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

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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

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;100 million turnovers</td>
<td>✓</td>
</tr>
<tr>
<td>~No dye desorption</td>
<td>✓</td>
</tr>
<tr>
<td>Loss of NCS-, substitution by I⁻, nitriles, imidazoles, etc.</td>
<td>?</td>
</tr>
<tr>
<td>Isomerisation, e.g. N- to S-bound SCN⁻</td>
<td>?</td>
</tr>
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<td>Decomposition of electrolyte components</td>
<td>?</td>
</tr>
<tr>
<td>Stability of electrocatalyst?</td>
<td>✓</td>
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</tbody>
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- No dye desorption
- Loss of NCS⁻, substitution by I⁻, nitriles, imidazoles, etc.
- Isomerisation, e.g. N- to S-bound SCN⁻
- Decomposition of electrolyte components
- Stability of electrocatalyst?

Lund et al vs Falaras et al. Low 80-85°C stability with nitrile solvents
Not significant according to micro-Raman (Falaras et al)
Little is known, more in situ spectroscopic work required
At least for Pt and certain electrolytes
At the cell level (Dyesol up to **250 mm** length): **Seals**

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Dyesol, Fujikura, Fraunhofer ISE</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Suppress ingress of O₂, H₂O</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Suppress egress of solvent</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Performance stability, 85°C/1,000h; -40°C/+85°C thermal cycling; 85°C/85% r.h./1,000h</td>
<td>✓</td>
<td>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</td>
</tr>
</tbody>
</table>

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


- **IEC 61646 85°C/1,000h and thermal cycling tests remain challenging for DSC**
20-year product life goal
System’s requirements

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
- 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 ($\leq 3.5\%$)
• At 1 sun N719 loses less $J_{sc}$, but some $ff$ (-2%) while Z907 loses more $J_{sc}$ and gains some $ff$ (+3%)
Some loss of IPCE over large part of spectrum over the first 300 h at 85°C, then almost complete recovery in the 400 to ~570 nm region (due to decreasing conduction band level?)
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

<table>
<thead>
<tr>
<th></th>
<th>300 h</th>
<th></th>
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<th>1,000 h</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Δ(IPCE) *)</td>
<td>Δ$J_{sc}$ (0.33 sun)</td>
<td>Δ$J_{sc}$ (1 sun)</td>
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<td>Δ$J_{sc}$ (0.33 sun)</td>
<td>Δ$J_{sc}$ (1 sun)</td>
</tr>
<tr>
<td>N719</td>
<td>-6.4%</td>
<td>-3.2%</td>
<td>-7.4%</td>
<td>-3.7%</td>
<td>-6.6%</td>
<td>-13.1%</td>
</tr>
<tr>
<td>Z907</td>
<td>-7.3%</td>
<td>-5.8%</td>
<td>-14.6%</td>
<td>-3.9%</td>
<td>-8.0%</td>
<td>-18.9%</td>
</tr>
</tbody>
</table>
$J_{sc}$ as a function of light level and storage time at 85°C

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

Transport resistance, TiO$_2$ resistance

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) $85^\circ \text{C}$: $R_{\text{br}} \downarrow$, $R_t$: no major change $\rightarrow \eta_{\text{coll}} \downarrow \rightarrow J_{\text{sc}} \downarrow$
- to a larger extent for Z907 than N719 (various batches)
- in contrast to light soaking (LS) where $\eta_{\text{coll}}$ hardly decreases
Conclusions from EIS

1) 85°C: $R_{br} \downarrow$, $R_t$: no major change $\rightarrow \eta_{coll} \downarrow \rightarrow J_{sc} \downarrow$
   - to a larger extent for Z907 than N719
   - in contrast to light soaking (LS) where $\eta_{coll}$ 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: $R_d \uparrow$, due to diffusion polarisation under photogeneration, particularly for Z907 $\rightarrow J_{sc} \downarrow$, diffusion limitation $\rightarrow V_{mpp} \downarrow$ ($V_{oc}$ is much less affected, no diffusion polarisation)
   $I_3^-$ (CE) $\downarrow \rightarrow R_{ct(photogeneration)} \uparrow$
   while $R_{ct(0.7 or 0.8V)} \downarrow$ due to ‘standard’ Pt activation
Conclusions from EIS

I$_3^-$ diffusion polarisation

I$_3^-$ diffusion resistance @ 0.33sun

N719

Z907

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Conclusions from EIS

$\text{I}_3^-$ diffusion polarisation

- Mainly occurs under increasing photocurrents, due to $\text{I}_3^-$ concentration polarisation
- Much less diffusion polarisation under net negative currents, due to high $\text{[I}^-]/[\text{I}_3^-]$ 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

Temperature of module (°C)

Maximum cycle time

100 °C/h max.

Minimum dwell time 10 min

Continue for specified number of cycles

Time (h)
Thermal cycling – IEC 61646
8×168 mm, MPN-based electrolyte

After 30 min illumination at 1 sun
• 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 $\eta_{coll}$
  - 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!

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