

Proc. Eurosensors XXVI, September 9-12, 2012, Kraków, Poland

## Rechargeable Lithium Film Batteries – Encapsulation and Protection

J. F. Ribeiro<sup>a</sup>, Rui Sousa<sup>a</sup>, J. A. Sousa<sup>b</sup>, B. M. Pereira<sup>b</sup>, M. F. Silva<sup>a</sup>,  
L. M. Goncalves<sup>a</sup>, M. M. Silva<sup>c</sup>, J. H. Correia<sup>a</sup> \*

<sup>a</sup>Algoritmi Centre, University of Minho, Guimarães, Portugal

<sup>b</sup>Electronics Department, University of Minho, Braga, Portugal

<sup>c</sup>Chemistry Centre, University of Minho, Braga, Portugal

---

### Abstract

Rechargeable solid-state lithium batteries were developed before [1] by physical vapour deposition (PVD). These batteries are fabricated with lithium-cobalt oxide (LiCoO<sub>2</sub>), lithium-phosphorus oxynitride (LiPON) and lithium (Li), respectively for cathode, electrolyte and anode. The LiCoO<sub>2</sub> and LiPON were deposited by RF sputtering and the metallic Li by thermal evaporation. The chosen material for current collectors was titanium (deposited by e-beam technique) to prevent chemical reactions in contact with lithium and provide good electrical conductivity.

In this work, the protection of lithium films from oxidation and delithiation is presented. Ti, LiPON, LiPO and layered films combining these materials were compared as protection for lithium. Titanium and LiPO films show good results and potential to be used as short-term protective materials in lithium batteries.

© 2012 Elsevier Ltd....Selection and/or peer-review under responsibility of the Symposium Cracoviense Sp. z.o.o.

Lithium batteries; Thin-films; Protection

---

### 1. Introduction

It's undeniable the fact that batteries are systems with the highest number of applications known up to know. Despite the developments made by the microelectronic industry, the battery technology didn't accompany these breakthroughs [2]. The increasing demand for even small stand-alone microsystems with integrated energy source (*e. g.* solar cells), led to the exponential interest in solid-state rechargeable

---

\* Corresponding author. Tel.: +351253510190; fax: +351253510189.

E-mail address: [jribeiro@dei.uminho.pt](mailto:jribeiro@dei.uminho.pt).

lithium batteries [3, 4, 5]. This battery technology [1] provides more energy density than conventional batteries (see Figure 1 (a)) and some safety issues like leaking or explosion are prevented since all materials are solid [6]. An artwork of battery is shown in Figure 1 (b).

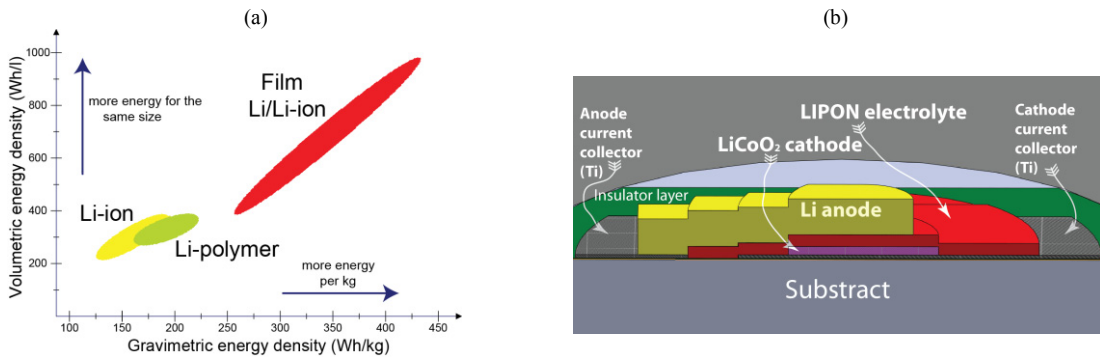


Fig. 1. (a) battery capacity compared for different technologies; (b) design of film battery with materials indication (not on scale for better visualization)

However, lithium is a very reactive element, and encapsulation of these batteries in microelectronic circuits is a major problem. The choice of the protection material depends on some constraints: The deposition process should not react with lithium; should offer protection to atmosphere and avoid delithiation. Some techniques were proved to provide effective protection, being parylene the most common material [7]. However, this process is not compatible with microfabrication techniques, and a separated fabrication process must be used. Moreover, sample must be always contained in inert atmosphere prior protection. The methods described in this work allow the manipulation of lithium films for a few hours at air, thus allowing sample transfer for a long-term encapsulation.

## 2. Results and Discussion

Protective films tests were conducted with Al/Ti contacts (300 nm Al / 300 nm Ti, by e-beam), deposited prior the evaporated lithium film (3 μm thickness) on glass substrate. Several of these samples were prepared for evaluation of different protection materials (Figure 2 (a)).

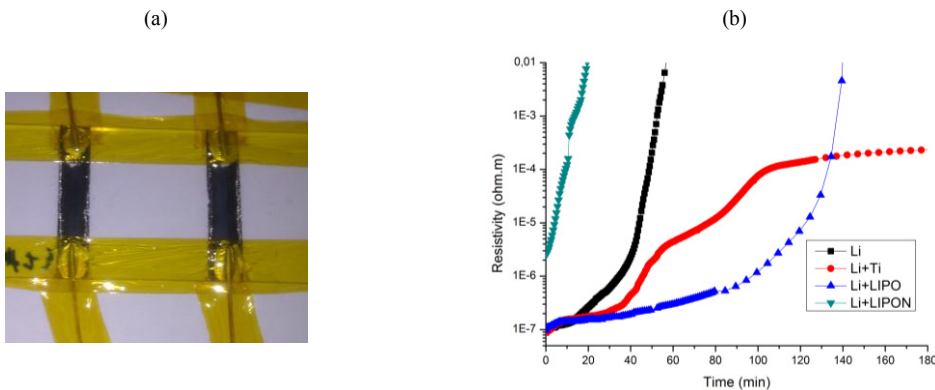


Fig. 2. (a) sample preparation for thermal evaporation of lithium and resistivity measurements; (b) shows resistivity of lithium measured after atmosphere contact and comparing different protective single layers

The film oxidation (without protection) was evaluated considering the resistivity change of lithium film when in contact with air. Other samples were covered with protection materials, and resistivity change when in contact with air was also evaluated. The protective layers tested were: 300 nm Ti; 300 nm LiPO; 300 nm LiPON; 3 successive layers of 100 nm Ti; 6 alternate layers of 50 nm LiPO and 50 nm Ti, all deposited on top of lithium without vacuum break. Figure 2 (b) shows the first four tests with and without deposition of a single thin-film on the lithium and the results show that LiPON react with lithium during deposition, so it can't be used for protection. The Ti and LiPO films show good results for protective materials and LiPO is the best for the first two hours and titanium for long-term protection. A multilayer protection was also investigated and in Figure 3 (a) and (b) is visible that the results are very similar to a single layer of Ti.

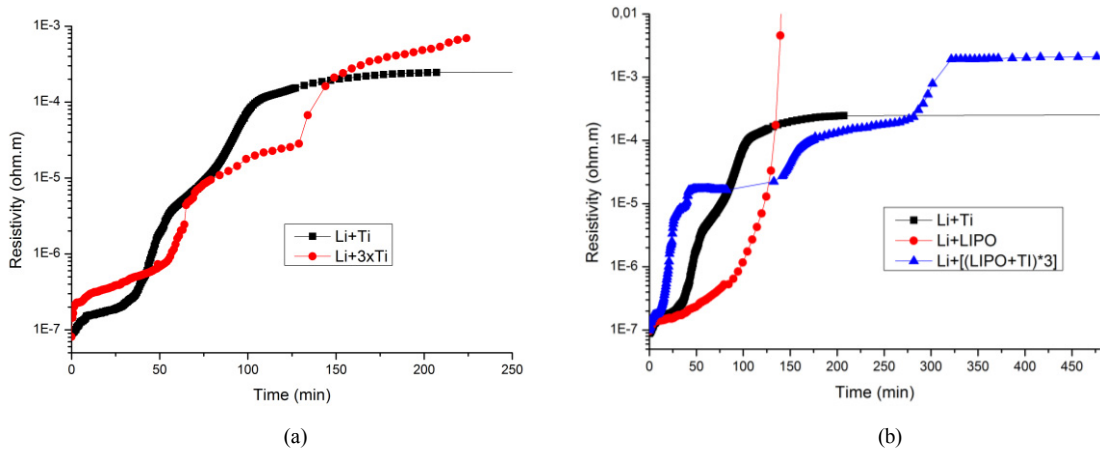


Fig. 3. (a) resistivity of lithium after atmosphere contact and comparing a thick protective layer of titanium with a three thin layers of titanium deposited consecutively and prefacing the same thickness of first; (b) resistivity of lithium after atmosphere contact comparing different protective layers

### 3. Conclusions

The oxidation of lithium is a major problem in lithium batteries. Rechargeable solid-state lithium batteries were developed before [1] by PVD. The  $\text{LiCoO}_2$  cathode and the LiPON electrolyte were deposited by RF sputtering and the metallic lithium anode by thermal evaporation. This paper presented short-term protective materials for lithium, allowing the contact with air for one hour without a major resistivity change. Ti, LiPO, LiPON and multilayers of these materials were investigated. LiPO and Ti single films have the best results, LiPO for first two hours and Ti for longer periods.

### Acknowledgements

This work was financial supported by FEDER/COMPETE and FCT funds with the project PTDC/EAAELC/114713/2009 and with first author scholarship SFRH/BD/78217/2011.

## References

- [1] L. M. Goncalves, et al.. Integrated solid-state film lithium battery. *Procedia Engineering* 2010;**5**:778-81.
- [2] M. Armand, J. M. Tarascon. Building better batteries. *Nature* 2008;**451**:652-7.
- [3] J. P. Carmo, L. M. Gonçalves, J. H. Correia. Thermoelectric microconverter for energy harvesting systems. *IEEE Trans. Ind. Electron.* 2010;**57**:861-7.
- [4] B. Fleutot, et al.. Characterization of all-solid-state Li/LiPONB/TiOS microbatteries produced at the pilot scale. *J. Power Sources* 2011;**196**:10289-96.
- [5] Thierry Djenizian, Ilie Hanzu, Philippe Knauth. Nanostructured negative electrodes based on titania for Li-ion microbatteries. *J. Mater. Chem.* 2011;**21**:9925-37.
- [6] Perrine Ribière, et al.. Investigation on the fire-induced hazards of Li-ion battery cells by fire calorimetry. *Energy Environ. Sci.* 2012;**5**:5271-80.
- [7] N. J. Dudney. Solid-state thin-film rechargeable batteries. *Materials Science and Eng.: B* 2005;**116**:245-9.