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**Mg₂Al₃, a complex and disordered intermetallic compound as
anode material for metal-air batteries**

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ABSTRACT

The intermetallic compound Mg_2Al_3 has been selected for this work to be tested as anode in a metal-air battery. The compound is prepared by a high temperature synthesis from elements and its cubic structure ($\text{Fd}\bar{3}\text{m}$, $a = 28.2341(3) \text{ \AA}$) has been refined from X-ray single crystal diffraction data. It is characterized by a high level of disorder with a large number of partially filled atomic sites, split positions and atomic mixing. The compound displays an interesting behavior towards self-corrosion in alkaline and saline environments but the better electrochemical performances are obtained in saline NaCl electrolyte. It is shown that both Al and Mg are involved in the oxidation reaction that occurs at the Mg_2Al_3 electrode used as anode in a metal-air battery. The operating voltage of an Mg_2Al_3 -air cell is remarkably stable over several hours and the Mg_2Al_3 anode efficiency is higher than that of a pure Mg anode in a saline environment.

KEYWORDS

Intermetallic compound, disordered structure, corrosion potential, metal-air batteries, anodic behavior, crystal structure

INTRODUCTION

Numerous and exciting researches have been reported up to now in the field of energy storage and energy conversion. In order to fit requirements for various applications that range from portable electronics to electrical transports, a great quantity of materials has been explored. For a long time, lithium batteries are considered as particularly interesting and powerful

systems. Yet widely commercialized, the Li-ion batteries still motivate scientists as indicated by the quantity of works aimed to improve their performances [1,2]. Nevertheless, their energy densities of current do not meet high-energy requests in specific areas as hybrid electric vehicles. In today's world, where environmental considerations gain in importance, with climate changes and fossil energy supply limitations, there is a substantial interest to turn towards non-polluting devices and renewable energies. Therefore, the search for alternative energy storage and conversion devices and for new electrode materials is still a challenge. Among energy sources, systems based on catalytic redox reactions such as fuel cells have acquired popularity due to their high efficiency and cleanliness. Currently the peculiar metal-air fuel cells (MAFC) that generate electricity through reaction between a metal and oxygen create a renewed and increasing interest. The electrochemical reactions that occur are the metal oxidation on anode and the oxygen reduction on cathode, output cell voltage being the potential difference between cathode and anode. With very high theoretical energy densities because the cathode active material is not incorporated in the battery, these electrochemical power sources are considered as promising candidates. Even displaying a quite low specific capacity, the Zn-air system has been studied for many years and primary Zn-air batteries are commercially available [3,4]. Recent reviews provide an overview of fundamentals, progress and limitations in the area of Li-air batteries [5-7]. It has been reported that capacity may depend on composition, porosity and morphology of the oxygen electro-catalyst employed for oxygen reduction at the cathode [8,9]. On the other hand, attention has also been paid to the nature of the electrolyte: aqueous saline or alkaline, with stabilizing additives or non aqueous, organic, ionic liquids [10-12]. Abundance on earth, low weight, low toxicity, high energetic theoretical capacities (2205 mAh g^{-1} for Mg and 2980 mAh g^{-1} for Al, Fig. 1) along with negative values of standard electrode potentials (-2.93 and -1.66 V relative to the standard hydrogen electrode) make Mg and Al very attractive elements [13,14].

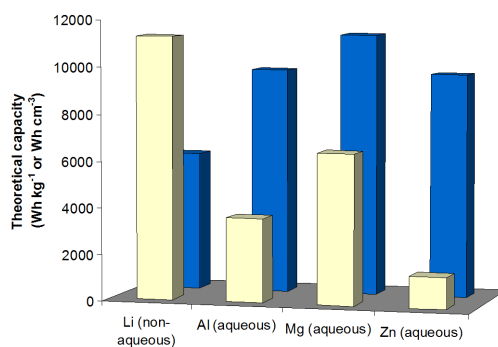


Fig. 1 Theoretical energy densities

Nevertheless, problems are encountered in MAFC built with pure Mg (or even pure Al) anodes. Severe self-corrosion associated with negative difference effect (NDE) during the battery discharge are major drawbacks responsible for losses in capacity and anodic efficiency that have delayed the development of these systems with respect to the Zn-air technology [15,16]. A lot of efforts have been devoted to the study of Zn-air [3] and Al-air batteries [17], but works relative to Mg-air batteries are scarcer. In search of the improvement of electrochemical performances of metal-air batteries, several Mg-based materials have been tested as anodes; most of them are multiphase or composite materials [18-21]. On the other hand, morphology effects (nano, meso...) of the anode materials have been reported [22,23]. Rechargeable systems implying reversible reactions remain a facing challenge but the Mg-air primary batteries, mechanically "refuelable", can still be improved through investigation of new electrode materials able to replace Mg [14].

In this paper, we report on the synthesis and characterization of a bimetallic material Mg_2Al_3 containing both magnesium and aluminum. The aim of the study is to explore the capabilities of this single-phase intermetallic compound used as anode in a metal-air fuel cell. Its electrochemical performances are analyzed comparatively with those of Mg and Al pure metals.

EXPERIMENTAL SECTION

Materials synthesis

Mg₂Al₃ is prepared from elements in stoichiometric ratio of Mg (Alfa Aesar, 99.8%, 20-100 mesh) and Al (Alfa Aesar, 99.5%, 325 mesh). Reagents are kept and handled in a glove box filled with controlled argon atmosphere. Weighed Mg and Al powders are intimately mixed and inserted in a tantalum container weld-sealed under argon atmosphere, which was in turn held within an Ar-filled sealed stainless steel jacket to avoid oxidation in air at high temperatures. Samples are heated to 700 °C in a tubular furnace and kept at this temperature for 24 h, during which they are submitted to a continuous rotation in order to ensure a good homogenization of the melt. Afterwards, samples are quenched in cold water and, to favor formation of the Mg₂Al₃ cubic polymorph, are annealed at 400 °C for 10 days. Then product is recovered and finally ground, either manually in a mortar or mechanically with a planetary ball mill.

Materials characterization

For identification and purity assessment purposes, powders are investigated by X-ray diffraction. The powder patterns are recorded on a Philips X'pert diffractometer equipped with a copper tube and a hybrid monochromator (parabolic multilayer mirror and two-crystal, Cu K α radiation). A single crystal isolated from the reaction product has been used to record diffracted intensities within the complete diffraction sphere on Xcalibur CCD (Oxford Diffraction) four-circle diffractometer. The crystal structure has been solved and refined using SHELX programs [24,25]. Details on experimental parameters for data collection and

structural refinements have been deposited (CSD-427957) and are available on demand*. The final refined composition $\text{Mg}_{37.3}\text{Al}_{62.7}$ is found in very good agreement with the EDX analyses of the crystal. Semi quantitative analyses of the samples are performed using a scanning electron microscope fitted with an energy dispersive detector unit.

Self-corrosion measurements

The Mg_2Al_3 powdered material has been pressed into pellets to be used as active material for the electrochemical experiments. Self-corrosion measurements are performed in 0.6 mol L^{-1} NaCl and 0.6 mol L^{-1} KOH solutions. The Mg_2Al_3 pellet (Mg rod) is immersed in the solution for reaction times ranging from 16 to 96 hours. Samples weights are determined with accuracy before and after experiment. Immersed samples are washed in de-ionized water after removal of the corrosion products formed at their surface and dried prior weighing. The corrosion rate is calculated using the weight loss method and expressed as the weight loss per surface area and per immersion time.

Electrochemical measurements

The Teflon test cell designed for the electrochemical measurements includes a working electrode (sample pellet) of 13 mm in diameter, a platinum foil used as counter electrode and a silver chloride Ag/AgCl-KCl saturated reference electrode (Fig. 2). The sample is fixed onto a stainless steel holder using a Teflon mask then the area of working electrode is 0.785 cm^2 . Either NaCl or KOH aqueous solutions are used as electrolytes. The solutions are prepared from analytical grade reagents and de-ionized water (resistivity $> 18 \text{ M}\Omega \text{ cm}$). Sodium chloride (Carlo Erba) or potassium hydroxide (Chem Lab) is added to water in adequate amount to make a solution at concentration 0.6 mol L^{-1} . Electrochemical measurements are

* CIF file may be obtained from FIZ Karlsruhe, www.fiz-karlsruhe.de/request_for_deposited_data.html

monitored using a Biologic VSP potentiostat controlled by the EC-Lab software. The potentiodynamic polarization curves have been recorded in a voltage domain that ranges from -1.8 to -0.5 V vs Ag/AgCl at a scan rate of 2 mV s^{-1} after OCP measurement.

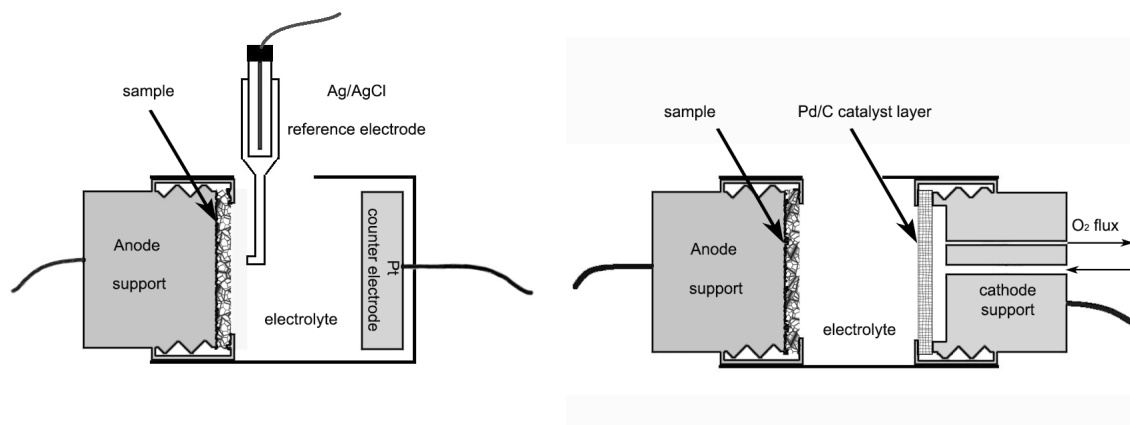


Fig. 2 Schematic representation of the experimental cell: 3-electrode configuration for electrochemical measurements (left) and metal-air battery configuration (right)

Battery tests

Battery tests are performed in the same cell mounted in a two-electrode configuration and the battery then consists of anode, cathode and electrolyte (Fig. 2). The experimental device allows the anode testing in the real conditions of a metal-air battery. Fig. 3 schematically shows how operates a full magnesium-air battery. In these experiments, anode is an Mg or Mg_2Al_3 sample, cathode is an air-electrode with nanostructured Pd/C catalyst and electrolyte is a 0.6 mol L^{-1} NaCl or KOH aqueous solution. The cathode is made of C-supported nano-Pd catalyst deposited onto a Ni-foam to form a diffusive layer allowing oxygen flow. Palladium nanoparticles are obtained by a solution route from palladium dichloride and acidified ethylene-glycol using the polyol process. The cathode conditioning consists in making a deposit onto nickel foam from a mixture of Pd nanoparticles, carbon black and aqueous polytetrafluoroethylene suspension.

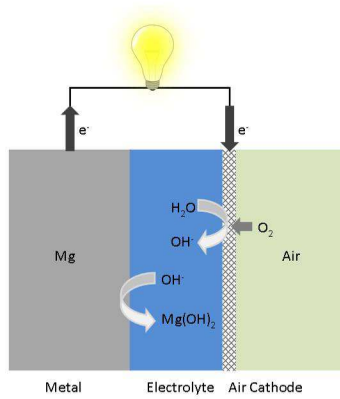


Fig. 3 Operating mechanism of a magnesium-air battery.

The discharge of the cell has been studied in galvanostatic mode at current densities of 5 and 10 mA cm⁻², the cell output potential is recorded for 16 hours. In order to evaluate the amount of anodic material that is consumed during the reaction, weight of the anode is determined before and after the discharge. The efficiency of the anode, η , can be then calculated using the following equation:

$$\eta = \frac{(Q/nF) \times M}{W_i - W_f} \times 100$$

In this expression Q is the electric charge (Coulomb) and n the number of electrons involved in the discharge reaction, F the Faraday constant ($F = 96485 \text{ C mol}^{-1}$) and M the atomic mass (g mol^{-1}). Weights of the sample before and after discharge, W_i and W_f , are expressed in grams.

RESULTS AND DISCUSSION

Material characterization

Owing to their low density, the Mg-Al compounds are of great interest for technological applications. Few intermetallic compounds are known in the binary system and display quite complex structures. The compound commonly referred to as Mg₂Al₃ actually corresponds to a

more complex stoichiometry and, according to the binary diagram, exists within a rather small composition domain [26]. Its structure is known from several decades [27]. A recent comprehensive study has revealed that it undergoes a polymorphic transition $\beta \rightarrow \beta'$ at 214 °C from cubic ($Fd\bar{3}m$, $a = 28.24 \text{ \AA}$) to rhombohedral ($a = 19.97$, $c = 49.91 \text{ \AA}$) symmetry [28]. In present work, alloys are prepared from high temperature synthesis at composition 60% Al and 40% Mg and then submitted to annealing treatment to obtain the pure compound in its cubic form. X-ray diffraction is used for purity evaluation and complete identification of the product.

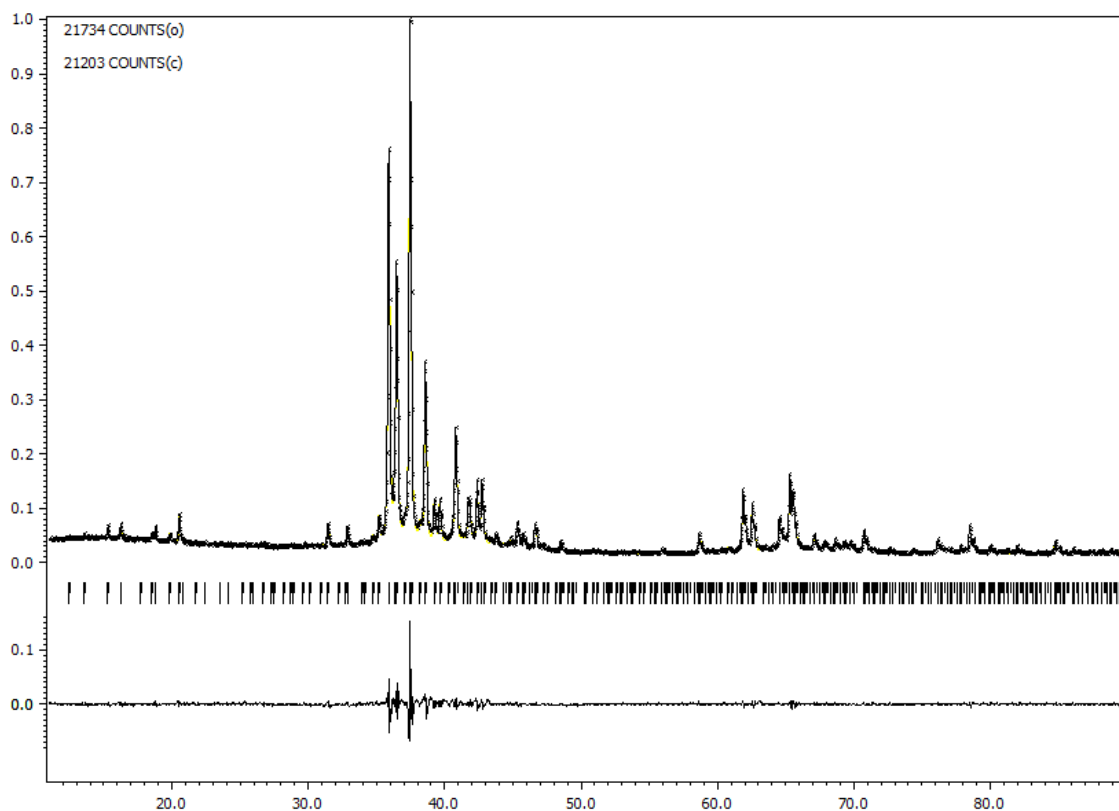


Fig. 4 Mg₂Al₃ experimental XRD powder pattern ($\lambda = 1.541 \text{ \AA}$) given comparatively with the calculated and difference powder diffraction profiles

Experimental XRD powder pattern (Fig. 4) has been analyzed using program JANA [29]. Profile refinement within a cubic $Fd\bar{3}m$ unit cell leads to agreement factors R_p/R_{wp} of 4.3/5.6% and lattice parameter refines to $a = 28.241(1) \text{ \AA}$. The absence of non-indexed lines

indicates the compound is obtained as a pure phase. Furthermore, the high temperature polymorph could not be detected any more after the annealing treatment.

The diffracted intensities collected from a single crystal, selected in the annealed material, display the $Fd\bar{3}m$ cubic symmetry with cell parameter $a = 28.2341(3)$ Å. Least squares refinement, with final agreement factors $R1 = 4.60\%$ ($wR2 = 8.46\%$), leads to the final composition $Mg_{435.7}Al_{732.8}$ for the compound, the unit cell of which contains 1168.5 atoms. This structure is characterized by a high level of disorder with a large number of partially filled atomic sites, atomic mixing and split positions. Our refined model perfectly fits the structures and stoichiometries established earlier for this specially complex structure described with 672 icosahedral clusters, 252 Friauf polyhedra and 244 other polyhedra [27,28]. Note that the refined composition (Al/Mg ratio of 1.68) markedly deviates from the Mg_2Al_3 formula commonly used for this compound. The disordered nature of the compound probably result for packing and/or electronic constraints and would account for specific properties. The behavior of Mg_2Al_3 compound as anode material in a metal-air battery is expected to be different from that of classical magnesium alloys as AZ31 etc... In the former case, the material is composed of a homogeneous distribution of a bimetallic compound while in the latter case the material rather consists of a distribution more or less uniform of Mg and Al within a composite material. Consequently these two situations are significantly different, particularly from the point of view of the atomic interactions and bonding types, which could result in discrepancies in electrochemical behavior.

Corrosion potentials of pure metals

Electrochemical experiments have been carried out in 3-electrode cells filled either with a 0.6 mol L⁻¹ NaCl or a 0.6 mol L⁻¹ KOH solution used as electrolyte. The corrosion potential determined for a pure Mg anode in these conditions with a salt electrolyte is -1.59 V vs

Ag/AgCl (−1.63 V vs. SCE) and compares well with values given in literature, as for example −1.57 V vs. SCE measured in a NaCl solution at a very slightly higher concentration (0.615 mol L^{−1} or 3.5 wt.%) [23]. On the other hand, when using the alkaline electrolyte, the measured potential of −1.55 V vs Ag/AgCl (−1.59 V vs. SCE) indicating a slightly lower reactivity (and a lower current density). It appears that the corrosion potential of the pure magnesium anode is not strongly affected when saline electrolyte is changed for alkaline electrolyte, at least at compositions and concentrations used in this work (table 1). Owing to chemical composition (~63 at.% Al) of the material investigated in this work, Mg₂Al₃, similar electrochemical experiments are also performed using a pure Al anode. The corrosion potential of metallic Al determined in aqueous NaCl electrolyte is −0.71 V vs Ag/AgCl while it is strongly shifted to −1.67 V vs Ag/AgCl when measured in aqueous KOH electrolyte. In contrast to results obtained for magnesium, the aluminum anode behavior is very different in saline or alkaline electrolytes with an important shift in the corrosion potential.

Table 1 Measured corrosion potential and OCP open circuit voltage (V vs Ag/AgCl) in 0.6 mol L^{−1} KOH and 0.6 mol L^{−1} NaCl aqueous electrolytes

Material	Corrosion potential		Open circuit voltage	
	NaCl	KOH	NaCl	KOH
Al	−0.71	−1.67	−0.71	−1.72
Mg	−1.59	−1.55	−1.62	−1.59
Mg ₂ Al ₃	−1.39	−1.35	−1.46	−1.41
Dense Mg ₂ Al ₃	−1.18	−1.46	−1.46	−1.52

It is well known that Al easily forms an Al₂O₃ protective layer on its surface which is responsible for the high potential in NaCl solution. Instead the alkaline solution is able to

attack this layer and clean the electrode from oxide, thus pure Al is available to be involved in a corrosion reaction. This well illustrates the pH effects on the corrosion potential of an aluminum electrode which passivates in saline media while it is relatively rapidly consumed in an alkaline electrolyte. A recent study has evidenced pH effects on the corrosion potential of an Al-based, Mg-containing, ternary alloy and, as could be expected, corrosion rate is lower in neutral solutions [30].

Corrosion potential in alkaline electrolyte

The corrosion potential of the intermetallic compound Mg_2Al_3 has been measured in alkaline electrolyte. Tafel representation of the voltametric curves $I = f(V)$ is given in Fig. 5 comparatively with magnesium and aluminum references. Experiments have been performed for different sample conditioning, starting from Mg_2Al_3 powder. As shown in scanning electron microscopy images, the original ground Mg_2Al_3 powder is homogeneous and formed of micron-sized particles (Fig. 6a).

For a sample prepared from Mg_2Al_3 powder pressed at room temperature, the corrosion potential measured in KOH electrolyte is -1.35 V vs Ag/AgCl. Nevertheless, pellets prepared by this technique are very fragile and difficult to handle, so various routes have been investigated to improve their mechanical solidity. When 10 wt.% of polyethylene powder is added to Mg_2Al_3 as a binder, the corrosion potential increases to -1.26 V vs Ag/AgCl. The material is globally more corrosion resistant, the reason for that would be the presence of an inert component resulting in no reactive domains (polyethylene grains) at the sample surface. Powdered samples have also been included in a poly(vinylidene fluoride) slurry and a similar effect is observed for the corrosion potential that shifts towards higher values beyond -1 V vs Ag/AgCl. It should be noted that in the latter two experiments the anode is actually a

composite material in which Mg_2Al_3 inter-grain contacts are greatly reduced because of the binder.

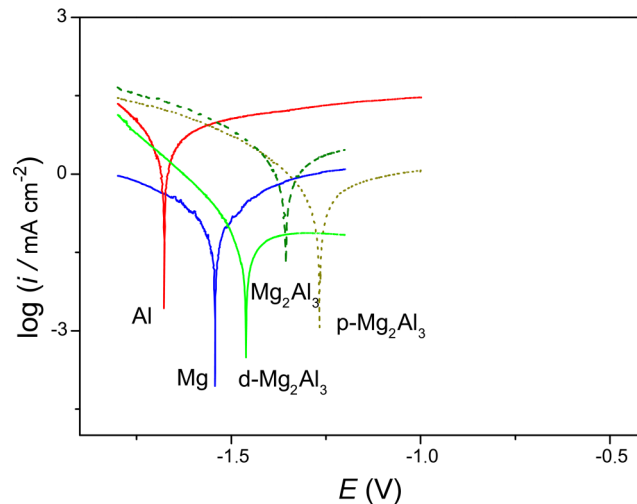


Fig. 5 Potentiodynamic polarization curves in KOH electrolyte

Mg_2Al_3 : pressed at room temperature, d- Mg_2Al_3 : pressed at 275 °C, p- Mg_2Al_3 : mixed with polyethylene binder

As one can see by looking at SEM images, the samples prepared from Mg_2Al_3 powder pressed at room temperature are composed of grains compacted together but still display some porosity (Fig. 6b). This is in agreement with the calculated density which is found about 60%. Definitely, sample surface displays roughness which could support some heterogeneity in the corrosion phenomena (preferential domains, inter granular attack, ...) and have some influence on the anode performances as reported for Mg samples of various controlled morphologies [22,23].

For the Mg_2Al_3 powder pressed at 275 °C, the sample density is significantly increased and calculated values are higher than 96%. This result is well illustrated by the SEM images of samples pressed at this temperature that show a very dense material in which no individualized grains can be observed neither on sample surface (Fig. 6c) nor on the section of a cut pellet (Fig. 6d).

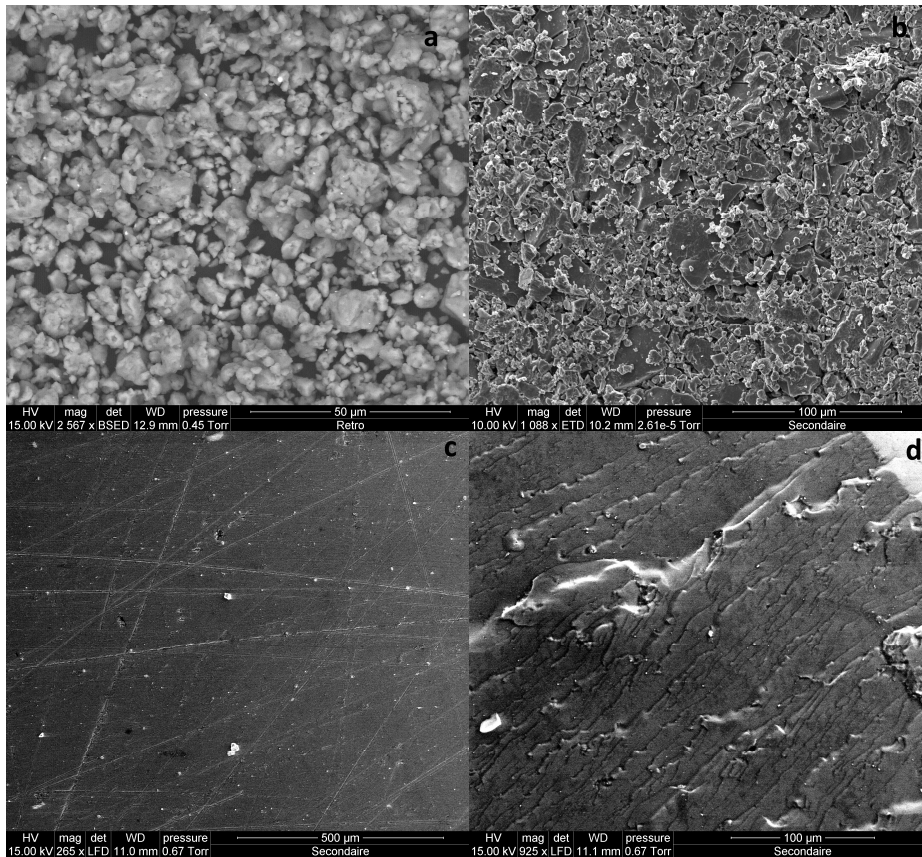


Fig. 6 SEM micrographs of Mg_2Al_3 : *up* (a)-powder, (b)-pressed at room temperature; *down* (c) surface of a dense pellet pressed at 275 °C and (d)-section

When measured using such dense samples, the corrosion potential reaches a more negative value of -1.46 V vs Ag/AgCl. In the mean time, the current density is found fairly lower than for samples pressed at room temperature indicating a smaller electrochemical activity.

The corrosion potential of Mg_2Al_3 moves from weakly negative values when powder is dispersed into a binder to clearly more negative values when it is well compacted into dense pellets. Such displacement associated with the sample conditioning would originate in some particle coalescence and densification phenomena that may have an effect on the material properties and its electrochemical behavior. With a corrosion potential of -1.46 V, the dense Mg_2Al_3 sample is found slightly more corrosion resistant than pure Mg (-1.57 V).

For Mg_2Al_3 samples conditioned differently, the corrosion potential is found to decrease towards more negative values as the sample compacity increases. Surprisingly, the Mg_2Al_3 denser samples are found the more reactive in alkaline electrolyte. In the mean time, the current density globally decreases indicating a better resistance to corrosion for the material; the weaker the current density, the slower the kinetics of the reaction.

Corrosion potentials in saline electrolyte

Analogous electrochemical potentiodynamic experiments are carried out using a 0.6 mol L^{-1} salt water electrolyte, the corrosion potentials measured for Mg_2Al_3 powders pressed at room temperature with and without polyethylene binder are very close (-1.37 and -1.39 V vs Ag/AgCl) as shown in Fig. 7.

Instead, values -1.18 and -1.17 V vs Ag/AgCl are measured for the corrosion potential of dense samples, the first is obtained for a hot pressed pellet and the second for a polished cast sample (bulk material). Note that a value of -1.33 V vs Ag/AgCl has been measured for corrosion potential of highly divided Mg_2Al_3 powder prepared by mechanical alloying and pressed at room temperature. This value is slightly higher than that of -1.39 V obtained starting from powder pressed under the same conditions, probably because of a higher density for the sample resulting from highly divided powder.

Contrary to what is observed in alkaline electrolyte, in saline electrolyte the denser samples provide the higher corrosion potentials (less negative values). Nevertheless lower current densities indicate that dense samples are characterized by a better resistance to corrosion and slow reaction rates. The Mg_2Al_3 denser samples display the lower reactivity in saline electrolyte.

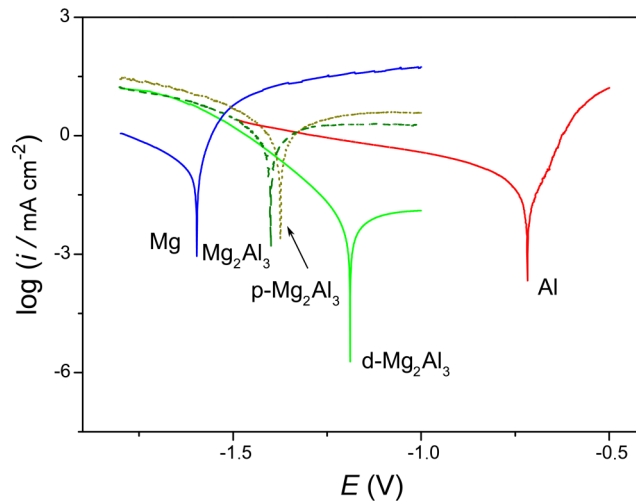


Fig. 7 Potentiodynamic polarization curves in NaCl electrolyte

Mg₂Al₃: pressed at room temperature, d-Mg₂Al₃: pressed at 275 °C, p-Mg₂Al₃: mixed with polyethylene binder

The results obtained in this work are quite unexpected since for a specific electrolyte (saline or alkaline) and same operating conditions, the corrosion potentials for the different kinds of Mg₂Al₃ are rather different. This indicates that potential is not only dependent on the material but could vary with parameters such as nature of electrode-electrolyte interface, surface morphology, sample density... The sample preparation is then an important parameter to consider. Mixing powders with binders have the effect of separating grains, lowering conduction properties and locally modifying the sample surface (composition, homogeneity, roughness...) Beyond the sample densification, the thermal treatment at high temperature modify the material morphology (porosity, sintering, surface smoothing...). These parameters would modify the material behavior towards the electrolyte mainly acting at interface (electrode-electrolyte interactions, oxidation coating, accessible surface, diffusion layer...).

Regarding the resistance to corrosion in NaCl, dense Mg₂Al₃ is nearly midway between Mg and Al, with a corrosion potential almost corresponding to the weighted average (according to the true stoichiometry) of the Mg and Al corrosion potentials. The corrosion current is found

smaller for Mg₂Al₃ anode than for Mg or Al pure electrodes. This is indicative of an electrochemical process characterized by lower reaction rates.

Looking now at general trends (variations of potential and current with electrolyte change), one can note that Mg₂Al₃ samples pressed at room temperature behave almost as Mg whereas dense Mg₂Al₃ samples rather have a behavior close to Al.

Self-corrosion rates

Before evaluating performances in electrochemical metal-air batteries, the self-corrosion behavior of the samples has been studied in alkaline and saline electrolytes. Actually, self-corrosion corresponds to chemical corrosion of the electrode, a side-reaction which should be as limited as possible.

The corrosion rates are measured by the weight loss method. As reported in table 2, pure Mg samples show a corrosion rate of 0.11 mg cm⁻² h⁻¹ in NaCl solutions, a value which is fairly lower than results reported in literature [18]. In contrast, dense Mg₂Al₃ samples (hot pressed or bulk) are found to display no measurable corrosion since no weight loss could be measured even after two weeks immersion. However, for long immersion times, samples are covered with a very slight white film indicating their surface could have been passivated.

Considering the Mg₂Al₃ good resistance to corrosion towards the electrolytes, it is reasonable to expect low self-discharge phenomena in assembled batteries.

Table 2 Self-corrosion rates determined in 0.6 mol L⁻¹ NaCl or KOH solutions

Corrosion rate (mg cm ⁻² h ⁻¹)	NaCl	KOH
Mg	0.11	0.008
Mg ₂ Al ₃	0	0

Battery tests

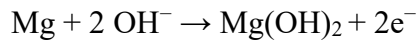
The compound Mg_2Al_3 has been employed as anode material in experimental metal-air batteries assembled in the laboratory with a Pd catalyst air-cathode. The discharge has been processed at constant current densities of 5 and 10 mA cm^{-2} . The starting potential of a battery using an alkaline electrolyte is found relatively high at ~ 1.2 V but continuously decreases and rapidly falls down, reaching nought after less than one hour. Therefore, no further investigation has been carried out using alkaline electrolytes.

Performances of Mg_2Al_3 anodes are more attractive in a battery containing a salt water solution used as electrolyte. The open circuit voltage OCV measured before discharge is found rather high at 1.4 V. Starting the discharge causes a rapid drop in the potential which stabilizes after few seconds to a value close to 0.7 V, the battery then operates at a constant voltage during several hours. This working potential value should be compared to 1.3 V, the operating potential of a pure magnesium anode in same experimental conditions (Fig. 8).

Such a discrepancy in the working potentials may be correlated to differences in interatomic interactions within materials. Actually, Mg is involved in metallic bonding in the elemental Mg while it is mainly surrounded by Al in the intermetallic Mg_2Al_3 compound where some covalent bonding occurs.

Typical experiments have been carried out up to 24 h for different sample conditionings. After discharge experiment, anodes made of room temperature pressed pellets are seriously dismantled while anodes made of dense pellets are only partially corroded. For a higher current density of 10 mA cm^{-2} , the operating potential of the battery still remains stable for several hours but is reduced to 1.0 V and ~ 0.4 V for Mg and Mg_2Al_3 anodes, respectively.

In the battery composed of a pure magnesium anode, the reaction that takes place at the anode is the oxidation of magnesium following



while in the mean time oxygen is reduced at the cathode

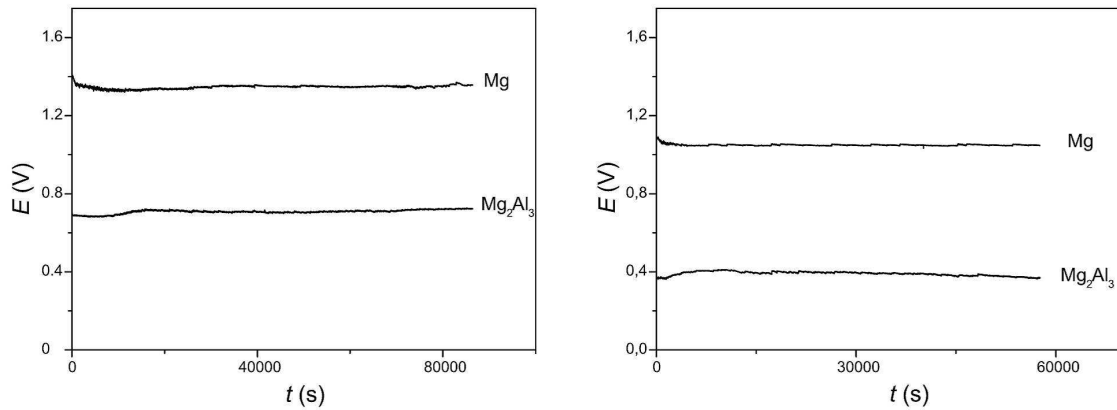
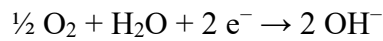


Fig. 8 Discharge of Mg and Mg₂Al₃ anodes in metal-air batteries using NaCl electrolyte and operating at 5 mA cm⁻² (left) and 10 mA cm⁻² (right)

During the discharge process of a battery containing Mg₂Al₃ as anode material, the oxygen reduction still occurs at the cathode but the oxidation reaction expected at anode could be more complex because it could involve the participation of the two elements, Mg and Al. Trying to elucidate what are the reactions, the product which is formed as a white precipitate at the bottom of the cell has been recovered for analysis. The XRD powder pattern of the raw precipitate indicates the presence of an amorphous component which cannot be thus identified and contains a few peaks that are characteristic of the aluminum hydroxide. At this stage the participation of aluminum in the reaction mechanism has been evidenced but no proof of the magnesium contribution is obtained. In a thermal analysis experiment, the collected precipitate is heated up to 1000 °C under N₂ atmosphere. The two endothermic events that are detected have been attributed to the dehydration and transformation of the product while a 45% total mass loss is measured. The XRD pattern of resulting product reveals the presence of a mixed Mg and Al oxide, MgAl₂O₄ and a small amount of MgO. This brings a

confirmation of both participation of magnesium and aluminum in the discharge reaction at the anode. Such finding corroborates the assumption that bonding nature around Mg plays a part in the oxidation phenomena occurring at the Mg_2Al_3 electrode.

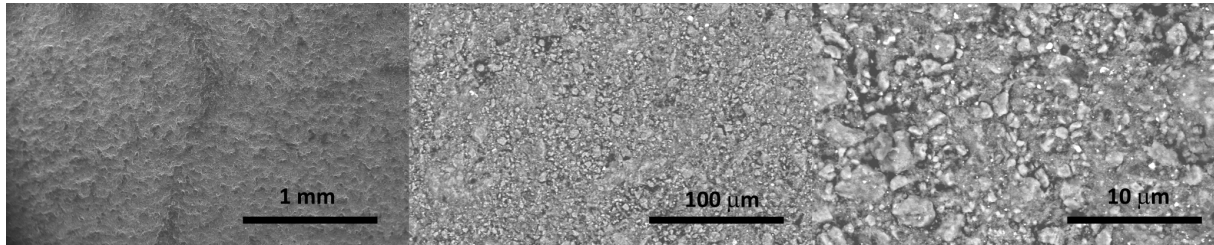


Fig. 9 Scanning electron microscopy images of sample surface of Mg_2Al_3 anode after 16 h of discharge in NaCl electrolyte

This result is confirmed by the energy dispersive X-ray spectrometry analyses of the white solid collected in the battery. Results indicate the presence in corrosion compound of both Mg and Al in Mg/Al ratio of 39.3/60.7, a value that compares well with ratios obtained for pristine compound, 37.6/62.4 from EDX analyses and 37.3/62.7 from X-ray diffraction data refinement. It can be then asserted that both elements contribute in the oxidation reaction at anode. Furthermore the intermetallic compound Mg_2Al_3 compound is steadily consumed at anode during the discharge reaction. It is reasonable to imagine that the Mg_2Al_3 oxidation reaction that takes place at the anode generates $Mg(OH)_2$ and $Al(OH)_3$ hydroxides.

After a long discharge of 16 hours operated in a battery that uses NaCl as electrolyte, the anode pellet of Mg_2Al_3 has been analyzed. It has been reported in literature that, for Mg alloys used as anodes, a part of the discharge product remains on the electrode surface and forms a layer with pore and crack that prevent passivation [31,18]. At a macroscopic scale, no thick corrosion layer covering the Mg_2Al_3 anode has been observed, the product which forms during discharge mainly deposits in the electrolyte at bottom of the cell. The surface of the anode still displays a great homogeneity with no breaks or deep holes (Fig. 9). It is widely

reported that pitting corrosion can be initiated at sample surface of alloys in which coexist different metallic micro-domains that behaves as micro-cells. In the case of dense intermetallic Mg_2Al_3 anodes, it would seem that such localized galvanic corrosion phenomena do not take place at the surface sample. The corrosion products mainly deposit and form an extremely thin layer which does not passivate the electrode, allowing a homogeneous corrosion process.

Table 3 Anode efficiency for a metal-air battery discharge (0.6 mol L^{-1} NaCl electrolyte)

	Current (mA cm^{-2})	Anode efficiency (%)
Mg	5	56.4
	10	52.2
Mg_2Al_3	5	69.4
	10	72.5

As indicated by the formula given above, anodic efficiency can be calculated from the weight loss during discharge. Its expression depends on the number of electrons involved in the reaction. For the Mg anode, the reaction that occurs at anode is well known and evaluation of this number is obvious. In case of Mg_2Al_3 , the calculated efficiency would depend on the reactions that take place at the electrode. Since proofs are provided that both Mg and Al are involved in oxidation reactions at anode, their both contributions will be considered in calculation. Most likely, the oxidation reaction of Mg_2Al_3 will provide Mg and Al at the respective oxidation states +2 and +3. Then, assuming the +2 oxidation state for Mg and +3 for Al, the number of electrons and the atomic mass should be replaced by average values calculated as weighted sums. The efficiency is then calculated according to the formula

$$\eta = \frac{(Q/n_a F) \times M_a}{W_i - W_f} \times 100$$

with $n_a = x_{\text{Mg}}z_{\text{Mg}} + x_{\text{Al}}z_{\text{Al}}$ and $M_a = x_{\text{Mg}}M_{\text{Mg}} + x_{\text{Al}}M_{\text{Al}}$ where x represents the mole fraction, z the oxidation state and M the atomic elemental mass for each component.

The calculated anodic efficiency for Mg and Mg₂Al₃ anodes experiments are given in Table 3. They are associated with 16 hour discharges of metal-air batteries using saline electrolyte. Compared to pure Mg, the Mg₂Al₃ anode displays an increase in the anodic efficiency of about 15%. In fact, the anodic efficiency calculated for an Mg anode is in the range 52-56%, either for current densities of 5 or 10 mA cm⁻². In the same conditions the Mg₂Al₃ anode efficiency is fairly higher and reaches a value comprised between 70 and 73%.

CONCLUSION

This study has been motivated by the investigation of Mg₂Al₃ electrochemical properties towards the corrosion. This intermetallic compound, known to undergo a polymorphic transformation has been prepared in its β-Mg₂Al₃ cubic low temperature form. Its very complex structure displays both positional and atomic disorder. Despite the important number of disordered positions (split and partially filled sites, atomic mixing) our refinement from single crystal data is in very good agreement with previously published works. The very close stoichiometries would indicate a very narrow composition domain for this intermetallic compound.

The intermetallic compound performances have been evaluated in metal-air devices. Results show a very good resistance to self-corrosion for Mg₂Al₃, highly improved compared with

pure Mg. Side reactions between electrode and electrolyte are almost suppressed either in alkaline or saline aqueous solutions.

As attested by its corrosion potential shifted towards positive region, Mg_2Al_3 is more corrosion resistant than pure Al and Mg in alkaline electrolyte. On the contrary, Mg_2Al_3 behavior in NaCl environment is intermediate between those of pure metals. Battery tests with an Mg_2Al_3 anode and an oxygen-air cathode show a rapid decrease in potential using KOH electrolyte but an extremely stable potential using NaCl, a behavior which is similar to that observed for a pure Mg anode. The participation of both Mg and Al has been evidenced in the corrosion process that appears to be homogeneous. This may be related to the single-phase nature of the compound which protects the electrode from localized corrosion phenomena (galvanic, pitting...) commonly observed for alloys. In spite of a lower electrochemical activity, Mg_2Al_3 displays a higher anodic efficiency than pure Mg. Anodic polarization effects are still observed which can be overcome by increasing electroactive surface, using highly divided materials or by adding stabilizing additives in the electrolyte [32]. Many routes can be explored to gain performance improvements.

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