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IN REPLY REFER TO:

Attorney Docket No. 84277 Date: 7 December 2004

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Serial Number 10/923,611

Filing Date 11 August 2004

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## 20041213 343

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## METHOD TO ACCELERATE WETTING OF AN ION EXCHANGE MEMBRANE IN A SEMI-FUEL CELL

TO ALL WHOM IT MAY CONCERN

BE IT KNOWN THAT (1) LOUIS G. CARREIRO, (2) CHARLES J. PATRISSI, AND (3) STEVEN P. TUCKER, employees of the United States Government, citizens of the United States of America, and residents of (1) Westport, County of Bristol, Commonwealth of Massachusetts, (2) Newport, County of Newport, State of Rhode Island and (3) Portsmouth, County of Newport, State of Rhode Island, have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

JEAN-PAUL A. NASSER, Esq. Reg. No. 53372 Naval Undersea Warfare Center Division, Newport Newport, RI 02841-1708 TEL: 401-832-4736 FAX: 401-832-1231 1 Attorney Docket No. 84277

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METHOD TO ACCELERATE WETTING OF AN 3 ION EXCHANGE MEMBRANE IN A SEMI-FUEL CELL 4 5 STATEMENT OF GOVERNMENT INTEREST 6 The invention described herein may be manufactured and used 7 by or for the Government of the United States of America for 8 governmental purposes without the payment of any royalties 9 thereon or therefore. 10 11 CROSS REFERENCE TO OTHER RELATED APPLICATIONS 12 This patent application is co-pending with a related patent 13 14 application entitled HIGH EFFICIENCY SEMI-FUEL CELL INCORPORATING AN ION EXCHANGE MEMBRANE (Navy Case No. 82737), 15 by, Maria G. Medeiros, Eric G. Dow, employees of the United 16 17 States government, Russell R. Bessette, Susan G. Yan, and Dwayne W. Dischert. 18 19 BACKGROUND OF THE INVENTION 20 21 (1) Field of the Invention 22 The present invention relates to semi-fuel cells, and more 23 specifically to a new treatment for ion exchange membranes that 24 accelerates the wetting of the membranes by aqueous electrolyte

solutions, thus reducing the start up time for metal/hydrogen
peroxide-based semi-fuel cells.

3 (2) Description of the Prior Art

A semi-fuel cell is essentially a hybrid of fuel cells and 4 batteries. Combining the refillable cathode or catholyte 5 oxidizer of fuel cells with the consumable anode fuel of 6 batteries. Semi-fuel cells are currently under investigation as 7 electrochemical power sources for unmanned undersea vehicles. 8 In a semi-fuel cell, a metal anode, such as magnesium or 9 aluminum along with a liquid catholyte, typically a strong 10 oxidizer like hydrogen peroxide, are consumed to produce energy. 11 The electrochemical reaction is given below for magnesium with 12 13 hydrogen peroxide in acid media. 14  $Mg -> Mg^{2+} + 2e^{-}$ Anode: 2.37 v 15 16  $H_2O_2 + 2H^+ + 2e^-$ 2 H<sub>2</sub>0 Cathode: 1.77 v 17 18  $Mg^{2+} + 2 H_20$ Cell Reaction: Mg +  $H_2O_2$  + 2H<sup>+</sup> 4.14v 19 20 In addition to the primary electrochemical reaction, 21 22 several parasitic reactions can also take place. 23 Decomposition:  $2 H_2 O_2 \rightarrow 2H_2 O_+ O_2$ 24

1 Direct Reaction:  $Mg + H_2O_2 + OH^- \rightarrow Mg^{2+} + 3 OH^-$ 

3 Corrosion: 
$$Mg + 2H_20 -> Mg^{2+} + 2 OH^- + H_2$$

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Of the three parasitic reactions listed above, the direct 5 reaction is the most detrimental to the operation of the semi-6 fuel cell since both magnesium and hydrogen peroxide are 7 consumed in a single step. Whereas magnesium corrosion can be 8 suppressed by pH adjustment and hydrogen peroxide decomposition 9 minimized by careful temperature control, prevention of the 10 direct reaction requires that the magnesium anode and hydrogen 11 peroxide catholyte be physically separated from each other. 12 То accomplish this, a semi-permeable membrane capable of ion 13 exchange is placed between the anode and cathode compartments of 14 the semi-fuel cell in order to isolate the anolyte and catholyte 15 solutions. 16

In order for ionic transport to occur across a membrane, 17 the membrane must first absorb the electrolyte solution. 18 The membrane's rate of absorption determines how quickly the semi-19 fuel cell reaches its operating voltage. In most applications, 20 semi-fuel cells are stored "dry" to prevent corrosion of the 21 magnesium anode. When electrical energy is needed, the semi-22 23 fuel cell's anode and cathode compartments are flooded with electrolyte so that power generation can begin. The membrane 24

must then wet immediately upon contact with the electrolyte, so 1 that the semi-fuel cell can begin to supply power. 2 In the 3 situation where the semi-fuel cell is being used with an unmanned underwater vehicle, the requirement for power 4 generation is within seconds of the vehicle's deployment. 5 Ion exchange membranes, such as Nafion®, require a long pre-soak 6 period (at least 12 hours) in aqueous electrolyte solution in 7 order to be fully wet and therefore fully functional in a semi-8 fuel cell. A method to accelerate the wetting of the membrane 9 is needed. 10

Several prior art methods exist for treating a Nafion® 11 membrane to make its performance more consistent and 12 reproducible. However, these techniques are designed to remove 13 impurities from the manufacturing process and/or exposure to the 14 environment rather than enhance the membrane's ability to absorb 15 liguid. Typical treatments involve boiling the membrane in 16 dilute acid followed by rinsing in boiling distilled water. 17 After treatment, the membrane must remain wet prior to use. 18 What is needed is a method that will allow an ion exchange 19 membrane such as a Nafion® membrane in a semi-fuel cell to be 20

stored dry and then to wet immediately when the semi-fuel cell

22 is activated.

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1	SUMMARY OF THE INVENTION
2	It is a general purpose and object of the present invention
3	to provide a method to increase the rate of absorption of
4	electrolyte solution by a Nafion® membrane.
5	This object is accomplished with the present invention by
6	providing a treatment method whereby a Nafion® membrane is
7	treated with glycerin (glycerol) to enhance its rate of
8	absorption of electrolyte solution
9	
10	BRIEF DESCRIPTION OF THE DRAWINGS
11	None.
12	
13	DESCRIPTION OF THE PREFERRED EMBODIMENT
14	The following is a detailed description of the treatment
15	method of the present invention. In the preferred embodiment a
16	membrane made of Nafion®, is used as the separating membrane in
17	a semi-fuel cell, however, other perfluorinated ionomer
18	membranes such as Felmion® and Aciplex-XR® could also be used.
19	In the preferred embodiment, the treatment method is applied to
20	Nafion® membranes NE-112, NE-1135, N-115 and N-117. Initially
21	the membrane is immersed in 1.5 M $H_2SO_4$ for 48 hours. The
22	membrane is then removed from the $H_2SO_4$ and rinsed in distilled
23	and or deionized $H_20$ . The membrane is then soaked in distilled .
24	and or deionized $H_20$ for 24 hours. The membrane is then removed

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1 from the  $H_20$  and then again rinsed in more distilled and or 2 deionized  $H_20$ . The membrane is then immersed in a polyhdric 3 alcohol for 48 hours. In the preferred embodiment of the method 4 the polyhdric alcohol is glycerin. After 48 hours the membrane 5 is removed from the glycerin and once again rinsed in distilled 6 and or deionized  $H_20$ . Finally the membrane is dried in air for 7 at least 48 hours prior to use.

8 Once treated in this manner, the Nafion® membrane may be 9 installed in the semi-fuel cell in the dry state and is ready to 10 instantaneously absorb electrolyte when the semi-fuel cell's 11 anode and cathode compartments are flooded with electrolyte, 12 thus allowing power generation to occur immediately.

The advantages of the present invention over the prior art 13 are that the present invention allows a Nafion® ion exchange 14 membrane to be stored dry within a semi-fuel cell module. This 15 is critical since the magnesium anode of a semi-fuel cell must 16 also be stored dry to prevent its corrosion. Upon activation of 17 the semi-fuel cell, the Nafion® membrane treated according to 18 the method of the present invention instantly allows ionic 19 transport to readily take place between the anode and cathode 20 compartments. The semi-fuel cell is then able to generate and 21 maintain sufficient voltage. In the situation where a semi-fuel 22 cell is used to power an unmanned underwater vehicle, the 23

present invention will reduce the vehicle's dependence on
standby/auxiliary batteries.

What has thus been described is a new treatment method for ion exchange membranes used in semi-fuel cells that accelerates the wetting of the membranes by aqueous electrolyte solutions, thus reducing the start up time for metal/hydrogen peroxide-based semi-fuel cells.

8 Obviously many modifications and variations of the present 9 invention may become apparent in light of the above teachings. 10 For example different types of ion exchange membranes may be 11 used. Different polyhydric alcohols may be used.

In light of the above, it is therefore understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

1	Attorney Docket No. 84277
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3	METHOD TO ACCELERATE WETTING OF AN
4	ION EXCHANGE MEMBRANE IN A SEMI-FUEL CELL
5	
6	ABSTRACT OF THE DISCLOSURE
7	A new treatment method for ion exchange membranes used in
8	semi-fuel cells that accelerates the wetting of the membranes by
9	aqueous electrolyte solutions, thus reducing the start up time
10	for metal/hydrogen peroxide-based semi-fuel cells.
11	Specifically, a Nafion® membrane that is intended for dry
12	storage in a semi-fuel cell is treated with glycerin (glycerol)
13	to enhance its rate of absorption of electrolyte solution when
14	the semi-fuel cell is activated.

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