The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1938-7

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Dye sensitized solar cells: toward a low cost, industrial viable, photovoltaics

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Aldo Di Carlo

CHOSE – Centre for Hybrid and Organic Solar Energy

Dept. Elect. Eng. - University of Rome “Tor Vergata”

EU Renewable Energy Road Map

The European Community has defined (10 Jan 2007) the following equation

20+20-20=2020

By 20**20** EU have to reduce by **20**% the CO_2 emissions increase by **20**% renewable energy and increase by **20**% the energy efficiency

http://ec.europa.eu/energy/index_it.html

Benefits:

- 443 billion euro investment 2001-2020
- 115.8 billion euro gained from fuel reduction
- 130 - 320 billion euro gained from additional costs
- 2 milioni additional jobs

Lazio Region activities on RES and efficiency

LAZIORINNOVABILE
RegioneLazio

REGIONE LAZIO

POLOIDROGENO
RegioneLazio

POLOMOBILITA'
RegioneLazio

POLOSOLAREORGANICO
RegioneLazio

CHOSE

Polo Solare Organico – Regione Lazio

CHOSE - Centre for Hybrid and Organic Solar Energy

2006

Objectives

- Research and Development on organic and hybrid photovoltaics
- Definition of a industrialization process for organic photovoltaics
- Technology transfer to Large and SME
- Reference point at Regional level on photovoltaic technologies
- Development of an Italian Network on photovoltaic technologies

- Today CHOSE involve 6 Tor Vergata teams (Engineering, Physics and Chemistry), 5 external teams (UniFerrara, UniSapienza, PoliTorino, UniTorino e CNR) ans several SME
- CHOSE has around 1000 m^2 of laboratories, with 35 Researchers (phD, PostDoc, Staff)

CHOSE – TT lab

CHOSE – Technology Transfer lab
@ Tecnopolo Tiburtino

CHOSE-TT lab is in the so called "Tiburtina Valley" of Rome where many high Tech companies have their R&D labs.

600 m^2 lab with 400 m^2 of Clean Room (ISO 7)

TT lab is mainly dedicated to the development of a pilot production line for DSC

CHOSE – ESTER lab

ESTER

ENERGIA SOLARE TEST E RICERCA
LABORATORI DI FISICA TECNICA AMBIENTALE
UNIVERSITÀ DEGLI STUDI DI ROMA 'TOR VERGATA'

Prof. Angelo Spena,
Prof.ssa Cristina Cornaro

Outdoor PV Test and meteorological station

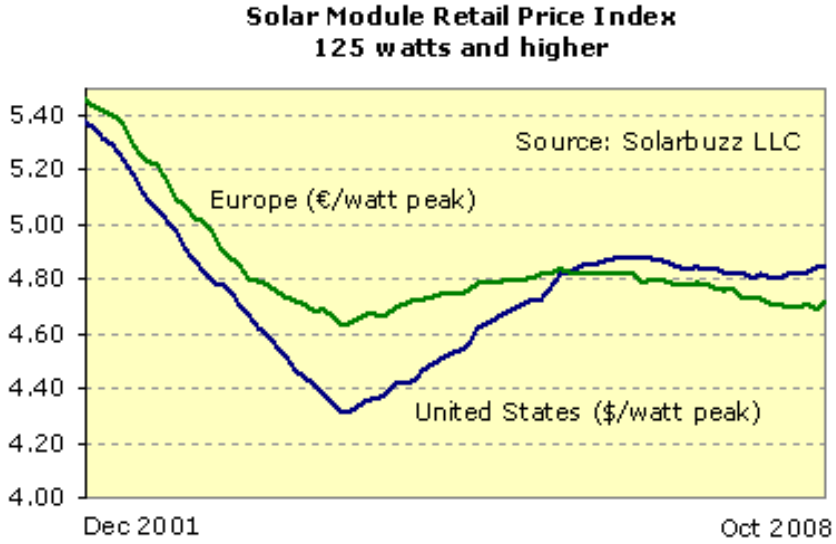
Main Characteristics:
- Meteorological station with also direct/indirect light intensity meas.
- up to 6 panel contemporary measurement with spectra meas.
- 2 rotation axis

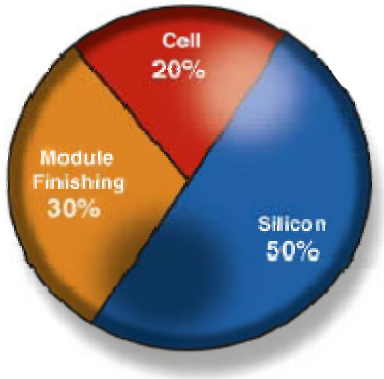
Energy from the sun

To satisfy the electricity needs of a typical family one needs 3kWp PV system, i.e. ~20m^2 of photovoltaic surface (assuming system efficiencies of 13%).

COST 20.000 euro

Cost reduction of PV systems per Wp/m^2 becomes paramount in order to make PV technology an important instrument for energy production.





Could we reduce cell cost ?

Silicon is quite expansive (2 euro/ Wp, one doping level)

Production plant are expansive (100 Meuro for 40 MWp/year amorphous silicon, 15Meuro for 30 MWp/year bulk silicon)

Energy payback is around 4 years for silicon cells, 2 years for a-Si

Is it possible to produce photovoltaic cell by reducting production and material costs ?

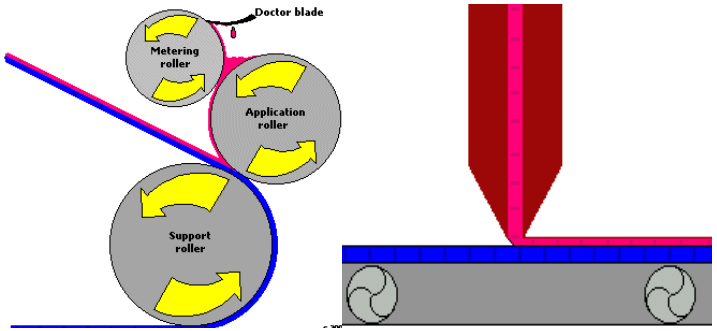
This is possible but we have to re-invent the cells

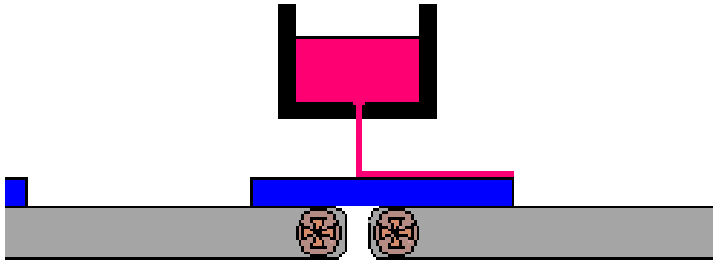
Organic photovoltaics

“New” manufacture processes

Conventional Electronics → **Organic Electronics**

Conventional semiconductor industry → **Printing methods**



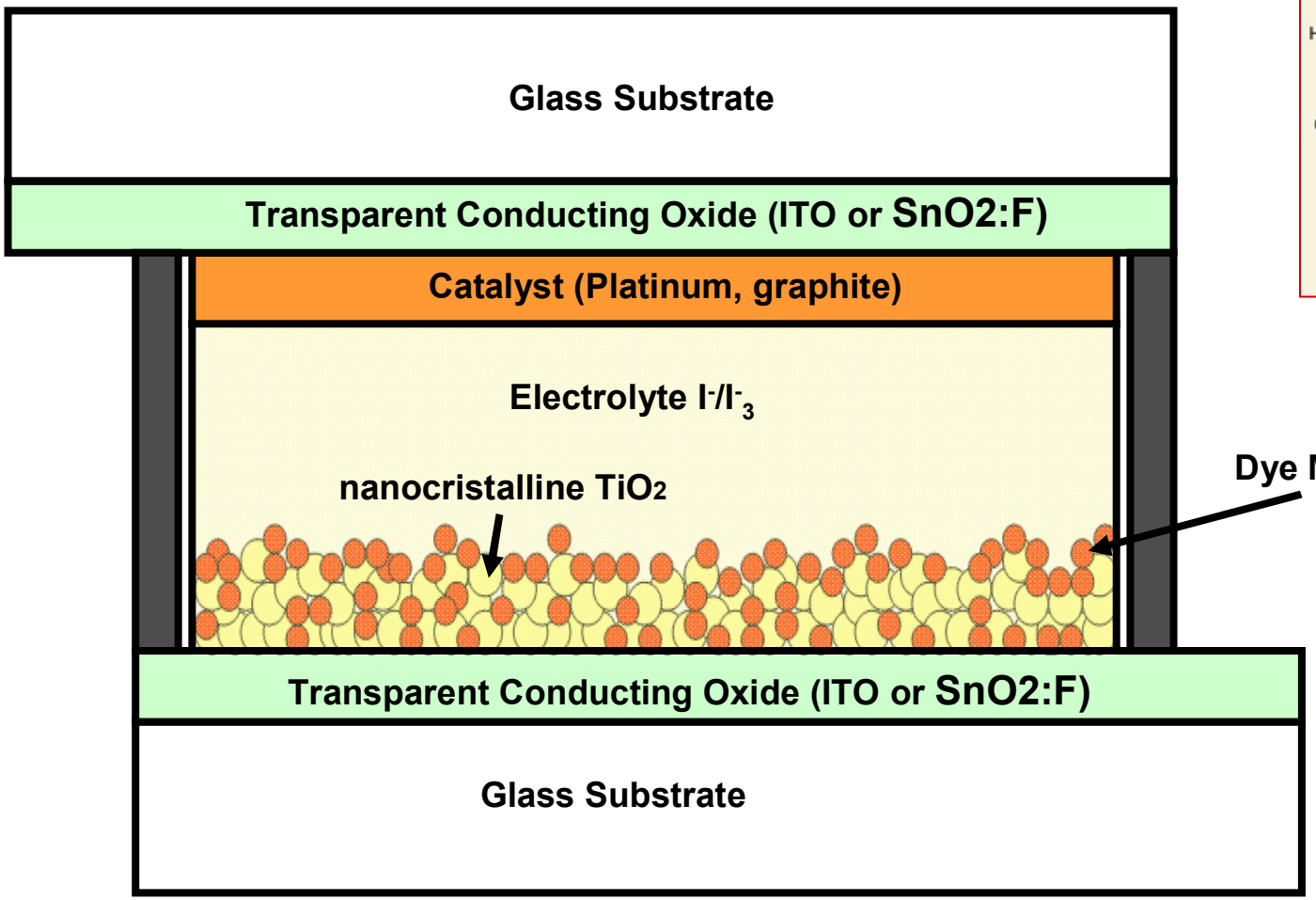


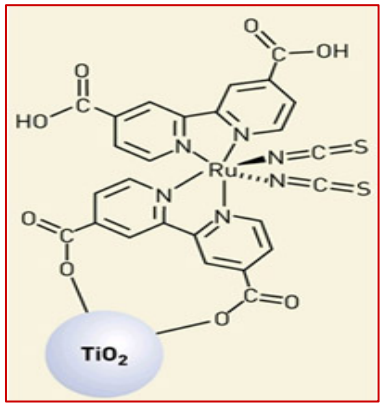
High temperature, doping, vacuum

Liquid deposition

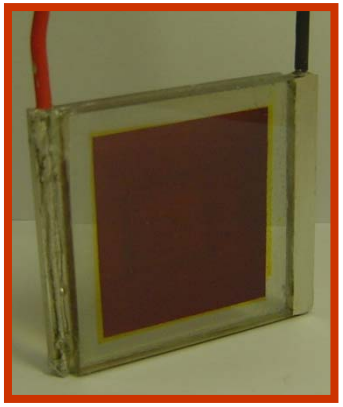
Large enterprises → **Small Medium enterprises**

Structure of Dye Sensitized Solar Cells

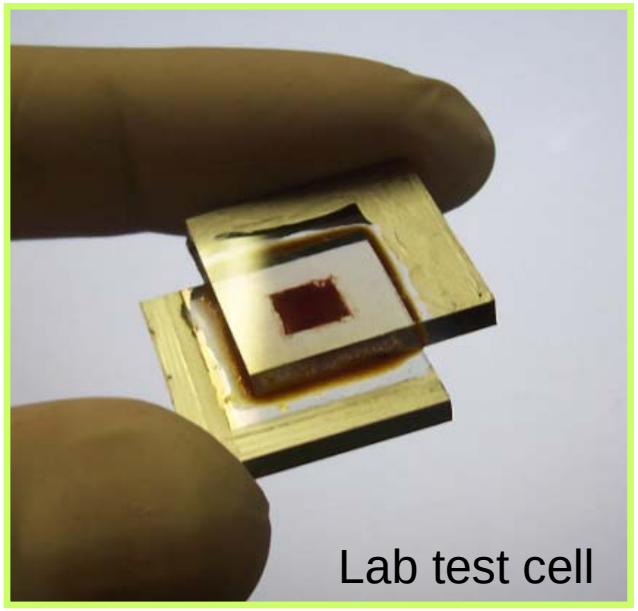


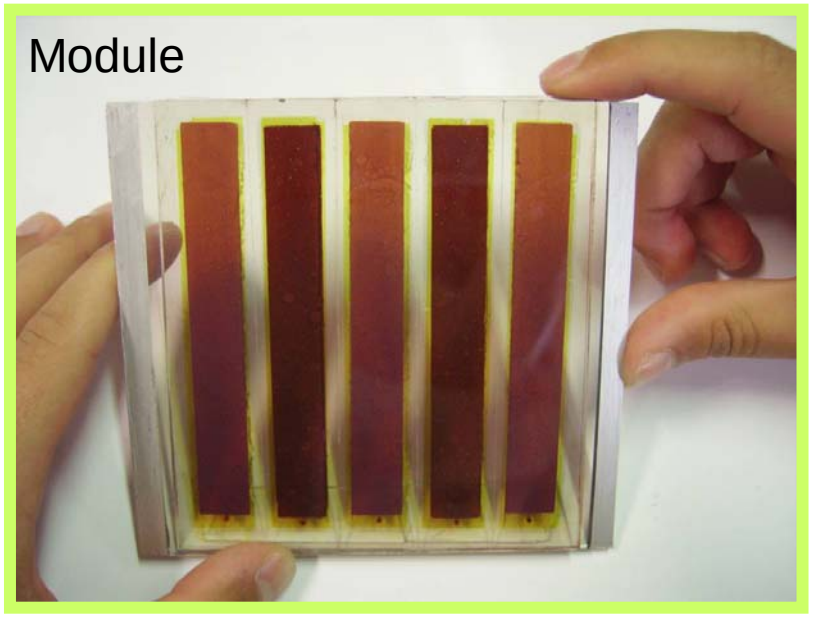


Dye Molecules on TiO_2



Cell and modules





- Optimization of the materials
- Optimization of the deposition
- Optimization of sealing

Cell optimization +

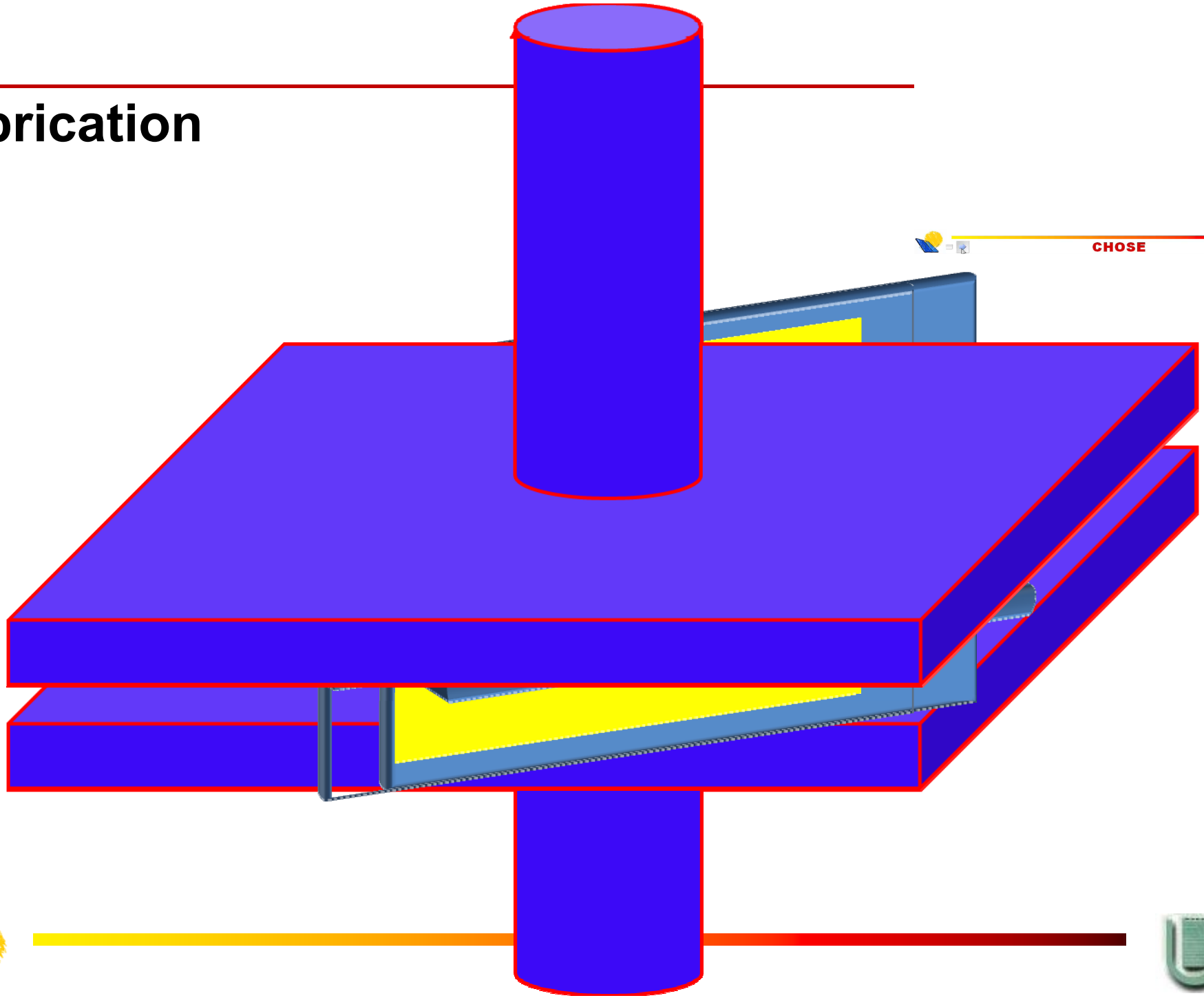
- inteconnections
- reduction of series resistance
- balance among cells
- Engineering of the module design

Scaling up is not trivial and it is one of the major problem !

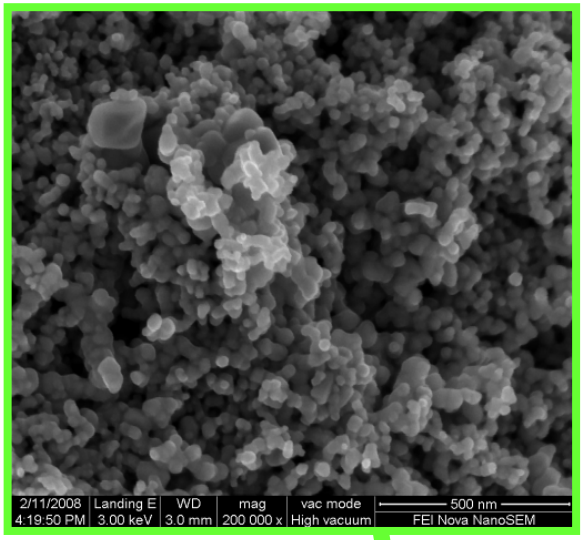
Fabrication

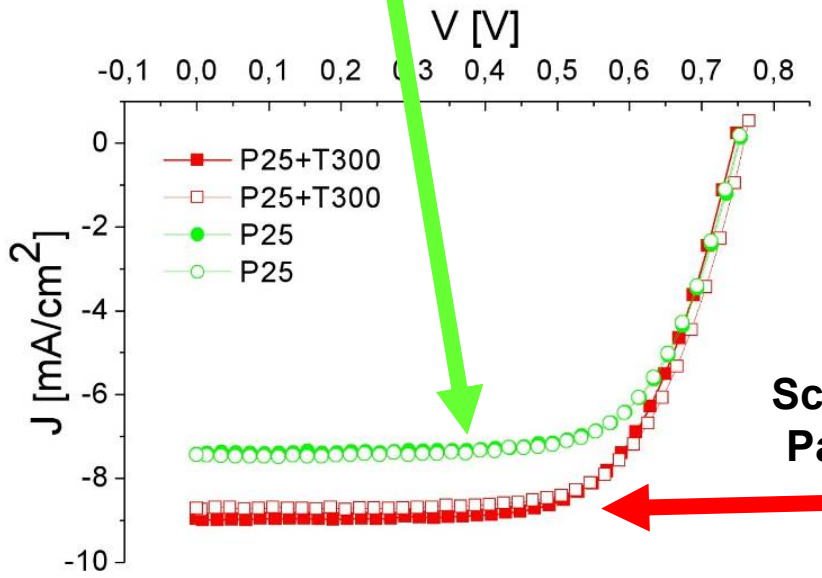
CHOSE

Movie

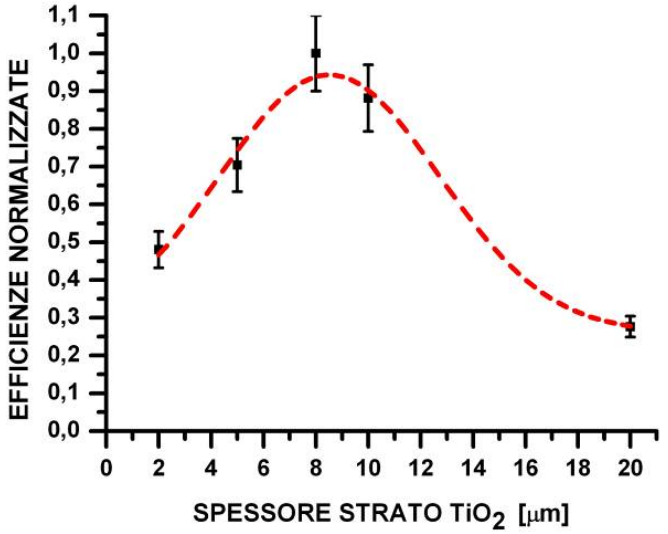


Optimization of TiO2 layer

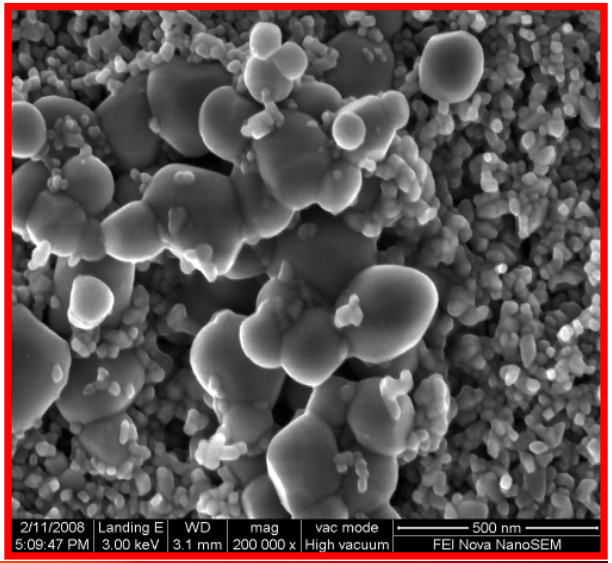




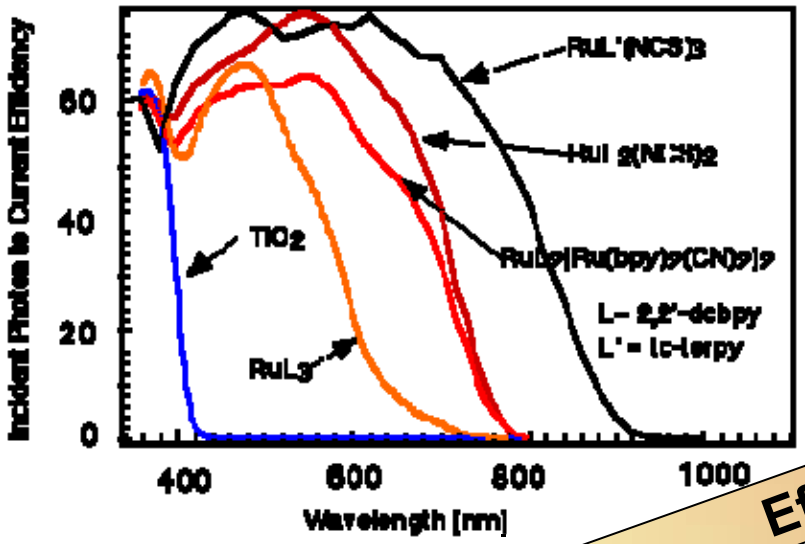
Thickness optimization



With Scattiering Particles



Dyes

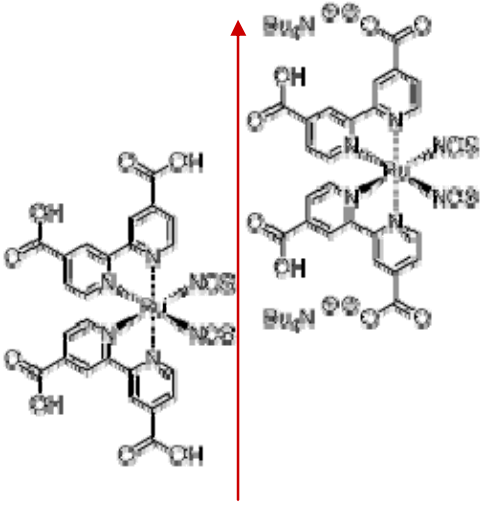


11%

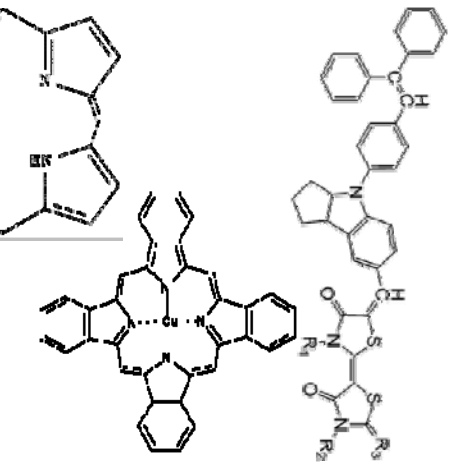
Efficiency

1%

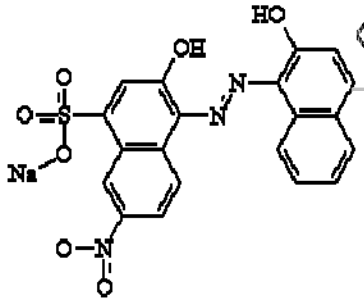
Rutenium-Based Dyes



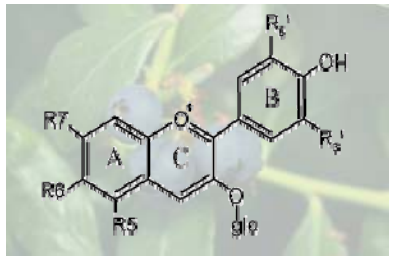
Organic Dyes



Industrial Dyes



Natural Dyes



CHOSE –UniFerrara

patent in progress

Electrolyte – Development @ CHOSE

Electrolyte optimization is related to the long term stability of the cell.

Electrolyte form:

Liquid Electrolyte:

- *organic solvent*: ACN, MPN, EC, PE, ecc....
- *redox couple*: I-/I3-, Br-/Br2, CoII/CoIII, SCN-/(SCN)2, SeCN-/(SeCN)2;
- *additive:* 4-tert-butylpiridine, N-Methylbenzimidazole, guanidine thiocyanate

Gel Electrolyte:

- High ionic conducibility;
- High chemical and electrochemical stability;
- Easy to prepare; Low cost; Good processability

PEO(polyethyleneoxide)
PEG(polyehtyleneglycole) **+ LiI / I_2**

Ionic Liquid based Electrolytes

In collaboration with the Chemistry Group of Tor Vergata we can synthesize different Ionic liquid. Suitable ionic liquid are for examples:

- **PMII : 1-methyl – 3 propylimidazolium iodide;**
- **HMII : 1-hexyl – 3 methylimidazolium iodide;**
- **BMIM : 1- butyl – 3 methylimidazolium iodide;**

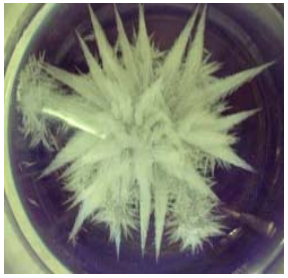
— **= High viscosity -> low conducibility**

io·li·tec
Ionic Liquids Technologies

Solaronix

- **EMIm-I : 1 ethyl - 3 methylimidazolium iodide;**
- **EMIm-SCN: 1 ethyl - 3 methylimidazolium thiocyanate;**
- **EMIm-DCA: 1 ethyl - 3 methylimidazolium dicyanamide;**
- **EMIm-BF4 : 1 ethyl - 3 methylimidazolium tetrafluoroborate;**

— **= Low viscosity -> high conducibility**



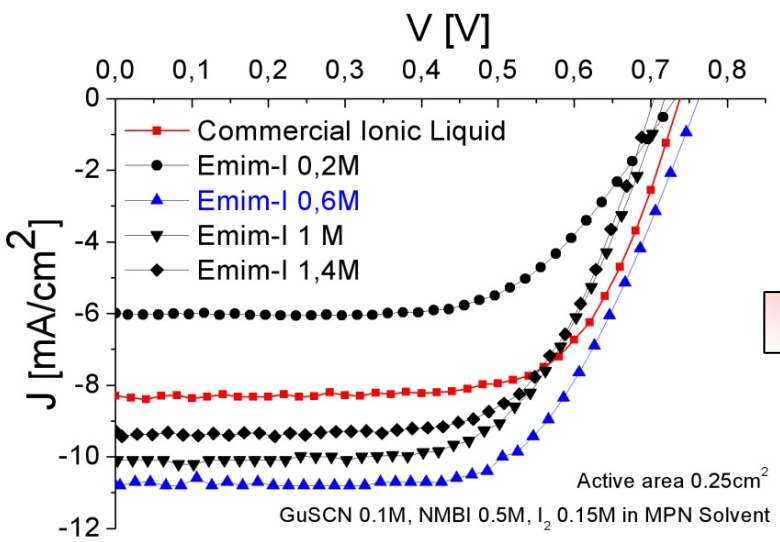
Ionic Liquid Electrolyte typical composition:

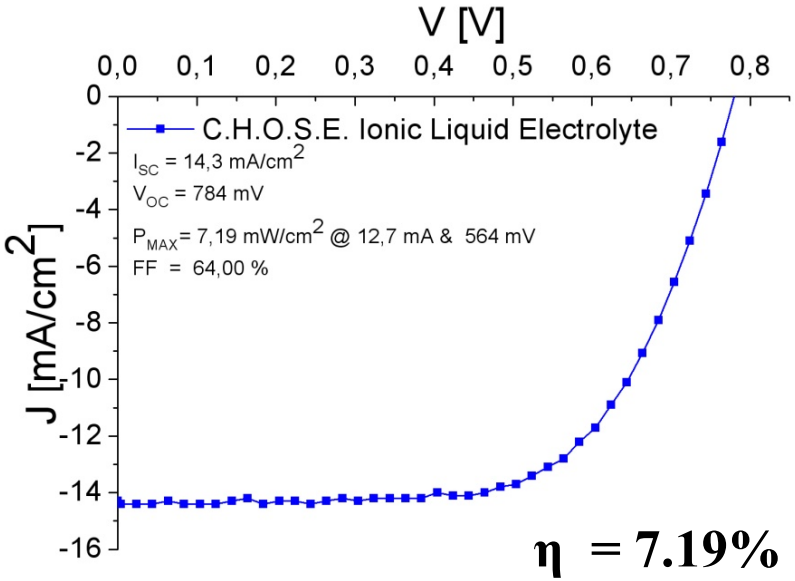
EMIm + **I^-, Dicyanamide, Trifluorometanesulfonilmide** + **I_2**

cation ***anion*** ***mediator***

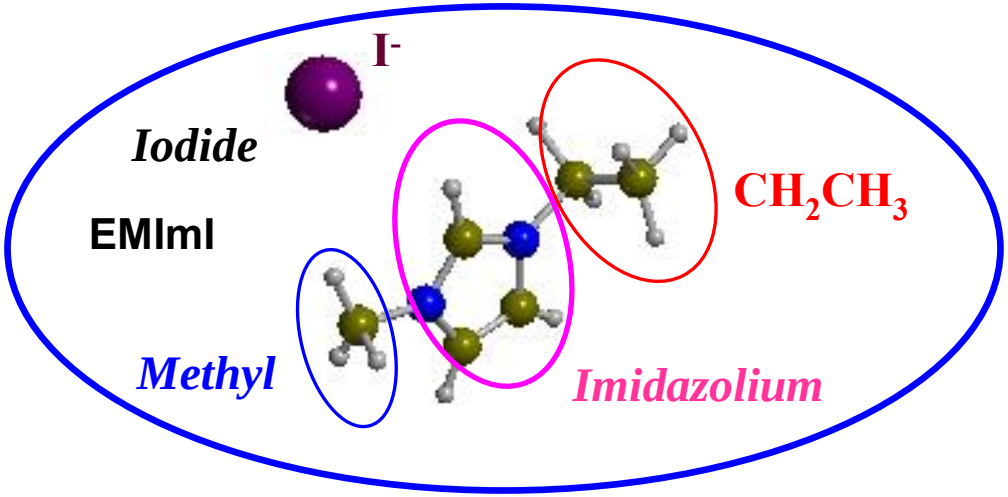
Particular attention is given to purification !

Ionic liquid based DSC





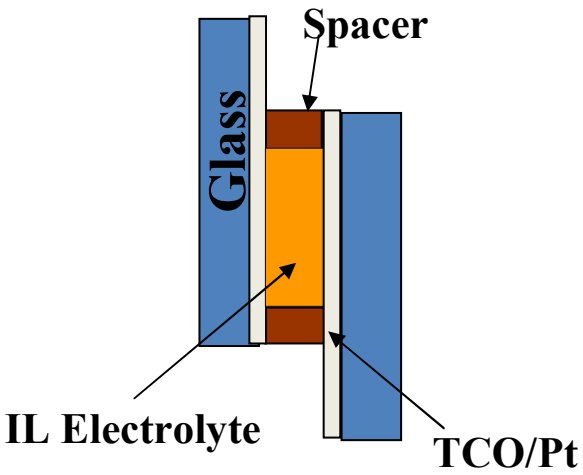
$\eta = 7.19\%$

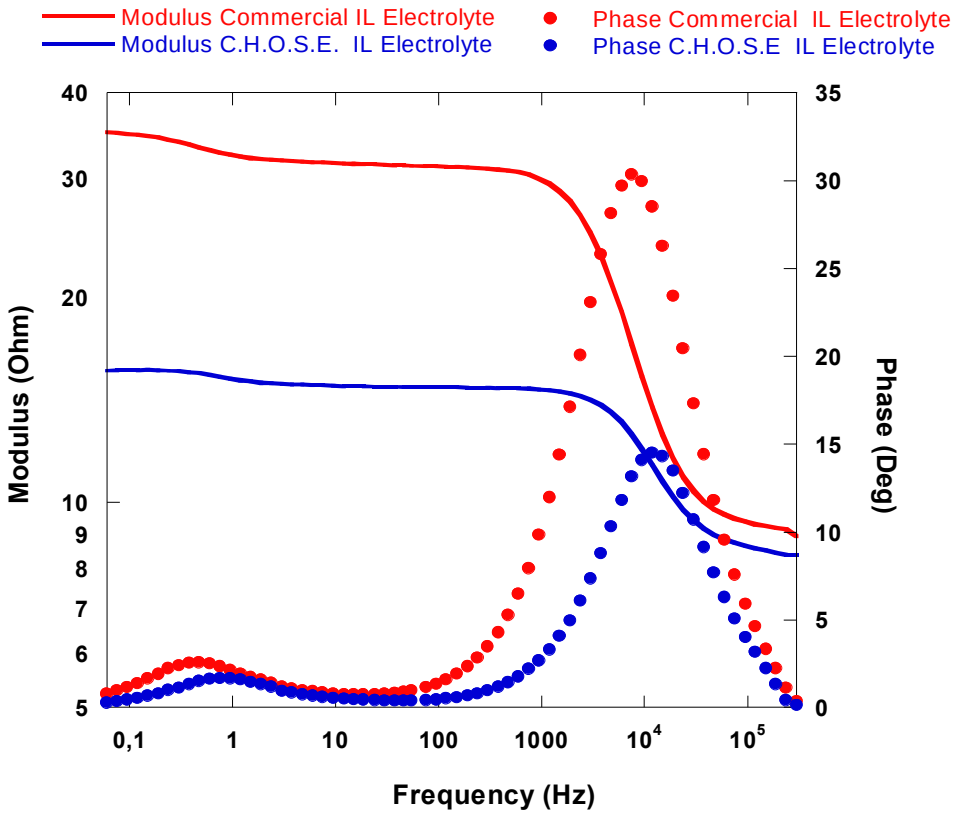


See Poster session

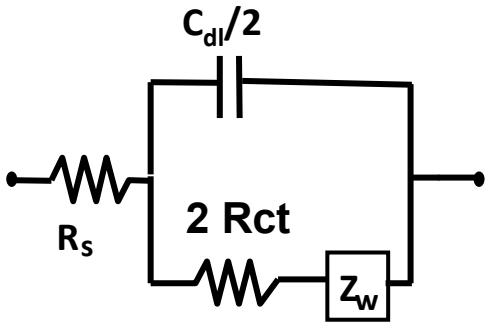
Electro-Impedance Spectroscopy

Symmetric cell



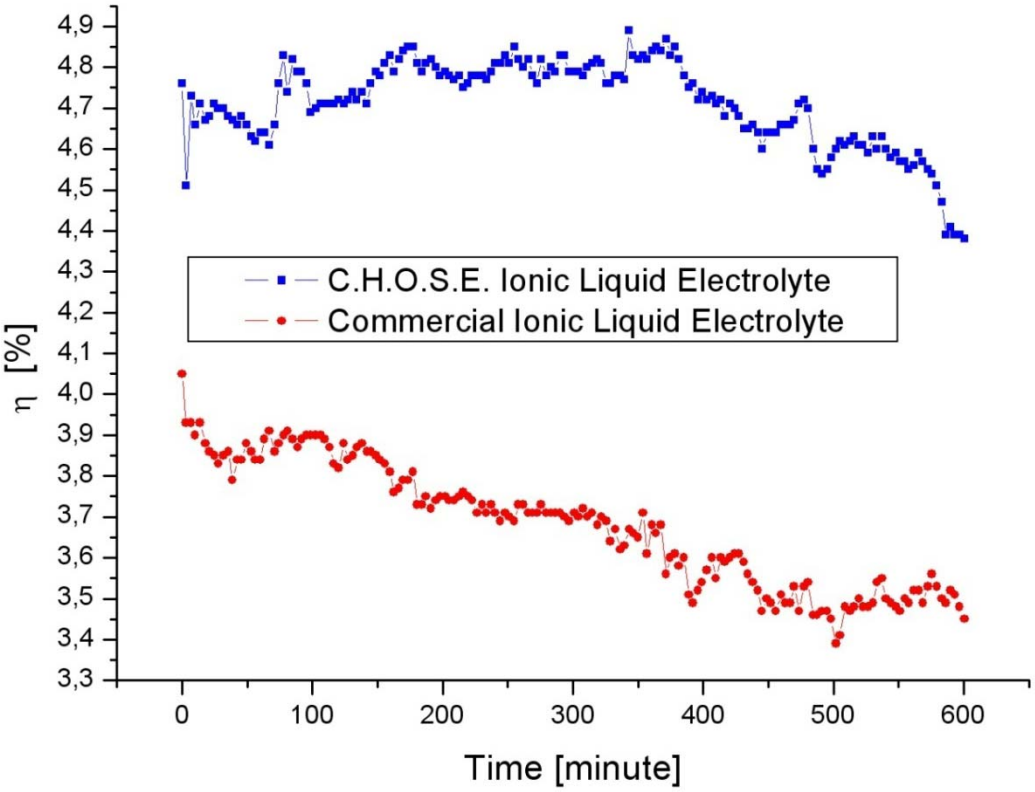


Equivalent circuit



Sample	R_{ct} (Ohm*cm^2)
Commercial IL	5.0
C.H.O.S.E. IL	1.5

Time evolution

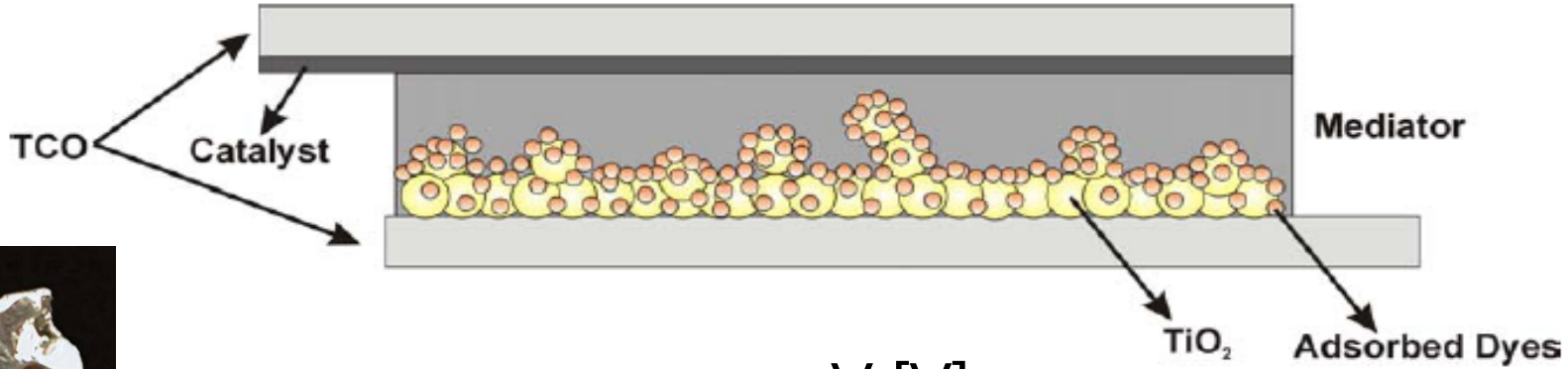


Comparison between:

- EMIM ionic liquid (CHOSE)
- EMIM ionic Liquid (Commercial)

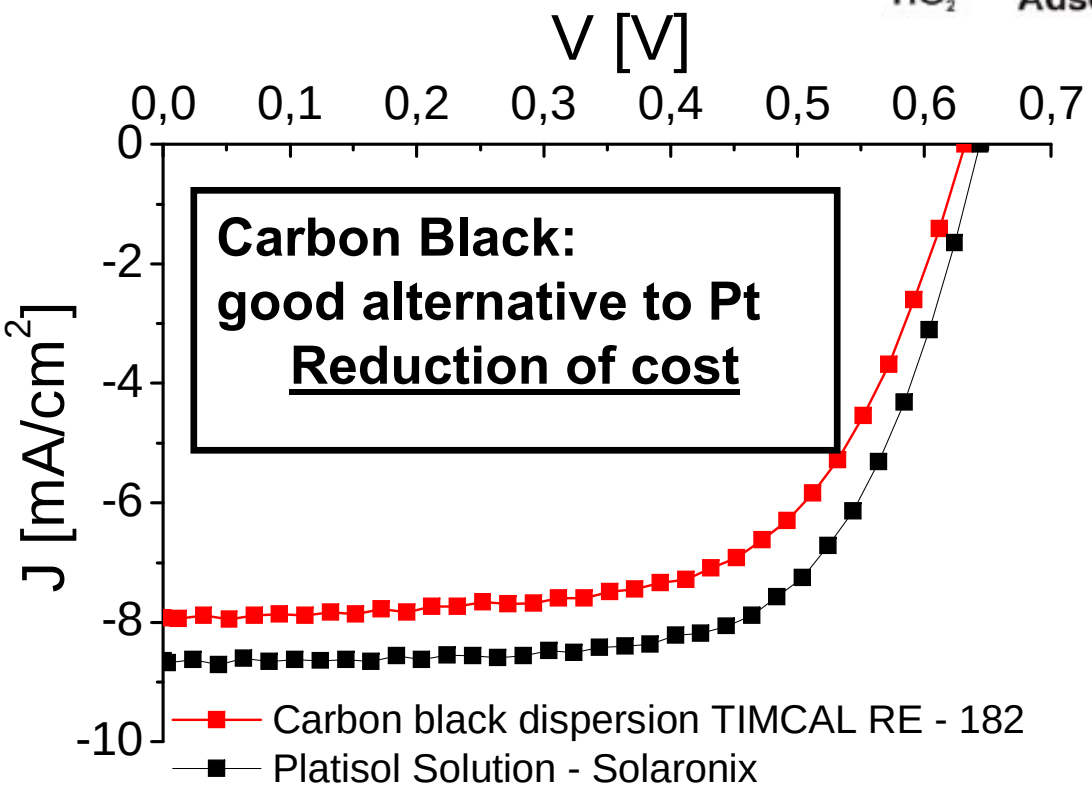
Cost of Ionic Liquid seems not to be a problem for a volume production

Counterelectrode development

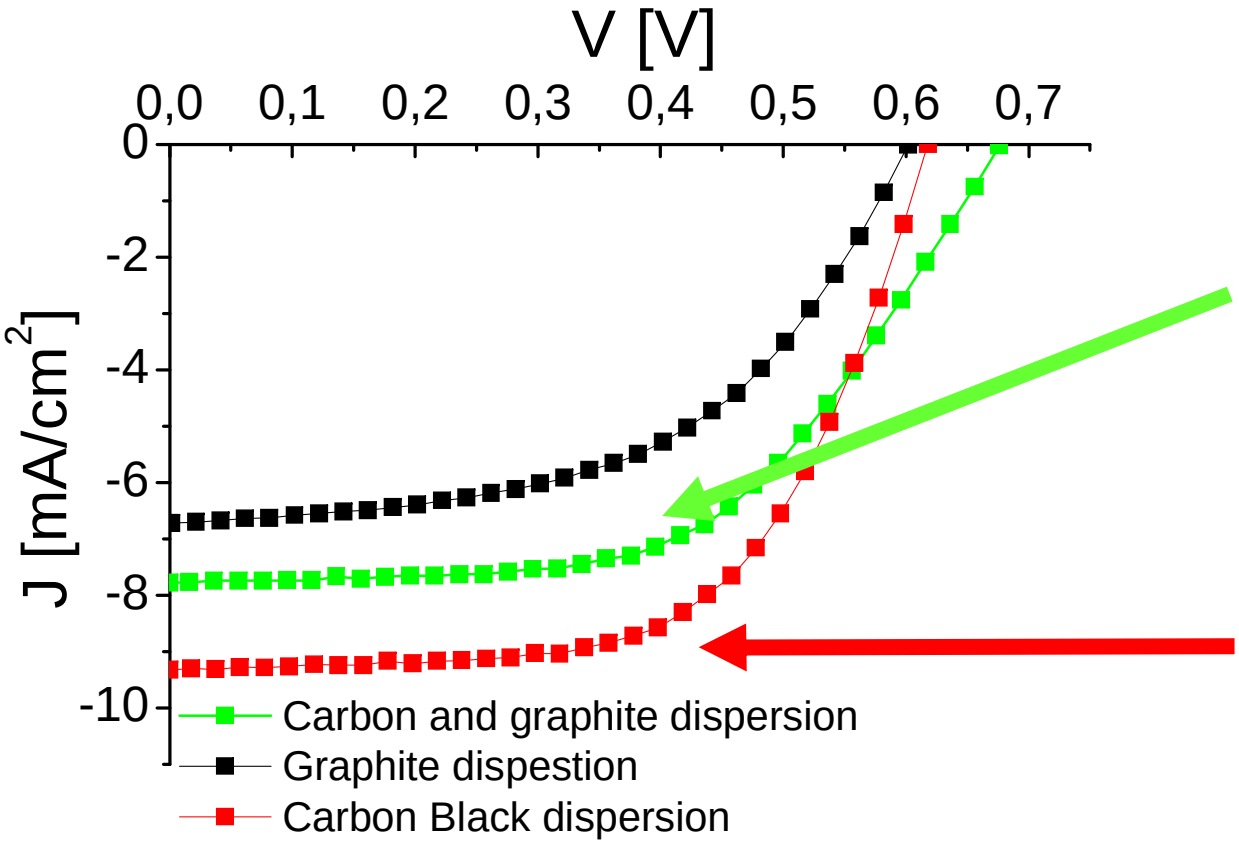


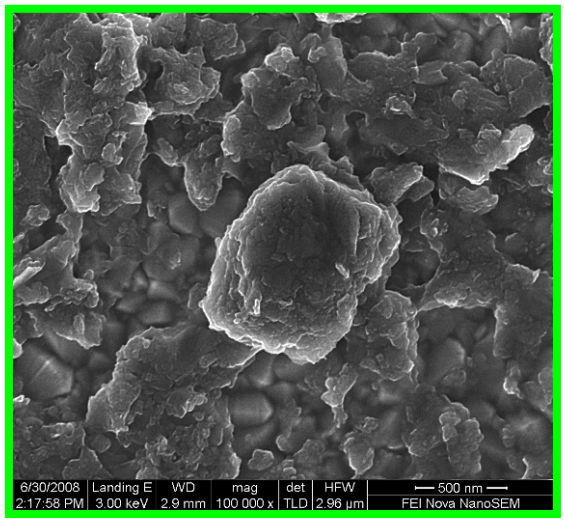
Carbon Black

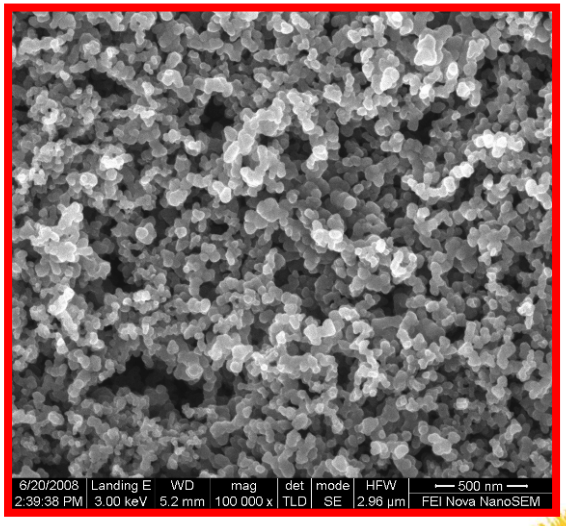
See Poster session



Carbon Black Counter-electrode





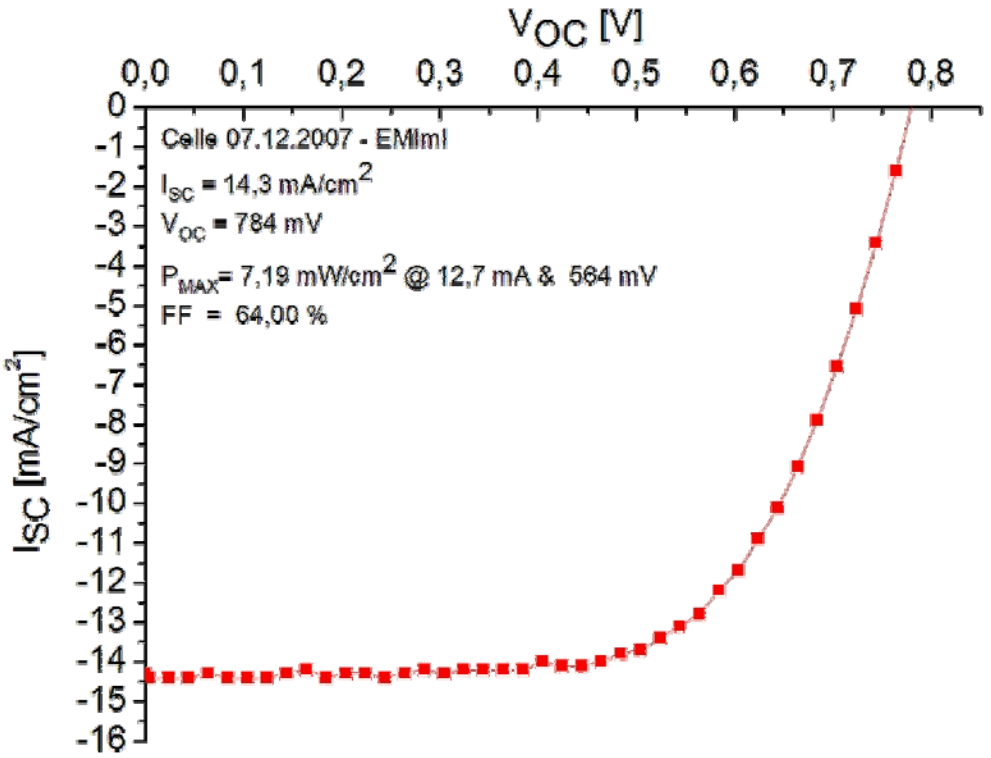


Nanometric “Carbon Black” particles improve catalysis and consequently efficiency

Typical Photovoltaic performance

- QE = 70-80%
- J_{sc} = 15 mA cm^{-2}
- V_{oc} = 0.8 V

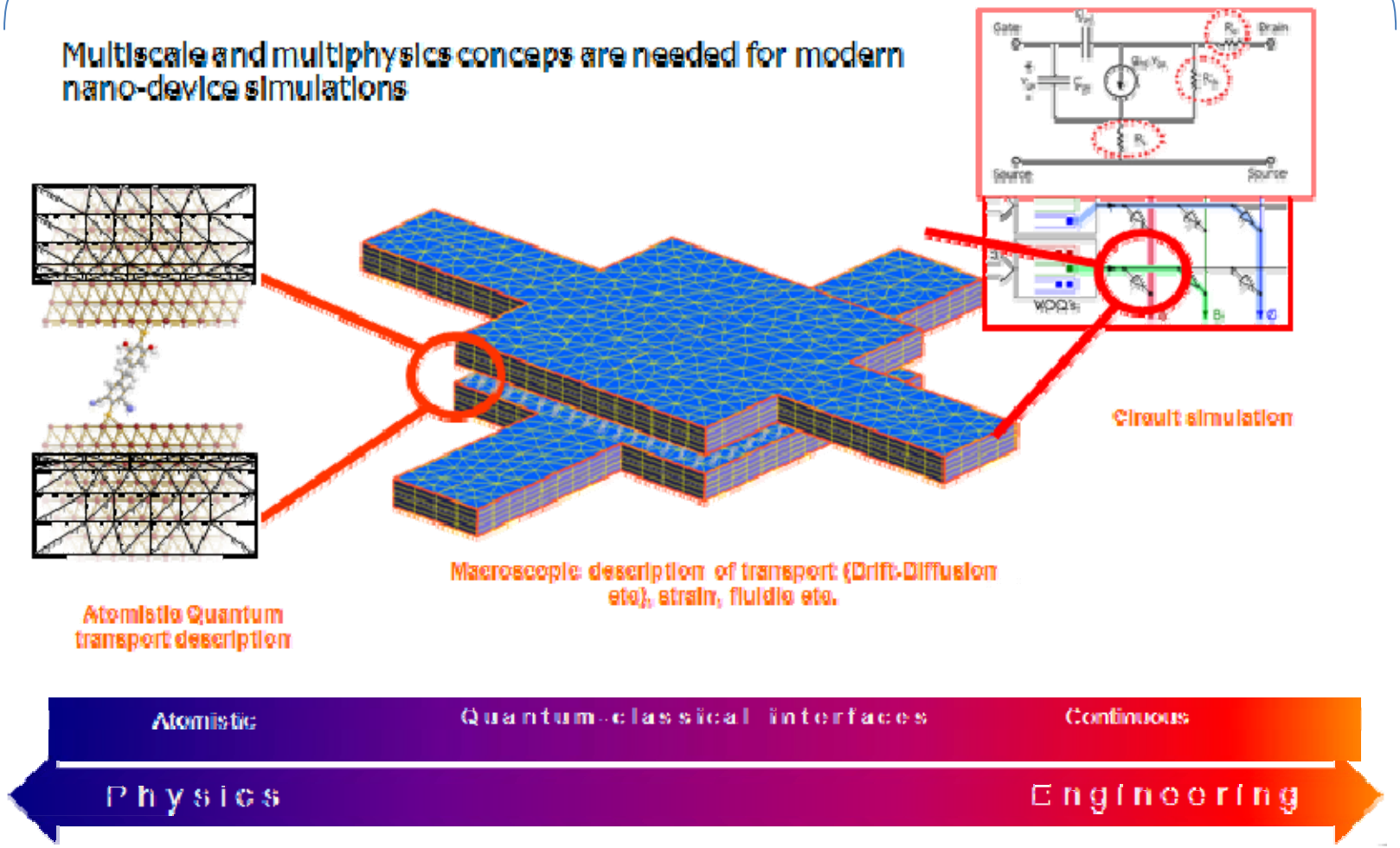
- η = 7 %
- Repeatability within 5%



- Challenges:
  - Improving photocurrent: dyes, light management
  - Improving photovoltage : minimise recombination
    alternative materials
  - Understand the Physics of the cell

Physical Device Modelling - TiberCAD

TiberCAD device simulator: www.tibercad.org



We are extending TIberCAD to account also for simulation of DSC

1D TiberCAD simulation of DSC (prel. res.)

$$j_\alpha = \mu_\alpha n_\alpha \nabla \phi_\alpha$$

$$\nabla j_\alpha = m_\alpha (G - R)$$

- **Note: α is related to the four carriers (redox pair, electrons in the semiconductor and cation)**
- **m_α is a coefficient which depends to the chemical reaction (1.5, 0.5, 1)**
- **G and R are the generation (dyes) and ricombination (TIO_2→ electrolyte) processes respectively**

Poisson equation:

$$\nabla\left(\varepsilon \nabla \varphi\right) = \left(n_C - n_e - n_{I^-} - n_{I_3^-} + N_{dye}^+\right)$$

R (Recombination model), electron from TiO_2 to the electrolyte:

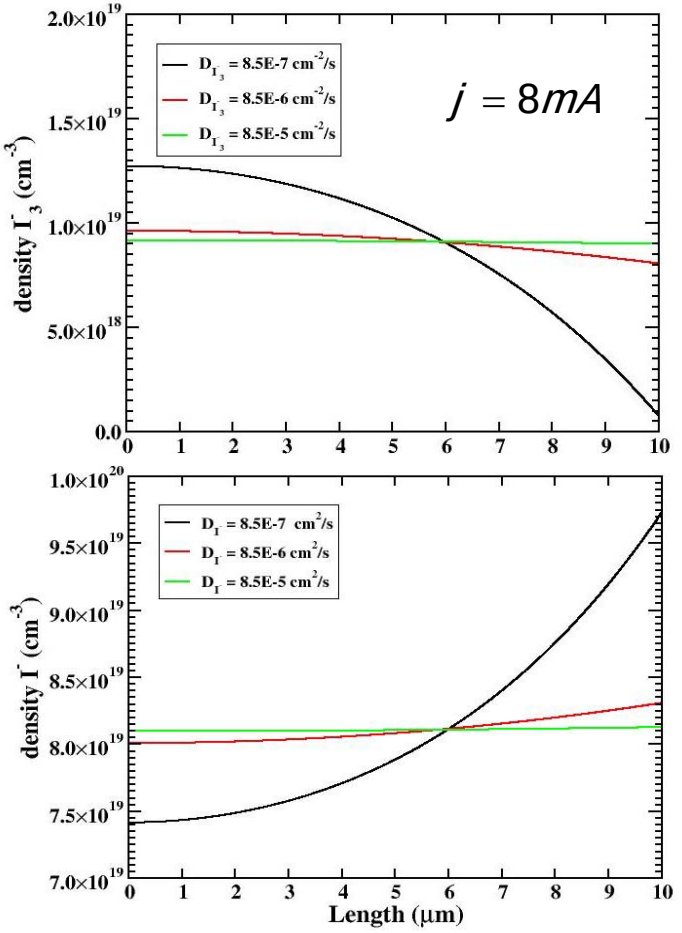
$$R = k_e \left[n_e \sqrt{\frac{n_{I_3^-}}{n_{I^-}}} - n_e^0 \sqrt{\frac{n_{I_3^-}^0}{(n_{I^-}^0)^3}} n_{I^-} \right]$$

Generalized Butler-Volmer equation (Cathode BC):

$$j = j_0 \left[\sqrt{\frac{n_{I_3^-} n_{I^-}^{OC}}{n_{I_3^-}^{OC} n_{I^-}}} e^{\frac{\alpha e U}{kT}} - \frac{n_{I^-}}{n_{I^-}^{OC}} e^{-\frac{(1-\alpha) e U}{kT}} \right]$$

Where U is the overvoltage:

$$U = E_{redox} - E_{redox}^{OC} = \Delta E_{redox}$$

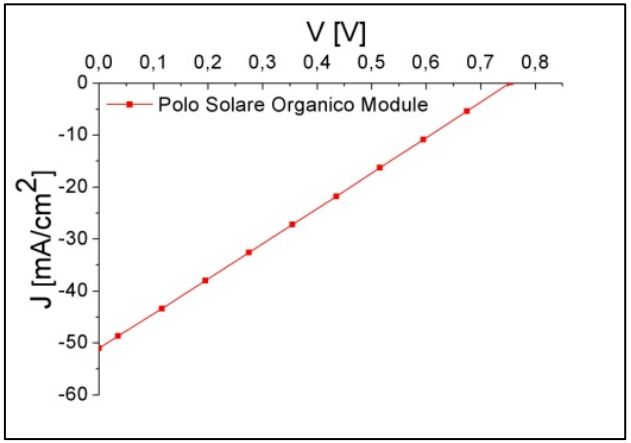


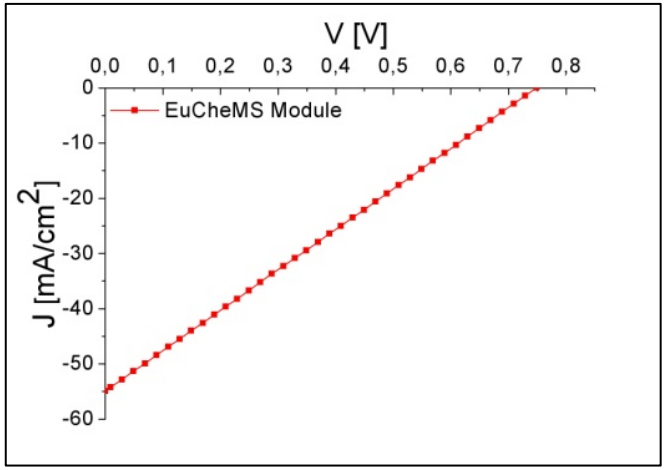
See Poster session

CHOSE

Large area: Modules

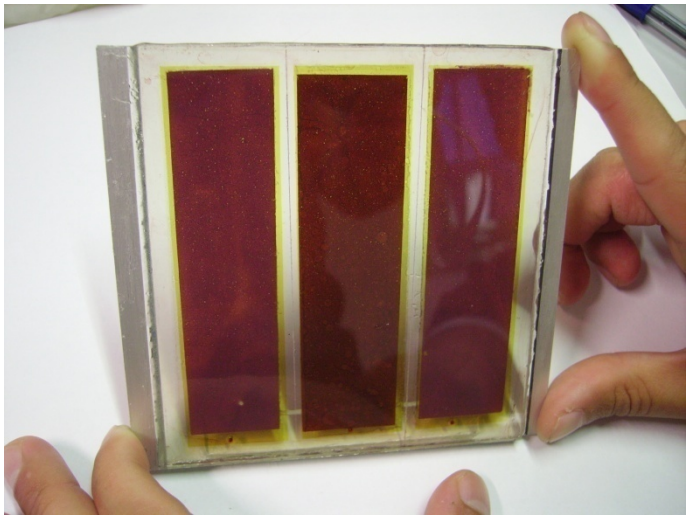
Example of DSC (sigle cells)





Series resistance is very critical !!!

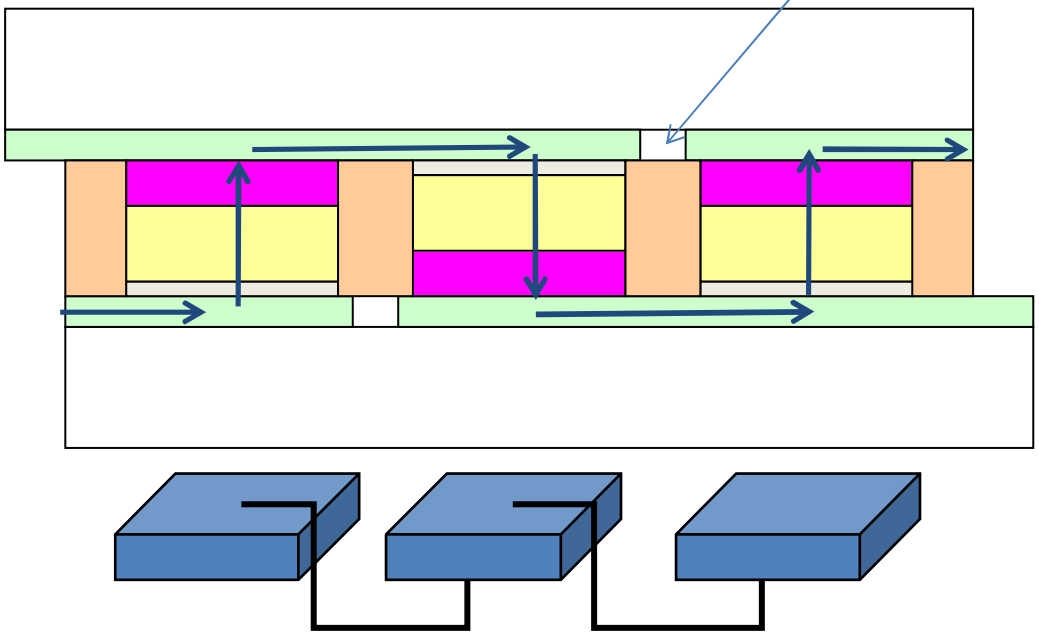
100cm² Module Fabrication with 3 cells series interconnected



- **Define contacts**
- **Coat the different layers**
- **Leave in Dye Solution**
- **Seal**

Laser scribed pattern

W - connection



Glass

TCO

Dye sensitized TiO2

Electrolyte

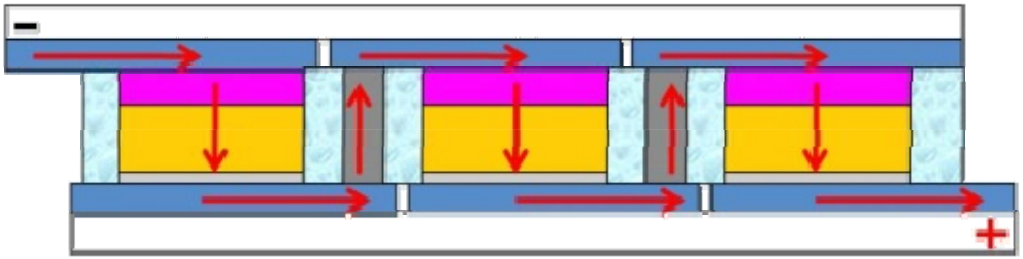
Pt catalyst

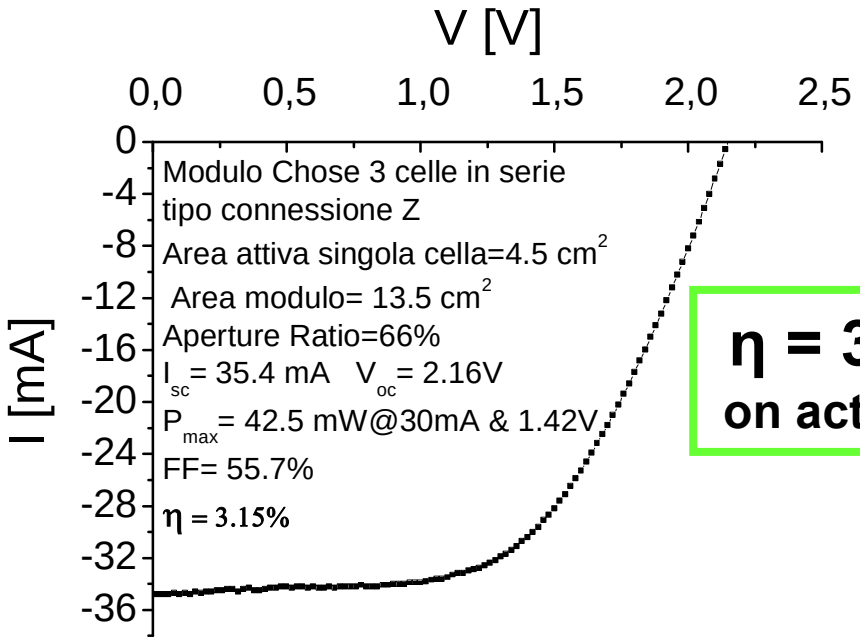
Encapsulant

Series interconnect of a number of cells

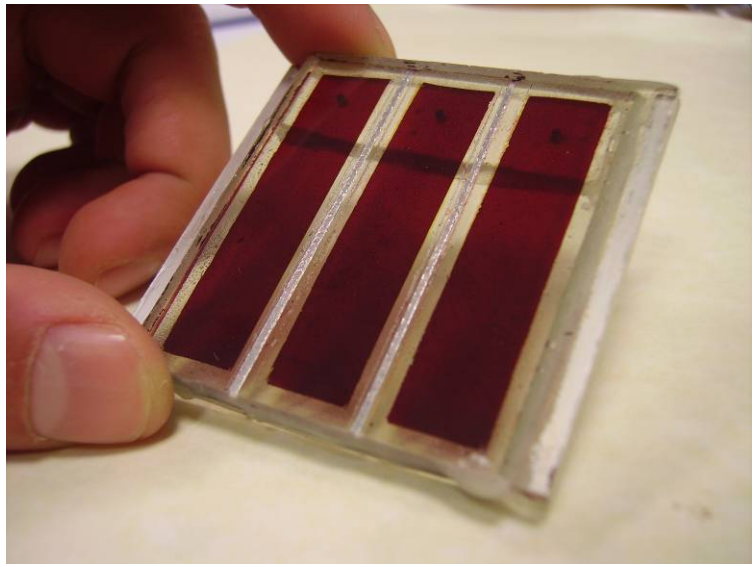
DSC Modules with Ionic Liquids

Z - connection



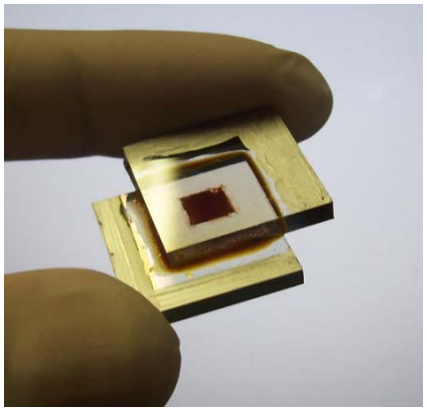


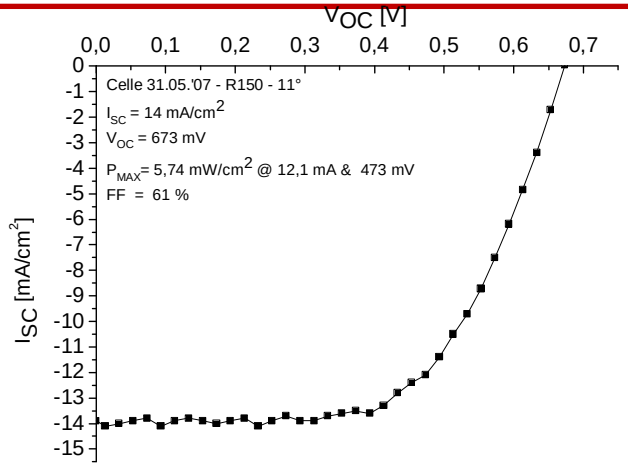
η = 3.15 %
on active area



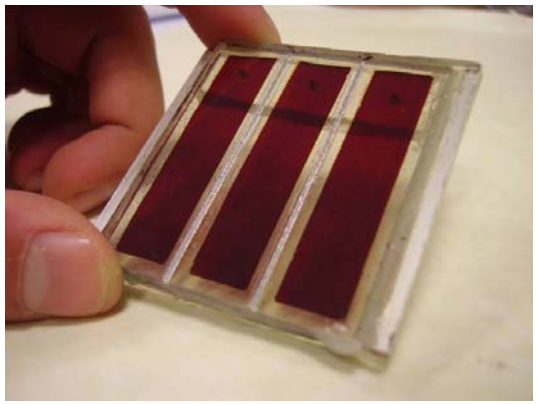
With Ionic Liquid

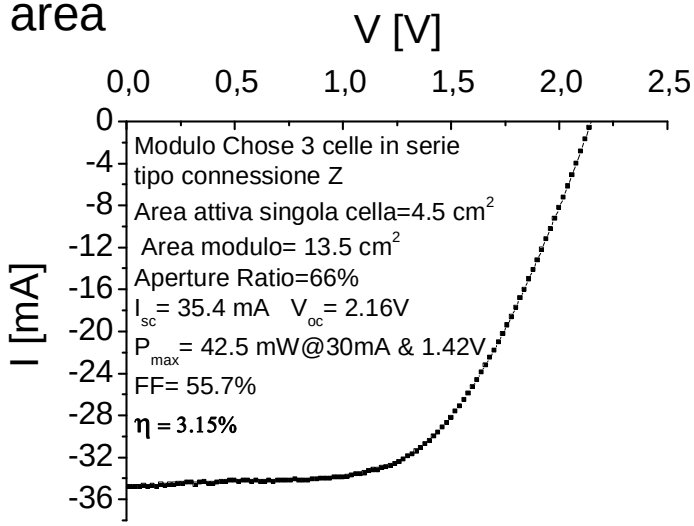
Summary cell and modules





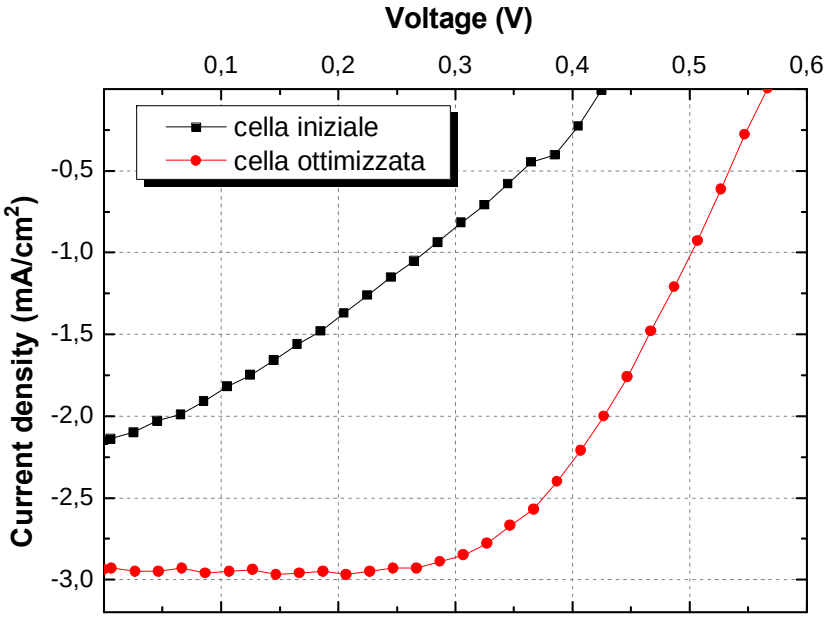
- Conversion efficiency single cell = 7-8% on small area (0.5 cm x 0.5 cm)
- Conversion efficiency module = 3-4% on active area
- Shelf life > year





Series Resistance limit module performance
Current collection grids can solve this but problems with corrosion

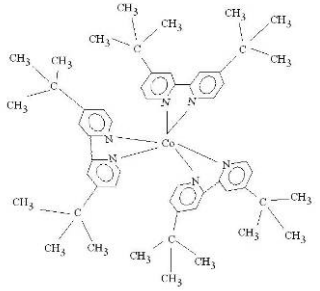
DSC with Cobalt Electrolyte



Comparison between standard Cobalt based cell and the optimized one. Light intensity 30 mW/cm²

	η [%]
Standar Cobalt Cell	0.95
Optimised Cobalt Cell	3.13
Improovement	+230%

Ref: S.Caramori, C.A. Bignozzi



PRO:

- **Low corrosive effect:**
  - **metal current collector, metal vertical connections**
  - **Easy to incapsulate**
- **Electrolyte is transparent:**

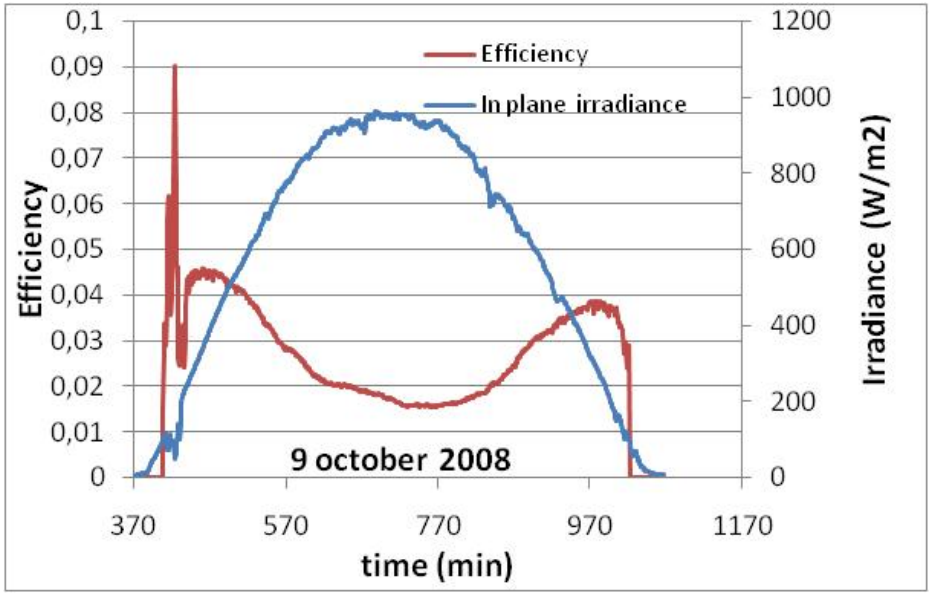
Problems :

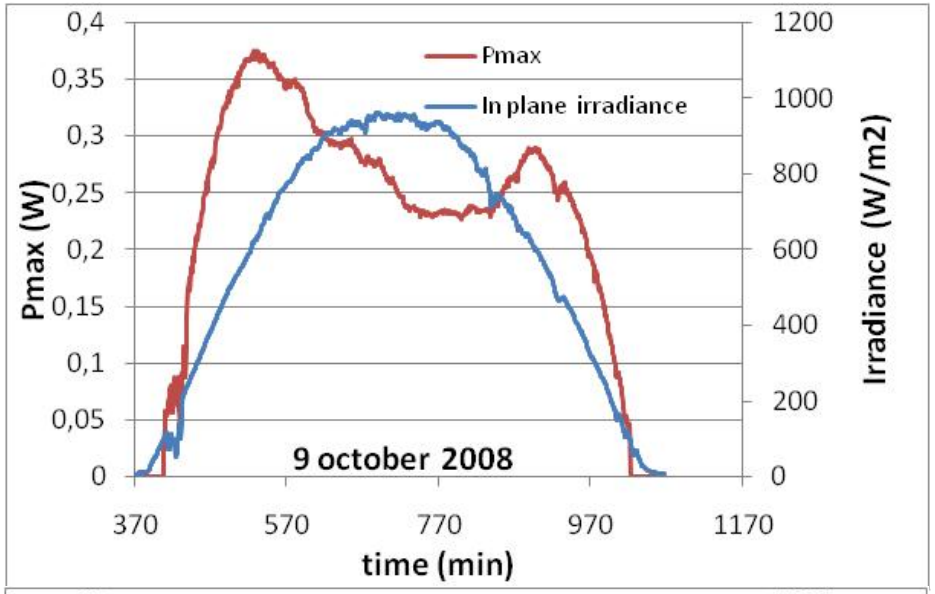
- **Mass-transport limited current**
- **Recombintaion at the TiO2 level.**

Solution: Al_2O_3 encapsulated TiO_2

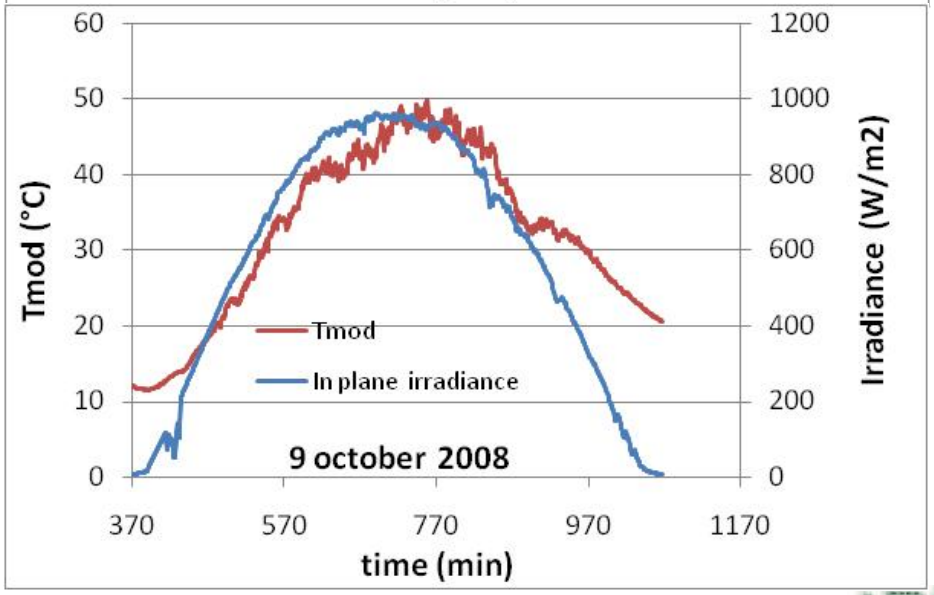
OUTDOOR Module measurements

Outdoor Module test – Clear day

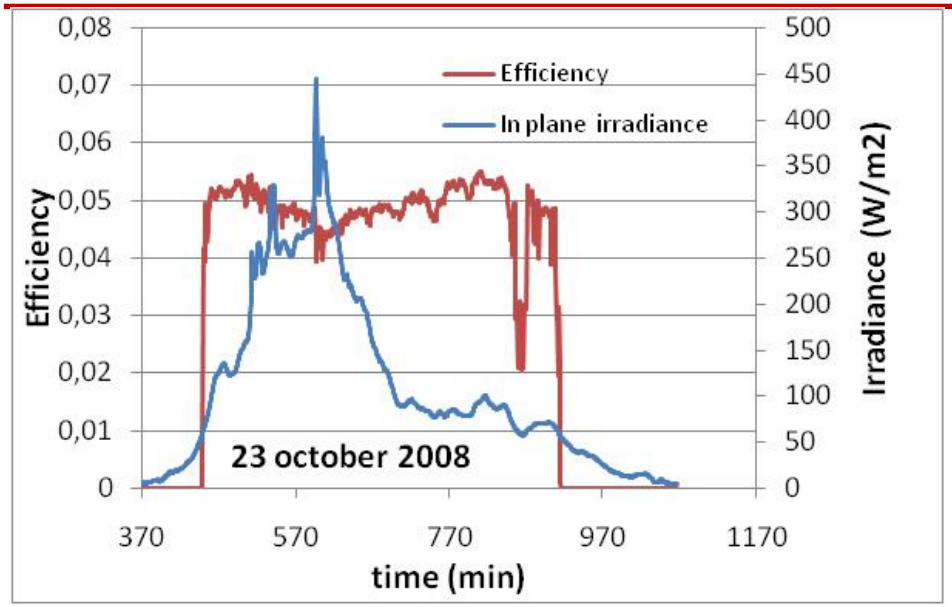


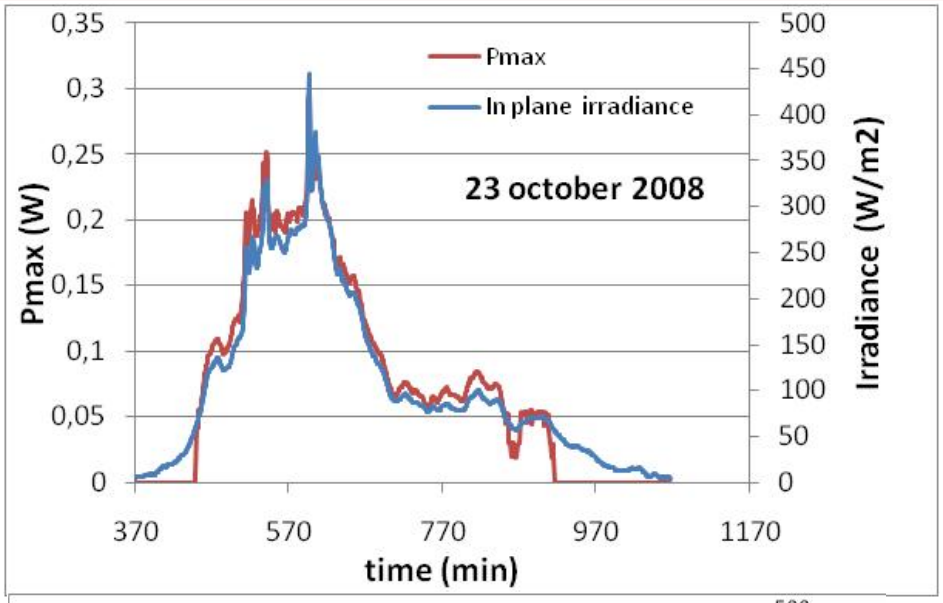


Light is mainly direct

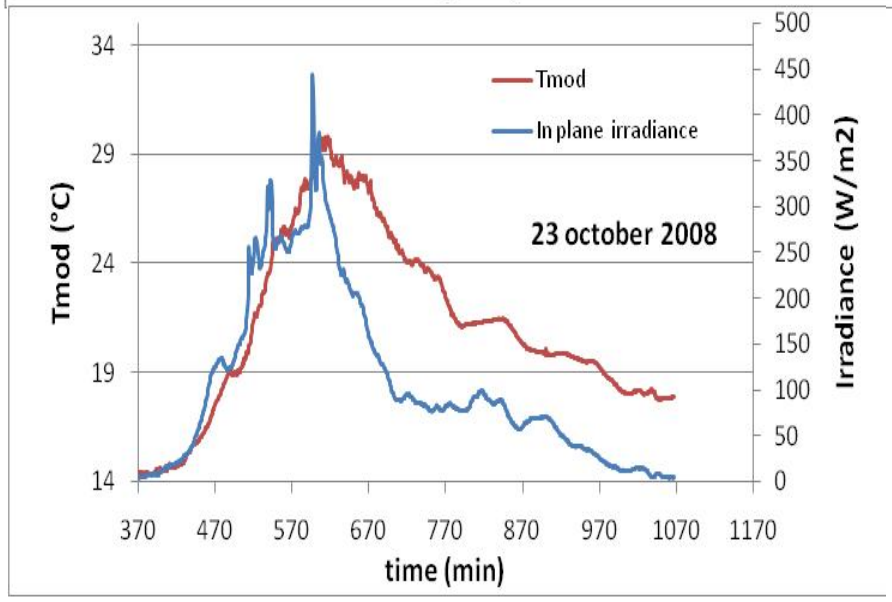


Outdoor Module test – Cloudy day





Light is mainly diffused



Energy production

[T. Toyoda et al. / Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 203–207]

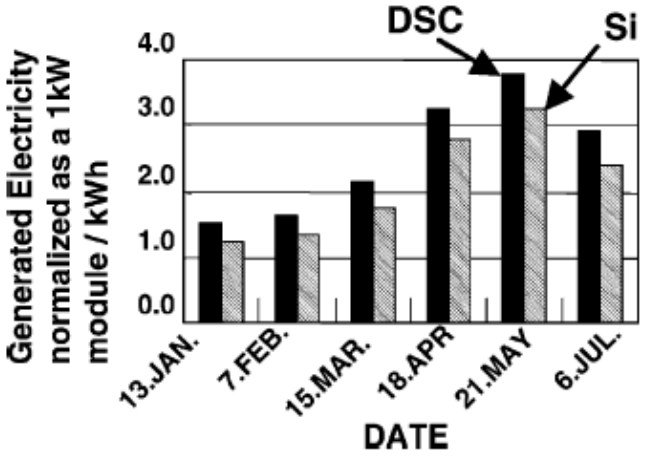


Fig. 5. Example of generated electricity for cloudy days between December and July for the DSC modules and the Si module. Output power is converted as a 1 kW module.

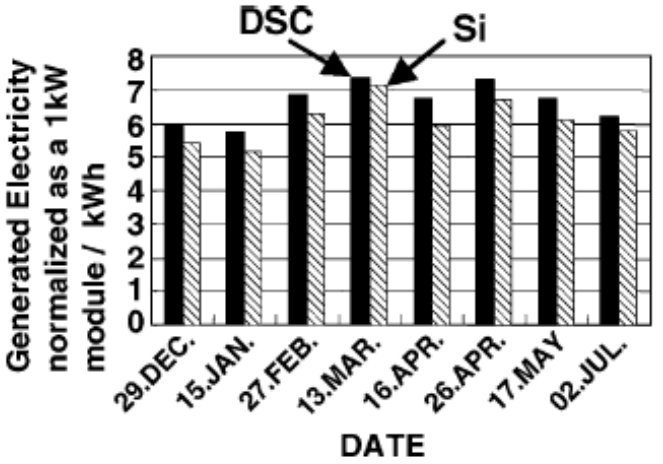


Fig. 4. Example of generated electricity for clear and sunny days between December and July for the DSC modules and the Si module. Output power is converted as a 1 kW module.

1 kWp of silicon based PV modules produce 1400 kWh / year.

1 kWp of DSC based PV modules produce 1600 kWh / anno

Actual Material Costs

For 50 W / m^2 panel we have a cost of 2 euro/watt of materials considering an annual production of 10.000 m^2.

This reduces to 1.6 euro/Wp for a production of 100.000 m^2

Dye, TiO2 paste and Electrolytes are under industrial scaling up (see for example the 400 million project of Basf, Merck and other in Germany) and we expect a strong reduction of their retail prices.

More critical is the situation for the glass-TCO where no strong reduction of the price is forecast (Pilkington)

However … Build integration PV

Compared to traditional photovoltaics, DSC has the following differentiation advantages:

Low dependence on angle of light
Stable operating voltage in all light conditions
Natural colours
Optional transparency
Aesthetically pleasing
Manufactured as a building product
Provides additional functionality for energy efficiency and noise reduction

Building Integration of Photovoltaics is quite convenient for DSC technology

Facade DSC photovoltaic glass can be manufactured on volume production for a price of the order 1/5 of the actual price for a silicon based glass photovoltaic façade

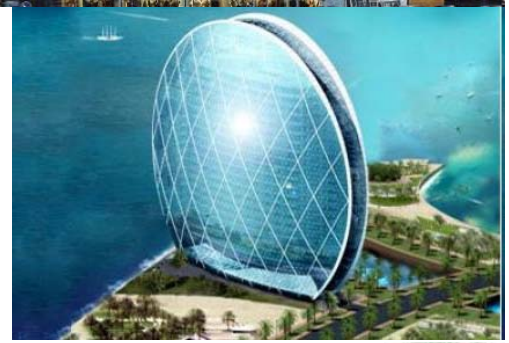
Silicon based PV glass Façade has 50-70 Wp/sqm quite comparable with DSC !

DYEPOWER consortium

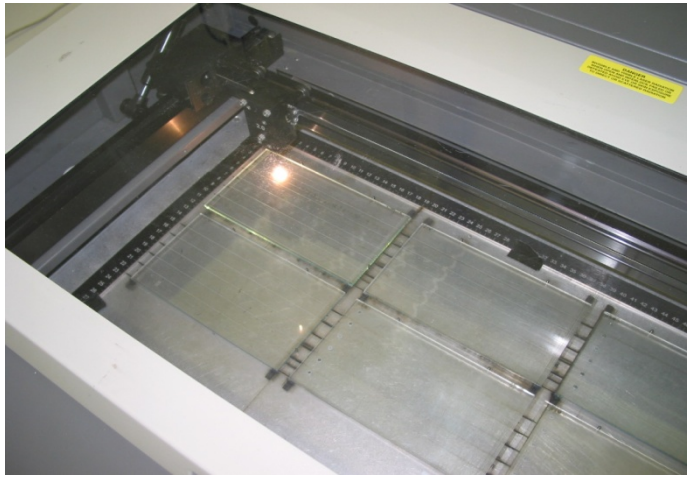
10 September 2008:

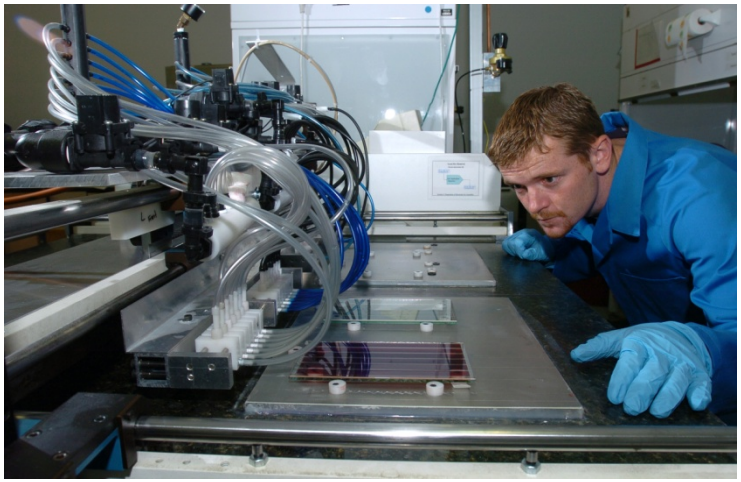
- ERG Renew S.p.A. (ERG group)
- Permasteelisa S.p.A.
- Dyesol Italia,
- CHOSE – Uni Tor Vergata,
- Uni. Torino,
- Uni. Ferrara

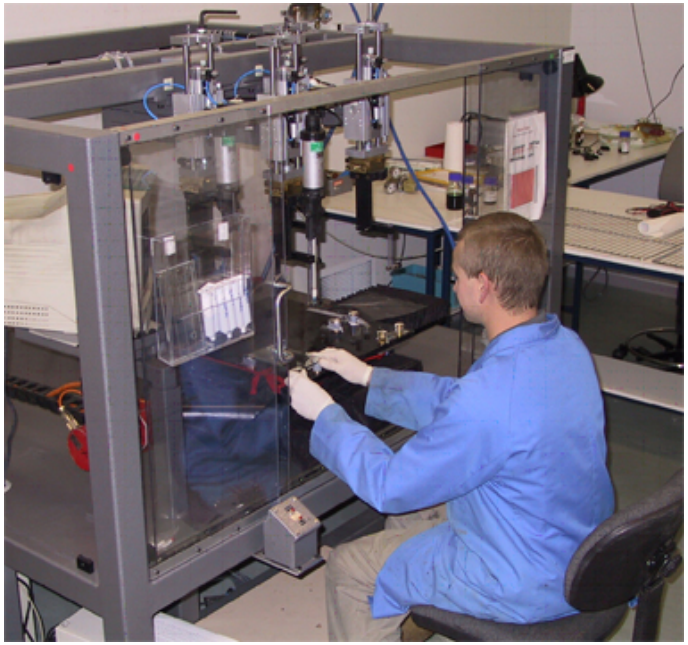
Signed a framework agreement
for the industrialization of DSC for BIPV



Dyesol Equipment for DSC Industrialization







CHOSE has recently acquired several DYESOL equipment for batch production of DSC.

Further development of these machines will be made to automatize the process

Industrialization

Dyesol has presented 14.000 hours acceletared life time test: this correspond to almost 20 years in normal operating conditions (II DSC-IC 2007)

See the Keith Brooks talk

Conclusions

- DSC represents a new way for silicon free photovoltaics. Large tunability, easy manufacture, low plant costs.
- Large area devices is not trivial and many issues are still open
- Industrialization is very close (see also SONY and SHARP patent activities !!!)
- Scale up of the materials with price reduction is request.
- We believe in BIPV

Acknowledgments

- UniFerrara (Bignozzi team)
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- UniTorino (Viscardi-Barolo team)

REGIONE LAZIO

Tor Vergata team

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A. Brunetti
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L. Salamandra
V. Guglielmotti

And many other PhDs