

Progress in nonaqueous magnesium electrochemistry

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Abstract

We report herein on recent studies related to nonaqueous magnesium electrochemistry and R&D of rechargeable magnesium batteries. Extensive attempts have been made to examine electrolyte systems based on ionic liquids as potential solutions for nonaqueous magnesium batteries. In general, magnesium electrodes are reactive with many imidazolium-based ionic liquids. In those liquids in which Mg electrodes are apparently stable, they develop a blocking passivation. It was possible to develop improved solutions for rechargeable magnesium batteries based on mixtures of THF, tetraglyme (where the high boiling point of the polyether improves the safety features), and complexes based on Lewis acid–Lewis base reactions between AlCl_2R and MgR_2 or RMgCl . The choice of the type of Lewis base, the R group and the appropriate acid–base ratios enables a reasonable specific conductivity to be obtained, 100% cycling efficiency of Mg electrodes, and a wide electrochemical window, up to 2.4 V.

This work included rigorous studies by Raman spectroscopy, electron microscopy, ICP, and a variety of electrochemical techniques. In parallel, Mg insertion cathodes based on cubic TiS_2 , NiS_x , NiSse and CuS_x were also investigated.

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1. Introduction

Success in the R&D and commercialization of primary and secondary Li and Li-ion batteries has demonstrated the application of active metals as anode materials in high energy density batteries. Another active metal that is widely used as the negative electrode in batteries is zinc. Other natural candidates used as anode materials in batteries are active metals such as Mg and Al. Over the years, magnesium electrochemistry has been explored in connection with R&D of battery systems. Practical, primary aqueous magnesium batteries were developed [1], and there have already been several studies on nonaqueous magnesium electrochemistry in connection with R&D of rechargeable Mg batteries [2–5]. About seven years ago, we reported on a new development of nonaqueous rechargeable magnesium battery systems that included magnesium metal anodes, $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($0 \leq x \leq 2$), Chevrel phase cathodes, and electrolyte solutions based on ethereal solvents and complexes that are the products of reactions between R_2Mg Lewis base and $\text{AlCl}_{3-n}\text{R}_n$ Lewis acid (R = alkyl groups) [6]. It was demonstrated that the acid–base ratio determines the electrochemical windows of these solutions, their conductivity, and the characteristics of Mg

deposition–dissolution in terms of over-potentials, reversibility, and deposition morphology [7–10].

In recent years, we have continuously studied several aspects of nonaqueous magnesium electrochemistry, including solution chemistry [11,12] and the electrochemical intercalation of magnesium [13,14]. Efforts are also underway by other groups to develop electrolyte solutions in which Mg electrodes behave reversibly (e.g., systems based on ionic liquids [15,16]) and Mg-insertion electrodes [17,18]. Hence, we can see that over the past few years there has been a continuous interest in nonaqueous Mg electrochemistry as part of ongoing efforts to develop rechargeable magnesium battery systems. This paper reports on further progress in that area, including the development and study of electrolyte solutions of wide electrochemical windows, improved kinetics of Mg electrodes, and reduced volatility. The paper also describes efforts to apply ionic liquids as electrolyte solutions for reversible Mg electrodes. Finally, some preliminary studies of Mg insertion electrodes are briefly reported.

2. Experimental

All solution preparations and electrochemical measurements were carried out under a pure argon atmosphere in M. Braun, Inc. glove boxes (less than 1 ppm of water and oxygen). Ionic liquids were obtained from Merck KGaA and Fluka Inc. and most

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of the other high purity chemicals were obtained from Aldrich. 1-butyl-3-methylimidazolium tetrafluoroborate IL (BMImBF₄) (Fluka, ≥97.0%) was dried over molecular sieves. Water content was determined by Karl Fischer titration. Mg(CF₃SO₃)₂ (Aldrich, 97%) was used as received. Two methods of preparation were used. In the first one, the Mg salt was added to a warm IL solution (70 °C) followed by agitation (magnetic stirrer). In the second method, the IL was added to the Mg salt and then the solution was agitated and heated to 70 °C. Electrochemical measurements were carried out at room temperature. It should be noted that Mg(CF₃SO₃)₂ is hardly soluble in this medium. Working electrodes included silver, platinum and magnesium. Magnesium foils were used as counter and reference electrodes.

Solutions comprising ether solvents and complexes of the (MgR₂)_n·(AlCl₂R)_m type were prepared by the dropwise addition of a chosen amount of a 1 M ethylaluminumdichloride (EtAlCl₂) solution in hexane (Aldrich, 97%) to a vigorously stirred, carefully measured amount of filtered 1 M dibutylmagnesium (Bu₂Mg) in heptane (Aldrich, 97%), or to an appropriate amount of 2 M ethylmagnesium chloride (EtMgCl) in THF (Aldrich, 99%). In this case, a mildly exothermic reaction took place, yielding immediately a powdery white precipitate. The suspension thus formed was stirred at room temperature for an additional 48 h, after which it was vacuum dried. Dry tetrahydrofuran (THF, J.T. Baker 99.99%), or mixtures of THF and tetraglyme were added to the dry, white solid to a desired concentration. The solutions were clear and colorless.

Another synthetic route involved the careful addition of an AlCl₃ solution in THF (prepared *in situ*) to an appropriate amount of 2 M ethyl(methyl)magnesium chloride (Et(Me)MgCl) in the same solvent, followed by evaporation and the final addition of the desired ether solvent mixture. Solutions containing complexes with methyl groups only, were prepared by reacting THF solutions of CH₃AlCl₂ and CH₃MgCl at desired stoichiometric ratios.

The electrochemical stability of the solutions and the characteristics of Mg deposition processes were determined by their voltammetric behavior in one-compartment, three-electrode cells, using an EG&G, Inc. 273 potentiostat. The electrochemical cells consisted of magnesium metal counter and reference electrodes, and platinum working electrodes. The scan rate used for electrochemical window determination was 25 mV/s, and the anodic limit of the electrochemical window was determined at the deflection point, where the *I* versus *E* curve showed a rapid increase in the positive currents, usually at *ca.* 5.0 μA/cm² above the background currents. We also studied, in similar cells, the behavior of Mg-insertion cathodes comprising 80% active mass (e.g., Mo₆S₈), 10% PVdF binder and 10% carbon black (by slow scan rate cyclic voltammetry).

The morphology of Mg deposition was studied by processing Mg or copper working electrodes in sandwich-type cells using magnesium metal counter and reference electrodes, followed by SEM analysis of the working electrodes (JEOL 840). Raman spectra were obtained using a micro-Raman spectrometer from Jobin-Ivon Inc. with an He–Ne laser (632.817 nm) in standard rectangular quartz tubes (Aldrich). All of the experiments were performed at room temperature (25 ± 2 °C).

We prepared and tested cathode active materials of the general formula, M'M_zS_xSe_y, in which M, M' = Cu, Ti, Fe, or Ni and z, x and y assume various proportions. The compounds that we tested included CuS, CuFeS₂, CuFe₂S₃, Cu₉S₈, Cu₂S, NiS, c-Ti₂S₄, l-Ti₂S₄, TiSSe and NiS_xSe_y (solid solutions in various x/y ratios). The general synthesis method was a simple high-temperature reaction of the palletized powdered pure elements under vacuum, in sealed quartz ampoules. In some cases, the raw materials used were the metal-sulfides, with the proportional stoichiometric addition of the other ingredients, namely sulfur, metal powder, or selenium. For most of the materials, the calcination temperatures ranged between 550 and 900 °C, with reaction times of 24 h to two weeks (as for cubic CuTi₂S₄). In cases where a tertiary metal was needed for the high-temperature synthesis stage, this was followed by an appropriate leaching procedure. For instance, with CuTi₂S₄ the Cu was leached out by reaction with iodine in acetonitrile over a period of 4–6 days. In all cases, the success of each synthesis stage was monitored by powder XRD analyses (Advance D 8 from Bruker Inc.) and, in some cases, also by elemental analysis by ICP (from Jobin-Ivon Inc.).

3. Results and discussion

3.1. ILs for Mg electrochemistry

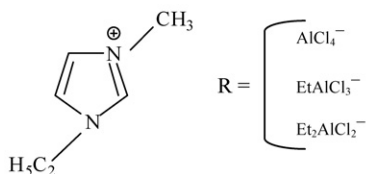
As an active metal, in a manner similar to lithium [19], magnesium is always covered by surface films in most kinds of atmospheres (ambient and inert), and in all polar aprotic solutions. However, in contrast to Li, whose surface films are usually Li-ion conducting [19], Mg electrodes in most electrolyte solutions are blocked, because surface films comprising Mg salts cannot conduct the bivalent Mg ions. In the search for inert polar aprotic solutions suitable for reversible Mg electrochemistry having wide electrochemical windows, ionic liquids (ILs) appear to be promising candidates. Indeed, recent work has demonstrated the possibility of reversible Mg deposition–dissolution in ILs comprising derivatives of imidazolium salts [15,16]. In parallel to those studies, we also studied the possibility of using ILs as electrolyte systems for Mg electrodes. Fig. 1 shows the various ILs systems studied and the relevant Mg salts. It should be noted that with none of these systems were we able to obtain reversible Mg deposition and dissolution, even in systems that could dissolve Mg salts up to high concentrations. Some very typical examples are demonstrated below.

Fig. 2 presents consecutive voltammograms, measured with a platinum working electrode in BMImBF₄ (see Fig. 1) containing 0.5 M Mg(CF₃SO₃)₂.

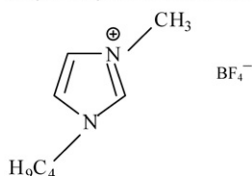
The background voltammetric behavior of BMImBF₄ is also presented (marked in the figure). The second CV related to the Mg salt solution, demonstrates a pronounced cathodic process due to the presence of the Mg salt and hence, should be attributed to magnesium deposition. The lack of corresponding anodic process indicates the irreversible nature of Mg deposition in this medium. The Mg deposited probably reacts with the ionic liquid (the BMIm⁺). The next, consecutive CV cycles reflect decaying cathodic currents, what means that the electrode is passivated.

Ionic liquids

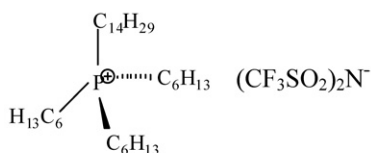
Ethylmethylimidazolium – R



Butylmethylimidazolium tetrafluoroborate



Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide

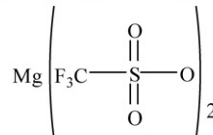


Magnesium salts

Magnesium chloride



Magnesium trifluoromethanesulfonate



Magnesium perchlorate



Dibutylmagnesium

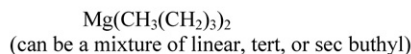


Fig. 1. Formulae of the ionic liquids and relevant salts tested in this work as potential electrolyte solutions for rechargeable magnesium batteries.

We did not identify yet the products of the possible reaction between Mg and BMIm^+ .

Fig. 3 shows the voltammetric behavior of a magnesium electrode in BMImBF_4 . The first cycle reflects both anodic and cathodic processes that should be attributed to magnesium dissolution and imidazolium reduction, respectively. However, in the second CV cycle the currents are very low, which reflects the passivation of the electrode. Similar results were obtained with all of the other systems.

It appears that magnesium electrodes, even if initially active, reach passivation in all of the IL-based systems presented in

Fig. 1, no matter which Mg salts are used. Passivation occurs due to reactions of magnesium with several types of ionic liquids (as is the case for imidazolium-based systems), or reactions with unavoidably present trace water. Our previous studies [20] may indicate the reactivity of bare Mg metal with anions such as ClO_4^- and BF_4^- . The results of such reactivity are the formation of insoluble Mg halides that completely block the Mg electrodes.

In certain IL systems, such as ethyl–methyl imidazolium– AlCl_4 , Mg metal visibly dissolves. We tried to repeat the experiments described in references [15,16], but were unable to obtain the reversible behavior of Mg electrodes nor the reversible Mg deposition–dissolution processes on noble metal electrodes in any of the IL systems. Hence, we have to conclude that most commonly used ILs, including those showing apparently high cathodic stability, are not suitable

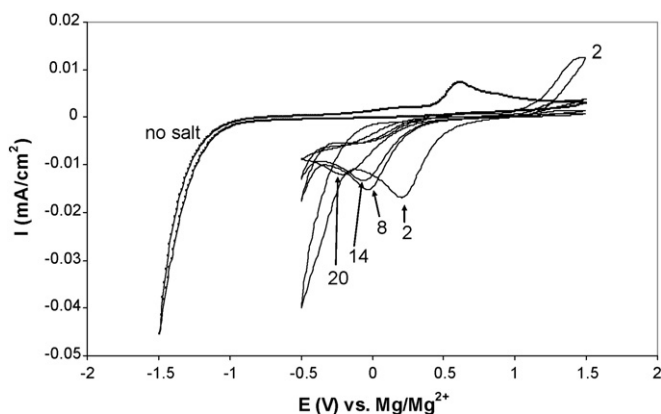


Fig. 2. Typical cyclic voltammograms measured with BMImBF_4 IL solutions and Pt working electrode at 50 mV/s. The CV related to the pure system (marked) and to solutions containing 0.5 M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ are presented, as indicated.

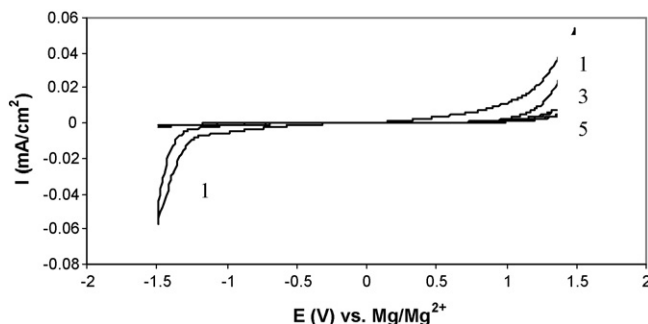
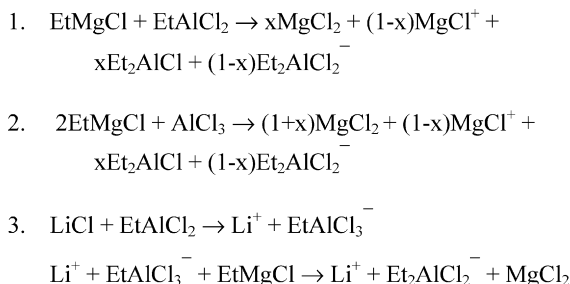


Fig. 3. Typical consecutive cycling voltammograms measured with an Mg electrode in BMImBF_4 , at 50 mA/s, as indicated.



Scheme 1. Major reactions used in this work for the preparation of solutions with “all ethyl complexes”.

solvents for reversible Mg electrodes. Thus, ILs cannot be considered as compatible or promising electrolyte solutions for Mg batteries.

3.2. Improved electrolyte solutions for magnesium batteries

Our first generation of electrolyte solutions for rechargeable magnesium batteries included THF solutions containing a complex with the formal stoichiometry of $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$, prepared by reacting MgBu_2 with AlCl_2Et at a ratio of 1:2. The anodic stability of this electrolyte solution is about 2.2 V (versus Mg R.E.). Mg electrodes are always bare and nonpassivated in these systems. We synthesized new solutions in which the R groups in the complexes were either all ethyl or all methyl. The all ethyl complexes were synthesized in three different ways, as presented in Scheme 1. Fig. 4 shows the Raman spectra of the solutions obtained by the three different synthetic routes, as indicated. The peak assignment is based on the Raman spectra of all the necessary reference solutions, prepared and measured within the framework of this study. These spectra confirm the product distribution presented for the reactions in Scheme 1. Solutions comprising complexes in which all the R groups were methyl were synthesized from the precursors, CH_3MgCl and AlCl_2CH_3 (usually at a 1:1 ratio).

Fig. 5 compares the steady state voltammograms of Pt electrodes in three THF solutions comprising “all methyl,” “all

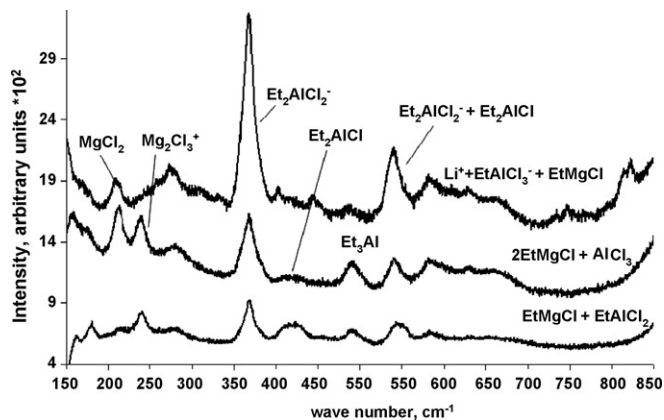


Fig. 4. Typical Raman spectra of a THF solution containing “all ethyl” complexes, prepared in three different ways, as indicated. The identification of the various peaks is based on a library of reference spectra prepared from reference solutions of known compositions [12].

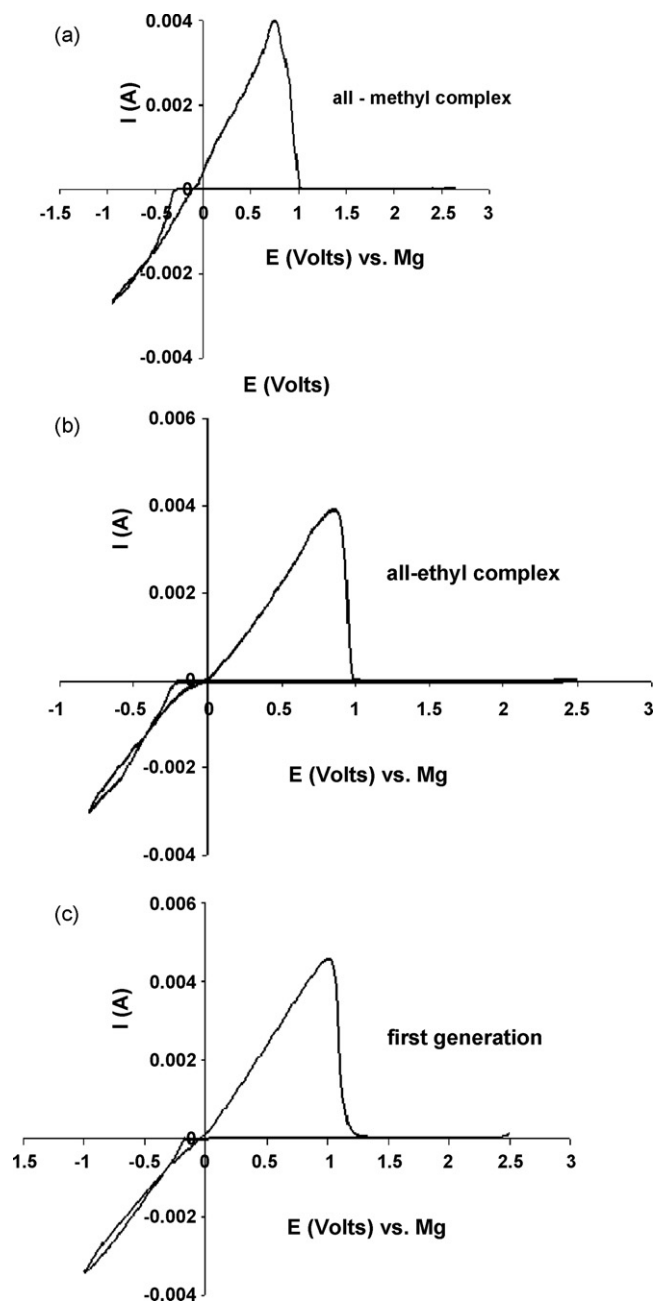


Fig. 5. Typical steady-state voltammograms of Pt electrodes in THF solutions containing various complexes. 25 mV/s. (a) The complex was prepared by reacting $\text{CH}_3\text{MgCl} + \text{AlCl}_2\text{CH}_3$; (b) the complex was prepared by reacting $\text{EtMgCl} + \text{EtAlCl}_2$; (c) the complex was prepared by reacting Bu_2Mg and EtAlCl_2 at a 1:2 ratio (the standard electrolyte) [6]. For the product distribution for a, b, see Scheme 1.

ethyl” and “ethyl–butyl” (our first, standard system) complexes, as indicated. In all three solutions, magnesium is deposited and dissolved reversibly, as well demonstrated by the CVs in Fig. 5, at efficiency close to 100%. However, it is clearly seen that the anodic stability of the solutions increases in the order of “ethyl butyl complex” < “all ethyl complex” < “all methyl complex.” As confirmed by previous studies [11,12], the reaction between the MgR_2 base and AlCl_2R acid at high acid/base ratios forms cations of the MgCl^+ or Mg_2Cl_3^+ type,

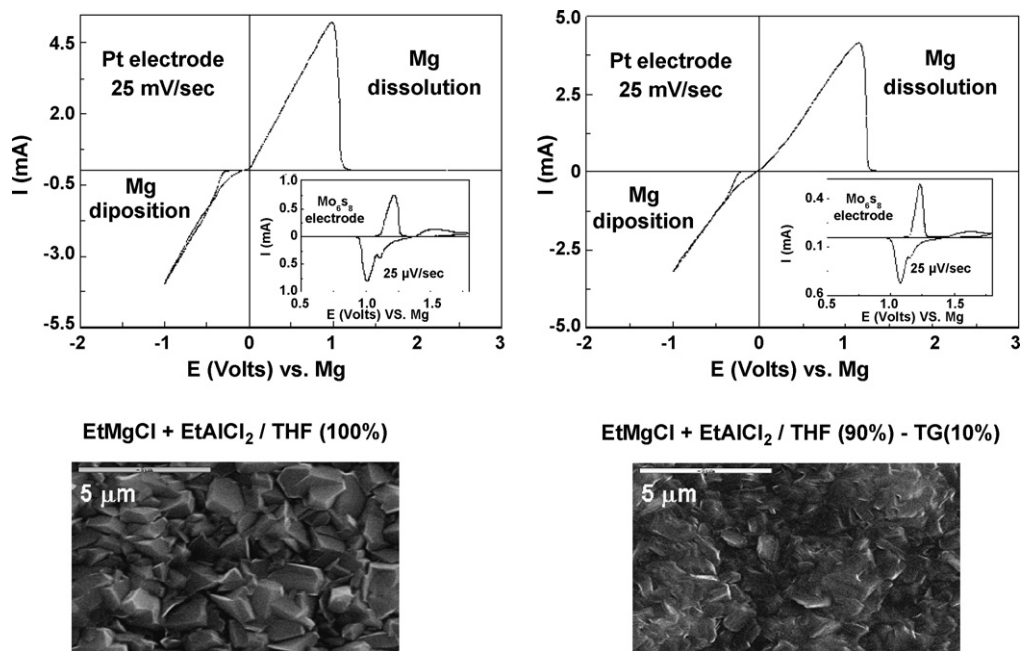


Fig. 6. A comparison between the performance of THF and THF–tetraglyme 9:1 solutions containing the complex electrolyte formed by reacting EtMgCl and EtAlCl₂ (see Scheme 1). Typical voltammograms of Pt electrodes and Mo₆S₈ composite cathodes, as well as SEM micrographs of Mg deposits, are presented, as indicated. The SEM micrographs reflect Mg deposition on copper substrates, 2 mA/cm², 2.8 C/cm². A scale appears in each micrograph.

and anions such as AlCl₂R₂[−]. Hence, the electrochemical windows of these solutions are determined by the anodic stability of the Al–R bonds. Thus, as the R group is smaller (Bu > Et > Me), its electron pushing tendency is likewise smaller, and, as expected, increases the resistance of the Al–R bonds to oxidation. It should be noted that in all three types of solutions, Mg insertion into Mg_xMo₆S₈ (0 ≤ X ≤ 2) is reversible, and therefore the behavior of the Chevrel phase cathodes is very similar in all of these solutions (since Mg insertion occurs from the same solution species, namely MgCl⁺ or Mg₂Cl₃⁺).

One of the problems related to the solutions described above is the high volatility of the solvent, THF. It would be preferable, from a safety point of view, to use far less volatile solvents in Mg batteries. It was found that all the above complexes can be prepared in solutions based in triglyme and tetraglyme (CH₃–O(CH₂–CH₂–O)_n–CH₃, n = 3 or 4, respectively). Mg electrodes behave reversibly in triglyme or tetraglyme solutions of (R₂Mg)_n•(AlCl₂R)_m complexes, and Mg ions can be intercalated reversibly into Mg_xMo₆S₈ Chevrel phases in the same solutions. However, the conductivity of these solutions is lower compared to that of THF solutions. In addition, the kinetics of Mg deposition, dissolution, and intercalation is more sluggish in the polyether solutions, compared to that of THF solutions. As a compromise, we checked the behavior of the above complex solutions in mixtures of THF and tetraglyme. We found that it was possible to use solutions with 10–20% tetraglyme (TG) in THF (by volume) without giving up on performance (compared to solutions based on pure THF).

Fig. 6 presents a comparison between the behavior of Mg deposition–dissolution and intercalation processes in THF and THF–TG 9:1 solutions of the (EtMgCl)•(EtAlCl₂)₂-complex. The figure shows typical steady state voltammograms of these

solutions with Pt and Mo₆S₈ (composite) electrodes, as well as typical SEM micrographs of Mg deposits on Cu substrates (obtained by Mg deposition processes with both solutions). The voltammograms measured with the platinum electrodes show the features of Mg deposition–dissolution processes and a similar anodic stability for both solutions. The slow scan rate CVs related to Mg ion intercalation–deintercalation into Mo₆S₈ composite electrodes also reflect the similar behavior of these processes in both solutions. However, the morphology of Mg deposition is slightly different, as demonstrated by the SEM micrographs. The Mg deposits have sharper crystallites in the THF solution, as compared to the THF–TG solution. Repeated experiments clearly demonstrated that Mg cycling efficiency in both solutions is the same, close to 100%. Hence, it is possible to use THF–TG mixtures with TG < 20% in rechargeable Mg batteries. The presence of the heavy ether reduces the overall volatility of the solution and prevents dangerous reactions between Mg deposits or dry complexes with moisture in the air, upon the unexpected exposure of battery components to ambient air.

3.3. On the search for new cathode materials

The Mg_xMo₆S₈ Chevrel phase is indeed a reversible cathode material for rechargeable magnesium batteries that can undergo thousands of discharge–charge cyclings at very low capacity fading [21]. One can definitely find possible commercial applications for rechargeable Mg batteries with Mo₆S₈ cathodes. However, the theoretical capacity of this cathode material is 122 mAh/gr, and its average operating voltage is around 1.1 V versus Mg anode. Thus, the practical energy density of rechargeable magnesium batteries using Mo₆S₈ cathodes is not

expected to exceed 60 Wh/Kg, even with the best engineering. In terms of engineering, Mg batteries with Mo_6S_8 may have some unique features. These include the possibility of using very thin Mg foil, with no need for a current collector and a low percentage of nonactive additives for the composite cathode, because the $\text{Mg}_x\text{Mo}_6\text{S}_8$ material is highly conductive. In addition, there are no side reactions in this battery system, and therefore there is no need to use any excess of Mg and electrolyte solutions to compensate for possible losses of active materials. Thus, the ratio between practical and theoretical energy densities of these batteries may be higher than usual in comparison to other rechargeable battery systems. However, in order to extend the possible application of rechargeable Mg batteries, it is important to develop new cathode materials of higher operational voltage and higher theoretical capacity, thus making it possible to compose Mg batteries with high energy density (a property that depends mostly on the cathode used). In the search for new cathode materials for Mg batteries, we synthesized materials of the following compositions: $\text{M}'\text{M}_2\text{S}_x\text{Se}_y$, in which M, $\text{M}' = \text{Cu}$, Ti, Fe, Ni or Cu and z , x and y assume various proportions. The compounds that we tested included CuS , CuFeS_2 , CuFe_2S_3 , Cu_9S_8 , Cu_2S , NiS , $\text{c-Ti}_2\text{S}_4$, $\text{l-Ti}_2\text{S}_4$, TiSSe , and NiS_xSe_y (solid solutions in various x/y ratios). In general, all of these compounds, except for $\text{c-Ti}_2\text{S}_4$, showed some reversible electrochemical activity in THF solutions containing complexes of the formal stoichiometry $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$. In all cases, repeated magnesium insertion–deinsertion could be observed. However, the capacity gradually declines from cycle to cycle. Since the results thus obtained are mostly preliminary, a detailed discussion on structural aspects and correlation between structures and rigorous electrochemical response is far beyond the scope of this paper, which is aimed mostly at reviewing progress and new directions of interest in the field of Mg electrochemistry. It can, however, be reported that in the case of CuS_x , NiS_x and NiSSe , Mg is inserted via the displacement of copper or nickel, while the insertion of Mg into cubic TiS_2 is an intercalation reaction. In addition, while the insertion of Mg into the above MS_2 compounds takes place only at elevated temperatures, the insertion of Mg into MSSe compounds is possible at room temperature. As an example, Fig. 7 shows several potential profiles obtained from a composite C-TiS_2 electrode upon galvanostatic insertion–deinsertion of magnesium at 60°C in $\text{THF}/\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ complex solutions.

The behavior of an electrode comprising layered TiS_2 is also presented. A common denominator for all the above-mentioned systems, which is demonstrated in Fig. 7, is the pronounced hysteresis between the discharge and charging processes (Mg ion insertion and deinsertion, respectively), and the decay in capacity upon repeated cycling. Hence, none of the above-mentioned systems can be considered as a practical cathode material for rechargeable magnesium batteries. However, all of them are interesting probe systems for the general study of electrochemical insertion of multivalent ions into inorganic hosts, comparison between mono- and multivalent ion insertion, and mechanistic studies of insertion via displacement reactions. The study of other potential cathode materials for rechargeable magnesium batteries is in progress.

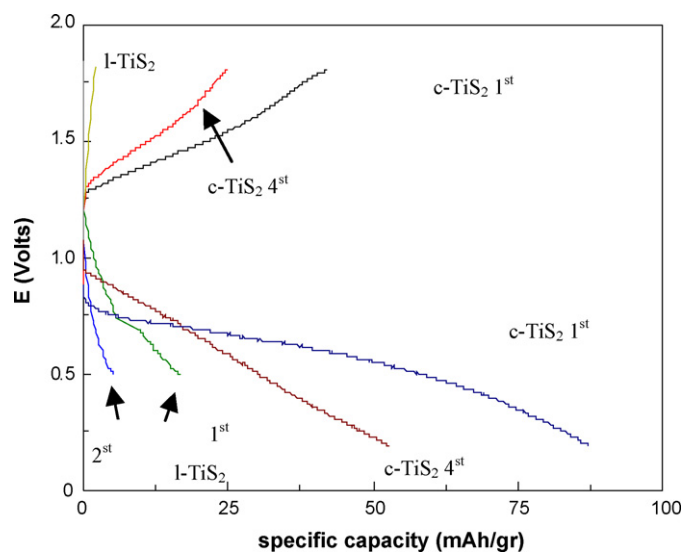


Fig. 7. Voltage profiles measured during galvanostatic magnesium intercalation and deintercalation of composite electrodes containing cubic TiS_2 as the active mass (80%). The composite electrodes contain 10% PVdF binder and 10% carbon black. $\text{THF}/\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ solution at 60°C , $0.1 \text{ mA}/\text{cm}^2$. The various cycle numbers are indicated.

4. Conclusion

In order to develop high energy density, rechargeable magnesium batteries, it is necessary to find electrolyte solutions with as wide an electrochemical window as possible in which Mg electrodes behave reversibly and, in parallel, to find new cathode materials that have a high red-ox potential (suitable for the electrochemical windows of the relevant electrolyte solutions) and high capacity. Natural candidates for high anodic stability, nonaqueous electrolyte solutions for Mg batteries are ionic liquids. However, our extensive studies of these as potential electrolyte systems for rechargeable Mg batteries showed two negative possibilities: several commonly used ILs, such as derivatives of imidazolium salts, are reactive with magnesium. In other systems in which magnesium is apparently stable, unavoidable passivation is developed on the Mg electrodes' surfaces due to possible reactions of magnesium with unavoidably present trace water or other contaminants. It was possible to develop improved electrolyte solutions based on ether mixtures: THF and tetraglyme (<20% TG) and Mg-Al-Cl-R complexes in which the R groups are comprised entirely of ethyl. For instance, the reaction between EtMgCl Lewis base and AlCl_2Et Lewis acid at a 1:2 ratio provided high quality electrolyte complexes in terms of the very high reversible behavior of Mg electrodes and Mg ion intercalation into a Mo_6S_8 Chevrel phase cathode, and in terms of anodic stability up to 2.4 V versus magnesium electrodes. These new solutions are better than the previously reported $\text{THF}/\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ solutions, and their synthesis is simpler. Several materials, including cubic TiS_2 , TiSSe , CuS_x , NiS_x and NiSSe , were tested as new cathode materials. All of them demonstrated some degree of reversible Mg insertion in solutions comprising THF and the above complexes (e.g., $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$). Mg is inserted into NiS_x , CuS_x or NiSSe via the displacement of the transition metal, while Mg ion insertion

into C-TiS₂ or TiSSe occurs only by intercalation. Mg insertion into the above sulfides requires elevated temperatures, while Mg insertion into MSSe compounds, can take place at RT. None of the above compounds are suitable as a practical cathode material for rechargeable Mg batteries, because a pronounced capacity fading upon initial cycling is recorded in all of the above cases. However, the above studies demonstrate the possibility that there are other compounds, apart from Chevrel phases, that can insert magnesium reversibly. A search for other Mg insertion compounds with better performance is currently in progress.

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