STABLE

THIRD NEWSLETTER

31ST OF AUGUST 2015

INNOVATIVE AUTOMOTIVE ELECTROCHEMICAL STORAGE APPLICATIONS BASED ON NANOTECHNOLOGY

In this issue:

Project presentation

STABLE focuses on innovations of battery anode, cathode, electrolyte materials and technologies, as well as assembly of batteries cells which are crucial on battery performance, cost and environmental impact.

Improvement of lifetime and cyclability of Li-air batteries through finding highly active bifunctional catalysts to effectively regenerate batteries, protecting the Li anode from dendrites formation using suitable membranes and obtaining stable electrolyte with additives to render solubility of Li2O2 that cause cathode clogging on cathode will be studied.

Activities will focus especially on 1) optimization of cathode structures; 2) the selection of active catalysts and dehydration membranes; 3) modification of anode structure with necessary protecting layers, additives or surfactants; 4) modification of electrolyte properties. The final aim is to obtain Li-air battery cells with specific capacity of >2000mAh/g and an improvement of cycle life to 100-150 cycles.

Work Progress

Work Package 1 — Synthesis and optimisation of anode material for Li-air battery: The overall objective of this WP is to synthesise and optimise lithium anode materials through different approaches. In this regard, significant results have been obtained.

The high efficiency of the standard NASICON membrane in protecting lithium anode was confirmed. However this membrane is highly expensive and extremely fragile. One strategy could be to try to prepare some similar protective membranes with other material (maybe polymers, but not PVDF) to enhance the mechanical properties.

TiO_2, Al_2O_3 and SiO_2 nanoparticles, as well as nanoclays such as montmorillonites and LDHs, have been used as additives for the PVdF protective polymeric layers for the anode, produced by melt intercalation with a weight load of 3% and a thickness up to 50 microns.

After electrochemical tests the protecting action of the membranes seems limited as the Li foil is quite corroded. Moreover the conductivity of these membranes is very low even if higher when additives are used.

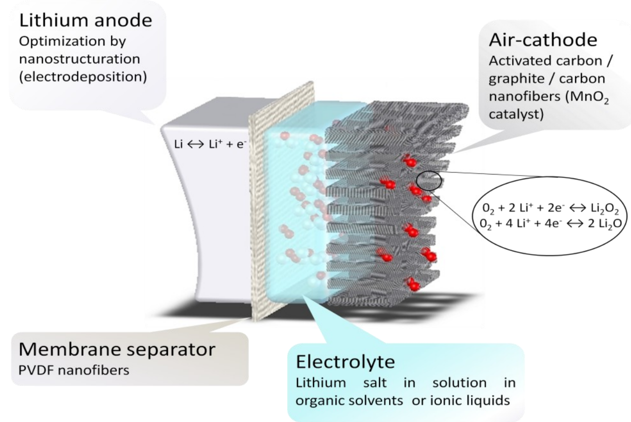
Different composition of Li-Ag and Li-Mg alloys were produced by using a high-energy planetary ball mill at room temperature. EDS dot-map analyses show that Ag/ Mg powders were distributed uniformly in the Li-Metal alloy matrix.

The addition of Mg powders into the lithium matrix couldn't show significant improvement on electrochemical performance of Li-air. Therefore, it is not recommended to use Li-Mg alloys as negative electrode.

"Electric car is considered as the most promising technical solution for automotive transports in 21st century"

LISICON based LAGP protective pellets and membranes have been synthesized by means of a sol-gel process or electrospinning.

Commercial LAGP membrane, synthesized LAGP membrane and PVDF nanofibers with 1% LAGP have been tested in Li-O_2 battery cell and enable to protect the metallic Li from passivation. No better capacity nor cyclability has been observed.



Composition and functioning of a Li-air battery

Production of LTO nanoparticles by different synthetic routes such as FSP and sol-gel methods. However, they did not match requirements specified.

Electrochemical deposition of copper nanorods onto copper and through an alumina membrane has been developed. Li has been then electrodeposited onto the nanorods. The electrochemical tests of this nano-structured anode show very low capacity and the electrodeposition setup needs to be optimized. Similar results have been obtained with the Li deposited onto CNFs.

As the performance of the protective layer did not show any significant improvement in the cell electrochemical performances, Li metal foil were used as anodes to build the prototypes.

Work Package 2 — Synthesis and optimization of cathode materials for Li-air battery: The objective of this WP is the development of the cathode materials, with good physical properties i.e. small thickness, big porosity and volume fraction of carbon.

The optimized air cathode with highly active catalysts, nano-structured carbon and moisture filtering membrane have been prepared. Mesoporous metal oxides (Co, Mn) as well as metal and metal oxide nanoparticles supported MWCT and graphene proved to increase the cell capacity and cycle ability. Among the various cathode materials tested Pd nanoparticles supported carbon nanofibers, showed excellent cycling performance.

The nanostructured mesoporous CNFs used as supporting the metal nanoparticles resulted to be porous enough to allow O_2 diffusion and at the same time to decrease the clogging of the formed by-products (Li_2O_2 , LiO_2). On the other hand, the presence of carbon graphite retained the good electronic conductivity of the cathode. Such cathodes enabled the cell to perform more than 90 reversible and stable discharge/recharge cycles with voltage gap of less than 0.5V in TEGDME-based electrolyte and pure oxygen feeding.

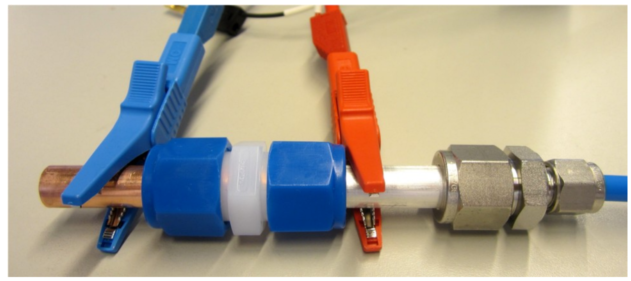
The results of WP2 further indicated that, for cell operating in ambient air, the cycling ability and the overall electrochemical performances can be largely improved with a suitable dehydration membrane located beyond the air cathode. Highly hydrophobic PVDF-HFP membranes loaded with silicon oil as an oxygen vector, acted as a moisture barrier and enabled the cell to cycle up to 650h . This behaviour was almost comparable to that of cells powered with pure oxygen.

Work Package 3 — Synthesis and optimization of electrolyte of Li-air battery: The objectives of this WP were to synthesize and characterize stable electrolytes with high conductivity and high oxygen solubility to increase the discharge current density and then determine the most suitable lithium-air battery materials and technology for the use in EVs.

The addition of ionic liquids in organic solvents significantly improved the ionic conductivity of electrolyte up to 9.5 ms cm-1 and more than 65 cycles were obtained at a discharge capacity of 835 mAh g-electrode. Moreover, the overall price of the electrolyte is then lower than conventional electrolyte due to the ratio of €/mol.

Besides, addition of metal oxide nanoparticles also showed slightly beneficial effects on the cell cycling. These additives are used to reduce the dendrites formation and to improve the oxygen solubility, the viscosity and the polarity of the electrolyte.

The up-scaling of the metal oxide nanoparticles production was carried out with brilliant results and samples were sent to POLITO for their incorporation in electrolytes to be tested at prototype scale.



Electrochemical setup to test Li-air cell

Work Package 4 — Simulation and modelling of Li-air battery: This aims to examine the nature of the important Li-O2 battery discharge product formation during operation, using Density Functional Theory modelling methods.

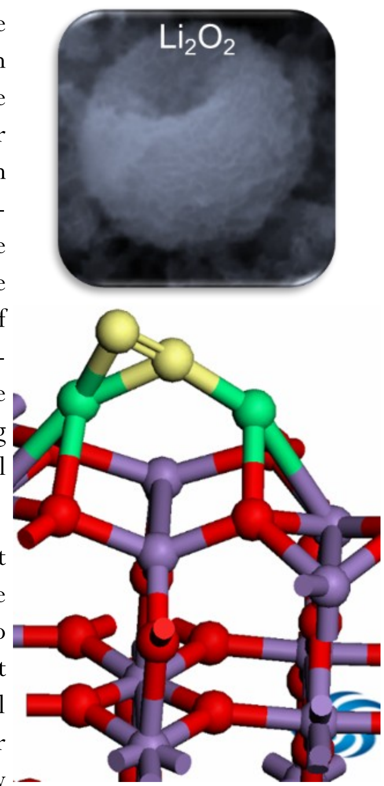
Density functional theory is a powerful method for examining atomic and molecular scale interactions, reactions and interfacial chemistry that happens on battery electrodes during use.

In this project, we developed models to understand the nature of the Li2O2, Li2O and LiO2 material formed during discharging and charging (the method by which the battery stores and delivers charge), and how the discharge product material nucleates and grows on the surface of metal oxide electrocatalysts, and compared to experimental battery tests using nanowires of this catalyst that we also synthesized in the laboratory.

Oxide electrocatalyst, especially those with 'active' surfaces are supposed to help improve reversibility and lower the charging over potential, to increase energy density in principle. The detail modelling conducted in STABLE showed that defective oxide surface favour the formation of Li2O2 and Li2O, and that the nature of the oxide surface plays a role in the rate formation of these species, even if they are formed via reactions involving solution-based LiO2* species.

Essentially, while the process that occurs in the battery electrolyte and with the O2 or H2O (or other high DN species) are important for reversible performance of these batteries, the nature of the permeable air electrode is found to be vital in determining the growth of the final Li2O2 phase.

The STABLE project can now apply these modelling methods to predict or screen-out useful bi-functional catalyst materials for improved reversibility and efficiency in the future.



Li_2O_2 formation on the surface of MnO_2 catalyst during Li-O_2 battery discharge

Work Package 5 — Assembly and optimisation of complete cell: While working with the cell, we noticed a few expected and a few unexpected challenges.

One thing to note is, we were only able to measure one cell, and therefore cannot pinpoint the cause of certain abnormal measurements.

Firstly, the difficulty of accurately measuring oxygen partial pressure, which would seem to affect voltage of the battery and is therefore important. It is also interesting to know in which way the oxygen concentration and oxygen partial pressure affects the cell. However, we would need a better and calibrated sensor to measure both parameters and larger number of cells to get appropriate statistics to make reliable conclusions.

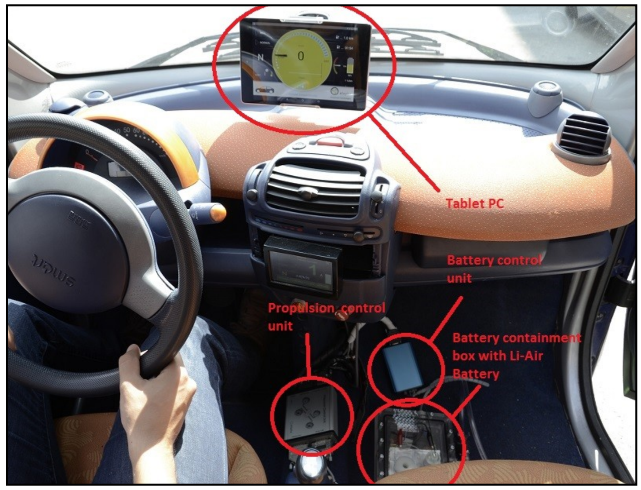
Another important detail about the cell is the need to apply pressure across the entire surface of the cell to ensure proper functionality of the cell.

It was also very important to measure cell voltage using instruments with sufficiently high input resistance, otherwise the measurement would both not be accurate, and the cell might be discharged.

Furthermore, it was not completely obvious what else affects battery voltage. For example, most of the time we would measure self-discharge as expected, yet it also happened we measured a higher voltage on the battery after it was disconnected for two days.

Overall, the cell looks promising, but apart from an increase in power it would also need to be able to work with oxygen from air to decrease the fire hazard of the battery system.

Different prototypes of cells were assembled by selecting the best performing components from every work package, namely the cathode, the electrolyte and the air dehydration membrane.



Li-air battery setup in a car

The first prototypes were assembled at Cegasa and delivered a capacity as high as 1268 mAh/g. Afterwards, different prototypes were assembled in coin and pouch cell configurations.

The pouch cell, comprising the Pd/CNF based cathode, a blended electrolyte and the oxygen selective membrane was tested in ambient air at 17%RH.

"The use of electric energy will not only slow down the consumption of petroleum resources but also contribute to the reduction of emission of carbon dioxide and toxic air pollutants"

Such cell performed over 150 cycles at 100% columbic efficiency, reaching the objectives proposed in the STABLE project.

Work Package 6 — Life cycle assessment: Electric vehicles are seen as the main answer to the transport sector´s problems of climate impact and diminishing oil supplies and lithium-air batteries, which theoretically can offer at least 10 times better energy density than the best battery technology (Lithium-Ion) of today, are therefore very interesting.

To detect and avoid other potential environmental problems with lithium-air cells, life cycle assessment (LCA) of environmental impact during manufacture, use and recycling of the Li-air battery has been done in work package 6.

The best prototype lithium-air cell developed in the project have been analysed from cradle to grave, i.e., from raw material production, cathode manufacturing, electrolyte preparation, cell assembly, use in a typical vehicle to end-of-life treatment and recycling. Life cycle impacts have been quantified in terms of climate impact, abiotic resource depletion and toxicity.

The LCA show that at the present level of lithium-air cell performance, production-related impacts dominate all environmental impact categories. However, as the performance of the lithium-air cell develops (and less cells are needed), battery-related losses during operation become the major source of environmental impacts, see figure below. The battery internal electricity losses become heat that may need considerable amounts of additional energy for its transportation out of the battery.

The LCA also show that by recycling, 10-30% of production-related environmental impact could potentially be avoided. Today no industrial recycling of lithium-based traction batteries is on-going and the economic incentive to invest in it is weak.

In view of above, it is recommended that future battery cell development projects already at the design stage ought to consider the methods and processes for efficient and environmentally benign cell-level recycling

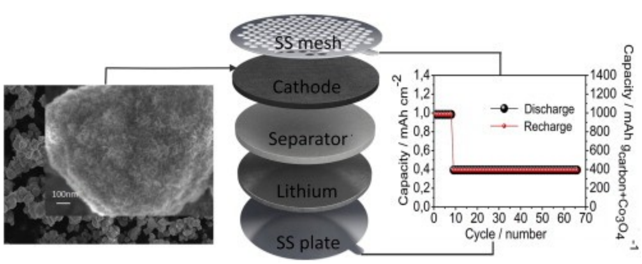
Work Package 7 — Scientific coordination: The scientific coordination of the project is done by Politecnico di Torino. The former coordinator, Prof Qiuping Chen, resigned and gave the task to Prof. Silvia Bodoardo on the 16th of February. Moreover, the leader of WP 2 has also changed to Dr. Carlotta Francia, also from Politecnico of Torino.

More information regarding the different meetings and workshops can be find under the meetings section of this newsletter on page 7.

Work Package 8 — Dissemination and exploitation strategy: The dissemination and exploitation strategy developed by Politecnico di Torino includes three main tasks: the project website. which website is regularly updated with the most recent news and activities related to the project, the workshops, and the periodic newsletters.

Furthermore, the project partners have participated in several conferences and published various articles and posters. Here is a list of the most recent ones:

- J. Zeng, C. Francia, J. Amici, S. Bodoardo, N. Penazzi. "Mesoporous Co_3O_4 nanocrystals as an effective electro-catalyst for highly reversible Li-O2 batteries" Journal of Power Sources 272 (2014)



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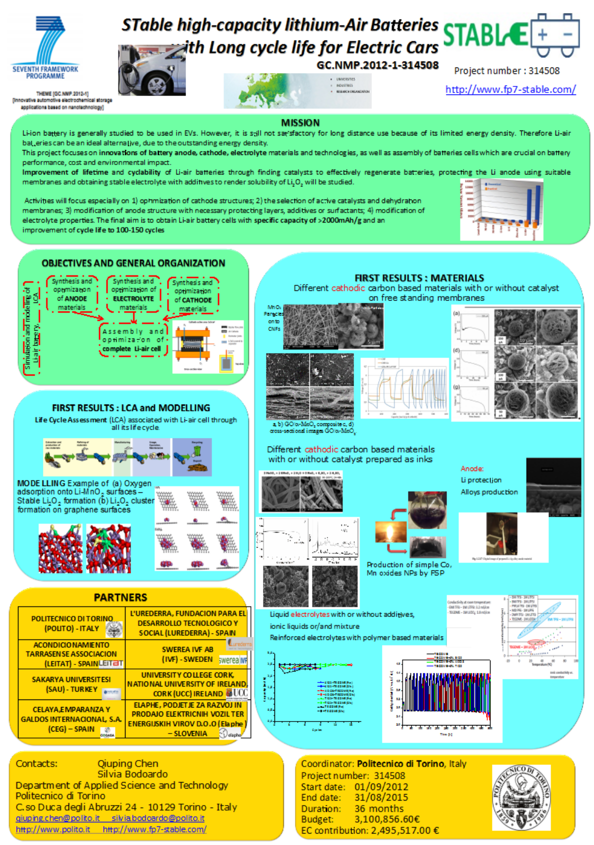
- IMLB 2014 - 17th International Meeting on Lithium Batteries (June 10-14, 2014 – Como, Italy - Poster). "Ionic liquid-based electrolyte for lithium-air battery" E. Knipping, C. Aucher, S. Martinez Crespiera, C.



Pelegrin, D. Amantia, L. Aubouy.

- ISE 2014 - 65th annual meeting of the international society of electrochemistry (September 1-5, 2014 – Lausanne, Switzerland - Poster). “Ionic liquid-based electrolyte for lithium-air battery” E. Knipping, C. Aucher, S. Martinez Crespiera, C. Pelegrin, D. Amantia, L. Aubouy.
- Batteries 2014 (September 23-26, 2014 – Nice, France - Oral). “Ionic liquid-based electrolyte for lithium-air battery” E. Knipping, C. Aucher, S. Martinez Crespiera, C. Pelegrin, D. Amantia, L. Aubouy. Speaker: Etienne Knipping
- 3rd International Conference on Electrospinning (August 4-7, 2014. San Francisco, CA, USA. - Oral). “Mesoporous metal-doped carbon nanofibers as cathode for lithium-air batteries” S. Martinez Crespiera, D. Amantia, C. Pelegrin, E. Knipping, C. Aucher, M. Faccini, L. Aubouy. Speaker: David Amantia
- MaBIC 2015 – Metal-air Battery International Congress (April 14-16, 2015 – La Coruña, Spain – Oral). “Ionic liquid -based electrolyte for lithium-air battery” E. Knipping, C. Aucher, S. Martinez Crespiera, C. Pelegrin, D. Amantia-

Meetings and Events

“Due to their high energy density, Li-ion batteries are being considered to meet the above mentioned demands.“

24 MONTH MEETING

29-30 September 2014

INDUSTRIAL WORKSHOP

29 September 2014

30 MONTH MEETING

3-4 March 2015

STABLE CLUSTERING WORKSHOP

The event took place on the 28th of May 2015 in Brussels and was organised by the Politecnico do Torino. Topics such as automotive battery materials and cell production in Europe were discussed. Then, the twelve projects member of the cluster presented their recent activities.

STABLE IN CHINA

From the 6-13 June, the coordinator of the project went to China to explore possible collaboration possibilities and learn more about recent research developments. The trip included a visit University

of Technology in Zhengzhou, a visit in Li-battery company in Luoyang, and a visit in JAC EV car manufacturing company.

IFAM EVENT

IFAM is traditional fair that takes place in Celje every year. It is focused on automation and robotization of industrial processes. This year organizers tried to add new fast-growing field of e-Mobility. The Electric Smart from the STABLE project and two other electric cars were the main

Exploitation

On the one hand, we will use the most promising typologies of nanoparticles developed during the project for new or deeper investigations on Li-air batteries' anodes, cathodes and electrolytes.

In addition, other investigations in the field of other kind of batteries will be carried out by using those and other nanoparticles' natures, as a consequence of the knowledge achieved during STABLE.

On the other hand, that know-how may be transferred to batteries' companies that might be interested in investigating new materials for their final products.

Exploitable Result	Description	Sectors of application	Time to Market (years)	IPR exploitation Forms	Partners involved
Lithium Anode for Li-O_2 or Li-air cells	Nano-structured lithium anode and/or anode protecting layers or surfactants to prevent dendrites formation for high safety and wide temperature operation range	Electrochemical Storage (Batteries)	5	Internal know-how, Patent, Licensing	POLITO, LEITAT, LUR, IVF, SAU
Cathode materials for Li-O2 or Li-air cells	Low cost synthesis of nano-structured carbon or graphene sheets with high pore volume and surface area as electrode support. Development of filter layer or membrane to prevent the moisture ingress and degradation of anode. Development and synthesis of multilayer highly active catalytic materials to increase the specific capacity to avoid the over-potential.	Electrochemical Storage (Batteries) Electrochemical Conversion (Fuel Cells)	5	Internal know-how, Patent, Licensing	POLITO, LEITAT, LUR, IVF, SAU
Electrolyte for Li-O_2 or Li-air cells	Stable low volatility electrolyte with low viscosity and high oxygen solubility to increase the discharge current density. Room temperature ionic liquids (RTILs) or combinations of solvents/additives.	Electrochemical Storage (Batteries)	3-5	Internal know-how, Patent, Licensing	POLITO, LEITAT, LUR, IVF, SAU
Simulation and modelling of Li-air battery	Complete modelling of the performance of the assembled cells by detailed density functional theory calculations of catalytic function, voltage stability, and phase formation influence on overall performance.	Electrochemical Storage (Batteries)	5	Internal know-how, Patent, Licensing	POLITO, LEITAT, LUR, IVF, SAU
Li-air cell	Assembly of complete cell using optimal anode and cathode materials and safe electrolytes. Test and evaluation of complete cell in laboratory scale.	Electrochemical Storage (Batteries)	>5	Internal know-how, Industrial Secret, Patent, Licensing	CEGASA, UCC, ELAPHE,LUR, POLITO, LEITAT
LCA data	Investigation of existing relevant Life Cycle Assessment (LCA) on lithium air batteries. Full LCA of cell concept to assess overall environmental performance with fabricated. Lab-test device. End-of-life management of Li-air batteries and assessment of their reuse and recycling .	Electrochemical Storage (Batteries) Life Cycle Analysis	3-5 years	Internal know-how, Consultancy	IVF, ELAPHE
In-wheel electric motor with batteries	Integration concept for an in-wheel electric motor including electrochemical storage.	Electrochemical Storage (Batteries) Electric Vehicle	>5 years	Internal know-how, Industrial Secret, Patent, Licensing	CEGASA

Upcoming Events

36 MONTH MEETING

This meeting will be the final one of the project and will take place in Sweden. The full list of results of STABLE with all the consortium partners will be discussed.

Project Partners

Visit the website!
www.fp7-stable.com

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