

Master Thesis - Chemistry

Using electrochemistry to graft
ethylenediamine as a blocking layer in
perovskite solar cells

by:

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Abstract - English

In this thesis, the use of cyclic voltammetry to graft non conductive molecules on the anode of methylamine-lead-triiodide perovskite solar cells to decrease the backward current was investigated. Ethylenediamine was used in an oxidative pathway onto fluorine doped tin oxide and aryl diazonium salt in a reductive pathway. Both compounds did not yield any increase in the efficiency compared to a standard without a TiO_2 blocking layer. The mechanism supposed to be at work in non conductive blocking layer is long distance electron tunneling. Given that the potential drop between forward and backward currents expected to be very small, only a very small window of thicknesses allows for the reduction of just one of them, thus increasing the overall efficiency. Unfortunately, the techniques to find the actual thickness of the blocking layer were not readily available.

Abstract - Français

Dans cette thèse, l'utilisation de la voltamétrie cyclique pour greffer des molécules non conductives sur l'anode de cellules solaires pérovskite à base d'iodure de méthylaminoplomb pour réduire le contre-courant a été étudiée. L'éthylènediamine a été utilisée en voie oxydative et l'aryle diazonium en voie réductive. Aucun des composés n'a montré d'augmentation de l'efficacité totale comparé aux cellules solaires sans couche de blocage. L'efficacité est tout au mieux 10 % inférieure, jusqu'à 80 %. Le mécanisme supposé à l'œuvre dans l'utilisation des couches de blocage non conductive est l'effet tunnel à longue distance. Étant donné que la différence de potentiel entre le courant et le contre-courant à l'interface anode-contact type-n est très petite, la fenêtre d'épaisseur où uniquement le contre-courant est diminué est très petite. Malheureusement, les techniques d'analyse à disposition ne nous ont pas permis d'identifier l'épaisseur de la couche greffée dans cette expérience.

Contents

1	Introduction	4
2	Perovskite solar cell	5
3	Blocking layer in solar cells	6
3.1	Grafting of Ethylenediamine	8
3.2	Grafting of aryldiazonium	8
4	Experiments	10
4.1	Materials and chemicals	10
4.2	Grafting method	10
4.3	Solar cell preparation	11
4.4	Charaterization of blocking layers	13
4.4.1	Cyclovoltametry	13
4.4.2	Ellipsometry	14
4.4.3	XPS	14
4.4.4	Kelvin probe force microscopy	14
4.5	Analysis methode	16
4.5.1	Solar simulator	16
5	Results and discussion	16
5.1	Preparatory work	16
5.1.1	Grafting	16
5.1.2	Cyclic voltammetry	16
5.1.3	XPS	17
5.1.4	Kelvin probe	17
5.2	solar cells	18

5.2.1	Solar simulator	19
5.2.2	Maximum power point	20
5.2.3	IPCE	21
6	Conclusion	22
7	Perspectives	23

1 Introduction

The research field of solar cells has changed quite a bit in the last decade. The discovery of the use of organometal halide perovskites as visible-light sensitizers for photovoltaic cells from A. Kojima et al. [5] started a new field for titanium based solar cells. At first, the perovskite was considered a black dye to make a traditional dye-sensitized cell, using the I^-/I_3^- as mediator. In 2012, H. Snaith et al. showed that using spiro-OMeTAD as a hole conducting layer and getting rid of the iodide mediator, which reacts with the perovskite, would prolonged the lifetime of the cells. Using Web of science, the publication relating to perovskite solar cell skyrocketed in the last years, as seen in figure 1.

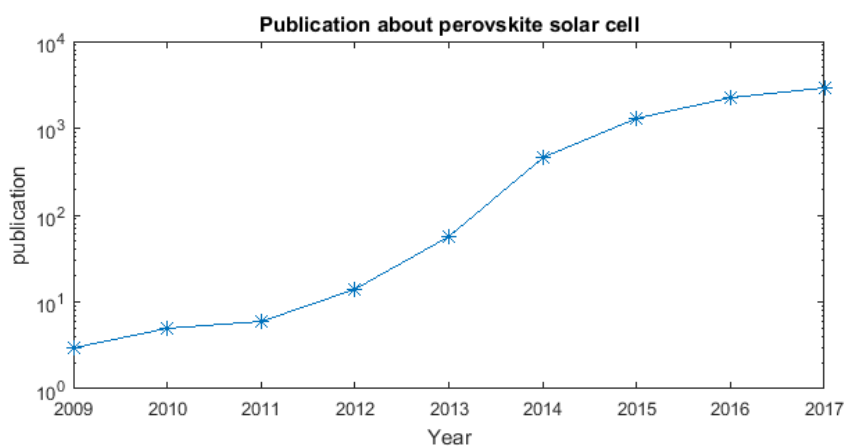


Figure 1: number of publication using perovskite solar cell in Web of Knowledge

The efficiencies are improving at a pace far greater than any other solar cell technology from 3.8% in 2009 to 22.1%[11] in 2016. This makes it on par with the commercial thin-film Si cells, as seen in figure 2

One of the biggest problems plaguing the perovskite cells are their lifetime. Until recently, the stability of the cells, both in short term and long term, was very poor with a lifetime extremely short. In 2017, a team achieved more than 7% loss in its initial power conversion efficiency (PCE) with an illumination of 1000 h[9].

For years now, the use of a blocking layer between the n-type contact and the anode, in perovskite and dye sensitized solar cells, to alleviate the problem of electron back current has been shown to increase the efficiency. The most used blocking layer being a compact layer of TiO_2 via thermally oxidized Ti at 500 °C, which is a semiconductor. The use of high temperatures is a problem in 2 major ways. First, the temperature used impose that the substrate it is deposited on top resist temperatures that high, which is a big problem if we don't use glass. Second, from a commercial point, it is an energy use that implies a big cost.

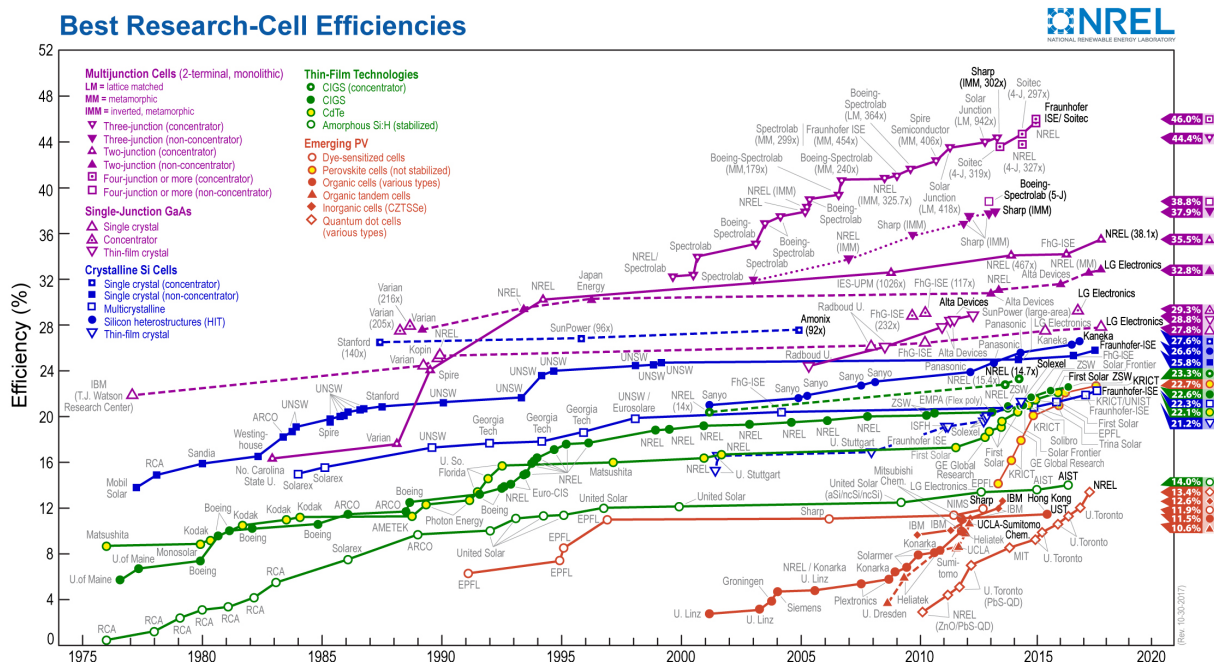


Figure 2: evolution of photo voltaic efficiencies. Si cells are in blue and perovskite in red with orange filled circles. From the NREL

The idea of using ethylenediamine (EDA) as a blocking layer, a non conductive compound arise from Song, Park et al. [10] and Gooding et al.[2]. In the former, polyethyleneimine ethoxylated was spin coated, giving a non conductive serving as blocking layer. The use of non conductive material instead of semi conductors implies a much bigger sensitivity to the thickness of the blocking layer. as a semiconductor can have an electron or hole transfer over "big" distances, non conductors allow transfer of electrons only through long distance electron tunneling. Their research showed an gain in efficiency from the original 13% just under 8 nm to peak at 15% at 9.1 nm. Once the thickness was increased to 10.8 nm, the efficiency collapsed down to 8.3%. [2] showed us the use of cycli voltammetry to graft EDA as a valid method and gave a baseline for the number of scans to use for grafting on fluorine doped tin oxide and indium doped tin oxide. The idea underlining this thesis is to find other sources for blocking layer which can be easily implemented and do not need high temperature (500 °C) to help in the usability and price of perovskite solar cells. If these cells want to become commercially viable, it need alternative cheap blocking layer and with the possibility to mass produce on different substrate which are sensitive to high temperature as plastic films.

2 Perovskite solar cell

A perovskite solar cell (PSC) is a solar cell where the absorbing layer is arranged in a perovskite structure with a general formula of ABC_3 with A and B as cations with

highly different sizes and C as the anion. In fig 3 we can see an example of a perovskite crystalline lattice. In nature, perovskites are metal oxides but the perovskite in solar cells, cation being an organic cation and Pb^{2+} and the anion I^- or another halide. A frequently used perovskite for solar cell is methylammonium lead triiodide ($MaPbI_3$). In PSC, in contrast to dye sensitized solar cells, the charges generated can easily separate and don't need a layer of TiO_2 to separate the hole-electron pair. to help the hole move away, a hole transport material is used to help. In our experiment, it is 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl amine)-9,9'-spirobifluorene (Spiro)

Today's best solar cells achieve an efficiency of 22.1% and the main problem of short and long term stability is being improved with the latest cells working for 1000 h, under equivalent to full sun light soaking conditions, with less than 7% loss compared to it's initial in light to electricity efficiency.

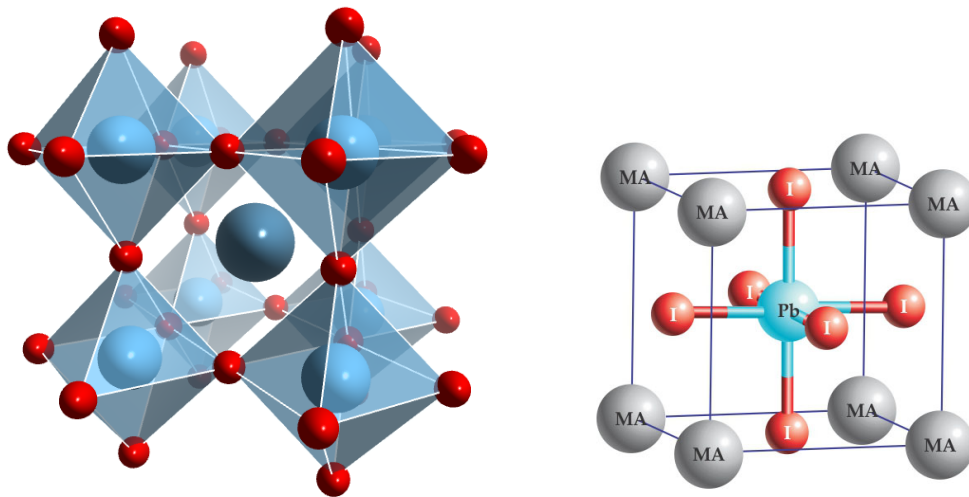


Figure 3: Scheme on the left of the Calcium titanate structure[1], in red the oxygen, in light blue the calcium and in dark blue the titanium. On the right, $MaPbI_3$

The structure of a perovskite solar cell is represented in figure 4. In 2 of the standards used, a scaffold of mesoporous TiO_2 was also used and it is embedded in the perovskite layer.

3 Blocking layer in solar cells

The use of blocking layer between the n or p-type contact and the electrode in solar cells has been in use for years and one of the most common being non porous TiO_2 deposited by proteolysis, described by Kavan & Grätzel in 1994 [4]. Most of the blocking layer are hole or electron-carrying measuring tens of nanometers. the use of semiconductors as blocking layer allows only for specific electron energies to transit through it and carefully calibrating the band gap of the blocking layer with the energy of the photon produced is

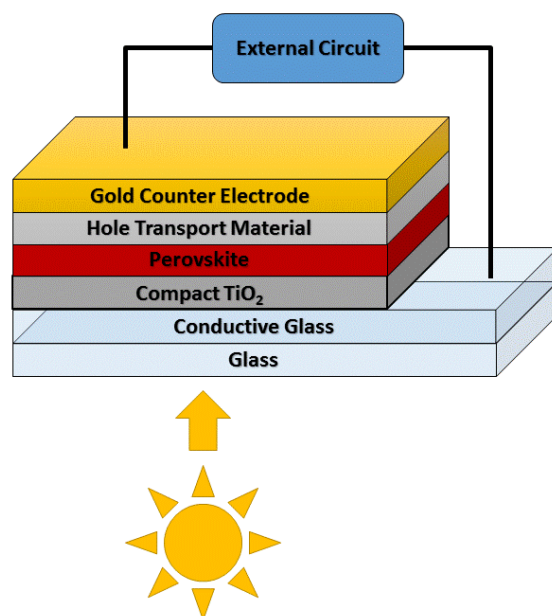


Figure 4: Scheme of a perovskite solar cell. In this experiment, the conductive glass is Fluorine doped tin oxide (FTO), cells are with with the compact TiO_2 blocking layer, the electrochemically grafted organic layer, or without as one of the standards. The perovskite is $MaPbI_3$

crucial.

Another way of limiting the backward current is by using a non conductive material. An example is given by Song et al.[10]. They used ethoxylated polyethyleneimine (PEIE). As said in the introduction, this method is very sensitive to the thickness of the blocking layer. As we can see in figure 5, in the 1st case, the blocking layer is too thin to impede current at any significant value. In case number 2, the blocking layer become thick enough that the potential of the electron going backward is low enough to lower the probability of tunneling effect but still lower than the forward electron potential. In case number 3, the blocking layer is at an optimal thickness, potential barrier, to completely block backward current and still let enough forward current go through. in case number 4, the thickness of the blocking layer become so important that even the slightly higher energy of the forward electron is not enough to easily tunnel through it and isolates the perovskite from the FTO.

Even with the same blocking layer, the nature of the solar cell can change the optimal thickness. Using PEIE, the optimal thickness is around 5.02 nm in P3HT:PCBM or PTB7:PC71BM polymer[7] but in an $CH_3NH_3I_{3-x}Cl_x$ perovskite cell and a mesoporous alumina scaffold, the optimal thickness goes to 9.1 nm.

To test the hypothesis of the non conducting layer, additionally, the experiment from Song et al. [10] was duplicated but could not be reproduced. Insufficient experience in the spin coating of the electrodes might have played a big role.

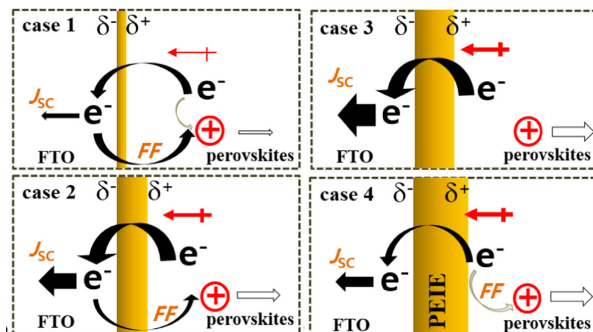
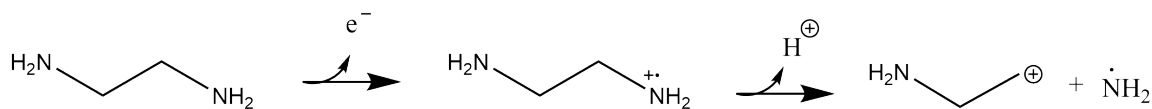


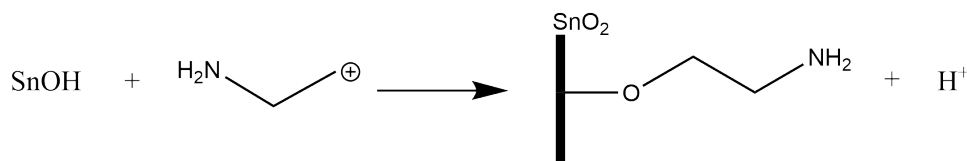
Figure 5: Scheme of the effect of the thickness of non conducting blocking layer on electron transmission from the perovskite to the FTO[10].

3.1 Grafting of Ethylenediamine

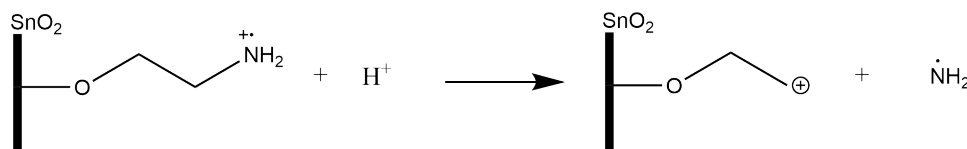
Ethylenediamine in acetonitrile in the presence of an anodic potential will make a covalent bond through a one-electron irreversible process.



then the reaction with the oxide

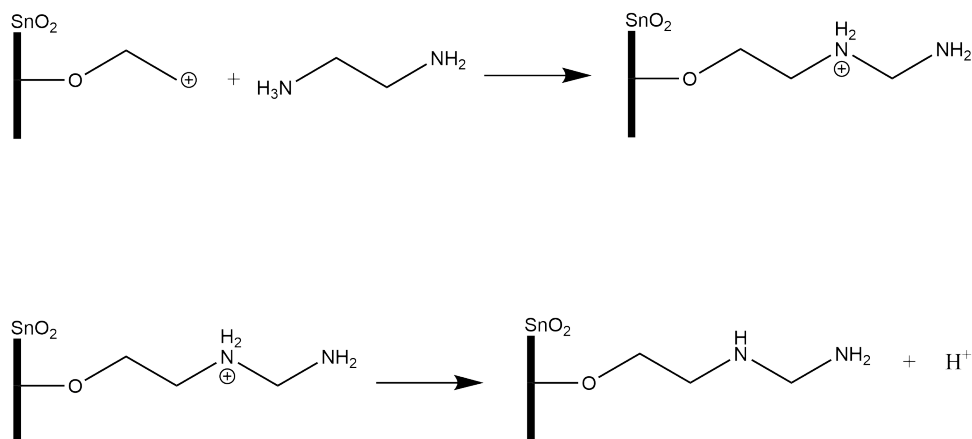


The process can continue further to polymerize the grafted amine with the oxidation of the grafted amine which will release NH_2^{\bullet} radical and have a positive CH_2^{\oplus} attacking an amine group then releasing a proton.



3.2 Grafting of aryldiazonium

The use of aryldiazonium in grafting of indium tin oxide by electrochemical reduction has already been studied [8]. The use of a polarisable molecule as non conductive blocking



layer can add some interesting properties, the main being the increase in potential difference between the p-type contact and the electrode. This increase in potential difference can increase the distance of the tunneling effect and decrease the backward current, leading to a wider range for the blocking layer to increase the overall efficiency. Unfortunately, the increase in electron density at the blocking layer/p-type contact might also induce a negative effect. The longer and the more electrons stay in the perovskite medium, the higher the chance of recombination, thus decreasing the overall efficiency of the solar cell. The mechanism can be seen in figure 6.

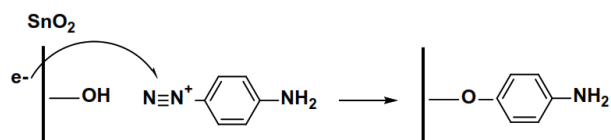


Figure 6: Scheme of the grafting of diazonium on tin oxide.

4 Experiments

4.1 Materials and chemicals

the materials and chemicals used were:

- Tetrabutylammonium tetrafluoroborate ($TBABF_4$)
- p-aminoaryldiazonium trifluoroborate (DIA)
- Ethylenediamine
- $CH_3NH_3 + PbI_3$ ($MaPbI_3$)
- Acetonitrile
- FTO and ITO glass plates
- Spiro-MeOTAD
- Zinc powder
- Hcl 1M
- Polyethyleneimine ethoxylated
- Ferrocene
- 0.2 M titanium tetraisopropoxide bis(acetylacetonate) and 2 M acetyl acetone in 2-propanol

4.2 Grafting method

The machine used is an Ametek VersaSTAT 3F potentiostat. FTO and ITO glass have been coated via cyclic voltammetry, with a glassy carbon electrode and a silver wire inserted in acetonitrile and 0.1 M $TBABF_4$ in a 20 ml glass vial. All the equipment is kept in an oven at 100 °C until used and the solution is degassed for 5 min with N_2 before each experiment. The number of cycles aimed for are taken from Gooding et al.[2] and extrapolated to achieve a thickness of 8 nm to be in the range given by Song et al.[10]. As the growth of the grafted layer follows a logarithmic trend, the number of scans soared to 300 cycles. These samples were test to have a preliminary idea. It showed that the signal was mostly killed as the efficiency of the cells were less than 2%. A decision was made then to restrict to 10 and 30 cycles for both.

The solution in which CV is done is a:

- EDA: 0.1 M $TBABF_4$ and 7mM ethylenediamine in ACN, with cycles from +0.35 V - +1.5 V at a scan rate of 40 mV/s
- DIA: 0.1 M $TBABF_4$, 1mM DIA in ACN, with cycles from +0.2 V - -0.5 V at 20 mV/s

The solutions were made new at least after every 100 cycles.

4.3 Solar cell preparation

The perovskite solar cells being made are $CH_3NH_3 + PbI_3$ -Spiro ($MaPbI_3$) based with gold counter electrode. The first step is cutting FTO glass from a big plate into bands of 3 by 12 cm then a band of about 4 mm is etched in the middle on the long side by Zinc powder and HCl 2 M for 2 min then washed. the next step is the cleaning of the glass in ultrasonic bath, 30 min in water with detergent, 15 min water, 15 min acetone and 15 min ethanol. The standards using TiO_2 blocking layer pass through a step of spraying of 0.2 M titanium tetraisopropoxide bis(acetylacetonate) and 2 M acetyl acetone in 2-propanol on a hot plate at 500 °C for 1 hour, seen in picture 7. Spraying is done from a distance of 9 cm for 2 seconds per band and 6 layers.

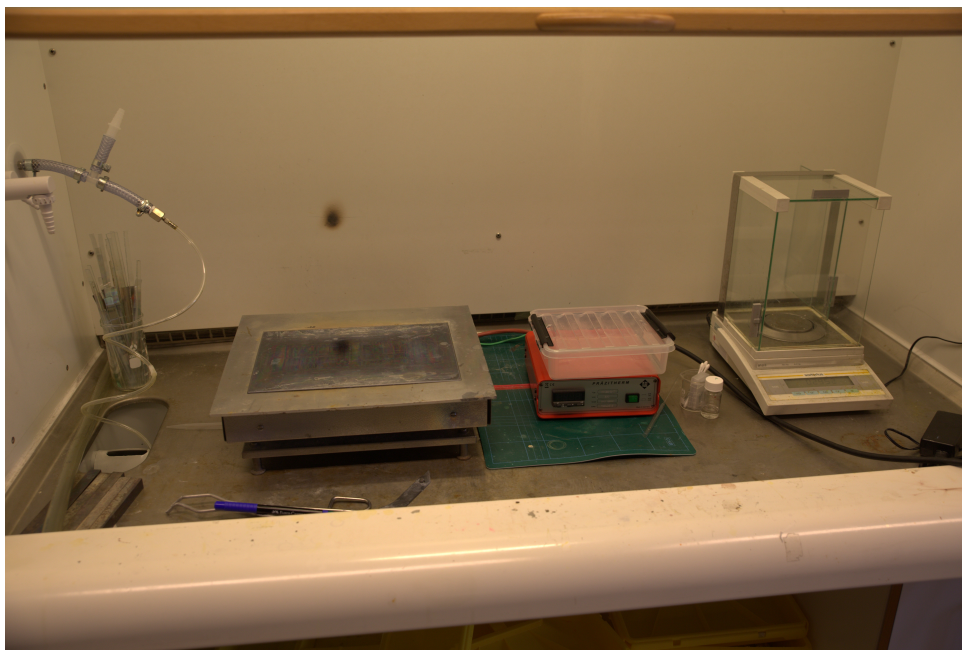


Figure 7: Hot plate to make the blocking layer via pyrolysis of TiO_2 at 500 °C.

Once cooled, the 3 by 12 cm plates are broken in smaller parts of 1.5 by 2.4 cm. The scaffolding of mesoporous TiO_2 is made by spin coating, see picture 8, a TiO_2 paste of 150 mg/ml in ethanol and put on a hot plate at 125 °C for drying then at 500 °C overnight. Finally, the plates are treated in a 0.02 M aqueous $TiCl_4$ at 70 °C for 20 min then washed with water and dried for 10 min at 80 °C. The perovskite, $MaPbI_3$ prepared by mixing methylamine iodide and lead(II) iodide (1:1) in DMSO, is done in a one step process. 75 μl is spin coated on the glass plate at 6000 RPM for 30 s. After 15 s, 140 μl chlorobenzene is added in the center. Then the plates are heated for 45 min at 90 °C. Once cooled again,

4.3 Solar cell preparation

the hole transporting layer, is added by spin coating at 4000 RPM for 30 s. The layer is made of spiro-OMeTAD, prepared by dissolving 85.8 mg of spiro-OMeTAD in 1 ml of chlorobenzene, 33.8 μl of 4-*tert*-butyl pyridine, μl of FK209 solution, 300 mg FK209 in 1 ml acetonitrile, and μl of lithium bis(trifluoromethanesulfonyl)imide solution, 520 mg in 1 ml acetonitrile is added. The next step is to manually etch the perovskite with a blade about 2 mm on the long side of the plate to be used as the anode contact.

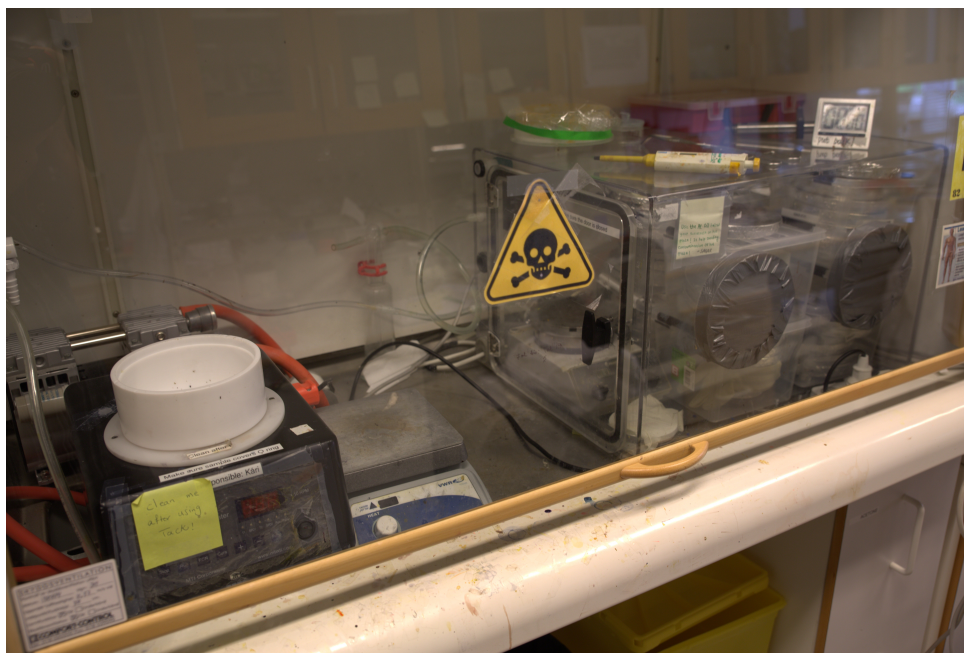


Figure 8: Spin coater on the left for the preparation of either the scaffold or the perovskite and spiro. On the left, dry box to store the cells when not in use.

For the third batch of experiments, the ambient humidity in air was making visually unsatisfying samples after the perovskite step. To try to remedy that problem, the whole process from the perovskite to the spiro spin coating has been done in a glove box at 23 °C in dry air, figure 9.

Once the spiro was done, the last part is depositing a layer of gold as the counter electrode. For that step, the glass plates are put in a support and optical mask, the spiro facing down, as seen in picture 10. The growth of the gold layer of 80 nm is done with increasing speed, with a rate of 0.02 nm/s until 5 nm then 0.05 nm/s until 10 nm and finally at 0.1 nm/s until 80 nm. The amount of gold used per deposition is from 130-145 mg. The final result of the cells are seen in picture 11. Once the cells are done, to minimize the degradation due to air, humidity and light, the cells are put in a opaque container in a dry box, which can be seen on the right side of picture 8

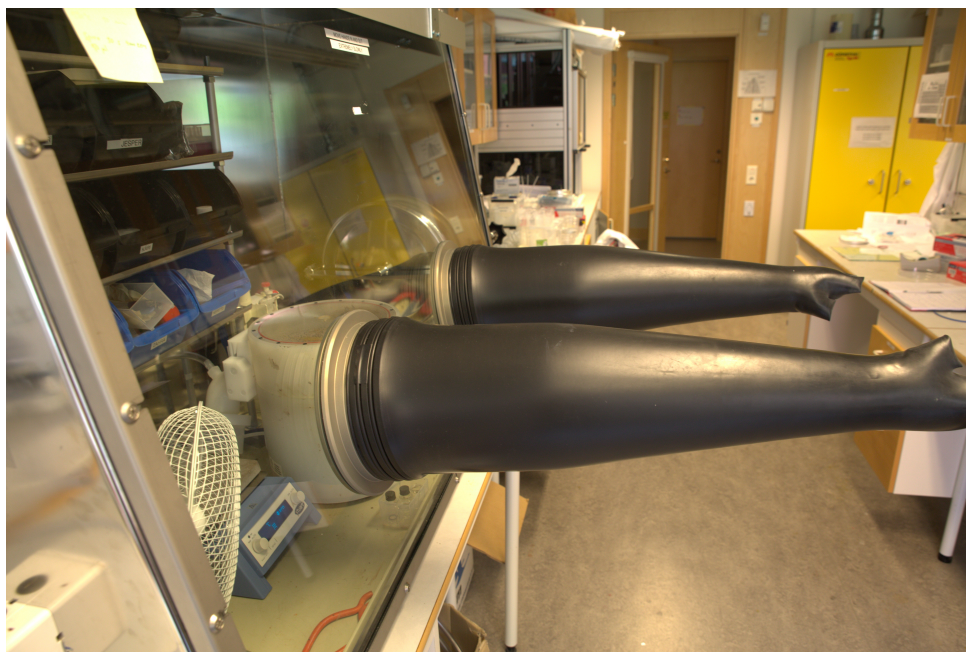


Figure 9: Glove box to work under more controlled atmosphere to limit the pollution of the solar cells.

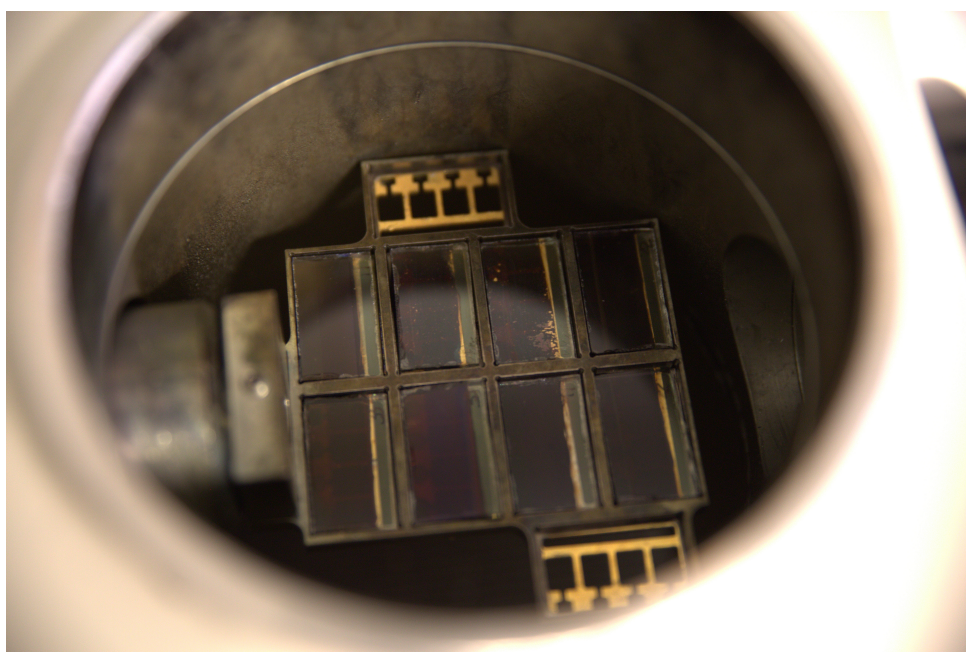


Figure 10: solar cells spiro side down in the holder of the vacuum ion electro deposition machine. adding the gold electrode of 8 nm.

4.4 Characterization of blocking layers

4.4.1 Cyclovoltametry

The grafted FTO and ITO samples are studied through cyclovoltametry against the Ferrocene/Ferrocene+ couple from 0 V - +1 V at 20 mV/s in a solution of 0.1 M $TBABF_4$

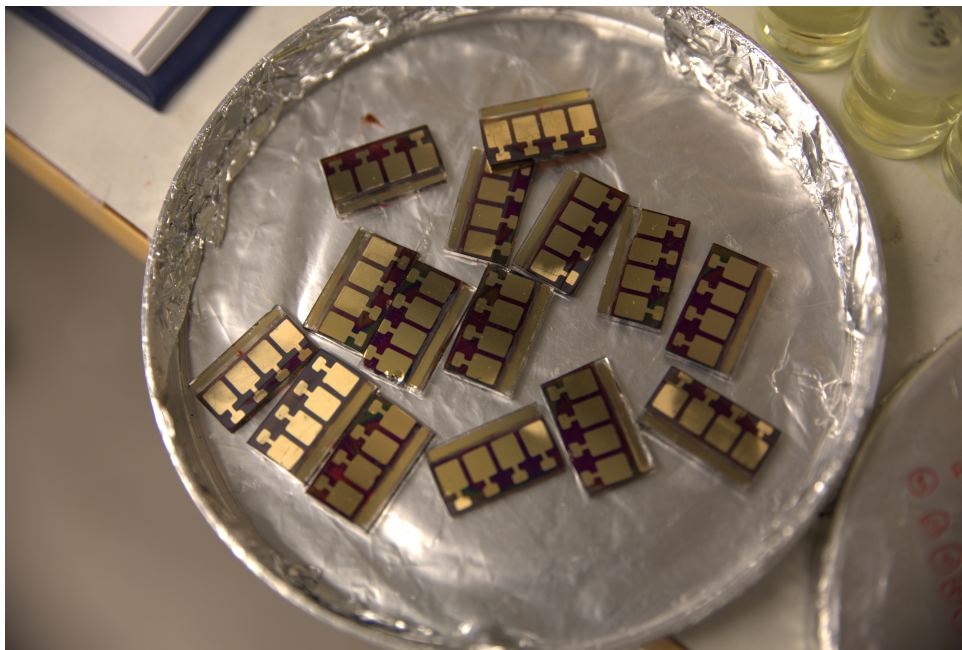


Figure 11: A batch of perovskite solar cells. Each bottle shaped electrode represents a cell. giving 4 cells per glass plate.

and 1mM Ferrocene. The setup used is the same as chapter 4.2

4.4.2 Ellipsometry

The thickness of the deposited layer was investigated via ellipsometry at the Danish Technical University (DTU). Unfortunately, no useful results were attainable for the FTO. For ITO, an interesting result appeared. The thickness of the ITO went from about 130 nm to a thickness of 4-10 nm. This pointed to the fact that the oxidative process used did in fact oxidize the ITO, as found by Folcher et al.[3] and Kraft et al.[6]

4.4.3 XPS

EDA coated samples were studied via X-ray photoelectron spectroscopy (XPS) at the i-Nano department at Aarhus University. XPS works by shining a high energy x-ray on a surface, ionizing it. Then the ionized surface relaxes itself by emitting photons with wavelengths specific to it's atomic number. Those photons are then captured by a detector. The emission spectra being known, the intensities at those wavelengths gives the prevalence of each atomic species.

4.4.4 Kelvin probe force microscopy

Kelvin probe force microscopy (KPFM) is used to determine the work function of the grafted FTO glass. KPFM is a scanning probe method where the potential between the tip and the surface is measured. An alternating current is passed through the cantilever

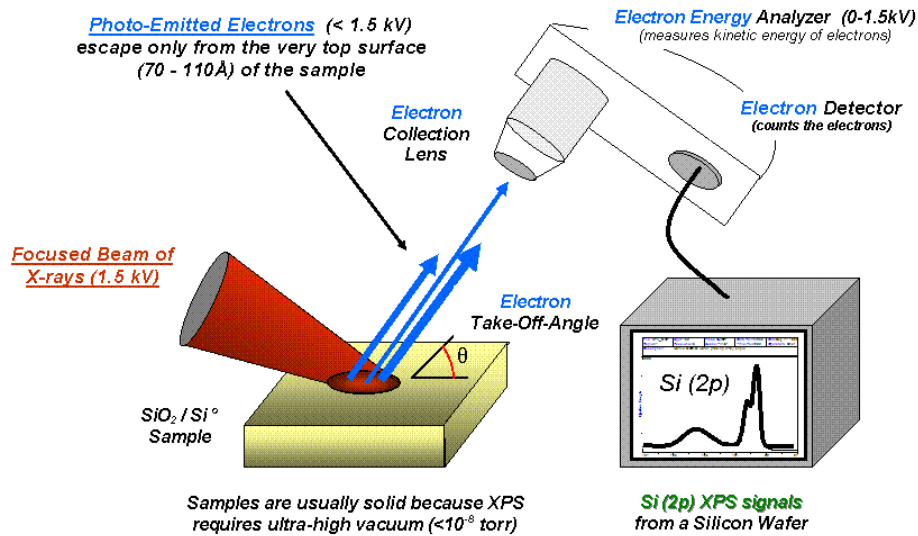


Figure 12: Scheme of an example of a Kelvin probe force microscope.[?]

tip at its resonance frequency ω_0 and a direct current passes through the sample. The voltage offset between DC and AC causes the tip to vibrate and a laser measures it. The energy of the cantilever tip-surface is given by

$$E = \frac{1}{2}C[2V_{DC}V_{AC}\sin(\omega_0 t) - V_{AC}^2\cos(\omega_0 t)] \quad (1)$$

This energy is stored in the vibration of it with the classical spring equation and the maximum amplitude x , $E = 1/2kx^2$.

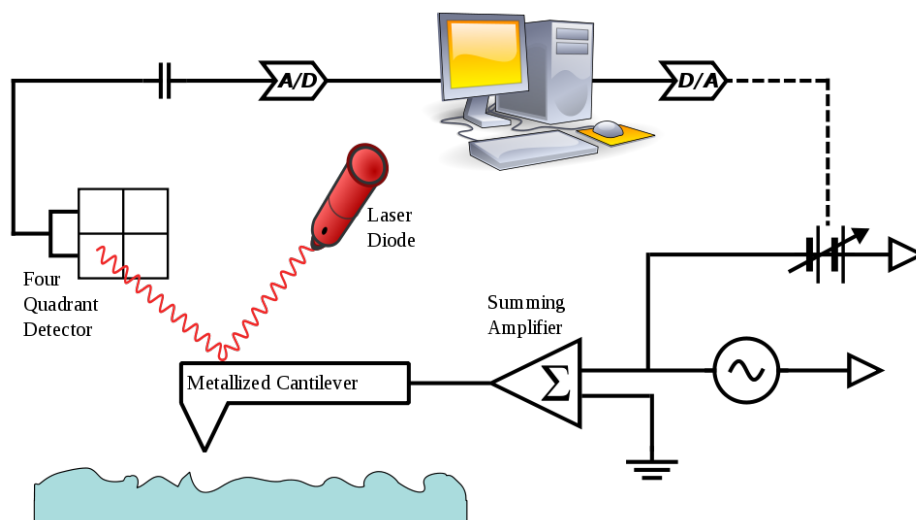


Figure 13: Scheme of a Kelvin probe force microscope.[?]

4.5 Analysis metode

4.5.1 Solar simulator

The solar cells are tested on a solar simulator of standard 1000 W/m^2 and air mass (AM) 1.5. The temperature of the room was $24\text{ }^\circ\text{C}$ at the moment of analysis. The calibration of the light intensity was done on a standard crystalline silicon solar cell. Short term maximum power point of the solar cell is made with illumination of 400 to 500 s Incident photon-to-electron conversion efficiency (IPCE) measurement are also done to see the quantum efficiency of the different cells.

Due to the inherent difficulty to have high reproducibility in the fabrication of perovskite solar cells, every time a new batch of organic blocking layer was tested, 4 standard cells have been produced for comparison and are labeled as such:

- PSC1: MaPbI_3 -Spiro with TiO_2 blocking layer and mesoporous TiO_2 scaffold
- PSC2: MaPbI_3 -Spiro with mesoporous TiO_2 scaffold
- PSC3: MaPbI_3 -Spiro with TiO_2 blocking layer
- PSC4: MaPbI_3 -Spiro
- PSC5: MaPbI_3 -Spiro with ethylenediamine 10 cycles
- PSC6: MaPbI_3 -Spiro with ethylenediamine 30 cycles
- PSC7: MaPbI_3 -Spiro with DIA 10 cycles
- PSC8: MaPbI_3 -Spiro with DIA 30 cycles

5 Results and discussion

5.1 Preparatory work

5.1.1 Grafting

The grafting of ethylenediamine on FTO did work well. The grafting CV signal. there is a clear dampening of the signal. After 10 cycles, the max current is already half compared to the first cycle.

5.1.2 Cyclic voltammetry

As seen in figure 15, grafting EDA on FTO does change very much the signal, both increasing the hysteresis and the maximum intensity. This implies that the amount of current and the reversibility of the reaction after grafting is highly affected and is correlated to the thickness of the grafted layer.

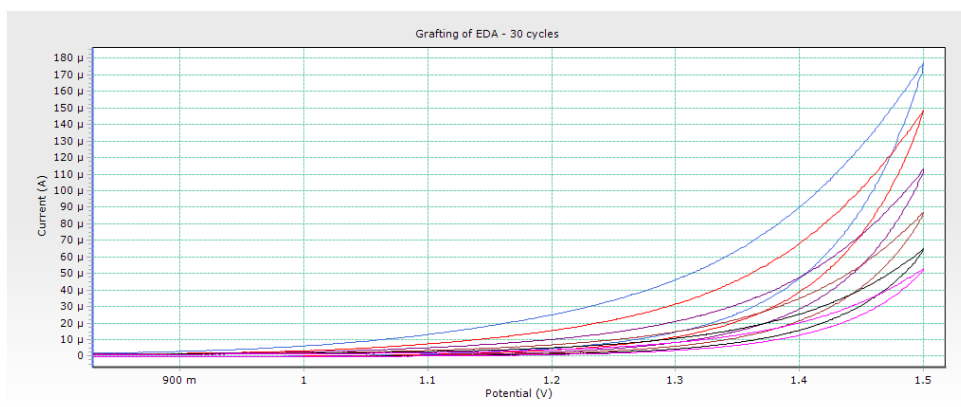


Figure 14: CV signal from the grafting of ethylenediamine on FTO. In blue 1 scan, in red 2 scans, in purple 5 scans, in brown 10 scans, in black 20 scans and in violet 30 scans

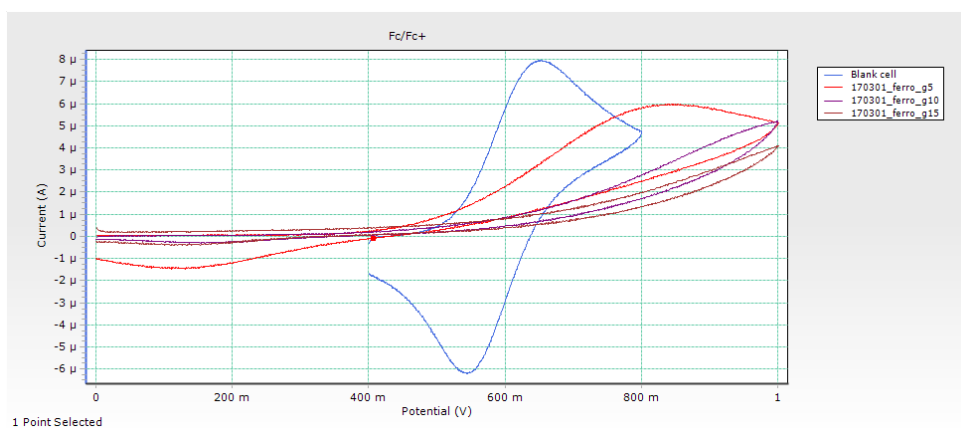


Figure 15: Fc/Fc⁺ signal from FTO, 5, 10 and 15 cycles of EDA grafting

5.1.3 XPS

Samples studied via XPS showed around 2.7% N and 36% C, this is a very high C/N ratio compared to what was expected. This could result either be the result of contamination by other organic compound. The result of polymerization of EDA would give an C/N ration much higher, with a theoretical limit of 2C/1N ratio for polyethylene amine. The Sn to C and N ratio cannot help us since the depth of XPS analysis stops in the middle of

5.1.4 Kelvin probe

The temperature at which the samples were tested was 20.8 ± 0.2 °C. As we can see in figures 16 and 17, the increase in number of cycles did influence the work function of the EDA grafted FTO. The work function value seen in the figures need to be corrected by 5 eV due to the calibration done with gold.

The average corrected work function of the system are seen in table 1. the increase in thickness of ethylenediamine does impact the work function of the blocking layer-FTO pair. The TiO_2 blocking layer is shown as example. Since the method of transporting the electron through the titanium and EDA is not hypothesized to be the same, the relative value of it between them is not as relevant.

Sample	Work function
EDA 10	-114
EDA 30	-182
TiO_2	-217

Table 1: corrected work functions of EDA 10 EDA 30 and TiO_2

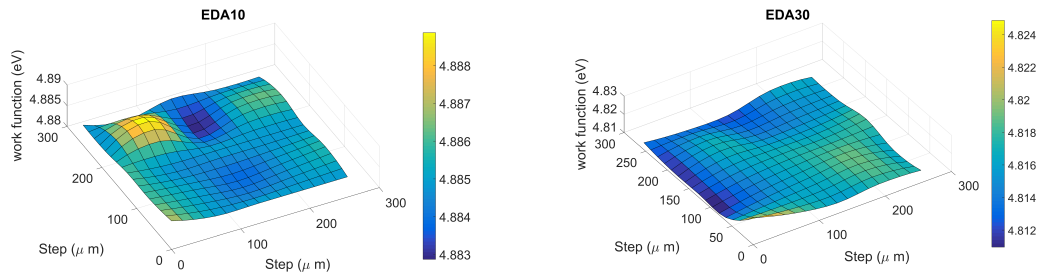


Figure 16: Total work function of the FTO-EDA-measuring tip over a surface of 0.09 mm^2 . With 10 cycles on the left and 30 on the right.

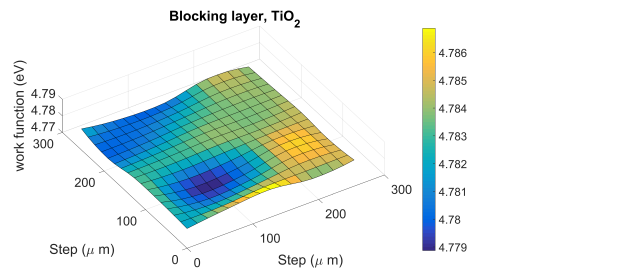


Figure 17: Total work function of the FTO- TiO_2 -measuring tip over a surface of 0.09 mm^2 .

The aim of finding the work function was to further a model of long distance electron tunneling. Unfortunately, such model worked upon did not yield any useful information.

5.2 solar cells

Of the 3 batches of perovskite solar cells made, only the 2 first ones, made with FTO grafted in advance at RUC worked. Unfortunately, the last batch, either the 4 references

and the samples where the layer of ethylenediamine was grafted on site with a more carefully controlled environment, did not work.

The glass plates made at RUC, during sonic cleaning or during transport might have scratched or degraded by some degree. They were made 10-13 days in advance.

5.2.1 Solar simulator

Efficiencies of perovskite solar cells are known to be hard to reproduce. Small factors like air humidity during preparation can render the cell much less efficient. Of the 3rd batch of experiments, due to high air humidity, the process took place in air controlled glove box. Unfortunately, none of the cells worked. The results can be seen in figures 18 to 21. du to the high variability of the samples, the values in table 2 are the best for each sample. The least variable results are the V_{OC} for PSC7 and the standards with Ti blocking layer, PSC1 and PSC3.

We can see that our samples do work worse than even the lowest standard PSC4. What can be summarized is that EDA works better than DIA and that 10 cycles are better than 30. Since the actual thickness is unknown, it is still possible for either to have a positive effect as blocking layers but the thickness should be reduced, what was tried for the 3rd batch.

Sample	PSC1	PSC2	PSC3	PSC4	PSC5	PSC6	PSC7	PSC8
Efficiency (%)	15.05	12.41	13.27	11.46	9.86	8.71	3.86	2.19
V_{OC}	1.055	0.975	1.08	1.03	1.06	1.025	0.765	0.72
Fill factor	0.710	0.641	0.667	0.587	0.568	0.535	0.420	0.377
Jsc (mA/cm^2)	20.1	19.9	18.4	19	16.4	15.9	12	8.09

Table 2: values for the best cell of each type

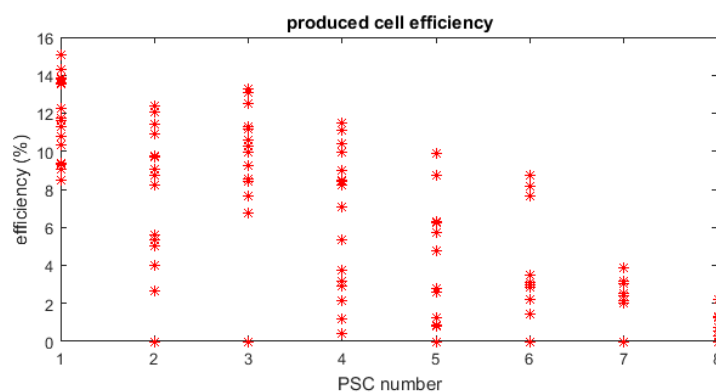


Figure 18

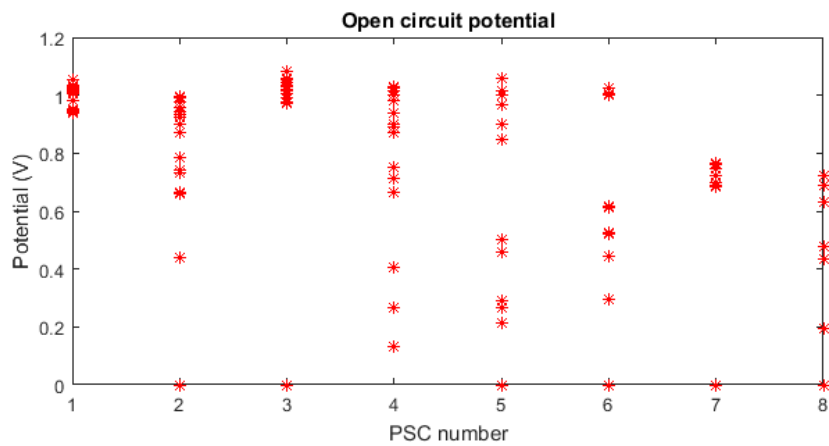


Figure 19

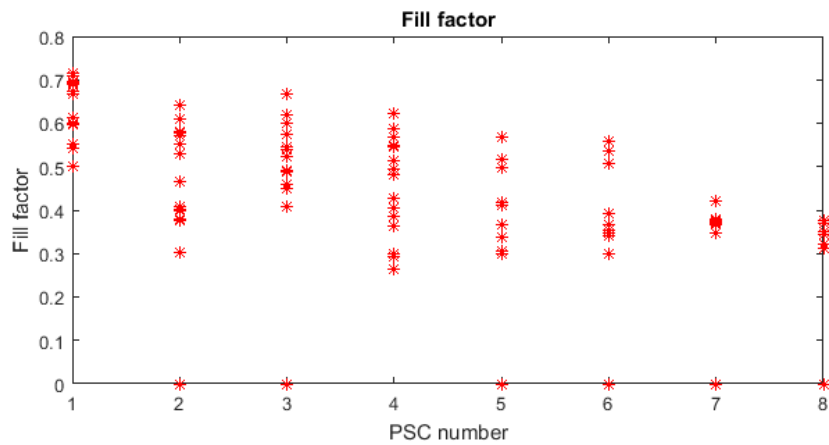


Figure 20

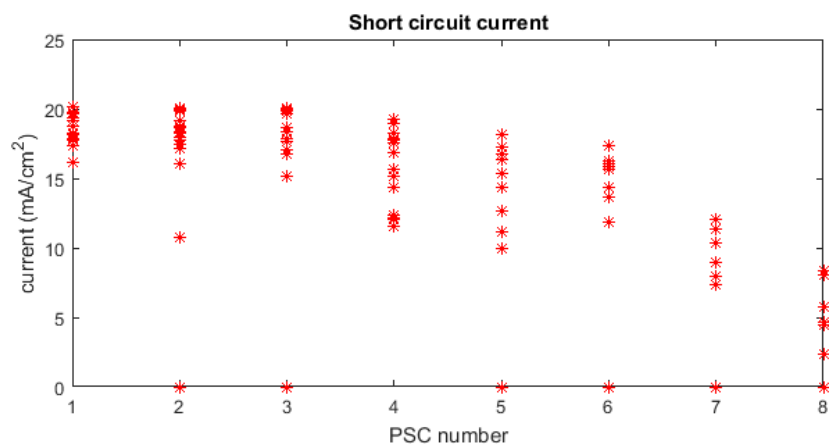


Figure 21

5.2.2 Maximum power point

When the short and mid term stability is studied, both standards with blocking layer do show a little dip in power and V_{OC} . For the other samples, over the first minute, the loss are from 25 to nearly 40% compared to their initial values.

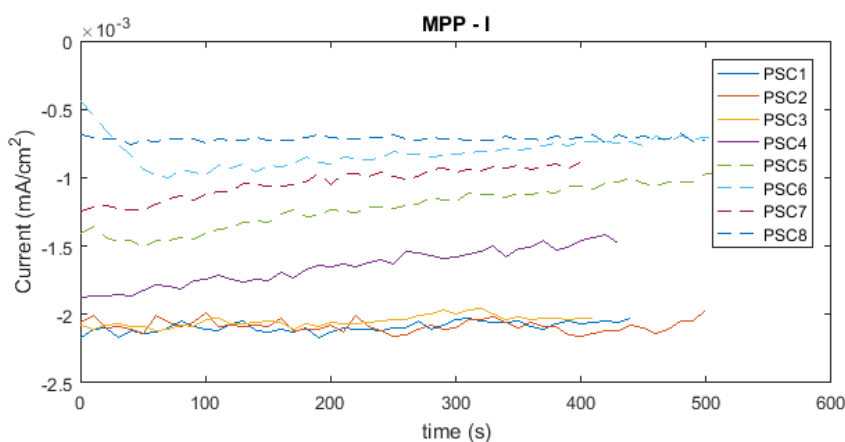


Figure 22: maximum current point of the solar cells over 400-500 s. Only EDA30 shows a current drop in the first minute.

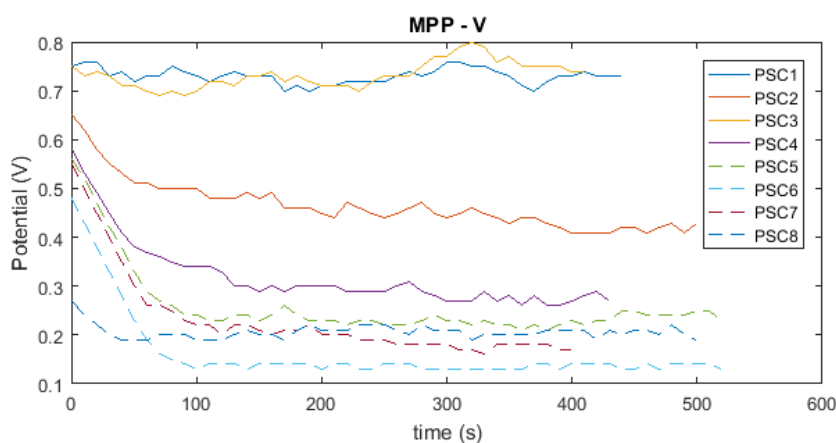


Figure 23: maximum V_{OC} point of the solar cells over 400-500 s.

For the current output in figure 22, only the sample using EDA 30 cycles did have a drop in the current in the first minute. All others are either stable or slightly increase due to the decrease in V_{OC} seen just before

5.2.3 IPCE

The incident photon to charge carrier efficiency can be seen in figure 25. the standards do all have a high IPCE over the whole spectrum, only having PSC3 dipping a little more than the others around 700 nm. PSC 4, being perovskite on bare FTO sits in between. For the samples. they all have poor values. EDA and fewer cycles being better.

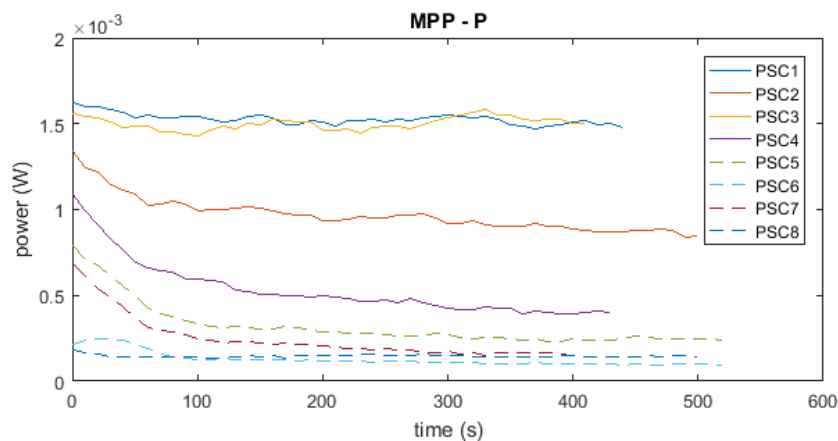


Figure 24: maximum power point of the solar cells over 400-500 s.

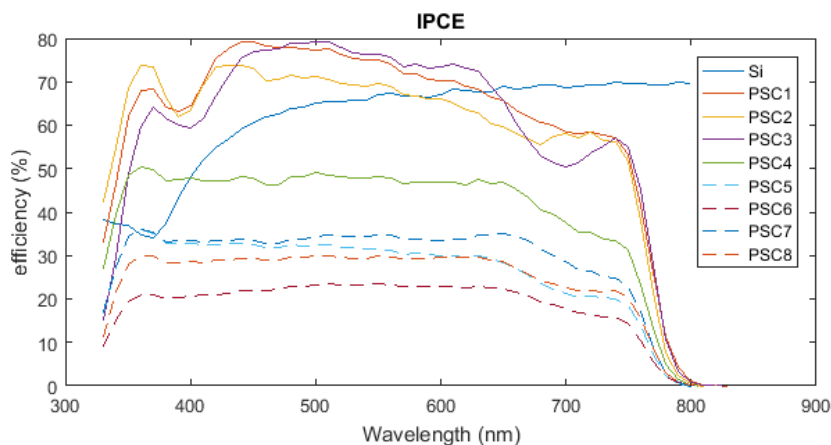


Figure 25

6 Conclusion

The experiment done so far do not show any improvement in efficiency in the *MaPbI3*-Spiro perovskite solar cells. The short and mid term stability are also very poor and IPCE is showing a graph resembling the bare standard with an even lower efficiency. Unfortunately, since the last experiment failed, optimization regarding the thickness of the EDA layer could not have been tested. The main problem that still holds is that the thickness of EDA layer is not known. Since the efficiency of non conductive blocking layer is extremely sensitive to the thickness, the possibility to be in the right thickness window is very small without an accurate analytical method being used. On the few samples done, it seems like ethylenediamine is a better contender as a blocking layer that p-aminoaryldiazonium, but it might just be that the thickness of the samples were just further from the optimum, thus making it too thick to actually let current flow free on either way. Another caveat is that we just assumed that the growth of the blocking layer on top of FTO is ideal. The FTO might have been corroded like what was seen on

ellipsometry for FTO, albeit at a much smaller extent due to its more stable nature. Or the fact that the growth of the blocking layer is not homogeneous at all, giving rise to some highly non-conductive areas and some with barely no layer, this would just behave like a cell without blocking layer with a much smaller surface contact to the electrode. Since the non conductive blocking layer done until now are with conjugated carbons, maybe the delocalization of the Pi electrons do play a non negligible role in the transport of the charges.

7 Perspectives

The most important work to continue this field of research would be to characterize precisely the thickness of the grafted layer. The lack of knowledge in that area is a big problem when we want to optimize the experiments. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) could give detailed images to see the homogeneity of the layer over FTO by scanning the same sample before and after grafting. High resolution transmission electron microscopy (HRTEM) and SEM would be tools to measure the thickness of the grafted layer, analyzing a slice of a grafted plate. It would also indicate if any corrosion to the FTO occurred.

To follow up on non conductive blocking layer, looking into other molecules that might be more polarisable to investigate if the potential increase in electron density in the n-type contact and the blocking layer is beneficial. The study of the accumulation of electron at the p-type contact and the blocking layer would be an interesting subject to see until which point, this increase can be optimized in conjunction of the perovskite thickness.

As discussed in chapter 3, the blocking layer's thickness is closely related to the incoming electron's energy. Thus a good model for predicting the electron tunneling will need to factor not only the work function of the electrode-block but also the energy of the electron produced by the active site.

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