

Enhanced electrochemical performance in the development of the aluminum/hydrogen peroxide semi-fuel cell

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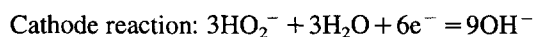
Abstract

Significant accomplishments from this research effort have defined and characterized the nature and rate of the chemical dynamics at the anode and cathode, thus allowing the development of the aluminum/hydrogen peroxide couple as an energy-dense semi-fuel cell system. This effort has included the investigation of new aluminum alloys, development of new electrocatalysts for the hydrogen peroxide, optimization of the operating parameters and modelling of the electrochemical performance of the couple. Furthermore, it has demonstrated a technique that will enhance the electrochemical properties of selected aluminum anodes, while controlling unwanted corrosion reactions at a tolerable level. The unique methodology described in this paper involves the use of additives to activate the surface of the aluminum anode-electrolyte, thus avoiding alloying, processing and heat treating. In addition to this anode development, we have identified a novel electrocatalyst that enhances effective and efficient electrochemical reduction of hydrogen peroxide, thus shifting the predilection of the peroxide from parasitic decomposition to desired high rate electrochemical reduction. The improved performance of this electrochemical couple has led to the attainment of current densities of 500 to 800 mA cm⁻², five to seven times that originally achievable at comparable cell voltages of 1.4 to 1.2. System-level modelling, based on the experimental evidence reported in this paper, indicates that the aluminum/hydrogen peroxide couple is a versatile and energetic electrochemical energy source.

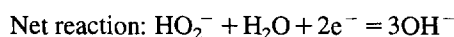
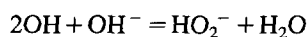
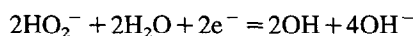
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1. Introduction

Over the past several years, the aluminum/hydrogen peroxide electrochemical semi-fuel cell system has been investigated through a wide range of parametric studies to develop it as an energy-dense power source for undersea vehicle propulsion. In alkaline media, the anode and cathode half-cell reactions are defined as:



It should be noted that, in a strongly alkaline medium, the reacting catholyte species is the deprotonated hydrogen peroxide, HO₂⁻, and that its reduction is more consistent with reduction to a neutral OH intermediate (1).



Operating cell voltages in the 1.2–1.7 V range, depending on current density, have been routinely obtained. On a theoretical basis [1], the aluminum/hydrogen peroxide (Al–H₂O₂) electrochemical couple compares favorably with the aluminum/silver oxide (Al–AgO) and other high energy density primary battery systems. As a result of this work, projections for an Al–H₂O₂ solution-phase catholyte system

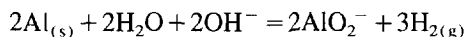
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indicate actual specific energy and energy densities of 330 Wh kg⁻¹ and 360 Wh dm⁻³, respectively, are achievable. This specific energy is comparable to the high specific energy of 290 Wh dm⁻³ projected for the similarly configured Al–AgO system, with the added benefit of one-third the cost.

In designing a system to incorporate Al–H₂O₂, the hydrogen peroxide presents a problem not typically associated with solid cathode materials such as silver oxide; specifically, unless isolated with a separator, the solution phase peroxide is in contact with both the aluminum anode and the electrocatalytic cathode. This means that the peroxide can create non-electrochemical energy-producing, 'parasitic', chemical pathways for the consumption of reactive anode and cathode materials. Specifically, one needs to be concerned with:

- (i) the corrosion reaction of the aluminum in a caustic medium;
- (ii) the direct reaction of aluminum with hydrogen peroxide;
- (iii) the parasitic homogeneous self-decomposition of the hydrogen peroxide;
- (iv) the heterogeneous decomposition of the hydrogen peroxide with substrate materials, such as the nickel substrate, silver catalyst or palladium/iridium catalyst.

Corrosion reaction:



Direct reaction: $2\text{Al}_{(s)} + 3\text{HO}_2^- = 2\text{AlO}_2^- + \text{OH}^- + \text{H}_2\text{O}$

Decomposition reaction: $2\text{H}_2\text{O}_2 = \text{O}_{2(g)} + 2\text{H}_2\text{O}$

For the Al–H₂O₂ semi-fuel cell to be viable, the efficiency of the electrochemical reactions must be maximized and the effects of the parasitic reactions minimized. Two approaches can be used to combat the corrosion of the aluminum in a caustic medium and the reaction of the aluminum with hydrogen peroxide. One is to fabricate an aluminum alloy with small amounts of other materials [2–7]; the other is to include additives in the electrolyte [8–12]. The efficiency of the electrochemical reduction of hydrogen peroxide with a concomitant decrease in its heterogeneous decomposition can be achieved through the use of a novel catalyzed cathode substrate [13].

This paper presents data on the activation of pure aluminum (99.999%) by the addition of additives to the electrolyte. The applicability of these electrolyte/additive combinations to the Al–H₂O₂ semi-fuel cell system wherein the H₂O₂ is reduced on a Pd/Ir catalyzed nickel substrate is discussed. System level modelling based on the experimental evidence reported in this paper is also presented. This modelling indicates that the aluminum/hydrogen peroxide semi-fuel cell is a versatile and energetic electrochemical energy source.

2. Experimental

For the aluminum anode-electrolyte additives investigations, a Princeton Applied Research (PARC) model 371

potentiostat was used and the data recorded using a Houston Instruments model RE 0092 X-Y recorder. The experimentation arrangement contained a three electrode system: a silver/silver chloride reference electrode, an isolated (via a porous ceramic cup) graphite rod (spectrographic grade, 6 mm (0.25") in diameter) as a counter electrode, and an aluminum button working electrode. This aluminum button was mounted in a holder available from Princeton Applied Research [14] with a hole in the center for the exposed area of the aluminum to come in contact with the electrolyte. The exposed area of the button was approximately 0.50 cm². Once the test was completed, the aluminum button was rinsed with distilled and deionized water and air dried. Initial and final weights were recorded and the exact corroded area of the button was measured. The electrochemical cell chamber consisted of a crystallization dish 170 mm in diameter and 90 mm deep. The cell chamber was then capable of holding one liter of electrolyte.

All experiments with aluminum anode-electrolyte additives were conducted by applying a potential range from –2.0 to 0.0 V versus Ag/AgCl, at a scan rate of 5 mV s⁻¹ at a current range to 1 A. The current data were recorded and converted to current density using the calculated area of the aluminum button. All experiments were conducted using a solution of 3.0 M NaOH, 0.50 M H₂O₂ and 40 g l⁻¹ of sea-salt, a temperature of 55°C and 99.999% Al obtained from Alcan International Inc.

The aluminum polarization was investigated with single additives added to the electrolyte at 0.10 g l⁻¹. The single additives investigated (with their referred symbols) were sodium stannate, Na₂SnO₃ (Sn), gallium oxide, Ga₂O₃ (Ga), sodium plumbate, Na₂PbO₃ (Pb), indium oxide, In₂O₃ (In), zinc oxide, ZnO (Zn), sodium borate, Na₂B₄O₇ (B), yttrium oxide, Y₂O₃ (Y), lanthanum oxide, La₂O₃ (La), bismuth oxide, Bi₂O₃ (Bi), manganese dioxide, MnO₂ (Mn), antimony oxide, Sb₂O₃ (Sb), sodium silicate, Na₂SiO₃ (Si), germanium oxide, GeO₂ (Ge), magnesium oxide, MgO (Mg), cobalt nitrate, Co(NO₃)₂ (Co) and nickel nitrate, Ni(NO₃)₂ (Ni).

Several binary combinations of additives were added to the electrolyte and the aluminum polarizations were observed. Eight of the binary combinations contained gallium oxide with each of the following: sodium plumbate, antimony oxide, sodium silicate, germanium oxide, sodium stannate, indium oxide, bismuth oxide, and magnesium oxide. Two other binary combinations of additives contained sodium stannate with magnesium oxide and sodium plumbate, respectively.

Three ternary combinations of additives were also investigated. These combinations all had gallium oxide and sodium stannate in combination with one of the following: sodium plumbate, magnesium oxide or bismuth oxide.

The full-cell Al–H₂O₂ tests were carried out using a 38×203 mm (1.5×8") electrolyte flow-through cell test system designed at NUWC, Newport. The cell body, made of pexiglass, is machined to accept a 1.5×8" aluminum

anode. Opposing the anode is a $1.5 \times 8''$ cathodic nickel substrate surface typically catalyzed with Pd and Ir as described in Ref. [13]. Both anode and cathode are mounted on individual current collector bus bars. The two electrodes are mounted vertically and are separated by a Vexar screen spacer. The catholyte and the electrolyte are pumped into the bottom of the cell, flowing between the anode and the catalytic surface and exiting at the top of the cell.

Electrolyte exiting the cell is returned to the two liter reservoir which consists of a round bottom flask in a heating mantle (Electromantle model MA). Electrolyte from the reservoir first enters the flow controller comprised of an Iswater model MV pump system and a Micropump 187-000 pump head. Upon exiting the flow controller the electrolyte enters a Cole Palmer Polystat constant temperature circulator. From this constant temperature bath the electrolyte enters the bottom of the test cell thus completing the electrolyte flow loop.

Cell current is controlled by a Hewlett Packard model 6253A d.c. power supply. A micro computer is used to monitor and record the cell voltage, cell current, the resultant power, the inlet, cell and outlet electrolyte temperatures, and the evolved gas flow rate. The software used for the data acquisition is LabTech NoteBook.

3. Results and discussion

The aluminum polarization curves for all of the materials used as single additives are shown in Fig. 1.

Gallium oxide is clearly the best additive, as it depolarizes the electrode to a much greater degree than any of the other additives. Of the remainder of the additives tested, manganese, indium, plumbate and stannate showed some slight depolarization enhancement.

Gallium in combination with bismuth and plumbate showed a slight increase in aluminum anode activity. Gallium

in combination with indium, silicate, magnesium and antimony passivated the aluminum at 350, 800, 900 and 1000 mA cm^{-2} , respectively.

Gallium alone passivated the aluminum at 800 mA cm^{-2} and the gallium–stannate combination activated the aluminum through the entire polarization profile. The results for matrix testing of various concentration combinations of gallium oxide and sodium stannate are given in Table 1.

These results indicate that the best combination for activation of the aluminum is:

$6.0 \times 10^{-4} \text{ M Ga}/6.0 \times 10^{-4} \text{ M Sn}$ because this combination activates the aluminum while not showing any passivation of the surface. Increased amounts of gallium and tin protect the surface from passivation. There is a maximum in the performance of the aluminum at $6.0 \times 10^{-4} \text{ M Ga}/6.0 \times 10^{-4} \text{ M Sn}$ that is diminished if the concentrations of Ga/Sn are increased further.

The gallium oxide–indium oxide matrix testing yielded poor aluminum activation performance with many of the concentration combinations resulting in aluminum passivation at rather low current densities. The results for this combination are summarized in Table 2.

Because the aluminum performs well at large concentrations of gallium and small concentrations of indium, it is evident that the indium has a deleterious effect on the activation of the aluminum.

The gallium oxide–bismuth oxide matrix testing resulted in violent gassing in all cases and the electrolyte turned yellow during the polarization runs. This combination was deemed to be impractical.

The sodium stannate combinations with magnesium oxide and sodium plumbate failed to yield any significant activation of the aluminum anode.

The ternary combinations of gallium–stannate–indium, gallium–stannate–plumbate and gallium–stannate–magnesium additives were also tested. All of these ternary

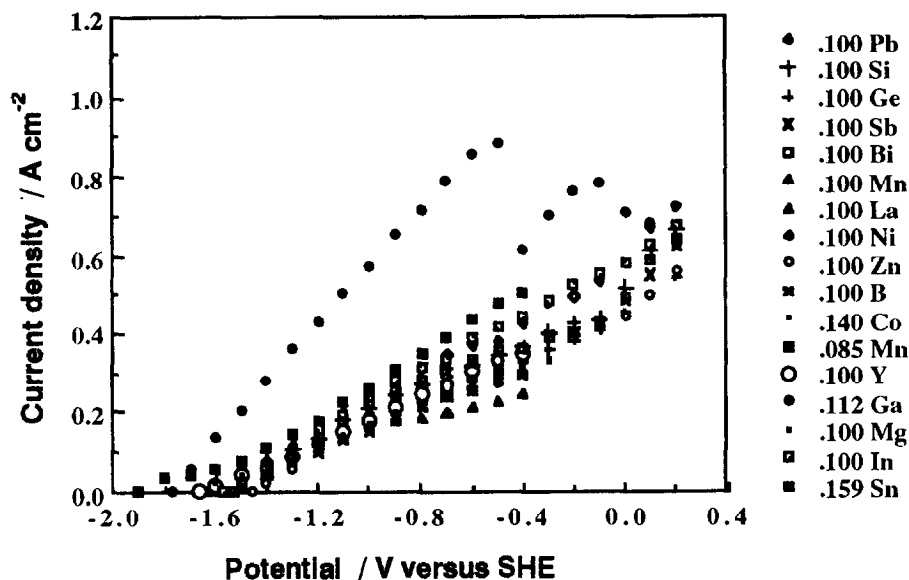


Fig. 1. Aluminum polarization for various electrolyte additives.

Table 1

Gallium oxide–sodium stannate matrix tests showing potential (V) at 500 mA cm⁻² with current density (mA cm⁻²) in brackets

Gallium oxide (mole l ⁻¹)	Sodium stannate concentration (mole l ⁻¹)			
	1.5 × 10 ⁻⁴	3.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴	1.2 × 10 ⁻³
1.5 × 10 ⁻⁴	(300)	(270)	(200)	(300)
3.0 × 10 ⁻⁴	-0.98 (800)	-0.98 (590)	-0.77 (> 710)	-0.72 (670)
6.0 × 10 ⁻⁴	-1.00 (620)	(450)	-0.93 (> 860)	-0.77 (> 730)
1.2 × 10 ⁻³	-0.94 (560)	-0.99 (820)	-0.93 (> 810)	-0.84 (> 750)

Table 2

Gallium oxide–indium oxide matrix tests showing potential (V) at 500 mA cm⁻² with current density (mA cm⁻²) in brackets

Gallium oxide (mole l ⁻¹)	Indium oxide concentration (mole l ⁻¹)			
	1.5 × 10 ⁻⁴	3.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴	1.2 × 10 ⁻³
1.5 × 10 ⁻⁴	-1.01(350)	+0.13(310)	+0.18(290)	+0.15(310)
3.0 × 10 ⁻⁴	-1.06(> 880)	-0.90(740)	+0.12(310)	+0.06(160)
6.0 × 10 ⁻⁴	-0.88(710)	+0.01(360)	+0.02(180)	+0.05(330)
1.2 × 10 ⁻³	-0.97(800)	-0.88(710)	+0.04(380)	+0.03(240)

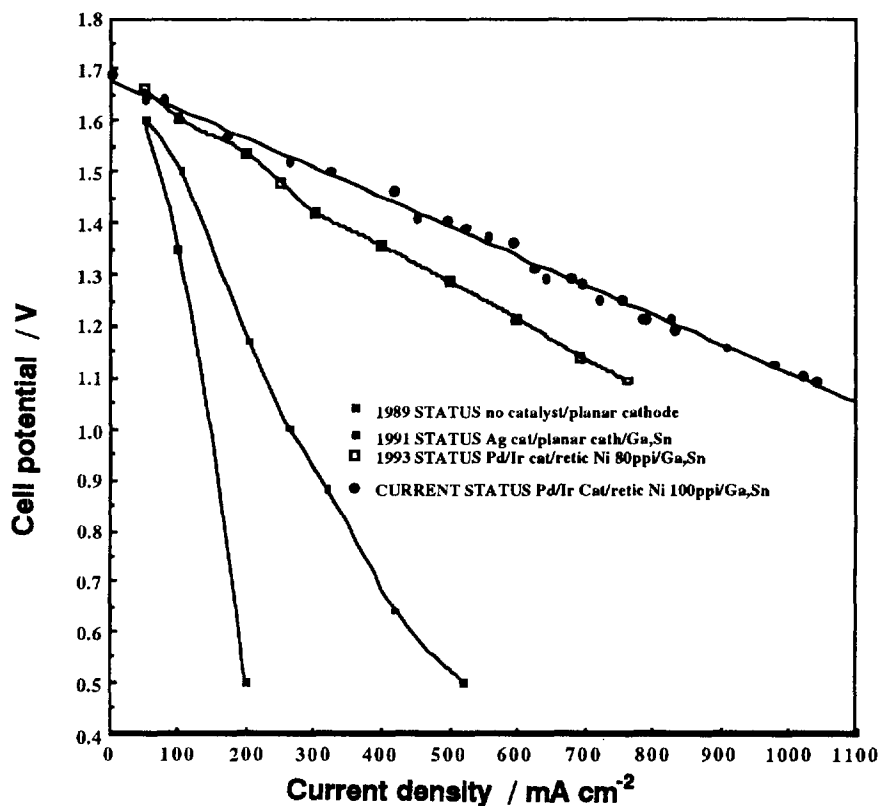


Fig. 2. Improvements in performance obtained during the development of the aluminum/hydrogen peroxide semi-fuel cell.

combinations showed little enhancement in the electrochemical performance of the pure aluminum.

Fig. 2 shows the dramatic improvement of the aluminum/hydrogen peroxide semi-fuel cell when the aluminum anode is activated with a combination of gallium and tin additives and a reticulated nickel substrate cathode is catalyzed for H₂O₂ reduction with palladium and iridium.

Not nearly as obvious, but certainly as impressive, are the subsequent improvements to the specific power of the overall

energy source as it would be configured for an undersea vehicle propulsion system. Numerical simulations have been developed [15] to quantify the effectiveness of various electrochemical systems employing aluminum aqueous couples; simulating not only the time-dependent energy producing electrochemical and chemical reactions, but also accounting for parasitic reactions, auxiliary hotel energy requirements as well as the necessary engineering components required to operate the system in the simulated vehicle configuration.

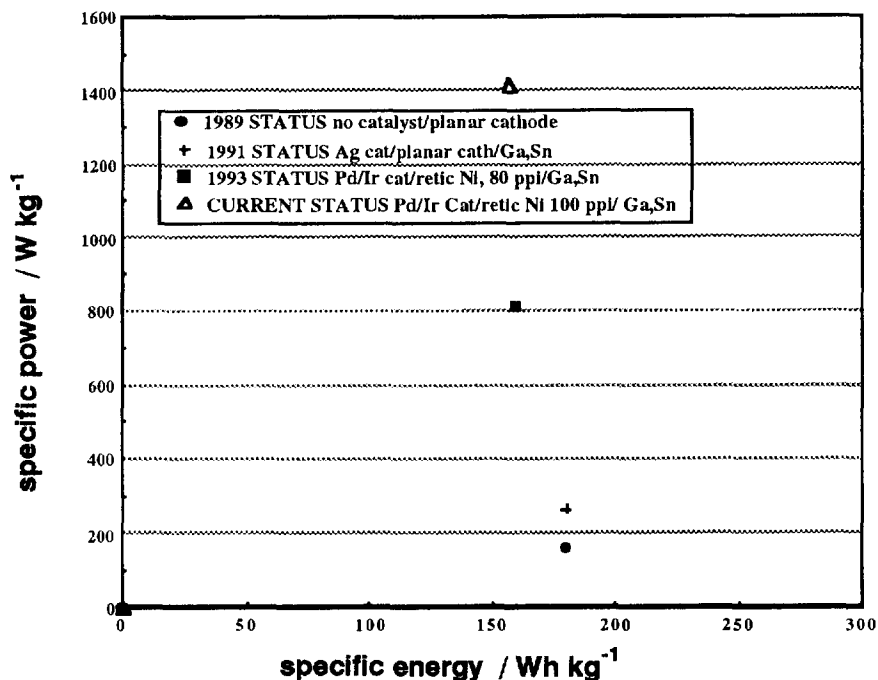


Fig. 3. Improvements in specific energy and power resulting from reductions in polarization based on numerical modeling.

The specific energy and power numbers resulting are extremely useful in determining the practical benefits resulting from the localized electrochemical improvements as well as determining their relative sensitivity to applied constraints, such as volume and weight of the allowable energy system.

Fig. 3 quantifies the relative improvements to the specific power of a semi-fuel cell system when configured for a high power application, as evidenced by the high specific powers.

The four points are directly applicable to the four polarization curves identified in Fig. 2. The improvements in specific power are directly related to the ability to maintain an average cell voltage of 1.2 while increasing current densities from 125 to 900 mA cm⁻². For all cases, concentrations of H₂O₂ are limited to 60% the limit for storage inboard the vehicle. Not shown in Fig. 3, but worth mentioning, are that the improvements to the overall system specific energy resulting from increasing the H₂O₂ concentration from 60 to 90% are marginal, being only 10%.

4. Conclusions

The two criteria measured in this study of the addition of small quantities of additives to the electrolyte for an Al–H₂O₂ semi-fuel cell were:

(i) activation of the aluminum as observed by a steep slope on a polarization curve;

(ii) elimination of aluminum surface passivation as observed by an unchanged slope on the polarization curve.

This work approaches the activation of the aluminum from the solution phase rather than the solid phase. Of the additives studied, the best combination was the gallium–stannate sys-

tem where both additives were present at 6.0×10^{-4} M concentration levels.

The improved performance of the aluminum/hydrogen peroxide semi-fuel cell is five to seven times that originally achievable, while maintaining comparable cell voltages of 1.2–1.4 V.

Numerical simulations employing the results of this study quantify the high power performance enhancements resulting from the ability to operate at higher current densities. The results are significant improvements in overall system specific power, 163 to 1412 W kg⁻¹, for the same constraints of weight, volume and bus voltage that are imposed by the underwater vehicle.

References

- [1] A.J. Bard, R. Parsons and J. Jordan, (eds.), *Standard Potentials in Aqueous Solution*, IUPAC, Marcel Dekker, New York, 1985.
- [2] G. Tarcy and R. Mazgaj, Aluminum alloys and associated anodes, *US Patent No. 4 808 498* (28 Feb. 1989).
- [3] J. Hunter et al. (Alcan International Ltd.), Aluminum batteries, *Eur. Patent Applic. No. 0 354 752* (1989).
- [4] G. Scamans, J. Hunter, C. Tuck, R. Hamlen and N. Fitzpatrick, Further development of aluminium batteries, in T. Keily and B.W. Baxter (eds.), *Power Sources 12*, International Power Sources Committee, Crowborough, UK, 1988, p. 363.
- [5] G. Scamans, J. Hunter and N. Holroyd, Surface engineering approach to the corrosion of aluminum, *Treatise on Materials, Science and Technology*, Vol. 31, Academic Press, New York, 1989.
- [6] C. Tuck, J. Hunter and G. Scamans, *J. Electrochem. Soc.*, 134 (1987) 2970.
- [7] D. MacDonald, K.H. Lee, A. Moccari and D. Harrington, *Corrosion*, 44 (1988) 652.

- [8] C. Marsh et al., Electrolytically activated aqueous alkaline battery having a pure aluminum anode and a method for providing a multi-performance battery therefrom, *Patent Applic. No. 72 909* (June 1990).
- [9] W. Bohnstedt, *J. Power Sources*, 5 (1980) 245.
- [10] M. Katoh et al., *US Patent No. 3 563 803* (1967).
- [11] K. Kordesch et al., *US Patent No. 3 880 671* (1975).
- [12] K. Sarangapani et al., *J. Appl. Electrochem.*, 14 (1984) 475.
- [13] C.L. Marsh, G.L. Seebach, J.W. VanZee, R.R. Bessette, H.G. Meunier and M.G. Medeiros, Preparation of an electrocatalytic cathode for an aluminum-hydrogen peroxide battery, *US Patent No. 5 296 429* (22 Mar. 1994).
- [14] EG&G, *Princeton Applied Research Electrochemical Accessories Manual, Model K0105 Flat Specimen Holder*, 1994, p. C2.
- [15] E.G. Dow, *Proc. 37th Power Sources Conf., Cherry Hill, NJ*, The Electrochemical Society, Pennington, NJ, 1996, pp. 39–42.