Ionic Liquids Today

Issue 3-05, Tuesday, 11th October, 2005.

Content of the second issue:

I. Editorial

By Thomas Schubert.

Aleae jactae sunt: *Grubbs, Schrock and Chauvin* were awarded with the nobel prize for chemistry 2005 for their development of the metathesis. After 2001 it was again a topic from the versatile field of catalysis, which received this most important price in chemistry.
On this occasion, we took of course a closer look at our ionic liquids database and found that indeed there exist a couple of papers, which describe the performance of ring-clothing metathesis (RCM) catalysts in ionic liquids. E.g. *Buijsman et al.* (the Dutch relative of our Scientific Director Mr. Bösmann?) reported 1-butyl-3-methyl-imidazolium hexafluorophosphate to be an efficient and recyclable medium for RCM, leading with a broad substrate tolerance to high conversions (*Org. Lett.* **2001**, *3*, 3785-3787.). Though we believe that there are some better ionic liquids, this publication stresses again, how versatile ionic liquids can be used.

With their program "Aurora" the ESA plans to send manned space ships to the moon and as well to mars until 2030. Inspired from these news we asked ourselves, if ionic liquids may help in this context. Many points of contact are given: batteries, super-capacitors and fuel-cells using ionic liquids as high-tech electrolytes are already in focus of research for a couple of years. Coatings with materials, e.g. metals such as Aluminium, Magnesium, Titanium or Tantalum, that are impossible to be deposited on other materials from aqueous media, are already or may be possible within the next years. And what about ionic liquids and nano-technology? Every week we find new publications about quantum-dots, new nano-materials, nano-tubes with interesting behaviour in ionic liquids and many more. And ionic liquids seem to be an ideal solvent for experiments under zero gravity, since they have no vapour pressure

(so no condensates will be found in the space-ship), they are non-flammable and the may be recycled. Therefore our answer is: We believe yes!

We encourage the engineers from ESA, NASA, India and China to define their problems and to check which interesting set of physical and/or chemical properties of an ionic liquid could improve a technology. Furthermore, we access our customers from industry and academia to think about the question *how* ionic liquids may help. Though there is no direct economical advantage from the several national space-programs, the new materials, energy-solutions and many other new technologies will find an entry into our daily life on planet earth, making it (with a close and serious look on sustainability) hopefully a bit easier, safer and cleaner.

We invite you to discuss this topic at our forum at www.iolitec.de!

This issue focuses on electrodeposition using ionic liquids. We try to present you some interesting facts, publications and materials about this "red hot" application of ionic liquids.

II. Bösmann says: "Hot stuff!"

By Andreas Bösmann.

Additive free electrodeposition of nanocrystalline aluminium in a water and air stable ionic liquid.

S. Zein El Abedin, E.M. Moustafa, R. Hempelmann, H. Natter and F. Endres

Electrochemistry Communications, In Press, Corrected Proof, Available online 6 September 2005.

Abstract:
This paper shows for the first time that nanocristalline aluminium can be deposited from a water and air stable ionic liquid, 1-butyl-1-methyl-pyrrolidinium-bis(trifluoromethanesulfonyl)imide. Without any additives, a shiny nanocristalline surface was obtained with an average grain size of 32 nm.

It has been known for a long time that most metals can be electrodeposited from ionic liquids. One disadvantage of the "classical" systems is the use of hygroscopic chlorometallate ionic liquids. The precursors for those ionic liquids are very hard to

dry, the chlorometallates are very sensitive to moisture and require an inert atmosphere to work with them.

This work uses 1-butyl-1-methyl-pyrrolidiniumbis(trifluoromethanesulfonyl)imide (BMPyrr-NTf_2), a hydrophobic and electrochemically stable ionic liquid as a solvent for aluminiumchloride. Since this ionic liquid has a very low viscosity and is thermally exceptionally stable, it can easily be dried under high vacuum at 100°C. Water contents of below 1 ppm can be reached very easily, making BMPyrr-NTf_2 an ideal ionic liquid for electrochemistry.
BMPyrr-NTf_2 dissolves up to 1.5mol/L $AlCl_3$ as a clear solution. Further addition of $AlCl_3$ leads to a biphasic mixture, which was described by *Wasserscheid et al.* (*Chemical Communications*, **2004**, 1552– 553). *Endres et al.* found that only the upper phase is active for electrodeposition of Al at room temperature. When the biphasic mixture is heated over ca. 80°C, it becomes monophasic and active for electrodeposition.

The deposits of Al that where obtained are dense, shining and well adherent to the substrate. A thickness of 10µm was electrodeposited at room temperature in 2h. Electrodeposition at 100°C appears to give a higher quality with finer crystallites.

So what we now have at hand is a process for the electrodeposition of aluminium that uses only substances that are non-flammable, easy to handle and easy to purify. Nonetheless, this process has one serious drawback: ionic liquids with the NTf_2-anion are comparable expensive. So one real important obstacle to overcome before commercialisation of this or a similar process is clearly the efficient recycling of the used ionic liquid or to find other, cheaper ionic liquids (we currently work on cheaper solutions!).

III. Electrodeposition and electroplating at IOLITEC

By Thomas Schubert.

As our name Ionic Liquids Technologies might imply, IOLITEC's overall concept is to combine ionic liquids with interesting and of course economically reasonable applications. Electrodeposition, electroplating and electropolishing are among the applications, which are very close to be realised on an industrial scale. If we take e.g. a closer look on the electrodeposition of aluminium on iron surfaces, we easily identify a couple of publications, which describe successful procedures using ionic liquids. But if we talk with specialists and users from the electroplating industry about feasibility, they express a lot of criticism about the described methods and the used materials. So there might be still a way to go.

Interesting coatings are e.g. Aluminium, Magnesium (and their alloys!), Titanium or Tantalum. All these metals can not be deposited from aqueous media, so ionic liquids with their large electrochemical window (which is equivalent to electrochemical stability) seem to be ideal solvents. Nevertheless, this is of course just the half truth: You have to combine the right ionic liquid with the right (also in terms of availability) metal-precursor.

At IOLITEC's well equipped electrochemical lab, which core is the Metrohm PGSTAT 30 Autolab, we are in the position to find out with a rational, systemized procedure which combination of a metal-salt corresponds well with a selected ionic liquid, to establish a method for the deposition of a new material. Furthermore, we are proud to employ Mr. Dipl.-Ing. Berthold Seßler, who is known as a leading specialist on this versatile field.

We'd like to encourage the academic work-groups to discuss with us about scope and limitations from a theoretical point of view and the colleagues from industry, to define interesting applications., we're sure to find a solution!

IV. Community

By Thomas Schubert (TS) and Andreas Bösmann (AB).

EuroMat 2005, Prag.

The "European Congress on Advanced Materials and Processes" EuroMat 2005 took place 5-8. September at the Technical University of Prague.
Over 1700 participants from more than 55 countries visited 16 parallel sessions covering topics from "Biomedical materials" to "Materials for Fusion Applications". In this very diverse range of topics, this was the first time Ionic Liquids where introduced. The symposium "Ionic Liquids: New Solvents for Chemical and Electrochemical Processing", organized by Prof. Endres attracted up to 150 visitors at a time, which is a bit more than its fair share among the other symposia.
AB

Surfacts 2005, Karlsruhe.

At the Surfacts 2005 IOLITEC presented potential applications for ionic liquids in surface and coating technologies, such as metal coating, liquid antistatic-additives (see also the "Wandres-process") and nano-technologies.
At the exhibition predominately exhibitors from metal-coating industry and cleaning technology presented their latest developments. Nano-technology was found more or less at the outlook of most companies and as topic at the forum.

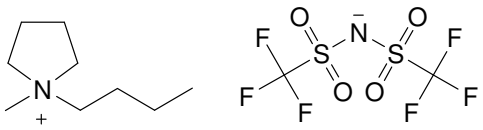
V. Interesting New Materials

By Tom Beyersdorff.

Ionic Liquids have attracted intensive interest as alternatives for classic electrolytes in electrochemical deposition over the past years. Several metals have been deposited from chlorometallate-based ionic liquids. These are corrosive and decompose in the presence of water. An alternative is a combination of a metal-salt and a stable Ionic Liquid such as BMIM BF_4 or BMIM PF_6. It has to be stressed that these Ionic Liquids are only thermally stable in the absence of water. This leads to complications during the drying process since these liquids can not be heated from the beginning.

With this issue of Ionic Liquids Today we would like present three thermally and electrochemically stable Ionic Liquids, which are promising alternatives for electrochemical applications as Prof. Endres has shown for the electrodecomposition of Aluminum from BMPyrr BTA (see also: "Bösmann says: ´Hot Stuff´").

1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide: BMPyrr BTA



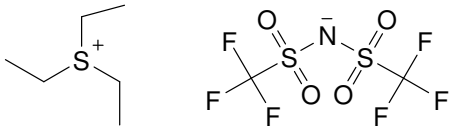
Endres et al. used this Ionic Liquid as solvent for the electrodeposition of aluminum (see also "Hot Stuff"). The high thermal (>180°C) and electrochemical stability (ECW/GC: 5.5 V) and as well the hydrophobicity of this material, which guarantees comparable low concentrations of water during electrochemical processes, makes it an ideal solvent for electrochemical applications.

Our Special offer:*

BMPyrr BTA (99%):	**IL-035-50 g**	**90,00 €**
	IL-035-100 g	**170,00 €**
	IL-035-250 g	**378,00 €**
	IL-035-500 g	**650,00 €**

BMPyrr BTA (99+%):	**IL-035+50 g**	**99,00 €**
	IL-035+100 g	**180,00 €**
	IL-035+250 g	**425,00 €**
	IL-035+500 g	**820,00 €**

Triethylsulfonium bis(trifluoromethylsulfonyl)imide: SEt_3 BTA

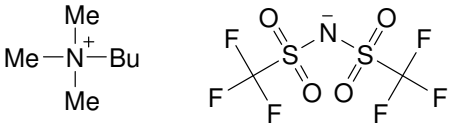


A conductivity of 7.1 mS/cm and an electrochemical window of 4.7 V (GC) make this Ionic Liquid an interesting alternative for some electrochemical applications. In addition this material is extremly hydrophobic and therefore very easy to dry.

Our Special offer:*

SEt_3 BTA (99%):	**IL-030-50 g**	**90,00 €**
	IL-030-100 g	**170,00 €**
	IL-030-250 g	**390,00 €**
	IL-030-500 g	**645,00 €**
SEt_3 BTA (99+%):	**IL-030+50 g**	**99,00 €**
	IL-030+100 g	**190,00 €**
	IL-030+250 g	**405,00 €**
	IL-030+500 g	**765,00 €**

N-Butyl-*N*-trimethyl-ammonium bis(trifluoromethylsulfonyl)imide: N_{1114} BTA

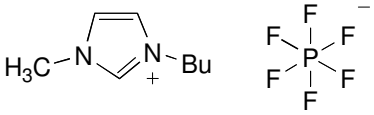


This material has many advantages compared to the well known higher homologue *N*-Methyl-*N*-trioctylammonium NTf_2, a much lower viscosity and a significant higher conductivity make it a real alternative in electrochemical applications.

Our Special offer:*

N_{1114} BTA (99%):	**IL-032-50 g**	**99,00 €**
	IL-032-100 g	**180,00 €**
	IL-032-250 g	**420,00 €**
	IL-032-500 g	**810,00 €**

1-Butyl-3-methyl-imidazolium hexafluorophosphate: BMIM PF_6

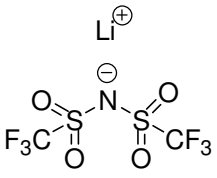


As our tribute to this year's nobel prize winners, we offer the most cited ionic liquid in this context for a special promotion price.

Our Special offer:*

BMIM PF_6 (99%):	**IL-011-50 g**	**65,00 €**
	IL-011-100 g	**105,00 €**
	IL-011-250 g	**240,00 €**
	IL-011-500 g	**430,00 €**

Lithium bis(trifluoromethylsulfonyl)imide: Li BTA

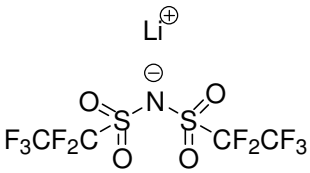


Li BTA is a widely used Li-source for batteries as well as a BTA-source for Ionic liquids, which are characterized in many cases by a high thermal and electrochemical stability in combination with a relatively high conductivity.

My special offer*:

Li BETI:	**KI-001-100 g**	**150,00 €**
	KI-001-250 g	**250,00 €**
	KI-001-500 g	**400,00 €**
	KI-001-1 kg	**750,00 €**

Lithium bis(pentafluoroethylsulfonyl)imide: Li BETI



This highly fluorinated lithium salt can be used as electrolyte in Li-batteries e.g. or as a precursor for highly hydrophobic and electrochemically stable Ionic Liquids.

My special offer*:

Li BETI:	**KI-016-25 g**	**125,00 €**
	KI-016-50 g	**200,00 €**
	KI-016-100 g	**380,00 €**
	KI-016-250 g	**900,00 €**

* All offers are valid until November 30th,2005.

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