

1 Publishable Summary

The LABOHR project, “Lithium-Air Battery with Split Oxygen Harvesting and Redox Processes” is a collaborative project funded by the European Commission under the FP7-2010-GC-ELECTROCHEMICAL-STORAGE. LABOHR aimed at developing a Li-air battery working prototype, using ionic liquid-based electrolytes. The specificity of the project is the use of the electrolyte as an oxygen carrier to harvest O_2 from ambient air through an external O_2 harvesting device, so that the O_2 saturated electrolyte is circulated via flowfield plates, instead of O_2 , with the goal of solving the cathode clogging problem, by a more homogeneous deposit of the reaction products within the porosity of the cathode. To achieve this goal, all the key issues of the cell chemistry are being addressed: The anode (lithium or silicon/carbon nanocomposites) as well as its interface with the electrolyte, the cathode (carbon or carbon functionalized with catalysts), the electrolyte (ionic liquid based) and the oxygen harvesting device. Beside the prototype, a full Li-air pack is being modeled, to assess the ability of the technology to meet the specifications of the automotive industry partner, as well as define realistic values to be reached at the prototype level for automotive powering. Finally, although the technology is still at the research level, eco-design and sustainability issues are being considered.

If practical long term cycling has not been reached for Li-air cells, accordingly to the state of the art of the technology, electrolyte flow cells and prototypes were developed and studied and many results were produced within the second period of the LABOHR project:

On the **cathode side**, it was shown that, in $PYR_{14}TFSI$ -based electrolyte, the oxygen reduction reaction (ORR) yields the insoluble LiO_2 and Li_2O_2 products which are reoxidized with O_2 evolution without electrolyte breakdown. **ORR in O_2 -saturated $PYR_{14}TFSI$ -LiTFSI** is not much influenced by carbon functionalization with transition metal catalysts, and **eco-friendly, cost-effective, catalyst-free meso-macro porous carbon, synthesized within LABOHR** delivers discharge capacities up to **ca. 3000 mAh g⁻¹ with voltage hysteresis \leq 1V**.

In $PYR_{14}TFSI$ -LiTFSI electrolyte, the O_2 mass transport limits the feasible currents and plays a crucial role for electrode capacity. While at low current density (0.05 mA cm^{-2}), the pore clogging by Li_2O_2 limits the electrode capacity at ca. 3000 mAh g^{-1} , at higher current densities (0.5 mA cm^{-2}), O_2 mass transport rate determines the electrode capacity. **O_2 mass transport** limitations were overcome by stirring O_2 -saturated $PYR_{14}TFSI$ -LiTFSI solutions and lab-scale full Li/ O_2 flow cells featuring 0.2 - 0.5 mA cm^{-2} discharge currents were developed. Rechargeability of these cells was demonstrated but the **recovered charge efficiency (η) is still an issue for cell long cycle-life**. For a long cycle-life the efficiency was not sufficiently high when carbon paper was used as ZL carbon support ($\eta \approx 80\%$), but a η value higher than 98% was reached at the very end of the project (at 4V vs. Li^+/Li).

Modeling explained different discharge behavior of carbons of different porosity in cells with stirred and unstirred electrolytes.

Novel promising soluble mediators were developed to enhance the rate of the oxygen reduction and evolution reactions in Li/ O_2 cells operating with $PYR_{14}TFSI$ -LiTFSI electrolyte.

On the **anode side**, in order to achieve the goals of the project for insertion anodes, **core-shell silicon-hard carbon nanoparticles attached to MWCNTs** were optimized and a combined electroless/pyrolysis method used to prepare Si-Ni-MWCNT composite material. Li/Si-C-MWCNT cells with IL-based electrolyte exhibited reversible **capacity 1700 mAh/g**

(Si) for more than 60 cycles. The Si-Ni alloy anodes provided stable cycling (at 1000 mAh/gSi) and **high-power capability for more than 180 cycles**.

In addition, graphite/nano-sized Si composites, prepared by different methods, allow improving sufficiently the electrochemical performance of nano-sized Si materials in terms of charge and discharge capacity, irreversible capacity loss and cycling performance. The cells, containing a composite (15% of Si) anode in 0.1M LiTFSI-PYR₁₄FSI electrolyte ran for over 70 cycles with c.a. **700 mAh/g of total anode**.

A total of twenty one ILs were synthesized and characterized: Among them, eight were synthesized in larger batches and **six different solid polymer electrolytes (SPEs)** were prepared and used for studying the **Li/electrolyte interface and the Li cycling performance**.

In particular, it was found that **separator, stabilization time and additives** are key issues for reaching long term cycling of Li metal with liquid electrolytes, especially for those which do not include the FSI anion (not suitable for Li-air). Long term cycling as well as high efficiencies were obtained for both liquid and solid electrolytes. In particular, with the use of additive, **11 months of continuous cycling at 0.1 mAh g⁻¹ were reached without shorts-circuits** (i.e. more than 3800 cycles of 2h without failing). **Li⁺ mass transport** was tested for different Li salt concentrations as well as the robustness and stability of the Li/electrolyte interface.

In addition, Li plating has been observed by use of **ex-situ SEM and in-situ optical microscope**, and it was shown **that it is possible to plate a full 50 μm foil of Li metal onto another without forming dendrites and maintaining a shiny Li surface**. It was possible to acquire videos showing that, if applying a potential of -1V vs Li^{+/}Li do trigger globular dendrite growth, it is not the case when cycling in the 0 - 150 mV range.

To demonstrate the applicability of the ternary SPEs, some full Li metal batteries have been assembled, leading to high energy densities and ex-situ SEM showed that at least **200 cycles can be reached without forming dendrites at C/10 and 40°C**.

From the automotive requirements and **(1-D and 3-D) modeling done at the cell level, a pack design was developed**, and the environmental impact of the Li-air technology was assessed through a Life Cycle Assessment approach.

An ancillary prototype for thermal- and electrolyte management was tested and realized so that flowrate and temperature distribution of the system can be monitored, recorded and evaluated. Moreover, a risk assessment for the LABOHR Li/air system was performed.

The main issue encountered for the realization of a practical oxygen harvesting device was the difficulty of allowing high O₂ flow through a membrane while blocking totally H₂O. This still require using unrealistic surfaces of permelective membranes.

During the prototype development of the 5 cm² final prototype, different electrolyte flow configurations were tested, as well as different active and inactive electrode components, and the focus has been on operating Li-O₂ cells with **cathode mass loading in the 3 mg cm⁻² range**, which, for Li-air, can be considered as rather high. At 60°C, c.a. **1500 mAh g⁻¹** were reached with a carbon developed within LABOHR, using a prototype including an **interdigitated flowfield plate**, which showed to be beneficial for limiting the O₂ mass transport issue.

The good discharge voltages of partners' carbons were confirmed in a more applied configuration. However, the rechargeability of the prototype was lower as compared with results obtained with different experimental set-up. This considered, rechargeability of 90% for full discharge was obtained at 40°C and cycling limited capacity (130 or **500 mAh g⁻¹**) at

'100 % recharge efficiency' was possible, although the high cut-off voltage used for charge (4.5 V vs. Li^+/Li) raises concern about the nature of electrochemical reaction taking place in presence of carbon at this potential.

Finally, it was shown that the IL based electrolyte is not significantly damaged after the cycling of the cells at 60°C up to 4.5V in presence of O_2 and can be easily separated from the Li salt by simple rinsing with water.

Project partners:

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4. Kiev National University of Technology and Design (KNUTD) (UKR)
5. University of Bologna (UNIBO) (IT)
6. University of Southampton (SOTON) (UK)
7. SAES getters S. p. A. (SAES) (IT)
8. ~~Chemetall (DE)~~ Rockwood Lithium (ROLi)
9. AVL List GmbH (AVL) (AT)
10. Volkswagen (VW) (DE)
11. European Research Services (ERS) (DE)