Transient phenomena and ion kinetics in triple-cation perovskites over a wide time range

Vladimir Dyakonov

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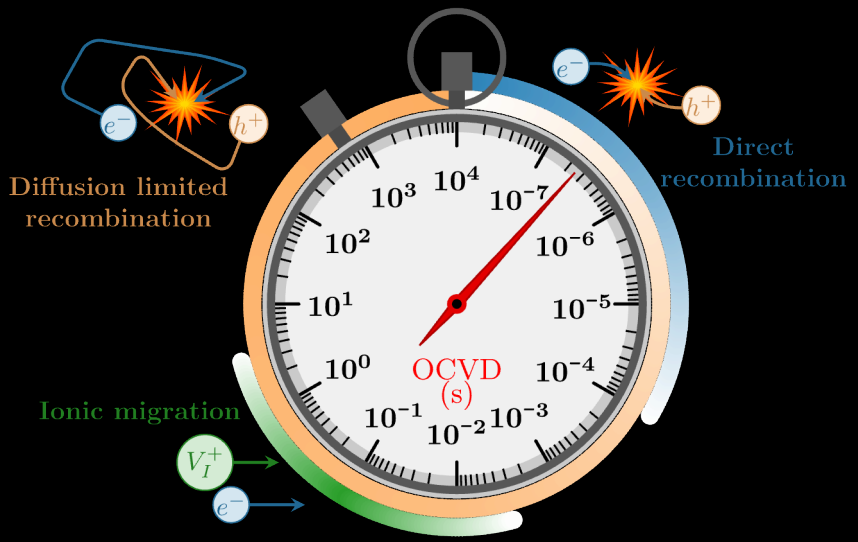
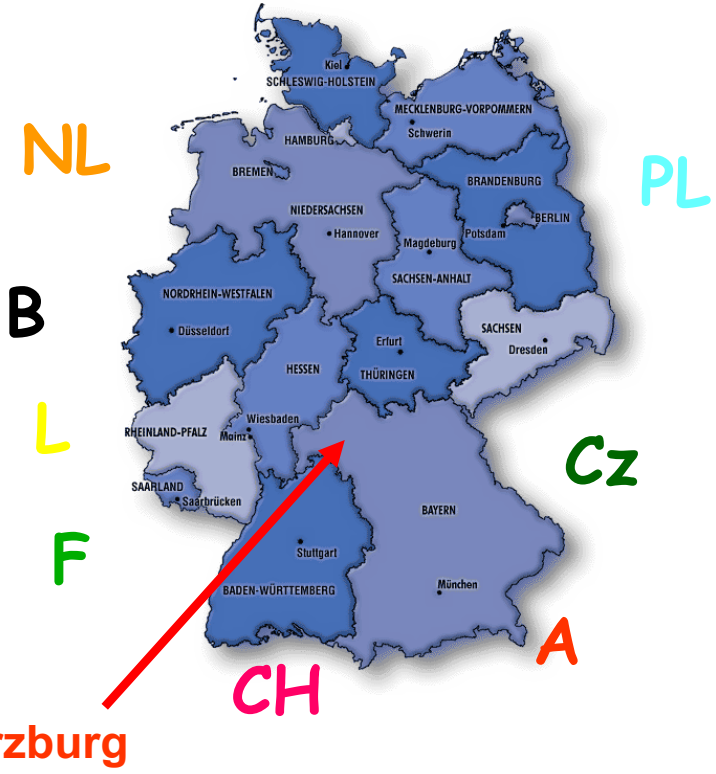
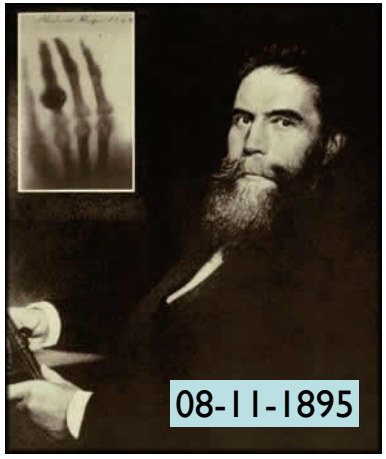


Summer School on Future prospects of perovskite based solar cells: 2023-05-15, Khiva, UZ

University of Würzburg





Multiple methods to study transient processes

- **Transient absorption and photoluminescence (TA, TRPL)**
  - Probing all absorbing excited states
  - Probing radiative recombination
- **Transient microwave conductivity (GHz) and OPTP**
  - Probing mobility and lifetime of charge carriers after pulsed excitation

non-contact

- **Transient photovoltage (OCVD) and photocurrent**
  - Probing recombination in solar cells under operating conditions
- **Transient conductivity (e.g., Time-of-Flight)**
  - Probing transit time of ***mobile*** charge carriers after pulsed excitation

contact

Study of ion migration in PSC using **O**pen-**C**ircuit **V**oltage **D**ecay (OCVD)

Challenges: Coupling between ions and electrons / holes makes the resulting dynamics and transient processes highly non-trivial

A. Baumann, VD et al., **APL Mater.** 2, 081501 (2014)
M. Fischer, VD et al., **Sustain. Energy Fuels** 5, 3578 (2021)

Open-Circuit Voltage Decay (OCVD)

1 sun illumination of the solar cell with a LED

↓

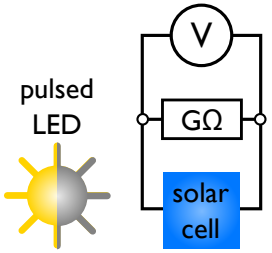
Built-up of steady-state under open circuit condition ➔ Constant V_{oc}

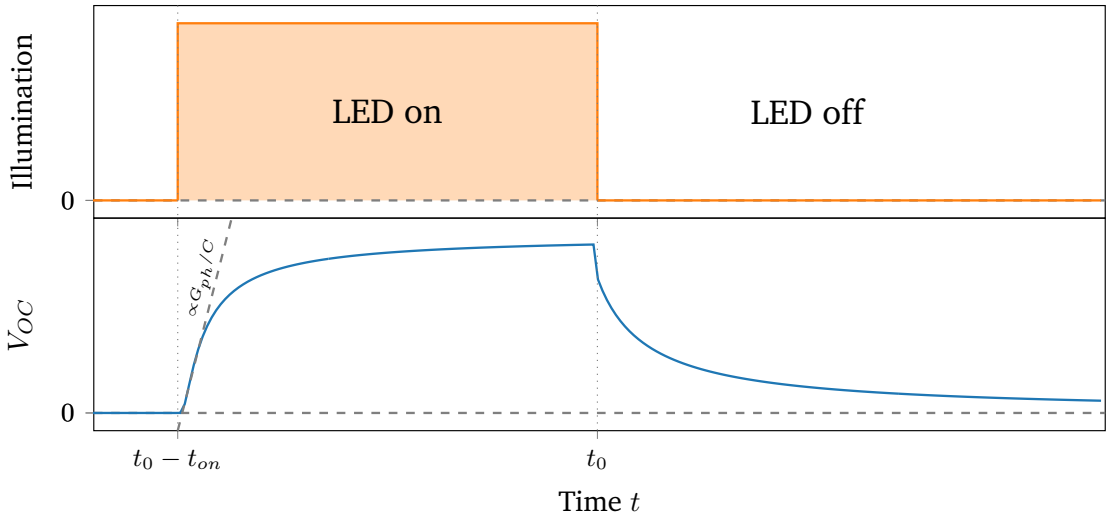
↓

LED off at t_0

↓

Monitoring of the voltage decay with high time resolution ($10^{-8} - 10^{3}$s)





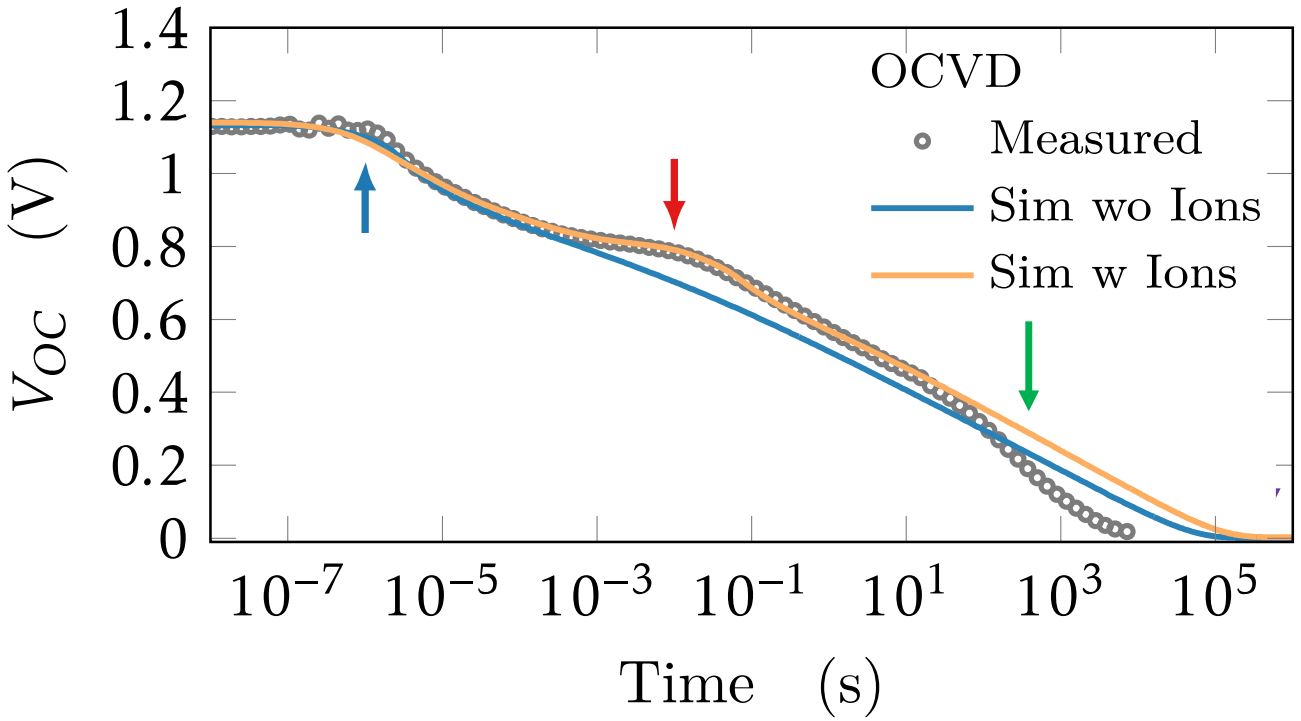
$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t}\frac{\mathrm{d}V}{\mathrm{d}Q} \approx qAG_{ph}\frac{1}{C_p}$$

Dr. Andreas Baumann

S. Lederhandler and L. Giacoletto, **Proc. IRE** 43, 477 (1955).
A. Baumann, VD et al., **APL Mater.** 2, 081501 (2014)

Features of an OCVD transient

Measured vs. simulated OCVD transients

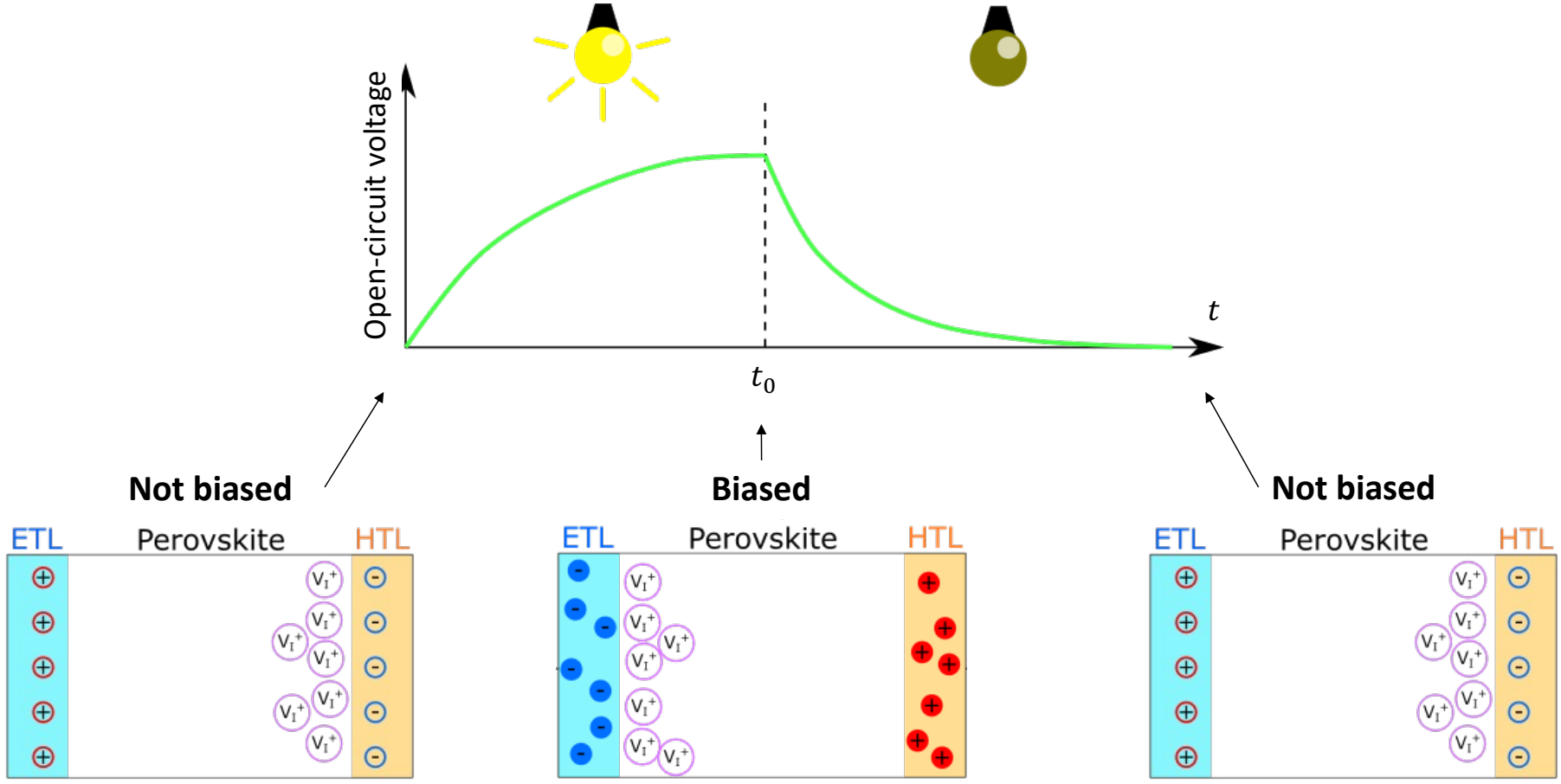


- Free carrier dynamics **~1-10µs**: electron/hole recombination
- Ion redistribution **~1-100ms**: slow down V_{oc} decay
- Shunt regime **>100s**: Leakage currents lead to a faster decay of V_{oc}

Mathias Fischer

M. Fischer, VD, K. Tvingstedt et al., **Sustain. Energy Fuels 5**, 3578 (2021)

Ion distribution during OCVD

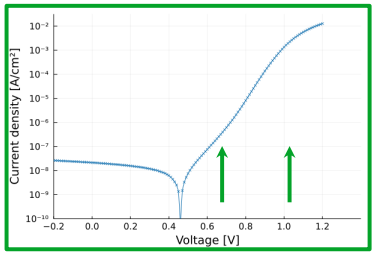


Calculating mobile ion properties from OCVD

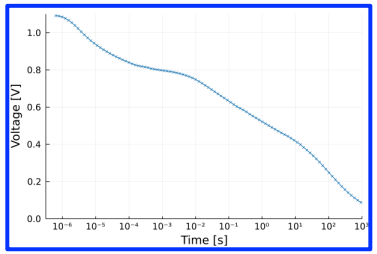
1. Device capacity $C(t)$

$$C\big(V(t)\big) = \frac{dQ}{dV} = \frac{dQ}{dt}\frac{dt}{dV} \approx -J\big(V(t)\big)\left(\frac{dV_{oc}(t)}{dt}\right)^{-1}$$

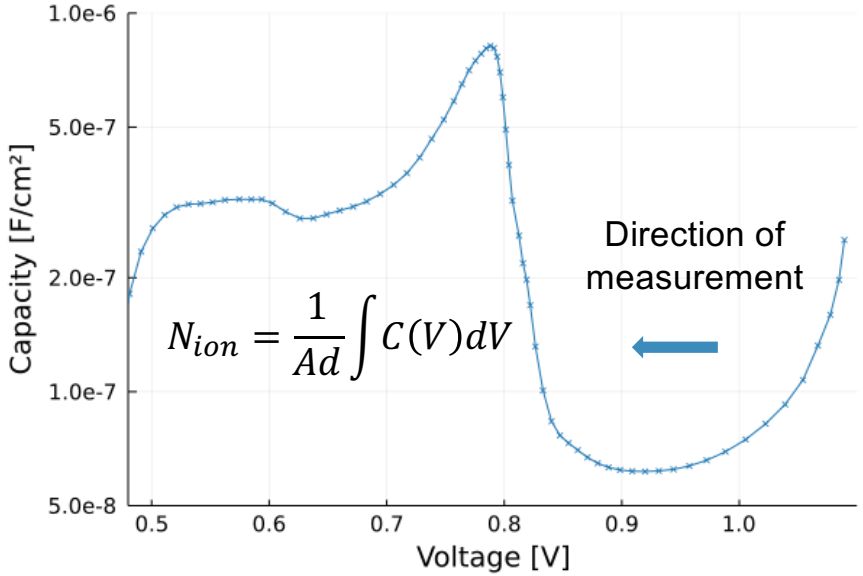
Dark JV



OCVD



Voltage-resolved device capacity $C(V)$



2. Total number of ions:

$$Q_{ion} = \int C(V)dV$$

3. Mobile ion concentration:

$$N_{ion} = \frac{Q_{ion}}{A * d}$$

Calculating mobile ion properties from OCVD

Device capacity $C(t)$:

$$C\big(V(t)\big) = \frac{dQ}{dV} = \frac{dQ}{dt}\frac{dt}{dV} \approx -J\big(V(t)\big)\left(\frac{dV_{oc}(t)}{dt}\right)^{-1}$$

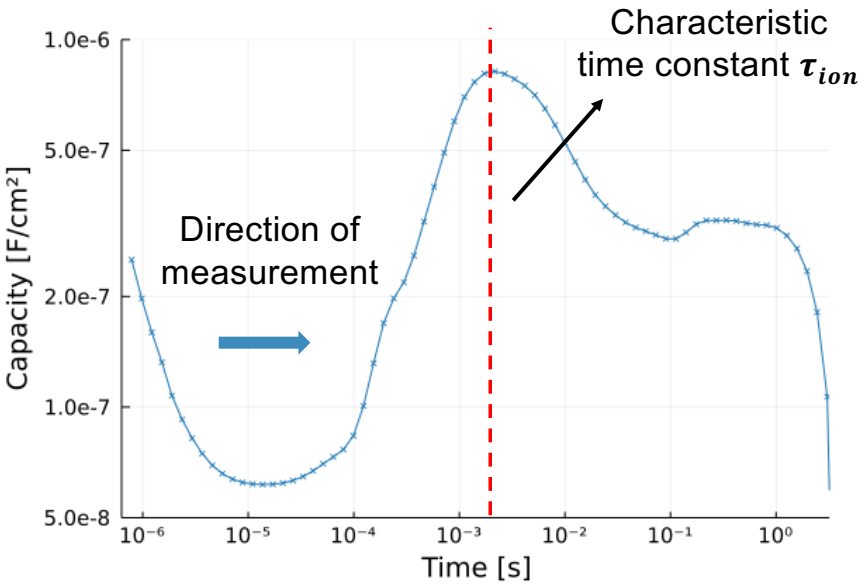
Ion diffusivity:

$$D_{ion} = \frac{d}{\boldsymbol{\tau_{ion}}}\sqrt{\frac{\epsilon_P \epsilon_0 k_B T}{q^2 N_{ion}}}$$

Ion density:

$$N_{ion} = \frac{1}{Ad}\int C(V)dV$$

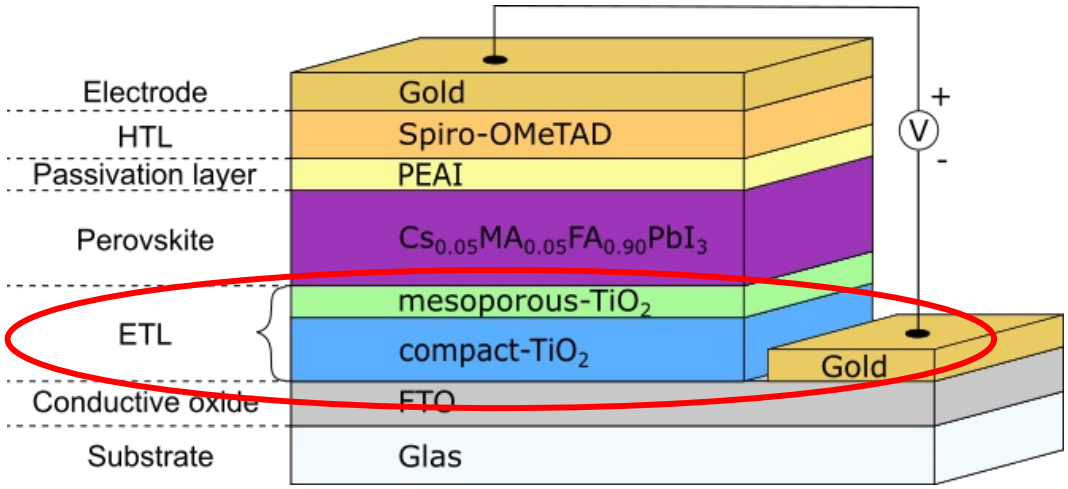
Time-resolved device capacity $C(t)$



Device structure

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Mesoporous n-i-p device



- Triple Cation perovskite composition
- Different types of m-TiO_2 as ETL

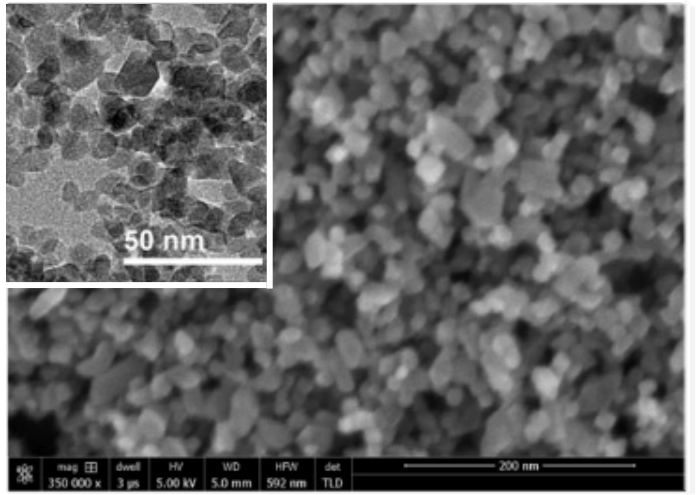
Dr. Yong Ding

Y. Ding, VD, MKN et al., **Nature Nanotechnology** 17, 598 (2022)

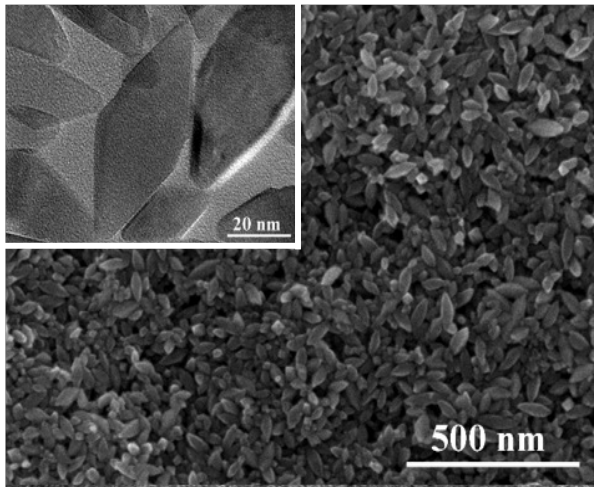
Different ETL layers

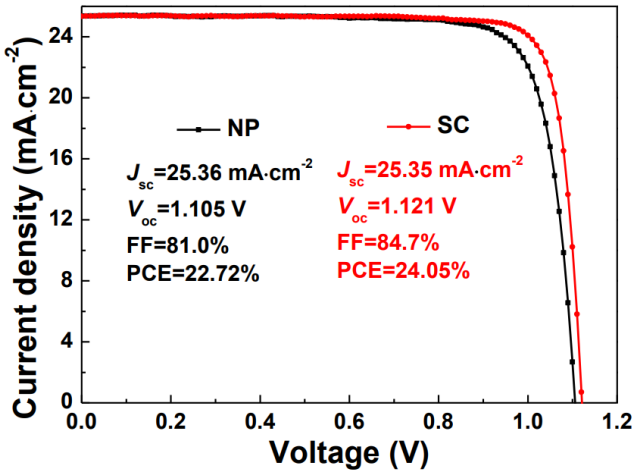
Two different types of m-TiO_2

Nanoparticle mesoporous-TiO_2
(NP m-TiO_2)



Single-crystalline mesoporous-TiO_2
(SC m-TiO_2)





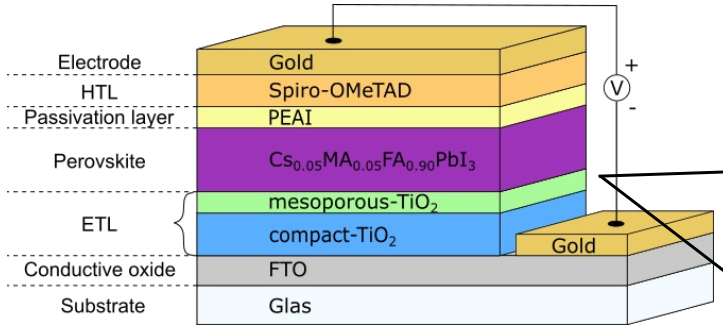
PCE: 22% *vs.* 24%
FF: 81% *vs.* 84%

Y. Ding, VD, MKN et al., **Nature Nanotechnology** 17, 598 (2022)

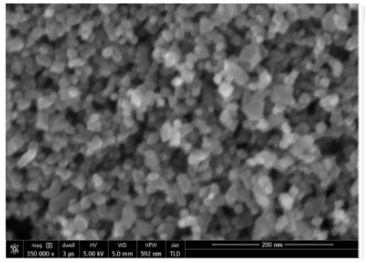
Morphology of mesoporous TiO_2 ETL

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Mesoporous n-i-p solar cell

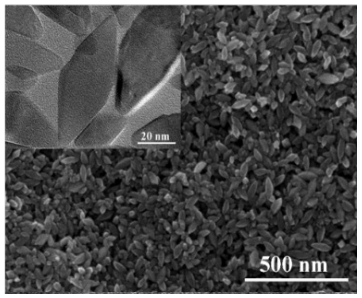


Nanoparticle mesoporous-TiO_2 (NP m-TiO_2)

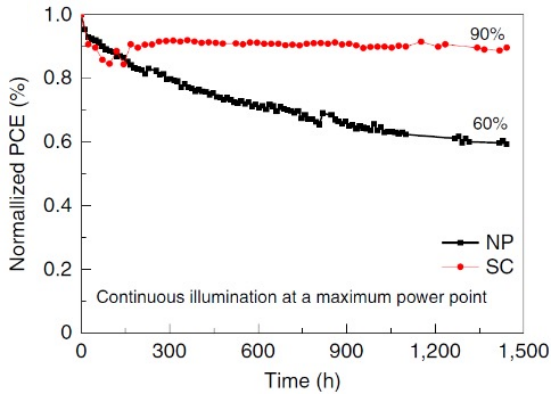


PCE: 22.7%
FF 81%

Single-crystalline mesoporous-TiO_2 (SC m-TiO_2)



PCE: 24.1%
FF: 85%



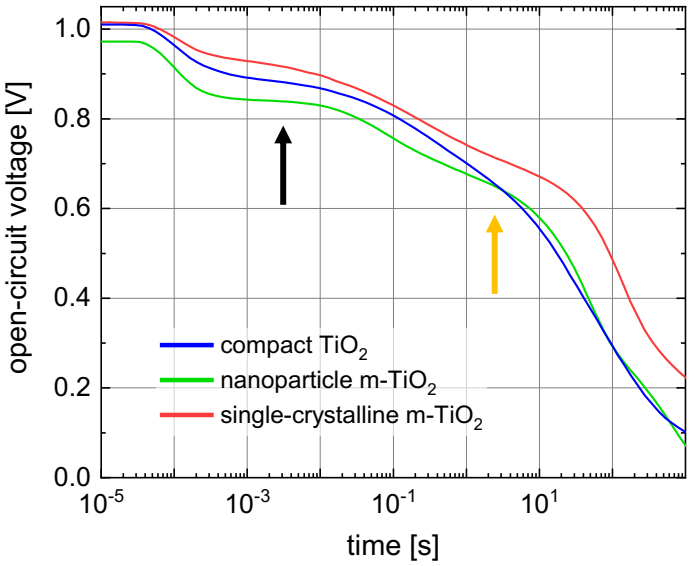
SC m-TiO_2:

- Increase in stability
- Lower lattice mismatch
- Higher mobility

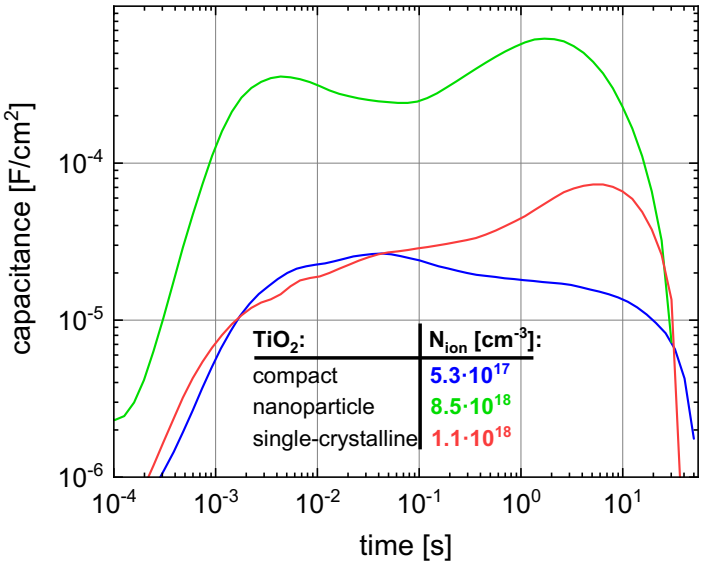
Y. Ding, VD, MKN et al., **Nature Nanotechnology** 17, 598 (2022)

OCVD transients

OCVD transient



Capacitance transient



Device capacity C(V(t)):

$$C\big(V(t)\big) = \frac{dQ}{dV} = \frac{dQ}{dt}\frac{dt}{dV} \approx -J\big(V(t)\big)\left(\frac{dV_{oc}(t)}{dt}\right)^{-1}$$

Dark *JV*

Inverse OCVD

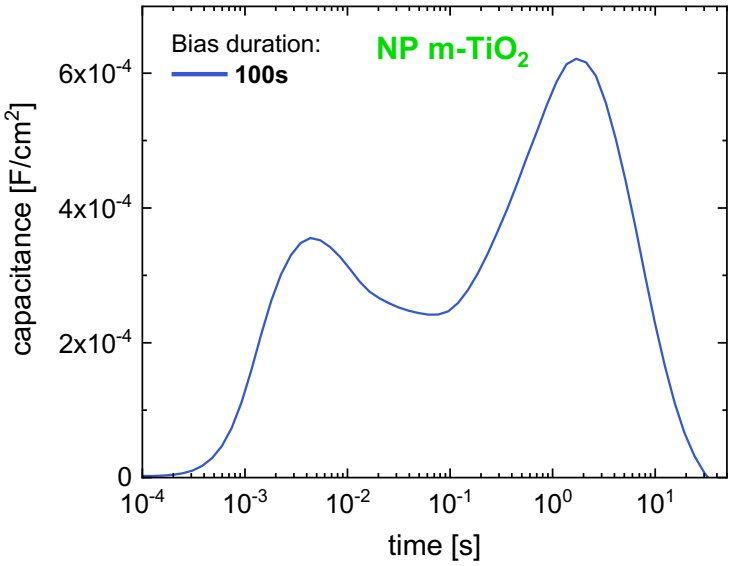
Mobile ion density:

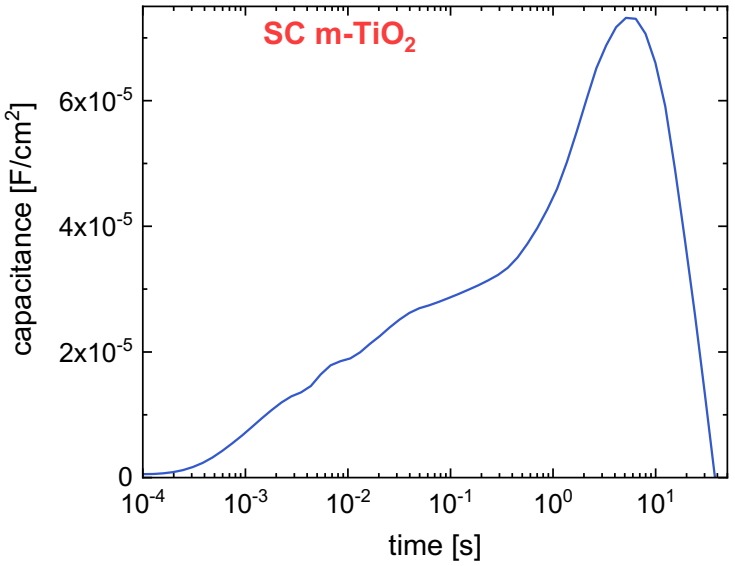
$$N_{ion} = \frac{\int C(V)dV}{A * d}$$

Valentin Schmid

Mobile ion dynamics

Time-resolved device capacity C(t)

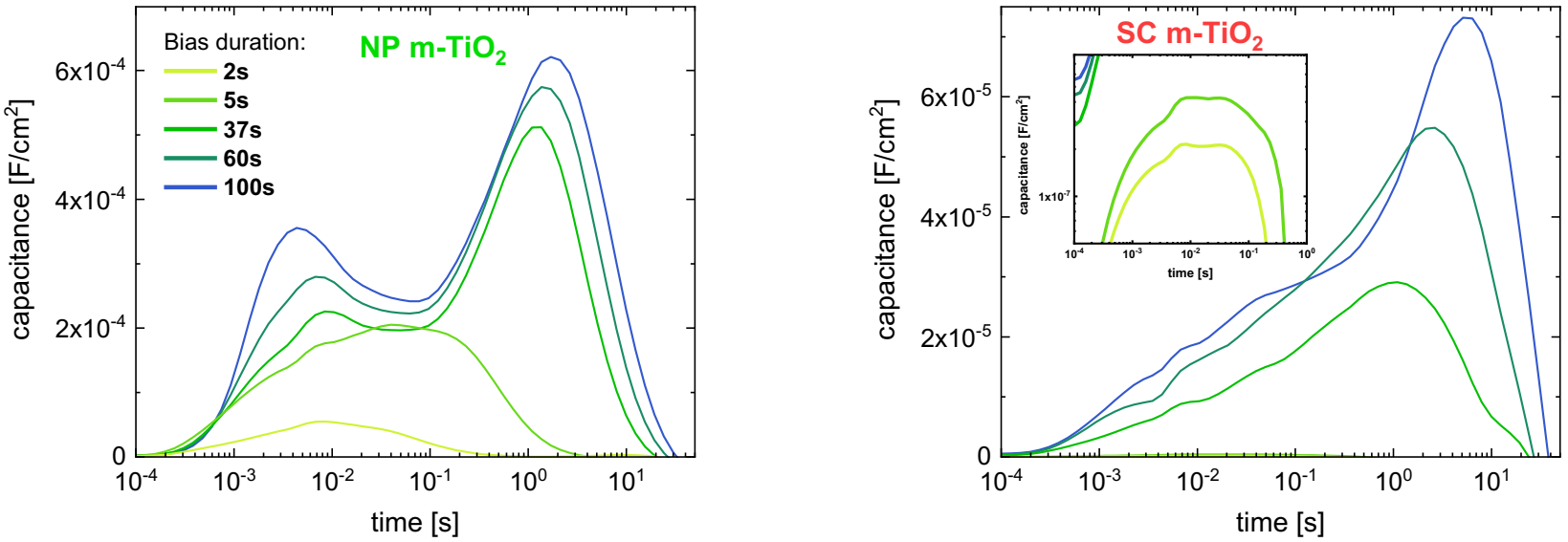




- Different ion kinetics, **fast and slow moving ions**

Mobile ion dynamics

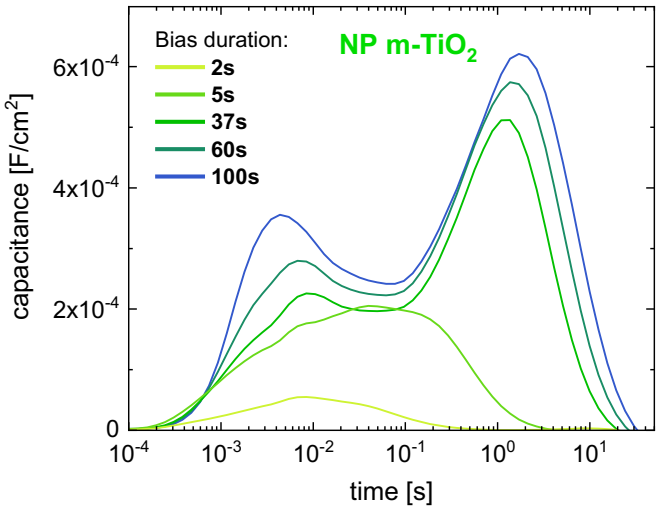
Time-resolved device capacity C(t)

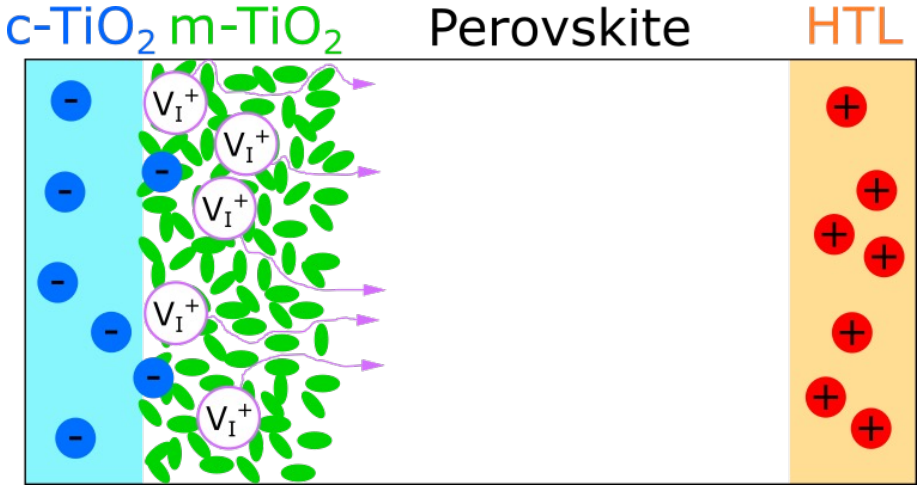


- Different ion kinetics, **fast and slow moving ions**
- Ionic contribution **increases and shifts** with increasing bias duration
- The slow moving ions are pronounced in the **SC m-TiO_2** device

→ mesoporous-TiO_2 slows down mobile ions – but why?

Why does mesoporous-TiO_2 slow down ions?



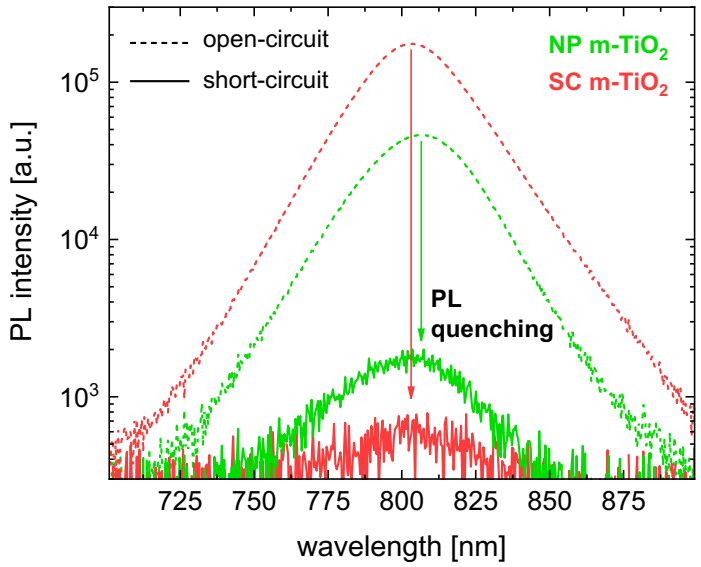


- **During bias:** Mobile ions either accumulate at the interface between m-TiO_2 and perovskite or diffuse into the perovskite-filled pores

- **During decay:** slowed diffusion of mobile ions out of pores

PL quenching & transient PL

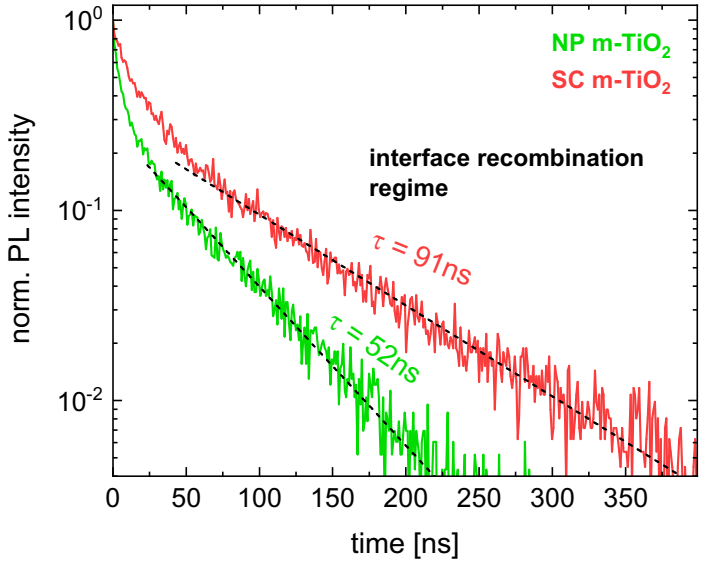
Steady-state PL



- Higher PL quenching between open and short circuit condition

→ **SC m-TiO_2 reduces the surface recombination at ETL/PVK interface**

Transient PL



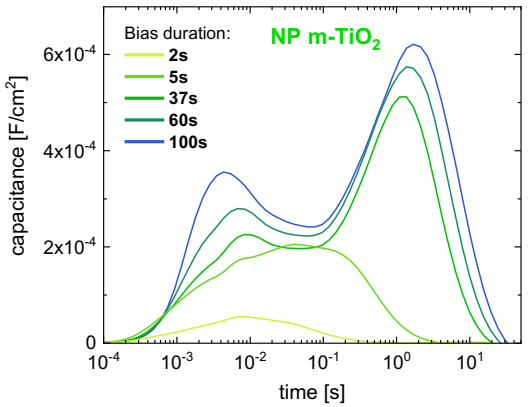
- **t < 50 ns**: extraction in transport layer & interface recombination
- **t > 50 ns**: reduced interface recombination

Summary OCVD

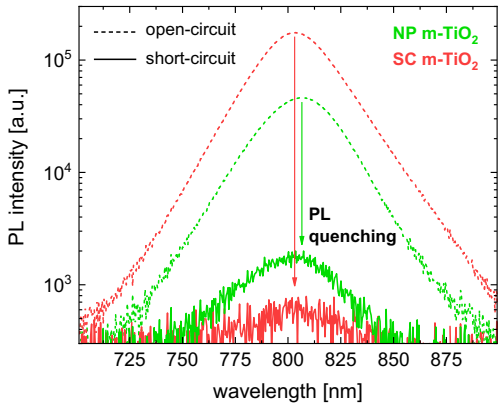
Single-crystalline (SC) vs. nanoparticle (NP) m-TiO_2 as ETL

- **OCVD** enables the study of the **kinetics of mobile ions** in fully operating PSC
- The **morphology of the nanoparticles** used for the m-TiO_2 layer influences both ion concentration and diffusivity
- **SC m-TiO_2**: successfully **slows down mobile** ions and decreases the ion density in the bulk perovskite
- PL quenching and transient PL reveals a **reduced surface recombination** at ETL/PVK interface for the **SC m-TiO_2**

OCVD



PL quenching

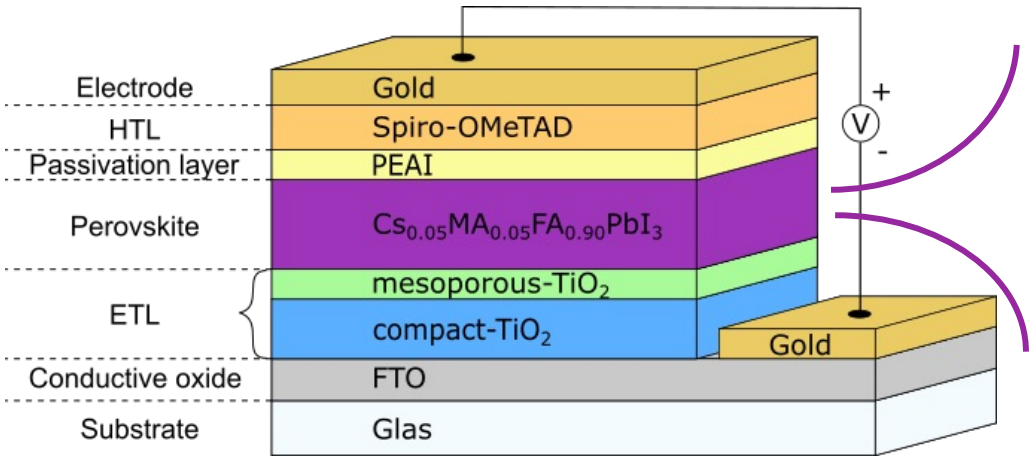


Influence of ionic liquids on charge carrier mobility in triple cation perovskite solar cells

Opportunities: ionic liquids (ILs) tend to improve thermal stability

Challenges: influence on structural and electronic properties unknown

Triple-cation perovskite films



Triple Cation perovskite

$Cs_{0.05}(CH_3NH_3)_{0.05}(CH(NH_2)_2)_{0.90}PbI_3$

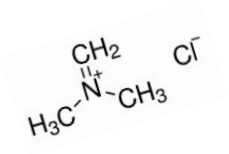
IL < 1%

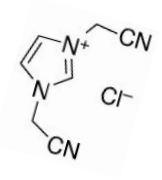
+

precursor solution

Ionic liquids

N,N-Dimethylmethylen-iminium chloride = [Dmmim]Cl





1,3-Bis-(cyanmethyl)-imidazolium chloride = [Bcmim]Cl

- [Dmmim]Cl: Incorporates into the crystal lattice, no influence on the crystallization
- [Bcmim]Cl: Deposits on the perovskite surface, improves crystallinity and growth

Time-Resolved Microwave Conductivity (TRMC)

Excitation of charge carriers in perovskite film leads to a change in photoconductance G

↓

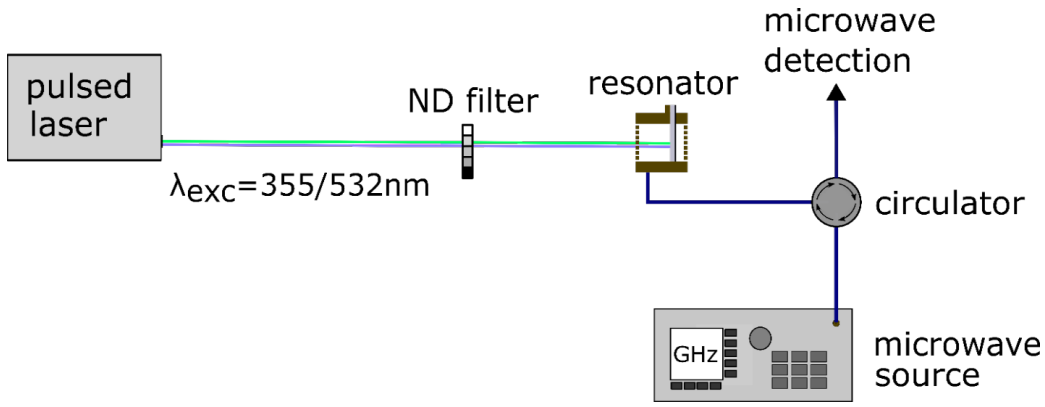
Change of reflected microwave power

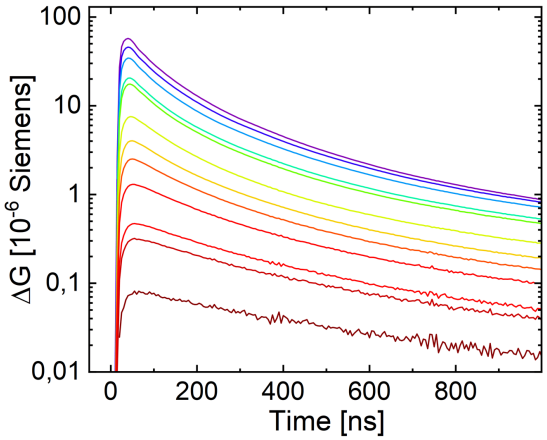
↓

Monitoring charge carrier mobility and lifetime

↓

Time resolution few tens of ns

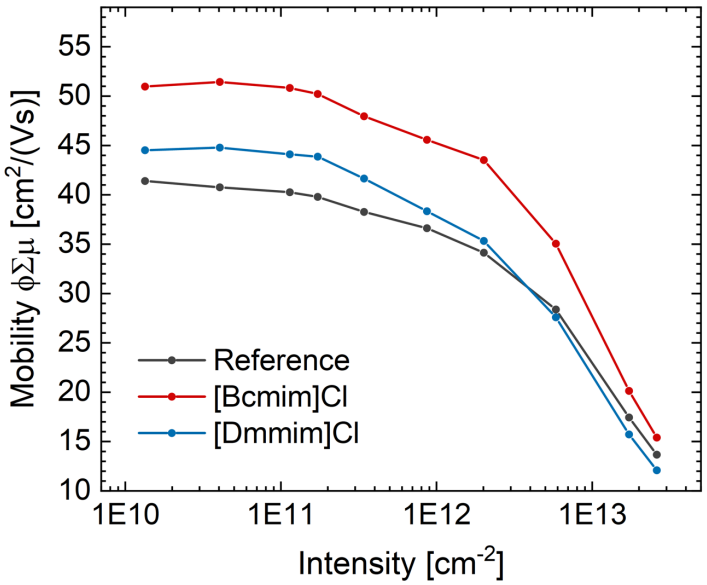




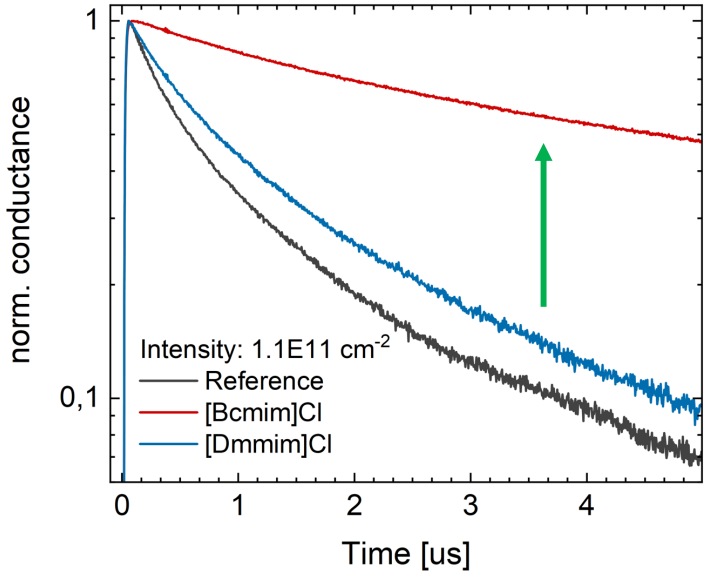
Patrick Dörflinger

Charge Carrier Dynamics

Charge carrier mobility



Charge carrier lifetime



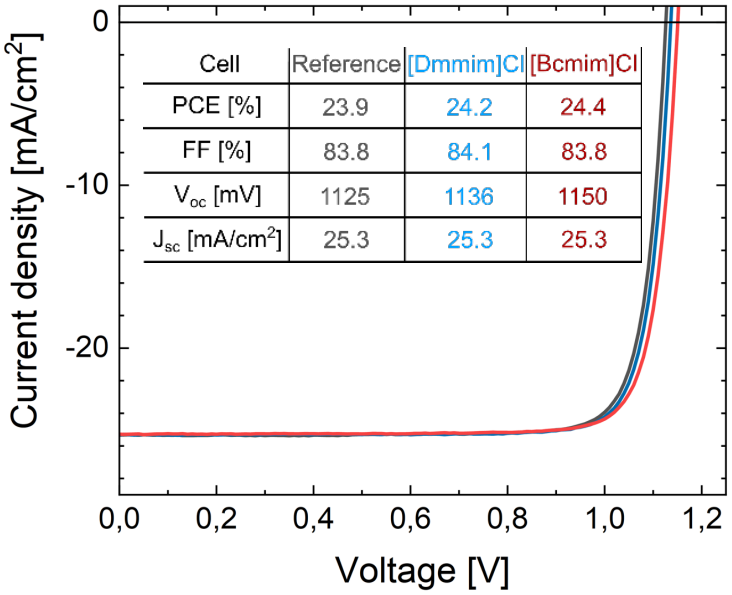
	Reference	Literature [*]	[Bcmim]Cl	[Dmmim]Cl
$\Sigma\mu\ \left[\frac{cm^2}{Vs}\right]$	41	32	52	45

- **Increase** in charge carrier mobility and lifetime for [Bcmim]Cl
- **Minor effects** on the charge carrier dynamics for [Dmmim]Cl

[*] H. Hempel, P. Dörflinger, VD et al., **Adv. Energy Mater.** 12, 2102776 (2022)

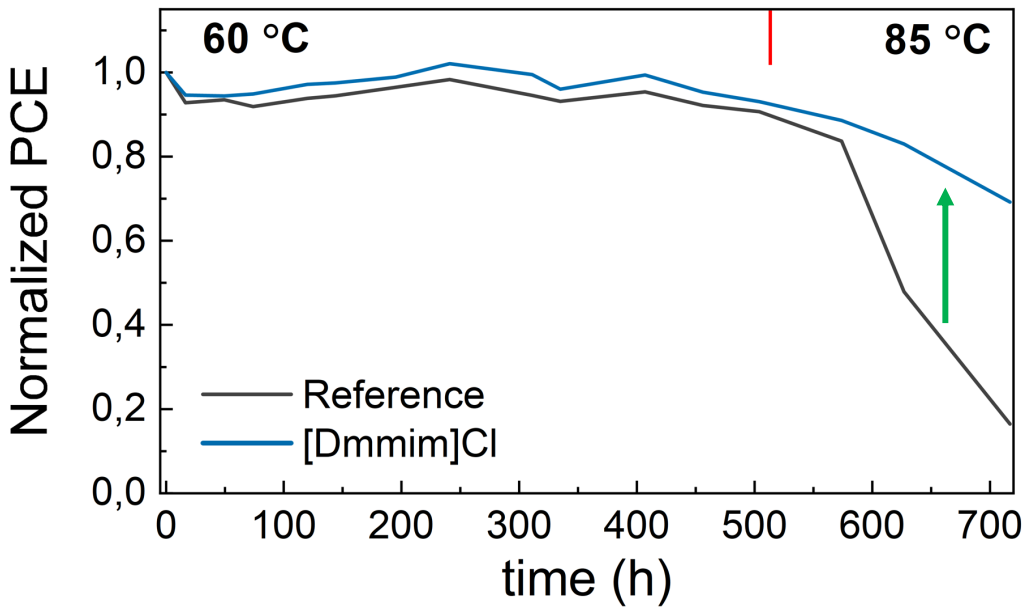
Impact of ILs on solar cells

Current-Voltage curve



Cell	Reference	[Dmmim]Cl	[Bcmim]Cl
PCE [%]	23.9	24.2	24.4
FF [%]	83.8	84.1	83.8
V_{oc} [mV]	1125	1136	1150
J_{sc} [mA/cm²]	25.3	25.3	25.3

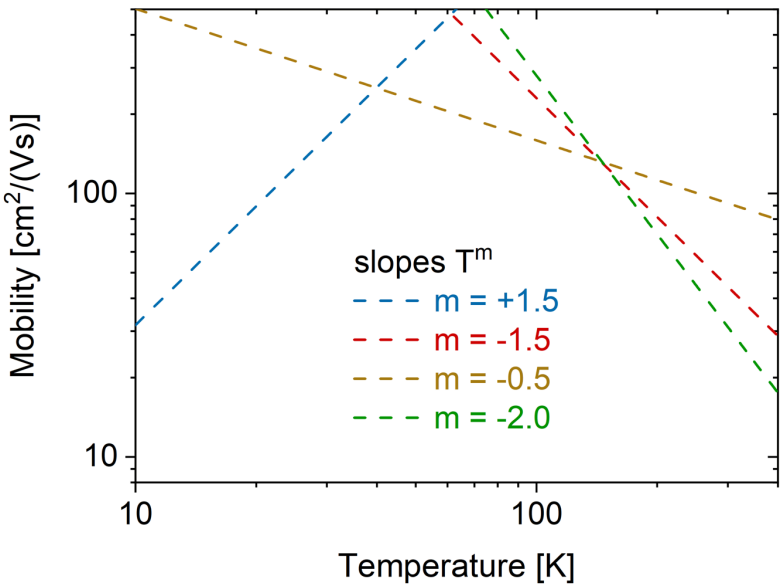
Heat resistance



- **Highest efficiency** (24.4%) for [Bcmim]Cl doped solar cells (24.2% for [Dmmim]Cl)
- Both ionic liquids increase the V_{OC}
- PCE tracking reveals a **higher heat resistance** for [Dmmim]Cl
- PLQY stable over 100h at 85˚C for [Dmmim]Cl, slight decrease for [Bcmim]Cl

Y. Ding, VD, MKN et al., **Nature Nanotechnology** 17, 598 (2022)

Temperature-dependent mobility



Why measuring temperature dependent mobility?

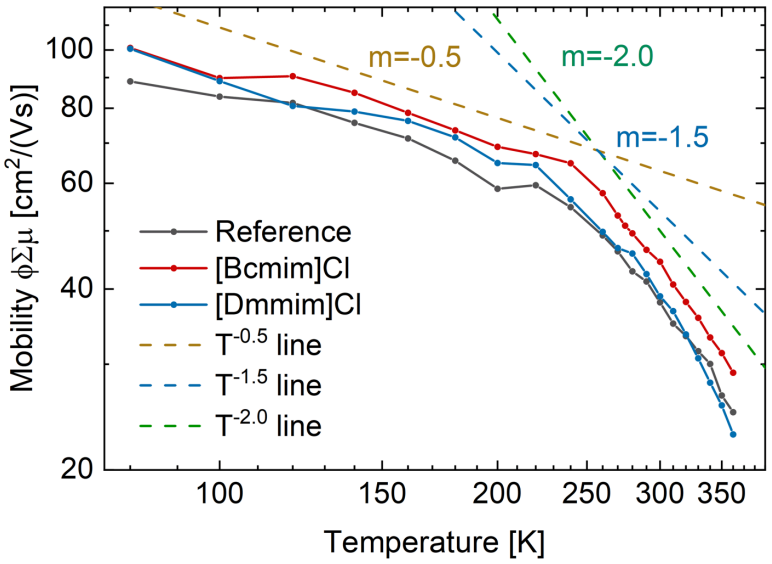
Slope gives information about the **predominating scattering mechanism!**

$$\mu \propto T^m$$

- $m = +\frac{3}{2}$: ionized impurity scattering
- $m = -\frac{3}{2}$: acoustic phonon scattering
- $m = -\frac{1}{2}$: LO phonon scattering
- $m = -2$: dynamic disorder (Pb-I bonds)

J. Frost, PRB 96, 195202 (2017)
M. Z. Mayers et al., Nano Lett. 18, 8041 (2018)

Temperature-dependent mobility



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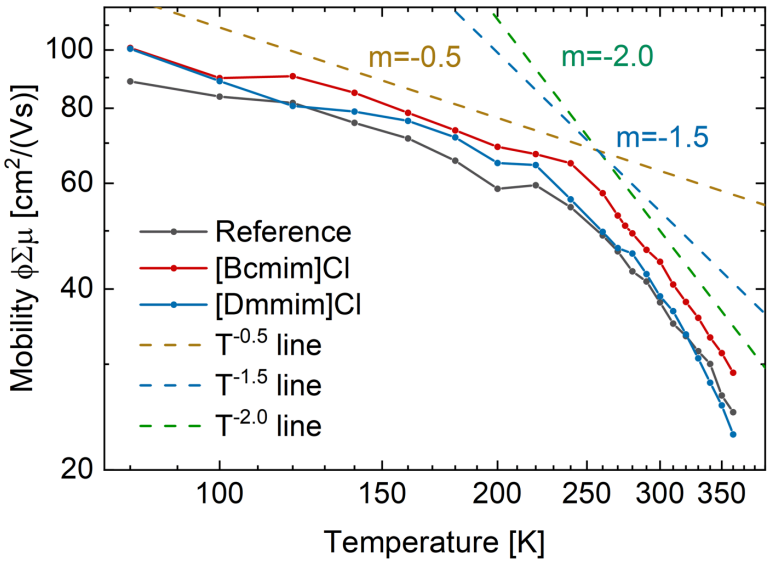


Why measuring temperature dependent mobility?

Slope gives information about the **predominating scattering mechanism!**

$$\mu \propto T^m$$

- $T < 260K$: scattering dominated by LO phonons
- $T > 260K$: scattering dominated by dynamic disorder

→ IL has **no influence** on the predominating scattering mechanisms

J. Frost, PRB 96, 195202 (2017)
M. Z. Mayers et al., Nano Lett. 18, 8041 (2018)

Summary TRMC

Ionic liquid doped perovskite absorbers:

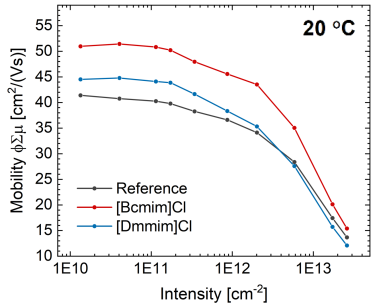
[Bcmim]Cl doped perovskite:

- Aggregates on the grain surface
- Higher **crystallinity**[***] and film quality
- Increase in **mobility and lifetime**
- High PCE

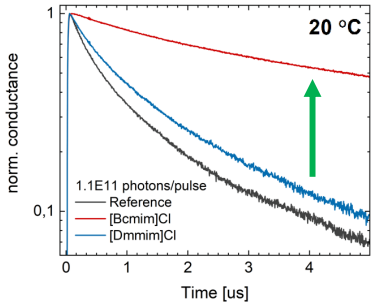
[Dmmim]Cl doped perovskite:

- **Incorporates** into the crystal lattice
- Minor changes in **mobility and lifetime**
- Increased **heat resistance** of the solar cells while maintaining high PCE

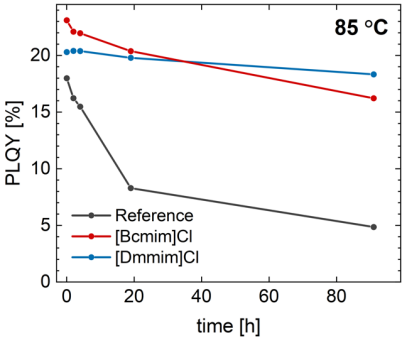
Mobility



Lifetime



PLQE



[***] Bin Ding et al., submitted (2022)

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