

## Project title

Hybrid gel electrolytes for all-solid-state Li-ion batteries

### BACKGROUND AND RATIONALE

Rechargeable lithium batteries are widely used for portables due to its large energy density. The Li-ion batteries (LIB) enable the development autonomous devices. The emerging market of smart devices in all areas asks for bendable miniaturized power sources and pushes the development of microbatteries, which are flexible and free in design. The miniaturization requires an even higher gravimetric and volumetric energy density. Therefore, lithium metal as negative electrode is tested for secondary batteries. Lithium metal is the anode material of choice because of its very high theoretical specific capacity of 3861 mAh/g, a low density of 0.59 g/cm<sup>3</sup>, and fast ion transfer. Lithium provides the lowest negative electrochemical potential (-3.040 V vs. the standard hydrogen electrode), which enlarges the potential difference between both electrodes. Furthermore, lithium is electronic conductive and does not require a current collector and it is cyclable for thousands of cycles. The use of Li metal as electrode brings the challenging problem of the inhomogeneous depositions of lithium on the negative electrode surface. These depositions are known as dendrites which reduce the life time and can even create a short circuit between the electrodes. The dendritic growth has hindered a wide commercialisation of Li-metal as anode material.

Solid electrolytes (SE) are advantageous because it can form a mechanical barrier against dendritic growth. Solid electrolytes can be Li-ion conducting ceramic materials, such as LiPON [1], or polar polymers, such as PEO [2] or PVDF [3], that dissolve a lithium salt. SEs reduce safety hazards because no volatile and flammable organic solvents are needed. In addition, the replacement of the liquid electrolyte by a solid electrolyte enabled the fabrication of microbatteries due to their form flexibility. Solid electrolyte nm-thin layers can be fabricated [1]. However, SEs have a low ionic conductivity. The Li-ions conduction happens along defects in inorganic and polymer SEs or along coordination centers along the polymer chains [4]. A new class of electrolytes were investigated that combine the mechanical stability of SEs and the high ionic conductivity of liquid electrolytes.

Quasi-solid electrolytes consist of an electrolyte solution mainly based on an ionic liquid, which is encapsulated in an inorganic or organic host matrix. Ionic liquids which display negligible vapor pressure and wide chemical, electrochemical, and thermal stability. IL-based electrolyte solutions can be immobilized in a 3 dimensional organic or inorganic network while trying to keep their properties. They are known as gel polymer electrolytes (GPEs) and ionogels (IGs), respectively. GPEs exhibit a high ionic conductivity and are flexible [5][6]. Various research groups have fabricated bendable batteries that [7] [8] [9]. However, GPEs are not stable enough to mechanical hinder dendritic growth in LMBs [10] [11]. IGs, most commonly with a silica scaffold, combine the high ionic conductivity and the mechanical stability of solid electrolytes. IGs were successfully tested in Li-ion batteries [12] [13] [14]. IGs can be prepared *via* a sol-gel process [15] [16] [17]. On one hand, the sol-gel technique brings multiple advantages. The sol-gel technique is a low-energy and low-cost process which is up-scalable. In addition, the direct deposition of the electrolyte precursor solution (EPS) on the positive electrode allows the EPS to penetrate the porous electrode material and to form a good contact of the electrolyte/electrode interface [18], which is an issue in all-solid batteries. On the other

hand, the process is very long. The gelation time of the EPS can take up to several days if uncatalyzed, and also the drying of the gel has to be done carefully to avoid cracks. The cracks may appear due to surface tension upon the removal of unreacted components and volatile products and by-products, whereby the IG shrinks. Formic acid (FA) is often used as catalyst in the IG synthesis to adjust the gelation time to tens of minutes or some hours [19]. The use of trifluoroacetic acid (TFA) with a lower  $pK_a$  value (0.23 vs. 3.75), allows to use a smaller volume, which is beneficial for the drying process. However, carboxylic acids are known to attack cathode materials such as LCO and LTO [20]. LFP was shown to maintain its properties in presence of carboxylic acids [21]. LFP is one cathode material of interest because of its excellent safety and long-life span.

IGs prepared *via* the sol-gel route reach ionic conductivities close to the one of the corresponding IL-based electrolyte solution (ILE) [22] [23]. The transference number was found to be higher than in the original ILE. The silanol groups on the silica matrix surface are believed to create pathways for Li-ions. Furthermore, dependent on the pore size and shape, the ions of the Li salt dissolved in the IL can be destructured, that means the ion mobility is increased [24]. On the contrary, too small pores can hinder ion movement due to increased ILE viscosity. The viscosity of the ILE plays an important role for the ionic conductivity. The conductivity increases with increasing salt concentration until the ILE viscosity becomes too important. Other research groups found similar effects [25]. 3-methacryloxypropyl and 3-glycidioxypropyl functional group on the silica surface can accelerate the Li-ion transport [26] [27]. Recently, an ice layer around the silica particles pushed the ionic conductivity above the corresponding ILE [Chen2020]. At the interface of the host matrix and the ILE, the IL ion and the Li salt ions form layers. Their arrangement is crucial for the Li-ion transport and has been studied for different IL/salt, IG and polymer electrolyte systems [28] [29] [30] [31] [32].

Despite all the advantages of the silica-based IGs, the rigid silica scaffold turns the IG brittle. Hence, hybrid electrolytes (HEs) are investigated. HEs are composed of both inorganic particles and polymers. The polymer ensures the electrolyte flexibility and the inorganic particles form a barrier against dendrites. Different inorganic nanoparticles such as clay [7] or silica [33] [34], were added to GPEs to increase the gel's stability and ionic conductivity. Likewise, polymers are added to IGs to improve the mechanical properties [35]. Hybrid electrolytes have been successfully tested [36] [37] [38] [39]. Hybrid electrolytes with a functionalized silica scaffold entwined with a flexible polymer matrix can create a quasi-solid electrolyte for lithium metal batteries resistant to dendritic growth and with high ionic conductivity.

## OBJECTIVES AND RESEARCH QUESTIONS

The aim of this project is to develop a hybrid electrolyte (HE) for LIBs based on a 3-dimensional silica-polymer matrix which hosts an IL-based electrolyte solution that enables a high ionic conductivity. The silica scaffold will be functionalized to facilitate the fast Li-ion transport. The HE will be synthesized by the inexpensive and up-scalable sol-gel process that allows a good contact between electrolyte and electrodes. The role of the silica precursor, ILE, polymer, catalyst and water on the resulting HE structure to optimize the HE structures regarding the ionic conductivity and mechanical stability.

The influence of ILs (mainly based on imidazolium) in the sol-gel synthesis has been reported for IGs [40] [41] [42]. Introducing the polymer further complicates the system. It is of interest to study these parameters to control and engineer the HE structure.

The HE will be compatible with LFP/Li metal systems. Dendrite-free flexible microbatteries with a long cycle life will be prepared for the application in autonomous smart devices.

## RESEARCH METHODOLOGY

The project objectives will be reached by developing the synthesis protocol towards an open-porous 3-dimensional with pathways for fast Li-ion travel. The synthesis will be based on the HE developed in the NCE laboratory and will happen over a sol-gel process with low water amounts and TFA as catalyst to adjust the gelation time suitable for the battery fabrication. The ILE is based on the IL PYR13-FSI and the lithium salt LiFSI. These materials resist the conditions in a galvanic cell and have proven to be excellent electrolyte solution in IGs. Especially the smaller size of the FSI- anion compared to TFSI- reduces the ILE viscosity. High Li salt concentration ( $\geq 3\text{M}$ ) and showed improved ionic conductivity and cycling behavior [43] [44]. PVDF-HFP is a suitable candidate for the polymer matrix because of its wide electrochemical stability window it is already used in GPEs [6]. It is soluble in acetone and mixable with the silica precursor and the ILE. Silica precursor such as 3-methacryloxypropyltrimethoxysilane or 3-glycidyloxypropyltrimethoxysilane can directly be used to produce a 3D scaffold with Li-ion paths. Traditional silica precursors such as TEOS (or TMOS for higher reactivity) can be used since the -OH terminated silica bounds water that interact with the FSI-ions due to increased dipole and liberates the Li-ions resulting in increased ionic conductivity [44]Chen2020]. The condition of the water layer formation will be studied. Especially, the interaction, role and influence of the components in different ratios, namely the Li salt, IL, silica precursor and polymer, water and catalyst during the sol-gel process and the resulting structure. Also, the interaction of the ILE with the combination of silica and polymer matrices will be determined to understand and tailor ion aggregation for fast Li-ion transport. Not only the silica scaffold, but also the polymer matrix enhances the ionic conductivity. The polar C-F bonds of the PVDF-HFP may help to dissociate the Li salt and facilitate the ion transport [45]. Raman, FTIR and NMR spectroscopy are applied in this context.

The HE structure can be analyzed by SEM, AFM and EDX to distinguish between both matrices and to identify their morphology. The ILE can be removed from the pores by Soxhlet extraction with a suitable solvent to study the porosity of the hybrid-matrix by gas sorption techniques and SEM. Dependent on the silica/polymer ratio, the silica scaffold might be self-standing so that it can be analyzed separately from the polymer matrix by SEM and nitrogen sorption. The mechanical stability of the HE will be tested by Young's modulus and tensile strength measurements.

After the profound structural characterization, the electrochemical properties will be studied. For this purpose, different deposition techniques such as spray coating and spin coating will be engaged to obtain  $\mu\text{m}$ -thin HE layers. For ionic conductivity measurements, the HE will be enclosed between two stainless steel disks in a coin cell in an argon-filled glovebox. The temperature dependence of the ionic conductivity will be studied. Equally, the Li-ion transference number will be determined. For the battery preparation, the HE layers will be directly deposited on the cathode and the penetration into the cathode pores will be verified by EXD. Coin cells of the LFP/HE/Li system will be prepared in an argon-filled glovebox to study

the PEIS and GC. The cycling-rate will be varied and the temperature will be controlled. The focus will also lie on the growth of dendrites that can be detected via the form of the charge and discharge curve during the GC measurements. The cathode stability will be tested *via* CV. In the last step, flexible batteries in a pouch cell design will be prepared to test the mechanical and electrochemical performance upon bending.



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