Ionic Liquids Today, 02-11 Monday, September 19th, 2011

Ionic Liquids Today www.iolitec.com

Issue 2-11, Monday, 19th September, 2011.



1 metric ton reactor at Heilbronn

Rare earth metals inside magnets.

- >>> Availability of Ionic Liquids
- >>> Rare Earth Recycling
- >>> Electrochemical Windows
- >>> Ultrapure and Low Viscous Ionic Liquids

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Ionic Liquids Today, 02-11 Monday, September 19th, 2011

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1 Editorial

The 4th conference on ionic liquids (COIL-4) was held in June at Washington, Crystal City, USA. Since I am involved in ionic liquids research and of course in their commercialization for 10 years now, the conferences of the COIL series acted for me (and I'm sure for many others) somehow as a benchmark for the interest of scientists, developers etc. in ionic liquids research. Though I don't know the concrete number of participants it seemed to me that there was no increase in the number of participants compared to COIL-3 at Cairns/Australia. Does it mean that ionic liquids are not as hot as they were a few years ago? Has the COIL format lost maybe a bit of attractiveness?

My own impression, which was confirmed by many other friends, was that from the scientific point of view the contributions were excellent. Anyway, I'd just liked to share my very personnel opinion with you, and I'm sure there are many other voices saying something completely different! What's your opinion?

I invite you to join our group **Ionic Liquids** at **Facebook** and discuss with us and others how conferences about ionic liquids, and in particular COIL-5 in 2 years, could or should look like in the future!

For me as an ionic liquid enthusiast (do I have a choice?) and CEO of a company that works in the field of ionic liquids, it is my duty to tell you that I see a strong increasing interest in ionic liquids and their applications, since many ideas turned into applications and will accelerate the development and importance of this field.

Best regards,

Moras Shal

Thomas J. S. Schubert, CEO & Founder, IOLITEC.

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2 Critical Essay: Availability of Ionic Liquids

By Thomas J. S. Schubert.

Over the past ten years the number of publications about ionic liquids exploded. Meanwhile the mark of 15'000 publications was scratched, but critical voices may ask "Where do I find ionic liquids in applications?" The answer to this question is not easy, because of its complexity.

Some Ionic Liquids Applications are already realized!

First of all: A number of applications are already realized! Sensor electrolytes are on the market now for eight years, introduced by the Swiss company Novasina, or additives based on quaternary ammonium salts, to avoid electrostatic charging, are on the market since 2004, or the liquid pistons (developed by Linde), where ionic liquids are used as functional fluids for the compression of gases, just to name a few.

A number of applications are developed in particular in the field of chemical processes, which were developed in narrow co-operations between companies, often just in bilateral projects. The results are enhanced processes leading internally to advantages in the production of other chemicals. It's also quite obvious that this information is disclosed and will not reach the public at conferences or fairs.

But an interesting, striking indicator is also the number of filed patents, which is far above the mark of 1'000!

Some Developments need their Time

Another important aspect is that there's a difference in time between invention and innovation. For me, as a scientist (who turned into a salesman...), it was an experience to learn that sometimes an obvious technical advantage does not necessarily result in a blockbuster application. The time that is needed for convincing people who make the decisions is often underestimated, since they are often not scientists or engineers.

Furthermore, the innovation cycles in major industries have to be considered. This is for example of great importance for the automotive industry. E.g. a developer from a

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global operating car producer said to me that if he just had today a fuel cell that is as efficient as combustion engine, it would take at least 7-10 years to introduce it into the market. By the way: In this context it was not considered, that there is no network of corresponding fuel stations (is the same true for e-mobility?).

And also a comparison to other technologies may be helpful: If we see the amazing development of liquid crystals, resulting today in billions of flat screen TVs, than we should know that it took more than 15 years of research until all problems were solved. I'm sure that during that period also less visionary critics asked "is it worth to put more money into this technology?"

The Prices: A Question of Scale

Finally, another important point that sometimes is not considered in a sufficient way is that at a certain point, you have to convince somebody that not only technical advantages are speaking for a certain material, but also a *value* is added. And the currency of value in the world of business is money. This means that by using an ionic liquid a customer is able to save money, e.g. by making a process more efficient, or he has to add an advantage to his product that somebody is willing to pay for.

This leads to the challenge that ionic liquids manufacturers have to have a close look on the complete value-added chain, to learn if advantages of ionic liquids are existing and, if yes, *where* they do.

As you can imagine, if I am writing an article about this topic, we learned already from many technologies where the benefits and where the drawbacks of ionic liquids are. In this context, over the past years the most critical point was the *price of ionic liquids*. And here comes the good message: If compared to the level of 2003, the price for ionic liquids used in industrial applications will decrease by significant factors and in some cases by magnitudes, if we go to ton's scale. This is true for a number of calculations we already made. Surprise, surprise, the economy of scale works also for ionic liquids!

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This may be common knowledge, but during a colloquium in Germany a metal plating specialist calculated the costs for a screw to be more than 100 times more expensive, when coated with aluminum by using an ionic liquid as electrolyte. To calculate this, he took the catalogue price from a lab-supplier for 100 g! Peter Wasserscheid remarked during the follow-up discussion, "if one buys sea-sand from a common lab-scale supplier (used for fixing the bed of a chromatography column), the price is $25 \in \text{per 100 g.}$ "

In summa, if ionic liquids are produced in larger batches or by novel techniques such as micro-reaction technologies, prices will drop significantly, since the working hours for the production of 10, 100 or 1'000 kg are nearly the same. As a consequence, the percentage for raw materials of the overall costs increases. If an ionic liquid manufacturer is able to order larger volumes of raw materials, the prices for them obviously also drop.

At our company we are already producing ionic liquids on a ton's scale, some of them by using batch techniques, some of them by using micro-reaction technology. Thus, we are prepared to deliver ionic liquids that fit best to your specific needs at fair prices!



Fig. 1. Left: Micro-reaction-system; right: 1 mt batch reactor at the Salzstraße Heilbronn, Germany.

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3 News from IOLITEC Inc.

By Tom F. Beyersdorff.

In April 2010 IOLITEC started its operations from the company's subsidiary in Tuscaloosa/AL with the import of ionic liquids from Germany and their distribution to customers in the USA, Canada and Mexico. After the successful launch of our US ionic liquids business and the processing of several hundred orders, IOLITEC Inc. will now make the next step and will start a new business unit in order to supply nanomaterials to customers in the USA, Canada and Mexico.

With the launch of the Nanomaterials division a selected portfolio of nanomaterials will be available on a catalog basis. A selection of fullerenes and carbon nanotubes is already available but more products (nano metals, metal oxides/carbides/nitrides) will be added in the near future. In addition, IOLITEC will offer the development of customized dispersions of nanoparticles as well as the manufacturing of dispersions from the gram to the multi kilogram and ton scale.

In order to provide a quotation for the production of a dispersion we need information on the nanomaterial (chemical composition, size, size distribution), the solvent matrix of the dispersion and the concentration of the nanoparticles in the dispersion. We will set up a matrix of experiments and will also determine the stability of the dispersion and the particle size in the dispersion using photon crosscorrelated spectroscopy.

We encourage all customers in North America to contact us with their inquiries for custom manufactured dispersions. With our knowledge in ionic liquids and nanomaterials we are the right partner for you and can offer fast and affordable solutions for your dispersion problems.

Please direct all inquiries to Dr. Tom Beyersdorff: Email: <u>Beyersdorff@iolitec.com</u> Phone: 1-205-348-2831

www.iolitec-usa.com

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4 Physico-chemical Properties of Ionic Liquids – Part II

By Maria Taige and Thomas J.S. Schubert.

4.1 Introduction

In our last issue of Ionic Liquids Today we presented in "Part 1" already viscosities and conductivities of selected ionic liquids from our product portfolio. In part II we now want to focus on the electrochemical stability of ionic liquids, which is another important property for many applications, like electrolytes for plating,¹ for lithium ion batteries², for electrochemical double layer capacitors,³ or for dye sensitized solar cells⁴.

All measurements were made by using an Autolab from Metrohm with platinum as working electrode, glassy carbon as counter electrode and a silver/silver chloride reference electrode.

4.2 Discussion of ECWs

In general the anion of an ionic liquid has a stronger influence on the electrochemical stability than the cation. This is shown in Figure 1 and in particular in Figure 2 on the example of ionic liquids with 1-ethyl-3-methylimidazolium as cation.



Figure 1: Influence of the anion on the electrochemical window of ionic liquids with 1-ethyl-3-methylimidazolium cation.

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Ionic liquids with bis(trifluoromethylsulfonyl)imide anion and with tetrafluoroborate anion are in this comparison the electrochemical most stable ionic liquids. 1-Ethyl-3methylimidazolium tetrafluoroborate (EMIM BF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide (EMIM BTA) have both an electrochemical window of 4.7 V (Figure 1). EMIM BTA has a slightly higher anodic limit while the cathodic limit of EMIM BF₄ is slightly higher than that of EMIM BTA, which is somehow interesting. By choosing the best ionic liquid for an electrochemical application, one should keep in mind that the BF₄ anion hydrolyzes in the presence of water. Therefore, EMIM BF₄ should not be used for applications with water or when the ionic liquid is exposed on air humidity during the application.

The same is true for 1-ethyl-3-methylimidazolium ethylsulfate (EMIM EtSO₄) which has also a wide electrochemical window of 4.0 V (Figure 1). While the cathodic limit of this ionic liquid is the same as for EMIM BF₄, the anodic limit of EMIM EtSO₄ is with 1.4 V significantly lower than for EMIM BF₄ (Figure 2). 1-Ethyl-3-methylimidazolium triflate (EMIM OTf) has an electrochemical window of 3.9 V (Figure 1). In this case the anodic limit is with 2.1 V slightly higher than the cathodic limit (Figure 2). 1-Ethyl-3-methylimidazolium acetate (EMIM OAc) and 1-ethyl-3-methyl-imidazolium thiocyanate (EMIM SCN) have the smallest electrochemical windows of the presented ionic liquids with 1-ethyl-3-methylimidazolium cations (Figure 1). EMIM OAc has the lowermost anodic limit while the cathodic limit of EMIM OAc is with -2.3 V even a little bit higher than that of EMIM BTA. EMIM DCA possesses the lowermost cathodic limit (Fig. 2).

Due to their high thermal stability⁵, which is often correlated to electrochemical stability, ionic liquids with bis(trifluoromethylsulfonyl)imide anions are interesting substances for electrolytes of lithium ion and other novel types of batteries.⁶ The electrochemical stabilities of selected ionic liquids with bis(trifluoromethylsulfonyl)imide anions are shown in Figure 3 and 4.

Among the selected ionic liquids Butyltrimethylammonium bis(trifluoromethyl-sulfonyl)imide (N_{1114} BTA) has the widest electrochemical window (Figure 3). It has an anodic limit of 2.9 V and a cathodic limit of -3.2 V (Figure 4). 1-Propyl-1-methyl-piperidinum bis(trifluoromethylsulfonyl)imide (PMPip BTA) has an electrochemical

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window of 5.9 V (Figure 3). The anodic limit of PMPip BTA is with 2.7 V a little bit less than that of N_{1114} BTA, while the cathodic limit is the same for both ionic liquids (Figure 4). Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide (S_{221} BTA) and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrr BTA) also have a wide electrochemical window of more than 5 V, while ionic liquids with aromatic cations like 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BuPy BTA) and 1-Butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide (BuPy BTA) and 1-Butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide (BuPy BTA) and 1-Butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide (Bu-2-Pic BTA) possess a significantly smaller electrochemical window of the presented ionic liquids with bis(trifluoromethylsulfonyl)imide anion (Figure 3).

The cathodic limit of the pyridnium-based ionic liquids BuPy BTA and Bu-2-Pic BTA of -1.3 V is very small while the anodic limit of 2.9 V is the same as that of N_{1114} BTA and S_{221} BTA (Figure 4).



Figure 2: Anodic and cathodic limit of ionic liquids with 1-ethyl-3-methylimidazolium cations and different anions.

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Figure 3: Electrochemical window of ionic liquids with bis(trifluoromethylsulfonyl)imide anions with different cations.



Figure 4: Anodic and cathodic limit of ionic liquids with bis(trifluoromethylsulfonyl)imide anions and different cations.

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4.3 Summary

In summary we were able to demonstrate that the electrochemical stability of an ionic liquid is strongly depending on the nature of the cation and the anion. Ionic liquids with bis(trifluoromethylsulfonyl)imide or tetrafluoroborate anions combined with aliphatic ammonium- or sulfonium cations lead to the electrochemically most stable ionic liquids.

- ⁴ Zakeeruddin, S. M.; Graetzel, M. *Adv. Funct. Mater.* **2009**, *19*, 2187–2202.
- ⁵ M. Götz, F. Ortloff, M. Taige, T. J. S. Schubert, Long-term stability of ionic liquids at temperatures over 180 °C, Green Solvents, October 10-13, **2010**.
- ⁶ Moosbauer, D.; Zugmann, S.; Amereller, M.; Gores, H. J. *J. Chem. Eng. Data* **2010**, *55*, 1794–1798.

1-Ethyl-3-methylimidazolium tetrafluoroborate, >98% Reduced			1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 99%			Reduced			
IL-0006-HP	[143314-16-3]	$C_6H_{11}BF_4N_2$	MW 197.97	IL-0044-HP	[2234	437-05-6]	$C_{10}H_1$	₈ F ₆ N ₂ O ₄ S ₂	MW 408.38
~	∕─\ BF₄ [⊖] ∨N∕¥⊕	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	65.00 € 86.00 € 130.00 € 295.00 € 525.00 € 945.00 € 3'780.00 €	~		(CF ₃ SO ₂);	₂N [⊖]	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$52.00 \in$ 69.00 ∈ 115.00 ∈ 235.00 ∈ 385.00 ∈ 695.00 ∈ 2'780.00 ∈

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%			1-Ethyl-3-methylimidazolium dicyanamide, >98% <i>Reduce</i>			Reduced
IL-0023-HP [174899-82-2] C	${}_{8}H_{11}F_{6}N_{3}O_{4}S_{2}$	MW 391.31	IL-0003-HP	[370865-89-7]	$C_8H_{11}N_5$	MW 177.21
$\sim N \sim \mathbb{P}^{(CF_3SO_2)_2 N^{\mathbb{C}}}$	25 g 50 g 250 g 500 g 1 kg 5 kg	55.00 € 75.00 € 120.00 € 260.00 € 440.00 € 745.00 € 2'980.00 €	~	/─\ [⊖] N(CN)₂ ∠N _√ N _√	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	71.00 € 95.00 € 160.00 € 345.00 € 995.00 € on request

¹ Koenig, U.; Sessler, B. *Trans. Inst. Met. Finish.* **2008**, *86*, 183–188.

² Moosbauer, D.; Zugmann, S.; Amereller, M.; Gores, H. J. *J. Chem. Eng. Data* **2010**, *55*, 1794–1798.

³ Balducci, A.; Henderson, W. A.; Mastragostino, M.; Passerini, S.; Simon, P.; Soavi, F. *Electrochim. Acta* **2005**, *50*,2233; Simon, P.; Gogotsi, Y. *Nature Materials* **2008**, *7*, 845.

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5 Ionic Liquids and the Recovery of Rare Earth Metals

by Thomas J. S. Schubert (TS).

Introduction

The increase of the world's population and in particular the economical rise of countries like BRIC (Brazil, Russia, India, China) and the N-11 countries (Iran, Mexico, Turkey, Philippines, Egypt, Indonesia, Nigeria, Vietnam, Pakistan and Bangladesh) leads generally to a bottleneck of the most important raw materials.

Though there are still enough sources in the world, rare earth metals became more and more a bottleneck, but for completely other reasons: Since China, which dominated 2010 with 96% the worldwide production of rare earth metals, has limited its exports in 2010 to a maximum of 30'300 tons per year, the prices increased dramatically. Rare earth metals are today of enormous technical importance e.g. for

- permanent magnets for applications in cell-phones or electric motors for wind engines (Neodymium, Dysprosium, Terbium, Samarium, and Praseodymium),
- Light Emitting Electrodes, (Yttrium, Europium)
- Laser (Neodym, Samarium, Dysprosium, Holmium, Erbium)
- Glass for optical applications (Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Erbium).

Because of China's export restrictions, it became essentially important to look for other sources of these important metals. We'll see surely soon novel mines in North America and Australia, where old mines are re-activated or novel mines explored. The most promising sources of rare earth metals in the western hemisphere are located in Greenland, where they will start mining in 2015.

In the meantime, the largest resource of rare earth metals except China's reserves is the recycling of waste, and electronic scrap, in particular. To activate this resource it is necessary to develop novel processes and techniques to realize it in an efficient way. In this context, the use of suitable ionic liquids for the extraction and deposition of the neat metal may play an important role.

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Fig. 1. Usage of rare earth metals in technical applications (Source: Öko-Institut e.V.).

Ionic liquids for extraction

The use of ionic liquids for extraction purposes is surely one of the earliest applications that were suggested, when the "antichrists" of ionic liquids (Ken Seddon) 1-butyl-3-methylimidazolium hexafluorophosphate and –tetrafluoroborate were introduced in the field of ionic liquids in the 1990s:

- The negligible vapor pressure,
- the fact that you'll find an ionic liquid that is miscible or non miscible with another solvent,
- and the fact that you'll find ionic liquids that may dissolve some metal compounds and/or have a strong affinity to some metal-ions

lead quickly to the idea to use them for metal extraction and metal recovery. As a consequence there are a number of data for miscibility of ionic liquids with other solvents available today, and also many partition coefficients.

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Ionic liquids for the extraction of rare earth metals

To our best knowledge, the dissolution of rare earth metal oxides was first reported by *Binnemans et al.*, who found that the a number of rare earth metal oxides such as Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, or Lu₂O₃, were soluble in a betaine ionic liquid.¹



Fig. 2. Betaine bis(trifluoromethylsulfonyl)amide, a powerful solvent for rare earth metal oxides.

Another interesting paper was published in 2009 by *Binnemans, Nockemann et al.* where they used ionic liquids based on the hexafluoroacetylacetonate-anion.²



Fig. 3. *Binnemans, Nockemann et al.* combined Imidazolium- and Pyrrolidinium-cations with the hexafluoroacetylacetonate-anion to form novel ionic liquids.

The BMIM hfac reacted in an aqueous solution with Neodymium(III) bis(trifluoromethylsulfonyl)imide to form a [Nd(hfac)₄]⁻-complex, which existence was confirmed by a crystal structure. As a consequence it might be possible to use this or a similar formation of complexes for the extraction and re-isolation of Neodymium and other rare earth metals e.g. from electronic scrap.

If the rare earth metals or metal oxides are once dissolved, it is possible to recycle them by

- simple extraction and chemical reduction to the metals or
- by metal deposition.

¹ P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner, K. Binnemans, *J. Phys. Chem. B* **2006**, *110*, 20979.

² H. Mehdi, K. Binnemans, K. Van Hecke, L. Van Meervelt, P. Nockemann, *Chem. Comm.* **2010**, *46*, 234.

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The electrochemical reduction to the metallic state of lanthanum, samarium, and europium was already described in 2005 by *May et al.*³ The rare earth metals recovered by this or similar procedures can be reused to build novel magnets, LEDs etc.

Finally it is worth to stress that independently from China's export restrictions and the discovery of novel sources, the recycling of rare metals is also interesting because of the enormous negative impact on the environment: To exhaust the materials by daylight mining it is necessary to move billions tons of ground earth and it is also energy intensive.



Scheme 1. Recycling concept of rare earth metals by using ionic liquids for extraction and recovery of the metals by electrodeposition.

³ A. I. Bhatt, I. May*, V. A. Volokovich, D. Collison, M. Helliwell, I. B. Polovov, R. G. Lewin, *Inorg. Chem.* **2005**, *44*, 4934.

6 Selected Applications

By Boyan Iliev (BI), Hülya Sahin (HS), Maria Taige (MT), Sven Sauer (SS), Tom F. Beyersdorff (TB) and Thomas J. S. Schubert (TS).

Autocatalytic Sonolysis of Iron Pentacarbonyl in Room Temperature Ionic Liquid BMIM NTf₂

L. Lartigue, R. Pflieger, S. I. Mikitenko, Y. Guari, L. Stievano, M. T. Sougrati, J. Larionova, *PhysChemChemPhys* **2011**, *13*, 2111-2113.

In recent years the number of publications that describe the synthesis of nanomaterials in IL has steadily increased. IoLiTec in co-operation with Prof. Janiak (Duesseldorf University/Germany) has filed two patents on the size controlled synthesis of nano metals in ionic liquids by either hydrogenation or thermal and/or photolytic decomposition of appropriate precursors. We could show that a variety of metal carbonyls decompose to form very small nanoparticles with a narrow size distribution upon heating. In addition it was shown that the choice of ionic liquid and especially of the anion had an influence on the particle size and the size distribution.

Guari et al. now report an addition to the previously published procedures. They could show that iron pentacarbonyl $Fe(CO)_5$ dissolved in BMIM NTf₂ decomposes if sonicated with 20 kHz ultrasound to form non aggregated uniform iron nanopartiles with a mean diameter of 3 nm. A drawback of this method is the long sonolysis time of almost 5h. However, this approach might provide access to nanomaterials that are often not accessible through conventional methods.

1,3-Dimethylimidazolium bis(trifluoromethylsulfonyl)imide, 99%							
IL-0198-HP	[174899-81-1]	$C_7H_9F_6N_3O_4S_2$	MW 377.28				
_N	N (CF₃SO₂)₂N ⊖ ⊕	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	67.50 € 90.00 € 150.00 € 320.00 € 545.00 € 925.00 € 3'930.00 €				

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Ionic Liquids as Electrolytes for the Development of a Robust Ampero-metric Oxygen Sensor (TS)

Zhe Wang, Peiling Lin, Gary A. Baker, Joseph Stetter, and Xiangqun Zeng, *Anal. Chem*, **2011**, *dx.doi.org/10.1021/ac201235w*

The authors use a simple Clark-type online electrochemical cell design, consisting of a platinum gauze working electrode and incorporating ionic liquids (IL) as electrolytes, which has been successfully applied for the amperometric sensing of oxygen. Ionic liquids (ILs) with their unique combination of physic-chemical properties have a number of advantages over common sensor electrolytes, such as high stability and long lifetimes.

Furthermore, the low volatility of ILs has been shown to eliminate the need for a gas-permeable membrane in the sensor system, simplifying device response since the diffusion layer no longer impinges upon a membrane. In addition, ILs frequently possess high thermal stability, which not only allows for facile sensor regeneration and decontamination, with favorable improvements in signal-to-noise (S/N) ratio, but also makes their use under nonstandard or extreme conditions (e.g. elevated temperatures, nonambient pressures) or in the presence of sensitive materials an intriguing possibility. With a variety of bis(trifluoromethylsulfonyl)imide (BTA)- based ILs the authors have achieved an oxygen detection limit as low as 0.05 vol %, good selectivity, full reversibility, and long-term stability over several months. IOLITEC has extensive competence on the subject and had its own IL-based water sensor for about 3 years.

Tributylmethylammonium bis(trifluoromethylsulfonyl)imide, 99%				1-Butyl-1-n bis(trifluoro	nethylpyrrolidini omethylsulfonyl)	um)imide, 99%	
IL-0117-HP	[405514-94-5]	$C_{15}H_{30}F_6N_2O_4S_2$	MW 480.53	IL-0035-HP	[223437-11-4]	$C_{11}H_{20}F_6N_2O_6$	4S ₂ MW 422.41
	CF ₃ SO ₂);	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	90.00 € 117.50 € 195.00 € 402.50 € 660.00 € 1'185.00 € 4'740.00 €	~~	\bigvee_{\bigoplus}^{N} (CF ₃ SO ₂)	2! 50 ₂N [⊖] 100 250 500 1 5	$\begin{array}{cccc} 5 & 52.00 \in \\ 0 & 69.00 \in \\ 0 & 115.00 \in \\ 0 & 235.00 \in \\ 0 & 385.00 \in \\ kg & 695.00 \in \\ kg & 2'780.00 \in \end{array}$

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1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%							
IL-0029-HP	[174899-83-3]	$C_{10}H_{15}F_6N_3O_4S_2$	MW 419.37				
1	/──\ N	25 g 50 g 250 g 250 g 500 g 1 kg 5 kg	54.00 € 72.00 € 122.00 € 260.00 € 440.00 € 750.00 € 3'000.00 €				

Green Bipropellants: Hydrogen-Rich Ionic Liquids that Are Hypergolic with Hydrogen Peroxide (TB)

S. Schneider, T. Hawkins, Y. Ahmed, M. Rosander, L. Hudgens, J. Mills, *Angew. Chem.* **2011**, *123*, DOI: 10.1002/anie.201101752

In recent years several research groups investigated ionic liquids as propellants with low vapor pressure. The general approach was to combine energetic cations and anions in the ionic liquid. In several cases cations were functionalized with nitrogroups and anions such as dicyanamide, dinitramide, azolate and many more were used.

In 2011 *Schneider et al.* published a different approach using hydrogen-rich ionic liquids that are hypergolic in contact with hydrogen peroxide. The new ionic liquids consisted of a phosphonium cation and a BH_4^- or an $Al(BH_4)_4^-$ anion and were synthesized by anion exchange between the phosphonium chloride and NaBH₄ followed by reaction with aluminum borohydride to form the complex $Al(BH_4)_4^-$ anion. Drop tests with standard propulsion oxidizers (H_2O_2 , N_2O_4 , white fuming nitric acid WFNA) were performed and ignition delays were measured. They could show that BH_4^- only ignited approx 3 sec after dropping on H_2O_2 , whereas $Al(BH_4)_4^-$ showed ignition delays in the millisecond range. In addition, $Al(BH_4)_4^-$ ignited in contact with N_2O_4 vapors before the liquids combined and exploded in contact with WFNA.

These first simple experiments show that this new class of IL is universally reactive with standard propulsion oxidizers and offers the potential of high-performing, noncryogenic, green bipropulsion.

IOLITEC offers a lot of Phosphonium-based ionic liquids. Please do not hesitate to contact us!

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High Performance Supercapacitor Based on Poly(ionic liquid)-Modified Graphene Electrodes (TB)

T. Y. Kim, H. W. Lee, M. Stoller, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, K. S. Suh, *Nano* **2011**, *5*, 436.

Supercapacitors or electric double layer capacitors (EDLCs) are a kind of electrochemical capacitors that store energy by reversible ion absorption onto active materials with high specific surface areas. In order to increase the capacitance of an EDLC the specific surface area of the electrodes has to be increased in order to allow a large number of ions to accumulate on the electrolyte/electrode interface and to build up the electronic double layer. Graphene and reduced graphene oxides are promising electrode materials for EDLCs due to their high surface area and excellent electronic conductivity. In addition, an increase of the energy density of an EDLC can be achieved by increasing the operating voltage and the availability of ions from the electrolyte. The wide electrochemical windows of some ionic liquids make these materials interesting alternatives to standard electrolytes.

Ruoff et al. recently published an approach that combines these two technologies. As electrode they used poly(ionic liquids)-modified reduced graphene oxide which was synthesized by reduction of graphene oxide in propylene carbonate in the presence of poly(ionic liquids) (PIL) at elevated temperature. The poly(ionic liquid) of choice was poly(1-vinyl-3-ethylimidazolium) NTf₂ which can be synthesized by polymerization of 1-Ethyl-3-vinylimidazolium NTf₂. Using these electrodes in combination with EMIM NTf₂ lead to a supercapacitor with a specific capacitance of 187 F/q, an energy density of 6.5 Wh/kg and a power density of 2.4 kW/kg.

Further research to further optimize the electrolyte/electrode combination has to be performed in order to yield an even higher capacitance and energy density.

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1-Ethyl-3-methylimidazolium chloride, >95%			
L-0093-TG	[65039-09-0]	$C_6H_{11}CIN_2$	MW 146.62
	, N , S , CI⊖ N , S ⊕ , CI⊖	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	60.00 € 75.00 € 105.00 € 165.00 € 260.00 € 495.00 € 2′095.00 €
Filled in as n	nelt!		

Selective Electrochemical Fluorination of Organic Molecules and Macromolecules in Ionic Liquids (BI)

T. Fuchigami, S. Inagi, *Chem. Commun.* **2011**, *47*, 10211.

Classic fluorination reactions are usually done in anhydrous HF, which is volatile and highly corrosive, and therefore very difficult to handle. Organic electrosynthesis has been known since the 1970s. The process involves anodic oxidation or cathodic reduction at the electrodes, followed by a chemical reaction step; therefore, no hazardous chemical oxidant or reductive agent is required in the electrochemical system. Furthermore, reactions can be carried out under mild conditions such as at room temperature and normal pressure. Some of the most widely used ILs for these purposes are adducts of trialkylammonium fluorides with HF in different ratios. The use of such salts, in particular in the absence of organic solvents, leads to high current densities with good to high current efficiencies (66–90%).

The authors have also found that a combination of Et₄NF–nHF (n=4, 5) and imidazolium ionic liquids was highly effective for the anodic fluorination of phthalides, the reduction of which was initially carried out successfully in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA). The yield of the anodic fluorination is low even in ionic liquid fluoride salts, mainly due to simultaneous oxidation of the fluoride salts during electrolysis. Even the use of 1-ethyl-3-methylimidazolium fluoride–2.3HF (EMIM F·HF_{2,3}) gave an unsatisfactory yield. In sharp contrast, when the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM OTf) was used, the yield increased noticeably.

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1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, 99%							
IL-0009-HP	[145022-44-2]	$C_7H_{11}F_3N_2O_3S$	MW 260.24				
~	∕─∖ CF₃SO₃ [⊖] ∕N _{∽∕} ⊕∖	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	72.50 € 97.50 € 140.00 € 310.00 € 550.00 € 990.00 € on request				

Transfer Layers: A Comparison across SWNTs, DWNTs, Graphite and an Ionic Fluid (HS)

Randy L. VanderWal, K. W. Street, Jr., K. Miyoshi, *Advances in Tribology*, **2011**, doi:10.1155/2011/929642.

The steady advancements of lubricants and their proper application is a substantial effort in economic terms. Optimally to the specific conditions adapted lubricants save energy, extend the durability of machines and reduce the abrasion whereby vastly cost-reduction could be achieved. It is self-evident to apply nanotechnology in the development of lubricants as the "nanoscale" plays a decisive role during the process associated with lubrication. In addition, an increasing attention is paid to the use of ionic liquids in tribology.

In order to combine tribological properties, *Miyoshi et al.* dispersed carbon nanomaterials and ionic liquids to get enhanced lubrication. They studied single-(SWNT) and double-walled (DWNT) carbon nanotubes and an ionic fluid individually and compared to SWNTs and graphite as additives within the ionic fluid. The combination of SWNTs with ionic fluid 1-ethyl-3-methylimidazolium tosylate yielded a >500 and 2.7 times lifetime improvement over the SWNTs alone and EMIM-Tosylate, respectively. An additional lifetime improvement is expected in vacuum due to the superior performance of ionic fluids in vacuum.

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Packaging: Powder in PE bottle

Single-Wall	ed Carbon Nanotub	es, 90%	MW 12.01	Graphite por	wder, 93%	C	MW/ 12 01
OD: < 2 nm L: < 20 μm SSA: > 450 n	n²/g	0.5 g 1 g 2 g 5 g	69.00 € 115.00 € 189.00 € 399.00 €	APS: 1.5-3 nm SSA: 540-650 PM: spherical Appearance: b	n m²/g plack powder	5 g 10 g 25 g 50 g	45.00 € 69.00 € 149.00 € 249.00 €
	Warning H 315, 319, 335 P 261, 280, 302+352, 3	305+351+338, 313	3+332, 362		Warning H 319, 335 P 261, 280, 305+353	L+338	
Packaging: Po	owder in PE bottle			Packaging: Po	wder in PE bottle		
Double-Wal	led Carbon Nanotul	oes, 90%		1-Ethyl-3-n	nethylimidazoliui	ntosylate, 9%	
CP-0013-SG	[308068-56-6]	С	MW 12.01	IL-0008-HP	[328090-25-1]	$C_{13}H_{18}N_2O_3S$	MW 282.36
OD: < 5 nm L: 20 μm SSA: > 450 n	n²/g	0.5 g 1 g 2 g 5 g	69.00 € 115.00 € 189.00 € 399.00 €	~		25 g 50 g 100 g 250 g	45.00 € 60.00 € 110.00 € 220.00 €
(٢)	Warning H 315, 319, 335 P 261, 280, 302+352, 3	805+351+338, 313	3+332, 362		v⊕ v v SO ₃ ⊖	500 g 1 kg 5 kg	395.00 € 675.00 € 2′840.00 €

Facile and Green Synthesis of ZnO Nanostructures in a Room Temperature Ionic Liquid 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide (HS)

K. E. Goharshadi, Y. Ding, X. Lai, P. Nancarrow, *Inorganic Materials*, **2011**, *47*, 379.

It has been shown that ionic liquids are suitable candidates to substitute organic solvents in many reactions. This qualification is due to their properties such as low melting temperature, high boiling temperature, non flammability and their thermal stability. The fact, that ionic liquids are recyclable, is an additional advantage.

Goharshadi et al. made use of these advantages and synthesized ZnO nano particles via microwave assisted decomposition of zinc acetate. Using 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as ionic liquid, they have been able to get a fast and controlled synthesis route for making pure hexagonal phase of ZnO nanoparticles. ZnO is applied in piezoelectrics, UV protection, electrodes for solar cells and pigments for paints, to name just a few examples.

The methodology described by *Goharshadi et al.* could be extended for fast and controlled production of a variety of nanoparticles.

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1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%	Reduced	Zinc oxide, 99.9% NO-0039-HP [1314-13-2]	ZnO	MW 81.3
$(CF_{3}SO_{2})_{2}N^{\bigcirc} $ $(CF_{3}SO_{2})_{2}N$	70.00 € 93.00 € 159.00 € 335.00 € 575.00 € 3'900.00 €	APS: 90-210 nm SSA: 5-7 m²/g PM: irregular Appearance: white powder Warning H 410 P 273, 501	25 g 100 g 500 g 1 k	25.00 45.00 189.00 299.00
		Packaging: Powder in PE bottle		

Extraordinarily Efficient Conduction in a Redox-Active Ionic Liquid (MT)

V. K. Thorsmølle, G. Rothenberger, D. Topgaard, J. C. Brauer, D.-B. Kuang, S. M. Zakeeruddin, B. Lindman, M. Graetzel, J.-E. Moser *Chem. Phys. Chem.* **2011**, *12*, 145-149.

Graetzel et al. recently published a very interesting paper on the conductivity pathways in mixtures of iodine and 1-methyl-3-propylimidazolium iodide (PMIM I) melts. They used tetrahertz time-domaine spectroscopy together with DC conductivity, diffusivity and viscosity measurements for their investigations.

They investigated the dynamical behavior of a mixture of a PMIM I melt and iodine and showed that the formation of polyiodides as well as the conductivity pathways in the mixture correspond with the iodine concentration. Up to iodine concentrations of ~3,6 M the triiodide anion is the predominant polyiodide, while the formation of higher polyiodides like I_5^- and I_7^- occurs at higher iodine concentrations.

The *Grotthuss-mechanism* is similar to a hole-transport-mechanism, which explains i. e. the mobility of protons in water. It has been often discussed that this mechanism also explains the conduction in redox-active ionic liquids. *Graetzel et al.* now demonstrated that this mechanism plays an important role for the conduction in a mixture of PMIM I and iodine.

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1-Methyl-3-propylimidazo iodide, >98%	lium	Reduced	1,3-Dimethy iodide, >98	ylimidazolium %		Reduced
IL-0025-HP [119171-18-5]	IL-0025-HP	[119171-18-5]	IL-0199-HP	[4333-62-4]	$C_5H_9IN_2$	MW 224.04
N N S⊕ N S⊕ N	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	45.00 € 60.00 € 95.00 € 195.00 € 309.00 € 495.00 € 1′980.00 €			25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	82.00 € 109.00 € 175.00 € 350.00 € 559.00 € 895.00 € on request

Rhodium-Phosphite SILP Catalysis for the Highly Selective Hydroformulation of Mixed C4 Feedstocks (MT)

M. Jakuttis, A. Schönweiz, S. Werner, R. Franke, K.-D. Wiese, M. Haumann, P. Wasserscheid *Angew. Chem. Int. Ed.* **2011**, *50*, 4492.

The hydroformylation reaction is an industrially very important homogeneous catalysed reaction. *Wasserscheid et al.* recently published a very interesting paper about the rhodium-phosphite SILP catalyzed continuous gas-phase hydroformylation of mixed C₄ raw materials. The SILP catalyst was prepared out of $[Rh(CO)_2(acac)]$, a diphosphite ligand, Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA) and calcinated silica. The reaction was carried out in a fixed bed reactor. Even though the C₄ raw material consists of 43.1 % isobutene, 25.6 % 1-butene, 9.1 % *trans*-2-butene, 7 % *cis*-2-butene and 14.9 % butane the SILP catalyst enables a highly regioselective conversion (>99 %) to the desired *n*-pentanal. In addition, the catalyst has a very high activity at temperatures of 120 °C and can be separated completely form the product after the reaction. These results make the SILP catalysis not only an interesting method for academic investigations but also applicable to industrial processes.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%							
IL-0023-HP [174899-82-2] C ₈	$H_{11}F_6N_3O_4S_2$	MW 391.31					
$\sim N \sim N \sim \mathbb{Q}^{\mathbb{Q}}$	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	55.00 € 75.00 € 120.00 € 260.00 € 440.00 € 745.00 € 2'980.00 €					

IL-0029-HP [174899-83-3] $C_{10}H_{15}F_6N_3O_4S_2$ MW 419.37 \bigwedge \bigwedge $(CF_3SO_2)_2N^{\bigcirc}$ $\begin{array}{c} 25 \text{ g} \\ 50 \text{ g} \\ 72.00 \in \\ 250 \text{ g} \\ 250 \text{ g} \\ 250 \text{ g} \\ 250 \text{ g} \\ 500 \\ 440.00 \in \\ 1 \text{ kg } \\ 750.00 \in \\ 5 \text{ kg } \\ 3'000.00 \in \end{array}$	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%					
$(CF_{3}SO_{2})_{2}N^{\bigcirc} (CF_{3}SO_{2})_{2}N^{\bigcirc} (CF_{3}SO_{2})_{2}N^{O} (CF_{3}SO_{2})_{2}N^{O} (CF_$	IL-0029-HP	[174899-83-3]	$C_{10}H_{15}F_6N_3O_4S_2$	MW 419.37		
	~~~!	/─\ V ∽ N ♥	25 g 50 g N [⊖] 100 g 250 g 500 1 kg 5 kg	54.00 € 72.00 € 122.00 € 260.00 € 440.00 € 750.00 € 3'000.00 €		

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1-Methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide, 99%				
IL-0024-HP	[216299-72-8]	$C_9H_{13}F_6N_3O_4S_2$	MW 405.34	
$\sim$	∕── N ∕∽ ⊕∽ (CF ₃ SO ₂ );	25 g 50 g 2N [⊖] 100 g 250 g 500 g 1 kg 5 kg	70.00 € 95.00 € 160.00 € 337.50 € 575.00 € 975.00 € 4'150.00 €	

# Room Temperature Ionic Liquid. A New Medium for Material Production and Analyses under Vacuum Conditions (TS)

S. Kuwabata, T. Tsuda, T. Torimoto, J. Phys. Chem. Lett. 2010, 1, 1377.

In ACS' new "Journal of Physical Chemistry Letters" a number of interesting ionic liquids papers were published as "Perspective" articles. One of them was released in 2010 by *Kuwabata et. al.* who gave an overview over the use of ionic liquids as medium for the production and analyses under vacuum conditions.

In the first part, they cited some examples of materials and, in particular, nanomaterial production under vacuum conditions, such as

- electrodeposition of Aluminum¹
- magnetron sputtering onto ILs²
- plasma deposition method³
- physical vapor deposition method⁴
- and electron beam and  $\gamma$ -ray irradiation⁵

¹ M. Johnston, J.-J. Lee, G. S. Chottiner, B. Miller, T. Tsuda, C. L. Hussey, D. A. Scherson, *J. Phys. Chem. B* **2005**, *109*, 11296.

² T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, *Appl. Phys. Lett.* **2006**, *89*, 24311.

³ S. A. Meiss, M. Rohnke, L. Kienle, S. Z. E. Abedin, F. Endres, J. Janek, *ChemPhysChem* **2007**, *8*, 50; S. Z. E. Abedin, M. Pölleth, S. A. Meiss, J. Janek, F. Endres, *Green Chem.* **2007**, *9*, 549; M. Brettholle, O. Höfft, L. Klarhöfer, S. Mathes, M. Friedrichs, S. Z. E. Abedin, S. Krischok, J. Janek, F. Endres, PhysChemChemPhys. **2010**, *12*, 1750.

⁴ K. Richter, A. Birkner, A.-V. Mudring, *Angew. Chem., Int. Ed.* **2010**, *49*, 2431; N. v. Prondzinski, J. Cybinska, A.-V. Mudring, *Chem. Commun.* **2010**, *46*, 4393.

⁵ A. Imanishi, M. Tamura, S. Kuwabata, *Chem. Comm.* **2009**, 1774; T. Tsuda, S. Seino, S. Kuwabata, *Chem. Comm.* **2009**, 6792.

In the second part, they gave an overview about analytical methods that are using vacuum techniques that have a significant benefit by using ionic liquids, such as

- XPS analysis⁶
- MALDI mass spectrometry⁷
- SEM observation and EDX analysis⁸
- and TEM observation⁹

From our point of view all of these techniques itself are each worth to be highlighted.

# Ionic liquids in vacuo; solution-phase X-ray photoelectron spectroscopy (TS)

E. F. Smith, I. J. Villar Garcia, D. Briggs, P. Licence, Chem. Comm. 2005, 5633.

The XPS analysis can be used for the elemental analysis of solids, but it gives also information about the electronic structure. As the authors mentioned, such information could be generally extremely useful for samples in solution, but common solvents simply evaporate in vacuum. And here ionic liquids enter the scene: As generally versatile solvents with a non measureable vapor pressure they seem to be ideal candidates for this application.

The authors selected the well explored Heck-reaction to demonstrate the power of this method: By using 1-ethyl-3-methylimidazolium ethylsulfate they observed the increase of Pd(0) and a corresponding decrease of  $Pd^{2+}$ , caused by the reduction of  $Pd^{2+}$  to the metal, leading to "Palladium black", presumably Pd nanoparticles.

⁶ E. F. Smith, I. J. Villar Garcia, D. Briggs, P. Licence, *Chem. Comm.* **2005**, 5633.

 ⁷ D. W. Armstrong, L.-K Zhang, L. He, M- L. Gross, *Anal. Chem.* 2001, *73*, 3679; M. Mank, B. Stahl, G. Boehm, *Anal. Chem.* 2004, *76*, 2938.

⁸ S. Kuwabata, A. Kongkanand, D. Oyamatsu, T. Torimoto, *Chem. Lett.* **2006**, *35*, 600.

⁹ P. Dash, R.W. J. Scott, *Chem. Comm.* **2009**, 812.

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IL-0033-HP         [342573-75-5] $C_8H_{16}N_2O_4S$ MW 236.29 $\sqrt{N} \sim N$ $\sum_{n=1}^{N} EtOSO_3^{\ominus}$ $25 \text{ g}$ $30.00 \in$ $100 \text{ g}$ $70.00 \in$ $250 \text{ g}$ $95.00 \in$ $250 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $250 \text{ g}$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $250 \text{ g}$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $100 \text{ g}$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $100 \text{ g}$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $100 \text{ g}$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $100 \text{ g}$ $100 \text{ g}$ $70.00 \in$ $500 \text{ g}$ $130.00 \in$ $1 \text{ kg}$ $195.00 \in$ $5 \text{ kg}$ $780.00 \in$	1-Ethyl-3-methylimidazolium ethyl sulfate, 99%						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	IL-0033-HP	[342573-75-5]	$C_8H_{16N_2O_4S}$	MW 236.29			
	~	∕─\ EtOSO ₃ ∕N,≪⊕,	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$30.00 \in$ $40.00 \in$ $70.00 \in$ $95.00 \in$ $130.00 \in$ $195.00 \in$ $780.00 \in$			

# Room temperature lithium polymer batteries based on ionic liquids (SS)

G. B. Appetecchi, G. T. Kim, M. Montanino, F. Alessandrini, S. Passerini, *J. Power Sources* **2011**, *196*, 6703.

*Passarini* describes in his work the effects of incorporated ionic liquids on rechargeable, allsolid-state, solvent-free, Li/LiFePO₄ polymer batteries. Those lithium metal polymer batteries are meant to be a good choice as power sources of the next gerenation regarding their energy density, cyclability and safety. One of the main drawbacks of those batteries is that they show only a very limited performance at room temperature, due to the low ionic conductivity of the solvent free electrolyte (poly(ethyleneoxide)lithium-salt). He showed that the incorporation of 1-Butly-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PMPyrr BTA) in those systems allows to reduce the operative temperature of those devices down to room temperature without depleting the chemical/electrochemical properties. Those IL containing batteries investigated in the article are able to deliver the theoretical capacity (170mAh g–1) at 30 °C and still large capacities (>100mAh g–1) at 20 °C with excellent cycle capability and coulombic efficiency close to 100%. At 40 °C large capacities are discharged even at medium rates.

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 99%					
IL-0035-HP	[2234	37-11-4]	$C_{11}H_2$	$_{0}F_{6}N_{2}O_{4}S_{2}$	MW 422.41
~~		(CF ₃ SO ₂ )	₂N [⊖]	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	52.00 € 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2'780.00 €

# Naked metal nanoparticles from metal carbonyls in ionic liquids: Easy synthesis and stabilization (SS)

C. Vollmer, C. Janiak, *Coord. Chem. Rev.* 2011, 255, 2039.

In this comprehensive review the authors describe the use of ionic liquids in the synthesis of metal-nanoparticles from metal carbonyls and salts and their stabilization in the ionic liquids.

The authors show a large number of different methods of synthesis including chemical reduction, photochemical decomposition, thermolysis, electroreduction, microwave and sonochemical irradiation.

One obvious advance for the use of metal carbonyls in synthesis results from the zero-oxidation state of the metal atom in the carbonyls. So during the synthesis no extra reducing agent is needed to release the free metal. In addition, many of the metal carbonyls precursors are commercially available and common industrial products. The side product CO could be removed very easily from the resulting dispersions. Another important point worked out by the authors is that the electrostatic and steric properties of ionic liquids allow the stabilization of metal nanoparticles without the need of additional stabilizers, surfactants or ligands. By choosing different ionic liquids and reaction conditions it is possible to adjust the resulting particle sizes for each specific application.

Therefore ionic liquids are very suitable media for the synthesis of metal nanoparticles.

1-Butyl-3-methylimidazolium hexafluorophosphate, 99%		Reduced	1-Butyl-3-methylimidazolium trifluoromethanesulfonate, 99%			Reduced
IL-0011-HP [174501-64-5] (	$C_8H_{15}F_6N_2P$	MW 284.18	IL-0013-HP	[174899-66-2]	$C_9H_{15}F_3N_2O_3S$	MW 288.29
$\bigvee_{N \swarrow \mathbb{P}_{6}^{\mathbb{O}}} PF_{6}^{\mathbb{O}}$	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$\begin{array}{c} 31.00 \in \\ 41.00 \in \\ 62.00 \in \\ 139.00 \in \\ 250.00 \in \\ 450.00 \in \\ 1'800.00 \in \end{array}$	~~	/─\ CF ₃ SO ₃ ∕_N ∕	25 g 50 g 250 g 250 g 500 g 1 kg 5 kg	61.00 € 82.00 € 123.00 € 275.00 € 497.00 € 895.00 € 3580.00 €

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### 7 New Products

By Thomas J. S. Schubert.

Driven by our customers' needs, we try to develop and extend our product range continuously. In this context, the most often asked questions are:

- Are products with lower viscosities and higher conductivities available?
- Are high-purities above 99% as colorless liquids available?
- Are smaller research quantities for <u>screening-tests</u> available?

As you can surely imagine, our answer is "yes!"

### Low viscous ionic liquids based on the Tricyanomethide-anion

The physical-chemical properties of ionic liquids are influenced mostly by the anion, while the cation is for fine-tuning or tailoring. Next to solvents, the use of ionic liquids as electrolytes is surely one of the most important applications and, as a consequence, the viscosity and conductivity are the most important properties.

When the dicyanamide- (DCA)-anion entered the ionic liquids world, the conductivity scratched 20 mS/cm, a value which in combination with the 1-ethyl-3-methylimidazolium-cation at that time only was achieved by highly corrosive ionic liquids and by the ionic liquids based on the thiocyanate-anion. Just a few years later, *Gores* introduced tetracyanoborate-based ionic liquids, which are even lower viscous and higher conductive, and thus are interesting materials.

In this context, the missing piece is the carbon-homologue, since in the periodic system carbon is located between boron and nitrogen. The tricyanomethide-anion (or methanide) is in principle very attractive, since the charge is delocalized in an optimum way, leading to a really weakly coordinating species, resulting in viscosities of 12.2 cP at 30°C and a conductivity of 17 mS/cm for 1-ethyl-3-methylimidazolium tricyanomethanide (IL-0316-HP).

We start now with the introduction of the EMIM-derivative, but a number of other cations combined with this novel and interesting anion will follow, soon.

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1-Ethyl-3-met tricyanometha	thylimidazolium anide, >98%		NEW
IL-0316-HP		$C_{10}H_{11}N_5$	MW 201.23
	C(CN)3 [⊖]	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	91.00 € 122.00 € 162.00 € 344.00 € 585.00 € 998.00 € on request

### **Colorless Ionic Liquids with purities above 99.5%**

Over the past years we were frequently asked for higher purities, and in particular for *colorless ionic liquids*. Even though only traces below 1 ppm can cause a slightly yellowish color, these traces may have a strong impact on those applications, where interfaces play an important role. This is in particular true for electrochemical applications, where traces can strongly influence the electrode surfaces, leading to misleading results. Another aspect are optical applications, where crystal clear fluids are required. If you are interested, please contact us, other ultrapure & colorless ionic liquids will follow, soon!

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99.5% <b>NEW</b>			1-Methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide, 99.5%			NEW
IL-0023-UP [174899-82-2]	$C_8H_{11}F_6N_3O_4S_2$	MW 391.31	IL-0024-UP	[216299-72-8]	$C_9H_{13}F_6N_3O_4S_2$	MW 405.34
$\bigvee_{N} (CF_3SO_2)_2 N$	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	75.00 € 100.00 € 170.00 € 365.00 € 615.00 € 1045.00 € on request	~~^N	/─\ (CF ₃ SO ₂ ) N ≪⊕ \	25 g 50 g 2№ 100 g 250 g 500 g 1 kg 5 kg	95.00 € 130.00 € 215.00 € 460.00 € 780.00 € 1325.00 € on request
1-Methyl-1-propylpyrrolidin bis(trifluoromethylsulfonyl)	ium imide, 99.5%	NEW	1-Butyl-1-me bis(trifluoror	ethylpyrrolidiniu methylsulfonyl)	um imide, 99.5%	NEW
1-Methyl-1-propylpyrrolidin bis(trifluoromethylsulfonyl)i IL-0044-UP [223437-05-6]	<b>ium imide, 99.5%</b> C ₁₀ H ₁₈ F ₆ N ₂ O ₄ S ₂	<b>NEW</b> MW 408.38	1-Butyl-1-me bis(trifluoror IL-0035-UP	ethylpyrrolidinio methylsulfonyl) [223437-11-4]	um imide, 99.5% C ₁₁ H ₂₀ F ₆ N ₂ O ₄ S ₂	<b>NEW</b> MW 422.41
<b>1-Methyl-1-propylpyrrolidin</b> <b>bis(trifluoromethylsulfonyl)</b> IL-0044-UP [223437-05-6]	ium imide, 99.5% $C_{10}H_{18}F_6N_2O_4S_2$ $N^{\ominus}$ 100 g 250 g 250 g 500 g 1 kg 5 kg	NEW MW 408.38 72.00 € 100.00 € 160.00 € 330.00 € 545.00 € 975.00 € on request	1-Butyl-1-me bis(trifluoror IL-0035-UP	ethylpyrrolidinin methylsulfonyl) [223437-11-4] $(CF_3SO_2)_2$	$\sum_{n=1}^{n} \frac{1}{n} \frac{1}{n} \frac{1}{20} F_6 N_2 O_4 S_2}{C_{11} H_{20} F_6 N_2 O_4 S_2}$	NEW MW 422.41 72.00 € 100.00 € 160.00 € 330.00 € 545.00 € 975.00 € on request

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## **Ionic Liquids for Screening-Tests: MyKit**

The introduction of our novel ionic-liquids-screening-kits is a consequence of many fruitful



discussions with our customers. First of all, we switched from 25 g to 10 g, which is surely enough for the most screening purposes. Secondly, we selected 58 common ionic liquids, which are now available at **unified prices**, independently from the particular ionic liquid, but depending on the number of

items:

- 5 to 9 items: 40 €/per ionic liquid
- 10 to 24 items: 35 €/per ionic liquid
- 25 to 50 items: 30 €/per ionic liquid

MyKit starts in general with 5 and is limited to maximum 50 items. Within the 59 different ionic liquids it is possible to combine any kind and/or number of items.

1-Ethyl-3-methylimidazolium	Triethylsulfonium	1-Hexyl-3-methylimidazolium
tetrafluoroborate (IL-0006-HP)	bis(trifluoromethylsulfonyl)imide (IL-0030-HP)	triflate (IL-0070-HP)
1-Butyl-3-methylimidazolium	Methyltrioctylammonium	1-Methyl-3-octylimidazolium
tetrafluoroborate (IL-0012-HP)	bis(trifluoromethylsulfonyl)imide (IL-0017-HP)	triflate (IL-0073-HP)
1-Hexyl-3-methylimidazolium	1-Ethyl-3-methylimidazolium	1-Butyl-1-methylpyrrolidinium
tetrafluoroborate (IL-0019-HP)	bis(trifluoromethylsulfonyl)imide (IL-0023-HP)	triflate (IL-0113-HP)
1-Methyl-3-octylimidazolium	1-Methyl-3-propylimidazolium	1-Ethyl-3-methylimidazolium
tetrafluoroborate (IL-0021-HP)	bis(trifluoromethylsulfonyl)imide (IL-0024-HP)	thiocyanate (IL-0007-HP)
1-Butylpyridinium	1,2-Dimethyl-3-propylimidazolium	1-Ethyl-3-methylimidazolium
tetrafluoroborate (IL-0089-HP)	bis(trifluoromethylsulfonyl)imide (IL-0134-HP)	dicyanamide (IL-0003-HP)
1-Butyl-3-methylpyridinium	1-Butyl-3-methylimidazolium	1-Butyl-3-methylimidazolium
tetrafluoroborate (IL-0081-HP)	bis(trifluoromethylsulfonyl)imide (IL-0029-HP)	dicyanamide (IL-0010-HP)
1-Butyl-4-methylpyridinium tetrafluoroborate (IL-0085-HP)	1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsufonyl)imide (IL-0104-HP)	1-Butyl-1-methylpyrrolidinium dicyanamide (IL-0041-HP)
1-Butyl-3-methylimidazolium	1-Hexyl-3-methylimidazolium	1-Ethyl-3-methylimidazolium
hexafluorophosphate (IL-0011-HP)	bis(trifluoromethylsulfonyl)imide (IL-0098-HP)	chloride (IL-0093-HP)
1-Hexyl-3-methylimidazolium	1-Hexadecyl-3-methylimidazolium	1-Butyl-3-methylimidazolium
hexafluorophosphate (IL-0018-HP)	bis(trifluoromethylsulfonyl)imide (IL-0103-HP)	chloride (IL-0014-HP)
1-Methyl-3-octylimidazolium	1-Allyl-3-methylimidazolium	1-Allyl-3-methylimidazolium
hexafluorophosphate (IL-0020-HP)	bis(trifluoromethylsulfonyl)imide (IL-0239-HP)	chloride (IL-0022-HP)
1-Butylpyridinium hexafluorophosphate (IL-0088-HP)	1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (IL-0044-HP)	Trihexyltetradecylphosphonium chloride (IN-0006-TG)
1-Butyl-3-methylpyridinium	1-Butyl-1-methylpyrrolidinium	1-Ethyl-3-methylimidazolium
hexafluorophosphate (IL-0080-HP)	bis(trifluoromethylsulfonyl)imide (IL-0035-HP)	bromide (IL-0015-HP)
1-Butyl-4-methylpyridinium	1-Methyl-1-propylpiperidinium	1-Butyl-3-methylimidazolium
hexafluorophosphate (IL-0084-HP)	bis(trifluoromethylsulfonyl)imide (IL-0045-HP)	bromide (IL-0037-HP)
1-Ethyl-3-methylimidazolium	1-Butylpyridinium	1,3-Dimethylimidazolium iodide
diethylphosphate (IL-0052-HP)	bis(trifluoromethylsulfonyl)imide (IL-0213-HP)	(IL-0199-HP)
1,3-Dimethylimidazolium	1-Butyl-3-methylpyridinium	1-Ethyl-3-methylimidazolium
dimethylphosphate (IL-0053-HP)	bis(trifluoromethylsulfonyl)imide (IL-0216-HP)	iodide (IL-0048-HP)
Choline dihydrogenphosphate	1-Butyl-4-methylpyridinium	1-Methyl-3-propylimidazolium
(IL-0042-HP)	bis(trifluoromethylsulfonyl)imide (IL-0219-HP)	iodide (IL-0025-HP)
1-Ethyl-3-methylimidazolium	Trihexyltetradecylphosphonium	1-Butyl-3-methylimidazolium
ethylsulfate (IL-0033-HP)	bis(trifluoromethylsulfonyl)imide (IN-0021-HP)	iodide (IL-0051-HP)
1-Ethyl-3-methylimidazolium	1-Ethyl-3-methylimidazolium triflate	1-Hexyl-3-methylimidazolium
hydrogensulfate (IL-0091-HP)	(IL-0009-HP)	iodide (IL-0026-HP)
1-Ethyl-3-methylimidazolium acetate (IL-0189-TG)	1-Butyl-3-methylimidazolium triflate (IL-0013-HP)	1-Allyl-3-methylimidazolium iodide (IL-0231-HP)
Ethylammonium nitrate (IL-0043-SG)		

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# 8 Community

### **IOLITEC@ Social Media**



Please follow IOLITEC at Facebook or connect yourself with IOLITEC's team at LinkedIn!

We invite you to become a member of the **Ionic Liquids group** on Facebook. Researchers, students, professionals from industry are welcome! From time to time we'll inform about latest publications on Facebook or we are open for any type of discussions!

### **Our current discussion on Facebook:**

How does the ionic liquids conference of the future looks like?



## Ionic Liquids @ Youtube:

### Ionic Liquids (German Language):

Prof. Dr. P. Wasserscheid explains the advantages of ionic liquids at the 20th anniversary of the foundation of the Deutsche Bundesstiftung Umwelt e.V.,

http://www.youtube.com/watch?v=3rnubz10-Ns

# <u>Ionic Liquids: Syrupy solvents promise new efficient ways to generate,</u> <u>store, and use energy (English Language):</u>

Dr. J. F. Wishart from Brookhaven National Lab explains the advantages and possibilities for the generations and storage of energy.

http://www.youtube.com/watch?v=MGl9g7Ob3fA

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### Lithium Battery Burnout:

An impressive example what might happen if a battery overheats. May ionic liquids help?

http://www.youtube.com/watch?v=jjAtBiTSsKY

### Non inflammability of ionic liquids:

Just a rhetorical question: A simple demonstration that (some) ionic liquids, that may be interesting electrolytes for batteries, are non flammable, recorded in our own labs.

http://www.youtube.com/watch?v=1LNzgC2ufaI

### Missed a conference? Here's our summary:

### Insight from the STLE Annual Meeting, May 15-19, 2011, Atlanta

In May 2011 the 66th annual meeting of the Society of Tribologists and Lubrication Engineers (STLE) took place at the Hilton in Atlanta. During the 4 day event more than 400 papers were presented to over 1000 participants from industry and academia and the newest developments in the field of tribology were presented. Unfortunately ionic liquids have not yet found their way into this conference as it was the case at the 17th International Colloquium Tribology held in January 2010 in Ostfildern/Germany, where a complete session was dedicated to the use of ionic liquids in lubrication.

Nevertheless 3 presentations directly addressed the use of ionic liquids in lubrication and each of these presentations has received a lot of interest from the audience.

The first presentation was given by Dr. Doerr from AC2T who discussed the thermaloxidative stability of ionic liquids and determined the degradation products of aged ionic liquids by different mass spectroscopic techniques. The results from these measurements were used to design and formulate new lubricants for long-term lubrication.

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In the second Presentation Dr. Beyersdorff (IoLiTec Inc.) gave a general introduction into ionic liquids and presented the use of ionic liquids in lubrication. In addition Dr. Beyersdorff presented IoLiTec's recent results in the stabilization of nanomaterial dispersions in water using ionic liquids as stabilizing agents. With the developed technique IoLiTec is able to manufacture dispersions of a variety of carbon allotropes in water with comparably low concentrations of ionic liquids as the dispersing agents.

During the third presentation Dr. Sutor reviewed the first ten years of work on ionic liquids in lubrication and discussed the use of ionic liquids as base oils for different applications.

Hopefully the interest and research in ionic liquids in the field of lubrication will increase until the next annual STLE meeting, providing enough interest and demand for a separate ionic liquids session.

# Impressions from the 1st Conference on Ionic Liquids for Separation and Purification Technologies (ILSEPT), September 4th-7th, Sitges, Spain

The aim of the "First International Conference on Ionic Liquids in Separation and Purification Technologies" was to provide a forum for people from academia and industry to share and discuss the cutting edge results that were obtained over the last years in establishing innovative separation and purification technologies that exploit the unique solvent properties of ionic liquids.

The conference was held at the Sitges resort village, some 35 km south of Barcelona. The weather was definitely on the side of the organizers from Elsevier, who did a wonderful job, and helped to keep the over 200 participants within the rooms of the convention centre of the Melia Sitges Hotel. The scientific program was split in two sessions in parallel over 3 days, with invited lectures from Prof. Richard Noble, (University of Colorado, USA, Title: Ionic liquids in membrane separations), Prof. Ilkka Kilpelainen, (University of Helsinki, Finland, Title: Ionic liquids in wood biorefining - possibilities and challenges), Prof. Dr. Bernd Jastorff, (University of Bremen, Germany, Title: Health, Safety and Environmental Aspects of Ionic Liquids in

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Separation Processes) and Dr. Wytze Meindersma, (TU-Eindhoven) together with Dr. Uwe Vagt, (BASF) Title: Opportunities and Limitations of Ionic Liquids in Extractive Distillation.

A big part of the program was allocated to  $CO_2$ -capture, resulting in two full sessions and over 12 presentations on this subject. Another important topic was extraction, recycling and purification of ionic liquids, for all of which industrial scale application is now available.







Both presentations, Dr. Schubert's on thermal fluids and Dr. Iliev's on sorption cooling were received well by the audience. If you are interested in a copy of the talks please contact us at <u>science@iolitec.de</u>

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#### Insights from COIL-4, June 15-18, 2011, Washington D.C., USA

By Tom F. Beyersdorff.

For the first time in the history of the COIL conference series the world's largest conference on ionic liquids was held in the USA. The venue of this 4 day event was the Hilton Crystal City Hotel in Arlington/Virgina, which is located just minutes away from all the sightseeing highlights of Washington D.C. The conference was organized by Dr. Robin Rogers from The University of Alabama in co-operation with the American Chemical Society and hosted more than 400 researchers from academia and industry. The scientific conference program included 8 plenary lectures, 35 keynote and featured lectures and a large number of contributed talks. The social events as well as the 3 poster sessions provided plenty of time for interactions with researchers from around the world and gave time for networking opportunities. In addition an exhibition with 8 companies accompanied the conference. IOLITEC was proud to be Gold Sponsor and exhibitor at the COIL-4 conference.

IOLITEC contributed two presentations to the conference program. In the first presentation Dr. Schubert talked about "Ionic Liquids – Solvents for the size controlled Synthesis and Stabilization of Nanomaterials" and presented IOLITEC's recent results on the stabilization of carbon allotrope dispersions in water using ionic liquids as stabilizing agents. The second presentation was given by Dr. Tom Beyersdorff on "Novel Electrolytes for Lithium-Ion Batteries". He presented IOLITEC's recent work on measuring physical properties of binary and ternary ionic liquid mixtures with and without LiNTf₂ additive as promising electrolytes for lithium-ion batteries. **Both presentations are available as PDF files on request at science@iolitec.de.** 

At this point IoLiTec would like to thank the organizers and their teams for organizing this exciting event. Special thanks should go out to all exhibitors and sponsors of COIL-4 who made this event possible with their financial contribution.

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### **Upcoming Exhibitions and Conferences:**

November 27th – December 1st, 2011: International Symposium on Molten Salts and Ionic Liquids, Cancun, Mexico (<u>www.flogen.com</u>)

### ACS National Meeting Spring 2012, San Diego/CA, USA, March 25-29, 2012

### http://www.acs.org

During the ACS Spring Meeting 2012 in San Diego two sessions will be held on Ionic Liquids.

The first session organized by Rani Jha has the title "**Green Solvents & Ionic Liquids as the Next Generation of Green Solvents**". The second session which is organized by Ann Visser (SRNL), Nick Bridges (SRNL) and Robin Rogers (The University of Alabama) is entitled "**Ionic Liquids: Science & Application**" Both sessions are part of the program of the Industrial and Engineering Chemistry Division.

In addition, a symposium in Honor of Robin Rogers who will become an Industrial & Engineering Chemistry Fellow will be held.

### Smart Coatings 2012, Orlando/FL, USA, February 22-24, 2012

### http://www.Smartcoatings.org

In February 2012 the Smart Coatings conference will be held in Orlando Florida.

IOLITEC will give a presentation entitled "**Ionic Liquids – Suitable Materials for** 

### Coating Technologies".

### **EUCHEM 2012**, Celtic Manor, Wales, August 5th-19th, 2012.

### http://www.euchem2012.org

The EUCHEM 2012 takes place at Celtic Manor, a really nice location. The EUCHEMseries brings together two separated twins: Molten salts and ionic liquids.

# Please keep us informed about other interesting events we could highlight in Ionic Liquids Today.

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### <u>Imprint</u>

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