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Efficient decommissioning and recycling of polymer solar cells: justification for use of silver†

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Large 100 m long polymer solar cell modules were installed in a solar park using fast installation (>100 m min^{-1}) and operated for 5 months ensuring a meaningful energy return factor (ERF > 1) followed by fast de-installation (>200 m min^{-1}) and end-of-life management. Focus was on recovery of silver that is an essential component of the two electrodes. We employed life cycle analysis as a tool to evaluate the most efficient silver extraction method as well as the impact on the overall life cycle of the solar cells. Silver from the electrodes could be recovered as silver chloride in 95% yield, which diminishes the overall energy payback time by 13%. The efficient recovery of silver justifies the use of silver electrodes in OPV even in a scenario where it is scaled to production volumes of 1 GW_p per day.

Broader context

Massive scale deployment of polymer solar cells for bulk energy production will require efficient decommissioning and end-of-life management. We have gained experience from solar parks based on OPV manufacture in a fully printed process that does not employ indium or vacuum. The device architecture does however include silver, the use of which is justified through the possibility for efficient recycling. We show that silver can be recovered in high yield and further demonstrate that recovery of silver positively influences the energy payback time by shortening it by as much as 13%.

1. Introduction

Pilot studies have shown that the polymer solar cell can be manufactured and installed at such a high speed and with such a low embodied energy that it can pay back the invested energy in a significantly shorter timespan than the operational lifetime. Not only does this confirm the viability of the polymer solar cell as a bulk electricity producing technology already with the presently available materials but it also highlights where invested effort is likely to give the highest impact. The unique properties of the polymer solar cell also enable one to explore deployment means and light harvesting methods that are not accessible to current state-of-the-art solar cells. The energy payback time can be exceptionally short (currently 138 days at the system level), as has been highlighted recently[1] and potentially as short as one day.[2]

One of the reasons for such low energy payback times is related to the replacement of indium–tin oxide (ITO) as the transparent electrode of the polymer solar cells with printable silver grids. Although this brings down both the cost and the invested energy, the low abundance of silver (the 65th most abundant element with around 0.075 ppm in the Earth's crust) will require efficient recycling schemes if its use on a larger scale is to be justified.

An excellent model for silver recovery from printed OPV already exists in the X-ray film industry. About 20% of the world's silver is used to make X-ray films on PET plastic film substrates and this silver is recycled industrially by several methods such as burning the film and recovering the silver from the ashes. Newer methods involve shredding of the film and dissolving the silver with cyanide or other proprietary chemical methods. Recycling of silver, gold and other metals from electronic equipment is also performed on an industrial scale and involves pyro- and hydrometallurgical processes.[3] Silver ion extraction from water solutions includes metallic replacement, ion exchange and electrolysis.

In the case of OPV the recovery process is made slightly more difficult because it is protected from degradation by lamination with a barrier plastic foil. The silver is thus not directly accessible to be dissolved by chemical treatment. A crucial factor for the success of the above mentioned recovery methods is the efficient gathering of the 'waste' to be recycled. Re-collection networks are required, preferably the same which handles distribution, which will ensure that it is easy and convenient for the end-user of the original product to hand over the 'waste'.

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We here present the de-installation of organic solar cell parks at a speed of 200 m min^{-1} by rewinding the flexible solar cell foil using a specially designed wagon (a video showing the de-installation of a 100 m module can be found in the ESI†). The de-installed solar cell foils can subsequently be handled in rolls ensuring easy gathering *via* a re-collection network aimed at recycling. Recovery of the silver from the solar cell foil was possible with up to 95% yield in the form of silver chloride with a simple laboratory scale setup. Treatment with nitric acid was chosen as the method to extract silver from the solar cell as it is a well-known reaction which is easily performed on a laboratory scale.

Based on the experimental work environmental impact analysis (EIA) was carried out following the life cycle assessment (LCA) guidelines with a consequential approach,[4,5] revealing that silver recovery can save energy to an extent which significantly brings down both the environmental load and the energy payback time of OPV modules.

2. Experimental

Solar cells

The solar cells were prepared according to the *IOne* process and installed as described previously.[6,7] De-installation of flexible organic solar cell modules is shown in this work to be possible using the same setup which has previously been used to install the modules. We achieved a manual de-installation speed of 200 m min^{-1} and recovered the solar cell foil that had been in operation for 150 days corresponding to an energy return factor‡ >1.

The final decommissioning product is a roll of similar character to the one that was used in the installation process. Such a roll allow for easy handling in a recollection network aimed for recycling and will also allow for the recycling process to occur using roll or roll-to-roll processing. Fig. 1 illustrates the dismounting and the shredding of the flexible solar cells.

Each roll of recovered solar cell foil had a length of 100 m and was mounted on the unwinder with tension control and was fed to a shredding machine making shreds that had a width of 5 mm. The shredder drove the foil at a web speed of 7 m min^{-1} while the unwinder kept the tension at 30 N. A series of experiments were carried out each using a stretch of 4 feet of solar cell foil (1.2192 m) with a width of 1 foot (0.3048 m). In order to examine the influence of lamination on silver extraction the shredding of the 4 feet sections was conducted on the dismounted stretch as they were (referred to as "non-delaminated") or after first delaminating the solar cells and the barrier foil, ensuring good exposure of the solar cell components (referred to as "delaminated"). The resulting long threads of solar cells were then cut into smaller pieces (2–3 cm) and placed in an Erlenmeyer flask. The pieces were treated with nitric acid (1 l) in different concentrations and left for 24 hours at room temperature followed by filtration through glass-wool. The shredded pieces were then washed with water (200 ml), which was combined with the filtrate (volume adjusted to 1200 ml).

Samples were taken from these (100 ml lots) and treated with brine (in the case of concentrated nitric acid this was first diluted with the same volume of water) causing the precipitation of silver chloride. The precipitate was allowed to settle followed by filtration and thorough washing with water. The amount of silver chloride was determined by weight after drying. To rule out the effect of the nitric acid on the precipitation some of the precipitation experiments were carried out after removing the nitric acid first by distillation and readjustment of the volume by dilution with water. The test showed no significant difference.

The amount of 'consumed' nitric acid in the process was determined by titration. The silver content of the silver inks used in the preparation of an equivalent length of solar cell was determined by dissolving gram quantities of the actual inks (1.7–4 g) in concentrated nitric acid followed by removal of the main part of the nitric acid by distillation, dilution with water, precipitation with water and weighing of the formed AgCl after thorough washing and drying of the filtered solid.

3. Life cycle assessment methodology

The focus of the EIA and LCA has been put on describing the impact on the environment when recycling silver. The life cycle assessment tool, highly recommended to identify hotspots and

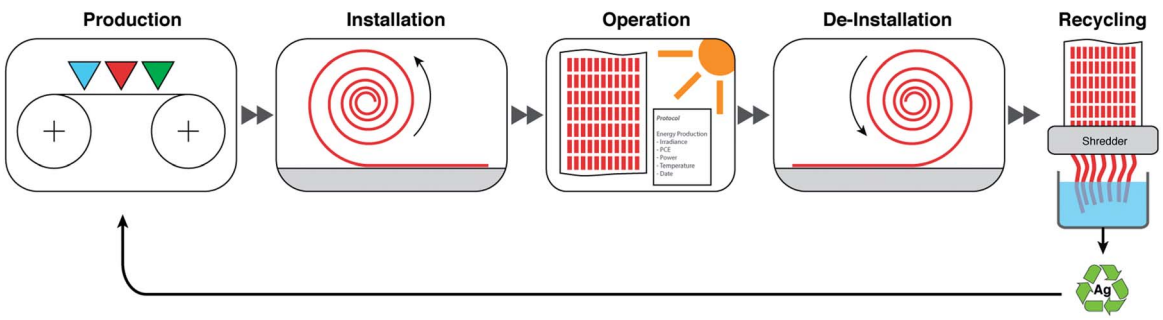

Fig. 1 Complete life cycle of OPV from manufacture of solar cell modules through their deployment in a solar park, operation until they have produced the same energy that was invested in their fabrication to the de-installation, reclaim and decommissioning once they have paid this energy back to finally the recycling of silver.

to help in the process of ecodesign,[8] has been selected to accomplish this goal. A hotspot analysis usually serves to prioritize areas for improvement in the development of a product. We have used this type of analysis extensively over the last three years to improve the production of OPV modules by minimizing their energy use, reducing the amount of materials used or replacing scarce materials.[2,9,10] Equally and furthermore we have now directed the efforts towards recycling one of the most harmful and scarce materials currently employed in the *IOne* technology, *e.g.* the silver electrode that we have so far not found a better replacement for when manufacturing on this scale (1000 m^2).

The complete process of recycling of the silver performed in our labs has been modelled using the SimaPro software. LCA includes all possible aspects of environmental impact, from the raw materials consumed during manufacturing (cradle) to disposal of the product after use in a landfill or incineration site (grave), or – in the case of recycling – its new life cycle (the next cradle). However no disposal stage is comprised in the study. Three key issues that must be settled to start conducting the LCA are the system boundary settings, the allocation and regional differences. The system boundary settings are aimed at correctly including everything within the limits of the model and ensure that the elements excluded from the boundary and modelling do not distort the results. The life cycle now includes the production of OPV modules, their lifetime, decommission and the recycling of silver, which is considered to start a new cycle – the recycled silver fraction.

With regard to allocation, industrial processes often result in more than one product (or service). There might be regional differences since a company in France will use energy from a different source (mainly nuclear) to a company in Denmark (mainly coal and some wind power) or Norway, (mainly hydro-electric power) which implies that identical production processes can have a different environmental impact depending on where they are carried out. Our process was carried out in Denmark, and so we have applied the Danish electricity mix and the corresponding inventory.[11] The electricity in the raw materials is essentially a black box taken from Ecoprofiles and from SimaPro and other databases such as PlasticsEurope. The functional unit (FU), or the unit everything is referred to, is an area related unit corresponding to 1 m^2 of processed area (or solar cell foil). Based on the results we have, as described in the Experimental section, two material recovery efficiencies for silver scrap have been considered: 95% recovery from the delaminated experiment (14.2 M HNO_3) and 72% recovery from non-delaminated foil (1.42 M HNO_3). Hence the LCA activity for 1 kg silver scrap also includes 0.05 kg for the best case or 0.28 kg disposal of silver waste for the worst case. Several methodologies have been used in the SimaPro software to assess the impact of this activity, as seen in Section 4.2. Three methods representing different approaches included in this software have been considered. CML 2000 (ref. 12) was selected as a midpoint method, ReCiPe[12] 2008 for the endpoint approach and Ecoindicator[12] since relevant categories for this work are comprised in it. Impact values in CML and ReCiPe are normalised to the maximum values the impact can have on air/water/soil/raw materials, so they are dimensionless. When Ecoindicator is used, the metric of the impact is given in the dimensionless unit Pt, obtained by weighting all the impact loads.

4. Results and discussion

4.1. Silver extraction

The original amount of silver present in the de-installed solar cells was 1.657 g per linear meter of solar cell – 2.119 kg silver ink (56% silver) was used to process 716 m solar cell foil. Table 1 shows the amount of recovered silver (in the form of silver chloride) for the solar cells after treating the shredded solar cells using various concentrations of nitric acid to dissolve the silver. The recovery at high nitric acid concentration is almost quantitative; something that would certainly be possible to optimize to complete recovery in an industrial process. Quite interestingly there is only a relatively little effect of using higher acid concentration and also the amount of acid consumed in the process seems to be closely related to the original acid concentration.

The explanation to why exposure to higher amounts of acid leads to higher acid consumption should probably be found in the fact that not only the silver reacts with the nitric acid. Fig. 2 shows the piles of 'non-delaminated' shredded material after the 24 hour treatment and besides an obvious color change it is clear that the volumes of the treated piles are very different although they started out the same. The shredded material exposed to 14.2 M HNO_3 has been exposed to a much higher degree of oxidation which has not only resulted in complete bleaching of the solar cell but also caused the shredded pieces to delaminate entirely resulting in a larger volume. As for the treatment with 4.74 M HNO_3 this has resulted in slight

Table 1 Silver chloride recovery and the amount of acid used after treatment of 4 feet solar cell segments (non-delaminated and delaminated) with concentrations of nitric acid for 24 h

	Non-delaminated		Delaminated	
HNO_3 concentration	AgCl recovery[a]	Consumed acid[b] (mmol)	AgCl recovery[a]	Consumed acid[b] (mmol)
14.2 M	95%	874 (6.1%)	95%	502 (3.5%)
4.74 M	84%	275 (5.8%)	87%	195 (4.1%)
1.42 M	72%	8 (0.6%)	77%	175 (12%)

[a] Average value. [b] Determined by titration before/after treatment for 24 h.

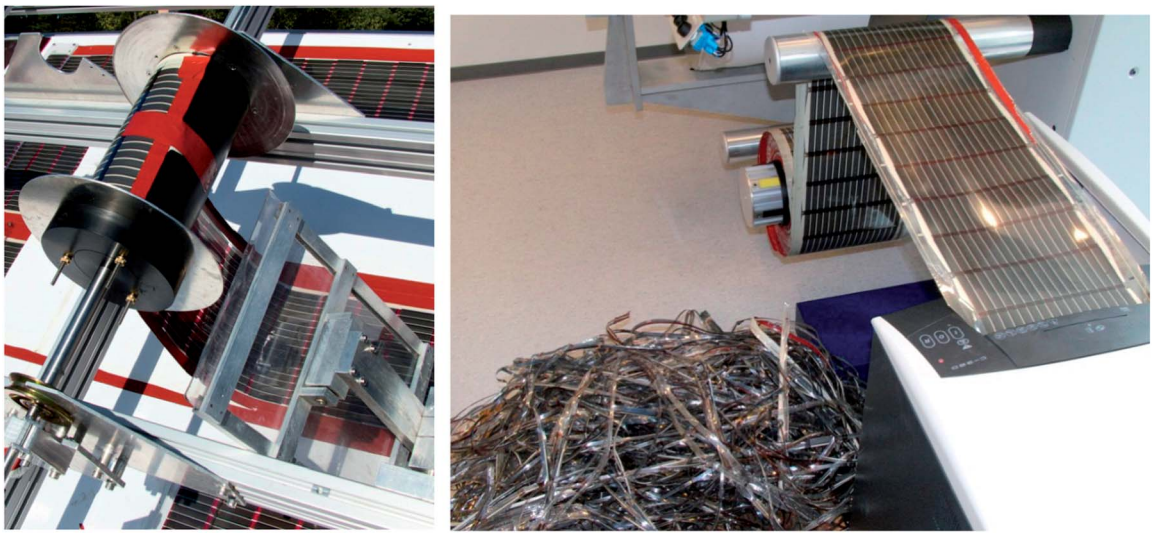

Fig. 2 Left. The start of the de-installation of a 100 m stretch of a flexible organic solar cell at 200 m min^{-1}. Right. Roll-to-shredding with continuous cutting of a roll of used OPV. The pile of shreds ready for silver recovery represents 10 m solar foil (width of 0.305 m).

bleaching and the shredded material has delaminated to some extent whereas almost no bleaching is observed for the treatment with 1.42 M HNO_3 and no or minimal delamination is observed. 3 foils are used in the preparation of the solar cell – one substrate upon which all processing is carried out and two barrier foils to encapsulate the substrate on the front and backside. We have not determined whether the barrier foils themselves (each comprising several layers) can delaminate in the acid treatment process but if a chemical reaction can occur at the surfaces of the foils then delamination will certainly allow for a larger degree of reaction as it increases the exposed surface. This could also explain why the 'delaminated' foil generally shows a slightly lower acid consumption although a larger portion of the silver is recovered. Before delamination and shredding the front laminate was removed as the front laminate has no contact with the processed layers of the actual solar cell. Consequently the potential free surface was less in the delaminated experiment as only two of the initial three foils were shredded and treated. In the case of weak acid (1.42 M) the 'non-delaminated foil' experiences no delamination as a result of the chemical treatment whereas the 'delaminated foil' is already fully exposed resulting in greater acid consumption. The results show that great care must be carried out when designing the silver extraction in order to target reaction with only the silver (Fig. 3).

Although complete recovery seems to require quite strong acid it is reassuring to observe that the main part of the silver can be extracted at much lower concentrations. This indicates that it will be possible to make a system where nitric acid is fed at one end and the solar cell in the other ensuring that the strong acid will be present to remove the last traces of silver and as the acid is consumed (resulting in lowering of the concentration) it moves towards the easier accessible silver in the solar cell where high acid concentration is of lesser importance. Such a system will probably allow for a very efficient usage of the nitric acid reducing the amount necessary for the extraction of silver. Combined with the use of chloride ions from seawater in the precipitation reaction could make this a very efficient method.

Fig. 3 Photograph of the remaining shredded pieces after the HNO_3 treatment from the 'non-delaminated' experiment (from left to right: 14.2 M, 4.74 M and 1.42 M). Besides the apparent difference in color there is a distinct difference in the subsequent volumes of the piles after the acid treatment. The volume differences are the result of different extents of delamination caused by the acid.

4.2. Environmental assessment

The process of recycling silver has been modelled in SimaPro creating a parameter named RE_rate that was given the different material recovery efficiencies: 0.95, 0.72 and 0, corresponding to nitric acid concentrations of 14.2 M (delaminated), 1.41 M (non-delaminated) and no recovery of silver. Nitric acid consumption has been modelled as if it could be reused up to 10 times – although it is potentially reusable many more times. The inventory of materials for each case has been created in SimaPro. We are here referring to the inventory of one square meter of OPV modules; a largely detailed description about the inventory calculation method can be found in the literature.[1] The life cycle of OPV modules when silver is recycled is modeled as if the silver recovered was again available to be processed in a new life cycle – without being refined. So that the energy content in silver is deduced from the cumulative energy demand (CED), or all the energy required to manufacture OPV modules.

In order to make a comparison with other energy technologies and provide meaningful numbers, we have calculated the energy payback time – EPBT – for the different cases under standard conditions. The conversion factors used from primary to electrical or thermal energy are 0.35 and 0.85, respectively. The modules are assumed to be installed in a location presenting 1700 kW h m^{-2} per year irradiation (typical of Southern-Europe), having a stabilized PCE of 1.6% on the active area (0.8% on the total area) and that they work with a performance ratio§ of 0.8.

Silver can be recovered in high yields but the higher the yield is, the larger the complete budget is since more energy and nitric acid volumes are required. The cumulative energy demand required for 1 m^2 of OPV modules when silver is recovered in a 95% yield is higher than for a 72% yield, which makes the EPBT higher as well, although it is still lower than when silver is not recycled (Table 2). The negative influence on the CED when having 95% silver recovery efficiency can also be seen in the global warming potential category under the CML methodology (Fig. 4) and in the climate change human health category in ReCiPe (Fig. 5). The rise of 14% in the footprint is shown in Table 2. This is caused by the higher consumption of nitric acid that while yielding a higher silver recovery does not balance in the CED thus leading to a longer EPBT.

Silver recycling has beneficial effects in terms of other environmental impacts if the recovery is high. The impact is reduced by half in almost all the categories when silver is recycled at the highest yield we could achieve in our setup (95%). Several environmental categories have a significantly smaller impact such as human toxicity, marine aquatic and terrestrial ecotoxicity, evaluated by the CML methodology (Fig. 4). When following the ReCiPe method in Fig. 5, positive effects can also be seen in metal depletion with an 87% reduction, which is also reflected in water ecotoxicities. Huge improvements in carcinogens assessed by Ecoindicator are expected if the silver is fully recycled, as well as in respiratory inorganic damages as illustrated in Fig. 6.

Table 2 Cumulative energy demand for the modules considering silver is not recycled; that silver is recovered with 72% and with 95% efficiency. Units are in MJ of primary energy, broken down into different types of energy, with the support of SimaPro software

LCI inventory	No silver recycled	Silver recycled – 72% rate	Silver recycled – 95% rate
Energy saved in materials (MJ_{EPE})	—	5	3.68
HNO_3 consumption (50%) (g)	—	27.5	275
Recycling processing energy	—	0.08	0.08
Cumulative energy demand (MJ_{EPE})	42.17	37.18	38.77
Greenhouse gases (CO_{2eq})	269.94	241.07	302.39
EPBT (year)	0.38	0.33	0.35

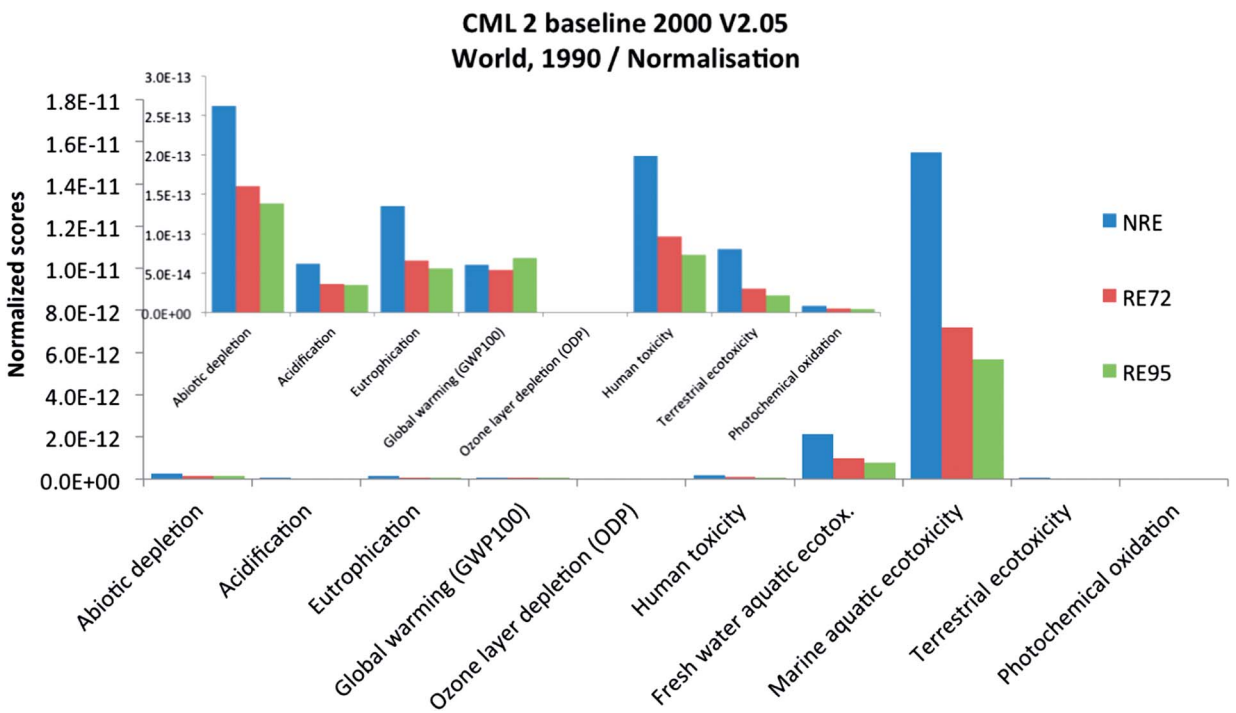

Fig. 4 Impact of one FU of OPV modules on several environmental categories under three assumptions: no recycled silver (NRE), modules with a recycling rate of 72% (RE72) and modules with a recycling rate of 95% (RE95). Evaluated using the CML midpoint methodology in SimaPro.

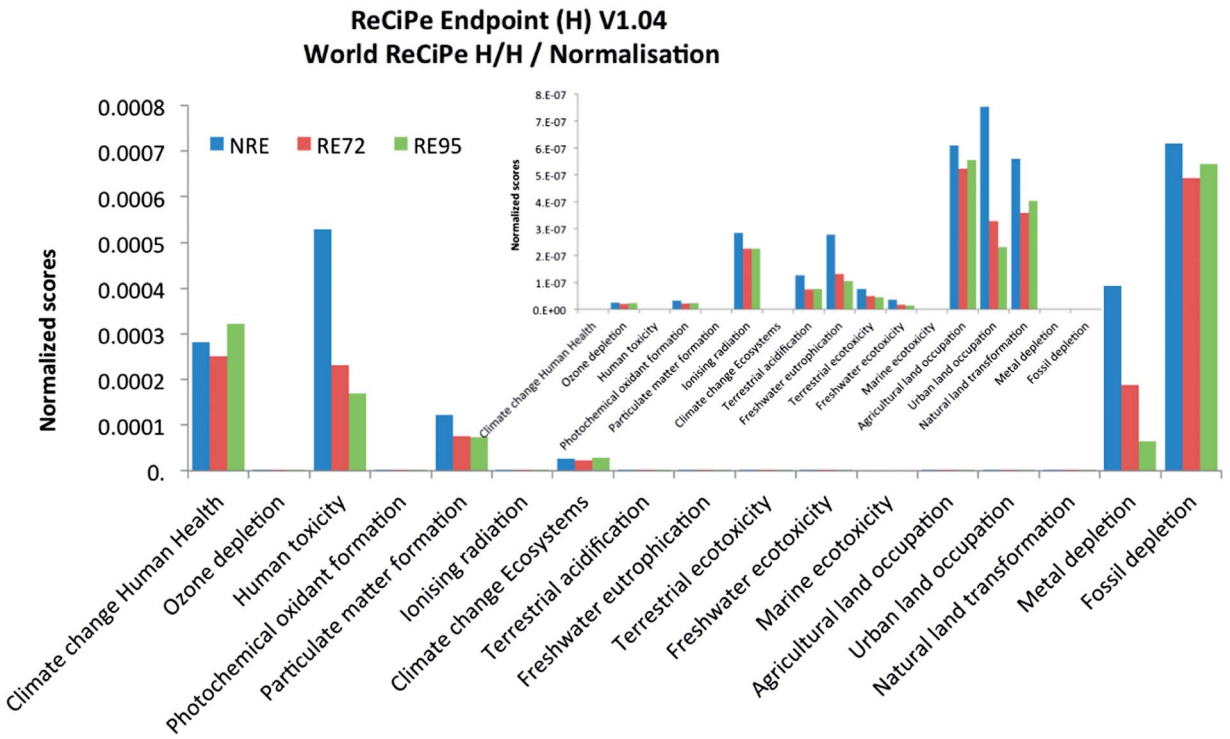

Fig. 5 Impact of one FU of OPV modules on several environmental categories under three assumptions: no recycled silver (NRE), modules with a recycling rate of 72% (RE72) and modules with a recycling rate of 95% (RE95). Evaluated using the ReCiPe endpoint methodology in SimaPro.

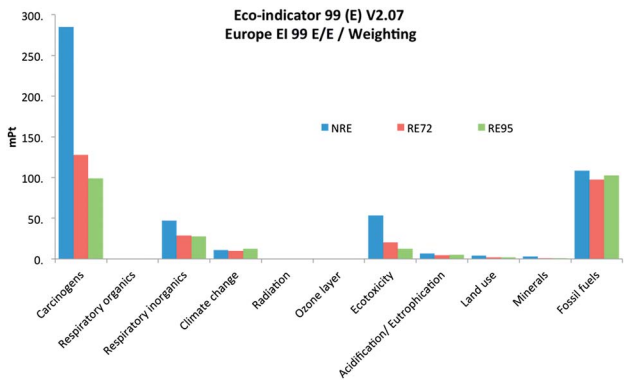

Fig. 6 Impact of one FU modules of OPV on several environmental categories under three assumptions: no recycled silver (NRE), modules with a recycling rate of 72% (RE72) and modules with a recycling rate of 95% (RE95). Evaluated using the Ecoindicator endpoint methodology in SimaPro.

5. Conclusions

The intention of the present work has been to establish potentially beneficial environmental effects resulting from the recycling of one of the materials that has been detected to be a hotspot along our trajectory in making organic solar cells a viable technology with low environmental impact: silver is not abundant, and certainly harmful in several impact categories such as water toxicity and carcinogens.

Silver extraction from the de-installed solar cells was found possible with an efficiency of up to 95% of what was originally used in their fabrication. We employed low energy intensive treatment with nitric acid after shredding the solar cell foil. Acid is consumed in the process which probably also include reaction with the various components of the solar cell other than silver including foils, adhesives and the actual solar cell components. Even low concentrations of acid were found sufficient to extract a significant part of the silver which in theory at least will allow for 'continuous consumption' of the acid in a manner where the acid itself does not have to be recovered.

We have performed recycling of silver trying to answer the following question: is it energy wise beneficial to recycle silver from decommissioned polymer solar cells – that can then be put more or less straight back into the printing inks used for manufacture of OPV – compared to the use of virgin material? We conclude that the process of recycling is environmentally beneficial and with a low degree of carbon emission. In any case the environmental benefits of recycling the silver have been clearly identified. Due to the low cumulative energy demand we end up having a shorter energy payback time by 11 days (decrease of 8%) in the case where the silver recovery efficiency is 95%, or 16 days shorter (decrease of 13%) when the silver is recycled with a 72% efficiency. Future work should explore the necessity for purification of the recycled silver and also address the recycling process of the silver content in OPV modules against their disposal and incineration. Incineration is a common activity in Denmark, OPV modules comprise >99%

plastic by weight and the calorific value of plastics is generally around 40 MJ kg^{-1} (dry plastics waste) that could be recovered as heat with possibly higher silver recovery yields from the ashes. The CO_2 emission would however also be increased. Although they are only present in very small amounts it might also be worth looking into the recycling of some of the other components of the solar cell such as fullerenes and metal oxides. The absorbing polymer can most likely not be recycled.

Acknowledgements

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Notes and references

‡ Energy Return Factor (ERF) indicates the total amount of energy saved per unit of invested energy, that is, the number of times the invested energy will be recovered by the system.

§ Performance ratio is the internationally introduced measure for an entire PV system. It accounts for the overall effect of losses due to the array temperature, incomplete utilization of the irradiation and failures of the system components.

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