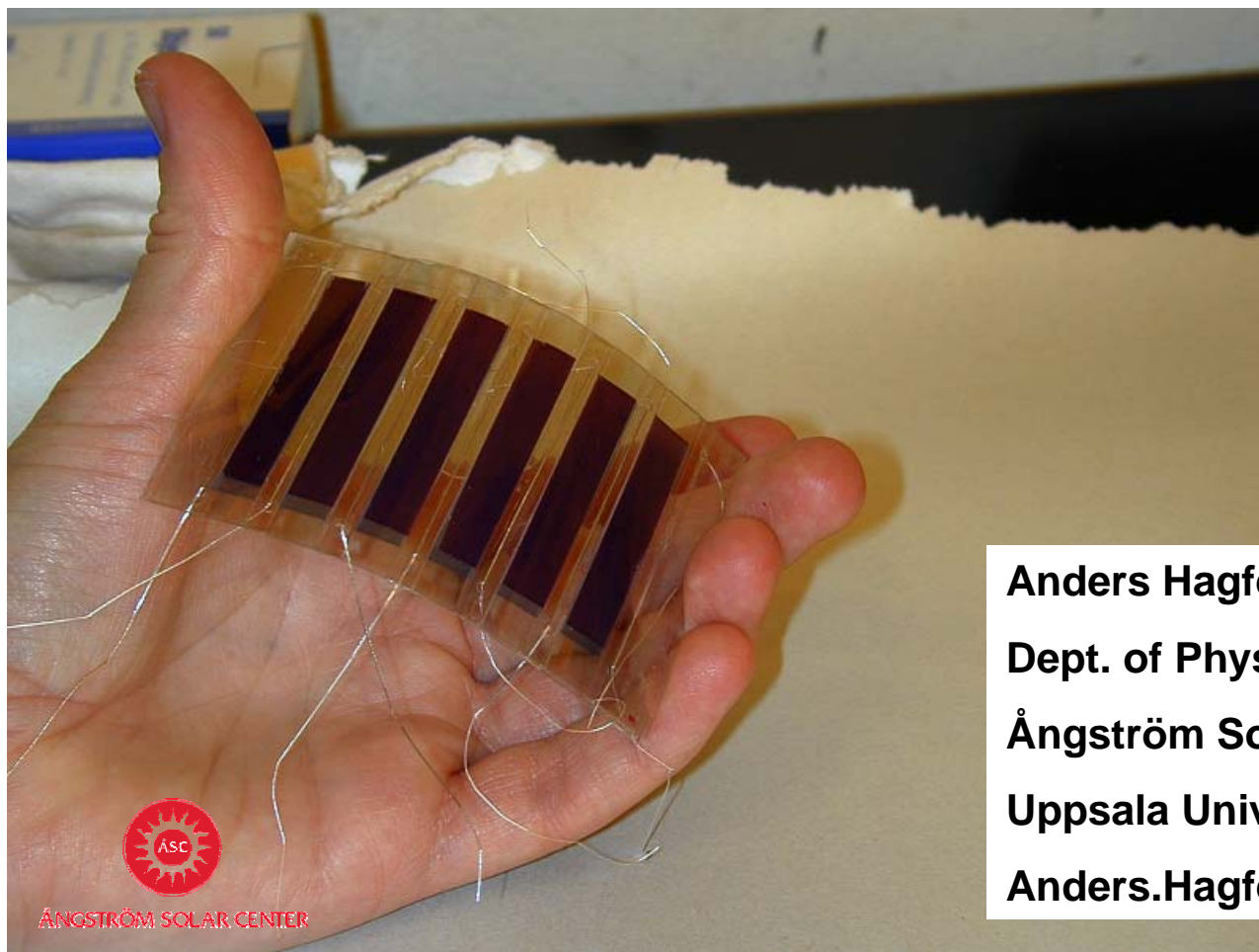


Stability of Organic Materials



Anders Hagfeldt

Dept. of Physical Chemistry

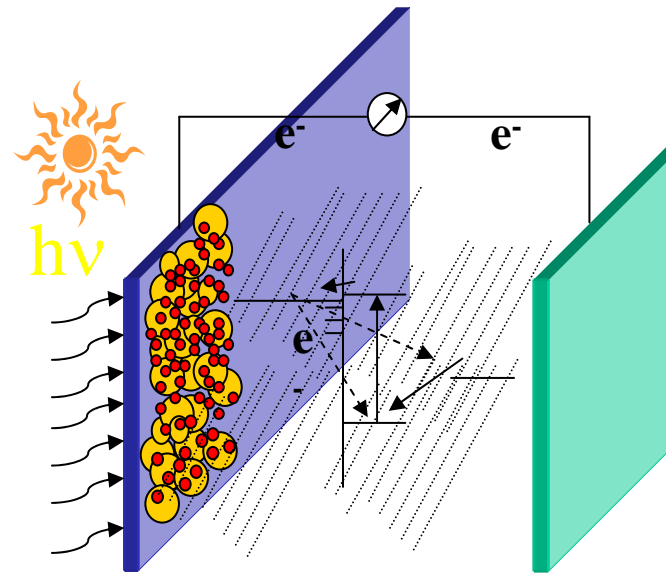
Ångström Solar Center

Uppsala University

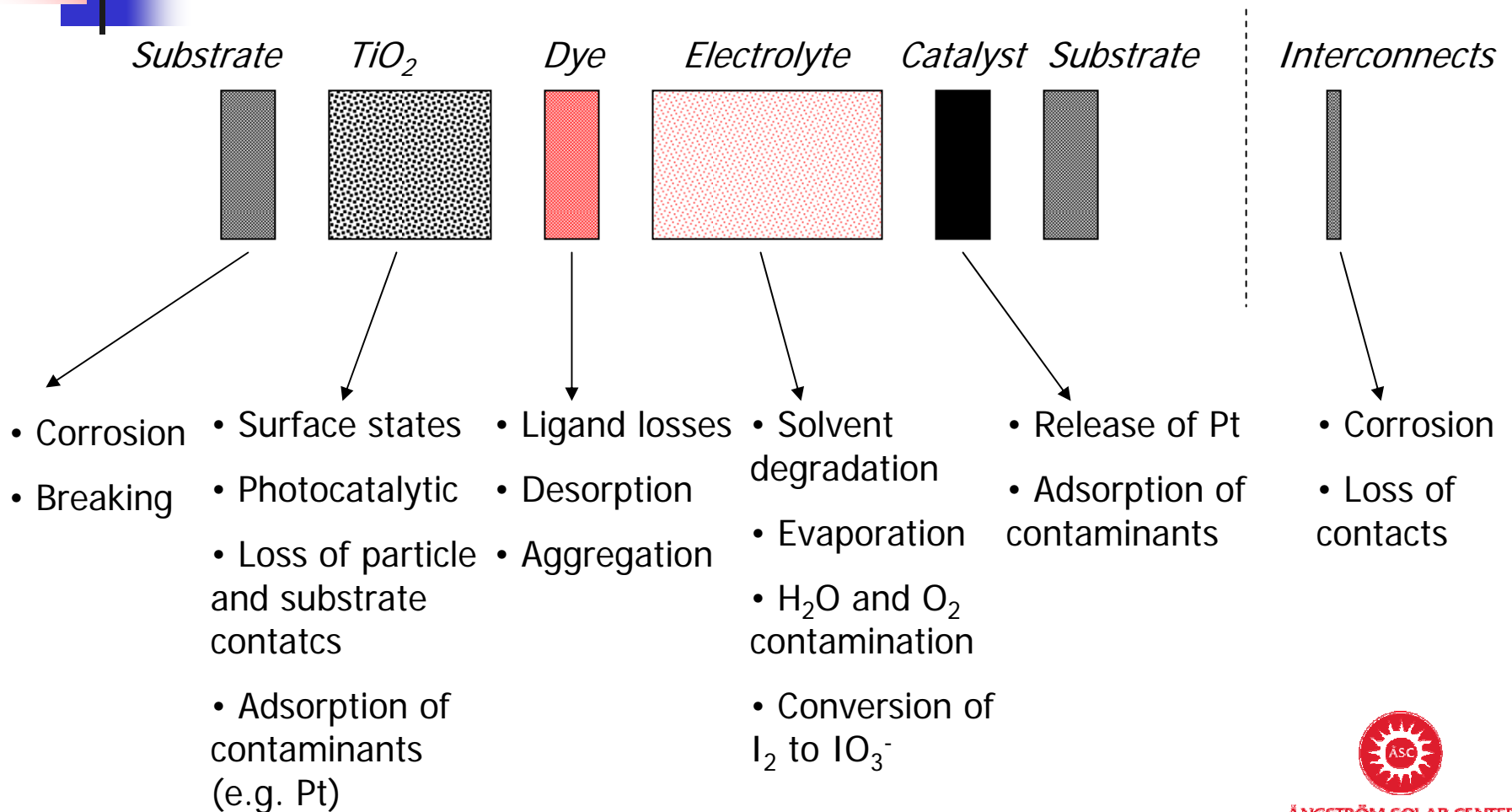
Anders.Hagfeldt@fki.uu.se

Specific features of DSC

- Charge separation and transport are separated
- Operation is based on kinetics and not a built-in electric field
- Kinetics and energetics are dynamic variables
- Dark and illumination measurements are not often correlated
- The processes are controlled at the semiconductor/dye/electrolyte interface



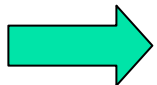
Possible degradation mechanisms in a DSC





Properties of the molecular components

- The dye is not stable in solution
- The oxidized dye in the DSC device has a life-time of about 1 second
- The intrinsic TiO_2 is an insulator
- The iodine based electrolyte is highly corrosive



Why does it work?





Stability arises from molecular interactions

Ex. The effect of the additive in the electrolyte

The additive improves the photovoltage

- reduce back reaction by blocking the surface
- shifting the CB – base effect

ECN, The Netherlands, showed that the additive improves stability

Additives: 4TBP (4-tert-butyle-pyridine)

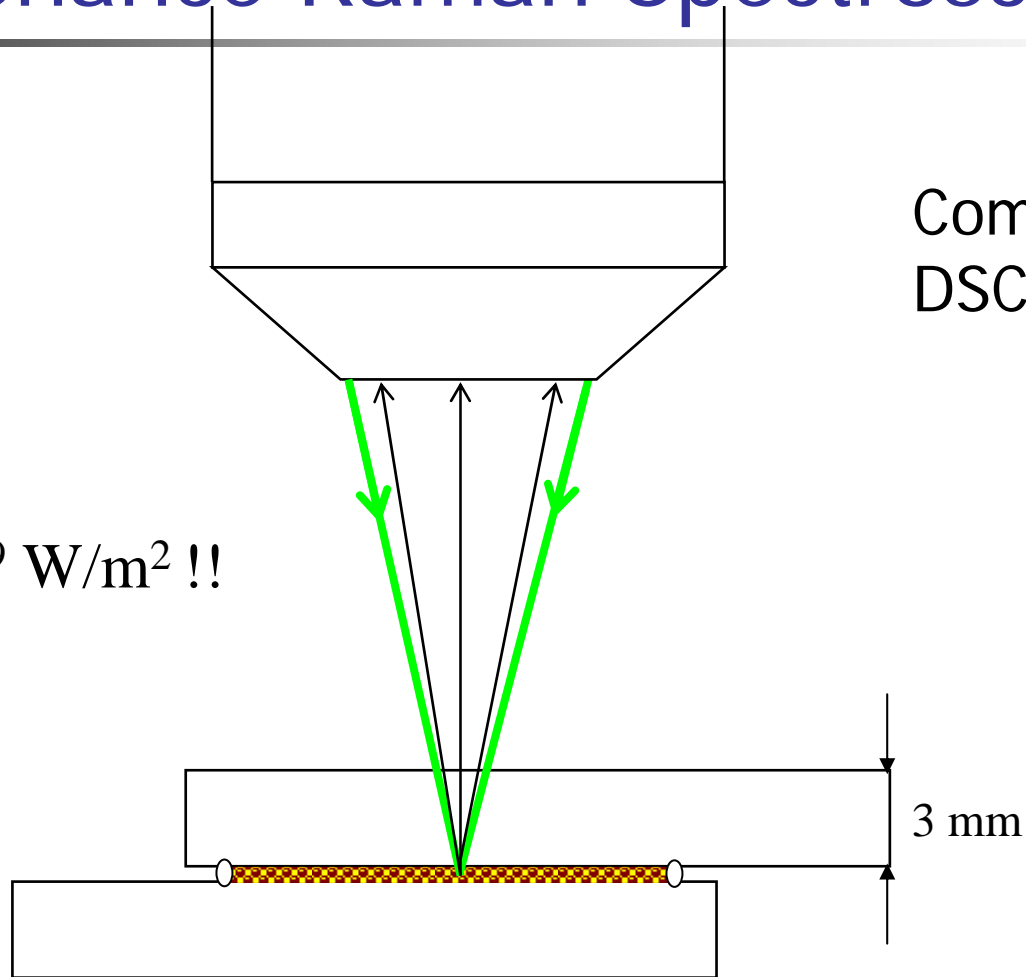


Resonance Raman Spectroscopy

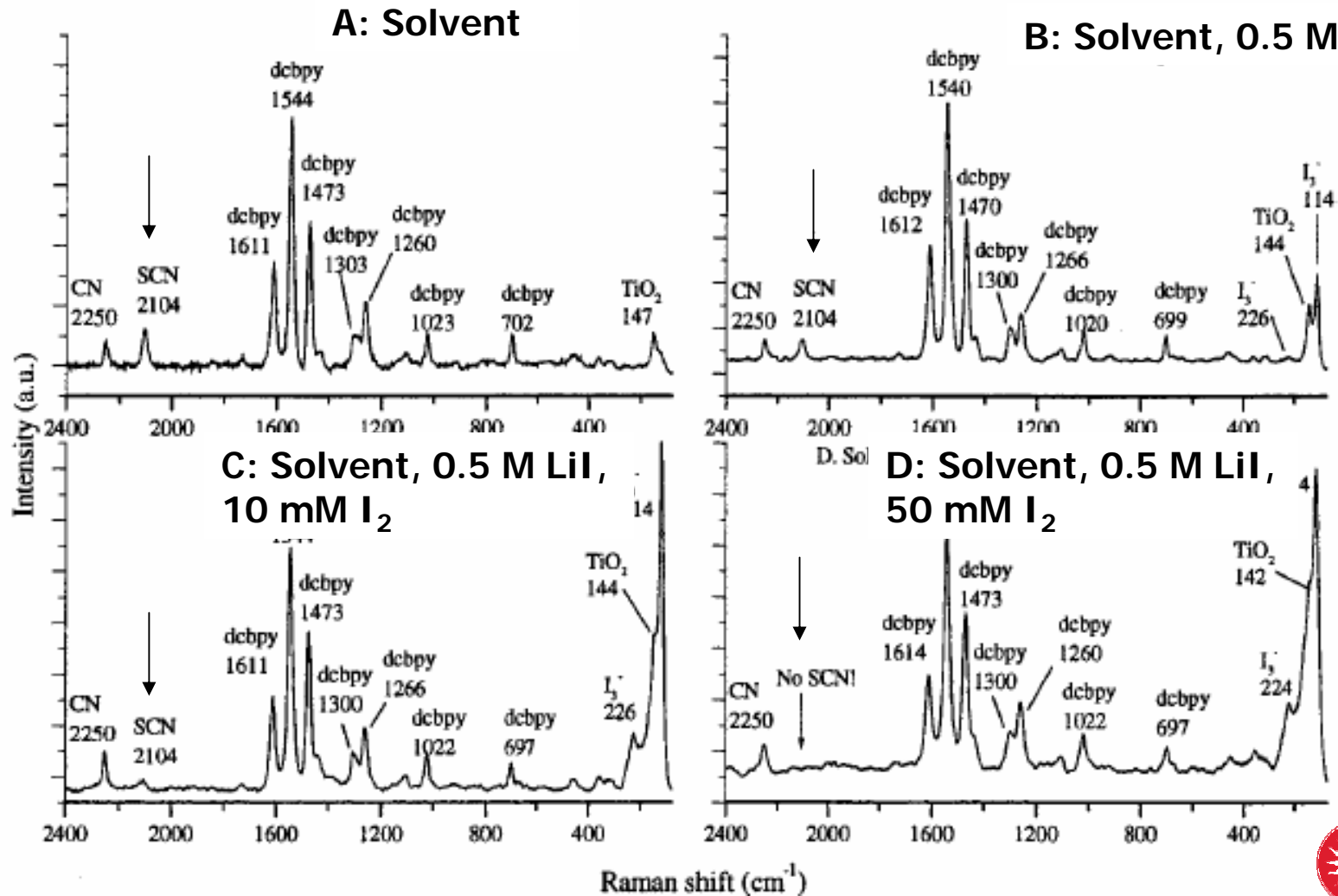
Green laser
 $\lambda=514 \text{ nm}$

Intensity: $2 \cdot 10^9 \text{ W/m}^2$!!

Complete
DSC devices

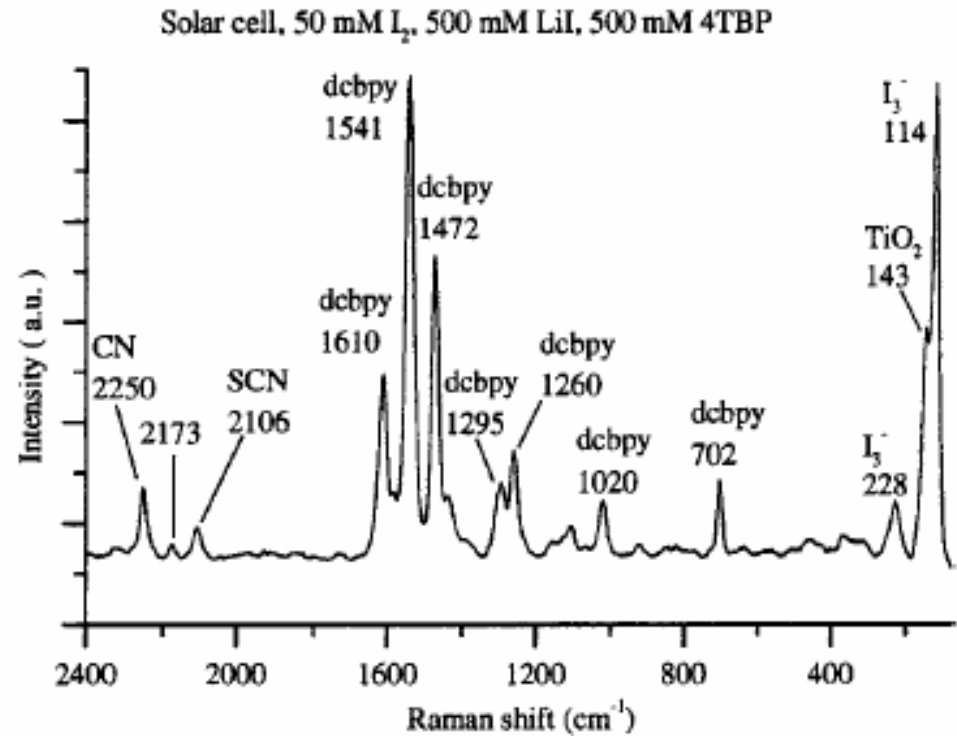


Variation of electrolyte composition



Effect of the additive

4-tert-butylpyridine
suppresses ligand
substitution





DSC Performance

■ *Efficiency*

- 11% for an area $< 0,2 \text{ cm}^2$
- 10,1% for an area $> 1 \text{ cm}^2$

Kroon et al., Proc. 19th EU PVSEC, June 2004, Paris

■ *Stability*

- Dye stability is at least 10^8 turnovers (corresponds to 15 years in sunlight)
- 6-7% efficiency (dark, $85 \text{ }^\circ\text{C}$, 1000h)
- 5% efficiency (1 sun, $45 \text{ }^\circ\text{C}$, 1000h)

Wang et al., Nat. Mater. 2 (2003) 498,

Sommeling et al., J. Photochem. Photobiol. A, 164 (2004) 137





Observations: DSC stability

- Results are lab-specific;
cell composition, purity of components, cell processing play an important role in the stability of the cells
- Compromise between top efficiencies and stability (dyes and electrolytes are modified)
- Importance of dye adsorption sites;
Photocurrent imaging techniques reveal that some spots of the cell degrade faster than others



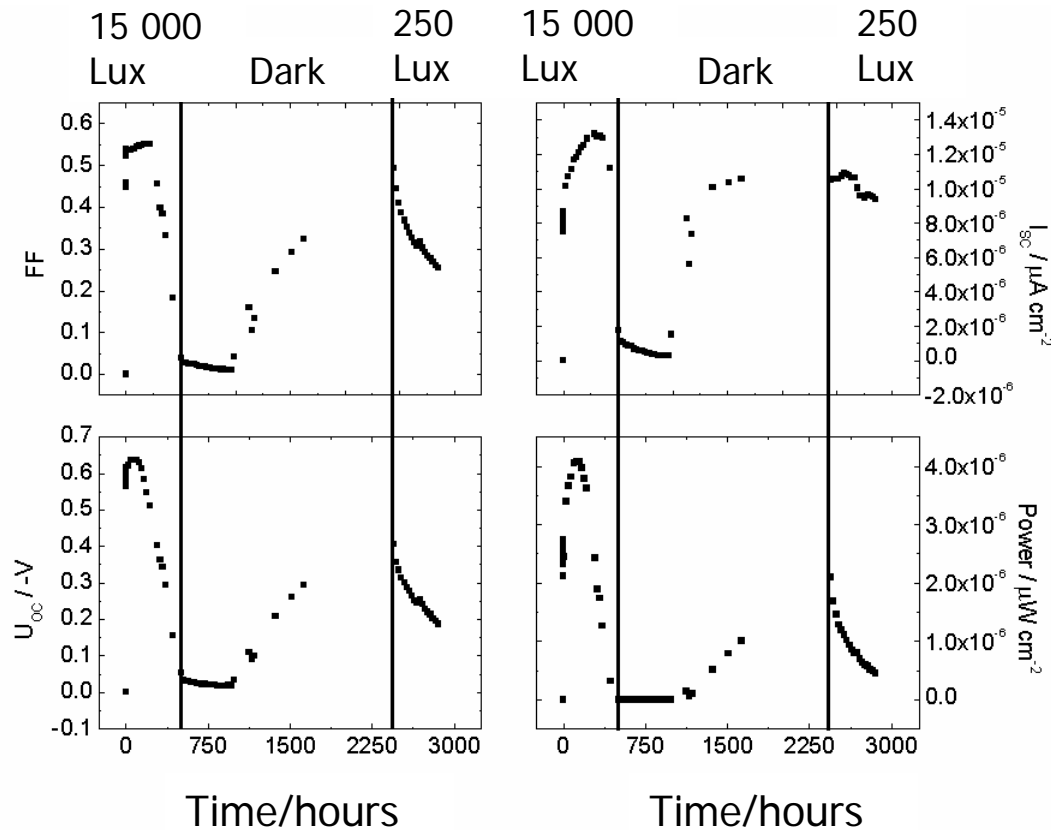


Observations: DSC stability, *cont.*

- Stability results depend on operating conditions (open circuit, short circuit, working point)
- Combined thermal annealing (85 °C) and illumination (1 sun) degrades the cell (loss of iodine)
- Recovery effects: Degradation of cells undergoing IEC tests (qualification test for Si-cells – dark, 85 °C) can be compensated by illumination, resulting in a recovery of the cell performance. Another recovery effect is shown on next slide. The effects depend on which electrolyte is used.



Example of a recovery effect



Plastic DSC cell developed for indoor applications

Exposed to light intensities where the photocurrent saturates, the power of the cell decreases. The power recovers after having kept the cell in darkness for some time.





Some conclusions

- Almost all scientific efforts have dealt with efficiency issues
- The molecular device is stable – not the molecular components on their own. The kinetics of the electron transfer processes between the molecular components need to be well balanced
- Standard tests for Si-cells are not relevant for DSC (IEC tests can be too pessimistic *and* too optimistic)



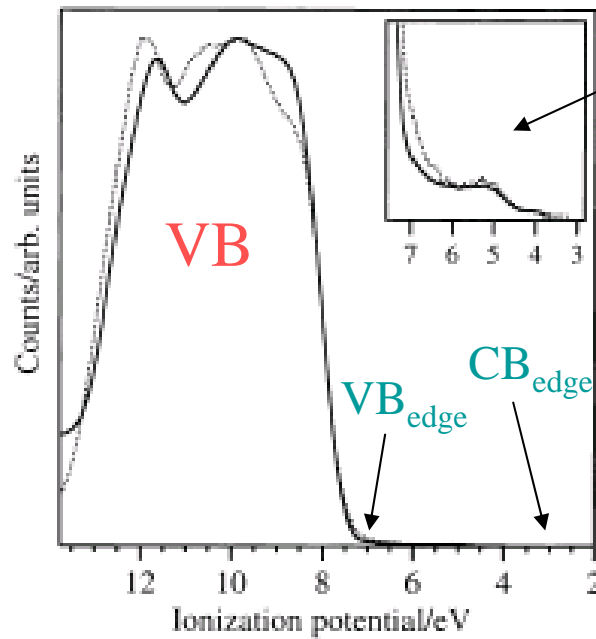


What do we do?

- Focus on improving cell *performance*, i.e. both efficiency and stability
- Need of general preparation protocols
- Develop relevant accelerated tests
- Tests under real outdoor conditions
- Develop an understanding of the molecular system – measurement techniques, simulations



Where are the traps?



Continuous
DOS in the
band gap

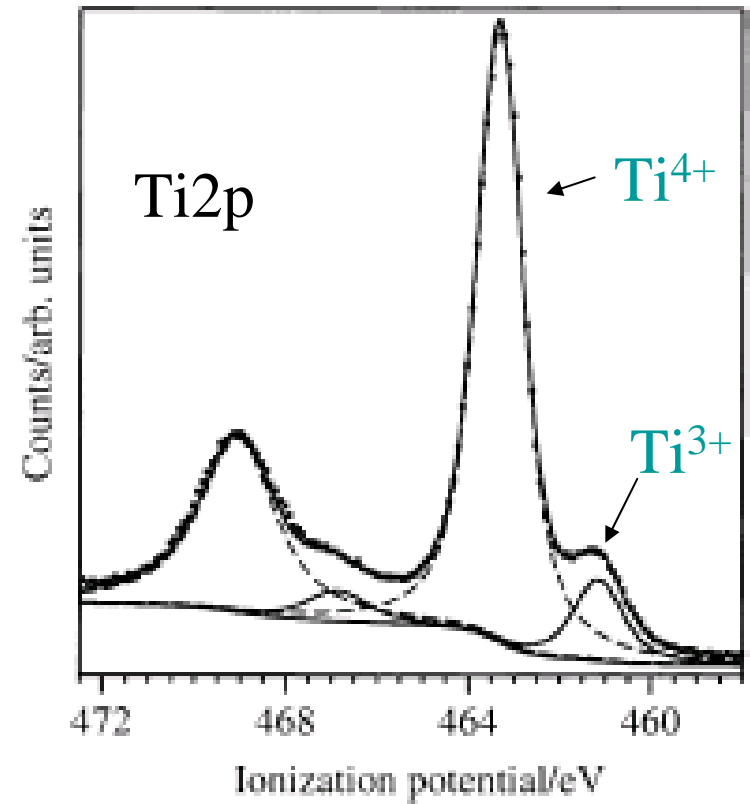
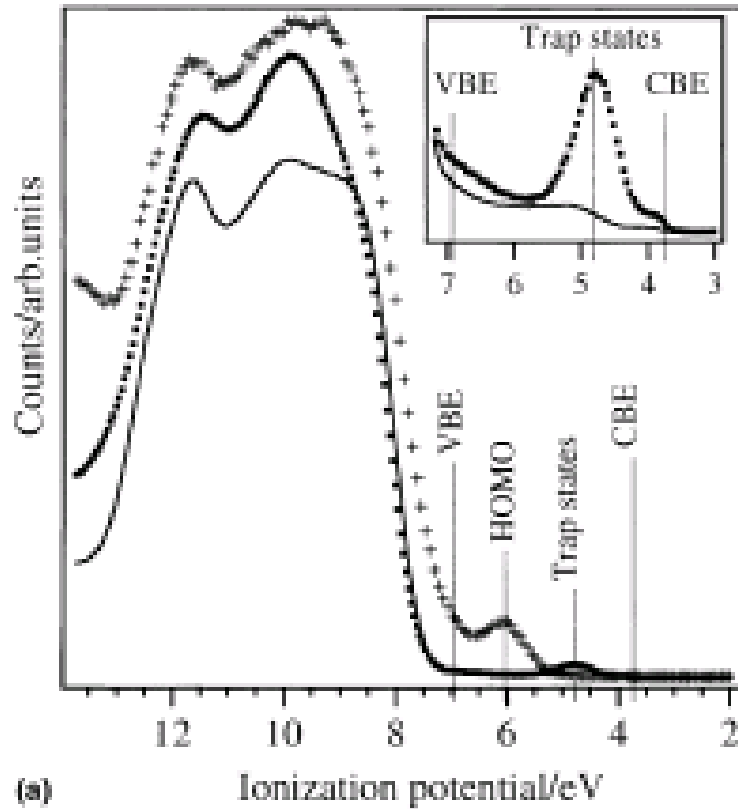
- Mesoporous TiO₂
- Single crystal rutile

Same number
of states

- Synchrotron radiation: 150 eV
- 10⁻⁷ mbar
- Resolution < 0.1 eV at FWHM



The TiO₂/Dye/Electrolyte Interface



- N3/TiO₂ Interface
- Electron injection followed by Li⁺ insertion

- Chemical nature of the trap states



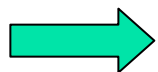
Development of measurement techniques – a DSC tool-box

The challenge:

- Determine the internal dynamics on *complete* devices under *working* conditions

Criteria

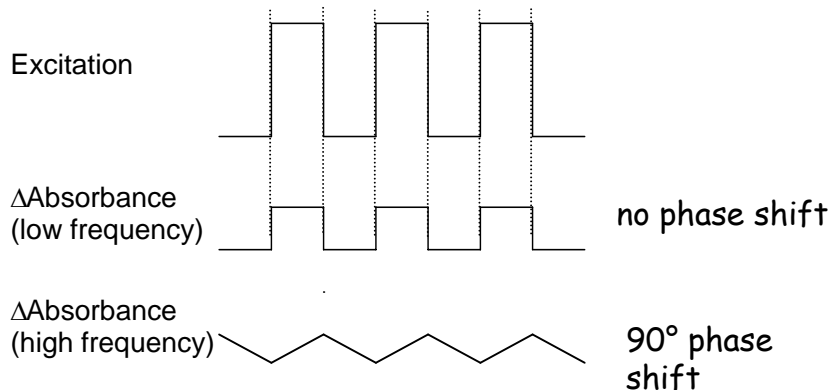
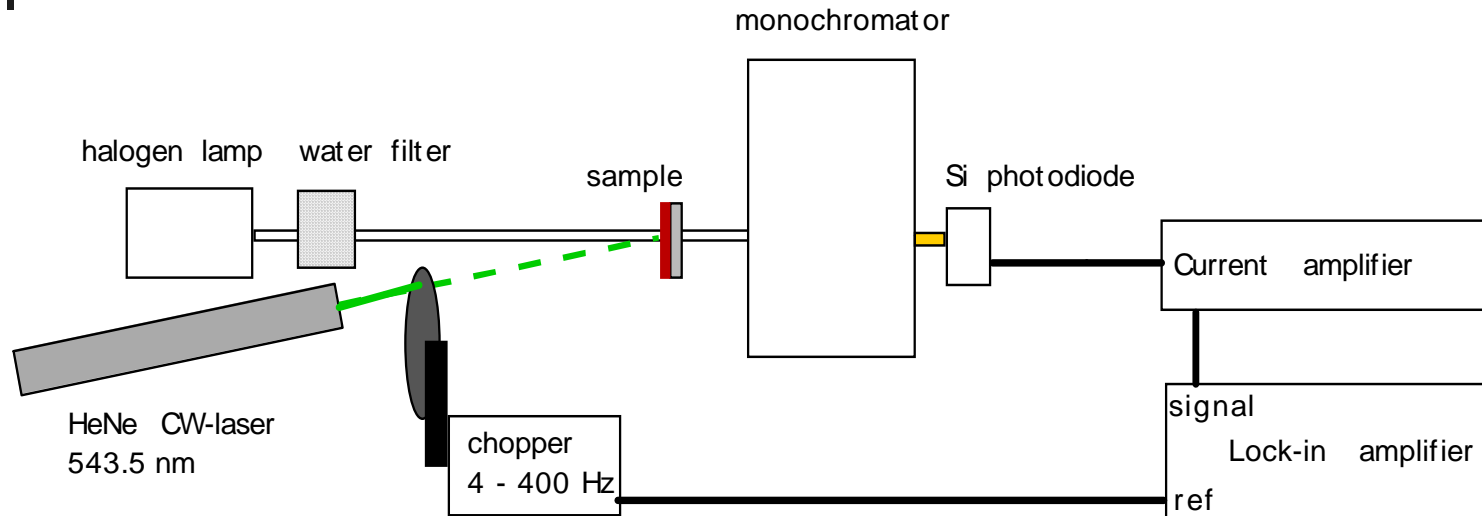
- Complete Devices
- Real Conditions
- Reasonable Measurement Time



IMPS, IMVS, PIA, Charge extraction, ...

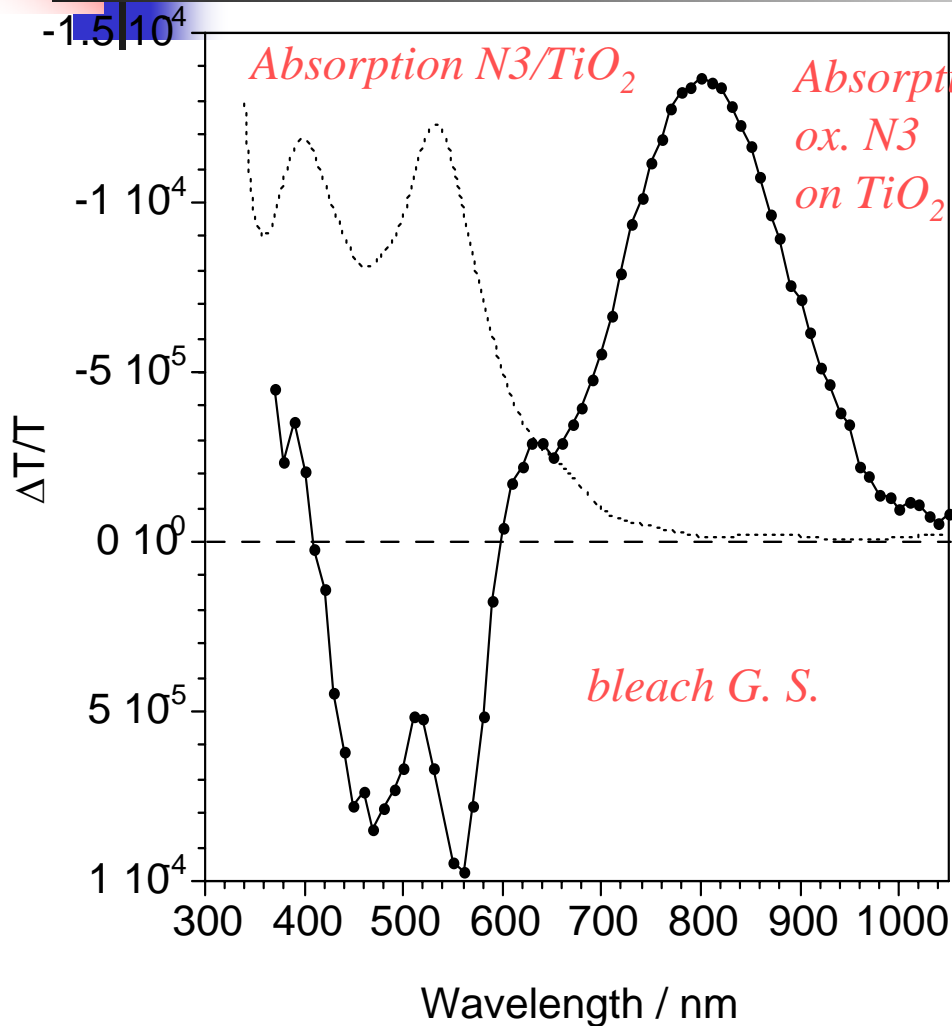


Ex. Photoinduced absorption spectroscopy



- $\Delta A \sim 10^{-6}$
- Complete solar cells or separate components
- 0.1 Hz – 10 kHz
- Combination with IMPS, ...

PIA of N3/ TiO₂

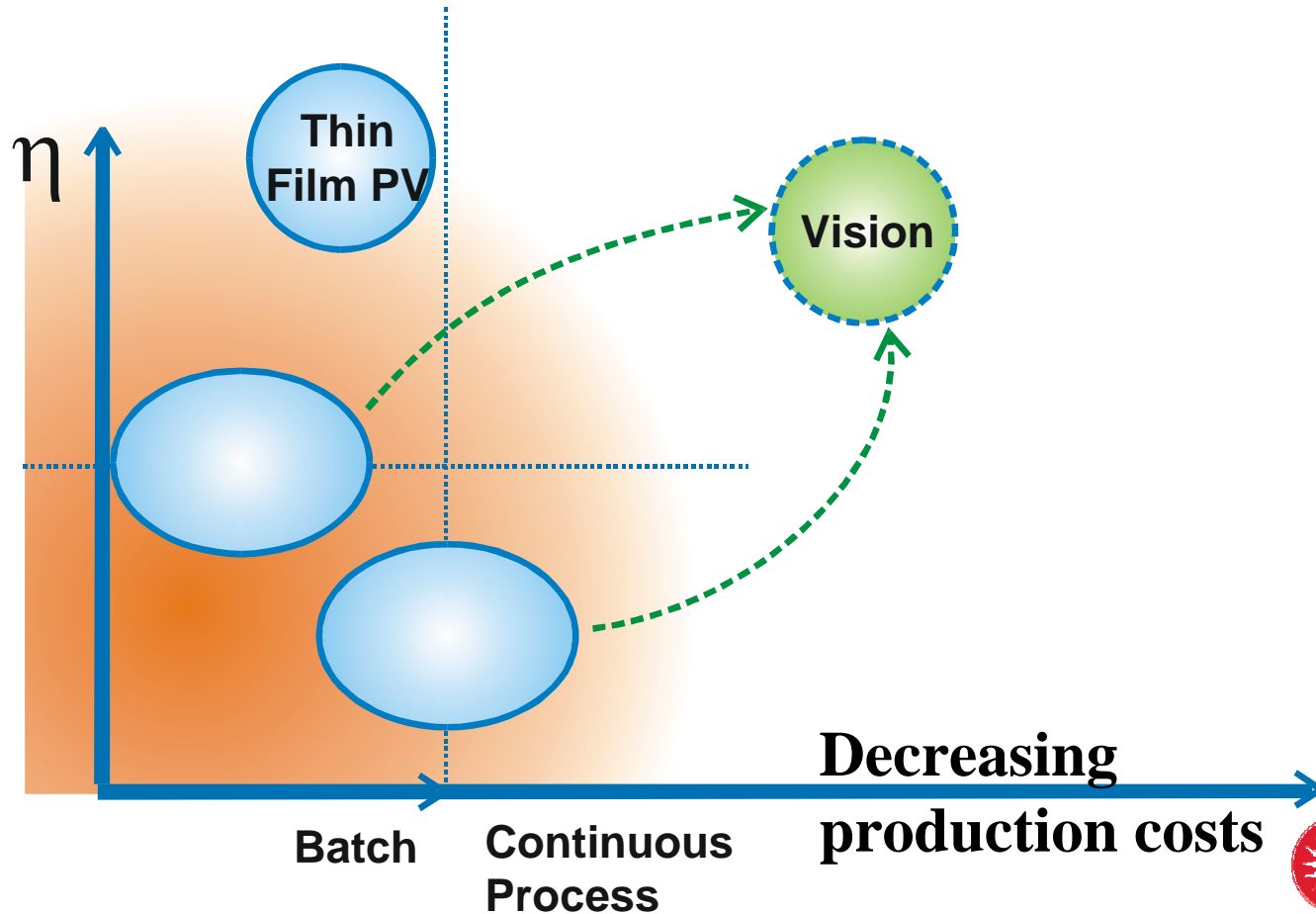


- 4 μm transparent mesoporous TiO₂
- Modulation frequency: 17 Hz
- Excitation 2.4 mW cm⁻²
- Measurement time: < 1h

*Life-time of Dye⁺ + e⁻(TiO₂):
1 ms under 1 sun*

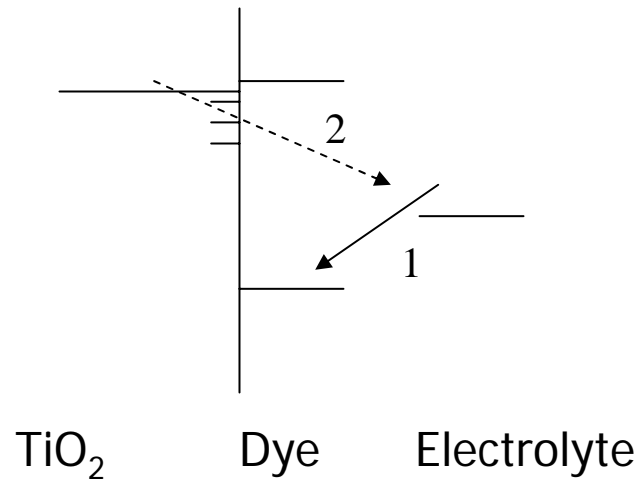


How to compete? Cost/Performance



How do we improve the performance?

Main losses

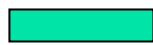


Design of new molecular components

- Oxide: Nanofibers
- Dye: HOMO/LUMO should be spatially separated
- Electrolyte: Efficient oxidant at the counter electrode and poor at the working electrode

How to decrease cost?

Low cost



Large volume production



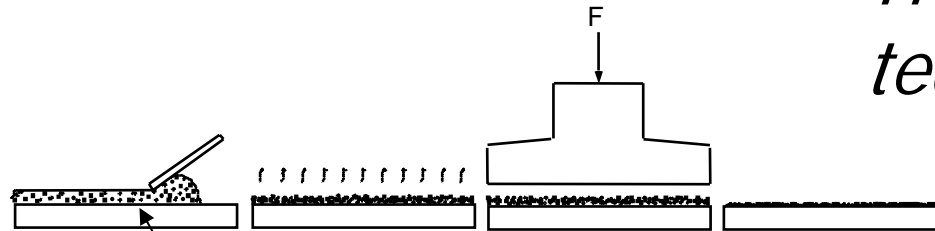
Continuous production process



Plastic substrates

*The Press-
technique*

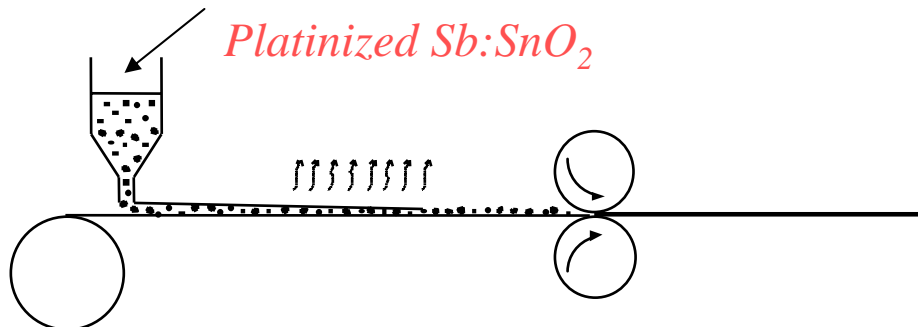
batch



TiO₂ powder,

Platinized Sb:SnO₂

continuous

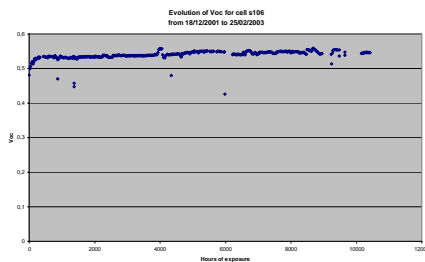


Plastic cell stability at indoor light

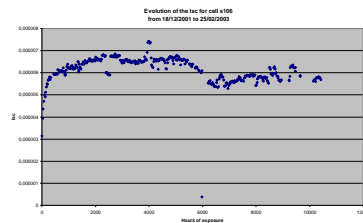
Proven stability for > 10 000 h under continuous indoor illumination (250 Lux)

Performance satisfactorily for different types of indoor applications

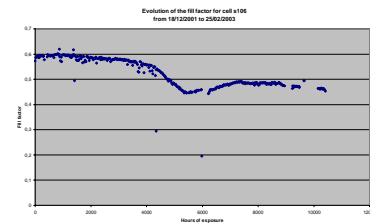
> 10 000 h illumination @ 250 Lux



$$V_{oc} = 0,55 \text{ V}$$



$$I_{sc} = 7,7 \text{ } \mu\text{A}/\text{cm}^2$$



$$ff = 0,48$$

Status Flexible DSC: Ångström Solar Center

	Technical Requirements	Market Potential
Indoor Applications	Yes	? → Yes
Outdoor Applications	No	Yes





Future work

- Basic research
 - Balancing the electron transfer processes
 - Control of the oxide/dye/electrolyte interface (why is the dye stable when it is adsorbed? Importance of adsorption geometry for stability, etc)
 - How to perform accelerated life-time tests
- Materials science aspects
 - For plastic cells in particular dyes and electrolytes
- Continuous processing (low-investment costs, reliability)
- Market entry through niche applications