Transient Ideality
Phil Calado
Imperial College London
SIMOEP, 2018
transient | 'tranzɪənt |
adjective

lasting only for a short time; impermanent

ideality | ,ɪdɪˈalɪti |
noun (pl. idealities) [mass noun]

the state or quality of being ideal
1. The impermanence of nature and life

2. The perfect day with a friend/loved one

3. The poor operational stability of perovskite solar cells
Diode ideality factor

Shockley diode equation:

\[
J = J_0 \left( \exp \left( \frac{qV}{n_{id}kT} \right) - 1 \right)
\]

\[
n_{id} = \left( \frac{q}{kT} \frac{dV}{d\ln(J)} \right)
\]

\begin{align*}
J & \quad \text{current density} \\
J_0 & \quad \text{dark saturation current} \\
V & \quad \text{voltage} \\
qu & \quad \text{elementary charge} \\
k_B & \quad \text{Boltzmann constant} \\
T & \quad \text{Temperature}
\end{align*}
### Ideality factor and recombination

<table>
<thead>
<tr>
<th>Recombination mechanism</th>
<th>Trap energy</th>
<th>Overlap</th>
<th>( n_{id} )</th>
</tr>
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<tbody>
<tr>
<td>Band-to-band</td>
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<td>( n &gt;&gt; p )</td>
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<td>SRH</td>
<td>Mid-gap</td>
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<td>1</td>
</tr>
<tr>
<td>SRH</td>
<td>Mid-gap</td>
<td>( n = p )</td>
<td>2</td>
</tr>
</tbody>
</table>

**Diagram:**
- **Bulk** and **Surface** regions.
- **Band to Band** and **SRH** recombination mechanisms.
- Carrier density vs. **Position**.
- **Electron**, **Hole**, **Photon** symbols.

**Notes:**
- **SRH** (Shockley–Read–Hall) mechanism.
- **Electron** and **Hole** concentrations.
- **Carrier density** graph with **p** and **n** labels.
In a real solar cell, series resistance, $R_S$ alters the slope:

$$n_{id} = \left( \frac{q}{kT} \frac{d(V + JAR_S)}{d\ln (J)} \right)$$

At open circuit $J = 0$

Reconstruct $J$-$V$ using $V_{OC}$ as a function of light intensity $\Phi$

’Suns vs $V_{OC}$’ plot gives $J$-$V$ without effects of $R_S$

$$n_{id} = \left( \frac{q}{kT} \frac{dV_{OC}}{d\ln (\phi)} \right)$$

• High mobile ionic defect densities:

<table>
<thead>
<tr>
<th>Label</th>
<th>Reaction</th>
<th>$\Delta H_S$ [eV]</th>
<th>$N_{ion} [\text{cm}^{-3}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\text{nil} \rightarrow V_{MA}' + V_{Pb}'' + 3V_1^0 + \text{MAPbI}_3$</td>
<td>0.14</td>
<td>$2 \times 10^{19}$</td>
</tr>
<tr>
<td>(2)</td>
<td>$\text{nil} \rightarrow V_{MA}' + V_1^0 + \text{MAI}$</td>
<td>0.08</td>
<td>$2 \times 10^{20}$</td>
</tr>
<tr>
<td>(3)</td>
<td>$\text{nil} \rightarrow V_{Pb}'' + 2V_1^0 + \text{PbI}_2$</td>
<td>0.22</td>
<td>$8 \times 10^{17}$</td>
</tr>
</tbody>
</table>

• Open circuit voltage, $V_{OC}$ changes in time

• At which time should we measure the ideality factor?

$V_{\text{preset}} = 0 \text{ V}$

$V_{OC}$ [V]

Time [s]

1. Hold device at preset voltage in the dark
2. Switch device to open circuit and simultaneously switch the illumination light on
3. Repeat for increasing light intensities!
Current-voltage scan results

Current-voltage hysteresis requires a combination of mobile ions and surface recombination\textsuperscript{1,2,3}

\textsuperscript{1}Van Reenen, J. Phys. Chem. Lett., 2015
\textsuperscript{2}Calado, P. Nat. Comms, 2016
\textsuperscript{3}Neukom, M. Sol. Energy Mater Sol., 2017
Transient ideality results

- $V_{\text{preset}} = +1.2 \text{ V}$
- $V_{\text{OC}}$ vs. time
- $\ln(\phi)$ vs. time
- $n_d$ values: $n_d = 1.0$, $n_d = 1.7$, $n_d = 2.0$, $n_d = 2.3$
- Time values: $t = 0.01 \text{ s}$, $t = 0.1 \text{ s}$, $t = 1 \text{ s}$, $t = 28 \text{ s}$

Surface to bulk recombination???
### Device simulation: Driftfusion

- Drift diffusion simulation using MATLAB’s PDEPE solver
- Solves for electrons, holes and *mobile ion* densities, and the electrostatic potential

![Graphical representation of the device simulation](image)

<table>
<thead>
<tr>
<th>Scheme no.</th>
<th>Dominant recombination mechanism</th>
<th>Trap energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Band-to-band only</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Surface SRH</td>
<td>Shallow</td>
</tr>
<tr>
<td>3</td>
<td>Surface SRH</td>
<td>Mid-gap</td>
</tr>
<tr>
<td>4</td>
<td>Bulk SRH</td>
<td>Shallow</td>
</tr>
<tr>
<td>5</td>
<td>Bulk SRH</td>
<td>Mid-gap</td>
</tr>
</tbody>
</table>
Equilibrium with ionic charge

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tr>
<td>$E_{CB}$</td>
<td>conduction band energy</td>
</tr>
<tr>
<td>$E_{VB}$</td>
<td>valence band energy</td>
</tr>
<tr>
<td>$E_{Fn}$</td>
<td>electron quasi Fermi level</td>
</tr>
<tr>
<td>$E_{Fp}$</td>
<td>hole quasi Fermi level</td>
</tr>
<tr>
<td>$n$</td>
<td>electron density</td>
</tr>
<tr>
<td>$p$</td>
<td>hole density</td>
</tr>
</tbody>
</table>
• Transient idealities for SRH surface recombination looked qualitatively like the results from the mesoporous Al$_2$O$_3$

• Ideality factor can change without the recombination mechanism changing
Ion migration causes change in overlap of $n$ and $p$ populations at interfaces.
Device state following forward bias

- More information encoded in the transient ideality than you would get in a standard measurement
- Steady state ideality factor is not necessarily the correct value
Transient ideality results

- mesoporous Al₂O₃ dominated by surface recombination
- mesoporous TiO₂ shows intermediate behaviour between surface and bulk recombination – we think this is because $n = p$ in the mesoporous region
Conclusions

- The value corresponding to the established ideality analysis can be obtained by forward biasing and taking an instantaneous measurement.
- Evolution of the $n_{id}$ curve gives allows the recombination mechanism to be distinguished further.
- The measured perovskite devices appear to be dominated by surface recombination.

Open questions

- Meaning of the initial large idealities following short circuit precondition.
- Generality of the results.

![Graph showing transient ideality over time for different materials.](image)
The Sun Doctors

Philip Calado (ICL)
Dr Piers R.F. Barnes (ICL)
Prof Jenny Nelson (ICL)
Jizhong Yao (Hangzhou Microquanta Semiconductor Co., Ltd.)

• Brian C. O’Regan (Sunlight Scientific)
• Daniel Burkitt (Swansea)
• Joel Troughton (Swansea)
• Triston Watson (Swansea)
• Matt Carnie (Swansea)
• Dan Bryant (Swansea)
• Xiaoe Li (ICL)
• Andrew M. Telford (Uni. New South Wales)
Driftfusion

Download and contribute at: https://github.com/barnesgroupICL/Driftfusion
Thank you for your attention
Supporting Information
J-V hysteresis

Belisle et al., Energy & Environmental Science, 2016
Transient Photovoltage (TPV)

Calado et al, Nat Comms., 2016
Transient photocurrent

![Graphs showing transient photocurrent](image)

- **Increasing Time at 0.8 V**
  - 120 μs
  - 600 μs
  - 1 ms
  - 10 ms
  - 100 ms
  - 1 sec
  - 20 sec

- **Planar**
  - Mesoporous

- **Time, μs**
  - 0
  - 5
  - 10
  - 15
  - 20

- **J [mA cm\(^{-2}\)]**
  - 0
  - 1
  - 2
  - 3

- **t\(_{\text{dwell}}\) [μs]**
  - 10
  - 20
  - 30
  - 40

- **J [mA cm\(^{-2}\)]**
  - 0
  - 1
  - 2
  - 3

- **J\(_{t=15\text{µs}}\) [mA cm\(^{-2}\)]**
  - 0
  - 1
  - 2
  - 3

- **t\(_{\text{dwell}}\) [s]**
  - 10\(^{-4}\)
  - 10\(^{-3}\)
  - 10\(^{-2}\)
  - 10\(^0\)
  - 10\(^1\)
  - 10\(^2\)
Time-Resolved Photoluminescence

Bi et al., Science Advances, 2016
Photo-Induced Impedence Spectroscopy

Measured

Simulated

Zarazua et al., Journal of Physical Chemistry Letters, 2016

Ilario Gelmetti (ICIQ)
Transient ideality, $V_{\text{pre}} = 0$ V

Recombination mechanism

<table>
<thead>
<tr>
<th></th>
<th>n $&gt;&gt;$ p</th>
<th>n $\approx$ p</th>
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<tbody>
<tr>
<td>Band-to-band</td>
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<td>SRH recombination</td>
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- Ion migration causes change in overlap of $n$ and $p$ populations at interfaces
Higher light intensity results in slower ion response.

- Ion drift current reduced due to field screening by electrons and holes.

Higher light intensity causes greater screening of the internal field.
Transient ideality $V_{\text{pre}} = 0 \, \text{V}$

![Graph a](image1.png)

![Graph b](image2.png)

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<td>Mid-gap</td>
<td>$n = p$</td>
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Legend:
- mp-TiO$_2$
- mp-Al$_2$O$_3$
- Bulk SRH mid
- Bulk SRH shallow
- Surf SRH deep
- Surf SRH shallow
- Band-to-band
Transient of the transient photovoltage measurement

1. Precondition device in the dark at voltage $V_{\text{pre}}$
2. Switch to open circuit, switch bias light on
3. Excite at periodic intervals with laser source (488 nm in this instance)
Transient of the transient mp-Al$_2$O$_3$
Transient of the transient mp-TiO$_2$

![Graph](image)

**Glass Side**

**TCA Side**

**mp-TiO$_2$**

**Diagram**

- TCA side
- Glass side
- $e^-$
- $h^+$

**Time [µs]**

- 0
- 10
- 20
- 30
- 40

**ΔV [mV]**

- -10
- 0
- 10
- 20
- 30

**Pulse**

- t=1.6s
- t=2.6s
- t=4.6s
- t=6.6s
- t=10.6s
- t=16.6s
- t=24.6s
- t=49.6s
4. Non-linear $\ln(\text{Suns})$ vs $V_{OC}$ relationship

Suns $V_{OC}$ and $n_{id}$ curve for a cell which has reached equilibrium at short circuit ($V_{pre} = 0$ V). Prior to illuminating the device the ion mobility was switched off.

**Value of average ideality or gradient of fit is dependent on the choice of range**
2. Ion distribution as function of light intensity

• Ionic charge dominates in perovskite phase

Ion distribution at steady state for different light intensities

• Ion distribution is a function of light intensity at steady state
Planar TiO$_2$ results

![Diagram showing a multilayer structure with labels for each layer: Gold, Spiro OMeTAD, Perovskite, base-TiO$_2$, FTO, Glass.]

**Graph a:**
- Plot of $J$ [mAcm$^{-2}$] vs. $V$ [V]
- Curves for Dark and 1 Sun eq.

**Graph b:**
- Plot of $n_{id}$ vs. Time [s]
- Experimental and Simulated surface rec.
PL and EL

(a) EL intensity vs. Time for mp-Al₂O₃
- Initial EL

(b) log10(EL Intensity) vs. log10(Injection Current)
- mp-Al₂O₃
- mp-TiO₂

(c) PL Intensity vs. Time for mp-Al₂O₃
- φ_{excite}

(d) Recombination Rate vs. Time
- SRH Interfacial
- BTB, Radiative

Imperial College
London
Fermi-level splitting and carrier density

\[ \Delta E_F = \frac{k_B T}{q} \ln \left( \frac{np}{n_i^2} \right) = \frac{k_B T}{q} \ln \left( \frac{n^\beta}{n_i^2} \right) \]

- \( \Delta E_F \): quasi Fermi level splitting (electron-hole potential)
- \( n \): electron density
- \( p \): hole density
- \( n_i \): intrinsic carrier density

Intrinsic

- \( E_{CB} \)
- \( E_{F_0} \)
- \( E_{F_p} \)
- \( E_{VB} \)

p-type

- \( E_{F_n} \)
- \( \Delta E_F \)

\( n = p, \quad \beta = 2 \)

\( p >> n, \quad \beta = 1 \)
Recombination reaction order

\[ \Delta E_F = \frac{k_B T}{q} \ln \left( \frac{np}{n_i^2} \right) = \frac{k_B T}{q} \ln \left( \frac{n^\beta}{n_i^2} \right) \]

\[ U = k_1 n + k_2 n^2 + k_3 n^3 \]

Assuming single reaction order is dominant:

\[ U = k_\alpha n^\alpha \]

At open circuit:

Generation = Recombination

\[ G = U \]

\[ n_{id} = \frac{q}{k_B T} \frac{dV_{OC}}{d \ln(U)} \]

\[ n_{id} = \frac{\beta}{\alpha} \]
Shockley Read Hall recombination

\[ U_{SRH} = \frac{(np - n_i^2)}{\tau_{n,SRH}(p + p_t) + \tau_{p,SRH}(n + n_t)} \]

For mid-gap traps the reaction order: \( \alpha = 1 \)

\[ U_{SRH} \propto n_{\text{min}} \]

\[ n_{id} = \frac{\beta}{\alpha} \]

<table>
<thead>
<tr>
<th>Carrier density to ( E_F ) exponent</th>
<th>Reaction order</th>
<th>Ideality factor</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Surface</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>Bulk</td>
</tr>
</tbody>
</table>
Leave no one behind policy
What does the simulation do?

1. You define a device- Energies, doping, dimensions
2. Tell it the starting conditions of the device e.g. dark equilibrium
3. Tell it whether you are shining light or an applying voltage
4. It tells you how the state of the device changes in time
5. Outputs: charge carrier densities, electrostatic potential => currents, quasi Fermi levels etc.
Crash course in energy-level diagrams

- $E_{CB}$: conduction band energy
- $E_{VB}$: valence band energy
- $E_{Fn}$: electron quasi Fermi level
- $E_{Fp}$: hole quasi Fermi level
- $n$: electron density
- $p$: hole density
1. Uses MATLAB’s PDEPE solver to solve the continuity and Poisson’s equations for electrons, holes and mobile ion densities.

2. High rates of recombination included in the p-type and n-type contact regions to simulate surface recombination.

Simulation code available for free at: https://github.com/barnesgroupICL/Driftfusion
Equilibrium with ionic charge

- Energy [eV]
- Carrier density [cm$^{-3}$]
- Ion density [x10$^{19}$ cm$^{-3}$]
- Position [nm]

- $E_{CB}$
- $E_{VB}$
- $E_{FP}$
- $E_{Fn}$

Mobile ions
Hysteresis: forward JV scan

Electrostatic Potential [V]

Carrier density [cm$^{-3}$]

Position [nm]

$U_{SRH} \propto n_{min}$

$U_{SRH}$: SRH recombination rate

$n_{min}$: minority carrier density
Hysteresis: reverse JV scan

Electrostatic Potential [V]

Carrier density [cm$^{-3}$]

Position [nm]

$U_{SRH} \propto n_{min}$

$U_{SRH}$: SRH recombination rate

$n_{min}$: minority carrier density
Key messages

- Hysteresis requires a combination of mobile ions and recombination at interfaces between perovskite and transport layers\(^1\)
- Absence of hysteresis does not equate to absence of mobile ions or improved stability
- Transient photocurrent shows presence of ions in inverted devices
- Illustrates of the power of the built-in field

\(^1\)Van Reenen et al., *The Journal of Physical Chemistry Letters*, 2015
hysteresis

Origin

GREEK → GREEK → GREEK
husteros → husterein → husterēsis → hysteresis
late → be behind → shortcoming, deficiency → late 19th century

late 19th century: from Greek husterēsis ‘shortcoming, deficiency’, from husterein ‘be behind’, from husteros ‘late’.
Why do some perovskite device architectures exhibit J-V hysteresis while others do not?

P. Calado et al. Nat Comms, 2016
Mobile ions and J-V hysteresis

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Formation energies and RT defect density $N_{ion}$

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Material</th>
<th>$V_{A}'$</th>
<th>$V_{B}''$</th>
<th>$V_{X}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[48]</td>
<td>MAPbI$_3$</td>
<td>0.88</td>
<td>2.31</td>
<td>0.58</td>
</tr>
<tr>
<td>[113]</td>
<td>MAPbI$_3$</td>
<td>0.46</td>
<td>0.80</td>
<td>0.08</td>
</tr>
<tr>
<td>[114]</td>
<td>MAPbI$_3$</td>
<td>0.57</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>[115]</td>
<td>MAPbI$_3$</td>
<td>0.70 - 1.12</td>
<td>1.39 - 1.78</td>
<td>0.28 - 0.45</td>
</tr>
<tr>
<td>[116]</td>
<td>MAPbI$_3$</td>
<td>0.74</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>[115]</td>
<td>MAPbBr$_3$</td>
<td>0.70 - 1.13</td>
<td>0.16 - 0.29</td>
<td>0.20 - 0.46</td>
</tr>
<tr>
<td>[116]</td>
<td>MAPbBr$_3$</td>
<td>0.80</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>[115]</td>
<td>CsPbI$_3$</td>
<td>0.59 - 1.16</td>
<td>0.81 - 0.99</td>
<td>0.29 - 0.36</td>
</tr>
<tr>
<td>[114]</td>
<td>FAPbI$_3$</td>
<td>0.56</td>
<td>-</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Calculated ionic migration activation energies for common perovskite materials.

Halides are mobile!

2References available upon request
3Eames, Nature Communications, 2015
Identifying recombination mechanisms in perovskite solar cells using transient ideality factors

Philip Calado
EXSS, Dept. of Physics, Imperial College London
Quantsol 2018, Rauris, Austria
22\textsuperscript{nd} March 2018
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P. Calado et al. Nat Comms, 2016
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Carrier density [cm$^{-3}$]

Position [nm]

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$U_{SRH}$: SRH recombination rate

$n_{min}$: minority carrier density
Hysteresis: reverse JV scan

Electrostatic Potential [V]

Carrier density [cm\(^{-3}\)]

Position [nm]

Applied Voltage [V]

Current Density [mA cm\(^{-2}\)]

\(U_{SRH} \propto n_{min}\)

<table>
<thead>
<tr>
<th>(U_{SRH})</th>
<th>SRH recombination rate</th>
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<tr>
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<td>minority carrier density</td>
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