Summary

Lithium-sulphur (Li-S) batteries have been considered as a promising storage system from the early sixties. Sulphur is cheap and abundant in nature. It has a high theoretical gravimetric capacity, high energy and high volumetric density. The Li-S battery offers many challenges that have to be overcome before the full commercialization of stable cells with high gravimetric energy density. The major issues are the lithium polysulphides diffusion and/or migration towards the anode, the so called lithium polysulphides shuttle mechanism and the cells self-discharge, which cause the capacity degradation.

In this work we investigate the effect of different cathode compositions either in charged state (carbon – sulphur composites) or in discharged state (cathode composites containing Li_2S). With aim to prevent or even completely stop polysulphides diffusion or migration from the positive electrode to the negative electrode, we have designed new separator interlayers based on chemically modified reduced graphene oxide and we have tested self-standing gel polymer electrolyte membranes

We show that pore volume and surface area of carbons play a role on the electrochemistry of Li-S batteries. By using *in operando* spectroscopy, such as UV-Vis and X-ray absorption spectroscopy on the Li_2S cathode material, we found that during the first oxidation Li_2S can be directly converted into sulphur, without going through the different lithium polysulphides steps.

The use of a chemically modified reduced graphene oxide with hydrophobic organic molecules or with directly bonded fluorine groups inhibit the diffusion of the lithium polysulphides towards the anode side. This was confirmed with different analytical techniques, such as *in operando* UV-Vis spectroscopy, a modified 4-electrode Swagelok cell and X-ray photoelectron spectroscopy.

Finally, the self-standing gel polymer electrolyte membrane used in an all solid-state and liquid Li-S cell configuration exhibit a decent electrochemical behaviour.

Keywords: Li-S batteries, cathode material, Li_2S as active material, reduced graphene oxide surface modification, separator interlayers, gel polymer electrolyte