EVS27 Symposium
Barcelona, Spain, November 17-20, 2013

EUROLIS - European lithium sulphur cells for automotive applications

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Short Abstract

EUROLIS is a European project started in October 2012 aimed at sustainable and advanced lithium sulphur (Li-S) batteries for automotive use with highly improved energy densities compared to today's Li-ion (LiB) technology. The combination of the promises of a Li-S battery based energy storage and the inexpensive and abundant materials used in the concept makes this research strategically valuable for Europe. Here we outline the basics of the Li-S battery concept, the main goals of EUROLiS and the partners involved, and how we aim to achieve the main goals.

1 Introduction

The on-going and foreseen increased electrification of the transport sector, the "electromobility" revolution, is one of the major driving forces for energy storage breakthroughs. The performance of the energy storage systems in XEVs is to a large extent totally dependent on the intrinsic promises of the battery cells used. While indeed the Li-ion battery (LiB) technology has advanced impressively the last decades, there are still severe limitations present which urge for improvement. Current rechargeable LiBs for XEVs are capable to deliver an energy density between 100-150 Wh/kg at the cell level, while a quite typical consumption of 1 litre of gasoline produces *ca* 2500 Wh of useful work – resulting in an order of magnitude difference between the energy delivered by 1 litre of gasoline and 1 kg of battery. Although we in our community all like to emphasize the advantages of XEVs, this in practice for the user *e.g.* translates into the autonomy of a car with similar weight driven by batteries alone is between 5-10 times shorter than with gasoline.

In addition, the LiBs of today absolutely need to be based on rather complex chemistries and manufacturing *e.g.* nano-coatings at both the electrodes, numerous additives in the electrolyte to ensure both performance and safety, and the use of expensive elements (Co,Ni) in the positive electrode (NMC *etc*). While the latter component of the LiB cells now at least partly is progressively being replaced by more abundant and also less expensive Fe-based materials (phosphates, silicates), mainly for safety and cost reasons – it does so with an intrinsic penalty in capacity.

However, to achieve or even approach the often quoted goal of a 500 km electric driving range using batteries to power our vehicles, and at the same time aim at less costly and complex, but still safe batteries, we need to explore new concepts different from the existing LiB technology and that can offer a real step further in energy storage.

1.1 The Li-S battery technology

One concept holding the promise to resolve the issues outlined above is the lithium-sulphur (Li-S) battery technology, the principle of which has been known for several decades, however without a real commercial breakthrough. Li-S batteries can in theory fulfil most important performance requirements as it possesses both a high volumetric (small size) and a high gravimetric (low weight) energy density. In addition, it can be produced as flexible, environmentally friendly and cost effective cells with in theory inherently safe & reliable operation [1].

Elemental sulphur (S_8) as the positive electrode material in the combination with lithium (Li) metal as negative electrode material offers an attractive rechargeable cell, with a theoretical possibility of giving energy values approaching 2500 Wh/kg (or 2800 Wh/l) assuming reaction to Li_2S. This is by virtue of *i)* the low equivalent weights of both lithium and sulphur and *ii)* an average 2.1 V redox voltage.

As an example the advantage of Li-S batteries in terms of specific capacity and relative price compared to different cathode materials for the LiB technology is presented in the Table 1.

Table 1: Properties for different cathode materials for Li-ion and Li-S batteries

Material	Theoretical Capacity ($mAhg^{-1}$)	Specific Capacity ($mAhg^{-1}$)	Relative Price
$LiCoO_2$	275	130-140	1
Li-NMC	~270	150-160	0.59
Li-NCA	~270	170-180	0.89
$LiMn_2O_4$	148	100-120	0.26
$LiFePO_4$	170	140-150	0.37
S	1675	200-1200	0.006

Thus, as sulphur is much less expensive than the typical cathode materials of other battery systems, the Li-S technology starts with a lower material cost. In addition, the manufacturing techniques for Li-S batteries are very similar to those used in other battery chemistries.

What are the main obstacles for Li-S implementation at large scale? The main problem is due to the fact that during the first discharge, elemental sulphur (S_8) accepts electrons leading to a sequential complex equilibrium of various lithium polysulphides and finally insoluble Li_2S is formed. Owing to the low solubility of Li_2S_2 and insoluble character of Li_2S, the end of the discharge curve shows poor kinetics which might translate to the low discharge efficiency at higher cycling rates. Thus, today, in practice discharge C-rates are rather limited. In addition, upon recharging, these products do not directly transform back into S_8, but go through the same polysulphide sequence. The higher polysulphides formed are now prone to diffuse to the lithium electrode where they directly react with lithium in parasitic reactions. While some parts of these reactions also ensure safe operation (overcharge protection via a shuttle mechanism) it deprives the cell of capacity – in each cycle cumulative.

Another weak point of the Li-S battery is nested in the insulating nature of sulphur (and polysulphides) requiring more advanced wiring (both electronic and ionic) to improve kinetics.

2. The EUROLIS project and goals

EUROLIS [2] is a collaborative small or medium scale focused research project (CP) funded by the European Union and coordinated by the National Institute of Chemistry, Ljubljana, Slovenia. The project started in October 2012 and will run for 4 years. The aim of the project is the development of advanced and sustainable Li-S batteries for automotive use.

2.1 The EUROLIS partners

This overall aim will be accomplished by intense collaboration between 7 research organizations (universities and research institutes) and 4 industrial partners (3 large enterprises and 1 SME). A continuously updated and more detailed description of the partners is to be found at our web-site [2]. The construction of the consortium is made to enable a fast progress from fundamental and applied understanding to optimisation of proper Li-S cells. The potential commercial use of Li-S cell will be tested within three generations of Li-S batteries.

2.2 The EUROLIS goals

The project includes basic research on various levels which will help understand the mechanisms governing the Li-S cell in different electro-chemical environments. The applied part of research will focus on optimisation and integration of materials into 18650 cells and cell testing for their appropriateness in the automotive applications.

Our goals in numbers are:

- An energy density of at least 500 Wh/kg with a specific power of at least 1000 W/kg during normal operation.
- A charge efficiency higher than 95 % in the entire cycle life in the operating temperature range from -25 °C to 80 °C.
- Durability reflected by a life time requested by automotive industry; at least 5 years and a cycle life of 1000 cycles

within the conditions of deep discharge – full charge.

- Meet or exceed safety standards and low costs: *i.e.* a maximum of 150 €/kWh.

Other important goals that are being targeted are; to enhance and protect European technology; to create new analytical techniques for reliable monitoring of Li-S battery processes during charging and discharging; to understand the mechanisms and properties needed for stable battery operation; to determine chemical environment (combination of electrolyte, electrode composition, required additives) and suitable morphology for stable operation of Li-S batteries; and finally to compare alternative configurations of Li-S battery with a classical configuration using metallic lithium as a negative electrode.

3 Research

As the project has merely started the detailed results so far are few – but a few examples of the type of general directions to be taken can be summarized here and more details are to be presented at the EVS-27 meeting. In general the overall goal and the sub-goals outlined above will be targeted by *e.g.* the following sub-projects:

i) Use composite cathodes to disperse sulphur over the high surface area of mesoporous carbon, to enable efficient supply of electrons and numerous ionic conductive paths. Such a framework can act as a mini electrochemical reaction chamber helping to prevent polysulphide diffusion out of the cathode composite. Additionally, functionalization of the outer surface of carbon particles can be performed.

ii) For Li-S batteries there are built-in paradoxes strongly linked to the properties of the electrolyte – both with respect to dissolution, solvation, and re-deposition. As the formation of soluble polysulphides leads to irreversible losses, these different stages must be interdependently approached. One way to both change the solubility and to increase the safety is to employ polymeric solvents and ionic liquids (IL). It is clear that the polysulphide species in IL solvents differs from those in organic solvents – often explained by a low solubility. The exploration of completely new electrolytes based on ionic liquids or mixed electrolytes is to be targeted.

iii) Life-cycle analysis, re-cycling and eco-design issues are all integrated parts of the project. Batteries are traditionally considered as potential environmental hazards due to use of toxic materials (Pb, Cd, Hg *etc*) and other metals like Ni, Co, RE's that requires recycling. While Li-S batteries do not contain any of these materials Li, S, and foremost hosting materials must be designed as environmentally acceptable materials. From a sustainability point of view, the Li-S battery will be considered as a source of lithium metal, and a wide usage of Li-S batteries for automotive applications will require, in the long term, an efficient method for lithium recycling.

Acknowledgments

The European Commission are gratefully acknowledged for the funding of the Collaborative Project EUROLIS (Contract No 314515) within the call FP7-2012-GC-MATERIALS. PJ and RD would like to thank all partners for all the effort put into making the project starting successfully.

References

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Authors

Patrik Johansson holds a PhD in Inorganic Chemistry and is currently Professor at Applied Physics, Chalmers, Sweden. He has published more than 80 scientific papers on Li-ion (LiB) battery materials, especially on new electrolytes and how to model these at a molecular level, and currently supervises 7 PhD students and mentors 2 post-docs. He leads the Alistore-ERI theory open platform and is work package leader for the Li-S battery electrolyte efforts within the EUROLIS project.

Robert Dominko is a senior research assistant at the National institute of Chemistry, Slovenia and the coordinator of the EUROLIS project. He has published over 70 papers in the field of lithium batteries and now he supervises 5 PhD students. Currently his main activities are in the field of Li-S batteries and partly also cathode materials for Li-ion batteries, along with a coordinating role for the group of positive electrode materials research within Alistore-ERI.