Silica-based thin film solid-state electrolytes for Lithium-ion microbatteries

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Introduction

The emerging market of the Internet of Things, smart objects, wearables 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. Electrolyte solution based on ILs with dissolved lithium salt can be confined into inorganic porous networks forming so-called ionogels, which are investigated as solid electrolyte [1]. Ionogels combine low hazard and good ionic conductivity. However, the growth of lithium dendrites may be observed during cycling, which reduce battery lifetime. In this project, we try to prepare a silica-ionogel to prevent dendritic growth by mechanical hindrance. The ionogel composition and the influence of trifluoroacetic acid (TFA) as catalyst were studied to obtain a fast condensation of the silica precursor.

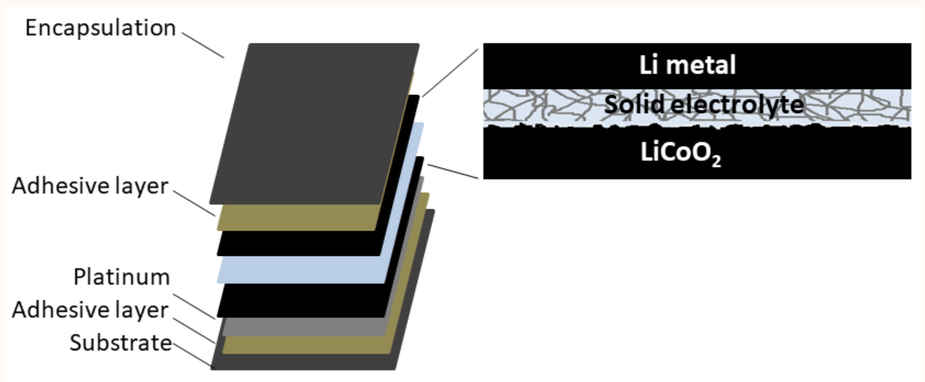


Figure 1. Scheme of a lithium ion microbattery with lithium anode, silica –based ionogel as solid electrolyte layer, and $LiCoO_2$ cathode.

Experimental Section

Ionogel preparation

Ionogels were prepared according to the literature [2] under ambient conditions with TFA. The lithium salt bis(trifluorosulfonyl)imide lithium salt (LiTFSI) was dissolved in the IL (N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR13-FSI)) to prepare the electrolyte solution. TMOS was used as a silicon precursor. The molar ratios of IL/TMOS was set to 2 or 3; the molar ratio of TFA/TMOS was between 0.1 and 0.5. Gelation and ageing were conducted at 25 °C or 50 °C. The gels were dried over 3 days with temperature increasing incrementally to 100 °C while stepping the pressure down to 1 mbar.

Characterization

The time of gelation was determined using the tilting method.

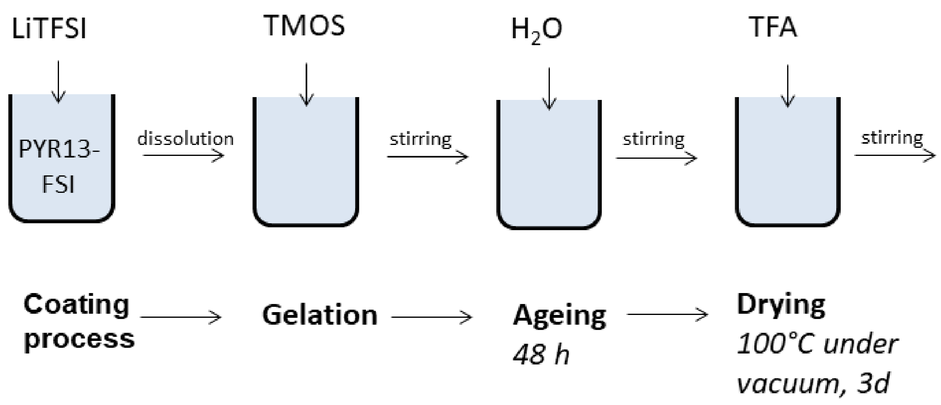
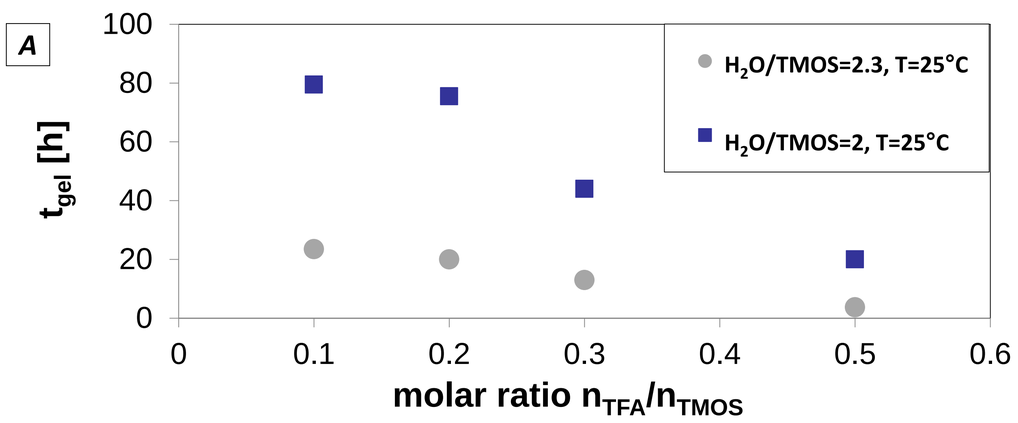


Figure 2. Scheme of the steps of the ionogel preparation via a one-step sol-gel process.

Results and discussion

The gelation is significantly accelerated by the addition of TFA and by increasing the water content for a fixed molar ratio n_{IL}/n_{TMOS} of 3 (*Fig. 3A*) and 2 (*Fig. 3B*). The added water amount is a crucial parameter since more than two methoxy groups per TMOS molecule have to be hydrolysed and condensed to obtain a 3-dimensional silica network. Also increasing the reaction temperature to 50°C shortens the gelation time. The comparison between Fig. *3A* and 3B shows that the gelation is accelerated when the IL concentration is increased. Indeed, it is known that interactions of the ions of the IL itself and the lithium salt as well as the silicon precursor can accelerate the condensation and overcome diluting effects [3].

The ionogels obtained are transparent (*Fig. 4*). A phase separation is avoided by keeping the water amount under the miscibility threshold (here n_{H_2O}/n_{TMOS} =2.3).



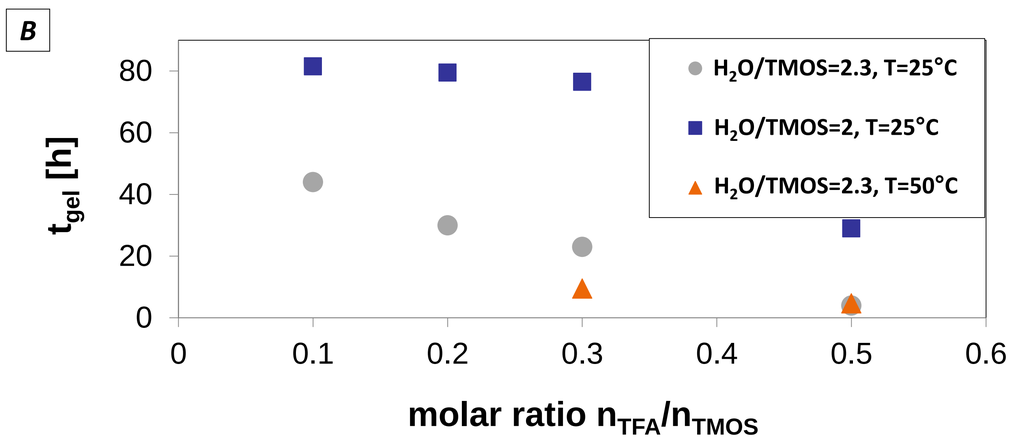


Figure 3. Gelation times in hours for the ionogel synthesis catalyzed by TFA. The molar ratio of IL and TMOS were 3 (A) and 2 (B). Two different water amounts (molar ration H_2O/TMOS= 2 (blue squares) and 2.3 (grey dots)) and four different TFA amounts were tested. The reaction was carried out at room temperature (blue and red) and at 50°C (orange triangles in B) for an molar ratio of H_2O/TMOS of 2.3. The gelation takes less time at high amount of catalyst. The gelation time can be significantly decreased by increasing water amount. Also increasing the reaction temperature to 50°C shortens the gelation time.

Figure 4. Transparent ionogels obtained with the molar ratios of IL/TMOS=2, H2O/TMOS=2.3 , TFA/TMOS=0.5 within 5 h (A) and IL/TMOS=2, H2O/TMOS=2.3 , TFA/TMOS=0.5 within 4 h (B).

Conclusions

Silica-based ionogels with confined IL were prepared in an one-step sol gel process catalyzed by TFA. Homogeneous and transparent gels were obtained with and a gelation time of less than 12 h. These promising ionogels will be tested in Li/$LiCoO_2$ microbatteries to investigate their electrochemical properties as solid-state electrolyte and their ability to hinder lithium dendritic growth.

References
[1] P.-E. Delannoy, . Power Sour., 2015, 274, 1085-1090.
[2] K. G. Sharp, J. Sol-Gel Sci. Technol., 1994, 2, 35-41.
[3] K. Donato, J. Sol-Gel Sci. Technol., 2015, 76, 414-427.