Life Cycle Environmental Impacts of Precursors Used in the Supply Chain of Emerging Perovskite Solar Cells

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***Abstract*— This paper presents estimations for life cycle energy demand, human toxicity, and climate change of industrial-scale production of A-site cation precursor chemicals that may be used in production of perovskite solar cells. We employed process scale-up concepts, updated data sources and industry-relevant process modelling assumptions to build commercially relevant life cycle inventories (LCIs) for each of the perovskite precursors. Life cycle assessment (LCA) was applied to characterize and compare the resulting life cycle impacts and comparisons were made with other module components. The main finding of this work is that precursor impacts are similar to each other and about 1,000 times less than solar glass. Therefore, selection of perovskite compositions for commercialization should be driven solely by efficiency and stability rather than environmental concerns.**

Keywords—Lead halide perovskite, Life cycle assessment, Supply chain sustainability, Critical material availability

I. Introduction

Lead halide perovskite photovoltaics (LHP PVs) spurred wide attention in the solar PV community due to their outstanding power conversion efficiencies, tunable optoelectronic properties, and projected low fabrication costs[1]. Single-junction LHP cells recently reached 25.2% just 10 years after their inception, exceeding the best performing CdTe modules and bordering on that of silicon solar cells. Key areas being addressed today for commercialization include improving the module operational lifetime, upscaling manufacturing lines and derisking the presence of toxic lead. Devices fabricated with a mixed cation perovskite absorber layer such as cesium/ methylammonium/ formamidinium ($Cs_xMA_yFA_{1-x-y}PbI_3$) show longer operational stability and higher efficiency than the most-studied $MAPbI_3$. The record efficiency LHP cell is fabricated with $MA_{0.05}FA_{0.95}PbI_3$ formulation. A-site alloying with inorganic Cs can improve the thermal and structural stability of the perovskite phase. A triple-cation formulation $Cs_{0.10}MA_{0.15}FA_{0.75}PbI_3$ achieved stabilized efficiency of 21.1% and sustained power output for 250 hours in an aging test under operating conditions [2]. Many groups have eliminated MA altogether. $Cs_{0.25}FA_{0.75}PbI_3$ achieved 19.1% efficiency while maintaining full performance after 150 hours at 85°C in air [3]. The same formulation was also used in perovskite-perovskite tandem device with 23.1% efficiency.

It is also important to understand the environmental impacts arising from the use of different precursors. Earlier LCA literature based on lab scale LCI analysis reported an outsized environmental impact for FA, raising concerns over commercializing high-performing compositions [4]. Additionally, cesium metal is in the top 33 elements of critical supply in the U.S. [5].

The objectives of this work are to (i) develop scalable LCI datasets for MAI, FAI and CsI using process scale-up concepts, (ii) quantify the resulting life cycle environmental, human health and energy use impacts, (iii) perform resource efficiency estimations for projected cesium use, (iv) evaluate the sensitivity of inputs to variability in environmental impact results, and (v) compare the resulting impact assessment results with those of other known module components to date.

II. Process Development for Life Cycle Inventories

A. Material demand

We calculated the precursor intensity to supply a PV manufacturing line of 100 MW of peak power (MWp) capacity. We assumed 100% precursor attribution in the perovskite A-site formulation as an upper limit estimation for MAI and FAI. We calculated CsI demand for 100% Cs and for $Cs_{0.15}FA_{0.85}$. We assumed 17% module efficiency, 1 µm film thickness and a national average solar insolation value of 1,700 $kWh/m^2/year$. Table I shows the results for material demand.

TABLE I. CATION PRECURSOR INTENSITY

Cation Precursor	Material needed (kg/100 MWp)
MAI	647
FAI	600
CsI	200

The material required would decrease slightly with increasing PV efficiency (~100 kg per 3%) and would decrease proportionally with smaller film thickness. Efficient lab-scale perovskite cells are made with 200-300 nm films, but industrial-scale film coating process might use thicker films to achieve better reproducibility. The calculated mass scales are relatively small and therefore can most efficiently be produced by batch processing in an on-demand production facility commonly used in the specialty chemicals industry in a once-a-year fashion, or more frequently if demand or shelf-life require it. If the demand is high enough (~1,000s of tons per year), solar manufacturers or their chemicals contractors might need to build a continuous production facility for steady precursor supply.

B. Process Scale-up and Fugitive Emissions Estimation

We used Reaxys© database libraries to identify high yield, industry-relevant process synthesis routes for each of the perovskite cationic materials. We then applied process design guidelines to sketch necessary unit operations for conversion steps and calculated the material and energy balances for unit operations. Scale-up methods by Piccino et al. [6] were used for heated liquid-phase, batch reactions for specialty chemicals. Fugitive emissions were estimated based on the phase and boiling points of the input materials. The LCA software tools SimaPro® 9.1, Ecoinvent version 3.6© and USLCI database libraries. The life cycle impact metrics studied here are climate change, cumulative energy demand (CED) and human toxicity (HT), calculated by ReCiPe v1.13.

III. Life Cycle Impacts and Process Contributions of Cation Production Processes

The climate change impact results per kg of cation precursor and a breakdown of their process contributions are shown in Fig. 1.

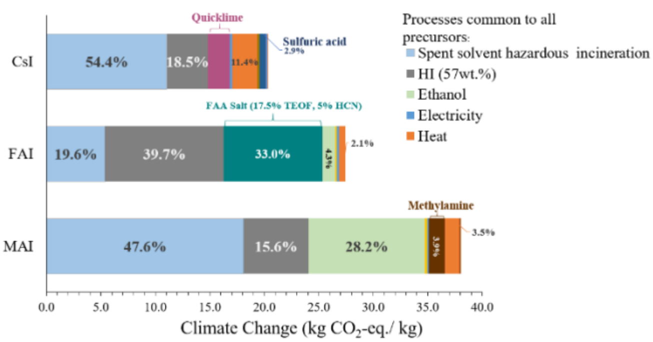

Fig. 1. Process contribution breakdown of the climate change impact category for scaled-up production of perovskite cation precursors.

A. MAI Production Process

We scaled up a synthesis route described by Lee et al.[7] that involves reaction between excess methylamine, dissolved in an anhydrous ethanol solution, and hydroiodic acid under nitrogen atmosphere and at room temperature.

Fig. 1 shows that climate change effect for producing 1 kg of MAI at industrial scale is 38.1 kg CO_2 eq. The CED is 463 MJ/kg and the HT is 2.47 kg 1,4-DCB eq./kg. Major process contributions include solvent incineration (~48%), large ethanol usage in reactor (~28%) and upstream heat operations for commercial hydroiodic acid production from hydrazine.

B. FAI Supply Chain

Fig. 2 shows the modelled supply chain for LCI compilation for FAI salt.

We scaled-up the synthesis route reported by Eperon et al. [8] that involves the reaction of formamidinium acetate (FAA) salt with 57 wt% hydroiodic acid (HI) at process conditions like those employed in MAI synthesis. FAA salt formation involves reacting liquid triethyl orthoformate (TEOF) with glacial acetic acid under ammonia refluxing at 135 °C for 45 minutes. TEOF production route involves the reaction between hydrocyanic acid (HCN) and anhydrous ethanol under dry hydrogen chloride (HCl) in petroleum ether solvent at subzero conditions (-15°C).

FAI has climate change effect of 27.4 kg CO_2 eq., CED of 198 MJ and HT of 3.62 kg 1,4-DCB eq. per kg of FAI. The

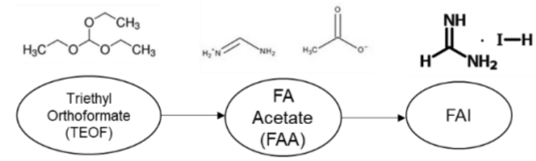

Fig. 2. Supply chain of FAI production.

largest process contributions to the climate change impact category include material usage of excess hydroiodic acid (~40%), FAA salt production (~33%) and spent solvent incineration (~20%). The direct heat and electricity consumption contribute a total of only 1.7% of the total impacts. This result contradicts that of a previous study that estimated a dramatically higher electricity and heat consumption for the FAI production process (~198 kWh/kg compared to 0.352 kWh/kg of FAI reported here).

C. Cesium Extraction, Refining and CsI production.

We scaled up the process of sulfuric acid digestion of cesium-bearing pollucite ore described by the patent published by Cabot Corporation [9]. The process involves using a 45 wt.% sulfuric acid to dissolve the pollucite ore in a calculated ratio of 0.36 kg of ore per 1 liter of acid at 115 °C for 16 hours followed by reacting recovered cesium alum with HI to form CsI salt. Process steps of slaking, polishing and neutralization of excess acids are modelled to obtain the pure CsI form. Waste allocation is performed as directed by Environmental Protection Agency (EPA) F-list.

CsI has a climate change impact of 20.3 kg of CO_2 eq., CED of 54.4 MJ and 1.86 kg 1,4-DCB eq. per kg of CsI. The hotspot process contributions are hazardous waste solvent incineration (~54%), HI usage (18.5%) and direct process heat operations (11.4%) due to the long reactor time.

Our calculations indicate that only 1.8% of current known cesium reserves would be needed to meet the entire U.S. solar PV electricity generation goal for 2022-2050 exclusively with $CsPbX_3$-based LHP PVs. Only 0.3% would be needed for state-of-the-art alloys with 15% Cs in the A-site, and likely far less than that considering the current dominant market share of silicon PV. The current commercial proven cesium reserves are estimated at ~90,000 metric tons.

IV. Life Cycle Impacts of Mixed Cation Perovskite Films

A perovskite thin film is synthesized by the reaction of ~1:1 mole ratio between the cation precursor and a lead halide salt in solution or vapor phase. We calculated the climate change, cumulative energy demand, and human toxicity midpoint categories for all alloy compositions in the ternary phase space, as shown in Fig. 3.

The impacts are not strongly dependent on A-site composition; an observation that is different from previous results that found that FAI is significantly more harmful across all impact categories. The variation in climate change and HT across all compositions is less than 30% [10]. MAI entails the

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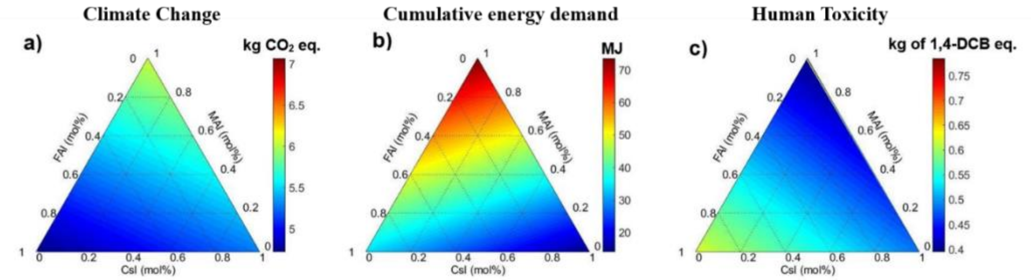

Fig. 1: Life cycle impact assessment results across the entire ternary phase space of cationic perovskite compositions a) climate change (CC) b) Cumulative energy demand (CED) , and c) Human toxicity (HT). Promising commercialization formulation ($F_{0.75}$ Cs $_{0.25}PbI_3$) has * symbol.

highest CED impact due to its large ethanol usage, but it is only a factor of 4 larger than CsI.

V. Hotspot analysis for synthesis solvent recovery

Solvent use and subsequent incineration are an environmental hotspot for all cation production processes. However, it may be uneconomical to recover solvents in small-scale batch production, except possibly the simple distillation to separate the reactor effluent stream in FAA production to recycle acetic acid. This stream is composed of ethanol byproduct with some ethyl acetate and unreacted acetic acid. Fig. 4 shows that FAA distillation on the batch scale may reduce climate change impacts by 6-8% on a molar basis for

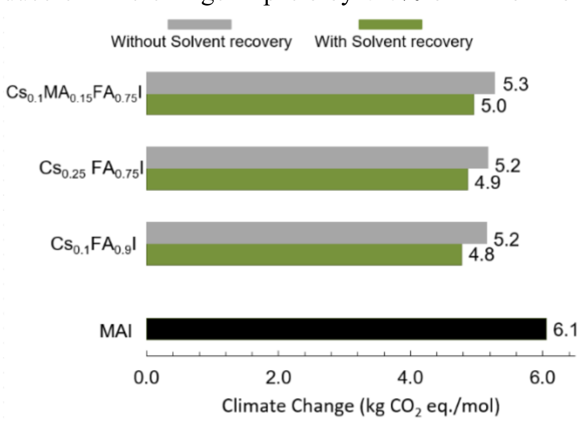

Fig. 4. Climate change impacts of selected cation formulations with and without solvent recovery in FAA production.

FA-based alloys. If perovskite PV capacity grows to capture large market shares (> ~10 GW), it becomes important to plan to recover and recycle significant volumes of synthesis solvents. For MAI, a possible recovery route for ethanol would include desorbing methylamine first followed by azeotropic distillation of ethanol/water mixture. Spent sulfuric acid mixtures from CsI production possess a greater environmental hazard because they contain heavy metals (i.e. Cd, Pb) and may require more complicated separations techniques.

VI. Comparison to other module components

We compiled a scaled-up LCI of lead (II) Iodide from Gong et al.[11] and used LCI of solar glass in Ecoinvent database to compare perovskite layer precursors to fixed solar glass. It is expected that a perovskite module would have glass-glass design. Table II shows the climate change (CC) impact for 1 m^2 of perovskite module is 1,000 times larger for solar glass than impacts of studied perovskite salts.

TABLE II. CLIMATE CHANGE IMPACTS OF PEROVSKITE PRECURSORS AND SOLAR GLASS

	$MAPbI_3$	$FA_{0.75}Cs_{0.25}PbI_3$	Solar glass
Material CC impact (kg CO_2 eq./kg)	15.9	13.3	1.0
Material in module (kg/m²)	4.29×10^{-3}	4.32×10^{-3}	15.0
Module CC impact (kg CO_2 eq./m²)	6.82×10^{-2}	5.74×10^{-2}	15.0

VII. Conclusions

The life cycle environmental and human toxicity impacts of considered perovskite precursors (MAI, FAI, CsI and PbI_2) are all similar to each other and much lower than those of solar glass. Therefore, perovskite formulations should be chosen solely based on efficiency and stability without additional constraints of environmental sustainability.

Acknowledgment

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