Silver recovery and removal using a Microbial Fuel Cell

Theofilos Kamperidis1, Asimina Tremouli*1, Pavlos K. Pandis1, Petros E. Tsakiridis2, Emmanoulla Remoundaki2, Gerasimos Lyberatos1,3

1School of Chemical Engineering, National Technical University of Athens, Heroon Polytechniou 9, Athens, 15780, Greece
2School of Mining and Metallurgical Engineering, National Technical University of Athens Heroon Polytechniou 9, Athens 15780, Greece
3Institute of Chemical Engineering Sciences (ICE-HT), Stadiou Str., Platani, 26504, Patras, Greece

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Presenting author: kamp.theo@gmail.com

Abstract: Photovoltaic (PV) panels contain various heavy metals in their thin film. The average life cycle of a PV panel is 25-30 years and there is a need to recycle their materials, in order to avoid their dispersion to the environment and to recover the maximum of their quantities. Silver is used as a conductor in first generation PV panels. A dual chamber microbial fuel cell was constructed and operated to study silver recovery, from a synthetic waste simulating a PV processed waste. The effect of conductivity and pH of the catholyte was examined. High silver recoveries were observed (>93%), at both pH 2 and 7. Silver reduction was delayed at lower conductivity (0.06 mS/cm 24 h versus 18.9 mS/cm 5 h). The system achieved higher power output (248 mW/m²) at pH 2 versus pH 7 (202 mW/m²). Using different supporting electrolytes (potassium chloride instead of sodium perchlorate) inhibited the reduction of silver due to the formation of silver chloride.

1. Introduction

Silver is a valuable heavy metal, because of its broad spectrum of applications. Common uses of silver are for jewelry construction and as a conductor in electrical circuits or batteries, among others [1]. Silver ends up in the environment through various anthropogenic pathways, including smelting operations, metallurgical and mining wastes, disposal of silver products and cloud seeding [2]. Due to silver’s high conductivity it is also used in photovoltaic (PV) panels. It is used in the solar cell of the panel to convert the energy from the sun to electricity as well as a conductive material [3, 4]. PV panels have a life cycle of about 30 years [5]. Following PVs end life, recycling and recovering the materials contained in PV panels is the best approach, in order to avoid the release of toxic and precious elements (such as silver, cadmium, copper) to the environment [6].

Silver is present in first generation PV panels. Silver’s price per ounce was 27.42$ on15-5-21 [7]. Due to silver’s high value, both economic and environmental issues arise [8]. Silver may be toxic to microorganisms and animals, depending on the concentration and the environment (aquatic, soil, air), as it is accumulated in their systems [2]. Apart from the effects on the eco-system, quantities of silver that could be recycled are lost upon disposal. Various methods have been developed to recover heavy metals in a cost-effective way [9]. Silver is usually recovered from wastewater by electrolytic recovery, ionic exchange, and precipitation among others [10]. Biosorption of silver has also been studied [11, 12]. Another innovative approach to the recovery of silver is by the use of bioelectrochemical systems [9].

Microbial fuel cells (MFC) have been examined as a technology to recover silver from synthetic wastewater at various inlet silver concentrations [8, 13]. The MFC technology converts the chemical energy of the bonds of organic compounds to electrical energy, by anaerobic microorganisms [14]. In the cathode an electron acceptor is reduced. Oxygen in air is a typical example of electron acceptor [14], whereas many alternative acceptors have been studied such as chromium [15], indium [16] and copper [17] etc. MFC technology is capable of simultaneously treating two effluents, one acting as electron donor in its anode and one as electron acceptor in the cathode. The biofilm is developed in the anode chamber of the cell, where the substrate is oxidized [18].

The aim of this work is to use MFC technology for the recovery of silver from a synthetic waste simulating the characteristics (concentration, pH) of the wastewater that is generated from a following hydrometallurgical process of 1st generation PV panels: acidic extraction using 5N nitric acid (HNO₃) for 3 h, at 25 °C of the PV panel’s thin film, [19].

2. Materials and Methods

A dual chamber MFC has been constructed for this work, similar to Tremouli et al. 2013. A Proton Exchange Membrane – (PEM) (Nafion ® 117, DuPont) was used with a total area of 3.77 cm². The membrane was pretreated
The anodic electrode was graphite paper. During the acclimation period, oxygen was the electron acceptor in the cathode, and graphite cloth with a platinum coating was used as the cathodic electrode. After acclimation, the carbon cloth was replaced with plain graphite paper. The dimensions for all the electrodes used were the same (2.5 cm x 3.8 cm). Titanium wire was connected to the electrodes using an epoxy resin (Conductive Epoxy, Circuit Works), for the electron collection. An external resistance set at 100 Ω, except stated otherwise, was connected to the two electrodes. The anolyte and catholyte were under continuous stirring. The system was placed inside a temperature controlled box, set at 32 °C.

A synthetic feed was prepared for the anode containing phosphate buffer (3.67 g/L NaH₂PO₄ and 3.45 g/L Na₂HPO₄), potassium chloride (0.16 g/L KCl), sodium bicarbonate (5 g/L NaHCO₃), trace elements (1% v/v, described elsewhere [21]) and glucose (1.5 g COD/L) as the electron donor. A high initial COD value was chosen for the anode feed, in order to ensure the adequacy of the substrate for the total reduction of silver. For the first three batch cycles, the MFC was inoculated with anaerobic sludge (10 % v/v) obtained from the Lykovrysi sewage treatment plant, Athens, Greece.

During the acclimation period, the cathode was continuously sparged with air and the catholyte contained phosphate buffer (pH 7) and potassium chloride (0.16 g/L KCl). Following acclimation period, the oxygen electron acceptor was replaced with silver. Four different recovery cases were examined (R1, R2, R3, R4). In the first experiment (R1) silver nitrate (AgNO₃) was diluted in DI water at the desired concentration and sodium perchlorate (NaClO₄) was added, to increase the conductivity of the catholyte. In the case of the second experiment (R2), silver nitrate was diluted in DI water and potassium chloride (KCl), instead of sodium perchlorate was added in order to increase the conductivity. The initial dissolved silver concentration was 0.5 mg/L, which indicated that the dissolved silver in the catholyte immediately reacted with chloride ions within the catholyte solution, forming silver chloride, by the following reaction:

\[ \text{KCl} + \text{AgNO}_3 \rightarrow \text{AgCl} (s) + \text{K}^+ + \text{NO}_3^- \] (Eq. 3)

For the third experiment (R3), silver nitrate was diluted in DI water with no supporting electrolyte. The fourth experiment (R4) was carried out with silver nitrate (AgNO₃) diluted in DI water, sodium perchlorate (NaClO₄) at pH 2 which was controlled using nitric acid (0.1 M HNO₃). Sodium perchlorate concentration (0.2 M) was kept constant. At the beginning of each batch cycle the cathode was sparged with nitrogen (N₂) in order to remove the oxygen from the chamber. Table 1 presents the characteristics of the catholyte for each case (R1, R2, R3 and R4).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inlet pH</th>
<th>Inlet conductivity (mS/cm)</th>
<th>Initial Silver concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>7</td>
<td>18.9</td>
<td>54</td>
</tr>
<tr>
<td>R2</td>
<td>7</td>
<td>19.5</td>
<td>0.5</td>
</tr>
<tr>
<td>R3</td>
<td>7</td>
<td>0.06</td>
<td>46</td>
</tr>
<tr>
<td>R4</td>
<td>2</td>
<td>18</td>
<td>49</td>
</tr>
</tbody>
</table>

Voltage was recorded every 2 min by (Agilent Keysight 34972A LXI Data Acquisition/Switch Unit) Linear Sweep Voltammetry (LSV) was carried out to assess the performance of the cells using Potentiostat – Galvanostat (PGSTAT128N – AUTOLAB) and an Ag/AgCl reference electrode. The pH and conductivity were measured by digital instruments (WTW INOLAB PH720) and (WTW INOLAB) respectively. Soluble COD was measured according to the standard methods [22]. To measure the silver diluted in the cathodic chamber, atomic absorption spectrometry (AAS) was used. At the end of each cycle, the electrode was removed from the cathode chamber replaced by a new one. The deposits on the carbon surface were examined using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS-EDX). Diluted silver was considered recovered once it had precipitated as pure silver, either deposited on the cathode surface of the cathode.
3. Results and Discussion

3.1. Silver recovery experiments

Figure 1 presents the results of four silver recovery experiments (R1, R2, R3 and R4). In the R1 experiment the silver was completely removed after 5 h of cell operation (Table 1). The dissolved ions form silver perchlorate react, as is presented in the following reaction:

\[ NaClO_4 + AgNO_3 \rightarrow AgClO_4 + Na^+ + NO_3^- \] (Eq. 1)

The anion of silver perchlorate is unstable, thus leading to the formation of silver cations [23]. Subsequently, the reduction of the silver takes place, as described by the following reaction:

\[ Ag^+ + e^- \rightarrow Ag(s) \downarrow \] (Eq. 2)

During the R2 experiment, silver chloride was immediately formed resulting to low concentration of dissolved silver at the beginning of the cycle (0.5 mg/L). After 27 h, the dissolved silver measured was 0 mg/L. For the R3 case, silver was reduced within 24 h with a recovery of 93% (Table 3). The slower reduction rate for R3 experiment in comparison with the R4 and R1 cycles, is attributed to the absence of the supporting electrolyte (sodium perchlorate 0.2 M) in the catholyte. In Table 1 the inlet conductivities are presented for the three cases (R1 18.9 mS/cm, R3 0.06 mS/cm and R4 18 mS/cm). During the R4 experiment, silver recovery occurred in less than 3 h while for the R1 case, the silver was completely reduced within 5 h.

![Figure 1: Recovery of silver versus time for the four experiments, each with different cathodic solution (R1=silver nitrate and sodium perchlorate at pH 7, R2=silver nitrate and potassium chloride at pH 7, R3=silver nitrate at pH 7 and R4=silver nitrate and sodium perchlorate at pH 2).](image)

<table>
<thead>
<tr>
<th>Experiment sets</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c = -10.451t + 53.38</td>
<td>-</td>
<td>c = 41.839exp(-0.112t)</td>
<td>c = -19.651t + 49.469</td>
</tr>
<tr>
<td>Fitted equations</td>
<td>R² = 0.9953</td>
<td>-</td>
<td>R² = 0.9887</td>
<td>R² = 0.9821</td>
</tr>
</tbody>
</table>

Table 2: Equations of the silver reduction rates, for the four experiments (R1, R2, R3, and R4).

In Table 2 are presented the different rates that were extracted after a fit on the silver reduction data from Figure 1. In the R1 and R4 cases, where the reduction was completed at 3 h and 5 h respectively, a linear equation (c=at+b)
was the best fit. Since R4 reduction was faster the R1, a smaller “t” coefficient was calculated (R1 a=-10.451 versus R4 a=-19.65). In the R2 case since there was no reduction, no rate was calculated. In the R3 case an exponential equation (c = 41.839exp(-0.112t)) fitted the data best.

Table 3: Measurements and calculations of the catholyte at the end of the cycle.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Silver concentration (mg/L)</th>
<th>I&lt;sub&gt;MAX&lt;/sub&gt; (mA)</th>
<th>Cathodic pH at the end of the cycle</th>
<th>Cathodic conductivity (mS/cm)</th>
<th>Recovery of silver (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>54</td>
<td>0.93</td>
<td>10.7</td>
<td>17.7</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>R2</td>
<td>0.5</td>
<td>0.40</td>
<td>10.3</td>
<td>18.5</td>
<td>0%</td>
</tr>
<tr>
<td>R3</td>
<td>46</td>
<td>0.02</td>
<td>7.9</td>
<td>0.23</td>
<td>93%</td>
</tr>
<tr>
<td>R4</td>
<td>49</td>
<td>0.95</td>
<td>7.7</td>
<td>15.3</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>

In the R1 experiment the maximum current output was 0.93 mA while the pH increased to 10.7 at the end of the cycle. A high silver reduction occurred (>99%). In the R2 experiment, by using potassium chloride as support to the electrolyte, the dissolved silver formed silver chloride, inhibiting the silver reduction. The pH at the end of the cycle increased to 10.3. In the case of R3 experiment, using silver nitrate and DI water, the maximum current output (0.02 mA) was lower in comparison to the other cases (R1: I<sub>MAX</sub> = 0.93 mA, R2: I<sub>MAX</sub> = 0.4 mA, R4: I<sub>MAX</sub> = 0.95 mA). This caused the slower reduction of silver, which lasted 24 h. When comparing R1 and R4 the silver reduction was completed after 5 h and 3 h of operation, respectively, indicating the significance of a high conductivity of the cathodic solution. In the R4 experiment, the maximum current was 0.95 mA and similarly to R1, a high percentage of silver (>99%) was reduced. An increase in the cathode pH was observed (initial pH 2, final pH 7.7). At the end of silver reduction, COD removal of the R1, R3 and R4 cases was approximately 50%.

3.2. SEM imaging and EDS analysis

R1 experiment

In the SEM images of the R1 electrodes, silver deposits on the carbon paper surface were observed. Pure silver crystals formed and in some cases chloride salts were observed (Figure 2). However, the operation of the cell was not inhibited by silver chloride, due to its small quantity. The formation of silver chloride is limited by the use of sodium perchlorate, since the reaction (Eq. 1) takes place.
Figure 2: SEM micrograph and EDS spectra of the cathodic electrode surface for the R1 recovery. Pure silver crystals (left) and formed chloride salts (right).

**R2 experiment**

During the R2 experiment, potassium chloride was used as the supporting electrolyte in place of sodium perchlorate. As soon as the synthetic wastewater was prepared it became blurred due to the presence of silver chloride. Subsequently, the MFC operation was initiated. After 27 h of operation, the cathodic solution was no longer blurred and deposits were observed on the cathodic electrode, as well as in the chamber. The silver concentration at the end of the cycle was 0 mg/L. The cathodic solution was filtered and the solid phase was analyzed with SEM and EDS.
The images of the SEM and EDS analysis indicated the formation of a silver chloride layer on the cathodic electrode, as well as precipitation of silver chloride (Figure 3). Due to the fact that all the silver was converted to silver chloride there was no silver reduction. The silver reducing operation of the MFC was inhibited. The use of potassium chloride to support the conductivity, as a cheap substitute of the sodium perchlorate proved ineffective.
3.3. Polarization experiments

Figure 4: Polarization and power curves for the two experiments (R1, R2 and R4).

Figure 4 presents the results of polarization experiments (conducted on the start of the batch cycles), for the three cases (R1, R2 and R4). No polarization curve was extracted for the R3 case, since the cell did not produce power, as presented in Figure 1 and Table 3. The maximum power was achieved for the R4 case and equal to 248 mW/m², while it generated 202 mW/m² for the R1 experiment and 60 mW/m² for the R2 experiment, respectively. Furthermore, a lower internal resistance (the resistance at which the polarization curve exhibits a maximum) was calculated for the R4 case in comparison with the R1 and R2 experiment (R4 = 604 Ω, R1=1103 Ω and R2=2010 Ω). The linear slope of the polarization curves indicated that the ohmic losses dominated in all cases. In the R2 experiment where the potassium chloride as supporting electrolyte the maximum power was the same to the power achieved when the cell operated with oxygen as the electron acceptor (Pmax=60 mW.m²). The precipitation of the silver as silver chloride led to the reduction of the dissolved oxygen in the catholyte.

4. Conclusion

Synthetic silver wastewater was prepared simulating 1st generation PV processed by hydrometallurgical method. Four cases of silver reduction using a microbial fuel cell were studied. The effect of the conductivity and pH on the silver reduction was examined in the cathode chamber. Silver recovery was high (>99%) in all cases, with the exception of potassium chloride, where silver precipitated as silver chloride. Silver was deposited on the cathode electrodes and in some cases chloride salts were observed. The best performance in terms of power output was achieved in the R4 case (248 mW/m²), with silver nitrate (49 mg/L), sodium perchlorate (0.2 M) and initial cathodic pH 2. By using the MFC technology the heavy metal recovery is feasible, but parameters such as the conductivity and the pH of the wastewater should be further examined in order to improve the MFC performance.

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