Electrochemical enhanced metal extraction from E-waste

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6.1 Introduction

The rapid development of technology and requirement of high performance electronic and electrical equipment has reduced the life expectancy's of electronic equipment's as everybody wants to have access to the latest technology. With progressive innovations and inventions, the life span of electronic equipment has become short and end up as obsolete waste products. This waste is now termed as electronic waste (E-waste) or waste electronic and electrical equipment (WEEE) and is one of the fastest growing waste streams in the past few decades (Frazzoli et al., 2010; Kaya, 2016; Zeng et al., 2017). With the rapid growth in the demand on new electronic equipment and the ability to cater a wider public with accessibility reaching to every corner of the world involves stress created on the natural resources that need to be used in making the electronics. This is evident from the exponential raise the prices of some of the metals that are used in the electronic industry (Graedel et al., 2015). The world has generated approximately 41.8 Mt of E-waste in 2014 and is expected to reach 49.8 Mt in 2018 (Cui and Anderson, 2016). Although WEEE constitutes only 8% of municipal solid waste, the amount of metals present in it exceeds than any other form of waste (Hossain et al., 2015). However, only 10%−15% of this waste is recycled and the majority end-up in landfills.

Electronic and electrical equipments uses a significant amount of valuable metals, precious metals, and rare earth which impart unique properties to this equipment and when discarded will become a waste of these resources. It is becoming increasingly difficult to source these metals especially rare earth metals to be used in the electronic industry (Boudesocque et al., 2019; Yazici and Deveci, 2013). The U.S. environmental protection agency suggests that recycling electronic waste would benefit in energy savings than the extraction of metals from the natural ores (EPA, 2007). Some of these metals are extremely toxic and adversely affect the

environment when discarded to the environment without proper care. Hence, these metals from WEEE should be recycled both as resource point of view and environmental view.

Electronic waste is categorized as hazardous waste due to the presence of toxic metals, organics which have a detrimental effect on the human health, environment, and imbalance the ecosystem due to improper handling during disposal (Pinto, 2008). Waste electronics and electrical equipments pose significant issues for its management for both the government and industry. The absence of strict government regulations made it difficult to handle or manage the growing WEEE (Salhofer et al., 2016). The efficiency of WEEE waste recycling involves many steps such as government legislation, consumer participation, the amount of waste that can be handled, and safe handling procedures. The handling practices of WEEE are not the same across the boards, making it difficult to coordinate the efforts. The majority of the WEEE is being dumped into developing countries like Indonesia, India, Bangladesh, Sri Lanka, Philippines, Nigeria and Liberia from the developed countries like United States, Australia, Japan, and European Union (Baldé et al., 2015). This calls for the requisite to treat the wastes that are valuable enough to go further for recovery to be in use as a secondary source.

6.1.1 Waste electronic and electrical equipment types

Electronic and electrical equipment can be classified into different types depending on their source, usage, and recyclability of these materials. The WEEE include batteries, lightbulbs and lamps, television, laptop, computers, tablets, and mobile phones with screens, fridges, freezers, chillers and air-condition units, printed circuit boards (PCBs), ink or toner cartridges, capacitors, cameras, power tools, lawn movers, photocopiers, projectors, display panels, microwaves, and printers (Khaliq et al., 2014; Vidyadhar, 2016). It is well known that the metals can be recycled infinitely irrespective of the form it is available. It is also identified that recovering metals from WEEE has significant advantages such as lesser secondary pollution and energy requirement compared to extracting the metals from natural resources (Zhang and Xu, 2016).

6.1.2 Metallic components in E-waste

The WEEE contains many components such as plastics, ceramics, metals, cables, CRT and LCD screens, cables, fire retardants, wires, and others, of which the metals constitute 60% by weight followed by plastics $\sim$15% and CRT and LCD screens at $\sim$11.8% (Zhang and Xu, 2016). The significant component of WEEE is the metals which can be recovered for reuse in the same industry. There are close to 54 metals that are identified in personal computers (Oguchi et al., 2013). However, the major components of metals include Cu, Al, Fe, Ni, Sn, Zn, Pb, Ag, Au, Li, Co, and others are present in ppm levels. Oguchi et al. (2013) have summarized different types of metals present in 24 different equipment types, as summarized in Table 6.1 (Oguchi et al., 2013). However, there are more metals used in the

Table 6.1 Hazardous and useful materials present in different WEEE.

Component	Useful materials	References
PCBs	Cu	Rajagopal et al. (2016)
CRT	Pb, REEs: Y and Eu	Önal and Binnemans (2019)
LCD panel	In_2O_3	Swain et al. (2016)
Wire	Copper, Aluminum	Vegliò et al. (2003)
Li-ion battery	Al, Cu, Li, Co	Li et al. (2012)
Ni-MH battery	Fe, Ni, Ce, La, Mn	Sobianowska-Turek (2018)

electronic equipment's in trace compositions. In WEEE precious metals contribute to the significant economic value, and the efforts are focused on extracting those metals during recycling operations. The primary hazardous and useful materials associated with WEEE are summarized in Table 6.1.

Apart from metals, the electronic waste is composed of ceramics which include SiO_2 and Al_2O_3 and plastics such as polyethylene, polypropylene, polyesters, epoxies, polyvinylchloride, nylon, and poly tetraflouroethane (Khaliq et al., 2014). In particular, PCBs constitute approximately 40% metals, 30% plastics, and 30% ceramics (Ogunniyi et al., 2009).

There are multiple approaches investigated in the literature to extract the metals from electronic waste. The methods include smelting, pyrometallurgical, vacuum pyrolysis, hydrometallurgical, and microalgal treatment, electrowinning, electrodeposition, and electroextraction. Each approach has its own advantages and disadvantages in relation to operation parameters and energy requirement (Ashiq et al., 2019; Veit et al., 2015). The complex composition of electronic waste warrants high-tech technologies to selectively extract these metals and reuse them. It is known that the metals can be recycled any number of times and recovering from the waste equipment gives an incentive of conserving the natural resources. Pyrometallurgy and hydrometallurgy are the most common methods used for the recovery of metals from WEEE. However, pyrometallurgy requires high temperatures to extract the metals from WEEE, which release toxic gases which need to be cleaned before releasing into the environment (Wang et al., 2017).

On the other hand, hydrometallurgy does not require high temperatures, high operation costs, reduced environmental impact, and reasonable metal recovery rates. Hydrometallurgical treatment of WEEE typically uses mineral acids such as HCl, H_2SO_4, or HNO_3 for the recovery of metals. Apart from that, it uses several reagents to such as cyanides, halide, thiosulfate, or thiourea for the extraction of precious metals. The section below provides a broad overview of the extraction of metals from WEEE using hydrometallurgical methods (Abdelbasir et al., 2018; Awasthi and Li, 2017).

6.1.3 Hydrometallurgical recovery methods

Conventionally, in hydrometallurgy, mostly acids are utilized to selectively leach out the targeted metals. Then, through a series of refining processes as in

Table 6.2 Leaching of WEEE from source and their recovery.

Leaching types	Leaching agents	Elements recovered	References
Thiourea leaching	$CS(NH_2)_2$, $Fe(III)/H_2SO_4$ as the oxidizing agent	82% Au	Zhang et al. (2012)
Thiosulphate leaching	$(NH_4)_2S_2O_3$, $CuSO_4$ Copper sulphate, NH_4OH Ammonium hydroxide	100% Ag, Au> 95%	Oh et al. (2003)
Acidic leaching	HCl/NaCl with HNO_3/$H2O_2$ leaching	9%−95% Pd	Quinet et al. (2005)

electrorefining, precipitation, and cementation, the metals get further concentrated (Abdelbasir et al., 2018). The valuable metals exist as complexes which become further demanding to extract them for secondary use. However, leaching has proven to be more promising than pyrometallurgical processes as it utilizes no external energy source and requires just the right solvents. The recovery rates are much higher compared to the pyrometallurgical processes. Table 6.2 shows a few examples of the different solvents used for the recovery of a few metals.

6.1.4 Electrowinning and electrorefining processes

Precious base metals are usually recovered through electrodeposition with lesser use of auxiliary materials as in leaching agents, lower environmental impacts, higher efficiency compared to energy requisites pyrometallurgical process and highly cost-effective (Ashiq et al., 2019; Fogarasi et al., 2015). Usually, the leaching process is followed by an electrorefining step. An electrochemical reaction that takes place spontaneously in the system, generates the requires ions for the current transfer, thereby, the noble metal of high purity gets migrated at the cathode and the less noble metal get oxidized at the anode. This is a normal scenario for any kind of electrochemical cell, involving electrodes and electrolytes and sometimes with an external power source for initial of the cell reactions (Işıldar et al., 2018; Roslan et al., 2017).

Electrowinning is a process by which the metal gets separated and recovered from the solution by electrolysis. The required metal gets deposited from the solution at the cathode, and the anode remains inert throughout the reaction. Whereas, electrorefining is another electrolytic process that involves the removal of impurities from the metal. The impure metal either gets deposited at the anode or remains in the electrolyte as insoluble sludge (Ozgur et al., 2016). Only the metal again gets migrated to the cathode. The rate of the electrolytic process is highly dependent on the current imparted by the half-cell reactions and can be enhanced through increasing the conductivity in the cell through maintaining the concentration of the metal

ion solution, adding some salts, providing heat, or even increasing the surface area of the electrodes (Walker, 1979).

6.2 Electrochemical enhancement methods for metal recovery

Electrochemical enhancement of elements from electronic scrap using electrolytic cells has gained tremendous attention over the last few years. Conventional cells utilizing aqueous solutions cannot be employed as electrolytes due to the high rates of electrolysis in the media and nonselective to the required elements to be extracted, lower stability in the cell due to heating and thereby less efficient (Simka et al., 2009). Thus, technologists and researchers focus on coming with electrochemical pathways to selectively refine the metals from leached solutions and by the use of nonaqueous solutions to selectively extract or electrodeposit the metal or the element. A brief graphics of electronic waste recovery is shown in Fig. 6.1.

6.2.1 Copper recovery

Metal wires in electronics appliances consist of copper, that has high electrical conductivity, thermal conductivity, and readily available. However, copper is a multivalent metal that oxidizes to copper oxides, viz., cuprite or cuprous oxide or cupric oxides. These oxides possess different physical properties that make them apt to be used in different applications as in varying from optical devises to high thermally resistant devices (Mezine et al., 2018). Lithium-ion batteries, photodetectors, solar cells, electronic equipments are some of the sources where these oxides have been applied. As is it a p-type semiconductor, copper oxides crystallize and thus suitable for many applications. PCBs contain polymers, metals, and certain amounts of ceramics. Of the 40% metals present in the circuit board, approximately 20% of copper can be found in a typical computer PCB whose quantity is much higher than the ore present naturally (around 0.6%). Copper recovery is of great economic interest in terms of its recovery as its degree of purity of obtaining is high and is of the declining market over the past decade (Zhang et al., 2017). Few recovery processes using electrochemical pathway is shown in Table 6.3.

The challenge revolves around the heterogeneity of the materials being used with copper in the manufacturing of the electronic equipment. Due to the formation of dioxins and furans from the halogenated flame retardants used in the PCBs processing, pyrometallurgical methods has its limitations and an added-costs in its high energy-driven processes (Guimarães et al., 2014; Puente-Siller et al., 2017; Wu et al., 2009). Moreover, the consumption of leaching agents for hydrometallurgy is high and leaches out large quantities of untreated wastewaters in the environment (Jha et al., 2012; Tuncuk et al., 2012). For these reasons, electrolysis is an efficient method for recovering copper and capable of obtaining high purity copper powders

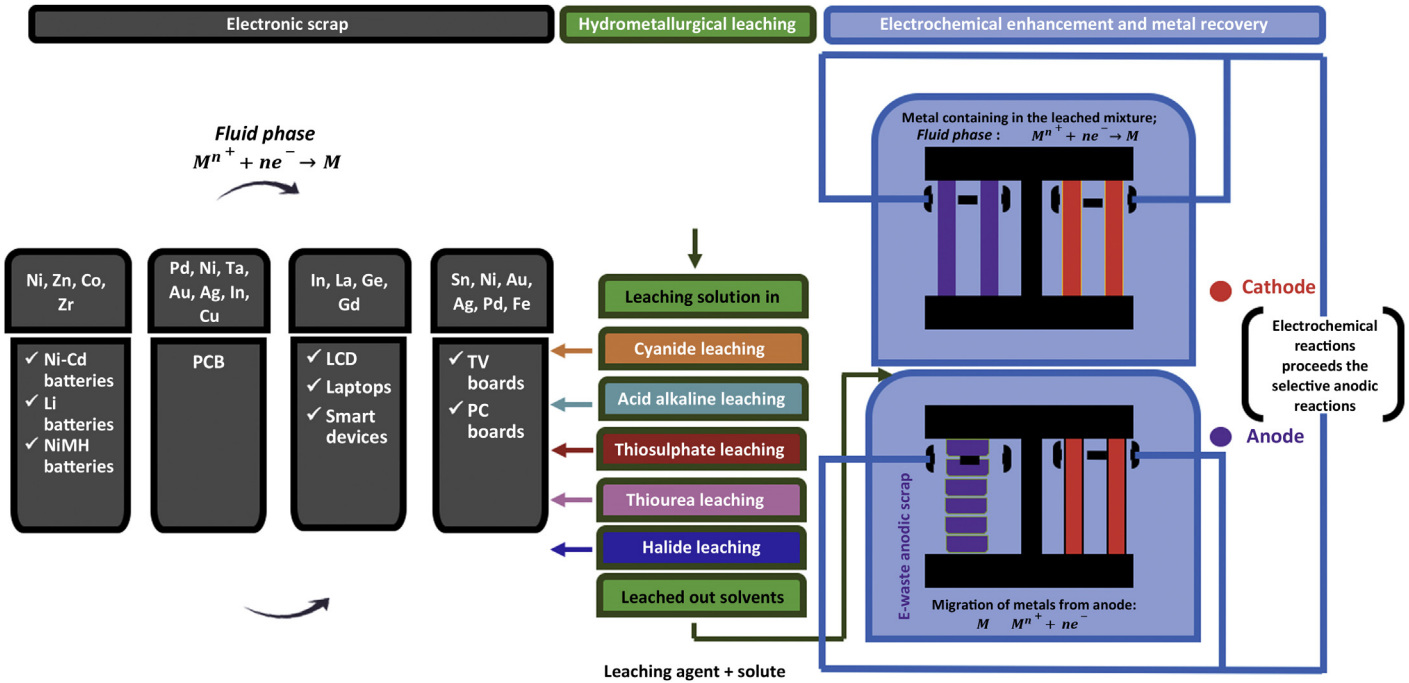

Figure 6.1 Graphical representation of electrochemical recovery of WEEE from leaching to electrowinning processes.

from the electronic wastes. The simultaneous leaching-electrodeposition process has been employed for a quick recovery of copper from PCBs.

Ideally, in the hydrometallurgical process, copper in the wastes gets leached out as Cu (1) utilizing Cu (II) through reduction. The purified Cu (I) reduced to copper metal at the cathode through electrowinning and leftover Cu (I) passes through the anode as Cu (II) and then further purified at the leaching process. This process recovers about 93% of copper and can be further improved while converting into final ultrafine powders of copper rather than copper collected on the cathode utilizing the right leaching agent (Oishi et al., 2008; Yang et al., 2012). Previous studies to further optimized the efficiency of the copper recovery by using ammonia-ammonium sulfate/chloride/carbonate were used as a leaching agent with supplied air for oxidation, achieved a recovery of 98% (Liu et al., 2010; Yang et al., 2012).

Another hydrometallurgical process known as slurry electrolysis is one of a kind recovery methods of pristine metals from electronic wastes and it utilizes chemical and electrochemical process combinations (i.e., leaching, solution purification, and electrowinning) in one reactor, all at once (Zhang et al., 2017). Copper recovered from these methods are mostly in particle size ranging from micropowders or even nanopowders depending on the conditions utilized. According to Li et al. (2019), ruthenium-plated titanium was used as the cathode and anode and a DC supply for current. A portion of CPU sockets containing a mixture of several elements are added to the anode chamber where 200 mL of a mixture of hydrochloric acid, sodium chloride, and hydrogen peroxide as an electrolyte were introduced into the cell (Li et al., 2019). The effects in the current density, pulp of CPU sockets dosage, and the residence time were all studied concerning the copper recovery rate. Hydrochloric acid leaches out copper to its chloride complexes and copper recovery rate significantly increased when hydrochloric acid concentration is increased (H^+ and Cl^- availability increases that contribute to the metal dissolution) up to a certain degree and show a declination in the recovery (Li et al., 2019; Zhu and Gu, 2002). Increasing the acid concentration recovered the other metals in the cell cathode, nickel powders being the impurity with the copper cathode (Ashiq et al., 2018; Li et al., 2019).

Electrolyzed copper powders were obtained from concentrated metal scraps of wasted PCBs, compressed and held at the anode were studied in Chu et al. (2015). Copper (99.5% purity) sheets were used as a cathode with copper sulfate pentahydrate, sodium chloride, and sulfuric acid as electrolytes were used with constant DC applied across. In this study, the rates of nucleation of copper have been further studied to see the mechanisms involved in the migration of copper from the scraps with respect to the particle sizes. Copper sulfate pentahydrate has a diverse effect on the migration of copper ions from the anode. The particle size increases to almost five-fold when the concentration of copper sulfate increases up to 90 g/L which is explained as a process called electro-crystallization which composed of rates: nucleation and growth throughout which the particle size differs in both the rates (Wang et al., 2010). If the rate of nucleation is faster than the growth rate, more crystals of copper formed that are fine in powders. However, when the concentration of the copper sulfate pentahydrate concentration increases, the rate of

growth enhances but producing a coarser copper particle (Yazici and Deveci, 2013). An optimum concentration is studied for these reasons, based on a constant current density supplied and the purity of the copper formed (Chu et al., 2015; Zhang et al., 2018a). Electronic items as in mixed motherboards and graphics cards are in high content of both copper and gold. These high valued materials are recycled via slurry electrolysis method that follows.

6.2.2 Gold recovery

Gold leaching process using cyanide were the norms for extraction from ores and has been carried over to extraction of gold from secondary resources as in electronic wastes. The toxicity in the environment leads to drastically reducing its usage and utilizes the applicability of using other leaching agents or other extraction pathways as in the electrochemical process. The recovery of gold using electrowinning and simultaneously leaching using copper ammoniacal thiosulfate solutions has been studied widely over the usage of cyanide (Ashiq et al., 2019; Bisceglie et al., 2017; Kasper et al., 2018). Because of the interference of copper ions in the recovery of gold, usage of this copper salt with additives such as sulfates, chlorides, and phosphate reduced the reduction rates of copper and thereby keeping the copper intact and increasing the volume of gold at the cathode. For instance, usage of EDTA stabilizes the thiosulphate by forming complexes with copper, and thus gold leaching was substantially achieved through the addition of EDTA. Amino acids have also been used as an excellent complexing agent for the selective gold recovery (Feng and Van Deventer, 2011; Kasper et al., 2011, 2018).

The rate of dissolution of gold in thiosulfate solutions that show poor solubility with gold is improved by the use of cupric amines or ferric oxalate or addition of sodium sulfite to the electrolytes. The presence of these sulfite ions prevents the thiosulfate from decomposing, which otherwise disproportionate to elemental sulfur and thereby decreasing the concentration of thiosulfate (Zelinsky, 2015; Zhang et al., 2012). Gold plated is used as a rotating disk electrode with the solution of sulfite and thiosulfate with the gold-containing solutions that need to be leached out (Zelinsky, 2015). Zelinsky and Novgorodtseva (2013) studied the gold anodic dissolution with additive thiourea on the graphite electrode. Graphite electrodes with Ag/AgCl (in saturated KCl) as a reference electrode and varying solutions concentrations of gold mixed with other elements of the waste electronic equipment were studied in Kasper et al. (2018).

Yap and Mohamed (2007) studied the usage of a galvanic cell for recovery of gold where different materials were utilized as a cathode. The drawback of utilizing an external cell that requires a power consumption has been addressed in this work and studied the use of the electrogenerated system without the use of an external supply (Hor and Mohamed, 2005; Spitzer and Bertazzoli, 2004; Yap and Mohamed, 2007). In an electro generative cell, the spontaneous cell reaction occurs, and the noblest of the elements deposits on the cathode and less noble metal is oxidized in the electrolyte, thereby creating the external current. The batch system is coupled

with carbon-based porous materials as cathode along with the zinc in the galvanic cell for recovery of gold from cyanide solutions. Reticulated vitreous carbon (RVC) has proven the most effective cathode in recovering 99% of gold from the solution and most of the gold been deposited exhibited the smallest grain size at nanolevel particles (Yap and Mohamed, 2007; Yap and Mohamed, 2008).

6.2.3 Silver recovery

As was the case of gold recovery, cyanidation is the most widely used hydrometallurgical technique to leach out precious metals like silver from different sources. It is due to the repercussions it created to the environment, an alternative of thiourea or thiosulfate to be used as lixiviants have been studied extensively (Ashiq et al., 2019; Zhang et al., 2012). The major drawbacks of using thiosulphate lixiviants are its oxidative degradation to polythionates through interactions with many oxidizing agents present in the lixiviants. It is also common for the silver particles, as in the case of gold, a coating of Cu-S from the degradation of thiosulphate that further inhibits the deposition of silver any further. Electrodeposition combined with leaching has been utilized for silver recovery from electronic scraps and printed circuits boards using an electrochemical cell. Carbon paste electrodes with electro-active species using graphite powder, silver sulfide as an electro-active species have been used.

Ionic liquids are seen as an alternative for recovery of many of the noble metals from the electronic wastes. Ionic liquids are solvents that consist of ion pairs. They are organic solvents with a low melting point that has low vapor pressure and thus environmentally friendly solvents. They have been used in the recovery of divalent metal ions as in copper, platinum, palladium, and gold. The physicochemical characteristics can be altered through combinations of salts used to tune the different cations and the anions (Sebastián et al., 2018; Zhang et al., 2015). Ionic liquids facilitate the migration of silver cations easily in an electrogenerated cell using the organic solvents (Molodkina et al., 2019). Silver deposition from these solvents is a "greener" alternative to silver electroplating using toxic cyanide-containing electrolyte environments (Zhang et al., 2015). Various polycrystalline substrates as in glassy carbon, polycrystalline gold, and platinum are used with ionic liquids to check the deposition rates from Ag^{+} to Ag^{0} and silver nucleation studies (Ispas et al., 2011; Molodkina et al., 2019; Simka et al., 2009).

6.2.4 Rare earth elements recovery

Permanent magnets, rechargeable batteries, and lamp phosphors utilize a significant portion of rare earth elements (REEs) due to their unique magnetic and electronic properties. Their shortage and rareness in natural forms led to several studies for its recovery from secondary sources that are otherwise end-of-life (EoL) products (Gutfleisch et al., 2011; Prakash et al., 2015).

6.2.4.1 Neodymium recovery

Neodymium iron is widely used in the synthesis of permanent magnets and are recovered from their EoL magnets using dissolution of the scrap by alkali hydroxides to precipitate into neodymium salts that are further refined to form their oxides. Selective recovery of REEs from these magnets that is composed of several other metals focuses on factors influencing the codissolution of ion and boron that coexists in the magnets. The differences in the standard reduction potential are used to selectively recover the rare metals through selective dissolution and thereby collecting the REEs at the cathode. The dissolution of neodymium or for many REEs, acidic solutions are mostly favored for its dissolution due to the passive layer it forms on the scraps (Lee et al., 2014; Prakash et al., 2015; Vander Hoogerstraete et al., 2014). Codissolution of iron and cobalt, that are also part of the system scraps, is a common phenomenon when attempting to recover neodymium. Sulfamic acids and a certain high current density applied could make the iron smelt at the bottom leaving the neodymium salts present in the leachate whose pH is made to drop to acidic conditions to precipitate to obtain the recovered REEs. The scrap magnets are used as an anode in a simple two-electrode electrochemical system with the REEs gets concentrated in the leachate that can be further recovered and extracted via precipitation by double salt or with hydrogen fluoride (Prakash et al., 2015).

6.2.4.2 Tellurium recovery

Tellurium (Te) is also used widely in electronics, photonics, photovoltaics, and metallurgy as it is a p-type semiconductor with extensive crystalline properties (Halpert and Sredni, 2014; Zhong et al., 2018). It is especially used as photovoltaic cadmium telluride (CdTe) cell of solar origin, Te is of high demand in its synthesis, and even a small level of purity could create a tremendous difference in the energy level for storage. Thus, its purification and recovery is crucial and goes through a series of hydrometallurgical processes that cause high energy consumption for its recovery and high equipment cost and reduction reactions at corrosive acidic media that in turn create repercussions in the environment. The low electrodeposition rate of tellurium and many of the kind semiconductors consumes heavy energy and often leading to loss of purity of the REEs thereby showing low conductivity in the diverse applications used (Chang et al., 2014). At a conventional level, tellurium compounds can be reduced to Te by slime solutions with the presence of hydrochloric acids or sulfuric acid leaching solutions (Jin et al., 2018; Makuei and Senanayake, 2018). Tellurium is recovered by electrodeposition at a large scale where electrowinning is done at an alkaline leach liquor. To increase the electrodeposition rate, photo-assistance is provided, and better film quality is obtained in the recovery electrode (Chang et al., 2014; Fan et al., 2016; Yang et al., 2015). The rate of nucleation and growth of Te deposition has been an interest, especially its film formation of stainless steel plate in an alkaline solution using a three-electrode cell. Stainless steel electrode is kept as a working electrode, a saturated calomel electrode as a reference and pure graphite plate as an auxiliary electrode. A light

source was used enhance the deposition rate onto the stainless steel substrate and kept to irradiate at a constant rate in a Te-rich leachate electrolyte containing sodium hydroxide as well (Dergacheva et al., 2014; Fan et al., 2016; Guo et al., 2014).

6.2.5 Ionic liquids for enhanced electrodeposition

Conventional aqueous solutions have its limitations in being selective to recover elements from their compounds and continuous liberation of a hydrogen molecule from the anodic reactions narrow the electrochemical window for elemental enhancement with lower stability and lesser efficient. Hydrogen evolution due to reduction half tends to hydroxylate the cathodic deposits due to pore formations and reduces the quality of the cathode (Simka et al., 2009). To overcome these problems, developments have been attempted to derive newer electrolytes extensively for elemental recovery using the cell and that can successfully reduce the reduction of the solvent to a great extent, maximizing the metal deposition (Sebastián et al., 2018; Su et al., 2010; Zhang et al., 2016).

Ionic liquids are free-water salt that is obtained from the dissolution of salts. They have incredibly high viscosity (20−100 mPa s) much higher than the traditional aqueous electrolytes (Fedorov and Kornyshev, 2014). They have much higher conductivity with low vapor pressure and low thermal stability but higher electrochemical stability which makes them unique to have a wider electrochemical window than the aqueous electrolyte (Conway et al., 1992; Dong and Zhang, 2012). Copper from waste PCBs showed a promising recovery when ionic liquids are utilized. Copper extracted using 1-butyl-3-methyl-imidazolium hydrogen sulfate showed almost full recovery (Huang et al., 2014). The driving force for high recovery rates is high electrochemical stability, electrical conductivity, adjustable polarity, and a wider electrochemical window compared to other electrodeposition methods (Zhang et al., 2009b,c; Zhang et al., 2018b). Zhang et al. (2018a) utilize N-butyl sulfonate pyridinium hydrosulfate, replacing sulfuric acid, to examine the recovery rates of copper in slurry electrolysis. As more sulfuric acid is replaced with IL, more copper is recovered and effectively reduced the particle size of the powder thereby forming fine powders with fine monocrystalline crystals with around 91% recovery (Zhang et al., 2018b).

REEs are progressively recovered using IL both at high and room temperature ILs. Owing to extremely high cathodic reduction potential for high ILs, room temperature ILs are preferred and studied for a varied range of REEs (Liu et al., 2016; Venkatesan et al., 2018; Zhang et al., 2016). In pursuit of recovering the waste elements from WEEEs, and electrochemical pathways to reduce to the base metal using ILs, Bagri et al. (2018) found the limit of using the conventional IL is the lack of reversibility that the metals/elements cannot be reoxidized once been reduced. Metals cannot be oxidized at anode, but they deposit on the cathode. Thus, they created a neutral ligand complexation of metal cations by increasing its size reducing the interactions between the cation and anion in the IL; this reduces the lattice energy which can diversify the recovery of a varied range of elements such as Nd, Dy, Gd, and Pr REEs recovery.

6.2.6 Process summary of the recovery of major elements present in waste electronic and electrical equipment

Table 6.3 Electrochemical recovery of selective metals from WEEEs.

WEEE	Elements in WEEE (weight%)	Recovered purity	Electrochemical conditions	References
Printed circuit boards (PCBs)	Cu 26	98	A mixture of copper sulfate pentahydrate, sodium chloride, and sulfuric acid as an electrolyte. Metal scraps obtained from mechanical processing of PCB are pressed to be used directly as anode and copper sheet of 99% purity as a cathode. The concentration of each of the solutions in the electrolyte was varied with different current density to examine the deposition effects separately	Chu et al. (2015) and Li and Zeng (2012)
		92	Electrowinning of synthetic copper sulfate solution and pregnant leach solution for PCB with polyoxometalate (POM), ammonium metatungstate hydrate as an additive to see the effect of current density on the migration of copper to the cathode. Copper and titanium sheets of the same dimensions were used as cathode and anode, respectively	Ehsani et al. (2016)
		99.6	Shredded WEEE up to 8 mm waste introduced in titanium basket as an anode. Pure copper sheets as cathode and ammonia and ammonium sulfate were used as the electrolyte. Optimum current density was identified, and copper recovered to a significant extent	Haccuria et al. (2017)
	24% Cu, 2% Au	94% Cu, 95% Au	Synthetic solutions containing thiosulfate, ammonia, copper, and gold were used for voltammetry studies with a three-electrode system: Pt rotating disk	Kasper et al. (2018)

(*Continued*)

Table 6.3 (Continued)

WEEE	Elements in WEEE (weight%)	Recovered purity	Electrochemical conditions	References
			electrode as the working electrode, Ag/AgCl as a reference electrode and Pt for the counter electrode	
From leached wastewaters of mobile equipment, laptop, tablets	Ni	99	Electrofloatation technique using both electrodes at aluminum and the electrolytes are synthetic wastewater with concentration series of nickel to check its influence on the current density	Coman et al. (2013)
		94	Electrodialysis and electro-leaching of nickel-containing rinse wastewaters using platinized titanium grids packed in beds of graphite powder. Instead of using a semipermeable membrane or ion exchange membranes, electrostatic shielding zones-ionic current sinks (ESZs- ICSs) were utilized	Dermentzis (2010)

6.2.7 Process flow chart

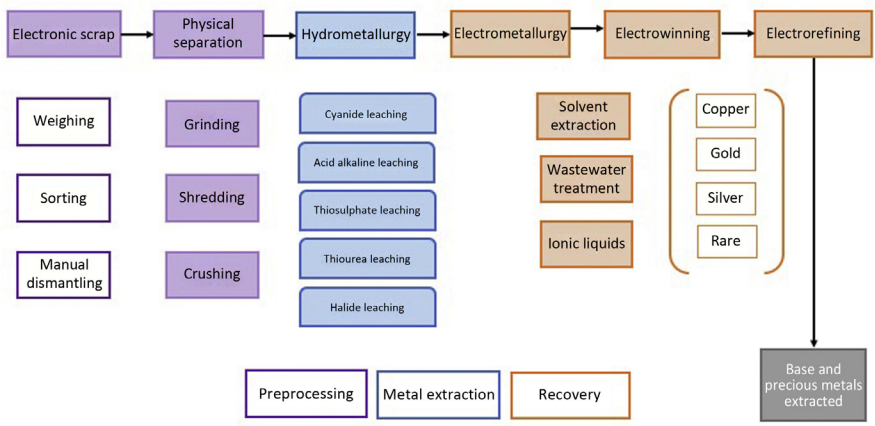

Figure 6.2 General flowsheet of electronic waste recovery to base metals.

6.3 Future outlook

The heterogeneous nature of the waste warrants special requirements for their metal recovery. The recovery of metals usually achieved through manual sorting as in crushing, screening, magnetic or even hydrometallurgical techniques that vary depending on the presence of other materials of the electronic equipment and the ease of separation (Fig. 6.2). Silver and other precious metals are of great importance to recover due to their rising prices and depletion of their parent ores. The most appropriate process must be initiated and studied further to recover these metals (Cortés López et al., 2017; Seisko et al., 2018).

Electrowinning, solvent extraction, precipitation, and ion-exchange are many of the several techniques used for the recovery of valuable metals from leach liquor (Kim et al., 2011; Yi et al., 2016; Yong et al., 2019). Major metals are recovered using electrowinning and then smelting to obtain the secondary usable raw materials. Precious metals being recovered at the anodic slimes in an electrochemical enhanced cell are predominantly recovered and rarely required further electrorefining (Alzate et al., 2017; Ashiq et al., 2018; Makuei and Senanayake, 2018). Table 6.3 lists out the major elements recovered from typical wastes with their purity and electrochemical conditions. Current efficiency needs to be studied further as the involvement of current density arising from the chemical reactions tends to make the system unstable to selectively refine the target elements (Lekka et al., 2015; Zhang et al., 2009a). One of the bigger pictures for sustainable usage of natural resources is to have the electronic equipment made from biodegradable materials so that they can be directly be converted to compost thereby, without the dependence of these expensive materials which still has a long way toward technological advancement in this electronic era.

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