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# Reversibility of electrochemical magnesium deposition from Grignard solutions

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The reversibility of electrochemical magnesium deposition from Grignard reagents was investigated with regard to potential application of magnesium as a negative electrode in rechargeable batteries. The reoxidation rate depends on the morphology of the magnesium deposit which is controlled by the substrate material. Good results were obtained using silver or gold substrates. Magnesium deposits on these materials was found to be of smooth and compact morphology. A nearly complete electrochemical reoxidation and a low self-discharge were observed.

## 1. Introduction

High charge density and low costs make magnesium an interesting material for the negative electrode in electrochemical energy storage devices. The electrochemistry of magnesium, however, has not hitherto been well investigated and many problems remain unresolved. Although some primary batteries are available [1, 2] rechargeable systems are still at an early stage of development [3]. This is caused by problems concerning the negative as well as the positive electrode [4–7].

As magnesium is oxidized by water and other protic solvents, only aprotic media are feasible as solvents for secondary magnesium cells. Thus, only a few organic electrolyte solutions containing Grignard reagents, aluminium or boron compounds, have been shown to be suitable for electrochemical magnesium deposition from organic solvents [8–12].

From voltammetric experiments on copper microelectrodes the equilibrium potential of the $Mg/Mg^{2+}$ - couple in ethyl magnesium bromide solution in THF was determined to be +850 mV vs $Li/Li^+$. The couple was also shown to be quite reversible with an exchange current density of $1\,mA\,cm^{-2}$ [13].

Deposit morphology, as described in the literature, varies from tree-like and dark to smooth and white. The bath composition has been modified to some extent as well as the current density during deposition, but the role of the substrate material has not yet been investigated.

The aim of this work has been to investigate the influence of the substrate material on the morphology of electrodeposited magnesium. As the system is considered as a possible negative electrode in rechargeable batteries the efficiency of electrochemical reoxidation of electroplated magnesium, as well as the self discharge during wet stand time in the electrolyte solution, should be characterized.

## 2. Experimental details

Ethyl magnesium bromide (EtMgBr) solutions were prepared by Grignard reaction in carefully dried tetrahydrofuran (THF). The EtMgBr content was determined by acidimetric and complexometric titration methods.

For nonstop-cyclization experiments a potentiostat PS5 (Sensortechnik Meinsberg) was used. Initially, a constant cathodic current of $0.5\ mA\ cm^{-2}$ was passed through the cell for 45 min. Then an anodic current ($i = 0.5\,mA\,cm^{-2}$) was applied up to a cutoff potential of 800 mV with respect to the magnesium reference electrode. The time of the anodic current divided by that of the cathodic current is defined as the reoxidation rate. Nickel, copper, gold and silver were used as working electrodes (area 2 $cm^2$), each being placed between two magnesium counter electrodes. The substrates were polished with corundum suspension and rinsed with dry acetone.

For cyclization experiments a magnesium sheet was used as reference electrode. It was abraded immediatly before insertion into the electrochemical cell. To evaluate the stability of these reference electrodes the open circuit voltage between two magnesium electrodes dipped into the Grignard solution were measured. Only a few millivolts were measured after an immersion time of hundreds of hours. For cyclic voltammetry experiments a $Ag/Ag^+$ (0.001 $mol\,dm^{-3}$, THF saturated with tetraethylammonium perchlorate) reference electrode was used. To prevent precipitation of AgBr a salt bridge filled with THF saturated with tetraethylammonium perchlorate was applied. Cyclic voltammograms were recorded at sweep rates from 1 to $25\,mV\,s^{-1}$. For microscopy studies, initially a complete deposition and dissolution cycle with a charge of $2.7\,C\,cm^{-2}$ (or $3.6\,C\,cm^{-2}$) was performed, then magnesium was deposited for 45 min with $0.5\ mA\,cm^{-2}$ ($1.35\,C\,cm^{-2}$) or for 120 min with $1\,mA\,cm^{-2}$ ($7.2\,C\,cm^{-2}$). Finally, the substrate electrodes were rinsed with dry acetone immediately after removing from the Grignard solution.

All operations were carried out in a dry argon atmosphere at room temperature.

## 3. Results and discussion

To simulate the charge and discharge behaviour of a negative electrode in a rechargeable battery, magnesium was galvanostatically electroplated for 60 min with a current density of 1 mA cm$^{-2}$. The deposited magnesium was then oxidized at the same current density until the cut-off voltage was reached.

The reversibility of the magnesium reduction was clearly found to depend on the substrate material. Figure 1 shows typical potential–time plots during the first deposition–dissolution cycle on different substrates. Dissolution from silver and gold electrodes gave flat potential plateaux, in contrast to nickel electrodes, where the potential depended on the dissolution state. The overpotential necessary for deposition or dissolution was influenced by the substrate material to a lesser degree. On silver and gold lower values were found. Best results were obtained in the case of silver electrodes, since a reoxidation rate of 100 % was found. On gold a complete reoxidation was observed, also in contrast to nickel and copper substrates where a considerable loss of electrochemically active magnesium during the first deposition-dissolution cycle was found. These experiments could be repeated many times. Non stop cycling of magnesium on gold substrates in a solution of Grignard reagent in THF gave a nearly complete reoxidation for more than a hundred cycles (Fig. 2). The same behaviour was found for cyclization on silver substrates. On copper substrates loss of electrochemically active magnesium was found only during the first cycles. Cyclization on nickel substrates showed a characteristic increase of reoxidation rate during the first cycles. The reoxidation rates finally reached values of 70–90 %, this being significantly lower than for silver and gold substrates. During the cyclization experiment electrochemically inactive magnesium accumulated on the nickel surface. These magnesium dendrites were weakly bound on the substrate.

Even after longer periods of wet stand time of the magnesium deposition in the electrolyte, a high reoxidation was found for silver and gold substrates (Fig. 3). The dissolution began at higher overvoltages which were not measured if the deposition was immediately followed by oxidation. After an immersion time of 1100 h 96 % of the magnesium could be electrochemically reoxidized. At the end of reoxidation the potential increased slowly. The high overvoltage with the start of dissolution could be caused by a thin, but dense passivation layer which is built up by reduction of the electrolyte on the surface of magnesium. The increasing potential at the end of dissolution and the loss of electrochemically active magnesium may be caused by the build up of the passivation layer and also by diffusion of magnesium atoms into the substrate material during the wet stand time.

Figure 4 shows a cyclic voltammogram recorded at 10 mV s$^{-1}$ for a silver electrode in a solution of EtMgBr in THF. The deposition of bulk magnesium is observed at potentials more negative than −2.58 V

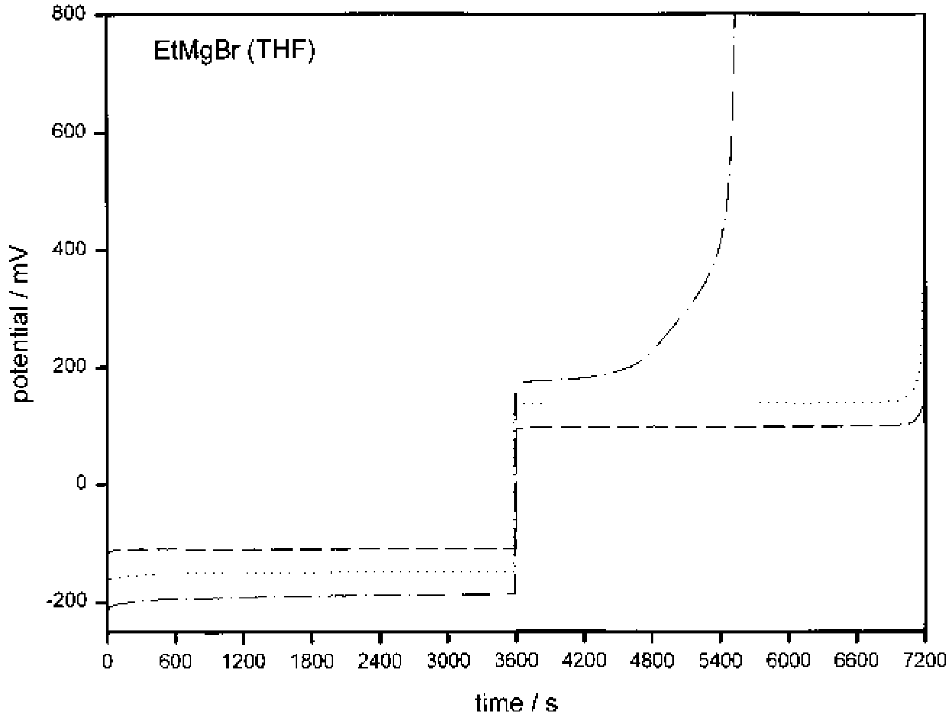

Fig. 1. Dependence of electrode potential on time during first galvanostatic reduction: 0–60 min, $I = -1$ mA cm$^{-2}$, followed by galvanostatic oxidation; 61–120 min, $I = +1$ mA cm$^{-2}$. Magnesium reference electrode. Substrate materials: (– –) silver, (· · ·) gold and (– · –) nickel.

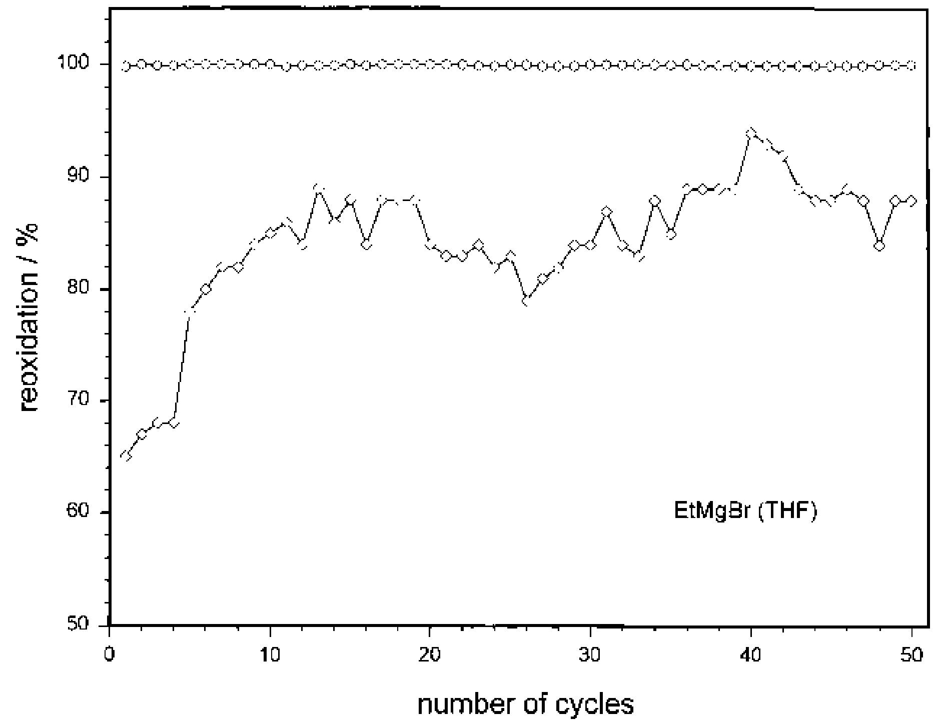

Fig. 2. Magnesium reoxidation on gold (○) and nickel (◇) substrates with respect to the cycle number. Deposition time 45 min; current density ∓0.5 mA cm$^{-2}$; $C$ = 1.7 mol dm$^{-3}$.

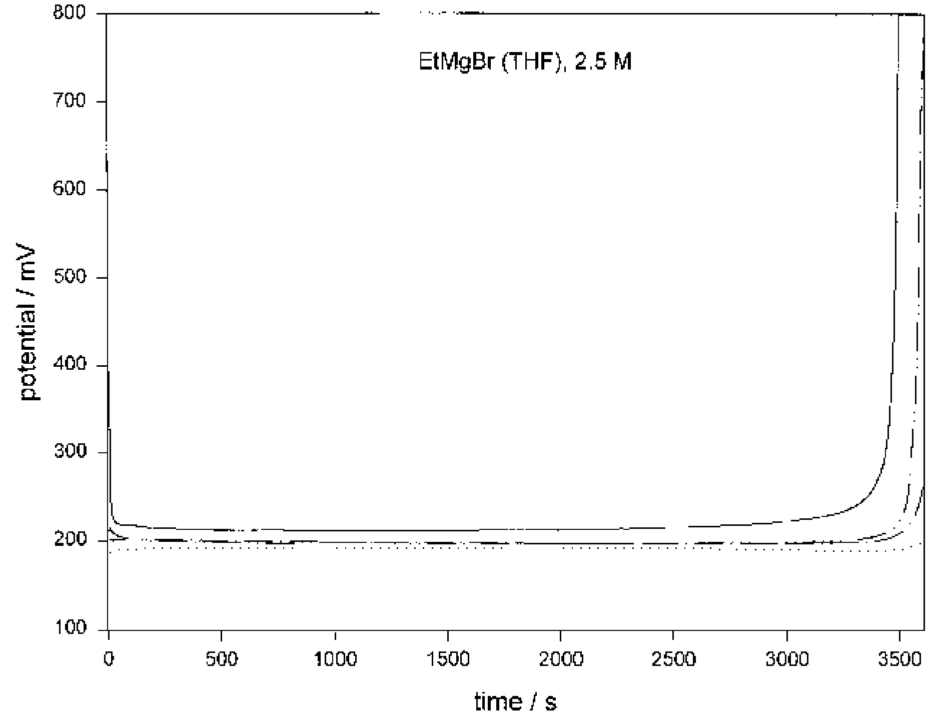

Fig. 3. Electrode potential during electrochemical reoxidation of 3.6 C cm$^{-2}$ magnesium in dependence from wet stand time in the electrolyte. Storage time: (···) 0, (– · – ) 100, (– ··) 350 and (—) 1100 h. Magnesium reference electrode; Ag substrate. $I$ = ± 1 mA cm$^{-2}$.

vs Ag/Ag$^+$. At about 2 V a reduction process begins which is partly reversible. At sweep rates of 25 mV s$^{-1}$ a charge of 0.5–2 mC cm$^{-2}$ was transferred during this underpotential process. This charge exceeds the amount necessary for the deposition of a two valent metal monolayer. This means that electrochemical alloying takes place by diffusion of magnesium into the bulk of the silver electrode. At slower sweep rates a higher amount of charge was transferred. During reoxidation two processes can be seen, the oxidation of bulk magnesium and a process at higher potentials which is connected with a charge transfer of 0.3–0.5 mC cm$^{-2}$, corresponding to the reoxidation of the magnesium monolayer. This means that the amount of magnesium diffused into the bulk of the silver electrode was not completely reoxidized in the course

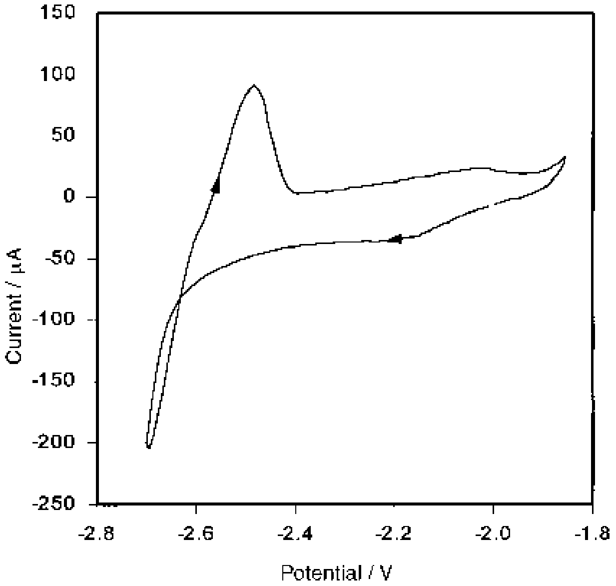

Fig. 4. Cyclic voltammogram of a silver electrode in EtMgBr in THF (1.2 M), potential vs Ag/Ag$^+$. $\nu$ = 10 mV s$^{-1}$; $A$ = 2 cm$^2$.

of this cyclicvoltammetric experiment. Electrochemical alloying was also found on gold electrodes. On nickel and copper no underpotential deposition or alloying was observed, as demonstrated in Fig. 5.

Figures 6 and 7 show micrographs of the magnesium deposit on different substrate materials. As can be seen from Fig. 6 magnesium is deposited on nickel in an irregular and dendritic manner, the substrate surface not being completely covered. An irregular deposition morphology was also found on copper substrates. On silver and gold electrodes a regular coverage of the substrate surface was found, as shown in Fig. 7.

It is known that, in those systems which show underpotential deposition or electrochemical alloying, even thicker metal deposits are plated more uniformly and homogeneously onto the substrate than in those cases where three-dimensional nucleation predominates [14]. The dendritic deposition morphology of magnesium on nickel and to a lower extent, on copper gives rise to side reactions of magnesium with electrolyte components followed by electrical isolation of magnesium particles from the electrode surface as in the case of lithium in organic electrolytes [15, 16].

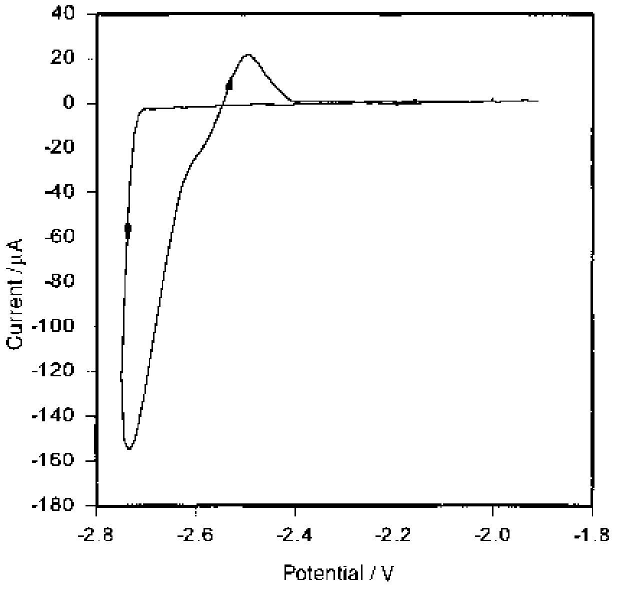

Fig. 5. Cyclic voltammogram of a nickel electrode in EtMgBr in THF (1.2 M), potential vs Ag/Ag$^+$. $\nu$ = 10 mV s$^{-1}$; $A$ = 2 cm$^2$.

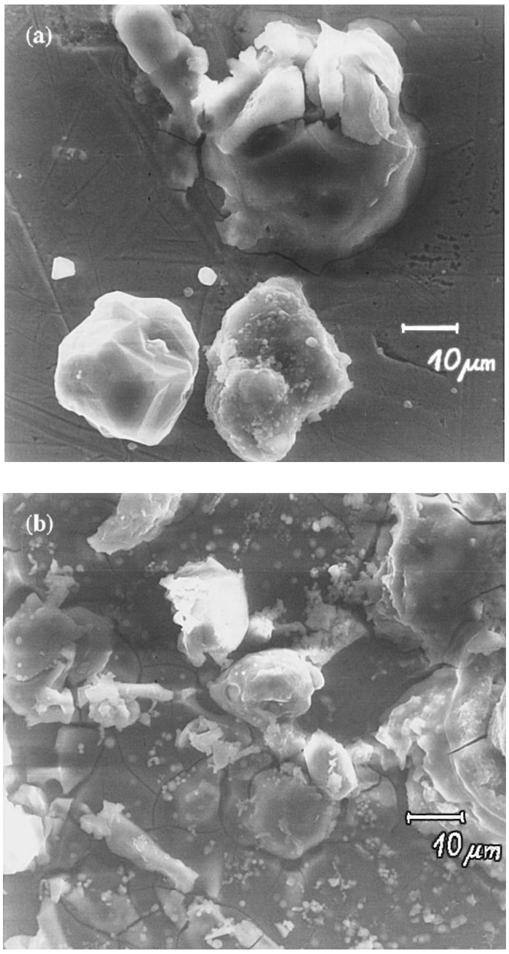

Fig. 6. SEM micrograph of magnesium deposit on nickel substrate. (a) $Q$ = 1.35 C cm$^{-2}$; (b) $Q$ = 7.2 C cm$^{-2}$.

## 4. Conclusions

Magnesium deposition on gold or silver substrates from Grignard solution show advantageous electrochemical behaviour regarding deposition morphology and reoxidation rates. However, many problems remain. The electrolyte chosen for these measurements was not optimized or adapted with regard to a complete cell system. EtMgBr-solutions in THF have low conductivity, insufficient oxidation stability and a poor compatibility towards potential cathode materials, for instance intercalation compounds. The last factor seems to be the main problem for construction of a working magnesium battery.

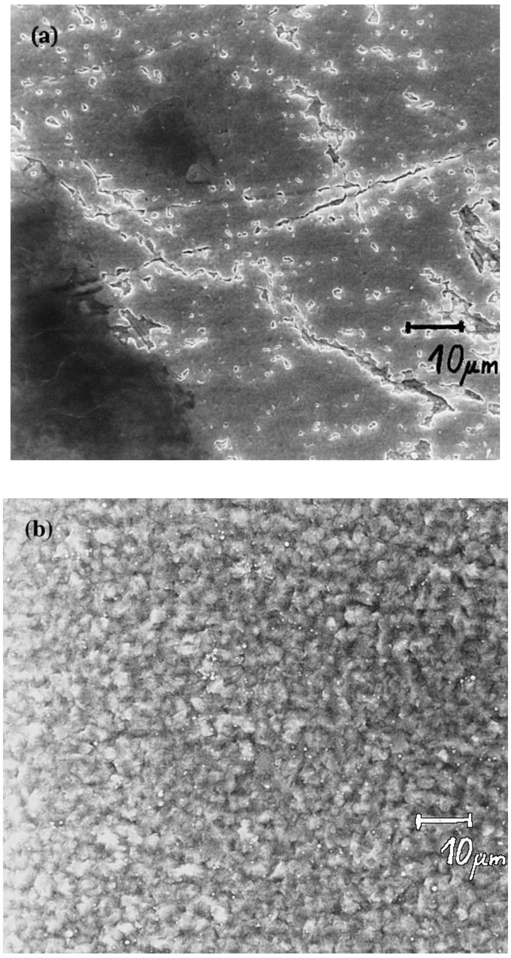

Fig. 7. SEM micrograph of magnesium deposit on silver substrate. (a) $Q$ = 1.35 C cm$^{-2}$; (b) $Q$ = 7.2 C cm$^{-2}$.

## Acknowledgements

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