



Recovery of critical and value metals from mobile electronics enabled by electrochemical processing



Tedd E. Lister^{a,*}, Peiming Wang^b, Andre Anderko^b

^a Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83404, United States

^b OLI Systems, Inc., 240 Cedar Knolls Road, Suite 301, Cedar Knolls, NJ 07927, United States

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ABSTRACT

Electrochemistry-based schemes were investigated as a means to recover critical and value metals from scrap mobile electronics. Mobile electronics offer a growing feedstock for replenishing value and critical metals and reducing need to exhaust primary sources. The electrorecycling process generates oxidizing agents at an anode to dissolve metals from the scrap matrix while reducing dissolved metals at the cathode. The process uses a single cell to maximize energy efficiency. E vs pH diagrams and metal dissolution experiments were used to assess effectiveness of various solution chemistries. Following this work, a flow chart was developed where two stages of electrorecycling were proposed: 1) initial dissolution of Cu, Sn, Ag and magnet materials using Fe^{+3} generated in acidic sulfate and 2) final dissolution of Pd and Au using Cl_2 generated in an HCl solution. Experiments were performed using a simulated metal mixture equivalent to 5 cell phones. Both Cu and Ag were recovered at ~97% using Fe^{+3} while leaving Au and Pd intact. Strategy for extraction of rare earth elements (REE) from dissolved streams is discussed as well as future directions in process development.

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1. Introduction

Mobile electronic devices such as smart phones and tablets are a significant source of valuable metals that should be recycled. Each year over a billion devices are sold world-wide and their average life is short. To some extent, valuable metals are already recycled to specifically recover precious metals such as Au. Metals contained in phones, which can be called value metals, are gold, palladium, silver, copper, cobalt and nickel. Devices contain increasing amounts of rare earth elements (REE) which have been designated critical materials. They are contained in displays, speakers and vibrators within the devices. The U.S. Department of Energy (2012) considers Nd, Dy, Eu, Tb and Y as REE critical materials. Other REEs such as Ce, La and Pr were deemed near critical. REEs are mined as a group where total REE concentrations in the ore are generally below 8% (Goonan, 2011). Many of the critical REEs have low abundance in the ore. Thus, when specific elements become critical, significantly more ore must be processed to capture the dilute but valuable critical elements. Targeted recycling of items containing these critical materials could address their future criticality.

Reviews of REE reserves, suppliers, applications and potential recycling sources are available (Buchert et al., 2012; Schüler et al., 2011). REEs are contained in mobile electronics, particularly Nd in magnet materials (Buchert et al., 2012). REEs are used in increasing amounts in green energy technologies such as direct drive windmills and hybrid

electric vehicle motors. Many of the devices that utilize large amounts of critical REEs have long service lives and thus are not currently available in significant amounts. Mobile electronics, which have very short useful lifetimes, offer a supply of critical REEs along with other value metals such as Au, Pd, Ag, Co and Cu.

Technology-rich devices such as smart phones and tablets continue to grow in use (CCS Insight, 2013). Mobile electronics recycling presents an enormous resource of critical and value metals. World sales for mobile phones (cell and smart phones) were approximately 1.7 billion in 2011 and 2012 (Gartner, Inc., 2013). The average device has a lifetime of 18 months in the United States (Environmental Protection Agency, 2004). Worldwide tablet sales for 2013 are estimated to be over 182 million, growing from 112 million in 2012 (Gartner, Inc., 2012). By the end of 2013 there will be 5.9 billion mobile devices in use (CCS Insight, 2013). Worldwide combined sales of smart phones and tablets are expected to reach 2.1 billion in 2017.

As mobile electronics have evolved, the size of circuitry has decreased as discrete components (processors, displays, speakers, cameras, microphones, etc.) are employed in lesser amounts. Unlike personal computers (PC), component by component (display, speakers, hard drive, etc.) separation for targeted recycling processes are less favorable due to small amounts of material involved. Value metals within mobile electronics are contained within circuitry and peripheral components such as displays and speakers. Cu is used to connect circuit elements. Solder is used to form permanent electrical connections. Pb-free solder is used to meet the Reduction of Hazardous Substances (ROHS) directive and contains Sn–Ag or Sn–Ag–Cu alloys. Surface

* Corresponding author.

E-mail address: tedd.lister@inl.gov (T.E. Lister).

contacts for non-permanent connections are coated with Au which may be deposited on interlayers such as Ni. Surface mount Ta capacitors utilize Ag and Pd in electrodes. High strength Nd–Fe–B magnets are used for speakers and vibrators (Buchert et al., 2012). Display backlighting in mobile devices use light emitting diode (LED) sources which contain small amounts of REE phosphors including Eu, Y and Tb (Buchert et al., 2012). The Li-ion batteries used to power devices contain significant amounts of valuable Co. In 2006, the USGS assessed the metal content of mobile phones (Sullivan, 2006). At that time a metal recycler estimated that 1 ton of cell phones contained 140 kg Cu, 3.14 kg Ag, 300 g Au, 130 g Pd and 3 g Pt. Precious metals comprise the greatest value (~91%) of recoverable metals (Hageluku, 2006). Mobile electronics (smart phones and tablets) pack more technology into a similar package and are likely to contain higher metal content per unit (Buchert et al., 2012). Thus, significant amount of critical, near critical and value metals are present with these devices and provide opportunity for economic and environmentally sound recovery methods.

Significant work has been reported on the recovery of metals from electronics printed circuit boards (PCB) (Hageluku, 2006; Cui and Zhang, 2008; Huang et al., 2009; Tuncuk et al., 2012). These methods are analogous to those in mining operations where metals can be in higher concentration than in ore bodies (Huang et al., 2009). The dissolution of PCB metals has largely been performed using one of three acids: HCl, H₂SO₄ and HNO₃. The choice of acid is generally a balance of dissolution speed and compatibility with downstream processing of the leachate solution. Both HCl and H₂SO₄ rely on dissolved O₂ as an oxidizing agent while HNO₃ is itself an oxidizer. Oxidizers, such as Cl₂, H₂O₂ and Fe³⁺, can be added to enhance dissolution rates (Tuncuk et al., 2012). Cu dissolution using FeCl₃ has been demonstrated (Z. Wang et al., 2010). In situ generated Cl₂ from mixing bleach and HCl is a powerful oxidizer (Herreros et al., 1999). For dissolution of precious metals aqua regia (HCl–HNO₃) is costly but effective, where NO₃[−] or nascent Cl₂ acts as the oxidizer and Cl[−] forms stable ion complexes (Huang et al., 2009). Complexing agents can be used to stabilize solution species and reduce the required oxidizing strength. Cyanide is common in mining (Huang et al., 2009) but is considered an environmental hazard. Molecular Cl, Br and I are well suited to dissolution of gold, acting as both the oxidizer and complexing agent. The order of stability for Au complexes increases going down the periodic chart from Cl to I. Cl₂ is manufactured by the electrochemical chlor-alkali process, providing a controlled means for on-site generation. Ag forms insoluble compounds with the halides, complicating the use of single step processes to dissolve all value metals.

Electrochemistry-based metal recovery schemes have been described for various metal recovery applications. Two functions have been described: 1) anodic generation of oxidizers to speed dissolution of metals from scrap or 2) cathodic electrowinning of leached metals for separation and recovery. Given proper consideration, the two processes may be performed in a single cell.

Electrowinning of metals is commonly reported where dissolved metal ions are electroreduced to capture and separate from the leach solution. Due to upstream chemistry unique to recycling, chemistry might be less than ideal compared with optimized electroplating or electrorefining chemistries. Electrowinning requires the reduction potential of the metal to be similar or more positive than the water reduction potential or primarily H₂ is produced. Several processes have been reported which use electrowinning to capture Cu or Ni from leachate solution (Oishi et al., 2007; Mecucci and Scott, 2002; Veit et al., 2006; Masavetas et al., 2009; Veglio et al., 2003). While electrowinning may be performed for many transition metals it is not possible to reduce REEs to metal from aqueous solutions. A mixed metal solution will also complicate the electroreduction process where more noble metals may prevent polarization to capture less noble ones. This can be used to electrorefine metals and thus enable separation.

Electrochemical processes have been developed to create a chemical environment to dissolve metals. Proton generation at the anode during

oxidation of water to O₂ can sustain low pH environments to enable dissolution. In situ generation of Cl₂ in HCl electrolytes has been reported for dissolving Cu in PCBs (Kim et al., 2008, 2010, 2011). This work used an anion exchange membrane (AEM) separated cell with a graphite anode. Leaching was performed at room temperature due to the limited solubility of Cl₂ gas at elevated temperatures. Leaching of Pb, Sn, and Zn from PCB material approached 100% with Cu being somewhat lower attributed to CuCl passivation (Kim et al., 2011). Ping et al. noted a significant increase in dissolution rate using electrogenerated Cl₂ versus dissolved O₂ from air as used for typical leaching (Ping et al., 2009).

Processes have also been described which perform both dissolution and electrowinning functions in the same cell, thus providing high electron efficiency. A system based on Cl[−] electrolytes was described, where Cl₂ was electrogenerated and fed to a dissolution vessel while dissolved metals were electrowon as a group at the cathode (Diaz et al., 1993; Brandon et al., 2001; Cheng et al.). Analogous schemes have also been investigated for mining applications. Copper matte was electrorefined by generating Fe³⁺ at the anode to dissolve Cu and electrowin at the cathode (Jiricny et al., 2002a, 2002b). These dissolution processes are analogous to electroplating methods utilizing a dissolving anode except the oxidizer/mediator acts as an electron shuttle in place of direct contact. This allows a complex partially conductive matrix, such as shredded electronic scrap, to be processed and separated in a single cell.

Recycling methods for REEs are not as well developed compared to value metals but are becoming of interest due to global demand. Reviews have recently outlined potential REE recycling feedstocks, existing recycling technologies and future needs (Binnemans et al., 2013; Tanaka et al., 2013; Anand et al., 2011). Projections suggest that particular REEs such as Dy will see increasing demand (Alonso et al., 2012; Hoenderdaal et al., 2013). Nd–Fe–B magnet alloys dissolve rapidly in acid solutions and are typically coated with Ni or layers of Ni and Cu for protection. Selection of the dissolution chemistry depends on the anticipated recovery process. REEs form insoluble trihydroxides species in basic medium (Pourbaix, 1974). This can be used to precipitate the REEs but requires a significant pH shift for acid-based leaching chemistries. The pH shift is also higher than for commonly dissolved metals such as Fe and Ni. REEs are very soluble in chloride and nitrate while having low solubility in sulfate except at low pH (Stevenson and Nervik, 1961). From moderate H₂SO₄, a slight increase in pH to slightly over 1 will precipitate the REEs as double salts ((REE)₂(SO₄)₃·Na₂SO₄·xH₂O using NaOH). This was used to capture REE from Ni–MH batteries (Pietrelli et al., 2002; Bertuol et al., 2009). Pietrelli described leaching with 2 M H₂SO₄ resulting in over 90% REE release then increased pH to 1.5 with NaOH to recover over 70% of REE content (2002). REEs were recovered from magnet scrap (swarf) using sulfuric acid to dissolve followed by NaOH addition to form double salt precipitate (Lyman and Palmer, 1995). Phosphoric acid dissolution followed by pH increase has been used to precipitate REEs from HCl leached Ni–MH battery material (Lyman and Palmer, 1995). Lamp phosphors show a wide variation in ease of dissolution (Binnemans et al., 2013). Specific recycling of REE from LEDs used for display backlighting was not found. Solvent extraction (SX) methods are commercially used to extract and separate dissolved REEs. SX has been used to recover dissolved REEs from Ni–MH batteries. Tzanetakis dissolved Ni–MH batteries in HCl and used 25% bis-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene (Tzanetakis and Scott, 2004). Extraction at pH 2.5 removed nearly 100% REEs, however, other metals were also extracted. Nuclear applications have extensively used SX for removing REE fission products for fuel reprocessing (Stevenson and Nervik, 1961).

Electrochemistry offers unique methods of enabling recovery of critical and value metals from mobile devices while minimizing chemical usage. Previous work has demonstrated processes using chlorine based solution to dissolve metals in a single chemistry (Kim et al., 2008, 2010, 2011). Other work has included dissolution and recovery

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