ORIGINAL PAPER

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Preparation by e-gun evaporation and study of cathode-electrolyte thin-film bi-layers for solid state microbatteries

Abstract In this paper, thin film bi-layers of $LiCoO_2$ cathode material and $xLi_2O\text{-}B_2O_3$ electrolyte glasses were prepared by e-gun evaporation. The ionic conductivity of the electrolyte films was measured by employing impedance spectroscopy technique and the results, for different chemical compositions of the electrolyte, are compared. Auger electron spectroscopy was employed to examine the successive thin-film layers of the bi-layer devices.

Keywords AC impedance spectroscopy · Cathode-electrolyte interface · Auger spectroscopy · Lithium boron-based electrolyte

Introduction

Solid state microbatteries are battery devices in which the cathode, the solid electrolyte, and the anode are deposited in thin-film form on an appropriate substrate. The high energy density necessary in microbattery devices is achieved by the utilization of the properties of intercalation host materials as cathodes. Intercalation cathodes, such as transition metal oxides, allow the insertion of the electrolyte mobile ions in their structure, thus obtaining a quasi-three dimensional redox chemical reaction. The electrolyte should act as an ionic conductor and electronic insulator, allowing the transfer of

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ions between the battery electrodes. The use of low-conducting materials, such as fast-ion conducting glasses, as electrolytes in solid-state batteries was made possible through the advantages of thin-film deposition techniques.

The properties of the interfaces between the solid electrolyte and the cathode or the anode in a micro-battery largely determine the rechargeability of the device. The interfaces, being responsible for the increase of the electrical resistance to the movement of lithium ions between the cathode and the anode through the electrolyte, limit the reversibility of the ion intercalation reaction in the electrodes, and consequently the rechargeability of the battery.

In this work, thin-film bi-layers of cathode material and solid electrolyte were prepared and their electrical and structural properties studied by impedance spectroscopy and Auger electron spectroscopy measurements, respectively. Lithiated cobalt oxide ($LiCoO_2$) was used as the cathode material and lithiated boron oxide glasses $xLi_2O\text{-}B_2O_3$, where $x = 0.5$ to $x = 3$, as the electrolyte.

Experimental

The cathode-electrolyte bi-layer samples were deposited in thin-film form on metallized alumina (Al_2O_3) or oxidized silicon (Si/SiO_2) substrates by e-gun evaporation. The metallization consisted of two successive layers of cobalt and platinum to provide electrical contacts to the thin films. The Co layer is used to enhance the adhesion of the Pt layer to the substrate.

The cathode material targets were prepared by sintering pellets of stoichiometric $LiCoO_2$ powder, provided by Aldrich, at 800 °C under oxygen flow and subsequent controlled cooling until room temperature. The lithiated boron oxide glasses $xLi_2O\text{-}B_2O_3$ were synthesized by melting the precursor materials Li_2CO_3 and B_2O_3 at 1100 °C. The melt was then poured in moulds to form the targets and allowed to cool at ambient temperature. The carbon contained in Li_2CO_3 is removed from the melt in the form of gaseous CO_2, produced by the thermal decomposition of Li_2CO_3 to Li_2O.

The successive thin-film layers of cathode material, of ~1 μm thickness, and solid electrolyte, of ~300 nm thickness, were deposited by e-gun evaporation under high vacuum, 10^{-7}–10^{-8} Torr. During the cathode layer deposition the substrate was kept at room

temperature. The thin-film cathodes were subsequently annealed at 350 °C in oxygen atmosphere. The solid electrolyte thin films were deposited on top of the cathode layers, with the substrate kept at room temperature. Finally, ohmic electrical contacts to the electrolyte layer were provided by thermal evaporation of gold.

Results and discussion

The electrical properties of ion-conducting materials used in batteries, as well as of the devices which they make up, are evaluated by the technique of impedance spectroscopy. The measured frequency response of the device impedance is simulated by an equivalent circuit, each element of which is attributed to a charge transfer mechanism or structural feature of the device.

In the case of thin-film lithium ionic conductors bounded on either side by ion-blocking metallic electrodes the equivalent circuit [1, 2, 3, 4, 5, 6] of Fig. 1 is used. The parallel combination of the constant phase element Q_1 and the resistor R corresponds to the film's bulk conductivity and is depicted in the Nyquist plot of the impedance spectrum as a semi-circular arc in the high frequency region. The second constant phase element Q_2 is depicted in the Nyquist plot of the spectrum as a straight line in the low frequency region, which is ideally normal to the real axis. The capacitive behavior of the device at low frequencies is attributed to the accumulation of lithium ions at the interfaces of the metallic electrodes with the bi-layer films and the consequent polarization [1] of the interfaces, due to the ion-blocking properties of the electrodes. The capacitive elements in the equivalent circuit have been replaced by non-ideal capacitances, which are modeled by constant phase elements, defined in the frequency domain as $Z_Q = Y^{-1}(j\omega/\omega_0)^{-n}$, where usually $\omega_0 = 1$ rad/s, the Y parameter is measured in conductance units, and $0 < n < 1$.

Contacts on the bi-layer devices that were prepared are lithium-ion blocking electrodes [1]. Despite the fact that two layers of materials were deposited between the metallic electrodes, the device impedance measured in the impedance spectrum represents solely the impedance of the electrolyte layer. The reason is that $LiCoO_2$ exhibits a relatively large electronic conductivity, of the order of 10^3 S/cm, as determined by the Van der Pauw technique, while the conductivity of $xLi_2O\text{-}B_2O_3$ glasses is at best of the order of 10^{-7} S/cm for $x = 3$ at room temperature [1]. Contributions to the total impedance due to the electrical properties of interfaces between any two successive layers in the bi-layer devices should
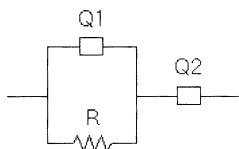
appear in the Nyquist plot of the impedance spectrum as additional semi-circular arcs, superimposed on its two basic constituents.

The Nyquist plot, drawn in logarithmic axes scale, of the impedance spectra of three bi-layers deposited under identical preparation conditions, but using electrolyte targets of different chemical composition, for $x = 0.5$, 1.5 and 3, is shown in Fig. 2. The measurements took place at room temperature. The semi-circular arcs corresponding to the electrical properties of the bi-layers at high frequencies, which were calculated through the fitting of the equivalent circuit to the experimental data, are also shown in Fig. 2. The resistance value that corresponds to the DC electrical behavior of the electrolyte film is deduced from the point of intersection of the above mentioned arc with the real axis. The resistivity of the electrolyte is then calculated by consideration of the device geometry. The results of the equivalent circuit fitting and the final resistivity values of the electrolyte thin films are presented in Table 1.

The resistivity of the electrolyte films decreases as the molar ratio x of the Li_2O glass network modifier in the B_2O_3 glass former increases, due to the fact that the oxygen atoms originating from Li_2O are integrated into the glass network, while the lithium atoms of Li_2O are connected to the network by electrostatic forces, thus being free to move on application of an electric field through the voids of the glass structure. An increase in the lithium ion concentration, as well as the induced structural changes of the glass network, imply the corresponding increase of lithium ion conductivity.

The conductivity of the electrolyte films is found to be smaller than the conductivity of the glass targets that were used to deposit the films, almost by an order of magnitude. The impedance spectrum of the bi-layer sample deposited with the $x = 3$ electrolyte target is correlated to the impedance spectrum of the target itself in Fig. 3. The measurement of the resistivity of the glass target at room temperature was achieved by applying carbon paste electrical contacts to a glass slab of ~ 1 mm thickness. The final value is $\rho = 3.16 \times 10^7$ Ωcm, approximately one order
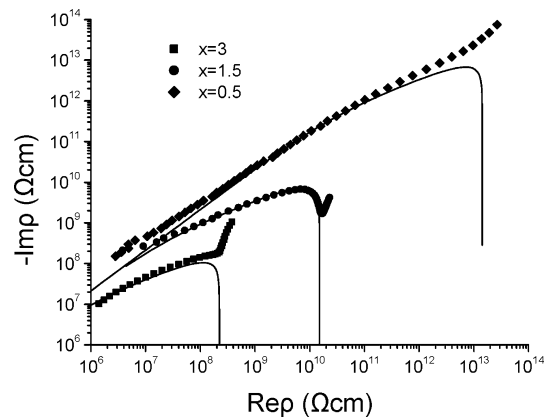

Fig. 2 Impedance spectra of bi-layer structures deposited with $x = 0.5$, 1.5, 3 targets

Fig. 1 Equivalent circuit

Table 1 Geometrical parameters and fitting results of the equivalent circuit to the impedance spectroscopy experimental data of the bi-layer structures

X	Contact diameter (mm)	Electrolyte film thickness (nm)	Q_1 and n_1 (S)	R (Ω)	Q_2 and n_2 (S)	ρ (Ωcm)
0.5	5	300	1.012×10^{-9} 0.970	2.183×10^{9}	1.338×10^{-9} 0.969	1.43×10^{13}
1.5	3	300	6.831×10^{-12} 0.971	6.423×10^{6}	9.548×10^{-8} 0.472	1.51×10^{10}
3	5	300	2.244×10^{-10} 0.961	3.426×10^{4}	2.026×10^{-9} 0.913	2.24×10^{8}

of magnitude smaller than the resistivity value of the corresponding film. A similar direct measurement at room temperature of the resistivity of the other glass targets used is not possible due to the very large resistance that slabs of ~1 mm thickness exhibit in their case. However, an estimation of the room temperature resistivity of these targets can be calculated by application of the Arrhenius equation to data found in the literature [1] that concern resistivity at high temperature and activation energy values.

It seems that the above mentioned observation can be generalized, that is, glass electrolyte thin films deposited on cathode material thin films exhibit lower conductivity than the corresponding glass targets, probably due to lithium losses during deposition by e-gun evaporation.

The electrolyte film conductivity is purely ionic, a fact which can be deduced from the DC electrical behavior of the bi-layer structures. Due to the lithium ion blocking metallic electrodes, the resistance of the structures, as measured with direct current instruments [4, 5, 6], should correspond to the electronic conductivity of the electrolyte film. In all cases, the DC resistance of the bi-layers was beyond the range of any instrument that was used, therefore the electrolyte films' electronic conductivity is too small to be measured. Consequently, the total conductivity determined by the impedance spectroscopy technique is solely ionic.

A bi-layer sample of electrolyte layer thickness ~100 nm, deposited on alumina substrate using the x = 3 glass target, was examined by means of Auger electron

spectroscopy combined with Ar ion bombardment erosion (Model PHI SAM 660). The primary electron beam had an energy of 2 kV while the Ar ions were accelerated to 3 kV. The sputtering rate, over a square area of 5×5 mm^2, was determined using a Ta_2O_5/Ta (National Physical Laboratory of the Community Bureau of References) reference sample to be about 10 nm/min. The depth profile of the sample is shown in Fig. 4. In order to illustrate the results more clearly, vertical lines were drawn to mark approximately the end of each layer. It is widely accepted that the depth where the signal of the characteristic element of each layer drops to half the value of its plateau is considered as the layer's end.

It can be seen that B was detected inside the cathode layer, but its presence is attributed to recoil implantation during sputtering rather than to diffusion during deposition. Co diffusion in the electrolyte layer, as well as deeper layers, is also observed. However, Co is a constituent element of the cathode material, and its diffusion throughout all layers in the structure cannot be considered harmful to the device's properties. The increase of O content in the Co adhesion layer was probably due to diffusion from the Al_2O_3 substrate. As far as Pt is concerned, its most intense transition (at 64 eV) partially overlaps with the Co low energy peak (at 53 eV). In order, then, to determine the Pt depth profile an Auger transition of Pt that was not affected by overlapping had to be utilized (at 168 eV), but the intensity of this transition was lower and for this reason
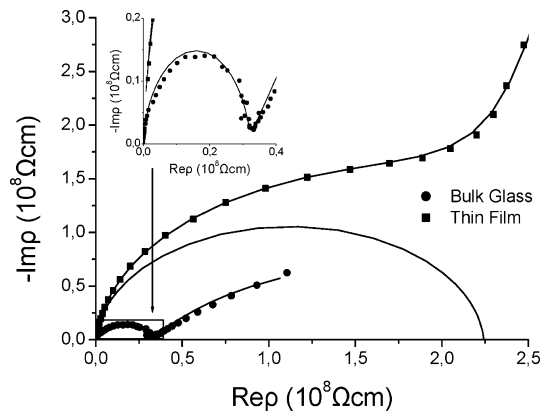
Fig. 3 Impedance spectra of x = 3 thin film and bulk electrolyte glass target
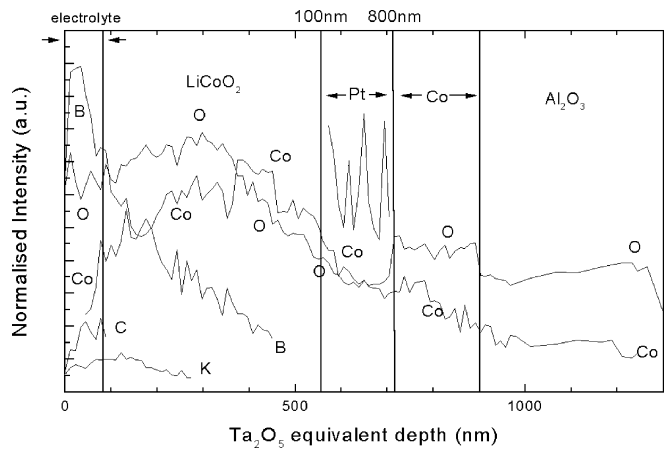
Fig. 4 Auger electron spectroscopy depth profile of a bi-layer sample with x = 3 electrolyte

the Pt depth profile in Fig. 4 is very noisy. However, it is clear that Pt did not diffuse into either the cathode layer or the substrate. Also Li (at 46 eV) was difficult to quantify due to partial overlapping with the Co low energy peak, but the obtained Auger spectrum hints to its presence. Moreover, there is some C and K contamination near the surface of the bi-layer device.

In general, the Auger electron spectroscopy examination of the bi-layer turned out the image of a very structured interface. It is extremely important, though, that Pt does not tend to diffuse into the cathode material thin film, as happens with Au, for instance, at high temperatures. The Co adhesion layer is the most suitable for $LiCoO_2$ cathode material, since its potential diffusion does not affect the cathode's qualitative chemical composition, as would happen with other adhesive layers, such as Ni or Ti.

Conclusions

The ionic conductivity of lithiated boron oxide glass thin films deposited on cathode material thin films by e-gun evaporation is one order of magnitude smaller than the conductivity of the corresponding glass targets, and increases as the lithium content in the film is increased. Practical applications of the electrolyte films to solid state microbatteries require the highest possible lithium ion conductivity. Auger electron spectroscopy reveals intermixing of the various layers induced by element diffusion, thus complicating the structural properties of the interfaces.

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