Li/sulfur and Li/polysulfide systems: an investigation on electrode protections and electrode/electrolyte interfaces

Catia Arbizzani, Francesca De Giorgio, Andrea La Monaca, Irene Ruggeri, Francesca Soavi
Department of Chemistry "Giacomo Ciamician" – Alma Mater Studiorum Bologna University, Via Francesco Selmi, 2 Bologna (Italy)

E-mail: *catia.arbizzani@unibo.it*

Li/S batteries are good candidates for large-size, stationary applications because of the abundance and low cost of sulfur. However, Li/S systems are far to be marketed for several reasons. During the discharge sulfur is reduced to S^{2-} and converted to Li_2S in a series of processes that involve the formation of soluble and insoluble polysulfides (PSs) from Li_2S_8 to Li_2S_2. The conversion of S to Li_2S determines a large volume expansion of the electrode that negatively contribute to the cycle life of the cell. In addition, the soluble PSs shuttle toward the anode and cathode and cause unwanted side reactions at Li electrode with a resulting decrease in coulombic efficiency and cell failure [1].
An approach to limit the PSs shuttle effect is the use of suitable interlayer membranes that hinder the PSs crossover without greatly affect the energy density [2]. The interlayers should be electrochemically and mechanically stable under battery cycling and they also should be cheap and commercially available. Another strategy is the use of PSs instead of the solid S-based electrode to improve the capacity and the stability of the cell [3].
Several challenges are, hence, still open in Li/S and Li/PSs cells. Although the finding that $LiNO_3$ forms a good passivation layer that protects Li from the chemical and electrochemical reactions with the dissolved PSs, the Li stability over cycling is still a challenge and the choice of the electrolyte plays a key-role, especially when novel design concepts such as flow cells are taken into account. The selection of suitable electrolytes and the development of free standing interlayers and of thin polymer layer directly grown on the electrode surfaces to minimize the PSs permeability will be presented and discussed for Li/S and Li/PSs systems.

Acknowledgements
The authors thank for financial support MSE-ENEA Electrical System Research 2015-2017 "Energy storage for electric system" Project.

References:
[1] J. Liang, Z.-H. Sun, F. Li, H.-M. Cheng, Energy Storage Mater. 2 (2016) 76-106.
[2] C. Zu, A. Manthiram, Phys.Chem. Chem. Phys., 15 (2013) 2291-2297.
[3] D-H. Lim, M. Agostini, F. Nitze, J. Manuel, J.-H. Ahn, A. Matic, Sci. Rep. 7 (2017) 6327.