Modeling hysteretic effects in perovskite solar cells

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Mathematical Modeling and Computational Physics (MMCP 2017), Dubna, July 3 - 7, 2017

Partial financial support within the Romania-JINR cooperation projects, JINR Order 220/10.04.2017, pp. 24 and 94 is acknowledged

Outline

- Perovskite solar cells

High power conversion efficiency (PCE>22%), Stability issues, Hysteretic effects

- Dynamic electrical model (DEM):

Equivalent circuit model, introducing a non-linear polarization component.

[1] G. A. Nemnes et al, *“Dynamic electrical behavior of halide perovskite based solar cells”*, Solar Energy Materials and Solar Cells 159, 197 (2017)

- Normal and inverted hysteresis effects:

Bias pre-poling and bias scan rate effects (theory and experiment)

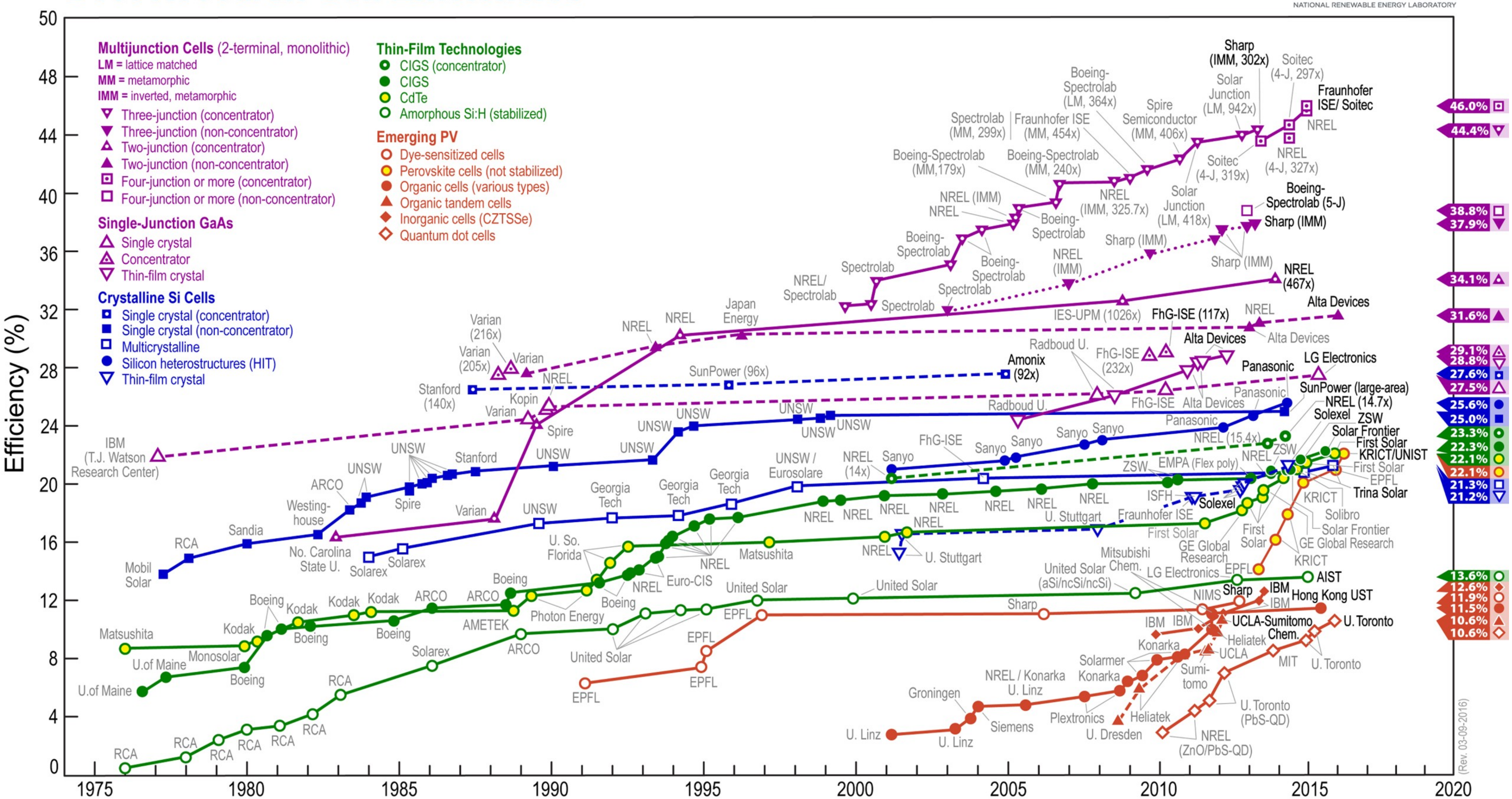
[2] G. A. Nemnes et al, *“Normal and inverted hysteresis in perovskite solar cells”*, J. Phys. Chem. C 121, 11207 (2017)

- Measurement protocol:

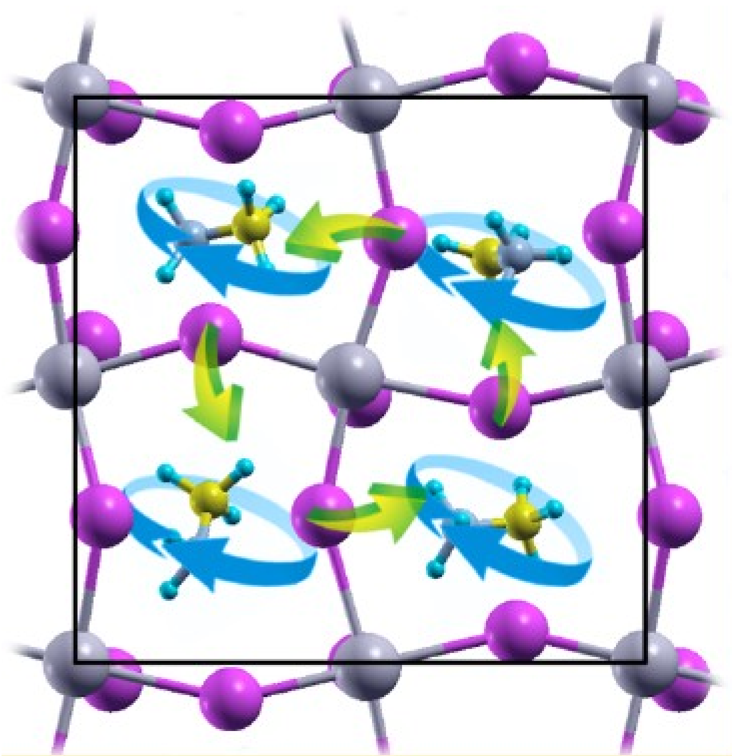
The importance of correlated forward and reverse bias scans

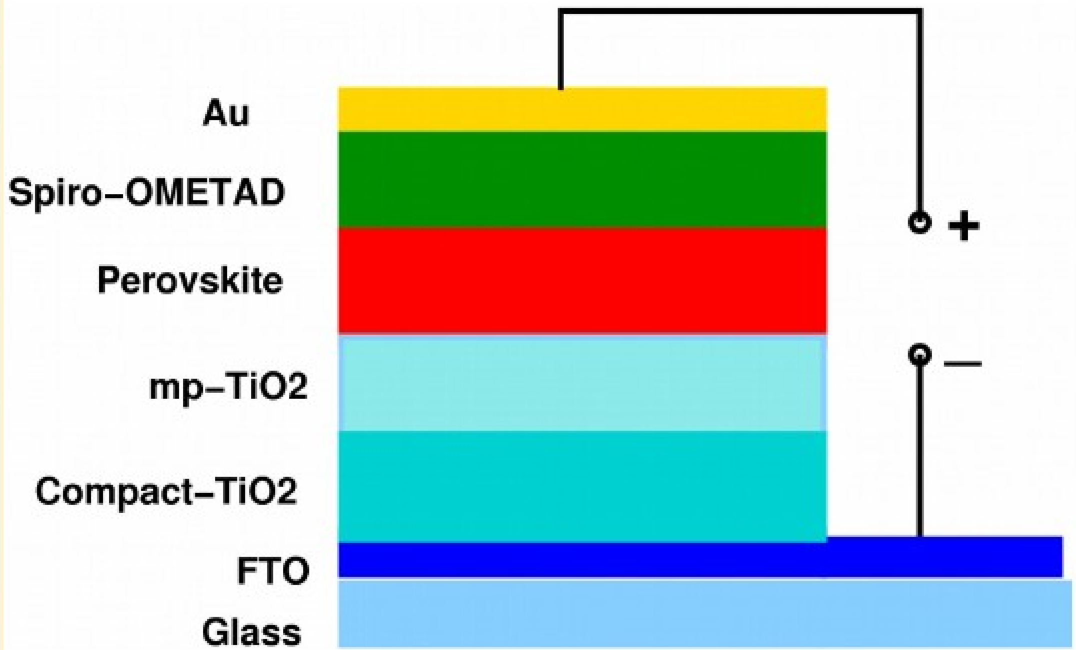
- Conclusions

Best Research-Cell Efficiencies



Material properties and device structure





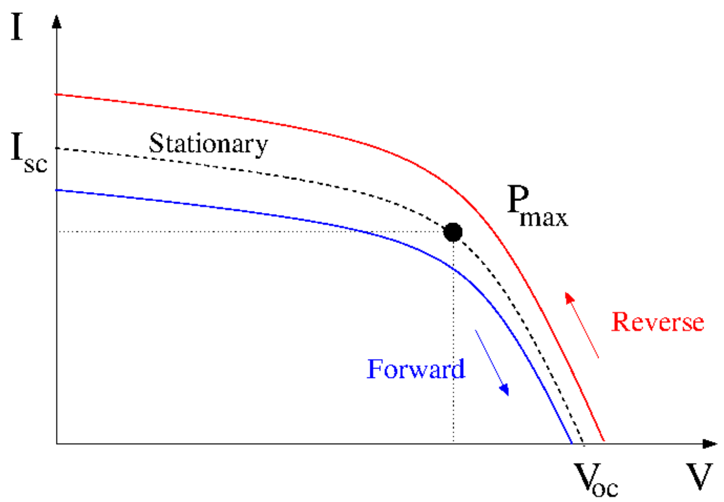
$CH_3NH_3PbI_3$ (MAPI)

High absorption coefficient, carrier mobility and diffusion length (> 1 μm)

Dynamic J-V hysteresis

- Dynamic hysteresis:
  - Forward and reverse bias scans yield different I-V characteristics (typically larger currents in reverse, explained by capacitive effects → *normal hysteresis*)
  - Depends on the pre-conditioning of the solar cell and on the bias scan rate

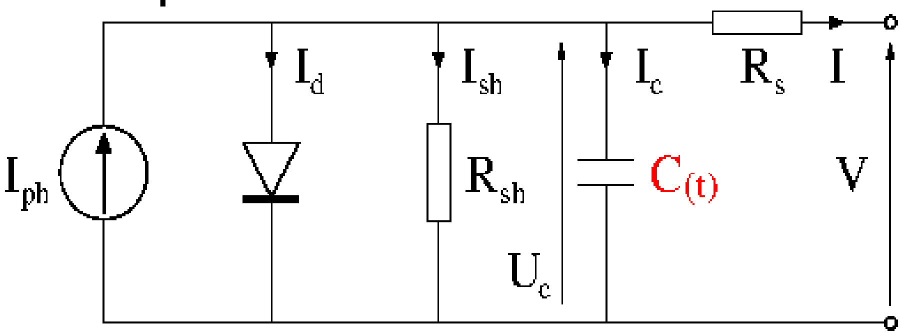
- Possible reasons for the hysteretic effects:
  - Giant dielectric constant
  - Ferroelectricity of the perovskite layer
  - Ion migration + accumulation of charges
  - Trapping-detrapping of charges
  - Unbalanced distributions of electrons and holes



- *Why investigate hysteretic effects ?*
  - A challenge for a *correct determination of the PCE.*
  - But it provides *further insight about the solar cell operation.*
  - Can be correlated *with solar cell degradation*

Dynamic electrical model (DEM)

Equivalent circuit:



$$I_{ph} = I_d + I_{sh} + I_c + I$$

C(t) modeled as P(t)

$P(t) = P_l(t) + P_{nl}(t)$

$$P_l(t) = \epsilon_0 \chi_l E(t)$$
$$\epsilon = (1 + \chi_l)\epsilon_0$$

Coupled system of equations:

(1)
$$-R_s C_0 \frac{\partial I}{\partial t} = I_s \left(e^{\frac{q(V+IR_s)}{nk_B T}} - 1 \right) + \left(\frac{R_s}{R_{sh}} + 1 \right) I + \frac{V}{R_{sh}} + C_0 \frac{\partial V}{\partial t} + \mathcal{A} \frac{\partial P_{nl}}{\partial t} - I_{ph}$$

Capacitor current:

$$I_c = C_0 \frac{\partial U_c(t)}{\partial t} + \mathcal{A} \frac{\partial P_{nl}(t)}{\partial t}$$

(2)
$$\frac{\partial P_{nl}}{\partial t} = \frac{P_{nl,\infty}(U_c(t)) - P_{nl}(t)}{\tau}$$
with
$$P_{nl,\infty} = (U_c / V_{oc}) P_\infty$$

Initial conditions: $I(t=0) = I_0 \quad P_{nl}(t=0) = P_0.$

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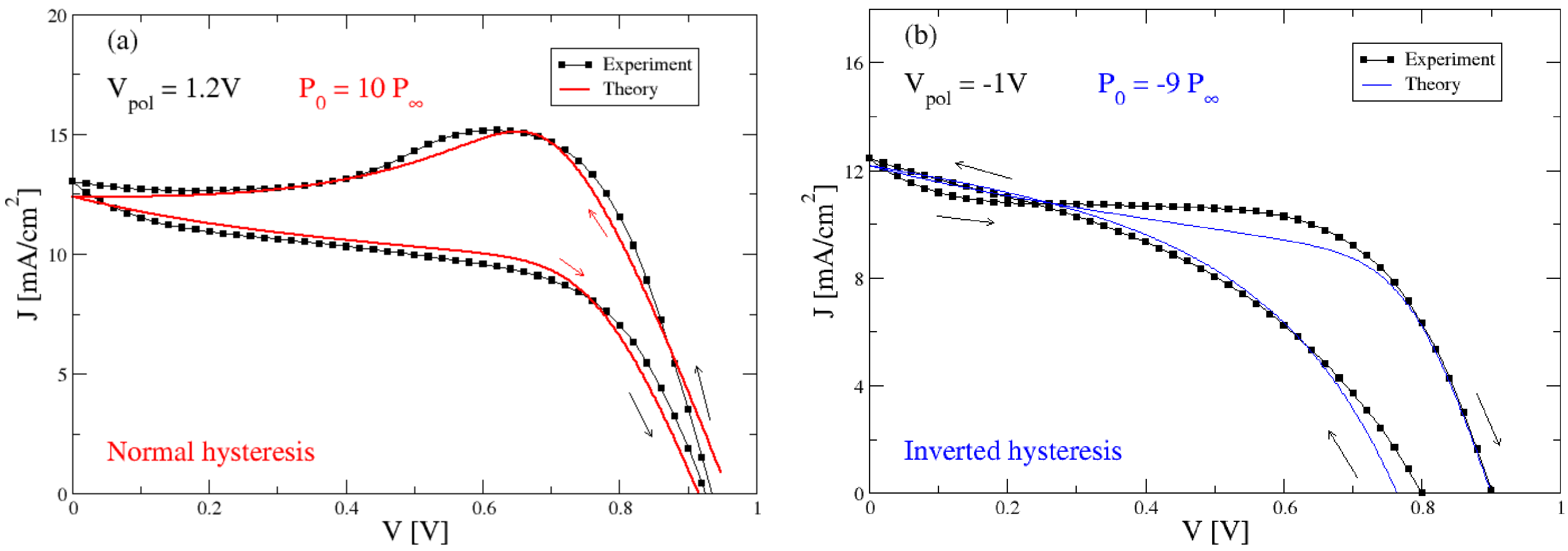
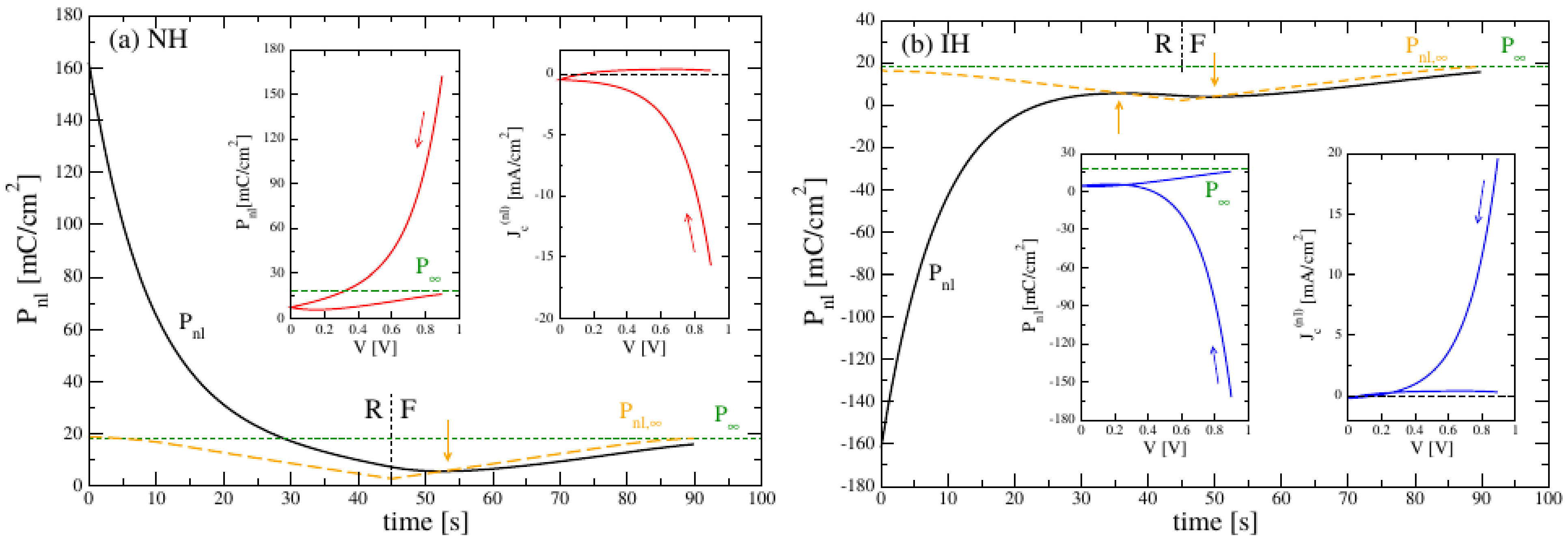
Normal and inverted hysteresis



Dynamic electrical behavior of perovskite solar cells under bias pre-poling:
(a) *normal* hysteresis and (b) *inverted* hysteresis.

Normal and inverted hysteresis : $P_{nl}(t)$

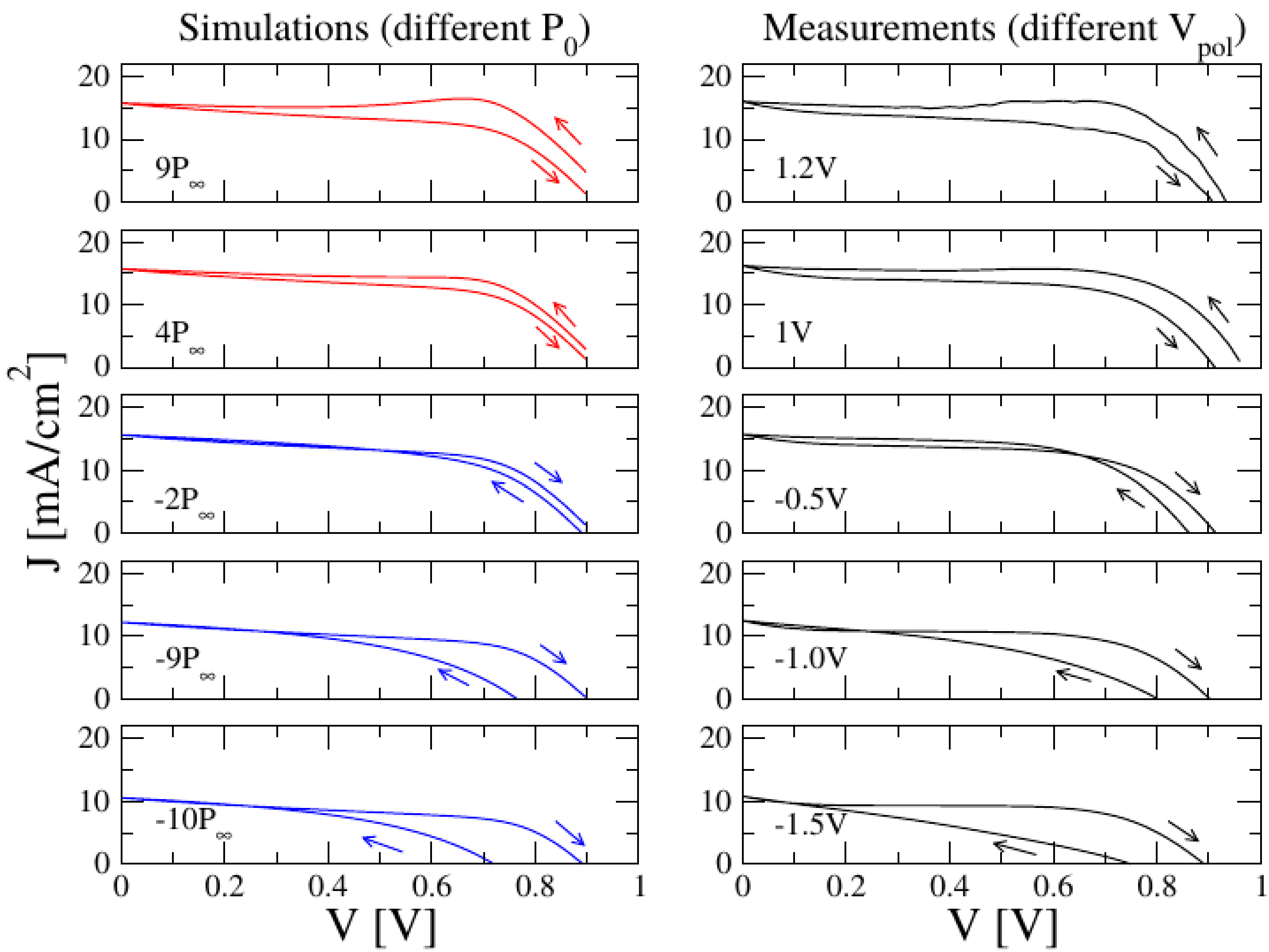


Normal hysteresis

Inverted hysteresis

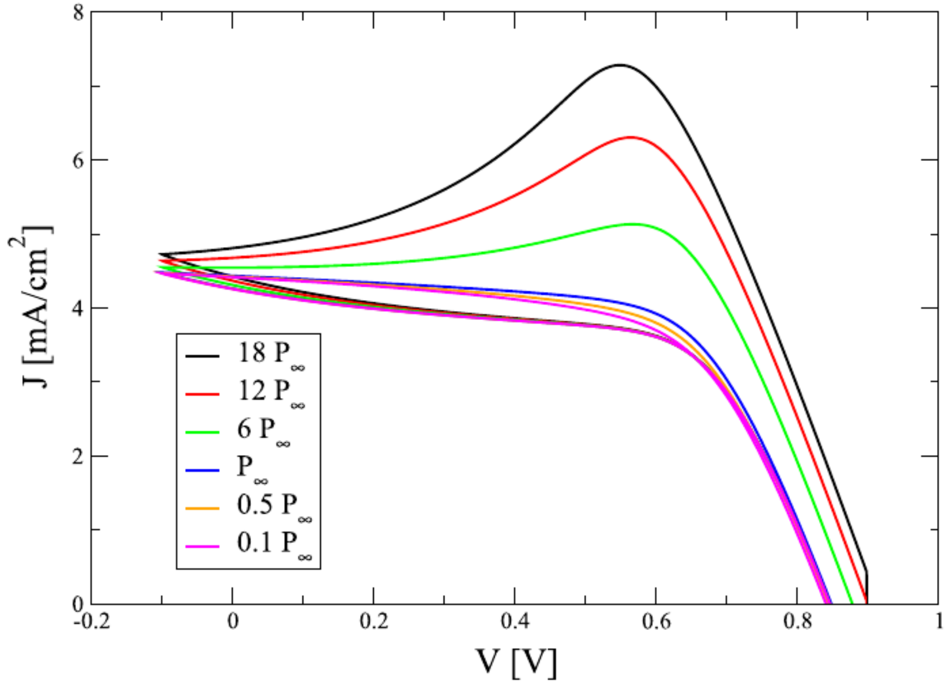
Time evolution of the non-linear polarization charge P_{nl} for NH (a) and IH (b).

Normal and inverted hysteresis

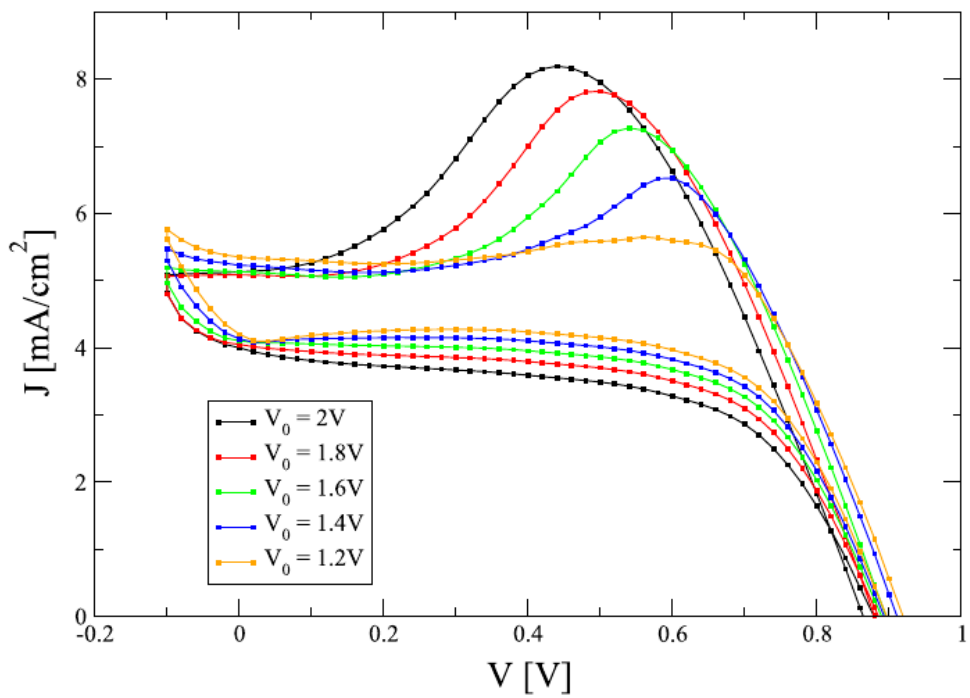


Simulation vs. experiment: effect of pre-poling bias.

Increasing the poling bias

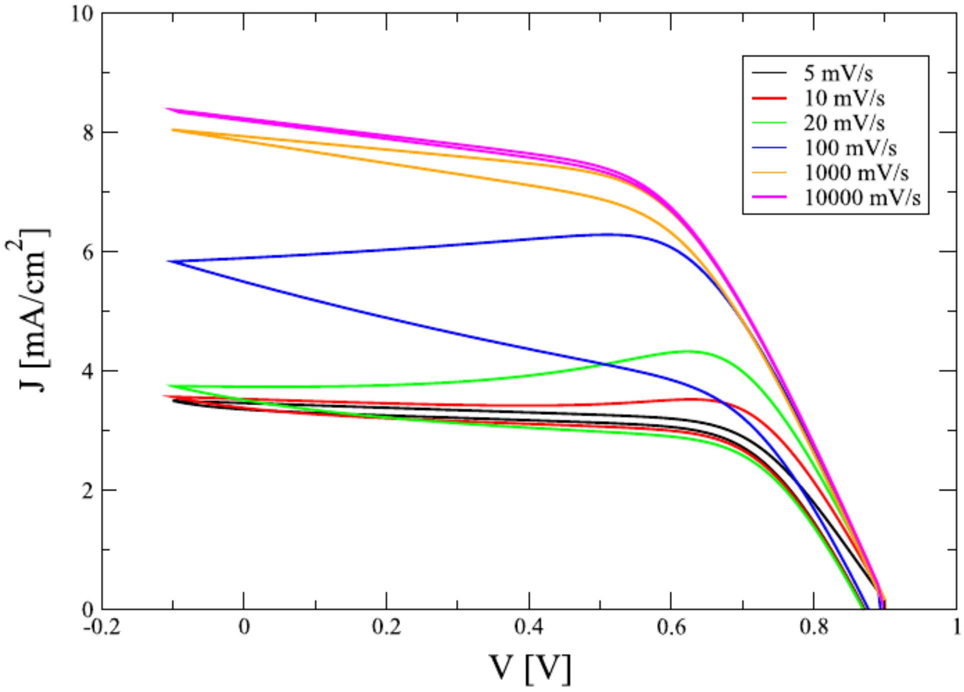


Theory (P0)

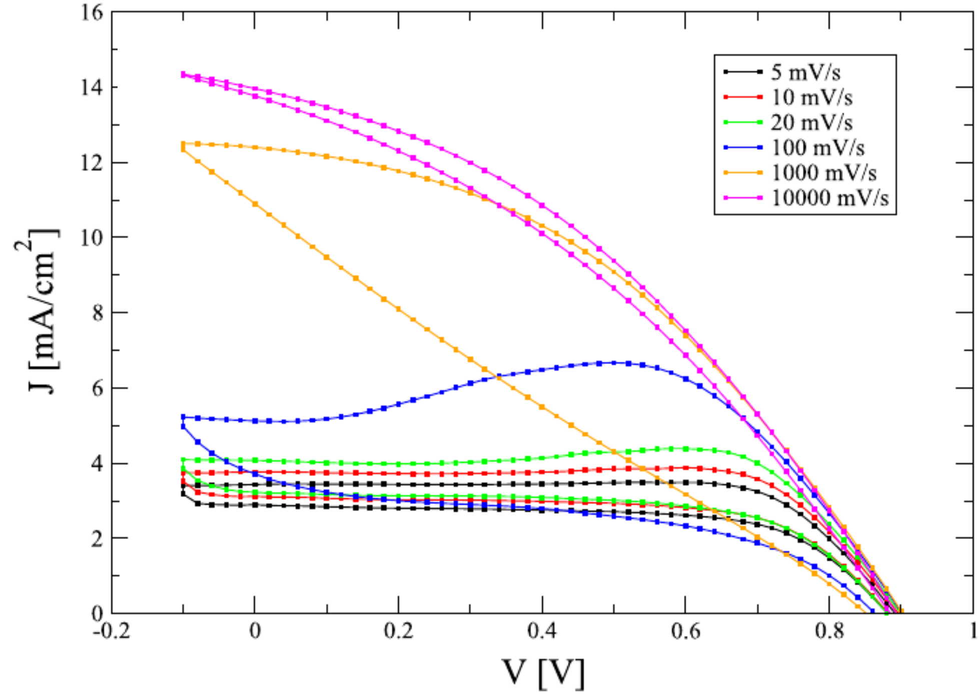


Experiment (V0)

Effect of the bias scan rate



Theory (dV/dt)



Experiment (dV/dt)

Measurement protocol

Three-step measurement protocol:

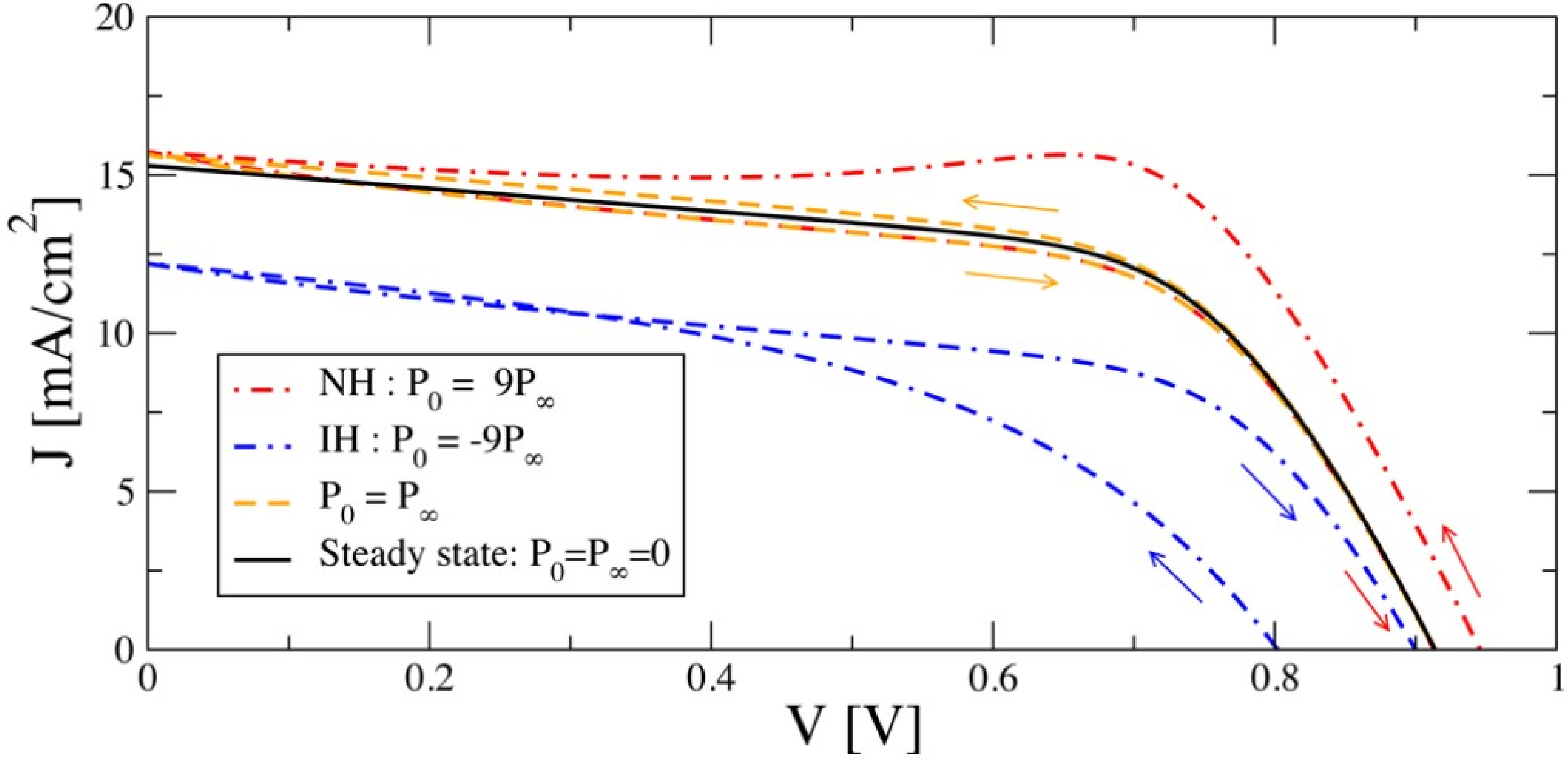
1. Stabilization at the open circuit bias → V_{oc}

2. Bias pre-poling at V_{oc} for a time t_{pol}

3. Actual measurement:

   A continuous reverse-forward sweep starting from V_{oc}

Measurement protocol



Comparing J-V characteristics at different bias pre-poling conditions: over-polarization (NH), inverse polarization (IH), minimal polarization and steady state.

Conclusions

- A dynamic electrical model (DEM) was proposed in form of an equivalent circuit, where the capacitor current is modeled by the time variation of the non-linear polarization.

- A particularly simple *Ansatz* for the time dependence of P_{nl} was introduced, explaining the hysteretic behaviors: pre-poling effects (overshoot in the reverse current), the enhanced hysteresis at intermediate scan rates and the increase (NH) / decrease (IH) of the short-circuit current at high rates.

- Normal and inverted hysteresis may be obtained in the same sample, with different poling conditions. *The DEM unifies two apparently different forms of hysteresis.*

- The analysis of the hysteretic effects represents an important issue for a correct determination of the PCE → reliable measurement protocols are required!

- The DEM provides the framework and is a practical tool for the calibration of microscopic descriptions.

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