A comparison between the electrochemical behavior of reversible magnesium and lithium electrodes

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Abstract

This paper describes briefly the difference between reversible lithium and magnesium electrodes. In the case of lithium, the active metal is always covered by surface films. Li dissolution–deposition is reversible only when the surface films contain elastomers and are flexible. Hence, they can accommodate the morphological changes of the electrode during the electrochemical processes without breaking down. In an ideal situation, lithium is deposited beneath the surface films, while being constantly protected in a way that prevents reactions between freshly deposited lithium and solution species. In contrast to lithium, magnesium electrodes are reversible only in solutions where surface film free conditions exist. Mg does not react with ethers, and thus, in ethereal solutions of Grignard reagents (RMgX, where R = alkyl, aryl, X = halide) and complexes of the following type: $Mg(AlX_{4-n}R_{n'}R'_{n''})_2$, R and R' = alkyl groups, X = halide, A = Al, $0 < n < 4$ and $n' + n'' = n$, magnesium electrodes behave reversibly. However, it should be noted that the above stoichiometry of the Mg salts does not reflect the true structure of the active ions in solutions. Mg deposition does not occur via electron transfer to simply solvated Mg^{2+} ions. The behavior of Mg electrodes in these solutions is discussed in light of studies by EQCM, EIS, FTIR, XPS, STM and standard electrochemical techniques. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The behavior of lithium electrodes in a large variety of non-aqueous systems has been extensively explored in depth. It is well known that lithium electrodes are always covered by surface films, due to reactions between the active metal and the reactive atmospheric components (e.g. O_2, N_2, H_2O, CO_2) and solution species (e.g. polar aprotic solvent molecules and many salt anions such as ClO_4^-, AsF_6^-, PF_6^-, BF_4^-, $N(SO_2CF_3)_2^-$, etc.). These form insoluble Li salts that precipitate on the lithium surface as thin films. Due to the unique properties of lithium bonds with many elements, many organic and inorganic Li salts in thin films conduct Li-ions under an electrical field. These surface films enable the use of lithium metal as a battery electrode, since they passivate and protect the active metal from continuous, thermodynamically favorable reactions with solution species, and yet, allow Li-ion migration through them when the

Li electrodes are polarized. This situation, in which the current distribution of Li deposition and dissolution depends on the transport characteristics of the surface film, may lead to highly non-uniform processes due to chemical and morphological non-uniformity (even at the submicroscopic level) of the surface films. Hence, a key issue in the use of Li metal anodes in rechargeable batteries is control and modification of the surface chemistry of the active metal in solutions in a way that induces formation of highly passivating, spatially homogeneous surface films. Magnesium is also highly reactive with atmospheric components, many polar aprotic solvents, and relevant anions of magnesium salts that may be soluble in non-aqueous systems. Therefore, in a similar manner to lithium, magnesium is usually covered by surface films [1]. However, in contrast to the case of lithium, the surface films which cover Mg electrodes in a large variety of non-aqueous systems (e.g. solutions based on alkyl carbonates, esters, acetonitrile, and other polar solvents) cannot conduct these bivalent Mg^{2+} ions. In view of this, electrochemical Mg deposition is impossible in such cases, and dissolution occurs at high over-potentials via a

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breakdown of the surface films. It is well known that Mg electrodes may behave reversibly in Grignard salt solutions in ethers (RMgX, where R = alkyl, aryl, X = Cl, Br) [2]. In addition, there was a report on the reversible behavior of Mg electrodes in THF/Mg(Br$_4$)$_2$ solutions (R = alkyl, aryl groups) [3]. This work is aimed at a rigorous study of Mg electrodes in solutions in which reversible deposition–dissolution of magnesium can be obtained. This paper describes the basic difference between reversible lithium and magnesium electrodes. It relates to previous extensive study of Li electrodes in polar aprotic systems [4], and to a recent study of magnesium electrochemistry, which benefited from the use of a variety of in situ spectroelectrochemical techniques, including FTIR, EIS, STM and EQCM, and ex situ surface sensitive tools such as SEM, EDAX and XPS in conjunction with standard electrochemical techniques.

2. Experimental

The use of EQCM, FTIR, EIS, electrode preparation, and the configuration of the electrochemical cells, as well as other details on the experimental set-up, has already been reported [1,5]. The application of in situ STM to highly reactive electrochemical systems is described in [6]. Grignard salts were purchased from Aldrich and Mg(Br$_4$)$_2$ were prepared as described in [3]. The preparation of ethereal solutions of Mg aluminate complexes, general formula Mg(AlCl$_2$RR′)$_2$ (R and R′ are alkyl groups) were described in [7].

3. Results and discussion

Fig. 1 presents situations common to both Li and Mg electrodes in non-aqueous solutions. Both metals are covered by native surface films comprised of metal oxide (inner layer) and metal hydroxide and carbonate (outer layer). Upon contact with solution species, complicated reactions take place (e.g. nucleophilic reactions between hydroxide, oxide and electrophilic solvent molecules). These reactions result in the surface films becoming mosaic-like and non-uniform on the microscopic level, as illustrated in Fig. 1 (upper part). Trace water, which is unavoidably present in all non-aqueous solutions (usually 10–100 ppm) complicates the picture, because H$_2$O hydrates surface species, diffuses through the surface films to the active metal, is reduced within the surface films to hydroxide, oxide, and possibly hydride (see Fig. 1, middle part). Electrochemical dissolution of the active metal through non-uniform surface films under non-uniform conditions leads to the breakdown of the surface films and the exposure of fresh metal to solution species. Repair of the surface films by obvious reactions between the active metal and solution species add more non-uniformity to the surface layers, as illustrated in Fig. 1 (lower part). Since the surface films formed on lithium

conduct Li-ions (the SEI model) [8], electrochemical Li deposition through the surface films is feasible. We can see two possibilities: irreversible behavior, in which the non-uniformity of the surface films leads to dendrite formation, which means a loss of the active mass and a reversible behavior in which Li deposits are protected by stable, highly passivating and flexible surface films.

The conditions for the reversible behavior of Li electrodes can be summarized as follows.

1. Reduced reactivity of the Li metal by surface doping (alloy formation).
2. Formation of elastic surface films that can accommodate the volume and morphological changes of the metal beneath them as Li is deposited or dissolved.

   In 1,3-dioxolane/LiAsF$_6$ solutions, the following two conditions exist:
   ○ Li is doped by arsenic (AsF$_6^-$ reduction), which reduces its reactivity towards solution species;
   ○ the surface films contain elastomers, which are oligomers for 1,3-dioxolane (OCH$_2$OCH$_2$CH$_2$)$_n$ with Li alkoxy (LiO) edges, which adhere well to the Li surface.

   Thereby, Li deposition in these solutions is very smooth and dendrite free.
3. When in contact with PEO-based solid electrolyte systems (i.e. polyethylene oxide and its branched derivatives), Li may behave reversibly, especially at elevated temperatures.

The surface films formed on lithium in contact with PEO contain Li$_2$O and oligomers of PEO with alkoxy (OLi) edges. The latter components make the surface films elastic (thus leading to the reversible behavior of the lithium electrodes).

In contrast to the case of Li electrodes in which there is no surface film free condition, reversible behavior of Mg electrodes can be obtained *only* in surface film free conditions. Such surface film free conditions can be reached in non-aqueous ethereal solutions, because, in contrast to lithium metal, the less reactive magnesium apparently does not react with ethers [1]. In addition to Grignard reagents (RMgX, where R = alkyl, aryl, X = halide), which form ethereal solutions in which Mg electrodes may behave reversibly, there are other families of complexes of the following type: Mg(AX$_{4-n}$R$_{n'}$R′$_{n''}$)$_2$, where A = Al, B, X = halide, R and R′ = alkyl aryl groups $0 < n < 4$, $n' + n'' = n$, which form electrolyte solutions with ethers, suitable for reversible magnesium electrodes. These complexes have a great advantage over Grignard salt solutions in terms of electrochemical applications, as their oxidation potentials may be 1 V higher than those of Grignard reagents. In this paper we demonstrate the reversible behavior of Mg electrodes in one of these complexes, namely, Mg(AlCl$_2$BuEt)$_2$.

Fig. 2 presents typical results of an EQCM experiment in which a cyclic voltammogram was measured together with
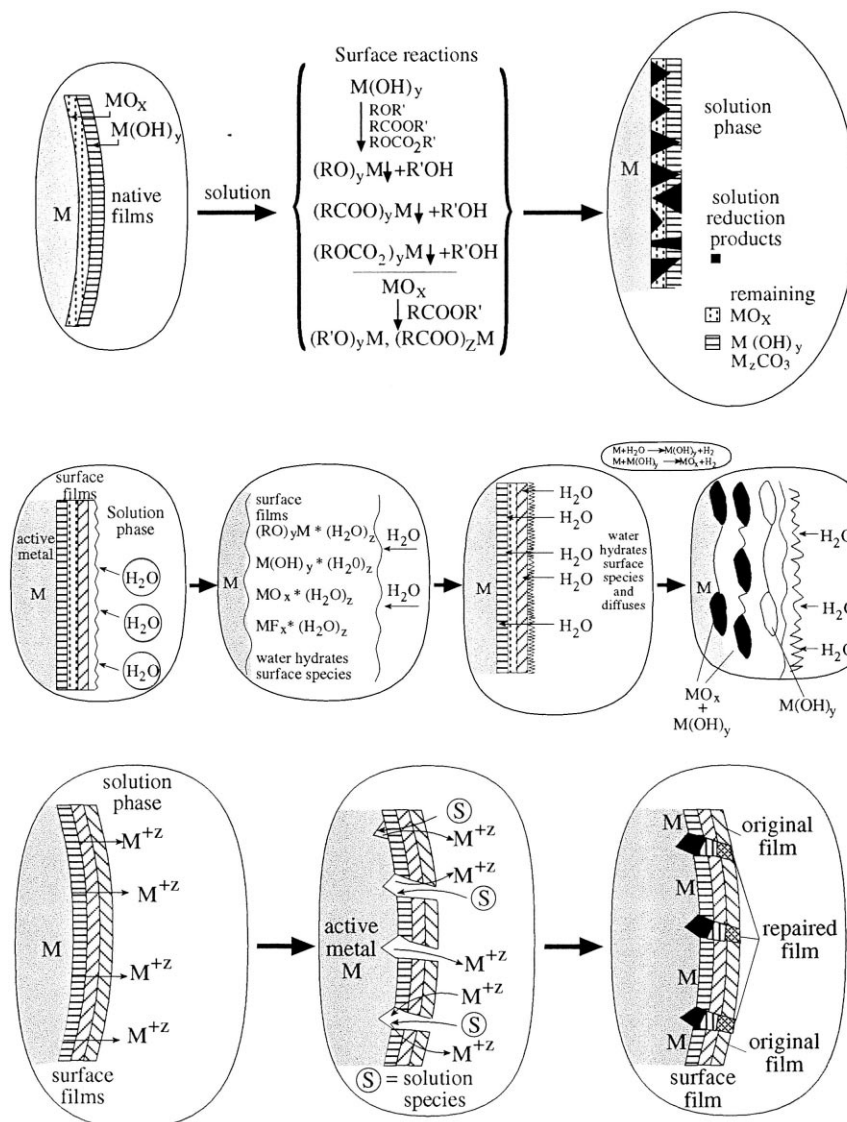
Fig. 1. A scheme of the situation of active metal surfaces in non-aqueous electrolyte solutions. Upper part: an active metal covered by native surface films is introduced into the electrolyte solution. Middle part: the role of trace water — H_2O hydrates surface species and diffuses through the surface films to the active metal electrodes. Lower part: electrochemical active metal (Mg, Li, etc.) dissolution takes place via breakdown and repair of the surface films.

the mass accumulation and depletion during Mg deposition–dissolution (Au electrode, $Mg(AlCl_2BuEt)_2$ 0.25 M/THF solution). The mass per mole of electrons (MPE) during the initial step of Mg deposition is higher than 12 g/mol, which is the equivalent weight of magnesium. As already discussed in relation to similar experiments with Grignard salt solutions [5], the high MPE calculated for the first step of Mg deposition reflects adsorption phenomena. Mg reduction may involve adsorption of species such as RMg^+, $RMgCl_2^-$, and other complexes. As is evident from EDAX measurements, the initial deposits have a complicated morphology, and also include elements such as Cl, Al and C, which compose possible complexes adsorbed to the surface. However, as Mg deposition intensifies (lower potentials, higher cathodic currents), the magnesium deposited forms a typical crystalline morphology. This is

demonstrated in Fig. 3, which shows SEM micrographs of Mg deposits. The relevant MPE calculated during intense Mg deposition in parallel EQCM experiments is close to 12 g/mol, reflecting deposition of pure magnesium. The consecutive Mg dissolution process is also characterized by MPE ≈ 12 g/mol. SEM–EDAX measurements of the substrates (Cu, Au, Ni, etc.) after deposition–dissolution cycles (last process of dissolution) revealed that the Mg deposited is completely dissolved electrochemically, leaving clean, film free surfaces. These EQCM, SEM and EDAX measurements definitely proved that Mg deposition–dissolution processes in the Mg-aluminate complex/ether solutions (e.g. THF, polyethers of the glyme family) are highly reversible with cycling efficiency close to 100% (confirmed by both charge and mass balance, and by surface element analysis).
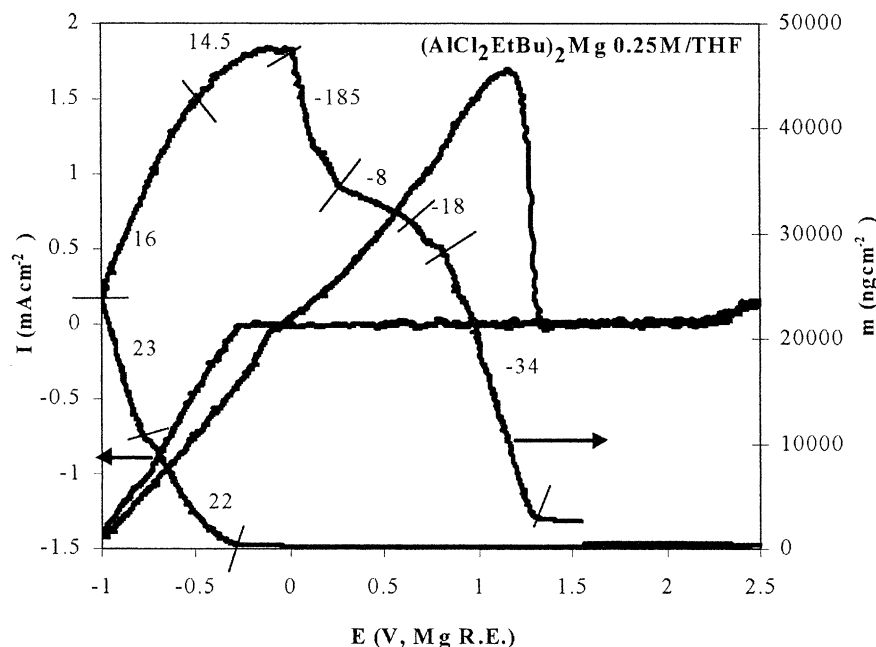
Fig. 2. Presentation of results of a typical EQCM experiment: Au electrode on quartz crystal, in 0.25 M Mg(AlCl$_2$BuEt)$_2$/THF solution. The cyclic voltammogram (5 mV/s) and the mass accumulation and depletion (Mg deposition–dissolution cycle) are shown together with the calculated mass (accumulated or depleted) per moles of electrons (MPE) during the process. Positive and negative MPE numbers refer to Mg deposition and dissolution, respectively.

Fig. 4 addresses an important feature of Mg electrodes in all ethereal solutions in which they behave reversibly (i.e. solutions of Grignard reagents or Mg-aluminate and Mg-borate complexes). This figure presents typical impedance spectra of Mg electrodes as a function of storage time in a THF/Mg(AlCl$_2$BuEt)$_2$ solution, and a typical chronopotentiogram of an Mg electrode during galvanostatic Mg deposition and dissolution processes. It is significant that the impedance of the Mg electrode, when at rest, is very high (>10,000 Ω cm^2), while the chronopotentiometric response reflects much lower impedance during the dynamic processes in which Mg is electrochemically deposited and dissolved (less than a few hundreds of Ω cm^2). We attribute the high impedance to adsorption processes, which were evidenced by the EQCM, FTIR, XPS and EDAX measurements, in which species such as RMg$^+$, RMgCl$_2^-$ and complexes are adsorbed to the electrode's surface. However, these adsorption processes *do not* lead to passivation of the Mg surfaces, and thus, overpotentials of several tens of milivolts are sufficient to break down the adsorbed layers, and so the adsorbed species do not adversely affect the dynamics of electrochemical Mg deposition and dissolution.
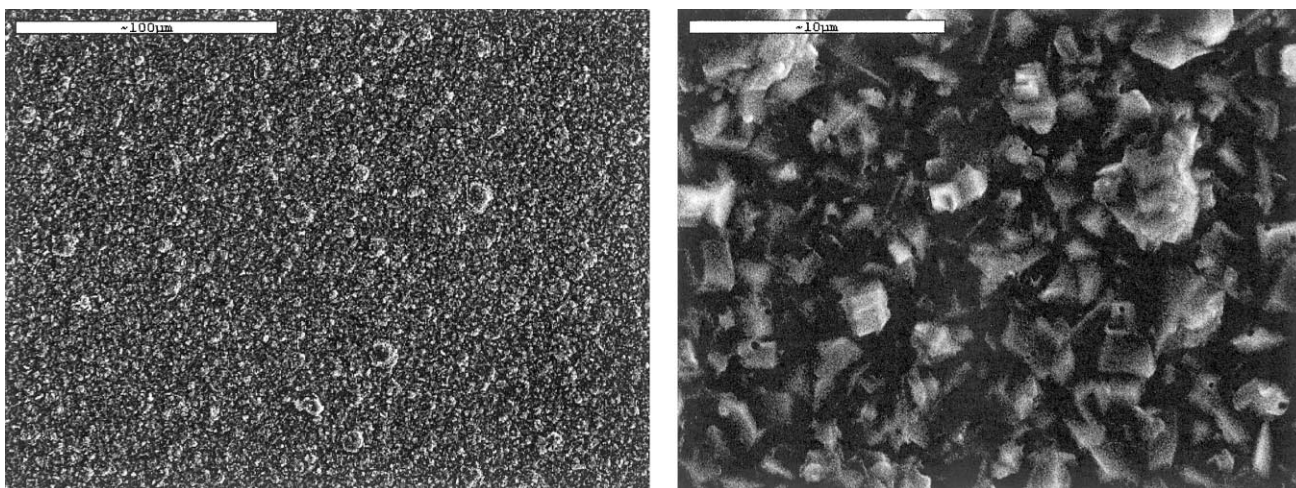

Fig. 3. SEM micrographs of Mg deposits on Cu foil, from a 0.25 M Mg(AlCl$_2$BuEt)$_2$/THF solution (two magnifications). A scale appears in each picture.
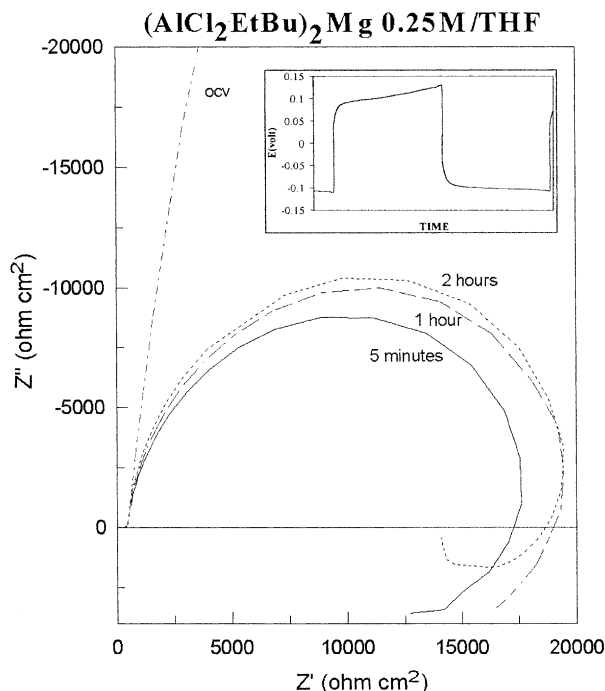
Fig. 4. Impedance spectra of Mg electrodes (Mg deposited on gold) in a THF/Mg(AlCl$_2$BuEt)$_2$ 0.25 M solution, presented as Nyquist plots (measured at different times after Mg deposition, as indicated). The insert shows a typical chronopotentiogram of Mg deposition–dissolution in the same solution, a galvanostatic process, 0.5 mA/cm^2, two Mg electrodes in a coin cell configuration.

4. Conclusion

The cyclic voltammograms of Mg deposition–dissolution in Mg(AX$_{4-n}$R$_{n'}$R$'_{n''}$)$_2$ solutions in ethers, where A = Al, B, etc.; X = Cl, etc.; R and R$'$ = alkyl or aryl groups, n, n', $n < 4$, $n' + n'' = n$ shows that these reactions are highly reversible. The electrochemical windows of the solutions containing the Mg-aluminate complexes are >2.5 V (oxidation occurs >2 V versus Mg/Mg^{2+}). A combination of EQCM, FTIR, STM and EIS measurements of Mg electrodes in these solutions seems to show that Mg electrodes are not covered by passivating surface films in these solutions. This is a condition for their reversible behavior. However, the processes are not simple reactions of the Mg/Mg^{2+} couple. Complicated adsorption phenomena accompany Mg deposition and dissolution in these systems. Because of these adsorption processes, the impedance of Mg electrodes in these solutions is high at rest (>10,000 Ω cm^2). However, during the electrochemical processes, the impedance of Mg electrodes is much lower (<100 Ω cm^2) due to an easy breakdown of the adsorbed layer.

Acknowledgements

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