Investigation of Local Ions Distributions in Polymer Based Light Emitting Cells

M. Gritsch[1], H. Hutter

Institute for Analytical Chemistry, TU Vienna, Getreidemarkt 9/151, A-1060 Vienna

L. Holzer, S. Tasch

Institute for Solid State Physics, TU Graz, Petersgasse 16, A-8020 Graz

Polymer based light emitting electrochemical cells have been analyzed by means of SIMS revealing a strongly inhomogeneous ions distribution that leads to an asymmetric behavior of such elements. This work shows that the separation of the ions already happens during the production of such cells.

1. Introduction

Light-emitting electrochemical cells (LECs) have a great potential for industrial applications due to their capability of blue color emission at low voltages. Such cells would be extremely cheap to produce and can also be designed to fill large scale areas. All in all those cells promise to be part of tomorrow's flat panel displays.

The typical behavior of the LECs is realized by adding an ionic salt to a conjugated polymer, often blended with a ionically conducting polymer to enhance the transport of the ions. For the cells investigated, m-LPPP (methyl substituted poly(para phenylene)) was used as semi-conducting polymer with PEO (Poly Ethylene Oxide) as ionic conductive and lithium trifluorsulfonate as ionic species, other set-ups for LEC's use lithium salt/crown ether complex as the solid electrolyte [1] or poly(1,4-phenylene-vinylene) (PPV) as polymer semiconductor [2]. This ionic species acts as counter ions for electrochemical doping during operation, where at the cathode the polymer is reduced (n-type doped) and on the anode oxidized (p-type doped) leaving a non doped region in-between. This doping is evidenced by absorption measurements of a LEC under operation [3]. The homogeneity of the polymer layer is most important for the quality of such devices, especially phase separation between the ionic conductive and the electronic conductive polymers strongly influences the performance of LEC's [4].

However, mLPPP based LECs show a different behavior than reported for LECs up to now, with ITO used as cathode. In forward direction with the ITO as anode the turn on voltages are significantly higher or no light emission can be observed [3]. We investigated the element distribution within the active layer by secondary ion mass spectroscopy (SIMS) depth profiling using both negative as well as positive secondary ions showing that already during the production of those cells the ionic species separate within the active layer thus pre-defining the direction in which those cells are to be operated.

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[1] Author to whom correspondence should be addressed

2. Experimental

The SIMS instrument used throughout those investigations was an enhanced CAMECA IMS 3f. The modifications refer mainly to the primary column to which a CAMECA Cs^+ fine focus ion source as well as a duoplasmatron for O_2^+ ions, extended lens systems and a digital raster generator have been added. The usage of a CAMECA Cs^+ Fine Focus ion source as well as O_2^+ duoplasmatron has been provided by the installation of a primary magnet. Furthermore the application of the primary magnet guarantees the purity of the primary ion species [5], [6].

As for the measurement of the local ions distribution in the LECs strongly electropositive species (Li^+ ions) as well as strongly electronegative species (F^- ions as tracer for the triflate ion) had to be detected to characterize the local ions distribution, the use of both primary ions was advisable. Thus, for each cell two measurements were necessary and the signals of the matrices (carbon for the polymer layer, indium for the ITO layer and aluminum or gold for the metallic top electrode, that could be observed in both measurements, were then used to fit the two measurements together resulting in a depth profile containing the information for both the lithium as well as the triflate distribution.

Within the scope of this work, Cs+ ions, accelerated to energies of 14.50 keV and focused to a spot diameter of some 10 µm resulting in a primary current of 15 nA have been used for the detection of negative secondary ions, the primary ion beam was projected onto an area of 350 x 350 µm in square with an analyzed area of 60 µm in diameter selected by the use of an aperture diaphragm. For the detection of positive secondary ions, O_2^+ primary ions accelerated to energies of 5.50 keV and focused to a spot diameter of some 10 µm resulting in a primary current of 500 nA have been used, the primary ion beam was projected onto an area of 250 x 250 µm in square with an analyzed area of 150 µm in diameter. Those conditions were chosen by trial in order to obtain optimum conditions for sputter removal rate, depth resolution and secondary ion yield.

The m-LPPP based LECs were prepared at the Institute for Solid State Physics, TU Graz, by L. Holzer. They were made by spincoating a cosolution of m-LPPP, PEO (molecular weight 5000 kDa) and $LiCF_3SO_3$, weight ratio 20:10:3 in cyclohexanone on an ITO coated glass substrate under argon atmosphere. The samples were annealed for half a day at 60 °C, and aluminum resp. gold was evaporated on top of the films under a pressure of about 10^{-6} Torr. This resulted in a 100 nm thick ITO base electrode, approximately 120 nm of polymer layer and 50 nm of metallic top electrode. Still, the actual thickness of the layers varied remarkably which resulted in short circuits on many of the pads as well as of course varying profile depths. Still this was no problem for the measurements as the criteria for the fitting of the depth profile was the thickness and position of the polymer layer, so the different depth profiles were stretched and shifted until the carbon distribution was in good agreement. To prevent the samples from oxidation and contamination under ambient air, they were operated and stored under argon atmosphere until they were transferred into the vacuum system of the SIMS instrument.

3. Results and Conclusion

Figure 1 shows a depth profile through a "standard" LEC system that has already been in use for some minutes. On the left hand (on top) the aluminum contact is situated, followed by the polymer layer and the ITO base electrode. Under operation, the ITO base electrode was set to negative potential. The relative thickness that can be observed

in the depth profile is not proportional to the actual thickness ratios in the samples due to differences in the sputter removal rates between the three layers; the polymer layer had the highest sputter removal rate. The profiles has been recorded until the interface to the glass substrate was reached where strong charging effects occurred. During measurement of the active layer the conductance was sufficient, so no charging effects could be observed. The profile broadness results mainly from the initial roughness of the samples and sputter induced effects.
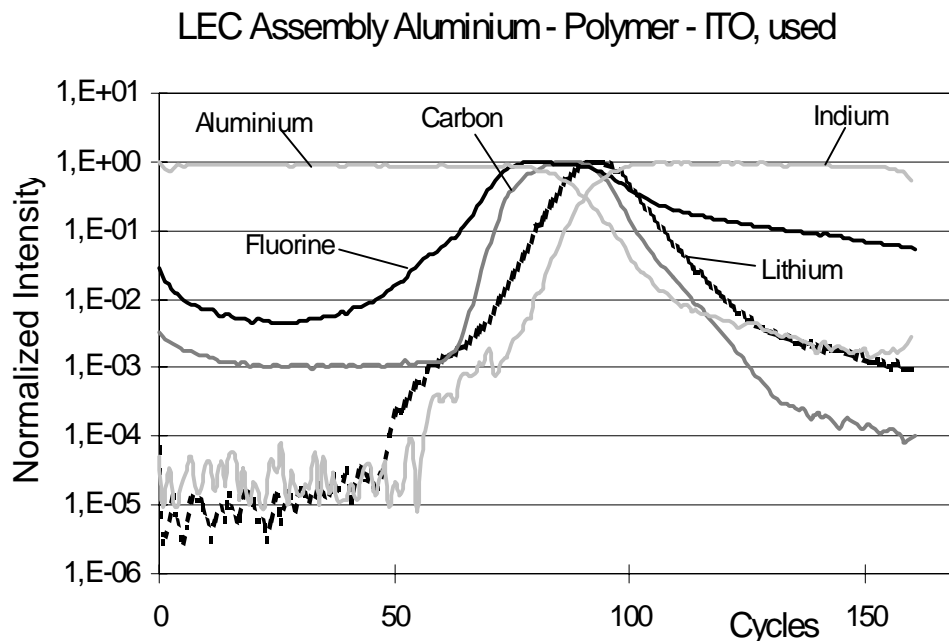
LEC Assembly Aluminium - Polymer - ITO, used

Fig. 1: Depth Profile through a used LEC.

One can clearly see that the ionic species have been separated under the influence of the applied electric field (some volts drop off over approximately 120 nm which results in an electric field of approximately $3 \cdot 10^7$ V/m) and that the lithium distribution is clearly shifted towards the interface ITO-polymer whereas the triflate distribution (represented by the fluorine ion) is shifted towards the interface aluminum – polymer. Especially remarkable, the fluorine and lithium distribution differ considerably from the carbon peak and they are of similar mass, so the observed shift of the peaks is most likely not an artifact of the sputter process. As no charging effects occurred, no effects of a local electric field from surface charging that would have driven the ions apart during measurement can be expected as it was reported for measurements on insulators [7], [8].
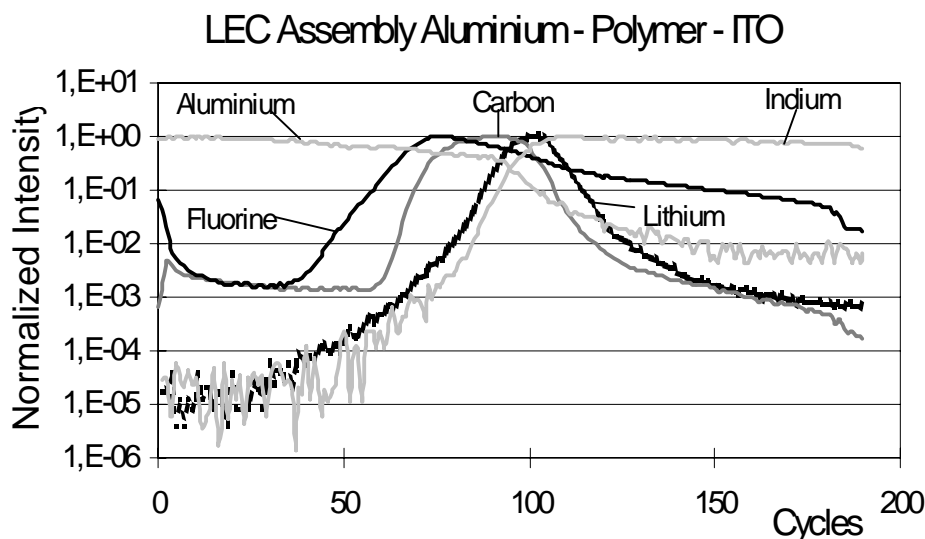
Fig. 2: Depth Profile through an unused LEC.

Figure 2 gives the depth profile for the identical LEC assembly, but this cell has not been used before so that one would expect the ions to be distributed homogeneously throughout the active layer, as no applied field could have driven them apart. But actually, the depth profile shows a separation of the ionic species, again lithium ions are enriched towards the interface polymer-ITO and the triflate ions at the opposite interface aluminum-polymer. This reveals, how the effect of an initial "polarity" of these devices comes up: as the ionic species separate already during production and the lithium ions enrich at the interface towards the ITO base electrode, the devices work properly with the ITO base electrode set to negative potential as many lithium ions are available for charge compensation. Reversing the polarity of this device would first afford to transport ions to the counter electrodes, and no light emission can be achieved. This explains the behavior of the devices, but still the question remains how this separation happens. For example different Fermi levels of the electrode materials build up an "inner" field: the energy difference of the Fermi levels of the two electrode materials is about 0.7 eV which could be the driving force for this process. when the two electrodes are in electric contact, the Fermi levels are equalized resulting in a built in field gradient within the polymer layer [9]. Further measurements on similar cells with other electrode materials resp. without top electrode attached showed that especially effects of solubility in the ITO electrode and fractional deposition of the components play an important role in the development of inhomogeneities on such cells [10].

It has been shown by depth profiling SIMS that within LEC's based on the system m-LPPP/PEO/LiCF$_3$SO$_3$ a significant separation of the ionic species happens. Different mechanisms can be held responsible for this effect: during spincoating, fractional deposition of the components happens leading to separation of the ionic species close to the electrode materials. During the following annealing the ions diffuse leading to broad, shifted peaks. To some extent also the solubility of lithium ions in the ITO base electrodes can be held responsible for this separation, and, last but not least, the built-in field that occurs when electrode materials with different Fermi levels are used leads to a separation of the anionic and cationic species. All in all those effects lead to an inhomogeneous distribution of the ionic species and thus to a more or less pre-set polarity of these devices.

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