Five approaches towards design of single-ion conducting poly(ionic liquid)s for safe all-solid-state Li batteries

A.S. Shaplov[a]
E.I. Lozinskaya[b], G. Lingua[c] and C. Gerbaldi[c]

[a]*Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg*
[b]A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, 119991, Moscow, Russia
[c]GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino 10129, Italy
alexander.shaplov@list.lu

The development of safe, efficient solid-state lithium batteries requires polymer electrolytes with high ionic conductivity (>10^{-5} S cm^{-1} at 25 °C) as well as good electrochemical and thermal stabilities. Among promising candidates, a new class of polyelectrolytes, namely poly(ionic liquid)s (PILs), has recently gained significant attention. PILs can be considered as the macromolecular analogs of ionic liquids (ILs), in the best cases combining the advantages of polymers (viscoelasticity, processability, film-forming properties, etc.) and ILs (high thermal and electrochemical stabilities, enhanced ionic conductivity, etc.). In this work, five approaches for the design and preparation of novel anionic PILs or "polymeric single-ion conductors" and their testing in Li batteries will be presented.

I. First approach consists in synthesis of **block copolymers** via RAFT polymerization. Such copolymers comprise poly(lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) (poly**LiM**) and poly(ethylene glycol) methyl ether methacrylate (poly**PEGM**) blocks. The "best" obtained PIL shows T_g=-61°C, ionic conductivity of 2.3×10^{-6} (25°C) S/cm, electrochemical stability (ESW) of 4.5 V vs Li^+/Li and lithium-ion transference number t_{Li+}=0.83.

II. Second approach deals with the synthesis of **triblock copolymers** by RAFT polymerization of **LiM** using PEG-based macroRAFT agents. This method provided solid PILs as self-standing films with T_g=-55÷7°C, σ=4.4×10^{-10}÷3.4×10^{-8} (25°C) and 10^{-4} (70°C) S/cm, t_{Li+}=0.91 and ESW=4.0V vs Li^+/Li.

III. Third method utilizes free radical copolymerization of anionic monomers with PEGM for the preparation of **random copolymers** showing T_g=-56÷-50°C, conductivity of 1.8×10^{-6} (25°C) S/cm, ESW=4.2 V vs Li^+/Li and t_{Li+}=0.91.

IV. Fourth approach involves **network formation** via copolymerization of **LiM**, PEGM and bifunctional dimetha-crylate in the presence of propylene carbonate as plasticizer. This allows to achieve the formation of solid films demonstrating conductivity of 10^{-4} S/cm (25°C), ESW=5.5 V vs Li^+/Li and t_{Li+}=0.86.

V. Fifth approach applies combination of ring opening polymerization of trimethylene carbonate by RAFT-agent with terminal hydroxyl group and further utilization of such macro-RAFT in RAFT copolymerization of **LiM** and PEGM. In these **block copolymers** one block is responsible for ionic conductivity (2.9×10^{-7}(25°C)), while the second block - for improved mechanical properties and outstanding electrochemical stability (ESW>4.8V vs Li^+/Li) [1].

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References

[1] Lingua, G.; Grysan, P.; Vlasov, P. S.; Verge, P.; Shaplov, A. S.; Gerbaldi, C. Macromolecules 54 (14) (2021) 6911–6924.

Figures

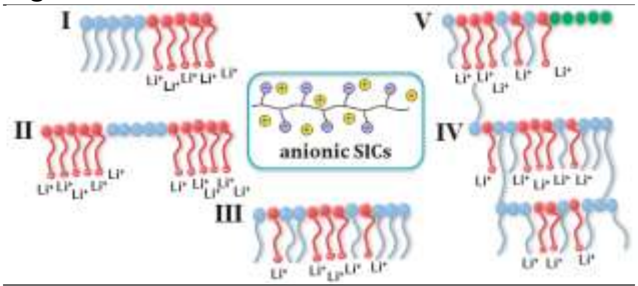

Figure 1: Five approaches for design of PILs.