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Water ingress into and climate dependent lifetime of organic photovoltaic cells investigated by calcium corrosion tests



Hannes Klumbies^{a,*}, Markus Karl^a, Martin Hermenau^a, Roland Rösch^b, Marco Seeland^b, Harald Hoppe^b, Lars Müller-Meskamp^a, Karl Leo^a

^a Institut für Angewandte Photophysik, Technische Universität Dresden, George-Bähr-Str. 1, 01062 Dresden, Germany

^b Institute of Physics, Technische Universität Ilmenau, Weimarer Str. 32, 98693 Ilmenau, Germany

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ABSTRACT

The degradation of non-encapsulated, small-molecule organic solar cells based on ZnPc (zinc phthalocyanine)/C₆₀ with an aluminum top electrode is investigated under different climate conditions and correlated with the water barrier performance of the aluminum electrode layer. The degradation of the solar cells turns out to be dominated by water and can be well predicted by the corrosion of calcium – a sensor for water – under the same conditions. By several independent techniques, an amount of $20 \pm 7 \text{ mg(H}_2\text{O) m}^{-2}$ is determined to reduce the solar cell efficiency to 50% of the initial value, independent of humidity and temperature between 20 and 65 °C. This experimental value for degradation sensitivity of an organic solar cell allows to translate the encapsulation requirements of the solar cell into a well-defined, objective quantity and allows to predict device lifetimes for different permeation barriers. Furthermore, electroluminescence imaging shows that the degradation is caused solely from a loss of active area caused by water ingress through defects in the aluminum top electrode. For this type of barrier, most of the permeation (> 72%) through the aluminum is thus caused by defects with a radius $r > 0.3 \mu\text{m}$ visible with an optical microscope. Hence, the water ingress through the aluminum top electrode and in turn the lifetime of the organic PV cell can be well predicted by a simple optical inspection.

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1. Introduction

Organic solar cells have reached a power conversion efficiency of 12% recently [1] and have great potential to open new applications for solar energy, e.g. in architecture or off-grid applications, reducing the need for fossil energy sources. In contrast to silicon solar cells, organic solar cells can be produced on flexible, light-weight, and low-cost polymer webs in a low-cost roll-to-roll process. While the intrinsic stabilities of organic solar cells seems to be sufficient [2–6], degradation due to external gases – especially water vapor [7–11] – still hampers their broader commercialization. According to an investigation on seven different state of the art organic photovoltaic devices, the dominant failure mode is the corrosion or delamination of electrodes [10].

To design appropriate permeation barriers for organic solar cells, the requirements of organic solar cells under realistic climate conditions have to be investigated. Since water turned out to play a crucial role in solar cell degradation, the water-uptake until the solar cell efficiency drops to 50% (T50-water-uptake) is an important

value required for barrier optimization. In literature, values for T50-water-uptake obtained by comparison with calcium corrosion tests under the same barrier films, e.g. 10 mg m^{-2} for a ZnPc/C₆₀-cell with an Al-cathode (100 nm) [12] and 21 mg m^{-2} for a P3HT/PCBM-cell with Ca/Al-cathode (20 nm/100 nm) [13] have been reported. However, the cathode acts as a barrier itself, which was not [13] or only ex post [12] taken in to account. Furthermore, it is not known how this T50-water-uptake depends on the temperature and whether the degradation is only proportional to or really dominated by water ingress.

In this work, we evaluate the water vapor transmission rate (WVTR) through aluminum cathodes with optical and electrical calcium corrosion tests at different climate conditions. By relating those WVTRs to the corresponding aging of ZnPc/C₆₀-cells, we calculate the T50-water-uptake for all climate conditions to check whether the degradation is fully determined by water ingress. We use ZnPc/C₆₀-cells because they represent a typical and well investigated material system for vacuum deposited small molecule organic solar cells. Furthermore, using the same material system as in our former work [12] allows us to refer differences in the results to the improvements of the method, i.e. the consideration of the aluminum cathode as a barrier as well as compensating increased water ingress from the edges of the solar cells. Finally, we

* Corresponding author. Tel.: +49 351 4634 2374.

E-mail address: hannes.klumbies@iapp.de (H. Klumbies).

investigate the relation between defect size and water permeation of defects in the Al-cathode to better understand the mechanism of water permeation.

2. Materials and methods

2.1. Solar cell architecture and materials

The solar cells were made up in a p–i–i-structure (p...p-doped, i...intrinsic) and were identical in design and materials to those described by Hermenau et al. [12] (see Fig. 1): On a glass substrate covered with a 95 nm thick, pre-structured layer of indium–tin–oxide (ITO) as the bottom-contact we evaporated a hole-transporting layer of BF-DPB (*N,N'*-((diphenyl-*N,N'*-bis) 9,9-dimethyl-fluoren-2-yl)-benzidine) p-doped with fluorinated C_{60} ($C_{60}F_{36}$, [14]) followed by intrinsic layers of 5 nm ZnPc (zinc phthalocyanine), a 30 nm thick bulk hetero-junction of ZnPc and C_{60} in a 1:1 weight ratio, additional 30 nm C_{60} , and 6 nm BPhen (bathophenanthroline; 4,7-diphenyl-1,10-phenanthroline). As top contact we evaporated 100 nm of aluminum at a pressure of 4.7×10^{-7} mbar with an average rate of 0.2 nm s^{-1} . The materials used and the evaporation system were carefully tracked and monitored by test runs to achieve reliable device quality. On each substrate, four devices \hat{a} 6.44 mm² were defined by the overlap of ITO and aluminum.

2.2. Calcium test architecture and materials

The calcium tests consisted of calcium as the corrodible sensor material covered with a C_{60} interlayer for mechanical decoupling and followed by the same top layers as for the solar cells to provide an identical permeation barrier (see Fig. 1.). On a glass substrate (Schott borofloat 33) we evaporated 60 nm calcium and 100 nm C_{60} . To ensure comparable growth behavior of the barrier layer, we added 6 nm BPhen before covering the stack with 100 nm aluminum. The aluminum was evaporated at a pressure of 2.4×10^{-7} mbar with an average rate of 0.2 nm s^{-1} . The calcium and the top aluminum layer had the shape of a rectangle of $17 \times 5 \text{ mm}^2$. Identical contacts (100 nm aluminum) below the calcium and on top of the aluminum top layer were used to monitor the lateral resistance of both layers together in a real 4-wire sense mode, i.e. with an electrode layout excluding series resistances as discussed by Schubert et al. [15]. Measuring the WVTR with the standard (100 nm C_{60}) and the doubled interlayer thickness (200 nm C_{60}) at 38 °C/11% rh (relative humidity) resulted in no differences ensuring that the C_{60} -interlayer does not influence the measurement. For the initial measurements at 38 °C/11% rh the stack was applied without the contacts for the aluminum layer. In consequence, leakage currents through the stack and over

the aluminum layer distorted the electrical measurement at this condition, which was improved by using the symmetrical contact scheme in all later measurements.

2.3. Aging setup

All samples were aged under four controlled climate conditions –3 Calcium tests and 3 solar cell substrates at each condition. The temperature was kept constant within a range of ± 1 °C. A defined humidity was provided by saturated salt solutions (see [16]): LiCl for 38 °C/11% relative humidity (rh), $Mg(NO_3)_2$ for 20 °C/54% rh, Na_2SO_4 for 38 °C/90% rh, and NaBr for 65 °C/50% rh. To avoid corrosion of the aluminum top layer under conditions with high humidities, we protected all samples aged by $> 11\%$ rh with a 175 μm thick PET-web (Melinex HCSTX1) degassed in a nitrogen-filled glovebox at 60 °C over 24 h and glued onto the samples with a UV-curable glue (Nagase XNR 5590). While this adds a small additional barrier, the comparison between solar cells and calcium tests is not affected.

2.4. Solar cell evaluation

Two solar cells per substrate, i.e. 6 per condition, were illuminated by a white-light LED (Seoul Z-LED P4, white, 240 lm). We set the light intensity to 1 sun proved by an equal short circuit current of the solar cell under both, our setup and a mismatch-corrected reference AM 1.5 light source with an intensity of 1 sun. Once per hour the *I*–*V*-curve of each solar cell was measured. Solar cells with macroscopic damages (scratches) in the aluminum cathode, i.e. extraordinary fast degradation, were removed from the evaluation. The aging at each climate condition was stopped when the efficiency of the solar cells dropped to 50% of the initial value (T50). Thereupon all solar cells as well as the related calcium tests aged at this condition were removed from the aging setup. The solar cells were investigated by electroluminescence-imaging (ELI, [10]) to evaluate the residual active area and to identify and compensate the fraction of degradation caused by edge diffusion (see Fig. 4). The defect density in the aluminum top layer was investigated under the microscope (Nikon Labophot 2, 10 \times magnification) on a total of 5 mm² by illuminating an unaged solar cell covered with PET from the bottom and counting the bright spots of light shining through the aluminum.

2.5. Electroluminescence-imaging

Exciting the solar cells with a constant forward voltage made them emit light from their photoactive layers. The light was collected with a back-illuminated and cooled silicon charge coupled device camera. However, light emission requires the injection of charge carriers from the electrodes. Hence, this method called electroluminescence-imaging allows to identify deficiencies related to charge carrier injection and thus the electrodes. Further information on this method can be found in the literature [17,18].

2.6. Calcium test evaluation

To corrode a 60 nm thick calcium layer $84 \text{ mg(H}_2\text{O) m}^{-2}$ are required, i.e. calcium corrosion is a quantitative sensor for water—but not oxygen [19]. Since calcium is an opaque conductor and calcium hydroxide is a transparent insulator, the corrosion can be monitored optically or electrically. While the optical evaluation was done only once per sample after the end of the aging procedure, the electrical resistance was monitored during the whole period of aging.

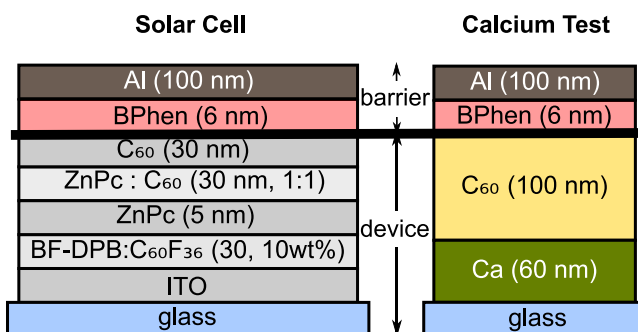


Fig. 1. Solar cell (left) and calcium test (right) stack design. The bottom of the stack is device-dependent, but the barrier (Al) and the layer it was grown on (BPhen) were identical to ensure an identical barrier on both stacks.

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