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A new magnesium-air cell for long-life applications

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A novel type of magnesium–air primary cell has been evolved which employs non-polluting and abundantly available materials. The cell is based on the scheme $Mg/Mg(NO_3)_2, NaNO_2, H_2O/O_2(C)$. The magnesium anode utilization is about 90% at a current density of $20\,mA\,cm^{-2}$. The anode has been shown to exhibit a low open-circuit corrosion, a relatively uniform pattern of corrosion and a low negative difference effect in the electrolyte developed above as compared to the conventional halide or perchlorate electrolytes. In the usual air-depolarized mode of operation, the cell has been found to be capable of continuous discharge over several months at a constant cell voltage of about 1 V and a current density of $1\,mA\,cm^{-2}$ at the cathode. The long service-life capability arises from the formation of a protective film on the porous carbon cathode and fast sedimentation of the anodic product (magnesium hydroxide) in the electrolyte. The cell has a shelf-life in the activated state of about a year due to the low open-circuit corrosion of the anode. These favourable features suggest the practical feasibility of developing economical, long-life, non-reserve magnesium–air cells for diverse applications using magnesium anodes with a high surface area and porous carbon–air electrodes.

1. Introduction

Electrochemical energy conversion based on metal–air systems is of great practical importance since the oxygen in the air is used directly and there is no need to store or transport active material for the battery cathode. The use of metal–air batteries is well established in practice in the form of wet zinc–air primary cells which have been employed for several decades in applications, such as railway signalling, where long service-life and high reliability are required.

The anode in the conventional wet air, depolarized primary cell is usually cast from zinc which is subsequently amalgamated with about 3% mercury. Two disadvantages of a widespread use of zinc–air cells are the environmental pollution caused by the toxic zinc and mercury salts and the relatively fast depletion of world resources of zinc which, it is estimated, will only last between twenty [1] and eighty [2] years at the present rate of growth of consumption.

The best long-term alternative to zinc as the anode in primary batteries is magnesium, for the following reasons:

(a) Resources: magnesium is available in unlimited quantities by extraction from sea water, the technology for which is well established.

(b) Environmental compatibility: the magnesium ion is nontoxic and so poses no pollution problems for battery sludge disposal, if amalgamation of the anode is avoided.

(c) Cost: magnesium, even when extracted from sea water, is fairly inexpensive, costing at present about twice as much as zinc of comparable battery-grade purity.

(d) Electrochemical reactivity: the standard potential of magnesium (− 2.37 V) is more negative than that of zinc (− 0.76 V) and the electrochemical equivalent of magnesium ($0.45\,g\,A^{-1}\,h^{-1}$) is less than that of zinc ($1.22\,g\,A^{-1}\,h^{-1}$); therefore, magnesium is considerably superior from an electrochemical point of view to zinc as an anode in primary cells.

Previous work on magnesium–air cells [3–9] is mainly concerned with the development of reserve-type cells which require activation (addition of electrolyte) before use and which, once activated, have a continuous discharge life of a few hours and a shelf-life on open circuit of only a few days.*

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* These performance limitations, which are not always mentioned in the references cited, can be inferred from a comparison of the data presented.

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The short life during discharge is mainly due to a deterioration of the porous carbon cathode by the deposition of magnesium hydroxide in the pores. The short shelf-life of cells after activation is mainly due to the high rate of corrosion, localized attack and spalling of the magnesium anode on open circuit.

The present work describes the development of a novel type of magnesium–air primary cell which is characterized by a continuous discharge capability over several months and by a shelf-life of several months in the activated state.

2. Experimental

2.1. *Anodes*

Strips of magnesium alloy anodes (alloy AZ-21, Dow Chemical Co.) were prepared by sectioning impact-extruded cans of this alloy. The strips were degreased in hot 20 wt% sodium hydroxide solution, rinsed with water, pickled in a mixture of 12 vol% acetic acid and 10 wt% sodium nitrate solutions for 2 minutes, rinsed with water, passivated in a solution containing 20 wt% chromic acid, 9 vol% orthophosphoric acid and 2 wt% magnesium nitrate for 2 minutes, rinsed with distilled water and dried before use. No amalgamation of the anode was carried out†.

2.2. *Cathodes*

Dry acetylene black, previously activated by a chemical oxidation step, was pressed in a die at about 5 $\mathrm{kg\,cm^{-2}}$ with about 13 wt% of polymethyl methacrylate (added as a 5% solution of the polymer in benzene) as the binder. The pressed electrode was dried at 60° C for about 6 hours to evaporate the benzene.

2.3. *Electrolyte*

At first, a large number of electolytes were screened to identify the electrolyte which satisfied the following objectives: a low and uniform corrosion rate of magnesium, low anodic polarization of magnesium at useful current densities and fast coagulation of the final anodic product (magnesium hydroxide) in the electrolyte. Some of the electrolytes studied in the pH range 5–8 were thus discarded, e.g. NaCl, $KHCO_3$, NH_4NO_3, $NaNO_3$, $NaNO_3 + HNO_3$, $NaNO_2$, Na_2SO_4, $MgCl_2$, $MgBr_2$ and $Mg(ClO_4)_2$, the last two being used both with and without potassium chromate as a corrosion inhibitor. In the presence of chromate ion, the corrosion rate was initially low but since a cathodic reduction of chromate took place at the carbon electrode during cell discharge, the inhibition of corrosion of the magnesium anode was eventually lost.

It was established as a result of these studies that a mixed electrolyte containing magnesium nitrate and sodium nitrite fulfilled the above objectives and should therefore be satisfactory for long-life, magnesium–air cells.

2.4. *Conductance measurement*

The conductance of the system $Mg(NO_3)_2$–$NaNO_2$–H_2O was measured with an a.c. conductance bridge in the usual way at 1000 Hz. The specific conductance of the electrolyte mixture chosen (2.6 M $Mg(NO_3)_2 \cdot 6H_2O$ and 3.6 M $NaNO_2$) was found to be 0.11 $\Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperatue (25 ± 5° C). There was no significant change in the conductance of the electrolyte after complete discharge of the cell.

2.5. *Measurement of the corrosion rate*

The rate of evolution of hydrogen from the magnesium alloy on anodic polarization was measured by the volume of solution displaced from a calibrated glass tube filled with electrolyte and with its closed end vertically above the test specimen (Fig. 1). The absence of glass joints and of residual gas space in the measuring glass tube ensured high accuracy of measurement. The magnesium rod was inserted directly from the bottom plug of the polythene container exposing only its crosssectional area. All measurements were carried out at room temperature (25 ± 5° C).

2.6. *Cell studies*

The cell Mg/$Mg(NO_3)_2$, $NaNO_2$, H_2O/C(air) was set up with a central, partially submerged, porous

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† In fact, amalgamation is to be avoided since it will enhance the corrosion rate of magnesium significantly by disrupting the passive film on the metal.

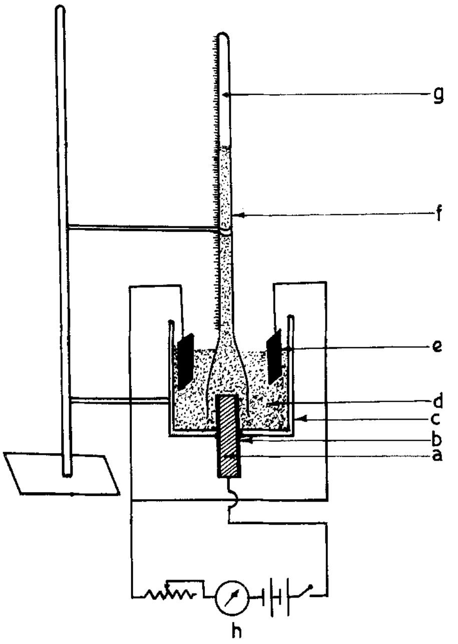

Fig. 1. Apparatus used to measure the volume of hydrogen gas evolved during the corrosion of magnesium under anodic polarization in different electrolytes. a, Rod of magnesium anode (AZ-21 alloy; diameter 2.25 cm); b, Polythene sleeve; c, Polythene container; d, Electrolyte solution; e, Magnesium plates (counter-electrodes); f, Glass tube of uniform bore (internal diameter 0.46 cm and length about 40 cm); g, Hydrogen gas collected; h, Ammeter.

carbon rod as the cathode, surrounded by strips of Mg anode. The cell was filled up with a magnesium nitrate solution (2.6 M) containing sodium nitrite (3.6 M). The concentrations of the salts are not critical.

Cell discharge studies were made, after a soaking period of two days, in the galvanostatic mode at different values of cell current, the cell voltage being allowed to attain a steady value at each cell current. The maximum value of the cell voltage was reached after a few hours of stabilization time at each cell current. The electrode potentials of the anode and cathode were measured separately using a saturated calomel electrode (SCE) as the reference electrode.

3. Results and discussion

3.1. *Nature of the cathodic reaction*

At the outset, it was proved that the cathodic reduction of NO_3^- or NO_2^- was not responsible for the current during cell discharge. This was established by measuring the single-electrode potential of the porous carbon cathode before and after de-aerating the electrolyte and the head-space of the cell with pure nitrogen gas, whilst maintaining the cell discharge current constant. It was found that, at a current density of 1 mA cm^{-2} at the cathode, the cathode potential shifted from − 0.4 V versus SCE in an air-saturated solution to − 0.8 V versus SCE after de-aeration. On bubbling air through the de-aerated electrolyte, the original potential (− 0.4 V versus SCE) was restored, thus clearly indicating the dominant role of oxygen as the cathodic reactant under normal conditions of cell discharge.

Moreover, a progressive increase in the pH of the electrolyte solution during continuous cell discharge was also observed. These facts indicate that the net cathodic reaction in the cell during spontaneous discharge is

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-.$$

3.2. *Nature of the anodic reaction*

The progressive build up of $Mg(OH)_2$ in the cell on continuous discharge indicates that the net anodic reaction is

$$Mg + 2OH^- \rightarrow Mg(OH)_2 + 2e.$$

It has been suggested [10] that the mechanism of anodic dissolution of Mg may involve the formation of Mg^+ at first, which will then interact with H_2O giving $Mg(OH)_2$ and H_2. If the efficiency of anodic dissolution is calculated assuming a two-electron loss per magnesium atom, i.e., on the basis of the formation of Mg^{2+} ion, this should not be more than 50% of the value when anodic dissolution leads to Mg^+ formation only. The present results, which show that the efficiency of anodic dissolution (Fig. 2) calculated on the basis of two-electron loss per Mg atom is about 90% if the current density is above 20 mA cm^{-2}, indicate that the mechanism involving univalent Mg^+ formation cannot be the predominant mode of anodic dissolution. The cell reaction which occurs during discharge is therefore

$$2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2.$$

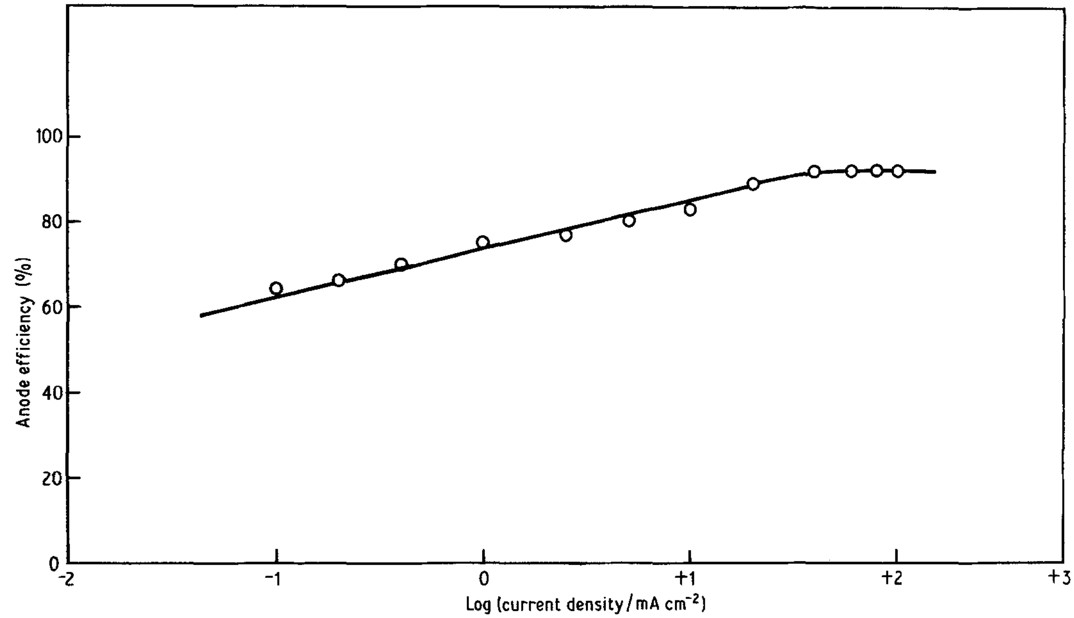

Fig. 2. The dependence of anode efficiency on anode current density for AZ-21 magnesium alloy in the cell electrolyte. The efficiency is calculated as the ratio $(Q_0 - Q_1)/Q_0$, where Q_0 is the total charge passed through the anode in a given time and Q_1 is the charge-equivalent of Mg corroded spontaneously (calculated through the volume of hydrogen gas evolved during the same time).

3.3. *Polarization curves*

The anodic and cathodic polarization curves obtained under steady-state conditions are shown in Fig. 3. The anode potential reached to within 100 mV of its steady-state value at a given current density within a few seconds of setting the current. The corresponding period was several minutes for the cathode potential.

The cathodic polarization curve indicates that the stationary potential established is a mixed potential, being considerably more negative than the thermodynamic value for the oxygen electrode reation (+ 1.06 V versus SCE in a solution of pH 7). Moreover, the charge transfer polarization is also fairly large, being about 0.5 V (from the rest potential) at 0.1 mA cm^{-2}. There is therefore considerable scope to improve the performance of the simple (noncatalysed) porous carbon, oxygen diffusion electrode in the nitrate–nitrite mixed electrolyte by incorporating a suitable electrocatalyst for the oxygen electrode reaction.

The tendency of the current to reach a limiting value at about 1.6 mA cm^{-2} of apparent area of the cathode is to be attributed to the exhaustion of oxygen at the three-phase boundary zone; an optimisation of the porous electrode structure, not attempted in this study, may be expected to enhance the limiting current for oxygen reduction.

The anode polarization curve (Fig. 3) also indicates the establishment of a mixed potential

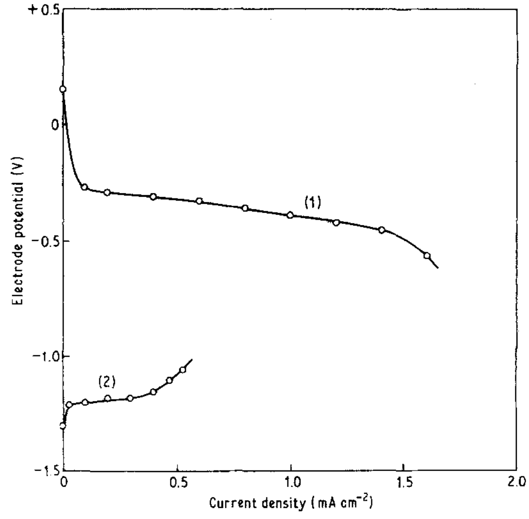

Fig. 3. Polarization curves for (1) the cathodic reduction of oxygen and (2) the anodic oxidation of AZ-21 magnesium alloy in $Mg(NO_3)_2$ (2.6 M) and $NaNO_2$ (3.6 M) electrolyte at room temperature.

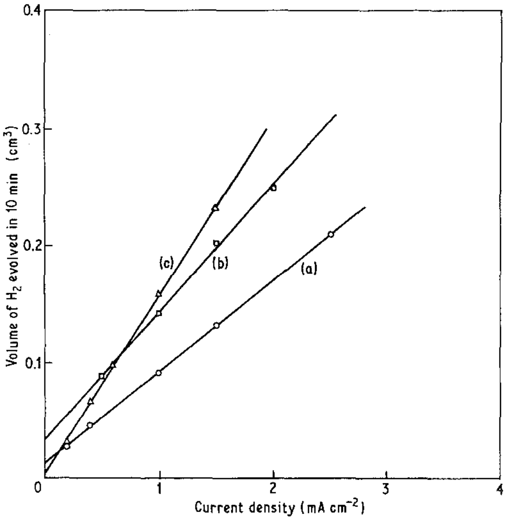

Fig. 4. Volume of hydrogen gas evolved at AZ-21 magnesium alloy on anodic polarization for 10 minutes at room temperature (25 ± 5° C) with various electrolytes. (Area of magnesium = 4.0 cm^2.) (a) $Mg(NO_3)_2$ (2.6 M) and $NaNO_2$ (3.6 M), pH of the electrolyte: 6.5; (b) $Mg(ClO_4)_2$ (1.6 M), pH of the electrolyte: 7.0; (c) $Mg(ClO_4)_2$ (1.6 M) and $K_2Cr_2O_7$ (0.5 g l^{-1}), pH of the electrolyte: 7.0.

at the Mg electrode at −1.3 V versus SCE, a value considerably more positive than the standard potential of the Mg^{2+}/Mg half-cell (− 2.37 V versus SHE). Since the corrosion rate at open circuit (Fig. 4) is quite low, it is to be inferred that the metal is in its natural passive state at its rest potential in contact with the electrolyte. The breakdown of passivity occurs within about 0.1 V of anodic polarization, beyond which the anodic dissolution of magnesium is found to take place more or less uniformly on the surface. The approach to a limiting current of anodic dissolution at about 0.5 mA cm^{-2} is due to the smoothness of the surface of the anode used which causes an early onset of secondary passivity by a deposition of $Mg(OH)_2$ on the surface.

3.4. *Cell discharge*

A typical curve for cell discharge at constant current is shown in Fig. 5. The remarkable constancy of cell voltage over the entire period of discharge indicates the long-term stability of the cell under continuous discharge. At point A in Fig. 5, almost the whole of the magnesium is anodically dissolved and the cell voltage tends to decrease rapidly. On replacing the anode with fresh magnesium strips, the cell voltage regained the value on the plateau of the discharge curve at the same cell current.

It is also interesting to note that the carbon electrode and the cell bottom were covered with a layer of $Mg(OH)_2$ but the bulk of the solution remained clear. The pH of the solution changed during this period of continuous cell discharge from an initial value of 6.5 to a final value of 8. Further, if the cell electrolyte at the end of cell discharge is filtered and stored, a slow precipitation of $Mg(OH)_2$ is observed in the filtrate.

These facts suggest that the long-term continu-

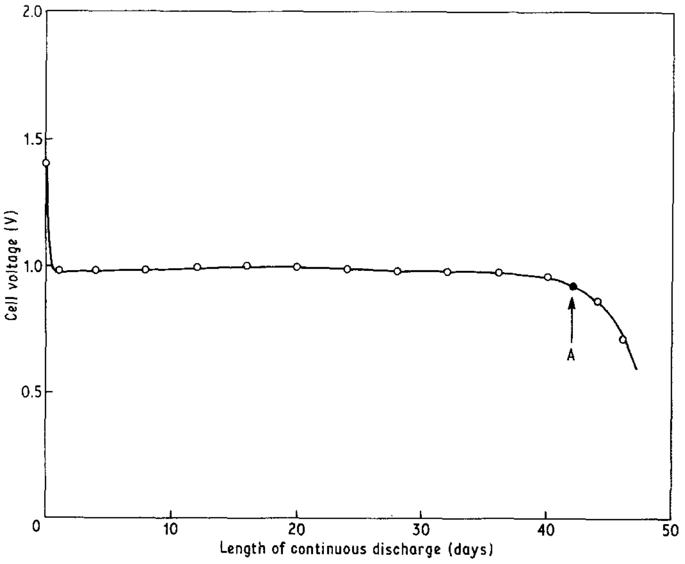

Fig. 5. Cell discharge curve at a constant current of 30 mA. The cell used had a magnesium anode of area 350 cm^2 and a porous carbon cathode of apparent area 180 cm^2. At the point A, the magnesium anode was almost completely dissolved.

ous discharge capability of the present magnesium–air cell is due to the magnesium nitrate–sodium nitrite electrolyte permitting either a certain degree of supersaturation or a very slow rate of precipitation of $Mg(OH)_2$, as a result of which there is no significant clogging of the electrolyte. Also, the layer of $Mg(OH)_2$ formed on the external surface of the carbon cathode prevents the diffusion and migration of Mg^{2+} into the pores of the carbon electrode, possibly because of the incipient formation of $Mg(OH)_2$ by interaction with the OH^- ions diffusing and migrating outward from the pores of the carbon electrode.

3.5. *Corrosion of the magnesium anode*

It is well known that magnesium electrodes undergo some corrosion under open circuit conditions and that the corrosion rate increases on anodic polarization ('negative difference effect'). Such corrosion losses should be minimized for practical applications in batteries.

The corrosion rates measured with AZ-21 magnesium alloy under anodic polarization in the nitrate–nitrite electrolyte and the conventional perchlorate electrolyte (with and without chromate inhibitor) are shown in Fig. 4. It may be seen from the figure that the 'negative difference effect' (which may be taken as the slope of the curves in Fig. 4) is substantially decreased in the nitrate–nitrite electrolyte as compared to the other electrolytes. The corrosion rate on open circuit, which amounts to about 45 $\mu A\ cm^{-2}$, is also small enough for galvanic anode applications. More significantly, the pattern of corrosion of the magnesium anode observed in the nitrate–nitrite electrolyte is of a relatively uniform type (Fig. 6), compared to localized attack in other electrolytes [11].

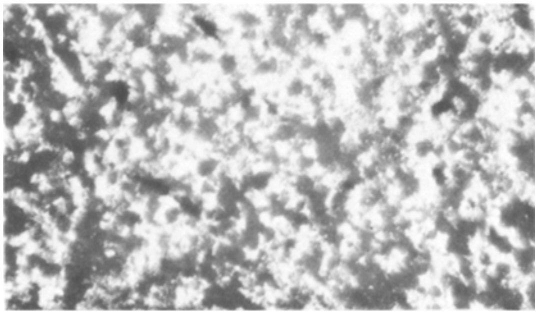

Fig. 6. Photomicrograph of the surface of AZ-21 magnesium alloy after anodic polarization in $Mg(NO_3)_2$ (2.6 M) and $NaNO_2$ (3.6 M) electrolyte at 1 mA cm^{-2} for 90 minutes. Magnification: 50×.

The uniform pattern of corrosion therefore leads to an effective penetration rate of the magnesium surface of less than 2 mm yr^{-1} under open circuit in the nitrate–nitrite electrolyte. This is a negligible value and permits a long shelf-life. In contrast, the localized corrosion of magnesium in perchlorate or halide electrolytes, with or without chromates, leads to large *effective* rates of penetration of the metal, thus curtailing the shelf-life.

While the mechanism of inhibition of magnesium corrosion in the nitrate–nitrite electrolyte requires further study, the high Faradaic efficiency for anodic dissolution (higher than 90% at a current density of 20 mA cm^{-2} or more, Fig. 2) and the relatively uniform or nonlocalized pattern of corrosion suggest that in this case a direct oxidation of Mg to Mg^{2+} takes place at the anode (i.e., without the intermediate formation of Mg^+). This occurs at the usual crystal defects such as kink sites and grain boundary sites, the rest of the sites being covered with an adsorbed layer of nitrate and nitrite ions.

4. Conclusions and implications

It may therefore be concluded that the magnesium–air cell

$$Mg/Mg(NO_3)_2, NaNO_2, H_2O/C(air)$$

holds promise as a primary source of electrical energy with a long wet-shelf-life and is based on widely available materials. Used batteries pose no pollution problems due to the ease of microbial oxidation of NO_2^- to NO_3^-, the assimilation of NO_3^- by plants and the compatibility of Mg^{2+} and Na^+ with the biosphere.

The relatively low power output of the as-yet unoptimized magnesium–air cells developed in the present work is comparable to, and makes them an obvious substitute for, the conventional 'wet air, depolarized cells' based on an amalgamated zinc anode. An extension of this work to develop high-power magnesium–air cells is, in principle, possible with design concepts (e.g., catalysed carbon electrodes; porous magnesium anode) similar to those which have led to modern high-power zinc–air cells. Moreover, the neutral electrolyte developed in the present work prevents any carbonation of the electrolyte even on prolonged exposure to air. Economical design of miniature magnesium–air cells with immobilized electrolytes is therefore also possible.

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