

The Use of Deep Eutectic Solvents Ionic Liquids for Selective Dissolution and Recovery of Sn, Pb and Zn from Electric and Electronic Waste (WEEE)

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The recovery of metals from a multi-component alloy obtained by crushing, melting and anodic dissolution of waste electric and electronic equipment (WEEE) has been investigated. The aim of this paper is to selective recover of Sn, Pb and Zn by a novel ecological technology using ionic liquids. Metallic Sn, Pb and Zn were electrochemically recovered from the WEEE dissolved in choline chloride-ethylene glycol-iodine ionic liquid. Cyclic voltammetry was used in order to determine the deposition potentials of the studied metals. XRD and SEM/EDX analysis methods were used to characterize the structure and morphology of the metallic deposits. Evolution of the cathodic deposition and of the chemical composition of the anode during the anodic dissolution process for Sn, Pb and Zn was also studied. This study has demonstrated the possibility of selective recovery of Sn, Pb and Zn from the multi-component alloy (which resulted from consecutive anodic dissolution of WEEE) by anodic dissolution/deposition in ionic liquids.

Keywords: waste electric and electronic equipment, ethaline ionic liquid, Sn, Pb and Zn, recovery, cyclic voltammetry

The processing of waste from electric and electronic equipment (WEEE, also called as electronic wastes or e-wastes) has been attracting more and more concerns from scientists all over the world. The key to WEEE recycle is waste from printed circuit boards (WPCBs), which are an essential part of almost all electric and electronic equipment, such as laptops, air conditioners, TV equipment, etc.). A novel method to recycle resources from WPCBs is by using organic solvents named ionic liquids as electrolytes.

Ionic liquids (ILs), also called as room temperature ionic liquids (RTILs), are basically liquid at low temperature. Typically, it consists of an organic cation with an inorganic or organic anion. ILs have a wide liquid temperature range and also possess numerous unique properties, such as negligible volatility, vapor pressure, thermal stability, high conductivity and wide electrochemical window [1]. ILs are powerful solvents and electrolytes with potential from high selectivity in both dissolution and recovery of metals. In the recent years, room temperature ionic liquids are increasingly applied for cathodic deposition of numerous metals, alloys or semiconductor compounds [2, 3]. The advantages of these novel baths include: electroplating of electronegative metals and their alloys; significantly reduced hydrogen evolution as compared with the acidic aqueous baths conventionally employed; lower electrical energy consumption comparing with aqueous solutions.

Ionic liquids show good electrical conductivity due to their complete ionic structure, are electrochemically robust with a large potential window and have an extremely low vapor pressure. The thermal stability of the ionic liquid is useful to obtain crystalline semiconductor films through direct electrodeposition at higher temperatures without subsequent annealing.

Currently, ILs were successfully applied in leaching metals from ores [4]. However, the literature on leaching metals from WPCBs by ILs is limited. In previous study [5]

we reported copper recovery in WEEE leachate by using DES ionic liquids based on choline chloride (ChCl). DESs are based on a mixture of ChCl with suitable hydrogen bond donors, like ethylene glycol (EG) [6]. In contrast to aqueous liquids where the solubility of metals is limited by the tendency of water to combine with metal ions and precipitate oxides and hydroxides, in water free ionic liquids much higher metal salt concentrations can be achieved. In last decade many authors has reported metals and alloys (and especially Sn, Pb and Zn) deposition by dissolution of metal/oxide salts in DES [7-12].

In this work we show that DES formed by an eutectic mixture of ChCl and EG can be used in the presence of iodine for the selective dissolution and recovery of Sn, Pb and Zn from electric and electronic waste (WEEE).

Experimental part

The background electrolyte (ethaline) was prepared by mixing ChCl (Aldrich 98%, dried for 24-120 h at 80°C) with EG (Aldrich 99%); by heating in a beaker the two components in 1:2 molar ratio at above 60°C for 30 min, until a homogeneous and colorless liquid was formed.

For the cyclic voltammetry measurements $\text{SnCl}_2 \times 2\text{H}_2\text{O}$, PbCl_2 , and ZnCl_2 (99%, Merck) reagents were used as precursors of Sn^{2+} , Pb^{2+} and Zn^{2+} ions without any purification, being dissolved in the supporting electrolyte ChCl-EG. In order to calculate the solution molarities we used a density value of ChCl-EG of $1.09 \text{ g} \times \text{cm}^{-3}$ determined in our laboratory at 70°C [13].

The WEEEs were processed through an innovative method of melting in a microwave installation, which allowed the complete separation of the organic and metallic fractions. The multi-component WEEE (sample 1) was obtained by melting in the microwave oven the cake resulting from PCB milling (dimensions < 5 mm). After melting, it was poured as a ingot into a metal ingotch,

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wt.%	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
Sample (S1)	67.18	10.93	6.48	5.22	4.00	1.11	4.40	0.4	0.01

Other elements (Mn, Si, Cr, V, etc) < 0.3%

Table 1
CHEMICAL COMPOSITION (wt.%) OF
THE PROCESSED WEEE

ingot dimensions 200 mm x 80 mm x 30 mm. Three samples were taken from different areas of the ingot, the samples were analyzed by inductively coupled plasma optical emission spectrophotometry ICP-OES for Cu, Sn, Zn, Pb, Fe, Ni, and by FAAS atomic absorption spectrometry for Au, Ag. The average of values is shown in the Table 1. More details for the obtaining of the anodic slime from consecutive anodic dissolution of cast WEEE was presented in a previous work [14].

In order to determine the mechanism of metals electrodeposition we used cyclic voltammetry (CV). For the CV measurements the electrochemical cell was connected to a PARSTAT 2273 potentiostat driven by PC computer. A platinum sheet (0.5 cm²) and a glassy carbon (GC) disk ($\phi=0.3$ mm) were used as working electrode, whereas the auxiliary electrode was a platinum mesh. A silver wire immersed in the working electrolyte was the quasi-reference electrode [15]. The working electrode was polished mechanically with alumina oxide paste, washed with bi-distilled water and dried prior to measurement. Electrochemical experiments were performed *via* a 100 mL jacketed cooling glass cell linked to a thermostated bath. The voltammograms were recorded with scan rates of 10-100 mV \times s⁻¹. Supplementary voltammetric measurement was performed for determining the electrochemical window of the above solvent. The temperature of the electrolyte was set at 70°C using a thermostat.

The selective deposition of the studied Sn, Pb and Zn from the WEEE sample was carried out in a electrolysis cell (250 mL) with one copper cathode (60 \times 30 \times 0.2 mm) and a central cast anode, immersed in the ChCl-EG electrolyte with 0.1 M of pure iodine (99.5%, Riedel-de-Haen) as oxidizing agent. In fact the dissolution of WEEE sample and the selective deposition of metals take place once. This method consists of the direct extraction of metals through an electrochemical process without a prior chemical dissolution. The electrodeposition process was realized using a stabilized power supply-I 4115 IEMI Romania of 30 V-15 A. In order to speed up the dissolution process the electrolysis cell was introduced into an ultrasonic bath. During the experiments the cell voltage was between 0.3-1.3 V depending on which metal we want to deposit and the anodic current density was 0.01-0.02 A \times cm⁻².

The chemical composition of the cathodic deposit and anode was determined using a Spectroflame PICP analyser. The thickness of metal deposits is determined with the aid of compact inverted metallurgical microscope GX41 with the accuracy of $\pm 0.1 \mu\text{m}$ on the polished end face of the substrate from copper with $d_{\text{Cu}}=0.5$ mm thickness and deposited coating layer. For characterization of the structure/microstructure of the metal deposits obtained we used X-ray diffraction (XRD) and scanning electron microscopy (SEM). The study of the metal deposits crystal structure was carried out in CuK α radiation by the modified diffractometer DRON-2 in the survey X-ray photographs regime by the points. A scanning electron microscope XL-30-ESEM TMP Philips-Netherlands, equipped with an energy dispersive X-ray analyzer (EDX) was used to ascertain deposit morphology and composition.

Results and discussions

Cyclic voltammetry investigations

A series of cyclic voltammetric experiments were performed for determining the dissolution/deposition potentials of the studied metals.

Figure 1 presents an example of the voltammogram in ChCl-EG (1:2 moles) eutectic as supporting electrolyte. It was noticed the large domain of potentials (from -1.3 V to +1.2 V) representing the *potential window* of more than 2V for selected ionic liquid, which is about 2 times wider in comparison with similar parameter of aqueous solutions (1.23 V).

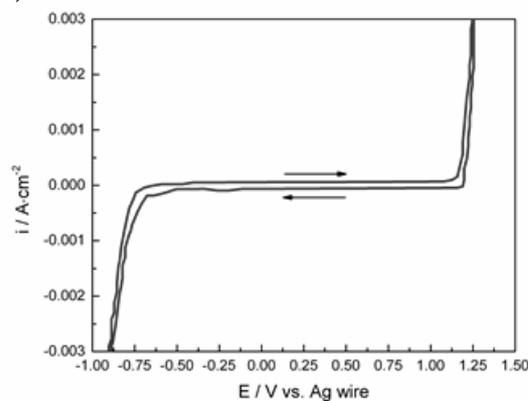


Fig.1 Cyclic voltammogram on Pt within extended potential range for (1ChCl-2EG) eutectic at 70°C; scan rate 100 mV \times s⁻¹

Figure 2 shows the voltammetric profile of Sn (II) on GC and Pt electrodes for the DES used. When Sn (II) is added to ethaline (1ChCl:2EG) a well-defined peak is observed at

-0.89 V in the cathodic scan, that can be attributed to the reduction of Sn²⁺ ion. By changing the working electrode the shape of the cyclic voltammogram is changing, *i.e.* Figure 2b shows that reduction of Sn²⁺ (on Pt electrode) started at -0.384 V. A mass transfer limiting current is again observed at potentials more negative than -0.5 V. The reverse sweep shows two stripping peaks: one anodic peak starting at a -0.250 V and another at -0.125 V. In a published work these peaks are attributed to the oxidation of two different tin ionic species present in the electrolyte [16]. However, we evidenced cathodic peak on both Pt and GC electrode representing the reduction of Sn²⁺ in a single step at -0.45 V and respectively at -0.89 V. Our results are in good agreement with literature data [7, 17, 18].

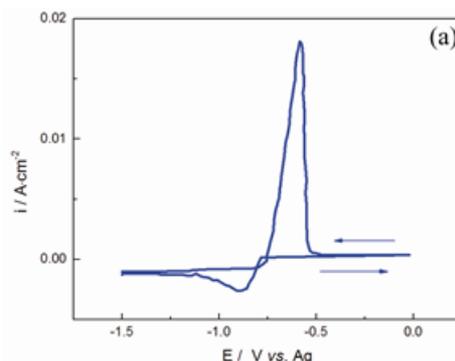


Fig. 2 Cyclic voltammogram in (1ChCl-2EG) containing SnCl₂ \times 2H₂O at 70°C: a) on GC, 0.05M SnCl₂ \times 2H₂O, scan rate 100 mV \times s⁻¹

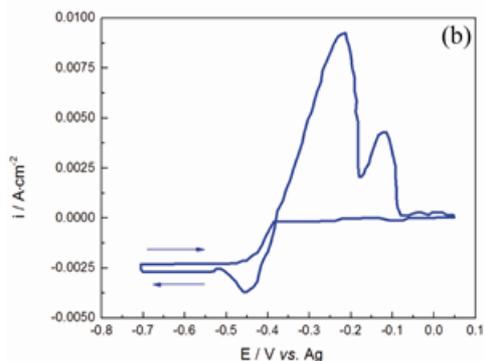


Fig. 2 Cyclic voltammogram in (1ChCl-2EG) containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at 70°C : b) on Pt, $0.1 \text{ M SnCl}_2 \cdot 2\text{H}_2\text{O}$, scan rate $10 \text{ mV} \times \text{s}^{-1}$

Figure 3 presents the cyclic voltammograms for Pb^{2+} and Zn^{2+} cathodic reduction. Figure 3a illustrates the deposition of Pb metal, a process that started at -0.25 V with an increasing current during negative going scan. The cathodic peak is at -0.311 V and it was assigned to the reduction of Pb^{2+} in one step with 2 electron transfer. The current increase at more negative potentials than -0.8 V , is due to the cathodic process of the cholinium cation of supporting electrolyte. These results are also in good agreement with literature data [19].

The cyclic voltammetry data for ChCl-EG eutectic with addition of ZnCl_2 is presented in figures 3b, c. Using Pt electrode (fig. 3b) the cathodic portion of the CV curve shows no well defined reduction peak but it is clear that the relative nucleation rate is slow. At more slow scan rates a cross-over of the current traces was observed at more negative potentials as evidence of nucleation and subsequent growth [11].

However, using glassy carbon (GC) working electrode (fig. 3b) the reduction of Zn is evidenced as a cathodic

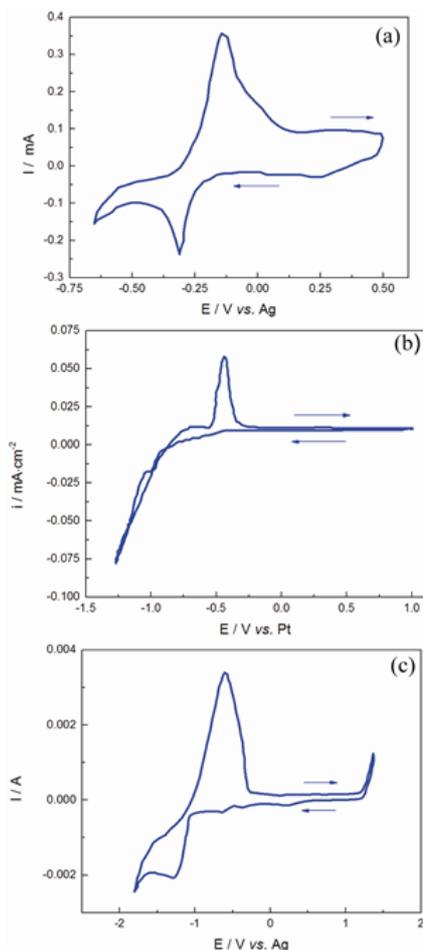


Fig. 3 Cyclic voltammograms in (1ChCl-2EG) eutectic containing Pb^{2+} or Zn^{2+} ions in different conditions: a) 0.1 M PbCl_2 at 50°C , Pt electrode, scan rate $100 \text{ mV} \times \text{s}^{-1}$; b) 0.3 M ZnCl_2 , 70°C , Pt electrode, scan rate $20 \text{ mV} \times \text{s}^{-1}$; c) 0.1 M ZnCl_2 , 70°C , GC electrode, scan rate $50 \text{ mV} \times \text{s}^{-1}$

peak assigned to potential of -1.273 V , by a mechanism in one step reduction. On the anodic branch of voltammogram, the rising current at more positive potentials than 1.5 V is attributed to chlorine evolution. All these results are also in good agreement with literature data [11, 20, 21].

The selective galvanostatic recovery of the studied metals was done in the ChCl-EG ionic liquid with addition of iodine as an oxidizing/catalytic agent. In order to be sure that iodine do not interfere with any of the studied metals we used cyclic voltammetry. Figure 4 shows that the reduction/oxidizing peaks for iodine appear at $+0.269 \text{ V}$ and respectively at $+0.638 \text{ V}$, which means that I_2 do not interfere with any of the voltammetric peaks for Sn, Pb or Zn.

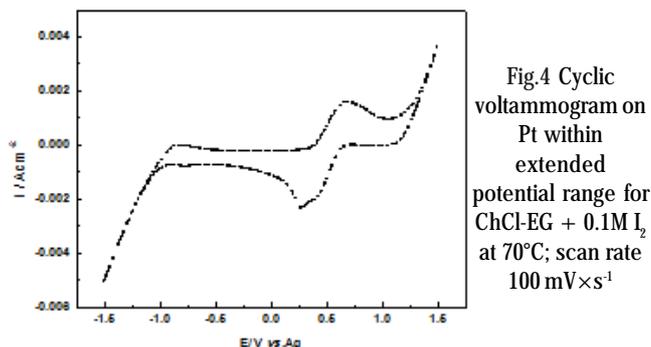


Fig.4 Cyclic voltammogram on Pt within extended potential range for ChCl-EG + 0.1 M I_2 at 70°C ; scan rate $100 \text{ mV} \times \text{s}^{-1}$

Metals recovery by electro dissolution/deposition

After we demonstrated the possibility of electrodeposition of Sn, Pb and Zn from ChCl-EG ionic liquid, we started to make selective dissolution of WEEE sample (of composition presented in table 1) and electrodeposition of the studied metals in ionic liquids.

Some preliminary experimental results [14] demonstrated that high purity Cu can be efficiently separated/recovered from the WEEE metallic fraction by anodic dissolution, so we extracted first of all the copper metal from the ingot and then we started the selective deposition of Sn, Pb and Zn.

The selective galvanostatic deposition tests for Sn from the WEEE sample led to smooth, uniform, glossy and adherent tin deposits at -0.45 V , current density $1.6 \text{ mA} \times \text{cm}^{-2}$, 60 min. It has been noticed that after this time, powdered tin is deposited over a cohesive, glossy and particularly smooth layer. The thickness of the deposited layer was 1.3 mm . The current efficiency for Sn deposition was calculated by gravimetric method and the obtained value was $\sim 85\%$. The Pb deposition experiments from WEEE sample led to a fairly adherent gray-silver deposit of thickness $\sim 2 \text{ mm}$ and the current efficiency of the $\sim 87\%$.

The Zn deposition from the same WEEE sample led to a bluish-white grey deposit with good adhesion and of $\sim 20 \text{ mm}$ thickness. The current efficiency of Zn deposition was found to be $\sim 95\%$.

The process was carried out for each metal for 168 hours, until the complete dissolution of the anode. After complete dissolution, the electrolyte was filtered and the anodic slime was washed with bi-distilled water and alcohol and then dried. After drying, the anodic slime was melted to produce new anodes of different composition.

Tables 2-4 show the chemical composition of the cathodic deposits during the selective anodic dissolution process, while tables 5-7 show the chemical composition of the anode during the anodic dissolution process.

As it can be observed in tables 2-7, during the metals recovery process the content of precious metals is continuously decreasing in the anode, it practically remains constant in the cathodic deposit.

Cathode deposit [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	-	-	-	-	-	-	-	-	-
	40 h	0.12	99.80	0.01	0.01	0.02	0.02	0.01	0.006	0.001
	80 h	0.09	99.82	0.01	0.02	0.01	0.02	0.01	0.007	0.001
	120 h	0.07	99.84	0.02	0.03	0.01	0.01	0.001	0.009	0.000
	168 h	0.04	99.85	0.03	0.04	0.01	0.01	0.005	0.010	0.000

Table 2
CHEMICAL COMPOSITION OF THE CATHODIC DEPOSIT DURING THE ANODIC DISSOLUTION PROCESS FOR Sn EXTRACTION

Cathode deposit [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	-	-	-	-	-	-	-	-	-
	40 h	0.12	0.03	0.02	99.77	0.02	0.01	0.02	0.006	0.001
	80 h	0.10	0.04	0.03	99.78	0.02	0.01	0.01	0.007	0.001
	120 h	0.06	0.10	0.03	99.80	0.01	0.01	0.005	0.009	0.001
	168 h	0.05	0.16	0.04	99.85	0.02	0.01	0.005	0.009	0.001

Table 3
CHEMICAL COMPOSITION OF THE CATHODIC DEPOSIT DURING THE ANODIC DISSOLUTION PROCESS FOR Pb EXTRACTION

Cathode deposit [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	-	-	-	-	-	-	-	-	-
	40 h	0.12	0.03	99.79	0.03	0.02	0.01	0.02	0.006	0.001
	80 h	0.07	0.04	99.82	0.02	0.02	0.01	0.01	0.007	0.001
	120 h	0.04	0.02	99.87	0.03	0.01	0.01	0.005	0.008	0.001
	168 h	0.02	0.02	99.88	0.03	0.02	0.01	0.005	0.012	0.001

Table 4
CHEMICAL COMPOSITION OF THE CATHODIC DEPOSIT DURING THE ANODIC DISSOLUTION PROCESS FOR Zn EXTRACTION

Anode [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	67.18	10.93	6.48	5.22	4.00	1.11	4.40	0.65	0.03
	40 h	68.50	6.56	7.50	6.20	5.00	1.56	4.00	0.65	0.03
	80 h	68.56	3.25	8.0	6.68	6.30	2.0	4.20	0.87	0.05
	120 h	69.32	1.68	8.72	6.62	6.85	2.1	4.30	0.88	0.05
	168 h	Complete dissolution								

Table 5
CHEMICAL COMPOSITION OF THE ANODE DURING THE ANODIC DISSOLUTION PROCESS FOR Sn EXTRACTION

Anode [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	67.18	10.93	6.48	5.22	4.00	1.11	4.40	0.65	0.03
	40 h	67.18	10.93	6.48	5.22	4.00	1.11	4.4	0.65	0.03
	80 h	68.12	8.56	7.34	3.25	4.27	2.41	4.58	0.63	0.02
	120 h	68.56	8.21	8.41	1.89	4.63	2.56	5.11	0.61	0.02
	168 h	Complete dissolution								

Table 6
CHEMICAL COMPOSITION OF THE ANODE DURING THE ANODIC DISSOLUTION PROCESS FOR Pb EXTRACTION

Anode [%]	Time	Cu	Sn	Zn	Pb	Fe	Ni	Al	Ag	Au
	0 h	67.18	10.93	6.48	5.22	4.00	1.11	4.40	0.65	0.03
	40 h	68.12	9.97	3.75	5.14	4.97	2.42	4.97	0.64	0.02
	80 h	68.56	9.93	1.75	5.24	5.42	2.97	5.48	0.63	0.02
	120 h	69.32	9.54	0.33	5.12	5.92	3.28	5.87	0.61	0.01
	168 h	Complete dissolution								

Table 7
CHEMICAL COMPOSITION OF THE ANODE DURING THE ANODIC DISSOLUTION PROCESS FOR Zn EXTRACTION

Metallic deposits characterization

X-ray diffraction patterns are presented in figure 5. Figure 5a shows the X-ray pattern of the sample-tin coating with thickness ~ (3.9-4.3 μ m) on copper substrate. The reflexes of the copper substrate are much less in the intensity comparing to the diffraction reflexes of tin. It is established that all reflexes in figure 5a, not relating to copper, correspond to tin of the tetragonal structure of space group S.G.: 14/ amd (141) [22]. The estimation of the unit cell parameters was made with the use *quadratic form* for the tetragonal structure [23, 24]. The obtained values of the Sn unit cell parameters are: $a=0.5829$ nm, $c=0.3185$ nm. The size of crystals, obtained by using the Scherrer equation is approx. 80-110 nm.

Figure 5b shows XRD analysis of the Pb deposit obtained on copper substrate. All peaks 2θ (30°, 35°, 50°, 60°, 76°, 84°, 87°, 98° and 106°) correspond to Pb metal on copper substrate. The resulting pattern was compared with the

standard JPCDS card, confirming the deposition of pure lead [24, 25]. The results of XRD pattern confirm that the Pb deposit consists only of Pb. The size of crystals, obtained by using the Scherrer equation is approx. 120-210 nm.

The XRD pattern of Zn deposit on copper substrate (fig.5c) detects signals of zinc at 36°, 39°, 42°, 54°, 71° and some copper signals from the substrate as the deposit was very thin [26]. The crystallites average sizes of 13-19 nm have been determined using the well-known Scherrer equation. The XRD pattern also confirms the deposition of pure zinc on copper cathode.

The scanning electron microscopy (SEM) images of the obtained metallic deposits are shown in figure 6 along with EDX analysis.

The silver white color of the deposit in the SEM image indicates the metallic Sn (fig. 6a). The EDX analysis (fig. 6b) confirmed the presence of mostly Sn with very small amount of Cl (<1%) in the deposit. The Cl in EDX spectrum

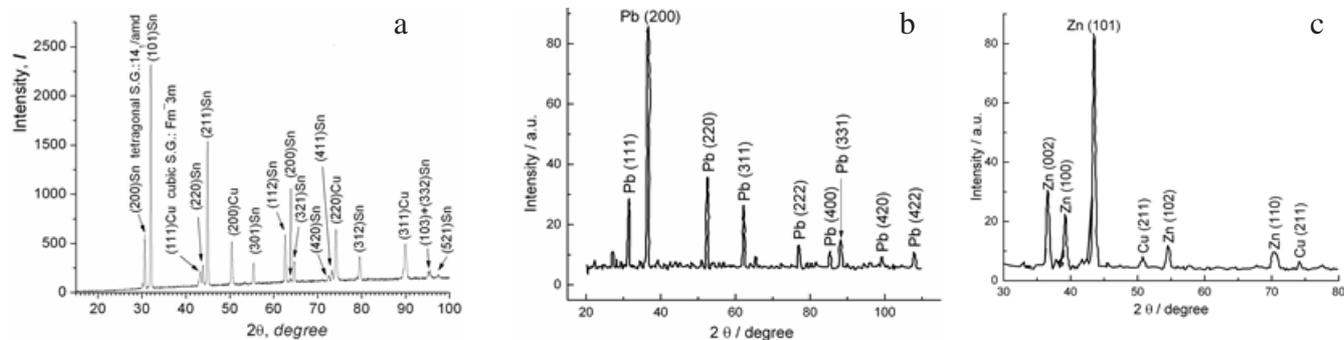


Fig.5 X-ray powder diffraction (XRD) patterns for the obtained metallic deposits: a) Sn; b) Pb; c) Zn

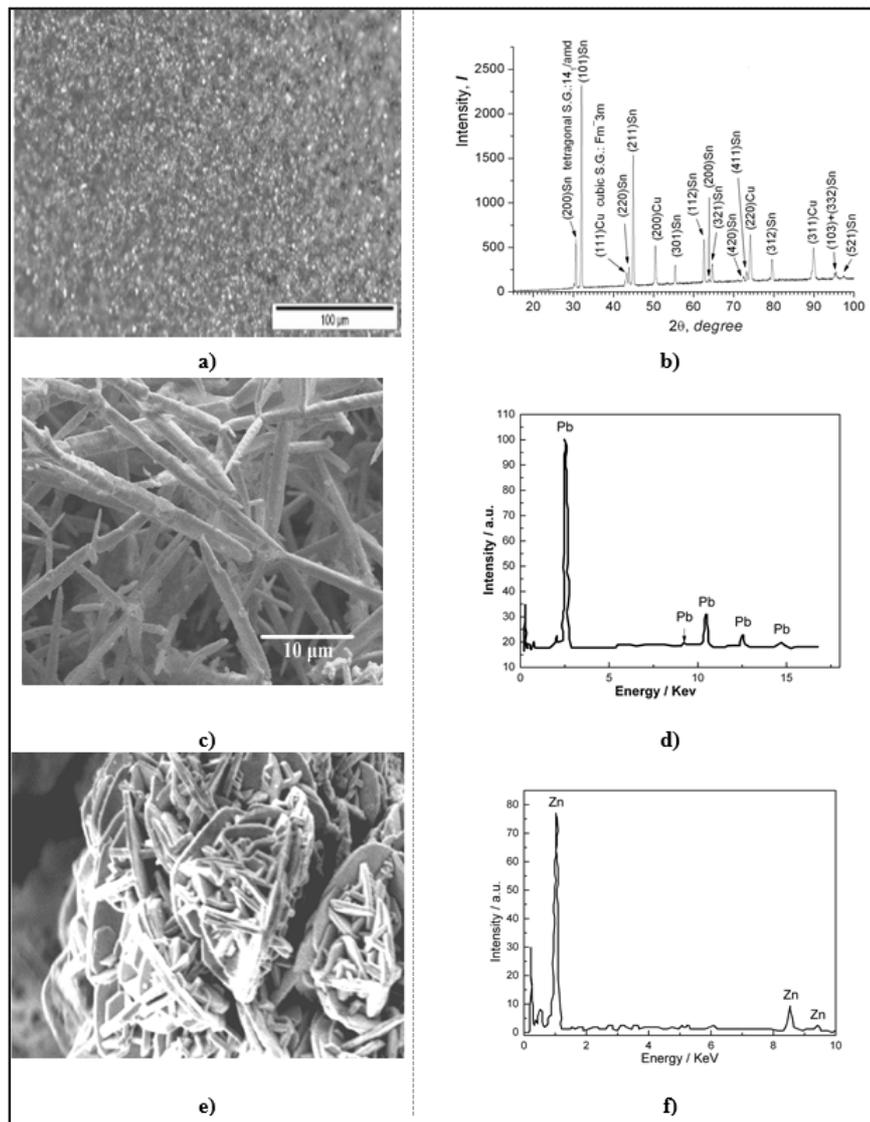


Fig.6 Microstructure (SEM image) and EDX analysis for the obtained deposits of : Sn (a,b); Pb (c,d); Zn (e,f)

might have originated from $\text{ChCl}_2\text{-EG}$ melt inclusion into the Sn deposit.

The Pb deposition experiments from WEEE sample led to a fairly adherent gray-silver deposit, for which the SEM images and EDX pattern are shown in figures 6c,d. The SEM image is bright. The deposit has a rod-like structure with an average diameter of $\sim 1 \mu\text{m}$ and length $\sim 200 \mu\text{m}$ as SEM image shows at $\times 2000$ magnification. The dendritic clusters are made of cubic crystals as seen in figure 6c. EDX analysis (fig.6d) of the deposit obtained at -0.3 V confirms that all peaks correspond to Pb. No other peaks were exhibited, suggesting that the main chemical constituent of the deposit is lead.

The SEM image of the Zn deposit obtained is shown in figure 6e and illustrates a thick, homogeneous bluish-white

grey layer. The average size of the deposited particulate Zn is about $20 \mu\text{m}$. The zinc deposit exhibits dendrite clusters, which are built up of crystal-like structure. The EDX analysis (fig.6f) shows only zinc peaks confirming that metallic zinc was obtained.

Conclusions

The paper demonstrates that deep eutectic solvent of choline chloride and ethylene glycol can be properly used as a solvent for metals extraction in the presence of iodine and using a sonicated bath in order to increase the dissolution process. The metallic complex alloy obtained from the WEEE melting in microwave furnace was

successfully dissolved and high purity Sn, Pb and Zn deposits were obtained for low current densities.

The electrodeposition of Sn, Pb and Zn from this ionic liquid has been studied.

The electrodeposition was carried out at potentials vs. Ag quasi-reference: -0.45 V for Sn, -0.31 V for Pb and -1.27 V for Zn. The current efficiency of selective electrodeposition of Sn, Pb and Zn was about 85-95%. The deposits were analyzed using XRD and SEM/EDX techniques and confirmed the deposition of pure metals on the copper cathodes. Successful extraction of tin, lead and zinc from anodic dissolution slime of electric and electronic waste (WEEE) was accomplished.

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