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CHAPTER 10

Environmentally Sustainable Solvent-based Process Chemistry for Metals in Printed Circuit Boards

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ABSTRACT

This chapter describes the development of several new processes relating to the fabrication, characterisation and recycling of printed circuit board (PCB) metal assemblies in alternative, sustainable solvent technologies based on an emergent class of liquids known as deep eutectic solvents (DES). It has been demonstrated that in many cases, the use of DES technologies can be disruptive to current process thinking and in principle can deliver benefits including increased efficiency,

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lower costs and better process control. These technologies offer the opportunity to incorporate new ideas into PCB fabrication and assembly that facilitate downstream, end-of-life recovery and separation consistent with a circular economy model. Current PCB manufacturing is carried out using many complex metal deposition processes involving aqueous solutions of toxic metal salts, strong inorganic acids, precious and expensive noble metals, and requires careful process control and monitoring. As a result, these processes are often costly to operate and inefficient. DES-based technologies can: (1) improve the economic and efficient use of essential metals; (2) reduce or eliminate use of precious and expensive metals; (3) reduce the use of complex and difficult to maintain process chemistry; (4) reduce reliance on toxic and noxious materials; and (5) improve recovery, recycling and reuse of PCB metals.

10.1 Introduction and Overview

Electronics manufacturing in general and specifically printed circuit board (PCB) fabrication and assembly requires processing of a wide range of metals, coatings, and surface finishes. The methods and approaches used for recovering and reusing these materials are covered in other chapters of this volume. Here we focus on the design and implementation of novel process chemistries for which the aims are to: (1) reduce the amounts of costly and strategically critical raw materials used in the manufacture; and (2) design an end of use strategy to facilitate more efficient downstream processing for either second life re-tasking, or end-of-life recycling and recovery.

Many of the materials and coatings used for electronics manufacture and PCB assembly are of high economic or strategic value. High value metals include platinum, palladium, gold and silver whilst others such as neodymium and lithium have strategic value added by the nature of the geopolitical constraints limiting market access.

Since 2011 the European Commission has produced a detailed list of raw materials critical for the EU economy, which are mainly in areas related to energy and digital technologies. Both of these are heavily reliant on the capability of electronics manufacturing.¹ These lists show that some key, high-value metals, such as gold, silver, platinum and rare earth metals such as neodymium, as well as more common metals, such as copper, are being consumed at an annual rate which represents a significant proportion of the global reserves. For example, copper is consumed at an annual rate of 16 million tonnes and there are thought to be global reserves of approximately 630 million tonnes (2.5% per annum). On the other hand, gold is consumed at an annual rate of 2500 tonnes with total reserves of 51 000 tons (4.9% per annum) and global resources of indium, used extensively in touchscreens and photovoltaic devices, are estimated at just 640 tonnes whilst the annual consumption is currently at 11 tonnes (1.7% per annum) and rising. It should also be noted that as these and other critical resources diminish,

they become more difficult and more expensive to obtain. Hence, these figures illustrate the urgent need to develop more efficient processes for the use of metals in PCB manufacturing and also indicate the necessity to recover and reuse materials from end of life devices (much of which resides in legacy landfill).

Currently, many of these materials are recovered from bulk mixed-waste electrical and electronic equipment (WEEE), for onward use by a combination of pyrometallurgical, hydrometallurgical and electrochemical processes (see Figure 10.1).²

In many cases these processes are often complex, not very efficient, require the use of strong inorganic acids, toxic and noxious chemicals and may be carried out in remote locations where legal governance and social responsibilities are regarded as a lower priority than they are in the EU and UK.³ For example, PCB assemblies are often burned in the open air in order to recover mixed metal oxides, and cyanide salts are used in aqueous processes to selectively recover gold and silver. Both of these processes represent a severe health risk to workers in these industries. Additionally, a proportion of the WEEE stream still goes to landfill, this is both wasteful and potentially dangerous. Although discrete individual components containing these metals (circuit elements, connectors, heat sinks *etc.*) can often be removed, recovered and processed separately, typically the remaining PCB waste is shredded and the metals must be recovered from a complex matrix. Furthermore, recovery and recycling of the high value metals is made even more challenging because they are only present in very low concentrations (mass fraction) in the PCB waste stream. Metals such as silver, palladium and gold are present in microgram to milligram quantities in assembled devices, either as discrete (often concealed) coatings on a copper substrate, connectors and so forth, or within the solder alloys of assembled devices.



Figure 10.1 Bulk PCB WEEE containing mixed metals and components.

Similarly, rare earth metals are present in vanishingly small quantities in assembled devices. However, even these amounts are significant given the global appetite for consumer electronics and mobile devices.

Consequently, the forward-looking strategy for a circular economy model of PCB and WEEE recycling should contain the following themes at least:

1. Materials segregation, recovery and reuse from existing manufacturing processes and from legacy waste streams such as land-fill.
2. Design and implementation of alternative, new process that can achieve the desired functionality whilst using existing resources more effectively (a more efficient process using less material).
3. Designing the recycling and recovery protocols during manufacture to enable more effective and efficient recycling at the end of life.

In keeping with this philosophy, the authors have recently developed alternative electrolytes for the chemical processing of materials and coatings using ionic liquids and choline chloride (ChCl) based deep eutectic solvents (DESS) for a range of metal finishing processes including electroplating of various metals and electropolishing of stainless steels, as well as other high-performance alloys for the automotive, aerospace and electronics surface finishing industries.⁴⁻⁹

Ionic liquids are non-aqueous solvents made up of salts which are liquid at ambient temperatures. They have many interesting properties such as a good electrical conductivity, high thermal stability and wide electrochemical windows, hence they are potential alternatives to existing process chemistries. However, ionic liquids are typically very expensive (often €1000's per kg) and therefore are not economically viable at the industrial scale. On the other hand, DESS have many of the attractive properties of ionic liquids but are formulated from binary mixtures of bulk commodity chemicals such as ChCl and ethylene glycol (EG) or urea (Ur), see Figure 10.2.

Choline chloride is a quaternary ammonium salt produced on the megaton per annum scale as an animal feed vitamin, whereas EG is most commonly used as an anti-freeze additive and Ur is a common fertiliser. The properties and uses of DESS have recently been reviewed in an open-access article.¹⁰ In addition, the general properties and specific applications of ionic liquids and deep eutectic solvent (DES) electrolytes in industrial processes and metal finishing have been described in detail.^{11,12} Typically, ionic liquids and DESS are a good solvent processing medium, offering a wide

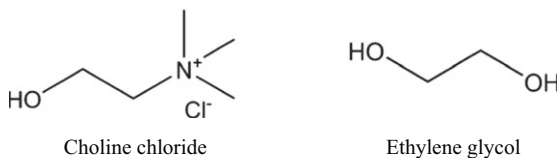


Figure 10.2 Chemical structures of ChCl and EG.

electrochemical window, high current efficiency and good solubility for metal salts. DESs in particular, are relatively low cost and have a low environmental impact. For example, the electropolishing of stainless steels from a DES comprising ChCl and ethylene glycol, (in a molar ratio of 1 ChCl:2 EG) has recently been described in detail by the authors.^{7,8} This electrolyte is marketed commercially by the trade-name of *Ethaline*. Current commercial electropolishing is typically carried out using sulphuric acid and phosphoric acid which can also contain CrO₃ and HF. However, the DES electrolyte functions in a similar manner to the commercial process but contains no strong inorganic acids.

The chemical and physical properties of the DES liquids provide access to metal deposition and dissolution reactions relevant to surface processing in PCB manufacturing which currently require aggressive or toxic reagents. The remaining sections of this chapter are focused on the outputs of several consortium projects funded by the European Union and Innovate UK. These consortia were assembled from groups of industrial end users, chemical manufacturers/distributors and academics focused on various aspects of PCB resource management, fabrication, assembly/testing, and recycling.

10.2 DESs as Alternative Solvents for PCB Coatings

Circuit boards are typically manufactured from a supporting substrate upon which patterned copper conduction tracks are placed, typically 50–100 μm thick, these are then coated with one of a variety of surface finishes depending on the application.¹³ The substrate is generally either a rigid fibre board, or more recently a flexible polymer allowing for movement in use and/or assembly. Surface finishes are intended both to facilitate the bonding of components during assembly, for example soldering, and also to protect the copper tracks from oxidation during the time between manufacture of the board and assembly of the finished product. Typical metal surface coatings include thin coatings of either silver or gold. These metals protect the copper from the aerobic oxidation that would inhibit or prevent subsequent soldering. Silver is a cheaper alternative to gold and although, like copper, it tarnishes in air, the silver oxide formed is soluble in the solder alloy and therefore this does not significantly affect the assembly or the properties of the solder joint. Typically, these coatings are much thinner than the copper substrate at around 50–250 nm. However, interfacial solid-state diffusion of copper in silver and gold is relatively fast, this results in rapid degradation of the surface finish owing to mixing of the copper substrate and silver/gold coating. In order to prevent this a further coating in the form of a hard metal such as nickel is required as a diffusion barrier. Consequently, Cu/Ni/Au is a common finish for PCB manufacture (Figure 10.3), but there are many others including palladium which is introduced to improve the reliability of the assembly in applications using gold wire bonding.

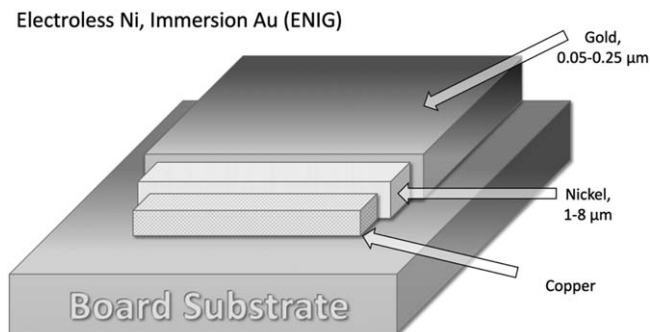


Figure 10.3 PCB conduction track: ENIG.

The various metals can be applied to the substrate board by a range of chemical and electrochemical processing techniques including electrolytic reduction, galvanic exchange of metal salts or autocatalytic processes using solution reducing agents in combination with a surface acting catalyst. These latter processes are generally referred to as electroless deposition. Current manufacturing processes make use of all of these, for example copper tracks can be deposited electrolytically, whilst nickel can be deposited electrolytically or using electroless methods. Subsequent coatings of palladium or gold are often deposited using electroless methods, whereas silver is commonly deposited by a galvanic immersion process. In all of these examples chemical and electrochemical processing is carried out in aqueous solutions of strong inorganic acids, often using toxic and noxious metal salts.

Copper and nickel electrodeposition are carried out from a sulphuric acid solution whilst electroless nickel baths are a complex mix of nickel sulphate, sulphuric acid, NaPH_2O_2 , glycine and malonic acid. Gold and silver are typically deposited using cyanide salts. In addition to the health and safety concerns, these processes are often complex, difficult to maintain and are resource inefficient. For example, a nickel deposition bath must be maintained at a constant temperature and over a very narrow operational pH range. Metal electrodeposition can be very inefficient in an acidic aqueous solution owing to intrinsic side reactions, such as the reduction of protons generating waste hydrogen gas. Alternative electroplating electrolytes using organic solvents are generally less attractive because they raise handling and safety issues, as well as additional costs. An exception to this is the electroplating of aluminium metal which is still achieved commercially in small volumes from a toluene-based electrolyte in the *AlumiPlate* process.¹⁴ In this case, aluminium coatings cannot be achieved from aqueous solution.

In contrast, DESs are non-flammable and relatively low cost. The high chloride content of DES electrolytes results in chemical speciation of the metal ions that generally render reduction processes more favourable energetically and this negates the need for specific and often toxic anions.⁶

Additionally, the wide electrochemical process window of DESs offers the potential benefit of a high current efficiency for electrolytic processing. The focus of the research and development in the applications of DES media to PCB coatings has been directed primarily at electrolytic and galvanic methods. These are described separately below.

10.2.1 Electrolytic Coatings from DES

Electrolytic coatings are achieved by the reduction of a metal ion species in solution in a Faradaic process in which the coating rate is generally controlled by the applied electrical current and the total amount of coating is related to the total charge passed. The application of the current and monitoring of the rate and deposited thickness is achieved using an external power source. The use of DES media for electroplating PCB metals such as copper, nickel and silver has been investigated under the IONMET EU FP6 project.⁹ The work showed that DESs based on eutectic mixtures of ChCl and hydrogen bond donors, such as Ur or EG can be used as electrochemical solvents for the electrodeposition of copper. Effective methods for the electrolytic deposition of bright, adherent copper metal from the simple chloride salt have been developed.¹⁵ In this case the electrolyte consisted of $0.1 \text{ M } [\text{CuCl}_2 \cdot (\text{H}_2\text{O})_2]$ in $\text{ChCl} : 2\text{EG}$ and contained no additives or acids. In addition, the work demonstrated through *in-situ* microgravimetry that in both liquids the current efficiency for copper deposition is close to 100%. Composites of copper with Al_2O_3 and SiC have also been produced and it was shown that the loading of these species in the resulting electroplated films is strongly dependent on the concentration of the particulate in solution, but largely independent of the concentration of copper salt or the timescale used. These wear resistant composite coatings, particularly of copper and silver, are often required for contact surfaces (connectors) and are difficult to achieve using conventional electrolytes.

Nickel is another important PCB metal, but it is more difficult to electroplate in aqueous solution and requires careful and diligent control of both the temperature and pH in the plating bath. This is both resource and time intensive. In contrast, nickel can be electroplated from DESs using a simple nickel salt, $[\text{NiCl}_2 \cdot (\text{H}_2\text{O})_6]$ and requires no acid formulation.¹⁶ In a direct comparison between deposition using aqueous solutions and DES (under otherwise identical conditions) it has been shown that nickel deposition can be carried out with similar deposition rates in aqueous and DES media despite the significant differences in viscosity and conductivity. It is, however, shown that in DES media the morphology of the deposits is markedly different from that achieved using a conventional (Watts) nickel bath and that one aspect of these differences manifests itself in a significant increase in the coating hardness and therefore in the mechanical durability (see Figure 10.4).¹⁷ The current efficiency in DESs is up to 90% which compares very well to the aqueous process. As with aqueous

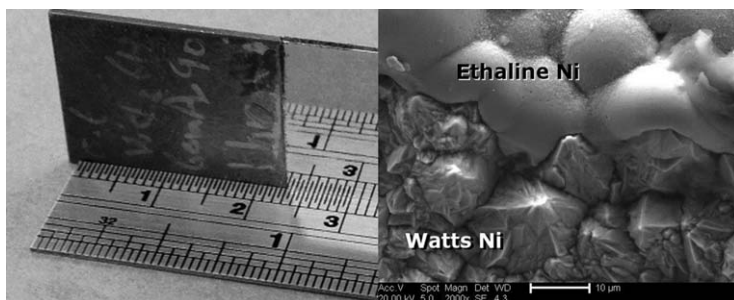


Figure 10.4 *Left:* Mirror-bright Ni coatings achieved on copper from DES. *Right:* Scanning electron micrograph of Ni deposits from aqueous solution (Watts) and a DES based on ChCl:2EG (*Ethaline*). Right side reproduced from ref. 16 with permission from the Royal Society of Chemistry.

electrodeposition, subtle control of the deposit finish and morphology for nickel and other metals can be exerted by the use of small molecule additives.^{18,19} Use of these additives in DESs can give equivalent nickel coatings at a lower metal ion concentration, thereby increasing the resource efficiency of this method.

Both silver and gold can be electroplated from DESs at essentially quantitative current efficiency.^{20,21} In PCB production, these metals are generally electroplated from aqueous solutions using cyanide salts, for example AuCN, AuCN₃ and AgCN. In the case of silver electrodeposition, the nitrate salt is often used in the presence of nitric acid. Electroplating in a DES electrolyte is achieved from the chloride salts for these metals, which presents a much lower health and safety risk, these salts are also much cheaper and more readily available. Silver can also be electroplated from DESs in the presence of particulates including silicon carbide and alumina in much the same way as copper (see details above).²² Hard and wear-resistant silver coatings have applications in connector design, but these coatings are difficult to achieve and control using aqueous solutions.

10.2.2 Galvanic Immersion Coatings

In contrast to the electrolytic methods, galvanic coatings are achieved by a chemical exchange process, exemplified in the scheme illustrated in Scheme 10.1. In this example atoms in the solid substrate, such as Cu, are dissolved into the solution in a spontaneous exchange of electrons with the ions already in the solution, Ag⁺. These ions in solution are then precipitated on the substrate surface as metallic silver.

Unlike electrolytic processes, the reaction detailed here is driven not by an external power source, but by the thermodynamic difference in the redox potential ($E'_{\text{Reaction}} = +0.4 \text{ V}$) between the two half reactions in Scheme 10.1. As a result of this, galvanic immersion coatings are often very difficult to

		<i>E'</i> /V	
Copper half reaction	$\text{Cu}^+_{(\text{DES})} + \text{e}^- \rightarrow \text{Cu}_{(\text{S})}$	-0.4	1
Silver half reaction	$\text{Ag}^+_{(\text{DES})} + \text{e}^- \rightarrow \text{Ag}_{(\text{S})}$	0.0	5
Overall reaction	$\text{Ag}^+_{(\text{DES})} + \text{Cu}_{(\text{S})} \rightarrow \text{Ag}_{(\text{S})} + \text{Cu}^+_{(\text{DES})}$	+0.4	

Scheme 10.1 Chemical exchange process for galvanic coatings. The values for the formal potential, E' , are relative to the $\text{Ag}^{+/0}$ couple in a DES consisting of $\text{ChCl}:2\text{EG}$. The subscripts indicate the state of matter in which (DES) corresponds to the solution in the liquid state and (S) represents the solid state. 10

control. Such processes derived from aqueous solutions have two major drawbacks: (1) the coatings are often very thin because once the substrate is covered with a deposit there is no longer a driving force for the reaction to continue, this limits the thickness of aqueous galvanic immersion coatings to typically 10–50 nm; (2) the salts required for immersion coatings are typically cyanide or acid based. 15

10.2.2.1 Immersion Silver from DESs

Galvanic immersion silver is used during PCB manufacturing as a medium/low cost finish to prevent degradation of exposed copper surfaces during storage between the manufacture of the PCB and the assembly procedure incorporating the board or component into a finished device. Typically, this can be up to several months. This method of protection for the copper surfaces is simple but effective, despite the fact that silver is thermodynamically much more susceptible to aerobic oxidation. This is because silver oxide (formed as a tarnish on silver surfaces), as well as the underlying silver metal, are very soluble in the common tin-based molten solders that are used in the surface mount assembly of the circuit board. On the contrary, copper oxides are poorly soluble in the molten solder, meaning that aerobic oxidation of the copper surface prior to soldering inhibits soldering and prevents bonding of the component. In a practical device, this can result in failure of the joint either through poor conductivity or because of low shock tolerance. Solder fluxes are often used to mitigate this problem by preventing aerobic oxidation of the copper surfaces, but this approach is not always successful or practical. The use of fluxes in assembly is discussed later in this chapter. 20

Commercial galvanic immersion silver processes typically use an aqueous silver nitrate solution in the presence of nitric acid. In addition to the social, health and environmental concerns that surround the use of strong inorganic acids, here the use of nitric acid has a detrimental effect because there is competitive etching of the copper tracks during silver plating. 25

As a result, component failures arise because of copper etching before the surfaces are silver plated. This is problematic for the electronics industry, particularly as integration densities continue to increase and consequently feature sizes become smaller. This is both wasteful in terms of valuable materials and also time, as failed components may require rework. Additionally, only very thin coatings of silver can be obtained from aqueous galvanic immersion, therefore catalysts are required to obtain thicker coatings for better protection (1–5 μm in thickness). This catalytic or electroless process results in further costs, materials and time. Hence this process has commercial, functional and environmental limitations.

We have described the deposition and morphology of metallic immersion silver coatings from solution in a DES based on a $\text{ChCl}:2\text{EG}$, eutectic mixture.²³ This process proceeds according to the overall reaction shown in Scheme 10.1, in which silver, Ag^+ , ions are present in the DES at a concentration of around 5 mM in the form of the AgCl salt. Silver chloride is profoundly insoluble in aqueous solution but dissolves well in the high ionic strength medium of the DES owing to the formation of AgCl_2^- . This has both practical and economic value as AgCl is one of the least expensive silver salts. Uniform, adherent, solderable finishes were obtained on test tokens and full-size boards simply by immersion of the copper substrates in a DES solution of AgCl . Crucially, the nature of the morphology of silver deposition facilitates the sustained growth of silver coatings. This is in contrast to the aqueous immersion process.

Studies using microgravimetric techniques have shown a rate of between 50 and 100 nm min^{-1} can be achieved for silver deposition and that although these rates can be sustained for long periods, at longer time periods the coatings increase in roughness and porosity.^{23,25} The use of small molecule additives such as ethylene diamine or EDTA, often used to control the rate of deposition and finish in metal coatings, has no benefit in the DESs and therefore are not required, giving a simpler and more environmentally friendly system.

Growth of the immersion coating in DESs beyond a monolayer surface coverage is facilitated by the microscopically porous morphology of the coating, allowing mobility of the substrate atoms to sustain silver deposition. The morphology of the coating and the rate of deposition are dependent on the silver ion concentration so that the surface finish can be tuned. The thickness and roughness, measured using atomic force microscopy (AFM), of a typical coating are shown in Figure 10.5. Here a coating thickness of around 0.5 μm was achieved and it can be seen that the roughness of the coating is greater than that of the copper substrate.

The process conditions for immersion silver deposition have been subsequently optimised for PCB deposition and are shown in Table 10.1. The pre-treatment and final rinse steps are consistent with existing manufacturing protocols.¹³

This protocol has produced a consistent surface finish on all test pieces which is comparable to samples processed using a commercial process

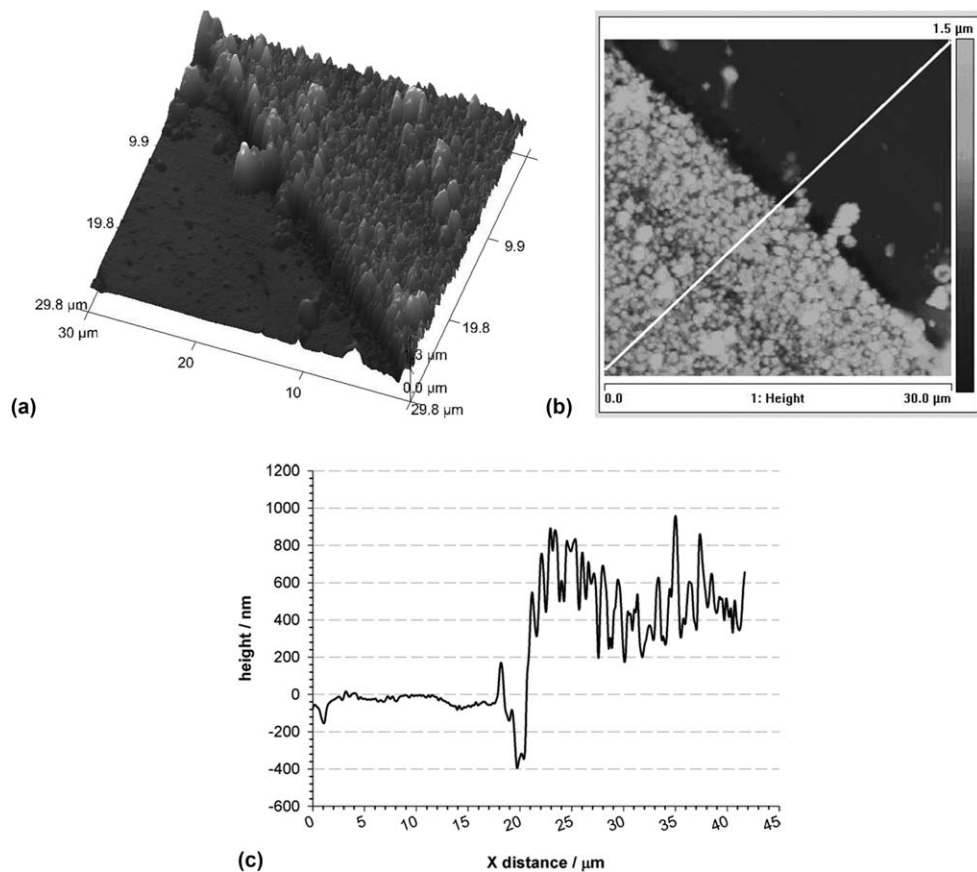


Figure 10.5 AFM image (tapping mode) of an Ag plated Cu sample: (a) 3D surface projection; (b) height contrast image for the same data; (c) height/distance data for the diagonal line trace shown in (b).
 Reproduced from ref. 23 with permission from the Royal Society of Chemistry.

Table 10.1 Immersion silver protocol for a bright adherent finish on copper track PCBs. The commercial name *Ethaline 200* is used for the DES comprising of $\text{ChCl} : 2\text{EG}$.

Ionic liquid immersion silver			
<i>Ethaline 200</i> , AgCl			
Process	Conditions	Temp ($^{\circ}\text{C}$)	Time (min)
Micro etch	10% HCl <i>Ethaline 200</i>	40	3
Rinse	<i>Ethaline 200</i> (neat)	<i>r.t.</i>	1
Rinse	<i>Ethaline 200</i> (neat)	<i>r.t.</i>	1
Deposit	5 mM AgCl <i>Ethaline 200</i>	48	2
Polish	0.5 mM AgCl <i>Ethaline 200</i>	48	2
Rinse	0.1 M Na acetate	30	2
Rinse	Hot water	48	2
Dry	Hot air	—	2

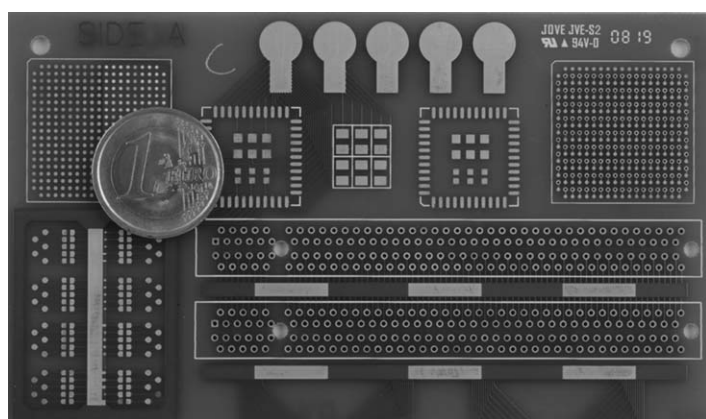


Figure 10.6 DES immersion silver test sample. Sample PCB processed with an ionic liquid process in a pilot plant at PW Circuits Leicester. The copper tracks are coated with silver to a semi bright and consistent finish.

(Figure 10.6). The test piece is coated with a uniform, bright silver surface with no copper streaking evident. Furthermore, this silver coating is abrasion resistant and in soldering tests, performs to an equivalent standard to commercial immersion silver.

As a deliverable element of the IONMET project, this process was scaled-up and pre-commercial trials were carried out with a PCB manufacturer (PW Circuits, Leicester).^{9,24,25} The scale-up process was based on full-sized multi-layered PCB substrates and consisted of 12×100 L process tanks.

Operation of the immersion process necessarily causes the build-up of copper in the DES solution (as well as the depletion of silver) resulting from the immersion reaction and this will eventually inhibit and slow the deposition of silver and limit the life of the bath. However, the Cu^+ and Ag^+ can be separated from the spent electrolyte and recovered for reuse along

with the DES. This can be achieved by precipitation of AgCl by adding water to the DES, followed by filtration to remove the silver salt. Copper can be recovered in a high yield by electrowinning (see above) and the DES can be dried and reused. In this way, the life-cycle of the process has minimal environmental impact.

Immersion processes in DESs are limited only by the redox potential and the solubility of the metal salts, which are generally very good.²⁶ Consequently, a range of other immersion coatings are possible, for example gold on silver, or gold on copper. Neither of these are of commercial significance because of rapid diffusion and interfacial mixing of the metals, however, the DES medium enables immersion coatings on other reactive metals such as aluminium. Here copper can be deposited as an immersion coating onto aluminium as a thin conversion coating that enables direct bonding (*e.g.* soldering) to other PCB substrates or else facile coatings of other metals such as nickel. Both of these possibilities offer opportunities to streamline electronics assembly processes and reduce the use of aggressive and toxic etchants and pre-treatment chemicals.

10.2.2.2 Immersion Gold and Palladium from DESs

Gold coating processes are widely used in the materials finishing, decorative and electronics industries owing to their high reliability, electrical conductivity and corrosion resistance. This is mainly because gold does not form insulating surface oxides. Electrolytic, electroless, and immersion plating are the three common methods used for the coating of conducting substrates with gold films and in each of these processes the conventional, commercial plating bath chemistry is dominated by the choice of the dicyanoaurate anion $[\text{Au}(\text{CN})_2]^-$ as the gold source owing its stability and its ability to yield fine grained deposits. However, there are significant safety concerns, as well as issues regarding the disposal of waste, where cyanide-based processes are concerned. Additionally, cyanide solutions are often used to recover the gold from PCB waste and the poorly regulated use of these processes in some countries is a major risk to human health and the environment. Nevertheless, immersion coatings are an important electrochemical process for the deposition of the thin gold coatings commonly used in the PCB and electronics industries. One such coating, electroless nickel/immersion gold (ENIG), is of particular importance in the maintenance of the solderable surface on printed circuit boards (PCBs) during storage, prior to solder reflow and assembly. In this case, nickel is liberated from the surface, providing electrons to the two gold ions in the solution, causing their reduction and creating a thin film of gold on the substrate surface. In the fabrication of ENIG coatings the electroless Ni is deposited on the copper substrate by the catalytic action of a solution phase reducing agent (NaPH_2O_2) in which the catalyst is a very thin coating of PdCl_2 applied to the copper. As a consequence, the resultant ENIG nickel coating contains 8–12 wt% phosphorus incorporated from the reducing agent. This is

generally favourable for the physical properties of the nickel coating in PCB applications and gives good adhesion and durability as well as providing an essential and effective diffusion barrier for the copper atoms of the substrate.

ENIG is a relatively expensive surface finish for PCBs because of the presence of gold and the palladium catalyst, but despite this it is increasing in popularity as it produces a level surface (important for automated electronics assembly) and good solderability, even when subjected to multiple heat/cool solder reflow cycles. However, ENIG coatings are susceptible to a fault phenomenon termed “*black pad*” which is generally accepted to be oxide formation on the surface of the underlying electroless nickel (EN) substrate, resulting from galvanic corrosion in the gold plating bath. The presence of “*black pad*” on a PCB results in poor quality, unreliable joints. The baths are generally acidic and conventional aqueous immersion gold processes fundamentally contribute to the formation of defects.

As DESs have shown promise in immersion coatings such as silver and copper (see above), from acid free formulations, the problems associated with commercial ENIG were addressed under an EU Framework 7 funded consortium entitled ASPIS (Advanced Surface Protection for Improved Reliability PCB Systems).²⁷ Here immersion gold coatings on commercial electroless nickel were achieved from 0.1 M DES solutions of AuCl, AuCN and K[Au(CN)₂] salts (see Figure 10.7).²⁸

Plating rates were determined using *in-situ* microgravimetric methods and ranged from 0.4–1.2 nm min⁻¹. This is much slower than the silver process (see above) and slower than the commercial immersion gold process. The deposition rate and surface finish was also dependant on the gold salt; the fastest deposition was observed for the AuCl salt and this also gave a rather rough and friable surface finish. The slowest deposition was exhibited by the

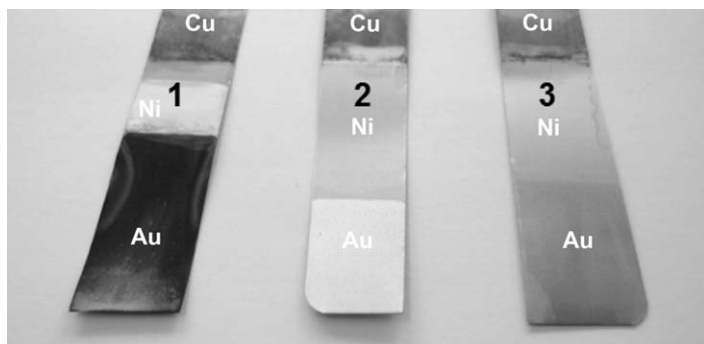
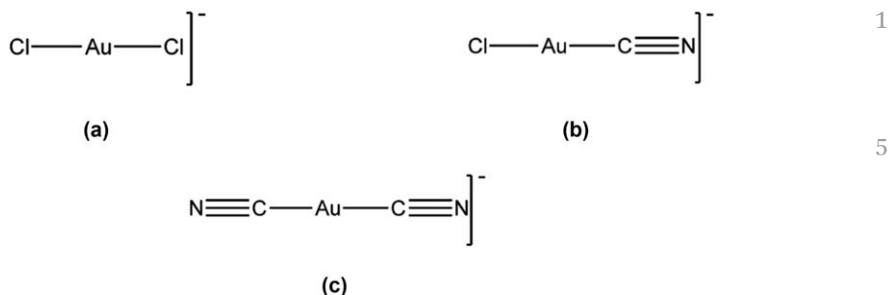


Figure 10.7 Photographs of immersion Au coatings, from different gold salts, onto electroless nickel of samples; **1** from AuCl, **2** from AuCN and **3** from KAu(CN)₂. The regions of the samples, Cu substrate, electroless Ni coating, and Au coating are labelled for clarity.

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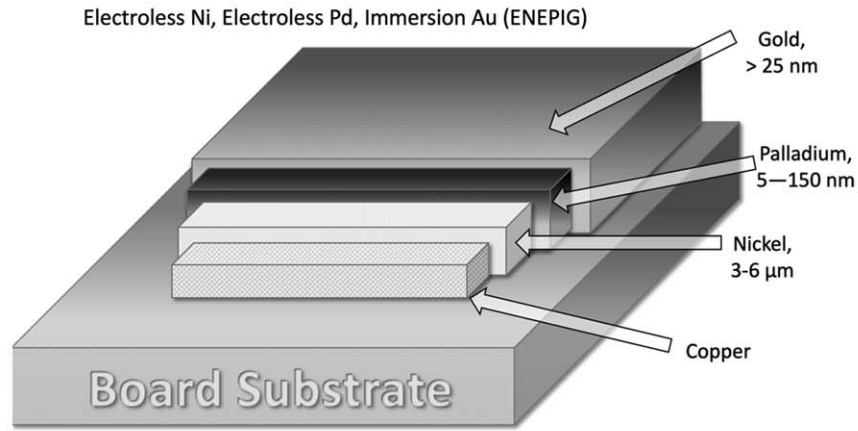
Scheme 10.2 Metal ion speciation, determined by EXAFS, for Au^+ in DES (*Ethaline*) from gold salts: (a) AuCl ; (b) AuCN and (c) $\text{K}[\text{Au}(\text{CN})_2]$.

cyanoaurate $[\text{AuCN}_2]^-$ which gave a very smooth, even and adherent finish (see Figure 10.7). The AuCN salt gave intermediate plating rates and surface finishing. These observations were correlated with the structural evidence for metal ion speciation gathered from X-ray scattering methods (EXAFS), as shown in Scheme 10.2.²⁸

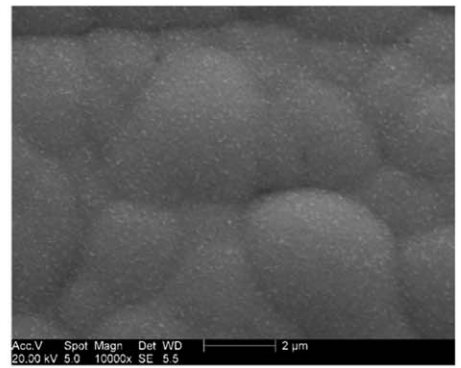
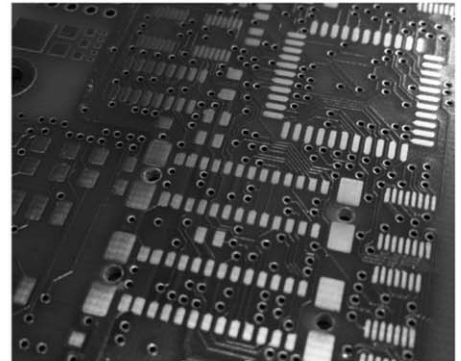
The presence of the strongly bound cyanide ligand in these cases is kinetically limiting to the rate of deposition, whereas the chloride ligand is generally less strongly bound and more labile. This insight has subsequently led to the design of a DES electrolyte for gold immersion plating in which control of the deposition rate is achieved by a competitive dissolution process using iodine as an oxidant.^{26,29} This formulation is capable of delivering smooth and even gold coatings in a process using a cyanide-free electrolyte.

The absence of the acidic component in the DES gold immersion process has delivered one of the key objectives of the ASPIS project in that there can be no corrosion of the nickel substrate and therefore the formation of “*black pad*” is avoided. In addition, this provides a process that is capable of competing with current commercial chemistries without the need for strong acids or cyanide, whilst increasing the efficiency by reducing waste and remedial rework.

This methodology has been further extended to encompass more modern developments in multi-layer surface finishes for PCB assembly. Recently, new and more complex surface finishes have emerged for PCB manufacture that specifically address reliability issues and in particular the need to maintain good component bonding under conditions of high thermal and mechanical stress. In addition, these finishes aim to provide a good bonding substrate for various assembly methods including surface-mount reflow soldering on copper, aluminium and gold wire bonding. One such finish is electroless nickel, electroless palladium, immersion gold, which is abbreviated to its acronym ENEPIG. As with ENIG, the amounts of metals used is small and the coatings of valuable metals are quite thin. The structure and dimensions of an ENEPIG finish are shown in Figure 10.8a. Although the ENEPIG finish achieves its objectives with respect to bonding performance and durability, the process is expensive and difficult to maintain. This is



(a)



(b)

Figure 10.8 (a) Structure and dimensions of the ENEPIG surface finish; (b) Images of the DES, ENIG finish on a test PCB (*top*), together with a scanning electron micrograph of the ENIG surface (*bottom*). The latter shows a smooth and even finish over the nodular electroless nickel.

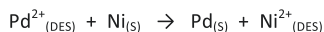
partly due to the demanding characteristics and narrow process windows (pH, temp, concentrations *etc.*) of the electroless processes. 1

In order to address these issues, a consortium of industry and academic partners were tasked with developing a simpler and more resource-efficient process that was functionally equivalent to the ENEPIG finish. The consortium was funded by Innovate UK under a project entitled “Manufacturing Coatings for Future Electronic Systems” (MACFEST).³⁰ The strategy was to use DESs without surface catalysts, acid solutions or complex process control to obtain a finish that was industry compliant, had good planarity and durability and that was capable of delivering good bonding during reflow soldering or gold-wire bonding. This was achieved by replacing the electroless process in the aqueous ENEPIG for a DES immersion process in an extension of the DES ENIG finish described earlier. The palladium metal is deposited directly onto the electroless nickel by a thermodynamic exchange with PdCl₂ in the DES solution (Scheme 10.3). 5 10 15

Gold metal can subsequently be deposited on top of the palladium in a similar immersion exchange process using a solution of either chloride, AuCl, or thiosulphate, Na₃[Au(S₂O₂)₂], gold salt. Hence, this process is operational using an acid- and cyanide-free plating formulation. This process has become known as electroless nickel, immersion palladium, immersion gold (ENIPIG). Figure 10.8 (b) shows an example of a board processed using DES ENIPIG and scanning electron micrograph of the surface; these show a smooth, bright and even deposit with the underlying nodular structure of the electroless nickel substrate. 20

Industry standard compliance for this, and other processes in new solvent media was established independently either by industrial partners or at the UK Catapult, Manufacturing Technology Centre (MTC). In the case of the ENIPIG coating, the effectiveness of the solder joint to the new coating was established using the wetting balance method. Here, the force of the interaction between the molten solder and the surface of the PCB is measured. The greater the force, the more effective the solder-substrate bond. Some representative data are shown in Figure 10.9, comparing the new DES immersion ENIPIG to some common alternatives (organic surface preservative OSP, ENIG (see above), tin and hot-air solder level (HASL)). The ENIPIG coating is shown to exhibit more consistent results than any other finish (evidenced from the small error bar). It is equivalent to commercial ENIG and better than either tin solder or copper OSP. 25 30 35

Hence a successful, simple, more environmentally sustainable process was developed as an alternative to commercial ENEPIG. The ENIPIG in DESs showed facile deposition of palladium and gold under easily managed process conditions giving a uniform coating on the PCB substrates with excellent planarity. The process is free from acids and cyanide, highly 40



Scheme 10.3 Immersion coating of palladium onto nickel in a DES electrolyte. 45

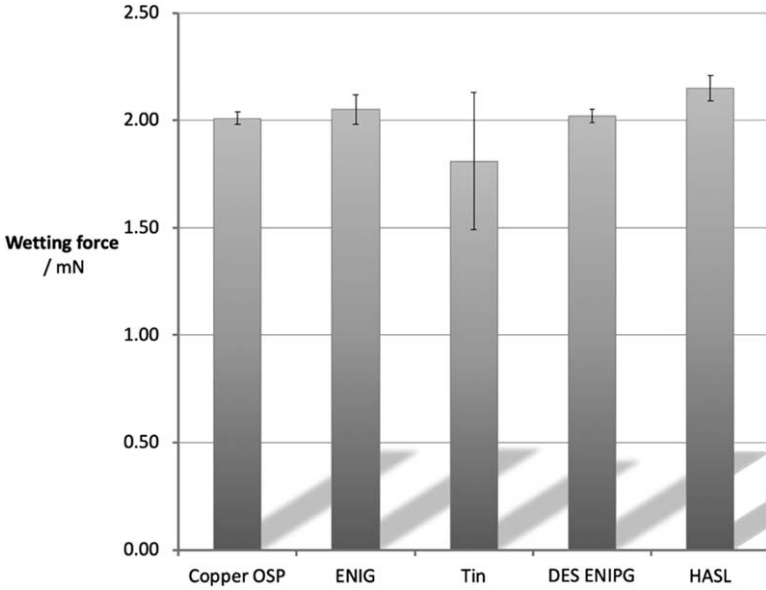


Figure 10.9 Solder wetting balance data comparing the DES immersion ENIPIG coating to a range of other common commercial PCB finishes.

solderable and shows limited corrosive effect on the substrate. This latter point is important in preventing downstream failures associated with *black-pad*.

10.3 DESs in PCB Assembly and Process Control

10.3.1 Soldering

PCB assembly relies on the soldering of components onto the PCB substrate and the assembly is often achieved with wave soldering or through solder reflow ovens. Effective wetting of the substrate by solder during reflow is essential to ensure the production of electronics with a high reliability. See for example the discussions regarding *black-pad* above. The wetting interaction by molten solder with the PCB substrate is maximised through the use of solder flux which, when heated, removes residual oxide from both the molten solder and the PCB substrate surface. The flux formulation has been demonstrated to have a significant impact on the strength of the solder joint.³¹ Additionally, bonding of metals with surface oxides that are either thick or of low solubility in common solder fluxes, such as Cu, Ni and Al, can be difficult and may require the use of more aggressive, noxious chemistries or the use of alternative solders.^{32,33} Solder fluxes are used in a variety of ways in PCB manufacturing including as a core within the solder wire, in wave soldering and as the flux medium in a solder paste.

Deep eutectic solvents provide an excellent environment for coordinating metal ions enabling high solubilities of metal salts, including oxides.³⁴ In the case of soldering, DESs are highly effective at removing residual oxide from the surface of a broad range of metals, behaving as successful solder fluxes and maximising the interaction between a freshly generated oxide free substrate and the molten solder, a pre-requisite for the generation of strong and reliable solder joints.³⁵ DESs can be used as solder fluxes for a wide variety of substrates. Figure 10.10 shows images of a several base metal samples bonded using a DES as a solder flux. In this case the DES consisted of a 1:2 molar ratio of ChCl and Ur respectively (known commercially as *Reline*), with a tin based solder. Strong and consistent solder joints could be formed with Cu, brass, Ni, stainless steel and even cast-iron substrates. In the case of Ni, cast iron and stainless steel, solder fluxes often rely on aggressive chemistries such as high concentrations of strong acids to break down the surface passivation layer or alternative joining methods such as brazing or diffusion bonding.^{36,37} In the case of DESs, the high metal ion coordinating ability of the liquid enables the removal of the surface oxide enabling effective soldering from environmentally benign chemicals. Given the effectiveness of DESs as a solder flux, their potential application in PCB assembly is clear, promising reliable soldering without the need for harmful chemicals.

PCBs are always surface coated to enhance the reliability of soldering by coating the Cu surface of the PCB to either prevent copper oxide formation, or generate an oxide that is readily removed from the surface.³⁸ The soldering efficacy of a range of DES fluxes based on ChCl with hydrogen bond donors such as Ur, EG, glycerol and oxalic acid were tested through commercial standard *Tri-Moore* wetting and solder wetting balance trials. *Tri-Moore* testing is a rotary wetting trial in which a fluxed PCB coupon is brought into contact with the surface of a molten solder pot, in this case SAC305, for a fixed period (*e.g.* 6 s). The extent of the soldering is then

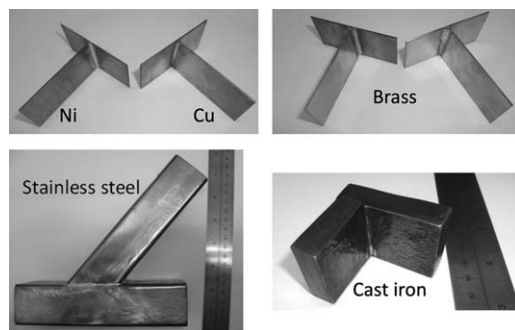


Figure 10.10 Images of metal samples bonded by soldering using the DES *Reline* as a flux and a tin based solder; Ni and Cu (*top-left*), brass (*top-right*), stainless steel (*bottom-left*) and cast iron (*bottom-right*) with a tin based solder. All show even and homogeneous solder wetting.

evaluated through quantification of the surface area coverage and micro-
sectioning to study the solder/substrate interface with a wide variety of PCB
substrates. Figure 10.11 shows soldering of a bare copper PCB, Figure 10.11a,
and a gold (ENIG) coated PCB, Figure 10.11d, in which full surface coverage
of the solder pads can be observed indicating that efficient wetting of the
PCB substrate was achieved with the solder flux effectively removing dirt
and residual oxide from the surface. Figure 10.11b and e show scanning
electron microscopy (SEM) images of the solder/substrate interface of a
soldered copper substrate in which an intermetallic region is observed
between the copper substrate and the Sn solder. The energy-dispersive X-ray
spectroscopy (EDX) line scan elemental analysis, Figure 10.11c and f, shows
the presence of an intermetallic region approximately 4 μm thick. In con-
trast, the sample prepared from the coupon that was coated with gold (ENIG)
had little discernible intermetallic structure between the nickel coating and
the solder.

A quantitative measure of the efficacy of a solder flux can be determined
from the solder wetting balance measurements. Solder wetting balance trials
measure the strength of the interaction between a fluxed PCB coupon and
molten solder. At initial contact between the solder and the PCB coupon
there is a buoyancy effect owing to the force exerted from the solder onto the
PCB. However, once the flux starts to affect the PCB surface, removing re-
sidual dirt and oxides, the solder is able to “wet” the substrate surface re-
moving the buoyancy effect. The rate at which this occurs and the final force
of wetting provides information about the effectiveness of the solder flux. In
trials supported by the Innovative Electronics Manufacturing Research
Centre (IeMRC, Loughborough University), and Innovate UK (project
MACFEST) wetting balance studies were carried out using DES fluxes and
these were compared to standard industry commercial fluxes on a range of
PCB finishes. A comparison of untreated Cu and electroless Ni finishes using
DESs and *Actiec5* (a standard moderately active solder flux) showed that the
wetting of Cu by the DES solder flux is considerably faster than the standard
flux. In a similar trial, an electroless Ni coated Cu wire was studied. In this
case no comparison with an existing flux was possible because *Actiec5* (and
commercial fluxes generally) does not enable the wetting of the electroless
Ni surface by molten solder at all. As with the Cu wire, soldering of the nickel
surface was observed rapidly. In addition, the results for copper soldering
are consistent with the solder wetting behaviour of all of the PCB surface
finishes tested, including an OSP, immersion tin, immersion silver, hot air
solder levelled (HASL) and ENIG, indicating that DES fluxes are effective
across a wide range of PCB surface finishes.

10.3.2 Surface-mount Assembly

Surface mount assembly requires the use of a solder paste. Here solder
particles are suspended in a thick flux medium that are deposited onto the
surface of the PCB pads for soldering through screen or inkjet printing.

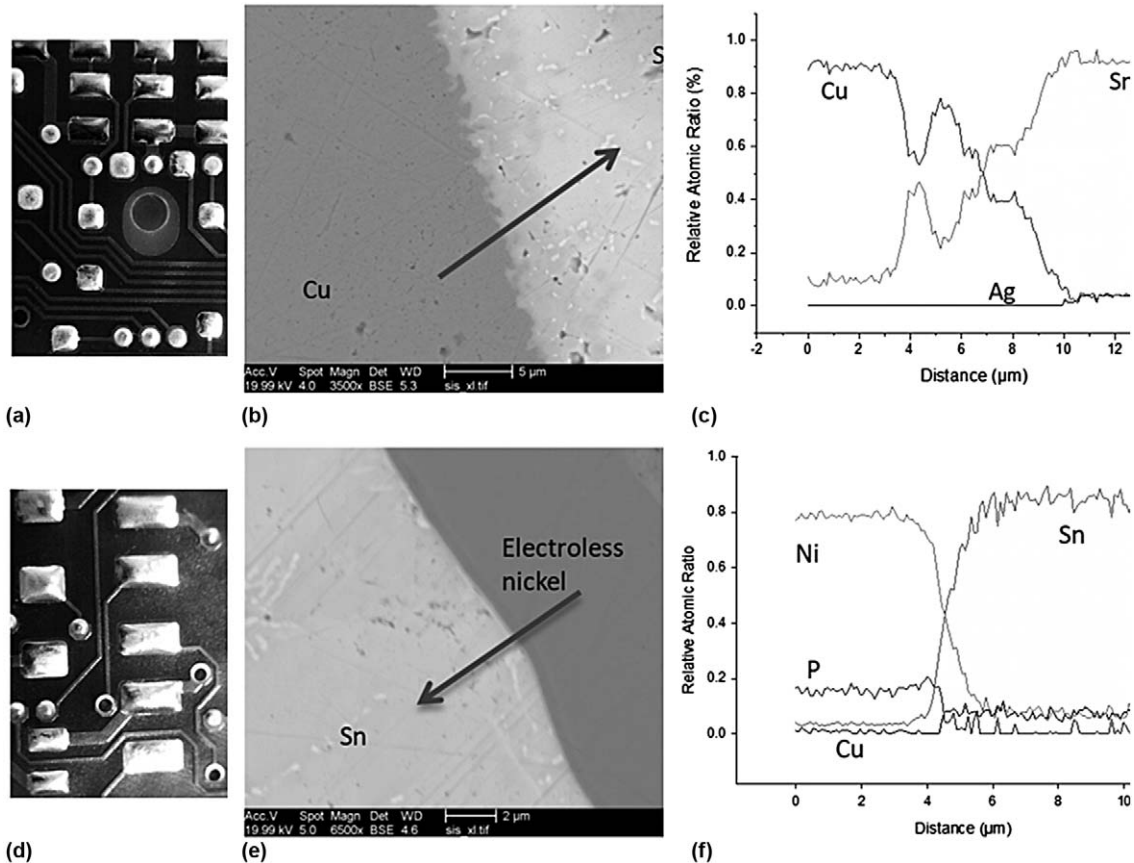


Figure 10.11 Data from *Tri-Moore* rotary wetting trials of Cu (a), and Au (ENIG) (d), finished PCB coupons, each fluxed with the *DES Reline*. SEM images of microsections (b) and (e) of the soldered Cu and Au (ENIG) coated PCB coupons respectively. EDX elemental line analysis, (c) and (f) of the solder joints shown in (b) and (e) respectively. The EDX spectra were acquired along the arrow indicated in the SEM images (b) and (e).

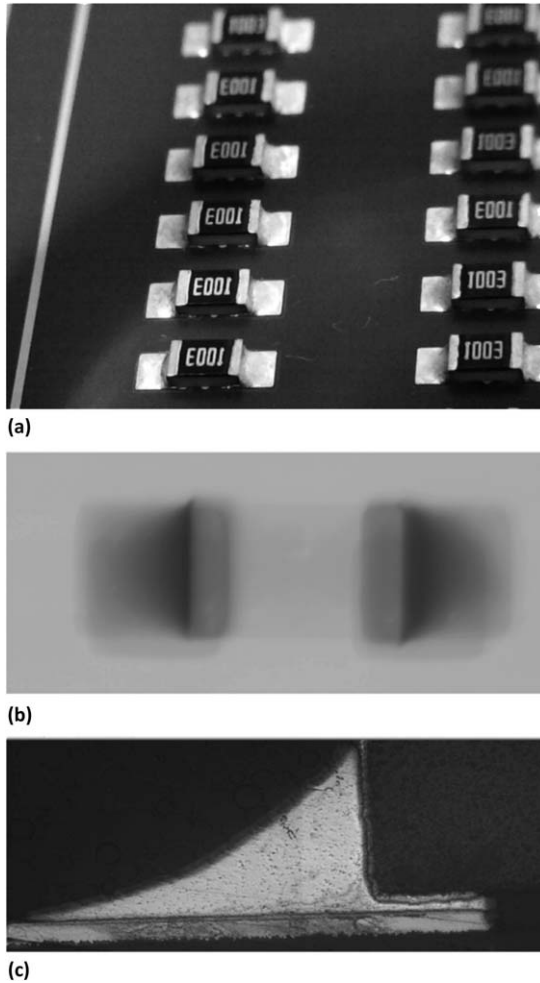
Subsequently, componentry is placed onto the solder paste, forming a conducting connection through solder reflow. It is necessary that the flux is viscous enough that the solder powder is held suspended within the solder flux. To this end, a rheology modifier utilising polyethylene glycols (PEGs) was mixed with the DESs at elevated temperature and left to cool forming a thick, gel like substance.³⁹ A *Reline* solder paste, containing 88.5 wt% SAC305 (standard solder alloy) was successfully applied in a surface mount PCB assembly performing as required in the screen printing and componentry placement while maintaining the excellent solderability consistent with the use of *Reline* as a solder flux.

Examples of assembled PCBs prepared using surface mount assembly are provided in Figure 10.12a–c as an optical image, an X-ray microscope image and an optical cross section of an electroless Ni coated PCB using a standard SAC305 solder paste. The soldering of the components to the PCB was uniform and showed wetting of the solder across the pad and up the full height of the component, demonstrating that in paste form the DES solder flux remains active. The X-ray microscope images also demonstrate the uniformity of the solder joint with little evidence of voiding. Cross sectioning confirms the findings from the X-ray microscope image that uniform and void free solder joints are present, suggesting that the wetting interaction between the molten solder with the PCB and component substrates has been maximised and the solder flux was acting effectively.

The prospect of a DES based solder paste offers numerous benefits over existing Rosin based ones. Namely, DESs perform their principal function of removing dirt and residual oxide rapidly and reliably. Additionally, owing to their efficacy in this regard they can be used to reliably solder a wider variety of substrates including bare copper and electroless nickel offering the potential of removing the costly and chemically hazardous coating processes. The DES is also easy to remove after soldering. Contamination testing of soldered PCBs that had been passed through a cold wash cycle had a NaCl contamination of only $0.04 \mu\text{g cm}^{-2}$, approximately 1% of the maximum permitted in a typical specification.⁴⁰

10.3.3 A New Solderable Surface Finish

In addition to their use as solder fluxes in PCB assembly, DESs have been used in the preparation of HASL finishes on PCBs. HASL is a standard protective coating technique in which a conventional copper track PCB is coated on a thin layer of tin-based solder, this is performed by first coating the PCB in a thin layer of a solder flux, secondly, immersing the PCB in a bath of molten solder with a short residence time (<5 s) and thirdly, the PCB is removed from the solder bath with excess molten solder removed from the surface of the pads through the use of compressed air knives. As the PCB panel cools, the remaining solder solidifies on the surface, protecting the copper from exposure to oxygen and subsequent formation of copper oxide.



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Figure 10.12 Tests data from pick and place surface mount assembly tests carried out at MTC (Coventry). Assembly carried out on an ENIG finished PCB token with components (size 2.5×2 mm) using a solder paste formulated from a mixture of 88.5 wt% SAC305 with a *Reline* based solder flux: (a) optical image, (b) X-ray microscope image and (c) optical image of a cross-section of the component joint (the PCB substrate is aligned on the bottom edge of the image).

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Figure 10.13a shows an optical image of the surface of a HASL PCB prepared using the *DES Reline*, a liquid prepared from a 1:2 molar mixture of ChCl and Ur and a solder of SN100C at 270°C . The solder coating is observed as a silver metallic layer of varying thickness depending on the size of the pad, and the location within each individual pad, with the thinnest solder being on the edge and the thickest in the centre. Figure 10.13c shows a cross sectional image of one of these pads, chemically etched to reveal the

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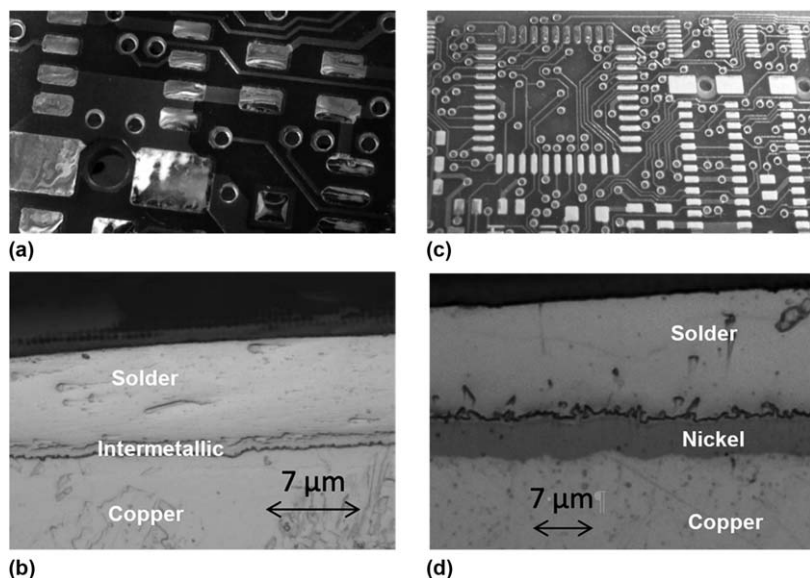


Figure 10.13 Optical images of the surface of (a) HASL and (b) HASLEN coatings of the respective PCBs prepared with a DES solder flux composed of *Reline* ($\text{ChCl} : 2\text{Ur}$) and cross-section images of their respective coatings (c) and (d). The discrete layers in each image are labelled for clarity. Reproduced from ref. 41 with permission from American Chemical Society, Copyright 2005.

microstructure. The solder coats the copper to a maximum thickness of $11 \mu\text{m}$ with the formation of a thin intermetallic Sn/Cu layer at the interface between the Cu substrate and a solder coating of between $1\text{--}2 \mu\text{m}$ thick.

Typically, HASL is the only form of solder coating found in PCBs as other surface finishes are thin and dissolve into the molten solder during soldering. However, the use of DESs as solder fluxes offers the opportunity to solder onto alternative coatings, such as electroless Ni, owing to their ability to quickly remove surface oxides at the elevated temperatures at which HASL takes place, in this example 270°C . This has led to the development of a novel PCB surface finish, hot air soldered electroless nickel (HASLEN), in which an additional electroless nickel coating is applied to the PCB prior to the HASL operation.⁴¹ Previously this concept was not possible owing to the lack of suitable solder fluxes for the soldering of electroless Ni. A cross section of a HASLEN coating is shown in Figure 10.13d, in which the electroless Ni coating can be observed as a thin band of approximately $7 \mu\text{m}$ thick. There is a comparatively thin intermetallic region between the electroless Ni and the solder.

When used in subsequent PCB assembly both HASL and HASLEN coatings perform similarly during reflow assembly in that, as the top surface is that of the solder, the resulting solder joint forms between the solder on the surface of the PCB and the component. However, the use of HASLEN offers

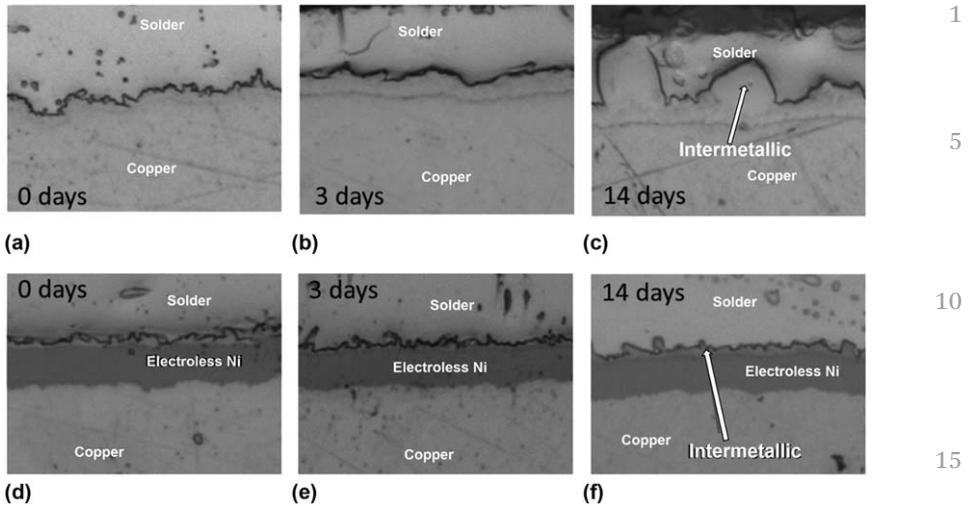


Figure 10.14 Cross sectional images of HASL (a), (b) and (c) and HASLEN (d), (e) and (f) that have been heated in an oven at 130 °C for 0, 3 or 14 days. The discrete layers in each image are labelled for clarity and the intermetallic phases are indicated at the end of the ageing period. Reproduced from ref. 41 with permission from American Chemical Society, Copyright 2005.

considerable promise in high reliability applications. Figure 10.14 shows a comparative accelerated ageing process in which the HASL and HASLEN coatings were aged at 130 °C for 0, 3 and 14 days. In the case of HASL the intermetallic region grows significantly over this time, eventually resulting in large and irregular intermetallic growth.⁴² These growths are linked to brittle fractures and failures. Additionally, the formation of tin whiskers is believed to occur through the generation of mechanical stress within solder joints caused through volumetric expansion of tin intermetallic growth.⁴³ In contrast, the accelerated ageing of HASLEN coatings shows minimal continued intermetallic growth formation (Figure 10.14d–f). Within a period of 14 days at 130 °C there was very little alteration in the composition of the coating. This suggests that HASLEN PCBs offer improvements compared to HASL PCBs as intermetallic growth through to the surface of the solder would take much longer giving a longer shelf life, the resulting solder joints would be less susceptible to brittle fracture causing more reliable electronics after manufacture and possible tin whisker mitigation owing to the formation of fewer stresses within the solder caused by intermetallic growth.

10.3.4 Process Control and Analysis

In any new or alternative process chemistry, minimisation of necessary resources during the manufacture of a PCB finish, as well as efficient reclamation, requires reliable analytical methods and procedures capable of

giving accurate information about feedstock waste streams, for example how much of a particular metal is present on a surface. Consequently, it is necessary to understand the waste stream in terms of the diversity of the materials present, their identity and the quantities of each.

In order to understand the detailed influences of the DES medium on various aspects of materials processing for thin-film coatings, the Leicester group have used sophisticated neutron scattering techniques at European large-scale facilities such as the International Spallation Source (ISIS, Oxford UK) and the Institut Laue–Langevin (Grenoble, France). These techniques give a detailed picture of the nature (thickness, roughness of buried interfaces) of a surface coating at the nano-scale, as well as fundamental insights into the mechanisms of deposition and dissolution.⁴⁴ However, the technical demands of sample preparation for such methods along with accessibility of the experimental facilities makes this type of analysis completely impractical for lab-based process monitoring. Fortunately, some of the more well-established analysis techniques also work very well in DES media. One such example is known as simultaneous thickness electrochemical potential (STEP). These methods have been described in aqueous metal finishing, although they are not often used. A test sample is subjected to a constant electrochemical current density whilst the potential is monitored as a function of time. The sample may be, for example, a multi-layer PCB substrate whose metal layers are being stripped away for analysis of the composition and thickness. Alternately, the method can be used to characterise and quantify deposition. Here, the STEP method provides information regarding the *identity* of the metal being removed using the unique value of the potential required to maintain a constant current, whilst information regarding the *quantity* of that metal is given from the time axis. The latter is directly related to the quantity of charge passed during the process using Faraday's law, as:

$$Q = i \cdot t \quad (\text{in which } Q = \text{charge (c)}, i = \text{electrical current (A)}, t = \text{time (s)}).$$

An example of the outcome of a STEP analysis for a test coupon is shown in Figure 10.15. Here a two-component Cu/Ag system is stripped by constant current dissolution in a DES. The values of the dissolution potential are clearly visible for the two metals and the time for which the potential remains constant gives the total charge and therefore the film thickness (see above). In addition to being able to provide identity/composition data, the STEP method in DESs is capable of providing information regarding the condition of the interface between two metals of a multi-layer and about the extent of metal mixing that occurs during ageing. This is useful for understanding processes such as interfacial diffusion and intermetallic formation during component assembly. The latter process can occur at soldered joints through temperature cycling or ageing and can cause brittle fractures in solder joints leading to component/device failure.

Consequently, such analytical techniques are aimed at providing a better understanding of new process chemistries and of the coatings they can

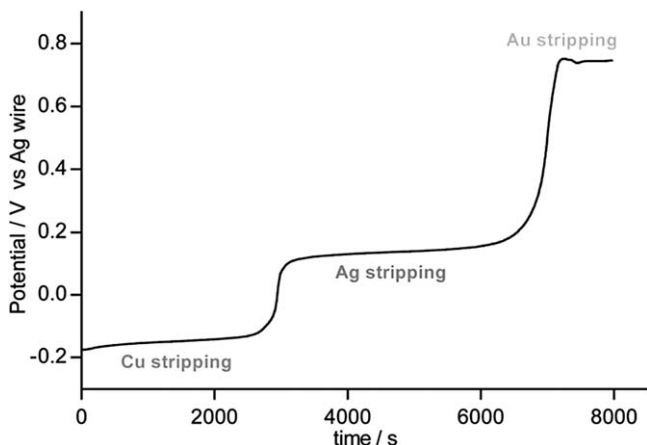


Figure 10.15 STEP experiment response for sequential metal stripping of an Ag/Cu bilayer from an Au (electrode). Bilayer fabrication: AgCl (10 mM in *Ethaline*), deposited potentiostatically at -0.1 V (7200 s); Cu (10 mM in *Ethaline*), deposited potentiostatically at -0.6 V (7200 s). Galvanostatic stripping in *Ethaline* at $i = 14.9 \mu\text{A cm}^{-2}$. Reproduced from ref. 44 with permission from the Royal Society of Chemistry.

deliver. The objective is a more reliable coating, with a longer-life cycle from a more efficient surface/solution chemistry that is often much simpler and easier to control than aqueous alternatives. Coatings can be subsequently designed to make the recovery of metals easier.

10.4 Waste Processing and Metal Recovery

Conventional methods for the recovery and separation of various metals from PCB waste involve burning of the bulk materials followed by dissolution of the remaining metal oxides. Alternatively, assembled components can be removed and then the PCB substrates shredded and treated separately. In either case, recovery of the metals is achieved by dissolution in aqueous acid followed by a series of neutralisation, precipitation, or electrochemical recovery processes. These processes can require careful process control and are often not very efficient. On the other hand, processing metals and metal compounds with ionic liquids and DES media is becoming increasingly attractive due to the ability to change speciation and therefore reactivity compared to aqueous solutions. The term *ionometallurgy* has been coined to describe this area of study and it has been reviewed in more detail elsewhere.⁴⁵ If we consider the oxidation of gold, as shown in Scheme 10.4.

The exact product will change depending on the solvent and it will produce either $[\text{Au}(\text{H}_2\text{O})_6]^+$ or $[\text{AuCl}_2]^-$ depending on whether it is in aqueous solutions or a DES, respectively. This can shift the redox potential by approximately -0.5 V in the DES.²⁶ This should mean that it is



Scheme 10.4 Oxidation of gold metal can be achieved by molecular iodine in a DES solution.

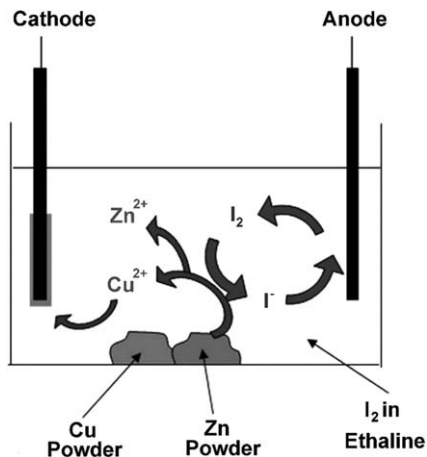
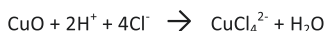


Figure 10.16 Schematic diagram showing the electrocatalytic dissolution of a mixture of metals in DES followed by their electrochemical recovery and separation. Reproduced from ref. 26 with permission from the Royal Society of Chemistry.



Scheme 10.5 Dissolution of copper oxide in a high [chloride] environment.

thermodynamically easier and kinetically faster to dissolve metals in DESs than in water. This has been demonstrated using iodine as an oxidant in *Ethaline*. It was shown that iodine is a strong oxidant in DESs that is able to oxidise most metals. We have demonstrated that not only is the oxidation of gold faster in DESs with iodine compared to traditional methods such as aqueous cyanide solutions, but the iodine can be regenerated electrochemically. This provides the opportunity to both dissolve a mixture of metals from shredded PCB waste and also then to selectively recover the separate metals. This concept is schematically indicated in Figure 10.16 for the separation of copper and zinc.

Using this concept, the selective recovery of metals from mixtures of Cu/Zn, Ga/As and Ag/Au has been successfully demonstrated.²⁹ This process applies not only to the recycling of metals, but also for the recovery of elements from minerals.⁴⁶ In addition to changing speciation, the high chloride media and low water content also destabilise the formation of metal oxides, as shown in Scheme 10.5.

More of the metal oxide will be in the form of the soluble anion if the water content of the liquid is low. The solubility of a range of oxides in DESs has been characterised and it has been found that the highest solubility occurs in the liquids with the lowest pH.³⁴ The solubility of the metal can be tailored by using different hydrogen bond donors. Acids such as oxalic and malonic have similar acidities in DESs but the anions have different chelating properties and so display different solubilities.^{47,48} The use of DESs to recycle metal oxides has been demonstrated on a 250 kg scale for electric arc furnace dust.⁴⁹ This is a mixture of aluminium, iron, zinc, lead and cadmium oxides. A DES was developed which only dissolved the last three of these. Once in solution, the lead and cadmium could be cemented from solution using zinc powder and the zinc chloride was subsequently recovered by precipitating it by adding water.

AQ-1

The destabilisation of metal oxides also enables the electrolytic processing of metals which is difficult in aqueous solutions. Most metals can be anodically dissolved without the formation of a passive film insulating the metal surface. This enables electropolishing and dissolution of metals such as titanium and nickel-based superalloys.^{50,51} The mechanism of dissolution is quite complex with the formation of porous solid films in many cases.⁵²

It has also recently been demonstrated that metal oxides, sulfides and arsenides can be electrochemically dissolved in DESs. In this method the metal compound is ground into a fine powder and mixed with a few drops of DES to create a thick paste. This can then be painted onto an electrode surface to create a thin layer. The viscosity of the film enables the paste to stick to the electrode surface and the conductivity allows the electrochemistry to be studied, even for materials which are quite poorly conducting such as sulfur. This technique is called paint casting and has been demonstrated for a variety of minerals including galena and pyrite.^{53,54} Such methods have a clear application in the recovery of low concentrations of strategic metals from touch screens, photovoltaic devices and small magnets found in surface mount transformers and inductive components.

Nickel is another example of a relatively high value metal which is present in a range of solid waste streams from many industry sectors in the presence of other metals from which it is difficult or impossible to separate using existing processes. Two industry sectors with closely related technological needs and challenges are surface finishing and battery recycling. Here the metal finishing sector includes metal recycling from the manufacture of PCB substrates (Ni plating) as well as from waste re-processing (WEEE). These challenges were the subject of an Innovate UK funded project into Ni recovery from plating waste generated by the PCB industry, amongst others, entitled, "*Recovery of Nickel from Filter Cake*" (RECONIF).

Within the surface finishing industry heavy metal pollutants from the facility liquid outfall are primarily removed *via* chemical precipitation as an insoluble, toxic hydroxide sludge which is then normally subjected to dewatering to generate a filter cake with a solid content of typically 30% which is destined for off-site disposal and ultimately to landfill. End-of-life

recycling of Ni-metal hydride, Ni-Cd batteries and more recent Li-ion battery chemistries is not carried out in the UK (see Chapter 9). Selective extraction of the valuable Ni content in a high purity form would have economic advantages, as well as enhancing the value of other recovered metals and enabling the safe handling of toxic cadmium. The RECONIF project addressed this loss of Ni from surface finishing and end-of-life batteries by developing an integrated system based on the selective dissolution of nickel from its hydroxide *via* a novel ionic liquid and DES media and the subsequent high efficiency electrowinning of the nickel in the pure metallic form for reuse. This development is highly innovative and addresses the loss of a valuable resource with its associated high environmental impact, for which no viable economic solution currently exists.

It was shown that the most effective nickel dissolution system to date is a eutectic solvent formulated from ChCl and lactic acid. The system is non-selective for nickel, however, it has the advantage of a very low viscosity. The dissolution of other minor metal components could be suppressed by further addition of other organic carboxylic acids. A hydrophobic task-specific ionic liquid based on the betainium cation ($[\text{Hbet}][\text{Tf}_2\text{N}]$) was chosen as this shows a selective solubility towards metal oxides and metal hydroxides. By acidifying the system, the recovered metals can be back-extracted from the DES into the water phase and the ionic liquid can be reused. The $[\text{Hbet}][\text{Tf}_2\text{N}]$ ionic liquid exhibits a well-known “phase switching” behaviour: after heating a two-phase system (ionic liquid-water) above the critical point of $55\text{ }^\circ\text{C}$, this results in a one-phase system. After cooling down the mixture below the critical point ($55\text{ }^\circ\text{C}$), the two-phase system is reformed. This process has been optimised for the recovery of Ni from mixed waste and operated at a pilot plant scale, 50 L, by C-Tech Innovation (Figure 10.17).



Figure 10.17 Pilot plant (50 L scale) for the operation of a DES-based process for Ni recovery and recycling from Ni plating waste generated by the surface finishing PCB supply chain and battery waste.

Nickel and cobalt waste streams from metal finishing and end-of-life batteries were also targeted under a separate EU Framework 7 consortium entitled Cobalt and Lanthanide Recovery from Batteries (CoLaBATS).⁵⁵ The CoLaBATS project comprised an international consortium, spanning academics, research institutes, recyclers, chemists and equipment producers, and brought together expertise to deliver a completely new and highly innovative hydrometallurgical process for leaching multiple metals from metal finishing and battery waste (electrodes and electrolytes). The CoLaBATS technology has been designed to provide a multi-stage process capable of extracting key high value individual metals (Ni, Co, Cu, Ln, Zn), plus the extraction of other metal mixtures suitable for further refining. The key outcome of the technology has been the ability to use novel DESs for selective leaching of metals from the waste stream. Compared to the current hydrometallurgical processes that employ strong acids, the DES method is much more benign and sustainable. Additionally, the DES has a low vapour pressure, making it easier to handle, and offering improved air quality in the workplace.

Furthermore, the benefit of the project outcome is the ability to reuse the chemistry. The DES can be stripped of the metals and reused in a closed loop process. The benefits of this are the reduction in chemical costs for operating the plant, the reduction of waste, and the improved environmental impacts compared to other hydrometallurgical recycling processes. Additionally, selective solvent and DES based extraction and recovery techniques were developed by consortium members for scale up and pre-commercial trials.⁵⁶

More recently, the UK government has identified recycling and recovery of important metals in electronics, particularly those from battery waste, as a key strategic effort. As a result, the *Faraday Challenge* (Innovate UK) and *The Faraday Institution* have been created and are funding various new initiatives in metal recovery and recycling.^{57,58}

10.5 Conclusion

We have described the development of several new processes relating to the fabrication, characterisation and recycling of PCB metal assemblies in alternative, environmentally sustainable solvent technologies. These solvent technologies are based on an emergent class of liquids known as DESs. The process and development work described here represents a summary of outputs from a range of collaborative consortium projects funded by various programmes under the European Union and Innovate UK actions. We demonstrate that in many cases, the use of DES technologies can be disruptive to current process thinking and in principle deliver benefits including increased efficiency, lower costs and better process control. In addition, these technologies offer the opportunity to incorporate new ideas into PCB fabrication and assembly that facilitate downstream end of life recovery and separation in a manner that is consistent with a circular economy model.

Current PCB manufacturing is carried out in many complex metal deposition processes including electrolytic, galvanic and catalytic mechanisms. Many of these chemistries involve aqueous solutions of toxic metal salts (e.g. cyanides), strong inorganic acids and precious and expensive noble metals (Au, Pd) and require careful process control and monitoring (e.g. pH and temperature). As a result, these processes are often costly to operate and inefficient. The emphasis of the processes described here is five-fold: (1) to improve the economic and efficient use of essential metals; (2) to reduce or eliminate the use of precious and expensive metals where these are superseded or unnecessary; (3) to reduce the use of complex and difficult to maintain process chemistry; (4) to reduce reliance on toxic and noxious materials; and (5) to improve recovery, recycling and reuse of PCB metals.

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