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Roadmap on Commercialization of Metal Halide Perovskite Photovoltaics

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Roadmap on Commercialization of Metal Halide Perovskite Photovoltaics

Shien-Ping Feng [2,27], Yuanhang Cheng [3], Hin-Lap Yip [3], Yufei Zhong [4], Patrick W.K. Fong [5], Gang Li [5], Annie Ng [6], Cong Chen [7], Luigi Angelo Castriotta [8], Fabio Matteocci [8], Luigi Vesce [8], Danila Saranin [9], Aldo Di Carlo [8,9,10], Wang Puqun [11], Ho Jian Wie [11], Hou Yi [11], Lin Fen [11], Armin Aberle [11], Zhaoning Song [12], Yanfa Yan [12], Xu Chen [13], Yang (Michael) Yang [13], Ali Ashgar Syed [1], Ishaq Ahmad [1], Tiklun Leung [1], Yantao Wang [1], JingYang Lin [1,14], Alan Man Ching Ng [14], Yin Li [1], Firouzeh Ebadi [15], Wolfgang Tress [15], Giles Richardson [16], Chuangye Ge [17], Hanlin Hu [17], Masoud Karimipour [18], Fanny Baumann [18], Kenedy Tabah [18], Carlos Pereyra [18], Sonia Raga [18], Haibing Xie [19], Monica Lira-Cantu [18], Mark V. Khenkin [20], Iris Visoly-Fisher [21,22], Eugene A. Katz [21,22], Yana Vaynzof [23,24], Rosario Vidal [25], Guicheng Yu [17], Haoran Lin [17], Shuchen Weng [17], Shifeng Wang [26] and Aleksandra B. Djurišić [1,27,28]

[1] Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

[2] Department of Advanced Design and Systems Engineering, City University of Hong Kong, Kowloon, Hong Kong

[3] Department of Materials Science and Engineering, City University of Hong Kong, Tat Chee Avenue Kowloon, Hong Kong

[4] School of Materials Science and Engineering, NingboTech University, No.1 South Qianhu Road, Ningbo, China

[5] Department of Electronic and Information Engineering, Research Institute for Smart Energy (RISE), The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

[6] Department of Electrical and Computer Engineering, Nazarbayev University, Nur-Sultan, Kazakhstan

[7] Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong

[8] CHOSE (Centre for Hybrid and Organic Solar Energy), University of Rome Tor Vergata via del Politecnico, Italy

[9] LASE (Laboratory of Advanced Solar Energy), National University of Science and Technology ‚MISiS‘, Russia

[10] Istituto di Struttura della Materia (ISM-CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy

[11] SERIS (Solar Energy Reserach Institute of Singapore), National University of Singapore, Singapore

[12] Wright Center for Photovoltaics Innovation and Commercialization, Department of Physics and Astronomy, The University of Toledo, Toledo OH 43606, USA

[13] State Key Laboratory of Modern Optical Instrumentation, Institute for Advanced Photonics, College of Optical Science and Engineering, Zhejiang University, Hangzhou, China

[14] Southern University of Science and Technology China (SUSTech), 1088 Xueyuan Blvd, Nanshan, Shenzhen, Guangdong Province, China

[15] Institute of Computational Physics, Zurich University of Applied Sciences, Winterthur, Switzerland

[16] Mathematical Sciences, University of Southampton, UK

[17] Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Nanshan District, Shenzhen, China

[18] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology (BIST), Building ICN2, Campus UAB, E-08193 Bellaterra, Barcelona, Spain

[19] Institute for Advanced Study, Shenzhen University, 3688 Nanhai Avenue, Shenzhen, Guangdong, China

[20] PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

[21] Swiss Institute for Dryland Environmental and Energy Research

[22] The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, Israel

[23] Chair for Emerging Electronic Technologies, Technical University of Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany

[24] Leibniz-Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany
[25] Department of Mechanical Engineering and Construction, GID, Universitat Jaume I, Castelló, Spain
[26] Innovation Laboratory of Materials for Energy and Environment Technologies, Tibet University, Lhasa, China

[27] Guest editors of the Roadmap.
[28] Author to whom any correspondence should be addressed.

E-mails: dalek@hku.ku, tony.feng@cityu.edu.hk

Abstract

Perovskite solar cells represent one of the most promising emerging photovoltaic technologies due to their high power conversion efficiency. However, despite of the huge progress made not only in terms of the efficiency achieved, but also fundamental understanding of relevant physics of the devices and issues which affect their efficiency and stability, there are still unresolved problems and obstacles on the path towards commercialization of this promising technology. In this roadmap, we aim to provide a concise and up to date summary of outstanding issues and challenges, and progress made towards addressing these issues. While the format of this article is not meant to be a comprehensive review of the topic, it provides a collection of the viewpoints of the experts in the field which covers a broad range of topics related to perovskite solar cell commercialization, including those relevant for manufacturing (scaling up, different types of devices), operation and stability (various factors), and environmental issues (in particular the use of lead). We hope that the article will provide a useful resource for researchers in the field and that it will facilitate discussions and moving forward towards addressing the outstanding challenges in this fast developing field.

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Section 1 - Overview of commercialization prospects of perovskite solar cells

Aleksandra B. Djurišić [1] and Shien-Ping Feng [2]
[1] The University of Hong Kong, Pokfulam Road, Hong Kong
[2] City University of Hong Kong, Kowloon, Hong Kong

1.1 Status

Perovskite solar cells (PSCs) have made impressive advances in efficiency as well as stability since initial reports, although there are still unresolved problems hampering the efforts towards their commercialization, as will be discussed in this roadmap. Nevertheless, a number of companies are working on PSCs, such as Oxford PV, Utmo Light Ltd., Imec, Microquanta Semiconductor, Solliance, Toshiba, Saule Technologies, Wonder Solar

Ltd., GCL New Energy, Xeger Sweden AB, Alta Devices, G24 Power Ltd, FlexLink Systems, Polyera Corporation Solar Print Ltd, New Energy Technologies Inc, Korver Corp., Solar-Tectic, Ubiquitous Energy Inc., Fraunhofer ISE, Raynergy Tek Incorporation, Xiamen Weihua Solar Co. Ltd, etc. [1,2]. Some of these companies, such as Oxford PV (in partnership with Meyer Burger, 125 MW capacity production line) and Saule Technologies, have been establishing new pilot production lines and/or expanding production capacity [1,2], and commercial prototypes have also been installed (72 modules in Henn-Na innovative Japanese hotel by Saule Technologies [1]). In addition, Microquanta Semiconductor has already established 5 GW-capacity production line, while GCL New Energy is building a production line in Kunshan with 100 MW capacity [2]. Commercialization efforts also include printing technologies (Saule Technologies, Wonder Solar Ltd) [1,2], and Wonder Solar Ltd. has already demonstrated a 110 m^2 outdoor power generation system [2]. In addition, various consortiums and partnerships involving universities, companies, research institutes and national labs have been established, such as European Perovskite Initiative (EPKI) [3] and US-MAP (Manufacturing of Advanced Perovskites) [4].

1.2 Current and Future Challenges

Generally, the greatest challenges towards commercialization are considered to be scaling up (including ambient manufacturing), achieving long term stability, reducing or eliminating the use of toxic solvents, and preventing Pb leakage into the environment [1,2,5,6]. In this article, challenges for different applications of PSCs and the current state of their commercialization are discussed (Sections 2&3), followed by the discussion of important challenges of scaling up, for both solution-based and vapour deposition-based methods, as well as ambient processing (Sections 4-6). It should be noted that different deposition methods not only affect the cost of the devices, but also they have important implications on their environmental impact. Since the scaling up requires not only the reliable deposition of high quality perovskite films over large areas, but also patterning and interconnections to connect individual cells into modules, these techniques and the perovskite modules are discussed in Sections 7 and 8. In addition, tandem devices, especially perovskite-Si tandems, are expected to play an important role in perovskite commercialization [7]. Therefore, different types of PSC-based tandems are discussed in Sections 9-11. As the perovskite materials and devices exhibit instability when exposed to illumination, ambient atmosphere, elevated temperature, and electrical bias, stability is commonly recognized as one of the most significant challenges in commercialization of perovskite solar cells [7,8]. Different factors affecting the stability and degradation mechanisms, as well as device encapsulation and stability testing are discussed in Sections 12-19. It should be noted that while considerable research efforts have been devoted to improving the intrinsic stability of PSCs under the assumption that extrinsic factors can be addressed by encapsulation [8], the issue of encapsulation is by no means trivial since there are commonly significant discrepancies between encapsulation approaches used in commercial modules and small lab-scale cells [9].

Other important issues which needs to be addressed are the issues of lead toxicity and environmental impact of PSCs. We can generally view the scaling up challenge as an engineering issue that can generally be solved, stability challenges as a mixture of fundamental scientific and engineering issues, while environmental impact is the most complex question, which requires complex and multidisciplinary analysis. This needs to include the evaluation of not only the environmental impact of manufacturing, use, and disposal of PSCs, but also the issue of material cost and availability to properly address the issue of sustainability [5]. Various aspects related to environmental issues are discussed in Sections 20-23. The discussion of environmental impact often, somewhat simplistically, reduces to the debate on lead-containing vs. lead-free PSCs. It should be noted that the performance of lead-free perovskites lags far behind that of Pb-based ones. Consequently, EPKI white paper [3] identified conventional lead-based PSCs as the most promising both in terms of environmental impact in CO_2/kWh g, as well as energy payback time and energy return of investment. Lead management was proposed to be achieved by optimizing containment and recycling the devices at the end of life [3]. Recycling strategies for these devices are particularly important, since they not only allow addressing the issue of the use of lead [5,6], but also allow for improved sustainability, lower cost, and lower environmental impact if transparent conductive oxides and metal back electrodes are recycled [6]. This important aspect of future perovskite commercialization is discussed in Section 24. In addition, further studies on scalability, environmental friendliness, and economic feasibility of recycling would be highly desirable, since these issues still represent open questions [10]. However, it should be noted that due to the toxicity of lead different views exist in perovskite community, and the use of lead remains a significant concern in the research community [5,10]. Thus, despite the fact that the negative environmental impact of other cell components is often found to be greater than that of the perovskite layer and the fact that lead replacement has been either unsuccessful in reducing environmental impact or the actual impact is unknown (depending on the perovskite composition) and for some of the proposed replacements there are issues in terms of cost and available supply [5,10], the need to develop better lead-free perovskite materials and devices is often highlighted in research literature. Among those Sn-based perovskites are commonly identified as the most promising, despite known environmental issues for this type of materials [5,10]. For example, it was claimed that tin-based PSCs may be commercialized sooner than lead-based for indoor photovoltaics once their efficiencies reach 15% [2]. However, in addition to not taking into account all the complexities of environmental impact of tin-based perovskites [10], this does not take into account the lag in stability of tin-based PSCs, as well as difficulties associated in developing ambient processing (due to tendency of Sn^{2+} to oxidize to Sn^{4+} [5]). Finally, in addition to challenges discussed in detail in this roadmap article, it is also necessary to recognize the challenges related to the organic materials used in these devices, which include costs and environmental impact associated with their synthesis and/or processing [6], as well as the associated stability issues arising from the use of organic materials [7]. Thus, we hope that this roadmap provides a useful snapshot of the current development of PSCs on their pathway towards commercialization, and that the issues covered will facilitate better understanding of relevant issues in a wide framework taking into account not only efficiency, scalability, and stability but also environmental impact and sustainability.

1.3 Advances in Science and Technology in perovskite material development to address the challenges

Among various advances directly related to commercialization which will be discussed in other sections of the roadmap, it is also worthwhile to highlight recent developments in perovskite materials. The use of 2D/quasi-2D perovskite materials to improve PSC stability has been attracting increasing attention in recent years [11-16]. These materials typically exhibit improved stability compared to commonly used 3D perovskites ABX_3 (where A denotes small organic cation or Cs^+, B is divalent metal cation commonly Pb^{2+} and X is halide anion), due to the presence of bulky organic spacer cations which separate layers of lead halide octahedra and contribute to increased hydrophobicity and reduced ion migration [11-13]. These materials can have different orientations, and the most common (100)-oriented 2D perovskites can have Ruddlesden-Popper (RP), Dion-Jacobson (DJ) or alternating cation in interlayer space (ACI) structure, with the corresponding formulas $C_2A_{n-1}B_nX_{3n+1}$, $CA_{n-1}B_nX_{3n+1}$ and $CA_nB_nX_{3n+1}$, respectively, where C denotes monovalent (RP, ACI) or divalent (DJ) spacer cation and n denotes the number of octahedral layers [12]. There are still lots of unknowns concerning the structure-property relationships and degradation mechanisms in these materials [11,12,17], in part due to large number of possible spacer cations. Generally, DJ and ACI materials are expected to exhibit improved stability compared to RP perovskites due to shorter interlayer distance and hydrogen bonding between the layers (both H-bonding and van der Waals interactions for ACI), while RP perovskites exhibit only weak van der Waals interactions between the layers. To compensate for the low conductivity or bulky organic cations and consequently poor charge transport in 2D (n=1) perovskites, these materials are commonly used in 3D/2D or quasi-2D (n>1) configurations for the active layer to achieve compromise between efficiency and stability [11-13]. While the efficiency of quasi-2D devices can exceed 19% [13], 3D/2D configuration can result in higher efficiencies approaching or even exceeding 25% [11,15,16], at least in part due to surface passivation of 3D perovskite achieved by 2D layer [11]. As these materials have been more recently developed and comparatively less studied compared to 3D perovskites, the commercially relevant stability tests, such as damp heat tests [16] or outdoor tests [18] are more scarce compared to 3D perovskites. Possible exception are the devices where bulky cations, such 5-aminovaleric acid, are used as additives to 3D perovskite, which have been commonly used in mesoporous PSCs and the reports include demonstrations of large areas and/or outdoor testing [14]. We expect that the use of 2D materials will become more common and that they will play a significant role in further development and ultimately commercialization of PSCs.

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Section 2 - Niche applications of perovskite solar cells

Yuanhang Cheng and Hin-Lap Yip

Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong

2.1 Status

Organic-inorganic hybrid metal halide perovskites are a star material for solar cell devices due to their intriguing optoelectronic properties such as high absorption coefficient, long carrier lifetime and diffusion length, tunable optical bandgap, and high defect tolerance. Perovskite solar cells (PSCs) have attracted much attention in both academic and industrial interests since 2009. Thanks to the efforts from the photovoltaic community, the world-record power conversion efficiency (PCE) of PSCs has increased rapidly from 3.9% to 25.7% during the last decade. Furthermore, in contrast to the conventional crystalline Si, perovskite materials offer advantages such as solution-processible, flexible, lightweight, and semi-transparent, making PSCs a promising PV technology, and especially favorable for certain niche applications, such as indoor PV for Internet of Things (IoT), flexible PV technology, and building-integrated PV (BIPV) as shown in Figure 1.[1-3]

Indoor PV for IoT. The development of IoT system requires millions of electronic devices to communicate wirelessly. Normally, the IoT devices consume low level of power and are supported by off grid power sources such as batteries. An alternative solution is using indoor PV devices to convert indoor light into electricity for supporting continuous operation of the IoT system. Unfortunately, commercial PV devices such as Si and Gallium Arsenide (GaAs) solar cells show unsatisfied performance under low light conditions, while the PSCs have been demonstrated to exhibit outstanding performance, e.g. over 40% PCE under indoor LED light.[4]

Flexible PV technology. With the rapid development of portable and wearable electronics, flexible PV devices as thin film power sources have attracted huge interest. Compared to the existing flexible PV devices such as amorphous-Si, CdTe and CIGS thin film solar cells, flexible PSCs show greater potential due to their high efficiency, low cost, and easy fabrication process.

Building-integrated PV. BIPV refers to PV devices that are not only acting as solar PV panels, but also as part of the building materials, such as building façades, skylines and windows. BIPV is particularly important for promoting more widespread solar adoption in urban area. In terms of power conversion efficiency and colour tunability, PSCs easy stand out among different PV technologies due to their broad bandgap tunability and high efficiency, making them an important candidate for BIPV.

Therefore, although the current PV market is dominated by the crystalline Si PV technology, particularly for grid-connected PV power system, the emerging perovskite PV technology could be very promising for the above-mentioned niche applications.

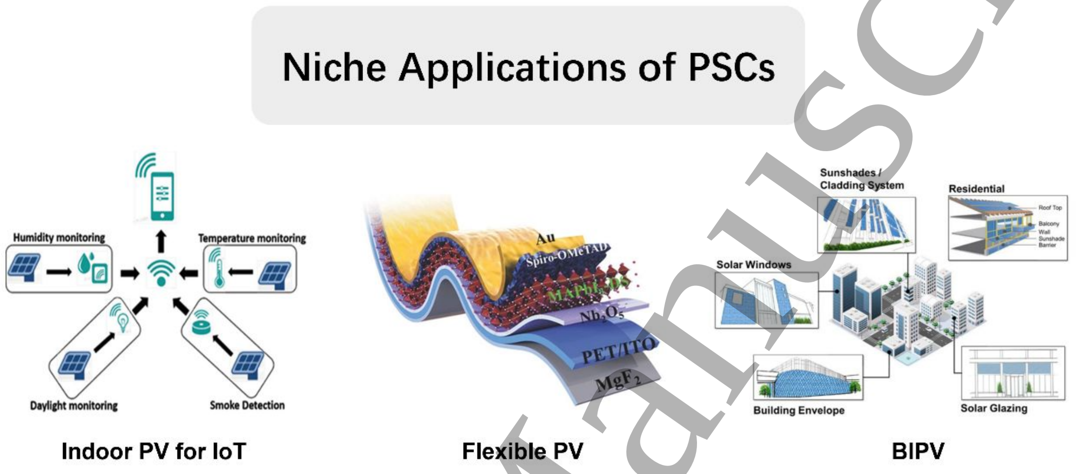

Figure 1- Niche applications of PSCs include indoor PV for IoT devices, flexible PV and BIPV.

2.2 Current and Future Challenges

Scaling up. Currently, the world-record efficiency of PSCs (25.7%) has exceeded that of multicrystalline Si solar cells (23.3%) and approaching that of single crystalline Si solar cells (26.1%). However, the best performance is only achieved in a ~0.1cm^2 small-area cell and the efficiency drops significantly to 17.9% when a large-area (such as 804 cm^2 from Panasonic) perovskite solar module is developed.[5] Such a large lab-to-fab gap can be ascribed to (i) the difficulty to achieve both high quality large-area perovskite films and charge transporting layers; (ii) the increased series resistance in large area devices due to the low conductivity of the transparent conductive oxide (eg. ITO) glass substrates. Therefore, the main challenges of scaling up perovskite PV technology include the development of large-scale deposition methods for uniform perovskite films and patterning processes for PV modules with high geometrical fill factor.

High performance conductive flexible substrates. Currently the most commonly used transparent conductive substrates for flexible solar cells are based on ITO coated-plastic substrates such as poly(ethylene 2,6-naphthalate (PEN) and polyethylene terephthalate (PET). To prevent the damage to the plastic substrates during the sputtering process, the ITO for flexible substrates is normally deposited by low-temperature (< 100°C) sputtering, resulting in lower transparency and conductivity. On the other hand, the mechanical property of ITO-coated plastic substrate is poor due to the intrinsic brittleness of metal oxide films. Therefore, developing high-performance electrode materials for flexible substrates is of great importance for flexible PSCs.

Stability. Long-term stability is another challenge for perovskite PV technology to enter the market. It has been demonstrated by different groups that the extrinsic (e.g. light, heat, moisture, oxygen, bias) and intrinsic factors (e.g. ion migration, materials degradation, chemical reaction at device interfaces), or their combinations can cause severe degradation of PSCs. However, there are no standard protocols for PSCs stability testing, thus it is still challenging to reveal the underlying degradation mechanism and find pathways to fabricate PSCs with operational lifetime comparable to current Si PVs.

Toxicity. The presence of water soluble toxic Pb ion in perovskite film could be a concern for indoor PV, wearable devices and BIPV applications. The potential leakage of Pb due to the damage of the PSCs may cause serious environmental contamination and pose potential risks to human health. Although Pb-free PSCs were proposed, they are suffering from either much lower in efficiency and poorer compared with their Pb-based counterparts. Therefore, the development of efficient Pb trapping and encapsulation technology will be important to ensure PSC to be safe to use.

2.3 Advances in Science and Technology to Meet Challenges

It is known that poor film uniformity would affect the device efficiency as well as its long-term stability. The uniformity of large-area perovskite film is largely affected by the deposition technology. Compared to the traditional spin coating method, large-scale processing such as blade coating, slot die coating, as well as thermal evaporation have been employed to produce large-area perovskite films with optimized film quality. For example, for solution process, the solvent systems of perovskite precursor materials have been carefully studied to control the nucleation and growth of large-area perovskite films.[6] For perovskite films prepared by vacuum-based thermal evaporation, controlling the evaporation rate of the organic cations and lead halides is of great importance to deposit large-area perovskite film with desired stoichiometric composition.[7] Other strategies include transporting layer engineering, interface engineering and defects passivation will also contribute to further improve the efficiency of large-area perovskite PV technology.

To improve the mechanical property of flexible PSCs, various conductive transparent materials have been recently developed to replace ITO for the flexible substrates. It has been demonstrated that Ag nanowires, metal mesh, carbon-based materials such as carbon nanotubes and graphene show better mechanical stability than crystalline ITO, but the corresponding flexible PSCs exhibit lower device performance. A recent work shows that the amorphous Cd-doped indium oxides with improved mechanical, electrical and optical properties can effectively replace ITO as transparent electrode for flexible PSCs, which exhibit very decent efficiency and stability.[8] Such development may pave the way for the development of new transparent conducting oxide films that are more suitable for flexible electronic applications, including flexible PSCs.

For device instability caused by environmental factors, it can be resolved via proper encapsulation to avoid chemical degradation of the perovskite film induced by moisture or oxygen. With the latest advancement in encapsulation technology, highly stable perovskite PVs were reported, which passed the demanding International Electrotechnical Commission (IEC) 61215:2016 Damp Heat and Humidity Freeze tests.[9] For the intrinsic stability of PSCs, recent works have successfully employed different spectroscopy techniques to monitor the evolution of defect states in perovskite films during device operation and reveal the device degradation mechanism[10], which is very important to provide insights to develop new strategies to stabilize PSCs.

The prevention of Pb leakage is also an important research field. The common method is to trap/absorb the Pb via capping molecules, so that Pb does not have chance to leak outside of the PV devices.[11] In addition, the state-of-art Sn-based Pb-free PSCs has achieved a record efficiency of over 14%.[12] It is calculated that Sn-based perovskite (1.1-1.4 eV) could deliver PCE with a theoretical Shockley-Queisser limit of 32%. Therefore, the development of Pb-free PSCs is still an important topic for PSC if effective strategies can be developed to resolve their current low efficiency and poor stability issues.

2.4 Concluding Remarks

Rapid advances of PSCs have been made in terms of both efficiency and stability at lab-scale device level. To compete with traditional Si PV technology, one possible pathway is to explore niche applications for perovskite PVs, such as indoor PV for IoT, flexible PV and BIPV. Although intensive efforts have been made in these areas, there are few remaining challenges still needed to be solved in the field. Scaling up perovskite PV to a desired size is the prime target to meet the requirements of IoT system or BIPVs. Developing high-performance flexible substrate is of great importance not only for the wearable electronic devices, but also for the BIPV applications for which light weight and conformal coating on curved building surface are required. Stability and toxicity of PSCs are also key problems to be addressed. These niche applications for perovskite solar cells provide a good entering point to the PV market for their initial phase of industrialization.

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Section 3 - Current state of commercialization efforts

Yufei Zhong[1, 2]
[1]School of Materials Science and Engineering, NingboTech University
[2]Ningbo Innovation Centre, Zhejiang University

Status

Photovoltaics (PVs) are one of the most important technologies to achieve net-zero purpose for our society in the future. The commercially available solar panels so far are mainly fabricated based on silicon materials, which already evolve into a well-matured industry after decades' efforts. There are, however, many other types of photovoltaic technologies, such as organic PV (OPV), quantum dot PV and metal halide perovskite (PVK) PV emerging as alternatives for power generation.[1-3] Among them, PVK appears as a "game changer" and leads its photovoltaic journey towards efficiency over 25% to date.[4] Such efficiency is already approaching that of crystalline silicon (c-Si) based device (26% in the lab) and far beyond that of commercially available c-Si panels (20%).[5] The great commercializing potential of this technology, such as high efficiency and solution compatibility (low-cost), therefore draws extensive attention from both the academia and the industry. Additionally, the functionalities such as flexibility, semi-transparency and indoor application render PVK panels broad range of contributions to future portable power generation.[6-8] Nevertheless, some obstacles are deemed to be conquered before finalizing a PVK PV product. First, the efficiency of the device needs to be competitive (>20%) and realized on module/panel size; second, the stability should be hold beyond at least 10 years (shorter lifetime compared to c-Si panels can be tolerable considering lower cost of PVK panels); third, a clear market positioning needs to be made for PVK PV, meaning maximizing achievable profit by knowing advantages of those competing products such as c-Si panels. These considerations should help to push PVK based panels to the market and also make sure its business lifetime is long enough for technological self-evolution, so as to take large share from future energy market in the long run.

Current and Future Challenges

First thing to consider for any types of PV trying for commercialization is their scalable fabrication. Although PVK based devices achieved remarkable efficiency in the lab scale, the device area of such proof of principle device is only 0.095 cm^2.[4] While the solution fabricating process on one hand enables making the devices fast and cost-efficient, it also induces inhomogeneous morphology in the photo-active layer during scalable fabrication. Such adverse effect can be induced by many factors such as purity of materials and structure defects during film formation.[9, 10] It can as well be induced by buffer layers near the metal contacts.[11, 12] Additionally, anti-solvent treatment is not possible during module/panel fabrication, alternative approach such as processing at elevated temperature or with solvent additive is thus essential to move current steps forward.[13, 14] From above factors, the biggest challenge at this moment is the degradation of efficiency as device/module areas scale up. Such challenge is evidenced by the champion efficiency of device dropping from 25% to 21.6%, 19.6%, 18.6% and 17.9% when device area scales up from 0.095 cm^2 to 1.024 cm^2, 7.92 cm^2, 29.54 cm^2 and 804 cm^2, respectively.[15] These results certainly raise the concern of future efficiency achievable by PVK based panels. As discussed above, to make competitive solar panels, c-Si panels would be a benchmark to compare to. Panel efficiency over 20% is therefore a “must” to achieve. Apart from efficiency, another obvious challenge is the stability. The typical reported literatures show stability over 1000 h without encapsulation and the longest stability tested are 10000 h after encapsulation, with efficiency loss smaller than 15%.[16] These results are however still far from ISOS standards, and non-comparable to that of c-Si panels. In particular, the PVK materials are water dissolvable. A dedicated stability test under high humidity or against resident heavy rain fall is required as the water dissolvable lead compound can contaminate underground water system.[17, 18]

Advances in Science and Technology to Meet Challenges

To solve above issues, efforts from the industry have been devoted to make efficient and stable PVK panels, as the huge potential of commercialization of PVK PV has attract their attention. Some key industrial players’ efforts are listed in Table 1. One can see that the continuously decreased efficiency upon larger device area is not inevitable here. However, one can also clearly see that the module efficiency achieved by the industry is far greater than that in academia, showing the future confidence towards this technology from the market. In particular, MicroQuanta has released its newly certified 21.4% efficiency with device area of 19.32 cm^2 (Nov. 2021), which is the highest efficiency for PVK based modules. Such results indicate future panel efficiency achieving 20% is realistic. Additionally, the largest area of 2925 cm^2 is released by Kushan GCL Optoelectronic Material (Nov. 2019), showing the advantage of solution-based printing methodology fabricating large area and low-cost PVK panels. Another effort concerning stability of PVK modules is also recently released by MicroQuanta.

It has released in Feb. of 2021 that its modules have passed the quality monitoring test by VDE Renewables GmbH (Ref No: TRPVM-ET 22110120-011-1). In both ultraviolet (UV) test (280-400 nm, 200 W/m^2, 60°C) and damp heat test (85°C, 3000 h), less than 5% degradation is observed. These testing parameters are 3-6 times higher than IEC61215 standards. Additionally, the modules kept the original efficiency after light soaking of 1000 h (irradiance: 1000 W/m^2, 70°C). Such impressive results certainly reveal the path ahead, showing the potential stability of PVK panels up to 20 years with proper passivation and encapsulation. Considering this estimated long lifetime of PVK modules, tandem device comprises of PVK and c-Si is thus of great interest. As released by both of OxfordPV and Helmholtz Center Berlin, the PVK/c-Si tandem can achieve efficiency over 29%, which shows promising application of such architecture. This means the stability of PVK sub-cell needs to be accommodated with c-Si cell. Achieving above long lifetime is thus a great step forward for both PVK single junction panels and PVK/c-Si tandem panels in the future.

Table 1. Device efficiency released by some industrial players.[5]

	Efficiency/Year	Device area	Certification
MicroQuanta Semiconductor	21.4%/2021	19.32 cm^2	JET
UtmoLight	20.1%/2021	63.98 cm^2	JET
Perovs	18.07%/2020	46.2 cm^2	Newport
Panasonic	17.9%/2019	804 cm^2	AIST
Kunshan GCL Optoelectronic Material	15.3%/2019	2925.0 cm^2	TÜV
OxfordPV (tandem)	29.52%/2020	1.12 cm^2	NREL
Helmholtz Center Berlin (tandem)	29.80%/2021	1.00 cm^2	ISE

Concluding Remarks

The continuous efforts in PVK based PV in the past decade have push it towards the dawn of commercialization. The remarkable achievement so far renders PVK panels competitive capability to take the future energy market by storm. Nevertheless, one should bear in mind that the main rival of PVK panels are c-Si panels, which also show advances in their technology and have recently released a record efficiency over 25% (TOPCon) with area as large as 242 cm^2.[5] Such news would provoke a reconsideration of how to apply PVK panels in future energy market. With currently less competitive efficiency and stability, PVK panels should take the advantage of applications which are beyond the reach of c-Si panels, such as flexible, semi-transparent and indoor applications. Such strategy would help to bypass the dominate power of c-Si in the market currently and renders enough time for technological breakthrough in the future.

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Section 4 - Scaling Perovskite Deposition: Solution-based Scalable Methods

Patrick W.K. Fong and Gang Li
Department of Electronic and Information Engineering, Research Institute for Smart Energy (RISE), The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

Status

In the light of the advancement in technology over the past decade, there were many revolutionary developments in perovskite solar cells (PSCs) to boost the power conversion efficiency (PCE) from its debut of 3.8% to 25.5% [1]. However, these remarkable results were predominately produced from device of active area ~0.1 cm^2 fabricated by solution-based spin coating method in research laboratory. However, this deposition technique results in the wastage of solar ink and is inherently unscalable. Recently, PCE as high as 22.6% has been demonstrated in laboratory-scale device of area ~1 cm^2 [1]. Nevertheless, the size of the device is still too small for commercialization.

It is widely acknowledged that the PCE of a solar cell follows the inverse scaling law (Figure 2), attributed to the increased series resistance contributed by the transparent conducting electrode. It is expected to be far more severe for large-area PSCs because of the difficulties in upscaling deposition of perovskite film while maintaining the uniformity and morphology. This provides the opportunities for the research in developing new techniques for scalable deposition of PSCs. Therefore, attempts on upscaling deposition of PSCs have been conducted concurrently to pave the road toward commercialization and the commonly used scalable solution-based deposition methods include inkjet printing, meniscus blade coating, slot-die coating, and spray coating. Among these scalable deposition techniques, promising results have been achieved by blade coating and inkjet printing of perovskite solar cell from stabilized efficiency of 17.8% (aperture area of 21.5 cm^2) [2] and PCE of 19.2% (aperture area of 50 cm^2) [3] demonstrated by blade coating method in research institute to a certified PCE of 17.9% for the champion perovskite small module (aperture area of 804 cm^2) by inkjet printing method produced by Panasonic Corporation [1, 4]. Despite these remarkable results, there is still a relatively large gap between the PCE of laboratory cells of area <0.1cm^2 and that of the small modules. This is because there is a big challenge in the technology transfer from laboratory-scale spin coating to manufacturing scalable coating and researchers should performed more in-depth investigation on tailoring the solar ink formulation favourite for individual scalable deposition method.

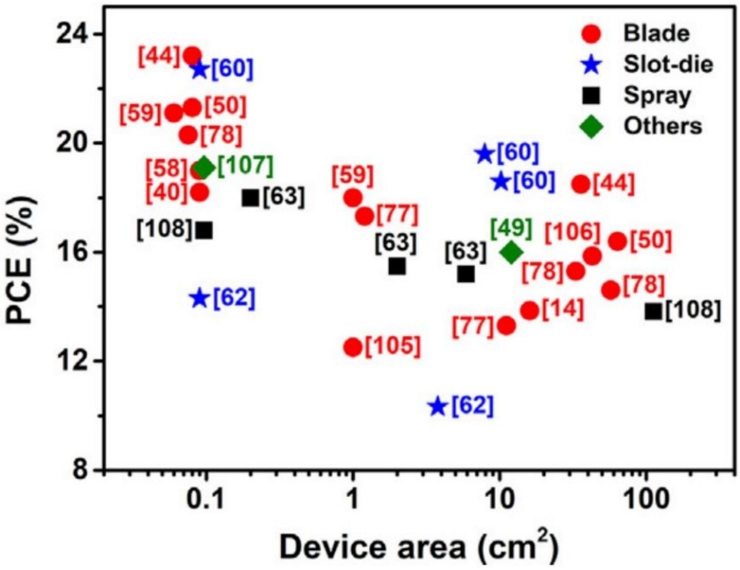

Figure 2: Power conversion efficiency obtained from small area to large area scalable deposited PSCs [5], showing the trend of the inverse scaling law. Reprint with permission from [5]. Copyright (2021) Elsevier.

Current and Future Challenges

It is known that the PCE of a solar cell follows the inverse scaling law. However, the loss in PCE over large area is far more significant in PSCs because of the challenges in maintaining film uniformity and morphology when scaling up the perovskite thin film by solution-based spin coating method. High-efficiency PSCs are deposited by manipulating the crystallization kinetics by solvent engineering (mixed solvent) or quenching protocols (anti-solvent, vacuum assisted or gas assisted drying) [6]. For scalable deposition method, it is doubtful that a direct technology transfer from the spin coating to scalable deposition of perovskite can be achieved [5]. Firstly, there is a large discrepancy in intrinsic precursor ink drying force. For spin-coating process, significant *dynamic* solvent evaporation happens during the spinning stage whereas it is rather *static* for scalable deposition. As such, the solidification process is different. Second, although the gas quenching is also scalable and air-knife assisted drying has been demonstrated [7], manipulation of the nucleation process by drop casting anti-solvent, which is widely used in high-efficiency spin coated PSCs, is difficult for large area deposition. Third, precursor ink wettability is another critical issue to consider for the deposition of compact and pinhole free large area perovskite thin film and the use of surfactant has been explored to address this issue [8]. The difference in the evaporation rate of solvent between spin coating and scalable coating technique affects the supersaturation of the wet film, which results in an impact on the film formation process and the processing window. In this regard, in-depth investigation on the precursor formulation, solvent engineering, chemical additives, and processing windows are needed to gain deeper understandings on the formation mechanisms prepared by specific scalable deposition method for reliable crystallization. Recently, there are some reports on the investigation on the processing window (Figure 3) and quenching protocol for scalable blade coating method using in-situ absorption spectrometry [9, 10] to gain further insight on the solidification kinetics with the aid of the LeMar model.

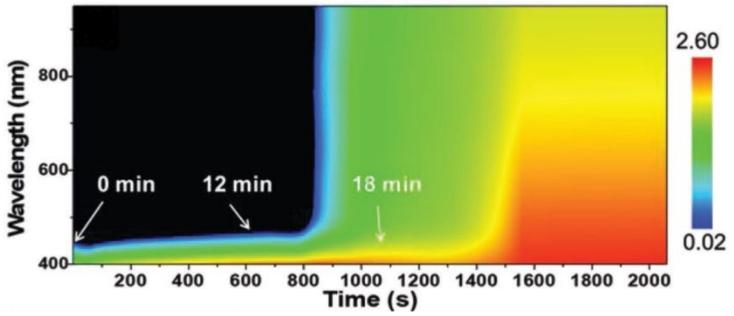

Figure 3: Time-resolved absorption spectrum of a blade coated perovskite film under natural drying, demonstrating a processing window up to 12 mins [9]. Reprint with permission from [9]. Copyright (2019) John Wiley and Sons.

Advances in Science and Technology to Meet

The critical factor for scalable deposition of large area perovskite film is the precise control of the nucleation and growth rate, which has been comprehensively discussed in previous report [6]. Physical (hot casting, gas quenching, vacuum extraction) or chemical (solvent engineering, additives) methodologies have been adopted. Blade coating and slot-die coating are conceptually the same, except that slot-die coating consumes more ink supply to fill up the reservoir and the pipelines down to the slot-die head. Hot casting has been adopted in blade coating and slot-die coating. The optimal temperature was found to be around 150^{o}C for blade coating [11]. Apart from hot casting, the acceleration of solvent evaporation can also be manipulated by solvent engineering by adding 2% volatile non-coordinating solvent into non-volatile coordinating solvent. A certified PCE of 16.4% was achieved from the PSC module of aperture area of 63.7 cm^2 [7]. Additive is another critical methodology in manipulating the growth kinetics and passivating the defects of perovskite film. Potassium hexafluorophosphate was added to the precursor solution for slot-die coating to reduce the nonradiative recombination defects. Perovskite mini-modules of 20.42% and 19.54% were obtained for areas of 17.1cm^2 and 65 cm^2, respectively [12]. Additive, L-α-phosphatidylcholine, could also be used to simultaneously enhance the wettability, the blade coating speed (180 m h^{-1}), and passive defects, resulting in stabilized minimodule efficiency of 14.6% with aperture area of 57.2 cm^2 [8]. At present, a certified PCE of 17.9 % on an area of 804 cm^2 has been demonstrated by Panasonic using inkjet printing strategy via optimizing ink formulation, concentration, and the coating amount and speed during the printing process [1]. However, the relatively slow printing speed, as compared to other scalable deposition methods, and the failures arising from nozzle clogging remain the obstacle for high throughput manufacturing. Furthermore, the tolerance of humidity on the perovskite film formation process should be considered for tailoring the ink formulation for scalable deposition in ambient environment.

Concluding remarks

Laboratory-scale perovskite solar cells have shown remarkable results over the past decade prepared by spin coating method. Toward industrialization, solution based scalable deposition of perovskite films has attracted many attentions in recent years. The biggest challenge is to develop the scalable process to precisely manipulate the nucleation and crystallization to deposit a compact and pinhole free perovskite film over large area. Technology transfer from laboratory spin coating to industrial scalable deposition is not straight forward despite the fact that some protocols, such as gas quenching, could re-apply to the scalable method. Even though the gap in PCE between small-area and large-area PSCs is narrowed, there remain challenges in the scalable deposition of perovskite in ambient condition especially the tolerance in humidity.

To realize a fully printable PSCs, in-depth scalable deposition of all the functional layers, hole and electron transport layers, should also be investigated.

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Section 5 - Scaling Up Perovskite Deposition: Vapor-based Scalable Methods

Annie Ng

Department of Electrical and Computer Engineering, Nazarbayev University, Nur-Sultan, Kazakhstan

5.1 Status

The vapor deposition techniques are the alternative methods for preparing perovskite thin films. These techniques have unique advantages such as formation of homogenous layers in a precise thickness over a large area, solvent-free deposition and good compatibility with sequentially deposited perovskite layers for fabrication of devices in heterostructures or tandem structures. Despite the fact that the current perovskite solar cells (PSCs) with record-high power conversion efficiencies (PCEs) are prepared by solution processes, it is predicted that the vapor deposition of perovskite materials will become more important in future manufacturing processes of scalable perovskite photovoltaics as they require a higher standard for commercial applications compared to the current research type of PSCs (e.g higher uniformity and lower defect density over a large area, ability to form a conformal films on a textured surface, fabrication of multiple junctions to overcome Shockley-Queisser limit of single junction solar cells etc.). The details of different vapor deposition techniques for preparing perovskites have been summarized in review papers [1]. Thermal evaporation and chemical vapor deposition (CVD) are the most established techniques for perovskite solar modules (PSMs). Qiu *et al* [2] have demonstrated a PCE of 9.34 % for a PSM with a designated area of 91.8 cm^2 by using hybrid chemical vapor deposition (HCVD), for which CsBr and PbI_2 were co-deposited by thermal evaporation followed by reacting CsBr–PbI_2 mixed film with FAI via a CVD process. Recently, Ritzer *et al*. [3] reported a record PCE of 16.6 % for a fully evaporated PSM with an area of 51.1 cm^2. It is noteworthy that the perovskite prepared by the vapor deposition technique is able to yield the lab-scale PSCs surpassing 21% [4]. The upscaling efficiency losses are mainly attributed to the difficulties in growing high-quality thin film over a large area and a non-ideal module design such as an increase of contact resistance from interconnections as well as sacrifice of active areas for forming interconnections. Continuous development of optimized vapor deposition methods along with advancement of scribing techniques and module layouts will definitely cause a breakthrough in device performance when scaling up the PSCs.

5.2 Current and Future Challenges

The versatile engineering approaches for improving the properties of perovskite materials and other functional layers leads to the most rapid enhancement in their device efficiency and stability during the last decade. However, most of the developed techniques for improving perovskite quality such as solvent engineering, the use of additives for assisting crystallization and defect passivation as well as chemical doping of perovskites for efficiency and stability enhancement are usually based on solution processes while the vapor depositions have less flexibility to adapt aforementioned techniques during perovskite growth. The compositional engineering for vapor deposited perovskite is also not straightforward. During thermal evaporation, the composition of perovskites can be adjusted by the evaporation rate of each precursor. The accurate stoichiometry of perovskites cannot be obtained if the evaporation of precursors cannot be precisely controlled. Intensive efforts are required to calibrate the evaporation rates of precursors since some of the material parameters and geometric factors are not known. Compared to the inorganic precursors, it is more difficult to control the evaporation of organic cation precursors such as methylammonium iodide (MAI) during vacuum deposition. The MAI has a relatively higher vapor pressure and it easily decomposes into intermediate species. Some possible MAI decomposition mechanisms have been reported [5] but more studies on MAI sublimation dynamics and effective strategies for precise control of MAI evaporation are still required. The composition of perovskites synthesized by CVD can be varied by adjusting the vapor pressures, flow rates and source temperatures etc. which also exhibit challenges in obtaining stoichiometrically balanced perovskites via indirect process control at the industrial scale. Furthermore, vapor deposition is not the common technique to synthesize perovskites with reduced dimensionality. For example, the perovskite quantum dots are synthesized by various solution methods such as hot injection and ligand-assisted precipitation. The preparation of PSCs based on quasi-2D or 3D/2D perovskites using vapor deposition is not as convenient as adopting solution engineering. It is generally believed that larger grain size with less grain boundaries leads to higher photovoltaic performance. However, the grain sizes of evaporated perovskites are usually smaller than the samples prepared by solution processes [6].

5.3 Advances in Science and Technology to Meet Challenges

The development of vapor deposition techniques for preparing perovskites are on their way. The continuous advancements in PSC fabrication technologies will bring a lot of possibilities to overcome the aforementioned challenges. It is worth to investigate the effects of different small molecules acting as additives or dopants that can be co-evaporated with perovskite precursors. The microstructures of the vapor deposited perovskites can be controlled via processing parameters such as substrate temperatures, surface properties of samples and deposition geometry etc. The post- deposition treatments can be performed on as-prepared perovskite samples for defect passivation [7] or optimization of microstructures [4]. To avoid the complication processes in maintaining the stoichiometry of multiple-cation mixed-halide perovskites during co-evaporation of a number of precursors, pre-synthesized perovskite powders can be used as a single source for deposition. The techniques such as flash evaporation and thermal ablation allow a rapid increase in temperatures to evaporate the source material and condense the perovskite on the substrates before decomposition [8]. Alternatively, the multi-component perovskites can be also obtained by selective substitution of the organic cations and/or halides during post-deposition treatments. This concept has been demonstrated successfully by interacting the pre-deposited perovskite films (e.g. $CH_3NH_3PbI_3$) with the appropriate gases (e.g. formamidine [9], Br_2 and Cl_2 [10]) to form a complex composition of perovskites. The vapor–solid reaction is another effective approach to grow multi-component perovskites [2]. The inorganic precursors which usually have a higher sublimation temperature can be thermally evaporated in a vacuum with an accurate control of the deposition rate. Then, the evaporated samples can be transferred to a CVD system to react with the vapor of organic cation precursors, for which, the aforementioned difficulties in controlling the thermal evaporation of organic cation precursors during vacuum deposition can be eliminated. In spite of different approaches to increase the flexibility for engineering the vapor deposited perovskite films, a lot of research efforts are still required to further optimize the processing conditions and verify their results in the large-scale manufacturing.

5.4 Concluding Remarks

The future development of vapor deposition techniques for preparing perovskites should be made along with their unique processing characteristics. The importance of these deposition techniques will be amplified when the PSCs are pushed towards scalable manufacturing during the stage of commercialization. To fully reveal the advantages of employing vapor deposition techniques for industrial productions (e.g. solvent free, high uniformity etc.), these techniques should be also used to prepare other functional layers of PSCs. Based on the current rapid advancement of this field, a scalable fully vapor deposited PSM with a good performance to satisfy the practical use can be achieved in the near future.

5.5 Acknowledgements

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Section 6 - Ambient processing of perovskite solar cells

Shien-Ping Feng[1] and Cong Chen[2]

[1] Department of Advanced Design and Systems Engineering, City University of Hong Kong, Hong Kong

[2] Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong

6.1 Status

Organolead halide perovskite materials have shown considerable promise for use in high-efficiency perovskite solar cells (PSCs).[1] A typical PSC consists of a several-hundred-nanometer-thick perovskite absorber (either with or without a mesoporous scaffold) sandwiched between the electron and the hole transport layers. The research works on perovskite deposition have mainly focused on solution-based processes because of their potential for industrial production.[2] The photovoltaic performance of PSCs is highly dependent on the morphology and crystalline structure of perovskite photoactive layer, which is very sensitive to ambient conditions like UV radiation, oxygen, temperature, and moisture.[3] Therefore, the fabrication of PSC usually requires a well-controlled atmosphere in glovebox to avoid the presence of moisture and oxygen. Most of the reported high-efficiency PSCs have been fabricated in an inert or controlled atmosphere, which hinders the real production. For commercialization, ambient fabrication is a desired technology and is of great importance for the development of large-scale perovskite solar modules at low prices. In this section, the challenges and techniques of efficient air-processed perovskite solar cells will be discussed.

6.2 Current and Future Challenges

Grain growth and crystallinity of perovskite are sensitive to the environmental stress factors (e.g., moisture, oxygen, heat, light). These ambient factors influence the morphology and crystalline growth of perovskite during thin film formation, which promote the formation of traps or charge carrier barriers within the perovskite absorber and deteriorate the device performance. Therefore, highly stable and efficient perovskite films are usually synthesized in a well-controlled glovebox under inert conditions.

The stability and toxicity of perovskite solar cells are the main issues for its industrial deployment and commercialization. Besides, there is also a requirement of ambient-processed high-quality perovskite to translate lab-scale fabrication to industrial compatible techniques for fabrication of PSCs in large-scale at low cost, such as spray coating, printing, slot-die, doctor blading, and roll to roll techniques. For example, the simple slot-die coating can fabricate high-quality and large-area air-processed PSCs. The doctor blade method is also a better process to deposit large area perovskite layers as compared to the spin coating process. Roll to Roll (R2R) process can be employed for the fabrication of flexible PSCs for industrial-scale manufacturing.

The influence of the ambient environment should be studied during the synthesis of the perovskite precursor solution. Moisture plays an important role in the ambient-processed perovskite films. Although water presence in organic halide perovskite solar cell can degrade the device, recent study shows that a particular ratio of the water molecule in the perovskite precursor solution may be an advantage during manufacturing [4]. There is an influence of moisture on the perovskite reaction process and the crystallization dynamics which can modify the morphology of the perovskite crystals and grains in the perovskite films. The next section provides an overview of techniques developed to fabricate air-processed perovskite solar cells with high efficiency and stability. The gap between efficiency for both air-processed PSCs and PCSs processed in an inert environment is reducing in recent years. The efficiency of air-processed PSC has increased from 5% to 22%[5], which is near that of the PSCs fabricated in an inert environment.

6.3 Advances in Science and Technology to Meet Challenges

The ambient environment affects both the perovskite conversion reaction and crystallization. Several advances have been employed to facilitate the development of air-processed perovskite solar cells from lab-scale to industry-compatible technologies. Both one-step and two-step solution deposition methods are most widely used to fabricate lab size (< 1cm^2) perovskite solar cells for fundamental studies, while spray coating, doctor blading, inkjet printing, and slot-die to integrate with a high- throughput R2R process are expected for upscaling the deposition of perovskite layer in a large area.

6.3.1 One/two-step deposition technique for ambient-processed perovskite solar cells

In a one-step process, typically, perovskite precursor is drop-casted onto substrates and followed by thermal annealing to form a perovskite film. In this process, the crystallization of perovskite in ambient air is rapid and uncontrollable under high humidity. To reduce the detrimental effect of moisture on perovskite formation, additive engineering with NH_4Cl addition in perovskite precursor solution can be applied to slow down the speed of perovskite crystallization due to the formation of an intermediate $CH_3NH_3X \cdot NH_4PbI_3(H_2O)_2$ after film deposition. Besides, the addition of antisolvents, such as ethyl acetate, during the one-step deposition process can absorb moisture and prevents the ingress of water from being involved in the crystallization process. In two-step process, a metal halide layer (e.g.,PbI_2) is first deposited onto the substrate followed by spin-coating of organic component solution. a preheating method was proposed to obtain a smooth PbI_2 layer with a high surface coverage in ambient air. Through preheating, the evaporation rate of DMF increased and the solvent vapor effectively prevented the ingress of water and oxygen into the perovskite layer. Further, an air-knife assisted two step recrystallization method was reported to prepare high-quality perovskite absorbers[6].

6.3.2 Vapor-based deposition technique for ambient-processed perovskite solar cell

Chemical vapor deposition (CVD) is a technique to achieve controlled film thickness and crystallization of perovskite in ambient conditions for photovoltaic applications. In this process, as-deposited PbI_2 film was first grown on a glass substrate then exposed to MAI vapor by using a CVD tube furnace and ambient air (with RH >60%). The PCE of reported perovskite solar cells with vapor-based deposition technique has exceeded 19%.[7]

6.3.3 R2R process for ambient-processed perovskite solar cells

R2R and doctor blade method facilitate deposition of the large area perovskite layers. Yang et al. first studied the impact of humidity in ambient air on perovskite film formation by using the doctor blading technique.[8] The perovskite films were grey, black, and dark brown with relative humidity of 60–70%, 40–50%, and 15–25%, respectively. By controlling the humidity, the air-blading based device could achieved a PCE of 20.08%.[9] Zuo et al. fabricated perovskite solar cell on a flexible substrate by using R2R method to achieve 15% PCE with negligible hysteresis.[10]

6.4 Concluding Remarks

There is a requirement of advancement of industrial compatible techniques for fabrication of PSCs in large-scale at low cost in the market. Other than the stability and toxicity, the translation of lab-scale fabrication to industrial-scale fabrication is another issue for PSCs. Perovskite materials are sensitive to ambient environment parameters such as air, water, light, and temperature. These ambient parameters influence the morphology and crystalline growth of perovskite during thin film formation. Therefore, the perovskite films are usually synthesized in a well-controlled glovebox under inert conditions. This section provides an overview of the techniques developed to fabricate ambient-processed PSCs for industrial deployment, including one/two-step deposition technique, vapor-based deposition technique, R2R process. With further research, it is likely that the efficiency between inert-environment-processed PSCs and ambient-processed PCSs will be reducing in the future. The up-scaling of ambient-processed PSC to industrial scale will be done by using industry compatible methods.

6.5 Acknowledgements

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Section 7 - Patterning and Interconnections for Modules and Tandems

Luigi Angelo Castriotta and Fabio Matteocci
Centre for Hybrid and Organic Solar Energy (CHOSE), Department of Electronic Engineering, University of Rome Tor Vergata, 00133 Rome, Italy

7.1 Status

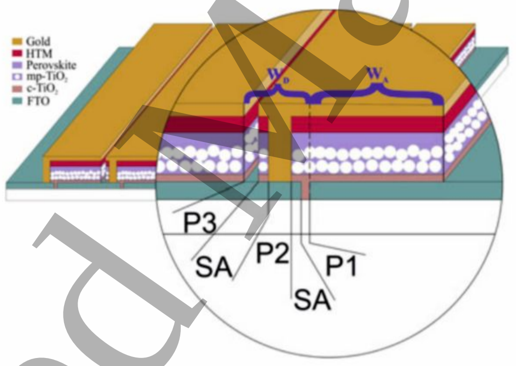
Perovskite solar cell (PSC) technology has reached impressive results during the last 10 years, with efficiencies up to 25.5% and 29.8% on single junction and Perovskite-Silicon tandem device. These results have been reached on relatively small area devices, with $0.1cm^2$ and $1cm^2$ active area respectively, far away from the exploitation of the PSC in the market. In this scenario, the results on scaling up process appears crucial. Patterning and interconnection manufacturing steps assist the fabrication of perovskite solar modules (PSMs) mitigating the resistive losses introduced by the use of transparent conductive oxides (TCOs) based substrate.

To fabricate PSMs, two main layout designs could be employed using series or parallel interconnections, as shown in Figure 4. In both configurations the overall performance of the PSM will be affected from the lowest performing cell limiting the current or the voltage in series or parallel interconnected PSM, respectively.

Series-connected PSMs are based on P1-P2-P3 interconnection design. P1, P2 and P3 refer to ablation processes performed during the PSM fabrication. In particular, P1 ablation insulates the front TCO electrode of neighbouring cells. The P2 ablation selectively removes the entire device stack without damaging the underlying TCO for the proper connection between cells. Finally, the P3 ablation insulate the back-electrodes. Laser assisted ablation is the most used patterning technique due to the high resolution and production speed. A maximum Power Conversion Efficiency (PCE) of 20.5% have been reached using series connection. Instead, only few studies report the fabrication of parallel-connected PSMs reaching a maximum PCE of 16.6%. Regarding the interconnection, the use of conductive grids is extremely needed to reduce the resistive losses and improve the current collection.

For tandem configuration, the device is based on the integration of cells based on a wider (>1.6eV) and a narrowed (<1.3eV) absorbers such like perovskite/perovskite, perovskite/OPV, perovskite/CIGS and perovskite/Si. The interconnection design is mainly dependent from the configuration (2 terminal or 4 terminal) and the integration (monolithic or mechanically stacked). The use of conductive grids is again crucial for the scaling up of tandem configuration where front electrode are generally based on low conductive TCOs.

a) Series-Connected PSM



b) Parallel-Connected PSM

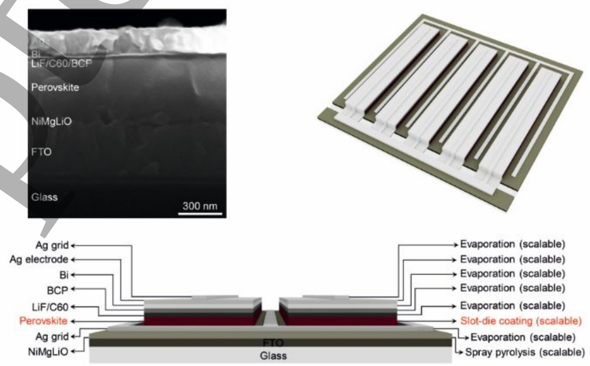


Figure 2 - Interconnection design in perovskite solar modules: a) Series-Connected PSM. Reproduced with the permission of IEEE publisher, b) Parallel-Connected PSM, Reproduced with the permission of Science publisher.

7.2 Current and Future Challenges

The investigation on the interconnection in series connected PSM is an important topic to evaluate by the scientific community in the next future. Although, scalable patterning procedure at high geometrical fill factors (up to 99%) have been demonstrated [1, 2], the role of the interconnection design on the long-term stability of the PSM is still an open issue.

Galagan reports on several degradation pathways induced by the monolithic interconnections in PSM, for the series connected module design, involving P1, P2 and P3 processes[3], as shown in Figure 5. Among those 4 degradation pathways, the P2 scribe will likely present the most challenge for device stability due to the direct contact of metal with the absorber material, which can result in chemical reactions, especially for perovskite materials with halide species. This process, involving P1, P2, P3, must have high yield and thus demands high coating uniformity and reproducibility: due to the series connected design, the current of an entire module and panel depends on the lowest performing sub-cell, thus limiting any imperfection occurred in the module, such as a pinhole, a particle induced shunts and/or an imperfect laser scribe. A strategy to overcome this limited interconnection design is necessary for the technology exploitation in the market.

In the parallel-connected PSMs case, a metal grid is needed to improve the charge transport through the TCO. The main challenge here relies on the metal grid design, with the aim to obtain a compromise between reducing resistive losses of the TCO, which improves fill factor, and minimizing optical losses through excess shadowing, which limits the current.

For tandem configuration, the main challenges rely on optimizing conductive grids/materials between top and bottom junction. A general issue related to interconnection and also for tandem is the reverse bias induced by partial shading of the PSMs: heating and irreversible electrochemical reactions can degrade the cell and the module because the illuminated cells can place a large reverse bias on the shaded cell/module to attempt to force current through it.

Overall, stability of perovskite solar cells, regardless for PSMs on single/multi junction, still drive the research community effort although great strides have been taken.

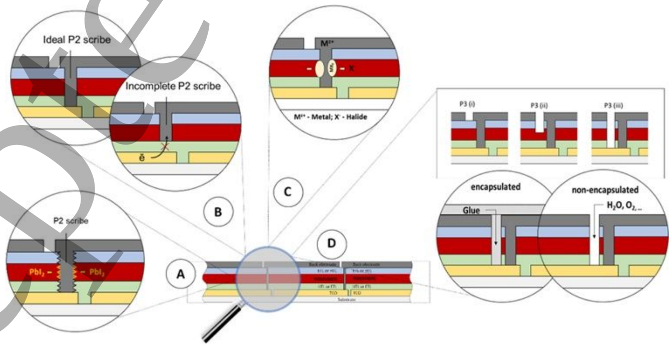


Figure 3 - Schematic illustration of the possible degradation mechanism in perovskite PV modules. (A) Degradation of the perovskite absorber and formation of a small amount of e.g. lead iodide (PbI_2) at the edges of the scribe; (B) incomplete removal of HTL or ETL materials which are located between the perovskite absorber and TCO; (C) direct contact between perovskite and metal electrode inside of the P2 scribe; (D) P3 scribe performed at different depths.

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7.3 Advances in Science and Technology to Meet Challenges

Very few works have been focused on the interconnection optimization for long-term stability, in the case of series-connected modules: what is clear is to avoid a direct contact between perovskite and metal, occurring at the P2 scribe. Bi et al. reported the application of a diffusion barrier layer at the P2 level to reduce the leakage rate of iodide, with best modules maintaining 95% and 91% of their initial PCE at 85°C and under light test over 1000h, respectively[4].

The limitation in the current, in the case of series-connected modules, might be addressed by looking at others thin film technologies solutions: companies like First Solar, in their CdTe modules, have introduced an additional scribe to mitigate this issue, called P4[5]. This process is performed perpendicularly to the P1, P2, P3 scribes, separating long cells into smaller ones. In this way, the shorter series connected strings are then connected in parallel. A similar approach, to avoid limitation in current by one sub-cells, is performed also by Xu et al., where alternation of series and parallel connected module is performed with a particular care on the design[6].

Hybrid series and parallel connected cells partially solve the possible shadowing problem, inducing reverse bias; to further reduce this effect, an important component to insert in a module/panel fabrication are the bypass diodes[7]: the function of the bypass diodes is to isolate a string of cells with unintentionally lower current (due to external factors) from the rest of the module. In this way, the voltage output is reduced, whereas the current output is preserved[8].

PSMs stability has been achieved by using parallel-module configuration by Yang et al.[9], where champion PSM maintain 96.6% of its initial PCE after 10.000 hours under day/night cycling illumination.

In tandem configuration, a way to boost the PCE and improve the stability of the perovskite/silicon tandem is to adopt the bifacial tandem configuration, as shown by Lehr et al., allowing for the reflected and scattered light from the ground (albedo) to be absorbed by the subcells junction[10].

7.4 Concluding Remarks

A massive study has been conducted on perovskite from an intrinsically and scientific point of view: what it is still missing is a systematic study on the effect of the interconnections for the long-term stability. Example of long-term stability on PSMs have been achieved by using diffusion barrier layers and parallel-connected subcells, avoiding contact between perovskite and metal, one of the main pathways of perovskite degradation. A major effort is necessary in these directions to clearly understand how to transfer what is reached on small area up to module size. Defining a set of specific stability protocols for PSMs and multi junction devices could step up perovskite upscaling, with also sharing important details such as subcells active area size, P1, P2, P3 parameters used and so on. A technological approach is needed to fill the gap between academia and industry, to further accelerate this technology into the market.

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Section 8 - Perovskite Modules

Luigi Vesce[1], Danila Saranin[2] and Aldo di Carlo [1, 2, 3]

[1] CHOSE (Centre for Hybrid & Organic Solar Energy), University of Rome Tor Vergata via del Politecnico, Italy

[2] LASE (Laboratory of Advanced Solar Energy), National University of Science and Technology ‚MISiS‘, Russia

[3] Istituto di Struttura della Materia (ISM-CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy

8.1 Status

Perovskite solar modules (PSMs) are fabricated resembling the thin-film photovoltaics (PV) technology on rigid (glass) or flexible (plastic, metal foils) substrates. Typically, the thickness of the multilayer device stack is in the range of 0.5 µm to few micrometers reducing the material consumption compared to first generation PV such as crystalline silicon (c-Si).

A proper tuning of the halide perovskite (HP) band gap and the use of transparent electrodes permit the realization of semi-transparent PSMs. The use of flexible substrates such as PEN (polyethylene naphthalene) allows for the integration of low-weight solar panels (<200 g/m^2) on curved surfaces. These characteristics open new application opportunities for PSMs such as building or vehicle integrated PV. The upscaling of HP technology from small area cells (PSCs) to modules (Figure 6) [1], and the related industrial exploitation, is achievable by proper scalable manufacturing processes module design, and interconnection patterning [2].

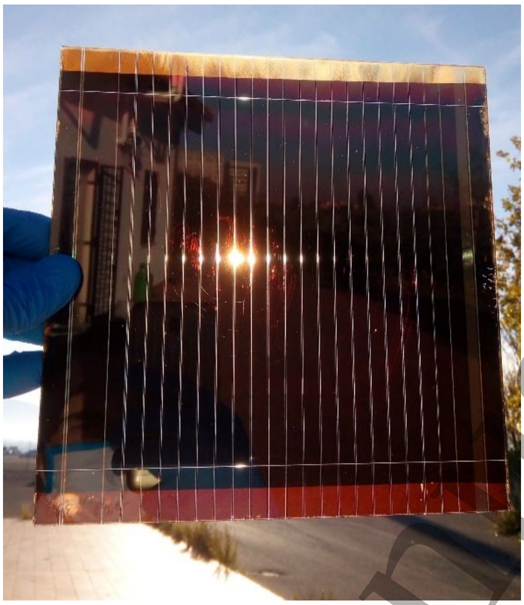

Figure 4 - Perovskite solar module of 300cm2 fabricated according to Vesce et al [1]

Besides fabrication, performance assessment of PSMs should follow international standards and compared with well-established PV technologies [3]. So far, the maximum reported PSC efficiency (25.7%) is about 18% lower than the theoretical Shockley-Queisser maximum efficiency (31.27%). A similar reduction is observed for c-Si PV [4]. However, scaling to module size the certified efficiency gap between cell and module is about 20% for PSM while reduces to only 8% for c-Si modules [5]. Scaling-up research efforts identified different strategies to improve PSM efficiency for both the inverted p-i-n and direct n-i-p module architectures. For the inverted architecture, the maximum certified efficiency is 20.1% on 16.4 cm^2 active area obtained by partially replacing DMSO with solid-state carbohydrazide in $MAFAPbI_3$ HP [6]. An efficiency of 20.2% (18.6% stabilized) on 27 cm^2 active area was achieved by compensating iodide vacancies and suppressing ion migration in a formamidinium-cesium HP [7]. The best certified n-i-p solar module has 19.3% efficiency on 17.1 cm^2 by exploiting $CsFAPbI_3$ HP formulation to inhibit the formation of a solvent-coordinated intermediate complex [8]. Recently, Liu et al. demonstrated that *o*-$PDEAI_2$ is an effective passivation agent to reach 21.4% efficient PSM on 26 cm^2 active area [9].

8.2 Current and Future Challenges

The uniform deposition of HP and transporting layers on large area is one of the most challenging aspects for module fabrication. Several coating techniques as well as post deposition treatments have been proposed to handle this issue. Since a PSM is made by interconnecting in series several cells, the current generated by each cell should be equal in order to avoid current mismatch that would impact on the overall module efficiency [4]. Module patterning is usually carried out by pulsed lasers (nano/pico-seconds) in the visible (532 nm) or ultra violet (355 nm) range. Here the target is to minimize the dead area (DA), that is the area between adjacent cells, maximizing the Active Area (AcA) for a given Aperture Area (ApA), i.e. maximizing the aperture ratio (AR, defined as AcA/ApA). On the other hand, an excessive reduction of DA will impact on the interconnection line width increasing the contact resistance and consequently reducing fill factor (FF) and module efficiency. Thus, the sheet resistance loss of the transparent conductive oxide (TCO), the interconnection dead area loss, and the interconnection contact loss, are some of the additional issues related to the scaling-up of the HP technology [1]. The module design and the interconnection patterning can face and limit these issues. In addition, the mentioned laser patterning process can generate defects across the layers [10].

An important aspect for real life module application is its encapsulation to face moisture, oxygen and contaminants, and to provide stability according to the international standards.

The back electrode (BE) deposition is one of the critical challenges for the high-throughput fabrication of PSMs. The all-printed process for the fabrication of PSMs is limited with the use of thermal evaporation metals for BE in vacuum. The fabrication of fully printable PSMs has been addressed by considering BEs based on carbon or nanostructured/low -dimensional materials (graphene, nanotubes etc.).

8.3 Advances in Science and Technology to Meet Challenges

Among all the layers, the HP absorber is the most challenging in the scaling up process. New optimized procedures and methods are required to obtain uniform, smooth and large-area HP films for highly efficient modules [4]. The development of scalable coating processes such as blade-coating, slot-die coating or spray-coating needs to address the issue of uniform deposition on very large area reaching the sqm size for industrial production. On this size, post deposition treatments needed for HP crystallization such as gas, solvent, vacuum quenching may not be effective as on small size cell/modules and the development of optimized/new processes is of paramount importance. Many of the deposition strategies for small area cells have been developed in glove-box with inert atmosphere and are not suitable for large area coating in ambient air. For ambient fabrication, the process window is very dependent on the HP precursor formulation as well as on the environmental parameters such as temperature and humidity. In this regard, a solid theory connecting crystallization process, environmental and coating parameters is needed to guide module development. Concerning the other layers, the most promising attempts for interface stabilization with passivation (2D materials, small molecules, or surface modifiers) or insulator buffers (polymer of oxide extra thin films) require advanced deposition methods. Carbon-based materials can substitute unstable and expensive metal electrode being low-cost, chemically inert, hydrophobic, thermally stable, and compatible with up-scalable techniques. The limited efficiency reached for carbon-based PSM (15.3% on 25 cm^2) deserve further developments mainly related to the conductance and contact resistance of the carbon electrode. Concerning the transparent electrode, TCO resistive losses are usually mitigated by patterning the substrate in small width (< 10mm) cells keeping the aperture ratio as large as possible. In less than a decade, the aperture ratio increased from 67% to about 95% due to the application of ultrashort laser pulse that permits the ablation of materials maintaining a very low heat diffusion through the target [11]. It is possible, however, to improve further the aperture ratio by using non-conventional solution like point contacts. The encapsulation of solar modules is another technological challenge. The process temperature limit of PSCs (around 100-120 ˚C) requires new encapsulation materials and edge sealants compliant with this low temperature budget.

8.4 Concluding Remarks

Nowadays, the fabrication of perovskite modules with a size comparable to conventional c-Si panel is mandatory for market exploitation of this new generation PV technology. A strong effort has been made in the last 10 years to increase efficiency, size and stability of PSMs. Nevertheless, available demonstrators are not comparable with conventional PV especially in terms of module size. In addition, there is significant reduction of efficiency scaling from small to large area. Several factors hamper such development, in particular the scalability of the solution-based coating and the HP crystallization process on large area. The use of additives, 2D materials and advanced deposition methods offers the possibility to increase the process window even out of the glove-box. This permits a facile approach to module manufacture reducing, at the same time, the capital expenditure for a large area process. In this respect, the realization of a PSM manufacture pilot line represents a required intermedium step toward industrialization. The pilot line is required to verify the entire automated fabrication process with specific throughput and performance constrains. In turn, this will permit a clear assessment of PSMs' stability following the IEC standard that comprises several accelerated life time tests in ambient air such as thermal cycles, damp heat, light soaking, reverse bias and mechanical stress. Last but not least, the PSM eco-profile must be addressed by lead-reduced formulations and/or lead-capture strategies together with specific recycling processes.

8.5 Acknowledgements

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Section 9 - Perovskite-based Tandem Cells: Perovskite/Si Tandems

Wang Puqun, Ho Jian Wei, Hou Yi, Lin Fen and Armin Aberle
SERIS (Solar Energy Research Institute of Singapore), National University of Singapore, Singapore

9.1 Status

With current photovoltaic (PV) panels accounting for only a fraction of the cost of terrestrial solar PV systems, and the sensitivity of the remainder to area and infrastructure, there is strong impetus for next-generation very high efficiency PV technologies. Tandem solar devices comprising two or more sub-cells offer higher power conversion efficiency, and thus higher power density, than single-junction devices, since each sub-cell utilizes the portion of the solar spectrum they are designed for more efficiently. Perovskite/Si tandems have been identified as one of the most promising tandem configurations for terrestrial 1-Sun PV systems thanks to the high-efficiency potential, low cost and bandgap tunability of perovskites, and the benefits from a partnership with established Si technologies. So far, studies on perovskite/Si tandems have focused on dual-junctions due to the greater process complexity of incorporating more junctions. Consequently, within the past few years, the 1-Sun efficiency of dual-junction perovskite/Si tandems has improved dramatically from 13.7% [1] to a remarkable 32.5% [2], far exceeding the record efficiency (26.7% [3]) of single-junction Si cells.

Various configurations of dual-junction perovskite/Si tandems have been reported. The popular two-terminal (2T) and four-terminal (4T) architectures have seen significant efficiency improvement (Figure 7). Interest in monolithic 2T is high because of its structural simplicity and compatibility with existing module technologies. The current 32.5% [2] record efficiency was achieved in 2T. Three-Terminal (3T) configuration is proposed as a promising option combining 4T's advantage of avoiding current matching requirement (thus more accommodating to spectral variation) and 2T's benefit of monolithic integration on the Si bottom cell [4]. However, present efficiencies are lower due to more complex device considerations. A detailed comparison of 2T, 3T and 4T dual-junction perovskite/Si tandems are summarized in Table 1.

Table 1. A detailed comparison of 2T, 3T and 4T dual-junction perovskite/Si tandem devices

Device structure	2-Terminal	3-Terminal	4-Terminal
1-Sun Efficiency potential (%)	45.1 [5]	45.3 [6]	45.3 [5]
Optimal bandgap (eV)	~1.70 [5], [7], [8]	1.60~1.90 (Less sensitive)	1.60~1.90 (Less sensitive)
Additional substrate and functional layers	No	No	Yes
Current matching	Yes	No	No
Integration complexity	High	High	Low
Compatibility with existing module technologies	Yes	No	No
Balance of system cost	Low	High	High
Spectral sensitivity	Moderate	Low	Low

The structure of the perovskite top cell and the Si bottom cell, as well as the integration between the two, are also subjects of active research. Although mainstream perovskite single-junction devices bear the n-i-p structure (defined by the deposition order) with the current record efficiency achieved with such, the highest efficiencies of perovskite/Si tandems are achieved with p-i-n perovskite cells. This has been attributed to the lack of efficient, conformal and optically transparent hole transporting materials and larger hysteresis in n-i-p structures. However, this may change with the advent of new materials. A variety of Si bottom cells have also been employed, including PERC (passivated emitter and rear cell), SHJ (Si heterojunction), TOPCon (tunnel oxide passivated contact) and IBC (interdigitated back contact) devices. SHJ cells are commonly used due to their high efficiency and readily available transparent conductive oxide (TCO) layers for top-bottom sub-cell integration. TCO-free options [1], [9]–[13] such as Si recombination junctions with the advantages of reduced parasitic absorption and matched refractive indices have also been explored as the integration layers.

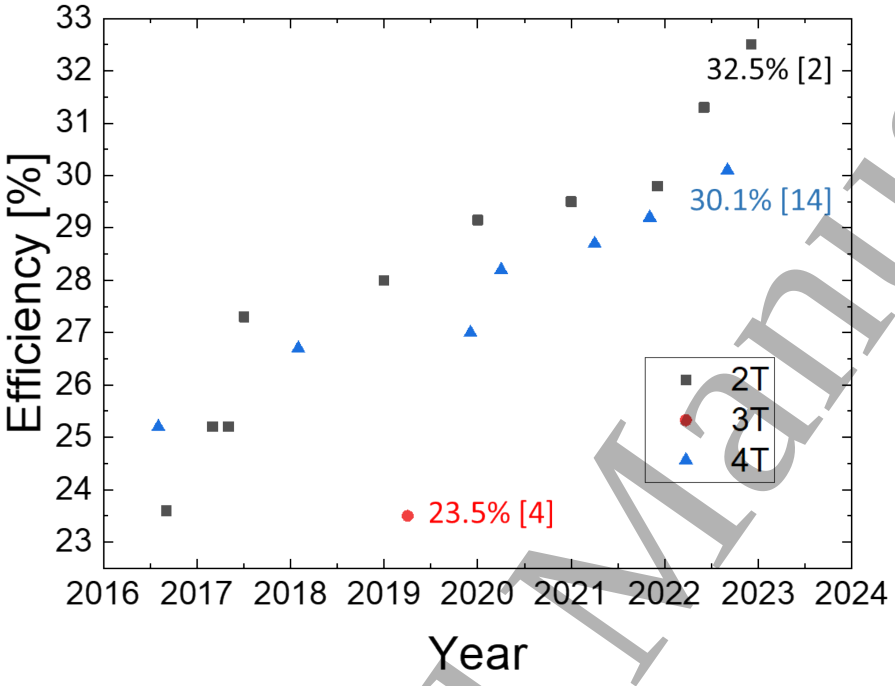

Figure 7. Efficiencies achieved to date for 2T, 3T, and 4T configurations of perovskite/Si tandem devices. Record 1-Sun efficiencies of 2T, 3T, and 4T configurations are achieved by references [2], [4] and [14] respectively.

Fabrication technologies of perovskite top cells are generally inherited from perovskite single-junction devices. They can be classified into solution-based processes, vapour-based processes and a hybrid of these two. Via hybrid two-step deposition methods, combining sequential co-evaporation and spin-coating, conformal growth of perovskite layers on textured Si bottom cells have been demonstrated [11], making it possible to boost the photocurrent density to > 20 mA/cm^2 and realize monolithic perovskite/Si tandem device exceeding 30%.

Current and Future Challenges

The main obstacles to the commercialization of perovskite/Si tandems are associated with the limitation of the perovskite top cell and can be categorized into four aspects: further efficiency improvement, scalability, stability and cost-effectiveness. These are outlined in Figure 8, along with the corresponding advances in science and technology required to address these challenges.

While the record efficiency of perovskite/Si tandems has significantly outperformed that of Si single-junction devices, there is still a large space for improvement, bearing in mind the theoretical 1-Sun efficiency limit of ~45% [5]. Such high efficiency devices present an avenue to significantly reduce the system-level cost. The potential for further efficiency improvement lies mainly in the perovskite top cell and the optimized integration of the two sub-cells.

A critical challenge towards commercialization lies with scaling up the small-area lab-scale devices to stable large-area devices for production while maintaining competitive efficiencies. Commonly reported areas are in the order of cm^2. Nonetheless, larger areas have also been explored with promising results, signifying the push towards scaling-up. Two notable examples are the 21.8% device with an active area of 16 cm^2 achieved by J. Zheng *et alia* [15] and the 26.7% device with an active area of 201.64 cm^2 announced by Oxford PV [16]. To compete with Si single-junction devices, a repeatable full-wafer efficiency beyond 28% should be targeted. Similarly, the instability of current perovskite devices has to be addressed with the aim to match the long lifetime and robust reliability of Si single-junction devices. Although perovskite/Si tandems have passed reliability tests of a few thousand hours [17], more developments are needed to assess their performance and reliability to add confidence in actual field operations.

In parallel, the manufacturing cost has to be adequately managed. The marginal cost of fabricating the perovskite top cell over the well-established Si bottom cell has to be compellingly low in order to reap the gains of efficiency. Although the material cost in perovskite solar cells and the cost of solution-based fabrication processes can be very low in principle, the current fabrication processes involve the use of expensive organic solvents and materials. The fabrication cost can be further reduced by reducing the use of these expensive organic solvents and materials. The costs also change with economies of scale. Combining competitive manufacturing cost of perovskite/Si tandems, remarkable efficiency and proven stability can significantly reduce the levelized cost of electricity (LCOE) of this PV technology, rendering it competitive to Si single-junction cells or even other sources of energy.

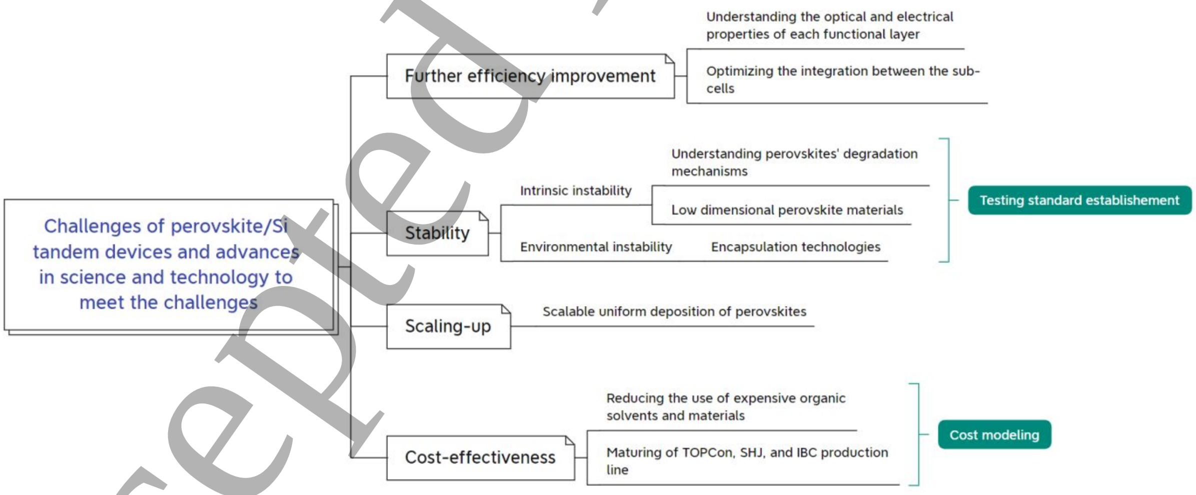

Figure 8. Challenges of perovskite Si tandem devices and advances in science and technology to meet challenges

Advances in Science and Technology to Meet Challenges

Corresponding advances in science and technology are required to address the above-discussed challenges (also outlined in Figure 2). To fully exploit the high-efficiency potential of perovskite/Si tandems, an in-depth understanding of the optical, electrical and optoelectronic properties of each functional layer is essential. Judicious design and engineering can then be applied to achieve optimized integration and implementation.

We believe that robust encapsulation technologies will be instrumental to tackle the stability issues associated with environmental exposure, whereas further understanding on perovskites' degradation mechanisms (especially photo-induced phase segregation) are required to solve the degradation of intrinsic material origin. Alternatively, low dimensional perovskite materials, demonstrated to be less susceptible to degradation, are worth exploring. Along with these developments, standards or protocols for testing the performance, stability and lifetime (including outdoor testing under operation) of perovskite-related devices have to be established.

Up to now, spin coating has been the prevalent method to form perovskite layers, having shown the best film quality and reproducibility. However, in the current state, it is not ideal for large-area deposition of perovskite absorbers due to requirements for process uniformity and low material consumption. Scalable uniform fabrication methods have to be developed for perovskite absorber layers as well as other functional layers. Alternative methods such as inkjet printing, slot-die coupled to roll-to-roll processes and physical vapor deposition methods are worth exploring for large scale manufacturing. Ultimately, streamlining the process deposition of all layers are necessary.

The learning rate of terrestrial 1-Sun solar PV dominated by Si technologies has been astounding (~23% according to the ITRPV). High efficiency Si PV will further benefit from maturation of next-generation Si single-junction cells (TOPcon, HIT and IBC). This exerts downward pressure to reduce the fabrication cost of the top perovskite cell. On the other hand, this can also favour the prospect of Si as a cost-effective substrate and bottom-cell for high efficiency tandem applications. Establishing relevant cost models and adapting them to the progress and advancement in technologies in this field would lend useful insights into the commercial viability of perovskite/Si tandems in various deployment scenarios.

Research to address toxicity of lead-containing devices (or other heavy metal) will allay health and environmental concerns. Already there has been work done on substitution for lead-free materials or that with reduced lead composition. More holistic approaches for lead-based perovskites will also need to be adopted. These include (1) robust packaging/encapsulation, (2) environmentally conscious manufacturing, and (3) responsible cradle-to-grave product design and recycling to minimize leakage of lead and exposure of living organisms to it. Such considerations are similar to First Solar's approach for thin film CdTe PV modules.

Advances in characterisation and metrology tailored for the peculiar properties (e.g. ion migration, phase segregation, and other light-induced changes) of perovskites will be relevant, not just in the laboratory but also in preparation for mass production. The motivation for this ranges from understanding fundamental materials properties, production monitoring, quantifying their performance, and reliability assessment. Developing failure analysis capabilities for probing perovskite and Si sub-cells individually in a tandem configuration will also rise in importance. Reliability benchmarking should take into consideration of the area and operational lifetime of the devices, and compared against prevailing Si single-junction devices. This calls for the establishment of consensus/standards on testing within the community.

Concluding Remarks

Perovskite/Si tandem solar cells have made remarkable progress in the laboratory and have surpassed the record efficiency of Si single-junction devices. However, a pre-requisite for the commercial deployment of this technology is scaling up of small-area devices to stable large-area production scale devices in a cost-effective way while maintaining sufficiently high efficiencies. To meet these challenges, advances in science and technology are needed on the entire commercialisation roadmap of perovskite/Si tandems. This ranges from developments in process technologies, device design, characterisation techniques, standards for testing, and addressing potential environmental and toxicity concerns of lead-containing perovskites. Solving these issues could pave the way for terawatt-scale deployment of perovskite/Si tandems.

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Section 10 - Perovskite-based Tandem Cells: Perovskite/Perovskite Tandems

Zhaoning Song and Yanfa Yan

Wright Center for Photovoltaics Innovation and Commercialization, Department of Physics and Astronomy, The University of Toledo, Toledo OH 43606, USA

10.1 Status

Perovskite/perovskite (PK/PK) tandem solar cells combine two perovskite absorber layers with complementary light absorption — typically a mixed-halide wide-bandgap (1.7 - 1.9 eV) perovskite and a mixed tin-lead (Sn-Pb) narrow-bandgap (1.1 - 1.3 eV) perovskite to reduce the thermalization loss and expand the utilization of the solar spectrum. This emerging perovskite-based thin-film tandem PV technology not only promises power conversion efficiencies (PCEs) beyond the thermodynamic limit of ~33% for single-junction devices but also offers some prominent attributes, such as flexibility in tuning the bandgaps of all subcells, simple fabrication techniques, suitability for processing on flexible and lightweight substrates, and projected low manufacturing and environmental costs [1]. Because of these merits, PK/PK tandems are recognized as a viable next-generation solar technology to render the lowest levelized cost of energy in the long term.

Along with the rapid development of single-junction perovskite solar cells, PK/PK tandems have experienced an astonishingly fast learning curve in performance enhancement in the past few years (Figure 9). In 2015, Jiang et al. [2] first realized the concept of monolithic two-terminal (2-T) PK/PK tandems by integrating two methylammonium lead iodide subcells using organic interconnecting layers. Later, Eperon et al. [3] made a breakthrough by developing 2-T PK/PK tandem architecture based on an infrared-absorbing Sn-Pb perovskite, enabling PCEs of up to 17%. This work has attracted substantial interest in the scientific community and inspired many follow-up studies. Most recently, several significant technological advances in PK/PK tandems have been accomplished, including Sn-Pb perovskite grain boundary passivation [4], compositional engineering and deposition process innovation [5, 6], inhibition of Sn^{2+} oxidation in the Sn-Pb perovskite precursor solution [7, 8], and the recombination layer modification [6, 9]. Thanks to all the efforts, the current record PCE of 26.4% for PK/PK tandems has surpassed the highest PCE of 25.7% for single-junction perovskite solar cells [10]. Notably, a certified PCE of 24.2% has been demonstrated for PK/PK tandems with an active area of over 1 cm^2 [8]. With the rapid momentum of technological progress and further exploration, PK/PK tandems are expected to become a leading photovoltaic (PV) technology with PCEs exceeding 30% in the foreseeable future.

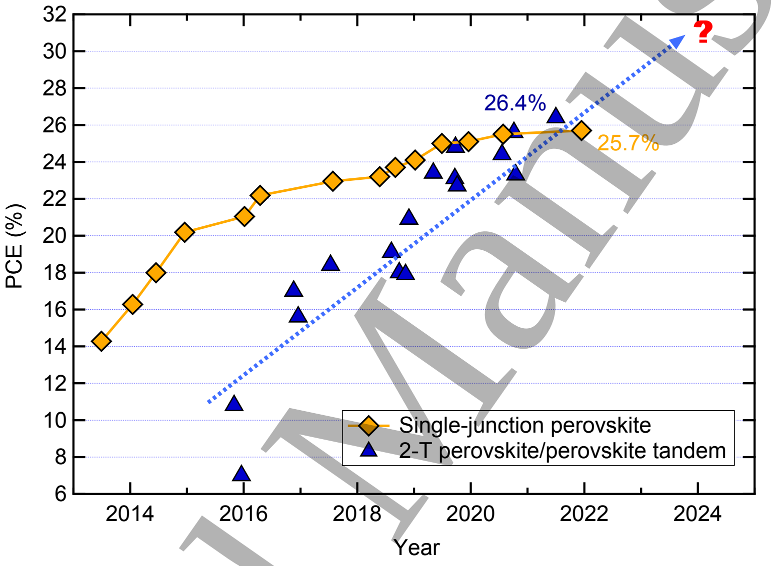

Figure 5 - Evolution of PCEs of single-junction perovskite and perovskite/perovskite tandem solar cells.

10.2 Current and Future Challenges

Though potentially promising, PK/PK tandems are facing significant obstacles on their way toward commercialization. Currently, the reported PCE of PK/PK tandems is still far below their theoretical limits. Their performance is limited by several materials-related issues, including mainly (i) large photovoltage losses and phase segregation in wide-bandgap perovskites, (ii) intrinsic instability and defectiveness in Sn-containing narrow-bandgap perovskites, and (iii) inevitable power loss at interconnecting layers. Particularly, wide-bandgap perovskite cells with Br- or Cs-rich stoichiometries typically suffer from a large open-circuit voltage deficit (V_{OC}-deficit) of more than 0.5 V, which is ascribed to compositional inhomogeneity, ion migration, and light-induced phase segregation. The ease of oxidation of Sn^{2+} to Sn^{4+} in Sn-based narrow-bandgap perovskites is responsible for a high defect density of Sn vacancies that lower the photocurrent generation and cause rapid performance degradation. Moreover, there is an urgent need to develop efficient and robust interconnecting layers that concurrently show small optical and electrical losses and have sufficient mechanical and chemical stability to protect the underlying first-deposited subcell from damages during the process of the second subcell.

While it is optimistic that high PCEs can eventually be achieved in PK/PK tandems, there are still profound manufacturing challenges associated with scalable fabrication, module design, and device reliability of this emerging technology. Most state-of-the-art PK/PK tandems reported in the literature were fabricated using spin-coating methods. However, industrial production requires scalable deposition techniques for all perovskite subcells and interconnecting layers. It is particularly challenging for Sn-Pb narrow-bandgap perovskites because of their high sensitivity to the processing environment. Additionally, integrating individual tandem cells into thin-film modules is technically challenging and practically unexplored. To enable the conventional thin-film monolithic integration in PK/PK tandem modules, strategies must be developed to avoid potential shunting through the interconnecting layers and corrosion at the scribing lines. Lastly, the device stability of PK/PK tandems is yet to be demonstrated. The intrinsic instability of Sn-Pb perovskites is currently the bottleneck that hinders the scalable production and practical applications of PK/PK tandems.

10.3 Advances in Science and Technology to Meet Challenges

To capitalize on the promise of PK/PK tandems, strenuous efforts are needed to collectively improve wide-bandgap perovskites, narrow-bandgap perovskites, and the interconnecting layers. PK/PK tandem research has been a growing field where the strategies for improving device performance and insights on the underlying tandem device working and degradation mechanisms are constantly evolving. Here, we only highlight some critical perspectives. First, holistic design and precise control of each component layer in the complex tandem structure is a prerequisite for enabling optimal current matching in perovskite subcells and, thus, maximizing the power output of tandems. The design and validation of tandem architectures need collaborative work of detailed device physics modelling, extensive expertise on device fabrication, and advanced optical and electrical characterization techniques. Moreover, each subcell requires delicate control to ensure the maximum conversion of solar energy. Strategies to mitigate large V_{OC}-deficit in wide-bandgap perovskite subcells include tailoring perovskite composition and grain growth, applying grain boundary and surface passivation, and identifying proper hole selective materials to match the deep valence band of wide-bandgap perovskites. Increasing the film thickness and minority carrier diffusion length of Sn-Pb narrow-bandgap perovskites is important for enabling a complete infrared photon conversion. Employing proper oxygen- and moisture-impermeable surface and grain boundary protection and engineering the Sn-Pb perovskites to reduce their reliance on oxygen- and moisture-free environment can be effective approaches to prevent the degradation of Sn-Pb perovskites. Furthermore, efficient interconnecting layers play a key role in connecting the subcells in the tandem devices. Tailoring the properties of recombination layers or tunneling junctions implemented in PK/PK tandems is critical to minimize the optical and electrical losses of the interconnecting layers.

Future work of PK/PK tandems will also focus on translating the deposition processes designed for small-area devices to the scalable manufacturing processes for tandem PV modules. Important lessons can be learned from the recent progress of scalable production of Pb-based perovskite solar cells and applied to the large-area coating of Sn-Pb perovskites. For industrial production, it is also important to develop suitable production tools to handle specifically the processing of Sn-Pb perovskites in a delicately controlled environment. The desirable manufacturing routes for the whole tandem structure should be scalable, high throughput, cost-effective, and uniform, like the processes used by the thin-film PV industry. Besides, the implementation of robust module encapsulation and packaging is necessary to ensure the long-term stable operation of PK/PK tandems.

10.4 Concluding Remarks

PK/PK tandems present an unprecedented opportunity for developing ultrahigh-efficiency and low-cost thin-film tandem PV modules. As laboratory-sized PK/PK tandem devices have been achieving PCEs higher than the record of single-junction perovskite solar cells, it is important to start considering pathways to implement this emerging PV technology at a commercially relevant scale. If the remaining scientific and technological challenges can be adequately addressed, PK/PK tandems will render their promise to become a low-cost leader in the future PV market.

10.5 Acknowledgements

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Section 11 - Other Perovskite Tandem Cells

Xu Chen and Yang (Michael) Yang

State Key Laboratory of Modern Optical Instrumentation, Institute for Advanced Photonics, College of Optical Science and Engineering, Zhejiang University, Hangzhou, China

11.1 Status

Cu(In,Ga)Se_2 (CIGS), Organic and $Cu_2ZnSnS_xSe_{4-x}$ (CZTS) materials are exceptional candidates as near-infrared absorbers in perovskite-based tandem configuration with significant advantages of tunable bandgaps, lightweight， and availability to flexible processing. It's available to realize the strong alliance between these near-infrared materials and perovskite. Figure 10 shows the record efficiencies of perovskite-CIGS (Pero-CIGS), perovskite-Organic (Pero-OPV) and perovskite-CZTS (Pero-CZTS) tandem cells published in the year 2014-2022. In Figure 10, the first 2-terminal (2T) perovskite-based tandem came out in IBM in 2014, with a Pero-CZTS tandem structure, and its efficiency was 4.6%.[1] Until 2022, the 4-terminal Pero-CZTS tandem has a high power conversion efficiency (PCE) of 22.27% developed in CITYU.[2] Furthermore, more researchers recently have focused on the Pero-CIGS and Pero-OPV tandem photovoltaics. The 4T Pero-CIGS tandem devices have achieved an outstanding PCE of 25.9% in NREL, while the responding 2T tandems have approached 23.26% efficiency in HZB.[3, 4] For Pero-OPV tandems, the monolithic tandem has demonstrated a good PCE up to 21.1% in WHUT, and the semi-transparent mechanically stacked tandem has demonstrated 14.05% PCE in SUDA.[5, 6] In addition to surpassing the single-cell devices in terms of efficiency, the tandems are also conducive to improved device stability. Compared to perovskite-silicon (Si), Pero-CIGS and Pero-CZTS have shown greater potentials to be applied to the space environment, benefitting from the excellent radiation hardness of CZTS and CIGS [7]. In addition, organic photovoltaics (OPVs) often suffer from insufficient UV-stability, but the UV-sensitivity of OPVs is settled by shielding blue-violet light with perovskite absorber in the Pero-OPV tandem solar cells (TSCs). However, these kinds of tandems are currently lagging behind the perovskite-Si and all-perovskite tandems in terms of efficiency. But further development can be expected for various new application scenarios, such as flexible, indoor, semi-transparent, and so on.

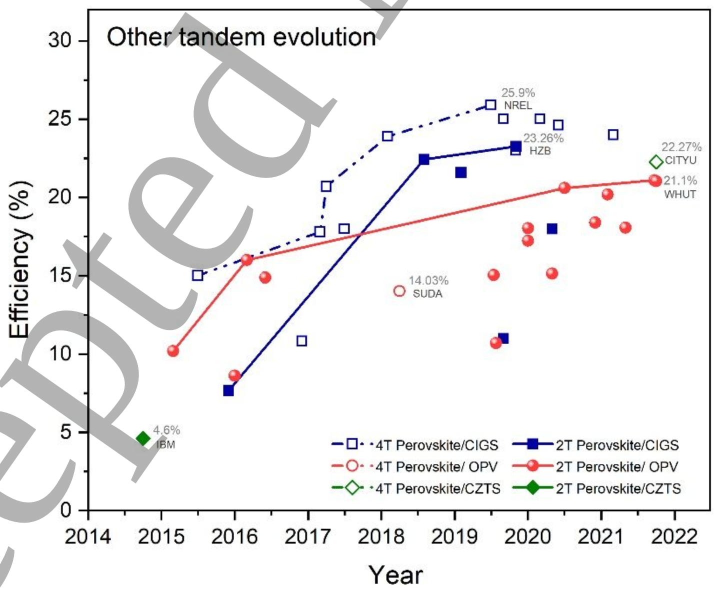

Figure 6- Efficiency evolution for Perovskite-CZTS[1, 2], Perovskite-CIGS[3, 4], and Perovskite-OPV[5, 6] tandem solar cells.

11.2 Current and Future Challenges

Critical light management. Parasitic absorption and reflection loss are mainly attributed to the optical losses in the TSCs, which contain multiple dielectric layers with unequal refractive index, acting as the charge transport layers, the blocking layers, and the light-absorbing layers, respectively. At present, the easiest and most widely used way is thermally evaporating a single magnesium fluoride (MgF_2) between the air and the ITO glass (or the glass substrate) as anti-reflection. CIGS and CZTS with the film thickness of micro-meters can absorb near-infrared light adequately, but OPVs are generally 100-115 nanometers thick. Thus, it is necessary to develop more specialized anti-reflection coatings for increasing the current density of OPVs.

Large open-circuit voltage (Voc) loss. Under ideal conditions, the Voc loss of the tandems is approximately equal to the sum of the loss of sub-cells. The champion CIGS with the PCE of 23.4% had a low Voc penalty of about 0.346 eV [8], compared to the CIGS, the best CZTS and organic solar cell showed high energy loss, reaching 0.589 [9] and 0.55 eV [10], respectively. Additionally, the optimal bandgap of the perovskite front subcells is above 1.65 eV, and the corresponding Voc loss generally exceeds 0.5 eV.

Unperfect interconnecting layer (ICL). The sputtered thick Indium-tin-oxide (ITO) layers are widely used in the Pero-CIGS and Pero-CZTS TSCs, resulting in good lateral charge conduction, optical losses, and the increment of the costs. Besides, the super-thin gold (Au) and silver (Ag) are often chosen as the recombination layers inside the Pero-OPV TSCs, inevitably leading to a trade-off between optical losses and charge conduction. Several reviews have given opinions on the ideal ICL for 2T tandems.[11] The perfect ICLs: (i) make the voltage addition of front and rear subcells, with reasonable energetic alignment; (ii) minimize the optical losses; (iii) possess good vertical charge conduction but less lateral charger conduction; (iv) low cost; and (v) protect the underlying subcells from solvent erosion, being quite difficult to fabricate. Considering, these challenges hinder the breakthrough of device efficiency, but also the delayed commercialization process.

11.3 Advances in Science and Technology to Meet Challenges

To face the challenge, it is bitterly necessary to figure out deep insights into photoelectric losses and the working mechanism of the perovskite-based TSCs. Lang et al [12] developed a subcell diagnosis methodology to calculate the practical efficiency limitations when the negative impact of different losses on device performance dominates, including bulk recombination, surface recombination, interface recombination, and transport losses (Figure 11a). Park et al [13] demonstrated that it’s useful to construct the 3-terminal (3T) measurement architecture for analyzing the charge dynamics of each subcell of a 2T tandem, separately and integrated (Figure 11b). In that case, it has been concluded that the perovskite front cell has microsecond-level kinetics while the Si bottom subcell has millisecond-level kinetics. However, there are still few relevant studies reporting whether this capacitance rule can apply to other perovskite-based TSCs, through the 3T measurement method. Moreover, continuous technological breakthroughs are also extremely important. Jiang et al [14] developed an In_2O_3:H film deposition method. Compared with the traditional transparent conductive electrodes (TCOs), the In_2O_3:H film has better mobility with a value up to 129 $cm^2V^{-1}s^{-1}$ and better NIR-transparent ability, which advantageously acted as an electrode in 4T TSCs, but not as an ICL inside a 2T TSC because of the high-temperature treatment of 230 degrees Celsius (Figure 11c). Wang et al [5] tuned the hole transport material (HTM) of the ICLs to minimize Voc loss and reduce the charge accumulation at the interfaces, indicating that the high-quality HTM, with adequate hole mobility, low absorption, and efficient quasi-Ohmic contact, plays a critical role in affecting the series capacity of two sub-cells of the Pero-OPV tandems (Figure 11d). Nevertheless, few researchers report whether the electron transport material

(ETM) has a similar effect to the HTM. Additionally, Li et al [15] fabricated a flexible Pero-OPV tandem device with a PCE of 13.61%, Voc of 1.80 V, short circuit current (Jsc) of 11.07 mA cm^{-2}, and a fill factor (FF) of 68.31%, which can drive water electrolysis systems to yield a solar-to-hydrogen efficiency of 11.21% (Figure 11e). Thus, accelerating the advancement of commercialization requires more exploration in applications with unique advantages for this type of tandem photovoltaics.

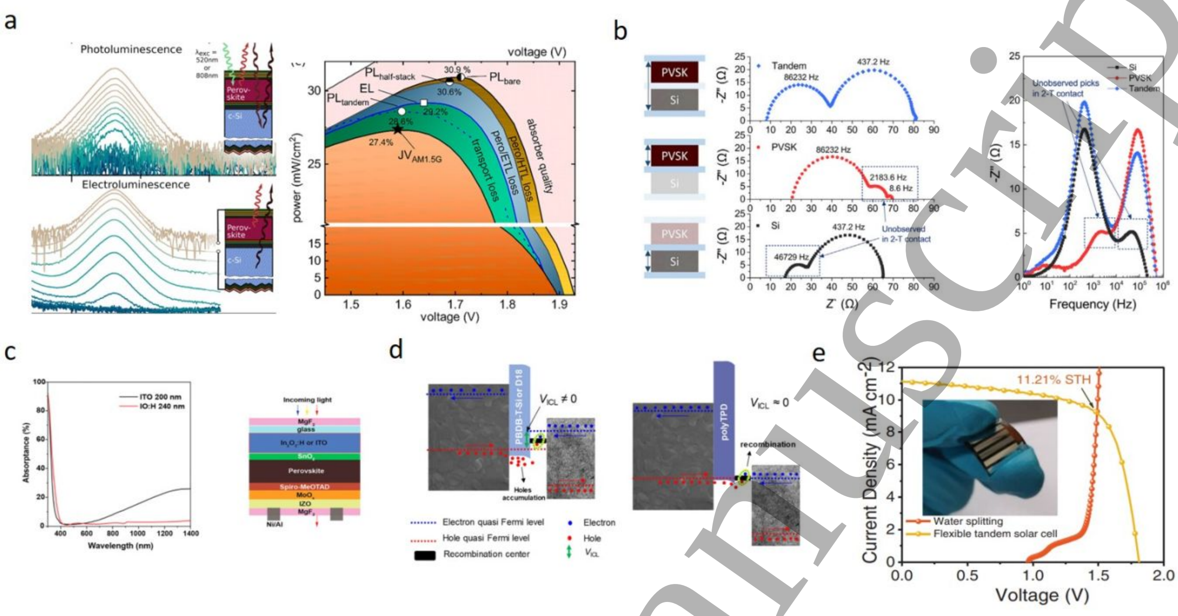

Figure 7- Advanced science and technology for meeting challenges. a, PCE potential of TSCs quantifying by intensity-dependent absolute photoluminescence (PL) and injection-dependent absolute electroluminescence (EL). b, Impedance spectroscopy of three-terminal tandem solar cells. Reproduced with permission. ***c****, Absorptance of the two kinds of transparent conductive electrodes: IO: H and ITO, and scheme of a semi-transparent perovskite solar cell.* ***d****, Mechanism of tuning the interconnecting layers for Pero-OPV TSCs.* ***e****, The J-V curves of flexible Pero-OPV TSCs. Figure reproduced with permission from ref. [5, 12, 14], Americal Chemical Society (***a****)(***c****)(***d****); ref. [13], Elsevier (***b****); ref. [15], Wiley (***e****).*

11.4 Concluding Remarks

In the review, we briefly introduced the evolution of the Pero-CIGS, Pero-CZTS, and Per-OPV tandem solar cells. Although more and more researchers are devoted to improving the performance of this type of tandem device, their efficiency is still far from the perovskite-Si and all-perovskite tandems solar cells. Next, we listed three common problems of critical light management, large Voc loss, and imperfect interconnecting layer, that hinder the improvement of those novel tandem applications. Finally, we emphasized subcell diagnosis methodology, 3-terminal measurement method, and some preparation techniques of better NIR-transparent TCOs, high-quality HTM, and flexible tandem photovoltaics that are worth learning from (Figure 11). We believe that, as long as such tandem cells show their unique advantages, they can also occupy a place in the huge photovoltaic market in the future market.

11.5 Acknowledgements

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Section 12 - Encapsulation of Perovskite Solar Cells

Syed Ali Asgher and Ishaq Ahmed
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

12.1 Status

Even though organic-inorganic halide perovskite Solar cells (OIHP) have achieved comparable power conversion efficiency (PCE) with Silicon solar cells ,[1] they are still facing barriers in large scale production. Up to some extent issues like higher photovoltaic performance with improved device stability are addressed. However, further progress of the field requires following standardized testing protocols, as well as establishing suitable encapsulation protocols for high performance.[2] As illustrated in Figure 12, the function of encapsulation is to restrict ingress of moisture and oxygen and restrict lead leakage, in order to achieve improvement in stability and reduce environmental hazards. While many encapsulation options are suitable for commonly reported stability tests (dark storage, or testing under 1 sun illumination at room temperature and under low to moderate humidity), it is considerably more difficult for encapsulation to satisfy more stringent device testing conditions, such as damp heat or outdoor testing.[2] To pass these stringent testing conditions, it is necessary to both develop a stable OIHP-based solar cell, and a suitable encapsulation. Several recent articles have discussed these issues,[2-6] but there has been no consensus in the community on wide adoption of a certain type of encapsulation material and/or encapsulation technique.

A number of different materials gave been reported to date, i.e., ethylene vinyl acetate (EVA), polyvinyl butyral (PVB), thermoplastic poly-urethane (TPU), Polyisobutylene (PIB), fluoropolymer coating, various polymer films, ethylene methyl acrylate, cyclized perfluoro-polymer (Cytop), organic − inorganic hybrid materials ORMOCERs, ORMOSIL aero-gel thin film,[3] as well as different polymer films, polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), poly (methyl methacrylate (PMMA) polycarbonate (PC), etc. [4] However, detailed comparisons between different materials have been scarce.

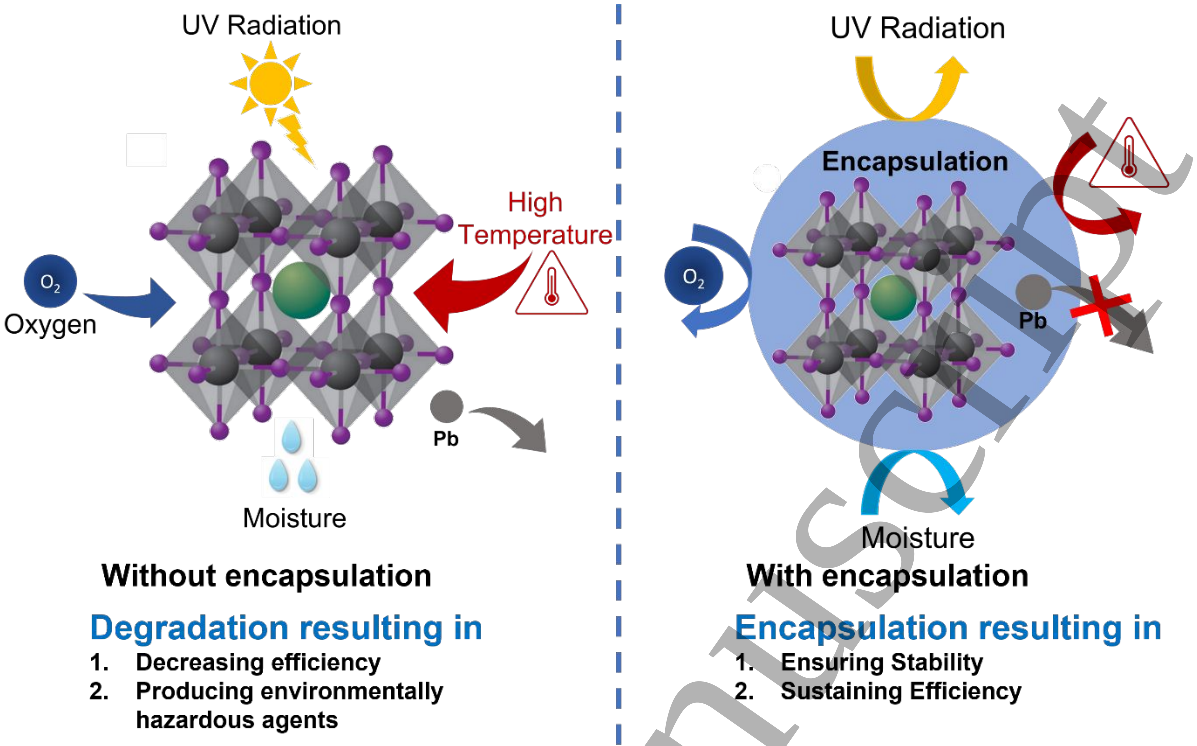

Figure 8 - Schematic illustration of perovskite with and without encapsulation.

12.2 Current and Future Challenges

It is well known that perovskite materials are highly moisture sensitive (regardless of illumination), as well as sensitive to the exposure to oxygen under illumination. Therefore, finding appropriate encapsulation materials and routes to adopt in perovskite field are highly desirable. Ideal materials for encapsulation require low oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) i.e., 10^{-4}–10^{-6} cm^3/m^2 day atm and 10^{-3}–10^{-6} cm^3/m^2 day respectively.[5] More importantly encapsulating material and perovskite properties should be compatible to avoid delamination and reaction risk to avoid a drop in the photovoltaic performance due to outgassing of solvent or sealant and/or reactions between solvent or sealant and device components during encapsulation process or during storage or application of different types of stress for accelerated stability testing. In other words, encapsulant and edge sealant should be inert with respect to perovskite device components, and should have suitable mechanical properties to ensure packaging integrity under thermal stress. In addition, it is highly desirable for the encapsulation material to have low cost and that its application is scalable for commercial production.

The encapsulation types can be roughly divided into two groups, thin film encapsulation and encapsulation with a cover (usually glass). While thin film encapsulation is highly desirable, especially for flexible devices, it should be noted that existing commercialized photovoltaics technologies use encapsulant+edge seal+cover method instead of thin film encapsulation. Nevertheless, thin film encapsulation remains of potential interest in research to improve its performance, and it can also be practically relevant for future commercialization when used in combination with cover glass/polymer encapsulation. Polymers like poly (methyl methacrylate) PMMA, PDMS, perylene C, fluoropolymers coating, spray-coated reduced graphene oxide (rGO) [6] etc., and inorganic films like silica or alumina[7] can be potential candidates for thin film encapsulation. These interlayers films can be incorporated with device via simple, low pressure deposition and low-cost methods like, atomic layer deposition (ALD), sputtering, evaporation, etc. Cover glass encapsulation further subdivided as blanket and edge encapsulation or both of them as shown in Figure 13 (a-c). The technique confines the devices between two surfaces with low OTR and WVTR, which limits possibility for moisture and oxygen ingress to the edge seal. While other oxygen and humidity sensitive technologies such as organic light emitting diodes have been successfully using encapsulation method using edge seal only with incorporated desiccant, this method is less suitable for perovskite solar cells since delamination commonly occurs at elevated temperatures. Thus, a combination of encapsulant and edge sealing is recommended for the best performance. This is complicated by the fact that some encapsulant common in Si photovoltaics industry, such as EVA, can react with perovskite.[2, 13] In addition, it is necessary to consider the package design, i.e. making contacts while simultaneously minimizing series resistance and ensuring stability of metal contact outside of the package, as well as ensuring that the width of the edge seal is compatible with chosen testing condition (i.e. ~12 mm of PIB needed for 1000 h under damp heat test).

Finally, it should also be noted that encapsulation not only limits moisture and oxygen ingress into the device, but also to restrict the lead (Pb) leakage in outside environment.[8] Thus, it is desirable to include lead containment features into the encapsulation package, as illustrated in Figure d and discussed in more detail in Section 23. In the case of integration of lead containment features into the packaging, it is necessary to verify both the device performance as well as lead containment under the entire range of different accelerated testing conditions (IEC 61 215:2021 or various ISOS protocols revised for perovskite solar cells[7]).

12.3 Advances in Science and Technology to Meet Challenges

There are different stability testing protocols, which can involve bias, illumination, humidity, and thermal stress, individually or in combinations,[9] under open circuit or maximum power point[9,10] testing. These testing protocols can thus be divided into testing protocols for device testing in dark, testing under light soaking, outdoor testing, thermal cycling, solar-thermal cycling, light cycling, and testing under bias. While the shelf-life testing (ISOS-D1) protocol remains very common and can be performed on devices without encapsulation, encapsulation is essential for other stability testing conditions, which include additional stress (illumination, temperature, high humidity) which accelerate perovskite material and device degradation. Great progress has been made in recent years in both improving the device stability and encapsulation method for perovskite solar cells to be able to pass ISOS-D3 damp heat testing conditions, which involve temperature of 85°C and relative humidity of 85%.[11] For a summary of device architectures and encapsulation methods suitable for these stringent tests, see Ref.[2] In 5 out of 7 reports on successful (>1000 h) damp heat testing, encapsulation with PIB as either blanket or edge sealant was used,[2] indicating its high suitability for perovskite encapsulation. Despite this progress, further research into encapsulant materials suitable for perovskite solar cells is needed, with particular attention devoted to performance at elevated temperature, not only due to the requirement to pass damp heat testing but also the fact that the temperature during outdoor operating condition was estimated to reach 70°C.[12]

12.4

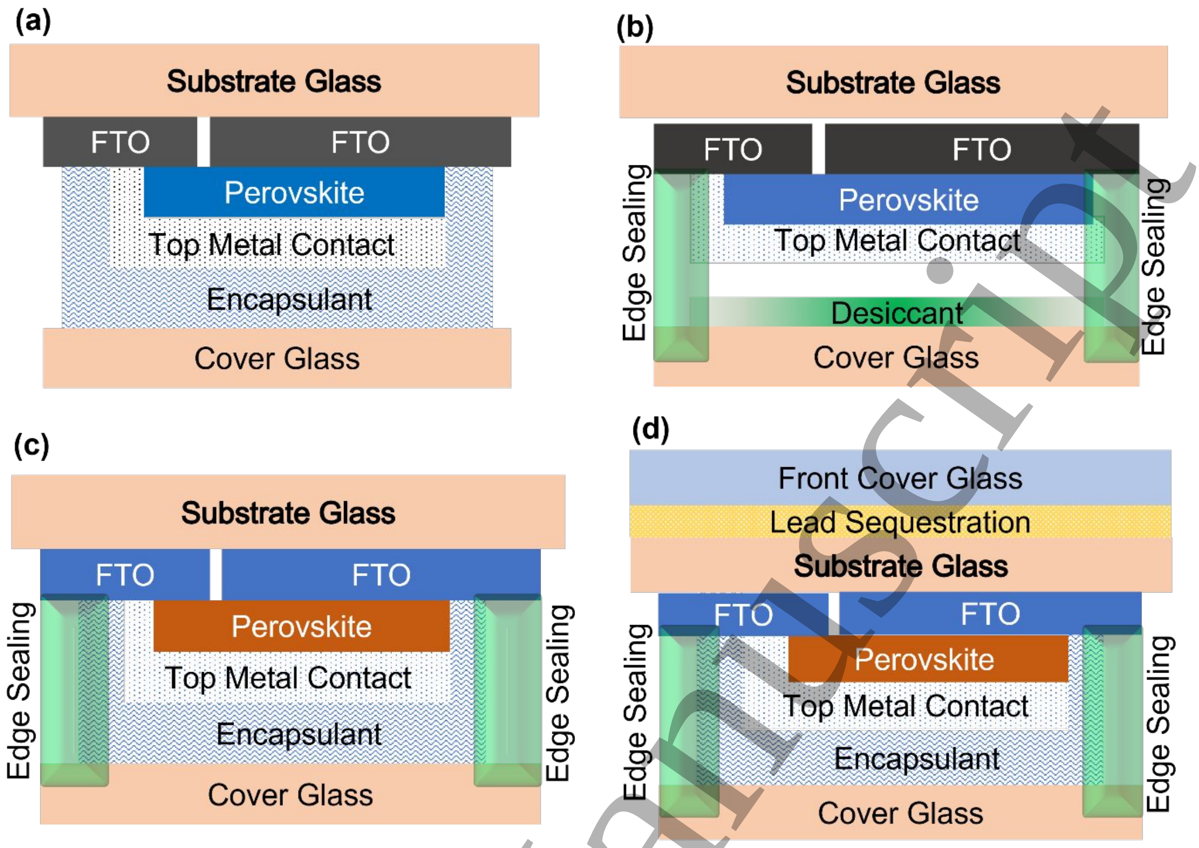

Figure 9 - Schematic illustration of different types of cover glass encapsulation. (a) blanket encapsulation, (b) edge encapsulation, (c) blanket encapsulation with edge sealing, and (d) sealed edge blanket encapsulation with added feature of lead containment. F Figure reprinted with permission from reference [2].

Concluding Remarks

Performance of solar cells under accelerated aging tests (damp heat, illumination with added thermal stress, outdoor testing, etc.) is a combination of their intrinsic stability and the ability of encapsulation to restrict the ingress of water and oxygen under the testing conditions. Advancement in both intrinsic stability and encapsulation will ultimately be beneficial for perovskite solar cell commercialization. An ideal encapsulation would consist of a thin film passivation layer (to further restrict outgassing of volatile decomposition products which would degrade metal electrodes and/or interconnects), compatible and stable encapsulant; edge sealant (possibly a bilayer combining PIB with additional sealant to minimize atmosphere ingress through any defects), impenetrable glass cover, and lead containment feature.

12.5 Acknowledgements

We would be happy to thank Prof. Aleksandra B. Djurišić, Department of Physics, The University of Hong Kong for her guidance and support.

12.6 References

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Section 13 - Stability of Perovskite Materials: Moisture and Oxygen

Aleksandra B. Djurišić [1], Tiklun Leung [1], Yantao Wang [1], JingYang Lin [1,2] and
Alan Man Ching Ng [2]

[1]Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong
[2]Southern University of Science and Technology China (SUSTech), 1088 Xueyuan Blvd, Nanshan, Shenzhen, Guangdong Province, China

13.1 Status

Halide perovskite materials, in particularly low bandgap iodide-based perovskites, exhibit instability when exposed to ambient, which is further enhanced upon ambient exposure under illumination. Since the solar cells are expected to operate under illumination in ambient, it is essential to understand the mechanisms of degradation in order to mitigate the degradation and achieve sufficiently stable performance. Another important implication of instability upon ambient exposure is the difficulty of commercialization if inert atmosphere processing is required, since possibility of ambient processing would significantly simplify the process and lower the cost.[1] Thus, improving the stability on exposure to ambient atmosphere is critical for future commercialization of these devices. All the layers in the perovskite solar cell can be affected by ambient exposure, and in some cases exposure to oxygen could be even beneficial, such as oxygen doping of 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (SpiroOMeTAD).[2,3] However, here we will mainly focus on the effect of oxygen and moisture on the halide perovskite material. Methylammonium (MA) lead iodide (MAPI) is thermodynamically unstable upon exposure to oxygen and water, and stability increases for different halides (Cl>Br>I) and it is also affected by the organic cation tendency towards deprotonation.[3] However, although MAPI is thermodynamically unstable in oxygen, the interaction is strongly affected by surface reaction kinetics, and consequently MAPI was found to be stable when exposed to oxygen in the dark, while it rapidly degraded when exposed to oxygen under illumination.[3] Upon exposure to moisture, MAPI initially transforms to hydrated form,[3-5] which is reversible, followed by irreversible degradation.[4,5] The degradation of the perovskite on exposure to humidity is dependent on the relative humidity and time of exposure,[4,5] and it is also affected by the hole transport layer covering the perovskite,[4] which offers the possibility to slow down the process by suitable selection of a hole transport layer (dopant-free hydrophobic materials forming smooth pinhole free films with good adhesion to perovskite are preferred). Initially a monohydrate $CH_3NH_3\ PbI_3{\cdot}H_2O$ forms (which can readily be converted back to MAPI), as shown in **Figure 14**, and then prolonged exposure results in the formation of dehydrate and ultimately decomposition to PbI_2.[5]

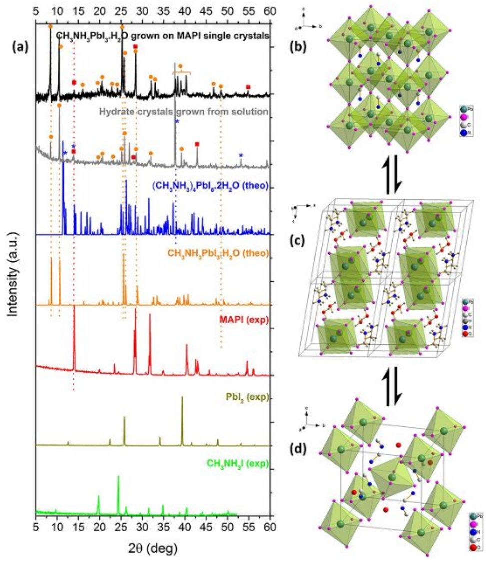

Figure 10 - (a) Identification of the composition of the hydrate species grown on MAPI single crystals (at long exposure to water vapors) and of MAPI hydrate crystals (polycrystalline, obtained from solution) by X-ray diffraction (XRD) (patterns in black and gray). The five patterns below these (either experimentally measured of simulated from crystal structures) show species the hydrated crystal material is likely to contain. Symbols are used to tag the main features according to the color of their respective spectra. Panel (b) shows the structure of MAPI in its cubic phase, while panel (c) shows the structure of the monohydrate phase, $CH_3NH_3PbI_3{\cdot}H_2O$ and (d) displays the structure of the dihydrate, $(CH_3NH_3)_4PbI_6{\cdot}2H_2O$. The position of the hydrogens on the $(CH_3NH_3)^+$ ions and the water is not assigned in panels (b) and (d).Fig. 2, Reproduced with permission from Chem. Mater. 27, 3397, 2015 (Ref. 5). Copyright 2015 American Chemical Society.

13.2 Current and Future Challenges

Significant have been made to understand the degradation processes and develop methods to address the degradation. Exposure of perovskite to moisture has been extensively studied,[3-6] and the degradation pathway for moisture exposure[3-5] is reasonably well understood. However, details related to the perovskite film properties (defects, stoichiometry, morphology, grain boundaries, surface termination) affect the degradation upon moisture exposure, and the influence of these factors need to be better understood. For example, rough surface can lead to faster degradation.[6] It is also important to note that moisture induced degradation is accelerated by illumination (even ambient illumination),[6] and this acceleration process, unlike the case of oxygen exposure, has not been as comprehensively studied. Furthermore, considering the fact that the perovskite films and devices tend to exhibit faster degradation in the presence of both oxygen and water compared to oxygen only or water only conditions, and the fact that ambient atmosphere contains both oxygen and water, it is important to improve our understanding of interactions involving both oxygen and water, in the dark and under illumination. As discussed, oxygen does not contribute significantly to the perovskite degradation in the dark.[3,7,8] Unlike water, oxygen does not diffuse into the grain interior and oxygen tends to adsorb at iodine vacancy sites on the surface where it remains relatively stable due to strong interaction with Pb.[7] The presence of water affects the adsorption of oxygen and its energy levels in the gap, similar to iodide vacancies, which makes it more likely that superoxide ions will be produced by reduction of oxygen by photoexcited electrons, and the magnitude of this effect is dependent on the surface termination.[7] Under illumination, superoxide ion is generated, which results in photooxidation of the perovskite.[7] The effects of oxygen are dependent on the partial pressure of oxygen and the composition of the perovskite, and the stability under illumination with oxygen exposure can be improved by simultaneous exposure to oxygen and iodine, as illustrated in **Figure 15**, although exact details of the ongoing processes in that case require further study.[8]

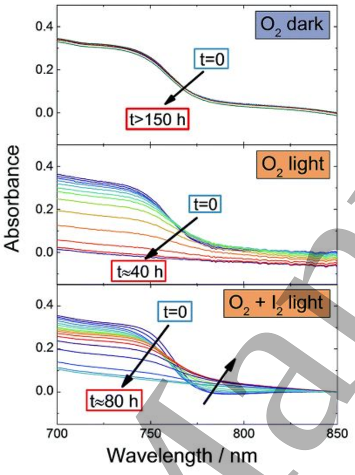

Figure 11 - Stability of MAPbI3 films under O2 exposure, in dark and under illumination (4.6 mW cm-2), monitored by UV-Vis spectroscopy. The samples are kept at 333 K under constant gas flow. After more than 150 hours, no changes are visible for samples kept in the dark between measurements, while 40 hours are sufficient to completely degrade samples exposed to light. As a comparison, a film kept under the same conditions (O_2 and light) but also under constant iodine partial pressure ($P(I_2)=1.4\times10^{-5}$ bar), shows doubled stability, with full degradation achieved after 80 hours. Note the formation of a tail in the absorption, indicating amorphization of $MAPbI_3$. Reproduced with permission from J. Mater. Chem. A 6, 10847, 2018 (Ref. 8).

13.3 Advances in Science and Technology to Meet Challenges

Different methods exist for improving the perovskite stability with ambient exposure (especially moisture), such as the use of hydrophobic layers, 2D perovskites, and/or encapsulation.[3,9] The use of bulky spacer cations which form a hydrophobic protective surface layer is particularly effective for reducing sensitivity to moisture.

However, dealing with instability under illumination is considerably more complex.[3] Even in encapsulated devices, there could be oxygen released from the metal oxide layer, which could result in degradation under illumination.[2] A reduction of superoxide ion generation and consequently reduction of photooxidation, as well as ion migration, has been demonstrated by optimizing the perovskite composition (Cs content),[2] since the photooxidation degradation is dependent on the perovskite composition.[8] In addition, improved stability under illumination can be achieved using additives combined with appropriate selection of device architecture.[10] For example, the use of aminovaleric acid additive resulted in increased superoxide ion generation for films on glass, but reduced superoxide ion generation when infiltrated into mesoporous $TiO_2/ZrO_2/C$ structure.[10] This was attributed to the dependence of superoxide ion formation on oxygen diffusion, grain morphology, and native defects.[10] Thus, significant stability improvements are possible by careful optimization of perovskite composition (including additives and/or passivation) and device architecture, introducing additional layers, and encapsulation.

In addition, progress has also been made towards the ambient processing of perovskite solar cells (for more details, see Section 6). For example, better understanding of the perovskite crystallization in the presence of water has led to the development of deposition process involving prenucleation by adjusting spin-coating and antisolvent application.[1] The increase in nuclei density achieved in this process prevented the growth of large needle–like crystals of $MA_2Pb_3I_8 \cdot 2DMSO$ intermediate, which resulted in smooth films and efficient devices.[1] However, while reports on ambient-prepared devices typically involve good shelf-life stability,[1] ambient-fabricated devices have rarely been subject to harsh stability testing conditions, such as damp heat test, outdoor test, and accelerated aging under illumination at elevated temperature. Such more stringent stability testing protocols are essential to establish whether any residual moisture arising from ambient processing affects device stability.

13.4 Concluding Remarks

Perovskite film and device stability is significantly affected by exposure to moisture and oxygen, in particular under illumination (although moisture also contributes to the degradation in the dark). The sensitivity to moisture and oxygen exposure hinders the development of ambient processing and it is detrimental to long term stability of the devices. The ambient-induced degradation processes are significantly affected by the composition and morphology of the perovskite and native defect concentrations. Moisture-related degradation is better understood and easier to address compared to photooxidation degradation in presence of oxygen and illumination. While encapsulation (discussed in more detail in Section 12) can significantly improve device lifetimes, due to the presence of surface-adsorbed oxygen in commonly used metal oxide charge transport layers, improved understanding of photooxidation and methods to suppress it are urgently needed to achieve high stability devices.

13.5 Acknowledgements

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Section 14 - Stability of Perovskite Materials: Illumination

Aleksandra B. Djurišić, Tiklun Leung and Yin Li
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

14.1 Status

In addition to extrinsic (oxygen, moisture induced) degradation, which is accelerated by illumination discussed in Section 13, illumination can result in intrinsic instabilities of the perovskite material, discussed in this Section. Furthermore, while illumination also results in an increase in temperature and affects the ion migration in the devices, the topics of temperature and ion migration will be discussed separately in Sections 15 and 16, respectively. In addition, while other device components (charge transport layers, electrodes) can also exhibit degradation under illumination,[1] the discussion in this section is limited to perovskite material. The intrinsic degradation under illumination is dependent on the type of illumination (UV, blue light, white light)[1] and involves irreversible[1-3] and reversible processes.[1,4-10] Degradation due to reversible processes can be reversed by storing the devices in the dark, and for this reason stability testing protocols involving light-dark cycling can yield different results compared to constant illumination. Among reversible photo-degradation processes, photo-induced halide segregation has been extensively studied, and while different hypotheses have been proposed to explain the observed experimental data[1,4-10] the process is still not fully clear. The irreversible photodegradation is somewhat better understood. It is strongly dependent on the halide perovskite composition, with perovskite films prepared with excess PbI_2 (common approach to increase efficiency of the devices) exhibiting degradation due to intrinsic decomposition of PbI_2 into Pb and I_2 under illumination,[2] with released I_2 resulting in a chain reaction and further degradation of the perovskite.[1,2] However, device performance degradation trends do not necessarily follow the same trend as perovskite film degradation due to complex interplay between different processes.[2] The methylammonium (MA) lead iodide (MAPI) is also susceptible to photodegradation under prolonged illumination, and it decomposes into MAI and PbI_2 (followed by further decomposition of PbI_2), and MAPI decomposition can even occur at temperatures as low as 5K.[1] It should be noted that many of these studies have been conducted in vacuum, which would result in inevitable loss of volatile organics. Recent experiment in Ar atmosphere clarified the process of MAPI photodegradation, and it was proposed the formation of $Pb^{(0)}@PbI_{2-x}$ nanoparticles, as illustrated in Figure 16.[3]

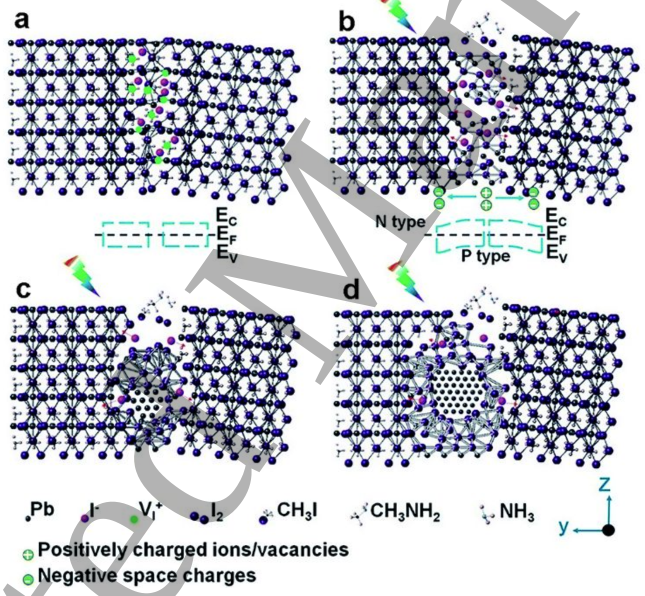

Figure 12- Illustration of the photodegradation mechanism of the MAPI film into the Pb@PbI2-x core–shell nanostructures. a) Lots of deficiencies exist at the grain boundary of the as-prepared perovskitefilm. . (b) Under light illumination, the iodide ions prefer to migrate away from the grain boundaries (red arrows) to inducea self-built electric field as shown below. (c and d) After extending the light illumination time, the preferential degradation at the amorphous PbI_{2-x} *and MAPI interface induced the formation of* $Pb@PbI_{2-x}$*. nanoparticles. Reproduced with permission from Ref.*[3]

14.2 Current and Future Challenges

Improving the stability of perovskite materials and devices under illumination is critical since the solar cells need to function under illumination. Due to practical importance of mixed composition halide perovskites for single cell PSCs as well as tandem devices, improved understanding of the photoinduced halide segregation (PHS) is of critical importance since its origins are still not fully understood.[1] Furthermore, due to complexity of the processes involved, differences in experiment designs, sample composition, sample morphology, and sample preparation, it is difficult to generalize conclusions of different studies. These variations result in large spread of reported segregation times from tens of seconds to tens of minutes even for similar perovskite compositions.[5] In particular, the measurement conditions (vacuum, air, nitrogen, polymer-protected in vacuum) determine whether the observed changes under illumination are reversible or not.[5] Consequently, different models have been proposed to explain PHS to date, which include polaron-induced lattice strain, defect mediated processes, and thermodynamic properties.[1,4] It was proposed that trapping of holes occurs exclusively in iodide phase of the perovskite, and selective expulsion of iodine from mixed halide film into the solvent occurs under illumination.[4] Hole trapping at iodide sites makes these sites unstable, triggering iodide migration through vacancy hopping, resulting in PHS.[4] In agreement with this, it was found that PHS is dependent on the trap state density, since photoexcited charge carriers which recombined through trap states were found to determine the rate of halide segregation.[5] It was proposed that electric field arising from trapped charge carriers initiates the segregation, and the process is further exacerbated by funnelling the carriers to lower bandgap segregated iodide phase.[5] The hypothesis of charge trapping is further supported by improved photostability by coating hole transport layer on perovskite surface which prevents hole accumulation in the perovskite.[6] However, further work is definitely needed to further understand the driving force for PHS, since neither polaron-based nor miscibility-based thermodynamic models fully explain existing literature data.[10] Based on temperature-independent terminal stoichiometry bandgap-based thermodynamic model instead of miscibility-based thermodynamic model was proposed.[10] However, before the matter can be considered settled, applicability to MA-free perovskites should also be investigated.

14.3 Advances in Science and Technology to Meet Challenges

A number of different approaches has been proposed to tackle photodegradation of halide perovskite materials and devices.[1] These include defect passivation (in particular surface and grain boundary),[1] adjusting perovskite composition[1,4,7] to reduce lattice distortion induced by photogenerated carriers, [1] avoiding the use of UV-sensitive charge transport layers such as TiO_2 and using photostable charge transport layers in general,[1] using UV-blocking layers and/or downconversion layers,[1] and interface modifications.[1,6] Due to the dependence of the photodegradation process on defects in the film, passivation of defects would obviously be beneficial, but it should be noted that complete elimination of the PHS would require low trap mediated recombination rate constant (10^5 s^{-1}), at least for MA-based perovskite.[5] Thus, composition optimization (cation mixing) and structural engineering is needed together with minimizing traps to suppress PHS.[5] Surface passivation of traps, for example using trioctylphosphine oxide (TOPO),[6] is particularly promising, since surfaces and interfaces typically contain higher defect concentrations compared to the bulk and charge carriers will tend to accumulate at interfaces.

Among different approaches to improve photostability, optimizing the perovskite composition and structure is also a highly promising approach. For example, Cs incorporation was found to improve photostability of mixed halide perovskite films,[4,8,9] and this phenomenon was attributed to reduced iodide mobility in mixed cation films.[4] However, the PHS exhibits complex dependence on the perovskite composition, which is likely an interplay between the effects of crystal structure as well as local electronic and chemical interactions.[8] As a result, PHS increased again when Cs concentration was increased above the optimal one,[8] which could not be fully explained by existing PHS models. In addition, prolonged illumination of a mixed cation sample can result in segregation of cations, which in turn could trigger halide segregation.[9] Another approach in optimizing perovskite composition to suppress PHS is the use of triple halide mixed perovskite.[7] These devices demonstrated significant improvement in the photostability even under significantly higher illumination intensity (up to 100 sun), as shown in Figure 17.[7]

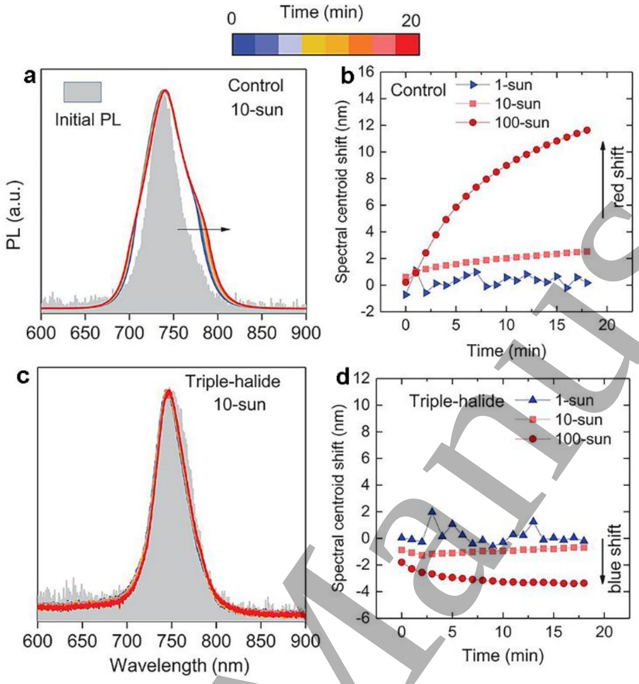

Figure 13 - Suppression of photoinduced phase segregation in triple-halide perovskites. (A) PL spectra of 1.67-eV control perovskite films (Cs25Br20) under 10-sun for 20 min. Arrows indicate the direction of the PL shift over time. (b) The shift of the spectral centroids of control films over time. The red shift becomes more obvious under higher injection. (c) PL spectra of 1.67-eV triple-halide perovskites (Cs22Br15+Cl3) under 10-sun illumination for 20 min. (d) The shift of the spectral centroids of triple-halide perovskites over time. The blue shift becomes more obvious under higher injection level.

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14.4 Concluding Remarks

Photostability of halide perovskite materials and devices has been extensively studied. Nevertheless, some phenomena, such as photoinduced halide segregation, are still not fully understood despite their practical significance. Thus, further work is needed in improving the understanding of the PHS process and its dependence on the halide perovskite material properties. From the practical applications point of view, since it is indisputable that defects play a significant role in a variety of degradation processes, both reversible and irreversible, progress has been made towards passivating the defects and improving the stability. Promising improvements have also been obtained in optimizing the perovskite composition, and it is likely that further improvements can be achieved by combining different approaches, such as simultaneous use of optimized perovskite composition, optimized processing including additives for defect passivation and achieving large grain sizes, and surface passivation.

14.5 Acknowledgements

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Section 15 - Stability of Perovskite Materials: Temperature

Firouzeh Ebadi and Wolfgang Tress

Institute of Computational Physics, Zurich University of Applied Sciences, Winterthur, Switzerland

15.1 Status

Thermal stability of a material is a crucial parameter that must be considered when the material is supposed to be used as a light harvester in a solar cell device. In metal halide perovskites elevated temperature can lead to reversible or irreversible changes. In addition to thermal decomposition, heat can cause significant adverse effects on optical and electronic properties of the material, e.g. by leading to phase changes. Since high power-conversion efficiency values have been achieved, the poor device stability, in particular under elevated temperatures, remains a major hurdle to commercialize perovskite solar cells (PSCs). There are several sources for degradation of PSCs under elevated temperatures including thermal instability of electron and hole transport layers and undesired diffusion of dopants or metals used for the electrode. Note that in this section, we will solely discuss the thermal stability of the perovskite materials themselves.

Already at the early stages of PSC research, studies have shown that $MAPbI_3$ ($MA = CH_3NH_3$), the first perovskite composition used in solar cells, is thermally instable. Decomposition of $MAPbI_3$ thin films was observed to already occur during annealing at 85 °C even in inert atmosphere[1]. Increasing the temperature towards 100 °C and higher causes decomposition of the material into methylamine, hydrogen iodide, and lead iodide. This observation is consistent with DFT calculations which have shown very low formation energies of the perovskite referred to its precursor salts. Since then, various attempts have been undertaken to increase the thermal stability. Those include optimizing the fabrication methods of the thin film and engineering the perovskite composition by introducing different cations, anions and mixtures thereof. In terms of halides, there are many reports showing that the addition of bromide increases the thermal stability.

Currently, mixed cation and mixed halide perovskite compositions are regarded as highly promising in terms of thermal stability [2]. However, it turned out that simple trends do not exist as displayed in Figure 18 showing a quantitative stability comparison of various mixed hybrid perovskites based on a TG-DTA analysis [3].

As the organic cation has been identified as the major weak point, all inorganic lead halide perovskites, e.g., $CsPbI_3$ are supposed to show much higher thermal stability.

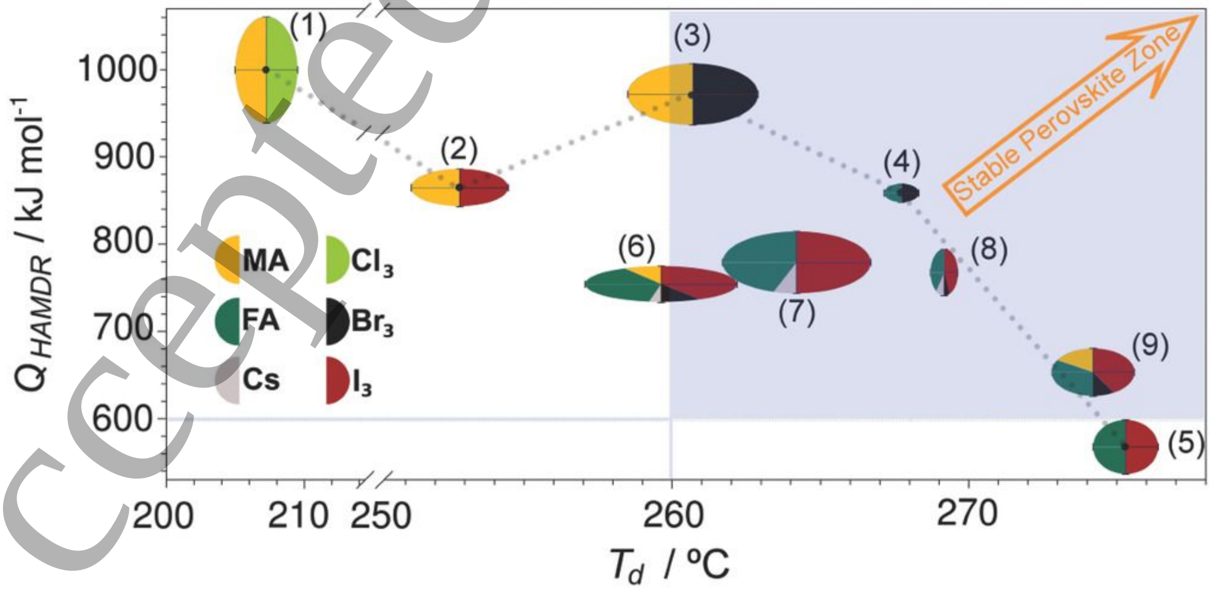

Figure 14 - Stability map of hybrid halide perovskites represented by Td (sample degradation temperature, x-axis) versus QHAMDR (sample heat absorbed at maximum degradation rate, y-axis) two parameters of thermal degradation experiments. Uncertainty of the measurement is represented by ellipses' x–y axis lengths. Colors in the left and right side of ellipses describe perovskite's A site composition and the X halide composition respectively. $MAPbCl_3$ (marked as (1) in the figure), $MAPbI_3$ (2), $MAPbBr_3$ (3), α-$FAPbBr_3$ (4), α-$FAPbI_3$ (5), $Cs_{0.05}MA_{0.16}FA_{0.79}PbI_{2.49}Br_{0.51}$ (6), $Cs_{0.1}FA_{0.9}PbI_3$ (7), $Cs_{0.2}FA_{0.8}PbI_{2.84}Br_{0.16}$ (8), and $MA_{0.33}FA_{0.67}PbI_{2.5}Br_{0.5}$ (9)[3]. Reproduced with permission. Copyright 2018, Wiley-VCH.

15.2 Current and Future Challenges

$MAPbI_3$ deteriorates during thermal stress. Replacing MA with formamidinium (FA = $CH(NH_2)_2$) can increase the thermal stability. This can be explained with FA having a greater number of H, leading to stronger H-bonding with the PbX_6 octahedra. However, the photoactive α-phase $FAPbI_3$ can quickly transform into a non-perovskite hexagonal (δ) phase of $FAPbI_3$. This holds similarly for the all-inorganic Cs lead-halides, whose thermodynamically stable phase at room temperature is commonly not the α phase. Therefore, the major challenge is to find compositions and ways of fabrication to obtain the optimum film regarding phase stability and thermal stability. When employing mixed compositions (especially mixed halides), demixing can occur leading to undesired phases enriched by certain elements.

Stabilizing α-phase $FAPbI_3$ is challenging. Various methods including additives, doping, and interfacial engineering have been reported. Lu *et al.* showed that an MASCN vapor-treated $FAPbI_3$ film remained in its pure black phase after 500 hours of annealing at 85°C[4]. Many reports have shown that partially replacing FA with MA in $FAPbI_3$, can stabilize the black phase. However, being under thermal stress over 500 h in 85 °C, the perovskite thin film degrades by releasing MA. Instead, partially replacing FA with Cs and I with Br, can help to stabilize the black phase and increase thermal stability of the material. It is shown that when stressed at 85 °C for 1000 h, $FACsPbI_3$ solar cells show no decline in power conversion efficiency whereas $FAPbI_3$ perovskites show signs of degradation[5]. However, excess Cs and Br would lead to phase instabilities due to large lattice stress. So, finding the right ratio of the cations and halides are major challenges.

On the other hand, there are reports on solar cells based on mixed compositions passing damp-heat tests and similar, proofing the excellent progress in the field. Nevertheless, it remains a future challenge when targeting 20-years-stable solar modules to avoid or control thermally activated migration of halide ions, which is an intrinsic property of the material (see Chapter 16).

15.3 Advances in Science and Technology to Meet Challenges

Recent advances in increasing the thermal stability of perovskite solar cells and characterization of the role of the perovskite and interfaces reveal the potential of the perovskite material to push the current limits and enter the solar market.

In order to accelerate this procedure from the perovskite material's perspective, there are a few strategies which can be taken: As mixed FA/Cs and I/Br combinations are one of the most promising for the hybrid perovskites, understanding more about the thermal decomposition kinetics in thin films of this material is the first essential step. Assisted by ab initio calculations, appropriate film preparation methods including the introduction of specific additives to the material are crucial. As in many cases degradation starts from the film surface, carefully tracking and characterizing changes at interfaces, e.g. using impedance spectroscopy can lead us towards fundamental understanding of the required passivation mechanism. Adding a thin 2D perovskite layer to the 3D perovskite film is another promising approach which can greatly enhance the stability of the PSCs [6]. Dedicated interfacial layers acting as ion blocking layers are needed to avoid that reversible losses due to unavoidable ion migration in the bulk of the material convert into irreversible losses, e.g. when constituents - thermally activated - diffuse out of the perovskite layer.

In addition to composition engineering, another approach toward thermally stable perovskite films is controlling the film growth to achieve almost tensile-stress-free compact films, with robust interfaces leading to a higher intrinsic thermal stability. Recently Dewi et.al. showed that un-encapsulated co-evaporated $MAPbI_3$ PSCs retain ≈80% of their original PCEs after 3600 h, when stored at 85 °C. This result indicates the importance of the growth process, allowing higher intrinsic thermal stability for films with minimum tensile stress [7]. Such an impressive thermal stability for solar cells with $MAPbI_3$ absorber shows the potential of control of the perovskite growth process to improve the stability of mixed perovskites even further.

In terms of materials, all-inorganic perovskites are the most promising compounds to address the stability challenge. Gaonkar *et al.*, reported thermally stable inorganic mixed halide perovskite solar cells with no loss in device performance at 200 °C for 72 h (Figure 19)[8]. However, the presence of point defects and not fully optimized preparation methods result in lower performance. In order to realize the full potential of these materials and maintain the α phase, e.g., during thermal cycling, further optimizations on the perovskite film including its interfaces are to be undertaken [9], [10].

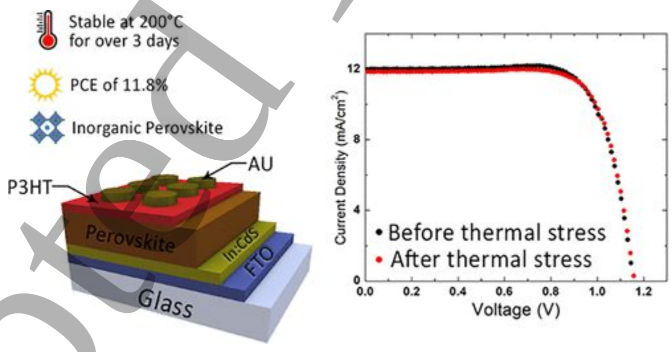

Figure 15 - All-inorganic CsPbIxBr(3−x) device performance showing no change with thermal stress at 200 °C for 72 h[8].

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15.4 Concluding Remarks

Fabricating thermally stable perovskite solar cells remains a challenge, although great progress has been made. Often, the main culprit of device degradation upon elevated temperatures are charge transport layers and electrodes, e.g., by diffusion of some of their constituents. The perovskite material itself does not instantaneously decompose under temperatures solar cells are exposed to. However, detrimental processes such as migration of intrinsic ions are accelerated, which might finally lead to a deterioration of the performance. To enhance the thermal stability of the perovskite itself, moving from $MAPbI_3$ to mixed compounds including FA and Br has proven a successful strategy. In the future, all-inorganic perovskites ($CsPbI_3$) hold the largest promise of being thermally stable for temperatures far above 100 °C. Challenging here is to maintain the perovskite phase also at ambient temperatures and facilitate a crystal and thin-film growth that avoids potential weak points such as stress in the lattice.

15.5 Acknowledgements

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Section 16 - Stability of Perovskite Solar Cells: Ion Migration

Giles Richardson
Mathematical Sciences, University of Southampton, UK

16.1 Status

Perovskite solar cells (PSCs) exhibit unusual physics that is not commonly observed in other photovoltaic technologies. This was first highlighted by Snaith *et al.* [1], who noted that the standard technique for assessing solar cell efficiency, by slowly scanning the applied voltage bias (V) across the cell and measuring the resulting current as a function of bias, to produce a current-voltage (J-V) curve, leads to different J-V curves depending on whether V is being scanned up or down, and on the rate at which it is scanned. This phenomenon is misleadingly termed current-voltage (J-V) hysteresis and disappears at very slow (and very high) scan rates. Consequently, it is largely irrelevant to the steady-state operation of a cell. However, the physics that underlies this phenomenon, namely the presence of slow-moving ion vacancies in the perovskite structure, plays a key role in cell performance and degradation. This is because the ion vacancies, which give rise to hysteresis, occur at much higher densities than the charge carriers (electrons and holes) and so largely determine the internal electrical environment of the perovskite absorber layer. In particular, they act to screen electric field from the perovskite by forming narrow space-charge layers at the edges of the perovskite material where they abut the transport layers (see figure 20). The exact distribution of the charged species across the space charge layers, which span the perovskite/transport layer interfaces, serves to determine the electric potential distribution across the device and so play a key role in determining the concentrations of charge carriers on these interfaces [2]. Thus, interfacial recombination, which is the predominant loss mechanism in efficient modern cells [3], is strongly dependant on the ion vacancy distribution. This opens the possibility of deliberately engineering devices to reduce interfacial recombination losses by, for example, changing the electric properties of the transport layers to modify the distribution of potential drops across the cell [2].

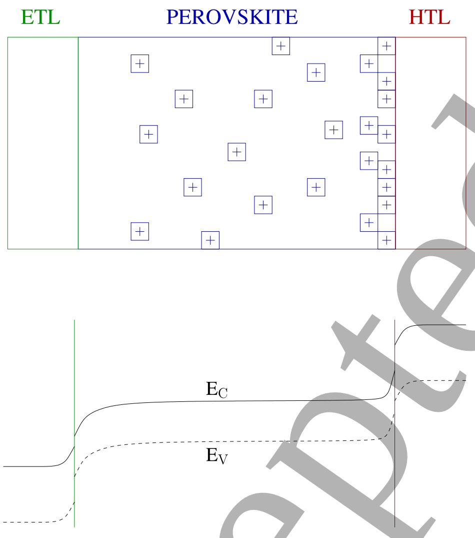

Figure 16 - (Top) Schematic of vacancy distribution in scenario where of a single mobile vacancy species (positively charged), (Bottom) associated conduction and valence band energies.

There is strong experimental evidence that the motion of halide vacancies, lying on the X-site of the perovskite structure, is predominantly responsible for hysteresis and the other short-time scale dynamics (0.1-100s) observed in PSCs. This is reinforced by *ab-initio* predictions of a low activation energy barrier for iodide ion hopping between neighbouring sites in the perovskite crystal structure of methylammonium lead tri-iodide ($CH_3NH_3PbI_3$), or MAPI for short [4]. Longer timescale dynamics, associated with reversible decays in cell efficiency (occurring over several hours) in highly-efficient mixed cation (formamidinium / methylammonium) mixed halide (Br^-/I^-) perovskite cells, have been

Notably, the absence of hysteresis in so-called “hysteresis-free cells" does not imply the absence of ion vacancy motion within the perovskite but often, as noted by Bryant *et al.* [6], signifies that the hysteresis timescale lies outside the range of timescales over which current- voltage scans are conducted. This alternative hypothesis can be confirmed by first cooling down (or heating up) the cell, in order to slow down (or speed up) ion motion, before repeating the J-V scans to see if hysteresis re-emerges. As noted in [2], transport layer properties play a significant role in determining the hysteresis timescale and can lead to marked differences in behaviour between cells of different construction but with identical perovskite absorber layers.

16.2 Current and Future Challenges

There is good evidence that the picture of the ionic behaviour of PSCs presented above is a simplification of their real physics, and that the chemistry of organometal perovskites exhibits other ionic behaviours, in addition to ion vacancy motion. In particular, *ab-initio* computations on perovskite structures [7], suggest that the barrier to the formation of certain ion vacancies, in reactions that may also spawn interstitial defects, is not particularly large. This suggests that that the accuracy of device models based on vacancy tracking alone could be improved by incorporating vacancy generation reactions and interstitial defect tracking. This is a significant challenge, which not only requires a full description of the set of vacancy generation reactions but also accurate estimates of the associated reaction rate constants [8]. Furthermore, since vacancy generation reactions also involve the generation (or annihilation) of charge carriers the resulting vacancy dynamics would be expected to display sensitivity to photogeneration; there is some evidence for this arising from Kelvin Probe Force Microscopy experiments [9].

The links between ion (and vacancy) motion and cell degradation are still not fully understood but are key to future advances in PSC design that can improve cell durability and are a prerequisite for long-lived commercially viable devices. At least in some cells degradation can be directly linked to the motion of ions (particularly halide ions sitting on the X-site) out of the perovskite absorber and into the adjacent transport layers [10]. This leads to the gradual degradation of the perovskite material. Various methods to reduce ion migration, and thereby control this degradation pathway, have been reviewed by Lee *et al.* [11]; these include passivation of grain boundaries between perovskite crystals and total, or partial, substitution of the methylammonium cation in the perovskite structure by other ions, such as formamidinium. Other works have suggested that the large mechanical stresses induced in the space charge layers lead to mechanical degradation of the cell in the vicinity of the transport layer interfaces. Smart cell construction based on a firm understanding of the degradation mechanisms should provide a method to minimise the deleterious effects of ion motion.

Another significant challenge presented by the atypical physics of PSCs is how photocarrier recombination in the cell can be monitored with simple non-destructive transient techniques, such as impedance spectroscopy (IS) and intensity modulated photocurrent spectroscopy (IMPS). Being able to detect the primary location of carrier recombination, particularly as it changes over time with cell degradation, is key to understanding cell stability and suggesting strategies to improve it. The presence of a high density of charged ion vacancies within the device, in addition to the usual charge carriers, means that the standard protocols for measuring the ideality factor (n_{id}) lead to non-integer values of this quantity that often lie well outside the normal range encountered in other photovoltaic technologies. It is therefore not possible to draw sensible conclusions about the location and type of recombination within a PSC from measurements of the ideality factor using these standard experimental protocols. This requires that new methods, based on an updated solar cell theory that is capable of accounting for mobile ion vacancies, be devised for extracting information from these non-destructive transient techniques. In the case of the ideality factor the protocols used to obtain its value need to be specifically redesigned to reflect the atypical PSC physics.

16.3 Concluding Remarks

The presence of charged ion vacancies in the perovskite absorber layer of perovskite solar cells plays a major role in the unusual physics of these devices. Improving the understanding of how ion vacancies (and related interstitial ionic defects) are generated and move within the device (including at the transport layers interfaces), is key to controlling device efficiency and limiting cell degradation.

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Section 17 - Stability of Perovskite Solar Cells: Electrode Choices

Chuangye Ge and Hanlin Hu

Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Nanshan District, Shenzhen, China

17.1 Status

The power conversion efficiency (PCE) of metal halide perovskite solar cells (MHPSCs) has been soared near 26%, recently research interest on the device stability have attracted more and more attention to prolong the duration of devices under operational conditions.[1,2] Up to now, substantial articles or reports have highlighted the rapid advance in this field, mainly concentrate on the study of new materials and their physical/chemical properties, design and construction of device with various configurations, and the operational mechanisms via compositional engineering, interfacial engineering and structural engineering. Electrode is essential for collecting charges in the device, which plays a substantial role to the PCE and stability of PSCs.[3–5] It accounts for a large share in the total fabrication cost, affecting the commercialization process of PSCs significantly. Less attentions have been devoted to electrode materials, compared with the rest components of PSCs. Apart from the photovoltaic performance and stability, electrode materials may affect other expected functions, including semi-transparency light-absorption, and flexibility. Furthermore, it is of importance to regulate the approach of the specific electrode during the fabrication of the entire device,[6] and consequently affect the cost of perovskite devices.

17.2 Current and future challenges

The electrode materials show suitable work function and excellent electric conductivity, which are necessary for the extraction, collection and transfer of the charge carriers. They can be summarized into different categories including metals, metal oxides, conducting polymers, carbonaceous materials, and their composites (Figure 1).[3] Typically, the benchmark metal electrodes of PSCs are noble-metals including gold or silver owing to their high light reflectivity and low sheet resistance ($R_{sq} \leq 1\ \Omega\ sq^{-1}$). Gold is the most typical electrode with excellent chemical robustness in PSCs, which could still react with the halide (iodide) in the hybrid perovskite under the synergistic effect of ion migration and perovskite decomposition, migrating through the hole transporting layer (HTL) to the perovskite layer, ultimately results in the degradation of the whole devices. Ag is another common electrode material, which is even more chemically unstable and may have a interaction with the react migrated iodine from absorbers, leading to a change of the interfacial electronic properties for the Ag/HTL interface.[3,4]

To replace these noble metals, some low-cost metals have been examined, including Al, Cu, Ni etc. Additionally, alloyed metallic or composite films have been introduced to address the stability issue in PSCs, such as NiAu, AgAl alloy, metal/metal oxide composites. Furthermore, several studies have examined the performance of molybdenum (Mo) and tungsten (W) electrode-based PSCs.[7,8]

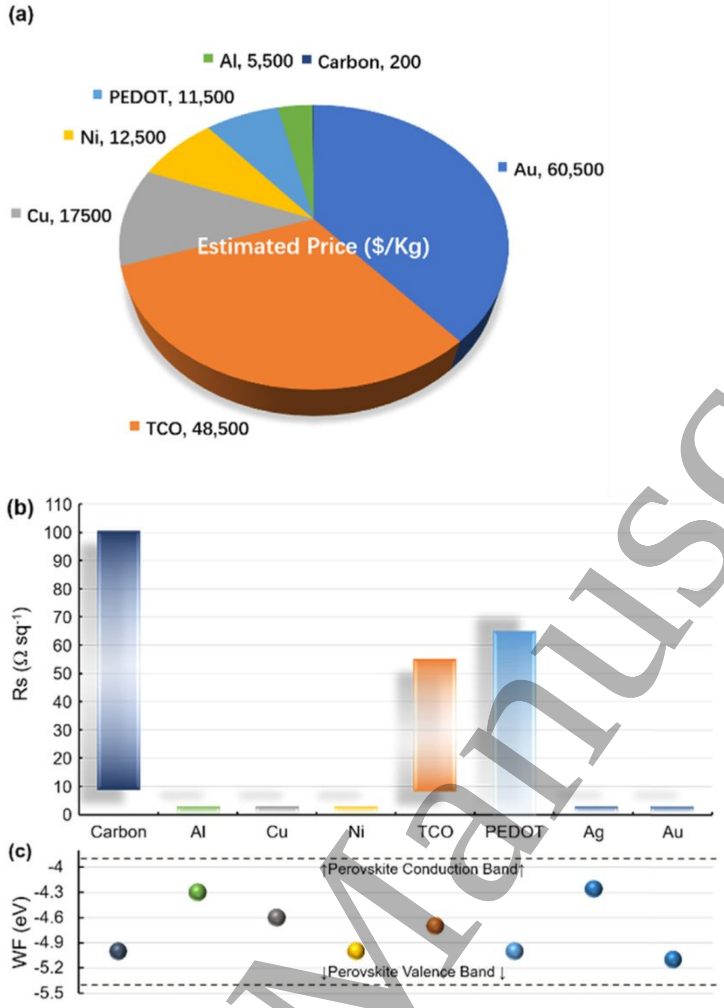

Figure 21. Analysis of electrode materials cost and property. (a) Summary of cost for various metallic electrodes; (b) Comparison of R_{sq} for different conductive electrode materials; (c) the work function of various electrodes materials. Reproduced with permission from Reference [1].

Carbon materials such as single-wall or multi-wall carbon nanotubes, graphite, graphene, and carbon black have been applied as electrodes for PSCs. Different from metal electrodes, carbon materials exhibit excellent diversity and modifiability, relatively high specific surface area, rich micropores and mesopores and high chemical stability, which ensures carbon materials work regularly in the monolithic structured PSCs.[1,9,10] Most importantly, the Fermi level of carbon (5.0 eV) is very close to the valence band edge of the perovskite (≈ 5.4 eV), facilitating the collection of holes from perovskites. It is notable that the carbon-based PSC have the superior advantage of being more stable than metals in damp-heat testing. However, the PCE of carbon-based (like HTL-free) PSCs is unsatisfied, thus it is necessary to concentrate on the improvement of PCE, such as introducing an electron blocking layer to suppress the carrier recombination.

Transparent conducting oxides (TCOs) has been widely used in PV modules, flat-pitanel displays, touch screens, and other applications due to well-established film deposition technique.[11–13] With respect to various TCO materials, fluorine doped tin oxide (FTO) and indium doped tin oxide (ITO) with excellent optical transparency and electrical conductivity are the most popular and commercial available materials, and have been widely utilized. Generally, they serve as substrates (bottom electrodes) in the thin film-based PV devices, providing ohmic connection with electron/hole transporting layer. However, owing to the high cost, lack of indium, poor flexibility for the glass substrates, alternative TCOs, e.g. gallium-doped zinc oxide (GZO), indium-doped cadmium oxide (ICO), and aluminum-doped zinc oxide (AZO), have also been explored in semi-transparent or tandem PSCs.

As a representative conducting polymer, PEDOT:PSS can serve as the HTM in PSCs. It shows similar work function as Au, around 5.0 eV, which makes it could be an ideal electrode material. However, aqueous solution is usually involved during the film preparation, which is harmful to stability of perovskite material.[5,7,8] Thus, it is of importance to develop suitable approach for the utilization of PEDOT:PSS. Other studies have shown that polymer-based PSCs with good stability can be obtained through transfer-lamination techniques, detachable stacking perovskite, and antireflection coating techniques, etc..

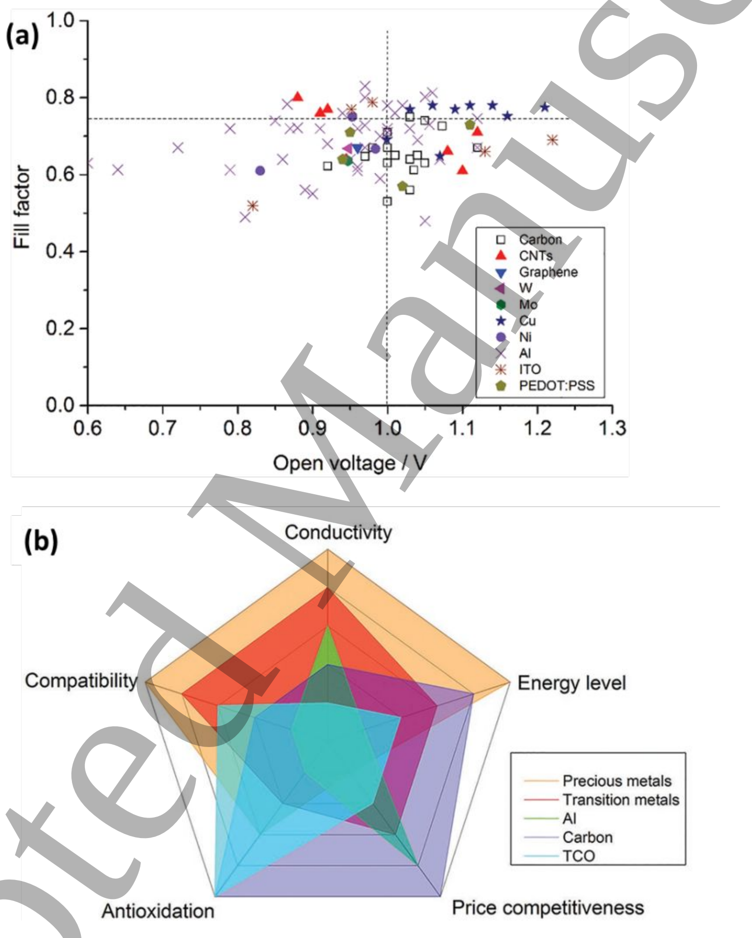

Figure 22. (a) Fill factor (FF) and PCEs of PSCs using various electrodes. (b) Summary of cost-effective electrode materials for PSCs. Different types of materials are ranked from poor to excellent according to their performance in corresponding factors. Reproduced with permission from Reference [3].

Rapid advances under intensive investigation towards the merits and drawbacks of electrodes have been highlighted and thoroughly understood (as shown in Figure 2). However, before their commercialization can be realized, some challenges need to be addressed.[14] First, in terms of electrode materials, their synthesis methods are usually costly and convoluted, making it difficult for them to be controlled precisely after purification. Second, modifications of carbon or polymer materials are required to align electronic bands with

PSCs, which is beneficial for the charge extraction.[10] It is possible to tune the work function by doping or mixing, and a variety of dopants have been investigated, but the unclear mechanism retard their commercial applications. Third, it is tough to prepare these materials massively with a low-cost technique. The fabrication of TCO electrodes requires high vacuum thermal evaporation or magnetron sputtering, which causes severe energy consumption.[5,13]

17.3 Advances in science and technology to meet challenges

The interface between charge carrier transporting layer and the metal electrode serves an important role in obtaining highly efficient PSCs with good duration stability. In order to collect charge carriers from electron transport layer (ETL) or hole transport layer (HTL) effectively, the energy gap between the work function of electrode and the valence band maximum (VBM) of HTL or conduction band minimum (CBM) level of ETL should be reduced as much as possible.[14] Various materials have been integrated to tune the work function of the metal electrode, and consequently improve the interfacial charge transfer. Moreover, an additionally thin layers such as ZnO, MoO_x, LiF, bathocuproine (BCP) could contribute to effective adjustment of the work function, the stability of PSCs as well. It is possible to fabricate carbon materials through many cost-effective techniques such as doctor-blading, screen printing, roll-to-roll printing, inkjet-printing, drop casting hot pressing, and press transferring.[10][15] Practical applications of carbon electrodes have been successful under various environmental conditions, demonstrating satisfactory robustness.[9,10] In terms of the electrodes in PSCs, it is preferable to consider energy level and stability before electrical conductivity and cost. In combination with their low cost, high performance, and excellent stability, carbon could be most likely to be commercialized in the future as long as the PCE can be further enhanced. Among low-cost metals, Cu is the most promising candidate due to its superior electrical conductivity and excellent contact with different HTLs. In addition, more evaluations are needed to discover the advances of Ni, Mo, and W.[11] Semitransparent, transparent, and tandem devices with TCO and conducting polymers like PEDOT are likely to perform well. The application of composite electrodes as alternatives towards the practical use of perovskite-based photovoltaics seems to be an option worth more exploring.

17.4 Concluding remarks

During the last several years, understanding and knowledge have been accumulated on electrodes for PSCs, ranging from materials, processing technique, and structure-property relationship, guarantee solid and advanced research and development of PSCs for diverse applications. Future efforts should be devoted to explore facile, simple, and low-cost fabrication approach, which allows the perovskite materials to integrate, constructing a highly efficient and stable architecture. We look forward to more and more outcomes to be achieved in developing electrodes materials that accelerates the commercialization of perovskite photovoltaics.

17.5 Acknowledgments

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Section 18 - Stability Testing of Perovskite Solar Cells

Masoud Karimipour[1], Fanny Baumann[1], Kenedy Tabah[1], Carlos Pereyra[1], Sonia Raga[1], Haibing Xie[2], Monica Lira-Cantu[1]

[1] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology (BIST), Building ICN2, Campus UAB, E-08193 Bellaterra, Barcelona, Spain

[2] Institute for Advanced Study, Shenzhen University, 3688 Nanhai Avenue, Shenzhen, Guangdong, China

18.1 Status

The different testing methods applied to assess the stability and lifetime of Halide Perovskite Solar Cells (PSCs) have evolved with time since the discovery of PSCs back in 2009. Due to the soft-material nature (materials with soft ionic lattice) that characterize halide perovskites (HPs), these testing methods are different from those employed for inorganic solar cells. The term ‘soft’ indicates the presence of van del Walls interactions and hydrogen bonds which are ideal binding modes for materials that can be fabricated by solution processing, resulting in thin films with excellent bendability and mechanical malleability. However, the combination of weak bonds and mobile ions make halide perovskites prone to ion migration which is one of the main causes of hysteresis, defect formation and phase separation, leading to device instability. Emerging photovoltaic technologies (EPVs) such as perovskite, organic, hybrid, dye-sensitized or quantum dot solar cells, observe differences in photo-response if compared to silicon or inorganic solar cells, and thus, distinct testing methods have been developed for PSCs. Back in 2011, the International Summit on Organic Photovoltaic Stability (ISOS) published the ISOS protocols, originally developed for Organic solar cells (OPVs), in an effort to normalize the testing approaches employed to characterize the stability of OPVs by different laboratories around the world [1]. Given the singular behaviour observed for halide perovskites, the PV community decided to upgrade these ISOS protocols to incorporate specific characterization procedures for PSCs [2]. This effort resulted in the introduction of specific testing conditions, for example the effect of bias voltage or light-dark cyclability [3], and the publication of the first technical report developed by the International Electrotechnical Commission (IEC TR 63228) [3]. The application of these protocols and the development of novel ones, are important steps towards the commercialization of the PSC technology. Nevertheless, further advances are necessary in order to improve PSCS lifetimes. It is imperative to mimic real operational conditions, which comprehends the application of many stress factors simultaneously. In real outdoor conditions, for example, devices and modules are subjected to coincident stress factors such as light irradiation, temperature, intermittent light load and dose, as well as light/dark cycles, just to mention a few.

18.2 Current and Future Challenges

A current challenge is the understanding of degradation mechanisms, which are still not completely clear. In-situ testing and advanced characterization techniques should be employed in order to understand degradation mechanisms observed in devices emulating real *operando* conditions [4]. In situ characterisation provides intermediate chemical and structural changes during operation under the light-illumination and heating. These changes are dynamic and can observe continuous transitions that are difficult to see under ex-situ testing [5]. Changes that can be monitored in-situ are related to materials morphology, optoelectronic properties (carrier generation and recombination) or crystallinity and thus the most employed techniques are related to in-situ SEM, TEM, X-Ray diffraction, among others. With respect to in-situ optoelectronic characterisation, analysis employing photoluminescence (PL) and time resolved photoluminescence (TRPL) or electrochemical impedance spectroscopy, are the most common tests. Advanced characterisation techniques should include the coupling of these test with temperature modulation, light irradiation or relative humidity [5]. Moreover, performing stability test at 65-85 ◦C instead of at the classical 25-45 ◦C, would permit to accelerate the degradation of the solar cells to make more accurate forecasts of long-term performance. Increasing the temperature of the testing by 10 ◦C accelerates reactions by a factor of 2.299 [5]. Increasing the irradiation dose to 5 suns instead of 1 will also accelerate degradation. Thus, stability testing for more than 1000 h at 65 ◦C-85 ◦C and 5 suns can give a lifetime estimate of 50 years approximately [6]. Determination acceleration factors by these means is also one of the pending assignments for the PSC technology.

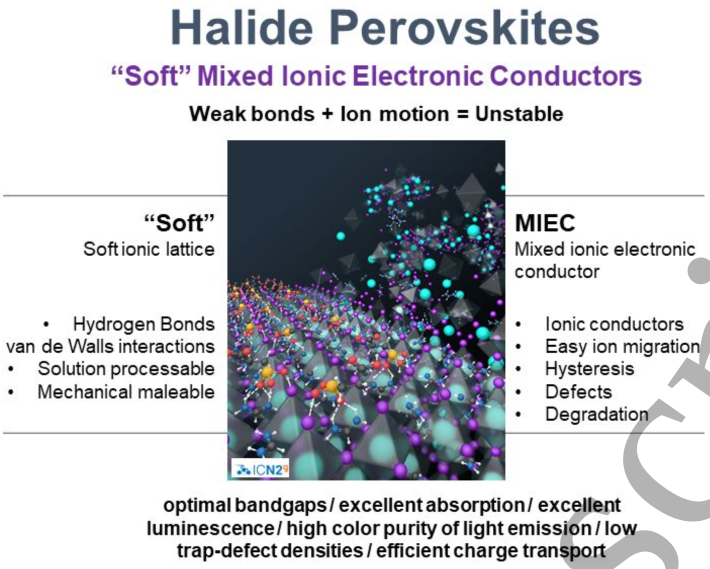

Figure 17 - Halide perovskites are "soft" ionic-electronic materials with weak bonds and high ionic motion. They must be engineered in order to make them stable.

The type of encapsulation or packaging of PSCs is a fundamental external issue affecting device lifetime. The adequate sealant must prevent the ingress of oxygen and moisture into the PSCs layers to avoid materials and device degradation, but, most important, to prevent the solubility and leakage of toxic Pb-based perovskites. At laboratory level, solar cell holders are usually employed to maintain the PSC under controlled conditions of atmosphere (N_2, Ar, or even Dry air), temperature or moisture with or without illumination. For outdoor testing, sealants usually made of epoxy resins or special encapsulants materials for glass-to-glass-encapsulation are employed. Holders applying inert gases usually employ continuous gas flow which can eliminate any residue that is produced under stability testing. Epoxy glues, on the contrary, can release vapours during PSC testing that stay within the encapsulation and can react with the halide perovskite or any of the materials of the PSCs. Thus, these two methods of testing result in completely different outcomes and more detailed protocols are required to overcome these limitations. Recommendations for how to encapsulate, as well as different reviews on encapsulants can be find in the literature [6].

18.3 Advances in Science and Technology to Meet Challenges

Density of defects in halide perovskites dictate the efficiency and stability of solar cells. Until very recent, defects associated with deep trap states were the focus of in-deep research since they promote non-radiative recombination, leading against a high photovoltage in detrimental of good power conversion efficiency. Shallow defects, on the contrary, have not been strongly considered since these are perceived as benign for classical semiconductors. However, halide perovskites are not classic semiconductors but mixed ionic-electronic (MIEC) conductors and the existence of shallow defects can have significant repercussions on the long-term stability of perovskite solar cells (PSCs) [7]. In HPs the metastability of the ubiquitous formamidinium lead triiodide (FAPbI3) perovskite and the migration of charged point defects provokes ion migration, phase separation and hysteresis that are the main causes of materials and device instability [8]. Shallow defects can be formed at very early stages of device and thin film fabrication and should be carefully controlled (Figure 23). Their presence can be observed at the bulk of the halide perovskite [7] or at the interfaces and surfaces [9] and can be the result of off-stoichiometric conditions during film formation [9] or due to strain [10]. Recent reports show the possibility for self-annihilation of charge-trapping ionic vacancies and interstitials upon illumination and/or biasing. More recent reports, employ organic additives which can passivate shallow point defects and immobilize ions resulting in PSCs with null efficiency loss after operational response under constant light illumination of 1 sun [7]. Thus, additive engineering can be employed to enhance solar cell efficiency but it is even more important, once highly efficient devices are fabricated, to analyse the passivation of shallow defect traps which will result in ion immobilization and enhance device lifetime.

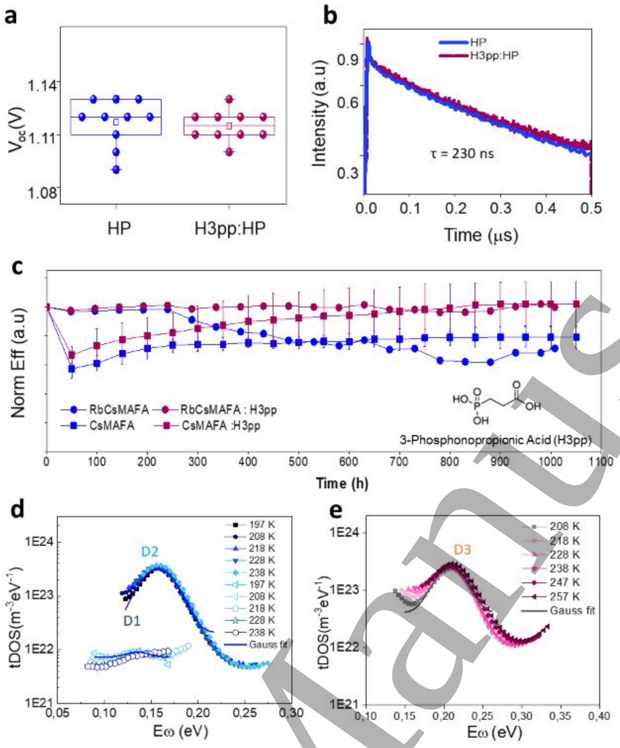

Figure 18- Shallow defect passivation dictates PSC stability. The use of the H3pp additive results in similar Voc (a), an indication of a similar non-radiative recombination (b) but excellent device stability (c). TAS analyses revealed the passivation of shallow defects (d) and (e). With permission of [7].

18.4 Concluding Remarks

Numerous are the efforts made to overcome instability issues of PSCs materials and devices. Protocols and technical reports are now in place to guide the researcher and industry on how to carry out stability testing of PSCs. Misinterpretation observed with ex-situ characterization techniques can be circumvented with the application of in-situ and advanced characterisation methodologies. However, there is still the need to develop testing methodologies resembling real *in-operando* conditions, especially those which can accelerate the degradation of the PSCs, as well as the use of acceleration factors. Accelerated tests under higher temperatures (56-85 ºC) and light irradiation doses above 1 sun can permit to calculate a more real estimate of the lifetime of PSCs. From a materials point of view, especial attention should be made to degradation factors such as ion migration and the possibility to eliminate this issue by the modification of materials. Different methods are being applied to immobilize ions. Additive engineering has demonstrated to be an effective method to passivate deep and shallow point defects. More in-depth studies should be carried out to better understand the relation between the type of defect and devices stability and efficiency. Right now, studies have demonstrated that passivation of deep defects improves devices voltage and efficiency, and the passivation of shallow defects is more related to ion immobilization and device lifetime.

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Section 19 - Outdoor Testing of Perovskite Solar Cells

Mark V. Khenkin[1], Iris Visoly-Fisher[2,3] and Eugene A. Katz[2,3]
[1]PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany
[2]Swiss Institute for Dryland Environmental and Energy Research
[3]The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, Israel

19.1 Status

Perovskite solar cells (PSC) are commonly expected to be utilized in terrestrial outdoor applications, i.e., in solar power plants or on rooftops. Outdoor environment presents a harsh combination of stress factors that is virtually impossible to reproduce in the lab due to its constantly changing nature. This highlights the importance of studying emerging PV technologies in the outdoor environment, but the same complexity makes it very rare, as yet. It has been shown that maximum power point (MPP) tracking is necessary for realistic PSC lifetime estimation, and proper device encapsulation is required to negate the external degradation by humidity and oxygen, further limiting the application of outdoor testing. Currently available outdoor data are therefore scarce and often not of the best quality (limited statistics, devices kept at open circuit in most cases). However, a few pioneering works demonstrated feasibility of good practices in outdoor experiments that will be discussed in this section (fig. 25) [1–5]. Recently several teams have shown encapsulated PSCs that passed the IEC damp heat tests (>1000 h under 85 °C and 85% RH) [6,7] and this was shown to be sufficient to achieve over a year of outdoor lifetime if matched with good material photo-stability [3]. Long-term outdoor research is therefore expected to become more widespread in the coming few years.

19.2 Current and Future Challenges

Outdoor data is required to address two key questions of vital importance for PSC technology maturing: 1) the detailed impact of weather parameters on the device power output, and 2) PSC outdoor stability. Answers to both questions are convoluted and determine the instantaneous efficiency at a given point of time, making it difficult to separate stability data from performance variations. This issue is challenging in PSCs due to the presence of transient processes at the timescale of several illumination hours (fig. 25a) [1] or several hundred hours (where seasonal changes occur, Fig. 1c,d), see below.

The impact of weather parameters includes sunlight intensity, module temperature, sunlight spectrum, and angle of incidence. The first two factors typically have the largest contribution and can be evaluated using performance matrix measurements, i.e., indoor measurements of J-V curves under different combinations of temperature and light intensity. From such measurements, the temperature coefficient (TC) can be calculated indicating the dependence of the output power on the device temperature, which is one of the most important factors determining PV energy yield. However, TCs obtained from the outdoor experiments can considerably differ from those implied from indoor measurements (and even have positive values [8]), possibly indicating significant artefacts. The solar spectrum has limited and predictable impact on single-junction PSCs, however, in the case of perovskite-based two-terminal tandem devices spectrum variation can lead to current mismatch between the sub-cells resulting in significant losses. Interestingly, in practice, temperature-induced bandgap changes and spectral variations during the day in outdoor conditions may limit this effect [9]. The angle of incidence is likely to have a minor effect on the energy yield, which is confirmed experimentally, at least in the case of a thick enough perovskite layer [10].

Long term stability is a challenge for the development of PSCs, and degradation of the active perovskite layer under influence of light, heat, electric bias and ambient oxygen and humidity has been demonstrated. Illumination enhances defect formation and ion migration, as well as phase segregation and perovskite decomposition in the active perovskite layer, resulting in both reversible and irreversible degradation mechanisms. Reversible degradation processes lead to significant performance variations during a day–night cycle, with various trends: degradation during the day/ restoration at night; or efficiency increase during the day/ degradation at night (Fig. 25a). In some studies these opposite trends were observed for the same devices at various aging stages [1]. This makes the quantitative assessment of PSC performance and stability significantly challenging. We have previously suggested the use of the daily energy output and the time needed to reach its 20% drop as alternative figures of merit for the outdoor performance and stability of PSCs [1].

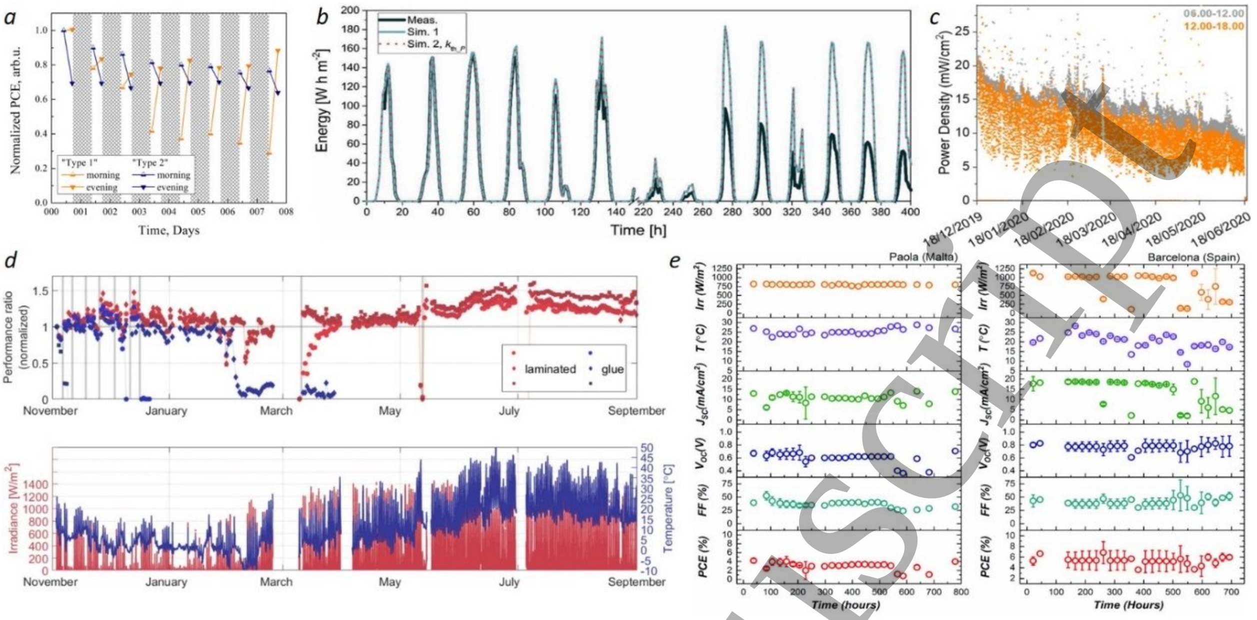

Figure 19 - PSCs outdoor measurements: (a) diurnal variations in PSC performance [1]; (b) comparison of modelled and measured power output at MPPT [2]; (c) power output of tandem devices showing reversible and irreversible degradation [4]; (d) long-term PSC performance and solar irradiance data showing seasonal changes [3]; (e) comparison of PSC output at two different locations (left: Malta, right: Spain) and climates [5]. Adapted from refs [1–5], with permissions.

19.3 Our Recommendations to Meet the Challenges

Electrical bias applied to the cells is known to have a significant effect on the PSC degradation rate and on the dominant degradation mechanisms [11]. Therefore, we recommend performing long-term outdoor studies of PSC stability at the device's MPP with continuous MPP tracking. The tracking losses should be considered and studied, including those associated with current-voltage hysteresis: static losses due to the perturbations introduced by the tracking algorithm, and dynamic ones due to the slow response to changes in the environmental conditions.

Outdoor data should be considered with respect to the time and geographical location they were obtained at. Significant conclusions can be drawn when data across multiple seasons (Figure 25c,d) and different climatic conditions is available and compared. At the moment such data is extremely rare (Figure 25e) and no conclusions were drawn on the peculiarities of PSC operation and stability with respect to particular climates. It is therefore advised to apply outdoor testing to a large number of devices and test locations, and to correlate the data with respect to the weather parameters noted above.

The comparison of outdoor data with modelled data was shown to be suitable to track the diurnal device degradation (fig. 25b) [2]. Comparison of outdoor data to the results of such modelling, using performance matrix measurements and weather data, can provide understanding of both the reversible and irreversible parts of degradation [12]. It is important to notice that reversible processes are also relevant for perovskite-based tandems (Figure 25c) [4].

19.4 Concluding Remarks

Real-world data is the most convincing proof of the technology readiness to enter the market. Therefore, we expect a rapid rise in the number of reports of PSCs' outdoor behavior in the coming years, including round-robin multiple-climates experiments. Such works will not only foster the understanding of PSCs' instabilities, but also lay the foundation for correlating outdoor lifetime with the indoor accelerated stress tests, and ultimately help to develop technology-specific qualification tests for perovskite-based modules.

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Section 20 - Environmental Impact of Perovskite Solar Cells: Life-cycle Analysis

Yana Vaynzof[1,2]
1Chair for Emerging Electronic Technologies, Technical University of Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany
[2]Leibniz-Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

20.1 Status

Life cycle assessment (LCA) is a holistic methodology that allows to evaluate the environmental, ecological and economic costs of the fabrication, use and disposal of a product. In the context of a photovoltaic module, the LCA must account for the mining of raw materials, their purification, the synthesis of new materials, manufacturing, operation, as well as the end-of-life recycling or disposal of the module's components.[1] Performing an LCA for a novel technology such as perovskite photovoltaics is complicated by the lack of data, for example regarding the lifetime of the device, its optimal architecture and costs of fabrication on a large-scale. Despite these limitations, several LCAs have already been performed to gauge the economic and environmental viability of perovskite photovoltaics. These include not only single-junction perovskite solar cells, but also several types of tandem devices such as Si/perovskite or perovskite/perovskite.[2-4] Regardless of architecture, all perovskite photovoltaic devices contain a substrate and a top metal electrode. These components are generally considered to be major contributors to both the embedded material and energy costs within the module. Glass - very commonly used as the solar cell's substrate - constitutes over 95% of the weight of the module, while rare metals such as Au or Ag (used as the top metal electrode) can account for up to 85% of the total embedded energy.[5] Future advances in replacing these materials with other alternatives would significantly reduce the primary energy consumption as well as other types of impacts.

Considering that perovskite materials can be deposited either by solution- or by vapor-processing,[6] several LCAs focused on comparing the impacts of both deposition methods.[7-8] It was found that generally both approaches lead to a similar impact, despite important differences in individual categories: solution processing led to higher impacts in acidification and eutrophication, human and water toxicity due to the extensive use of solvents, while deposition by vapor method led to higher electrical energy consumption for the deposition under vacuum. Since these studies were predominantly based on data for small area devices, significantly more technological advances in upscaling perovskite layer fabrication are required in order to be able to truly assess which deposition method is preferable.

20.2 Current and Future Challenges

One of the key difficulties in performing an LCA of perovskite photovoltaics is the lack of reliable data to be used for analysis, resulting in the necessity to incorporate various assumptions into the evaluation. Two recent reviews examining the existing literature of perovskite solar cell LCAs highlight this issue. For example, Leccisi and co-workers found that the reported primary energy consumption varied by over three orders of magnitude for similar perovskite compositions and deposition methods.[9] Similarly, a recent review by Vidal and colleagues reported that unlike other thin film technologies (e.g. a:Si, CdTe and CIGS), the spread in the reported global warming potential (GWP), cumulative energy demand (CED) and the estimated energy payback time (EPBT) vary greatly between different reports on perovskite single junction as well as tandem solar cells (**Figure 26**) making a meaningful comparison to other technologies very speculative.[10]

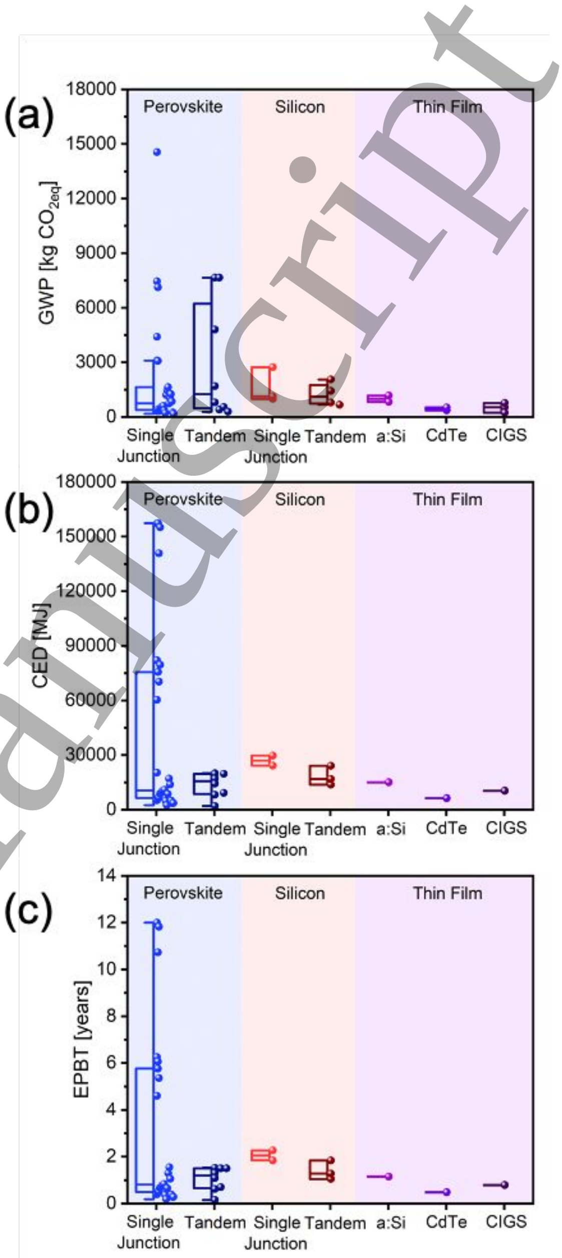

Figure 20 - (a) GWP and (b) CED compared for 1 kWp (c) EPBT. Adopted with permission from Ref 10.

Both reviews conclude that the assumptions made regarding the upscaling of perovskite modules from lab-scale to industrial scale are the key source for the discrepancies observed in the different LCAs. Interestingly, the only available LCA performed at an industrial scale led to very promising results with a CED of 3613 $MJkWp^{-1}$ and a short EPBT of only 0.28 years.[11] This highlights that the key challenge to be addressed in the context of LCA of perovskite photovoltaics is in the optimization of the large-scale deposition processes for the perovskite active layers. Indeed, the ideality coefficient (IC) - defined as the % ratio of the environmental impact of an ideal process to the existing one - is estimated to be <0.1% for the deposition of perovskite layers.

Another challenge that requires attention is the use of certain materials in the perovskite device structure that introduce significant material, energy and environmental costs. For example, the very commonly used hole-transporting layer (HTL) Spiro-OMeTAD introduces significant environmental costs due to its complex synthesis, purification and the common use of dopants to enhance its conductivity.[Error! Bookmark not defined.-Error! Bookmark not defined.] This can be addressed by using a more environmentally friendly HTL material or by exploring HTL-free device architectures. Similarly, commonly used electron transporting layers, such as metal oxides or organic materials, are also associated with high costs and need to be optimized,[Error! Bookmark not defined.] not only in terms of their impact on device performance and stability, but also in terms of their impact on the LCA of perovskite photovoltaics. Finally, as already mentioned above, the use of rare metals as electrode materials in perovskite solar cells is highly disadvantageous. Some LCAs suggest that the use of Au electrodes represents am 85% of the total embedded energy[5] and that its replacement would reduce many of the environmental impact categories by up to 90%.[12]

20.3 Advances in Science and Technology to Meet Challenges

To address the challenges outlined above, the focus of perovskite photovoltaics community should shift from predominantly optimizing the device power conversion efficiency towards the development of more sustainable, large-scale device architectures. In particular, while spin-coating is utilized by the vast majority of perovskite researchers due to its simplicity and wide-scale availability,[6] it is highly unlikely to be scalable, considering that roughly 90% of the material is wasted in this process. This exemplifies that significantly more research has to be dedicated to scalable deposition methods, including for example, thermal evaporation or blade-coating. In this context, lessons could be learned from other emerging photovoltaic technologies which have already undergone the transition to the market. For example, similarly to perovskite photovoltaics, the vast majority of academic research in the field of organic solar cells is dedicated to devices fabricated by solution-processing, but among the most successful examples of industrial application of organic solar cells are devices fabricated by thermal evaporation (e.g. Heliatek, Germany). Significantly more research and new comparative LCAs that evaluate the impacts of both deposition techniques on an industrial scale are needed to identify if this will also be the case for perovskite photovoltaics.

The advancements in the development of scalable deposition techniques for perovskite active layers have to be complemented by further optimization of the other layers in the device structure, such as charge transport layers and electrodes. Importantly, their development cannot be achieved independently, since the properties of perovskite materials can be strongly impacted by choice of extraction layer on top of which the perovskite active layer is deposited. This suggests that once novel, particularly promising and environmentally-friendly charge extraction layer materials are identified, the focus of scalable perovskite processing optimization should lie on the use of specifically these materials. In the case of metal electrodes, a particularly promising strategy is their replacement with carbon-based electrodes. While these electrodes can be deposited at low temperature and are significantly less costly than those made from rare metals, the efficiency of perovskite solar cells with such electrodes is rather moderate, and significantly more research is required to demonstrate that state-of-the-art, high efficiency devices can be fabricated using carbon-based electrodes.

20.4 Concluding Remarks

In summary, several challenges are yet to be addressed in the context of LCAs of perovskite photovoltaics. On the methodological side, the lack of data and the need for certain assumptions make perovskite solar cell LCAs very difficult to compare, since widely varying results are often reported for very similar devices. This can be addressed by further advancing the scalable deposition processes for perovskite solar cells, which would enable the use of reliable costs associated with this process in the LCAs. Moreover, new materials, in particular for charge extraction layers and electrodes, need to be identified and investigated, since these are often recognized to be major contributors to environmental costs. Despite these challenges, certain LCAs suggest that perovskite photovoltaics is highly competitive with respect to other technologies, including the long-established silicon solar cells. These suggest that with further advancements, this technology has a strong potential to enter the market as an efficient and more sustainable alternative.

20.5 Acknowledgements

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Section 21 - Environmental Impact of Perovskite Solar Cells: Use of Green Solvents

Rosario Vidal
Department of Mechanical Engineering and Construction, GID, Universitat Jaume I, Castelló, Spain

21.1 Status

The deposition of the perovskite layer by solution is a strength for the expansion of this technology due to its potential low cost and lower environmental impacts, as it requires less energy consumption. However, the toxicity to human health and the environmental impacts of solvents are important aspects that deserves attention.

N,N-dimethylformamide (DMF), the most widespread solvent used for the deposition of perovskite layer, is included in the Candidate List of Substances of Very High Concern (SVHC), as part of Regulation by the European Chemical Agency (ECHA). The objective of this authorization process is to ensure that less hazardous substances or technologies, which are technically and economically feasible, progressively replace SVHCs. Moreover, DMF and other polar aprotic solvents used for perovskite deposition, such as N,N-dimethylacetamide (DMAC) and N-methyl-2-pyrrolidone (NMP) are toxic to the human reproductive system. Other more favorable solvents such as gamma-butyrolactone (GBL), acetonitrile, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1H)-one (DMPU) and tetrahydrofuran (THF) are labelled “dangerous”. In addition, DMPU is labelled potentially toxic, THF as potentially carcinogenic and DMSO is not classified. Other solvents used as anti-solvents or for the deposition of another layers, e.g. toluene, diethyl ether, 2-methoxyethanol, etc., may also be of concern, although they are outside the scope of this section.

The greenest solvent is the solvent that is not used [1]. Since this is not possible, efforts are needed to minimize their environmental footprint. This includes both minimizing the amount and minimizing the impacts across the life cycle (LCA). Potential green alternatives include solvent mixtures of the above polar aprotic solvents, but also other possible formulations such as PolarClean, methylamine+acetonitrile, γvalerolactone, 1,3-dimethylimidazolidin-2-one (DMI), etc. However, before large-scale industrialization of perovskite, a comprehensive LCA, including use, recycling and solvent disposal, is still needed.

21.2 Current and Future Challenges

Hamill et al. [2] demonstrated the Gutmann's donor number [3] (DN) as a viable parameter to indicate the coordinating ability of a solvent with the Pb^{2+} center of perovskites. Different alternatives to toxic polar aprotic solvents are screened, either pure or mixtures, based on the DN or related such as Mayer bond unsaturation order and Kamlet parameters, in conjunction with properties such as vapor pressure, boiling point, lower explosive limit (LEL), molecular size or Hansen solubility. However, there is still much room for improvement to fully understand the role of solvents as ligands, retarding the reaction rate, controlling the nuclei/growth, coarsening grains for preparing high-quality perovskite film. A thorough understanding of the multiplicity of roles during perovskite film formation will help to understand the mechanism of perovskite film formation [4] and will open the door to select green solvents. This challenge is the core of Figure 27.

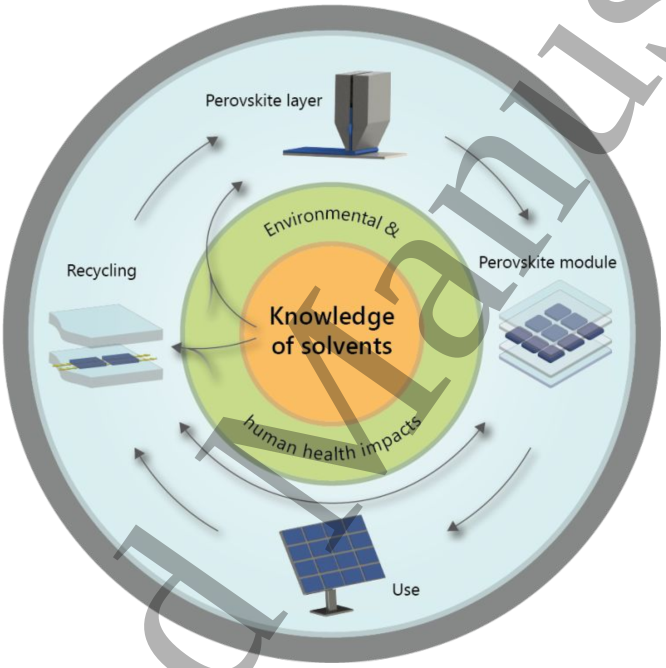

Figure 27 - Challenges for perovskite photovoltaics circularity: 1. Understanding of solvent role in perovskite film formation. 2. Updating and extending our knowledge of their environmental impacts.

For perovskite photovoltaics circularity, a proper end-of-life is essential to avoid the lead leachates and to recover valuable components, such as the substrate and the electrodes. DMF is the solvent most used for the removal of the substrate. Other solvents are alkylamines, chlorobenzene chloride and ethylene glycol (DES), etc. The same solvent used to separate the substrate often dissolves the perovskite layer. In other cases, polar aprotic solvents, mainly DMF, are used. However, in this case it is easier to select green solvents, focusing mainly on solubility, boiling point and LEL.

Whether for the deposition of perovskite or for the recycling of modules, it is essential to consider the LCA of the solvent, i.e. its manufacture from raw materials, the application of the solvent and its recycling or safe disposal, avoiding evaporation or wastewater once applied. Updating and extending our knowledge of their environmental impacts is another challenge, second ring of Figure 27. New or updated toxicity characterization factors for solvents and for perovskite precursors are essential to properly perform LCAs.

For this purpose, fate and exposure models based on available toxicity data from ECHA, U.S. EPA, etc. could be applied.

21.3 Advances in Science and Technology to Meet Challenges

A starting point of how to accomplish a LCA of solvents is recently tested for eight polar aprotic solvents: DMF, DMSO, DMAC, NMP, DMI, GBL, THF and DMPU [5]. The environmental impacts affecting human health are plotted in Figure 28, comprising the full life cycle of the solvents. The human health environmental impacts include human toxicity, global warming, particulate matter and other impacts (stratospheric ozone depletion, ionizing radiations, ozone formation and water consumption). Clearly, the circular scenario (C), in which the solvent is recycled, is more advantageous than the linear scenario (L), in which the solvent evaporates after film deposition. The only exception is THF.

Human toxicity characterization factors are obtained by applying fate and exposure models with available data published in the ECHA, with which USEtox [6], the best available model for characterizing human health toxicity of chemicals, is modified. As a result, DMF is the solvent with the largest human toxicity characterization factor followed by DMAC (coincidently, both are SVHC). However, when considering the entire life cycle, the most impactful is NMP, both for human toxicity and total environmental impacts affecting human health, because manufacturing is energy-intensive.

Figure 28 highlights the comparatively lower human environmental impacts of DMSO during the full life cycle, which is in good agreement with recommendations in other sectors, although DMSO does present its own challenges.

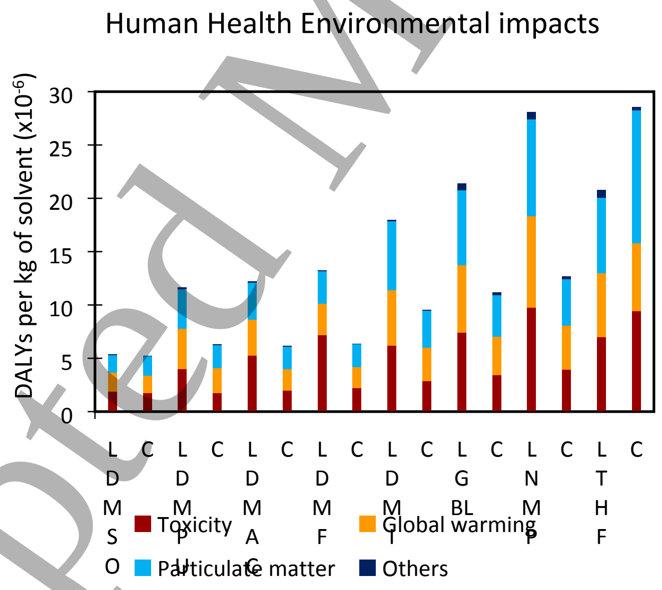

Figure 28 - Life cycle assessment of eight aprotic solvents for perovskite film manufacturing with evaporation or linear scenario (L) and solvent recycling or circular scenario (C), data in [5]. USEtox is modified for human toxicity impacts. The rest of impacts are obtained from ReCiPE 2016

This work [5] should be considered a roadmap to further develop less harmful solvent systems. Recently, new strategies to tune the interactions between the solvate and the solute, in order to optimize the nucleation and crystallization dynamics during the film formation, are proposed, for example mixing PbS quantum dots into the perovskite solution in pure DMSO [7]. Also noteworthy are the promising results of DMSO/2-butoxyethanol [8] and acetonitrile/methylamine [9] in roll-to-roll processes.

21.4 Concluding Remarks

Future work in the field of perovskite photovoltaic should take into consideration the possible environmental impact of the solvents used to become a viable alternative "green" energy technology. A thorough understanding of the multiplicity of roles during perovskite film formation will help to understand the mechanism of perovskite film formation and will open the door to select green solvents. In addition, we need to update and extend our knowledge of their environmental impacts of solvents. A starting point of how to accomplish a comprehensive assessment of the solvents is recently tested for eight polar aprotic solvents used for perovskite layer deposition. Among these, DMSO promises low environmental impacts on a large scale but must be optimized for achieving suitable performance parameters such as power conversion efficiency and module stability.

21.5 Acknowledgements

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Section 22 - Environmental impact of PSCs – lead-containing vs. lead-free

Guicheng Yu, Haoran Lin and Shuchen Weng
Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, Shenzhen 518000, China

22.1 Lead-free and lead-less perovskites materials for solar cells

1.1 Isovalent element substitution strategy:

In principle, other less toxic, environmentally benign metals can replace lead. Tin and germanium are the intensively investigated alternatives because they share similar chemical properties with lead as group VI elements. Krishnamoorthy and his colleague firstly reported germanium-based $AGeI_3$ (A=Cs, MA) perovskite solar cells (PSCs) in 2015 with a power conversion efficiency (PCE) of 0.2%.[1] Pure inorganic tin halide PSCs, $CsSnX_3$ (X=Cl, Br, I), were proposed by Chen et al. with a PCE of 12.96% and impressive water stability.[2] Although Ge/Sn or mixed elements-based solar cells developed rapidly, their PCE are generally still below 10%, far behind that of the Pb-based analogs.[3-4] Also, the rapid oxidation of Sn and Ge from +2 to +4 determined by their high energy s orbitals questions their long-term stability in practical devices. On the other hand, the bandgaps of Sn/Ge-based perovskites are usually higher than the ideal bandgap for single-junction solar cells (1.34eV). Moreover, Sn and Ge-based perovskites possess lower enthalpy, lower defect formation energy, leading towards faster film growth, poor film morphology, and therefore more defect formation and high carrier recombination.[5] The poor film morphology results in a reduction in the filling factor (FF) of the PSCs, which ultimately gives rise to an underperforming PCE. Lastly, with eco-friendly elements compositions, chalcogenide perovskites based solar cells are promising candidates with their high resistance to water and temperature.[6] In 2016, $BaZr_{0.75}Ti_{0.25}S_3$, reported by Meng and his teams, has a bandgap of 1.43eV that almost reached Shockley–Queisser limit.[7] Recently, Wei et al. fabricated n-type $BaZrS_3$ thin films by plasma laser deposition. And these films are great light absorber with absorption coefficient > 10^5 cm^{-1} under 2eV photon test condition.[8] Although chalcogenide perovskites were predicted to have amazing theoretical PCE for single junction solar cells, few satisfying devices were reported due to the lack of valid film processing methods.

1.2 Heterovalent elements substitution strategy:

Double perovskite, another lead-free derivative with a chemical formula of $A_2M(I)M(III)X_6$, has monovalent M^+ and trivalent M^{3+} ions alternatively replacing lead in the perovskite structure. The vacancy-ordered double perovskites $A_2\square M(IV)X_6$ and $A_3\square M_2(III)X_9$ (□ stands for vacancy) with reduced-dimensional structures sometimes are also regarded as heterovalent derivatives of conventional lead-based perovskites. Practical double perovskite solar cells were first prepared by Greul et al. in 2017 which unveiled reasonable degradation resistance and exhibited a PCE of 2.43%.[9] Considering the structural versatility of double perovskites, researchers evaluated their light-absorbing properties using theoretical calculations and found that several double perovskites such as $Cs_2AgInBr_6$, $RbCuInCl_6$, $Cs_2InSbCl_6$ have direct bandgap and high theoretical maximum PCE for solar cell applications.[10] Lab-scale double perovskite solar cell devices to date mainly focused on $Cs_2AgBiBr_6$ and $Cs_2AgInCl_6$ material systems due to their good processability and stability.[11] Vacancy-ordered double perovskite solar cells are also developed using Cs_2SnI_6, Cs_2TiI_6, $Cs_3Bi_2I_9$, $MA_3Bi_2I_9$ and $MA_3Sb_2I_9$ materials.[12] Nevertheless, none of these devices has a PCE exceeding 4%, which is not attractive for single-junction solar cell applications at this point. The poor photovoltaic performance of these double perovskites could be attributed to their indirect bandgap and the parity-forbidden transition effect, which result in poor optical absorption. In most of these materials, intrinsic defects would introduce deep levels in the bandgap, which is another factor accounting for their inferior performance.[13] Significant efforts have to be made on band structure manipulation, defect suppression and transporting layer optimization before the potential breakthrough may occur.

1.3 Lead-less strategy:

Lead-free PSCs solved toxicity issues of lead at the cost of their photovoltaic performance, hence the commercialization opportunity was hindered. One possible solution was to find a balance between toxicity and efficiency by lowering lead usage in PSCs via Sn/Ge substitution.[14] This strategy has serval advantages: first and foremost, reduced lead content would reduce toxicity to meet the strict environmental standard. Secondly, doped Sn/Ge can be stabilized in its bivalent state, improving the device stability under ambient conditions. Thirdly, the bandgap of PSCs can be readily tuned to the optimized value for solar cells (1.34 eV) by alternating the lead content. **Table 1** summarized some of the less lead PSCs in the past 10 years. As shown, the percent of lead content gradually decrease while the photovoltaic parameters remained close to pure lead PSCs.[15]

Table 1. Photovoltaic parameters of less lead perovskites solar cells.

Perovskites	**Pb content [%]**	**V_{OC} [V]**	**J_{SC} [mA/cm^2]**	**FF [%]**	**PCE [%]**	**Year**
$CsPb_{0.9}Sn_{0.1}IBr_2$	90	1.26	14.3	63.0	11.33	2017
$MAPb_{0.75}Sn_{0.25}I3$+0.05mg/mL C_{60}	75	0.736	23.5	79.0	13.7	2017
$FA_{0.7}MA_{0.3}Pb_{0.7}Sn_{0.3}I_3$+12%GABr+0.03mmol SnF_2	70	1.02	26.61	76.0	20.63	2020
$FAPb_{0.5}Sn_{0.5}I_3$+ 10mol% SnF_2	50	0.782	28.1	73.0	16.27	2018
$(FASnI_3)_{0.6}(MAPbI_3)_{0.34}(MAPbBr_3)_{0.06}$+10mol% SnF_2	40	0.888	28.72	74.6	19.03	2018
$CsSnI_3$	0	0.86	23.2	65.0	12.96	2016

2. Toxicity

Lead compounds are undoubtedly toxic, and toxicology of lead has been well established. Lead enters the bloodstream through ingestion, inhalation or dermal contact. Even a small concentration of lead in blood is accused to have reproductive toxicity, neurotoxicity, carcinogenicity and is harmful to blood pressure, renal function, immune system and so on.[16] For perovskite solar cells, in case of device failure, water systems are the most vulnerable to lead toxicity when compared with the soil system.

Tin toxicology is more complex and not understood thoroughly. There are some evidence showing that tin could be inhaled and accumulate in blood and skeletal sites, causing genotoxicity, carcinogenicity, and reproductive defects.[17] When tin was released to the environment, its toxicity may decrease instead due to its oxidation to the insoluble SnO_2 compound. On the contrary, germanium is believed to have low or no toxicity to human. Therefore, it is widely used in pharmacy, cosmetics, semiconductors, and nanotechnology. Nevertheless, recent studies suggest organic germanium may have negative impact on human health and environmental systems to some extent.[18]

Within the elements utilized in the double perovskite solar cells, silver is considered as nontoxic to human beings that tableware is made by silver from ancient times. The toxicity of bismuth is controversial. On the one hand, bismuth is classified as nontoxic heavy metal that can be entirely metabolized from the body within a satisfactory time. So that the Bi (III) compounds have been used in the medical field for many centuries. On the other hand, some research suggest that bismuth may induce slight cytotoxicity in kidney and chronic diseases.[19] It would be safer to further investigate the toxicity of bismuth before a firm conclusion is drawn. For antimony compounds, inhalation exposures could cause respiratory irritation, pneumoconiosis, antimony spots on the skin and gastrointestinal symptoms.[20] Toxicity of indium lead to indium-related lung disease when inhaled by human.[21] It should be handled with cautious on the fact that some semiconductors such as ITO (indium tin oxide) and InP are widely used in optoelectronic devices. The copper is also known to have neurotoxicity and aquatic toxicity despite its excessive usage in different forms.[22] Titanium is considered as a bio-inert material that is used commonly for implants but, in rare cases, health issues were also reported.[23]

In summary, most of these elements designed to substitute lead are toxic to some extent. Even the elements regarded as “bio- and environmental-safe” (Ge, Bi, Ti) also have negative reports in some cases and require for further investigation. Although we have good intention to eliminate the negative environmental impact of lead, whether the newly introduced substituents are capable remain questionable in the aspect of toxicity.

3. Cost and environmental assessment of lead-free perovskite solar cells

3.1 Abundance

Mineral paragenesis is common in nature. Lead, in the form as the Galena (PbS) or the Cerussite ($PbCO_3$), usually coexists with zinc ores. Bismuthinite (Bi_2S_3) and silver ores are prone to coexist with metallic mines such as lead or zinc ones. Some of these ores are relatively easier to be purified with valuable by-products. However, Cassiterite (SnO_2) as one of the major ores of tin, is always found along with arsenic mines. The hazardous arsenic by-products may cause severe problems to the environment and human health near the minefield. Also, mineral paragenesis means the production of the low content elements in ores is subject to the production capacity of the high content product.

Despite the paragenesis, germanium and antimony, which belong to the “disperse elements”, are with high abundance and scattering distribution. In other words, more energy and water are required for the concentration and extraction processes of these metallic products.

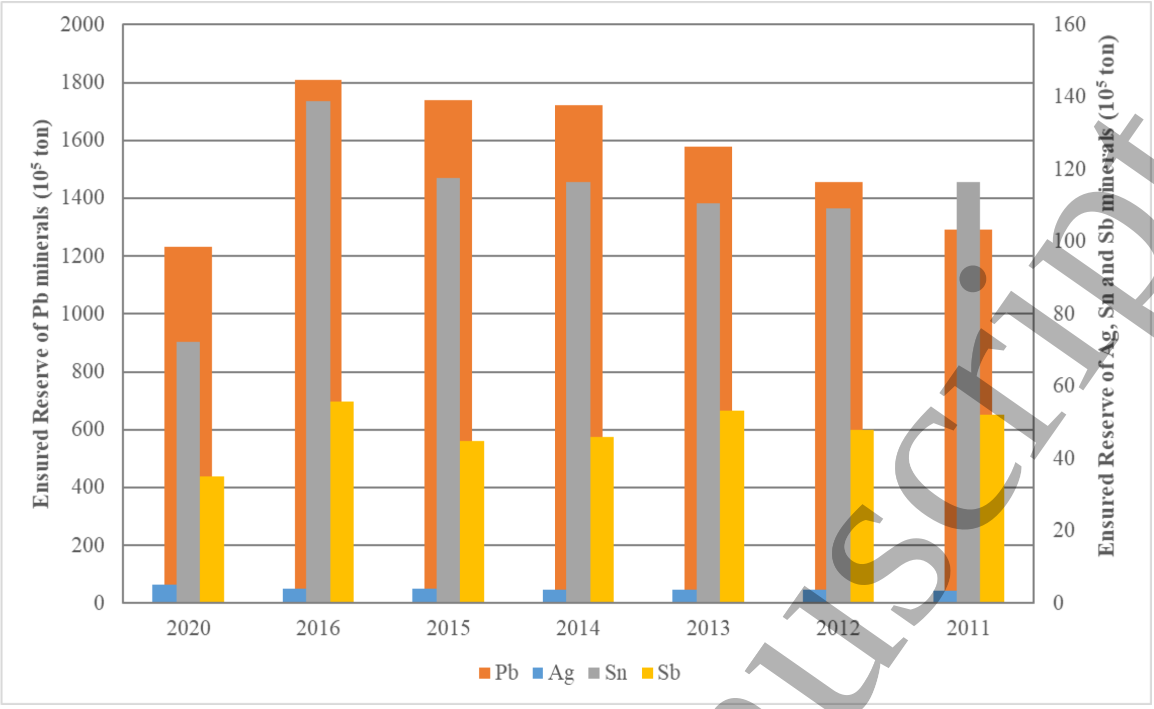

Figure 29. Annual mineral base reserves of lead, silver, tin, and antimony from 2011-2016[24] and in 2020[25], mainland China.

Figure 29 shows that the ensured reserve of minerals follows the trend of Pb>Sn>Sb>Ag in 2011-2016 and 2020 in mainland China. For the elements (Bi, In, Ge) not listed on the figure, they have even lower annual production than silver (<20000 tons per year). A low abundance or high degree of dispersion of an element usually results in a high energy refinement process, high production cost and high environmental impact potential.

3.2 Cost of production

Since the lead-free perovskite solar cell technology is far from mature, only several reports of tin-based solar cells have gone through Life Cycle Assessment (LCA). **Table 2** demonstrates and compares the LCA parameters of some of the lead-based and tin-based PSCs from the previous studies. According to the LCA results, the mass of these raw materials to produce 1 kWh electricity for the module can be calculated and are listed in the table and graphed in **Figure 2**.

Table 2. Comparison of Lead-based PSCs and Tin-based PSCs from the recent studies.

Metal	**LCA study**	**Material**	**PSC structure**	**Pb/Sn Inventory[d] (kg/kWh)**	**Corresponding compounds and cost (¥/kWh)**		**GWP[a,d] (Kg CO$_{2\text{-eq}}$/kWh)**	**EPBT/year**	**Efficient area/%**	**Module convers. efficiency/%**	**PR[a]**	**LT[a]/year**
Pb	Ramamurthy Rao et al., 2021[26]	NP[a,]	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	1.24E-04	PbBr$_2$/PbI$_2$	46.58	$0.18^{+0.17}_{-0.08}$	$0.97^{+0.78}_{-0.41}$	NP	17.6	0.85[b]	3
Pb	Zhang et al., 2017[27]	MAPbI$_3$	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	2.04E-04	PbI$_2$	76.59	2.63	0.9-3.5	60	20[c]	0.75	1
		FAPbI$_3$	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	2.16E-04	PbI$_2$	75.93	3.18	0.9-3.5	60	20[c]	0.75	1
		CsPbBr$_3$	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	2.03E-04	PbBr$_2$	76.48	6.78	0.9-3.5	60	20[c]	0.75	1
		MAPbI$_2$Cl	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	9.06E-05	PbCl$_2$	9.17	3.56	0.9-3.5	60	20[c]	0.75	1
Pb	Celik et al., 2016[28]	MAPbI$_3$	FTO/SnO$_2$/perovskite (SC[a])/CuSCN/MoO$_x$/Al	1.74E-06	PbI$_2$	0.65	0.15	1.30[c]	65	15	0.75	5
		MAPbI$_3$	FTO/SnO$_2$/perovskite (VD[a])/CuSCN/MoOx/Al	2.16E-06	PbI$_2$	0.81	0.18	1.55[c]	65	15	0.75	5
		MAPbI$_3$	FTO/SnO$_2$/perovskite (HTL free)/c-paste	1.74E-06	PbI$_2$	0.65	0.12	1.05[c]	65	15	0.75	5
Pb	Gong et al., 2015[29]	MAPbI$_3$	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	1.75E-06	PbI$_2$	0.66	0.08	0.27±0.0542	70	9.1	0.8	2
		MAPbI$_3$	ITO/ZnO/perovskite/S-OMeTAD/Ag	1.45E-06	PbI$_2$	0.54	0.06	0.20±0.0392	70	11	0.8	2
Pb	Espinosa et al., 2015[30]	MAPbI$_3$	FTO/TiO$_2$/perovskite/S-MeOTAD/Ag	5.23E-06	PbCl$_2$	0.53	5.48	17.32	NP	15.4	0.8	1
		MAPbI$_3$	ITO/PEDOT: PSS/perovskite/PCBM/Al	9.07E-06	PbCl$_2$	0.92	5.24	16.54	NP	11.5	0.8	1
Sn	Zhang et al., 2017e[27]	MASnI$_{3\text{-}x}$Br$_x$	FTO/TiO$_2$/perovskite/S-OMeTAD/Au	4.09E-04	SnI$_2$/SnBr$_2$	335.00[e]	6.75	0.9-3.5	60	5[c]	0.75	1
Sn	Serrano-Lujan et al.,2015[31]	MASnI$_3$	FTO/TiO$_2$/perovskite+TiO$_2$/S-MeOTAD/Au	6.11E-04	SnI$_2$	572.48	10.70	NP	NP	6.4	0.8	1

[a] Abbreviation for **0**:GWP: Global Warming Potential (kg CO$_{2\text{-eq.}}$/kWh); PR: Performance Ratio; LT: Lifetime; NP: not provided; SC: solution-based: VD: vacuum-based.

[b] 0.75 is used in Southern Europe and 0.95 is used in the US. The average of the two is chosen.

[c] Not given by the author, recalculating according to Celik et al.[28], Serrano-Lujan et al and Zhang et al in this review.

[d] Some researchers including Zhang, Celik, Gong and their colleges mentioned in this review chose a unit area (1cm^2 or 1m^2) as the functional unit for the LCA, others chose 1 kWh electricity production. To compare the difference between Lead-based and Lead-free perovskites, we exchange all data in functional unit 1cm^2 or 1m^2 into 1kWh according to the Equation 1.[28]

$$Impact_{kWh} = \frac{Impact_{m^2}}{I \times \eta \times PR \times LT} \quad (1)$$

where, I=insolation constant, assigned as 1700 kWh/m^2-year in this paper （except the one calculated by Ramamurthy Rao et al with 1513.5 kWh/m^2-year）, η=module efficiency (%), PR=performance ratio of the module (%), LT=lifetime of the PV (year)

[e] The author didn't provide the ratio of SnI_2 and $SnBr_2$. Since the purity of $SnBr_2$ regent from the suppliers is not high enough, we assumed the SnI_2 with high concentration and therefore used the price of SnI_2 for the calculation.

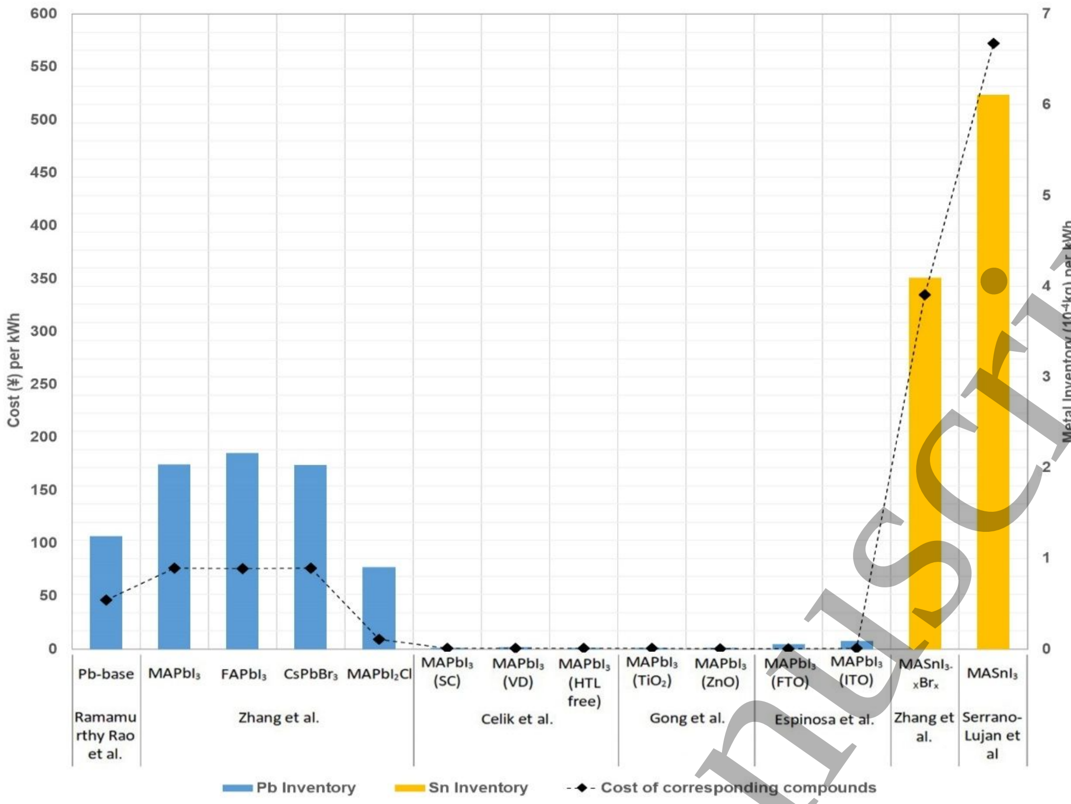

Figure 30. Comparison between the cost of lead-based PSCs and tin-based PSCs. The mass inventory (blue histograms for lead and yellow ones for tin) in these PSCs have been recalculated in kg/kWh electricity the module produced in the assigned lifetime, according to the mass inventory provided by the corresponding researchers and **equation 1**. The cost for the raw materials containing Pb or Sn (black rhombus) is calculated by the mass of these raw materials times the average prices listed in **Table 3.**

Generally, when the PSCs are still in the lab scale, the fabrication cost comparison between lead-based and lead-free PSCs can be simplified as the comparison between the cost of raw materials, with the premise that the fabrication process is similar for both devices. Price of high-purity PbX_2 (X=I, Cl, Br) and SnX_2 (X=I, Br) are collected from the regent suppliers (Aladdin, Sigma-Aldrich, and Alfa Aesar, **Table 3**) and the average prices are used to calculate the production cost of raw materials in lab-scale, demonstrated as the black rhombus marks in **Figure 30**.

Table 3 Price of raw materials provided by three main suppliers in December 2021.

Material	**Price from suppliers (¥/100g*)**			**Average price (¥/100g)**
	Aladdin	Sigma - Aldrich	Alfa Aesar	
PbI_2	6,729 (Anhydrous, 99.999%, metal basis)	36,300 (Perovskite grade, 99.999% metal basis)	7,478 (Anhydrous, 99.999%, metal basis)	16,836
$PbCl_2$	5,098 (Anhydrous, 99.999% metals basis)	11,790 (AnhydroBeads™, 10 mesh, 99.999%)	5,672 (Anhydrous, 99.999% metals basis)	7,520
$PbBr_2$	3,584	27,993	32,160	21,246

	(99.999% metals basis)	(Anhydrobeads™, 99.999% metals basis)	(Anhydrous, 99.999% metals basis)	
SnI_2	23,836 (Anhydrous, 99.99% metal basis)	39,204 (10 mesh, 99.99% metal basis)	26,472 (Anhydrous, 99.999%, metal basis)	29,837
$SnBr_2$	3,596 (99%)	- -	4,096 (99.20%)	3,846

*Calculate by the price with the maximum package the regent suppliers offered online. The price may be lowered with a mass demand.

From **Figure 2**, the mass inventory of lead used in lead-based PSCs is under 2.5×10^{-4} kg/kWh, while those for tin-based PSCs can be above 6×10^{-4} kg/kWh in maximum. Since the tin-based PSCs are with higher raw material prices and lower module efficiency (**Table 3**) compared with the lead-based ones, their fabrication cost increment brought by raw materials can be a maximum of three magnitudes higher when producing 1 kWh electricity.

3.3 Global warming potential and energy payback time

The global warming potential (GWP) of the PSCs can be quantified by the mass of equivalent CO_2 per kWh electricity production. We plot the GWP of different PSCs with and without lead in **Figure 31**. Lead-based PSCs are with GWP from 0.06-6.78 kg $CO_{2\text{-eq.}}$/kWh, the lead-free counterparts with SnI_2/$SnBr_2$ or pure SnI_2 as raw materials, however, own relatively higher GWP of 6.75 and 10.70 kg $CO_{2\text{-eq.}}$/kWh, respectively.

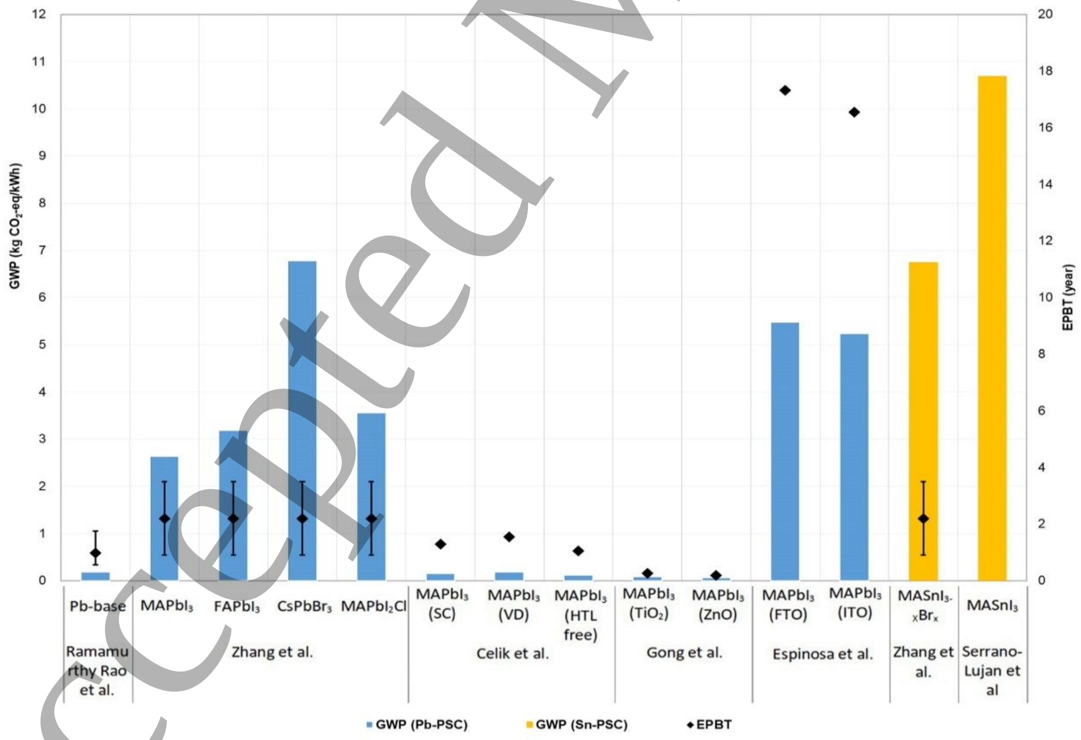

Figure 31. Comparison of GWP and EPBT data from previous studies. The GWP (blue histograms for lead and yellow ones for tin) have been recalculated in kg/kWh electricity the module produced in the assigned lifetime, according to the **equation 1**. The lifetime selection and other parameters are

shown in **Table 2**. The EPBT (black rhombus) and their deviations are provided by the corresponding researchers. Serrano-Lujan et al. do not provide the EPBT data in their research paper, so these data are remained blank in the graph.

Energy payback time (EPBT, year) values the required time for a system to recover from the energy consumption of a certain module.[26] The EPBT results of PSCs mentioned above are listed in **Table 2**. Zhang et al. gave the range of EPBT in 0.9-3.5 years in their research,[27] while Gong's are with merely 0.25 and 0.30 years,[29] respectively. The EPBT of Pb-PSCs can be as high as 17.32 years in this table, which should be corrected to around 1 year by selecting different criteria as suggested by Espinosa et al.[30] Since Serrano-Lujan et al. does not provide the EPBT of their tin-based PSC, however, we can assume that with a relatively higher energy consumption during the fabrication process and lower module efficiency compared with lead-based PSCs, a longer EPBT for tin-based PSCs will be reasonable.

Concluding remarks

To conclude this section, lead-free perovskite based solar cells are still lagging far behind lead-containing solar cells, not only because of their mediocre PCEs, but also because of their observable toxicity, low material abundance, high production cost and high environmental impact during material production and device fabrication. It seems that, at this point, lead-based PSCs are more feasible for mass production and industrialization. And rather than developing new lead-free alternatives, encapsulation and recycling of lead-based solar cells are more feasible and reliable ways in reducing the environmental impact of lead.

Acknowledgement

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Section 23 - Environmental Impact of Perovskite Solar Cells: Safe-by-design Devices and Lead Sequestration

Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong

23.1 Status

Despite of high PCE of lead-based PSCs, stability and hazardous environmental impacts of PSCs have been challenging factors for their scalable industrial production for commercialization since the degradation of the perovskite not only results in reduced PCE but also in releasing toxic components into the environment [1]. Lead (Pb) is the essential part of PSCs with high PCE and high stability. Thus, exposure of PSCs to elevated temperature, humidity, oxygen, and UV light causes degradation and production of soluble PbI_2 or $PbBr_2$ with water solubility product constant (K_{sp}) of 10^{-8} which is much larger compared to other heavy metals compounds (e.g., CdTe < 10^{-34}), resulting in increased bioavailability and therefore increased toxicity. While addressing the environmental impact of PSCs, it is of great importance to estimate the amount of Pb in the fabricated PSC device and amount of lead compounds released to the environment after degradation, and the amount of bioavailable lead [2]. The amount of Pb in the PSCs devices has been calculated to ~0.4 g/m^2 if the planar absorbing layer of methylammonium lead iodide (MAPI) is having 300 nm thickness [3]. To produce MAPI-based PSCs with PCE of 25%, it has been estimated that ~160 tons of Pb will be needed yearly to meet the electricity demand of USA considering an energy intensity of 38 μg/kWh [4]. Besides PSC modules, monitoring the use of Pb in the electronic solders is very important to address environmental impact of PSCs. It has been reported that 6200 tons of Pb content of electronic solder including commercial photovoltaic (PV) panels was required annually in 2012 [4]. Different Pb emission sources in US have been summarized in the Figure 32. Thus, all commercial PV panels contain Pb in the solder, which is the reason for the exemption on the restrictions for the use of Pb in PV modules in different regulations to control the use of hazardous materials in electrical and electronic equipment. While this would technically allow commercialization of Pb-containing PSCs [2], an important distinction from environmental point of view is water solubility of Pb compounds in PSCs.

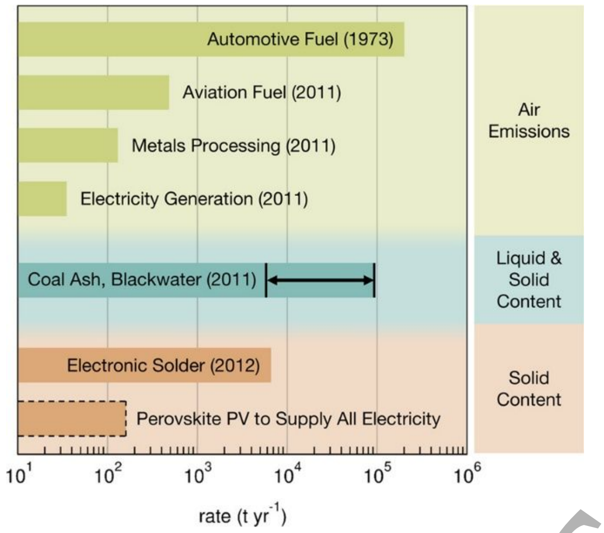

Figure 21 - Different Pb emission sources in US. Figure reprinted with permission from [4]

23.2 Current and Future Challenges

Considering the facts that perovskite solar cells contain toxic Pb, which can be released into the environment in water soluble form (lead halide compounds), alternative approaches to reduce or eliminate Pb by partial or complete replacement with other metals have failed to produce devices with competitive efficiencies and lifetime compared to Pb-based devices. Thus, current commercialization efforts are primarily concerned with Pb-based devices, therefore, it is necessary to address the issue of possible release of Pb into the environment. The release of Pb can be in the form of air-born deposits, leaching into soil with rainwater or release on complete decomposition in fire incidents. A study finds that under a 1 hour of simulated rain (1 mL/h), a non-encapsulated MAPI layer with 400 nm thickness and 3.6 cm^2 area will release 0.5 mg of Pb into the environment. The authors revealed the complete dissolution of Pb compounds under the simulated effect of rainfall with the passage of time thus increasing the Pb content by ~70 ppm of the first cm of soil under the targeted device [3]. While the PSCs are normally encapsulated to prevent degradation of their performance due to exposure to moisture and oxygen, damage of the panel (for example by hail) can still result in the discharge of Pb into the environment. Thus, an advancement in the technology of PSCs is required to minimize the amount of Pb in PSCs and control its release to the environment. Different strategies have been explored to prevent the Pb leakage from encapsulated solar cells, which typically involve the integration of lead-trapping materials within the encapsulation package, so that the encapsulation has dual purpose to both prevent the ingress of oxygen and moisture and to prevent the leaching out of Pb. While promising preliminary results have been obtained and significant reduction in lead emissions has been demonstrated, considerable further work will be needed to conclusively and extensively demonstrate the safety and effectiveness of the proposed strategies since the research on lead sequestration in PSCs is still in its infancy.

23.3 Advances in Science and Technology to Meet Challenges

Due to the need to use Pb to achieve high efficiency, safe-by-design device fabrication strategies and alternative Pb sequestration technologies are being developed to minimize the lead leakage [5-10]. One of the most safe-by-design strategy for Pb sequestration is encapsulating the PSCs devices with some suitable material which can prevent Pb leakage into the environment as well as serve as a barrier for oxygen and moisture ingress into the devices for operational stability. For example, the use of self-healing epoxy resin-based polymers with a glass transition temperature around 42 ^oC has been proposed to be used as encapsulant. The self-healing of the epoxy resin at elevated temperature can prevent water ingress resulting in the reduced Pb leakage by 375-fold as compared to UV-curable resins [5]. Few other encapsulating materials have also been reported for preventing Pb leakage such as transparent Pb-binding polymer composite films [6], built-in polymer resins [7] and Pb-sequestering iron (III) benzene tricarboxylic acid (FeBTC):poly(dopamine) (PDA) metal organic framework (MOF) polymer composites [8]. An alternative proposed approach for safe-by-design lead sequestration strategy is use of cation exchange resins (CER) as coating materials for PSC devices. The CER can be used on both sides of the PSCs package as well as on the cell electrode and prevent the Pb leakage to about 90% and reduce Pb level below the safe drinking water Pb level according to the US Federal 40 CFR 141 regulation without compromising the cell performance [9]. Recently, it has also been proposed that if monomer additives are used within the device package, which on in-situ polymerization produce Pb entrapping polymer networks, the Pb leakage can be mitigated [10]. However, further work is needed to simultaneously optimize the PSCs cell performance, operational stability, and the Pb sequestration in the outdoor environment for passing the industrial standards for commercialization.

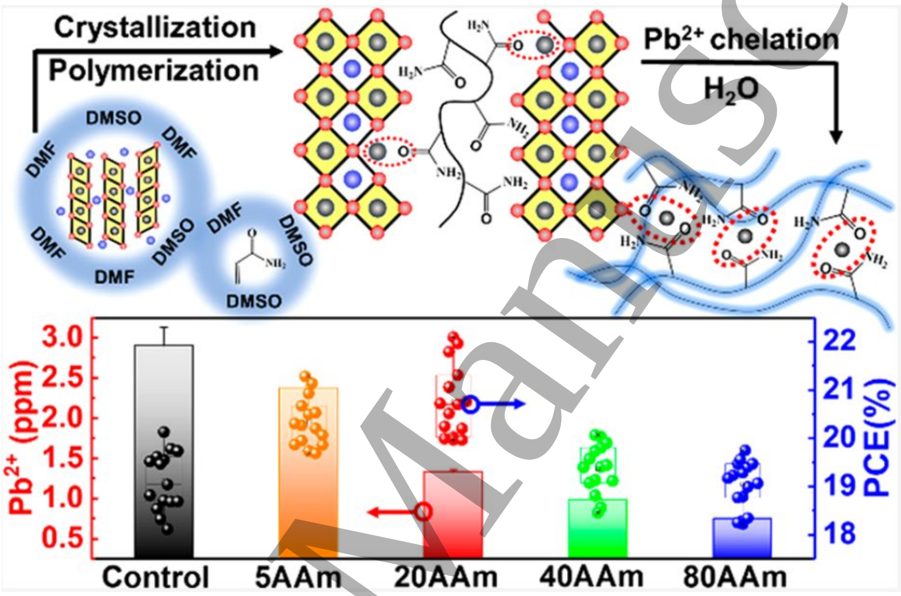

Figure 22 - Mitigating the lead leakage of high-performance PSCs via in-situ polymerized networks. Figure reprinted with permission from [10]

23.4 Concluding Remarks

The lead halide perovskite solar cells have achieved highest PCE with relatively cost-effective processing techniques; however, the leakage of Pb to the environment from the degraded PSCs has been a challenging factor for their commercialization. While impressive reductions of Pb leakage have been demonstrated since 2019 using several different approaches, lead sequestration and safe-by-design PSCs are new concepts which require further testing. In particular, it is critical to investigate whether Pb leakage mitigation is achieved under all operational conditions, including elevated temperature (~70ºC can be reached during outdoor operation) and prolonged operation. In other words, devices with packaging containing Pb-sequestration solution need to demonstrate the ability to pass standard accelerated aging tests both in terms of PCE retention as well as retention of Pb-containment capability.

23.5 Acknowledgements

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Section 24 - Environmental Impact of Perovskite Solar Cells: Recycling Prospects

Shifeng Wang
Innovation Laboratory of Materials for Energy and Environment Technologies, Tibet University, Lhasa, China

24.1 Status

With the rise in global temperature due to the increasing amount of CO_2 emissions arising from the burning of fossil fuel, carbon neutrality has become a worldwide consensus. Currently, 137 countries around the world have set carbon neutrality targets in various ways, such as policy declarations or legislation, and most of them plan to achieve carbon neutrality by 2050. To achieve these goals, emission reduction and sink enhancement are usually adopted as the two main lines. One effective and efficient approach to reducing emissions is the utilization of renewable and clean energy, among which perovskite solar cells (PSCs) have been regarded as the rising star of the third-generation solar cells [1,2] holding the great potential for efficiently delivering large scale, low-cost solar electricity.

PSCs have experienced a rapid development and attracted extensive studies since 2012 when the first solid-state PSC was reported with a power conversion efficiency (PCE) of 9.7% [3]. To date, a record reported efficiency of 25.7%, which is very close to the Shockley–Queisser limit for a single junction solar cell, was achieved by the research team from Ulsan National Institute of Science and Technology (UNIST)[4]. However, the environmental impacts of PSCs, including the use of organic solutions, the leakage of toxic metals, have been always the major concerns since the born of PSCs, impeding to some extent the commercialization and large-scale applications. For instance, Pb inside the perovskite crystal once is discharged into soil or water, it can accumulate in human bodies gravely damaging multiple body systems and causing sever heath issues.

As there is still a long way from commercialization for PSCs, a complete recycling strategy has not been developed up to now. However, investigations on the recycling technologies are drawing increasing attention by both academia and industry, such as reuse of the components and materials constituting the solar cells or modules. Actually, successful recycling solutions have been built for many other solar technologies such as silicon and CdTe solar modules, providing important practical basis and reference for PSCs recycling mechanism. Only is the environmental footprint of PSCs reduced, the large-scale applications of renewable energy can be sustainable and contribute to the carbon neutral society, and people can benefit from the clean electricity without any fears from environment pollution and contamination.

24.2 Current and Future Challenges

The challenges for recycling and recovery of PSCs can be divided into two stages, one is the manufacturing procedure, while the other is the application through their working lifetime. From the angle of reality, most of the state-of-the-art PSCs fabricated contain lead in the light-absorbing materials with a high level far exceeding the concentration limit of regulations for electronic devices, although a large number of researchers have tried to replace Pb with Sn as an environmentally-friendly alternative but suffering from severer instability and substantially lower PCE in comparison with their lead-based counterparts. Besides the Pb-containing absorber, PSCs are assembled by integrating tightly the valuable charge transport layers with the expensive transparent conductive oxide (TCO) substrates serving as the front electrodes and the noble metals like gold coating entirely on the rear in the sandwich configuration, which not only increases the fabrication cost, but also raises the difficulty in separating every component for recycling and recovery of degraded modules. In addition, PSCs are usually fabricated and encapsulated on TCO coated glasses with a fragile structure and poor properties of corrosion resistance and moisture blocking, making them easy to fail and release toxic materials into the environment. Considering the economic aspects, if PSCs enter practical use on a large scale, the consumption of valuable materials for manufacturing will rise sharply, leading to a significant increase in cost and losing the competitive edge, because of the energy-intensive treatment process with high temperature and high price of TCO substrates and noble metals used in PSCs. From the perspective of policies, few laws and regulations across the world have been uniformly formulated on the practical use of solar modules regarding to the environmental impacts, as well as the recycling mechanism at their end of life. Currently, PV modules are classified into the category of electronic devices. Therefore, if failure or end-of-life, they will be collected in accordance with international electronic waste disposal regulations. Overall, challenges are increasingly emerging with the growth of public concerns about environment issues relating to the renewable energy applications.

24.3 Advances in Science and Technology to Meet Challenges

Before PSCs enter commercial markets, many efforts have been made to develop recycling technologies for sustainability and environmental protection. However, the technologies vary largely depending on the diverse architectures and materials of PSCs, which can be categorized into four parts: TCO substrates, perovskite absorbing films and carrier transport layers, mitigation of Pb toxic elements, and the valuable metal electrodes. Between the inorganic TCO substrate and Au rear contact, the perovskite and charge transport layers exhibit good solubility in organic solvents, facilitating the separation and extraction of all components and enabling the recycling viable. For instance, the TCO/glass substrate can be easily recovered by the dimethylformamide (DMF) immersing, ultrasonicating and solvents rinsing (chlorobenzene, deionized water, ethanol and acetone) [5,6]. The perovskite materials can be dissolved in a polar aprotic solvent through the ion reaction, leaving Au electrodes and the mesoporous TiO_2 coated transparent conductive glass to regenerate PSCs [7]. The PbI_2 from degraded devices can be nearly 100% recycled by using commercial zeolite in an aqueous solution, where toxic Pb^{2+} are absorbed and stabilized through ion exchange while rare iodine is recovered for PSC refabrication [8]. By immersing the used devices into chlorobenzene after peeling off the metal electrode, the valuable hole transport material Spiro-OMeTAD can be selectively removed without damaging the remaining films, which are used to remake new PSCs with identical PCE [9]. Very recently, a “one-key-reset” recycling approach was reported [10] to separate and extract simultaneously all the constituent materials at once from the used perovskite solar cell to remake new one retaining efficiency of more than 20%, by applying a brand-new bleacher which is composed of methylamine and nonpolar solvents. Finally, encapsulation materials can be recycled by pyrolysis and chemical decomposition. To conclude, all components and materials of PSCs can be recycled through selective extraction or a package solution, whereas PSCs can also be refabricated with comparable PCE using the recycled materials to eliminate the environmental impacts and reduce the production cost.

24.4 Concluding Remarks

The PCE of PSCs has already surpassed 25.7%, comparable with commercialized technologies, such as CdTe and Si solar cells. Nevertheless, the toxicity of Pb element with the risk of leaking into the environment and the high cost of TCO/glass substrates and the noble gold electrodes hinder the industrialization and commercialization of PSCs and make the recycling routes crucially important. Researchers worldwide have made progress towards developing recycling and recovery technologies, such as solvent extraction, ion exchange, chemical reaction. The refurbished PSCs using the recycled materials still retain impressive PCE or even better than that of the pristine cells, demonstrating the feasibility of double-way recycling approaches, one is to recycle the used or degraded PSCs, and the other is to reuse the recycled materials for producing new PSCs. These technologies and efforts offer promising recycling routes for PSCs to alleviate the environmental concerns and promote the sustainability as well as the competitiveness.

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24.6 References

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