TECHNICALLY speaking

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Ambient Temperature Ionic Melts in Magnesium Electrodeposition

Safety, ease of handling, high-energy density considerations in a secondary battery, obviously, makes magnesium-based electrochemical system a potential candidate for the requirement of developing a high energy, environment friendly secondary battery. Ionic melt has the advantage of having only ions which is not possible in usual electrolyte solutions where ions are enveloped by solvent molecules through primary and secondary solvation sheaths.

INORGANIC MELTS:

Low melting point binary mixtures of magnesium halide are as follows:

MgI_2 – KI	250°C
$MgCl_2$ – $AlCl_3$	184°C
$Mg(NO_3)_2$ – KNO_3	178°C
$Mg(NO_3)_2$ – $NaNO_3$	135°C

These low melting systems have iodide and nitrate as anions which are not sufficiently stable in the positive potential range and, therefore, may not be compatible with the positive electrode material in a magnesium-based electrochemical system. $AlCl_3$ containing melts is prone to Al co-deposition and does not require a considerably low temperature. Ternary or multi-component systems containing magnesium halide and having a melting point lower than 100°C may be explored on the lines of work reported for Al deposition.[1]

ORGANIC MELTS:

The electrodeposition of aluminium below 100°C from melts containing Butylpyridinium chloride (BPC) or Ethyl-methyl-imidazolium chloride (EMIC) and $AlCl_3$ has been demonstrated. The industrial utilization of these processes has been reported.[2] Ionic liquids have been defined as solvents solely composed of ions and having melting points below 100°C. Typical cations are substituted imidazolium ions, such as 1-butyl-3-methylimidazolium, or tetraalkylammonium ions, e.g., trioctylmethyl-ammonium. Some important anions are hexafluorophosphate, trifluoromethylsulfonate, bis(trifluoromethylsulfonyl)imide. Many ionic liquids have negligible vapor pressures, even at temperatures of 300°C, have viscosities similar to water, ionic conductivities of up to 0.1 $(\Omega\ cm)^{-1}$, and wide electrochemical windows of more than 6 V. Ionic liquids will gain a rising interest in electrochemistry as elements and compounds can be made electrochemically which are not accessible by conventional aqueous or organic electrochemistry.[3] Electrochemical magnesium deposition and dissolution on silver substrate with 100% cycling efficiency could be realized in the ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide containing 1 M $Mg(CF_3SO_3)_2$.

Overpotential for the steady-state deposition-dissolution processes at 0.1 and 0.2 $mAcm^{-2}$ was only several tens of millivolts against magnesium at room temperature. The cyclic voltammograms also demonstrated reversible magnesium steady-state deposition-dissolution around 0 V (vs Mg reference electrode). Impedance measurements of the electrode revealed a large electrochemical resistance during the initial Mg deposition. This resistance, however, became much smaller during steady-state cycling. Results from scanning electron microscopy showed that Mg deposition was not smooth and compact, and could be completely dissolved electrochemically.[4]

A metallic aluminum (Al) layer was successfully electrodeposited onto a magnesium (Mg) alloy in a Lewis acidic aluminum chloride–1-ethyl-3-methylimidazolium chloride ($AlCl_3$–EMIC) ionic liquid under galvanostatic condition at room temperature. The electrochemical impedance spectroscopic data indicated that a bare Mg alloy had a polarization resistance of only 470 $\Omega\ cm^2$ in 3.5 wt% NaCl solution, whereas the Al-coated Mg sample showed its resistance as high as 8700 $\Omega\ cm^2$ in the same environment. Moreover, it was also found that the Al layer deposited at a lower current density was more compact and uniform when compared to that deposited at a higher current density; consequently, this coating revealed a superior protection capability for the Mg substrate against corrosion.[5]

Room temperature, magnesium ion-conducting molten electrolytes were prepared using a combination of acetamide, urea and magnesium triflate or magnesium perchlorate. The molten liquids showed high ionic conductivity of the order of $mScm^{-1}$ at 25°C. Vibrational spectroscopic studies based on triflate/perchlorate bands revealed that the free ion concentration was higher than that of ion-pairs and aggregates in the melt. Electrochemical reversibility of magnesium deposition and dissolution was demonstrated using cyclic voltammetry and impedance studies.[6]

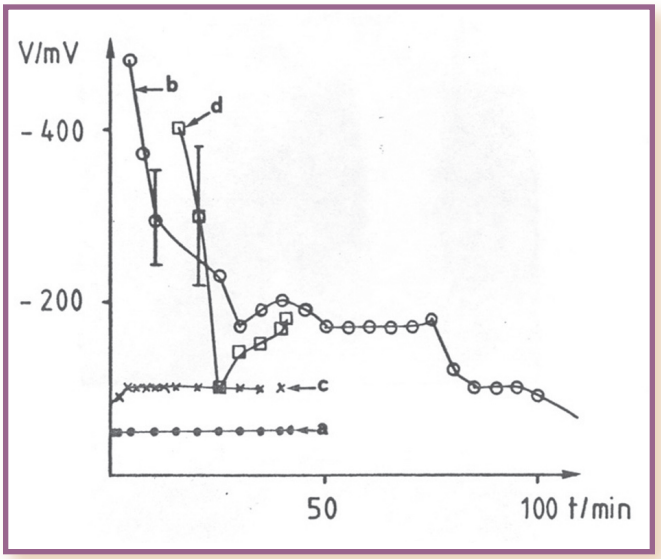

Figure 1. Potential-time characteristics for galvanostatic deposition in different solutions, j=5 mAcm^{-2}
a: EMIC- $AlCl_3$ /40-60 (weight %)
b: EMIC-$AlCl_3$ -$MgCl_2$ / 39.5 – 59.1–1.4
c: EMIC-$AlCl_3$ -$MgCl_2$ / 38.8 – 58.3–2.9
d: EMIC-$AlCl_3$ -$MgCl_2$ / 37.8 – 56.6–5.6

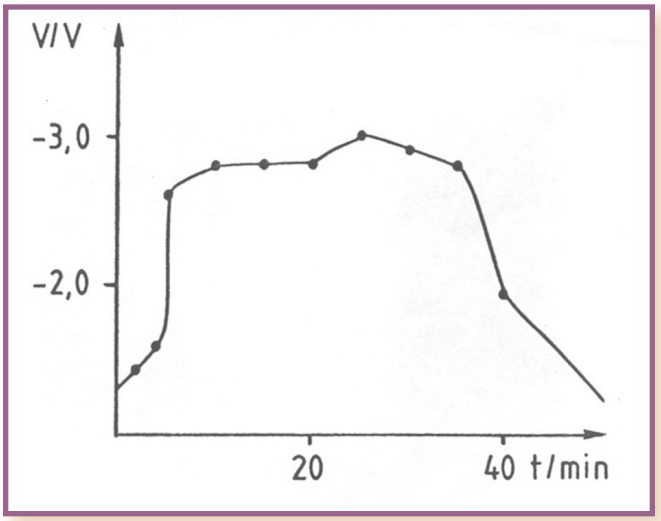

Figure 2. Potential-time characteristics for galvanostatic deposition in a EMIC-$AlCl_3$ -$MgCl_2$ / 78 – 2–20 (weight%) solution, j=5 mAcm^{-2}

Electroplating of Al on Mg and its alloy from $AlCl_3$-EMIC ionic liquid at the lower temperature of 5°C and 20°C with observations of surface morphologies of Al deposits and of interfaces between the Al layer and the substrates are reported.[7]

The magnesium insertion (in MoO_3 reversibly) at 80°C from the $MgCl_2$/EMIC/$AlCl_3$ molten salt electrolyte system was demonstrated.[8]

Perhaps for the first time the possibility of EMIC forming ionic melt with $MgCl_2$ was shown. However, galvanostatic deposition in such a melt at 90°C did not reveal even trace of Mg deposition. Ternary ionic melts of EMIC, $MgCl_2$ and $AlCl_3$ did show Mg deposition along with Al[S. Sultan and H. Tannenberger, CSEM technical report no. 477, 1991]. In view of enhanced quantum of electrochemical research in ambient temperature ionic melts with reference to magnesium electrochemistry (as reported in literature), it seems appropriate to publish briefly the findings of pioneering work done in this field decades ago (1991).

	EMIC	$MgCl_2$	$AlCl_3$
a	39.5	1.40	59.3
b	38.8	2.90	58.3
c	37.8	5.60	56.6
d	78	20	2

Table 1. Ternary ionic melt EMIC-MgCl2-AlCl3 (composition in weight %).

	Al	Mg
a	99.6	0.4
b	97.7	2.3
c	99.3	0.7

Table 2. Microprobe analyses: (% weight).

MATERIALS AND METHODS

All experiments have been carried out in a glove box (Mecaplex) under nitrogen with continuously controlled moisture and oxygen content: $CH_2O \leq 4$ ppm, $CO_2 \geq 4$ ppm.

Small electrochemical cells (10 ml) have been used to avoid excessive use of the expensive chemicals: Ethylmethyl imidazolium chloride (EMIC) and a stock solution (liquid at room temperature) of 60% $AlCl_3$ -40% EMIC (by weight) was provided by Paul Scherrer Institute, Villigen, Switzerland. The three electrodes consisted of three wires, the nature of which depended on the investigated system. The area of the working electrode was only estimated, admitting an error of up to a factor of 2.

All electrochemical measurements have been carried out with standard AMEL equipment.

EMIC – $MgCl_2$ melt:

$MgCl_2$ (Aldrich, 98%, dry) was dried in vacuum at 300°C for 60 hours. The solubility of $MgCl_2$ in EMIC at 80°C was checked by adding increasing amounts of $MgCl_2$ to the melt. Up to 24% (weight) of $MgCl_2$ have been added without reaching the limit of solubility. However, dissolution is slow (~ tens of hours) in spite of magnetic stirring.

Ternary EMIC – $MgCl_2$ – $AlCl_3$ melt:

Different compositions of ternary system was prepared by adding $MgCl_2$ in the stock solution (liquid at room temperature) of 60% $AlCl^3$ -40% EMIC (by weight). Table 1 gives the composition (in weight%) of four such melts