

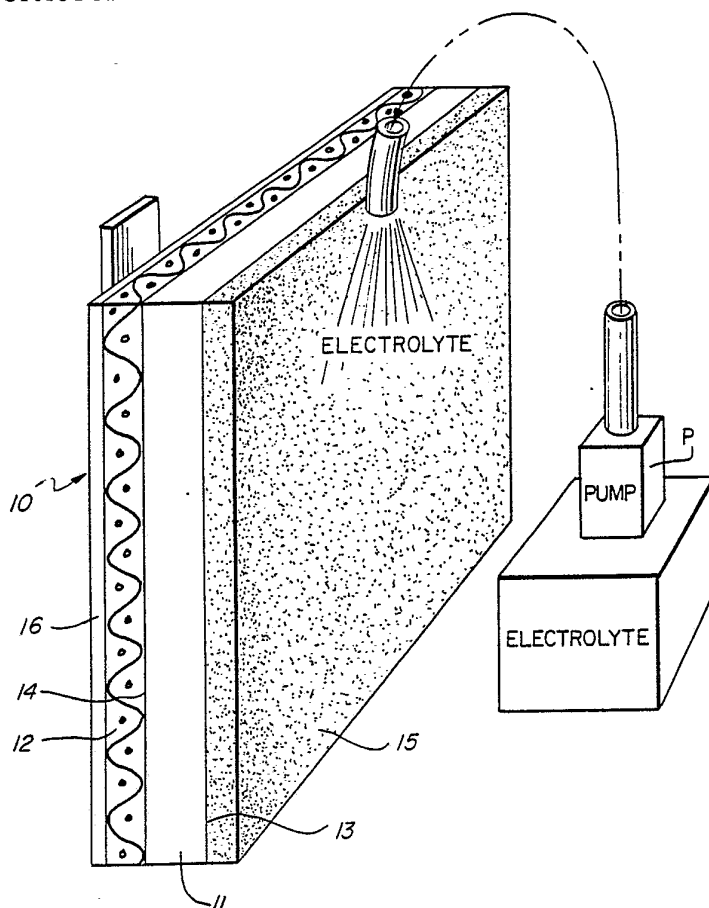


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US84/00202 (22) International Filing Date: 13 February 1984 (13.02.84) (31) Priority Application Number: 474,502 (32) Priority Date: 11 March 1983 (11.03.83) (33) Priority Country: US (71) Applicant: LOCKHEED MISSILES & SPACE COMPANY, INC. [US/US]; 1111 Lockheed Way, Sunnyvale, CA 94086 (US). (72) Inventors: MOMYER, William, Raymond ; 695 Toyon Place, Palo Alto, CA 94306 (US). LITTAUER, Ernest, Lucius ; 27305 Deer Springs Way, Los Altos Hills, CA 94022 (US). (74) Agents: EDGELL, G., Paul et al.; 10 Gould Center, Rolling Meadows, IL 60008 (US).		(81) Designated States: AU, BE (European patent), BR, DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent), NO. Published <i>With international search report.</i>

(54) Title: AIR CATHODE STRUCTURE MANUFACTURE**(57) Abstract**

An improved air cathode structure (10) for use in primary batteries and the like. The cathode structure includes a matrix active layer (11), a current collector grid (12) on one face of the matrix active layer, and a porous, nonelectrically conductive separator (15) on the opposite face of the matrix active layer, the collector grid and separator being permanently bonded to the matrix active layer. The separator has a preselected porosity providing low IR losses and high resistance to air flow through the matrix active layer to maintain high bubble pressure during operation of the battery. In the illustrated embodiment, the separator was formed of porous polypropylene. A thin hydrophobic film (16) is provided, in the preferred embodiment, on the current collecting metal grid.



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AIR CATHODE STRUCTURE MANUFACTURE

Technical Field

The United States Government has rights in this invention pursuant to Purchase Order No. 5513309 with The Continental Group, Inc. under Prime Contract No. W-7405-ENG-48 between The University of California and the U. S. Department of Energy. This invention relates to primary battery structures and, in particular, to air cathode structures for use therein.

Background Art

In one form of known electrochemical cell for use as a primary battery, aqueous electrolyte is flowed between a reactive metal anode and an air cathode. The anode is conventionally formed of a chemically and electrochemically reactive metal, such as lithium and sodium. Illustratively, such electrochemical cells are disclosed in U.S. Letters Patent 3,791,871 of Leroy S. Rowley, 4,001,043 of William R. Momyer, and 4,269,907 of William R. Momyer, et al, disclosures of which are hereby incorporated by reference.

It has been found that air cathode structures, such as those developed for fuel cells, are not adaptable for use in such electrochemical cells as they have been found to have insufficient durability to withstand degradation by the electrolyte flowing across the electrolyte face of the cathode element, and the pressure imbalances which are present at the cathode structure during discharge of the electrochemical cell.

Illustratively, in U.S. Letters Patent 4,364,805 of Douglas K. Rogers, an air cathode is disclosed utilizing air blow-through at pressures in the range of 2 to 15 psig.

In U.S. Letters Patent 4,269,907 of William R. Momyer et al, an electrochemical cell is disclosed wherein the reactive metal anode is separated from the cathode by a nonconductive flow screen.

In U.S. Letters Patent 3,438,815 of Jose D. Giner, an electrochemical device is disclosed wherein at least one of the anode and cathode comprises an integral porous metal layer in physical contact



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with a separate catalytic layer. The integral porous metal layer is in contact with the electrolyte of the cell in operation thereof.

In the above indicated U.S. Letters Patent 4,269,907 of William R. Momyer et al, a nonconductive porous element is disposed between the anode and cathode to maintain proper spacing therebetween.

Disclosure of Invention

The present invention comprehends an improved air cathode structure for use in a primary battery having a reactive metal anode and an aqueous electrolyte which is flowed against one surface of the air cathode structure. The invention comprehends provision of such an air cathode structure having a matrix active layer, a current collector grid on one face of the matrix active layer, and a porous, nonelectrically conductive separator on the opposite face of the matrix active layer, the collector grid and separator being permanently bonded to the matrix active layer, the separator having a preselected porosity providing low IR losses and high resistances to air flow through the matrix active layer to maintain high bubble pressure characteristics thereof.

In the illustrated embodiment, the separator comprises porous polypropylene.

In a modified embodiment, the separator comprises asbestos paper.

The invention further comprehends the improved method of forming such an improved air cathode structure for use in a primary battery wherein an electrically insulative porous separator is integrally bonded to a face of a matrix active layer opposite the current collector face thereof.

In the illustrated embodiment, the step of integrally bonding the separator to the matrix active layer comprises a step of thermal bonding.

In the illustrated embodiment, the thermal bonding is carried out under pressure.

Illustratively, the separator, in the illustrated embodiment, is bonded to the matrix active layer by hot pressing thereof thereagainst.

The porosity of the insulative separator is preselected to minimize IR drop therethrough while maintaining a high resistance to air



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flow through the matrix active layer.

The improved air cathode structure and method of manufacture thereof are extremely simple and economical while yet providing the highly improved primary battery means discussed above.

Brief Description of the Drawing

Other features and advantages of the invention will be apparent from the following description taken in connection with the accompanying drawing wherein the figure is a fragmentary perspective view of the air cathode structure embodying the invention.

Best Mode for Carrying Out the Invention

In the illustrative embodiment of the invention as disclosed in the drawing, an improved air cathode structure generally designated 10 for use in a reactive metal-aqueous electrolyte-air primary battery is shown to include a matrix active layer 11. A current collector grid 12 is provided on one face of the cathode layer 11.

As indicated briefly above, in such reactive metal-aqueous electrolyte-air cathode batteries, the electrolyte flowing from a delivery pump P tends to degrade surface 13 of the cathode against which it is flowed, i.e., opposite the air surface 14 to which the collector grid 12 is bonded.

As indicated briefly above, the invention comprehends the provision of a porous control layer 15 on surface 13. In the illustrated embodiment, porous layer 15 comprises a layer of porous polypropylene, which is permanently bonded to the matrix active layer 11 surface 13 as by thermal bonding thereto. Illustratively, the polypropylene layer is permanently bonded to the layer 11, in the illustrated embodiment, by a hot pressing operation.

As further shown in the drawing, a hydrophobic, thin protective film 16 is provided on the current collector grid 12, and in the illustrated embodiment, this film comprises a polytetrafluoroethylene film, which is similarly permanently bonded to the grid in the hot pressing operation.

Porous layer 15 effectively defines a separator for effectively preventing electrical shorting between the cathode and anode at the



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narrow electrode spacings conventionally utilized in reactive metal-H₂O-air primary batteries.

Further, the porous layer 15 permits the pressurized air directed to surface 14 through the layer 16 and grid 12 to be at a positive pressure, such as in the range of 2 to 15 psig, relative to the electrolyte pressure.

Still further, the porosity of the separator layer 15 is preselected to minimize IR losses in the battery while maintaining the desired back pressure, i.e. maintaining a high "bubble pressure" for the air electrode structure. By maintaining the high bubble pressure, air is effectively precluded from percolating through the porous structure into the electrolyte, while yet being efficiently provided to the matrix active layer 11 in the operation of the battery.

Other porous materials may be utilized within the scope of the invention and, illustratively, the porous layer 15 may be formed on Quinterra asbestos paper.

Air cathodes manufactured as discussed above showed high resistance to degradation by the flowing electrolyte, while providing high electrical performance at discharge rates, such as 200 milliamperes per square centimeter.

In the illustrated embodiment, the matrix active layer had a thickness of approximately 8 to 10 mils, the collector grid had a thickness of approximately 4 to 5 mils, the polypropylene porous layer had a thickness of approximately 3 to 5 mils, and the porous polytetrafluoroethylene layer had a thickness of several mils. All of the layers were permanently bonded together by the hot pressing operation. As indicated above, the insulating porous layer 15 effectively prevents shorting of the cells during discharge, while providing improved prevention of degradation by the flowing electrolyte and maintained high bubble pressure in the operation of the battery.

The foregoing disclosure of specific embodiments is illustrative of the broad inventive concepts comprehended by the invention.



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Claims

1. For use in a primary battery having a reactive metal anode, and an aqueous electrolyte, air cathode structure comprising:
 - a matrix active layer;
 - a current collector grid on one face of the matrix active layer; and
 - a porous, nonelectrically conductive separator on the opposite face of the matrix active layer, said collector grid and separator being permanently bonded to the matrix active layer, said separator having a preselected porosity providing low IR losses and high resistance to air flow through the matrix active layer to maintain high bubble pressure characteristics thereof.
2. The air cathode structure of Claim 1 wherein said separator comprises porous polypropylene.
3. The air cathode structure of Claim 1 wherein said separator comprises asbestos paper.
4. The air cathode structure of Claim 1 further including an outer protective layer permanently bonded on the collector grid.
5. The air cathode structure of Claim 1 further including an outer protective polytetrafluoroethylene layer permanently bonded on the collector grid.
6. The method of forming an improved air cathode structure for use in a primary battery, comprising integrally bonding an electrically insulative porous separator to a face of a matrix active layer opposite the current collector face thereof.
7. The method of forming an air cathode structure of Claim 6 wherein said step of integrally bonding the separator to the matrix active

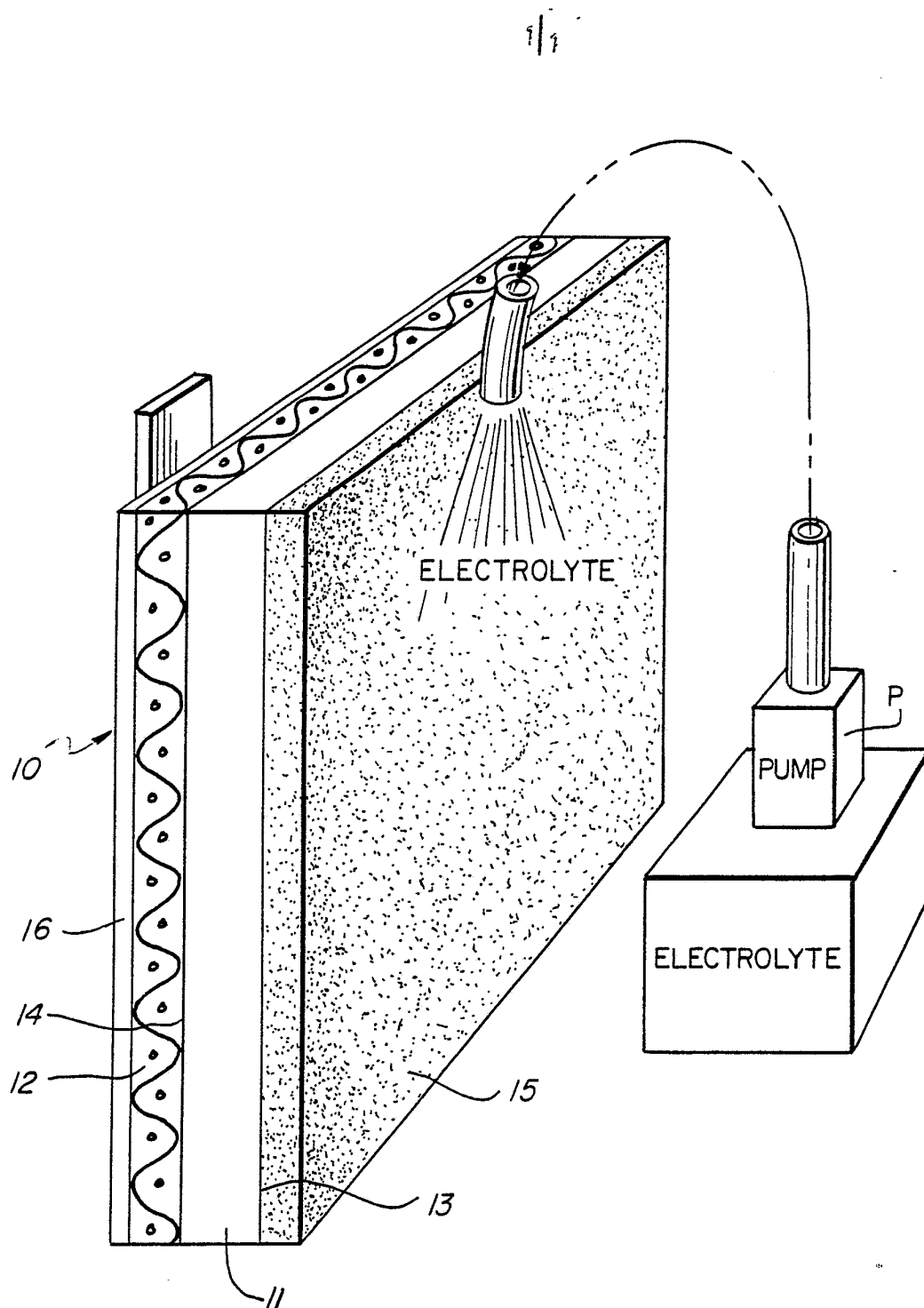


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layer comprises a step of thermal bonding.

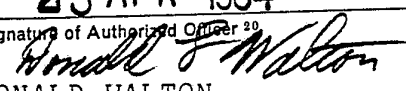
8. The method of forming an air cathode structure of Claim 6 wherein said step of integrally bonding the separator to the matrix active layer comprises a step of thermally bonding the separator to the matrix active layer under pressure.
9. The method of forming an air cathode structure of Claim 6 wherein said step of integrally bonding the separator to the matrix active layer comprises a step of hot pressing the separator to the matrix active layer under pressure.
10. The method of forming an air cathode structure of Claim 6 wherein the porosity of the insulative separator is preselected to minimize IR drop therethrough while maintaining a high resistance to air flow through the matrix active layer.





INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/00202

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INT CL 9 HO1M 2/16 US CL 429/27		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	429/27, 28, 29, 40, 41, 44	
U.S.	427/115 156/308.2	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	U.S., A, 3,043,898 (MILLER ET AL) 10 JULY 1962	
Y	U.S., A, 3,615,852 (GEHRING ET AL) 26 OCTOBER 1971	1-10
A	U.S., A, 4,104,197 (HEFFLER) 01 AUGUST 1978	
Y	U.S., A, 4,221,846 (ARMSTRONG ET AL) 09 SEPTEMBER 1980	1-10
A, P	U.S., A, 4,389,466 (JOY) 21 JUNE 1983	
A	U.S., A, 3,438,815 (GINGER) 15 APRIL 1969	
A	U.S., A, 3,791,871 (ROWLEY) 12 FEBRUARY 1974	
A	U.S., A, 4,001,043 (MOMYER) 04 JANUARY 1977	
A	U.S., A, 4,269,907 (MOMYER ET AL) 26 MAY 1981	
A	U.S., A, 4,364,805 (ROGERS I) 21 DECEMBER 1982	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
16 APRIL 1984	23 APR 1984	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 DONALD WALTON	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A

U.S., A, 4,364,806 (ROGERS II)
21 DECEMBER 1982V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.