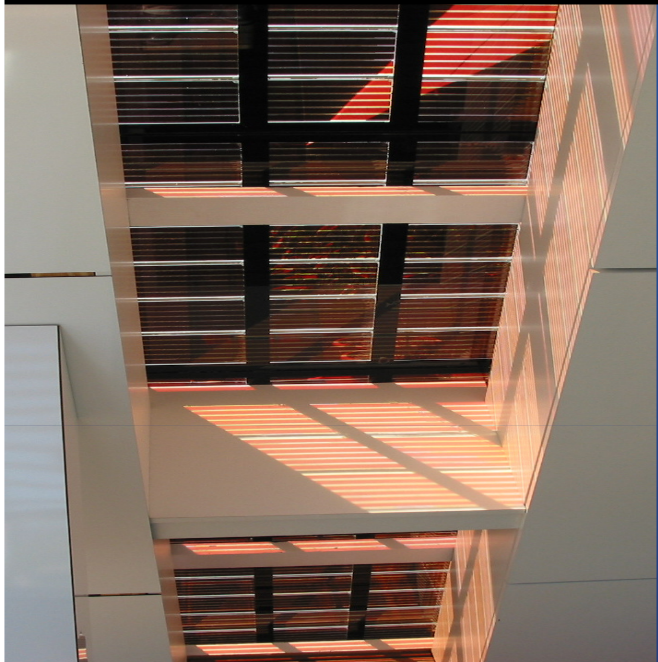


Long term stability of dye solar cells – meeting IEC 61646 requirements

Hans Desilvestro, Nancy Jiang,
Martin Berry and Paul Murray
Presenter: Ben Wilkinson (Dyesol UK)

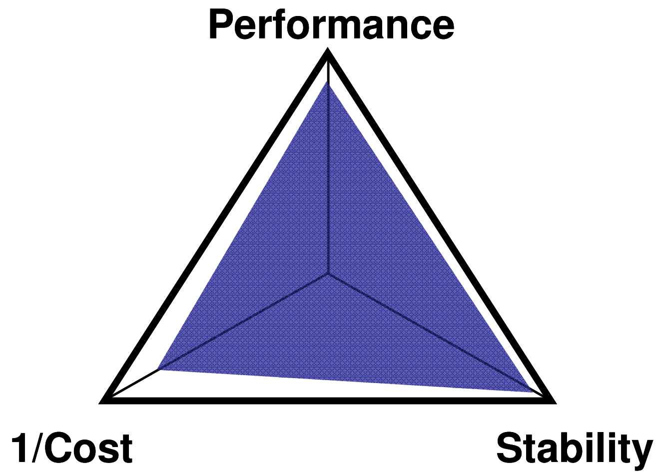
4 April 2012

Outline

- **Motivation**
- **The challenge**
- **Disentangling degradation mechanisms through DSC accelerated testing**
  – Hydrophilic vs hydrophobic dye
  – IV data
  – IPCE (Incident Photon-to-Electron Conversion Efficiency)
  – EIS (Electrochemical Impedance Spectroscopy)
- **Towards larger devices**
- **Summary**

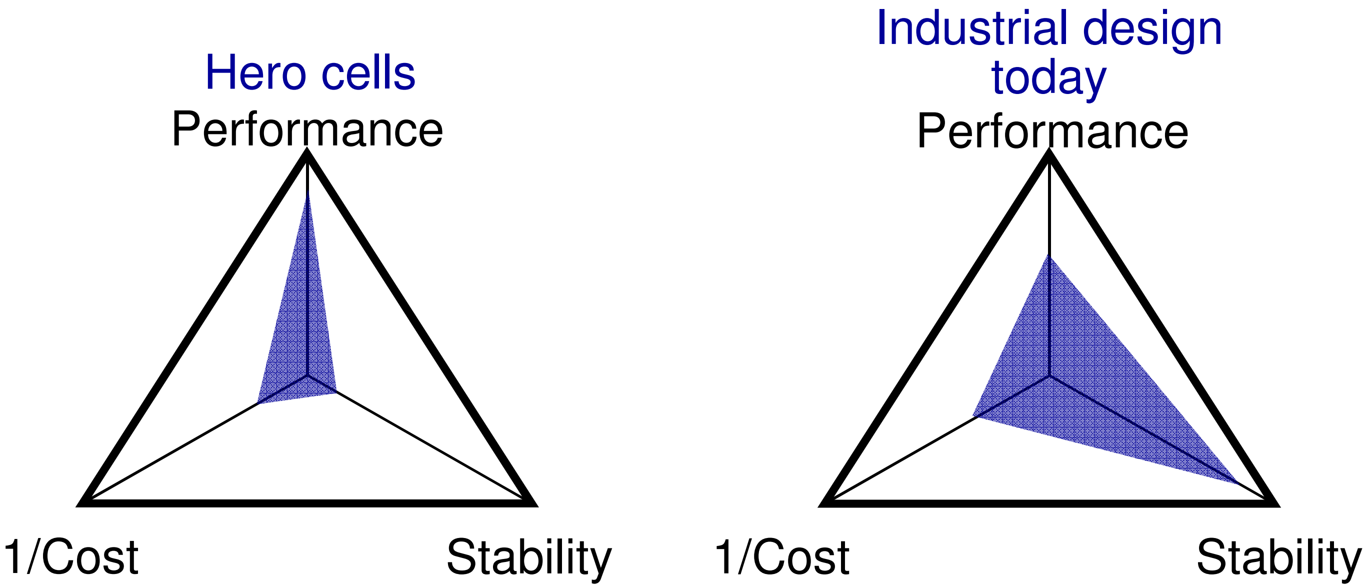
Motivation

- **Develop integrated understanding of all materials and design aspects of dye solar cells (DSC)**
  - To best serve and advise our commercial partners
  - Optimum focus on most promising materials and technologies
- **Achieve optimised LCOE for any given application**
  - Performance
  - Stability
  - Cost



The challenge

- **To achieve grid parity under a moving target of declining PV prices**
- **Performance – Stability - Cost**



- **20+ years life time in building applications**
- **Standards: PV-specific + Building Standards**

20-year product life goal

System's requirements

At the molecular level

>100 million turnovers	✓	at least for certain dyes/electrolytes
~No dye desorption	✓	at least for certain dyes/electrolytes
Loss of NCS-, substitution by I^-, nitriles, imidazoles, etc.	?	Lund et al vs Falaras et al. Low 80-85°C stability with nitrile solvents
Isomerisation, e.g. N- to S-bound SCN^-	?	Not significant according to micro-Raman (Falaras et al)
Decomposition of electrolyte components	?	Little is known, more in situ spectroscopic work required
Stability of electrocatalyst?	✓	At least for Pt and certain electrolytes

20-year product life goal

System's requirements

DYESOL

At the cell level (Dyesol up to 250 mm length): Seals

Suppress ingress of O_2, H_2O	✓	Dyesol, Fujikura, Fraunhofer ISE
Suppress egress of solvent	✓	Dyesol, Fujikura, Fraunhofer ISE
Performance stability, 85°C/1,000h; -40°C/+85°C thermal cycling; 85°C/85% r.h./1,000h	✓	at least for certain dyes/electrolytes, 85°C/85% r.h.: requires glass-based encapsulation (i.e. similar to CIGS or CdTe), best assessed at the panel level

- **Excellent DSC durability under light soaking conditions (~60°C). E.g. Dyesol >25,000 h quasi-continuous illumination ⇨ 25-40 years life time extrapolated, depending on location**

R. Harikisun, H. Desilvestro, Sol. Energy, **85**, 1179 (2011), "Long-term stability of dye solar cells"

- **IEC 61646 85°C/1,000h and thermal cycling tests remain challenging for DSC**

20-year product life goal

System's requirements

DYESOL™

At the module level

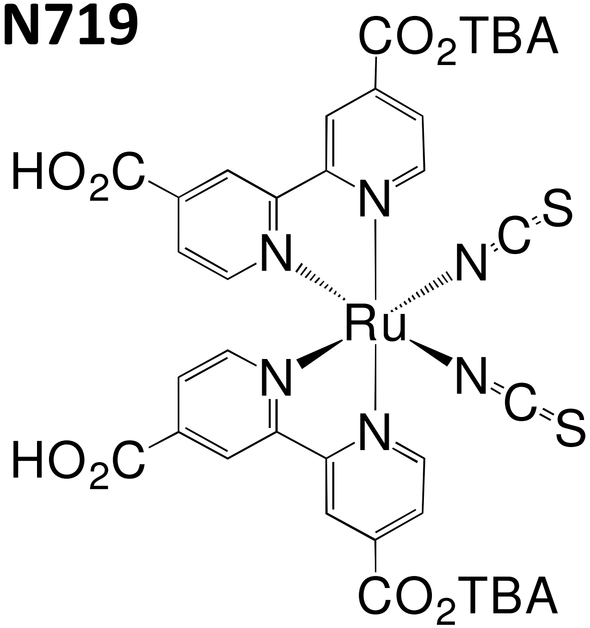
- Cell-to-cell interconnects
- Corrosion protection of current collectors
- Potential shunt paths
- Sealing

At the system's level

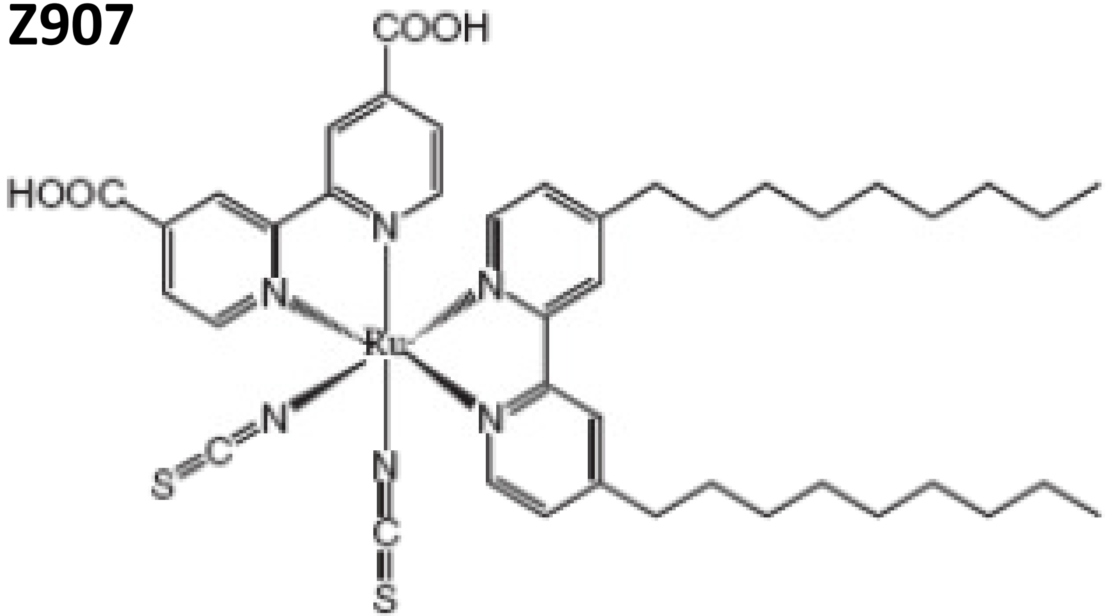
- Environmental, temperature extremes, hail, etc.
- Building code requirements
- Maximum power point tracking independent of any ageing phenomena

Cell chemistry

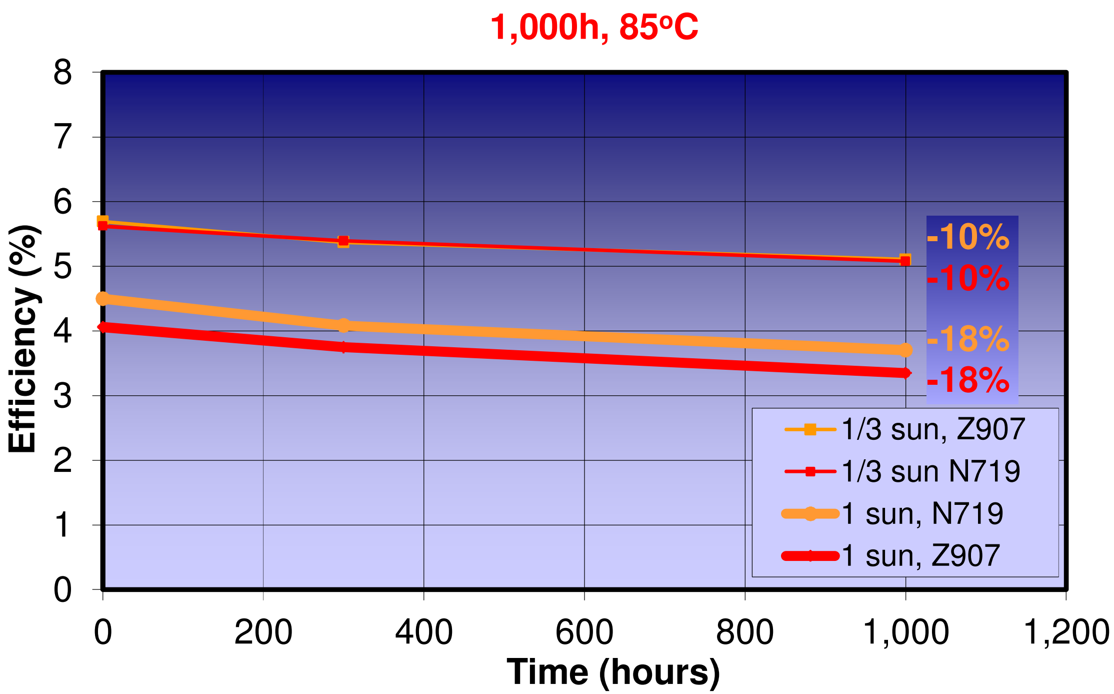
N719



Z907



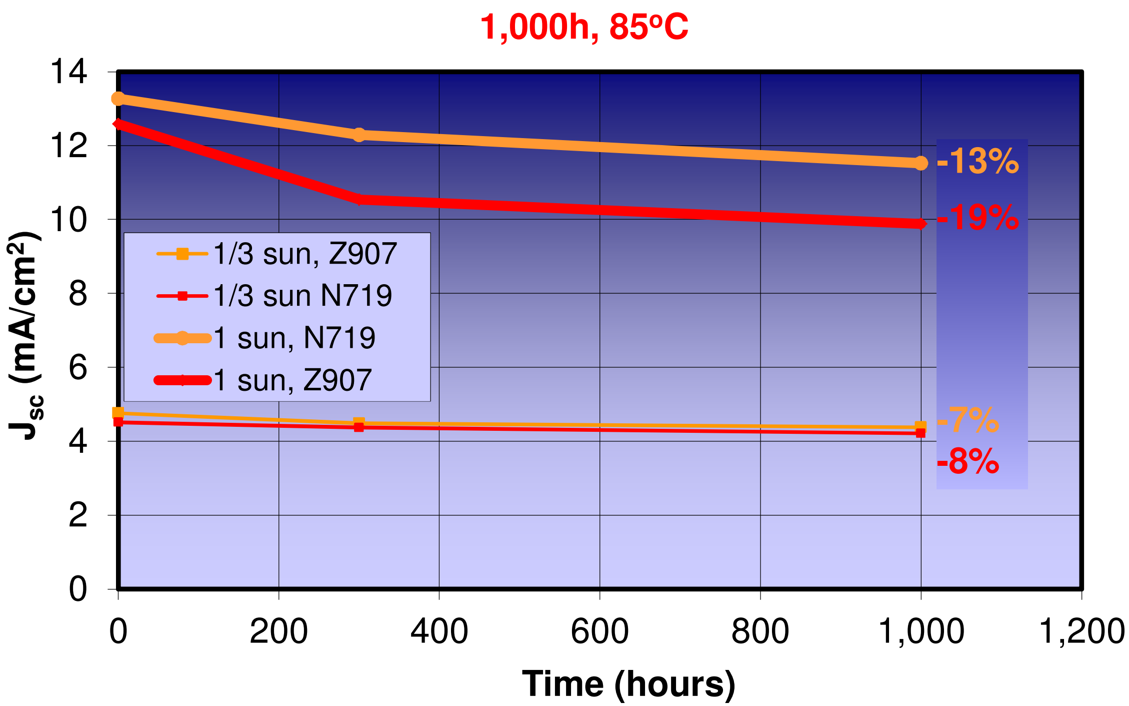
- **N719 (hydrophilic) vs Z907 (hydrophobic)**
- **High-boiling solvent, non-nitrile**
- **Pt catalyst based on Dyesol Platinum Paste PT1**
- **8×11 or 8×168 mm active area**



Effectively meeting IEC 61646 for most practical light levels

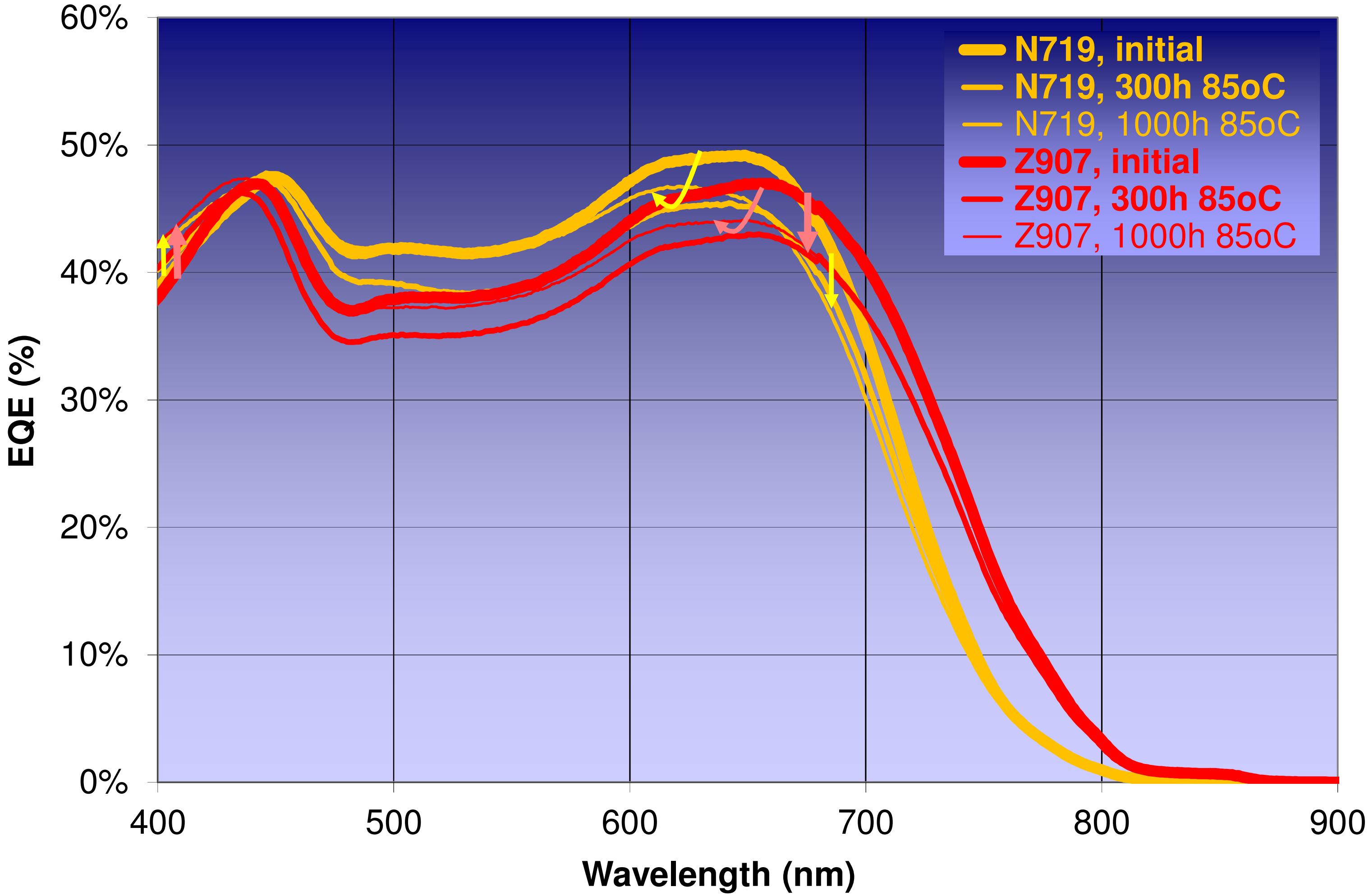
Loss mainly due to loss of J_{sc} - Why?

- **Virtually no loss of V_{oc} for either dye (≤3.5%)**
- **At 1 sun N719 loses less J_{sc}, but some ff (-2%) while Z907 loses more J_{sc} and gains some ff (+3%)**



IPCE (after 85ºC storage)

Incident Photon-to-Electron Conversion Efficiency



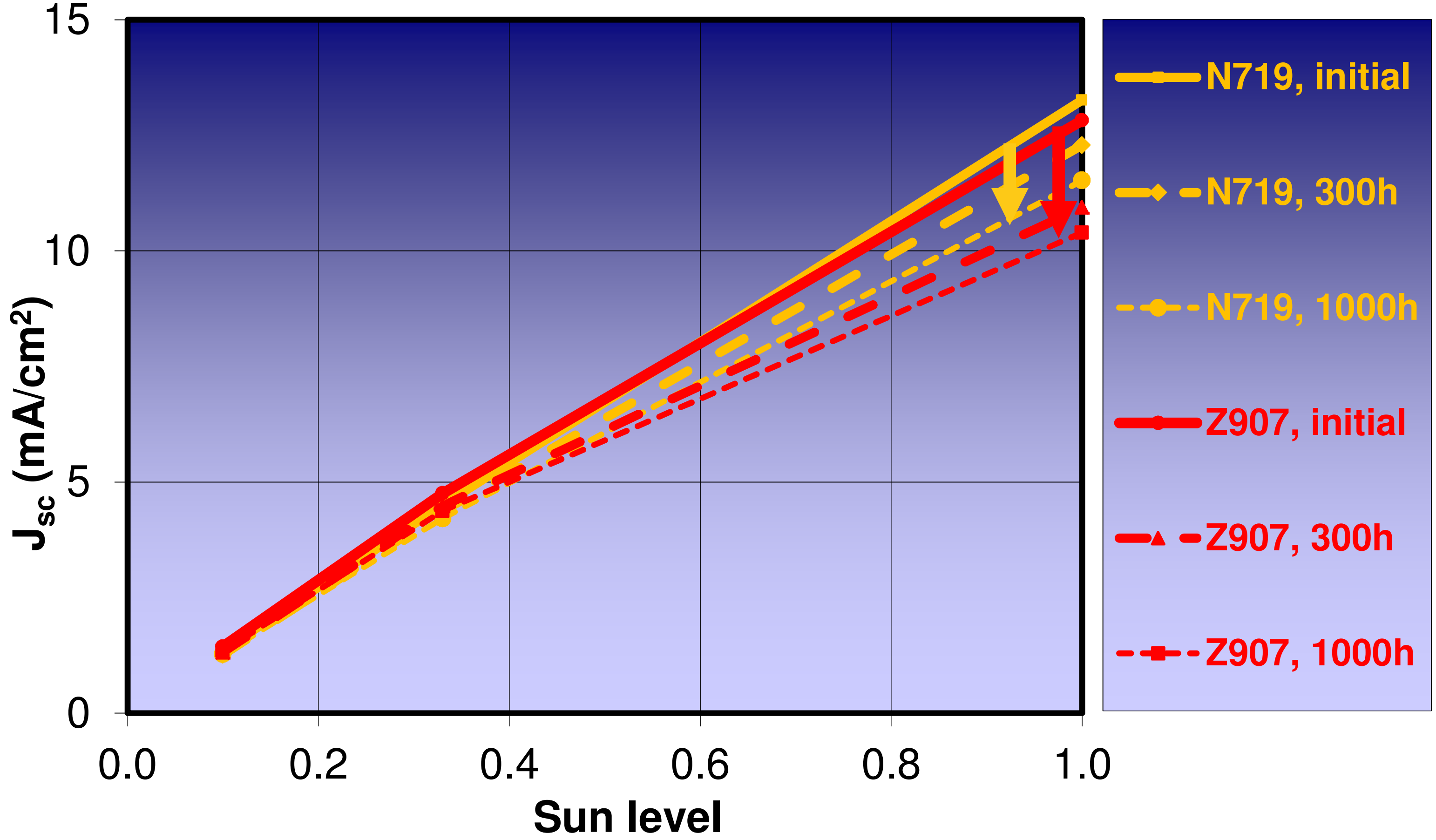
Some loss of IPCE over large part of spectrum over the first 300 h at 85ºC, then almost complete recovery in the 400 to ~570 nm region (due to decreasing conduction band level?)

IPCE

- **No major dye desorption or decomposition such as ligand exchange**
- **Loss of IPCE under low intensity monochromatic light is only partly responsible for loss of J_{sc} under higher intensity light, particularly**
  - after 1,000 h 85°C storage
  - at the higher light levels of 1 sun
  - for Z907

	300 h			1,000 h		
	Δ(IPCE) *)	ΔJ_{sc} (0.33 sun)	ΔJ_{sc} (1 sun)	Δ(IPCE) *)	ΔJ_{sc} (0.33 sun)	ΔJ_{sc} (1 sun)
N719	-6.4%	-3.2%	-7.4%	-3.7%	-6.6%	-13.1%
Z907	-7.3%	-5.8%	-14.6%	-3.9%	-8.0%	-18.9%

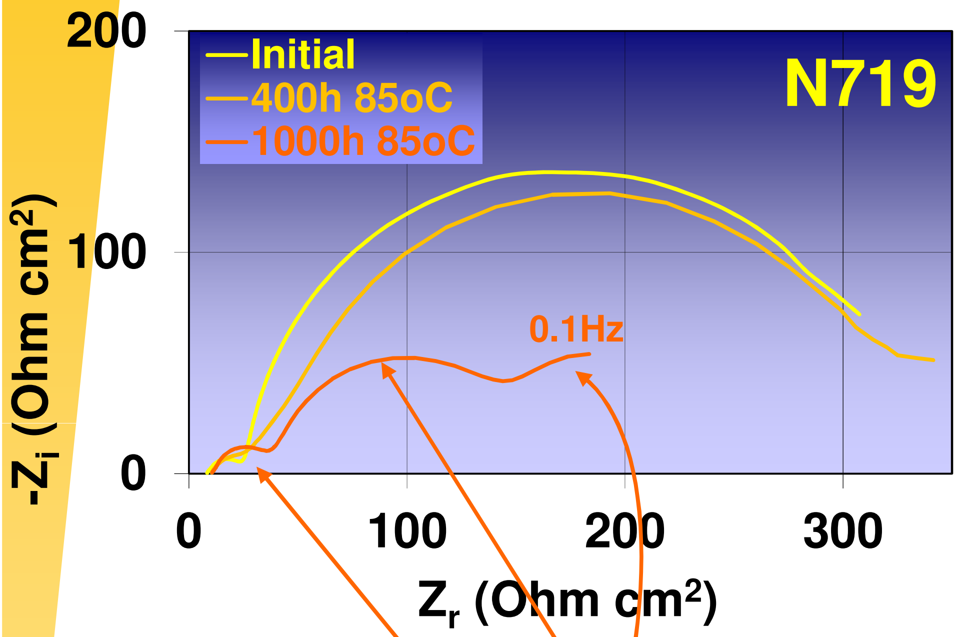
J_{sc} as a function of light level and storage time at 85ºC

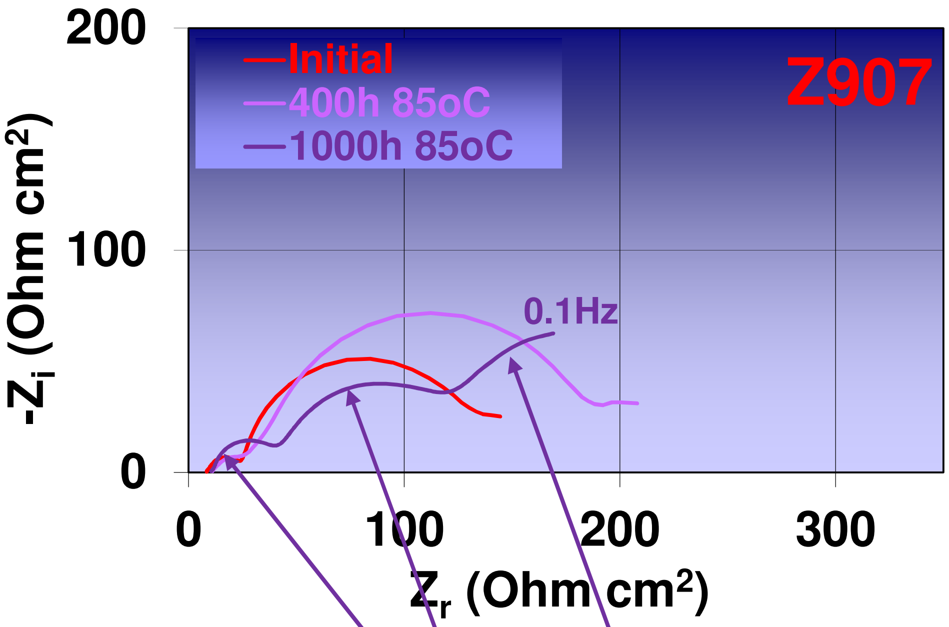


Serious current limitation at the higher light levels as a result of thermal stress testing, particularly for Z907

EIS

Electrochemical Impedance Spectroscopy, 0.4V, 0.33 sun

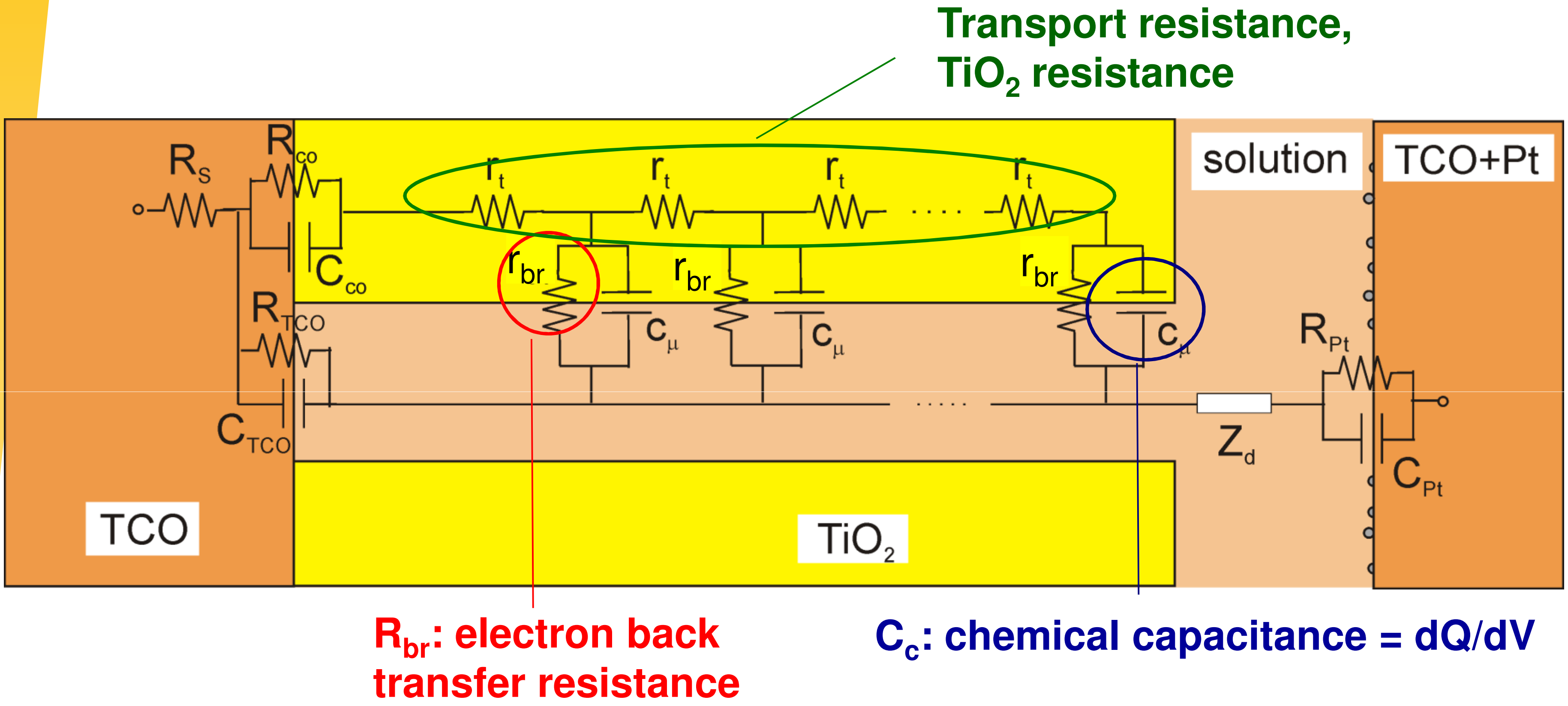




- Significant decrease of R_{br} with prolonged 85°C storage, mainly from 400 to 1,000h
- Significant increase of R_d with prolonged 85°C storage from 400 to 1,000h
- Significant increase of CE R_{ct} at 0.4 V, vs decrease at 0.7 or 0.8 V

- Initial increase of R_{br} then decrease from 400 to 1,000h
- More significant increase of R_d with prolonged 85°C storage compared to N719
- Significant increase of CE R_{ct} at 0.4 V, vs decrease at 0.7 or 0.8 V

EIS (AC impedance)
Transmission line model



a) F. Fabregat-Santiago, et al Solar Ener. Mat. and Solar Cells 87, (2005) 117-131. b) Hoshikawa, et al. *J. Electroan. Chem.*, *588 (2006)* 59

Electron collection efficiency = $R_{br}/(R_{br}+R_t)$

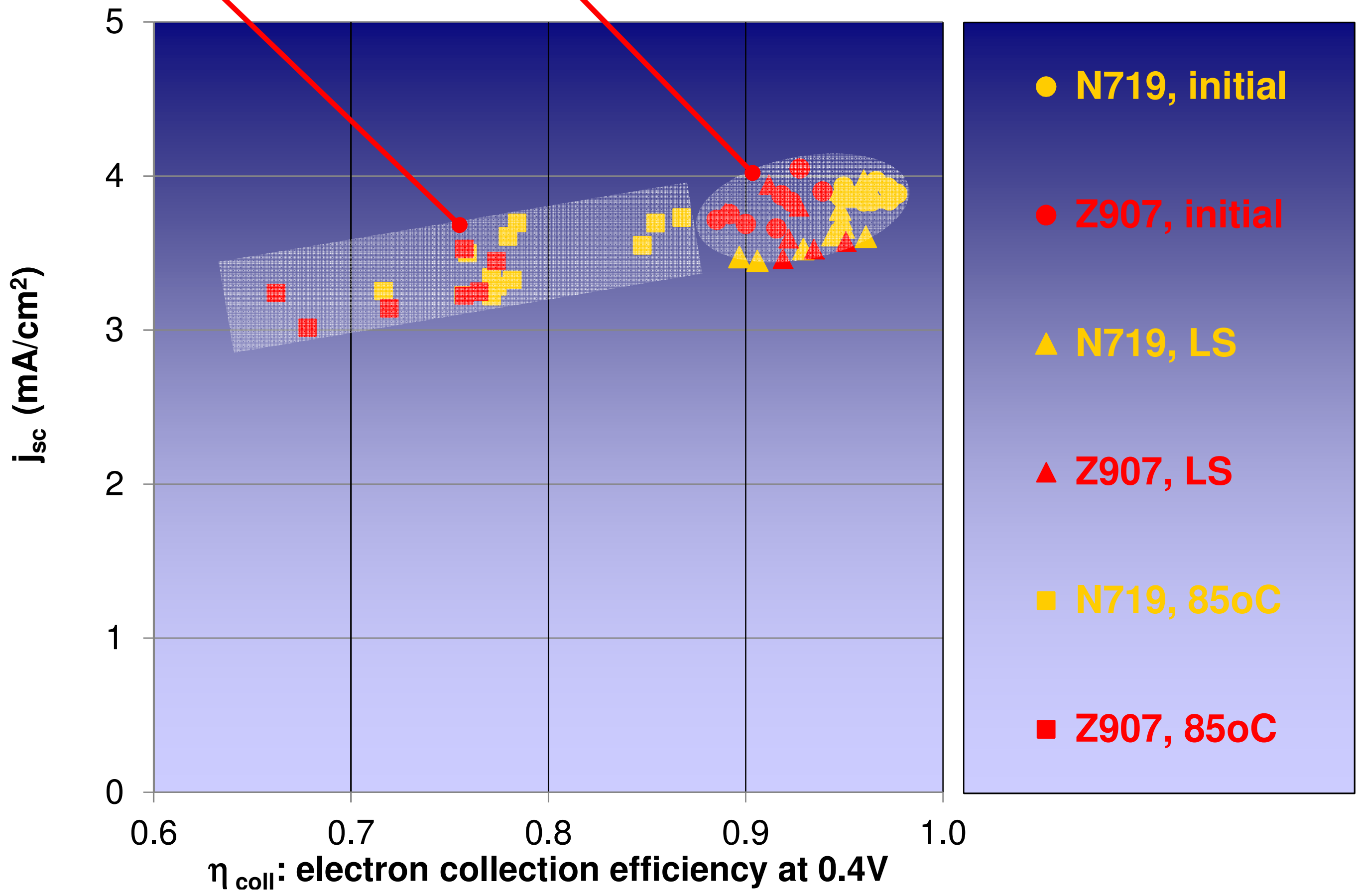
Electron diffusion constant $D_e = d^2 / (R_t C_c)$

Electron diffusion length $L_n = d\,(R_{br}/R_t)^{1/2}$ **d = TiO_2 layer thickness**

Conclusions from EIS

1) 85°C: R_{br} ⇩, R_t: no major change → η_{coll} ⇩ → J_{sc} ⇩

- to a larger extent for Z907 than N719 (various batches)
- in contrast to light soaking (LS) where η_{coll} hardly decreases



Conclusions from EIS

1) **85°C: R_{br} ⇩, R_t: no major change → η_{coll} ⇩ → J_{sc} ⇩**
   - to a larger extent for Z907 than N719
   - in contrast to light soaking (LS) where η_{coll} hardly decreases

2) **85°C: evidence of conduction band downward shift by ~50-100 mV.** Possibly reason for increased IPCE over large part of spectrum. In contrast to light soaking with no significant shift of V_{cb} over 1,000h

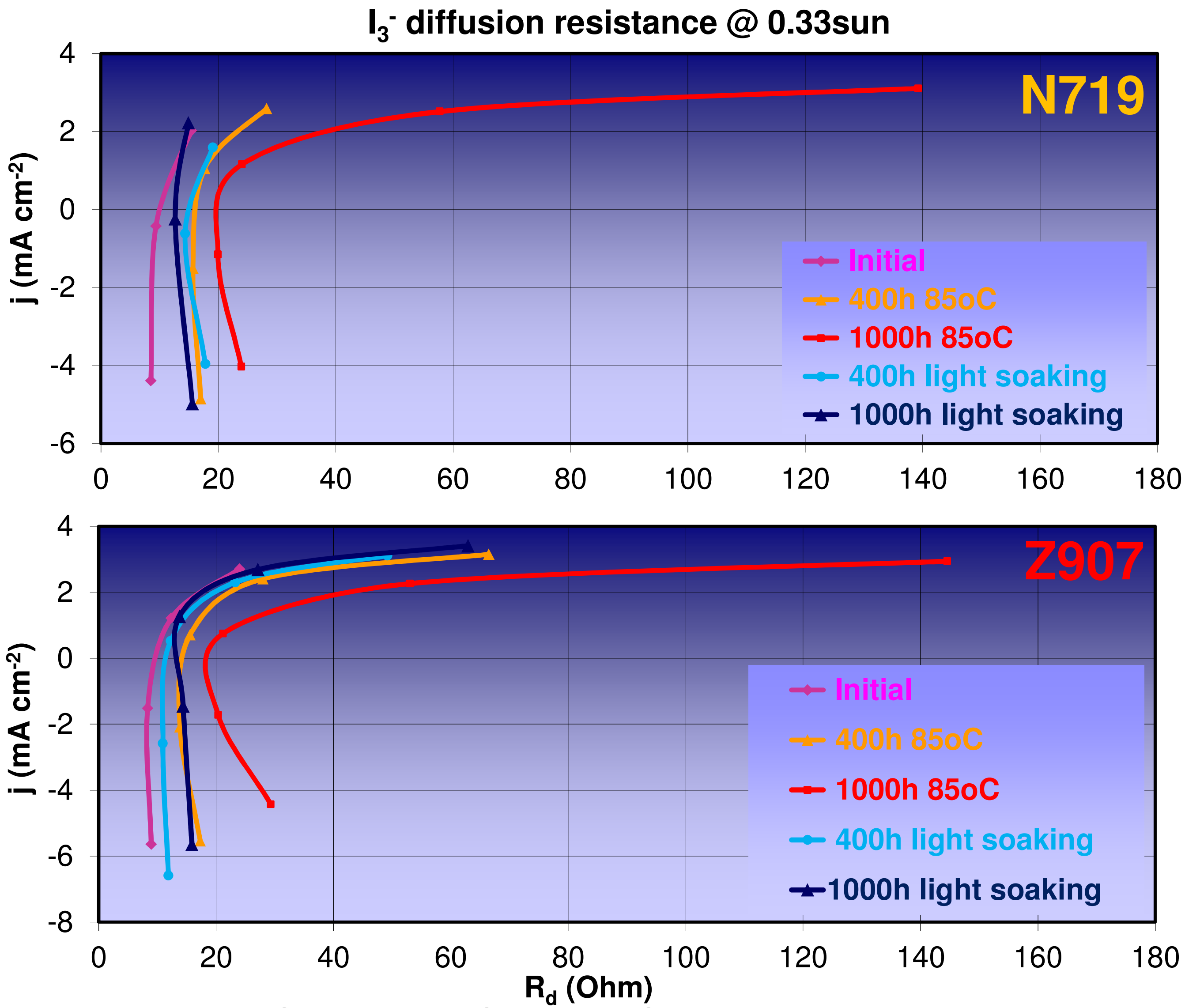
3) **85°C: R_d ⇧, due to diffusion polarisation under photogeneration, particularly for Z907 → J_{sc} ⇩, diffusion limitation → V_{mpp} ⇩** (V_{oc} is much less affected, no diffusion polarisation)

   I_3^- (CE) ⇩ → $R_{ct(photogeneration)}$ ⇧

   while $R_{ct(0.7\ or\ 0.8V)}$ ⇩ due to 'standard' Pt activation

Conclusions from EIS

I_3^- diffusion polarisation

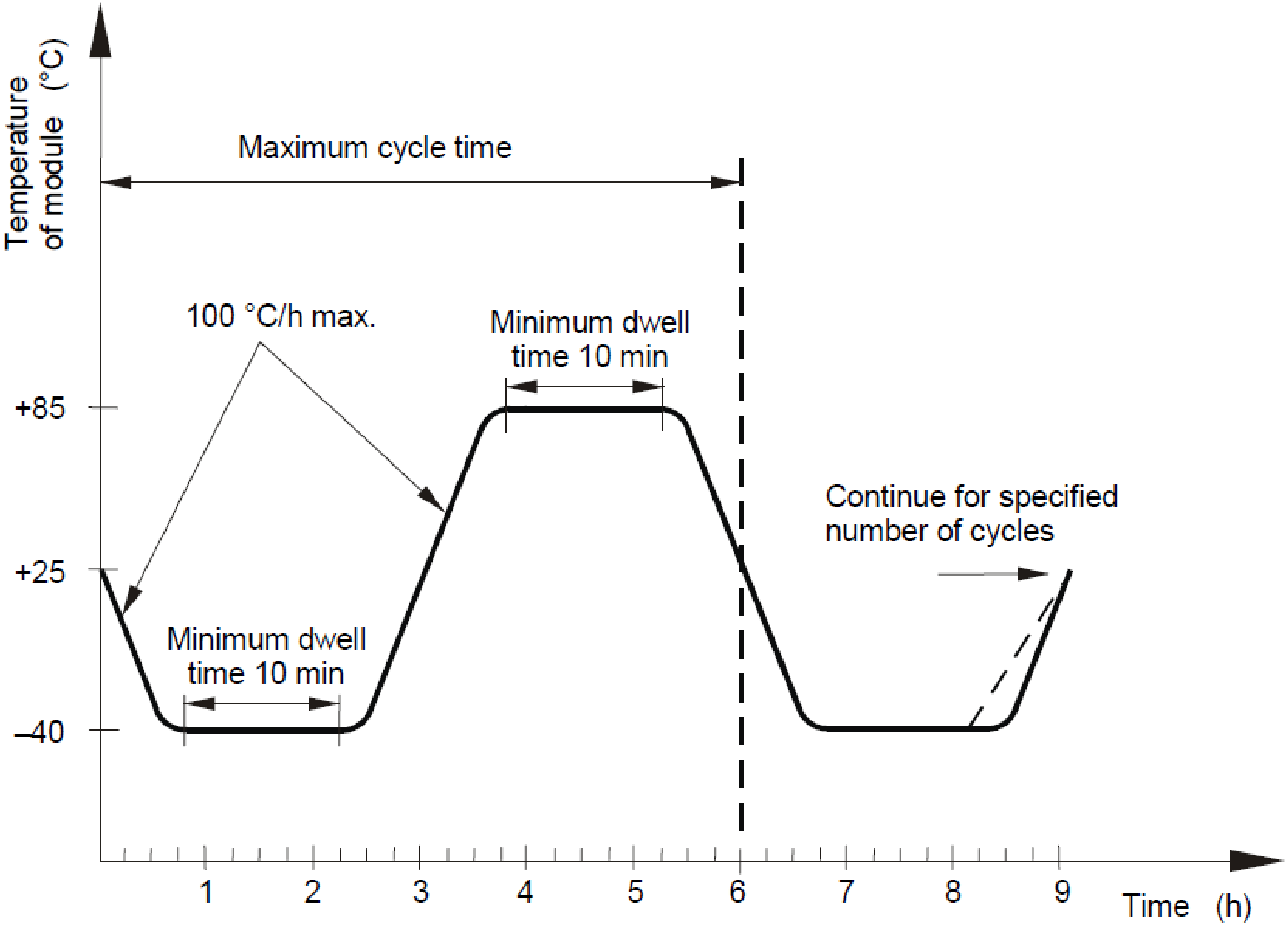


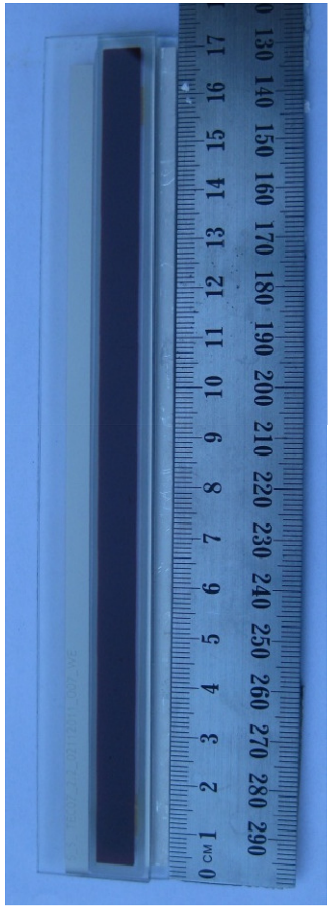
Conclusions from EIS

I_3^- diffusion polarisation

- **Mainly occurs under increasing photocurrents, due to I_3^- concentration polarisation**
- **Much less diffusion polarisation under net negative currents, due to high $[I^-]/[I_3^-]$ concentration ratio**
  - most notable with Z907 as a result of 1,000 h at 85°C
- **Much more pronounced for Z907:**
  - significant increase of R_d as a result of light soaking
  - significant increase of R_d as a result of 400 h at 85°C
  - very significant increase of R_d as a result of 1,000 h at 85°C
- **Much less pronounced for N719:**
  - almost no increase of R_d as a result of light soaking
  - some increase of R_d as a result of 400 h at 85°C
  - very significant increase of R_d as a result of 1,000 h at 85°C

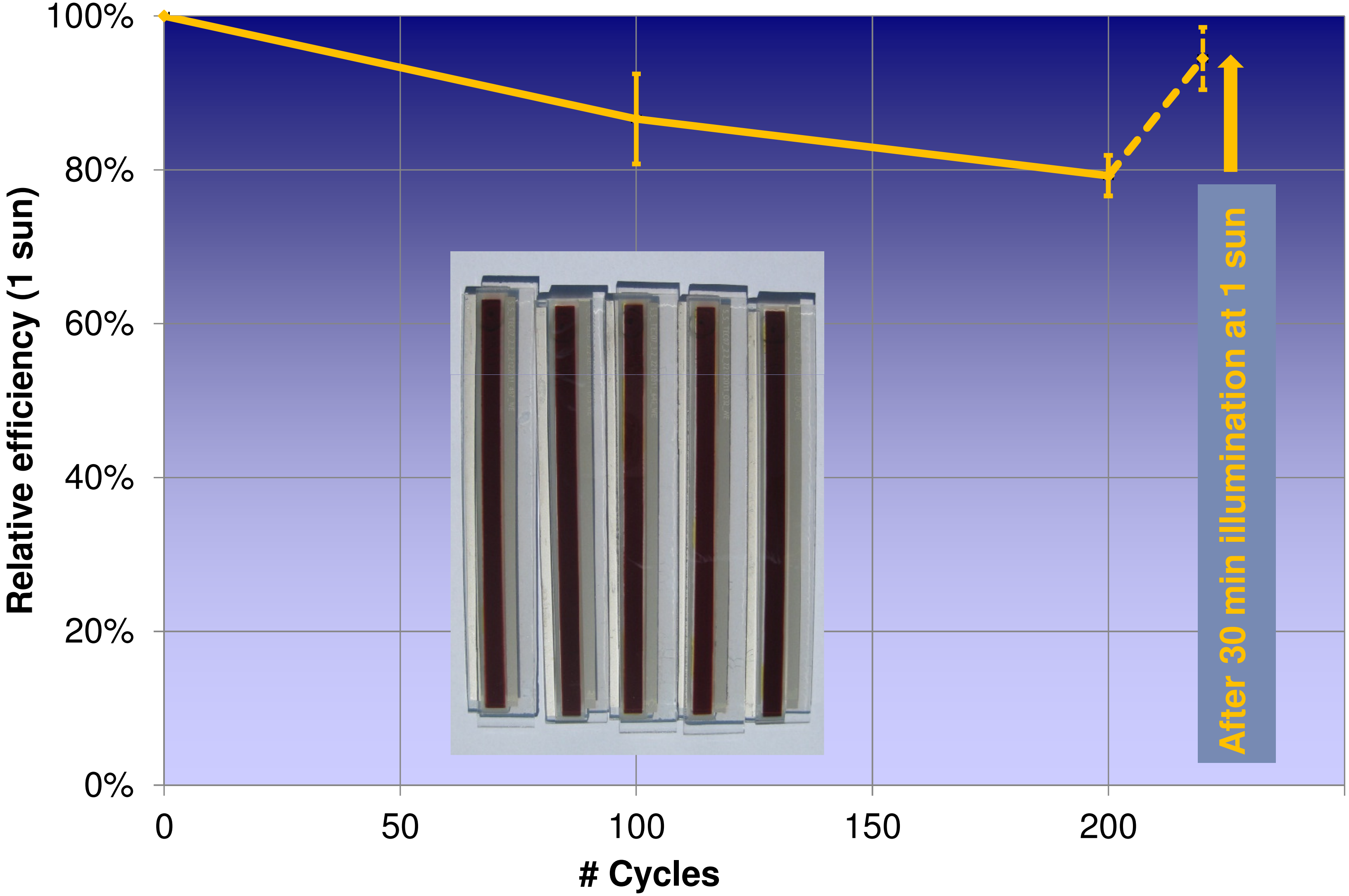
Thermal cycling – IEC 61646





Thermal cycling – IEC 61646

8×168 mm, **MPN**-based electrolyte



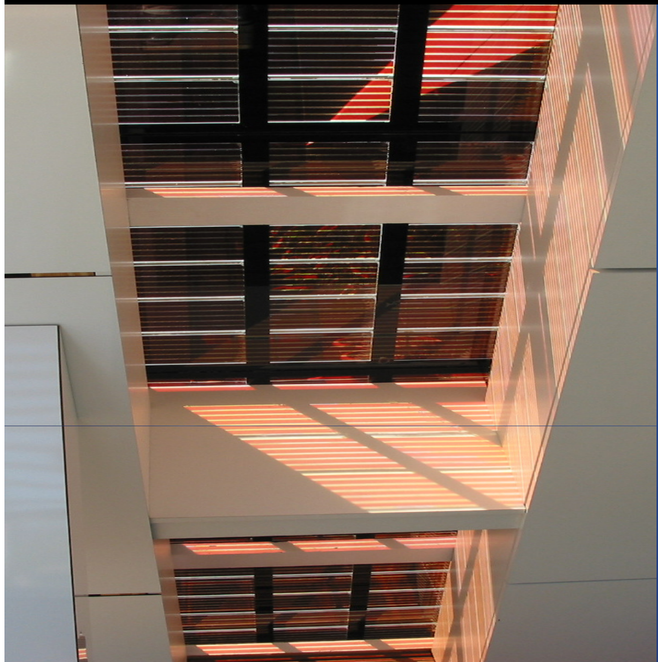
Thermal cycling – IEC 61646

Results / towards larger devices

- **No visual changes**
- **No electrolyte leaks**
- **After 200 thermal cycles with 168mm long cells**
  - temporary loss of 20% efficiency, probably due to nitrile-based solvent
  - largely recoverable after 30 min illumination (@ 1 sun)
- **Similar tests for larger multi-cell devices and with electrolytes offering improved high temperature stability**

Conclusions

- **Very promising chemical and mechanical stability achievable under IEC 61646 85°C storage and thermal cycling**
- **Loss of J_{sc} (rather than V_{oc} or ff) under 85°C storage with the specific cell chemistry is due to**
  - decreasing electron collection efficiency η_{coll}
  - increasing I_3^- diffusion resistance
- **Chemical reasons for increased diffusion resistance upon high temperature exposure are presently not known**
  - more in situ spectroscopic and electrochemical work required
- **Strategies in place to further improve DSC high temperature stability**



Thank you for your attention!

www.dyesol.com