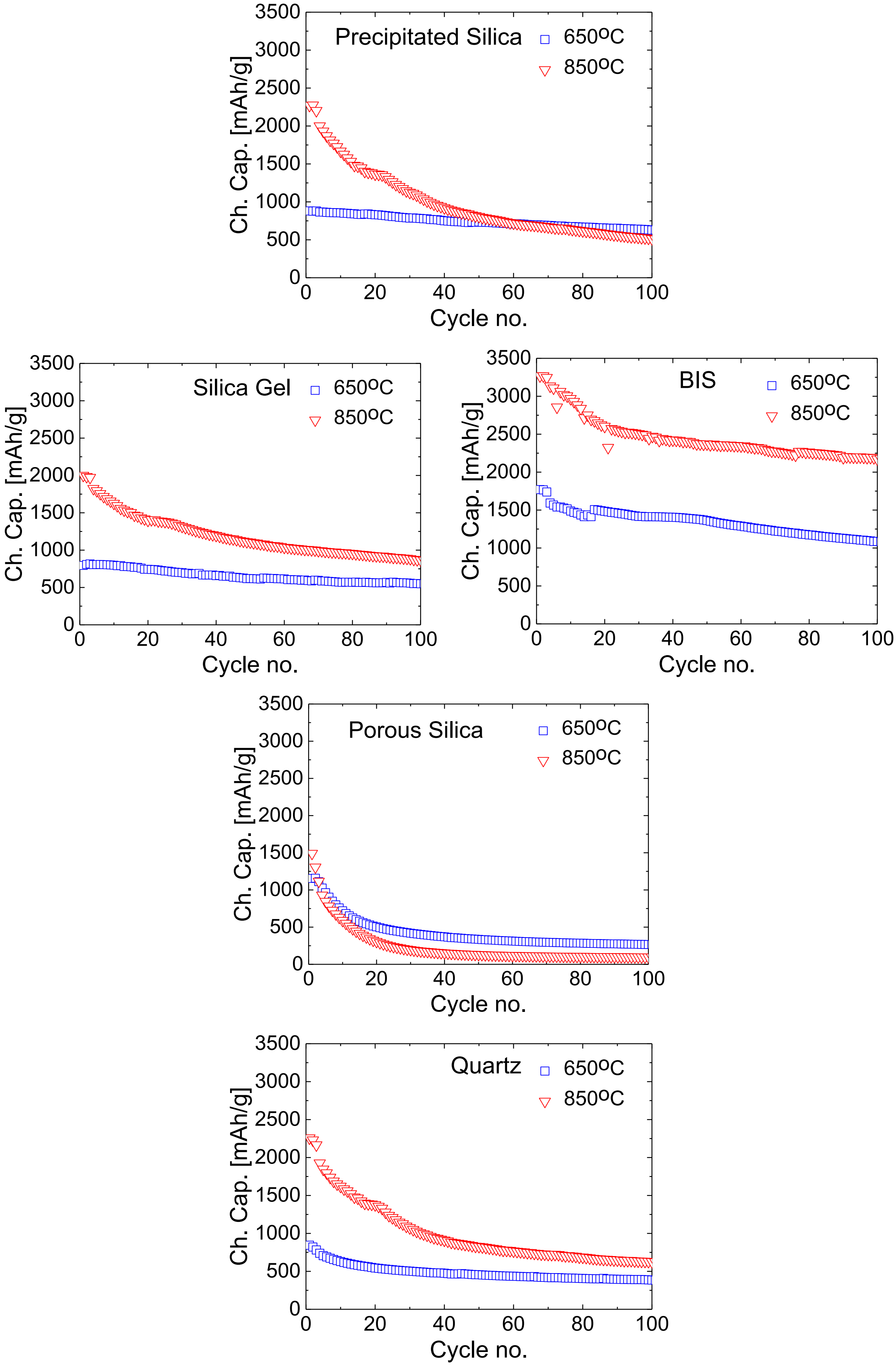

Precipitated Silica
650oC
850oC
Ch. Cap. [mAh/g]
Cycle no.
Silica Gel
650oC
850oC
Ch. Cap. [mAh/g]
Cycle no.
BIS
650oC
850oC
Ch. Cap. [mAh/g]
Cycle no.
Porous Silica
650oC
850oC
Ch. Cap. [mAh/g]
Cycle no.
Quartz
650oC
850oC
Ch. Cap. [mAh/g]
Cycle no.

Figure S 11. Discharge capacity of porous silicon/silica composites reduced at 650 and 850 °C

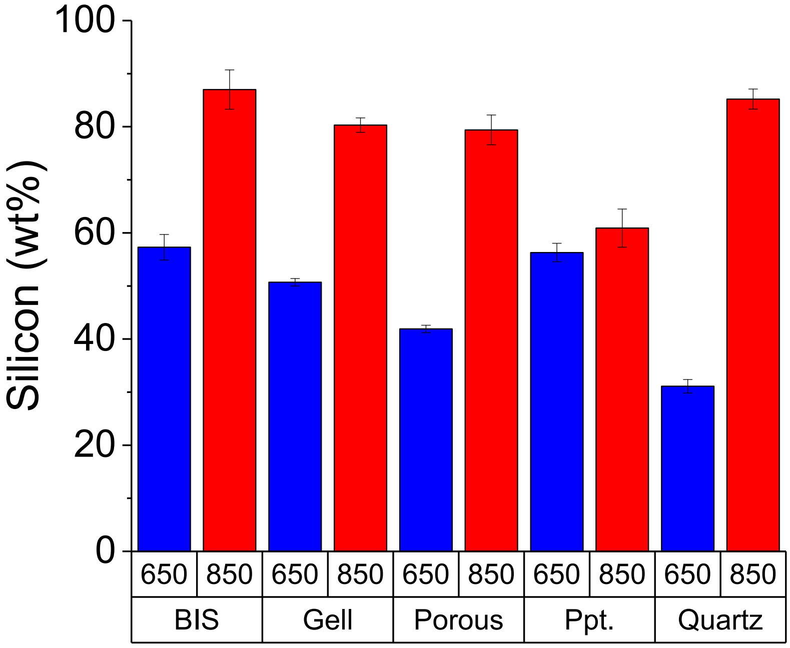
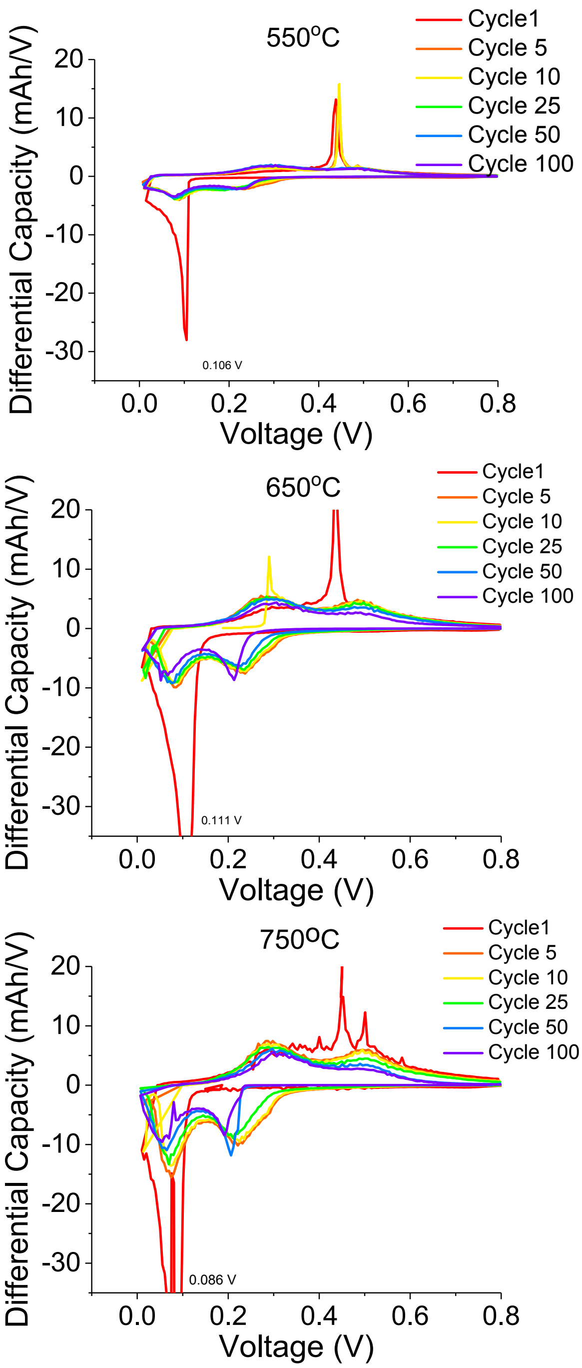


Figure S 12. Purity of silicon reduced from silica sources at 650 and 850 °C

Anode performance



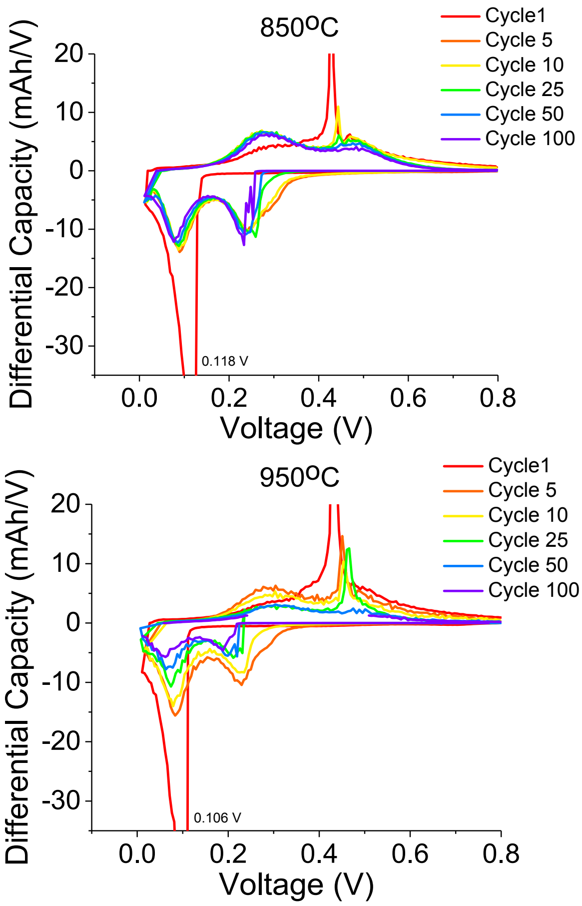


Figure S 13. Differential capacity plots of the 1st, 5th, 10th, 25th, 50th and 100th cycles for silicon reduced between 550-950 °C

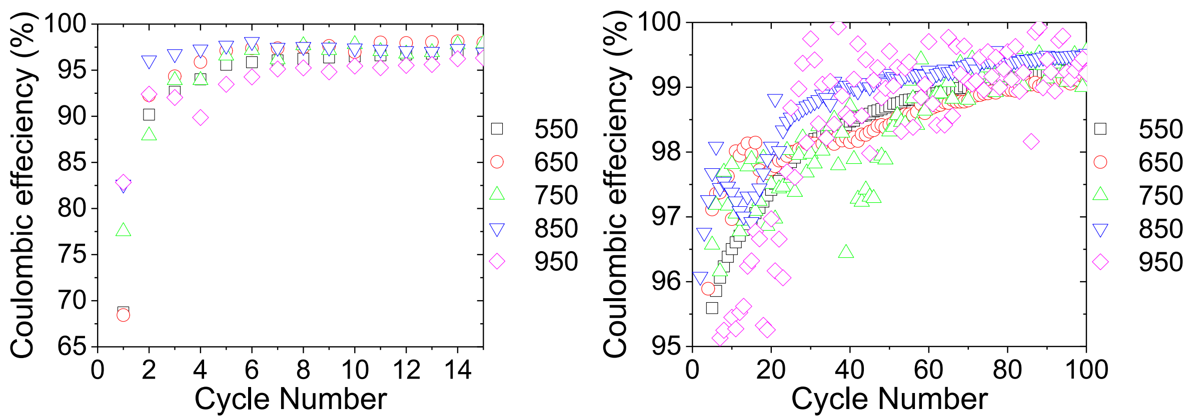


Figure S 14. Columbic efficiencies (a) during the first 10 cycles, (b) for 100 cycles of silicon's reduced at 550-950 °C

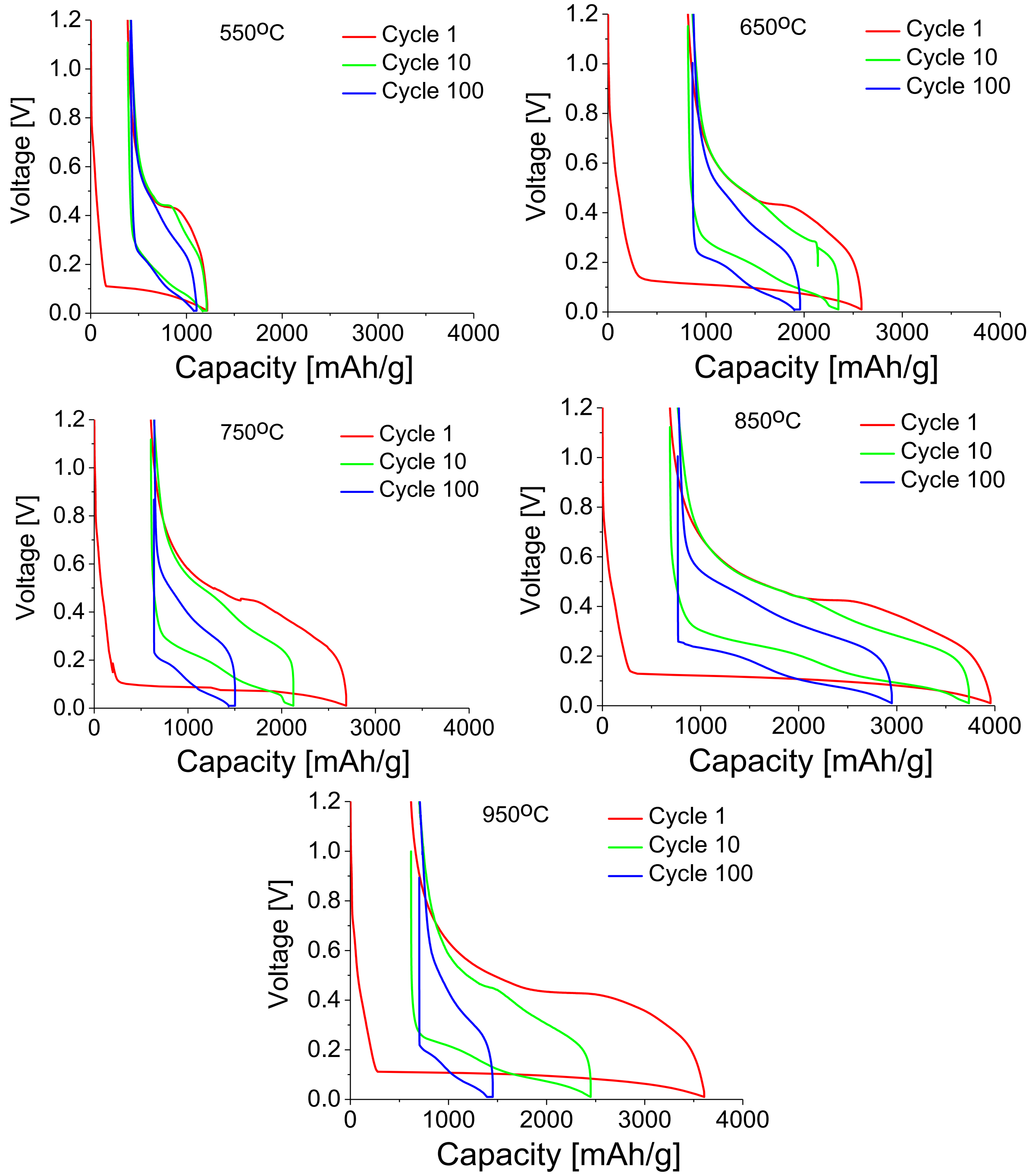


Figure S 15. Voltage capacity profiles of the 1st, 10th and 100th cycles for silicon reduced from 550-950 ºC

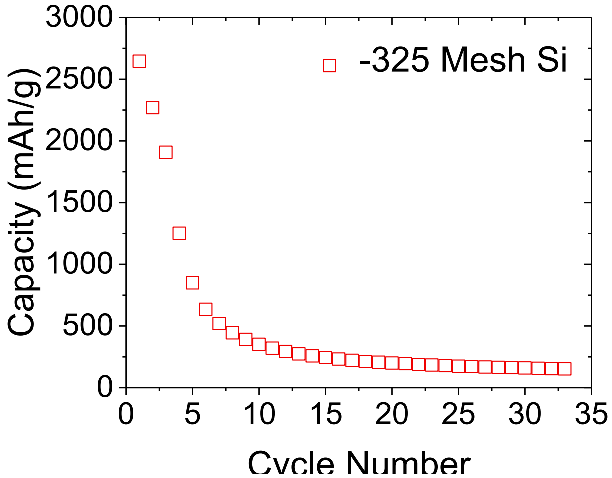


Figure S 16. Capacity vs cycle life of micron sized silicon particles (-325 mesh)

Figure S 17. Steel trough reactor with lid used in this study.