

# Synthesis of single-ion BAB triblock nanostructured copolymers as efficient electrolytes for lithium metal batteries

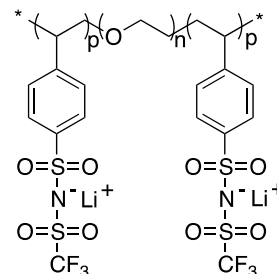
Didier Gigmes

Aix Marseille Université, CNRS, Institut de Chimie Radicale  
13397, Marseille cedex 20, France  
didier.gigmes@univ-amu.fr

The development of alternative transportation modes such as electric or hybrid vehicles, has become a key need for a sustainable long term development<sup>1</sup>. In this context, the increase of energy density for the battery systems is crucial and imposes necessary to explore original strategies for both the active electrode materials and electrolyte<sup>2,3</sup>. Among the different systems, battery technology based on a lithium metal anode would be particularly attractive notably in combination with Li-S and Li-air systems<sup>4</sup>. Unfortunately, the use of lithium metal associated with liquid electrolyte, led to safety problems due to a possible irregular metallic lithium electrodeposits during the recharge. In some cases, this phenomenon could result in dendrite formation responsible for dramatic explosion hazards. The use of a solid polymer electrolyte (SPE), could solve most of the safety issues encounter with liquid electrolyte. However, the development of SPE has been hampered by two hurdles i/ the inability to design a SPE that exhibits both a high ionic conductivity and good mechanical properties and ii/ during battery operation, the motions of lithium ions carry only a small fraction of the overall ionic current which leads to the formation of strong concentration gradient resulting in undesired effects like favored dendritic growth<sup>5</sup> and limited energy density especially when power increases.

In recent years, increasing research efforts have been focused on SPE made from block copolymers such BAB, where A represents an ionic conductor typically poly(ethylene oxide) (PEO) block and B a polymer providing the mechanical strength. Indeed, thank to their ability to self-assemble at the nano-scale, block copolymers represent a unique class of materials allowing the combination of different properties in a single material. The main advantage of the block copolymers is based on the covalent attachment of two different polymers, thus avoiding the unwanted macrophase separation when the blocks are immiscible.

In this presentation we will demonstrate the potential of the Nitroxide Mediated Polymerization technique to prepare a series of block copolymers fulfilling the specific criteria of solid polymer electrolytes films designed for lithium metal battery. More particularly, we will present the synthesis of a series of new type of BAB nano-structured symmetric triblock copolymers with an A block consisting of a linear poly(ethylene oxide) (PEO) as a template for lithium ion conduction, and a B block consisting of poly(4-styrene sulfonyl(trifluoromethylsulfonyl)imide) lithium salt.



The conductivity of these copolymers is almost one order of magnitude higher than that of the state of the art for such materials ( $1.310^{-5} \text{ Scm}^{-1}$  at 60°C) combined with a lithium ion transport number close to unity. Moreover the mechanical strength is drastically improved and the electrochemical window stability is extended to more than 5 V. The battery tests show that the power performances and cycling are outstanding particularly at 60°C which makes these materials highly attractive for next battery generation<sup>6</sup>.

## References

- [1] J. Tollefson, Nature, **456** (2008) 436-440.
- [2] F. Cheng, J. Liang, Z. Tao, J. Chen, Advanced Materials, **23** (2011) 1695-1715.
- [3] M. Armand, J-M Tarascon, Nature, **451** (2008) 652-657.
- [4] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J-M. Tarascon, Nature Materials, **11** (2012) 19-29.
- [5] J-N Chazalviel, Physical Review A, **42** (1990) 7355-7367.
- [6] R. Bouchet, S. Maria, R. Meziane, A. Aboulaich, L. Lienafa, J.-P. Bonnet, T. N. T. Phan, D. Bertin, D. Gigmes, D. Devaux, R. Denoyel, M. Armand, Nature Materials (2013) *accepted*.