

This paper is published as part of a PCCP Themed Issue on:
Physical Chemistry of Ionic Liquids

Guest Editor: Frank Endres (Technical University of Clausthal, Germany)

Editorial

Physical chemistry of ionic liquids

Phys. Chem. Chem. Phys., 2010, DOI: [10.1039/c001176m](https://doi.org/10.1039/c001176m)

Perspectives

Ionicity in ionic liquids: correlation with ionic structure and physicochemical properties

Kazuhide Ueno, Hiroyuki Tokuda and Masayoshi Watanabe, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921462n](https://doi.org/10.1039/b921462n)

Design of functional ionic liquids using magneto- and luminescent-active anions

Yukihiro Yoshida and Gunzi Saito, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920046k](https://doi.org/10.1039/b920046k)

Accelerating the discovery of biocompatible ionic liquids

Nicola Wood and Gill Stephens, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b923429b](https://doi.org/10.1039/b923429b)

Ionic liquids and reactions at the electrochemical interface

Douglas R. MacFarlane, Jennifer M. Pringle, Patrick C. Howlett and Maria Forsyth, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b923053j](https://doi.org/10.1039/b923053j)

Photochemical processes in ionic liquids on ultrafast timescales

Chandrasekhar Nese and Andreas-Neil Unterreiner, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b916799b](https://doi.org/10.1039/b916799b)

At the interface: solvation and designing ionic liquids

Robert Hayes, Gregory G. Warr and Rob Atkin, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920393a](https://doi.org/10.1039/b920393a)

Ionic liquids in surface electrochemistry

Hongtao Liu, Yang Liu and Jinghong Li, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921469k](https://doi.org/10.1039/b921469k)

Discussion

Do solvation layers of ionic liquids influence electrochemical reactions?

Frank Endres, Oliver Höfft, Natalia Borisenko, Luiz Henrique Gasparotto, Alexandra Prowald, Rihab Al-Salman, Timo Carstens, Rob Atkin, Andreas Bund and Sherif Zein El Abedin, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b923527m](https://doi.org/10.1039/b923527m)

Papers

Plasma electrochemistry in ionic liquids: deposition of copper nanoparticles

M. Brettholle, O. Höfft, L. Klarhöfer, S. Mathes, W. Maus-Friedrichs, S. Zein El Abedin, S. Krischok, J. Janek and F. Endres, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b906567a](https://doi.org/10.1039/b906567a)

Size control and immobilization of gold nanoparticles stabilized in an ionic liquid on glass substrates for plasmonic applications

Tatsuya Kameyama, Yumi Ohno, Takashi Kurimoto, Ken-ichi Okazaki, Taro Uematsu, Susumu Kuwabata and Tsukasa Torimoto, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b914230d](https://doi.org/10.1039/b914230d)

Electrostatic properties of liquid 1,3-dimethylimidazolium chloride: role of local polarization and effect of the bulk

C. Krekeler, F. Dommert, J. Schmidt, Y. Y. Zhao, C. Holm, R. Berger and L. Delle Site, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b917803c](https://doi.org/10.1039/b917803c)

Selective removal of acetylenes from olefin mixtures through specific physicochemical interactions of ionic liquids with acetylenes

Jung Min Lee, Jelliarko Palgunadi, Jin Hyung Kim, Srun Jung, Young-seop Choi, Minserk Cheong and Hoon Sik Kim, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b915989d](https://doi.org/10.1039/b915989d)

Screening of pairs of ions dissolved in ionic liquids

R. M. Lynden-Bell, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b916987c](https://doi.org/10.1039/b916987c)

Double layer, diluent and anode effects upon the electrodeposition of aluminium from chloroaluminate based ionic liquids

Andrew P. Abbott, Fulian Qiu, Hadi M. A. Abood, M. Rostom Ali and Karl S. Ryder, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b917351j](https://doi.org/10.1039/b917351j)

A comparison of the cyclic voltammetry of the Sn/Sn(II) couple in the room temperature ionic liquids *N*-butyl-*N*-methylpyrrolidinium dicyanamide and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide: solvent induced changes of electrode reaction mechanism

Benjamin C. M. Martindale, Sarah E. Ward Jones and Richard G. Compton, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920217j](https://doi.org/10.1039/b920217j)

Ionic liquids through the looking glass: theory mirrors experiment and provides further insight into aromatic substitution processes

Shon Glyn Jones, Hon Man Yau, Erika Davies, James M. Hook, Tristan G. A. Youngs, Jason B. Harper and Anna K. Croft, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b919831h](https://doi.org/10.1039/b919831h)

Nitrile-functionalized pyrrolidinium ionic liquids as solvents for cross-coupling reactions involving *in situ* generated nanoparticle catalyst reservoirs

Yugang Cui, Ilaria Biondi, Manish Chaubey, Xue Yang, Zhaofu Fei, Rosario Scopelliti, Christian G. Hartinger, Yongdan Li, Cinzia Chiappe and Paul J. Dyson, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920025h](https://doi.org/10.1039/b920025h)

Ionic liquid as plasticizer for europium(III)-doped luminescent poly(methyl methacrylate) films

Kyra Lunstroot, Kris Driesen, Peter Nockemann, Lydie Viau, P. Hubert Mutin, André Vioux and Koen Binnemans, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920145a](https://doi.org/10.1039/b920145a)

***Ab initio* study on S₂ reaction of methyl *p*-nitrobenzenesulfonate and chloride anion in [mim][PF₆]**

Seigo Hayaki, Kentaro Kido, Hirofumi Sato and Shigeyoshi Sakaki, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920190b](https://doi.org/10.1039/b920190b)

Influence of imidazolium bis(trifluoromethylsulfonylimide)s on the rotation of spin probes comprising ionic and hydrogen bonding groups

Veronika Strehmel, Hans Rexhausen and Peter Strauch, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920586a](https://doi.org/10.1039/b920586a)

Thermo-solvatochromism in binary mixtures of water and ionic liquids: on the relative importance of solvophobic interactions

Bruno M. Sato, Carolina G. de Oliveira, Clarissa T. Martins and Omar A. El Seoud, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921391k](https://doi.org/10.1039/b921391k)

[Patterns of protein unfolding and protein aggregation in ionic liquids](#)

Diana Constatinescu, Christian Herrmann and Hermann Weingärtner, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921037g](#)

[High vacuum distillation of ionic liquids and separation of ionic liquid mixtures](#)

Alasdair W. Taylor, Kevin R. J. Lovelock, Alexey Deyko, Peter Licence and Robert G. Jones, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920931j](#)

[Designer molecular probes for phosphonium ionic liquids](#)

Robert Byrne, Simon Coleman, Simon Gallagher and Dermot Diamond, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920580b](#)

[States and migration of an excess electron in a pyridinium-based, room-temperature ionic liquid: an *ab initio* molecular dynamics simulation exploration](#)

Zhiping Wang, Liang Zhang, Robert I. Cukier and Yuxiang Bu, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921104g](#)

[J-aggregation of ionic liquid solutions of meso-tetrakis\(4-sulfonatophenyl\)porphyrin](#)

Maroof Ali, Vinod Kumar, Sheila N. Baker, Gary A. Baker and Siddharth Pandey, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920500d](#)

[Spontaneous product segregation from reactions in ionic liquids: application in Pd-catalyzed aliphatic alcohol oxidation](#)

Charlie Van Doorslaer, Yves Schellekens, Pascal Mertens, Koen Binnemans and Dirk De Vos, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920813p](#)

[Electrostatic interactions in ionic liquids: the dangers of dipole and dielectric descriptions](#)

Mark N. Kobrak and Hualin Li, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920080k](#)

[Insights into the surface composition and enrichment effects of ionic liquids and ionic liquid mixtures](#)

F. Maier, T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid and H.-P. Steinrück, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920804f](#)

[Ionic liquids and reactive azeotropes: the continuity of the aprotic and protic classes](#)

José N. Canongia Lopes and Luís Paulo N. Rebelo, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b922524m](#)

[A COSMO-RS based guide to analyze/quantify the polarity of ionic liquids and their mixtures with organic cosolvents](#)

José Palomar, José S. Torrecilla, Jesús Lemus, Víctor R. Ferro and Francisco Rodríguez, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920651p](#)

[Solid and liquid charge-transfer complex formation between 1-methylnaphthalene and 1-alkyl-cyanopyridinium bis\(trifluoromethyl\)sulfonyl imide ionic liquids](#)

Christopher Hardacre, John D. Holbrey, Claire L. Mullan, Mark Nieuwenhuyzen, Tristan G. A. Youngs, Daniel T. Bowron and Simon J. Teat, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921160h](#)

[Blending ionic liquids: how physico-chemical properties change](#)

F. Castiglione, G. Raos, G. Battista Appetecchi, M. Montanino, S. Passerini, M. Moreno, A. Famulari and A. Mele, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921816e](#)

[NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids](#)

Jinming Zhang, Hao Zhang, Jin Wu, Jun Zhang, Jiasong He and Junfeng Xiang, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920446f](#)

[Electrochemical carboxylation of *m*-chloroethylbenzene in ionic liquids compressed with carbon dioxide](#)

Yusuke Hiejima, Masahiro Hayashi, Akihiro Uda, Seiko Oya, Hiroyuki Kondo, Hisanori Senboku and Kenji Takahashi, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920413j](#)

[A theoretical study of the copper\(I\)-catalyzed 1,3-dipolar cycloaddition reaction in dabco-based ionic liquids: the anion effect on regioselectivity](#)

Cinzia Chiappe, Benedetta Mennucci, Christian Silvio Pomelli, Angelo Sanzone and Alberto Marra, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921204c](#)

[Fragility, Stokes–Einstein violation, and correlated local excitations in a coarse-grained model of an ionic liquid](#)

Daun Jeong, M. Y. Choi, Hyung J. Kim and YounJoon Jung, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921725h](#)

[Reactions of excited-state benzophenone ketyl radical in a room-temperature ionic liquid](#)

Kenji Takahashi, Hiroaki Tezuka, Shingo Kitamura, Toshifumi Satoh and Ryuzi Katoh, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920131a](#)

[In search of pure liquid salt forms of aspirin: ionic liquid approaches with acetylsalicylic acid and salicylic acid](#)

Katharina Bica, Christiaan Rijkssen, Mark Nieuwenhuyzen and Robin D. Rogers, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b923855g](#)

[Nanocomposites of ionic liquids confined in mesoporous silica gels: preparation, characterization and performance](#)

Juan Zhang, Qinghua Zhang, Xueli Li, Shimin Liu, Yubo Ma, Feng Shi and Youquan Deng, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920556j](#)

[An ultra high vacuum-spectroelectrochemical study of the dissolution of copper in the ionic liquid \(*N*-methylacetate\)-4-picolinium bis\(trifluoromethylsulfonyl\)imide](#)

Fulian Qiu, Alasdair W. Taylor, Shuang Men, Ignacio J. Villar-Garcia and Peter Licence, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b924985k](#)

[Understanding siloxane functionalised ionic liquids](#)

Heiko Niedermeyer, Mohd Azri Ab Rani, Paul D. Lickiss, Jason P. Hallett, Tom Welton, Andrew J. P. White and Patricia A. Hunt, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b922011a](#)

[On the electrodeposition of tantalum from three different ionic liquids with the bis\(trifluoromethyl sulfonyl\) amide anion](#)

Adriana Ispas, Barbara Adolphi, Andreas Bund and Frank Endres, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b922071m](#)

[Solid-state dye-sensitized solar cells using polymerized ionic liquid electrolyte with platinum-free counter electrode](#)

Ryuji Kawano, Toru Katakabe, Hironobu Shimosawa, Md. Khaja Nazeeruddin, Michael Grätzel, Hiroshi Matsui, Takayuki Kitamura, Nobuo Tanabe and Masayoshi Watanabe, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b920633g](#)

[Dynamics of ionic liquid mediated quantised charging of monolayer-protected clusters](#)

Stijn F. L. Mertens, Gábor Mészáros and Thomas Wandlowski, *Phys. Chem. Chem. Phys.*, 2010, DOI: [10.1039/b921368f](#)

Plasma electrochemistry in ionic liquids: deposition of copper nanoparticles

M. Brettholle,^a O. Höfft,^a L. Klarhöfer,^b S. Mathes,^b W. Maus-Friedrichs,^b S. Zein El Abedin,^a S. Krischok,^c J. Janek^d and F. Endres^{*a}

Received 1st April 2009, Accepted 8th July 2009

First published as an Advance Article on the web 5th August 2009

DOI: 10.1039/b906567a

We report on the synthesis of copper nanoparticles in two different water- and air-stable ionic liquids using plasma electrochemical deposition. The copper nanoparticles were deposited in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]Tf₂N) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf₂N). To get information on the dimensions of the particles made, we have applied *in situ* transmission electron microscopy (TEM) (particles in ionic liquid). The chemical composition was investigated by *ex situ* X-ray photoelectron spectroscopy (XPS). We found that the copper particles produced in [Py_{1,4}]Tf₂N were larger in size compared to the particles obtained in [EMIm] Tf₂N (roughly 20 vs. 10 nm). The chemical composition of the particle surface differs too. In both cases the particles are partly oxidised leading to a CuO shell, but the particles obtained in [Py_{1,4}]Tf₂N carry a lot of residues from the ionic liquid.

1. Introduction

Metal nanoparticles have found extensive attention due to their unique electronic properties, chemical reactivity and potential applications in optical, magnetic or electronic devices and in catalysis. As the particle size approaches the nanometre scale, the number of atoms in the grain boundaries at the particle surface increases. This leads to dramatic effects on the physical properties as well as on the catalytic activity of the bulk material. A number of different methods have been developed to prepare metal nanoparticles, such as chemical,¹ photochemical,² and electrochemical ones.³

Since metal nanoparticles are often quite reactive, inert gas environments and addition of stabilising agents, such as polymers and surfactants, are usually employed in preparation.^{4,5} However, for the optimal application, a pure metal colloid solution is preferred because the additives can interfere with the particle surface, inducing a negative effect on the properties.

Ionic liquids have successfully been employed for the synthesis and stabilisation of metal nanoparticles without the addition of stabilising agents.^{6–9} It was reported⁶ that very fine and stable nanoparticles of Ir(0) and Rh(0) with 2.0 nm–2.5 nm diameter can be synthesised in the dry ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate from [Ir(cod)Cl]₂ (cod = 1,5-cyclooctadiene) and RhCl₃·3H₂O, respectively,

by chemical reduction. The isolated nanoparticles can be re-dispersed in the ionic liquid, in acetone, or used in solventless conditions for the liquid–liquid biphasic, homogeneous or heterogeneous hydrogenation of arenes under mild reaction conditions (75 °C and 4 atm).⁶ Stable Pt(0) nanoparticles of 2–3 nm diameter and with a narrow size distribution can be easily obtained *via* decomposition of Pt-organometallic precursors, *e.g.*, Pt₂(dba)₃ (dba = bis-dibenzylidene acetone), in 1-butyl-3-methylimidazolium hexafluorophosphate.⁷ These nanoparticles are recyclable catalytic systems for the solventless or biphasic hydrogenation of alkenes and arenes under mild reaction conditions. Itoh *et al.*⁸ reported the synthesis and functionalisation of gold nanoparticles modified with ionic liquids based on the imidazolium cation. Gold and platinum nanoparticles with diameters of 2–3.5 and 2–3.2 nm, respectively, can also be synthesised using novel thiol-functionalised ionic liquids (TFILs).⁹

As ionic liquids have very low vapour pressures (at or near room temperature typically between 10^{−9} and 10^{−8} Pa and at 100 °C in the region of 10^{−4}–10^{−2} Pa depending on the particular liquid), they can be employed in vacuum experiments as fluid substrates or solvents. Torimoto *et al.* reported *e.g.* that very fine gold nanoparticles can be obtained by sputter deposition of gold onto ionic liquids.¹⁰

Quite recently we have reported that free, isolated silver nanoparticles can be obtained in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [EMIm]TfO by applying plasma as a mechanically contact-free electrode.^{11,12a,12b} We could show that ionic liquids are well suitable as electrolytes for plasma electrochemical processes, as their vapour pressure is extremely low, thus facilitating stable and homogeneous plasmas.¹¹ The plasma electrochemical approach is hitherto the only electrochemical route to the synthesis of free nanoparticles. A glow discharge plasma was employed as a

^a Institute of Particle Technology, Clausthal University of Technology, Robert-Koch-Str, 42, D-38678 Clausthal-Zellerfeld, Germany. E-mail: frank.endres@tu-clausthal.de

^b Institut für Physik und Physikalische Technologien, Clausthal University of Technology, Leibnizstr, 4, D-38678 Clausthal-Zellerfeld, Germany

^c Institute of Micro- and Nanotechnologies and Institute of Physics, TU Ilmenau, P.O. Box 100565, 98684 Ilmenau, Germany

^d Physikalisch-Chemisches Institut, Justus-Liebig-University Gießen, Heinrich-Buff-Ring 58, D- 35392 Giessen, Germany

gaseous electrode and the other (solid) electrode was immersed in the ionic liquid containing the desired metal salt. This method was also successfully applied for the reduction of HAuCl_4 and PdCl_2 in 1-butyl-3-methylimidazolium tetrafluoroborate $[\text{BMIm}]\text{BF}_4$ by Xie and Liu.¹³

In this paper we report on the synthesis of free, dispersed copper nanoparticles in the air- and water-stable ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ($[\text{EMIm}]\text{Tf}_2\text{N}$) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ($[\text{Py}_{1,4}]\text{Tf}_2\text{N}$), by employing plasmas as mechanically contact-free electrodes. Cu nanoparticles are interesting due to their catalytic and electrocatalytic properties. Nanocrystalline compact copper layers with an average crystallite size of about 50 nm can *e.g.* be electrodeposited without additives in the ionic liquids $[\text{Py}_{1,4}]\text{TfO}^{12a}$ and $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$.¹⁴ As ionic liquids can—in our experience—strongly influence the particle size of electrochemically made materials it raises the question to which extent the ionic liquid influences the particle size in the plasma electrochemical experiment.

2. Experimental

2.1 Preparation of the samples

Copper was dissolved electrochemically in $[\text{EMIm}]\text{Tf}_2\text{N}$ or in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ from a copper wire (Alfa Aesar: 99.999%) by using salt bridge separating working and counter electrode compartments. The concentration and the oxidation state of copper were determined with Faraday's laws. The benefit of this preparation method is that the copper is dissolved in the Cu^{1+} state in the liquid. Another hint for the oxidation state is the colourlessness of both prepared solutions, because Katase *et al.* show that a Cu^+ trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)amide solution is colorless in contrast to dissolved Cu^{2+} .¹⁵ Thus, there is just one reduction step from Cu^{1+} to Cu needed and the oxidative attack of Cu^{2+} on freshly made Cu nanoparticles leading to Cu^+ is avoided. At room temperature the efficiency of copper oxidation to Cu^+ is 100% at low overvoltages, providing that extremely pure ionic liquids are used. Two copper concentrations were investigated, 62 mmol L^{-1} in both liquids and 24 mmol L^{-1} in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$. Cyclic voltammetry has shown that it is possible to electrodeposit copper from both prepared solutions. The results are in good agreement with our previous results.¹⁴ The setup for the particle production consists of a dc plasma reactor with controlled argon atmosphere inside an inert gas glove box (OMNI-LAB from Vacuum Atmospheres). The plasma reactor consists of a glass cell with usual KF (Klein Flange) vacuum connectors. The glass cell is made of two parts, connected with KF vacuum parts, which facilitates filling of the cell. One of the two platinum electrodes is fused in the cell, the other one is welded on a feed through flange. The cell is evacuated with a common rotary pump. The control of the argon gas flow for the plasma (we use the argon directly from the glove box, oxygen content < 1 ppm) is done with an easy to handle dosing valve (Pfeiffer Company). The plasma was ignited with a common dc power supply. All experiments were done at room temperature.

2.2 Spectroscopic and microscopic measurements

The particle size of the copper particles was determined by transmission electron microscopy (TEM). The TEM used is a JEOL JEM-2100 and the acceleration voltage was 120 kV. For the TEM measurements a small drop of the ionic liquid with the produced nanoparticles was placed onto a TEM grid. The chemical composition of the used ionic liquids, with and without Cu, as well as that of the particles was analysed *ex situ* with X-ray photoelectron spectroscopy (XPS). For the *ex situ* measurements the particles were separated by centrifugation and washed several times with acetone to remove most of the ionic liquid. After washing, a droplet of acetone with highly concentrated particles was put onto a doped oxidised silicon (100) wafer. Desorbing of the acetone leads to a thin layer of particles on the silicon substrate. XPS was performed using a commercial X-ray source (Fisons XR3E2-324). The spectra were recorded under UHV conditions ($\sim 10^{-8}$ Pa), using Al-K_α primary radiation (14 kV, 20 mA, 1486.6 eV). After acquisition of the spectra, various data handling procedures were carried out on the raw data. Survey (broad energy range, low resolution) spectra were collected to determine the elemental composition of the sample surfaces. High resolution spectra (resolution of 1.5 eV) of the Cu 2p core levels were collected to determine chemical/bonding states. All given values in eV are referenced to the C 1s peak (in this case C 1s = 285 eV). XPS is a highly surface sensitive technique, providing information on the outermost 5–10 nm of the sample. XPS peaks were fitted mathematically using overlapping Gauss profiles. The fitting was performed applying OriginPro7 including the Peak Fitting Module (OriginLab Corporation).

3. Results and discussion

3.1 Copper in $[\text{EMIm}]\text{Tf}_2\text{N}$

An appropriate amount of the ionic liquid $[\text{EMIm}]\text{Tf}_2\text{N}$ containing 62 mmol L^{-1} Cu^+ (2 ml) was put in the glass cell and carefully out-gassed at 0.1 Pa. Then the plasma was ignited at a pressure of 100 Pa at a current of 10 mA. In our experiments the electrode above the liquid acted as a cathode and the other one as an anode. After ignition the voltage drops immediately from 1000 V to 450–500 V. A typical plasma experiment (30 minutes) is shown in Fig. 1. Shortly after ignition (Fig. 1b) a dark cloud appears at the plasma–ionic liquid interface. With ongoing time this cloud grows downwards the cell. The rest of the liquid stays clear. At the anode some small bubbles are formed. This is likely to be due to decomposition of the liquid at the anode of the cell.

Fig. 2 shows a TEM image of the obtained copper nanoparticles inside the used ionic liquid. Small particles with an average size of about 11 nm are clearly seen. Unfortunately a better resolution could not yet be achieved and thus electron diffraction pattern could not be obtained. This might be due to the ionic liquid layer adsorbed on the particles. Recent AFM studies from Atkin *et al.* show that ionic liquids can be strongly adsorbed to metallic or non-metallic surfaces delivering several solvation layers.¹⁶ $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ is adsorbed on Au(111) up to 3 times more strongly than $[\text{EMIm}]\text{Tf}_2\text{N}$.¹⁷ Thus, in all

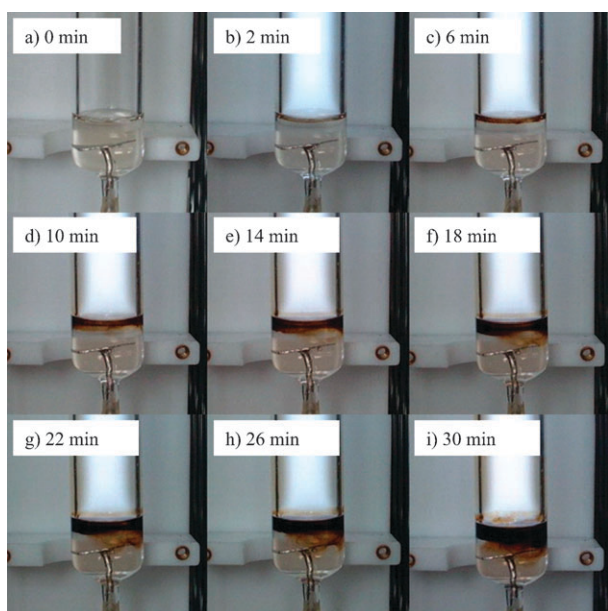


Fig. 1 Plasma experiment (30 min) Cu^+ -[EMIm]Tf₂N.

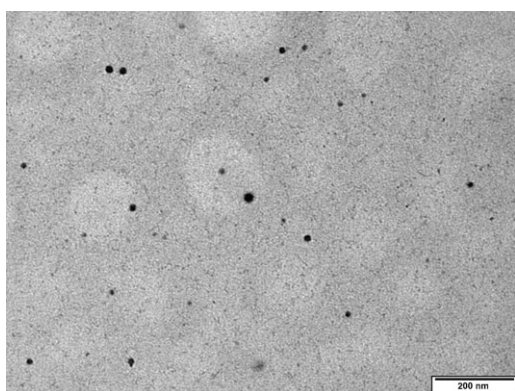


Fig. 2 TEM image of Cu particles in [EMIm]Tf₂N.

interface reactions in/with ionic liquids solvation layers have to be expected, which might be quite difficult to remove. On the other hand these solvation layers might have a varying stabilising effect on the particles and thus vary the particle size. An XPS analysis of a thick and closed layer of particles as deduced from the missing signal of the Si wafer support (see Fig. 3) reveal that the major spectral contributions consist of copper, carbon, oxygen and fluorine. Carbon and fluorine are due to some residues from the ionic liquid. Heating of the film to 400 °C at a pressure of $\sim 10^{-8}$ Pa removes the carbon nearly completely and most of the fluorine. Under these conditions the bulk phase of the ionic liquid is evaporated. The oxygen part decreased as well but not as strongly as the other elements.

The XPS survey spectrum of such a prepared particle film after heating in vacuum to 400 °C is presented in Fig. 3 together with a spectrum of a copper sheet. Detailed spectra of the Cu 2p_{3/2} peak of the heated particles are shown in Fig. 4. The dotted line represents the original data, peak fits of the individual components are displayed using coloured solid

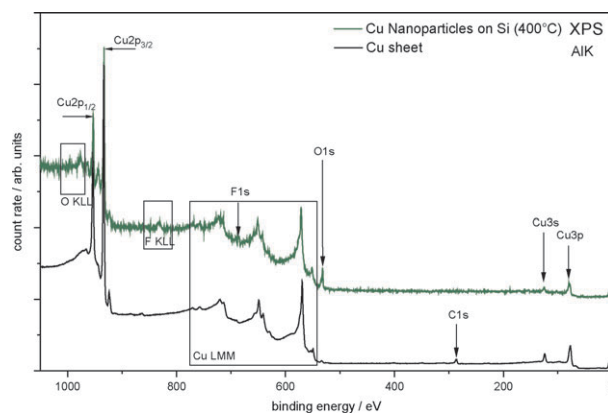


Fig. 3 XPS survey spectrum of a Cu nanoparticle film ([EMIm]Tf₂N) after heating to 400 °C compared to clean copper sheet.

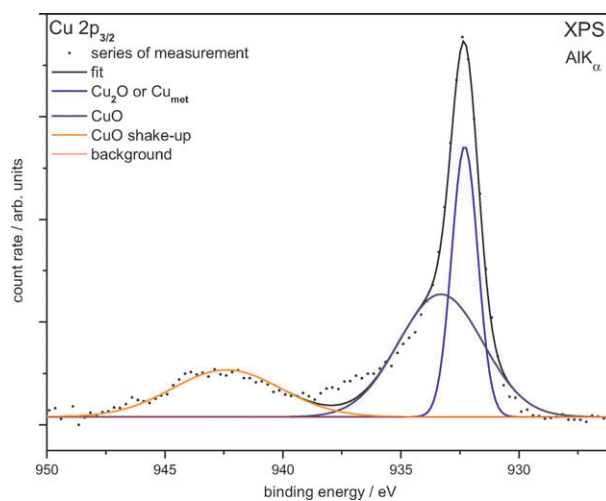


Fig. 4 XPS Cu 2p_{3/2} region of the nanoparticle film ([EMIm]Tf₂N) after heating to 400 °C.

lines, while their sum is shown as the black solid line. The Cu 2p_{3/2} peak comprises two contributions with binding energies at 932.3 (blue line) and 933.3 eV (dark blue line). The additional peak around 943 eV (orange line) in the Cu 2p_{3/2} peak region is due to a shake up process (the ejected core electron simultaneously transfers some of its energy to another electron). This structure is an indication of CuO,^{18,19} because this shake up is due to the open 3d⁹ shell of Cu²⁺ (see for comparison the detailed copper 2p spectra in Fig. 6). The energetic peak position for the Cu 2p_{3/2} around 933.3 eV is in very good agreement with the value given in the literature for CuO.¹⁹ The structure at 932.3 eV could be either assigned to clean copper or to copper in Cu₂O. In vacuum CuO can be easily reduced to Cu₂O.¹⁹ The change from CuO to Cu₂O could be seen in the strong decrease of the shake up peaks in the Cu 2p_{3/2} peak region. Under the assumption that no contribution of metallic copper or Cu₂O is visible in the detail spectra of the Cu 2p region for the as-deposited (unheated case) particles, we could calculate a minimum CuO film thickness of about 3 nm for the particles. This is just a rough approximation, but it seems possible that the smaller particles

are completely oxidised and some have an oxide shell. This oxide layer is most likely due to oxygen attack during (unavoidable) *ex situ* handling of the samples under air leading to CuO. Currently it is an open question whether the particles are completely oxidised or consist of a metallic core and an oxide shell. For electrodeposited aluminium and silicon nanoparticle films from ionic liquids it was shown that these particles have a core shell structure.²⁰ In order to obtain direct information on the chemical composition of the ionic liquids and possible changes by the plasma treatment XPS experiments on ionic liquids surfaces containing the particles itself have been performed (Fig. 5). Briefly, the as-deposited [EMIm]Tf₂N exhibits no unexpected elements and the relative carbon, nitrogen, sulfur, oxygen and fluorine peak areas reflect the stoichiometry of the ionic liquid as previously reported.²¹ The detailed spectrum of the Cu 2p_{3/2} peak of the particles in the liquid is shown in Fig. 6. The spectrum for the particles in the liquid looks like CuO in comparison with clean copper, oxidised copper and a CuO reference spectrum. As there was a quite long *ex situ* transfer time between the production and the measurements it is an open question whether an *in situ* or an

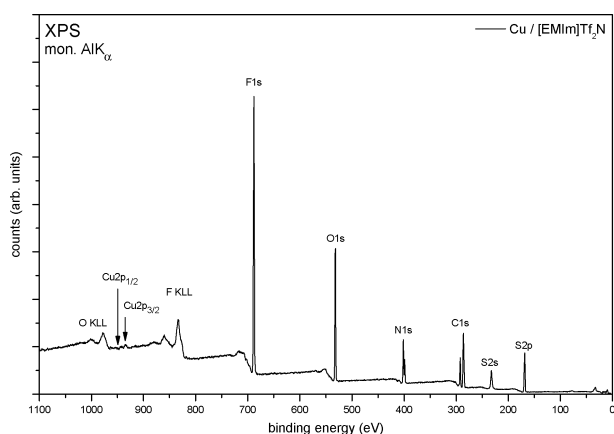


Fig. 5 XPS survey spectrum of [EMIm]Tf₂N containing the copper particles after the plasma process.

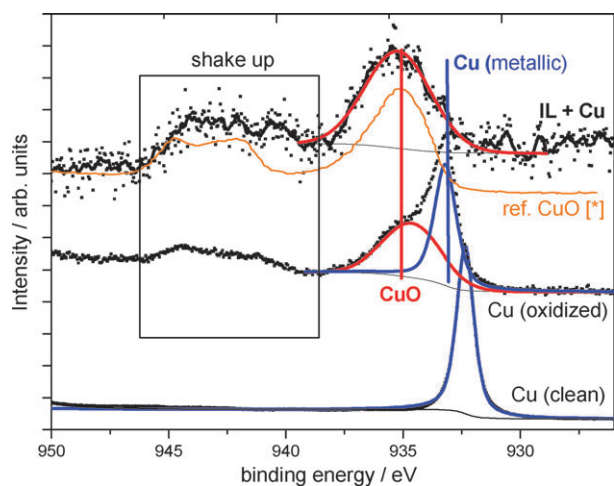


Fig. 6 XPS Cu 2p_{3/2} region of the nanoparticles in [EMIm]Tf₂N, Moulder *et al.*²⁵

ex situ oxygen attack is responsible for the oxidation of the copper at this point. Detailed XPS studies on the influence of the dissolved copper and copper ions on the surface properties of the ionic liquids will be presented elsewhere.²²

3.2 Copper in [Py_{1,4}]Tf₂N

The Cu-[Py_{1,4}]Tf₂N solution was prepared and subjected to plasma electrochemical reduction as in the case of the Cu⁺-[EMIm]Tf₂N solution. In contrast to [EMIm]Tf₂N an additional colour change could be observed during the plasma experiment. This is due to an interaction of the liquid with the plasma itself. Because of the higher viscosity of [Py_{1,4}]Tf₂N ($\eta \approx 80$ mPa s at room temperature²³) the cloud containing the particles moves more slowly downwards compared to [EMIm]Tf₂N ($\eta \approx 36$ mPa s²³). The corresponding TEM image is shown in Fig. 7. Again a high resolution image could not be acquired as the layer of the ionic liquid was too thick. The average diameter of the copper particles is 26 nm. Also in this case we could not get information on the crystallinity of the particles by electron diffraction. The XPS analysis of the copper particles exhibited some different features compared to the particles created in [EMIm]Tf₂N. The XPS survey spectrum of a vacuum heated film still shows (Fig. 8) contributions from fluorine, carbon, oxygen and sulfur. The particle film was not as dense as in the [EMIm] case; this explains the silicon 2s and

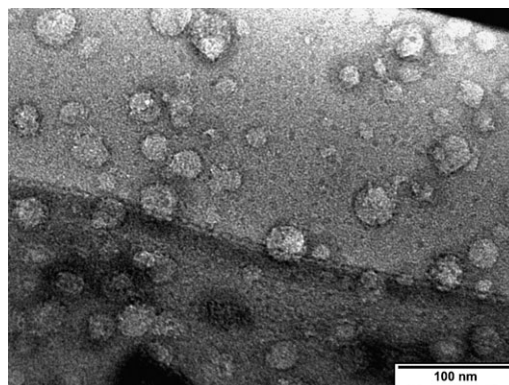


Fig. 7 TEM image of Cu particles in [Py_{1,4}]Tf₂N.

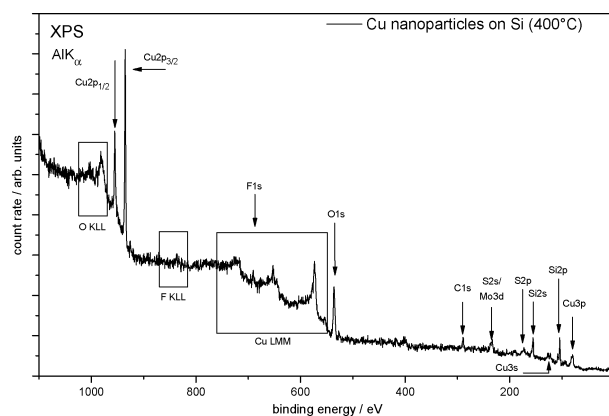


Fig. 8 XPS survey spectrum of a Cu nanoparticle film ([Py_{1,4}]Tf₂N) after heating to 400 °C.

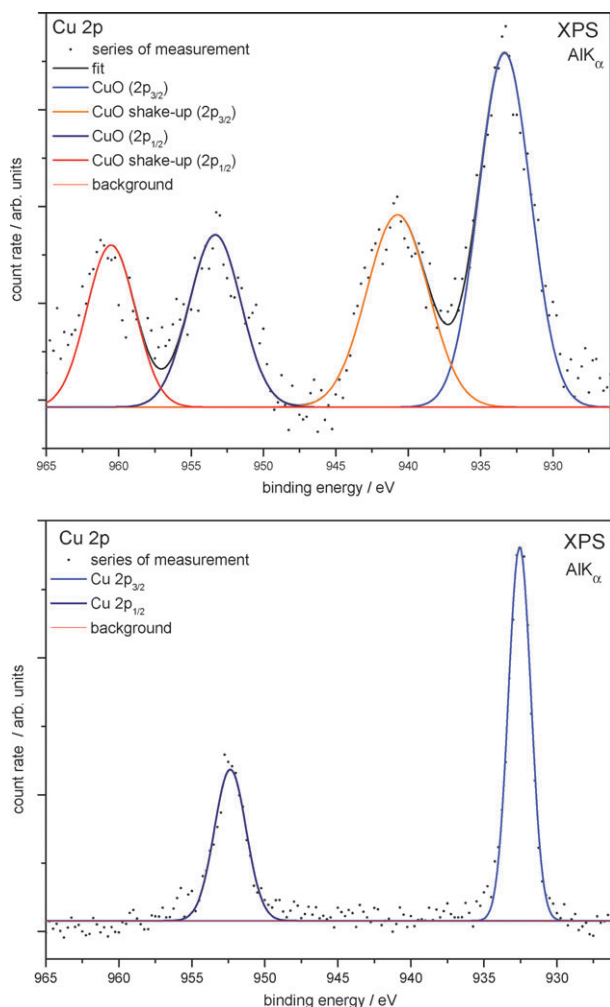


Fig. 9 XPS Cu 2p region of the nanoparticle film ([Py_{1,4}]Tf₂N) before and after heating to 400 °C.

2p peaks from the substrate in the survey spectrum. These fractions of residues, especially fluorine and sulfur, on the particles surfaces are another indication of a different interaction of the two liquids with the plasma and the copper. To some extent the contributions of oxygen and carbon have to be attributed to the silicon substrate, as heating to 400 °C is not sufficient to clean the wafer entirely. The detailed spectra of the Cu 2p peaks before and after heating are shown in Fig. 9. Again the dotted line represents the original data, peak fits of the individual components are displayed using coloured solid lines, while their sum is shown as the black solid line. Before and after heating the main Cu 2p_{3/2} (Cu 2p_{1/2}) structures (blue lines) consist of only one peak at different energetic positions 933.4 eV (953.4 eV) and 932.5 eV (952.4 eV), respectively. Additionally before heating the typical shake up peaks are visible at 940.8 eV (orange line) and 960.7 eV (red line). After heating the shake up peaks have completely vanished. Thus the oxidation state of the particles has changed. The purified particles consist of a high amount of CuO and by heating in vacuum they were, in contrast to the particles, produced in [EMIm]Tf₂N, completely reduced (most likely to Cu₂O). Under the same assumption as before, the as-deposited particles exhibited a minimum oxide film thickness of about 3 nm.

Thus it seems possible that most of the particles have, due to their larger size, an oxide shell. The XPS for the surface of the liquid analysis again provides no evidence for impurities and the peak areas well reflect the expected stoichiometry of the ionic liquid within the accuracy of this method. Moreover, no evidence for a modification of the ionic liquid by the Cu and the plasma treatment was observed. In contrast, to the Cu⁺-[EMIm]Tf₂N solution we have not been able to detect Cu so far.

3.3 Discussion

The interaction between plasma and Cu⁺ containing two different ionic liquid solutions delivers a similar but slightly different result, showing that the ionic liquid clearly influences the particle growth/size. Obviously the different physico-chemical properties of both employed liquids play a role in the interaction process. First, the particles prepared in [EMIm]Tf₂N are slightly smaller compared to [Py_{1,4}]Tf₂N (~11 nm vs. 26 nm). The particles are to a certain amount oxidised to CuO and Cu₂O in both cases, (in our opinion) due to a surface attack during the intensive *ex situ* treatment, although an *in situ* oxidation inside the reactor cannot be excluded totally. Earlier results on the electrodeposition of Cu-, Al- and Si-films from ionic liquids support this assumption.^{14,20} The different fractions of residues on the particles raise more questions, thus an interaction of the liquid with the plasma seems to play a role. The observed colour change during plasma treatment of [Py_{1,4}]Tf₂N supports the XPS findings for the deposited particles. At a first glance the decomposition of the [Py_{1,4}] cation might cause the colour change. However in ultrapure ionic liquids the [Py_{1,4}] cation is under typical electrochemical conditions roughly 700 mV more stable than the [EMIm] cation. It might be possible that the Cu⁺ ion has an influence on the IL decomposition. In the literature, there are two publications dealing with the interaction of cold plasmas with ionic liquids.^{13,24} Xie and Liu did not report any decomposition of [BMIm]BF₄-HAuCl₄ and [BMIm]BF₄-PdCl₂ solutions during plasma treatment as analysed with IR spectroscopy and NMR.¹³ In contrast, Baba *et al.* found a colour change of pure [BMIm]BF₄ through irradiation with 220 eV plasma ions.²⁴ The colour did not change when the liquid was irradiated with 20 eV plasma ions. The XPS measurements of the plasma treated ionic liquid vacuum interface of both liquids ([EMIm]Tf₂N and [Py_{1,4}]Tf₂N) with the dispersed particles have shown no difference between the untreated IL surface and the plasma treated one.

From our experience with electrochemical deposition of copper we would rather expect that the particles made in [EMIm]Tf₂N are wider in diameter than those made in [Py_{1,4}]Tf₂N. Both on mica and on Au(111) the ionic liquid [Py_{1,4}]Tf₂N is more strongly adsorbed than [EMIm]Tf₂N leading, in our opinion, to different grain sizes. Furthermore, from the TEM experiments reported here, there is strong evidence that [Py_{1,4}]Tf₂N is more strongly adsorbed on the particles than [EMIm]Tf₂N. Consequently, the particles made in [Py_{1,4}]Tf₂N should be smaller than those made from [EMIm]Tf₂N. These unexpected results might be due to a

different behaviour of the Cu^+ ions at the plasma–ionic liquid interface. For example the viscosity of $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ is 2 times higher compared to $[\text{EMIm}]\text{Tf}_2\text{N}$, therefore one can expect a longer residence time of the copper ions and the resulting copper particles at the liquid–plasma interface leading to a wider diameter. Our studies show that ionic liquids clearly influence the plasma electrochemical deposition of copper nanoparticles. Furthermore, the surface oxidation of the particles is also influenced by the ionic liquid.

4. Conclusion

We have reported on the synthesis of free, dispersed copper nanoparticles in air- and water-stable ionic liquids $[\text{EMIm}]\text{Tf}_2\text{N}$ and $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ by employing plasmas as mechanically contact-free electrodes. We have shown that the particles produced in $[\text{EMIm}]\text{Tf}_2\text{N}$ are smaller in diameter (~11 nm) compared to those ones produced in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ (~26 nm). This is in contrast to the classical electrochemical deposition of copper in these liquids and might be due to the viscosity of the liquids. Moreover from the experiments there are strong hints that $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ is more strongly adsorbed on these particles than $[\text{EMIm}]\text{Tf}_2\text{N}$. In both liquids the particles are to a certain extent oxidised to CuO , most likely due to a surface attack during *ex situ* treatment. In contrast to earlier published results on the plasma electrochemical deposition of Ag nanoparticles, the production of copper nanoparticles is surprisingly much more complicated. In order to elucidate the surface chemistry future studies will involve further ionic liquids as reaction media as well as higher resolution TEM measurements.

Acknowledgements

Financial support from the German Research Foundation (DFG) within the priority research program “Ionic liquids” (projects DFG En370/16-2, DFG Ja648/13-1 and 13-2, DFG Kr2228 5-1) is gratefully acknowledged.

References

- 1 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924.
- 2 H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Peng and G. Q. Xu, *Langmuir*, 1996, **12**, 909.
- 3 M. A. Anderson, S. Gorer and R. M. Penner, *J. Phys. Chem. B*, 1997, **101**, 5895.
- 4 I. Lisieki and M. P. Pileni, *J. Am. Chem. Soc.*, 1993, **115**, 3887.
- 5 A. C. Curtis, D. G. Duff, P. P. Edwards, D. A. Jefferson, B. F. G. Johnson, A. I. Kirland and A. S. Wallace, *J. Phys. Chem.*, 1988, **92**, 2270.
- 6 G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira and J. Dupont, *Chem.–Eur. J.*, 2003, **9**, 3263.
- 7 C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner and S. R. Teixeira, *Inorg. Chem.*, 2003, **42**, 4738.
- 8 H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, **126**, 3026.
- 9 K. S. Kim, D. Demberelnyamba and H. Lee, *Langmuir*, 2004, **20**, 556.
- 10 T. Torimoto, K. Okaszaki, T. Kiyama, K. Hirahara, N. Tanaka and S. Kuwabata, *Appl. Phys. Lett.*, 2008, **89**, 243117.
- 11 S. A. Meiss, M. Rohnke, L. Kienle, S. Zein El Abedin, F. Endres and J. Janek, *ChemPhysChem*, 2007, **8**, 50.
- 12 (a) S. Zein El Abedin, M. Pölleth, S. A. Meiss, J. Janek and F. Endres, *Green Chem.*, 2007, **9**, 549; (b) J. Janek, M. Rohnke, M. Pölleth and S. A. Meiss, *Plasma electrochemistry with ionic liquids*, In *Electrodeposition from Ionic Liquids*, ed. F. Endres, D. MacFarlane, A. Abbott, Wiley-VCH, Weinheim, 2008, p. 259.
- 13 Y. B. Xie and C. L. Liu, *Plasma Processes Polym.*, 2008, **5**, 239.
- 14 S. Zein El Abedin, A. Y. Saad, H. K. Farag, N. Borissenko, Q. X. Liu and F. Endres, *Electrochim. Acta*, 2007, **52**, 2746.
- 15 T. Katase, K. Murase, T. Hirato and Y. Awakura, *J. Appl. Electrochem.*, 2007, **37**, 339.
- 16 R. Atkin and G. G. Warr, *J. Phys. Chem. C*, 2007, **111**, 5162.
- 17 R. Atkin, S. Zein El Abedin, R. Hayes, L. H. S. Gasparotto, N. Borissenko and F. Endres, *J. Phys. Chem. C*, 2009, **113**, 13266.
- 18 P. E. Larson, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **4**, 213.
- 19 G. Schön, *Surf. Sci.*, 1973, **35**, 96.
- 20 F. Bebensee, N. Borissenko, M. Frerichs, O. Höfft, W. Maus-Friedrichs, S. Zein El Abedin and F. Endres, *Z. Phys. Chem. (Munich)*, 2008, **222**, 671.
- 21 O. Höfft, S. Bahr, M. Himmerlich, S. Krischok, J. A. Schaefer and V. Kempter, *Langmuir*, 2006, **22**, 7120.
- 22 A. Keppler, O. Höfft, F. Endres and S. Krischok, in preparation.
- 23 J. M. Crosthwaite, M. J. Muldoon, J. K. Dixon, J. L. Anderson and J. F. Brennecke, *J. Chem. Thermodyn.*, 2005, **37**, 559.
- 24 K. Baba, T. Kaneko and R. Hatakeyama, *Appl. Phys. Lett.*, 2007, **90**, 201501.
- 25 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, ed. J. Chastain and R. C. King Jr., Physical Electronics, Inc., USA, 1995.