Silica-based ionogels as a promising solution for all-solid-state Lithium-ion microbatteries

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The emerging market of the Internet of Things, smart objects and others increase the demand for micro energy sources. Rechargeable lithium-ion batteries are a well-known technology for energy storage. However, safety issues and high production costs constrain progress. Research on solid electrolytes, such as LiPON, was performed to evade leakage. But LiPON suffers from low ionic conductivity and a cost and time intensive production process. Another approach is the substitution of volatile and flammable organic electrolyte solvents with ionic liquids (IL), 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 [1]. The use of polymers as host structure obtaining gel polymer electrolytes offers good ionic conductivity. However, the growth of lithium dendrites may be observed during cycling, which reduce battery lifetime. Electrolyte solution based on ILs can be confined into inorganic porous networks forming so-called ionogels, which are investigated as solid electrolyte materials. Ionogels combine low hazard and good ionic conductivity [2].

Silica-based ionogels compatible with $Li/LiCoO_2$ systems were prepared in a one-pot sol-gel process. The composition of the ionogel precursor solution and the influence of trifluoroacetic acid (TFA) as catalyst were studied to obtain a fast condensation. The time and the extent of the gelation were determined using the tilting method and ^{29}Si solid-state NMR, respectively. Homogeneous and transparent ionogels were obtained with a gelation time of less than 12 h.

First, the physical properties of the host matrix were characterized by N_2 sorption, Hg porosimetry and SEM. The silica host matrix is a 3D network predominantly built from 3-fold condensed silicon centres. The SEM images of the dried SiO_2 host matrix reveal two different structures (Fig. 2). For the lowest IL amount (molar ratio IL/Si precursor = 1), spheres (diameter 0.7 µm) are obtained, which form macropores of 5 µm. The other gels (molar ratio IL/Si precursor = 3 or 5) present smaller particles, which are more densely packed. All ionogels present micropores and a BET surface area around 800 cm²/g.

Then, the electrochemical performances of the ionogel were evaluated with complex impedance spectroscopy measurements and galvanostatic cycling (GCPL). The ionogels were tested in $Li/LiCoO_2$ microbatteries to investigate their electrochemical properties as solid-state electrolyte and their ability to hinder lithium dendritic growth. A first result shows that these promising ionogels may be successfully used as electrolyte in $Li/LiCoO_2$ cells. A first battery was prepared, which cycles more than 100 cycles at a rate of C/2 with no evidence of dendritic growth (Fig. 3a). Impedance characterization reveals the high internal resistivity of this battery, which explains the decrease of the discharge capacity over time (Fig. 3b).

The next step is to understand the correlation between the structure of the SiO_2 host matrix and the electrochemical performances of the ionogel electrolyte layer in $Li/LiCoO_2$ batteries.

References

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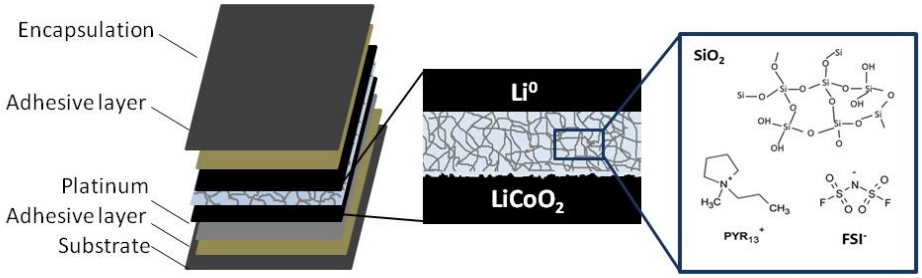

Figure 1: Solid SiO_2/ionic liquid electrolyte for all solid-state Li-ion microbatteries.

a) b)

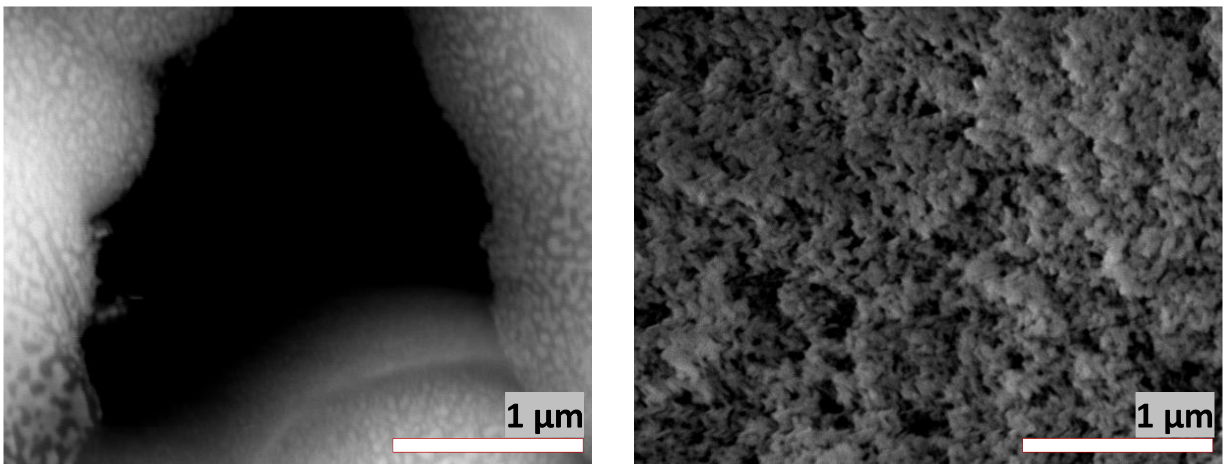

Figure 2: SEM images of a) the ionogel with molar ratios: IL/TFA/Si precursor = 1/0.3/1 and b) the ionogel with molar ratios: IL/TFA/Si precursor = 3/0.3/1.

a) b)

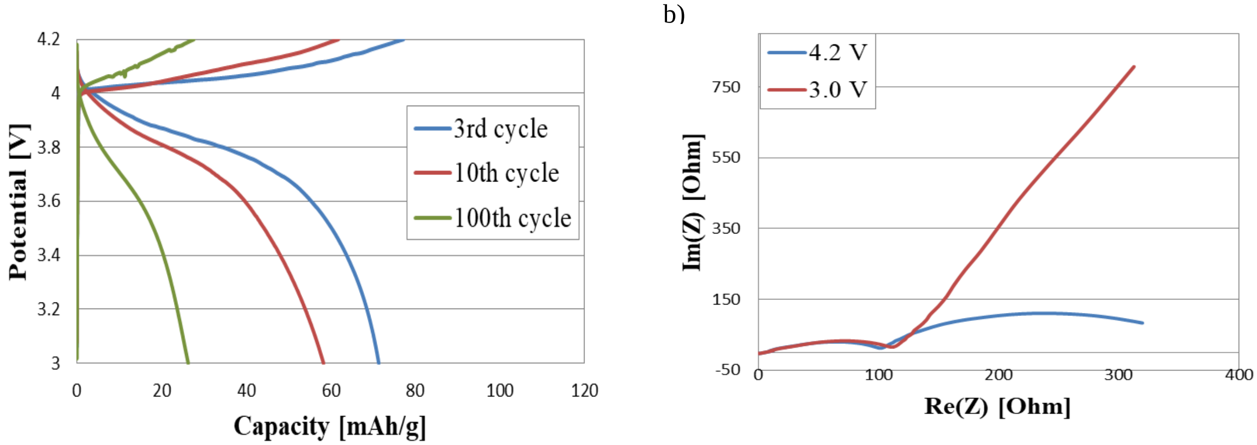

Figure 3: a) Galvanostatic discharge/charge curves of a Li/ionogel/$LiCoO_2$ cell at a cycling rate of C/2. The composition of the ionogel is: molar ratios IL/TFA/Si precursor = 3/0.3/1. b) Corresponding impedance spectra of the charged (4.2 V) and discharged cell (3.0 V).