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(54) Title: AN ENERGY STORAGE DEVICE, AN INORGANIC GELLED ELECTROLYTE AND METHODS THEREOF

(57) Abstract: The present invention is related to hybrid capacitors specifically to PbO_2/Activated Carbon hybrid ultracapacitors with an inorganic thixotropic-gelled-polymeric-electrolyte. The hybrid ultracapacitor of the present invention is simple to assemble, bereft of impurities, and can be charged/discharged rapidly with high faradaic efficiency.

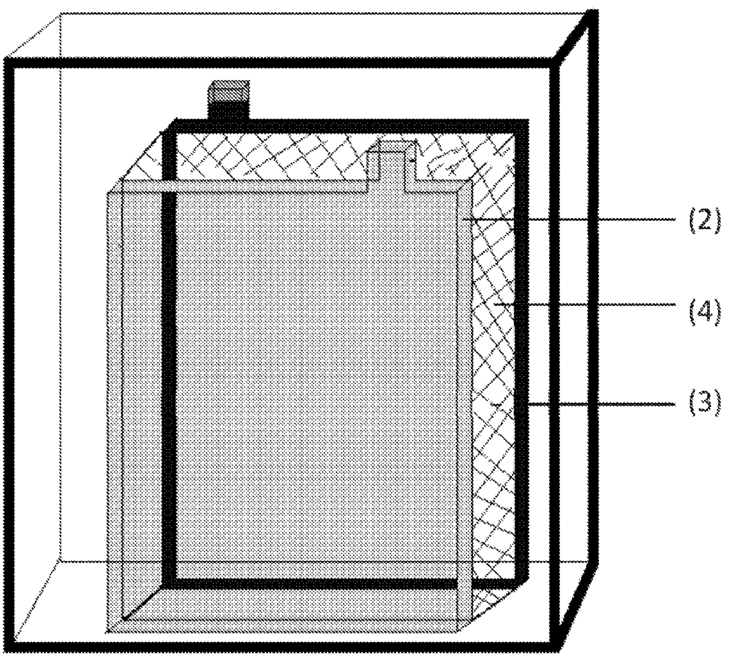

FIGURE 1

WO 2013/011464 A1

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"AN ENERGY STORAGE DEVICE, AN INORGANIC GELLED ELECTROLYTE AND METHODS THEREOF"

TECHNICAL FIELD

The present disclosure is related to hybrid capacitors, specifically to PbO_2/Activated Carbon hybrid ultracapacitors with an inorganic thixotropic-gelled-polymeric-electrolyte. The hybrid ultracapacitor of the present disclosure is simple to assemble, bereft of impurities and can be charged / discharged -rapidly- with high faradaic efficiency.

BACKGROUND OF THE INVENTION

Supercapacitors (also termed as ultracapacitors) are being projected as devices that could enable major advances in energy storage. Supercapacitors are governed by the same physics as conventional capacitors, but utilize high-surface-area electrodes and thinner dielectrics to achieve greater capacitances, allowing energy densities greater than those of conventional capacitors and power densities greater than those of batteries. Supercapacitors can be divided into three general classes, namely, electrical-double-layer capacitors, pseudocapacitors and hybrid capacitors. Each class is characterized by its unique mechanism for charge storage, namely faradaic, non-faradaic, and the combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte as in a battery electrode, while a non-faradaic mechanism does not use a chemical mechanism - rather, charges are distributed on surfaces by physical processes that do not involve the making or braking of chemical bonds similar to "the electrical double-layer". A hybrid supercapacitor combines a battery electrode where the energy is stored in chemical form, and an electrical-double-layer electrode where the energy is stored in physical form. A PbO_2/Activated Carbon supercapacitor comprises a positive plate akin to a lead acid cell and a high surface-area activated carbon electrode as negative plate. The charge-discharge reactions at the positive and negative plates of such a hybrid supercapacitors are as follows.

(+) plate: $PbSO_4 + 2H_2O \leftrightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e^-$

(-) plate: $2C + 2H^+ + 2e^- \leftrightarrow 2(C^-H_{ads}^+)_{dl}$

Accordingly, the net charge-discharge reactions for the hybrid supercapacitor can be written as follows.

$PbSO_4+2H_2O+2C \leftrightarrow PbO_2+ H_2SO_4+2(C\text{-}H_{ads}^{+})_{dl}$

The (+) plate is realized by electrochemical formation and subsequent cycling in sulfuric acid / perchloric acid, while the (-) plate is prepared by pasting activated carbon onto a graphite sheet. The said hybrid supercapacitor stores energy both in chemical and physical forms.

The hybrid capacitors known in the prior art employ conventional PbO_2 plates that require sizing and mixing of the active materials of appropriate compositions, pasting, drying, curing and formation. Such electrodes are not fully amenable to fast charge/discharge processes desired in a capacitor.

STATEMENT OF THE INVENTION

Accordingly, the present disclosure relates to an energy storage device (1), as shown in figure 1, comprising: a) substrate-integrated-lead-dioxide electrode (2), b) an activated carbon electrode (3), and c) a thixotropic inorganic-gel-polymer electrolyte (4) intercepted between the substrate-integrated-lead-dioxide electrode and the carbon electrode; an energy storage unit comprising plurality of energy storage device (1) as mentioned above, connected in series; a method of manufacturing an energy storage device (1), said method comprising acts of: a) preparing substrate-integrated lead dioxide electrode (2), b) preparing activated carbon electrode (3), and c) mounting the substrate-integrated lead dioxide electrode (2), the activated carbon electrode (3) with a thixotropic inorganic-gel-polymer electrolyte (4) in between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy storage device; a method of using energy-storage device (1) or energy storage unit as mentioned above, said method comprising act of conjugating said energy-storage device or unit with electrical device for generating electrical energy to supply energy to devices in need thereof; and an inorganic thixotropic-gelled-polymer-electrolyte.

BRIEF DESCRIPTION OF THE ACCOMPANYING FIGURES

Figure 1 shows schematic diagram of a cell [energy storage device (1)] from the 12V substrate-integrated PbO_2/activated-carbon ultracapacitor with inorganic thixotropic-gelled-electrolyte.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an energy storage device (1) comprising:

a) a substrate-integrated-lead-dioxide electrode (2),
b) an activated carbon electrode (3), and
c) a thixotropic inorganic-gel-polymer electrolyte (4) intercepted between the substrate- integrated-lead-dioxide electrode.

In an embodiment of the present disclosure, the energy storage device (1) is a hybrid capacitor.

In another embodiment of the present invention, the electrolyte acts as a separator.

In yet another embodiment of the present invention, the electrolyte is selected from a group comprising sulfuric acid, methanesulfonic acid and perflourosulfonic acid, preferably sulfuric acid.

In yet another embodiment of the present invention,, the electrolyte is a thixtropic-gel obtained by cross-linking silica with sulfuric acid.

In still another embodiment of the present disclosure, the sulfuric acid has concentration ranging from about 4M to about 7M, preferably about 6M.

In still another embodiment of the present disclosure, the energy storage device (1) is of faradaic efficiency ranging from about 88% to about 90%, preferably about 89%.

The present disclosure relates to an energy storage unit comprising plurality of energy storage device (1) as mentioned above, connected in series.

The present disclosure relates to a method of manufacturing an energy storage device (1), said method comprising acts of:

a) preparing substrate-integrated lead dioxide electrode (2),
b) preparing activated carbon electrode (3), and
c) mounting the substrate-integrated lead dioxide electrode (2), the activated carbon electrode (3) with a thixotropic inorganic-gel-polymer electrolyte (4) in between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy storage device.

In another embodiment of the present invention, the electrolyte acts as a separator.

The present invention relates to a method of using energy-storage device (1) or energy storage unit as mentioned above, said method comprising act of conjugating said energy-storage device or unit with electrical device for generating electrical energy to supply energy to devices in need thereof.

The present invention relates to an inorganic thixotropic-gelled-polymer-electrolyte.

In an embodiment of the present invention, the electrolyte is prepared by cross-linking fumed silica with sulfuric acid.

In another embodiment of the present invention, the sulfuric acid has concentration ranging from about 4M to about 7M, preferably about 6M.; and wherein the electrolyte is capable of acting as a separator between electrodes of an energy storing device.

The present invention is related to realizing substrate-integrated PbO_2/Activated-carbon hybrid ultracapacitor bereft of impurities. The hybrid ultra capacitors of the present invention are simple to assemble, bereft of impurities, and can be charged / discharged rapidly with faradaic efficiencies as high as 89%.

In the current invention, the positive electrodes, namely substrate-integrated PbO_2, are made by electrochemical formation of pre-polished and etched lead metal sheets. Specifically, the substrate-integrated PbO_2 is obtained by oxidizing $PbSO_4$ which is formed when lead sheets come in contact with sulfuric acid. Subsequent to their formation, the electrodes are washed copiously with de-ionized water to wash off all the impurities.

Generally, electrodes in batteries are charged at C/10 rate (10h duration) and discharged at C/5 rate (5h duration). If the battery electrodes are charged/discharged at the rate C (1 hour) or at higher rates, their cycle-life is affected. Faradaic efficiency of the battery electrodes depends on the particle size of the active materials, porosity of the electrode, internal resistance of the electrode, etc. The battery electrodes have low faradaic efficiency.

The present invention provides electrochemically formed and substrate-integrated PbO_2 as battery-type electrode, which can be charged and discharged at higher rates, while retaining faradaic efficiencies as high as 89% with thixotropic gelled polymeric electrolyte.

The capacitance is calculated from the discharge curve using the equation:

$$C(F) = I(A) \times t(s)/(V_2-V_1)$$

where V_2 is the voltage at the beginning of discharge and V_1 is the voltage at the end of discharge.

Pulsed cycle-life test involves the following four steps.

Step 1. Charging the ultracapacitor at 3A for 1 s.
Step 2. Open-circuit voltage measurement for 5s.
Step 3. Discharge the ultracapacitor at constant current at 3A.
Step 4. Open-circuit voltage measurement for 5s.

The hybrid capacitor of the present invention is connected in series to obtain capacitors wherein the cell voltage gets added up, while the effective capacitance decreases, akin to conventional capacitor.

The method of manufacturing substrate-integrated PbO_2/activated-carbon hybrid ultracapacitor (1) essentially comprises: preparing substrate-integrated lead dioxide electrode (2), preparing activated-carbon electrode (3), and mounting the substrate-integrated-lead-dioxide electrode (2), the activated-carbon electrode (3) with an inorganic thixotropic-gelled-polymeric-electrolyte (4) in between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy-storage device.

The present invention discloses substrate-integrated PbO_2/activated-carbon hybrid ultracapacitors(HUC) with an inorganic thixotropic-gelled-polymer-electrolyte, which also acts as a separator. The gelled separator herein enhances the overall performance of the HUC with respect to critical parameters, such as capacitance and cycle-life.

The devices of the present invention can be easily conjugated with electrical devices for generating electrical energy as supply energy to devices in need thereof.

The technology of the instant invention is elaborated in detail with the help of following examples. However, the examples should not be construed as limiting the scope of the invention.

Example:

Preparation of substrate-integrated PbO_2/Activated Carbon Hybrid Ultracapacitors

A. Preparation of Substrate-Integrated PbO_2 Electrodes.

Substrate-integrated- PbO_2 electrodes are prepared by etching pre-polished lead sheets (thickness approximately 300 μm) in 1M HNO_3 for 60s and subsequently washed copiously with deionized water. The sheets were then immersed in 6 M aqueous H_2SO_4 with 0.1 M $HClO_4$ as additive at room temperature. On immersing in aqueous sulfuric acid, a thin layer of lead sulfate is formed on the surface of the lead sheet which is oxidized to PbO_2 by using it as anode in an electrochemical cell fitted with a counter electrode. The process is repeated about five times to prepare the fully-formed substrate-integrated PbO_2 electrodes.

B. Preparation of PVDF bonded activated carbon electrodes.

Activated-carbon electrodes are prepared by pasting activated carbon ink containing polyvinylidene difluoride (PVDF) as a binder. In brief, a carbon paste was obtained by mixing 85 wt.% of high-surface-area carbon (BET surface area is about 2000 m^2/g and particle size of about 10 μm) with 10 wt. % of carbon black (particle size = ~ 1 μm) and 5 wt. % of binder like PVDF dissolved in an appropriate quantity of dimethylformamide solvent or Teflon (PTFE, poly-tetrafluoroethylene). Typically, 0.1 g of PVDF is dissolved in 10 ml of DMF and 1.7 g of high surface area carbon (Meadwestvaco product No. 090177) and 0.2 g of carbon black was added. The mixture was mixed well in an ultrasonicator for 5 min. The resulting carbon ink was brush coated onto two graphite electrodes of area 4.5 cm x 7 cm, which had a tag area of 0.5 cm width and 0.5 cm length. The carbon paste was applied on both sides of the carbon electrodes so that each side of the electrode in order to get a 0.5 g of active material. Then the electrodes were dried in air oven for overnight (about 10 h) at 80°C.

C. Assembly of 12V Substrate-Integrated PbO_2-AC Hybrid Ultracapacitors (HUCs)

A 12V substrate-integrated PbO_2/Activated carbon hybrid ultracapacitor was realized by connecting six single cells in series in a commercial lead-acid battery container. Each cell of this 12V hybrid ultracapacitor comprises 9 positive and 8 negative plates, each of size 4.5 cm x 7 cm, with the tag area of 0.5cm x 0.5 cm and 0.3 mm thickness for the positive plate and 0.8 mm thickness for negative plates. An inorganic thixotropic-gelled-polymer-electrolyte that was also used as a separator was prepared by cross-linking fumed silica with 6 M sulfuric acid. A unique method was used to interconnect the graphite electrodes. The tag portion of the negative electrodes is electroplated with tin, followed by electroplating with lead, which facilitates the graphite electrode tags to be soldered to each other. The graphite electrodes in each cell were soldered with lead by torch-melt method using an appropriately designed group-burning fixture. Subsequently, the cells were interconnected in series.

The gelled electrolyte separator used herein enhances the overall performance of the HUC with respect to critical parameters such as cycle-life and capacitance. The comparative data for the 12V Absorbent Glass-Mat (AGM)-HUC and 12 V Gelled-HUC are given in Table 1 below.

	AGM-HUC	Gelled-HUC
Internal Resistance	90 m ohm	120 m ohm
Faradaic Efficiency	91%	89%
Capacitance		
300mA	184 F	269 F
600mA	163 F	255 F
900mA	150 F	239 F
1.2A	138 F	222 F
1.5A	130 F	208 F
Leakage Current after 24h	15 mA	35 mA
Self Discharge after 24 h	13 %	16 %

Table 1: Comparison between AGM-HUC and Gelled-HUC.

While various aspects and embodiments of the present invention have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

We Claim

1. An energy storage device (1) comprising:
    a) a substrate-integrated-lead-dioxide electrode (2),
    b) an activated carbon electrode (3), and
    c) a thixotropic inorganic-gel-polymer electrolyte (4) intercepted between the substrate- integrated-lead-dioxide electrode and the carbon electrode.
2. The energy storage device as claimed in claim 1, wherein the energy storage device (1) is a hybrid capacitor.
3. The energy storage device as claimed in claim 1, wherein the electrolyte acts as a separator.
4. The energy storage device as claimed in claim 1, wherein the electrolyte is selected from a group comprising sulfuric acid, methanesulfonic acid and perflourosulfonic acid, preferably sulfuric acid.
5. The energy storage device as claimed in claim 4, wherein the electrolyte is a thixotropic gel obtained by cross-linking silica with sulfuric acid.
6. The energy storage device as claimed in claim 4, wherein the sulfuric acid has concentration ranging from about 4M to about 7M, preferably about 6M.
7. The energy storage device as claimed in claim 1, wherein the energy storage device (1) is of faradaic efficiency ranging from about 88% to about 90%, preferably about 89%.
8. An energy storage unit comprising plurality of energy storage device (1) of claim 1 connected in series.
9. A method of manufacturing an energy storage device (1), comprising acts of:
    a) preparing substrate-integrated lead dioxide electrode (2),
    b) preparing activated carbon electrode (3), and
    c) mounting the substrate-integrated lead dioxide electrode (2), the activated carbon electrode (3) with a thixotropic inorganic-gel-polymer electrolyte (4) in between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy storage device.
10. The method as claimed in claim 9, wherein the electrolyte acts as a separator.
11. A method of using energy-storage device (1) as claimed in claim 1 or energy storage unit as claimed in claim 7, said method comprising act of conjugating said energy-storage

device or unit with electrical device for generating electrical energy to supply energy to devices in need thereof.

12. An inorganic thixotropic-gelled-polymer-electrolyte.
13. The electrolyte as claimed in claim 12, wherein the electrolyte is prepared by cross-linking fumed silica with sulfuric acid.
14. The electrolyte as claimed in claim 13, wherein the sulfuric acid has concentration ranging from about 4M to about 7M, preferably about 6M.; and wherein the electrolyte is capable of acting as a separator between electrodes of an energy storing device.

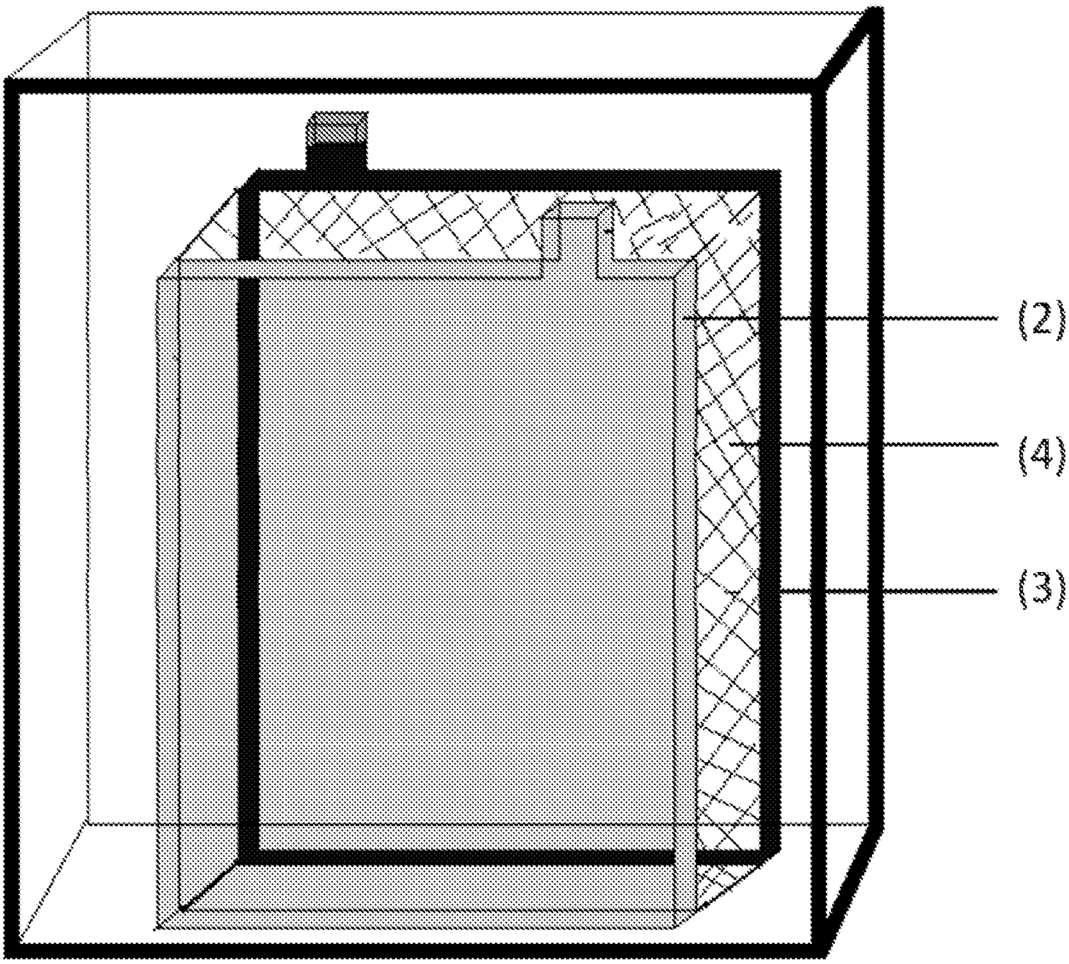

FIGURE 1