# Vacuum Electrochemistry in Ionic Liquids

***by Oliver Höfft and Stefan Krischok***

In recent years, ionic liquids (IL) have been introduced as new electrolytes in electrochemistry.[1] Their physical and chemical properties facilitate new and exciting applications for electrochemical processes. For example, ILs are characterized by their large electrochemical windows, which permit the electrodeposition of metals like aluminium and even semiconductors like silicon.[2,3] Furthermore, through careful selection of the IL, one can influence and tune the electrodeposition process.

The electrodeposition of aluminum is a good example, nanocrystalline aluminum deposits can be synthesized from $AlCl_3$ in 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)amide ($[Py_{1,4}]$ $Tf_2N$), whereas microcrystalline deposits can be obtained in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm] $Tf_2N$), although the Al species are virtually identical.[4] The reasons for this behaviour are different adsorption structures ("solvation layers") of the cations and anions on the electrode.[5] [Please refer to article by Ipsas *et al.* in this issue for more details of electrodeposition in ILs – Ed.]. Furthermore, the interaction processes between ionic liquids and interfaces (in particular the adsorption of the IL ions on electrode materials) have been extensively studied using *in-situ* scanning tunnelling microscopy (STM), atomic force microscopy (AFM) and spectroscopic techniques like sum frequency generation and X-ray diffraction.[6-9] [Please refer to article by Borisenko *et al.* in this issue for further details – Ed.].

The (usually) very low vapor pressure of ILs, which range between $10^{-9}$ and $10^{-8}$ Pa at or near room temperature and between $10^{-4}$ and $10^{-2}$ Pa, at 100 °C, opens up many additional approaches for the investigation of ILs. In particular, it is possible to apply vacuum-based methods to study ILs. X-ray photoelectron spectroscopy (XPS) has proven to be a powerful technique to study IL interfaces in a controlled environment.[10-14] Due to the fact that monolayer of ILs can be prepared by evaporation in ultra high vacuum (UHV), adsorption structures can readily be analysed with XPS and monitored with STM.[15,16]

The logical next step is to study the electrochemistry of IL-electrode interfaces directly in vacuum. Kuwabata *et al.* developed an *in situ* electrochemical scanning electron microscope (ECSEM) for the monitoring of electrodeposition processes.[17] Figure 1 shows their first electrochemical cell design. With this cell they studied the oxidation and reduction of a poly(pyrrole) film on platinum in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BMIm] $Tf_2N$). It was clearly visible that the film thickness decreased and increased, respectively, during oxidation and the reduction.

In addition, with *in situ* EDX measurements, the doping of the poly(pyrrole) film with potassium ions was investigated. With a new cell, produced from fluorine doped tin oxide-coated glass (FTO), Kuwabata *et al.* imaged silver electrodeposition in $[BMIm]Tf_2N$.[18] With the ECSEM, they observed a dendritic growth of silver on FTO. These measurements were accompanied by *in situ* EDX studies. Such observations have helped to close the gap between the *in situ* STM/AFM experiments at the nanoscale and the *ex situ* SEM measurements of thicker, micro-scale deposits. Precise fabrication and accurate filling of the cell are necessary to image the electrode surface, because a thick IL film on top of the surface can hinder the penetration of the secondary electrons (used for imaging) through the liquid film to obtain proper image. Such requirements become especially important for *in situ* XPS measurements, as the inelastic mean free path of electrons excited by the x-ray radiation is only a few nanometers.

Electrochemical cells for *in situ* XPS were introduced by the groups of Licence, Compton and Kötz.[19-21] Taylor *et al*.[19] studied the electrochemical reduction of iron in an [EMIm] $EtOSO_3$ and [BMIm] $FeCl_4$ mixture, whereas Kötz *et al*[21] analyzed the boundary between a Pt anode and an [EMIm] $BF_4$ electrolyte. Wibowo *et al.*[20] investigated potassium electrodeposition from $[Py_{1,4}]$ $Tf_2N$ onto a nickel mesh. This field presents many promising avenues for investigation of the IL-electrode interface and of electrochemical processes using ILs.

## Synthesis of Materials in Vacuum

The synthesis of nanoparticles is a hot topic in the field of IL research. The synthesis of a variety of nanoparticles from ILs in vacuum is possible by different methods, such as sputter deposition or physical vapor deposition of metals onto surfaces of the liquids in vacuum, reduction with free electrons in a scanning electron microscope and plasma electrochemical approaches.[22] The advantage of using ILs as a medium for nanoparticle synthesis is that the derived nanoparticles can be stabilized without the presence of any adventitious stabilizing agent.[23] An overview on the different methods to produce nanoparticles in ILs and their applications can be found in three recent reviews.[23-25] With respect to the electrochemical route for nanoparticle synthesis in ILs, Dupont and Scholten have stated in their review, *"Electrochemical reductions of metal compounds in ILs are likely the cleanest methods for preparing metal NPs since only electrons are*

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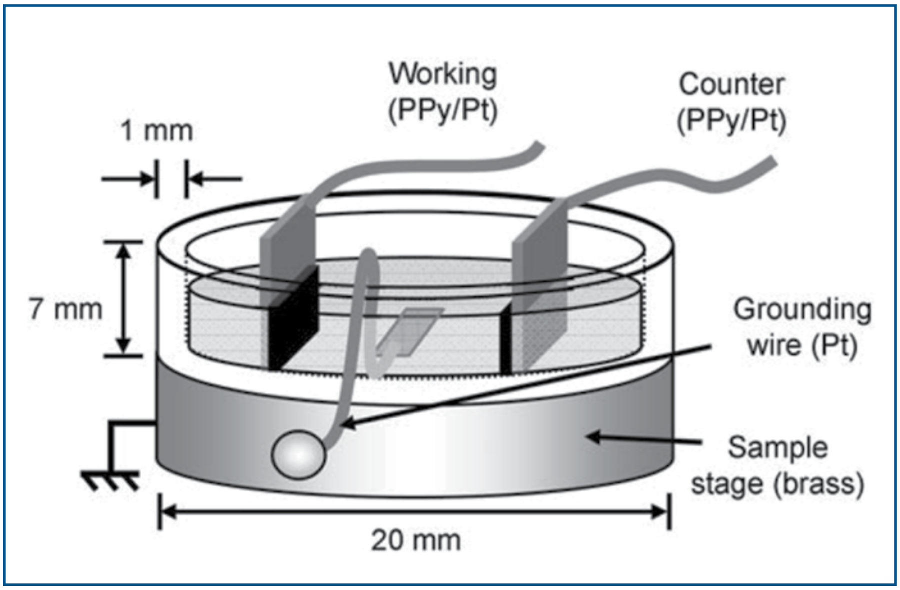

**Fig. 1.** *Electrochemical cell by Kuwabata* et al.[17] *Figure from Kuwabata* et al.[13] *(Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)*

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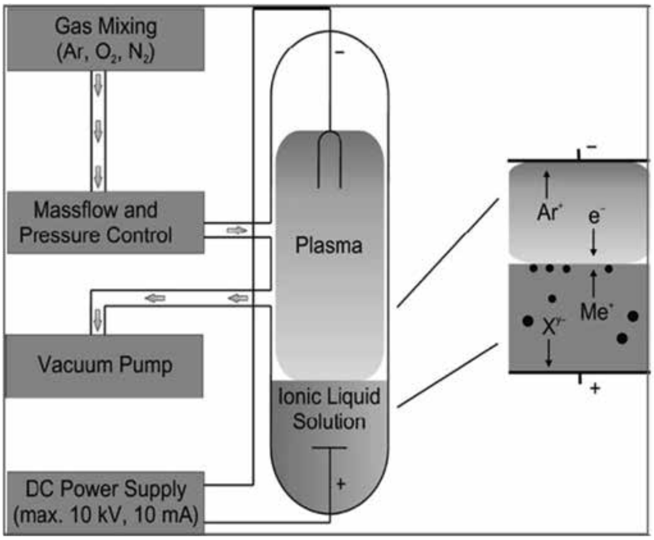

**Fig. 2.** *Sketch of a plasma reactor. Figure from Meiss,* et al.[36] *Copyright Wiley-VCH Verlag GmbH & Co. KGaA. (Reproduced with permission.)*

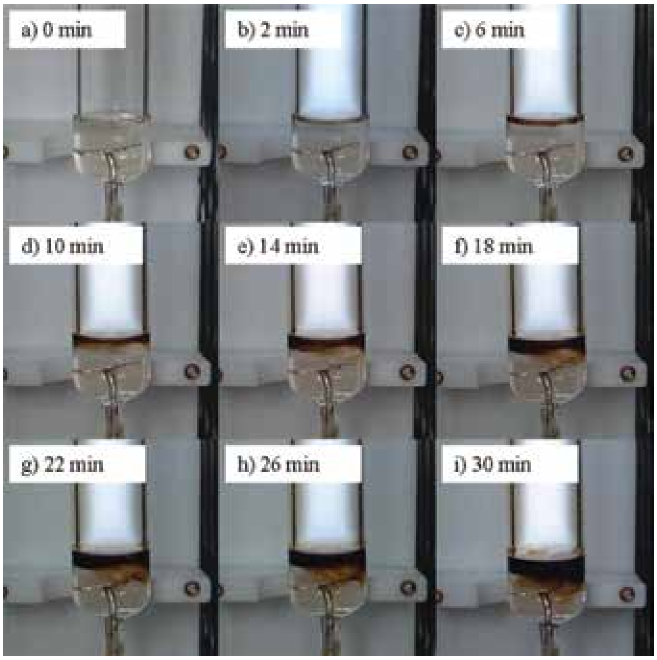

**Fig. 3.** *Temporal evolution of the plasma electrochemical reduction (30 min) of Cu$^+$ in [EMIm]Tf$_2$N. Figure from Brettholle,* et al.[32] *(Reproduced by permission of the PCCP Owner Societies.)*

*involved.”*[23] One can extend this statement, since the entire process takes place in the highly controlled environment of a vacuum chamber.

The synthesis approaches involving scanning electron microscopes and scanning Auger electron microscopes were introduced by Roy *et al*.[26] and Imanishi *et al*.[27] Here, the electrons were used both for the reduction of precursor to yield the nanoparticles and for monitoring the process. In this context one has to be aware that the electrons might not only induce the desired precursor reduction but might also interact with the IL medium, leading to their decomposition.

The plasma approach is different since the electrons for the reduction are provided from a plasma, which is in direct contact with the IL. Consequently, electrons are able to reduce dissolved metal or semiconductor compounds directly at the IL/plasma interface. Generally speaking, the idea of using free electrons for precursor reduction is not new, as Gubkin used a plasma in conjunction with an aqueous solution of silver nitrate more than hundred years ago[28] to synthesise silver at the water surface.

Nowadays atmospheric-pressure microplasmas or plasma jets are available to provide electrons to aqueous interfaces for precursor reduction.[29,30] With these techniques, the high vapor pressure of water can be circumvented.

The low vapor pressure of ILs further facilitates obtaining a stable plasma above the interface. The ignition of such a plasma can be achieved with different systems.[22,31] One of the easiest ways is to use DC plasma reactors. In Fig. 2, a sketch of such a reactor is shown. It consists of a glass cell with two metal electrodes, which are connected to a DC power supply. The cell is pumped using a rotary pump and the gas flow for the plasma can be regulated using a vacuum valve. Argon is usually used as the plasma gas.

A typical experiment starts by filling the reactor with the IL electrolyte containing the desired metal precursor. Thereafter, the electrolyte is carefully outgassed at a pressure of $10^{-3}$ mbar. The plasma gas is then fed into the cell, a pressure of around 1 mbar is maintained, and a voltage between 500 and 1000 V is applied between the electrodes. The exact parameters depend on the distance between the electrodes and on the electrolyte used. When the upper electrode acts as the cathode, the electrons move towards the electrolyte and the gas ions move towards the counter electrode. At the plasma/IL interface, the electrons can react with the dissolved metal ions and particles are formed.

In Fig. 3 a typical temporal evolution of the plasma electrochemical experiment is shown, with reference to the generation of copper nanoparticles from a [EMIm]Tf$_2$N/ Cu Tf$_2$N solution.[32] It is clear that the reaction starts directly at the plasma/IL interface and, with time, a dark cloud grows in the downward direction in the cell, whereas the rest of the liquid remains clear. Some small bubbles are formed at the anode, likely due to the decomposition of the IL at this electrode.

Plasma electrochemistry using DC reactors was divided into two modes (A and B mode) by Hatakeyama *et al*.[33] These modes depend on the polarisation of the electrodes. Nanoparticles can, in principle, be synthesised in both modes. In the A-mode, where the cathode is immersed in the liquid, secondary electrons, created due to the interaction of the plasma gas ions with the IL interface, act as the reducing agents. In the B-mode, where the cathode is above the liquid, the primary electrons in the plasma reduce the dissolved species.

Another DC plasma reactor concept was introduced by Liu *et al*., wherein no electrode is immersed in the liquid (both electrodes are in the gas phase). The electrolyte is placed in a quartz crucible and is located at the “positive column” of the glow discharge.[34] In addition Liu *et al*., showed that a sub-atmospheric dielectric barrier discharge (SADBD) plasma can also act as a reducing agent.[35] Radio frequency discharge plasma setups have also been used for plasma electrochemistry.[36] With these approaches, the generation of silver, gold, platinum, palladium and copper nanoparticles in different ILs have been reported[22,31-34]

The particle sizes have been determined by transmission electron microscopy (TEM) and, in the case of ILs, this can be done directly with the particles in the IL. Thus, secondary reactions induced during separation of the particles from the IL, and the resultant convolution in particle size data, can be avoided. This is especially important for the particles made from reactive metals. However, this approach also has a possible disadvantage in that a detailed analysis of the particle structure is rendered difficult by the presence of an IL film around the particles. In general, all particles thus synthesized and reported in the literature were found to exhibit sizes well below 100 nm. No correlation between IL physical properties (like surface tension) and particle size has hitherto been conclusively established. The particles synthesised in ILs have mostly been equivalent or larger in size compared to the particles generated with the chemical reduction method or the sputtering technique. For example the copper nanoparticles produced by physical vapor deposition in [BMIm]Tf$_2$N and [BMIm]PF$_6$ exhibit particles sizes around 3 nm.[37] By chemical reduction, comparable particle sizes were observed.[38] The copper nanoparticles produced in [BMIm]dca were also in this size regime, while the Cu particles in [EMIm]Tf$_2$N and [Py$_{1,4}$]Tf$_2$N were larger.[52]

A comparison of the particle dimensions achieved from plasma electrochemistry in ILs consisting of imidazolium cations and different anions, with the particles generated by reduction with low-energy electrons in a SEM yielded similar size regimes.[39] Interestingly, Kuwabata *et al*. found that the anion plays an important role on the particle size, whereas the change of the alkyl chain length of the cation has a minor influence on the particle size.[39] Here, the particles derived from imidazolium liquids containing the [Tf$_2$N] anion were around a factor of two larger compared particles derived from imidazolium ILs containing the [PF$_6$] anion. This is in good agreement with our own observations.

Due to the very low vapor pressure of ILs, XPS can be used as a powerful tool for characterization. It provides detailed insights into the surface stoichiometry, possible surface enrichments, and the chemical state of the detected elements. Thus, it is possible to investigate the original chemical state of the dissolved species, to perform the characterization of the synthesized material, including, *e.g.*, the oxidation state (valence) of the produced material, and to analyse the residuals from the ILs.

Using more sophisticated experimental setups, it is even possible to obtain direct insights into the electrochemical mechanisms in play.[19-21] As an example of XPS studies on salts dissolved in ILs and the characterization of electrodeposited materials, data for the TaF$_5$/[PMIm]Tf$_2$N system are shown in Fig. 4 (for more details see Krischok, *et al*.[40]). In Fig. 4a the influence of the Ta salt concentration on the N 1s signal is shown. The Tf$_2$N related signal at about 399 eV decreases with respect to the PMIm related N-signal at about 402 eV (from the expected 1:2 ratio) with increasing amounts of TaF$_5$. Obviously the cation:anion ratio of the IL at the surface is strongly modified by the Ta salt. In Fig. 4b the obtained Ta spectra are shown. The Ta signal is different for the dissolved Ta salt in the IL, the Ta near the surface of the deposited Ta film after short sputtering (note that in this particular case the sample was exposed to ambient conditions after film production), and the Ta after longer sputtering. The data for the electrodeposited film show that the surface is oxidized (see signal after 20 min sputtering). With increasing sputtering time, an additional metallic Ta component appears. Moreover, the XPS of the as prepared film reveals the

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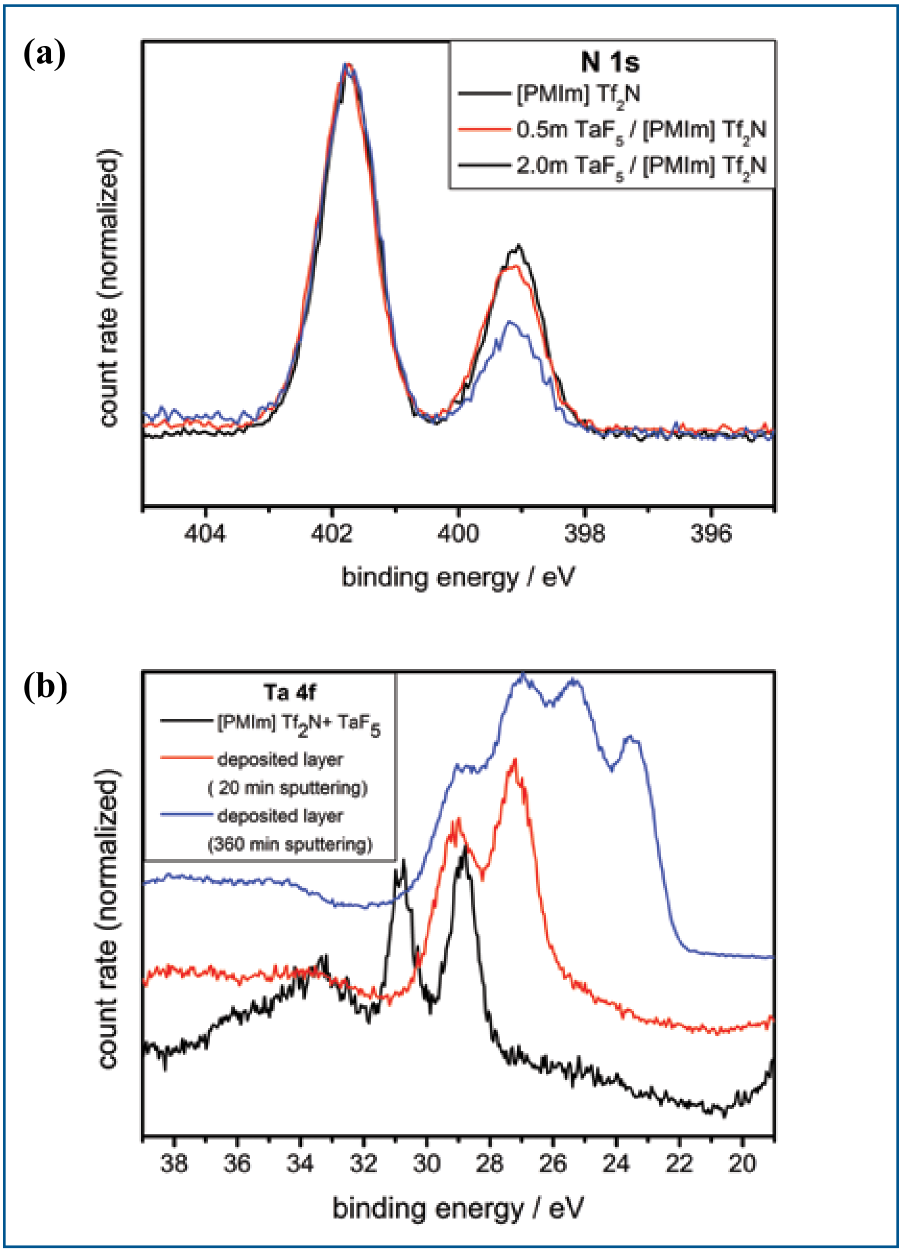

**Fig. 4.** *(a) Changes of the N1s XPS core level spectra of [PMIm] Tf$_2$N in dependence of the dissolved Ta-salt concentration. The shown spectra have been normalized and the binding energy was adjusted by shifting the PMIm related signal to 401.7 eV for charge compensation. (b) Ta signal for the dissolved salt and for the deposited film after short and longer sputtering time. The spectra have been normalized and a vertical offset was added for better visualisation. All XPS spectra were recorded using monochromatized Al Ka radiation.*

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presence of large amounts of IL residuals. Similar studies have also been performed for the production of Cu nanoparticles from ILs by plasmaelectrochemical methods.[32]

But what is the advantage of the plasma electrochemical approach in combination with ionic liquids compared to the other methods? One advantage might be that this technique opens the way to the generation of semiconductor particles like germanium and silicon. Kareem and Kaliani were able to produce ZnS nanoparticle in [BMIm]BF$_4$ with plasma electrochemistry,[41] therefore the synthesis of other semiconductor compounds should also be feasible. Endres *et al.* have shown by electrodeposition experiments that nanoscale silicon and germanium films can be easily made from different SiCl$_4$ and GeCl$_4$ containing IL solutions.[42,43] Not too surprisingly, the first attempts to reduce SiCl$_4$ and GeCl$_4$ by plasma electrochemistry failed as the precursors were simply pumped off due to too high vapor pressures. Then, a solid GeCl$_2$·*dioxane complex* (GeCl$_2$C$_4$H$_8$O$_2$) was selected as germanium source.[44] Compound particles with sizes smaller than 50 nm have been obtained using this solid.

With XPS, the chemical composition of the solution before and after the plasma treatment has been analyzed. At the electrode-solution interface, germanium can be detected in both cases. The detailed spectrum of the Ge 2p region shows, for the untreated solution, only germanium in the Ge$^{2+}$ oxidation state. After the plasma interaction, an additional component is visible in the spectrum, which can be attributed to a lower oxidation state of Ge. This demonstrates that the plasma process leads to germanium reduction via Ge$^{2+}$ and Ge$^{+}$ to Ge$^{0}$.

For attempts to produce silicon particles, SiI$_4$ was chosen, a solid that cannot be pumped off from the reactor. An electrodeposition experiment performed by Bund *et al.* revealed that from SiI$_4$/[Py$_{1,4}$]Tf$_2$N solutions, elemental Si could not be obtained, but rather subvalent Si$_x$I$_y$ compounds were produced. Nevertheless, these first results showed that SiI$_4$ can be reduced electrochemically.[44] XPS investigation of silicon electrodepositon from ILs has not been successful until now. As there are only a few Si precursors available, we have developed a new reactor design that permits the use of high vapor pressure precursors in future.[45]

A further application for plasma electrochemistry using ILs is the direct functionalization of materials with metal particles. Hatakeyama *et al.* impregnated carbon nanotubes with gold and palladium salts, followed by plasma treatment.[46] They observed the formation of metal particles between the bundles of the carbon nanotubes. They expected that this resulted in the formation of more uniform particles because the small spaces inside the nanotubes inhibited particle agglomeration.[46] Obviously, plasma electrochemistry in ILs can also be used for the production of hybrid materials as described above.

Finally, a possible "disadvantage" of vacuum electrochemistry has to be addressed. In all presented cases, the ILs interact with high-energy electrons or photons in the case of SEM or XPS experiments, and with low energy electrons in the plasma experiments. Thus the IL might degrade. For example, from pulse radiolysis measurements it is known that aromatic cations, especially imidazolium cations, serve as electron trapping centers during radiolysis, resulting in the formation of neutral radicals and radical ions.[47,48] These radicals can activate secondary reactions in the system. Additionally we have shown that there is an influence of non-monochromated AlKa X-rays and electron beams on the surface composition of the IL [EMIm]Tf$_2$N.[49] In plasma experiments Hatakeyama *et al.* have observed strong color change in an IL containing an imidazolium cation.[33] With optical emission spectroscopy, methylidyne radicals (CH) in the plasma could be detected,[33,46] arising from a loss of an alkyl chain from the imidazolium cation. Such radicals can also act also as reducing agents in solution, thereby convoluting the electrochemical process.

## Conclusions and Outlook

Ionic liquids have created a pathway for performing electrochemistry under vacuum. The electrons from electron microscopes or from a plasma can be used directly as reducing agents in such a process/experiment. One can monitor and investigate electrochemical processes at the IL/vacuum interface and at the IL/electrode interface in classical electrochemical cells using SEM or photoelectron spectroscopy, provided the precursors used have a low vapor pressure. The need for low vapor pressure precursors is one of the disadvantages of vacuum electrochemistry. However, with an optimized cell design, such challenges can be overcome. Some interesting preliminary results that demonstrate the possibility to produce even compound semiconductors by plasma electrochemistry have been presented. Moreover, electrochemistry in the monolayer regime might be possible since the production of very thin layers of ILs in UHV by evaporation or other deposition methods is possible and not too difficult. This might lead to a deeper understanding of electrochemical processes at the atomic scale.

In closing, ILs enable a versatile platform for fundamental electrochemical studies in vacuum, as well as processes of interest, such as nanoparticle synthesis. These areas are poised for growth.

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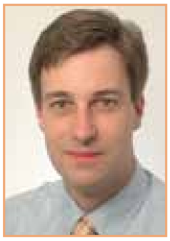

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