

A Review of magnesiothermic reduction of silica to porous silicon for lithium-ion battery applications and beyond

*Jake Entwistle, Anthony Rennie, Siddharth Patwardhan**

Supporting Information

Table S1. Key data abstracted from literature sources to quantify: 1 silica properties, 2 Magnesiothermic reduction conditions, 3 Silicon production properties, 4 Anode Performance properties and testing criteria, 5 key electrode parameters.

Phyto derived silica (excluding diatoms)

<u>1.Source Silica</u>	<u>2.Reduction Methods</u>		<u>3.Product Silicon</u>		<u>4.Performance</u>	<u>5.Testing Variables</u>
Surface area m ² /g Porosity Pore volume	Molar ratio Mg:SiO ₂ Temperature Duration Ramp rate		BET Surface Area Porosity Pore volume		Initial Stable Capacity Charging Rate Number of cycles %capacity retn	% active material mass in electrode Electrolyte additives Binder
Rice Husks ^[42] 289 m ² /g Mesoporous 0.45 cm ³ /g	(a) 2.5:1 650°C 2hours 5°C/min	(b) 2.5:1 650°C 2hours 40°C/min	(a) 245 m ² /g Mesoporosity 0.74 cm ³ /g	(b) 54 m ² /g Few Mesop 0.11 cm ³ /g	(a) 1750 mAh/g ^a 2.1 A/g 300 cycles 86%	65% active mass 1%VC PVDF
Rice Husks ^[50] 221 m ² /g 0.49 cm ³ /g	(a) 2.5:1 650°C 7 hours 1°C/min	(b) 2.5:1 650°C 7 hours 5°C/min	(a) 267 m ² /g Mesoporosity 1.1 cm ³ /g ^b	(b) 7.5 m ² /g 0.11 cm ³ /g	(a) 2294 mAh/g ^c 0.2 A/g 100 57%	60% active mass 2%VC additive Alginate

Rice Husks ^[62] 213 m ² /g Mesoporous 2-10nm Mesoporous 0.29 cm ³ /g	2.5:1 650°C 7 hours	150 m ² /g Mesoporous Mesoporous vol 0.60 cm ³ /g	≈1600 mAh/g 1.0 A/g 100 cycles 76%	60% active mass 'Contained' VC Alginate
Rice Husks ^[61] ^d 234 m ² /g Mesoporous 1.4-4.3nm 0.425 cm ³ /g	2.5:1 500°C 7 hours 5°C/min	42 m ² /g Meso-Macroporous 0.31cm ³ /g	1400 mAh/g 0.08 A/g 50 cycles 65%	60% active material 1.5% VC Alginate
Rice Husks ^[68] 286 m ² /g Mesopores 5nm	2:1 850°C 3 hours	47 m ² /g 10-50nm pores	1600mAh/g 0.2A/g 100%*	60% active material 5w%FEC PAA binder *Testing with Carbon Coating only Very low mass loading reported 72% cap retention for 100 cycles with more conventional loading.
Reed ^[84] 101 m ² /g Mesoporous 0.22 cm ³ /g	2.5:1 650°C 6hours 5°C/min	224 m ² /g Mesoporous 0.70cm ³ /g	2435 mAh/g 2.1 A/g 200 cycles 45%	70%active mass Carbon coating PVDF
Reed Horsetail ^[56] 233 m ² /g 0.35 cm ³ /g 6nm APD	2:1 600°C 1 hour 1:1 w-ratio reactants:NaCl	117 m ² /g 0.24 cm ³ /g 9nm APD	N/a	N/a
Bamboo Silk ^[56] 0.47 m ² /g 0.35 cm ³ /g 19nm APD	2:1 600°C 1 hour 1:1 w-ratio reactants:NaCl	356m ² /g 0.56 cm ³ /g 8nm APD	N/a	N/a

^a5°C/min sample ^btypo present in paper 1.1 m³/g unlikely ^c1°C/min silicon APD =Average Pore Diameter ^dleached and unleached comparison

Micro and mesoporous silicon

<u>Source Silica</u>	<u>Reduction Methods</u>		<u>Product Silicon</u>	<u>Performance</u>	<u>Testing Variables</u>
Surface area m ² /g Porosity Pore volume	Molar ratio Mg:SiO ₂ Temperature Duration Ramp rate		BET Surface Area Porosity Pore volume	Initial Stable Capacity Charging Rate Number of cycles %capacity retn	% active material mass in electrode Electrolyte additives Binder
Silicon Particles ^[64] <74um nonporous	Step 1 2.1:1 500°C 10 hour	Step 2 Air atm 650°C 10hours	86.6 m ² /g Mesoporous 4nm pores	3200 mAh/g 0.36 A/g 85cycles 64%	60% active mass Alginate SiO ₂ passivated layer
Aerogel ^[63]	5:1 500°C 10 hour	Air atm 650°C 5 hours	239 m ² /g Mesoporous 4nm pores	1782 mAh/g 0.36 A/g 100 cycles 82%	60% active material 5% FEC Alginate SiO ₂ passivated layer
Sand ^[63]	5:1 500°C 10 hour	Air atm 650°C 5 hours	23.9 m ² /g Mesoporous ≈30nm APD	≈1782 mAh/g 0.36 A/g 100 cycles 82%	60% active material 5% FEC Alginate SiO ₂ passivated layer
Diatom ^[63]	5:1 500°C 10 hour	Air atm 650°C 5 hours	74 m ² /g Mesoporous ≈30 APD	≈1400 mAh/g 0.36 A/g 100 cycles 71%	60% active material 5% FEC Alginate SiO ₂ passivated layer
SBA-15 ^[63]	5:1 500°C 10 hour	Air atm 650°C 5 hours	103 m ² /g Mesoporous Majority 4-16nm	≈1300 mAh/g 0.36 A/g 100 cycles 77%	60% active material 5% FEC Alginate SiO ₂ passivated layer
SBA-15 ^[39]	2.5:1 650 °C 7 hours 5°C/min		74 m ² /g Mesoporous 28nm APD 0.56cm ³ /g	2727 mAh/g 4.2 A/g 100 53%	60% active material 1:1 CMC:SBR 2w%VC

SBA-15 ^[39]	2.5:1 650°C 7 hours 5°C/min	74 m ² /g Mesoporous 28nm ave 0.56 cm ³ /g	1500 mAh/g 4.2 A/g 100 cycles 94.4%	60% active material 1:1 CMC:SBR 2w%VC CVD carbon coating
SBA-15 ^[54]	3.5:1 500°C ^e	162 m ² /g Mesoporous 2-10nm	2918 mAh/g 0.05A/g 50 cycles 34%	40% active material PVDF Ni foam cc
Nanorods ^[69] 666 m ² /g 3.4nm diam pores 1.49 cm ³ /g	2:1 650°C 5 hours 10°C/min	128 m ² /g Mesoporous nanoparticles 3.5nm diam pores + distribution around 42nm 0.66 cm ³ /g	≈2600 mAh/g 0.4 A/g 80 cycles 40%	80% active material Polyimide binder
Nanorods ^[85]	2.5:1 670°C 5 hours	255 m ² /g Mesoporous Nanorods (~50nm dia) 12nm ave diam 0.64 cm ³ /g	1400 mAh/g 0.2A/g 170 cycles 74%	70%active material Alginate
Nanowires ^[86]	3.125:1 600°C 5 hours	157 m ² /g Mesoporous cross-linked Nanowires 40-65nm diam 0.33cm ³ /g	1300 mAh/g 2.5 A/g 1000 cycles 49%	80% active mass CMC
Nanowires ^[40] 10-20nm diameter Length several ~20μm	2:1 500°C 6 hours 10°C/min	3-5nm particles accumulated alone original nanowire shape	1200 mAh/g 0.045 A/g 55 cycles 54%	80% active mass PVDF

Microspheres ^[83]	2.5:1 650°C 2 hours		200 m ² /g Mesoporous <6nm 0.25cm ³ /g	≈3000 mAh/g 0.1 A/g 100 cycles ≈100%	70%active material PVDF
Purified Sand ^[59] Nonporous >5um-50nm particles	2.25:1 700°C 6 hours 5°C/min 5:1 w-ratio reactants:NaCl		323 m ² /g Mesoporous	≈1700mAh 1.8 A/g 1000 cycles 70%	70% Active material PAA Carbon coating 2% VC
Stöber Spheres ^[51] 400nm diameter	3:1 800°C 12 hours		Porous Silicon Spheres composed submicron nanoparticles	2300 mAh/g 0.1A/g 50 cycles 10%	60%active material PVDF Carbon coating improved performance
Stöber Spheres ^[57] 200nm 12 m ² /g	1:2.25 700°C 5°C/min 6hours 1:10w SiO ₂ :NaCl		215 m ² /g Meso and microporous	≈1700mAh/g 1.8 A/g 500 cycles >80%	70% active material Alginate
Diatomite ^[67]	Step 1 Al powder 900°C 3 hour	Step 2 Mg reduction 700°C 3 hours 5°C/min	Mesoporous	1750 mAh/g 1.8A/g 100 cycles 86%	70% active material (70w%Si 30w%Al) PAA+CMC 10w% FEC

Diatomaceous Earth ^[80] 6 m ² /g Mainly Microporous	2.5:1 650°C 6 hours 5°C/min	96 m ² /g Mainly Mesoporous	1300mAh/g 0.2mA/cm ² 30 cycles 29%	75% active material Alginate 2% VC
Glass bottles ^[58]	1:2.10 1:2.25 700°C 5°C/min 6hours 1:10w SiO ₂ :NaCl	-	1420 mAh/g 1.8A/g 400 cycles 72%	70% active material PAA 1:1, v/v FEC:DMC

≈denotes numerical data not stated, approximated from graphical data inferred from report

Macroporous silicon

<u>Source Silica</u>	<u>Reduction Methods</u>	<u>Product Silicon</u>	<u>Performance</u>	<u>Testing Variables</u>
Surface area m ² /g Porosity Pore volume	Molar ratio Mg:SiO ₂ Temperature Duration Ramp rate	BET Surface Area Porosity Pore volume	Initial Stable Capacity Charging Rate Number of cycles %capacity retn	% active material mass in electrode Electrolyte additives Binder
Mesoporous Powder ^[70] 10nm APD	2.5:1 650°C 6 hours 5°C/min	Macroporous Particles Ave 200nm	≈2400 mAh/g 0.72 A/g 100 cycles 69%	80% active material 2% VC PVDF
Silica spheres 200nm average diameter ^[46]	1.9:1 700°C 5 hours 5°C/min	Macroporous ~200nm	1162 mAh/g 2.0 A/g 800 cycles 91%	70% active material (of which 13.5%=Carbon coating via CVD) CMC 3%VC

Notable non-electrochemistry papers

<u>Source Silica</u>	<u>Reduction Methods</u>		<u>Product Silicon</u>	
Surface area m ² /g Porosity Pore volume	Molar ratio Mg:SiO ₂ Temperature Duration Ramp rate		BET Surface Area Porosity Pore volume	
Diatom frustules ^[36] 1.65 m ² /g	2.5:1 650°C 2.5hour 3 °C/min		541 m ² /g 0.7 cm ³ /g Significant micropores	
Diatomaceous earth ^[43]	(a) 2.25:1 650°C 2.5 hour	(b)2.25:1 650°C 2.5 hour 1:10 wt-ratio reactants:NaCl	(a) 5.2 m ² /g 0.01 cm ³ /g	(b) 295 m ² /g 1.2 cm ³ /g 22nm APD
SBA-15 ^[34] 542 m ² /g 1.13cm ³ /g 8.34nm ave pore diam	1.5:1 670°C 1.5hour 3 °C/min		Shape Retained 605m ² /g 1.54cm ³ /g 10.17nm APD	
SBA-16 ^[34] 679 m ² /g 0.65cm ³ /g 5.63nm APD	1.5:1 670°C 1.5hour 3 °C/min		Ordered porosity destroyed 230m ² /g 0.63cm ³ /g 8.25nm APD	