SOLID-STATE DYE-SENSITIZED SOLAR CELLS: CURRENT STATE OF THE ART – CHALLENGES AND OPPORTUNITIES

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ABSTRACT: The first generation of dye-sensitized solar cell technology is based on a liquid electrolyte component. Today, this technology is on the verge of commercialization. The step towards the market and real applications is supported by the prospect low manufacturing costs, good efficiency as well as the expectation that the current stability level of this technology is at least sufficient for applications in mobile electronics. These favorable developments may be reinforced and accelerated even further, if the corrosive liquid electrolyte could be replaced by a non-corrosive solid, since this would ease a number of stringent requirements in the production process. A successful exchange of the liquid electrolyte by a solid-state holeconductor requires to at least maintain, preferably improve, the most relevant technical parameters of the solar cell (efficiency, stability, cost). First pioneering work with solid-state holeconductors was carried out 10 years ago with an initial efficiency level below 1%. Until 2007, the record efficiency could be improved to 5%. This paper gives an overview of the solid-state concept as an early stage approach with good perspectives for the mid-term future (~ 5-10 years).

Keywords: Dye-Sensitized Solar Cells, Solid State, spiro-OMeTAD

1 INTRODUCTION

Compared with liquid electrolyte based systems, solid-state dye sensitized solar cells (SDSC) offer the prospect of possible benefits in manufacturing processes, e.g., less stringent requirements for sealing and interconnection schemes on the module level and safe handling in a production process. In the liquid electrolyte DSCs the presence of a corrosive liquid, containing iodine leads to the requirement of protective coatings for internal interconnects or current collector grids.

However, the solid state DSCs are currently at a significantly earlier research stage and still inferior to their liquid electrolyte counterparts in terms of efficiency by a factor of about 2. The best results to date have been achieved with an amorphous molecular holeconductor, 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9' spirobifluorene (spiro-OMeTAD).

The efficiency gap between the solid-state and liquid electrolyte based DSCs (LDSC) - published record data are 5 % vs. 11 % on small, sub-cm^2 surface areas - is explained primarily by the fact that the best performance of current SDSC devices is achieved with TiO_2 layers, which are only 2-3 μm thick [1]. This is about 5 times less than required for optimal light absorption with typical dye sensitizers (maximum absorption coefficients are in the range of $1\text{-}2\cdot10^4$ $M^{-1}cm^{-1}$). This undesirable thickness limitation of the TiO_2 layers is related to an suboptimized kinetic competition between charge transport and interfacial recombination [2] as well as preparative challenges to achieve complete pore-filling of the regenerator into the porous TiO_2 films [3].

Here, we give a selective overview of promising recent developments in the field.

2 RESULTS AND DISCUSSION

2.1 Comparison between liquid-electrolyte and solid-state dye-sensitized solar cells (state-of-the-art)

The data in the following table show published data of important technical and economic solar cell characteristics (efficiency, stability, module costs).

	Liquid electrolyte	Solid-state
Record η	11% [4]	5% [5]
Stability	98 % after 1000 hrs, 1 sun, 80°C [6]	?
Cost	70-150 €/m^2 (<1 – 2.5 €/W_p [7]	?

For solid-state DSC reliable stability data and cost estimations have not yet been published, which reflects the early stage, pre-commercial nature of this concept. It is clear from the (missing) data in the table, that the solid-state approach – despite the expected benefits, described in the introduction – has currently not yet matured to a level, where it is competitive with the liquid electrolyte based systems.

2.2 Current technological challenges

This subchapter focusses on device efficiency exclusively due to a lack of sufficient data about device stability. The efficiency gap by a factor of 2 is related almost entirely to a lower current output of the solid-state DSCs (6-9 mA/cm^2 vs. 15-20 mA/cm^2). Voltage (> 800 mV) and fill factor (> 70%) on the other hand, are high and compare very well with the electrolyte based systems.

The straightforward reason for the substantially lower current output is that the peak performance for solid-state DSCs is currently obtained for a thickness of the TiO_2/Dye/spiro-OMeTAD layer of only 2-3 μm, which is about 5 times less than required for optimal light absorption. For comparison, LDSCs reach peak performance levels for layer thicknesses of typically ~10-15 μm. In other words, while any additional light absorption is transformed into an increase of the current output until reaching optical saturation according to Lambert-Beer´s law for LDSC devices, other current limiting factors come into play for SDSC devices before reaching optical saturation. These relations are illustrated schematically in figure 1, which shows the maximum expected current output for a dye sensitized solar cell as a function of the active layer thickness, assuming that no factors other than light absorption are limiting. The dotted line shows, in which way SDSC devices depart from this idealized behavior. The current output of LDSC devices on the other hand shows close to ideal behavior and follows the continuous line in the figure.

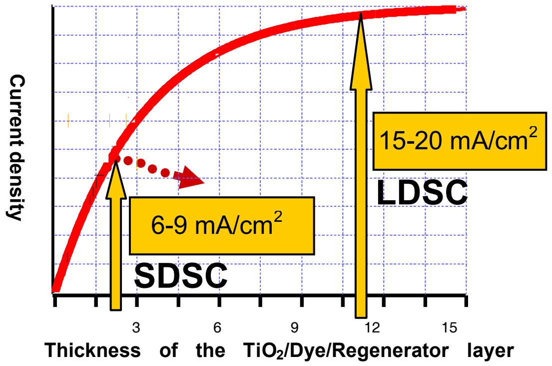

Figure 1: Maximum expected current output for DSC devices as a function of active layer thickness.

The question, which other factors than light absorption start to limit the current output of SDSC devices when increasing the layer thickness beyond 2-3 µm has been investigated by several groups. There is consensus, that both, incomplete infiltration of the solid-state holeconductor into the porous matrix of the TiO_2/Dye film (**pore-filling**) and faster **interfacial recombination** kinetics (for recombination of electrons in the TiO_2 with holes in the spiro-OMeTAD) are the key factors.

As far as pore-filling is concerned, two undesirable consequences can be differentiated, as proposed by Schmidt-Mende et. al [8].:

(1) In case that incomplete infiltration leads to areas inside the film, where dye molecules are not within the required intimate electronic contact to the spiro-OMeTAD, these dye molecules will not be able to contribute to the current output of the device.

(2) In case that incomplete infiltration can be rather imagined as the formation of a thin, but more or less quantitative coating of the internal TiO_2/Dye surface area, voids in the spiro-OMeTAD phase would be present which are not at the same time removing the intimate contact with the dye molecules. This case could lead to diminished electrical conductivity of the spiro-OMeTAD phase due to the reduced effective conduction cross-section as well as to an increased recombination probability (related to the confinement of the hole transport close to the TiO_2/Dye interface).

Both cases can be present and the experimental evidence available today does not allow to rule out one or the other.

As far as interfacial recombination is concerned, substantially faster kinetics of more than one order of magnitude have been measured for SDSC, compared with LDSC devices. This leads to an unfavorable shift of the kinetic competition between charge transport and recombination, which can be expressed as a decrease in electron diffusion length. Despite first studies investigating the dependence between diffusion length and applied bias, which indicate that the fill factor and the open circuit voltage, rather than the short-circuit current should suffer from increased recombination kinetics, this question is not yet fully resolved. Earlier studies with devices employing another solid-state holeconductor, the inorganic compound CuSCN, have shown, that all characteristic parameters (Isc, Voc and FF) were negatively affected by fast recombination kinetics [9].

2.3 Selected routes to overcome the efficiency gap

In the following, examples for three promising routes to overcome the limitations responsible for the efficiency gap will be shown: new dyes with increased absorption coefficients, interfacial engineering and advanced hole-conductor deposition methods. Two of them, new dyes and interfacial engineering, are investigated intensely since several years, profiting from the fact that this type of research is equally relevant for liquid electrolyte based cells. For SDSC devices, the largest share of efficiency progress since 1997 was related to innovations in interfacial engineering. The third route, advanced holeconductor deposition methods, is only starting to play a role in the current research agenda in the SDSC field and is specific to the solid-state concept.

A) New dyes: It is beyond the scope of this text to present a comprehensive picture of the exponentially increasing amount of work in this field. Next to new ruthenium dyes, there is a large number of new organic dyes. These latter ones often have maximum molecular extinction coefficients 5-10 times as high as the "traditional" N-719 or Z-907 dyes. Quantitative light harvesting within the absorption range of these dyes is feasible even with films as thin as 2-3 microns. For cases, where the absorption range is sufficiently broad, these dyes are clearly favorable compared with the "traditional" Ru-dyes in terms of overall light harvesting in thin TiO_2 layers. Despite that, new record efficiency values have not yet been obtained with these organic dyes. Less favorable charge transfer kinetics may be the reason for that, but further optimizations are expected to lead to the desired success.

As an example of this development, figure 2 shows the chemical structure of an indoline dye, D-102, with wich 4% efficiency was achieved using a 1.6 µm thin TiO_2 film [11].

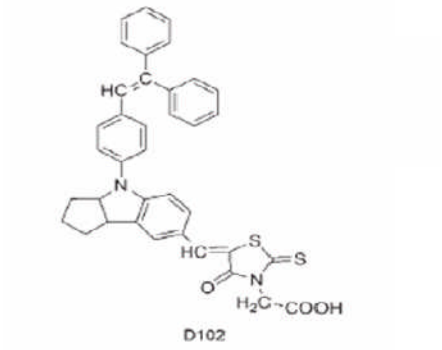

Figure 2:
The indoline dye D-102, an organic sensitizer with excellent light harvesting properties in the visible range.

B) Interfacial engineering: One way, that interfacial engineering can benefit the development of SDSC devices is by slowing down interfacial recombination processes. Recombination is believed to occur via trap states at the surface of the TiO_2 particles. These states may be exposed directly to the holeconductor molecules at the interstitial gaps between the dye molecules. A direct interface between the electron conducting TiO_2 particles and the hole conducting spiro-OMeTAD molecules is undesirable and enhances recombination. Saturating such trap states by the adsorption of small molecules, like tert-butylpyridine (tbp) can avoid the formation of such a direct interface. In SDSC devices the application of this concept, using tbp, resulted in a doubling of the Voc (from ~ 400 mV to ~ 800 mV). Another example of interfacial engineering is the application of dyes with different hydrophilic or hydrophobic side groups. This allows changing the surface wettability of the dye coated TiO_2 surface with the holeconductor solution during the solution deposition of the holeconductor and also with the solid holeconductor itself after solvent evaporation. Systematic studies of this type have not yet been carried out, but the hydrophobic side chains of the Z-907 sensitizer have been postulated to be beneficial in terms of wettability.

3) Advanced holeconductor deposition methods: Currently the holeconductor is deposited by spin-coating from a chlorobenzene solution. Apart from the fact that spin-coating is not a credible method for future up-scaling, the choice for a solution based deposition method in general may not be optimal. In fact, complete pore-filling should be hard to obtain using a solution based method: even if one speculates that the pores of the TiO_2 film are fully filled with the spiro-OMeTAD solution at a certain time after the application of the holeconductor solution to the porous TiO_2/Dye film and before spinning, a large fraction of the filled porous space consists of solvent molecules at this point. The volume fraction of the solvent in typical spiro-OMeTAD solutions is between 85 – 90 % (!). When the film dries after spincoating, the solvent molecules, leaving the porous matrix can indeed be expected to leave behind voids.

As indicated at the beginning of section 2.3, very little work has been dedicated to tackle this issue so far. It would seem obvious that an increased holeconductor concentration would be desirable. This has indeed been observed when varying the spiro-OMeTAD concentration in the initial optimization work of this system. The current concentration is therefore already close to the saturation limit of spiro-OMeTAD in chlorobenzene, which was chosen as a solvent for the same reason (highest solubility of the spiro-OMeTAD compared with other common solvents like toluene, for example). As far as the solubility limit and corresponding solid/solvent fraction is concerned, new innovations are required, e.g. by systematic studies with new holeconductor materials in combination with extensive solvent screening. Removing solvents from the deposition process entirely by using solvent-free deposition methods could also be of evident interest in this context as long as the chemical integrity of the holeconductor is not affected and the holeconductor molecules are provided with sufficient molecular mobility to diffuse into the pores of the TiO_2/Dye matrix.

5 CONCLUSIONS

The current status and challenges of the field of solid-state dye-sensitized solar cells was discussed as well as a selection of possible solutions to these challenges. Current bottlenecks for further progress in efficiency are expected to be overcome in the near future.

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