

Understanding degradation mechanism of perovskite solar cell

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This is to certify that this dissertation entitled **Understanding degradation mechanism of perovskite solar cell** for the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represent study/work carried out by Ankit kumar under the supervision of professor Atikur Rahman, department of physics, Indian institute of science Education and Research, Pune during the academic year 2017-2018.



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Declaration

In hereby declare that the matter embodied in report entitled **Understanding degradation mechanism of perovskite solar cell** are the results of works carried out by me at the department of physics, Indian Institute of Science Education and Research, Pune, Under the supervision of professor Atikur Rahman and the same has not been submitted for any other degree.



Ankit Kumar

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This thesis is dedicated to my family.

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Table of Contents

ABSTRACT	7
Introduction	9
Chapter 1) Theory and instrumentation	13
(1.1) Theory of solar cell	13
(1.1.1) Working principle	13
(1.1.2) Solar cell parameters	13
(1.2) measurement technique	15
(1.2.1) I-V characteristics	15
(1.2.2) Capacitance measurement	15
(1.2.3) Noise spectroscopy	16
(1.3) Controlled environment chamber	17
Chapter 2) Anomalous effect of UV light on the humidity dependence of photocurrent	19
(2.1) Introduction	19
(2.2) Measurements and discussion	20
(2.3) Conclusion	23
Chapter 3) Perovskite solar cell parameters in moderate humidity condition (without permanent degradation)	24
(3.1) Introduction	24
(3.2) Measurement and discussion	25
(3.3) Effect on ideality factor –	29
(3.4) Conclusion	32
Chapter 4) Degradation of perovskite solar cell in high humidity condition and a recipe for its recovery	33
(4.1) Introduction –	33
(4.2) Measurement and discussion	34
(4.4) Recovery of perovskite solar cell	37
(4.5) Non-recoverable degradation	Error! Bookmark not defined.
Chapter (5)-Temperature induced degradation in perovskite solar cell	45
(5.1) Introduction-	45
(5.2) Measurement and discussion	45
(5.3) Conclusion	51
Conclusion	51
Reference	52

ABSTRACT

Effect of oxygen on the humidity dependence of photocurrent in presence of UV light has been studied for perovskite solar cells. We observed that the magnitude of photocurrent increases with decreasing humidity initially, but below certain humidity, the photocurrent starts to decrease when the humidity is reduced by sending dry nitrogen gas. If we decrease the humidity by sending dry air (keeping nitrogen to oxygen ratio same), then this effect is absent. This phenomenon is related to the presence of oxygen in the environment. When humidity is decreased by flowing dry nitrogen, the oxygen present in the environment of perovskite solar cell also reduces. We found that, in a reduced oxygen environment, the presence of UV light helps to remove oxygen from the mesoporous TiO₂ which is responsible for the reduction of photocurrent. In presence of white light, this effect is not observed. To understand the phenomenon we studied low-frequency noise characteristics, current-voltage and dielectric properties of the perovskite solar cells under various conditions.

In next chapter we studied the effect of humidity on perovskite solar cell in the moderate humidity condition (upto 50%). We Found that in moderate humidity condition, in short time interval, there is no significant degradation of perovskite solar cell occurs. which we proved by studying the change in conventional solar cell parameters such as- open circuit voltage (**Voc**), Fill factor and power conversion efficiency. At the moderate humidity (up to 50% humidity), significant increase of the trap states have been observed through low frequency noise measurements in different humid environment (go up to the 50% humid environment). This increase in trap states is due to the fact that in humid environment water molecules get accumulated at the interface (between active perovskite layer (**CH₃NH₃PbI₃**) and hole collecting layer (**Spiro-MeOTAD**)) and started to form hydrated ions near the interface. Which we also confirmed by capacitance measurement in low frequency region.

In **chapter 4**, we observed rapid degradation in perovskite solar cell parameters in presence of high humidity condition (RH > 60%). Using the noise and capacitance measurement in the low frequency region we showed that as we go to the very high humidity condition, this quick degradation of perovskite solar cell is related to the loss of selectiveness of hole collective layer (**Spiro-MeOTAD**). By observing the change in photocurrent and the fact that this rapid degradation of solar cells parameters such as- open circuit voltage and fill factor can be

recovered if we quickly keep the sample in vacuum condition for few hours, we showed that at the beginning hole selective layer is not degrading, it is the water molecule which reacting with the hole transporting layer (**Spiro-MeOTAD**) and providing a conducting channel for charge carriers. We further demonstrated the fact that keeping the perovskite solar cell in high humidity (RH ~ 70%) condition for long time (more than 5 hours), resulted in permanent degradation of hole collective layer and solar cells become non-recoverable. Perovskite (**CH₃NH₃PbI₃**) material is also degrading in high humidity and as we increase the time in high humidity significant amount of **CH₃NH₃PbI₃** also degrade into **PbI₂** ions but the drastic drop in open circuit voltage is related to the degradation in hole transporting layer.

In the next chapter, we demonstrate the heat induced degradation of perovskite solar cell. We observed no significant decrease in solar cell parameters after treating the solar cell in moderate temperature (T < 65 °C) condition for few hours (5 hours), but large decrease in the open circuit voltage (**V_{oc}**) is observed when the solar cell are exposed to the high temperature (~ 80 °C) for 5 hours. We showed that No significant decrease in the photocurrent and drastic drop in open circuit voltage is due to the hole collective layer which goes bad quickly at high temperature. Some amount of perovskite material (**CH₃NH₃PbI₃**) also degraded into the **PbI₂** ions which we confirmed by measuring capacitance in low frequency.

Introduction

Perovskite solar cell has a perovskite structured compound as the light harvesting active layer. Perovskite compound has an ABX_3 crystal structure, in which A is an organic material, B is metal and X is halide. The site **A** is mostly occupied by methyl ammonium (CH_3NH_3), the site **B** is occupied by the metal for example (Lead (**Pb**), Tin (**Sn**)) and the site **X** is occupied by halide. Perovskite material active layer is sandwiched between electron transport layer and hole transport layer on a conducting and transparent glass which makes the complete solar cell. Methyl ammonium lead halide ($CH_3NH_3PbX_3$) is the best example of perovskite structure compound which is mostly used as an active layer in a solar cell. In 2009, Kojima reported the first application of Methyl ammonium lead halide perovskite material as an active layer for photovoltaic devices ([1][2]).

In our study, we have used methyl ammonium lead iodide ($CH_3NH_3PbI_3$) solar cell, which has TiO_2 as an electron selective layer and **Spiro-MeOTAD** as a hole selective layer. Methyl ammonium lead iodide perovskite material has many characteristics which are suitable and beneficial for photovoltaic devices application, for example high absorption coefficient (10^3 to 10^4 cm^{-1}), large diffusion length ($\sim 1 \text{ micrometre}$), direct bandgap, high mobility ($2-66 \text{ cm}^2 \text{ V}^{-1}\text{S}^{-1}$) and solution-based deposition synthesis process. All these properties make this material as an ideal next-generation photovoltaic device([3][4][5][6][7][8]).

With already achieved more than 20% efficiency, perovskite solar cells have few issues which are stopping them to be commercialized. One of them is the uses of Lead (**Pb**) in the perovskite material (due to its toxic nature for the environment) and another main problem is their long-term stability. The first problem could be solved by using the other metal for example Tin (**Sn**) instead of Lead (**Pb**) in perovskite compound, but in that case, stability further decreases ([9][10][11]).

Long-term stability is the major problem for perovskite solar cells. There are four main factors which are responsible for the perovskite solar cell degradation, namely humidity, heat, UV light, and O_2 environment. A lot of studies have been done for degradation of perovskite solar cell due to these four factors and several groups are trying to make perovskite solar cell stable over a long period of time, so that it will be possible to bring this photovoltaic technology to the industries and we will be able to solve many problems related to energy.

Humidity is a crucial factor in perovskite solar cell degradation, in high humidity condition perovskite solar cells degrade within few hours, and even in moderate humidity condition perovskite solar cell degrade in few days ([12]). There have been lots of studies done with humidity degradation and making the perovskite solar cell stable in humid environment. Several groups trying to improve the stability in humid environment by encapsulation of solar cell, substitution of hole and electron selective layer and inserting an organic material thin film into the solar cell which can prevent the water molecule from getting inside the solar cell ([13][14]). With these efforts scientists were able to increase the stability to some extent but long-term stability is still one of the major problems for the solar cells.

UV light also degrades the perovskite solar cell, in presence of UV light Methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) degrades to PbI_2 ions and then these ions act as the traps which are responsible for degradation of perovskite solar cell parameters, for example- fill factor, open circuit voltage and their efficiency. In solar radiation, the UV light intensity is around ($4.3\text{mW}/\text{cm}^2$) on the earth surface. Many groups have studied the perovskite solar cell degradation under the UV light while the other factors were eliminated, their UV light intensity was higher than the solar radiation UV intensity. They studied the change in fill factor or efficiency of solar cell over a range of time under UV illumination and it takes few days to see the considerable degradation of solar cell parameters. Solar cell degradation in UV light is a slow process compared to the humidity and heat-induced degradation ([15])

Oxygen can also degrade perovskite solar cell, once we kept the perovskite solar cell in oxygen environment, O_2 will start to go inside the perovskite solar cell and in the presence of light there will be formation of highly reactive superoxide species which are responsible for decreasing the solar cell parameter but degradation due to oxygen is not that fast process, and comparative to humidity degradation it takes a long time to degrade the solar cells.

The fourth factor is the degradation due to the heat, if the perovskite solar cell is kept in high-temperature condition, Methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) material starts to degrade into PbI_2 ions. Heat-induced degradation could be very fast and slow depending on at what temperature we are going to address the solar cell degradation. If we go to high-temperature condition, for example more than 100°C environment than perovskite solar cell made of methylammonium lead halide degrades in few hours ([16][17]).

So far many studies have done on how the solar cell parameter degrades with these factors (humidity, heat, UV light and O₂) and what are the chemical and physical changes in perovskite material (Methyl ammonium lead halide) once the solar cell is exposed to these environments. All the four factors degrade solar cell parameter by increasing the trap density into interface or in the active materials. The reaction could change with types of degradation, for example, water molecule first make the hydrated ions with Methyl ammonium lead halide (**CH₃NH₃PbI₃**) and then further degrade it into the **PbI₂** ions, while the UV Light and heat directly degrade the material into **PbI₂** ions. On the other hand oxygen makes the reactive superoxide in presence of light which degrades the Methyl ammonium lead halide into **PbI₂** by deprotonating it, but final degradation in solar cell is related to the increase in the defect concentration and degrading of Methyl ammonium lead halide (**CH₃NH₃PbI₃**) into **PbI₂**.

Several groups studied the degradation of Methyl ammonium lead halide (**CH₃NH₃PbI₃**) thin film alone, and compare it with the degradation of a complete solar cell. Degradation of a complete solar cell can be different, because it has hole and electron selective layer which cover Methyl ammonium lead halide active layer and make the interfaces, the solar cell also has electrodes which can also create the problem in the open environment. It turned out from these studies that degradation of perovskite thin film is slow while the degradation of complete solar cell is very fast in same extreme environmental condition, which makes people think that it is not only the perovskite material (Methyl ammonium lead halide) degradation which kills the solar cell fill factor and power conversion efficiency, it could be the interfaces of solar cell which are responsible for quick degradation, few groups started to study about the interface effect on degradation of perovskite solar cell and making solar cell stable by replacing the hole or electron selective layer, which turn out to be favourable for the perovskite solar cell stability([18][19]).

Humidity is the main devil for perovskite solar cell, even in the low humidity environment it can degrade the solar cell in few days, and in presence of light this process becomes faster and can degrade the solar cell in few hours. Degradation of Methyl ammonium lead iodide (**CH₃NH₃PbI₃**) in the humid environment happen in two steps, initially it forms the hydrated ions with Methyl ammonium lead iodide (**CH₃NH₃PbI₃**) and further degrade it into the **PbI₂** ions. These ions act as defects and reduces the power conversion efficiency. The first step of the degradation process (hydrated ions of Methyl ammonium lead iodide) is reversible, while

The other process is not (can't recover once it degrades into the PbI_2 ions([20],[21]). As we already mention that degradation of complete solar cell could be different than the degradation of perovskite thin film because there is no direct exposure of Methyl ammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbX}_3$) film to the environment. There are two possible paths for the degradation of perovskite solar cell in a humid environment. First path is related to the degradation of Methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) which is obvious and second path is related to degradation due to the interfaces in the extreme environment.

There have been large number of studies devoted on how the Methyl ammonium lead iodide material degrade in perovskite solar cell within high humidity condition. By using various methods, for example such as XRD, PL, external quantum efficiency measurement, it has been proposed that in humid environment condition Methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) degrade in PbI_2 . [22]. The first step of the degradation process (hydrated ions of Methyl ammonium lead iodide) is reversible, while the other process is not (can't recover once it degrades into the PbI_2 ions)[21]. As we already mention that degradation of complete solar cell could be different than the degradation of perovskite thin film because there is no direct exposure of Methyl ammonium lead halide film to the environment. There are two possible paths for the degradation of perovskite solar cell in a humid environment. One is related with the perovskite layer degradation and other is interface is going bad with high humidity. There is not much study has been done on how the interfaces are going bad within extreme environment condition (high humidity) and which interface of perovskite solar cell is responsible for rapid degradation in high humidity condition.

Many groups studied the chemical change with time in perovskite material In humid environment, but only a few studies are devoted to understanding the mechanism behind the solar cell degradation in term of electronic transport, for example how the defects are responsible for solar cell degradation, what is the defect concentration, their energy levels, how are they responsible for making interface bad. The second thing we need to understand is that how the interface is responsible for solar cell degradation in high humidity and which interface is going bad in high humidity condition, is it the transporting layer which is degrading in extreme environment condition or is there defects energy levels which provides the channel for charge carriers, causing the loss of selectivity of charge transporting layer which in turn decreases the solar open circuit voltage and fill factor.

Chapter 1) Theory and instrumentation

(1.1) Theory of solar cell

A solar cell is an electric device which converts light energy into the electric energy by the photovoltaic effect. A semiconductor p-n junction is a good example of the solar cell. When light falls on the solar cell surface, photons give their energy to the electron present in the semiconductor and if the given energy is sufficient (equal or more than the band gap of semiconductor material) then electron moves to the conduction band. Due to the electric field between P-N junctions, this newly generated electron will move to n-type layer and the hole in valence band will move to the P side and we will get electric energy to an external load. Solar cells can be made from both the organic and inorganic materials. Inorganic solar cells are made of the semiconductor materials in the periodic table (examples are **Si**, **GaAs**, **CdTe** solar cell), Organic solar cells have an organic layer to absorb the photon energy. Newly discovered perovskite solar cells are made of organo-metallic halide compound.

(1.1.1) Working principle

Perovskite solar cell behaves as almost similar to organic solar cell. They have an active layer which acts like a sensitizer, this layer has perovskite structure that absorbs light and generates electron-hole pairs. This layer is sandwiched between electron and hole transporting layers, so that electron can move only in one direction while hole can move in the other direction. These three layers are deposited on the transparent and conductive glass (FTO). Once we keep the solar cell in light, perovskite layer absorbs energy from the photons and photo-generated electrons can move to the conduction band and holes remain in the valence band, the electrons can pass through the electron transport layer (TiO_2 , NiO_2 etc.) and hole can move through the hole transporting layer, providing current to the outside load.

(1.1.2) Solar cell parameters

Before we start studying about solar cell, we need to define some of its parameters, which are very important for solar cell characterization. I-V characteristic of the solar cell is an important measurement because it provides the required parameters of solar cell needed to characterize the solar cell. From the I-V characteristics of a solar cell we get the following parameters.

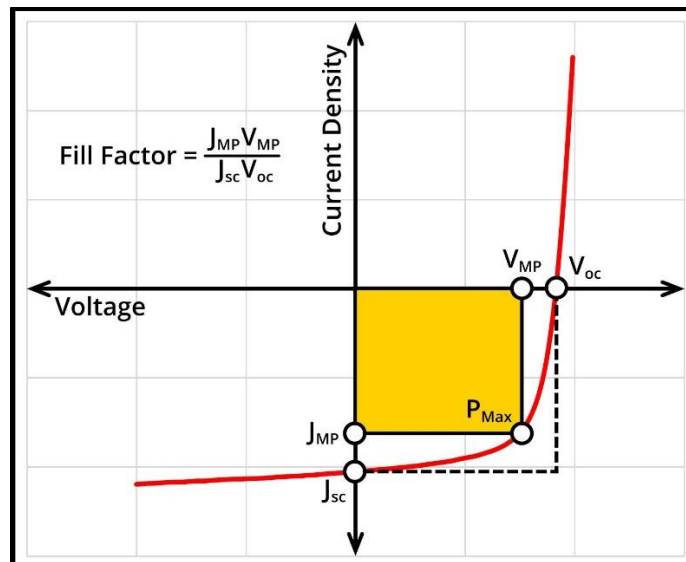


Figure (1) I-V curve of a standard solar cell (image is taken from google images)

- (1) Short circuit current- This is the maximum current we can get from a solar cell without harming its construction. So if we short the solar cell terminals than the maximum current flowing in the circuit is the short-circuit current.
- (2) Open circuit voltage- This is the maximum voltage we can get across the solar cell terminal so if we measure the voltage difference across its terminal while it does not have any external circuit to flow the current. In other words, we can say that voltage drop across the solar cell if the current in external circuit is zero.
- (3) Maximum power point- The point on the I-V curve at which we can get maximum power output from the solar cell is its maximum power point. The current at this point is called I_m (maximum current) and voltage call is V_m (maximum voltage).
- (4) Fill factor – fill factor is an important parameter in solar cell characterization. It is the ratio between maximum power and product of J_{sc} (short circuit current) to V_{oc} (open circuit Voltage)

$$\text{Fill factor} = P_m / (J_{sc} * V_{oc}) \text{ where } p_m = I_m * V_m$$

- (5) Efficiency – it is the ratio between the output power of solar cells given as electricity to the 1 sun solar irradiation. We know the solar radiation on the earth surface is around 100 mW/cm^2 so the efficiency will be output power by 100 mW/Cm^2 .

Efficiency is also an important parameter in deciding the solar cell characteristics and its quality. Higher the efficiency means it can provide more electrical power by converting the sunlight efficiently

(1.2) measurement technique

In this study, we use different measurement techniques to understand the quality of a solar cell. Some of them are standard technique some of them we design for our purpose. Here I am going to address most of the techniques we used to demonstrate the perovskite solar cell quality.

(1.2.1) I-V characteristics

All the DC electrical characteristics were measured using Keithley 2450 source-measure unit. We measured I-V characteristic of a solar cell in the different environment in presence of different LED as well as in the dark. Measuring the I-V characteristics in different environment condition can provide us information about how the solar cell quality is changing with different environments. As well as we measure some parameter for example photocurrent with continuously varying the environment which can provide us more information how the solar cell quality continuously changing with varying the environment condition. Change in photocurrent by continuously increasing or decreasing the humidity, temperature, O₂ from the environment can be more informative. For data acquisition, we used the LabVIEW programming.

(1.2.2) Capacitance measurement

Capacitance spectroscopy is important measurement technique as it gives us information about the dielectric properties of the sample. For a solar cell, the capacitance can provide us information about the trap density and ionic contribution. So as we change the environment how the capacitive or dielectric properties and ionic contribution are changing can provide us information about the solar cell quality the contribution of ions and changes in defect concentration.

For capacitance measurement, we used Stanford Research System SR 865A, 4MHz DSP lock-in amplifier and Keysight 33621A waveform generator. The technique we used to measure the capacitance is simple and depend on the theory of impedance, as we all know a solar cell has both the resistive and capacitive element. The total impedance of solar cell will be its resistance and its reactance which is $(1/j(2\pi f) c)$ where j is a complex number, f is frequency and c is capacitance, so the reactance is frequency dependent. For capacitance measurement, we put a 10-ohm resistance in series with the solar cell and measure the complex current across this 10-ohm resistance. The purpose behind using the small resistor is that most of the voltage drop will be across the solar cell, by sending a sinusoidal voltage from the function generator over a range of frequency which will give us capacitance value for different frequency. For data acquisition, we use LabVIEW programming which automatically plots the capacitance as a function of frequency over a given range of frequency in the program.

(1.2.3) Noise spectroscopy

Noise spectroscopy could be the best tool to measure the quality of a solar cell. $1/f$ noise in semiconductor arises due to the trapping or recombination of charge carrier with traps. As it is the voltage fluctuation measurement, even a small change in traps and defect density can increase the trapping and recombination by a large amount and which can be revealed by noise spectroscopy.

To measure the $1/f$ noise we measure the voltage fluctuation over a range of time and amplify the signal using low-frequency voltage preamplifier whose background noise is very less. We used the LabVIEW program for data acquisition which store the voltage fluctuation over a time into the DAQ and once we got the voltage fluctuation over a range of time using FFT algorithm, we convert the time domain into the frequency domain.

$1/f$ noise spectroscopy is a very sensitive tool and used for characterizing many photovoltaic devices. For the characterization of perovskite solar cell, it's not have been much explored. Small quality change in a solar cell can be revealed by noise spectroscopy which is not possible by some other old technique.

Before starting the measurement on a solar cell we standardize our instrument by checking capacitance of a standard capacitor which comes out to be exact to its standard value and the second thing we should be careful about the background noise of preamplifier which is

around ($S_v - 10^{-17} \text{ v}^2/\text{Hz}$) in the desired frequency range (1-1000Hz). This noise is very small comparative to noise in perovskite solar cell, so we confirmed that preamplifier background noise cause no harm to our measurement.

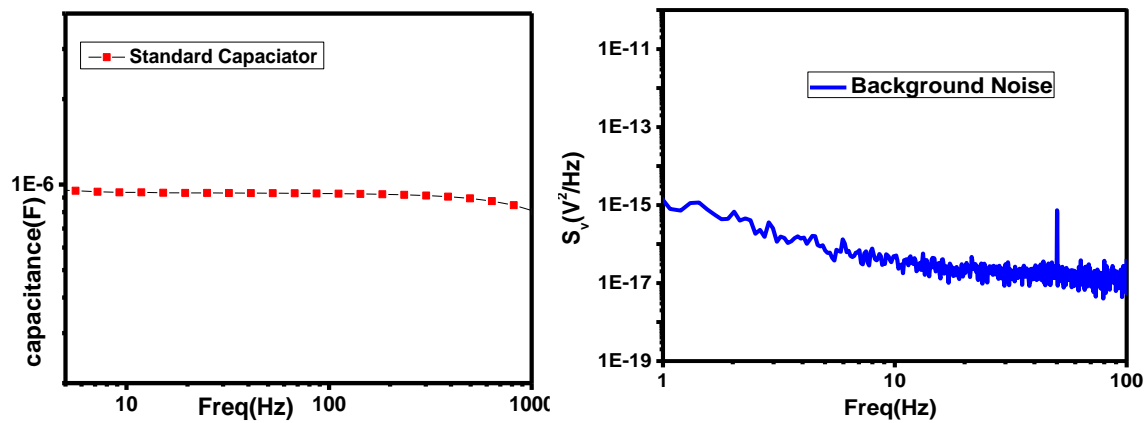
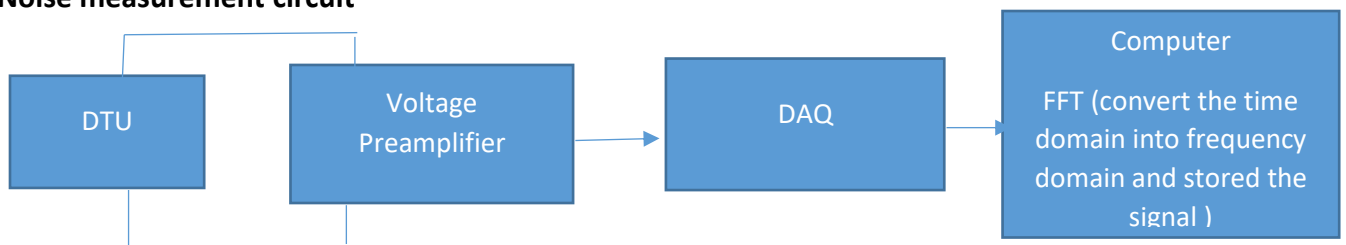


Figure (2) (a) standard capacitor (98 Nanofarad) was measured using lock-in amplifier (to standardized our instrument) (b) $1/f$ low-frequency noise measurement of the current pre-amplifier (to prove that background noise are not going to affect our measurement because their value is Very small)

Noise measurement circuit –



Time dependent voltage data (after the amplification) were sampled using National Instrument PCIe-6321, X series DAQ card (capable of sampling at 250 kS/s).

(1.3) Controlled environment chamber

As we all know the perovskite solar cell degrade by many factors, so to see the change in parameters due to a particular factor is very hard, for that we need very controlled environment in which we can control all the factors, which are responsible for degradation.

By minimizing the other factors we can see the degradation and change in solar cell parameters due to a particular factor, in open environment it is very hard.

So we design a chamber where we can control environment precisely, in the chamber we can flow any gas with controlled rate. For example to reduce the humidity we flow dry O₂ through the chamber and to reduce both the humidity and O₂ we can flow dry N₂ further to increase the humidity alone in absence of O₂ we flow humid N₂. For humidity measurements, we used a DHT22 sensor, which we connect with the Arduino and for data acquisition from the sensor we used LabVIEW programming. To control the temperature of the solar cell we used PID controller.

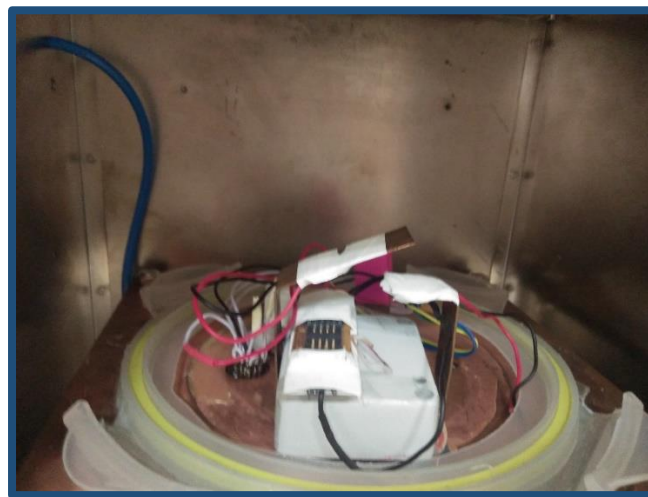


Figure (3) control environment chamber, we kept this setup in a square aluminium box to avoid any electromagnetic interface in our measurements.

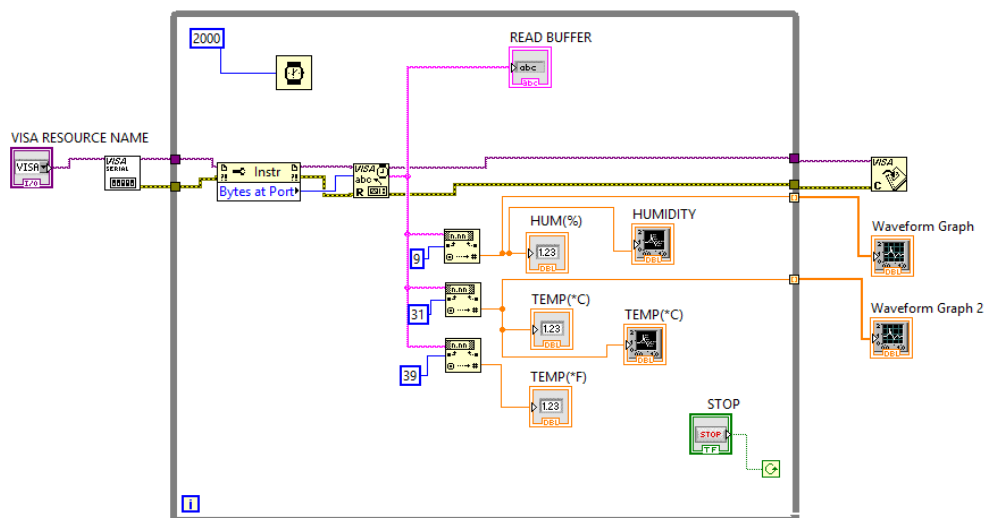


Fig (4) LabVIEW program to measure the continues change in humidity (DHT22 sensor with Arduino)

Chapter 2) Anomalous effect of UV light on the humidity dependence of photocurrent

(2.1) Introduction

Humidity is one of the mostly studied parameters in the context of stability of perovskite solar cell and it has been reported that reduced humidity environment is beneficial for the longer stability. Several reports mentioned the effect of humidity on the photocurrent and found that, photocurrent increases with decreasing humidity. However, the details of how the humidity is being controlled can provide some important information regarding the effect of other parameters, such as presence of oxygen, whose effect might have been overlooked in the process. Understanding the effect of each factor is important for the development of reliable and stable perovskite solar cell.

The effect of ultraviolet light on the stability of perovskite solar cell has also been studied by several groups and there have been reports that performances of perovskite solar cells degrade under UV light exposure in presence of oxygen. Though the speed and extent of degradation by UV light is not very clear. It has been reported that, under inert condition the effect of UV light is not dramatic and causes slow degradation. However, other reports claim that Oxygen can cause rapid degradation of perovskite solar cells in presence of light. In case of solar cells made of mesoporous TiO_2 , it has been proposed that the degradation is related to the light-induced desorption of surface-adsorbed oxygen.

Here we demonstrate an anomalous effect of UV light on the humidity dependence of photocurrent in perovskite solar cells. We found that, if the humidity is reduced by flowing dry nitrogen then, in presence of UV light, the magnitude of photocurrent initially increases with decreasing humidity and below a certain humidity it starts to decrease. If the humidity is decreased using dry air then this phenomenon is absent. Also, in presence of white light, the photocurrent always increases independent of whether the humidity is decreased by flowing dry nitrogen or air.

Our results suggest that, the decrease of photocurrent below certain humidity level in presence of UV light, is related to the depletion of oxygen. When humidity is reduced by flowing dry nitrogen, along with water vapor it also replaces the oxygen present in the

surrounding environment of perovskite solar cell. To understand the mechanism behind this phenomenon, we have studied low-frequency $1/f$ noise characteristics, current-voltage (I-V), capacitance-voltage (C-V) and capacitance-frequency (C-f) under various conditions. We found that, in reduced oxygen environment, the presence of UV light helps to remove oxygen from the mesoporous TiO_2 which is responsible for the reduction of photocurrent.

(2.2) Measurements and discussion

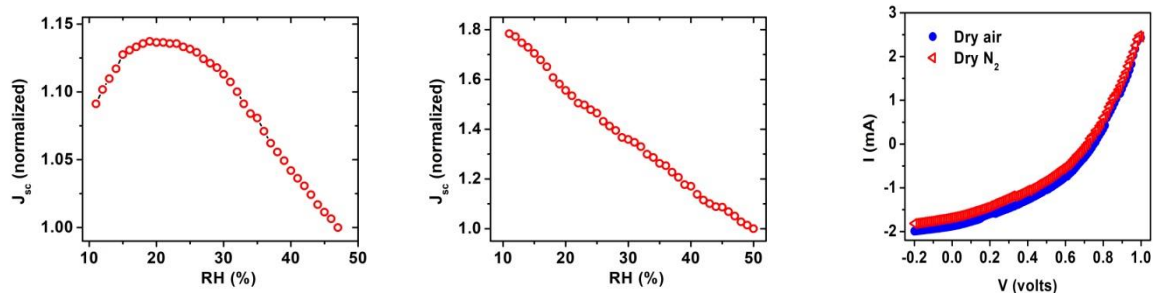


Figure 1. Humidity dependent J_{sc} in presence of (a) UV (385 nm) and (b) white light. The humidity is reduced by sending dry N_2 gas. (c) I-V characteristics at 10% humidity in presence of UV light when humidity is decreased by dry air (solid circle) and dry nitrogen (open triangle).

In figure 1(a) we have shown the variation of photocurrent (normalized) as a function of humidity when the humidity is reduced by sending dry nitrogen gas and the sample is illuminated using a 365nm UV led (3.5 mW.cm^{-2} at the sample surface). The magnitude of photo current initially increases with decreasing humidity but below a certain level (in this case around 20% humidity), the photocurrent starts to decrease.

In presence of white light (20 mW.cm^{-2} at the sample surface), the magnitude of photocurrent increases with decreasing humidity without showing any decrease (see Fig. 1(b)). Similar effect has also been observed for any wavelength other than UV. In general, the enhancement of photocurrent with decreasing humidity is considered due to the removal of water molecule from the device (inside the grain or grain boundary), which reduces the charge traps hence recombination reduces and photocurrent increases. If we reduce the sample environment humidity by sending dry air, then the photocurrent keeps increasing with decreasing humidity

for any wavelength of light. In Figure 1(c) we have shown I-V characteristics in presence of UV light when sample was kept in dry air (solid circle) and dry nitrogen (open triangle).

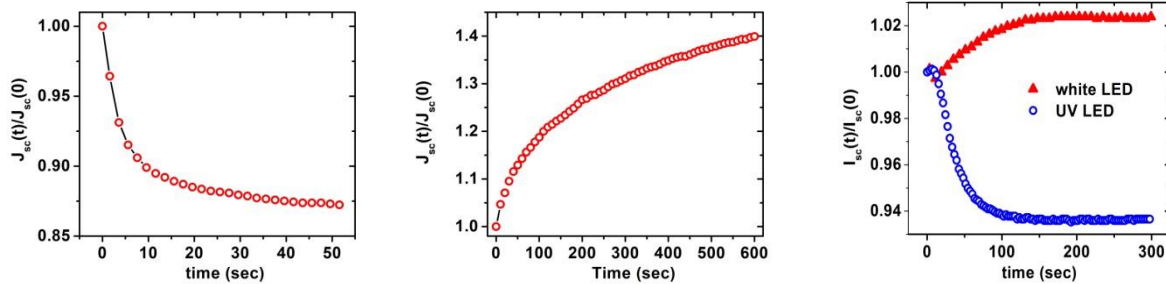


Figure 2 (a) Photocurrent as a function of time after rapid removal of oxygen. In (b) both humidity and oxygen are removed initially then photocurrent is measured after introducing oxygen by sending dry air and photocurrent is measured as a function of time. (c) Time dependence of photocurrent (normalized) in presence of UV (open circle) and white light (solid triangle) when humidity is reduced by sending dry nitrogen.

To further confirm that the effect is indeed related to oxygen and UV light, we have done the following experiments. We have reduced the humidity initially by sending dry air and then we flush the sample environment by quickly sending large amount of dry nitrogen to remove the oxygen and measured the J_{sc} as a function of time. In Figure 2(a), we have shown one such representative data which shows that, after removing the oxygen from the vicinity of the perovskite sample, the photocurrent starts to decrease as a function of time though the humidity remains unchanged. On the other hand, if we reduce the humidity and oxygen by flushing the sample environment with dry nitrogen first and then introduce oxygen by sending dry air, photocurrent increases with time in presence of UV light (Fig. 2(b)). These results clearly demonstrate the role of oxygen on photocurrent in presence of UV light.

To rule out any time dependent effect, we have studied time dependence of photocurrent in presence of UV and white light. In Figure 2(c), we have shown time dependence of J_{sc} in presence of UV (open circle) and white light (solid triangle) when humidity is reduced by sending dry nitrogen (oxygen is removed). It is evident from the data that, in presence of white light, J_{sc} increases slightly and become constant. On the other hand, in presence of UV light photocurrent reduces initially before it reaches a steady state value. The initial decrease of photocurrent in presence of UV illumination is probably due to further desorption of oxygen from the sample interface. In presence of white light, the photocurrent increases slightly and reaches to a steady value quickly.

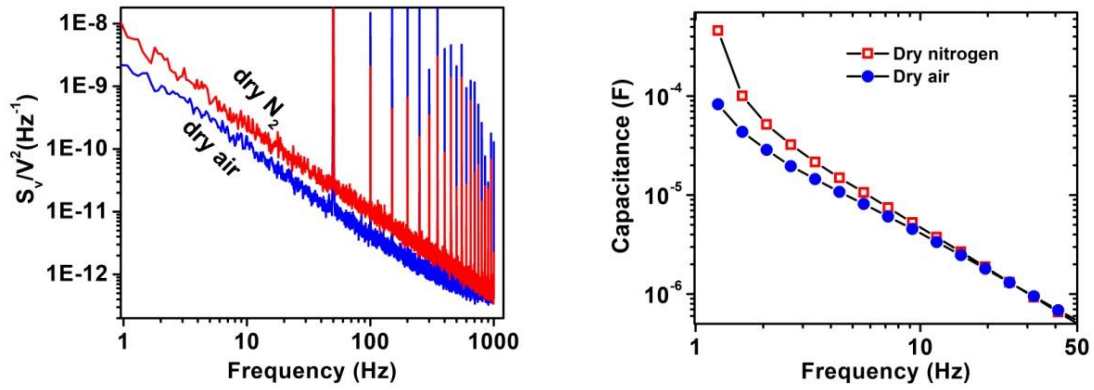


Figure 3 (a) Low frequency noise power (in log-log scale) is shown when humidity is reduced by dry air (blue line) and dry nitrogen (red line). From the plot it is clear that noise follows $1/f^\alpha$ behavior over more than three decades. (b) Measured capacitance in the low frequency region. Capacitance in dry nitrogen environment is higher (open square) than dry air (solid circle). The difference is pronounced in the low frequency regime.

To further investigate the effect of oxygen and UV light on photocurrent, we measured the low frequency noise characteristics and dielectric properties of these samples under various conditions. Figure 3(a) shows low frequency noise characteristics in presence of dry nitrogen (both moisture and oxygen removed) and dry air (only moisture removed). In presence of UV light, the normalized noise power shows $1/f^\alpha$ dependence over at least 3 decades. In both the conditions we observed value of $\alpha \approx 1.3$. In presence of dry nitrogen, normalized noise power is higher than dry air.

Oxygen vacancies in TiO_2 act as deep level trap states which is one of the major problems for the application of this material as electron transporting layer.[23] In presence of UV illumination, oxygen can release from TiO_2 and these vacancies act as deep trap states. The presence of deep level trap states is also consistent with the observed noise behavior. As the carrier trapping and de-trapping mechanism is much slower for the deep level trap states, the relative contribution of the low frequency noise increases which is consistent with the observed value of the exponent, $\alpha \approx 1.3$. We also found that, noise is higher in presence of UV compared to white light illumination. This enhancement of fluctuation can be due to desorption of oxygen which modulates the energy barrier at the TiO_2 /perovskite interface. Similar effect has been observed in the case of resonant tunnelling diode.

We measured the dielectric properties of these samples in presence and absence of oxygen after UV illumination. In Figure 3(b) we have shown capacitance as a function of frequency

for these two conditions. It is evident that the value of capacitance in the low frequency region increases after removal of oxygen from the perovskite solar cell environment. This result is consistent with our previous observation of increasing noise after removing the oxygen. The removal of oxygen in presence of UV increases interfacial polarization due to desorption of oxygen from TiO₂. The interfacial polarization can only follow the slowly varying field as a result the capacitance in the low frequency region increases.

Oxygen plays an important role in determining the degradation of perovskite solar cells. In presence of O₂ the degradation is rapid and has been attributed to the formation of O₂⁻ ions. However our result suggests that O₂ plays a positive role in determining the photocurrent, especially at low humidity condition. Removal of O₂, in presence of UV light reduces the photocurrent. In our perovskite solar cells, mesoporous TiO₂ is used as the electron transporting layer. Recent studies show that the interface between TiO₂ and perovskite layer plays an important role in determining the device performance and stability. Any degradation of the TiO₂ layer will have effect on the charge collection efficiency i.e. in photocurrent. It has been observed that reducing the oxygen vacancy in TiO₂ layer by annealing the TiO₂ layer in presence of oxygen improves the perovskite solar cell efficiency.[23] The observed improvement is mainly due to the reduction of trap states which enhances the carrier lifetime thus increases photocurrent. In reduced O₂ environment, in presence of UV light, desorption of O₂ from the mesoporous TiO₂ surface enhances. This reduces the charge collection efficiency hence the photocurrent.

(2.3) Conclusion

In this study, we have shown role of oxygen in determining the humidity dependence of photocurrent in presence UV light. At low humidity condition in presence of UV light, photocurrent reduces if oxygen is removed. This is probably due to the enhancement of oxygen desorption from the mesoporous TiO₂ layer in presence of UV light. These oxygen vacancies act as deep level trap states whose signatures are observed in the enhancement of low frequency noise and capacitance. These results show that, when studying the effect of UV and humidity in the context of degradation or stability of perovskite solar cell, one should also take care about the presence of oxygen in the environment. Our findings will help to understand the effects of UV light, humidity and oxygen in determining the various properties and stability of perovskite solar cells.

Chapter 3) Perovskite solar cell parameters in moderate humidity condition (without permanent degradation)

(3.1) Introduction

After seeing the effect on the photocurrent with changing the humidity condition in presence of UV light in our previous study, and the result provided by the noise spectroscopy and capacitance, it is the time that we should study the effect of humidity alone on the perovskite solar cell parameter. In this study, we are going to address the effect of moderate humidity on perovskite solar cell parameters. First we kept the solar cell in the N_2 environment for some time (10 mint) so that O_2 and humidity can be removed from the solar cell environment and then further increase the humidity with the flow of humid N_2 (flowing the dry N_2 through a water bubbler with controlled flow rate) so that changes are only due to the Humidity. Once we start increasing the humidity of the environment, water molecules will start to get inside the perovskite solar cell through the HTL. So far lot of studies has done on how much the perovskite solar cell parameter reduces once we kept it in the humid environment condition with time. Many study demonstrate that in low or moderate humidity condition only over a long time period perovskite solar cell parameters such as power conversion efficiency and fill factor changes, but not much exploration on the study of how the trapping and defect concentration are going to change and how the charge collective layer and interface between the charge collective layer and perovskite material is going to behave in moderate humidity condition.

Here we are going to demonstrate the problem that how the defects and traps change once we start increasing the humidity up to a moderate humidity where there is no permanent degradation in perovskite material for the initial time period. The changes in various parameters of perovskite solar cell such as photocurrent, capacitive behaviour, noise (in presence of light) get affected in moderate humidity condition. Our study suggest that even in the moderate humidity condition where there is no degradation in perovskite active material for initially time interval (quick measurement were done by just going to moderate humidity condition) but there is huge increase in the defects and traps density was observed, which increases the trapping of the charge carries and responsible for change in photocurrent.

Further we demonstrate that once you keep the solar cell in moderate humidity condition for some time we observed only a small decrease in solar cell fill factor and power conversion efficiency which is not related to perovskite material degradation (the time for which we kept the solar cell was small) but related to increase in the traps concentration because as the time pass more water molecule get inside the perovskite solar cell and accumulate at the interface and they started to form hydrated ions with perovskite material near the interface (between the perovskite and HTL).

(3.2) Measurement and discussion

To avoid the effect of O_2 First we removed the oxygen by flowing the dry N_2 into the chamber for a long time (Around 10 mint) and then used humid N_2 (obtained by sending dry N_2 gas through a gas bubbler filled with water) to increase the humidity and dry N_2 to reduce it. We started our experiment by measuring the change in photocurrent with changing the humidity alone (this time O_2 was absent in all the experiment so the effect is only due to humidity). We increase the humidity only up to a moderate value ($RH < 55\%$) so that we can avoid the degradation of perovskite solar cell for the initial time period. We used WHLED (intensity $20mW/cm^2$ on the solar cell surface).

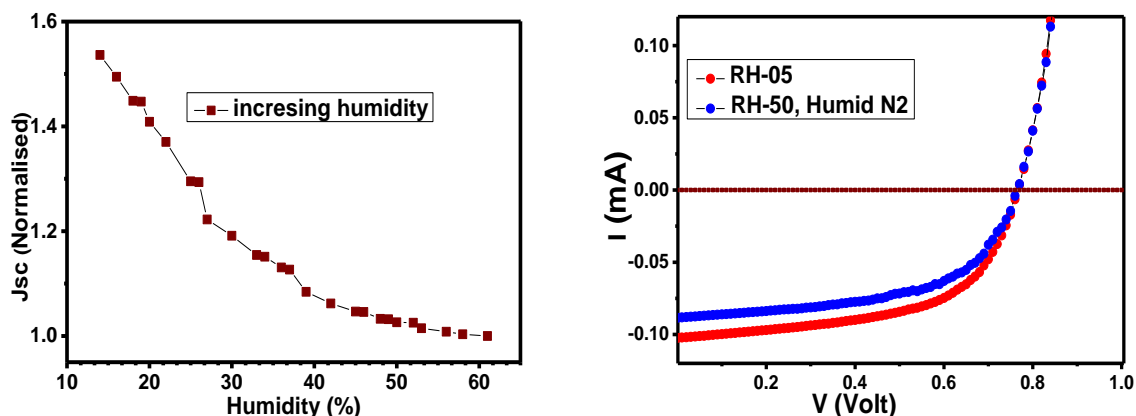


Figure (1) (a) change in photocurrent with increase humidity (continuous flow of humid N_2 into the chamber) in presence of white LED ($20mW/Cm^2$ at the surface of the solar cell) (b) I - V characteristics of the solar cell in presence of WHITE LED (intensity $20 mW/Cm^2$) in two different humidity Red (RH-05%) and Blue (RH-50%), humidity was fixed at particular humidity during the measurements.

We observed that with increasing the humidity photocurrent start to decrease (similar to our previous study) this is due to the fact that with increasing humidity water molecule first

diffuse through the hole collective layers and get accumulate at the interfaces and also accumulate across the grain boundaries of the perovskite material which increases the trapping of photo generated charge carriers as a result, photocurrent decreases. As long as the water can't get inside the perovskite grain they can't degraded significant amount of perovskite it into the PbI_2 ions. So this change is not related to permanent degradation of perovskite material, in moderate humidity condition degradation of the perovskite material take hours (19, 20). So this decrease in photocurrent is related to trapping of charge carrier with water molecule and with perovskite hydrated ions at the grain boundaries.

To further confirm the accumulation of water molecule at the perovskite and HTL interface and at the perovskite grain boundaries, we did noise spectroscopy and capacitance measurement which confirm the water molecules accumulation at the interface and formation of hydrated ions at the grain boundaries of $CH_3NH_3PbI_3$, which act as traps for charge carriers.

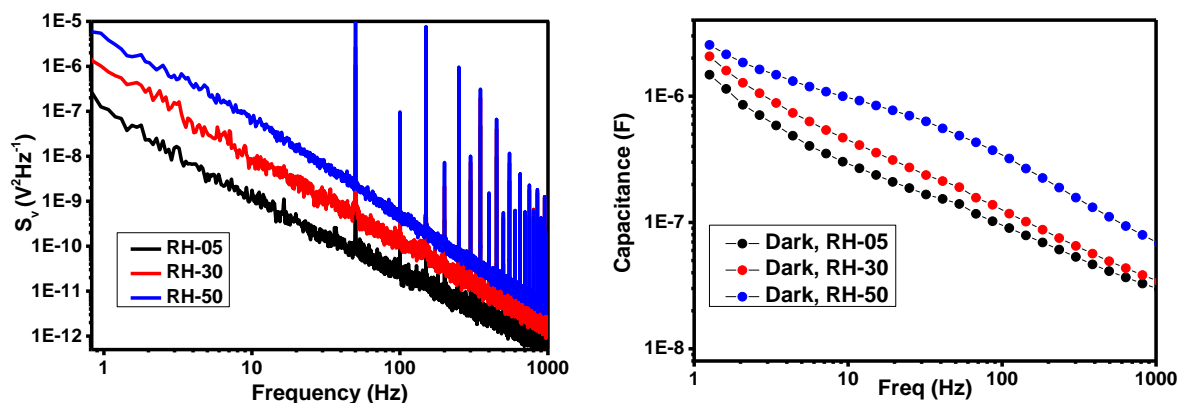


Figure 2 (a) Low frequency noise power (in log-log scale) is shown in presence of white led (intensity - 20 mW/cm^2) where black (humidity -2%, Dry N_2 environment) and when humidity is increased by humid N_2 Red (RH-30% and keep fixed to that throughout the measurement), Blue (RH-50%, Keep fixed throughout the measurement). From the plot it is clear that noise follows $1/f^\alpha$ and increase with increase humidity (b) Measured capacitance in the low frequency region in the dark and humidity condition were same as the Noise measurement.

From the data it clear that with increasing humidity $1/f$ noise increases which is related to increase in trapping and recombination of charge carrier at the interface and grain boundaries of $CH_3NH_3PbI_3$. It is interesting to mention that compared to the solar cell conventional

parameters (such as **Voc**, **Jsc** and **Fill factor**) noise change is significantly, this clearly shows the importance of Noise spectroscopy as a sensitive tool to investigate the quality of perovskite solar cells. Studies of other parameters do not provide detail mechanism about the carrier transport in perovskite solar cells. Noise study can provide important information about trapping and de-trapping for charge carrier at the interface, Noise data in presence of white light easily confirms, water molecules accumulation at the interface and at the grain boundaries of **CH₃NH₃PbI₃** and they act as traps and these traps increase with humidity.

Study of dielectric behaviour as function of humidity shows significant changes in the capacitance value in the low frequency region. This Lower frequency region is related to bulky ions such as perovskite hydrated ions, PbI₂ and other heavy ions present in the solar cell, for example, Li ions present in the Spiro-MeOTAD (hole selective layer) layer. As we go to moderate humidity water molecules get accumulated at the interface and at the grain boundaries of **CH₃NH₃PbI₃** which further form the hydrated ions at the grain and at the surface of perovskite material. These water molecules accumulation at the interface and hydrated ions at the interface and grain boundaries contribute to capacitance of perovskite solar cell. The increase in capacitance in lower frequency region (less than 10HZ) is less which telling the fact that formation of hydrated ions is less but large increase in capacitance in $F > 100$ Hz is related to the water molecule accumulation at the interface.

To further see the effect how the parameters of perovskite solar cell changes if we keep the samples in moderate humidity conditions for some time. At the beginning most of the changes are only due to water accumulation at the interface and grain boundaries of **CH₃NH₃PbI₃** and nothing to do with degradation of the perovskite material. We kept the sample for 1 hrs in 30% and 50% humidity in the presence of light and then took the measurements to find out how parameters changes within this time interval.

From the I-V characteristics **fig(3)** it is clear that in the 30% humidity there is no significant change in the open circuit voltage (**Voc**) and fill factor observed in small time interval (1 hour) there is already water molecule which get accumulated once we increase the humidity further diffusion of water can't take place inside the perovskite solar cell through HTL.

Once we keep the sample at 50% humidity than in the small time interval some more water molecule can diffuse through the HTL and can increase the accumulation at the interface with

time. As with time concentration of accumulated water near the interface increase which result in decrease in open circuit voltage (V_{oc}) and fill factor to some extent.

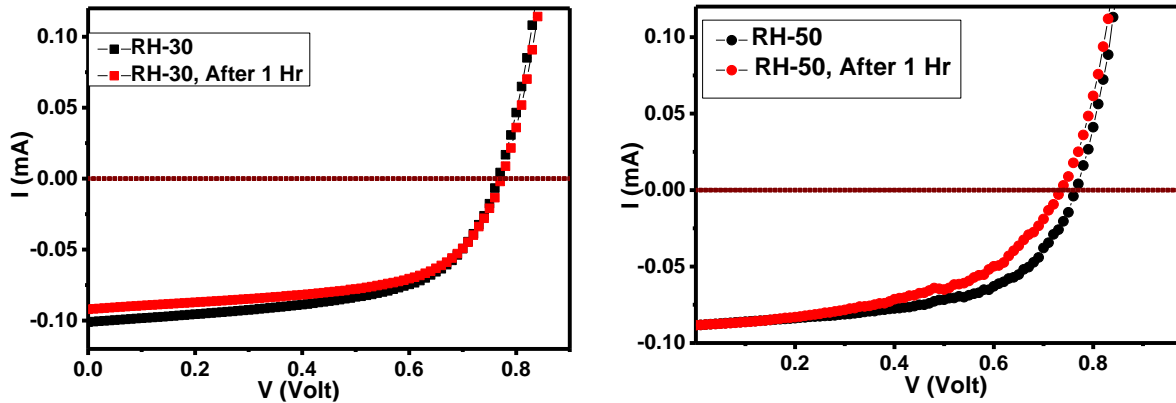


Figure (3) I-V characteristics of perovskite solar cell in presence of White Led (intensity $-20\text{mW}/\text{cm}^2$) (a) humidity of the chamber was at RH-30% during complete measurement black (at the beginning), red (after keeping the sample at 30% humidity for 1 hour) (b) humidity of the chamber was at RH-50% during complete measurement black (at the beginning), red (after keeping the sample at 50% humidity for 1 hour). We keep fix the humidity at certain point by controlled flow of humid N_2 and oxygen was absent in the chamber during all the measurement.

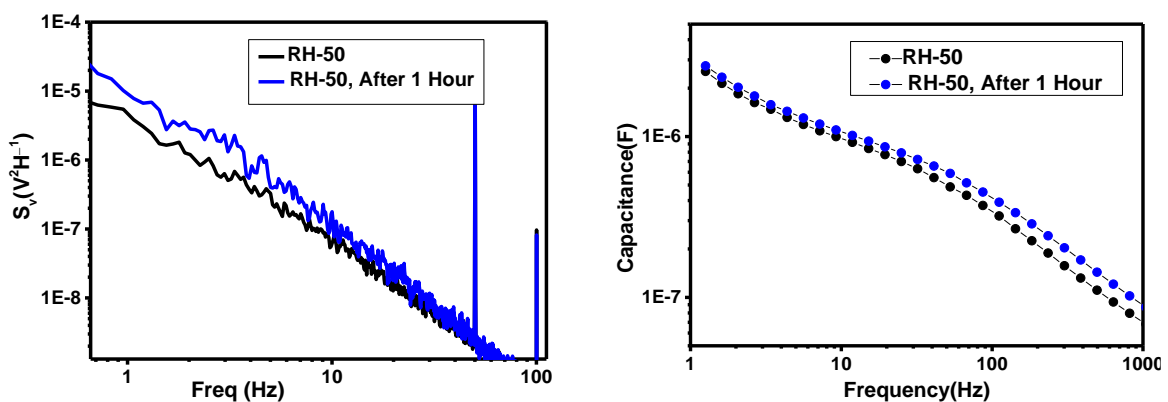


Figure (4) (a) Low frequency noise power (in log-log scale) with white LED (intensity $20\text{mW}/\text{Cm}^2$) in humid environment (RH-50%), black (at the beginning) blue (After we keep the sample in this environment for 1 hour)(b) Measured capacitance in the low frequency region in humid environment (RH-50) in the dark condition black(at begging) and blue (after we keep sample for 1 hour at RH-50% humidity)

Our observed data can be confirmed by measuring noise in these time interval. There is only a small increase in $1/f$ noise at lower frequencies (Fig-4), which confirm that as we kept the solar cell at a particular humidity, some more water can diffuse through the HTL and concentration of accumulated water increase with time but at moderate humidity condition not enough water can further diffuse through the HTL. So only a bit increase in water assisted traps have been seen with time.

Capacitance (fig. 4) also changes a bit in 100-1000 Hz frequency range that increase is mostly related to some more water molecules accumulation at the interface, but as already water molecule get accumulated at the interface further diffusion of water can't take place at moderate humidity within a short time period (1 hour) in moderate humidity condition. Capacitance and noise data are consistent with each other.

(3.3) Effect on ideality factor –

To further confirm increase in water molecule assisted trap states in the Solar cell as we go to humid environment, we studied variation of ideality, which can provide useful information about trapping and de-trapping into the perovskite solar cell. The value of Ideality factor for ideal solar cell should be one but as the quality of solar cell decrease due to increase in photo generated charge carrier recombination with the traps, the ideality factor increase. From the ideality factor, we can get valuable information about the solar cell quality and recombination rate and traps concentration.

To calculate the ideality factor we studied intensity depended of open circuit voltage (V_{oc}). Solar cell open circuit voltage is related to its short circuit current by Shockley equation. Changing the light intensity will change short circuit current (J_{sc}) which will further change the open circuit voltage (V_{oc}) of a solar cell. By plotting open circuit voltage (V_{oc}) vs the logarithm of J_{sc} we can calculate the ideality factor using Shockley equation for a solar cell.

We first kept the solar cell at lower humidity condition (2% humidity in an N_2 environment) for some time and then measured the change in open circuit voltage (V_{oc}) by varying the light intensity. The second measurement was done by increasing the humidity by the flowing Humid N_2 into the chamber and keeping the solar cell at moderate humidity (humidity was

fixed at 35% for entire period of measurement) for some time (around 30 mint) and then did the intensity depended measurements.

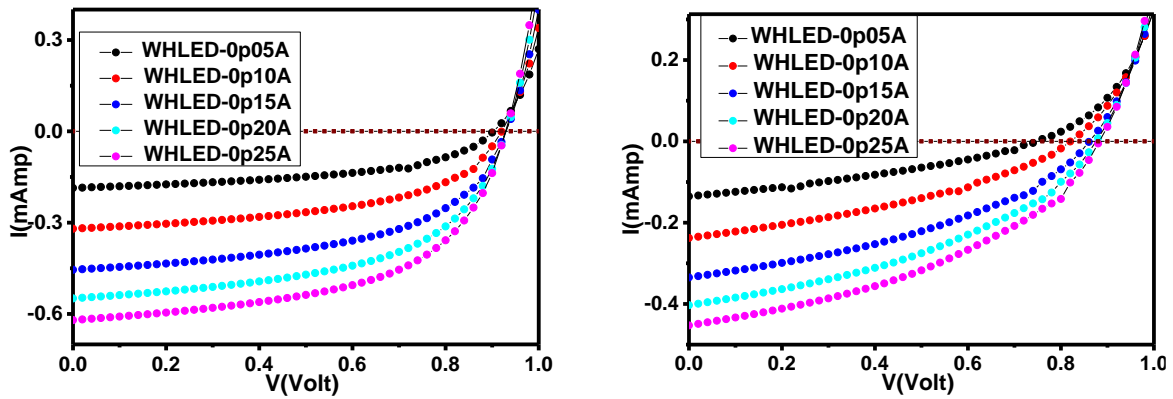


Figure (5) I-V characteristics of solar cell with different intensity of white Light in (a) In Dry N₂ environment (humidity was 1% during the complete measurement) (b) Moderate humidity (RH-35% with the humid N₂ and keep fixed at this humidity by controlled humid N₂ Flow into the chamber) environment.

Current through white LED (Amp)	Open circuit voltage in RH- 2% (mV)	Open circuit voltage in RH- 35% (mV)
0.05	897.5	740.0
0.10	919.0	820.4
0.15	929.4	860.3
0.20	935.2	876.6
0.25	935.8	882.6

Further using equation (1) of solar cell we calculated the ideality factor in these humidity condition.

$$V_{OC} = \frac{nk_B T}{q} \ln\left(\frac{J_{ph}}{J_0} + 1\right)$$

..... Equation (1)

J_{ph} – photocurrent in the solar cell

J_0 – saturation current

V_{oc} - Open circuit voltage

T – Temperature

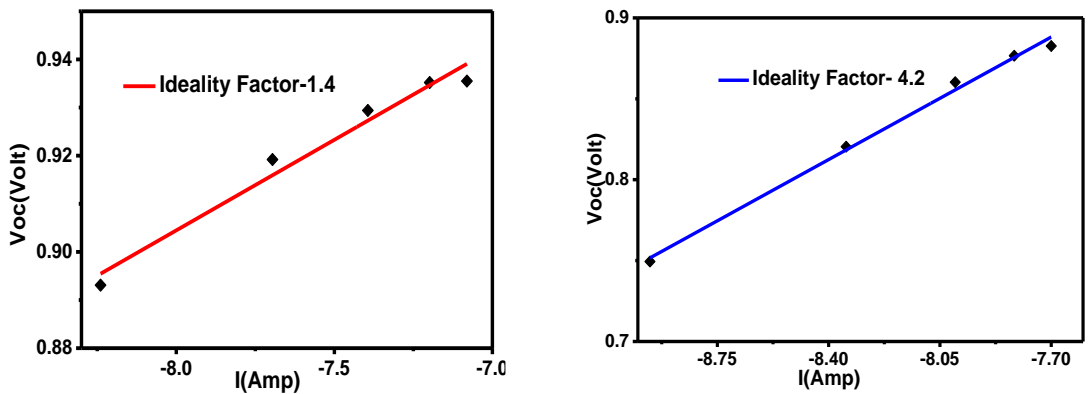


Figure (6) open circuit voltage (Voc) with logarithm of photocurrent (Amp) in two different environment condition (a) RH-1% (Dry N2 environment) (d) RH-35% (humid N2 Environment), ideality factor was calculated using the slop of the Graphs

Ideality factor calculated in lower humidity condition is 1.4 and in high humidity condition 4.2. This tell us that in high humidity condition recombination rate increase, which is due to the accumulation of water molecules at the perovskite and HTL interface and at the grain boundaries of perovskite material. Some hydrated ions also form near the interface and at the grain boundaries of perovskite and they act as traps for charge carriers. This is consistent with our previous study that with increasing humidity or by keeping perovskite solar cell in moderate humidity condition, water assisted traps increase. This increase in water assisted traps increases the recombination of photo generated charge carrier, as the recombination or trapping of charge carrier increase results in decreasing the solar cell quality.

(3.4) Conclusion

In this chapter we showed that even if the perovskite solar cell are kept in moderate humidity condition, for certain time interval there is not much change in perovskite solar cell convention parameters such as- open circuit voltage (**V_{oc}**), fill factor and power conversion efficiency. But we observed significant increase in traps density due to the water molecule accumulation at the interface of perovskite and HTL and at the grain boundaries of perovskite which shows strong Signature in the low frequency noise characteristics.

Further we showed that as we keep the solar cell in moderate humidity condition for some time further water molecule induced trap states at the surface start to increase which result in small decrease in fill factor and power conversion efficiency of solar cell. With increasing time in humid environment water molecules also start to react with the perovskite material (**CH₃NH₃PbI₃**) at the surface and at the grain boundaries form the hydrated ions. The concentration of these hydrated ions is very small if the time of exposing to humid environment is small).

Ideality factor calculation also consistent with our result, as the humidity increase water assisted traps at the surface and at the grain boundaries of perovskite increaser. As the recombination of charge carriers increase ideality factor of the perovskite become higher. We also observed an enhancement in the ideality factor if we kept the perovskite solar cell in moderate humidity condition for long time.

Chapter 4) Degradation of perovskite solar cell in high humidity condition and a recipe for its recovery

(4.1) Introduction –

In high humidity condition (RH > 60%) perovskite solar cell will degrade in few hours, Several studies have done focusing on changes in fill factor and power conversion efficiency with time in high humidity condition and it is proven fact that in high humidity condition solar cell degrade in few hours. Several other groups also did measurements on a thin film of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) in high humidity condition and the result showed that the degradation of methyl lead iodide into the PbI_2 is not that quick and takes several hours.

The chemical change in methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) in presence of high humidity occurs in the following way, first methylammonium lead iodide form the hydrated ions with water which further result in PbI_2 ions. Hydrated ions formation is recoverable process and we can recover $\text{CH}_3\text{NH}_3\text{PbI}_3$ back if we quickly remove the water from methylammonium lead iodide, but once it is degraded into PbI_2 ions then it is not a recoverable.[20][21][22]

So what causes perovskite solar cell degrade quickly in the high humidity condition while the degradation of methyl lead iodide is not that fast process. Several studies have shown that it is the interface which is responsible and several other studies showed that it is the hydrated ions on the surface of perovskite which degraded the solar cell. Some groups also showed that hole transporting layer is degrade in high humidity condition but so far we don't have clear idea about the factors responsible for the degradation in high humidity condition.

In this chapter, we will study how the solar cell parameters changes in high humidity condition, we studied the change in open circuit voltage, fill factor and the photocurrent at high humidity condition. To get further inside about underlying mechanism, we did noise measurement which can provide us information about deep traps states in high humidity condition. We also perform Capacitance measurements to get insight about the condition of interface. These measurement helped us single out the degradation of the interface from the active perovskite layer.

(4.2) Measurement and discussion

From our previous study, we found that in moderate humidity, perovskite solar cells do not degrade rapidly. Whereas, at high humidity condition, the rate of the degradation is much faster and open circuit voltage (Voc) and fill factor become almost zero within 2-3 hours in 70% humidity (Fig. 7 and table 1). **All the I-V characteristics were done in presence of white led (intensity ~ 20 mW/cm² at the sample surface).**

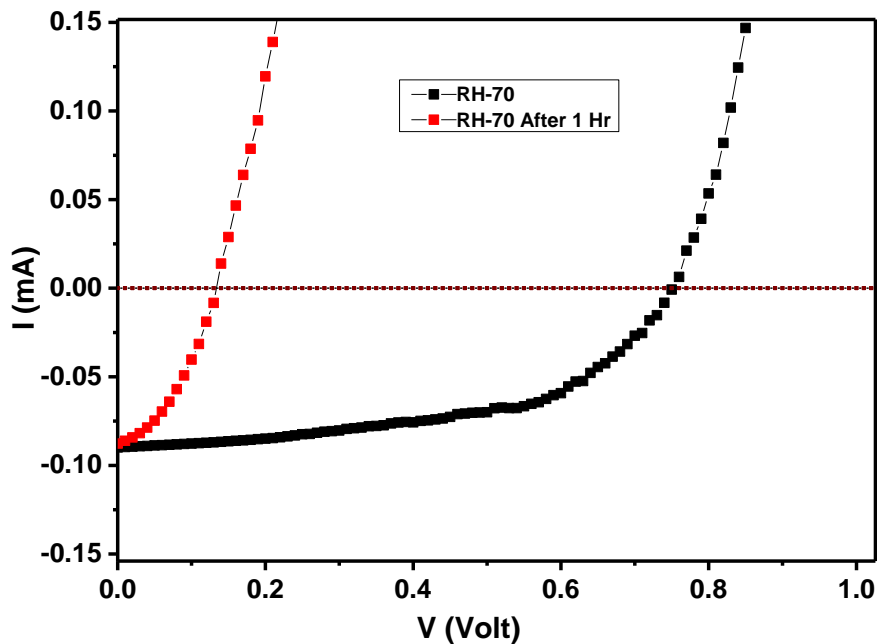


Figure (7) I-V characteristics of solar cell in high humidity condition, Black (At the beginning) and Red (After 1 hour we keep the solar cell In RH -70% humidity environment), from the graph it is clear that open circuit Voltage drop drastically.

Table-1

Time	Open circuit Voltage (Volt)	Photocurrent- I (μ A)
At beginning	0.75	89.0
After 1 hour	0.13	86.3

To study the effect of high humidity, we first kept the solar cell in a dry N₂ environment for some time which will remove the O₂ from the environment (and we can to avoid any oxygen effect from our measurements). Then we increase the humidity by flowing humid N₂ and measure the I-V characteristics in presence of white light (intensity - 20mW/cm²). We kept the solar cell in 70% humid environment for 1 hour and then measured the I-V. We found

large decrease in open circuit voltage. After 1 hour in this humidity condition, open circuit voltage decrease from 0.75V Volt to 0.13 volt (**Table 1**) and the fill factor decreases drastically. While the change in Photocurrent is not that significant 89.0 μA to 86.3 μA (**Table 1**).

So in high humidity condition, open circuit voltage is decreases quickly while the decrease in photocurrent is not that much, which tell us that the perovskite material does not degrade considerably and can give sufficient photocurrent. Hence, it is the interface which is degrading quickly in high humidity condition. These observations are based on the I-V measurement which cannot provide precise details about the process behind the quick degradation of the solar cell in high humidity condition.

We studied low frequency noise characteristics and capacitance to get more information about the defect and interface. We did the noise measurement in presence of White LED (intensity 20mW/cm²) and capacitance in the dark condition.

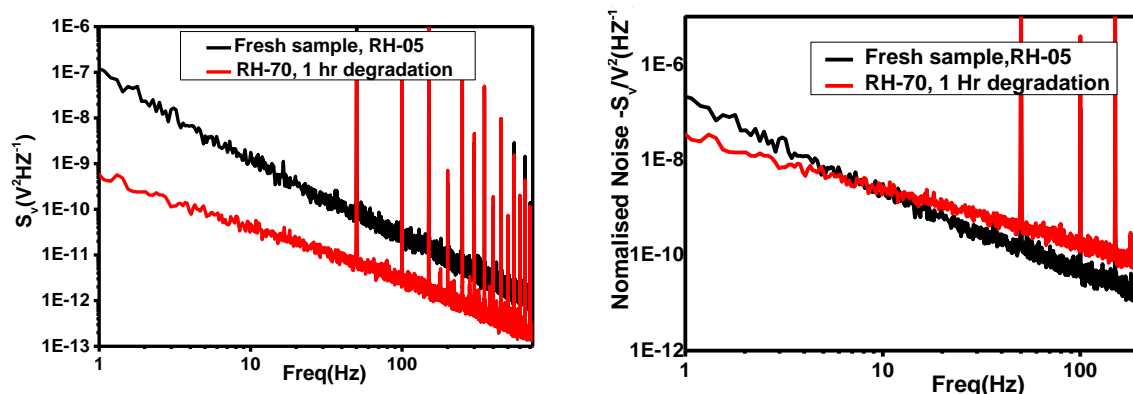


Figure (8)) Low frequency noise power (in log-log scale) with white LED, black (Dry N₂ environment, Rh-5%) and Red (humid N₂ environment, RH-70%) after we keep the sample at this humid environment for 1 hour) (b) Normalised Noise with open circuit Voltage. for normalised 1/f^α Noise the value of α is 1.6 for Fresh sample and α - 1.1 for degraded sample.

As we can see from (Fig. 8), there is a decrease in noise once we kept the perovskite solar cell in high humidity condition for some time. This decrease in noise power is related to the decrease in open circuit voltage (V_{oc}) (which reduces drastically in high humidity condition) so, for more precise analysis, we need to normalize the noise with the voltage to see changes

in normalized noise power. The normalized noise power increases with degradation and Slope of $1/f^\alpha$ noise starts to decrease with the degradation and the $1/f^\alpha$ corner shifted towards lower frequency. This is probably due to formation of heavier ions (hydrated ions start to form quickly at the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer in this humid environment) in the high humidity condition.

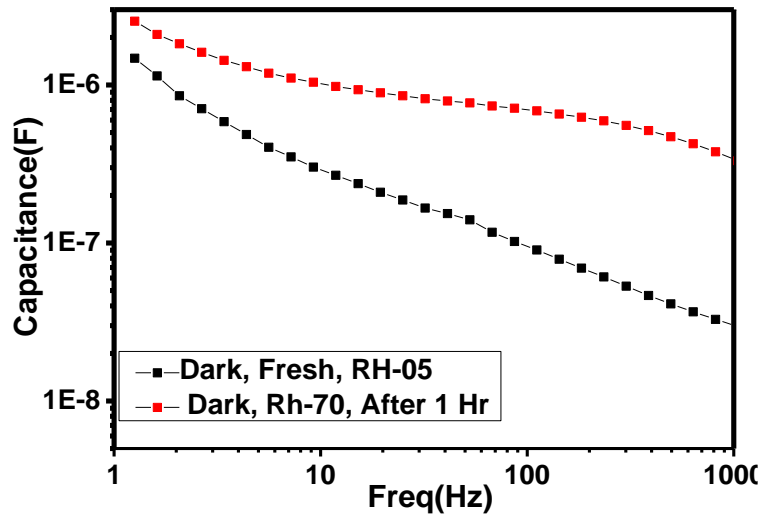


Figure (9) capacitance as a function of frequency in dark condition, black (Dry N2 environment (RH-5) and Red (humid environment (RH-70%) after we keep the sample at this humid environment for 1 hour), from the graph we can see large change in capacitance in (10-1000 HZ frequency range)

From (Fig. 9) we see that capacitance increase a lot as we go to high humidity condition. The increase in the lower region is related to bulky ions like hydrated methylammonium lead iodide, PbI_2 and some other heavy hydrated ions while the higher frequency region is related to water molecule accumulation at the interface. So as we go to high humidity large amount of water diffuse through the HTL layer and accumulate at the HTL and perovskite layer interface and further diffuse in perovskite material and accumulate at the grain boundaries of perovskite material. In the high humidity water start to form lot of $\text{CH}_3\text{NH}_3\text{PbI}_2 \cdot \text{H}_2\text{O}$ ions at the interface and at the grain boundaries. So we observe a huge increase in capacitance which is large in 100-1000Hz frequency range due to presence of large water accumulation and hydrated ions at the interface. Still in the small time scale water molecule at the grain can't get inside the perovskite material and large amount of perovskite still remain intact.

Conclusion -

From the above data we can conclude that in high humidity, as the large amount of water molecule going inside the perovskite solar cell, two processes are responsible for solar cell degradation. First process is methyl ammonium lead halide start to make the hydrated ions at the surface and at the grain boundaries of perovskite which increases the trap density, as the time goes more and more hydrated ions starts to form and they can further degrade in PbI_2 . Even in high humidity for small time interval (1 hour) water molecules not able to get inside the perovskite material (only accumulate at the grain boundaries) so we still have most of our perovskite material intact and only small part at the grain and the surface form hydrated ions.

The second process is the degradation of interface at high humidity. From the data it is clear that solar cell open circuit voltage and fill factor decreases rapidly even though degradation of perovskite material is not that much (still have good amount of photocurrent). The leakage current in solar cell increase significantly this indicates of HTL layer is going bad at high humidity and as a result the solar cell leakage current and open circuit voltage degrades precipitously.

From this study we confirm that interface is mainly responsible for rapid degradation of perovskite solar cell open circuit voltage but still not clear how the interface (between $\text{CH}_3\text{NH}_3\text{PbI}_3$ active material and hole selective layer) is going bad in high humidity conditions. is it the permanent degradation of hole selective layer (**Spiro-MeOTAD**) or is it the water molecules provide a channel to the charge carriers, in which case carrier transporting layer lost its selectiveness resulting large decrease in the open circuit voltage. We will discuss about this problem in the next section.

(4.4) Recovery of perovskite solar cell

In the previous section we have shown that it is the interface which going bad quickly in the high humidity condition and contributes mostly in the decrease of perovskite solar cell open circuit voltage, but we still need to figure out how the interface is going bad.

To see whether the degradation caused by the interface is permanent or is it recoverable? So after keeping the solar cell in high humidity condition for **1 hour** we transfer the sample to a vacuum desiccator quickly and kept in absence of any light for more than 10 hours, then measure the I-v characteristics of this solar cell in low humidity condition to avoid any further degradation. We compared the parameters of these perovskite solar cells with pristine ones and got some interesting result.

As we can see from the I-V graph (Fig. 10) that perovskite solar cell recovered after keeping it in vacuum for 10 hours. There is a decrease in photocurrent which is related the fact that some part of perovskite active layer at the surface and grain boundaries undergo degradation in **PbI₂** ions which not recoverable. Hydrated ions can't be recovered completely, and some hydrated ions go to further degradation and converted into **PbI₂** which is responsible for the photocurrent decreases but most of perovskite material is still intact. Fill factor and power conversion efficiency also decreases slightly, which is again related to the fact that some hydrated ions are not recoverable (degraded into the PbI₂ ions).

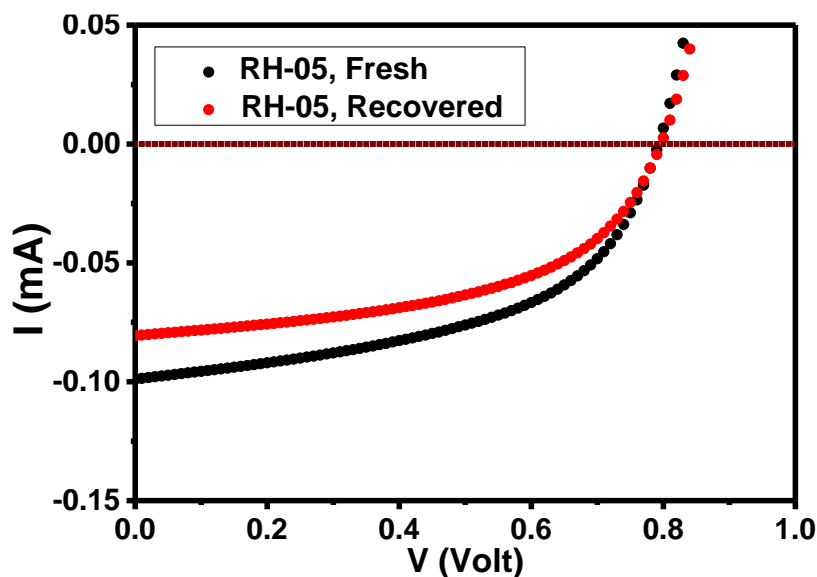


Figure (10) I-v characteristics of fresh (black) and recovered (red) solar cell in presence of white light (intensity 20mW/cm² at the sample surface) in the dry N₂ environment (humidity around 05%)

Open circuit voltage is recovered mostly which indicates the fact that rapid drop in the open circuit voltage in high humidity condition is mostly due to the interface and it is not due to

the permanent degradation of hole transporting layer, which imply that hole transporting layer is not going bad that quickly but it is the water molecule that react with the layer and providing a conducting channel to the charge carriers, As a result solar cell lost its HTL selectivity and we see a rapid decrease in open circuit voltage and fill factor.

Noise and capacitance measurement in fresh and recovered sample can provide us more information. From the graph (Fig. 11), it is clear that noise again increase comparative to degraded sample and show the same $1/f^\alpha$ behaviour (value of α is more and less same, in degraded case α decrease a lot which was related to rapid degradation of open circuit voltage).

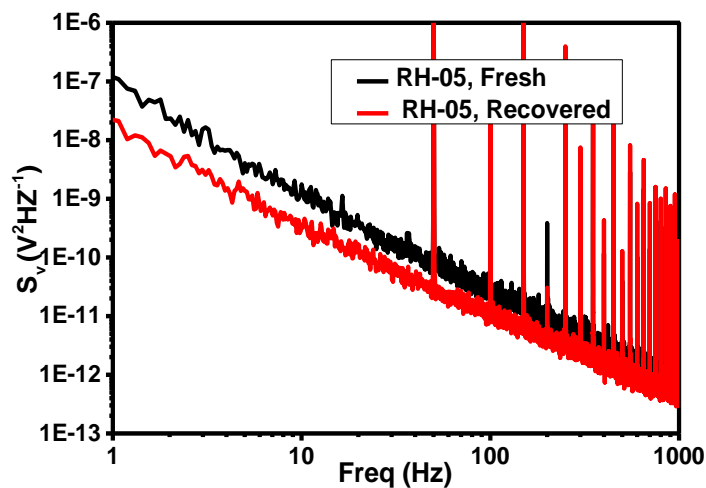


Figure (11) Low frequency noise power (in log-log scale) with white LED (intensity $\sim 20\text{mW}/\text{cm}^2$) in the Dry N₂ environment black (Fresh perovskite solar cell), Red (Recovered perovskite solar cell)

The magnitude of noise decreases a bit in the recovered solar cell comparative to Fresh, this indicates reduction of trap states in the recovered solar cell. Earlier as we proposed that the slight reduction of photocurrent in the recovered solar cell is due to the fact that some part of perovskite material degraded in PbI_2 , These PbI_2 can passivate the traps and decrease the probability of trapping and de-trapping of charge carriers as a result noise gets reduced in the recovered solar cell. Passivation of traps by PbI_2 is well known phenomena and several groups show that PbI_2 ions have a beneficial effect on solar cell by passivating the trap sites ([24],[25]).

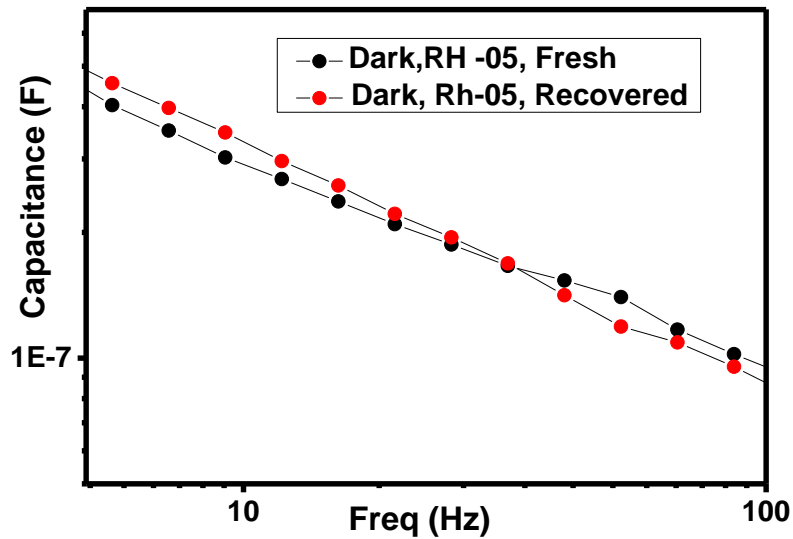


Figure (12) capacitance measurement as function of frequency in Dry N2 Environment (humidity around 5%), black (fresh sample) and Red (recovered solar cell), all the capacitance measurement were done in dark condition

To strengthen our claim further we have performed capacitance measurements which show that capacitance in the lower frequencies region (Fig. 12), which is related to the presence of heavy ions like PbI_2 increases little bit in the recovered sample compared to the fresh solar cell. The increase is very small, because only small fraction of perovskite material converts into PbI_2 ions.

(4.5) Non-recoverable degradation

For this study, we kept the solar cell in high humidity condition for a longer time (more than 3 hours) and then put them back to vacuum for 1 day and next day we performed all the measurements. We compare the parameters of these solar cells with pristine solar cells parameters. From the I-V characteristics it is clear that once we keep the sample in high humidity condition for a longer time, we cannot recover them back and the samples degrade permanently.

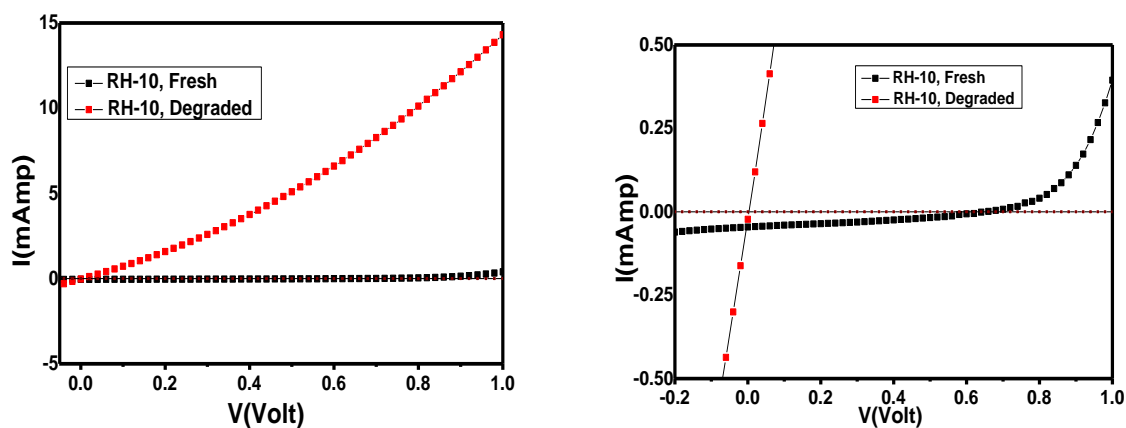


Figure (13) (a) I-V characteristics of black (Fresh) and Red (permanent degraded) perovskite solar cell in the N₂ environment (humidity 10%) (b) Zoomed I-V characteristics to see the change in photocurrent. From the graph it is clear open circuit voltage (Voc) is almost Zero. All I-V measurements were done in White Led (intensity ~ 20 mW/cm² at the sample surface)

Types	Open circuit voltage (Volt)	I (μA)
Fresh Solar cell	0.65	40.0
Degraded solar cell	0.01	23.7

From the I-V data of (Fig. 13 and table) it is clear that, open circuit voltage is almost zero which will make the fill factor and power conversion efficiency of solar cell also around zero. Interestingly change in the photocurrent is only half was observed.

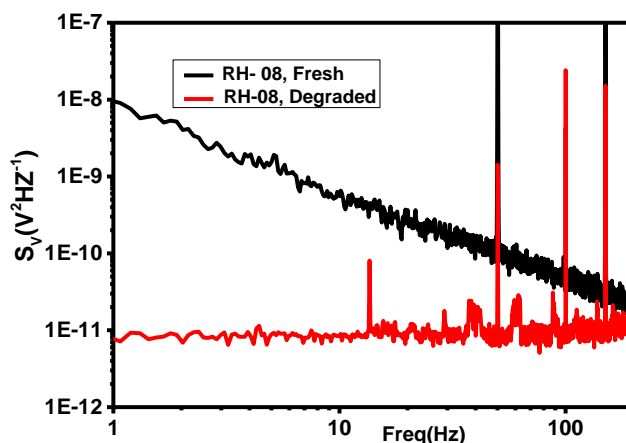
As we explained earlier, once we kept the solar cell in high humidity condition, degradation will start mainly due to two processes. This time as we kept the solar cell in high humidity for long time water at the grain boundaries of perovskite can also diffuse inside the perovskite material and started to form the hydrated ions and further degrade them into PbI₂ ions. From

the fact that $\text{CH}_3\text{NH}_3\text{PbI}_2 \cdot \text{H}_2\text{O}$ is reversible process and the decrease in photocurrent of degraded solar cell is only half, tell us that still we have good amount of perovskite material which is intact.

The second process, in which water molecule degrading the hole transporting layer (**Spiro-MeOTAD**), is a fast process and result in rapid degradation of solar cell open circuit voltage and fill factor. At earlier stage in high humidity water molecules are providing a conducting channel for charge carrier which is responsible for drastic drop in open circuit voltage but once we kept it for a long time (more than 3 hours) in high humidity, water molecule start to degrading the hole transporting layer. This process is comparatively slow but if it gets enough time then it damage the hole transporting layer form he big void into the HTL which is not recoverable and the solar cell degrades permanently. Some groups reported that, after the solar cell degradation if the hole transporting layer is changed then the solar cell can be recoverable up to some extent. This is consistent with our observation.

Noise and capacitance data further confirms our results. The measured noise in the degraded solar cell is almost flat because, for these solar cells, the open circuit voltage is almost zero. To know the normalized noise power we need to divide it with the square of open circuit voltage. We see that (Fig. 14 (b)) the normalized noise power is significantly large but does not change with frequency. The shift of $1/f^\alpha$ corner frequency to the lower frequency region is probably related to the presence of heavier ions (lot of PbI_2) in the sample shows dynamics is very slow.

(a)



(b)

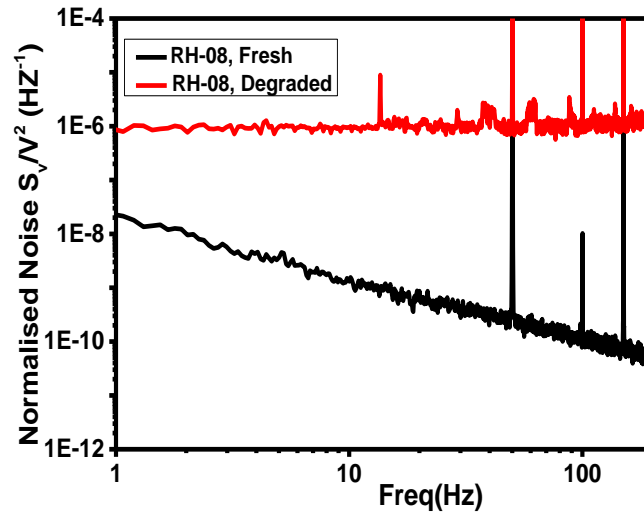


Figure (14) (a) Low frequency noise power (in log-log scale) with white LED (intensity 20mW/Cm²) black (fresh solar cell cell) and Red (Degraded solar cell) (b) normalised low frequency noise power with open circuit voltage

(c)

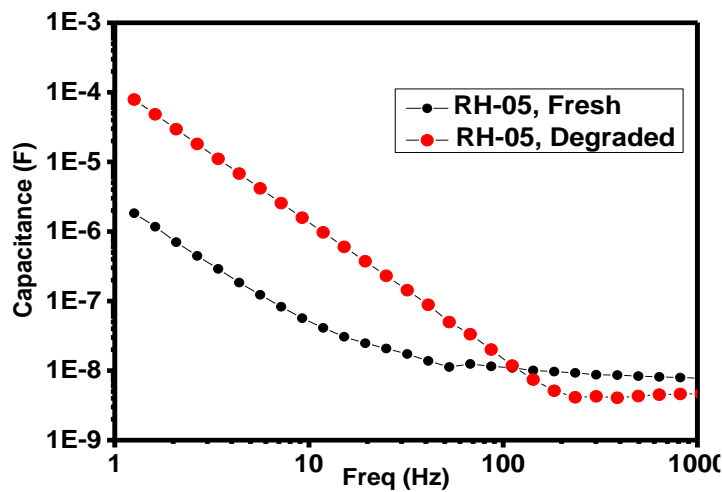


Figure (14) (c) Capacitance measurement as function of frequency in dark condition, black (Fresh sample), Red (permanent degraded sample)

In capacitance data we see a huge increase in the low frequency region, which is probably due to the presence of PbI_2 ions. This is consistent with the fact that, once we keep the solar cell in high humidity condition for long time, enough water molecule will go inside the perovskite solar cell and form the hydrated ions which further degraded into PbI_2 ions. As already mentioned in this humidity environment for long time water can diffuse into the

perovskite material itself and started to degrade it give lot of PbI_2 ions. This result is consistent with the fact the photocurrent reduces to half of its value.

The decrease in capacitance in (100-1000Hz) frequency region (Fig. 14(c)) needs more explanation. Once we kept the solar cell high humidity for long time we know it deteriorated the HTL. Once the hole transporting layer is degraded permanently, relatively lighter ions and charge carrier can move easily throughout the solar cell. The region ($f > 200$ Hz) is mostly due to the charge accumulation at the interface and with the reduction of charge accumulation at the interface due to its permanent degradation and big void in it capacitance decreases in this frequency region.

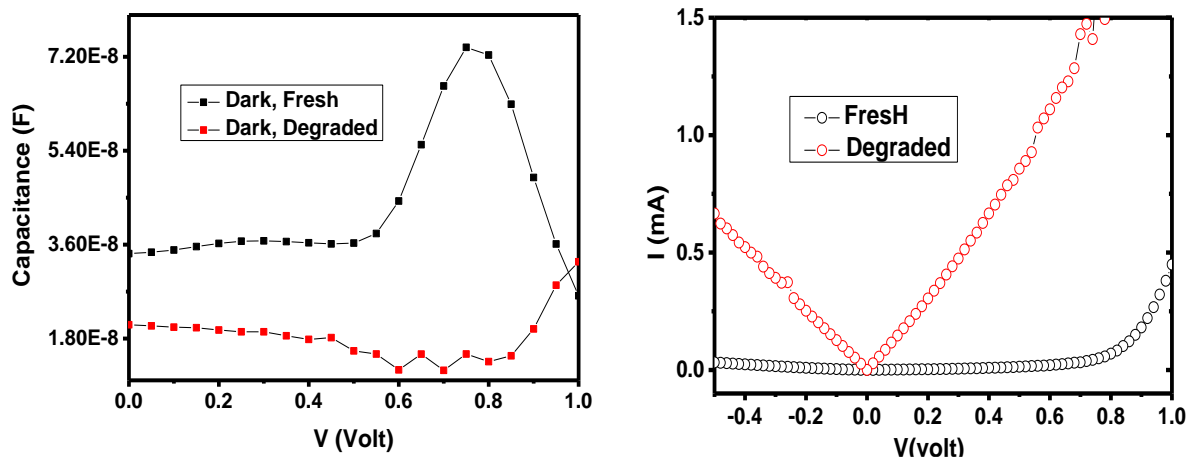


Figure (15) (a) capacitance (at frequency 217 Hz) as a function of applied Dc voltage in dark condition, black (Fresh sample) and Red (permanent degraded sample). All the Capacitance measurement were done in dark (b) I-V characteristics of fresh (Black) and degraded (Red) solar cell in dark condition, leakage current increase a lot in degraded solar cell which is due to the loss of HTL (Spiro-OMeTAD)

We also perform capacitance-voltage measurement for these perovskite solar cells. For degraded solar cell, C-V (Fig. 15) does not show the normal p-n junction like behaviour. Which indicates the degradation of hole transporting layer. The capacitance in degraded sample is less because we measuring it at 217 Hz frequency and at this frequency it's the capacitance due to accumulation at the interface. Once the HTL degraded so as well as the capacitance. This c-v characteristic is consistent with drastic increase in leakage (fig. 15 (b)) current because as the leakage current increase the diffusion capacitance decrease ($f > 200$ Hz) and both are due deterioration in HTL.

Chapter (5)-Temperature induced degradation in perovskite solar cell

(5.1) Introduction-

To understand the perovskite behaviour in high temperature we did temperature dependent study. As we know that heat can also degrade perovskite solar cell. In high temperature condition methylammonium lead iodide starts to degrade and forms PbI_2 ions.

(5.2) Measurement and discussion

We studied the I-V characteristics of the perovskite solar cell with increasing temperature (Fig. 1). From the Schottky diodes equation (**equation 1**), it is clear that with increasing temperature open circuit voltage decrease because of large increase in reverse saturation current. Photocurrent also increases with increasing temperature, which is due to the fact that at high temperature more electron can get into the conduction band due to their thermal energy.

$$V_{OC} = \frac{nk_B T}{q} \ln\left(\frac{J_{ph}}{J_0} + 1\right)$$

.....equation (1)

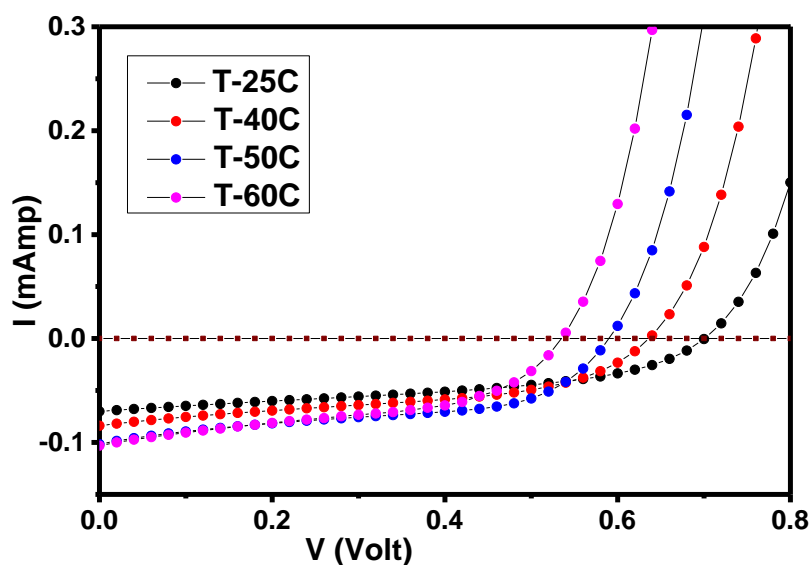


Figure (1) I-V characteristics of solar cell in presence of white light (intensity around $20\text{mW}/\text{cm}^2$) for different temperature in the N_2 environment (humidity - 1%)

The capacitance of solar cell increase with increasing temperature (Fig. 2) which is due to the fact that as we go to the higher temperature, the contribution from ions increases which result in increasing capacitance.

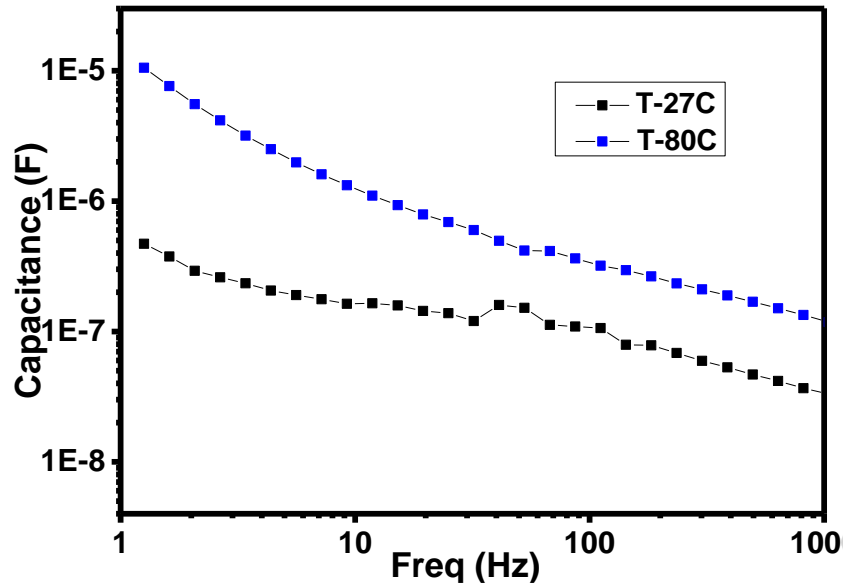


Figure (2) Capacitance measurement as a function of frequency for two different temperature T-27 °C (black) and T-80 °C (blue) in the dark condition, sample was in the Dry N2 environment during all the temperature dependent measurement(Humidity of chamber -1%)

Next we studied how the solar cell parameters change if we keep the solar cell at an elevated temperature for relatively longer time. We studied the change in open circuit voltage, fill factor and photocurrent with time as we kept the sample at a higher temperature. We start our time dependent measurement at moderate temperature condition for example 50 °C and kept the sample at this temperature of 5 hours and studied its degradation. Gradually we increased the temperature and go up to higher temperature, for example 80 °C. All these measurements were done in a chamber where we maintained N2 environment (humidity was around 1%) throughout the experiment so there is no effect of humidity and O₂ on the degradation.[26]

From I-V characteristics (fig. 3) it is clear that moderately high temperature conditions do not degrade the solar cell in a small time interval. After keeping the solar cell at 50 °C or 60 °C for 5 hours and then bringing them back to room temperature, we do not see any significant change in the open circuit voltage. There is a small increase in current observed which is large in 60 °C case and small in 50 °C. This increase in photocurrent is related to the fact that a small part of perovskite material degrade in these conditions and produces PbI_2 which has a beneficial effect on photocurrent through the passivation of defects (discussed earlier).

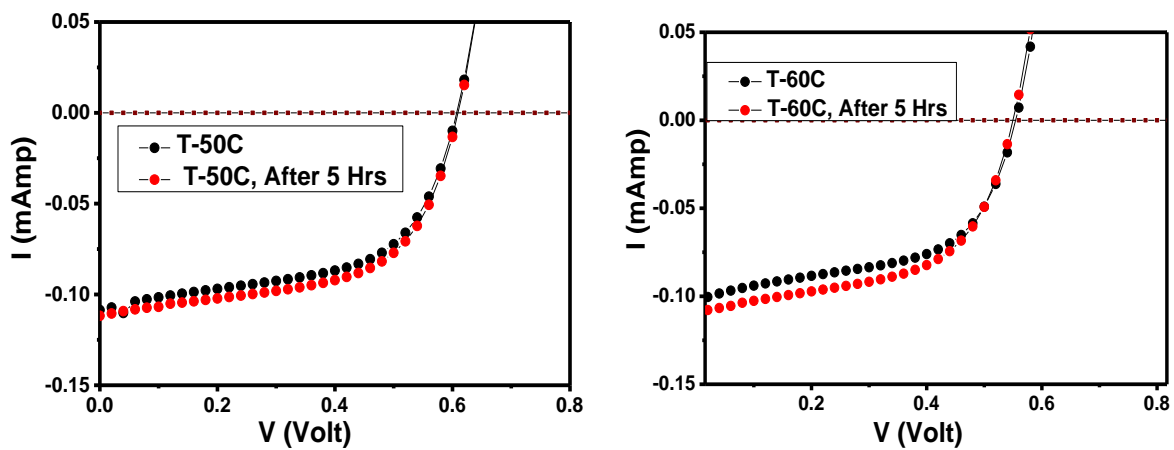


figure (3) (a) I-V characteristics of solar cell at room temperature in presence of white led, Black (fresh solar cell), Red (after treating the perovskite solar cell At 50°C for 5 hours) (b) I_V characteristics of perovskite solar cell at room temperature in presence of white Led, black (fresh solar cell, Red (after treating solar cell at 60°C for 5 hours). During all the measurement solar cell was in a Dry N2 environment chamber

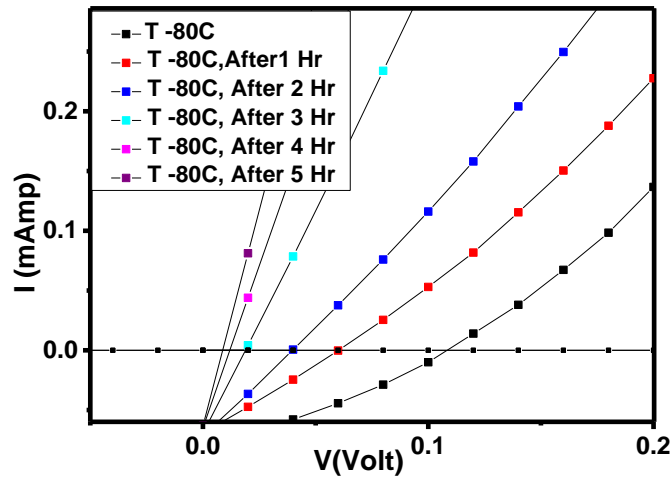


Figure (3)(b) I-V characteristics of perovskite solar cell at T=80°C in presence of white Light for different time (solar cell was kept at 80°C for 5 Hours in dry N₂ environment and I-V characteristics were measured after each 1 hours).

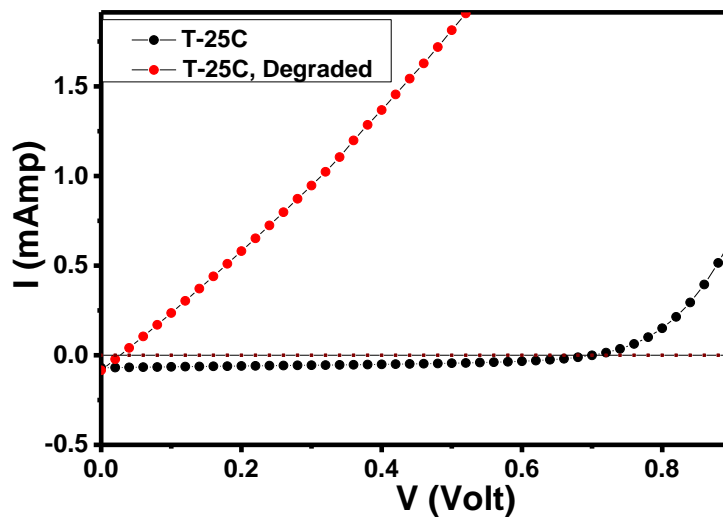


Figure (4) I-V characteristics of a solar cell, black (fresh sample), Red (permanent degraded solar cell after treating in 80 °C temperature condition for 5 Hours). From the graph it is clear that open circuit almost goes to zero, but change in photocurrent is not that large.

Table -1

Types	Open circuit voltage (Volt)	I (μA)
Fresh solar cell	0.70	75.8
Degraded solar cell	0.02	66.5

In 5 hrs degradation at high temperature perovskite solar cell open circuit voltage (V_{oc}) almost go to Zero (fig. 4 and Table 1).

From the I-V characteristic (fig. 3 , fig. 4 and table 1) it is clear that once we go to 80 °C, perovskite solar cell start to degrade quickly, we still need to find that this quick degradation is related to the interface or is it the perovskite material ($CH_3NH_3PbI_3$) which is degrading fast. From our previous study we know that as we go to extreme environment condition (high humidity), both the perovskite material and interface start to degrade but the degradation of perovskite material comparative to degradation of interface is very slow.

As we go to the high temperature its degrade the perovskite material in PbI_2 ions, but we still have a large photocurrent in solar cell and the reduction in solar cell photocurrent was not that much, its open circuit voltage which reduces a lot after keeping the solar cell in high temperature condition (At 80 °C). So from this it is the clear that we still have perovskite material which is converting the light into the photocurrent. Open circuit voltage and fill factor again implying that it is the interface between the perovskite material and HTL, which is goes bad. This time it is the temperature which is degrading the hole transporting layer.

Further we measure the leakage current (reverse saturation current) in degraded solar cell and compare it with the pristine solar cell. From fig. (5) It is clear that leakage current increase significantly in degraded solar cell which is consistent with the fact that HTL layer is now degraded.

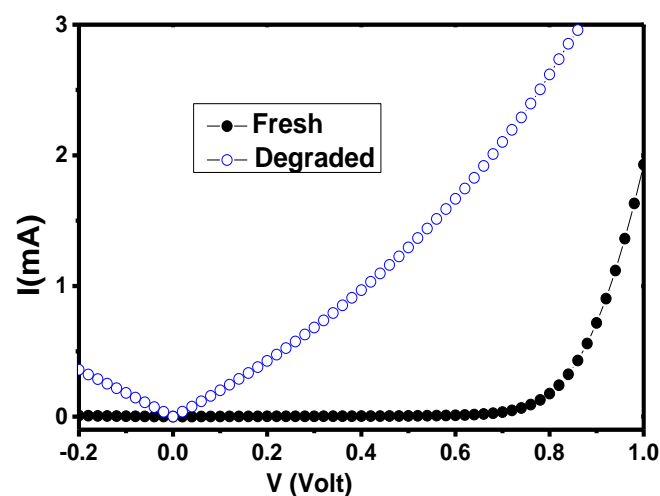


Fig (5) I-V characteristics of pristine (black) and degraded (blue) solar cell in dark condition

We further measured the capacitance of the degraded solar cell in dark condition (Fig. 6). There is a large increase in capacitance of the solar cell in the low frequency region but it decreases in the high frequency region. Which is related to the fact that as we go to the high temperature methyl ammonium lead iodide will start to degrade into PbI_2 ions and as we kept the solar cell at high temperature condition for a long time which degraded some part of perovskite into PbI_2 ions and some other ions also form as we degraded at high temperature. Due to contribution of these ions capacitance value at lower frequencies increase significantly ($f < 100 \text{ Hz}$).

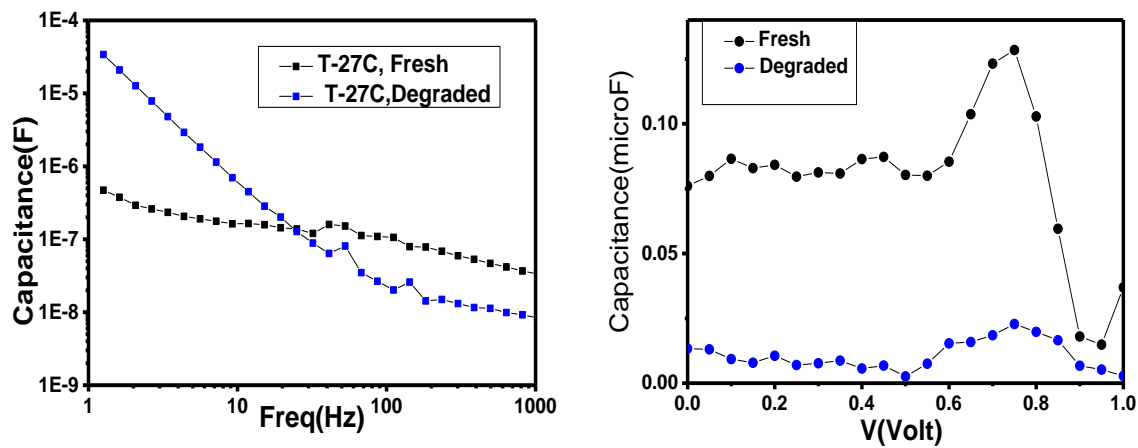


Figure (6) capacitance measurement as a function of frequency, Black (fresh solar cell) and Blue (permanent degraded solar cell after high heat treatment) at room temperature (b) capacitance (at frequency 217Hz) measurement as a function of applied voltage for Black (fresh solar cell) and Blue (permanent degraded solar cell). All the capacitance measurement were done In dark condition and the sample was in Dry N2 environment during all the measurements.

As we kept the solar cell in high heat condition for a long time the hole transporting layer is almost distorted so the lighter ions and charge carrier can easily pass through. So once the hole transporting layer is degraded, charge and ions accumulation near to the interface reduce. Capacitance at higher frequency range is mostly related to the ions and charge accumulation at the interface, which result in a decrease in the capacitance in this frequency range ($f > 200 \text{ Hz}$).

Capacitance-voltage data confirm that our degraded perovskite solar cell do not follow the P-N junction behaviour because of degradation in HTL layer (Fig. 6). C-V data was taken at 217 HZ frequency and the capacitance is low in degraded solar cell comparative to pristine one because once we lost the HTL layer accumulation of charge near the interface (perovskite and HTL) reduces result in decrease capacitance. Very high Leakage current in degraded solar cell (fig. 5) is also consistent with decrease in capacitance

(5.3) Conclusion

Thermal study also suggest that for the perovskite solar cell degradation, interface is the main factor for damaging the performance. Perovskite material also degrades at high temperature which is shown in the capacitance measurement by significant increase in the capacitance in lower frequencies region which is related to the heavy ions contribution. Degradation of methylammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is a slower process than the degradation of its interface, it is the interface which kills the solar cell in high heat and high humidity condition quickly and responsible for drastic drop in open circuit voltage and high leakage current.

Conclusion

Our study was basically on the characterization of perovskite solar cell in different environment condition using current-voltage, noise spectroscopy and capacitance measurement as the main tool. Through these study we try to understand origin of the degradation of the perovskite solar cells in various environmental condition. In moderate humidity condition, there is no significant degradation of perovskite solar cells has been observed over a small time interval. Though the photocurrent show some changes, which are related to the increase in concentrations of defects and traps assisted by accumulation of water molecules at the interface between the perovskite and HTL.

In extreme condition (either high humidity or high temperature) condition Rapid degradation in solar cell parameters is related to the degradation of the hole transporting layer. Some part of perovskite also undergo degradation into PbI_2 ions. To determine the role of interface, noise spectroscopy and capacitance characteristics were found to be very useful.

Perovskite solar cell is one of the most important photovoltaic materials these days, and to improve its stability we need to understand the possible origin behind its degradation. Our study suggests that perovskite solar cell interface (between perovskite and HTL layer) plays major role in quick degradation under extreme environmental conditions. Perovskite material also degrades but the process is comparatively slow and solar cell should be stable for a longer time, but it is the interface between the perovskite and HTL which goes bad quickly. So to make perovskite solar cell stable we need to replace the hole selective layer -Spiro-MeOTAD with a different HTL layer which can survive in the extreme condition.

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