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TRADE – IT

An EIS study of metals dissolution mechanism in bromide-based electrolytes used as lixiviants for waste printed circuit boards

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INTRODUCTION

Waste printed circuit boards (WPCBs) contain substantial amounts of metals (Cu, Fe, Zn, Sn, Pb, Ni, Au, Ag) and include epoxy resin, glass fibers, ceramics and other non-metallic fractions, which embody large numbers of brominated flame retardants and other harmful substances, that might create serious pollution problems upon disposal. In view of the environmental and economic benefits, increasing attention has been paid to the development of different processes for hazardous components separation and metals recycling from WPCBs.

In an attempt to develop an innovative and eco-friendly technology for the advanced electrochemical recovery of the metals from WPCBs, the dissolution behavior of Zn, Sn, Fe and Pb in different bromide-based electrolytes has been investigated using electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) measurements. Different electrical equivalent circuits have been proposed to broaden understanding the dissolution mechanism of the metals in acidic Br-/Br_2 solutions that could be used as lixiviants in the hydrometallurgical route of metals recovery from WPCBs.

EXPERIMENTAL

Dissolution test solutions

sol. A: 2 M KBr (pH=6)
sol. B: 2 M KBr + 0.5 M HBr (pH=0.3)
sol. D: 2 M KBr + 0.5 M HBr + **0.001 M Br_2**
sol. C: 2 M KBr + 0.5 M HBr + **0.01 M Br_2**

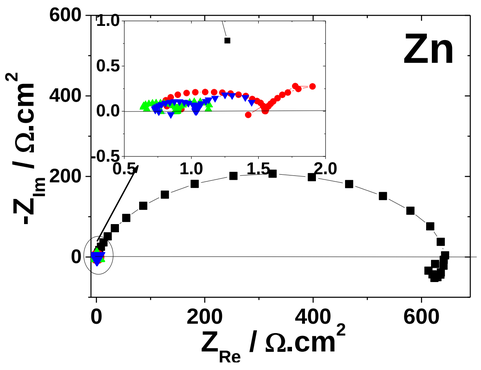
Electrodes

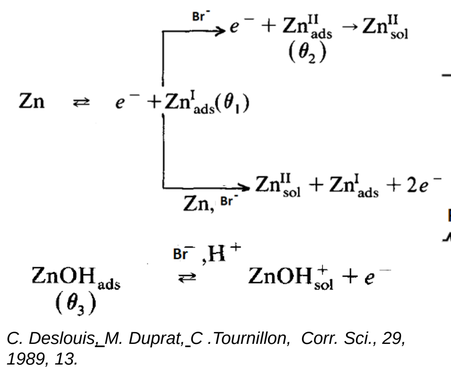
Zn (5.9mm); Sn (6mm); Fe (6mm); Pb (5.9 mm) disks as working electrodes
$Ag/AgCl/KCl_{SAT}$ as reference electrode (Ref.)
Pt wire (ϕ = 0.5 mm, L 10 cm) as counter electrode

Electrochemical impedance spectroscopy measurements - PARSTAT 2273 Potentiostat/Galvanostat

XPS measurements - ESCALAB 250 Xi XPS (Thermofisher) spectrometer equipped with a scanning electron microscope and an X-ray detector for EDX data acquisition

RESULTS AND DISCUSSION





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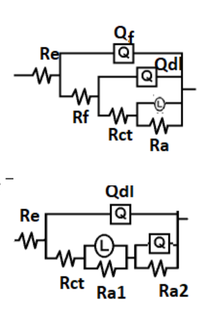
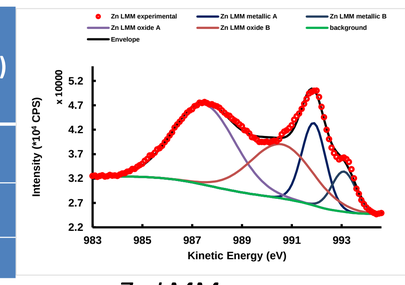


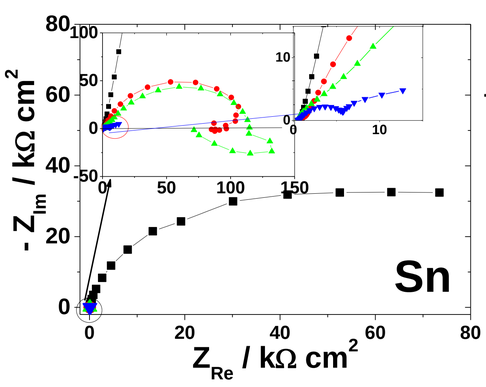
Table 1. Impedance data for Zn dissolution in different bromide-containing electrolytes

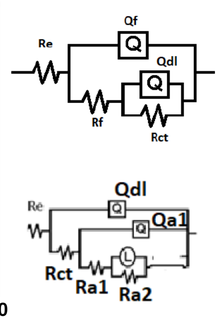
Solution	R_e (Ω cm²)	R_f (Ω cm²)	C_f (μF/cm²)	R_{ct} (Ω cm²)	C_{dl} (μF/cm²)	R_{a1} (Ω cm²)	L (H cm²)	R_{a2} (Ω cm²)	C_2 (F/cm²)
A	1.07	283.6	4.97	372.7	16.1	-	-	-	-
B	0.74	-	-	3.10	235	0.04	2E-4	1.27	**5.07**
C	0.64	-	-	0.26	188.4		-	0.28	**8.15**

$$C = \left(R^{1-n}Q\right)^{1/n}$$



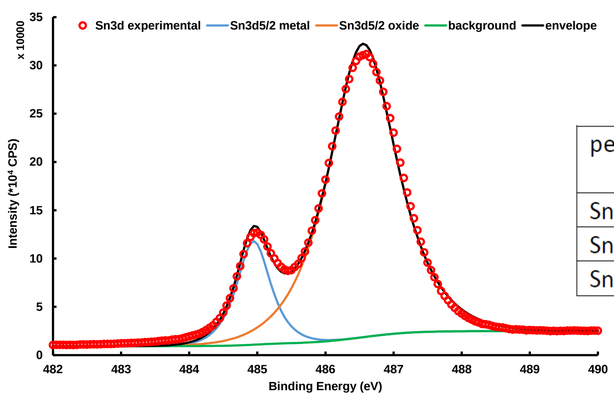
Zn LMM narrow scan





$Sn \rightarrow Sn^{2+} + 2e^-$

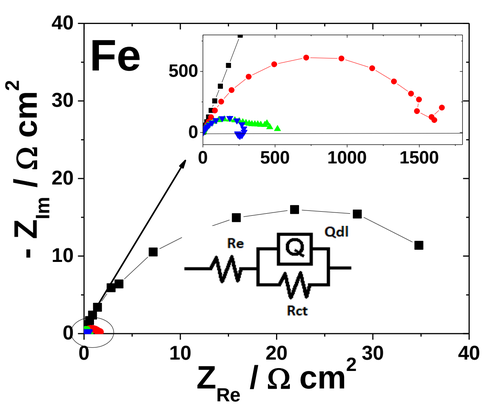
$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$



Sn3d narrow scans

Table 2. Binding energies of the observed Sn species

peak	state	observed BE (eV)	database BE (ev)	FWHM (eV)	possible compound
Sn3d5	0	484.97	485.2	0.6	Sn
Sn3d5	2+	-	486.0	-	SnO
Sn3d5	4+	486.57	486.6	1.2	SnO_2



$Fe - 2e^- \rightarrow Fe^{2+}$

$Fe + H_2O \leftrightarrow (FeOH)_{ads} + H^+ + e^-$

$(FeOH)_{ads} \rightarrow FeOH^+ + e^-$

$Fe + (FeOH)_{ads} \rightarrow Fe(FeOH)_{ads}$

$Fe(FeOH)_{ads} + OH^- \rightarrow FeOH^+ + (FeOH)_{ads} + e^-$

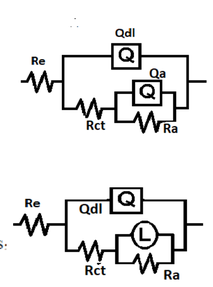
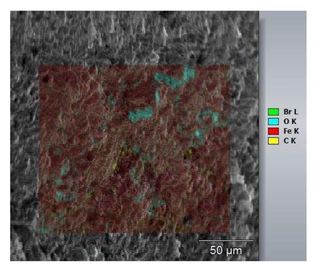
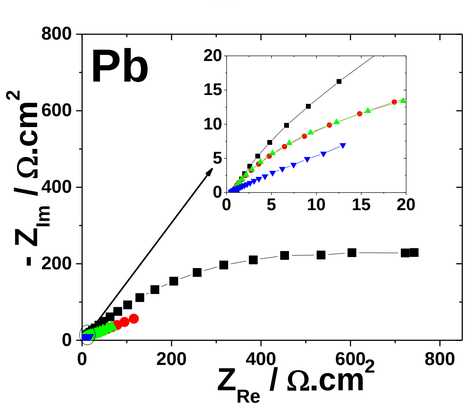


Table 3. Impedance data for Fe dissolution in different bromide-containing electrolytes

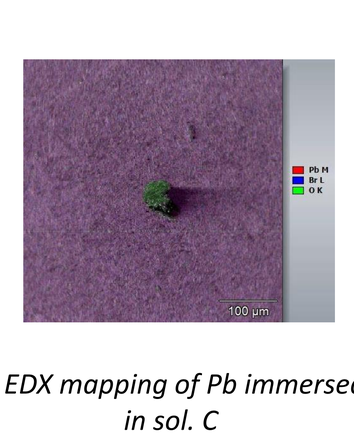
Solution	R_e (Ω cm²)	R_{ct} (Ω cm²)	C_{dl} (μF/cm²)	R_a (Ω cm²)	C_a (μF/cm²)	R_a' (Ω cm²)	L (H cm²)
A	1.00	42290	155	-	-	-	-
B	0.83	21.43	31.1	1633	89	-	-
C	0.616	863.9	29.5	-	-	439.1	**129.9**



EDX mapping of Fe immersed in sol. C



Nyquist diagrams corresponding to metals corrosion in different electrolytes: (–■–) Sol. A; (–●–) Sol. B; (–▲–) Sol. D; (–▼–) Sol. C



EDX mapping of Pb immersed in sol. C

CONCLUSIONS

- Electrochemical measurements showed that the addition of bromine in the system favours to great extents the dissolution process of all studied metals as compared to bromine-free electrolytes.
- In the investigated experimental conditions, the highest dissolution rates of the metals were obtained in acidic bromide solution containing 0.01 M Br_2 and they vary in the following order: Zn >> Sn > Pb > Fe.
- XPS chemical assessment allowed the identification of the dissolution products formed on the metallic surfaces after exposure to the electrolytes.

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Materials and Electrochemical Processing & Electrochemical Engineering

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MAT-P-4	Mila N. Krstajić Pajić, Sanja I. Stevanovic, Vuk V. Radmilović, Piotr Zabinski, Nevenka R. Elezović, Velimir R. Radmilović, Snezana L). Gojković, **Vladislava M. Jovanović** (*Department of Electrochemistry, ICTM, University of Belgrade, Belgrade, Serbia*)	***Catalysis at nano level: promoting Pt nanoparticle activity by Au decoration***
MAT-P-5	**Marijana Pantović Pavlović** (*Institute of Chemistry, Technology and Metallurgy, Department of Electrochemistry, University of Belgrade, Belgrade, Serbia*), Sanja Eraković, Miroslav Pavlović, Ljiljana Veselinović, Jasmina Stevanović, Vladimir Panić, Nenad Ignjatović	***Surface modification of titanium implants by adherent hydroxyapatite/titanium oxide composite coatings using novel in-situ synthesis***
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MAT-P-9	**Simona Varvara** (*University "1 Decembrie 1918" of Alba Iulia, Department of Exact Sciences and Engineering, Alba Iulia, Romania*), Sorin Aurel Dorneanu, Alexandru Okos, Roxana Bostan, Maria Popa, Liana Maria Muresan , Petru Ilea	***An EIS study of metals dissolution mechanism in bromide-based electrolytes used as lixiviants for waste printed circuit boards***
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