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Synergistic aqueous biphasic systems: a new paradigm for the ‘one-pot’ hydrometallurgical recovery of critical metals

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ABSTRACT

Acidic aqueous biphasic system (AcABS), in which the inorganic salt component of traditional aqueous biphasic system (ABS) is replaced by the inorganic acid inherently present in typical hydrometallurgical leachate solution, is shown to selectively separate cobalt from nickel, a separation relevant to the recycling of NiMH batteries. To overcome the limitation of electrodeposition in the presence of high acid concentration, a mixed ABS-AcABS approach is developed in which HCl is partially substituted by addition of a predictable amount of NaCl. This synergistic ABS-AcABS system retains the metal extraction efficiency of AcABS whilst diminishing the acid concentration required to induce phase separation as well as its distribution to the ionic liquid-rich phase. Selective deposition of cobalt in the presence of co-extracted manganese impurities was achieved in AcABS, ABS and ABS-AcABS systems. The morphology and composition of the obtained deposits as well as the Faradic efficiency of the process can be altered by varying the NaCl to HCl ratio and water content, resulting in highly tailored cobalt deposits. These results highlight the potential of AcABS derived systems as a new extraction-separation platform for the integrated hydrometallurgical treatment of critical metals, from leaching to electrodeposition.

KEYWORDS: acidic aqueous biphasic systems, critical metals, ionic liquids, waste electrical and electronic equipment, electrodeposition

1 INTRODUCTION

2 The extraction, separation and purification of critical metals from complex matrices such as
3 minerals or electronic wastes is technologically challenging, often requiring a series of demanding
4 processing steps. A traditional flowsheet for the hydrometallurgical treatment of metal feedstocks
5 follows a series of concentration (leaching), purification (solvent extraction) and refining stages
6 (electrodeposition or precipitation).¹⁻⁵ Process intensification, i.e. the ability to conduct multiple
7 hydrometallurgical operations within a single processing unit, is of great interest industrially as
8 this can reduce the economic and environmental impact associated with metal consumption. In
9 this context, a sustainable, effective and affordable metal extraction process is an issue of critical
10 importance. To alleviate metal criticality and reduce the environmental impact of mining
11 operations, the development of a simple, robust and flexible platform is of particular relevance for
12 the recycling of metals from secondary ‘ores’.

13 We recently proposed a ‘one-pot’ solution for the simultaneous leaching and selective extraction
14 of various critical metals using an ionic liquid-based acidic aqueous biphasic system (AcABS).⁶
15 Ionic liquids (ILs) are salts composed of asymmetric ions with disperse charge that are liquid at
16 room temperature.⁷ In the newly reported AcABS composed of the IL tributyltetradecyl
17 phosphonium chloride ([P₄₄₄₁₄]Cl), the very acid present in the leaching solution was used to salt-
18 out the IL. This is markedly different from conventional aqueous biphasic systems (ABS), such as
19 the previously reported [P₄₄₄₁₄]Cl – NaCl – based ABS for metal extraction,⁸ in which the molar
20 entropy of hydration of an inorganic salt dictates the formation of a reversible biphasic system
21 composed of a salt-rich phase and organic-rich phase.⁹ Performing the extraction in aqueous media
22 reduces the overall environmental impact associated with IL application as (i) lower quantities are
23 required compared to solvent extraction, (ii) hydrophilic ILs are less toxic and more biodegradable

24 than their hydrophobic counterparts and (iii) mass transfer properties are significantly improved
25 due to the lower solution viscosity, resulting in faster extraction kinetics.¹⁰⁻¹⁴

26 In this work, the scope AcABS processes is extended to investigate the extraction and separation
27 of Co(II), a critical metal,¹⁵ from Ni(II) and Mn(II) – a separation relevant to the recycling of nickel
28 metal hydride and lithium-ion batteries.¹⁶ To this end, a mixed ABS-AcABS approach is proposed
29 in which the HCl content required to induce phase separation in AcABS is predictably substituted
30 by small amounts of NaCl, further accentuating the versatility of the proposed approach.
31 Synergistic ABS-AcABS systems retains the advantages of AcABS whilst diminishing the acid
32 concentration required to induce phase separation as well as its distribution to the IL-rich phase.
33 This enables the use of more environmentally friendly operating conditions and facilitates the
34 subsequent metal deposition from the IL-rich phase. Selective deposition of Co(II) is optimized as
35 a function of various parameters including water content, HCl concentration and NaCl
36 concentration. The ability to directly deposit metals from the IL-rich phase opens the possibility
37 for a fully integrated approach to the leaching, separation and deposition of critical metals from
38 complex sources.

39

40 **METHODOLOGY**

41 **Materials and Instrumentation**

42 A detailed description of the compounds used as well as the instrumentation employed is
43 provided in the ‘Methodology’ section of the Supplementary information. The chemicals were
44 used as received without further purification.

45 Determination of mixed ABS-AcABS systems for metal extraction

46 It is important to emphasise that three different separation systems are employed in this work:
 47 two ternary systems composed of $[P_{44414}]\text{Cl-HCl-H}_2\text{O}$ (AcABS) and $[P_{44414}]\text{Cl-NaCl-H}_2\text{O}$ (ABS)
 48 respectively and a quaternary system $[P_{44414}]\text{Cl-HCl-NaCl-H}_2\text{O}$ referred to as ABS-AcABS. The
 49 phase diagrams for the quaternary system ABS-AcABS containing a fixed NaCl concentration (1
 50 wt.%, 2 wt.% and 4 wt.%) were determined through the cloud point titration method in a
 51 temperature-controlled cell at 298 K under agitation and atmospheric pressure. The concentration
 52 of NaCl was identical (1 wt.%, 2 wt.% and 4 wt.%) in all solutions used as to keep its concentration
 53 constant throughout the cloud point titration procedure. The quaternary system compositions were
 54 determined by the weight quantification of all components added within an uncertainty of $\pm 10^{-3}$ g.
 55 The detailed experimental procedure adopted is described in a previous work.¹⁷ The extraction and
 56 separation of Co(II) from Ni(II) and Mn(II) in different ABS-AcABS mixtures of total mass 5 g
 57 containing 30 wt.% $[P_{44414}]\text{Cl}$ was studied as a function of the HCl to NaCl ratio. A mixed metal
 58 ion solution containing $0.1 \text{ mol.L}^{-1} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$, $0.1 \text{ mol.L}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.1 mol.L^{-1}
 59 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was used for all experiments. Solutions were mechanically agitated for 5 min at 298
 60 K until the complete dissolution of the IL. The resulting mixture was left to phase separate 60 min
 61 in a thermostatic bath at 298 K. The volume of each phase of the ABS-AcABS was measured and
 62 aliquots of the upper and lower phases were collected for metal concentration analysis by
 63 inductively coupled plasma optical emission spectroscopy (ICP-OES) after appropriate dilution.
 64 The chloride, acid and water content of the IL-rich phase (top phase) was also determined after
 65 separation of the phases. The extraction efficiency (%EE) was calculated as follows:⁶

$$66 \quad \%EE = \frac{\frac{[M]_0 V_{\text{initial}}}{V_{\text{low}}} - [M]_{\text{low}}}{[M]_0} \times 100 \quad - (1)$$

where $[M]_0$ is the initial metal concentration of the metal in solution before extraction (*i.e.* before addition of the IL). $V_{initial}$ is the volume in mL of the mixture before extraction whilst V_{low} is the volumes, expressed in mL, of the lower phase after extraction. $[M]_{low}$ is the concentration of the metal ion in the lower phase after extraction.

Electrodeposition of Co(II) from ABS-AcABS

Electrochemical investigations including chronoamperometry and cyclic voltammetry (CV) were carried out using a Metrohm Autolab potentiostat controlled with the GPES software. A three-electrode system was used consisting of a glassy carbon (GC) working electrode (3 mm diameter), an iridium counter electrode and a silver chloride (Ag/AgCl) reference electrode. The working electrode was polished with diamond paste, rinsed and dried prior to all measurements. All cyclic voltammograms of single 0.1 mol.L⁻¹ Co(II) aqueous solutions were obtained at 298 K and at a scanning rate of 0.01 V.s⁻¹ with varying [P₄₄₄₁₄]Cl (from 0 to 20 wt.%) and HCl concentrations (0 to 8 mol.L⁻¹).

Chronometric deposition experiments were performed in the following three systems: ABS, AcABS and ABS-AcABS (with and without the addition of water). Compositions of all systems are presented in Table S1 in the ESI. After extraction from a single metal solution containing 0.1 mol.L⁻¹ of CoCl₂.6H₂O or a mixed solution of 0.1 mol.L⁻¹ of CoCl₂.6H₂O, NiCl₂.6H₂O and MnCl₂.4H₂O, the IL-rich phase was isolated from the aqueous one. CV experiments were carried out under agitation in a potential range of -2.50 to 2.00 V *vs.* Ag/AgCl at a scan rate of 0.01 V.s⁻¹. Electrodeposition of metals was undertaken by chronoamperometry agitation at a fixed potential of -2.00 V *vs.* Ag/AgCl during one hour. The three systems namely, AcABS, ABS and ABS-AcABS depicted in Table S1 were studied. A fourth system was considered to investigate the

impact of the water content on the deposition. After separating and isolating the phases from the system ABS-AcABS, the IL-rich phase was diluted in a minimum of water (0.2 g of water per gram of isolated IL-rich phase) until the solution colour transitioned from deep blue to light red. This well-known colour change is due to the transition of blue chloride-complexes (CoCl_4^{2-} or CoCl_3^{2-}) to the formation of a red cobalt hexahydrate complex, $\text{Co}^{2+}(\text{H}_2\text{O})_6$.¹⁸ This system is referred to as “ABS-AcABs-diluted” in this work.

Obtained deposits were analysed by SEM-Energy Dispersive Spectroscopy (SEM-EDS) for single metal extractions. Metallic deposits obtained after selective deposition of cobalt in multielemental solutions were analysed through X-ray Diffraction (XRD). In the latter case, the metal was fully leached in 5 mL of 4 mol.L⁻¹ nitric acid (HNO_3) in order to investigate (i) the purity of the metal and (ii) the Faradic efficiency of the electrodeposition (E_F). The Faradic yield corresponds to the ratio between the experimental and theoretical conversion of Co(II) to Co(0) during electrodeposition. E_F was calculated according to the following equation:

$$E_F = \frac{C_{\text{Co}} \times V_{\text{HNO}_3}}{\frac{\int_0^t I(t) dt}{nF}} \times 100 \quad (2)$$

where C_{Co} represents the concentration of cobalt in mol.L⁻¹ in the aqueous phase containing nitric acid, used to leach the deposits. V_{HNO_3} is the volume of the nitric acid solution in L. I (A) represents the current produced during chronoamperometry measurements for a given time t in seconds. F and n stand for the Faraday constant and the number of moles of electrons exchanged during the reduction respectively.

110 RESULTS AND DISCUSSION

111 Development of mixed ABS-AcABS systems for metal extraction

112 The innovation of AcABS lies in its ability to extract metals directly from leachates just by
113 adding a carefully selected IL. However, optimal extraction and separation of Co(II) in the
114 $[P_{44414}]\text{Cl-HCl-H}_2\text{O}$ AcABS was shown to occur for highly concentrated solutions of HCl above
115 8 mol.L^{-1} or $\sim 25 \text{ wt.}\%$, considerably more concentrated than most common leaching solutions (*cf.*
116 Figure S1 of the ESI). A full description Co(II), Ni(II) and Mn(II) extraction in AcABS is provided
117 in the “Metal extraction in the $[P_{44414}]\text{Cl-HCl-H}_2\text{O}$ AcABS” section in the ESI. This includes the
118 effect of HCl concentration in AcABS on the partition of $[\text{H}_3\text{O}]^+$, Cl^- and H_2O to the IL-rich phase
119 (Table S2, ESI), the IL-rich phase viscosity before and after metal extraction (Figure S2, ESI) and
120 the influence of Co(II) feed concentration on the extraction efficiency and system properties of
121 AcABS (Figure S3 and S4, ESI).

122 However, the addition of extra HCl to leachates to induce AcABS formation and the efficient
123 extraction of Co(II) is not realistic from an industrial perspective due to i) the corrosivity of HCl
124 and ii) the increased cost of solution neutralisation after extraction. Furthermore, even small HCl
125 concentrations can inhibit the subsequent electro-deposition of Co(II) due to the narrowing of the
126 electrochemical window caused by the reduction of $[\text{H}_3\text{O}]^+$ (*cf.* Figure S5 in ESI). $[P_{44414}]\text{Cl}$ was
127 shown to form ABS with a wide range of chloride salts.¹⁹ As such, we propose a mixed ABS-
128 AcABS system using mixtures of HCl/NaCl capable of efficiently separating Co(II) from Ni(II)
129 and Mn(II) from any chloride-containing aqueous solution, even at low HCl concentrations. It is
130 important to stress that some degree of solution acidity is required leach metals and to prevent
131 metal hydrolysis common at the high pH of typical ABS.

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2
3 132 The binodal curves for [P₄₄₄₁₄]Cl-HCl-H₂O systems containing 1 wt.%, 2wt% and 4wt% of NaCl
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5 133 at $T=298$ K are presented in Figure 1A. As expected from the lower cloud point of the [P₄₄₄₁₄]Cl-
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7 134 NaCl-H₂O system compared to that of HCl,¹⁹ the addition of a small concentration of NaCl results
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9 135 in a large decrease in the corresponding HCl concentration required to induce phase separation.
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11 136 For 15 wt.% [P₄₄₄₁₄]Cl, approximately 21 wt.% of HCl is required compared to 6.5 wt.% HCl for
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13 137 a mixed ABS-AcABS containing 4 wt.% NaCl. An additional benefit of the presented ABS-
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15 138 AcABS system is the predictable shift in the binodal position with increasing NaCl concentration
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17 139 as shown in Figure 1B. For [P₄₄₄₁₄]Cl concentrations above 5 wt.%, the binodals in Figure 1A are
18
19 140 roughly parallel. This allows the following simplification to be made: the addition of 1 wt.% NaCl
20
21 141 decreases the HCl requirement by approximately 3.4 wt.%. The proposed linear correlation is only
22
23 142 valid for ABS-AcABS containing up to of 4 wt.% NaCl. Addition of NaCl above 4 wt.% does not
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25 143 provide the same relative HCl decrease as below this salt concentration (Figure S6 in ESI). This
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27 144 appears as the limit for the synergistic effect of NaCl with HCl in ABS-AcABS.
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Figure 1. (A) The effect of NaCl concentration on the binodal curve of $[P_{44414}]Cl$ -HCl- H_2O system at 298 K (binodal data is provided in Table S3 in the ESI). **(B)** Reduction in the HCl concentration required to induce phase separation at a fixed NaCl concentration for 10 wt.%, 15 wt.% and 20 wt.% $[P_{44414}]Cl$

The partition of Co(II), Ni(II) and Mn(II) from a multielement solution containing 0.1 mol.L^{-1} of each respective metal ion was attempted for eight ABS-AcABS systems at different HCl:NaCl ratio ($T=298 \text{ K}$). The system compositions are given in Table S4 of the ESI and their respective metal extraction efficiency and the concentration of Cl^- , $[H_3O]^+$ and H_2O in the IL-rich phase after extraction and phase separation are presented in Figure 2-3 and Table S4. The concentration of the $[P_{44414}]^+$ cation in the aqueous phase was found to be below the detection limit for all tested systems

158 and is not included. The results in Figure 2 show that for all systems, there is little variation in the
159 extraction efficiency of the studied metal ions as one moves from and ABS to AcABS despite the
160 large variation in the total chloride concentration. Co(II) was extracted to the IL-rich phase whilst
161 Ni(II) remained in the aqueous phase and Mn(II) partitioned between the two, with a slight increase
162 in Mn(II) extraction at higher NaCl concentrations. These results are in accordance with previously
163 reported Co(II) and Ni(II) extraction from [P₄₄₄₁₄]Cl-NaCl-H₂O ABS and [P₄₄₄₁₄]Cl-HCl-H₂O
164 AcABS^{6,8} as well as those using hydrophobic phosphonium based-ILs in traditional liquid-liquid
165 extraction.^{13-14,16,20}

166 ILs incorporating quaternary phosphonium cations are known to extract anionic metal
167 complexes such as those formed by Co(II), Cu(II), Fe(III), Pd(II), or Pt(IV) at high halide
168 concentrations through the formation of a hydrophobic pair between the anionic metal complex
169 and the cation of the IL.^{6,8,13-14,20-21} Ni(II) exhibits a limited coordination with chloride anions,
170 highlighted by the low complexation constant of NiCl⁺ ($k_1^{\text{Ni}^{2+}} = 0.07$).¹⁸ The inability of Ni(II) to
171 form anionic chloro-complexes in water results in low extraction yields due to its inability to form
172 an ion pair with the IL cation. The intermediate complexation constant of Mn(II) with Cl⁻ ($k_1^{\text{Mn}^{2+}}$
173 = 0.33) compared to Ni(II) and Co(II) ($k_1^{\text{Co}^{2+}} = 0.40$)¹⁸ is reflected in its extraction efficiency
174 (Figure 2). The speciation of Co(II) is highly dependent on the ratio of Co(II) concentration to
175 chloride concentration in solution, the anionic species CoCl₃⁻ and CoCl₄²⁻ can be found at high
176 HCl concentrations.¹⁸ This transition from Co(H₂O)₆²⁺ found in aqueous solutions to negatively
177 charged Co(II) complexes can be visually observed as the solution changes color from pinkish red
178 to deep blue, the same as the color of the IL-rich phase after extraction. A previous study on the
179 extraction of Co(II) using [P₄₄₄₁₄]Cl confirmed that Co(II) is predominantly extracted as the

CoCl₄²⁻ species within the IL phase.^{6,8} The speciation of Co(II) is highly relevant for its subsequent electrodeposition from IL solutions and will be addressed further on.²²

Figure 2. Co(II), Mn(II) and Ni(II) extraction efficiencies in ABS-AcABS system with varying NaCl to HCl concentrations at 298 K. System compositions are provided in Table S4 of the ESI.

On a molar basis, significantly less Cl⁻ is required to induce ABS phase separation and Co(II) extraction when NaCl is employed compared to HCl. NaCl was shown to be a more efficient salting-out agent than HCl for the liquid-liquid demixing of [P₄₄₄₁₄]Cl-based ABS.¹⁹ Extraction of Co(II) is close to quantitative for HCl:NaCl ratio of 0.7 or greater. It is postulated that in such systems, the Cl⁻ provides the necessary chloride to form anionic chlorocobalt complexes whilst the greater salting-out effect of Na⁺ compared to that of [H₃O]⁺ promotes the transition of the less hydrophilic CoCl₃⁻ and CoCl₄²⁻ species to the IL-rich phase. This supports the claim that a mixed ABS-AcABS system for metal extraction combines the advantages and flexibility of AcABS with those of ABS with no loss in metal extraction efficiency.

196 The partition behaviour of the acid and water to the IL-rich phase in mixed ABS-AcABS
197 presents an interesting behaviour based on the ratio of HCl to NaCl as shown in Figure 3. The
198 water content of the IL-rich phase is low for all the studied systems, decreasing down to a minimum
199 of 7 wt.% H₂O for an ABS-AcABS composition of 30 wt.% [P₄₄₄₁₄]Cl, 10.8 wt.% HCl and 4.0
200 wt.% NaCl. The water content increases as NaCl is substituted by HCl from 10.6 wt.% in ABS
201 and reaching 21.1 wt.% for the pure AcABS in line with the greater salting-out potential of NaCl
202 compared to HCl.¹⁹ Furthermore, the acid concentration in the IL-rich phase does not significantly
203 increase whilst NaCl is the primary driver (HCl:NaCl molar ratio <0.89) for the phase separation
204 of ABS-AcABS. From the presented results, two conclusions can be inferred of great relevance
205 for the subsequent electrodeposition of Co(II) from a [P₄₄₄₁₄]Cl-rich phase. Firstly, a mixed ABS-
206 AcABS system can be predictably tuned with little appreciable variation in metal extraction
207 compared to simple ABS or AcABS systems. Secondly, a compromise is required in the HCl to
208 NaCl ratio of ABS-AcABS. Higher NaCl concentrations reduce the acid and chloride migration to
209 the IL-rich phase at the expense of a lower water content compared to simple AcABS. The high
210 viscosity of loaded [P₄₄₄₁₄]Cl solutions can reduce the diffusion of Co(II) as well as cause losses
211 during manipulation. However, minimizing the acid concentration will facilitate the deposition of
212 Co(II) from [P₄₄₄₁₄]Cl solutions. An additional consideration is that the water content, and
213 therefore the viscosity, of the loaded [P₄₄₄₁₄]Cl-rich phase once isolate can be controlled by dilution
214 with water.

Figure 3. Concentration of acid ($[H_3O]^+$), chloride anion and water in the $[P_{44414}]Cl$ -rich phase after metal extraction in ABS-AcABS system with varying NaCl to HCl concentrations at 298 K. System compositions, including the partition behavior of the acid and water to the IL-rich phase, are provided in Table S4 of the ESI.

Electrochemical behaviour of Co(II) in ABS-AcABS systems

Having demonstrated the separation of Co(II) from Ni(II) and Mn(II) in AcABS and ABS-AcABS as well as the partitioning of the system components relevant to the subsequent deposition of Co(II), the electrochemical behaviour of studied system is now investigated. The influence of the hydrophilic $[P_{44414}]Cl$ in aqueous solutions on the reduction potential of Co(II) is presented in Figure 4. The presence of the IL in aqueous solution lowers the kinetics of water to hydrogen reduction (*cf.* Figure 4A), in line with the wide electrochemical window of phosphonium-based ILs.²³⁻²⁴ Co(II) is known to reduce to metallic cobalt at a potential of -0.28 V *vs.* ENH, this is to say, -0.50 V *vs.* Ag/AgCl.²⁵ In accordance with the literature, the CV of an aqueous 0.1 mol.L⁻¹ Co(II) solution (Figure 4A, dashed line) presents an inset reducing peak at -0.42 V and a minimum at -1.0 V *vs.* Ag/AgCl. A large oxidation peak is also observed from 0.42 to 0.59 V *vs.* Ag/AgCl,

confirming that cobalt can be oxidized reversibly. The addition of increasing amounts of [P₄₄₄₁₄]Cl from 0 to 10 wt. % IL results in a decrease in the cathodic peak potential for cobalt ($E^{\text{Red}}_{\text{Co}}$) from -0.42 to -1.06 V vs Ag/AgCl. When the concentration of IL exceeds 10 wt.%, the reduction peak potential remains constant (*cf.* Figure 4B). This shift in the reduction peak is a strong indication of a change in the complexation of Co(II) in the presence of the chloride anions from the IL. The anionic cobalt complexes CoCl_3^- and CoCl_4^{2-} are the predominant complexes reported in chloride based ILs.^{13-14,22,26} Furthermore, whilst the CoCl_3^- was shown to be electrochemically active in ILs, the complex CoCl_4^{2-} was not.²² This suggests that a high chloride concentration is inhibiting the deposition of Co(0). This is in accordance with the Nernst law, which states that changes in the speciation has an influence on the standard reduction potential of metallic species.

However, complexation of chlorides is insufficient to explain the magnitude of the shift in the reduction potential. The electrochemical kinetic behaviour of nickel electrodeposition was previously studied in acidic aqueous phases and lead to the intermediate formation of Ni(OH) adsorbed species.²⁷⁻²⁹ Similarly, cobalt is assumed to present the following reduction mechanism in water:

Elevated concentrations of ILs could inhibit the formation of the intermediate complex cobalt(I) hydroxide adsorbed species and therefore reduce the kinetic of reduction of Co(II).

The intensity of all reduction peaks decreases with the increasing IL concentration due to the higher viscosity and therefore lower kinetics of the IL-concentrated systems compared to the pure water system. Finally, an unveiled trend can be observed for mixtures containing 5 wt. % [P₄₄₄₁₄]Cl

or more with the emergence of a small reduction peak close to -0.5 V vs. Ag/AgCl (Figure 5A, inset). This is attributed to the reduction of Co(II) to Co(I). ILs provide a better environment for the stabilisation of intermediate metal oxidation states compared to water. For example, the presence of water was shown to significantly affect the voltammetric behaviour of Co(II) in the ethylammonium nitrate IL and the oxidation of Co(II) to Co(III).³⁰

Figure 4. (A) CV experiments at a 0.01 V.s⁻¹ scan rate of various solutions containing 0.1 mol.L⁻¹ of Co(II) and concentration of [P₄₄₄₁₄]Cl ranging between 0 (black dotted line) and 20 wt. % (light to dark blue colours). (B) Evolution of the inset peak corresponding to the reduction of Co(II) to Co(0) as a function of the concentration of [P₄₄₄₁₄]Cl.

CV analysis at a scan rate of 0.01 V.s^{-1} and 298 K on a GC working electrode was carried out in the four systems AcABS, ABS and ABS-AcABS (both undiluted and diluted) after extraction from $0.1 \text{ mol.L}^{-1} \text{ Co(II)}$ solutions. The solution compositions of the studied systems are listed in Table S1. The CV scans are presented in Figure 5. Electrodeposition of Co(II) was performed during one hour on a GC electrode under agitation. The electrodes were qualitatively and semi-quantitatively analyzed via SEM-SE and SEM-ESD respectively. The morphology and composition of the obtained deposits are presented in Figure 6 and Table 1 respectively.

Figure 5. CV of various systems after extraction of cobalt in an aqueous solution containing $0.1 \text{ mol.L}^{-1} \text{ Co(II)}$. Scanning rate: 0.01 V.s^{-1} . Current densities (J) are multiplied by 25 for the ABS, AcABS and ABS-AcABS systems.

Starting with the ABS system, first reported by Onghena et al.⁸ composed of $[\text{P}_{44414}]\text{Cl-NaCl-H}_2\text{O}$, a reduction peak (Co(II) to Co(0)) with an onset point at $-1.07 \text{ V vs. Ag/AgCl}$ can be observed (Figure 5, orange line). This is in full agreement with our previous result showing that $E_{\text{Co}}^{\text{Red}} = -1.06 \text{ V vs. Ag/AgCl}$ for systems containing 10 wt. % or more $[\text{P}_{44414}]\text{Cl}$. After inducing a potential

of -2.00 V vs. Ag/AgCl to the solution, EDS analysis of the obtained deposit on the GC electrode surface indicates a high purity cobalt deposit of 98.9 mol.% (Table 1). No significant quantities of chloride or phosphonium are recorded. The morphology of the obtained deposit is that of micrometre-scale dendrites, characteristic of metallic cobalt in aqueous solutions.³¹ Despite the lack of visible Co(0) reduction peak in the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS (Figure 5, purple line), small particles were identified on the GC electrode after electrodeposition. This is a direct consequence of the large concentration of acid after extraction in the top phase ([H₃O]⁺ = 3.0±0.26 mol.L⁻¹). In such an acidic environment, Co(0) particles can be leached back in the aqueous solution after deposition. Two concomitant but opposing phenomena emerge: (i) the reduction of Co(II) at the negative overpotential and (ii) the oxidation of Co(0) due to the HCl concentration. As a result, the particle seen in Figure 6 is composed of only 52.7 mol.% of cobalt and 44.7 mol.% of chloride, characteristic of an ongoing leaching phenomenon.

Figure 6. SEM-SE images (magnification $\times 1000$) of working electrodes after 1 hour of electrodeposition at -2.00 V vs. Ag/AgCl.

Table 1. Elemental analysis of the electrodeposited deposits obtained in ABS, AcABS and ABS-AcABS (undiluted and diluted) systems after extraction from solutions containing 0.1 mol.L⁻¹ Co(II).

Systems	Elemental analysis (mol.%)		
	Co	Cl	P
ABS	98.9 ± 12.3	1.1 ± 0.5	-
AcABS	52.7 ± 23.3	44.7 ± 18.3	2.6 ± 1.6
ABS-AcABS	92.6 ± 12.5	6.9 ± 6.3	0.5 ± 0.1
ABS-AcABS-diluted	95.6 ± 16.3	3.3 ± 2	1.1 ± 0.6

To avoid leaching just after the electrodeposition step, a mixed ABS-AcABS system containing [P₄₄₄₁₄]Cl-NaCl-HCl-H₂O is evaluated (composition provided in Table 1). As shown in Figure 3, the partial substitution of HCl by NaCl reduces the [H₃O]⁺ concentration of the IL-rich phase whilst maintaining the required solution acidity to perform the leaching of metals. This system was studied both in its undiluted and diluted form to establish the impact of water and therefore Co(II) complexation, on the quality of the Co(0) deposits. In the CV of undiluted ABS-AcABS, E^{Red}_{Co} appears at -1.12 V vs. Ag/AgCl (Figure 5, grey line), similar to that obtained in the ABS system. The composition of the obtained deposit is 92 mol.% of cobalt and only 7 mol.% chloride. This represents a significant increase in the deposit purity compared to that obtained in AcABS. The presence of Cl⁻ is assigned to (i) the presence of residual [P₄₄₄₁₄]Cl in the final deposit and (ii) to the small leaching effect from the persistent presence of HCl ([H₃O]⁺ = 0.35±0.04 mol.L⁻¹). SEM-SE analysis of the working electrode surface after deposition reveals its complete coverage by a large layer of deposit (*cf.* Figure 6). The deposit presents a sheet-like structure with no observable

dendrites. This is probably due to the etching of the deposit surface by the remaining HCl after oxidation of Co(0) present in the dendritic structures of high surface area.

To gain a better understanding on the role of water in the studied system, the IL-rich phase (top phase) of the mixed system ABS-AcABS was isolated after extraction and diluted (0.2 g of water per gram of isolated IL-rich phase). The system was diluted through dropwise addition of water until a shift in the solution colour from blue to light red was observed. By varying the water content of the IL-rich phase after AcABS extraction, essentially transitioning from a water in IL environment to IL as electrolytes in aqueous solutions, the mass transport and interfacial structure at the electrode can be altered resulting in potentially different deposit properties.³²⁻³³ An additional positive effect of dilution on the Faradic efficiency is the change in Co(II) coordination from chlorocobalt complexes to Co(II) hexahydrate. Dilution of the system results in a positive shift in the onset of the reduction peak from -1.12 V *vs.* Ag/AgCl for ABS-ACABS to -0.90 V *vs.* Ag/AgCl for ABS-AcABS-diluted. The dilution influences the complexation of cobalt-chloride complexes, thereby increasing the reduction potential in accordance with Nernst's law. A deposit composed of large dendrites was visually observed, further confirmed by SEM-SE (*cf.* Figure 6). Elemental analysis of the deposit highlights a quasi-pure material composed of 95.5 mol.% cobalt. In light of these results, [P₄₄₄₁₄]Cl-NaCl-HCl-H₂O mixture stands out as promising medium for the recovery of metallic cobalt. The morphology and composition of the obtained deposits can be altered by varying the NaCl to HCl ratio and water content, resulting in highly tailored cobalt deposits. However, extraction results displayed in Figure 2 indicate that up to 40 wt.% of Mn(II) can be co-extracted with Co(II). The question of the selectivity of such a process, starting from an aqueous solution containing a mixture of Co(II), Mn(II) and Ni(II) thus arises.

Selective electrodeposition of Co(II) from Ni(II) and Mn(II)

After extraction of a mixture of 0.1 mol.L⁻¹ of Co(II), Ni(II) and Mn(II) from ABS and ABS-AcABS systems (Table S1 of the ESI), chronoamperometry experiments at -2V vs Ag/AgCl were carried out to selectively reduce cobalt to its metallic state. Results are given in Figure 7. Current densities for all experiments suffer from some oscillations as a result of hydrogen evolution from the reduction of water and/or of [H₃O]⁺. The current density slowly decreases with time during deposition in all systems, characteristic of metallic deposition. The reduction of a conductive material such as cobalt can increase the surface area of the electrode and thus the current density in absolute value. This phenomenon is particularly pronounced in the ABS-AcABS-diluted system where the current density is multiplied by a factor of 8 in one hour. The lower viscosity and chloride complexation of this system are beneficial for an efficient deposition of metals. Quantitative compositional analysis of the deposits for the systems presented in Figure 7 and their respective Faradic efficiencies are displayed in Table 2.

Figure 7. Chronoamperometry experiments using a potential of -2.00 V vs. Ag/AgCl for 1 hour. Current densities (J) are multiplied by 25 for the ABS and ABS-AcABS systems.

For all studied systems, no trace of Mn(II) and Ni(II) were recorded, confirming that solely Co(II) is reduced as a metallic species. This is to be expected as Ni(II) is not extracted to the IL-rich phase (*cf.* Figure 1), and Mn(II) presents a reduction potential of -1.41 V *vs.* Ag/AgCl, lower than that of Co(II) (-0.5 V *vs.* Ag/AgCl).²⁵ The efficiency of Co(II) reduction is low in the undiluted ABS and ABS-AcABS systems with a final deposit mass of 0.30 mg and 0.29 mg respectively. Faradic efficiencies indicate that around 30 % of the electrons generated by the potentiostat are devoted to the reduction of Co(II) to metallic Co(0) in these systems. Inducing a potential of -2.00 V *vs.* Ag/AgCl results in an important reduction of water and/or proton to hydrogen. The low energetic yields hinder the industrial application for such processes.

Table 2. ICP analysis performed for ABS, ABS-AcABS, and ABS-AcASB-diluted systems. The composition of the deposits and Faraday efficiencies (E_F) are given for all systems.

Deposit Composition	Extraction Systems		
	ABS-AcABS	ABS	ABS-AcABS-diluted
Co (mg)	$0.30 \pm 5 \times 10^{-3}$	$0.29 \pm 5 \times 10^{-3}$	7.2 ± 0.1
Mn (mg)	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
Ni (mg)	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
E_F (%)	28.9	31.6	59.7
Co electroplated (mol.%)	0.91	0.82	2.51

Deposition yields are significantly improved after dilution, with close to twenty fourfold increase in the deposit mass to 7.2 mg in the system ABS-AcABS-diluted. This results in a twofold increase

in the Faradic efficiency to a value of 59.7 %. The Faradic yields reported here are reasonably satisfying and were obtained without any optimisation of the electrochemical process. At -2 V vs. Ag/AgCl, water or $[H_3O]^+$ present in the medium is expected to be reduced significantly. Carrying out the experiments at a more positive potential would most probably lead to better yields due to a less pronounced reduction of water or $[H_3O]^+$. Experiments carried out at -1.5 V vs. Ag/AgCl revealed that deposition of Co(II) was possible, whereas assigning a potential of -1 V at the GC electrode did not yield any reduction of Co(II). It is worth highlighting that the electric charge is of 0.3 and 14 C for the undiluted and diluted ABS-AcABS systems respectively. As a result, even if the Faradic yield is twice higher with the ABS-AcABS-diluted, more electrons will be devoted to the reduction of water in the latter system. However, the cobalt deposition kinetic is more than 24 times faster in the diluted systems which significantly improves results obtained compared to pure ILs. After 1 hour of chronoamperometric measurements, only 2.5 mol. % of Co(II) ions were reduced. This proves that the bath did not suffer from any significant concentration depletion. Larger surface electrodes are required to recover the metal in an acceptable length of time. The current-time transient for the deposition of Co(II) from the ABS-AcABS-diluted system was studied to determine the nucleation process (Figure S7 of the ESI) and was found to follow a 3D instantaneous nucleation growth process.

The crystalline structure of the deposits obtained at the end of the chronoamperometry experiments were analysed by XRD analysis with the spectra depicted in Figure 8. NaCl crystals are highlighted in the ABS-AcABS and ABS systems. This is not surprising as these two solutions contain an important initial NaCl concentration (7.6 wt.%) to induce the formation of two phases. Near the electrode, the deposition of cobalt in ABS-AcABS and ABS systems will most likely release chloride anions from the metallic complexes and locally saturate the solution in NaCl

inducing the crystallisation of the latter salt. All deposits are composed of metallic Co(0) crystallised in a hexagonal close packed lattice. However, there are differences in the crystallisation of Co(0) in the ABS and ABS-AcABS compared to the ABS-AcABS-diluted system. Focusing on the cobalt metallic peaks 2 (p_2) and 3 (p_3) at 44.6° and 47.5° respectively, the ratio $R = p_2 / p_3$ differs from one system to another. These two peaks correspond to the crystal orientation (111) and (101) respectively of metallic cobalt.³⁴ Concerning the ABS-AcABS-diluted system, p_2 presents a higher intensity than p_3 resulting in a ratio R of 1.51. The opposite phenomenon is reported for ABS-AcABS and ABS systems leading to a ratio of 0.51 and 0.47 respectively. This phenomenon highlights a preferential crystalline orientation of metals electrodeposited in concentrated IL solutions compared to diluted IL solutions. Such changes in the crystalline nature of deposits due to the presence of IL was previously reported for the deposition of copper in the presence of $[C_4mim][HSO_4]$ as additive.³⁵

The versatility of IL-based ABS and AcABS was recently highlighted for its application in metal extraction^{6,8,36-37} but it is here shown that it can be extended to the electrodeposition of metals. The hydrophilicity of the extracting solution allows to tune and enhance the efficiency of the recovery of pure cobalt and to modify the properties of the resulting deposits.

Figure 8. XRD diffractograms of deposits obtained after extraction of metals from a mixed solution containing 0.1 mol.L⁻¹ Co(II), Ni(II) and Mn(II) and electrodeposition at a potential of -2.00 V vs. Ag/AgCl during 1 hour.

CONCLUSIONS

AcABS and its ABS-AcABS derivative stands out as an efficient, flexible and integrated extraction-separation-purification platform for the recovery of critical metals from primary and secondary ores. By varying the HCl concentration and the chloride source (either NaCl or HCl), selective separation of Co(II) from Ni(II) was achieved whilst controlling the partition of the various system constituents. The distribution of HCl was found to have a profound influence on the subsequent electrodeposition of Co(II). To address this, a mixed ABS-AcABS extraction system was proposed which combines the advantages of the AcABS and ABS systems. By varying the water content of the [P₄₄₄₁₄]Cl-rich phase after extraction and separation of Co(II) from Ni(II), high quality dendritic deposits of pure metallic cobalt were obtained in presence of Mn(II) impurities. Furthermore, ABS-AcABS systems can be tailored to obtain metal deposits with varied properties. The results presented in this work demonstrate the applicability of AcABS for a ‘one-

pot' approach for the sequential leaching, solvent extraction and electrodeposition of metals. Moreover, this work provides an understanding of the fundamental mechanisms governing the extraction and electrodeposition in AcABS required to extend these findings to the recovery of other critical metals.

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ASSOCIATED CONTENT

Supporting Information. detailed list of chemicals and instruments used, extraction of Co(II), Ni(II) and Mn(II) in AcABS as a function of HCl concentration, IL-rich phase viscosity before and after Co(II) extraction, extraction in AcABS as a function of Co(II) concentration, composition of IL-rich phase after extraction in ABS and ABS-AcABS systems, CV of aqueous Co(II) solutions in the presence of HCl, electrochemical behavior of Co(II) in $[P_{44414}]Cl$ aqueous solutions, chronometric measurements of Co(II) deposition from $[P_{44414}]Cl$ -rich phase after extraction in AcABS, ABS and ABS-AcABS, nucleation mechanism of Co(II) in mixed ABS-AcABS-diluted system during electrodeposition.

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Notes

The authors declare no competing financial interest.

REFERENCES

- 1) Ayres, R.U., Metals *Recycling*: Economic and Environmental Implications. *Resour. Conserv. Recy.*, **1997**, 21, 145–173. DOI 10.1016/S0921-3449(97)00033-5.
- 2) Cui, J., Forssberg, E., Mechanical recycling of waste electric and electronic equipment: a review. *J. Hazard. Mater.*, **2003**, 99, 243–263. DOI 10.1016/S0304-3894(03)00061-X.
- 3) Nuss, P., Eckelman, M., Life Cycle Assessment of Metals: A Scientific Synthesis. *PLoS One*, **2014**, 9, e101298. DOI 10.1371/journal.pone.0101298.
- 4) Cui, J., Zhang, L., Metallurgical recovery of metals from electronic waste: a review. *J. Hazard. Mat.*, **2008**, 158, 228–256. DOI 10.1016/j.jhazmat.2008.02.001.

- 1
2
3 473 5) Wilson, A.M., Bailey, P.J., Tasker, P.A., Turkington, J.R., Grant, R.A., Love, J.B., Solvent
4
5 474 extraction: the coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.*, **2014**,
6
7 475 43, 123-134. DOI 10.1039/C3CS60275C.
8
9
10 476 6) Gras, M., Papaiconomou, N. Schaeffer, N., Chainet, E., Tedjar, F., Coutinho, J.A.P., Billard,
11
12 477 I., Ionic-Liquid-Based Acidic Aqueous Biphasic Systems for Simultaneous Leaching and
13
14 478 Extraction of Metallic Ions. *Angew. Chem. Int. Ed.*, **2018**, 57, 1563-1566. DOI
15
16 479 10.1002/anie.201711068.
17
18
19 480 7) Hallett, J.P., Welton, T., Room-temperature ionic liquids: solvents for synthesis and catalysis.
20
21 481 2. *Chem. Rev.*, **2011**, 111, 3508–3576. DOI 10.1021/cr1003248.
22
23
24 482 8) Onghena, B., Opsomer, T., Binnemans, K., Separation of cobalt and nickel using a
25
26 483 thermomorphonic ionic-liquid-based aqueous biphasic system. *Chem. Commun.*, **2015**, 51,
27
28 484 15932-15935. DOI 10.1039/C5CC06595J.
29
30
31 485 9) Shahriari, S., Neves, C.M.S.S., Freire, M.G., Coutinho, J.A.P., Role of the Hofmeister Series
32
33 486 in the Formation of Ionic-Liquid-Based Aqueous Biphasic Systems. *J. Phys. Chem. B*, **2012**,
34
35 487 116, 7252. DOI 10.1021/jp300874u.
36
37
38 488 10) Thuy Pham, T.P., Cho, C.W., Yun, Y.S., Environmental fate and toxicity of ionic liquids: a
39
40 489 review. *Water Res.*, **2010**, 44, 352. DOI 10.1016/j.watres.2009.09.030.
41
42
43 490 11) Fu, J., Yang, Y.I., Zhang, J., Chen, Q., Shen, X., Gao, Y.Q., Structural Characteristics of
44
45 491 Homogeneous Hydrophobic Ionic Liquid–HNO₃–H₂O Ternary System: Experimental Studies
46
47 492 and Molecular Dynamics Simulations. *J. Phys. Chem. B*, **2016**, 120, 5194. DOI
48
49 493 10.1021/acs.jpcb.6b01214.
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 494 12) Mazan, V., Boltoeva, M.Y., Tereshatov, E.E., Folden III, C.M., Mutual solubility of water and
4
5 495 hydrophobic ionic liquids in the presence of hydrochloric acid. *RSC Adv.*, **2016**, 6, 56260. DOI
6
7 496 10.1039/C6RA06791C.
8
9
10 497 13) Vander Hoogerstraete, T., Wellens, S., Verachtert, K., Binnemans, K., Removal of transition
11
12 498 metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid:
13
14 499 separations relevant to rare-earth magnet recycling. *Green Chem.*, **2013**, 15, 919. DOI
15
16 500 10.1039/C3GC40198G.
17
18
19 501 14) Wellens, S., Thijs, B., Binnemans, K., An environmentally friendlier approach to
20
21 502 hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with
22
23 503 undiluted phosphonium ionic liquids. *Green Chem.*, **2012**, 14, 1657–1665. DOI
24
25 504 10.1039/C2GC35246J.
26
27
28 505 15) European Commission, *Study on the review of the list of Critical Raw Materials*. Luxembourg:
29
30 506 Publications Office of the European Union, **2017**. DOI 10.2873/876644.
31
32
33 507 16) Larsson, K. Binnemans, K., Selective extraction of metals using ionic liquids for nickel metal
34
35 508 hydride battery recycling. *Green Chem.*, **2014**, 16, 4595-4603. DOI 10.1039/C3GC41930D.
36
37
38 509 17) Neves, C.M.S.S., Ventura, S.P.M., Freire, M.G., Marrucho, I.M., Coutinho, J.A.P., Evaluation
39
40 510 of Cation Influence on the Formation and Extraction Capability of Ionic-Liquid-Based
41
42 511 Aqueous Biphasic Systems. *J. Phys. Chem. B*, **2009**, 113, 5194–5199. DOI 10.1021/jp900293v
43
44
45 512 18) Högfeldt, E. *IUPAC Stability constants of metal-ion Complexes Part A: Inorganic ligands*;
46
47 513 IUPAC; Pergamon Press, **1982**.
48
49 514 19) Schaeffer, N., Passos, H., Gras, M., Mogilireddy, V., Leal, J.P., Pérez-Sánchez, G., Gomes,
50
51 515 J.R.B., Billard, I., Papaiconomou, N., Coutinho, J.A.P., Mechanism of ionic-liquid-based
52
53
54
55
56
57
58
59
60

- acidic aqueous biphasic system formation. *Phys. Chem. Chem. Phys.*, **2018**, 20, 9838-9846. DOI 10.1039/c8cp00937f.
- 20) Onghena, B., Valgaeren, S., Vander Hoogerstraete, T., Binnemans, K., Cobalt(II)/nickel(II) separation from sulfate media by solvent extraction with an undiluted quaternary phosphonium ionic liquid. *RSC Adv.*, **2017**, 7, 35992-35999. DOI 10.1039/C7RA04753C.
- 21) Papaiconomou, N., Svecova, L., Bonnaud, C., Cathelin, L., Billard, I., Chainet, E., Possibilities and limitations in separating Pt(IV) from Pd(II) combining imidazolium and phosphonium ionic liquids. *Dalton Trans.*, **2015**, 44, 20131–20138. DOI 10.1039/c5dt03791c.
- 22) Hsieh, Y.T., Lai, M.C., Huang, H.L., Sun, I.W., Speciation of cobalt-chloride-based ionic liquids and electrodeposition of Co wires. *Electrochim. Acta*, **2014**, 117, 217–223. DOI 10.1016/j.electacta.2013.11.120.
- 23) Tsunashima, K., Sugiya, M., Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes. *Electrochem. Commun.*, **2007**, 9, 2353–2358. DOI 10.1016/j.elecom.2007.07.003.
- 24) MacFarlane, D.R., Tachikawa, N., Forsyth, M., Pringle, J.M., Angell, C.A., Energy applications of ionic liquids. *Energy Environ. Sci.*, **2014**, 7, 232–250. DOI 10.1039/C3EE42099J.
- 25) Bard, A., Parsons, J., Jordan, R., *Standard potentials in aqueous solutions*, CRC Press, **1985**.
- 26) Lechat, S., Khan, M.A., Bouet, G., Spectrophotometric study of cobalt(II) chloride complexes in ethanol and propan-2-ol. *Inorg. Chim. Acta*, **1993**, 211, 33–36. DOI 10.1016/S0020-1693(00)82840-6.

- 537 27) Matulis, J., Slizys, K., On Some Characteristics of Cathodic Processes in Nickel
538 Electrodeposition. *Electrochim. Acta*, **1964**, 9, 1177-1188. DOI 10.1016/0013-
539 4686(64)85009-X.
- 540 28) Piatti, R.C.V., Arvia, A.J., Podesta, J.J., The Electrochemical Kinetic Behaviour of Nickel in
541 Acid Aqueous Solutions Containing Chloride and Perchlorate Anions. *Electrochim. Acta*.
542 **1969**, 14, 541-560. DOI 10.1016/0013-4686(69)87040-4.
- 543 29) Chassaing, E., Jousselein, M., Wiart, R., The Kinetics of Nickel Electrodeposition Inhibition by
544 Adsorbed Hydrogen and Anions. *J. Electroanal. Chem.*, **1983**, 157, 75-88. DOI
545 10.1016/S0022-0728(83)80377-5.
- 546 30) Suryanto, B.H.R., Lu, X., Chan, H.M., Zhao, C., Controlled electrodeposition of cobalt oxides
547 from protic ionic liquids for electrocatalytic water oxidation. *RSC Adv.*, **2013**, 3, 20936-20942.
548 DOI 10.1039/C3RA43614D.
- 549 31) Crundwell, F.K., M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, W.G.,
550 *Extractive metallurgy of nickel, cobalt and platinum group metals*, Elsevier, **2011**.
- 551 32) Abbott, A.P., Model for the Conductivity of Ionic Liquids Based on an Infinite Dilution of
552 Holes. *Chem. Phys. Chem.*, **2005**, 6, 2502-2505. DOI 10.1002/cphc.200500283.
- 553 33) Kornyshev, A.A., Double-Layer in Ionic Liquids: Paradigm Change? *J. Phys. Chem. B*, **2007**,
554 111, 5545–5557. DOI 10.1021/jp067857o.
- 555 34) Qin, W., Yang, C., Ma, X., Lai, S., Selective synthesis and characterization of metallic cobalt,
556 cobalt/platinum, and platinum microspheres. *J. Alloys Compd.*, **2011**, 509, 338–342. DOI
557 10.1016/j.jallcom.2010.09.022.

- 35) Zhang, Q.B., Hua, Y.X., Wang, Y.T., Lu, H.J., Zhang, X.Y., Effects of ionic liquid additive [BMIM]HSO₄ on copper electro-deposition from acidic sulfate electrolyte. *Hydrometallurgy*, **2009**, 98, 291–297. DOI 10.1016/j.hydromet.2009.05.017.
- 36) Blesic, M., Nimal Gunaratne, H.Q., Jacquemin, J., Nockemann, P., Olejarz, S., Seddon, K.R., Strauss, C.R., Tunable thermomorphism and applications of ionic liquid analogues of Girard's reagents. *Green Chem.*, **2014**, 16, 4115–4121. DOI 10.1039/C4GC01159G.
- 37) Vander Hoogerstraete, T., Onghena, B. Binnemans, K., Homogeneous Liquid–Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid. *J. Phys. Chem. Lett.*, **2013**, 4, 1659–1663. DOI 10.1021/jz4005366.

1
2
3
4
5
6
7
8
9
10
11
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TABLE OF CONTENT (TOC)

SYNOPSIS

The potential of acidic aqueous biphasic system (AcABS) is extended and proposed as a new extraction-separation platform for the integrated hydrometallurgical treatment of critical metals from leaching to electrodeposition.