The Development of Aluminum Aqueous Batteries for Torpedo Propulsion

Prototype Development of a Replenishment Electrolyte Management System for Activation and Control of a Pile Configured Battery Cartridge

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ABSTRACT

Development of electric propulsion systems for torpedo applications imposes significant challenges with regards to system energy and power densities, both gravimetric and volumetric. Energy and power goals of 200 Wh/kg and 1200 W/kg, respectively, for the overall battery system have necessitated the development of recirculating aqueous electrolyte systems capable of run-time optimized molar concentrations of both the products and the reactants. Several electrolyte operating concepts have been evaluated, ranging from closed system (no active control of the electrolyte concentration) to delayed and variable rate controlled injection of both solute (NaOH) and solution (sea water and NaOH solution). The development of an intelligent electrolyte management concept, utilizing a Replenishment Electrolyte Management System (REMS) results in projected improvements in energy density of an Al-Ago battery, for a particular torpedo application, from 100 Wh/kg to 200 Wh/kg, enabling the Al-Ago battery system to meet the torpedo propulsion performance requirements, which otherwise could not be met with other primary or secondary battery systems.

Background

The Navy's development of aluminum-aqueous batteries for torpedo applications has been ongoing, at varying levels of intensity, since the original patent for aluminum-silver oxide (Al-Ago) was filed in 1973 and awarded in 1976 (1). The interest in this electrochemical couple stems primarily from its capability to provide extremely high rates, in excess of 1600 mA/cm², while maintaining very high energy densities in excess of 200 Wh/kg (2). In 1975, the Navy began development of an advanced lightweight (12.75 inch diameter) torpedo utilizing electric propulsion employing an Al-Ago primary battery. Several Navy patents (3,4) were awarded in 1978 for improving the aluminum anode alloy, at the same time the Al-Ago couple was successfully demonstrated (5) in a 12.75 inch diameter pile cartridge configuration at 150 Wh/kg. From 1981 through 1990, the French Navy, with the support of the French contractor SAFT, successfully developed and demonstrated Al-Ago for a 12.75 inch diameter lightweight torpedo propulsion application, the Murenne V-9. At nearly the same time, 1986-1990, the US Navy resumed development of the Al-Ago battery for a 21 inch heavyweight application, successfully demonstrating several 21 inch diameter cartridges at unprecedented current densities in excess of 1600 mA/cm² in a 200 Wh/kg configuration, op. cit. (2). With the exception of the French effort, development up to this point had focused on the battery cartridge electrochemistry. Development of the electrolyte management system, required to control the thermal, hydraulic and chemical conditions of the flowing electrolyte, began in earnest in 1992. Recent experimental efforts in the field of passive hydrocyclone gas/liquid separation enabled the Al-Ago technology to be applicable for operational scenarios over a broad power range, previously considered unattainable.

Replenishment vs. One Fill

The terminology used to discriminate the different types of electrolyte management systems are subjective, therefore warranting sufficient definition at this juncture. The battery, as a whole, consists of the battery cartridge hydraulically coupled to the electrolyte management system. The electrolyte management system consists of the electrolyte solute and solution together with the various valves, pumps, gas/liquid separators and heat exchangers required to control the chemical and thermodynamic states of the electrolyte solution before, during and after the battery cartridge is discharged. What uniquely characterizes a particular type of system is the method of integrating and activating the various components.

The Al-Ago replenishment electrolyte management system (REMS), shown schematically in Fig. 1, contains...
dry NaOH solute stored in the electrolyte reservoir prior to activation. Activation is initiated when sea water floods the reservoir, mixing with the dry solute and creating a predetermined solution of NaOH.

Subsequent to the initial mixing process, the replenishment system undergoes three (3) serial processes, depicted in Fig. 2, to optimize the electrolyte concentration.

Phase I is a 'closed system' phase. The electrolyte concentration, at this point, varies as a result of the overall electrochemical oxidation-reduction and parasitic corrosion reactions, Eqs. 1 and 2, respectively.

\[
2\text{Al} + 3\text{AlO}_2^- + 2\text{OH}^- \rightarrow 2\text{AlO}_2^- + 3\text{Al} + \text{H}_2\text{O} \quad E^0 = 2.85\text{V} \quad (1) \\
\text{Al} + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{AlO}_2^- + \frac{3}{2}\text{H}_2 + 100 \text{ kcal/gmole H}_2 \quad (2)
\]

Phase II is an 'electrolyte spew' phase, which initiates the flow, \( Q_2 \), of electrolyte from the system via pump \( P_2 \). While this happens, fresh sea water flows into the electrolyte reservoir, \( V_{\text{res}} \), via the sea water hull penetration, \( SV_1 \), to replace the volume discharged overboard. This action prevents the increase of the concentration of sodium aluminate, \( \text{NaAlO}_2 \), at the expense of a rapid decay in the concentration of NaOH.

Phase III is a 'replenishment/spew' phase which consists of the additional flow, \( Q_3 \), of high concentration, typically 50% weight fraction, liquid NaOH from the replenishment tank, \( V_{\text{rep}} \), into the electrolyte reservoir, \( V_{\text{res}} \), via pump \( P_3 \). This maintains the NaOH concentration of electrolyte flowing into the battery. In the event the volumetric rates of the two metering pumps are unequal, which is typically the case, ingress or egress of sea water via the sea water hull penetration, \( SV_1 \), will occur.

By contrast, the one fill electrolyte system consists of only a phase I mode of operation. The electrolyte concentration profile for this system is shown in Fig. 3.
One of the attributes of the Al-AgO electrochemistry is its ability to discharge safely over a wide spectrum of electrolyte concentrations and temperatures for current densities ranging from 50 to 1600 mA/cm². None the less, the efficacy of this system, particularly the cell voltage, $E$, is strongly dependent on the relative concentrations of the sodium hydroxide and sodium aluminate, as can be clearly represented by the Nernst Equation when applied to Eq. 1.

$$E = E^0 - \frac{RT}{nF} \ln \left( \frac{[\text{AlO}_2^-]^2 [\text{Ag}]^3 [\text{H}_2\text{O}]}{[\text{Al}]^2 [\text{AgO}]^2 [\text{OH}^-]^2} \right)$$  (3)

Thorough analyses by Moden (6) of numerous electrochemical experiments have determined that the optimum electrolyte concentration of NaOH gravitates toward 4 molar, at current densities ranging from 800 to 1600 mA/cm². An example of this is clearly shown in Fig. 4, which emphasizes the preference to operate on the 4 molar NaOH 'ridge'.

Fig. 5 portrays the undesirable decrease in aluminum coulombic efficiency, $\eta$, symptomatic of increasing electrolyte molar concentrations of NaAlO₂. Such excursions promote an increased rate of the parasitic corrosion reaction, Eq. 2, and the subsequent increased generation of both the $H_2$ gas, which must be contended with via the gas/liquid separator, and the run limiting NaAlO₂.

Based on this information, the operation of the electrolyte management system will be highly effective if it is capable of maintaining a constant 4 molar NaOH concentration while limiting the NaAlO₂ concentration to 2 molar.

For the sake of control and efficiency, the electrolyte temperature must also be optimized. Avoiding electrode passivation and maintaining steady, continuous electrochemical activation of the aluminum anode is realized for electrolyte solution temperatures in excess of 130°F to 150°F, depending on the current density and the electrolyte concentration. For current densities in excess of 800 mA/cm², temperatures in excess of 180°F are desired. Initial starting temperatures of the electrolyte solute and H₂O are typically 50°F to 60°F. A temperature rise in excess of 130°F is dependent on the final electrolyte solution concentration, as is evident in Fig. 6.
the electrolyte reservoir volume, at the expense of an equally rapid increase of the run limiting NaAIO₂ concentration, as shown in Fig. 8.

Electrolyte solution temperatures, Tₒ, of this magnitude must be realized within 5 seconds or less for most torpedo applications. The magnitude and rate of the electrolyte reservoir solution temperature change, shown in Fig. 7, is realized from the heat of reaction subsequent to the ingestion of sea water into the electrolyte reservoir and its mixing with dry NaOH powder, loosely dispersed in the reservoir.

The necessity for an initial startup concentration of 8-10 molar NaOH conflicts with the optimized electrolyte concentration of 4 molar, as previously shown in Fig. 4. Therefore, for a given discharge profile, a rapid transition from 10 molar to 4 molar is accomplished by minimizing the electrolyte reservoir volume, at the expense of an equally rapid increase of the run limiting NaAIO₂ concentration, as shown in Fig. 8.

It is also evident from inspection of Fig. 8 that the one fill system will never achieve its optimum 4 molar/2 molar NaOH/NaAIO₂ concentration. Much of the NaOH cannot be utilized, rendering the one fill system inefficient.

In order to extend the run time beyond the volume limiting one fill condition, the concentration of NaAIO₂ and NaOH must be controlled by simultaneous dilution and replenishment of the electrolyte with sea water and NaOH, respectively.

By establishing control volumes around each REMS component depicted in Fig. 1., and performing a mass balance,

\[ \frac{d}{dt} \int \rho \, dV = \left( \int \rho \, \vec{V} \, dA \right)_t - \left( \int \rho \, \vec{V} \, dA \right)_0 \] (4)

assuming non deformable control volumes, results in the following relation for the molar concentration for each species, \( C_n \).

\[ \left( \frac{d}{dt} C_n \right)_{cv} = \left( \frac{C_n}{\Theta} \right)_t - \left( \frac{C_n}{\Theta} \right)_0 \] (5)

Where the residence time, \( \Theta \), for a given control volume, \( V_{cv} \), and volumetric flow rate, \( Q \), is defined as,

\[ \Theta = \frac{V_{cv}}{Q} \] (6)

Therefore, the assumption of complete mixing of each species allows for the relationship,
which results in the following relation for the molarity of a given species, \( C_n \), in solution exiting a particular control volume.

\[
\frac{d}{dt} C_n = \sum \left( \frac{C_n}{\theta} \right)_i = \sum \left( \frac{C_n}{\theta} \right)_i
\]  

For the electrolyte system depicted in Fig. 1, Eq. (8) is written for a control volume around each component, and again for each species traveling through the component. What results is a series of \( N \) first order differential equations with \( N \) unknowns, solutions of which readily determine the concentration, \( C_n \), of the electrolyte at any point in the electrolyte system as a function of time. This is accomplished for any electrochemical discharge profile.

Of critical significance is the determination of two unknowns. The first is the replenishment (ingress) flow rate, \( Q_9 \), of the high concentrate NaOH required to offset the mass of NaOH which is dropping as a result of the electrochemical and parasitic reactions. This can be written in the form,

\[
Q_{OH} = (CQ)_{Rx} \left( \frac{C_{OH} + 1.0}{C_{AlO_2}} \right) \frac{1}{C_{OH}}
\]  

where the first and second terms in the second set of parenthesis account for the NaOH discharged overboard along with the NaAlO\(_2\) and the NaOH consumed by the electrochemical and parasitic reactions, respectively. The subscript 2, identifies the state point at the entrance to the egress control volume, \( CV_2 \), Fig. 1.

The consumption of NaOH via the load current, \( I_{load} \), leakage current, \( I_{leak} \), and corrosion is written,

\[
C_{Q_{Rx}} = \frac{(I(t)_{load} + I(t)_{leak})}{\eta} \frac{1}{W_{Al}} \frac{1}{M_{Al}} \frac{1}{60} \text{ 100} \]  

in units of \( \left( \text{gmoles/sec} \right) \). For the sake of this analysis, only constant power (varying current density) discharges were evaluated. Empirical data for various current densities characterizing the voltage slope, \( m \), under various electrolyte and electrode conditions was programmed into the model in the form,

\[
\frac{d}{dt} \left( \frac{E}{E_{peak}} \right) = - \frac{m}{T}
\]  

allowing the load current to be determined as a function of time, for substitution into Eq. (10).

The second critical flow to control in this system is the egress flow, \( Q_3 \), used to expel the undesirable products of reaction, NaAlO\(_2\). This is defined based on the operational upper limit of the NaAlO\(_2\) concentration, \( C_{AlO_2} \),

\[
Q_3 = (CQ)_{Rx} \frac{1}{C_{AlO_2}}
\]  

This identical process has been applied to another type of aluminum-flowing aqueous electrolyte primary battery, the aluminum-hydrogen peroxide (Al-H\(_2\)O\(_2\)) battery, which can be better characterized as a semi fuel cell. The overall electrochemical reaction is

\[
2Al + 3H_2O_2 + 2OH^- \rightarrow 2AlO_2^- + 4H_2O \quad E^0 = 3.23V
\]

The Al-H\(_2\)O\(_2\) electrolyte management system is identical to the Al-AgO REMS shown in Fig. 1 with the addition of a liquid hydrogen peroxide, H\(_2\)O\(_2\), storage container and a metering pump for injecting the liquid H\(_2\)O\(_2\) catholyte into the electrolyte stream.

The result is an increased number of equations attributed to the additional control volume for the liquid H\(_2\)O\(_2\) ingress, thus requiring the control of a third flow parameter. The increased number of parasitic reactions, three as compared to one in the Al-AgO system, further complicates the algebra, but is otherwise straightforward.

Application of these REMS algorithms and comparison to a one fill configuration results in dramatic projected improvements in both the power and energy density of the Al-AgO and Al-H\(_2\)O\(_2\) battery systems for both 21 inch and 12.75 inch diameter torpedoes, as shown in Figs. 9 and 10.

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Fig. 9. Gravimetric Comparison of REMS system to a one fill electrolyte system.
For each curve in Figs. 9 and 10, the point on the lower left represents the one fill configuration, while the point on the upper right represents the REMS configuration. The point in the middle of each curve represents a simplified REMS configuration, it has no replenishment tank and is capable of performing only phases I and II of the REMS system as depicted in Fig. 2. The Al-H\(\text{2O}_2\) system, represented by a single point, was modeled only in the REMS configuration.

![Graph](image)

**Fig. 10. Volumetric Comparison of REMS system to a one fill electrolyte system.**

The advanced heavyweight torpedo propulsion requirements are consistent with the upper point on the 'Al-AgO 21" curve; displaying that without REMS, the one fill system would be inadequate.

In practical application of the REMS, however, errors associated with controlling \(Q_0\) and \(Q_1\), measuring load current, \(I_{\text{load}}\), determining the leakage current, \(I_{\text{leak}}\), and projecting the coulombic efficiency, \(\eta_1\), will result in increased errors in \(C_{\text{AlO}_2}\) and \(C_{\text{OH}_1}\), over the course of the discharge. Therefore, for long duration applications, a closed form control methodology where concentration is determined explicitly is required.

One method of determining \(C_{\text{AlO}_2}\) and \(C_{\text{OH}_1}\) is presently under investigation by the author. Conducting a number of experiments involving the measurements of the electrolyte conductivity, viscosity and temperature, it appears feasible, using correlations developed by Van Zee (7) involving these parameters, to determine the absolute concentration of \(C_{\text{AlO}_2}\) and \(C_{\text{OH}_1}\). Commercially available in-line viscometers and conductivity sensors are being evaluated to determine the accuracy and precision of this process.

**Conclusion**

The implementation of a REMS system for the Al-AgO battery in a torpedo application will yield a 60-70% improvement in the volumetric power and energy density over traditional one fill electrolyte management systems.

Using optimized REMS configurations, both the Al-AgO and Al-H\(\text{2O}_2\) battery systems are projected to have comparable gravimetric energy and power densities, Al-AgO having a 12% advantage. The significant difference is that Al-AgO is nearly 1.6 times more power and energy dense than Al-H\(\text{2O}_2\) on a volumetric basis, making this system much more practical for volume limited, high power applications.

**Acknowledgment**

The author would like to thank Dr. R. Nowak and Mr. J. Fein of the Office of Naval Research for their enthusiastic support and sponsorship of electric propulsion under the Undersea Weaponry Program Element.

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