7 Summary and outlook

The present study focused on the development of environmentally sustainable and low-cost dye sensitized solar cells (DSSC). A new cell concept was developed that aims to replace the toxic and volatile organic solvent of liquid DSSC. At the same time the standard DSSC used as a reference in many experiments was significantly advanced in terms of initial efficiency and long term stability. Finally a diffusion model for electron transport in nanoporous TiO_2 was developed based on the parameters extracted from photovoltage/photocurrent measurements.

In detail the following points were worked on:

1) Nano Surface Conductivity Solar Cell (NSCSC)

The NSCSC utilizes the ambient humidity as a solvent. Hygroscopic salts are deposited on the nanoporous TiO_2-particles that are partly dissolved by the humidity of the ambient atmosphere to form a supersaturated electrolyte film. The main advantage is that the cell does not have to be sealed and that there is still a percolating network of pores present that allows the deposition of coadsorbents through the gas phase.

A conversion efficiency of 2 % could be demonstrated so far. The lower conversion efficiency compared to liquid DSSC is mainly due to a lower short circuit current and a lower fill factor. Transient photovoltage measurements revealed that the poor IPCE of NSCSC is mainly due to an enhanced recombination rate at the TiO_2/electrolyte interface, which is in average 50 times higher. At the same time it was demonstrated that hole mobility in the electrolyte film does not limit the overall charge transport for a light intensity < 10 $mWcm^{-2}$. At higher light intensity the hole transport is rate limiting and the short circuit current levels off at about 3.5 $mAcm^{-2}$ for a standard NSCSC.

Thus further development of the NSCSC needs to focus on the reduction of the recombination rate constant and the improvement of the hole conductivity within the electrolyte film.

Progress to slow down the recombination rate was made by adsorbing carboxylic acids, phosphonic acids and thiols through the gas phase. Using standard GC-MS equipment an apparatus was built that allows the deposition of any volatile compound in the nanomol range on the TiO_2-particles. Some of the coadsorbents could significantly improve the V_{OC} and I_{SC} of the NSCSC. For example after deposition of $1.3*10^{-10}$ mol benzylmercaptan on an active cell area of

1 cm² the open circuit potential increased by ca. 19 % and the short circuit current by ca. 8 %. The deposition of coadsorbents through the gas phase is believed to be a very promising technique to improve the rectifying properties of the TiO_2/electrolyte interface since it is applicable to millions of other organic compounds. It is believed that combinatorial experiments might play a key role in the future development of NSCSC.

With the same experimental equipment the influence of the solvent concentration on the V_{OC} and I_{SC} was quantified. It was demonstrated that about 6 monolayers of water are adsorbed on the TiO_2-nanoparticles in an atmosphere of 60 % relative humidity at 22 °C.

Upcoming work on the device should focus on the long term stability of NSCSC. Up to now a reasonable stability at room temperature in darkness could be demonstrated for one year. However, no systematic studies were undertaken so far. Furthermore stability test under illumination and/or elevated are needed to assess the limits of this new cell concept.

2) Aging of liquid DSSC

Systematic studies on long term stability at 80 °C in darkness for ca. 1000 h were done within a two month research internship at the Energy Center of the Netherlands, ECN. The so-called masterplate concept was applied, which allows the assembly of cells with highly reproducible IV-parameters. Five different parameters were investigated:

- water in the electrolyte

  It was demonstrated that the addition of up to 5 % water to the electrolyte can enhance the efficiency for certain electrolyte/dye combinations and does not effect the long term stability in accelerated aging tests. The highest conversion efficiency was 5.6 %. Employing the Z907-sensitizer and an electrolyte with 0.6 M DMPII, 0.5 M NMBI, 0.1 M iodine in propionitrile/water 95:5, 97 % of the initial conversion efficiency could be retained after 1000 h at 80 °C, demonstrating for the first time that the presence of water does not necessarily affect the long term stability of DSSC. By photovoltage transient measurements it was shown that a reduced recombination rate mainly contribute to the improved conversion efficiency. These findings raise hope that open cell concept of the NSCSC, which equilibrates with the ambient humidity, might be a feasible alternative to sealed DSSC.

- oxygen in the electrolyte

  It was proven that the saturation of the electrolyte with oxygen has no impact on the long

term stability of DSSC. By oxidation of iodide to iodine at the counter electrode according to

$$4I^- + 2O_2 + 4H^+ \rightarrow 2I_2 + 4OH^-$$

the oxygen depletes quickly in the electrolyte and already after 600 hours no differences compared to the reference cells were observed. However, by the reaction with unidentified contaminants in the electrolyte the initial short circuit current was found to be over 40 % lower.

- $TiCl_4$-treatment of the electrode

  The $TiCl_4$-treatment of the TiO_2-particles and successive annealing is known to increase the short circuit current and the conversion efficiency. In this study it was shown that an increased dye uptake and a shift of the TiO_2 conduction band to lower energy contribute to a higher I_{SC}. At the same time the recombination rate is significantly reduced. In long term stability test $TiCl_4$-treated cells degraded much slower. That stresses the importance of the TiO_2-film morphology and the binding mode of dye molecules for the performance of DSSC and further optimization of the TiO_2-particles are believed to be of fundamental importance for stable devices.

- purity of the electrolyte solvent

  The requirements on chemical purity for the performance and stability of DSSC have not been investigated so far. By comparing different batches of propionitrile in DSSC it could be proven that both initial efficiency and long term stability correlate very well with the amount of impurities. That stresses the importance that only purified chemicals should be employed in DSSC. By GC-MS most contaminants could be identified and quantified, however, the detrimental effect of each compound was not determined separately.

- layer thickness

  Some indications were found the additional dye stored in thicker TiO_2-layers act like a buffer in long term stability tests. Degradation or desorption of dye molecules is better compensated in thicker cells and a lower degradation rate was observed after exposure to 80 °C.

3) Transport model for semiconductor electrodes

A transport model based on the continuum equation for charge carriers in solar cells was

developed. It was demonstrated that the electron transport in the nanoporous TiO_2 electrode of DSSC can be treated independently from the hole transport in the electrolyte. The absence of a macroscopic electric field in the TiO_2 allowed further simplifications. The input parameters could be directly measured, thus no adjustable parameters were needed.

The model aims to understand electron transport in dye sensitized solar cells under various conditions. It was especially useful for the simulation of photovoltage/photocurrent transients at different points on the IV-curve. Furthermore it was used in the analysis of degradation in liquid DSSCs and charge transport limitations in NSCSC.