Summary of Phase 3 of the SEE 8 Project

In this stage studies regarding perovskite solar cells (PSC) with standard geometry FTO/electron transporter/halide perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) /spiro-OMeTAD/Au, the $CH_3NH_3PbI_{3-x}Cl_x$ was obtained both through the standard two-step method (2S) and through the new one-step synthesis method (1S). Multiple optimizations at each layer were performed in order to obtain larger and more reproducible power conversion efficiency (PCE) values. Studies regarding the stability in time have shown an important improvement of the PSC. After repeated tests for more than 3.000 hours it was observed that fabricated PSC have a maximum 10% drop of the PSC value, even if they are heated to 70°C, the cells being uncapsulated and stored in low humidity conditions (~10%). The PCE values of a standard PSC ($FTO/TiO_2/CH_3NH_3PbI_{2.6}Cl_{0.4}$) obtained through 1S or 2S method with Au or Ag electrodes are shown in Fig. 1. It has been proven that not only the deposition method but also the type of top electrode is important. A degradation of the PSC always occurs when Ag is used as top electrode material and in the case of Au electrode only for the case of 2S fabricated cells. The cause of degradation, proven by HRXPS studies, is the migration of iodide to and through spiro-OMeTAD, facilitated by the pinholes (microscopic perforations in the active layer caused by the incomplete coverage of the perovskite) and by the Ag electrode. Fig. 2 shows the processes that lead to the degradation of a PSC with Ag electrode, the primary cause being the migration of iodine from the methylammonium lead iodide (MAPI) composition that leads to the formation of PbI_2 and AgI. The stability of PSC can be increased using Au for top electrodes (that do not react with I) on pinhole free cells (that are obtained only through 1S technique).

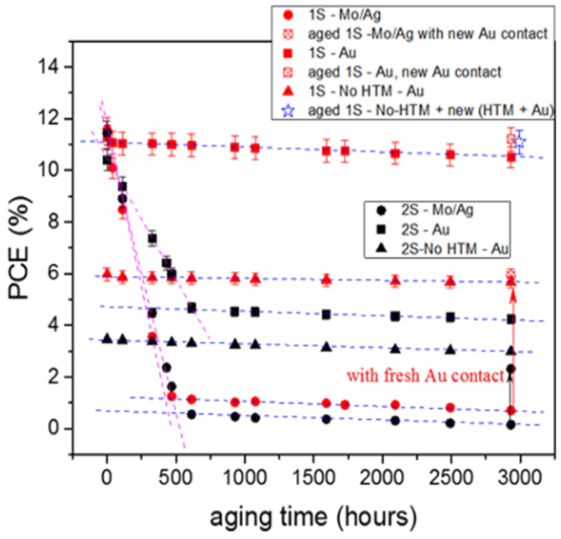

Figure 1

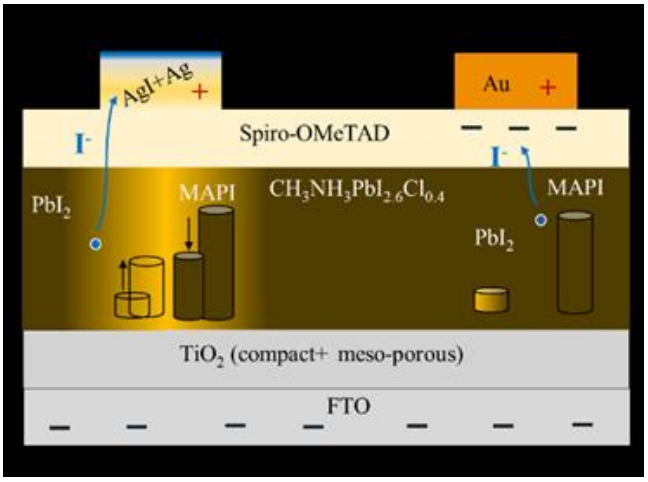

Figure 2

Studies regarding the possibility of replacing the standard ITO/FTO electrodes with transparent AZO or flexible metallic network electrodes have been performed. Although the AZO layer fabricated on both glass and networks of metallic microfibers have a very good conductivity, the integration in a PSC leads

to a decrease of AZO conductivity resulting in a reduction of the conversion efficiency of the PSC (PCE~ 2.5%). The cause identified was the migration of oxygen from the oxide layer into AZO during the crystallization treatment at 450°C of the TiO_2 layers deposited over the AZO layer which then lowers the conductivity of the electrode. The substitution of the TiO_2 with a ferroelectric (PTO and BTO) was done using multiple fabrication techniques. Although PTO and BTO have excellent ferroelectric properties, the incorporation in PSC has not lead to an increase of PCE. Still, the experimental data have clearly shown that charge collection efficiency can be improved by the presence of a ferroelectric layer, a increase of the polarization load leads to a better orientation of the spontaneous polarization and as an effect of a larger P in the ferroelectric layer, an increase of the short-circuit current is obtained. The polarization in the ferroelectric layer should be oriented from MAPI to the FTO electrode in order to increase the short-circuit current, as obtained from the atomistic simulations (see Fig. 3). For the opposite orientation no signal from the illuminated PSC is recorded.

A dynamic electric model was developed that is capable of describing the hysteresis phenomena experimentally observed in the J-V characteristics of the cells. Using a simple hypothesis of electrical polarization relaxation of the device it is possible to accurately reproduce the experimental J-V characteristics. The developed theoretical model is also capable of reproducing the J-V characteristics obtained at different scan speeds, being a good tool for the calibration of relevant microscopic models for the operation of this type of solar cells. An example of experimental and simulated J-V curves are shown in Fig. 4.

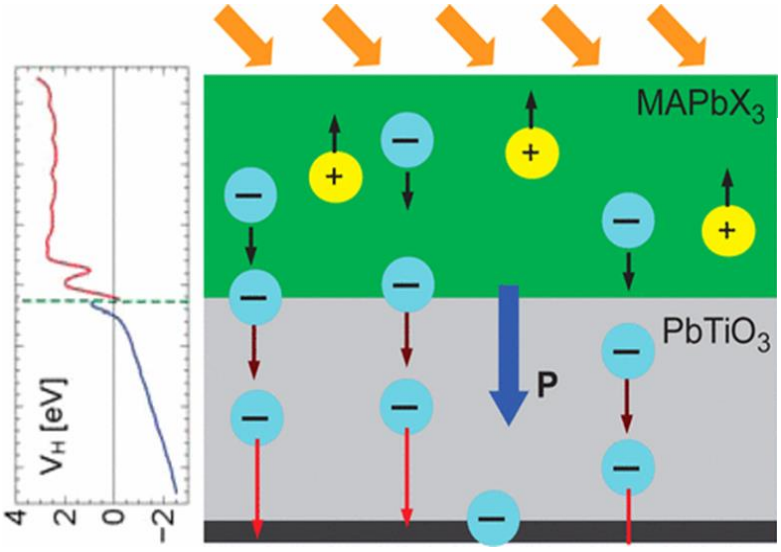

Figure 3

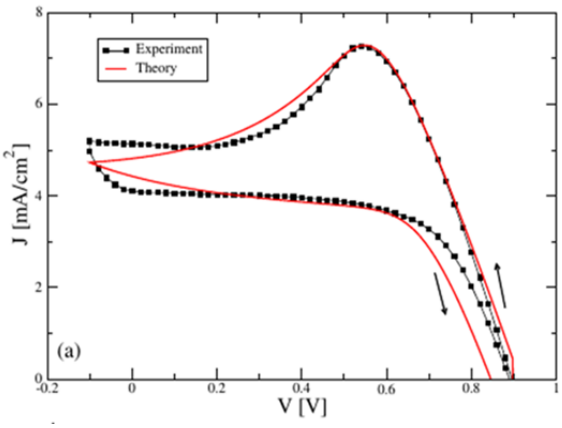

Figure 4

Other activities involved optimization of the deposition methods of compact and mesoporous TiO_2 layers, to facilitate large area deposition, and as a result, an increase to 15.4% PCE was obtained. Using the lab scale experimental results, the „PERPHECT" modular printing prototype was completed, offering the possibility of using three different deposition techniques for thin films.