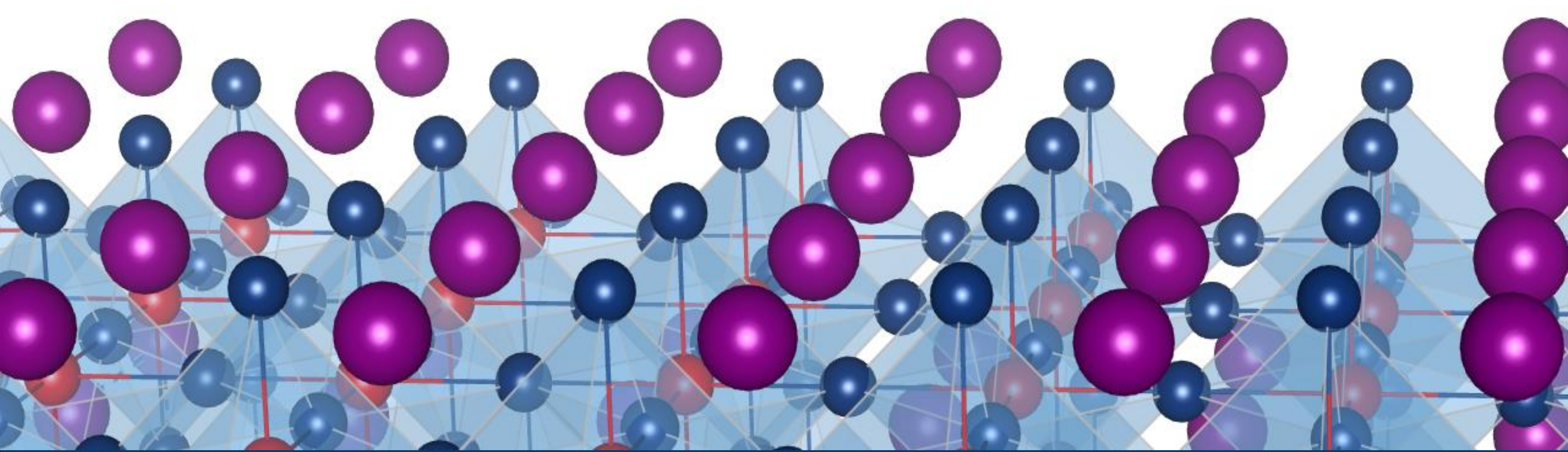

Modelling Charge Extraction and Recombination Losses in Perovskite Solar Cells

**Sandheep Ravishankar, Lukas Frommel,
Thomas Kirchartz and Uwe Rau**
IMD-3 Photovoltaik, Forschungszentrum Jülich

Emmy
Noether-
Programm
DFG Deutsche Forschungsgemeinschaft

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

SPP 2196
Perovskite Semiconductors:
From fundamental properties to devices
DFG

JÜLICH
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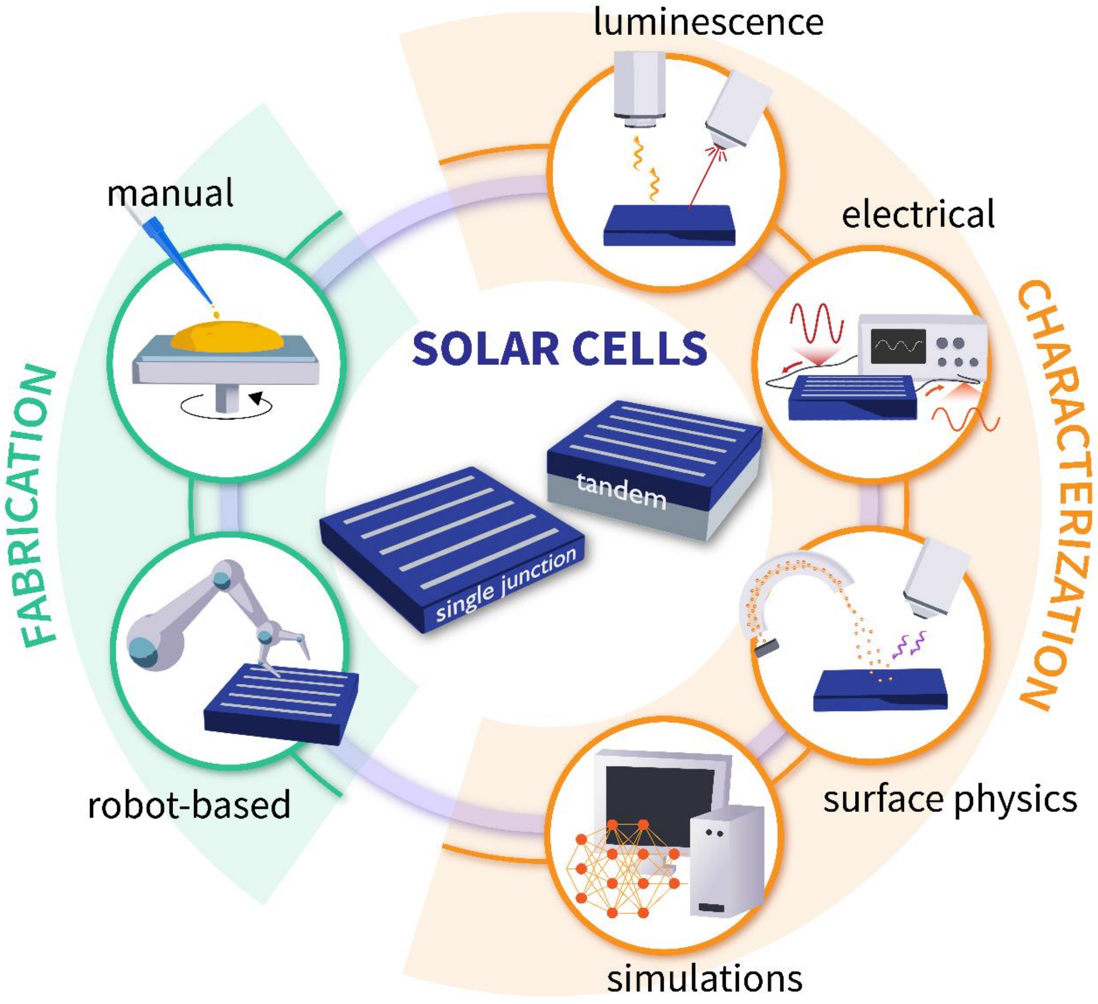
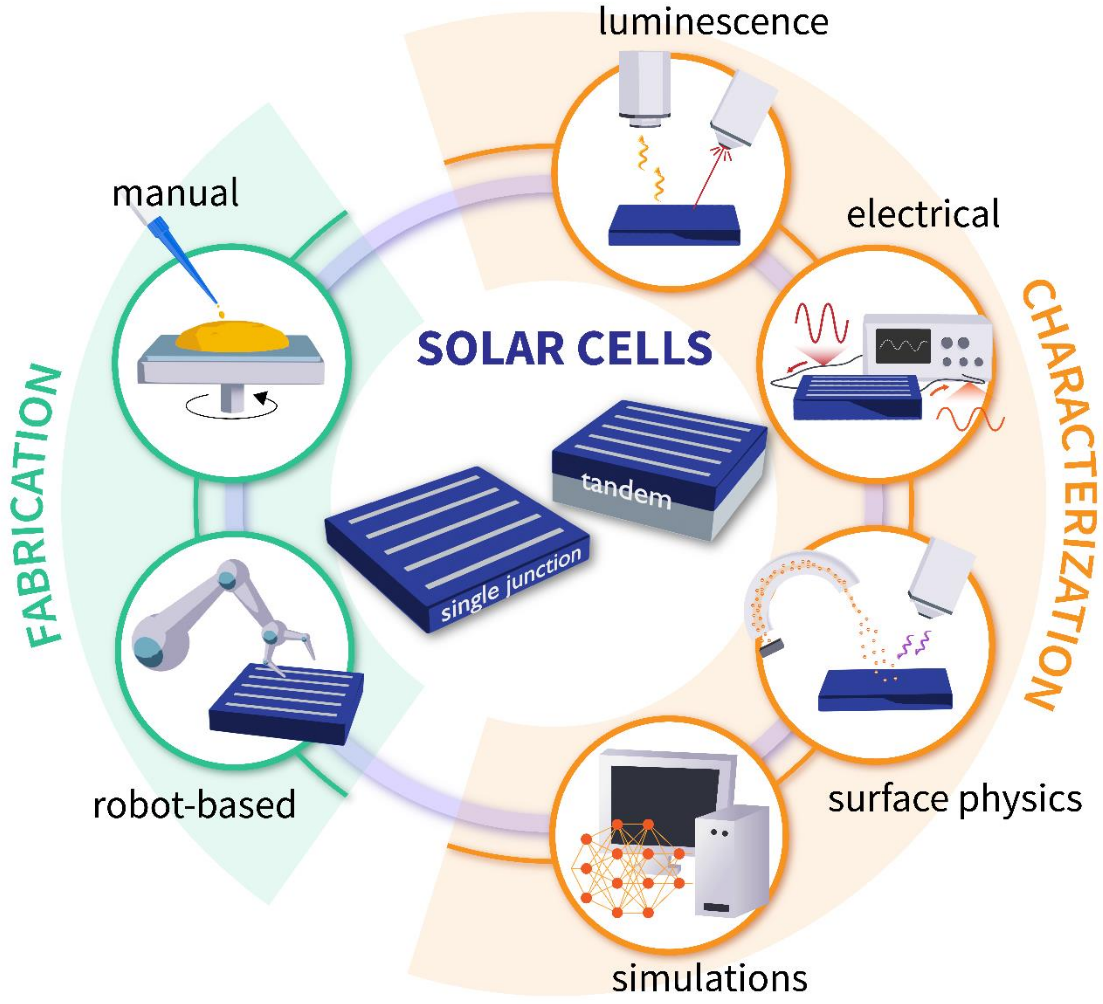
my team



advanced characterization of the loss mechanisms and device physics

https://www.fz-juelich.de/en/imd/imd-3/research/knowledge-based-pv/electrical-spectroscopy.

my team



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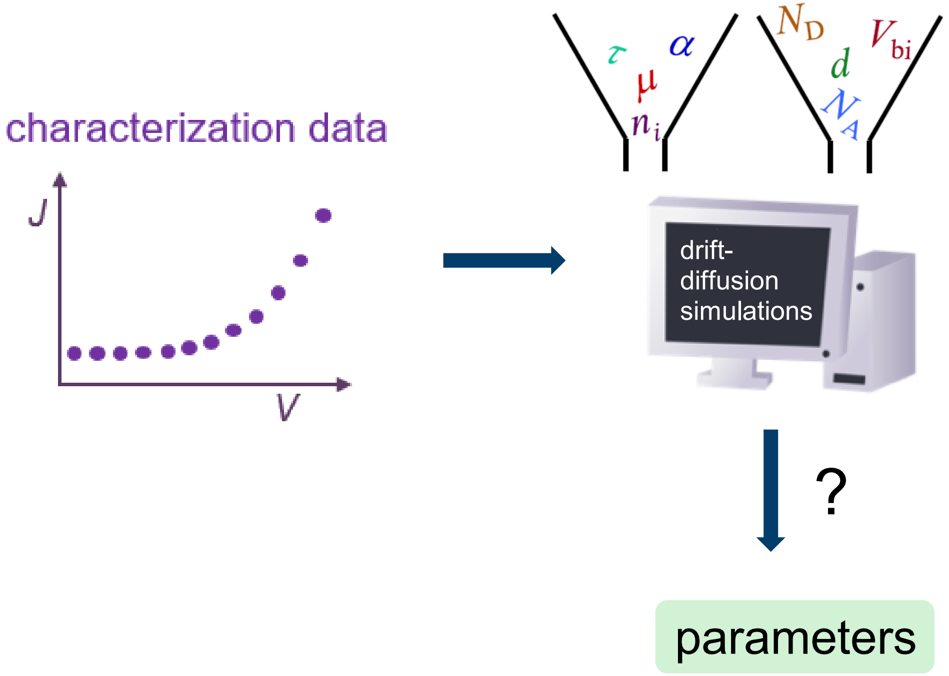

characterization data

drift-diffusion simulations

parameters

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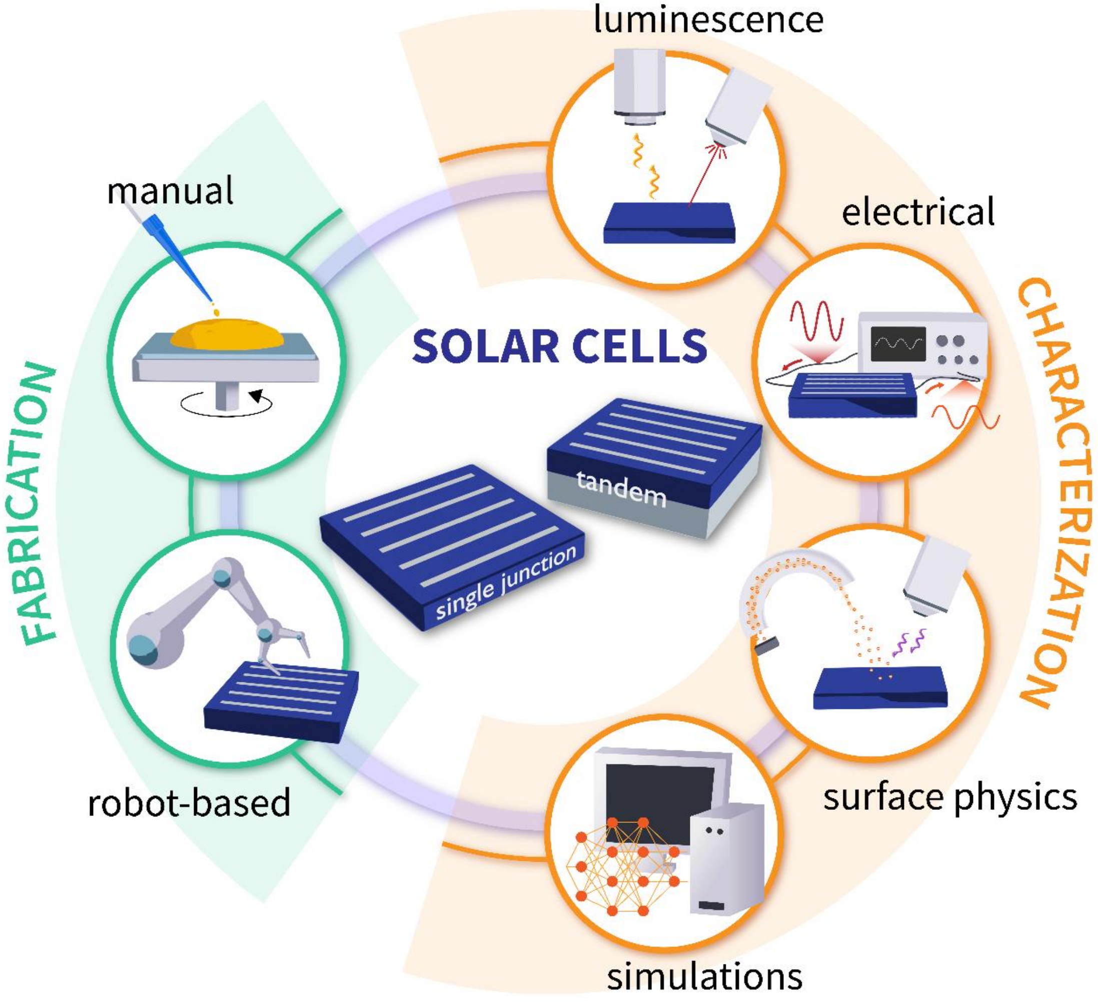
my team



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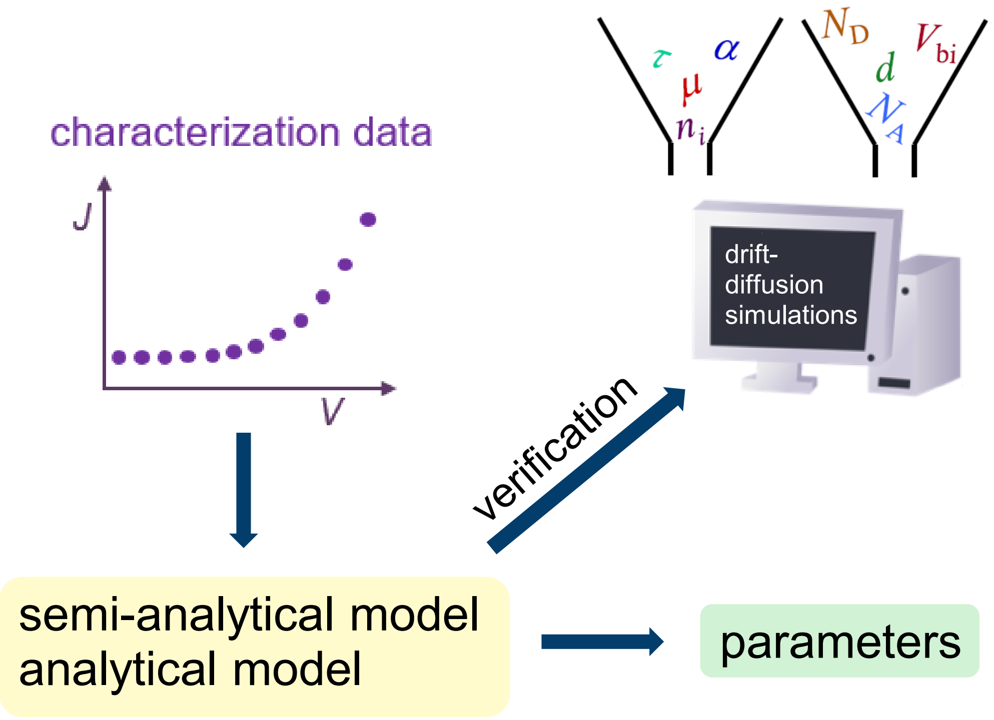


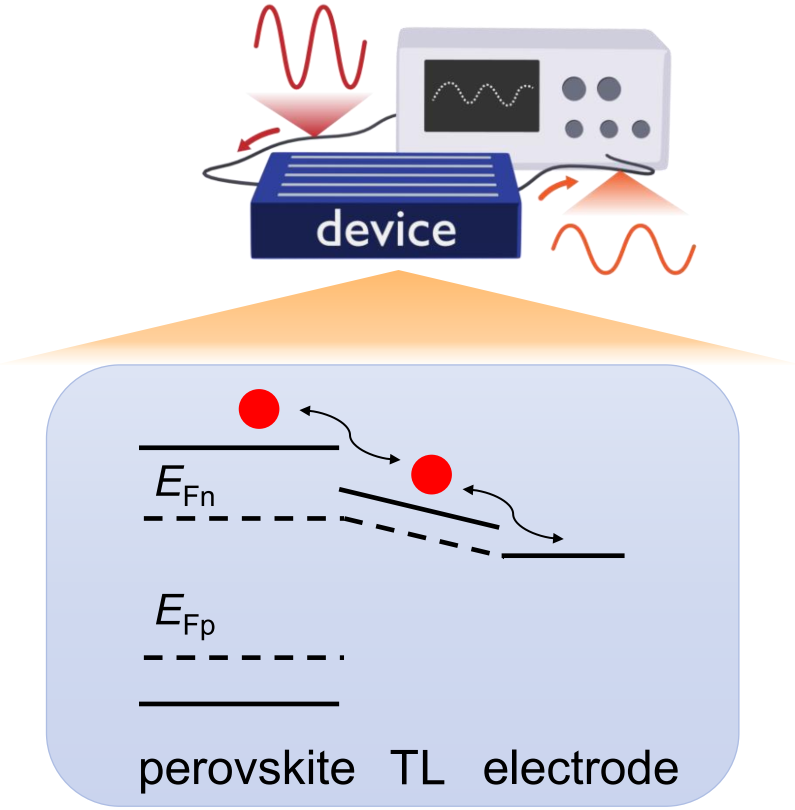
characterization data

semi-analytical model
analytical model

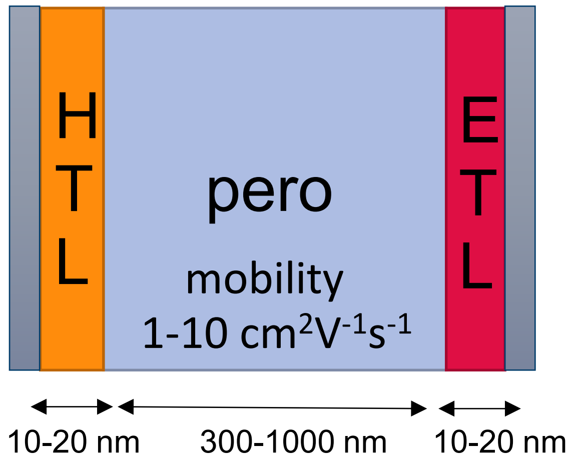
parameters

https://www.fz-juelich.de/en/imd/imd-3/research/knowledge-based-pv/electrical-spectroscopy.

characterizing charge extraction losses using small-perturbation methods



perovskite solar cell - effect of transport layers



HTL

pero

mobility

1-10 cm^{2}V^{-1}s^{-1}

ETL

10-20 nm

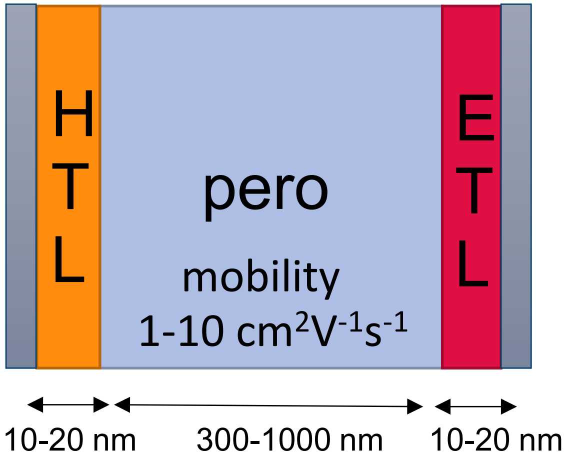
300-1000 nm

10-20 nm

PTAA	PCBM/BCP
P3HT	C_{60}/BCP
SAMs	CMC/BCP

mobility – 10^{-5}-10^{-2} cm^{2}V^{-1}s^{-1}

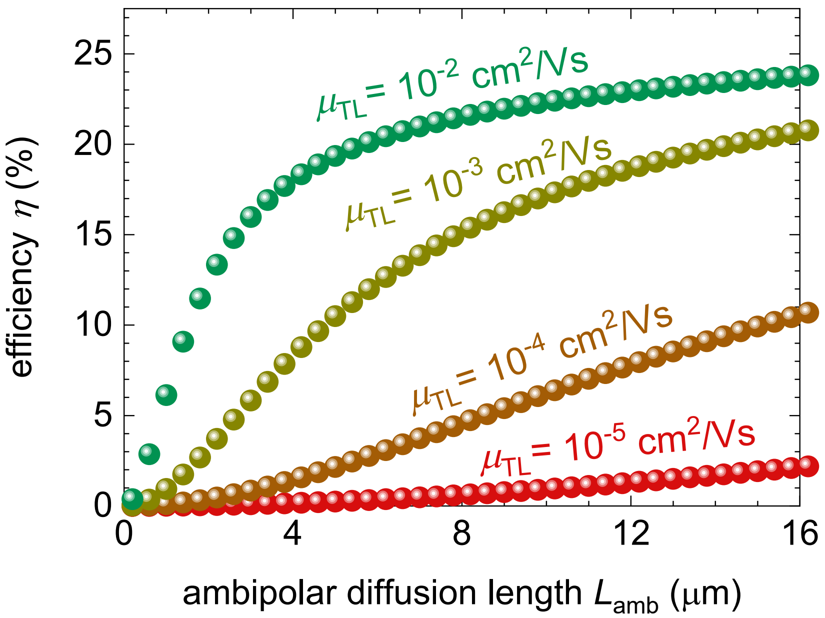
perovskite solar cell - effect of transport layers

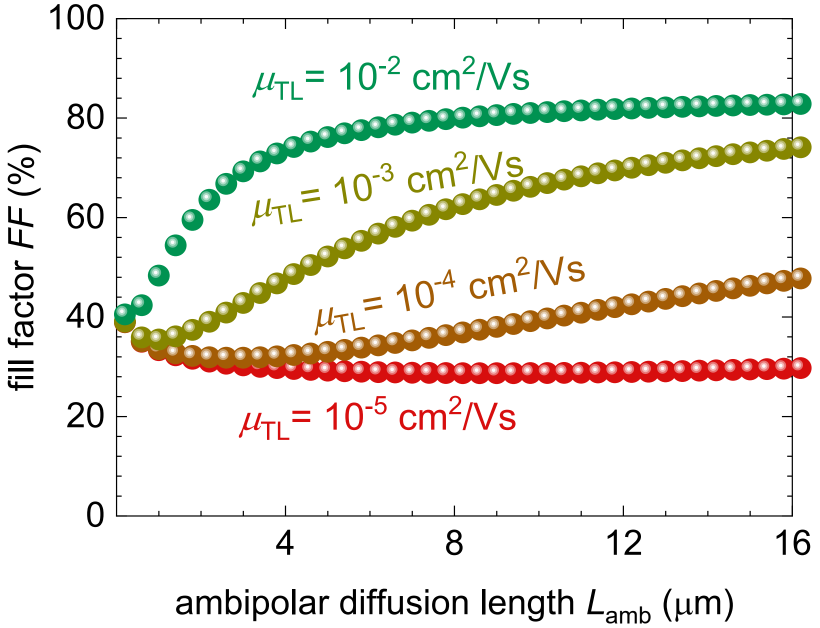


PTAA
P3HT
SAMs

PCBM/BCP
C_{60}/BCP
CMC/BCP

mobility – 10^{-5}-10^{-2} $cm^2V^{-1}s^{-1}$

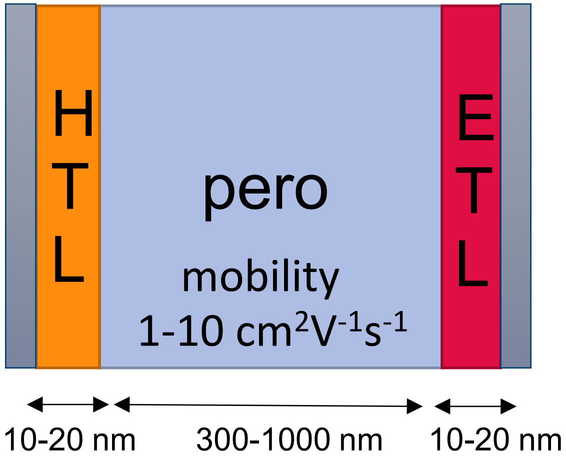




large diffusion lengths in the perovskite are irrelevant if transport layers do not extract charge efficiently

Akel, S. et al., 2023. *PRX Energy*, *2*, p.013004.

perovskite solar cell - effect of transport layers



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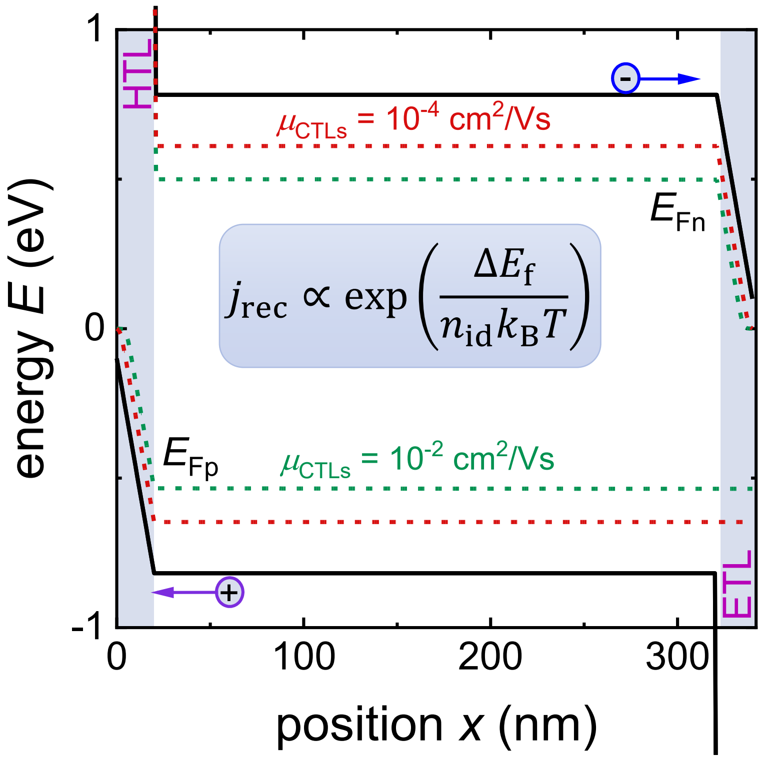
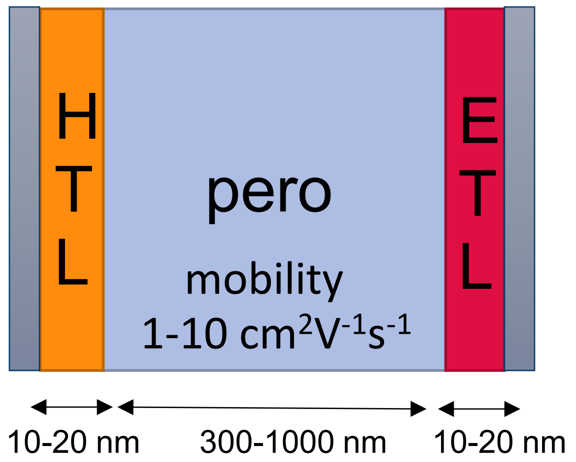


$$j_{rec} \propto \exp\left(\frac{\Delta E_f}{n_{id} k_B T}\right)$$

quasi-Fermi level splitting in the perovskite is coupled to potential drop across the transport layers

Akel, S. et al., 2023. *PRX Energy*, *2*, p.013004.

perovskite solar cell - effect of transport layers



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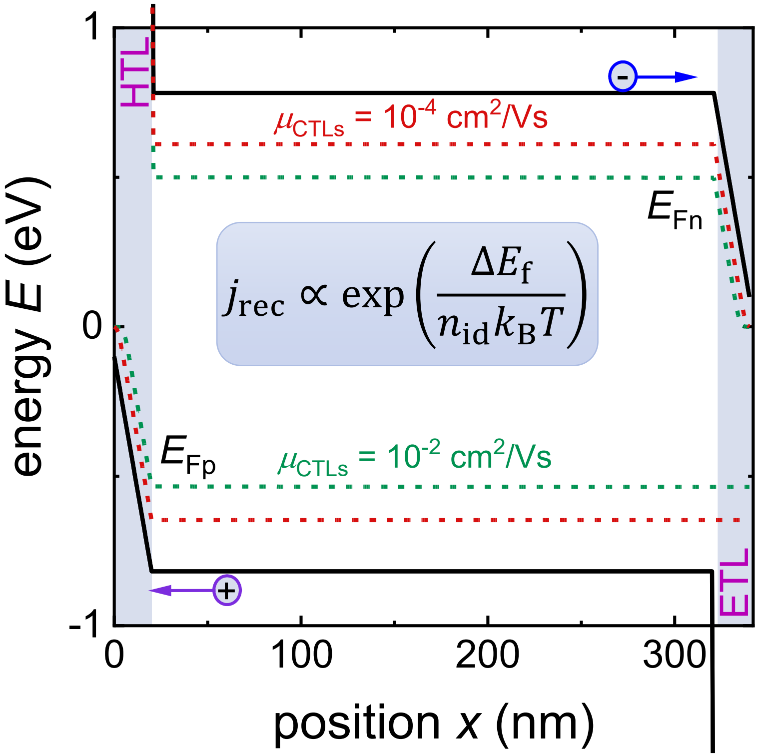
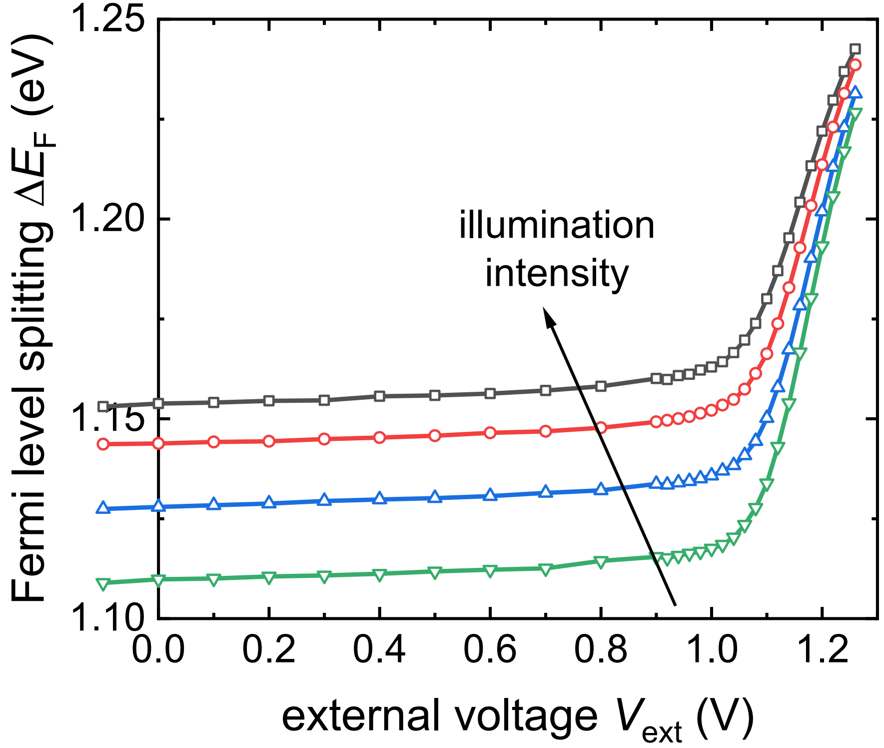




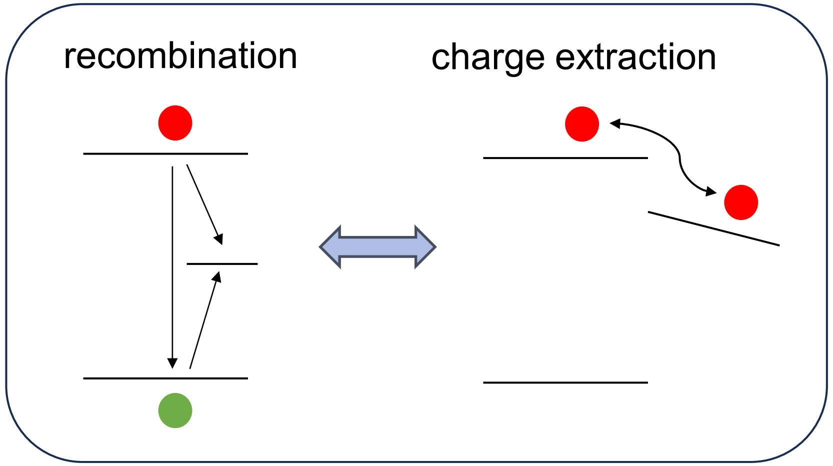
quasi-Fermi level splitting in the perovskite is coupled to potential drop across the transport layers

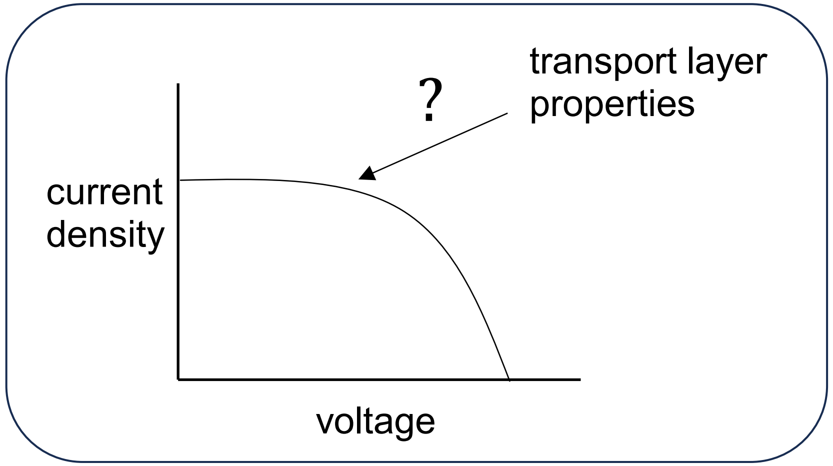
Akel, S. et al., 2023. *PRX Energy*, *2*, p.013004, D. Grabowski et al., 2022. *Solar RRL*, *6*(11), p.2200507.

key questions

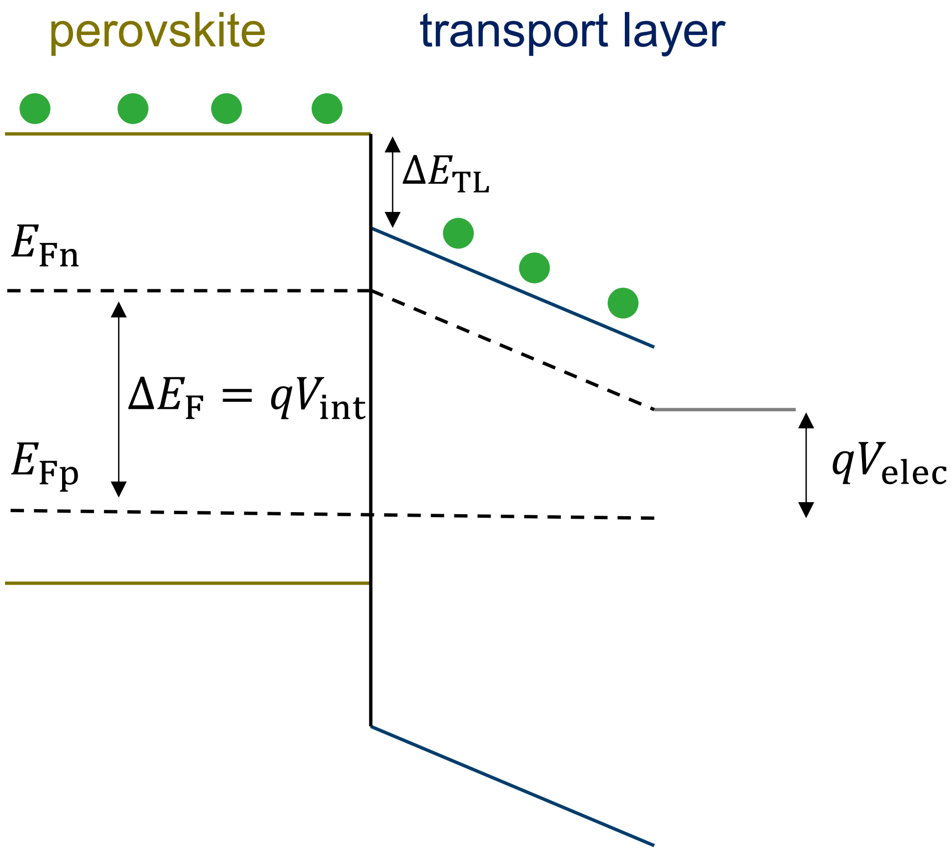
can we separate transport layer effects from bulk effects in typical characterisation techniques?

can we account for the effect of the transport layers on the PSC performance?





charge extraction through the transport layers



$$F_{\mathrm{TL}} = \frac{V_{\mathrm{bi,TL}} - V_{\mathrm{elec}}}{d_{\mathrm{TL}}}$$

assumptions

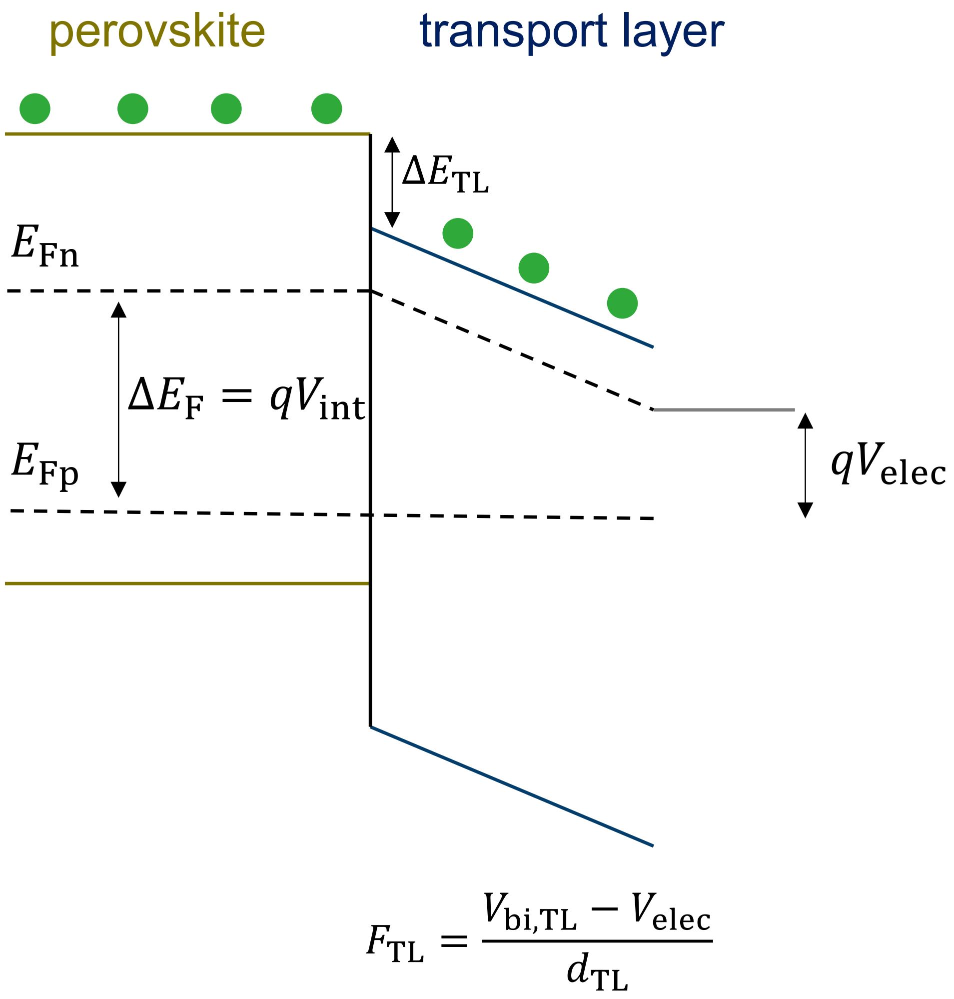
flat quasi-Fermi levels in the perovskite

mobile ions fully shield the electric field

symmetric transport layers

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

charge extraction through the transport layers



$$F_{TL} = \frac{V_{bi,TL} - V_{elec}}{d_{TL}}$$

current density

$$j = qn_i S_{exc} \times \left[\exp\left(\frac{qV_{int}}{2k_B T}\right) - \exp\left(\frac{V_{elec}}{2k_B T}\right)\right]$$

charge extraction velocity

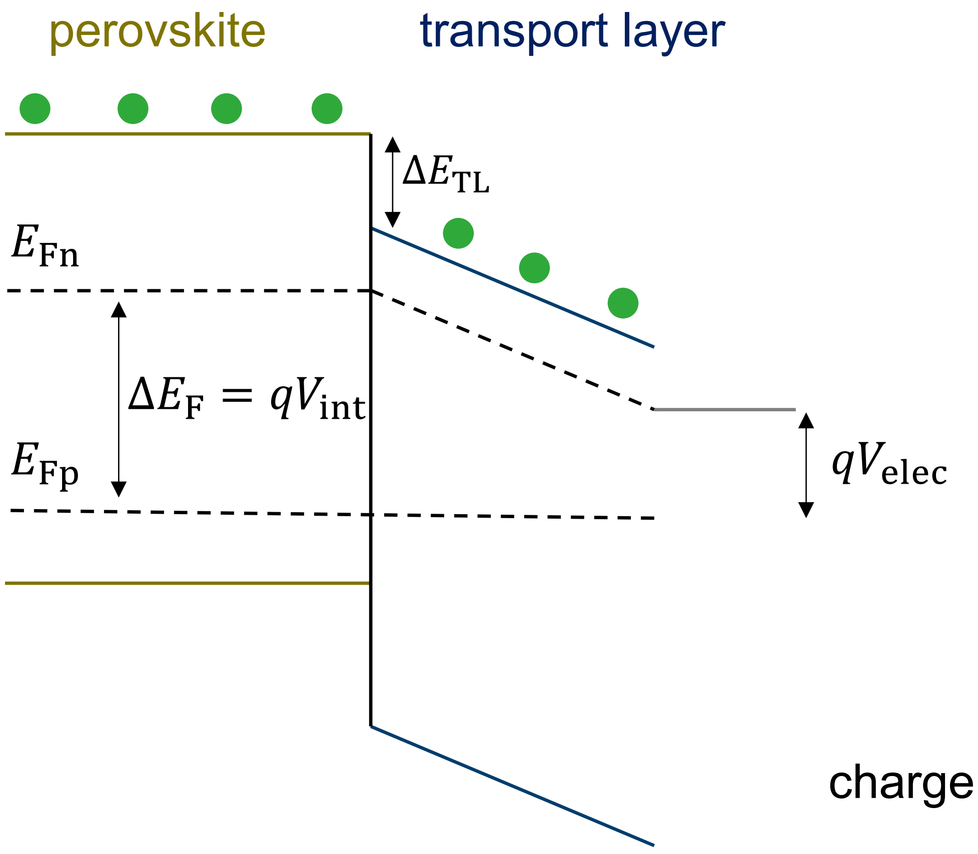
$$S_{exc}(V_{elec}) \cong \mu_{TL} F_{TL} \exp\left(\frac{\Delta E_{TL}}{k_B T}\right)$$

charge extraction time constant

$$\tau_{exc} = \frac{d_{pero}}{S_{exc}}$$

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

charge extraction through the transport layers



$$F_{\mathrm{TL}} = \frac{V_{\mathrm{bi,TL}} - V_{\mathrm{elec}}}{d_{\mathrm{TL}}}$$

current density

$$j = qn_{\mathrm{i}}S_{\mathrm{exc}} \times \left[\exp\left(\frac{qV_{\mathrm{int}}}{2k_{\mathrm{B}}T}\right) - \exp\left(\frac{V_{\mathrm{elec}}}{2k_{\mathrm{B}}T}\right)\right]$$

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charge extraction time constant

$$\tau_{\mathrm{exc}} = \frac{d_{\mathrm{pero}}}{S_{\mathrm{exc}}}$$

→

charge extraction resistance

$$R_{\mathrm{exc}} = \frac{2k_{\mathrm{B}}T}{q^2 S_{\mathrm{exc}} n_{\mathrm{i}}}\exp\left(\frac{-qV_{\mathrm{elec}}}{2k_{\mathrm{B}}T}\right)$$

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

figure of merit accounting for charge extraction losses

$$j = qd\left[G - \frac{n_\mathrm{i}}{\tau_\mathrm{rec}(V_\mathrm{ext})}\exp\left(\frac{qV_\mathrm{ext}}{2k_\mathrm{B}T}\right)\right]$$

current-voltage curve – balance of generation and recombination

figure of merit accounting for charge extraction losses

$$j = \left[\frac{1}{1 + \frac{\tau_{\mathrm{exc}}(V_{\mathrm{ext}})}{\tau_{\mathrm{rec}}(V_{\mathrm{ext}})}}\right] qd \left[G - \frac{n_{\mathrm{i}}}{\tau_{\mathrm{rec}}(V_{\mathrm{ext}})} \exp\left(\frac{qV_{\mathrm{ext}}}{2k_{\mathrm{B}}T}\right)\right]$$

current-voltage curve including generation, recombination and extraction

L. Krückemeier et al., 2023. *Advanced Materials* 35, 2300872.
S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

figure of merit accounting for charge extraction losses

$$j = \left[\frac{1}{1 + \frac{\tau_{\mathrm{exc}}(V_{\mathrm{ext}})}{\tau_{\mathrm{rec}}(V_{\mathrm{ext}})}}\right] qd \left[G - \frac{n_{\mathrm{i}}}{\tau_{\mathrm{rec}}(V_{\mathrm{ext}})} \exp\left(\frac{qV_{\mathrm{ext}}}{2k_{\mathrm{B}}T}\right)\right]$$

$$\mathrm{FOM} = \frac{1}{1 + \frac{\tau_{\mathrm{exc}}(V_{\mathrm{ext}})}{\tau_{\mathrm{rec}}(V_{\mathrm{ext}})}}$$

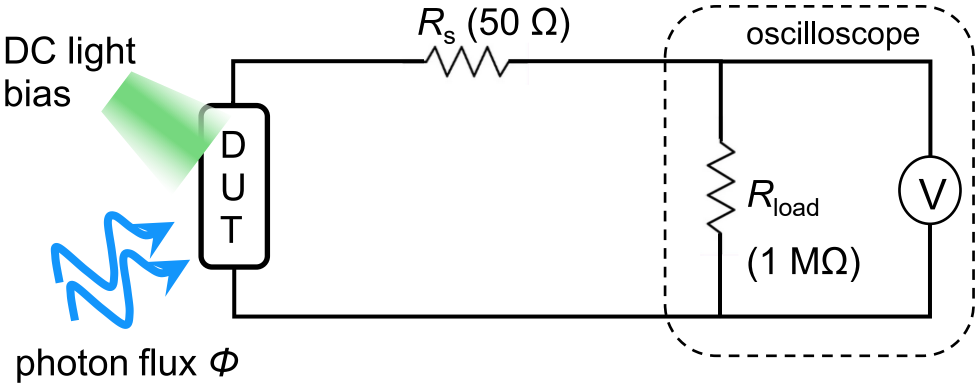
FOM = 1
perfect charge extraction

FOM < 1
non-ideal charge extraction

L. Krückemeier et al., 2023. *Advanced Materials* 35, 2300872.
S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

small-perturbation methods

transient photovoltage (TPV) – time domain



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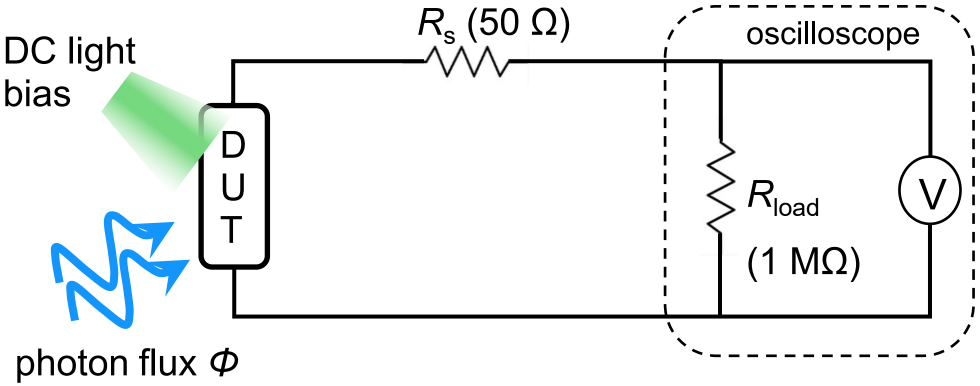
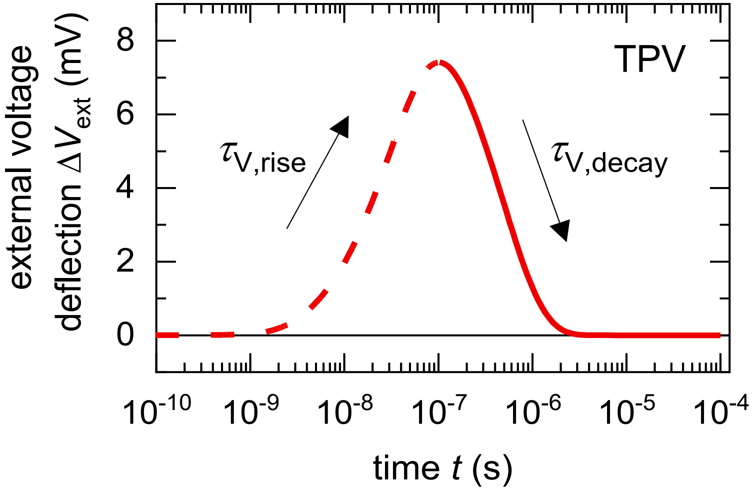
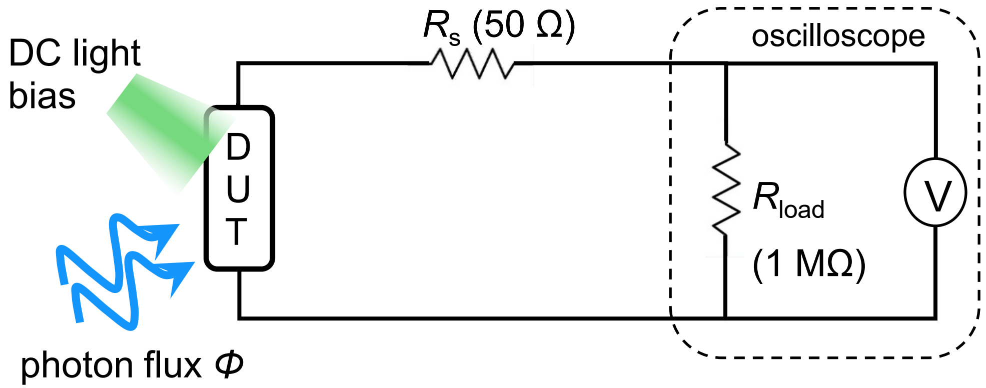


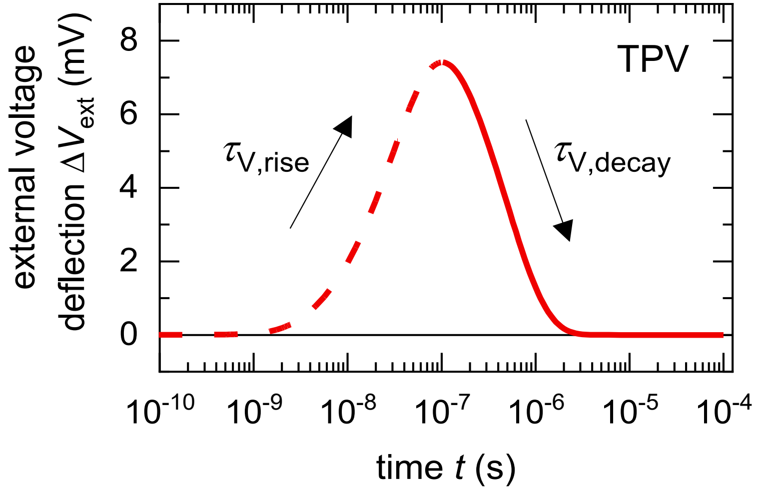


$$\Delta V_{\text{ext}}(t) = \Delta V_{\text{ext},0}\left(e^{-t/\tau_{\text{V,decay}}} - e^{-t/\tau_{\text{V,rise}}}\right)$$

small-perturbation methods

transient photovoltage (TPV) – time domain





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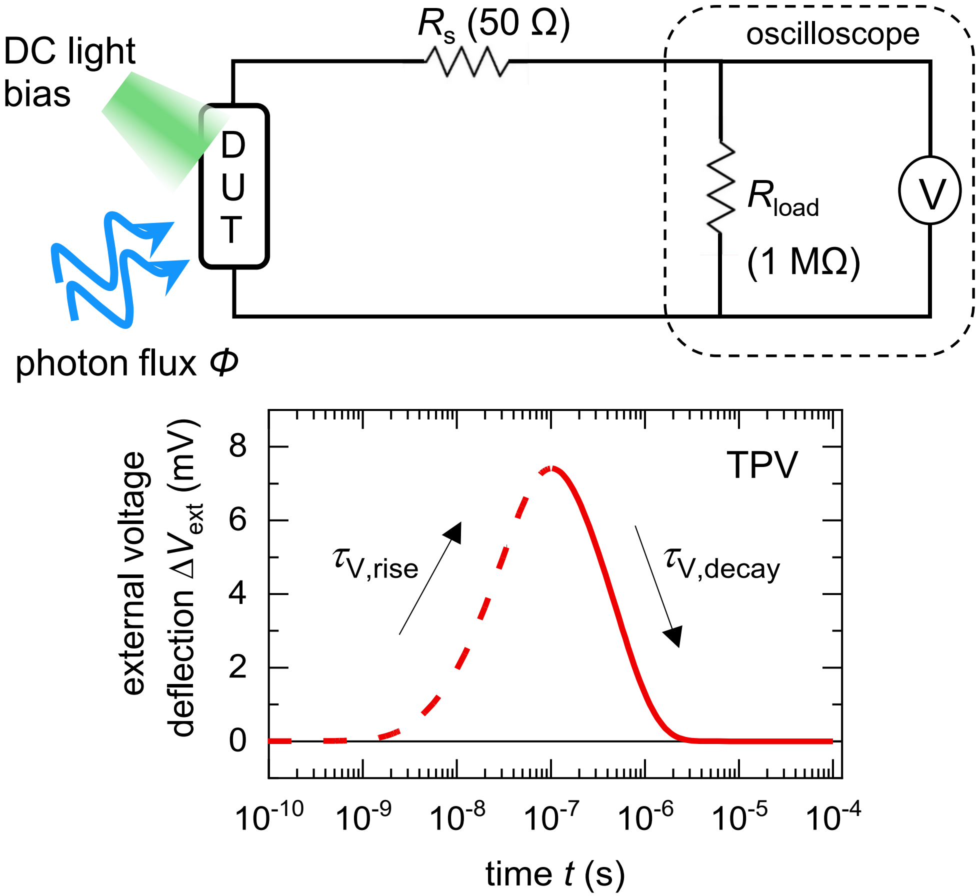
intensity modulated photovoltage spectroscopy (IMVS) – frequency domain

$$W(\omega) = \frac{\tilde{V}}{q\tilde{\Phi}} \longrightarrow \omega = 10\ \mathrm{MHz} - 1\ \mathrm{mHz}$$

small-perturbation methods

transient photovoltage (TPV) – time domain



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intensity-modulated photovoltage spectroscopy (IMVS)

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intensity modulated photocurrent spectroscopy (IMPS)

$$Q(\omega) = \frac{\tilde{J}}{q\tilde{\Phi}} \longrightarrow \omega = 10\text{ MHz} - 1\text{ mHz}$$

small-perturbation methods

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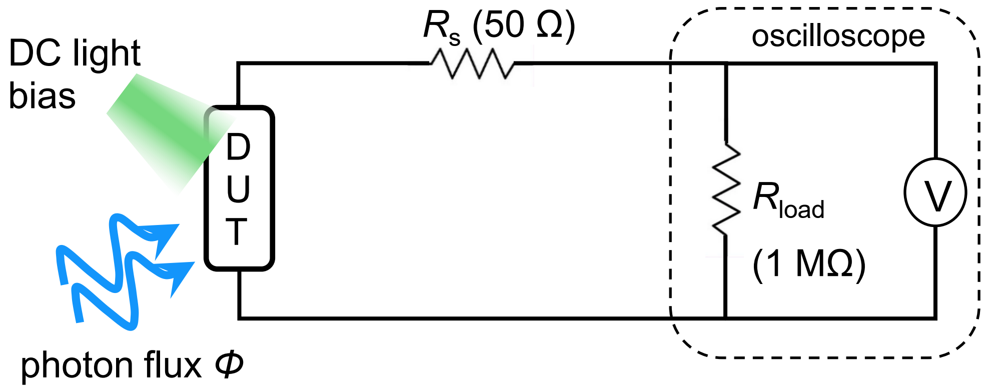

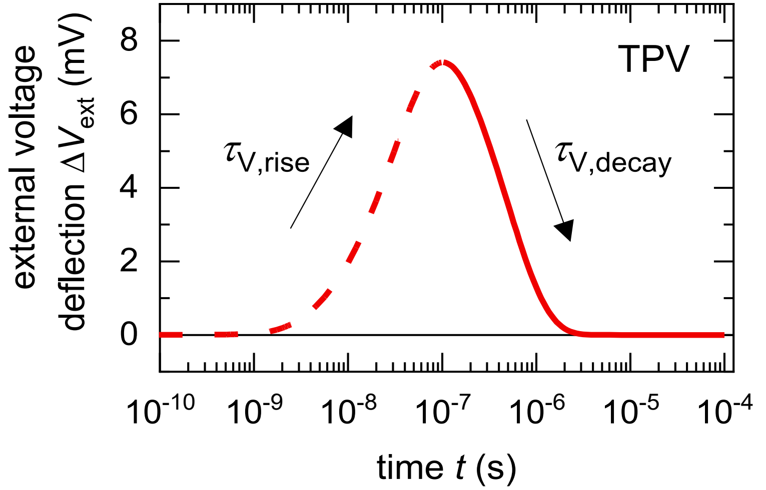

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intensity modulated photocurrent spectroscopy (IMPS)

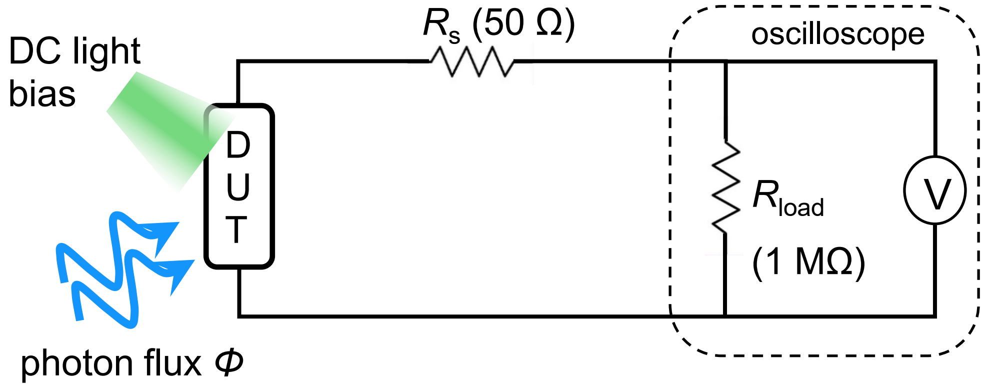
$$Q(\omega) = \frac{\tilde{J}}{q\tilde{\Phi}} \longrightarrow \omega = 10\ \mathrm{MHz} - 1\ \mathrm{mHz}$$

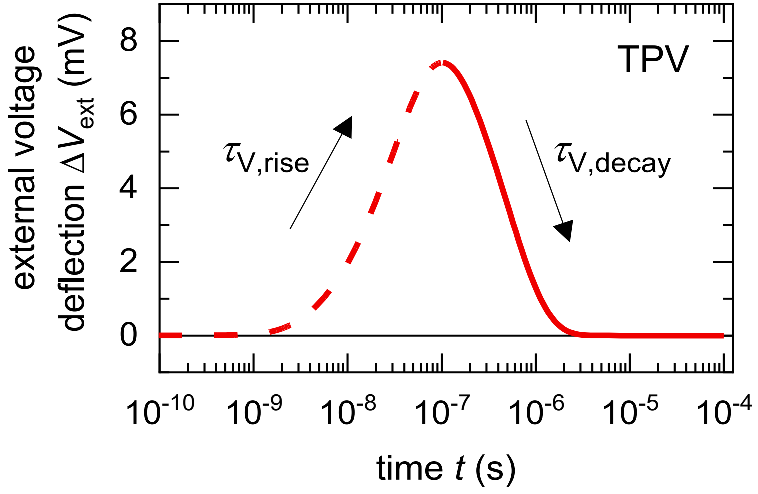
impedance spectroscopy (IS)

$$Z(\omega) = \frac{\tilde{V}}{\tilde{J}} \longrightarrow \omega = 10\ \mathrm{MHz} - 1\ \mathrm{mHz}$$

small-perturbation methods

transient photovoltage (TPV) – time domain





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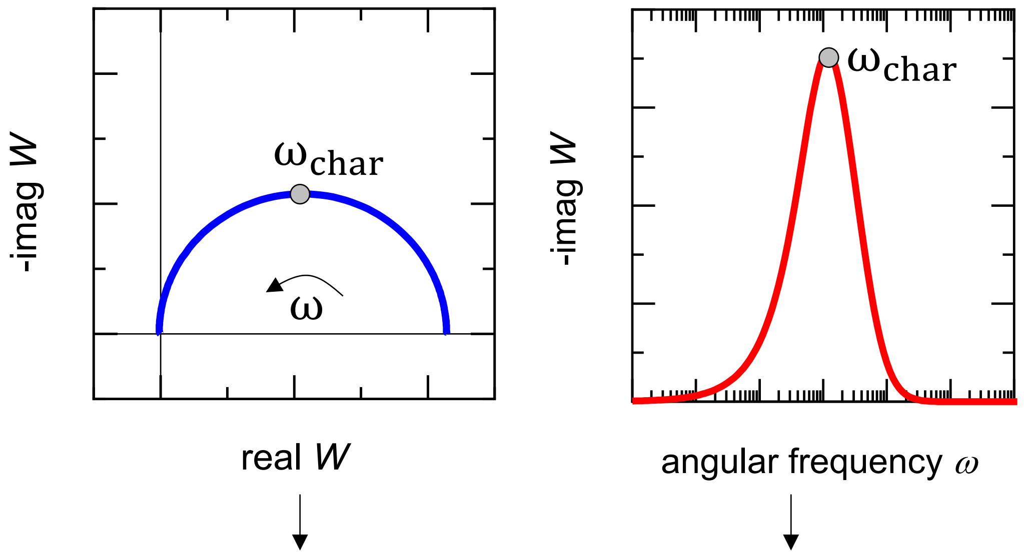
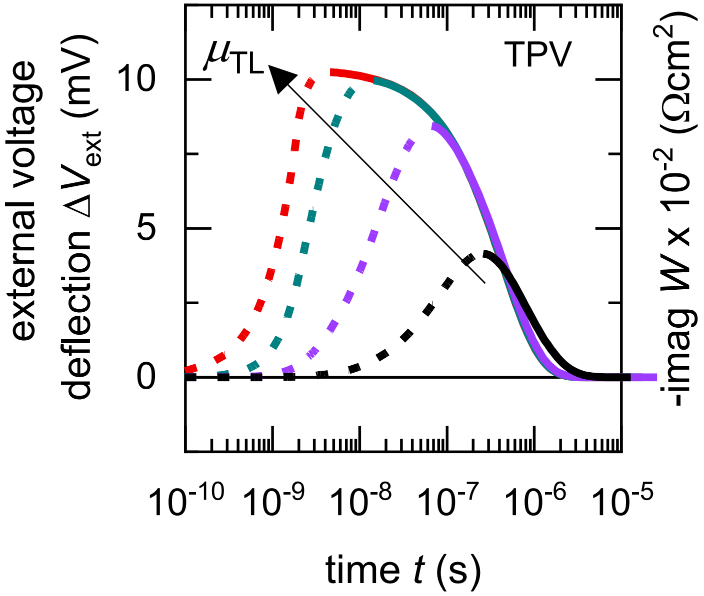
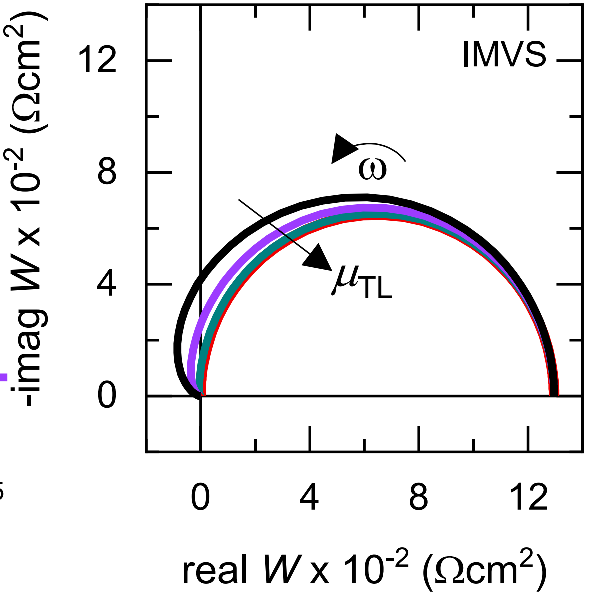


$$\frac{d(-\text{imag}\,W)}{d\omega} = 0 \rightarrow \omega_{char} = \frac{1}{\tau_{char}}$$

time constants

drift-diffusion simulations





S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

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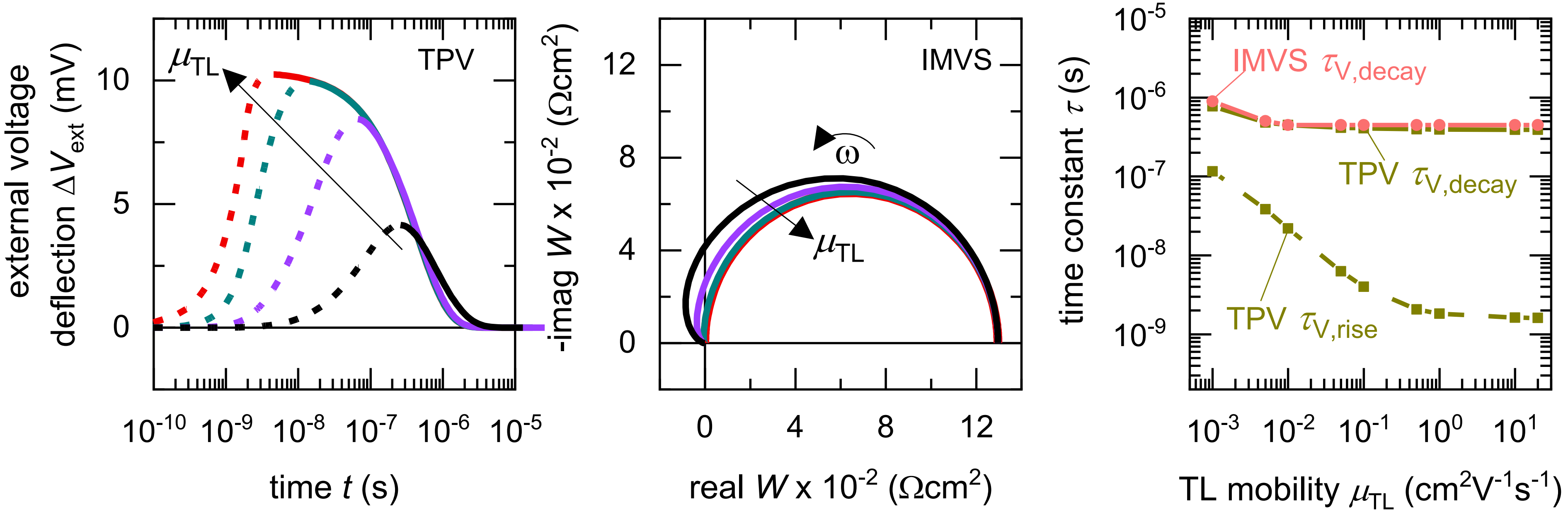
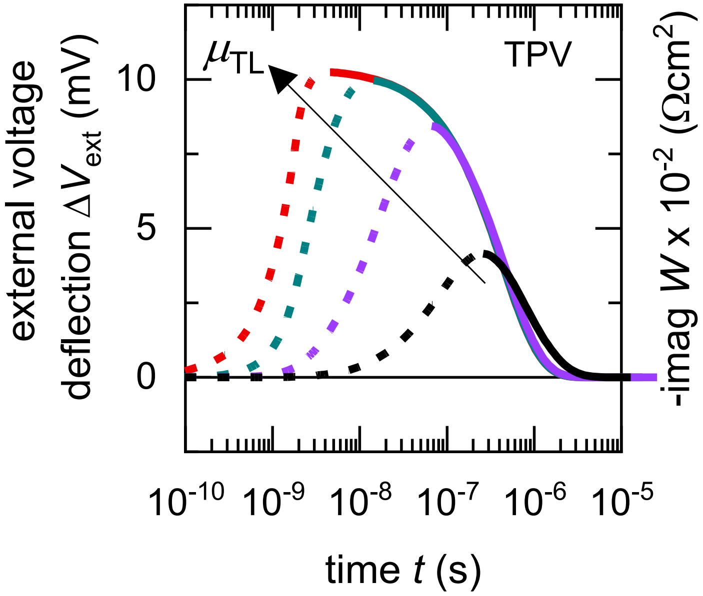
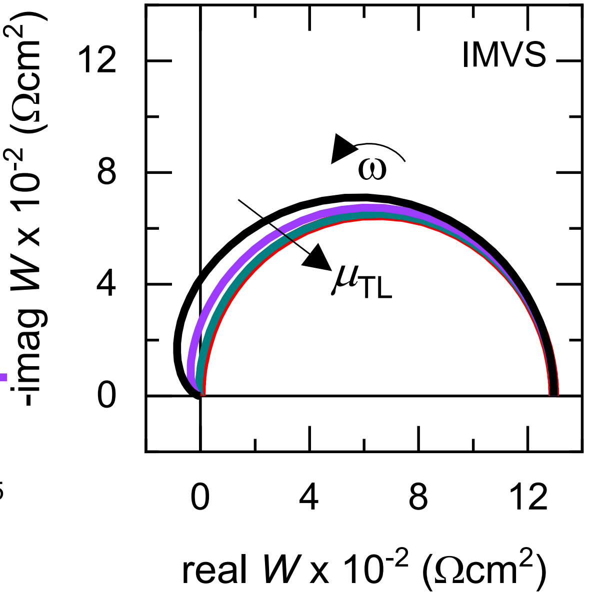


why do time domain methods show two time constants while frequency domain methods show only one time constant?

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

modified transfer function





logic

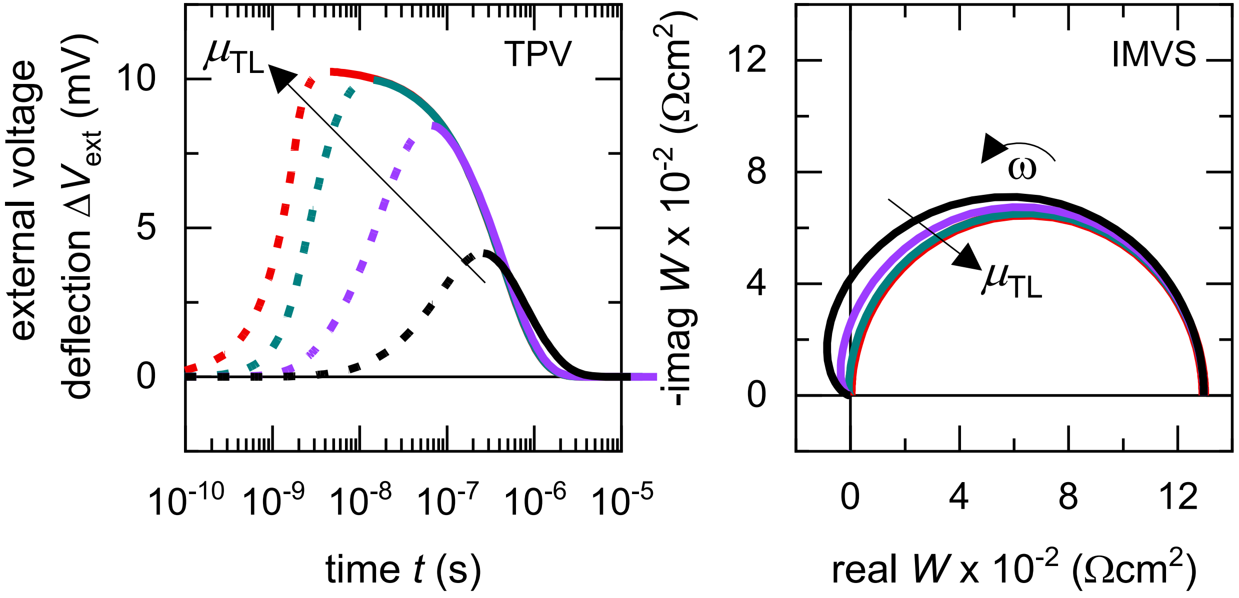
time domain methods show absolute value and slope of the voltage/current

frequency domain methods show no information about the slope

$$V \rightarrow \frac{dV}{dt} \xrightarrow{\text{laplace transform}} i\omega V$$

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

modified transfer function



<u>logic</u>

time domain methods show absolute value and slope of the voltage/current

frequency domain methods show no information about the slope

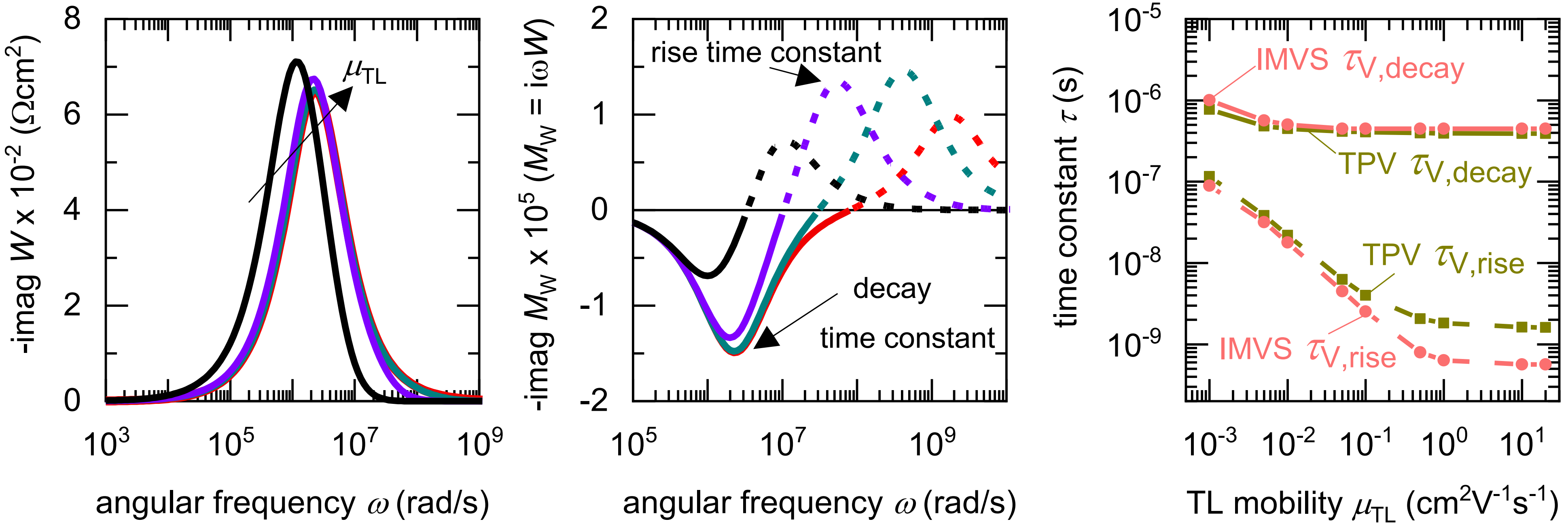
$$M_W = i\omega W \longrightarrow \begin{matrix} \text{real } M_W = -\omega \times \text{imag } W \\ \text{imag } M_W = \omega \times \text{real } W \end{matrix}$$

$$\longrightarrow$$

$$\frac{d(-\text{imag } M_W)}{d\omega} = 0 \rightarrow \omega_{char} = \frac{1}{\tau_{char}}$$

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

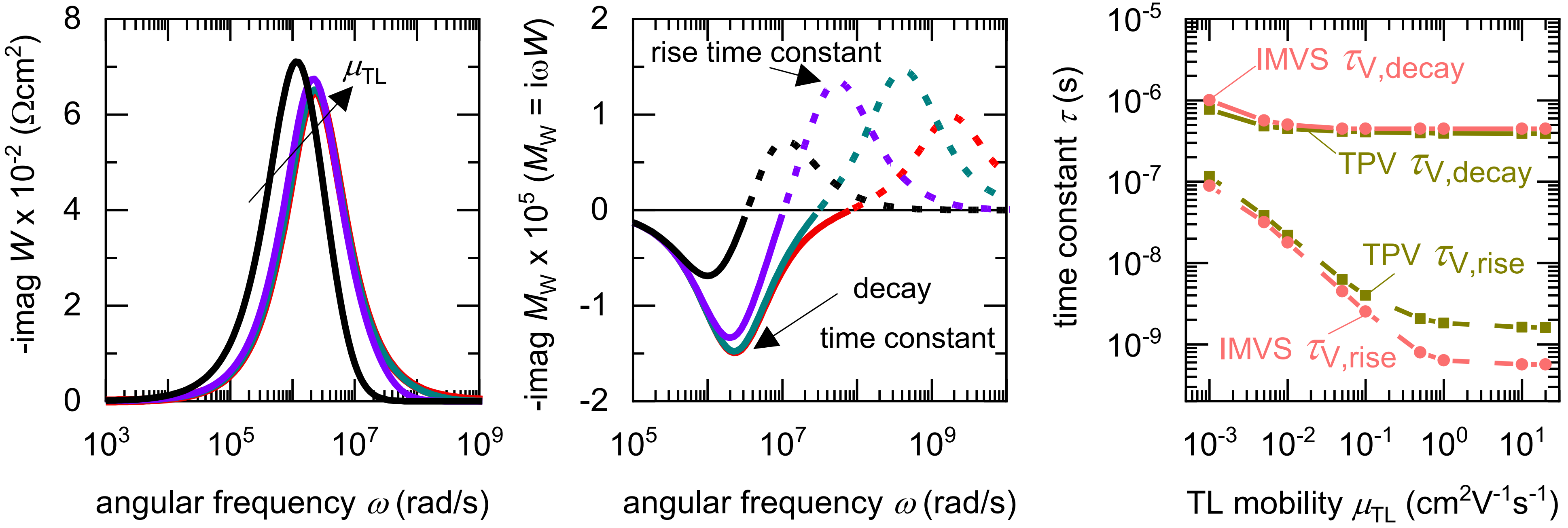
modified transfer function



rise time constant embedded in the transition of real part of transfer function to negative values at high frequencies

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

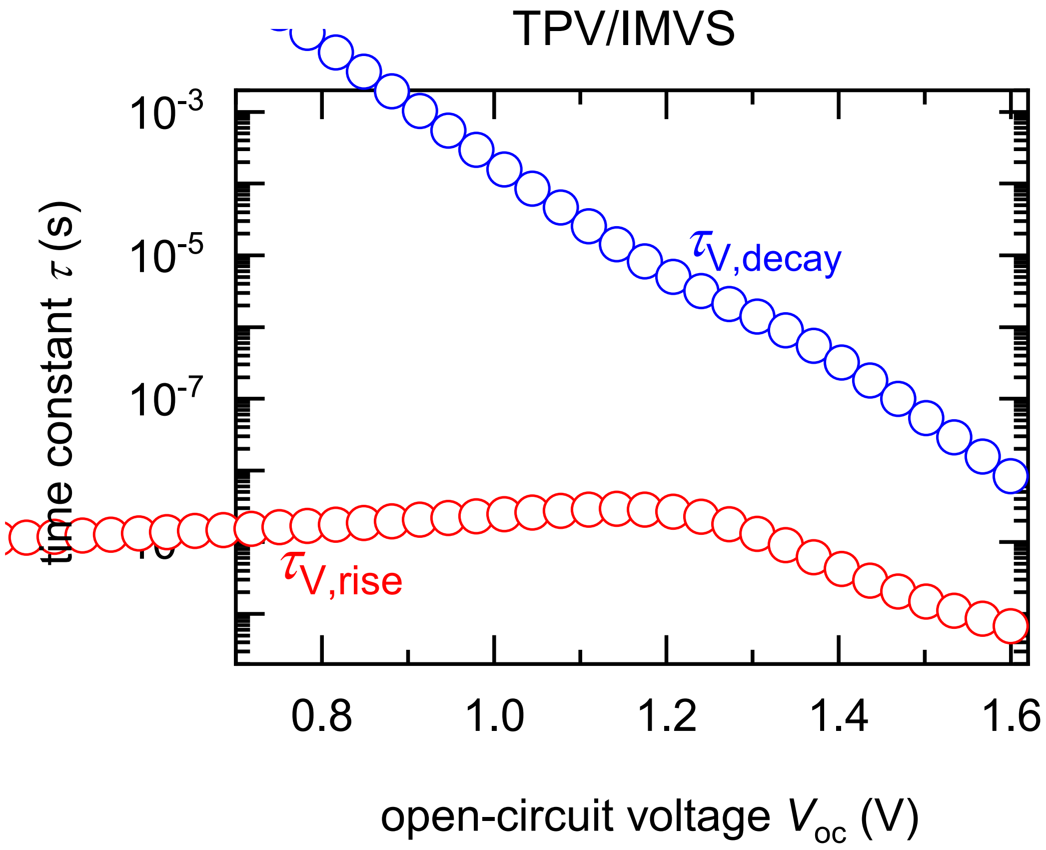
modified transfer function



which mechanisms generate the rise and decay time constants?

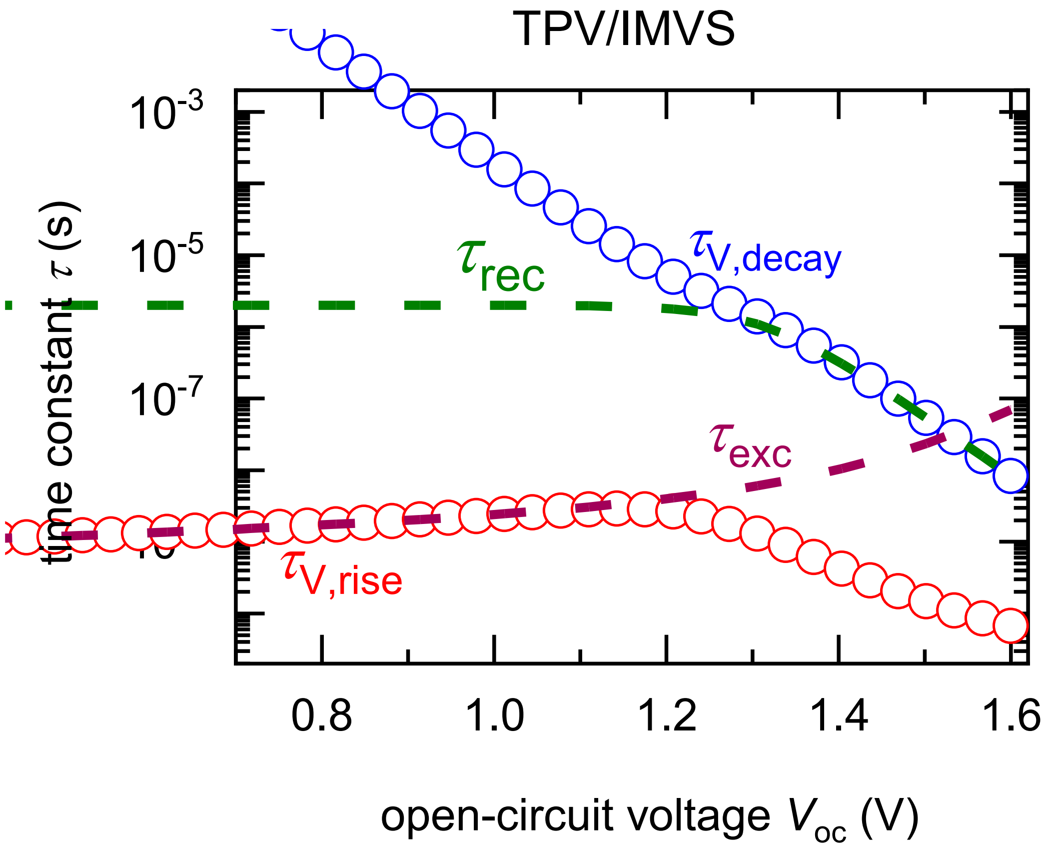
S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

predicted time constants



S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

predicted time constants



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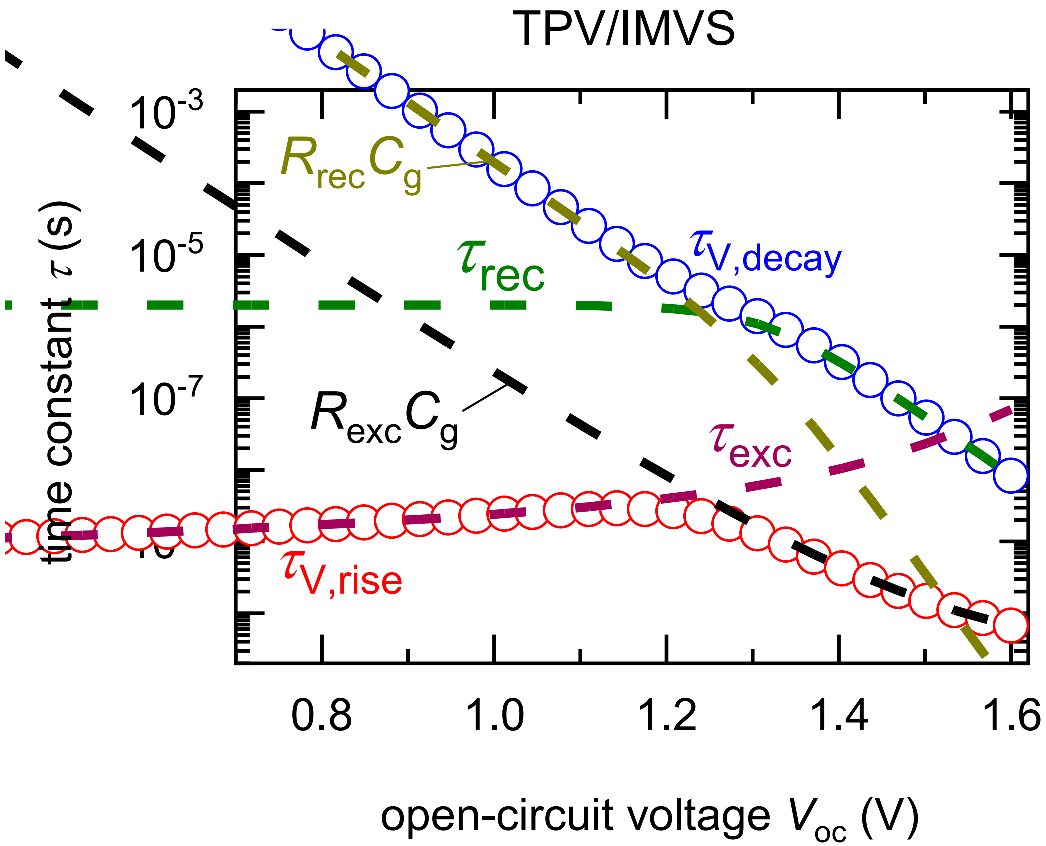

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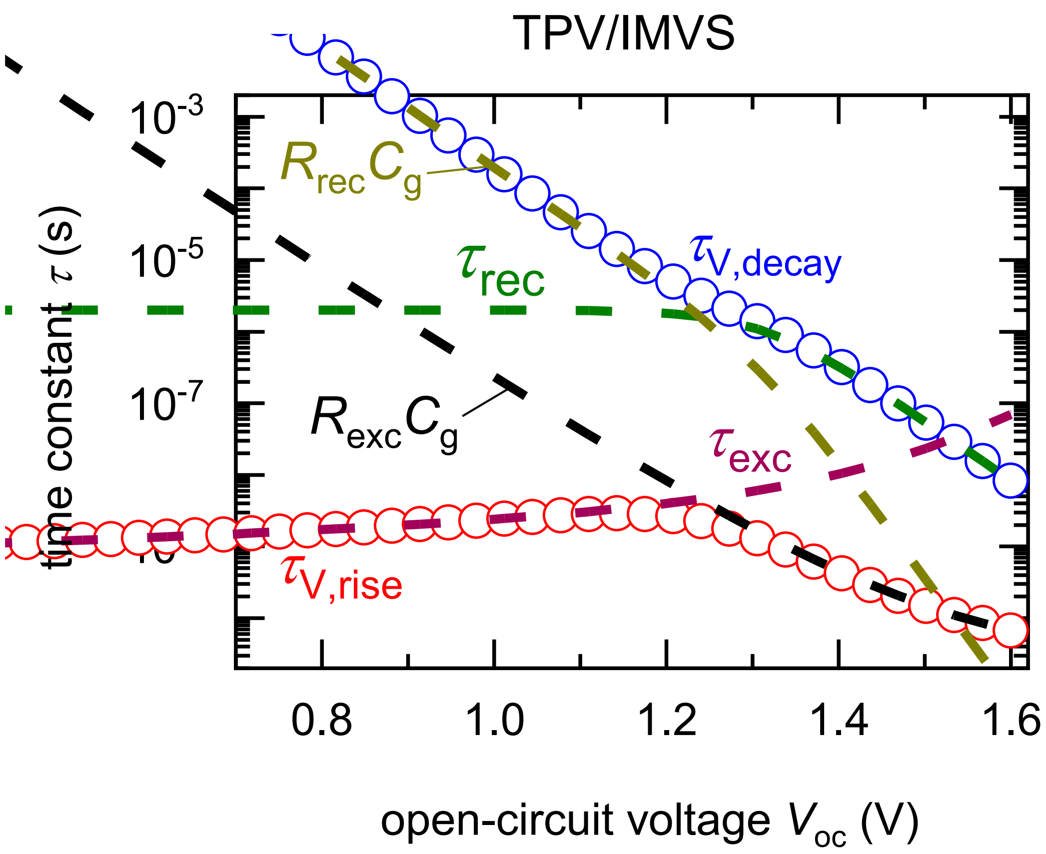
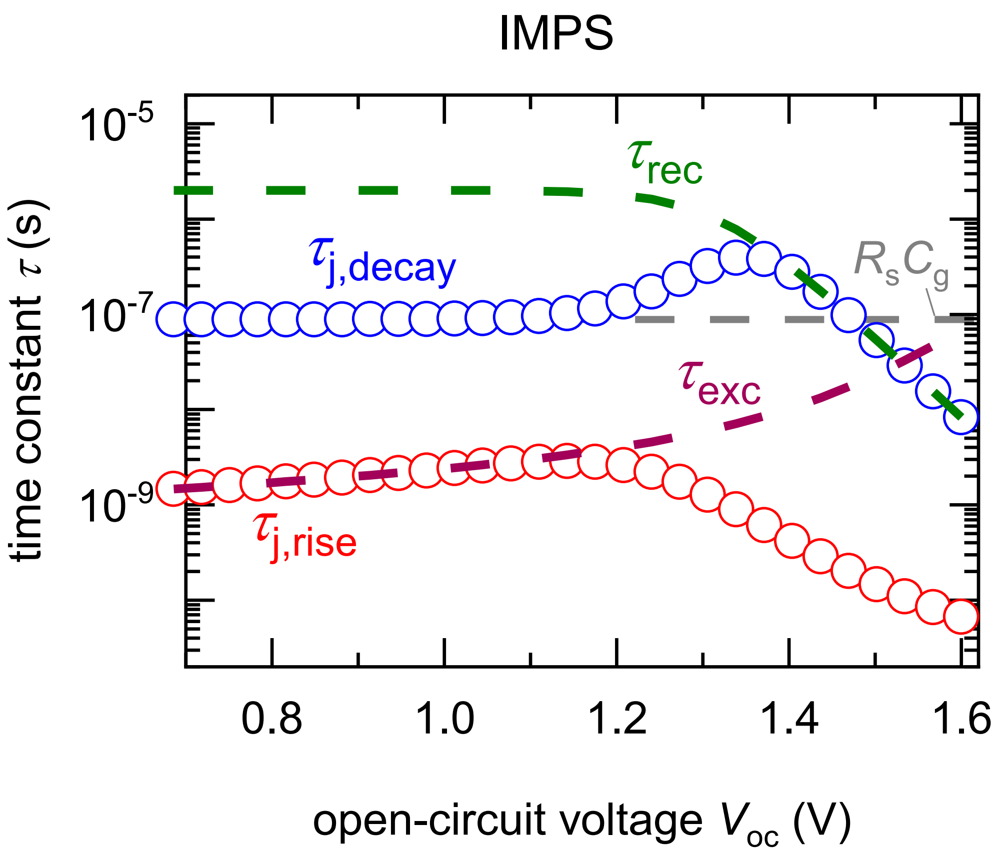
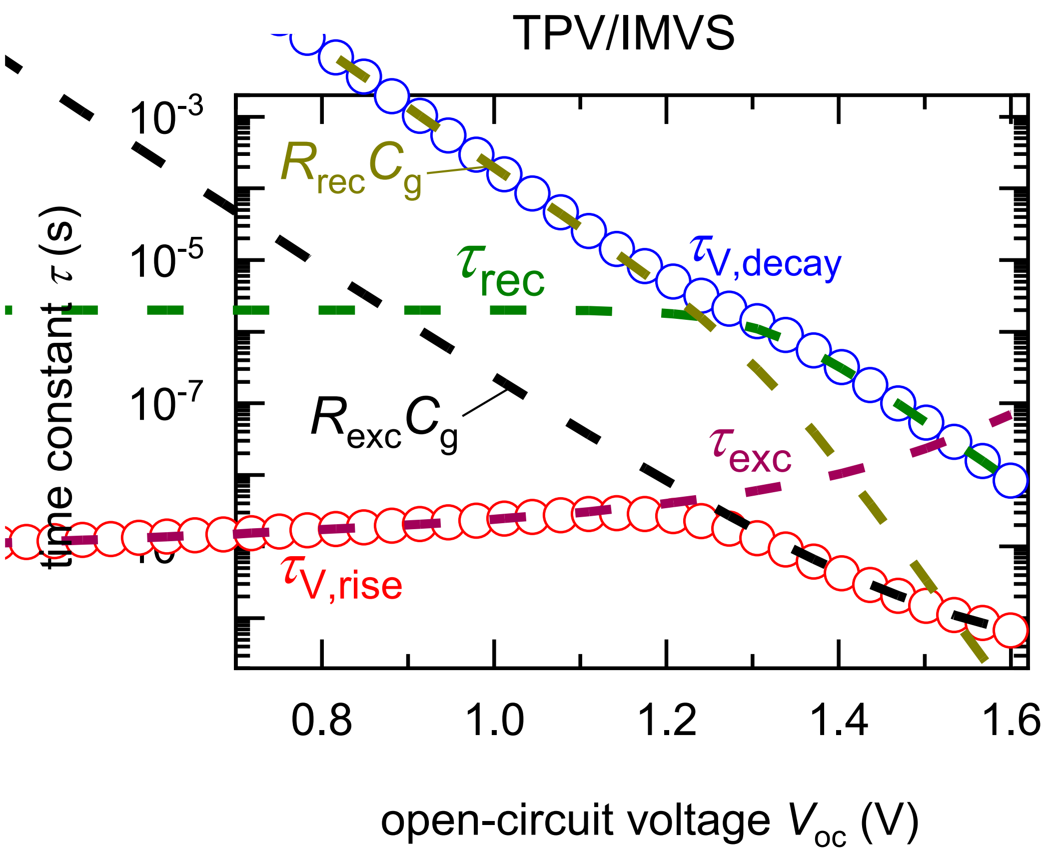
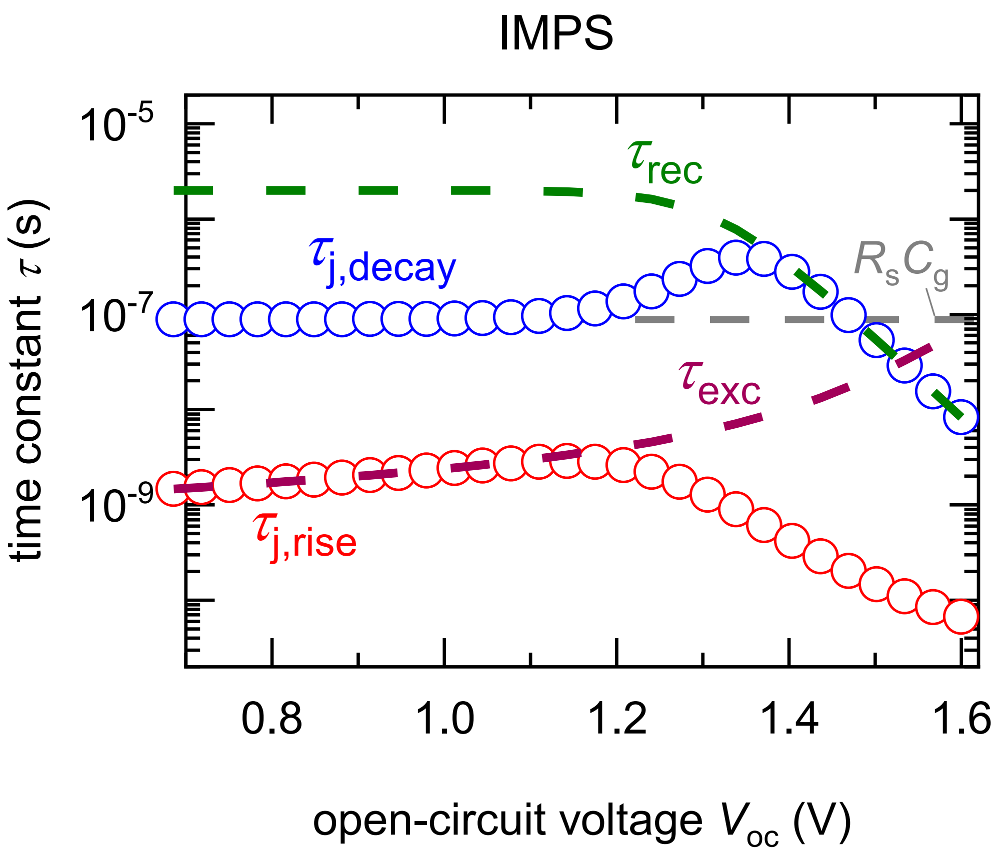




S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

predicted time constants





rise time constant → charge extraction

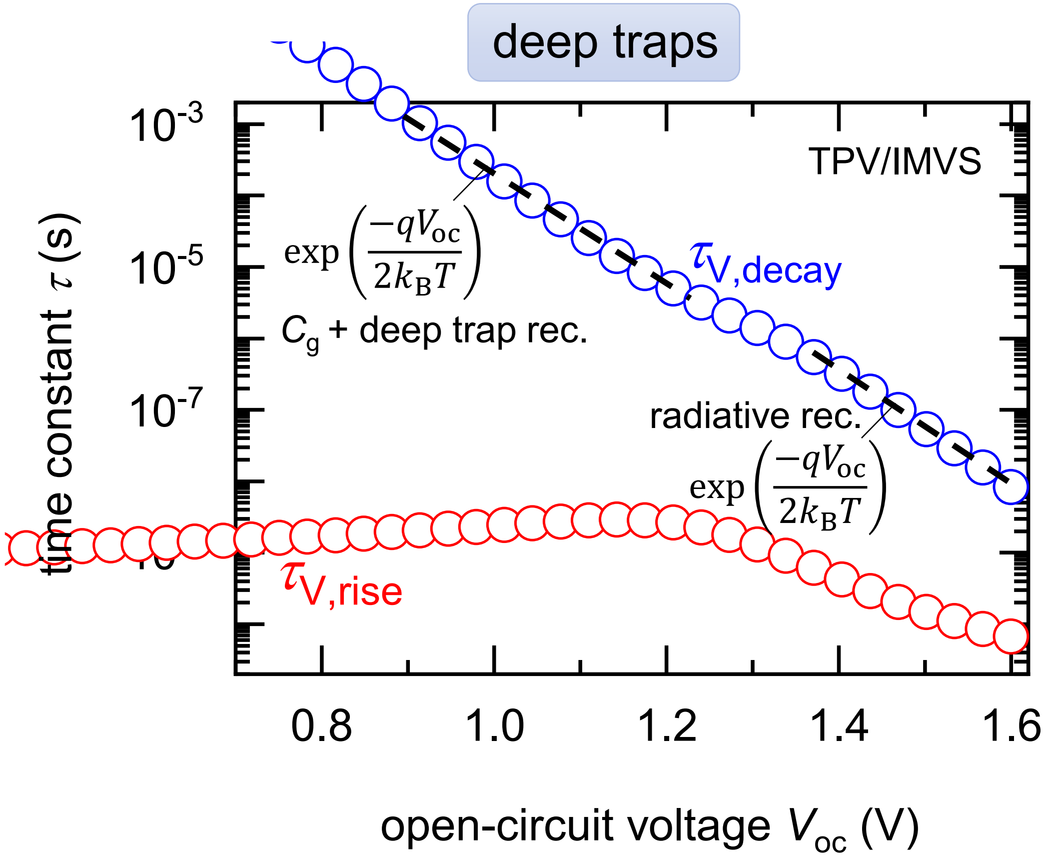
decay time constant → recombination

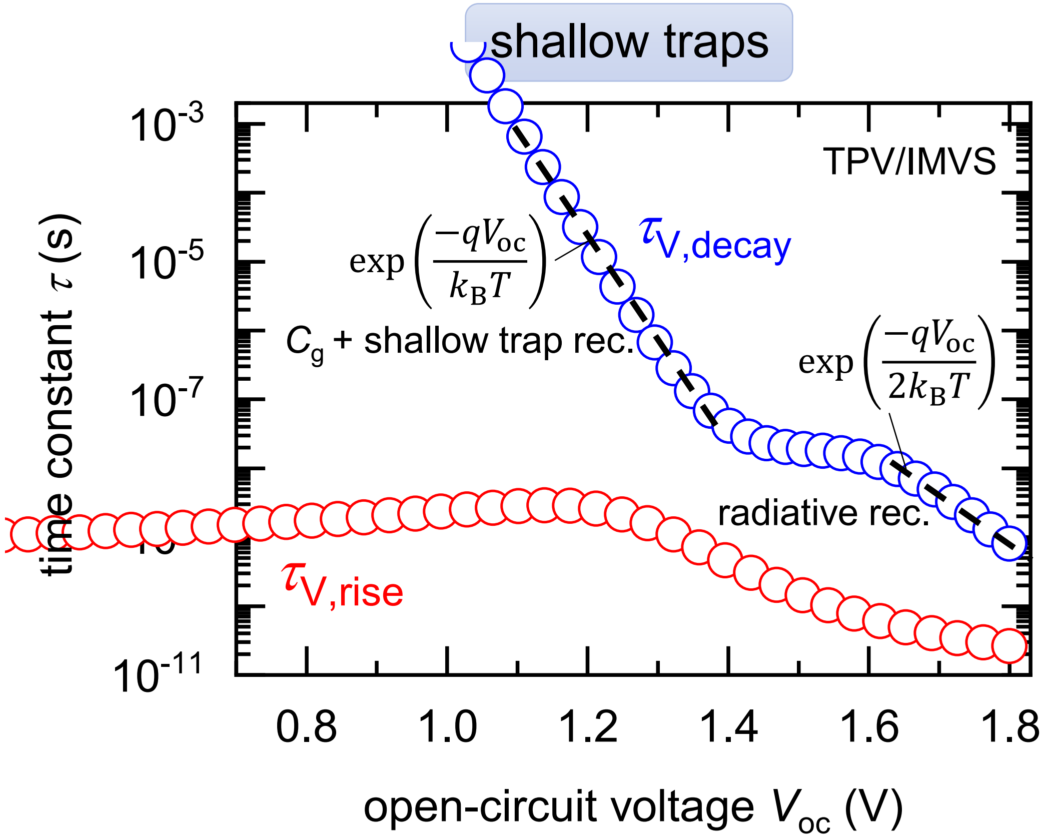
rise time constant → charge extraction

decay time constant → R_sC_g attenuation

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

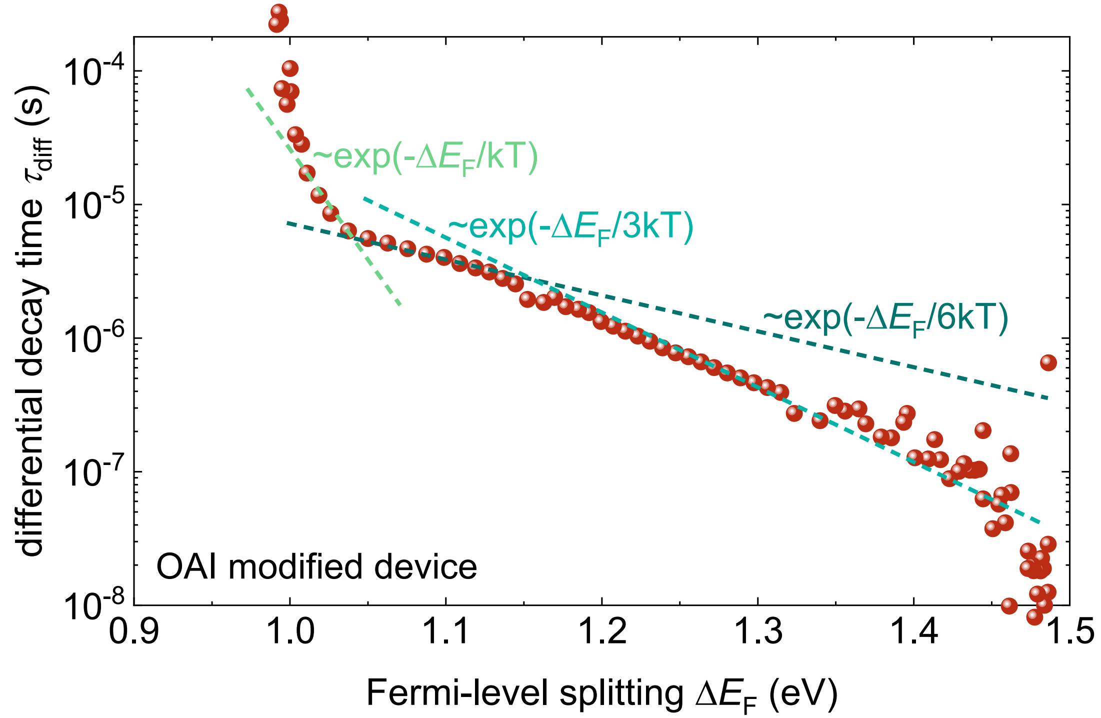
predicted time constants

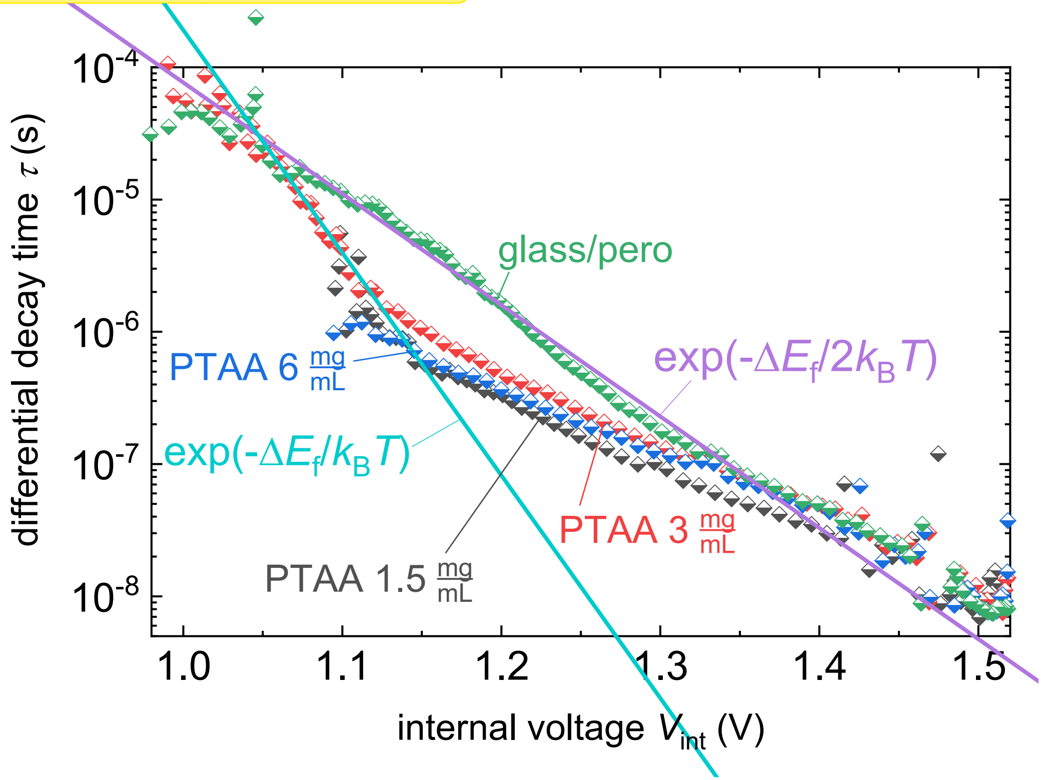

deep traps


shallow traps

shallow traps in perovskite solar cells

transient photoluminescence (tr-PL) measurements

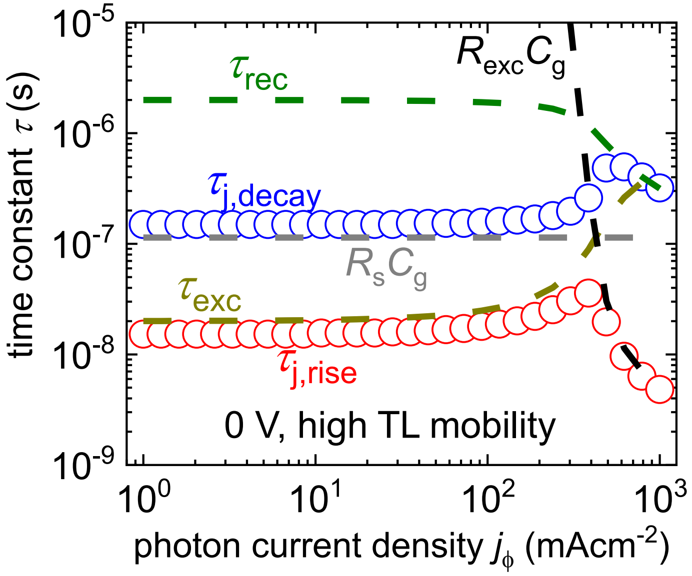


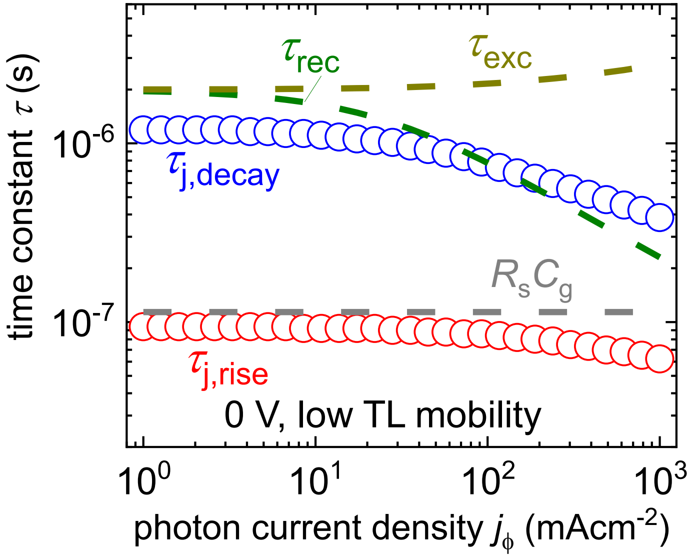


Y. Yuan et al., 2024. *Nature Materials*, *23*(3), pp.391-397. C. Dreessen et al., 2024. *Solar RRL*, *8*(23), p.2400504.

IMPS time constants versus light intensity

model

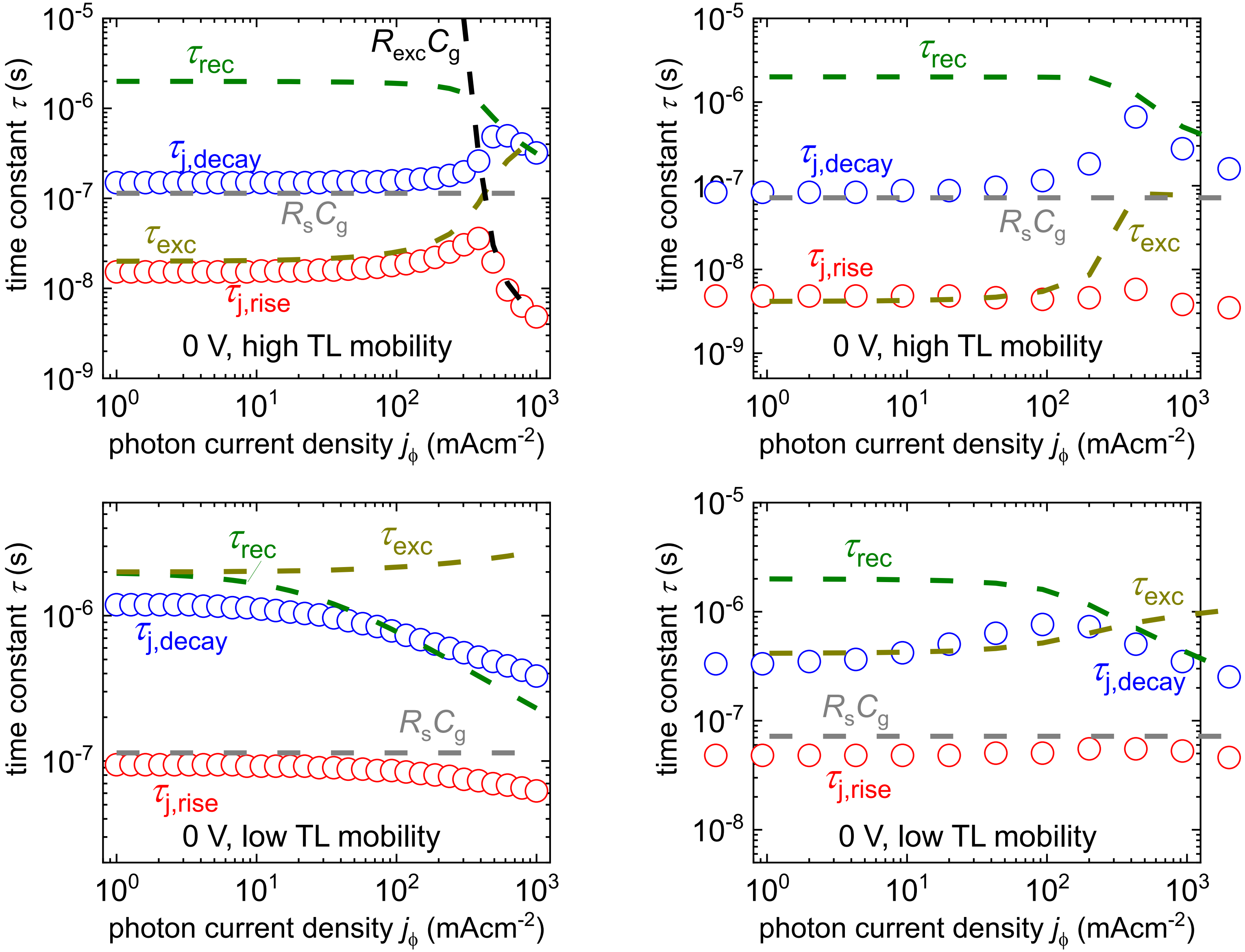




IMPS time constants versus light intensity

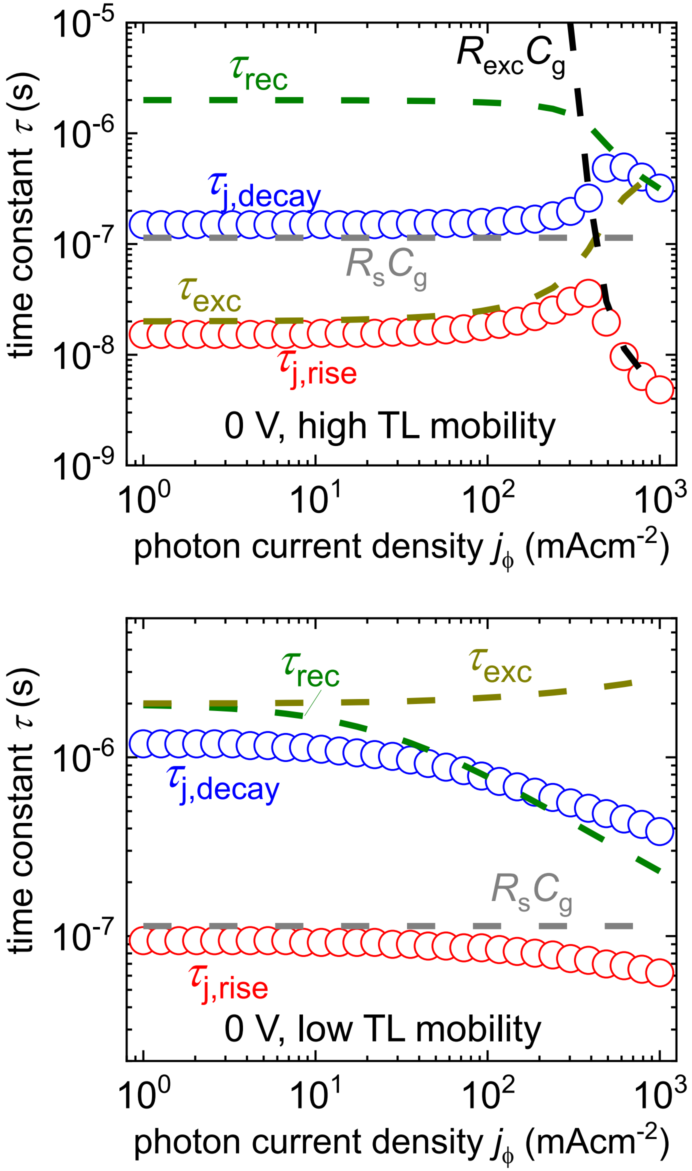
model

drift-diffusion

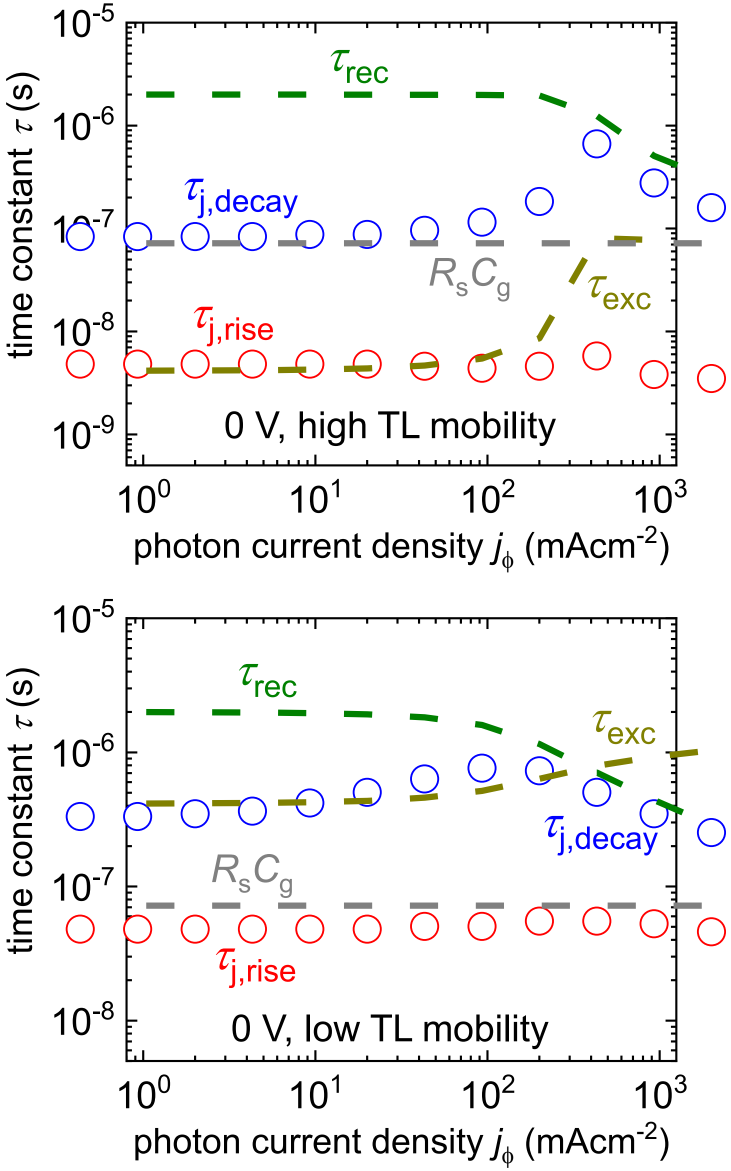


IMPS time constants versus light intensity

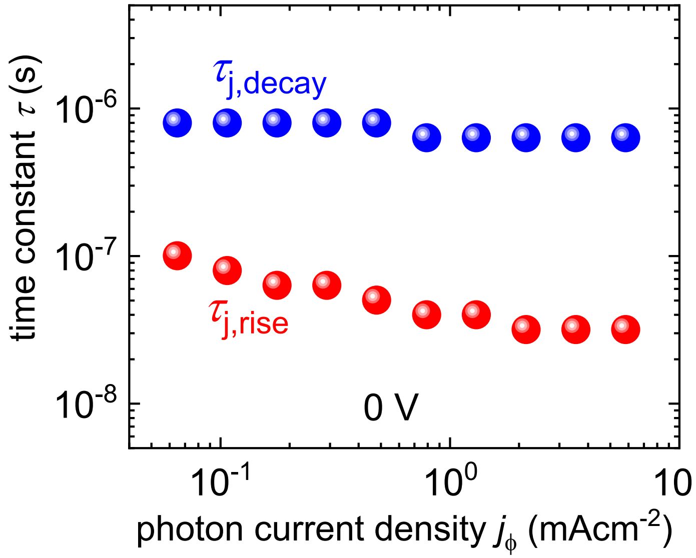
model



drift-diffusion

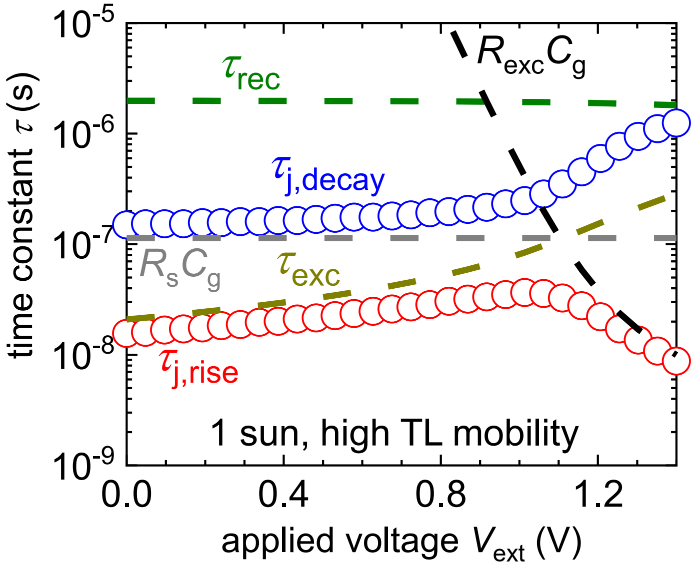


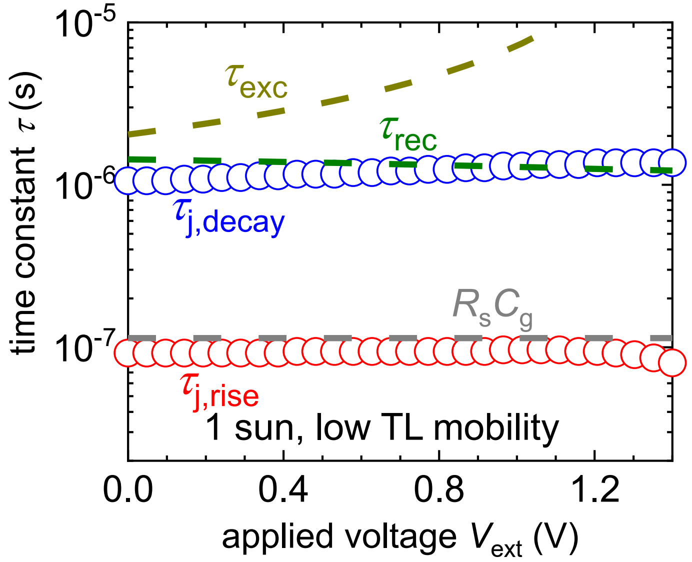
experiment



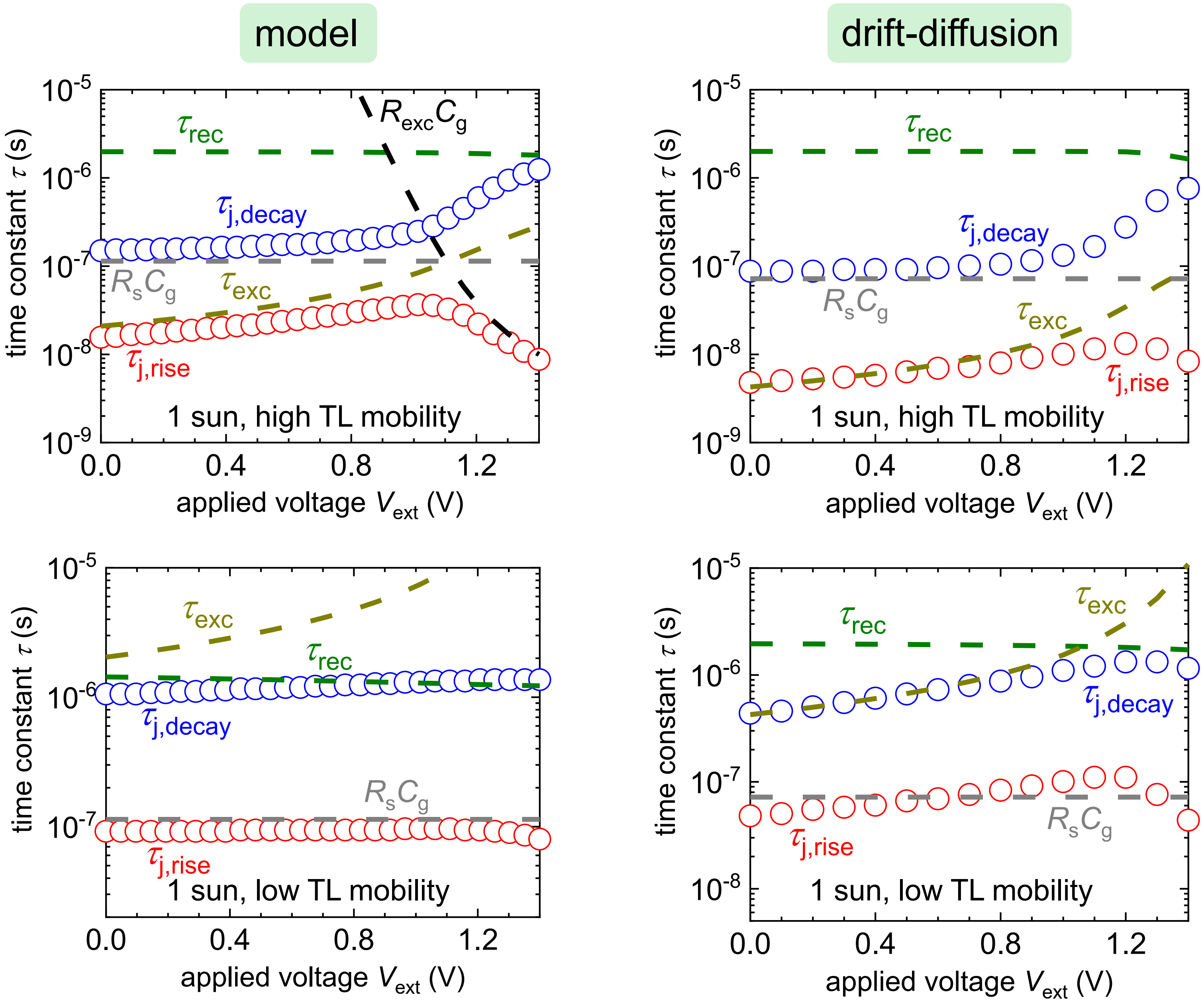
IMPS time constants versus voltage

model



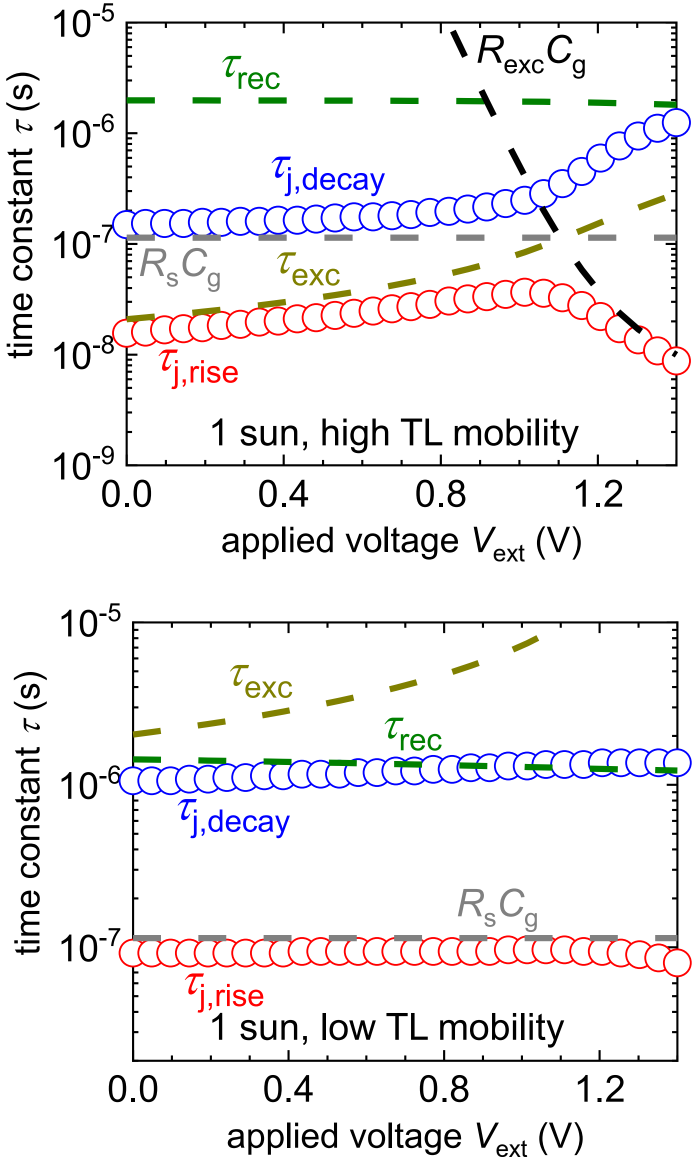


IMPS time constants versus voltage

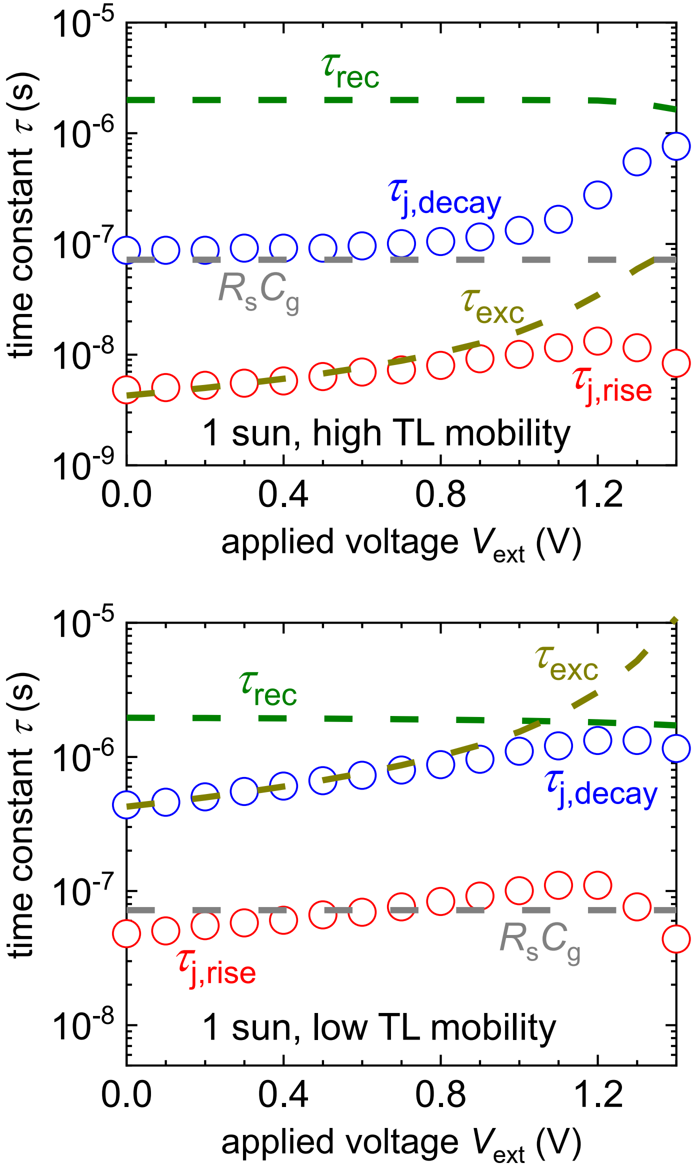


IMPS time constants versus voltage

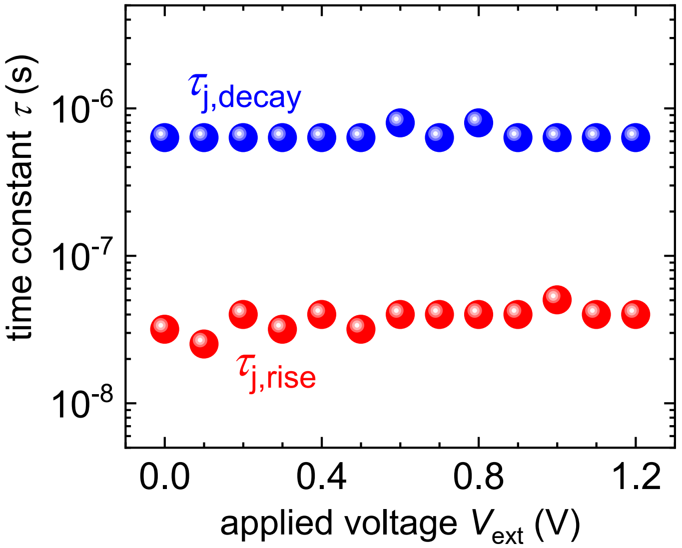
model



drift-diffusion



experiment



transfer functions

IMVS

$$W = \left[\left(\frac{\tau_{\mathrm{exc}}}{\tau_{\mathrm{rec}}} + i\omega\tau_{\mathrm{exc}}\right)\left(\frac{1}{R_{\mathrm{exc}}} + i\omega C_{\mathrm{g}}\right)\right]^{-1}$$

IMPS

$$Q = \left[1 + i\omega R_{\mathrm{s}} C_{\mathrm{g}} + \left(\frac{\tau_{\mathrm{exc}}}{\tau_{\mathrm{rec}}} + i\omega\tau_{\mathrm{exc}}\right) + \left(1 + \frac{R_{\mathrm{s}}}{R_{\mathrm{exc}}} + i\omega R_{\mathrm{s}} C_{\mathrm{g}}\right)\right]^{-1}$$

IS

$$Z = \frac{W}{Q}$$

transfer functions

IMVS open-circuit

$$W = \left[\frac{1}{R_{\mathrm{rec}}} + i\omega C_{\mu} + i\omega C_{\mathrm{g}}\left(1 + \frac{R_{\mathrm{exc}}}{R_{\mathrm{rec}}} + i\omega R_{\mathrm{exc}} C_{\mu}\right)\right]^{-1}$$

IMPS open-circuit

$$Q = \left[1 + \frac{R_{\mathrm{s}} + R_{\mathrm{exc}}}{R_{\mathrm{exc}}} + i\omega (R_{\mathrm{s}} + R_{\mathrm{exc}}) C_{\mu} + \left(\frac{\tau_{\mathrm{exc}}}{\tau_{\mathrm{rec}}} + i\omega \tau_{\mathrm{exc}}\right) + i\omega C_{\mathrm{g}}\left(1 + \frac{R_{\mathrm{exc}}}{R_{\mathrm{rec}}} + i\omega R_{\mathrm{exc}} C_{\mu}\right)\right]^{-1}$$

IS open-circuit

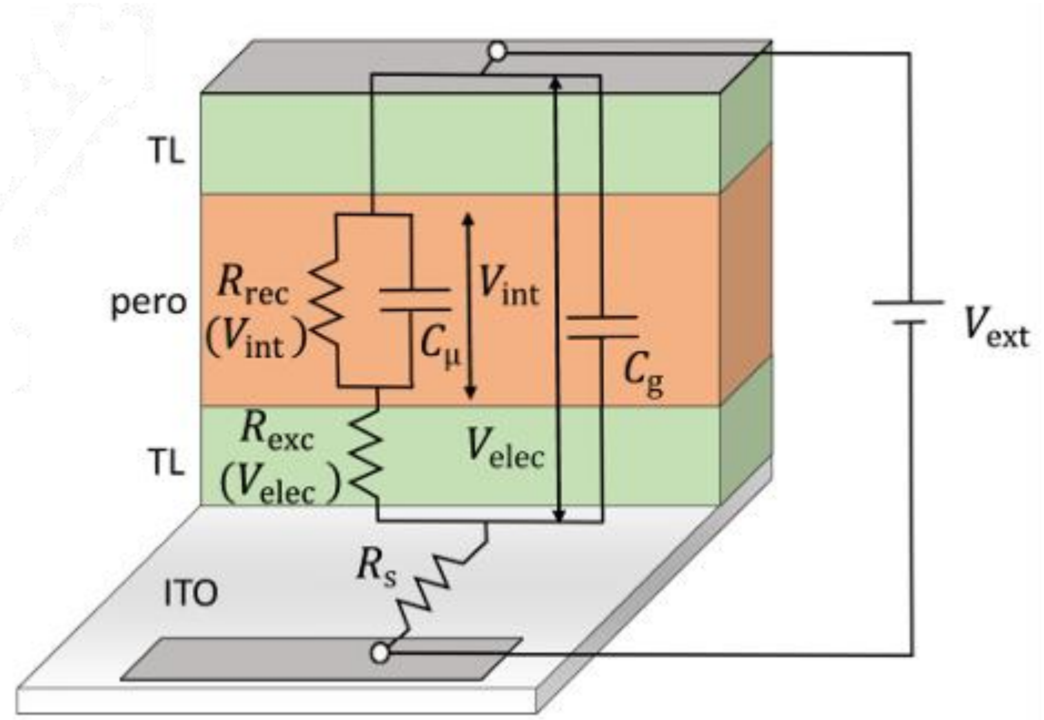
$$Z = R_{\mathrm{s}} + \left[\frac{1}{R_{\mathrm{exc}} + \left(\frac{1}{R_{\mathrm{rec}}} + i\omega C_{\mu}\right)^{-1}} + i\omega C_{\mathrm{g}}\right]^{-1} = \frac{W}{Q}$$

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

equivalent circuit

IS open-circuit

$$Z = R_\mathrm{s} + \left[\frac{1}{R_\mathrm{exc} + \left(\frac{1}{R_\mathrm{rec}} + i\omega C_\mu \right)^{-1}} + i\omega C_\mathrm{g} \right]^{-1}$$



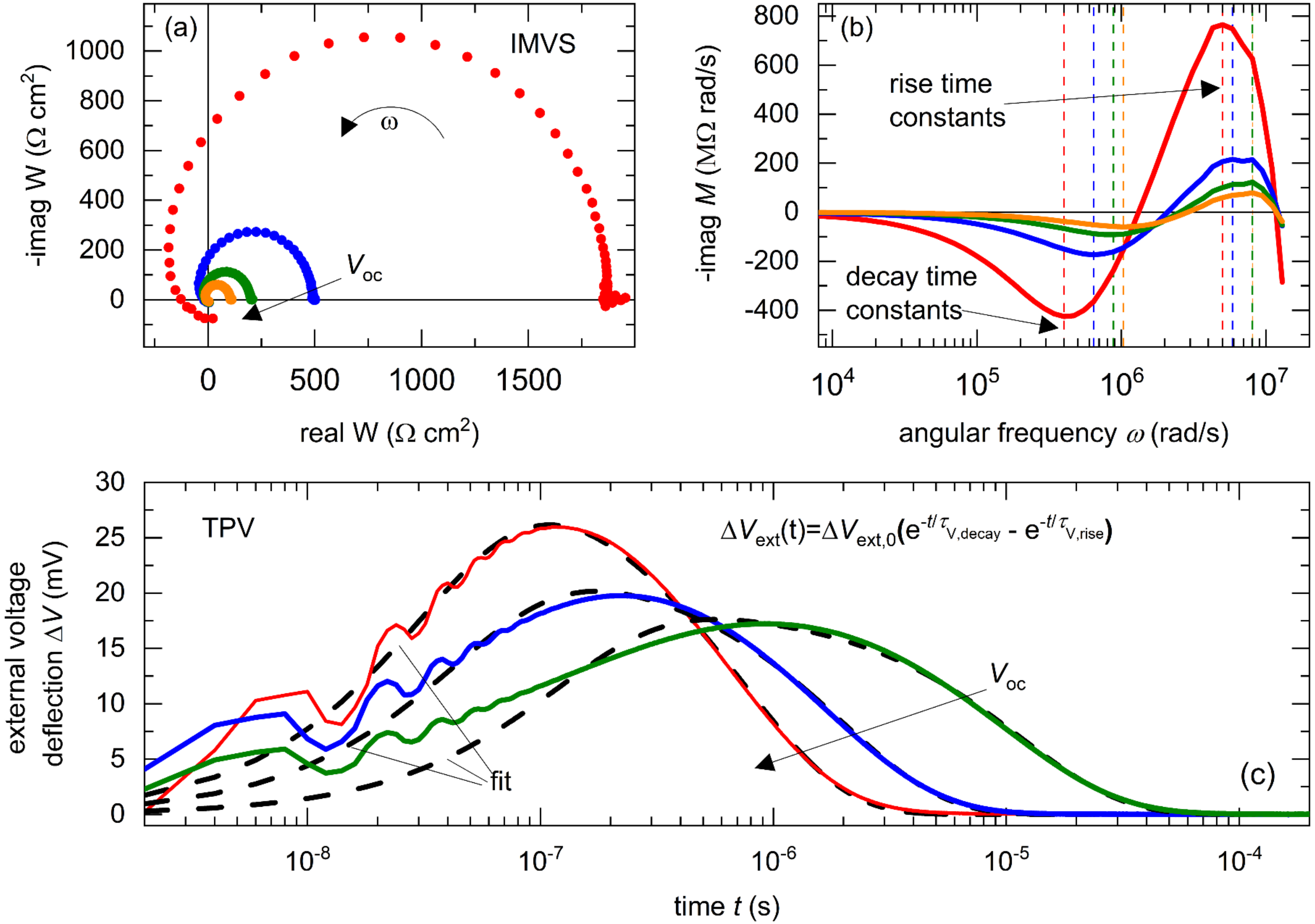
equivalent circuit can be defined only at open-circuit ($V_\mathrm{int} = V_\mathrm{elec}$)

$$j = q n_\mathrm{i} S_\mathrm{exc} \times \left[\exp\left(\frac{qV_\mathrm{int}}{2k_\mathrm{B}T} \right) - \exp\left(\frac{V_\mathrm{elec}}{2k_\mathrm{B}T} \right) \right]$$

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

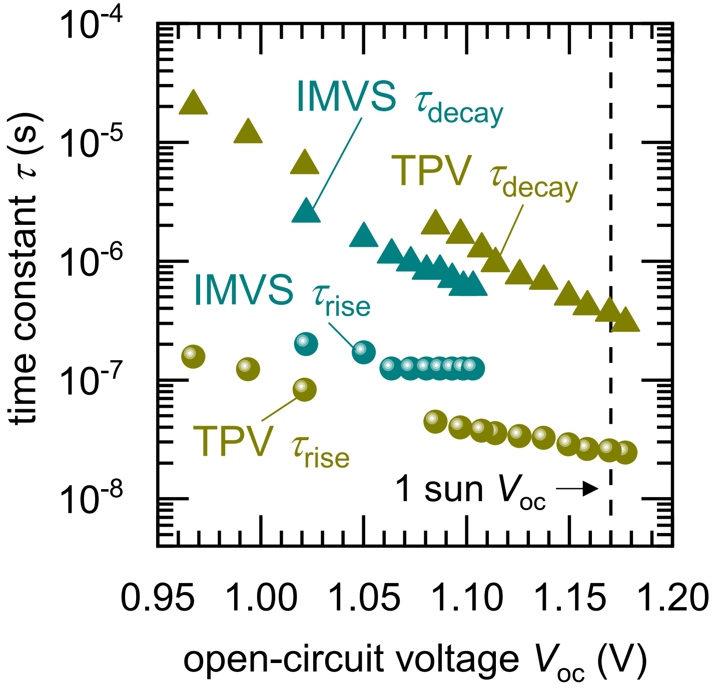
application to experimental data

ITO/SAMs/PTAA/$Cs_{0.05}FA_{0.8}MA_{0.15}PbI_{2.25}Br_{0.75}$ (1.68 eV)/C_{60}/BCP/Ag devices



S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

experimental rise and decay time constants



S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

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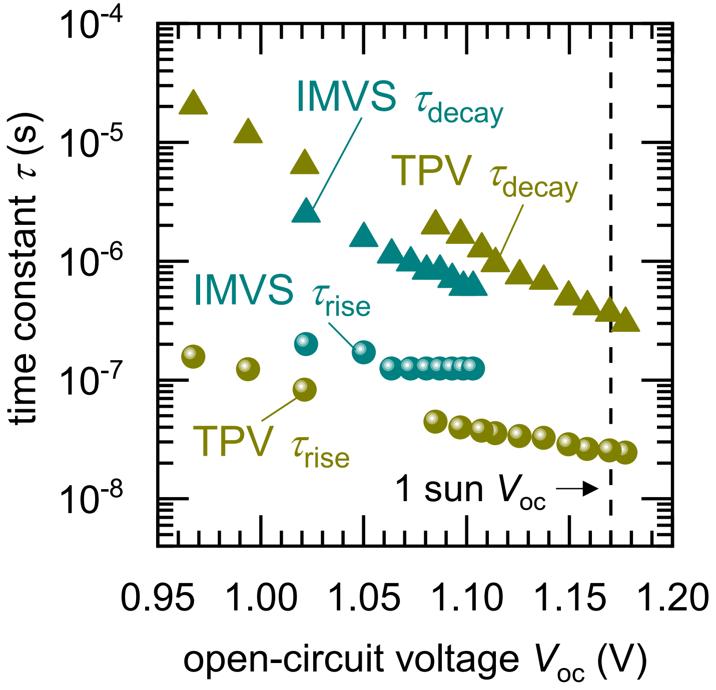
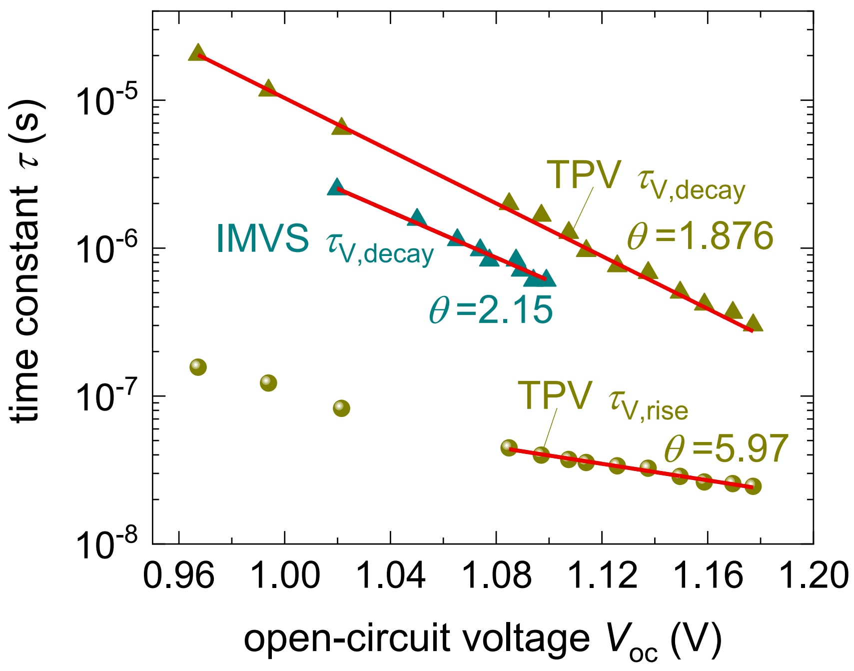


$$\tau = \tau_0 \exp\left(\frac{-qV_{oc}}{\Theta k_B T}\right)$$



S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

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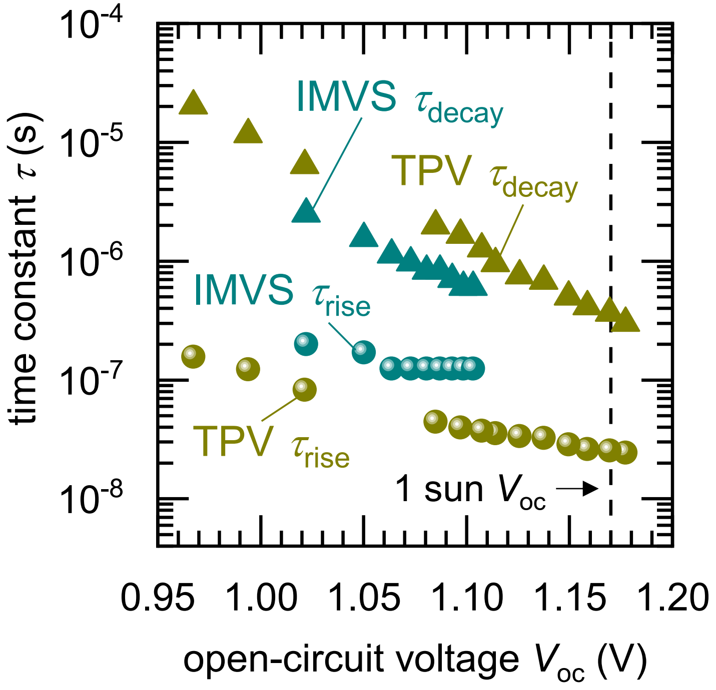
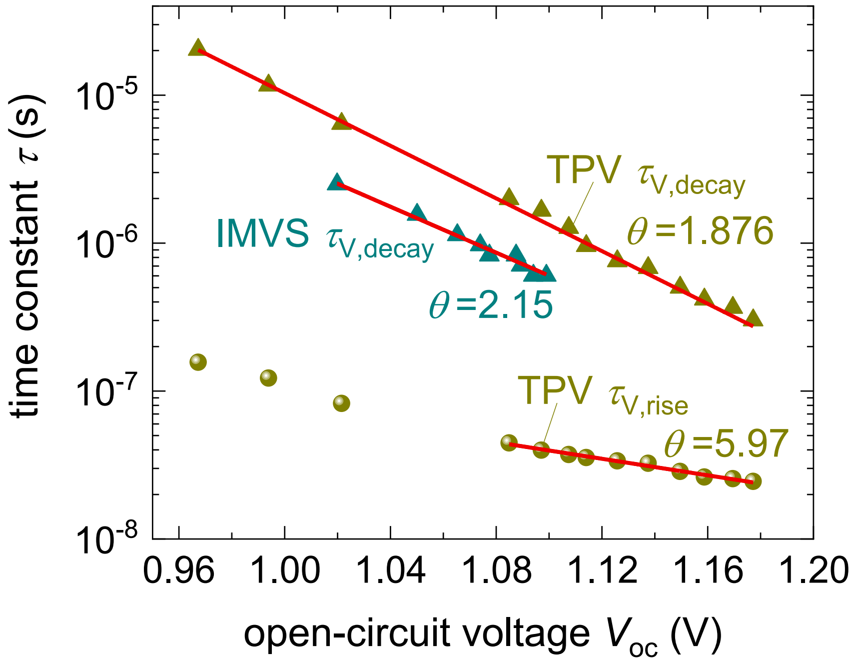


$$\tau = \tau_0 \exp\left(\frac{-qV_{\mathrm{oc}}}{\Theta k_{\mathrm{B}} T}\right) \longrightarrow$$

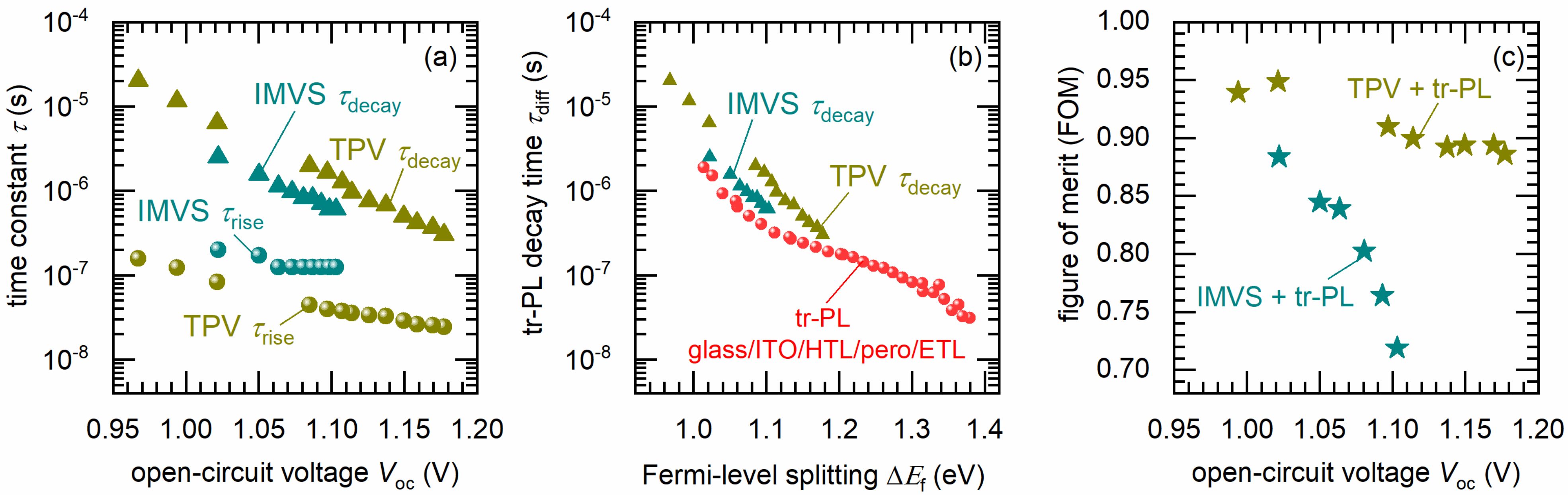


rise times correspond to charge extraction

decay times correspond to recombination limited by charge re-injection from the electrodes

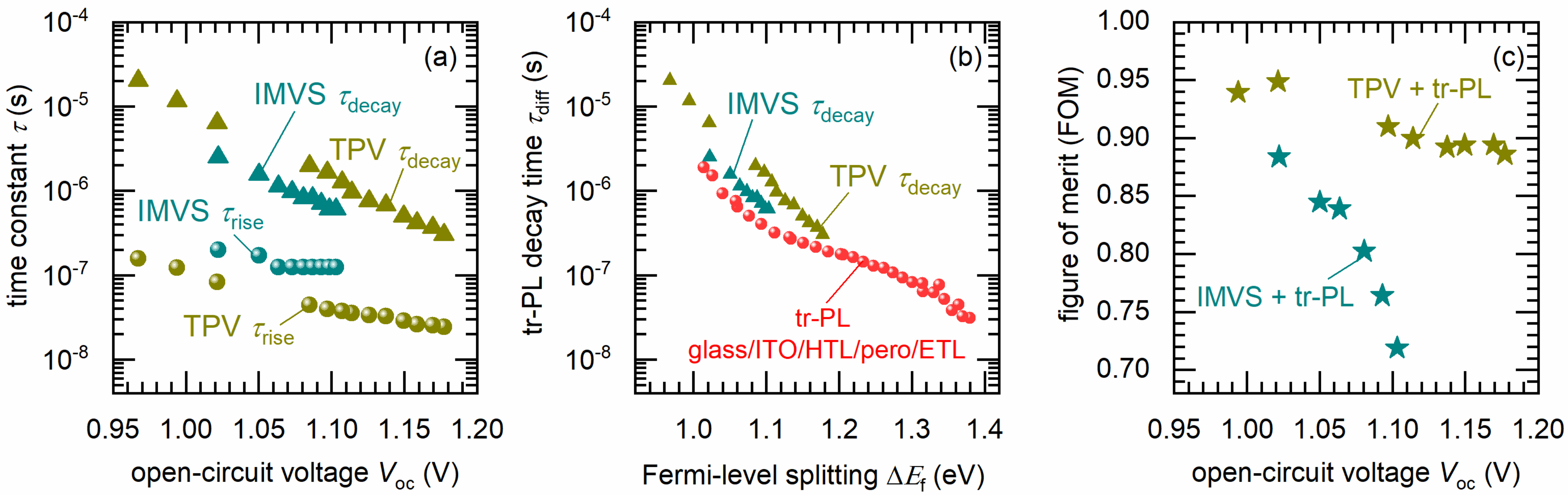
S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

experimental FOM



S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

experimental FOM



FOM values close to 1 imply a significant electric field in the transport layers that allows fast charge extraction

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

conclusions

can we separate transport layer effects from bulk effects in typical characterization techniques?

$\xrightarrow{i\omega \times \text{transfer function}}$

verify using time-domain methods

rise time constant → charge extraction

decay time constant → recombination

→ depends on bias condition

conclusions

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→ depends on bias condition

can we account for the effect of the transport layers on the PSC performance?

→

charge extraction efficiency

$$FOM(V_{\text{ext}}) = \frac{1}{1 + \frac{\tau_{\text{exc}}(V_{\text{ext}})}{\tau_{\text{rec}}(V_{\text{ext}})}}$$

conclusions

can we separate transport layer effects from bulk effects in typical characterization techniques?

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charge extraction efficiency

$$FOM(V_{\text{ext}}) = \frac{1}{1 + \frac{\tau_{\text{exc}}(V_{\text{ext}})}{\tau_{\text{rec}}(V_{\text{ext}})}}$$

future work

determination of FOM and influence of shallow traps versus voltage and light intensity

Acknowledgements: Yueming Wang and Dr. Bingbing Chen for the samples, DFG for funding.

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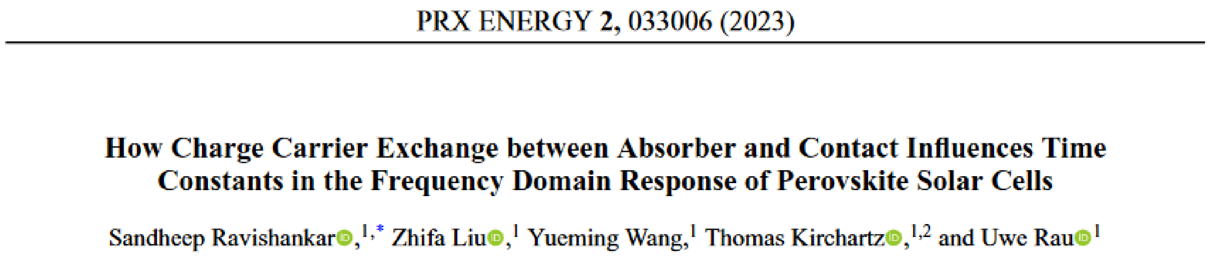
Discerning rise time constants to quantify charge carrier extraction in perovskite solar cells†

Sandheep Ravishankar,[*a] Lennard Kruppa,[a] Sandra Jenatsch,[b] Genghua Yan[a] and Yueming Wang[a]



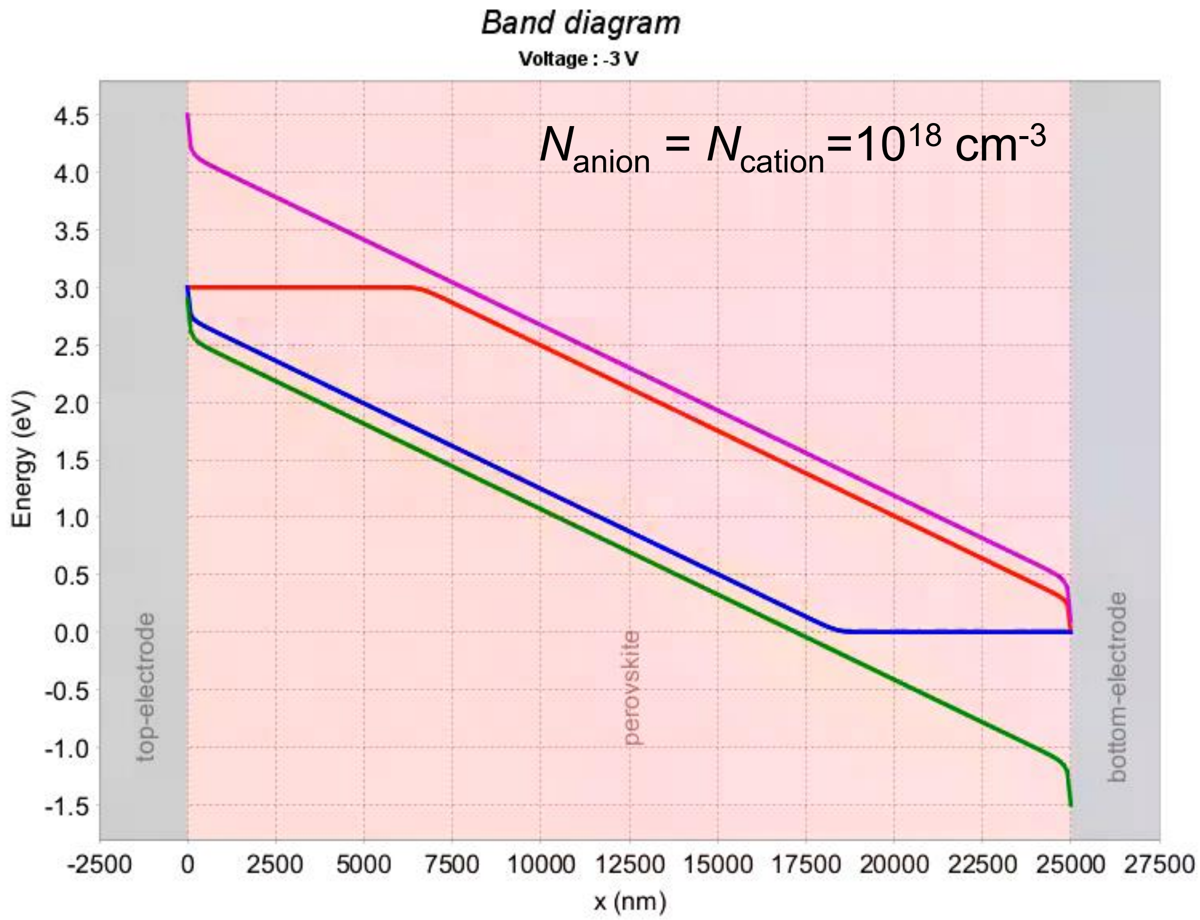
PRX ENERGY **2**, 033006 (2023)

How Charge Carrier Exchange between Absorber and Contact Influences Time Constants in the Frequency Domain Response of Perovskite Solar Cells

Sandheep Ravishankar,[1,*] Zhifa Liu,[1] Yueming Wang,[1] Thomas Kirchartz,[1,2] and Uwe Rau[1]

effect of mobile ions

single crystal device – drift-diffusion simulation



Acknowledgement: Lukas Frommel, Forschungszentrum Jülich.

effect of mobile ions

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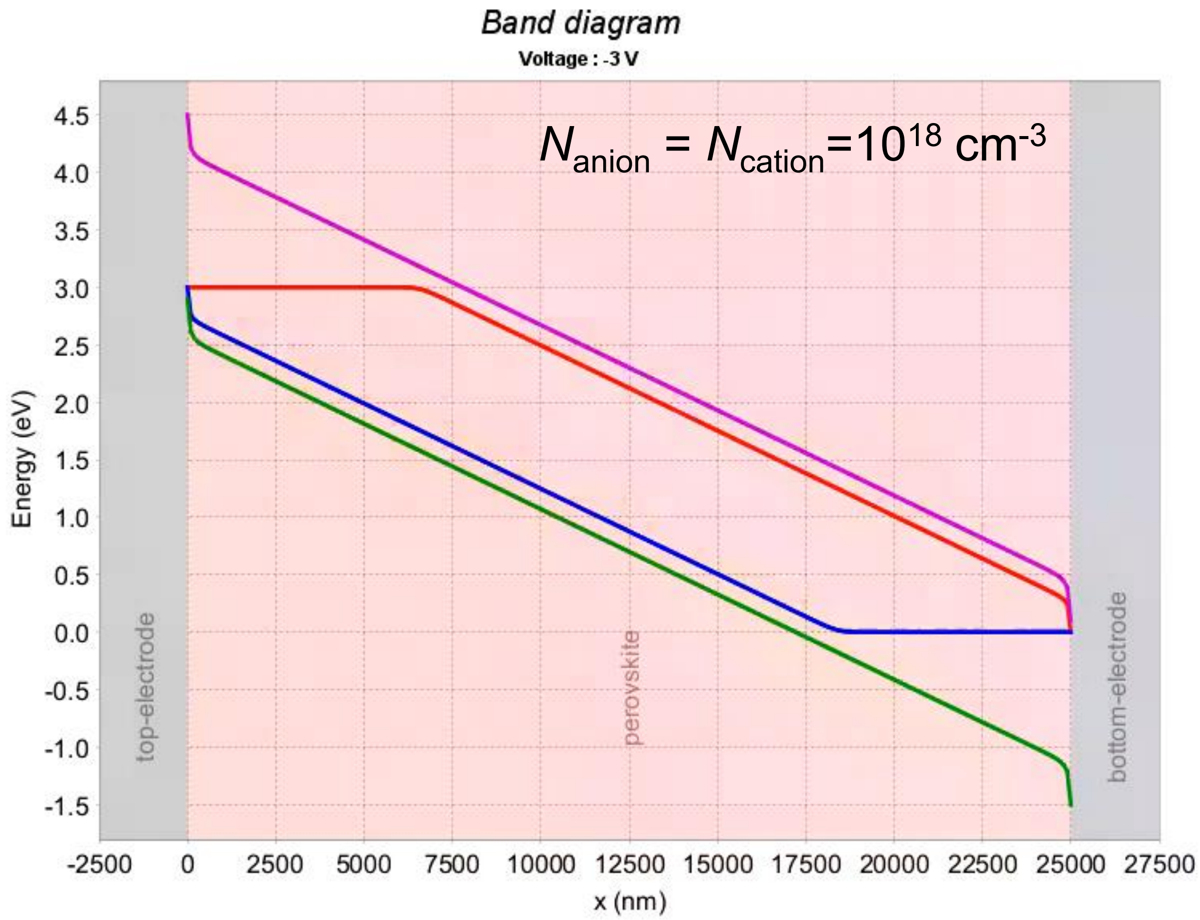
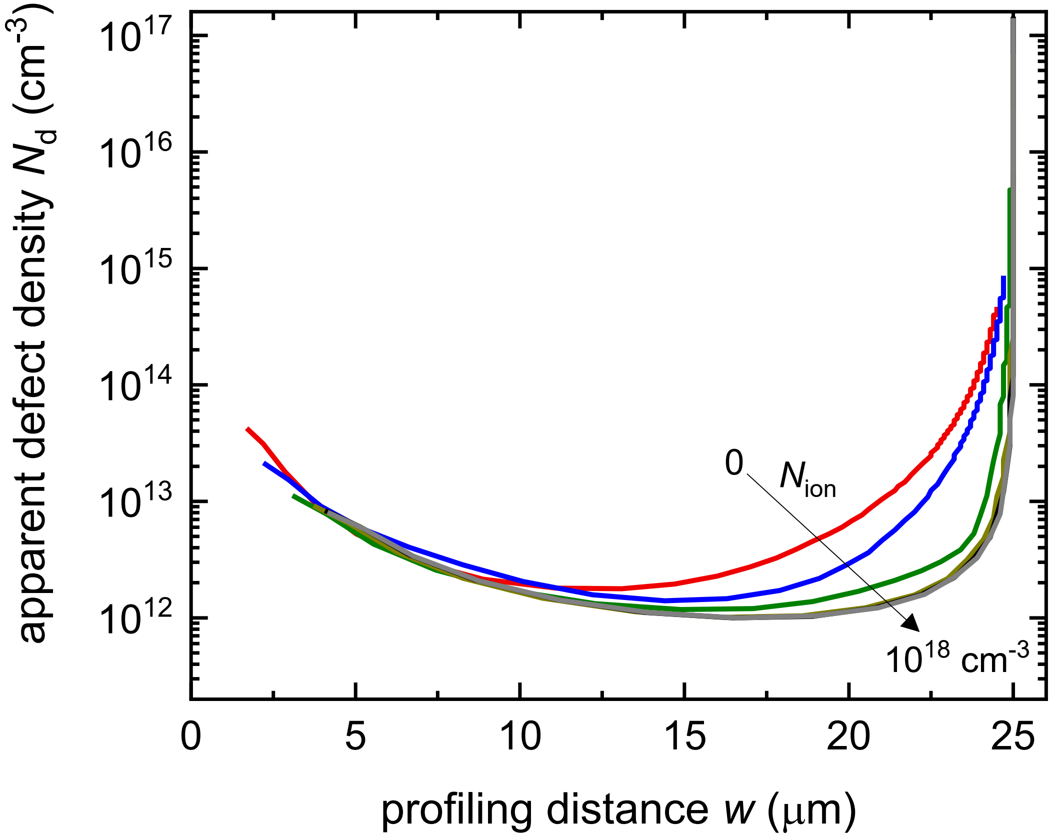
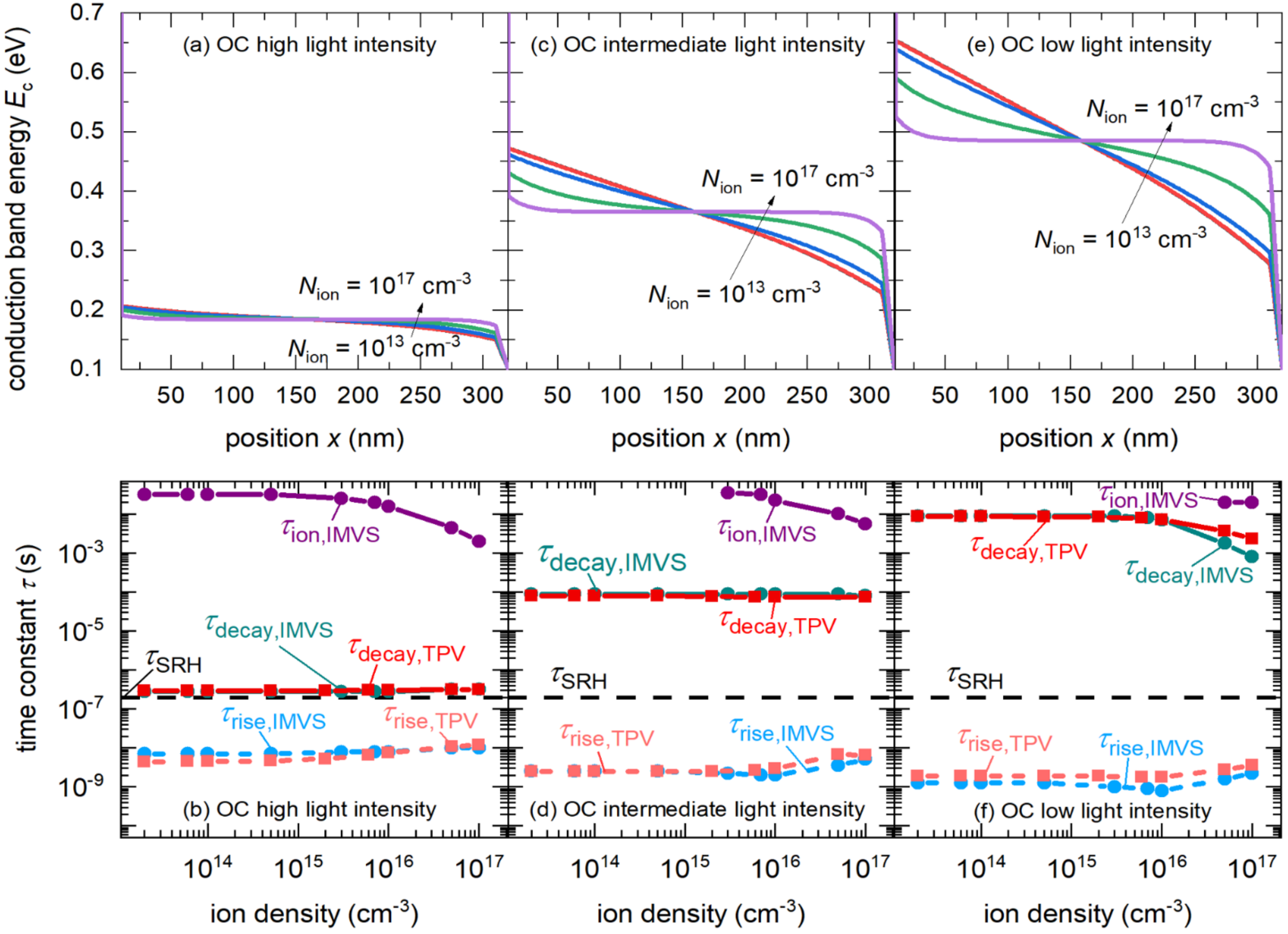




Acknowledgement: Lukas Frommel, Forschungszentrum Jülich.

influence of mobile ions

drift-diffusion simulations



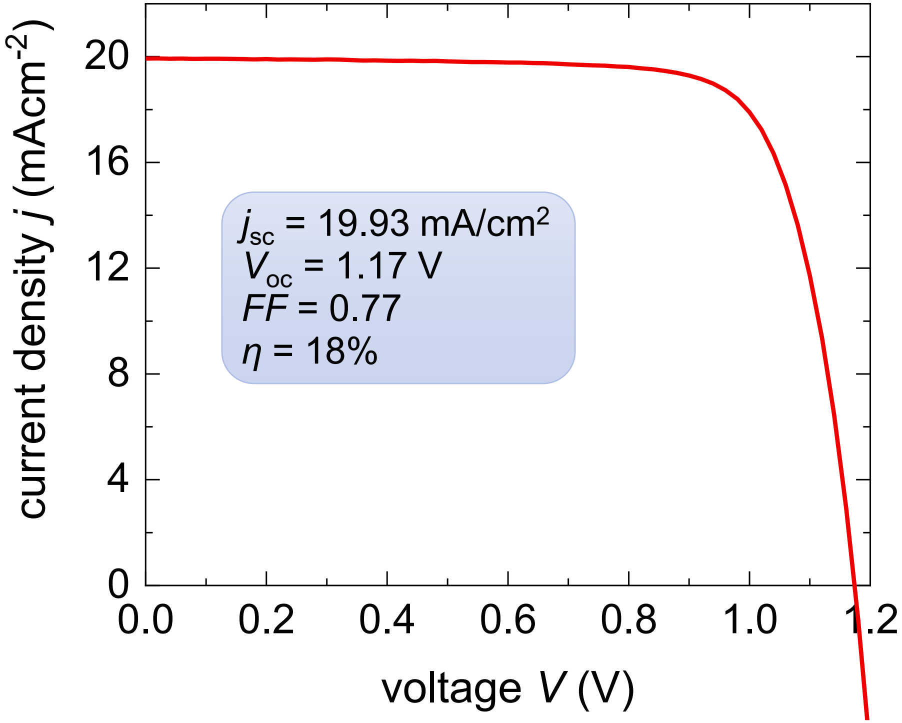
developed analysis using the modified transfer function is valid for devices with mobile ionic densities

additional time constant at low frequencies due to the slow movement of the ions

S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

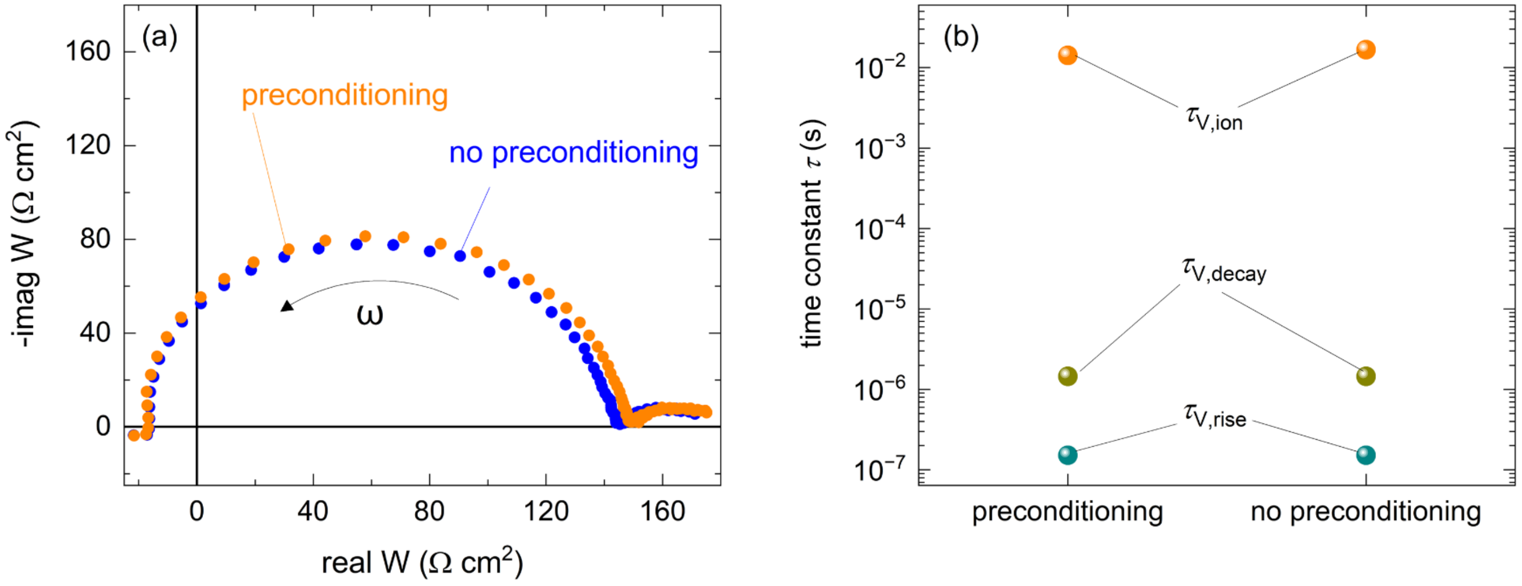
application to experimental data

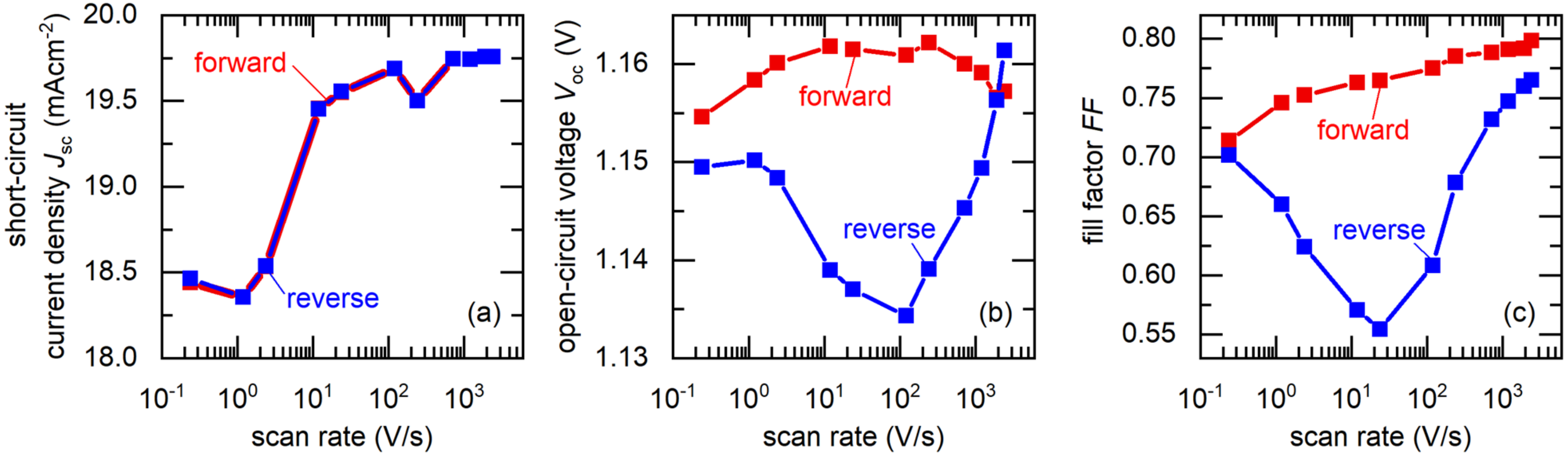
ITO/SAMs/PTAA/$Cs_{0.05}FA_{0.8}MA_{0.15}PbI_{2.25}Br_{0.75}$ (1.68 eV)/C_{60}/BCP/Ag devices



S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

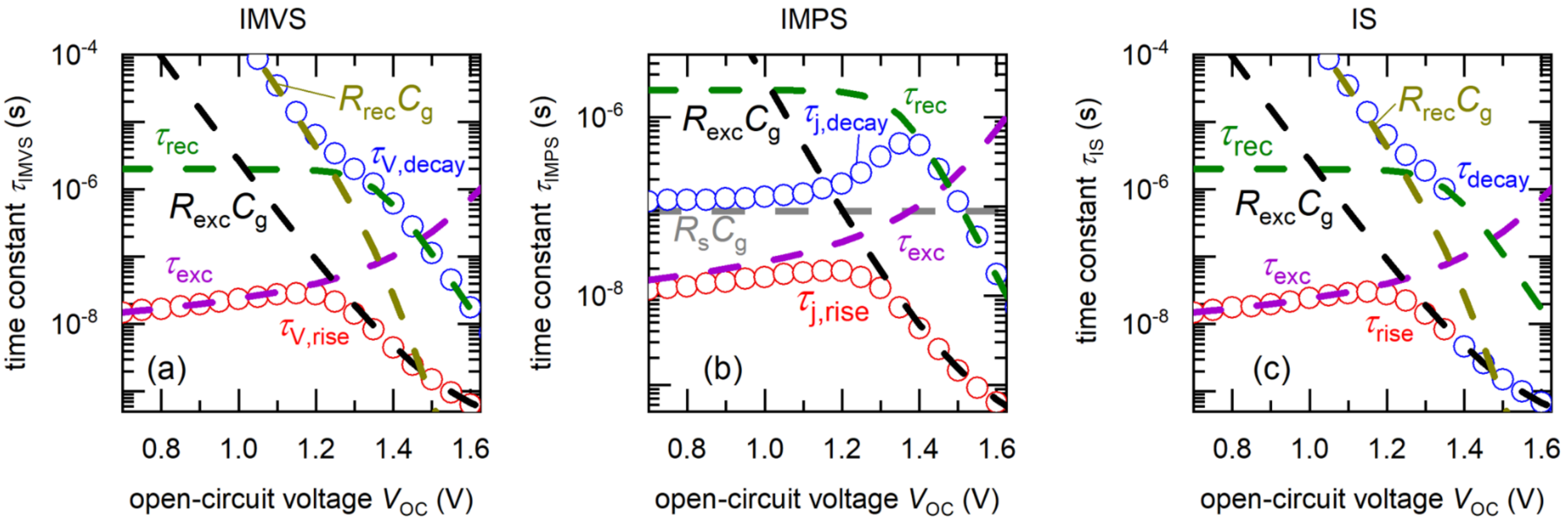
ionic influence on measured spectra





S. Ravishankar et al., 2024. *Energy & Environmental Science*, *17*(3), pp.1229-1243.

predicted time constants



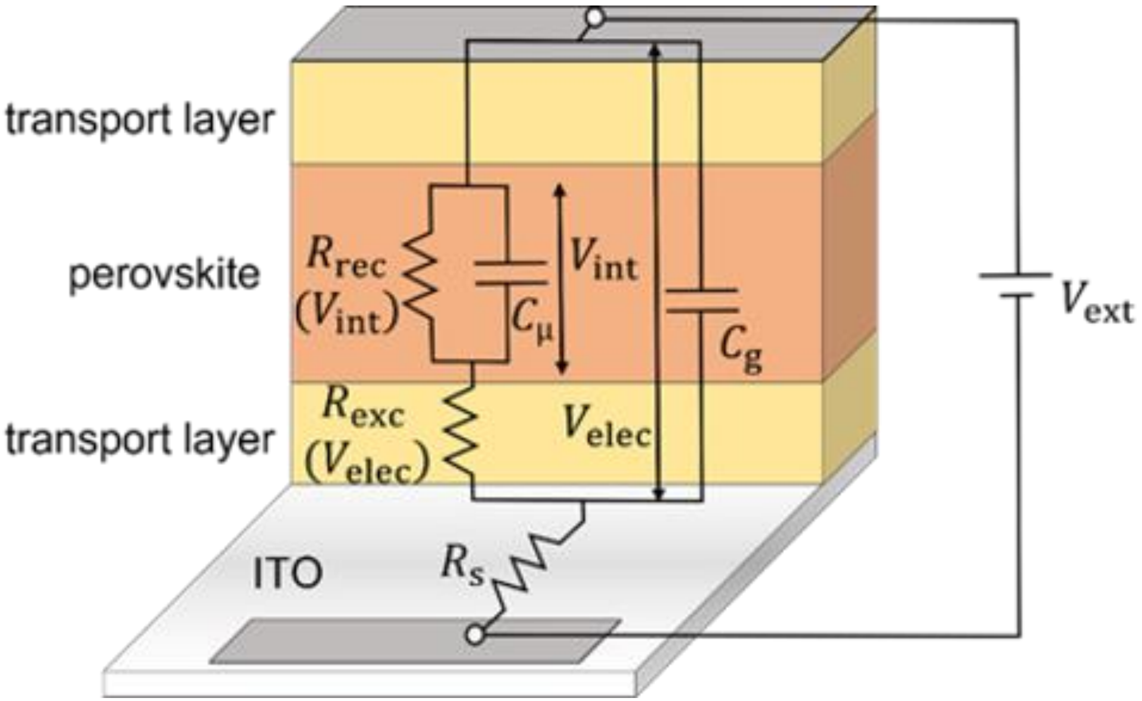
different time constants expressed due to the voltage dependence of resistances and capacitances

rise time constants generally correspond to charge extraction

decay time constants generally correspond to recombination or R_sC_g attenuation

S. Ravishankar et al., PRX Energy **1**, 013003 (2022).

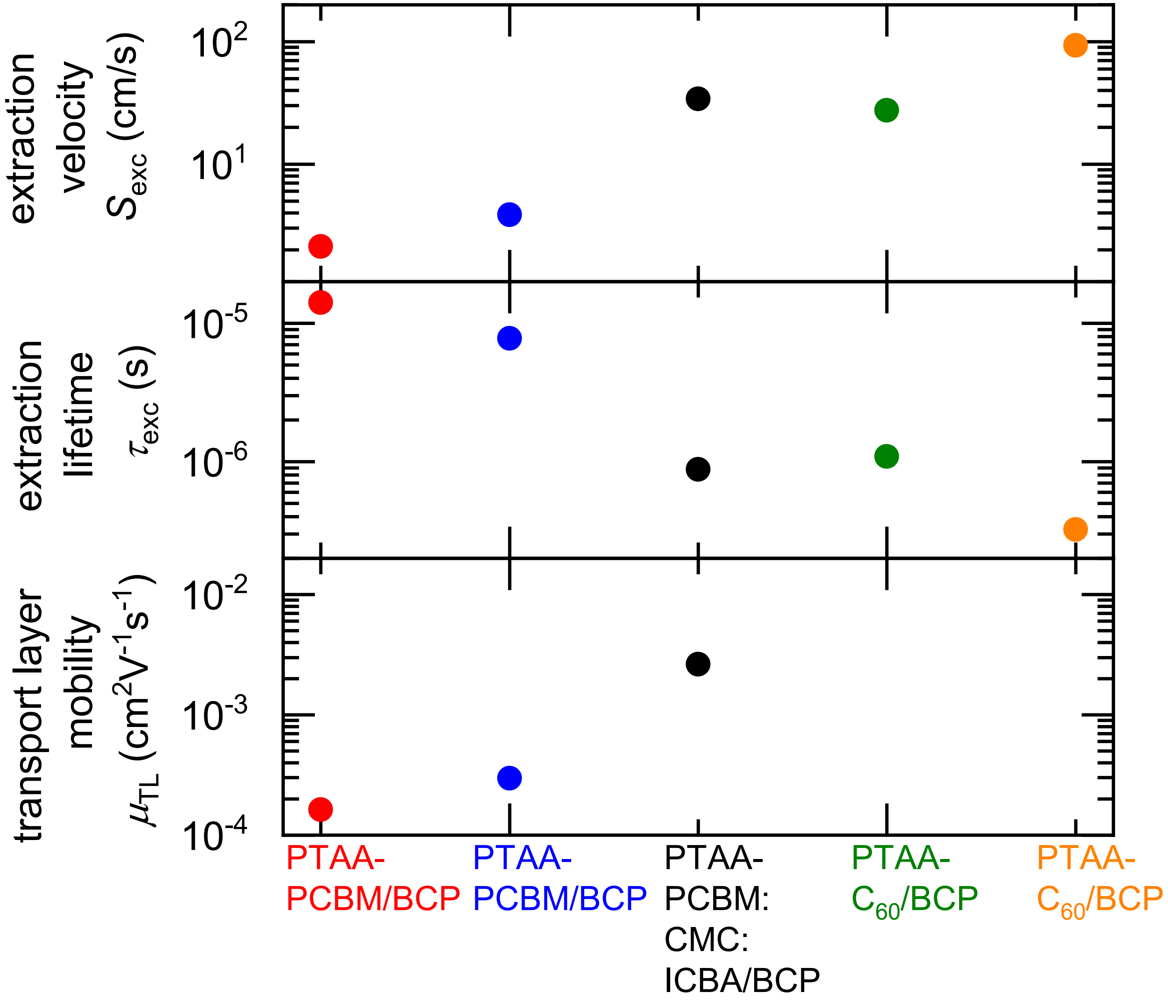
derived equivalent circuit



accounts for effects related to the difference between the internal voltage V_{int} (quasi-Fermi level splitting) and the external voltage under illumination

S. Ravishankar et al., 2023. *PRX Energy* 2, 033006.

IS data analysis



transport layer mobilities between 10^{-4} – 3×10^{-3} $cm^2V^{-1}s^{-1}$ calculated for PTAA-based PSCs

S. Ravishankar et al., PRX Energy **1**, 013003 (2022).

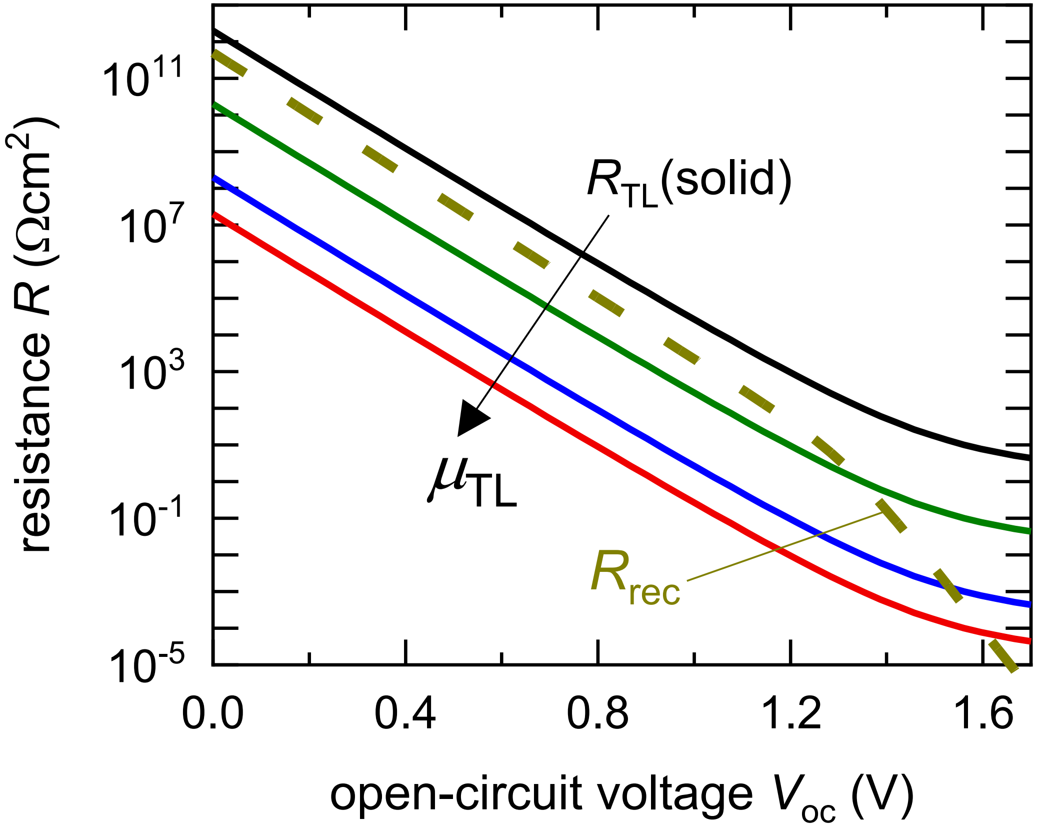
transport layer resistance

recombination resistance

$$R_{\mathrm{rec}} = \left(\frac{1}{R_{\mathrm{rec,SRH}}} + \frac{1}{R_{\mathrm{rec,rad}}}\right)^{-1}$$

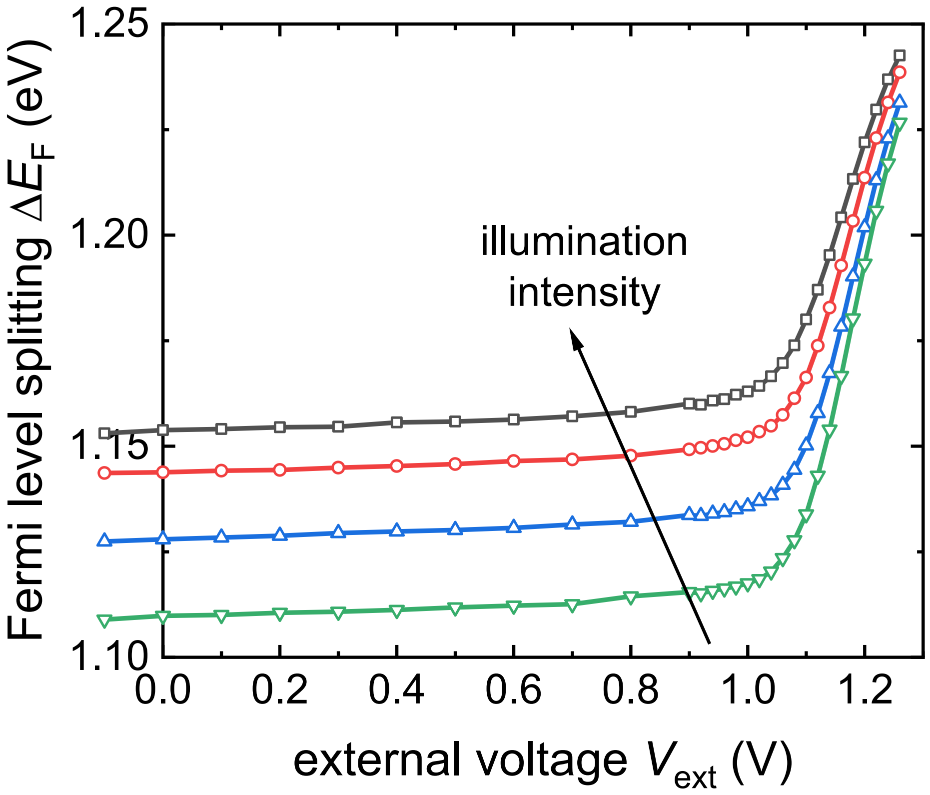
transport layer resistance

$$R_{\mathrm{exc}} = \frac{2k_{\mathrm{B}}T}{q^2 n_{\mathrm{i}} S_{\mathrm{exc}}} \exp\left(\frac{-qV_{\mathrm{elec}}}{2k_{\mathrm{B}}T}\right)$$



S. Ravishankar et al., PRX Energy **1**, 013003 (2022).

the internal and external voltage



$$j_{rec}(V_{ext}) = j_{rec,0}\exp\left(\frac{\Delta E_F\ (V_{ext})}{n_{id}k_B T}\right)$$

D. Grabowski et al., 2022. *Solar RRL*, *6*(11), p.2200507.

j-V curve

$$j = j_{\mathrm{sc}} - j_{0,\mathrm{sat}}\left(\exp\left(\frac{qV_{\mathrm{ext}}}{n_{\mathrm{id}}k_{\mathrm{B}}T}\right) - 1\right)$$

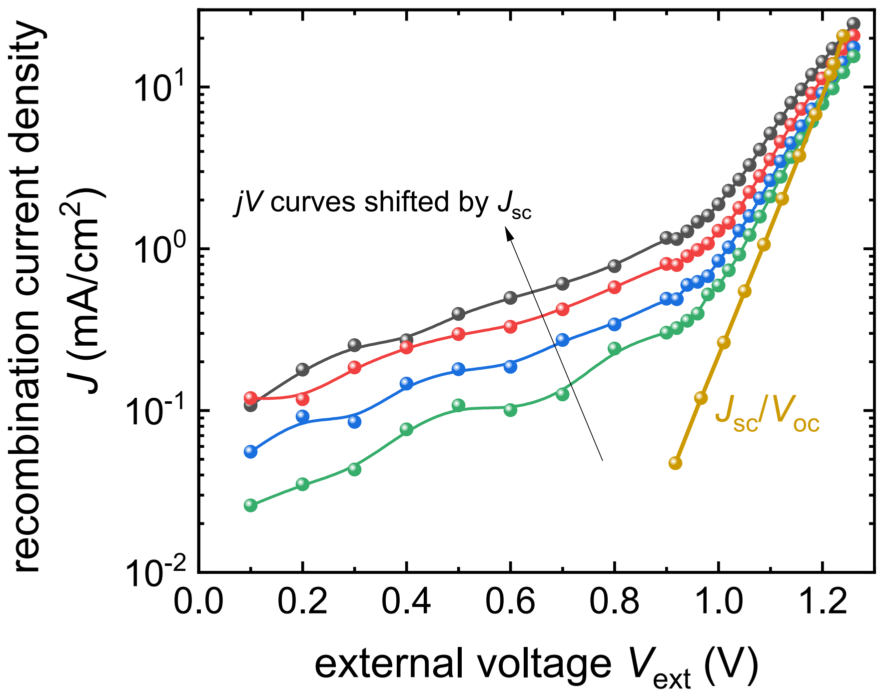
assumptions

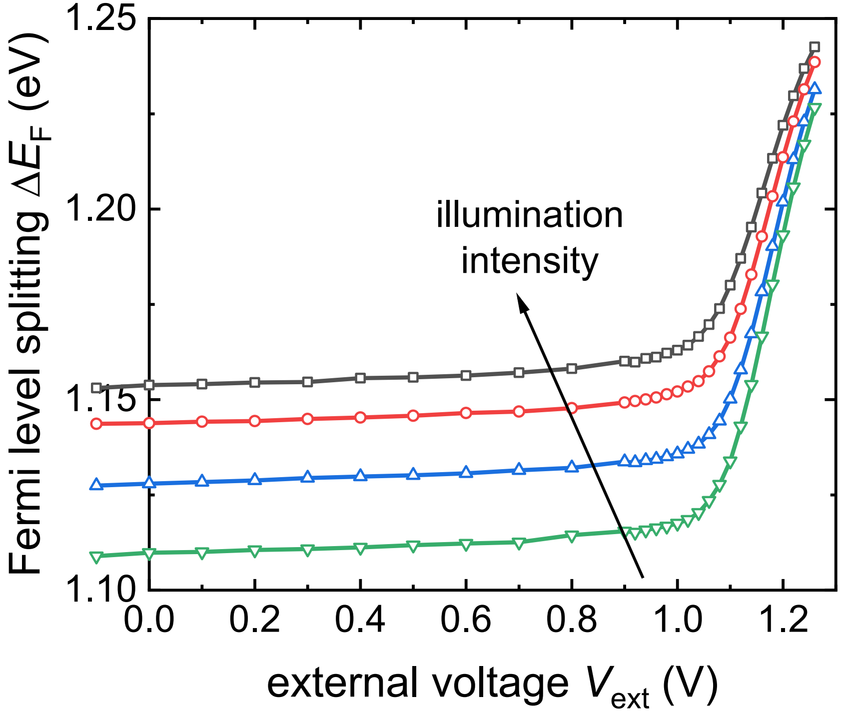
quasi-Fermi level splitting is equal to the external voltage, with and without illumination

current due to photogeneration of charge carriers can be superimposed on the dark jV curve

D. Grabowski et al., 2022. *Solar RRL*, *6*(11), p.2200507.

j-V curve

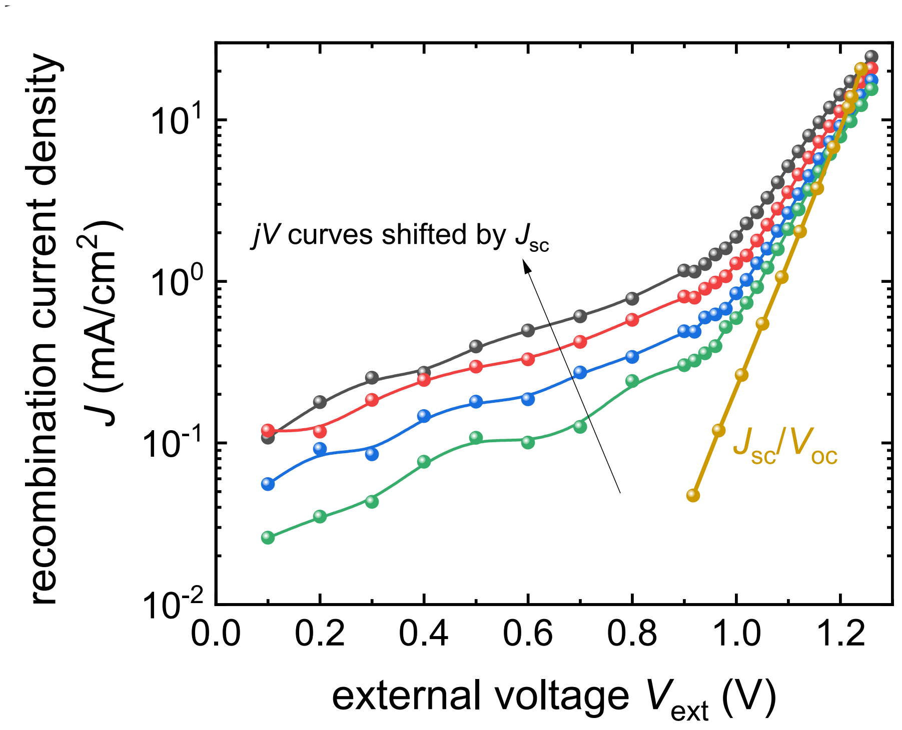


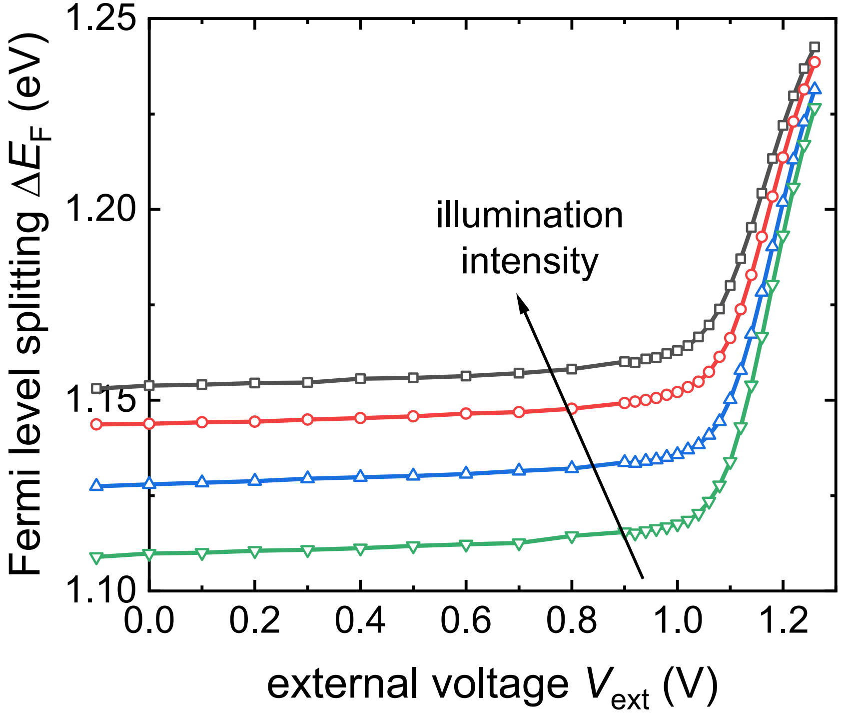


$$j = j_{\mathrm{sc}} - j_{0,\mathrm{sat}}\left(\exp\left(\frac{qV_{\mathrm{ext}}}{n_{\mathrm{id}}k_{\mathrm{B}}T}\right) - 1\right)$$

D. Grabowski et al., 2022. *Solar RRL*, *6*(11), p.2200507.

j-V curve with influence of transport layers





$$j = qS_{\mathrm{exc}}n_0\left[\exp\left(\frac{qV_{\mathrm{int}}}{n_{\mathrm{id}}k_{\mathrm{B}}T}\right) - \exp\left(\frac{qV_{\mathrm{ext}}}{n_{\mathrm{id}}k_{\mathrm{B}}T}\right)\right]$$

accounts for recombination losses
at all points of the jV curve

O. Breitenstein, IEEE Journal of Photovoltaics **4**, 899 (2014), U. Rau et al., Physical Review Applied **14**, 014046 (2020).
S. Ravishankar et al., PRX Energy **1**, 013003 (2022).