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Collaborative project

Nanomaterials for future generation Lithium-Sulfur batteries

Funded by Bundesministerium für Wirtschaft und Technologie (BMWi)

Beneficiary: Dresden, University of Technology Department for Inorganic Chemistry I	Reference number: 01MX12011
Title of the project: Nanomaterials for future generation <u>L</u> ithium <u>S</u> ulfur batteries (MaLiSu) Title of the subproject: Nanostructured carbons for carbon-sulfur nanocomposites	
Project manager: Prof. Dr. Stefan Kaskel	Phone.: Fax: Email: Stefan.kaske@chemie.tu-dresden.de
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Project partner:

1. University Dresden
2. Fraunhofer IWS, Dresden
3. SGL Carbon GmbH, Meitingen
4. Uppsala University, Sweden
5. Varta Micro Innovation GmbH, Graz, Austria

Content

I. Summary

1. Aim and objectives

One approach to significantly enhance the energy density of state-of-the-art lithium ion batteries is the lithium sulfur system (Li/S). Sulfur as the active cathode material has a theoretical specific capacity of 1672 mAhg^{-1} (considering the reaction of S^0 to S^{2-}) and a discharge potential of 2,2 V using lithium anodes. While for lithium ion batteries using intercalation cathodes a limit in energy density of about 200 Whkg^{-1} is expected, for the lithium sulfur battery energy densities of up to 600 Whkg^{-1} might be in reach. Safety and costs also can be improved as sulfur is available, less expensive and less toxic when compared to cobalt based cathodes. However, various challenges are connected to the lithium sulfur cell chemistry, which need to be solved within systematic studies and by the development of new material concepts. Following effects negatively affect the cycle stability and efficiency of Li/S-batteries:

- Low electric and ionic conductivity of sulfur
- Solubility of polysulfides in common electrolytes leading to the “shuttle” mechanism
- Low stability of lithium metal anodes (dendrite formation)

In this proposed project, these effects will be addressed and a lithium sulfur battery with significantly improved properties will be developed. Key aspects are

- Carbon materials with defined pore structure in the nanometer regime as conductive and stabilizing framework for the sulfur cathodes
- Polymer electrolytes to reduce the “shuttle” mechanism
- Coating of lithium anodes to reduce the dendrite formation

Besides fundamental studies on mechanisms and material research, the project aims for a potentially fast transfer of the results to industrial realization.

Objectives:

Full cell concept

Main objective is the development of a new full cell concept for a next generation lithium sulfur battery with significantly enhanced properties. Prototype cells with energy densities larger than 400 Whkg^{-1} and cycle life over **hundreds of cycles** are expected as a result of this project.

To reach this goal, close cooperative work on different components of the battery cells is necessary. Most important aspects are the material chemistry of the sulfur cathode and the electrolyte system to be combined with lithium anodes.

Role of nanostructure in carbon materials for sulfur nanocomposite cathodes

Nanomaterials most likely play an important role as carrier to contact and stabilize the sulfur species during charging and discharging processes. One aim is to study the influence of pore geometry of **porous carbons** (with pores in the nanometer regime) on the performance of carbon / sulfur composites. Micropores are expected to reduce the dissolution of lithium polysulfide species, causing the shuttle mechanism, while mesopores may enhance the ionic transport and thereby the rate capability. Highly conductive carbons will be studied as additive to enhance the electric conductivity and thereby, the rate capability of the cathode. **Carbon nanotubes** are most promising for this purpose due to the unique electrical properties and the large aspect ratio.

Processing electrodes

Not only the materials but also reliable and scalable processes need to be developed in order to provide a technology towards future generation battery production. Roll-to-roll processing of the desired nanocomposite materials including paste formulation, coating and calendaring will be major objectives. Cathodes with stable capacities of **600 mAhg⁻¹ (mass of sulfur)**, stability over at least **50 cycles** and a **rate capability of 0,5 C** are targeted as a result of the project.

Polymer electrolytes

The nature of the electrolyte has a drastic effect on electrochemical behaviour of the sulfur electrodes in the Li/S battery (e.g. shape of the capacity curves, length of the first vs. second plateau). Recent progress, however, in the field of electrolyte formulation moving away from the use of non-aqueous multicomponent liquid electrolytes to gel polymer membranes, has revived the whole Li/S battery area. In general, it is lithium sulfide saturated electrolytes combined with polymers/gels that provide a physical barrier that appears to minimize problems such as the solubility of sulfide anions and capacity fade. PEO-systems with Litriflate or LiTFSI salts in the matrixes are shown to be promising. The target in this project is a polymer/gel electrolyte with a **conductivity in the order of 10⁻⁴ S cm⁻¹**.

2. Preconditions and starting point for the project

In this project, the group of Prof. S. Kaskel at TUD was responsible for the synthesis and characterization of nanostructured carbons with defined pore geometry as well as their sulfur composites (WP 1.1, 1.3 and 1.4). In the beginning of the project, the group had over 40 staff members focused its research on synthesis and characterization of porous and nanostructured materials for energy storage applications. At this time, nanoporous materials thereby were applied in gas storage and in electrode materials, mostly for Supercaps. Materials with specific surface areas of over 4000 m²/g (DUT-n (Dresden University of Technology)) are a highlight example of the research results. The group was already working in different projects on carbon-based electrodes for supercapacitors and Li/S batteries. Sulfur/carbon composite cathodes with specific capacity of 900 mAh/g were already demonstrated in cooperation with Fraunhofer IWS.

Additionally, the group was involved in the proposal named "WING-Zentrum: Batterie - Mobil in Sachsen - BamoSa" to be funded by the German Federal Ministry of Education and Research (planned: 01.05.2012 – 30.03.2015, and finally actually approved: 1.6.2013-30.5.2016) and "Basta - Batterie stationär in Sachsen" planned and approved for the period 11/2012-10/2015. At this time, Prof. Dr. S. Kaskel was author of over 160 publications with key aspects of his research activities being metal organic frameworks (MOF), porous carbons and nanocomposites. In personnel unity he led and is leading a group of over 40 staff members at TUD as well as the department "chemical reaction and surface technologies" at Fraunhofer IWS. He was and still is responsible for various research programmes and large scale projects within his research activities.

3. Work-, time- and cost-plan

In the first phase of the project, material development will be done on carbon/sulfur composite cathodes and polymer electrolytes. First reliable results for a decision on the continuation of the proposed material approach are expected for MS 1 (M9). In an iterative process, materials will be optimized in terms of electrochemical performance (WP 1, WP 3 and WP 4). Tasks within WP 2 (electrode processing), WP 3 and WP 4 are necessary to bring the results to the next level: a running, scalable and balanced full cell configuration. After the selection of a material combination at MS 2 (M15), components and cells will be optimized until MS 3 (M27). The last step of the project is to concentrate on demonstration of the results. Selected components will be produced and integrated into demonstrator cells. Evaluation of the cells

against state of the art energy storage devices will be performed within the last period of the project and will be finished by the successful demonstration in MS 4 (M36).

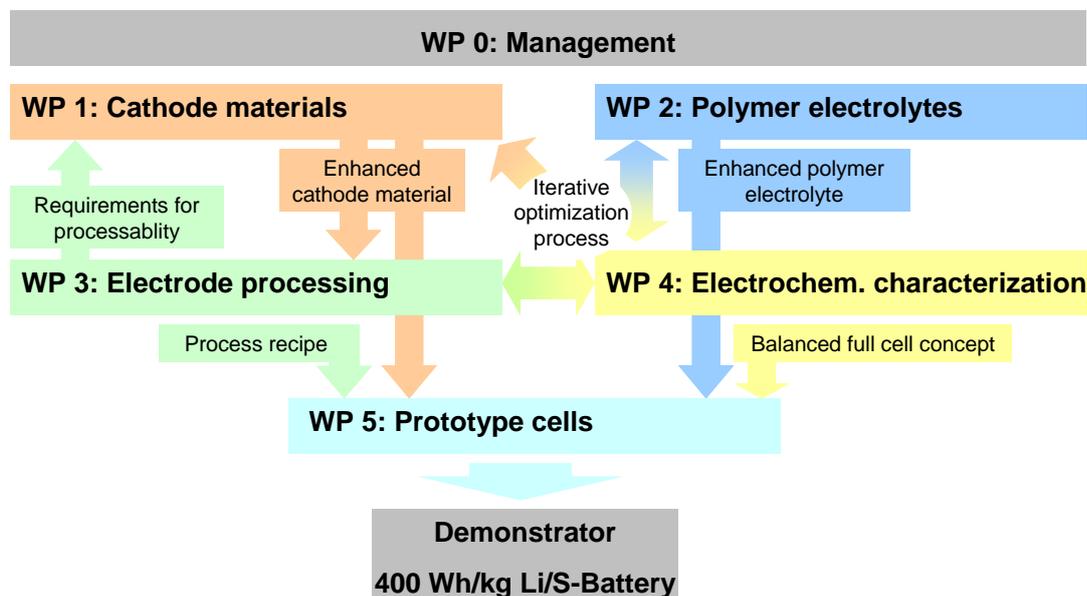


Figure 1: Graphical presentation of the components showing their interdependencies

Table 1: Timing of the work packages

Work Packages		Project duration											
WP		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
0 Management													
0.1	Project management and coordination												
1 Cathode materials													
1.1	Pore design in porous carbon materials												
1.1.1	Synthesis of microporous carbons												
1.1.2	Synthesis of mesoporous carbons												
1.1.3	Synthesis of hierarchical carbons												
1.2	Industrial processed carbons												
1.2.1	to be defined												
1.2.2	to be defined												
1.2.3	to be defined												
1.3	Preparation of carbon / sulphur composites												
1.3.1	Melt infiltration and thermal treatment												
1.3.2	Up-scaled material preparation for WP 2 + 5												
1.4	Material characterization												
1.4.1	Material structure and pore characterization												
1.4.2	Characterization of polysulfide retention (UV/VIS)												
2 Electrode Processing													
2.1	Powder and paste formulations												
2.2	Coating process												
2.3	Electrode characterization												
3 Polymer electrolytes													
3.1	Polymer electrolyte formulation												
3.2	Composite (gel) electrolyte formulation												
3. Mrz	Polymer electrolyte characterization												
4 Electrochemical characterization													
4.1	Evaluation of cathode materials												
4.1.1	Capacity and cycle stability testing												
4.1.2	Rate capability testing												
4.1.3	Mechanism study												
4.2	Evaluation of polymer electrolytes												
4.3	Electrode balancing												
5 Prototype cells													
5.1	Electrode fabrication on prototype level												
5.2	Fabrication of prototype cells												
5.3	Evaluation of prototype cells												

Milestone plan

Table 2

Milestone number	Milestone name	Work package(s) involved	Expected date ¹
1	Feasibility of material approach	1, 3, 4	M 9
2	Materials for enhanced performance	1, 3, 4	M 18
3	Full cell concept and testing results	2, 4, 5	M 27
4	Prototype demonstration (400 Whkg ⁻¹)	5	M 36

MS 1 Feasibility of material approach (M 9)

- First results on capacity values of microporous carbon / sulfur nanocomposites will be presented. A specific capacity of higher than 500 mAhg⁻¹ (mass of sulfur) is aimed for to demonstrate the general feasibility of the approach (TUD, SGL)

MS 2 Materials for enhanced performance (M 18)

- Detailed results on influence of pore geometry on performance of carbon / sulfur composite materials (TUD, IWS)

MS 3 Full cell concept and testing results (M 27)

- Enhanced cathodes with stable capacity of > 600 mAhg⁻¹ (mass of sulfur) (TUD, IWS, SGL)
- Materials for prototype cell manufacturing available and functionality in test cells (TUD, IWS, SGL)

MS 4 Prototype demonstration (400 Whkg⁻¹) (M 36)

Prototype cell is available with following specifications:

- Pouch cell design
- Energy density > 400 Whkg⁻¹
- Cycle stability > 50
- Rate capability > 0.5 C

WP 1 Cathode materials

WP 1.1 Pore design in porous carbon materials (TUD)

Objectives

The nanostructure in carbon materials plays an important role in sulfur nanocomposite cathodes. Electrical contact, mechanical stabilization and retention of soluble polysulfide species are the main function of the carbon material. Micropores and large surface areas are expected to enhance the sulfur utilization and stabilization, while mesopores are expected to enhance transport phenomena.

In this work package, carbons with defined micropores (diameter < 2 nm) and mesopores (2 - 50 nm) will be synthesized via template based methods. Finally, hierarchical carbons will be developed with a high micropore volume and an additional accessible mesopore system.

WP 1.1.1 Synthesis of microporous carbide-derived carbons

Microporous carbons will be synthesized via silicon carbide templates. Silicon is removed by high temperature chlorination, leaving a microporous carbon skeleton with defined pore

structure. SiC precursors and chlorination temperature will be varied to adjust a narrow pore geometry within the micropore regime. Material characterization and optimization takes place in exchange with WP 1.4.

A series of samples with defined pore geometry between 0.5 and 2 nm pore diameter and different particle size will be provided for sulfur infiltration (WP 1.3) and electrochemical testing (WP 4).

WP 1.1.2 Synthesis of mesoporous carbons

Mesoporous carbons with pore diameters in the range of 2-50 nm will be synthesized using nanostructured metal oxide templates. Carbon will be deposited from various organic precursors on the particulate or porous templates, carbonized by temperature treatment and wet-chemical (etching) or gas phase extraction (chlorination).

A series of samples with defined pore geometry between 2 and 50 nm pore diameter and different particle size will be provided for sulfur infiltration (WP 1.3) and electrochemical testing (WP 4).

WP 1.1.3 Synthesis of hierarchical mesoporous carbide derived carbons

By combination of methods 1.1.1 and 1.1.2 hierarchical mesoporous carbide-derived carbons will be synthesized.

A series of samples with defined pore geometry with one fraction in the micropore and the other in the mesopore regime will be provided for sulfur infiltration (WP 1.3) and electrochemical testing (WP 4).

The material synthesis will be adapted and optimized according to results from sulfur infiltration (e.g. enhancement of wettability) and electrochemical testing.

Table 3

WP 1.1	Year 1				Year 2				Year 3				MM	Partner
WP 1.1.1													4	TUD
WP 1.1.2													4	TUD
WP 1.1.3													4	TUD
MM	6				6								12	TUD

WP 1.3 Preparation of carbon / sulfur nanocomposites (TUD, IWS, SGL)

Objectives

Carbon / sulfur nanocomposites will be prepared by melt and / or solution infiltration of elemental sulfur into the porous carbon materials. For this process step, an optimized method will be developed to receive reproducible results. Main aim is to obtain sulfur loadings as high as possible, while achieving a good utilization and cycling performance. Experimental results on optimum loading levels will be opposed to theoretical considerations on accessible pore volume and volume expansion during cycling for the different carbon host materials.

WP 1.3.1 Melt infiltration

For a representative carbon sample, optimized conditions (temperature, time, ratio of components, mixing) for the melt infiltration step will be defined. In case melt infiltration does not lead to satisfying results, sulfur solutions in organic solvents will be applied.

When optimized conditions are defined, various carbon samples from WP1.1 and WP 1.2 will be infiltrated by sulfur with a series of different loading levels.

In iterative steps with the electrochemical and structural characterization in WP 1.4 and WP 4, optimization will be achieved.

Thermal treatment is expected to be the most important process step for the preparation of carbon sulfur nanocomposites. Additional rows of experiments will be defined to optimize the temperature program during and after infiltration.

Weight loss on composites will be monitored in thermogravimetry experiments in dependence of temperature and time. Influence of various temperature treatments (variation of time,

temperature, gas phase pressure) on electrochemical properties will be tested in exchange with WP 4.

Table 4

WP 1.3	Year 1				Year 2				Year 3				MM	Partner
WP 1.3.1													4	TUD
MM	2				2				0				4	TUD/

WP 1.4 Materials characterization (TUD, SGL)

Objectives

Materials characterization is required to provide control over material synthesis and information on their structure and composition. Only by detailed analysis of the results conclusions on structure – property relations can be drawn.

WP 1.4.1 Material structural analysis

Porous carbons and carbon / sulfur nanocomposites will be analyzed by structural characterization methods to determine sulfur distribution, particle size and ordered structure. Methods to be applied include transmission and scanning electron microscopy (TEM, SEM), x-ray diffraction (XRD) and small angle x-ray scattering (SAXS).

Elemental composition is determined by energy dispersive x-ray analytic (EDX) and by inductive coupled plasma measurements (ICP). Further information is acquired by ash content determination.

Gas adsorption experiments will be applied for determination of specific surface area, pore volume and pore size distribution

At TUD the methods will be applied for characterization on porous CDC materials. At SGL the same methods will be applied for characterization on industrial processed carbons. At IWS structural characterization will be applied on up-scaled sulfur / carbon nanocomposites. Whenever required, characterization results and equipment will be shared between the partners.

WP 1.4.2 Investigations on polysulfide retention

One aim of the project is to gather know-how on the influence of pore structure in porous carbons on polysulfide retention during cycling. Interaction of polysulfides with the different carbon materials will be monitored by UV/Vis-spectroscopy and/or elemental analysis on polysulfide solutions being in contact to the porous materials.

All results of WP 1.4 will be provided and communicated on a day-by-day exchange. Findings will be incorporated directly in material optimization in WP 1.1, 1.2 and 1.3.

Close cooperation will be also drawn to WP 4, as relations of structural properties on electrochemical performance are expected to be the key for an optimized material concept.

Table 5

WP 1.4	Year 1				Year 2				Year 3				MM	Partner
WP 1.4.1													7	TUD
WP 1.4.2													4	TUD
MM	2				4				5				11	TUD

4. Scientific and technical state of the art
a. R&D results (publications and patents) being relevant for the implementation of the project?

Tomorrow's Energy Storage: the Lithium Sulfur Battery

Current energy storage solutions on the basis of Li-ion intercalation compounds have almost reached their energy density limit and it will be quite difficult to reach the desired 300 km range for electric vehicles without enormous compromises with respect to their construction. Besides the limited energy and high costs for current Li-ion batteries there are also huge challenges concerning safety aspects for this energy storage generation.

In contrast to classical intercalation compounds, the charge and discharge of Li/S batteries is based on processes which lead to the formation and cleavage of covalent bonds. Generally, the assembly of a lithium sulfur battery consists of a solid lithium anode and a solid sulfur cathode. Lithium ions will be transported to and from the two electrodes using a liquid electrolyte like a solution of LiPF_6 in carbonate based organic solvents. At the cathode, lithium ions will react with sulfur in a stepwise reduction to form polysulfides and in the completed discharged state Li_2S . The cell voltage for the complete reaction lies in this case at about 2.2 V, while the cathode has a theoretical specific capacity of 1672 mAhg^{-1} . Current cells based on sulfur technology are capable of an energy density of about 350 Wh kg^{-1} [1], whereas Li-ion batteries based on intercalation compounds are limited to a maximum of about 200 Wh kg^{-1} .

The challenges preventing the break-through of the Li/S technology for mass production are mainly

- Improving the electrical conductivity of sulfur by suitable composites [2]
- Improving the coulomb efficiency by inhibiting the „shuttle“ mechanism (migration and reduction of soluble polysulfide species from cathode to anode) [3]
- Improving the cycle stability by balance the mechanical stress caused by volume expansion during discharge process [4]

Carbon materials for Li/S-Cathodes

An interesting approach to address the mentioned challenges is to add carbon materials to the cathode and form sulfur/carbon composites. Carbon black [2] and carbon nanotubes [5] were added to improve the electrical conductivity. First investigations on porous materials reported the synthesis of a blend of elemental sulfur with active charcoal [6]. Sulfur is infiltrated into the pores of the carbon by using its melt at elevated temperatures. It was shown by using liquid electrolytes that this strategy successfully led to a higher energy density and a prolonged cycle life. In another work by Gao et al., microporous carbon spheres were infiltrated with sulfur. The authors demonstrated a cycle stability of 500 cycles and explain the better performance with a stronger retention of soluble species within the micropores [7]. Recently, Nazar et al. synthesized the first composite of mesostructured carbon with sulfur using melt impregnation [8]. The highly ordered pore structure of the carbon matrix leads to an excellent contact with sulfur and therewith referred to the amount of sulfur to an unmatched reversible capacity of about 1300 mAhg^{-1} , which is about 80 % of the theory (1672 mAh g^{-1} correspond to 100 %). Nevertheless, even in that case there is still a migration of soluble species. The addition of polymeric electrolyte to that system was reported to enhance the cycle stability and the coulomb efficiency.

Lithium Conducting Membranes and Solid Electrolytes

Nazar et al. were not the first using lithium conducting membranes as a strategy. In fact there are several works in recent years demonstrating the use of solid electrolytes or its application in all-solid-state configurations. Scrosati et al. reported recently in renowned trade journals the application of polyethyleneoxide-based gel or solid electrolytes [9,10], respectively, which lead to prolonged cycle stability and in addition to advantages concerning safety aspects

because of the avoidance of liquid electrolytes. Similarly, Tatsumi et al. prepared a Li/S-battery with the glass electrolyte $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$ which leads to high discharge capacity and good coulombic efficiency [11]. Problems arising with the use of solid electrolytes certainly are the moderate conductivity for lithium ions. Nevertheless, there is a huge potential for fundamental research in order to overcome this issue.

Another interesting approach is the utilization of complex membrane composites. First patents of Sion describe for instance a lithium conducting sol-gel layer, which is coated on a conventional battery separator, by that it is possible to avoid the migration of polysulfide species to the anode side [12]. Currently, Sion is working in close collaboration with BASF in order to generate such multifunctional membranes to cover the metallic lithium anode [13]. Sion states on their website that by using this technology discharge capacities for full LiS-battery cells of about 350 Whkg^{-1} are possible. For the near future, Sion predicts discharge capacities of up to 600 Whkg^{-1} .

It is also possible to use solid electrolytes consisting of complex ceramic phosphate compounds like Lisicon (is used in the field of lithium air batteries) to cover the Lithium [14]. Attention has to be paid on the cycle stability of such composites with regard to the mechanical stability. Another problem is the thickness of such solid electrolytes. Techniques have to be developed in order to obtain thinner membranes and to provide fast lithium conduction.

In conclusion, the future of lithium sulfur batteries relies inevitably on an interaction interdisciplinary work on the different materials and components. It is thus essential not only to concentrate on one of these topics, but also to keep in mind that the interplay of all these components is a quite challenging affair. A fast transfer of the fundamentals into industrial applications will strongly rely on that.

New aspects of this proposal beyond the state of the art include:

- Development of full battery cells with energy densities $> 400 \text{ Whkg}^{-1}$
- Study on the role of nanostructure and pore geometry in carbons on performance of carbon / sulfur composite electrodes
- Evaluation of industrially processed porous carbons in Li/S-batteries
- Development of new gel- and polymer electrolytes with a conductivity $>10^{-4} \text{ S cm}^{-1}$.
- Study of the electrode/electrolyte interfaces for improved battery stability.

b. Reference list

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5. Collaborations with third parties

This EraNet-Project involved 4 further partners from Austria (Varta Microinnovation) and Sweden (Uppsala University and Scania, Södertälje) and Germany (SGL Carbon, Meitingen). A close collaboration between all partners was essential for the success of the project. Therefore, project meetings involving all partners were planned and carried out every 6 month. Exchange of information, samples and results was done permanently. Exchange of informations, samples and results were done on a week-by-week basis.

II. Detailed Description and presentation

1. Use of funding and technical / scientific results, comparison with the original proposed work- time and cost plan

Scientific and technical results

1.1. Microporous carbide-derived carbons (CDCs) (WP 1.1.1 and WP 1.4.1)

The work package of TUD within the project is focused on the pore design in porous carbon materials and their structural characterization as well as the preparation of carbon/sulfur nanocomposites in cooperation with the partners at IWS.

Microporous carbons (part of work package 1.1.1) with pore diameters below 2 nm have been prepared by the selective etching of silicon atoms out of silicon carbide using hot chlorine gas. This special class of microporous carbons is named carbide-derived carbon (CDC). A high temperature chlorine treatment was performed to transfer the metal atoms to volatile SiCl_4 leaving behind of a porous CDC material. The properties of carbide-derived carbons are known to be a function of the halogenation conditions and the properties of the carbide precursor. We have prepared different materials samples starting either from crystalline or amorphous SiC with regard to obtain different micropore structures which should result in different properties. On the one hand the liquid polycarbosilane SMP-10 (purchased from Starfire Systems) was converted to amorphous silicon carbide at 800°C followed by chlorine treatment at the same temperature (the sample is denoted as SMP-10-CDC). Nitrogen physisorption isotherms taken at 77 K (Table 6) appears to be of type I according to the IUPAC classification representing a typical microporous material. The SMP-10-CDC shows a specific surface area of 1938 m^2/g , a total pore volume of 0.91 cm^3/g , and a micropore volume of 0.87 cm^3/g . A second microporous CDC material was prepared starting from crystalline silicon carbide precursor particles ($\sim 1.2 \mu\text{m}$) by a chlorine treatment at 900°C (the sample is denoted as SiC-CDC). Due to the highly crystalline precursor the pores of the resulting carbon material are smaller in size as compared to the SMP-10-CDC resulting in slightly lower specific surface area (1170 m^2/g), total pore volume (0.58 cm^3/g), and micropore volume (0.53 cm^3/g). The high purity of both samples was determined via EDX analyses showing a carbon content of more than 99 wt.%, while chlorine, oxygen, and silicon are below the detection limit. Both samples were provided to the partners at IWS for the characterization as a sulfur host material in lithium-sulfur battery cathodes.

Table 6: Porosity data summary and EDX analyses of the microporous CDCs.

Sample	$\text{SSA}_{\text{BET}}^{\text{a)}}$ [m^2/g]	Total pore volume $^{\text{b)}}$ [cm^3/g]	Micropore volume $^{\text{c)}}$ [cm^3/g]	Carbon content (EDX) [wt.%]
SMP-10-CDC	1938	0.91	0.87	>99
SiC-CDC	1170	0.58	0.53	>99

a) Specific surface area calculated by the Multi-Point BET equation.

b) Total pore volume calculated at 0.9 P/P_0 .

c) Micropore volume calculated at 0.2 P/P_0 .

1.2 Colloidal arginine-based SiO₂ nanoparticle templates for micro, meso and micro/meso-porous carbons (WP 1.1.1, 1.1.2, 1.1.3 and 1.4.1)

We successfully prepared different microporous and mesoporous carbon materials as well as hierarchical micro- and mesoporous carbide-derived carbons. For that purpose, we have used the nanocasting method (hard-templating) of commercially available fumed silica (Aerosil, Evonik) with either carbon or carbide precursors. Different mesopore sizes were adjusted by using template particles of different size. However, the maximum achievable diameters are limited to values below 20 nm making the use of specifically tailored colloidal particles necessary for the implementation of larger pores in the resulting carbon material.

For the synthesis of large silica sphere templates, we have applied a method using arginine as the stabilizer for the controlled growth of SiO₂ nanoparticles in an ethanol/water mixture (Figure 2). Tetraethyl-orthosilicate (TEOS) was used as the silica source. The size of the particles is precisely controllable by the composition of the growth solution (Table 7 and Figure 3A). SEM images show a highly mono-modal size distribution. Due to the relatively slow evaporation of the solvents, the spheres generate ordered arrays. The SiO₂ particles with the lowest diameters of 34 nm even show constructive low-angle X-ray scattering due to oscillation as a result of the highly uniform sphere diameter throughout the whole sample (Figure 3B).

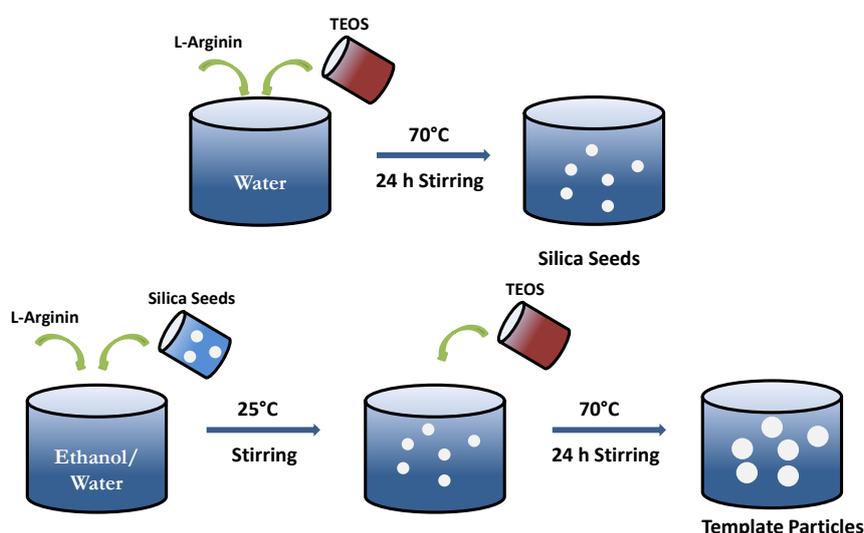


Figure 2: Schematic of the synthesis procedure for colloidal SiO₂ nanoparticle templates.

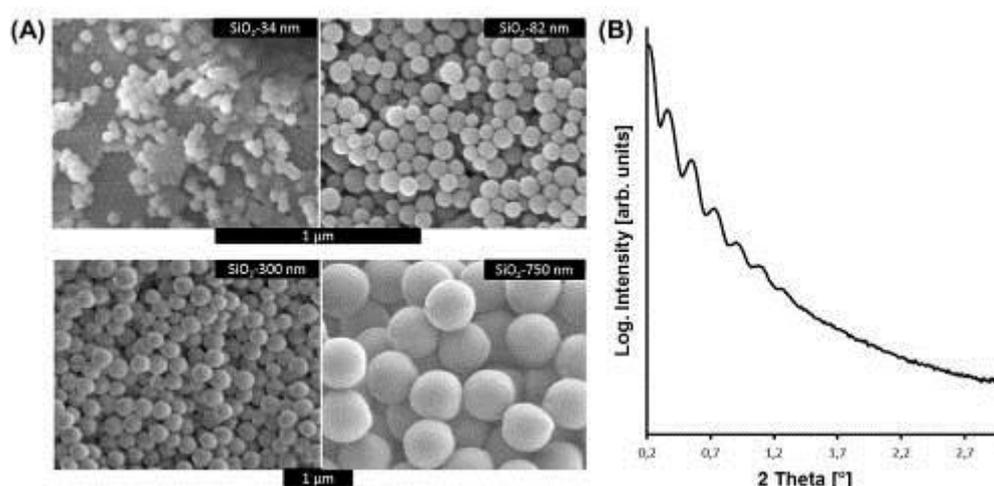


Figure 3: (A) SEM images of the SiO₂ nanoparticle templates and (B) low-angle X-ray scattering curve of the particles with a diameter of 34 nm.

Table 7: SEM and SAXS data of the Colloidal SiO₂ nanoparticle templates.

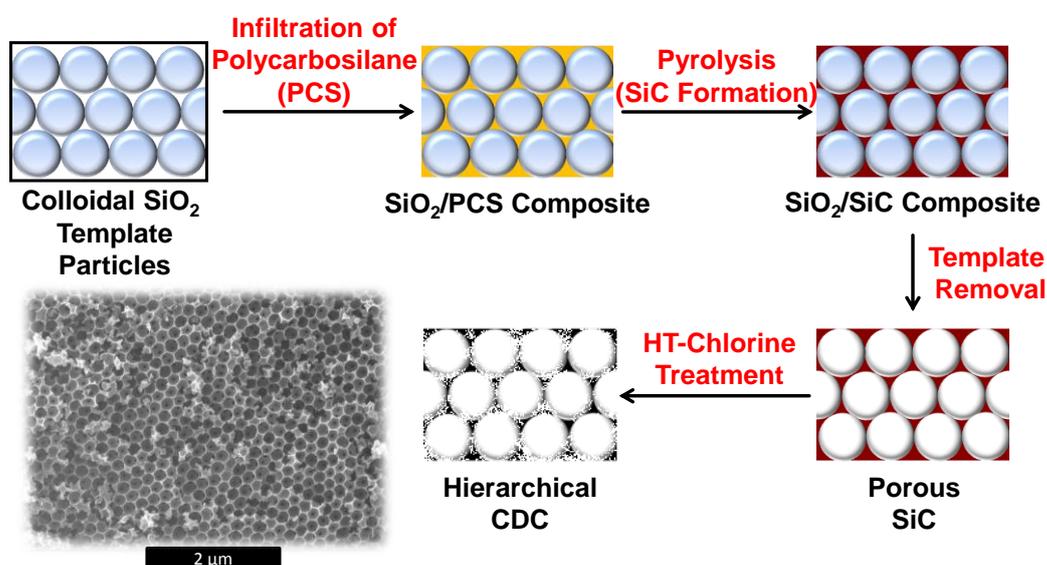
Name	Diameter _{SEM} [nm] ^{a)}	Diameter _{SAXS} [nm] ^{b)}
SiO ₂ -34 nm	34.4 ± 3.0	47.2
SiO ₂ -82 nm	82.3 ± 7.2	-
SiO ₂ -300 nm	300.4 ± 18.2	-
SiO ₂ -750 nm	750.7 ± 30.0	-

a) Particle diameter obtained from SEM-Images was determined using the software "ImageJ". For every size 150 particles were measured.

b) To obtain the particle size by SAXS measurements the scattering curves were fitted with the software "Scatter" assuming spherical particles.

1.3 Hierarchical micro- and large pore carbide-derived carbons (CDCs) using colloidal template particles (WP 1.1.3 and 1.4.1)

The colloidal template particles prepared by the arginine-route were used as templates (i.e. placeholders for the formation of pores) for the production of hierarchically structured carbide-derived carbon materials. For this purpose, the particle powder was infiltrated with polycarbosilane polymer SMP - 10 followed by pyrolysis under inert atmosphere transforming the SMP-10 into silicon carbide (Figure 4). Template removal was achieved by dissolution of the silica particles in aqueous hydrofluoric acid (HF) solution. The resulting porous silicon carbide (SiC) material was then subjected to a high-temperature chlorine treatment at 800°C leading to the selective removal of the silicon atoms due to the formation of volatile SiCl₄ species. The resulting CDC materials are of a strongly hierarchical character because the walls of the SiC are equipped with a large volume of micropores during the halogenation (Figure 5).

**Figure 4:** Schematic of the synthesis procedure for hierarchical micro- and large-pore CDCs prepared from colloidal SiO₂ nanoparticle templates and representative SEM image of one obtained sample.

Scanning electron microscopy (SEM) images (Figure 4 and Figure 5A) prove highly uniform pore sizes of the resulting materials. The hard templating method starting from the as described arginine-based colloidal silica particles allows adjusting the pore size in a range from 30 nm up to ~600 nm. The smaller size of the pores (compared to the particle diameter) is related to slight shrinkage processes during the high-temperature chlorine treatment but that does not negatively affect the pore uniformity (Table 8). The ordered packing structure of the template particles can be successfully transferred to the CDC replica materials as transmission electron microscopy (TEM) images reveal the presence of periodically arranged pore walls and pores (Figure 5 B). The interconnected void-window type pore system of the CDCs allows rapid accessibility of the pores for e. g. electrolyte ions throughout the entire material

which is highly demanded for the application in Li-S battery cathodes. The narrow pore entrances can also prevent the undesired dissolution and diffusion of solvable polysulfide species out of the cathode. For the CDCs with pores below 100 nm, the interconnections in the pore system are not visible in SEM images and thus, high-resolution TEM investigations were carried out (Figure 6A). In addition to the large mesopores of 30-40 nm in size, their rather narrow pore entries in the range of 10 - 20 nm are visible. Furthermore, the microporous pore walls consisting of mostly disordered sp^2 hybridized carbon fringes can be seen.

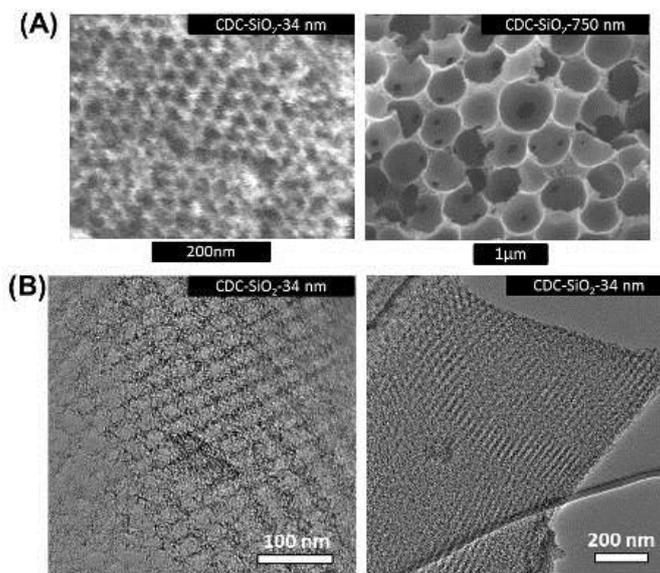


Figure 5: SEM (A) and TEM (B) images of micro- and large-pore CDCs from colloidal SiO_2 nanoparticle templates of different size.

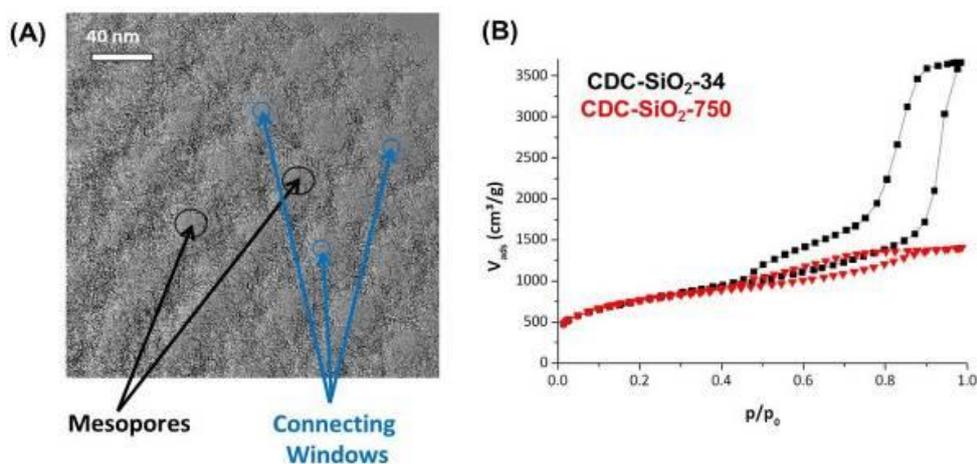


Figure 6: TEM image of CDCs from 34 nm colloidal SiO_2 nanoparticle templates (A) and nitrogen physisorption (77 K) isotherms of CDCs prepared by colloidal SiO_2 nanoparticle templates with two different sizes (B).

Due to the insertion of a large amount of micropores into the pore walls of the SiC precursor during the high-temperature chlorine treatment, the resulting CDCs have very high surface areas of more than $2700 \text{ m}^2/\text{g}$ as determined by nitrogen physisorption measurements at 77 K (Figure 5 B and Table 8). Moreover, outstanding nanopore volumes as high as $5.7 \text{ cm}^3/\text{g}$ are achieved for the CDCs prepared from 34 nm SiO_2 spheres as indicated by the large uptake of nitrogen and the distinct hysteresis loop in the nitrogen physisorption isotherm of this sample. The pore sizes of 32.7 nm and 36.1 nm calculated from SEM and quenched solid density functional theory methods (from nitrogen adsorption data), respectively, reflects the high precision of this synthesis method because the values are certainly close to the size of the template particles. The actual pore volume of the CDC prepared from

the larger SiO₂ particles is higher than the value of 2.2 cm³/g determined by nitrogen physisorption because this measurement captures only the narrow nano-scaled micro pores and the larger voids of several 100 nm in size do not fully contribute to the calculated value. As a consequence, both of these samples are highly suitable for hosting a large amount of active sulfur material in their pore structure and therefore, high loadings can be achieved with regard to high electrochemical capacities related to the mass of the whole cathode.

The purity of the CDCs was determined with electron dispersive X-ray spectroscopy measurements (Table 9). The carbon content is above 98 atom% in both samples while potential impurities of silicon are not detected due to the complete removal of these species in the high-temperature chlorine treatment step. Minor impurities of chlorine remained in the pores of the CDCs but their concentration is certainly low because all samples were purified by a post-reductive treatment under an atmosphere of flowing hydrogen after the silicon extraction. Due to this post-synthesis treatment and due to the absence of oxygen during synthesis, the oxygen content of these materials is far below that of comparable porous carbon materials derived from other precursors.

Table 8: Porosity, SEM, and SAXS data of the CDCs from colloidal arginine-based SiO₂ nanoparticle templates.

Name	SSA _{BET} [m ² /g] ^{a)}	V (nanopore) _{total} [cm ³ /g] ^{b)}	Pore Diameter _{SEM} [nm] ^{c)}	Pore Diameter _{QSDFT} [nm] ^{d)}
CDC-SiO₂-34 nm	2708	5.7	32.7 ± 2.5	36.1
CDC-SiO₂-750 nm	2753	2.2	602.3 ± 25.6	-

a) Specific surface areas were calculated using the BET equation in the relative pressure range from 0.05-0.2.

b) Total nanopore volumes were determined at a relative pressure of 0.99.

c) Pore diameter obtained from SEM-Images was determined using the software ImageJ. For every size 150 pores were measured.

d) Pore diameters were calculated using a QSDFT-Kernel at the adsorption branch of the isotherms assuming slit, cylindrical and sphere pores.

Table 9: EDX data summary of the CDCs from Colloidal SiO₂ nanoparticle templates.

Name	Carbon [atom%]	Silicon [atom%]	Oxygen [atom%]	Chlorine [atom%]
CDC-SiO₂-34 nm	98.0	not detected	1.0	1.0
CDC-SiO₂-750 nm	98.7	not detected	0.1	1.2

1.4 Mesoporous and Macroporous carbons (MCs) prepared by sucrose as carbon precursor and colloidal template particles (WP 1.1.2 and 1.4.1)

The arginine-based colloidal SiO₂ template particles were additionally used as templates for the synthesis of carbon materials with a monomodal distribution of pores. Therefore, the precursor was changed from polycarbosilane polymer to sucrose as a direct carbon feedstock (without chlorination step). The template spheres are impregnated with a hydrocarbon solution and the sucrose composite is transferred to carbon by pyrolysis under inert atmosphere. Finally, the template particles are removed in hydrofluoric acid solution leading to the formation of the mesopores (Figure 7).

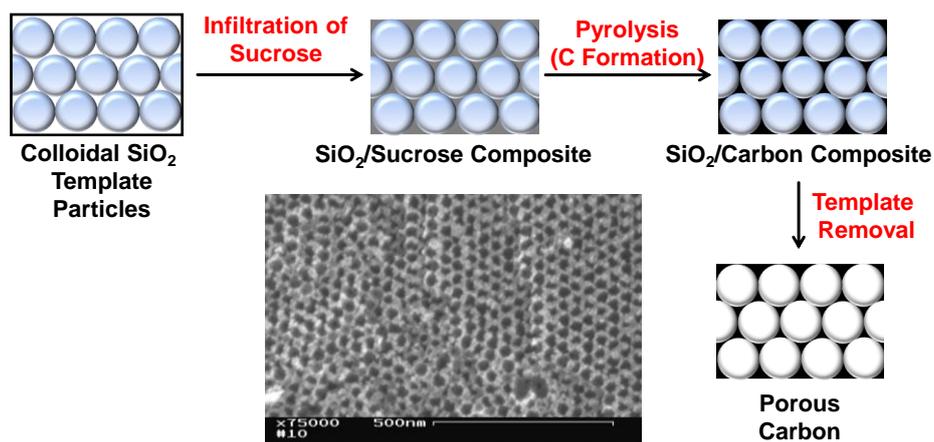


Figure 7: Schematic of the synthesis procedure for large-pore carbons prepared from arginine-based colloidal SiO₂ nanoparticle templates and representative SEM image of one obtained sample.

As for the carbide-derived carbon materials, the Meso- or Macroporous carbons (MCs) can be also prepared with a well-defined pore size according to the elevated template particle diameter. In a first set of samples, all of the above-described silica samples were infiltrated with equal amounts of sucrose and further processed to MC products. SEM images (Figure 7 and Figure 8) of the obtained materials show a system of uniformly sized and interconnected spherical pores of different sizes depending on the template. In case of the smallest pores obtained from the 34 nm template particles, even a regularly ordered arrangement of pores can be obtained. The pore sizes calculated from the SEM investigations are in good accordance with the used SiO₂ template particle dimensions.

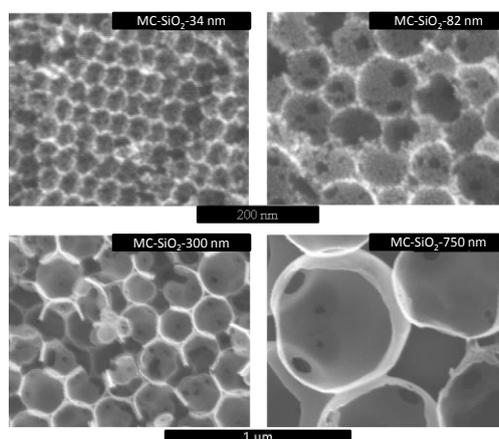


Figure 8: SEM images of Meso- or Macroporous carbons (MCs) from arginine-based colloidal SiO₂ nanoparticle templates of different size.

Nitrogen physisorption isotherms (Figure 9) reflect the structure of the MCs already indicated by the SEM investigations, as well. Because the larger pores do not contribute as much to the specific surface area (SSA) of the materials as rather narrow micro- or mesopores do, the values considerably decrease from the smallest (993 m²/g) to the largest pores (412 m²/g). The obtained SSAs are lower compared to the CDCs due to the absence of micropores (Table 10). However, high pore volumes of up to 5.5 cm³/g can be obtained for the 34 nm sized particles. As for the CDCs obtained from the larger templates, the total pore volumes of the MCs from the template particles of 82 nm (and above) are also underestimated by the nitrogen physisorption measurements. The carbon content of the materials determined by EDX is above 99.9 atom% while any potential impurity is below the detection limit revealing their high purity.

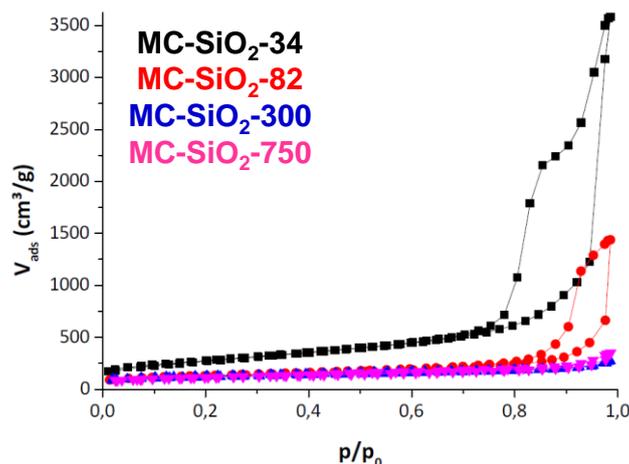


Figure 9: Nitrogen physisorption (77 K) isotherms of MCs prepared from arginine-based colloidal SiO₂ nanoparticle templates of different size.

Table 10: Porosity, SEM and SAXS data of the MCs prepared from arginine-based from colloidal SiO₂ nanoparticle templates.

Name	SSA _{BET} [m ² /g] ^{a)}	V (Nanopore) _{total} [cm ³ /g] ^{b)}	Pore Diameter _{SEM} [nm] ^{c)}
MC-SiO ₂ -34 nm	993	5.5	40.9 ± 0.6
MC-SiO ₂ -82 nm	446	2.2	80.8 ± 5.9
MC-SiO ₂ -300 nm	397	0.5	249.8 ± 13.8
MC-SiO ₂ -750 nm	412	0.4	726.6 ± 32.6

- a) Specific surface areas were calculated using the BET equation within the relative pressure range from 0.05-0.2.
 b) Total nanopore volumes were determined at a relative pressure of 0.99.
 c) Pore diameter obtained from SEM-Images was determined using the software "ImageJ". For every size 150 pores were measured.

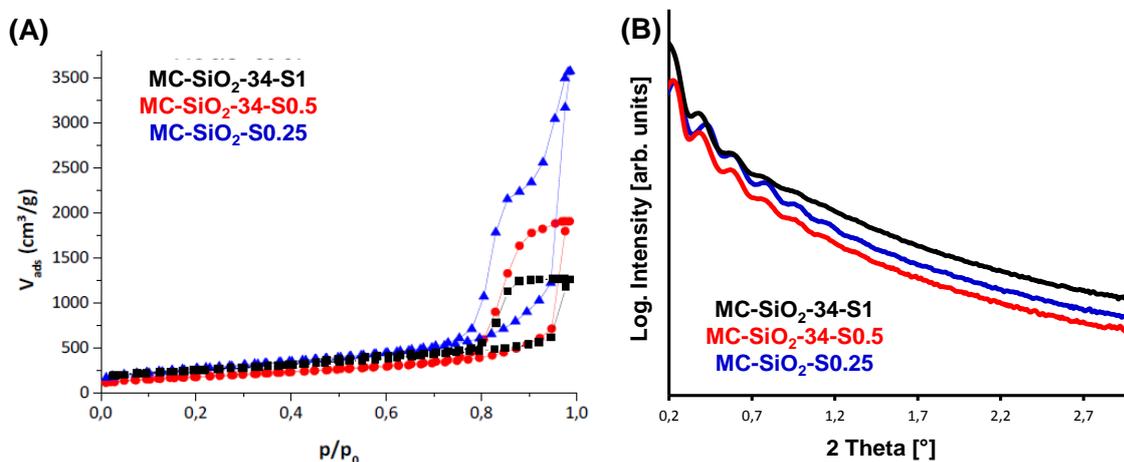


Figure 10: Nitrogen physisorption (77 K) isotherms of MCs prepared from 34 nm arginine-based colloidal SiO₂ nanoparticle templates with different amounts of sucrose (A) and SAXS curves of the samples (B).

In addition to different template particle sizes, we have investigated the influence of the adjusted sucrose/silica ratio using the 34 nm silica spheres as the template. Sucrose/silica ratios between 0.25 and 1 were used to achieve different filling degrees of the template and therefore, different wall thicknesses in the resulting MCs. Due to the fact that the hysteresis loops in the nitrogen physisorption isotherms (Figure 10) of the different materials are located at equal relative pressures, their pore size is similar despite the different amounts infiltrated into the template particles. Furthermore, all materials are of a highly uniform structure as shown by the constructive scattering in the SAXS curves of the MCs and similar calculated

pore sizes (Table 11). Due to the thicker walls, the total nanopore volumes decrease at higher sucrose contents. On the first view, this might be a disadvantage but at the same time, thicker walls do not offer so many defects in their carbon microstructure and might be of a higher conductivity and therefore show better suitability as sulfur host structures in Li-S cathodes.

Table 11: Porosity, SEM and SAXS data of the MCs prepared from arginine-based Colloidal SiO₂ nanoparticle templates.

Name	$m_{\text{Sucrose}}/m_{\text{Silica}}$ [g/g]	SSA_{BET} [m ² /g] ^{a)}	$V(\text{Nanopore})_{\text{total}}$ [cm ³ /g] ^{b)}	Pore Diameter _{SEM} [nm] ^{c)}	Pore Diameter _{SAXS} [nm] ^{d)}
CDC-SiO₂-34-S1	1	914	2.0	40.5 ± 0.9	44.6
CDC-SiO₂-34-S0.5	0.5	662	3.0	n. determined	44.8
CDC-SiO₂-34-0.25	0.25	993	5.7	32.7 ± 2.5	44.2

- Specific surface areas were calculated using the BET equation within the relative pressure range from 0.05-0.2
- Total nanopore volumes were determined at a relative pressure of 0.99
- Pore diameter obtained from SEM-Images was determined using the software "ImageJ". For every size 150 pores were measured.
- For pore size calculation using SAXS curves they were fitted with the software "Scatter" assuming spherical particles with a homogeneous core.

From the electrochemical testing of these model substances as sulfur host performed at Fraunhofer IWS it could be concluded that a combination of micro- and mesopores is highly beneficial for an optimal performance. The elevated templating approaches are suitable for the tailoring of materials. However, they are not suitable for scaling up and hence, the carbon materials are comparably expensive. In order to focus on scalable production of porous carbons as host material in Li/S cathodes, a commercially available conductive porous carbon black "Ketjenblack EC-600JD" (KB, produced by AkzoNobel) with large mesopore content was activated with carbon dioxide to enhance the pore volume and specific surface area.

1.5 CO₂ Activation of Ketjenblack (KB)

In general, the "activation" of carbon materials is performed with regard to introduce or enhance their porosity by controlled etching under oxidative conditions. It can be distinguished between chemical activation (oxidation based on ZnCl₂, H₃PO₄, or KOH) and physical activation (oxidation based on H₂O vapor, CO₂, or oxygen). Especially CO₂ activation is a promising method when compared to chemical activation procedures because it does not require an additional washing step to remove side products and provides sufficient control over the pore size of the activated carbons. CO₂ activation is usually performed in the range of 800-1000°C and by using the Boudouard reaction for carbon oxidation (Figure 11). Hence, CO₂ activation is widely used in industry for the production of porous carbons.

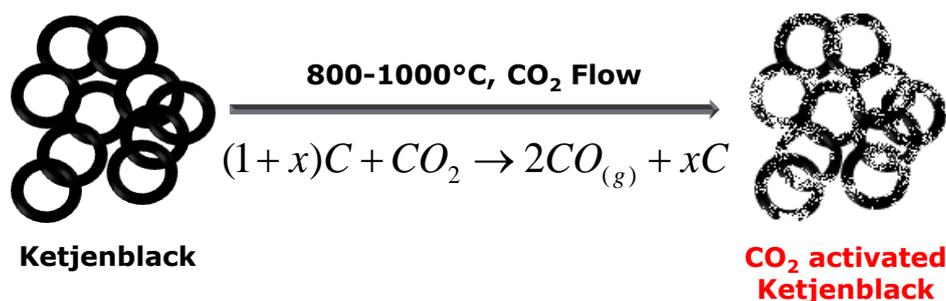


Figure 11: Schematic of the CO₂ activation procedure for KB.

The as-received KB material was characterized with nitrogen physisorption at -196°C (Figure 12). The measured specific surface area (SSA) of $1344\text{ m}^2/\text{g}$ is close to the value given by the manufacturer ($1400\text{ m}^2/\text{g}$). The high total pore volume of $2.72\text{ cm}^3/\text{g}$ potentially provides high sulfur loadings into the carbon host structure. At this point, it should be noticed that all the given values for the total pore volume are determined from the nitrogen physisorption isotherms at relative pressure $p/p_0 = 0.99$, i.e. the values refer to pores $> \sim 180\text{ nm}$. As the adsorption does not reach saturation for all of the materials presented, it can be expected that the overall pore volumes are even higher. For the optimization of the activation procedure (i.e. the generation of additional porosity), different batches of materials were prepared at different activation temperatures and with different activation times under constant CO_2 flow. Due to the generation of additional porosity, the activation procedure increases the porosity of the pristine KB even at the lowest temperature of 950°C and the shortest time of 2 h (Table 12). At a slightly higher temperature of 975°C , the increase of porosity does not significantly change and the burn off of KB material during oxidation remains comparable. At a temperature of 990°C and when the activation is performed for 4 h, the SSA and total pore volume increase more significantly to $1800\text{ m}^2/\text{g}$ and $5.58\text{ cm}^3/\text{g}$, respectively. These changes are related to the additional generation of micropores and the oxidation of the mesopore walls leading to higher porosity values. However, the burn-off of the KB during activation is still below 50 wt% indicating no major changes in the materials structural features. This is further evidenced by the comparable shape of the nitrogen physisorption isotherms before and after activation (Figure 12).

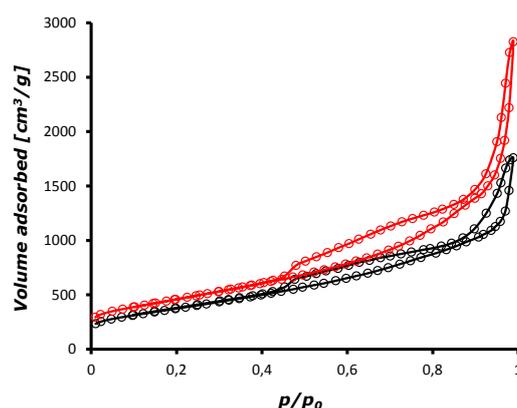


Figure 12: Nitrogen physisorption isotherms (-196°C) of the pristine KB (black) and one CO_2 activated (4h, 990°C) KB (red).

Table 12: Nitrogen physisorption data summary and burn-offs of the pristine KB and the KB materials activated under different conditions.

Sample	SSA_{BET} [m^2/g] ^{a)}	Total pore volume [cm^3/g] ^{b)}	Burn off [%]
Pristine Ketjenblack (KB)	1344	2.72	-
KB-activated at 950°C for 2 h	1400	3.38	7.2
KB-activated at 975°C for 2 h	1411	3.49	9.8
KB-activated at 990°C for 4 h	1800	5.58	47.3

^{a)} Specific surface area calculated using the multi-point BET equation ($p/p_0 = 0.05-0.2$).

^{b)} Total pore volume calculated from the volume of adsorbed nitrogen at $p/p_0 = 0.99$.

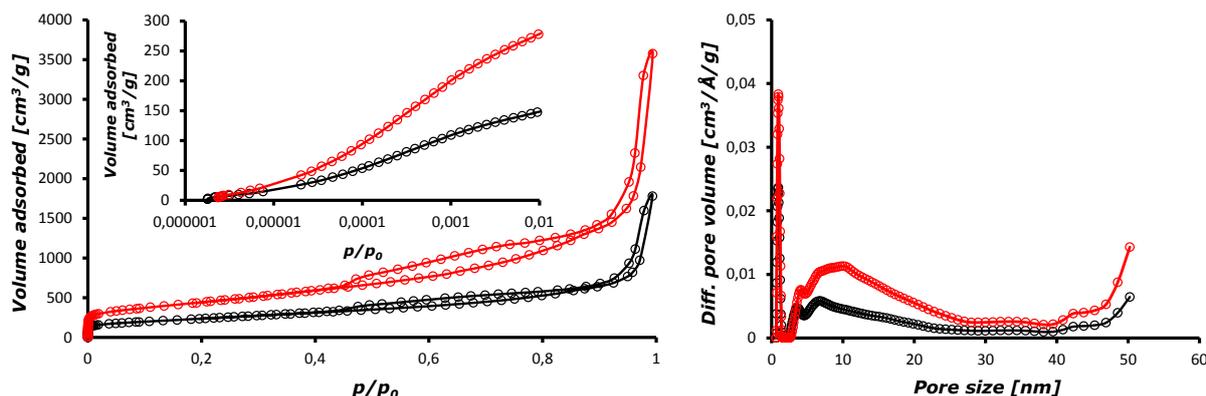


Figure 13: Left: Low-pressure nitrogen physisorption isotherms (-196°C) of the pristine KB (black) and one CO₂ activated (4h, 990°C) KB (red). The details of the low-pressure area are shown in the inset. Right: Differential pore size distributions calculated by the quenched solid density functional theory (QSDFT) method for nitrogen adsorption on carbon materials at -196°C (adsorption branch) assuming slit/cylindrical pores.

Pore size distributions (PSDs) of the materials are calculated by the so-called quenched solid density functional theory (QSDFT) method from nitrogen physisorption isotherms measured at -196°C and low pressure (Figure 13). According to the higher volume of adsorbed nitrogen at relative pressures below $p/p_0 = 0.1$, the PSDs show a significant increase of the micropore volume. The size of these small cavities remains nearly unchanged at a diameter of 0.9 nm. The diameter and volume of the small mesopores of 5-30 nm in diameter increase due to the partial oxidation of their pore walls. In addition, larger mesopores with diameters > 40 nm are detected before and after the activation procedure.

Transmission electron microscopy (TEM) images of the materials do not show a significant textural difference after activation (Figure 14). In accordance with the PSD calculated from the nitrogen physisorption data, the Ketjenblack consists of agglomerates of nm-sized, hollow, near-spherical carbon structures with internal cages of 10-30 nm in diameter. Larger mesopores of up to 100 nm in size are located between these hollow structures.

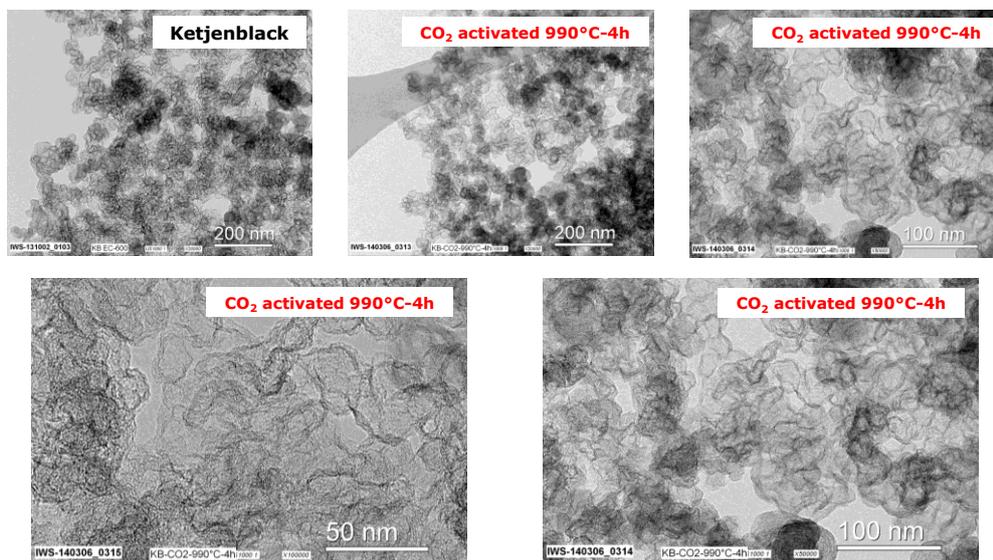


Figure 14: Transmission electron microscopy images of the pristine and CO₂ activated (4h, 990°C) KB at different magnifications.

TEM micrographs at higher magnifications (Figure 15) further underline the decreasing thickness of the mesopore walls during CO₂ activation. Additionally, it can be seen that the carbon microstructure within these walls is relatively graphitic, e.g. when compared to standard activated carbons or carbide-derived carbon materials with random orientation of the carbon layers (i.e. a high degree of disorder) previously reported in this project. Many of the carbon

fringes show nearly parallel orientation over a wide range can be observed. This property is highly beneficial for the use in Li-S battery cathodes because it serves for high electric conductivity and hence, efficient electrical contacting of the insulating sulfur by the carbon host. This is of crucial importance for sufficient operation of the cathode, especially at high charge-discharge rates.

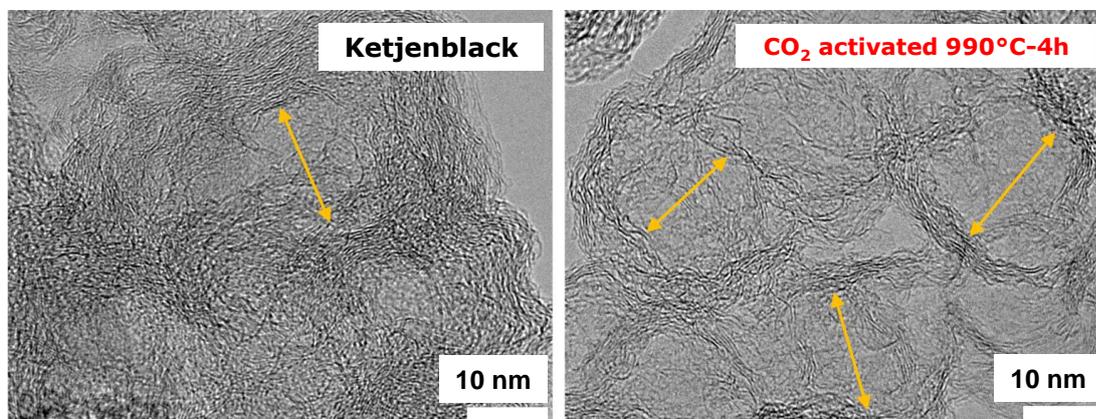


Figure 15: Transmission electron microscopy images of the pristine and CO₂ activated (4h, 990°C) KB at high magnification. The arrows indicate the hollow mesopore structures.

Besides the pore structure and the electrical conductivity, the surface properties of the carbon material are crucial for its performance in Li-S batteries. One suitable method for the estimation of the surface polarity of porous carbon materials is the adsorption of water vapor. The water vapor physisorption isotherms at 25°C (Figure 16) show a significant uptake at relative pressures $p/p_0 > 0.6$. This indicates a very hydrophobic surface of the KB materials before and after activation. Despite the presence of oxygen atoms from CO₂ during activation, no additional oxygen-containing functional groups are inserted during activation. The non-polar surface of KB and activated KB is attractive as it enhances the interaction with non-polar sulfur and ensures sufficient wetting of the pore system with the electrolyte.

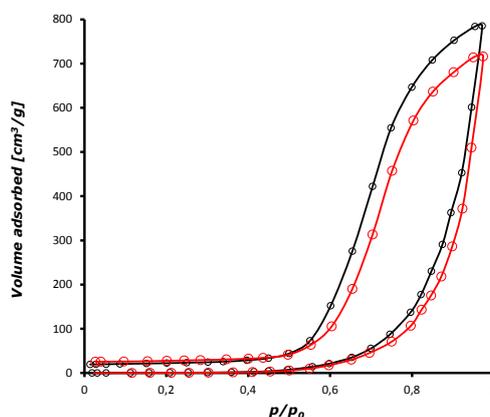


Figure 16: Water vapor physisorption isotherms (25°C) of the pristine KB (black) and one CO₂ activated (4h, 990°C) KB (red).

1.6 Activated KB/Sulfur Composites (WP 1.3.1)

Due to the highest porosity values of all activated carbons in combination with the non-polar surface properties and the graphitic carbon nanostructure, the KB activated at 990°C for 4 h was loaded with sulfur (1:2 weight ratio carbon:sulfur) for the electrochemical testing in Li-S battery cathodes by melt infiltration procedure. Scanning electron microscopy (SEM) images of the KB/sulfur composite (Figure 17Figure 20) show no large sulfur agglomerates or blocking of pores, i.e. the active material is completely infiltrated into the nanopores of the KB framework.

In addition, electron dispersive X-ray spectroscopy (EDX) analysis of the composites of sulfur with pristine KB and sulfur with activated KB shows homogeneous sulfur distribution on microscale and the strong attachment of the active material throughout the carbon host (Figure 18).

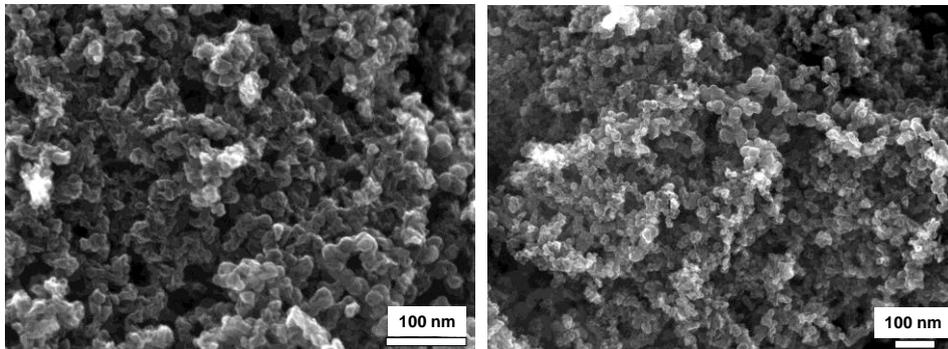


Figure 17: Scanning electron microscopy images of an activated KB infiltrated with sulfur (1:2 by weight).

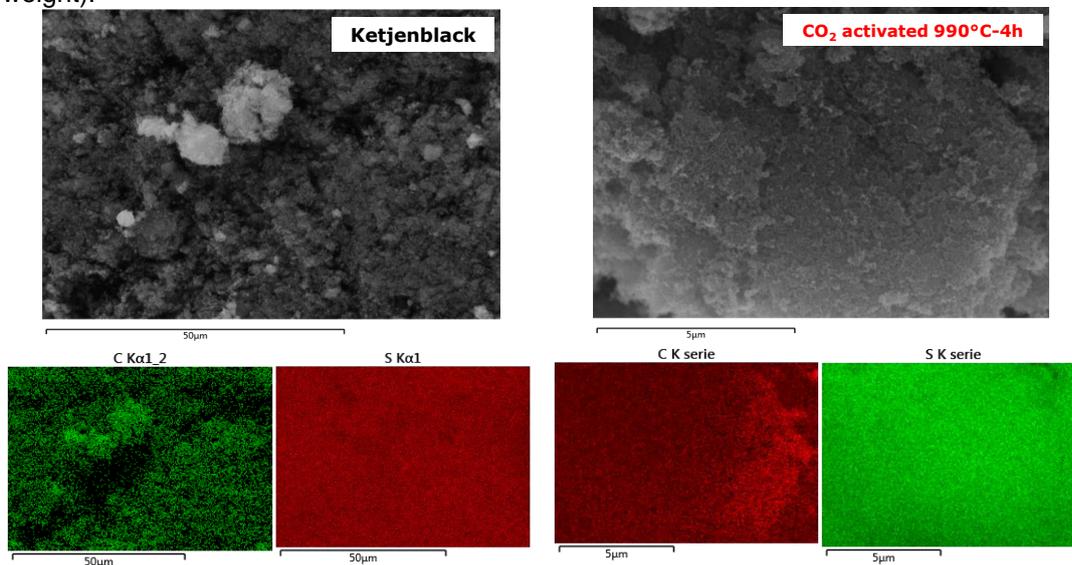


Figure 18: Scanning electron microscopy images and EDX mapping analyses (carbon:red; sulfur:green) of KB (left) and activated KB (right) infiltrated with sulfur (1:2 by weight).

In conclusion, we have optimized a commercially available Ketjenblack material for the use in Li-S battery cathodes by physical activation in flowing CO₂ gas under different conditions. The SSA was increased by up to 34% and the total pore volume was significantly increased, as well. The carbon texture remains highly graphitic and the surface of the activated KB is of non-polar character. After optimization of the activation procedure, the materials were homogeneously infiltrated with 66% sulfur and delivered to the project partners at Fraunhofer IWS Dresden for detailed electrochemical characterization.

1.6 Synthesis of CDC Nanospheres from Miniemulsions

Besides the activation of commercially available carbon materials, we have further investigated the influence of the particle size of the carbon material used in Li-S battery cathodes. Therefore, we have developed a novel synthesis route towards carbide-derived carbon nanospheres based on the use of oil-in-water miniemulsions. The latter consist of a water phase and organic oil droplets stabilized by the ionic surfactant sodium dodecyl sulfate (SDS). The driving forces for the homogeneous distribution of the polycarbosilane oil phase are introduced by ultrasonic treatment. The polycarbosilane chains in the oil phase are then cross-linked and solidified, followed by drying (i.e. removal of the water phase) and pyrolysis to

silicon carbide under inert atmosphere. In the final step, silicon atoms are removed by a high-temperature chlorine treatment leading to the formation of a highly microporous CDC material (Figure 19). Since this transformation is known to be a conformal process, the nanospherical shape of the silicon carbide materials can be maintained during the silicon removal.

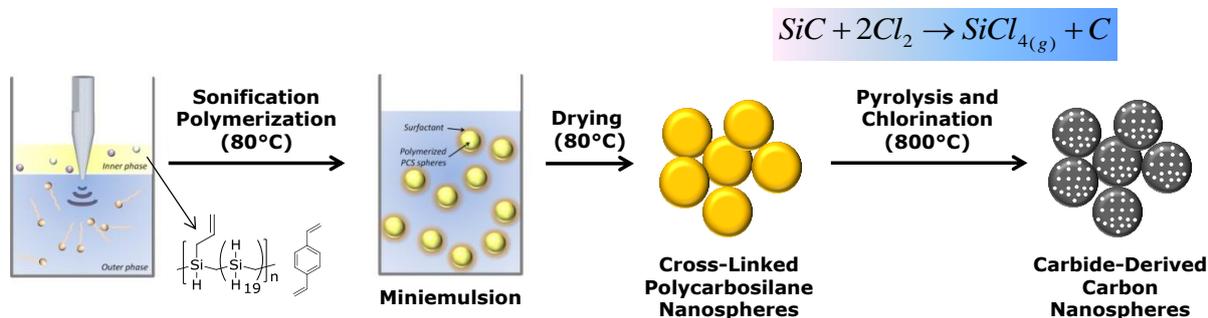


Figure 19: Procedure for the preparation of CDC nanospheres from miniemulsions.

The particle size of the spherical CDC structures is analyzed by SEM investigations and is in the range of 20-200 nm. Although the CDCs are not absolutely homogeneous regarding their size distribution, they show a perfect spherical shape (Figure 20). Due to the large amount of micropores, the CDC nanospheres exhibit high SSA of more than 2500 m²/g and a total pore volume as high as 1.8 cm³/g. Due to these high porosity values, these materials are promising candidates for the use in Li-S battery cathodes. Their very small particle size will facilitate complete sulfur utilization due to short diffusion pathways for ions and electrolyte. The CDC nanospheres were delivered to the project partners at Fraunhofer IWS Dresden for detailed electrochemical characterization.

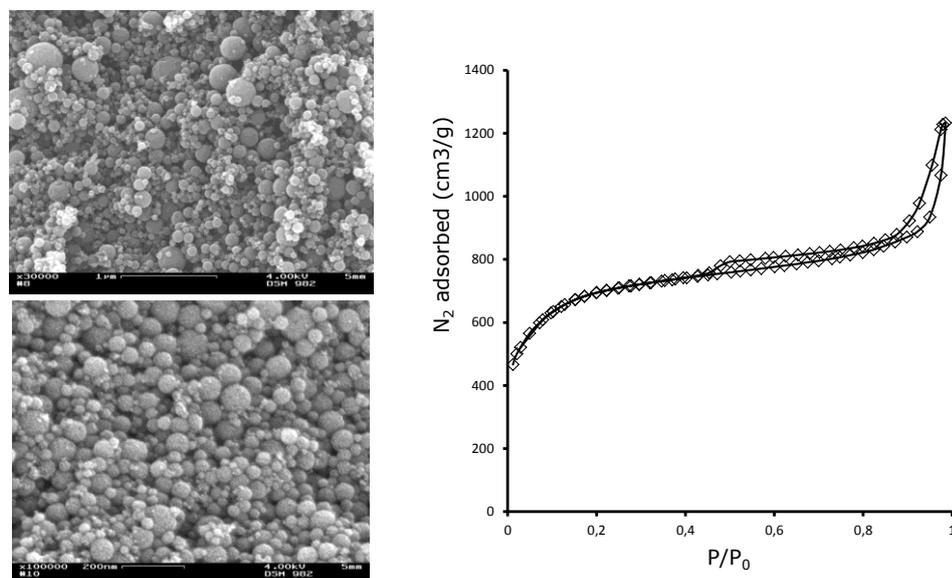


Figure 20: SEM micrographs and nitrogen physisorption isotherms (-196°C) of CDC nanospheres from miniemulsions.

1.7 Investigations on polysulfide retention – liquid phase adsorption studies (WP 1.4.2)

One main reason for the limited cycle life and capacity loss of lithium sulfur cells can be attributed to the so-called lithium polysulfide shuttle. A promising approach to avoid this shuttle effect is to minimize the polysulfide diffusion towards the anode by applying a diffusion barrier between cathode and anode or by using a sulfur host which shows a high affinity towards, both, sulfur and polysulfides. We studied the latter approach by means of ex-situ liquid phase

adsorption of polysulfides to find promising cathode materials without time-consuming electrochemical testings.

Liquid phase adsorption studies strongly depend on the solvent environment of the adsorbate. Hence, experiments were performed using a Li_2S_6 solution in a 50:50 organic ether DME/DOL mixture, to mimic a lithium sulfur cell environment as best as possible. The solution was diluted to three different concentrations and incubated with a defined amount of adsorbent until the equilibrium was reached. The cathode material was filtered off and the polysulfide concentration in the supernatant solution was determined by UV/Vis-spectroscopy. Different types of adsorbents were tested with regard to their polysulfide uptake. Several model carbons that contained basically no hetero-atoms were used to investigate the influence of the pore structure. Those materials can be categorized as highly hydrophobic and show pore structures from purely micro to purely mesoporous. A second set of adsorbents consisted of some highly hydrophilic adsorbents with different pore geometry ranging from micro to micro and mesopores.

The hydrophobic set of carbons consisted of TiC-CDC chlorine treated at 600 (TiC-CDC-600) and 1000°C (TiC-CDC-1000), commercially available activated carbon Norit DLC Super 50 (Norit DLC), CMK-3, Ketjenblack (KB), OM-CDC, and CO₂ activated Ketjenblack (act. KB), which was developed within this project. DLC exhibits a broad pore size distribution ranging from micropores ($d < 2$ nm) to smaller mesopores ($d = 2-4$ nm). OM-CDC displays a material with a more defined micro- ($d = 0.8$ nm) and mesoporosity ($d = 4$ nm). CMK-3 exhibits exclusively mesopores ($d = 4.5$ nm) whereas both CDC-600 ($d = 0.6$ nm) and CDC-1000 ($d = 0.8$ nm) contain only very narrow and defined micropores. KB and act. KB contain only small amounts of micropores and very large mesopores, while the activation process lead to higher amount of both pores (Figure 21).

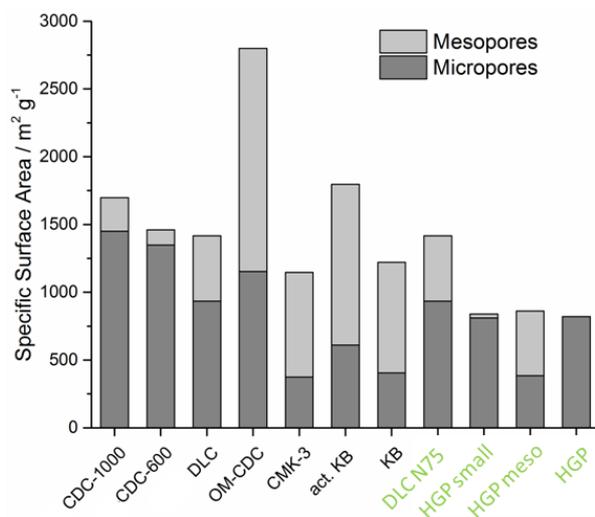


Figure 21: Composition of micro- and mesoporosity based on nitrogen physisorption isotherms (-196°C) and DFT based pore size distribution. Hydrophilic and hydrophobic adsorbents are labeled green and black, respectively.

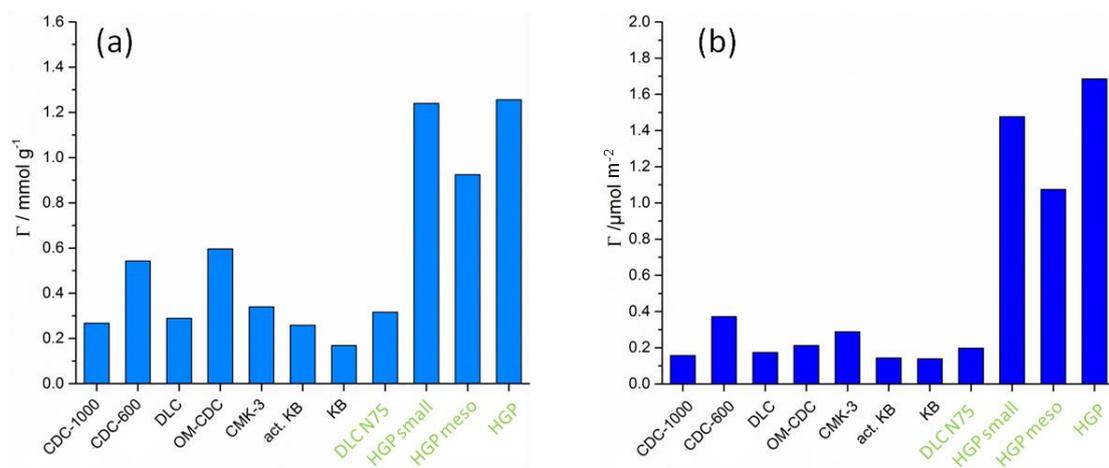


Figure 22: (a) gravimetric lithium polysulfide capacity determined by UV/Vis-spectroscopy, (b) specific surface normalized lithium polysulfide capacity determined by UV/Vis-spectroscopy. Hydrophilic and hydrophobic adsorbents are labeled green and black, respectively.

The gravimetric polysulfide capacity for DLC reaches a value of 0.29 mmol g^{-1} corresponding to a theoretical pore filling of below 10%. The good solubility of Li_2S_6 in DME/DOL makes the carbon surface less attractive for adsorption and DME/DOL may also co-adsorb at the carbon surface and displace some of the polysulfides. OM-CDC shows the highest uptake (0.6 mmol g^{-1}) among the hydrophobic carbons. The surface normalized uptake shows that also the mesopores must adsorb some polysulfides because as well as CDC-1000 and OM-CDC show nearly the same uptake in $\mu\text{mol m}^{-2}$. A vague trend can be observed when the gravimetric uptake is plotted against the micropore volume of the hydrophobic adsorbents showing that with increasing micropore content of the adsorbent the polysulfide uptake is increased (Figure 23). But its broad distribution indicates that other pores adsorb polysulfides as well. Interestingly, the surface normalized uptake is increased for CDC-600 ($0.37 \mu\text{mol m}^{-2}$), which contains even smaller pores than CDC-1000. As a consequence, pores are filled to a higher degree. This indicates that micropores, especially the ones smaller than 0.6 nm, adsorb polysulfides stronger than bigger pores.

Because of their ionic nature, polysulfides are expected to face stronger interactions with hydrophilic adsorbents. Several metal oxides were described to favor polysulfide adsorption but lack electrical conductivity. Nitrogen doped carbons combine electrical conductivity and hydrophilic properties. We modified the pore surface of DLC with nitrogen functionalities (7%). Water physisorption proved a more hydrophilic surface. Nevertheless, no increase in polysulfide uptake could be observed. An even more hydrophilic carbon sample, which contains more nitrogen (14%) and oxygen (10%) and exclusively small micropores around 0.6 nm, increases dramatically the polysulfide uptake (1.25 mmol g^{-1}). Two different particle sizes (HGP and HGPsmall) were tested with nearly identical results. By salt template methods, mesopores were introduced in this heavily doped material (HGPmeso). As a consequence, the micropore surface decreases but the nitrogen content stays nearly the same (10%). The gravimetric uptake decreases to 0.9 mmol g^{-1} following the same trend observed for hydrophobic adsorbents. Micropores seem to play a predominant role for polysulfide adsorption, which is even more pronounced when the pore wall is of hydrophilic nature (Figure 23).

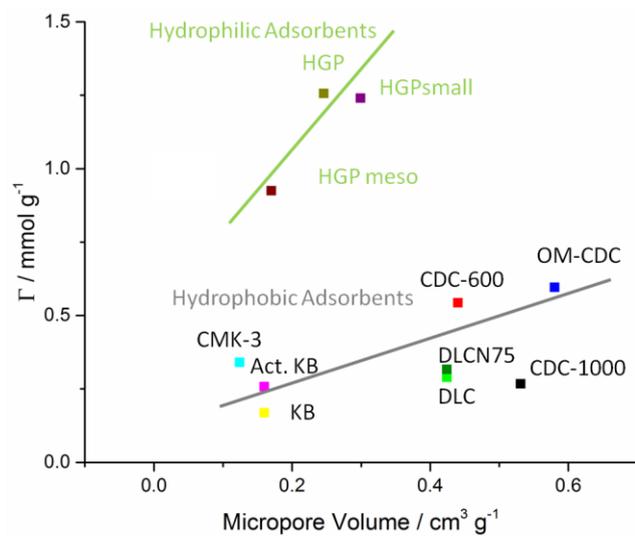


Figure 23: Lithiumpolysulfide capacity plotted against micropore volume. Strongly hydrophilic samples are clearly shifted to higher values, while hydrophilic as well as hydrophobic samples follow a vague trend with increasing micropore concentration. Hydrophilic and hydrophobic adsorbents are labeled green and black, respectively.

2. Most important costs of the report on expenditure of funds

The most important costs were personal costs for the scientific staff (E 13) and the student co-workers. Moreover, for the investigation by scanning electron microscopy, the SEM equipment of the department for Physical Chemistry was used. For the detailed analysis of the composites, the equipment of the department for Organic Chemistry was used. For the synthesis being carried out, several carbon precursors, HF and HF decontamination chemicals as well as small laboratory equipment were needed. For technical meetings (in Meitingen, Uppsala, Södertälje, Graz) and conferences, travel costs were used.

3. Necessity and adequacy of the work carried out

As documented under 1. and 2., the funding was spend to undertake the work according to the approved project proposal. This work contributed significantly to the development of enhanced Lithium-Sulfur batteries.

27 MM of scientific staff (E 13) were needed for the tasks as described in the description of work. Due to the high innovation degree of the work that was carried out, the staff needed to have a university degree in chemistry or related fields for

- The synthesis of the stabilized nanoparticles and the respective carbon materials using chlorination and HF treatment, respectively
- The realisation of the CO₂ activation
- Interpretation of the nitrogen and water physisorption measurements and SEM images and correlation between measurements and synthesis
- design of a method for the liquid phase (polysulfide) adsorption

The scientific staff was supported by student workers that help with the preliminary laborious and time consuming preparation steps of all synthesis and adsorption measurements.

4. Prospective exploitation, especially in regard of the proposed exploitation plan

Proposed exploitation plan TUD

For TUD as university, the **scientific** exploitation, the **academic connectivity** and **transfer of knowledge to students** / young researchers is crucial. In contrast, the economic exploitation plays a subordinated role or is mainly addressed by the preparation of **proposals** for **follow-up projects**, respectively.

TUD was planned to gain and indeed gained **further knowledge about porous carbon** material development for Li sulfur batteries with the proposed project. This know-how will be **transferred** in short **term to other complementary projects** at TUD in the area of battery research, but also **for other applications**, such as gas separation, catalysis and electro-adsorption. Moreover, the development of carbon precursors and materials plays an important role for novel silicon-hardcarbon structures for anode application – in lithium ion batteries as well as lithium-sulfur batteries. In mid-term, the experience gained by this project is expected to **enhance the position of TUD as strong R&D partner** for material development with a focus on next generation batteries, e. g. lithium-sulfur batteries as well as sodium-sulfur batteries. **Follow-up projects** and **industrial cooperations** have been the main goals for exploitation of the project results and one project proposal in regard of Li/S batteries has been already **approved** and one will start in the beginning of 2016.

One aim for the long term is the further development of materials towards other energy storage technologies, such as Li-air batteries and hybrid supercapacitors. For TU Dresden as university, the **scientific connectivity** to the battery/carbon research community was developed and will be further expanded (e. g. ongoing cooperation with G. Yushin & P. Pré).

Table 13: Prospective exploitation

Lfd. Nr.	Description	Time horizon
1	further knowledge about porous carbon material development for Li sulfur batteries	2015-2017
2	enhance the position of TUD as strong R&D partner for material development	2015-2020
3	Young researcher group (funded by BMBF) working on mechanochemical synthesis of porous carbon materials for electrochemical energy storage devices	2015-2019
4	Follow-up projects: proposal for a young researcher group (ESF) working on Li ₂ S/C and Sn/C composites elongated	2015
5	Follow-up project ("ALISE", Horizon 2020): porous carbon material development for Li/S cathodes and anodes	2015-2019
6	Follow-up project ("StickLiS", BMBF): nitrogen-doped carbons for cathodes in Lithium/Sulfur batteries:	2016-2019
7	Successful cooperation between Dr. P. Pré (University Nantes) regarding detailed microscopic investigations of CDC structure by TEM, measurements finished and manuscript draft in preparation	2015
8	further development of materials towards sodium-sulfur batteries in a project financed by the free state of saxony	2015-2017
9	Ongoing cooperation with Prof. Gleb Yushin (Georgia Institute of Technology, USA) regarding Li-S batteries based on CDC structures.	2015-2016
10	Cooperation with Utrecht: nanostructured carbon materials as catalyst supports for the iron-catalyzed production of lower olefins by the Fischer-Tropsch process (Postdoc grant for student who finished his Ph.D. working on carbon materials or sulfur cathodes)	2015-2017

5. Progress during the project in regard of third parties

No R & D results were published by third parties, which were relevant for the implementation of the project.

6. Publications (planned and already published)

- Poster presentations at the 1st, 2nd and 3rd work shop "Lithium Sulfur Batteries" 2012, 2013 and 2014
- Poster presentation at the conference "Nanofair 2014" in Dresden, Germany
- Oral presentation at the "Carbon 2013" in Rio de Janeiro
- Oral presentation at 26. Deutsche Zeolith-Tagung 2014, Paderborn
- Oral presentation at CellMAT 2014, Dresden, Germany, Oktober 2014 ;
- Oral presentation at GDCh Fachgruppe Festkörperchemie und Materialforschung, 17.Vortragstagung, Dresden September 2014
- Kim, Hyea; Wu, Feixiang; Lee, Jung Tae; Nitta, Naoki; Lin, Huan-Ting; Oschatz, Martin; Cho, Won Il; Kaskel, Stefan; Borodin, Oleg; Yushin, Gleb, In Situ Formation of Protective Coatings on Sulfur Cathodes in Lithium Batteries with LiFSI-Based Organic Electrolytes, *Advanced Energy Materials*, 2014, DOI: 10.1002/aenm.201401792

- Oschatz, Martin; Borchardt, Lars; Pinkert, Katja; Thieme, Soeren; Lohe, Martin R; Hoffmann, Claudia; Benusch, Matthias; Wisser, Florian M.; Ziegler, Christoph; Giebeler, Lars; Ruemmeli, Mark H.; Eckert, Juergen; Eychmueller, Alexander; Kaskel, Stefan; Hierarchical Carbide-Derived Carbon Foams with Advanced Mesostructure as a Versatile Electrochemical Energy-Storage Material, *Advanced Energy Materials*, 2013, DOI: 10.1002/aenm.201300645
- Hoffmann, Claudia; Thieme, Soeren; Brueckner, Jan; Oschatz, Martin; Biemelt, Tim; Mondin, Giovanni; Althues, Holger; Kaskel, Stefan, Nanocasting Hierarchical Carbide-Derived Carbons in Nanostructured Opal Assemblies for High-Performance Cathodes in Lithium–Sulfur Batteries, *ACS Nano* 2014, DOI: 10.1021/nn503394u
- Thieme, Soeren; Brueckner, Jan; Bauer, Ingolf; Oschatz, Martin; Borchardt, Lars; Althues, Holger; Kaskel, Stefan; A lithium–sulfur full cell with ultralong cycle life: influence of cathode structure and polysulfide additive, *Journal of Materials Chemistry A*, 2014, DOI: 10.1039/C4TA06748G
- Lee, Jung Tae; Zhao, Youyang; Thieme, Soeren; Kim, Hyea; Oschatz, Martin; Borchardt, Lars; Magasinski, Alexandre; Cho, Won-Il; Kaskel, Stefan; Yushin, Gleb; Sulfur-Infiltrated Micro- and Mesoporous Silicon Carbide-Derived Carbon Cathode for High-Performance Lithium Sulfur Batteries, *Advanced Materials*, 2013DOI: 10.1002/adma.201301579
- Strubel, Patrick; Thieme, Soeren; Biemelt, Tim; Helmer, Alexandra; Oschatz, Martin; Brueckner, Jan; Althues, Holger; Kaskel, Stefan; ZnO Hard Templating for Synthesis of Hierarchical Porous Carbons with Tailored Porosity and High Performance in Lithium-Sulfur Battery, *Advanced Functional Materials*, 2014, DOI: 10.1002/adfm.201402768

No further publications in preparation/planned.

Berichtsblatt

1. ISBN oder ISSN	2. Berichtsart Abschlussbericht
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3b. Titel der Publikation	
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	16. Zusätzliche Angaben
17. Vorgelegt bei (Titel, Ort, Datum)	
18. Kurzfassung Elektromobilität verspricht ein großes Potential, aber weitere Innovationen sind nötig, um die Nachteile der Elektrofahrzeuge gegenüber Verbrennungsmotor betriebenen Fahrzeugen auszugleichen. Limitierend wirken sich vor allem die Kosten und die Energiedichte der Batterie aus. Letztere begrenzt im Wesentlichen die rein elektrische Reichweite der Elektrofahrzeuge. Lithium-Ionen-Batterien nach Stand der Technik erreichen ca. 200 Wh kg ⁻¹ . Neue Batterien mit signifikant höherer Energiedichte wären ein großer Schritt, um die Elektromobilität Massentauglich zu machen. Zukünftige Batteriegenerationen sind dabei eine große Chance für Europa den Technologievorsprung in Asien aufzuholen. Die Lithium-Schwefel-Technologie hat dabei das Potential, deutlich höhere Energiedichten zu erreichen und gleichzeitig Materialkosten zu senken. Im Rahmen des MaLiSu Projektes wurde ein signifikanter Beitrag zum fundamentalem Verständnis der Lithium-Schwefel Batteriechemie geleistet. Kohlenstoffmaterialien agieren als leitfähiges und stabilisierendes Gerüst für die nicht-leitfähigen Schwefelspezies. Der Einfluss der Nanostruktur des Kohlenstoffs auf die Performance in Schwefel-Kompositelektroden wurde grundlegend untersucht. Kohlenstoffmaterialien mit verschiedenen spezifische Oberflächen sowie verschiedenen Porenvolumina wurden von der TU Dresden als Projektpartner synthetisiert und den Partner des Fraunhofer IWS ¹ übergeben. Aus der elektrochemischen Charakterisierung ergab sich, dass Durchmesser von Transportporen ≥40 nm, Oberflächen von über 1000 m ² /g und hohe Porenvolumina von > 3 cm ³ g ⁻¹ entscheidend sind, um hohe Schwefelbeladungen und gleichzeitig eine hohe Schwefel-Ausnutzung zu erreichen. Für die Überführung der Ergebnisse in die Zellproduktion und die Anwendung in Elektrofahrzeugen sind jedoch weitere F&E-Arbeiten nötig.	
19. Schlagwörter Poröse Kohlenstoffe, Elektrodenprozessierung, Energiespeicher, Lithium-Schwefel-Batterien	
20. Verlag	21. Preis

*) Auf das Förderkennzeichen des BMBF soll auch in der Veröffentlichung hingewiesen werden.