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Chemical Bonding and Physical Trapping of Sulfur in Mesoporous Magnéli Ti_4O_7 Microspheres for High-performance Li-S Battery

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Abstract:

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Various host materials have been investigated to address the intrinsic drawbacks of lithium sulfur batteries (LSBs), such as the low electronic conductivity of sulfur and inevitable decay in capacity during cycling. Besides the widely investigated carbonaceous materials, metal oxides have drawn much attention because they form strong chemical bonds with the soluble lithium polysulfides. Here, mesoporous Magnéli Ti_4O_7 microspheres were prepared via an *in-situ* carbothermal reduction that exhibited interconnected mesopores (20.4 nm), large pore volume ($0.39 \text{ cm}^3 \text{ g}^{-1}$) and high surface area ($197.2 \text{ m}^2 \text{ g}^{-1}$). When the sulfur cathode was embedded in a matrix of mesoporous Magnéli Ti_4O_7 microspheres, it exhibited a superior reversible capacity of $1317.6 \text{ mAh g}^{-1}$ at moderate current (C/10) and a low decay in capacity of 12 % after 400 cycles at C/5. Strong chemical bonding of the lithium polysulfides to Ti_4O_7 , as well as effective physical trapping in the mesopores and voids in the matrix, were considered responsible for the improved electrochemical performance. A mechanism of the physical and chemical interactions between mesoporous Magnéli Ti_4O_7 microspheres and sulfur is proposed based on systematic investigations.

Introduction

Rechargeable batteries with high energy density and long cycle life are highly sought-after for electric vehicles and large-scale energy storage systems, such as smart grids.^[1] The lithium-sulfur battery (LSB) has attracted considerable attention due to its high specific capacity of 1675 mAh g^{-1} , which is based on the redox reaction that converts sulfur to lithium sulfide (Li_2S) reversibly via various intermediate lithium polysulfides (Li_2S_n , $n = 2-8$).^[2] This and the abundance of low-cost sulfur makes the LSB one of the more promising future battery technologies.^[2b, 3d, 3] However, commercialization of LSBs has generally been hampered by low sulfur utilization and poor long-term cyclability. This is due to the poor conductivity of the pristine sulfur, large volumetric expansion during the discharge process (80 % volumetric expansion from S to Li_2S), high solubility of the lithium polysulfides and passivation of the reactive surface of the metallic lithium anode.^[2d, 4] Dissolution of lithium polysulfides triggers capacity loss via the so-called ‘shuttle effect’ during cycling, which lowers the Coulombic efficiency (CE) of the cell. This problem can be addressed, in part, by producing a cathode in which the sulfur is encapsulated.^[5]

To tackle these issues, novel host materials have been developed for the sulfur cathode to limit the movement of the lithium polysulfides. These include various carbonaceous materials such as mesoporous carbon,^[3b, 6] porous carbon capsules,^[7] graphene,^[8] conductive polymers (such as polypyrrole^[9] and polyaniline^[10]), and carbon interlayers.^[11] While carbonaceous host materials on the cathode all give the desirable properties of low density and high electronic conductivity, the non-polar nature of the carbon surface offers limited attraction to the polar lithium polysulfides. Therefore, while improved electrochemical performance can be achieved with the available carbonaceous materials, the general reliance on physical trapping and/or weak chemical bonding limits the level of sulfur loading.^[8b] Furthermore, modest improvements have been realized through different morphologies of the carbonaceous materials. Hierarchically porous nanostructures interconnected with conductive walls such as microspheres composed of graphene and nanotubes, demonstrated enhanced entrapment of lithium polysulfides.^[8c, 12] Overall, even the best carbonaceous host materials do not appear likely to meet the ultimate demands of LSB technology.

A number of inorganic oxides have attracted research attention as cathode additives due to the prospect of providing superior chemical bonding with lithium polysulfides.^[13] For instance, SiO_2 ,^[14] TiO_2 ,^[15] Al_2O_3 ,^[16] V_2O_5 ,^[17] and Co_3O_4 ,^[17] in a variety of forms, have been investigated to restrain the capacity loss associated with the dissolution of lithium polysulfides during cycling, known as the 'shuttle effect'.^[2c, 5a, 18] Among these, Ti-based materials are particularly promising additives to the cathode, as electronic conductivity can be maintained for various morphologies and porosities.^[3c, 4a] Recently, hollow TiO_2 microspheres in a close-packed matrix have been successfully implemented to bind sulfur within the cathode for improved performance and long-term cycling.^[15b] A TiO_2 /graphene interlayer has been prepared, that delivered a high reversible cathode capacity of 1040 mAh g^{-1} over

300 cycles at C/2.^[19] However, while this and other studies demonstrated some improvements, significant loss of capacity was inevitable, due to the lithium polysulfides dissolving, especially in long term cycling at high sulfur loading.^[8c, 12c] One interpretation of this results is that stoichiometric TiO₂ has only a limited capacity for strong interaction with polysulfide species.

Some special titanium sub-oxides (so-called ‘Magnéli phase’, Ti_nO_{2n-1} (3 < n < 10)) have been noted to have high electronic conductivity, due to regular oxygen vacancies in the lattice.^[20] Similar to edge-shared TiO₆ octahedra in rutile, there is periodic shearing every n^{th} octahedron derived from the reduction of Ti.^[20a, 20b, 21] The resultant unsaturated Ti³⁺ centers in the crystal lattice of the suboxide could provide sites with high affinity for sulfur and lithium polysulfides.^[22] A study in which Ti₄O₇ nanotubes were incorporated into the sulfur cathode revealed excellent cycling performance (0.012 % capacity decay per cycle at C/2), which was ascribed to a strong chemical affinity between sulfur and the sub-oxide.^[22b] Due to lattice transitions at high temperature, nanotubes reduced by hydrogen are inclined to form aggregates which are detrimental to the electrochemical performance. Moreover, the nanotube aggregates are open structures and therefore do not playing a role in trapping lithium polysulfides during cycling. Notably, optimized morphologies with high surface area and more complex packing should endow the cathode materials with enhanced properties, such as superior capacity and prolonged cyclability.

In this work, mesoporous Magnéli Ti₄O₇ microspheres were prepared via an *in-situ* carbothermal reduction. The synergistic effect of high conductivity with the capability of binding lithium polysulfides, together with tailored mesoporosity, allows a sulfur cathode hosted on Magnéli Ti₄O₇ to deliver unrivalled performance. As a result, the mesoporous Magnéli Ti₄O₇ microspheres with a large specific surface area (197.2 m² g⁻¹) and high specific pore volume (0.39 cm³ g⁻¹) greatly facilitate

lithium ion diffusion. Due to their affinity for sulfur species, these active LSB cathode materials containing up to 70 wt% sulfur exhibited a high discharge capacity, even at elevated rates (1317.6 mAh g⁻¹ at C/10 and 861.0 mAh g⁻¹ at 2C), along with an excellent long-term cycling performance (< 1 % capacity fading over 250 cycles at C/5). In addition to the characterization of the porous structure and electrochemical properties, energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the strong Ti₄O₇-lithium polysulfides interaction, and a mechanism for high retention during cycling was proposed based on cryoSEM results.

Results and discussion

The Magnéli Ti_nO_{2n-1} phases are a homologous series of sub-stoichiometric compositions of titanium oxides between TiO₂ and Ti₂O₃.^[20a, 20b] Among these, Ti₄O₇ has been employed as a thermal electronic material due to its high conductivity, resistance to acids and thermal stability.^[23] It has already been demonstrated that Ti_nO_{2n-1} nanoparticles can chemically bond with lithium polysulfides.^[22a, 22b] For the first time, we have combined this effect with a porous hierarchical morphology, with large mesopore diameter, that could provide enhanced diffusion of lithium ions. The polymeric precursor (resol) was infiltrated into pre-made mesoporous TiO₂ microspheres and then reduced to mesoporous Ti₄O₇ microspheres via an *in-situ* carbothermal reduction that did not destroy the porous structure (**Scheme 1**).

Scheme 1. Schematic representing resol infiltration into mesoporous anatase TiO_2 microspheres to produce mesoporous Magnéli Ti_4O_7 microspheres via an *in-situ* carbothermal reduction. Sulfur impregnates the mesopores and forms particles in the voids between microspheres.

The molar ratio of $\text{TiO}_2\text{:C}$ in the preparation of the different samples (MM- x , where x indicates the volume of resol solution in mL used during synthesis) were roughly 3:1 for MM-0.5, 3:2 for MM-1, and 3:4 for MM-2. The more carbon precursor impregnated in the mesoporous TiO_2 microspheres could lower the n value in the final Magnéli $\text{Ti}_n\text{O}_{2n-1}$ phase, which has been demonstrated in a previous report.^[22d] The morphology and crystal structure of rutile TiO_2 microspheres (RM) and Magnéli Ti_4O_7 microspheres were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), **Figure 1**. After carbothermal reduction at high temperature, the microspheres maintained a particle diameter of 2 μm without appreciable destruction and shrinkage, compared with RM (**Figure 1a and c**). The coarse surface of MM-1, determined by the packing of crystals of ~ 100 nm in diameter, was clearly observed (**Figure 1d**). Internal porosity was shown from the cross-section view of the Ti_4O_7 microsphere (**Figure S1b**), revealing the presence of mesopores across Ti_4O_7 microsphere. The reaction between TiO_2 and the carbonized polymer in the microspheres resulted in complete conversion at high temperature of the

TiO₂ to Ti₄O₇ crystals, the crystal size being larger than that of the raw material. When a lower proportion of resol was used the microsphere structure was not retained (MM-0.5 in **Figure S1a**), whereas when the resol portion was doubled, similar morphologies were achieved (MM-2 in **Figure S1c**). A small crystal from the MM-1 sample in the form of an octagon shaped nanoparticle of 40 nm in size, surrounded by amorphous carbon derived from resol is seen in the TEM image (**Figure 1e**). The high-resolution TEM image in **Figure 1f** reveals the crystalline Magnéli Ti₄O₇ with a d-spacing of 4.2 Å, which was indexed to the (10 $\bar{2}$) plane. This was confirmed by selective area electron diffraction (SAED) of the same region (**Figure S1d**).

Figure 1. SEM images of a, b) mesoporous rutile microspheres (RM), and c, d) mesoporous Ti_4O_7 microspheres (MM-1). e) TEM images of a Ti_4O_7 crystal in MM-1 and f) HRTEM image of the same crystal.

To identify the carbonaceous content of the different MM-x samples, thermogravimetric analysis (TGA) was conducted under an oxygen atmosphere (**Figure S2a**). The small mass loss below 100 °C was attributed to absorbed water in the porous structure, and the weight gain from 200 °C to 400 °C attributed to synergy effect of Ti^{3+} oxidation (**Figure S2b**). The mass loss between 400 °C and 550 °C was attributed to the decomposition of carbon (with some mass gain occurring due to Ti^{3+} oxidation),^[24] which amounted to 5, 12, and 21 wt% of MM-0.5, MM-1, and MM-2, respectively. The approximate carbon content of the composites was calculated as 8.1, 16, and 25 wt% of MM-0.5, MM-1, and MM-2, respectively, as shown in the Supporting Information (page S3).

X-ray powder diffraction (XRD) patterns indicated that Magnéli Ti_4O_7 (JCPDS Card No. 50-787) was the main crystal phase in MM-1 and MM-2 (**Figure 2a**). The rutile phase (JCPDS Card No. 21-1276) was observed for RM, which was produced after the same calcination treatment of the mesoporous anatase microspheres that had not been infiltrated with resol. The Magnéli Ti_6O_{11} phase (JCPDS Card No. 50-788) was obtained when a lower proportion of resol was used (MM-0.5 in **Figure S2c**). The crystallite size of MM-1, calculated using the Scherrer equation and the strongest Magnéli Ti_4O_7 peak at 26.3°, was 60 nm which is larger than that of RM (42 nm). Although the cross-linked carbon framework can retain the porous structure and spherical morphology, obvious crystal growth occurs from elemental transfer at high temperature. No diffraction pattern for graphitic carbon was

observed, implying that only amorphous carbon was formed at 1000 °C without a catalyst.^[25] With a higher proportion of resol, the Magnéli Ti_4O_7 content increased slightly. Magnéli Ti_5O_9 (JCPDS Card No. 51-641) and anatase TiO_2 (JCPDS Card No. 21-1272) peaks were revealed in the Rietveld refinement of MM-1 and MM-2 XRD patterns (**Figure S2d and e**).

After infiltration of resol precursor, nitrogen gas sorption isotherms (**Figure S2f**) of the TiO_2 /resol mixtures (TiO_2 /resol-*x*) were measured, and the very low surface area ($< 0.01 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($< 0.001 \text{ cm}^3 \text{ g}^{-1}$) of the resulting samples indicated that mesopores of the anatase microspheres were successfully filled with resol precursors. Nitrogen sorption isotherms (**Figure 2b**) of RM and MM-*x* samples exhibited type IV absorption behavior with a sharp capillary condensation step at $P/P_0 = 0.8\text{--}0.9$ and H1 type hysteresis loops that are typical of mesoporous materials with large spherical pores.^[26] Compared with the low microporous absorption below $P/P_0 = 0.2$ of RM, the MM-*x* samples exhibited higher microporous absorption. The hysteresis loop at $P/P_0 = 0.5\text{--}0.8$ revealed the corresponding distribution of small mesopores formed in the MM-*x* samples during calcination. The pore size distributions (calculated from the adsorption branch based on the BJH model) of RM, MM-1 and MM-2 centered at 20.4 nm, 20.9 nm and 18.0 nm, respectively (**Figure 2c**). Both MM-1 and MM-2 contained mesopores less than 10 nm, likely due to the carbonaceous material formed during the carbothermal reduction. Owing to the hierarchical mesoporous features, MM-1 exhibited the highest surface area ($197.2 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.39 \text{ cm}^3 \text{ g}^{-1}$); the corresponding V-t plot analysis (**Figure S3**) revealed that the mesopores contributed $160 \text{ m}^2 \text{ g}^{-1}$ (81.1 %) towards the total surface area (**Table 1**). Additionally, the pore volume of MM-1 was primarily attributed to the mesopores (95.5 %). A higher carbon content distributed in the Magnéli Ti_4O_7 framework of MM-2 led to a smaller mesopore contribution to surface area and pore volume (**Table**

1). Mesoporous microspheres with high surface area and pore volume can be obtained by carbothermal reduction; however, residual carbon infiltrated in the Ti_4O_7 framework will partially fill or block the porous structure.

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Figure 2. a) XRD patterns of RM, MM-1, and MM-2. b) Nitrogen sorption isotherms of RM, MM-1, and MM-2. c) Pore size distribution of RM, MM-1, and MM-2 determined by BJH analysis.

Table 1. Physical properties of RM, MM-1 and MM-2.

Sample	PD ^{a)} (nm)	S _{total} (m ² g ⁻¹)	S _{meso} ^{b)} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{meso} ^{c)} (cm ³ g ⁻¹)
RM	20.4	63.4	60.6 (95.6 %)	0.34	0.34 (99.7 %)
MM-1	20.9	197	160 (81.1 %)	0.39	0.37 (95.9 %)
MM-2	18.0	174	117 (67 %)	0.27	0.23 (86.7 %)

a) Peak of the pore size distribution; b) Contribution of surface area from mesopores within total BET surface area; c) Contribution of pore volume from mesopores within total pore volume.

It has been demonstrated that oxygen defects in the Magnéli Ti₄O₇ have the capacity to adsorb oxide species.^[21-22] Given sulfur and oxygen are located in the same periodic table group, they have similar electron configurations and chemical bonding properties. Besides the enhanced chemical interaction, optimized morphology and porous structure of nanocrystalline Magnéli Ti₄O₇ should play a role in improving the electrochemical properties as a cathodic host material for LSB. Sulfur was impregnated into RM, MM-1, and MM-2, and the sulfur loadings were determined by TGA to be approximately 70 wt% for all composites (RM/S, MM-1/S, and MM-2/S) (**Figure S4a**). Nitrogen sorption isotherms of sulfur impregnated composites (labelled as RM/S, MM-1/S, and MM-2/S)

revealed extremely low absorbed volume, implying that the mesopores were almost completely impregnated with sulfur (**Figure S4b**).

The electrochemical behaviour of the mesoporous Magnéli Ti_4O_7 microspheres (MM-x) was first assessed with cyclic voltammetry (CV), as shown in **Figure S5**. MM-0.5 was not included in electrochemical characterization due to the destruction of the microsphere morphology. CV curves conducted from 1.5 to 3.5 V at scan rate of 0.05 mV s^{-1} were collected for the 1st and 5th cycle of the MM-x/S samples. The cathodic scan of MM-1/S indicated two reduction peaks and the onset reduction potentials started at around 2.3 and 2.1 V. This represents the conversion of high-order lithium polysulfides (Li_2S_x , $4 < x < 8$) to low-order lithium polysulfides (Li_2S_y , $2 < y < 4$) and further conversion to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively (**Figure S5a**). In contrast, the corresponding peaks of MM-2/S (**Figure S5b**) were at slightly lower potentials due to higher polarization of the electrodes. Different from a previous report of sulfur hosted by carbon,^[27] no reduction peak related to LiNO_3 decomposition (1.5–1.6 V) could be observed in the cathodic scan when in the presence of mesoporous Ti_4O_7 microspheres. Comparing the first, fifth, and 400th cycle obtained from MM-1/S (**Figure S5a**), the peaks were retained, without LiNO_3 decomposition, indicating enhanced reversibility of lithium polysulfides bonded to the Ti_4O_7 surface. Only one broad oxidation peak at 2.5 V was observed in the anodic scan of MM-x/S, presenting continuous conversion from $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ to high-order lithium polysulfides and ultimately to sulfur. Besides the main oxidation peak, shoulders were observed at higher voltage in the anodic scan of MM-x/S, which could be attributed to a higher energy barrier of Li_2S delithiation in the voids of the microspheres.^[28] The corresponding CEs of MM-x/S, calculated from CV scans, were 98 % for MM-1/S and 89 % for MM-2/S. CV curves at various

sweep rates are shown in **Figure S5**, where MM-1/S demonstrated lower polarization especially at high sweeping rate (2 mV s^{-1}).

The galvanostatic profiles of various composite electrodes were observed with two typical well-defined plateaus (**Figure 3a**), corresponding to the formation of high-order (2.3 V) and low-order (2.1 V) lithium polysulfides.^[22b] The charge/discharge profiles were obtained within cut-off voltages of 1.8–2.8 V and the voltage of the discharge plateaus corresponded to the peak voltages in the CVs mentioned above. The first-cycle capacities calculated from discharge curves at a moderate current of C/10 were 502 mAh g^{-1} , $1317.6 \text{ mAh g}^{-1}$, and $1198.8 \text{ mAh g}^{-1}$ for RM/S, MM-1/S, and MM-2/S, respectively (**Figure 3a**). From the galvanostatic results, the calculated CEs were 98 %, 98 %, and 89 % for RM/S, MM-1/S, and MM-2/S, respectively. The Nyquist plots of electrochemical impedance spectra (EIS) obtained from the electrodes are shown in **Figure 3b**. In general, the high frequency semicircle and the low frequency line can be ascribed to charge transfer resistance and Warburg impedance, respectively.^[22b] The electrolyte solution resistance (R_s) and charge-transfer resistance (R_{ct}) are compared according to the equivalent circuit shown in **Figure S5e**. The MM-1/S exhibited the lowest charge transfer resistance due to the high content of conductive Ti_4O_7 and hierarchical structure of the packed mesoporous microspheres. The large transfer resistance of RM/S and MM-2/S could be attributed to a higher resistance of TiO_2 and an amorphous carbon excess, respectively.

The dependence of charge/discharge capacity on rate for different samples showed a steady decrease from C/10 to 2C (**Figure 3c**). The average reversible capacities at 2C were 178.1 mAh g^{-1} for RM/S, 861.0 mAh g^{-1} for MM-1/S, and 425.1 mAh g^{-1} for MM-2/S. A dramatic loss in capacity for rates beyond 1C was not observed for the mesoporous Magnéli Ti_4O_7 microspheres (MM-1), that dramatic loss in capacity has been observed for mesoporous carbon foams,^[6] porous carbon

nanospheres,^[7a] and hollow carbon capsules.^[7b] A higher capacity at 2C was obtained for the Ti₄O₇ microspheres with larger surface area and pore volume (MM-1/S), as a result of the high electronic conductivity of Ti₄O₇ and fast mass transfer in the porous microsphere structure.^[2b] The initial discharge capacity of MM-1/S was 1198 mAh g⁻¹ and the capacity remained at ~1000 mAh g⁻¹ after 400 cycles at C/5, thus exhibiting excellent cyclability when compared with previous studies (**Figure 3d**).^[4, 5d, 12c] Remarkably, obvious decay only occurred after 250 cycles, indicating only 0.073 % decay per cycle between the 250th and 400th cycle. Given the development of an erratic voltage-time response, the limitation on cycle life appears to be ascribed to dendritic growth of the lithium anode.^[29] This indicates that even after several hundred cycles, the capacity of the cathode is essentially unchanged.

Figure 3. a) Voltage versus specific charge/discharge capacity profiles of the initial galvanostatic cycles of RM/S, MM-1/S, and MM-2/S at $C/10$. b) EIS profiles of fresh cells containing RM/S, MM-1/S, and MM-2/S, and c) Rate performance from $C/10$ to $2C$ of RM/S, MM-1/S, and MM-2/S. d) Cyclability with calculated CE of RM/S and MM-1/S at $C/5$. All capacities were calculated based on the sulfur mass. In c) and d), the open and solid markers represent charge and discharge capacities, respectively.

Figure 4a shows the XPS Ti 2p spectrum of the pristine Ti_4O_7 microspheres without sulfur loading.

Due to the inevitable oxidation of Ti^{3+} on the surface, only a small shoulder centered at 457.8 eV could be assigned to Ti^{3+} sites, overlapped partially by main Ti^{4+} peak.^[30] Due to more abundant active sites derived from the higher pore volume, surface area and Ti_4O_7 content of MM-1/S, it exhibited the highest electrochemical capacity. To investigate the interaction between lithium polysulfides and MM-1/S further, XPS spectra were obtained for samples of the electrode that had been galvanostatically discharged to 1.8 V. Because of sensitivity to ambient air and moisture, discharged cells were disassembled in an argon-filled glovebox. The Ti 2p spectrum in **Figure 4b** shows two characteristic peaks of Ti_4O_7 at 458.8 and 464.6 eV.^[23a] The small shoulder at 457.4 eV could be indexed to the Ti-S bond in the composite.^[29] In the S 2p spectrum (**Figure 4c**), various sulfur-related environments could be observed. Strong peaks at 170 eV and 164 eV were assigned to sulfate, probably from residual electrolyte, and lithium polysulfides of various chain lengths, respectively.^[29] Peaks centred at 162 eV could be attributed to S in metal sulfide (Ti-S), which matched well with the corresponding peaks in the Ti 2p spectrum.^[29] In addition, peaks around 165 eV were attributed to the S-S bridge in lithium polysulfides. Corresponding peaks derived from the Ti-S bond in the Ti 2p and S 2p spectrum after discharge demonstrated the existence of bonds between lithium polysulfides and the low coordinated Ti of Magnéli Ti_4O_7 .

Previous research has shown that sulfur, especially in the nanoscale form, is very volatile under electron beam irradiation and therefore the accurate elemental content is difficult to determine.^[32] CryoSEM images (**Figure 5**) of electrodes were obtained at -140 °C to hinder evaporation of sulfur under irradiation of the electron beam. The theoretical Ti:S atomic ratio (0.39) in mesoporous Magnéli Ti_4O_7 microspheres (MM-1/S) was calculated according to the total pore volume and values

of density for Ti_4O_7 and S (**Table S1**). EDS results taken in different areas of the samples showed that the atomic ratio of Ti/S inside the microspheres was 0.41 (site 1 in **Figure 5a**), while S was also observed outside the microspheres (site 2 in **Figure 5a**). After 400 cycles, the morphology of the electrode samples taken in the charged state was relatively similar to the initial state, and the atomic ratio of Ti/S (0.43) barely changed (**Figure 5a and b**). Micrometer-sized sulfur remained in and wrapped around the microspheres due to strong chemical bonding and physical entrapment. Because little change was observed in the Ti/S ratio in the microspheres during cycling, sulfur and its soluble intermediates were trapped successfully within the confines of the mesopores and within the voids formed between microspheres (**Figure S6a and b**). In addition, the elemental

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Figure 4. a) Ti 2p XPS spectrum of as-prepared mesoporous Ti_4O_7 microspheres (MM-1), b) Ti 2p XPS spectrum and c) S 2p XPS spectrum obtained from fully discharged MM-1/S (1.8 V).

Figure 5. CryoSEM images and corresponding EDS spectra of MM-1/S from fully charged cells a) before and b) after 400 cycles at C/5. Red rectangular frames in SEM images mark different EDS sites on microspheres (sites 1 and 3) or sulfur particles in the void (sites 2 and 4). Ti/S ratios are shown.

distribution across the microspheres and voids demonstrated periodic change in Ti and S content (Figure S6c and d).

TGA under nitrogen flow and slow ramping rate ($3\text{ }^{\circ}\text{C min}^{-1}$) of the cathode materials before and after cycling are shown in **Figure S7**. Pristine sulfur mixed with super P carbon and PVDF evaporated at $260\text{ }^{\circ}\text{C}$, whereas when encapsulated in mesoporous Ti_4O_7 microspheres evaporated at higher temperature ($300\text{ }^{\circ}\text{C}$) due to the strong chemical bonding with the sub-oxide surface and entrapment in mesopores. Remarkably, evaporation of the as-prepared and cycled cathode materials showed a two-step mass loss in the TGA curves, which could be attributed to sulfur and lithium polysulfides absorbed in the electrodes.^[33] The sulfur content derived from mass loss before $400\text{ }^{\circ}\text{C}$ was 55 wt% on the fresh electrode, coinciding well with theoretical calculation (56 wt%). After 400 cycles, there was a 10 wt% sulfur loss from the electrode, which is consistent with the capacity loss derived from the electrochemical characterization (**Figure 3d**).

The mechanism of interaction between mesoporous Ti_4O_7 microspheres and S during cycling is proposed in **Figure 6**. Top-view (**Figure 6a-c**) and cross-section images (**Figure 6d-f**) of the fresh electrodes, and corresponding electrodes in the charged/discharged state were obtained. Initially, it can be seen that micrometer-sized sulfur formed irregular shaped particles and was located in the microsphere voids (**Figure 6a and d**). After being fully charged, sulfur particles have deposited on the exterior of the microspheres, presumably due to the high electronic conductivity and porosity of the Ti_4O_7 microspheres providing pathways for both electron flow and electrolyte diffusion (**Figure 6b and e**). During the discharge process, the SEM images strongly suggest that swelling within the electrode as sulfur is converted to Li_2S (**Figure 6c and f**). Despite the large volumetric expansion, the integrity of the electrode coating is preserved, without any sign of cracking (**Figure S8**), implying that the voids formed between the microspheres are able to accommodate this expansion. Besides strong chemical bonding provided by Ti_4O_7 , the large mesopores and abundant voids in the Ti_4O_7

microspheres show excellent stability despite the volumetric changes of the sulfur species during long-term cycling.

Figure 6. SEM images of MM-1/S in a, d) a fresh electrode, b, e) a fully charged and c, f) a fully discharged electrode in a-c) top-view and d-f) cross-section-view. g) Schematic representation of the active electrode materials during the charge/discharge process demonstrating the morphological transition of mesoporous Ti_4O_7 microspheres and sulfur particles in the voids.

Conclusion

A cathode host for LSBs, based on a packed ensemble of mesoporous Magnéli Ti_4O_7 microspheres, is capable of delivering outstanding levels of performance, in terms of discharge capacity, cycle-life and rate-performance. The synthesis approach combines mesoporous anatase TiO_2 microspheres with a soluble polymer (resol, carbon source for *in-situ* carbothermal reduction) to produce mesoporous Magnéli Ti_4O_7 microspheres with large mesopore (~ 20 nm), high specific surface area (~ 200 m^2 g^{-1}), and pore volume (~ 0.4 cm^3 g^{-1}). These physical properties permit up to 70 wt% loading with sulfur, with the resulting electrodes having a discharge capacity around 1320 mAh g^{-1} at moderate current density, with excellent capacity retention (88 % after 400 cycles).

Characterization of the cathode material before and after charge-discharge shows that the packed matrix of Magnéli Ti_4O_7 microspheres provides a highly optimised physical network for efficient electrode operation, and the chemical characteristics of the sub-oxide surface also enhance the trapping of sulfur species through specific Ti-S interactions. The porosity and conductivity of these electrodes support charging and discharging up to relatively high rates, with the additional feature of a strong interaction between the host surface and lithium polysulfides that promotes the redeposition of S during the charging phase. The features of these materials improve the long-term cyclability and high rate performance when applied in LSBs.

Experimental Section

Chemicals: Titanium (IV) isopropoxide (TIP, 97 %), hexadecylamine (HDA, 90%) and sulfur powder (99.98 %) were purchased from Sigma-Aldrich. Phenol crystals (AR), 1-butanol (99.8 %), absolute ethanol (> 99.5 %), formaldehyde aqueous solution (25 wt%, AR), sodium hydroxide (NaOH, AR)

were purchased from Chem-Supply. Hydrochloride solution (HCl, 32 wt%) and ammonia aqueous solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt%) were purchased from Merck. Ammonium chloride (NH_4Cl , AR) came from BDH, and carbon disulfide (CS_2 , reagent grade) from Scharlau. All chemicals were used as received. The water used was collected from a Milli-Q Millipore academic purification system with a resistivity higher than $18.2 \text{ M}\Omega \cdot \text{cm}$.

Synthesis of Resol: The resol precursor ($\text{MW} < 500$) was prepared according to previous report.^[25] In a typical synthesis, phenol (0.61 g) was melted at 42°C in a flask and mixed with aqueous NaOH solution (0.13 g, 20 wt%) under stirring. Formaldehyde solution (1.05 g) was added dropwise and the mixture was stirred for 1 h at 75°C . After cooling to room temperature, the pH of the solution was adjusted to 7 with aqueous HCl (2 M). The solvent was removed by vacuum evaporation at 45°C . The final product, denoted as resol solution, was dissolved in ethanol (50 wt%), and NaCl was collected by centrifugation.

Synthesis of Mesoporous Anatase TiO_2 Microspheres: Amorphous TiO_2 microspheres were prepared in 1-butanol via a sol-gel procedure with HDA as structure directing agent.^[34] Typically, HDA (11.92 g) was dissolved in 1-butanol (600 mL) at room temperature, followed by the addition of aqueous NH_4Cl solution (4.8 mL, 0.1 M). Under intense stirring, TIP (13.57 mL) was added quickly and stirred for 1 min. The solution was kept static for 18 h, then the white precipitate was collected by centrifugation and washed 3 times with ethanol. Finally, the amorphous microspheres were dried at room temperature.

A solvothermal treatment was performed to prepare mesoporous anatase TiO_2 microspheres with highly crystalline framework. Typically, amorphous TiO_2 microspheres (3.2 g) were dispersed in a

mixed solution of ethanol (40 mL), water (20 mL) and ammonia solution (2 mL), and stirred for 30 min at room temperature. The mixture was heated in a Teflon-lined autoclave (100 mL capacity) at 160 °C for 16 h. Mesoporous anatase TiO_2 microspheres were obtained after calcination at 550 °C for 4 h in air.

Synthesis of Mesoporous Magnéli Ti_4O_7 Microspheres: Mesoporous Magnéli Ti_4O_7 microspheres (MM-x) were prepared by a thermal reduction procedure. Mesoporous TiO_2 microspheres (0.8 g) were dispersed in resol solution (50 wt%, x mL) and stirred at room temperature until all solvent evaporated. The resol/microspheres mixture was thermopolymerized at 100 °C for another 24 h, and then calcined at 1000 °C in argon for 6 h (ramping rate of 5 °C min⁻¹). The final products were denoted as MM-x, where x was the volume of resol solution. That is, for MM-0.5, 0.5 mL of resol solution (50 wt% resol) was added to the mesoporous TiO_2 microspheres (0.8 g). Pristine mesoporous rutile TiO_2 microspheres, denoted as RM, were calcined following the same procedure but without prior polymer infiltration.

Loading S in Mesoporous Magnéli Ti_4O_7 Microspheres: To infiltrate sulfur into the mesoporous microspheres, S solution (6 mL, 0.25 g mL⁻¹ in CS_2) was added to the microsphere powder (0.5 g) so that the MM-x/S weight ratio was 1/3, then the CS_2 was evaporated with continuous stirring. The dried mixture was sealed in a Teflon-lined autoclave (30 mL capacity) and heated at 155 °C for 24 h to obtain the final composites which were labelled as MM-x/S and RM/S.

Material Characterization: Morphology characterization was performed on an FEI Quanta 200F environmental scanning electron microscopy (SEM) at an accelerating voltage of 15 kV and without Au coating in order to study sample morphology, while EDS was performed using an INCA SDD X-ray

microanalysis system. TEM and high resolution TEM (HRTEM) were conducted on an FEI Tecnai F20 transmission electron microscope operating at 200 kV. Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance Diffractometer using Cu K α radiation. The diffractometer was set at a 40 kV working voltage and 40 mA working current, with samples scanned from 5° to 80° 2 θ . TGA was conducted on a Mettler Toledo TGA/SDTA851^e thermogravimetric analyser heating from 25 °C to 900 °C at a ramp of 3 or 10 °C min⁻¹ under a flow of oxygen or nitrogen (30 mL min⁻¹). Nitrogen sorption isotherms were measured at -196 °C using a Micromeritics TriStar 3000 Surface Area and Porosity Analyser. Prior to measurement, calcined samples were degassed at 150 °C for at least 8 h on a vacuum line. The specific surface areas were calculated by a standard multipoint Brunauer-Emmett-Teller (BET) method using adsorption values in the range $P/P_0 = 0.05\text{--}0.20$. The Barrett-Joyner-Halenda (BJH) model was applied to the adsorption branch of the isotherm to determine pore size distributions, and total pore volume (V_{total}) was estimated from the adsorbed amount at $P/P_0 = 0.983$. The mesopore volume (V_{meso}) and mesopore surface area (S_{meso}) were calculated by the V-t plot method using the equation $V_{meso} = 0.001547I$, representing the ordinate axis intercept on the V-t plot. The t values were calculated as a function of the relative pressure using the de Bore equation, $t = [13.99/(0.034 - \log(P/P_0))]^{1/2}$. The X-ray photoelectron spectrometer (XPS) data were recorded on a VG ESCALAB 220i-XL spectrometer equipped with a twin crystal monochromated Al K α X-ray source, which emitted a photon energy of 1486.6 eV at 10 kV and 22 mA. The C 1s peak at 285 eV was used as a reference for the calibration of the binding energy scale.

Electrochemical measurements: Electrochemical experiments were evaluated by testing CR2032 type coin cells. Working electrodes with S loading (0.4 ~ 0.6 mg cm⁻²) were prepared by mixing 80 wt% of active materials (MM-x/S or RM/S), 10 wt% of carbon black (Super P, TIMCAL) and 10 wt% of

polyvinylidene fluoride (PVDF, Aldrich) dissolved in N-methyl-2-pyrrolidinone (NMP, 99 %, Aldrich). The homogeneous slurry was coated onto etched aluminium foil (30 μm thickness, JCC Co. Ltd.) and dried at 50 $^{\circ}\text{C}$ for 24 h in vacuum. Coin cells were assembled in the argon-filled glove box using lithium as the counter electrode. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI, 1M) dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with LiNO_3 additive (0.2 M) was used as the electrolyte, and the polypropylene membrane (7P09B, SOLUPOR[®], Lyndall) as the separator. Galvanostatic cycling was carried out using the Maccor battery test system (series 4000) with the potential ranging from 1.8 to 2.8 V versus Li/Li^+ at room temperature. The current rate values were based on the theoretical capacity of sulfur (1C equals to 1672 mA g^{-1}). Specific capacity values were calculated based on the mass of sulfur in the samples, which was determined using TGA. Electrochemical impedance spectroscopy (EIS) measurements were carried out on the Solartron frequency response analyzer (model 1255b) with the frequency ranging from 10 Hz to 100 kHz. Cyclic voltammetry (CV) was conducted on the Solartron battery test unit (model 1470) at different sweeping rates (0.05–2 mV s^{-1}) and between cut off voltages of 1.5–3.5 V (vs. Li/Li^+).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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The table of contents: Mesoporous Magnéli Ti₄O₇ microspheres were synthesized by an *in-situ* carbothermal reduction. The microspheres have a large mesopore diameter and high surface area, allowing up to 70 wt% sulfur loading. As host material of sulfur, composite microspheres showed a high discharge capacity (1320 mAh g⁻¹) and long-term cyclability (12 % fading after 400 cycles).

Keyword: mesoporous materials, lithium sulfur battery, high capacity, long cyclability, Magnéli phase

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