



Performance of commercial aluminium alloys as anodes in gelled electrolyte aluminium-air batteries



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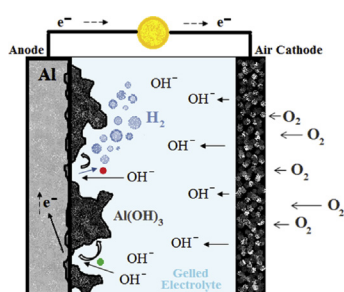
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HIGHLIGHTS

- Al7475 alloy gives successful results for inexpensive Al-air primary batteries.
- Pure Al cladmed alloys performs better for discharges at low current rates.
- At high current rates Zn or Mg as alloying element in Al provides better results.
- The gelled electrolyte is easy to manufacture and resolves leakage problems.

GRAPHICAL ABSTRACT



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ABSTRACT

The evaluation of commercial aluminium alloys, namely, Al2024, Al7475 and Al1085, for Al-air batteries is performed. Pure Al cladmed Al2024 and Al7475 are also evaluated. Current rates from 0.8 mA cm^{-2} to 8.6 mA cm^{-2} are measured in a gel Al-air cell composed of the commercial alloy sample, a commercial air-cathode and an easily synthesizable gelled alkaline electrolyte. The influence of the alloying elements and the addition to the electrolyte of ZnO and ZnCl₂ as corrosion inhibitors is studied and analysed via EDX/SEM. Specific capacities of up to 426 mAh/g are obtained with notably flat potential discharges of 1.3–1.4 V. The competition between self-corrosion and oxidation reactions is also discussed, as well as the influence of the current applied on that process. Al7475 is determined to have the best behaviour as anode in Al-air primary batteries, and cladding process is found to be an extra protection against corrosion at low current discharges. Conversely, Al1085 provided worse results because of an unfavourable metallic composition.

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1. Introduction

Metal-air batteries have drawn considerable attention from companies and researchers since they are a promising source of energy for future generations of electric vehicles (EVs). Lithium-air,

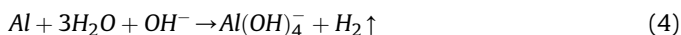
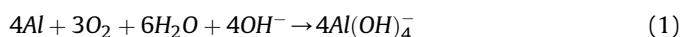
zinc-air, magnesium-air, aluminium-air, etc. are the most evaluated electrochemical pairs because they use oxygen from the air as one of the main battery reactants, reducing the weight and the cost of the battery and permitting higher space for energy storage. Metal-air flow batteries are also promising because of the reduction of the cost and their application in large scale energy storage [1].

Mg-air and Al-air batteries are in the early stages of development and have gathered considerable research attention. Zn-air batteries have been the most studied ones, and are currently used

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for hearing aids and other common applications [2]. Aluminium is the fourth most abundant element on earth and, compared to zinc, is less expensive, not only in terms of weight but also in terms of the cost per ampere hour [3–5]. Furthermore, Al is a well-known construction and manufacturing material due to its lightness and toughness and is extensively used in industries such as the auto-motion and construction. There has been a great development among commercial alloys with well-classified properties in the 9 series as a function of the principal alloying metals, such as 2XXX Cu and 7XXX Zn. The study of the commercial Al alloys as anodes in Al-air batteries could be the basis for progress in inexpensive and easily producible energy storage sources. This extended development in commercial alloys could provide the opportunity for metal-air cells to be competitive against currently well-established energy accumulation technologies. The main problem is that Al exhibits a spontaneously formed oxide film on the electrode surface when in contact with air or aqueous solutions. Due to the presence of this protective oxide film, the corrosion potential of the anode is shifted in the positive direction, and the active dissolution of Al is slowed considerably. This change results in a significant reduction of the extractable energy. A priori, Al becomes unattractive as an energetic anode material. Nevertheless, batteries with Al anodes are interesting because they exhibit a high theoretical cell voltage of 2.4 V in an alkaline electrolyte due to reaction (1), as well as a high theoretical energy density of 8076 Wh kg⁻¹ [6]. Aqueous electrolytes are widely used in metal-air batteries because of their high ionic conductivities. However, their fluidity may lead to penetration and leakage through capillaries in the porous air cathode. Therefore, gelled electrolytes are proposed as a straightforward solution in order to avoid these problems, with low conductivity losses. Concentrated solutions of KOH or NaOH lead to optimal battery performance, but self-corrosion is a highly important reaction in the process. For this reason, research has focused on enhancing the aluminium oxidation rate (2) in alkaline media, while inhibiting self-corrosion (4), which consumes Al as a means to spontaneously generate H₂.



The rechargeable Al-air battery is one of the most promising developments, but several issues must be solved, such as: anode corrosion, sluggish discharge products, the high self-discharge rate, cell irreversibility and shelf life. On the other hand, if electrochemical recharging is not feasible, the battery system could offer rapid mechanical recharging by replacing the used Al electrode with a new one [7,8].

In alkaline media, the major problem for the Al-air system is the decrease of the coulombic efficiency due to the high rate of hydrogen evolution from self-corrosion. The latter induces fuel loss during standby [9,10], forcing the system to continuously discharge. In addition, the cell potential is much lower than the theoretical value as a result of polarisation resistance caused by passivation of the Al surface under current load. To solve these problems, many researchers have studied high-purity-grade aluminium alloys doped with Ga, In, Sn, or Mg, which act as corrosion inhibitors and decrease the overvoltage for Al dissolution, shifting the potential towards more negative values [11–14]. These alloys result in higher cell potentials, which made this system more attractive. Additives

in the electrolyte have also been widely used, including ZnO, SnO₃²⁻, and In(OH)₃ [15,16]. The influence of these doping elements on the corrosion behaviour in saline and/or alkaline solutions has been studied, and better electrochemical performance and lower self-corrosion rates, including lower H₂ generation, have generally been observed.

The behaviour of commercial Al alloys as anodes for high capacity Al-air primary alkaline gel batteries is analysed. Laboratory-scale prototypes were designed to investigate the value of these alloys. Conventional techniques such as static and dynamic galvanostatic discharges, weight loss measurements and EDS were employed to understand the processes. The effect of the minority elements in the Al alloys and the limiting factors in the death of the battery were examined. Finally, the feasibility of using commercial alloys as an anode material in an Al-air battery is discussed.

2. Experimental

2.1. Electrodes and materials

Commercial aluminium alloys Al2024 and Al7475 with different metal compositions were evaluated as anodes in Al-air batteries with a gelled alkaline electrolyte; Cu and Zn, respectively, were the dominant alloying elements. Both unclad and clad specimens were examined for both alloys. Additionally, Al1085 unclad was tested for comparison with the other alloys; in this case the alloy has a high aluminium content. Table 1 reports the complete compositions. The cladding specimens have on top a three micron thick pure aluminium film, which facilitates the formation of the passive layer, protecting the alloy from corrosion. The three alloys are well-known construction materials because of their good balance between hardness and lightness. Al2024 is a typical aircraft fuselage material, Al7475 is used in applications where corrosion is a limiting factor, such as aeroplane air collision zones, and Al1085 is used in construction/decoration after polishing, which results in a bright and clear metal. These alloys were chosen because since they represent an inexpensive and an accessible input for industries.

A commercial air cathode, *Electric fuel* EA4, was used as the positive electrode in the Al-air cells. It is a Ni mesh on which carbon with a MnO₂ catalyst, is pasted. On the air-exposed face, a film of O₂-permeable Teflon[®] is pressed to prevent liquid electrolyte leakage and water inlets, while allowing oxygen from the air to enter.

For the gelled electrolyte synthesis, KOH, acrylic acid (AA), ZnO or ZnCl₂, K₂S₂O₈, and N,N'-methylene-bisacrylamide (MBA) were used; all are of >99% purity from Sigma–Aldrich.

2.2. Electrode preparation and gelled electrolyte synthesis

Pieces of 3 cm² exposure area were cut from a 2 mm thick sheet of aluminium alloy. The unclad samples were polished with emery paper (grade 200–800) and then cleaned with distilled water and acetone. Clad Al alloys were used by simple removal of the plastic protection film on the surface without sanding, to avoid the elimination of the pure Al layer.

The alkaline gel electrolyte was synthesized by casting a mixture of KOH solution, with or without additives, a gel agent (AA + MBA) and a polymerization initiator as described by Y. Zuo et al. [17]. KOH (10 g) and ZnO (0.35 g) or ZnCl₂ (0.25 g) were dissolved in distilled water (16 ml). ZnO and ZnCl₂ additives were added as inhibitors to the aluminium in alkaline solutions [15,16]. A cross-linker, MBA (0.25 g), was dissolved in AA (liquid, 1.58 ml). The alkaline solution was added to the gel agent to obtain a clear dissolution with white granular precipitates. The latter were subsequently removed through filtration and the viscous liquid was collected in a Petri

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