Novel Method of Recycling Perovskite Solar Cells Using Iodide Solutions

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Abstract

A novel recycling method utilizing aqueous iodide solutions has shown promise at selectively dissolving lead perovskite and preserving the glass substrate of lead perovskite solar cells (PSCs). Perovskite compounds are notorious for degrading upon contact with moisture into lead iodide which can be capitalized upon for recycling. When iodide ions reach a critical concentration in aqueous solutions, the solubility of lead iodide begins to rapidly increase as several complex ions are formed. Iodide solutions selectively interact with the perovskite material which dissolves from the edge inwards, allowing for exfoliation of the back contact and retention of the glass substrate and electron transport layer. PbI_2 solubility studies using KI, HI, and NH_4I were conducted to determine an effective iodide source to develop a scalable recycling process. Retaining the coated glass substrate intact preserves the possibility to manufacture new solar cells from the same materials, by also omitting the use of organic solvents the costs as well as the human and environmental hazards of recycling PSCs can be minimized.

Introduction

The implementation of renewable energy products is becoming increasingly common as the global demand for electricity continues to rise along with concerns regarding the environmental release of CO_2 and heavy metal pollutants. Environmentally sustainable or carbon neutral energy can be captured using solar cells, wind mills, hydroelectric plants, and many other green technologies. Interest in solar energy has led to the development of many different types of solar devices including the promising PSCs which offer competitive power conversion efficiencies (PCE), low production cost, simple fabrication, and recyclability for remanufacture compared to existing technologies.

PSCs utilize the compound methylammonium lead triiodide ($CH_3NH_3PbI_3$) as a light harvesting material and have shown rapid advancements in PCE from 3.8% in 2009 to 25.7% in 2022.[1-2] A common type of PSC structure is the inverted n-i-p which has the lay up of glass, a transparent conductive oxide (TCO) coating, an electron transport material (ETM), a light harvesting material (perovskite), a hole transport material (HTM), and a conductive back contact . Perovskite compounds are relatively reactive and degrade when exposed to moisture, ambient humidity, ultraviolet light, and high temperatures. This reactivity has proved challenging to overcome in their integration into solar devices.[3] The HTM and ETM within the PSC are in direct contact with perovskite, and consequently, may also cause degradation and reduce PCE over time. Extensive research has been undertaken with regards to material selection and fabrication methods of PSCs to overcome these challenges.[4] Doping the perovskite to obtain phases of higher stability, altering the interfaces / selection of materials used as HTMs and ETMs, and utilizing encapsulation to reduce external environmental exposure has led to impressive advancements in the stability and lifetimes of PSCs from minutes to thousands of hours.[3-4] As improvements continue to be made in the stability of the PV materials used in PSCs extended lifetimes can be expected to reach those required for large-scale industrial implementation.[4] PCSs are also reletively cheap to produce at 35.30$ to 60.75 $ per m^2 making lead PSCs a strong competitor.[5]

While the use of lead compounds in PSCs has raised concern due to environmental toxicity, attempts to replace lead with similar metals such as tin, antimony, germanium, and bismuth have resulted in considerably lower PCEs of 13.24%, 3.34%, 7.11%, and 3.17% respectively.[2,7-10] Due to the considerable gap in PCE between PCSs utilizing lead and those utilizing alternative materials, lead options have maintained their prominence in ongoing research efforts and continue to be on the forefront of perovskite technologies. Previously, researchers have investigated the ecotoxity of the other PSC components, such as the aluminum frame and back contact layer, and found their life cycle toxicity concerns on par with those of lead.[11] Recycling methods for aluminum framing and back contact materials such as silver, copper, and gold are already established in industry. Various methods have been investigated to recycle lead from PSCs, with the aim of capturing the heavy metal and allowing for the direct reuse of TCO and ETM coated glass for the manufacture of new cells. Through efficient PSC recycling strategies lead introduced to landfills or that released to the environment can be minimized and the monetary costs, environmental costs, and pay back periods compared to producing new cells can be reduced[12] Unfortunately, many of the current recycling processes that are able to recover the coated glass utilize ecotoxic, flammable, and expensive solvents that are more environmentally impactful than manufacturing virgin glass and coatings.[12]

A life cycle assessment study conducted by Rodriguez-Garcia et al. identified that these processes use BA: butylamine, CB: chlorobenzene, DMF: N,N-dimethylformamide, DMSO: dimethyl sulfoxide, EA: ethyl acetate, EtOH: ethanol, GBL: γ-butyrolactone or combinations of these chemicals.[12] By reusing the solvents several times they become less environmentally impactful than producing virgin glass and coatings at which point the recycling breakeven is achieved. Rodriguez-Garcia et al. determined that after using DMF and DMSO to recover coated glass the solvents must be recovered and reused on the order of 23 and 89 times respectively to reach the recycling break even point.[12] Processes using chemicals or solvents for recycling have the strongest capability of becoming sustainable as processes using physical and thermal separations of the PV layers continuously require the high input of energy or materials for every panel.[12] Rodriguez-Garcia et. al. also made mention of the Global Harmonized System of Classification and Labeling of Chemicals categorization of all solvents excluding water as hazardous, the waste of the aforementioned solvents is also classified as hazardous waste due to concerns of flammability and corrosion.[12-13] A PSC recycling process based on the use of water can be expected to have considerably lower environmental impacts, material cost, hazards to humans, and increased sustainability compared to processes using solvents.

Lead perovskite or methylammonium lead triiodide degrades upon contact with moisture into lead iodide and methylammonium iodide (MAI), a reaction which is catalyzed by water according to Eq. 1.[14]:

$$MAIPbI_3 + H_2O \rightarrow MAI + PbI_2 + H_2O \qquad \textbf{(1)}$$

At room temperature lead iodide is sparingly soluble in water at 630 mg/L or 1.366×10^{-3} M.[15] According to solubility work conducted by Oscar et al. above the critical concentration of 0.1 M $[I^-]$ lead iodide solubility can be improved by the formation of complex ions as shown in Eq 3-4.[16] In water alone

Eq. 2 is the dominant dissociation reaction, however the complex ions shown in Eq. 3 and Eq. 4 begin to occur when iodide reaches 0.1 M and are responsible for an observed increase in solubility.[16]

$$PbI_{2(s)} \leftrightharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \quad \textbf{(2)}$$

$$PbI_{2(s)} + I^{-}_{(aq)} \leftrightharpoons PbI_{3}^{-}{}_{(aq)} \quad \textbf{(3)}$$

$$PbI_{2(s)} + 2I^{-}_{(aq)} \leftrightharpoons PbI_{4}^{2-}{}_{(aq)} \quad \textbf{(4)}$$

Oscar et al. conducted solubility experiments up to 0.4 M using potassium iodide, the reactions in Eq. 2-4 are only dependent on the presence of [I^-] by increasing the iodide concentration the reactions in Eq 3-4 begin to be enhanced and more lead iodide is dissolved. . In theory any highly dissociable iodide compound should be able to supply [I^-] ions to show similar results.[16]

Materials and Methods

Iodide Compound Solubility Studies

The purpose of this research is to compare the efficiencies of iodide compounds at dissolving lead iodide, to determine if the iodide ion alone or the respective cations have influence on lead solubility, and explore concentrations above 0.4 M. Solubility studies were conducted using 50 mL solutions of KI, ammonium iodide (AMI), and HI at the concentrations shown in Table 1. The solutions were added to 100 mL beakers along with 0.5 g of PbI_2 powder and a stir bar before being covered with parafilm and placed on magnetic stir plates set to 300 rpm for 24 hours. The ambient temperature during the experiments was approximately 18.3 ℃. After 24 hours, each of the beakers were visually inspected to confirm the presence of undissolved PbI_2. Remaining solids were desired to ensure that the maximum [Pb^{2+}] concentration and equilibrium conditions had been achieved. A syringe was used to draw 5 mL samples from each of the beakers and then dispensed through a 0.5 mm syringe filter into individual ICP-MS sample tubes. The filtered samples were then prepared for ICP-MS via serial dilution from 1:1000 into a solution of 2% trace metals grade nitric acid.

Scanning Electron Microscope Imaging

An Axia™ ChemiSEM™ scanning electron microscope (SEM) with focused ion beam (FIB) and energy dispersive spectroscopy (EDS) attachments was used to view cross sections of the PV layers of PSCs. A 5 mm by 5 mm sample was produced from an untreated PSC using a glass cutter to create scores in the desired dimensions and dipping the cell in liquid nitrogen which induced fracturing. The sample fragments were mounted to SEM buttons using copper tape and silver paste to create electrical contact to the PV layers. A tungsten back stop was deposited on the PSCs surface and FIB was used to mill a stair step pattern though the PV layers and EDS was used to create quantitative element maps.

PSC Digestion Scoping Study

In an effort to test the transferability of the solubility studies from PbI_2 to PSCs a scoping study was conducted by submerging a PSC in a 4 M ammonium iodide solution. Once the PSCs were subjected to the iodide delamination processing the TCO and ETM layers are expected to be retained on the glass substrate while the perovskite, HTM, and back contact were physically removed.

Results & Discussion

Solubility Studies

The lead content of the diluted samples was attained using ICP-MS along with the potassium concentration as shown in Table 1, the data was also based to create the solubility curves in Figure 1. The relative standard deviation (RSD) reported in table 1 is based of three repeated measurements of the same sample by ICP-MS.

Table 1: Results of solubility studies for potassium and lead

Iodide Compound Conc. [M]	Lead Conc. [mM]	RSD [mM]
KI:		
0	1.5144	0.0015
0.2	0.0487	0.0021
0.4	0.1134	0.0069
0.6	0.3045	0.0026
0.8	0.6947	0.0054
1.0	1.4583	0.0016
AMI		
0	1.4770	0.0034
0.2	0.0434	0.0028
0.4	0.1190	0.0020
0.6	0.2366	0.0027
0.8	0.2876	0.0039
1.0	0.4096	0.0029
HI		
0	-	-
0.2	0.0239	0.0048
0.3	0.0677	0.0033
0.4	0.0698	0.0021
0.5	0.1165	0.0041
0.6	0.1763	0.0053
0.8	0.3896	0.0090
1.0	0.7568	0.0059

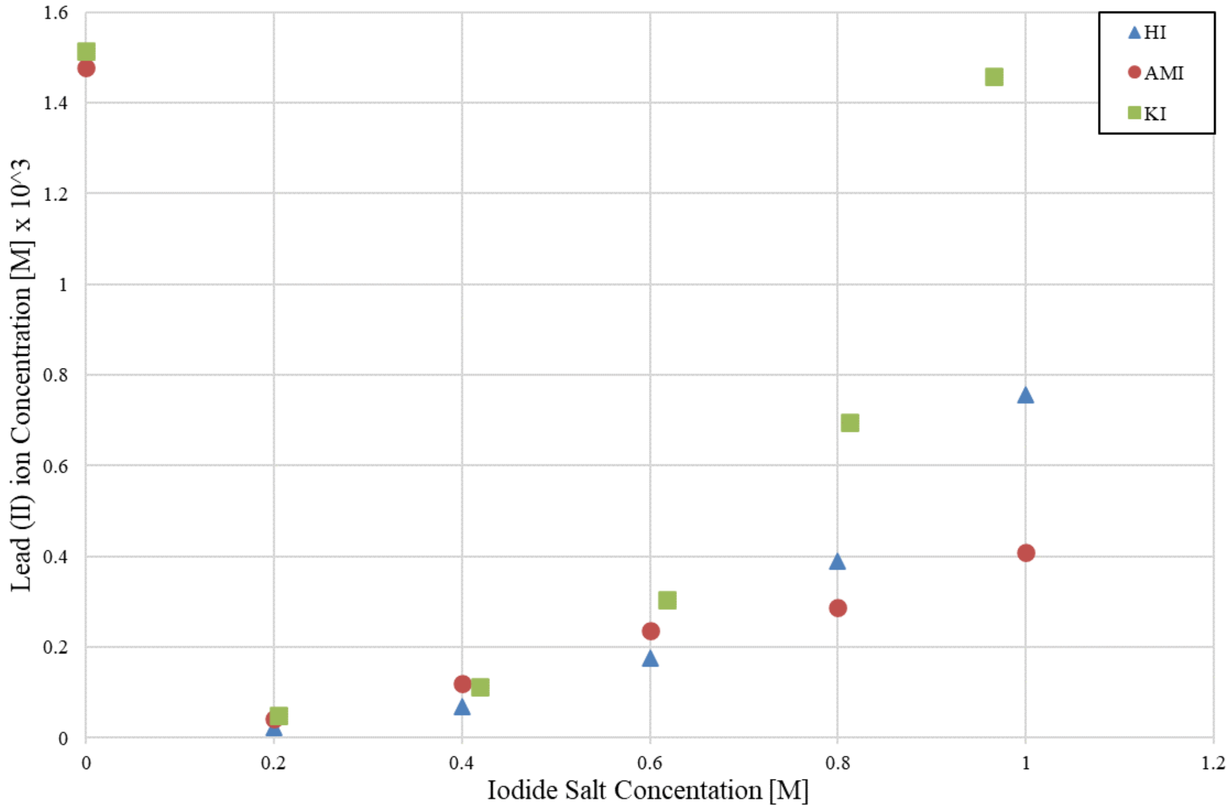

Figure 1: Plotted solubility study data for HI, AMI, and KI solutions vs. measured lead (II) concentrations

The solubility studies point to KI as being the most effective iodide compound for dissolving higher concentrations of Pb^{2+} when compared against AMI and HI. As shown in Table 1 the concentration of PbI_2 soluble in water is higher than the solubilities using the iodide salts thus further exploration above 1.0 M will need to be conducted. The solubility curves in Figure 1 appear to have an exponential trend and much higher concentrations of lead may be attainable in higher molar iodide solutions. KI being formed from a strong base and strong acid is a neutral salt, AMI being formed from a strong acid and weak base is a weakly acidic, and HI being a strong acid is highly acidic. The pH of these salts versus concentration are reflected in Figure 2:

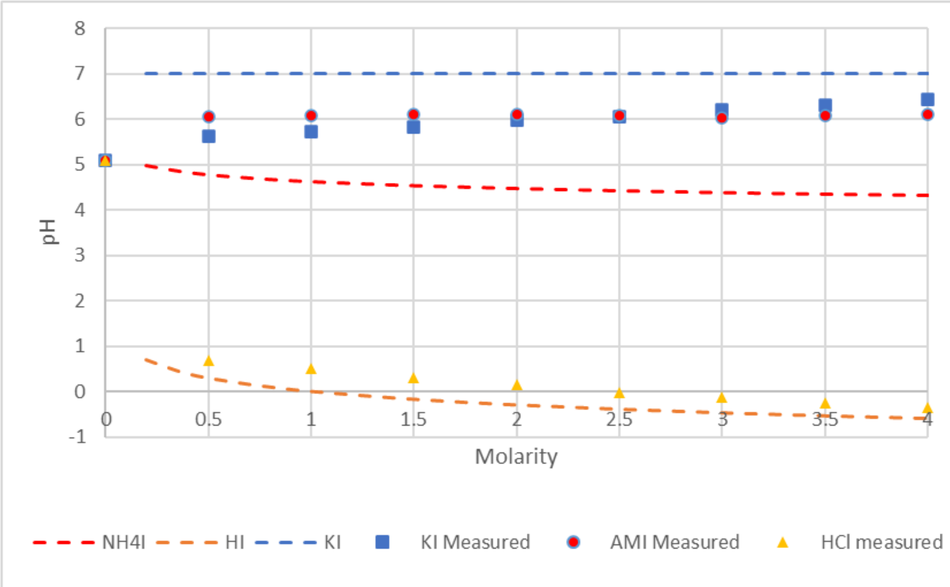

Figure 2: pH vs Molarity of Ammonium Iodide, Hydroiodic acid, and Potassium Iodide; dashed lines are calculated values, while data points were measured.

In order to explain the difference in lead iodide solubility in the iodide salts pH of the various salt solutions was explored. Tabular K_a values was used to determine the hydronium concentrations of the various salts at different molarities and then the pH values. The dashed lines represent the calculated pH values and the dotted lines represent measured values of the same salts. The measured line of HCl was added as an analog for HI. The cause of the discrepancy between the calculated and measured values and the theoretical values is unknown. It is also interesting to note that the distilled water used to make the solutions is slightly acidic at a pH of around 5.1, which would cause some shift in the measured values but does not entirely explain the difference between the theoretical values. The measured trendlines of the KI and AMI are also close enough to one another that pH does not explain the change in solubility of lead iodide in these solutions. The reactions in Eq. 3-4 could be shifted by Le Chatelier's principle when more iodide ions are added to the system which explain the increase in solubility and align with the research by Oscar et al.

Scanning Electron Microscope Imaging

The PV materials can be seen in Figure 2 A-I as the key elements composing the individual layers are highlighted. Perovskite and the organic compounds used in the HTM and ETM appear to have degraded under the heat of the FIB process, this is evident by the cratering in the central perovskite layer. The HTM and ETM were not visible as the SEM is not capable of accurately quantifying the content of carbon. However, SEM images of PSCs before and after recycling will be useful in the future for visual confirmation that the process is successful.

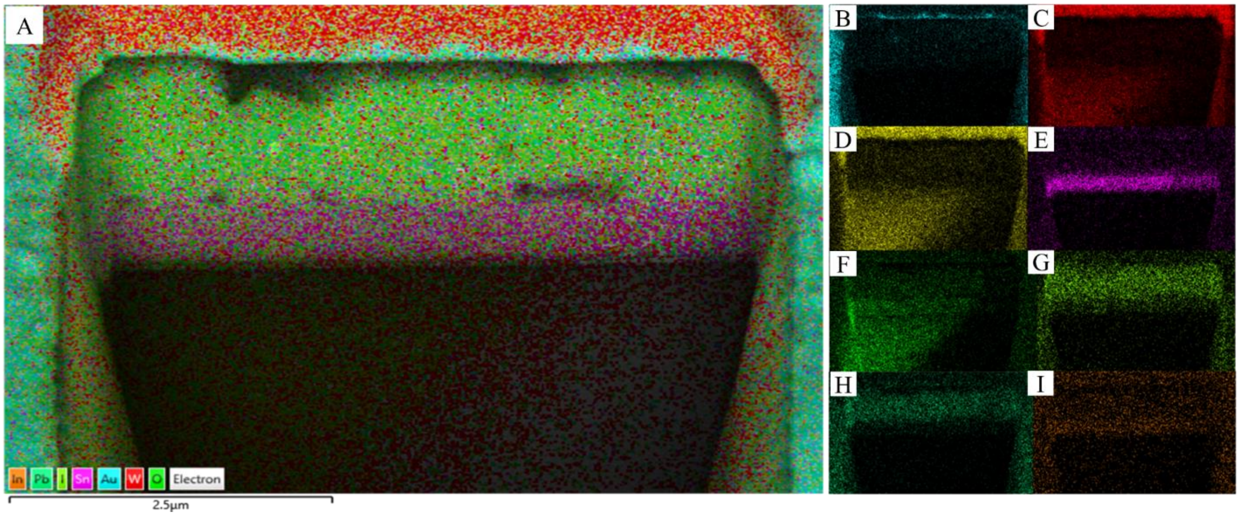

Figure 2: A: SEM/EDS image of the PSC PV layer cross section highlighting major elements, B-I: individual quantity maps of the elements gold, tungsten, silicon, tin, oxygen, iodine, lead, and indium respectively

Digestion Scoping Study

After approximately 24 hours the back contact and HTM layers had completely exfoliated from the ETM, TCO, and glass substrate as can be seen in Figure 3: A-C. The exfoliated layers were mechanically affixed via the lead perovskite and after its dissolution via the reactions shown in Eq. 3-4 the layers became small flakes capable of being rinsed off and separated from the substrate layers (Figure 3B). It is expected that the dissolution process begins on the edge of the PSC and migrates inward as the perovskite is degraded and leaves a gap between the remaining PV materials. The solution containing the exfoliated solids was then filtered which effectively separated the solids from the aqueous phase, ICP-MS of the leaching solution confirmed the presence of elevated lead levels compared to the distilled water used to prepare the 4 M iodide solution.

The leaching investigation showed that the process was effective for PSCs and can strip the perovskite from the cells effectively without causing obvious damage to the coated glass substrate. The back contact was easily collected from the leach solution through filtration leaving the lead ions behind. Image analysis (e.g., ImageJ) will be a valuable method for quantifying the removal of the PV layers given the stark contrast in the appearance of the PSCs seen in Figures 3A & 3C. A small amount of remaining adhesive material can be seen as vertical striations in Figure 3C.

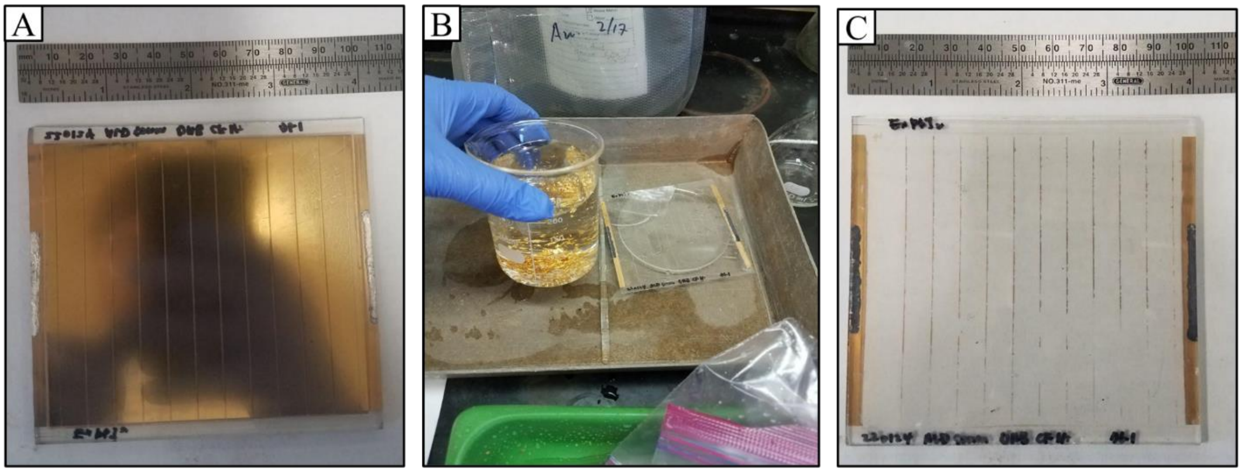

Figure 3: Images of PSC digestion scoping study. Fig. A: Pre-digested PSC, B: stripped cell and exfoliated back contact materials with lead ions in the leach solution, C: cleaned PSC after digestion process

Conclusions

In this study a series of experiments were performed to explore the possibility of a novel method for the recycling of PSC's. Three iodide compounds, KI, HI, and NH_4I were investigated as possible solvents for lead iodide. KI appears to be the most effective salt at dissolving lead iodide, and there appears to be a strong relationship between KI concentration and lead iodide solubility after a local minimum is reached, however higher concentrations need to be explored to show improved solubility over water. These results point to a new PSC recycling process that will be further investigated in future studies.

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Conflict of Interest

No conflicts of interest have been identified by the authors at this time

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