

# High stability perovskite solar cells under ambient conditions

ISSN 1752-1416  
 Received on 28th January 2020  
 Revised 4th June 2020  
 Accepted on 17th August 2020  
 E-First on 15th December 2020  
 doi: 10.1049/iet-rpg.2020.0098  
 www.ietdl.org

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**Abstract:** Though perovskite solar cells have outstanding commercialisation potential, perovskite materials are very vulnerable to moisture and oxygen. So the main issue for perovskite solar cell is very fast degradation. In order to elaborate on this concern, the stability of perovskite solar cells were investigated in this study. The effect of oxygen and moisture on perovskite solar cells decreased with encapsulation of the cells. Encapsulation has been carried out with ultraviolet cured epoxy resin. Stability tests were taken place in laboratory conditions under solar simulator and also shelf-life tests. Perovskite solar cells showed the highest power conversion efficiency (PCE) of 9.77% with a short circuit current density of 22.5 mA/cm<sup>2</sup>, the open-circuit voltage of 0.94 V and fill factor of 0.46. After 2800 h, perovskite solar cells were still 85% stable in atmospheric conditions. Perovskite solar cells exhibited distinctive durability for shelf-life test in laboratory conditions. The PCE of perovskite solar cells were decreased only 15% of its initial value after 2800 h. In order to elaborate the degradation of perovskite solar cells, the cells are exposed to solar irradiation AM1.5G. Perovskite solar cells degraded gradually with time under solar irradiation; however, this stability test indicated that the solar cells were durable 20% after 500 h exposure to solar irradiation.

## 1 Introduction

Photovoltaic solar cells are promising technologies for producing electricity from sunlight; in particular, silicon solar cells with a superior efficiency of around 27% [1, 2]. Though fabrication of silicon solar device is needed detrimental chemicals in complex purification process [2] and silicon-based panels are very expensive. Hybrid metal-halide perovskites emerge as an alternative to inorganic solar cells because of their good electronic properties and variety of coating methods [3, 4]. Perovskite solar cells (PSCs) are preferred since it is solution processable, low cost and superior efficiency [5]. Power conversion efficiency (PCE) of this type of solar cells 3.8% was first reported by Kojima *et al.* in 2009 [6]. The highest PCE of PSCs is over 22% [7]. The chemical formula of perovskite structure is defined ABX<sub>3</sub>; A: Organic cation, B: Inorganic cation, X<sub>3</sub>: Halogen anion [8]. The main drawback of perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>Cl<sub>3</sub>) solar cells is low durability [9–11]. PSCs lose around 80% of their PCE within 3 h after their production [11]. Oxygen and water vapour in the atmosphere degraded perovskite and that leads to a decrease in the efficiency and stability of PSCs. Besides, ultraviolet (UV) radiation is a crucial factor that negatively affects the stability of PSCs. High temperature also causes degradation of PSC's chemical structure [12–14].

In the literature, lead-free PSCs showed high stability, with 90% durable after 500 h of continuous operation in the glovebox atmosphere under AM1.5G illumination [15]. Large area perovskite solar module was investigated with printing technologies, having very high ambient stability for 2000 h [16]. It was also reported PSCs with NiOx nanoparticles as the hole transport layer and ZnO nanoparticles as an electron transport layer (ETL), showed 1440 h stability in ambient conditions [9]. At ambient temperature and zero humidity, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells seen high stability, high temperature and in moisture degradation. Hydrogen iodide (HI), which decomposes in the perovskite cell, provides faster decomposition [17]. A total of 40% relative humidity (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> – PbI<sub>2</sub> + CH<sub>3</sub>NH<sub>3</sub>I) was reported to cause a reaction. This indicates that PbI<sub>2</sub> is more reactive [18].

In this paper, we have fabricated PSCs and then determined the photovoltaic parameters of PSCs under solar illumination. We have studied shelf life test (ISOS-D-1) and laboratory weathering testing (ISOS-L-1) [10–12] were carried out. It is a studied mixture of halides of lead (II) iodide (PbI<sub>2</sub>) and lead chlorides (PbCl<sub>2</sub>) for the fabrication of PSCs. It is focused on solution-based processing especially perovskite layers and also hole transport layers. This is a very cost-efficient method for obtaining the PSCs. In this paper, we compared both ISOS-D-1 and ISOS-L-1 stability tests and PSC degradation were also discussed.

## 2 Materials and methods

### 2.1 Materials

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was obtained from HERAUS [\*6\*,\*6\*]-Phenyl C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM) which is used as the ETL, was obtained from LUMTEC. Indium tin oxide (ITO) coated glass substrates (15 Ω/sq) that was obtained from KINTEC. Methylammonium iodide (MAI), PbI<sub>2</sub> and PbCl<sub>2</sub>, were obtained in powder form LUMTEC and ALDRICH, respectively. N,N-dimethylformamide (DMF), 1,2-dichlorobenzene (DCB) solvents were also obtained from SIGMA ALDRICH and MERCK. The UV epoxy resin used for the encapsulation materials was obtained from OSSILA.

### 2.2 Device fabrication & characterisation

The PEDOT:PSS were spin-coated on cleaned ITO coated glass substrates and heat treatment at 120°C for 20 min. (Fig. 1). The mixture of MAI, PbI<sub>2</sub>, PbCl<sub>2</sub> with a mole ratio 2:1:1 was spin-coated onto PEDOT:PSS coated the substrates and then thermally annealed at 80°C for 2 h. (Fig. 1) The weight percentages of the MAI, PbI<sub>2</sub>, PbCl<sub>2</sub> were 16, 7, 11%, respectively.

The PC<sub>61</sub>BM concentration was 50 mg/ml in DCB. Then, the PC<sub>61</sub>BM solutions were coated on the perovskite layer at a spinning rate of 1000 rpm for 30 s. Finally, Ca (10 nm) and Al (100 nm)

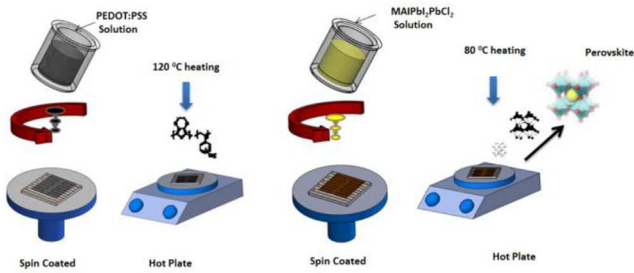


Fig. 1 Schematic diagram of preparation of PSCs [19]

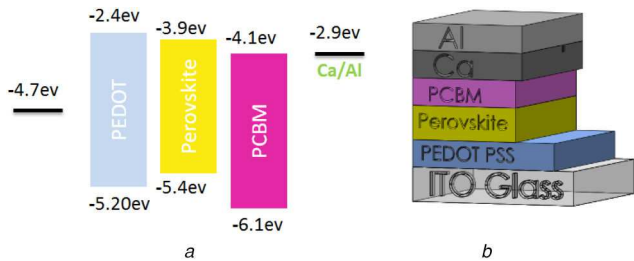


Fig. 2 Device structure and energy level diagrams of a complete perovskite solar cell  
(a) Energy diagram of PSCs [20], (b) Solar cell architecture

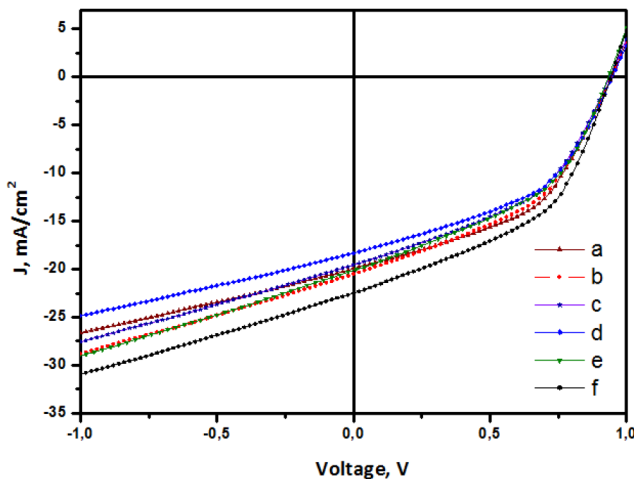


Fig. 3  $J$ - $V$  characteristics of PSCs

Table 1 Photovoltaic parameters of PSCs

Device	$V_{oc}$ , V	$J_{sc}$ , mA/cm <sup>2</sup>	FF	PCE
a	0.94	19.94	0.47	8.95
b	0.94	20.5	0.44	8.61
c	0.94	19	0.46	8.41
d	0.94	18.32	0.46	8.01
e	0.93	20.12	0.43	8.22
f	0.94	22.5	0.46	9.77

were deposited using a thermal evaporator at a deposition rate of 2.5 Å/s.

### 3 Results and discussion

#### 3.1 Photovoltaic characterisation

PSCs have a hybrid structure since they contain both organic and inorganic structures. The band diagram and energy levels of PSC is seen in Fig. 2a. The conventional perovskite solar cell device structure is depicted in Fig. 2b. The conventional device structure consists of ITO/PEDOT:PSS/Perovskite/PCBM/Ca/Al. In the device structure, it is used MAI, PbCl<sub>2</sub> and PbI<sub>2</sub> to construct perovskite. The  $I$ - $V$  characteristics of the cells were shown in Fig. 3. The highest PCE of PSC was 9.77%, and open circuit

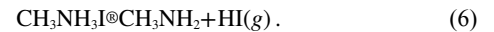
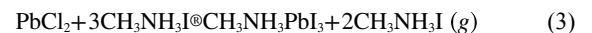
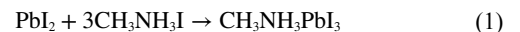
voltage ( $V_{oc}$ ) of the cell was 0.94 V. PSCs are of high efficiency, we fabricated six devices for reproducibility and exhibited in Fig. 3. The photovoltaic parameters of the PSCs are given in Table 1. Power conversion efficiencies are about in the range of 8.01–9.77%. The current–voltage measurements were carried out under AM 1.5G irradiation via a mask.

#### 3.2 Device stability

The fundamental parameters of the experiments are temperature, solar irradiation and moisture for stability tests [21]. In order to understand the stability of the cells, we measured the photovoltaic parameters of the cells for 2800 h in time intervals. The stability of the solar cells measured with ISOS-D-1, ISOS-L-1 protocols [10]. PCE and short circuit current density ( $J_{sc}$ ) of solar cells decreased slightly with time. It was indicated that PSC seems quite stable under ambient conditions (ISOS-D-1).

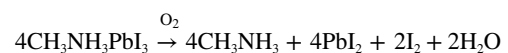
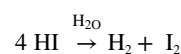
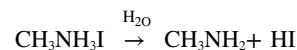
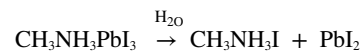
The results showed that PSCs are quite durable at ambient conditions in dark (ISOS-D-1). O<sub>2</sub> and moisture parameters affect slightly the PSC stability at ambient conditions. The normalised current density of PSC changed about 20% from the initial value with time (Fig. 4). When time increases, normalised  $V_{oc}$ , fill factor (FF),  $J_{sc}$  of PSC changed very slightly. However, normalised PCE decreased 20% of its initial value, since PCE affected all PV parameters. Nevertheless, the stability of PSC is quite good that is 80% durable at ambient conditions after 2800 h.

The reactions during perovskite formation are as follows [13, 22]:



We supposed that since PbI<sub>2</sub> is more reactive than PbCl<sub>2</sub> during the formation of perovskite structure PbI<sub>2</sub> first interact with CH<sub>3</sub>NH<sub>3</sub>I and therefore CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> occurs [23]. In reaction 3, PbCl<sub>2</sub> reacts with CH<sub>3</sub>NH<sub>3</sub>I to form MAPbI<sub>3</sub> and MAI or PbI<sub>2</sub>. It is seen that CH<sub>3</sub>NH<sub>3</sub>I formed as a result of the reaction creates HI with the effect of moisture, oxygen and UV radiation and the perovskite structure decomposes. This indicates that PbI<sub>2</sub> is more reactive. Following the MAI interacts with PbCl<sub>2</sub> during thermal annealing process and colour changes. After the thermal annealing process, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>2</sub>Cl<sub>2</sub> perovskite structure occurs. Changes in the colour of the film during the annealing process are shown in Fig. 5.

During the degradation of PSCs, some chemical reactions occur with oxygen, moisture and solar irradiation. Fig. 6 shows some possible reactions that may occur when the perovskite films are affected by O<sub>2</sub> and moisture



[24]

The process of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> decomposition was displayed schematically in Fig. 6 [23]. In the reaction shown in Fig. 6, PbI<sub>2</sub>, which is more reactive than PbCl<sub>2</sub>, interacted with MAI to form

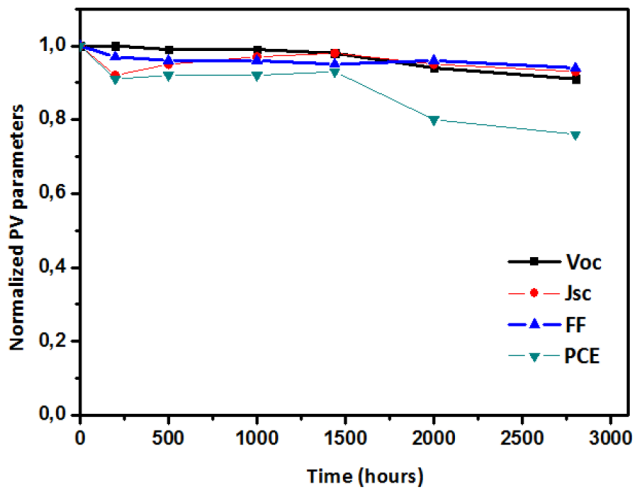


Fig. 4 ISOS-D-1 stability study of PSCs ambient conditions:  $V_{oc}$ ,  $J_{sc}$ , FF, PCE versus time graph

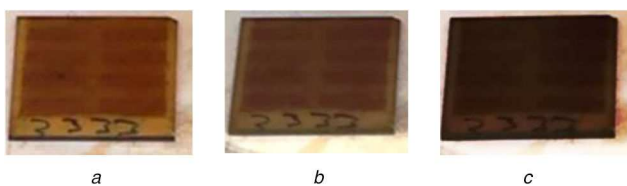


Fig. 5 From the beginning of the annealing process (a) 12 s later, (b) 30 min later, (c) 2 h later

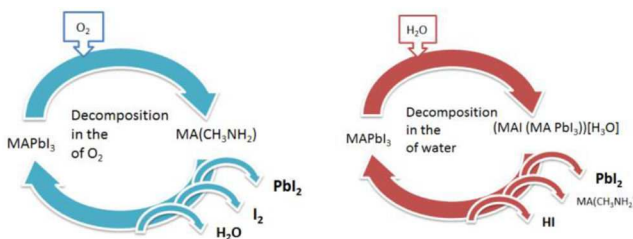


Fig. 6 Decomposition of perovskite structure [23, 24]

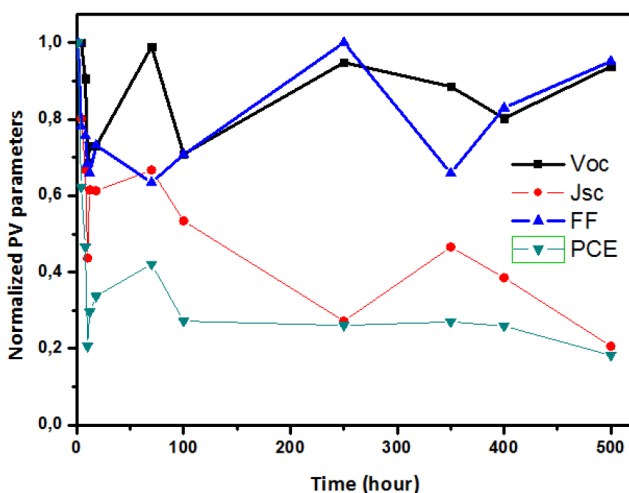


Fig. 7 ISOS-L-1 stability test of PSCs with time

$\text{CH}_3\text{NH}_3\text{PbI}_3$ . Since  $\text{PbI}_2$  is more reactive, it is first affected by moisture and perovskite structure can be degraded. However, Fig. 4 indicated that PSC stability is quite good for ISOS-D-1 test protocols since it is stable for 2800 h. It is revealed that ambient conditions slightly affect perovskite device performance after encapsulation.

A situation similar to the degradation of perovskite structure due to moisture can also occur under UV light. ISOS-L-1 test was

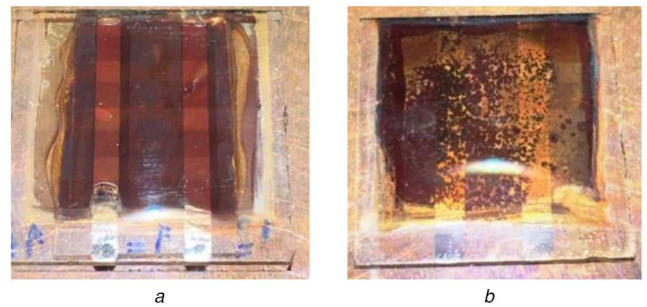


Fig. 8 Images of PSCs

(a) Before exposure to solar irradiation, (b) After exposure to solar irradiation

applied to the solar cells produced under the same conditions, and their stability was determined under solar simulator for 500 h. Fig. 7 presents normalised  $V_{oc}$ ,  $J_{sc}$ , FF and PCE as a function of time for PSCs. At the beginning of the ISOS-L-1 test, PCE and  $J_{sc}$  values of the PSCs decreased quite sharp. A few hours later, PCE of the solar cells stabilised 20% durability and last 500 h. The FF and  $V_{oc}$  values decreased 20% of initial values, whereas the  $J_{sc}$  and PCE values decreased about 80%. ISOS-L-1 test claimed that devices were stable for 500 h with low durability of 20% (Fig. 7).

Fig. 8 shows photographs of the cells before and after ISOS-L-1 test for 500 h. It was shown that the final images of the PSCs were exposed to solar irradiation after 500 h. It was seen that solar irradiation degrades very quickly the cells by breaking the bond between  $\text{CH}_3\text{NH}_3$  and  $\text{PbI}_2$ . Since the yellow colour indicates the presence of  $\text{PbI}_2$  and cleavage of perovskite bond.

Although the shelf life test of PSCs showed very good durability, ISOS-L-1 test stability is quite low. It is seen that UV radiation substantially affects PSC stability. Since it is known that oxygen molecules diffuse into the active layer and trap  $\text{I}_2$  vacancies. After exposing solar irradiation, UV light leads to forming electron-hole pairs. The electron transfer to  $\text{O}_2$  produces highly reactive superoxide species. These superoxides attack perovskite layer starting to degradation. [24]

## 4 Conclusions

In this study, the PSCs kept at ambient conditions (ISOS-D-1) remained quite stable for about 2800 h.  $\text{O}_2$  and moisture seem to effect very little on the degradation of solar cells under ambient conditions. However, the ISOS-L-1 test of PSCs under the solar simulator, solar cell stability was quite smaller than that of ISOS-D-1. The reason for this result was UV irradiation of PSCs during ISOS-L-1 test. Perovskite layer produces electron-hole pair with UV irradiation and it transfers electrons to oxygen. Forming superoxides degrade perovskite devices excessively [24]. This effect can overcome very advanced encapsulation methods such as atomic layer deposition technique (ALD) and distinct barrier layers. We will try to develop new encapsulation methods with ALD in the future study. Furthermore, we will try to decrease  $\text{PbI}_2$  concentration and increase MAI concentration improve the stability of PSCs in the new projects.

## 5 References

- [1] Philipps, S.: 'Photovoltaics Report', updated: 27 August 2018
- [2] Green, M.A., Hishikawa, Y., Dunlop, E.D., *et al.*: 'Solar cell efficiency tables (version 52)', *Prog. Photovoltaics Res. Appl.*, 2018, **26**, pp. 427–436
- [3] Wang, D., Liu, Z., Zhou, Z., *et al.*: 'Reproducible one-step fabrication of compact  $\text{MAPbI}_{3-x}\text{Cl}_x$  thin films derived from mixed-lead-halide precursors', *Chem. Mater.*, 2014, **26**, pp. 7145–7150
- [4] Zuo, L., Gu, Z., Ye, T., *et al.*: 'Enhanced photovoltaic performance of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells through interfacial engineering using self-assembling monolayer [supporting information]', *J. Am. Chem. Soc.*, 2015, **137**, pp. 2674–2679
- [5] Ye, T., Lim, S.L., Li, X., *et al.*: 'Pinhole-free mixed perovskite film for bending durable mixed perovskite solar cells', *Sol. Energy Mater. Sol. Cells*, 2018, **175**, pp. 111–117
- [6] Kojima, A., Teshima, K., Shirai, Y., *et al.*: 'Organometal halide perovskites as visible-light sensitizers for photovoltaic cells', *J. Am. Chem. Soc.*, 2009, **131**, pp. 6050–6051

- [7] Yusoff, A.R.B.M., Nazeeruddin, M.K.: 'Organohalide lead perovskites for photovoltaic applications', *J. Phys. Chem. Lett.*, 2016, **7**, pp. 851–866
- [8] Hodes, G.: 'Perovskite-based solar cells', *Science*, 2013, **342**, pp. 317–318
- [9] You, J., Meng, L., Song, T., *et al.*: 'Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers', *Nat. Nanotechnol.*, 2016, **11**, pp. 75–81
- [10] Reese, M.O., Gevorgyan, S.A., Jørgensen, M., *et al.*: 'Consensus stability testing protocols for organic photovoltaic materials and devices', *Sol. Energy Mater. Sol. Cells*, 2011, **95**, pp. 1253–1267
- [11] Unay, H., dos Reis Benatto, G.A., Beliatas, M.J.: 'High stability of benzotriazole and benzodithiophene containing medium band-gap polymer solar cell', *Sol. Energy Mater. Sol. Cells*, 2018, **174**, pp. 433–444
- [12] Jørgensen, M., Norrman, K., Krebs, F.C.: 'Stability/degradation of polymer solar cells', *Sol. Energy Mater. Sol. Cells*, 2008, **92**, pp. 686–714
- [13] Niu, G., Guo, X., Wang, L.: 'Review of recent progress in chemical stability of perovskite solar cells', *J. Mater. Chem. A*, 2015, **3**, pp. 8970–8980
- [14] Philippe, B., Park, B.W., Lindblad, R., *et al.*: 'Chemical and electronic structure characterization of lead halide perovskites and stability behavior under different exposures-A photoelectron spectroscopy investigation', *Chem. Mater.*, 2015, **27**, pp. 1720–1731
- [15] Chen, M., Ju, M.G., Garces, H.F., *et al.*: 'Highly stable and efficient all-inorganic lead-free perovskite solar cells with native-oxide passivation', *Nat. Commun.*, 2019, **10**, pp. 1–8
- [16] Priyadarshi, A., Haur, L.J., Murray, P., *et al.*: 'A large area (70 cm<sup>2</sup>) monolithic perovskite solar module with a high efficiency and stability', *Energy Environ. Sci.*, 2016, **9**, pp. 3687–3692
- [17] Han, Y., Meyer, S., Dkhissi, Y., *et al.*: 'Degradation observations of encapsulated planar CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells at high temperatures and humidity', *J. Mater. Chem. A*, 2015, **3**, (15), pp. 8139–8147
- [18] Shirayama, M., Kato, M., Miyadera, T., *et al.*: 'Degradation mechanism of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite materials upon exposure to humid air', *J. Appl. Phys.*, 2016, **119**, p. 115501
- [19] Adam, G., Kaltenbrunner, M., Glowacki, E. D., *et al.*: 'Solution processed perovskite solar cells using highly conductive PEDOT:PSS interfacial layer', *Sol. Energy Mater. Solar Cells*, 2016, **157**, pp. 318–325
- [20] Kim, H. P., bin Mohd Yusoff, A.R., Jang, J.: 'Polystyrene enhanced crystallization of perovskites towards high performance solar cells', *Nanoscale Adv.*, 2018, **1**, pp. 76–85
- [21] Kavak, P., Parlak, E.A.: 'Investigation of indoor stability testing of polymer solar cell', *Hindawi*, 2016, **2016**, pp. 1–8
- [22] Berhe, T.A., Su, W.-N., Chen, C.-H., *et al.*: 'Organometal halide perovskite solar cells: degradation and stability', *Energy Environ. Sci.*, 2016, **9**, (2), pp. 323–356
- [23] Wang, D., Wright, M., Elumalai, N.K., *et al.*: 'Stability of perovskite solar cells', *Sol. Energy Mater. Sol. Cells*, 2016, **147**, pp. 255–275
- [24] Aristidou, N., Eames, C., Sanchez-Molina, I., *et al.*: 'Fast oxygen diffusion and iodide defects mediate oxygen-induced degradation of perovskite solar cells', *Nat. Commun.*, 2017, **8**, p. 15218