

Evolution of the iodine crystals in dye-sensitized solar cells

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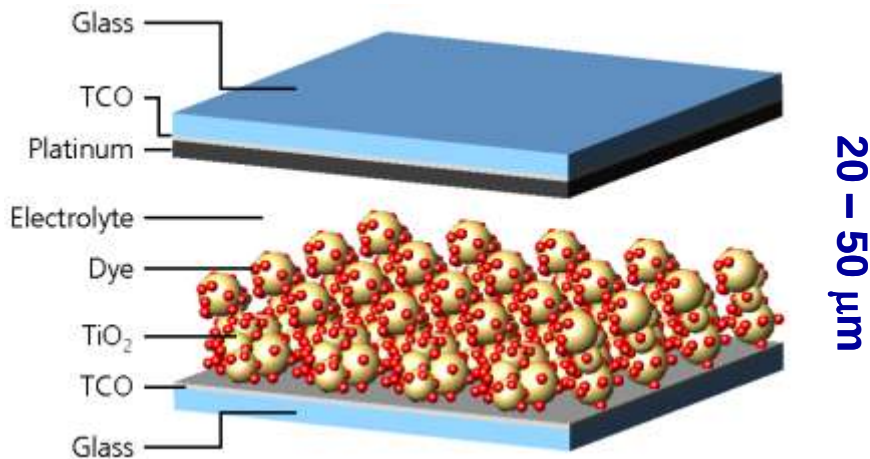


Outline

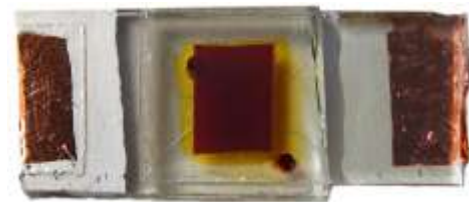
- Motivation
- Results of the DSSCs:
 - › stored at room temperature in the dark
 - › temperature treatment at 60 °C and 80 °C (T_C outdoors could exceed 60 °C)
 - › reverse current treatment (to simulate a shaded DSSC connected in series in a PV module)
 - › forward current treatment (to simulate a shaded DSSC connected in parallel in a PV module)
- Conclusions

Dye-sensitized solar cell

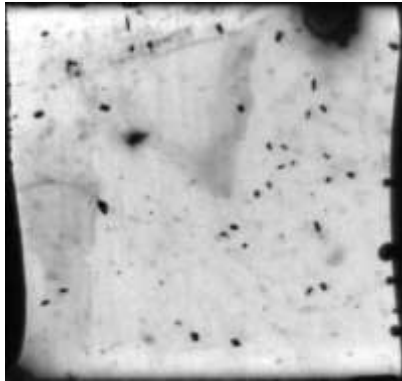
- simple and low cost technology and materials
- the highest reported efficiency exceeds 12%
- stability is still a problem



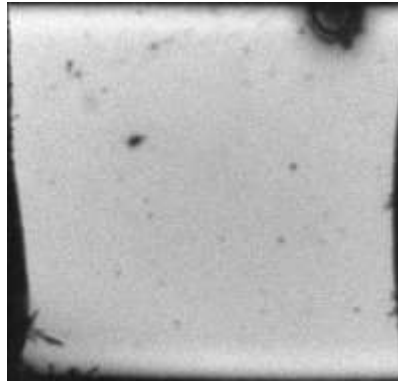
Our cell:



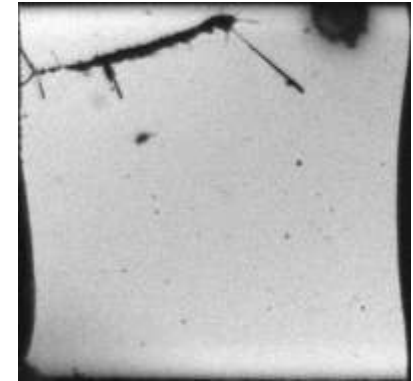
Motivation



→
245 kWh/m²



→
660 kWh/m²



fresh

$$J_{SC} = 9.52 \text{ mA/cm}^2$$

$$V_{OC} = 0.658 \text{ V}$$

$$\eta = 3.80\%$$

$$J_{SC} = 9.99 \text{ mA/cm}^2$$

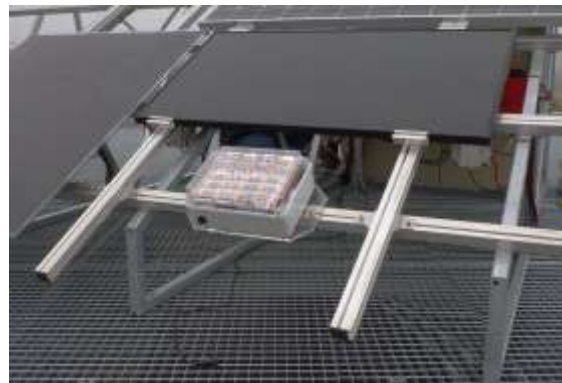
$$V_{OC} = 0.626 \text{ V}$$

$$\eta = 4.06\%$$

$$J_{SC} = 9.12 \text{ mA/cm}^2$$

$$V_{OC} = 0.599 \text{ V}$$

$$\eta = 3.45\%$$



Electrolyte:

1-propyl-3-methyl-imidazolium iodide:

1-ethyl-3-methyl-imidazolium
tetracyanoborate, vol. 13:7

0.5 M N-methylbenzimidazol

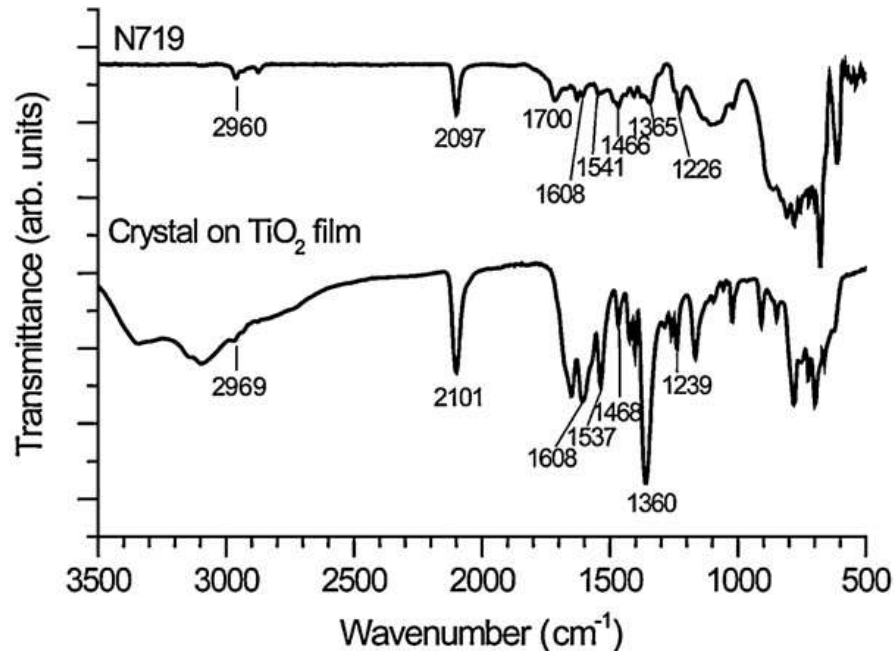
0.1 M guanidinium thiocyanate

0.2 M I₂

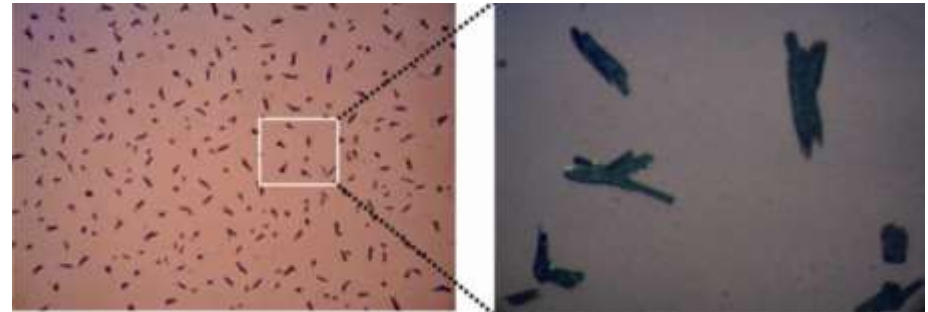
Outdoor ageing: April-October 2012, Ljubljana

Motivation

Fourier transform infrared spectroscopy



Optical microscope image

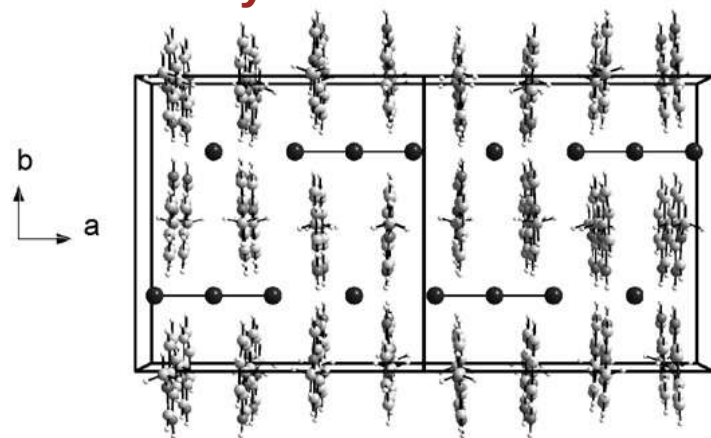
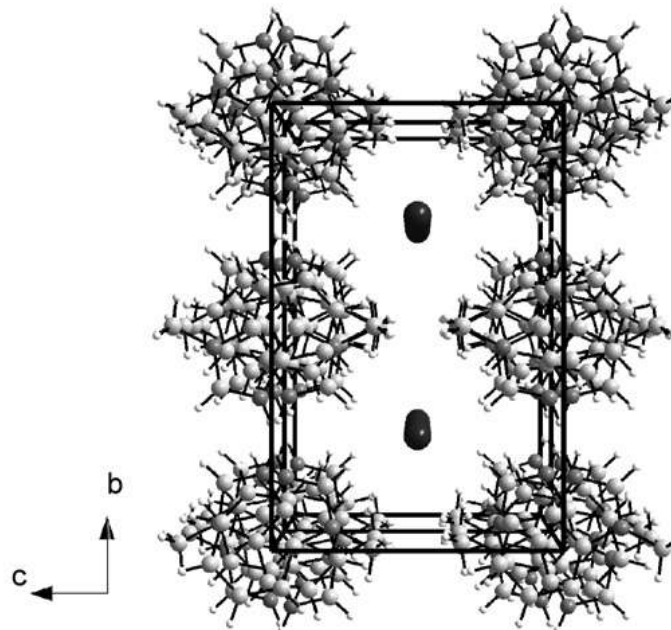


- dark needle-shaped solid **crystals** appeared on the TiO₂ after 10 days
 - they are related to dye detaching in the presence of guanidinium thiocyanate
- guanidine reacts with H₂O residues and forms ammonia - a dye desorbing agent**

M.J. Kim *et al. Appl. Surf. Sci.* **258** (2012) 8915

Motivation

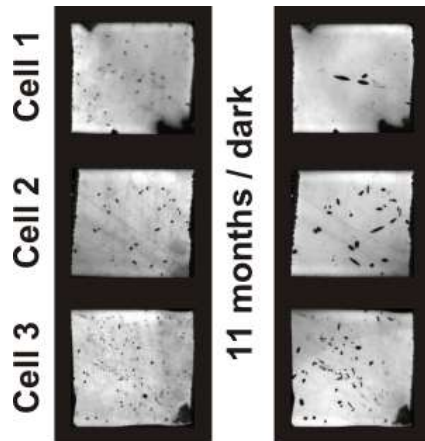
X-ray diffraction



- dark brown, almost black **crystals** appeared after 1-2 weeks
- *N*-methylbenzimidazole (MBI) interacts with I_3^- ions to form neutral and/or ionic complexes, such as $(MBI)_6(MBI-H^+)_2(I^-)(I_3^-)$
- they consisted of six neutral and two protonated MBI fragments, I^- and I_3^- anions balance the overall charge, the organic layers are separated by inorganic layers with alternating I^- and linear I_3^- anions forming infinite chains

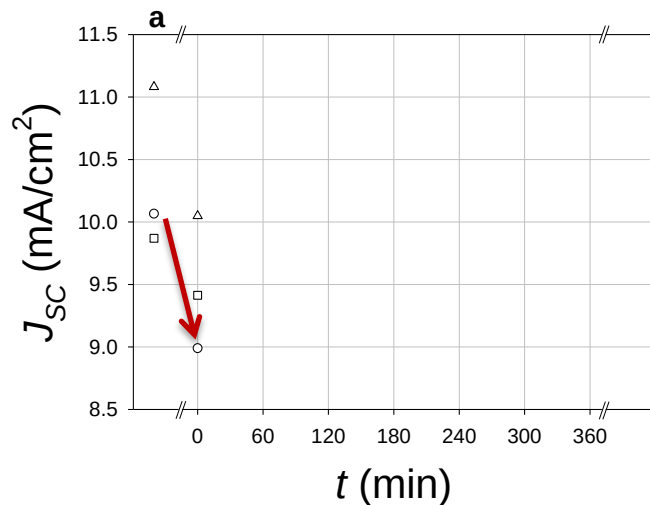
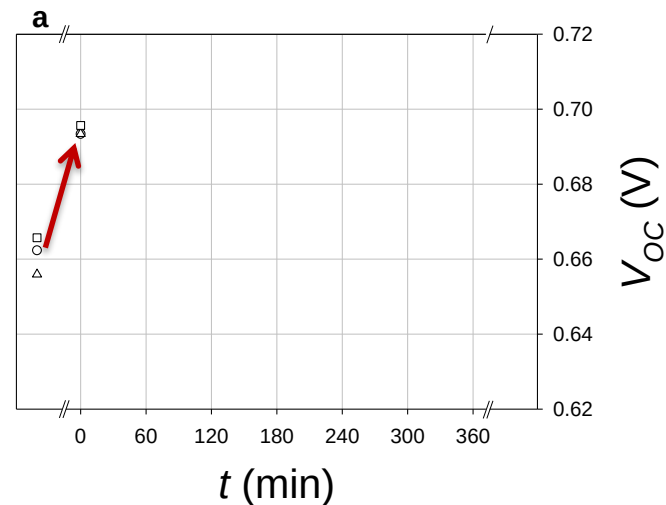
A. Fischer *et al.* *Sol. Energ. Mat. & Sol. C.* **91** (2007) 1062

Storing cells in the dark

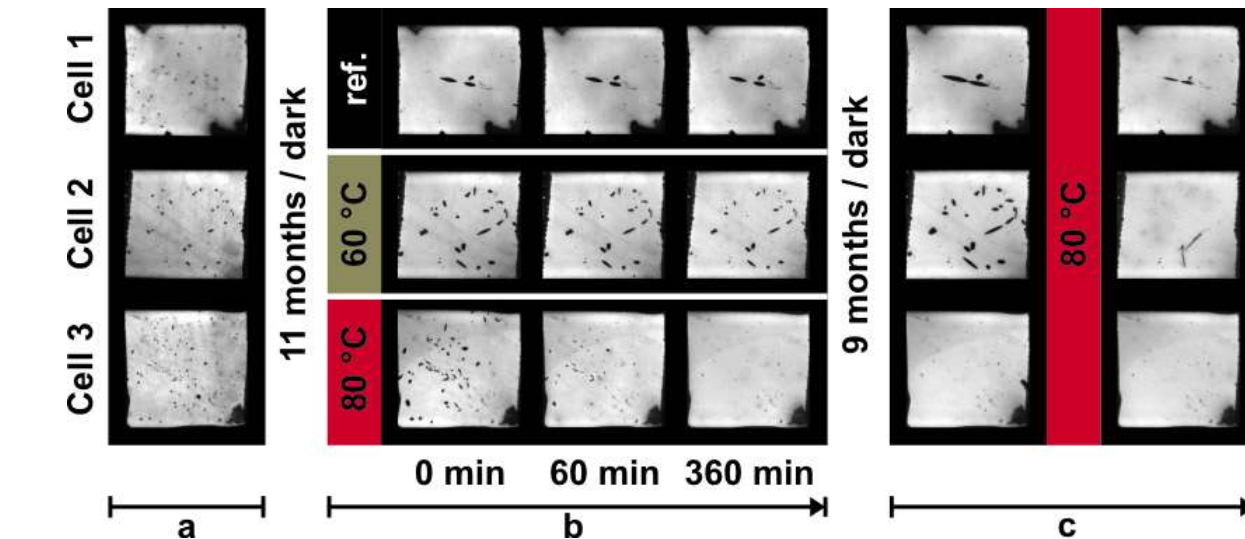


- cells have small crystals after fabrication
- the crystals grow when the cells are stored in the dark:

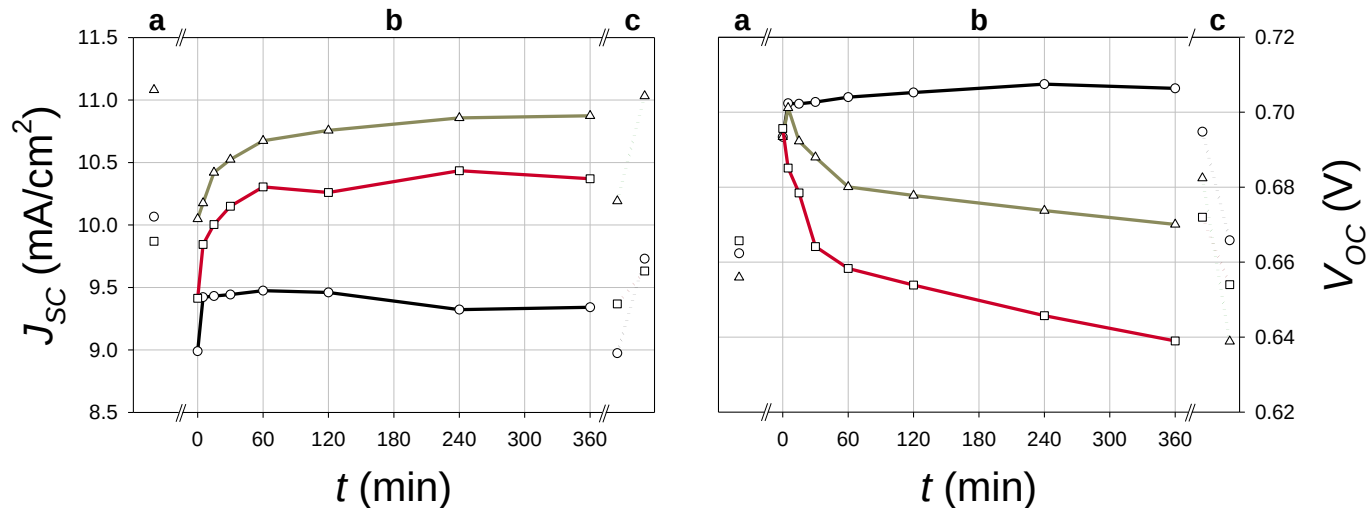
- > reduce $[I_3^-]$
- > decrease J_{SC} (approx. 1 mA/cm²)
- > increase V_{OC} (approx. 40 mV)



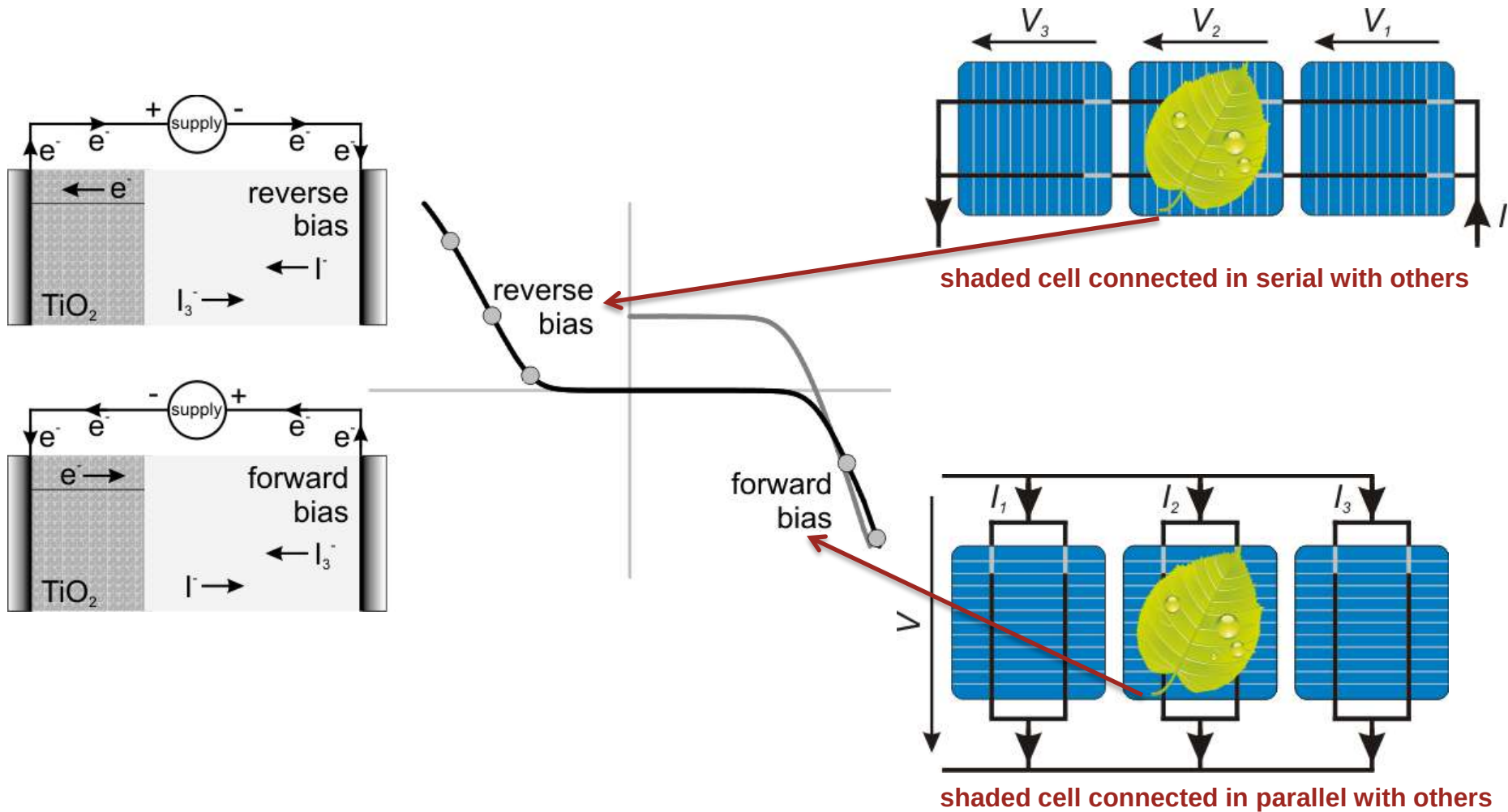
Temperature treatment



- crystals dissolve
 $> J_{SC} \uparrow$
 $> V_{OC} \downarrow$
- crystals do not reappear if previously dissolved

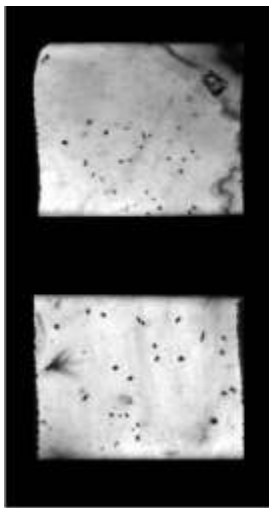


Current treatment



Current treatment

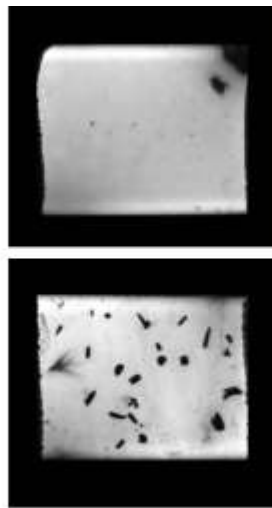
$J_{SC} = 9.74 \text{ mA/cm}^2$
 $V_{OC} = 0.664 \text{ V}$
 $\eta = 3.63\%$



$J_{SC} = 10.17 \text{ mA/cm}^2$
 $V_{OC} = 0.658 \text{ V}$
 $\eta = 4.18\%$

11 months / dark

$J_{SC} = 7.52 \text{ mA/cm}^2$
 $V_{OC} = 0.758 \text{ V}$
 $\eta = 4.03\%$



$J_{SC} = 9.37 \text{ mA/cm}^2$
 $V_{OC} = 0.695 \text{ V}$
 $\eta = 4.29\%$

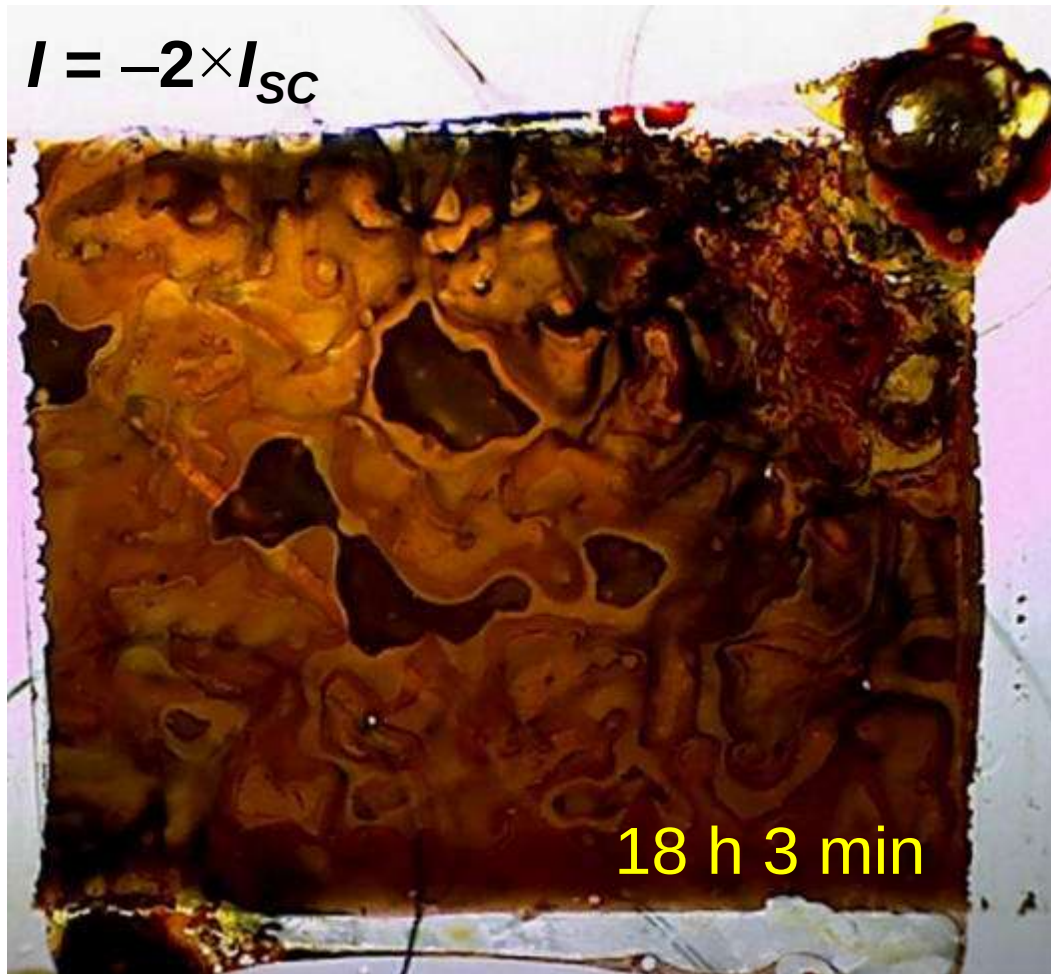
reverse

Similar conclusion:

- small crystals are present after fabrication
- the crystals grow when the cells are stored in the dark:

- > reduce $[I_3^-]$
- > decrease J_{SC}
- > increase V_{OC}

Reverse current treatment



- appearance of small bubbles
- small bubbles combine
- bubble size gradually decreases
- dye molecules detaching off
- **severe damage of the DSSC**

<http://www.rsc.org/suppdata/cp/c4/c4cp01463d/c4cp01463d2.mp4>

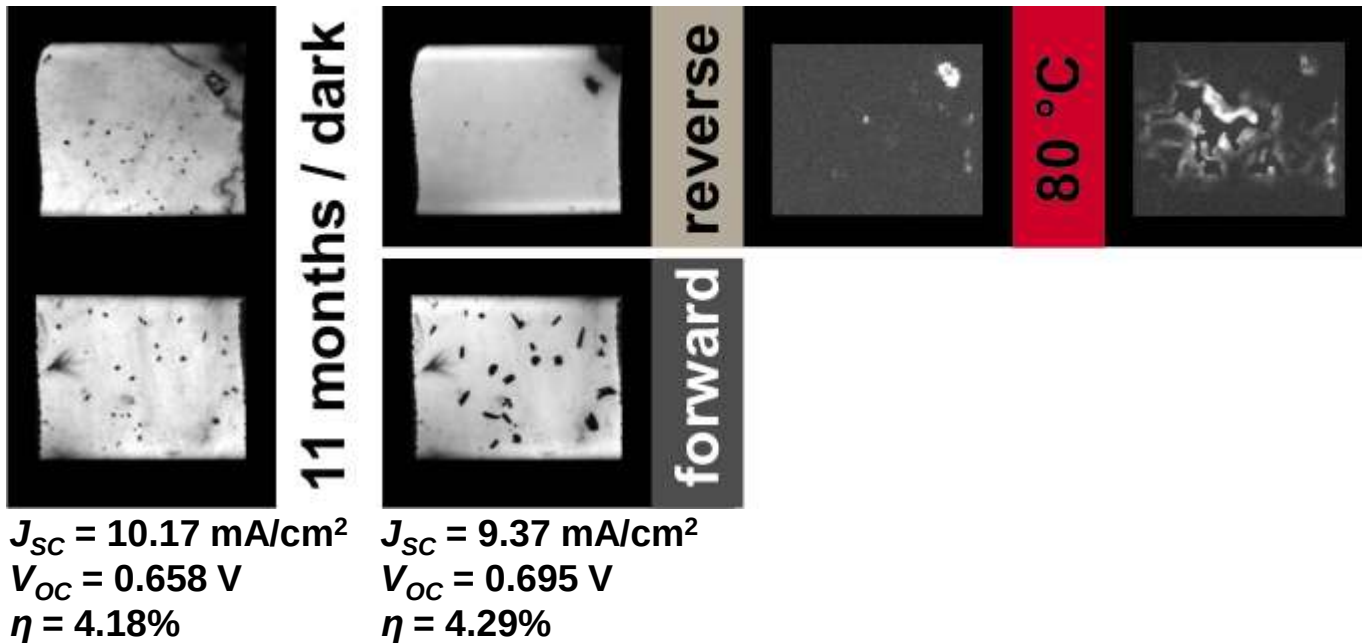
Current treatment

$J_{SC} = 9.74 \text{ mA/cm}^2$
 $V_{OC} = 0.664 \text{ V}$
 $\eta = 3.63\%$

$J_{SC} = 7.52 \text{ mA/cm}^2$
 $V_{OC} = 0.758 \text{ V}$
 $\eta = 4.03\%$

$J_{SC} = 0.00 \text{ mA/cm}^2$
 $V_{OC} = 0.007 \text{ V}$
 $\eta = 0.00\%$

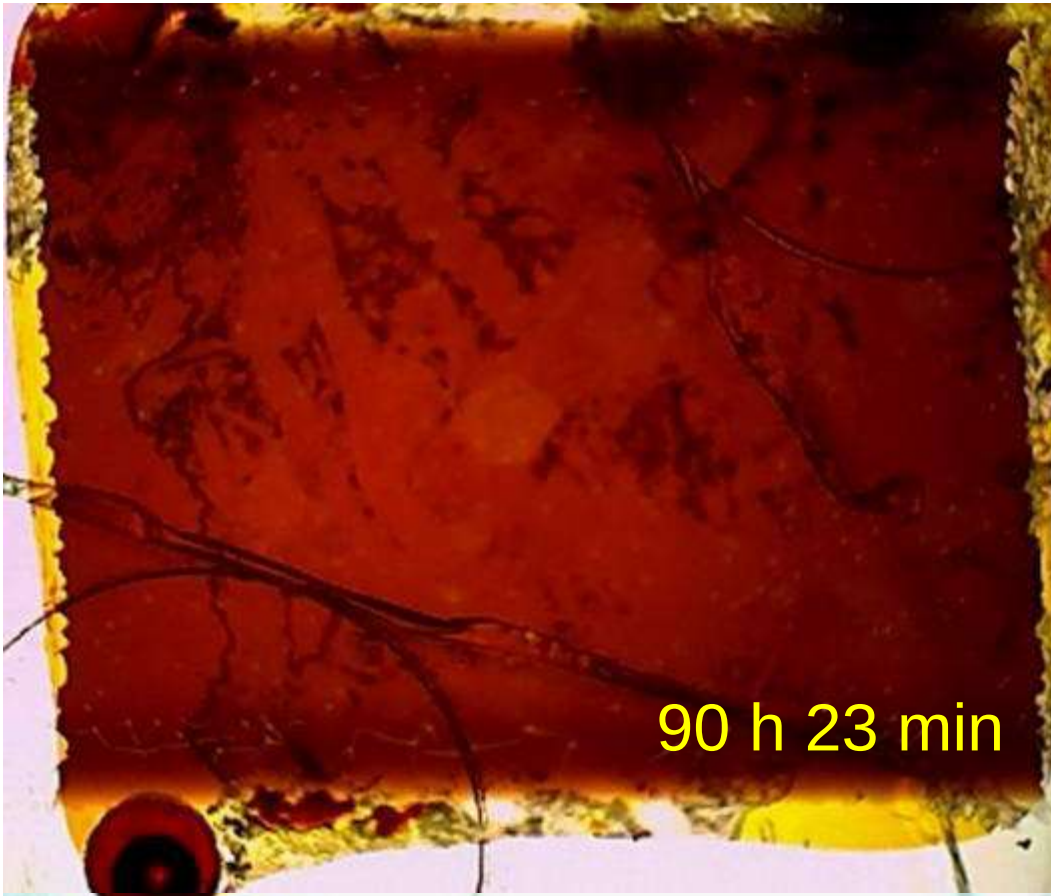
$J_{SC} = 0.08 \text{ mA/cm}^2$
 $V_{OC} = 0.254 \text{ V}$
 $\eta = 0.01\%$



DSSC performance is not recovered

Forward current treatment

$$I = -2 \times I_{sc}$$



- rapid growth of the crystals
- crystals grow in all directions (dendritic pattern)
- crystals became brighter
- **electrolyte collapse**

<http://www.rsc.org/suppdata/cp/c4/c4cp01463d/c4cp01463d2.mp4>

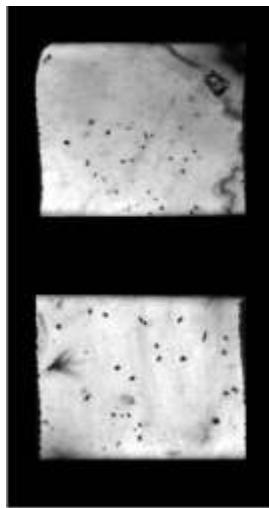
Forward current treatment

$J_{SC} = 9.74 \text{ mA/cm}^2$
 $V_{OC} = 0.664 \text{ V}$
 $\eta = 3.63\%$

$J_{SC} = 7.52 \text{ mA/cm}^2$
 $V_{OC} = 0.758 \text{ V}$
 $\eta = 4.03\%$

$J_{SC} = 0.00 \text{ mA/cm}^2$
 $V_{OC} = 0.007 \text{ V}$
 $\eta = 0.00\%$

$J_{SC} = 0.08 \text{ mA/cm}^2$
 $V_{OC} = 0.254 \text{ V}$
 $\eta = 0.01\%$



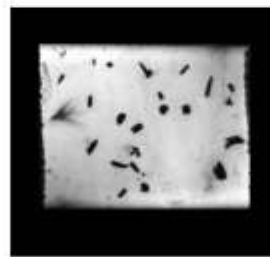
11 months / dark



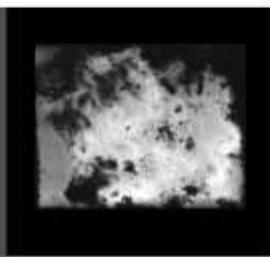
reverse



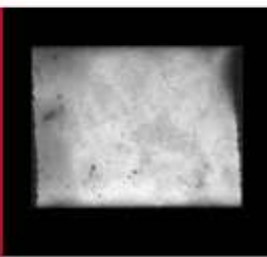
80 °C



forward



80 °C



$J_{SC} = 10.17 \text{ mA/cm}^2$
 $V_{OC} = 0.658 \text{ V}$
 $\eta = 4.18\%$

$J_{SC} = 9.37 \text{ mA/cm}^2$
 $V_{OC} = 0.695 \text{ V}$
 $\eta = 4.29\%$

$J_{SC} = 1.90 \text{ mA/cm}^2$
 $V_{OC} = 0.605 \text{ V}$
 $\eta = 0.52\%$ →

$J_{SC} = 10.64 \text{ mA/cm}^2$
 $V_{OC} = 0.630 \text{ V}$
 $\eta = 4.16\%$

recovery of DSSC performance by heat treatment

Conclusions

- different treatments (storing in the dark, heat treatment at 60 °C or 80 °C, reverse and forward current treatment) of the ionic liquid based DSSC with a I_3^-/I^- redox couple influence the spatial distribution of the iodine containing crystals (defects) and therefore the cell performance
- storing the cells in the dark: crystals grow, $[I_3^-] \downarrow$, $J_{SC} \downarrow$, $V_{OC} \uparrow$
- heat treatment at 60 - 80 °C: crystals dissolve, $[I_3^-] \uparrow$, $J_{SC} \uparrow$, $V_{OC} \downarrow$
- reverse current : rapid formation of H_2 bubbles, detachment of dye molecules from TiO_2 , irreversible breakdown of the cell
- forward current: crystals grow rapidly, η decreases by 88% but the following heat treatment at 80 °C can restore the performance

Conclusions

- crystals do not reappear even after a resting period of 9 months if they had been completely removed by heat treatment
- the study agrees with a theory that the electrolyte the additive *N*-methylbenzimidazole reacts with iodine and forms iodine containing crystals such as $(\text{MBI})_6(\text{MBI-H}^+)_2(\text{I}^-)(\text{I}_3^-)$ complex
 [A. Fischer *et al. Sol. Energ. Mat. & Sol. C.* **91** (2007) 1062]
- **heat treating DSSCs at 80 °C is recommended to either initially stabilize or restore an I_3^-/I^- redox couple based electrolyte and in turn cell performance**

Thank you for your attention