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Environmentally friendly recovery of Ag from end-of-life c-Si solar cell using organic acid and its electrochemical purification

Eun-Hyuk Yang [a,c], Jun-Kyu Lee [a,c], Jin-Seok Lee [a,*], Young-Soo Ahn [a], Gi-Hwan Kang [b], Churl-Hee Cho [c,*]

[a] Advanced Materials and Devices Laboratory, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea
[b] Photovoltaic Laboratory, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea
[c] Graduate School of Energy Science and Technology, Chungnam National University, Daejeon 305-764, Republic of Korea

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ABSTRACT

Environmentally friendly and reusable methanesulfonic acid (MSA) was used with the addition of an oxidizing agent to extract Ag from solar cells. Recovery using varying MSA:H_2O_2 mixing ratios of 100:0, 90:10, 75:25, 50:50, and 0:100 revealed that Ag can be effectively extracted in a MSA-rich solution. The concentration of Ag ions dissolved in each mixture was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which established that the optimal extraction condition is a MSA:H_2O_2 ratio of 90:10. The addition of HCl to the leaching solution used for Ag recovery prompted the precipitation of AgCl, which was then reacted in turn with NaOH and H_2O_2 to recover Ag metal powder. This Ag metal powder was analyzed by glow discharge mass spectrometry (GDMS) and found to have a low purity of around 99% (2N), but this was found to be improved through subsequent electrorefining to a purity of 99.995% (4N5).

1. Introduction

Photovoltaic (PV) is highly efficient and non-polluting power generator that utilize solar energy, and therefore have great potential in alternative energy applications due to the fact that they neither produce noise or toxic gases, nor consume large amounts of material resources. Indeed, many countries have already gained benefits through the use of PVs; and as a result of this, the market for PV modules is rapidly expanding (Yi et al., 2014). This increase in the popularity of PV modules, however, is likely to create problems in relation to the generation and disposal of associated waste in the near future (Doi et al., 2001). It is certain that the accumulating amount of PV module waste and the significant amount of retired PV modules arising over the next few decades will need to be safely recycled (Choi and Fthenakis, 2014).

The average life of a crystalline silicon PV module is estimated to be around 25–30 years, as they are prone to defects such as delamination, EVA discoloration, and burn markings (Park et al., 2013). In response to this, the European Union recently issued Guideline 2012/19/EU (replacing the previous 2002/96/EC) to establish rules relating to end-of-life (EOL) PV modules (Granata et al., 2014). These consider EOL PV modules to be waste electrical and electronic equipment (WEEE), and so specific goals pertaining to their collection, recovery and recycling need to be established (Granata et al., 2014). For this reason, many researchers are now actively investigating the recycling of PV modules. The current PV market mainly consists of crystalline Si PV modules that, in order of mass, are made from glass with an Al frame, Ag-printed Si solar cells, an encapsulant, a backsheet and a junction box. The recovery of Ag from these components of solar cells has not been considered to be worth the effort because Ag represents only ~0.08% of the total weight of the module and is fairly well dispersed throughout the solar cell (Olson et al., 2013). Even so, this amount is not negligible, as there is an estimated 18 g of Ag in every 22 kg 200 W PV module. Furthermore, as Ag is much more expensive than the other three metals (Si, Al, and Cu) used in PV modules, it accounts for nearly half of the cell processing cost. This Ag content also corresponds to 1% of the total embedded energy, which means that it represents the largest amount of embedded energy of all the materials in a PV module when their weight proportion is taken into account.

There are several methods that can be used for the recovery of Ag, including extraction using a cyanide solution (Hiskey and Sanchez, 1990) or nitric acid (Lee et al., 2013). However, these methods can cause further environmental problems, such as the generation of waste acid solutions and toxic fumes. This study therefore utilizes a reusable and environmentally friendly methanesulfonic acid (MSA) solution in combination with an oxidizing agent to initiate the oxidation of Ag, which offers the advantage of a high saturation metal salt solubility, high conductivity, simple effluent treatment method, and relatively low toxicity (Gernon, 1999). The MSA can also be regenerated through the substitution of H^+ for Ag^+ by adding HCl acid during AgCl precipitation, and so can be reused for further reaction (Wolfram, 2014). The ratio at which the MSA is mixed with the oxidizing agent is the most important parameter when attempting to efficiently dissolve Ag from a c-Si solar cell, as this directly affects the extraction rate. With the aim of maximizing the

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* Corresponding authors.
E-mail addresses: jslee@kier.re.kr (J.-S. Lee), choch@cnu.ac.kr (C.-H. Cho).

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Table 1
The mixing ratios and reaction times used to extract Ag from solar cells.

Sample	(A)	(B)	(C)	(D)	(E)
Mixing ratio (MSA:H_2O_2)	100:0	90:10	75:25	50:50	0:100
Extraction time	1–12 h				

efficiency of the chemical process, the ratio of MSA to oxidizing agent was varied to find an optimal value, which was then subsequently applied to the dissolution of Ag in c-Si wafers from EOL PV modules containing 4″ solar cells. The Ag material recovered by the conversion of AgCl via a wet chemical process then underwent electrorefining for purification to >4N level purity, which is needed for the recovery of Ag from PV modules to become a viable recovery technology.

2. Experimental procedure

2.1. Recovery of Ag using an organic solvent

6″ mono c-Si commercial solar cells with three bus bars were used to determine the optimum conditions for the chemical extraction of their Ag content by means of a series of steps. First, the 6″ solar cells were divided into 36 uniform pieces, which were then immersed in a mixed solution of MSA (99 wt.%) with H_2O_2 (30 wt.%) for 1–12 h at room temperature for each experiment. For this, a beaker filled with the mixed solution was placed into a cold water bath in order to maintain a temperature of 25 °C, and the solar cells were immersed into the beaker. As shown in Table 1, various mixing ratios of MSA and H_2O_2 were used (100:0, 90:10, 75:25, 50:50 and 0:100), which are hereafter referred to respectively as (A), (B), (C), (D) and (E). The optimal mixing conditions for the 6″ cells were also applied to a 4″ solar cell that was recovered from an actual EOL PV module by pyrolysis in a furnace (Lee et al., 2015a; Lee et al., 2015b) in order to demonstrate the recovery of Ag using an existing system.

To precipitate the Ag leached from the solar cells, a 35 wt.% aqueous solution was added to the MSA-based leaching solution, which was then stirred for 1 h at 200 rpm. The resulting precipitates were recovered by centrifuging to separate the liquid from the solid component. To convert the AgCl to Ag metal powder, it was first reacted with an aqueous solution of NaOH (2 wt.%) while stirring at 200 rpm for 1 h, followed by the addition of H_2O_2 (30 wt.%) and further reaction for 0.5 h. The recovered Ag metal powder was manufactured into an ingot using a thermal torch.

2.2. Purification of Ag by electrorefining

All electrochemical experiments were conducted using a PGSTAT 302N Autolab system (Eco Chemie, The Netherlands). During electrorefining, the anode was made to remain in uniform contact with the Ag ingot by using a spiral rolling of Pt wire. An Ag plate measuring 45 mm × 10 mm × 1 mm in size was used as the cathode. Current was applied to the system using an electrolyte concentration of 10 wt.% $AgNO_3$ and a Ag/AgCl (3 M KCl) reference electrode. A 2.3 cm^2 area of the cathode was exposed to the electrolyte solution, which was maintained at room temperature during electrorefining at a current density of 86.96 A/m^2.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu ICPS-1000IV) was used to analyze the concentration of Ag in the mixed solution. An X-ray diffractometer (XRD; Rigaku DMAX-2500) was also employed to investigate the phases of the recovered and refined Ag, and energy dispersive X-ray spectroscopy (EDS; Horiba EMAX 7200-H) was used to analyze the impurities generated by electrorefining. The concentrations of the various impurities in the Ag materials were measured using a glow discharge mass spectrometer (GDMS; Thermo VG 9000).

3. Results and discussion

Although MSA provides excellent solubility when used with Ag compounds, it does not react with Ag metal unless a specific additive is employed. As an oxidizing agent needs to be added to MSA to initiate the extraction of Ag from solar cells (Gernon, 1999), it is very important to optimize the mixing ratio to achieve the most efficient dissolution of Ag. Fig. 1 shows a comparison of the dissolution outcomes of Ag depending on the mixing ratio of MSA and the oxidizing agent (H_2O_2) with the reaction time. The change in the color of the Ag grid on the solar cell surface provides an approximation of the degree of Ag dissolution, in that if the Ag electrode is fully dissolved then the color should change from white to the gray color of the Si underneath the Ag grid. The fact that the color of the Ag grid did not change after 12 h when only MSA or H_2O_2 was applied suggests that it is not possible to extract

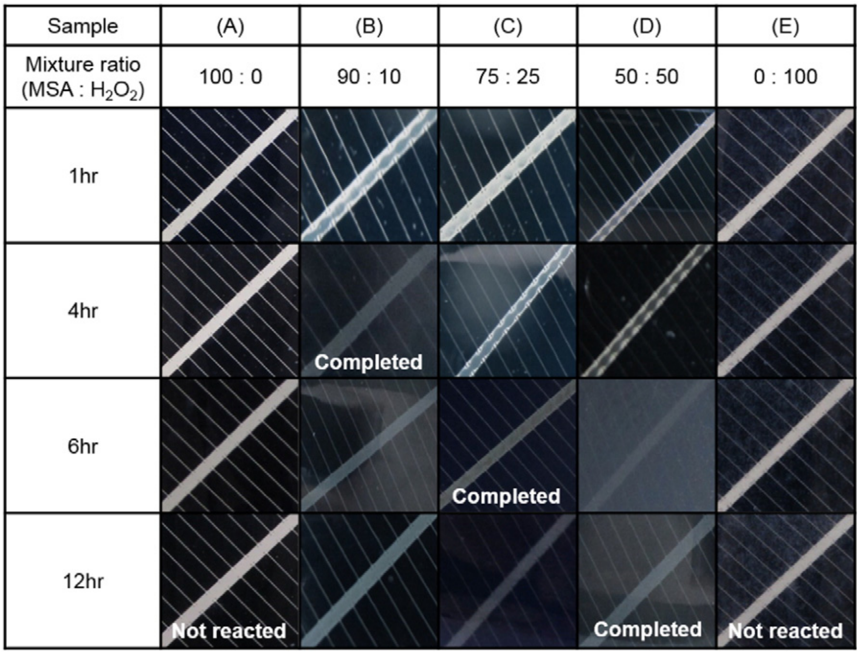

Fig. 1. The dissolution behaviors of Ag electrodes according to the mixing ratio and reaction time.