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PROMISES AND CHALLENGES OF PEROVSKITE SOLAR
CELLS IN PORTABLE APPLICATIONS

Bachelor of Science thesis

Examiner: Prof. Nikolai Tkachenko

ABSTRACT

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In the process of reducing fossil fuel consumption and continuous development of clean energy, photovoltaic technologies will play an increasing role. Current mainstream solar cell technology, crystalline silicon solar cells, has the disadvantage of high processing costs. In addition, there is a growing interest to incorporate solar cells into a wider variety of applications, such as building integrated or portable devices. Silicon-based solar cells are not necessarily the best technology for these applications, and alternatives have been sought from new, low-cost photovoltaic technologies such as organic, dye-sensitized or hybrid organic-inorganic perovskite solar cells.

Perovskite solar cells seem to combine the high efficiencies typical of silicon-based solar cells with low production costs, good mechanical properties, wide tunability and some other favourable properties of organic photovoltaics. They appear to be potential candidates for portable photovoltaic devices. There are, however, some challenging issues that need addressing before the realistic implementation of perovskite solar cells in commercial applications.

This thesis discusses the advantages and current problems in employing perovskite solar cells in portable photovoltaic devices, as well as possible solutions to said problems. First, the mechanism of operation and essential properties of perovskite solar cells will be explained. Then, promises of perovskite solar cells will be discussed from a point of view of using them in portable solar cell applications. Finally, some of the most significant challenges in the upscaling of perovskite solar cells and their use in portable photovoltaics will be reflected.

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LIST OF ABBREVIATIONS AND SYMBOLS

DSSC	Dye-sensitized solar cell
EPBT	Energy payback time
ETL	Electron transporting layer
HTL	Hole transporting layer
OPV	Organic photovoltaics
PCE	Power conversion efficiency
PHJ	Planar heterojunction
PSC	Perovskite solar cell
PV	Photovoltaic

1. INTRODUCTION

Considering the world's constantly growing need for energy, the research on efficient, clean and renewable energy sources is of great importance. Fossil fuels continue to provide the vast majority of world's primary energy, but the decrease in fossil fuel resources and their undeniable negative effect on the environment have created a high demand for efficient renewable energy sources. Solar energy is one of the strongest candidates among the possible sources of renewable energy, as it is both abundant and environmentally friendly. Solar energy can be harvested either via solar heating or the generation of electricity by photovoltaic effect. The first exploitation of the photovoltaic effect was by the silicon solar cell, and to this day, silicon-based solar cells continue to be predominant in photovoltaic applications. Despite having some indisputable strengths, such as high efficiency, and being rather difficult to replace as the leading solar cell technology, silicon solar cells are generally not cost-effective for large-scale implementation due to their high processing costs. The drive to find more affordable types of solar cells has led to the research and development of new technologies, such as dye-sensitized, organic and hybrid organic-inorganic photovoltaics. [1]

Perovskite solar cells (PSCs) have recently been the object of growing interest and investigation. This is mainly due to their impressive efficiencies that, at least on laboratory scale and short-term observations, can compete with efficiencies of commercial silicon cells. The efficiency of PSCs has improved from 3,8% to over 20% in just a few years. [5] Along with efficiency and relatively low production cost, PSCs offer high absorption coefficients [4], easy fabrication and wide tunability of material properties [6] that make them a promising photovoltaic technology. There are, however, some challenges in upscaling PSCs from laboratory to commercial production, including long-term cell instability and toxicity of the materials.

The research in developing new low-cost photovoltaics not only helps in answering to the constantly growing need for energy, but also creates new opportunities to utilize solar cells in for example portable, building integrated or indoor applications. Perovskite solar cells have quite a few characteristics that make them potential candidates for portable photovoltaic applications. In this thesis, perovskite solar

cells are discussed particularly from this viewpoint. First, their operational principle along with their most essential properties are introduced. Second, the advantages employing them into portable solar cell devices are discussed and finally, the current challenges in upscaling perovskite solar cells into portable applications are reviewed, along with some possible solutions to said challenges.

2. OPERATION AND KEY PROPERTIES OF PEROVSKITE SOLAR CELLS

The conversion of sunlight into electricity in perovskite solar cells, as in all solar cell types, is based on photovoltaic effect. As light is absorbed into the cell's semiconducting material, the photons with energy larger than the semiconductor's band gap can excite electrons from the valence band to the conduction band of the material. The excited electrons crossing the band gap lead to a higher electron density on the conduction band and consequently lower density on the valence band. This is often referred to as formation of electron and hole pairs, hole being the place that the excited electron used to fill, and therefore a carrier of a positive charge. [1, 20, 26]

The excited electrons can move freely within the material. Eventually, the electrons are extracted into the conduction band of an electron transporting material, which is slightly lower in energy than the conduction band of the semiconductor. From there the electrons are transported to the external circuit through a conductive substrate, producing an electric current. The holes are correspondingly injected into a hole transporting material and out of the cell through a metal electrode. The operational principle of a perovskite solar cell is visualised in Figure 2.1.

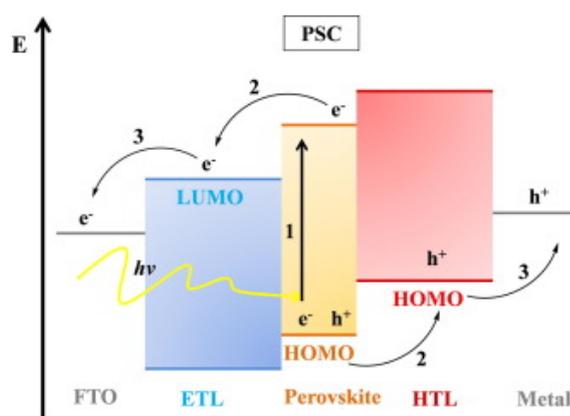


Figure 2.1 Energy diagram of electron excitation and charge separation in PSC. [20] In the figure, HOMO (highest occupied molecular orbital) is analogous to the valence band mentioned in the text, and LUMO (lowest unoccupied molecular orbital) corresponds to the conduction band.

A typical perovskite solar cell is composed of light absorbing perovskite material placed between electron transporting layer (ETL), and a hole transporting layer (HTL). The ETL usually consists of mesoporous, but sometimes also planar TiO_2 . In the standard device architecture, the front electrode placed before ETL is made of transparent conducting oxide such as fluorine doped tin oxide (FTO) (see Figure 2.1) deposited on a substrate, usually glass. After HTL there is a back electrode, which in the case of PSCs is usually made of noble metals such as silver or gold. [10]

The light harvesting layer of a perovskite solar cell consists of a semiconducting hybrid halide perovskite material with a basic crystal structure of ABX_3 . The structure is illustrated in Figure 2.2. In the formula, A is an organic cation, B is a metallic cation and X is a halogen. The halogen is usually iodine, but chlorine and bromine can also be used. Lead and tin are generally used as the metallic cation, and methylammonium, formamidinium or other monovalent cation as the organic species, methylammonium being the most common. The valence and conduction bands of perovskites are formed only from the orbitals of the metallic cation and the halogen, so B and X are the elements that determine the electronic properties of the perovskite material. The organic cation A does not contribute to the electronic properties, but governs the 3D crystal structure of the perovskite and therefore affects its optical properties. The most widely used perovskite material in photovoltaics is methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), or its analogues with mixed halides $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ or $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$. [20]

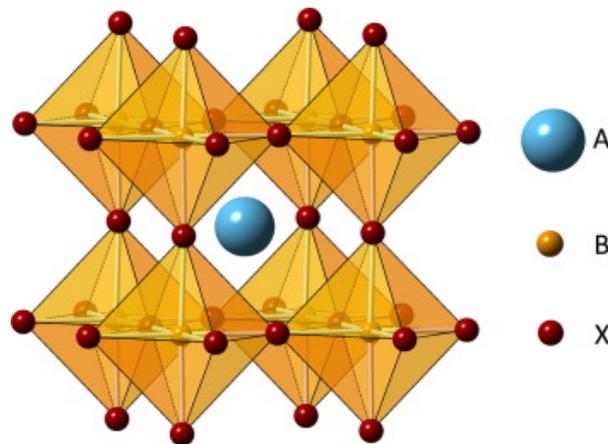


Figure 2.2 Crystal structure of perovskite, where A is a monovalent organic cation, B a metallic cation and X a halogen. [20]

When talking about solar cells and comparing different technologies, it is important to quantify how well light can be absorbed into a certain material. The absorption coefficient tells how far incident light of a certain wavelength can penetrate into a material before being absorbed. It is determined by the material and the wavelength

of light, or photon energy. [1] Perovskite materials in general have an absorption coefficient of about 10^5 cm^{-1} in the range of visible light. This is quite high compared to other semiconductive materials used in photovoltaics, and it means that effective light absorption is possible with thin perovskite layers. [4, 20] Absorption coefficients of different semiconductors are presented in Figure 2.3A.

Considering the operation and performance of solar cells, the process of electrons stabilizing back to their initial energy level is as relevant as light absorption and electron excitation. This process is called recombination. If the excited electrons are not provided with an external driving force, they will quickly lose the extra energy acquired by light absorption, return back to their equilibrium position, and combine with the holes losing the absorbed energy as heat or emitting photons. [1] Diffusion length is the distance which a charge carrier can travel before recombining with a carrier of opposite charge. In perovskites, diffusion length can be longer than one micrometer for both electrons and holes, which is sufficiently long for efficient operation even in planar solar cell architectures. [26]

The theoretical thermodynamic upper limit of efficiency in solar cells is defined by so-called Shockley-Queisser limit. When light is absorbed into a material, only the photons having energy greater than the band gap of the semiconductor are absorbed. Those with lower energy are not, and therefore do not generate charge carriers. If the energy of an absorbed photon is much greater than the band gap of the semiconductor, the excess energy is lost as heat or emitting photons. Because of this, the energy of all the photons in the spectrum can never be fully harvested, and consequently, the efficiency of a solar cell can never reach 100 %. In fact, a solar cell can theoretically reach a maximum efficiency of around 33 %. Perovskite materials have band gaps ranging from approximately 1.2 to 2.3 eV [4], which correspond to Shockley-Queisser limits between 20 and 30 %. [1] Shockley-Queisser limit as a function of band gap of the material is visualised in Figure 2.3B.

Besides efficiency, other important quantities in solar cell performance are open circuit voltage (V_{OC}) and short circuit current (J_{SC}). Where one of these quantities has its maximum value, the other has a value of zero, and vice versa. Therefore, when designing solar cells one has to find a balance between the two quantities and try to determine a point where their product reaches its maximum value. [1] A J-V curve is a typical way of visualizing the behaviour of solar cells.

The first PSCs were derived from dye-sensitized solar cells by replacing the organic sensitizer in a liquid-based DSSC with a perovskite material. In these cells, the perovskite acted as a light absorber. Later an all-solid-state PSC was intro-

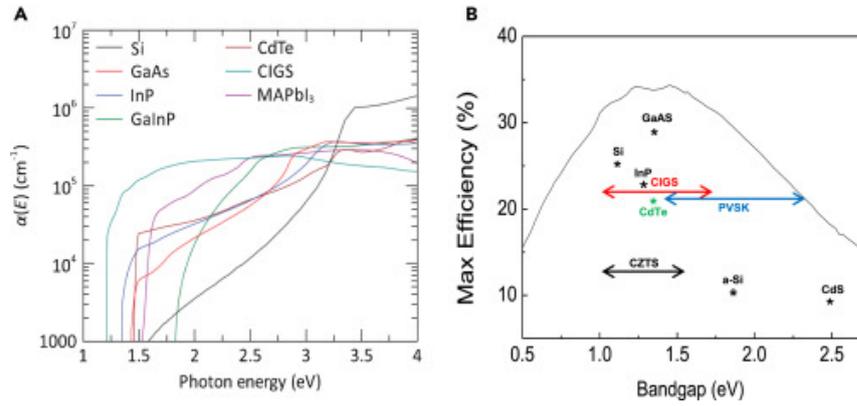


Figure 2.3 (A) Absorption coefficients of selected materials and (B) Shockley-Queisser limits according to band gap and material. The arrows show the band gap range that can be achieved via band gap tuning of compound semiconductors [1]

duced with spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9-spirobifluorene) hole transport layer, and with further understanding of the operation mechanisms it was discovered that replacing the typically used mesoporous TiO₂ with Al₂O₃ maintained the high efficiencies. [1, 4] This indicates that perovskites can operate not only as light absorbers, but also as electron transporters, seeing as Al₂O₃ acts only as a scaffold rather than as an electron transporting material. [14] The next step in device architecture was planar heterojunction PSC, which is constructed entirely without a mesoporous scaffold and where the perovskite acts both as a light absorber and a bipolar charge transporter. [1, 32] In the simple planar structures, a thin light-harvesting perovskite film is sandwiched between a compact electron transport layer and a hole transport layer. Planar heterojunction solar cells are defined by structure as either n-i-p or p-i-n ones, based on the sequence of the functional layers, starting from the layer facing the incoming light. In the general n-i-p configuration the ETL is on top of the transparent conducting substrate and HTL shares an interface with the back metal electrode. In the inverted p-i-n architecture, the relative order of charge selective layers is opposite. [32]

The composition and properties of PSCs are easily modifiable by making changes in the metal halides and organic species of the perovskite material. For example, replacing some of the iodine with bromine to form a mixed halide perovskite CH₃NH₃PbI_{3-x}Br_x improves the stability in comparison to MAPbI₃, while maintaining the high efficiency. In comparison to the most widely used perovskite material MAPbI₃, formamidinium lead iodide (FAPbI₃) has a broader absorption of the solar spectrum and a narrower band gap of 1.48 eV compared to MAPbI₃'s 1.55 eV. Currently, the best certified efficiencies of 22.1 % are achieved with FAPbI₃-based cells. [12, 30] However, FAPbI₃-based perovskite materials tend to be less stable than MAPbI₃-based. [30]

The materials used in ETL and HTL affect the properties of PSCs as well. For example, PSCs are otherwise promising candidates for preparing flexible solar cells, but the widely used TiO_2 as scaffold and ETL requires high-temperature processes that limit the choice of flexible substrates. Planar heterojunction (PHJ) PSCs have been investigated as an alternative to mesoporous structures, and some ETL materials, such as ZnO , have been found to be suitable for application on flexible surfaces. However, the best efficiencies are still achieved with TiO_2 electron transport layer.

Aside of mechanical properties, also the appearance of PSCs can be modified by altering either the materials of ETL and HTL or by making changes into the perovskite material itself. PSCs can be fabricated into semitransparent and/or colorful designs. Different colors can be achieved via band gap tuning, i.e. substituting iodine with other halogens, for example bromine [23]. In order to prepare efficient semitransparent devices, all layers of the cell should be transparent. This is relatively easy to achieve for all other layers except the opaque metal electrode. Some replacements for currently used silver and gold electrodes have been found for example in thin metal films, conductive polymers, carbon nanotubes and silver nanowires [10, 32]. Similarly to attempts with flexible solar cells, semitransparent PSCs do not currently reach the efficiencies of their rigid and opaque counterparts. [32]

3. PROMISES OF PEROVSKITE SOLAR CELLS

So called first generation photovoltaics, mainly silicon-based solar cells, have traditionally been quite expensive, which has prompted the research for more cost-effective solar cell technologies. Lately, the cost of silicon solar cells has dropped to a level where they could be employed into the energy grid, at least in some parts of the world. Due to this, it is difficult for other technologies to compete with silicon solar cells unless they exhibit similar or better efficiencies and then beat them in manufacturing costs. [9]

The main reason why perovskite solar cells are under such extensive research is their impressive efficiency, that competes with silicon solar cells and exceeds other low-cost photovoltaic technologies. Best silicon solar cells have efficiencies of over 25 %, and gallium arsenide (GaAs) cells can reach PCEs as high as 28.8 %. Perovskite solar cells can achieve efficiencies of around 22 %, which is roughly twice the efficiency of the best organic and dye-sensitized solar cells. [13] Considering commercial applications, advantages of PSCs include relatively cheap raw materials, low production costs and simple processing techniques, as well as high absorption coefficients in the range of visible light, which corresponds to thin perovskite layers in devices. Perovskite solar cells are also easily modifiable because of the modular structure of the perovskite, meaning that one or several components of the perovskite material can be altered to achieve desired features. It has also been shown that the energy payback time (EPBT) of perovskite solar cells can be as low as 0.22 years, which is notably shorter than EPBTs of 2.4 and 0.7 years for silicon and thin film photovoltaics, respectively. [27]

The traits mentioned above make PSCs a considerable alternative for current commercial solar cells, and perhaps also the most competitive one in comparison to other low-cost photovoltaics such as organic or dye-sensitized solar cells. PSCs still have some issues that may limit the potential for energy grid integration for some time, cell stability being the most determinative. [27] The problems with PSC upscaling and implementation will be further discussed in Chapter 4. Instead of energy grid integration, PSCs could contribute to applications where silicon solar cells are not necessarily the best options, such as portable, building integrated and indoor

photovoltaics. [8]

To be usable in portable applications, solar cells must meet certain requirements. First, they need to be relatively light-weight, for the device to be easily moved around. Second, they have to perform sufficiently well in diffuse or otherwise non-ideal lighting conditions, because portable devices cannot be constantly positioned in perfect conditions. Production cost of the solar cell is also an important factor, considering that the consumer price of the final product corresponds to it, and the price has to be affordable enough for someone to actually buy a device. Flexibility is not essential but it helps in moving the device around if the device can be folded or rolled. This makes the use of solar cells on curved surfaces possible, and might even make the devices less breakable if there is no need to use brittle glass substrates. Also, possibilities to tune for example the color (as pictured in Figure 3.1) or transparency of the solar cell are, again, not essential but can increase the range of possible applications. This chapter will briefly review how well perovskite solar cells meet these requirements and how feasible portable PSCs could be.



Figure 3.1 Example of the color tunability of $CH_3NH_3PbI_{3-x}Br_x$ mixed halide perovskite [23]

One of the main advantages of perovskite solar cells in comparison to conventional silicon-based photovoltaics is the simplicity and low cost of processing. Perovskite solar cells mostly utilize abundant and non-precious materials and perovskites can achieve a crystalline structure by simply precipitating out of a solution. [4] Although so far perovskite solar cells have been fabricated mostly in small scale (1 cm^2 or less), large area, roll-to-roll compatible deposition techniques are under research. Thin-film PSCs can be fabricated via simple, low-temperature solution processing techniques such as screen printing, blade coating and slot die R2R-coating, as well as evaporation techniques. It is worth noting that processing method has an impact on the PCE of the fabricated cell. As an example, screen printing produces cells with a PCE of 15 %, while for blade coating and slot die R2R-coating the PCEs are around 10 % and 9 %, respectively (all measured in cells with area less than 1 cm^2). [27]

In portable applications, solar cells have to operate sufficiently well under very

different levels of illumination, compared to the optimised outdoor conditions of stationary solar panels, which can always be positioned in the ideal illumination conditions and tilt angles. Conventional silicon, copper indium gallium selenide (CIGS), and cadmium telluride (CdTe) solar cells generally perform quite poorly in low levels of illumination. Perovskite solar cells, however, exhibit good performance over a wide range of lighting conditions and even in artificial light, being able to reach power conversion efficiencies as high as 24 % under 200 lx indoor compact fluorescent lighting, and 25.4 % under 400 lx. [11] Satisfactory performance under varying illumination conditions is essential in portable devices, as they are used in many different environments and not only outdoors in direct sunlight, and so far PSCs show promising results. Performance of different types of PSCs in simulated sunlight and indoor light depending on the processing technique is presented in Figure 3.2

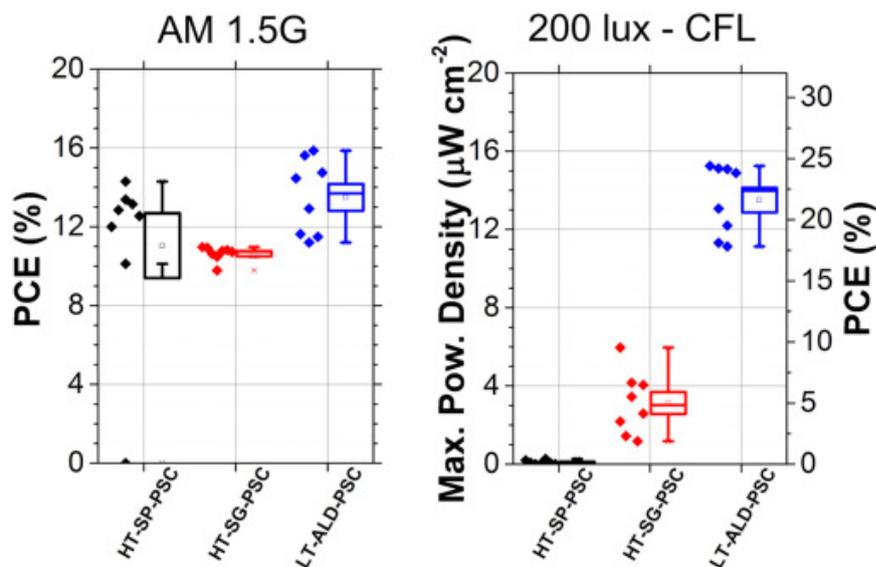


Figure 3.2 Performance of different types of perovskite solar cell devices in simulated sunlight (left) and 200 lx compact fluorescent light (right). Different processing techniques used: Glass/FTO/Spin Coating based PSCs (black), Glass/FTO/Spray Pyrolysis based PSCs (red), and Glass/ITO/Atomic Layer Deposition based PSCs (blue) [11]

As mentioned earlier, perovskite materials have remarkably high absorption coefficients over a wide range of the spectrum. Besides efficient light absorption, this contributes to less material needed in preparation of a functioning solar cell, and to more light-weight devices. PSCs can also be processed at quite low temperatures, meaning that instead of glass substrates they can be applied on plastic, which further reduces the weight. In comparison, silicon solar cells tend to need rather thick light absorbing layers because of the rather low absorption coefficient of silicon and their preparation includes high-temperature processing steps, which prevents the application on lighter plastic substrates. In addition to light-weight solar cells, both

the high absorption coefficient and low processing temperatures enable the preparation of flexible solar cells, as thin layers and flexible plastic substrates allow the cell to bend.

Most of the research on perovskite solar cells has been performed on glass substrates, but since perovskites can be processed at low temperatures and their high absorption coefficient enables thin perovskite layers, PSCs could be used in flexible devices. The bending radius of perovskite solar cells can be as small as some millimeters. [8] Many flexible substrates, such as widely used polymers polyethylene terephthalate (PET) and polyethylene naphthalene (PEN), have to be processed at temperatures below 150 °C. [19] Currently, many high-efficiency perovskite solar cells utilize a mesoporous metal oxide layer, often TiO_2 , both as a mesoporous scaffold for the perovskite light absorber and as a electron transport material. To obtain high quality TiO_2 it has to be processed at temperatures over 400 °C, which prevents application to some flexible substrates. Planar heterojunction (PHJ) PSCs have been investigated as an alternative for cells based on mesoporous TiO_2 and it has been shown that satisfactory performance is possible without mesoporous structures. However, to produce flexible solar cells, it is essential to develop low-temperature processable charge transport materials. [18]

To date, the highest efficiencies of flexible PSCs have been achieved by using amorphous TiO_2 which can be processed at low temperatures. It can therefore be applied on plastic substrates such as PET, and it yields a PCE as high as 15.07 %. [28] Replacing TiO_2 altogether with another material is also possible and has been done with ZnO, which has higher electron mobility than TiO_2 and doesn't need high-temperature processing. Devices with ZnO nanoparticle ETL fabricated on PET substrate have been reported to achieve 10.2 % power conversion efficiency and 1.03 V open circuit voltage, and to endure bending with losing less than 15 % of the initial PCE. [18] Another study reports a flexible device with TiO_x ETL achieving an open circuit voltage of 0.95 V and PCE of 12.2 %. 95 % of the initial PCE was maintained after 1000 bending cycles with 10 mm bending radius. [17] The results are visualized in Figure 3.3.

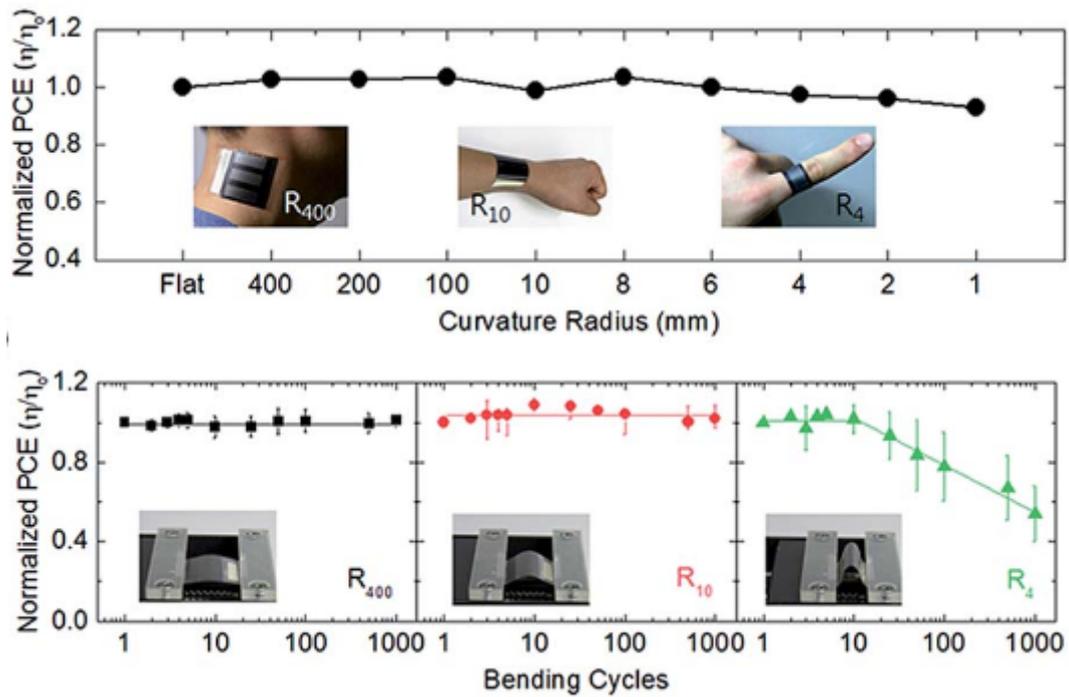


Figure 3.3 Normalised PCE of flexible PSC after bending within radius from 400 mm to 4 mm (upper figure) and as a function of bending cycles with different radii of 400, 10 and 4 mm (lower figure). [17]

Another way to make use of the strong absorbance of perovskite materials is to incorporate them into tandem solar cells. In tandem cells, a wide band gap absorber is stacked with a narrow band gap absorber in order to improve efficiency. The most used perovskite material MAPbI_3 has a band gap of around 1.6 eV and it can be tuned up to almost 2.3 eV by substituting some of the iodine with other halogens, such as bromine. Seeing as the ideal band gap for the top cell in tandem architectures with silicon or CIGS is 1.7-1.8 eV, perovskites seem to be promising candidates in this sense. [2] In some tandem structures, the top cell needs to be semitransparent. This, while resulting in a drop in efficiency, is achievable for perovskite solar cells by replacing the opaque noble metal electrode with a transparent one, such as conducting polymer or metal nanowire electrode. [10] A tandem cell with silicon or CIGS bottom cell and a 1.76 eV band gap perovskite top cell is estimated to be able to achieve efficiency of 30.4 %. [2]

While the estimated efficiency of tandem cell structures is indeed impressive, combining a perovskite solar cell with a silicon cell strips away some of PSCs other favourable properties, such as flexibility or light weight. It is also worth noting that while tandem structures combine the best properties of silicon and perovskite solar cells, they also combine the major disadvantages of both cell types. Therefore, by fabricating a silicon-perovskite tandem cell, one essentially ends up with a device

that has the high production cost of a silicon cell, and the poor durability and short lifetime of a perovskite solar cell.

It seems that perovskite solar cells naturally have quite a few characteristics that make them suitable candidates for portable photovoltaic devices. Many of the properties can also be modified due to the great tunability of perovskite materials. While it appears that the PSCs that would otherwise be most fitting for portable applications don't reach the top efficiencies, in portable and other smaller scale applications a bit lower efficiencies could be acceptable.

4. CURRENT CHALLENGES IN PEROVSKITE SOLAR CELL APPLICATIONS

Despite being a promising photovoltaic technology and showing impressive results in terms of efficiency and performance, perovskite solar cells still have some issues that need to be resolved before they can be commercialised. Perhaps the most urgent one is the long-term stability of the cells, which currently isn't very convincing. Solar cells are used in ambient conditions, preferably for longer periods of time, and therefore need to sustain daily and seasonal changes in temperature, as well as moisture and oxygen in the air. Degradation of a solar cell can be caused by environmental conditions such as elevated temperature, UV illumination and exposure to ambient atmosphere, but it can also be a result of intrinsic instability. [5, 27] Another problem, particularly troublesome considering portable, personal devices, is the possible toxicity of lead included in the perovskite material. The overall environmental impact of PSCs is also something that needs more research before they can enter the market. In this chapter, the above mentioned, major challenges of perovskite solar cells are discussed, especially from a viewpoint of portable PV applications.

The biggest challenging issue in the realistic implementation of perovskite solar cells is their long-term stability. Cell stability strongly determines what markets PSCs can contribute to and even though the stability requirements for portable devices are not as high as for devices integrated into the energy grid, most of the high-efficiency PSCs only have a lifetime of a few hours. [25] Clearly, the stability of perovskite solar cells is something that needs to be drastically improved if they are to be employed in any applications outside of the laboratory.

Most of the PSC instability can be attributed to the unstable perovskite materials, which readily decompose under environmental stress. [29] Perovskite solar cells are remarkably sensitive to humidity because of the hygroscopic ammonium ion. This was discovered already with the very first PSCs derived from dye-sensitized solar cells, when the perovskite material was corroded by the liquid electrolytes. [22] The perovskite (here $\text{CH}_3\text{NH}_3\text{PbI}_3$) tends to decompose into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$, resulting in a decrease in the PCE of the cell. PSCs stored in either dry air or

nitrogen maintain 80 % of their initial performance after 24 hours and 20 % after six days, whereas similar cells stored in ambient air retain less than 20 % of their initial performance after 24 hours and 6 % after six days. [31] It appears that humidity does indeed have an effect on the degradation of perovskite solar cells. [5]

Besides humidity, other causes for the instability of the perovskite material include illumination, interaction with ETL and HTL materials or components of solution processing, and thermal conditions. In UV light the lead-halide parts of perovskites may decompose and form metallic lead. [24] Under illumination, any excess PbI_2 in the perovskite layer can also result in degradation even in inert atmosphere, and the degradation of the cell is faster in ambient atmosphere than that of cells with no excess PbI_2 . TiO_2 , widely used as electron transport material, can extract electrons from iodine in the interface of the perovskite and ETL, resulting in the degradation of MAPbI_3 into PbI_2 . This process is visualised in Figure 4.1. Some additives used in hole transport layers, such as 4-tert-butylpyridine (TBP), or residues of solvents from the solution process can promote the corrosion of the perovskite. Perovskites are also very sensitive to impurities in the solvent and solute, as well as any moisture during the fabrication, which means that the preparation of the cells has to be carried out in a controlled and air-tight environment. [22]

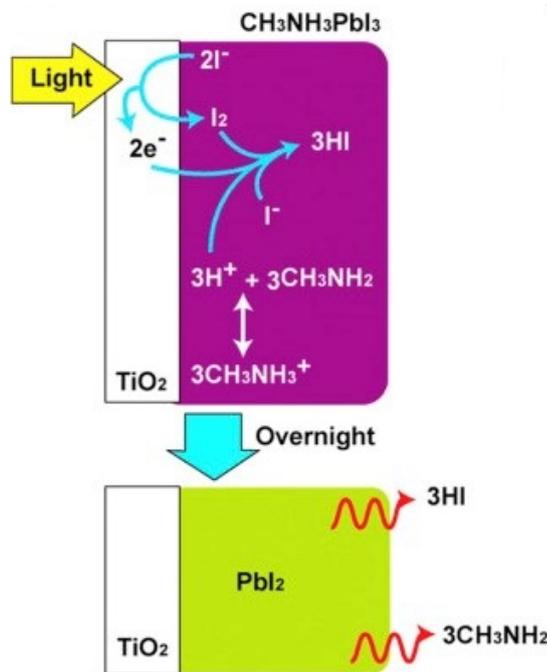


Figure 4.1 Degradation of the perovskite as a result of TiO_2 /perovskite interface reactions [5]

The degradation can also result from the intrinsic thermodynamic instability of the perovskite crystal structure. At around 55°C MAPbI_3 experiences a phase transition from a tetragonal crystal structure into a cubic one, which decreases the

cell performance. [29] The decomposition of MAPbI_3 into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ is exothermic, implying that the tetragonal structure is thermodynamically unstable at room temperature regardless of outside factors such as moisture or oxygen. It has also been shown that perovskites exhibit similar degrading behaviour in both air and vacuum, suggesting that the degradation mechanism may indeed be intrinsic and independent of environmental factors. [5] It should also be remembered that the stability of each individual layer affects the stability of the whole cell, so similarly to the perovskite layer, also the stabilities of ETL and HTL need to be considered in order to produce long-lasting cells.

The stability of PSCs can be improved by perovskite material modification, engineering of perovskite/ETL and perovskite/HTL interfaces, and encapsulation of the device. For example, partially replacing iodine with bromine or chlorine prevents the spontaneous phase separation into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ and increases chemical stability. Overall, strengthening the interaction between the organic cation and inorganic anion in the lattice results in better chemical stability. Bromine, being a smaller atom than iodine, creates a more compact and stable crystal structure than iodine, and also improves the resistance towards humidity. Complete replacement of iodine with bromine results in a drop in efficiency, so in order to achieve better stability without losing in PCE, it is better to use mixed halides. [22] It is also possible to replace halogens with pseudohalogen polyanions such as SCN^- to improve stability. Substituting some of the organic cation and creating mixed perovskites such as $\text{FA}_x\text{MA}_x\text{PbI}_3$, or replacing it completely to form inorganic perovskites such as CsPbI_3 also improves thermal stability. [5]

Degradation caused by the interactions of perovskite and charge carrying materials can be reduced by installing blocking layers of other materials into the interfaces of perovskite and charge transport layers. For example, a layer of Al_3O_2 or Sb_2S_3 can be inserted into the perovskite/ETL interface in order to block the corroding interaction between them. The effect of a Sb_2S_3 blocking layer in PCE is visualized in Figure 4.2. The ETL material can also be doped with other atoms, for example doping ZnO with aluminium or magnesium increases stability. Since UV illumination promotes the corroding interaction between perovskite and TiO_2 ETL, it can be suppressed by installing a UV filter in front of the ETL. [22] Buffer layers can also be used in the perovskite/HTL interface in order to prevent the harmful additives such as TBP in HTL materials from corroding the perovskite. Possible materials for the interfacial buffer layers are for example methylcyclopentadienyl manganese tricarbonyl (MMT) or Al_3O_2 . [5]

Aside of material and interface engineering, encapsulating the cell against humidity,

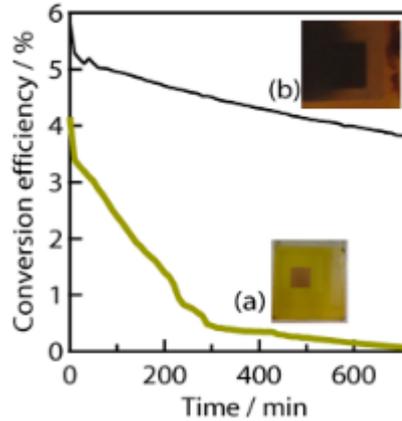


Figure 4.2 Degradation of uncapsulated solar cells a) without blocking layer and b) with Sb_2S_3 blocking layer between TiO_2 ETL and perovskite [15]

oxygen and other ambient conditions is a means to improve stability. Encapsulation is also used in other thin-film photovoltaics. Besides the materials used for sealing the cell, the sealing procedure itself has an effect on the PCE of the resulting device. Thermal stress, high pressure and UV curing, often used in the sealing process, can in fact damage the cell after the encapsulation. With optimized encapsulation processes, the PSC can maintain its initial power conversion value for more than 1300 hours of shelf life, while similar but unsealed devices can have a decrease of 20 % in PCE over the first 50 hours. [21]

Besides cell stability, another issue that needs to be addressed is the possible toxicity of lead and overall environmental impact of perovskite solar cells, as well as the disposal and recycling of cells at the end of their service life. The European Union regulates the amounts of hazardous substances in consumer electronics. This includes for example the lead currently used in the best-performing perovskite solar cells. Stationary photovoltaic installations are excluded from the regulations, however, portable devices such as solar powered calculators or telephones are not. The lead content in electronic devices can be no larger than 0.1 % of weight. [7] Therefore, in order to realistically produce portable PSC devices with the current legislation, either the lead content has to fall under the limit, or the lead has to be completely replaced.

Unfortunately, current research suggests that the direct replacement of lead with other metal cations usually results in a decline in device efficiency. Substitution of lead with tin has been attempted and while this is theoretically possible, the PCE of such cells is significantly lower than the PCE of their lead-based counterparts. In addition to poor performance, tin-based cells are even more unstable than lead-based due to the tendency of Sn^{2+} ion to oxidize into Sn^{4+} . [16] According to a

life cycle assesment made for tin- and lead-based PSCs, tin-based cells have higher environmental impact in all categories, and all in all appear to have no advantages over their lead-based analogues. [25] Another alternative under research is bismuth, and while it shows good stability in ambient conditions, the efficiency of such a cell is extremely low, less than 2 %. [29] Development of lead-free perovskites with high efficiency still faces serious challenges, and as it is, attention should be drawn into effective encapsulation technologies in order to address the potential environmental problems.

It is of somewhat common consensus that when it comes to environmental effects of the perovskite production, the lead content in the perovskite layer is not the main concern. Instead, processing of other layers in perovskite solar cells requires energy intensive production steps. This includes for example the high-temperature sintering of TiO_2 and the manufacturing of the FTO-coated glass substrate, which alone consumes 36 % of all the primary energy of embedded materials. [16] Based on a life cycle assessment of perovskite solar cells, their total environmental impact per unit of electricity generated is lower than that of monocrystalline silicon solar cells, but greater than any other commercial technology. The main reason for the higher enviromneltal impacts is the shorter lifetime of perovskite solar cells. Solution processing was found to decrease the overall electricity consumption, but the organic materials used for preparing the precursors for perovskite deposition seem to cause high marine eutrophication. The toxicity impact of lead appears to be negligible in all categories of the life cycle assessment. [3] The manufacturing environmental impacts of selected PV technologies are presented in Figure 4.3.

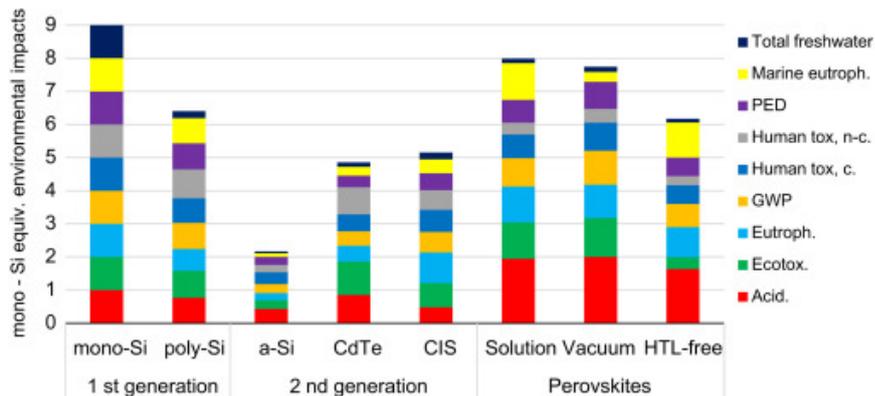


Figure 4.3 Comparison of environmental impacts of perovskite devices and commercial PV technologies. In each category, the impact of each technology is divided by the impact of mono-Si cells. In the figure, GWP stands for global warming potetial and PED for primary energy demand. [3]

Aside of possible alterations to the fabrication processes, it is important to develop easy and effective recycling processes in order to reduce the environmental impacts

of PSCs. This is true especially if the lifetimes of perovskite solar cells remain short. Recycling contributes also in the recovery of some of the scarcer materials, such as noble metals from the electrodes. It is worth noting that although the lead content is not necessarily the main contributor to the environmental impacts, it is highly toxic to the environment and unless properly recycled, adds greatly to the impacts. Landfilling PSCs - where most of the lead leaches into soil and water - implies environmental impacts five times larger than incineration of the cells, where the lead is recovered. [25] It has been shown that PSC devices can be dismantled at room temperature and that materials can be extracted with high purity for either direct reuse or further recycling. Most importantly, new PSC devices can be fabricated from materials recycled at least twice without significant losses in device performance. [16]

Naturally, there are also other challenges that need answers before PSCs can enter the market. For one, the use of noble metals in the electrodes is not necessarily the best option, seeing as noble metals are quite expensive and they can also contribute to the instability of the cell by interacting with the perovskite layer. [5] As mentioned in the context of tandem cells, alternatives for gold or silver electrodes are under research. Overall, the PSC technology is still quite young, and currently the fact is that the best efficiencies and performances are still achieved only in laboratory scale cells. Upscaling PSCs and finding solutions to the challenges discussed in this chapter is still very much under research, but if satisfactory solutions are found, PSCs could well be employable into consumer electronics.

5. CONCLUSIONS

Perovskite solar cells have attracted great interest during the recent years, and with good reason. With their excellent light absorbing properties, simplicity of processing and wide tunability, they offer a competitive alternative for conventional photovoltaics, performing well in many areas where the current commercial technologies fail. While their lab-scale efficiencies are impressive, whether similar values are ever achievable in larger scale cells remains to be seen. Nevertheless, perovskite solar cells may well be the best-performing low cost photovoltaic technology.

Partially due to the constantly dropping cost of silicon solar cells, and also because of the issues with cell stability, perovskite solar cells may have a hard time replacing silicon-based photovoltaics in energy grid integration. They do, however, exhibit better performance in non-ideal lighting conditions and can achieve mechanical properties, such as flexibility, that silicon cells cannot. Therefore they could be considerable candidates for portable photovoltaics. Through fundamental research addressing cell instability, as well as less ecotoxicity and other environmental impacts, perovskite solar cells have great potential to enter the market, and in the light of current research it appears that portable PSC devices might indeed be a feasible application.

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