THIN FILM LI-ION BATTERIES WITH CARBON ANODE

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The number of portable computational and communicational devices increases rapidly in the multimedia age, and the need for miniaturised energy sources becomes a necessity. An ideal microbattery (MB) should be inexpensive, compact, lightweight, and theoretically infinitely rechargeable. The development of thin film Li-ion MBs supported in the framework of NATO SfP Programme aims at fabrication of MBs capable of use in integrated circuits (ICs). The operational acceptability is based on low power requirements of ICs and the high energy density of MBs. In previous period we report on the optimisation of deposition parameters for radio frequency (RF) and direct current (DC) magnetron sputtering of single layer components of Li-Ion MBs [1]. Recently, three-layer thin film samples of MBs were prepared by a sequentional sputtering and their electrochemical properties are introduced in this contribution.

Experimental

All-solid-state microbatteries were composed of $LiCoO_2$ cathodes, LIPON electrolytes and carbon anodes. The films were deposited onto alumina substrates with sputtered NiCr contacts. First, $LiCoO_2$ cathodes were deposited by RF magnetron sputtering in argon-oxygen atmosphere at 200^0 C without any post-deposition annealing. The thickness of cathode layers varied from 1000 to 1500 nm. Then, LIPON electrolytes were sputtered onto the cathodes in argon-nitrogen atmosphere at 70^0 C; the thickness was 1500 – 3000 nm. Lastly, carbon anodes were sputtered onto the electrolytes in the DC regime in argon atmosphere at 300^0 C; the thickness was 2500 – 4000 nm. A complete three-layer structure is shown in Fig. 1.

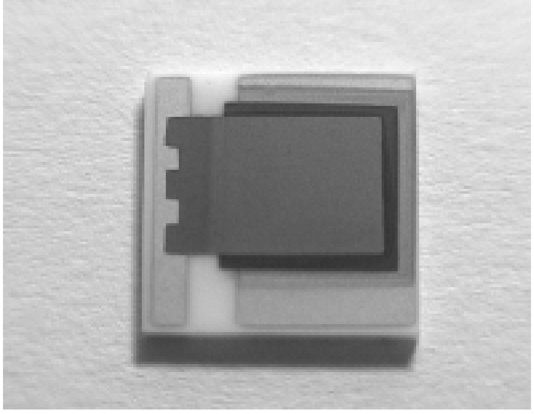

Fig. 1 *Sample of a $LiCoO_2$/LIPON/C microbattery*

The MBs were subjected to impedance and charge/discharge measurements. Impedance measurements were carried out with initial/final frequency of 100 kHz / 5 mHz at DC potential of 0 V and AC amplitude of 5 mV. Charge/discharge characteristics were measured with the constant current of 0.01 mA, cut off voltage 2.8 - 3.8 V for charge, 0 – 2 V for discharge and cut off time of 42 h.

Deposition temperature

The deposition temperature is the most important parameter that affects the physical and electrochemical properties of both single layers and the microbattery. It affects the crystallinity, stoichiometry and also the adhesion and strain inside the carbon and $LiCoO_2$ films, which consequently influence the stability of the layers during charge/discharge cycling. In the case of the electrolyte, the deposition temperature strongly affects the resistivity of the film, which plays the crucial role in the resistivity of the entire microbattery. Higher deposition temperature leads to an intermixing at interfaces of buffer layer/electrode as well as in double-layers cathode/electrolyte and electrolyte/anode, which results in a broadening of interfaces, but it improves the adhesion.

Considering the compatibility of MBs' technology with ICs' technology, the deposition temperature should not exceed 400°C. Nevertheless, it was proved that it is possible to produce functional samples of MBs with carbon anode even at the deposition temperature lower than 400^0 C, as it is demonstrated below.

Deposition pressure

The pressure in the discharge chamber is an important deposition parameter that significantly influences the density and morphology films. It was found that increasing of the deposition pressure increases the number of mutual collisions of atoms during the deposition and results in lower density and more imperfections in layers. The number and size of defects promote in the subsequent layers and can cause serious problems, *e.g.* short circuits between cathode and anode layers, which lead to the failure of the battery.

Other important deposition parameters

Target - substrate distance and the rate of deposition are other important factors that influence the density and morphology of single layers and have to be optimised for each of them. The stoichiometry of layers is influenced by the partial pressure of gases in the chamber and both the deposition temperature and pressure. The stoichiometry of a layer often differs from the stoichiometry of the target used for the deposition, which can change even in the course of the deposition.

Results and Discussion

After optimisation of the deposition parameters, ten samples of MBs were produced and subjected to impedance and charge/discharge measurements.

Impedance spectra

Impedance spectra were measured under conditions given above. The following theoretical fitting model can describe the description of the behaviour of a MB (see Fig. 2).

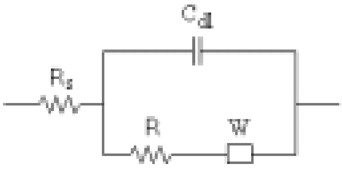

Fig. 2 *Equivalent circuit for a MB*

In Fig. 2, R_s stands for the series resistance corresponding with the ohmic resistance of the cathode and anode layers, and the contact resistance of the interfaces between the electrodes and the metallic current collectors. C_{dl} represents the electric double-layer capacitance of the Helmholtz charge formed across the cathode/electrolyte and anode/electrolyte interfaces. A small contribution to this capacitance is due to the geometrical capacitance, the origin of which is the presence of three layers of materials with a finite dielectric constant between the parallel metallic current collectors. R is the resistance of the solid electrolyte layer, corresponding to the lithium-ion conductivity of the electrolyte material. The contribution of the charge transfer resistance of the redox processes taking place at the electrodes to this resistance is considered as negligible.

The W element is the Warburg impedance which corresponds with the diffusion of lithium ions into and out of both electrodes.

The porous nature of the device interfaces was considered to be the cause of the experimentally observed frequency dispersion of the capacitive elements of the circuit. For this reason, the double-layer capacitance and the Warburg impedance were substituted by constant phase elements Q_1 and Q_2 in a practical fitting model: $R_S(Q_1[R_1Q_2])$. The values of the elements in this simplified equivalent circuit are summarized in the following table.

Circuit element	*Value (S.I.)*
R_s	1.33E+03
Q_1	1.09E-07
R_1	6.26E+05
Q_2	3.42E-06

The fitted impedance spectra are introduced in Figs. 3 - 4.

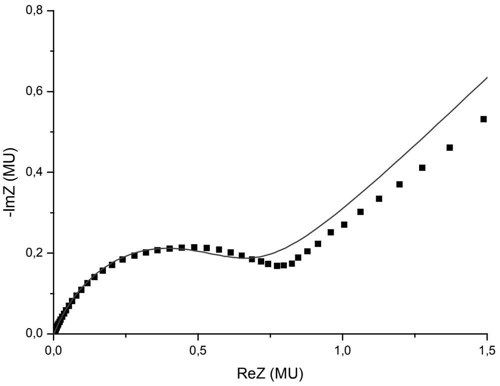

Fig. 3 *Nyquist plot of the impedance spectrum*

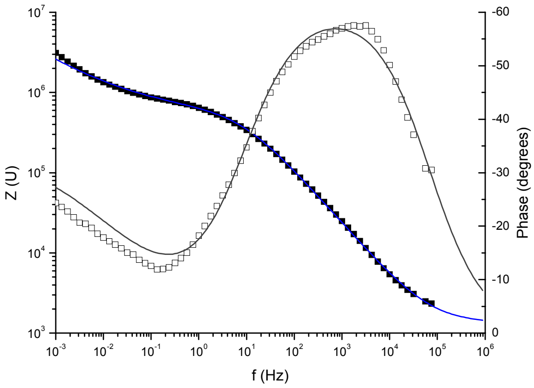

Fig. 4 *Bode plots of the impedance spectrum*

The point of intersection of the semicircle with the x-axis in Fig. 3 corresponds with the DC electrical behaviour of the electrolyte film, while the straight line demonstrates the capacitive behaviour attributed to an accumulation of Li-ions at the interfaces and the consequent polarization [2].

In Fig. 4, there is a continues decrease of the impedance, which suggests the presence of ionic conductivity in the whole frequency range. However, it follows from measured capacity values given below that the conductivity of the electrolyte is still far from optimum.

Capacities

Results of the cycling of a MB are demonstrated in Figs. 5 – 7. In the first run of cycling the MB was charged/discharged in the potential range 2.0 – 2.8 V (see Fig. 5). After 24h relaxation time the potential range was broadened and the MB was subjected to the second run of cycling (see Fig. 6). The capacity in the first charge cycle of the second run was the highest capacity measured on this sample (3.5 μAh). The highest capacity loss was observed between the first and second cycle, similarly as in the first run; the difference between later cycles was not so dramatic.

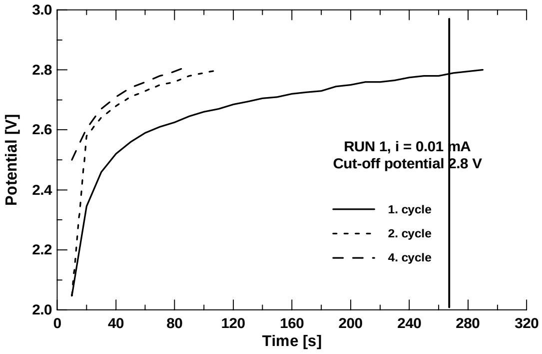

Fig. 5 *Charge of the MB in the 1st run*

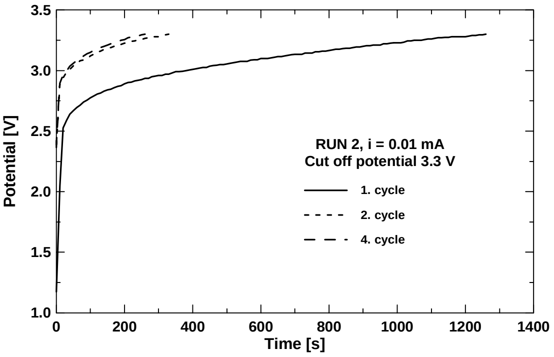

Fig. 6 *Charge of the MB in the 2nd run*

After another 24h relaxation period the MB was subjected to 30 charge/discharge cycles in the third run (see Fig. 7).

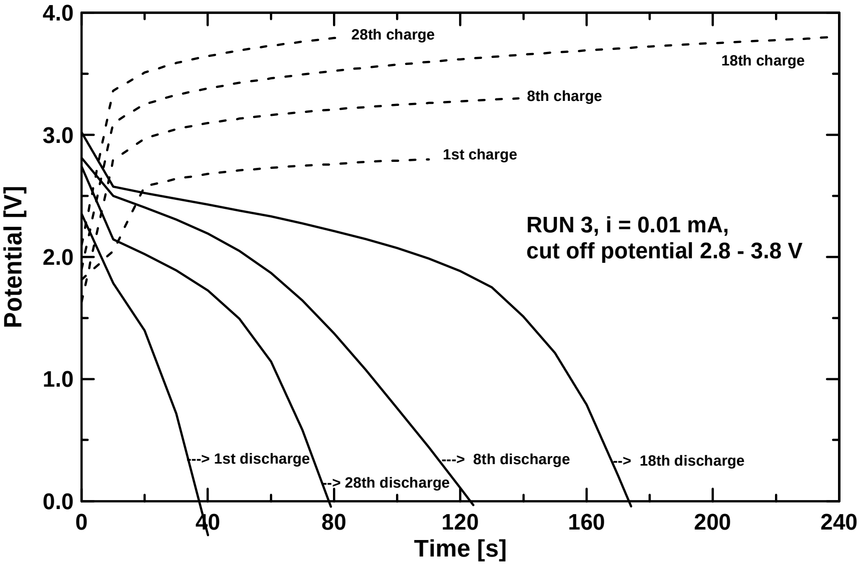

Fig. 7 *Charge/discharge in the 3rd run*

The charge capacity of MB increased with the number of cycles up to the 25th cycle, then decreased as a result of worsening adhesion of the carbon anode, as was obvious from the microscope picture of the MB made after the cycling. However, there is only a small difference between values of the charge and discharge capacities in later cycles of the third run.

Conclusions

Functional samples of all-solid state MBs with carbon anodes were prepared at deposition temperatures not exceeding 400°C to meet the requirement of the compatibility of the MBs‘ and ICs‘ technology. The thin film batteries were charged/discharged in the potential range 0 – 3.8 V in ten cycles at least. The capacity of the MBs as well as the value of the capacity loss are expected to be improved after the optimisation of the solid electrolyte composition and the perfection of the deposition technology for the electrolyte/carbon anode interface.

[1] J. Prachařová et al., *J. Power Sources* **108** (2002), 204.

[2] Ch. Julien et al., Solid State Batteries: Materials design and optimization, Kluwer. Boston 1994.