Capping Layers Design Guidelines for Stable Perovskite Solar Cells via Machine Learning

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Abstract—After reaching a device efficiency level comparable to silicon, perovskite solar cell’s next big challenge is to tackle its environmental instability issue. To solve this problem, researchers have started incorporating a buffer layer called ‘capping layer’, consisting of low dimensional (LD) perovskite, sandwiched between perovskite absorber and hole transport layer. However, there is no conclusive agreement on how to select capping layer material that best extends the stability. By using feature importance rank on the regression models, we can start to see which molecular properties on capping layer have significant impact in suppressing degradation.

Keywords—perovskite solar cell, buffer layer, capping layer, degradation, stability

I. INTRODUCTION

Perovskite solar cell (PSC) has reached 25.2% efficiency [1], yet its stability is still behind silicon’s 25-year stability. To improve PSC stability, researchers have started to deposit capping layer consisting of a more stable Ruddlesden-Popper (RP) perovskite series atop of the perovskite absorber [2]. This capping layer has also been shown to improve surface passivation, and hence, overall device performance [2].

Various capping layer materials have been explored, including benzene rings/ phenyl with amine (e.g. phenylethlammonium iodide [3]), long carbon chains with amine (e.g. n-octylammonium iodide [4], n-butylammonium iodide [5]), or large, complex structures (e.g. Eu-porphyrin complex [6]). However, comparing the materials’ stability is challenging, due to non-standardized degradation test protocols across different studies. The design guideline for capping layer materials is therefore, hard to conclude, and slows down the development to push PSC into the market.

This work was supported by National Science Foundation (NSF) SusChem Grant CBET-1605547, Skoltech grant 1913/R as part of the Skoltech NGP Program, and TOTAL Sustng Mbr 9/08, RPP.

II. EXPERIMENTAL RESULTS

A machine-learning framework is introduced to pinpoint the most significant organic molecular properties of the capping layer materials responsible for the stability improvement. The capping layer materials properties from PubChem 2019 database [7] and the capping layer fabrication process conditions (annealing temperature and precursor concentration) serve as input to the regression models. The degradation test results from the various capping layer materials deposited atop of an unstable absorber, methylammonium lead iodide (MAPbI$_3$), serves as output to the models. Feature importance rank from the regression models is then extracted, to find which properties affect the stability most significantly. Materials characterization is then performed to investigate the underlying mechanisms behind the stability improvements in these capping layers. Finally, devices with capping layer are fabricated to see how they perform. The experimental method is summarized in Fig. 1.

![Fig. 1. The experimental method for investigating capping layer design guidelines.](image)

A. Machine Learning and Feature Importance Rank

The 21 capping layer materials, including tetrapropylammonium iodide (TMAI) and phenyltriethylammonium iodide (PTEAI), with various concentrations (5-15 mM) are deposited and annealed at temperatures between 50°C-125°C. While the
films are degraded in a controlled environmental chamber, under 0.16 Sun illumination, 85% relative humidity and 85°C heat, the image of the films is taken every 3 minutes. The image data is then extracted for the red, green, blue (RGB) values. The color change in the films from black to yellow correspond to an increase in red and green (RG) values. Since RG values both overlap, either values can represent the degradation process.

We define a degradation onset, which is the time-intercept of extrapolated slope coming from a sharp increase in red values, that serves as machine learning model output. The onsets for bare, TPAI-capped, and MAPbI3 films are shown in Table I, showing that both TPAI- and PTEAI-capped films are more environmentally stable.

| Capping Materials         | Degradation Onsets (minutes) |
|---------------------------|------------------------------|
| Bare MAPbI3               | 107 ± 45                     |
| TPAI-capped MAPbI3        | 353 ± 66                     |
| PTEAI-capped MAPbI3       | 462 ± 115                    |

The 13 material properties extracted from PubChem 2019 database [7] serve as the input. Decision-tree-based regression models are trained, using scikit-learn library [8]: random forest regression and gradient boosting regression with decision trees. For each model, the feature importance rank is extracted using SHAP (SHapley Additive exPlanations) [9]. The feature importance rank result for random forest regression (Fig. 2.) shows that both the topological polar surface area and the number of hydrogen-bond donor in the capping layer organic molecules affect the stability of the capping layer the most.

The red color represents that the higher feature value leads to better stability, and the blue color represents the opposite. Therefore, to design a stable capping layer, we need a smaller area of topological polar surface and a fewer number of hydrogen-bond donor. Gradient boosting regression with decision trees model also shows similar trend in top two features.

B. In-depth Materials Characterization

To better understand how the presence of the organics in capping layer affect the films during the degradation, we also perform Fourier-transform infrared spectroscopy (FTIR). This measurement shows how the methylammonium coming from capped-MAPbI3 films, indicated by the NH3+ stretch at 3,176 cm⁻¹, is preserved during degradation in PTEAI-capped film.

C. Device Performance

To see how both TPAI and PTEAI capping layers perform in terms of efficiency, devices are fabricated with the following architecture, from bottom to top: a fluorine-doped tin oxide (FTO) layer as the contact, a SnO2 layer as the electron transport layer, a MAPbI3 layer as the photoabsorber layer, a capping layer, a spiro-OMeTAD layer as the hole transport layer, and a gold layer as the contact.

Under 1 Sun, AM1.5G illumination, the PTEAI-capped devices perform the best (median efficiency: 15.5%) among bare (median: 13.6%), TPAI-capped (median: 13.5%), and PTEAI-capped MAPbI3 devices, which is due to high open-circuit voltage ($V_{OC}$) and short-circuit current density ($J_{SC}$), as shown in Fig. 3.

Fig. 3. The reverse device measurements for bare, TPAI-capped, and PTEAI-capped MAPbI3 absorbers. The bottom and top 25% of the device results, respectively. The red bar represents the median. PCE is power conversion efficiency, $V_{OC}$ is open-circuit voltage, and $J_{SC}$ is short-circuit current.
III. DISCUSSION

This study demonstrates the first-time machine-learning approach is used to find the guideline for selecting the capping layer for PSCs. Both decision-tree-based algorithms show consistent results in feature importance ranking. The top two features affecting the stability, which are the number of hydrogen-bond donor and the polar surface area of the molecule, are related. The presence of lone pairs from electronegative atoms can act as hydrogen-bond donor and affect the polarity of the molecules by creating permanent dipoles. Though, how the presence of hydrogen-bond donor accelerates the degradation requires further investigation. It is clear, however, that the excess of PbI₂ in the capped-film is reduced, because the capping layer material reacts with the excess PbI₂ in MAPbI₃ layer. The reduction of excess of PbI₂ in initial perovskite absorber material is known to improve stability [10].

Looking at the device results, the increase in JSC exhibited by devices with capping layer, can be attributed to the surface passivation improvement [11] and / or the higher diffusion length. To understand which one causes the change in JSC, we need to further investigate the charge-carrier diffusion length, which is proportional to the charge-carrier mobility and lifetime. Regardless, the high JSC coming from capping layer is beneficial for boosting the efficiency.

On the other hand, the improvement in VOC can be caused by an increase in bandgap. Hence, bandgap measurement is needed to understand the underlying cause. Nevertheless, similar to the JSC, an improvement in VOC gives an additional benefit of using the capping layer.

IV. SUMMARY

The capping layer has been shown to improve the environmental stability of the perovskite thin-films, and also to boost their device performance. The machine-learning framework also helps to pinpoint which 13 capping layer molecular properties taken from the database governs the framework also helps to pinpoint which 13 capping layer material reacts with the excess PbI₂ in MAPbI₃ layer. The guideline of choosing organic capping layer molecules with small polar surface area fewer number of hydrogen-bond donors to extend stability enlightens the photovoltaic community to bring the PSCs closer to mainstream photovoltaic market. In addition, the ~14% relative boost in efficiency from depositing an optimum capping layer also provides an extra benefit.

ACKNOWLEDGMENT

N. T. P. H. thanks National Science Foundation (NSF) SusChem Grant CBET-1605547 and Skoltech grant 1913/R as part of the Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through MITel Sustng Mbr 9/08, RPP. A. T. thanks Alfred Kordelin Foundation and MITeI thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program. J. T., C. B., Z. L., and S. S. thank TOTAL SA research grant funded through Skoltech NGP Program.

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