Press Information

Dr. Andrew Abbott – Senior Lecturer
Chemistry Department
University of Leicester, LE1 7RH
Tel: 0116 252 2087
Fax: 0116 252 3789
www.le.ac.uk/chemistry

Dr Khalid Shukri – Business Manager
Scionix Limited
298 Regents Park Rd, London N3 2UA
020 8371 3905
020 8371 3958
www.scionix.co.uk

- Ionic liquids are non-volatile and hence do not pollute the atmosphere. They can replace strong mineral acids and volatile organic solvents for many applications.

- Scionix is a joint venture company formed between the University of Leicester and Genacys Ltd. to develop ionic liquids for industrial applications.

- Current projects include chrome plating, electropolishing, catalyst reprocessing and organic reactions.

- University of Leicester is currently collaborating with the aerospace industry to develop a hard chromium deposition process, replacing chromic acid. The improvements of are economic (improves process efficiency) social (it is far less hazardous to work with) and environmental (less polluting).

- University of Leicester is a world-leader in Green Technology. The ionic liquids research is carried out by a multidisciplinary research team, which combines a wide range of chemical expertise with the business experience of Genacys.

Background to Industrial Applications

Chromium Electroplating Using Ionic Liquids

The corrosion of metals in the environment costs most developed countries between 3 and 5% of their GNP every year. For the UK this amounts to approximately £40bn p.a. A key method of reducing corrosion is the electrodeposition of a metallic coating that passivates on contact with the environment and prevents the oxidising agent reaching the substrate. This kind of surface engineering occupies a fundamental position within global engineering industries, with applications in a wide range of industrial sectors. In 1990, the electroplating market in the UK was valued at £700m, with a projection in excess of £1.3bn by 2005. Hard chrome plating has been regarded with unparalleled status in terms of wear resistance and corrosion resistance, while providing a hard, tough, low friction surface. Consequently, the process plays a critical role in, for example, civil and military aerospace, industrial hydraulic applications, the automotive industry, and the maritime and naval industries.

The major disadvantage of the current process of chrome plating is that it requires the use of chromic acid-based electrolytes comprising hexavalent chromium – Cr(VI). The toxicity and carcinogeneity associated with Cr(VI) has resulted in wide-ranging environmental legislation in the USA and Europe to reduce its use. For example, the EU End-of-Life Vehicles (ELV) Directive aims to ban the use of Cr(VI) in the manufacture of vehicles from July 2003, although limits of 2g of metallic chromium per car may be permitted for the foreseeable future. Other disadvantages of the existing technology are economic, such as the low current efficiency of the reduction of Cr(VI) in acid media. Furthermore, the difference in overpotential between chromium and hydrogen reduction results in the evolution of hydrogen gas, which can lead to embrittlement in the substrate, thus reducing quality and yield.

We have developed a series of ionic liquids containing a variety of metals that can be used for electrodeposition. Our chromium deposition processes use Cr(III) salts, which are significantly less toxic than the carcinogenic Cr(VI) species. In addition, our processes operate with >90% current efficiency. This reduced power consumption not only reduces the cost but also greatly reduces the overall environmental impact of the chromium deposition process, making our ionic liquid technology a more environmentally benign form of plating. Moreover, since these are not aqueous solutions, there is negligible hydrogen evolution, hence essentially crack free, highly corrosion resistant deposits are possible. This may also allow thinner deposits thus reducing overall material and power consumption even further.

Furthermore, as our plating baths do not produce any toxic chromic acid vapours, the working conditions for operators are also dramatically improved. Further benefits include; required effluent treatment is minimised and air pollution control measures are also made redundant. Our initial results indicate that the low cost of the ionic liquids developed at the University of Leicester coupled with the considerable increase in electrical efficiency and superior surface finish of the deposited chromium should provide a viable industrial alternative.

The project, currently funded by the sustainable technologies initiative (STI) from the DTI and EPSRC, addresses the replacement of chromic acid for chromium electroplating by a new sustainable technology based upon Cr(III) containing ionic liquids. The project involves close co-operation between; (i) the University of Leicester which is developing the new methodologies, (ii) Poeton Industries Limited which will develop and test the technologies on a pilot industrial scale (baths up to 1000 litres), (iii) Smiths Aerospace Actuation Systems-Cheltenham which will apply and validate these techniques on high-tech industrial examples and (iv) Whyte Chemicals Limited, which will formulate the novel ionic liquids and supply them to the end users. The whole project is managed by Scionix Ltd, which is a joint venture company between the University of Leicester and Genacys Limited.

It is anticipated that the development of ionic liquid-based chromium plating processes will have a significant impact on industrial sustainability for hard chromium plating. Another important part of the project is the life cycle assessment for the reuse of the ionic liquids. Formulation of the ionic liquid does not require organic solvent, high pressure, high temperature or extended reflux conditions. Vapour pressure characteristics mean that losses to the atmosphere are negligible, and the resulting potential for reuse and recycling of ionic liquid materials is high. The materials employed are far less toxic than those currently used, and energy requirements for electroplating processes will be significantly reduced.

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 a major industrial process.

Environmentally-friendly electropolishing

Electropolishing of stainless steel is an effective way of increasing corrosion resistance. Electropolished components also decrease wear and increase lubricity in engines, decreasing a major cause of engine failure. And they offer several other functional benefits. Current electropolishing technology uses harsh aqueous mineral acids such as sulphuric and phosphoric acids. These are naturally corrosive, harmful to work with and must be neutralised before disposal. Acid-based electropolishing is an inherently inefficient process: only 10–20% of the energy supplied is utilised for electropolishing. The scale of this activity worldwide represents a significant environmental concern.

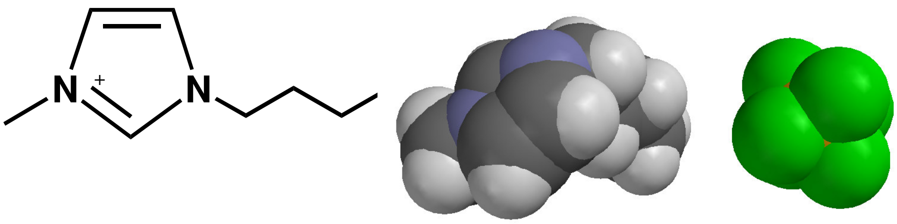
A group at the University of Leicester, through its joint venture company Scionix, is developing alternative electropolishing electrolytes using novel eutectic mixtures (types of ionic liquids). The ionic liquids are based on the biodegradable pro-vitamin choline chloride, a bulk commodity chemical produced on a Mtonne scale. The new polishing baths are also non-toxic, non-flammable and non-corrosive, showing significant social benefits over current technology. The ionic liquids allow electropolishing with high current efficiency, improved surface finish and improved corrosion resistance.

The group is currently developing a commercially viable medium-to-large-scale electropolishing plant process using these novel electrolytes in collaboration with UK companies Anopol and Whyte Chemical. This development project will optimise electropolishing parameters and develop a protocol for commercial electropolishing surface treatment using these electrolytes. They are also evaluating the long-term stability, recyclability and reprocessing of the ionic liquids. A medium-scale plant to be constructed, based initially on a 500-litre electrochemical cell, will be the largest industrial application of this type of solvent.

The new process reduces significantly the total volume of effluent and its toxicity. There are no highly corrosive compounds in the ionic liquid formulation. When the metal, and it is usually iron, is electrochemically oxidised it complexes with the hydrogen bond donor and the insoluble complex precipitates to the base of the cell. The cell liquid can be filtered periodically and the metal complex collected. This allows for suitable recycling of both the ionic liquid and the metal, preventing environmental emissions.

The Background to Ionic Liquids

Ionic compounds tend to be solid at ambient temperatures. This is because the interaction between ions are high and ions can easily organise themselves into stable lattices. The melting point of an ionic compound is related to the size and charge of the ions; the larger the ions and the smaller the charge the less energy is required to break the ionic bonds. At the extreme, organic cations with quaternary ammonium groups (R_4N^+) have low lattice energies and large anions such as PF_6^- and BF_4^- can also be made. The symmetry of the ions is also important; non-symmetrical ions are more difficult to fit into a lattice and hence the lattice energy and melting point will be lower. A large amount of work has been carried out on compounds known as imidazomium salts e.g. butyl-methyl imidazolium hexafluorophosphate (BMIM PF_6). This compound is liquid at room temperature (in fact it freezes at –40°C).

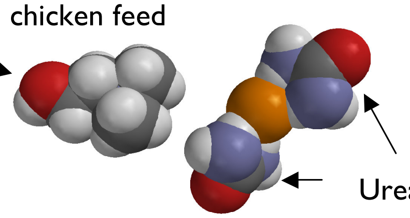


PF_6^-

Conventional liquids consist of small neutral molecules that have only weak intermolecular forces between them. As a result it is relatively easy for individual molecules to escape into the gas phase *i.e.* these liquids are volatile. This loss of volatile organic compounds (VOCs) used as solvents is the larges source of toxic compounds in the atmosphere. Ionic liquids are of interest because it does not evaporate and hence does not pollute the atmosphere. They are also non-flammable which makes them safer to work with as solvents. They are, however, quite difficult to make and is therefore extremely expensive. The toxicity of imidazolium salts has also not yet been ascertained.

Another alternative approach is to take a simple organic halide salt and complex the anion with something that will form a hydrogen bond. The complexing agent will decrease the interaction between the anion and the cation and decrease the freezing point of the mixture. An example of this is choline (2-hydroxyethyl-trimethylammonium) chloride (this is vitamin B4 and is produced on the Mtonne p.a. scale as an additive for chicken feed) mixed with urea ($NH_2C{=}ONH_2$) which is a common fertiliser

Choline chloride – A vitamin in chicken feed



Urea – A common fertiliser

This is not only cheap and easy to make, but it is non-toxic and even biodegradable. This approach is also applicable to a wide variety of salts and an even wider range of hydrogen bond donors.

This is just part of the work carried out at the University of Leicester into environmentally compatible solvents to find out more look at the Green Chemistry web site

www.le.ac.uk/chemistry/lgcg