

Thin Nanostructured Solar Cells on Metal Sheets

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ABSTRACT

Direct integration of nanostructured, dye-sensitized solar cells (DSC) on industrial sheet metals, used e. g. as building materials has been studied. To demonstrate a flexible, roll-to-roll manufacturable, and mechanically stable DSC, counter electrodes made of platinized ITO-PET plastic foils, and solidified iodine electrolyte were employed in the cells, where the photoelectrodes were deposited on stainless steel sheets. Total power conversion efficiency of 3.8 % was obtained with a DSC consisting of a stainless steel photoelectrode, Pt-plastic counter electrode, and gel electrolyte (for a reference, 4.3 % and 4.7 % with a Pt-glass counter electrode and gel and liquid electrolytes, respectively). The simple manufacturing process of the cells and the flexible, low-cost steel substrate show potential for cost-efficient, high throughput mass production of the DSC.

Keywords: dye-sensitized solar cell, steel substrate, flexible

1 INTRODUCTION

Due to mostly low-cost materials and simple manufacturing process, nanostructured dye-sensitized solar cells (DSC) [1] present a potential alternative to the traditional silicon and thin film photovoltaic devices. Unlike the solid semiconductor solar cells, a DSC is an electrochemical device, consisting of two electrodes interconnected by a layer of redox electrolyte. Electricity is generated on the photoelectrode, which is a porous, high surface area network of TiO_2 -nanoparticles, sensitized with a light-absorbing dye and permeated with the electrolyte. Figure 1 presents the operating principle of the DSC.

While the highest reported energy conversion efficiencies of the DSC exceed already 11 % [2], the rigid, heavy, and fragile glass substrate conventionally used in the cells is still a hindrance to their high throughput industrial manufacturing. Conducting glass is also the most expensive part of the cell. To address these problems, we have studied direct integration of the dye solar cell structure onto industrial sheet metals used e. g. as building materials. Roofing and façade materials with solar-active functional coatings would lead to considerable savings in the implementation of the new technology, since a significant part of the cost of photovoltaic systems is due to the additional structures needed in the installation and support of the panels.

Metal substrate has many advantages, such as superior conductivity, which is important especially when the cell size is upscaled, cost-efficiency, mechanical sturdiness, and flexibility. It also stands high temperatures, which makes it a suitable substrate for the photoelectrode, where sintering in elevated temperatures is required to form a high quality, nanoporous TiO_2 film. On the other hand, metal sheet is opaque, which requires lighting of the cell from the counter electrode side, resulting in optical losses. These losses can be minimized, however, with careful optimization of the counter electrode and the electrolyte composition.

To demonstrate a flexible, roll-to-roll producible DSC, we have used ITO-PET conductive plastic foils as the counter electrode substrate and semi-solid (gelatinized) electrolyte to improve the mechanical stability of the cells.

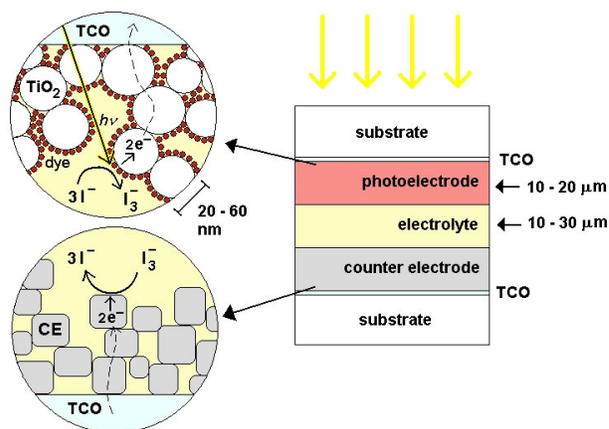


Figure 1: Operating principle of the DSC.

2 EXPERIMENTAL

2.1 Substrates

The studied metal materials included zinc-coated and plain carbon steel, stainless steel (StS, type 1.4301) and copper (thickness 1 – 1.25 mm, supplied by Outokumpu Ltd., Ruukki Ltd. and Luvata Ltd.). Electrodes were also prepared on FTO-glass (Pilkington TEC-15, sheet resistance 15 $\Omega/\text{sq.}$, thickness 2.5 mm; supported by Hartford Glass Company, Inc.) and ITO-PET plastic foils (NV-CT-CH-1S-M-7, sheet resistance 60 $\Omega/\text{sq.}$, thickness 200 μm ; supplied by Bekaert Specialty Films, Inc.).

2.2 Corrosion Stability of the Metals

The iodine electrolyte typically used in the DSC is corrosive towards many metals, which is why soaking and encapsulation tests were performed to find out the studied metal materials' suitability for DSC substrates. In the soaking tests, metal pieces were immersed in the liquid electrolyte for several months, after which the metal ion concentrations in it were analyzed with atomic absorption spectrometry (AAS). In the encapsulation tests, small amount of the electrolyte was sealed between a metal sheet and a glass, mimicking the situation in a real cell.

2.3 Cell Preparation

Nanoporous TiO₂-photoelectrodes (PE) were prepared with the doctor-blading method and high temperature sintering, using commercial titania paste (Sustainable Technologies International). Counter electrodes (CE) were prepared both on glass substrates (as a reference) with the standard thermal platinization method [3], and on ITO-PET foils, using either sputtered platinum or conducting polymer PEDOT as the catalyst. Thermally platinized StS sheets were also tested as the CEs. The liquid electrolyte composition was 0.5 M LiI, 0.03 M I₂, and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile. Semi-solid electrolyte was made of the liquid by gelatinizing it with 5 wt% PVDF-HFP [4]. More detailed descriptions of the cell preparation can be found in our previous publications [5, 6].

2.4 Cell Performance Characterization

The cell performance was characterized with *IV* (current-voltage) -curve measurements in a solar simulator, electrochemical impedance spectroscopy (EIS), steady-state polarization, and open-circuit voltage decay (OCVD) measurements. Optical measurements on the UV-VIS spectral range were also performed to examine the light absorption in the cell components.

3 RESULTS AND DISCUSSION

3.1 Stability of the Metals in the Electrolyte

Soaking and encapsulation tests verified that StS was the only metal suitable as a DSC substrate without a protective coating [5]. StS sheets were employed both as PE and CE substrates, as illustrated in Figure 2. Encapsulation tests also showed that even if the metal was instable in the electrolyte, the corrosion of the metal surface is not detrimental to the cell operation but the loss of triiodide ions from the electrolyte, due to the redox reaction $I_3^- + M \rightarrow 3I^- + M^{2+}$ ($M = \text{metal}$). Gradual loss of the electrolyte layer color indicated the proceeding of the redox reaction, and this simple visual inspection proved to be a

quick and straightforward method to preliminarily test the stability of the metals in unpolarized state.

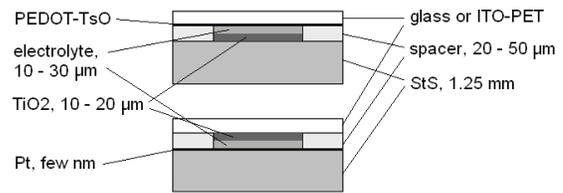


Figure 2: StS-based cell geometries. StS as the PE (upper; here with a PEDOT-CE) or CE substrate (lower).

3.2 Cell Performance

Table 1 lists the *IV*-parameters (I_{sc} = short circuit current, V_{oc} = open circuit voltage, FF = fill factor, η = energy conversion efficiency) of the different cell types (cell active area 0.32 cm², TiO₂ film thickness 10-15 μm), and Figure 3. presents the *IV*-curves of the best StS-PE cells, both obtained with 100 mW/cm² AM1.5 G equivalent light intensity. For the measurements, the cells were equipped with masks to reduce stray light [7].

Cell types in Table 1 are the following: 1: glass PE, liquid electrolyte, Pt-glass CE (standard DSC); 2: glass PE, liquid electrolyte, StS-CE; 3: StS-PE, liquid electrolyte, Pt-glass CE; 4: StS-PE, gel electrolyte, Pt-glass CE; 5: StS-PE, gel electrolyte, Pt-sputtered ITO-PET CE; 6: StS-PE, gel electrolyte, PEDOT ITO-PET CE.

| Cell type | I_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | η (%) |
|-----------|--------------------------------|--------------|----------|------------|
| 1 | 14.0 | 0.704 | 0.58 | 5.8 |
| 2 | 13.6 | 0.663 | 0.40 | 3.6 |
| 3 | 12.2 | 0.675 | 0.57 | 4.7 |
| 4 | 12.4 | 0.618 | 0.57 | 4.3 |
| 5 | 11.8 | 0.597 | 0.54 | 3.8 |
| 6 | 5.9 | 0.603 | 0.59 | 2.1 |

Table 1: *IV*-parameters of the StS-based cells vs. the standard DSC configuration.

The StS-PE cell configuration was chosen for further research because, in order to maintain flexibility in a StS-CE cell, the PE should be deposited on plastic. Since plastic foils cannot stand high temperature treatments such as 450 – 500 °C sintering of the TiO₂ film, it leads to poorer PE quality and lower cell performance. StS-PEs on the other hand, can be sintered in elevated temperatures, which yields good and mechanically stable electrodes. As it can be seen from Figure 3, the performance of an StS-PE, Pt glass CE and gel electrolyte cell is almost equal to that of a similar cell with a glass PE. The efficiencies of our uncoated StS-PE DSCs are among the highest reported [8-9].

The performance of the platinized StS CE was not satisfactory. The charge transfer resistance (R_{ct}) on the Pt-StS – electrolyte interface was larger than that obtained with the standard DSC CE, platinized glass (data not

shown) and the fill factors of the StS-CE cells were low. The latter can be explained with the larger R_{ct} , and possibly also with the different adhesion of platinum on these two substrates. The adhesion of thermally deposited Pt on StS is not as good as on FTO-glass [5], which can lead to inefficient charge transport and additional resistive losses between the Pt layer and the substrate. It is also possible that the iron and/or other ingredients of the steel have a harmful effect on the Pt's catalytic function.

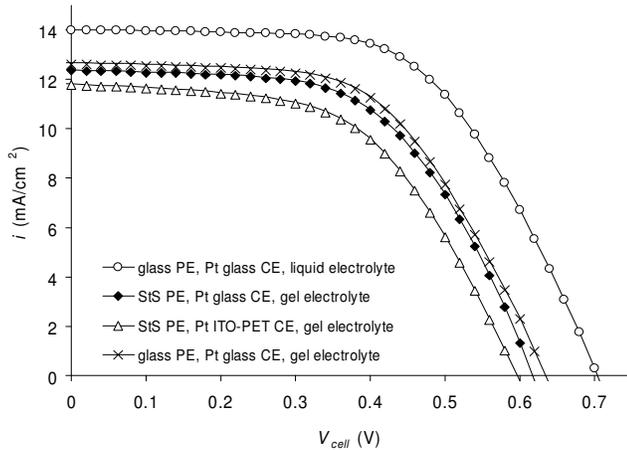


Figure 3: *IV*-curves of the best StS-PE cells (glass PE cells as a reference).

3.3 Optimization of the StS-PE Cell Structure

In order to reduce the optical losses, caused by light absorption in the counter electrode and the electrolyte, these cell components have to be optimized. In the case of the CE, this requires a trade-off between high enough transmittance but still high enough catalytic activity (amount of the catalyst) for the triiodide-iodide redox reaction in the electrolyte. Of the catalysts tested on ITO-PET, 1-4 nm layer of sputtered platinum gave the best results (cell type 5 in Table 1 and "Pt ITO-PET CE" in Figure 3).

To minimize the losses in the electrolyte, caused by the triiodide ion's strong absorption on the visible wavelengths, both the electrolyte layer thickness and the I_3^- concentration $[I_3^-]$ were reduced. Decreasing the electrolyte layer thickness from the standard 40 μm to 20 μm increased the I_{sc} and the efficiency 9 %. A 16 % increase in efficiency was gained when both the electrolyte layer thickness and $[I_3^-]$ were reduced, the latter from the standard 0.05 M to 0.03 M. Dilution of the whole electrolyte was also tried and it increased the efficiency to some extent, but not as much as in the case of dilution of only the triiodide concentration. The decreased concentrations of the other electrolyte species may have a negative effect on the cell operation

which is why decreasing the concentration of I_3^- alone is a better way to optimize the electrolyte.

3.4 Leakage Current from the Substrates

Substrate-mediated recombination, i. e. leakage current from the PE substrate has been suggested to necessitate the use of a barrier layer between the substrate and the nanoporous TiO_2 film [8]. We have measured the leakage currents from different substrates and investigated the use of atomic layer deposited (ALD) compact TiO_2 thin films (4 nm and 35 nm) as a recombination barrier and their effect on the DSC performance.

In our measurements, leakage current from bare StS was smaller than that from FTO glass [10]. In the case of dye-covered substrates (representing the situation in the real cells, where the substrate on the bottom of the pores of the TiO_2 film is covered with a monolayer of dye), the leakage currents were about the same both with the StS and the FTO glass. This verifies that substrate-mediated recombination is not a problem with StS.

However, other interaction mechanisms seem to exist between the dyed TiO_2 film and the StS substrate, even though the exact nature of these mechanisms has not yet been clarified. For example, based on the electron lifetime (τ_{eff}) measurements in the TiO_2 film (EIS and OCVD), TiO_2 -mediated recombination appears to be enhanced in the StS-PE cells. This didn't cause notable changes in the *IV*-curves, but showed as shorter τ_{eff} in the StS-PE cells, compared to the glass PE cells, at typical DSC operating voltages, where recombination via the TiO_2 film dominates over the substrate-mediated process [10]. Barrier layer might prove useful in inhibiting these mechanisms, were they identified as detrimental to the cell operation or long-term stability.

3.5 Cell Size Upscaling

Upscaling the StS-PE based DSC is one of the main focuses of current research. This far, cells up to 6 cm x 6 cm have been prepared (Figure 4). While the superior conductivity of the StS substrate obviates the use of additional current collectors on the PE, the lateral resistance of the CE substrate is still the main problem in the cell size upscaling. To reduce this resistance, current collector stripes were either hand-painted with conductive silver paint, or deposited by inkjet-printing with silver nanoparticle ink on the CE substrate (ITO-PET and as a reference, FTO-glass). At the moment, the best energy conversion efficiency gained with a 6 cm x 6 cm DSC with an StS-PE, sputtered Pt ITO-PET CE and liquid electrolyte has been 1.4 % (in comparison, 1.5 % with a thermally platinized glass CE). Research with the CE current collector structures continues, as well as further optimization of the cell structure (e. g. incorporating carbon nanomaterials into the electrode films to improve charge transport and

conductivity) along with long-term stability tests of the StS-based cells.

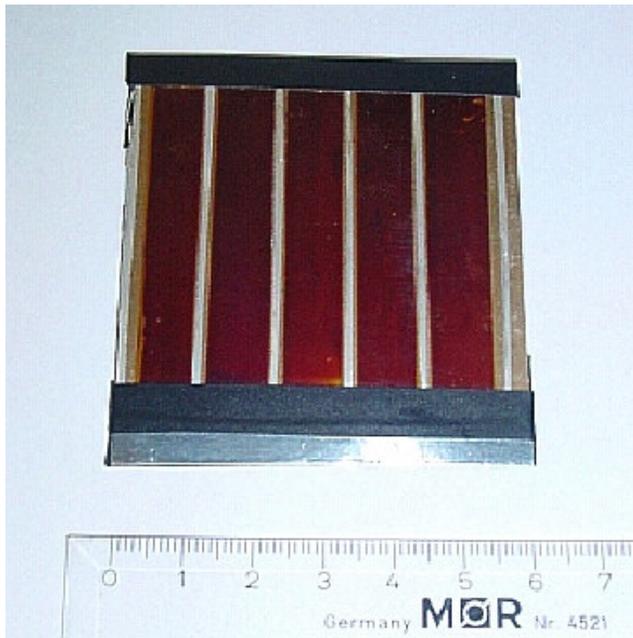


Figure 4: A 6 cm x 6 cm DSC with a StS-PE. Grey lines are the current collector stripes, red color the active area of the PE.

4 CONCLUSIONS

We have demonstrated an all-flexible, roll-to-roll producible, metal-based dye solar cell. The corrosive iodine electrolyte typically used in the DSC narrows the range of metal materials suitable as a substrate, but based on our soaking and encapsulation tests, stainless steel is stable enough in the electrolyte to be used as a substrate uncoated. In our cells, StS works as the photoelectrode substrate, while a Pt-sputtered, conductive ITO-PET plastic foil is employed as the counter electrode. The electrolyte is gelatinized to improve the mechanical stability of the cells.

StS substrate has many advantages, such as superior electrical conductivity, cost-efficiency, flexibility and mechanical robustness, in comparison to the traditionally used conductive glass. Our research has also shown that substrate-mediated recombination is even slower from StS than from glass. The opaqueness of the StS sheet requires lighting of the cell from the CE side. This results in optical losses, which can be minimized, however, with optimization of the electrolyte and CE structures. After optical loss reduction, with StS-PE (uncoated StS, active area 0.32 cm², 1 sun illumination), gelatinized iodine electrolyte, and Pt-glass or Pt ITO-PET CE, respectively, 4.3 % and 3.8 % total energy conversion efficiencies have been obtained [10].

With large, 6 cm x 6 cm StS-PE test cells the efficiencies are around 1.5 % at the moment but the goal is a 5 % efficient, stable cell/array. Room for improvement still exists, though on the other hand, the cell manufacturing process is upscaleable into industrial mass production and together with the cost-efficiency of the steel substrate, this makes manufacturing of even modest efficiency cells economically feasible.

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REFERENCES

- [1] B. O'Regan, M. Grätzel, *Nature*, 353, 737, 1991.
- [2] Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Seró, J. Bisquert, T. Bessho, H. Imai, *J. Phys. Chem. B*, 110, 25210, 2006.
- [3] N. Papageorgiou, W. Maier, M. Grätzel, *J. Electrochem. Soc.*, 144, 876, 1997.
- [4] P. Wang, S. Zakeeruddin, M. Grätzel, *J. Fluorine Chem.*, 125, 1241, 2004.
- [5] M. Toivola, F. Ahlskog, P. Lund, *Sol. Energy Mater. Sol. Cells*, 90, 2881, 2006.
- [6] M. Toivola, L. Peltokorpi, J. Halme, P. Lund, *Sol. Energy Mater. Sol. Cells*, 91, 1733, 2007.
- [7] S. Ito, K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. Zakeeruddin, M. Grätzel, *Prog. Photovolt: Res. Appl.*, 14, 581, 2006.
- [8] M. Kang, N.-G. Park, K. Ryu, S. Chang, K.-J. Kim, *Sol. Energy Mater. Sol. Cells*, 90, 574, 2006.
- [9] Y. Jun, J. Kim, M. Kang, *Sol. Energy Mater. Sol. Cells*, 91, 779, 2007.
- [10] K. Miettunen, J. Halme, M. Toivola, P. Lund, *J. Phys. Chem. C*, published on Web 02/19/2008.