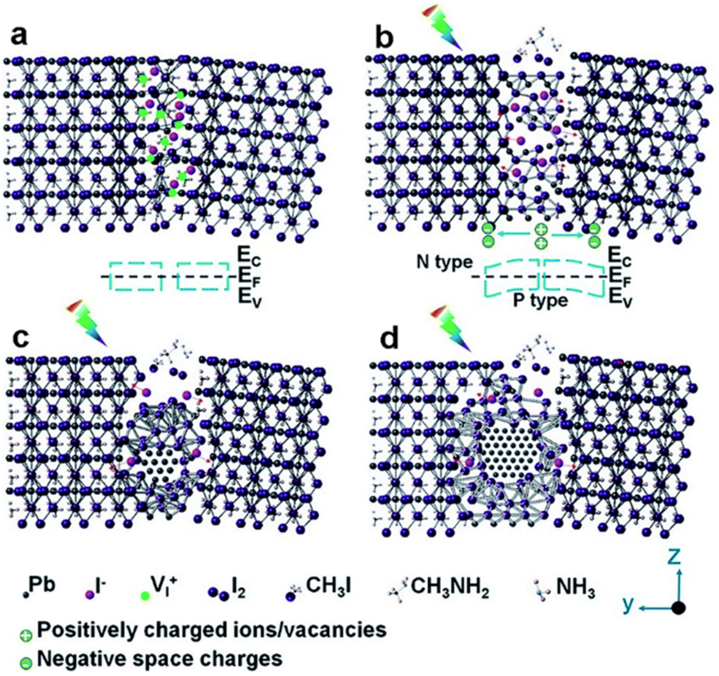

Figure 16. Illustrations of the photodegradation mechanism of the MAPI film into the Pb@PbI2-x core–shell nanostructures. (a) Numerous deficiencies exist at the grain boundary of the as-prepared PVK film. (b) Under light illumination, the iodide ions prefer to migrate away from the grain boundaries (red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

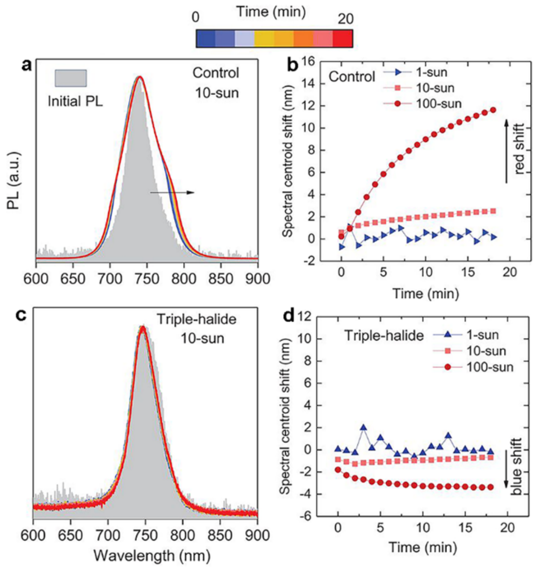

Figure 17. Suppression of photoinduced phase segregation in triple-HPs. (a) Photoluminescence (PL) spectra of 1.67 eV control PVK films (Cs25Br20) under 10-sun for 20 min. The arrows indicate the direction of the PL shift over time. (b) The shift of the spectral centroids of control films over time. 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.

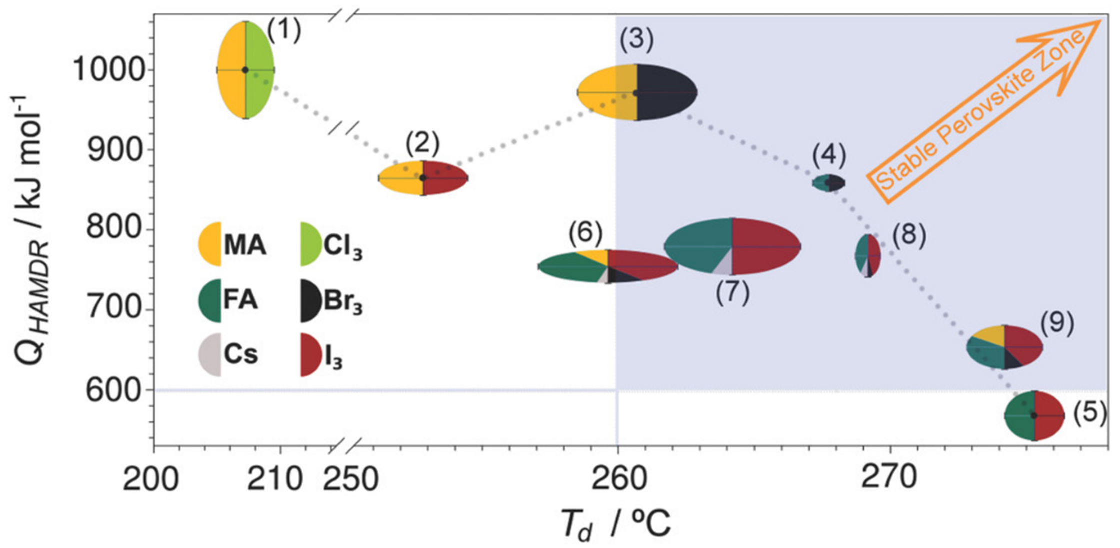

Figure 18. A stability map of hybrid HPs represented by Td (sample degradation temperature, *x*-axis) versus QHAMDR (sample heat absorbed at maximum degradation rate, *y*-axis), two parameters of thermal degradation experiments. Uncertainty of the measurement is represented by the ellipses' *x*–*y* axis 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.)

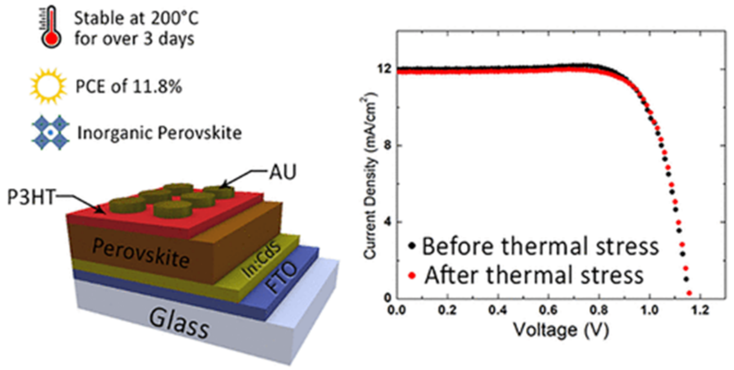

Figure 19. All-inorganic CsPbIxBr(3 − x) device performance showing no change with thermal stress at 200 °C for 72 h [173]. Reprinted with permission from [173]. Copyright (2020), American Chemical Society.

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

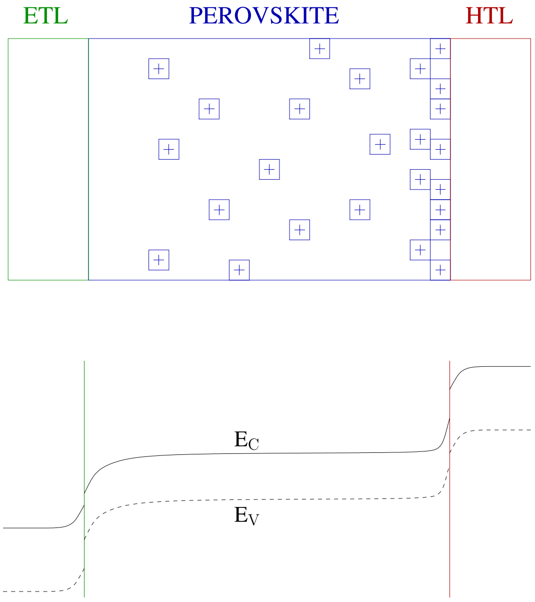

Figure 20. (Top) A schematic of vacancy distribution in a scenario of a single mobile vacancy species (positively charged). (Bottom) The associated conduction and valence band energies.

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 ($\approx$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

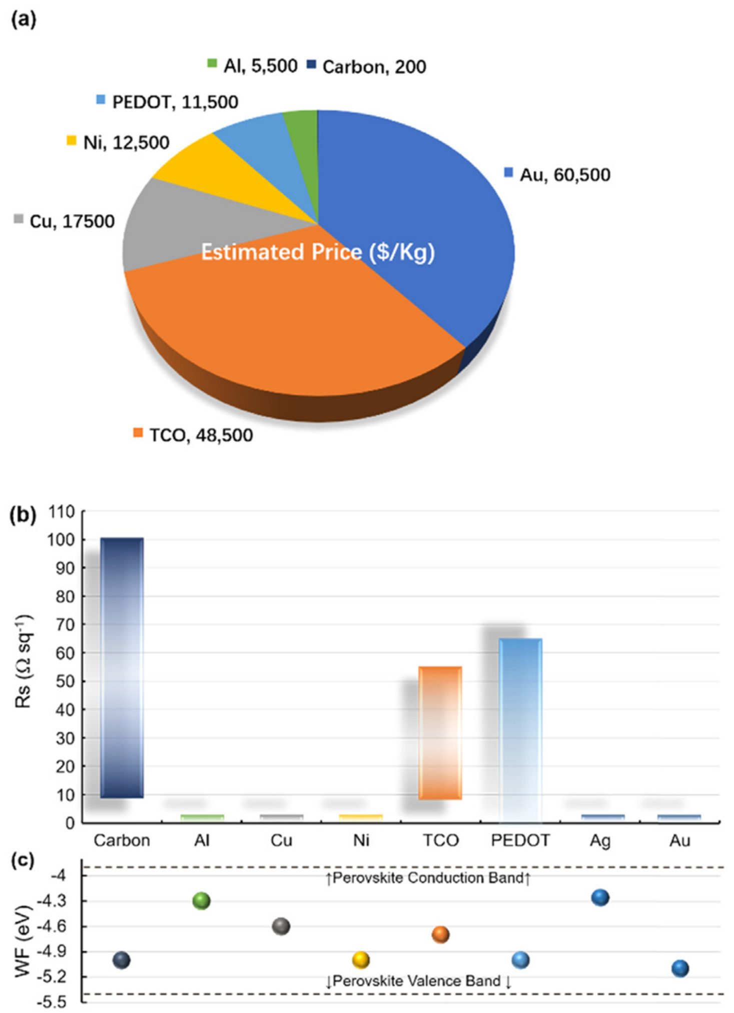

Figure 21. Analysis of electrode material costs and properties. (a) A summary of the costs of various metallic electrodes; (b) comparison of R_{sq} for different conductive electrode materials; (c) the work function of various electrode materials. Reproduced with permission from [187]. Reprinted from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

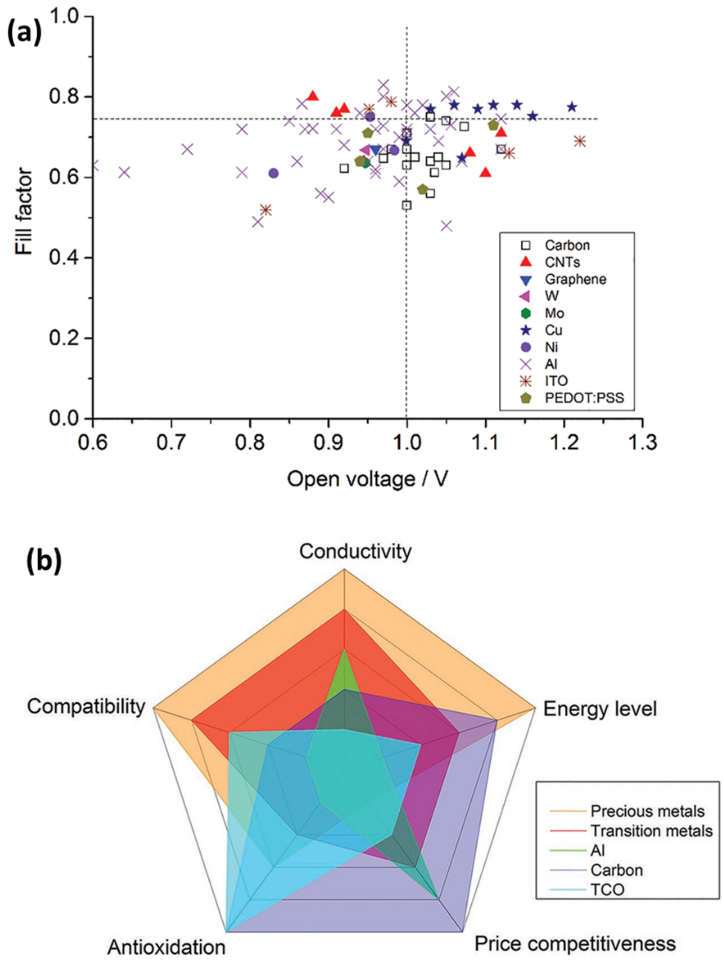

Figure 22. (a) Fill factors and PCEs of PSCs using various electrodes. (b) A summary of cost-effective electrode materials for PSCs. Different types of materials are ranked from poor to excellent according to their performance in corresponding factors. Reproduced with permission from [189], [199] John 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,

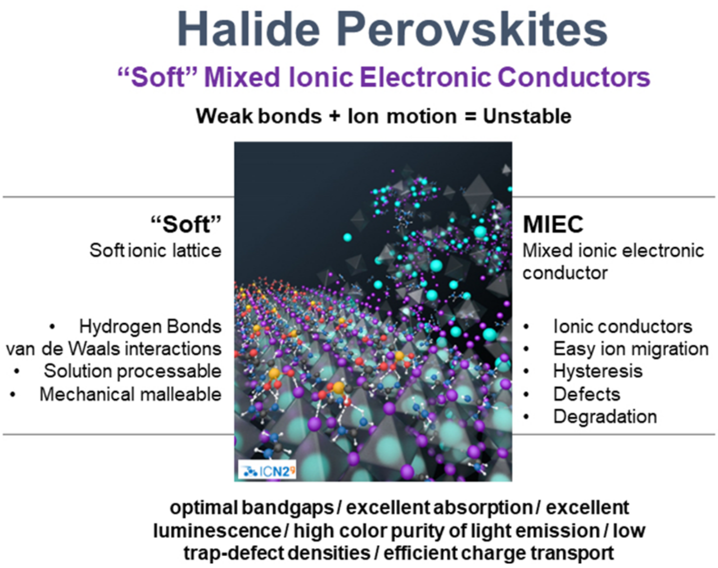

Figure 23. Halide perovskites are 'soft' ionic-electronic materials with weak bonds and high ionic motion. They must be engineered to make them stable.

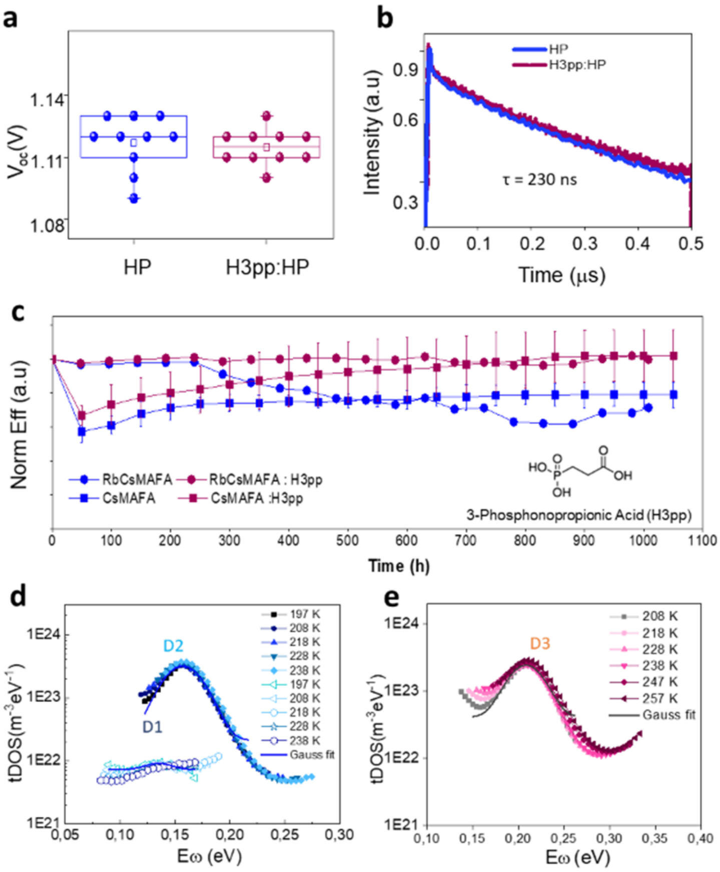

Figure 24. Shallow defect passivation dictates PSC stability. The use of the H3pp additive results in similar Voc (a), an indication of a similar non-radiative recombination (b), but excellent device stability (c). TAS analyses revealed the passivation of shallow defects (d) and (e). Reprinted from [205].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

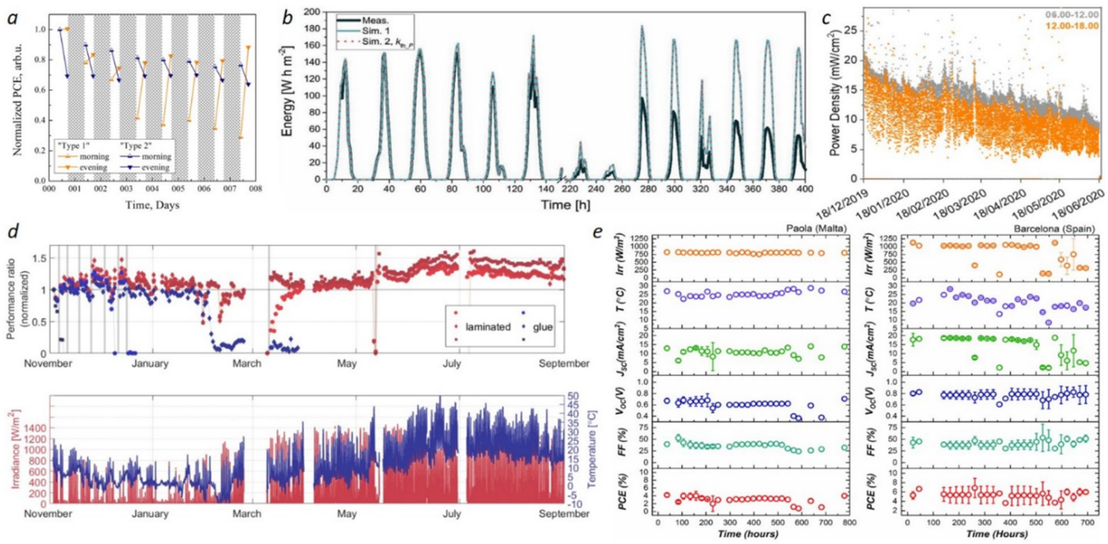

Figure 25. PSC outdoor measurements: (a) diurnal variations in PSC performance [209]. Reproduced from [209]. CC BY 3.0. (b) Comparison of modeled and measured power output at MPPT [210]. Reproduced from [210]. CC BY 4.0. (c) The power output of tandem devices showing reversible and irreversible degradation [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 $\mathrm{MJkWp^{-1}}$ 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,

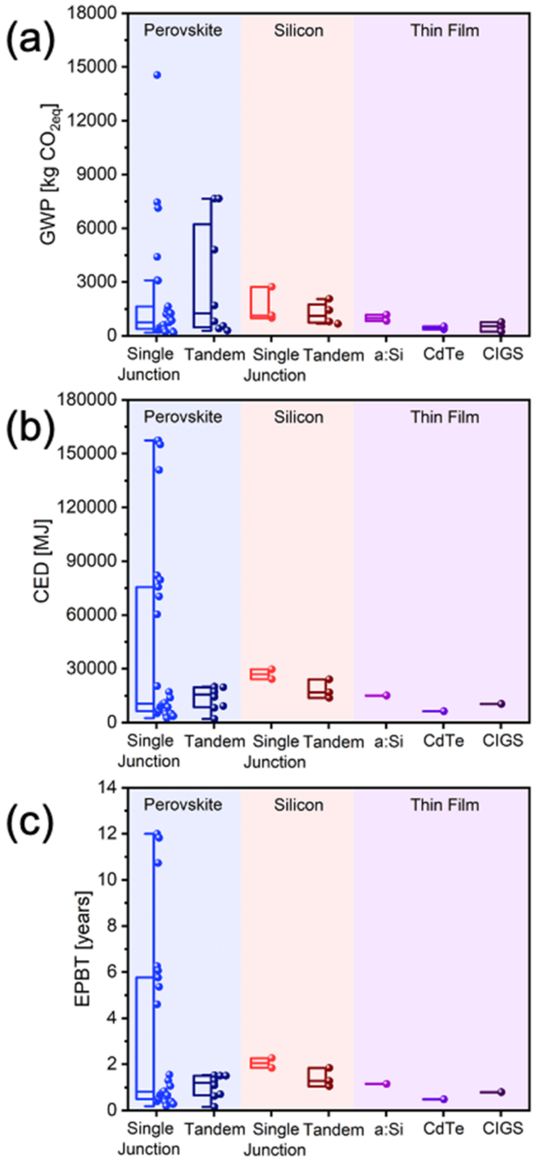

Figure 26. (a) GWP and (b) CED compared for 1 kWp (c) EPBT. Reproduced from [225]. CC BY 4.0.

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

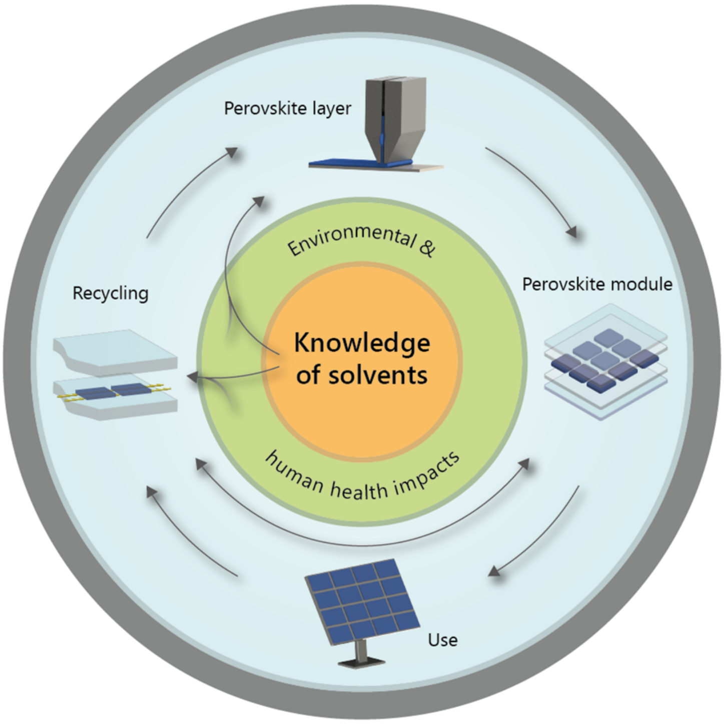

Figure 27. Challenges for PVK PVs circularity: 1. understanding of the solvent role in PVK film formation. 2. Updating and extending our knowledge of their environmental impacts.

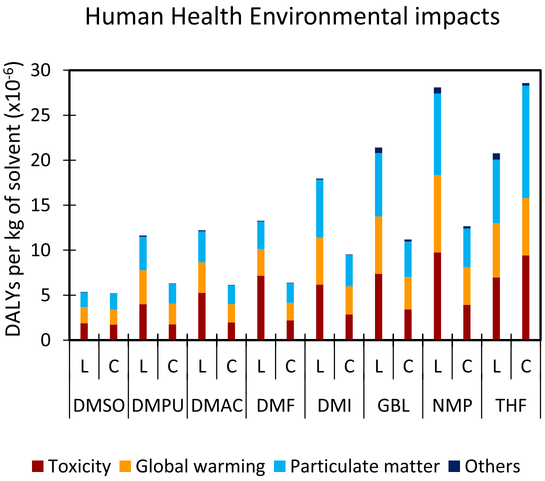

Figure 28. Life cycle assessment of eight aprotic solvents for PVK film manufacturing with evaporation or linear scenario (L) and solvent recycling or circular scenario (C), data in [233]. USEtox is modified for human toxicity impacts. The rest of the impacts are obtained from ReCiPE 2016.

(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.

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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 $A_3\square M_2(III)X_9$ (□ 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.

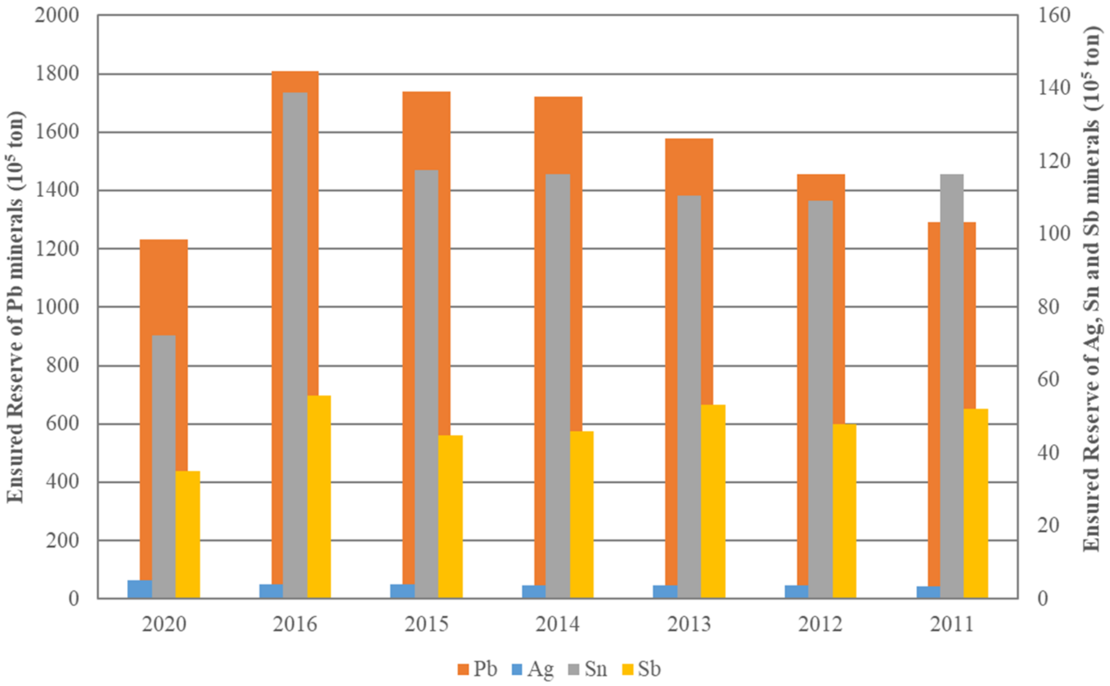

Figure 29. Annual mineral base reserves of lead, silver, tin, and antimony from 2011–2016 [261] and in 2020 [262], mainland China.

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
		$MAPbI_2Cl$	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.

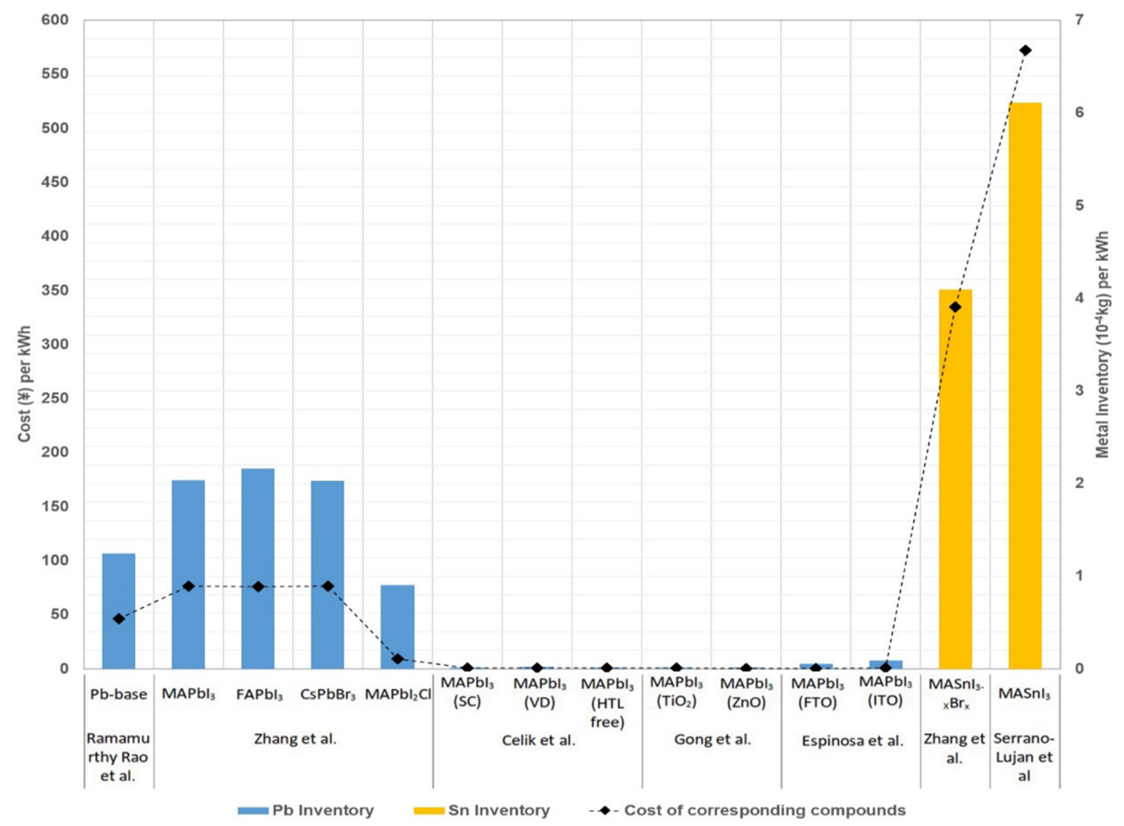

Figure 30. A comparison between the cost of lead-based PSCs and tin-based PSCs. The mass inventory (blue histograms for lead and yellow for tin) in these PSCs have been recalculated in kg kWh^{-1} electricity, the module produced in the assigned lifetime, according to the mass inventory provided by the 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.

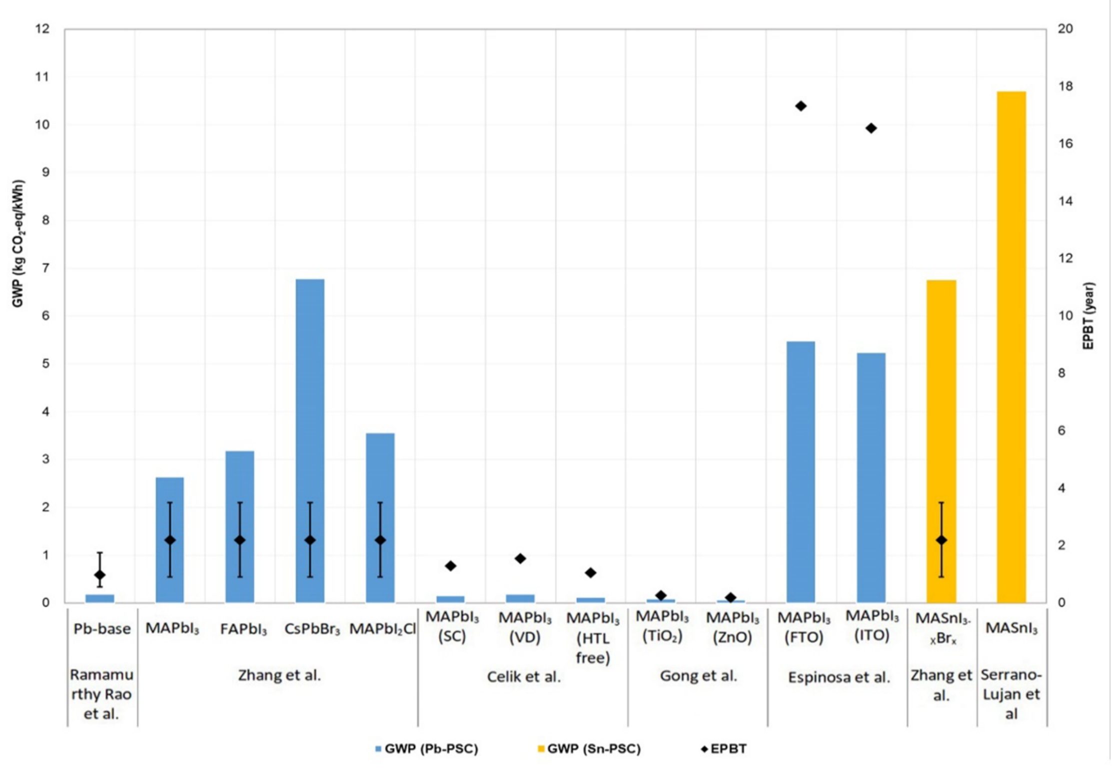

Figure 31. A comparison of GWP and EPBT data from previous studies. The GWP (blue histograms for lead and yellow for tin) have been recalculated in kg/kWh electricity, the module produced in the assigned lifetime, according to equation (1). The lifetime selection and other parameters are shown in table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

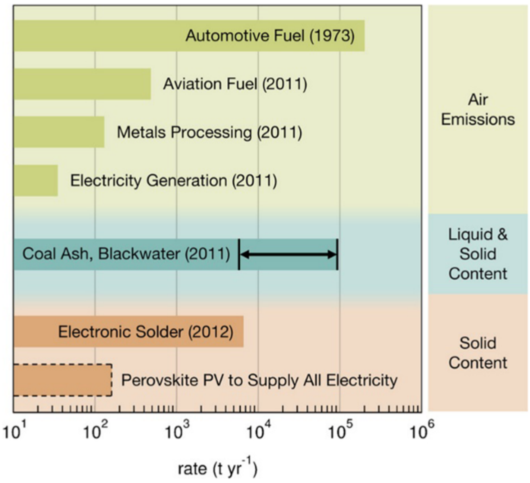

Figure 32. Different Pb emission sources in the US. Reprinted with permission from [268]. Copyright (2015), American Chemical Society.

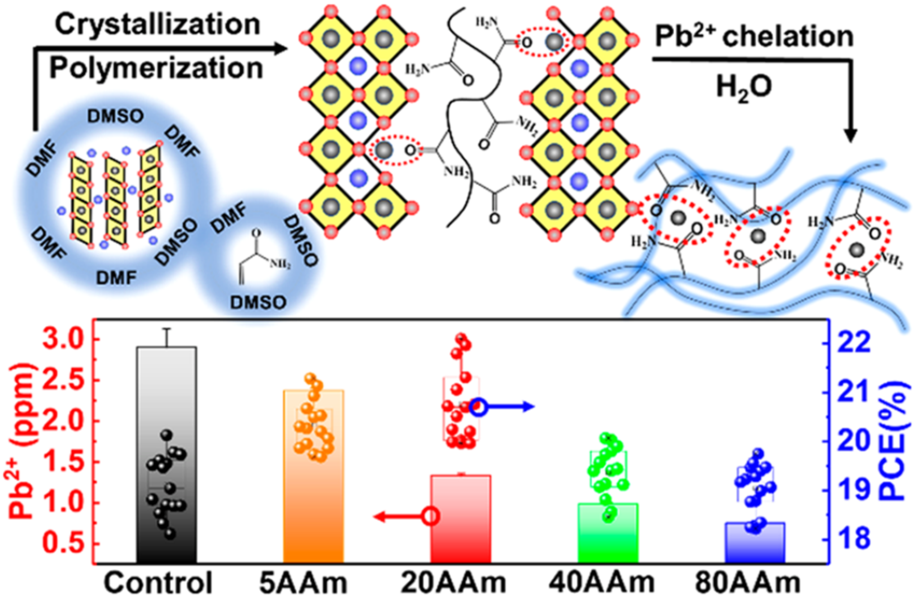

Figure 33. Mitigating the Pb leakage of high-performance PSCs via *in situ* polymerized networks. Reprinted with permission from [274]. Copyright (2021), American Chemical Society.

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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