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SiO_2 precursors for Si-based negative electrode materials for Li-ion batteries

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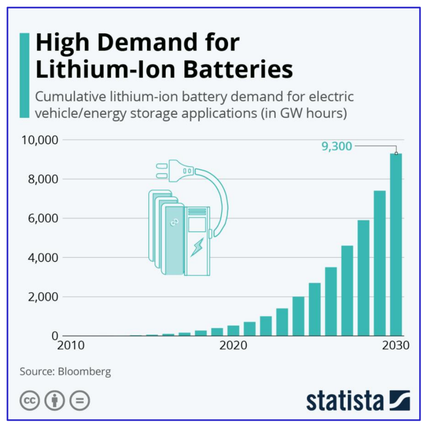
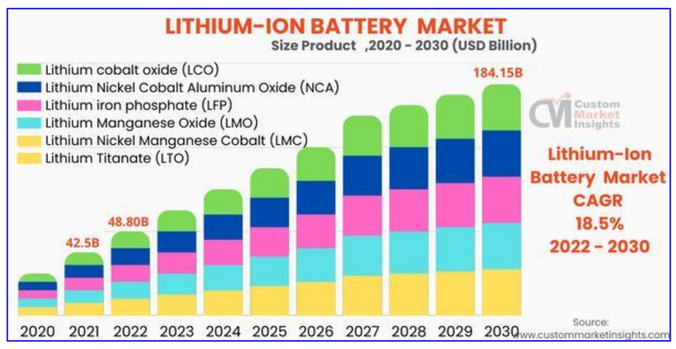
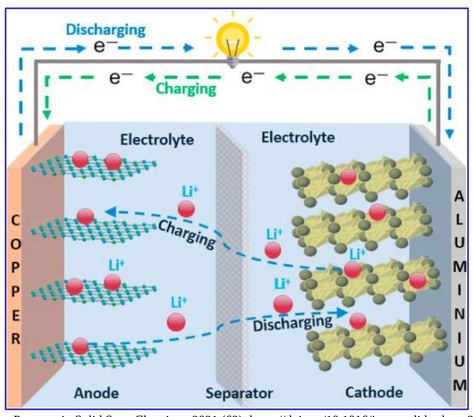
Prospects for Li-ion batteries development



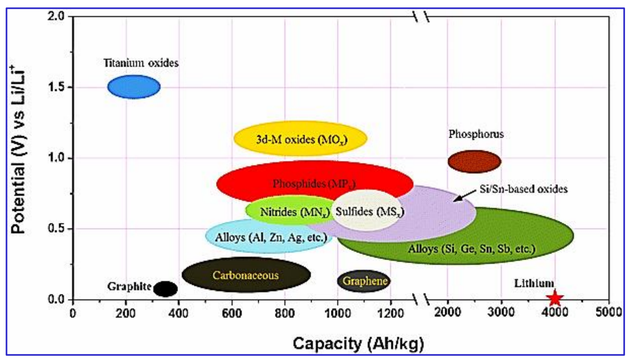


Schematic theoretical charge-discharge process in Li-ion batteries



A. M. Divakaran, Progress in Solid State Chemistry 2021 (62), https://doi.org/10.1016/j.progsolidstchem.2020.100298

Electrochemical characteristics of negative electrode materials for LBs



J. Lu, Electrochemical Energy Reviews 2018 (1), https://doi.org/10.1007/s41918-018-0001-4

The aim is to investigate silica precursors for magnesiothermic reduction to produce silicon-based materials and compare Si-based materials electrochemical properties in LIBs.

Tasks are:

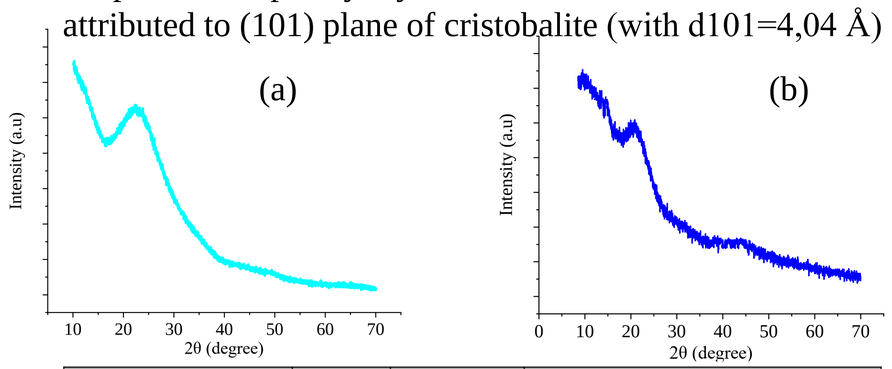
1.Characterize silica synthesized from tetraethoxysilane (TEOS) and commercial fumed silica used as precursors for magnesiothermic reduction; 2. Study Si-based materials of the reduction reaction and washing; 3. Explore their electrochemical properties in Li-ion half-cells.

Characterization of silica precursors

- The ***synthesized*** silica precursor was obtained with *hydrolysis of TEOS* in presence of *ammonia*. 25 ml of TEOS was mixed with 132 ml of ethanol, then 4 ml of HCl (0.1 M) and 1.5 ml of ammonia (4 M) were added and stirred for a night. The obtained product was dried at 80°C overnight under vacuum to remove residual solvent and further at 600°C in air for 1 hour. The obtained silica was ball-milled in a zirconia bowl.
- The ***commercial*** fumed silica was purchased from Sigma Aldrich.

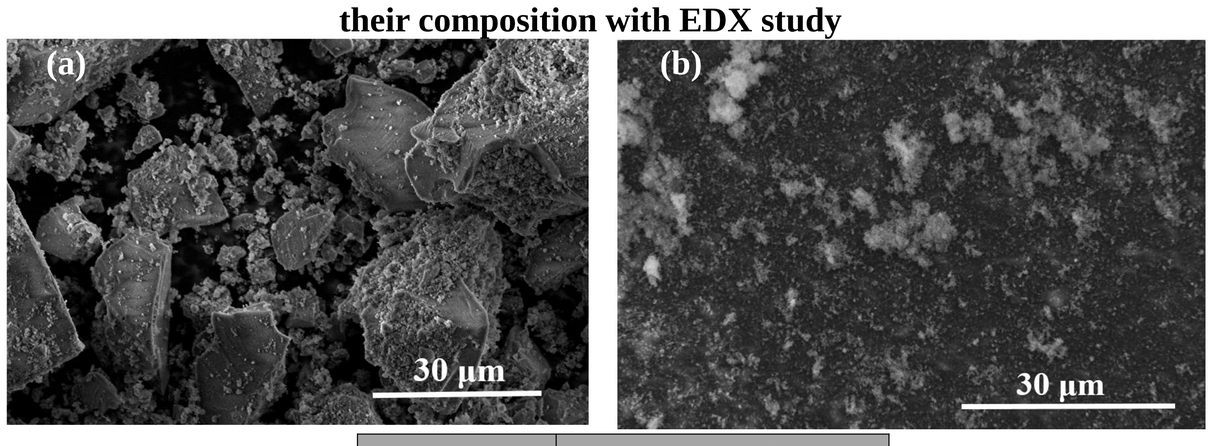
Experimental X-ray diffraction patterns of the synthesized (a) and commercial (b) silica materials

Both samples reveal poorly crystalline nature and one clear broad peak attributed to (101) plane of cristobalite (with d101=4,04 Å)



Sample	2θ, °	d101, Å	Crystallite size from Scherrer equation, nm
Synthesized	23	3,95	1,9
Commercial	21	4,26	1,2

SEM images of the synthesized (a) commercial (b) silica and their composition with EDX study

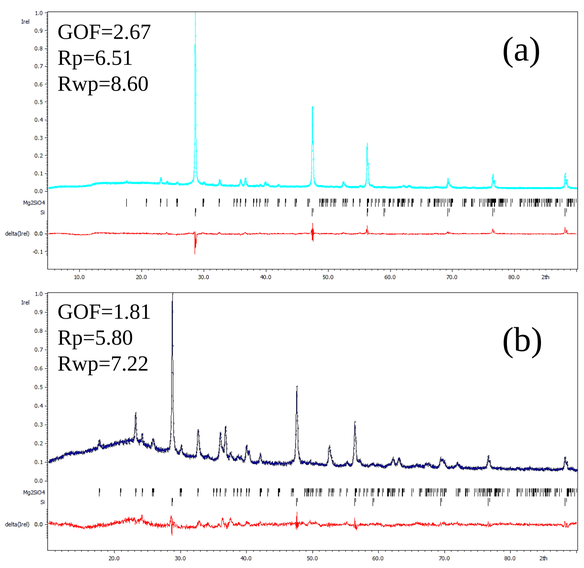


Sample	Atom. % of element	
	O	Si
Synthesized	70	30
Commercial	66,7	33,3

Si-based anode materials

The Si-based materials for anodes are synthesized via magnesiothermic reduction of silica samples at (SiO_2: Mg: MgO (added to decrease the intensity of the reaction and prevent a possible explosive eruption) = 1: 0.8: 0.4) was conducted in the muffle furnace at 550 °C in air for 1 hour. The reaction products were washed in the mixture of 40 ml of HCl (38 wt. %) with 200 ml of deionized (DI) water and in DI-water. Materials from the synthesized and commercial precursors are “S” and “C”.

PXRD patterns of samples: a) S, b) C

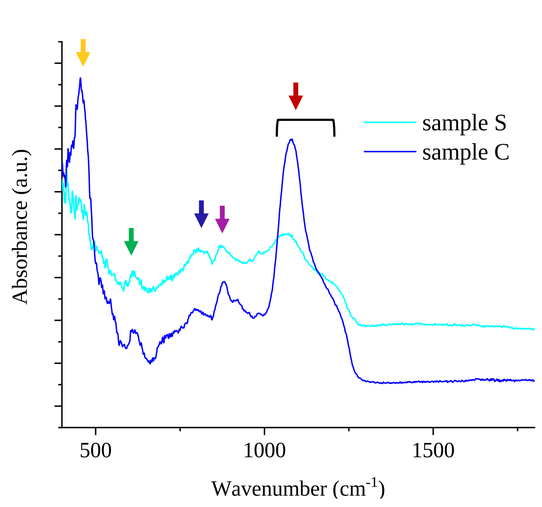


Possible reactions during magnesiothermic reduction of SiO2:

SiO2 + 2Mg = Si + 2MgO
SiO2 + 4Mg = 2MgO + Mg2Si
Mg2Si + SiO2 = 2MgO + 2Si
Si + 2Mg = Mg2Si
2Mg + 3SiO2 = 2MgSiO3 + Si
MgO + SiO2 = MgSiO3
2MgO + SiO2 = Mg2SiO4

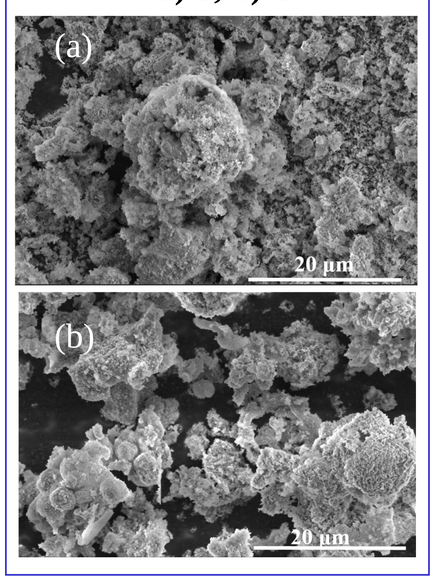
Sample	Wt. % of phases after the Rietveld refinement	
	Si	Mg2SiO4
S	69	31
C	33,5	66,5

FTIR spectra of the samples



Absorbance, cm^{-1}	Mode
609	Si-Si
1075	ν_{as} (Si-O-Si)
800	ν_s (Si-O-Si)
460	δ_r (Si-O-Si)
890	ν_s (SiO4)

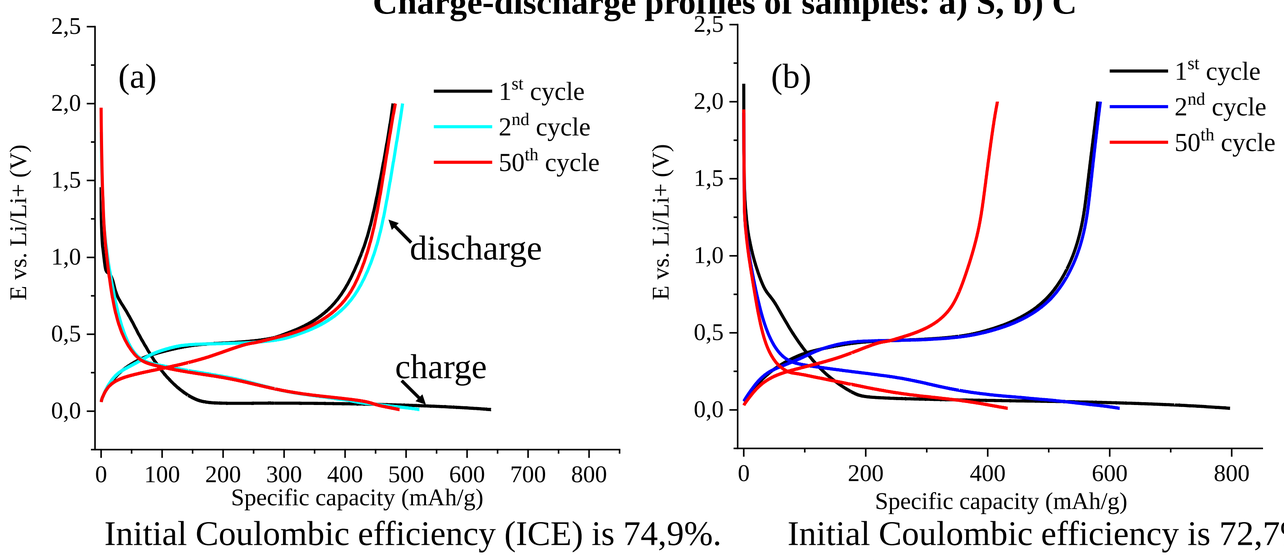
SEM images of the samples: a) S, b) C



Electrochemical performance of Si-based materials in half cell configurations

The electrode slurry consists of Si-based anode material, carbon black Super P (Timcal), single-walled carbon nanotubes (CNT; TUBALL), carboxymethyl cellulose (CMC; Sigma-Aldrich) and styrene-butadiene rubber (SBR) in 65:18:3:7:7 mass ratio. An average electrode active mass was 1.2 mg.

Charge-discharge profiles of samples: a) S, b) C



Initial Coulombic efficiency (ICE) is 74,9%.
Specific discharge capacity is 477 mAh/g.
Capacity retention after 50 cycles is 98%.

Initial Coulombic efficiency is 72,7%.
Specific discharge capacity is 580 mAh/g.
Capacity retention after 50 cycles is 72%.

Conclusions:

1. Synthesized and commercial silica precursors revealed poor crystallinity with peaks at 2θ of about 21° and 23° corresponding to (101) plane of cristobalite. Particles of both precursors are of irregular shape, but the commercial sample has smaller agglomerates.
2. After the magnesiothermic reduction and washing both samples demonstrate high degree of crystallinity with Si and Mg2SiO4 formation. FTIR spectroscopy study reveals SiO2 presence in both samples. The reduction of fumed silica comes amid powder sintering and particle agglomeration as well as larger interaction of MgO and SiO_2 compared to the TEOS-derived synthesized precursor. The yield of Si for S sample is about twice higher compared to C (69% and 33,5% respectively).
3. Both C and S samples demonstrate close ICE more than 70%. C sample shows higher specific capacity but worse cycling stability of 72% compared to S sample with 98%.

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