RENEWABLE AND SUSTAINABLE ENERGY INSTITUTE

**NSF International Research Experience for Students (IRES)**
*Perovskites – A Solution to Global Energy Conversion Needs*

# Uncovering the Effect of Mobile Ions on Degradation in Perovskite Solar Cells Under Reverse Bias

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*Perovskite solar cells (PSCs) pass current and degrade quickly in reverse bias, limiting their operational stability. However, simple band diagrams indicate that PSCs should not pass current in reverse bias. Asymmetry in the mobile ion distribution has been hypothesized to cause steep band bending and allow a tunneling current to flow, but typical reported mobile ion concentrations of* $\sim 10^{17}$ *ions/cm*$^3$ *are too small to explain the strong observed current. Here, we explore the distribution of mobile ions and dopants in PSCs throughout reverse bias and recovery. Changes in the amount and distribution of mobile ions and dopants are linked to loss in PCE during reverse bias, and restoration of PCE during recovery in forward bias.*

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## Introduction

Perovskite solar cells (PSCs) have the potential to increase efficiency and reduce the cost of solar panels. However, PSCs experience extreme degradation under reverse bias when some cells in a series-connected panel become shaded due to fallen leaves, dust, snow, or other factors. In reverse bias, PSCs degrade quickly, often losing over 70% of their initial power conversion efficiency (PCE) in minutes.[1] Understanding the cause of degradation under reverse bias is an important step towards preparing PSCs for commercial implementation.

Under reverse bias conditions, PSCs are expected to behave as a typical diode in the "off" direction, passing no current. However, holding devices at reverse bias voltages results in current flow and extreme degradation. Bowring et al. proposed that positively charged mobile ions, most likely iodine vacancies ($V_I^+$), drift to the hole transport layer (HTL) under reverse bias while negatively charged ions are immobile.[1] The resulting asymmetric ion distribution causes asymmetric band bending, leading to holes tunneling through the electron transport layer (ETL) into the perovskite valence band, causing current flow. Oxidation of iodide by the injected holes is proposed as the cause of degradation. Density functional theory calculations, alongside measurements under rapidly changing voltage and illumination conditions, support the existence of pronounced differences in the mobilities of cations and anions.[1–3] However, typical reported mobile ion densities in perovskite solar cells range from about $10^{17}$ to $10^{18}$ ions/cm$^3$ which are too low to bend the energy bands enough to cause the strong current observed in PSCs under reverse bias.[4,5]

We propose a model to explain reverse bias current in PSCs by adding electrochemical reactions to the asymmetric ion distribution model. Electrochemical reactions in the perovskite layer create ionic defects which increase the mobile ion density enough to cause a strong tunneling current. In this model, iodine is oxidized likely near the ETL forming highly mobile iodine vacancies ($V_I^+$). At the same time a species is reduced near the HTL, forming low mobility species ($X^-$). Iodine vacancies ($V_I^+$) then drift to the HTL, leading to flat bands near the HTL and center of the perovskite, with steep bending near the ETL, letting holes tunnel into the perovskite valence band.

## Results & Discussion

The model developed to explain current flow in reverse bias relies on the creation of mobile ions through electrochemical reactions, which requires the perovskite layer to be able to transfer charge to the contacts. Figure 1a shows how the ITO typically used as a bottom contact in PSCs has large spikes which are not covered completely by a spin cast HTL. The ITO will penetrate through the HTL, causing ITO-perovskite contact (Figure 1b) which allows electrochemical reactions to occur.

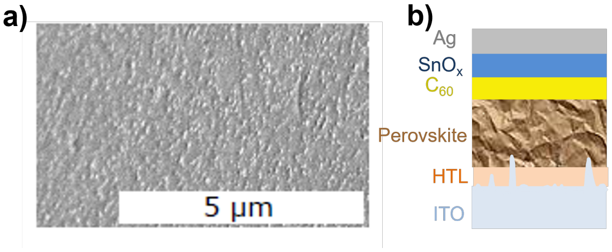

Figure 1. (a) SEM image of ITO with 5nm of spin cast HTL on top. (b) Diagram of perovskite solar cell including ITO spikes.

Current transient measurements were used to extract mobile ionic density in PSCs using the method shown in Figure 2a. When held at a negative voltage, the ions in a PSC reorganize due to the electric field. Upon switching to 0V the electronic current will stabilize quickly, and the ion re-equilibration current can be measured. Integrating the resulting current provides the number of mobile ions in the PSC. Figure 2b shows the displaced charge increasing after time under reverse bias, indicating that mobile ions are being created. In forward bias, the mobile ion density decreases towards its initial value (Figure 2b). These observations support the proposed model by indicating that mobile ions are created in reverse bias, and indicate that the reaction can be reversed in forward bias, decreasing the number of mobile ions.

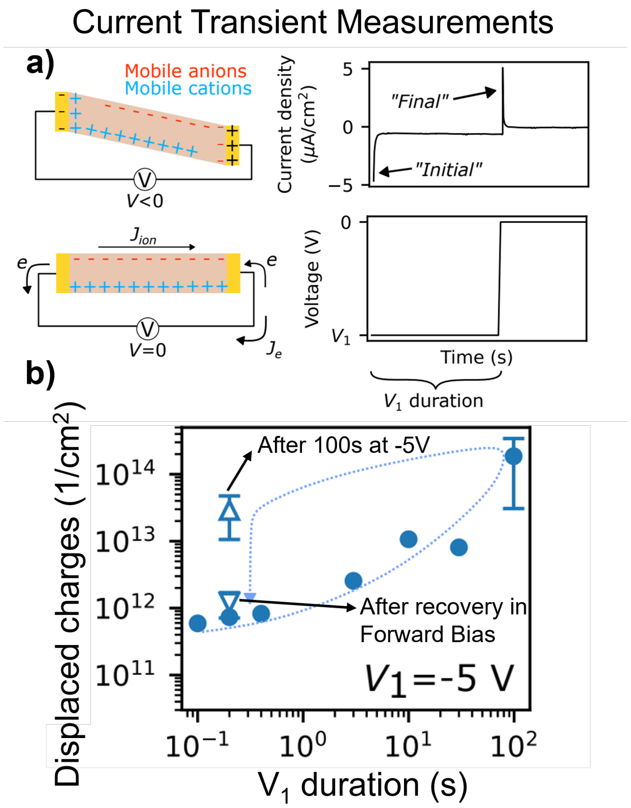

Figure 2. (a) Diagram showing how switching the voltage from V1 to 0 V can measure the mobile ion density in a PSC. (b) Measured mobile ion density in a PSC with no HTL during reverse bias.

The reversibility of the mobile ion density after recovery in forward bias is interesting because PSCs sometimes show partial recovery in PCE after reverse bias.[6] To explore how recovery in PCE is related to ion density, the capacitance vs. voltage of PSCs after reverse bias and recovery was measured. Using the well-known Mott Schottky equation $\frac{1}{C^2} = \frac{2(V_{bi}-V)}{qN_{charge}\epsilon_r A^2}$, $N_{charge}$ represents the defect density at high frequencies and the mobile ion density at low frequencies. The frequencies used in these measurements were chosen based on a measured capacitance vs. frequency plot in accordance with previous literature.[7,8] Figure 3a shows the resulting capacitance-voltage data measured at 5 Hz. The linear region present initially disappears after 15 hours at -3 V, making it difficult to measure the mobile ionic density, however, the device slowly approaches its initial measurement during recovery at +0.2 V. The data at 10 kHz has a clear linear region that is affected by reverse bias and recovery. Figure 4 shows the normalized $N_{defects}$ from the 10 kHz C-V data and the normalized PCE. The initial point is after reverse biasing the device for 15 hours at -3 V, then as the device is held at +0.2V, both the PCE and defect density recover at very similar rates.

From all the collected data, it appears that reverse bias increases the mobile ion density while decreasing the defect density and PCE. During recovery, the mobile ion density decreases back towards its initial value, while the defect density and PCE both increase towards their initial values. The PCE decrease is caused mainly by a decrease in fill factor, indicating the formation of a charge extraction barrier during reverse bias. Including the increase of mobile ions, likely iodine vacancies near the HTL, it is possible that $PbI_2$ may be forming a charge extraction barrier near the HTL in reverse bias. The $PbI_2$ layer may be trapping or recombining charges, leading to the perceived lower defect density after reverse bias at low voltages (Figure 4), due to the charges being trapped in this layer.

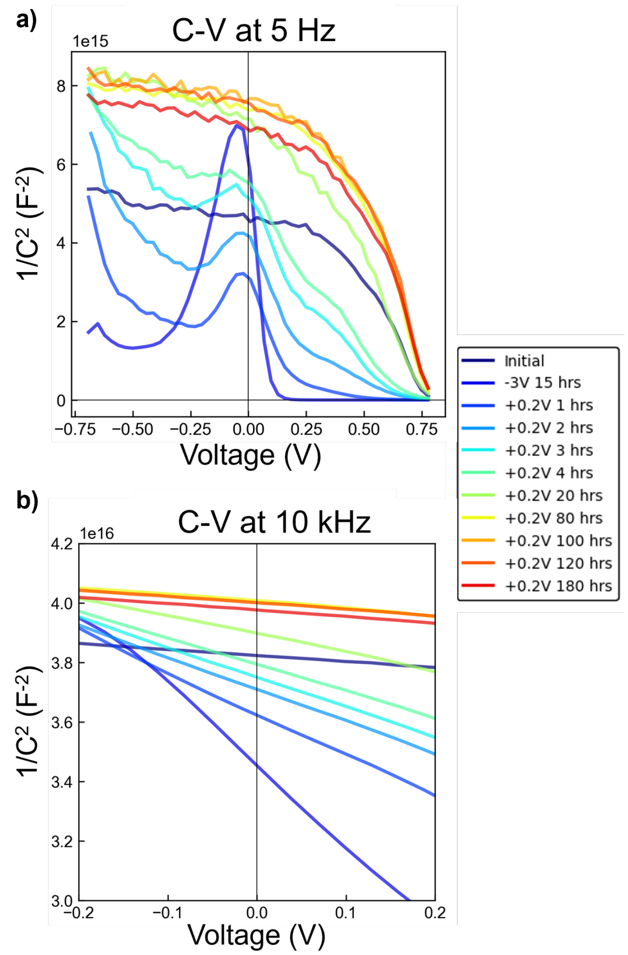

Figure 3. (a) Capacitance vs. Voltage of a PSC (ITO/5nm PTAA/PVSK/$C_{60}$/$SnO_x$/Ag) at 5 kHz during reverse bias and recovery. (b) C-V of the same PSC at 10 kHz.

Future work must be done to further refine the proposed model and incorporate the low and high frequency capacitance vs. voltage data, PCE data, and voltage-switch data to understand exactly what mechanisms cause degradation and current flow under reverse bias, and how devices can be recovered. Next steps include modeling the capacitance vs. voltage curves of PSCs at low frequencies to compare with experimental data, repeating testing on small-area devices to avoid defects which significantly affected the collected data, and doing x-ray diffraction and XPS to look for evidence of $PbI_2$ and electrochemical reaction products at the interfaces of the perovskite layer.

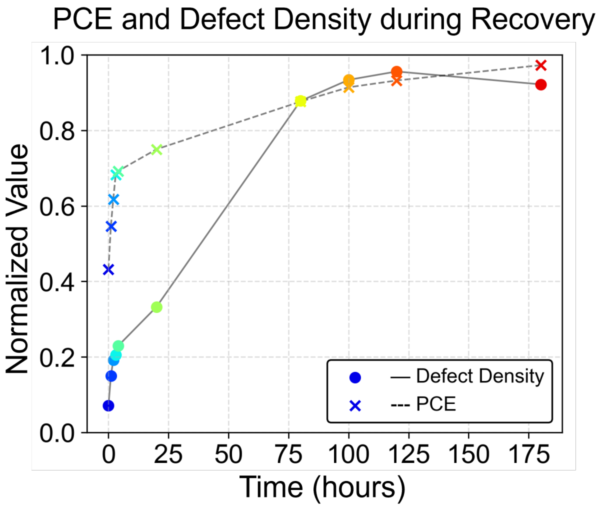

Figure 4. Normalized PCE and defect density during recovery at +0.2V after reverse biasing at -3V for 15 hours.

## Conclusions

Perovskite solar cells unexpectedly pass current under reverse bias conditions, resulting in extreme degradation which limits their stability in real-world conditions. The current flow under reverse bias is likely caused by electrochemical reactions creating mobile ions which then distribute asymmetrically, allowing a tunneling current to flow. The loss in performance during reverse bias may be caused by accumulation of mobile ions at the device interfaces leading to the formation of a charge extraction barrier. Forward bias voltages can partially recover devices by reducing the number of mobile ions in the device, likely through opposite reactions. Future work is recommended to explore what specific electrochemical reactions occur, and how the charge extraction barrier forms.

## Acknowledgements

I would like to thank Dr. Emil List-Kratochvil and Dr. Stefan Gall for their assistance with this project.

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