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Why Use Ionic Liquids for Electrodeposition?

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At the start of the first edition, it seemed pertinent to pose the question “Why use ionic liquids for electrodeposition?” With over 8 years more experience, it is more suitable to ask “What are the limitations of ionic liquids for electrodeposition?” The previous edition highlighted the lack of background information on many ionic liquid systems, and this edition will fill in quite a bit of this.

The growing interest in the topic in the intervening period is evidenced by the number of publications per year. With about 60 papers per year in 2007, it had grown to 200 papers in 2014. The body of literature that needs to be reviewed has trebled, which highlights the activity. This topic has an h-index of 70.

Electroplating has been carried out for over 200 years, and despite electroplated goods entering many aspects of manufacturing industry, very little has changed about the physical processes involved in electrodeposition for about 100 years. It was only with the advent of the electronics industry in the middle of the twentieth century that significant changes occurred in the hardware and chemistry of the plating solutions [1]. The postwar period saw an increase in gold plating for electronic components and the use of less hazardous plating solutions. This trend has continued with increased control of hazardous materials to the environment. Improved solution composition and power supply technology have also allowed the development of fast and continuous plating of wire, metal strips, semiconductors, and complex substrate geometries.

Many of the technological developments seen in the electronics industry depend on sophisticated electroplating, including the use of exotic metals, and this is one of the drivers for new technology within the electroplating sector. The other main driver is the search for alternative technologies for metals such as chromium, nickel, and cadmium. Anticorrosion and wear-resistant coatings are predominant in the market for electroplating, and environmental directives will evidently limit their usage in the future.

The main metals that are commercially deposited are Cr, Ni, Cu, Au, Ag, Zn, and Cd together with a number of copper- and zinc-based alloys [1]. The

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whole electroplating sector is based on aqueous solutions. There are some niche markets based on organic solvents such as aluminum, but these are very much exceptions. Metals not included in this list are generally deposited using plasma vapor deposition (PVD) or chemical vapor deposition (CVD) techniques. These methods allow the coating of most substrates (metal, plastic, glass, ceramic, etc.) not only with metals but also with alloys or compounds (oxide, nitride, carbide, etc.), without damaging the environment. Although these techniques are technically interesting, it is regrettable that they always involve high capital investment and it is difficult to prepare thick coatings; thus, they are only applied to high-value niche markets.

Clearly, the key advantages of using aqueous solutions are as follows:

- Cost
- Nonflammability
- High solubility of electrolytes
- High conductivities resulting in low ohmic losses and good throwing power
- High solubility of metal salts
- High rates of mass transfer.

For these reasons, water will remain the mainstay of the metal plating industry; however, there are also limitations of aqueous solutions including the following:

- Limited potential windows.
- Gas evolution processes can be technically difficult to handle and result in hydrogen embrittlement.
- Passivation of metals can cause difficulties with both anodic and cathodic materials.
- Necessity for complexing agents such as cyanide.
- Water used for almost all of the process steps must been treated before discharge.

These prevent aqueous solutions being applied to the deposition of several technically important materials. In addition, probably the most pressing issue facing the electroplating sector is the introduction of legislation such as Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) in the European Union and similar legislations in other countries, which seek to limit metal precursors such as CrO_3, Ni(II), and Co(II) salts as well as metals such as cadmium.

The key technological goals include replacement of environmentally toxic metal coatings, deposition of new alloys and semiconductors, and new coating methods for electronegative metals. The main driving force for nonaqueous electrolytes has been the desire to deposit refractory metals such as Ti, Al, and W. These metals are abundant and excellent for corrosion resistance. It is, however, the stability of their oxides that makes these metals difficult to extract from minerals and apply as surface coatings.

1.1 Nonaqueous Solutions

There are clearly a range of alternative nonaqueous solutions that could be used for electrodeposition. Ideally, to obtain the properties required for an electrolyte solution, polar solvent molecules have to be used, and these should preferably be small in molecular weight and volume, in order to obtain the requisite high fluidity. Unfortunately, all polar solvents result from electronegative elements, which by their nature makes them good electron donors. Accordingly, they will strongly coordinate with metal ions, making them difficult to reduce. While a number of metals have been deposited from polar organic solvents, these tend to be more electropositive metals, and the processes offer few advantages over aqueous solutions. Some studies have been conducted using nonpolar organic solvents, predominantly aromatic hydrocarbons, but these suffer from the serious disadvantage that the dissolved electrolytes are highly associated and the solutions suffer from poor conductivity. The solutions do, however, have wide potential windows, and it has been demonstrated that metals such as aluminum and titanium can be deposited from them. One of the most successful nonaqueous processes is the SIGAL process developed in the late 1980s for the deposition of aluminum from toluene [2, 3]. The aluminum source is triethyl aluminum, which is pyrophoric, and despite the high flammability of the electrolyte solution, the process has been commercialized and is still the only electrochemical method for the deposition of aluminum. A review of electrochemistry in nonaqueous solutions is given by Izutsu [4] and Simka *et al.* [5].

1.2 Ionic Fluids

Clearly, an alternative to molecular solvents is the use of ionic fluids. Ionic materials typically melt at elevated temperatures due to their large lattice energies. High-temperature molten salts have been extensively used for the electrowinning of metals such as Li, Na, Ti, and Al [6–8]. They have wide potential windows, high conductivities, and high solubilities for metal salts; in fact, they have most of the advantages of aqueous solutions and overcome most of their limitations, but clearly, they suffer from the major limitation that the operational conditions are difficult to achieve and limit the range of substrates that can be used for deposition.

The alternative to high-temperature molten salts is to use an ionic substance that melts at a low temperature. While this may sound as an oxymoron, it is logical to suppose that the melting point of an ionic substance is related to ionic size, since the greater separation between the charges lowers the lattice energy, and if the ions are made large enough, the material will eventually melt under ambient conditions. A significant amount of work was carried out in the middle of the twentieth century with the aim of developing lower temperature molten salts. One of the key aims was to develop a lower temperature melt for aluminum deposition, which led to the formation of $Li^+/K^+/AlCl_3$ eutectics having freezing points close to 100 °C [9]. The use of quaternary ammonium salts particularly pyridinium and imidazolium salts eventually pushed the freezing point down to ambient conditions. The term “ionic liquids” was coined to differentiate these lower temperature ionic fluids from their high-temperature analogs, which are composed predominantly of inorganic ions.

The synthesis and properties of a range of ionic liquids are detailed in the following chapter, while the history and chemical properties of these liquids are covered in well-known reviews [10, 11]. Since the previous edition, numerous applications of ionic liquids have been commercialized. The most well known of these is BASF's BASIL process [12]. This uses the ionic liquid as a phase transfer catalyst to produce alkoxyphenylphosphines, which are precursors for the synthesis of photoinitiators used in printing inks and wood coatings. The imidazole acts as a proton scavenger in the reaction of phenyl-chlorophosphines with alcohols to produce phosphines. The Dimersol® process [13] has also been commercialized and uses a Lewis-acid catalyst for the dimerization of butenes to produce C_8 olefins, which are usually further hydroformylated giving C_9 alcohols used in the manufacture of plasticizers.

A review of successes and applications of ionic liquids is out of date almost as soon as it is published, but some areas where some significant developments have been made include batteries, supercapacitors, actuators, dye-sensitized solar cells, gas storage, antistatic agents, and cleaning agents. These applications are covered in numerous reviews [14–17]. Advances in the commercialization of electrodeposition are covered later in this book, but it is sufficient to say here that some processes have been taken to a scale where hundreds to thousands of amperes have been applied to working electrodes.

1.3 What Is an Ionic Liquid?

The recognized definition of an ionic liquid is "an ionic material that is liquid below 100 °C," but this leaves significant question as to what constitutes an ionic material. Some authors limit the definition to cations with discrete anions, for example, BF_4^- and NO_3^-. This definition excludes the original work on chloroaluminate systems and the considerable work on other eutectic systems and is therefore unsatisfactory. Systems with anionic species formed by complex equilibria are difficult to categorize as the relative amounts of ionic species depend strongly on the composition of the different components.

Ionic liquids have also been separated into first- and second-generation liquids, where first-generation liquids are those based on eutectics and second-generation liquids have discrete anions [18]. Others have sought to further divide the first-generation liquids into different types depending on the nature of the Lewis or Brønsted acid, which complexes (see Chapter 3.2) [19]. While there is some dispute as to whether eutectics with Brønsted acids constitute ionic liquids at all, there are others who seek to widen the description of ionic liquids to include materials such as salt hydrates [20].

In general, the first-generation ionic liquids form because the charge on the ions is delocalized, and this gives rise to a reduction in lattice energy. The majority of ionic liquids are described by equilibrium:

$$\text{cation} + \text{anion} + \text{complexing agent} \leftrightarrow \text{cation} + \text{complex anion} \tag{1.1}$$

Potentially complex cations could also be formed using species such as cryptands or crown ethers.

$$\text{cation} + \text{anion} + \text{complexing agent} \leftrightarrow \text{complex cation} + \text{anion} \tag{1.2}$$

The confusion arises from the magnitude of the equilibrium constant. For discrete anions such as BF_4^- and even $((CF_3SO_2)_2N)^-$, the equilibrium lies clearly to the right of Eq. (1.1). For some eutectic-based liquids, the equilibrium constant is also to the right, for example,

$$\mathrm{Cat^+Cl^- + AlCl_3 \leftrightarrow Cat^+ + AlCl_4^-} \tag{1.3}$$

But the addition of more Lewis acid produces other anionic species,

$$\mathrm{Cat^+Cl^- + 2AlCl_3 \leftrightarrow Cat^+ + Al_2Cl_7^-} \tag{1.4}$$

The use of less Lewis-acidic metals, for example, $ZnCl_2$ or $SnCl_2$, will lead to a small amount of Cl^- being present in the mixture. The species formed between the anion and the complexing agent becomes weaker when a Brønsted acid, for example, urea, is used.

$$\mathrm{Cat^+Cl^- + urea \leftrightarrow Cat^+ + Cl^- \cdot urea} \tag{1.5}$$

Others have claimed that, in the extreme, water can act as a good Brønsted acid and hydrate salts can act as ionic liquids [20].

$$\mathrm{LiClO_4 + 3.5H_2O \leftrightarrow Li^+ \cdot \mathit{x}H_2O + ClO_4^- \cdot \mathit{y}H_2O} \tag{1.6}$$

This idea has recently been extended to include metal salts with complexants such as acetonitrile and MeCN [21, 22].

$$\mathrm{AgTf_2N + MeCN \rightleftharpoons Ag^+ \cdot MeCN + Tf_2N^-}$$

Metal salts such as $AlCl_3$ and $ZnCl_2$ have been found to disproportionate to give both anionic and cationic metal-containing species [23].

$$\mathrm{2AlCl_3 + \mathit{n}\,Amide \rightleftharpoons [AlCl_2 \cdot \mathit{n}\,Amide]^+ + AlCl_4^-}$$

These latter ideas are relatively new and point to a wide range of other metal-containing species being possible. They do, however, illustrate that the current definition of ionic liquids (only ions, m.p. <100 °C) may indeed be precise but, at the same time, not very useful from the perspective of chemical applications.

Ionic liquids with discrete anions have a fixed anion structure, but in the eutectic-based liquids at some composition point, the Lewis or Brønsted acid will be in considerable excess and the system becomes a solution of salt in the acid. A similar scenario also exists with the incorporation of diluents or impurities; hence, we need to define at what composition an ionic liquid is formed. Similarly, many ionic liquids with discrete anions are hydrophilic, and the absorption of water is found to sometimes have a significant effect on the viscosity and conductivity of the liquids [24–26]; at some point, these mixtures become better considered as concentrated aqueous solutions.

It has recently been shown that water mixtures with DESs can in some cases be beneficial for metal deposition, as the presence of water changes speciation and mass transport. Water–ionic liquid mixtures have been shown to be non-homogeneous microemulsions in some cases and so diffusion will be complex, depending on the phase behavior of the metal salt. Recent approaches to overcome this difficulty have been to classify ionic liquids in terms of their charge mobility characteristics [27] and the correlation between the molar conductivity and fluidity of the liquids [28].

In this book, a broad range of ionic liquids will be assumed, encompassing all of the aforementioned types because in the discipline of electrodeposition, it is the resultant deposit that is important, rather than the means by, or medium from, which it was obtained. As will be seen later, there is also a very fine line between a concentrated electrolyte solution and an ionic liquid containing diluents.

1.4 Technological Potential of Ionic Liquids

A series of transition- and main-group-metal-containing ionic liquids have been formulated, and the feasibility of achieving electrodeposition has been demonstrated for the majority of these metals. Figure 1.1 shows the elements in the periodic table that have been deposited using ionic liquids. Details of these systems are given in the subsequent chapters, and concise summaries exist in reviews [19, 29].

While ionic liquids could potentially be used for all electrodeposition processes, it is quite clear that technically and economically their influence will be most significant in specialist, possibly niche, applications. The most important of these will probably include the following.

1.4.1 Removal of Toxic Reagents

One of the biggest challenges in electroplating will be the need to comply with legislation such as REACH, which is attempting to limit the use of hazardous metal precursors in aqueous processes such as CrO_3, $NiSO_4$, and $CoCl_2$ [30–32]. The first of example of a response to this has been scaled up to semiproduction plant scale by OCAS in Belgium [33, 34] (see Chapter 11). Attempts are also being made to substitute strongly acidic solutions for common metal processing systems [35].

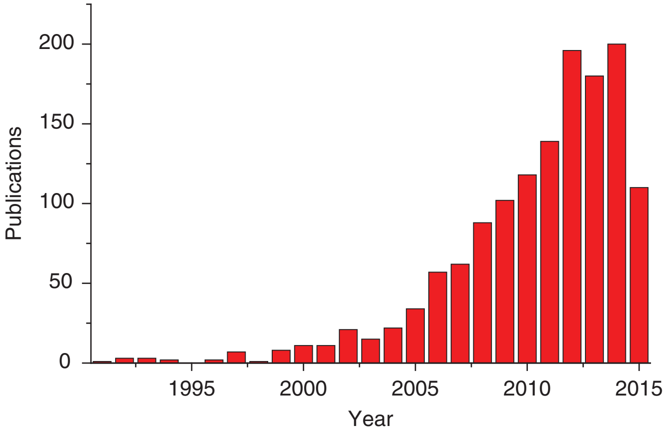

Figure 1.1 Publications on the topic of electrodeposition using ionic liquids, 1991 to mid-2015 (Web of Science).

Direct comparison has recently been carried out between nickel deposition in ionic liquids and the commercial electrolyte. It was shown that similar deposition rates could be obtained despite the differences in viscosity, but improved metal hardness was achieved in the ionic liquid resulting from different deposit morphologies [36].

1.4.2 Water-Sensitive Metals

This is understandably the area that is most interesting as it could enable the deposition of metals that cannot be deposited using aqueous solutions. Initially, aluminum was the main drive, and this is covered in-depth in Chapter 4. This area has been reviewed by El Abedin and Endres [37] and Alemany *et al.* [38]. The wide potential windows of some ionic liquids have been used for the deposition of several other reactive metals including magnesium [39] and group I metals [40, 41]. Other metals, which are difficult to deposit from molecular solvents, have recently been deposited, for example, Ta and Ru using a variety of pyrrolidinium and imidazolium salts [42–44].

A key advantage of using ionic liquids for this task is that redox potentials can change with metal speciation and can thus be adjusted to the requirements of a particular deposition process. This allows metals that would have disparate redox potentials in aqueous solutions to be codeposited in ionic media. Recent additions to this field include the study of Al–Zn [45], Ti–Al [46], Al–Mn [47], and Al–Li [48] alloys.

1.4.3 Deposition on Water-Sensitive Substrates

Several groups have studied the deposition of metals onto water-sensitive substrates, for example, zinc onto magnesium [49] and aluminum on to magnesium alloys [50].

1.4.4 Semiconductor Electrodeposition

The deposition of well-characterized semiconductors is an important technological goal. In a similar manner to that practiced with water-sensitive metals, electroplating systems have been developed for a variety of p-block elements including most of groups III, IV, and V. Of particular note is the ability to deposit silicon, germanium, gallium, and indium [51–53] and their alloys such as Si_xGe_{1-x} [54], Bi–Te, Sb–Te [55], CdTe [56], and CdS [57]. Ternary and quaternary systems, for example, AlInSb [58] and Cu_2ZnSnS_4, have also been produced [59]. The topic of semiconductor deposition is covered in Chapter 6.

1.4.5 Deposition of Nanoarchitectures

In aqueous solutions, metals tend to deposit with a macrocrystalline morphology, whereas in ionic liquids, crystallites for many metals are orders of magnitude smaller. The exact cause of this is not fully understood, but it was shown that there is a definite cation effect [60, 61] suggesting that the double-layer structure affects deposit morphology. Many authors have shown the importance of a specific ionic liquid in controlling the morphology of a metallic deposit [62]. It seems that ionic liquids with bulky cations, particularly those with aromatic moieties, tend to yield smaller architectures compared to those without aromatic moieties. A variety of nanoscale deposits have been produced with the majority aimed at making catalytic surfaces either for synthesis or for sensors [63].

Two- and three-dimensional microstructures such as wires and macropores can be electrodeposited on an electrode surface by using a templating mask. This is not unique to ionic liquids, but it does enable a wider range of metals to be used. Three-dimensional ordered macroporous (3DOM) films can be created by deposition around ordered polymer spheres, and this has been done for Cu [64] and Si [65]. Electrodeposition through nanoporous polycarbonate films has been carried out to produce silver [66] and aluminum [67] nanorods with high aspect ratios ($l/d \sim 80-100$). The deposition of structured architectures is covered in more detail in Chapter 8.

In the longer term, specialist ionic liquids will enable technically complex high-added value products to be introduced, for example, semiconductor coatings, special magnetic alloys, nanoparticle composite coatings with special erosion/corrosion properties, and metal foams for energy-storage activated surfaces for self-sterilization purposes (e.g., through photocatalysis).

Also, metals have significantly different reduction potentials in ionic liquid solutions compared to water. For example, the difference in reduction potential between the Cr and Pt in ionic liquids may be as little as 100 mV, whereas in aqueous solutions, it is in excess of 2 V. One consequence of this characteristic is that alloy coatings may be prepared more readily and that it should be possible to develop many novel alloy coatings. The first comparison between aqueous and ionic liquid redox potentials has now been published [68].

A fundamental advantage of using ionic liquid electrolytes in electroplating is that, since these are nonaqueous solutions, there is negligible hydrogen evolution during electroplating and the coatings possess the much superior mechanical properties of the pure metal. Hence, essentially, crack-free, more corrosion-resistant deposits are possible. This may allow thinner deposits to be used, thus reducing overall material and power consumption still further.

The electrodeposition of metals from ionic liquids is a novel method for the production of nanocrystalline metals and alloys, because the grain size can be adjusted by varying the electrochemical parameters such as overpotential, current density, pulse parameters, bath composition, and temperature. Recently, for the first time, nanocrystalline electrodeposition of Al, Fe, and Al–Mn alloy has been demonstrated.

1.4.6 Health and Safety

The properties of the new electrolyte media could also provide much higher health and safety standards for employees in the workplace, that is, elimination of hazardous vapors, elimination of highly corrosive acidic/alkaline solutions, and substantially reduced use of toxic chemicals. Current aqueous processing systems have a strongly negative impact on the environment (risk of groundwater contamination, soil pollution), which obliges the treatment of wastewater and the dumping of the ultimate waste in landfill. The metal finishing industry in general estimates that at least 15% of turnover is related to the cost of treatment for environmental protection. A significant issue for the metal finishing industry is the introduction of REACH, a European Community Regulation (EC 1907/2006) started in June 2007. It unified a variety of directives and regulations into a single system to protect human health and the environment. The main aims are to handle chemical substance data through supply chains and regulate the use of chemicals of higher concern. The legislation places the burden to manage chemical risks on industry both during manufacture and at the import/export stage. REACH also provides the European administrators with more powers to restrict usage. Similar legislation has been, or is in the process of being, implemented in other countries. Thus, industries using metal finishing processes must search for new techniques to achieve these environmental goals. In addition to the growing costs and negative effects on competitiveness, it is a question of survival in the years to come. The technology developed by this project is generic to most metal plating systems and as such should represent a significant advancement for the environmental sustainability of the metal finishing and electronics manufacturing sectors.

Of value from a health and safety point of view, many ionic liquids have insignificant vapor pressure (thus odorless), some are nontoxic (and even completely biodegradable), and most are highly conductive.

There are, however, numerous risk elements in the development of processes based on these new liquids:

- Coatings must achieve quality standards and a large amount of process development is required.
- A life cycle analysis (LCA) and an environmental impact study have only been carried out for a limited number of systems.
- Information of scale-up and integration design of generic prototype systems has been gathered, but it is proprietary information.
- Some applications are at fundamental research stage with associated higher risk, that is, electroless, semiconductor, anodizing, and nanocomposite coatings.
- Process economics have been determined for a limited number of processes, but this again is proprietary information.
- For improved existing products, customer acceptance is likely to be a significant factor, that is, reluctance to change product specifications.

Some processes are now reaching a scale of development where these issues have been addressed [34]. One has even reached a scale where >1000 A is applied to the working electrode and the electrolyte has been used for >1 year. Most of the information is still proprietary. This does, however, show that many of the issues with ionic liquid scale-up can be overcome. The potential impact is extremely broad and fundamental in nature, because the research will explore a totally innovative approach to metal finishing technology, which has never been exploited previously. The use of this completely different type of solvent/electrolyte system entirely changes the normal behavior of metal finishing processes seen in traditional aqueous electrolytes, and an extensive range of entirely new processes and products can be expected. Information gained to date from pilot studies shows that deposit morphology is fundamentally different from current aqueous deposits.

There are several physical plating parameters that are different in an ionic liquid from those in an aqueous solution.

1.4.7 Temperature

Ionic liquids have wide liquid regions typically in the range from −40 to 250 °C, which allow more thermodynamic control than is possible in aqueous solutions. This may have potential benefits for the development of new alloys. While most studies have been carried out in the range of 25–50 °C, some recent investigations have shown that operating conditions at ~100 °C can lead to significantly different morphologies.

1.4.8 Diluents

Ionic liquids can be diluted with a range of organic and aqueous solvents, and these significantly affect conductivity, viscosity, and metal speciation. Some new data has been obtained, especially with water as a diluent. It has also been found that ionic liquids added to aqueous plating baths can act as brighteners. These effects have been ascribed to double-layer effects and changes in speciation.

1.4.9 Cation and Added Electrolytes

Cationic structure and size will affect the viscosity and conductivity of the liquid and hence will control mass transport of metal ions to the electrode surface. They will also be adsorbed at the electrode surface at the deposition potential; hence, the structure of the double layer is dominated by cations. Some studies have shown that changing the cationic component of the ionic liquid changes the structure from microcrystalline to nanocrystalline (see Chapter 9). While these changes are undeniable, more studies need to be carried out to confirm that it is a double-layer effect. If this is in fact the case, then the potential exists to use the cationic component in the liquid as a built-in brightener. The double layer in ionic liquids is now better understood [69]. Most of the electrode charge is compensated in the first layer of counterions, and this is followed by a series of layers of opposite charges. AFM - atomic force microscopy has been used to determine the structure at the electrified interface, and electrolytes such as LiCl have been shown to disrupt this interfacial structure [70].

1.4.10 Anode Material

In aqueous solutions, the anodic processes are either breakdown of the electrolyte solution (with oxygen evolution at an inert anode being favored) or the use of soluble anodes. The use of soluble anodes is limited by the passivation of many metals in aqueous solutions. In ionic liquids, however, the first option is not viable due to the cost and nature of the anodic breakdown products. New strategies will therefore have to be developed to use soluble anodes where possible or add a sacrificial species that is oxidized to give a benign gaseous product.

1.4.11 Brighteners

Brighteners are added to most aqueous electroplating solutions and work by either complexing the metal ions and decreasing the rate of nucleation or by acting as an interfacial adsorbate blocking nucleation and hindering growth. Aqueous brighteners have not been studied in ionic liquids, and it is doubtful that they will function in the same way as they do in water because of the difference in double-layer structure and mass transport.

A small amount of work has been carried out into brighteners that complex the metal ions in solution (see Chapter 11), but again no systematic studies have been carried out. Brighteners, which rely on electrostatic or hydrophobic interactions, may function in ionic liquids, but their efficacy is likely to be surface- and cation/anion-specific. As with other solutes in ionic liquids, the general rule of “like dissolving like” is applicable, that is, ionic species will generally be soluble as will species capable of interacting with the anion. Aromatic species tend to exhibit poor solubility in ionic liquids consisting of aliphatic cations and vice versa.

1.5 Conclusions

Since the first edition was published, many of the fundamental issues have begun to be addressed. Researchers have focused on the areas where ionic liquids display a clear advantage over aqueous electrolytes, such as controlling architectures and the deposition of semiconductors. Models of the physical properties are now more developed, and the types of systems that form ionic liquids have been expanded. Aspects such as the activity of brighteners and double-layer structures have now been developed. This topic has become a broad church with a less stringent definition of what constitutes an ionic liquid. Ionic liquids are now becoming more mainstream, and their success in other application fields is making their adoption easier. We expect that there will be rather rapid further development in the near future as the technologies become truly practical and the special advantages and outcomes possibly become more widely accepted (Figure 1.2).

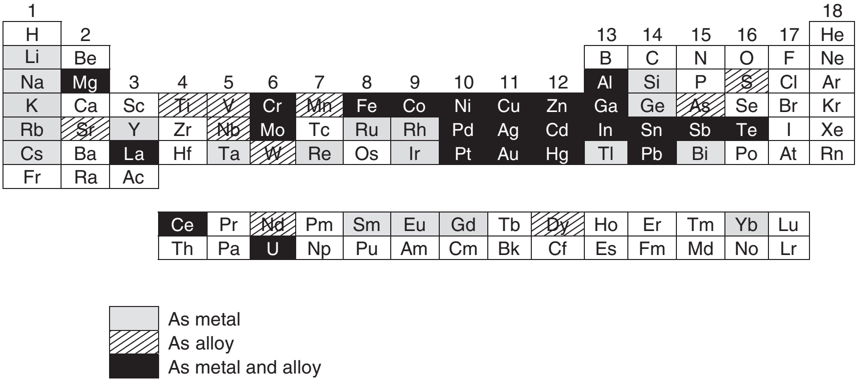

Figure 1.2 Summary of the elements deposited as single metals or alloys.

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