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Assessment of the Li-air battery technology for automotive applications through the development of a multi-electrode solid-state prototype

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Summary

This report highlights the results of a project carried out at the National Research Council of Canada (NRC), with the overall objective to address the major issues of the Li-air battery technology and assemble a multi-electrode pilot-scale prototype. Several innovative ideas and technologies were investigated along the core concept of a polymer-based solid-state technology. The assessment of the Li-air technology is discussed through the results of the project as well as other sources, especially concerning its readiness and perspectives for automotive applications.

1. INTRODUCTION

The improvement of battery performance and their price decrease will be the key enablers of vehicle electrification. In this regard, an increase in the energy density of batteries is particularly sought after, because it is the obvious main driver to cost reduction and range anxiety mitigation. Consequently, a number of higher energy density technologies, often referred as "beyond Li-ion technologies", are being extensively studied : lithium-sulfur, metal-air, multivalent chemistries, solid-state batteries, etc.

Among them, the lithium-air technology clearly stands as the most promising system in terms of energy density, reaching a theoretical capacity of 3500 Wh/kg, almost 20 times the current Li-ion automotive cells. In practical batteries, only about half of the theoretical energy density is usually obtained, but if only 30 % of the theoretical energy density of Li-air batteries was indeed available, it would allow common vehicles to travel for ca. 800 km (500 miles) between charges, even more than what a typical internal combustion engine (ICE) vehicle is capable of. These impressive numbers have triggered an intense research activity worldwide, mostly in the last decade.

However, this promising technology also comes with a set of major challenges, both at the scientific and technical levels. A non-exhaustive list of the issues to be solved includes 1) the use of metallic lithium at the anode side, which has to be protected from the oxidative atmosphere of the cathode side and whose dendrite growth must be inhibited ; 2) the realization of a fast, reversible and steady electrochemistry at the cathode (where the reaction product, lithium peroxide is being generated), 3) the finding of an electrolyte that does not evaporate and is both stable towards the lithium anode and the ultra-oxidative electrochemistry occurring at the cathode; 4) the engineering of a 3D porous cathode with triple-point functionality (gas diffusion, ion diffusion and electron percolation), and so on…

In order to tackle these challenges, a tremendous amount of work has been carried out, in order to better understand the Li-air electrochemistry, reveal its major failure modes and find solutions to them [1-3]. Due to the complexity of the issues, the great majority of the work has been carried out at the laboratory scale, often targeting a single phenomenon. Consequently, no practical lithium-air battery prototype has ever been designed and tested so far.
This publication highlights the results of a project carried out at the National Research Council of Canada, with the overall objective to address the major issues of the Li-air battery technology and assemble a multi-electrode pilot-scale prototype, and in the meantime assess the readiness of this technology, especially for automotive applications.

2. RESULTS AND DISCUSSION

2.1 Development of Li-air battery components

All the components of a Li-air battery have been investigated in the project, keeping in mind the overall objective of building a realistic Li-air battery, including 3D porous current collectors, cathode catalysts, carbon supports for the catalysts, and a solid polymer electrolyte.

2.1.1 3D current collectors development

Commercially available nickel foams typically used in metal-air batteries (INCO foams) have a typical porosity of 97 % and a thickness over 1.3 mm [4]. The only way to decrease their thickness to a suitable value for Li-air battery electrodes (~ 700 µm in this project) is to press the foam, which directly decreases the porosity to ca. 53 %, which affects the gas flow and increases the electrode weight.
Therefore, foams were designed at NRC with specific characteristics needed for Li-air application, namely a thickness of 700 µm, a minimal pore size and a high surface area (cf. Fig. 1). A NRC-patented technology was adapted for this purpose. The principle is the foaming of a nickel powder formulation comprising selected foaming agents and binders, and then to de-bind and sinter the foam in a reductive environment at high temperature. Thanks to its very high porosity (96 %) and low thickness (700 µm), the foam weight by surface unit was decreased by 30 % compared to the commercial foams.

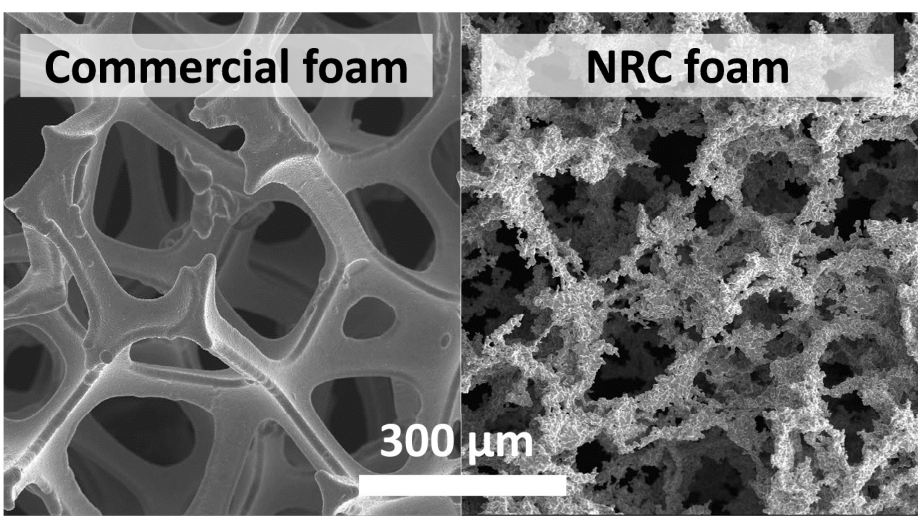

Figure 1 : Scanning electron microscopy images of commercial nickel foams and foams developed at CNRC.

2.1.2 Cathode catalyst screening

A catalyst is needed to enable the Li-air reaction : $2\ Li^+ + O_2 + 2\ e^- \leftrightarrows Li_2O_2$.
Accordingly, a number of catalysts families were investigated : metals, alloys, metal oxides, perovskites, pyrochlores, etc. Figure 2 shows the comparative electrochemical performances of a selection of tested catalysts. The first observation is that the carbon supports themselves (CP = carbon paper ; KB = Ketjenblack) are able to catalyze the reaction, as already reported in the literature [5-6]. However, the addition of catalysts can increase the capacity of the cell in certain cases, even if a real effect of the

presence of catalysts is not obvious and still debated in the community. In our study for instance, the presence of various catalysts failed to decrease the large overpotential observed during the recharge (corresponding to the dissolution of Li_2O_2 and the evolution of oxygen) (cf. Fig. 2a). However, the use of catalysts helped increase the cyclability of cells during shallow cycling (discharge capacity limited to 1000 mAh/g, cf. Fig. 2b). Overall, the best catalysts tested were the lead ruthenium oxide pyrochlore (PbRuO) [7] and the nickel cobalt oxide spinel ($NiCo_2O_4$).

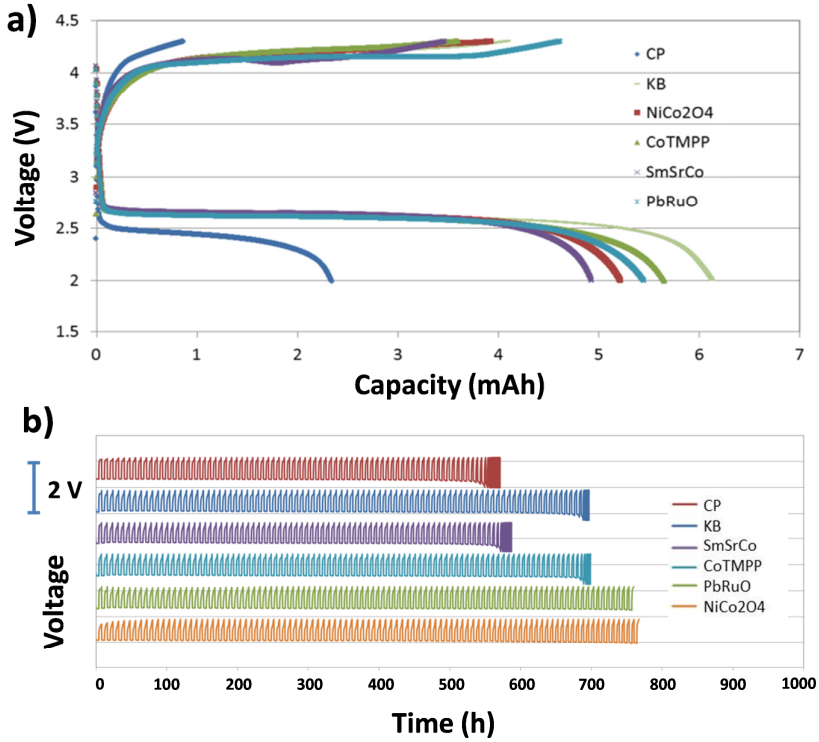

Figure 2 : Comparative electrochemical performances of some of the catalysts tested. a) Galvanostatic cycling at 0.2 mA/cm^2 and 100 % DOD ; b) galvanostatic cycling with a discharge capacity limitation at 1000 mAh/g of active material.

2.1.3 Solid polymer electrolyte development

Li-air battery electrolytes face a number of unprecedented requirements : 1) given that these are open systems with flowing gas, the electrolyte must not evaporate, 2) they have to be chemically stable versus metallic lithium, the cathode's product (lithium peroxide) and the ultra-oxidative oxygen radical species generated during the cell discharge, 3) they must prevent lithium dendrite growth to ensure operational safety and 4) they have to protect the lithium metal towards the cathode's oxygen atmosphere.

Looking at the current technologies available, the only type of electrolytes that have a chance to fulfill all those requirements are solid-state electrolytes. And the only lithium metal-containing batteries today are Bolloré's LMP batteries, that power the Blue Car EVs [8]. Their solid-state electrolyte is polymer-based and already demonstrated a number of these requirements. We therefore used this strategy in the development of our Li-air technology.

A formulation of solid polymer electrolyte (SPE) was developed, based on cross-linked PEO and a PVDF mechanical support. A number of additives were investigated, in order to increase the conductivity, stabilize the anode interface and enhance the O_2 permeability. All SPEs were produced using a melt-extrusion process in an anhydrous room (H_2O < 30 ppm, dew point -60 °C). The film thickness was set between 80 and 100 µm.

Figure 3 presents the conductivity of SPE formulations containing different additives. PYR14TFSI is an ionic liquid that allows to significantly increase the ionic conductivity of the SPE. It is also effective in promoting the formation of a stable solid electrolyte interface (SEI) with lithium metal, which helps

prevent the initiation of dendrites. Its use as an additive in PEO-based SPEs has already been reported in the literature [9-10].

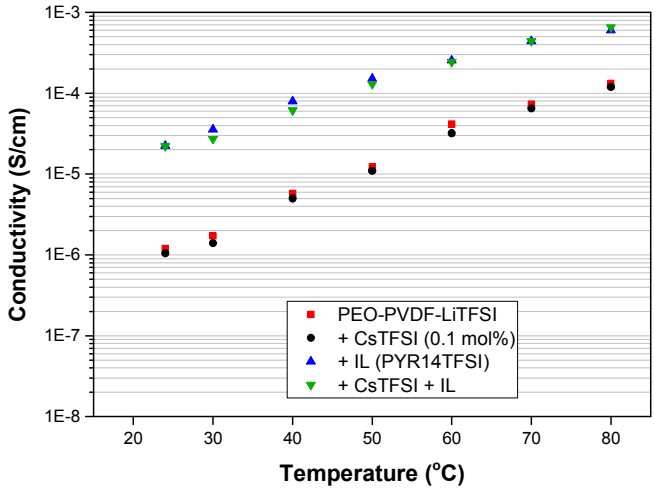

Figure 3 : Ionic conductivity of several SPE formulations

The cesium salt CsTFSI has been recently proposed as a dendrite suppressing additive for liquid electrolytes [11], but it has never been investigated in polymer electrolytes. Figure 3 shows that the addition of 0.1 mol% of CsTFSI has no effect on the SPE conductivity, which was expected. However, it proved to have a significant impact on the dendrite formation : Figure 4 shows a Li stripping/plating experiment designed to accelerate the growth of lithium dendrites. It can be observed that the addition of 0.1 mol% of CsTFSI allows an effective stabilization of the interface (lower overvoltage) as well as a 5 times improvement in the prevention of dendrite growth. When a lower concentration of CsTFSI was used the effect was much lower, but with higher concentrations, a quick increase of the interface resistance lead to poor performance (results not shown).

Finally, an optimized formulation was reached, incorporating all additives and showing enhanced characteristics relative to the reference SPE.

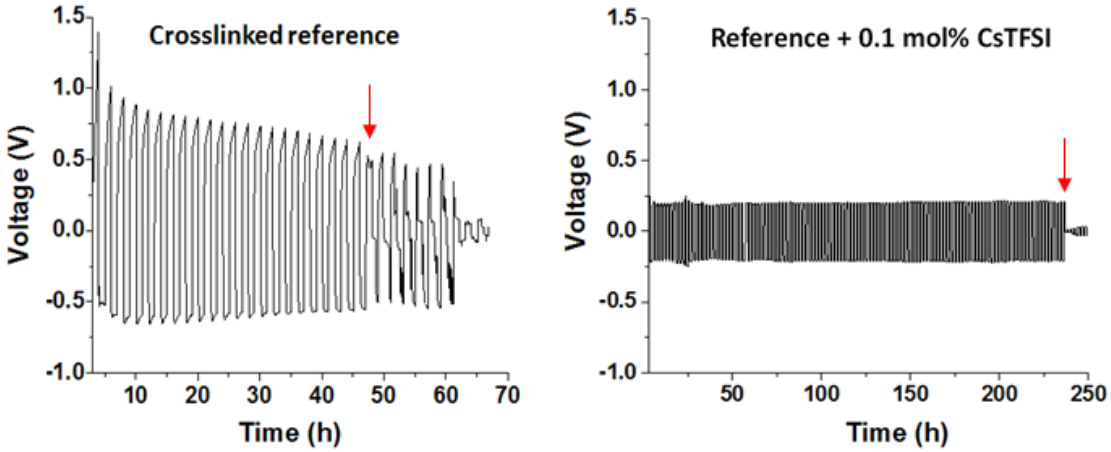

Figure 4 : Lithium Stripping/plating experiment of Li/SPE/Li cells at 70 °C and 0.5 mA/cm^2 with current inversion each hour. The red arrow shows the crossing of the first dendrite through the SPE, causing a sudden drop of voltage.

2.2 Integration of Li-air battery components

The integration of the different components is critical to optimize the battery electrochemistry. Two steps of integration were investigated : the incorporation of the catalytic layer onto the nickel foam current collector, and the compatibilisation of the 3D cathode with the SPE electrolyte.

2.2.1 Catalyst and carbon support integration

Several studies were carried out to optimize the cathode fabrication method. Spray deposition was then selected for its effectiveness in coating homogeneously the active layer on the nickel foam. A number of optimization studies were carried out, including the active material formulation (type of binder, catalyst and carbon support, relative ratios of components, ink viscosity) as well as spray deposition parameters (substrate temperature, spraying distance and speed, etc). The final formulation included 64 wt% of Ketjenblack EC-600JD (KB) as the carbon support, 16 wt% of catalyst (KB:catalyst = 8:2), 10 wt% of PTFE as a structural binder and O_2 diffusion enhancer, and 10 wt% of PEO as co-binder, bringing adhesive properties towards the current collector and compatibility with the PEO-based SPE.

Figure 5a displays the results of a carbon loading study, with both specific and absolute capacities as criteria. It can be observed that the lower loading reached the best specific capacities (4400 mAh/g). However, the surface capacity of the cell was low (< 2 mAh/cm^2). The cell delivering the higher suface capacity had a loading around 3 mg/cm^2, even if the KB was working less ideally (2800 mAh/g). Figure 5b shows SEM pictures of a commercial INCO foam bare (left) and loaded with 3 mg/cm^2 of active layer (right), clearing showing that the nickel surface is totally and homogeneously covered without blocking the cathode's porosity to O_2 and electrolyte.

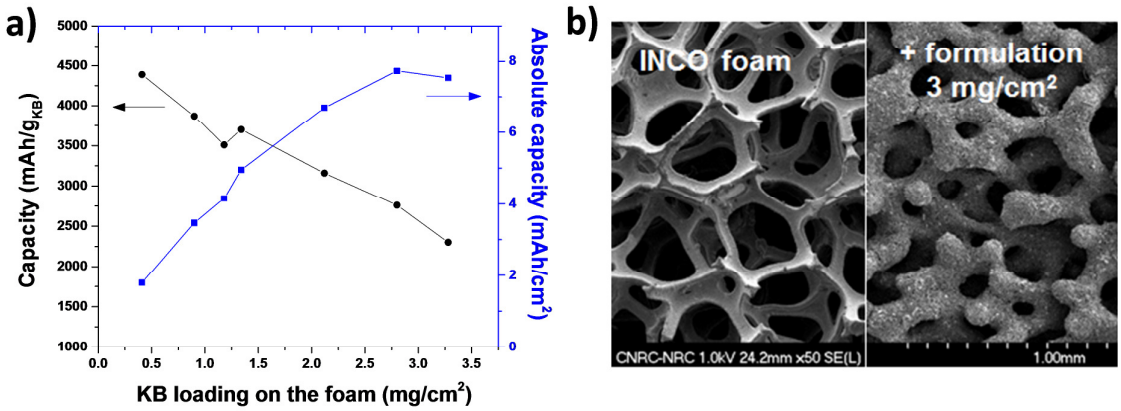

Figure 5 : a) Carbon loading optimization ; b) SEM images of a commercial INCO foam coated at an optimized loading of 3 mg/cm^2.

2.2.2 Cathode-SPE integration

One of the most critical interfaces of a solid-state Li-air battery is the cathode-electrolyte interface. Because the electrolyte is a solid-state extruded flat membrane, its compatibilisation with a highly porous 3D cathode is a complex challenge. A number of solutions were investigated, all involving the use of an integration layer. The latter is meant to be a Li^+ ion link between the cathode and the SPE, and can be considered as a second layer of electrolyte.

Figure 6a shows the comparative performances of Li-air cells assembled with different electrolyte integration layers. When no integration layer was used, the cell's electrochemistry was limited to the cathode regions in direct contact with the SPE, providing poor capacity. When a liquid integration layer was used (here a blend of LiTFSI with PYR14TFSI, chosen for its compatibility with the SPE and its negligible volatility), the cell delivered a much higher capacity. However, the average discharge voltage was low (2.5 V), demonstrating a sluggish electrochemistry with poor rechargeability. When the cathode was totally impregnated with the ionic liquid integration layer, the electrochemistry was better but still not optimal. Finally, the best integration method was obtained by melt-pressing a PEO-based integration layer (PEO+LiTFSI) into the cathode's porosity. Interestingly, this means that O_2 diffusion into the PEO-based

integration layer was sufficient to allow a good electrochemistry, at least at the low current rates usually used to test Li-air batteries (0.1 mA/cm^2). Figure 6b shows a cross-sectional view of a solid-state Li-air cell assembled with a PEO-integrated cathode.

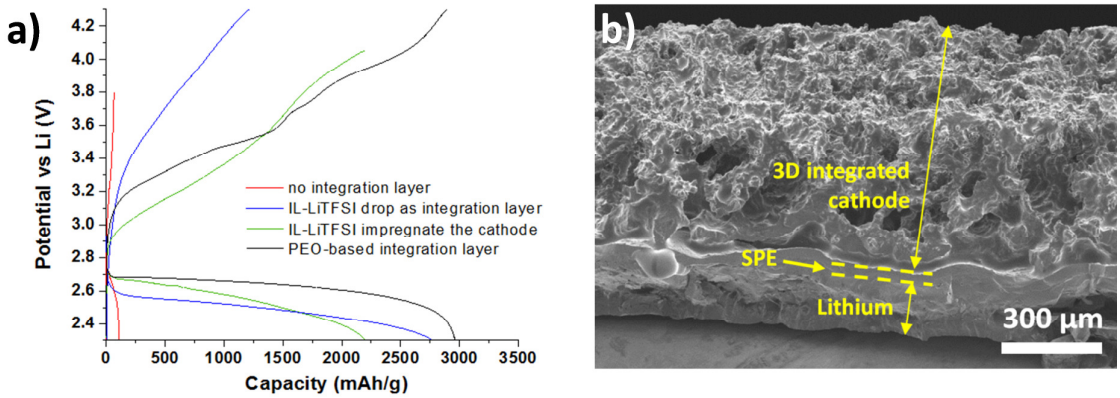

Figure 6 : a) Discharge/charge curves of cells assembled with different integration layers ; b) SEM cross-sectional image of a solid-state Li-air cell assembled with a PEO-based integration layer.

2.3 Design and assembly of a large-scale Li-air battery prototype

In order to fully assess the Li-air technology, it is important to understand not only its electrochemistry at the cell level, but also the engineering feasibility of large-scale systems. All the Li-air large-scale prototypes reported in the literature are based on soft pouch cases with areas open to the atmosphere for O_2 intake. These are often 2-electrode designs or 3-electrodes designs (a lithium metal anode sandwiched between two cathodes) for the more elaborated ones [12-13] and unfortunately do not represent real prototypes that can be extrapolated to larger scales. The only way to achieve a realistic Li-air battery prototype is to develop a multi-electrode stack design with integrated gas channels. Therefore, such a design was realized, with the strategy to limit the penetration of the SPE integration layer into the nickel foam, in order to use the upper part of the foam as the gas channel.

Selected Li-air components were upscaled. Unfortunately, the NRC foams could not be reproducibly obtained at a larger scale, and commercial INCO foams were used instead. The spray deposition of the active materials onto nickel foams was upscaled to a 12x12 cm^2 dimension using an automated scanning spray deposition technique. Methods of integration and component alignment were also designed and fabricated. A few of them are displayed in Figure 7.

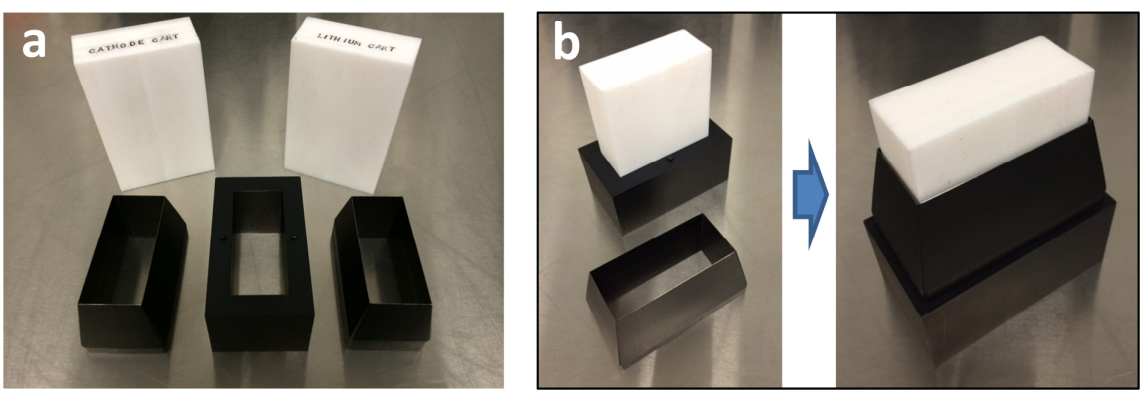

Figure 7 : a) a set of specifically designed punches and component alignment tools ; b) example of a manual stacking method of two components of different dimensions, achieving a precise concentric alignment.

Finally, 10-electrode prototypes were assembled (5 electrodes per polarity), each electrode having a 19.5 cm^2 active area (6.85 x 2.85 cm^2 ; total area : 97.5 cm^2). Figure 8 shows the different components and assembly steps of a prototype. The design of a number of stacked air-electrodes requires efficient gas channels to provide oxygen to the electrodes. In the developed design, two main gas tunnels are located at

the vertical of the gas inlet/outlets (cf. Fig 8a : removable alignment pins). These vertical tunnels provide gas to each level of the stack. The gas is then channeled through the upper part of the nickel foams and reaches the outlet on the other side of the stack, hence providing oxygen to the whole active area. Fig. 8c shows an image of a prototype's electrode stacking, from a 3D reconstruction obtained by X-ray microtomography. Because of the X-ray high contrast between polymers and metals, only the metal parts appear clearly, such as the nickel foams and the nickel and copper current collectors. The X-ray microtomography allowed to characterize the quality of the stack assembly and figure out the efficiency of gas channels.

The SPE dimension was slightly bigger than the lithium (and cathode) dimension, in order to protect lithium from the oxygen atmosphere at the stack edges.

The prototypes were assembled in an anhydrous room, then inserted into a soft pouch that was thermally sealed on all sides (cf. Fig. 8b). The last side was vacuum sealed in order to remove all atmospheric contaminants before flushing with oxygen. The prototypes were then transferred to the testing lab.

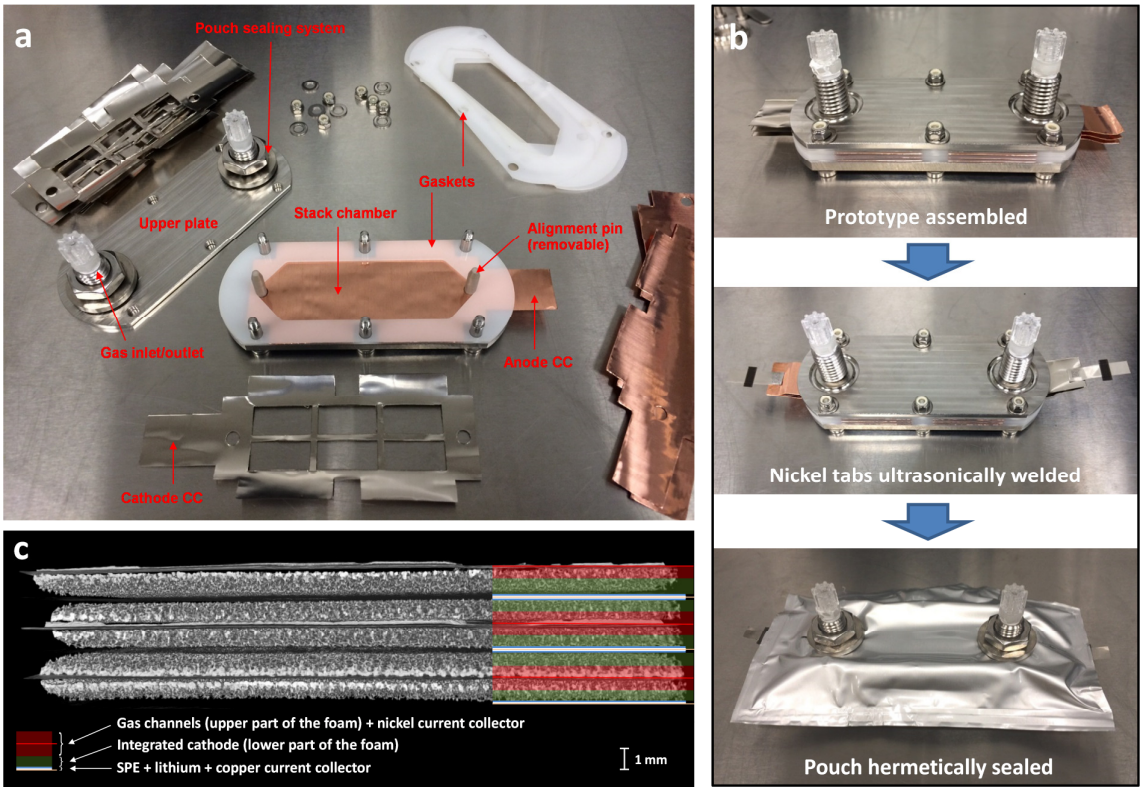

Figure 8 : **a)** Components of the prototype. Plain copper sheets (20 µm thick) are used as anode current collectors, whereas pierced nickel sheets (30 µm thick) are used as cathode current collectors. Gaskets made of polypropylene (1.1 mm thick to accommodate 100 µm lithium, ~100 µm SPE and ~900 µm integrated cathode) are being used as stack chambers. The removal of the alignment pins provides gas inlet/outlet channels to each stack layer ; **b)** final steps of prototype assembly. The stack is being assembled in an anhydrous room (DP : -60°C) and finally sealed under vacuum, in order to remove all air contaminants. **c)** X-ray microtomography image of a section of the prototype.

2.4 Performance testing

The solid-state cells were tested under dry oxygen. Laboratory cells were assembled in ECC-air cells (EL-CELL, Germany). Prototypes were continuously flushed with oxygen during cycling. All testing was done at 70 °C in order to impart a sufficient ionic conductivity to the polymer electrolyte. Figure 9 displays the comparative electrochemical performances of the solid-state Li-air cells. The impedance spectroscopy of the prototypes before cycling was quite similar to the lab-cells, demonstrating the quality of the upscaling and prototype assembly. A Warburg-type diffusion contribution was however observed in the medium frequencies of the prototype's impedance curves, that could be caused by a less efficient oxygen diffusion.

The first discharge of a typical lab-cell and prototype is displayed in Figure 9b. The prototype specific capacity was quite similar to the lab-cell capacity, demonstrating that all active area is functioning in a proper manner. It reached an absolute capacity of 790 mAh, which corresponds to a delivered energy of 2 Wh. When only considering the mass of the stack (anode+cathode+electrolyte+ integrated O_2), this leads to a gravimetric energy density of 204 Wh/kg, similar to current Li-ion batteries. The use of the lighter foams developed within the project (instead of the INCO foams) would have boosted the energy to ~230 Wh/kg, still far from expectations for the Li-air technology.
Moreover, as in fuel cell systems, a metal-air battery needs a gas delivering system, a holding frame and gaskets to accurately channel the gas to the cathode side. These requirements add a very important mass to the system. All additional components (gaskets + plates + screws & washers + pouch) represented a total weight of 500 g. Therefore, considering the total prototype weight, the delivered gravimetric energy density reaches 3.9 Wh/kg. It is important to indicate that the optimization of the prototype's weight and volume was not an objective of the project.
Besides, when considering the volumetric energy density of the stack only (not considering the frame), these 2 Wh of energy converts into an energy density of 180 Wh/L, which is less than half the volumetric energy density of current Li-ion batteries (typically over 400 Wh/L).

These numbers clearly put in evidence the significant challenges related to system engineering which remain to be overcome to bring to success any alkali metal-air technology. Unfortunately, these challenges have barely been investigated so far [14-15].

Figure 9b shows also that the prototype discharge voltage was lower than the lab-cell, indicating a more important discharge overvoltage, which could be related to either the prototype construction (design), inefficiencies in the current extraction from the cell (electrical contacts), or inefficiency in the oxygen provision, as could be suggested by the impedance data. The recharge after a full discharge also showed a higher overpotential than the lab-cell and systematically experienced a sudden drop of the voltage after reaching only a partial recharge. This behaviour was also observed in lab-cells incorporating cathodes obtained with the upscaled scanning spray deposition method, and could be related to non-optimized active layer deposition conditions. It is unlikely to be caused by lithium dendrites since the same behaviour was also observed in liquid electrolytes with separators as thick as 650 µm. A partial delamination of the electrolyte integration layer from the active layer after the dissolution of Li_2O_2 could be an hypothesis, but requires further investigations.

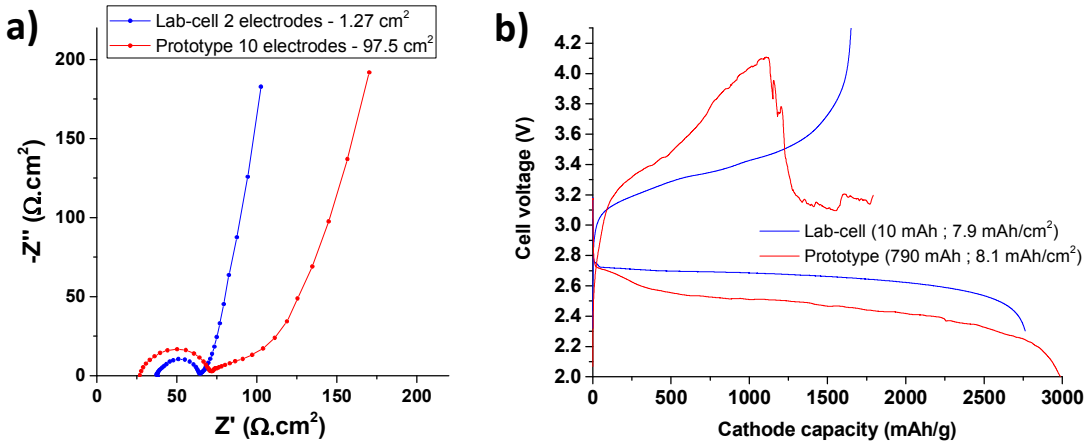

Figure 9 : a) Impedance spectroscopy of a typical lab cell and prototype ; b) First galvanostatic cycle of a lab cell and prototype at 0.1 mA/cm^2.

Post-mortem analysis (SEM and XRD) revealed that an amorphous phase of Li_2O_2 was produced in solid-state cells instead of the toroïds and nanoplatelets usually observed in liquid electrolytes (cf. Figure 10). Such an amorphous phase of Li_2O_2 has already been reported, and is thought to be caused by special conditions of nucleation and growth [16-18]. In the case of solid-state electrolytes, it could be caused by the inability of Li_2O_2 to grow crystals at a solid-solid interface due to steric hindrance.

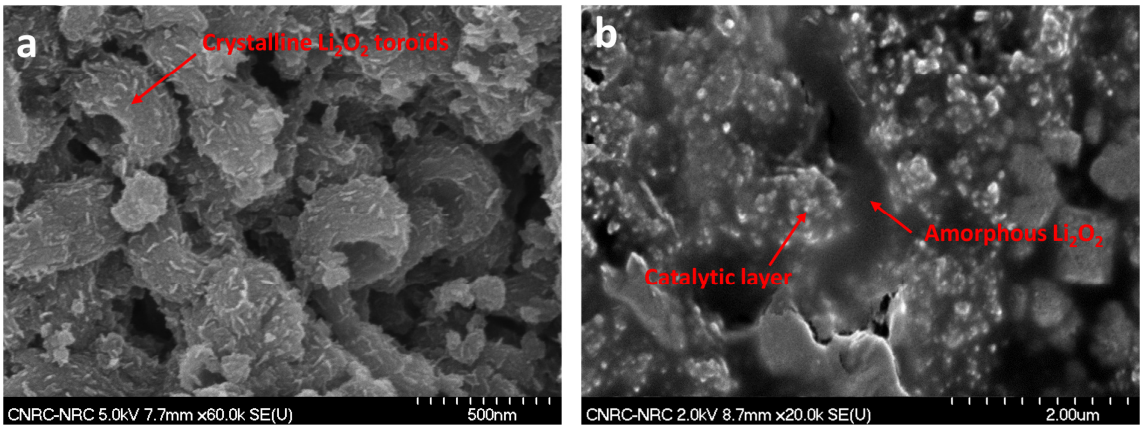

Figure 10 : SEM images of cathodes after a full discharge in liquid (a) and solid-state (b) electrolytes. Liquid electrolyte is 1M $LiCF_3SO_3$ in TEGDME, tested at ambient temperature. Image b) is a cross-sectional view of a cryogenic-ruptured cathode.

Figure 11 displays the results of a typical cyclability experiment of a solid-state lab-cell with a partial depth of discharge (500 mAh/g ; ~20 % DOD). As can be observed, even with a partial DOD, the cell cyclability is poor, delivering only a few cycles at 500 mAh/g. After ~10 cycles, the electrochemistry stabilizes around 420 mAh/g before the sudden death of the cell, usually between 20 to 40 cycles. The total number of cycles varies from cell to cell without any clear correlation, indicating that the cause of failure is common to all cells and not depending to specific components tested in the cell. Renewal of the oxygen (at cycle 32 in this experiment) did not succeed in improving the cell cycling, demonstrating that the cause of cell failure is not related to the total consumption of the oxygen present in the cell.
Post-mortem investigations did not reveal a clear indication of the cause of cell failure. Further studies would be necessary to clearly establish the causes of cell performance decay and failure in this particular case. However, a number of other studies suggest that the product of the reaction (Li_2O_2) actively reacts with the electrolyte and the cathode's active materials (especially carbon) as revealed by *in-situ* mass spectroscopy analysis [5, 19-22]. This fundamental issue definitely needs to be solved before any Li-air technology can be brought to the market.

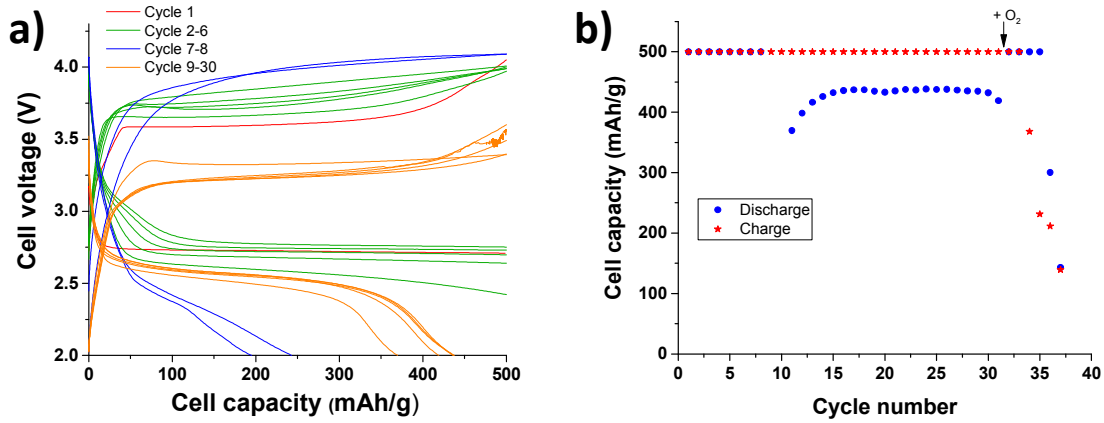

Figure 11 : a) galvanostatic cycling of a solid-state Li-air battery at 0.1 mA/cm^2 with a capacity limitation at 500 mAh/g ; b) Variation of the cell capacity during cycling. At cycle 32, the oxygen in the cell was renewed.

3. CONCLUSIONS AND PERSPECTIVES

The Li-air technology holds great promises for the development of high energy density batteries needed to extend the range of electric vehicles. However, a number of fundamental challenges need to be overcome to enable this technology. This project aimed at investigating these challenges and possibly find solutions to a number of them.

On the anode side, the use of metallic lithium requires the development of a solid-state electrolyte layer that can protect it while preventing the growth of dendrites during the recharge. Such a solid-state electrolyte, formulated with specific additives was successfully developed.

The cathode needs to keep a high porosity, while integrating a significant load of active materials and ensure an efficient triple phase (O_2-ions-electrons). For this purpose, ultra-porous nickel foams were developed, allowing to decrease the foam weight contribution by 30 % compared to commercially available INCO foams. The formulation of the active layer was extensively studied, with the screening of multiple carbon supports, catalysts, binders and deposition methods. It was found that the use of catalysts did not clearly lead to performance improvements relative to carbon-based cathodes. The loading of active materials was optimized to reach the highest energy per surface area. An optimum of 3 mg/cm^2 was established for this cathode technology, higher than the sub-1 mg/cm^2 usually reported in the fundamental studies. However, it still needs to be improved for real applications.

The development of a cathode-electrolyte compatibilization layer was necessary to enable an efficient triple-phase in the porous structure of the cathode. The melt-integration of a PEO-based electrolyte formulation into the porosity of the cathode proved to be the best way to integrate both components.

The overall performances of the solid-state cells did not meet the expectations in terms of energy density and power density, and more fundamentally, in terms of electrochemical stability. A number of studies carried out within the last three years revealed that the major issue of the Li-air technology lies in the reactivity of its lithium peroxide product, which corrodes both the electrolyte layer and the carbon of the cathode's active layer. No definitive answer to that problem has been found so far, but a few recent reports might lead to interesting perspectives, all of them avoiding the formation of lithium peroxide : Liu et al. developed a specific electrochemistry that directly transforms Li_2O_2 into LiOH, which can then be redecomposed using a specific redox mediator [23]. On the other hand, Lu. et al. demonstrated an iridium-based catalyst that specifically leads to the production of lithium superoxide (LiO_2), which is both more conductive and more stable than lithium peroxide [24]. Another interesting avenue is the development of sodium-air batteries, which have also been shown to lead to the superoxide rather than the peroxide [25-27].

Finally, a large-scale multi-electrode prototype was designed and fabricated to investigate the Li-air upscaling challenges. The prototypes reached similar performances as the lab-cells in terms of cell capacity, which demonstrated that gas distribution could be possible in the upper part of the cathode foam, suppressing the necessity to use specific gas distribution plates as typically required in fuel cells technology. However, the significant weight added to the stack by the frame and gaskets – even if non-optimized – pointed out the important challenges still lying at the system level.

The overall results of the project concord well with other recent reports to conclude that this technology, despite its important promises, is still far from commercialization [14, 28-29]. A number of critical issues and challenges need to find solutions before an application can be envisioned.

Acknowledgments

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