REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
31-03-2004

2. REPORT TYPE
Final Report

3. DATES COVERED *(From - To)*
August 2003 - March 2004

4. TITLE AND SUBTITLE
Final Report on Research of Air Cathodes for Aluminum Air Batteries

5a. CONTRACT NUMBER
N00014-03-M-0388

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Dobley, Arthur
Robak, Jan

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Yardney Technical Products, Inc.
82 Mechanic Street
Pawcatuck, CT 06379

8. PERFORMING ORGANIZATION REPORT NUMBER
3873-04

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Ballston Tower One
800 North Quincy St.
Arlington, VA 22217-5660

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This SBIR Phase I goal was to improve the efficiency of a lightweight aluminum-air battery and use a greater portion of the potential energy available in the aluminum anode. Specifically, the aim was to advance aluminum-air batteries by focusing on an efficient air cathode structure with an increased oxygen diffusion rate. Typical problems are air cathodes with low oxygen diffusion rates. By improving the structure of the air cathode, the battery system will greatly improve. The air cathode structure is a carbon composite with a binding agent and metal catalysts. We investigated different carbon morphologies, varied surface areas, and catalysts. Yardney produces several air cathodes and the effort was to improve their performance by modifying the existing cathode formulations. Different carbons and catalysts were used to produce new cathodes. Several new cathodes were produced, characterized, and tested in actual aluminum-air cells in atmospheric air. One new cathode displayed an improvement as high as 21% at current densities of 5 and 10 mA/cm2.

15. SUBJECT TERMS
Aluminum air battery, air cathodes, oxygen cathodes

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU	16	**19b. TELEPHONE NUMBER** *(Include area code)*

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Table of Contents

1.0 INTRODUCTION AND OBJECTIVE

The dismounted marine currently uses portable power systems mainly for radio communications, however the future will require a wide range of portable power systems for an "electronics rich" environment. The marine is already burdened with traditional equipment and the addition of new equipment will likely add to this load. This places a premium on reducing the weight of the power sources to maintain the mobility and effectiveness during combat. This need for lightweight power sources is the catalyst for developing higher energy density (Wh/kg) power sources.

Current power source requirements are met with the $LiSO_2$ (BA-5590) primary batteries and any possible substitute power sources shall be compared to this baseline. A power source that offers promise in this application is the Aluminum-air system (for the chemistry see the Appendix). This system actually has a higher energy density than the $LiSO_2$ system and could be significantly higher, if a larger portion of its theoretical energy density could be realized. The system displays a significant difference between the practical and theoretical energy densities (Table I). Part of the inefficiency is due to the difference in the theoretical Al-air voltage (2.7V) and the practical operating Al-air voltage (1.35V). The goal of this program was to improve the practical energy density of the Al-air system. The focus of this Phase I program was to identify and evaluate alternative cathode materials to reduce this difference between the practical and theoretical energy density of the aluminum anode. Several new air cathodes were developed using different catalysts and carbons. These new cathodes were characterized and then discharged in actual aluminum air cells. One new air cathode formulation performed better than our existing cathode. The new Vulcan cathode performed better than the existing Mn cathode at the current densities of 5 and 10 mA/cm^2 with an improvement as high as 21%.

Table I: Gravimetric Energy Density of Various Battery Systems[1]

System	Electrochemical Equivalent of Metal (Ah/g)	Theoretical Cell Voltage (V)	Practical Operating Voltage (V)	Theoretical Energy Density of Metal (Wh/kg)	Practical Energy Density of Cells (Wh/kg)
Al-air	2.98	2.7	1.35	8,100	690 (Dry Cell) 320 (Wet cell)
Zn-air	0.82	1.6	1.2	1,300	340 (Button cell)
$LiSO_2$	3.86	3.1	2.8	13,000	260 (Cylindrical)
$LiMnO_2$	3.86	3.5	2.7	13,000	230 (Cylindrical)

2.0 TECHNICAL APPROACH

The goal of the Phase I program was to improve the energy density of the aluminum air system by changing the air cathode chemistry. During the Phase I study, the cathode formulation was modified by investigating new catalysts and carbons. A critical component of the aluminum-air battery is the air cathode, which serves as the oxygen-reducing electrode during battery discharge. The main factors affecting performance of this electrode are as follows:

- Type of catalyst for oxygen reduction reaction (to increase voltage)
- Type of carbon for oxygen reduction capacity (to increase capacity)

The type of catalyst used in the air cathode, and method of application onto the carbon, affects the operating voltage of the cell. Effective catalysts will increase the voltage of the cell. The catalyst also reduces the amount of energy needed to reduce molecular oxygen, and fully reduces oxygen to a two minus oxidation state producing more electrons for the cell. More electrons correspond to more energy available for the cell to produce. The carbon type is another important factor in the air cathode. Carbon affects the reduction rate of oxygen and the capacity of the cell. Carbons come in many types, forms, shapes, and surface areas. The carbons directly affect the porosity of the air cathode structure with our cathode fabrication technique. The main modifications we investigated were: the new ruthenium catalyst, a Vulcan carbon, and a carbon called VGCF. The three main modifications and the reasoning behind each will be discussed below.

---

[1] Data from Handbook of Batteries and Fuel Cells 3rd Edition (David Linden), except for the Al-air system which is based on previous Alupower Al-air cell.

2.1 Ruthenium Catalyst

Catalysts used in the existing cathodes include: platinum, silver, manganese and cobalt. Ruthenium is known for its catalytic ability and has received much attention in the fuel cell industry. Because cathodes for metal air cells are essentially the same for fuel cells, since they both reduce oxygen, ruthenium was selected to be investigated. Ruthenium metal (5 wt. % on carbon, from Aldrich) was used as a catalyst. Using the metal on the carbon saved time and money because the reactive site of the molecular oxygen is on the surface of the carbons. The carbon had a surface area of about 900 m^2/g, and the type was listed as "proprietary" by the manufacturer. The ruthenium catalyst should increase the voltage of the cell.

2.2 Vulcan Carbon

Vulcan XC-72R is carbon black with a surface area of 254 m^2/g (Cabot Corp.). It was chosen because it is a different form of carbon that is highly conductive. Vulcan XC-72R is an amorphous carbon that is more conductive than typical carbon blacks. It also has good processing characteristics. This form also has a lower surface area than the typical carbon used. Yardney uses Black Pearls, which has approximately 1500 m2/g. The Vulcan carbon should result in a cell with increased voltage, since it is highly conductive, and has the possibility of increasing capacity.

2.3 VGCF (Vapor Grown Carbon Fiber)

The vapor grown carbon fibers are nanoscale tubes (nanotubes) from Mitsubishi. This carbon is widely used as an additive in lithium ion batteries to increase conductivity. These highly conductive nanotubes were added to the air cathode structure in an attempt to decrease the resistance of the cathode. These carbon nanotubes will mix with the carbon and provide an electrical path from the catalyzed carbon particles, where the oxygen reduction takes place, to the metal current collector. VGCF should increase the conductivity, thus increasing the voltage at high rates of discharge. There is a chance of capacity gain also.

Another cathode was made with no catalysts present to verify that metal catalysts improve the performance of the cathodes. All modifications mentioned above involved a change in only one parameter to test its effect on our existing cathodes structures. This way the change in the cathodes performance can be attributed to the new modification.

3.0 WORK COMPLETED

3.1 Cathode Formulation and Construction

Air cathodes were made using different catalysts and carbons (see Table II) following the procedure in the proposal. The low-cost air cathode patented by Alupower consists of two active carbon/catalyst layers sandwiching a nickel current collector with a hydrophobic Teflon film on the airside of the cathode (Figure 1). The parameters tested were particular types of catalysts and carbons. The cathodes contained metals such as: manganese, silver, cobalt, platinum, and ruthenium. The carbons used were Black Pearls 2000, proprietary carbons, Vulcan XC-72R, and Vapor Grown Carbon Fibers (VGCF). There were nine different types of cathodes, and each batch was large enough in area to produce several electrodes for testing.

Table II Cathode types with designated catalysts and carbons. The '*' represents new cathode formulations tested. BP2000 is Black Pearls 2000, Vulcan is Vulcan XC-72R, and 'not designated' means the supplier of catalyzed carbon has 'proprietary' carbon, VGCF is vapor grown carbon fibers (nanoscale).

Cathode Type	Catalyst	Carbon
1	Mn	BP2000
2	Ag	BP2000
3	Co and Mn	BP2000
4	Co	BP2000
5	Pt	Not designated
6*	Ru	Not designated
7*	Mn	Vulcan
8*	No catalyst	BP2000
9*	Mn	BP2000 + VGCF

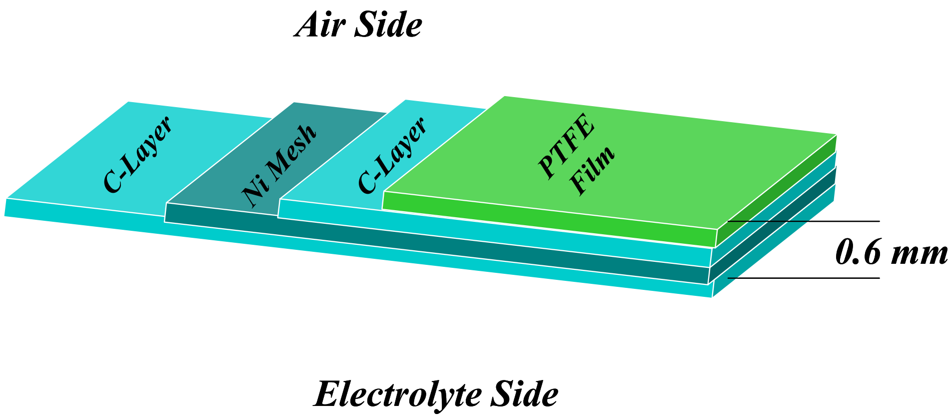

Figure 1 Diagram of the layered carbon electrode used as an air cathode in aluminum air cells. The PTFE is a Teflon membrane to repel water from the atmosphere. The "C" is the carbon layer that contains the metal catalysts. The nickel mesh is the current collector.

3.2 Cathode Characterization

The structure, elemental composition, and catalyst distribution of the cathodes was studied by Scanning Electron Microscopy (SEM). This provided detailed images of the cathodes to investigate porosity and coating. Elemental analysis was useful for determining the efficiency of mixing, coating, and distribution of the catalysts.

3.3 Cathode Testing

The cathodes' performance was tested by two methods: polarization with a three-electrode measurement, and by discharging in a SOFAL cell which are detailed below.

The polarization test set up consists of a test cell with removable electrodes (Figure 2). An anode and the air cathode to be tested are fitted into the sides of the test cell. These electrodes are discharged at different rates to observe the polarization. Polarization is essentially the electrical energy expended to drive the reaction forward. Lower polarization corresponds to less wasted energy, which means more of the potential energy in the aluminum anode is being utilized. Polarization tests were done both in 9% NaCl (aq) and 6.5 M KOH (aq) electrolytes. The NaCl (aq) electrolyte was used to test the new cathodes since the existing cathodes were tested in that electrolyte previously. 6.5 molar KOH (aq) is the optimal concentration for performance as it allows for the precipitation of the aluminum from the electrolyte.

New cathodes were also tested as components in actual SOFAL cells (Figure 3). SOFAL stands for Special Operations Forces Aluminum-Air Battery. These are aluminum air primary battery hybrid systems manufactured here (Figure 4). Each unit contains 16 cells for the aluminum battery and these were the cells we tested the new cathodes in. In the SOFAL cell, each cell contains two air cathodes around a patented aluminum alloy anode consisting of 99.995% Aluminum and a smaller percentage of magnesium and tin (see Figure 3). The anode's dimensions were is 3.5" x 2 " which corresponds to 7 in^2 (45 cm^2). The cathodes are about 2.5" x 4" in dimension which has an area of 10 in^2 (65 cm^2). The electrolyte was 6.5 M KOH (aq) solution with an additive of sodium stannate. This additive reduces the corrosion of the aluminum alloy and evolution of hydrogen gas. These cells fit into the SOFAL unit but were not tested in the full battery design. SOFAL cells were discharged on a computer controlled battery cycling system at 2.0 amps, 22mA/cm^2, 22°C and with a pressure about 1 atmosphere in air.

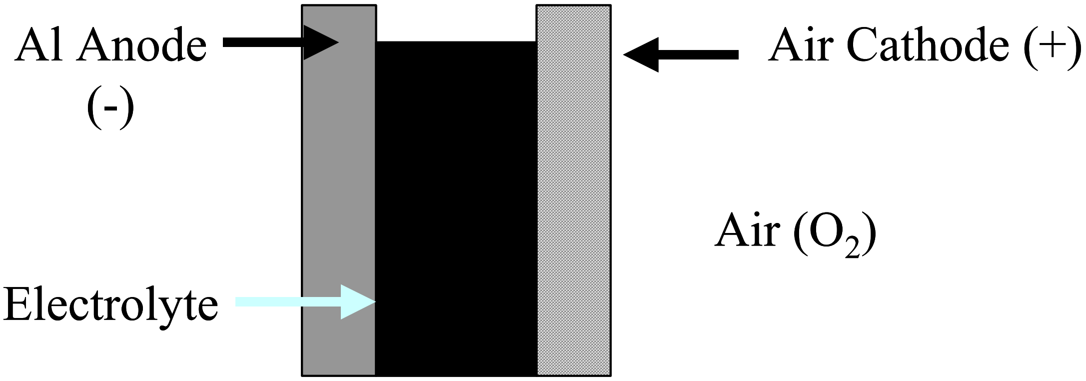

Figure 2 Diagram of the test cell used to measure polarization. The reference electrode would be located in the electrolyte.

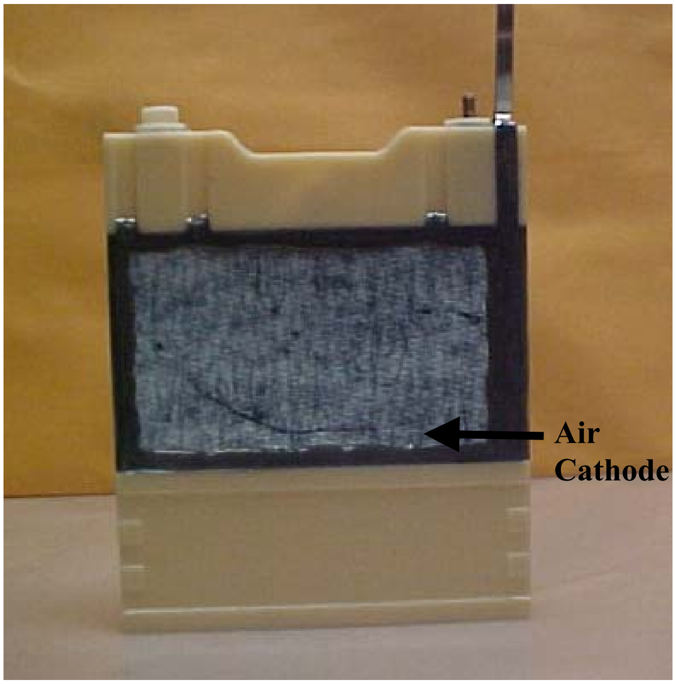

Figure 3 Picture of the actual SOFAL cells used to test the new air cathodes.

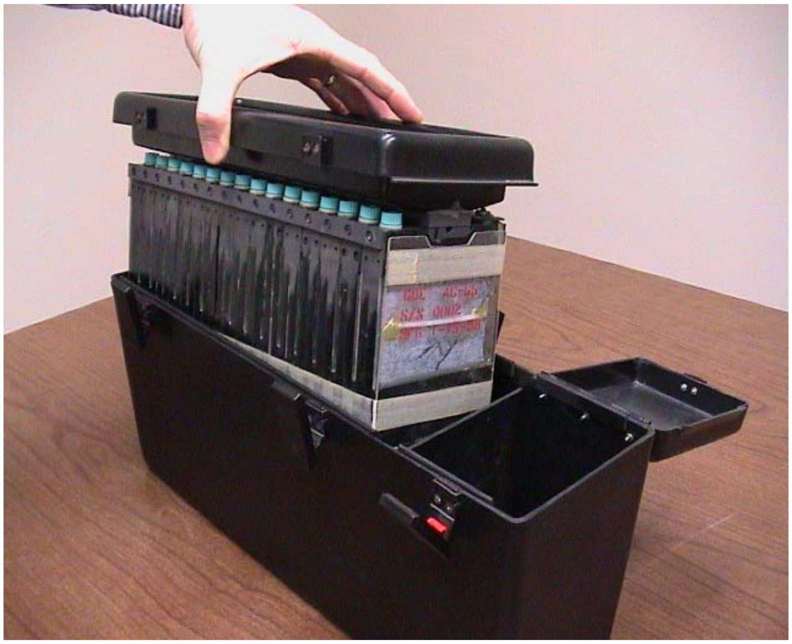

Figure 4 View of the SOFAL aluminum air battery unit. This unit is an aluminum air battery produced by the company. The SOFAL cells are stacked together inside the unit. The cells are about four inches across.

4.0 RESULTS

Several new cathodes were constructed with different catalysts and carbons (Table II). These cathodes were then analyzed by SEM for structural and elemental characteristics. Images were taken to view overall construction and pores. The cathode must contain pores to allow both the oxygen gas and electrolyte to come in contact with the catalysts and carbon. Due to the catalysts' role and the cost of precious metal catalysts it is important to evenly distribute the catalysts in the air cathode and prevent clumping. Distributing the catalysts increases the reactivity of the cathode, and decreases material cost. Elemental analysis was done to view the elements present and the distribution of the metal catalysts. The image below (Figure 5) is representative of the cathodes constructed. The images of the cathodes were similar and a representative sample from the Mn catalyzed air cathode (number 1 in Table II) is used to illustrate the porosity and distribution of catalysts in both Figure 5 and Figure 6.

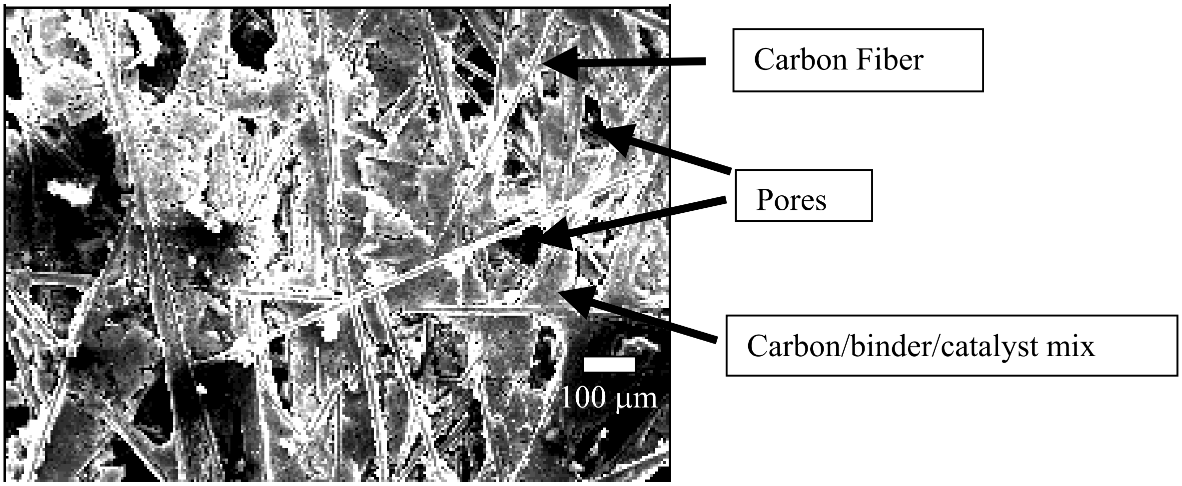

Figure 5 Scanning electron microscope (SEM) image of the Mn catalyst air cathode showing porosity and an open nature.

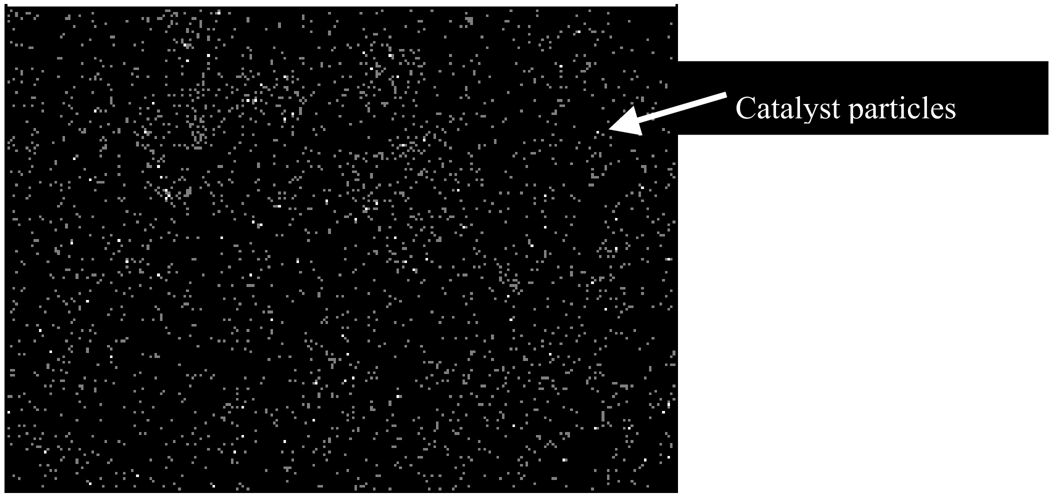

Figure 6 SEM image of the Mn catalyst air cathode (same as Figure 5) showing the Mn catalyst well distributed over the cathode structure.

Figure 5 show the fibrous non-woven carbon mat with the carbon/binder/catalyst mixture (white and gray portions) bound to the mat with many large and small pores (black portions) through out the air cathode to allow passage of electrolyte and oxygen. Figure 6 is the elemental analyses showing the distribution of the Mn catalyst of the same exact portion seen in Figure 5 with the white dots representing the Mn particles. Note how the particles are small and widely distributed in the air cathode. Overall, these pictures represent very good air cathode construction with open pores and a highly distributed catalyst.

4.1 Polarization Tests

Polarization tests were done on the new cathodes in two types of electrolytes; 9% NaCl (aq) and 6.5 M KOH (aq). The NaCl (aq) electrolyte was used to test the new cathodes since the existing cathodes were tested in that electrolyte previously. The 6.5 molar KOH (aq) is the optimal concentration for performance for basic electrolytes (high pH values). Low voltage values close to zero (on the y-axis) correspond to low polarization. Lowering the polarization essentially increases the energy obtained from the aluminum anode. The first graph (Figure 7) is the polarization in the NaCl (aq) electrolyte. This is a comparison of the new cathodes (ruthenium, Vulcan, and VGCF) with the existing cathode catalyzed by Mn (respectively cathodes numbered 6,7,9, and 1 in Table II). These tests were run in air at 22^{o}C and no heating of the cell or electrolyte was done. The conditions were 9%NaCl (aq) electrolyte with no additives, a nickel anode, and a standard calomel reference electrode (CRE). The Vulcan cathode (#7 in Table II) performed significantly better than all of the new cathodes and the existing cathode (Mn, #1). This can be due to Vulcan's highly conductive nature. At the lower current densities, the new Vulcan cathodes improved over 10% over the existing Mn cathode (Table III). At the higher densities of 30 mA/cm^2 they were equal.

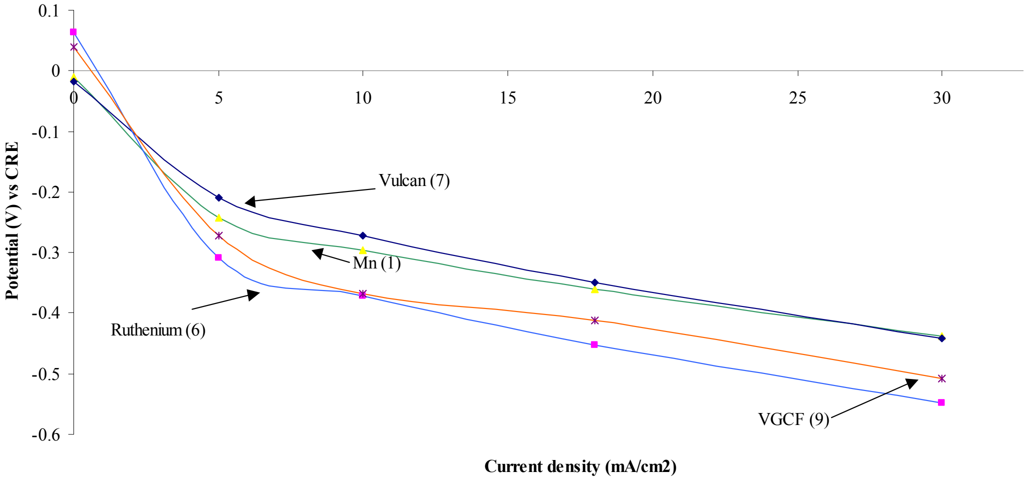

Figure 7 Polarization graph of the new air cathodes compared to the existing Mn catalyzed cathode in NaCl (aq) electrolyte. The labels and numbers of each curve refer to specific cathode formulations in Table II.

Table III Improvement of polarization with the new Vulcan cathode with the NaCl (aq).

		Current Densities	
	5 mA/cm^2	10 mA/cm^2	18 mA/cm^2
Existing Cathode (Mn) Potential	-.24 V	-.30 V	-.36 V
New Cathode (Vulcan) Potential	-.21 V	-.27 V	-.35 V
% Improvement	13	10	3

The second graph (Figure 8) is the polarization in the KOH (aq) electrolyte. This is a comparison of the new cathodes (Ruthenium, Vulcan, no catalyst, and VGCF) with the existing cathode catalyzed by Mn (respectively cathodes numbered 6, 7, 8, 9, and 1 in Table II). These tests were run at 22°C and no heating of the cell or electrolyte was done. The atmosphere was air. The conditions were 6.5 M KOH (aq) electrolyte with no additives, a nickel anode, and a standard calomel reference electrode (CRE). The new Vulcan cathode performed better than all of the other new cathodes formulations in the range of current densities tested. The new Vulcan cathode performed better than the existing Mn cathode at the current densities of 5 and 10 mA/cm^2, but at 18 mA/cm^2 the situation was reverse (Table IV). This can be due to the porosity of the Vulcan cathode not being optimized for higher rates (which can be done in the Phase II).

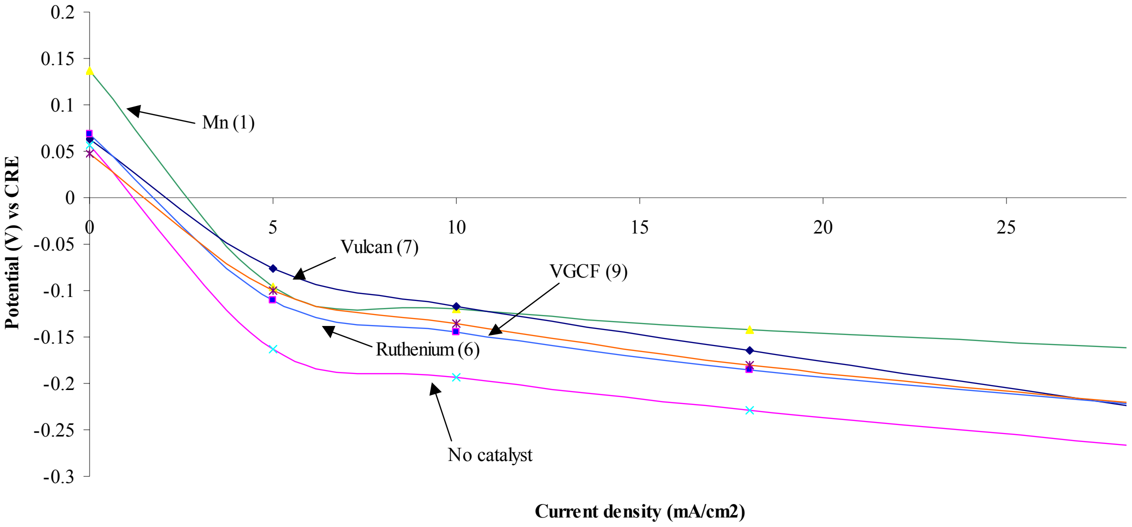

Figure 8 Polarization graph of the new air cathodes compared to the existing Mn catalyzed cathode in KOH (aq) electrolyte. The labels and numbers refer to specific cathode formulations in Table II.

Table IV Polarization comparison of the existing Mn cathode with the new Vulcan cathode with the KOH (aq) electrolyte.

		Current Densities	
	5 mA/cm^2	10 mA/cm^2	18 mA/cm^2
Existing Cathode (Mn) Potential	-.096V	-.120 V	-.142 V
New Cathode (Vulcan) Potential	-.076 V	-.117 V	-.165 V
% Improvement	21	2	-16

4.2 **Cell Discharge Testing**

Three new cathodes were tested by incorporating them into SOFAL cells and discharging. They were the Ruthenium, Vulcan, and VGCF cathodes (respectively cathodes numbered 6, 7, and 9 in Table II). The cells were discharged at a constant current of at 2.0 amps, a current density of 22mA/cm^2, at 22^{o}C in air at about 1 atm. of pressure (Figure 9). Better results would be obtained if the atmosphere was pure oxygen, and especially if it was pressurized. With oxygen gas at about 20% in the atmosphere, the cells rate of discharge would increase 5 times in pure oxygen presuming the same chemistry. If the pure oxygen was pressurized the cells performance would increase further and now the system would become more of a fuel cell. In the graphs the peaks around 20 hours are due to addition of more electrolyte that is according to the test procedure to maintain an adequate level of electrolyte. It is important to note that these cells did not leak electrolyte nor weep electrolyte. Some electrolyte was lost due the rate of evaporation. Each air cathode was run in duplicate and displayed very similar graphs showing the reproducibility of the cells. The air cathodes with VGCF additive had a higher voltage than those without. The main purpose of the VGCF additive was to increase the voltage of the cell. This was expected since the VGCF carbon was added with the intention to increase conductivity. This carbon additive only replaced 10% (weight) of the Black Pearls 2000. Higher amounts should further increase the conductivity and voltage. During the Phase I only one concentration was investigated to test feasibility. The VGCF air cathodes displayed the greatest energy produced, in terms of watt-hours, since it had the highest voltage. The Vulcan carbons (Vu) had the shortest discharge times around 32 hours. Surprisingly the Vulcan carbon air cathodes, which performed so well during the polarization tests, were not the top performers in the cell discharge testing. This is probably due the long discharge time of the SOFAL cell compared to the short discharge times of the polarization tests. The structure of the air cathode due to the morphology of the carbon is also a factor in the long-term discharge. The Vulcan carbons are more round in nature while the VGCF nanotubes are very long. The nanotubes should provide longer conductive paths for the electrons through the air cathode structure providing a structure with better endurance. The graph of the Ruthenium catalyzed cathode (Ru) was about the average of the other two in terms of voltage, but did have a 10% longer discharge. The ruthenium catalyst did not perform better than the lower cost manganese (Mn) catalysts used in both the VGCF and Vulcan air cathodes. Since the current was 2 amps the capacity is twice the discharge hours. The Vulcan, VGCF, and Ruthenium cathodes produced 65, 71, and 75 amp hours respectively, until the 1.2 cutoff voltage.

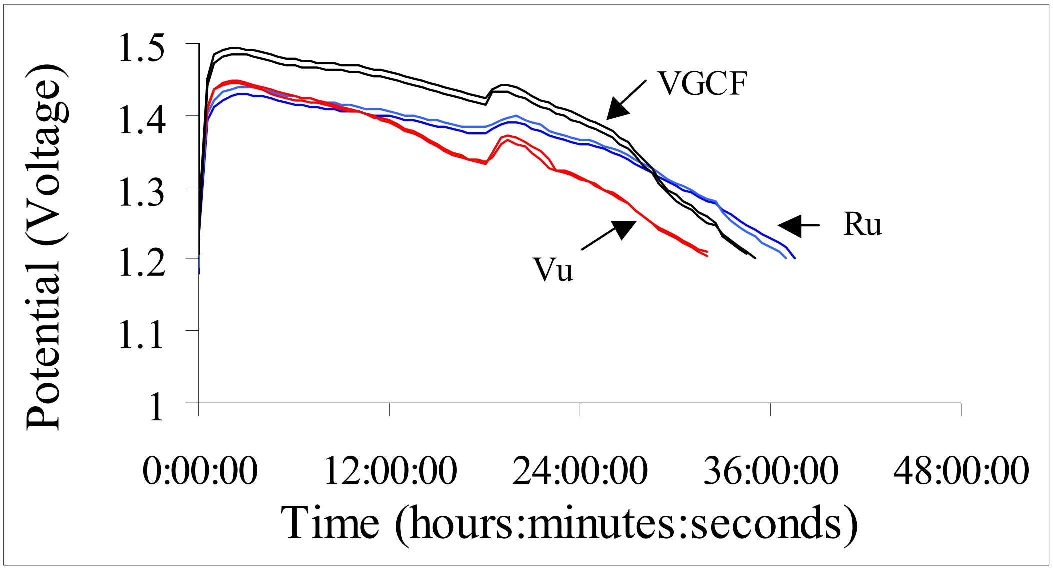

Figure 9 Discharge graph of three new cathodes in SOFAL cells.

5.0 CONCLUSIONS

The Phase I work demonstrated the feasibility of improving the air cathodes to use more available energy in the aluminum anode. The air cathodes chemistry was improved by using two different carbons: Vulcan and VGCF nanotubes. The Vulcan carbons decreased polarization and increased the efficiency of the system. The VGCF nanotubes increased the conductivity and voltage. In this study the chemistry was investigated and the air cathode structure was not optimized. The structure will be optimized in Phase II. The next generation air cathode will combine the strengths of all three carbons investigated in the Phase I. The Black Pearls 2000 will be used for its capacity, the Vulcan will decrease polarization, and the VGCF nanotubes will increase the voltage. All three carbons combined in one cathode will install the strength of each carbon to produce a superior cathode. This combined with the manganese (Mn) catalyst that performed well and has a low cost, should provide an energy efficient air cathode capable of harnessing more potential energy of the aluminum anode than current air cathodes.

The Phase II ideas and work include combining the new carbons together in one cathode, optimizing the structure, and further improving the conductivity of the cathode. The next area of improvement for the air cathodes appears to be conductivity. The best catalyst and the carbon types have been identified in these Phase I tests. The Vulcan and VGCF carbons and Mn metal catalyst appear to reduce oxygen at the required rates but the means of conducting the electrons to the tab of the cell needs further improvement. Modification of the current collector, binder, or Teflon layer will improve the performance of the cathode and thus the aluminum air system. These components can be investigated next to increase the useable energy form the aluminum air system. Improving the conductivity, using a blend of three carbons, and using the low cost Mn catalyst will provide an aluminum air battery capable of providing portable power for military equipment.

6.0 APPENDIX

The chemical reaction that occurs in an Al-air cell, using alkaline electrolyte, proceeds according to the following reaction:

$$4\ \mathrm{Al} + 3\ \mathrm{O_2} + 6\ \mathrm{H_2O} + 4\ \mathrm{OH^-} \rightarrow 4\ \mathrm{Al(OH)_4^-}$$

During discharge, the dissolved aluminate ion produced in this reaction precipitates out as crystalline hydrargillite (aluminum hydroxide):

$$\mathrm{Al(OH)_4^-} \rightarrow 4\ \mathrm{Al(OH)_3} \downarrow + \mathrm{OH^-}$$

In addition to producing energy in this reaction, a parasitic corrosion occurs at the anode that contributes to the dissolution of aluminum, generating minute quantities of hydrogen gas and heat.

$$2\mathrm{Al} + 6\mathrm{H_2O} + 2\mathrm{OH^-} \rightarrow 3\ \mathrm{H_2} \uparrow + 2\ \mathrm{Al(OH)_4^-}$$

This corrosion of the anode, in an alkaline electrolyte, is one of the factors that reduce the coulombic efficiency and the energy density of the Al-air cell.