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ROADMAP

Roadmap on commercialization of metal halide perovskite photovoltaics

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Abstract

Perovskite solar cells (PSCs) represent one of the most promising emerging photovoltaic technologies due to their high power conversion efficiency. However, despite the huge progress made not only in terms of the efficiency achieved, but also fundamental understanding of the relevant physics of the devices and issues which affect their efficiency and stability, there are still unresolved problems and obstacles on the path toward 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 the progress made toward 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 PSC 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 move forward toward addressing the outstanding challenges in this fast-developing field.

Contents

1. Overview of commercialization prospects of perovskite solar cells

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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 toward their commercialization, as will be discussed in this roadmap. Nevertheless, a number of companies are working on PSCs, such as Oxford photovoltaic (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, and Xiamen Weihua Solar Co. Ltd [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 a 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 laboratories have been established, such as European Perovskite Initiative (EPKI) [3] and US-MAP (Manufacturing of Advanced Perovskites) [4].

Current and future challenges

Generally, the greatest challenges toward 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 and 3), followed by a discussion on the important challenges of scaling up, for both solution-based and vapor-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 have important implications on their environmental impact. Since the scaling up requires not only the reliable deposition of high-quality perovskite (PVK) films over large areas, but also patterning and interconnections to connect individual cells into modules, these techniques and the PVK modules are discussed in sections 7 and 8. In addition, tandem devices, especially PVK-Si tandems, are expected to play an important role in PVK commercialization [7]. Therefore, different types of PSC-based tandems are discussed in sections 9–11. As the PVK 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 the commercialization of PSCs [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 need to be addressed are the issues of lead toxicity and the environmental impact of PSCs. We can generally view the scaling-up challenge as an engineering issue that can generally be solved, and 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 PVKs lags far behind that of Pb-based ones. Consequently, an 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 (EPBT) 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 one to address 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 (TCOs) and metal back electrodes (BEs) are recycled [6]. This important aspect of future PVK commercialization is discussed in section 24. In addition, further studies on the 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 the PVK 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 PVK layer and the fact that lead replacement has been either unsuccessful in reducing the environmental impact or the actual impact is unknown (depending on the PVK 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 PVK materials and devices is often highlighted in research literature. Among these, Sn-based PVKs 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 PVs once their efficiencies reach 15% [2]. However, in addition to not taking into account all the complexities of the environmental impact of tin-based PVKs [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 the tendency of Sn^{2+} to oxidize to Sn^{4+} [5]). Finally, in addition to the challenges discussed in detail in this roadmap article, it is necessary to recognize the challenges related to the organic materials used in these devices, which include costs and the 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 toward commercialization, and that the issues covered will facilitate better understanding of relevant issues within a wide framework, taking into account not only efficiency, scalability, and stability but also environmental impact and sustainability.

Advances in science and technology in PVK 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 PVK materials. The use of 2D/quasi-2D PVK 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 PVKs ABX_3 (where A denotes a small organic cation or Cs^+, B is a divalent metal cation, commonly Pb^{2+}, and X is a 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 PVKs can have a 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 a monovalent (RP, ACI) or divalent (DJ) spacer cation, and n denotes the number of octahedral layers [12]. There are still numerous unknowns concerning the structure-property relationships and degradation mechanisms in these materials [11, 12, 17], in part due to a large number of possible spacer cations. Generally, DJ and ACI materials are expected to exhibit improved stability compared to RP PVKs due to shorter interlayer distance and hydrogen bonding between the layers (both H-bonding and van der Waals interactions for ACI), while RP PVKs 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 ($n = 1$) PVKs, these materials are commonly used in 3D/2D or quasi-2D ($n > 1$) configurations for the active layer to achieve a compromise between efficiency and stability [11–13]. While the efficiency of quasi-2D devices can exceed 19% [13], the 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 PVK achieved by the 2D layer [11]. As these materials have been more recently developed and comparatively less studied compared to 3D PVKs, the commercially relevant stability tests, such as damp-heat tests [16] or outdoor tests [18], are more scarce compared to 3D PVKs. Possible exceptions are the devices where bulky cations, such as

5-aminovaleric acid, are used as additives to 3D PVK, 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 the commercialization of PSCs.

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2. Niche applications of PSCs

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Status

Organic–inorganic hybrid metal halide perovskites (HPs) are a star material for solar cell devices due to their intriguing optoelectronic properties, such as their high absorption coefficient, long carrier lifetime and diffusion length, tunable optical bandgap, and high defect tolerance. PSCs have attracted considerable attention in both academic and industrial fields since 2009. Due to the efforts of the PV community, the world-record power conversion efficiency (PCE) of PSCs has increased rapidly from 3.9% to 25.8% during the last decade. Furthermore, in contrast to the conventional crystalline Si, PVK materials offer advantages such as being solution-processable, flexible, lightweight, and semi-transparent, making PSCs a promising PV technology, and especially favorable for certain niche applications, such as indoor PVs for the Internet of Things (IoT), flexible PV technology, and building-integrated PV (BIPV), as shown in figure 1 [19–21].

Indoor PV for IoT. The development of the IoT system requires millions of electronic devices to communicate wirelessly. Normally, IoT devices consume a low level of power and are supported by off-grid power sources, such as batteries. An alternative solution is to use indoor PV devices to convert indoor light into electricity to support continuous operation of the IoT system. Unfortunately, commercial PV devices, such as Si and gallium arsenide (GaAs) solar cells, show unsatisfactory performance under low-light conditions, while the PSCs have been demonstrated to exhibit outstanding performance, e.g. over 40% PCE under indoor light-emitting diode (LED) light [22].

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 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.

BIPV. 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 areas. With regard to PCE and color tunability, PSCs easily 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 crystalline Si PV technology, particularly for grid-connected PV power systems, the emerging PVK PV technology could be very promising for the above-mentioned niche applications.

Current and future challenges

Scaling up. Currently, the world-record efficiency of PSCs (25.8%) has exceeded that of multicrystalline Si solar cells (23.3%) and is approaching that of single crystalline Si solar cells (26.1%). However, the best performance is only achieved in a $\sim$0.1 cm^2 small-area cell, and the efficiency drops significantly to 17.9% when a large-area (such as 804 cm^2 from Panasonic) PVK solar module is developed [23]. Such a large lab-to-fab gap can be ascribed to: (i) the difficulty to achieve both high-quality large-area PVK films and charge transporting layers; (ii) the increased series resistance in large-area devices due to the low conductivity of the TCO (e.g. indium-tin-oxide (ITO)) glass substrates. Therefore, the main challenges of scaling up PVK PV technology include the development of large-scale deposition methods for uniform PVK films and patterning processes for PV modules with a high geometrical fill factor (GFF).

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. In addition, the mechanical properties of ITO-coated plastic substrates are poor due to the intrinsic brittleness of metal oxide films. Therefore, the development of high-performance electrode materials for flexible substrates is of great importance for flexible PSCs.

Stability. Long-term stability is another challenge for PVK PV technology to enter the market. It has been demonstrated by different groups that the extrinsic (e.g. light, heat, moisture, oxygen, electrical bias) and intrinsic factors (e.g. ion migration, material degradation, chemical reaction at device interfaces), or their

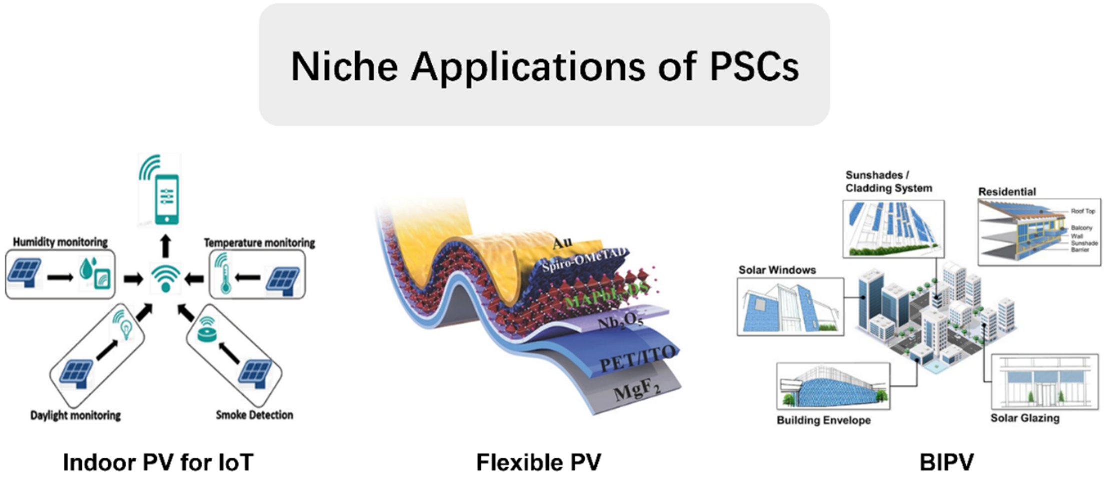

Figure 1. Niche applications of PSCs include indoor PVs for IoT devices, flexible PVs and BIPV. [20] John Wiley & Sons. (Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). [21] John Wiley & Sons. (Copyright © 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). [19] John Wiley & Sons. (Copyright © 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

combinations can cause severe degradation of PSCs. However, there are no standard protocols for PSC stability testing; thus it is still challenging to reveal the underlying degradation mechanism and find pathways to fabricate PSCs with operational lifetimes comparable to current Si PVs.

Toxicity. The presence of water-soluble toxic Pb ions in PVK film could be a concern for indoor PVs, 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 efficiency and poorer stability compared with their Pb-based counterparts. Therefore, the development of efficient Pb trapping and encapsulation technology will be important to ensure that PSCs are safe to use.

Advances in science and technology to meet challenges

It is known that poor film uniformity will affect the device efficiency as well as its long-term stability. The uniformity of large-area PVK film is largely affected by the deposition technology. Compared to the traditional spin-coating method, large-scale processing methods, such as blade coating, slot-die coating, and thermal evaporation, have been employed to produce large-area PVK films with optimized film quality. For example, for solution processing, the solvent systems of PVK precursor materials have been carefully studied to control the nucleation and growth of large-area PVK films [24]. For PVK films prepared by vacuum-based thermal evaporation, controlling the evaporation rate of the organic cations and lead halides is of great importance to deposit a large-area PVK film with desired stoichiometric composition [25]. Other strategies include transporting layer engineering, interface engineering, and defects passivation, which will also contribute to further improve the efficiency of large-area PVK PV technology.

To improve the mechanical properties of flexible PSCs, various conductive transparent materials have been recently developed to replace ITO as the flexible substrates. It has been demonstrated that Ag nanowires, metal mesh, and 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 amorphous Cd-doped indium oxides with improved mechanical, electrical, and optical properties can effectively replace ITO as the transparent electrode for flexible PSCs, which exhibit very decent efficiency and stability [26]. 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.

With regard to device instability caused by environmental factors, this can be resolved via proper encapsulation to avoid chemical degradation of the PVK film induced by moisture or oxygen. With the latest advancement in encapsulation technology, highly stable PVK PVs were reported, which passed the demanding International Electrotechnical Commission (IEC) 61215:2016 Damp Heat and Humidity Freeze tests [27]. With regard to the intrinsic stability of PSCs, recent works have successfully employed different spectroscopy techniques to monitor the evolution of defect states in PVK films during device operation and reveal the device degradation mechanism [28], which is very important to provide insights to enable the development of 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 [29]. In addition, the state-of-the-art Sn-based Pb-free PSC has achieved a record efficiency of over 14% [30]. It is calculated that Sn-based PVK (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 PSCs if effective strategies can be developed to resolve their current low efficiency and poor stability issues.

Concluding remarks

Rapid advances in PSCs have been made in terms of both efficiency and stability at the laboratory-scale device level. To compete with traditional Si PV technology, one possible pathway is to explore niche applications for PVK PVs, such as indoor PVs for IoT, flexible PVs and BIPV. Although intensive efforts have been made in these areas, there are several remaining challenges that still need to be solved in the field. Scaling up PVK PV to a desired size is the prime target to meet the requirements of an IoT system or BIPVs. The development of high-performance flexible substrates is of great importance not only for wearable electronic device but also for BIPV applications for which lightweight and conformal coatings on curved building surfaces are required. Stability and toxicity of PSCs are also key problems to be addressed. These niche applications for PSCs provide a good entry point to the PV market for their initial phase of industrialization.

3. Current state of commercialization efforts

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Status

PVs are one of the most important technologies to achieve a net-zero purpose for our society in the future. The commercially available solar panels so far are mainly fabricated based on silicon materials, which have already evolved into a well-matured industry after decades of efforts. There are, however, many other types of PV technologies, such as organic PV (OPV), quantum dot PV and metal halide PVK PV, which are emerging as alternatives for power generation [31–33]. Among them, PVK appears as a 'game changer' and leads its PV journey toward efficiency over 25% to date [34]. Such efficiency is already approaching that of a crystalline silicon (c-Si)-based device (26% in the laboratory) and far beyond that of commercially available c-Si panels (20%) [35]. The great commercializing potential of this technology, such as high efficiency and solution compatibility (low cost), therefore draws extensive attention from both academia and industry. Additionally, functionalities, such as flexibility, semi-transparency, and indoor application, render PVK panels able to make a broad range of contributions to future portable power generation [36–38]. Nevertheless, some obstacles need 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 hold beyond at least ten years (a shorter lifetime compared to c-Si panels can be tolerable considering the lower cost of PVK panels); third, a clear market positioning needs to be made for PVK PV, meaning maximizing achievable profit by knowing the 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, to take a large share from future energy markets in the long term.

Current and future challenges

The first thing to consider for any type of PV trying for commercialization is their scalable fabrication. Although PVK-based devices achieved remarkable efficiency at the laboratory scale, the device area of such a proof of principle device is only 0.095 cm^2 [34]. While the solution fabrication process on one hand enables the devices to be made fast and cost-efficient, it also induces inhomogeneous morphology in the photo-active layer during scalable fabrication. Such adverse effects can be induced by many factors, such as the purity of materials and structure defects during film formation [39, 40]. They can also be induced by buffer layers near the metal contacts [41, 42]. Additionally, antisolvent treatment is not possible during module/panel fabrication. An alternative approach, such as processing at an elevated temperature or with solvent additive, is thus essential to move the current steps forward [43, 44]. From the above factors, the biggest challenge at this moment is the degradation of efficiency as device/module areas scale up. Such a challenge is evidenced by the champion efficiency of the device dropping from 25% to 21.6%, 19.6%, 18.6%, and 17.9% when the 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 [2]. These results certainly raise concerns regarding the 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. Achievement of panel efficiency over 20% is therefore a 'must'. Apart from efficiency, another obvious challenge is the stability. The typical reported literature shows stability over 1000 h without encapsulation, and the longest stability tested is 10 000 h after encapsulation, with efficiency loss smaller than 15% [45]. These results are however still far from International Summit on Organic Photovoltaic Stability (ISOS) standards, and are non-comparable to those of c-Si panels. In particular, 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 systems [46, 47].

Advances in science and technology to meet challenges

To solve the above issues, efforts from the industry have been made to make efficient and stable PVK panels, as the huge potential of the commercialization of PVK PV has attracted their attention. Some key industrial players' efforts are listed in table 1. One can see that the continuously decreased efficiency upon a 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 toward this technology from the market. In particular, MicroQuanta has released its newly certified 21.4% efficiency with a device area of 19.32 cm^2 (November 2021), which is the highest efficiency for PVK-based modules. Such results indicate that future panel efficiency achieving 20% is realistic. Additionally, the largest area of 2925 cm^2 has been

Table 1. Device efficiency released by some industrial players [35].

	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

released by Kushan GCL Optoelectronic Material (November 2019), showing the advantage of solution-based printing methodology when fabricating large-area and low-cost PVK panels. Another effort concerning the stability of PVK modules has also recently been released by MicroQuanta.

It was released in February 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) tests (280–400 nm, 200 W m^{-2}, 60 °C) and damp-heat tests (85 °C, 3000 h), less than 5% degradation was 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 appropriate passivation and encapsulation. Due to this estimated long lifetime of PVK modules, a tandem device comprised of PVK and c-Si is thus of great interest. As released by both 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 a PVK sub-cell needs to be accommodated with a c-Si cell. The achievement of the above long lifetime is thus a great step forward for both PVK single-junction panels and PVK/c-Si tandem panels in the future.

Concluding remarks

The continuous efforts in PVK-based PV in the last decade have pushed it toward the dawn of commercialization. The remarkable achievement so far renders PVK panels with the competitive capability to take the future energy market by storm. Nevertheless, one should bear in mind that the main rivals 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 [35]. Such news would provoke a reconsideration of how to apply PVK panels in the future energy market. With currently less competitive efficiency and stability, PVK panels should embrace the advantages of applications which are beyond the reach of c-Si panels, such as flexible, semi-transparent, and indoor applications. Such a strategy would help to bypass the dominant power of c-Si in the market currently, and renders enough time for a technological breakthrough in the future.

Acknowledgments

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4. Scaling PVK deposition: solution-based scalable methods

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Status

In view of the advancement in technology over the past decade, there were many revolutionary developments in PSCs to boost the power conversion efficiency (PCE) from its debut of 3.8%–25.5% [35]. However, these remarkable results were predominantly produced from a device of active area (AcA) $\sim$0.1 cm^2 fabricated via a solution-based spin-coating method in a 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 a laboratory-scale device of area $\sim$1 cm^2 [35]. 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 PVK film while maintaining the uniformity and morphology. This provides opportunities for research into the development of 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 PSCs, from stabilized efficiency of 17.8% (aperture area (ApA) of 21.5 cm^2) [48] and PCE of 19.2% (ApA of 50 cm^2) [49] demonstrated by the blade coating method in a research institute to a certified PCE of 17.9% for the champion PVK small module (ApA of 804 cm^2) via the inkjet printing method produced by Panasonic Corporation [35, 50]. Despite these remarkable results, there is still a relatively large gap between the PCE of laboratory cells of area $<$0.1 cm^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 a manufacturing scalable coating, and researchers should perform more in-depth investigation into tailoring the solar ink formulation favorite for individual scalable deposition methods.

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 a large area is far more significant in PSCs because of the challenges in maintaining film uniformity and morphology when scaling up the PVK thin film using a solution-based spin-coating method. High-efficiency PSCs are deposited by manipulating the crystallization kinetics via solvent engineering (mixed solvent) or quenching protocols (antisolvent, vacuum-assisted or gas-assisted drying) [52]. For the scalable deposition method, it is doubtful that a direct technology transfer from the spin coating to scalable deposition of PVK can be achieved [51]. Firstly, there is a large discrepancy in the intrinsic precursor-ink drying force. With the spin-coating process, significant *dynamic* solvent evaporation happens during the spinning stage, whereas it is rather *static* in 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 [53], manipulation of the nucleation process by drop casting antisolvent, 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 PVK thin film, and the use of surfactant has been explored to address this issue [54]. The difference in the evaporation rate of solvent between the 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 investigations into the precursor formulation, solvent engineering, chemical additives, and processing windows are needed to gain deeper understandings of the formation mechanisms prepared by specific scalable deposition methods for reliable crystallization. Recently, there have been reports on the investigation of the processing window (figure 3) and quenching protocol for the scalable blade-coating method using *in-situ* absorption spectrometry [55, 56] to gain further insight into the solidification kinetics with the aid of the LeMar model.

Advances in science and technology to meet challenges

The critical factor for scalable deposition of large-area PVK film is the precise control of the nucleation and growth rate, which has been comprehensively discussed in a previous report [52]. Physical (hot casting, gas quenching, vacuum extraction) or chemical (solvent engineering, additives) methodologies have been

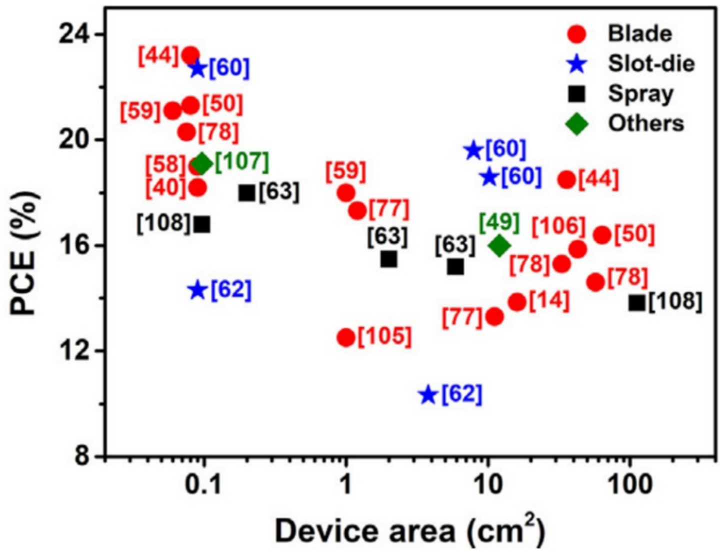

Figure 2. Power conversion efficiency obtained from small-area to large-area scalable deposited PSCs [51], showing the trend of the inverse scaling law. Reprinted from [51], Copyright (2021), with permission from Elsevier.

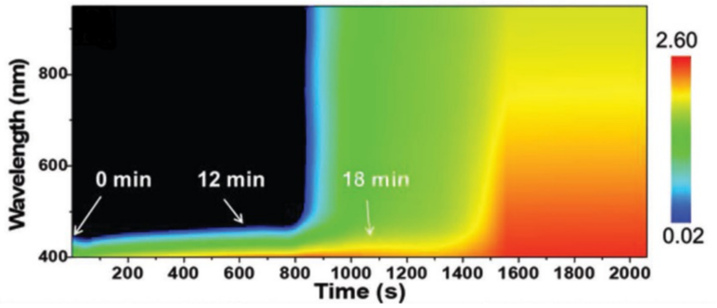

Figure 3. The time-resolved absorption spectrum of a blade-coated PVK film under natural drying, demonstrating a processing window up to 12 mins [55]. John Wiley and Sons [55]. (Copyright © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

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 °C for blade coating [57]. 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 ApA of 63.7 cm^2 [53]. The use of an additive is another critical methodology for manipulating the growth kinetics and passivating the defects of PVK film. Potassium hexafluorophosphate was added to the precursor solution for slot-die coating to reduce the nonradiative recombination defects. PVK mini-modules of 20.42% and 19.54% were obtained for areas of 17.1 cm^2 and 65 cm^2, respectively [58]. The 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 ApA of 57.2 cm^2 [54]. At present, a certified PCE of 17.9% on an area of 804 cm^2 has been demonstrated by Panasonic using an inkjet printing strategy by optimizing the ink formulation, concentration, and the coating amount and speed during the printing process [35]. However, the relatively slow printing speed, when compared to other scalable deposition methods, and the failures arising from nozzle clogging remain the obstacles for high-throughput manufacturing. Furthermore, the tolerance of humidity on the PVK film formation process should be considered when tailoring the ink formulation for scalable deposition in ambient environments.

Concluding remarks

Laboratory-scale PSCs have shown remarkable results over the past decade when prepared using the spin-coating method. With regard to industrialization, solution-based scalable deposition of PVK films has attracted considerable attention 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 PVK film over a large area. Technology transfer from laboratory spin coating to industrial scalable deposition is not straightforward 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 has narrowed, challenges remain in the scalable deposition of PVK in ambient conditions, especially the tolerance in humidity. To realize a fully printable PSC, in-depth scalable deposition of all the functional layers, holes, and electron transport layers (ETLs), should also be investigated.

Acknowledgments

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5. Scaling up PVK deposition: vapor-based scalable methods

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Status

Vapor deposition techniques are the alternative methods for preparing PVK thin films. These techniques have unique advantages, such as the formation of homogeneous layers in a precise thickness over a large area, solvent-free deposition, and good compatibility with sequentially deposited PVK layers for fabrication of devices in heterostructures or tandem structures. Despite the fact that the current PSCs with record-high power conversion efficiencies (PCEs) are prepared by solution processes, it is predicted that vapor deposition of PVK materials will become more important in future manufacturing processes of scalable PVK PVs 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 conformal films on a textured surface, fabrication of multiple junctions to overcome the Shockley–Queisser limit of single-junction solar cells, etc.). The details of different vapor deposition techniques for preparing PVKs have been summarized in review papers [59]. Thermal evaporation and chemical vapor deposition (CVD) are the most established techniques for perovskite solar modules (PSMs). Qiu *et al* [60] demonstrated a PCE of 9.34% for a PSM with a designated area of 91.8 cm^2 by using hybrid CVD, 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* [61] 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 PVK prepared by the vapor deposition technique is able to yield the laboratory-scale PSCs surpassing 21% [62]. 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 in contact resistance from interconnections as well as the sacrifice of active areas for forming interconnections. Continuous development of optimized vapor deposition methods together with the advancement of scribing techniques and module layouts will definitely cause a breakthrough in device performance when scaling up PSCs.

Current and future challenges

Versatile engineering approaches for improving the properties of PVK materials and other functional layers have led to the most rapid enhancement in their device efficiency and stability during the last decade. However, most of the developed techniques for improving PVK quality, such as solvent engineering, the use of additives for assisting with crystallization and defect passivation, as well as chemical doping of PVKs for efficiency and stability enhancement, are usually based on solution processes, while the vapor depositions have less flexibility to adapt the aforementioned techniques during PVK growth. The compositional engineering for vapor-deposited PVK is also not straightforward. During thermal evaporation, the composition of PVKs can be adjusted by the evaporation rate of each precursor. The accurate stoichiometry of PVKs 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. MAI has a relatively higher vapor pressure and it easily decomposes into intermediate species. Some possible MAI decomposition mechanisms have been reported [63], but more studies on MAI sublimation dynamics and effective strategies for precise control of MAI evaporation are still required. The composition of PVKs 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 PVKs via indirect process control at the industrial scale. Furthermore, vapor deposition is not the commonly used technique to synthesize PVKs with reduced dimensionality. For example, PVK quantum dots are synthesized using various solution methods, such as hot injection and ligand-assisted precipitation. The preparation of PSCs based on quasi-2D or 3D/2D PVKs 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 PV performance. However, the grain sizes of evaporated PVKs are usually smaller than the samples prepared by solution processes [64].

Advances in science and technology to meet challenges

The development of vapor deposition techniques for preparing PVKs is imminent. The continuous advancements in PSC fabrication technologies will bring a lot of possibilities to overcome the aforementioned challenges. It is worth investigating the effects of different small molecules acting as additives or dopants that can be co-evaporated with PVK precursors. The microstructures of the vapor-deposited

PVKs can be controlled via processing parameters, such as substrate temperatures, surface properties of samples, and deposition geometry. The post-deposition treatments can be performed on as-prepared PVK samples for defect passivation [65] or optimization of microstructures [62]. To avoid the complication processes associated with maintaining the stoichiometry of multiple-cation mixed-halide perovskites during co-evaporation of a number of precursors, pre-synthesized PVK 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 PVK on the substrates before decomposition [66]. Alternatively, the multi-component PVKs can also be 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 PVK films (e.g. $CH_3NH_3PbI_3$) with the appropriate gases (e.g. formamidine [67], Br_2 and Cl_2 [68]) to form a complex composition of PVKs. The vapor–solid reaction is another effective approach used to grow multi-component PVKs [60]. The inorganic precursors, which usually have a higher sublimation temperature, can be thermally evaporated in a vacuum with 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 of engineering vapor-deposited PVK films, many research efforts are still required to further optimize the processing conditions and verify their results in large-scale manufacturing.

Concluding remarks

The future development of vapor deposition techniques for preparing PVKs should be made together with their unique processing characteristics. The importance of these deposition techniques will be amplified when the PSCs are pushed toward scalable manufacturing during the commercialization stage. To fully reveal the advantages of employing vapor deposition techniques for industrial productions (e.g. solvent-free, high uniformity, etc.), these techniques should also be 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 practical use can be achieved in the near future.

Acknowledgments

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6. Ambient processing of PSCs

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Status

Organolead halide perovskite materials have shown considerable promise for use in high-efficiency PSCs [69]. A typical PSC consists of a several-hundred-nanometer-thick PVK absorber (either with or without a mesoporous scaffold) sandwiched between the electron and the hole transport layers (HTLs). The research works on PVK deposition have mainly focused on solution-based processes because of their potential for industrial production [70]. The PV performance of PSCs is highly dependent on the morphology and crystalline structure of the PVK photoactive layer, which is very sensitive to ambient conditions like UV radiation, oxygen, temperature, and moisture [71]. Therefore, the fabrication of PSCs usually requires a well-controlled atmosphere ina glove box 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 PVK solar modules at low prices. In this section, the challenges and techniques of efficient air-processed PSCs will be discussed.

Current and future challenges

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

The stability and toxicity of PSCs are the main issues facing its industrial deployment and commercialization. Moreover, there is also a requirement for ambient-processed high-quality PVK to translate laboratory-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 (R2R) techniques. For example, 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 PVK layers when compared to the spin-coating process. The 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 PVK precursor solution. Moisture plays an important role in ambient-processed PVK films. Although water presence in organic halide PSC can degrade the device, a recent study shows that a particular ratio of the water molecule in the PVK precursor solution may be an advantage during manufacturing [72]. There is an influence of moisture on the PVK reaction process and the crystallization dynamics, which can modify the morphology of the PVK crystals and grains in the PVK films. The next section provides an overview of techniques developed to fabricate air-processed PSCs with high efficiency and stability. The gap between efficiency for both air-processed PSCs and PCSs processed in an inert environment has been reducing in recent years. The efficiency of air-processed PSCs has increased from 5% to 22%[73], which is near that of PSCs fabricated in an inert environment.

Advances in science and technology to meet challenges

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

One/two-step deposition technique for ambient-processed PSCs

In a one-step process, typically, the PVK precursor is drop-casted onto substrates and followed by thermal annealing to form a PVK film. In this process, the crystallization of PVK in ambient air is rapid and uncontrollable under high humidity. To reduce the detrimental effect of moisture on PVK formation, additive engineering with NH_4Cl addition in PVK precursor solution can be applied to slow down the speed of PVK crystallization due to the formation of an intermediate $CH_3NH_3X{\bullet}NH_4PbI_3(H_2O)_2$ after film deposition. Moreover, 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 the two-step process, a metal halide layer (e.g. PbI_2) is first deposited onto the substrate followed by spin coating of an organic component solution. A preheating method was proposed to obtain a smooth PbI_2 layer with high surface coverage in ambient air. Through preheating, the evaporation rate of N,N-dimethylformamide (DMF) increased and the solvent vapor effectively prevented the ingress of water and oxygen into the PVK layer. Further, an air-knife-assisted two-step recrystallization method was reported to prepare high-quality PVK absorbers [74].

Vapor-based deposition technique for ambient-processed PSC

Chemical vapor deposition (CVD) is a technique used to achieve controlled film thickness and crystallization of PVK in ambient conditions for PV applications. In this process, as-deposited PbI_2 film was first grown on a glass substrate and then exposed to methylammonium iodide vapor using a CVD tube furnace and ambient air (with RH $>$60%). The power conversion efficiency (PCE) of reported PSCs with the vapor-based deposition technique has exceeded 19% [75].

R2R process for ambient-processed PSCs

The R2R and doctor-blade method facilitate deposition of the large-area PVK layers. Yang *et al* first studied the impact of humidity in ambient air on PVK film formation using the doctor-blading technique [76]. The PVK 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 achieve a PCE of 20.08% [77]. Zuo *et al* fabricated PSCs on a flexible substrate using the R2R method to achieve 15% PCE with negligible hysteresis [78].

Concluding remarks

There is a requirement for the 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 laboratory-scale fabrication to industrial-scale fabrication is another issue for PSCs. PVK materials are sensitive to ambient environment parameters, such as air, water, light, and temperature. These ambient parameters influence the morphology and crystalline growth of PVK during thin-film formation. Therefore, the PVK films are usually synthesized in a well-controlled glove box 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 techniques, the vapor-based deposition technique, and R2R process. With further research, it is likely that the efficiency between inert-environment-processed PSCs and ambient-processed PCSs will be reduced in the future. The upscaling of ambient-processed PSC to industrial scale will be carried out using industry-compatible methods.

Acknowledgments

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7. Patterning and interconnections for modules and tandems

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Status

PSC technology has achieved impressive results during the last ten years, with efficiencies up to 25.5% and 29.8% on single-junction and PVK-silicon tandem devices. These results have been reached on relatively small-area devices, with 0.1 cm^2 and 1 cm^2 active area (AcA), respectively, far away from the exploitation of the PSC in the market. In this scenario, the results on the scaling-up process appear 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 oxide (TCO)-based substrates.

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 a P1-P2-P3 interconnection design. Here, P1, P2, and P3 refer to ablation processes performed during the PSM fabrication. In particular, P1 ablation insulates the front TCO electrode of neighboring cells. The P2 ablation selectively removes the entire device stack without damaging the underlying TCO for proper connection between cells. Finally, the P3 ablation insulates the back-electrodes. Laser-assisted ablation is the most-used patterning technique due to its high resolution and production speed. A maximum power conversion efficiency (PCE) of 20.5% has been reached using series connection. Instead, only a 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 needed to reduce the resistive losses and improve the current collection.

For a tandem configuration, the device is based on the integration of cells based on a wider (>1.6 eV) and a narrowed (<1.3 eV) absorber, such as PVK/PVK, PVK/OPV, PVK/CIGS, and PVK/Si. The interconnection design is mainly dependent on 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 the tandem configuration, where front electrodes are generally based on low conductive TCOs.

Current and future challenges

The investigation on the interconnection in-series connected PSM is an important topic for the scientific community to evaluate in the future. Although, scalable patterning procedures at high geometrical fill factors (FFs) (up to 99%) have been demonstrated [79, 80], 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 [81], as shown in figure 5. Among those four degradation pathways, the P2 scribe will likely present the greatest challenge for device stability due to the direct contact of metal with the absorber material, which can result in chemical reactions, especially for PVK materials with halide species. This process, involving P1, P2, and 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 occurring in the module, such as a pinhole, particle-induced shunts, and/or an imperfect laser scribe. A strategy to overcome this limited interconnection design is necessary for technology exploitation in the market.

In the parallel-connected PSM 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 the FF, and minimizing optical losses through excess shadowing, which limits the current.

For the tandem configuration, the main challenges rely on optimizing conductive grids/materials between the top and bottom junction. A general issue related to interconnection, and also for the tandem configuration, 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 PSCs, regardless of whether PSMs are on single/multi junctions, still drive the research community effort, although great strides have been taken.

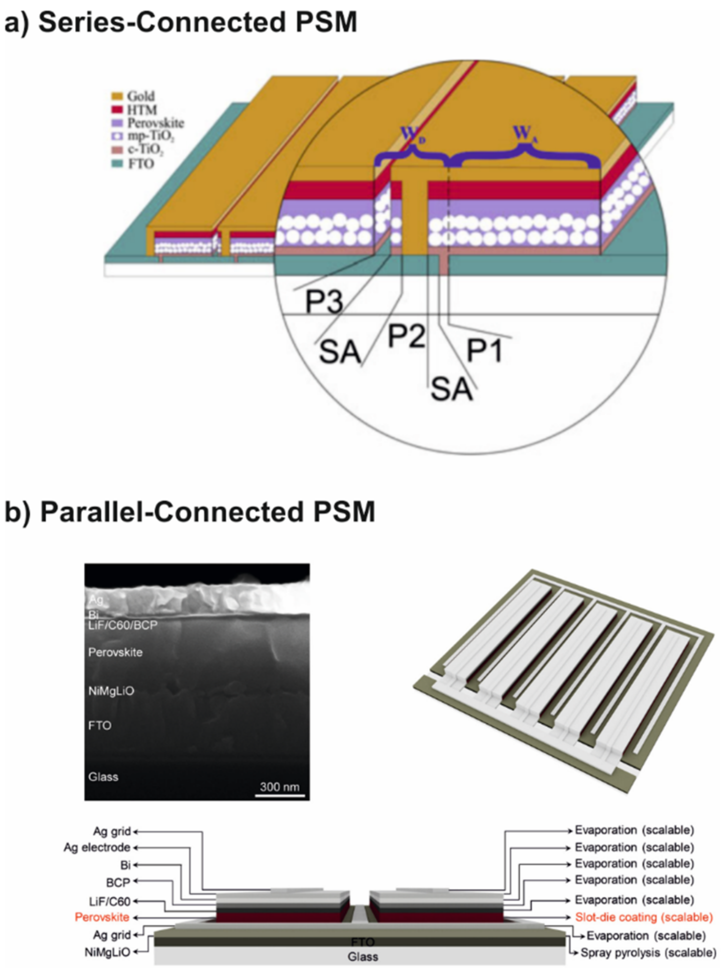

Figure 4. Interconnection design in PVK solar modules: (a) a series-connected PSM. Reproduced with the permission of IEEE publisher. (b) A parallel-connected PSM. Reproduced with the permission of Science publisher. Copyright (2017) IEEE. Reprinted, with permission, from [79]. From [24]. Reprinted with permission from AAAS.

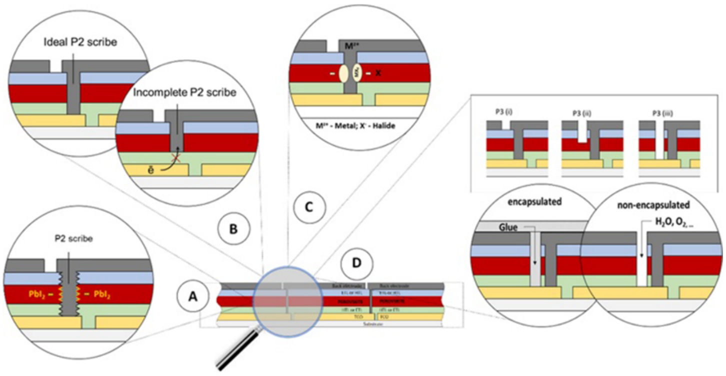

Figure 5. A schematic illustration of the possible degradation mechanism in PVK PV modules. (A) Degradation of the PVK absorber and formation of a small amount of e.g. lead iodide (PbI_2) at the edges of the scribe; (B) incomplete removal of hole transporting layer or electron transport layer materials, which are located between the PVK absorber and TCO; (C) direct contact between PVK and the metal electrode inside the P2 scribe; (D) P3 scribe performed at different depths. Reproduced from [81]. Copyright IOP Publishing Ltd. CC BY 3.0.

Advances in science and technology to meet challenges

Very few works have focused on the interconnection optimization for long-term stability, in the case of series-connected modules: what is clear is to avoid direct contact between PVK 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 the best modules maintaining 95% and 91% of their initial PCE at 85 °C and under light test over 1000 h, respectively [82].

The limitation in the current, in series-connected modules, might be addressed by looking at other thin-film technologies solutions: companies like First Solar, in their CdTe modules, have introduced an additional scribe to mitigate this issue, called P4 [83]. This process is performed perpendicularly to the P1, P2, and 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 the current by one sub-cell, was also performed by Xu *et al*, where alternation of series and parallel connected modules is performed with particular care taken with the design [84].

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 [85]: the function of the bypass diodes is to isolate a string of cells with an 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 [86].

PSM stability has been achieved using a parallel-module configuration by Yang *et al* [24], where a champion PSM maintained 96.6% of its initial PCE after 10.000 h under day/night cycling illumination.

In the tandem configuration, a way to boost the PCE and improve the stability of the PVK/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 sub-cell junction [87].

Concluding remarks

A massive study has been conducted on PVK from an intrinsically and scientific point of view: what is still missing is a systematic study on the effect of the interconnections for the long-term stability. Examples of long-term stability on PSMs have been achieved using diffusion barrier layers and parallel-connected sub-cells, avoiding contact between PVK and metal, one of the main pathways of PVK degradation. A major effort is necessary in these directions to clearly understand how to transfer what is reached on a small area up to module size. Defining a set of specific stability protocols for PSMs and multi-junction devices could step up PVK upscaling, also sharing important details, such as sub-cell AcA size, P1, P2, and 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.

Acknowledgments

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8. PVK modules

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Status

Perovskite solar modules (PSMs) are fabricated resembling the thin-film PVs 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 a few micrometers, reducing the material consumption compared to first-generation PV, such as crystalline silicon (c-Si).

Appropriate 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 polyethylene naphthalene (PEN) 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) [88], and the related industrial exploitation, is achievable by appropriate scalable manufacturing process module design and interconnection patterning [89].

Besides fabrication, performance assessment of PSMs should follow international standards and be compared with well-established PV technologies [90]. 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 [91]. However, when scaling to module size the certified efficiency gap between the cell and module is about 20% for PSM, while it reduces to only 8% for c-Si modules [92]. 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 (AcA), obtained by partially replacing dimethyl sulfoxide (DMSO) with solid-state carbohydrazide in MAFAPbI$_3$ HP [49]. An efficiency of 20.2% (18.6% stabilized) on 27 cm^2 AcA was achieved by compensating iodide vacancies and suppressing ion migration in a formamidinium-cesium HP [93]. 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 [94]. Recently, Moore *et al* demonstrated that *o*-PDEAI$_2$ is an effective passivation agent to reach 21.4% efficient PSM on 26 cm^2 AcA [95].

Current and future challenges

The uniform deposition of HP and transporting layers on a 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 to avoid current mismatch that would impact on the overall module efficiency [91]. 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 ApA, i.e. maximizing the aperture ratio (AR, defined as AcA/ApA). However, an excessive reduction of the DA will impact on the interconnection line width, increasing the contact resistance and consequently reducing the fill factor and module efficiency. Thus, the sheet resistance loss of the transparent conductive oxide (TCO), the interconnection DA loss, and the interconnection contact loss, are some of the additional issues related to the scaling-up of the HP technology [88]. The module design and the interconnection patterning can face and limit these issues. In addition, the aforementioned laser patterning process can generate defects across the layers [96].

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 by the use of thermal evaporation metals for BEs 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).

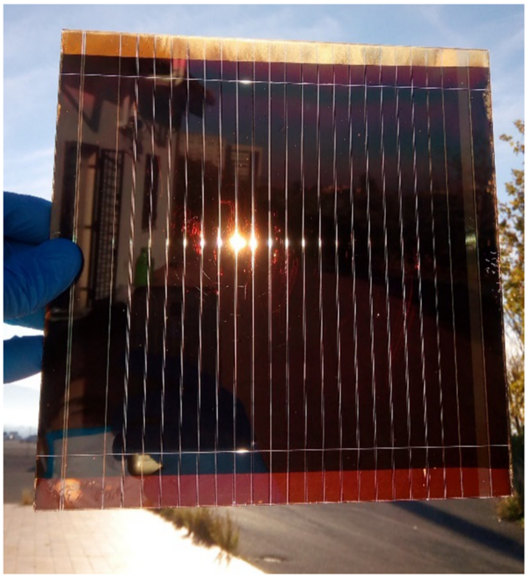

Figure 6. A PSM of 300 cm^2 fabricated according to Vesce *et al* [88].

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 [91]. 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. At this size, post-deposition treatments needed for HP crystallization, such as gas, solvent, and vacuum quenching, may not be as 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 a glove box with an 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, and environmental and coating parameters are 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 electrodes as they are low-cost, chemically inert, hydrophobic, thermally stable, and compatible with upscalable techniques. The limited efficiency reached for carbon-based PSM (15.3% on 25 cm^2) deserves further development, 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 ($<$10 mm) cells, keeping the AR as large as possible. In less than a decade, the AR increased from 67% to about 95% due to the application of an ultrashort laser pulse that permits the ablation of materials, thus maintaining a very low heat diffusion through the target [79]. It is possible, however, to further improve the AR by using a non-conventional solution like point contacts. The encapsulation of solar modules is another technological challenge. The process temperature limit of PSCs (around 100 °C–120 °C) requires new encapsulation materials and edge sealants that are compliant with this low-temperature budget.

Concluding remarks

Today, the fabrication of PVK modules with a size comparable to conventional c-Si panels is mandatory for market exploitation of this new-generation PV technology. A strong effort has been made in the last ten years to increase the 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 when scaling from a small to a large area. Several factors hamper such development, in particular the scalability of the solution-based coating and the HP crystallization process on a large area. The use of additives, 2D materials, and advanced deposition methods offer the possibility to increase the process window, even out of the glove box. This permits a facile approach to module manufacture reduction and, 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 intermediate step toward industrialization. The pilot line is required to verify the entire automated fabrication process with specific throughput and performance constraints. In turn, this will permit a clear assessment of the PSMs' stability following the IEC standard that comprises several accelerated lifetime tests in ambient air, such as thermal cycles, damp heat, light soaking, reverse bias, and mechanical stress. Finally, the PSM eco-profile must be addressed by lead-reduced formulations and/or lead-capture strategies together with specific recycling processes.

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9. PVK-based tandem cells: PVK/Si tandems

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Status

With current 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. PVK/Si tandems have been identified as one of the most promising tandem configurations for terrestrial 1-Sun PV systems due to the high-efficiency potential, low cost, and bandgap tunability of PVKs, and the benefits from a partnership with established Si technologies. So far, studies on PVK/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 PVK/Si tandems has improved dramatically from 13.7% [97] to a remarkable 33.2% [98], far exceeding the record efficiency (26.7% [35]) of single-junction Si cells.

Various configurations of dual-junction PVK/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 33.2% [98] record efficiency was achieved in 2T. The three-terminal (3T) configuration is proposed as a promising option, combining the 4T's advantage of avoiding current matching requirements (thus more accommodating to spectral variation) and the 2T's benefit of monolithic integration on the Si bottom cell [99]. However, present efficiencies are lower due to more complex device considerations. A detailed comparison of 2T, 3T, and 4T dual-junction PVK/Si tandems is summarized in table 2.

The structure of the PVK top cell and the Si bottom cell, as well as the integration between the two, are also subjects of active research. Although mainstream PVK 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 PVK/Si tandems are achieved with p-i-n PVK 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 [97, 104–108], such as Si recombination junctions with the advantages of reduced parasitic absorption and matched refractive indices, have also been explored as the integration layers.

Fabrication technologies of PVK top cells are generally inherited from PVK single-junction devices. They can be classified into solution-based processes, vapor-based processes, and a hybrid of these two. Via hybrid two-step deposition methods, combining sequential co-evaporation and spin coating, conformal growth of PVK layers on textured Si bottom cells has been demonstrated [106], making it possible to boost the photocurrent density to $>$20 mA cm^{-2} and realize a monolithic PVK/Si tandem device exceeding 30%.

Current and future challenges

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

While the record efficiency of PVK/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 $\sim$45% [100]. Such high-efficiency devices present an avenue to significantly reduce the system-level cost. The potential for further efficiency improvement lies mainly in the PVK top cell and the optimized integration of the two sub-cells.

A critical challenge toward commercialization lies in scaling up the small-area laboratory-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 toward scaling-up. Two notable examples are the 21.8% device with an active area (AcA) of 16 cm^2 achieved by Zheng *et al* [110] and the 26.7% device with an AcA of 201.64 cm^2 announced by Oxford PV [111]. To compete with Si single-junction devices, a repeatable full-wafer efficiency beyond 28%

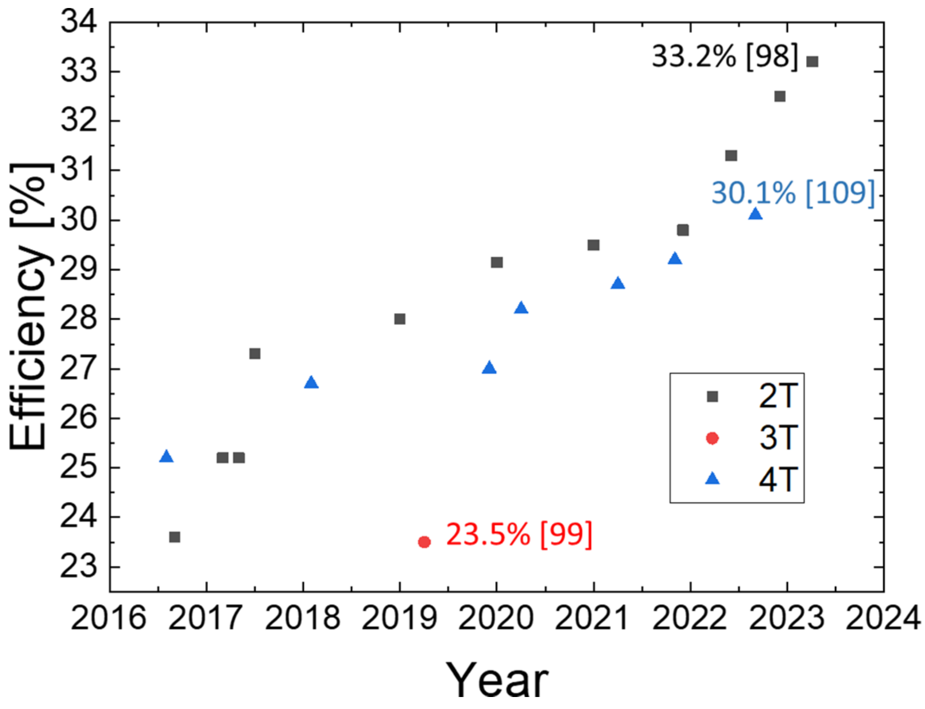

Figure 7. Efficiencies achieved to date for 2T, 3T, and 4T configurations of PVK/Si tandem devices. Record 1-Sun efficiencies of 2T, 3T, and 4T configurations are achieved by [98, 99] and [109], respectively.

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

Device structure	2-Terminal	3-Terminal	4-Terminal
1-Sun efficiency potential (%)	45.1 [100]	45.3 [101]	45.3 [100]
Optimal bandgap (eV)	∼1.70 [100, 102, 103]	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

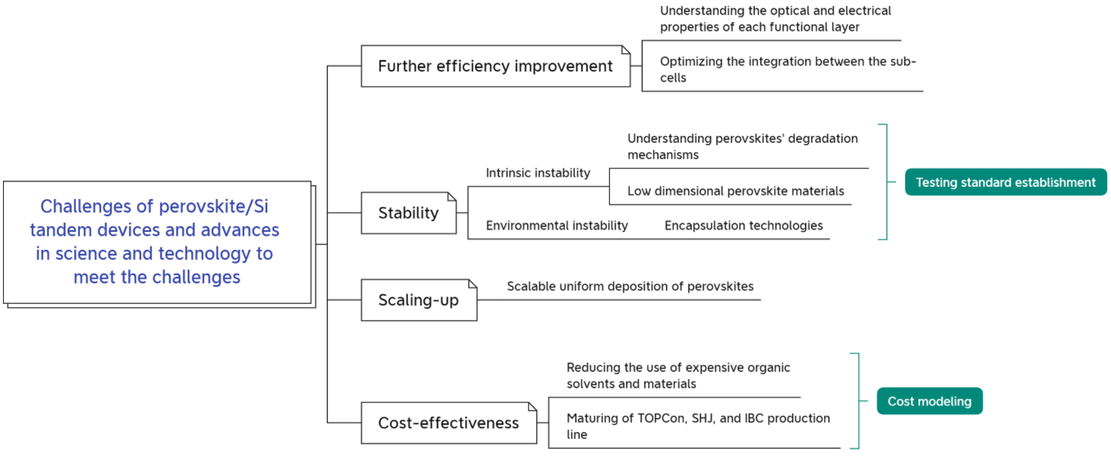

Figure 8. The challenges of PVK Si tandem devices and advances in science and technology to meet challenges.

should be targeted. Similarly, the instability of current PVK devices has to be addressed with the aim to match the long lifetime and robust reliability of Si single-junction devices. Although PVK/Si tandems have passed reliability tests of a few thousand hours [112], 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 PVK top cell over the well-established Si bottom cell has to be compellingly low to reap the gains of efficiency. Although the material cost in PSCs 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 the competitive manufacturing costs of PVK/Si tandems, remarkable efficiency, and proven stability can significantly reduce the levelized cost of electricity of this PV technology, rendering it competitive to Si single-junction cells or even other sources of energy.

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 8). To fully exploit the high-efficiency potential of PVK/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 a further understanding of PVKs' degradation mechanisms (especially photo-induced phase segregation) is required to solve the degradation of intrinsic material origin. Alternatively, low-dimensional PVK materials, demonstrated to be less susceptible to degradation, are worth exploring. Together with these developments, standards or protocols for testing the performance, stability, and lifetime (including outdoor testing under operation) of PVK-related devices have to be established.

Until now, spin coating has been the prevalent method used to form PVK layers, having shown the best film quality and reproducibility. However, in the current state, it is not ideal for large-area deposition of PVK absorbers due to requirements for process uniformity and low material consumption. Scalable uniform fabrication methods have to be developed for PVK 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 is necessary.

The learning rate of terrestrial 1-Sun solar PV dominated by Si technologies has been astounding (∼23% according to the international technology roadmap for photovoltaic (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 PVK cell. However, this can also favor 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 PVK/Si tandems in various deployment scenarios.

Research to address toxicity of lead-containing devices (or other heavy metals) will allay health and environmental concerns. Already there has been work carried out on substitution for lead-free materials or that with reduced lead composition. More holistic approaches for lead-based PVKs 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 characterization and metrology tailored to the peculiar properties (e.g. ion migration, phase segregation, and other light-induced changes) of PVKs 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 to production monitoring, quantifying their performance, and reliability assessment. Developing failure analysis capabilities for probing PVK and Si sub-cells individually in a tandem configuration will also rise in importance. Reliability benchmarking should take into consideration the area and operational lifetime of the devices, and should be compared against prevailing Si single-junction devices. This calls for the establishment of consensus/standards on testing within the community.

Concluding remarks

PVK/Si tandem solar cells have made remarkable progress in the laboratory and have surpassed the record efficiency of Si single-junction devices. However, a prerequisite for the commercial deployment of this technology is the 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 commercialization roadmap of PVK/Si tandems. This ranges from developments in process technologies to device design, characterization techniques, standards for testing, and addressing potential environmental and toxicity concerns of lead-containing PVKs. Solving these issues could pave the way for terawatt-scale deployment of PVK/Si tandems.

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10. PVK-based tandem cells: PVK/PVK tandems

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Status

Perovskite/perovskite (PK/PK) tandem solar cells combine two PVK absorber layers with complementary light absorption—typically a mixed-halide wide-bandgap (1.7–1.9 eV) PVK and a mixed tin–lead (Sn-Pb) narrow-bandgap (1.1–1.3 eV) PVK to reduce the thermalization loss and expand the utilization of the solar spectrum. This emerging PVK-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 sub-cells, simple fabrication techniques, suitability for processing on flexible and lightweight substrates, and projected low manufacturing and environmental costs [113]. 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.

Together with the rapid development of single-junction PSCs, PK/PK tandems have experienced an astonishingly fast learning curve in performance enhancement in the last few years (figure 9). In 2015, Jiang *et al* [114] first realized the concept of monolithic two-terminal (2-T) PK/PK tandems by integrating two methylammonium lead iodide (MAPI) sub-cells using organic interconnecting layers. Later, Eperon *et al* [115] made a breakthrough by developing 2-T PK/PK tandem architecture based on an infrared-absorbing Sn-Pb PVK, enabling power conversion efficiencies (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 PVK grain boundary passivation [116], compositional engineering and deposition process innovation [117, 118], inhibition of Sn^{2+} oxidation in the Sn-Pb PVK precursor solution [119, 120], and the recombination layer modification [118, 121]. Due to all these efforts, the current record PCE of 26.4% for PK/PK tandems has surpassed the highest PCE of 25.7% for single-junction PSCs [35]. Notably, a certified PCE of 24.2% has been demonstrated for PK/PK tandems with an active area of over 1 cm^2 [120]. With the rapid momentum of technological progress and further exploration, PK/PK tandems are expected to become a leading PV technology with PCEs exceeding 30% in the foreseeable future.

Current and future challenges

Although 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 PVKs, (ii) intrinsic instability and defectiveness in Sn-containing narrow-bandgap PVKs, and (iii) inevitable power loss at interconnecting layers. Particularly, wide-bandgap PVK 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 PVKs 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 sub-cell from damage during the process of the second sub-cell.

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 PVK sub-cells and interconnecting layers. It is particularly challenging for Sn-Pb narrow-bandgap PVKs 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 PVKs is currently the bottleneck that hinders the scalable production and practical applications of PK/PK tandems.

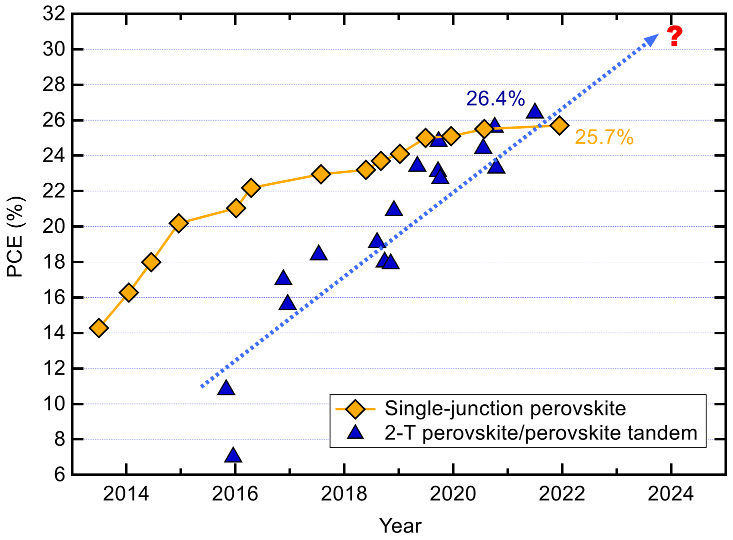

Figure 9. Evolution of PCEs of single-junction PVK and PVK/PVK tandem solar cells.

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 PVKs, narrow-bandgap PVKs, and the interconnecting layers. PK/PK tandem research has been a growing field where the strategies for improving device performance and insights into 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 PVK sub-cells and, thus, maximizing the power output of tandems. The design and validation of tandem architectures need collaborative work of detailed device physics modeling, extensive expertise on device fabrication, and advanced optical and electrical characterization techniques. Moreover, each sub-cell requires delicate control to ensure the maximum conversion of solar energy. Strategies to mitigate large V_{OC}-deficit in wide-bandgap PVK sub-cells include tailoring PVK composition and grain growth, applying grain boundary and surface passivation, and identifying appropriate hole-selective materials to match the deep valence band of wide-bandgap PVKs. Increasing the film thickness and minority carrier diffusion length of Sn-Pb narrow-bandgap PVKs is important for enabling a complete infrared photon conversion. Employing appropriate oxygen- and moisture-impermeable surface and grain boundary protection and engineering the Sn-Pb PVKs to reduce their reliance on oxygen- and moisture-free environments can be effective approaches to prevent the degradation of Sn-Pb PVKs. Furthermore, efficient interconnecting layers play a key role in connecting the sub-cells 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 PSCs and applied to the large-area coating of Sn-Pb PVKs. For industrial production, it is also important to develop suitable production tools to specifically handle the processing of Sn-Pb PVKs 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. Moreover, the implementation of robust module encapsulation and packaging is necessary to ensure the long-term stable operation of PK/PK tandems.

Concluding remarks

PK/PK tandems present an unprecedented opportunity for the development of 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 PSCs, 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.

Acknowledgments

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11. Other PVK tandem cells

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Status

$Cu(In,Ga)Se_2$ (CIGS), organic and $Cu_2ZnSnS_xSe_{4-x}$ (CZTS) materials are exceptional candidates as near-infrared absorbers in a PVK-based tandem configuration with significant advantages of tunable bandgaps, lightweight, and availability for flexible processing. It is possible to realize the strong alliance between these near-infrared materials and PVK. 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 years 2014–2022. In figure 10, the first 2-terminal (2T) PVK-based tandem came out in IBM in 2014, with a Pero-CZTS tandem structure, and its efficiency was 4.6% [122]. Until 2022, the 4-terminal Pero-CZTS tandem had a high power conversion efficiency (PCE) of 22.27% developed in CITYU [123]. Furthermore, more researchers have recently focused on the Pero-CIGS and Pero-OPV tandem PVs. 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 [124, 125]. 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 [126, 127]. In addition to surpassing the single-cell devices in terms of efficiency, the tandems are conducive to improved device stability. Compared to PVK-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 [128]. In addition, OPVs often suffer from insufficient UV stability, but the UV sensitivity of OPVs is settled by shielding blue-violet light with a PVK absorber in the Pero-OPV tandem solar cells (TSCs). However, these kinds of tandems are currently lagging behind the PVK-Si and all-PVK tandems in terms of efficiency. But further development can be expected for various new application scenarios, such as flexible, indoor, semi-transparent systems.

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 indices, acting as the charge transport layers, the blocking layers, and the light-absorbing layers, respectively. At present, the easiest and most widely used method involves thermally evaporating a single magnesium fluoride (MgF_2) between the air and the indium tin oxide (ITO) glass (or the glass substrate) as antireflection. CIGS and CZTS with the film thickness of micrometers can absorb near-infrared light adequately, but OPVs are generally 100–115 nanometers thick. Thus, it is necessary to develop more specialized antireflection coatings to increase 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 [129]; compared to the CIGS, the best CZTS and organic solar cell showed high energy loss, reaching 0.589 [130] and 0.55 eV [131], respectively. Additionally, the optimal bandgap of the PVK front sub-cells is above 1.65 eV, and the corresponding Voc loss generally exceeds 0.5 eV.

Imperfect interconnecting layer (*ICL*). The sputtered thick 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. Moreover, 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 [132]. The perfect ICLs: (i) make the voltage addition of front and rear sub-cells, 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 sub-cells from solvent erosion, being quite difficult to fabricate. Overall, these challenges hinder the breakthrough of device efficiency, but also the delayed commercialization process.

Advances in science and technology to meet challenges

To face the challenge, it is extremely necessary to identify deep insights into photoelectric losses and the working mechanism of the PVK-based TSCs. Lang *et al* [133] developed a sub-cell 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,

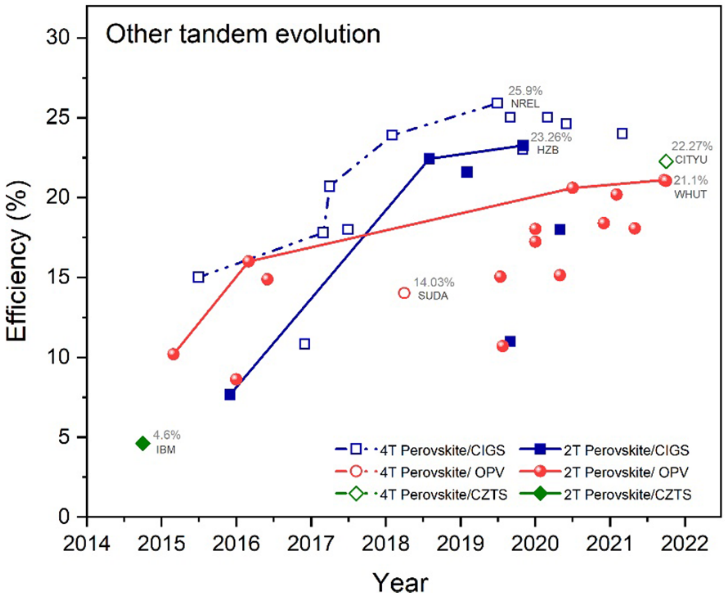

Figure 10. Efficiency evolution for PVK-CZTS [122, 123], PVK-CIGS [124, 125], and PVK-OPV [126, 127] TSCs.

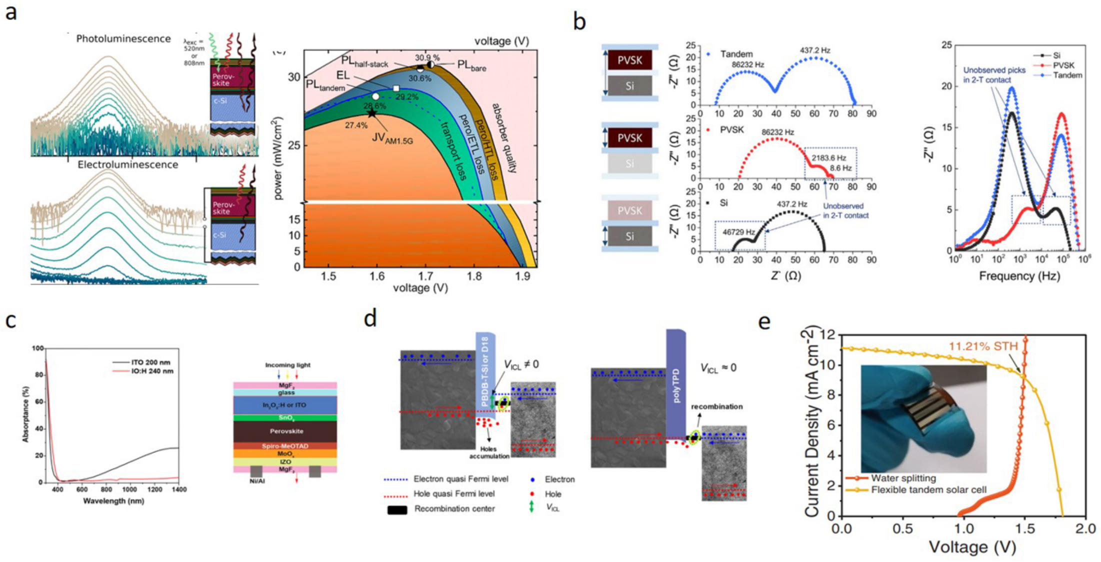

Figure 11. Advanced science and technology for meeting challenges. (a) The PCE potential of TSCs quantified by intensity-dependent absolute photoluminescence (PL) and injection-dependent absolute electroluminescence (EL). (b) Impedance spectroscopy of three-terminal TSCs. Reproduced with permission. (c) Absorptance of the two kinds of transparent conductive electrodes: IO: H and ITO, and a scheme of a semi-transparent PSC. (d) The mechanism of tuning the interconnecting layers for Pero-OPV TSCs. (e) The J-V curves of flexible Pero-OPV TSCs. (a) Reprinted with permission from [133]. Copyright (2021) American Chemical Society. (b) Reprinted with permission from [99]. Copyright (2020), American Chemical Society. (c) Reprinted from [134], Copyright (2019), with permission from Elsevier. (d) Reprinted with permission from [126]. Copyright (2021), American Chemical Society. (e) [135] John Wiley & Sons. (Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

and transport losses (figure 11(a)). Park *et al* [99] demonstrated that it is useful to construct the 3-terminal (3T) measurement architecture to analyze the charge dynamics of each sub-cell of a 2T tandem, separately and integrated (figure 11(b)). Here, it has been concluded that the PVK front cell has microsecond-level kinetics, while the Si bottom sub-cell has millisecond-level kinetics. However, there are still few relevant studies that report whether this capacitance rule can apply to other PVK-based TSCs, through the 3T measurement method. Moreover, continuous technological breakthroughs are also extremely important. Jiang *et al* [134] developed an In_2O_3:H film deposition method. Compared with the traditional TCOs, the In_2O_3:H film has better mobility with a value up to 129 $cm^2 V^{-1} s^{-1}$ and better Near-infrared (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 11(c)). Wang *et al* [126] 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 11(d)). Nevertheless, few researchers report whether the electron transport material has a similar effect to the HTM. Additionally, Li *et al* [135] 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 11(e)). Thus, acceleration of the advancement of commercialization requires more exploration in applications with unique advantages for these types of tandem PVs.

Concluding remarks

In this review, we briefly introduced the evolution of the Pero-CIGS, Pero-CZTS, and Per-OPV TSCs. Although increasing numbers of researchers are devoted to improving the performance of this type of tandem device, their efficiency is still far from the PVK-Si and all-PVK tandems solar cells. Next, we listed three common problems of critical light management, large Voc loss, and the imperfect interconnecting layer, that hinder the improvement of these novel tandem applications. Finally, we emphasized sub-cell diagnosis methodology, the 3-terminal measurement method, and some preparation techniques of better NIR-transparent TCOs, high-quality HTM, and flexible tandem PVs 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 PV market in the future market.

Acknowledgments

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12. Encapsulation of PSCs

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Status

Even though organic–inorganic halide perovskite solar cells (OIHP) have achieved comparable power conversion efficiency with silicon solar cells [136], they are still facing barriers in large-scale production. To some extent, issues like higher PV performance with improved device stability have been addressed. However, further progress in the field requires the following of standardized testing protocols, as well as establishing suitable encapsulation protocols for high performance [9]. As illustrated in figure 12, the function of encapsulation is to restrict ingress of moisture and oxygen and restrict lead leakage, 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 [9]. 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 [9, 137–140], 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 have been reported to date, i.e. ethylene vinyl acetate (EVA), polyvinyl butyral, thermoplastic polyurethane, polyisobutylene (PIB), fluoropolymer coating, various polymer films, ethylene methyl acrylate, cyclized perfluoro-polymer (Cytop), organic–inorganic hybrid materials, ORMOCERs, ORMOSIL aero-gel thin film [137], as well as different polymer films, polydimethylsiloxane (PDMS), PET, polytetrafluoroethylene, poly (methyl methacrylate (PMMA) polycarbonate, etc [138]. However, detailed comparisons between different materials have been scarce.

Current and future challenges

It is well known that PVK materials are highly moisture sensitive (regardless of illumination), as well as sensitive to the exposure to oxygen under illumination. Therefore, the discovery of appropriate encapsulation materials and routes to adopt in the PVK field is highly desirable. Ideal materials for encapsulation require a low oxygen transmission rate (OTR) and water vapor 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 [139]. More importantly, encapsulating material and PVK properties should be compatible to avoid delamination and reaction risks to avoid a drop in the PV performance due to outgassing of solvent or sealant and/or reactions between the solvent or sealant and device components during the encapsulation process, or during storage or application of different types of stress for accelerated stability testing. Specifically, the encapsulant and edge sealant should be inert with respect to PVK 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 be 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 PV technologies use an 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 PMMA, PDMS, perylene C, fluoropolymer coatings, and spray-coated reduced graphene oxide [140], and inorganic films like silica or alumina [141] can be potential candidates for thin-film encapsulation. These interlayer films can be incorporated with the device via simple, low-pressure deposition, and low-cost methods, such as atomic layer deposition, sputtering, and evaporatio. Cover-glass encapsulation can be further subdivided into blanket and edge encapsulation or a combination of both, as shown in figures 13(a)–(c). The technique confines the devices between two surfaces with low OTR and WVTR, which limits the possibility of moisture and oxygen ingress to the edge seal. While other oxygen- and humidity-sensitive technologies such as organic light-emitting diodes have successfully used the encapsulation method using the edge seal only with incorporated desiccant, this method is less suitable for PSCs 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 the Si PV industry, such as EVA, can react with PVK [9, 142]. 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

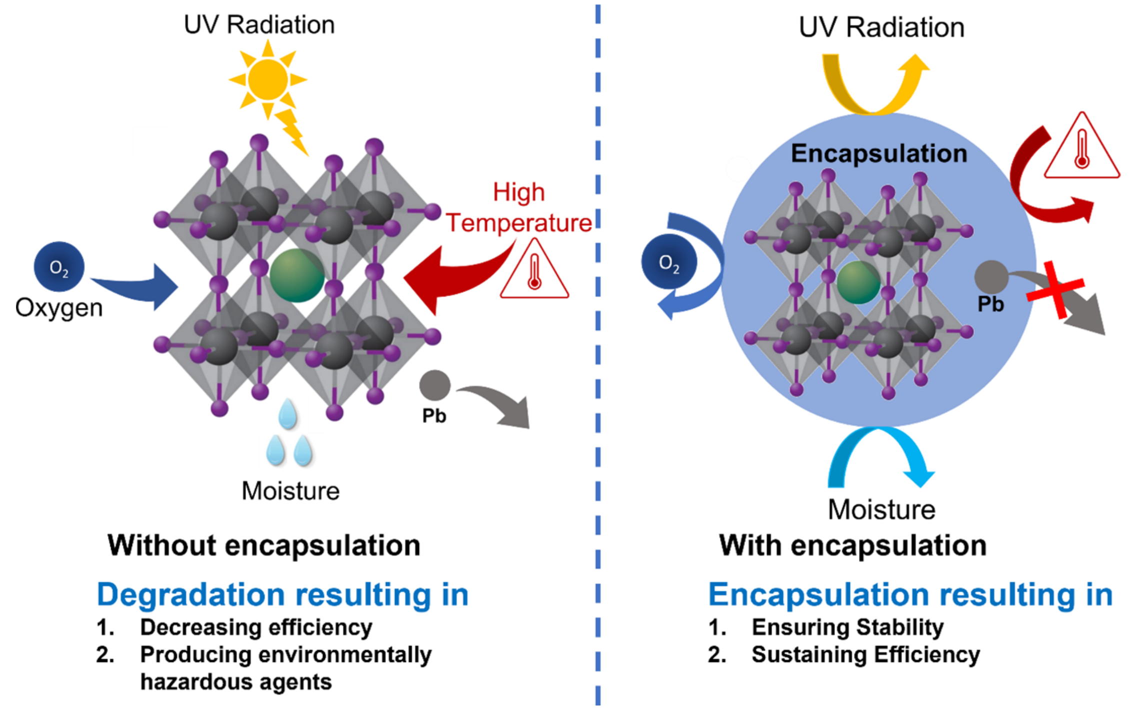

Figure 12. A schematic illustration of PVK with and without encapsulation.

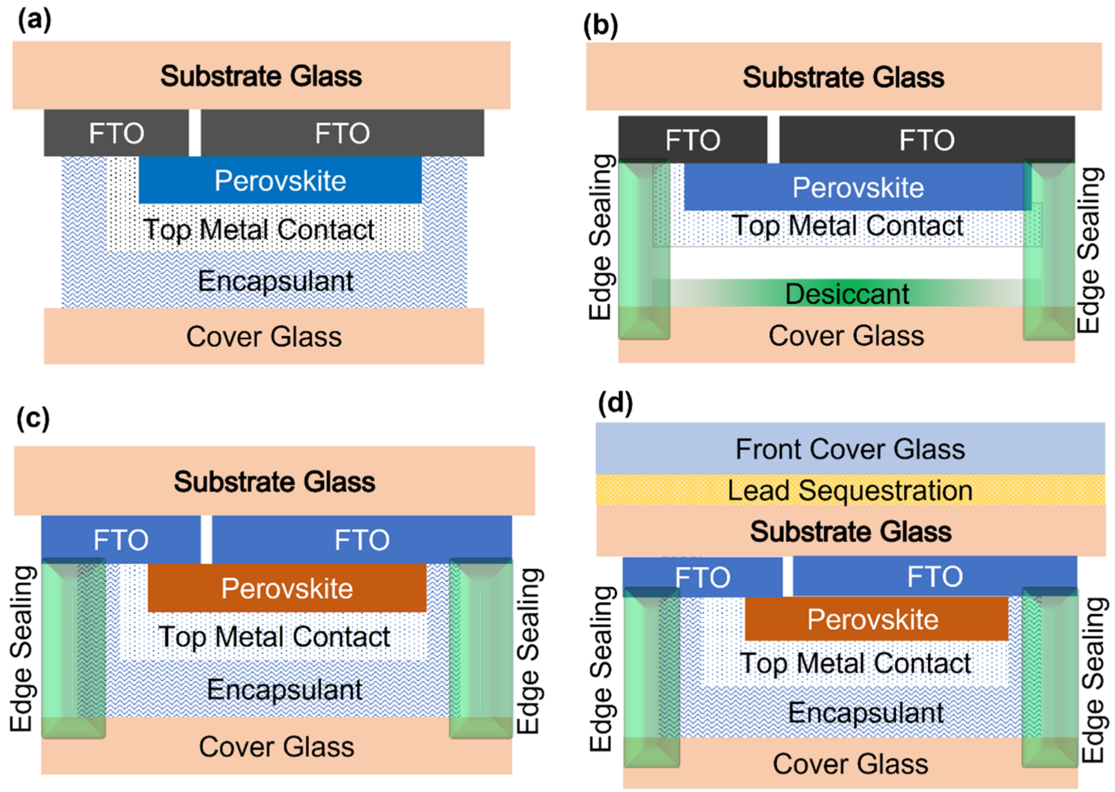

Figure 13. A schematic illustration of different types of cover-glass encapsulation: (a) blanket encapsulation, (b) edge encapsulation, (c) blanket encapsulation with edge sealing, and (d) sealed-edge blanket encapsulation with the added feature of lead containment. Reprinted with permission from [9]. Copyright (2022), American Chemical Society.

the package, as well as ensuring that the width of the edge seal is compatible with the chosen testing conditions (i.e. ∼12 mm of PIB is needed for 1000 h under the damp-heat test).

Finally, it should also be noted that encapsulation not only limits moisture and oxygen ingress into the device, but also restricts the lead (Pb) leakage in the outside environment [143]. Thus, it is desirable to include lead containment features into the encapsulation package, as illustrated in figure 32 and discussed in more detail in section 23. With the 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 PSCs [141]).

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 combination [45], under open-circuit or maximum power point (MPP) [45, 144] testing. These testing protocols can thus be divided into testing protocols for device testing in the 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) that accelerate PVK material and device degradation. Great progress has been made in recent years in both improving the device stability and encapsulation method for PSCs to be able to pass ISOS-D3 damp-heat testing conditions, which involve temperature of 85 °C and relative humidity of 85% [141]. For a summary of device architectures and encapsulation methods suitable for these stringent tests, see [9]. In five out of seven reports on successful (>1000 h) damp-heat testing, encapsulation with PIB as either blanket or edge sealant was used [9], indicating its high suitability for PVK encapsulation. Despite this progress, further research into encapsulant materials suitable for PSCs is needed, with particular attention devoted to performance at elevated temperatures, not only due to the requirement to pass damp-heat testing but also the fact that the temperature during outdoor operating conditions was estimated to reach 70 °C [145].

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 PSC commercialization. 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), an impenetrable glass cover, and a lead-containment feature.

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13. Stability of PVK materials: moisture and oxygen

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Status

Halide perovskite (HP) materials, in particular low-bandgap iodide-based PVKs, exhibit instability when exposed to an ambient environment, which is further enhanced upon ambient exposure under illumination. Since the solar cells are expected to operate under illumination in an ambient atmosphere, it is essential to understand the mechanisms of degradation 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 the possibility of ambient processing would significantly simplify the process and lower the cost [146]. Thus, improving the stability on exposure to ambient atmosphere is critical for future commercialization of these devices. All the layers in the PSC can be affected by ambient exposure, and in some cases exposure to oxygen could even be beneficial, such as oxygen doping of 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (SpiroOMeTAD) [147, 148]. However, here we will mainly focus on the effect of oxygen and moisture on the HP 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 toward deprotonation [148]. 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 [148]. Upon exposure to moisture, MAPI initially transforms to a hydrated form [148–150], which is reversible, followed by irreversible degradation [149, 150]. The degradation of the PVK on exposure to humidity is dependent on the relative humidity and time of exposure [149, 150], and it is also affected by the hole transport layer (HTL) covering the PVK [149], which offers the possibility to slow down the process by suitable selection of a HTL (dopant-free hydrophobic materials forming smooth pinhole-free films with good adhesion to PVK 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 a dehydrated species and ultimately decomposition to PbI_2 [150].

Current and future challenges

Significant efforts have been made to understand the degradation processes and to develop methods to address the degradation. Exposure of PVK to moisture has been extensively studied [148–151], and the degradation pathway for moisture exposure [148–150] is reasonably well understood. However, details related to the PVK film properties (defects, stoichiometry, morphology, grain boundaries, surface termination) affect the degradation upon moisture exposure, and the influences of these factors need to be better understood. For example, a rough surface can lead to faster degradation [151]. It is also important to note that moisture-induced degradation is accelerated by illumination (even ambient illumination) [151], and this acceleration process, unlike oxygen exposure, has not been as comprehensively studied. Furthermore, considering the fact that PVK 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 PVK degradation in the dark [148, 152, 153]. 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 interactions with Pb [152]. 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 [152]. Under illumination, a superoxide ion is generated, which results in photooxidation of the PVK [152]. The effects of oxygen are dependent on the partial pressure of oxygen and the composition of the PVK, 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 this case require further study [153].

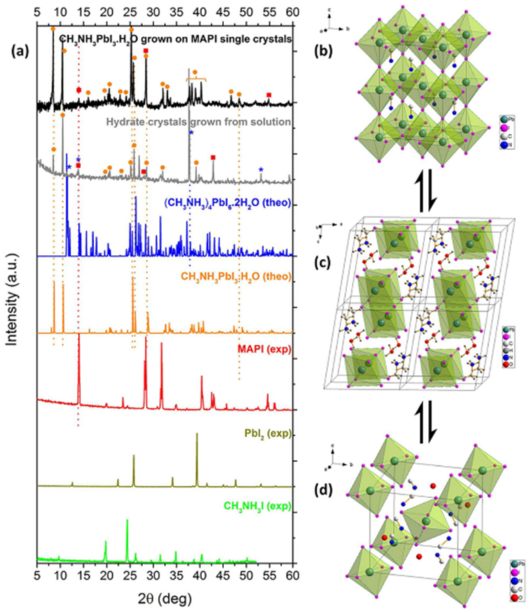

Figure 14. (a) Identification of the composition of the hydrated species grown on MAPI single crystals (at long exposure to water vapors) and of MAPI hydrated crystals (polycrystalline, obtained from solution) by x-ray diffraction (patterns in black and gray). The five patterns below these (either experimentally measured or simulated from crystal structures) show the species that 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). Reprinted with permission from [150]. Copyright (2015), American Chemical Society.

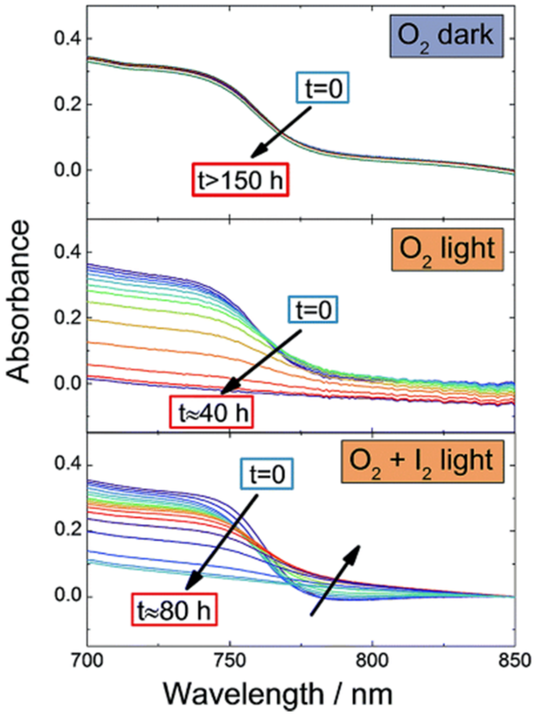

Figure 15. Stability of MAPbI3 films under O_2 exposure, in the dark and under illumination (4.6 mW cm^{-2}), monitored by UV–vis spectroscopy. The samples are kept at 333 K under constant gas flow. After more than 150 h, no changes are visible for samples kept in the dark between measurements, while 40 h 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 ($P(I_2) = 1.4 \times 10^{-5}$ bar), shows doubled stability, with full degradation achieved after 80 h. Note the formation of a tail in the absorption, indicating amorphization of $MAPbI_3$. Reproduced from [153]. CC BY 3.0.

Advances in science and technology to meet challenges

Different methods exist for improving the PVK stability with ambient exposure (especially moisture), such as the use of hydrophobic layers, 2D PVKs, and/or encapsulation [148, 154]. 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 [148]. Even in encapsulated devices, there could be oxygen released from the metal oxide layer, which could result in degradation under illumination [147]. A reduction of superoxide ion generation and consequently reduction of photooxidation, as well as ion migration, has been demonstrated by optimizing the PVK composition (Cs content) [147], since the photooxidation degradation is dependent on the PVK composition [153]. In addition, improved stability under illumination can be achieved using additives combined with appropriate selection of device architecture [155]. For example, the use of an aminovaleric acid additive resulted in increased superoxide ion generation for films on glass, but reduced superoxide ion generation when infiltrated into a mesoporous $TiO_2/ZrO_2/C$ structure [155]. This was attributed to the dependence of superoxide ion formation on oxygen diffusion, grain morphology, and native defects [155]. Thus, significant stability improvements are possible by careful optimization of PVK composition (including additives and/or passivation) and device architecture, introducing additional layers, and encapsulation.

In addition, progress has been made toward the ambient processing of PSCs (for more details, see section 6). For example, better understanding of PVK crystallization in the presence of water has led to the development of a deposition process involving prenucleation by adjusting spin coating and antisolvent application [146]. The increase in nuclei density achieved in this process prevented the growth of large needle–like crystals of a $MA_2Pb_3I_8 \cdot 2DMSO$ intermediate, which resulted in smooth films and efficient devices [146]. However, while reports on ambient-prepared devices typically involve good shelf-life stability [146], ambient-fabricated devices have rarely been subject to harsh stability testing conditions, such as the damp-heat test, outdoor test, and accelerated aging under illumination at elevated temperatures. More stringent stability testing protocols are essential to establish whether any residual moisture arising from ambient processing affects device stability.

Concluding remarks

PVK 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 the long-term stability of the devices. The ambient-induced degradation processes are significantly affected by the composition and morphology of the PVK and native defect concentrations. Moisture-related degradation is better understood and easier to address compared to photooxidation degradation in the 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.

Acknowledgments

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14. Stability of PVK materials: illumination

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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 PVK 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 exhibit degradation under illumination [156], the discussion in this section is limited to PVK material. The intrinsic degradation under illumination is dependent on the type of illumination (UV, blue light, white light)[156] and involves irreversible [156–158] and reversible processes [156, 159–165]. 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 [156, 159–165] the process is still not fully clear. The irreversible photodegradation is somewhat better understood. It is strongly dependent on the halide perovskite (HP) composition, with PVK films prepared with excess PbI_2 (a common approach to increase efficiency of the devices) exhibiting degradation due to intrinsic decomposition of PbI_2 into Pb and I_2 under illumination [157], with released I_2 resulting in a chain reaction and further degradation of the PVK [156, 157]. However, device performance degradation trends do not necessarily follow the same trend as PVK film degradation due to complex interplay between different processes [157]. The methylammonium (MA) lead iodide (MAPI) is also susceptible to photodegradation under prolonged illumination, and it decomposes into methylammonium iodide and PbI_2 (followed by further decomposition of PbI_2), and MAPI decomposition can even occur at temperatures as low as 5 K [156]. It should be noted that many of these studies have been conducted in vacuum, which would result in the inevitable loss of volatile organics. Recent experiment in an Ar atmosphere clarified the process of MAPI photodegradation, and the formation of $Pb^{(0)}@PbI_{2-x}$ nanoparticles was proposed, as illustrated in figure 16 [158].

Current and future challenges

Improving the stability of PVK materials and devices under illumination is critical since the solar cells need to function under illumination. Due to practical importance of mixed composition HP 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 [156]. Furthermore, due to the complexity of the processes involved, differences in experimental designs, sample composition, sample morphology, and sample preparation, it is difficult to generalize the conclusions of different studies. These variations result in a large spread of reported segregation times from tens of seconds to tens of minutes, even for similar PVK compositions [160]. In particular, the measurement conditions (vacuum, air, nitrogen, polymer-protected in vacuum) determine whether the observed changes under illumination are reversible or not [160]. Consequently, different models have been proposed to explain PHS to date, which include polaron-induced lattice strain, defect mediated processes, and thermodynamic properties [156, 159]. It was proposed that trapping of holes occurs exclusively in the iodide phase of the PVK, and selective expulsion of iodine from mixed halide film into the solvent occurs under illumination [159]. Hole trapping at iodide sites makes these sites unstable, triggering iodide migration through vacancy hopping, resulting in PHS [159]. 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 [160]. It was proposed that an electric field arising from trapped charge carriers initiates the segregation, and the process is further exacerbated by funneling the carriers to a lower bandgap segregated iodide phase [160]. The hypothesis of charge trapping is further supported by improved photostability by coating HTL on the PVK surface, which prevents hole accumulation in the PVK [161]. 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 the existing literature data [165]. Based on temperature-independent terminal stoichiometry, a bandgap-based thermodynamic model instead of a miscibility-based

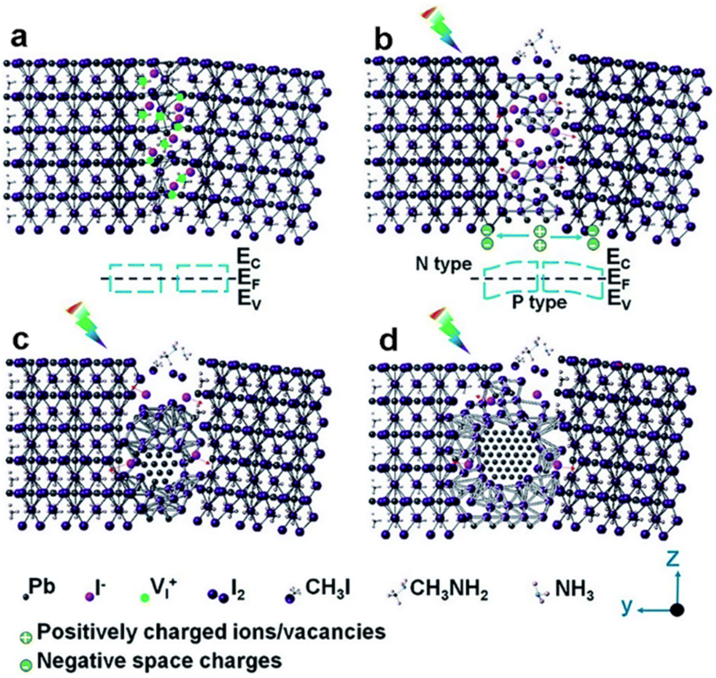

Figure 16. Illustrations of the photodegradation mechanism of the MAPI film into the Pb@PbI2-x core–shell nanostructures. (a) Numerous deficiencies exist at the grain boundary of the as-prepared PVK film. (b) Under light illumination, the iodide ions prefer to migrate away from the grain boundaries (red arrows) to induce a 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 from [158] with permission from the Royal Society of Chemistry.

thermodynamic model was proposed [165]. However, before the matter can be considered settled, applicability to MA-free PVKs should also be investigated.

Advances in science and technology to meet challenges

A number of different approaches has been proposed to tackle photodegradation of HP materials and devices [156]. These include defect passivation (in particular surface and grain boundary) [156], adjusting the PVK composition [156, 159, 162] to reduce lattice distortion induced by photogenerated carriers [156], avoiding the use of UV-sensitive charge transport layers, such as TiO_2, and using photostable charge transport layers in general [156], using UV-blocking layers and/or downconversion layers [156], and interface modifications [156, 161]. 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 a low trap-mediated recombination rate constant (10^5 s^{-1}), at least for MA-based PVK [160]. Thus, composition optimization (cation mixing) and structural engineering are needed together with minimizing traps to suppress PHS [160]. Surface passivation of traps, for example, using trioctylphosphine oxide [161], 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 the different approaches to improve photostability, optimizing the PVK composition and structure is also a highly promising approach. For example, Cs incorporation was found to improve the photostability of mixed HP films [159, 163, 164], and this phenomenon was attributed to reduced iodide mobility in mixed cation films [159]. However, the PHS exhibits complex dependence on the PVK composition, which is likely an interplay between the effects of crystal structure as well as local electronic and chemical interactions [163]. As a result, PHS increased again when the Cs concentration was increased above the optimal concentration [163], 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 [164]. Another approach for optimizing PVK composition to suppress PHS is the use of triple halide mixed PVK [162]. These devices demonstrated significant improvement in the photostability, even under significantly higher illumination intensity (up to 100 sun), as shown in figure 17 [162].

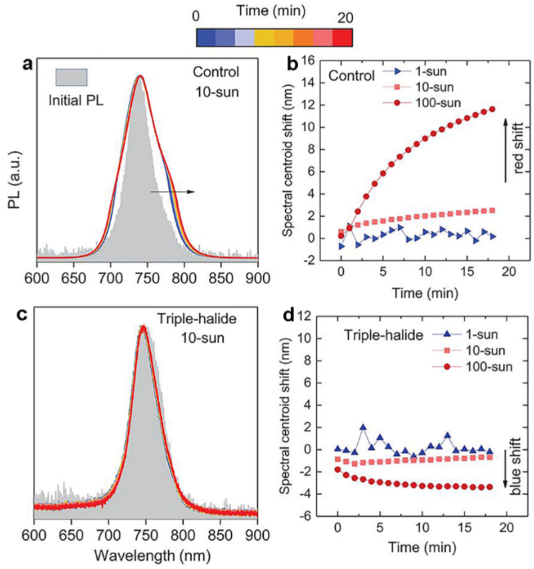

Figure 17. Suppression of photoinduced phase segregation in triple-HPs. (a) Photoluminescence (PL) spectra of 1.67 eV control PVK films (Cs25Br20) under 10-sun for 20 min. The arrows indicate the direction of the PL shift over time. (b) The shift of the spectral centroids of control films over time. The red shift becomes more obvious under higher injection. (c) PL spectra of 1.67 eV triple-HPs (Cs22Br15 + Cl3) under 10-sun illumination for 20 min. (d) The shift of the spectral centroids of triple-HPs over time. The blue shift becomes more obvious under higher injection levels. From [162]. Reprinted with permission from AAAS.

Concluding remarks

Photostability of HP materials and devices has been extensively studied. Nevertheless, some phenomena, such as PHS, are still not fully understood despite their practical significance. Thus, further work is needed to improve the understanding of the PHS process and its dependence on HP 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 toward passivating the defects and improving the stability. Promising improvements have also been obtained in optimizing the PVK composition, and it is likely that further improvements can be achieved by combining different approaches, such as simultaneous use of optimized PVK composition, optimized processing, including additives for defect passivation and achieving large grain sizes, and surface passivation.

Acknowledgments

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15. Stability of PVK materials: temperature

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Status

The 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 (HPs), 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 (PCE) values have been achieved, the poor device stability, in particular under elevated temperatures, remains a major hurdle to the commercialization of PSCs. There are several sources for degradation of PSCs under elevated temperatures, including thermal instability of electrons 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 PVK materials themselves.

Already, at the early stages of PSC research, studies have shown that $MAPbI_3$ ($MA = CH_3NH_3$), the first PVK composition used in solar cells, is thermally unstable. Decomposition of $MAPbI_3$ thin films was observed to already occur during annealing at 85 °C, even in inert atmosphere [166]. Increasing the temperature toward 100 °C and higher causes decomposition of the material into methylamine, hydrogen iodide, and lead iodide. This observation is consistent with density functional theory (DFT) calculations, which have shown very low formation energies of the PVK referred to its precursor salts. Since then, various attempts have been undertaken to increase the thermal stability. These include optimizing the fabrication methods of the thin film and engineering the PVK 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 HP compositions are regarded as highly promising in terms of thermal stability [167]. However, it transpires that simple trends do not exist, as displayed in figure 18, showing a quantitative stability comparison of various mixed hybrid PVKs based on a thermogravimetry differential thermal analysis (TG-DTA) analysis [168].

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

Current and future challenges

$MAPbI_3$ deteriorates during thermal stress. Replacing MA with formamidinium ($FA = CH(NH_2)_2$) can increase thermal stability. This can be explained by 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-PVK 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 methods 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 a MASCN vapor-treated $FAPbI_3$ film remained in its pure black phase after 500 h of annealing at 85 °C [169]. 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 PVK 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 the 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 PCE, whereas $FAPbI_3$ PVKs show signs of degradation [170]. However, excess Cs and Br would lead to phase instabilities due to large lattice stress. Therefore, finding the right ratio of cations and halides is a major challenge.

Meanwhile, there are reports on solar cells based on mixed compositions passing damp-heat tests and similar, proving 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 Section 16).

Advances in science and technology to meet challenges

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

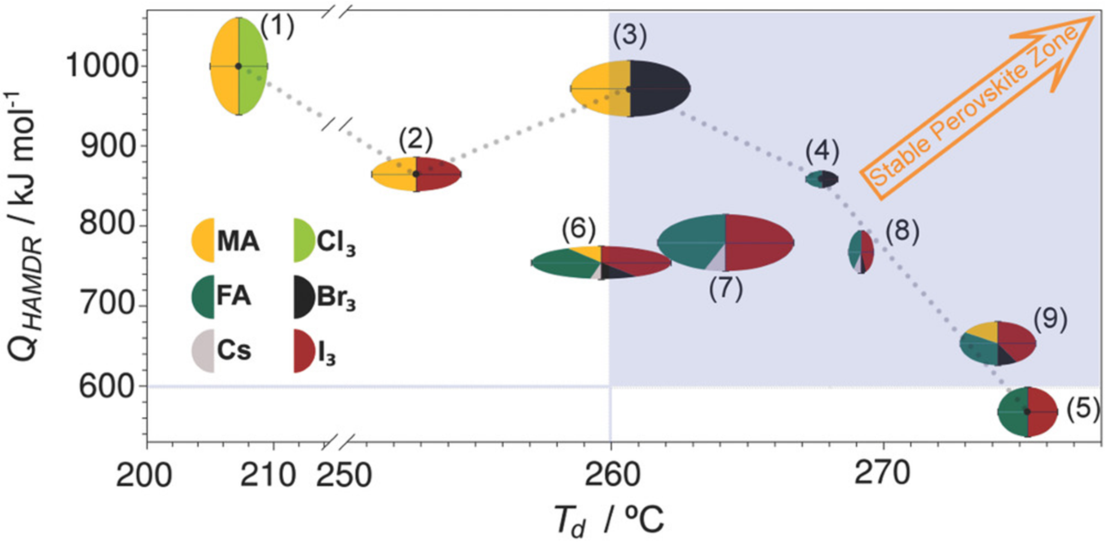

Figure 18. A stability map of hybrid HPs represented by Td (sample degradation temperature, *x*-axis) versus QHAMDR (sample heat absorbed at maximum degradation rate, *y*-axis), two parameters of thermal degradation experiments. Uncertainty of the measurement is represented by the ellipses' *x*–*y* axis lengths. Colors in the left and right side of ellipses describe the PVK'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). [168] John Wiley & Sons. (Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

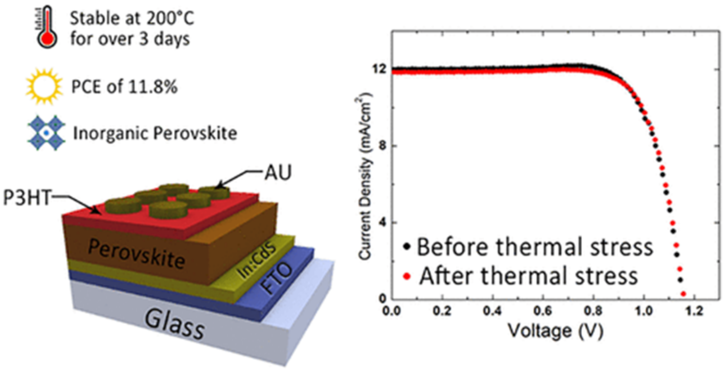

Figure 19. All-inorganic CsPbIxBr(3 − x) device performance showing no change with thermal stress at 200 °C for 72 h [173]. Reprinted with permission from [173]. Copyright (2020), American Chemical Society.

To accelerate this procedure from the PVK 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 PVKs, 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; therefore, carefully tracking and characterizing changes at interfaces, e.g. using impedance spectroscopy can lead us toward a fundamental understanding of the required passivation mechanism. Adding a thin 2D PVK layer to the 3D PVK film is another promising approach, which can greatly enhance the stability of the PSCs [171]. Dedicated interfacial layers acting as ion-blocking layers are needed to avoid the fact 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 PVK layer.

In addition to composition engineering, another approach toward thermally stable PVK films is to control 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 [172]. Such impressive thermal stability for solar cells with a $MAPbI_3$ absorber shows the potential for control of the PVK growth process to improve the stability of mixed PVKs even further.

In terms of materials, all-inorganic PVKs are the most promising compounds to address the stability challenge. Gaonkar *et al* reported thermally stable inorganic mixed halide PSCs with no loss in device performance at 200 °C for 72 h (figure 19)[173]. However, the presence of point defects and not fully optimized preparation methods resulted in lower performance. To realize the full potential of these materials and maintain the α phase, e.g. during thermal cycling, further optimizations on the PVK film, including its interfaces, are to be undertaken [174, 175].

Concluding remarks

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

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16. Stability of PSCs: ion migration

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Status

PSCs exhibit unusual physics that is not commonly observed in other PV technologies. This was first highlighted by Snaith *et al* [176], 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 PVK 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 PVK absorber layer. In particular, they act to screen the electric field from the PVK by forming narrow space-charge layers at the edges of the PVK 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 PVK/transport layer interfaces, serves to determine the electric potential distribution across the device and so plays a key role in determining the concentrations of charge carriers on these interfaces [177]. Thus, interfacial recombination, which is the predominant loss mechanism in efficient modern cells [178], is strongly dependent on the ion vacancy distribution. This opens up 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 [177].

There is strong experimental evidence that the motion of halide vacancies, lying on the X-site of the PVK 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 neighboring sites in the PVK crystal structure of methylammonium lead tri-iodide ($CH_3NH_3PbI_3$), or MAPI for short [179]. 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^-) PVK cells, have been associated with the very slow motion of cation vacancies [180].

Notably, the absence of hysteresis in so-called ‘hysteresis-free cells’ does not imply the absence of ion vacancy motion within the PVK but often, as noted by Bryant *et al* [181], 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, to slow down (or speed up) ion motion, before repeating the J-V scans to see if hysteresis re-emerges. As noted in [177], transport layer properties play a significant role in determining the hysteresis timescale and can lead to marked differences in behavior between cells of different constructions but with identical PVK absorber layers.

Current and future challenges

There is good evidence that the picture of the ionic behavior of PSCs presented above is a simplification of their real physics, and that the chemistry of organometal PVKs exhibits other ionic behavior, in addition to ion vacancy motion. In particular, *ab initio* computations on PVK structures [182] 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 [183]. 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 [184].

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 PVK absorber and into the adjacent transport layers [185]. This leads to the gradual degradation of the PVK material. Various methods to reduce ion migration, and thereby control this degradation pathway, have been reviewed by Lee *et al* [186]; these include passivation

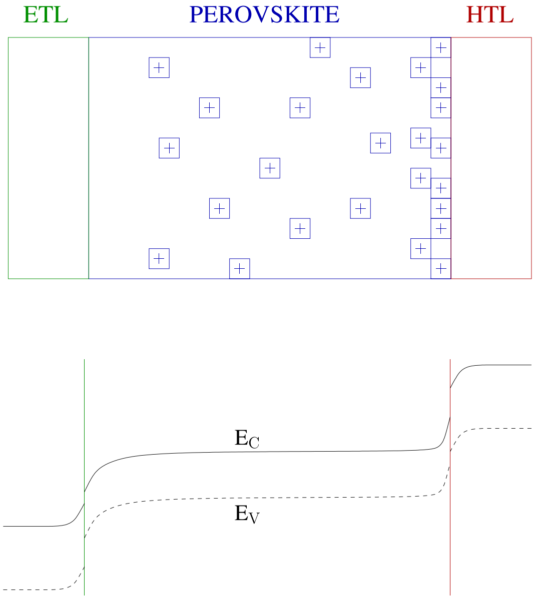

Figure 20. (Top) A schematic of vacancy distribution in a scenario of a single mobile vacancy species (positively charged). (Bottom) The associated conduction and valence band energies.

of grain boundaries between PVK crystals and total, or partial, substitution of the methylammonium cation in the PVK 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 minimize 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 and intensity modulated photocurrent spectroscopy. 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 PV 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.

Concluding remarks

The presence of charged ion vacancies in the PVK absorber layer of PSCs 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 layer interfaces) is key to controlling device efficiency and limiting cell degradation.

17. Stability of PSCs: electrode choices

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Status

The power conversion efficiency (PCE) of metal halide perovskite solar cells has soared to near 26%. Recently, research interest in device stability has attracted increasing attention with the aim to prolong the duration of devices under operational conditions [187, 188]. To date, substantial articles or reports have highlighted the rapid advances in this field, and mainly concentrate on the study of new materials and their physical/chemical properties, the design and construction of the device with various configurations, and the operational mechanisms via compositional engineering, interfacial engineering, and structural engineering. The electrode is essential for collecting charges in the device, and plays a substantial role in the PCE and stability of PSCs [189–191]. It accounts for a large share in the total fabrication cost, affecting the commercialization process of PSCs significantly. Less attention has been devoted to electrode materials compared with the other components of PSCs. Apart from the PV performance and stability, electrode materials may affect other expected functions, including semi-transparency light absorption and flexibility. Furthermore, it is importnat to regulate the approach of the specific electrode during the fabrication of the entire device [192], and consequently affects the cost of PVK devices.

Current and future challenges

The electrode materials show suitable work functions 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 21) [189]. Typically, the benchmark metal electrodes of PSCs are noble metals including Au or Ag due to their high light reflectivity and low sheet resistance ($R_{sq} \leqslant 1\,\Omega\,sq^{-1}$). Au is the most typical electrode with excellent chemical robustness in PSCs, which could still react with the halide (iodide) in the hybrid PVK under the synergistic effect of ion migration and PVK decomposition, migrating through the hole transporting layer (HTL) to the PVK layer, ultimately resulting in the degradation of the whole device. Ag is another common electrode material, which is even more chemically unstable and may have a interaction with the reacted migrated iodine from absorbers, leading to a change in the interfacial electronic properties of the Ag/HTL interface [189, 190].

To replace these noble metals, various 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, and metal/metal oxide composites. Furthermore, several studies have examined the performance of molybdenum (Mo) and tungsten (W) electrode-based PSCs [193, 194].

Carbon materials, such as single-wall or multi-wall carbon nanotubes, graphite, graphene, and carbon black, have been applied as electrodes for PSCs. In contrast to metal electrodes, carbon materials exhibit excellent diversity and modifiability, a relatively high specific surface area, rich micropores and mesopores, and high chemical stability, which ensures carbon materials work regularly in the monolithic structured PSCs [187, 195, 196]. Most importantly, the Fermi level of carbon (5.0 eV) is very close to the valence band edge of the PVK (≈5.4 eV), facilitating the collection of holes from PVKs. It is notable that carbon-based PSCs 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 by introducing an electron blocking layer to suppress the carrier recombination.

Transparent conducting oxides (TCOs) have been widely used in PV modules, flat-panel displays, touch screens, and other applications due to well-established film deposition techniques [31, 197, 198]. 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 commercially 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 the electron/HTL. However, due to the high cost, lack of indium, and poor flexibility for the glass substrates, alternative TCOs, e.g. gallium-doped zinc oxide, indium-doped cadmium oxide, and aluminum-doped zinc oxide, have also been explored in semi-transparent or tandem PSCs.

As a representative conducting polymer, PEDOT:PSS can serve as the hole transport material in PSCs. It shows a similar work function to Au, around 5.0 eV, which makes it an ideal electrode material. However, aqueous solution is usually involved during the film preparation, which is harmful to the stability of PVK material [191, 193, 194]. Thus, it is important to develop a suitable approach for the utilization of

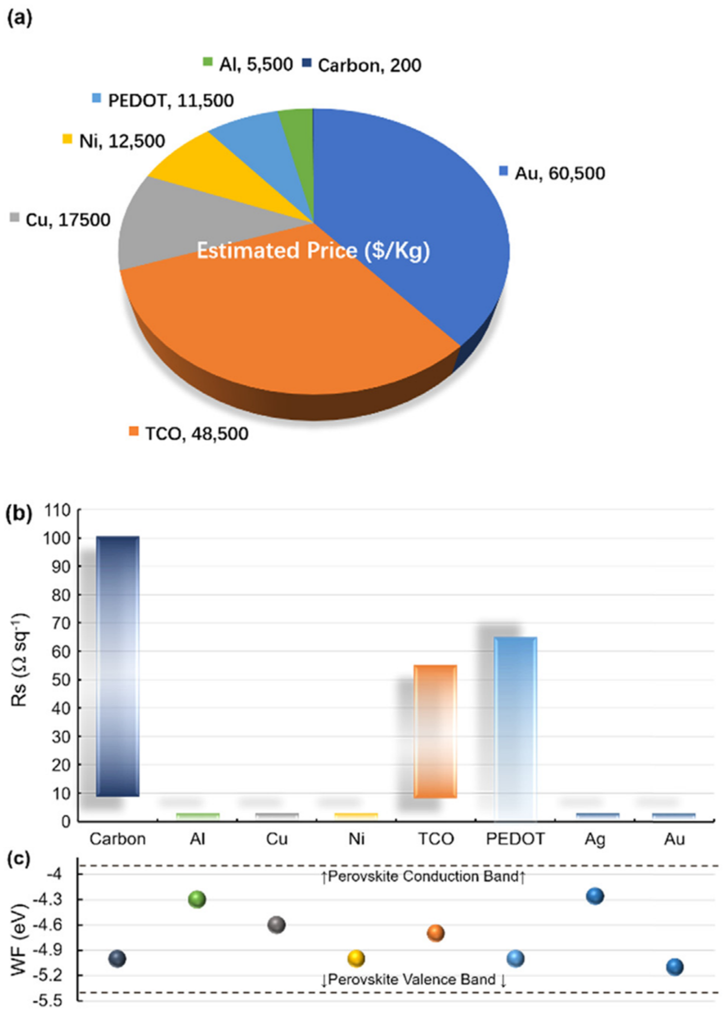

Figure 21. Analysis of electrode material costs and properties. (a) A summary of the costs of various metallic electrodes; (b) comparison of R_{sq} for different conductive electrode materials; (c) the work function of various electrode materials. Reproduced with permission from [187]. Reprinted from [189]. Copyright (2018), with permission from Elsevier.

PEDOT:PSS. Other studies have shown that polymer-based PSCs with good stability can be obtained through transfer-lamination techniques, detachable stacking PVK, and antireflection coating techniques, etc.

Rapid advances under intensive investigation toward the merits and drawbacks of electrodes have been highlighted and thoroughly understood (as shown in figure 22). However, before their commercialization can be realized, various challenges need to be addressed [199]. 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 [196]. It is possible to tune the work function by doping or mixing, and a variety of dopants have been investigated, but the unclear mechanism retards their commercial applications. Third, it is tough to prepare these materials on a large scale using a low-cost technique. The fabrication of TCO electrodes requires high-vacuum thermal evaporation or magnetron sputtering, which causes severe energy consumption [191, 198].

Advances in science and technology to meet challenges

The interface between the charge carrier transporting layer and the metal electrode plays an important role in obtaining highly efficient PSCs with good duration stability. To collect charge carriers from the electron transport layer (ETL) or HTL effectively, the energy gap between the work function of the electrode and the valence band maximum of the HTL or conduction band minimum level of the ETL should be reduced as much as possible [199]. Various materials have been integrated to tune the work function of the metal electrode, and consequently improve the interfacial charge transfer. Moreover, additional thin layers, such as

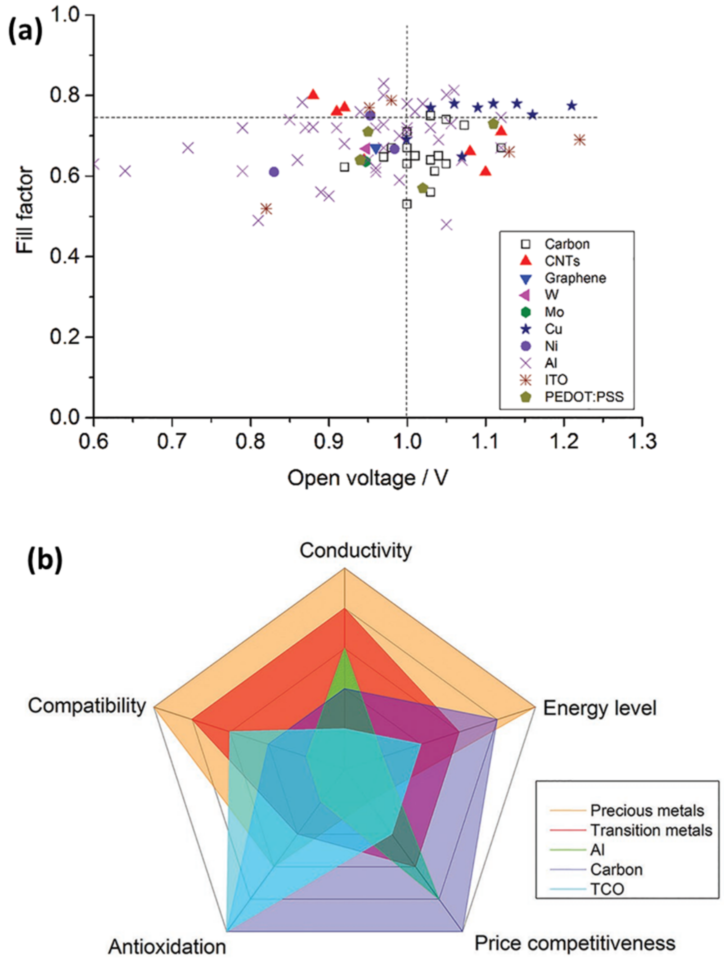

Figure 22. (a) Fill factors and PCEs of PSCs using various electrodes. (b) A summary of cost-effective electrode materials for PSCs. Different types of materials are ranked from poor to excellent according to their performance in corresponding factors. Reproduced with permission from [189], [199] John Wiley & Sons. (Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

ZnO, MoO_x, LiF, and bathocuproine, could contribute to effective adjustment of the work function and the stability of the PSCs. It is possible to fabricate carbon materials using many cost-effective techniques, such as doctor blading, screen printing, roll-to-roll printing, inkjet printing, drop casting hot pressing, and press transferring [7, 196]. Practical applications of carbon electrodes have been successful under various environmental conditions, demonstrating satisfactory robustness [195, 196]. 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 the 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 [197]. Semitransparent, transparent, and tandem devices with TCO, and conducting polymers like PEDOT are likely to perform well. The application of composite electrodes as alternatives toward the practical use of PVK-based PVs seems to be an option worth more exploration.

Concluding remarks

In recent years, understanding and knowledge have been accumulated on electrodes for PSCs, ranging from materials, processing techniques, and structure–property relationships, guaranteeing solid and advanced research and development of PSCs for diverse applications. Future efforts should be devoted to the exploration of facile, simple, and low-cost fabrication approaches, which allow the PVK materials to integrate, constructing a highly efficient and stable architecture. We look forward to increasing numbers of outcomes to be achieved in the development of electrode materials that accelerate the commercialization of perovskite PVs.

Acknowledgments

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18. Stability testing of PSCs

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Status

The different testing methods applied to assess the stability and lifetime of halide PSCs have evolved with time since the discovery of PSCs back in 2009. Due to the soft-material nature (materials with a 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 der Waals interactions and hydrogen bonds, as shown in figure 23, 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 HPs prone to ion migration, which is one of the main causes of hysteresis, defect formation, and phase separation, leading to device instability. Emerging PV technologies 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 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 [200]. Given the singular behavior observed for HPs, the PV community decided to upgrade these ISOS protocols to incorporate specific characterization procedures for PSCs [45]. This effort resulted in the introduction of specific testing conditions, for example, the effect of bias voltage or light-dark cyclability [201], and the publication of the first technical report developed by the IEC (IEC TR 63228) [201]. The application of these protocols and the development of novel ones, are important steps toward the commercialization of PSC technology. Nevertheless, further advances are necessary to improve PSC lifetimes. It is imperative to mimic real operational conditions, which comprehend 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.

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 to understand degradation mechanisms observed in devices emulating real *operando* conditions [202]. *In situ* characterization provides intermediate chemical and structural changes during operation under light illumination and heating. These changes are dynamic and can observe continuous transitions that are difficult to see under *ex situ* testing [203]. Changes that can be monitored *in situ* are related to material morphology, optoelectronic properties (carrier generation and recombination), or crystallinity and thus the most employed techniques are related to *in situ* SEM, TEM, and x-ray diffraction, among others. With respect to *in situ* optoelectronic characterization, analysis employing photoluminescence and time-resolved photoluminescence or electrochemical impedance spectroscopy are the most common tests. Advanced characterization techniques should include the coupling of these tests with temperature modulation, light irradiation, or relative humidity [203]. Moreover, performing a stability test at 65 °C–85 °C instead of at the classical 25 °C–45 °C would permit one 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 [203]. 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 [204]. Determination of acceleration factors by these means is also one of the pending assignments for PSC technology.

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 PSC layers to avoid material and device degradation but, most importantly, to prevent the solubility and leakage of toxic Pb-based perovskites. At the 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 encapsulant materials for glass-to-glass encapsulation, are employed. Holders applying inert gases usually employ continuous gas flow,

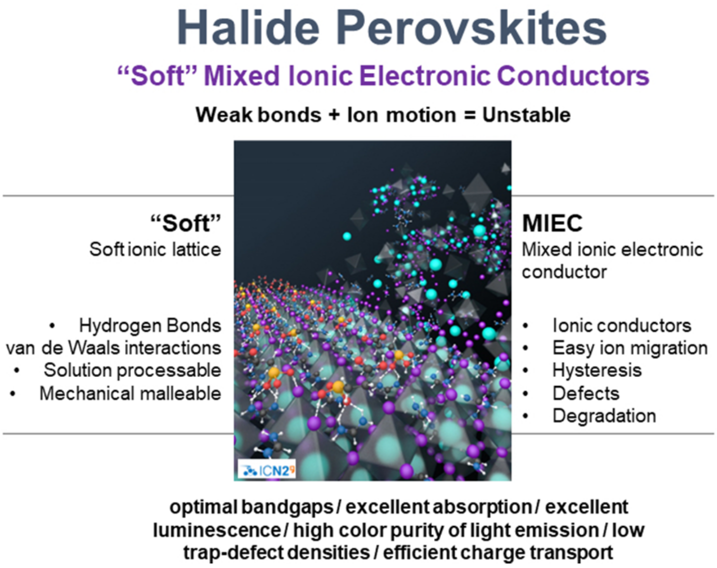

Figure 23. Halide perovskites are 'soft' ionic-electronic materials with weak bonds and high ionic motion. They must be engineered to make them stable.

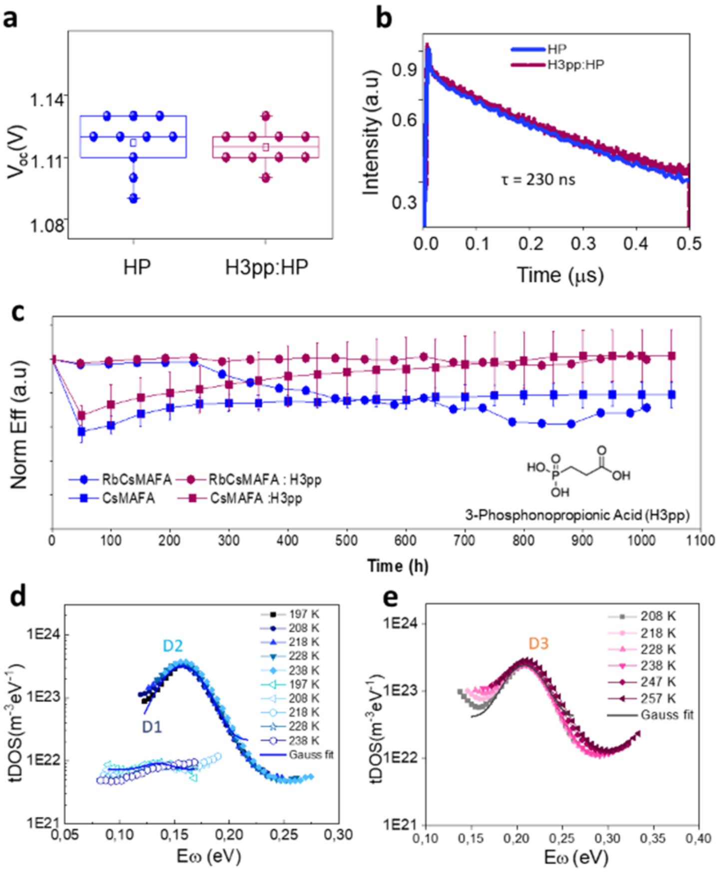

Figure 24. Shallow defect passivation dictates PSC stability. The use of the H3pp additive results in similar Voc (a), an indication of a similar non-radiative recombination (b), but excellent device stability (c). TAS analyses revealed the passivation of shallow defects (d) and (e). Reprinted from [205]. Copyright (2021), with permission from Elsevier.

which can eliminate any residue that is produced under stability testing. Epoxy glues, however, can release vapors during PSC testing that stay within the encapsulation and can react with the HP or any of the materials of the PSCs. Thus, these two testing methods 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 found in the literature [204].

Advances in science and technology to meet challenges

The density of defects in HPs dictates the efficiency and stability of solar cells. Until very recently, defects associated with deep trap states were the focus of in-depth research since they promote non-radiative recombination, limiting the photovoltage in detrimental of good PCE. Shallow defects, in contrast, have not been strongly considered since these are perceived as benign for classical semiconductors. However, HPs are not classic semiconductors but mixed ionic–electronic conductors and the existence of shallow defects can have significant repercussions on the long-term stability of PSCs [205]. In HPs the metastability of the ubiquitous formamidinium lead triiodide (FAPbI3) PVK and the migration of charged point defects provokes ion migration, phase separation, and hysteresis that are the main causes of material and device instability [206]. Shallow defects can be formed at very early stages of the device and thin-film fabrication and should be carefully controlled (figure 24). Their presence can be observed at the bulk of the HP [205] or at the interfaces and surfaces [207] and can be the result of off-stoichiometric conditions during film formation [207] or due to strain [208]. 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 [205]. Thus, additive engineering can be employed to enhance solar cell efficiency; however, it is even more important, once highly efficient devices are fabricated, to analyze the passivation of shallow defect traps, which will result in ion immobilization and enhance the device lifetime.

Concluding remarks

Numerous efforts have been made to overcome the 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 characterization 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 °C–85 °C) and light irradiation doses above 1 sun can permit the calculation of a more real estimate of the lifetime of PSCs. From a materials point of view, special attention should be paid to degradation factors, such as ion migration and the possibility to eliminate this issue via the modification of materials. Different methods are being applied to immobilize ions. Additive engineering has been 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 device's stability and efficiency. To date, studies have demonstrated that passivation of deep defects improves the device's voltage and efficiency, and the passivation of shallow defects is more related to ion immobilization and the device lifetime.

Acknowledgments

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19. Outdoor testing of PSCs

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Status

PSCs are commonly expected to be utilized in terrestrial outdoor applications, i.e. in solar power plants or on rooftops. The outdoor environment presents a harsh combination of stress factors that is virtually impossible to reproduce in the laboratory 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, to date. It has been shown that maximum power point (MPP) tracking is necessary for realistic PSC lifetime estimation, and appropriate 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 the feasibility of good practices in outdoor experiments that will be discussed in this section (figure 25) [144, 209–212]. Recently, several teams have shown encapsulated PSCs that passed the IEC damp-heat tests (>1000 h under 85 °C and 85% relative humidity (RH) [27, 213], and this was shown to be sufficient to achieve over a year of outdoor lifetime if matched with good material photo-stability [211]. Long-term outdoor research is therefore expected to become more widespread in the near future.

Current and future challenges

Outdoor data are required to address two key questions of vital importance for PSC technology maturation: (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 (figure 25(a)) [209] or several hundred hours (where seasonal changes occur, figures 25(c) and (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 that determines PV energy yield. However, TCs obtained from outdoor experiments can considerably differ from those implied from indoor measurements (and even have positive values [214]), possibly indicating significant artefacts. The solar spectrum has a limited and predictable impact on single-junction PSCs; however, in PVK-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 [215]. 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 PVK layer [216].

Long-term stability is a challenge for the development of PSCs, and degradation of the active PVK layer under the 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 PVK decomposition in the active PVK 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 (figure 25(a)). In some studies these opposite trends were observed for the same devices at various aging stages [209]. 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 [209].

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 [217]. 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

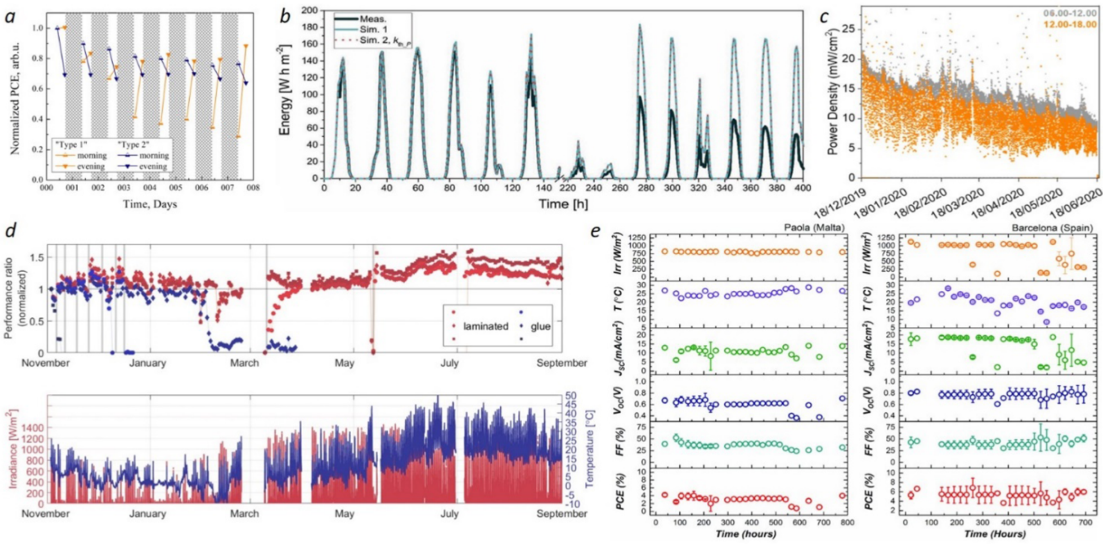

Figure 25. PSC outdoor measurements: (a) diurnal variations in PSC performance [209]. Reproduced from [209]. CC BY 3.0. (b) Comparison of modeled and measured power output at MPPT [210]. Reproduced from [210]. CC BY 4.0. (c) The power output of tandem devices showing reversible and irreversible degradation [144]. Reprinted with permission from [144]. Copyright (2021), American Chemical Society. (d) Long-term PSC performance and solar irradiance data showing seasonal changes [211]. Reproduced from [211]. CC BY 4.0. (e) A comparison of PSC output at two different locations (left: Malta, right: Spain) and climates [212]. Reproduced from [212]. CC BY 4.0.

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 cross multiple seasons (figures 25(c) and (d)) and different climatic conditions are available and compared. At the moment such data are extremely rare (figure 25(e)) 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 modeled data was shown to be suitable to track the diurnal device degradation (figure 25(b)) [210]. Comparison of outdoor data to the results of such modeling, using performance matrix measurements and weather data, can provide an understanding of both the reversible and irreversible parts of degradation [218]. It is important to note that reversible processes are also relevant for PVK-based tandems (figure 25(c)) [144].

Concluding remarks

Real-world data are the most convincing proof of the technology's 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-climate experiments. Such works will not only foster the understanding of PSCs' instabilities, but will also lay the foundation for the correlation of the outdoor lifetime with the indoor accelerated stress tests, and ultimately help to develop technology-specific qualification tests for PVK-based modules.

20. Environmental impact of PSCs: life-cycle analysis

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Status

Life-cycle assessment (LCA) is a holistic methodology that allows one to evaluate the environmental, ecological, and economic costs of the fabrication, use, and disposal of a product. Within the context of a PV module, the LCA must account for the mining of raw materials, their purification, the synthesis of new materials, manufacturing, and operation, as well as the end-of-life recycling or disposal of the module's components [10]. Performing an LCA for a novel technology such as PVK PVs 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 PVK PVs. These include not only single-junction PSCs, but also several types of tandem devices, such as Si/PVK or PVK/PVK [219–221]. Regardless of architecture, all PVK PV 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 [222]. 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 PVK materials can be deposited either by solution- or by vapor-processing [64], several LCAs focused on comparing the impacts of both deposition methods [223, 224]. 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, and human and water toxicity due to the extensive use of solvents, while deposition using the 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 of PVK layer fabrication are required to be able to truly assess which deposition method is preferable.

Current and future challenges

One of the key difficulties in performing an LCA of PVK PVs 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 PSC 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 PVK compositions and deposition methods [226]. 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 PVK single junctions as well as tandem solar cells (figure 26), making a meaningful comparison to other technologies very speculative [225].

Both reviews conclude that the assumptions made regarding the upscaling of PVK modules from laboratory-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 [227]. This highlights that the key challenge to be addressed within the context of the LCA of PVK PVs is in the optimization of the large-scale deposition processes for the PVK 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 PVK layers.

Another challenge that requires attention is the use of certain materials in the PVK 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 [223, 224]. 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 [222], not only in terms of their impact on device performance and stability, but also in terms of their impact on the LCA of PVK PVs. Finally,

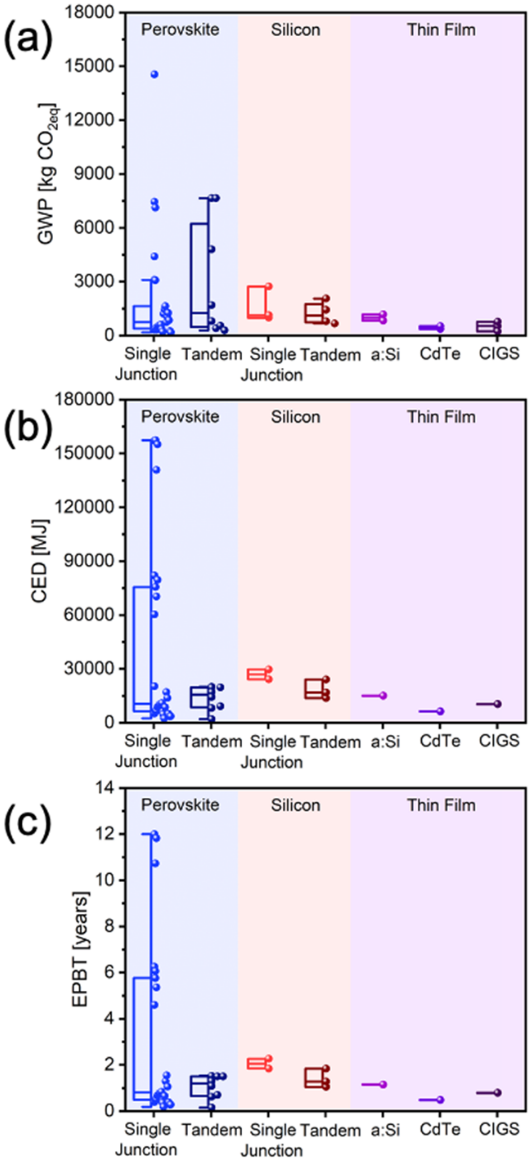

Figure 26. (a) GWP and (b) CED compared for 1 kWp (c) EPBT. Reproduced from [225]. CC BY 4.0.

as already mentioned above, the use of rare metals as electrode materials in PSCs is highly disadvantageous. Some LCAs suggest that the use of Au electrodes represents am 85% of the total embedded energy [222] and that its replacement would reduce many of the environmental impact categories by up to 90% [228].

Advances in science and technology to meet challenges

To address the challenges outlined above, the focus of the PVK PV community should shift from predominantly optimizing the device power conversion efficiency toward the development of more sustainable large-scale device architectures. In particular, while spin coating is utilized by the vast majority of PVK researchers due to its simplicity and wide-scale availability [64], 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. Within this context, lessons could be learned from other emerging PV technologies, which have already undergone the transition to the market. For example, similarly to PVK PVs, the vast majority of academic research in the field of organic solar cells is dedicated to devices fabricated using solution processing, but among the most successful examples of industrial application of organic solar cells are devices fabricated using 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 PVK PVs.

The advancements in the development of scalable deposition techniques for PVK 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 PVK materials can be strongly impacted by the choice of extraction layer on top of which the PVK active layer is deposited. This suggests that once novel, particularly promising, and environmentally friendly charge extraction layer materials are identified, the focus of scalable PVK processing optimization should lie specifically on the use of 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 PSCs 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.

Concluding remarks

In summary, several challenges are yet to be addressed within the context of LCAs of PVK PVs. On the methodological side, the lack of data and the need for certain assumptions make PSC 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 PSCs, 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 PVK PVs are 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.

Acknowledgments

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21. Environmental impact of PSCs: use of green solvents

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Status

The deposition of the PVK 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 deserve attention.

N,N-dimethylformamide (DMF), the most widespread solvent used for the deposition of the PVK 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 PVK 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 labeled 'dangerous'. In addition, DMPU is labeled potentially toxic, THF as potentially carcinogenic, and DMSO is not classified. Other solvents used as antisolvents or for the deposition of other 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 [229]. 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 (life-cycle assessment (LCA)). Potential green alternatives include solvent mixtures of the above polar aprotic solvents, but also other possible formulations, such as PolarClean, methylamine + acetonitrile, γ-valerolactone, and 1,3-dimethylimidazolidin-2-one (DMI). However, before large-scale industrialization of PVK, a comprehensive LCA, including use, recycling, and solvent disposal, is still needed.

Current and future challenges

Hamill *et al* [230] demonstrated the Gutmann's donor number (DN) [231] as a viable parameter to indicate the coordinating ability of a solvent with the Pb^{2+} center of PVKs. Different alternatives to toxic polar aprotic solvents are screened, either pure or mixtures, based on the DN or related, such as the 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, and coarsening grains for preparing high-quality PVK film. A thorough understanding of the multiplicity of roles during PVK film formation will help to understand the mechanism of PVK film formation [232] and will open the door to the selection of green solvents. This challenge is the core of figure 27.

For PVK PVs 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 PVK 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 PVK 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 PVK 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.

Advances in science and technology to meet challenges

A starting point of how to accomplish an LCA of solvents was recently tested for eight polar aprotic solvents: DMF, DMSO, DMAC, NMP, DMI, GBL, THF, and DMPU [233]. 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

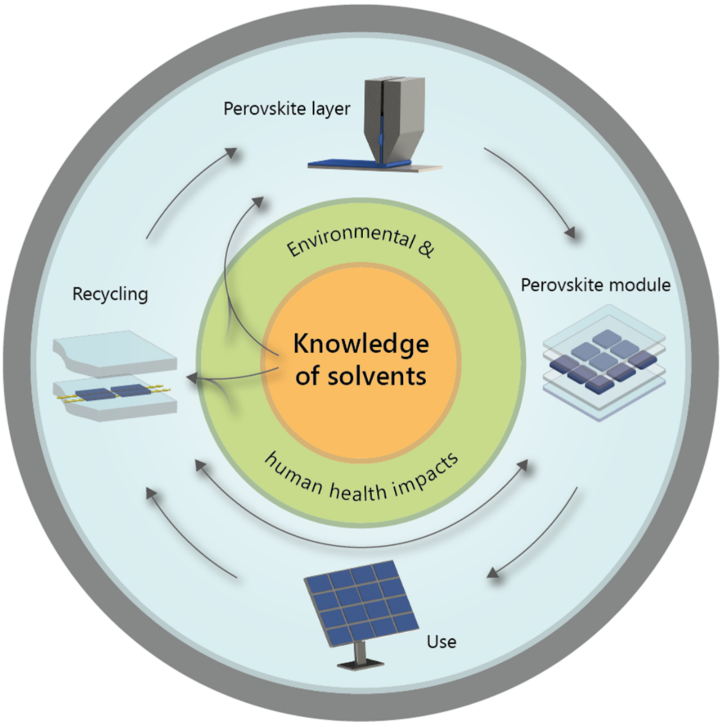

Figure 27. Challenges for PVK PVs circularity: 1. understanding of the solvent role in PVK film formation. 2. Updating and extending our knowledge of their environmental impacts.

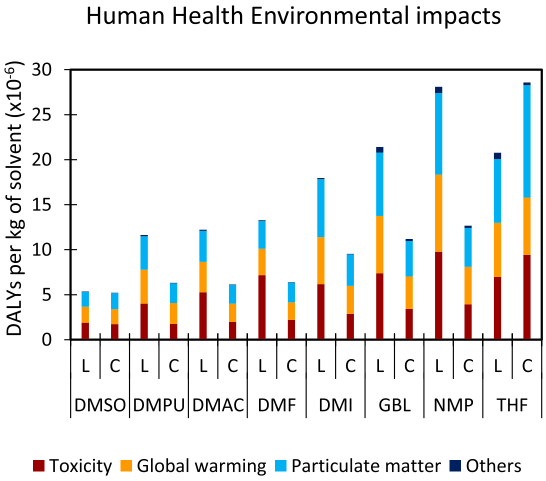

Figure 28. Life cycle assessment of eight aprotic solvents for PVK film manufacturing with evaporation or linear scenario (L) and solvent recycling or circular scenario (C), data in [233]. USEtox is modified for human toxicity impacts. The rest of the impacts are obtained from ReCiPE 2016.

(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 [234], 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.

This work [233] 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, to optimize the nucleation and crystallization dynamics during the film formation, are proposed, for example, mixing PbS quantum dots into the PVK solution in pure DMSO [235]. Also noteworthy are the promising results of DMSO/2-butoxyethanol [236] and acetonitrile/methylamine [237] in roll-to-roll processes.

Concluding remarks

Future work in the field of PVK PV 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 PVK film formation will help to understand the mechanism of PVK film formation and will open the door to the selection of green solvents. In addition, we need to update and extend our knowledge of the environmental impacts of solvents. A starting point of how to accomplish a comprehensive assessment of the solvents was recently tested for eight polar aprotic solvents used for PVK layer deposition. Among these, DMSO promises low environmental impacts on a large scale but must be optimized to achieve suitable performance parameters, such as power conversion efficiency and module stability.

Acknowledgments

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22. Environmental impact of PSCs—lead-containing vs lead-free

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Lead-free and lead-less PVK materials for solar cells

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) PSCs in 2015 with a power conversion efficiency (PCE) of 0.2% [238]. 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 [239]. Although Ge/Sn or mixed-elements-based solar cells developed rapidly, their PCEs are generally still below 10%, far behind that of the Pb-based analogs [240, 241]. 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. Meanwhile, the bandgaps of Sn/Ge-based PVKs are usually higher than the ideal bandgap for single-junction solar cells (1.34 eV). Moreover, Sn and Ge-based PVKs possess lower enthalpy, lower defect formation energy, leading toward faster film growth, poor film morphology, and therefore more defect formation and high carrier recombination [242]. The poor film morphology results in a reduction in the fill factor (FF) of the PSCs, which ultimately gives rise to an underperforming PCE. Lastly, with eco-friendly element compositions, chalcogenide PVK-based solar cells are promising candidates with their high resistance to water and temperature [243]. In 2016, $BaZr_{0.75}Ti_{0.25}S_3$, reported by Meng and his teams, had a bandgap of 1.43 eV that almost reached the Shockley–Queisser limit [244]. Recently, Wei *et al* fabricated n-type $BaZrS_3$ thin films via plasma laser deposition. And these films are great light absorbers with an absorption coefficient $> 10^5$ cm^{-1} under 2 eV photon test conditions [245]. Although chalcogenide PVKs were predicted to have amazing theoretical PCEs for single-junction solar cells, few satisfying devices were reported due to the lack of valid film processing methods.

Heterovalent elements substitution strategy

Double PVK, 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 PVK structure. The vacancy-ordered double PVKs $A_2\square M(IV)X_6$ and $A_3\square M_2(III)X_9$ ($\square$ stands for vacancy) with reduced-dimensional structures are also sometimes regarded as heterovalent derivatives of conventional lead-based PVKs. Practical double PSCs were first prepared by Greul *et al* in 2017, which unveiled reasonable degradation resistance and exhibited a PCE of 2.43% [246]. Considering the structural versatility of double PVKs, researchers evaluated their light-absorbing properties using theoretical calculations and found that several double PVKs, such as $Cs_2AgInBr_6$, $RbCuInCl_6$, and $Cs_2InSbCl_6$, have direct bandgap and high theoretical maximum PCEs for solar cell applications [247]. Laboratory-scale double PSC devices to date have mainly focused on $Cs_2AgBiBr_6$ and $Cs_2AgInCl_6$ material systems due to their good processability and stability [248]. Vacancy-ordered double PSCs have also been developed using Cs_2SnI_6, Cs_2TiI_6, $Cs_3Bi_2I_9$, $MA_3Bi_2I_9$, and $MA_3Sb_2I_9$ materials [249]. 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 PV performance of these double PVKs 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 [250]. Significant efforts have to be made in band structure manipulation, defect suppression, and transporting layer optimization before the potential breakthrough may occur.

Lead-less strategy

Lead-free PSCs solved the toxicity issues of lead at the cost of their PV 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 [251]. This strategy has several 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 3 summarizes some of the less-lead PSCs in the past ten years.

Table 3. Photovoltaic parameters of less-lead PVK 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	11.33	2017
$MAPb_{0.75}Sn_{0.25}I3 + 0.05$ mg ml^{-1} C_{60}	75	0.736	23.5	79	13.7	2017
$FA_{0.7}MA_{0.3}Pb_{0.7}Sn_{0.3}I_3 + 12\%GABr + 0.03$ mmol SnF_2	70	1.02	26.61	76	20.63	2020
$FAPb_{0.5}Sn_{0.5}I_3 +$ 10 mol% SnF_2	50	0.782	28.1	73	16.27	2018
$(FASnI_3)_{0.6}(MAPbI_3)_{0.34}(MAPbBr_3)_{0.06} +$ 10 mol% SnF_2	40	0.888	28.72	74.6	19.03	2018
$CsSnI_3$	0	0.86	23.2	65	12.96	2016

As shown, the percentage of lead content gradually decreases, while the PV parameters remained close to pure-lead PSCs [252].

Toxicity

Lead compounds are undoubtedly toxic, and the toxicology of lead has been well established. Lead enters the bloodstream through ingestion, inhalation, or dermal contact. Even a small concentration of lead in the blood is accused of reproductive toxicity, neurotoxicity, and carcinogenicity and is harmful to blood pressure, renal function, the immune system, and so on [253]. For PSCs, in the 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 is some evidence showing that tin could be inhaled and accumulate in blood and skeletal sites, causing genotoxicity, carcinogenicity, and reproductive defects [254]. When tin is released to the environment, its toxicity may decrease instead due to its oxidation to the insoluble SnO_2 compound. In contrast, germanium is believed to have low or no toxicity to humans. Therefore, it is widely used in pharmaceuticals, cosmetics, semiconductors, and nanotechnology. Nevertheless, recent studies suggest organic germanium may have a negative impact on human health and environmental systems to some extent [255].

Within the elements utilized in the double PSCs, silver is considered as nontoxic to human beings in that tableware has been made from silver since ancient times. The toxicity of bismuth is controversial. First, bismuth is classified as a nontoxic heavy metal that can be entirely metabolized from the body within a satisfactory time. Therefore, Bi (III) compounds have been used in the medical field for many centuries. Second, some research suggests that bismuth may induce slight cytotoxicity in kidney and chronic diseases [256]. 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 [257]. Toxicity of indium led to indium-related lung disease when inhaled by humans [258]. It should be handled with caution based on the fact that some semiconductors, such as indium tin oxide (ITO) and InP are widely used in optoelectronic devices. Copper is also known to have neurotoxicity and aquatic toxicity despite its excessive usage in different forms [259]. Titanium is considered as a bio-inert material that is commonly used for implants but, in rare cases, health issues have also been reported [260].

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

Cost and environmental assessment of lead-free PSCs

Abundance

Mineral paragenesis is common in nature. Lead, in the form of 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 purify with valuable by-products. However, cassiterite (SnO_2) as one of the major ores of tin, is always found together 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.

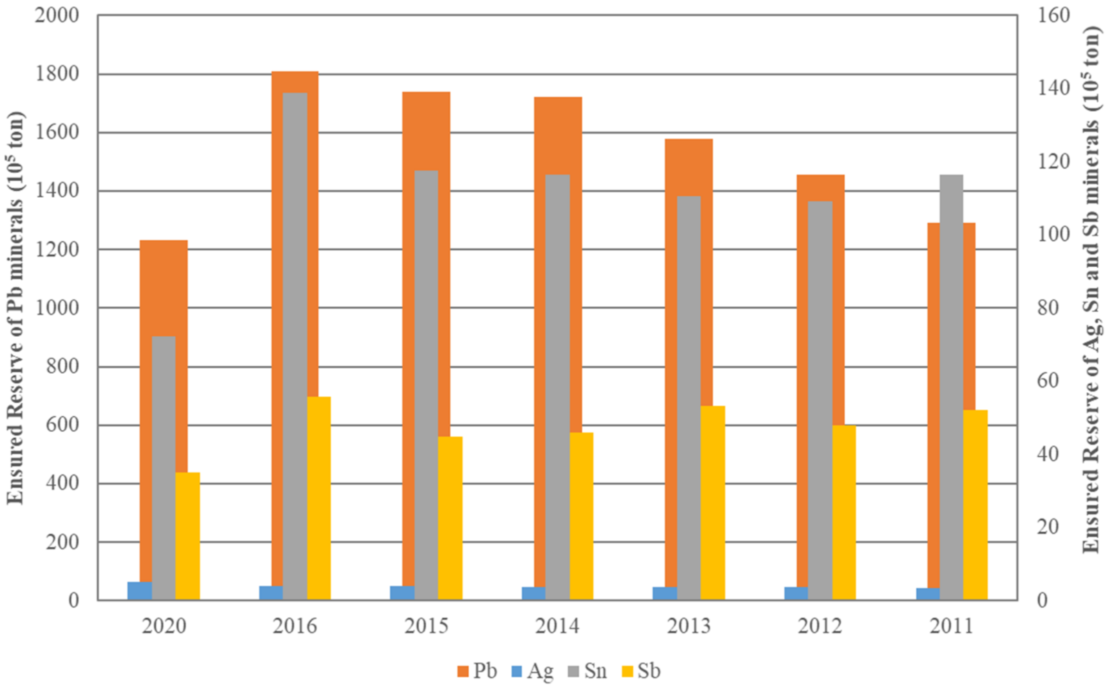

Figure 29. Annual mineral base reserves of lead, silver, tin, and antimony from 2011–2016 [261] and in 2020 [262], mainland China.

Despite the paragenesis, germanium and antimony, which belong to the 'disperse elements', have high abundance and scattering distribution. Specifically, more energy and water are required for the concentration and extraction processes of these metallic products.

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 in the figure, they have even lower annual production than silver (<20 000 tons per year). A low abundance or high degree of dispersion of an element usually results in a high energy refinement process, high production costs, and high environmental impact potential.

Cost of production

Since lead-free PSC technology is far from mature, only several reports of tin-based solar cells have gone through life-cycle assessment (LCA). Table 4 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 masses 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 30.

Generally, when the PSCs are still at the laboratory 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. The prices of high-purity PbX_2 (X = I, Cl, Br) and SnX_2 (X = I, Br) are collected from the reagent suppliers (Aladdin, Sigma-Aldrich, and Alfa Aesar, table 5), and the average prices are used to calculate the production cost of raw materials at laboratory-scale, demonstrated as the black rhombus marks in figure 30.

From figure 30, the mass inventory of lead used in lead-based PSCs is under 2.5×10^{-4} kg kWh^{-1}, while those for tin-based PSCs can be above 6×10^{-4} kg kWh^{-1} at maximum. Since the tin-based PSCs have higher raw material prices and lower module efficiency (table 5) compared with the lead-based PSCs, their fabrication cost increment brought by raw materials can be a maximum of three magnitudes higher when producing 1 kWh electricity.

Global warming potential and energy payback time (EPBT)

The 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 have a GWP from 0.06 to 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, have relatively higher GWPs of 6.75 and 10.70 kg $CO_{2\text{-eq}}$./kWh, respectively.

Table 4. 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^{-1})	Corresponding compounds and cost (¥ kWh^{-1})		GWP[a,d] (kg CO$_{2\text{-eq}}$ kWh^{-1})	EPBT/year	Efficient area (%)	Module convers. efficiency (%)	PR[a]	LT[a]/year
Pb	Ramamurthy Rao *et al* [263]	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* [228]	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* [224]	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* [222]	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* [223]	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* [228]	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* [264]	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] Abbreviations for table 3: 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, recalculated according to Celik *et al* [224], 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 (1 cm^2 or 1 m^2) as the functional unit for the LCA, others chose 1 kWh electricity production. To compare the difference between lead-based and lead-free PVKs, we exchange all data in functional units 1 cm^2 or 1 m^2 into 1 kWh according toequation (1) [224].

$$Impact_{kWh} = \frac{Impact_{m^2}}{I \times \eta \times PR \times LT}. \tag{1}$$

where I = insolation constant, assigned as 1700 kWh m^{-2}-year in this paper (except for that 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 did not provide the ratio of SnI$_2$ and SnBr$_2$. Since the purity of the SnBr$_2$ reagent 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.

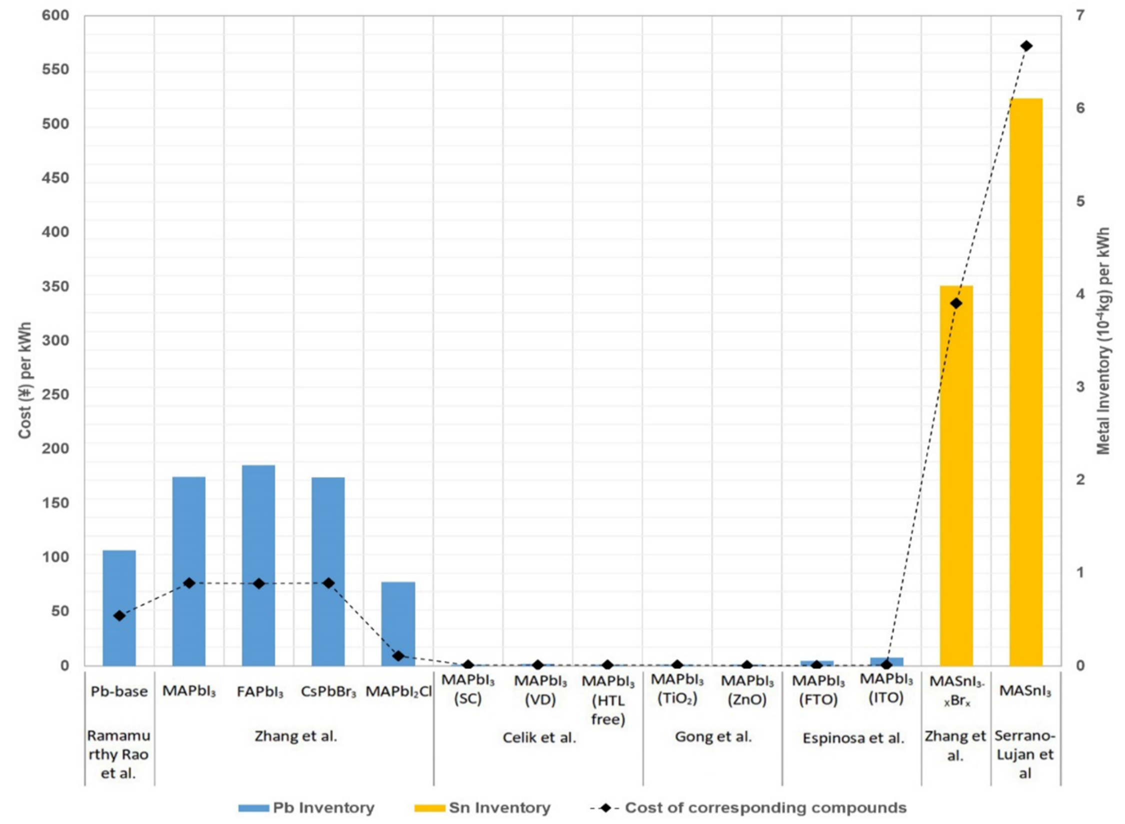

Figure 30. A comparison between the cost of lead-based PSCs and tin-based PSCs. The mass inventory (blue histograms for lead and yellow for tin) in these PSCs have been recalculated in kg kWh^{-1} electricity, the module produced in the assigned lifetime, according to the mass inventory provided by the corresponding researchers and equation (1). The cost for the raw materials containing Pb or Sn (black rhombus) is calculated using the mass of these raw materials times the average prices listed in table 5.

Table 5. The prices of raw materials provided by three main suppliers in December 2021.

Material	Price from suppliers (¥/100 g[a])			Average price (¥/100 g)
	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 (99.999% metals basis)	27 993 (Anhydrobeads™, 99.999% metals basis)	32 160 (Anhydrous, 99.999% metals basis)	21 246
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

[a] Calculated by the price with the maximum package the reagent suppliers offered online. The price may be lowered with a mass demand.

EPBT (year) values are the required time for a system to recover from the energy consumption of a certain module [263]. The EPBT results of the PSCs mentioned above are listed in table 4. Zhang *et al* gave the range of EPBT in 0.9–3.5 years in their research [228], while Gong's are given as merely 0.25 and 0.30 years [222], 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* [223]. Serrano-Lujan *et al* do 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.

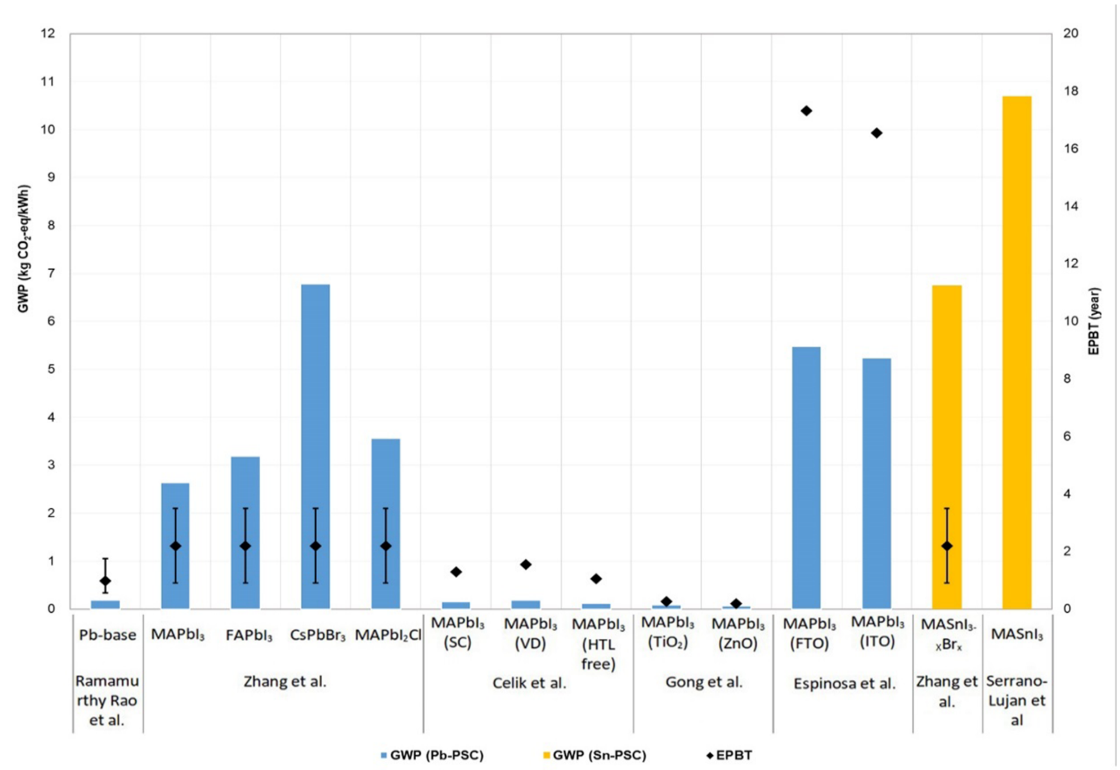

Figure 31. A comparison of GWP and EPBT data from previous studies. The GWP (blue histograms for lead and yellow for tin) have been recalculated in kg/kWh electricity, the module produced in the assigned lifetime, according to equation (1). The lifetime selection and other parameters are shown in table 4. 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; therefore, these data remain blank in the graph.

Concluding remarks

To conclude this section, lead-free PVK-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 costs 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 to reduce the environmental impact of lead.

Acknowledgment

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23. Environmental impact of PSCs: safe-by-design devices and lead sequestration

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Status

Despite the high power conversion efficiency (PCE) of lead (Pb)-based PSCs, the stability and hazardous environmental impacts of PSCs have been challenging factors for their scalable industrial production for commercialization. This is because the degradation of PVK not only results in reduced PCE but also in releasing toxic components into the environment [265]. 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 a water solubility product constant (K_{sp}) of 10^{-8}, which is much larger compared to other heavy metal 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, the amount of Pb compounds released to the environment after degradation, and the amount of bioavailable Pb [266].

The amount of Pb in PSC devices has been calculated to $\sim$0.4 g m^{-2} if the planar absorbing layer of methylammonium lead iodide (MAPI) has 300 nm thickness [267]. To produce MAPI-based PSCs with PCE of 25%, it has been estimated that $\sim$160 tons of Pb will be needed yearly to meet the electricity demand of the USA, considering an energy intensity of 38 μg kWh^{-1} [268]. Besides PSC modules, monitoring the use of Pb in the electronic solders is very important to address the environmental impact of PSCs. It has been reported that 6200 tons of Pb content of electronic solder including commercial PV panels was required annually in 2012 [269]. Different Pb emission sources in the US are summarized in 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 [266], an important distinction from an environmental point of view is the water solubility of Pb compounds in PSCs.

Current and future challenges

Considering the fact that PSCs contain toxic Pb, which can be released into the environment in water-soluble form (Pb 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 lifetimes 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 airborne deposits, leaching into soil with rainwater or released on complete decomposition in fire incidents. A study finds that under 1 h of simulated rain (1 Ml h^{-1}), 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 $\sim$70 ppm of the first cm of soil under the targeted device [267]. While PSCs are normally encapsulated to prevent degradation of their performance due to exposure to moisture and oxygen, damage tothe 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 Pb leakage from encapsulated solar cells, which typically involve the integration of Pb-trapping materials within the encapsulation package, so that the encapsulation has a 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 a significant reduction in Pb 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 Pb sequestration in PSCs is still in its infancy.

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 Pb leakage [269–274]. One of the most safe-by-design strategies for Pb sequestration is to encapsulate the PSCs devices with a 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 °C has been proposed to be used as an encapsulant. The self-healing of the epoxy resin at elevated temperature can prevent water ingress, resulting

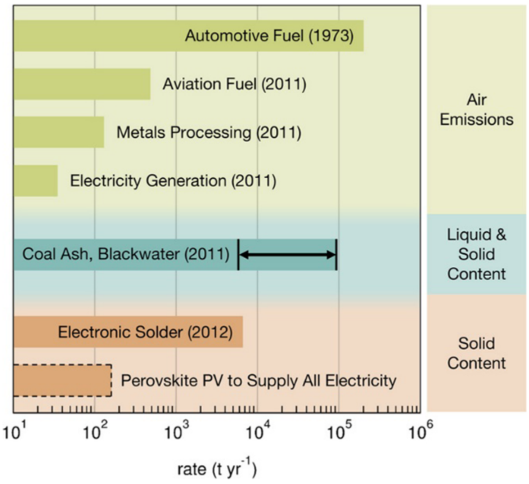

Figure 32. Different Pb emission sources in the US. Reprinted with permission from [268]. Copyright (2015), American Chemical Society.

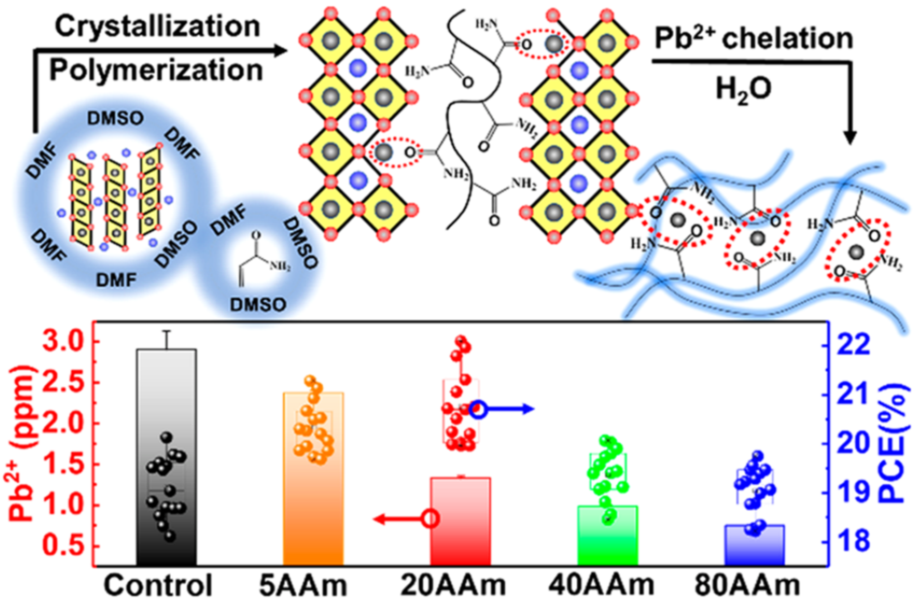

Figure 33. Mitigating the Pb leakage of high-performance PSCs via *in situ* polymerized networks. Reprinted with permission from [274]. Copyright (2021), American Chemical Society.

in a 375-fold reduction in Pb leakage when compared to UV-curable resins [269]. Several other encapsulating materials have also been reported for the prevention of Pb leakage, such as transparent Pb-binding polymer composite films [270], built-in polymer resins [271], and Pb-sequestering iron (III) benzene tricarboxylic acid (FeBTC):poly(dopamine) (PDA) metal organic framework polymer composites [272]. An alternative proposed approach for a safe-by-design Pb sequestration strategy is the use of cation exchange resins (CER) as coating materials for PSC devices. The CER can be used on both sides of the PSC package as well as on the cell electrode and prevents Pb leakage to about 90% and reduces the Pb level below the safe drinking water Pb level according to the US Federal 40 CFR 141 regulation without compromising the cell performance [273]. Recently, it has also been proposed that if monomer additives are used within the device package, in which *in situ* polymerization produces Pb-entrapping polymer networks, the Pb leakage can be mitigated [274]. However, further work is needed to simultaneously optimize the PSC's performance, operational stability, and the Pb sequestration in the outdoor environment to pass the industrial standards for commercialization.

Concluding remarks

The Pb halide PSCs have achieved the 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 in Pb leakage have been demonstrated since 2019 using several different approaches, Pb 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 (∼70 °C can be reached during outdoor operation) and prolonged operation. Specifically, 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.

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24. Environmental impact of PSCs: recycling prospects

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Status

With the rise in global temperature due to the increasing amount of CO_2 emissions arising from the burning of fossil fuels, 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 PSCs have been regarded as the rising star of the third-generation solar cells [275, 276], with great potential for the efficient delivery of large-scale low-cost solar electricity.

PSCs have experienced a rapid development and have attracted extensive studies since 2012, when the first solid-state PSC was reported with a power conversion efficiency (PCE) of 9.7% [277]. 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) [278]. However, the environmental impacts of PSCs, including the use of organic solutions, and the leakage of toxic metals, have always been the major concerns since the birth of PSCs, impeding to some extent the commercialization and large-scale applications. For instance, once the Pb inside the PVK crystal is discharged into soil or water, it can accumulate in human bodies, gravely damaging multiple body systems and causing severe health issues.

As there is still a long way from commercialization for PSCs, a complete recycling strategy has not been developed to date. However, investigations on the recycling technologies are attracting increasing attention from both academia and industry, such as reuse of the components and materials constituting the solar cells or modules. In fact, 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 PSC's recycling mechanism. When the environmental footprint of PSCs is reduced, the large-scale applications of renewable energy can be sustainable and contribute to the carbon-neutral society, and people can benefit from clean electricity without any fears from environment pollution and contamination.

Current and future challenges

The challenges for the 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 fabricated PSCs contain Pb 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; however, these suffer from severe instability and substantially lower PCE in comparison with their Pb-based counterparts. Besides the Pb-containing absorber, PSCs are assembled by tightly integrating 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 increases 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 easily fail and release toxic materials into the environment. When 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 temperatures and the 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 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 they fail or reach their 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 environmental issues relating to renewable energy applications.

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, PVK absorbing films and carrier transport layers, mitigation of Pb toxic elements, and valuable metal electrodes. Between the inorganic TCO substrate and Au rear contact, the PVK and charge transport layers exhibit good solubility in organic solvents, facilitating the separation and extraction of all components and enabling the recycling to be viable. For instance, the TCO/glass substrate can be easily recovered by dimethylformamide (DMF) immersion, ultrasonication, and solvent rinsing (chlorobenzene, deionized water, ethanol, and acetone) [279, 280]. The PVK 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 [281]. The PbI_2 from degraded devices can be nearly 100% recycled using commercial zeolite in an aqueous solution, where toxic Pb^{2+} is absorbed and stabilized through ion exchange while rare iodine is recovered for PSC refabrication [282]. 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 PCEs [283]. Very recently, a ‘one-key-reset’ recycling approach was reported [284] to simultaneously separate and extract all the constituent materials at once from the used PSC to remake a new one that retained 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 the components and materials of PSCs can be recycled through selective extraction or a package solution, whereas PSCs can also be refabricated with comparable PCEs using the recycled materials to eliminate the environmental impacts and reduce the production costs.

Concluding remarks

The PCE of PSCs has already surpassed 25.7%, and is comparable with commercialized technologies, such as CdTe and Si solar cells. Nevertheless, the toxicity of the 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 toward developing recycling and recovery technologies, such as solvent extraction, ion exchange, and chemical reactions. The refurbished PSCs using the recycled materials still retain impressive PCEs or PCEs that are even better than those 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 to produce new PSCs. These technologies and efforts offer promising recycling routes for PSCs to alleviate the environmental concerns and promote their sustainability as well as their competitiveness.

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Data availability statement

No new data were created or analysed in this study.

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