Energy &
Environmental
Science

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Energy Environ. Sci.*, 2016, **9**, 857

Received 4th January 2016,
Accepted 29th January 2016

DOI: 10.1039/c6ee00021e

www.rsc.org/ees

Incineration of organic solar cells: efficient end of life management by quantitative silver recovery†

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Recovery of silver from the electrodes of roll-to-roll processed organic solar cells after incineration has been performed quantitatively by extraction with nitric acid. This procedure is more than 10 times faster than previous reports and the amount of acid needed for the extraction is reduced by a factor of 100–150. LCA studies show that the resulting environmental impacts from silver extraction of incinerated ashes are more favourable on almost all standard factors compared to extraction from shredded organic solar cells. The so lessened environmental impacts by efficient recovery fully justify the use of Ag as an electrode in scaled production of organic solar cells.

Broader context

Silver is widely used as an electrode in organic solar cells because of its high conductivity and it is so far the only metal that can be printed efficiently in roll-to-roll processes. At the same time mining of silver is associated with heavy pollution. This puts the rapidly evolving technology in a dilemma where efficient recycling of silver is needed if deployment on a massive scale is to be justified. In this work we have demonstrated the complete recovery of silver from incinerated organic solar cells. The extraction of silver from the incineration ashes can reduce the amount of acid needed for extraction by a factor of 100–150 when compared to previous studies performed on shredded organic solar cells. The extraction time can also be reduced by a factor of 12. Life cycle assessment scenarios show that recycling of silver by extraction from the ash generally has a 20% lower environmental impact compared to extraction from shredded cells.

Introduction

In parallel with the rapid advancement of the organic solar cell technology by roll-to-roll (R2R) processing the choice of materials becomes increasingly important. Energy payback times of 120 days have already been demonstrated for organic solar cells in solar parks with an energy return factor of 6.[1] With the prospect of massive scale deployment of solar cells it is paramount that the materials used for their manufacture are abundant – or that the materials can be easily recycled and re-entered into the production of new solar cells after decommission. Silver (Ag) has so far proven to be the best material and the only metal suitable for R2R processing of electrodes. This constitutes a challenge not only for organic solar cells, but for all thin film photovoltaic technologies relying on Ag, if the latter cannot be recycled efficiently. Though not classified as a "critical raw material" for the overall economy,[2] in particular the renewable energy sector crucially relies on Ag and may suffer from limitations to expand production capacities and political risks (by geographical concentration of ores in a few countries).[3] Massive environmental pollution and energy requirements associated with mining of primary ores make Ag the main contributor to the overall environmental impact for state-of-the-art R2R processed organic solar cells.[4–6] In terms of sustainability, all metals that enter the supply chain from the mining industry pose a challenge not only with respect to environmental pollution and energy consumption, but also for aspects related to health and operator safety. Therefore, recycling of metals is an efficient means to achieve true sustainability of photovoltaic technologies.

In a previous report we described how the use of Ag in organic solar cells is justified by efficient decommission and recycling. By shredding the solar cells followed by a chemical treatment with nitric acid it was possible to recover up to 95% of the Ag used in the manufacture of the solar cells.[7] Here we describe how a complete recovery of Ag can be achieved if the solar cells are decommissioned by combustion in a heat

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ee00021e

and power plant with subsequent chemical treatment of the remaining ashes.

In this work we demonstrate the efficient re-extraction of Ag by lowering the overall volume and increasing the surface/volume ratio of the material to be chemically treated by incineration. The combustion of the organic fraction of the solar cell also contributes to power production and heat conservation. A complete (101.3 ± 3.8%) Ag recovery from the ashes is now achieved using less than 1% of the amount of acid employed previously. Furthermore, by combustion of the solar cell, acid treatment time is reduced from 24 h to 2 h compared to mechanical shredding, which is crucial to decrease the foot-print of recycling facilities. Also, diluted nitric acid can be used instead of concentrated nitric acid because of the higher acid accessibility of Ag.

Experimental

Incineration procedure

1 m^2 of organic solar cell foil (width: 0.3048 m, length: 3.28 m) was cut into smaller pieces which were tied up with heat resistant stainless steel wire (EN 1.4835/AISI 252MA from INOX) and placed in a heat resistant metal container fitted with a tubular air inlet and an exhaust tube. The container was then put into a high temperature oven with a continuous air supply (Fig. 1). The electric oven was placed outside and the temperature was gradually increased over 20 min to 400 °C at which it was left for an additional 20 min before gradually increasing the temperature (1 h) to either 800 °C or 1000 °C at which it was kept for an additional hour. After this, the oven was turned off and the system was allowed to cool down. The steel wires were then removed and the ashes were isolated (Fig. 1 right). Incineration experiments were performed using single encapsulated solar cells (single encap.) at 800 °C and 1000 °C, and double encapsulated solar cells (dbl. encap.) at 1000 °C. The isolated ashes (24.38 g from single encap. at 800 °C incineration, 18.55 g from single encap. at 1000 °C incineration, 36.38 g from dbl. encap. at 1000 °C incineration) were ground and intimately mixed to a homogeneous powder before acid extraction and further analysis.

Determination of Ag recovery by ICP-MS analysis

Ashes from the OPV combustions at a maximal temperature of 800 °C (971 ± 43 mg) as well as at 1000 °C (339 ± 13 mg; 993 ± 12 mg for double encapsulated cells) were extracted in 1.42 M and 0.78 M HNO_3 in a liquid to solid ratio of 10 : 1 (semiconductor grade, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland) using an orbital shaker (SM 30 A control, Edmund Bühler GmbH, Hechingen, Germany) at 130 rpm and room temperature. Every extraction was done at least in duplicates. Samples were taken after 2 h extraction time and subsequently centrifuged (Centrifuge 5804R, Vaudaux-Eppendorf AG, Schönenbuch, Switzerland) at 4500 × g at room temperature for 5 min. The Ag content in the supernatants (diluted with 1% HNO_3) was measured by analysing the isotope ^{107}Ag and ^{85}Rb (internal standard) on an Agilent 7500cx ICP-MS (Agilent Technologies AG, Basel, Switzerland) using a dwell time of 0.3 s per isotope and standard settings.[8] To remove polyatomic interferences, the octopole collision cell was pressurized with 4.5 mL min^{-1} helium. The Ag was quantified using matrix-matched calibration solutions (1% HNO_3) prepared from multi-element standards (Sigma-Aldrich Chemie GmbH, Buchs, Switzerland). Furthermore, the Ag content in the solid phase was determined by μXRF. For this, ground ashes were mixed with XRF wax (1 : 4 wt/wt wax : sample; CEREOX® Licowax C, Fluxana, Bedburg-Hau, Germany) and were pressed to 5 mm pellets for 3 min at 2.0 t with a manual hydraulic press (Specac's Atlas Series, Biel-Benken, Switzerland). The Ag content was quantified on a M4 Tornado system (Bruker Nano, Berlin, Germany)

Fig. 1 Left: Picture of 1 m^2 of an organic solar cell rolled out on the ground. On the bottom left of the same picture an additional 1 m^2 has been cut into smaller pieces, tied up with heat resistant steel wire and put in a ceramic bowl inside the steel container. Middle: Picture of the oven setup with the steel container placed inside the high temperature oven with a controlled air flow. Right: Pictures of the cut up solar cells before and after incineration.

Table 1 Silver recovery efficiencies from the ashes of single encapsulated OPV incinerated at 800 °C and 1000 °C, and double encapsulated solar cells at 1000 °C

$[HNO_3]$	800 °C (single encap.) [% of printed Ag]	1000 °C (single encap.) [% of printed Ag]	1000 °C (double encap.) [% of printed Ag]
0.78 M[a]	3.1 ± 0.5	41.6 ± 1.8	3.0 ± 0.1
1.42 M[b]	101.3 ± 3.8	78.5 ± 2.7	78.7 ± 3.7

[a] Triplicate. [b] Duplicate.

on maps of 2 × 2 mm, under the following conditions: a Rh tube, 50 kV accelerating voltage, 600 μA beam current, 25 μm distance between spots, 50 ms per pixel. The accuracy has been assessed on pellets of a similar reference material (fly ash, BCR 176R), spiked with ~1 and ~2% weight Ag (Table S1, ESI†) by using the same procedure. Ag extraction efficiencies were calculated based on the amount of Ag added during printing and ICP-MS analysis. The recovery efficiencies were then verified by the difference in solid phases of Ag contents by means of μXRF (owing to challenging absolute quantification of the latter in complex matrixes; ESI,† Table S1).

Life cycle assessment (LCA)

Comparing the Ag recycling experiments from incineration with those from shredding/wet processing, there are four distinguishing improvements that were considered for LCA:

- The extraction time was decreased by a factor of 12.
- Additional energy recovery upon burning of the OPV.
- Less acid was used for extraction (by a factor of >100 times).
- The Ag recovery efficiency was increased from 95 to effectively 100%.

These facts indicate *a priori* the supremacy of recycling Ag from the ashes through incineration. However, for a more qualified assessment it is necessary to use a more rigorous methodology for the two scenarios, which accounts for emissions and their effects during the whole lifetime. Following standards defining the LCA procedures ISO 14040 and 14044 the influence of Ag recycling *via* shredding/wet processing was compared to Ag recycling from ashes after incineration. It has to be stressed that both scenarios were based on experimental data. The experimental procedure for the shredding/wet processing can be found elsewhere, as can the model used here for the manufacturing of the organic solar cells that has been thoroughly reported elsewhere.[6,7] The inventory has been created in SimaPro software together with Ecoinvent database in SimaPro software.[9,10] The scenarios have been modelled according to experimental procedures as well (details in the ESI†). The environmental categories evaluated are a set of categories commonly used in LCA assessments to enable comparisons. They are taken from International Reference Life Cycle Data System (ILCD) methodology[11] and they reflect the impact that a product has in different categories, such as climate change, terrestrial eutrophication, human and ecosystems toxicity (complete list in the ESI†).

Results and discussion

Polymer solar cells were incinerated at 800 °C and 1000 °C with the aim of quantitative Ag recovery from the electrodes. Based on ICP-MS, virtually complete extraction of the Ag added during printing of the electrodes was achieved, *i.e.* 101.3 ± 3.8% (Table 1). The extraction efficiencies were confirmed by μXRF, which showed a decrease in the Ag content of 96.7% between original and extracted pellets at 800 °C (77.8% and 86.3% for single and double encapsulated cells at 1000 °C, respectively; Table S2, ESI†). It has to be noted that, despite the virtually complete Ag extraction, also the 800 °C ash residuals still showed an Ag signal in μXRF, being within the analytical uncertainty of ICP-MS (101.3 ± 3.8% of the theoretical content). This was assigned to the high inhomogeneity of samples (containing some residual Ag hot spots). Still, Ag recovery using 800 °C incineration can be considered virtually complete.

In contrast, incineration at elevated temperature (1000 °C) yielded lower extraction efficiencies (~20% less, Table 1) in contrast to moderate temperatures. Generally, lower recovery at high incineration temperatures may either be due to losses through volatilization of Ag (after reaction with halides)[12] or by formation of solid phases with different acid accessibility. Volatilization could be excluded based on the Ag contents of the original ashes by μXRF (Table S2, ESI†). Lower incineration temperatures have been shown to favor the formation of (nitric acid accessible) elemental Ag, whereas at 1000 °C melting of the latter will occur (melting point at 962 °C).[13] Once melted, Ag may react further and/or be incorporated in recalcitrant fractions, lowering eventual extraction efficiencies. Therefore, despite the more complete combustion, higher incineration temperatures are not recommendable for Ag recovery as presented here.

Decreasing the acid concentration to 0.78 M led to a considerably decreased recovery in all cases assumingly due to an elevated pH of the mixture. Due to the formation of silver chloride, it was not possible to directly measure the supernatant pH with lab-electrodes (containing KCl). Comparing the extraction efficiency of the single encapsulated cells (1000 °C; 0.78 M) with other efficiencies (both at low and high acid concentrations) points to the direction that 0.78 M acid is indeed close to a threshold concentration: minute changes in the buffer capacity of the formed solid phases may thus cause extraction of a more easily available Ag fraction. This certainly warrants further investigation. However, since the LCA results (see below) demonstrated already the higher acid concentration having a beneficial impact, this was considered outside the scope of the present study. In any case, there is further optimization potential for an industrial process in regard to contact times, liquid to solid ratios, temperatures, *etc.* making combustion and acid leaching a real option for OPV recycling.

Compared to our previous study where shredded organic solar cells were extracted directly without incineration[7] the Ag extraction process presented here poses advantages at several levels. First of all, the acid concentration needed to recover ≥95% of Ag from the electrodes could be decreased by a factor of 10 from 14.2 M to 1.42 M. In the previous study, direct wet processing with 1.42 M HNO_3 only led to a lower recovery efficiency of 72% for non-delaminated and 77% for delaminated solar cells. Secondly, the volume of the acid needed for the extraction of 1 m^2 of organic solar cell could be decreased by a factor of 10–15. Combined with the lower acid concentration this means that 100–150 times less HNO_3 is necessary for extraction of Ag from the ashes. Finally, the extraction time could be considerably lowered from 24 h to 2 h easing potential industrial application by lower reactor foot-print and associated investment costs. Together with these improvements come the advantages of heat energy recovery during incineration as well as simplification of the handling due to a homogenous ash powder instead of shredded cells. As a result, the volume of waste to be treated is reduced considerably facilitating industrial implementation.

The polymer solar cells applied here only contain a small amount of zinc as an additional metal to Ag. For the recycling of the cells this is a considerable advantage in comparison to other thin-film photovoltaic technologies. Although the metals from technologies such as CuInGaSe solar cells can be recovered quantitatively as a mixture, the separation into individual elements is highly challenging and requires separation techniques such as nanofiltration and liquid–liquid extraction by complexing agents.[14] Ag can be straightforwardly separated from zinc in acidic solutions using simple chloride precipitation. Recovery of zinc from municipal waste incineration fly ashes is already carried out on an industrial scale, *e.g.* in Switzerland,[15] though mono-incineration of e-waste is not yet in place. Mono-incineration of organic solar cells and acid leaching of the ashes containing Ag and zinc can therefore be considered as a simple and industrially feasible process.

Given the material composition of the organic solar cells, state-of-the-art incineration plants are furthermore expected to be fully capable of removing hazardous byproducts from the process. The organic solar cells in this work constitute (by weight) 95% PET foil and adhesive, 3.74% silver, 1.00% printed polymers, 0.11% zinc oxide and 0.04% fullerene. The main part of the solar cells is organic polymeric materials, which are ideal for incineration and optimized incineration processes followed by flue gas treatment, deals very efficiently with hazardous gases, such as dioxins and SO_x, formed in the process. In addition, further nanomaterials (*e.g.* TiO_2, ZnO,…) applied in OPV (and PV in general) – even if inert during combustion – can be expected to be removed in the filters of state-of-the-art incineration plants, as demonstrated in full scale for CeO.[16] Also the fullerenes, which under inert conditions can be stable up to 950 °C, will be fully oxidized to gas phase products at temperatures above 500 °C.[17]

Environmental impact of Ag recovery

One of the main utilities to conduct a life cycle impact assessment is to evaluate how the environmental impacts of a product can be diminished. The solar cells as any other product can cause a radically different impact depending on the end of life that they go through. With the use of life cycle assessment it is possible to answer the question of which scenario is the most beneficial in terms of environmental impact.

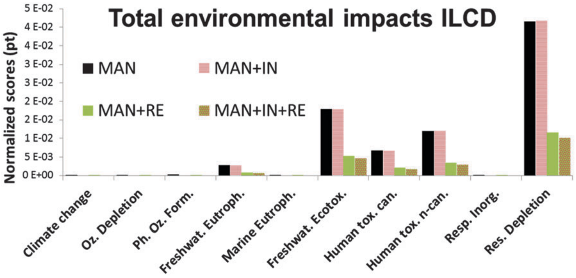

Fig. 2 Normalized impact scores with ILCD methodology in Simapro when evaluating different stages of 1 kW h of solar cells, the manufacturing (MAN) and its disposal considering three end of life scenarios: (1) silver recycling (MAN + RE), (2) incineration of solar cells (MAN + IN), (3) incineration of solar cells followed by silver recovery from the ashes (MAN + IN + RE). Selected impact categories are: climate change (kg-CO2eq per pers); Oz. depletion: ozone depletion (kg CFC-11 eq); Ph. Oz. Form.: photochemical ozone formation (kg NMVOC eq); Freshwat. Eutroph.: freshwater eutrophication (kg-Peq per pers); Marine Eutroph.: marine eutrophication (kg-Neq per pers); Freshwat. Ecotox.: freshwater ecotoxicity (CTUe per pers); Human tox. can.: human toxicity, cancer effects (CTUh per pers); Human tox. n-can.: Human toxicity, non-cancer effects (CTUh per pers); Resp. Inorg.: respiratory inorganics (kg-PM2.5eq per pers); Res. Depletion: resource depletion (kg-Sbeq per pers). Four impact scores have been omitted for their insignificant contribution. They can be consulted along with the characterized values in Tables S7 and S8 in the ESI.†

The environmental impacts of the whole life cycle of solar cells undergoing three-end of life scenarios have been calculated. In the first scenario, after the manufacturing (MAN) and use, the Ag is recycled *via* shredding/wet processing (MAN + RE), the second is the pure incineration after the use without Ag recovery (MAN + IN) and the third one consists of the Ag recycling from the incineration ashes (MAN + IN + RE). The evaluation of the three scenarios are represented against the manufacturing of the solar cells in Fig. 2. All impact categories are on average 20% lower when the Ag is recovered from the ashes (MAN + IN + RE) as compared to recycling *via* shredding/wet processing (MAN + RE), with the exception of ozone depletion that is 126% higher. However, incineration without recycling (MAN + IN) has very similar impact to the pure manufacture (MAN) meaning that the recovered energy by incineration therefore has very little influence on the total impact. In consequence, it is indeed the more efficient recovery of Ag that positively impacts the environmental profile of the organic solar cells over the whole life cycle.

Conclusions

Recovery of Ag from the electrodes of organic solar cells can be performed quantitatively from ashes of incinerated cells. Extraction from the ashes instead of the shredded cells reduces the treatment time and the required acid equivalents significantly (by a factor of 12 and a factor of 100–150 respectively) with the potential for heat recovery during incineration. LCA scenarios show that recycling of Ag by ash extraction generally has a 20% lower environmental impact compared to extraction from shredded cells.

These results cement previous justifications of the use of silver as an electrode for mass production, in spite of its scarcity, under the precondition that appropriate recycling procedures are in place.

Acknowledgements

This work was supported by Energinet.dk (Project No. 12144) and by the Danish Ministry of Science, Innovation and Higher Education under a Sapere Aude Top Scientist Grant (no. DFF-1335-00037A). The School of Life Sciences (HLS) of the University of Applied Sciences and Arts Northwestern Switzerland (FHNW) is gratefully acknowledged for the internal strategic research fund. The support of the European Commission's *StableNextSol* COST Action MP1307 is acknowledged.

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