

Recent progress in long-term stability of perovskite solar cells

Seyedali Emami, Luísa Andrade, ¹Adélio Mendes

LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy Engineering, Faculdade de Engenharia da Universidade do Porto. ¹(mendes@fe.up.pt)

Abstract

Perovskite solar cells made a huge breakthrough among the nanostructured thin film photovoltaics. They exhibited certified power conversion efficiency (PCE) as high 24 % in 2015. A vast amount of research were spent on improvement of PCE and lowering the fabrication process temperature, resulting in outstanding outcomes in these areas. In contrast, the long-term stability and commercialization of these devices were not well studied. The review briefly summaries the challenges of perovskite solar cells in the road of stabilization and commercialization.

Subject Headings. Photovoltaic Cell, Solar Energy.

Author Keywords. Perovskite Solar Cell, Stability, Long-Term, Commercialization.

1. Introduction

Solar energy is the most reliable renewable energy sources to replace traditional energy resources such as coal, oil and natural gas. In this context, solar cells have gained tremendous attentions during past decades. To date, silicon solar cells are the most common photovoltaic devices on the market. The high power conversion efficiency of around 25 % is the major advantage of silicon solar cells which makes them the leader in the market (Green et al. 2015). High production costs and complex manufacturing of Si-based photovoltaics, are the drawback of these devices.

Thin-film solar cells are the next generation in line, solar cells such as copper indium gallium selenide (CIGS) with efficiencies reaching 20 % (Jackson et al. 2011), and cadmium telluride (CdTe) photovoltaics (Britt and Ferekides 1993) are the most famous devices of this type. The production process of these cells involves high temperature, toxic raw materials, and high cost vacuum vapor deposition. Therefore, these types of photovoltaics may not grow into the market higher than their current share.

Emerging solar cells are the most recent devices in the research field. Dye-sensitized solar cells (DSCs) are the pioneer in this group. The first DSC was reported on 1991 (O'Regan and Grätzel 1991) which opened the doors to low-cost and easy roll-to-roll fabrication solar cell technology. Commonly, dye-sensitized solar cells are consist of a photoanode (*e.g.*, TiO₂), a dye (*e.g.*, N719), an electrolyte (*e.g.*, iodide/triiodide redox couple), and a counter electrode (*e.g.*, platinum). DSCs working principle is different from common p-n junction solar cells, since light adsorption and charge transport occur separately at dye sensitizer and photoanode. The generated electrons are transported to the conduction band of the photoanode, and the electrolyte delivers the holes to the counter electrode (Hagfeldt et al. 2010). Conventional dye-sensitized solar cells were constructed with liquid-state electrolytes and they have reached to PCE near to 13 % with cobalt-based redox shuttle and an engineered donor- π -acceptor dye (Mathew et al. 2014). The biggest challenge for DSC is to improve their long-term stability. The most common issues are including degradation of photoanode and counter electrode, concentration drop in electrolyte redox couple, and encapsulation related concerns (Asghar

et al. 2010). Stability issues related to temperature, electrolyte leaking, and moisture presence in the cell could be reduced through suitable encapsulation of the liquid-state electrolyte DSC devices (Ribeiro et al. 2012). In contrast, the liquid electrolyte of DSCs could be replaced with solid state organic hole transport material (HTM) to minimize the stability issues (Bach et al. 1998). The power conversion efficiency of solid-state DSCs were relatively lower than the conventional liquid ones. To date, the highest PCE reported for solid-state DSCs is around 6 % with 2,2',7,7'-tetrakis(N,N-dimethoxyphenylamine)-9,9'-spirobifluorene (*spiro-OMeTAD*) as the organic HTM and C220 dye (Cai et al. 2011).

On 2009 Miyasaka and co-authors, were reported the first application of organometal halide perovskite materials in photochemical solar cells (Kojima et al. 2009). The device had a structure similar to DSCs, photoanode of TiO₂, CH₃NH₃PbX₃ (where X= Br, I) perovskite as light harvesting agent, iodide/triiodide redox couple as electrolyte, and platinum for counter electrode. The best working cell had PCE of 3.81 %, but it was quite unstable when exposing to air. This pioneer work lead the research to focus more on organometal halide perovskite and to date, more stable cells with certified PCE as high as 24 % has reported (Green et al. 2015).

Research has mainly dedicated to improving the power conversion efficiencies of perovskite solar cells (PSCs) while less attentions were focused on stability, lead content and commercialization issues of this new type of devices. Therefore, a brief review of these challenges is presented in this review.

2. Working principle of perovskite solar cells

Perovskite is a term used for referring to a crystal structure identical to calcium titanium oxide (CaTiO₃). The mineral was first discovered in Russia and it is named after Russian mineralogist, Count Lev Alekseevich Perovskii (1792-1856). The general chemical formula for perovskite is AMX₃, where "A" and "M" are cations of very different sizes, and "X" is an anion. Organometal halide perovskites containing cation metal of carbon family (such as Ge²⁺, Sn²⁺, and Pb²⁺) and anion halogens (F, Cl, Br, and I) are of the most interest for their good photovoltaic application (Mitzi 1996). The most common organic compound used for perovskite solar cells are; methylammonium (CH₃NH₃⁺), ethylammonium (CH₃CH₂NH₃⁺), and formamidinium (NH₂CH=NH₂⁺) (Kim et al. 2012, Hao et al. 2014, Im et al. 2012). Perhaps the most common perovskites used in photovoltaic applications are methylammonium lead triiodide (CH₃NH₃PbI₃) or others with mixed halides structures (CH₃NH₃PbI_{3-x}Br_x or CH₃NH₃PbI_{3-x}Cl_x) (Green, Ho-Baillie, and Snaith 2014, Ball et al. 2013).

Working principle of a solar cell involves, light absorption, charge separation, charge transport, and charge collection. Organometallic perovskites such as CH₃NH₃PbI₃ have showed both electron and hole transport properties (Xing et al. 2013). Therefore, perovskite solar cells could be constructed both as p-n junction and p-i-n junction. Perovskite cells are typically fabricated with two structures; mesoporous and planar.

The structure of mesoporous perovskite cells (Figure 1a) includes a mesoporous metal oxide (*e.g.*, TiO₂, Al₂O₃) which is coated with perovskite sensitizer. In contrast, planar perovskite solar cell architecture (Figure 1b) involves a perovskite layer deposited between electron and hole transport materials. Comparing these two structures, recombination rate of planar configuration is lower than mesoporous cells while, the charge transport rate of them was similar (Gonzalez-Pedro et al. 2014). Planar structure cells are interesting for flexible cells since their fabrication does not involve typical high temperature sintering stages. Apart from these

two configurations, an HTM-free structure was also reported with moderate power conversion efficiencies reaching to 12.8 % (Mei et al. 2014).

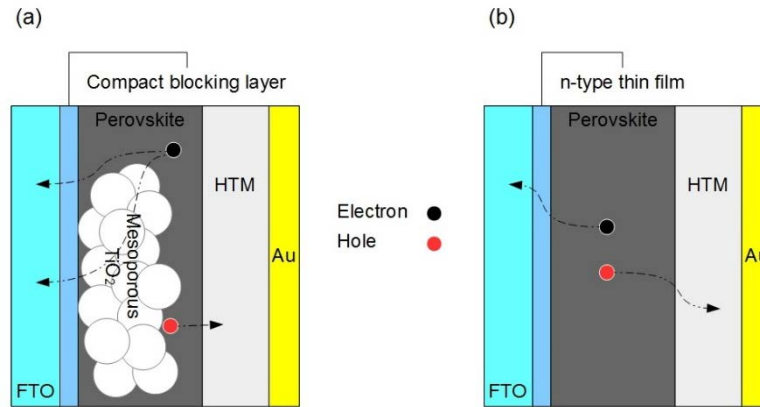
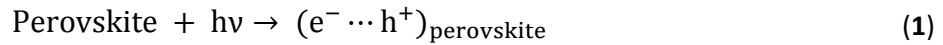


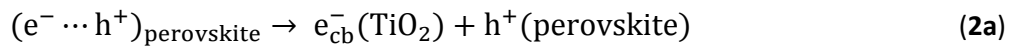
Figure 1: Schematic illustration of (a) mesoporous perovskite solar cell with TiO₂ layer as electron transport material; (b) planar perovskite structure in which perovskite acts as ambipolar transport

The energy level for mesoporous perovskite constructed with TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au junction is well matched for charge transport and separation (Figure 2a). For similar mesoporous configuration the electron transfer process involves (Figure 2b) (Marchioro et al. 2014):

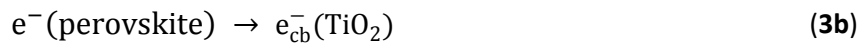
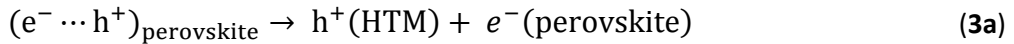
Photoexcitation of perovskite;



Electron injection;



Hole injection;



Photoluminescence;



Non-radiative recombination;



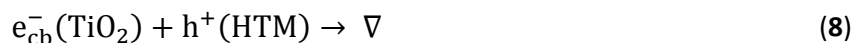
Back electron transfer at TiO₂-perovskite junction;



Back charge transfer at perovskite-HTM junction;



Charge recombination at TiO₂-HTM interface;



The overall photovoltaic conversion efficiency of mesoporous structure perovskite cell is controlled through above processes. In order to achieve high PCE, charge generation and transport (1)-(3) should have faster rate comparing to undesired recombination (4)-(8).

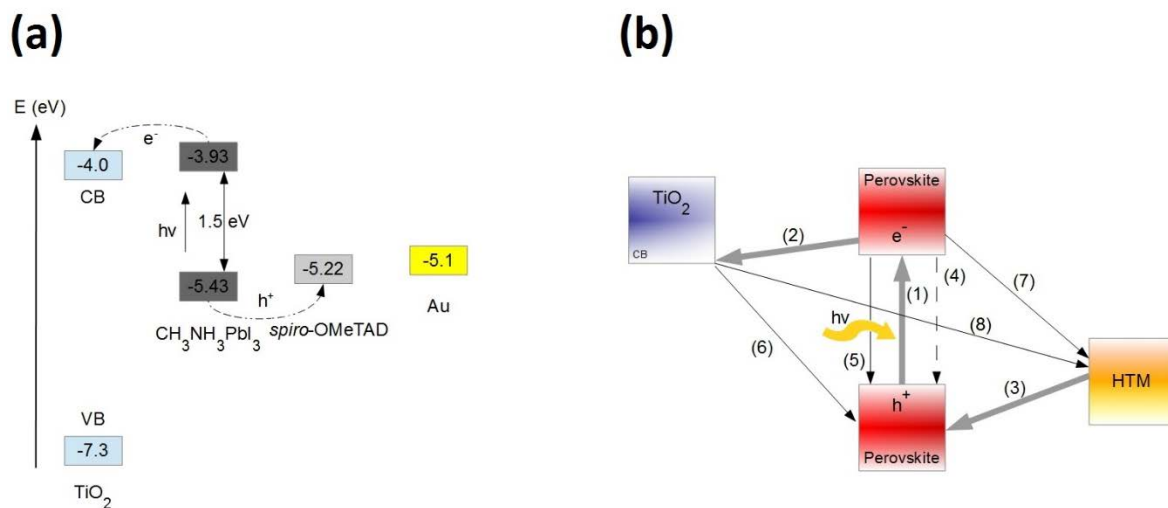


Figure 2: (a) Vacuum energy levels for perovskite cell with TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au configuration. (b) Electron and hole transport process for mesoporous perovskite

The ideal bandgap for single-junction photovoltaic cell should be ranging from 1.1 to 1.4 eV (Meillaud et al. 2006). One of the most remarkable properties of perovskite material is that they could adopt different bandgaps by varying their composition. For instance, by changing the halide composition of CH₃NH₃Pb(I_{1-x}Br_x)₃ (where, 0 ≤ x ≤ 1), the bandgap could be altered from 1.2 to 2.3 eV (Figure 1a) (Noh et al. 2013). Alternatively, Snaith *et al.* showed that by increasing the cation size APbI₃ perovskites, the bandgap could decrease. They have explored the change in bandgap energy and absorbance at UV-Vis spectra for three perovskite structure by substituting large radius formamidinium with slightly smaller methylammonium and very small cesium (Figure 1b) (Eperon et al. 2014).

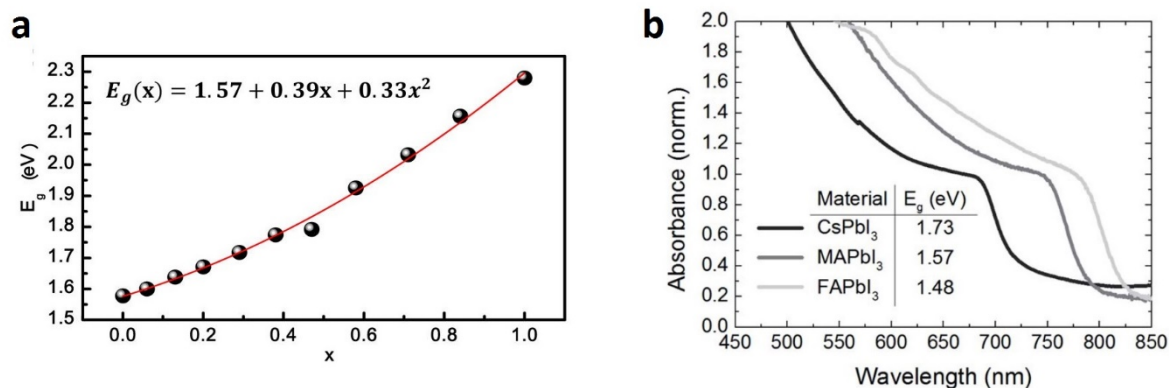


Figure 3: The influence of perovskite composition on the bandgap energy. (a) Bandgap energy change for CH₃NH₃Pb(I_{1-x}Br_x)₃ as a function of x. (b) bandgap and absorbance change for APbI₃ perovskites where, A being cesium (Cs), methylammonium (MA) or formamidinium (FA). Adapted with permission from (Eperon et al. 2014) and (Noh et al. 2013). © 2013, American Chemical Society, and 2014, Royal Society of Chemistry

Solid-state hole transport material (HTM) was first used in DSCs as a substitute to liquid electrolyte and it exhibited increase in V_{oc} of the device because of their high redox potential. Moreover, the aggressive liquid electrolyte was not quite compatible with perovskites materials, leading to fast degradation of the device. In contrast, solid-state HTM had shown improvements in the stability of PSCs (Kim et al. 2012). Perhaps the most common HTM used in perovskite-sensitized cells is *spiro*-OMeTAD which has resulted devices with PCE reaching to 19 % (Zhou et al. 2014). A high conductive HTM, reduces the series resistance and improves the fill factor of the cell (Lee et al. 2012). For example, Seok *et al.* reported improvement in

V_{oc} and fill factor when replacing *spiro*-OMeTAD ($12.7 \Omega \cdot \text{cm}^2$) with polymeric PTAA, poly-triarylamine, ($5.4 \Omega \cdot \text{cm}^2$) hole conductor (Heo et al. 2013).

To date, various approaches were applied to construct perovskite solar cells. These include substituting traditional TiO_2 photoanode with Al_2O_3 (Carnie et al. 2013, Edri et al. 2014, Lee et al. 2012), ZrO_2 (Bi et al. 2013), or ZnO_2 nanorod (Kumar et al. 2013, Son et al. 2014), as well as application of different organo halide perovskite such as common $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Kim et al. 2013, Jeon et al. 2014, Liu and Kelly 2014, Qin et al. 2014), $\text{CH}(\text{NH}_2)_2\text{PbI}_3$ (Koh et al. 2014, Eperon et al. 2014), or $\text{CH}_3\text{NH}_3\text{SnI}_3$ (Hao et al. 2014, Noel et al. 2014). Moreover, diverse fabrication routes of sequential deposition (Burschka et al. 2013, Zheng et al. 2014), vacuum deposition (Liu, Johnston, and Snaith 2013), and vapor-assisted deposition (Chen et al. 2014), provides a wide range of process temperature.

3. Commercialization and stability challenges

To date, the highest PCE of perovskite sensitized solar cells were reached with Pb-based perovskite light absorbers. Taking into account the toxic nature of lead and regulation related to material restriction laws, perhaps the major challenge is to replace lead with non-toxic, environmental friendly substances such as tin (Sn). Fabricated Sn-based PSCs have reached 6.4 % conversion efficiency (Noel et al. 2014) which comparing to Pb-based devices, are way less efficient. Moreover, tin halide perovskites such as $\text{CH}_3\text{NH}_3\text{SnI}_3$ and $\text{CH}(\text{NH}_2)_2\text{SnI}_3$ crystal structure suffers from $\text{Sn}^{2+}/\text{Sn}^{4+}$ conversion. In which, they display n-type semiconductor behavior at their 2+ oxidation state, while accommodated Sn^{4+} centers results in self doping and acting as p-type metal-like material (Stoumpos, Malliakas, and Kanatzidis 2013). Therefore, the stability of these type of device remain as a challenge until reaching more advanced sealing techniques (Hao et al. 2014).

The current lead-based PSCs are reported to be sensitive to humidity and oxygen (Noh et al. 2013). Additionally, degradation issues under ultraviolet exposure was reported for mesoporous TiO_2 structured lead-based devices (Leijtens et al. 2013). Overcoming these challenges is only possible through degradation mechanisms study of all components of the device.

In terms of cost, most of the component of the perovskite cells are relatively cheap. The main cost is related to FTO-coated glass substrates and gold counter electrode. However, the Au contact could be replaced by printable carbon counter electrode, to decrease of these costs (Ku et al. 2013). The production process is mostly done through cost-effective techniques such as spin-coating and screen-printing which makes these devices a promising candidate for future efficient photovoltaic industry. Graetzel *et al.* estimated the energy payback time of less than one year for dye-sensitized solar cells (Graetzel et al. 2012). Assuming a similar payback time approach for PSCs, reveals another advantage of these devices comparing to silicon solar cells with three years of payback (Boix et al. 2014).

The stability issue of the perovskite solar cells were not studied in details. Clearly, the research has focused on improving the performance of the device rather than paying attention to its long-term stability. Although there are some reported stable devices, but the degradation mechanisms are not well understood. Some studies stated, perovskite material as the major oxygen or UV light sensitive material, while some others identified HTM as the source of the stability issue of these photovoltaic cells.

Burschka et al. have examined long-term stability of an encapsulated (at argon atmosphere) cell with $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{spiro}$ -OMeTAD/Au configuration, at 45°C and $100 \text{ mW} \cdot \text{cm}^{-2}$ light intensity for 500 hours. They reported 20 % loss in PCE and small decay in V_{oc} and fill factor

(FF) while the J_{sc} remained stable. The stable J_{sc} was indicating no photodegradation in perovskite sensitizer and decays was associated to shunt resistance decrease (Burschka et al. 2013).

A non-encapsulated HTM-free cell with $TiO_2/ZrO_2/CH_3NH_3PbI_3/C$ structure was tested for 840 hours at room temperature in the dark. The initial PCE of the device was around 6.5 % and it stayed unchanged after stability experiment and even no notable change in the other characteristics of the cell (Ku et al. 2013).

Snaith et al. revealed a UV sensitive behavior for $TiO_2/CH_3NH_3PbI_{3-x}Cl_x/spiro-OMeTAD/Au$ cell, which they stated to be attributed to light desorption of surface-adsorbed oxygen. The degradation issue could be decelerated through using UV filter and encapsulation. However, replacing TiO_2 with Al_2O_3 has solved the UV issue and showed relatively 1,000 hour stable performance for the cell at 40 °C and 76.5 mW.cm⁻² light intensity (Leijtens et al. 2013).

A series of non-sealed perovskite solar cells with $TiO_2/CH_3NH_3Pb(I_{1-x}Br_x)_3/PTAA/Au$ structure, were exposed to 35 % humidity for 22 days at room temperature, to study their degradation behavior. While cells with no Br, or low fraction of Br ($X=0, 0.06$) had higher PCE (ca. 11 %), they acted absolutely unstable to humidity and lost 60 % of their initial conversion efficiency. In contrast, device with slightly higher Br content ($X=0.2, 0.29$) retained their initial conversion efficiency (ca. 9.2 %) along the test (Noh et al. 2013).

While most of the non-encapsulated devices consist of $CH_3NH_3PbI_3$ exhibited stability issue, Ito *et al.* explored copper(I) thiocyanate (CuSCN) as HTM in a device with $TiO_2/CH_3NH_3PbI_3$ and reported better stability comparing to cells constructed with *spiro-OMeTAD* and PTAA based. They indicated that humidity effects are mainly related to HTM (or the interface of the perovskite and hole-transport material) rather than $CH_3NH_3PbI_3$ itself (Ito et al. 2014).

A similar approach was applied by Park et al. to study 1,000 hour performance of devices with $TiO_2/CH_3NH_3PbI_3/HTM/Au$ configuration to investigate the influence of 20 % humidity on three different HTMs. These hole-transport materials were P3HT (poly(3-hexylthiophene-2,5-diyl)), PDPPDBTE (poly[2,5-bis(2-decyldodecyl)-pyr-olo[3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-di(2,20bithiophen-5-yl)-ethene]), and *spiro-OMeTAD*. They concluded that cell with *spiro-OMeTAD* lost 28 % of its initial PCE while P3HT and PDPPDBTE cells maintained their PCE over the aging test. The excellent stability of polymer-based perovskite cells, is due to hydrophobic nature of these materials which prevents water from penetrating to perovskite surface (Kwon et al. 2014).

Recently, the study of HTM effect on the stability of perovskite solar cells, have begun to attract more attention (Zhang, Liu, et al. 2015, Zhang, Lyu, et al. 2015, Yeo et al. 2015, Christians, Miranda Herrera, and Kamat 2015, Guarnera et al. 2015, Misra et al. 2014, Mei et al. 2014). Nonetheless, most of these studies are testing low efficient (<10 %) cells which are not quite suitable for commercialization purposes. Some of these studies are only considering humidity exposure test which are not proper for outdoor objectives. For outdoor application, an aging test should include temperature, humidity and light exposure.

In this challenge, two notable achievements have reached for stable PSCs with conversion efficiencies higher than 12 %. Snaith *et al.* used a buffer layer of Al_2O_3 nanoparticles between perovskite and HTM which increased both PCE and stability of the cell. A sealed device with $TiO_2/CH_3NH_3PbI_{3-x}Cl_x/Al_2O_3/spiro-OMeTAD/Au$ structure were exposed to light illumination equal to one sun, for 350 hours. The initial 13 % PCE of the device was slightly changed after the aging test, while a similar device without buffer layer have lost 50 % of its PCE (Guarnera et al. 2015). Mei *et al.* have fabricated an HTM-free cell consisting of $TiO_2/ZrO_2/(5-AVA)_x(MA)_{1-x}$.

$x\text{PbI}_3/\text{C}$ (where, MA= CH_3NH_3 , and 5-AVA= $\text{HOOC}(\text{CH}_2)_4\text{NH}_3$). Non-encapsulated cell with 12.8 % of this study, illustrated a remarkable stability over 1008 hours of $100 \text{ mW}\cdot\text{cm}^{-2}$ light exposure at room temperature. This excellent stability behavior is attributed to protection provided by thick carbon counter electrode ($10 \mu\text{m}$) which is acting as water-retaining layer (Mei et al. 2014).

4. Conclusions

The most efficient perovskite solar cells are constructed with $\text{CH}_3\text{NH}_3\text{PbI}_3$ and *spiro*-OMeTAD and the main long-term stability issue of PSCs are found to be related to these two main components of the device. Some reports related stability issue to *spiro*-OMeTAD, and tried to replace it with polymeric materials (*e.g.*, PTAA, P3HT, and PDPPDBTE) which they seem to be suitable alternatives. Additionally, HTM-free cells exhibited excellent stabilities when used with thick back contacts such as carbon. Therefore, these two strategies seems to be in the front line for reaching stable non-sealed cells. In contrast, an airtight encapsulation could solve many related humidity issue of these photovoltaic devices without modifying efficient state-of-the-art components. Hence, another trend of research would be to development a decent encapsulation technology.

The current Pb-based state-of-the-art perovskite solar cells are having a hazardous heavy metal drawback similar to CdTe solar cells. European Union Restriction on Hazardous Substances (RoHS) made an exception for CdTe, perhaps the same approach may be considered for PSCs as well. However, production capacity of 1,000 GW per year could be reached by less than 10,000 tons of Pb which is much lower lead-content comparing to 4 million tons per year needed for lead-acid batteries (Hodes 2013).

Long-term stability and lead content, were found to be the largest drawbacks of perovskite solar cells. Study of the degradation mechanism of the device would result in cells with enhanced long-term stability. In addition, further research is required in order to find a suitable alternatives to replace Pb with non-toxic substances.

References

- Asghar, M. I., K. Miettunen, J. Halme, P. Vahermaa, M. Toivola, K. Aitola, and P. Lund. 2010. "Review of stability for advanced dye solar cells." *Energy and Environmental Science* no. 3 (4):418-426.
- Bach, U., D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel. 1998. "Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies." *Nature* no. 395 (6702):583-585.
- Ball, J. M., M. M. Lee, A. Hey, and H. J. Snaith. 2013. "Low-temperature processed meso-structured to thin-film perovskite solar cells." *Energy and Environmental Science* no. 6 (6):1739-1743.
- Bi, Dongqin, Soo-Jin Moon, Leif Haggman, Gerrit Boschloo, Lei Yang, Erik M. J. Johansson, Mohammad K. Nazeeruddin, Michael Gratzel, and Anders Hagfeldt. 2013. "Using a two-step deposition technique to prepare perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) for thin film solar cells based on ZrO_2 and TiO_2 mesostructures." *RSC Advances* no. 3 (41):18762-18766. DOI: [10.1039/C3RA43228A](https://doi.org/10.1039/C3RA43228A).
- Boix, P. P., K. Nonomura, N. Mathews, and S. G. Mhaisalkar. 2014. "Current progress and future perspectives for organic/inorganic perovskite solar cells." *Materials Today* no. 17 (1):16-23.

- Britt, J., and C. Ferekides. 1993. "Thin-film CdS/CdTe solar cell with 15.8% efficiency." *Applied Physics Letters* no. 62 (22):2851-2852.
- Burschka, J., N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel. 2013. "Sequential deposition as a route to high-performance perovskite-sensitized solar cells." *Nature* no. 499 (7458):316-319.
- Cai, N., S. J. Moon, L. Cevey-Ha, T. Moehl, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, and M. Grätzel. 2011. "An organic D- π -A dye for record efficiency solid-state sensitized heterojunction solar cells." *Nano Letters* no. 11 (4):1452-1456.
- Carnie, M. J., C. Charbonneau, M. L. Davies, J. Troughton, T. M. Watson, K. Wojciechowski, H. Snaith, and D. A. Worsley. 2013. "A one-step low temperature processing route for organolead halide perovskite solar cells." *Chemical Communications* no. 49 (72):7893-7895.
- Chen, Q., H. Zhou, Z. Hong, S. Luo, H. S. Duan, H. H. Wang, Y. Liu, G. Li, and Y. Yang. 2014. "Planar heterojunction perovskite solar cells via vapor-assisted solution process." *Journal of the American Chemical Society* no. 136 (2):622-625.
- Christians, Jeffrey A., Pierre A. Miranda Herrera, and Prashant V. Kamat. 2015. "Transformation of the Excited State and Photovoltaic Efficiency of CH₃NH₃PbI₃ Perovskite upon Controlled Exposure to Humidified Air." *Journal of the American Chemical Society*. DOI: [10.1021/ja511132a](https://doi.org/10.1021/ja511132a).
- Edri, E., S. Kirmayer, M. Kulbak, G. Hodes, and D. Cahen. 2014. "Chloride inclusion and hole transport material doping to improve methyl ammonium lead bromide perovskite-based high open-circuit voltage solar cells." *Journal of Physical Chemistry Letters* no. 5 (3):429-433.
- Eperon, G. E., S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, and H. J. Snaith. 2014. "Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells." *Energy and Environmental Science* no. 7 (3):982-988.
- Gonzalez-Pedro, V., E. J. Juarez-Perez, W. S. Arsyad, E. M. Barea, F. Fabregat-Santiago, I. Mora-Sero, and J. Bisquert. 2014. "General working principles of CH₃NH₃PbX₃ perovskite solar cells." *Nano Letters* no. 14 (2):888-893.
- Graetzel, M., R. A. J. Janssen, D. B. Mitzi, and E. H. Sargent. 2012. "Materials interface engineering for solution-processed photovoltaics." *Nature* no. 488 (7411):304-312.
- Green, M. A., K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop. 2015. "Solar cell efficiency tables (Version 45)." *Progress in Photovoltaics: Research and Applications* no. 23 (1):1-9.
- Green, Martin A., Anita Ho-Baillie, and Henry J. Snaith. 2014. "The emergence of perovskite solar cells." *Nature Photonics* no. 8 (7):506-514. DOI: [10.1038/nphoton.2014.134](https://doi.org/10.1038/nphoton.2014.134).
- Guarnera, Simone, Antonio Abate, Wei Zhang, Jamie M. Foster, Giles Richardson, Annamaria Petrozza, and Henry J. Snaith. 2015. "Improving the Long-Term Stability of Perovskite Solar Cells with a Porous Al₂O₃ Buffer Layer." *The Journal of Physical Chemistry Letters*:432-437. DOI: [10.1021/jz502703p](https://doi.org/10.1021/jz502703p).
- Hagfeldt, A., G. Boschloo, L. Sun, L. Kloo, and H. Pettersson. 2010. "Dye-sensitized solar cells." *Chemical Reviews* no. 110 (11):6595-6663.
- Hao, F., C. C. Stoumpos, D. H. Cao, R. P. H. Chang, and M. G. Kanatzidis. 2014. "Lead-free solid-state organic-inorganic halide perovskite solar cells." *Nature Photonics* no. 8 (6):489-494.
- Heo, J. H., S. H. Im, J. H. Noh, T. N. Mandal, C. S. Lim, J. A. Chang, Y. H. Lee, H. J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, and S. I. Seok. 2013. "Efficient inorganic-organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors." *Nature Photonics* no. 7 (6):486-491.

- Hodes, G. 2013. "Perovskite-based solar cells." *Science* no. 342 (6156):317-318.
- Im, J. H., J. Chung, S. J. Kim, and N. G. Park. 2012. "Synthesis, structure, and photovoltaic property of a nanocrystalline 2H perovskite-type novel sensitizer (CH₃CH₂NH₃)PbI₃." *Nanoscale Research Letters* no. 7:1-14.
- Ito, S., S. Tanaka, H. Vahlman, H. Nishino, K. Manabe, and P. Lund. 2014. "Carbon-double-bond-free printed solar cells from TiO₂/CH₃NH₃PbI₃/CuSCN/Au: Structural control and photoaging effects." *ChemPhysChem* no. 15 (6):1194-1200.
- Jackson, P., D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, and M. Powalla. 2011. "New world record efficiency for Cu(In,Ga)Se₂ thin-film solar cells beyond 20%." *Progress in Photovoltaics: Research and Applications* no. 19 (7):894-897.
- Jeon, Nam Joong, Jun Hong Noh, Young Chan Kim, Woon Seok Yang, Seungchan Ryu, and Sang Il Seok. 2014. "Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells." *Nat Mater* no. 13 (9):897-903. DOI: [10.1038/nmat4014](https://doi.org/10.1038/nmat4014).
- Kim, H. S., C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Grätzel, and N. G. Park. 2012. "Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%." *Sci Rep* no. 2:591. DOI: [10.1038/srep00591](https://doi.org/10.1038/srep00591).
- Kim, H. S., J. W. Lee, N. Yantara, P. P. Boix, S. A. Kulkarni, S. Mhaisalkar, M. Grätzel, and N. G. Park. 2013. "High efficiency solid-state sensitized solar cell-based on submicrometer rutile TiO₂ nanorod and CH₃NH₃PbI₃ perovskite sensitizer." *Nano Letters* no. 13 (6):2412-2417.
- Koh, T. M., K. Fu, Y. Fang, S. Chen, T. C. Sum, N. Mathews, S. G. Mhaisalkar, P. P. Boix, and T. Baikie. 2014. "Formamidinium-containing metal-halide: An alternative material for near-IR absorption perovskite solar cells." *Journal of Physical Chemistry C* no. 118 (30):16458-16462.
- Kojima, A., K. Teshima, Y. Shirai, and T. Miyasaka. 2009. "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells." *Journal of the American Chemical Society* no. 131 (17):6050-6051.
- Ku, Z., Y. Rong, M. Xu, T. Liu, and H. Han. 2013. "Full printable processed mesoscopic CH₃ NH₃ PbI₃ /TiO₂ heterojunction solar cells with carbon counter electrode." *Scientific Reports* no. 3.
- Kumar, M. H., N. Yantara, S. Dharani, M. Graetzel, S. Mhaisalkar, P. P. Boix, and N. Mathews. 2013. "Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells." *Chemical Communications* no. 49 (94):11089-11091.
- Kwon, Y. S., J. Lim, H. J. Yun, Y. H. Kim, and T. Park. 2014. "A diketopyrrolopyrrole-containing hole transporting conjugated polymer for use in efficient stable organic-inorganic hybrid solar cells based on a perovskite." *Energy and Environmental Science* no. 7 (4):1454-1460.
- Lee, M. M., J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith. 2012. "Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites." *Science* no. 338 (6107):643-647.
- Leijtens, T., G. E. Eperon, S. Pathak, A. Abate, M. M. Lee, and H. J. Snaith. 2013. "Overcoming ultraviolet light instability of sensitized TiO₂ with meso-superstructured organometal tri-halide perovskite solar cells." *Nat Commun* no. 4:2885. DOI: [10.1038/ncomms3885](https://doi.org/10.1038/ncomms3885).
- Liu, D., and T. L. Kelly. 2014. "Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques." *Nature Photonics* no. 8 (2):133-138.
- Liu, M., M. B. Johnston, and H. J. Snaith. 2013. "Efficient planar heterojunction perovskite solar cells by vapour deposition." *Nature* no. 501 (7467):395-398.

- Marchioro, A., J. Teuscher, D. Friedrich, M. Kunst, R. Van De Krol, T. Moehl, M. Grätzel, and J. E. Moser. 2014. "Unravelling the mechanism of photoinduced charge transfer processes in lead iodide perovskite solar cells." *Nature Photonics* no. 8 (3):250-255.
- Mathew, S., A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, and M. Grätzel. 2014. "Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers." *Nature Chemistry* no. 6 (3):242-247.
- Mei, A., X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Grätzel, and H. Han. 2014. "A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability." *Science* no. 345 (6194):295-298.
- Meillaud, F., A. Shah, C. Droz, E. Vallat-Sauvain, and C. Miazza. 2006. "Efficiency limits for single-junction and tandem solar cells." *Solar Energy Materials and Solar Cells* no. 90 (18-19):2952-2959.
- Misra, Ravi K., Sigalit Aharon, Baili Li, Dmitri Mogilyansky, Iris Visoly-Fisher, Lioz Etgar, and Eugene A. Katz. 2014. "Temperature- and Component-Dependent Degradation of Perovskite Photovoltaic Materials under Concentrated Sunlight." *The Journal of Physical Chemistry Letters*:326-330. DOI: [10.1021/jz502642b](https://doi.org/10.1021/jz502642b).
- Mitzi, D. B. 1996. "Synthesis, crystal structure, and optical and thermal properties of (C₄H₉NH₃)₂MI₄ (M = Ge, Sn, Pb)." *Chemistry of Materials* no. 8 (3):791-800.
- Noel, Nakita K., Samuel D. Stranks, Antonio Abate, Christian Wehrenfennig, Simone Guarnera, Amir-Abbas Haghighirad, Aditya Sadhanala, Giles E. Eperon, Sandeep K. Pathak, Michael B. Johnston, Annamaria Petrozza, Laura M. Herz, and Henry J. Snaith. 2014. "Lead-free organic-inorganic tin halide perovskites for photovoltaic applications." *Energy & Environmental Science* no. 7 (9):3061. DOI: [10.1039/c4ee01076k](https://doi.org/10.1039/c4ee01076k).
- Noh, J. H., S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok. 2013. "Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells." *Nano Letters* no. 13 (4):1764-1769.
- O'Regan, B., and M. Grätzel. 1991. "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films." *Nature* no. 353 (6346):737-740.
- Qin, P., S. Tanaka, S. Ito, N. Tetreault, K. Manabe, H. Nishino, M. K. Nazeeruddin, and M. Grätzel. 2014. "Inorganic hole conductor-based lead halide perovskite solar cells with 12.4% conversion efficiency." *Nature Communications* no. 5.
- Ribeiro, F., J. MaçAira, R. Cruz, J. Gabriel, L. Andrade, and A. Mendes. 2012. "Laser assisted glass frit sealing of dye-sensitized solar cells." *Solar Energy Materials and Solar Cells* no. 96 (1):43-49.
- Son, D. Y., J. H. Im, H. S. Kim, and N. G. Park. 2014. "11% efficient perovskite solar cell based on ZnO nanorods: An effective charge collection system." *Journal of Physical Chemistry C* no. 118 (30):16567-16573.
- Stoumpos, C. C., C. D. Malliakas, and M. G. Kanatzidis. 2013. "Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties." *Inorganic Chemistry* no. 52 (15):9019-9038.
- Xing, G., N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, and T. C. Sum. 2013. "Long-range balanced electron-and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃." *Science* no. 342 (6156):344-347.

- Yeo, J. S., R. Kang, S. Lee, Y. J. Jeon, N. Myoung, C. L. Lee, D. Y. Kim, J. M. Yun, Y. H. Seo, S. S. Kim, and S. I. Na. 2015. "Highly efficient and stable planar perovskite solar cells with reduced graphene oxide nanosheets as electrode interlayer." *Nano Energy* no. 12:96-104.
- Zhang, M., M. Lyu, H. Yu, J. H. Yun, Q. Wang, and L. Wang. 2015. "Stable and low-cost mesoscopic CH₃NH₃PbI₂Br perovskite solar cells by using a thin poly(3-hexylthiophene) layer as a hole transporter." *Chemistry - A European Journal* no. 21 (1):434-439.
- Zhang, Y., W. Liu, F. Tan, and Y. Gu. 2015. "The essential role of the poly(3-hexylthiophene) hole transport layer in perovskite solar cells." *Journal of Power Sources* no. 274:1224-1230.
- Zheng, L., Y. Ma, S. Chu, S. Wang, B. Qu, L. Xiao, Z. Chen, Q. Gong, Z. Wu, and X. Hou. 2014. "Improved light absorption and charge transport for perovskite solar cells with rough interfaces by sequential deposition." *Nanoscale* no. 6 (14):8171-8176.
- Zhou, H., Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang. 2014. "Interface engineering of highly efficient perovskite solar cells." *Science* no. 345 (6196):542-546.

Acknowledgments

S. Emami and L. Andrade acknowledge European Research Council for funding within project BI-DSC – Building Integrated Dye sensitized Solar Cells (Contract Number: 321315). The authors also acknowledge Project WinDSC SI&IDT (ref. 21539/2011) for financial support.