BFE SI/501816-01 UPERO Final report

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Short report on toxicity of lead halide-based perovskite solar cells

1. Introduction

Since lead is a natural constituent of the earth's crust, trace amounts are found in plants, soil and water. Due to mining and the fabrication of man-made objects and chemicals, lead can be ingested and deploy its toxic potential. When accumulated in the body severe health problems may occur. In past times, notorious sources for lead intoxication were lead-based sweetening agents, e.g., used by the Romans in many dishes and similarly during the 17th century in Germany. Later, "modern" sources from gasoline exhausts, smelter emissions, fly ash from coal power plants, peeling paint, etc., have massively dispersed lead throughout the environment. Nevertheless thanks to the increasing knowledge and awareness, today's daily intake of lead per person is about 100-1000 times smaller than during Roman times.

Still lead is a major public health concern, since it has the potential of causing irreversible health damage, interfering with body functions such as the central nervous, hematopoietic, hepatic and renal system. [1] Lead uptake can lead to oxidative stress by creating an imbalance between production of free radicals and the biological system's ability to annihilate the reactive intermediates or to repair the resulting damage. [2] Free radicals have numerous effects and can attack the cell membrane, oxidize proteins and nucleic acids like DNA and RNA leading to cancer. [3] Besides oxidative stress, the ion mechanism is another reason for lead toxicity. Pb^{2+} can easily substitute other bivalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+} and to a lesser extent monovalent cations like Na^{+}.[4]

Today, lead emission is of course a concern for all technologies involving lead as one of its constituents, and therefore the young organic lead-halide perovskite semiconductors used as efficient solar cell absorbers are looked at critically. Before tackling the latter subject it is however interesting to consider lead emission involved in c-Si technology that shared 95% of the global PV module production in 2019. [5] Silver is ubiquitously used as current collectors. To interconnect individual cells in modules, PV are conventionally soldered to the silver electrodes using $Sn_{37}Pb$ and $Sn_{36}Pb_2Ag$ alloys[6]. The precise amount of lead used in c-Si modules depends on the type of solder, but on average, the amount of lead used in a typical c-Si panel is about 6.1 g/m^2. Accordingly, the estimated amount of lead used in PV industry increased greatly due to the large deployment in recent years approaching 20'000 tons in 2018 (see Figure 1). Environmental impact becomes relevant as soon as Pb is leaching out of the modules. According to the leaching test procedure (TCLP) for commercial c-Si modules, Pb leaching out of modules varied from 3 to11 mg/L, the regulatory limit being 5 mg/L. [7,8] Thus, hazardous waste stemming from modules coming to their end-of-life will become an important challenge in the next 5 to 10 years. Fortunately this situation will be relaxed in the in the future as silver based solders will gradually replace lead based ones. [9]

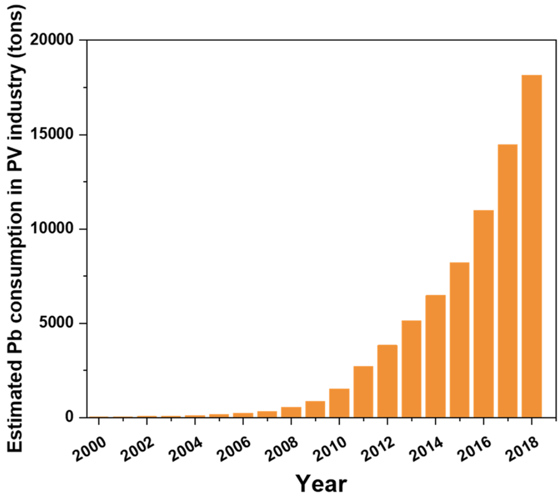

Figure 1. Estimated Pb consumption in photovoltaic industry based on annual electricity capacity, as listed by the international renewable energy agency. [10]

2. Lead content in halide perovskite solar cells (PSC)

The total lead content in a thin film solar cell incorporating a 400 nm thick lead halide perovskite absorber is about 0.4 g/m^2, which is a relatively small amount of lead compared to other sources of lead contaminating the environment. First of all, the amount of lead found in a 1 cm thick slice of soil per square meter is 0.3-1.2 g/m^2 and therefore is of the same order of magnitude as in lead-based perovskite solar cells. [11] However, with widespread implementation of this technology, considerable amounts of lead may accumulate. If for example the U.S. electricity production would be covered by perovskite/c-Si tandem solar cells (PCE of 25%) alone and estimating a 25-year lifetime, around 160 t/year of lead would be required for solar cell production. [12] This is much less than the solid lead emission from electronic solder of 7'000 t/year, or the lead content of 100'000 t/year in coal ash and black water. For comparison, the airborne emission from automotive fuels before 1973 was of a similar order of magnitude. In the light of these massive emissions from other industry sectors, the upper weight limit of lead fixed by the European Union’s Restriction of Hazardous Substances (RoHS) of 0.1% by weight of the full device[13] may seem adequate. Even though this regulation only relates to portable devices, it is interesting to note that PSC modules on glass would pass the regulations, while PSC modules on plastic foil would not. PV panels on rooftop and facades are exempt from this regulation, but as we discussed above, the lead content of c-Si modules of 6 g/m^2 is already higher than the one of the thin lead halide perovskite absorber and from this point of view nothing precludes the implementation of PSC technology. However, recent studies discuss the difficulty of introducing a safe threshold, because lead salts leaching out of PSC modules may be more bioavailable. [14]

3. Toxicity of lead-based PSC

In view of the continuing effort of industrializing PSC technology, several toxicity studies have been carried out. [14-20] First of all, these studies use different cytotoxicity assays to investigate cellular properties, metabolic activity, morphology and viability. For example murine primary hippocampal neurons and human dopaminergic neuroblastoma cells, suffered apoptotic cell death after $CH_3NH_3PbI_3$ treatment, while for human lung epithelial cells, only the proliferation capacity and mitochondrial activity changed without noticeable cell death. One of the studies established that the toxicity degree ranked as Pb^{2+} > $CH_3NH_3PbI_3$ > PbI_2 = PbO. PbI_2 is the degradation product after irreversible degradation of the perovskite with water[21], while PbO is mainly produced in a fire hazard.[22] It has to be noted that PbI_2 is already listed as acutely toxic based on the EC Regulation No. 1907/2006.

Other bioassays employed microorganisms such as aquatic and soil bacterial species, invertebrate animals and more complex forms of life.[18] It was found that the release of Pb^{2+} ions in the exposure medium was the determining fact for toxicity. Thereby bacterium V. fischeri proved to be the most sensitive species to lead-halide perovskite materials (Figure 2).

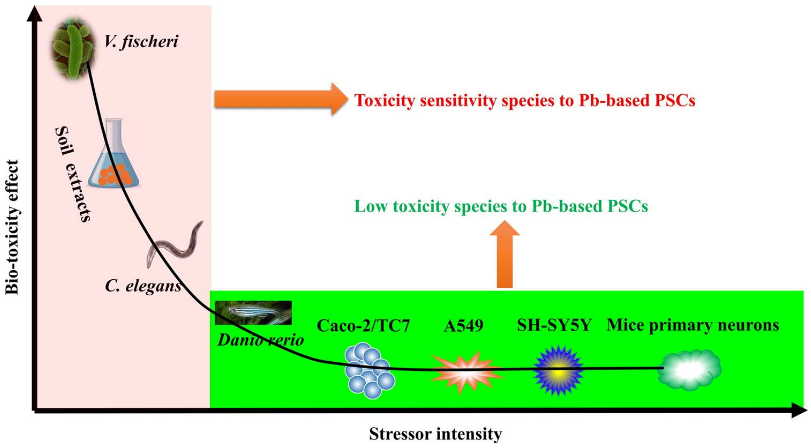

Figure 2. Toxicity sensitivity of certain biological species. A549 represented for human lung adenocarcinoma epithelial cells, SH-SY5Y represented for human dopaminergic neuroblastoma cells, Caco–2/TC7 represented for human colonic epithelial cells[18]

In summary, lead-based perovskites pose significant risks to the ecosystem, as well as to animal and human health. It is therefore judicious to look at the leaching process of PSC modules. Since the lead-halide perovskite based solar cells are very sensitive to humidity and oxygen, a thorough module encapsulation is mandatory. Under extreme weather conditions or due to fire, however, the encapsulation can break and lead species can escape to the ground under heavy rainfalls or escape into the atmosphere in the case of fire. In the case of water, non-encapsulated $CH_3NH_3PbI_3$ films immediately degraded to yellow colored films composed of PbI_2.[21] After only 5 minutes of exposure in simulated rain, 72% of the lead content was lost in the form of Pb^{2+} ions and PbI_2 colloids. Damaged cells with different encapsulation methods were also investigated.[23] For extreme conditions, where simulated rain lasted for 72h lead leaching was almost complete with amounts of 0.54 g/m^2 escaping to the ground.[23] At the present stage, further studies are needed to assess the soil sequestration of toxic Pb^{2+} ions under outdoor conditions, i.e., natural soil and weather.

4. Fail-safe encapsulation of PSC

In recent years, there have been many reports on avoiding lead leaching out of a broken cell or module encapsulation by implementing lead capturing films into the device structure. This has been achieved either by endowing the hole or electron transport layer, the electrode layer with lead adsorbing property. For example a tetraethylene-glycol substituted thiadiazole hole transmitting layer with Pb^{2+} chelating ability was introduced by Lee et al..[24] An ammonium sulfide layer was deposited directly on top of the lead-halide perovskite film to passivate the absorber surface and prevent Pb^{2+} to leach out of the film due to the very strong binding energy of PbS.[25] A thiol functionalized metal-organic framework was used as an electron transmitting layer to stabilize the device and also to potentially capture Pb^{2+} ions released during leaching. The metal organic framework showed a lead adsorption capacity of 355 mg/g.[26] X. Li et al.[27] used phosphonic acid derivatives with strong Pb^{2+} binding capacity to be deposited outside of the perovskite electrodes. These films are able to swell when soaked into water and can retain up to 96 % of the lead leakage (Figure 3).

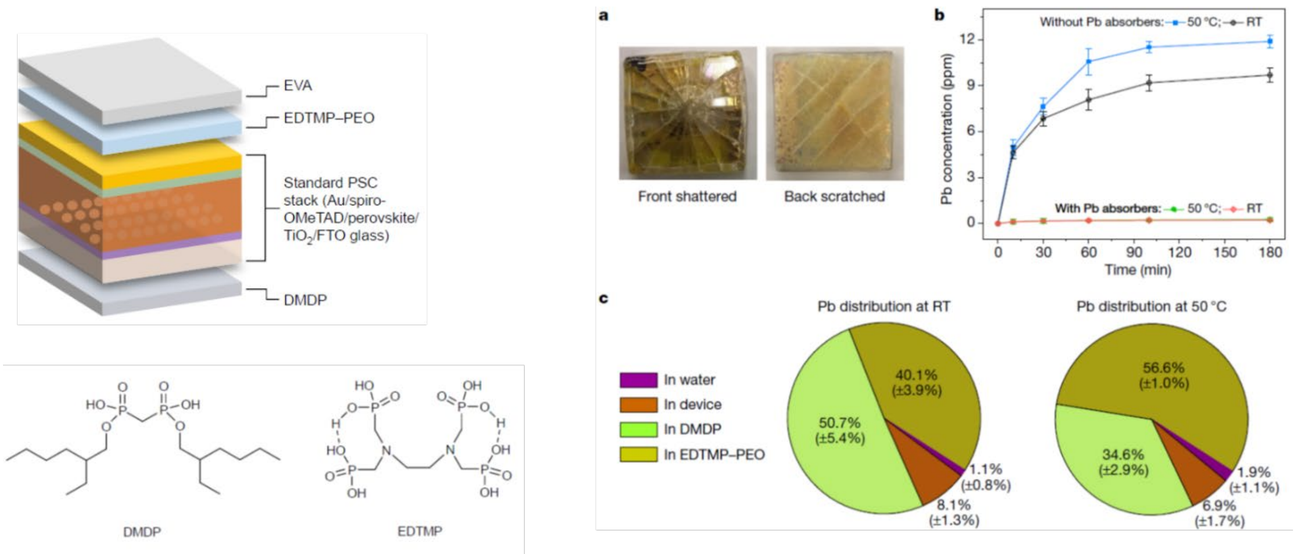

Figure 3. Typical perovskite device structure using additional layers of the phosphonic acid derivatives DMDP and EDTMP on top and bottom of the device structure (left). Shattered device glass and back scratched back layer (a), Leaching concentration (b) and lead distribution using in the damaged devices at room temperature and 50°C (c).[27]

Fire safety too has been tackled by some research groups. Among other strategies, a glass-glass encapsulation has been proven to be an effective strategy to avoid emission of lead into the atmosphere (evaporated PbI_2). The simulated fire scenario consisted of annealing the encapsulated cell at a temperature of 760 °C under a constant supply of fresh air. The reason for the effectiveness of the encapsulation is that most of the PbI_2 can be oxidized into PbO and PbO_2 species, and remain in the glass cover.[22]

5. Lead-free halide perovskites

Another approach that already started almost a decade ago consists of replacing the lead atom by other atoms of the periodic table.[28] Pb^{2+} can be replaced by other metal ions with low or with none toxicity at all. Examples of equivalent cations are Sn^{2+} and Ge^{2+} which have been most studied.[29] It is also possible to replace 2 Pb^{2+} cations by one tetravalent ion such as Sn^{4+}, Ge^{4+}, Ti^{4+} or Pd^{4+} to form so-called double perovskites with chemical formula $A_2M(iv)X_6$, where, A is an organic or inorganic monovalent cation, M(IV) is the tetravalent metal cation and X is the halide anion.[29] Air-stable molecular semiconducting iodosalts for solar cell applications: Cs_2SnI_6). Yet another possibility is to replace three Pb^{2+} cations by two trivalent metal cations such as In^{3+}, Sb^{3+} or Bi^{3+} to form semiconductors with $A_3M(III)2X_9$ stoichiometry.[30] In order to allow for a denser packing, quaternary double perovskite compounds with $A_2M(I)M(III)X_6$ composition were also studied.[31] To date, lead-free halide perovskite cells still show quite modest to poor power conversion efficiencies compared to lead-based halide PSCs. A comprehensive review of the field is given in the article by J. Li et al..[29] The highest efficiency of 13.24% reported in the latter review relates to a Sn^{2+}-based iodide semiconductor comprising two larger organic cations. Despite this remarkable achievement, efficiencies are still far away from the best lead-based PSC cells that reached an efficiency of 25.6 %.

There have also been attempts to reduce the amount of lead by using mixed Sn^{2+}/Pb^{2+}-based PSCs with $APb_{1-x}Sn_xX_3$ composition. Indeed, power conversion efficiencies up to 20% could be achieved by this method[32], but still this would only cut the lead content by approximately a factor of two (Figure 4).

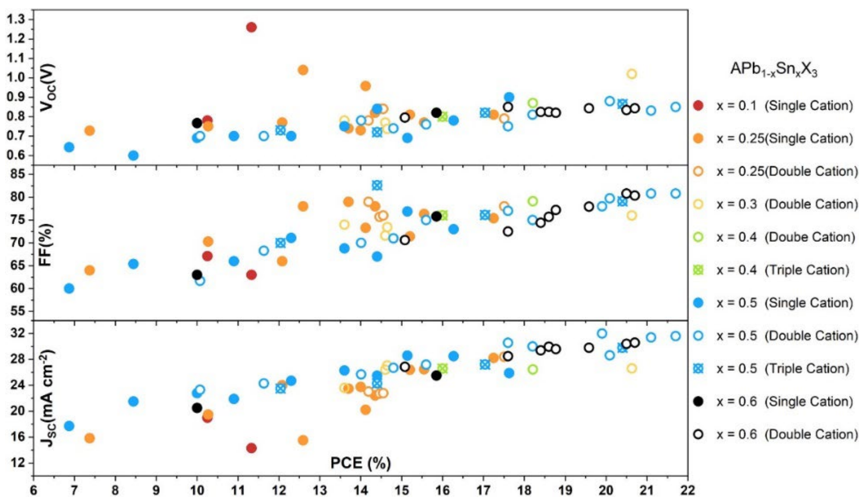

Figure 4. Progress of single-junction champion Pb-Sn mixed PSCs (laboratory tested values) reported so far with the device parameters V_{OC}, J_{SC}, and FF plotted against the device PCE. The Sn content (x) and A-site cation composition are shown in different colors and symbols[32]

Replacing Pb^{2+} by other metal cations is therefore not a straight forward approach, and will have to accept losses in power conversion efficiency. It therefore seems quite clear that lead-based perovskite solar cells will head the way also regarding technological development. Fail-safe encapsulation is the way to go and strategies have to be found for end-of-life disposal and recycling.

6. Recycling of perovskite based solar cells

In the view of having to live with lead-based PSCs, selecting appropriate disposal methods of degraded exhausted modules coming to their end-of-life is as important as taking precautionary measures against potential lead leaching. Dumping expended modules in landfill would cause 70% of the lead leaching to the soil and water during the first year, while lead can be recovered in fly ashes during incineration process. [33] A better, more environmental-friendly way for the final disposal of modules would be the recycling of end-of-life panels. By this approach, the risk of lead leaching out into the environment can be minimized. Moreover, PbI_2 could be reutilized to manufacture new modules or refurbishing degraded ones. [34] Another strategy aims at refurbishing PSC cells and modules once exhausted. Mesoscopic carbon-based solar cell architectures as the ones developed at Solaronix SA are particularly interesting for this purpose, since the porous oxide scaffold as well as the conductive oxide bottom electrode and glass substrate can be reused in the refurbished solar cells (Figure 5). Impressively, 90% of the initial power conversion efficiency can be retained for the remanufactured encapsulated devices. The refurbishing process allows to reduce the green-house warming potential (expressed in kg of CO2-equivalent per kWp of nominative power) by as much as 30%.[35]

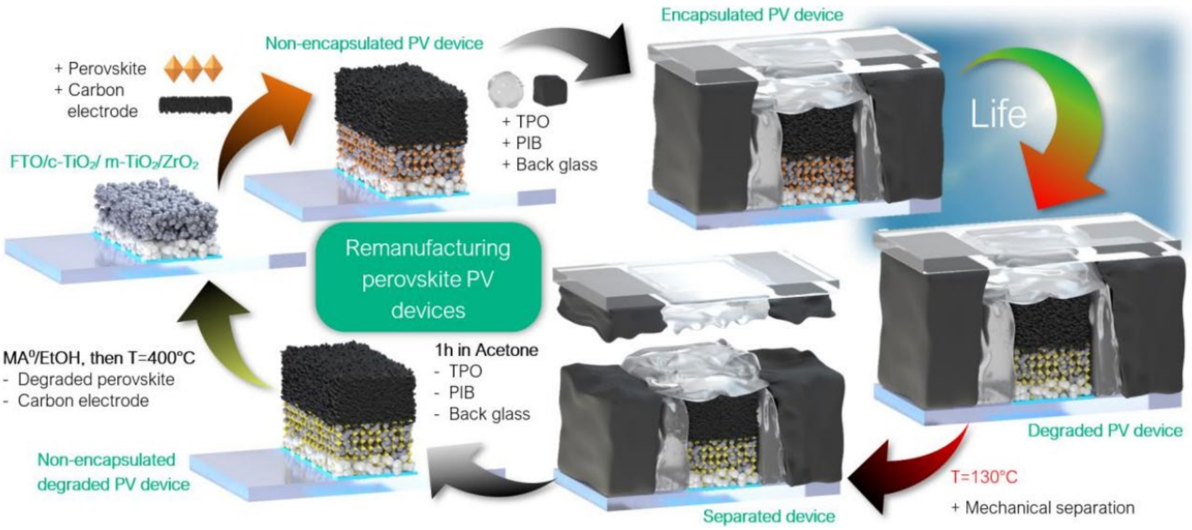

Figure 5. Mechanical, thermal and chemical route to separate back-glass, encapsulants, degraded perovskite and carbon layer. [35]

It is not the purpose of this short report to give a comprehensive overview of the proposed recycling processes. Such processes have been reported in the literature. [36]

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