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$Li_7La_3Zr_2O_{12}/LiCoO_2$ - cathode for all-solid-state batteries

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A battery is a device that converts the chemical energy contained in its active materials directly into electric energy through an electrochemical oxidation-reduction reaction. The battery is composed by an anode (the negative electrode) where, upon discharging, the oxidation reaction takes place, a cathode (the positive electrode) where the reduction reaction takes place, and an electrolyte (usually an organic, flammable liquid) that allows the migration of the ions between the electrodes. Currently, some research on this topic tends towards the manufacturing of flexible Li-ion micro-batteries for uses in microsystems. To do so, it is necessary to replace the widely used liquid electrolyte by a solid-type one because the flexible/micro configuration is not compatible with liquid electrolytes: (i) it is difficult to process microsystems with liquid electrolytes and (ii) the flexibility of the battery may lead to leakages. In addition, this replacement could also open the way to new battery types in order to solve the safety issues related to the use of flammable organic electrolytes in larger batteries.[1]

Recently, a low-cost and energy-efficient spray-coating process of lithium cobalt oxide (LCO), *i.e.* a cathode material, has been developed in our lab to obtain flexible microelectrodes. As the final objective is to use a solid state electrolyte such as Gel Polymer Electrolyte (GPE) or Lithium Phosphorous Oxynitride (LiPON), the coating process still needed to be adapted to the production of solid state batteries. In fact, due to the presence of 50-60% porosity inside the cathode layer, the migration of the lithium ions is hindered, which leads to the decrease of the ionic conductivity. The main challenge was to use a nanostructured electrolyte such as $Li_7La_3Zr_2O_{12}$ (LLZO) to fill the LCO coating porosity (between 50 - 60 %) in order to improve the ionic conductivity of the layer without changing the electrochemical properties of the LCO, to finally be able to build an all solid-state battery (Figure 1).

Three different crystalline structures of LLZO can be synthesized. The first one, the high-temperature cubic phase (HT-LLZO), is obtained at temperature over 1000°C and is not stable at room temperature; the second one is the tetragonal phase (t-LLZO), which is obtained above 700°C; recently, Murugan *et al.*[2] have shown that a second cubic phase could be obtained at temperature below 700°C. Among these three polymorphs, the low temperature cubic phase (c-LLZO) has been chosen because it is possible to synthesize it using a low-temperature sol-gel process and because the obtained material is stable at room temperature[3,4]. Moreover, c-LLZO is a very promising material for solid state electrolyte applications due to its chemical stability in contact with Li metal and its relatively high ionic conductivity ($\sim 10^{-6}$ S/cm)[5].

Nanostructured LLZO samples obtained by the above-mentioned sol-gel synthesis were characterised by Transmission Electron Microscopy (TEM, Figure 2), mixed (30% w/w) with LCO in ethanol, and then coated by spray-coating on stainless steel disks (used as current collector) in order to prepare µm-thick films as battery cathodes without the use of any binder or conductive additive. X-Ray Diffraction was used to analyse the obtained film and shows that the crystalline structure of the two materials (c-LLZO, LCO) was not modified (Figure 3). The LLZO/LCO cathode film was then inserted into a coin-cell with a liquid electrolyte. Preliminary electrochemical characterisation was performed, consisting in checking the capacity during battery discharge. Figure 4 shows the potential (V) versus the capacity (mAh/g): the two curves (LCO and LLZO/LCO) reach close values of capacity around ~137 mAh/g, which means that mixing the solid electrolyte with LCO did not modify the electrochemical properties of the latter. Finally, pore texture measurements using Archimedes' principle[6] showed that the void fraction of the LCO film was decreased from 50% to 37% without changing the crystalline structure of c-LLZO or LCO or the capacity of the battery.

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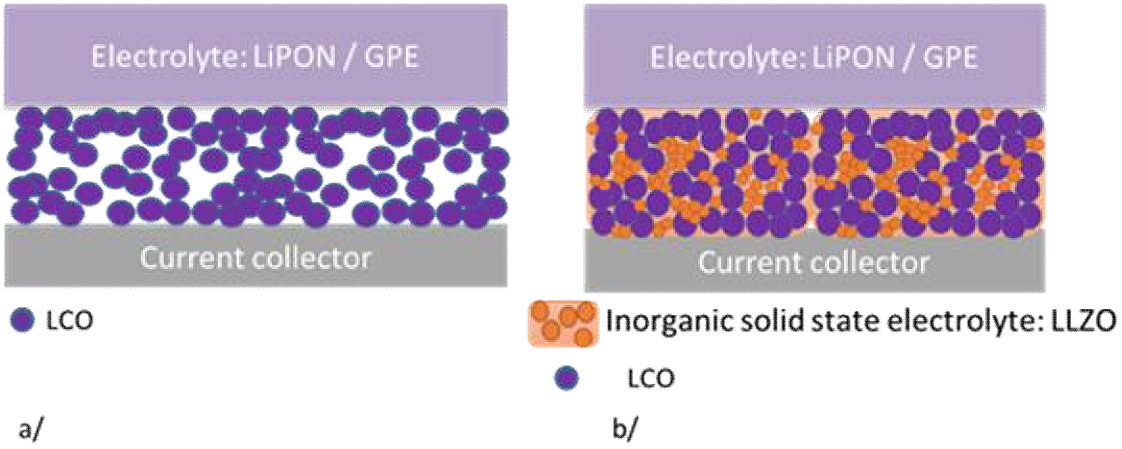

Figure 1. Cathode layer a/ without and b/ with c-LLZO.

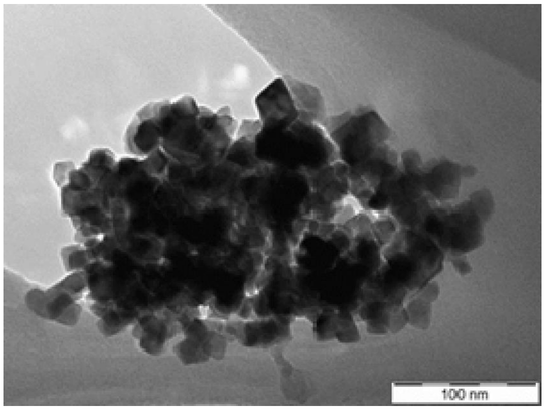

Figure 2. TEM image of cubic LLZO.

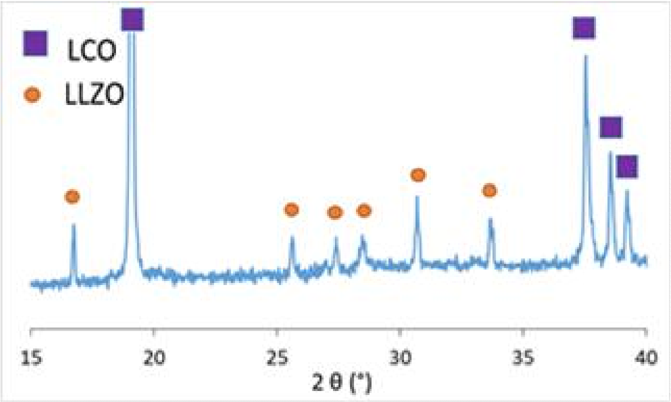

Figure 3. XRD Diffractogram of an LLZO/LCO coating.

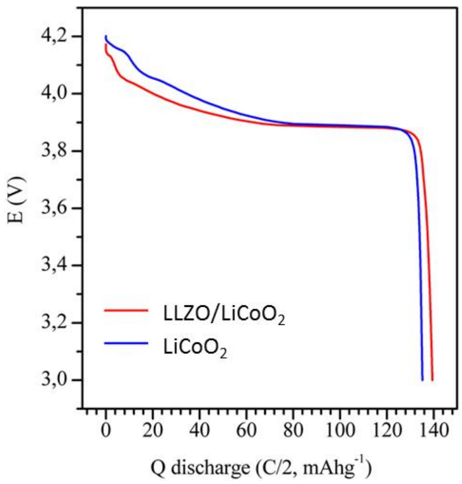

Figure 4. Discharging curve of LCO coating and mixed LLZO/LCO coating.