Cronfa - Swansea University Open Access Repository

_____

Cronfa URL for this paper:

_____

_____

Platinized counter-electrodes for dye-sensitised solar cells from waste thermocouples: A case study for resource efficiency, industrial symbiosis and circular economy

Rhys G. Charles [a, *], Peter Douglas [b, c], Jenny A. Baker [d], Matthew J. Carnie [d], James O. Douglas [e], David J. Penney [f], Trystan M. Watson [d]

[a] COATED Engineering Doctorate, Materials and Manufacturing Academy (M2A), Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, UK
[b] Chemistry Group, School of Medicine, Swansea University, Singleton Park, Swansea, SA2 8PP, UK
[c] School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban, 4000, Republic of South Africa
[d] SPECIFIC, Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, Wales, UK
[e] Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK
[f] College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, UK

ARTICLE INFO

ABSTRACT

A study of a local industrial symbiosis involving the recovery of platinum from waste thermocouples which is then used for the preparation of catalytic electrodes suitable for dye-sensitized solar cell production is reported. The small quantity of platinum in the filaments of used thermocouples, thousands of which are discarded each year by metal foundries, can be economically recovered by conversion to chloroplatinic acid hydrate, an 'added value' product, which can then be used in the fabrication of dye-sensitized solar cell counter-electrodes. 91% recovery of platinum from filaments as chloroplatinic acid hydrate has been achieved by *aqua regia* digestion of manually isolated filaments. Cost-benefit analysis shows the proposed process derives sufficient value to cover landfill costs for what is left of the waste thermocouples after platinum removal; provide ~5 days employment; and provide 63% materials cost savings for electrode preparation in comparison to purchasing commercially available chloroplatinic acid hydrate. The proposed local industrial symbiosis would, per year, divert ~50 g of platinum from landfill, avoid up to 1400 kg of CO_2 emissions associated with primary production of an equivalent quantity of platinum, and give enough platinum to produce catalytic electrodes for ~500 m^2 of dye-sensitized solar cells, which could supply clean energy for 12 homes in the locality. The process exemplifies the environmental, economic and social benefits available through adoption of circular practices, which make use of secondary materials available within the local economy by valorizing wastes. The process also overcomes economic barriers to critical raw materials (CRMs) recovery from dissipative applications.

1. Introduction

The world faces the limits of current 'linear' economic models due to resource security issues, growing population and increasing per-capita consumption. Transition is necessary to a new 'circular economy': a resource-efficient industrial economy which decouples economic growth from resource consumption (EC, 2014b; Ellen MacArthur Foundation, 2013; O'Connor et al., 2016). In a circular economy, the concept of 'waste' is replaced with one of 'resource' and process waste is reduced through industrial symbiosis, whereby process waste becomes the feedstock of another process. In this way, materials are retained in an economically productive capacity, cascading across multiple product lifecycles. Enhanced resource-efficiency will deliver synergistic economic, environmental and social benefits (Ellen MacArthur Foundation, 2013). Of significant importance to sustainable economic growth and transition to a low-carbon society is a secure supply of critical raw materials (CRMs), (The ad-hoc Working Group, 2011; EC, 2008;
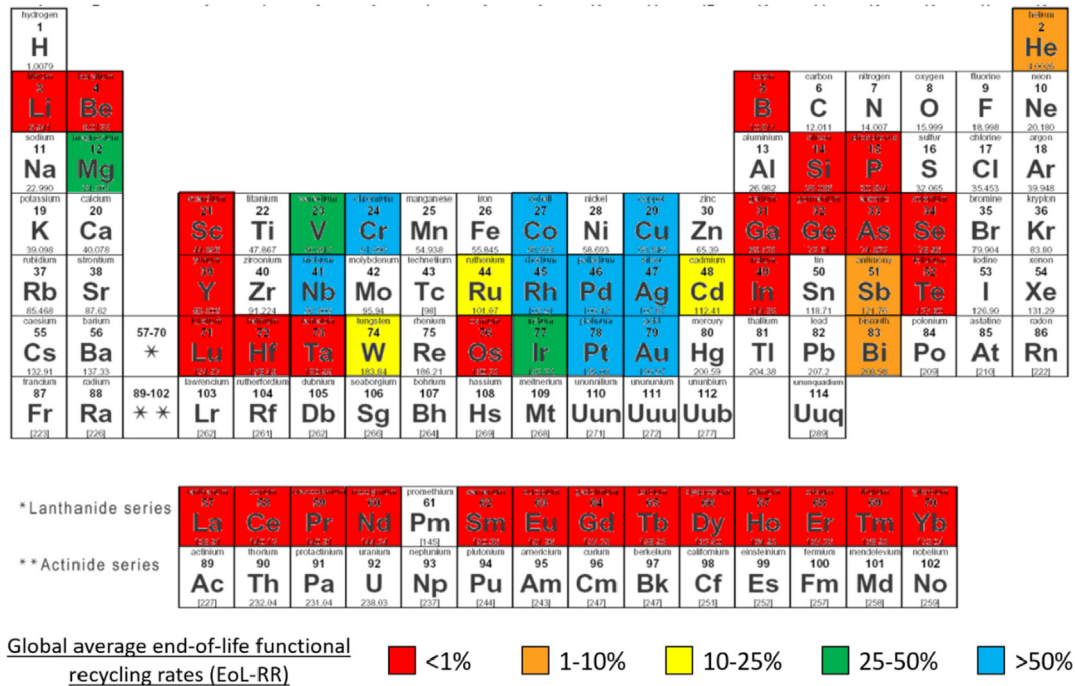
Fig. 1. Global end-of-life functional recycling rates (EoL-RR) of elements highlighted as critical in recent assessments (adapted from Graedel et al., 2011); critical materials identified by (EC, 2011, 2014a; Harfield et al., 2014; Deloitte Sustainability et al., 2017b); data on recycling rates from (Graedel et al., 2011; Deloitte Sustainability et al., 2017a).

EC, 2014a; Deloitte Sustainability, 2017b), and widespread deployment of low-carbon renewable energy technologies. CRMs face future supply bottlenecks and their global recovery rates are currently low as shown by Fig. 1 which shows average end-of-life functional recycling rates (EoL-RR) of elements highlighted as critical in recent criticality assessments (Reck and Graedel, 2012). Average EoL-RR is a metric which presents the quantity of given material recovered from end-of-life products as a percentage of the quantity of the amount of materials present in end-of-life products (Graedel et al., 2011).

CRMs are vital to the functionality of many low-carbon technologies upon which reductions in global emissions and achieving sustainability with the planet rely (Buchert et al., 2008; EC, 2014a; Reck and Graedel, 2012). The scale of deployment of renewable technologies, particularly photovoltaics (PV) may well be constrained by access to CRMs (de Castro et al., 2013). Elshkaki and Graedel (2013) analysed the future development of electricity generation technologies and the metals required for their components using a multi-level dynamic material flow model which showed that all PV technologies face future resource supply constraint. Moss et al. (2013) examined the future materials demand to 2020 and 2030 resulting from six low-carbon technologies of the EU's Strategic Energy Technology Plan (SET-Plan) for comparison with known global production volumes in 2010. This revealed that supply of neodymium (Nd), dysprosium (Dy), indium (In), tellurium (Te) and gallium (Ga) represent high risk to technology deployment, particularly for wind and solar power. Increasing CRM recovery rates will be crucial if demand for widescale deployment of sustainable technologies, particularly PV, is to be met (Tao and Yu, 2015).

A reason for low recovery rates of CRMs, even for valuable metals like platinum (Pt), is the use of these metals in dissipative applications, i.e. where they are present in low concentrations and the consequent high costs of recovery and low total recoverable value make traditional recycling routes unfeasible, resulting in loss

of these elements from the economy (Charles, 2015; Reller et al., 2009; Richter and Koppejan, 2016; Rotter and Chancerel, 2012; Zimmermann and Gößling-Reisemann, 2013). This is exemplified by the low recycling rate of Pt from electronics.

Platinum is a CRM with high economic value (>\$37/g)[1] reflecting its low abundance in the Earth's crust as well as the economic and environmental costs of its production (13,954 t CO_2/t)[2] (Schluep et al., 2009). Table 1 gives global demand and recycling rates for Pt by end use sector. The high value of platinum has driven efficient recycling from applications such as industrial chemical catalysts and bullion where use and management of these materials is carefully controlled and where recycling rates are very high, ~95% when collection and recovery processes are efficient. As a result of low collection rates, recycling rates from auto catalysts are only ~50% despite available efficient recycling processes. Recycling rates from electronics are very low, 0–5%, mainly due to the dissipative use of platinum in electronics, low collection rates for waste electrical and electronic equipment (WEEE), and poor product design for recycling and recovery (Hagelüken, 2012).

Low recycling rates are typical for many of the CRMs in electronics, where they are often used in trace amounts within complex systems. The dissipative nature of the application of many CRMs in WEEE represents considerable economic and technical barriers to their recovery. Ueberschaar et al. have shown this to be the case for Ga recovery from LEDs and ICs on PCBs in which small amounts of Ga are diluted within a complex mixture of materials (Ueberschaar et al., 2017). If cost-effective recovery of CRMs in dissipative applications in WEEE could be achieved, then utilisation of this rich secondary resource could mitigate the issue of CRM supply bottlenecks (Buchert et al., 2008, 2012; Huisman et al., 2016) and offset costs and emissions associated with their production. Menikpura

---

[1] LME 10/7/15, converted from GBP at 1.32 \$/£.
[2] 4100 times greater CO_2 emitted per unit mass of metal produced than copper.

Table 1
Global demand for platinum by end use sector in 2015 and estimated end-of-life (EoL) recycling rates.

Application	Global Demand		Recycling Rate (%)
	(10^3 Troy Oz) (O'Connell et al., 2016)	% of demand	(EC, 2015; Graedel et al., 2011)
Autocatalyst	3011	40	50–55
Jewellery	2456	32	90–100
Industrial Total	1629	22	80–90
Chemical	494	7	≤90[a]
Electronics	151	2	0–5
Glass	163	2	
Petroleum	100	1	≤90[a]
Other Industrial	721	10	10–20[b]
Retail Investment	474	6	90–100[c]
Total	7570		60–70[b]

[a] recovery from catalysts used by this sector
[b] includes sensors, crucibles, medical/dental and decorative applications
[c] excludes coins and bullion-no typical end-of-life management, reuse is common

et al. have used LCA to demonstrate that recycling of WEEE in Japan under the Home Appliances Recycling Law (HARL) would result in considerable green house gas emission savings as a result of the avoidance of virgin materials production (Menikpura et al., 2014). Hong et al. have demonstrated that recycling of WEEE is environmentally beneficial in comparison to alternative landfill or incineration scenarios as a result of a reduction in human toxicity, terrestrial ecotoxicity, freshwater ecotoxicity and marine ecotoxicity (Hong et al., 2015).

Enhancing recycling rates of CRMs from dissipative applications relies on improving the cost-benefit of recovery. This can be achieved through enhancement of eco-design in products to reduce costs of disassembly and retain CRMs in closed-loop applications as demonstrated by Richter and Koppejan (2016) in their study of extended producer responsibility systems for gas discharge lamps in Nordic countries. However, for existing products achieving the necessary cost-benefit for recovery of CRMs requires reduction in costs of recovery through other means. Hydrometallurgical processes for recovery of materials from WEEE, involving digestion of metals with subsequent recovery from solution, have been demonstrated to be more efficient and environmentally friendly than physical separation and pyrometallurgical processes, and through reduction of the use of reagents the costs of such processes can be minimized. This is a strategy that has been used to create more cost-effective recovery processes for CRMs from WEEE. Diaz et al. (2016) have demonstrated an electrochemical recovery process, which relies on the regeneration of ferric ions as weak oxidizers for selective recovery of base metals leaving precious and critical materials for extraction, with reduced chemical demand. Rocchetti et al. (2015) have developed a cross-current leaching process for recovery of In from LCD screens, in which a single quantity of nitric acid is used to leach low quantities of In from multiple screens until a concentration of In in solution is achieved which can be economically recovered.

Recycling of materials from WEEE for fabrication of solar cells is not only environmentally beneficial in comparison to primary resource based production, but offers a potential pathway to reduced energy payback times (EPBT), reduce levelised cost of energy generation (LCOE), and enhanced competitiveness and intangible value for PV manufacturers in a global market in which consumers are becoming increasingly environmentally aware (Charles et al., 2016). In light of this, numerous processes for fabrication of solar cell components from wastes have been developed at lab scale recently. Chen et al. (2014) developed a process by which lead (Pb) halide perovskite solar cells could be manufactured from waste lead-acid car batteries. The Pb based electrodes are converted to high purity PbI_2, the precursor necessary for reaction with methylammonium iodide in order to deposit the photoactive methylammonium lead iodide perovskite layer in solar cells. Nair et al. (2014) have created carbon counter electrodes for dye-sensitized solar cells (DSSCs) from waste zinc (Zn) batteries, which represents a potential method enabling substitution of critical Pt. Through isolation of carbon in battery electrodes from other materials present, a suspension can be produced and cast onto indium tin oxide (ITO) glass substrates. The ITO glass in LCD screens from WEEE has also been successfully used as substrates for solar cells by both Ayaz et al. (2016) and Chen et al. (2015), which represents a route through which solar cell manufacturing can be decoupled from the primary supply of In. Conversion of each of these waste materials into added-value materials for solar cell production represents an alternative pathway for recovery, which may result in greater cost-benefit than is achievable through traditional recycling pathways for these wastes. Such strategies may be used to achieve the financial driving force necessary to enhance recovery efficiency of CRMs from dissipative applications in WEEE, which at present are not economically recoverable, while reducing manufacturing costs for new devices.

A significant application of Pt in industrial electronics is in thermocouple wire. The thermocouple temperature sensors market is estimated at $1.6 billion in 2018 with a growth rate of 6.6%/year over the period 2014–2020 (Mordor Intelligence, 2017). Measurement of molten metal temperatures in foundries and steel plants is almost exclusively conducted using single use thermocouples (Fig. 2) containing a pair of filaments, one of which is either pure Pt or PtRh6% alloy, and the other is Pt alloyed with 10–30% Rh depending on the required working temperature range. Recovery of platinum group metals (PGMs) from waste thermocouples (WTCs) is hindered by the small quantities of PGMs present in each thermocouple (Godley, 2014). However, opportunities exist within the circular economy for innovative recovery models which valorize materials that may otherwise be lost when recovery through traditional recycling chains is not economic (Chamberlin et al., 2013). As shown here, a circular economy approach involving industrial symbiosis i.e. "an association between two or more industrial facilities or companies in which the wastes or by-products of one become the raw materials for another" (WRAP, 2015), may be used to drive cost effective recovery of platinum from waste thermocouples (Fig. 3).

Although the term industrial symbiosis has developed with the field of industrial ecology, and the principle has gained popularity as interest in circular economy has grown, the principle itself can be seen enacted throughout history. Industrial symbiosis is tied to the very birth of the chemical industry. Perkin's manufacture of mauveine laid the foundations for the synthetic dye industry. These 'synthetic colours were the product of a completely new industry that was based on the hydrocarbons distilled out of coal tar, previously the inconvenient waste of coal gas works' (Travis, 1993). For the past 30 years, symbiotic industry has grown around the sugar industry, benefiting from the availability of sugarcane waste residues, such as bagasse and leaves. This has become the feedstock of a number of industries which employ lignocelluslosic biconversions to create chemicals, such as luvelinic acid and itaconic acid, from which an enormous variety of value-added commercial products are produced. Speciality enzymes, organic acids and bio-ethanol are all produced from the waste biproduct of the sugar industry (Chandel et al., 2012; Geilen et al., 2010). Perhaps the most well-known example of industrial symbiosis today is in Kalundborg, Denmark. The Kalundborg symbiosis is a partnership between the Kalundborg Municipality and eight other organisations i.e. Novo Nordisk, Novozymes, DONGEnergy, RGS90, Statoil, Gyproc, Kalundborg Supply and KaraNoveren. These buy and sell waste
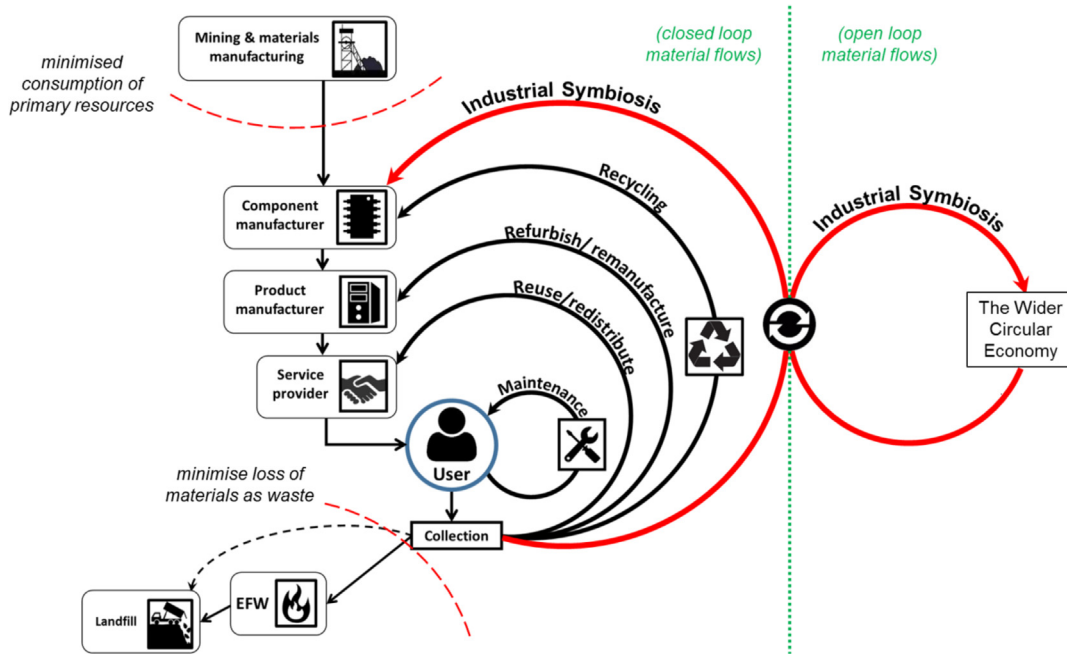
Fig. 2. Material flows in a circular economy drawing on secondary raw materials from the wider circular economy through industrial symbiosis, (adapted from Ellen MacArthur Foundation, 2013).
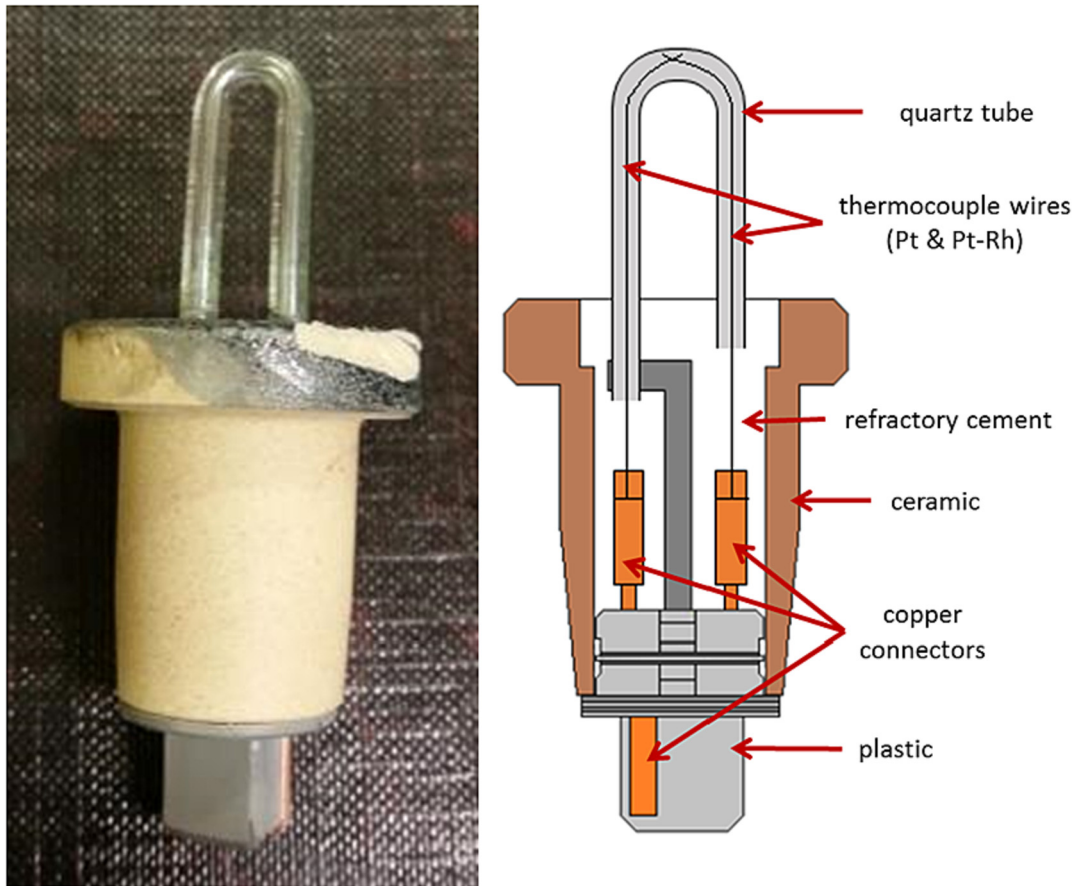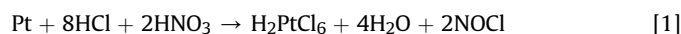

Fig. 3. Waste Heraeus Electro-Nite Positherm expendable immersion thermocouple (schematic diagram adapted from Van der Perre, 2000).

from each other in a closed cycle of industrial production. This is the world's first example of 'well-functioning' industrial symbiosis which has been driven by economic benefits resulting from energy and resource savings. A number of products are traded including steam, ash, gas, heat and sludge with over 30 exchanges of water, energy and other by-products between partners (Ehrenfeld and Gertler, 1997). Industrial symbiosis in the chemical industries has been reviewed by Cui and Liu (2017) who highlight a number of studies that confirm the environmental and economic benefits to organisations who establish symbiotic relationships, including the Midong Chemical Industrial Park, China which has resulted in > ¥380 million savings through avoidance of 5.86 million tonnes of resource consumption and waste emissions. Recent research into potential industrial symbiosis processes includes an LCA assessment conducted by Ilias et al. (2018) on a proposed industrial symbiosis between crystalline silicon photovoltaics (Si-PV) manufacturing and recycling in which Si wafers are recovered from EoL modules, and remelted into ingots for use in fabrication of wafers for new modules. The results confirm that 'energy payback time' for the new modules is drastically reduced and that energy return on investment is ~17 times that initially invested, indicating that the proposed process is both environmentally and commercially viable. If the economic benefits of industrial symbiosis can be harnessed through use of WTCs for creation of added-value Pt compounds for manufacturing, then the economic barriers to recovery of Pt from these devices may be overcome.

1.1. Description of the industrial symbiosis strategy

Chloroplatinic acid hydrate is an important precursor in many applications of platinum (Chen and Holt-Hindle, 2010). It is more expensive than platinum ($102/g at ~38 wt% Pt), and conversion of the Pt in waste thermocouples to chloroplatinic acid hydrate, an 'added value' Pt compound, could significantly increase the derivable value from Pt in the filaments. Following manual isolation of Pt filaments from WTCs it is possible to convert these to chloroplatinic acid hydrate by digestion in *aqua regia* through reaction 1, followed by removal of nitric acid from the resulting solution by boiling and evaporation to dryness following addition of hydrochloric acid (HCl) to yield solid $H_2PtCl_6.xH_2O$, reaction 2 (Renner et al., 2001).

$$Pt + 8HCl + 2HNO_3 \rightarrow H_2PtCl_6 + 4H_2O + 2NOCl \quad [1]$$

$$3HCl + HNO_3 \rightarrow Cl_2 + 2H_2O + NOCl \quad [2]$$

This simple process requires no specialist equipment other than a fume hood, and produces no solid or liquid waste other than WTCs minus filaments. The potential for small scale recovery close to the source of generation of WTCs offers interesting possibilities at low economic and environmental cost in comparison to traditional recycling routes. If a suitable partner organization could be found that uses chloroplatinic acid hydrate, then an industrial symbiosis strategy could potentially lead to:

- increased levels of PGM recovery from end-of-life devices;
- reduced waste management costs for producers of WTCs;
- mitigation of materials criticality issues;
- reduced environmental and economic costs for organizations using chloroplatinic acid hydrate.

A local foundry[3] operating in Baglan, South Wales produces

>43,000 WTCs annually. Currently, these are landfilled at a cost (2015 data) of $158.40/tonne ($132/tonne landfill tax + $26.40 gate fee) for lack of viable recycling options. Conscious of resource security concerns over PGMs, this company sought a recycling route which recovers PGMs from WTCs. A local research centre[4] conducts research into the manufacture and optimization of DSSCs at their site, also in Baglan, South Wales, and currently buys chloroplatinic acid hydrate, in 1 g quantities, for fabrication of DSSC catalysts (Hagfeldt et al., 2010) (Fig. 4). (The role of the Pt catalyst in a DSSC is to catalyse the reduction of tri-iodide to iodide at the counter electrode, which allows the iodide to regenerate the dye in the reverse reaction at the working electrode.) These two organisations are excellent partners for the proposed local industrial symbiosis: the foundry generates waste of potential value to the research centre.

$$I_3^- + 2e^- \rightarrow 3I^- \quad [3]$$

To evaluate the potential industrial symbiosis, the following question was asked: can chloroplatinic acid hydrate of sufficient quality for use in DSSCs be synthesized from WTCs in sufficient quantity and at sufficient cost-benefit to justify the process? Here, the answer to this question is shown to be 'yes' and that the barriers to recovery of Pt from this dissipative application in thermocouples may be overcome by local industrial symbiosis. This example also illustrates the benefits of the circular economy/industrial symbiosis approach.

Although this article focuses on the example of Pt from WTCs for DSSC counter-electrode catalysts in a relatively small scale local operation, chloroplatinic acid hydrate is important in numerous applications where Pt deposition is required. A major example for low-carbon technologies is in the preparation of catalysts for fuel cells (He et al., 2004; Pozio et al., 2002; Prabhuram et al., 2003). Furthermore, small-scale local operations such as this are of significant importance to a healthy circular economy. Economies require a balance of various size businesses to thrive in the long term with larger enterprises bringing volume and efficiency and smaller ones offering alternative models when crises occur (Ulanowicz et al., 2009). A multitude of similarly sized operations throughout the circular economy could deliver material cost savings and domestic sources of CRMs for manufacturing as shown by this example, while providing economic resilience through diversity (Ellen MacArthur Foundation, 2013). It should be noted that Pt is only one of the many elements facing future supply bottlenecks that may be sourced from available 'wastes', and in particular, from WEEE (Buchert et al., 2008, 2012).

2. Experimental

To verify the suitability of this industrial symbiosis process WTCs were collected and inspected and filaments were isolated and converted to chloroplatinic acid hydrate from which DSSC counter electrodes were prepared. To verify the suitability of WTCs as a Pt source for DSSC catalysts and the procedure of chloroplatinic acid hydrate synthesis, purchased Pt wire was also digested to produce chloroplatinic acid hydrate, and yields compared. These two chloroplatinic acid hydrate samples, along with a standard purchased sample, were used to create counter electrodes. Electrical impedance spectroscopy (EIS) was used to compare the electrochemical performance of counter electrodes created from the different chloroplatinic acid hydrate samples in 'dummy cells'.

---

[3] Weartech International Ltd. Unit 1, Moor Road, Baglan Industrial Estate, Port Talbot SA12 7BJ, UK.

[4] SPECIFIC IKC, Baglan Bay Innovation Centre, Central Avenue, Port Talbot, SA12 7AX, UK.
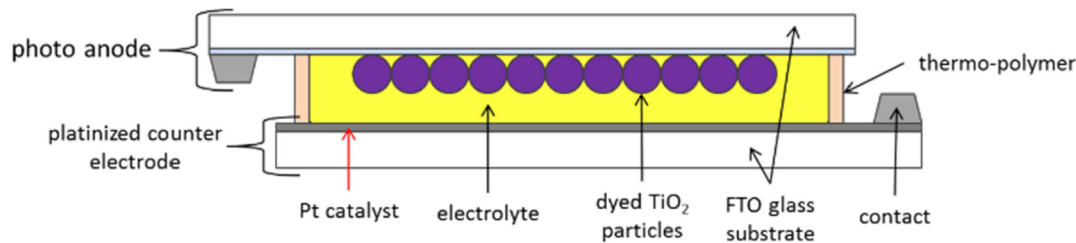
Fig. 4. Structure of a dye-sensitized solar cell (DSSC).

A cost-benefit analysis for the proposed industrial symbiosis was conducted for comparison with current costs incurred by the WTC producer and chloroplatinic acid hydrate user.

2.1. Materials

A 5.5 kg sample of WTCs was obtained from the local foundry, and was coned and quartered to give a representative sub sample of 82 individual WTCs for further study. 99.998% Pt wire (Johnson Matthey) was used as received. HCl (31.5–33.0%) and HNO$_3$ (69–72%) (CertiFied AR (analytical reagent), Fisher Chemicals). Chloroplatinic acid hydrate (≥99.9% trace metal basis); isopropyl alcohol (IPA) (≥99.7%); TraceCERT® 1000 mg/L Rh in HCl standard solution; TraceCERT® 1000 mg/L Pt in hydrochloric acid (HCl) standard solution; 1-methyl-3-propylimidazolium iodide (98%); benzimidazole (98%); iodine (99.8% trace metal basis); and guanidinium thiocyanate (99%) were purchased from Sigma-Aldrich. 3-methoxypropionitrile (98%) was obtained from Acros Organics. All chemicals were used as received.

2.2. Methods

The overall procedure of isolation of filaments, chloroplatinic acid synthesis and fabrication of DSSC counter electrodes is outlines in Fig. 5. Visual inspection of thermocouple filaments following isolation from WTC (Fig. 5, stage 1) was conducted with a Hampshire Micro:Wessex WSL1 long arm stereo microscope. Diameters of filaments were measured from scanning electron microscope (SEM) images and their alloy composition was measured using Energy dispersive x-ray spectroscopy (SEM/EDS) analysis conducted with a Hitachi TM3000 table top microscope running BrukerQuantax 70 software for EDS analysis. Alloy composition was confirmed by x-ray fluorescence (XRF) analysis using Fischer Instrumentation Fischerscope XDAL-FD system and Fischer WinFTM software. A 50 keV x-ray beam with circular cross-section of 0.07 mm was used with 60 s scan times and aluminium primary filter applied. Pt analysis was quantified from x-ray emission signals at 9.42 keV (Lα_1) and 11.07 keV (Lβ_1), and Rh was quantified from x-ray emission signals at 20.22 keV (Kα_1) and 22.72 keV (Kβ_1).

2.2.1. Synthesis and analysis of chloroplatinic acid samples

~100 mg of Pt filaments, or wire, were digested by boiling in 10 ml of *aqua regia* (3:1 HCl/HNO$_3$) for 3 h. Following digestion, solutions were evaporated to near dryness to remove nitric acid before dissolution of the residue in 10 ml 1:1 HCl/H$_2$O. Chloroplatinic acid hydrate was obtained from 5 ml of this solution by evaporation to dryness with further drying at 80 °C for 12 h (Fig. 5, stage 2). The remaining 5 ml of solution was retained for analysis and fabrication of DSSC counter electrodes.

Pt analyses by atomic absorption spectroscopy (AAS) was carried out using a PerkinElmer AAnalyst 200 with a single element PerkinElmer 50 mm Lumina Universal hollow cathode lamp and an air-acetylene flame, using the method of multiple standard additions (Skoog et al., 2014). Analysis was conducted at 265.95 nm using a slit width of 1.05 mm (2.7 nm bandpass), flow rates for air and acetylene of 10 and 2.5 L/min respectively, and a signal integration time of 3 s. The instrument was calibrated with TraceCERT® 1000 mg/L Pt in HCl standard solution. Inductively coupled plasma − optical emission spectroscopy (ICP-OES) analyses were carried out using an Agilent Varian 710 ES ICP-OES instrument with an axial torch, Varian SPS 3 autosampler, ICP expert II software. A plasma flow of 15 L/min, nebuliser pressure of 240 kPa, sample uptake delay of 30 s, 10 s rinse time, and dry argon as carrier gas were used. Quantitative analysis was conducted at 3 wavelengths for platinum (203.646 nm, 214.424 nm, 265.945 nm -1st to 3rd order spectra) with 3 replicates at each wavelength. Results for platinum are taken as the mean result from three wavelengths. Analysis of Rh was conducted at a single wavelength only (343.488 nm − first order spectrum) as poor calibration of 2nd and 3rd order spectra were obtained, probably due to interference from other elements present. Analyses were performed in duplicate for each sample. Pt content of synthesized chloroplatinic acid hydrate samples is given as the mean of the results obtained from AAS and ICP-OES analyses.

2.2.2. Fabrication and characterization of platinized counter-electrodes

NSG Tec7 FTO glass (7 Ω/sq) was cut into 25 mm × 15 mm pieces. A small hole was drilled into the non-conductive surface adjacent to the upper right hand corner of a 1 cm^2 area at their centre to allow filling of cells with electrolyte. The glass was cleaned with distilled water and detergent, and rinsed with distilled water and then IPA before drying with compressed air. 100 μL of ~5 mM chloroplatinic acid in IPA was spin coated onto the FTO at 2000 rpm for 40 s, accelerating at 2000 rpm/s and then heated to 400 °C for 30 min to generate the platinized electrode (Fig. 5, stage 3). Pairs of counter-electrodes were used to produce 'dummy cells' (Baker et al., 2015; Fang et al., 2004a, 2004b; Hauch and Georg, 2001; Liberatore et al., 2009), sealed together with a 1 cm × 1 cm, 25 μm Surlyn™ gasket (Fig. 6a). Cells were filled with electrolyte (0.8 M 1-methyl-3-propylimidazolium iodide, 0.3 M benzimidazole, 0.1 M iodine, and 0.05 M guanidinium thiocyanate in 3-methoxypropionitrile) via channels drilled through the glass. Cells were sealed with Surlyn™ and a glass slip. An MBR electronics USS-9210 ultrasonic soldering system was used to apply CERA-SOLZER GS155 solder to the conductive side of each electrode at its terminus.

EIS was performed on the cell using a GAMRY Reference 600 Potentiostat at open circuit voltage. An AC voltage of 10 mV$_{rms}$ was applied over the frequency range 150,000−0.1 Hz. Charge transfer resistance (R_{CT}) and double layer capacitance (C_{dl}) values were measured from Nyquist plots of impedance spectra fitted to a Randles equivalent circuit with a short Warburg element (Fig. 6b) (Raistrick et al., 1987), to reflect the finite diffusion within the
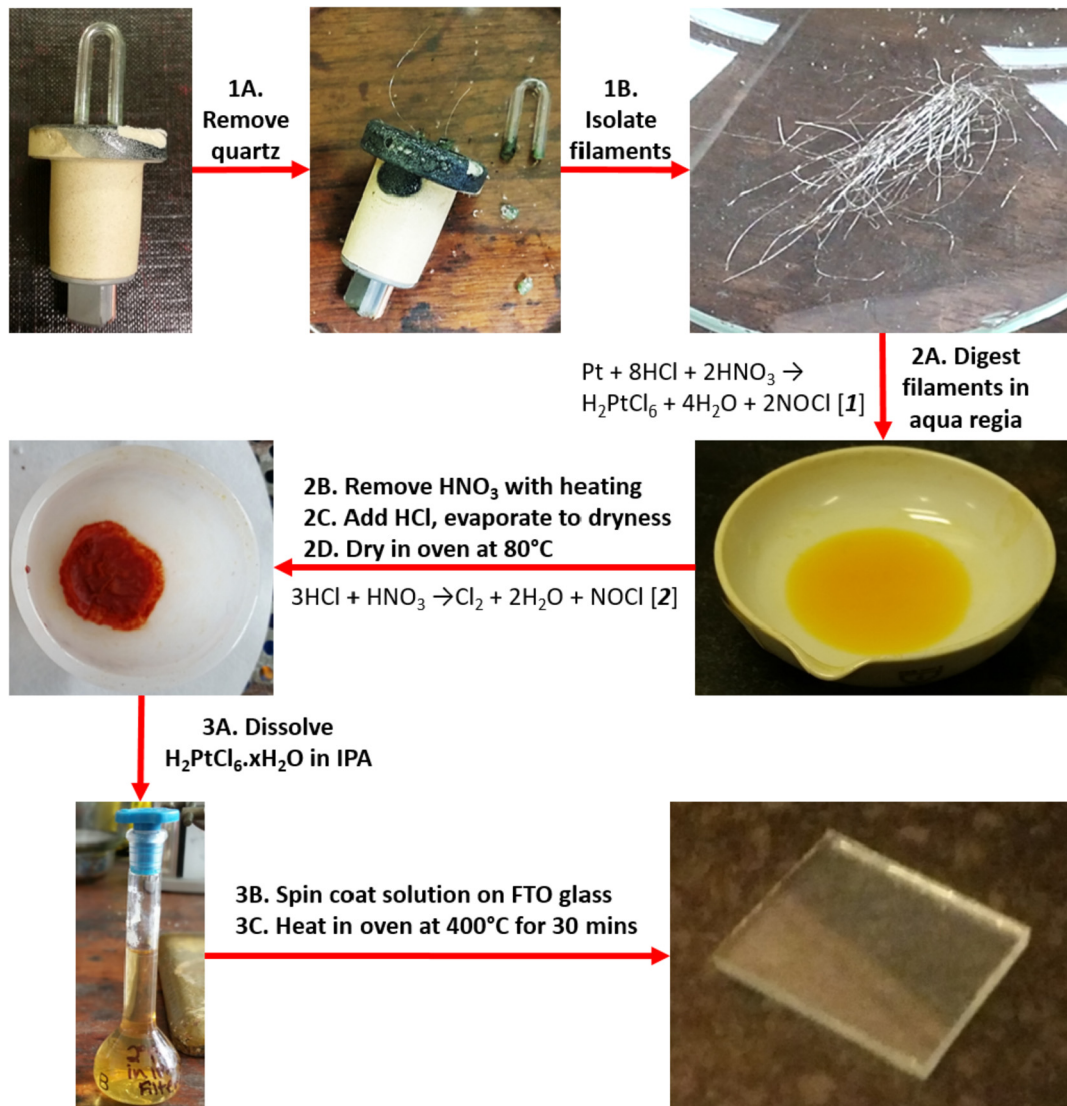
Fig. 5. Procedure for synthesising DSSC counter electrodes from waste thermocouples. The process includes 3 stages: 1) isolation of Pt filaments; 2) synthesis of chloroplatinic acid hydrate; 3) creation of DSSC counter electrodes.

25 μm distance between electrodes in cells, using Z-view software.

The area tested by EIS analysis was 1 cm^2 per electrode as defined by the Surlyn gasket. Exchange current densities at each electrode (j_0) were calculated from measured R_{CT} values using equation i, where F is Faraday's constant, T is temperature, R the gas constant, and n the number of electrons involved in the reaction (Baker et al., 2017).

$$R_{ct} = \frac{RT}{j_0 nF} \qquad (i)$$

SEM imaging of platinized counter-electrodes was carried out at 5 kV using a 30 μm aperture Secondary Electron (SE2) detectors and InLens detectors on a Zeiss Nvision using a Gemini SEM column.

2.2.3. Cost benefit analysis

Cost benefit analysis was carried out by comparison of the cost of purchasing chloroplatinic acid hydrate with the cost of production via the industrial symbiosis process shown in Fig. 7. Labour times for processing WTCs were scaled up from the time taken to process the 82 WTC samples, with labour and overhead costs in line

with the local recycling company overhead rate of $20.91/hour. It was assumed WTC filaments are to be sold by the supplier for conversion into chloroplatinic acid hydrate at a price (d), which covers the costs of isolating the filaments (a) and disposing of processed WTCs in landfill ($158.40/tonne) ($b$). Transport costs ($c$) are incurred by the user of WTCs at a rate of ($0.59/mile). Costs incurred for chloroplatinic acid hydrate synthesis (e) are scaled up from production of 1 g of chloroplatinic acid and take account of chemical costs (HCl ACS reagent grade, 2.5 L: $75.11; HNO$_3$ ACS reagent grade, 2.5 L: $115.63) and electricity costs ($0.20/kWh, UK average 2015). Cost of electricity for the oven used to dry the sample was not included as the oven used is in operation 24 h a day regardless. No waste disposal costs are included in the chloroplatinic acid hydrate production as the process produces no solid or liquid waste, and no labour costs for the synthesis are included as minimal staff time is required for addition of acids during the process and during the digestion process and drying of the product. The total cost of synthesized chloroplatinic acid hydrate to the user (f) is calculated as the sum of transport costs, costs of synthesis, and the price of filaments ($c + d + e$).

A cost-benefit analysis was conducted by comparison of the
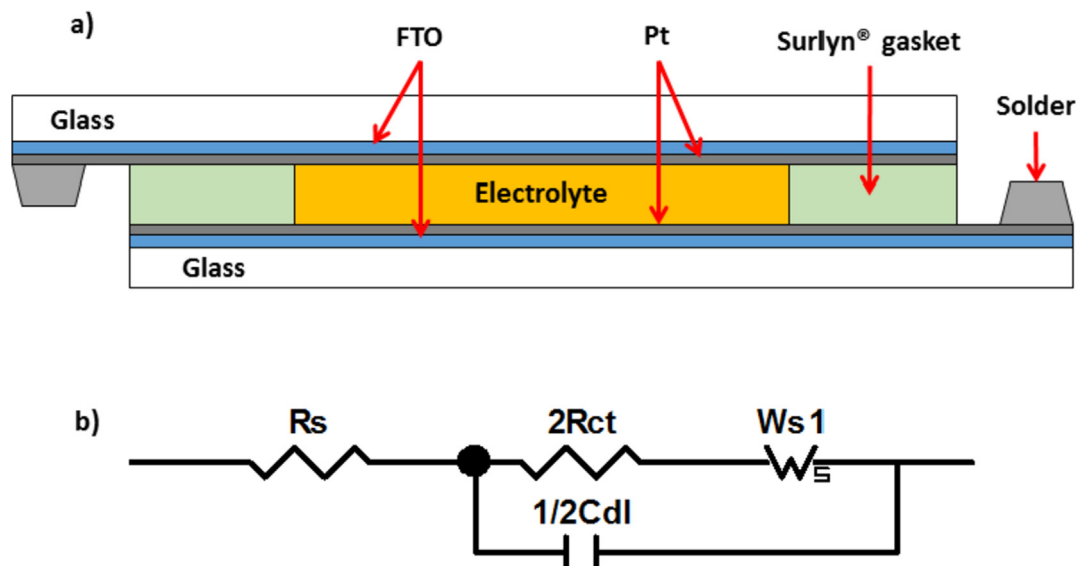
Fig. 6. a) Electrochemical symmetrical 'dummy cells' used for EIS measurements. **b)** Equivalent circuit for 'dummy cells': Randles equivalent circuit with Warburg element. R_S — electrolyte solution resistance; C_{dl} — double layer capacitance; R_{ct} — charge transfer resistance at electrolyte|platinized counter electrode interface; Ws1 — ~short Warburg diffusion.
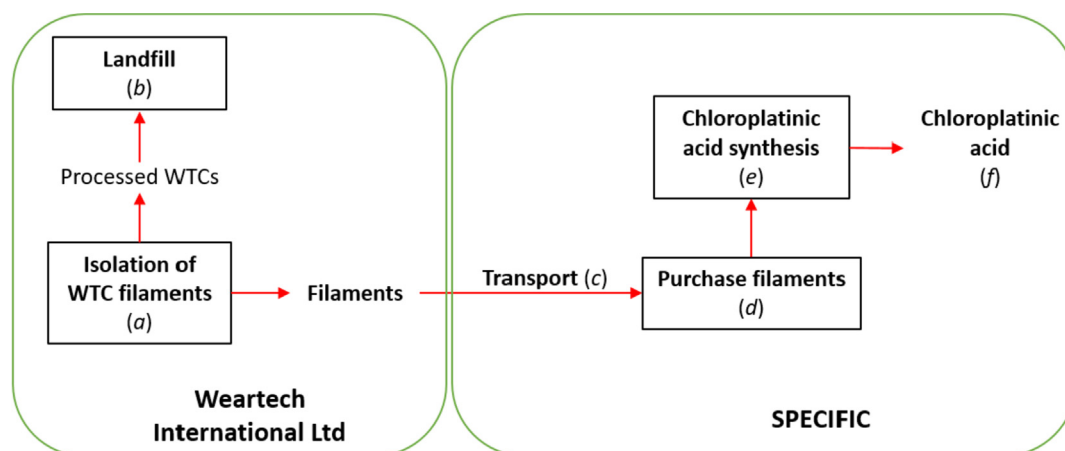
Fig. 7. Industrial symbiosis operations and associated costs of each operation indicated by letters in square brackets: (a) labour and overheads; (b) landfill tax + gate fee; (c) transport; (d) price of filaments (a+b); (e) chemicals + energy; (f) total cost of chloroplatinic acid (c + d + e]).

total cost of chloroplatinic acid hydrate synthesis, with commercial prices of chloroplatinic acid hydrate when purchased in 1 g and 25 g lots from a supplier, and administrative overheads associated with buying chloroplatinic acid hydrate are not included. As chloroplatinic acid hydrate is used to deposit Pt metal on DSSC counter electrodes, the true cost benefit is shown by comparison of the cost per gram of Pt as chloroplatinic acid hydrate with wt%Pt taken into account.

3. Results and discussion

It is convenient to discuss the results in terms of: the isolation of filaments from waste thermocouples; the chemical analysis of the chloroplatinic acid hydrate prepared from these filaments and the suitability of this chloroplatinic acid hydrate for DSSC electrode manufacture; and the environmental impact, and cost benefit, of the proposed industrial symbiosis.

3.1. Isolation of filaments from waste thermocouples

Inspection of WTCs revealed their physical condition to be variable with some in close to 'as new' condition (e.g. Fig. 3) and others damaged extensively with some cracked, and/or quartz missing, and/or caked in the alloy they were used to measure (Fig. 8). Despite damage, most WTCs were found to contain both filaments in their entirety and WTCs without filaments were rare.

The quartz tube was removed with pliers to access the base of filaments protruding from the refractory cement. Filaments were snipped as close to their base as possible to minimise the quantity remaining within the refractory cement of WTCs (Fig. 5, stage 1). This process was timed, and masses of isolated filaments were recorded for subsequent costing exercises. Microscopic analysis of isolated filaments revealed each WTC contained 2 filaments of different diameters, larger filaments with a mass of 1.1 (±0.3) mg and diameter of ~74 μm, and lighter thinner filaments with a mass of 0.4 (±0.1) mg and diameter of 40.5 μm. Diameters of thin and
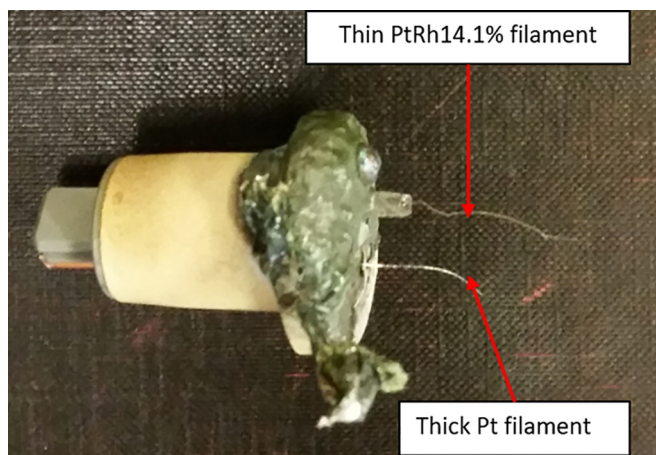
Fig. 8. Waste thermocouple in poor condition with exposed filaments and alloy compositions as determined by SEM/EDS.

Table 2
Pt content of chloroplatinic acid hydrate and Pt recovery yield from WTCs and 99.998% Pt wire.

	Pt source	
	WTCs	Pt wire
Metal Digested		
Mass (*mg*)	97.3 (±0.3)	97.3 (±0.3)
Wt%Pt	95 (±1)	100
Chloroplatinic acid hydrate product		
Mass (*mg*)	173.2 (±0.3)	204.0 (±0.3)
Wt%Pt	49 (±2)	47 (±1)
Pt recovered in product		
Yield (*mg*)	84 (±3)	96 (±2)
%yield	91 (±3)	99 (±3)

thick filaments were measured from images at 1200 to 1800 times magnification, respectively (Fig. 9).

SEM/EDS analysis revealed that thick filaments are ~100% Pt and thin filaments are ~ PtRh14% alloy, (close to the alloy composition of PtRh13% given for ANSI-type R thermocouple filaments in the manufacturer specification and within the tolerance of the EDS (Van der Perre, 2000)). XRF analysis confirmed the thicker filament to be 100% Pt and the lighter filament to be PtRh12.75% alloy. Assuming filaments are present in a 1:1 length ratio, then the average composition of filaments is Pt96%Rh4%.

WTCs have an average PGM concentration of ~120 ppm, considerably higher than the majority of ores refined for Pt production (Nishnij-Tagil, Russia: 10–20 ppm; South African Bushveld complex: 3–20 ppm) (Renner et al., 2001). 97.3 (±0.3) mg of Pt bearing filaments were isolated from the 82 WTC sub-sample, an average of 1.2 mg per thermocouple.

3.2. Chloroplatinic acid hydrate

AAS analysis of the solution after filament digestion shows the average Pt content of WTC filaments to be 95 (±1)%, in line with expectation. Table 2 gives details of yields and metal content for chloroplatinic acid hydrate synthesized from thermocouple filaments and 99.998% Pt wire for comparison. Both chloroplatinic acid

hydrate samples synthesized have significantly higher Pt content than commercial chloroplatinic acid hydrate (38.6 (±0.2) wt% Pt), probably as a result of the oven drying at 80 °C.

3.3. Assessment of suitability for DSSC electrode manufacture

The mean values of R_{CT} for dummy cells produced from chloroplatinic acid hydrate derived from different sources are given in Table 3. The slightly higher R_{CT} value observed for cells made from the bought material is likely due to a lower quantity of Pt deposited on the electrode surface as a result of the slightly lower concentration Pt solution used, possibly as a consequence of deliquescence of commercial chloroplatinic acid hydrate sample during weighing due to its highly hygroscopic nature. Column j_0/[Pt] gives exchange current densities for the deposited Pt layer per unit concentration of Pt in IPA used to deposit the layer and within experimental error the results are the same.

The data in Table 3 show that all three sources of Pt are equally suitable for the preparation of DSSC electrodes. The presence of Rh and any other contaminants in WTC-derived chloroplatinic acid hydrate does not have any detrimental effect on the catalytic activity of the platinized electrodes prepared. It was not possible to identify localised metal deposits on the electrodes using SEM across the 5000–100,000× magnification range (the size range of ~1 μm–~10 nm), and so the metal particles are presumed to be smaller than ~10 nm. What is most important for this work is that across this magnification range SEM showed no gross differences in electrodes made from recycled thermocouples compared to those made from pure Pt wire or purchased chloroplatinic acid hydrate.
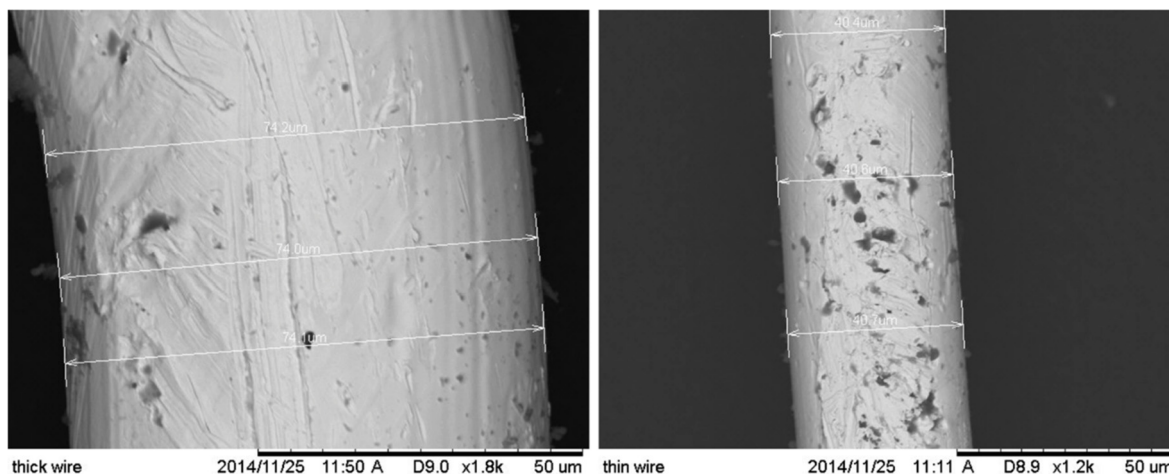

Fig. 9. Diameter measurements of thick (left) and thin (right) waste thermocouple filaments from SEM images at 1800 and 1200 times magnification, respectively.

Table 3
Average charge transfer resistances (R_{CT}), double layer capacitances (C_{dl}) and exchange current densities (j_0) at the electrolyte|electrode interface for electrodes in 'dummy cells' produced with platinum from different source; and corresponding j_0 expressed per unit concentration of Pt in IPA used for creation of electrodes (j_0/[Pt]).

Chloroplatinic acid hydrate source	[Pt] in IPA (mM)	R_{CT} ($\Omega\ cm^{-2}$)	C_{dl} (μF)	j_0 ($mA\ cm^{-2}$)	j_0/[Pt] ($mA\ cm^{-2}M^{-1}$)
Pt wire	4.41($\pm$0.06)	5.15($\pm$0.31)	10.05($\pm$0.46)	2.47($\pm$0.15)	0.56($\pm$0.03)
WTC	4.70($\pm$0.06)	4.80($\pm$0.58)	10.73($\pm$0.55)	2.65($\pm$0.32)	0.56($\pm$0.07)
Purchased from supplier	3.84($\pm$0.05)	7.00($\pm$0.56)	9.20($\pm$0.23)	1.82($\pm$0.15)	0.47($\pm$0.04)

Errors are standard error on the means, (N = 6)

3.4. Supply and environmental impact

The local foundry currently generates ~43,340 WTCs per year, which would yield 51.4 ($\pm$0.2) g of filaments, more than enough to support the current activities of the local research centre. Recovery of this quantity of Pt offsets demand for an equivalent quantity from primary sources, negating the requirement to mine and process between 2.5 and 17 tonne of ore and saving ~200–1400 kg CO_2. Counter-electrodes for highly efficient DSSCs require 5–50 µg/cm^2 of Pt (Chen et al., 2010; Liberatore et al., 2009; Papageorgiou, 2004), therefore WTCs from the foundry could be used to produce 100–1000 m^2 of electrodes for DSSC annually. 500 m^2 of DSSCs is sufficient to provide enough solar electricity for ~12 households in South Wales UK, based on the local solar irradiance and a cell efficiency of ~12%.

3.5. Cost benefit analysis

The associated costs of the potential industrial symbiosis operation shown in Fig. 7 are given in Table 4 with a cost benefit analysis given in Table 5.

The cost of producing WTC-derived chloroplatinic acid hydrate was calculated to be $47.39/g (Table 4), less than half the current commercial price of chloroplatinic acid hydrate when purchased in 1 g quantities (Table 5). This equates to a cost of 97.51 $/g for the WTC Pt rather than the 265.71 $/g Pt for commercially available $H_2PtCl_6.xH_2O$, and a material cost saving of 63% for the chloroplatinic acid hydrate user. The majority of cost is incurred in the manual isolation of filaments at the foundry. Despite this, there is sufficient cost benefit to justify ~5 days of employment per year at 37 h/week on UK national living wage, whilst also covering the foundry landfill costs for what is left of the WTCs after removal of the platinum.

Process costs could be reduced further by an increase of scale by extension of the process to take waste thermocouples from other foundries, steel works and glass works, along with the development of semi-automated isolation of WTC filaments. Although traditional automated recycling processes (grinding, with subsequent automated materials separation stages) without prior removal of filaments would render efficient recovery of Pt impossible (Chancerel et al., 2009; Hagelüken, 2006; Hagelüken and Meskers, 2013; Van schaik and Reuter, 2012), a semi-automated process for isolation of filaments from whole WTCs could

Table 5
Comparative cost of platinum as chloroplatinic acid hydrate synthesised from WTCs and purchased in minimum and maximum available quantities.

Pt Source	Cost ($/g)	Wt%Pt	Pt cost ($/g)	Cost benefit ($)
WTC	47.39	48.6	97.51	
Purchased $H_2PtCl_6.xH_2O$		38.6		
1 g quantity	102.56[a]		265.71	168.20
25 g quantity	41.03[a]		106.28	8.77

[a] Commercial price of chloroplatinic acid hydrate from supplier (Sigma-Aldrich, 2016).

accelerate the process whilst reducing costs. In addition, chemical costs - the second most significant in the process, could be reduced by processing greater numbers of filaments simultaneously. Although 10 ml of *aqua regia* was used in this case, a higher solid/liquid ratio could still achieve efficient digestion.

Additional cost benefit may be achievable through automated recycling of the remaining portions of WTCs. Comminution followed by eddy current and density separation techniques could produce Cu, plastic and refractory oxide fractions for recycling in order to valorize this material, which would generate additional revenue whilst reducing landfill cost.

4. Conclusions

The proposed industrial symbiosis valorizes a source of Pt in the waste arising from its use in a dispersive application, for which traditional recycling pathways are uneconomic. Manual isolation of filaments from waste thermocouples (WTCs) with subsequent digestion in *aqua regia* and precipitation from HCl yields chloroplatinic acid hydrate of sufficient quality for use in production of platinized electrodes for dye-sensitized solar cells. The specific foundry-research centre industrial symbiosis described here would result in the annual transfer of ~50 g of Pt from waste to resource. Through conversion of WTC filaments to the 'added value' product chloroplatinic acid hydrate sufficient value is derivable to: cover landfill costs of what remains of WTCs after platinum filaments are removed; provide ~5 days employment; and give 63% materials cost saving on chloroplatinic acid hydrate in comparison to other commercial suppliers.

The diversion of Pt from landfill enhances resource-efficiency and mitigates materials criticality issues by decoupling supply

Table 4
Cost analysis for production of 1 g chloroplatinic acid hydrate from WTCs via the industrial symbiosis process indicated in Fig. 7.

Operation	Costs	supplier costs	user costs	% of total cost
(a)	Labour & overheads	$41.25		87.0
(b)	Landfill	$0.73		1.5
(c)	Transport		$0.32	0.7
(d)	Price of filaments ($a+b$)		$41.98	88.6
(e)	Energy		$1.39	2.9
	Chemicals		$3.70	7.8
(f)	**Total cost** ($c+d+e$)		**$47.39**	

from primary production. The recovery of 50 g Pt from the single foundry discussed here offsets demand for an equivalent quantity from primary sources, negating the requirement to mine and process between 2.5 and 17 tonne of ore, and saving ~200—1400 kg CO_2. Enough chloroplatinic acid hydrate can be synthesized annually from WTCs from this single foundry alone to produce platinum coated counter-electrodes for ~500 m^2 of DSSCs, sufficient to supply clean energy for ~12 households in South Wales.

Acknowledgements

References

Ayaz, M., Kasi, J.K., Kasi, A.K., Samiullah, Ali, M., 2016. Toward eco green energy: fabrication of DSSC from recycled phone screen. Int. J. Relig. Educ. 4 (1), 17—22.

Baker, J., McGettrick, J.D., Gethin, D.T., Watson, T.M., 2015. Impedance characteristics of transparent GNP-Pt ink catalysts for flexible dye sensitized solar cells. J. Electrochem. Soc. 162 (8), H564—H569.

Baker, J.A., Worsley, C., Lee, H.K.H., Clark, R.N., Tsoi, W.C., Williams, G., Worsley, D.A., Gethin, D.T., Watson, T.M., 2017. Development of graphene nano-platelet ink for high voltage flexible dye sensitized solar cells with cobalt complex electrolytes. Adv. Eng. Mater. 19 (3), 1600652.

Buchert, M., Manhart, A., Bleher, D., Pingel, D., 2012. Recycling Raw Materials from Waste Electronic equipment. Oeko Institute e.V.

Buchert, M., Schuler, D., Bleher, D., 2008. Critical Metals for Future Sustainable Technologies and Their Recycling Potential. Oko-Institut & UNEP & UNU, Darmstadt, Germany.

Chamberlin, L., Jasmin, E., Raksit, A., 2013. Wales and the Circular Economy: Favourable System Conditions and Economic Opportunities. Ellen MacArthur Foundation on Behalf of the Waste and Resources Action Programme (WRAP) and the Welsh Government.

Chancerel, P., Meskers, C.E.M., Hagelüken, C., Rotter, V.S., 2009. Assessment of precious metal flows during preprocessing of waste electrical and electronic equipment. J. Ind. Ecol. 13 (5), 791—810.

Chandel, A.K., da Silva, S.S., Carvalho, W., Singh, O.V., 2012. Sugarcane bagasse and leaves: foreseeable biomass of biofuel and bio-products. J. Chem. Technol. Biotechnol. 87 (1), 11—20.

Charles, R., 2015. From E-waste to Green Energy: Waste as a Critical Material Source for Photovoltaic Technologies: a Case Study for Industrial Symbiosis, the Asian Conference on Sustainability, Energy and the Environment 2015 (ACSEE 2015) iafor, Kobe, Japan.

Charles, R.G., Davies, M.L., Douglas, P., 2016. Third Generation Photovoltaics: Early Intervention for Circular Economy and a Sustainable Future, 2016 Electronics Goes Green 2016+ (EGG), pp. 1—8.

Chen, A., Holt-Hindle, P., 2010. Platinum-based nanostructured materials: synthesis, properties, and applications. Chem. Rev. 110 (6), 3767—3804.

Chen, C.-M., Chen, C.-H., Wei, T.-C., 2010. Chemical deposition of platinum on metallic sheets as counterelectrodes for dye-sensitized solar cells. Electrochim. Acta 55 (5), 1687—1695.

Chen, C.C., Chang, F.C., Peng, C.Y., Wang, H.P., 2015. Conducting glasses recovered from thin film transistor liquid crystal display wastes for dye-sensitized solar cell cathodes. Environ. Technol. 36 (23), 3008—3012.

Chen, P.-Y., Qi, J., Klug, M.T., Dang, X., Hammond, P.T., Belcher, A., 2014. Environmentally-responsible fabrication of efficient perovskite solar cells from recycled car batteries. Energy Environ. Sci. 7, 3659—3665.

Cui, H., Liu, C., 2017. Applying industrial symbiosis to Chemical Iindustry: a literature review. In: AIP Conference Proceedings.

de Castro, C., Mediavilla, M., Miguel, L.J., Frechoso, F., 2013. Global solar electric potential: a review of their technical and sustainable limits. Renew. Sustain. Energy Rev. 28, 824—835.

Deloitte Sustainability, British Geological Survey, Bureau de Recherches Géologiques et Minières, Netherlands Organisation for Applied Scientific Research, 2017a. Study on the Review of the List of Critical Raw Materials: Critical Raw Materials Factsheets. European commission, Brussels.

Deloitte Sustainability, TNO, British Geological Survey, Bureau de Recherches Géologiques et Minières, 2017b. Study on the Review of the List of Critical Raw Materials - Final Report. European Commission.

Diaz, L.A., Lister, T.E., Parkman, J.A., Clark, G.G., 2016. Comprehensive process for the

recovery of value and critical materials from electronic waste. J. Clean. Prod. 125, 236—244.

EC, 2008. Commission staff working document accompanying the communication from the commission to the european parliament and council: the raw materials initiative. In: Meeting Our Critical Needs for Growth and Jobs in Europe, Brussels.

EC, 2011. Critical raw materials for the EU - report of the working group on defining critical raw materials. In: DG Enterprise and Industry. European Commission. http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical/index_en.htm.

EC, 2014a. Report on Critical Raw Materials for the EU - Report of the Ad Hoc Working Group on Defining Critical Raw Materials.

EC, 2014b. Speaking points by environment commissioner Janez Potočnik on circular economy. In: Press Conference on Circular Economy and Green Employment Initiative, Brussels, 2 July, 2014.

EC, 2015. Report on critical raw materials for the EU - critical raw materials profiles. In: DG Enterprise and Industry.

Ehrenfeld, J., Gertler, N., 1997. Industrial ecology in practice: the evolution of interdependence at Kalundborg. J. Ind. Ecol. 1 (1), 67—79.

Ellen MacArthur Foundation, 2013. Towards a Circular Economy - Economics and Business Rationale for an Accelerated Transition. Ellen MacArthur Foundation. http://www.ellenmacarthurfoundation.org/business/reports.

Elshkaki, A., Graedel, T.E., 2013. Dynamic analysis of the global metals flows and stocks in electricity generation technologies. J. Clean. Prod. 59, 260—273.

Fang, X., Ma, T., Guan, G., Akiyama, M., Abe, E., 2004a. Performances characteristics of dye-sensitized solar cells based on counter electrodes with Pt films of different thickness. J. Photochem. Photobiol. Chem. 164 (1—3), 179—182.

Fang, X., Ma, T., Guan, G., Akiyama, M., Kida, T., Abe, E., 2004b. Effect of the thickness of the Pt film coated on a counter electrode on the performance of a dye-sensitized solar cell. J. Electroanal. Chem. 570 (2), 257—263.

Geilen, F.M.A., Engendahl, B., Harwardt, A., Marquardt, W., Klankermayer, J., Leitner, W., 2010. Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system. Angew. Chem. Int. Ed. 49 (32), 5510—5514.

Godley, M., 2014. Thermocouple Recycling, GC Metals, Personal Communication, 2014.

Graedel, T.E., Allwood, J., Birat, J.-P., Buchert, M., Hagelueken, C., Reck, B.K., Sibley, S.F., Sonnemann, G., 2011. Recycling Rates of Metals - a Status Report, International Resource Panel, International Resource Panel, Working Group on the Global Metal Flows. UNEP.

Hagelüken, C., 2006. Improving Metal Returns and Eco-efficiency in Electronics Recycling - a Holistic Approach for Interface Optimisation between Pre-processing and Integrated Metals Smelting and Refining. IEEE International Symposium on Electronics & the Environment, San Francisco, pp. 218—223.

Hagelüken, C., 2012. Recycling the platinum group metals: a european perspective. Platin. Met. Rev. 56 (1), 29—35.

Hagelüken, C., Meskers, C., 2013. Recycling of technology metals. In: Hieronymi, K., Kahhat, R., Williams, E. (Eds.), E-waste Management, from Waste to Resource. Routledge, Oxon, pp. 63—64.

Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., Pettersson, H., 2010. Dye-sensitized solar cells. Chem. Rev. 110 (11), 6595—6663.

Harfield, P., Harris, C., Sanders, C., 2014. Mapping Critical Resources for Wales. Literature Review, Ecodesign Centre, Cardiff.

Hauch, A., Georg, A., 2001. Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. Electrochim. Acta 46 (22), 3457—3466.

He, Z., Chen, J., Liu, D., Zhou, H., Kuang, Y., 2004. Electrodeposition of Pt-Ru nanoparticles on carbon nanotubes and their electrocatalytic properties for methanol electrooxidation. Diam. Relat. Mater. 13 (10), 1764—1770.

Hong, J., Shi, W., Wang, Y., Chen, W., Li, X., 2015. Life cycle assessment of electronic waste treatment. Waste Manag. 38 (1), 357—365.

Huisman, J., Habib, H., Brechu, M.G., Downes, S., Herreras, L., Løvik, A.N., Wäger, P., Cassard, D., Tertre, F., Mählitz, P., Rotter, S., Chancerel, P., Söderman, M.L., 2016. ProSUM: Prospecting Secondary Raw Materials in the Urban Mine and Mining Wastes, 2016 Electronics Goes Green 2016+ (EGG), pp. 1—8.

Ilias, A.V., Meletios, R.G., Yiannis, K.A., Nikolaos, P., 2018. Integration and assessment of recycling into c-Si photovoltaic Module's life cycle. Int. J. Sustain. Eng. 11 (3), 1—10.

Liberatore, M., Decker, F., Burtone, L., Zardetto, V., Brown, T.M., Reale, A., Di Carlo, A., 2009. Using EIS for diagnosis of dye-sensitized solar cells performance. J. Appl. Electrochem. 39 (11), 2291—2295.

Menikpura, S.N.M., Santo, A., Hotta, Y., 2014. Assessing the climate co-benefits from waste electrical and electronic equipment (WEEE) recycling in Japan. J. Clean. Prod. 74 (0), 183—190.

Mordor Intelligence, 2017. Global Thermocouple Temperature Sensors Market - by Type (Nickel Alloy Thermocouples, Platinum or Rhodium Alloy Thermocouples, Tungsten or Rhenium Alloy Thermocouples), Industry, Geography, Trends, Forecast - (2017-2022), Industry Reports. Mordor Intelligence.

Moss, R.L., Tzimas, E., Kara, H., Willis, P., Kooroshy, J., 2013. The potential risks from metals bottlenecks to the deployment of strategic energy technologies. Energy Pol. 55, 556—564.

Nair, G., Shafawi, M., Irwanto, M., Yusoff, M.I., Fitra, M., Mariun, N., 2014. Performance improvement of dye sensitized solar cell by using recycle material for counter electrode. Appl. Mech. Mater. 446—447, 823—826.

O'Connell, R., Tankard, W., Alexander, C., Strachan, R., Nambiath, S., Litosh, S.,

Tourney, J., Wiebe, J., Wong, L., Rannestad, E., Li, S., Aranda, D., Scott-Gray, N., Imangaliyeva, T., Rodwell, G., Ji, A., Cheng, H., Salmon, B., 2016. GFMS Platinum and Palladium Survey. Thompson Reuters, London, UK.

O'Connor, M.P., Zimmerman, J.B., Anastas, P.T., Plata, D.L., 2016. A strategy for material supply chain sustainability: enabling a circular economy in the electronics industry through green engineering. ACS Sustain. Chem. Eng. 4 (11), 5879–5888.

Papageorgiou, N., 2004. Counter-electrode function in nanocrystalline photoelectrochemical cell configurations. Coord. Chem. Rev. 248 (13–14), 1421–1446.

Pozio, A., De Francesco, M., Cemmi, A., Cardellini, F., Giorgi, L., 2002. Comparison of high surface Pt/C catalysts by cyclic voltammetry. J. Power Sources 105 (1), 13–19.

Prabhuram, J., Wang, X., Hui, C.L., Hsing, I.M., 2003. Synthesis and characterization of surfactant-stabilized Pt/C nanocatalysts for fuel cell applications. J. Phys. Chem. B 107 (40), 11057–11064.

Raistrick, I., Macdonald, J., Franceschetti, D., 1987. Theory. In: Macdonald, J. (Ed.), Impedance Spectroscopy. John Wiley and Sons, p. 74.

Reck, B.K., Graedel, T.E., 2012. Challenges in metal recycling. Science 337 (6095), 690–695.

Reller, A., Bublies, T., Staudinger, T., Oswald, I., Meißner, S., Allen, M., 2009. The mobile phone: powerful communicator and potential metal dissipator. GAIA 18 (2), 127–135.

Renner, H., Schlamp, G., Kleinwächter, I., Drost, E., Lüschow, H.M., Tews, P., Panster, P., Diehl, M., Lang, J., Kreuzer, T., Knödler, A., Starz, K.A., Dermann, K., Rothaut, J., Drieselmann, R., Peter, C., Schiele, R., 2001. Platinum Group Metals and Compounds, Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co, KGaA.

Richter, J.L., Koppejan, R., 2016. Extended producer responsibility for lamps in nordic countries: best practices and challenges in closing material loops. J. Clean. Prod. 123, 167–179.

Rocchetti, L., Amato, A., Fonti, V., Ubaldini, S., De Michelis, I., Kopacek, B., Vegliò, F., Beolchini, F., 2015. Cross-current leaching of indium from end-of-life LCD panels. Waste Manag. 42, 180–187.

Rotter, V.S., Chancerel, P., 2012. Recycling of critical resources - upgrade introduction, electronics goes green 2012+. In: ECG 2012-Joint International Conference and Exhibition, Proceedings.

Schluep, M., Hagelueken, C., Kuehr, R., Magalini, F., Maurer, C., Meskers, C., Mueller, E., Wang, F., 2009. Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling–From e-Waste to Resources. United Nations Environment Programme & United Nations University, Bonn, Germany.

Sigma-Aldrich, 2016. Chloroplatinic Acid Hydrate ≥99.9% Trace Metals Basis, 2016. http://www.sigmaaldrich.com/catalog/product/aldrich/520896?lang=en&region=GB. (Accessed 14 July 2016).

Skoog, D.A., West, D.M., Holler, F.J., Crouch, s.R., 2014. Standard Addition Methods, Skoog and West's Fundamentals of Analytical Chemistry (International Edition), ninth ed. Brooks/Cole - Cengage Learning, Toronto, Canada, p. 185.

Tao, J., Yu, S., 2015. Review on feasible recycling pathways and technologies of solar photovoltaic modules. Sol. Energy Mater. Sol. Cell. 141, 108–124.

The ad-hoc Working Group (a sub group of the Raw Materials Supply Group of the European Commision), 2011. Annex V to report of the ad-hoc working group on defining critical raw materials. In: DG Enterprise and Industry. European Commission. http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/annex-v-b_en.pdf.

Travis, A.S., 1993. The Rainbow Makers, the Origins of the Synthetic Dyestuffs Industry in Western Europe. Associated University Presses, London and Toronto.

Ueberschaar, M., Otto, S.J., Rotter, V.S., 2017. Challenges for critical raw material recovery from WEEE – the case study of gallium. Waste Manag. 60, 534–545.

Ulanowicz, R.E., Goerner, S.J., Lietaer, B., Gomez, R., 2009. Quantifying sustainability: resilience, efficiency and the return of information theory. Ecol. Complex. 6 (1), 27–36.

Van der Perre, I.W., 2000. Temperature Measuremet in Liquid Metal. http://heraeus-electro-nite.com/media/webmedia_local/media/downloads/steel_2/temperaturecontrol/temperature_wvdp_2000.pdf. (Accessed 11 July 2015).

Van schaik, A., Reuter, M.A., 2012. 9-Shredding, Sorting and Recovery of Metals from WEEE: Linking Design to Resource Efficiency, Waste Electrical and Electronic Equipment (WEEE) Handbook. Woodhead Publishing, pp. 163–211.

WRAP, 2015. What Is Industrial Symbiosis? http://www.wrap.org.uk/content/what-industrial-symbiosis. (Accessed 11 July 2015).

Zimmermann, T., Gößling-Reisemann, S., 2013. Critical materials and dissipative losses: a screening study. Sci. Total Environ. 461–462, 774–780.