

Electrochemical Behavior of Magnesium and its Alloys in non-Aqueous Solutions

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Abstract

Magnesium and its alloys are widely used in creation of chemical sources of current, because possesses a number of characteristics: highly negative standart potential, low equivalent weight, high melting point, low cost, relative abundance, ease of handling, machining, and disposal, and low toxicity of most its compounds. Therefore study of magnesium behavior and isolation is actually and perspective. However results of researches in this area are separated and have no a general direction. In this connection, the given article supposes by the purpose to generalize last achievements, available in the modern literature in electrochemistry of magnesium and its alloys in non-aqueous media.

Introduction

The development and tendency of using non-aqueous solvents as media for realization of electrochemical processes on active metals

Investigation of non-aqueous solutions is of great importance in the development of many branches of the general theory of solutions [1]. Practical importance of non-aqueous solutions as media for analytical determinations, realization of various syntheses and electrochemical processes has considerably increased recently. Investigations of electrochemical processes in non-aqueous media do not only contribute to our knowledge about their nature, but also frequently allow to carry out processes which do not proceed in aqueous solutions [2]. This arouses a heightened interest of chemists as well as representatives of other branches of natural sciences for the problem of non-aqueous solutions. This interest is reflected in the growth of the number of papers devoted to non-aqueous solutions that is remarkably noticeable even against the increased amount of information in the field of chemistry. However, the number of generalizations - monographs or survey articles - in the field of chemistry of non-aqueous solutions does not answer the abundance of the accumulated information yet. This circumstance is one of the reasons that induced the authors to write the given paper.

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The investigations of non-aqueous solutions begun as far back as the forties [3] attracted chemist's, attention at once first of all with their doubtless originality and the use of some of them has considerably expanded the variety of possible electrochemical reactions. In particular, some non-aqueous solvents are much more effective, than water, especially in reactions of organic and metal-organic compounds. Many of them are oxidized or reduced with more difficulty, than water and, hence, can be used in a wider range of potentials. Many compounds being inert in water can become active in other solvents and, on the contrary, compounds reacting with water, for example, alkaline metals, in non-aqueous solvents can be stable [4].

Non-aqueous solvents are characterized by an extremely wide range of various properties [5], depending on different nature of intermolecular interactions. Due to the peculiarities of interparticle interactions the role of association and specific solvation processes is of great importance for them. The use of the non-aqueous solvents has required new theoretical and experimental approaches to researches. This situation is aggravated by great methodical difficulties of work with dehydrated solvents, the necessity to develop new special experimental engineering, impossibility to use directly the great theoretical and experimental material obtained in aqueous solutions.

The perspectives of the development of the chemistry of non-aqueous solutions are conditioned

by the necessity to study the ways of creation and introduction of new materials as well as intensification of the existing methods of material production in various industries. As a result, the problems of optimization of these processes, ecology and creation of wasteless technologies, realization of processes principally impossible in aqueous solutions are solved.

A development of modern engineering is based on the use of new substances and materials having a complex of physicochemical properties. New groups of chemical sources of current (CSC) [6] are being developed. Now these are the sources of current in which alkaline and alkaline earth metals are used, and those with solid electrolytes having ionic conductivity. The application of such metals as negative electrodes of the current source has always been attractive because of high negative potential and large exchange currents. However, in water solutions the use of these metals is encountered with extremely great difficulties. In modern variants of current sources with alkaline and alkaline earth metals salt alloys, organic (aprotic solvents) or solid electrolytes are used, the second and the third ones being the most perspective. In CSC with aprotic solvents as the anode lithium (magnesium) is used, that allows to achieve significant values of electromotive force (EMF) (up to 3-4 V) and high values of specific energy. Halides, sulphides, metal oxides and other compounds are used as the material for the cathode. Attempts are being made to create accumulators using lithium (magnesium) electrode in electrolytes on the basis of aprotic solvents. Lithium sources of current are widely used as power supply for radioelectronic equipment, electrical clocks.

Over the past 25 years, a considerable amount of attention has been paid to the use of alkali metals, particularly Li [7], in non-aqueous secondary batteries, but comparatively little work has been done with the alkaline earth metals. In work Thomas et. al. [8] non-aqueous electrochemistry of magnesium in more details is considered and assess the feasibility of constructing a secondary battery operable at ambient temperatures. For receiving of such battery the following components in work are used: anodes on the basis of magnesium or its alloys, positive electrode (PE), which are capable reversible to intercalate of magnesium, electrolytes – organomagnesium halide compounds (methyl-, ethyl-, butyl magnesium chloride) in tetrahydrofuran (THF) It is noted, that the number of combinations of the solvent, electrolyte and PE for which satisfactory characteristics can

be achieved is limited in comparison with alkaline metals. Sulphides, oxides and borides of transition metals as PE are considered. The behavior of magnesium in THF solutions is analysed. It is shown that electrolytes in which magnesium is deposited and dissolved frequently contain magnesium-organic compounds, ethers or amines. Ethers and amines are unstable in the presence of oxides and sulphides of transition metals.

In this connection, researchers showed a keen interest in the study of electrochemical behavior of various metals in non-aqueous solutions. One of these metals is magnesium being a promising anode material by a number of parameters when creating CSC, and, consequently, the study of its behavior in non-aqueous solutions of electrolytes is a perspective direction in electrochemistry.

The purpose of the given work is the generalization of theoretical and experimental data in the field of electrochemical behavior of magnesium and its alloys in non-aqueous systems.

Magnesium corrosion processes in non-aqueous solutions

All main properties of a magnesium electrode at polarization are determined first of all by the properties of surface formations on account of corrosion.

The investigation [9] of the behavior of magnesium and its amalgam in electrolytes on the basis of dimethyl formamide (DMF), acetonitrile (AN) and propylene carbonate (PC) containing oxygen and water additives showed that even in carefully purified solutions electrode process rate constant is very small owing to, presumably, the passivation of the surface on account of the reaction with the solvent. This is confirmed by the fact, that constant renovation of magnesium electrode surface in $\text{Mg}(\text{ClO}_4)_2$ solutions in PC and AN results in the shift of a stationary potential to the negative part and the increase of kinetic characteristics of the electrochemical process [10]. It follows from this that the kinetics of the electrode process is determined by a charge transfer through a film, and the stationary potential depends on the ratio of its cationic and electrode conductivity. In work [11] it is shown, that the electrode potentials of lithium and magnesium are conditioned by uniformly proceeding processes on the surface. The displacement of the potential to the positive part from equilibrium is determined by part of electronic conductivity of the film. The stationary potential reaches equilibrium with the

film conductivity becoming purely ionic, when the contribution of the electronic component is negligibly small.

The main increase of the film during corrosion occurs in the first 2-4 hours [12]. Later on the process becomes much slower as it was shown for $\text{Mg}(\text{ClO}_4)_2$ solutions in PC and AN.

Kedrynsky with his co-workers [13] investigated the influence of surface formations on chemical and electrochemical behavior of active metals, in particular, of lithium and magnesium. The rate and nature of lithium and magnesium corrosion in electrolytes on the basis of aprotic bipolar solvents are determined. The rate of anode dissolution of magnesium was found to be four orders lower than that of lithium at small polarization and two orders lower at large ones. It is explained by an essential difference in cationic conductivity of the surface film, and also by the greater part of electronic conductivity of this film on magnesium.

The electrochemical behavior of magnesium in solutions of magnesium and lithium perchlorates in PC, AN, nitromethane (NM) is investigated in [14]. The electrode potential of magnesium in electrolytes on the basis of the above-mentioned solutions has the properties of the stationary one [15]. The electrochemical behavior of magnesium in the solutions being studied was stated to be determined by a passivating film formed on the metal surface. The electrochemical behavior of magnesium at constant updating of the surface under the solution is satisfactorily described from the point of view of a charge transfer through a film. The study of magnesium activation by different methods (cathode polarization, mechanical removal of the film, the use of alloys) has shown that it is practically impossible to reach the equilibrium state on the surface of the electrode. The possible reason of the presence of anode current maximum on potentiodynamic curves taken after cathode polarization, is the dissolution of magnesium deposited from the solution. It is shown that at transition from aqueous solutions to non-aqueous ones the decrease of capacity and substantial increase of film resistance is observed. Corrosion behavior of magnesium essentially depends on the content of water [16]. Water acts as the process activator: with the increase of its concentration in solutions from 0.01 up to 10 % (weight) the film becomes thinner and changes its properties, as the capacity of the electrode grows, and the resistance of the film decreases. Currentless electrode potential of magnesium shifts

to a more negative area, and the anode dissolution is considerably facilitated.

With the purpose of finding out the opportunities of using magnesium as CSC anode material with electrolytes on the basis of aprotic donor solvents (ADS) the values of stationary potentials (E_{sp}) of a rotating disk electrode of magnesium in solutions of lithium and magnesium perchlorate in PC, NM, AN [17] were measured. It is shown that in all cases the stationary potential does not reach its equilibrium value because of corrosion processes. The dependence of the stationary potential on of the electrode rotation speed (ω) and concentration of Mg^{2+} ions (C) is expressed by the following ratio:

$$E_{sp} = A + (aRT/nF) \times \ln(W_{1/2} - \ln C),$$

where A - const.

Magnesium corrosion process rate is supposed to be determined by the presence of corrosion-active substances, in particular, water admixtures. It is shown, that the corrosion products form a film on the surface of magnesium, the growth rate of which is described by the logarithmic law.

Magnesium is corroded in these solutions with the rate $\sim 10^{-8}$ A/cm² [16], most part of corrosion products being deposited on the metal surface. In the course of corrosion rearrangement of the surface layer takes place with the replacement of oxides by the products of the reaction with electrolytes. Apparently, the surface layer passivates the electrode as there is a wide range of potentials (~ 1.5 V), where the rate of magnesium charge - ionization processes does not depend on the potential. The surface layer essentially complicates the kinetic characteristics of magnesium electrode. The linear dependence in semi-logarithmic coordinates is only observed at constant scraping out the surface of the electrode under the solution and is satisfactorily explained from the point of view of the related charge transfer through the film. On the bases of the obtained data optimal conditions under which magnesium can be used in CSC are determined.

A similar linear dependence in Tafel coordinates for magnesium electrode in thionyl-chloride is obtained in [18]. High values of the slope angle in these dependences are accounted by the author for the fact that at polarization the main potential fall occurs in the surface film and the exponential dependence between the current and the potential characterizes the charge transfer through the film volume in the fields of high strength. thionyl-chloride electrolyte investigated in this work forms a film when interact-

ing with magnesium consisting, mainly, of MgCl_2 . Exposition of magnesium electrode in the solution is shown to result in the considerable passivation of the surface and superimposition of anode polarization there occurs activation due to the destruction of the film under the current. This phenomenon is well known for a lithium electrode and determines the so-called «voltage drop» in CSC. If the anode process in thionyl-chloride solutions proceeds with a noticeable rate, the cathode polarization of magnesium electrode in them is superpressing that can be indicative of an extremely low cationic conductivity of the film as well as anionic one. Comparison of cathode and anode processes in thionyl-chloride solutions does not agree well with the expected cationic conductivity of the film in the anode process.

The behaviour of magnesium in thionyl-chloride solutions is not only of practical interest but also attracts by the fact that allows to a great extent to exclude from consideration strong interactions between magnesium cation and the main solvent being very helpful when explaining cation transfer from the liquid phase through the film during cathode polarization.

The cathode isolation of magnesium from non-aqueous media

In the earlier work by Peled [19] it was shown that in magnesium electrode polarization field up to 20 mV the current of cathode reduction is only little less than the current of anode dissolution in $\text{Mg}(\text{AlCl}_4)_2$ and $\text{Mg}(\text{FeCl}_4)_2$ solutions in thionyl-chloride. Polarization curves in this field are rectilinear which is accounted for the transfer of magnesium cation through the film volume. On chronopotentiograms of galvanostatic isolation of magnesium on a nickel support in $\text{Mg}(\text{FeCl}_4)_2$ solutions in SOCl_2 one can distinctly observe an area corresponding to the formation of metal on the surface of nickel. When cutting of the polarizing current the potential of the polarized nickel electrode corresponds to the potential of compact magnesium.

Both the anode dissolution and the cathode reduction of magnesium in thionyl-chloride solutions result in a considerable modification of the film, it being the greater, the higher is polarization [18]. If the anode polarization activates the process in time, the cathode polarization results in its blocking. Taking into consideration the fact that in the first case the boundary capacity grows and in the second one it drops one can formally speak about the decrease

of the film thickness at anode polarization and the increase of it at cathode, but it is impossible to explain this from the point of view of cation transfer through the film.

The problem of cathode isolation of magnesium as well as other active (alkaline and alkaline earth) metals is in the fact that the metal being isolated easily reacts with solution components, many of them being often reduced at more positive electrode potentials. This results in the fact that instead of isolation of compact metal on the electrode one can observe decomposition of the solvent accompanied, as a rule, by the formation of layers of an insoluble product on the surface. If alkaline metals, in particular lithium, have a sufficiently high mobility of cation in the solid phase of the product on the electrode surface that allows the metal to be deposited under the film and be isolated from the solution, alkaline earth metals form compounds with a considerably lower mobility of cation in the solid phase that greatly slows down the isolation of the metal according to the above mentioned mechanism.

Furthermore, alkaline earth metal cations, in particular magnesium, exhibit much more acid properties in the reaction with the solvent that, in its turn, complicates the discharge process by slowing down cation desolvation and accelerates anion - radical disproportionation reactions in the cathode process, i.e. increases the rate of electrochemical decomposition of the solvent.

Consideration of the process of electrochemical isolation of active metals to which magnesium belongs is impossible without considering the interaction of the metal with medium. The most interesting precondition for the discussion of this matter is the concept of Trassatty [20] which implies that on the surface of a metal electrode not only the equality of electrochemical potentials of cations in the metal and in the solution is established but also the equality of electrochemical potentials of electron in the same phases. If the solution is stable in relation to the solvated electron, equilibrium between the metal and the metal solution in a liquid phase is established. The formation of similar solutions is typical of alkaline and alkaline earth metals. In this case instead of isolation of metal at cathode polarization generation of solvated electrons is observed. For magnesium such a case is described in the electrolysis of MgBr_2 solution in liquid ammonia when a dark blue colouring of the solution is formed which is characteristic of metal solutions containing a solvated electron [21]. But in

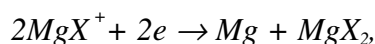
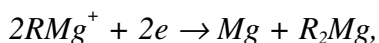
practice, as a rule, stability of solution components to the solvated electron is most often insignificant and their decomposition (reduction) with takes place to form the corresponding magnesium compound.

In this sense the processes of electron transfer into the solution or magnesium cation charge on the electrode surface are determined, on the one hand, by magnesium cation solvation degree, i.e. the main properties of the solvent, and, on the other hand, by the ability of the solvent to accept the electron, i.e. acid properties of the solvent. The more pronounced are both acid and basic properties of the solvent, the less probable is isolation of metal not complicated by the surface passivation processes.

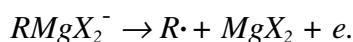
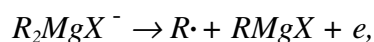
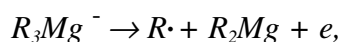
The resulting necessity of preferring less coordinating (basic) substances when choosing solutions for magnesium electrolysis is encountered by a counter tendency for solubility and electroconductivity of magnesium compounds to decrease in more «indifferent» solvents. The main compromise between these tendencies is the offer to use metalloorganic compounds of magnesium where acid properties of cation are greatly levelled, and affinity for relatively indifferent solvents is increased on account of a hydrocarbon radical.

The solutions of complex salts of magnesium for electroisolation of magnesium are perspective. It first of all concerns to solutions of Grignard reagent having huge importance in organic synthesis. During dissociation of such solutions the complex is formed, which is easily reduction and less solvation, therefore organomagnesium compounds are widely used for isolation of magnesium [22].

With the help of the radioactive magnesium was shown that magnesium enters into composition of cation in Grignard reagent [23]. During the anode discharge of anions, the free alkyl-radicals are formed. The following electrode processes are possible: on the cathode:



on the anode:



In [24] electroisolation of magnesium was carried

out from Grignard reagent solutions. On platinum electrodes there was observed luminescence on the on anode. Then electrolysis of phenylmagnesiumbromide was carried out in systems with a platinum cathode and anode of different metals: aluminium, bismuth, gold, nickel, silver, tin, zinc, cadmium and magnesium. Of the listed materials, anodes of magnesium, aluminium, cadmium and zinc were found to be corroded under these conditions.

Gender and Pletcher [25] studied electrodeposition and dissolution of magnesium from Grignard reagent solutions C_2H_5MgBr (0.5 mol/dm^3) in THF. The deposition current increases in the presence of $MgBr_2EtO$ (0.5 mol/dm^3). It is shown that magnesium is not deposited from solutions of other salts ($MgBr_2$ and $Mg(ClO_4)_2$) in THF and PC. Deposition of metal magnesium powder from $LiAsF_6$ and $MgBr_2O(C_2H_5)_2$ solutions in THF is detected. However, this process is of a secondary character - magnesium is reduced by metal lithium isolated electrolytically. Lossins and Emmenegger [26] state that metallic magnesium is effectively, with small overpotential anode ionized in $Mg(CF_3SO_3)_2$ solutions in DMF, dymethylacetamide (DMA) and binary mixtures on their basis; ionization potential area comes nearer to -1.8 V in relation to Fc/Fc^+ (ferrocene/ferrocenic picrate) electrode. At a negative potential shift beginning with -3.2 V the rise of cathode current is identified attributed to the reduction of Mg^{2+} , though cathode mass increase is not indicated. In case of using inert (Pt, Au, carbonglass (CG)) supports electrodeposition is not observed either (anode peaks on reverse branches of cyclic voltamperograms are not registered).

The choice of an appropriate solvent for carrying out electrolyses is not the only problem in the extraction of magnesium. So, in the electrolysis of solutions of simple magnesium salts in organic solvents (alcohols, pyridine, DMF, formamide, AN, aniline etc.) deposition of metal magnesium does not occur [27, 28]. Similar results [29] are observed in liquid ammonia.

Bytrych and his colleagues [30] investigated electrodeposition of magnesium from DMF and pyridine in detail. Magnesium bromide solutions in pyridine and magnesium chloride solutions in DMF were exposed to electrolysis in a closed bath with cathodes of Pt, Mg or Hg when mixed in a current of nitrogen. In the electrolysis of magnesium bromide in pyridine magnesium was not extracted, the same results are obtained in the electrolysis of magnesium chloride solutions in DMF with solid cathodes, magnesium amal-

gam is formed with mercury cathode. In the electrolysis of magnesium chloride hydrate solutions in DMF magnesium hydroxide and $\text{MgCl}_2 \cdot 4\text{DMF} \cdot 2\text{H}_2\text{O}$ are formed. In anhydrous DMF with Pt-anode chlorine is extracted but with Mg-anode chlorine is not extracted and on the cathode gelatinous substance is formed which on hydrolyzing gives $(\text{CH}_3)_2\text{NH}$ and HCHO .

Alongside with the nature of the solute and the solvent the nature of the support material is one of the main criteria effecting the electrochemical process. It is known that in the course of magnesium extraction on aluminium electrode magnesium implants into the crystalline lattice of aluminium with the formation of an intermetallic compound [31], while on nickel electrode magnesium extraction is observed and on iron electrode passivation takes place [32]. Apparently, this is connected with the fact that, unlike other electrodes, nickel electrode has the nature and quality favouring magnesium extraction. Some available in literature data on the results of electrochemical extraction of magnesium are summarized in the Table 1.

The electrochemical behavior of magnesium alloys in organic solvents

Alongside with magnesium, magnesium alloys having necessary qualities and being resistant to corrosion are widely used in motor industry, in such fields of industry as electrical engineer, transport, in space researches in the production of rockets and artificial satellites, in nuclear engineering [33].

According to the review of Loodmaa and Toir, work [34] on the study of anode materials of alloys of Al and Mg, MnO_2 cathodes and Al/ MnO_2 elements the results of measurements in aqueous, mixed and organic solvents were obtained. It is shown that when choosing suitable alloys, solution composition and anode corrosion inhibitors it is possible to compose Al/ MnO_2 electrolytes characteristics of which are comparable with those of Zn/ MnO_2 electrolytes. When working with the electrolytes being discussed the main difficulties are noted to be pitting corrosion of anodes and a negative differential effect.

Investigations of the anode made of Mg-Hg alloy in LiClO_4 solution in ADS were carried out in [35]. Stationary potentials (E_s) anode polarization curves on magnesium and its alloy with Hg in 1M LiClO_4 solutions in AN, DMF, PC were measured. In the case of magnesium EC values are close to -1.08 (AN)

and -1.71 V in relation to water saturated calomel electrode (DMF), and for the alloy they are -1,70 and -1,99 V respectively. Introduction of carbon tetrachloride (CCl_4) into DMF is accompanied by EC value of magnesium and EC value of Mg-Hg system (-1.92 and -1.95 V respectively) becoming close.

At current density equal up to 20 mA/cm^2 the electrode polarization remains, but in AN it increases considerably. The conclusion is made that in carefully purified DMF with CCl_4 additives the behavior of magnesium hardly differs from electrochemical characteristics of Mg-Hg alloy due to the destroying effect of CCl_4 on the passivating film. In not purified DMF EC values appear to be less negative by 0.5 V.

The available data do not explain essential differences in the anode behavior of magnesium-mercury alloys, pure magnesium and its alloys with other metals [36]. At the same time it is magnesium-mercury alloys that find a wide application in the production of water activated CSC.

The essential features of anode behavior of magnesium-mercury alloys are the following:

1) Unlike magnesium, the dependency of hydrogen isolation rate on the current density on magnesium-mercury alloys is of a non-linear character; at the initial site of increases with the current density and then becomes constant;

2) Measurements of the double layer capacity by the method of a potential drop after cutting the current off showed that the double layer capacity on pure magnesium and some of its alloys increased with the current density just as the rate of hydrogen isolation. On magnesium-mercury alloys the capacity is less and becomes practically constant at 130-150 $\mu\text{F}/\text{cm}^2$ at definite current densities that, taking into account the roughness of the metal surface, is characteristic of anode processes not complicated by side reaction phenomena.

On the basis of the investigations carried out it is concluded that anode dissolution of magnesium-mercury alloys proceeds according to the amalgam mechanism, i.e. via dissolution of magnesium in the mercury film formed on the metal surface followed by transition of magnesium $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}$ into the solution, that satisfactorily explains the regularities observed.

A wide application of CSC of magnesium-air type with a free electrolytes is restricted nowadays by a relatively little period of their work because of a sharp decrease of electrical characteristics at a short discharge time. A variant of CSC with a semi-bound

Table 1

Literary data on electrochemical extraction of magnesium from non-aqueous systems

Solvents	DN	AN	Salt	Material of electrode	Results of electrolysis		Note	Literature
					Extraction of magnesium	Others		
1	2	3	4	5	6	7	8	9
NH ₃ (liq)	59		MgBr ₂	Mg	No	Form blue metal solutions		[21]
pyridine	33,1	17,2	MgBr ₂	Pt	No		Remixing in a current of nitrogen	[30]
				Mg	No			
				Hg	Mg amalgam			
DMSO (dimethyl sulphoxide)	29,8	19,3	Mg(ClO ₄) ₂	Al	Intermetallic compound			[31]
DMA	27,8	13,6	Mg(CF ₃ SO ₃) ₂	Mg	No			[26]
				Hg	No			
				Pt	No			
				Au	No			
				GC	No			
DMF	26,6	16	MgCl ₂	Pt	No			[24]
				Mg	No			
				Hg	Mg amalgam			
			MgCl ₂ ×H ₂ O	Pt Mg	No	Mg(OH) ₂	The stage of introduction Mg ²⁺ limits	[25]
			Mg(ClO ₄) ₂	Al	Intermetallic compound			
			Mg(CF ₃ SO ₃) ₂	Mg	No			A rise of a cathode current at shifting of a potential with -3.2V. Increase of the cathode mass due to magnesium deposition is not revealed.
				Hg	Mg amalgam			
				Pt	No			
				Au	No			
				GC	No			
THF	20	8	MgBr ₂	Cu	No			[25]
			Mg(ClO ₄) ₂	Cu	No			
			LiAsF ₆ and MgBr ₂ O(C ₂ H ₅) ₂	Cu	Yes	Metallic powder	The secondary character of deposition	[37]
			MgBr ₂ +LiBH ₄	Pt	Yes	90%Mg +10%V	The output on a current is less than with ethereal solutions	
			CH ₃ MgCl+AlCl ₃	Mg	Yes	Dendritic deposit	i =1.25 mA/cm ² E _{cell} =0.5 V	

Table 1*Continued*

1	2	3	4	5	6	7	8	9
THF	20	8	$C_2H_5MgCl + AlCl_3$	Mg	Yes	Excellent, small grain	$i = 1.25 \text{ mA/cm}^2$ $E_{\text{cell}} = 1.5 \text{ V}$	[7]
			$C_2H_5MgCl + AlCl_3$	Mg	Yes	Excellent, large grain	$i = 1.25 \text{ mA/cm}^2$ $E_{\text{cell}} = 0.6 \text{ V}$	
			$C_4H_9MgCl + AlCl_3$	Mg	Yes	Excellent, large grain	$i = 1.25 \text{ mA/cm}^2$ $E_{\text{cell}} = 1.0 \text{ V}$	
$(C_2H_5)_2O$	19,2	3,9	C_2H_5MgBr	Pt	Yes		On polarizing curve	[38]
			C_4H_9MgBr	Pt	Yes			[38]
			$MgBr_2 + LiBH_4$	Pt	Yes	90% Mg		[37]
			Grignard reagent $RMgX$	Pt	Yes			[24]
			Grignard solutions	Pt	Yes		Mg deposition proceeds in 2 stages.	[39]
				Al	Yes			
				Zn	Yes			
				Cd	Yes			
				Sn	Yes			
				Pb	Yes			
				Sb	Yes			
				Bi	Yes			
toluene	0,1	8	CsF , $(C_2H_5)_2Mg$, $(C_2H_5)_3Al$, iso- $(C_4H_9)_3Al$, (1:2:4:2:3)		Yes	99,4%Mg	An electrolysis is carried out at 40°C and $i = 1 \text{ A/dm}^2$	[40]
γ - BL			$Mg(CF_3SO_3)_2$	Mg	No			[26]
				Hg	No			
				Pt	No			
				Au	No			
				GC	No			
PC			$MgBr_2$	Cu	No			[25]
			$Mg(ClO_4)_2$	Cu	No			
			$Mg(ClO_4)_2$	Al	Intermetallic compound		The rate is limited by crystallization C chemical stage.	[31]
$SOCl_2$			$Mg(FeCl_4)_2$	Ni	Yes	Electrode passivation	On galvanostatics curve	[19]
				Mg	No	The passivating film	The film has properties of a solid electrolyte	[41]

electrolyte in an inert matrix is investigated in work [42]. According to the results of the experiments recommendations on optimization of the electrolyte matrix, interelectrode distance, configuration and modification of CSC were worked out.

Electrochemical properties of lithium and its binary alloys with magnesium (10 % and 20 %) at their anode oxidation in 1 M LiBF₄ solution in γ -butyrolactone (γ -BL) were investigated. The electrodes were made by a fit pressing of lithium or its alloy tablets on a nickel net [43].

Anode polarization characteristics were investigated when quietly immersing electrodes by the potentiostatic method within the range of the designed potential change from 0 up to 2.5 V in relation to the lithium electrode in the same solution and by the galvanostatic method at current density within 0.2-15 mA/cm². Currentless potentials of lithium and its alloys with magnesium are close to each other and are in the range 0 - 4 mV. In comparison with the anode of pure lithium, polarization of anodes of alloys in the range of current density from 10 to 15 mA/cm² and at current density up to 1 mA/cm² has the following values: 20 % Mg 0.9-1 and 0.5-0.6 V, 10 % Mg 0.9 - 1 and 0.2-0.3 V.

The highest coefficients values of using lithium were observed in magnesium alloys (93-95 %) which is apparently due to oxidation of magnesium. Relative capacities of most alloys do not depend on polarization current indicating the identity of the nature of side reactions proceeding both on lithium electrode and its alloys.

Conclusions

The electrochemical behaviour of magnesium electrode is conditioned by a passivating film which is characterized by the properties of a solid electrolyte. The rate of anode dissolution of magnesium is determined by the conductivity of the film on magnesium ions. At high current densities electrode polarization increases resulting in the puncture of the film and activation of the electrode.

Depending on the polarization type the state of the film considerably changes. By the results of capacity measurements it is possible to assume that the film thickness decreases at anode polarization and at cathode polarization it increases.

High electronegative potential characterizes magnesium as a potentially highly effective anode material for CSC, in particular, for current sources with electrolytes on the basis of organic solvents. The

major factors determining the discharging characteristics of magnesium electrode in the investigated solution electrolytes are the value of polarization, electrochemical activity of the solvent, the support material as well as adsorption characteristics of electrolyte components. The microstructure of the cathode precipitated magnesium changes owing to the formation of a passivating film, which inhibits the process of anode dissolution and imposes diffusion limits on magnesium ions transfer through a film.

The basic direction in the solution of the problem of cathode deposition of magnesium from electrolytes on the basis of organic solvents is in optimization of properties of electrolytes and choice of conditions allowing to remove by effects.

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Received 21 December 2000.