ECS Transactions, 45 (29) 139-142 (2013)
10.1149/04529.0139ecst ©The Electrochemical Society

Thin-film Materials for Solid-State Rechargeable Lithium Batteries

J. F. Ribeiro[a], R. Sousa[a], M. F. Silva[a], L. M. Goncalves[a],
M. M. Silva[b], and J. H. Correia[a]

[a]Algoritmi Centre, University of Minho, 4800-058 Guimarães, Portugal
[b]Chemistry Centre, University of Minho, 4700-057 Braga, Portugal

Thin-film materials for solid-state rechargeable lithium batteries were fabricated by physical vapor deposition. The cathode is a lithium cobalt oxide ($LiCoO_2$) film, separated from the anode (metallic lithium) by an electrolyte of lithium phosphorus oxynitride (LiPON). The $LiCoO_2$ was deposited by RF sputtering, annealed after deposition and x-ray diffraction patterns showed higher crystallinity with 2 hours of annealing in vacuum with a temperature of 650 ºC. LiPON was deposited by reactive RF sputtering (nitrogen) and metallic lithium by thermal evaporation. Ionic conductivity of LiPON films was measured at room temperature of 26 ºC and 6.3×10^{-7} $S.cm^{-1}$ obtained. Electrical resistivity of a 3 µm thickness lithium film was 7.6×10^{-8} Ω.m, measured during deposition.

Introduction

Energy storage is a huge challenge of 21st century [1, 2], mostly achieved with batteries. Despite the development of the microelectronic industry, the battery technology didn't follow these breakthroughs [3]. Batteries are ideal power sources of electronic devices because they provide stable voltage and allow the leveling of energy consumption [4, 5]. This is of special concern when the target applications are in the biomedical field or for long cycle operations without requiring human activity [6, 7].

Solid-state film lithium batteries present the highest volumetric energy density (800 $Wh.L^{-1}$) and gravimetric energy density (350 $Wh.g^{-1}$), very high cycle-life and charge-discharge rates up to 5C (only exceeded by super-capacitors) [7, 8, 9]. The integration of batteries with solid-state circuits requires the use of a solid-state anode, cathode and electrolyte. These batteries are intrinsically safe since all materials are solid and no leaking or explosion could occur. Film battery chemistry is being developed at ORNL (Oak Ridge National Laboratories) [6] with a LiPON solid electrolyte between the anode and cathode. These batteries have a potential of 4.5 V, typical capacities below 100 $\mu A.cm^{-2}$ and charge rate from 2C to 5C. However, due to the thin-films deposition process, the thickness is limited to few micrometers, resulting in a small capacity. The increase demand for even smaller power sources has driven the market of thin-film batteries and is predictable that reach $5.6 billion in 2015 [10]. This work presents the fabrication parameters and the characterization of a lithium cobalt oxide ($LiCoO_2$) cathode, a lithium phosphate nitride (LiPON) electrolyte and a metallic lithium (Li) anode.

Experimental and Results

Cathode

The $LiCoO_2$ is mostly used as cathode material in lithium batteries due to its excellent electrochemical stability, high lithium-ion diffusion and ability to provide a high voltage in the battery. The full crystalline structure of $LiCoO_2$ facilitates the diffusivity of lithium ions and decreases the electrical resistivity. The $LiCoO_2$ thin-film was deposited by RF sputtering and presented the best characteristics when deposited with a power source of 150 W, a pressure of 2×10^{-3} mbar, 40 sccm of argon and an annealing at 650 °C during 2 h in vacuum. The lowest electrical resistivity (3.7 Ω.mm) was achieved at this temperature and the crystallization proven by x-ray diffraction (XRD). Figure 1 shows de XRD pattern of films deposited as described, annealed at temperatures from 500 ºC to 800 ºC. Increasing the annealing temperature, the main peaks of $LiCoO_2$ XRD pattern are identified, however the film resistivity greatly increases for annealing temperatures above 650 °C. Annealing temperature of 650 ºC showed the best compromise between a high crystallization and low resistivity of the $LiCoO_2$ film.

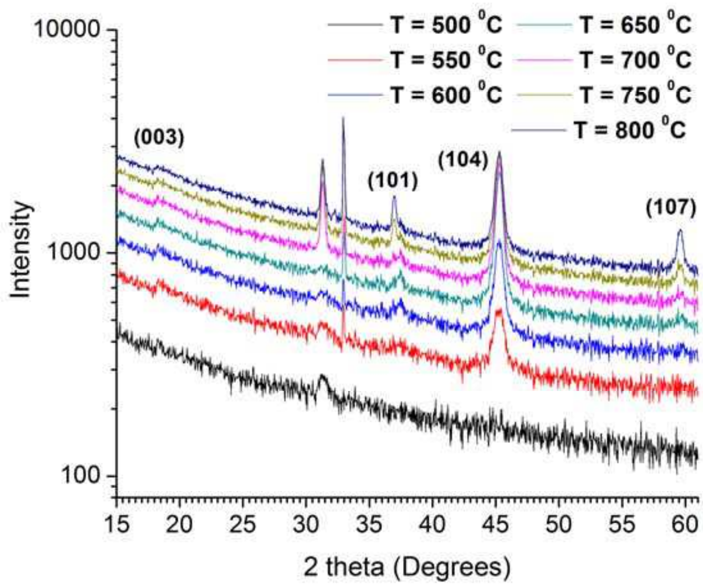

Figure 1. XRD diffraction analysis of $LiCoO_2$ thin-films at several annealing temperatures.

Electrolyte

LiPON is a glassy electrolyte with high ionic conductivity and high electrical resistivity. Electrical resistivity of LiPON films was reported before as greater than 10^{14} Ω.cm [8]. Thin-films of LiPON were deposited by RF sputtering with a RF power source of 150 W, 20 sccm of nitrogen and a pressure of 3×10^{-4} mbar. An ionic conductivity of 6×10^{-7} $S.cm^{-1}$ was measured at 26 ºC. Figure 2 shows de dependence of ionic conductivity with the temperature during measurement.

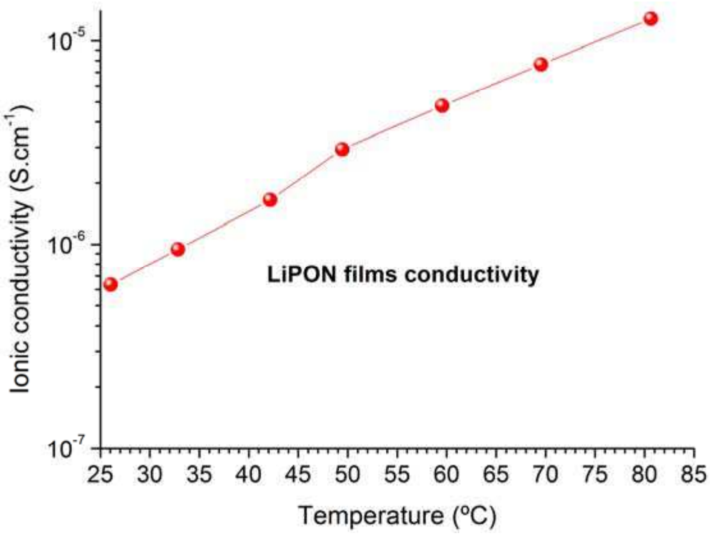

Figure 2. Ionic conductivity of LiPON thin-films at several measurement temperatures.

Anode

Metallic lithium is the most common material used as anode in lithium batteries, due to the high gravimetric and volumetric capacity, despite the rapid oxidation that occurs when lithium is exposed to contact with air. Lithium was deposited by thermal evaporation, using tantalum boxes in a vacuum chamber at base pressure of 6×10^{-6} mbar, with a deposition rate of 50 $Å.s^{-1}$. The resistivity of $7,6\times10^{-8}$ Ω.m was measured during the deposition of a lithium film with 3 µm thickness (Figure 3).

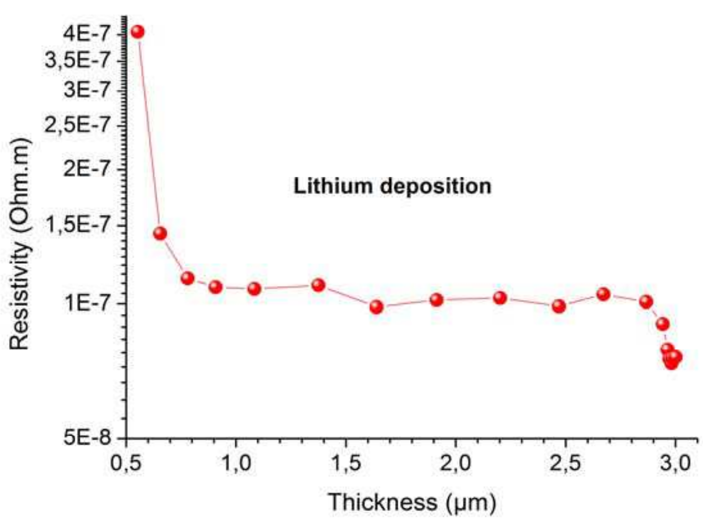

Figure 3. Lithium resistivity during deposition.

The whole battery design, including the substrate ($Si+SiO_2$) and current-collector thin-films (Ti) are presented in Figure 4. This structure is under development.

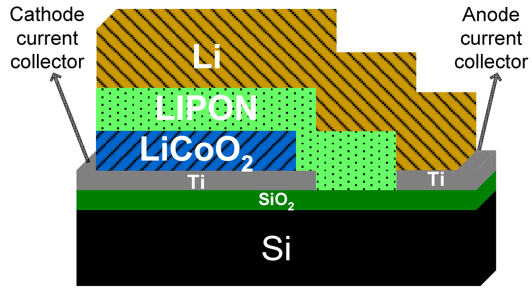

Figure 4. Battery design (not on scale for better visualization).

Conclusions

This paper presented fabrication and characterization of active materials for rechargeable lithium batteries. $LiCoO_2$ (cathode) and LiPON (electrolyte) were deposited by RF sputtering and metallic lithium (anode) by thermal evaporation. XRD and electrical resistivity measurements showed that $LiCoO_2$ thin-films annealed at 650 ºC during 2 hours in vacuum are good candidates for cathode films. The LiPON electrolyte was deposited also by RF-sputtering (in N_2 atmosphere) and ionic conductivity of 6.3×10^{-7} $S.cm^{-1}$ was measured with a room temperature of 26 ºC. Electrical resistivity of $7{,}6\times10^{-8}$ Ω.m was measured in 3 μm thickness lithium film.

Acknowledgments

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

References

1. S. Suzuki, N. Sakai and M. Miyayama, *Key Engineering Materials*, **388**, 37 (2009).
2. P. G. Bruce, B. Scrosati and J.M. Tarascon, *Angewandte Chemie*, **47**, 2930 (2008).
3. M. Armand and J.M. Tarascon, *Nature*, **451**, 652 (2008).
4. J. P. Carmo, *et al.*, *J. Micromech. Microeng.*, **20**, 1 (2010).
5. B. Fleutot, *et al.*, *J. Power Sources*, **196**, 10289 (2011).
6. N. J. Dudney and B.J. Neudecker, *Solid State & Materials Science*, **4**, 479 (1999).
7. B. Kang and G. Ceder, *Nature*, **458**, 190 (2009).
8. N.J. Dudney, *Materials Science and Engineering - B*, **116**, 245 (2005).
9. A. Patil, *et al.*, *Materials Research Bulletin*, **43**, 1913 (2008).
10. T. Djenizian, Ilie Hanzu and P. Knauth, *J. Mater. Chem.*, **21**, 9925 (2011).