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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.

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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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 m² 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) 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 HNO₃ 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% HNO₃) was measured by analysing the isotope ¹⁰⁷Ag and ⁸⁵Rb (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.

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% HNO₃) 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 (Spectac’s Atlas Series, Biel-Benken, Switzerland). The Ag content was quantified on a M4 Tornado system (Bruker Nano, Berlin, Germany).
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 ver-
cified by the difference in solid phases of Ag contents by means
of µXRF (owing to challenging absolute quantification of the
latter in complex matrices; 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
used here for the manufacturing of the organic solar cells that has
after incineration. It has to be stressed that both scenarios were
shredding/wet processing was compared to Ag recycling from ashes

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

| [HNO₃]     | 800 °C (single encap.) | 1000 °C (single encap.) | 1000 °C (double encap.) |
|------------|------------------------|------------------------|------------------------|
|            | [% of printed Ag]      | [% of printed Ag]      | [% of printed Ag]      |
| 0.78 M⁶    | 3.1 ± 0.5              | 41.6 ± 1.8             | 3.0 ± 0.1              |
| 1.42 M⁶    | 101.3 ± 3.8            | 78.3 ± 2.7             | 78.7 ± 3.7             |

⁻ Triplet. ᵇ Duplicate.

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; re-
spectively; 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)‡
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).¹⁷ 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 incineration⁷ the Ag

Results and discussion

Polymer solar cells were incinerated at 800 °C and 1000 °C
with the aim of quantitative Ag recovery from the electrodes.
incineration plants, as demonstrated in full scale for CeO.

be expected to be removed in the filters of state-of-the-art
e.g.

considered as a simple and industrially feasible process.
leaching of the ashes containing Ag and zinc can therefore 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
together as 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
feasibly.

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 technolo-
gies 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 nanofiltra-
tion 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 SOx formed in the process.
In addition, further nanomaterials (e.g. TiO2, 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 fullerences, 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 assess-
ment 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.

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 signifi-
cantly (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.

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