HIGHLY STABLE PEROVSKITE FILM WITH IONIC LIQUID ADDITIVES FOR AMBIENT AIR DEPOSITION

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Abstract

Perovskite solar cells (PSCs) technology has emerged as a highly promising photovoltaic (PV) option due to remarkable advancements in power conversion efficiency (PCE). Nevertheless, the stability of PSCs continues to pose a challenge for commercialization, as factors such as moisture, oxygen, light, and temperature can lead to degradation during fabrication and actual use stage. The stability of the perovskite film is crucial for extending the device's lifetime and performance. This research seeks to explore the degradation mechanism and improve the perovskite film's stability by incorporating 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) and 1,3-dimethyl-3-imidazolium hexafluorophosphate ($DMIMPF_6$) ionic liquids into a perovskite precursor using the two-step deposition technique in ambient air. The perovskite film's degradation and PSCs' stability were evaluated under high relative humidity conditions, averaging 73%RH without encapsulation. UV-visible spectroscopy results indicate that the most stable perovskite film, containing the $BMIMBF_4$ ionic liquid additive, maintains its α phase perovskite structure for 144 hours without alterations in absorbance and persisted for over 336 hours before degrading into an undesirable δ phase perovskite. Furthermore, PSCs retained 74.1% of their initial PCE after 28 days of exposure to ambient conditions. This research offers promising findings for the large-scale fabrication of stable PSCs.

Keywords: **Air Ambient Fabrication; Ionic Liquid Additives; Perovskite Film Degradation; Perovskite Solar Cells Stability; Two-Step Deposition Techniques**

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Introduction

The demand for solar energy has been steadily increasing due to the ongoing climate change crisis and achieving the Net Zero target goal by 2030 has become a top priority. Despite the fact that the crystalline silicon photovoltaic technology remains the dominant commercial solar cell due to its high performance, durability, and long lifespan, its use of silicon, a valuable resource in the electronics industry, raises concerns about potential scarcity and high energy and material requirements involved in its production. To address these issues, perovskite photovoltaic technology has emerged as a promising third-generation photovoltaic technology that offers impressive performance (National Renewable Energy Laboratory, 2022) with low energy and material requirements. However, the ambient instability of perovskite solar cells (PSCs) due to their sensitivity to moisture, oxygen, light, and temperature (Kundu and Kelly, 2020) makes device fabrication under an inert atmosphere remains a major obstacle to their large-scale commercialization. This instability not only poses a significant barrier to their fabrication but also affects their lifespan in actual use, leading to a drop in device performance (He *et al*., 2020). Therefore, improving the stability of perovskite solar cells is an urgent challenge that needs to be addressed in order to establish a sustainable photovoltaic option. While perovskite solar cells are currently limited to laboratory-scale in an inert atmosphere, addressing their stability issues will enable their large-scale commercialization and pave the way for a sustainable future.

In the general laboratory-scaled PSCs, the formal planar architecture is commonly utilized, consisting of five layers; Transparent conductive oxide (TCO) coated glass layer, Electron transport layer (ETL), Absorber layer or Perovskite layer, Hole transport layer (HTL), and Back electrode. While each layer is susceptible to degradation, the absorber layer or Perovskite layer is particularly vulnerable to the ambient atmosphere, especially moisture which can cause destruction to the perovskite structure (Schlipf *et al*., 2018). This research aims to enhance the stability of PSCs by fortifying the perovskite layer with various types of ionic liquid (IL) as an additive to perovskite precursor. The experiment comprises two main procedures, focusing on perovskite film degradation and the improvement of PSCs stability.

Methods

In the experiment aimed at improving the degradation of perovskite films, the Fluorine-doped Tin Oxide glass (FTO) was utilized as the transparent conductive oxide (TCO), while SnO_2-doped NH_4Cl served as the electron transport layer (ETL). The perovskite layer employed three different recipes of triple cation perovskite precursor. For the improvement of PSCs stability, the same materials were used as in the perovskite film experiment, with the addition of Spiro-OMETAD as the hole transport layer (HTL), and Gold (Au) as the back electrode layer, to fabricate the perovskite solar device. The experiments were carried out under controlled humidity in an ambient air atmosphere, except for the HTL, which was deposited under an inert atmosphere. Subsequently, all perovskite films and perovskite solar cells were exposed to the extremely high relative humidity in an ambient air atmosphere without encapsulation. The film degradation was evaluated periodically using a colorimeter and UV-visible spectroscopy to observe changes in color and absorbance. The film's properties, morphology, and crystallinity were examined using Contact angle, Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) methods, respectively. For the device stability, the power conversion efficiency (PCE), Short-circuit current density (Jsc), and Open-circuit voltage (Voc) were monitored on a weekly basis using a solar simulator.

Perovskite Precursor and Ionic Liquid Addition

In this research, two types of high-potential ionic liquids (ILs) were chosen to be doped into the triple cation perovskite precursor, with an optimized concentration for each type. To facilitate the deposition process, the precursor was divided into two sets.

The first set consisted of a solution containing 1.5M PbI_2 and 5% vol./vol. CsI in a DMF:DMSO solvent with a ratio of 0.95:0.05. The solution was stirred at 80°C for an hour until it became clear and then continued to be stirred without heat overnight. Next, for recipe no.2, 0.2% vol./vol. of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) was added to the precursor, while for recipe no.3, 0.2% weight/weight of 3-dimethyl-3-imidazolium hexafluorophosphate ($DMIMPF_6$) was added. Finally, both solutions were stirred without heat overnight.

The second precursor set was composed of 0.4M Formamidinium iodide (FAI), 0.1M Methylammonium iodide (MAI), and 0.3M Methylammonium chloride (MACl) in Isopropanol (IPA) with a volume of 1 ml. The solution was stirred overnight without applying heat.

Deposition Method

The deposition process for all perovskite recipes followed the same parameters and conditions. The electron transport layer, perovskite layer, and hole transport layer were deposited using the spin-coating technique, while the back electrode layer was deposited through thermal evaporation. To ensure large-scale potential and low toxicity, a two-step deposition technique was developed for the perovskite layer that does not require the use of an anti-solvent. The perovskite layer was deposited under controlled humidity of approximately 40-50% RH in an ambient air environment with the aid of a humidifier. The first step involved dropping and spinning 40 µl of the first precursor set at low speed, followed by spinning at high speed (1900 rpm) for 30 seconds. The resulting CsI/PbI_2+(IL) layer, which had a yellow color, was annealed at 70°C for 1 minute and then allowed to cool for 5 minutes. The second step involved dropping and spinning 300 µl of the second precursor set at high speed (2500 rpm) for 40 seconds. The perovskite film was formed by annealing at 160°C for 10 minutes, resulting in a black-colored film that was then allowed to cool for 30 minutes.

Results and Discussion

Perovskite Film Degradation Results

The unencapsulated FTO/SnO_2+NH_4Cl/Perovskite film of each recipe was examined under uncontrolled humidity in ambient air at room temperature with an average of 73%RH. The observation included two types; the first type is related to the film hydrophobicity, crystallinity, and morphology, while the second type is related to the film degradation.

1. Film Hydrophobicity, Crystallinity, and Morphology

Ionic liquids were chosen to improve the perovskite film due to their ability to control crystallization kinetics, form strong ionic bonds, and provide hydrophobicity (Silva *et al.*, 2020; Shahiduzzaman *et al.*, 2021; Zhu *et al.*, 2021). This makes them promising additives for enhancing the morphology and crystallinity of the perovskite film as well as improving the interlayer between the ETL and perovskite layer (Bai *et al.*, 2019; Shahiduzzaman *et al.*, 2021). The contact angle

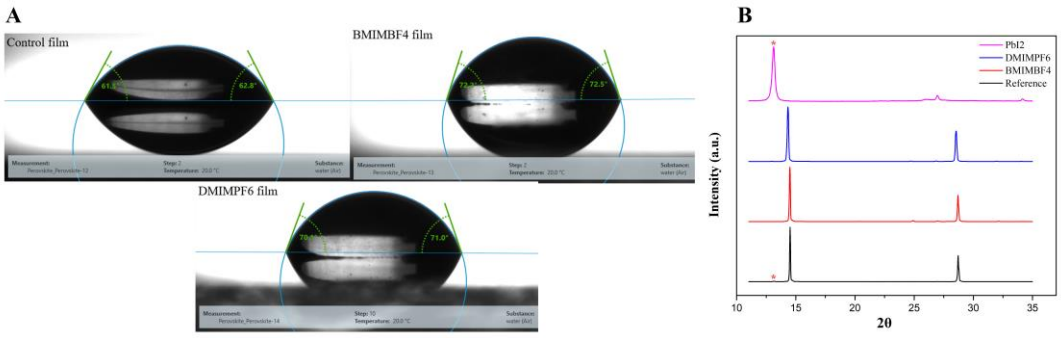

Figure 1. Perovskite film hydrophobicity and crystallinity A. Contact angle results and B. XRD results

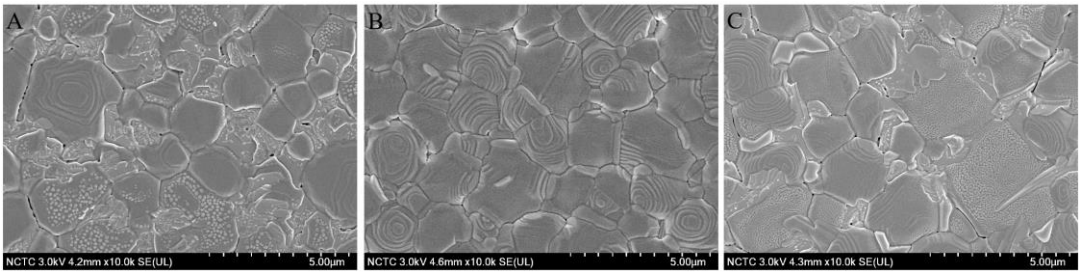

Figure 2. SEM results of FTO/SnO_2+NH_4Cl/Perovskite (A) Control film with an average grain size of 1.9 µm, (B) $BMIMBF_4$ additive film with an average grain size of 2.5 µm, and (C) $DMIMPF_6$ additive film with an average grain size of 2.8 µm

measurement revealed that the addition of ionic liquids enhances the hydrophobicity of the perovskite film. In comparison to the control film, the film with $BMIMBF_4$ and $DMIMPF_6$ additives displayed a higher angle, indicating better resistance to moisture-induced through the perovskite film during deposition. (Figure 1(a)). Moreover, the XRD result indicated that the film with ionic liquid additives also inhibited the residual PbI_2 (Bai *et al*., 2019). The control film showed a small peak that corresponds to the peak of PbI_2, while this peak was not observed in the film with $BMIMBF_4$ and $DMIMPF_6$ additives. (Figure 1(b))

In Figure 2, the SEM results demonstrate that the doping of ionic liquid benefits the crystallization kinetics by slowing down the growth process, resulting in larger grain size, compact crystal structure, and reduced gap between grain boundaries. With the hydrophobic properties and strong interionic bond at the ETL-perovskite layer interface, the film with $BMIMBF_4$ additives exhibits a uniform and smooth grain without any porosity inside. Similarly, the film with $DMIMPF_6$ additives has a larger grain size and smaller grain boundaries, but the presence of moisture pores inside the grain has been observed. Although the hydrophobicity of the $DMIMPF_6$ film is similar to that of the $BMIMBF_4$ film, it may not have a strong interfacial bond, resulting in moisture penetration during the deposition. Nonetheless, the moisture-pore size is smaller than that of the control film, which is more hydrophilic.

2. Film Degradation

To track the degradation progress of the perovskite film, its color, and absorbance was monitored. A black-colored perovskite film or α phase perovskite film can degrade into a yellow non-perovskite film or δ phase undesirable-perovskite film (Ma *et al*., 2017). The film color at the center of the perovskite film area was checked daily, and the degree of color change was calculated. At color change degree level 10, the results showed that the control film without ionic liquid additives had the fastest color change rate, degrading by the 6^{th} day. In contrast, the films with $BMIMBF_4$ and $DMIMPF_6$ degraded on the 11^{th} and 7^{th} days, respectively. (Figure 3(a))

Similarly, UV-Visible spectroscopy results indicate that the absorbance edge of the perovskite film with no additives, $BMIMBF_4$ additive, and $DMIMPF_6$ additive started to change on days 5^{th}, 7^{th}, and 7^{th}, respectively. The gradual change in absorbance edge and intensity of the $BMIMBF_4$ film is influenced by its uniform and non-moisture porous morphology, resulting in the $BMIMBF_4$ film still not completely degraded even after 14 days of observation. In contrast, both the control film and $DMIMPF_6$ film, which have moisture-porous inside the grain, showed a rapid change in absorbance edge and intensity after the α phase started to change. The control film had completely degraded to δ phase undesirable-perovskite on day 7^{th}, while the $DMIMPF_6$ film, with a better morphology, degraded slower than the control film on day 11^{th}. (Figure 3B)

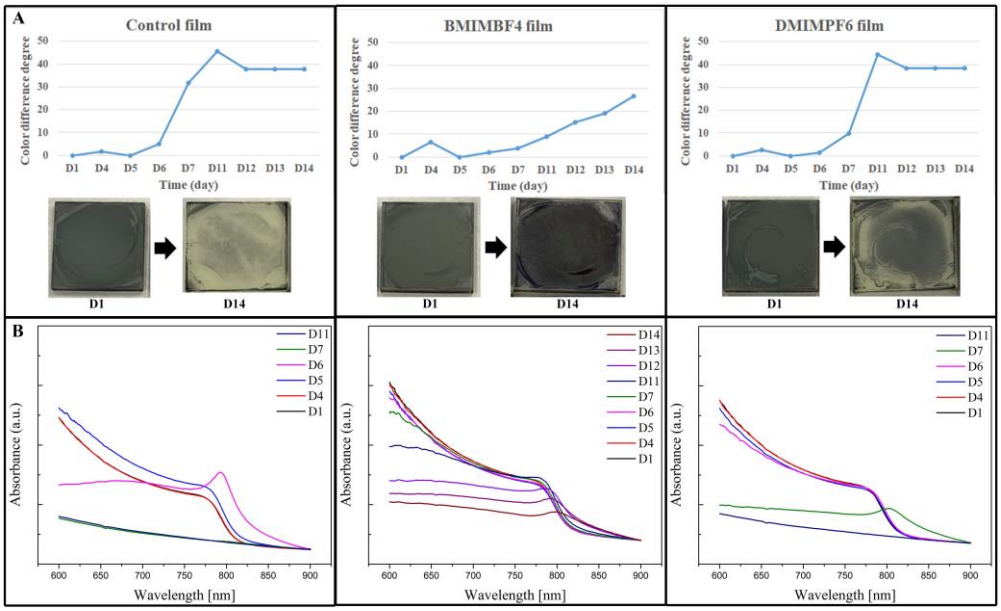

Figure 3. Perovskite film degradation 2 weeks observation results under air ambient, 73%RH without encapsulation A. color-changing check results B. film absorbance by UV Visible spectroscopy results

Perovskite Solar Cells Stability Results

The solar cells were constructed with FTO/SnO_2+NH_4Cl/Perovskite layer with three different recipes/Spiro-OMETAD/Au architecture and were left exposed to ambient air with an average humidity of 73% without any encapsulation or humidity control. The performance of the cells was monitored weekly for 28 days using a solar simulator, and the average value of 10 points/recipe was reported as a Figure 4 result.

1. Initial Efficiency and Long-Term Stability

The initial efficiency results (D_0) indicate that the highest-performing solar cell is the control perovskite film without ionic liquid additives, which achieves a PCE of 20.4%. In comparison, the PSCs with $BMIMBF_4$ and $DMIMPF_6$ additives achieve PCE of 18.5% and 16.3%, respectively. The presence of pores within the smaller perovskite grain enhances charge separation, leading to greater carrier extraction and increased Voc (Im *et al*., 2014). Despite the control PSC having the highest initial efficiency, it experienced a 14.2% decrease in initial efficiency since the first week (D_7) due to a reduction in Jsc, while the $BMIMBF_4$ and $DMIMPF_6$ PSC maintained their initial efficiency. This drop in Jsc indicates a decrease in absorbance performance caused by moisture-induced perovskite layer degradation, which penetrates through the perovskite layer at grain boundaries due to the loose structure, resulting in ion migration and perovskite phase change (Kundu and Kelly, 2020). The PSC with ionic liquid additives has a superior interface quality, larger grain size, dense structure, and smaller grain boundary gap, which enhances its moisture protection ability (Shahiduzzaman *et al*., 2021; Bai *et al*., 2019). However, the $DMIMPF_6$ PSC also experienced a slight drop in Jsc, while the $BMIMBF_4$ PSC maintained both Voc and Jsc perfectly.

The second week (D_{14}) results indicate the drastic drop in PCE for the control PSC and $DMIMPF_6$ PSC, while the $BMIMBF_4$ PSC experienced a lesser decline. The control and $DMIMPF_6$ PSCs suffered drops of over 40% and 25%, respectively, due to the deterioration of the film morphology, which resulted in low charge carrier mobility, high trap density, and high recombination losses. Consequently, both Voc and Jsc decreased. The initial efficiency of $BMIMBF_4$ PSC decreased by about 13.5%, primarily due to the degradation of the interface between layers, which resulted in increased recombination and decreased Voc. Starting from the third week (D_{21}) up to the fourth week (D_{28}), the PCE, Voc, and Jsc values of all PSCs showed a gradual decline due to degradation. However, the Jsc of $BMIMBF_4$ PSC remained at the same level as the initial condition during 28 days of observation, indicating efficient light absorption by the perovskite layer.

The results at the end of the fourth week (D_{28}) indicate that $BMIMBF_4$ PSC was the most stable among all PSCs, maintaining 74.1% of the initial PCE, while the control PSC and $DMIMPF_6$ PSC were able to maintain only 58.8% and 65.6% of their initial PCE, respectively.

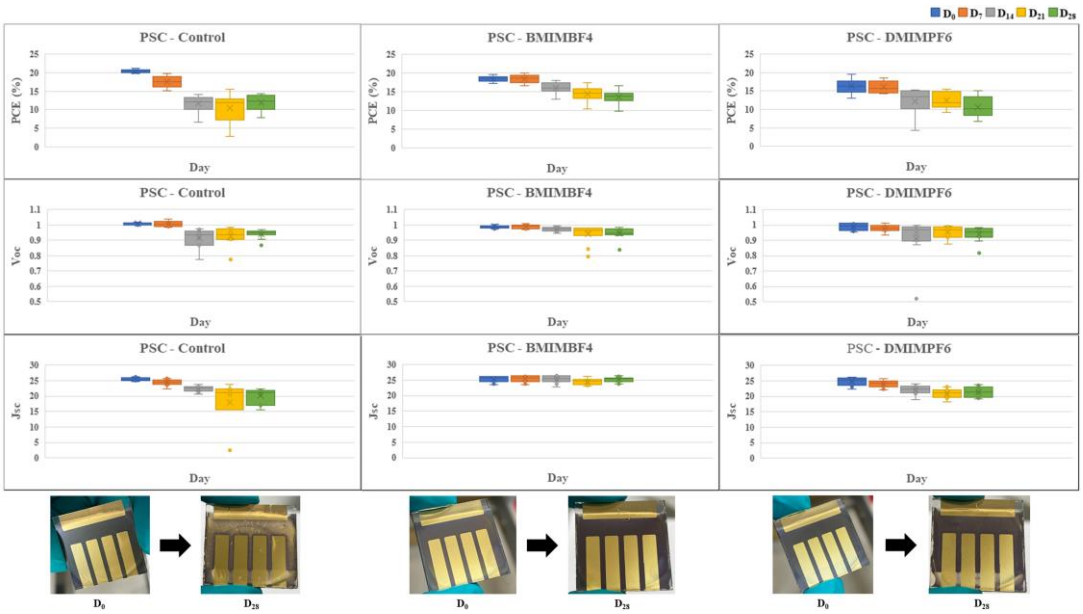

Figure 4. Perovskite solar cell performance and stability results for 28 days

Conclusions

Perovskite solar cells (PSCs) are vulnerable to degradation in ambient conditions, with the perovskite layer being particularly affected and moisture acting as the primary damaging factor. The incorporation of ionic liquids into the perovskite film has proven effective in counteracting the adverse effects of moisture, improving film morphology, hindering perovskite phase transitions, and enhancing the perovskite layer's stability. A stable perovskite layer helps maintain the Jsc and Voc values, contributing to the long-term stability of the PSC. Overcoming fabrication constraints will aid in advancing large-scale commercialization via ambient air fabrication. Nonetheless, moisture is only one of several factors that must be addressed, with light- and heat-induced factors also requiring consideration. Enhancing stability is essential not only for the perovskite layer but also for the electron transport layer (ETL) and hole transport layer (HTL) to promote efficient charge carrier extraction, charge transfer, and reduced recombination losses.

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References

Bai, S., Da, P., Li, C., Wang, Z., Yuan, Z., Fu, F., Kawecki, M., Liu, X., Sakai, N., Wang, J, T-W., Huettner, S., Buecheler, S., Fahlman, M., Gao, F., and Snaith, H.J. (2019). Planar perovskite solar cells with long-term stability using ionic liquid additives. Nature, 571:245-250. https://doi.org/10.1038/s41586-019-1357-2

He, S., Qiu, L., Ono, L.K., and Qi, Y. (2020). How far are we from attaining 10-year lifetime for metal halide perovskite solar cells?. Materials Science and Engineering: R: Reports, 140:100545. https://doi.org/10.1016/j.mser.2020.100545

Im, J-H., Jang, I-H., Pellet, N., Grätzel, M., and Park, N-G. (2014). Growth of $CH_3NH_3PbI_3$ cuboids with controlled size for high-efficiency perovskite solar cells. Nature Nanotechnology 9(11):927-932. https://doi.org/10.1038/nnano.2014.181

Kundu, S. and Kelly, T.L. (2020). In situ studies of the degradation mechanisms of perovskite solar cells. EcoMat, 2(2):e12025. https://doi.org/10.1002/eom2.12025

Ma, F., Li, J., Li, W., Lin, N., Wang, L., and Qiao, J. (2017). Stable α/δ phase junction of formamidinium lead iodide perovskites for enhanced near-infrared emission. Chemical Science, 8(1):800-805. https://doi.org/10.1039/C6SC03542F

National Renewable Energy Laboratory. (2022). Best Research-Cell Efficiency Chart. Retrieved February, 2023 from https://www.nrel.gov/pv/cell-efficiency.html

Schlipf, J., Bießmann, L., Oesinghaus, L., Berger, E., Metwalli, E., Lercher, J.A., Porcar, L., and Müller-Buschbaum, P. (2018). In Situ Monitoring the Uptake of Moisture into Hybrid Perovskite Thin Films. The Journal of Physical Chemistry Letters, 9(8):2,015-2,021. https://doi.org/10.1021/acs.jpclett.8b00687

Shahiduzzaman, M., Muslih, E.Y., Hasan, A.K.M., Wang, L., Fukaya, S., Nakano, M., Karakawa, M., Takahashi, K., Akhtaruzzaman, M., Nunzi, J-M., and Taima, T. (2021). The benefits of ionic liquids for the fabrication of efficient and stable perovskite photovoltaics. Chemical Engineering Journal, 411:128461. https://doi.org/10.1016/j.cej.2021.128461

Silva, W., Zanatta, M., Ferreira, A.S., Corvo, M.C., and Cabrita, E.J. (2020). Revisiting Ionic Liquid Structure-Property Relationship: A Critical Analysis. International Journal of Molecular Sciences, 21(20):7,745. https://doi.org/10.3390/ijms21207745

Zhu, X., Du, M., Feng, J., Wang, H., Xu, Z., Wang, L., Zuo, S., Wang, C., Wang, Z., Zhang, C., Ren, X., Priya, S., Yang, D., and Liu, S. (2021). High-Efficiency Perovskite Solar Cells with Imidazolium-Based Ionic Liquid for Surface Passivation and Charge Transport. Angewandte Chemie International Edition, 60(8):4,238-4,244. https://doi.org/10.1002/anie.202010987