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Non-haloaluminate ionic liquids for low-temperature electrodeposition of rare-earth metals—A review

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Abstract: The inherent advantages of ionic liquids (ILs) in electrochemistry have received extensive attention in recent two decades. As a new generation of ILs, non-haloaluminate ILs exhibit better benefits and fewer drawbacks compared to haloaluminate based ILs, which are more qualified for metal electrodeposition, especially reactive metals. In this brief review, the recent developments regarding the application of non-haloaluminate ILs as solvents for low-temperature electrodeposition of rare-earth (RE) metals are outlined. In addition, the current problems and an outlook on future research are presented.

Keywords: ionic liquids; electrochemistry; rare earths; low-temperature electrodeposition

Due to the unique unpaired f-electrons configuration and rich structures of energy levels, rare-earth (RE) metals and their alloys exhibit interesting optical, electric, magnetic, and hydrogen storage properties that have been widely studied for their potential applications in various functional materials[1–6]. The high reactivity of lanthanide metals requires an electrodeposition route utilizing aprotic electrolytes. Production of RE metals is conventionally operated in high temperature molten salts electrolytes, i.e., oxide, fluoride or chloride, depending on the raw material[7]. However, molten salts are highly corrosive and high energy consumption limited by high-temperature operation. Organic solvents have also been selected as electrolytes for electrodeposition of RE metals[8]; nevertheless they are generally volatile and inflammable.

Ionic liquids (ILs) have attracted increasing attention as novel aprotic media and potential replacements for high-temperature molten salts and organic solvents in electrodeposition processes on both a laboratory and industrial scale owing to their unique chemical and physical properties, such as negligible vapor pressure, nonflammability, thermostability, property tunability, high ionic conductivity, wide electrochemical potential windows, and good solubility for metal salts[9,10]. As the first generation of ILs, haloaluminate based ILs (mixtures of aluminum halides with the corresponding halide salt of an organic cation) have been extensively investigated for the electrodeposition of reactive metals, such as Li, Na, Al[11–13]. Metal halides (most usually the chloride) generally serve as precursors for their ready solubility in these ILs. However, the highly hygroscopic nature of haloaluminate based ILs has delayed progress to larger scale applications, since they must be carefully prepared and handled under essentially anhydrous conditions[14]. To combat this, studies on development of ILs based on hydrophobic anions, defined as air- and water-stable ILs, have spurred enormous research interests. Air- and water-stable ILs, are normally composed of unsymmetrical organic cations, such as alkyl-imidazolium alkyl-pyridinium, tetraalkyl-ammonium, etc., and hydrophobic anions, for example, PF_6^-, OTf^-, and NTf_2^-, which could be prepared and safely stored outside of an inert atmosphere. In comparison with the haloaluminate based ILs, air- and water-stable ILs exhibit larger electrochemical windows (generally more than 4.0 V) and lower viscosity, which not only creates an opportunity to the electrodeposition of reactive metals at room temperature, but also offers more efficient mass transport and higher conductivity for electrochemical applications. In fact, many reactive and refractory metals including Li, Mg, Al, Ta, Nb, Ti, and semiconductors such as Si and Ge were successfully prepared from the air- and water-stable ILs[15–18]. Moreover, "task specific" ILs that contain carboxyl-functionalized cations show high solubility for metal oxides[19–21], in particular lanthanide oxides, which may open up a promising route for the preparation of RE metals in ionic liquid media from their oxides at room temperatures, though investigations on the sequent electro-

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deposition are lacked. Similarly, deep eutectic and dicyanamide based ILs also behave as versatile solvents for electrochemistry.

To obtain further information, several comprehensive books[15,22,23] and reviews[24–27] that give detailed descriptions of the synthesis, purification, physicochemical properties, and applications of these ILs are recommended. This brief review focuses on the recent developments in the application of non-haloaluminate ILs, including air- and water-stable, task specific, deep eutectic and dicyanamide based ILs for electrodeposition of RE metals at low temperatures (<473 K). Furthermore, some currently facing issues and the promising direction on future research are also addressed.

1 Air- and water-stable ionic liquids

1.1 Organic precursors

RE element La was firstly reported to be successfully electrodeposited from a haloaluminate based IL system, $LaCl_3$ saturated EMIC-$AlCl_3$ with the addition of LiCl and $SOCl_2$; however, due to the high hygroscopic and reactive nature of this system, complex solid phases, such as $La(OH)_2$, La_2O_3, LaOCl and $LaCl_3$, were also formed[28]. The following investigations are then mainly focused on air- and water-stable ILs, particularly for NTf_2^- anion based solvents. Unfortunately, NTf_2^- anion is demonstrated to be a poor ligand, for instance, in comparison to Cl^- [29,30], that means the abundant sources of metals salts such as RE chlorides, oxides and fluorides cannot be used as precursors directly, since they are hardly dissolved in the neutral melts[31]. Consequently, the synthesis of RE intermediate salts, $RE(NTf_2)_3$, which are treated as the introducing precursors, is generally indispensable and the typical extraction procedure for RE metals in NTf_2-based ILs can be schematically drawn in Fig. 1.

Bhatt et al.[32] have firstly reported the synthesis of lanthanum bistriflimide complexes $[LnNTf_2)_3(H_2O)_3]$ (where Ln=La^{III}, Sm^{III} or Eu^{III}) and their electrochemical reduction behaviors in N,N,N-trimethyl-n-butyl-ammonium bis(trifluoromethanesulfonyl)imide (Me_3NBu-NTf_2). The all three lanthanide complexes were shown to be reducible to the metallic state, where the reduction of La(III) was electrochemical irreversible with three- electron transfer in a single step, La^{III}→La^0, while for both Sm(III) and Eu(III), reduction processes involved two consecutive irreversible reactions, Sm^{III}→Sm^{II} and Sm^{II}→Sm^0, and Eu^{III}→ Eu^{II} and Eu^{II}→Eu^0, respectively. In addition, the redox reactions between trivalent and divalent of Sm, Eu and Yb in 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-NTf_2) with their corresponding NTf_2 complexes as precursors were studied[33]. In all cases, the electrode reactions of the Sm(III)/Sm(II), Eu(III)/Eu(II), and Yb(III)/Yb(II) couples at a glassy carbon electrode exhibited poor reversibility owing to the shielding effect of NTf_2^- anions surrounding the redox center. However, the studies were restricted only to the redox conversion of trivalent to divalent, while their electrochemical conversions to metallic form were not reported. Rao et al.[34] further investigated the electrodeposition of Eu on either glassy carbon (GC) or stainless steel (SS) electrode from a solution of $Eu(NTf_2)_3$ in BMP-NTf_2 at 298–373K. Similar to the observations in Me_3NBu-NTf_2, the reduction of Eu(III) in BMP-NTf_2 was demonstrated to undergo a two-step redox conversion to metallic form involving a quasi-reversible reaction, Eu^{III}→Eu^{II} and followed by an irreversible reaction, Eu^{II}→Eu^0, with an estimated charge transfer rate-constant (ks) value of 6.15×10^{-5} cm^2/s at 373 K. A diffusion coefficient of Eu(III) was determined to be in the range of 10^{-7} cm^2/s at 373 K. A gray colored metallic Eu was obtained after electrolysis of 100 mmol/L $Eu(NTf_2)_3$ in BMP-NTf_2 at −2.6 V vs. Fc/Fc^+ on SS electrode for 5 h.

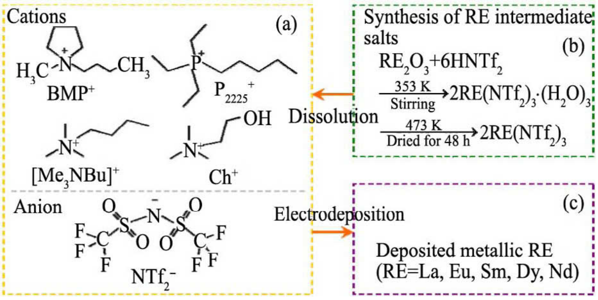

Fig. 1 Schematic illustration of NTf_2-based ILs normally investigated (a), synthesis of RE intermediate salts (b), and electrodeposition process (c)

Matsumiya et al.[35] were the first to report the electrochemical behavior of Sm(III) and Eu(III) in a novel class of phosphonium/ammonium cations based ILs. It was found that the diffusivities of these trivalent complexes in phosphonium ttriethyl-pentyl-phosphonium bis (trifluoromethyl-sulfonyl)imide (P_{2225}-NTf_2) IL were more facile than that in the corresponding ammonium ttriethyl-pentyl-ammonium bis(trifluoromethyl-sulfonyl) imide (N_{2225}-NTf_2) IL, due to a weaker electrostatic interaction in P_{2225}-NTf_2 compared to that of N_{2225}-NTf_2. The diffusion coefficients of Sm(III) and Eu(III) in these ILs were calculated to be in the range of 10^{-12} cm^2/s at 298 K. Further works[36–38] in the same research group showed that P_{2225}-NTf_2 was qualified as a novel electrolytic solvent for the electrodeposition of Dy and Nd. The diffusion behaviors of Dy(III) and Nd(III) in P_{2225}-NTf_2 were satisfied with the Arrhenius law, and the corresponding activation energies were estimated to be 53.4 kJ and 61 kJ/mol, respectively. Their diffusion coefficients were found to be in the order of 10^{-11} cm^2/s at 373 K. Deposits with average size in 0.8–0.9 µm for Dy and 1.68 µm for Nd were obtained on the Cu substrate by potentiostatic deposition at –3.8 V vs. Fc/Fc^+ in 0.1 mol/L