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Use of Cascade Reduction Potential for Selective Precipitation of Au, Cu, and Pb in Hydrochloric Acid Solution

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Abstract−Optimization of reduction potential for electroseparation was studied for the recovery of gold, copper, and lead from acidic solution. A linear sweep voltammetric method enabled us to determine characteristic reduction potentials for each metal and the kinetics of the metal deposition indicated by current-voltage curves. In order to precipitate the metal species sequentially, reduction potentials were examined for the individual and mixed solutions of Au(III), Cu(II), and Pb(II). The three metals were reasonably well isolated from the mixed solutions such as Cu(II)/Pb(II) and Au(III)/Cu(II)/Pb(II) in the order of the corresponding reduction potentials, in particular, the mass transfer controlled reduction potentials, obtained from linear sweep voltammetry (LSV) measurement.

Key words: Reduction Potential, Electroseparation, Linear Sweep Voltammetric Method, Mass Transfer Controlled Potential

INTRODUCTION

As the electronic and mobile communication industries have expanded tremendously, printed circuit board (PCB) manufacturing has become one of the fastest growing industries. Consequently, a large amount of waste PCBs, as scrapped electronics, has been abandoned into the environment, which has led to heavy metal pollution and caused loss of metal resources. This has forced us to introduce a waste minimization strategy to reuse recoverable waste as well as to prevent waste generation at the source [Fresner et al., 1996; Bernardes et al., 1997]. As a well known and generally used procedure, chemical precipitation under a controlled pH has been used to remove metals in a solution as insoluble metal forms, or sludge. There are, however, several incentives for the introduction of recovery and recycling of resources without generating secondary wastes, i.e., stimulation of lowering discharge limits, limitation of disposal sites, the increasing cost of sludge discharge, and the monetary value of the recovered materials. Of the methods currently being employed for the recovery of metals [Fu et al., 1995; Armstrong et al., 1996; Pesic et al., 1997; Kim and Cho, 1997; Kim et al., 1998; Chang and Huang, 1998; Juang et al., 1999; Voropanova and Velichko, 1999], removal and recovery by electrochemical methods from the source is the most attractive due to its potential as a one-step cleanup method for metal recycling which does not trigger any secondary problem [Walsh and Gabe, 1981; Armstrong et al., 1996, 1997].

The purpose of this study is to investigate the optimum reduction potentials and operating conditions for selective recovery of the metals from mixed metal solutions and to measure their chemical and electrochemical characteristics in chloride-complexed acid solutions. Their characteristics have been examined theoretically and experimentally for a single metal solution and in a mixed metal solution where strong complexation exists, and then selective electrodeposition of individual metals was evaluated. Electrodeposition of metals has been found in earlier publications [Walsh and Gabe, 1981; Armstrong et al., 1996, 1997]. The principle of the studies was the change in the reduction potentials for each of the metals present in the solutions. However, they have not studied a metal solution in the presence of strong complexation caused by high acid concentrations, though Armstrong et al. [1996] took into account slight complexation. In this study, cascade reduction potentials were applied for the selective electrodeposition of Cu(II), Pb(II), and Au(III) in strong acid that may be used in an actual process for dissolution of the metals.

EXPERIMENTAL

1. Chemicals and Materials

All reagents and chemicals used were of analytical grade. The supporting electrolyte was prepared by using a hydrochloric acid solution (Merck, 37%). The Au(III) solution was prepared with $AuCl_3$ (Aldrich, 99.99%), the Pb(II) solution with $PbCl_2$ (Aldrich, 98%), and the Cu(II) solution with $CuCl_2 \cdot 2H_2O$ (Junsei, 97%). The initial metal ion concentration was within the range of 0.5 mM to 1 mM. Each sample solution was prepared by using a hydrochloric acid solution of 1 M to 4 M. The anolyte consisted of the supporting electrolyte only at the same concentration of the catholyte which consisted of the supporting electrolyte and metal(s). The initial pH was the same in both solutions. Distilled water was used in preparing all the solutions.

2. Apparatus

Fig. 1 shows the three-electrode system used for the separation and recovery of metals from acidic solutions. An electrolytic cell, divided into two compartments by a cation exchange membrane (CMX, NEOSEPTA, Tokuyama Corp., Japan), was used as a metal recovery system in a strong acid medium. This membrane plays an important role in performing effective electrolysis. Metal precipitation occurs only in the cathode compartment. If the electrolysis were carried out to recover metals from the acidic solution such

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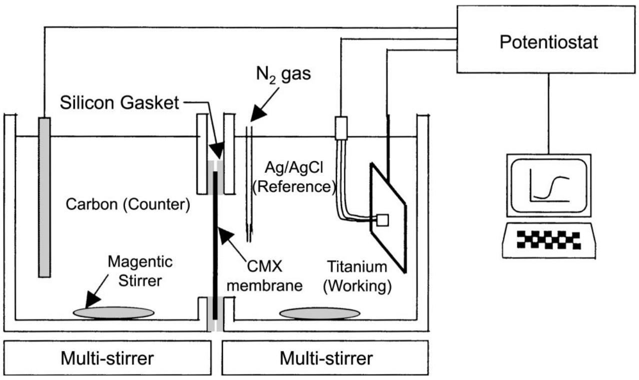

Fig. 1. Schematic experimental set-up for controlled reduction experiments.

as HCl in one-compartment reactor, a deleterious product such as chlorine gas would be generated so that this process must be inferior. By dividing the electrolysis reactor into two compartments, an inorganic solution such as Na_2SO_4, which is indifferent to undesired anodic reactions, can be used just to provide sufficient conductivity to carry out the electrolysis. A plate titanium oxide electrode and a rod type carbon electrode, acting as a working electrode and a counter electrode, respectively, were placed in the separate compartments of a batch-type cell, each compartment volume being 200 mL. The acid solution with metals was present in the working-cathode compartment. Metals deposited can be collected easily on the plate titanium oxide electrode in the system, leading to sequential recovery of the individual metal species. A potentiostat used in this study was an EG&G Princeton Applied Research model 263A controlled by a 486DX computer via an IEEE-488 GPIB/TNT card. PAR M270/250 Research Electrochemical Software was used in all electrochemical measurements. The potentiostat was used in performing the linear sweep voltammetry (LSV), chronopotentiometry, and chronoamperometry. A water jacket maintained the reaction temperature at 25 °C. The cathode was a 2×2 cm titanium plate and the anode was carbon rod. The reference electrode, saturated KCl-Ag/AgCl (SSE), was placed in the cathode compartment and was arranged to be contacted with the working electrode via a Luggin capillary in all experiments. An MS-4 (Iuchi, Japan) multi-stirrer was used to agitate the solution.

3. Procedure

All electrochemical experiments were performed in the three-electrode cell. All solutions were deoxygenated by purging with nitrogen for 30 min prior to each experiment. A titanium oxide plate, the working electrode, was prepared by polishing the electrode with alumina, immersing it in diluted nitric acid for 5 min, rinsing it with deionized water, cleaning with acetone, and rinsing again with deionized water prior to all runs. The open-circuit potential (OCP) was determined by chronopotentiometry at a zero current for each experiment. The OCP was the initial potential in performing electrochemical analyses. The LSV was carried out by scanning potential from the OCP (or initial potential) and increasing to the cathodic potentials by using a linear sweep of 5 mV/sec (2 mV traversed in 0.4 sec) while stirring the solutions well in the electrolytic reactor.

In order to examine the selective electrodeposition, controlled potential electrolyses were performed by using chronoamperometry at a fixed cathode potential. During the chronoamperometry, the potential was kept at the value that was obtained in the LSV experiments with a single or mixed metal solutions. The reduction potentials for a mass transfer controlled operation were employed in the range of the limiting current plateau.

Concentrations of each metal were determined by using AAS (Atomic Absorption Spectrophotometer, Perkin-Elmer 5100PC) for Cu (324.8 nm) and Pb (283.3 nm) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometer, Jobin Yvon 38 plus) for all mixed metal solutions including Au, with the wavelengths used for Au, Cu, and Pb set at 242.795 nm, 324.754 nm, and 220.353 nm, respectively.

RESULTS AND DISCUSSION

1. Chloride-Complexed Speciation of Metals

The electrodeposition of metal ions is influenced by the types and concentrations of complexes. These complexes consist of one or more central ions, such as metals with a number of ligand ions or molecules surrounding and attached to them [Snoeyink and Jenkins, 1980]. Three metals, copper, lead, and gold, in hydrochloric acid solution also have a tendency to form complexes with chloride. The complexes could be neutral, cationic, or anionic, depending upon the charge of the central ion and the ligands. Portions of each species in the complex solutions were estimated by taking into account the concentration of the chloride ion and pH.

$$M^{n+}+Cl^{-}\Leftrightarrow MCl^{(n-1)}, \qquad [MCl^{(n-1)}]=\beta_1[M^{n+}][Cl^{-}] \tag{1}$$

$$M^{n+}+2Cl^{-}\Leftrightarrow MCl_2^{(n-2)}, \qquad [MCl_2^{(n-2)}]=\beta_2[M^{n+}][Cl^{-}]^2 \tag{2}$$

$$\vdots \qquad\qquad \vdots$$

$$M^{n+}+xCl^{-}\Leftrightarrow MCl_x^{(n-x)}, \qquad [MCl_x^{(n-x)}]=\beta_x[M^{n+}][Cl^{-}]^x \tag{3}$$

$$C_{T,\,Cl}=[MCl^{(n-1)}]+2[MCl_2^{(n-2)}]+\cdots+x[MCl_x^{(n-x)}] \tag{4}$$

$$C_{T,\,M}=[M^{n+}]+[MCl^{(n-1)}]+[MCl_2^{(n-2)}]+\cdots+[MCl_x^{(n-x)}] \tag{5}$$

In general, the concentrations of complexes of a metal species with the inorganic ligand such as chloride can be obtained by using equilibrium relations from Eqs. (1) to (3) and the mass balance equations from Eqs. (4) and (5). Table 1 shows the stability constant (β) and the possible reaction that can participate. The mass balance in the concentration of chloride [Eq. (4)] is also expressed as

$$C_{T,\,Cl}=\beta_1[M^{n+}][Cl^{-}]+2\beta_2[M^{n+}][Cl^{-}]^2+\cdots+x\beta_x[M^{n+}][Cl^{-}]^x \tag{6}$$

Table 1. Stability constants of metal-chloride complexes

Reaction	log K	Reference
$H_2O\Leftrightarrow H^{+}+OH^{-}$	−14	[Snoeyink and Jenkins, 1980]
$HCl \Leftrightarrow H^{+}+Cl^{-}$	3	[Snoeyink and Jenkins, 1980]
$Au^{3+}+2Cl^{-}\Leftrightarrow AuCl_2^{+}$	9.8	[Raubenheimer and Cronje, 1999]
$Au^{3+}+4Cl^{-}\Leftrightarrow AuCl_4^{-}$	26	[Snoeyink and Jenkins, 1980; Raubenheimer and Cronje, 1999]
$Cu^{2+}+Cl^{-}\Leftrightarrow CuCl^{+}$	0.1	[Ringbom, 1963]
$Cu^{2+}+2Cl^{-}\Leftrightarrow CuCl_2$	−0.5	[Ringbom, 1963]
$Pb^{2+}+Cl^{-}\Leftrightarrow PbCl^{+}$	1.62	[Ringbom, 1963]
$Pb^{2+}+2Cl^{-}\Leftrightarrow PbCl_2^{-}$	2.44	[Ringbom, 1963]
$Pb^{2+}+3Cl^{-}\Leftrightarrow PbCl_3$	1.71	[Ringbom, 1963]
$Pb^{2+}+4Cl^{-}\Leftrightarrow PbCl_4^{2-}$	1.56	[Ringbom, 1963]

Table 2. Composition of metal-chloride complexes at various total acid concentrations

Metal	Complexes (eq/L)	1 N HCl	2 N HCl	3 N HCl	4 N HCl
Au(III)	Au^{3+}	1.53×10^{-29}	9.53×10^{-31}	1.88×10^{-31}	5.98×10^{-32}
	$AuCl_2^+$	9.57×10^{-20}	2.38×10^{-20}	1.06×10^{-20}	5.97×10^{-21}
	$AuCl_4^-$	0.0015	0.0015	0.0015	0.0015
	NNS*	≈100%	≈100%	≈100%	≈100%
Cu(II)	Cu^{2+}	7.77×10^{-4}	4.2×10^{-4}	2.63×10^{-4}	1.81×10^{-4}
	$CuCl^+$	9.77×10^{-4}	1.053×10^{-3}	9.92×10^{-4}	9.09×10^{-4}
	$CuCl_2$	2.453×10^{-4}	5.276×10^{-4}	7.446×10^{-4}	9.09×10^{-4}
	NNS*	12.27%	26.38%	37.23%	45.46%
Pb(II)	Pb^{2+}	4.94×10^{-6}	9.08×10^{-7}	2.82×10^{-7}	1.13×10^{-7}
	$PbCl^+$	2.05×10^{-4}	7.54×10^{-5}	3.51×10^{-5}	1.87×10^{-5}
	$PbCl_2$	1.35×10^{-3}	9.93×10^{-4}	6.93×10^{-4}	4.93×10^{-4}
	$PbCl_3^-$	2.45×10^{-4}	3.60×10^{-4}	3.77×10^{-4}	3.57×10^{-4}
	$PbCl_4^{2-}$	1.94×10^{-4}	5.70×10^{-4}	8.94×10^{-4}	1.13×10^{-4}
	NNS*	89.50%	96.18%	98.23%	99.06%

*NNS is the ratio of neutral and negative species to total complexes formed with chloride ion.

The chloride concentration was obtained by using a trial and error approach and was used to solve the concentration of the uncomplexed metal with the modified equation from Eq. (5)

$$[M^{n+}]=\frac{C_{T,M}}{\beta_1[Cl^-]+\beta_2[Cl^-]^2+\cdots+\beta_x[Cl^-]^x} \tag{7}$$

With the concentrations of chloride and uncomplexed metal, the concentrations of each metal complex were calculated. Table 2 shows the chloride-complexed speciations for each metal. As the concentration of the hydrochloric acid increased, the corresponding concentration of the chloride ion increased. It was confirmed that this chloride ion concentration affected the complexes formed with metal ions in the solution. With the increasing total concentration, the percentage of neutrally or negatively complexed metals increases. Neutral or negative chloride-complexed metals might influence the electrochemical characteristics of the electrodeposition of the metals by demanding a greater electrical potential for them to be deposited on the cathode than the free ions or positive complexes [Scott, 1995] and by reducing the current efficiency for deposition of each metal. Nevertheless, a metal dissolution process for waste PCBs should be performed with high concentrations of hydrochloric acid to maintain the high solubility for metals on PCBs.

2. Determination of Deposition Potential for Metal Solutions

The standard electrode potentials for each reaction

$Au^{3+}+3e^- \Leftrightarrow Au(s)$
$Cu^{2+}+2e^- \Leftrightarrow Cu(s)$
$Pb^{2+}+2e^- \Leftrightarrow Pb(s)$

are known as 1.50, 0.337, and −0.126 (SHE), respectively [Dean, 1992]. The reduction potentials showed wide gaps among the three metals, in the order of Au(III), Cu(II), and Pb(II), in the negative direction. It implies that gold, copper, and lead could be sequentially recovered by increasing a potential cathodically.

All the experiments were started at the open circuit potential and proceeded in the reductive direction, and showed good reproducibility. As shown in Fig. 2, the voltammogram for Pb(II) shows the shifting of the reduction potential with the concentration of hydrochloric acid toward the negative potential. The change in the HCl concentration caused the change in the activity of Pb(II) species, as well as in the composition of the copper species so that the NNS value increased with the increase in the HCl concentration as shown in Table 2. It implies that the increase in NNS value needed more electrical power to reduce the metal species. Moreover, the reduction potential of complexes of Pb(II) with chloride ion was more cathodic than the standard reduction potential of non-complexes of Pb(II). The reduction potential of non-complexed lead ion is 0.096 V (SSE), but one of the complexes of Pb(II) in 1 M HCl is 0.25 V (SSE) as shown in Fig. 2. A limiting current (or mass transfer controlled potential) was observed in each concentration of HCl from a steady-state plateau at −0.3 V to −0.5 V (SSE). The potential, where currents went up rapidly, was caused by powder formation in accord with

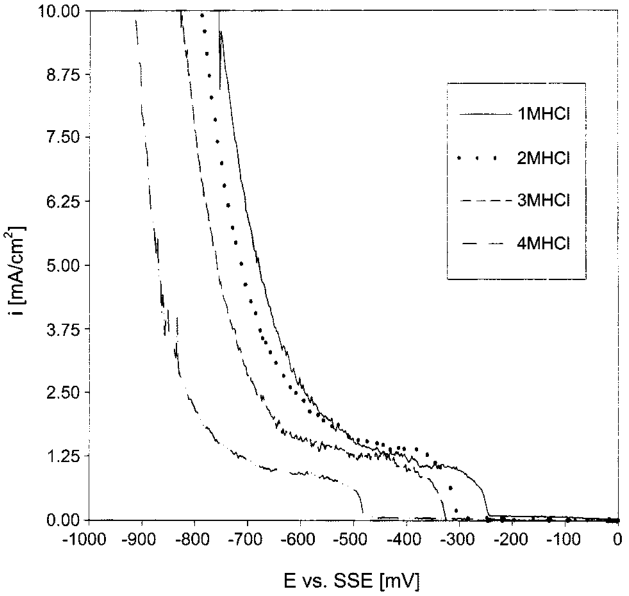

Fig. 2. Linear sweep voltammograms of the 1 mM Pb(III) solution on titanium oxide. Scan rate 5 mV sec^{-1} and 25 °C.

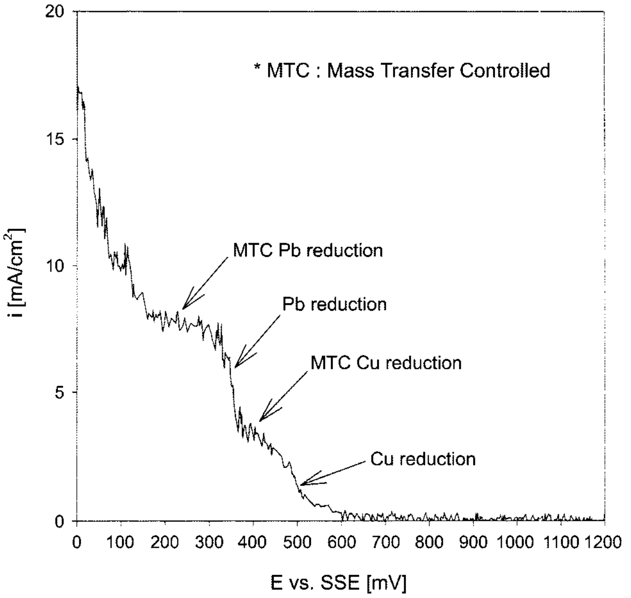

Fig. 3. Linear sweep voltammogram for a mixed solution of copper and lead, 1 mM Cu and 1 mM Pb in 1 M HCl, on titanium oxide; scan rate 5 mV sec^{-1} and 25 °C.

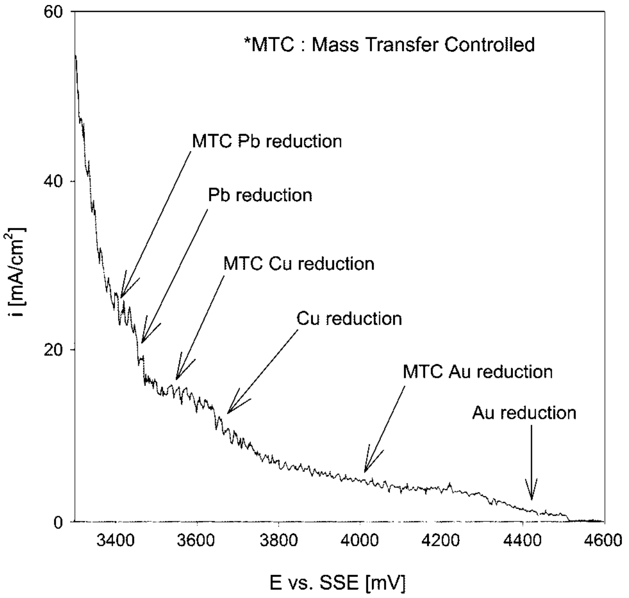

Fig. 4. Linear sweep voltammogram for a mixed solution bearing all three metals, 0.5 mM Au, 1 mM Cu, and 1 mM Pb in 1 M HCl, on titanium oxide; scan rate 5 mV sec^{-1} and 25 °C.

the results of Armstrong et al. [1996], and was recorded as an increasingly negative value with the increasing concentration of HCl.

Consecutive electrode reactions can occur in the case where two or more reducible substances are present in the same solution. In the most favorable situation for a mixed solution including two reducible substances, the first metal species would be reduced at less extreme potentials than the others while the second metal species would not be reduced yet until the mass transfer controlled region for the first metal has been reached. Therefore, the reduction of the first metal can be achieved without interference of the second unless the current by the reduction of the second metal species is superimposed on the current caused by the mass-transfer-limited flux of the first metal. In this regard, LSV was performed for mixed solution [Bard et al., 1980]. As shown in Fig. 3, two appreciable steps are observed for copper and lead. The first deposition of metal was initiated at about 0.6 V (SSE). According to the reduction potential difference among the three metals, it was expected that copper would be reduced first. This was confirmed partly by observing the deposited metal, tinged with the color of copper, on the working electrode. After the mass controlled region of copper, the second step corresponds to the deposition of lead occurring at 0.35 V (SSE). The working electrode readily turned black in the second step. The mass transfer controlled region of lead, from 0.32 to 0.15 V (SSE), shows a broader response than that of copper, from 0.47 V to 0.35 V (SSE).

Reduction characteristic for a system in which three metal species are reduced in three steps is examined as shown in Fig. 4. As mentioned earlier, the increase of the current followed by a plateau indicates the deposition of gold, copper, and lead, respectively. The deposition of gold was initiated at 4.5 V (SSE). A limiting current was observed in the range of 4.3 V to 3.8 V. The deposition of copper did not occur to any appreciable extent from 4.5 to 3.8 V (SSE). The current increase caused by the deposition of copper can be seen between 3.8 and 3.48 V (SSE). Finally, the deposition of lead follows at 3.48 V to 3.38 V (SSE) after the current increase caused by the deposition of copper. The potential jump toward anodic direction is due to a lower rank of Au(III) than Cu(II) or Pb(II) in the ionization series. Au(III) can be precipitated even without electrical energy in the presence of Cu(II) and Pb(II) which have much higher ionization potential. This results in lowering the activation energy for the cathodic reaction of Au(III), shifting the reduction potential of Au(III) toward the more oxidative condition from the standard electrode potential.

Consequently, the reduction potentials of metals were significantly different from the type of solution containing the metal(s). It indicates that it is necessary to optimize the reduction potential from the appropriate LSV result to effectively isolate each metal from the solution.

3. Selective Electrodeposition from Mixed Metal Solutions

Controlled potential electrolyses were performed to investigate the selective recovery by means of a sequential deposition in the batch electrochemical reactor used for previous experiments. The experiments were carried out at a preselected potential until the majority of a relatively preferential metal was separated. The first reducible metal was removed from the cathode compartment, and then the next step was continued at a higher reduction potential. Each experiment took about 3 hours. A two-metal solution, Cu(II)/Pb(II) in 1 M HCl, and a three-metal solution, Au(III)/Cu(II)/Pb(II) in 1 M HCl, were examined since they are typical combinations occurring in waste PCBs. In order to reuse metals, metal ions should be transformed into solid forms that can be handled easily. The reduction potentials used in all the experiments were in the mass transfer controlled region, indicated by the plateau of the voltammogram (or limiting-current density). In general, in the mass transfer controlled potential region, the deposit often exhibits flask, dendrite, or powder, depending upon the normalized current density by limiting current density [Pletcher and Walsh, 1990].

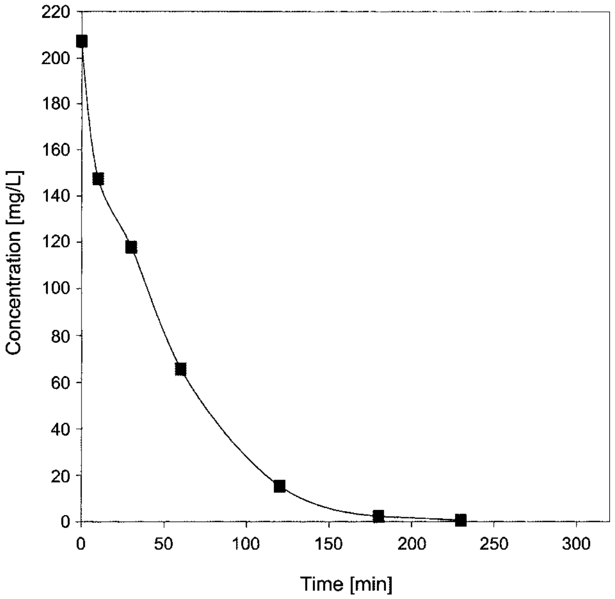

Fig. 5. Variation in the concentration of lead - voltages were set at −0.3 V (SSE) for the 1 mM lead deposition.

Electrodeposition of the lead solution was carried out at a preselected potential under mass transfer controlled conditions. Fig. 5 shows the time profiles of the lead concentration. The preselected potential for the lead deposition was at −0.5 V (SSE). Even though the potential was reductive enough to generate hydrogen on the cathode, the powder deposit at the mass transfer controlled potential resulted in increasing the surface area of the electrode so that lead was removed faster than expected. It indicates that the potential selected in the mass transfer controlled potential region would be successfully used to recover lead in solutions. The concentration of hydrochloric acid did not change during the electrolysis, which was confirmed by titration, and therefore can be recycled to dissolve the metals on waste PCBs.

As discussed earlier, the first choice of the potential determined from the LSV of the single metal solution for isolating the first reducible metal from a mixed metal solution was inappropriate. Therefore, it was necessary to employ the first step potential at 0.45 V (SSE) from the LSV measurement of the Cu(II)/Pb(II) solution to isolate Cu(II) from the mixed solution as shown in Fig. 3. After isolating copper, we selected −0.5 V (SSE) from the LSV of Pb(II) to recover the lead left in the solution. Both copper and lead were removed effectively at 0.45 V and –0.5 V (SSE), respectively, as shown in Fig. 6. Employment of the potentials resulted in reasonably selective electrodeposition. The recovery efficiencies of copper and lead were 88.3% and 98.9%, respectively, in 180 min.

In a similar manner, for the case of the three-metal solution, the first [4 V (SSE)], the second [0.45 V (SSE)], and the third potential [–0.5 V (SSE)] were adopted from the voltammograms of the Au(III)/Cu(II)/Pb(II) solution, the Cu(II)/Pb(II) solution, and the Pb(II) solution, respectively, to isolate each metal sequentially because Au, Cu, and Pb were orderly deposited by stepping them toward the cathodic potentials. Fig. 7 shows that this potentiostatic control led to selective electrodeposition. Gold was recovered completely within 240 min, the concentration of copper fell down to 1.7 ppm [97.4%] during the second step, and lead was recovered to 32.8 ppm [84.2%] during the third step.

The above results showed that cascade reduction potential enabled us to isolate gold, copper, and lead from individual [Pb(II)] solution and mixed [Cu(II)/Pb(II) and Au(III)/Cu(II)/Pb(II)] solutions.

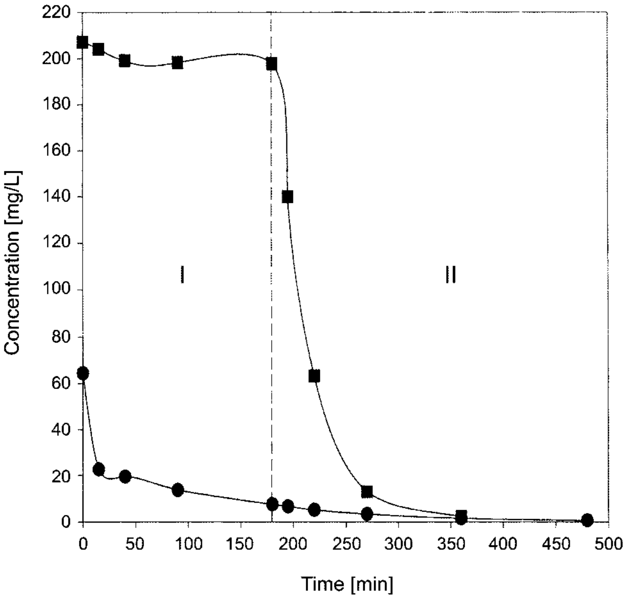

Fig. 6. Selective electrodeposition for the solution including 1 mM Cu and 1 mM Pb in 1 M HCl. The first step [I] (0.45 V vs. SSE for 180 min) for the copper deposition and the second step [II] (–0.5 V vs. SSE for 300 min) for the lead deposition: ●, copper; ■, lead.

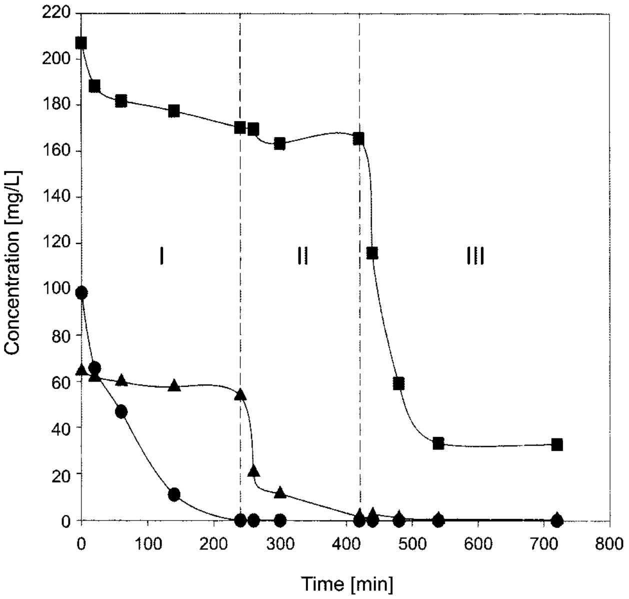

Fig. 7. Selective electrodeposition for the solution including 0.5 mM Au, 1 mM Cu, and 1 mM Pb in 1 M HCl. The first step [I] (4 V vs. SSE for 240 min) for the gold deposition, the second step [II] (0.45 V vs. SSE for 180 min) for the copper deposition, and the third step [III] (–0.5 V vs. SSE for 300 min) for the lead deposition: ●, gold; ▲, copper; ■, lead.

Table 3. Reduction potentials selected by LSV and mass transfer controlled regions

(V vs. SSE)	Au	Cu	Pb
Pb(II)			−0.5 (−0.3 to −0.5)
Cu(II)/Pb(II)		0.45 (0.47 to 0.35)	−0.5 (−0.3 to −0.5)
Au(III)/Cu(II)/Pb(II)	4 (4.3 to 3.8)	0.45 (0.47 to 0.35)	−0.5 (−0.3 to −0.5)

( ): Mass transfer controlled regions

The potential that was used for the electrodeposition of the corresponding step was successfully determined by the LSV for the solution containing the metals that remained. The optimum potential for the fast and selective electrodeposition of metal from mixed solutions without simultaneous deposition was selected at the potential in the mass transfer controlled region before the electrodeposition of other metals begins. These values are summarized in Table 3 with the potential ranges for mass transfer controlled region.

CONCLUSIONS

A cascade electrolysis operation using optimized reduction potentials for gold, copper, and lead, was presented. This operation led to a reasonable electroseparation from individual and mixed metal solutions and proposed the optimized operation method for each metal solution. Linear sweep voltammetry was shown to be a useful tool for providing the optimized reduction potential for each metal. The reduction potentials of each metal were found to be in the order of Au(III), Cu(II), and Pb(II) in the cathodic direction and to sequentially separate the metals in the same order by means of a cascade electrolysis operation. The results show that heavy metals in waste PCBs can be recovered economically and separated effectively without any secondary pollution.

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