**Institution:** University of Leicester

**Unit of Assessment:** 8 Chemistry

**Title of case study:** Leaner, Greener Material Processing using Ionic Liquids

## 1. Summary of the impact

Ionic liquids (liquid salts) offer a more energy efficient and environmentally sustainable method of coating and processing metals than other more traditional methods. The generic technology developed at Leicester for plating and etching metals significantly decreases the power consumption, uses less hazardous chemicals and produces less aqueous waste. Many of the current acid-based liquids are restricted by legislation. The spin-out company, Scionix Ltd has developed numerous processes for metal processing through collaborative grants with the University of Leicester and the end users. Probably the largest impact has been through the development of a breakthrough technology for the electroplating of chromium removing the use of carcinogenic chromic acid. In April 2013 [text removed for publication] (one of the world's largest steel producers) signed an exclusive license with Scionix Ltd for [text removed for publication] using the ionic liquid technology developed at the University.

## 2. Underpinning research

*Origins*: Leicester has developed a series of ionic liquids based on eutectic mixtures of quaternary ammonium salts with either metal salts or hydrogen bond donors (**Abbott** and **Davies** (1999-present)). The research originated from a consultancy for Johnson Matthey in 1997 on the electrodeposition of aluminium alloys using traditional chloroaluminate based ionic liquids. The original patents covered over $10^6$ liquids and it was immediately clear that the almost limitless formulations had significant commercial application. This led directly to the formation of a University of Leicester spinout company, Scionix Ltd., in 1999. A joint venture model was adopted with a partner who has the capacity to manufacture the liquids on the multi-tonne scale (Whyte Chemicals). Customers range from academic groups through to large scale industry (see below). The term Deep Eutectic Solvents (DESs) was coined to differentiate them from ionic liquids with discrete anions. The advantages of these liquids are that they can be easily prepared in bulk, they are comparable in cost to bulk molecular solvents, and can be prepared from bulk commodity chemicals such as choline chloride with hydrogen bond donors such as glycerol, and urea which have negligible ecotoxicity [1,2]. The unusual solvent properties make them ideal for metal processing applications such as metal deposition, dissolution or recycling. The Leicester Group of **Abbott, Davies, Frisch,** and **Ryder** have published 75 papers on DESs covering topics such as metal deposition and dissolution, mass transport and redox properties. This has been pertinent to all of the metal deposition and dissolution processes developed to date by helping design liquids specific to each application.

*Fundamental Studies:* To be able to design and apply a new class of liquids **Abbott** and **Ryder** developed fundamental new insight into the viscosity, conductivity and mass transport in all types of ionic liquids [3]. It was shown by the Leicester group that the large ion size means that mass transport is limited by the availability of holes for ions to move into. This means that viscosity can be modelled using hole theory and conductivity can be modelled using a Nernst Einstein model because the holes are effectively at infinite dilution. It was shown that classical diffusion does not occur in ionic liquids with ions moving by a series of jumps between suitably sized voids. It was also shown that some liquids form ideal solutions allowing concentration effects of redox potentials to be modelled [4]. This has led to the development of liquids with some of the lowest viscosities and highest conductivities yet reported and these are being applied to the latest generation of liquids for chromium plating.

In addition **Abbott, Ryder** and **Frisch** coined the term *Ionometallurgy* to describe the dissolution and selective recovery of metals using ionic liquids [5]. They produced the first galvanic series in an ionic liquid and showed that in some ionic liquids metal salts form ideal solutions. This has allowed the first standard redox potentials to be determined which were shown to be related to speciation in different ionic liquids. This has helped with the development of a new class of liquids which do not involve quaternary ammonium salts which is now being exploited for aluminium electrodeposition through an EU project.

Since 2009 the group has been engaged in detailed studies of surface morphology and chemistry using a unique combination of electrochemical acoustic resonator as well as X-ray techniques and liquid phase probe microscopy to understand the correlations between macroscopic effects such as surface finish, brightness and appearance with the microscopic environment at the electrochemical interface. This environment encompasses the molecular structure of metal ions in the liquids as well as complex kinetic phenomena such as electrochemical nucleation and growth. Both of these can be affected by addition of molecular ligands that are known colloquially as levellers and brighteners in the metal finishing industry. In 2010 these facilities were augmented by holographic microscopy (giving orders of magnitude faster data acquisition) and in 2012 optical profiling for non-contact characterisation. This has informed the development of novel brighteners for use in electroplating baths [6].

*Developing Impact:* Most of the ionic liquid based metal plating processes were initially developed through the Leicester group who instigated a consortium consisting of 33 partners for the EU-funded IONMET project (EU, FP7 contract No.: 515743) between 2008 and 10. This covered not only the fundamental aspects of deposition mechanism but also developed additives to make electroplate brighter. It was able to produce efficient, environmentally-compatible techniques for depositing thin layers of metals such as copper, nickel, aluminium and silver together with alloys such as Zn/Sn. Other outputs were developed through two further EU grants, 6 TSB grants, a Royal Society Industry Fellowship (Ryder) Rolls-Royce) and a KTP grant all of which involved industrial partners such as Corus, Rolls Royce, Anopol Ltd and CTech.

## 3. References to the research


1) Novel Solvent Properties of Choline Chloride/ Urea Mixtures” A. P. **Abbott**, G. Capper, D. L. **Davies**, R. Rasheed and V. Tambyrajah *Chem. Commun,* 2003, 70-71.

2) “Deep Eutectic Solvents Formed Between Choline Chloride and Carboxylic Acids” A. P. **Abbott**, D. Boothby, G. Capper, D. L. **Davies**, R. Rasheed and V. Tambyrajah *J. Am. Chem. Soc.* 2004, ***126**, 9142* Refs 1 and 2 are the standard citation for what DESs are. There have been in excess of 300 publications in the field of DESs since 2008, all of which built upon the original Leicester publication. (1) and (2) have received over 500 citations.

3) Model for the Conductivity of Ionic Fluids Based on an Infinite Dilution of Holes” A. P. **Abbott**, *Chem. Phys. Chem.* 2005, ***6**,* 2502-2505 Paper that proposed a new model for mass transport in ionic liquids.

4) "Ionic liquids form ideal solutions", A.P. **Abbott**, G. **Frisch**, H. Garrett, and J. Hartley, *Chem Commun*, 2011, 47(43), 11876-11878.

5) “Ionometallurgy: Designer Redox Properties for Metal Processing”, A.P. **Abbott**, G. **Frisch**, S.J. Gurman, A.R. Hillman, J. Hartley, F. Holyoak and K.S. **Ryder**, Chem. Commun., 2011, 47, 10031.

6) Electrodeposition of Metals from Ionic Liquids, F. Endres, A. P. **Abbott**, and D. MacFarlane (Eds.) Wiley VCH 2008 This is the standard book on metal deposition in ionic liquids. A second edition is currently being written.


## 4. Details of the impact

Traditional metal processing techniques involve strong mineral acids and bases. These processes evolve large volumes of aqueous effluent which must be treated before emission and this can be a significant environmental hazard. The processes also have inherently poor power inefficiency due to the electrochemical instability of water. Scionix Ltd was formed as a University spin-out (1999) to commercialise ionic liquid technology as an alternative and currently holds 4 key patents [1]. Scionix Ltd. is now one of the world's major producers and innovators in the field of ionic liquids [2], disseminating technologies and techniques which simultaneously benefit industries such as electronics manufacturing, aerospace engineering, metal finishing and surface coatings. These benefits include reduced energy costs, reduced environmental emissions and reduced user hazard. Each process is underpinned by recycling protocols and economic evaluations. Typically the company produces 1000 to 3000 kg of ionic liquids p.a. which is significant for such a nascent technology. The company has developed several commercial scale processes in collaboration with UoL and the end users. These include chromium plating [text removed for publication] electropolishing (Rolls Royce, Anopol and Northbridge Motorsport) and silver plating (P W Circuits) and each process delivers environmental and efficiency improvements over the aqueous process.

Rolls Royce, PWCircuits and [text removed for publication] were engaged through industry briefing events organised by national/international trade associations (Institute of Material Finishers/ European Institute of Printed Circuit Boards). The technology was showcased through the Ionic Liquid Demonstrator which is an industry facing showcase based at UoL containing six pilot plants each using > 50 kg of ionic liquids [3]. Since its opening in June 2009 more than 25 businesses have used the Ionic Liquids Demonstrator Unit including Dow, MacDermid, HydroQuebec and Silberline. All have trialled new processing techniques with their products including printed circuit boards, batteries and colloidal dispersions. Prototype materials, devices and processes have been produced. A European consortium POLYZION used the facilities and was successful in developing rechargeable zinc batteries with a specific current density of 1000 W $kg^{-1}$**,** excellent cycleability (>1000 cycles) and a large open circuit potential (~1.9V) [4].

<u>Chromium Plating</u>: Chromium is the industry standard for hard metal coatings and is currently solely carried out using highly carcinogenic chromic acid. The establishment of the first Cr(III) route to hard chrome is a significant development. The process developed with [text removed for publication] is coating steel tubes with hard chromium using a novel rotating electrode arrangement to decrease the volume of ionic liquid needed and further improve the safety of the plating process. The exclusive license signed between [text removed for publication] and Scionix sees private sector investment of >2M Euro. The original work in this area led to Abbott being awarded the Industry and Green Medals by the Royal Society of Chemistry [5, 6].

<u>Electropolishing</u>: Rolls-Royce Aerospace was assisted by Ryder working at their Derby site (originally under the auspices of the Royal Society Industry Fellowship scheme (2010-2012) and then under a HEIF funded Fellowship). He developed a new approach to superalloy processing using electrochemical etching. To deliver the impact it was necessary to understand the role of ionic liquids in electrolytic removal of oxide films and dissolution of metals from Ni super alloy castings. The mechanism of scale formation was elucidated in collaboration with Rolls Royce. The surface chemistries, morphologies and mathematical modelling of the cooling process were also studied in high temperature melts.

The scale removal is greatly simplified using ionic liquids and is not possible from conventional aqueous acid electrolytes. Typically these parts are deployed in the Trent series of engines that power Boeing and Airbus passenger aircraft. The project succeeded in streamlining production of the blade components by scale removal (using ionic liquids) prior to the expensive heat-treatment and annealing processes. This cannot currently be achieved because alternative techniques for scale removal, before heat-treatment, cause solid state recrystallisation in the alloys producing grain boundaries that lead to stress fractures. Rolls Royce Aerospace has now embarked on a technology readiness pathway leading to the use of Leicester's ionic liquids technology. The company is now collaborating with Ryder to solve specific production problems associated with surface scale in engine production parts, with a view to fully implementing ionic liquids technology in its production processes.

<u>Silver Plating</u>: Since October 2009, PW Circuits of Leicester has operated a full coating process

developed by the Leicester Ionic Liquids Group based on an 8 tank line using c.a. 1 tonne of ionic liquid. Simple immersion of a copper coated printed circuit board in a mixture of ethylene glycol and choline chloride with silver chloride produces boards which not only meet all industry requirements but actually improve over existing techniques in functions such as solderability. The liquid developed significantly reduced the cost of immersion coating as it used a less expensive silver salt than the current industry standard. The quality of the product in terms of its solderability and resistance to tarnishing was independently verified by the European Institute of Printed Circuits [7].

The processes commercialised to date and their key impacts are listed below and many of the impacts have been independently verified. [8]

| ***Process (Users)*** | ***Current Technology Issues*** | ***Impact of New Technology*** |
|---|---|---|
| Chromium plating [text removed for publication] | chromic acid (carcinogenic) | Three-fold decrease in power consumption<br>Uses $CrCl_3$ |
| Electropolishing (*Rolls Royce, Anopol, Northbridge Motorsport*) | $H_2SO_4$, $H_3PO_4$, HF, chromic acid | Safe in contact with skin<br>Four-fold decrease in power consumption<br>Metal recoverable<br>Greatly decreased failure rate (superalloys) |
| Silver Plating (*PWCircuits*) | Acid based – leads to board failure through track etching<br>Silver cyanide complexes | Reduced cost (uses silver nitrate)<br>Reduced light sensitivity<br>Non-acidic – no track etching<br>Improved solderability |

**5. Sources to corroborate the impact**

1) International Patents WO2000 056700; WO 2001 022670; WO 2001 022638; WO 2007 003956
2) www.scionix.co.uk
2) http://www.ionmet.eu/fileadmin/ionmet/Dissemination/IONMET_brochure_200711.pdf
3) http://www.le.ac.uk/ebulletin-archive/ebulletin/news/press-releases/2000-2009/2009/06/nparticle.2009-06-01.html
4) http://www.polyzion.eu/
5) June 2007 Royal Society of Chemistry - Green Chemistry Medal to Prof Abbott
6) June 2008 Royal Society of Chemistry - Industrial Chemistry Lectureship to Prof Abbott
7) http://pcb007.com/pages/columns.cgi?clmid=26&artid=54911&_pf_=1 Review of the silver plating process by the silver plating process and the dissemination event by the EIPC (Printed circuit board Trade Body)
8) http://www.pfonline.com/articles/are-ionic-liquids-the-future-of-the-surface-treatment