

# FLEXIBLE SOLID-STATE LI – ION BATTERY USING GE THIN FILM ANODE AND LiCoO<sub>2</sub> CATHODE

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**Abstract** — Flexible and solid – state Li-ion batteries (LIBs) can offer flexibility, lightweight and easy portability in large-scale energy storage, with significantly higher power and long cycle life. The anode is a crucial component affecting the performance of LIBs. Here, we investigate the electrochemical performance of e-beam deposited Ge anode (300 nm thick) coupled with LiCoO<sub>2</sub>/LiPON (cathode/solid-state electrolyte) in a microbattery system fabricated only by PVD techniques. LiCoO<sub>2</sub> cathode was deposited by rf-sputtering with 120 W of power source and 17/3 sccm of Ar/O<sub>2</sub>, respectively. The LiPON was also deposited by rf-sputtering at 100 W of RF power. Microstructure and battery performance were investigated by scanning electron microscopy (SEM) and electrochemical measurements (open circuit potential (OCP), charge/discharge cycles and electrochemical impedance spectroscopy (EIS)).

**Keywords:** Design, flexible Li-ion batteries, germanium, LiPON electrolyte

## I – Introduction

Li-ion batteries (LIBs) are the state-of-the-art technology among electrochemical energy storage and conversion cells, and are still considered the most attractive class of battery in the future due to their high specific energy density, high efficiency, long cycle life and environmental friendliness [1], [2]. Due to the fast development of small, portable and flexible electronics, flexible LIBs with thickness below 10  $\mu\text{m}$  attracts great attention as a future power source for flexible and wearable electronic devices (e.g. roll-up displays, touch screens, wearable sensors and medical devices) [2]. Flexible LIBs have a better form factor than conventional rechargeable LIBs since they can be flexed or bent into the microsystems.

The key challenge to fabricate flexible LIBs is to design reliable materials with high capacity, cycling stability, and good adhesion properties coupled with high performance and stability electrolytes, when they are deformed to fit the powered devices [3]. In this context, the ceramic solid electrolyte of lithium phosphorus oxynitride (LiPON) can offer more security than liquid electrolytes because no leaking or explosion can

occur and offer stability and high ionic conductivity [4]. Moreover, an all solid-state thin-film battery offers several advantages, such as the packaging can be much more light and small and good endurance to adverse environmental conditions [5].

High-energy LIBs depend on the high capacities of the electrode materials. Lithium cobalt oxide (LiCoO<sub>2</sub>) is commonly used as cathode material in LIBs. In particular, the high-temperature form of LiCoO<sub>2</sub> (HT-LiCoO<sub>2</sub>) exhibits excellent electrochemical behavior with theoretical capacity of 140 mAh/g at potential of 4V vs Li/Li<sup>+</sup>, when compared with the low-temperature phase of LiCoO<sub>2</sub> (~80 mAh/g) [6]. From the point of view of capacity, germanium (Ge) and silicon (Si) are promising anode materials for high-generation LIBs. Ge has high volumetric capacity (see figure 1) and compared with Si-based materials, Ge exhibits higher diffusivity of lithium (400 times higher than Si at room-temperature[7], better Li insertion/extraction kinetics and lower volume change during lithiation/delithiation process, which can support much higher charge/discharge rates leading to a better cycling performance at comparable capacity [8].

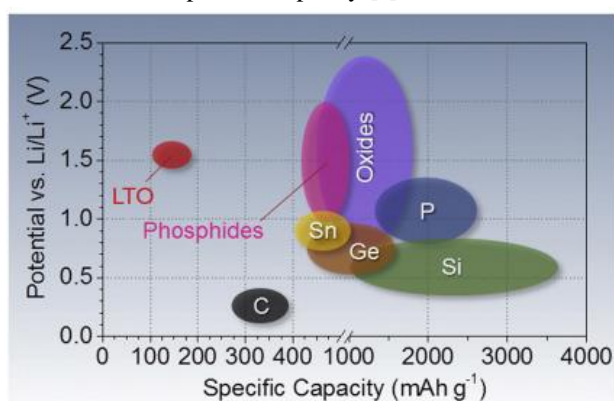


Figure 1: Potential vs Li/Li<sup>+</sup> and capacity of promising materials for next generation LIB anodes [9].

In this work, a different design of a flexible Li ion battery microsystem based on Ge thin film anode and LiCoO<sub>2</sub>/LiPON was developed by only PVD techniques. Current electrolytes in Li ion batteries are typically ionic liquid/solution. LiPON as Li-ion battery electrolyte has advantage of be implemented in various microsystems without risk for human health.

## II - Experimental Details

The flexible solid-state Li-ion battery was fabricated only by PVD techniques and using shadow masks to have the format shown in figure 2. The cross-sectional drawing of the battery with all steps of fabrication is presented in figure 2. For better visualization, height is in a different scale from other dimensions.

The battery was fabricated onto 35 x 25 mm polyimide substrates (Kapton® 500 HN with 127µm thick) that provides flexibility, good thin-film adhesion and supports all deposited layers. RF-sputtered silicon nitride ( $\text{Si}_3\text{N}_4$ ) layer (100 nm thick) was first deposited onto the Kapton substrate as Li barrier layer, avoiding the diffusion of lithium ions to the substrate. A first Ti layer was deposited before the platinum cathode current collector to promote adhesion. Ti (30 nm deposited by e-beam) was used for platinum adhesion and Pt (150 nm deposited by DC-sputtering) is the current collector for  $\text{LiCoO}_2$ , without reacting with it.  $\text{LiCoO}_2$  cathode (500 nm thick) was fabricated on top of Pt layer, by RF magnetron sputtering technique, with power source of 120 W, pressure of  $6 \times 10^{-3}$  mbar and atmosphere of 17/3 sccm of Ar/ $\text{O}_2$  flow, respectively. After  $\text{LiCoO}_2$  deposition, the  $\text{LiCoO}_2$  film was annealed at 400 °C in an oven for 1 hour, at atmospheric conditions (air). A ramp of 3 °C/min was maintained during the oven heating and cooling. Ti anode current collector (300 nm thick) was deposited before the LIPON electrolyte to prevent undesirable chemical reactions between LIPON and Ti during the deposition of e-beam Ti Layer. LIPON electrolyte was deposited over the cathode material and also by RF magnetron with conditions explained before in J.F. Ribeiro, et al.[10], Two thin layers of  $\text{Si}_3\text{N}_4$  (20 nm) and LIPO (50 nm) were after deposited by RF-sputtering in order to prevent accidental internal short circuits in the limits of battery electrodes and contacts. Moreover, since  $\text{Si}_3\text{N}_4$  is a lithium barrier, will prevent lithium ions to flow between cathode and anode in the limits of the battery, thus only the top section of the battery becomes the active area, where film thickness is controlled. LIPO and  $\text{Si}_3\text{N}_4$  materials offer the advantage of compatibility with underlying layers. The e-beam deposited Ge (300 nm thick) was connected by the current collector Ti layer. Layer's thickness, deposition temperature and PVD technique used are summarized in table I. The battery total thickness is about 2,15 µm plus the Kapton® thickness (127 µm).

Microstructure of the as-deposited battery cross-section was examined using a NanoSEM – FEI Nova 200 (FEG/SEM) by making use of Si substrate, instead of Kapton, to facilitate the cross-section SEM image of figure 3. Electrochemical tests (open circuit potential (OCP), charge/discharge cycles and electrochemical impedance spectroscopy (EIS)) were performed in the flexible battery, after Ge deposition, and without breaking the vacuum. All measurements were done with Gamry Reference 600TM potentiostat/galvanostat where the working electrode was connected to Pt

cathode current collector and the reference and counter electrode connected to anode current collector (titanium).

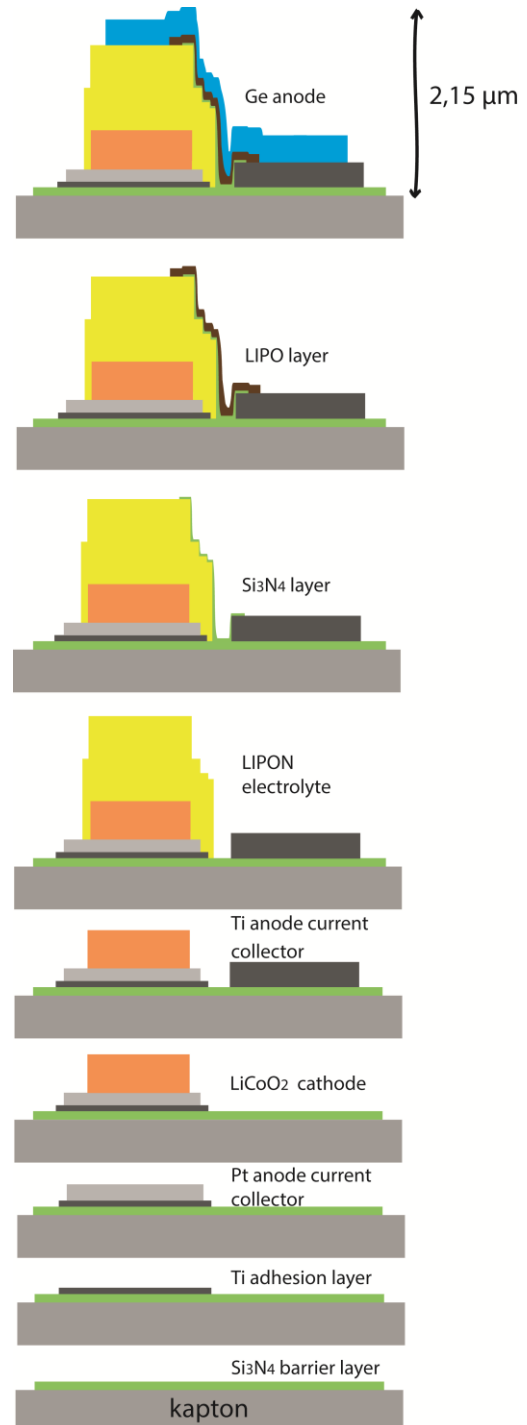


Figure 2: Schematic representation of the fabrication steps for thin-film Ge- $\text{LiCoO}_2$  battery on Kapton substrate (not on scale for better visualization). Total thickness of the battery (excluding the thickness of the substrate) is also shown.

## III - Results and Discussion

In figure 3, the result of a SEM investigation of the whole Li – ion microbattery structure, before cycling tests, is reported. As shown in this cross-section image, a well-organized columnar structure with smooth

interfaces at  $\text{LiCoO}_2/\text{Pt}$ ,  $\text{LiPON}/\text{LiCoO}_2$  and  $\text{LiPON}/\text{Ge}$  are observed. Furthermore, a good adhesion between all layers is also shown. The  $\text{Si}_3\text{N}_4$  and  $\text{LiPO}$  thin layers are not shown in this region. Measured thickness of each layer is also presented in figure 3. The thickness measured by SEM is equivalent (error > 5%) to the thickness measured by the microbalance during deposition. However, the thickness of  $\text{LiPON}$  film appears significantly thinner than expected ( $\sim 1\mu\text{m}$ ) which could be justified with acoustic properties settled in microbalance system.

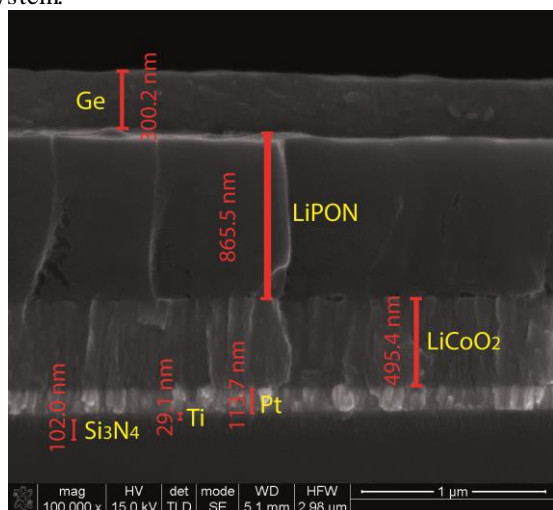


Figure 3: Cross-sectional SEM image of the as-deposited thin-film  $\text{Ge-LiCoO}_2$  battery on silicon substrate.

An open circuit potential (OCP) was the first electrochemical measurement performed in the thin-film battery. Before the charging test, a negative voltage of 267 mV is observed (not shown here). The OCP measurement was realized (during 2 minutes) in the end each charge or discharge cycle, as presented in figure 4. After the first charge at 4,1 V, a voltage of 1,836 V is observed. Furthermore, after the 8th charge, the OCP increase to 2,113 V. A self-discharge of the battery is also observed, since voltage decreases about 174 mV in 2 minutes. In a 30 minutes OCP measurement (not shown), a decrease from 2.11 V to 1.56 V was also observed, despite the high impedance input of the acquisition system (above 10 GOhm). This self-discharge was not expected due to well know negligible self-discharge of thin-film batteries [11]. This self-discharge could be related to a possible thinner electrolyte ( $\text{LiPON}$ ) in some area between the cathode and the anode (probably in the lateral limits). Furthermore, after discharge processes residual voltages between 0,9 V and 1,20 V are observed. The voltage profiles of the battery during discharge cycles in the region of 0 - 2V at current of 100 and 200 nA are shown in figure 5. In the first discharge cycle, the initial capacity of 46 nAh/cm<sup>2</sup> was calculated, with a discharge current of 100nA. However, this capacity reduces in the next cycles, as can be calculated from data in figure 4. Despite the bad capacity retention observed, a flexible and solid-state  $\text{Ge-LiCoO}_2$  battery was developed only by PVD techniques.

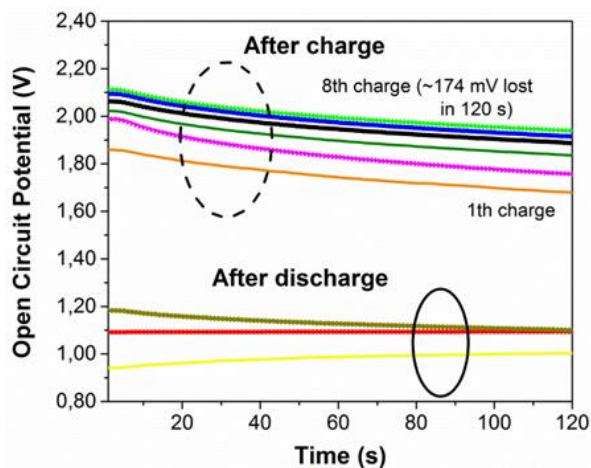


Figure 4: Variation in OCP of flexible thin-film  $\text{Ge-LiCoO}_2$  battery during rest after several charge/discharge rates.

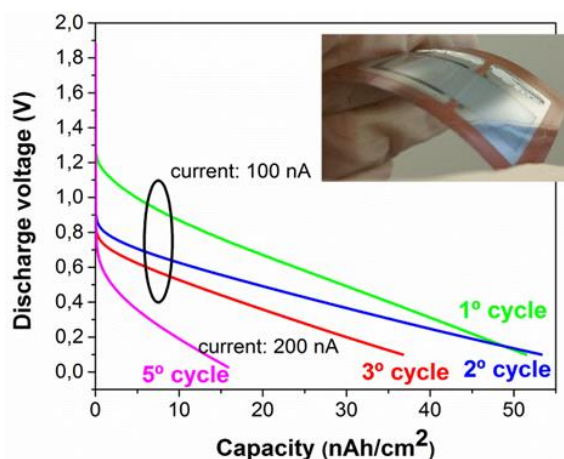


Figure 5: Discharge data for the flexible thin-film  $\text{Ge-LiCoO}_2$  battery are shown.

Electrochemical impedance spectroscopy (EIS) measurements were performed on the fully charged  $\text{Ge-LiCoO}_2$  battery. The applied AC signal for the impedance measurement was 10 mV, with frequency between 1MHz and 1 mHz. There was a 1.5 h rest between the charge and EIS test. Figure 6 shows the obtained Nyquist plot of the  $\text{Ge-LiCoO}_2$  battery after 3th cycles, which show two over-lapped semicircles through high to middle frequency and a straight line at low frequency. The solid line in the figure is the result of the fitting procedure using the equivalent circuit presented in figure 6 modelled with the *Gamry Echem Analyst*. The intersection of the diagram with real axis refers to a bulk resistance ( $R_1$ ) that reflects sum of ohmic resistances (resistance of electrolyte, current collectors and cell connectors). The semicircle at high frequency is related to resistance ( $R_2 = 1.450 \times 10^6 \Omega$ ) with and double layer capacitance ( $C$ ) of the solid electrolyte interface. The semicircle at middle frequency reflects the charge – transfer resistance ( $R_3 = 6.822 \times 10^6 \Omega$ ) and Warburg impedance ( $W = 5.700 \times 10^{-6} \text{ S.s}^{0.5}$ ) reflecting the Li ions diffusion process.

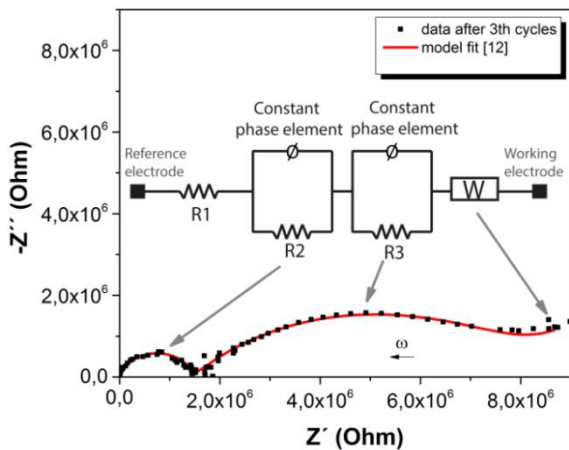


Figure 6: Nyquist plot showing the experimental data and equivalent circuit used to fit.

#### IV - Conclusion

A new design of flexible solid-state thin-film Ge-LiCoO<sub>2</sub> battery was successfully fabricated only with PVD techniques. A plastic Kapton with 127 μm thickness was used as substrate in order to provide flexibility to the battery. E-beam Ge thin-film (300 nm thick) was deposited as anode of the battery. LiCoO<sub>2</sub> cathode (500 nm thick) was deposited by RF-sputtering with 17/3 sccm of Ar/O<sub>2</sub> flow. Solid LiPON electrolyte was deposited under conditions published before by our group [10]. A well-organized battery structure with smooth interfaces and good adhesion was observed by SEM analysis. AC impedance data was modelled by the proposed equivalent circuit by which it was possible the extraction of several parameters. A large self-discharge was observed and related to a possible thinner electrolyte between the active electrodes. Despite the observed low potential, small initial capacity (46 nAh/cm<sup>2</sup>) and retention fading along charge/discharge cycles, a flexible solid-state battery was developed using techniques compatible with those used in MEMS industry.

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