

Short communication

Development of a novel composite aluminum anode

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Abstract

This paper presents a novel composite fabrication of aluminum anodes for use in moderate rate Al/Air cells in alkaline media. The polymer composite/particulate aluminum structure allows control of electrolyte contact with the aluminum surfaces during discharge. This ability could lead to improved deliverable energy density and allow the anode discharge characteristics, in some measure, to be tailored to need.

A limited first round lab testing of these composite anodes has been carried out. Current capabilities were moderate, ranging up to about 2 mA/cm². Observed cell discharge potentials were mostly above 1 V. Delivered energy densities were generally comparable to those of planar anodes of comparable metal weight and alloy. It is of particular significance, however, that the discharge lifetimes of the composite anodes for certain formulations, on a per gram basis, were considerably longer than those of their planar counterparts. Further formulation optimization and fabrication uniformity should lead to improved energy density and lifetime.

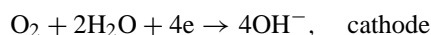
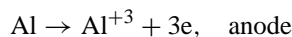
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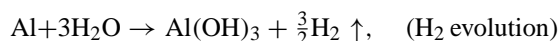
1. Introduction

Aluminum is an attractive anode material for electrochemical air cells. It is abundant, quite inexpensive, environmentally benign and metallurgically workable without special equipment. Its electrochemical equivalent (2.98 Ah/g) and theoretical specific energy (8.1 kWh/kg) are second only to lithium. The aluminum/oxygen cell is principally operated as a primary reserve type battery. It can be designed to contain the oxidizer within the cell, for example as H₂O₂ held separately in the electrolyte, with a mechanism to introduce the latter to initiate cell activity. More commonly, the configuration is an Al/air cell, which derives its oxygen from the atmosphere, and is usually termed a “semi-fuel cell”. Historically, the couple has been developed for use with neutral saline and alkaline electrolytes as, essentially, single use, field-activated batteries for certain military [1] and marine applications. Its full potential to operate in the semi-fuel cell mode, however, has heretofore not been exploited. Of particular interest for portable applications, is the possibility of attaining quite high mass energy densities by designing the cells for periodic anode/electrolyte replacement in the course of use [2]. The energy productive

reactions are:



Along with the parasitic corrosion reaction:



Special aluminum alloys have been developed to minimize corrosion, particularly in the neutral electrolytes (NaCl, KCl). In these electrolytes, the no-load (open circuit) corrosion rate can be made quite low and is proportional to the current drawn. These special alloys also reduce the corrosion rate to some extent in the more aggressive alkaline electrolytes [3]. The actual wet lifetime of ordinary planar thin aluminum anodes, however, in normal or even in “stand-by” (no-load) operation is still normally only on the order of perhaps several days or 3–10 h/g of anode. The anode continuously dissolves, since no surface passivation occurs. Corrosion proceeds rather expeditiously, whether or not current is being drawn.

The purpose of this short paper is to introduce and document a novel composite fabrication of the aluminum anode. The goal of this fabrication is to extend the working life

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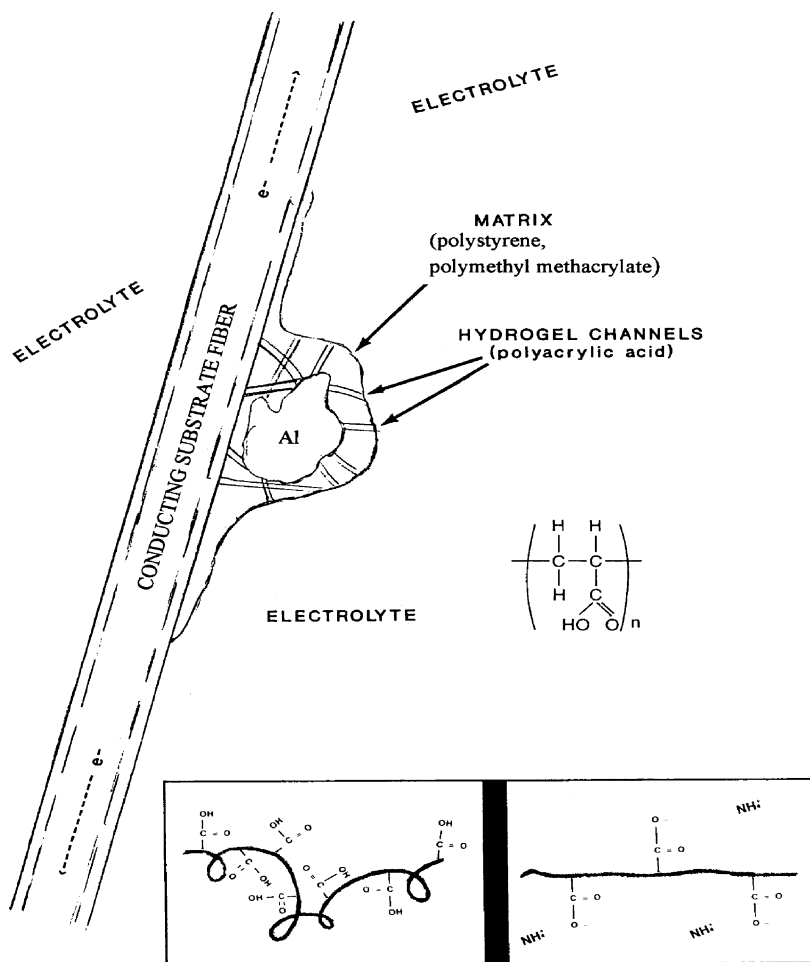


Fig. 1. Schematic representation of composite Al electrode.

of the aluminum anode in the alkaline electrolytes (NaOH, KOH), which, by virtue of their higher conductivity, are of primary interest for most applications.

2. Approach—the structure

A polymer mixture, containing particles of aluminum powder, has been applied and bonded by pressing onto an aluminum metal substrate current collector. This polymer mixture consists of two components. An active component of polyacrylic acid (PAA) is capable of supporting ionic conduction via water molecules along its length. An “inert” structural component (polymethyl methacrylate, polystyrene, or the like) supports and isolates the PAA molecules. The linearized structure of PAA is that of a long chain molecule which can adsorb and immobilize aqueous electrolyte molecules along its length. The anode operates with the movement of OH^- ions along the molecular chain while current is being drawn from the cell. This can be considered as a kind of “ion hopping” mechanism. When a quantity of such chain molecules are incorporated into an inert polymer medium, relatively isolated one from another,

a physical barrier can be created between the active species (Al particles) and the bulk electrolyte, while maintaining the ionic conduction. This is shown schematically in Fig. 1. Both the productive and parasitic reactions compete for available hydroxyl ions at the particle interfaces.

In the ideal, this composite fabrication has some potential benefits. Since direct electrolyte contact with the working anode surfaces (particles) can be controlled, contribution from the corrosion reaction equation above may be somewhat attenuated. In particular, the contribution due to “local action” may be reduced by the relative isolation of the metal particles provided by the encapsulating polymers. This corrosion mechanism arises from current paths between electropositive and electronegative electrode regions, probably caused by impurity inclusions.

3. Experimental

The PAA polymer portion was stirred into methanol at moderately high shear using a small paddle impeller. After dissolving, the PAA was linearized by neutralizing the solution with NH_4OH or an organic amine. In the neutral

solution, the PAA stretches out due to the net mutual repulsion of the negative charges along its length. The length of a PAA 2MMW linearized molecule is of the order of 0.1 mm. The process of linearization is shown in the inset of Fig. 1.

A second inert polymer component (polystyrene or polymethyl methacrylate) was first dissolved in tetrahydrofuran (THF) and then added to the PAA solution. Sufficient solvent was used to produce a combined polymer solution. This second polymer, essentially impervious to the electrolyte and inert to the system, is used for structural stability. High purity Al powder (99.97%) or a specially developed reduced corrosion alloy designated EB50 V [4] in powder form was added to the combined solution. Composite anodes of approximate dimensions $4.5 \text{ cm} \times 6.25 \text{ cm} \times 0.1 \text{ cm}$ were fabricated using the described mixture. A perforated thin Al sheet or multi-ply expanded mesh Al screen substrate was placed on a warmed surface (-60°C) and infiltrated with the solution/Al powder mixture by dripping or spraying. It was necessary to periodically agitate the mixture during the application process to prevent the Al powder from settling.

After solvent evaporation, the impregnated substrate was pressed to about one thousand psi between two flats at -200°C , somewhat above the softening temperature of the thermoplastic polymers, to consolidate the composite structure. This is roughly depicted schematically in Fig. 1. In the idealized structure, the linearized PAA molecules form a filamentary network intermeshed with the metal particles and conducting substrate. During discharge, the immersed anode absorbs, and largely fixes, the water-based electrolyte along the PAA molecules, effectively suppressing bulk metal–electrolyte contact. The hydroxyl ions hop along the chains of water molecules to reach the Al particles, which release electrons into the substrate/load and form the $\text{Al}(\text{OH})_3$. The latter remains mostly in place within

the structure and eventually converts to the oxide. Fig. 2 shows a composite Al anode as fabricated and after 122 h immersion/discharge in 1 M KOH. This illustrates the sequestering of the discharge product within the composite electrode structure. This property should provide some benefit in maintaining electrolyte conductivity throughout the discharge.

The number of fabrication variables is quite formidable. They include: proportion and length distribution of the PAA polymer, type and quantity of inert polymer, particle size, proportion and alloy type of the Al powder and, finally, the type of substrate. A special order was made for the EB50V alloy in powder form (the Aluminium Powder Co., Forge Lane, Sutton Coldfield, UK). The alloy was carefully formulated using pure Al (99.999%), spray atomized and sieved to produce powders of particle size 11.5, 38, 45 μm and larger. Electrodes also were fabricated from available 99.97% Al powder (CERAC, Milwaukee, WI 53233) of about 38 μm particle size. Unfortunately, The optimized alloy EB50 V was not available in expanded metal form for substrate comparison. Obtaining the latter by special order was priced well beyond the scope of this effort. The EB50 V substrates used in these tests were limited thus to thin perforated sheets. Expanded metal substrate screen was obtained in Al 1145, the highest purity aluminum readily available. In general, these latter substrates produced cell potentials several tenths of a volt below those with the EB50 V substrates and, of course, are not optimized for corrosion resistance. The expanded metal substrates did allow multiple layers of current collector to be used which should increase the electronic conductivity within the electrode. It is, perhaps, a current limiting weakness of this composite fabrication that a more distributed conducting Al substrate analogous to that of sintered nickel is not available.

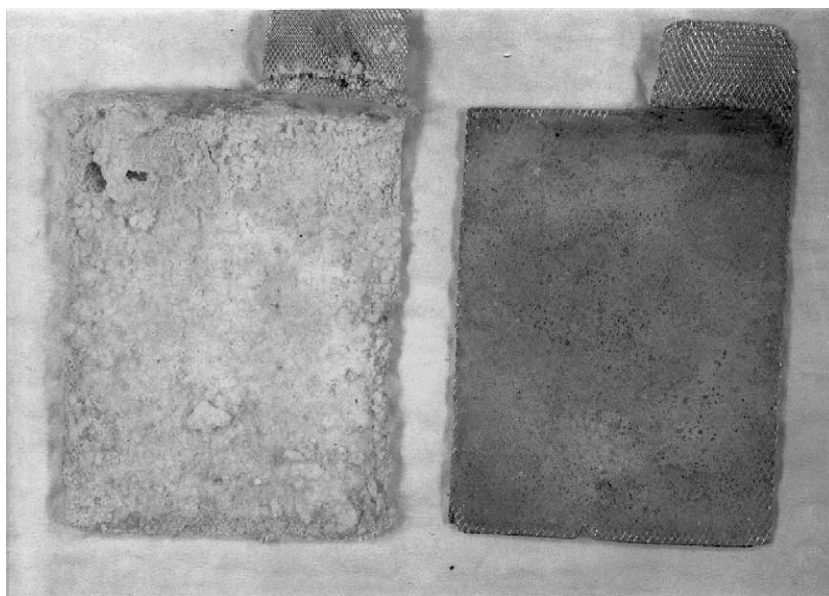


Fig. 2. Composite Al anode—As fabricated (right), after discharge (left). Anode no. 12, Table 1.

The electrodes were tested in unsealed prismatic lab cells fitted with a commercial catalyzed carbon air electrode on one face (Yardney Technical Products, Inc. #AC-65). Anode–cathode separation was about 3–5 mm. The test cells held about 30 cm³ of electrolyte (1 M NaOH or KOH), which was maintained at constant level during discharge. Constant current discharge was set using a regulated power supply. Cell potential was monitored continuously at the various current loads using a chart recorder.

4. Discussion

Fig. 3 (above) compares the discharge of a composite aluminum anode with that of an aluminum control. In this case, the 99.97% purity aluminum metal was used for both anodes, –325 mesh (45 μm) powder in the composite and perforated Al sheet for the control. The aluminum expanded metal control (diamonds) delivered a discharge time at 40 mA (–1 mA/cm²), of about 2.5 h to dissolution. The composite anode (squares) was discharged initially at 40 mA for 2 h. The load then was reduced to 20 mA with discharge for an additional hour. Finally, the load was reduced to 5 mA with further discharge for 34 h. While the control exhibited a somewhat greater potential during its discharge at 40 mA, the composite anode maintained a potential well above 1 V throughout most of its discharge period.

Examination of the plot of Fig. 3 reveals that the composite anode exhibits a kind of “threshold” behavior, which was observed to be fairly typical of the composite formulations. The anode can be discharged for a period at given current (40 mA, in the example above) to low potential. Upon reducing the load current (to 5 mA in the example), the anode

can be discharged many more hours at constant potential to ultimate failure. This discharge behavior may be attributable to the presence of some lower and many higher impedance current paths in the structure. Applying a high initial load exhausts the low impedance current paths, leaving most of the higher impedance paths available to carry the current as the load is reduced. Similar behavior can be observed in several composite anodes of Table 1 (below), where multiple discharge currents are recorded.

Formulations and structural data for representative composite anodes and controls are presented in Table 2 and identified by number. The electrical discharge properties are given for the numbered electrodes in Table 1. The formulation entries of Table 2 require some explanation. The entry for anode #4, for example, indicates that 0.066 g of 90 kMW. PAA and 0.05 g of 450 kMW. PAA polymers were dissolved in solvent (methanol) and linearized. This solution then was combined with a solution of 1.0 g polystyrene dissolved in a cosolvent (THF). Two grams of 45 μm Al powder were added to this mixture. The powder was maintained in solution by agitation while being deposited on the 4.5 cm × 6.25 cm anode substrate.

The discharge data is shown in Table 1. The 6 g EB50 V sheet control (#2) did achieve the highest specific energy output of the group, but not a particularly long discharge life in terms of hours/aluminum gram of anode. The two remaining controls (#1, 3) were fabricated from aluminum metal of the same degree of purity as that used as substrates in the composites. For proper comparison, they were fabricated to the same total aluminum weight of the composite test anodes. These controls achieved moderate energy output, with relatively short working lives. In particular, the 3 g Al 1145 Xmet anode delivered 154 Wh/kg with a working life of

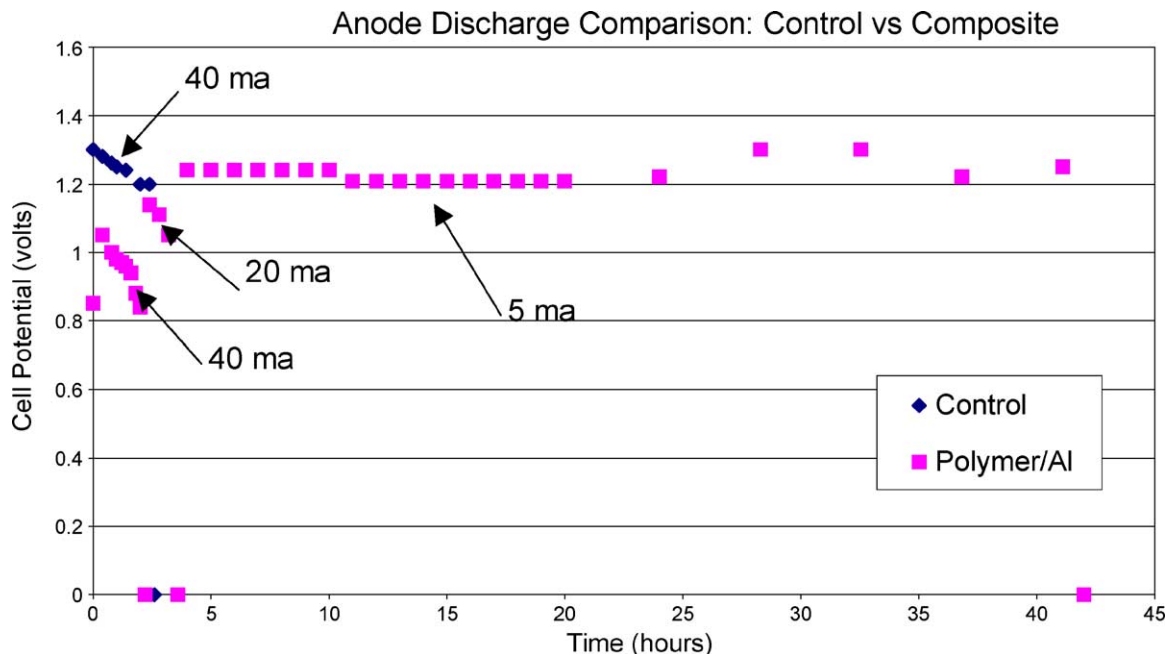


Fig. 3. An anode discharge comparison: Al control vs. composite (anode no. 4, Table 2).

Table 1
Discharge of Al test anodes in alkaline media

No.	Discharge current (mA)	Discharge time (h)	Potential range (V)	A (h)	W (h)	W (h)/kg (total)	Operational life (h/g of Al)
1	40	10.5	1.2–1.0	0.42	0.462	154	3.5
2	80	43	1.62–1.2	3.438	5.158	897	7.48
3	80	16	1.25–0.8	1.28	1.34	268	3.2
4	40	2	1.0	0.08	0.08		
	20	1	1.14	0.02	0.023	102	12.33
	5	34	1.2 (constant)	0.170	0.204		
5	40	88	0.55	3.52	1.93	322	14.66
6	40	7.75	1.0	0.31	0.31		
	0	16	–	0	0	240	14.66
	20	19.5	1.05	0.39	0.41		
7	20	0.5	1.0–0	0.010	0.005		
	0	24	–	0	0	–30	60.0
	0.5	338	1.22–0.4	0.174	0.169		
8	20	5.5	1.19–1.13	0.110	0.128		
	0	13	–	0	0		
	10	5	1.034–0.70	0.050	0.048	162	26.5
	5	56	1.13–1.08	0.280	0.311		
9	20	4	1.22–0.85	0.080	0.092		
	10	4	1.20–0.80	0.040	0.046	108	17.33
	5	34	1.23–0.75	0.170	0.187		
10	20	5	1.14–1.05	0.10	0.108		
	10	2.4	1.19–0.94	0.024	0.027	124	16.0
	5	40.6	1.23–1.1	0.203	0.236		
11	10	7	1.25–0.96	0.07	0.081	199	25.0
	5	55.6	1.56–1.4	0.278	0.417		
12	20	4	1.15–0.75	0.080	0.087		
	10	3.5	1.17–0.95	0.035	0.038		
	5	25.6	1.22–1.18	0.128	0.154	107	40.66
	0	70	–	0	0		
	5	8	1.12–0.80	0.040	0.042		

10.5 h. A composite anode (#6), also containing 3 g of aluminum, delivered 240 Wh/kg over an immersed working life of some 43 h. Other composite anodes attained significantly longer working lives with a roughly inverse relationship with delivered energy. Thus far, the data seems to show improved working parameters when the encapsulating polymer mix-

ture weight ratio of PAA/polystyrene or PAA/polymethyl methacrylate lies in the range 4.6:1–1:1, with total polymer weight of about 0.05–0.25 that of the aluminum powder. Optimum formulation for the best combination of working parameters, however, certainly has not yet been achieved.

Table 2
Composition data for selected test anodes

Anode no.	Formulation	Aluminum type/quantity	Substrate
1	Control—expanded grid	Al 1145, 3 g	Multi-ply, Xmet
2	Control	EB50 V, 5.75 g	Sheet
3	Control	99.9% Al, 5 g	Sheet
4	(0.066 gA + 0.05 gB):1.0 g-polystyrene	2 g-99.97%, 45 μm	3 ply Xmet Al 1145
5	(0.13 gA + 0.1 gC):0.05 g-polystyrene	5 g-99.97%, 45 μm	3 ply Xmet Al 1145
6	(0.13 gA + 0.1 gB + 0.1 gC):0.25 g-polystyrene	2 g-EB50 V, 38 μm	3 ply Xmet Al 1145
7	(0.22 gA):0.33 g-poly(methyl methac)	5 g-EB50 V, 38 μm	3 ply Xmet, Al 1145
8	(0.13 gA + 0.1 gC):0.05 g-poly(methyl meth)	2 g-EB50 V, 38 μm	3 ply Xmet, Al 1145
9	(0.26 gA + 0.05 gC):0.5 g-polystyrene	2 g-EB50 V, 11.5 μm	3 ply Xmet, Al 1145
10	(0.26 gA + 0.05 gC):0.25 g-polystyrene	2 g-EB50 V, 11.5 μm	3 ply Xmet, Al 1145
11	(0.26 gA + 0.05 gC):0.5 g-poly(methyl meth)	2 g-EB50 V, 11.5 μm	EB50V sheet, 0.75 g
12	(0.26 gA + 0.05 gC):0.3 g-poly(methyl meth)	2 g-EB50 V, 11.5 μm	3 ply Xmet, Al 1145

where A: PAA, MWt-90K; B: PAA, MWt-450K; C: PAA, MWt-750K.

The above all being stated, the main point of this paper, in the Author's opinion, is to introduce a potentially interesting alternative aluminum anode structure, rather than focusing too closely on details of the present test electrodes. The general results of the test data, of course, are necessary for proof of concept. With greater experimental resources and an expanded scope of effort, however, this composite anode fabrication might be able to contribute to an improved Al/air cell, tailored to specific applications.

5. Conclusions

1. The conductive polymer encapsulated powder aluminum anode can be tailored to produce an enhanced discharge lifetime in the alkaline electrolytes.
2. Both the polymer blend composition and mixture/application uniformity are critical in achieving a successful electrode. Variation of this encapsulating medium allows, in principle, a range of control over the discharge characteristics of the aluminum species with respect to electrode life and current capability. (Reproducibility is a problem with the very small mixture batches and hand methods employed in this study.)
3. The self-sequestering of the reaction products within the anode as it discharges should help maintain electrolyte conductivity, enabling a more constant cell potential.
4. Composite fabrication of the anode allows the possibility of introducing performance enhancing additive compounds throughout the electrode structure.
5. Considering the large number of parameters and the variability of hand fabrication, the optimum combination of anode energy output and discharge lifetime, cannot yet be determined. The general viability of the approach can be asserted, however, from the data acquired thus far.

Acknowledgements

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