Aluminum as anode for energy storage and conversion: a review

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Abstract

Aluminum has long attracted attention as a potential battery anode because of its high theoretical voltage and specific energy. The protective oxide layer on the aluminum surface is however detrimental to the battery performance, contributing to failure to achieve the reversible potential and causing the delayed activation of the anode. By developing aluminum alloys as anodes and solution additives to electrolytes, a variety of aluminum batteries have been extensively investigated for various applications. From molten salt and other non-aqueous electrolytes, aluminum can be electrodeposited and therefore be suitable for developing rechargable batteries. Considerable efforts have been made to develop secondary aluminum batteries of high power density. In the present paper, these research activities are reviewed, including aqueous electrolyte primary batteries, aluminum-air batteries and molten salt secondary batteries. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Aluminum is a very attractive anode material for energy storage and conversion. Its relatively low atomic weight of 26.98 along with its trivalence give a gram-equivalent weight of 8.99 and a corresponding electrochemical equivalent of 2.98 Ah/g, compared with 3.86 for lithium, 2.20 for magnesium and 0.82 for zinc. From a volume standpoint, aluminum should yield 8.04 Ah/cm^3, compared with 2.06 for lithium, 5.85 for zinc and 3.83 for magnesium. Additionally, aluminum is both an abundant and relatively inexpensive metal.

Aluminum has been considered as a battery electrode since 1850s when Hulot [1] described a cell with zinc (mercury) as anode, aluminum as cathode and dilute H$_2$SO$_4$ as electrolyte. Aluminum as anode was first used in the Buff cell in 1857 [2]. In 1893, an amalgamated aluminum–zinc alloy was proposed for use as anode in a cell with carbon cathode [3]. The use of aluminum or amalgamated aluminum as anode in heavy-duty chlorine-depolarized batteries was reported in 1948 [4]. With amalgamated aluminum, the open circuit voltage was as high as 2.45 V.

Serious efforts were first made on utilization of aluminum anodes in Leclanche-type dry cells after the 1950s, when an aluminum/aqueous NaOH + ZnO/porous membrane/ MnO$_2$(C) system was disclosed [5]. Further development was made on an Al/MnO$_2$ cell with manganese chloride tetrahydrate as electrolyte [6].

The aluminum/oxygen system was first demonstrated in the early 1960s by Zaromb [7] and Trevethan et al. [8], who found that the addition of zinc oxide or certain organic inhibitors, e.g. alkyldimethylbenzyl-ammonium salts, to the electrolyte significantly decreased the corrosion of amalgamated aluminum anodes in 10 M sodium or potassium hydroxide solutions.

These early efforts, however, did not succeed to use the aluminum anode in any commercial battery products. This is due to the protective oxide film on aluminum metal, which causes a decrease in the reversible electrode potential, i.e. the cell voltage is considerably lower than the theoretical value. This is also the reason that aluminum appears cathodic to zinc in neutral or acid electrolytes [9]. Therefore, a zinc cell is possible to exhibit a higher voltage than the analogous aluminum unit in these electrolytes. The oxide film also causes the phenomenon of so-called "delayed action", that is, the time lag before the cell reaches its maximum operating voltage when the circuit is closed.

The oxide film can, of course, be removed by dissolution in concentrated alkali solutions or by amalgamation. However, any gain in the anode potential in this way is accompanied by accelerated wasteful corrosion and poor shelf life. These and other difficulties have long delayed the

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development of a satisfactory aluminum cell. Considerable effort has been made to develop aluminum alloy anodes and electrolyte additives for aluminum batteries with aqueous electrolytes, especially for aluminum-air batteries [10]. Concerning aluminum alloys as anode, it should be remarked that lithium–aluminum alloys have also been extensively investigated both for molten salt secondary batteries [11] and for lithium ion batteries [12]. In those cases, aluminum is used for lithium storage and the lithium–aluminum alloys are therefore not included in the present review.

Molten salts or other non-aqueous media provide an alternative electrolyte, in which aluminum does not form the surface oxide film. Moreover, aluminum can be electro-deposited from the non-aqueous media. Such electrolytes are suitable for developing rechargeable aluminum batteries. Considerable research has been carried out for developing aluminum secondary batteries since the 1970s.

In this review, aluminum cells are classified according to the used electrolyte, i.e. aqueous or non-aqueous solutions. As the most active subject, aluminum-air (oxygen) batteries use also aqueous solution as electrolyte. However, they belong to a category of semi-fuel cells since the oxidant is supplied from outside the battery system. A separate section is therefore created for the aluminum-air batteries.

2. Aluminum batteries with aqueous electrolytes

Compared with molten salt or organic solution electrolytes, aqueous solutions are simple to operate, low in cost, and with less environmental pollution. So far, aluminum batteries based on aqueous solution electrolytes have received wide attention and the following systems have been investigated: Al/MnO_2, Al/AgO, Al/H_2O_2, Al/S, $Al/FeCN$ and $Al/NiOOH$.

The conventional aqueous solution batteries such as lead-acid batteries and Ni-Cd batteries suffer from low energy density and environmental pollution. As seen in Table 1, the electrochemical characteristics of Al batteries are superior.

Table 1
Conventional aqueous solution batteries and aluminum batteries

| Batteries	Open circuit voltage (V)		Capacity (Ah/kg)	Theoretical energy density (Wh/kg)
	Theoretical	Measured		
Lead-acid	2.0	2.0	83	170
Ni-Cd	1.4	1.2	181	240
Zn-AgO	1.6	1.4	199	310
Al-AgO	2.7	2.0	378	1020
Al-H$_2$O$_2$	2.3	1.8	408	940[a]
Al-FeCN	2.8	2.2	81	230
Al-S	1.8	1.4	595	1090

[a] Calculated for 30% H_2O_2.

2.1. Al-MnO$_2$ batteries

MnO_2 is the typical cathode materials for dry batteries, e.g. in the Zn/MnO_2 system. With aluminum as anode instead of zinc, $Al-MnO_2$ batteries exhibit a theoretical voltage about 0.9 V higher than Zn/MnO_2 batteries. However, due to the surface oxide film on aluminum anodes, the measured voltage for Al/MnO_2 batteries is found to be only 0.2 V higher than Zn/MnO_2 batteries. Earlier research was then concentrated on development of aluminum alloys in order to promote the anode potential [13]. It was found that addition of a small amount of Zn, Cd, Mg or Ba led to an increase in the anode potential by 0.1–0.3 V, while addition of Ga, Hg, Sn or In gave an increase in the anode potential by 0.3–0.9 V [14]. Combination of two or more of the above mentioned elements could also improve the anode efficiency [15]. More detailed discussion on anode alloying elements and electrolyte additives will be given in Sections 3.1 and 3.2, respectively.

The used electrolytes include $AlCl_3\cdot6H_2O$, $CrCl_3\cdot6H_2O$ and later alkaline solutions KOH and NaOH. The cell reaction can be expressed as:

$$Al + 3MnO_2 + 3H_2O = 3MnOOH + Al(OH)_3 \qquad (1)$$

The application of this type of batteries, is, however, limited to some special situations, e.g. as an underwater power source when seawater is used as electrolyte [16]. Recently a combination of the permanganate (Mn(VII), MnO_4^-) cathode with the aluminum anode has been studied, which gives the following cell reaction [17]:

$$Al + MnO_4^- + 2H_2O = Al(OH)_4^- + MnO_2,$$
$$E_{cell} = 2.9\,V \qquad (2)$$
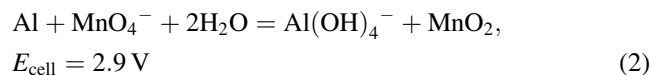
2.2. Aluminum-silver oxide battery

Silver oxide is widely used as cathode materials for various types of batteries [18]. With zinc as anode and alkaline solutions as electrolyte, silver oxide batteries are one of the commercial products with the highest energy density. Being superior to zinc, aluminum has received attention for use in silver oxide batteries, especially as underwater driving power mainly for military purposes [19,20]. The cell reaction can be expressed as

$$2Al + 3AgO + 2OH^- + 3H_2O = 2Al(OH)_4^- + 3Ag,$$
$$E_{cell} = 2.7\,V \qquad (3)$$
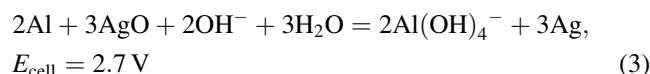
An Al/AgO battery system of 140 V and 1.66 kWh with an energy density of 82 Wh/kg has been developed for submarine applications [21]. With polymer as binder for the silver oxide electrode, an alkaline battery using aluminum alloy anode was reported to have a capacity as high as 1.2 Ah/cm^3 at near 100% Coulombic efficiency [22].

2.3. Aluminum-hydrogen peroxide battery

The use of H_2O_2 as the cathodic reactant for aluminum batteries was first proposed by Zaromb [23]. The system, with hydrogen peroxide as an alternative source of oxygen, is of special interest for applications where gaseous oxygen is difficult to reach, for example, underwater. In alkaline media, the cell reaction of an Al-H_2O_2 battery is:

$$2Al + 3H_2O_2 + 2OH^- = 2Al(OH)_4^-, \quad E_{cell} = 2.3\,V \quad (4)$$
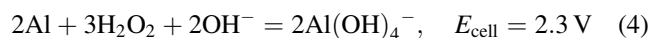
A main issue for developing Al/H_2O_2 batteries is to achieve an efficient reduction of peroxide at a high cathode potential and to prevent the reaction of hydrogen peroxide with the aluminum anode. For this purpose, two types of battery designs have been proposed. One is the direct addition of H_2O_2 into the liquid electrolyte [24,25]. By this means, Hasvold et al. [26] constructed an Al-H_2O_2 battery system as the power source for an unmanned underwater vehicle. Rao et al. [27] designed a multi-functional battery—a low power operation (1 kW) is achieved when seawater is added as electrolyte while a high power operation is achieved (20 kW) when a mixture of seawater and hydrogen peroxide is added.

Another design is a dual-channel cell in order to reduce the non-electrochemical reactions between hydrogen peroxide and aluminum anode [28]. The catholyte and anolyte compartments are separated by an Ir/Pd modified porous nickel cathode. It was reported that such a battery system exhibited an open circuit voltage of 1.9 V, a polarization loss of 0.9 mV/(mA/cm^2) and a power density of 1 W/cm^2.

2.4. Al-sulfur battery

Recently Licht and co-workers [29,30] have coupled the high Faradaic capacity of aqueous sulfur with an aluminum anode to exemplify a novel class of Al/S battery. The aqueous electrolyte is an alkaline solution containing K_2S. The anions are, besides OH^-, various sulfide complexes such as HS^-, S^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, etc. The overall cell reaction can be written as:

$$2Al + S_4^{2-} + 2OH^- + 4H_2O = 4HS^- + 2Al(OH)_3,$$
$$E_{cell} = 1.79\,V \quad (5)$$
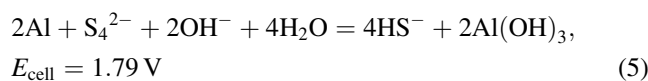
Based on the potassium cation, the Faradaic capacity of the Al/S battery is found to be 361.7 Ah/kg, and the theoretical specific energy of the system is 647 Wh/kg. This is an interesting system. The aluminum anode behavior [31], the chemistry and electrochemistry of sulfur [32,33] as well as the low current domain [34] and high current domain [35] of the system have been investigated.
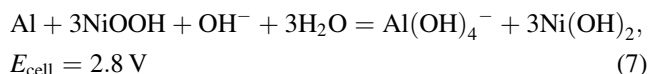
2.5. Other batteries

Al-ferricyanide battery: $Fe(CN)_6^{3-}$ has been widely employed in electrochemical and other systems. Coupled with an aluminum anode, a novel battery system has been proposed [36]. In alkaline media the cell reaction can be expressed as:

$$Al + 3OH^- + 3Fe(CN)_6^{3-} = 3Fe(CN)_6^{4-} + Al(OH)_3,$$
$$E_{cell} = 2.76\,V \quad (6)$$
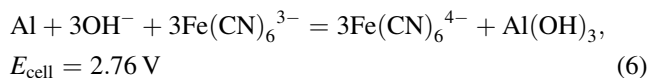
Taking KOH as the electrolyte, this battery system is reported to exhibit an open circuit voltage of 2.2 V, a discharging current density of 2000 mA/cm^2 and a power density of 2 W/cm^2.

Al-NiOOH Battery: A combination of aluminum with the most popular cathode candidate, NiOOH, gives the following cell reaction [37]:

$$Al + 3NiOOH + OH^- + 3H_2O = Al(OH)_4^- + 3Ni(OH)_2,$$
$$E_{cell} = 2.8\,V \quad (7)$$

3. Aluminum-air batteries

Metal/air batteries contain metal (negative) anodes and oxygen (positive) cathodes, with the oxygen usually obtained from air. These batteries are classified according to the type of metal anode since air (oxygen) is a common feature. Table 2 summarizes the electrochemical features for various metals in metal/air cells containing alkaline electrolytes. Reviews with emphasis on the technical and application respects of Al/air batteries are available [10]. The present review is more concentrated on the chemistry and electrochemistry of aluminum alloy anodes, electrolytes and additives.

3.1. Aluminum anodes

Thermodynamically an aluminum anode should exhibit a potential of -1.66 V in saline and -2.35 V in alkali electrolyte. However, practical aluminum electrodes operate at a significantly lower potential because (a) aluminum is normally covered by an oxide film which causes a delay in reaching a steady-state voltage due to internal resistance; (b) aluminum undergoes a parasitic corrosion reaction, resulting in less than 100% utilization of the metal and the evolution of hydrogen.

The discharging reaction of an aluminum electrode in alkaline media is:

$$Al + 4OH^- = Al(OH)_4^- + 3e^-, \quad E = -2.35\,V \text{ vs. SHE} \quad (8)$$
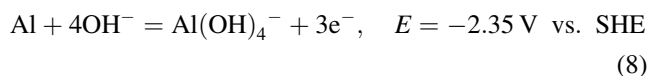
The progressive consumption of hydroxyl ions at the aluminum electrode makes the electrolyte more saturated with the aluminate. Eventually the aluminate concentration exceeds the super-saturation and a crystalline form of aluminum hydroxide precipitates with the regeneration of hydroxyl ions:

$$Al(OH)_4^- = Al(OH)_3 + OH^- \quad (9)$$

Table 2
Summary of metal/air cells with alkaline electrolytes

Pair	Anode reaction	Anode potential (V)[a]	Metal equiv. (Ah/)g	Cell voltage (V)[b]		Specific energy (kWh/kg)	
				Theoretical	Operating	Of metal	Of cell reactants
Li/air	$Li + OH^- = LiOH + e^-$	−3.05	3.86	3.45	2.4	13.3	3.9
Al/air	$Al + 3OH^- = Al(OH)_3 + 3e^-$	−2.35	2.98	2.70	1.2–1.6	8.1	2.8
Mg/air	$Mg + 2OH^- = Mg(OH)_2 + 2e^-$	−2.69	2.20	3.09	1.2–1.4	8	2.8
Ca/air	$Ca + 2OH^- = Ca(OH)_2 + 2e^-$	−3.01	1.34	3.42	2.0	4.6	2.5
Fe/air	$Fe + 2OH^- = Fe(OH)_2 + 2e^-$	−0.88	0.96	1.28	1.0	1.2[c]	0.8
Zn/air	$Zn + 2OH^- = Zn(OH)_2 + 2e^-$	−1.25	0.82	1.65	1.0–1.2	1.3	0.9

[a] The anode potential was vs. the standard hydrogen electrode (SHE).
[b] When coupled with an oxygen cathode.
[c] 1.8 kWh/kg for Fe^{3+}.

In addition to the electrochemical consumption of the anode, aluminum is thermodynamically unstable in an alkaline electrolyte and reacts with the electrolyte to generate hydrogen:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2 \qquad (10)$$
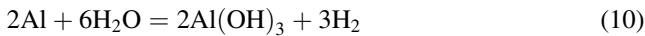
This parasitic corrosion reaction, or self-discharge, degrades the Coulombic efficiency of the anode and must be suppressed in order to minimize the capacity loss.

There are two ways to improve the anode behavior. One is to dope aluminum with other elements in order to render it less corrodible in the electrolyte. The second is to modify the electrolyte by adding inhibitors, additive agents or complexing agents in order to make the electrolyte less corrosive.

Aluminum reacts rapidly and irreversibly with oxygen to form a strongly-adhering oxide film, which largely determines the electrochemical behavior of aluminum in aqueous electrolytes. Modification of the behavior of the oxide layer by means of specially designed aluminum alloys has been extensively explored [38–44]. Aluminum alloys based on high purity grade metal doped with elements such as Ga, In, Sn, Zn, Mg, Ca, Pb, Hg, Mn and Tl have been investigated. Besides corrosion processes of pure aluminum [45,46] the electrochemical behavior of a number of aluminum alloys have been studied, showing that alloying with certain metals can improve the voltage.

The route of controlling the behavior of the aluminum anode by addition of alloying agents is known as "activation". The mechanism of the aluminum activation is related to (a) moderating the thickness of the oxide film; (b) reducing the rate of the direct reduction of water by aluminum and (c) controlling the dissolution morphology.

For example, the surface of an aluminum–gallium alloy becomes enriched with gallium during anodic polarization. This reduces the oxide film barrier and increases the voltage efficiency. By this means a number of alloys have been prepared by the controlled, low-level (50–1000 ppm) addition of alloying elements to super-purity aluminum. The incorporation of small concentrations of metals such as magnesium, calcium, zinc, gallium, indium, thallium, lead,

mercury, and zinc, usually in combinations as ternary or quaternary alloys, has been found to be effective in achieving activation (high current capability) and inhibition of corrosion [43,44].

Earlier investigations showed that the presence of certain impurities such as iron and copper in the aluminum can markedly affect the electrochemical behavior. For example, the corrosion rate is found to be particularly sensitive to the concentration of iron in the metal [47]. Super-purity metal (at least 99.999% purity) has therefore been used to prepare anodes. From an economic point of view, it is desirable to develop aluminum anodes based on high-purity smelter-grade metal (99.8%) instead of the high-cost super-purity metal. In combination with the electrolyte additives, this has been recently demonstrated and expected to reduce the cost of the anode metal significantly.

Doche et al. [48] examined four types of aluminum alloys: (a) ALCAN alloy made of 99.999% Al doped with 0.1 wt.% Sn and 0.5 wt.% Mg; (b) 2N7 commercial grade (99.7%); (c) 3N5 grade (99.95%, refined to decrease Fe content below 10 ppm); and (d) 5N grade (pure 99.999% obtained by an electrorefining process). In 4 M NaOH containing 0.05 M Na_2SnO_3 and 20 g/l $Al(OH)_4^-$ at 60 °C, 2N7 grade aluminum showed too high corrosion rate to be measured. For the other three samples, the measured corrosion currents at open circuit potential and a potential of −1.65 V versus Hg/HgO are summarized in Table 3. All three samples undergo substantial corrosion under open circuit conditions, the

Table 3
Corrosion current of the ALCAN, 5N and 3N5 aluminum alloys in 4 M NaOH containing 0.05 M Na_2SnO_3 and 20 g/l $Al(OH)_4^-$ at 60 °C

	ALCAN	5N	3N5
Open circuit potential			
E_a (V vs. Hg/HgO) at $I = 0$	−1.87	−1.79	−1.78
$I_{corrosion}$ (mA/cm^2)	12.1	13.5	15
$E_a = -1.65$ V vs. Hg/HgO			
I_{total} (mA/cm^2)	75	65	55
$I_{corrosion}$ (mA/cm^2)	2.4	3	5.3

3N5 exhibits a corrosion rate 10% higher than the 5N and 24% higher than the ALCAN sample, indicating a detrimental effect of the presence of impurities in the aluminum. Under discharge conditions ($E_a = -1.65$ V versus Hg/HgO), the corrosion current is clearly reduced, resulting in Coulombic efficiencies ($\eta = I/(I + I_{corrosion})$) of 96.8, 95.6, and 91.2% for the ALCAN, 5N and 3N5 samples, respectively.

2N-aluminum (not less than 99% purity), however, has been used in Al-air batteries with 4 M NaOH containing 20% sodium citrate and 0.4% CaO as electrolyte [49]. Quaternary alloys based on 99.8% pure aluminum containing lead, gallium and indium have been tested in NaOH based solutions [50,51]. It is reported that 99.8% pure aluminum can be used successfully to make alloy anodes in the alkaline electrolyte containing citrate and stannate.

The properties of aluminum alloy electrodes for use in seawater or other neutral electrolytes have been explored, including addition of gallium, indium, thallium, and small quantities of phosphorus and manganese [39].

3.2. Electrolytes and additives

The major development effort to date has focused on metal/air cells with two types of electrolytes, i.e. alkaline and saline electrolytes.

3.2.1. Alkaline electrolytes

The development of the Al/air battery with alkaline electrolytes can be traced to the efforts of Zaromb [7] and Trevethan et al. [8] in the early 1960s. The studies demonstrated the technical feasibility of alkaline Al/air batteries. Thereafter, most of the studied aluminum-air batteries operate with strongly alkaline electrolytes.

The alkaline electrolyte permits optimal performance for the air cathode and a low-level of aluminum polarization under normal operation. The alkaline solution can absorb carbon dioxide when the cell is open to air. This can result in the crystallization of carbonate in the porous air electrode, which may impede air access and cause mechanical damage and a decreasing electrode performance.

Concerning the mass production of aluminum-air batteries, KOH solution does not allow the retreatment of alumina via the industrial Hall–Héroult process, because potassium ions have harmful effects on the cathode of electrolysis cell. Consequently, NaOH is suggested by Doche et al. [48]. In this connection, a concentration range around 3–5 M is preferred when considering the precipitation of $Al(OH)_4^-$ into $Al(OH)_3$ in the regenerator.

Earlier effort was made to modify the electrolyte by adding inhibitors, additive agents or complexing agents in order to make the electrolyte less corrosive [7,8]. Addition of alloying elements to electrolyte solutions can avoid alloying, processing and heat-treating [52], though it was found less effective than the alloying techniques [53]. Among a long list of investigated additives, oxides of gallium, indium, calcium and zinc as well as stannates and citrates were found to be effective in inhibiting corrosion and/or boosting the electrode potential when added into the solution phase rather than the solid phase.

Doche et al. [48] used sodium stannate (Na_2SnO_3) as a corrosion inhibitor in NaOH solution. In 4 M NaOH containing 20 g/l $Al(OH)_4^-$ at 65 °C, the optimal concentration of sodium stannate was found to be around 0.04 M. A solution based on 4 M NaOH containing 20% sodium citrate and 0.4% CaO has been developed as electrolyte with 2N-aluminum (not less than 99% purity). Albert et al. [47] used $CaCl_2 \cdot 2H_2O$ (2.5%) and NaCl (0.1–3.0%) as additives to 4 M NaOH containing 20% sodium citrate. Kapali et al. [50] reported that, in the alkaline electrolyte containing citrate and stannate, aluminum of 99.8% purity can be successfully used to prepare quaternary alloy anodes with lead, gallium and indium. This alloy anode is also suitable for use in alkaline electrolyte containing ZnO [51].

3.2.2. Saline electrolytes

Despic et al. [39] were the first who explored Al/air batteries with saline electrolyte. A suitable electrolyte is a 12% solution of sodium chloride, which is near the maximum conductivity. The conductivity of salt water is, however, lower than that of an alkaline electrolyte. To minimize the power loss due to internal resistance, a narrow anode–cathode gap is required. The anodic dissolution of aluminum in saline solutions results initially in soluble complexes with either hydroxyl or chloride ions, and subsequently in an aluminum hydroxide gelatinous precipitate [54]. The gel product of hydrated aluminum hydroxides is undesirable for several reasons. First, it can cause anode passivation due to the accumulation of aluminum hydroxide on the electrode. Secondly, it binds water and increases the water requirement. For example, gelation increases the water requirement from 0.33 ml/Ah to approximately 5 ml/Ah. This increased water requirement reduces both the gravimetric (Wh/kg) and the volumetric (Wh/l) energy density. Thirdly, gelation makes cleaning the cell for reuse more difficult.

Additives such as sodium phosphate, sodium sulfate, sodium fluoride, and sodium bicarbonate to sodium chloride solutions have been investigated in order to increase the compactness of aluminum hydroxide and therefore reduce the water requirements. These additives serve as coagulants to precipitate the reaction product. Addition of flocculating agents to precipitate aluminum hydroxide has also been examined [55]. It seems that NaF is the most effective additive for obtaining a crystalline precipitate. Moreover, it has been found that an acidic electrolyte is beneficial to improve the battery performance [56,57]. Holzer et al. [58] and Muller et al. [59] have therefore investigated this possibility.

Another way is to generate turbulence in the electrolyte or to use a crystallizer/separator, involving seeding and then the precipitation of large particles from the electrolyte. The separator retains the precipitated solids, and the remaining liquid is circulated back to the cells.

3.3. Air/oxygen cathodes

The reaction at the cathode is the electroreduction of oxygen, which can only be sustained at practical rates by using a gas diffusion electrode. The required oxygen may be obtained from air for terrestrial applications. Systems designed for space or underwater applications may employ cryogenic oxygen or chlorate candles. A huge amount of literatures concerning the development of gas diffusion electrodes in connection with metal/air batteries as well as fuel cells have been published, which are not, however, included in the present review.

3.4. System designs and operations

The overall system concept for the aluminum-air battery and its use in vehicles has been described [10]. The battery can be mechanically recharged by addition or replacement of aluminum anode plates and by addition of water. The concentration of aluminate increases during discharge to three times the saturation level. In order to maintain a stable electrolyte composition during discharging and to prevent undesirable precipitation, the aluminum ion is allowed to precipitate slowly as aluminum trihydroxide by seeding with $Al(OH)_3$.

Different approaches to achieving mechanical refuelability have been experimentally investigated in test cells, bicells or multi-cell stacks, i.e.

(a) *Moving electrode:* Aluminum anode plates are soldered to copper-clad circuit board and placed between air-cathode modules. The modules feature an air-electrode suspended on a flexible diaphragm which advances toward the anode during discharge [60]. Another solution is to fix the anode slab between two air electrode modules, which are advanced pneumatically.

(b) *Wedge-shaped cells:* A wedge-shape anode is consumed between two rigid air electrodes held at an acute angle to form a dimensionally stable cell [61]. Anode current collection is achieved by parallel tracks of metal, which also define the internal electrode separation. This cell is designed for continuous, gravity feed of rectangular slab anodes into the cell, with partial recharge capability, and full utilization of anode material.

(c) *Aluminum chips/pellets:* Techniques have been developed to use aluminum in forms of chips or pellets in order to realize a continuous feeding [62]. One design uses aluminum particles having diameters of 1–5 mm [63].

3.5. Applications

The alkaline aluminum/air batteries cover a wide range of applications from emergency power supplies to field-portable batteries for remote power applications, to batteries for electric vehicles and underwater vehicles. For electric vehicle propulsion, aluminum contains approximately one-half the energy content of gasoline per unit weight and three times the energy per unit volume. Most of the batteries are designed as reserve batteries, being used with conventional lead-acid batteries to provide a standby power supply with extended service life. Another application of alkaline aluminum-air batteries is the power supply for underwater vehicles. Examples include unmanned vehicles for submarine and mine surveilance, long-range torpedoes, swimmer delivery vehicles and submarine auxiliary power. In these applications the oxygen can be carried in pressurized or cryogenic containers or obtained from the decomposition of hydrogen peroxide or from oxygen candles.

The advantages of aluminum-air salt water batteries include a long shelf life on dry storage and innocuous electrolyte involved. As a "reserve" or "standby" power source, the battery is stored dry, and an aqueous solution of sodium chloride can be added by the consumer prior to use. A number of batteries using saline electrolytes have been designed as portable power sources such as a mooring light for barges, field recharger of nickel-cadmium and lead-acid storage batteries.

4. Aluminum batteries with non-aqueous electrolytes

Compared with aqueous electrolytes the advantages of molten salts are mainly three-fold, namely high electrical conductivity, fast electrode kinetics and hence less polarization, and high decomposition potential. Aluminum can be electrodeposited from the non-aqueous media and therefore the electrolytes are suitable for developing rechargeable aluminum batteries.

4.1. Alkali chloroaluminate melts

Binary NaCl–AlCl$_3$ and ternary NaCl–KCl–AlCl$_3$ systems are the most widely used alkali chloroaluminate melts for developing aluminum batteries. Reviews of chemistry [64] and electrochemistry [65,66] of these AlCl$_3$-based systems were made in 1970s. Thereafter, additional investigations of the NaCl–AlCl$_3$ system have been made concerning, among others, density [67], potentiometry [68–70], electrical conductivity [71], vapor pressure [70], phase equilibrium [72], and the nature of sulfur and sulfides [73]. In these systems the melts with molar ratio of MCl/AlCl$_3$ (where M is commonly Na and/or K) larger than unity are defined as basic, whereas those with molar ratio less than unity as acidic. In an acidic melt, $Al_2Cl_7^-$ is the major anion species. As the acidity (AlCl$_3$ content) of the melt decreases, $AlCl_4^-$ becomes the major species [74]. The principal solvent equilibrium in these systems is as follows:

$$2AlCl_4^- = Al_2Cl_7^- + Cl^- \tag{11}$$

4.1.1. Cathodic process of aluminum deposition

Much work has been carried out to study the cathodic deposition of aluminum. Early work on electrochemistry of aluminum in aluminum-containing molten salt systems was reviewed by Malachesky [75]. Electrochemical deposition of aluminum from molten alumina-cryolite melts [76], non-aqueous organic electrolytes and room temperature molten salts [77,78] as well as chloroaluminate melts [79] has been comprehensively discussed.

It has been reported that, on tungsten, platinum and gold electrodes, underpotential deposition was observed and alloying of platinum and gold with aluminum from the melt occurs in the initial stage of the deposition [80–82]. The cathodic deposition of aluminum is possible by discharge of either of the two aluminum-containing complexes, $AlCl_4^-$ and $Al_2Cl_7^-$. In a basic melt, the deposition reaction is due to the discharge of $AlCl_4^-$ anions:

$$AlCl_4^- + 3e^- = Al + 4Cl^- \tag{12}$$

and in an acidic melt, the $Al_2Cl_7^-$ anion is reduced to give the aluminum deposit:

$$4Al_2Cl_7^- + 3e^- = Al + 7AlCl_4^- \tag{13}$$

As shown from the early kinetic studies, reaction (13) appeared quasi-reversible [83,84]. A very strong dependence of the electrode exchange current density for charge transfer of aluminum on the composition of the melt, i.e. on the mole fraction of $AlCl_3$, was found and a multi-step electrode reaction mechanism was proposed [85,86]. The governing role of the nucleation process for reduction of $AlCl_4^-$ and $Al_2Cl_7^-$ in chloroaluminate melts was been emphasized [87,88]. The predominant role of the electronucleation in the cathodic deposition of aluminum was supported by the fact that the addition of some surface active agents can significantly affect the process [89]. By means of voltammetry and chronoamperometry, the nucleation process was found to be progressive [90].

4.1.2. Dendrite formation and inhibition

As early as in the 1930s, it was found that aluminum dendrites were easily formed during the cathodic deposition at high current densities from $NaCl–AlCl_3$ melts [91]. This was later studied by Midorikawa in a series of papers [92]. Thereafter many investigations have been performed, including a kinetic model [93]. The spacing between electrodes in batteries is usually very small, and hence the compactness of the deposited aluminum is of special importance for the capacity and cycling life of the batteries.

In molten salt media, the charge transfer process is generally fast and the cathodic deposition is normally diffusion controlled. Fundamentally a much faster growth of a dendritic protrusion than the rest of the electrode surface lies in the difference in diffusion conditions. Consequently two aspects must be considered in order to suppress dendrite formation. One is to improve the diffusion process of the depositing species and the other is to change the rate of the charge transfer/nucleation processes. Parameters that affect the aluminum dendrite formation based on these considerations have been extensively investigated, as briefly reviewed below.

Melt compositions: Investigations have shown that the aluminum chloride content in the melt has a dominant effect on the appearance of aluminum deposits. Grjotheim and Matiasovsky [89] reported that at current densities up to 50 mA/cm^2 aluminum was deposited on a steel substrate in the form of fine crystallites from an alkali chloroaluminate melt containing 63.6 mol% $AlCl_3$. Fellner et al. [88] observed a similar critical value on an iron cathode in a ternary $NaCl–KCl–AlCl_3$ system containing 56.8–63.6 mol% $AlCl_3$. With a glassy carbon electrode, Qingfeng et al. [90] reported that smooth aluminum deposits could only be obtained in a narrow current density range from 2 to 10 mA/cm^2 in a slightly basic $NaAlCl_4$ melt. It is known that $AlCl_4^-$ is the major anion species in equimolar $NaCl–AlCl_3$ melts, whereas $Al_2Cl_7^-$ exists in acidic melts. It seems that complexing of aluminum in a form of $Al_2Cl_7^-$ is beneficial to inhibit the dendrite formation.

Organic additives: Addition of organic agents is a common method in order to suppress the dendrite formation. Usually these additives are absorbed preferentially at the active sites on the tips of protrusions, and therefore a slowing down of the rate of their growth occurs. For aluminum deposition from alkali chloroaluminate melts, the favorable organic additives are found to be tetramethyl-ammonium chloride (TMA) [89] and urea, among others.

Inorganic additives: The influence of inorganic additives has been investigated by addition either in the form of compounds (mainly chlorides) or by electrolytic dissolution of auxiliary anodes of the respective metals. Among the additives investigated [94–98] KCl, $BaCl_2$, and NH_4Cl were found to have little effect, while $PbCl_2$, $SnCl_2$, $MnCl_2$, LiCl, NaBr, NaI and HCl were found to have some beneficial effects, improving the quality of the aluminum deposits. Iron chloride as an impurity in the chemicals had a bad effect on the deposits.

Substrate materials: In $NaCl–AlCl_3$ melts, lead was also found to be the most favorable substrate for aluminum deposition, followed by zinc, copper, iron, silver, aluminum, and carbon in that order [99,100]. Even for a mild steel substrate, an electropolishing pretreatment in the melt itself was found to be useful [101]. Reversibility of aluminum deposition and dissolution on nickel, tungsten and glassy carbon electrodes has been studied [102].

The fact that substrate materials have a pronounced effect on the quality of aluminum deposits suggests, in addition to the diffusion controlled mass transport process, the importance of the nucleation processes. This was confirmed by the beneficial effects of current tailoring (pulsed current, reversal current and ac superposition current) [98]. It is therefore of significance to recognize the different types of dendrites and their mechanisms. In a basic $NaAlCl_4$ melt at high current densities, needle-like and fur-tree-like dendrites or

very porous deposits were obtained, attributable to the slow diffusion controlled process of aluminum-containing species. At lower current densities, aluminum was deposited in a form of spongy deposits, supposedly due to the slow nucleation process. The spongy deposits can be inhibited by means of Al-Mn co-deposition or by use of a pulsed current [90].

4.1.3. Development of aluminum batteries

The earliest attempt was made to develop the Al/Cl_2 battery system by using $NaCl–(KCl)–AlCl_3$ as electrolyte [103]. Due to the difficulty associated with the chlorine storage, metal chlorides were proposed as the cathode materials. However, the high solubility of metal chlorides in the melts limited the development of such battery systems [104].

Sulfur and its group elements were then suggested as the cathode candidates [105–107]. Once again the problems associated with the storage and solubility of sulfur in the molten chlorides led one to investigate transition metals [108,109] and their sulfides [110] such as FeS_2, FeS, TiS_2, Cr_2S_3, $NaFeS_2$, CoS, NiS, Ni_3S_2, MoS_3, especially in Japan [111–115] and Denmark [90,98,102,116]. From consideration of cost and other technical aspects, FeS_2 and FeS are the most commonly used cathodes for the system.

At 175 °C, an $Al/NaCl–AlCl_3/MeS_2$ molten salt battery system exhibits high discharging capacity, though a significant capacity loss is observed due to the solubility of metal sulfides [117]. Another technical problem is the formation of aluminum dendrites during the recharging. It has been shown that use of pulsed current or addition of inorganic chlorides such as $MnCl_2$ can improve the deposition of aluminum and the reversibility of electrodes depends on the electrode substrates [90,98].

In order to lower the operational temperature, low melting point systems have been developed. Hjuler et al. [118] developed an inorganic salt mixture for the Al/Ni_3S_2 battery operating at around 100 °C. Takami and Koura [119] employed $NaCl–AlCl$-organic salts as electrolyte for Al/FeS_2 battery operating also at around 100 °C.

4.2. Room temperature molten salts

Another main interest in the field is room temperature molten salt systems. Aluminum chloride forms room temperature electrolytes with organic chlorides such as *n*-butyl-pyridinium-chloride (BuPyCl), 1-methyl-3-ethylimidazolium-chloride (MEICl), and 2-dimethyl-3-propylimidazolium-chloride [120–123]. A molten mixture of 1,4-dimethyl-1,2,4-triazolium chloride (DMTC) and $AlCl_3$ has also been suggested as the secondary battery electrolyte [124].

For binary systems, when $AlCl_3$ content is less than 50 mol%, the melt is basic and the major ionic species in the melt are $AlCl_4^-$ and Cl^-. The equimolar melt is neutral. When the $AlCl_3$ content is more than 50 mol%, the melt is acidic and the major ionic species is $Al_2Cl_7^-$. Aluminum metal can only be deposited from the acidic melt. Therefore, the basic melts can be used as electrolyte for primary batteries and the acidic melts can be used as electrolyte for both primary and secondary batteries. It has been proved that the electrodeposited aluminum can be efficiently discharged without decomposing the electrolyte melt [125]. Therefore, the melts have been widely employed for development of primary and secondary batteries based on aluminum anode, including $Al-Cl_2$, $Al-FeCl_3$, $Al-CuCl_2$ and $Al-FeS_2$ systems [126–128].

4.3. Other systems

With a number of attractive features such as high conductivity, good thermal stability [129], ability to dissolve numerous metallic salts, and weak coordination with metallic cations [130,131], dimethylsulfone (DMSO) has been considered as a promising organic solvent for rechargeable aluminum cells [132]. It has been shown [133] that aluminum can be reversibly plated and stripped in a mixture (2:1 mole ratio) of $AlCl_3–LiCl$ dissolved in DMSO while no aluminum plating was observed in that of 1:1 mole ratio.

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