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PROJECT FINAL REPORT

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Project acronym: STABLE

Project title: Stable high-capacity lithium-Air Batteries with Long cycle life for Electric cars

Funding Scheme

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4.1 Final publishable summary report

- **Executive summary**

The objective of this project was to develop innovative materials and technologies for Li-air battery with improved performance in terms of life cycle and specific capacity. In order to achieve this objective, different activities have been designed for innovation study of the anode materials in WP1, cathode materials in WP2, electrolyte in WP3, simulation and modelling in WP4, assembly of battery cells in WP5, life cycle assessment in WP6.

Low cost synthesis of the cathode materials starting from easily available compounds which should also satisfy easy conductivity of Li ions have been employed and studied. Different techniques such as hydrothermal, flame spray pyrolysis etc. Several different cathodic materials were produced and have been used in prototype cells and compared. In particular, materials with different porosity, electronic conductivity, different catalyst and catalysts loading have been produced and tested both as self-standing electrodes and as inks on conductive supports.

Electrolyte mixture was optimized in term of performance and of environmental impact.

The optimized solution and results generated from WP1-WP3 were simulated through WP4, and employed for the assembly and optimization of complete cell (WP5), as well as for the implementation of life cycle assessment (WP6).

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.

The assembled prototypes 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.

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

- **A summary description of project context and objectives**

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 have been studied 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 Li_2O_2 that cause cathode clogging.

Activities were focused especially on optimization of cathode structures; 2) the selection of active catalysts and de-hydration 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.

The project is organized in 9 workpackages.

- **Work Package 1 — Synthesis and optimization of anode material for Li-air battery.**

The overall objective of this WP is to synthesize and optimize 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.

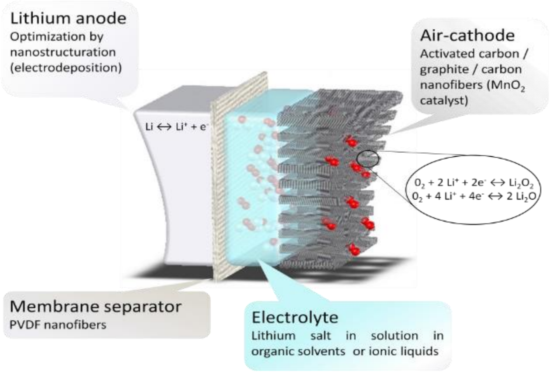


Fig. 1. Schematic representation of a Li-Air cell with membrane protected anode

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

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 nano-rods onto copper and through an alumina membrane has been developed. Li has been then electrodeposited onto the nano-rods. 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 behavior 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 $g^{-1}_{electrode}$. 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.

- **Work Package 4 — Simulation and modelling of Li-air battery.**

The Work Package 4 aims to examine the nature of the important Li-O_2 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 Li_2O_2, Li_2O and LiO_2 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 Li_2O_2 and Li_2O, 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 LiO_2 species.

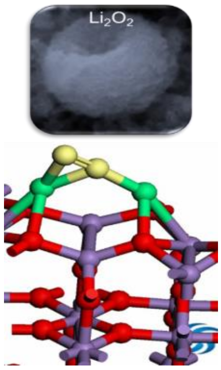


Fig. 2. FESEM picture of Li_2O_2 crystal (above), structural representation of Li_2O_2 (below)

Essentially, while the process that occurs in the battery electrolyte and with the O_2 or H_2O (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 Li_2O_2 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.

- **Work Package 5 — Complete cell.**

The Work Package 5 aims to the realization of the final prototype. Several generation of prototypes have been developed to show high capacity and long cycle life.

While working with the cell, we noticed a few expected and a few unexpected challenges.

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. The last produced prototypes were working with air at ambient pressure. 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. 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.

Fig. 3. Picture of a pouch-cell prototype

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.

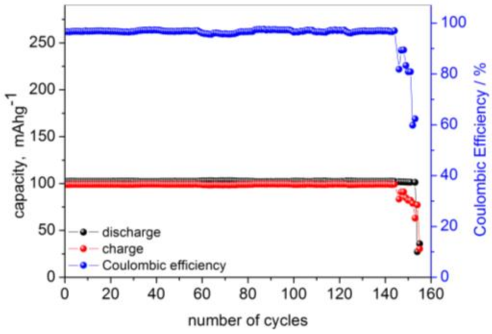


Fig. 4. Charge/Discharge Capacity and Coulombic Efficiency of the pouch cell final prototype

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. Such cell performed over 150 cycles at 100% columbic efficiency, reaching even overcoming 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 analyzed 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. 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 ongoing and the economic incentive to invest in it is weak.

Fig. 5. Car with the integrated Lithium Air system

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.

- **Work Package 8 — Dissemination and exploitation strategy.**

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

Furthermore, the project partners have participated in several conferences and published various articles and posters.

Some interesting and well attended workshops were also organized:

INDUSTRIAL WORKSHOP

29th September 2014

STABLE CLUSTERING WORKSHOP

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

STABLE IN CHINA

From the 6-13th June, the coordinator of the project went to China to explore possible collaboration and learn more about recent research developments. The trip included a visit at the University of Technology in Zhengzhou, a visit in Li-battery company in Luoyang, and a visit in JAC EV car manufacturing company.

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

Further information on www.fp7-stable.com

- **A description of the main S&T results/foregrounds,**

STABLE project is focused on the study of materials for Li-air cells.

ANODE

The main objectives are:

1. Development of anode protecting layers or surfactants with high safety operation range
2. Synthesis and characterization of good quality fillers or additives for protecting anode from dendrites formation
3. Discover the most suitable lithium air battery materials and technology for the use in EV

TiO_2, Al_2O_3 and SiO_2 nanoparticles, as well as nanoclays such as montmorillonites (MM) 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. The cycling time of these cells is impressing however most of the systems showed a low columbic efficiency linked to a high resistivity of the membranes. Lower columbic efficiency on the 1st cycles → Swelling with electrolyte allows crossing of Li ions through the membrane.

The best results are obtained with the membranes PVDF+Si and PVDF+LDH. In general, nanoclays showed better performance than NPs

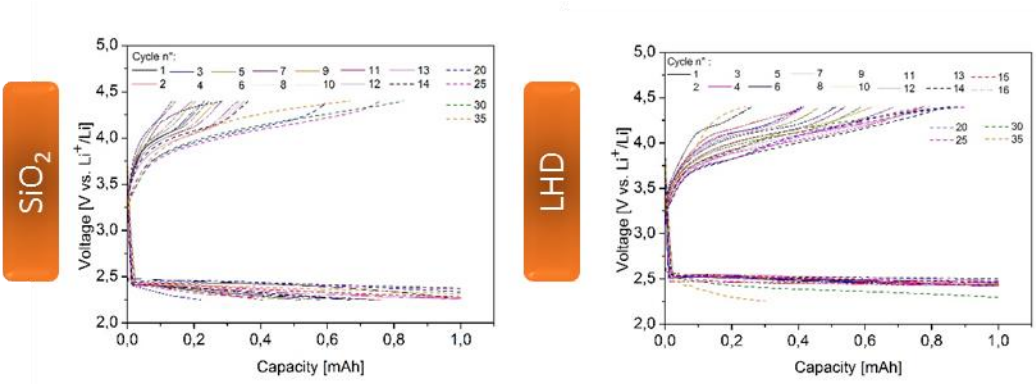


Fig. 6. Cycling profiles of the different polymeric layers tested.

Pure NASICON membrane was also prepared: The cycling is fairly regular and so is the cell capacity, for around 25 cycles, then it began dropping. After 1000h inside the cell the lithium anode was not entirely corroded, proving the cell failing wasn't caused by anode corrosion.

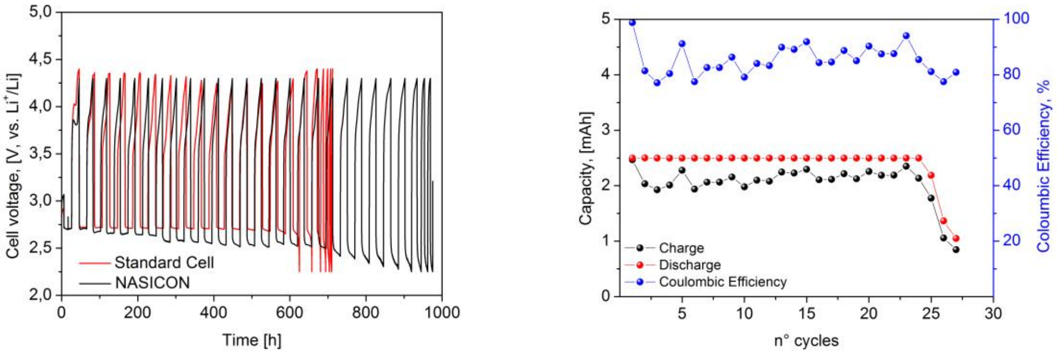


Fig. 7. Cycling profile (left), Charge/Discharge capacity and Coulombic Efficiency (on the right) of the cell with NASICON protected anode

The downside of this membrane is its cost and its extreme fragility.
The coulombic efficiency of the standard cell is steady around 100% for 16 cycles before drastically dropping, while the coulombic efficiency of the NASICON cell is less regular, oscillating around 90% for 25 cycles, thus demonstrating a longer lifetime while maintaining a fairly good efficiency, probably thanks to the lithium protection.

NASICON membrane was also covered with PVDF layer: It was observed :
Very high resistivity inside the cell. On the first cycle, the cell does not discharge. Subsequent re-charge probably occurs due to parasitic reactions (nothing to do with the decomposition of lithium peroxide).
As cycling proceeds, the liquid electrolyte inside the separator probably diffuses in both the NASICON and PVDF membranes and a decrease of the internal resistance of the cell is observed for a while. These problems can probably be explained by a poor intrinsic Li-ion conductivity of the 2 membranes and of the poor adhesion between each other, and by a probable reaction between PVDF and lithium

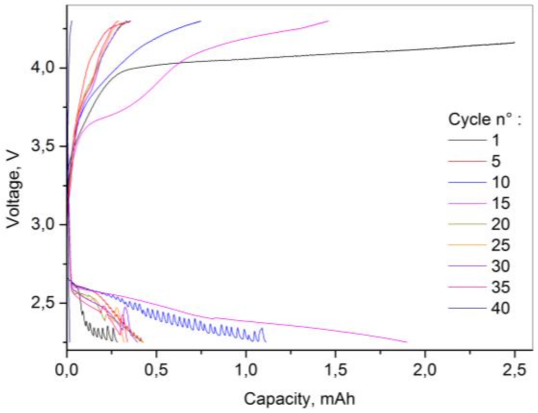


Fig. 8. Cycling profile of cell with PVDF coated NASICON protected anode

Alloys with Ag and Mg have been produced.
According to electrochemical cycling tests, Li-Ag anode containing 8 %wt. Ag was shown the best cycling performance compared with other Li-Ag alloys.

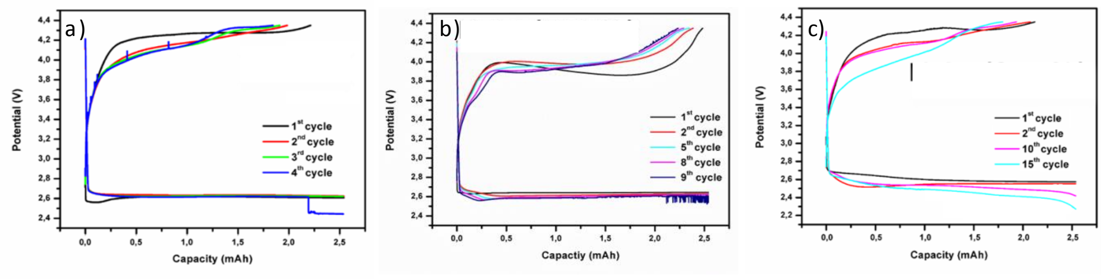


Fig. 10. Cycling profile of cells with pure Li anode (a), and Li-Ag anode 5wt.% (b) and 8wt.% (c)

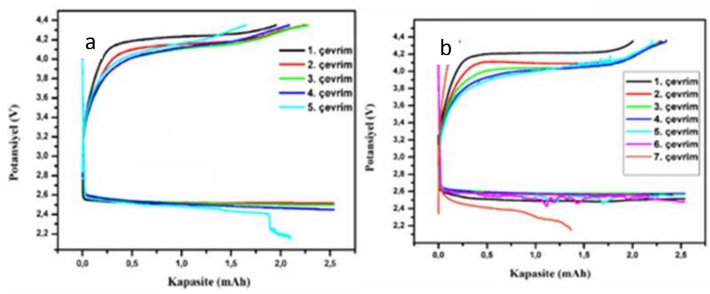


Fig. 11. Cycling profile of cells Li-Mg anode 5wt.% (a) and 8wt.% (b)

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

CATHODE

The objectives are:

1. Low cost synthesis and characterization of nano-structured and morphology of carbon / graphene with high pore volume, morphology and surface area as electrode supports.
2. Synthesis and optimization of nano-structured /multilayered active catalysts to increase the capacity and avoid the over-potential of cathode.
3. Fabrication and characterization of dehydration (or nano-structured hydrophobic) membrane for air cathode
4. Selection of the most suitable cathode and dehydration membrane for the cell prototype development.

Several materials have been developed:

Different nanostructured carbon based materials:

- Ordered mesoporous carbons (C16-C15) as replicas of silica templates
- Hollow core mesoporous shell carbons (HCMSC)
- Multiwalled carbon nanotubes (MWCNT) based buckypapers
- Different mesoporous carbon nanofibers (CNFs)

Graphene and Reduced Graphene Oxide (RGO):

- Graphene oxide (GO) was produced via Hummer's method
- Multilayered graphene production

Cathodes:

- Composite cathodes (Ni mesh support)
- Ink type cathodes-coatings (commercial GDLs supports with and without microporous layer)
- Self-standing cathodes

As reported in D2.3, several materials have been synthesized and optimized with and without catalysts.

Here a list of produced materials follows.

- Crystalline mesoporous α-MnO_2, α-MnO_2 supported on carbon black, mesoporous Co_3O_4,
- TiO_2 /RGO, Ru NPS supported on ITO
- α-MnO_2 nanowires, Graphene Oxide (GO)/α-MnO_2 , (GO)/α-MnO_2 /Pt , α-MnO_2/CNT

- Pt nanoparticles and Pt nanoparticles decorated MWCNT, (CNT)/α-MnO_2 /Pt bifunctional catalysts
- α-MnO_2 doped mesoporous CNF, nanostructured M-doped MnOx/C (M=Co or Pd) and PtAu/C
- High surface area metal doped nanofibers Pd and Co
- Co, Co_3O_4 and MnO_2 NPs produced by flame pyrolysis, preparation of Co_3O_4 and Co_3O_4/ MnO_2 supported on MWCNTs electrocatalysts
- Highly hydrophobic PVDF-HFP membranes prepared by non-solvent induced phase separation and loaded with silicon oil.
- Preparation of sandwich structured membrane: the core membrane is eletrospun PVDF membrane with high porous structure and sheath membrane is porous cellulose acetate membrane which casted from acetone and water mixed solvent

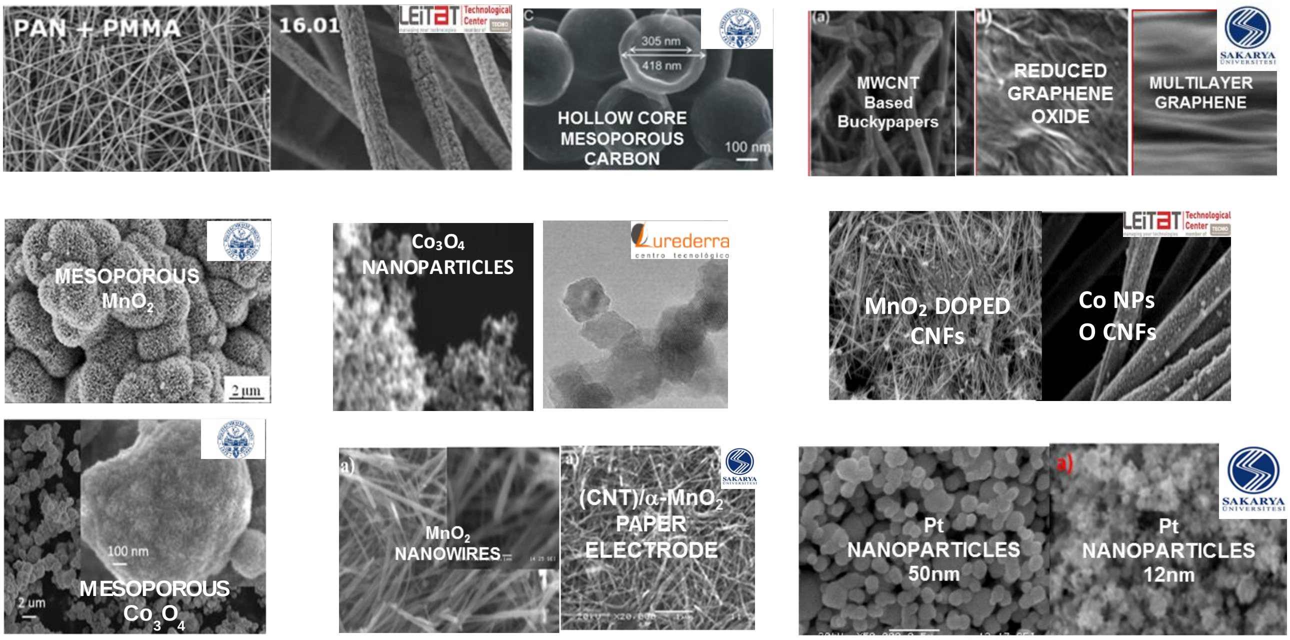


Fig. 12. FESEM pictures of nanostructured cathode materials prepared by the different partners

All produced materials were characterized by a chemical-physical point of view. Here are reported the electrochemical results.

In the case of Nanostructured M-doped MnOx/C (M=Co or Pd) and PtAu/ self-standing cathodes were prepared.

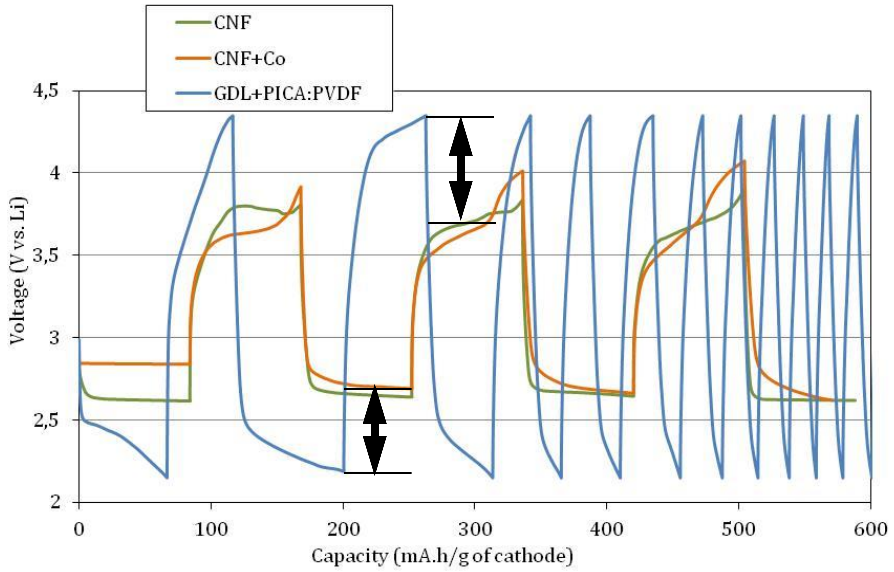
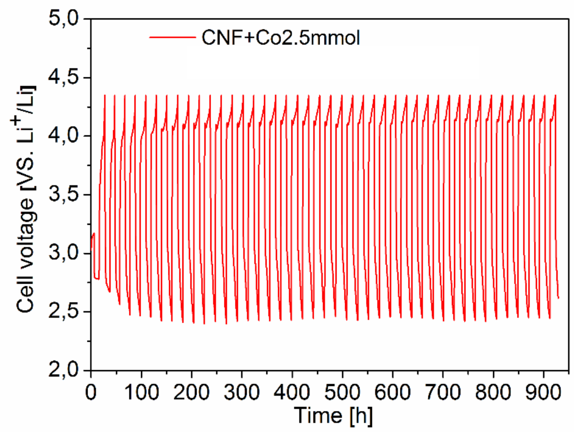


Fig. 13. Charge/discharge curves of Li-O_2 battery cells using different cathodes with CNFs with catalyst and/or additives (applied current: 10 mA/g of cathode).

As shown in Fig.12.the use of CNF lowers the overpotential

The same materials were also used as coating for GDL. Again a reduction of the overpotential was observed.



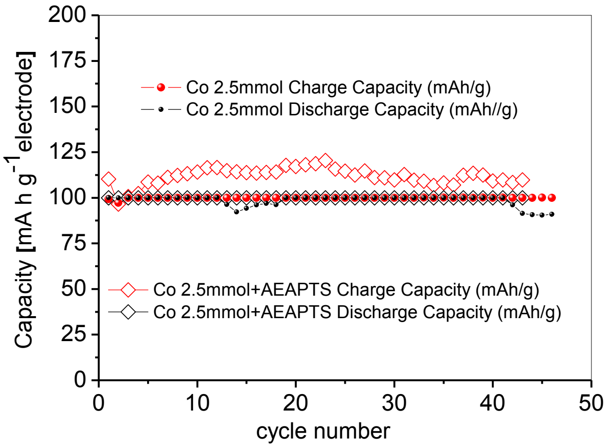


Fig. 15. Charge/discharge curves of Li-O_2 battery cells using cathodes made of GDL 24BA coated with CNFs supported Co catalyst (applied current: 10 mA/g).

Fig. 14. Charge/Discharge capacity of Li-O2 battery cells using cathodes made of GDL 24BA coated with CNFs supported Co catalyst and additive (applied current: 10 mA/g).

As self-standing cathode, outstanding results were achieved by using Co.CNFs: more than 40 days of cell operation and more than 45 reversible cycles for CNF + Co2.5mmol were measured (see Fig.15. and Fig.16.). The capacity is 100mAh/g based on the total mass of the electrode (Fig.13.)

In order to reduce the difference in voltage between charge and discharge, noble metals were used as coatings on GDL24BA with Pd2,5 mmol AEPTS/CNFs. The cell span more than 70 days without losing capacity.

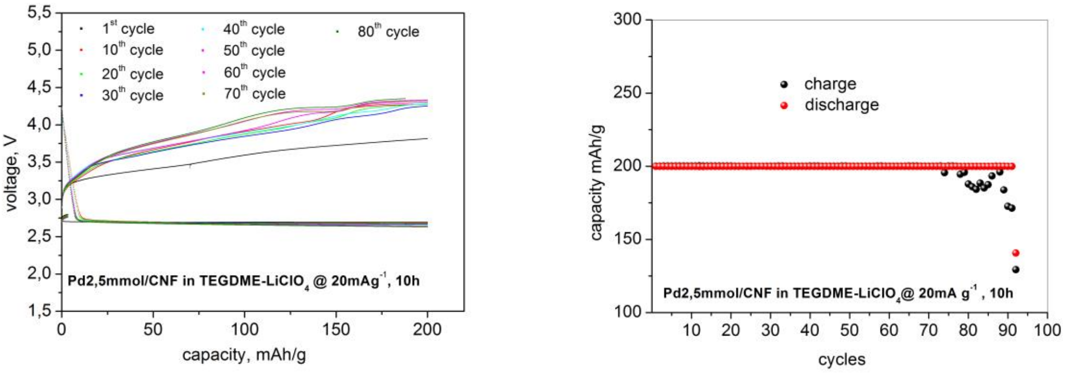


Fig. 16. Galvanostatic discharge-charge of a Li-oxygen battery cell using CNFs deposited as an ink to GDL-24BA as air-cathode with: Pd 2.5mmol+ AEPTS. Electrolyte: TEGDME with 5wt. % of LiClO4. (left) cell voltage vs. time and (right) capacity vs. the number of cycles.

Also in the also of Pd overpotential in the order of 1.1,5 V were obtained. Those values are very interesting and promising.

Flame Spray pyrolysis (FSP) was used to synthesize several ceramic nanopowders used as high capacity material the cathode. In particular the cathodes containing Cobalt oxides were coated on GDL and on multiwall carbon nanotubes – the cyclability is high and the capacity is outstanding in the order of 15000 mAh/g. (Fig.17.)

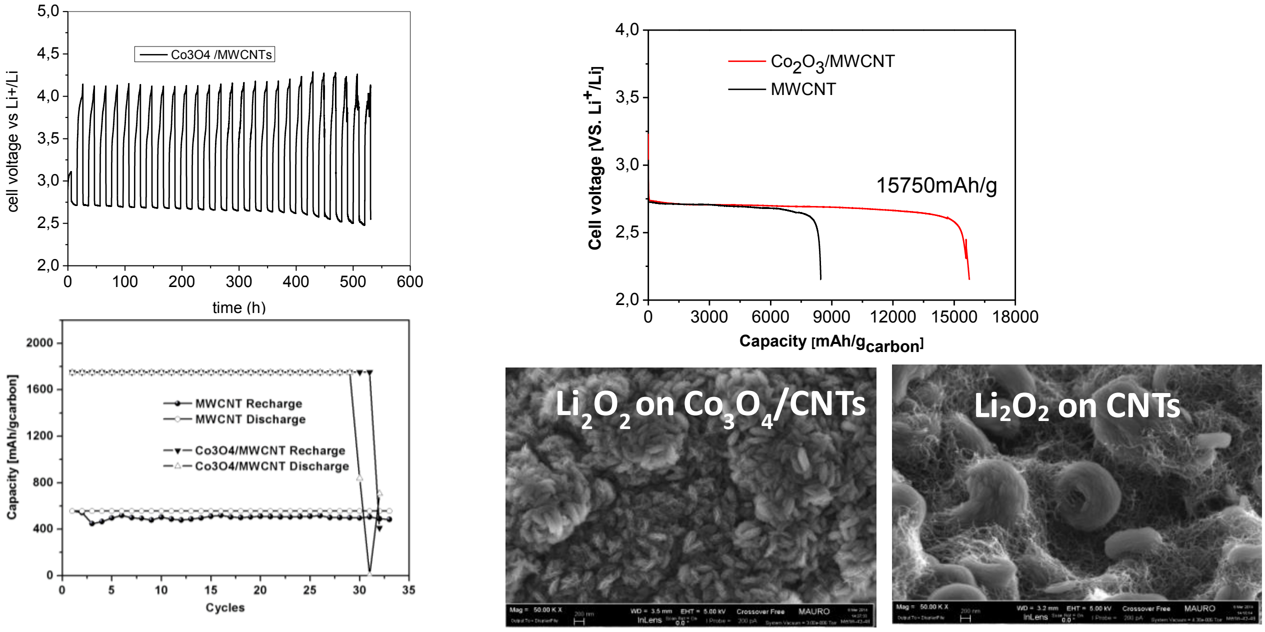


Fig. 17. Cell testing with coatings on GDL 24BC + Co_3O_4/MWCNTs as cathode
ECC-Air (EL-Cell); Anode: Li foil, Electrolyte: TEGDME – 0.5M $LiClO_4$; O_2 flow rate: 3.5 mL/min; 0.1mA/cm^2, 2.15-4.35V, 10h max

Many other materials were studied by changing the noble metal and changing the support. So that meosporous carbons, CNT and other were studied.

Graphene was also prepared by exfoliating graphite: Self-standing electrodes were produced from Pt nano powder (10 nm), α-MnO_2 powder and multiwalled carbon nanotubes in the form of thickness controllable air breathing paper electrode for Li-air cells (Fig.18.)

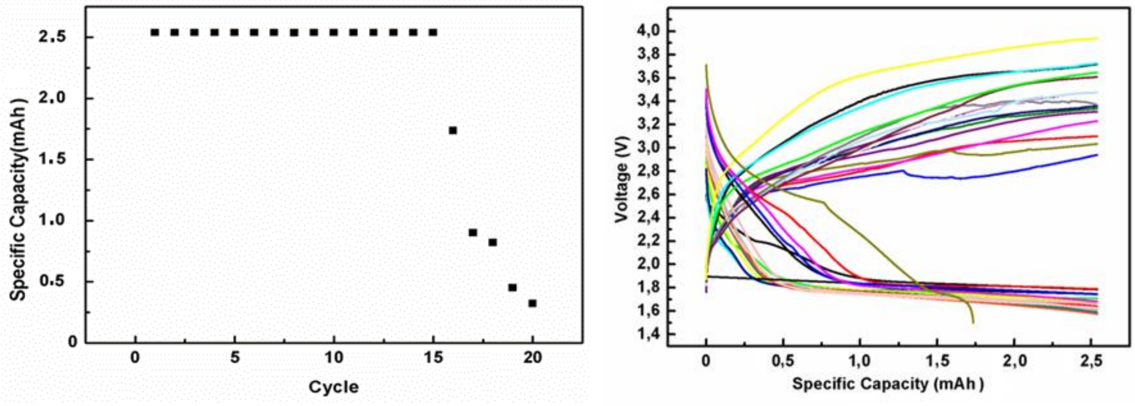


Fig. 18. Cycling capacity (left) and cycling profile (right) of ECC-Air (EL-Cell), Anode: Li foil, Electrolyte: 1M LiPF6 dissolved in NMP, with PEO and Al_2O_3 additives, 0.1mA/cm^2, 10h discharge.

Finally two types of membranes were prepared to prevent the moisture inlet in the cell.

Highly hydrophobic PVDF-HFP membranes were prepared by non-solvent induced phase separation in 240 micron thin sheets. Optimum porosity was achieved by adding sacrificial silica nanoparticles. After silica removal the pores of the membrane were loaded with silicon oil acting as “an oxygen vector”.

The membrane was characterized and tested in different conditions (Fig.19.)

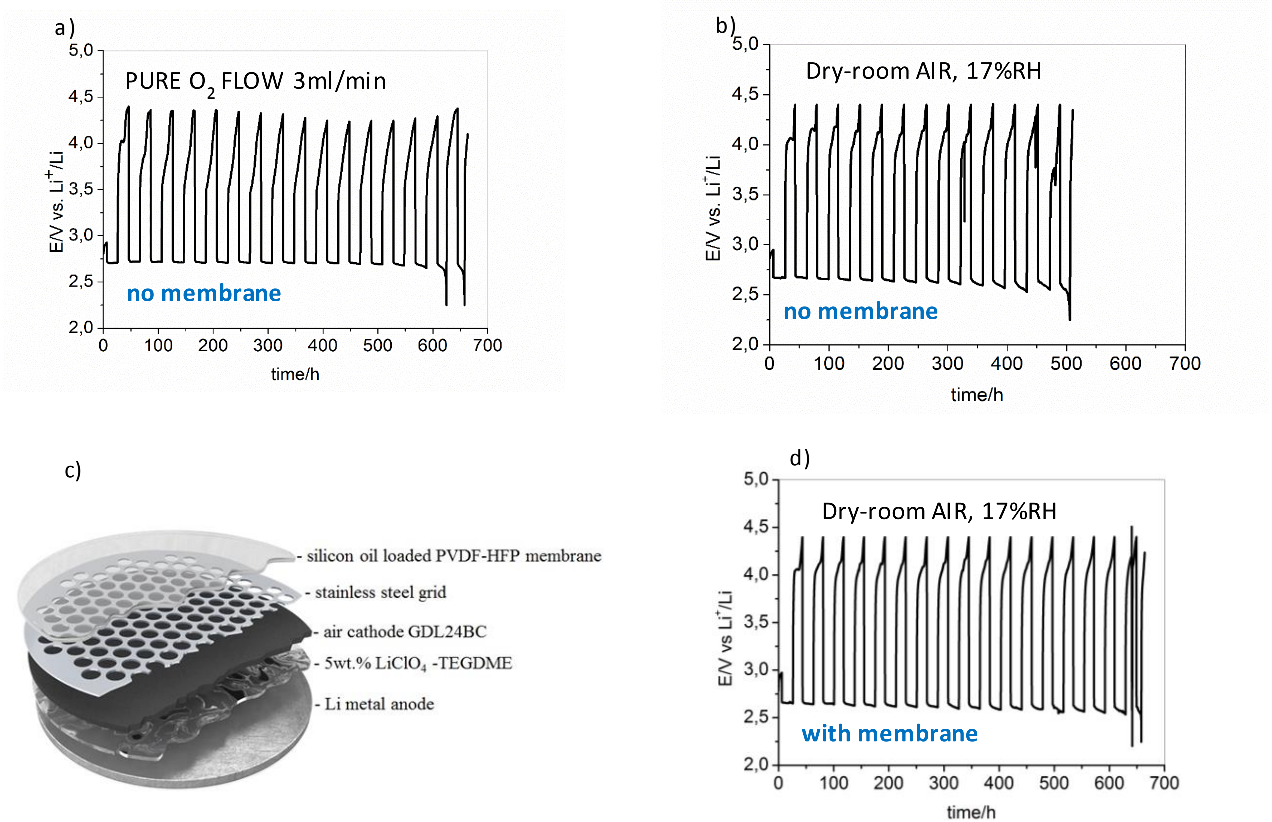


Fig. 19. Sketch of electrodes/electrolyte assembly, with the actual position of the membrane beyond the GDL (c), cycling profiles of: cell fed with O_2, without membrane (a), cell in ambient air (17%RH) without membrane (b) and cell in ambient air (17%RH) with membrane. CYCLING TESTS: i=0,05mAcm-2, 20hs discharge, between 2,25÷4,3V, TEGDME + LiClO4, Cathode: GDL24BC, anode lithium

All materials for cathode, produced by FSP, are available at large scale (Carbon sources such as Graphene, CNT and MnO2 structures).

As conclusions can be stated that:

- Nevertheless the main materials for cathode or components are not extremely expensive, the noble metals content has to be kept at reasonably low quantities. Carbon was used in any case as the main cathode material.
- However, in case there are some noble metals such as Pt and Pd etc., which can be used as catalyst on the cathode and these materials are expensive and not cost effective.
- The final answer will depend on the final design of the air cathode. If noble metals are used, this would be a significant contributor to price. This would be highly dependent upon the weight loading of the catalyst material (assuming the use of a much cheaper carbon support). In some literature reports, high catalyst loadings of up to 40% weight compared to carbon are used.
- From production process point of view, cathode preparation and cell assembly are lab-made, thus the mass production is not considered at this stage.

ELECTROLYTES

Electrolyte used can be organized in the following groups:

Organic solvents:

- Carbonate-based solvents (EC, DEC, PC)
- Tetraethylene glycol dimethy lether (TEGDME)
- N-methyl-2-pyrrolidone (NMP)
- Dimethyl sulfoxide (DMSO)

Ionic liquids (ILs):

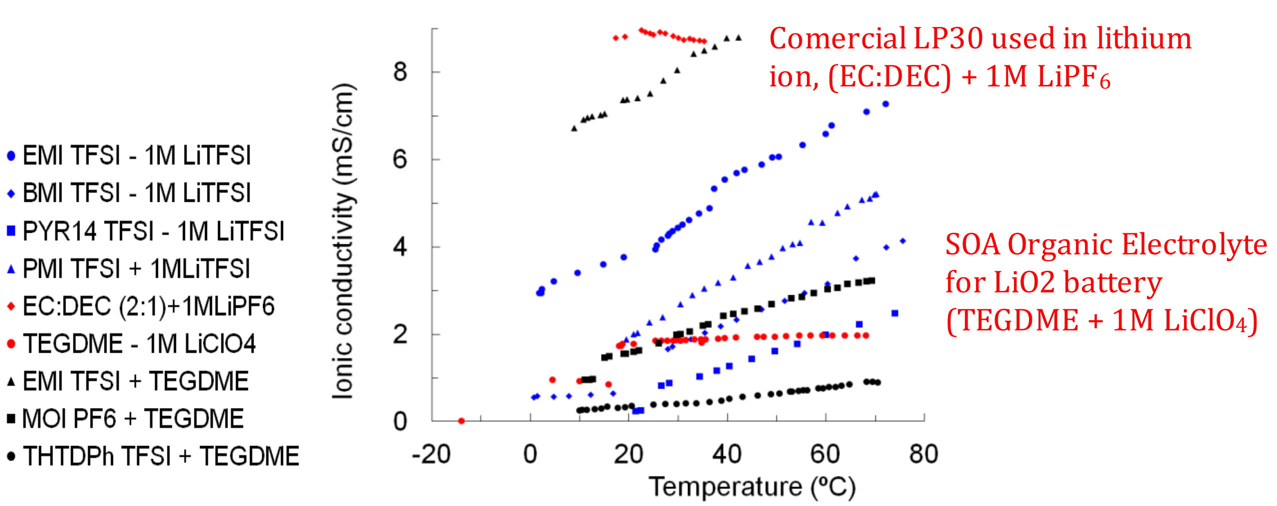
- cation: imidazolium, pyrrolidinium, piperidinium
- anion: bis(trifluoromethylsulfonyl)imide, hexafluorophosphate

Mixture ILs + organic solvent

Additives: Nanoparticles of CeO_2, ZrO_2, SiO_2, Al_2O_3, TiO_2

As organic solvents are concerned, Carbonate-based mixtures show very low cycle life (<10 cycles) due to gassing (EC) and Li_2CO_3 formation. TEGDME + $LiClO_4$ showed good results.

Ionic liquid are safer than organic electrolytes and present comparable conductivity (10 mS/cm @RT for EMITFSI). The performance are also increasing with temperature, make sense for high temperature application (Fig.20.)



Comercial LP30 used in lithium ion, (EC:DEC) + 1M $LiPF_6$

SOA Organic Electrolyte for LiO2 battery (TEGDME + 1M $LiClO_4$)

Fig. 20. Ionic conductivities in function temperature for different electrolytes

Additives based on ceramic compounds have been produced and used to stabilize the electrolytes (Fig. 22 *a*) Electrochemical results by using TEGDME are interesting in particular by using $LiNO_3$ as salt, which increases the durability of the cell. NO_3^- can react with Li metal to form soluble nitrite anions and a passivating layer of Li_2O on the surface of Li electrode (Fig.21.)

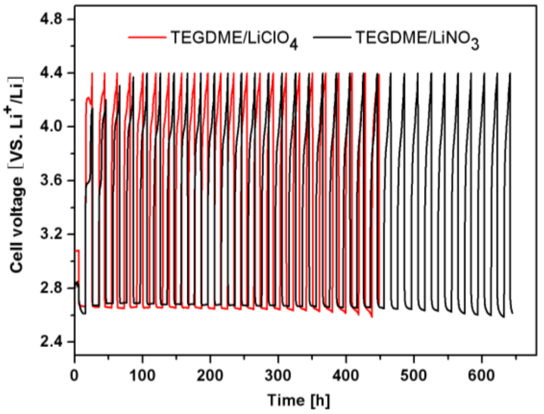


Fig. 21. Cycling profiles of cells tested with different Li salts in the electrolyte

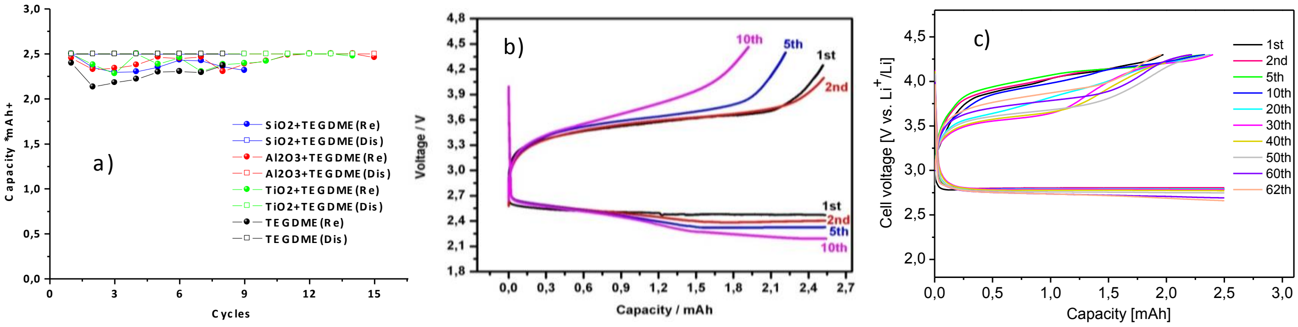


Fig. 22. Capacity profile of cells tested with different additive's electrolyte (a), cycling profile of a cell tested with EMITFSI-LiTFSI-0.1%PeO (b) and cycling profile of a cell tested with 5wt.%Al_2O_3+95wt.%DMSO electrolyte (c)

The use of additives increases the coulombic efficiency as can be seen on Fig.22.a .Higher stability is also achieved with the use of PeO or Al_2O_3 and ILs (Fig.22.b.). The use of DMSO strongly increased the overall performance in particular with the addition of 5% of Al_2O_3(Fig.22.c.).

With the IL-DMSO electrolyte, 80 % of the recharge process was realized at a voltage inferior to 4.0 V. More than 65 cycles were executed with a capacity retention of more than 80%. (Fig.23.)

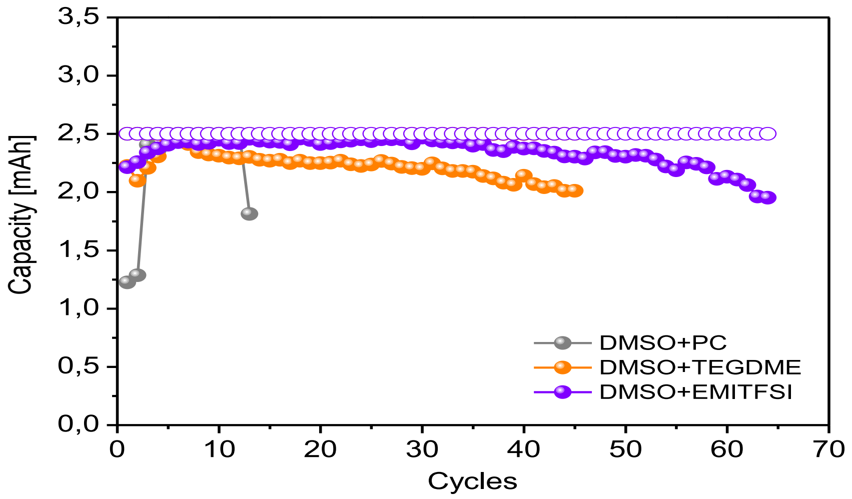


Fig. 23. Number of cycles vs. capacity of the cells with different mixed electrolytes

COMPLETE CELL

One of the objectives of STABLE was to produce a Li-air battery cell with specific capacity of >2000mAh/g and an improvement of cycle life to 100-150 cycles. Two generations of cells have been produced: one fuel cell type proving both high capacity and long cycle life and a second generation in which the fuel cell type was used to reach the high capacity and coffee bag and coin cell types were used for long cycling.

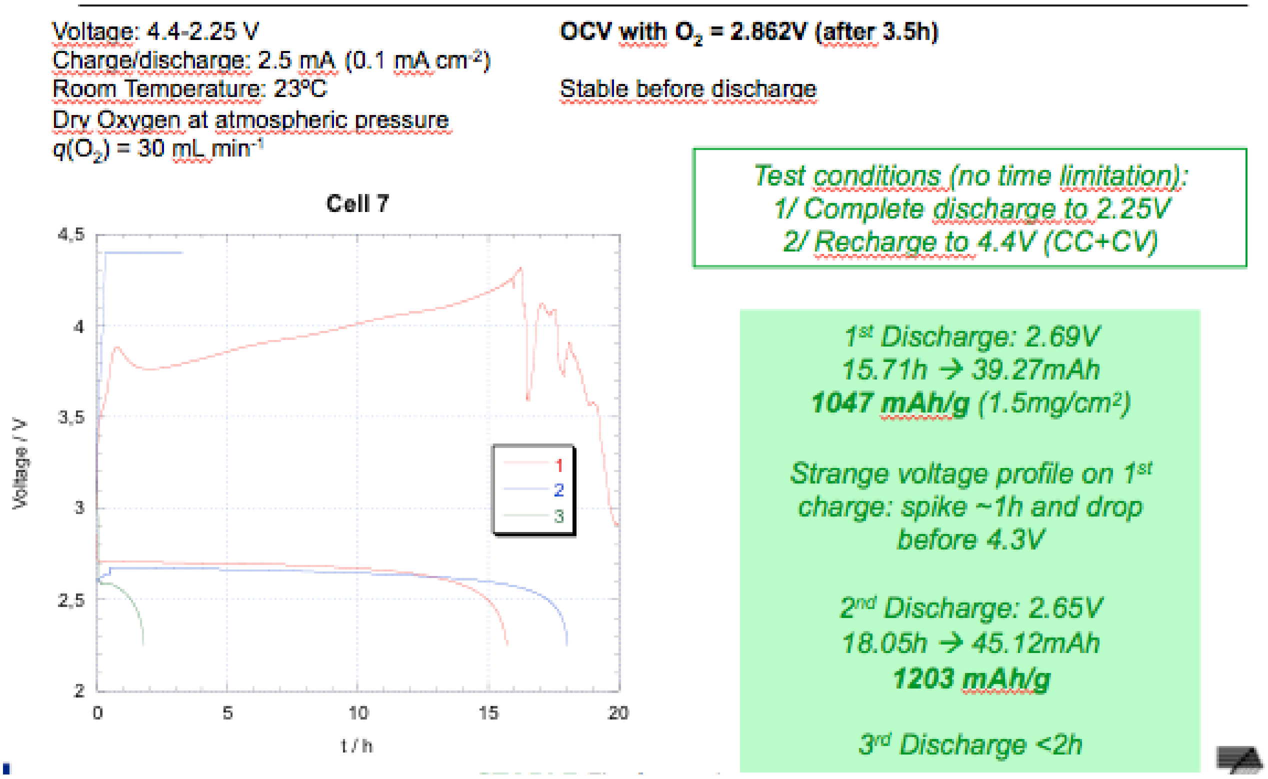
Several cells were prepared with different composition. These are reported in the corresponding deliverable. Here only best results are reported for sake of brevity.

The fuel cell type was assembled with different materials. Hereafter are reported some of the best performing.

Component	Material	Units	Mass (g)	**Mass %**	**Weight % (wo/ housing)**
Electrolyte	5wt% LiClO$_4$ TEGDME	1	12	**0,619**	**66,6**
Lithium Foil	Li	1	0,67	**0,035**	**3,7**
Separator	**Glass Microfibre POLITO**	1	0,6655	**0,034**	**3,7**
Tab	Cu	1	1,537	**0,079**	**8,5**
Cathode (POLITO)	**GDL24BC + Co$_2$O$_3$/CNT (1,5 mg/cm^2)**	1	0,2865	**0,015**	**1,6**
Anode sealing gasket	Polyester sheet + silicone layer	2	1,941	**0,100**	**10,8**
Cathode sealing gasket	Polyester sheet + silicone layer	1	0,927	**0,048**	**5,1**
Housing					
screw + washer + nut	Stainless steel	12	265,92	**13,73**	
End plate + collector plate + monopolar plate (flow field) + racors	Stainless steel + graphite composite + Copper	2	1653	**84,34**	

Table 1. The BoM for the fuel cell type prototype.

With the above reported composition, the following electrochemical results are obtained:



Voltage: 4.4-2.25 V
Charge/discharge: 2.5 mA (0.1 mA cm^{-2})
Room Temperature: 23°C
Dry Oxygen at atmospheric pressure
$q(O_2)$ = 30 mL min^{-1}

OCV with O_2 = 2.862V (after 3.5h)

Stable before discharge

Test conditions (no time limitation):
1/ Complete discharge to 2.25V
2/ Recharge to 4.4V (CC+CV)

1st Discharge: 2.69V
15.71h → 39.27mAh
***1047 mAh/g** (1.5mg/cm^2)*

Strange voltage profile on 1st charge: spike ~1h and drop before 4.3V

2nd Discharge: 2.65V
18.05h → 45.12mAh
1203 mAh/g

3rd Discharge <2h

Fig. 24. Electrochemical results obtained with the fuel cell type prototype

The capacity was higher than 1200 mAh/g. Unfortunately the cyclability is very low. Better results were obtained with the following cell composition:

Component	Material	Units	Mass (g)	**Mass %**	**Weight % (wo/ housing)**
Electrolyte	5wt% $LiClO_4$ TEGDME	1	11	**0,568**	**64,6**
Lithium Foil	Li	1	0,67	**0,035**	**3,9**
Separator	**Glass Microfibre POLITO**	1	0,6655	**0,034**	**3,9**
Tab	Cu	1	1,537	**0,079**	**9,0**
Cathode (POLITO)	**GDL24BC + Co_2O_3/CNT (1,2 mg/cm^2)**	1	0,2835	**0,015**	**1,7**
Anode sealing gasket	Polyester sheet + silicone layer	2	1,941	**0,100**	**11,4**
Cathode sealing gasket	Polyester sheet + silicone layer	1	0,927	**0,048**	**5,4**
Housing					
screw + washer + nut	Stainless steel	12	265,92	**13,74**	
End plate + collector plate + monopolar plate (flow field) + racors	Stainless steel + graphite composite + Copper	2	1653	**84,39**	

Table 2.The BoM for the coin cell type prototype.

Coin cells were prepared: Reproducibility of the cells was significantly lower than the standard El-Cell.

The nature of pressing for the cells and requirement for a number of metal spacers in the casing meant that a high percentage of the cells shorted prior to testing or showed unstable OCV values during the two hour rest period. Nevertheless, a number of cells were successfully created and the results were compared with parallel tests run in the El-cells.
Asymmetric discharge/charge tests run with CNT tests in DMSO at a fixed capacity (1000 mAhg^{-1}). Better capacity retention seen than for pure Super P cathodes. Reduced OER overpotential was obtained with reduced charging current. The capacity retention was improved at slower rates and best performance for slowest symmetric test (50 µA±).

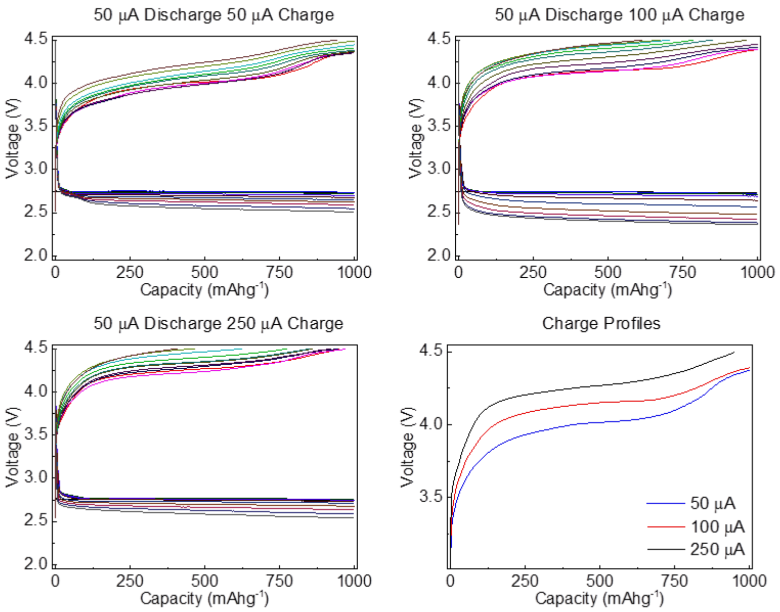


Fig. 25 Discharge/charge profiles of CNT cathodes in DMSO/LiTFSI electrolyte at 50 µA and recharged at 50 µA, 100 µA and 250 µA. Comparison of the first charge profiles at the different currents are provided for comparison.

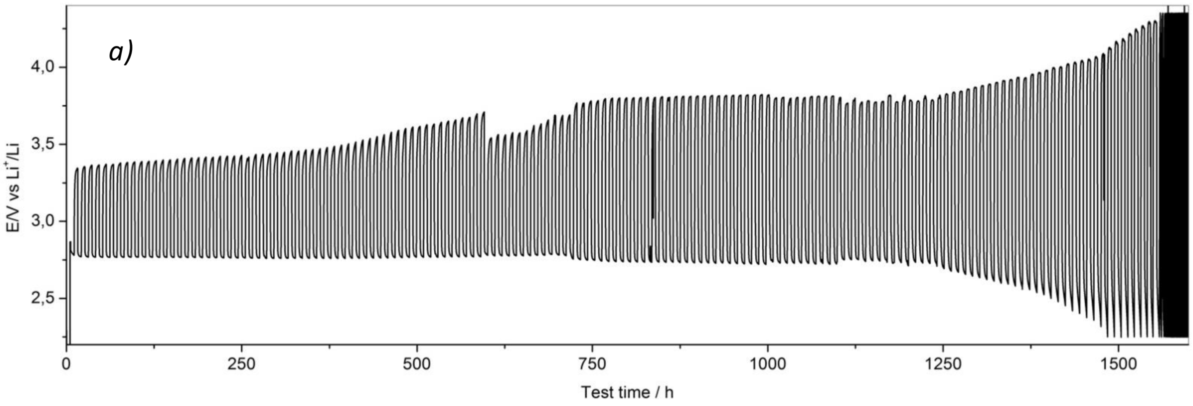
Some prototypes were assembled as pouch cells, and tested with a maximum time of charge and discharge of 5h. The cells were assembled with selected electrodes and electrolytes and with the optimized membrane to prevent the moisture inlet in the cell. The composition of cells and the results achieved can be summarized as follow:

Prototype n°	Housing	Nickel	Copper	Cathode	Separator	Electrolyte	Lithium	Membrane + Si Oil	Current density	Feeding	N° of cycles
1	-	-	-	GDL 24BC	Fiber Glass	TEGDME LiClO4 5%	-	-	0,05 mA/cm^2	Ambient Air 17%RH	41
2	2,8891 g			PdCNF on GDL24BA 0,0698 g	Fiber Glass 0,1579 g	DMSO80 + IL20 $LiClO_4$ 5% 1,1581 g	0,2050 g	0,8558 g	20mA/g	Ambient Air 17%RH	38
3	5,42 g	0,1071 g	0,2526 g	PdCNF on GDL24BA 0,0685 g	Fiber Glass 0,0,0954 g	DMSO80 + IL20 $LiClO_4$ 5% 1,1869 g	0,2662 g	0,1045 g	20mA/g	Ambient Air 17%RH	42
4	3,00 g	0,0758 g	0,1074 g	PdCNF on GDL24BA 0,0191 g	Fiber Glass 0,0636 g	DMSO80 + IL20 $LiClO_4$ 5% 0,9010 g	0,1522 g	-	20mA/g	Dry Air 0% RH	40
5	5,18 g	0,0422 g	0,1180 g	PdCNF on GDL24BA 0,0640 g	Fiber Glass 0,0769 g	DMSO80 + IL20 $LiClO_4$ 5% 0,5793 g	0,9515 g	0,1341 g	20mA/g	Ambient Air 17%RH	105

Table 3 The BoM for the pouch cell type prototypes

Cell 4 was tested in dry air for comparison, while the other ones were tested in air with the 17% of humidity.

The best results were obtained with the cell 5 and 151 cycles:



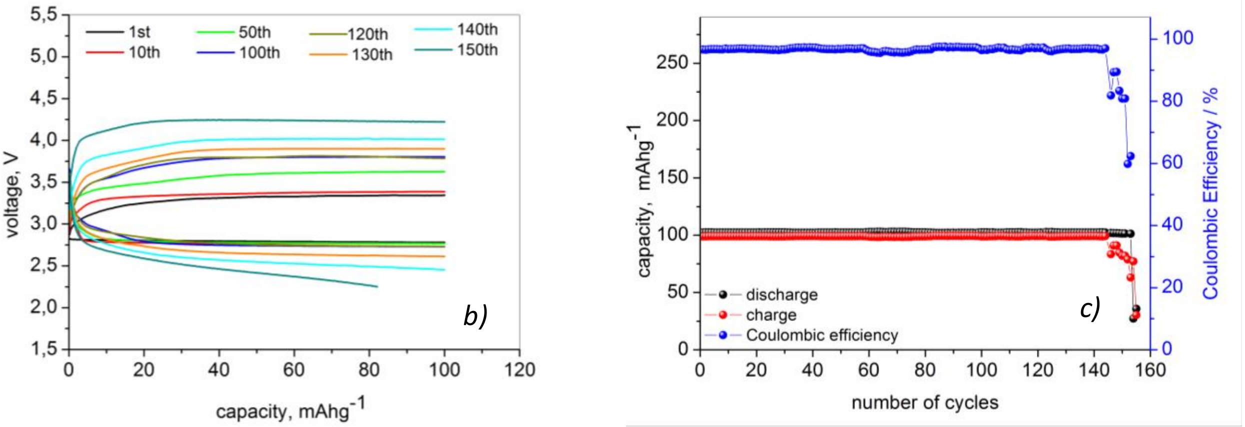


Fig. 26 Electrochemical characteristics of the pouch cell prototype 4: a) cell voltage vs. time, b) cell voltage vs. capacity, c) capacity vs. number of cycles.

Modelling

Large-scale density functional theory models were performed to investigate the influence of electrocatalysts on the formation of Li_2O_2, LiOH and Li_2O during operation of Li-O_2 batteries. The modelling effort elucidated a general basis for the influence of important electrocatalyst crystallinity and surface defects on the overpotential associated with discharging and recharging of the Li-O_2 battery

Life Cycle Assessment-LCA

Lithium-air batteries are investigated for propulsion aggregates in vehicles as they theoretically offer at least 10 times better energy density than the best battery technology (lithium-ion) of today. A possible input to guide development is expected from life cycle assessment (LCA) of the manufacture, use and recycling of the Li-air battery.

For this purpose, lithium-air cells are analyzed 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. The aim of this investigation is highlighting environmental hotspots of lithium-air batteries to facilitate their improvement, in addition to scrutinizing anticipated environmental benefits compared to other battery technologies. Life cycle impacts are quantified in terms of climate impact, abiotic resource depletion and toxicity. Data is partly based on assumptions and estimates guided from similar materials and processes common to Li-ion technologies. Laboratory scale results for Li-air systems are considered, which include expectations in their future development for efficiency gains.

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. The battery internal electricity losses become heat that may need considerable amounts of additional energy for its transportation out of the battery.

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. LCA could provide additional arguments and a quantitative basis for lithium battery recycling. This emphasizes the need to develop LCA toxicity impact methods in order to properly assess lithium.

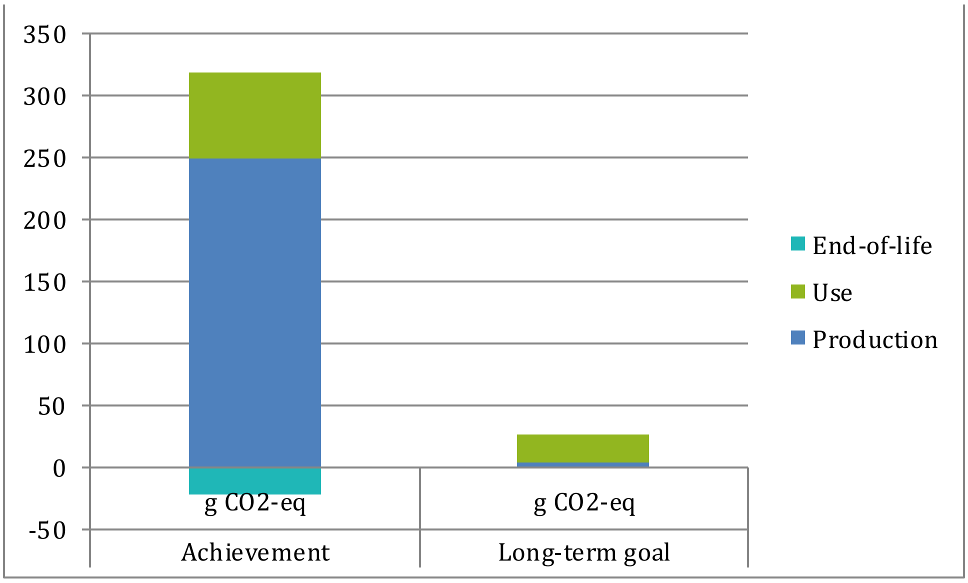


Fig. 27 Climate impact per vehicle km for the two scenarios.

- **The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results).**

The objective of the project is to obtain Li-air battery cells with specific capacity of >2000mAh/g and an improvement of cycle life to 100-150 cycles. This so high capacity and cyclability can allow the production of EVs with performance closer to those of current internal combustion vehicles if compared to other storage systems, e.g. Li-ion batteries. It is so evident the potential impact and use of the results of Stable project, translated into socio-economic impact and the wider societal implications of the project.

The objectives are well reached with a high capacity of 1200 mAh/g obtained with fuel cell type batteries, Such design permits to multiply the capacity adding more cells together. The cycle life was here improved to 151 cycle in air with 17% of relative humidity. This is one of the best results actually present in the literature.

The EU is a major contributor to the world's automotive industry manufacturing over a quarter of all vehicles including third of passenger cars. The industry accounts for more 6.5% of the EU GDP. This project is expected to contribute to reduce such an economic impact by creating a competitive platform through the development of new technologies. The developed new technologies could be exploited by the industrial partners as also demonstrated during the industrial workshop organized in Torino.. The lithium air batteries and their processing technologies developed in the STABLE project will generate a larger influence for European academic research. This was also discussed during the cluster workshop in Brussels. Consequently an increasing market for material production in Europe will arise through generation of new companies. The quantitative increase in highly skilled workforce, together with the knowledge acquired during the project activities will help to enhance the competitiveness of European industry.

The European Community will profit from the reduction of waste production and improvement of resource efficiency through a more efficient recycling of critical materials. On a project scale, it can be expected that new and skilled engineers and scientists will stand out from the STABLE project. The skilled workforce will ensure, together with the knowledge produced, the increase of the competitiveness of the European industries

Exploitable Foreground and its Use

Based on the positive outcome of the assessment procedures in WP1-WP6 and taking into account the outcomes of the costs estimation, the industrial partners promote the developed batteries within their own companies and among companies cooperating with them in the EU, taking care of IPR protection in each case.

To carry out this synthetic work, the following table has been filled with the **first proposal of identified exploitable results**:

#	Exploitable Result	Description of Exploitable Foreground	Sector(s) of application	Time to Market	Patents or other IPR exploitation Forms/Claims	Owner & Other Partner(s) involved
1	*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 years*	*Internal know-how, Patent, Licensing*	*Owner to be defined depending on the specific result* *Partners involved: LUR, POLITO, LEITAT, IVF, SAU*

#	Exploitable Result	Description of Exploitable Foreground	Sector(s) of application	Time to Market	Patents or other IPR exploitation Forms/Claims	Owner & Other Partner(s) involved
2	*Cathode materials for Li-O_2 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 and to avoid the over-potential.*	*Electrochemical Storage (Batteries)* *Electrochemical Conversion (Fuel Cells)*	*5 years*	*Internal know-how, Patent, Licensing*	*Owner to be defined depending on the specific result* *Partners involved: POLITO, LEITAT, LUR, IVF, SAU*
3	*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 years*	*Internal know-how, Industrial Secret, Patent, Licensing*	*Owner to be defined depending on the specific result* *Partners involved: LEITAT, POLITO, CEGASA, SAU*

#	Exploitable Result	Description of Exploitable Foreground	Sector(s) of application	Time to Market	Patents or other IPR exploitation Forms/Claims	Owner & Other Partner(s) involved
4	*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 years*	*Internal know-how (Consultancy) for further use in materials development and cell design*	*UCC* *Partners involved: LEITAT, CEGASA, ELAPHE*
5	*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 years*	*Internal know-how, Industrial Secret, Patent, Licensing*	*CEGASA* *(UCC, ELAPHE)* *Partners involved: LUR, POLITO, LEITAT*
6	*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*	*Partners involved: IVF, ELAPHE*

#	Exploitable Result	Description of Exploitable Foreground	Sector(s) of application	Time to Market	Patents or other IPR exploitation Forms/Claims	Owner & Other Partner(s) involved
7	*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*	*Elaphe* *(CEGASA)*

Dissemination Plan

The STABLE dissemination plan as part of the PUDF (D8.3, D8.5, D8.9, D8.12) includes activities such as project website, flyers, newsletters, scientific publications, workshops, presentations at conferences and fairs. In addition, STABLE project will participate in clustering activities with other EU funded lithium based batteries projects (LISSEN, EUROLIS) and workshops organised by PPP Green Cars and EGVI in Brussels. Participation in other workshops organized by other projects in the area relevant to the STABLE will be ensured, such as during the ECS conferences or others organized by ALISTORE-ERI.

All partners participated in dissemination activities. The partners will disseminate the project through their networks and newspaper, marketing departments, clusters, magazines and information days.

The research leading to these results has received funding from the Seventh Framework Programme FP7/2007-2013 under grant agreement n°314508.

Website

The aim of building a website homepage is to set up the project community, that is the worldwide group of organisations and professionals that share an interest in potential results, are possibly impacted by those results, or are in a position that may affect the actual use and exploitation of the innovative concepts of the project. Additionally, another objective is to facilitate the exchange of information and knowledge between the partners forming the consortium through a private area.

The project website has been developed, set-up and is maintained by POLITO. It is public and accessible from month 3 of the project (Deliverable 8.1) at: http://www.fp7-stable.com/

It includes a public area navigation menu divided in the following sections: Home (general presentation of the project), About us, Partners (links to partner's websites), Meeting (project meetings), Workpackages (WP description), News, Gallery, Contact us, Login (to restricted area).

The restricted area with secure FTP access has also been implemented for sharing sensitive information between the STABLE partners.

The site will be updated at least every two months in order to disseminate the findings of the project and stimulate further interest in its growth and activities. A web analytic tool (such as Google Analytics) may be used to monitor access and hits received in order to evaluate the outreach of this on-line dissemination tool.

The **electronic newsletters** will be published every 12 months (Deliverables 8.4, 8.7 and 8.11), outlining the current/planned activities of the STABLE project and the newest results, both through the website and via the email subscription service. This will ensure continued stimulation of other parties' interest in the STABLE project over its lifecycle. The first year newsletter (D8.4) reported on conference attended by the partners presenting STABLE results an upcoming event such as project meetings.

Other media like project logo, flyer and poster have been designed and promoted through the web and on the international and national meetings (conferences, workshops, fairs, etc.).

Already included in the website, as part of the Visual Identity for the project, the **logo** has been adopted. The STABLE logo shown attached is simple and distinctive, integrating the project acronym with a scheme of an electrical plug and a battery with a shape that evokes the wheels of a car, thus summarising the project aim of developing a new battery technology suitable for electromobility. Newsletters are distributed by the partners' contacts and are collected on the website.

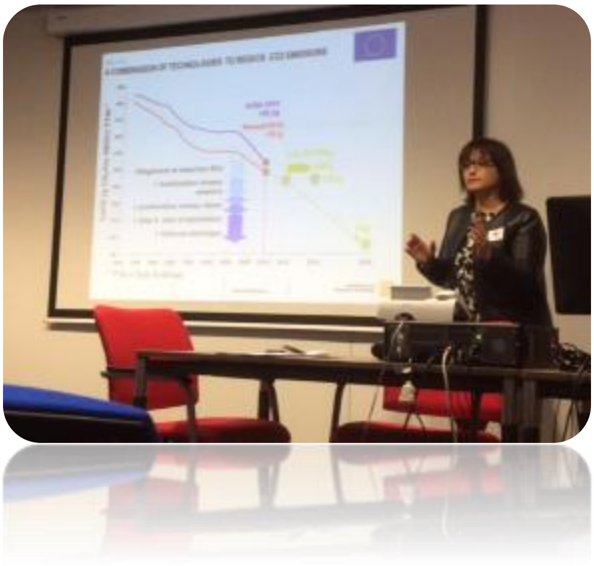
Workshops

The STABLE consortium has also planned to organize 3 workshops which will invite technical agents in the automotive sector and urban mobility (companies, research institutes, public research organizations and universities). Participation in these workshops for government representatives (national, regional and local), would allow them to see first-hand the degree of maturity of technologies and the possible timetable for its implementation in the market.

1.- Elaphe foresees a **dissemination event** (D8.6 - month 19) in order to promote electric vehicle technologies, battery technologies and STABLE project results in Slovenia.

2.- An open **Industrial workshop on electric mobility vehicles** was organized in month 24 by POLITO as a forum for the exchange of STABLE research results and industrial experience on selected topics of mutual interest. It is expected that this workshop will lead to closer interaction between industrial partners from outside the consortium and the project partners.

3.- A **Scientific workshop in coordination with other EU funded battery projects** was organized in M32 in Brussels. **Clustering** activities with other EU funded lithium based batteries projects was organized. All experts from other EU lithium batteries were invited for the better communication and dissemination, exchange of information and for developing new cooperation projects etc. The results from the STABLE project will also be presented in this workshop through the posters or oral presentations.



Projects presentation

Thursday, 28th May 2015

14:55 APPLE—Scrosati B.
15:05 BATTERIES 2020 - Virreal I.
15:20 GREENLION - Urdampilleta I.
15:35 MARSEV - Urdampilleta I.
15:50 MATS4BAT —Martinet S.
16:05 eCAIMAN—Ganev B.
16:15 SOMABAT—Gil-Agustí M.
16:30 Coffee Break
17:00 ALISE/ALION— Aucher C.
17:20 EUROLIS/HELIS—Dominko R.
17:40 LISSEN —Scrosati B.
17:55 BiLiLuBat—Tesfu T.
18:10 STABLE- Bodoardo S.
18:25 Conclusions

Lithium-ion

Beyond lithium-ion

Brainstorming cluster
Brusselles–May 29th,2015

In conclusion the above dissemination activity will be directed towards researchers in materials science, students who will be part of the future generation of scientists and professionals in industry (experts in material, process and production).

For future month some more activities are already planned e.g. the participation at the Researcher Night in Torino (24th September 2015) and the participation in EEVC (December 2015).

Clustering Activities

Clustering activities with other EU lithium based battery projects will be promoted, especially those funded in the same Call (LISSEN, EUROLIS). These activities will also culminate in a workshop organised at the end of these projects that follow the same timeline, as mentioned in section 3.3.

In addition, STABLE is funded under the European Green Cars Initiative (EGCI). The EGCI is one of the three Public Private Partnerships (PPP) of the European Economic Recovery Plan announced by the President of the European Commission on the 26th of November 2008. The topics of the initiative include research on trucks, internal combustion engines, biomethane use, and logistics. However, a main focus is on the electrification of mobility and road transport.

In the framework of the initiative, there has been a continuous process of strategic stakeholder consultations, it consist on multiannual implementation plans which rest upon the long-term roadmaps and strategic research agendas of the European Technology Platforms, and it also includes workshops. Within the new framework program "Horizon 2020", a new PPP following EGCI has been set up: EGVI (European Green Vehicle Initiative). The STABLE project will be active in these forms.

Journal Publications and Conferences

The STABLE scientific and technical foreground, approved for public dissemination by the project consortium, will be published in international peer review journals and presented on scientific conferences. It is reminded that in any communication (written or oral) a clear reference to the STABLE project as an FP7 project co-funded by the EC shall be made:

The research leading to these results has received funding from the Seventh Framework Programme FP7/2007-2013 under grant agreement n°314508.

Also at conferences, within the Task 8.1, networking activities with other networks/projects/peer groups dealing with EVs on European and national levels are envisaged. This is to mutually benefit from expertise/experience in the field and to broaden the dissemination of the STABLE project results.

The initial draft of a technical or scientific paper should be distributed to the rest of the partners in order to know if partners have any objection to publish the requested paper, article or communication. Every 6 months a list of published articles and conference dissemination performed will be shared with the consortium. Complete references shall be made available to the Commission and will be included in the updated PUDF every 12 months.

STABLE will actively present key findings and progress also at key conferences and events in each and all areas of importance to the industrial and scientific goals of the overall description of work the conferences attended are reposted in the corresponding deliverable.