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Work package: WP 2: System definition and benchmarking
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Title: D2.1 Definition of the starting chemical environment

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1 SUMMARY

The purpose of deliverable is to define starting chemical environment which will be used at the beginning of the project. Materials selections and characterization tools are derived out form the EUROLIS project (Grant agreement No. 314515).

Li-S battery electrochemical behaviour is a function of different parameters and this deliverable setup starting point for the following parameters:

- a) microstructural and physicochemical (e.g. electrical) properties of cathode host matrices,
- b) sulphur impregnation procedure,
- c) ratio between sulphur and electrolyte,
- d) areal capacity for the composite cathode,
- e) composition of cathode composite (binder, carbon black, and ratio between components)
- f) composition of electrolyte, type of separator and lithium metal.

Definition of parameters is based on the recent results in the EUROLIS project and objectives written in the grant agreement for the HELIS project.



2 OUTLINE

The starting materials for the Li-S battery configuration to be used in the first series of Li-S prototype cells are partially based on the achievements in the EUROLIS project. A carbon host matrix with a high porosity will be used for the impregnation with sulphur. Ideally, the carbon should be doped with nitrogen or other sulphur absorption surface sites to enable high affinity to polysulphides during cycling. The amount of sulphur should exceed 50 wt.% (overall electrode composition). The areal capacity is important and the objective is 3-5 mAh/cm². It is recommended to embark away from PVdF based binders – interesting alternatives are water based binders or using polymerised ionic liquids. Preferentially the electrolyte is based on a binary or multi-component solvent mixture with different concentrations of LiTFSI or LiTDI salts. The separator design should enable the storage of the required amount of electrolyte and prevent polysulphide diffusion from the cathode to the lithium metal anode. Besides preventing the polysulphide shuttle effect, protection of the lithium metal surface is needed. All components need to be properly characterised before they are used in the battery. This is crucial for the cell model development/validation as well. Electrochemical tests include starting (formation) cycle and continuous cycling with constant current. Results are to be given both as capacity per mass of sulphur (mAh/g_s) and as areal capacity (mAh/cm²).



3 CATHODE

3.1 Host matrices

Host matrices properties determining the sulphur impregnation, such as pore volume, pore size distribution, surface area and level of adsorption sites, play important roles in achieving specific capacity, cycling stability, and adequate Coulombic efficiency. Figure 1 shows the microstructure of some different carbons prepared at MPI. The optimal electrochemical behaviour was achieved using the carbon matrix presented in the middle of the figure, where the pore network provides enough space for the formation of Li_2S and at the same time storage volume for the electrolyte. The obtained specific capacity per mass of sulphur is *ca.* 1200 mAh/g_S at 60% of sulphur loading. Based on this, the requirements for the starting carbon host matrices are:

- Surface areas of 2000-2500 m²/g
- > 5cm³/g pore volume
- > 6 wt.% of N doped into the structure

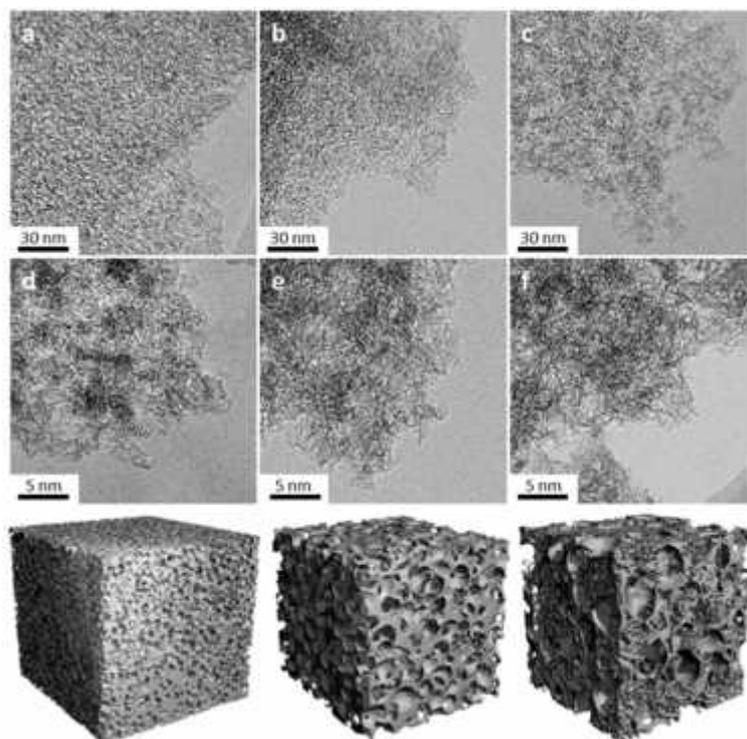


Figure 1: HRTEM images of different carbons. Bottom: Scheme of carbon structure (ref. doi:10.3390/met2020122).

Out of three listed requirements, the most important seems to be pore volume, since a larger amount of the electrolyte in the cathode composite leads to a higher sulphur conversion and more stable cycling (probably less diffusion out from the cathode). Based on the literature, surface area has no large influence, however, with a high surface area we can introduce a larger amount of adsorption sites, which may lead to more stable cycling. Type of porosity needs to be checked since bottle neck pores or pores interconnected with small throats can be problematic for long term running (passivation or precipitation can completely stop interconnection between pores).

3.2 Sulphur impregnation

The classical sulphur impregnation method is made at 155°C in argon (Ar) atmosphere. Prior to this heat treatment, the carbon/sulphur mixture has to be thoroughly mixed to obtain a homogenous distribution of carbon and sulphur. Large quantities of material may lead to heterogeneities and consequently to sulphur particles being left after the impregnation as shown in Figure 2. This must clearly be avoided.

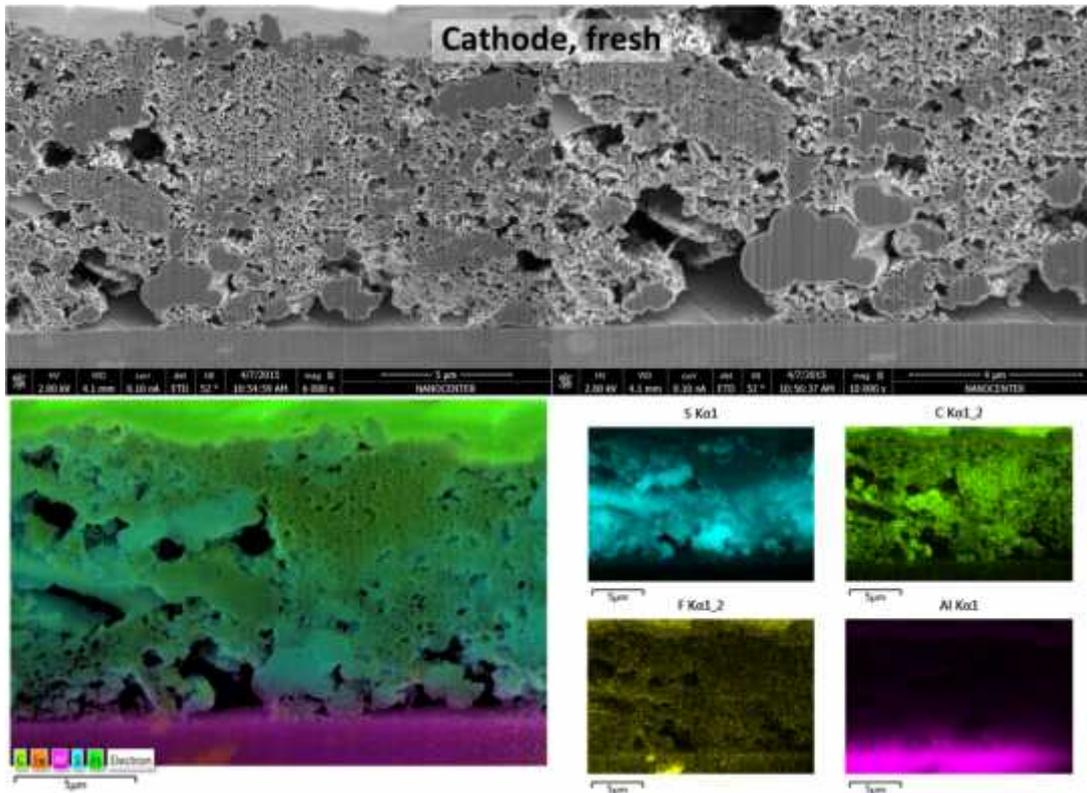


Figure 2: SEM-FIB images and EDX analysis of the fresh cathode cross section showing non homogenous sulphur distribution. Sulphur impregnation was obtained by sulphur infiltration method at 155°C.

The here suggested conditions to avoid this non-optimal sulphur distribution are:

- a) a longer dwell time for sulphur impregnation (a typical time is 6 h) or
- b) a wet impregnation method, where sulphur is dissolved in an organic solvent and the carbon host matrix is dispersed in the resulting solution.

For both a) and b) above, the obtained mixture needs to be further treated at 155°C in the inert atmosphere (after evaporation of excess solvent). All prepared samples, especially the more large scale samples, need to be checked by XRD and a few selected electrodes also by FIB-SEM-EDX analysis.

Any host matrices unable to accommodate at least 60 wt.% of sulphur are out of interest as this will lead to overall specific capacities of the composite too low for the project objectives.

4 ELECTROLYTE AND BINDER

The solubility of the polysulphides in the electrolytes is mainly influenced by the type of solvent used. Therefore, basic studies of interactions between solvents and polysulphides are important to reveal e.g. the influence of properties such as donor number, polarity, and viscosity to further understand solubility, disproportionation reactions, precipitation of non-soluble products, etc. The emphasis is solvents with high polysulphide solubility as the amount of electrolyte required for complete conversion of sulphur into Li_2S and back during cycling can then be reduced (and large quantities substantially reduce the energy density of the Li-S cell). According to our predictions the quantity of electrolyte should preferably be less than 5 $\mu\text{L}/\text{mg}$ of sulphur.

The Li-S cell electrolyte is a mixture of two or more solvents with a defined salt concentration and several different compositions are still needed to be explored including varying the Li-salt(s) (LiTFSI and LiTDI) and Li-salt concentration(s). Based on the EUROLIS project, it is recommended to consider an ionic liquid (IL) as one of the components.

In the EUROLIS project we have especially identified ILs with a methoxyethyl chain grafted onto the nitrogen atom of the cation to have superior performance as compared to other standard ILs. However, due to their high viscosities, such ILs (Figure 3) have only been used together with standard organic solvents. Further investigations in terms of polysulphide solubility, changes in viscosity and ionic conductivity, etc. have to be done in order to understand how different solvent mixtures influence the performance of Li-S batteries, especially cycling.

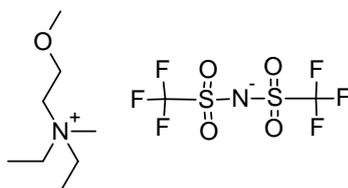


Figure 3: $N_{1,2,2,(201)}$ TFSI, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide

As for the binder, we need to embark away from classical PVdF based binders to binders more suitable for Li-S batteries. Aspects related to the binder self-organization (location/microstructure) at the vicinity of the solid phases within the host matrix should be addressed. In the project we plan to use polymerised ILs based binders, which already have shown improved properties compared to PVdF. Other potential binders allowing low drying temperatures should be tested and benchmarked.

5 SEPARATOR AND LITHIUM

The role of the separator is to electrically insulate the positive and the negative electrodes, while still enabling ionic conduction (Li^+). Additionally, the separator acts as an electrolyte buffer, especially important for Li-S cells due to the large amount of electrolyte required for the sulphur conversion reaction. Classical separators used in the Li-ion technology are therefore not appropriate; they can typically store only *ca.* 0.8 and $1.4 \mu\text{l}/\text{cm}^2$, while we need at least $3\text{--}5 \mu\text{l}/\text{cm}^2$. The separator also aims at completely stopping polysulphide diffusion between the electrodes. A lithium conductive ceramic membrane, LATP from Ohara, was demonstrated to completely stop polysulphide diffusion why a Coulombic efficiency up to 99.95% could be obtained (Figure 4). However, after a certain number of cycles, depending on the amount of lithium, we observed cell failure. Careful analysis showed complete destruction, with degradation products found throughout the whole cross section of the lithium electrode (Figure 5).

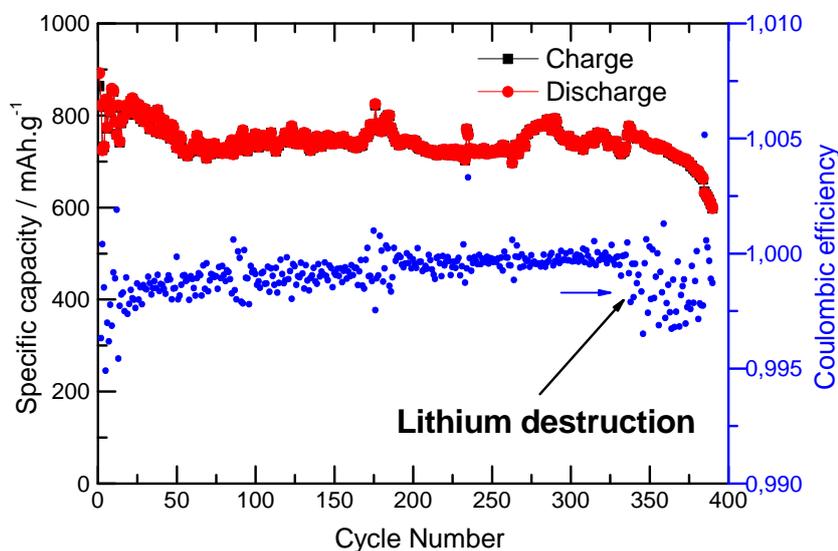


Figure 4: Specific capacity and Coulombic efficiency as a function of number of cycles.

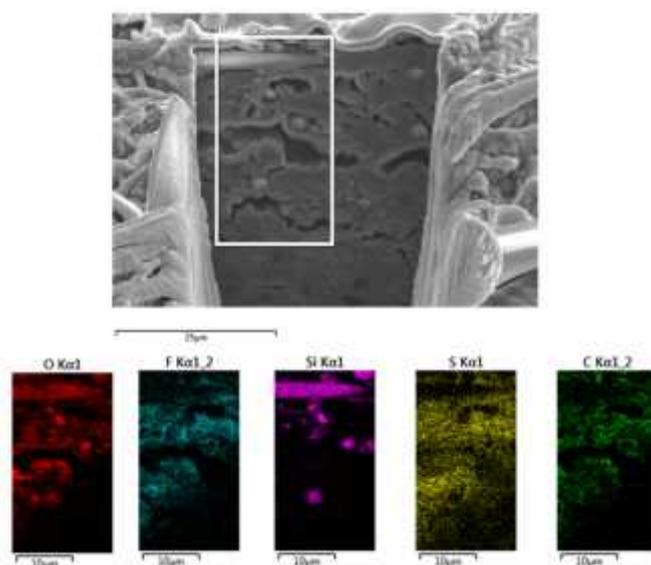


Figure 5: SEM-FIB images and EDX analysis of the cycled lithium foil.

Based on Figures 4 and 5 the following guidelines for the further development of the separator and the lithium negative electrode can be suggested:

- a) One alternative separator concept is carbon felt (as suggested by prof. Peled at the KO).
- b) The separator has to be selective for different polysulphides (long-, mid- and short-chain).
- c) An inorganic or organic protection layer is required for long term cycling.

6 CHARACTERISATION AND ELECTROCHEMICAL TESTS

6.1 Characterisation of cell components

A proper characterisation of all cell components is important for understanding the consequences of changes in the cell chemistry and finally meet the project objectives and for the models validation in WP5.

- For the carbon host matrices we need to obtain materials' parameters by typical characterisation tools like BET surface area, porosity and pore size distribution, composition (obtained by CHNS and TGA), electrical resistivity of the host matrix would be also useful since the increase of pore volume may result in a decrease in conductivity.
- For the electrolytes solubility tests for polysulphides including different chain lengths needs to be evaluated for different compositions.

6.2 Electrochemical tests

Since electrolyte can dissolve high amount of PS and has a strong influence on capacity and life, it would be interesting to figure the total amount of electrolyte per mg of sulphur and also the volume of the porosity of the set (separator + positive electrode) expressed in $\mu\text{l}/\text{mgS}$.

The typical galvanostatic charge/discharge procedure is performed on the laboratory scale. The current densities used should always be based on the quantity of sulphur in the electrode and the current should be calculated on the basis of $1672 \text{ mA}/\text{g}_\text{S}$. An electrochemical window between 3.0 V and 1.5 V should be used if not determined differently during the project. Results are to be presented as capacity calculated from the charge used for charging and the charge obtained during discharging. The ratio between charge obtained during discharge and charge used for battery charging determines the Coulombic efficiency, which is an indicator of the success of both the cell chemistry and the cell design. Formation cycle is typically to be made at low current densities corresponding to C/20 or C/50 rates (i.e. $0.836 \text{ mA}/\text{g}_\text{S}$ or $0.334 \text{ mA}/\text{g}_\text{S}$) while the main part of the cycling should be made at C/10 to C/5. The life cycle tests should aim at least 50 cycles (laboratory scale) to validate a specific chemistry. For EV application, energy density is measured at C/3 rate; therefore a cycle at C/10 charge rate and C/3 discharge rate would give indication on the energy density for the targeted application. The observed capacities always need to be re-calculated to the electrode level (including the weight of the current collector) and in addition the areal capacity (mAh/g) should be provided to evaluate the appropriateness of the Li-S cell chemistry – our objective is to reach 5 mAh/g. All electrochemical results should be accompanied with the electrolyte to sulphur ratio used and the temperature, which should be provided and also continuously measured if not stable within $\pm 2^\circ\text{C}$.



7 CONCLUSIONS

This deliverable defines some of the starting points in the materials selection for the Li-S batteries. Most of the recommendations are based on the results and the experiences from the EUROLIS project. Within the deliverable recommendations for carbon host matrix properties, sulphur impregnation method, electrolyte composition, binder selection, separator properties, characterisation techniques, and electrochemical tests are provided.

The recommendations within this deliverable do not prevent the use of any other component available in any partner's laboratory that can lead to improved performance of Li-S prototype cells. Work package leaders should initiate discussions between partners involved in the preparation of the Li-S cell prototypes.



ABBREVIATIONS:

Li₂S – lithium sulphide

HRTEM – high resolution transmission electron microscope

Ar – argon

SEM – scanning electron microscope

FIB – focus ion beam

EDX - energy-dispersive X-ray spectroscopy

XRD – X-ray diffraction

N_{1,2,2,(201)}TFSI - N,N-diethyl-N-methyl-N(2methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide

PVdF – Polyvinylidene fluoride

LATP - Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O₁₂

BET - Brunauer–Emmett–Teller

TGA - Thermogravimetric analysis

CHNS – carbon, hydrogen, nitrogen, sulphur

LiTFSI - Lithium bis(trifluoromethanesulfonyl)imide

LiTDI - Lithium 4,5-dicyano-2-(trifluoromethyl) imidazolidide

IL – Ionic liquid

