Advanced optoelectronic tools to interrogate solution-processed solar cells

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New generation solar cells
The next step: biological electronics
Transients of the transient photovoltage spectroscopy (TrOTTr TPV)

Dan Bryant (ICL, Chemistry)
Xiaoe Li (ICL, Chemistry)
Jenny Nelson (ICL, Physics)
James Durrant (ICL, Chemistry)
Matt Carnie (Swansea, Specific)
Joel Troughton (Swansea, Specific)
Hysteresis in perovskite solar cells

Anomalous Hysteresis in Perovskite Solar Cells

Henry J. Snaith,* Antonio Abate, James M. Ball, Giles E. Eperon, Tomas Leijtens, Nakita K. Noel, Samuel D. Stranks, Jacob Tse-Wei Wang, Konrad Wojciechowski, and Wei Zhang

- Current-Voltage scans exhibit hysteresis between forward and reverse scans
- Short circuit current and open circuit voltage exhibits relaxation on the timescale of seconds

CH$_3$NH$_3$PbI$_3$ (MAPI)
Ion migration

Anode

Cathode

$E_{\text{ions}}$

$E_{\text{cell}}$

Current Density [mA/cm$^2$]

Voltage [V]

$V_{\text{precon}} < V_{\text{oc}}$

$V_{\text{oc}}$

Dark

Light

Time

Voltage
Transients of the transient (TrOTTr) photovoltage measurements
The TrOTTr rig
**TiO\textsubscript{2} bottom cathode architecture**

![Diagram showing the TiO\textsubscript{2} bottom cathode architecture with layers of Au, Spiro OMeTAD, CH\textsubscript{3}NH\textsubscript{3}Pbl\textsubscript{3}, TiO\textsubscript{2}, and FTO.]

![Graph showing the current density vs voltage with different conditions: 'Dark Reverse', 'Dark Forward', '1 Sun Reverse', and '1 Sun Forward'.]

![Graph showing the variation of open-circuit voltage (Voc) with time (t). The Voc stabilizes at 800 mV after 1.2 seconds.]
Ionic charge accumulation

a) $t = -60\,\text{s}$, Short Circuit
b) $t = -1\,\text{s}$, Short Circuit
c) $t = 0\,\text{s}$, Open Circuit
d) $t = 45\,\text{s}$, Open Circuit

Hysteresis-free devices!

Hysteresis-free and highly stable perovskite solar cells produced via a chlorine-mediated interdiffusion method†

Neeti Tripathi,¹ Masatoshi Yanagida,¹ Masayoshi Shirai,³ Takuya Masuda,² Liyuan Han³ and Kenjiro Miyano³

- Changing contact materials appears to alter J-V hysteresis
Hysteresis depends on the contact materials

Bottom cathode – TiO₂

<table>
<thead>
<tr>
<th>Layer</th>
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<tbody>
<tr>
<td>Au</td>
</tr>
<tr>
<td>Spiro OMeTAD</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>FTO</td>
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</tbody>
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Top cathode - PCBM

<table>
<thead>
<tr>
<th>Layer</th>
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<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>PCBM</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
</tr>
<tr>
<td>ITO</td>
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</tbody>
</table>

Top cathode - ZnO

<table>
<thead>
<tr>
<th>Layer</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
</tr>
<tr>
<td>ITO</td>
</tr>
</tbody>
</table>
PCBM top cathode architecture
The role of interfacial recombination

- Without surface recombination, photogenerated charge carriers flood device and screen ionic charge.

![Diagram showing the role of interfacial recombination](image-url)
The role of interfacial recombination

- With surface recombination, photo-carrier concentrations are low, ionic charge dominates E-field distribution.

Van Reenen et al. JPCL 2015, DOI: 10.1021/acs.jpclett.5b01645
No bias light $\rightarrow$ few background carriers

**Positive transient photocurrent observed in both architectures indicating reverse field**
Conclusions

- Mobile ions are present in the device regardless of hysteresis.

- Surface recombination determines whether a reverse electric field at Voc is detectable or not. It also affects the extraction efficiency at 0<V<Voc.

- Hysteresis can be reproduced in JV curves by switching ON or OFF the surface recombination, while allowing for ion migration.
How Does the Photo-oxidation of Fullerenes Affect the Behaviour of OPV Devices?

James R. Durrant (Imperial, Chemistry)
Jiaying Wu (Imperial, Chemistry)

Jason Röhr
Beth Rice
Alexandre De Castro Maciel
Jenny Nelson

Wing C. Tsoi (Swansea)
Zhe Li (Swansea)
Harrison K. H. Lee (Swansea)
Emily Speller (Swansea)
Photo-oxidation of fullerene

![Graph showing current density (mA/cm²) vs. voltage (V) for different times and compositions of PCDTBT:PCBM and PCDTBT:PCBM:O-PCBM.](image)

- **0 min, fresh**
- **10 mins**
- **30 mins**
- **60 mins**
- **600 mins**

- **PCDTBT:PCBM:O-PCBM**
- **PCDTBT:PCBM**

- **Current density (mA/cm²)**
- **Voltage (V)**

- **PCE (%)**
- **Relative O-PCBM (%)**

- **Ca/Al**
- **PEDOT:PSS**
- **ITO**
- **Glass**

Harrison K. H. Lee
Photo-oxidation of PCBM

\[ \text{PCBM} \rightarrow \text{PCDTBT:PCBM:O-PCBM} \]
Photo-oxidation products

Xiao et al. JACS 2007, DOI: 10.1021/ja0763798
Matsuo et al. Chem Comm 2012, DOI: 10.1039/c2cc30262d

Epoxide

Di-carbonyl

LUMO

HOMO

Beth Rice
Mass spectrometry

(a) 910.1

(b) 910.1, 926.1, 958.1, 974.1

(c) 910.1, 926.1, 942.1, 958.1, 974.1, 990.1, 1006.1, 1022.1

Fresh PCBM

Degraded PCBM in blend with PCDTBT

Degraded PCBM in solution

Mark F. Wyatt
IR spectroscopy

Photo-oxidation time

- 0min
- 10min
- 40min
- 100min
- 280min
- 610min
- 970min
- 1950min

Wavenumber (cm⁻¹)

1737 cm⁻¹

1782 cm⁻¹

Normalised Absorbance

Emily Speller
Sub-band gap states in PCBM

-3.6 eV

-5.5 eV

-4.3 eV

-6.0 eV
Effect on RECOMBINATION #1: solar cell

-3.6 eV

-5.5 eV

-4.3 eV

-6.0 eV
What happens in the device?

Charge Extraction

Transient Photovoltage
Voc reconstruction

![Graph showing Voc (V) vs. light intensity (sun equivalents)]

- **0% measured**
- **0% reconstructed**
- **0.4% measured**
- **0.4% reconstructed**
- **1% measured**
- **1% reconstructed**
Effect on RECOMBINATION #2: LED

-3.6 eV

-5.5 eV

-4.3 eV

-6.0 eV
Electroluminescence

O-PCBM

Normalised EL
Energy [eV]

Energy [eV]
EL of pure blend components

Red-shift or change in oscillator strengths?

![Graph showing normalised EL versus energy (eV) for PCBM and PCDTBT in fresh and degraded states.](image)

- PCBM
- PCDTBT
- PEDOT:PSS
- ITO
- Glass

![Diagram showing device stack with Ca/Al, PCDTBT, PEDOT:PSS, ITO, and Glass layers.](image)
Electroluminescence and external quantum efficiency

\[ J_{0,rad} = q \int_0^\infty EQE \cdot \phi_{bb} dE \]

\[ V_{OC,rad} = \frac{kT}{q} \ln \left( \frac{J_{sc,rad}}{J_{0,rad}} + 1 \right) \]
Open-circuit voltage losses

![Graph showing open-circuit voltage losses for various O-PCBM content](image)

- Voc
- Non-rad. loss
- Abs. loss
- SQ loss

- Open-circuit voltage losses
- EL-QE
- SQ limit
- Solar Simulator
- Eg/q
Conclusions

TRAPS!

HOMO-LUMO simulations

Transport

Recombination at the D/A interface

Voltage losses from non-radiative recombination
Thanks

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