Understanding Ion-Related Performance Losses in Perovskite-Based Solar Cells by Capacitance Measurements and Simulation

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[2] Fraunhofer ISE, Germany
[3] IMEC, Belgium

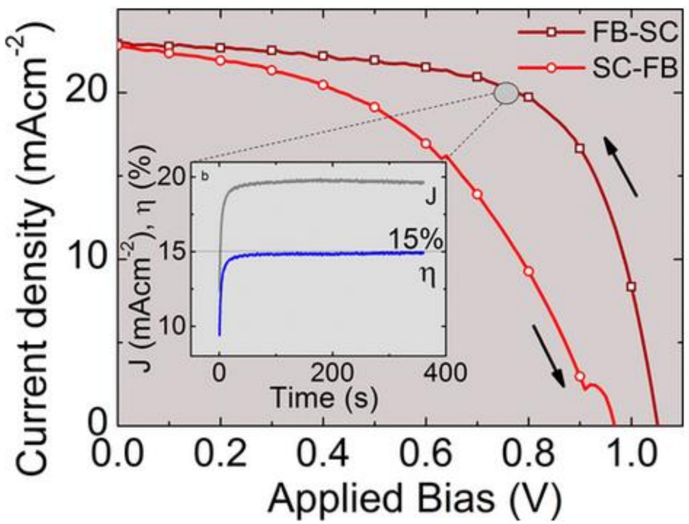
EU PVSEC, Vienna, Austria, 25th September 2024

Motivation

Understand Ion-related losses in Perovskite-Based Solar Cells (PSCs)

- **Hysteresis effects** impact the performance of PSCs [1-3]
- Origin: **Ion migration** within the perovskite absorber
- Goal: Understand and mitigate ion-related performance losses
- Approach: Small AC signal analysis [3,4]
  - Investigate frequency-dependent capacitances of PSCs
- **Learn about** device properties, e.g., ion diffusivities, built-in potential, …

[1] Snaith *et al.*



Experiments

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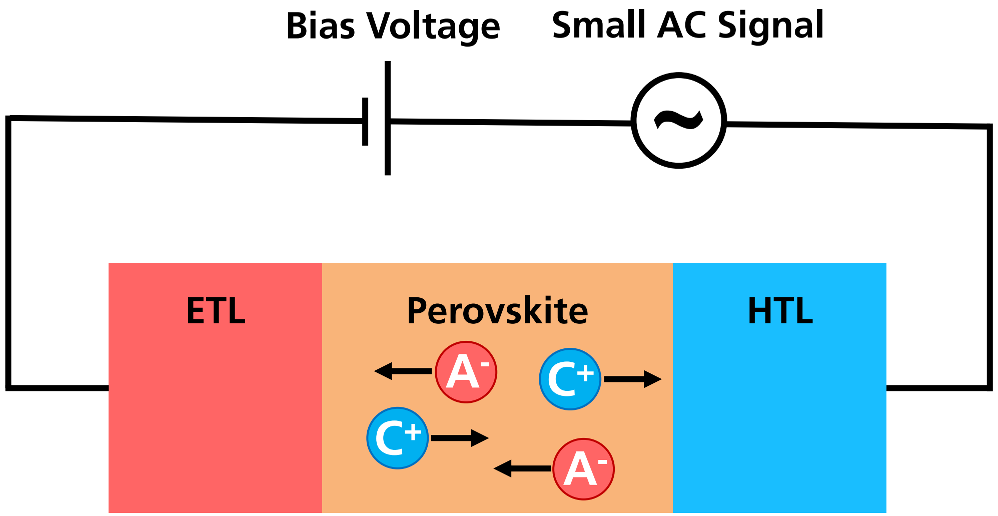

Simulation

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[1] Snaith *et al.*, „Anomalous Hysteresis in Perovskite Solar Cells", J. Phys. Chem. Lett. 2014
[2] Le Corre *et al.*, „Quantification of Efficiency Losses Due to Mobile Ions …," Sol. RRL, vol. 6(4), 2022
[3] Ravishankar *et el.*, "Multilayer Capacitances: How Selective Contacts Affect …," PRX Energy, vol. 1(1), 2022
[4] Recart, Cuevas, "Application of junction capacitance measurements…," IEEE Trans. Electron Dev., vol. 53(3), 2006

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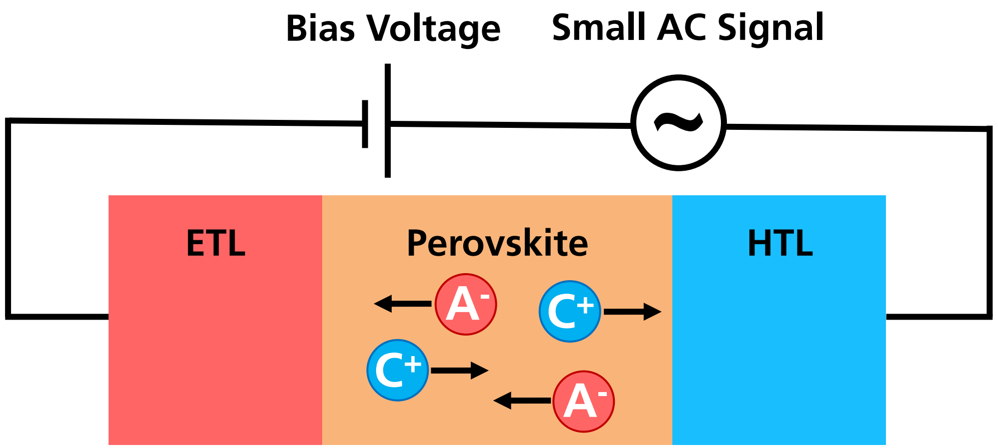
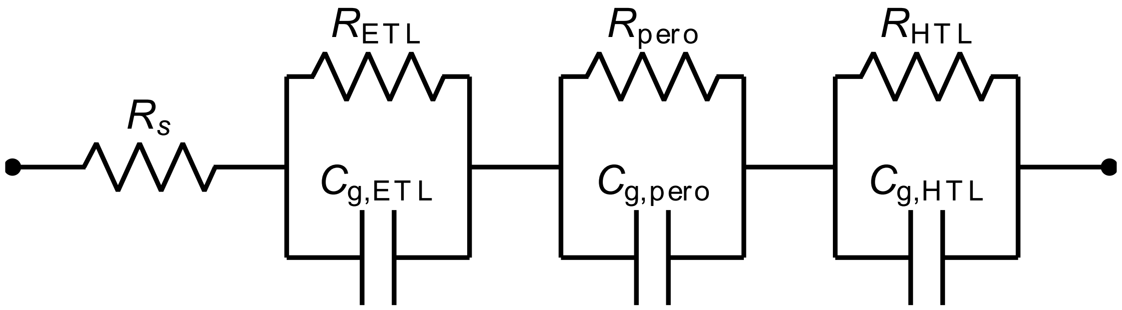
Modelling Approaches

Small AC signal analysis



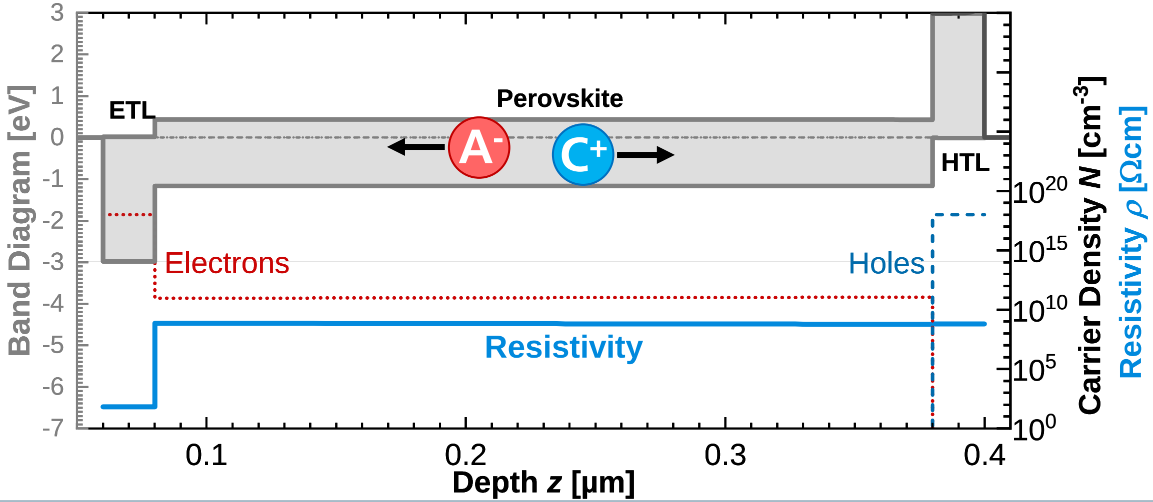
- **Equivalent-Circuit Modelling Approach:**
  - Each layer: RC circuit [1]
  - Geometrical capacitance (plate capacitor):

$$C_{g,L}/A = \epsilon_0\,\epsilon_r/d_L$$



Equivalent Circuit

- **TCAD Modelling (this work):**
  - Detailed device modelling with Sentaurus TCAD [2]
    - Poisson equation and electron/hole drift diffusion (DD)
  - TCAD model was extended to AC signal analysis [3]
    - Compared to Eq.-Circuit Model
  - **Advantages**:
    - DD-Modelling of (several types of) ions incl. preconditioning
    - Study interfaces, full (tandem) stacks, tunneling transport, …
    - Same model for simulation of *JV* curves, …



TCAD Model

[1] Ravishankar *et al.*, „Multilayer Capacitances: …“, PRX Energy, vol. 1, no. 1, 2022
[2] Messmer *et al.*, „Toward more reliable measurement procedures…“, Prog Photovolt Res Appl. 2024
[3] Messmer *et al.*, „Understanding Ion-Related Performance Losses…“, submitted to Solar RRL

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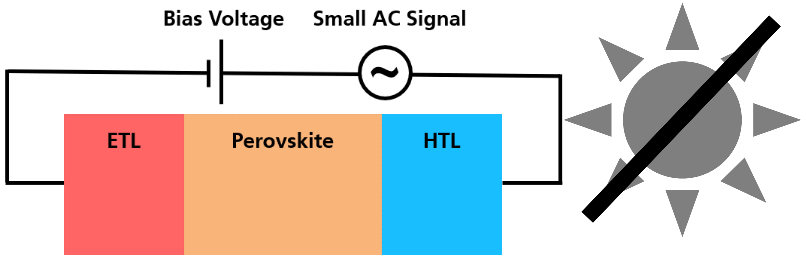
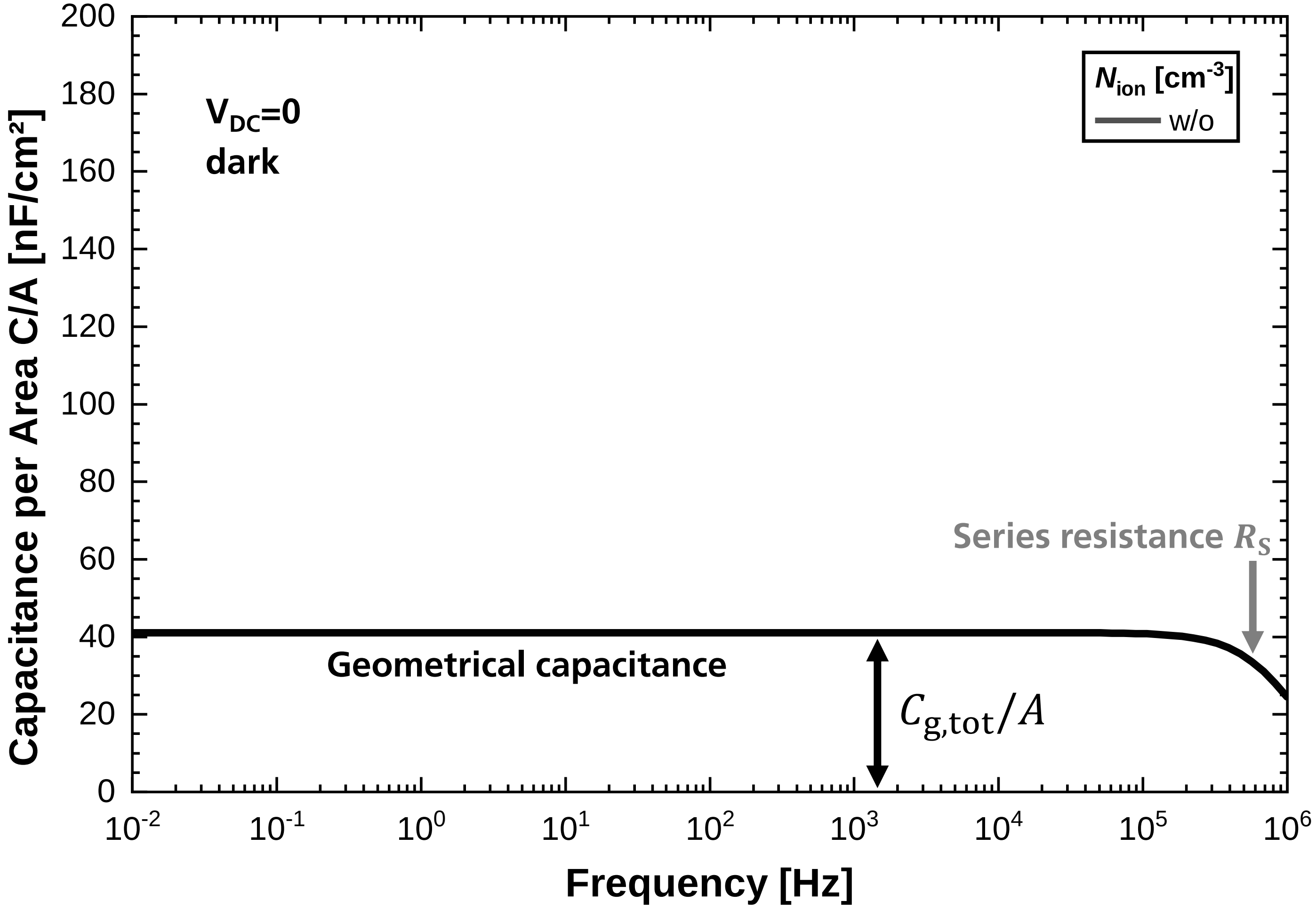
Ion-induced Capacitances in Perovskite Solar Cells

TCAD Simulation: Dark State



- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection
  - High-frequency capacitance reduced by series resistance



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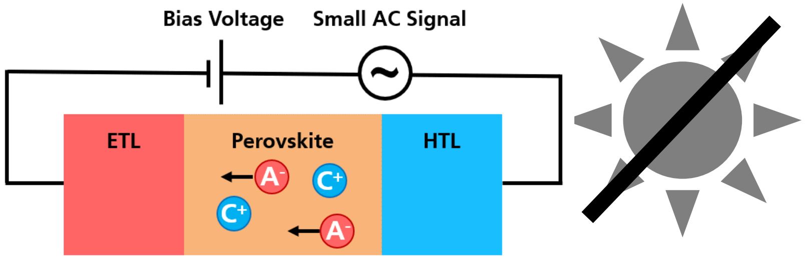

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- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection:
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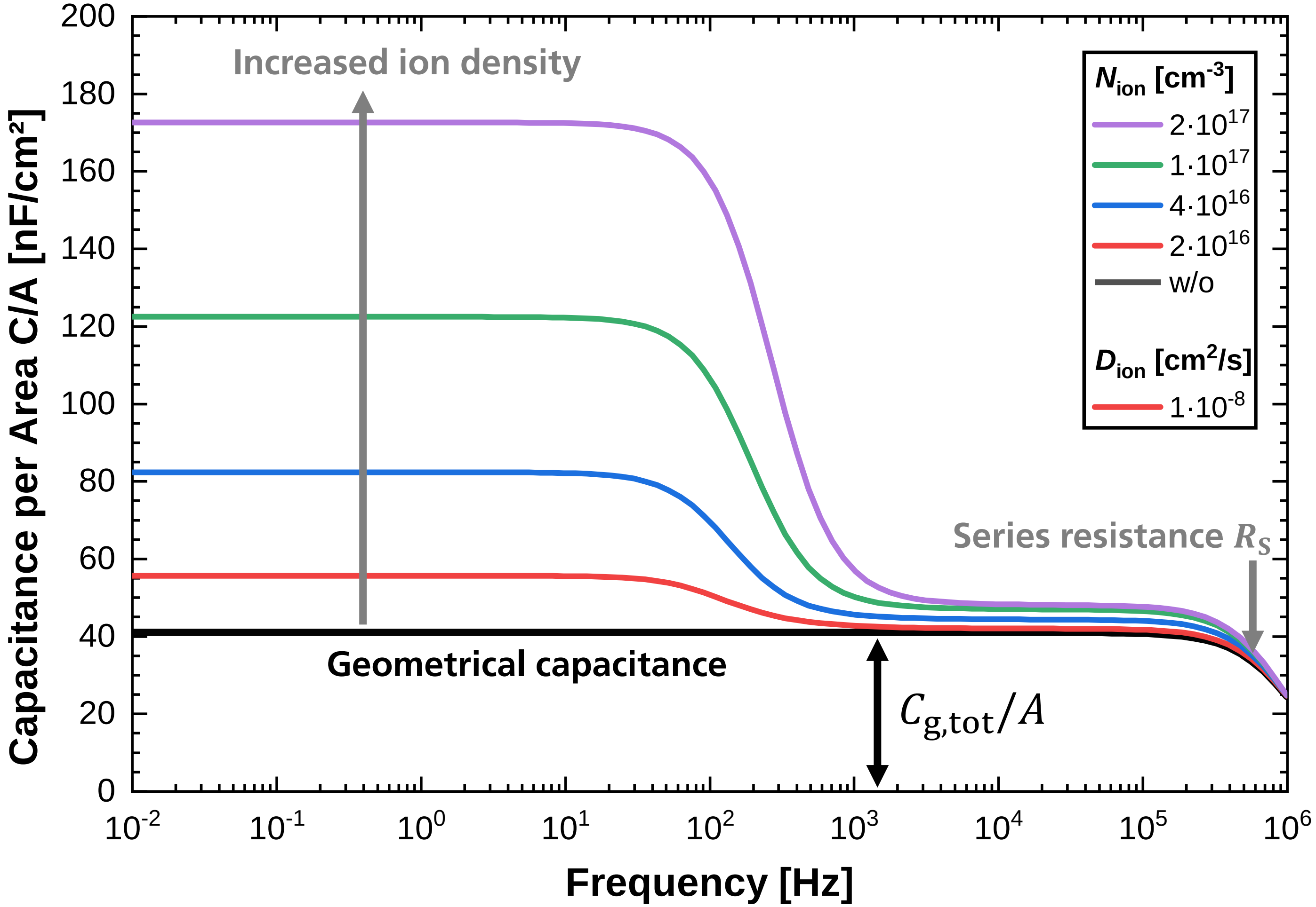
- Mobile anions with varied concentration (immobile cations)
  - Increased low-frequency response of capacitance



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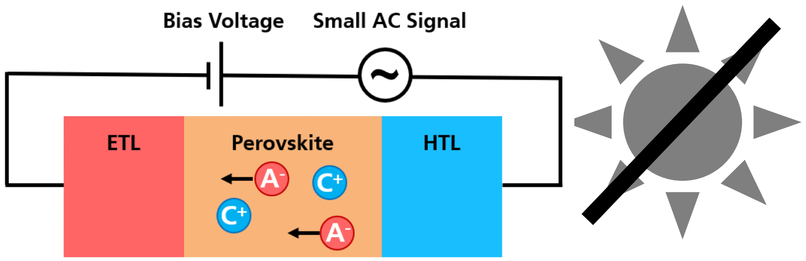
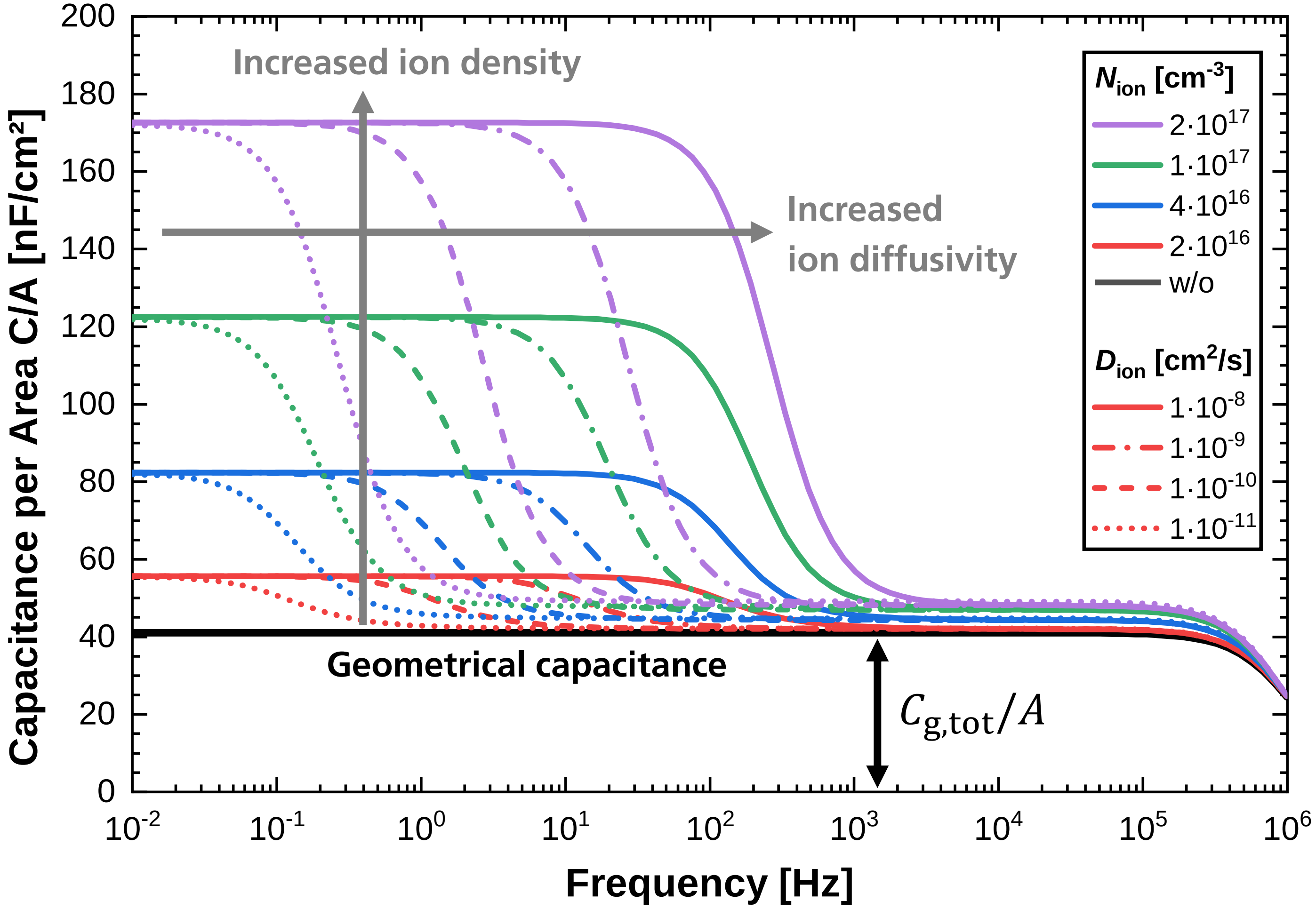
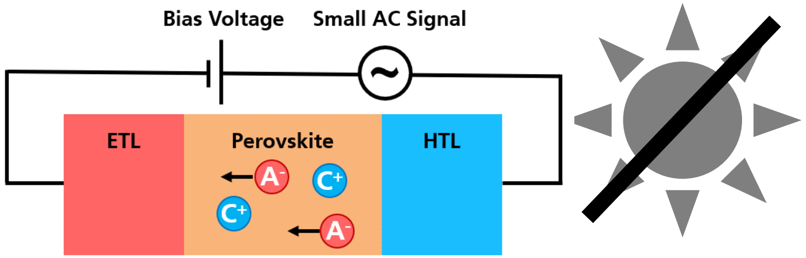


- Dark state, w/o DC bias, w/o ions, varied AC frequency
  - Geometrical capacitances in series connection:
  - High-frequency capacitance reduced by series resistance
- Mobile anions with varied concentration (immobile cations)
  - Increased low-frequency response of capacitance
- Mobile anions with varied diffusivity
  - Characteristic frequency shifts



Ion-induced Capacitances in Perovskite Solar Cells

Experimental Evidence



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- Perovskite single junction fabricated and measured at IMEC

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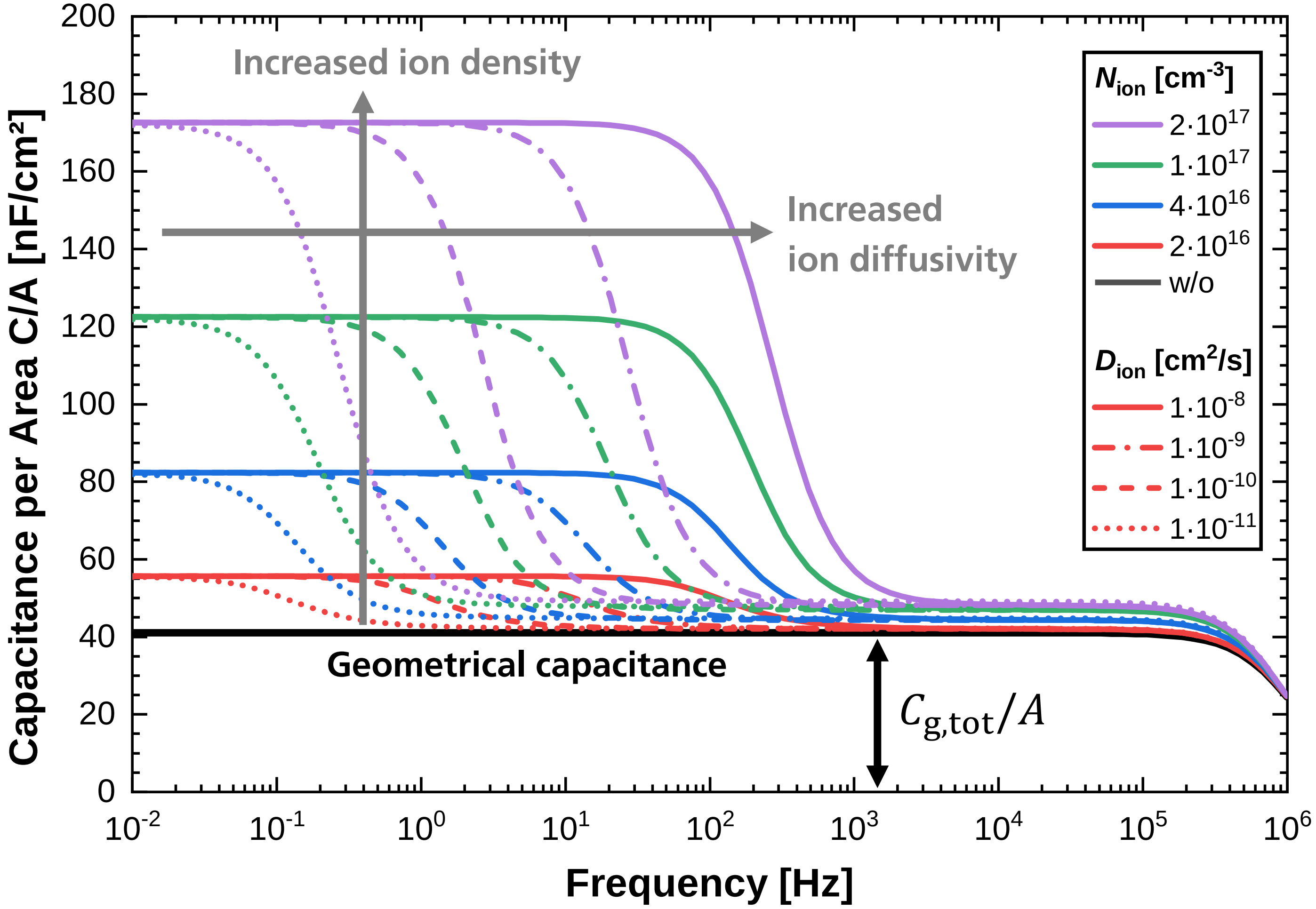

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Ion-induced Capacitances in Perovskite Solar Cells

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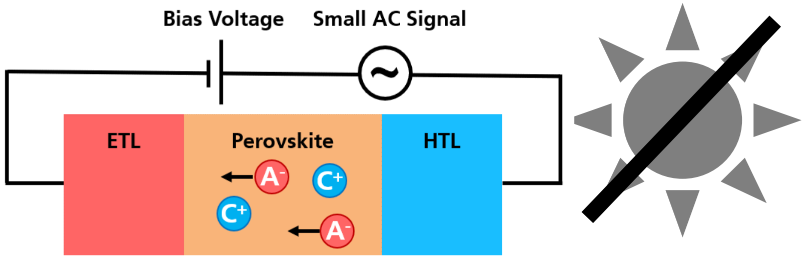

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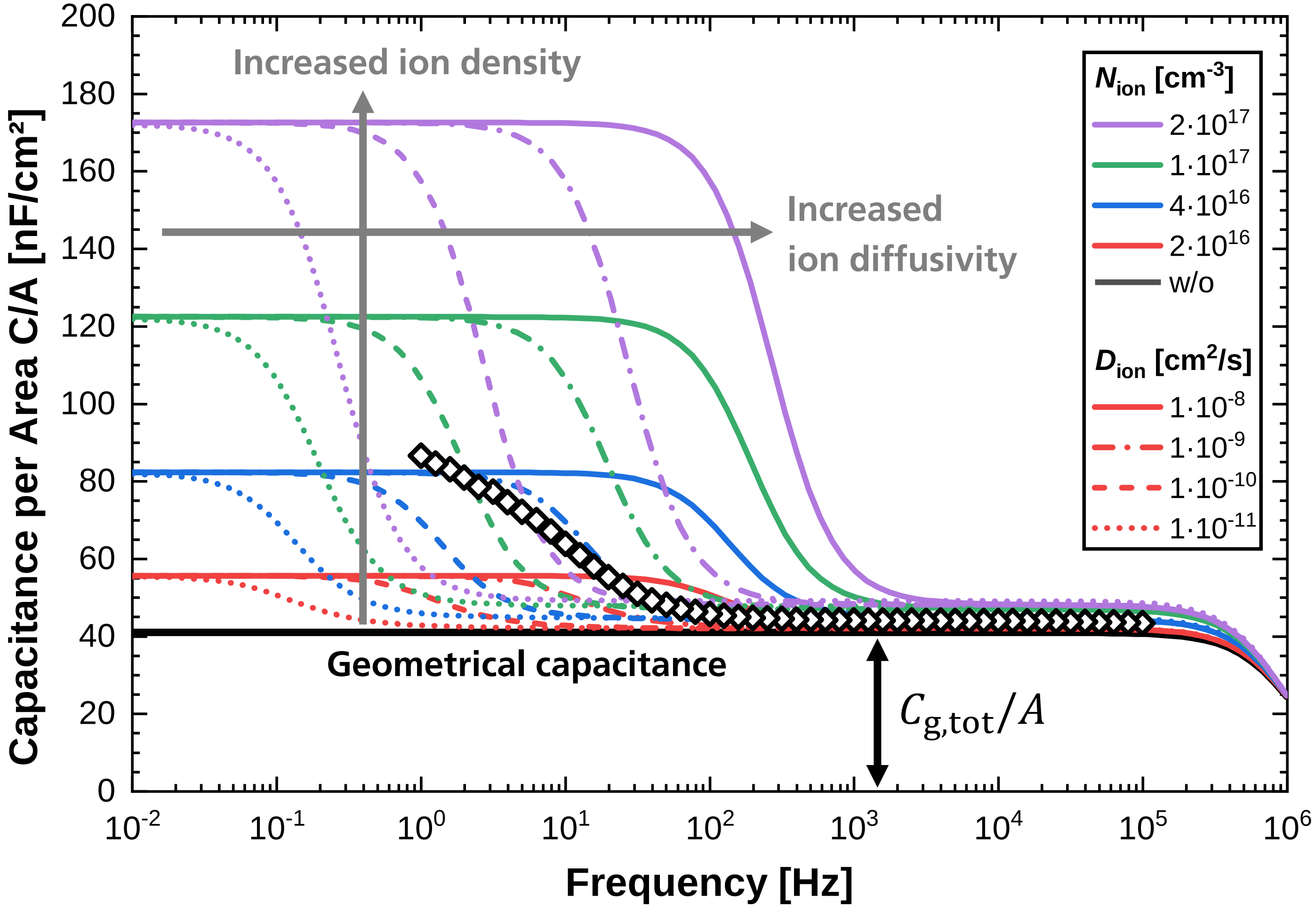

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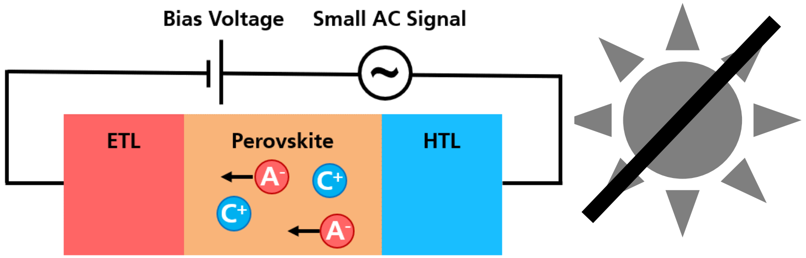
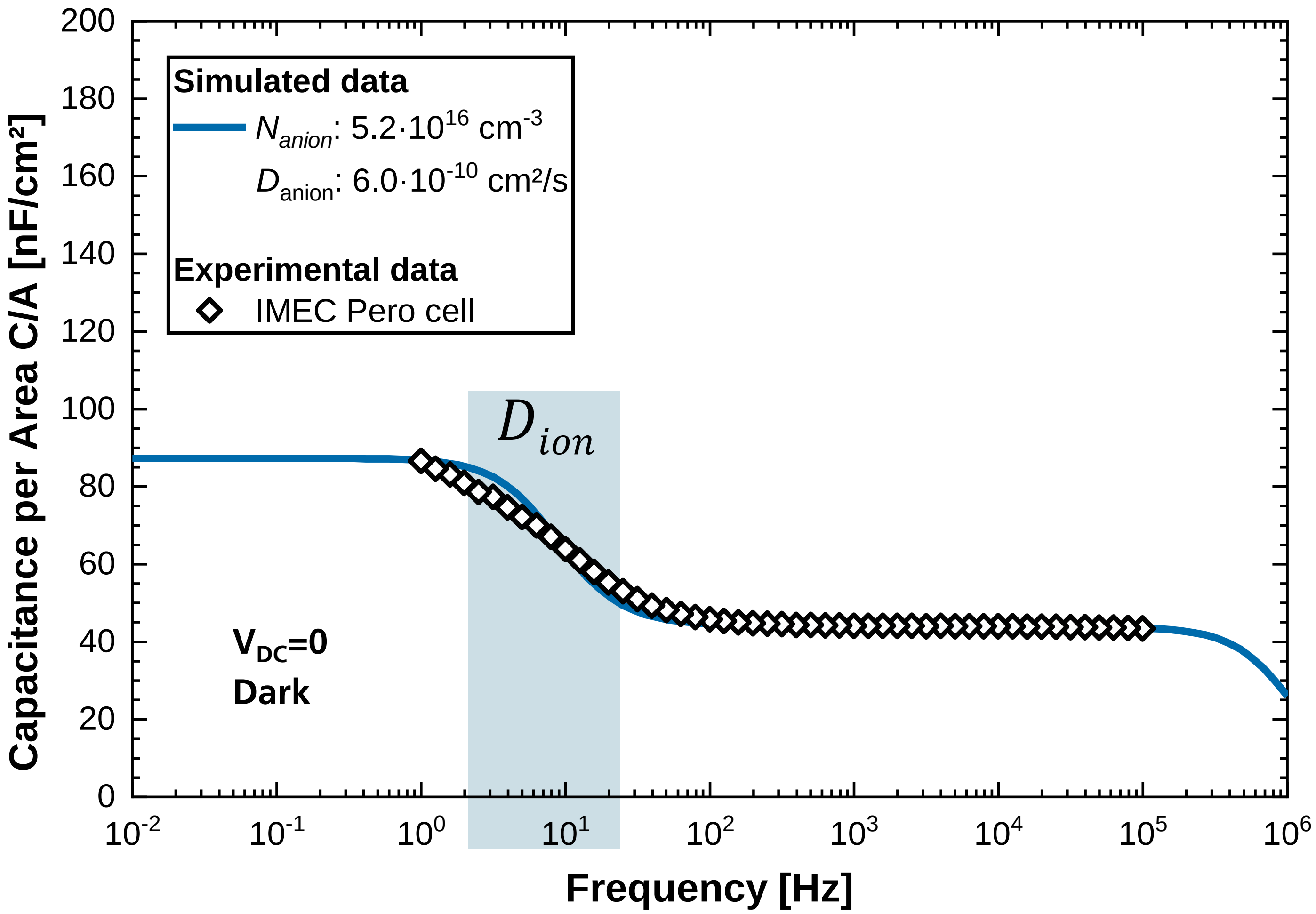


- Perovskite single junction fabricated and measured at IMEC
- What can we deduce from *C-f* characteristics?
  - Characteristic frequency *f*, here around 10 Hz
    → **Ion diffusivity** of $6{\cdot}10^{-10}$ cm²/s



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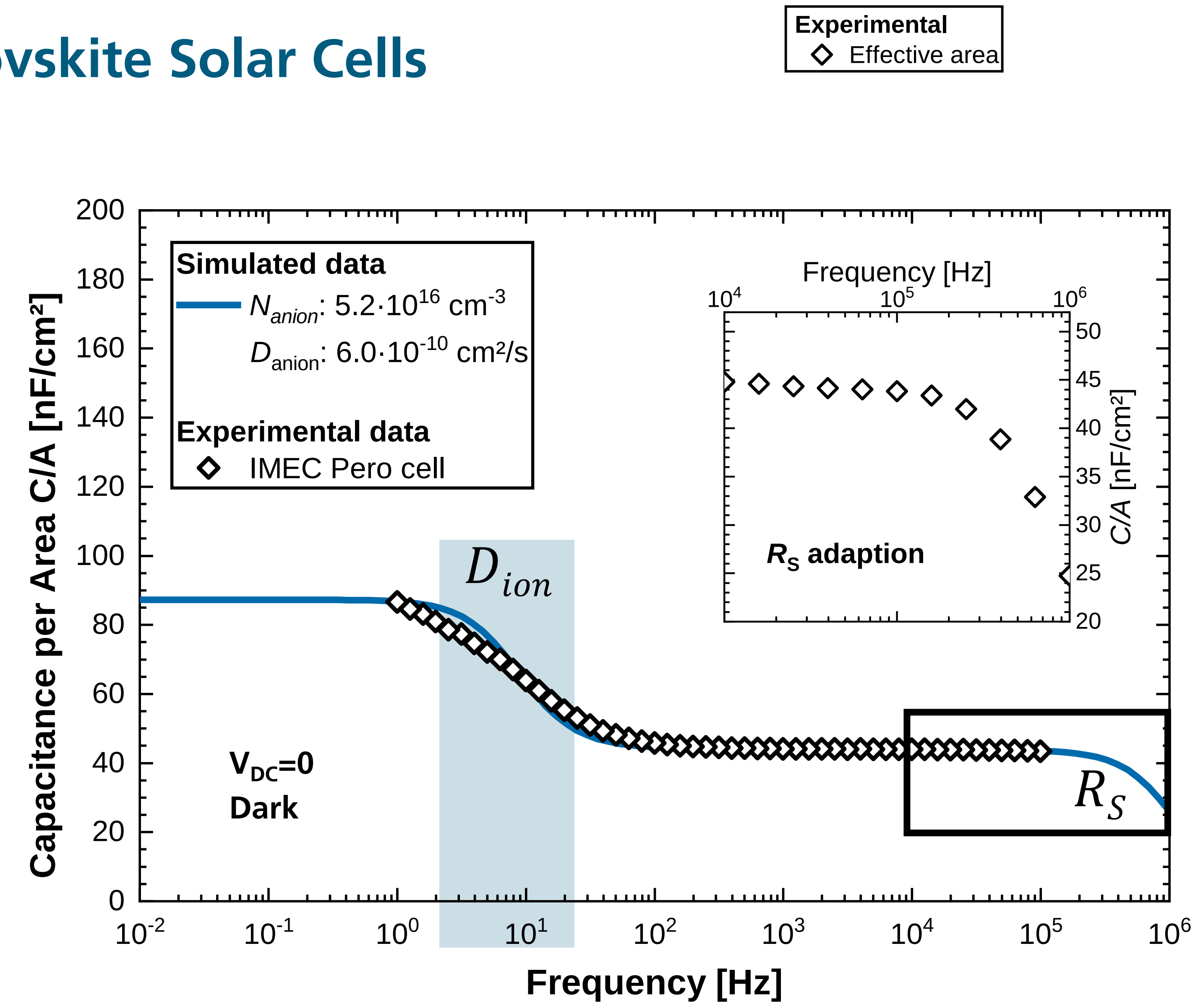

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Experimental Evidence

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- What can we deduce from *C-f* characteristics?
  - Characteristic frequency f, here around 10 Hz
    → **Ion diffusivity** of $6\cdot10^{-10}$ cm²/s
  - High-frequency regime (measured on similar sample)
    → **Series resistance** of device is about 3 Ω·cm²
  - C_{IF} (for negligible capacitances of CTLs):
    → **Dielectric permittivity** of perovskite (for known d_{Pero})

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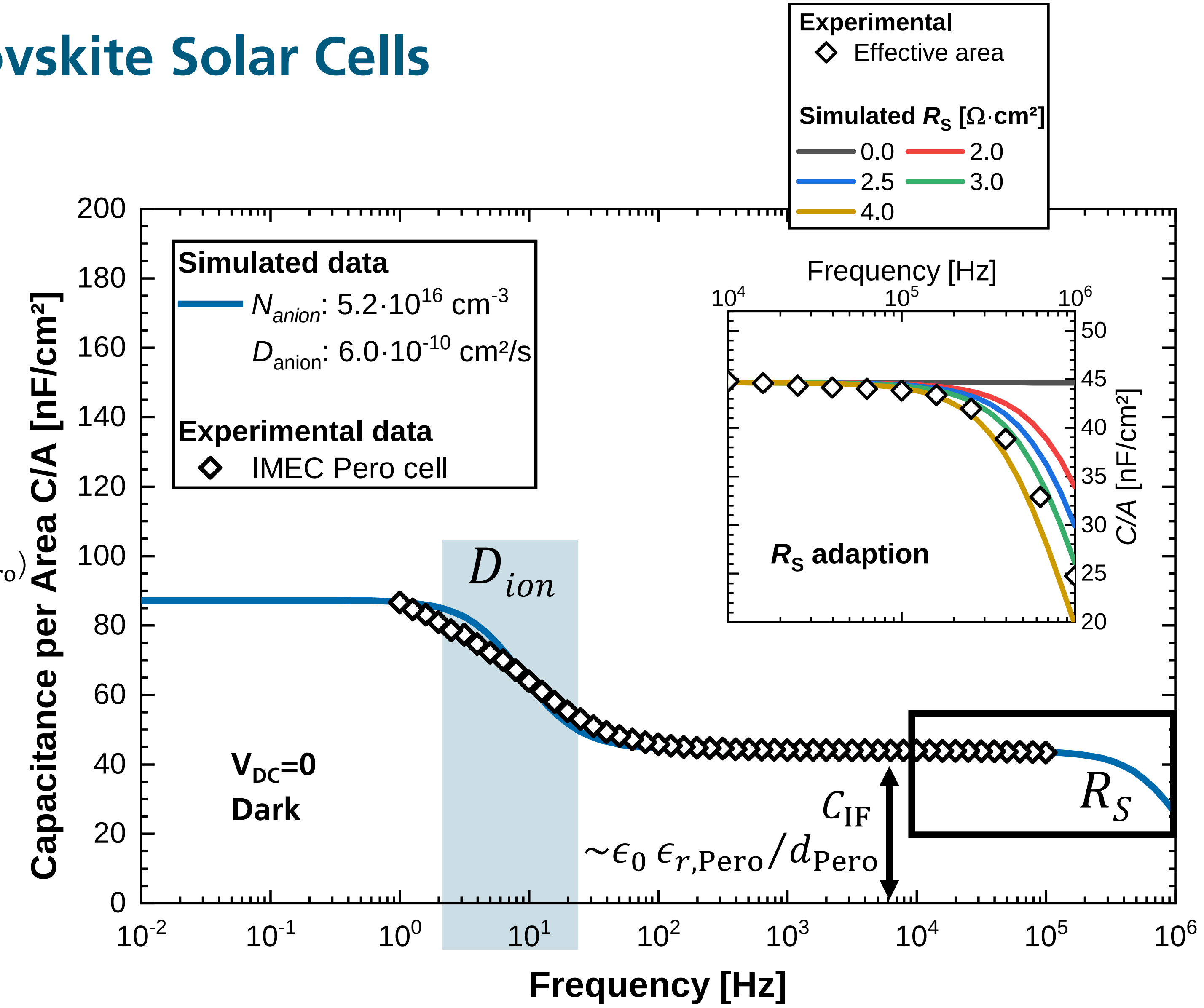

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Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis

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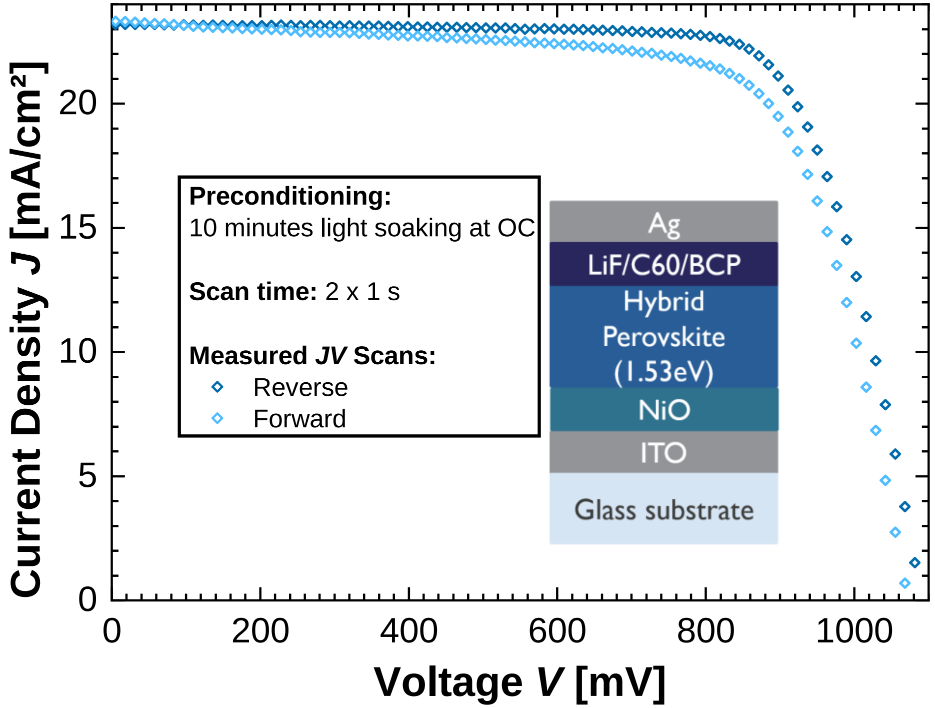
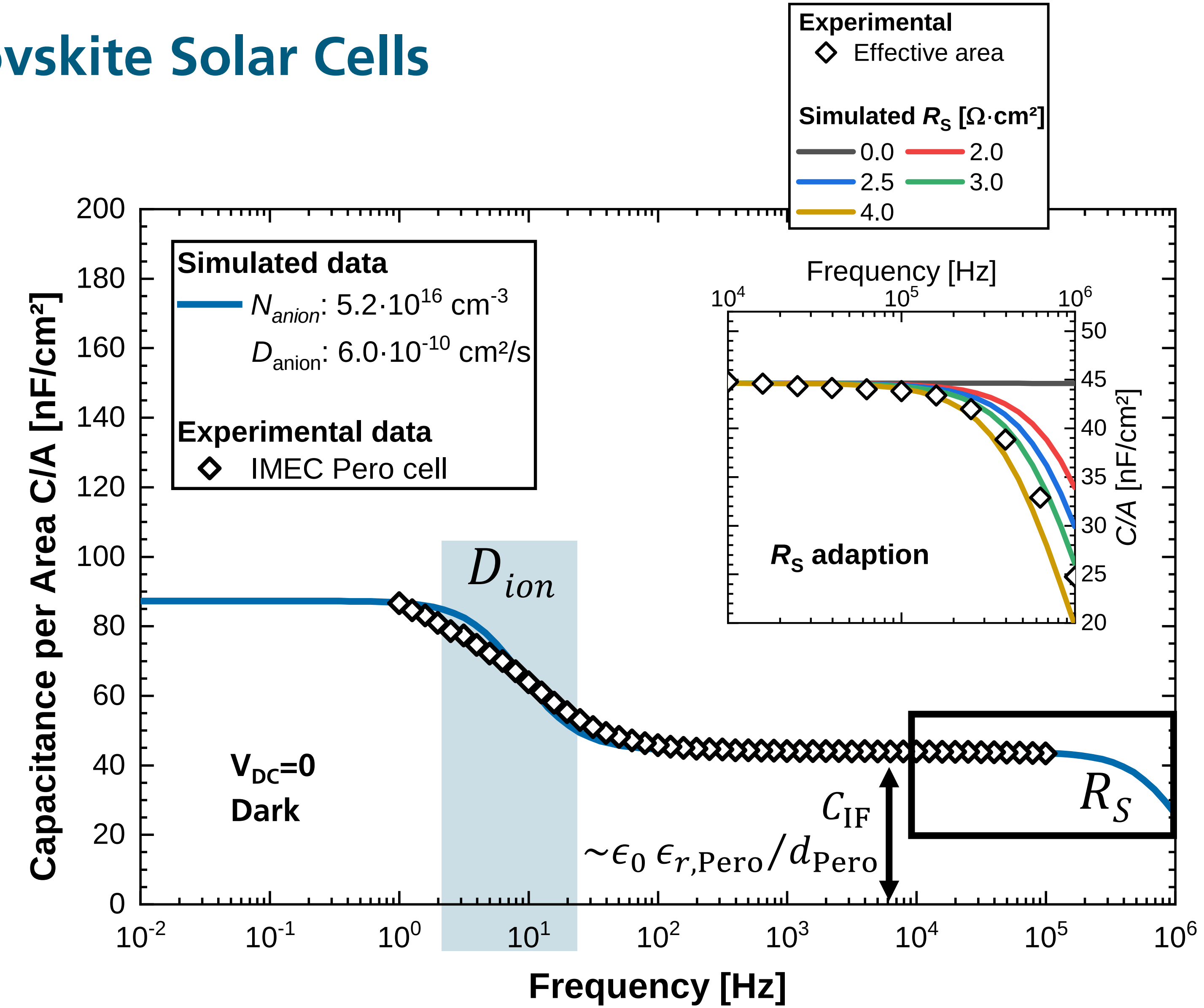
- Measured *JV* reverse and forward scan for same sample





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Ion-induced Capacitances in Perovskite Solar Cells

Relation to *JV* Hysteresis

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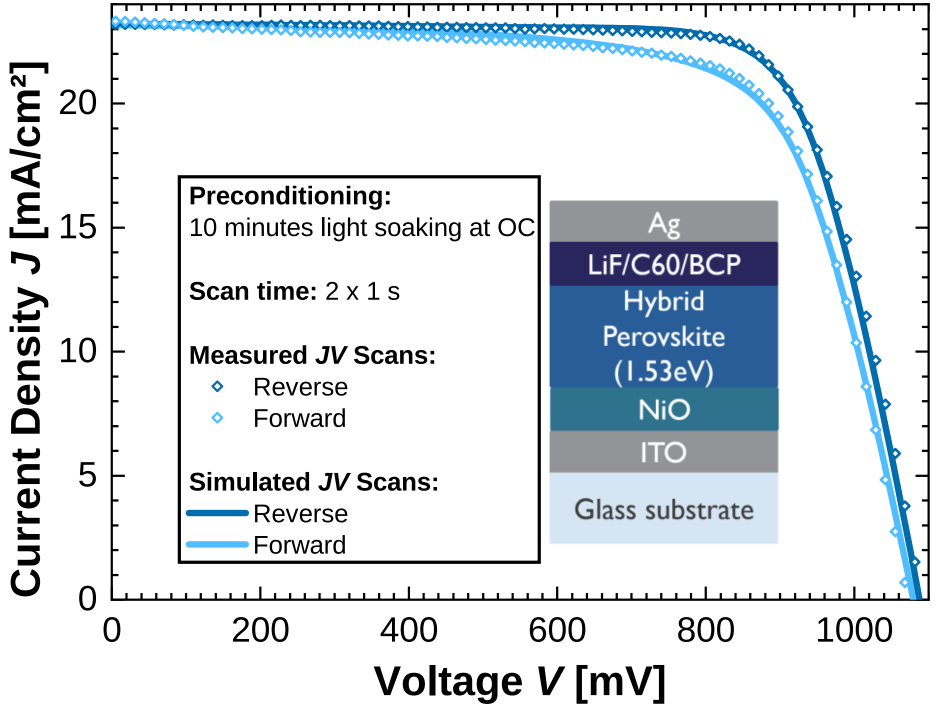

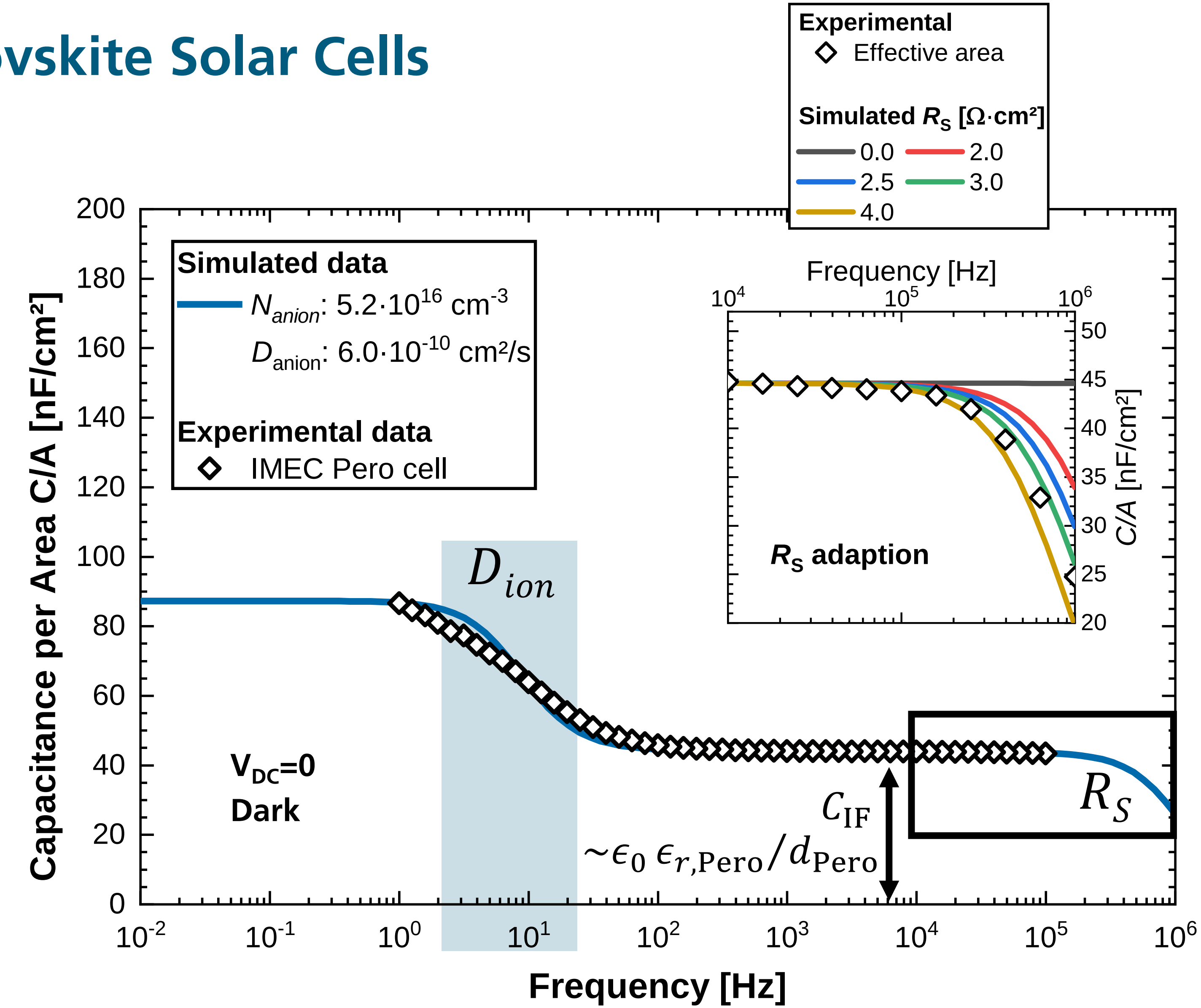

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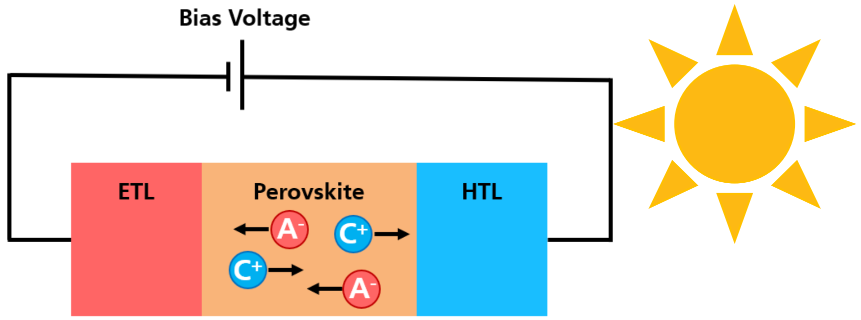

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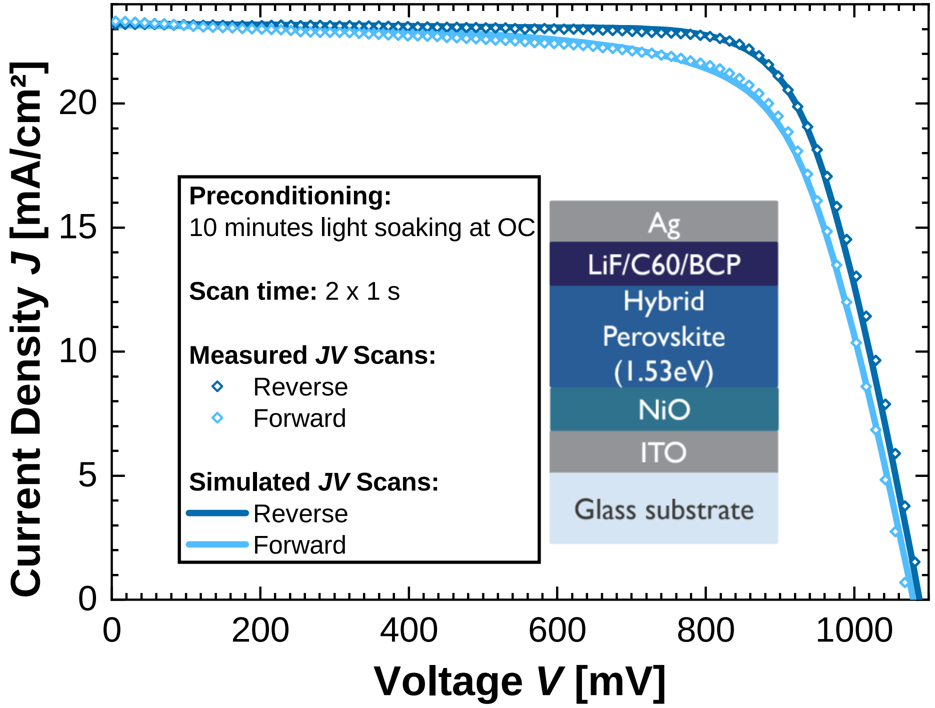

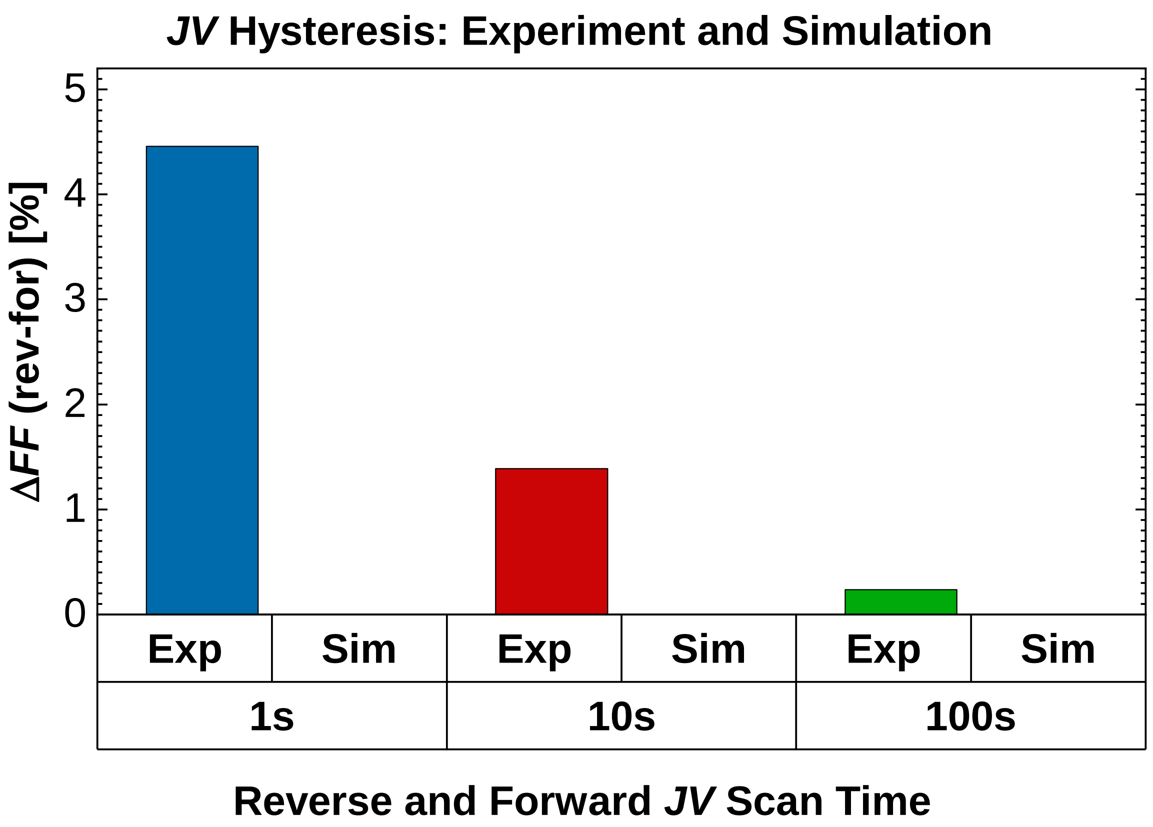

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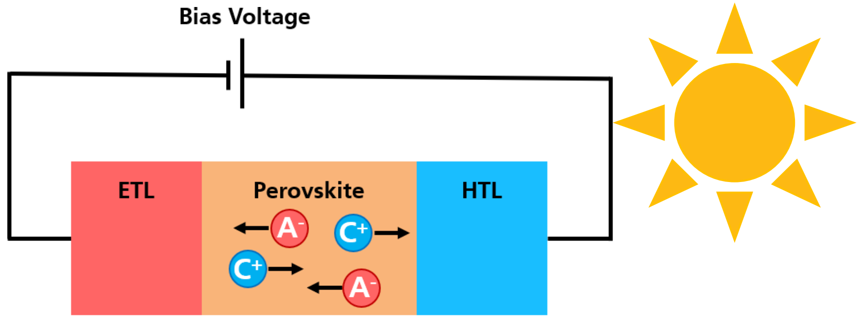

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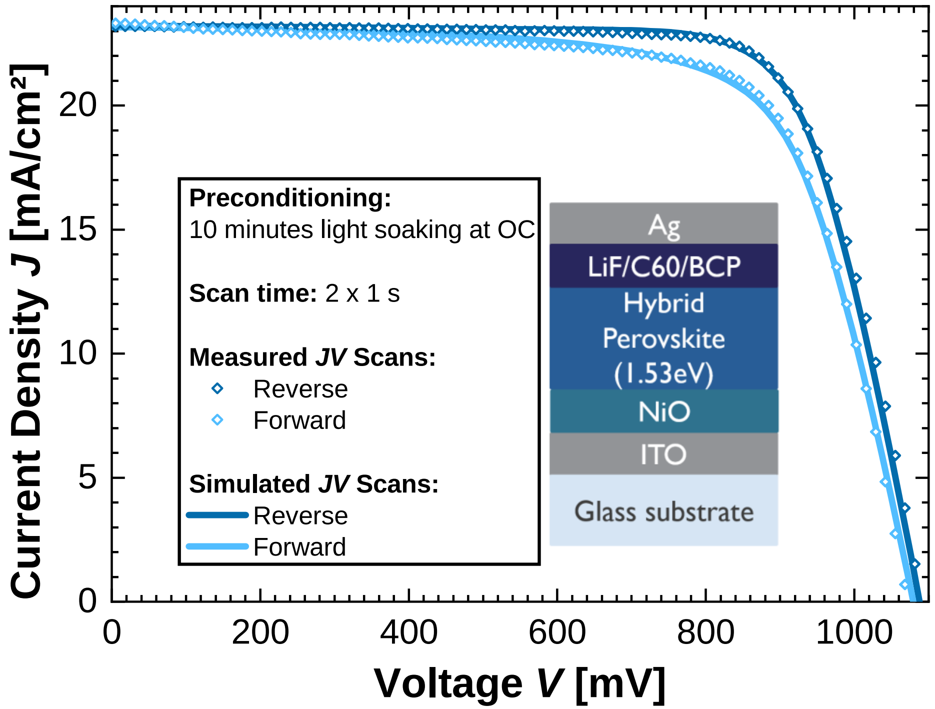

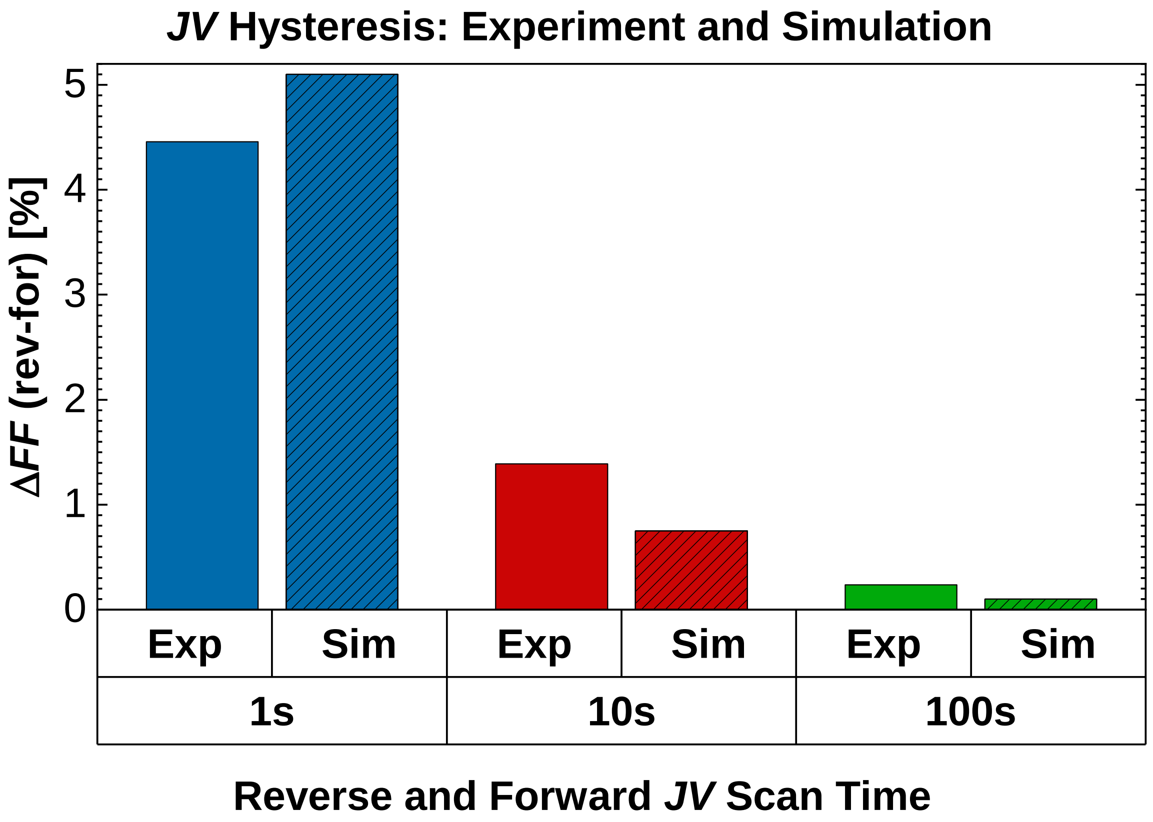

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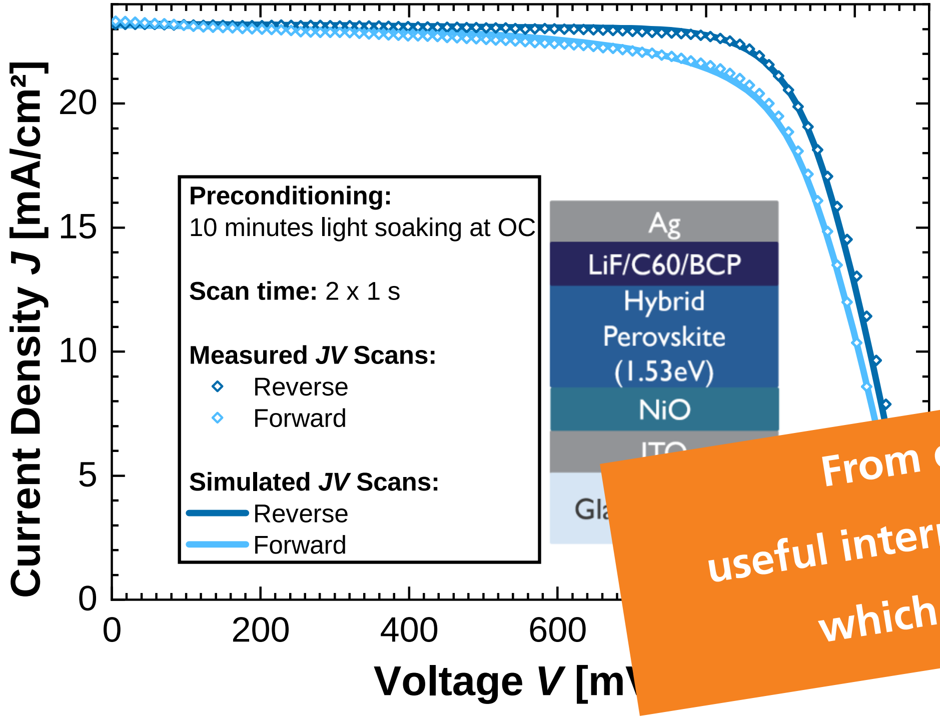

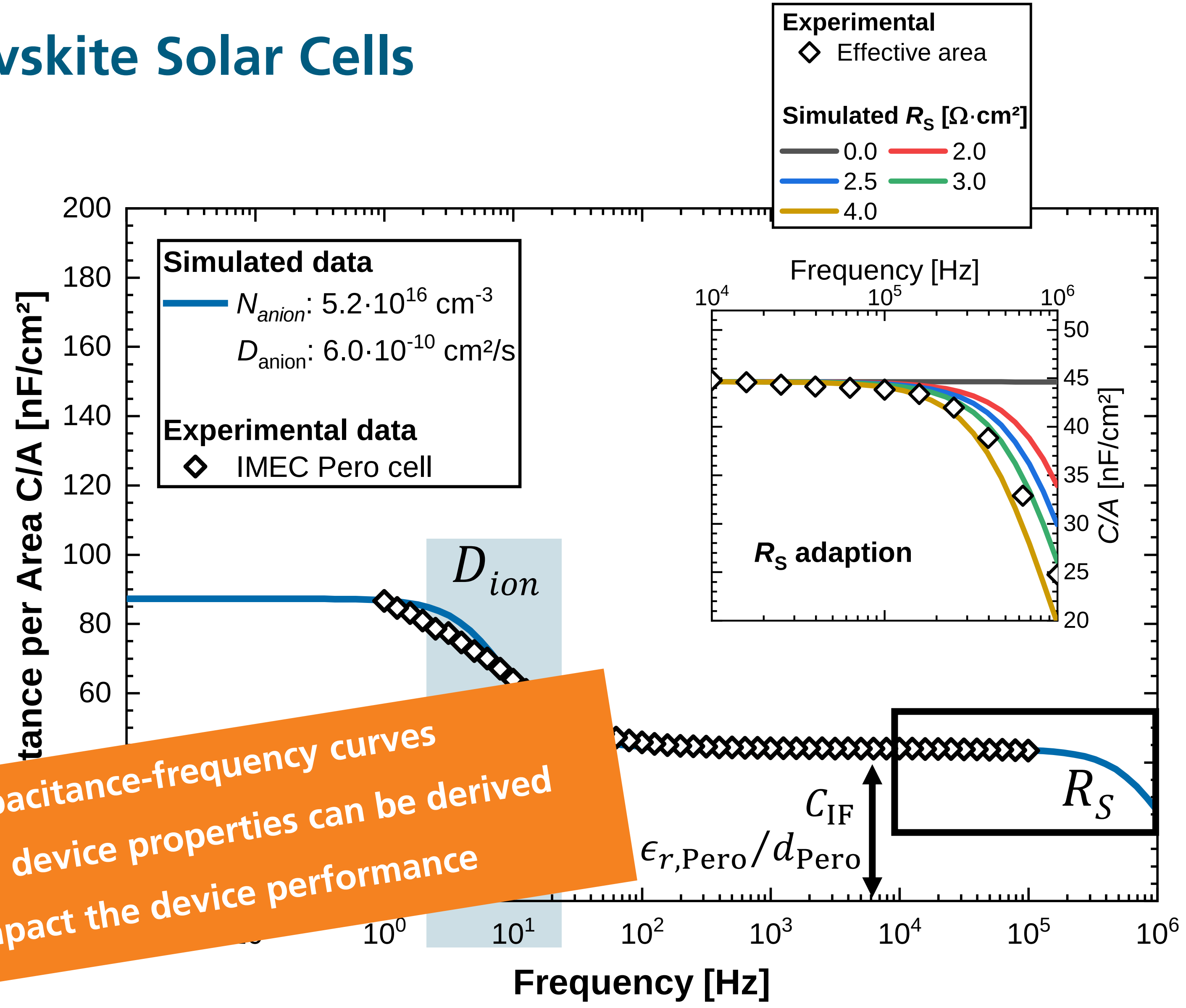

From capacitance-frequency curves useful internal device properties can be derived which impact the device performance

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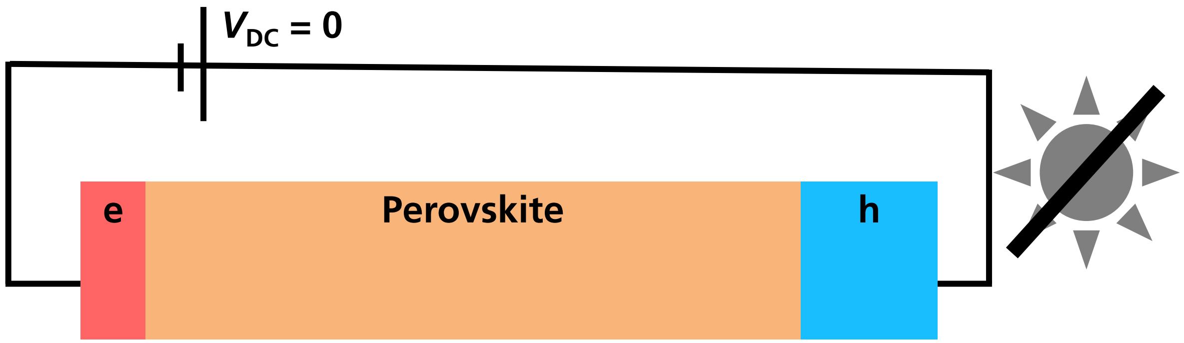
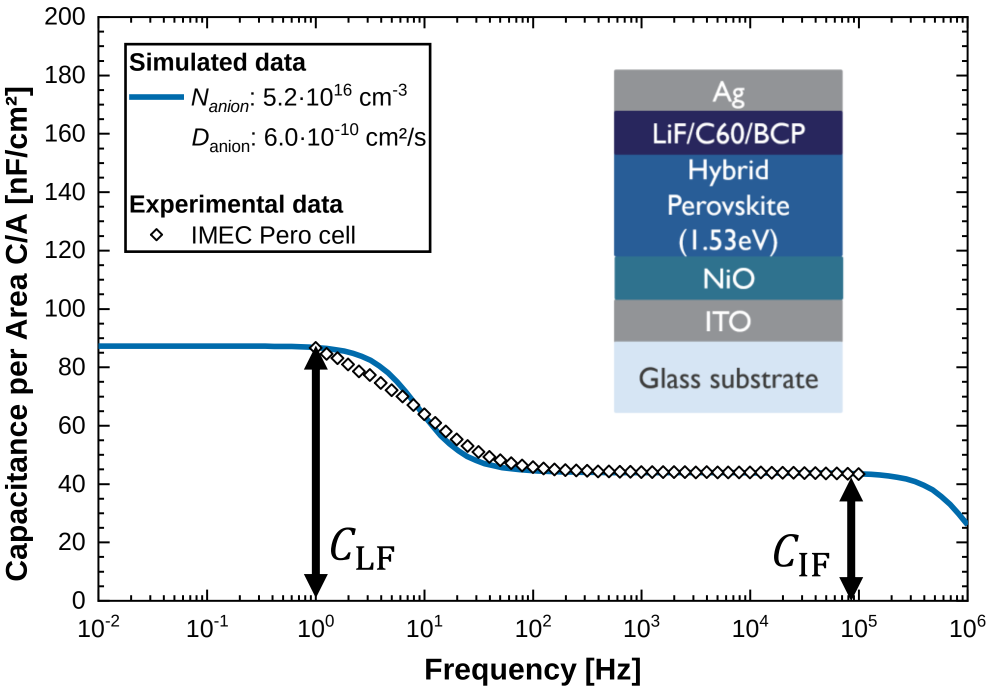
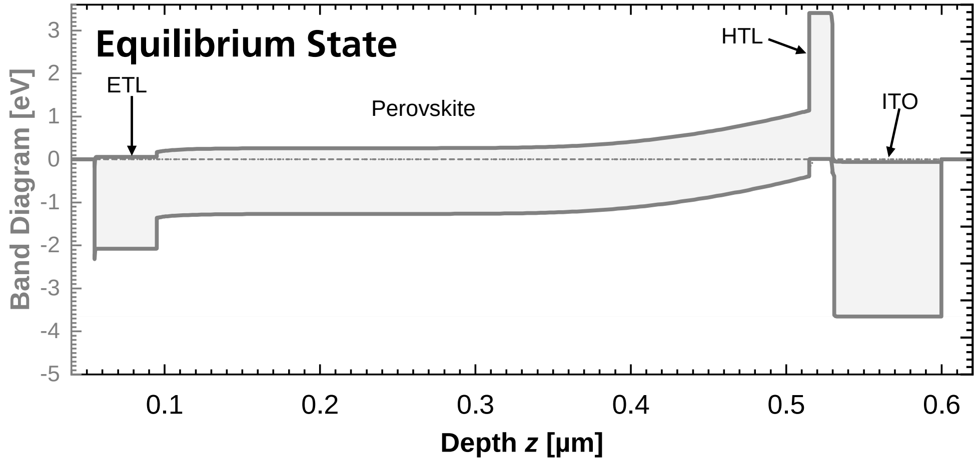
Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau







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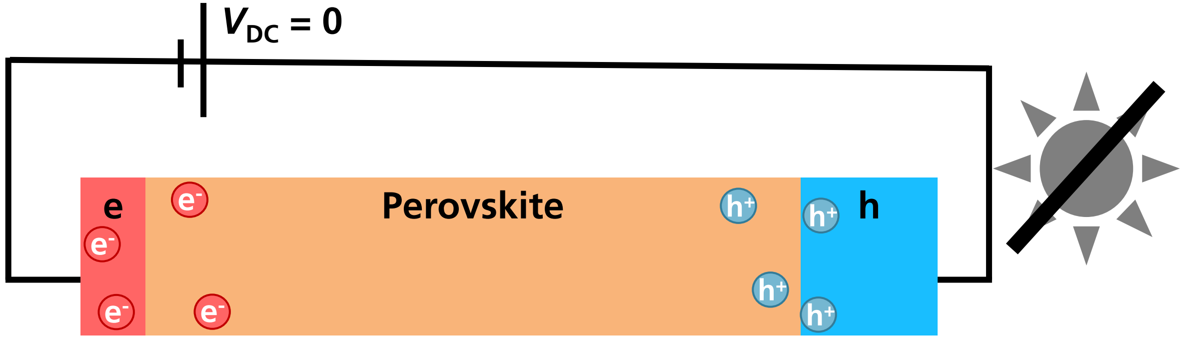

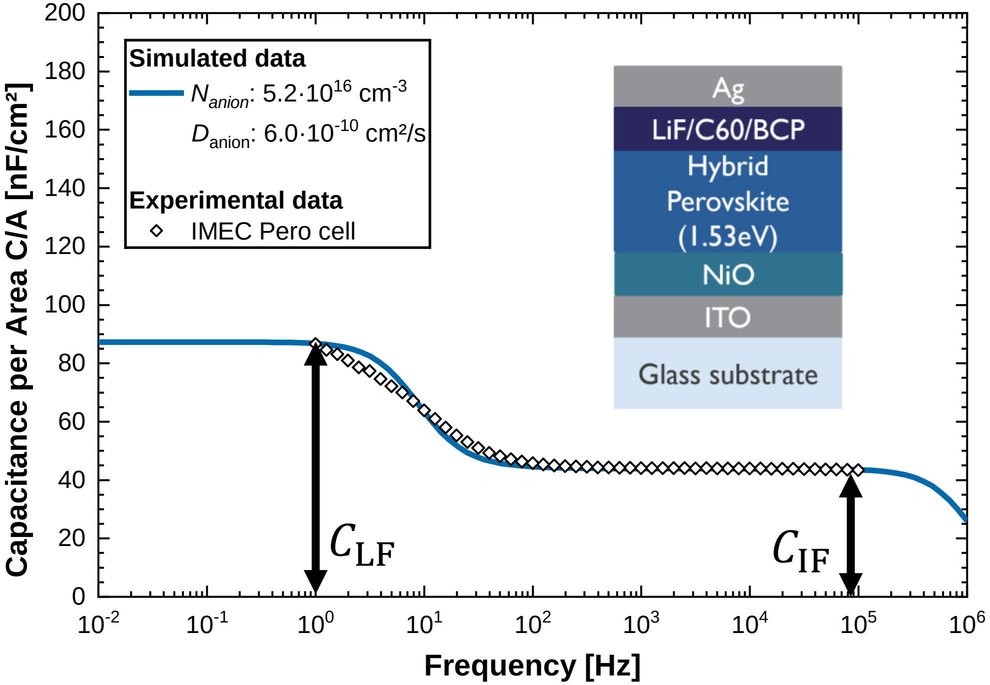

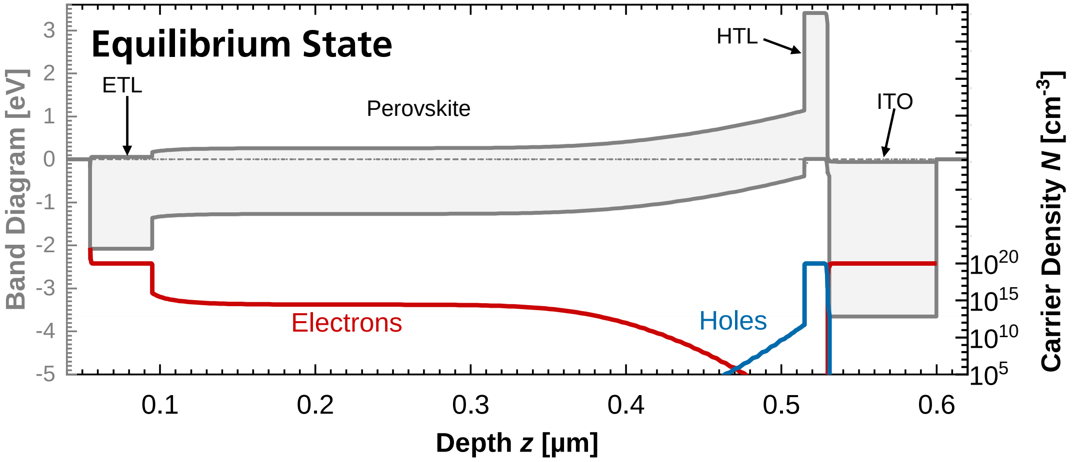

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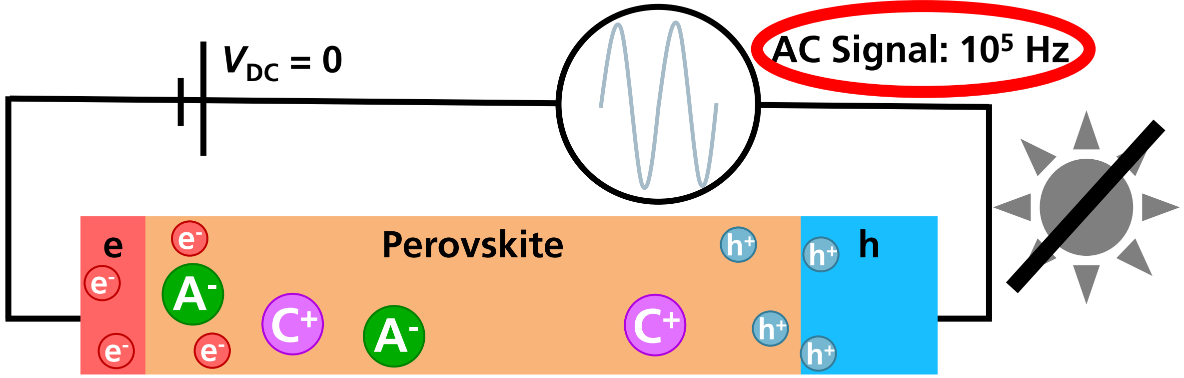

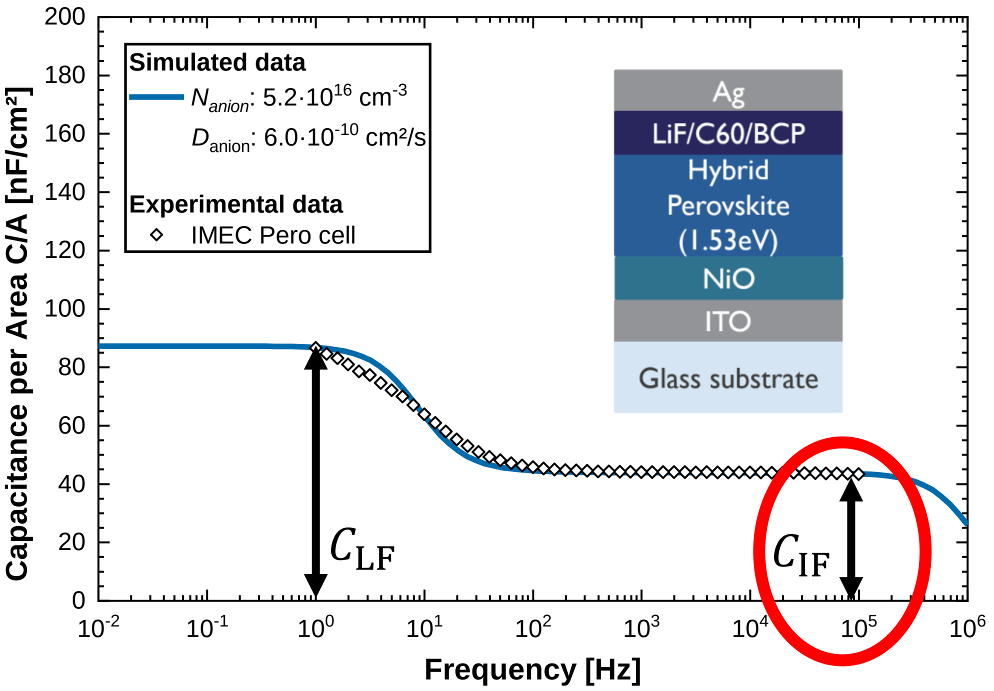

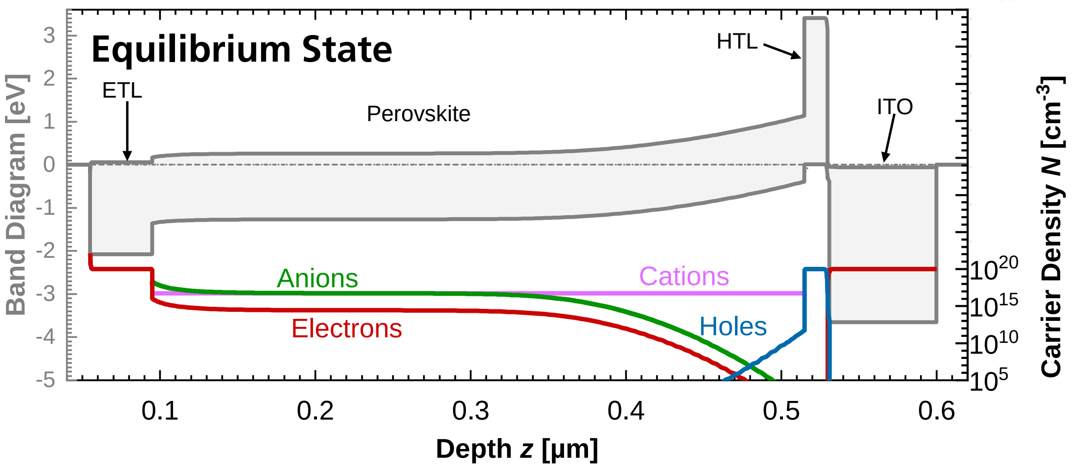

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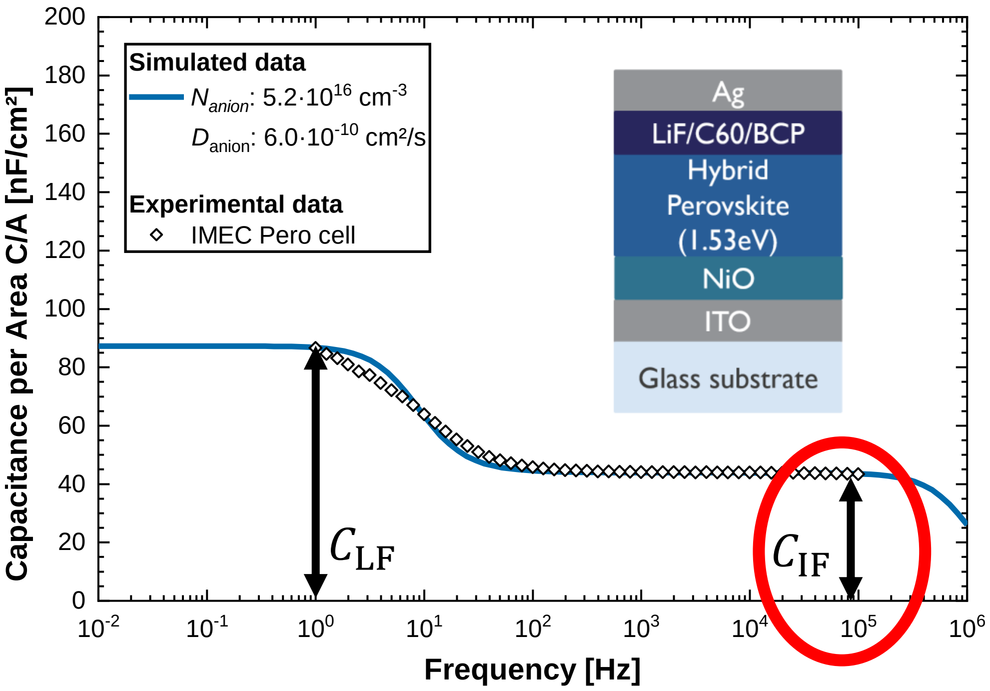
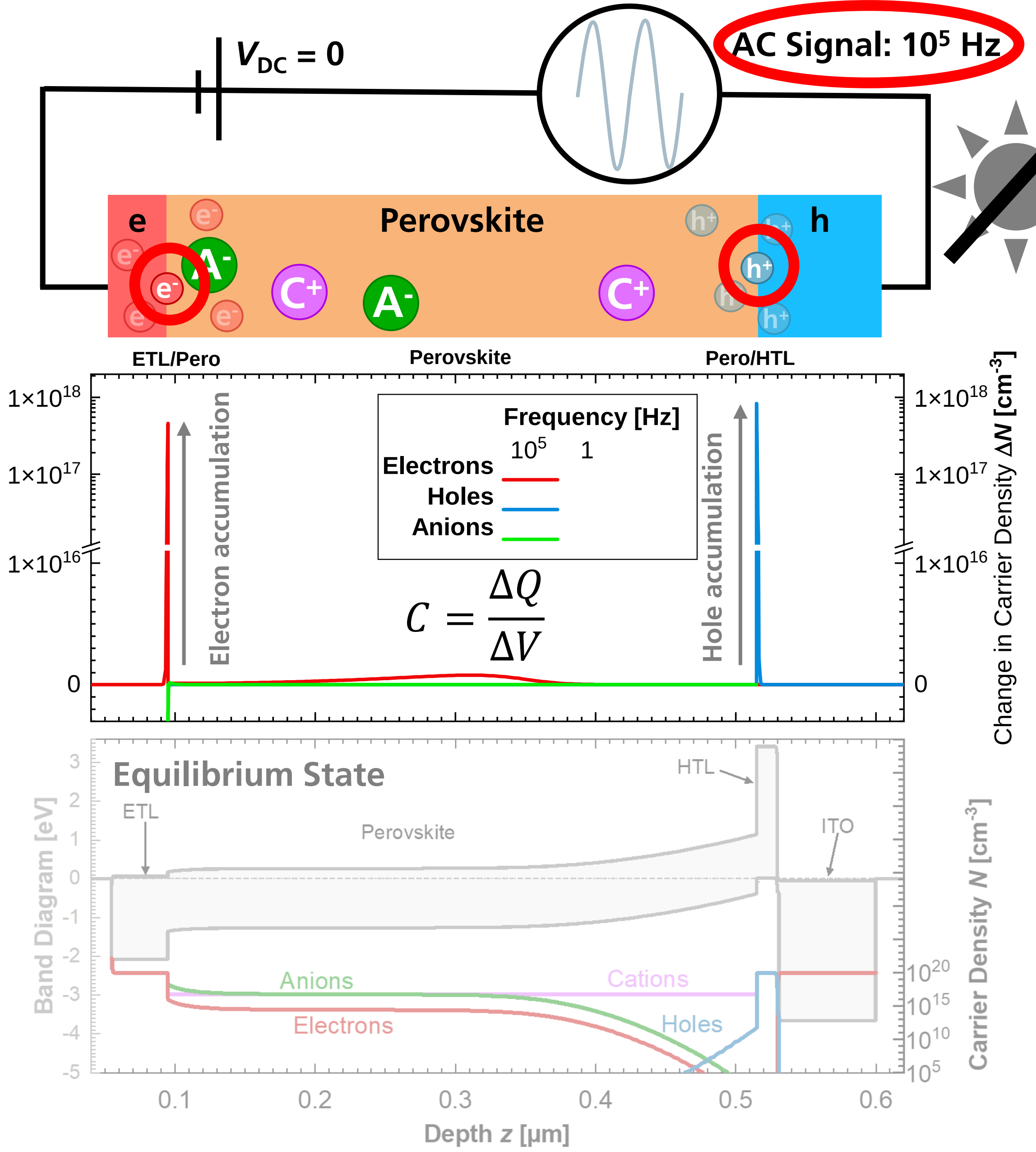
- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface





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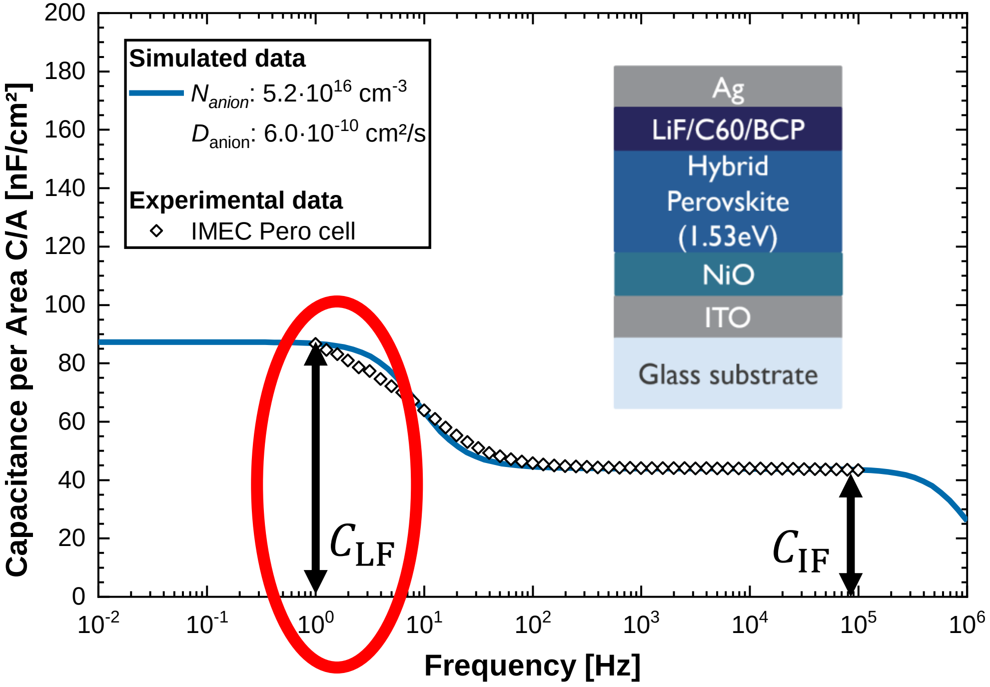

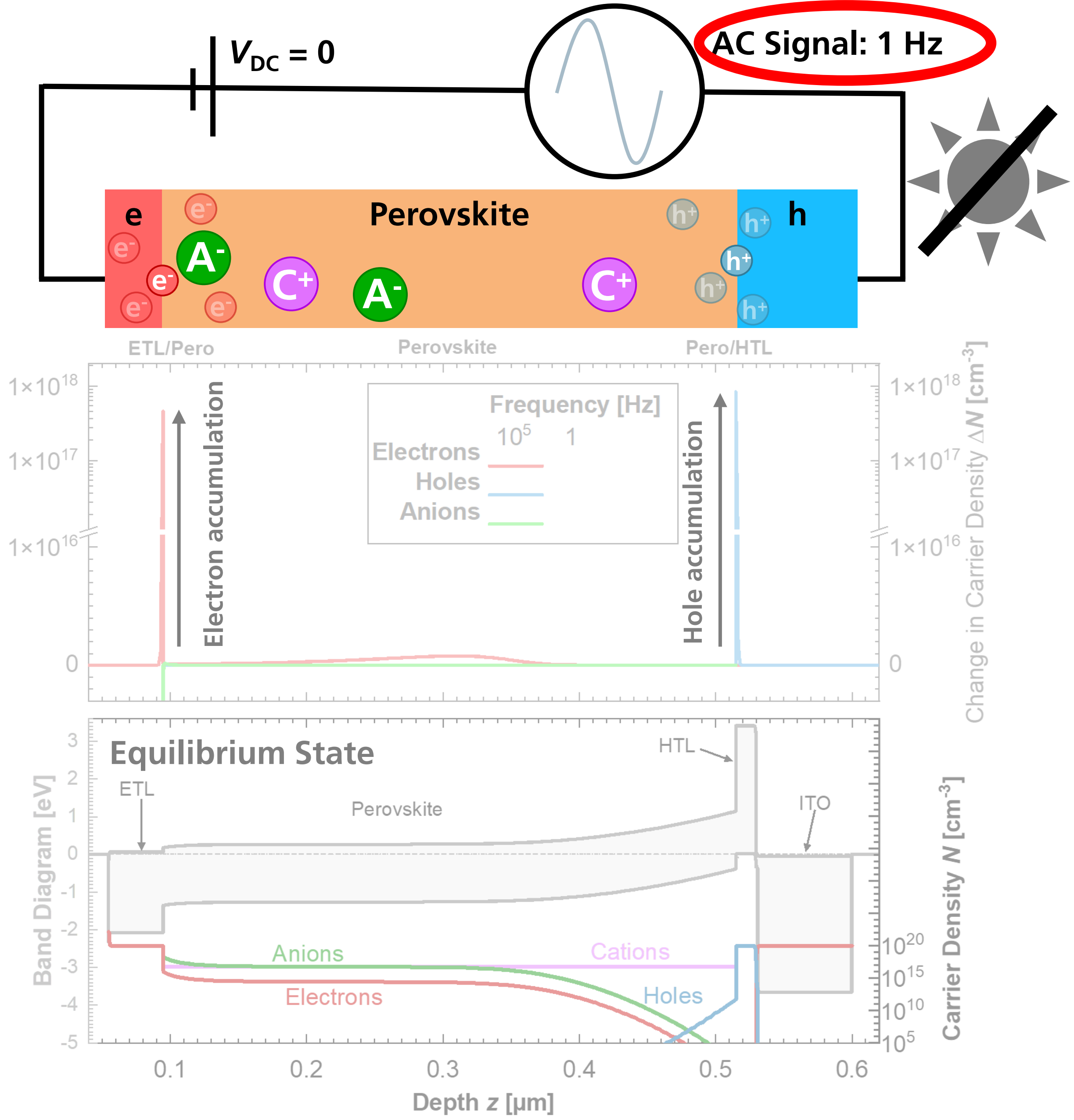

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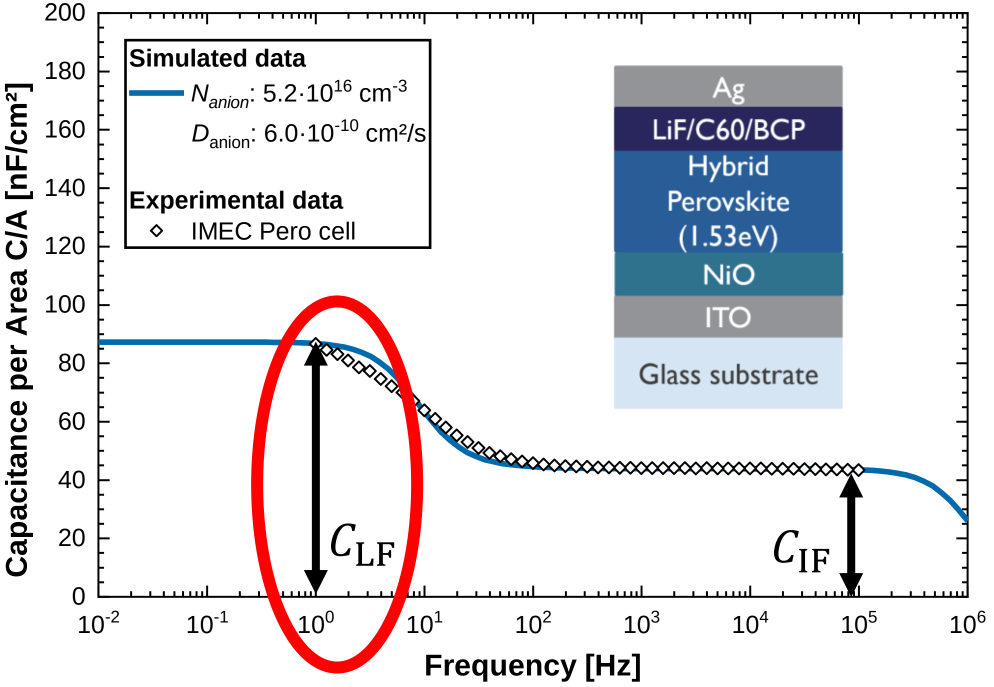

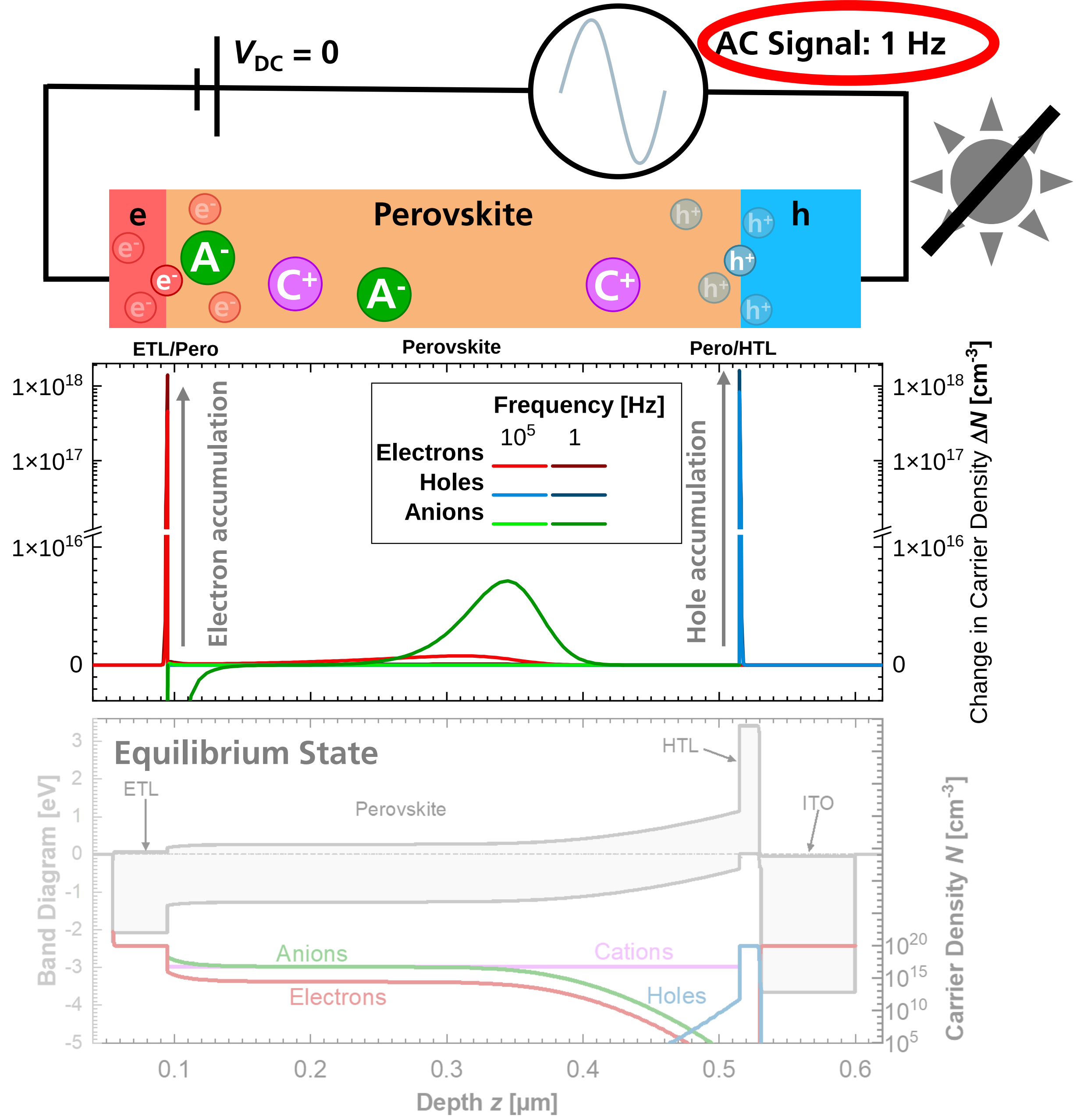

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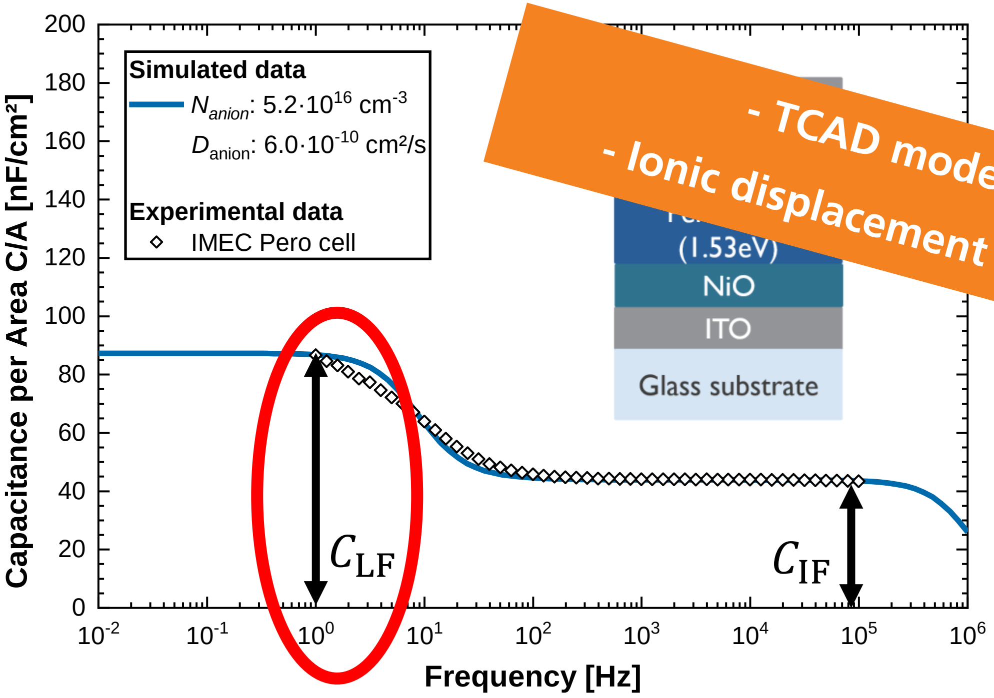
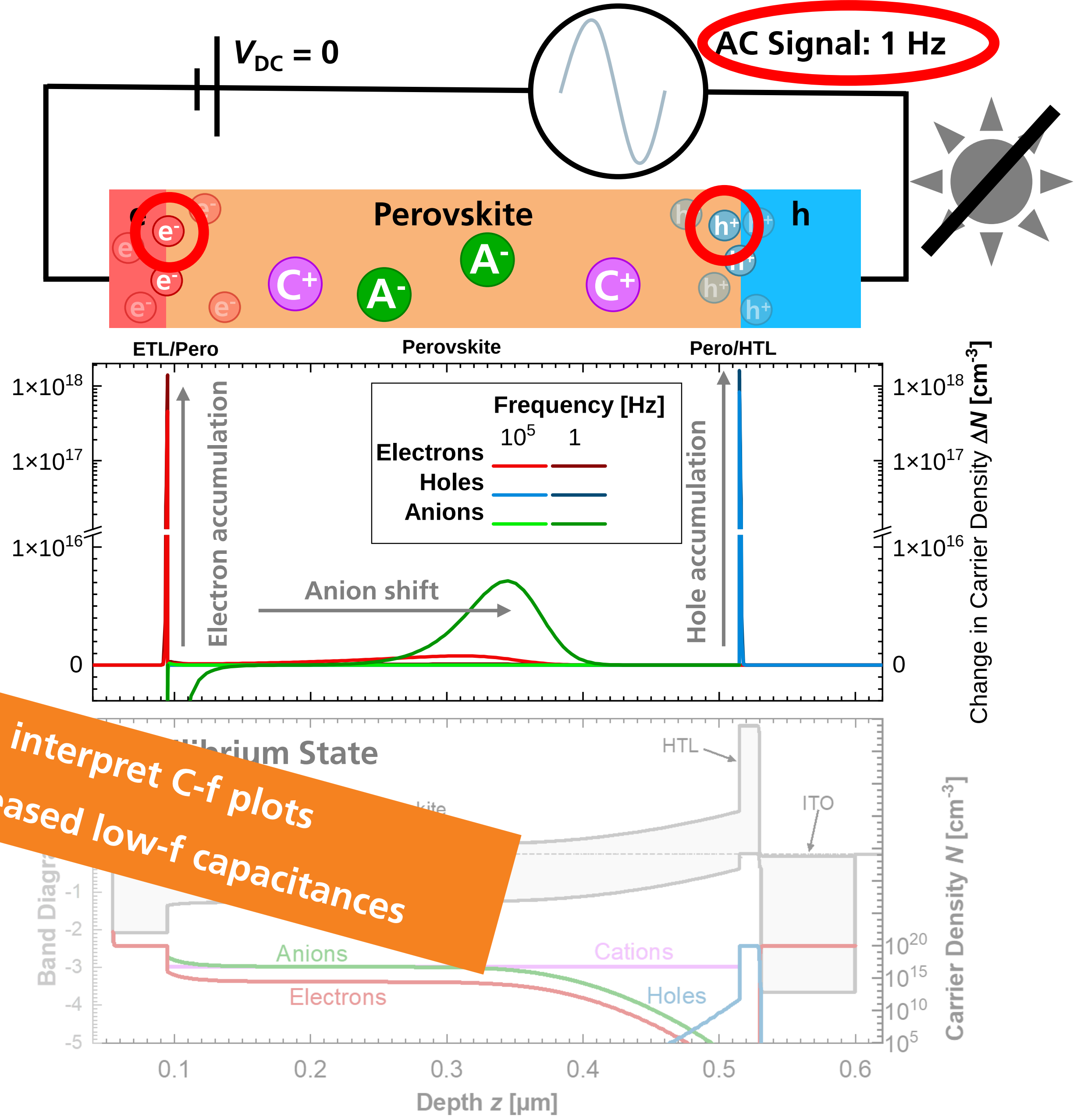
Ion-Induced Capacitances

In-Depth Analysis of the Capacitance Plateau

- C_{IF} corresponds to charge accumulation at Pero/ETL, Pero/HTL interface
- C_{LF}: **Anion displacement** from ETL interface towards bulk leads to further charge carrier accumulation
  - → C_{LF} depends on N_{ion}, **but also on** built-in potential, cations, …





- TCAD modelling helps to interpret C-f plots
- Ionic displacement leads to increased low-f capacitances

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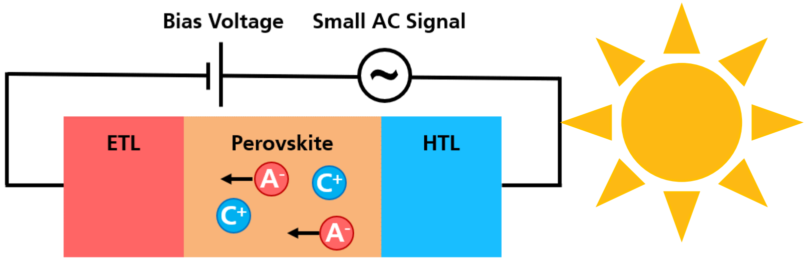
Ion-Induced Capacitances under Illumination

TCAD Simulation



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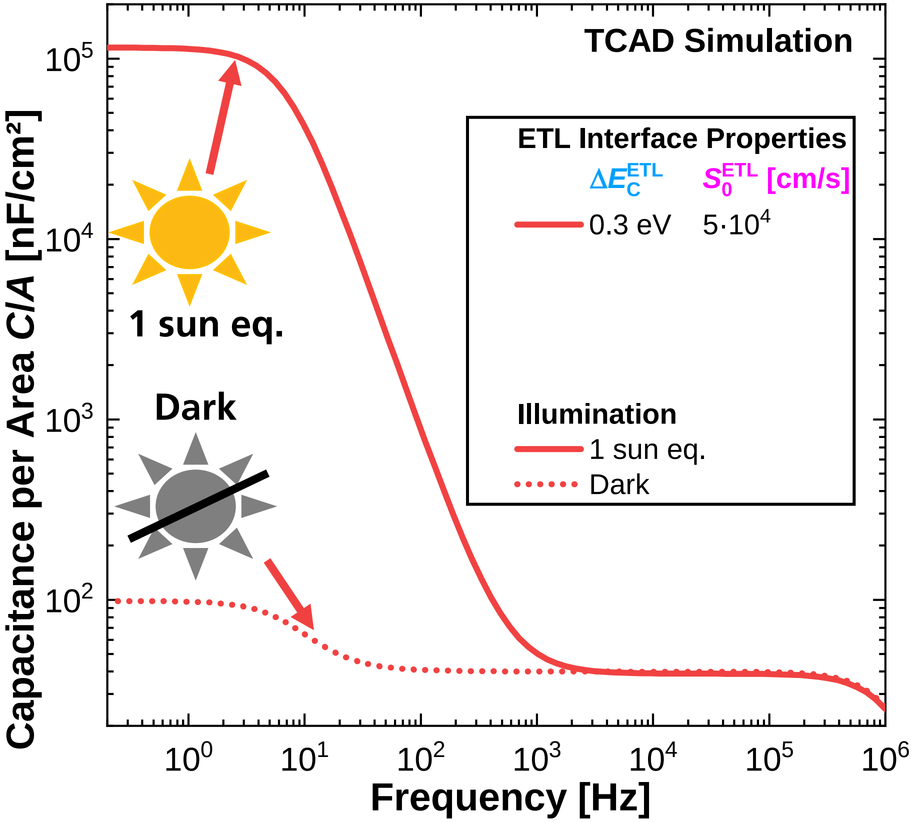

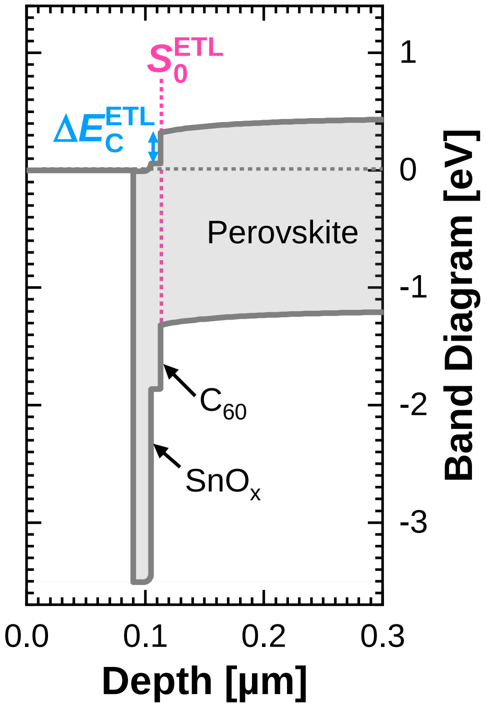

- **Simulated dark and light *C-f* curves** for different ETL interface properties
  - Capacitance under illumination increases by several orders of magnitude

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Ion-Induced Capacitances under Illumination

TCAD Simulation

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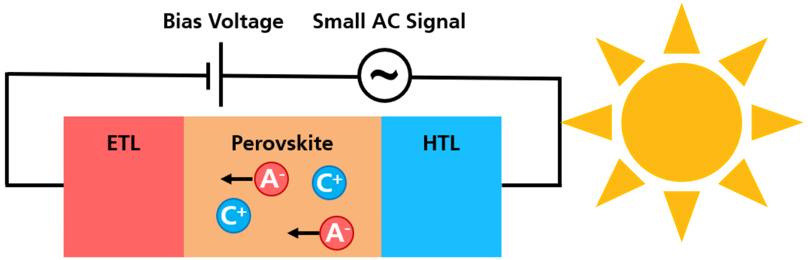

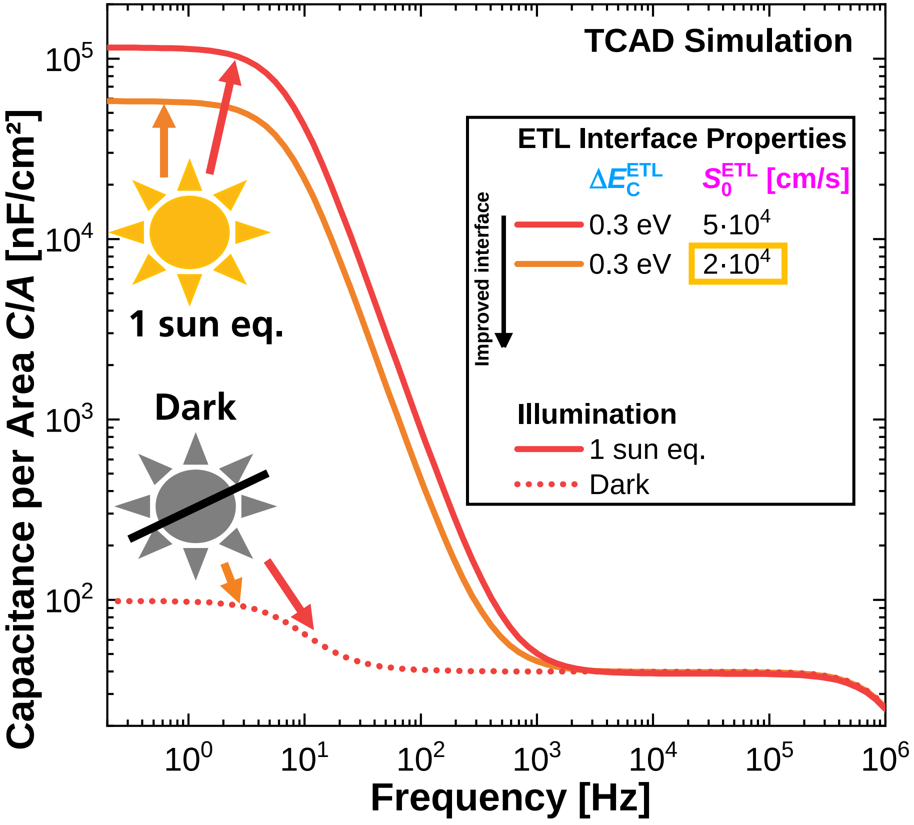

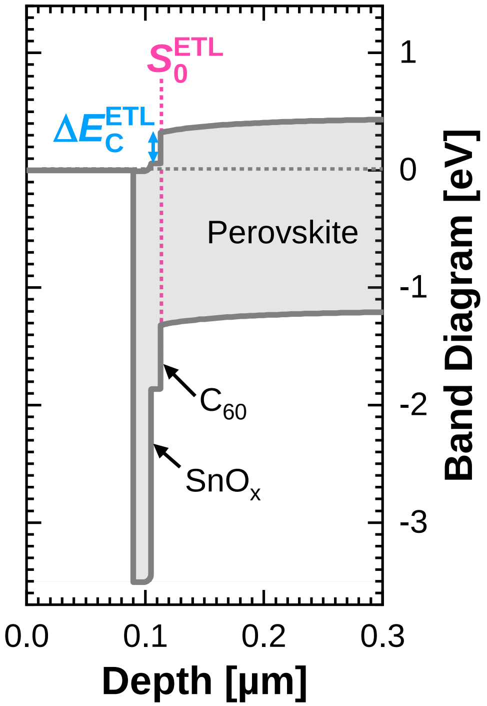

- **Simulated dark and light *C-f* curves**
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  - Capacitance under illumination increases by several orders of magnitude
- **For lower surface recombination velocity (SRV) at ETL/Pero interface:**
  - Illuminated *C-f* curve shifts down
  - Dark *C-f* curve is unchanged

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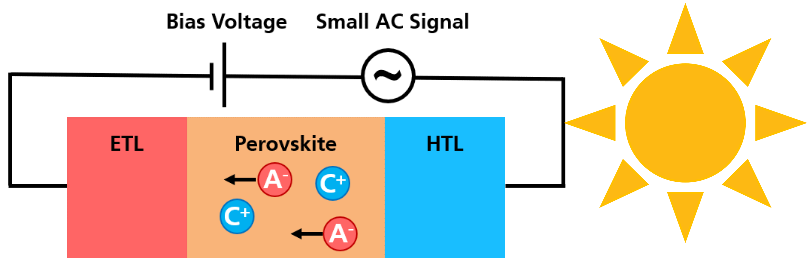

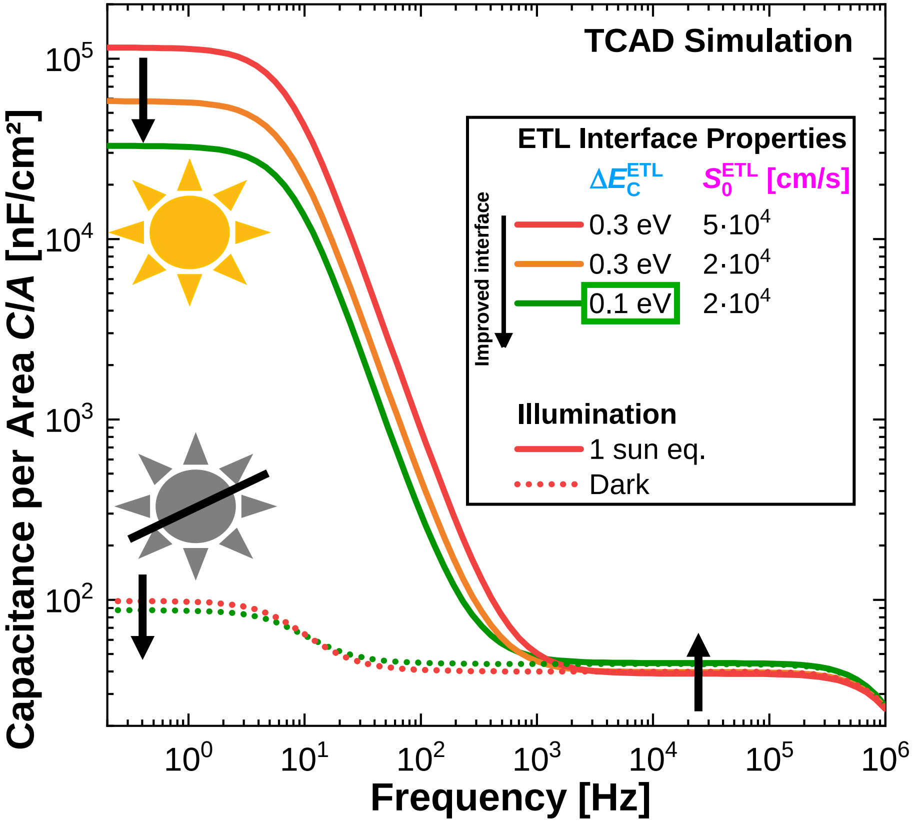

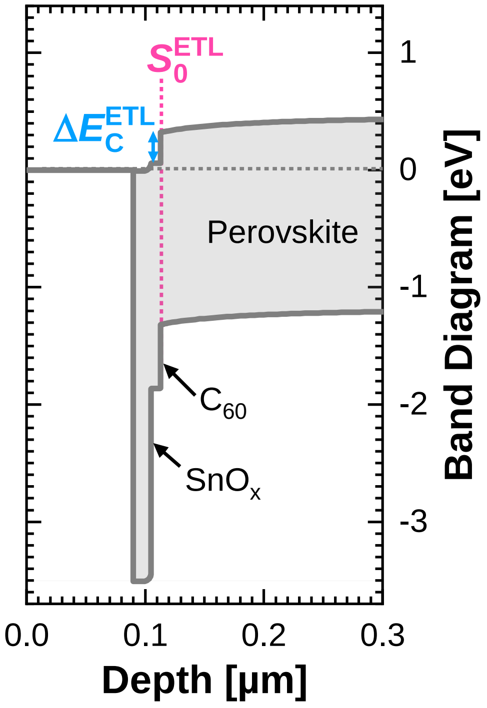

- **Simulated dark and light *C-f* curves**
  for different ETL interface properties
  - Capacitance under illumination increases by several orders of magnitude
- **For lower surface recombination velocity (SRV) at ETL/Pero interface:**
  - Illuminated *C-f* curve shifts down
  - Dark *C-f* curve is unchanged
- **For change in band alignment (reduced ETL/Pero conduction band offset):**
  - Both illuminated and dark *C-f* curve change
  - **Low frequency plateau**: Capacitance decreases
  - **High frequency plateau**: Capacitance increases

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Ion-Induced Capacitances under Illumination

Experimental Comparison

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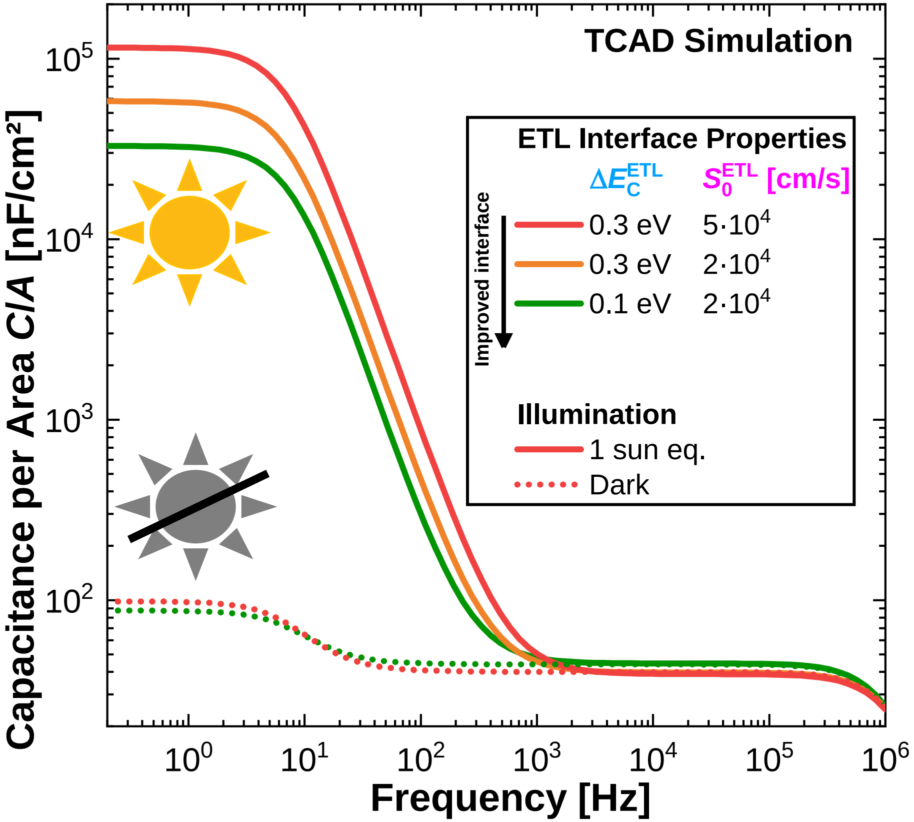

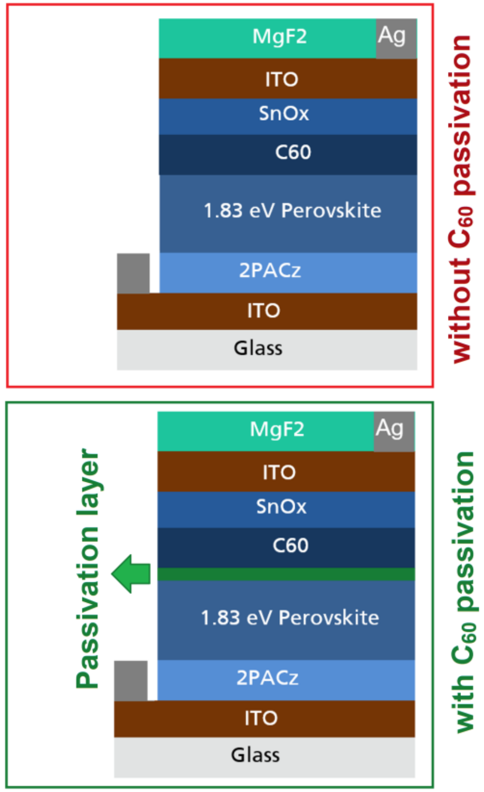

- Perovskite single junctions (used as top cells) fabricated at Fraunhofer ISE and measured at IMEC
  1. **ETL/Pero interface unpassivated**
  2. **ETL/Pero interface passivated with PI***

*PI = piperazinium iodide

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Ion-Induced Capacitances under Illumination

Experimental Comparison

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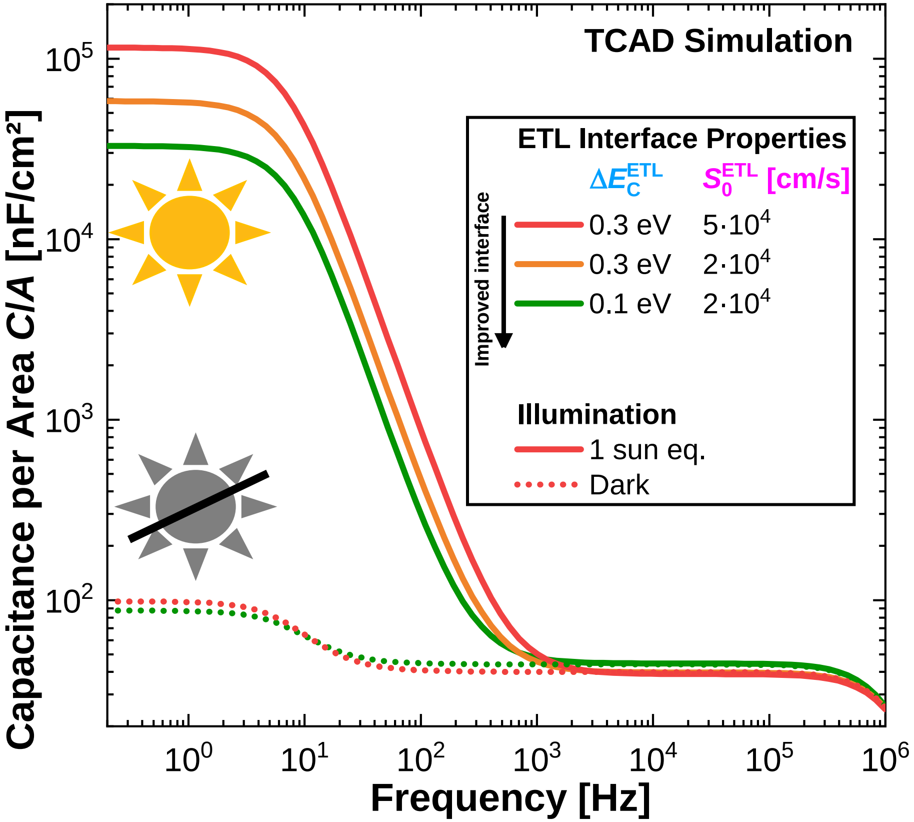

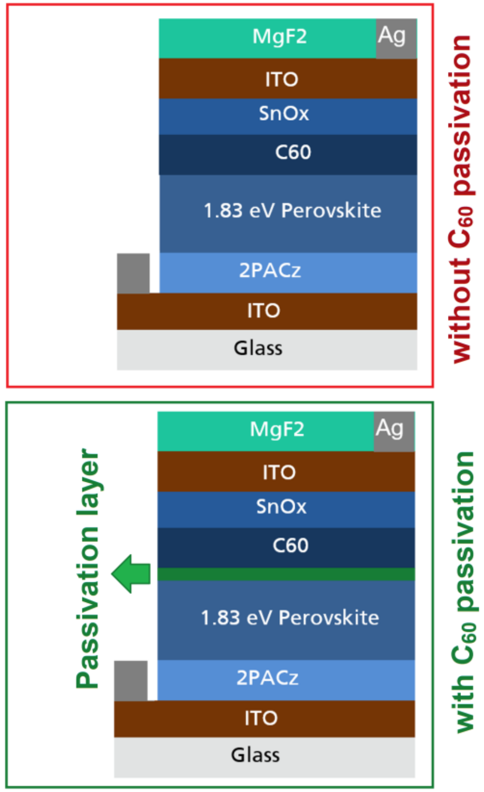

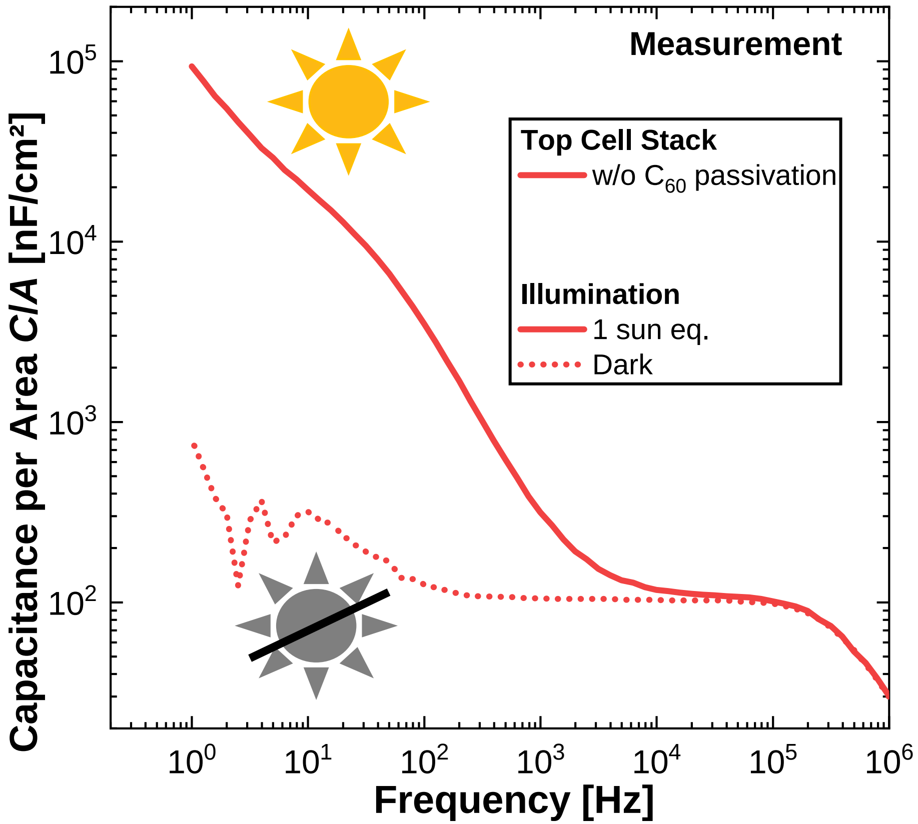

Ion-Induced Capacitances under Illumination

Experimental Comparison

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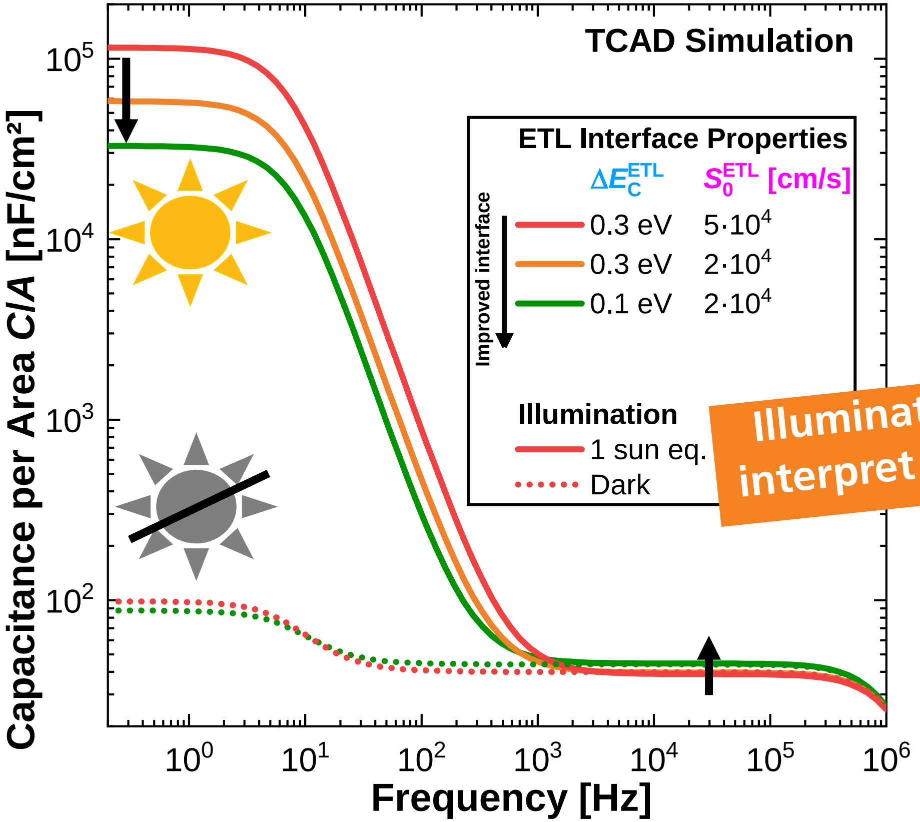
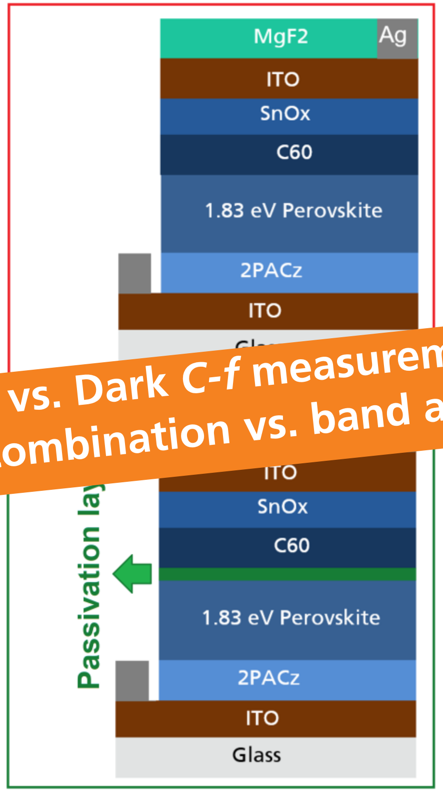
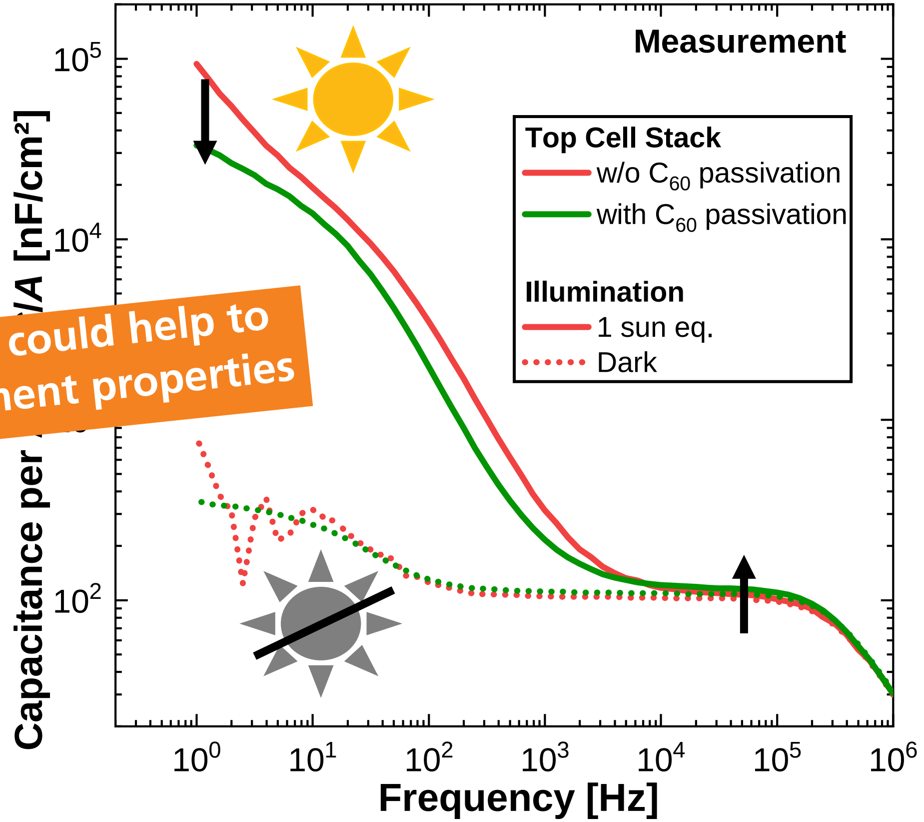
- Good qualitative agreement of TCAD model and measurements

Passivation layer leads to:

- Reduced low-f capacitance → Indicates lower recombination
- Increased high-f capacitance → Possibly also better ETL/Pero band alignment







Illuminated vs. Dark *C-f* measurements could help to interpret recombination vs. band alignment properties

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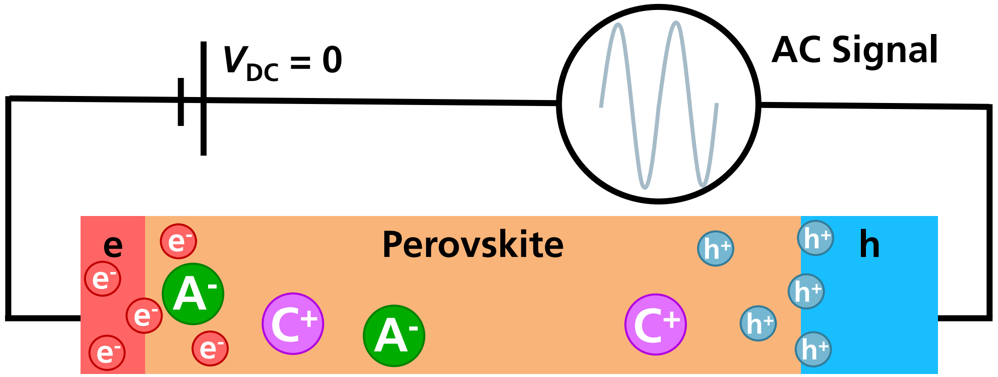
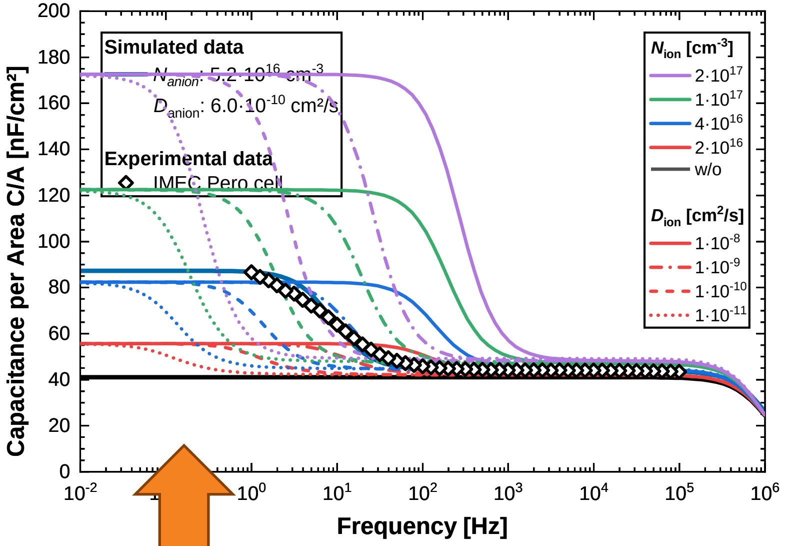
Conclusion



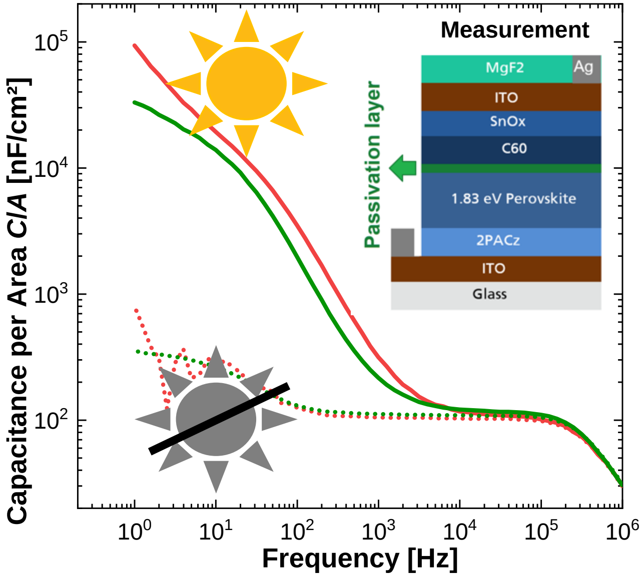


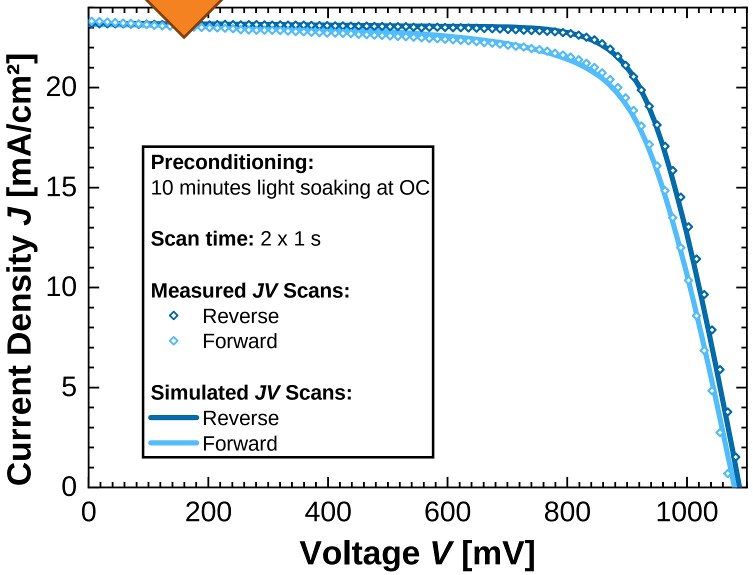
- TCAD Simulation of capacitance response of PSCs:
  - Impact of ionic properties
  - Good agreement with experimental data
  - Insights into physical origin of ionic capacitance

- Link ***C-f* response** to scan-time dependent ***JV* hysteresis**

- Investigation of ***C-f* curves under illumination**
  - Effect of band alignment and interface recombination
  - Experimental evidence

→Simulation-aided analysis of *C-f* curves contributes to **enhanced understanding**
→**Careful interpretation** of data is essential
→Measurements are **non-destructive** and on device level





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Thanks for your attention!

Upcoming Journal Publication in Solar RRL [1]

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[1] Messmer *et al.*, „Understanding Ion-Related Performance Losses in Perovskite-Based Solar Cells by Capacitance Measurements and Simulation", submitted to Solar RRL

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Federal Ministry for Economic Affairs and Climate Action

on the basis of a decision by the German Bundestag