Supplementary information

Comparative Life Cycle Assessment of Lead-Free Halide Perovskite/Polymer Composites for Piezoelectric Energy Harvesting

Keywords: Piezoelectric, lead zirconate titanate, PZT, life cycle assessment, perovskite, energy harvesting.

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Inventories

This section includes the detailed inventory tables used to model the life cycle inputs of the studied materials. Tables S1 and S2 present the inventory data for PZT synthesis at laboratory scale, based on the work by Ibn-Mohammed.[1] Table S2 includes adjustments such as an increased PbO input to account for evaporation losses during high-temperature synthesis, and the use of isopropanol as a solvent.[2] For the $FASnI_3$–PVDF composite, Tables S3 and S4 contain the input data derived from the synthesis procedures reported by Pandey.[3]

Certain materials required to model the environmental impacts of the halide perovskite composite $FASnI_3$–PVDF are not available in the Ecoinvent database. These are tin(II) iodide (SnI_2), formamidinium iodide (FAI), and polyvinylidene fluoride (PVDF).

The inventory for SnI_2 synthesis was constructed from stoichiometric ratios and reaction temperatures reported in the literature (Table S5).[4] To promote the formation of SnI_2, an excess of Sn was used and is considered to be recovered, minimizing material losses. It was assumed that all iodine sublimates during the synthesis process, as the reactants are kept at 170 °C for two hours and iodine is known to sublimate at significantly lower temperatures This assumption is supported by iodine's well-known ease of sublimation, which is facilitated by its weak van der Waals forces and high triple point, making iodine a classic example of sublimation.[5,6]

For the synthesis of FAI, the inventory reported in previous work was used.[7] The same data from their study were adopted, except for electricity consumption, which was recalculated at an industrial scale (Table S6).[8]

As Ecoinvent provides data only for polyvinyl fluoride (PVF) and not for polyvinylidene fluoride (PVDF), we relied on the dedicated last PVDF inventory developed (Tables S7-S9),[9] who highlighted that previous LCA studies often approximated PVDF using proxies such as PVF, PTFE, or PVC due to the lack of a specific inventory. Chopra et al. proposed two synthesis routes: organometallic polymerization using R-132b, and gas-phase polymerization using HFC-152. We selected the gas-phase route due to its wider industrial application[10] and its comparatively lower environmental impacts. Upon reviewing the proposed inventory, we identified a high excess of chlorine used during synthesis, which was confirmed by cross-checking the original patent. Additionally, we found that hydrogen chloride (HCl) is produced as a by-product in the reactor. While it is neutralized with KOH and water in the base case, its recovery is potentially feasible at an industrial scale. We also observed that the inventory tables lacked proper representation of process outputs, resulting in incomplete datasets. After updating the inventory to reflect all relevant outputs, we recalculated the impacts using the ReCiPe 2016 Midpoint method. Our results showed lower environmental impact compared to the original study: 39.4 kg CO_2-eq/kg PVDF (versus 55.8 kg CO_2-eq/kg) for climate. After updating the inventory to include all relevant outputs, we recalculated the impacts using the ReCiPe 2016 Midpoint method, as in the referenced study. Our results showed a lower environmental impact for climate change: 39.4 kg CO_2-eq per kg of PVDF, compared to 55.8 kg CO_2-eq/kg reported in the original publication. Upon investigating the source of this difference, we found that the choice of electricity mix significantly influences the results, as also discussed in the supplementary material of the cited article. Their reported values range from 60.6 kg CO_2-eq/kg PVDF when using electricity from China to 54.1 kg CO_2-eq/kg when using electricity from the US. In our case, the initial calculations were based on the European electricity mix, yielding the 39.4 kg CO_2-eq/kg result. When using electricity from China, our model showed an increase to 48.0 kg CO_2-eq/kg PVDF. In addition to regional electricity differences, the lack of detail regarding the specific inputs used in the original article's software model limits the possibility of a direct comparison. Moreover, the use of a recent version of the Ecoinvent database likely contributed to the different value obtained in our study. For comparison, the PVF inventory available in ecoinvent reports values of 198.9 kg CO_2-eq/kg PVF, indicating that even the revised PVDF scenario carries nearly twice the climate impact, underscoring the importance of using a dedicated and accurate inventory in LCA studies.

The following tables present the inventories used in the calculations for this study:

Table S1: Inventories of the material inputs and outputs for laboratory and industrial manufacturing 1 m² of piezoelectric $PbZr_{52}Ti_{48}O_3$

Input/Output	Parameters	Unit	Quantity (Laboratory)	Quantity (Industrial)	Quality Data
Input	TiO_2	Kg	$1.34\cdot10^{-3}$	$8.61\cdot10^{-4}$	(4,3,1,1,3,1.05)
Input	ZrO_2	Kg	$2.24\cdot10^{-3}$	$1.44\cdot10^{-3}$	(4,3,1,1,3,1.05)
Input	PbO	Kg	$8.58\cdot10^{-3}$	$5.52\cdot10^{-3}$	(4,3,1,1,3,1.05)
Input	Isopropanol	Kg	$3.00\cdot10^{-2}$	$1.50\cdot10^{-3}$	(4,3,1,1,3,1.05)
Input	Argon	Kg	$1.04\cdot10^{-3}$	$1.04\cdot10^{-3}$	(4,3,3,1,3,1.05)
Input Electricity	Heating	MJ	7.96	$1.48\cdot10^{-2}$	(4,3,3,1,3,1.05)
Input Electricity	Electricity without deposition	MJ	1.98	$4.92\cdot10^{-2}$	(4,3,1,1,3,1.05)
Input Electricity	Electricity with deposition	MJ	$1.14\cdot10$	9.46	(4,3,1,1,3,1.05)
Output	Isopropanol to air	Kg	$3.00\cdot10^{-2}$	$1.50\cdot10^{-3}$	(4,3,1,1,3,1.05)
Output	Pb to air	Kg	$7.24\cdot10^{-4}$	$2.46\cdot10^{-8}$	(4,3,1,1,3,1.05)
Output	Argon to air	Kg	$1.04\cdot10^{-3}$	$1.04\cdot10^{-3}$	(4,3,1,1,3,1.05)
Output	Sputtering slag	Kg	$7.43\cdot10^{-3}$	$3.91\cdot10^{-4}$	(4,3,1,1,3,1.05)

Table S2: Inventories of the material inputs and outputs for 1 kg of lead (II) oxide (PbO)

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	SiO_2	Kg	0.27	(4,3,1,1,3,1.05)
Input	NH_3	Kg	0.08	(4,3,1,1,3,1.05)
Input	Water	Kg	0.08	(4,3,1,1,3,1.05)
Input	Acetic acid	Kg	0.37	(4,3,1,1,3,1.05)
Input	Pb	Kg	0.93	(4,3,1,1,3,1.05)
Input Electricity	H_2O_2 50%	Kg	0.11	(4,3,1,1,3,1.05)
Input Electricity	Electricity	MJ	0.59	(4,3,1,1,3,1.05)
Output	SiO_2 to air	Kg	0.27	(4,3,1,1,3,1.05)
Output	CH_3COOH to air	Kg	0.37	(4,3,1,1,3,1.05)
Output	NH_3 to air	Kg	0.08	(4,3,1,1,3,1.05)
Output	H_2O_2 to air	Kg	0.004	(4,3,1,1,3,1.05)

Table S3: Inventories of the material inputs and outputs for laboratory and industrial manufacturing of 1 m^2 of perovskite FASnI$_3$ embedded within PVDF matrix

Input/Output	Parameters	Unit	Quantity (Laboratory)	Quantity (Industrial)	Quality Data
Input	$FASnI_3$ solution	Kg	$1.70\cdot10^{-3}$	$1.68\cdot10^{-5}$	(2,1,1,1,1,1.05)
Input	PVDF solution	Kg	$7.00\cdot10^{-4}$	$6.69\cdot10^{-6}$	(2,1,1,1,1,1.05)
Input	Electricity without deposition	MJ	$2.44\cdot10^{-6}$	$2.44\cdot10^{-8}$	(4,1,2,1,3,1.05)
Input	Electricity with deposition (spin coating)	MJ	2.14	1.55	(4,1,1,1,3,1.05)
Input	Heat	MJ	$5.30\cdot10^{-3}$	$5.27\cdot10^{-5}$	(4,1,1,1,3,1.05)
Output	DMF to air	Kg	$5.70\cdot10^{-3}$	$2.85\cdot10^{-4}$	(4,1,1,1,3,1.05)
Output	Perovskite Waste	Kg	$2.33\cdot10^{-3}$	0.00	(4,1,1,1,3,1.05)

Table S4: Inventory for preparing 1 kg of FASnI3 perovskite solution

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	SnI_2	g	677.42	(3,1,2,1,1,1.05)
Input	FAI	g	312.72	(3,1,2,1,1,1.05)
Input	DMF	g	1716.36	(3,1,2,1,1,1.05)
Input	Electricity	MJ	$9.35\cdot10^{-4}$	(4,1,2,1,3,1.05)

Table S5: Inventory for manufacturing 1 kg of SnI_2

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	Tin	g	318.68	(4,3,3,1,3,1.05)
Input	Iodine	g	700.00	(4,3,3,1,3,1.05)
Input	Water	g	175.00	(4,3,3,1,3,1.05)
Input	N_2	g	30.00	(4,3,3,1,3,1.05)
Input	HCL	g	12.76	(4,3,3,1,3,1.05)
Input	Chemical plant	p	$4.00\cdot10^{-10}$	(4,3,1,1,3,3)
Input	Electricity	MJ	13.89	(4,3,1,1,3,3)
Output	Water to air	g	175.00	(4,3,3,1,3,1.05)
Output	HCl to air	g	13.89	(4,3,3,1,3,1.05)
Output	N_2 to air	g	30.00	(4,3,3,1,3,1.05)
Output	Iodine (I_2) to air	g	18.68	(4,3,3,1,3,1.05)

Table S6: Inventory for manufacturing 1kg of FAI

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	Hydrogen cyanide	g	157.15	(4,3,1,1,3,1.05)
Input	Hydroxylamine	g	192.06	(4,3,1,1,3,1.05)
Input	Acetic anhydride	g	296.82	(4,3,1,1,3,1.05)
Input	Hydrogen iodide	g	743.79	(4,3,1,1,3,1.05)
Input	Water	g	319.83	(4,3,1,1,3,1.05)
Input	Chemistry Plant	p	$4.00\cdot10^{-10}$	(4,3,1,1,3,3)
Input	Electricity	MJ	2.60	(4,3,1,1,3,1.05)
Output	Acetic acid to air	g	349.18	(4,3,1,1,3,1.05)
Output	Water to air	g	319.83	(4,3,1,1,3,1.05)

Table S7: Inventory for manufacturing 1kg of PVDF

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	VDF	Kg	1.0652	(4,3,1,1,3,1.05)
Input	DTBP	Kg	0.0084	(4,3,1,1,3,1.05)
Input	Ultrapure Water	Kg	3.0458	(4,3,1,1,3,1.05)
Input	Wax	Kg	0.0017	(4,3,1,1,3,1.05)
Input	Electricity	kwh	12.3691	(4,3,1,1,3,1.05)
Output	Waste Water	Kg	3.1211	(4,3,1,1,3,1.05)

Table S8: Inventory for manufacturing 1kg of VDF

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	Activated carbon	Kg	0.100	(4,3,1,1,3,1.05)
Input	HFC-152a	Kg	1.032	(4,3,1,1,3,1.05)
Input	Chlorine	Kg	24.366	(4,3,1,1,3,1.05)
Input	Copper	Kg	0.010	(4,3,1,1,3,1.05)
Input	Palladium	Kg	0.0001	(4,3,1,1,3,1.05)
Input	Nitrogen	Kg	0.125	(4,3,1,1,3,1.05)
Input	Hydrogen	Kg	0.250	(4,3,1,1,3,1.05)
Input	KOH	Kg	0.005	(4,3,1,1,3,1.05)
Input	Ultrapure Water	Kg	4.278	(4,3,1,1,3,1.05)
Input	Cadmium sulfate	Kg	0.100	(4,3,1,1,3,1.05)
Input	Electricity	kwh	1.230	(4,3,1,1,3,3)
Output	Waste Water	Kg	8.941	(4,3,1,1,3,1.05)
Output	Hydrogen to air	Kg	0.156	(4,3,1,1,3,1.05)
Output	Nitrogen to air	Kg	0.125	(4,3,1,1,3,1.05)

Table S9: Inventory for manufacturing 1kg of tert-butylpyridine (DTPB)

Input/Output	Parameters	Unit	Quantity	Quality Data
Input	Hydrogen peroxide	Kg	2.508	(4,3,1,1,3,1.05)
Input	Sulfuric acid	Kg	2.029	(4,3,1,1,3,1.05)
Input	Butene	Kg	1.774	(4,3,1,1,3,1.05)
Input	Decarbonized water	Kg	0.571	(4,3,1,1,3,1.05)
Input	Sodium hydroxide	Kg	0.339	(4,3,1,1,3,1.05)
Input	Ultrapure water	Kg	5.421	(4,3,1,1,3,1.05)
Input	Magnesium sulfate	Kg	0.565	(4,3,1,1,3,1.05)
Input	Electricity	KWh	0.296	(4,3,1,1,3,3)
Output	Waste water	Kg	12.208	(4,3,1,1,3,1.05)

Environmental Impacts

This section presents the environmental impacts assessed using the Environmental Footprint (EF) 3.1 methodology for the various scenarios examined in the study. The assessment encompasses cradle-to-gate scenarios at both laboratory (Table S10) and industrial scales (Table S11), as well as cradle-to-grave scenarios that account for the environmental benefits associated with avoided impacts during the use phase and end-of-life management.

Table S10: Environmental impacts from laboratory cradle-to-gate for 1m^2 of PZT ceramic and FASnI$_3$-PVDF composite

Category	Unit	PZT	FASnI$_3$-PVDF
Acidification	mol H+ eq	$9.10\cdot10^{-3}$	$1.37\cdot10^{-3}$
Climate Change	kg CO2 eq	1.86	$2.66\cdot10^{-1}$
Ecotoxicity, freshwater	CTUe	7.81	1.51
Particulate matter	disease inc.	$3.66\cdot10^{-8}$	$6.17\cdot10^{-9}$
Eutrophication, marine	kg N eq	$1.32\cdot10^{-3}$	$3.08\cdot10^{-4}$
Eutrophication, freshwater	kg P eq	$1.07\cdot10^{-3}$	$2.36\cdot10^{-4}$
Eutrophication, terrestrial	mol N eq	$2.08\cdot10^{-2}$	$2.26\cdot10^{-3}$
Human toxicity, cancer	CTUh	$4.53\cdot10^{-9}$	$1.02\cdot10^{-10}$
Human toxicity, non-cancer	CTUh	$1.30\cdot10^{-6}$	$3.60\cdot10^{-9}$
Ionising radiation	kBq U-235 eq	$7.38\cdot10^{-1}$	$1.45\cdot10^{-1}$
Land use	Pt	4.65	$8.91\cdot10^{-1}$
Ozone depletion	kg CFC11 eq	$5.30\cdot10^{-8}$	$1.49\cdot10^{-8}$
Photochemical ozone formation	kg NMVOC eq	$1.45\cdot10^{-2}$	$7.30\cdot10^{-4}$
Resource use, fossils	MJ	$3.71\cdot10$	5.74
Resource use, minerals and metals	kg Sb eq	$2.81\cdot10^{-5}$	$1.08\cdot10^{-5}$
Water use	m3 depriv.	$3.29\cdot10^{-1}$	$1.91\cdot10^{-1}$
Total Energy	GJ	$4.22\cdot10$	6.74

Table S11: Environmental impacts from industrial cradle-to-gate for various PZT compositions and $FASnI_3$-PVDF composite

Category	Unit	PZT(60/40)	PZT(56/44)	PZT(52/48)	PZT(48/52)	PZT(44/56)	PZT(40/60)	$FASnI_3$-PVDF
Acidification	mol H+ eq	$6.47\cdot10^{-3}$	$6.53\cdot10^{-3}$	$6.54\cdot10^{-3}$	$6.60\cdot10^{-3}$	$6.65\cdot10^{-3}$	$6.69\cdot10^{-3}$	$7.50\cdot10^{-4}$
Climate Change	kg CO2 eq	1.00	1.01	1.01	1.02	1.02	1.03	$1.51\cdot10^{-1}$
Ecotoxicity, freshwater	CTUe	5.14	5.18	5.20	5.26	5.30	5.34	$4.36\cdot10^{-1}$
Particulate matter	disease inc.	$2.55\cdot10^{-8}$	$2.57\cdot10^{-8}$	$2.57\cdot10^{-8}$	$2.60\cdot10^{-8}$	$2.62\cdot10^{-8}$	$2.64\cdot10^{-8}$	$2.56\cdot10^{-9}$
Eutrophication, marine	kg N eq	$9.14\cdot10^{-4}$	$9.21\cdot10^{-4}$	$9.21\cdot10^{-4}$	$9.30\cdot10^{-4}$	$9.35\cdot10^{-4}$	$9.41\cdot10^{-4}$	$1.34\cdot10^{-4}$
Eutrophication, freshwater	kg P eq	$8.56\cdot10^{-4}$	$8.63\cdot10^{-4}$	$8.62\cdot10^{-4}$	$8.70\cdot10^{-4}$	$8.75\cdot10^{-4}$	$8.80\cdot10^{-4}$	$1.37\cdot10^{-4}$
Eutrophication, terrestrial	mol N eq	$1.34\cdot10^{-2}$	$1.35\cdot10^{-2}$	$1.35\cdot10^{-2}$	$1.37\cdot10^{-2}$	$1.38\cdot10^{-2}$	$1.39\cdot10^{-2}$	$1.18\cdot10^{-3}$
Human toxicity, cancer	CTUh	$4.60\cdot10^{-10}$	$4.64\cdot10^{-10}$	$4.65\cdot10^{-10}$	$4.70\cdot10^{-10}$	$4.74\cdot10^{-10}$	$4.77\cdot10^{-10}$	$4.74\cdot10^{-11}$
Human toxicity, non-cancer	CTUh	$2.52\cdot10^{-8}$	$2.54\cdot10^{-8}$	$2.56\cdot10^{-8}$	$2.59\cdot10^{-8}$	$2.61\cdot10^{-8}$	$2.63\cdot10^{-8}$	$1.35\cdot10^{-9}$
Ionising radiation	kBq U-235 eq	$5.99\cdot10^{-1}$	$6.04\cdot10^{-1}$	$6.03\cdot10^{-1}$	$6.09\cdot10^{-1}$	$6.12\cdot10^{-1}$	$6.16\cdot10^{-1}$	$9.74\cdot10^{-2}$
Land use	Pt	3.56	3.59	3.59	3.63	3.65	3.67	$5.18\cdot10^{-1}$
Ozone depletion	kg CFC11 eq	$1.92\cdot10^{-8}$	$1.94\cdot10^{-8}$	$1.93\cdot10^{-8}$	$1.95\cdot10^{-8}$	$1.97\cdot10^{-8}$	$1.98\cdot10^{-8}$	$2.80\cdot10^{-9}$
Photochemical ozone formation	kg NMVOC eq	$3.46\cdot10^{-3}$	$3.49\cdot10^{-3}$	$3.49\cdot10^{-3}$	$3.53\cdot10^{-3}$	$3.55\cdot10^{-3}$	$3.57\cdot10^{-3}$	$3.80\cdot10^{-4}$
Resource use, fossils	MJ	$2.30\cdot10$	$2.32\cdot10$	$2.32\cdot10$	$2.34\cdot10$	$2.35\cdot10$	$2.36\cdot10$	3.44
Resource use, minerals and metals	kg Sb eq	$1.73\cdot10^{-5}$	$1.75\cdot10^{-5}$	$1.76\cdot10^{-5}$	$1.78\cdot10^{-5}$	$1.80\cdot10^{-5}$	$1.82\cdot10^{-5}$	$4.00\cdot10^{-7}$
Water use	m3 depriv.	$2.57\cdot10^{-1}$	$2.59\cdot10^{-1}$	$2.56\cdot10^{-1}$	$2.61\cdot10^{-1}$	$2.62\cdot10^{-1}$	$2.64\cdot10^{-1}$	$4.68\cdot10^{-2}$
Total Energy	GJ	$2.71\cdot10$	$2.73\cdot10$	$2.73\cdot10$	$2.75\cdot10$	$2.77\cdot10$	$2.78\cdot10$	4.10

NET Cumulative Energy Demand

In Figure 6 of the main text, the impact on cumulative energy demand (CED) of eliminating battery use is calculated using Equations 6 and 7. Meanwhile, Figure S1 illustrates how the CED would evolve if only the energy recovered by the piezoelectrics, as calculated using Equation 5, were considered. As expected, the recovery times are significantly longer. Specifically, for perovskites, more than 10^8 cycles are required at 10 MPa and 10^6 cycles at 100 MPa. In comparison, a piezoelectric material with a similar d_{33} coefficient would require over 10^{12} and 10^9 cycles at 20 Hz, respectively. Commercially available PZT materials would need approximately 10^{10} and 10^8 cycles. This represents a difference of two orders of magnitude when the impact of eliminating batteries is not taken into account.

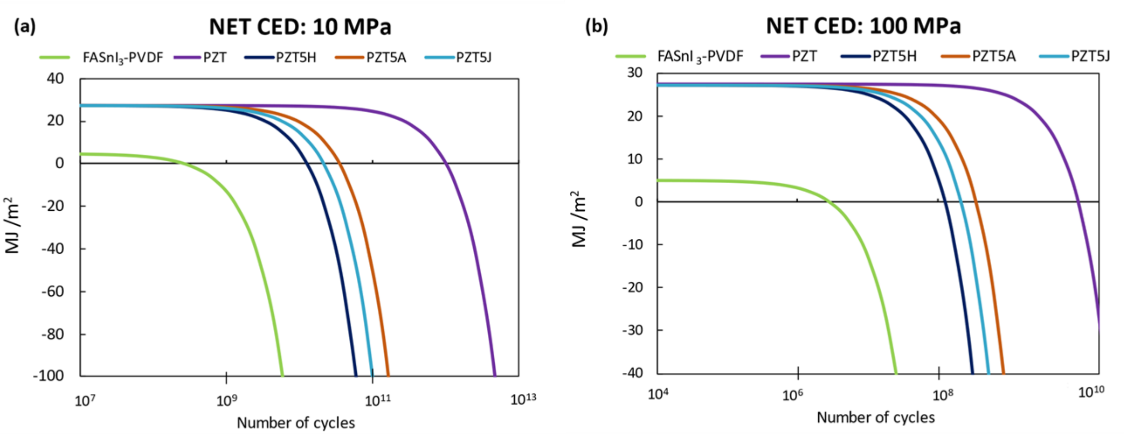

Figure S1: NET cumulative energy demand (CED) of PZTs and FASnI$_3$-PVDF perovskite at (a) 10 MPa and (b) 100 MPa. The operating time required is indicated next to the dashed line for a frequency of 20 Hz. Note that the NET CED is calculated by subtracting the cumulative energy recovered through energy harvesting, as determined by Equation (5), considering only the piezoelectric layer.

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