

Interfacial Electrochemistry of Ionic Liquids

by Andreas Bund and Frank Endres

Ionic liquids (ILs), which were in their infancy about 15 years ago, have today been accepted as versatile materials in various fields of chemistry. There is now an overwhelming number of publications dealing with ILs. In comparison to molecular liquids, they show certain remarkable properties. For one, they are an extraordinarily disparate class of materials. Millions of different ILs can potentially be synthesized by combination of various cations and anions. Since even slight changes in the side group of an anion or cation can lead to considerably altered properties of the resultant IL, a wide matrix of ILs with tailored properties can be envisaged.

Currently there are about 1000 ILs commercially available. They have wide thermal windows, i.e., most of them can be handled between 0 and 200 °C, which closes the gap between conventional solvents and high temperature molten salts.¹ This property, together with their wide electrochemical windows, makes ILs interesting candidate materials for the electrodeposition of refractory metals like tantalum and niobium that in the past could only be deposited from high temperature molten salts. From selected ILs, these metals can now be deposited in thin crystalline layers at temperatures between 150 and 200 °C. However, there seem to be limits to the use of ILs for metal electrodeposition, for example the electrodeposition of titanium remains quite challenging. The composition of the IL plays an important role in the electrochemical process. These interesting aspects are addressed in the article contributed by Ispas *et al.* in this issue.

Apart from their wide thermal and electrochemical windows, most of the ILs have negligible vapor pressures at room temperature, which allows studies to be performed even in an ultrahigh vacuum. This allows researchers to monitor species that are generated during an electrochemical process using techniques such as photoelectron spectroscopy. In a low temperature plasma, electrochemistry can be performed at the IL/plasma interface. Metal and semiconductor nanoparticles (e.g., Si and Ge) can also be obtained via this plasma-synthesis route. Höfft *et al.* summarize these aspects in their article.

The focus of electrochemists vis-à-vis ILs has hitherto been on their electrochemical window, which in some cases can be as wide as ± 3 V vs NHE. But the electrochemical window in itself does not explain certain phenomena, for example, obtaining microcrystalline metal deposits in one IL medium, but nanocrystalline deposits in a slightly different one under comparable conditions. The first advances toward resolving these were made about seven years ago in papers showing that ILs formed solvation layers at interfaces. These solvation layers were so strongly adsorbed that they could be probed with an atomic force microscope. Shortly afterwards, it was shown that ILs were also adsorbed on metal surfaces and that the adsorption and orientation of the liquids varied with the electrode potential. Thus, it is likely that ILs can strongly influence electrochemical reactions.² Borisenko *et al.* summarize these aspects of ILs in their contribution in this issue.

Meanwhile these experimental observations on the electrochemical aspects of ILs have been well supported by theory and computer simulations. Interfacial properties can already be predicted to a good extent, and there has been remarkable progress on the theoretical chemistry front, as discussed by Ivaništšev and Fedorov in this issue. It is evident that theory is an important tool to understand the complicated

interfacial electrochemistry of ILs. In our opinion there must be a focus on these aspects in the future, as a deep understanding of the interfacial electrochemistry is needed to develop viable technical processes that lie at the confluence of electrochemistry and ILs. ■

About the Authors



ANDREAS BUND studied Chemistry at the University of Saarland during 1989-1995. His PhD (1999, *summa cum laude*) was on the application of piezoelectric quartz crystals for rheological and microgravimetric in-situ measurements. In 1999 he moved to Dresden University of Technology where he did his habilitation thesis in 2004. The habilitation thesis was on tribological, rheological, and magnetohydrodynamic effects at electrochemical interfaces. In 2005 he was awarded the renowned Heisenberg fellowship of the Deutsche Forschungsgemeinschaft. During the time of his fellowship he was twice a visiting scientist at the University of Utah where he worked with Henry S. White on electrochemical magnetohydrodynamics and the numerical simulation of electrochemical processes. From 2009 to 2010 he held a visiting professorship at TU Munich, Faculty of Physics, Chair Interfaces and Energy Conversion. In August 2010 he was appointed full professor at Technische Universität Ilmenau, group of Electrochemistry and Electroplating. Andreas Bund has about 90 ISI refereed journal articles. He may be reached at Andreas.Bund@tu-ilmenau.de.



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