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Attorney Docket No. 83879
Date: 1 August 2005

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Serial Number 11/121,711

Filing Date 05 May 2005

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# A HYBRID ELECTROCHEMICAL ENERGY SOURCE

TO ALL WHOM IT MAY CONCERN

BE IT KNOWN THAT (1) CHARLES J. PATRISSI, (2) ERIC G. DOW, and (3) MARIA G. MEDEIROS, employees of the United States Government, citizens of the United States of America, and residents respectively of (1) Newport, County of Newport, State of Rhode Island, (2) Barrington, County of Bristol, State of Rhode Island, and (3) Bristol, County of Bristol, State of Rhode Island, have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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Reg. No. 53372

Attorney Docket No. 83879

# A HYBRID ELECTROCHEMICAL ENERGY SOURCE

## STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefore.

## CROSS REFERENCE TO OTHER RELATED APPLICATIONS

Not applicable.

## BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to electrochemical energy sources, and more specifically to a hybrid electrochemical energy source that combines a lithium/water battery with a hydrogen/oxygen powered fuel cell.

(2) Description of the Prior Art

There continues to be a need for energy sources with a high energy density. In particular, there is a need for high energy density energy sources that can power unmanned undersea vehicles. Such energy sources when used to power such vehicles

are required to have an energy density greater than 600 Wh $kg^{-1}$. They also need to have long endurance and quiet operation. Additionally, they must be relatively inexpensive, environmentally friendly, safe to operate, reusable, capable of a long shelf life and not prone to spontaneous chemical or electrochemical discharge.

The zinc silver oxide (Zn/AgO) electrochemical couple has served as a benchmark energy source for undersea applications. Because of its low energy density, however, it is not suitable for unmanned undersea vehicles whose energy density requirements are seven times those of the Zn/AgO electrochemical couple.

In an effort to fabricate power sources for unmanned undersea vehicle with increased energy density (over zinc-based power sources), research has been directed towards aqueous lithium-based power sources. Lithium water and lithium silver oxide batteries have demonstrated high lithium coulombic efficiencies at high discharge rates. A low discharge rate lithium water battery has been engineered having high lithium efficiency during extended periods of operation (i.e. at least one year of continuous operation). Much of the development of both high discharge rate and low discharge rate aqueous lithium batteries focused on optimizing the coulombic efficiency of the lithium anode by reducing the corrosion rate. To accomplish this, a specific electrolyte composition must be developed for

each set of operating parameters, such as power, energy density and cell temperature.

The electrochemical and corrosion reactions during battery operation of lithium anode batteries, such as the lithium water battery, produce hydrogen ($H_2$ in gaseous state). Normally the hydrogen gas is vented as an unwanted byproduct. Venting hydrogen gas, however, creates unwanted noise in unmanned undersea vehicles. What is needed is an energy source that utilizes the hydrogen byproduct and by doing so increases the coulombic efficiency of the lithium anode battery and eliminates the noise associated with venting the hydrogen, resulting in a quiet operation energy source with high energy density.

## SUMMARY OF THE INVENTION

It is a general purpose and objective of the present invention to establish an electrochemical energy source for use in an underwater environment that utilizes the hydrogen byproduct of a lithium anode battery, such as the lithium water battery, and by doing so increases the coulombic efficiency of the lithium anode battery and eliminates the noise associated with venting the hydrogen, resulting in a quiet operation energy source with high energy density.

This objective is accomplished by combining a lithium water battery with a proton exchange membrane fuel cell. The reaction

between the lithium and water in the battery will generate electrical energy and hydrogen ($H_2$) gas. The hydrogen gas will then be collected and used as the fuel component for the proton exchange membrane fuel cell. The resulting hybrid electrochemical energy source has a low current density, long endurance, and a higher energy density for the entire system over the sum of its individual components.

## BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the invention and many of the attendant advantages thereto will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

FIG. 1 is a block diagram of the apparatus hybrid electrochemical energy source;

## DESCRIPTION OF THE PREFERRED EMBODIMENT

A hybrid power source is defined as "... combinations of multiple energy storage and conversion technologies into an integrated power system that provides optimal energy efficiency and appropriate operating parameters over a broad range of power levels." Referring now to FIG. 1 there is illustrated a diagram of the hybrid electrochemical energy source 10 composed of a

lithium water battery 12 and a proton exchange membrane fuel cell 14. The battery 12 is joined to an electrolyte reservoir 18. In alternate embodiments, the reservoir 18 could actually be the seawater surrounding an underwater vehicle containing the present invention. In the preferred embodiment, the reservoir contains an aqueous solution composed of potassium hydroxide (KOH), methanol and lithium hydroxide (LiOH). The battery 12 is also joined to a water reservoir 22 that can replenish the water as it is consumed via reaction with lithium. In the preferred embodiment, sensors 24 and control equipment 26 such as pumps are used to maintain the proper water level during operation. The battery 12 has a gas transfer means that accumulates and feeds the hydrogen gas byproduct to the fuel cell 14. In the preferred embodiment, a hose 16a is connected to the battery 12. The hydrogen gas vents through the hose to an accumulation tank 16 that collects the hydrogen gas until it is needed by the fuel cell 14. Another hose, 16b, is connected from the accumulation tank 16 to the fuel cell 14 to feed the hydrogen gas to the fuel cell 14. A regulator 28 in the fuel cell 14 maintains hydrogen gas pressure. In the preferred embodiment, the fuel cell 14 will also require oxygen as a fuel component. An oxygen source 20 is therefore attached to the fuel cell to feed it oxygen. In the preferred embodiment the oxygen source 20 is an oxygen containing species such as hydrogen peroxide ($H_2O_2$), however it

is not limited as such and could also be pressurized oxygen gas ($O_2$).

The electrochemical reactions in the lithium water battery 12 are shown in Equations 1-3:

Anode: $2Li \rightarrow 2Li^+ + 2e^-$ $E^\circ = 3.04$ V (1)

Cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^\circ = -0.83$ V (2)

Overall: $2Li + 2H_2O \rightarrow H_2(g) + 2OH^- + 2Li^+$ $E^\circ = 2.21$ V (3)

During the electrochemical production of electricity, the battery produces hydrogen gas ($H_2$) as shown in equation (3). Lithium water batteries are designed for long duration applications at low power. In a preferred embodiment, the lithium water battery 12 delivers a specific energy of 1800 to 2400 Wh per kg of lithium. The lithium water battery 12 uses an aqueous electrolyte 18 composed of potassium hydroxide (KOH), methanol and lithium hydroxide (LiOH) as illustrated in FIG. 1. The electrolyte 18 minimizes the corrosion reaction between the lithium and the water as illustrated in Equation 4 below:

Corrosion: $2Li + 2H_2O \rightarrow H_2(g) + 2OH^- + 2Li^+$ (4)

Since both corrosion and the production of electrochemical energy produce the hydroxide ion ($OH^-$) and hydrogen gas, it is critical to the battery performance to control the electrolyte concentration of the hydroxide ion and thereby minimize corrosion. Hydrogen gas and the hydroxide ion are produced in a 1:1 molar ratio. So, the increase in the hydroxide ion in the

lithium water battery 12 can be determined by measuring hydrogen gas with a mass flow meter 30. To keep the hydroxide ion within normal limits for the current density expected, two valves 32a, 32b, and a pump 34 would be required. A determination of hydroxide ion concentration in real time would be based on the starting concentration plus the amount produced by corrosion and electricity. To lower the hydroxide ion concentration, the two valves 32a and 32b would open and the control equipment 26 would add water while the pump 34 forces out lithium hydroxide into a holding tank 36. Pumping duration would control the amount of water necessary to reduce the hydroxide ion to the required concentration range. Simple calculations (i.e. converting hydrogen to hydroxide ion concentration) and pump control could be performed with the UUV onboard computer (not shown).

Although corrosion of the lithium does produce hydrogen, it is undesirable because it consumes lithium and produces no electrochemical energy, thereby reducing the overall coulombic efficiency of the energy source.

In the preferred embodiment, the fuel cell 14 is designed to deliver from 1 kW to 1 MW powered by hydrogen ($H_2$) and oxygen ($O_2$) regulated at 30 psig. The fuel cell 14 is capable of functioning at low temperatures, which is necessary for underwater vehicle applications. The fuel cell 14 is designed to work simultaneously with the battery 12 or independently.

Before use, the lithium water battery is stored dry (under argon). Therefore, it contains nothing that is reactive towards lithium so it can be transported and stored using procedures normally used in the art by the producers of lithium and lithium batteries.

The advantages of the present invention over the prior art are the increase in energy density and the increase in quiet operation. Generating electricity from excess hydrogen produced by the lithium water battery significantly increases the specific capacity of the lithium anode. Hydrogen gas is generated when lithium reacts with water electrochemically and parasitically as expressed above. Since hydrogen production is inevitable, the practical specific capacity of the hybrid electrochemical energy source is two times higher than a lithium water battery alone. Consuming the hydrogen gas rather than venting it eliminates the noise involved with the venting process allowing much quieter operation of the energy source for use in underwater vehicles where stealth is required. This invention is environmentally friendly in that the present invention is intended for use in underwater vehicles and must remain neutrally buoyant therefore there is no discharge of it's contents into the surrounding seawater. The hybrid electrical energy source of this invention has a low current density, long

endurance, and a higher energy density for the entire system over the sum of its individual components.

Obviously many modifications and variations of the present invention may become apparent in light of the above teachings. For example the exact composition of the electrolyte will be a function of the specific operating requirements of the power source, such as power, temperature, and energy density. In addition, it is likely that compounds other than those specified above will be used to minimize lithium corrosion and increase the energy density of the hybrid electrochemical energy source.

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.

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# A HYBRID ELECTROCHEMICAL ENERGY SOURCE

## ABSTRACT OF THE DISCLOSURE

A hybrid electrochemical energy source that combines a lithium/water battery with a hydrogen/oxygen powered fuel cell. The reaction between lithium and water in the battery generates electricity and hydrogen. Rather than vent the hydrogen and discard it, the generated hydrogen is collected and then used as fuel for the hydrogen/oxygen fuel cell, resulting in a quiet operation energy source with high energy density.

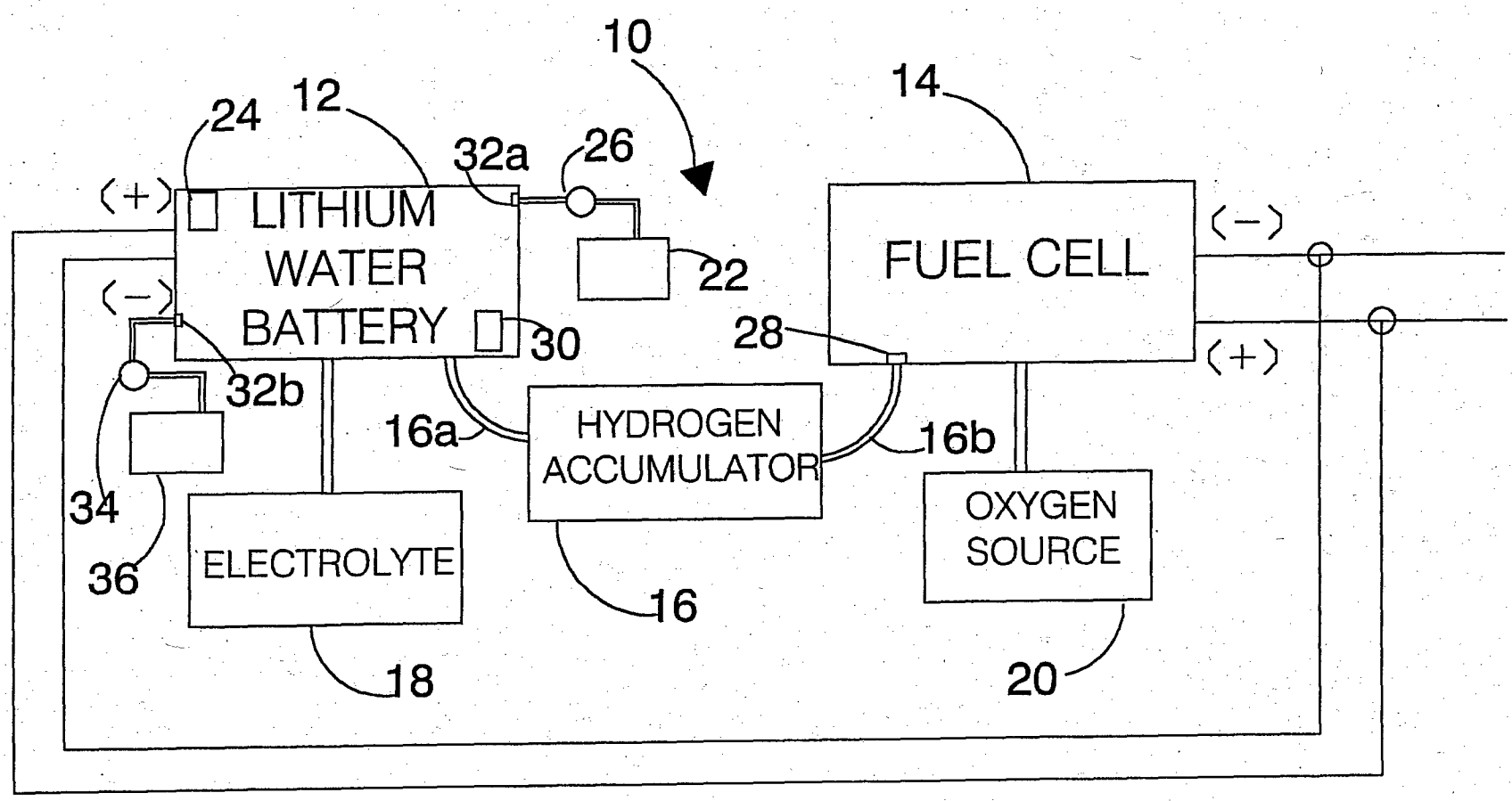
10
12
14
24
32a
26
(+)
LITHIUM
WATER
BATTERY
22
FUEL CELL
(−)
(−)
30
28
(+)
32b
16a
HYDROGEN
ACCUMULATOR
16b
34
OXYGEN
SOURCE
ELECTROLYTE
36
16
18
20

FIG. 1