Investigation of Degradation in Perovskite Solar Cells Using Thermal Hysteresis of Photocurrent

Dhruba B. Khadka[1], Masatoshi Yanagida[1] and Yasuhiro Shirai[1]

[1] Photovoltaics Materials Group, Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

Abstract — **Investigating the degradation mechanisms of perovskite solar cells (PSCs) is paramount to addressing stability-related issues. Our study delves into the deterioration of PSC by probing thermal hysteresis of photocurrent (THPC) and thermally active ionic dynamics. THPC emission reveals alterations influenced by interfacial ionic or charge accumulation. Photogenerated current exhibits a significantly higher degree of variation in degraded devices with a wide range of ionic charge densities. This highlights the substantial influence of thermally active ionic charge on PSC performance degradation, particularly in devices with lower photocurrent. This study highlights the direct correlation between the degradation of PSC devices and the presence of thermally activated charges.**

I. Introduction

Perovskite solar cell (PSC) under operation accelerates the loss of power conversion efficiency (PCE).[1], [2] The degradation is caused by external factors such as irradiation, heat, moisture, oxygen, electric bias, and strain. [3], [4], [5] The degradation mechanism is stimulated with increased chemical kinetics at elevated temperatures. Since the photocurrent loss is usually observed in degraded PSCs, monitoring photocurrent under different conditions could provide insights for understanding the intrinsic factor of the device degradation.[6]

Direct monitoring of the electrically active defects in the absorber layer has been reported by thermal spectroscopy techniques;[7],[8] such as thermal admittance spectroscopy,[4], [9], [10], [11], [12] and thermally stimulated photocurrent (TSC).[13] The cause of operational instability of PSCs at elevated temperatures remains elusive. The temperature of PSC could easily reach 35–55 ºC under working conditions and the photocurrent is driven by varying temperatures. Thermally driven photocurrent could have a significant effect on fresh and aged PSC. [14]

Here, to understand the degradation mechanism, we have collected thermally triggered photocurrent. Then, the thermal hysteresis of photocurrent (THPC) characteristic extracted from photocurrent difference under heating and cooling of PSC is used to unravel the factors contributing to the reduction in photocurrent in PSCs operating under conditions akin to the real-world perovskite working temperature range. we monitored the thermal-driven photocurrent in the PSC. The THPC data of fresh and degraded devices demonstrated a stark difference in photocurrent variation under different rates of temperature variation. A degraded device revealed deeper traps than a fresh device. This report presents the mechanism behind the degradation of PSCs driven by photocurrent loss.[15]

II. Experimental Sections

A. Device fabrication:

The details of the precursor solution and device fabrication can be found in the earlier reports.[16], [17] In brief, for the fabrication of inverted PSCs, we have used ITO substrate and NiO_x deposited by sputtering mentioned earlier.[18], [19] For the fabrication of perovskite films, we adopted two-step depositions PbI_2 deposition followed by dripping of the MAX precursor solution (a mixture of MAI+MACl.[11], [20] For completion of the device, PCBM as ETL, AZO layer, and Ag. Devices were sealed by encapsulation glass and UV-curable resins before the subsequent measurement in ambient conditions.

B. For operational stability testing:

The J–V curves were measured under 1 sun with an AM 1.5G spectral filter (100 $mWcm^{-2}$) coupled to an MPPT system. We placed the encapsulated PSCs in an enclosed system under air ambient for stability monitoring. The devices were kept under illumination and heat stress (50-60 ºC).

For THPC measurement, the devices were placed under 1 sun white light illumination and photocurrent was monitored using the PAIOS measurement system by changing temperature from 240 to 360 K under different heating and cooling rates (dT/dt= x K/min).

C. Equations

Considering the thermal dynamics of photocurrent hysteresis, THPC spectra can be resolved by assigning resonance temperature or thermal energy with multiple peak analyses. The following equation was used for evaluating charge accumulation or ionic defects in THPC in fresh and aged PSCs.

$$Q_{THPS} = \frac{1}{\beta T} \int_{T_1}^{T_2} I_{THPC}^{T_t} \, dT \qquad [1]$$

where T_t is a resonance temperature peak and β (K/s) is the heating or cooling rate.

III. RESULTS AND DISCUSSION

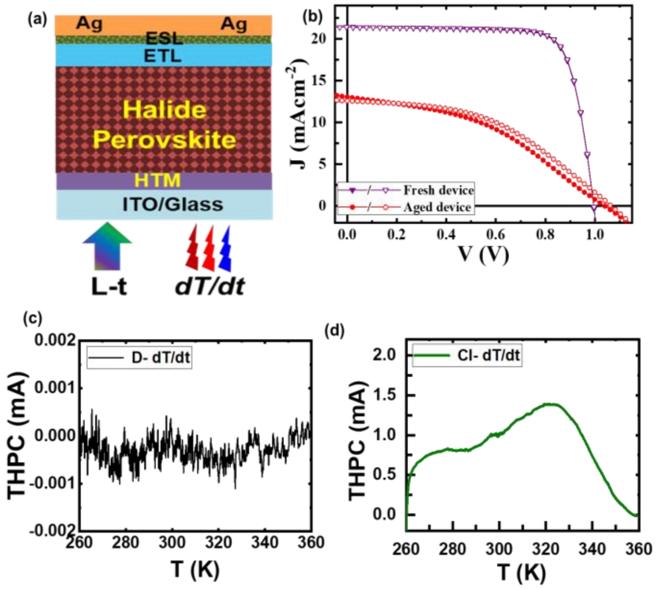

Fig. 1. Schematic of the THPC spectra measurement (a), J-V curves of fresh and aged PSCs (b). THPC spectra (c) under dark and (d) under continuous illumination (CI).

Fig. 1a shows the schematic of THPC measurement across a temperature spectrum spanning from 240 to 360 K. Current-voltage (*J-V*) curves of fresh and aged PSCs are shown in Fig. 1b. The fresh device of PCE is ~ 15.677% (J_{SC}~ 20.53 mAcm^{-2} and V_{OC}~ 0.998 V). The PCE of the PSCs dropped to 6.14% (J_{SC}~ 12.59 mAcm^{-2} and V_{OC}~ 1.06 V) for the aged PSCs placed at under heat and light stress (at 50 ± 5 ºC and t >1000 hrs under continuous illumination). The figure shows that the photocurrent and FF dropped to 40 and 33% in the aged PSCs. This observation is parallel to other reports. The drop in PCE driven by photocurrent has been widely reported in degradation studies.[21], [22]

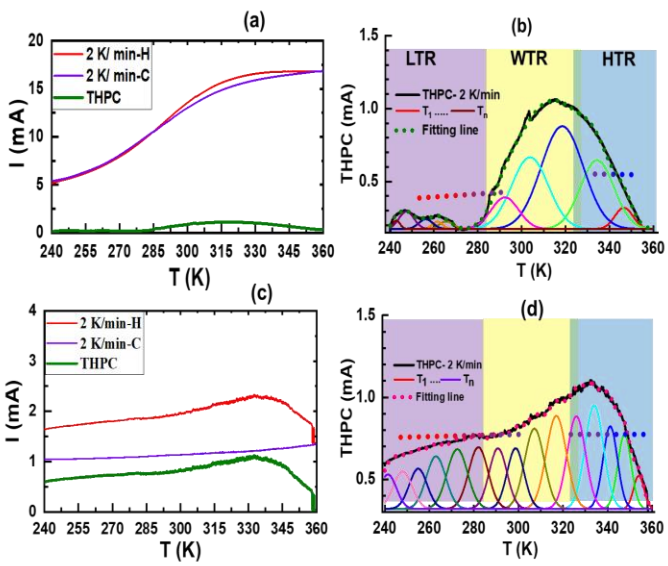

Fig. 2. THPC spectra of the fresh (a, b) and aged (c, d) PSCs under temperature drifting rate of 2 K/min in the temperature range (240-360 K) and corresponding fitting spectra, respectively. Here the shaded regions indicate a low-temperature range (LTR), working temperature range (WTR), and high-temperature range (HTR). The three curves under THPC spectra display representative spectral fitting under the LTR, WTR, and HTR regimes. The dotted arrows represent arbitrary multiple peaks (T1, …. ,Tn) fitting of THPC spectra. The accumulated charge is calculated by evaluating the area under respected fitted curves (Table 1).

For monitoring the THPC, we have collected the THPC data under dark, and continuous illumination (CI) (Figure 1c, d). Out of these three, the THPC under CL demonstrates a distinct feature.

The photocurrent in PSC and THPC at varying temperatures from 240-360 K with a heating or cooling rate of 2 K/min for the fresh (Fig. 2a) and aged (Fig. 2c). For the aged PSC, the photocurrent driving under heating and cooling revealed a stark difference compared to the fresh PSCs. The fitting of these THPC spectra with multiple resonance temperatures (T_t) is depicted in Fig. 2b,d. Th charge accumulation is summarized in Table 1. We observed a notable dominance of charges triggered by thermal agitation. This suggests that, in aged PSCs, the charges or ions accumulated at the interface and the material have become more responsive to changes in temperature under a wide range. These results indicate that the photocurrent loss in aged devices could be a consequence of the dominance of thermally active ions or charges accumulated at deteriorated interfaces under light and heat stress.

Table 1.THPC spectra analysis: accumulated charge (Q_{THPC}) and percentage sharing in aged PSC in defined temperature ranges.

	Fresh		Aged	
	Q_{THPC} (mC)	Q_{THPC} (%)	Q_{THPC} (mC)	Q_{THPC} (%)
LTR (240-283 K)	0.429	10.24	1.927	33.95
WTR (283-323 K)	2.452	58.52	2.105	37.08
HTR (323-363 K)	1.309	31.24	1.644	28.97
Total	4.191	100	5.677	100

IV. SUMMARY AND CONCLUSIONS

This report presents the degradation of PSCs by THPC analysis. The intrinsic point defects and defect density in fresh and degraded PSCs were investigated by fitting THPC spectra. It shows THPC emissions with a complex thermally active charge or ion accumulations due to interfacial deterioration. These photoactive mobile charges are found to be more pronounced in aged PSC with higher charge densities. This plays a detrimental role in the loss of photo-current in the degraded PSCs. Our report corroborates a direct link between PSC device degradation and thermally triggered charge accumulation.

REFERENCES

[1] K. Domanski, E. A. Alharbi, A. Hagfeldt, M. Grätzel, and W. Tress, 'Systematic investigation of the impact of operation conditions on the degradation behaviour of perovskite solar cells', *Nat Energy*, vol. 3, no. 1, pp. 61–67, Jan. 2018, doi: 10.1038/s41560-017-0060-5.

[2] D. B. Khadka *et al.*, 'Advancing Efficiency and Stability of Lead, Tin, and Lead/Tin Perovskite Solar Cells: Strategies and Perspectives', *Solar RRL*, vol. 7, no. 21, p. 2300535, Nov. 2023, doi: 10.1002/solr.202300535.

[3] D. Wang, M. Wright, N. K. Elumalai, and A. Uddin, 'Stability of perovskite solar cells', *Solar Energy Materials and Solar Cells*, vol. 147, pp. 255–275, Apr. 2016, doi: 10.1016/j.solmat.2015.12.025.

[4] D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, 'Degradation of encapsulated perovskite solar cells driven by deep trap states and interfacial deterioration', *J Mater Chem C Mater*, vol. 6, no. 1, pp. 162–170, 2018, doi: 10.1039/C7TC03733C.

[5] D. B. Khadka, Y. Shirai, M. Yanagida, K. Uto, and K. Miyano, 'Analysis of degradation kinetics of halide perovskite solar cells induced by light and heat stress', *Solar Energy Materials and Solar Cells*, vol. 246, p. 111899, Oct. 2022, doi: 10.1016/j.solmat.2022.111899.

[6] D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, 'Insights into Accelerated Degradation of Perovskite Solar Cells under Continuous Illumination Driven by Thermal Stress and Interfacial Junction', *ACS Appl Energy Mater*, vol. 4, no. 10, pp. 11121–11132, Oct. 2021, doi: 10.1021/acsaem.1c02037.

[7] V. G. Litvinov *et al.*, 'Investigation of Deep-Level Defects Lateral Distribution in Active Layers of Multicrystalline Silicon Solar Cells', *MRS Adv*, vol. 2, no. 53, pp. 3141–3146, Nov. 2017, doi: 10.1557/adv.2017.376.

[8] X. Mathew, 'Photo-induced current transient spectroscopic study of the traps in CdTe', *Solar Energy Materials and Solar Cells*, vol. 76, no. 3, pp. 225–242, Mar. 2003, doi: 10.1016/S0927-0248(02)00276-3.

[9] D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, 'Attenuating the defect activities with a rubidium additive for efficient and stable Sn-based halide perovskite solar cells', *J Mater Chem C Mater*, vol. 8, no. 7, pp. 2307–2313, 2020, doi: 10.1039/C9TC06206H.

[10] D. B. Khadka, Y. Shirai, M. Yanagida, T. Tadano, and K. Miyano, 'Interfacial Embedding for High-Efficiency and Stable Methylammonium-Free Perovskite Solar Cells with Fluoroarene Hydrazine', *Adv Energy Mater*, vol. 12, no. 38, p. 2202029, Oct. 2022, doi: 10.1002/aenm.202202029.

[11] D. B. Khadka, Y. Shirai, M. Yanagida, T. Masuda, and K. Miyano, 'Enhancement in efficiency and optoelectronic quality of perovskite thin films annealed in MACl vapor', *Sustain Energy Fuels*, vol. 1, no. 4, pp. 755–766, 2017, doi: 10.1039/C7SE00033B.

[12] D. B. Khadka, S. Y. Kim, and J. H. Kim, 'A Nonvacuum Approach for Fabrication of Cu2ZnSnSe4/In2S3 Thin Film Solar Cell and Optoelectronic Characterization', *Journal of Physical Chemistry C*, vol. 119, no. 22, pp. 12226–12235, Jun. 2015, doi: 10.1021/acs.jpcc.5b03193.

[13] J. Plans, M. Zieliński, and M. Kryszewski, 'Theory of the thermally-stimulated-current transport peak. Application to a dispersive transport case', *Phys Rev B*, vol. 23, no. 12, pp. 6557–6569, Jun. 1981, doi: 10.1103/PhysRevB.23.6557.

[14] A. Baldini and M. Bruzzi, 'Thermally stimulated current spectroscopy: Experimental techniques for the investigation of silicon detectors', *Review of Scientific Instruments*, vol. 64, no. 4, pp. 932–936, Apr. 1993, doi: 10.1063/1.1144145.

[15] D. B. Khadka, M. Yanagida, and Y. Shirai, 'Assessing degradation in perovskite solar cells via thermal hysteresis of photocurrent and device simulation', *Solar Energy Materials and Solar Cells*, vol. 281, p. 113319, Mar. 2025, doi: 10.1016/j.solmat.2024.113319.

[16] D. B. Khadka, Y. Shirai, M. Yanagida, J. W. Ryan, and K. Miyano, 'Exploring the effects of interfacial carrier transport layers on device performance and optoelectronic properties of planar perovskite solar cells', *J Mater Chem C Mater*, vol. 5, no. 34, pp. 8819–8827, 2017, doi: 10.1039/C7TC02822A.

[17] D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, 'Ammoniated aqueous precursor ink processed copper iodide as hole transport layer for inverted planar perovskite solar cells', *Solar Energy Materials and Solar Cells*, vol. 210, p. 110486, 2020, doi: https://doi.org/10.1016/j.solmat.2020.110486.

[18] M. G. M. Pandian *et al.*, 'Effect of surface treatment of sputtered nickel oxide in inverted perovskite solar cells', *Thin Solid Films*, vol. 760, p. 139486, Oct. 2022, doi: 10.1016/j.tsf.2022.139486.

[19] M. Yanagida, T. Nakamura, T. Yoshida, D. B. Khadka, Y. Shirai, and K. Miyano, 'Surface modification of sputtered NiOx hole transport layer for CH3NH3PbI3perovskite solar cells', *Jpn J Appl Phys*, vol. 62, no. SK, p. SK1054, Aug. 2023, doi: 10.35848/1347-4065/acd5dc.

[20] D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, 'Investigation of Degradation Kinetics of Perovskite Solar Cells by Accelerated Aging', in *2022 IEEE 49th Photovoltaics Specialists Conference (PVSC)*, IEEE, Jun. 2022, pp. 0001–0003. doi: 10.1109/PVSC48317.2022.9938939.

[21] S. Wang, Y. Jiang, E. J. Juarez-Perez, L. K. Ono, and Y. Qi, 'Accelerated degradation of methylammonium lead iodide perovskites induced by exposure to iodine vapour', *Nat Energy*, vol. 2, no. 1, p. 16195, Jan. 2017, doi: 10.1038/nenergy.2016.195.

[22] M. Saliba, M. Stolterfoht, C. M. Wolff, D. Neher, and A. Abate, 'Measuring Aging Stability of Perovskite Solar Cells', *Joule*, vol. 2, no. 6, pp. 1019–1024, Jun. 2018, doi: 10.1016/j.joule.2018.05.005.