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ภูมิอากาศเขตร้อนชื้น

Understanding parameters affecting operational stability of perovskite solar cells in
hot-humid climate

เสนอ

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Chapter 1: Introduction

With increasing energy demand from the population growth requiring more energy production from fossil fuel, those extra greenhouse gas released will exacerbate climate change problems. There is a need to harvest energy from a cleaner source that does not deteriorate the environmental situation. The sun is the most abundant source of energy that can be extracted to different usable form of energy, including heat and electricity. Photovoltaic (PV) device transform solar energy into electricity. Current commercial Silicon PV technology can produce electricity with record power conversion efficiency (PCE) above 26%. However, this requires hundred micrometers thick of materials to transform solar energy. Second and third generation of PV, namely vacuum-processed and solution-processed thin film PV, only require tens and less than one of micrometer, respectively, to convert solar energy.

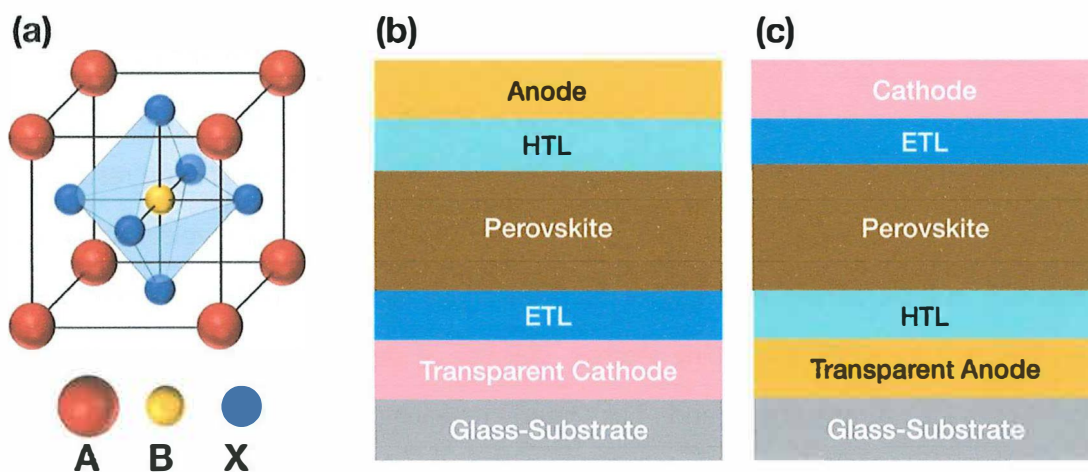


Figure 1 (a) Perovskite chemical structure where A, B and C represent cation (MA, FA), metal (Pb, Sn), and anion (I, Br), respectively. Standard (b) and inverted (c) architecture of perovskite solar cells

Organic-inorganic lead halide solar cells, referred to as perovskite solar cells, are the most promising third generation solar cells that can harvest solar energy as efficiently as 25.2% PCE in a single junction configuration and 29.1% PCE in tandem with silicon solar cells¹. On top of that, perovskite is a defect tolerant material, yielding high PCE solar cells even fabricated via low cost

solution-processing. As a result, variety of applications can be made utilizing perovskite materials, including large module solar cells, flexible electronics, light emitting diode, and smart windows. According to Li et al, single junction perovskite solar cells are 78% of the cost of silicon solar cells², making it economically feasible for real implementation. However, stability of perovskite solar cells is the bottleneck limiting commercialization.

Lead halide perovskites are hygroscopic and prone to decompose at elevated temperature.³ Moreover, conventional perovskite solar cells with titanium dioxide as an electron transporting layer are also UV-sensitive, catalyzing decomposition of perovskite when oxygen is presence.⁴ Mechanical stability of perovskites is also a big concern because perovskite absorber itself requires minimal force to fracture⁵ and there are multiple layers with thermal expansion coefficient mismatched that can lead to delamination between adjacent layers and thus loss of solar cell performance.⁶

Because there is no stability testing consensus or standard for perovskite solar cells, most stability testing of perovskite have been carried out in storage, referred to as shelf-stability, which does not provide a good control of environment, making it hard to compare the result between different research groups. Since perovskite is sensitive to heat, the second typical stability testing is carried out in inert atmosphere with extra stress from heat, referred to as thermal stability testing. This test is crucial in probing intrinsic stability of perovskite against decomposition at realistic operating temperature and has been revealing insightful mechanism such as decomposition with prolong aging at 85°C⁷ and metal counter electrode-perovskite reaction.^{8,9} The last commonly used condition for stability test includes light, ambient environment, and electrical bias (for some of the time), referred to as light stability. This test is the closest but not ideal in measuring operational lifetime of perovskite solar cells. Grancini et al. demonstrated one year stability of perovskite solar cells under 1 sun, 55°C in ambient without electrical bias of encapsulated perovskite solar cells.¹⁰ However, their test without electrical bias overlook a big issue of ion migration that complicates perovskite solar cells operation.

Due to ionic nature of lead halide perovskite^{11,12}, introducing high energy stressors, such as light or electrical field, can move mobile species, causing a change in electrical band or interface.^{13,14} Once those factors are removed, the mobile species diffuse back to normal, causing reversible effect. These effects are concerning especially for perovskite solar cells in operation. Figure 1 shows performance of perovskite solar cells in three different architecture: planar, mesoporous, and inverted solar cells, which were set to light-dark cycle every 12 hours.¹³ Depending on the solar cells architecture, the recovery time can take almost ten hours.

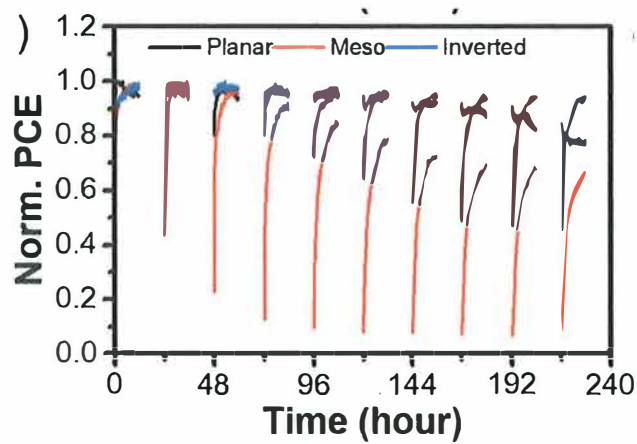


Figure 2 Normalized power conversion efficiency (PCE) of perovskite solar cells of three architecture: planar (black), mesoporous (red), and inverted (blue) as they go through 12-hour light-dark cycle.¹³

From all of above, there is still a need to understand perovskite solar cells behavior under operation when all the environmental stressors are presence and how to minimize the perovskite solar cells recovery to maximize energy production during daytime.

Objectives of this work

- 1 To diagnose critical factors affecting operational stability of perovskite solar cells
- 2 To understand recovery behavior of perovskite solar cells in operation

Chapter 2: Perovskite Solar Cell Fabrication

A typical perovskite solar cells architectures are shown in **Figure 1**– inverted and standard architecture. Since perovskite material is hygroscopic, the fabrication process requires low-humidity level environment for solution making and thin-film formation. A controlled atmosphere glovebox with moisture level below 0.1ppm is required for nice quality of perovskite film. While, for the hole and electron transport layer adjacent to the perovskite layer, a spin coater outside of the glovebox would be sufficient, even though some solution mixing might require a low moisture level atmosphere. Below are summary of required equipments for the fabrication process for each layer.

2.1 Equipments for perovskite solar cells fabrication

Electron transport layer (ETL)/ Hole transport layer (HTL) fabrication equipments:

1. Ultrasonic bath – to clean the substrate by sonicating the transparent conductive oxide (TCO) coated glass in alcronox, DI water, Acetone, and Isopropanol, respectively.
2. UV-ozone cleaner – to clean all organic residue and prepare the surface for ETL/HTL coating
3. Weighing scale and hotplate – to prepare ETL/HTL solution
4. Spin coater – to coat the ETL/HTL layer onto the TCO glass.
5. Hotplate – to anneal the coated ETL/HTL to promote crystallization and remove all the solvent.

Perovskite layer fabrication equipments:

1. Glovebox or environmental controlled box equivalent – to control and minimize moisture and oxygen in the environment for the best quality perovskite film.
2. Spin-coater – to coat the perovskite layer
3. Hotplates – two of them to let the crystallization take place gradually. Normally, one hotplate is fixed at 50°C and the other at 100°C. Once the spun-coated film turned slightly brown

Electrode deposition equipments (to complete the solar cells)

1. Thermal evaporation attached to a glovebox – to deposit metal electrode on top of already deposited ETL/HTL of a perovskite solar cells.
2. Sputtering machine – to deposit transparent conductive oxide as an alternative to the metal electrode, which will give a “semitransparent” solar cell
3. Doctor blading or screen printing machine – to deposit carbon electrode on top of perovskite. This technique is the simplest but requires a careful selection of carbon paste such that the solvent will not degrade the perovskite film.

2.2 Lab visits

At the beginning of this project, I did not have a lab space designated to my research activity, neither did I have a spin-coater to prepare the film. Therefore, I had visited various laboratories in Thailand and abroad, in hope that I can find a place to fabricate some perovskite solar cells for stability testing.

Trip 1: Semiconductor Physics Research Laboratory, Department of Physics, Chulalongkorn University, Thailand

Back when the project started, this lab only had an acrylic box flushed with Nitrogen gas for solutions preparation and device fabrication. With this setup, it takes a few hours for the moisture level to drop or to get all the solvent out of the system after solution-making or film-processing. Therefore, only one activity can take place in a day and the box needed to be flushed with nitrogen overnight prior to thin-film fabrication to get the moisture level down really low. As a result, only one batch of solar cells can be fabricated per week. However, this laboratory is equipped with a thermal evaporator not connected to a glovebox to deposit top counter electrode with limited choice of materials, silver and aluminum. They also have a sputtering machine mostly for aluminum doped zinc-oxide layer. In terms of characterization, they have a setup for efficiency, external quantum efficiency, photoluminescence, and absorption.

Trip 2: Mahidol University, Salaya Campus, Thailand

This lab has four hands glovebox to control the atmosphere down to below 0.1ppm for both oxygen and moisture. Also, they have a thermal evaporator, which is also not connected to a glovebox. So solution-processed fabrication should not be an issue in this lab, but the sample interfaces could inhibit high performance solar cells if the sample is exposed to humid atmosphere before thermal evaporation. However, perovskite solar cells fabrication here is not possible because the glovebox is always full with their own students.

Trip 3: Visiting Suranaree University of Technology (SUT), Thailand

I visited this university to explore sputtering options on top of perovskite solar cells. As previously mentioned in the introduction about metal-perovskite interaction. It is necessary to fabricate metal free perovskite solar cells. One option is to use transparent conductive oxide (TCO) layer as an electrode. There are three ways to deposit TCO: sol-gel processing, nanoparticle deposition, and sputtering. Sol-gel processing requires annealing at temperature above 200°C, which will degrade most perovskite layers. Nanoparticles are usually synthesized and dispersed in water or ethanol, both of which will degrade perovskite. Unless, there is a way to disperse nanoparticle in non-chemically reactive with perovskite, this is not a good route to complete perovskite solar cells. Third option, sputtering, is the best technique to deposit TCO on top of the perovskite because sputtering gives a high quality-dense film and can be done at temperature below 100°C.

At Assoc. Prof. Dr. Worawat Meevasana's lab at SUT, they can sputter various HTL, ETL, and TCO: NiO_x , Al_2O_3 , ZnO , TiO_2 , FTO , ITO , ZTO , WO_3 , and WS_2 . However, each of the sputtering process still need to be optimize prior to actual deposition on perovskite solar cells. Another thing to consider is that, there is no facility to fabricate solution-processed perovskite layers here at SUT yet, so ones need to think of a solution to improve the interface between solution-processed perovskite and sputtered layer.

Trip 4: Visiting University of Wuppertal, Germany

Since the lab of Prof. Dr. Thomas Riedl at the University of Wuppertal used to do vast research in organic light emitting diode, they are well equipped with a thermal evaporator and sputtering machine connected to a glovebox for solution-processed film fabrication (Figure 3). Their specialty is semitransparent perovskite solar cells fabrication with SnO_2 as electron transport layer and aluminum doped zinc oxide as TCO. During my visit, we discussed over solar cells fabrication and encapsulation techniques. They agree to provide semitransparent perovskite solar cells when needed.

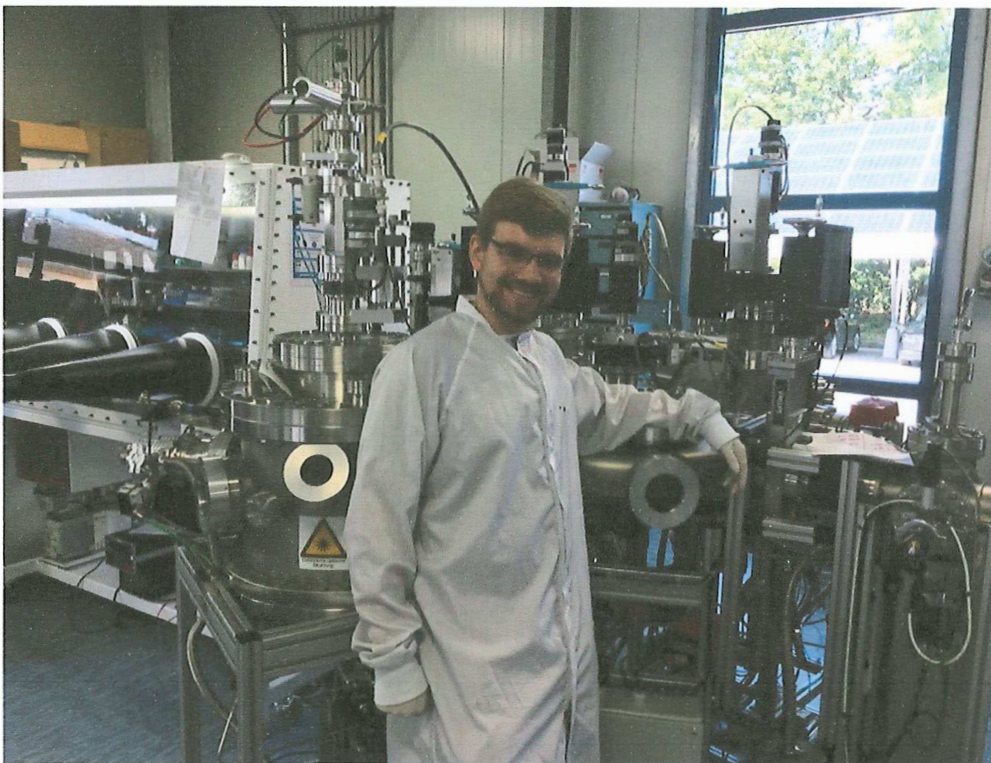


Figure 3 Colleague at the University of Wuppertal in front of sputtering and thermal evaporator that's integrated to a glovebox.

Trip 5: Visiting Solliance Solar Research, the Netherlands

I made this visit because Solliance is the world leader in flexible thin film encapsulation for perovskite solar cells. They have IP protected multilayer barrier films which has high moisture

barrier quality close to a glass slide. Therefore, when I first got there, I hope to gain some experience of such simpler encapsulation. However, when I got there, I learned that such high quality barrier film can be simply made, but the way to apply it onto perovskite solar cells can be tricky. Therefore, a durable and stable adhesive needed to be researched. At the end of the trip, we still could not find appropriate way to encapsulate perovskite with flexible films. So this is still an open end research.

Trip 6: Visiting King Mongkut's University of Technology Thonburi (KMUTT), Thailand

Facilities at KMUTT is very similar to Mahidol. They have a glovebox and thermal evaporator. Recently, they just added sputtering tools in their lab, as shown in **Figure 4**. They allow others to fabricate solar cells at their lab but it is too crowded and they could not offer any time slot for me to go fabricate perovskite there.



Figure 4 Left (glovebox) where the perovskite layer is formed (middle) thermal evaporator (right) fume hood with a spin coater for ETL/HTL layer formation.

Trip 7: Visiting Kasetsart University (KU), Thailand

Facilities at KU is very similar to KMUTT and Mahidol.

Conclusion of the lab visits:

- The high quality facilities in Thailand (MU, KU, KMUTT) are not available to use unless I share a project with them. Even at those facilities, the power conversion efficiency and reproducibility of perovskite solar cells are still low.
- If I need high performance solar cells for stability testing, I am better off getting perovskite solar cells from international collaborators such as University of Wuppertal, Stanford University, or Solliance.
- Encapsulation technique for perovskite needed to be further researched for a low-cost and high quality package such that the encapsulated solar cells can withstand hot and humid environment in Thailand during operation.

2.3 Perovskite solar cells fabrication

Despite previous unsuccessful lab visit, I was able to convince two institutes to allow me to fabricate perovskite solar cells in Thailand.

Trip 1: Fabricate Solar cells at Chiangmai University, Thailand

At Asst. Prof. Dr. Pipat Ruankham's lab, I shared with them my knowledge of how to fabricate double cation (Cs/FA) perovskite solar cells. Combining their specialty on metal oxide transport layer with my experience on fabricating perovskite layer, we were able to fabricate full stack perovskite solar cells with 2.15% on the first day I was there, **Figure 5**. This was done only inside a stainless-steel environmental box with controllable humidity level down to 10%RH. The top counter electrode we used was commercial carbon paste, which can be easily applied and baked without needing thermal evaporation. I have learned a lot spending two days in this lab including a solution-making technique without the need to use glovebox. I hope we can continue working together to make low-cost perovskite solar cells fabrication possible. With further optimization, we were able to obtain 9.94% a few months after, **Figure 6**.

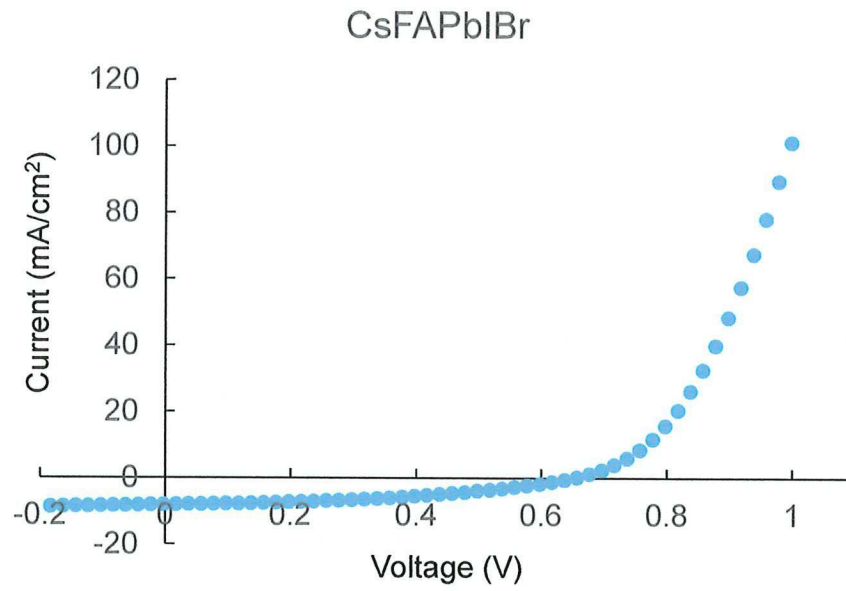


Figure 5 JV curve of the best solar cell fabricated for the first time at CMU.

Table 1 Figure of merits of the first-time fabricated CMU solar cell

PCE (%)	FF (%)	J _{sc} (mA.cm ⁻²)	V _{oc} (V)
2.15	41.3	-7.99	0.65

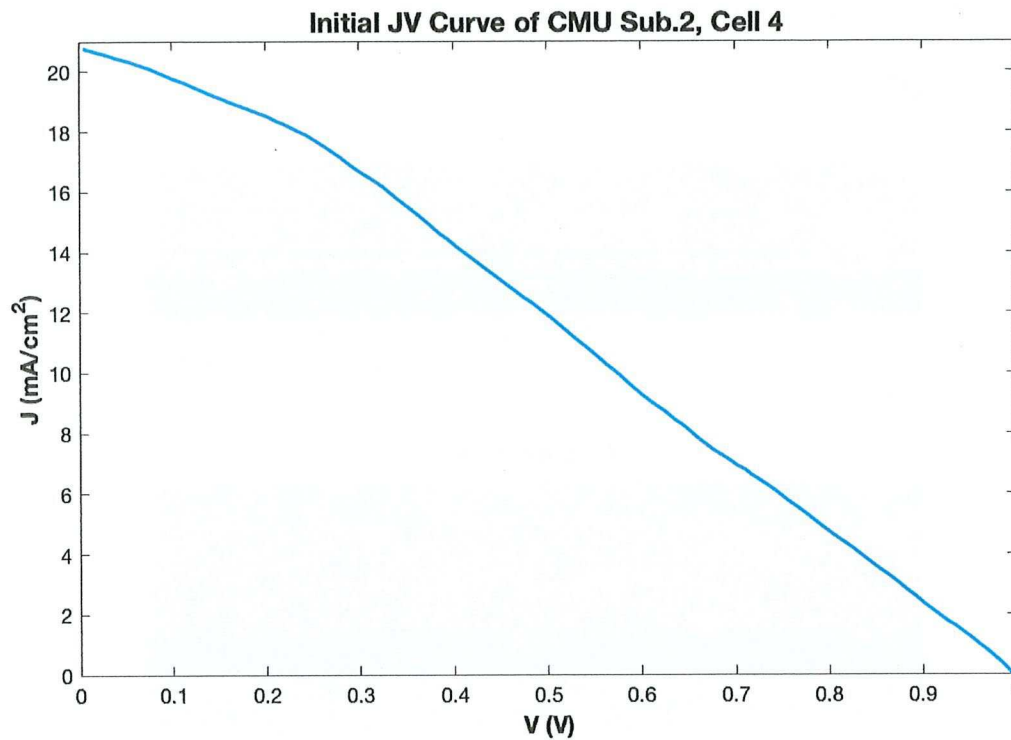


Figure 6 Initial JV profile of CMU Substrate 2 Cell 4 sample after optimization

Trip 2: Learning Solar cells encapsulation at National Science and Technology Development Agency, Thailand

Since Dr. Pisist Kumnorkaew at NSTDA is one of the perovskite solar cells leader in Thailand, he has connections with perovskite startup in China and got lots of knowledge transfer regarding encapsulation. He offered to train us how to easily encapsulate perovskite using carbon as an electrode together with MU and CMU. This process can be done simply by sprinkle carbon powder on solution-processed perovskite films, cover the powder with a piece of TCO coated glass, and mounted two pieces of substrate together by a binder clip. In my opinion, this process is simple enough to be done but does require lots of carbon materials. Furthermore, it is quite hard to control the density of the film. Therefore, the conductivity of the electrode could be an issue. In my opinion, it would be more reproducible if carbon electrode is coated from a solution instead.

2.4 Perovskite Solar Cells used for stability testing

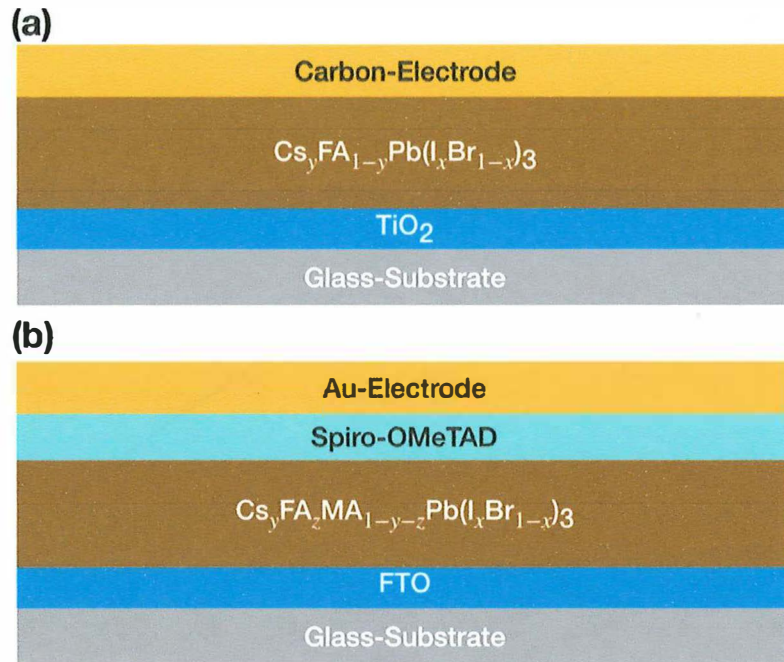


Figure 7 Comparing schematic of CMU (a) and NSTDA (b) device stack

Table 2 Figure of merits of NSTDA and CMU solar cells

	NSTDA	CMU
PCE (%)	4.9±1.6	9.9±5.7
V_{oc} (V)	0.6±0.2	0.8±0.1
I_{sc} (mA)	1.2±0.7	1.5±0.7
FF (%)	32.5±14.9	28.9±4.7

Chapter 3: Low-cost characterization

3.1 JV measurement

The traditional JV measurement is commonly used for solar-cell power conversion efficiency (PCE) determination. This measurement needs a source-meter to generate voltage sweeping which applied to a photovoltaic device and measure output current. After that, output current and voltage sweeping are plotted and utilized to calculate the PCE of a device.

3.1.1 Hardware setup

Hardware List

- Test Cell: Si solar cell 6V 2W
- Variable Resistor: 0-500 Ω range
- High Precision Multimeter: Keithley model 2700
- Light Source: LED Lamp (6500K-Light temperature)

Measurement Setup

We designed a low-cost setup to measure JV of a solar cell. We connect a variable resistor to a photovoltaic device as shown in **Figure 8**. During the JV measurement, we placed the solar cell under a LED lamp and measured voltage of the solar cell and output current by Keithley model 2700 while we swept variable resistor from ~0-500 Ω

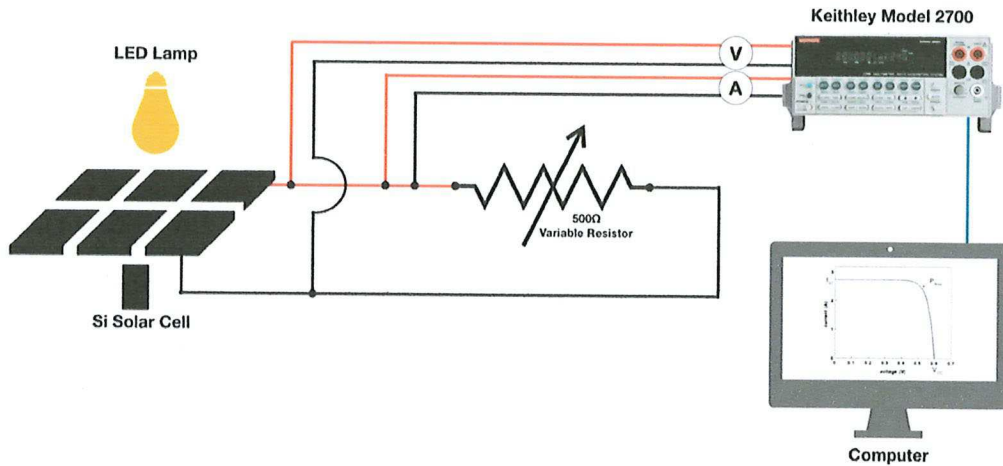


Figure 8 Low-cost JV measurement setup Schematic

3.1.2 Software setup

In our measurement, we used Excelinx software to collect the voltage data from Keithley model 2700. This software run on the Microsoft Excel (the program interface is shown in Figure 9). We set the delay time at 0.02 second to collect the JV data.

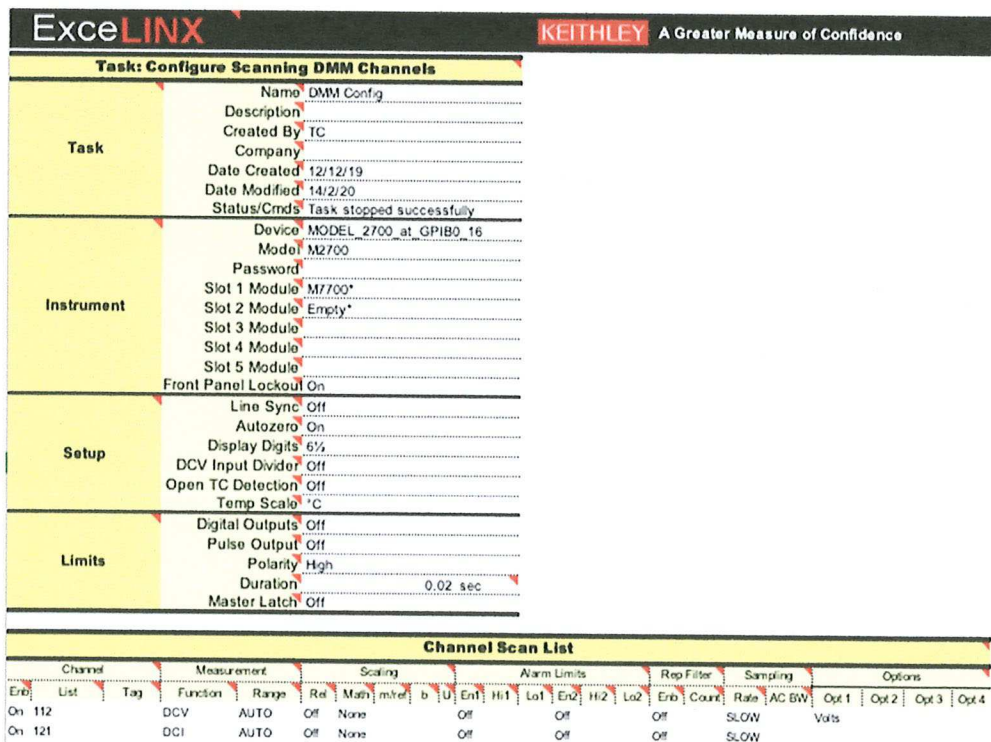


Figure 9 Excelinx software interface

3.1.3 Results

We ran the low-cost measurement on the 6V 2W Si solar cell then we got the IV curve for the device as shown in Figure 10.

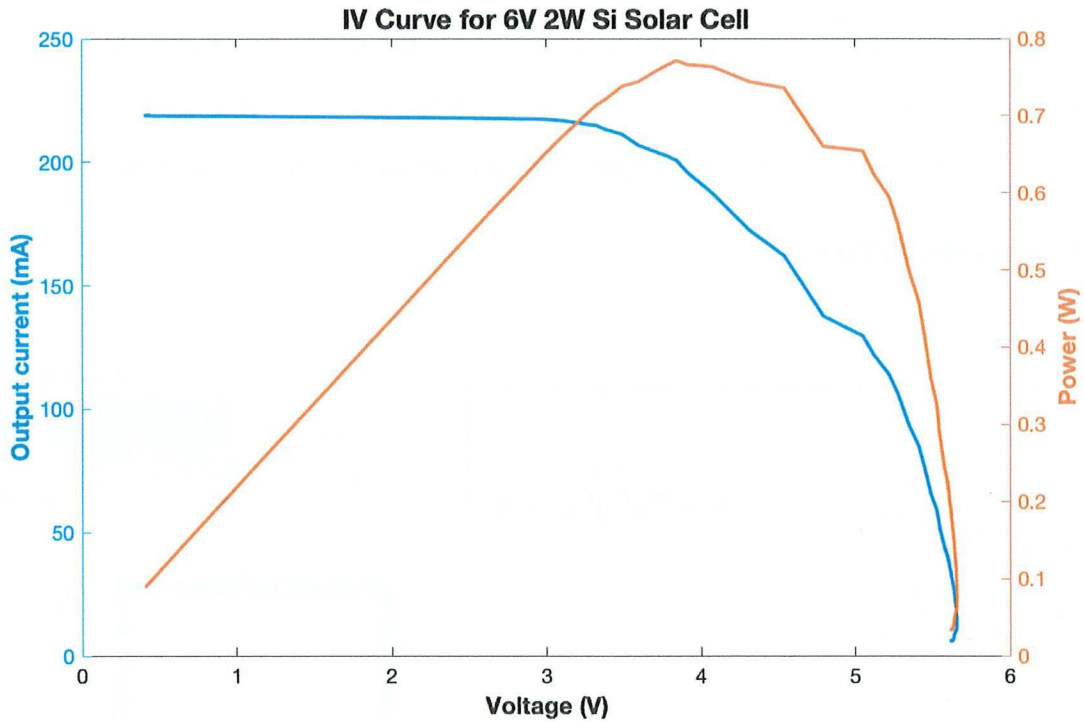


Figure 10 IV curve of Si solar cell which measured by low-cost IV measurement

3.1.4 Technical problems

The IV-curve from low-cost IV measurement in Figure 10 is not smooth because of two reasons. The first reason is uncontrollable voltage sweeping speed from manually turning the variable resistor knob. The second reason, the resistor is not precise enough, therefore, caused instability voltage scanning speed.

So, this low-cost JV measurement setup was not used in further IV characterization in this project due to the issues stated above.

3.2 Low-cost stability tracking

In normal operation, solar cells are put under an applied voltage bias such that will yield highest PCE. To probe operational stability, a maximum power point tracking (MPPT) is necessary to set the voltage. However, the existing commercialized MPPT only supports high voltage and high current solar module with limited resolution if used to control lab-scale solar cells. For the stability tracking setup, we decided to use a fixed resistor that will put a voltage across a solar cell to around the maximum power-voltage and measure the current across that resistor.

3.2.1 Hardware setup

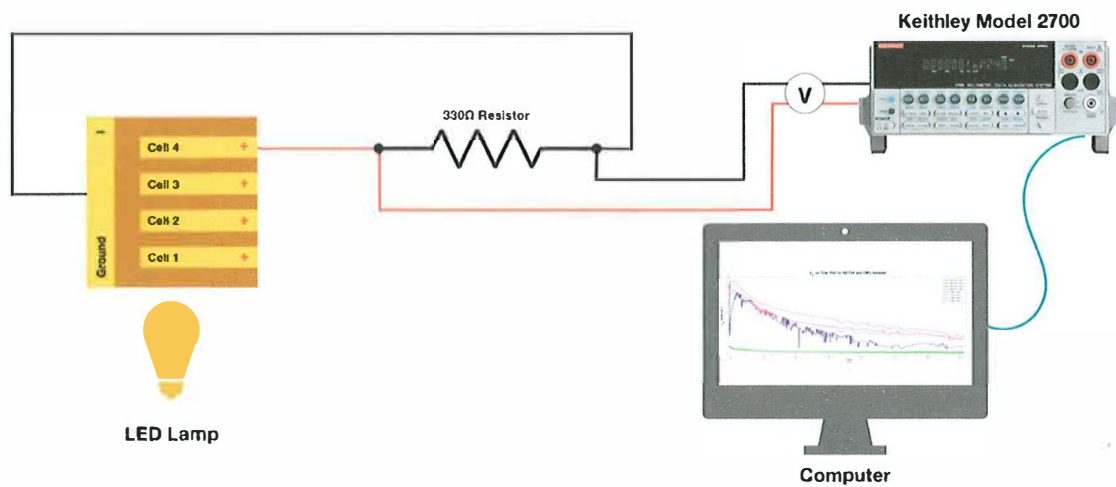


Figure 11 Low-cost stability tracking setup for each cell.

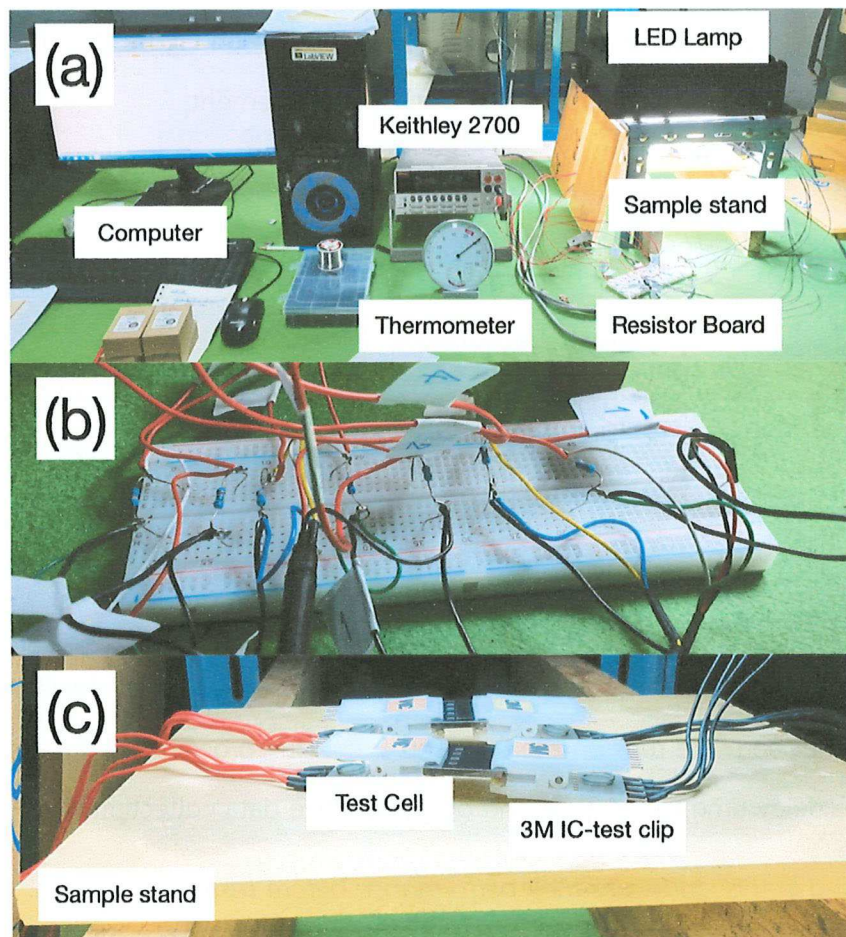


Figure 12 Stability tracking setup (a), resistor board (b) and cell connections (c)

The measurement setup for stability tracking is shown in Figure 11 with equipment details below:

- Test cells: NSTDA and CMU perovskite solar cell
- Fixed resistor: 330Ω
- High Precision Multimeter: Keithley model 2700
- Light Source: LED Lamp (6500K-Light temperature)
- House thermometer-hygrometer
- 3M IC-test clip

We connected the anode of perovskite solar cells (both NSTDA and CMU sample) to fixed 330Ω resistors and cathode to another side of the resistor as in **Figure 11**. Then, we attached a pair of measuring probes to the resistor for voltage measurement.

Test Conditions

Table 3 Measuring condition during measurement

Active Area	Ambient Description	Temperature	Humidity	Light Intensity
0.04 cm ²	room ambient with no control	30-38 °C	32-46%RH	~1 Sun

3.2.2 Software setup

In this measurement, we also used Excelinx software to collect the voltage data from Keithley model 2700. This software runs on the Microsoft Excel (the program interface is shown in **Figure 9**). We set the delay time to 112.5 second output voltage data collection.

Solar cells used in this study and their performance before testing

We use the perovskite samples from two groups, NSTDA and CMU, which provide device stack as illustrated in **Figure 7***Error! Reference source not found.*. Before the test, we performed JV measurement on the samples so that we can determine which figure of merits – J_{SC} , V_{OC} , or FF-drop and cause degradation of the solar cells.

Table 4 Initial and final PCE of NSTDA and CMU samples

Cell	Group			
	NSTDA (Substrate 2)		CMU (Substrate 1, 06/01/20 Fab.Date)	
	%PCE Before	%PCE After	%PCE Before	%PCE After
1	10.94	0.30	Cell Broken	
2	4.56	0.12	0.67	0.10
3	3.68	0.17	0.27	0.31
4	2.95	0.39	1.92	2.28

3.2.3 Results and discussion

JV before vs after stability tests

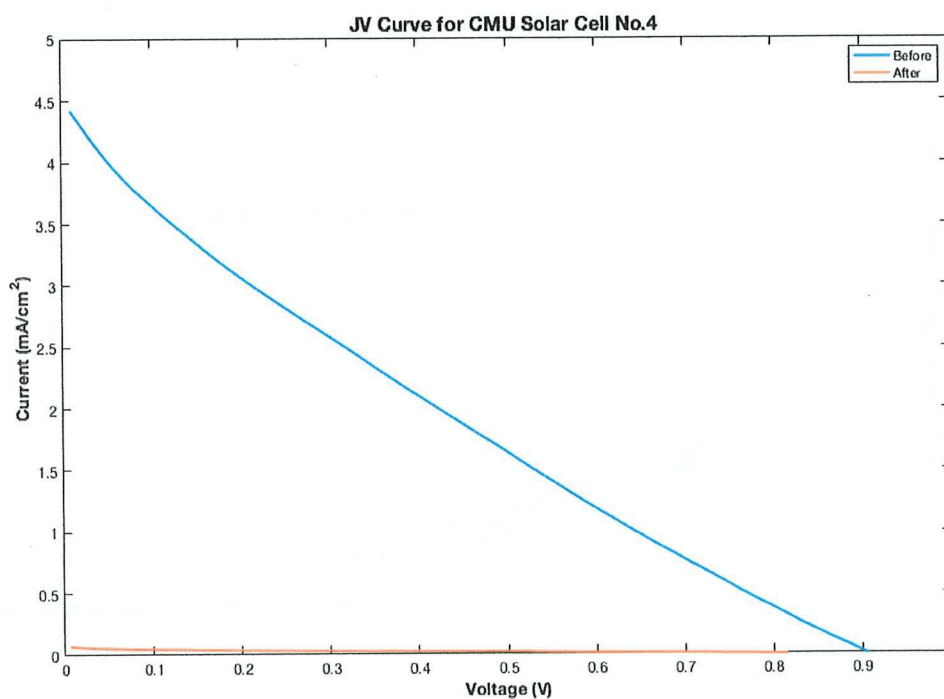


Figure 13 JV-curve of CMU Cell 4 sample before (blue) and after (orange) long-term stability tracking

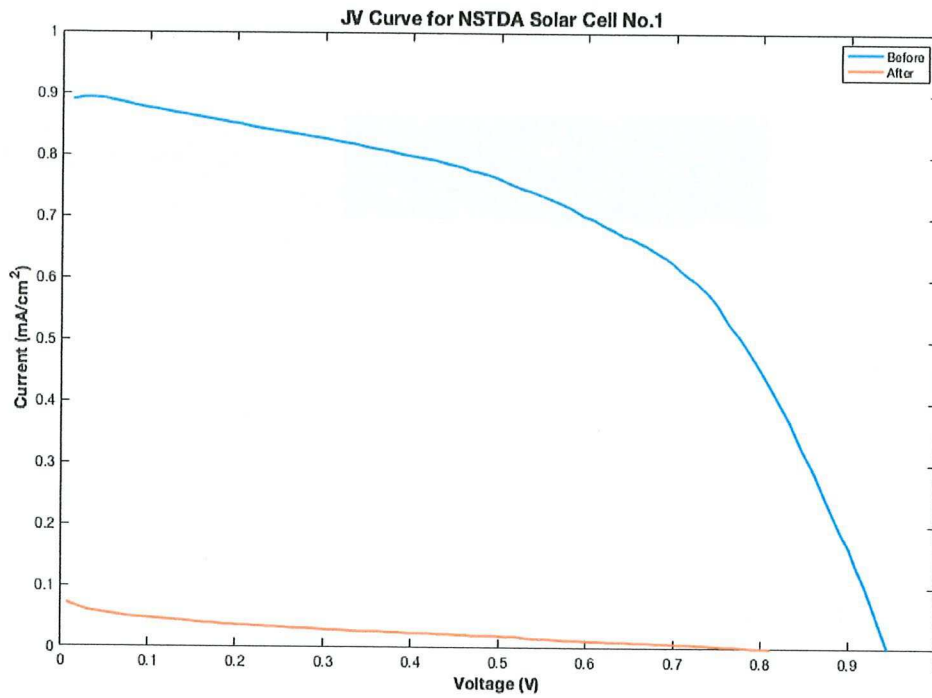


Figure 14 JV-curve of NSTDA Cell 1 sample before (blue) and after (orange) long-term stability tracking

J vs. time (CMU vs. NSTDA)

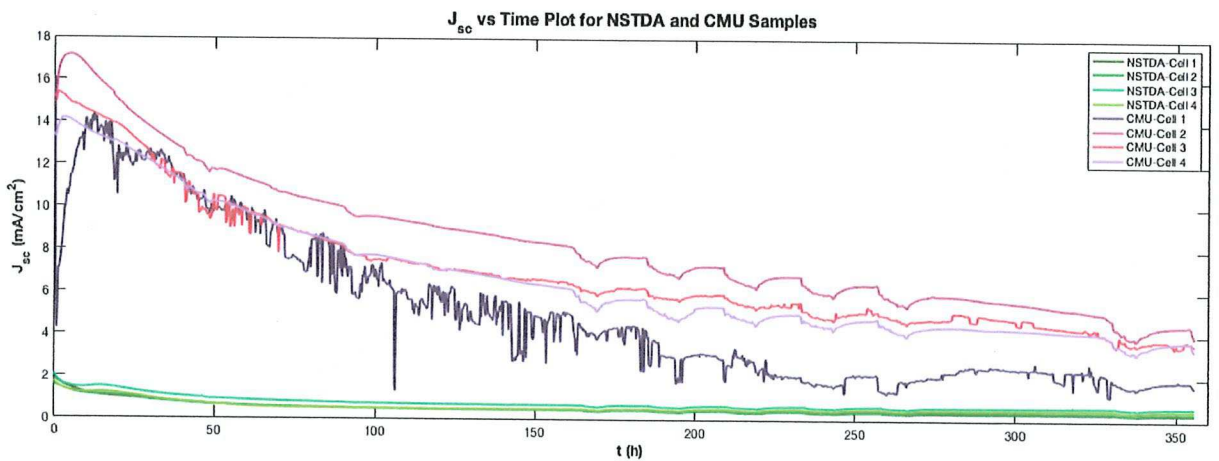


Figure 15 Plot of current density vs time of NSTDA (green tone) and CMU (purple tone) samples

Figure 15 shows the current density passing through resistors vs time evolution. The perovskite solar cells from CMU is higher in efficiency and also more stable than the ones from

NSTDA. This is most likely due to a lack of metal electrode, which can catalyze a degradation of perovskite materials, unlike the solar cells with gold counter electrode from NSTDA. All solar cells seem to need some time to reach their highest efficiency then the decay in performance would take place. The cyclic pattern between 160 and 260 hours are from turning on and off the air-condition during workdays. Therefore, for a proper stability testing setup, a room with controlled temperature is necessary.

3.3 Conclusion

The low-cost JV measurement can be used to measure the JV curve of a photovoltaic device, but this system is not accurate and stable enough for the perovskite solar cell. So, this setup was not utilized in perovskite solar cell PCE determination.

We succeeded in setting up a low-cost stability tracking; this system can perform ~360 h continuously without any issue. The result in **Figure 15** shows that the samples from CMU group perform with higher stability which compare to sample from NSTDA group, which is due to the lack of metal counter electrode in the solar cell stack.

Chapter 4: Stability Measurement

In order to properly probe stability of perovskite solar cells, one needs a standardized equipments to be able to report the lifetime for high quality publication. I was fortunate enough to secure some other funding to purchase a reliability setup from infinityPV company, Denmark, which provides close to the solar spectrum light source and CE certified equipments. Throughout this chapter, I will report my approach to test hypotheses regarding stability of perovskite solar cells.

Hypothesis:

1. The devices with carbon top electrode can perform more stably because the carbon electrode does not react with the perovskite layer unlike the metal electrode.
2. Moisture induces degradation of a perovskite solar cell. However, the solar cells without metal top counter electrode should degrade less than the ones with metal electrodes.
3. Perovskite solar cells can recover their performance after resting in dark and dry (humidity < 5%RH) conditions.

Solar cells used in these studies

The samples which utilized in stability measurements consist the device stack that shown in Figure 7.

4.1 Stability of perovskite solar cells with metal vs. carbon top counter electrode

4.1.1 Hardware setup

Light Source

This system consists ISOSun as the light source. The ISOSun is a metal-halide lamp which provides the spectral distribution close to AM 1.5g shown in **Figure 16** and intensity close to 1000 W/m², as called 1-sun intensity. Furthermore, the ISOSun can generate light intensity in 1-100 sun range.

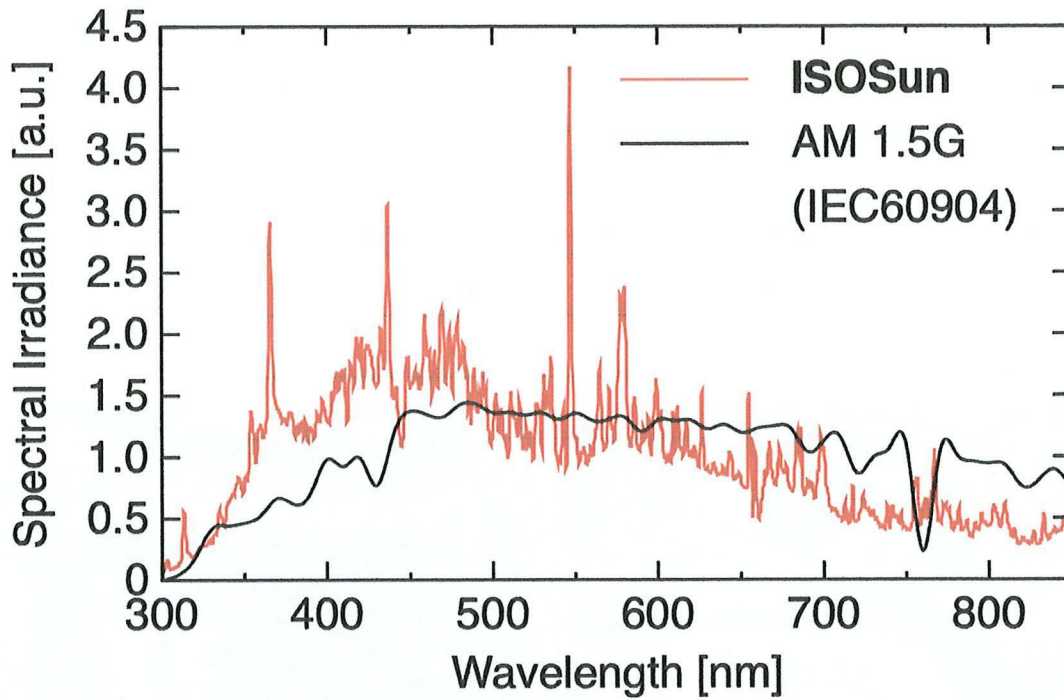


Figure 16 Spectral distributions of ISOSun (red) and AM 1.5G (black) light sources

Cooling System

The ISOS testing system consists of 6 fans totally, 4 fans flow cool air into chamber surface or testing area and other 2 fans that flow hot air out. However, it's also recommended the system to be operated in a controlled room with temperature below 27°C.

Source Measurement Unit

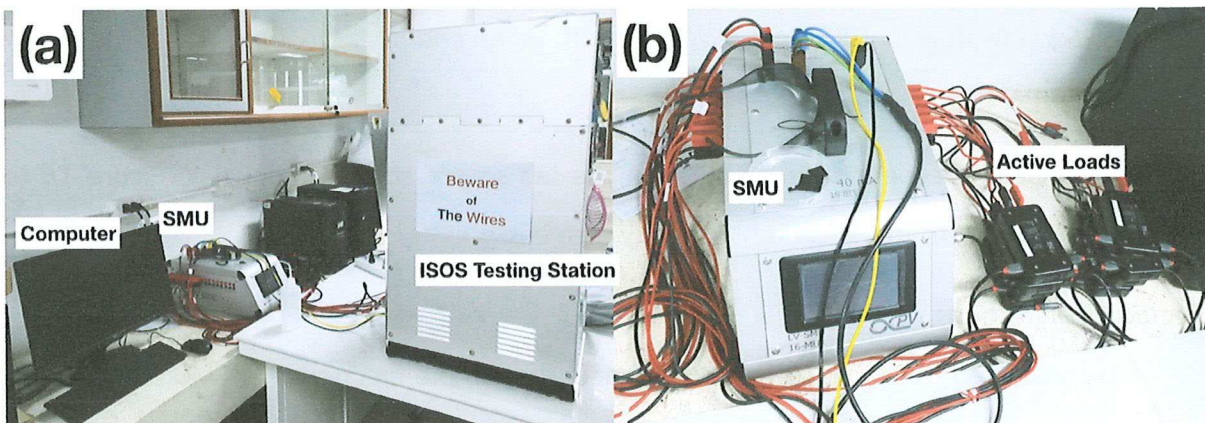


Figure 17 Hardware setup overview (a) and SMU and active loads connections (b).

The source measurement unit (SMU), **Figure 17(b)**, is a device which used to applied voltage into solar cells and measure output current for JV measurement.

Active Loads

The active load (**Figure 17(b)**) is utilized to hold a solar cell at a voltage point which the device yield the highest power (this point is called maximum power point, MPP).

Sample stage

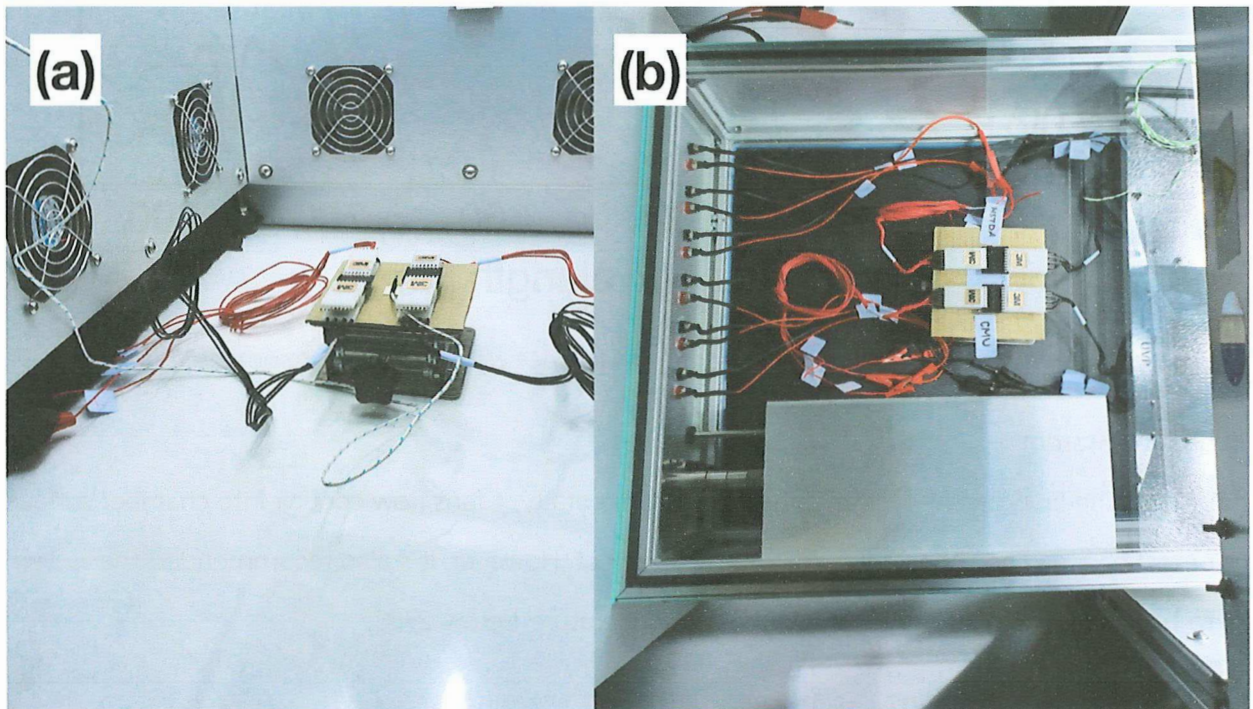


Figure 18 Sample stage and sample alignment with (a) no chamber (dry env. setup) and (b) chamber (humid env. Setup)

We placed the perovskite samples on the lab scissor stand as shown in **Figure 18** to elevate the samples to the 1 sun light intensity area easily.

Electrical connections

We also used the 3M IC test-clip to connect the sample electrodes to SMU as illustrated in **Figure 18**.

4.1.2 Software setup for measurement

In the stability measurement, we used InfinityPV-IV software to control the SMU and performed stability measurement. This test start with the JV scan to search for the maximum power voltage (voltage that a solar cell produces the highest power). After that, the software commands the SMU to hold a solar cell at the maximum power voltage throughout the setting time interval. Then, JV scan is repeated and MPP adjustment will take place at each set interval.

4.1.3 Testing conditions (humidity vs. dry)

Table 5 Measuring conditions for dry and humid environment tests

Condition	IV Scan Step	Active Area	Temperature (°C)	Humidity (%RH)	Chamber	Light Source	Light Intensity
Dry	10 mV/step	0.04 cm ²	44-47	~15	Not include	Metal	~1 Sun
Humid			40-43	45-58	Include	Halide (ISOSun)	

4.1.4 Results

NSTDA Samples

Figure 19: shows the stability test result of perovskite solar cells from NSTDA in low and high humidity condition as shown in the legend. It can be seen that perovskite solar cells degrade slower in a higher humidity level, but also the performance drop to 0 at a shorter time. Table 6 shows PCE before and after the perovskite solar cells went through their respective test in low and high humidity condition.

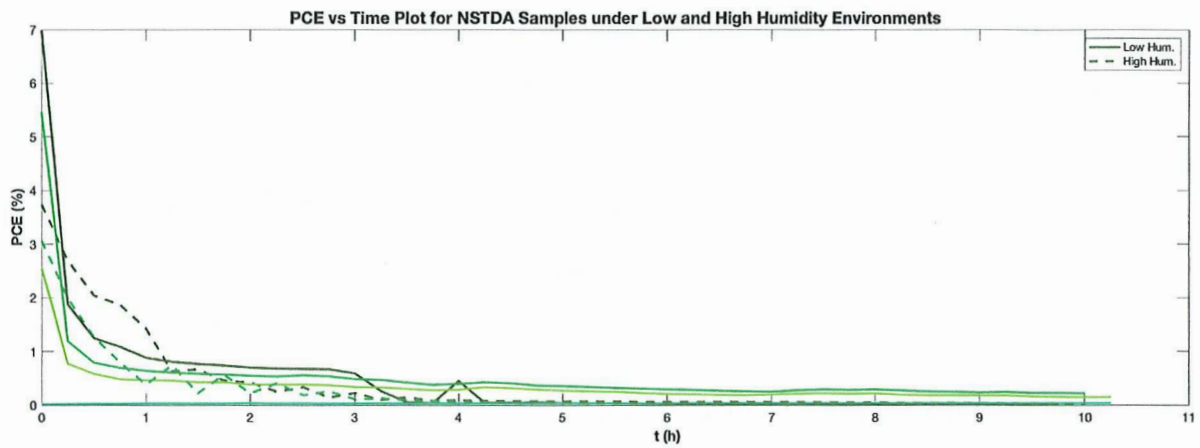


Figure 19 Stability test results of NSTDA samples in dry (solid line) and humid (dash line) environments

Table 6 PCE change of NSTDA sample before and after stability test

Cell	Testing Environments			
	Dry		Humid	
	%PCE Before	%PCE After	%PCE Before	%PCE After
1	6.99	0.11	3.65	0.04
2	5.47	0.22	3.07	0.02
3	Cell Broken			
4	1.67	0.15	-	-

Moreover, we plotted the JV profiles of the best PCE NSTDA sample in each environment which illustrated in Figure 20-Figure 21. These results show that PCE of NSTDA sample drop significantly after stability tests in two environments.

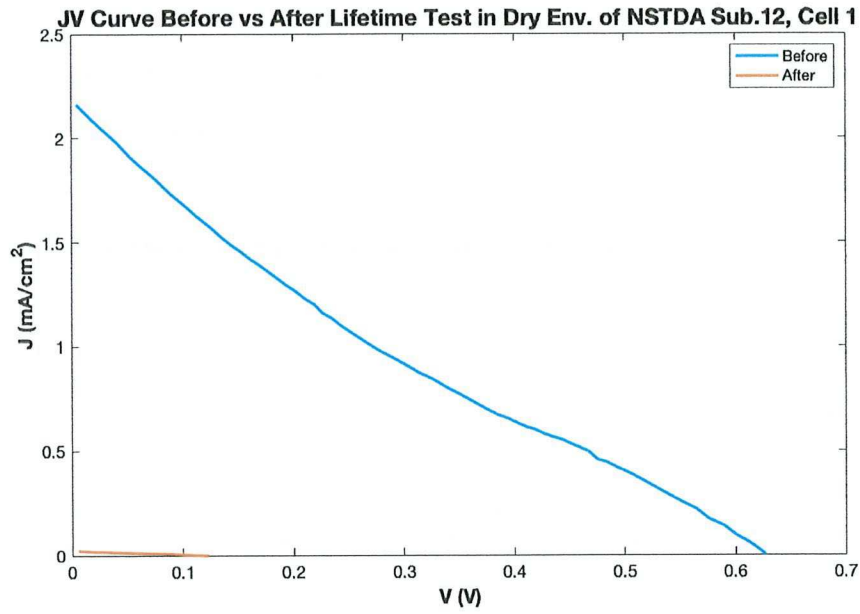


Figure 20 JV curve before and after stability test of NSTDA substrate 12 cell 1 in dry environment

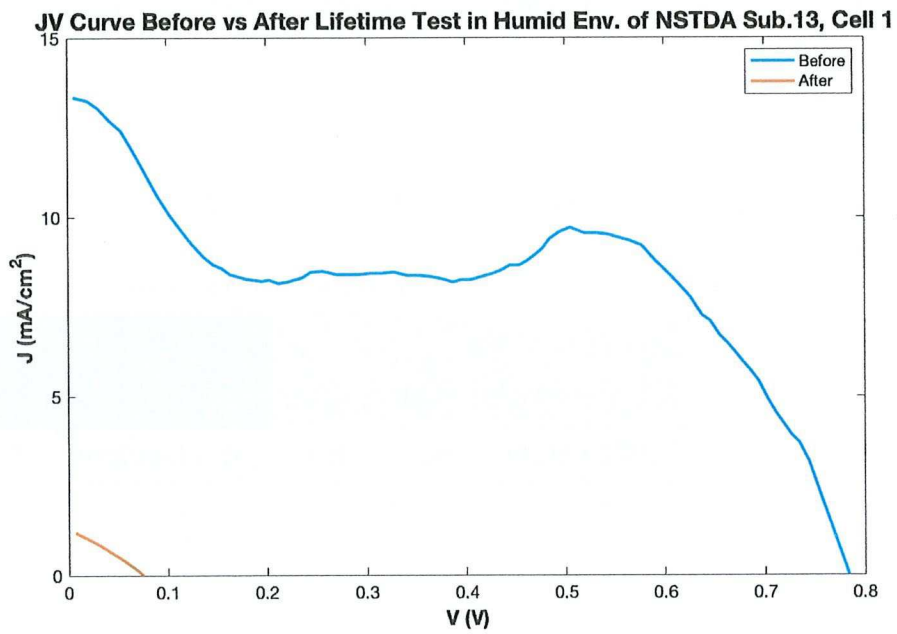


Figure 21 JV curve before and after stability test of NSTDA substrate 13 cell 1 in humid environment

CMU Samples

Figure 22: shows the stability test result of perovskite solar cells from CMU in low and high humidity condition. Surprisingly, we found the PCE increase after stability test mostly in high humidity condition. This is most likely due to the growth of perovskite grain size¹⁵.

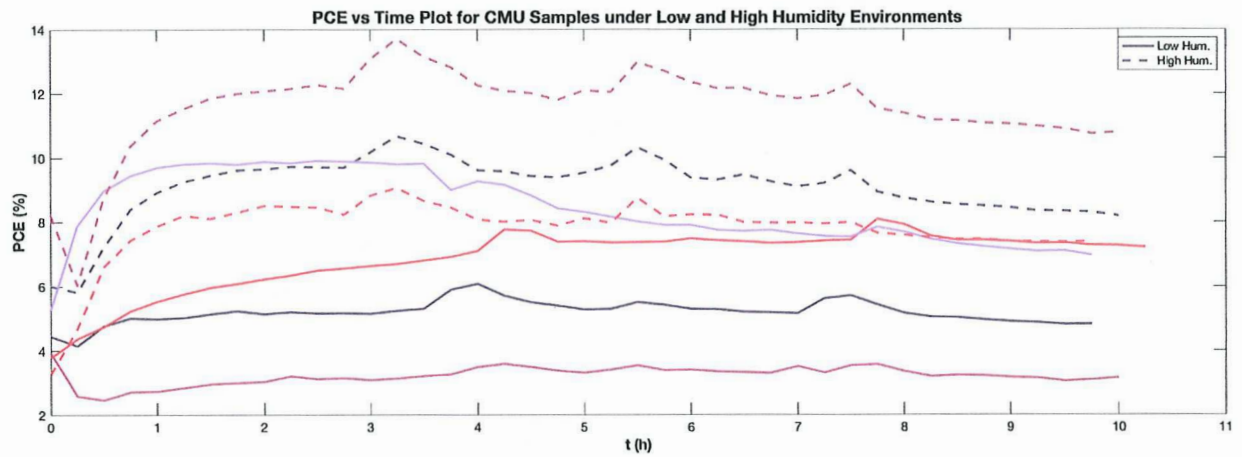


Figure 22 Stability test results of CMU samples in dry (solid line) and humid (dash line) environments

Table 7 PCE change of CMU sample before and after stability test

Cell	Testing Environments			
	Dry		Humid	
	Substrate 12, 03/01/20 Fab.Date		Substrate 13, 03/01/20 Fab.Date	
	%PCE Before	%PCE After	%PCE Before	%PCE After
1	4.45	4.81	6.01	8.18
2	3.94	3.15	8.23	10.78
3	3.78	7.21	3.27	7.28
4	5.26	6.94	-	-

Moreover, we plotted the JV profiles of the best PCE CMU sample in each environment which illustrated in Figure 23-Figure 24. These results show that the fill-factor of CMU sample increase which correspond to the growth of PCE.

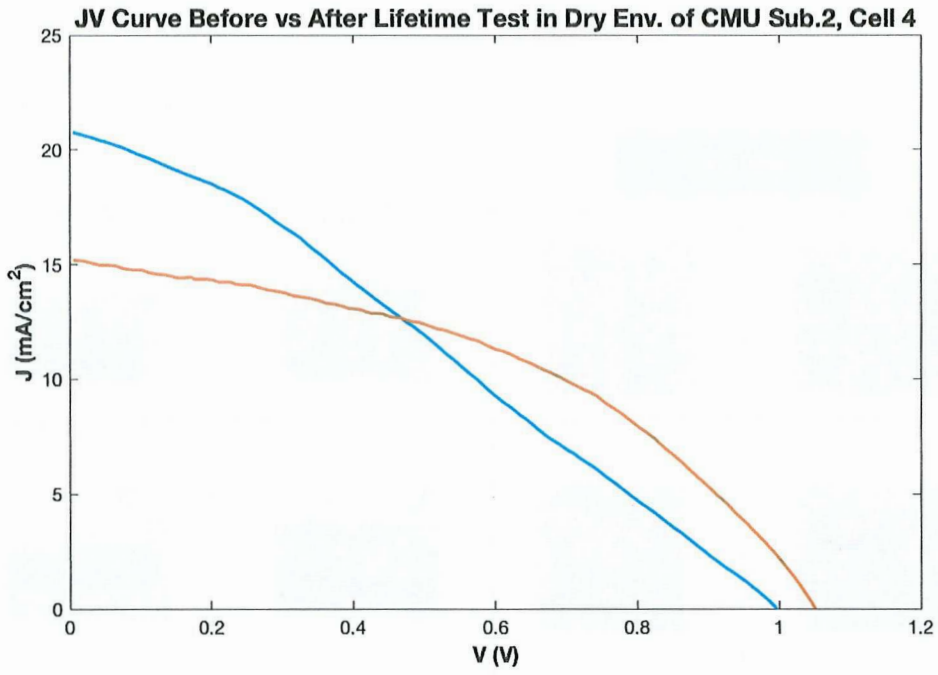


Figure 23 JV curve before and after stability test of CMU substrate 2 cell 4 in dry environments

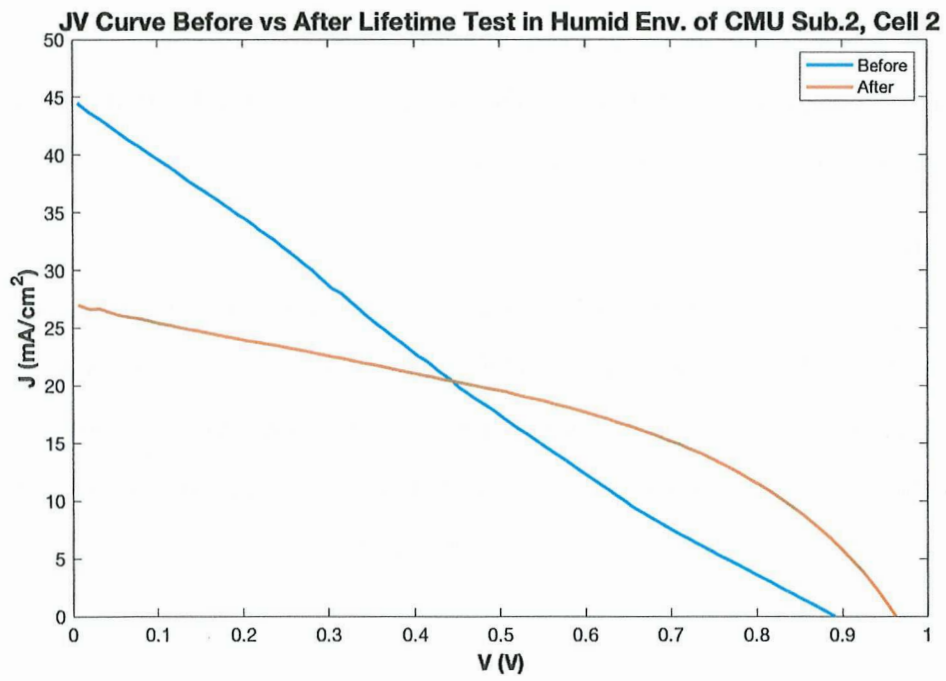


Figure 24 JV curve before and after stability test of CMU substrate 2 cell 2 in humid environment

4.1.5 Sample Evolution

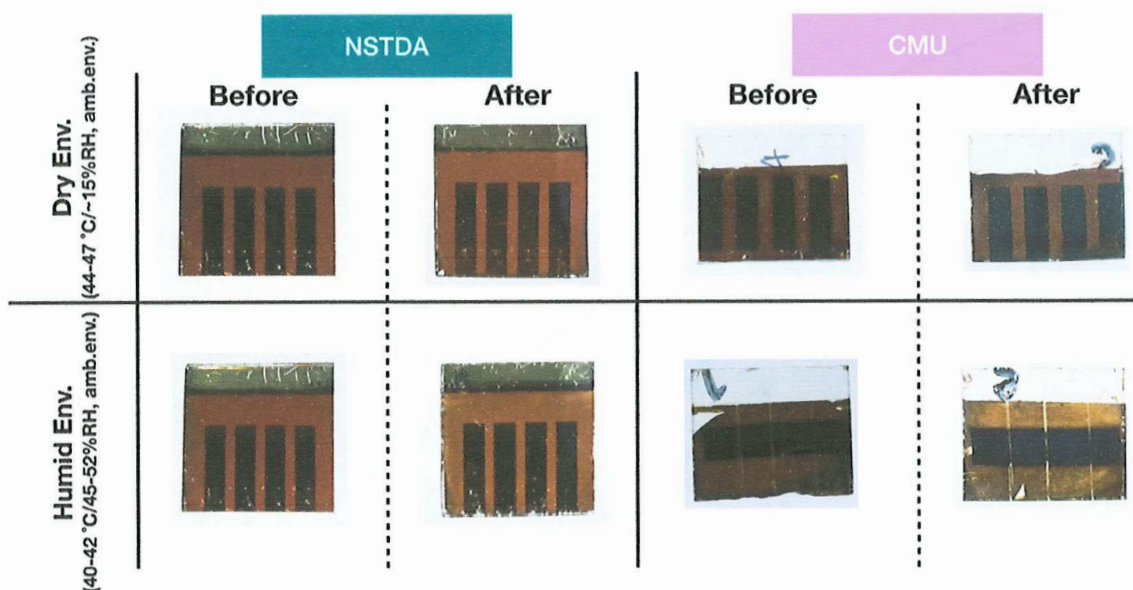


Figure 25 NSTDA and CMU sample evolutions before and after stability test

After stability test in dry and humid environments, the perovskite layer in the samples from both groups turned to yellow as shown in Figure 25. The yellow color that appear is PbI_2 which indicates the degradation of the perovskite layer.

4.1.6 Discussion

Surprisingly, the performance or PCE of CMU sample increased during stability tests in dry and humid environment despite the visual degradation observed. I suggest that the moisture in atmosphere penetrate into the perovskite layer and increase the grain size of perovskite. In the case of NSTDA, the sample PCEs drop significantly in few hours. I suppose that the perovskite layer was easily degraded by moisture in atmosphere because the perovskite of NSTDA samples consist of MA which is sensitive to moisture.

4.1.7 Conclusion

- The samples with carbon top electrode are more stable than the ones with metal electrodes in both dry and humid environments.

- The increase in PCE which appears in CMU sample comes from the effect of moisture that induce perovskite grains growth, increasing the carrier diffusion length and performance of the solar cells.
- Metal electrode on top the perovskite layer induce the degradation of perovskite which leads to a drop in PCE.

4.2 Diurnal testing

4.2.1 Hardware setup (testing equipment)

The hardware setup for the diurnal test is the same as the setup for stability test in humid environment.

4.2.2 Testing conditions

Testing and Resting Conditions

Table 8 Conditions for each light cycle

	IV Scan Step	Active Area	Temperature (°C)	Humidity (%RH)	Light Source	Light Intensity
Testing Cycle	10 mV/step	0.04 cm ²	40-43	45-58	Metal Halide (ISOSun)	~1 Sun

Aging Procedure

Table 9 Conditions for each resting (dark) cycle

	Aging Environment	Temperature (°C)	Humidity (%RH)
Resting Cycle	Dry-Dark	25-31	<5

After each diurnal testing cycle was finished, the samples were stored in covered petri dish under the conditions which shown in Table 9.

4.2.3 Results

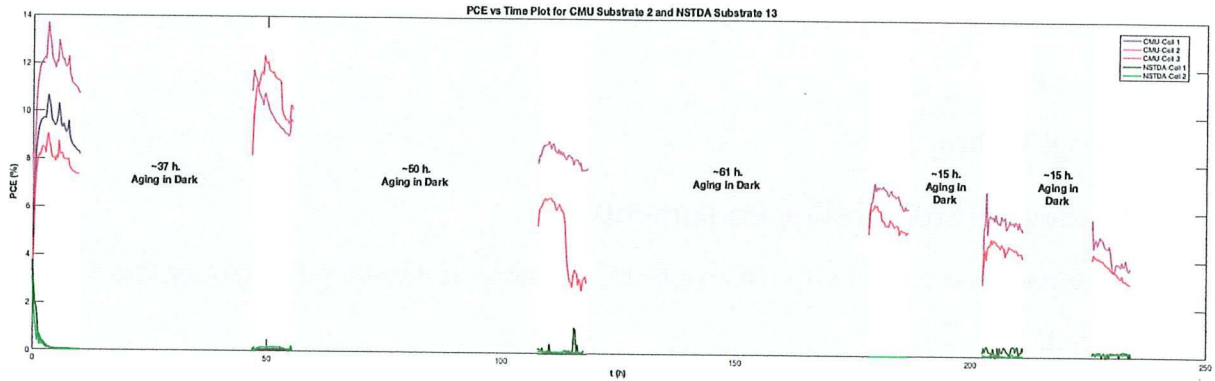


Figure 26 Diurnal test results of NSTDA (green tone) and CMU (purple tone) samples

After 37, 50 and 61 h of resting in the dark-dry condition, we found that the PCE can recover to the local maximum in 1.35 h, 2.45 h and 1.3 h, respectively. In the real condition, the duration which has no light starts around 5.00 pm and ends at 8.00 am (15 h) so we changed the resting in the dark time to 15 h that corresponds to the real condition for later cycles. The recovery times after the first and second 15 h aging intervals are 1.5 and 0.8 h, respectively. Following the results, the recovery time is not proportional to the resting in the dark time. During the PCE decay measurement in the light condition, the PCEs in each cycle increase to the local maximum PCE before decrease to the local minimum PCE at the end of the cycle (as shown in Table 10). Curiously, the initial PCE after aging in dry-dark condition is lower than the final PCE at the end of light cycle (the samples continually degrade during aging in the dark condition). The JV profiles of the best PCE NSTDA and CMU samples before and after the diurnal test can be found in Figure 27-Figure 28. More in-depth study on this issue needs to be further investigated, which is beyond the scope of this study.

Table 10 %PCE of each CMU sample at initial and final of each light cycle

Cell	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5		Cycle 6	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
1	Cell Broken											
2	6.04	10.78	10.88	9.60	7.94	7.76	5.09	6.14	3.00	5.24	5.77	3.75
3	3.27	7.39	8.18	10.09	5.33	2.94	5.38	5.15	3.38	4.11	4.07	3.04

Table 11 PCE of NSTDA and CMU samples before and after diurnal test

Cell	Group			
	NSTDA (Substrate 13)		CMU (Substrate 2, 03/01/20 Fab.Date)	
	%PCE Before	%PCE After	%PCE Before	%PCE After
1	3.65	0.16	6.01	2.09
2	3.07	0.01	8.23	3.63
3	Cell Broken		3.27	2.93

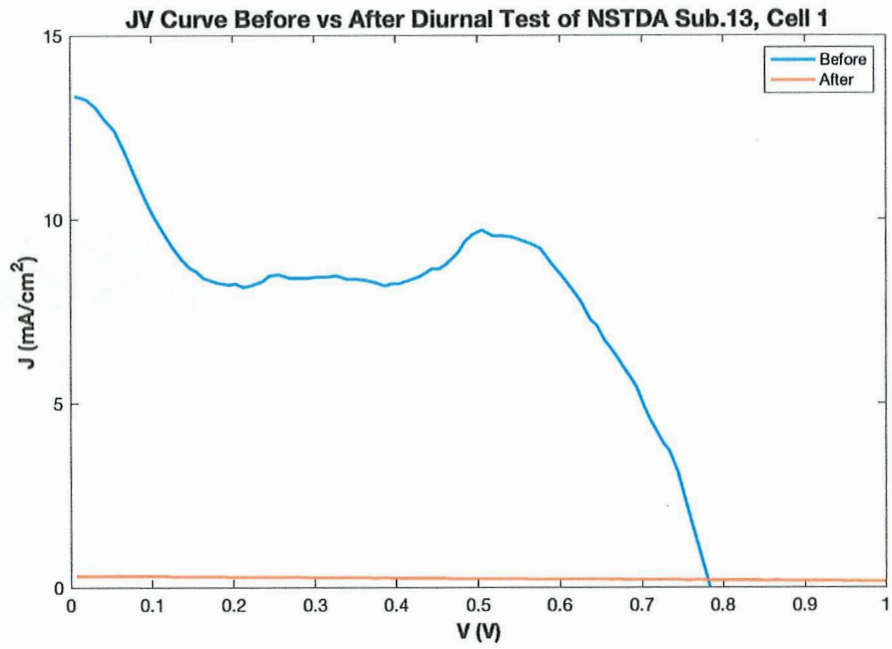


Figure 27 JV curve before and after diurnal test of NSTDA substrate 13 cell 1

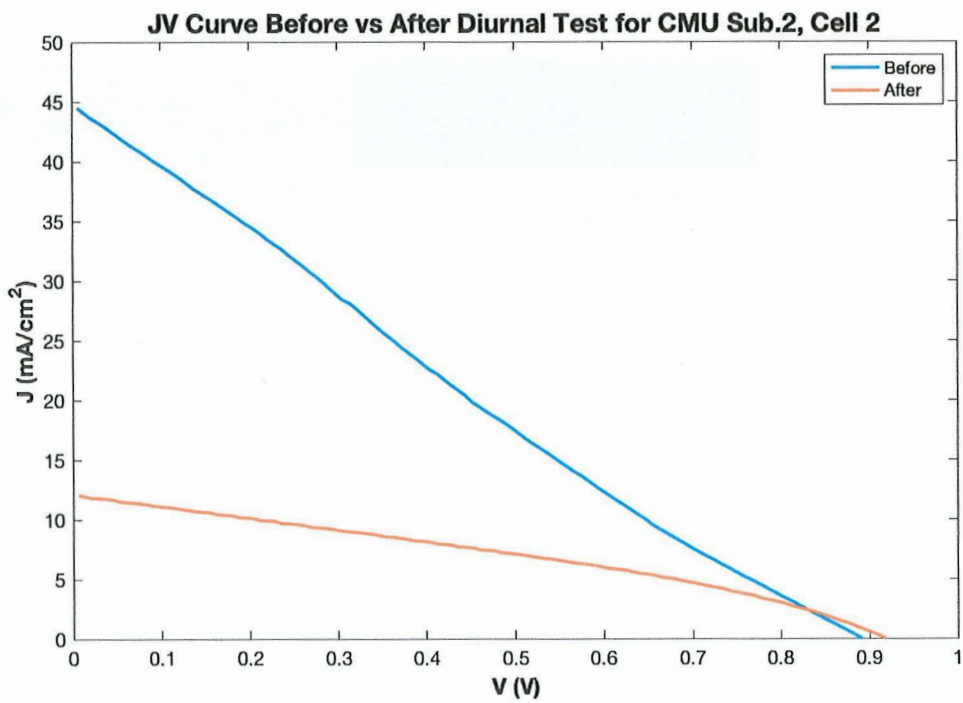


Figure 28 JV curve before and after diurnal test of CMU substrate 2 cell 2

4.2.4 Discussion

Following the result in **Figure 26**, moisture induces PCE of NSTDA samples drop significantly to nearly 0% during the first light cycle test. This PCE drop is from the perovskite degradation in light and humid environment. In the case of CMU samples, the PCE of each sample increases to a maximum PCE point of each cycle then drop until the end of each operating cycle under the light. The drop of PCE from the local maximum is from the degradation of perovskite layer by moisture in the atmosphere and light. After resting in the dry-dark condition, the starting PCE in each cycle of CMU samples is still lower than the final PCE on the prior day due to the permanent degradation of perovskite layer.

4.2.5 Conclusion

- The PCE recovery in the dark storage only occurs in the samples without metal electrode.
- The recovery time of devices do not depend on the aging time, so the optimized recovery time is not confirmed.
- Moisture still plays the crucial role on the perovskite degradation in devices, especially during operation with light and heat at plays.

Chapter 5: Conclusion and Output

Perovskite solar cells fabrication require well-controlled environment with very low moisture level. Even though, some semi-premier facilities existed in Thailand, their access are very limited. At the moment, high quality solar cells can only be obtained from abroad. Despite having research scientist who graduated from the world's leaders in perovskite, there is no easily access facility to let them continue their high impact research. We need to build regional central facilities where everyone can go try their idea if the country wants to push this field forward and produce low-cost perovskite solar panels to replace silicon solar module.

Low-cost setup for performance measurement of perovskite solar cells do not work well. Ones need proper source meter unit to source the voltage and measure high resolution current coming out from a solar cell. However, low-cost setup for stability testing could work. Using the LED light source removes the effect of UV light and prevents the solar cells from getting too hot. Assuming that a solar cell can be well-packaged with UV filtered and constantly cooled in real world, operation, one can use LED and resistor setup that we demonstrated in the chapter 3. We can see that regardless of the UV and high temperature, the solar cells with carbon electrode is more stable than the cells with metal electrode. However, performance of the solar cells with carbon electrode are usually not as high as ones with metal electrode. Therefore, future work would be improving performance of perovskite solar cells with carbon-based electrode.

With proper stability setup, perovskite solar cells with carbon-based electrode still surpass the stability of cells with metal electrode. With further maximum power point tracking, the carbon electrode solar cells get more than 100% better within the first two hours of operation in either humid and dry environment with heat. This is a promising sign for perovskite solar cells to be used in Thailand. Further day-night replication of the perovskite solar cells shows that the solar cells take up to at least an hour to stabilize each initialization, morning, then the performance would drop throughout the day. This drop in performance is likely due to heat and moisture induced degradation as can be seen by a change in solar cells colors from brown (perovskite) to yellow (PbI_2), degradation product. To more accurately replicate the day/night behavior, one

needs to track operating behavior on an encapsulated solar cells, which will naturally be one of the future works of this project.

Lastly, the experience gained from testing reliability of perovskite solar cells in tropical climate in this project brought me a realistic perspective of what stress factor causes degradation the most. The most aggressive factor is indeed moisture and the degradation worsen when light is present. Therefore, I was invited to be a part of international committee and voice in my opinion on reliability testing of the perovskite solar cells from tropical climate standpoint. I have provided various feedback and requirement to test perovskite solar cells at high temperature and controlled humidity. As a result, we published the first consensus statement in Nature Energy journal for stability testing of perovskite solar cells as can be seen in the next page.

Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures

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Improving the long-term stability of perovskite solar cells is critical to the deployment of this technology. Despite the great emphasis laid on stability-related investigations, publications lack consistency in experimental procedures and parameters reported. It is therefore challenging to reproduce and compare results and thereby develop a deep understanding of degradation mechanisms. Here, we report a consensus between researchers in the field on procedures for testing perovskite solar cell stability, which are based on the International Summit on Organic Photovoltaic Stability (ISOS) protocols. We propose additional procedures to account for properties specific to PSCs such as ion redistribution under electric fields, reversible degradation and to distinguish ambient-induced degradation from other stress factors. These protocols are not intended as a replacement of the existing qualification standards, but rather they aim to unify the stability assessment and to understand failure modes. Finally, we identify key procedural information which we suggest reporting in publications to improve reproducibility and enable large data set analysis.

To ensure economic feasibility and competitive leveled cost of electricity, new photovoltaic (PV) technologies must offer long-term stability alongside high power conversion efficiency (PCE). For instance, the lifetime expectation for a PV module in a power plant is 20–25 years, to match the reliability of silicon-wafer-based modules. At present, the long-term stability of emerging technologies such as organic photovoltaic (OPV) cells, dye-sensitized solar cells (DSSCs) and halide perovskite solar cells (PSCs) is not meeting this target and improvements are hampered by a lack of understanding of the module failure modes.

The existing qualification tests described in the International Electrotechnical Commission (IEC) standards on terrestrial PV modules (such as IEC 61215)^{1–3} are designed for the field performance of silicon panels to screen for well-understood degradation modes generally associated with issues at the module level. These tests, however, are unlikely to be well-suited to OPV cells, DSSCs and PSCs because of their fundamentally different material properties and device architectures. In fact, various reports have shown that the

stability of these devices cannot be fully assessed by the procedures developed for conventional PV products^{4–10}, which led to the publication of various studies that attempted to understand the degradation mechanisms in emerging PV systems. Unfortunately, these studies lacked consistency in the assessment and reporting procedures, which prevented data comparison and, consequently, the identification of various degradation factors and failure mechanisms.

In light of such shortcomings, in 2011, a broad consortium of researchers developed recommendations for evaluating the stability of OPV cells¹¹. These standardized ageing experiments (the so-called ISOS protocols) were established at the International Summit on Organic PV Stability (ISOS) held in Roskilde, Denmark, in 2010. They outline a consensus between researchers in the OPV field on performing and reporting degradation studies in a controlled and reproducible way. These protocols are not intended to be a standard qualification test, nor are they suited for application by industry or insurance agencies; however, it is worth mentioning that tests based on the ISOS protocols were recently considered at the IEC level

A full list of affiliations appears at the end of the paper.

NATURE ENERGY

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