Formation of artificial solid electrolyte interphase by radiolysis

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Among energy storage devices, Lithium ion batteries (LIBs) are efficient power sources used for many applications including mobile microelectronics. However, ageing phenomena are not yet fully understood. These phenomena are a crucial issue to provide safe and stable batteries[1]. LIBs are usually composed of a negative electrode where the active material is graphite, a positive electrode usually a lithium metal oxide and an organic liquid electrolyte. Ortiz *et al.* have shown that radiolysis is a powerful tool to simulate the degradation of the latter one in short time: minutes/hours instead of weeks/months by electrolysis (Fig. 1). Moreover, radiolysis allows performing experiments at the picosecond time scale thus giving access to reaction mechanisms[2,3]. During the first cycles of the battery, the reduced surface of the negative electrode reacts with the electrolyte producing a solid interphase (solid electrolyte interphase, SEI)[4] which is responsible for the capacity loss of the battery[5]. In this work, we investigated the SEI formation by radiolysis at the surface of various carbonaceous materials including crystalline graphite (lithiated or not) and carbon nanoparticles (amorphous as well as organized) prepared by laser pyrolysis[6]. Materials were dispersed in a mixture of carbonate solvents containing $LiPF_6$. Composition and morphology of SEI were investigated by XPS and TEM while the composition of gas and liquid phases was studied by gas chromatography and high resolution mass spectrometry, respectively. We show that an artificial SEI can be produced by radiolysis. We observe always the same degradation mechanisms of the electrolyte but interestingly the SEI composition depends on the carbonaceous material. The artificial SEI formed at the surface of graphite is composed of Li carbonate, oxalate and oligomers of poly(ethylene oxide) while the SEI formed at the surface of carbon nanoparticles contains Li salts as Li_2CO_3. Radiolysis allows producing materials with modified surface that will be tested as new materials for negative electrode.

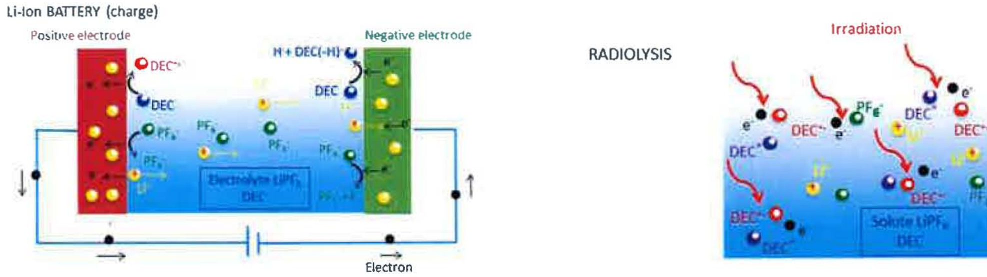

Fig. 1. *Comparison between primary electron transfers at the electrodes in the electrolytic charge/ageing processes of a Li-ion battery (in $LiPF_6$ 1 M/diethylcarbonate solution as a model electrolyte) (left), and after ionization in the bulk during radiolysis with the same medium (right)*[3].

References: [1]Larcher D., Tarascon J. M. *Nature Chem.* **2015**, *7*, 19-29. [2]Ortiz D., Steinmetz V., Durand D., Legand S., Dauvois V., Maître P., Le Caër S. *Nat. Comm.* **2015**, *6*, 6950. [3]Ortiz D., Jiménez Gordon I., Baltaze J.-P., Hernandez-Alba O., Legand S., Dauvois V., Si Larbi G., Schmidhammer U., Marignier J.-L., Martin J.-F., Belloni J., Mostafavi M., Le Caër S. *ChemSusChem* **2015**, *8*, 3605-3616. [4]Yan J., Zhang J., Su Y.-C., Zhang X.-G., Xia B-J. *Electrochim Acta* **2010**, 55, 1785-1794. [5]Peled E. *J. Electrochem. Soc.* **1979**, *126*, 2047-2051. [6]Galvez A., Clinard C., Rouzaud J.N., Herlin-Boime N., Reynaud C. *Carbon*, **2002**, *40*, 2775-2789.