Abstract
The PhD thesis was embedded in the Energy for Smart Objects (EnSO) project, which is part of the Electronic Components and Systems for European Leadership (ECSEL) Joint Undertaking in collaboration with the European Union’s H2020 Framework Program (H2020/2014-2020) and National Authorities, with the aim to develop Autonomous Micro Energy Sources (AMES) for smart objects. In the framework of the EnSO project, the goal of the thesis was to develop a solid electrolyte for all-solid Li-metal microbatteries as energy storage device in AMES. Lithium metal is the anode material of choice because of its very high theoretical specific capacity of 3861 mAh/g, which is one of the important requirements for miniaturized batteries. However, inhomogeneous lithium depositions known as dendrites, which reduce the life time and can connect both electrodes and create a short circuit, are often observed when using Li-metal as anode. The aim is therefore to develop a solid electrolyte, which presents a high ionic conductivity for the Li ion transport and a high mechanical stability to hinder dendritic growth. Electrolyte solutions based on ionic liquids (ILs) with dissolved lithium salt can be confined into inorganic porous networks forming so called ionogels (IGs), which are investigated as quasi-solid electrolyte materials.

In a first step, the synthesis in a one-pot sol-gel process for silica-based ionogels is developed and in a second step tested as quasi-solid electrolyte in Li/LiCoO2 systems. IGs were obtained by a sol-gel reaction between TMOS as silica precursor and TFA as catalyst in PYR13-FSI (IL) and LiTFSI (Li+ source). It was possible to synthesize transparent IG monoliths with gelation times of 2-3 h, which is a suitable time for the IG film preparation on the LCO cathodes. Four IGs with different compositions were prepared and characterized. Two types of silica matrices built of mostly threefold-condensed Si centers could be distinguished: a densely packed structure and an open-porous structure, the latter one corresponding to IG B with the molar ratios IL/TMOS=3, TFA/TMOS=0.3, H2O/TMOS=2.3. The ionic conductivity of the IGs could be linked to the silica matrix structure. Only the IG with the open-pore structure (IG B) has a good ionic conductivity (10⁻⁴ S/cm). Equally, the examination of the four IGs as thin film electrolytes in LCO/Li batteries show promising results for batteries containing IG B. However, the capacity lies under the theoretical value (89 mAh/g instead of 136 mAh/g) due to high cell resistance.

Therefore, the ionic conductivity of IG B was improved by changing the synthesis process while keeping the composition unaltered. The new IG B⁺ has a very good ionic conductivity (10⁻³ S/cm) but a poor mechanical stability due to a matrix structure of loosely connected silica particles. IG B⁺ was not able to hinder dendritic growth. Thus, the PVDF-HFP polymer (20 wt.%) was added to B⁺ (B⁺-p), which enhanced the mechanical stability and the cyclability of the Li-ion batteries with B⁺-p as electrolyte layer. No indication of dendrites was visible in the charge/discharge curve for minimum 30 cycles at C/5. The capacities are low (≤ 80 mAh/g) due to the decreased liquid (IL) to solid (SiO2 + PVDF-HFP) ratio, which results in a lower lithium ion mobility.

In order to increase the battery capacity, the silica amount in the IG formulation was reduced, the LiTFSI lithium salt concentration was increased, and the Li⁺ source was modified by taking IL-based electrolyte solution with different concentrations of LiFSI. Indeed, the capacity increases with decreasing silica amount due to improved ion mobility. The change of the lithium concentration from 1M to 3M and 5M enhanced the capacity. A battery with the combination of the reduced silica amount (0.5 TMOS) and 5M electrolyte solution has a good capacity (> 100 mAh/g) for at least 10 cycles at C/5. The lithium salt LiFSI has a smaller anion than LiTFSI and thus, it can further improve the ion mobility in the IG electrolyte film. All IGs containing LiFSI have a higher ionic conductivity than the corresponding gels with LiTFSI.
Overall the battery performance and reproducibility could be greatly improved. Batteries containing a solid electrolyte with 20 wt.% PVDF-HFP and the reduced TMOS amount with a 3M LiFSI solution are able to cycle without the appearance of dendrites for 13 cycles at C/5 followed by 12 cycles at C/2 with a rather good coulombic efficiency around 95%. However, the capacity remains under the theoretical maximum. 

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