

Electrodeposition in Ionic Liquids

by Adriana Ispas and Andreas Bund

In practice, the electrodeposition of most metals and alloys is almost exclusively performed from aqueous solutions. Chromium, nickel, zinc, copper, silver and gold are some of the metals that are largely used in various technical applications. They can be obtained from aqueous solutions that in some cases are based on toxic components (e.g., cyanide) and using processes that have rather low current efficiencies (e.g., chromium).

There are a number of metals with a Nernst potential well below that of water decomposition and that therefore cannot be electroplated from aqueous baths (e.g. aluminum, magnesium, tantalum and others). Ionic liquids (ILs) have now caught the attention of electroplaters, hitherto mostly in the research labs. ILs consist of an organic cation (e.g. pyrrolidinium, imidazolium, ammonium) and an inorganic anion (e.g. chloride, bromide, tetrafluoroborate, triflate). They have a wide range of solubilities and miscibilities; for example, some of them are hydrophobic, while others are hydrophilic (Fig 1). ILs do not readily evaporate and most ILs are nonflammable and nontoxic, thereby providing key environmental advantages when compared to organic solvents. ILs are liquid at temperatures far below 100°C,

which makes them interesting alternatives to high temperature molten salts. Some ILs are stable up to several hundred degrees Celsius and have an electrochemical window of up to 4-5 V. Furthermore some precursors for the deposition of reactive elements are either not soluble or decompose in water, but are highly soluble and stable in ILs. On the flip side, one drawback of ILs is their relatively low electrical conductivity compared to aqueous systems — a direct consequence of their high viscosity. However due to their good thermal stability, IL based electrolytes can be operated at elevated temperatures, thereby somewhat alleviating this problem. The aforementioned useful physico-chemical properties make ILs interesting candidates for the electrodeposition of reactive metals, semiconductors and polymers that cannot be plated from aqueous baths. Possible applications include electrorefining, decoration, corrosion protection or other functional surface finishings.^{1,2}

One subclass of ILs that has garnered interest are deep eutectic solvents (DES). They are eutectic mixtures of two components: one, a simple quaternary ammonium halide, and the other, an inorganic metal salt or an organic hydrogen-bound donor, such as an amide or an

alcohol. Popular DES are based on the mixture of choline chloride with urea, or with ethylene glycol, glycerol or propylene glycol. Compared to real ILs, DES are much cheaper but have more limited thermal and electrochemical stabilities.³

In the spring 2007 edition of *Interface* there were a series of articles from Keith E. Johnson, Tetsuya Tsuda and Charles L. Hussey that discussed the properties of ILs and their possible applications in electrochemical process: as electrolytes in lithium ion batteries; in supercapacitors; for treatment of nuclear wastes; in dye-sensitized photoelectrochemical cells, to mention a few. However, one important aspect of ILs is that they can concomitantly serve both as solvents and supporting electrolytes, a fact that make them an attractive alternative to organic or toxic solvents in the electroplating industry. The choice of salt used is very important for electrodeposition in ILs. From some precursor salts it is possible to precisely electrodeposit the target element, while the choice of other precursor salts preclude total reduction to metal (Fig. 2). To improve the deposition rates and plating process efficiency, special ILs have been designed that contain the metal species to be plated.¹¹

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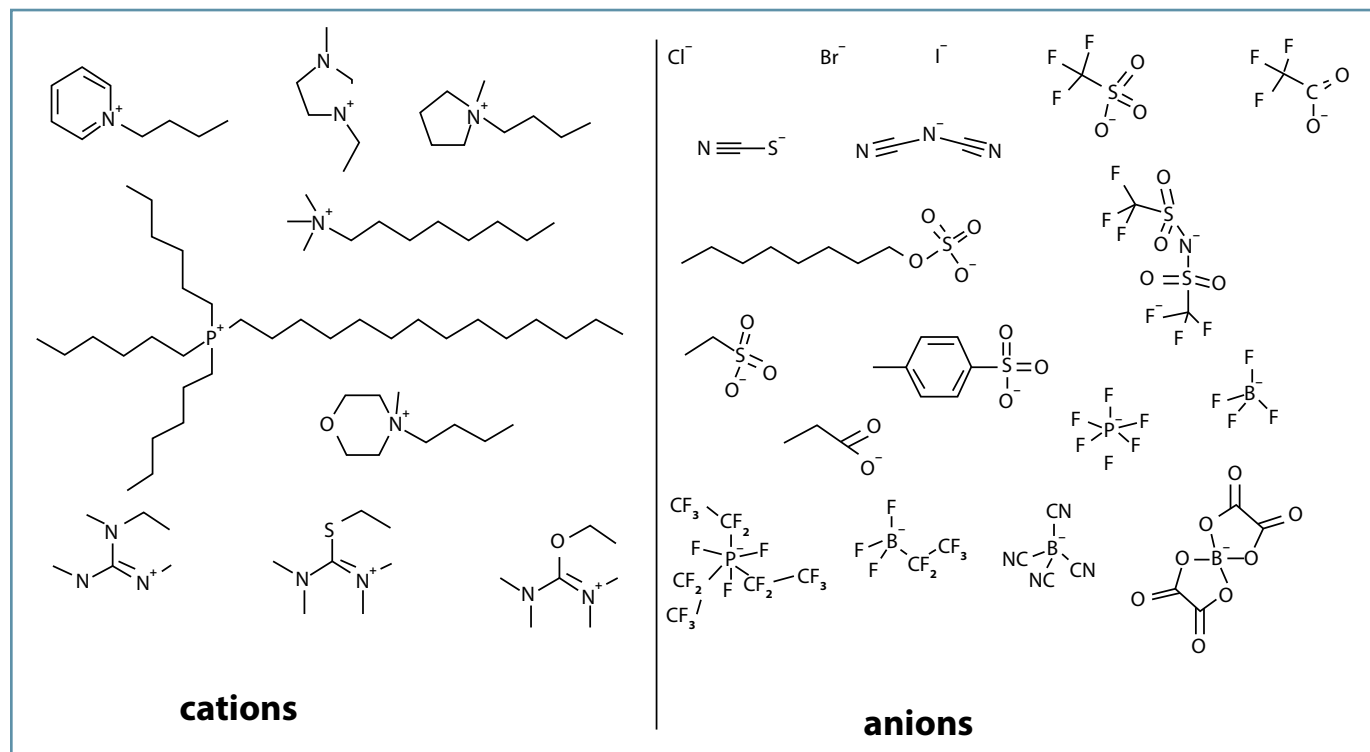


FIG. 1. Structures of cations and anions of commonly used ILs. Theoretically, 10^{12} to 10^{18} possible combinations between the cations and anions are possible. However, not all of these envisaged ILs will have good conductivity and electrochemical windows that make them useful for electrochemical applications.

With such ILs, very high current densities can be employed, which can considerably reduce plating times and thus costs. An important book on electrodeposition in ILs appeared in 2008.² However, the first reviews on the various materials (metals, semiconductors or conducting polymers) that can be plated from ionic liquids, on the physico-chemical properties of ILs, and on the challenges of conducting electrochemistry in ILs appeared starting from 2002.^{1,4-10}

Most reviews have hitherto focused on the type of metals/alloys/semiconductors or polymers that one can deposit in ionic liquids. The above mentioned reviews discuss recipes for plating metals and alloys from ILs, such as Al, Pd, In, Sb, Te, Cd, Cu, Ag, Ni, Co, Zn, Sn, Ga, Ge, Si, Ta and many more. This short overview will focus on some other aspects, namely on the use of additives, co-deposition, and pulse plating in ILs.

Use of Additives for Electrodeposition from ILs

Additives added to the plating bath can be adsorbed chemically or physically on the surface to be coated. In the case of chemisorption, there can be partial transfer of electrons between the substrate and adsorbate, while for physisorption, electrostatic or van der Waals forces are prevalent.¹² The additives act both on kinetics of the electrodeposition and on the growth mechanism. Plating in the presence of additives generally yields deposits with a better morphology and improved mechanical or electrochemical properties. Some additives reduce the internal stress within the deposits, some facilitate bright surfaces or reduce the roughness of the deposits. All

these beneficial properties of additives have been observed for layers electrodeposited in aqueous solutions.

The brightness of deposits (*e.g.* Fe, Co, Ni) and their grain size can be increased by increasing the plating bath temperature even in the absence of additives in ILs.¹³⁻¹⁵ This is due to the stronger adsorption of cations on the electrode surface at lower temperatures, which hinders the nucleation and growth of the deposits and results in grain refining.¹⁶

In passing, we note that ionic liquids themselves can be used as additives during plating from aqueous electrolytes, *e.g.* for grain refining.¹⁷⁻²⁰ However, this application of ILs in aqueous baths is beyond the scope of this article. There is not much literature to be found on the effect of additives in deposition from ILs. Herein, some studies are presented wherein additives have been used in ILs to improve the properties of electrodeposited layers.

This issue of *Interface* also contains articles by Fedorov and Ivaniššev, Borisenko, Atkin, and Endres where the structure and dynamics of the IL/electrode interface is discussed. One important point discussed in those contributions is that the double layer in ILs is different from that in aqueous solutions. In the following paragraph, we present a simple description of cation adsorption on the electrode surface to describe the role of additives during electrochemical plating.

In the absence of additives, the cations of an IL will accumulate near the electrode surface when it is negatively polarized. The reduction of metal cations is expected to occur slowly, through the adsorbed layer of cations (for example, the 1-butyl-1-methylpyrrolidinium cation, [BMP]⁺). As a consequence, the reduction of the metal ions is hindered. In the presence of additives, a cationic complex of the metal ions with the

additive can be formed, and this can partly compensate for the electrostatic barrier at the interface by facilitating charge transfer to the metal ions. Other mechanisms can be based on the adsorption of the additives on the electrode surface. By replacing some of the bulky adsorbed IL cations, the additive molecules can induce a more facile electrode reaction. As a consequence, a smoother and shinier surface is obtained in the presence of additives (such as acetonitrile, coumarin, thiourea, benzotriazole or acetone)^{11,14,21} with better adhesion on the substrate also observed in the case of coumarin.^{13,22}

For example, acetonitrile has been added as an additive during Fe deposition from 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, [BMP][TFSA], containing Fe(TFSA)₂.¹³ Acetone,^{14,21} coumarin²² and thiourea^{21,22} have been added during Co and Ni electrodeposition from [BMP][TFSA], containing Co(TFSA)₂ or Ni(TFSA)₂. Changes in the coordination environment in the presence of thiourea,²² acetonitrile and acetone are higher (the coordination number of acetonitrile or acetone is 14) compared to those induced by the [TFSA]⁻ anion (coordination number 7).¹³ The changes in the coordination environment indicated the formation of a complex product between the metal ions and the additives, which could facilitate the reduction of the Co²⁺. However, the coordination was not affected when coumarin was used in Co deposition from [BMP][TFSA] ILs containing Co(TFSA)₂²² suggesting that no complex of Co²⁺ ions with coumarin was formed. In this latter case, the reduction of cobalt occurred from the divalent cobalt species [Co(TFSA)₃]⁻.

When nicotinamide was used as additive during Al electrodeposition from AlCl₃ in 1-butyl-3-methylimidazolium chloride²³ an inhibition of Al deposition was observed,

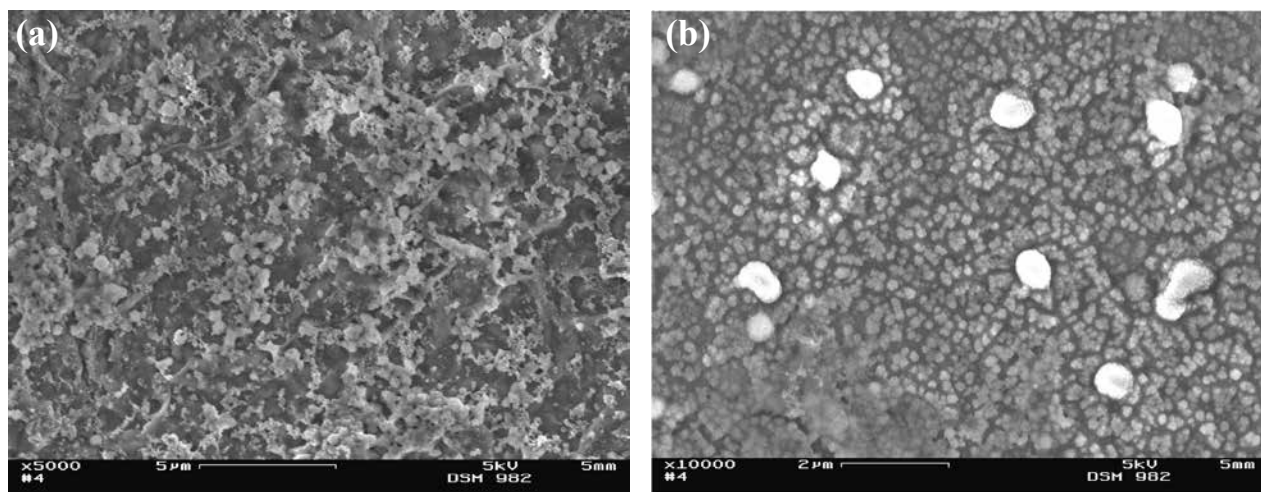


Fig. 2. (a) Silicon layer (thickness ca 180 nm) deposited from 1 M SiCl₄ in [BMP][TFSA] at room temperature (25°C) and $E = -2.3$ V on Au electrodes. The counter and reference electrodes used were Pt wires. The presence of elemental Si is supported by the mass charge balance via in-situ microgravimetry. (b) Si-containing layer (thickness ca. 300 nm) deposited from 1 M Si₄ in [BMP][TFSA] at room temperature (25°C) and $E = -2.3$ V on Au electrodes. In-situ microgravimetry indicated that the deposited layer did not consist solely of elemental Si.

but, at the same time, highly uniform and smooth surfaces were obtained. This example shows that additives can have opposing contributions to the various important parameters in a plating process (time, quality etc.).

Zinc electrodeposition from DES (1:2 choline chloride: urea and 1:2 choline chloride: ethylene glycol) in the presence of acetonitrile, ethylene diamine and ammonia has been studied in Abbott *et al.*²⁴ The use of ammonia promoted mass transport, enhanced deposition rates and engendered a specific morphology. The addition of ethylene diamine inhibited the reduction of Ni but favored the reduction of Zn. Brighter deposits could be obtained in the presence of either ethylene amine or ammonia. Acetonitrile had a negligible effect on the electrochemical deposition of Zn from ILs.

Additives can also be used in lithium-ion batteries to improve the cycling ability of lithium in ILs.^{25,26} Propylene carbonate^{27,28} and ethyl alcohol²⁷ have been used in the electrodeposition of Co and Zn-Co from ILs and toluene. LiCl has been used in Al electrodeposition²⁹ and LiF in Ta electrodeposition.³⁰ In all these studies, it was shown that the grain size and morphology of the deposits, and the electrochemical behavior could be altered by addition of suitable additives to the IL-based plating baths. This area remains of considerable interest and it is in theory possible to tune the properties of the plating bath for any metal by choosing a suitable combination of IL solvent and additive.

Codeposition

Electrocodeposition implies the simultaneous deposition of a metal matrix (e.g., Ni, Cu, Zn) or a polymeric matrix (PEDOT) and of nano or micro sized particles. The nanoparticles to be deposited can be oxides (Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , CeO_2), carbon based materials (Cr_3C_2 , SiC, WC, diamond, carbon nanotubes), magnetic particles (Fe_3O_4 , Co) or insulating particles (Teflon). Usually the aim is to obtain codeposits with better mechanical, optical, magnetic properties or corrosion resistance than the matrix itself. Therefore, in some industrial applications (e.g. automotive or aerospace industry), codeposited materials have already replaced pure metals.^{12,31}

Hitherto electrocodeposition has mostly been performed in aqueous baths. Reports on electrocodeposition in ILs are very scarce. Abbott and co-workers have reported the electrocodeposition of Cu and Cr from DES in the presence of Al_2O_3 and SiC particles.^{32,33} The stability of the DES based suspensions with various particles such as Si_3Ni_4 , SiC, BN, Al_2O_3 and diamond was reported to be quite good: 1 μm Al_2O_3 particles sedimented within 24 h from the suspension, while 50 nm particle suspensions were stable for more than 1

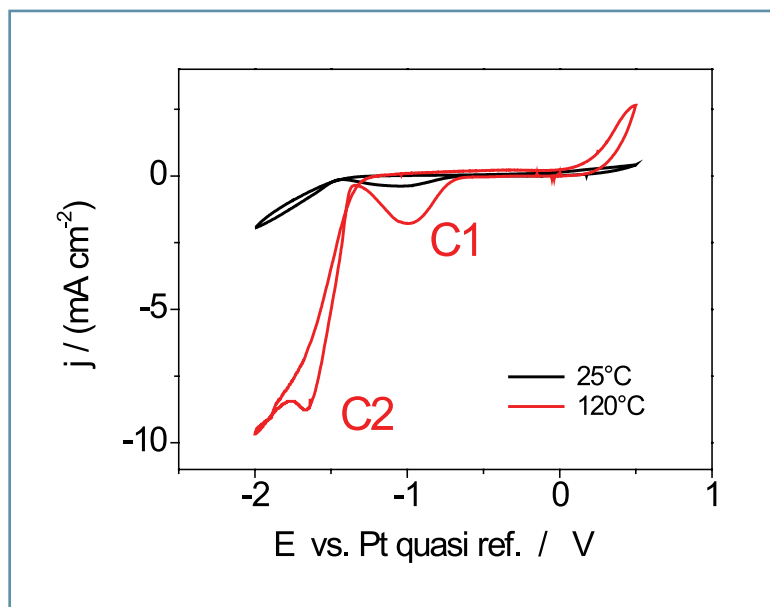


Fig. 3. Cyclic voltammograms (scan rate = 10 mV/s) in 0.5 M TaF_5 in [BMP][TFSA], obtained on Au electrodes, at 25 and 120°C. Platinum wires were used as counter and reference electrodes. Wave C1 is attributed to a partial reduction of Ta^V , and C2 to the deposition of a Ta⁰ rich layer.

week.^{32,33} The codeposition of Cu- Al_2O_3 and Cu-SiC films from DES was shown to be different compared to codeposition from aqueous solutions, in terms of deposition thermodynamics and kinetics, or in terms of the complexing mechanisms of the metal ions. This will remain an area of interest in the future.

Pulse Plating in ILs

Most electrodeposition from the ILs is performed in constant current or constant potential mode. In some studies, cyclic voltammetry is also used as a deposition technique. Pulsed electrodeposition is a powerful technique widely used by the plating industry to improve the morphology (e.g., finer grains) or the throwing power (e.g., covering through holes in printed circuit boards by pulse reverse plating). Pulsed electrodeposition can also improve the adhesion of the deposit to the substrate, and, in the case of alloy deposition, it can be used to tailor the composition of the electrodeposit. Pulse plating (PP) implies a splitting of the Nernst-Diffusion layer into two regions, a pulsating and a stationary diffusion layer.¹² The concentration of the active species that will be reduced in the pulsating layer varies with the frequency of the pulsating current.

A short review on pulse plating from ILs can be found in Ispas and Bund.³⁴ Most papers are on Al electrodeposition³⁵⁻⁴² and its alloys with Co, Cu, Sb or Ni.⁴³⁻⁴⁶ Other alloys that have been obtained by pulse plating from ILs and deep eutectic solvents, respectively, are In-Sn⁴⁷ and BiSbTe.⁴⁸ Some conducting polymers have also been synthesized by pulse plating in ILs.^{49,50} Most of the

studies have focused on the morphological aspects of the deposited layers, i.e., these studies describe the improvement in the morphology of the deposits, in the adhesion of the deposited layers on different substrates, and the reduction of the grain size of the deposits when compared to the layers obtained by direct plating. Moreover, no surface pretreatment was necessary to obtain an adherent and structured Al film on Al^{36} electrodes when pulse plating was used.

Another powerful application of pulse plating is alloy deposition. Different alloy compositions can induce varied physico-chemical properties in the resultant films. For example, by varying the alloy composition, magnetic properties can be altered,⁴³ the morphology can be improved^{44,45} or the electronic properties can be modulated.⁴⁵ Sometimes, contamination of the deposited layers with impurities from the bath, or with species that arise from the partial decomposition of electrolytes has been observed in the deposited layers obtained from IL-based baths. However, this contamination can be reduced if pulse plating is used instead of dc plating.⁴⁴ Selectivity in terms of crystalline phases can also be achieved using pulse plating in ILs. For example, a single phase of Al-Ni alloy (Ni_3Al) can be obtained by pulse plating, while multiple intermetallic phases are usually detected in the dc plated deposits.⁴⁶

There are metals for which the reduction process is quite complex as it involves the transfer of many electrons, e.g. tantalum or niobium (Fig. 3). The electrodeposition of Ta using potentiostatic pulses in ILs produces smoother and more compact

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layers when compared to dc plating at elevated temperatures.^{34,51} At the same time, potentiostatic pulses favor the electrodeposition of Ta at room temperature⁵² (Fig. 4). Hard magnetic layers (Co-Sm) can also be obtained by using the pulse plating technique in ILs.⁵³

Outlook

Electrochemistry is an economic technique for obtaining coatings on substrates of complicated geometrical shape (e.g. screws, springs). Deposits with smooth surfaces, good resistance against corrosion and high hardness, and low levels of contamination with foreign species are usually desired for specific functional coatings. For layers that cannot be deposited from aqueous baths, ILs are the media

of choice. If ILs are to be employed for electrodeposition on a larger (industrial) scale, it is highly probable that additives in conjunction with pulse plating techniques will be used. We anticipate intensive research on optimizing deposition processes in ILs in the presence of additives, or under different plating conditions. Another key aspect that should be kept in mind is the effect of impurities. These could be byproducts arising from the synthesis of ILs (such as Li) or traces of water. Some effects of the impurities have been addressed in the literature^{2,5,7} and therefore are not detailed here. When one implements an IL-based plating process on an industrial scale, minimization of impurities will be essential. The precursors that one can use in the deposition process are also very important, as well as the anion/cation combination employed. We envision that an important role will be played by tailored ILs in this context.¹¹

About the Authors



ADRIANA ISPAS studied physics at the “Alexandru I. Cuza” University in Iasi, Romania, where she obtained her MSc in applied physics in 2001. In 2003 she moved to Germany to the Dresden University of Technology, in the department of

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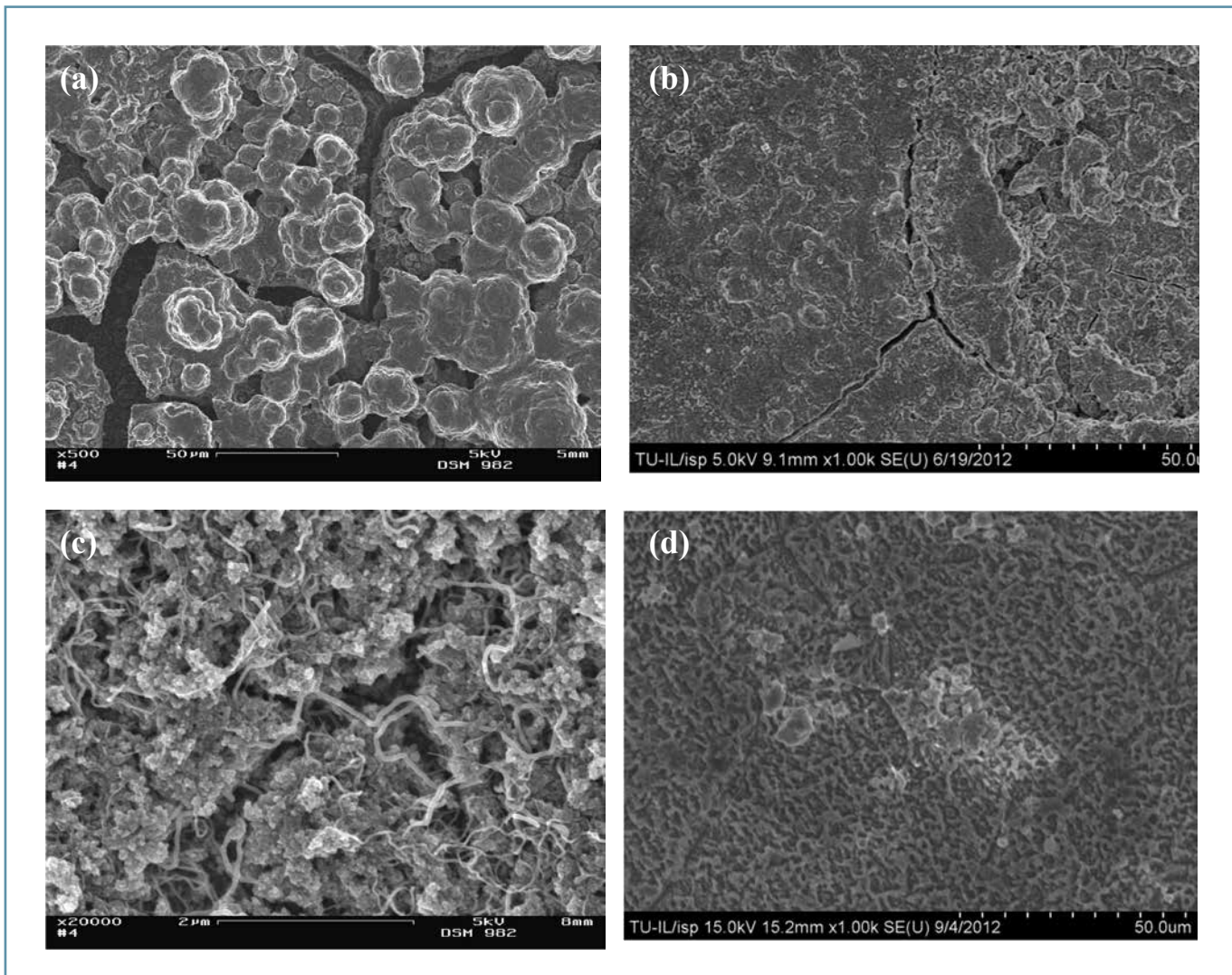


FIG. 4. Scanning electron micrographs of layers electrodeposited from ILs: (a) 0.5 M TaF₅ in 1-methyl-3-propyl-imidazolium bis(trifluoromethylsulfonyl)amide, [PMIm][TfSA]: at 130°C and E = -1.6 V; (b) 0.5 M TaF₅ in [PMIm][TfSA], 1 s at E = -0.8 V and 1 s at E = -1.7 V; (c) 0.5 M NbF₅ in [PMIm][TfSA]: 130°C and E = -1.3 V; (d) 0.5 M NbF₅ in [PMIm][TfSA]: at 25°C, 1 min at E = -2.5 V and 1 min at E = -1.0 V, Working electrode was Au, counter and reference electrodes were Pt wires.



ANDREAS BUND studied Chemistry at the University of Saarland during 1989-1995. His PhD was on the application of piezoelectric quartz crystals for rheological and microgravimetric *in situ* measurements. He obtained his PhD in 1999 with *summa cum laude*. 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 Universitaet 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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