Title: AN ENERGY STORAGE DEVICE AND METHOD THEREOF

Abstract: The present disclosure is related to hybrid capacitors specifically to PbO2/Activated Carbon hybrid capacitors. The hybrid super capacitor of the present disclosure is simple to assemble, bereft of impurities and can be fast charged/discharged with high faradic-efficiency.

Figure - 3

Declarations under Rule 4.17:

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(1v))

Published:

— with international search report (Art. 21(3))
AN ENERGY STORAGE DEVICE AND METHOD THEREOF

TECHNICAL FIELD
The present disclosure is related to hybrid capacitors specifically to PbO₂/Activated Carbon hybrid ultracapacitors. The hybrid ultracapacitor of the present disclosure is simple to assemble, bereft of impurities and can be fast charged/discharged with high faradiac efficiency.

BACKGROUND

Supercapacitors (also termed as ultracapacitors) are being projected as potential 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 and rather charges are distributed on surfaces by physical processes that do not involve the making or braking of chemical bonds "similar to 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 PbO₂/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.

(+): PbSO₄ + 2H₂O ↔ PbO₂ + H₂SO₄ + 2H⁺ + 2e⁻
Accordingly, the net charge-discharge reactions for the hybrid supercapacitor can be written as follows.

\[
PbSO_4 + 2H_2O + 2C \rightarrow PbO_2 + H_2S_0_4 + 2(C-H_{ads}^+)_{d,i}
\]

The (+) plate is realized by electrochemical plating and cycling in sulphuric acid/perchloric acid while the (-) plate is prepared by pasting activated carbon onto a lead 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 desirous of a capacitor.

**STATEMENT OF DISCLOSURE**

The present disclosure is in relation to an energy-storage device (1) comprising: a substrate-integrated-lead-dioxide electrode (2), an activated-carbon electrode (3), and a separator (4) soaked in an electrolyte (5) and placed in-between the substrate-integrated-lead-dioxide electrode and the carbon electrode in a container (6); an energy storage device (7) comprising plurality of energy storage device (1) of claim 1 connected in series; a method of preparing substrate-integrated lead dioxide comprising acts of, a) etching pre-polished lead sheets; b) washing the etched lead sheets with deionized water; c) immersing the washed lead sheets in mixture of sulphuric acid and perchloric acid to obtain a layer of lead sulphate; and d) oxidizing the lead sulphate to lead dioxide to obtain substrate-integrated lead dioxide; 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) in a container (6) with separator (4) soaked in an electrolyte (5) in-between the substrate-integrated-lead-dioxide and the carbon electrodes to manufacture the energy-storage device; a method of using energy-
storage device (1 or 7), said method comprising act of conjugating said energy-storage device with electrical device for generating electrical energy to devices in need thereof for working.

**BRIEF DESCRIPTION OF ACCOMPANYING FIGURES**

Figure 1: Schematic diagram of substrate-integrated PbO₂/activated-carbon ultracapacitor.

Figure 2: Schematic diagram of substrate-integrated PbO₂/activated-carbon ultracapacitors connected in series.

Figure 3: Schematic diagram of electrochemical cell employed for preparing substrate-integrated PbO₂ electrodes.

Figure 4: XRD patterns for the positive electrodes.

Figure 5: Cyclic voltammograms for a PbO₂/Activated Carbon Hybrid Ultracapacitor.

Figure 6: Constant current charge/discharge cycles.

Figure 7: Life-cycle test.

Figure 8: Constant current charge/discharge characteristics.

Figure 9: Constant-potential charge and constant-current discharge characteristics.

Figure 10: Cycle-life test for PbO₂/PVDF-bonded Activated-Carbon Hybrid Ultracapacitor.

Figure 11: Constant-current discharge characteristics for 6V/40F PbO₂/Activated Carbon Hybrid Ultracapacitor.

**DESCRIPTION OF DISCLOSURE**

The present disclosure is in relation to an energy storage device (1) comprising:

a) a substrate-integrated-lead-dioxide electrode (2),

b) an activated-carbon electrode (3), and
c) a separator (4) soaked in an electrolyte (5) and placed in-between the substrate-integrated-lead-dioxide electrode and the carbon electrode in a container (6).

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

In still another embodiment of the present disclosure, the separator (4) is made of material selected from a group comprising porous glass and porous polymers, preferably porous glass.

In yet another embodiment of the present disclosure, the electrolyte is selected from a group comprising sulphuric acid, methanesulfonic acid, perflurosulphonic acid, and preferably sulphuric acid.

In yet another embodiment of the present disclosure, the sulphuric acid is concentrated in range from about 4M to about 7M, preferably about 6M.

In yet another embodiment of the present disclosure, the energy storage device (1) is of faradiac efficiency ranging from about 94% to about 96%, preferably 95%.

The present disclosure is also in relation to an energy-storage device (7) comprising plurality of energy-storage device (1) connected in series.

The present disclosure is also in relation to a method of preparing substrate-integrated lead dioxide comprising acts of,

a) etching pre-polished lead sheets;

b) washing the etched lead sheets with deionized water;

c) immersing the washed lead sheets in mixture of sulphuric acid and perchloric acid to obtain a layer of lead sulphate; and

d) oxidizing the lead sulphate to lead dioxide to obtain substrate integrated lead dioxide.

In still another embodiment of the present disclosure, the etching is carried out using Nitric acid.

In yet another embodiment of the present disclosure, the Nitric acid is of concentration ranging from about 0.5M to about 1.5M, preferably about 1M.

In yet another embodiment of the present disclosure, the sulphuric acid is concentrated in the range from about 4M to about 7M, preferably about 6M.
In yet another embodiment of the present disclosure, the perchloric acid is concentrated in the range from about 0.05M to about 0.2M, preferably about 0.1M.

In yet another embodiment of the present disclosure, the oxidation of lead sulphate to lead dioxide is by using the lead sulphate as an anode in an electrochemical cell.

The present disclosure is also in relation to 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) in a container (6) with separator(4) soaked in an electrolyte (5) in-between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy storage device.

In yet another embodiment of the present disclosure, the container (6) is made of material selected from a group comprising porous glass and porous polymer, preferably porous glass.

The present disclosure is also in relation to a method of using energy-storage device (1 or 7), said method comprising act of conjugating said energy-storage device with electrical device for generating electrical energy to devices in need thereof for working.

The present disclosure is related to realizing substrate-integrated PbO₂/Activated-carbon hybrid ultracapacitor bereft of impurities. The hybrid ultra capacitors of the present disclosure are simple to assemble, bereft of impurities, and can be fast charged / discharged with faradaic efficiencies as high as 95%.

In the current disclosure, the positive electrodes, substrate-integrated PbO₂ are made by electrochemical formation of pre-polished and etched lead metal sheets. Specifically, the substrate-integrated PbO₂ is obtained by oxidizing PbSO₄ 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. The XRD patterns for the formed electrodes were recorded and found to be free of impurities. The XRD
patterns provided in the figure 4 clearly suggest the formation of lead dioxide. The negative electrode is an activated carbon electrode.

In the current disclosure of PbO2/Activated carbon hybrid ultracapacitor, PbO2 electrode is a battery-type electrode and activated carbon is a double-layer-capacitor electrode. Figure 5 is a cyclic voltammogram for PbO2/activated carbon hybrid ultracapacitor at a scan rate of 10 mV/s showing a peak for the oxidation of PbS04 to PbO2 at 2V during the anodic scan and the corresponding reduction of PbO2 to PbS04 at 1.5V during the cathodic scan. The oxidation and reduction peaks reflect the PbO2/Activated carbon to be a hybrid device.

Generally, the battery electrodes are charged at C/10 rate (10h duration) and discharged at C/5 rate (5h duration). If the battery electrodes are charged/discharged at C rate 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 disclosure provides, electrochemically formed and substrate-integrated PbO2 as battery-type electrode that can be charged and discharged at higher rates with faradaic efficiencies as high as 95%. The same has been illustrated in Figure 8. The figure 8 shows current charge and discharge curve at 50 mA for the substrate-integrated PbO2/Activated hybrid ultracapacitor exhibiting faradaic efficiency as high as 95%.

Figure 6 shows the charge and discharge polarization curves at 25 mA, 50 mA and 100 mA for a substrate-integrated PbO2/Activated carbon hybrid ultracapacitor prepared by using Teflon as binder in the carbon electrodes. The capacitance is calculated from the discharge curve using the equation:

\[ C(F) = \frac{I(A) \times t(s)}{(V_2-V_1)} \]

where \( V_2 \) is the voltage at the beginning of discharge and \( V_1 \) is the voltage at the end of discharge. It is found that the hybrid ultracapacitor has a capacitance of 10.79F at 25mA, 10.05F at 50 mA and 9.738F at 100 mA.
The figure 7 shows the cycle-life data for the substrate-integrated PbO$_2$/Activated carbon hybrid ultracapacitor at 0.1 A suggesting the hybrid ultracapsacitors to have high cycle-life. The cycle-life test involves the following four steps.

Step 1. Charging the ultracapacitor at 2.3V for 10 min.

Step 2. Open-circuit voltage measurement for 5s.

Step 3. Discharge the ultracapacitor at constant current at 0.2A.

Step 4. Open-circuit voltage measurement for 30s.

Figure 10 shows the cycle-life data for the substrate-integrated PbO$_2$/Activated-carbon hybrid ultracapacitor.

Figure 9 illustrates the discharge curves at varying currents for the substrate-integrated PbO$_2$/Activated-carbon hybrid ultracapacitor followed by their charging at 2.3V for 10min.

The hybrid capacitor of the present disclosure is connected in series to obtain capacitors wherein the cell voltage gets added up while their effective capacitance decreases akin to conventional capacitor. Figure 11 shows the discharge curves at 0.2A current for substrate-integrated PbO$_2$/Activated-carbon hybrid ultracapacitor cell comprising two and three cells connected in series. The figure indicates that the cell voltage is added up when two or more cells are connected in series while their effective capacitances decrease akin to conventional capacitors.

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) in a container (6) with separator(4) soaked in an electrolyte (5) in-between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy-storage device.
The devices of the present disclosure can be easily conjugated with electrical devices for generating electrical energy to devices in need thereof for working.

The technology of the instant application is elaborated in detail with the help of following examples. However, the examples should not be construed to limit the scope of the disclosure.

Example:

**Preparation of substrate-integrated PbO₂/Activated Carbon Hybrid Ultracapacitors**

**A. Preparation of Substrate-Integrated PbO₂ Electrodes.**

Substrate-integrated- PbO₂ electrodes are prepared by etching pre-polished lead sheets (thickness 300 µm) in 1M HNO₃ for 60s and subsequently washed copiously with deionized water. The sheets were then immersed in 6 M aqueous H₂SO₄ with 0.1 M HC₁₀₄ 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 PbO₂ by using it as anode in an electrochemical cell fitted with a counter electrode. The process is repeated for about five times to prepare the fully-formed substrate-integrated PbO₂ electrodes. The electrochemical cell employed for this purpose is connected to a constant current dc supply as shown schematically in figure3.

**B. Preparation of PVDF bonded activated carbon electrodes.**

Activated-carbon electrodes are prepared by pasting activated carbon ink containing polyvinylidene difluoride as a binder. In brief, a carbon paste was obtained by mixing 85% of high-surface-area carbon (BET surface area is about 2000 m²/g and particle size < 10 nm) with 10 wt. % of carbon black (particle size is about 1 µm) and 5 wt. % of binder like PVDF dissolved in an appropriate quantity of dimethylformamide solvent or teflon. Typically, 0.1 g of PVDF is dissolved in 10 ml of DMF and 1.7 g of high surface area carbon (Meadwestvaco 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 3.5 cm x 6.0 cm with that had a tag area of 1 cm width and 3 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 Substrate-Integrated PbO$_2$-AC Hybrid Ultracapacitors (HUCs)

a) 6V substrate-integrated PbO$_2$-AC hybrid ultracapacitor.

6V substrate-integrated PbO$_2$-AC HUCs were assembled by connecting three 2V HUCs in series. 2V/100F substrate-integrated PbO$_2$/PVDF-bonded AC HUCs comprising a substrate-integrated PbO$_2$ electrode of size 3.5 cm x 6 cm with a tag of 1 cm width and 3 cm length formed by aforementioned method and a PVDF-bonded carbon electrode prepared as described above were assembled using a 3 mm thick AGM (adsorbed glass mat) soaked with 6 M H$_2$SO$_4$ acid as the separator and electrolyte. The complete assembly, PbO$_2$-(AGM+H$_2$SO$_4$) - AC, was then assembled into a plexiglass container. The cell was then tested for its electrochemical characteristics.

b) 12V substrate-integrated PbO$_2$-AC hybrid ultracapacitor.

12V PbO$_2$-AC HUCs were assembled by connecting six HUCs in series. The details for assembling the HUCs are given as under.

2V/100F substrate-integrated PbO$_2$/PVDF-bonded AC HUCs comprising a substrate-integrated PbO$_2$ electrode of size 3.5 cm x 6 cm with tags (6a, 6b) of 1 cm width and 3 cm length formed by aforementioned method and a PVDF-bonded carbon electrode prepared as described above were assembled using a 3 mm thick AGM (adsorbed glass mat) soaked with 6 M H$_2$SO$_4$ acid as the separator and electrolyte. The complete assembly, PbO$_2$-(AGM+H$_2$SO$_4$) - AC, was then assembled into a plexiglass container. The cell was then tested for its electrochemical characteristics.

c) 12V substrate-integrated PbO$_2$-AC hybrid ultracapacitor.
A 12V substrate-integrated Pb0.2/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 of size 4.5cm x 7 cm with the tag (6b) area of 0.5cm x 0.5 cm and 0.3mm thickness for the positive plate and 0.8mm thickness for negative plates (6a); 1mm thick AGM sheets were used as separator. A unique method was used to interconnect the graphite electrodes. The tag portion of the negative electrodes (6a) is electroplated with Tin followed by electroplating with lead which facilitates the graphite electrode tags (6b) to solder with 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.

It is found that these hybrid ultracapacitors yield a capacitance value of 120F at 5C rate of discharge.

While various aspects and embodiments 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 separator (4) soaked in an electrolyte (5) and is fixed in-between the substrate-integrated-lead-dioxide electrode and the carbon electrode in a container (6).

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 separator (4) is made of material selected from a group comprising porous glass and porous polymers, preferably porous glass.

4. The energy-storage device as claimed in claim 1, wherein the electrolyte is selected from a group comprising sulphuric acid, methanesulfonic acid, perflourosulphonic acid, preferably sulphuric acid.

5. The energy storage device as claimed in claim 4, wherein the sulphuric acid is concentrated in range from about 4M to about 7M, preferably about 6M.

6. The energy storage device as claimed in claim 1, wherein the energy storage device (1) is of faradiac efficiency ranging from about 94% to about 96%, preferably 95%.

7. An energy storage device (7) comprising plurality of energy storage device (1) of claim 1 connected in series.

8. A method of preparing substrate-integrated-lead-dioxide comprising acts of, etching pre-polished lead sheets;
   a) washing the etched lead sheets with deionized water;
   b) immersing the washed lead sheets in mixture of sulphuric acid and perchloric acid to obtain a layer of lead sulphate; and
   c) oxidizing the lead sulphate to lead dioxide to obtain substrate-integrated lead dioxide.

9. The method of preparation of substrate-integrated lead dioxide as claimed in claim 8, wherein the etching is carried out using nitric acid.
10. The method of substrate-integrated lead dioxide as claimed in claim 9, wherein the nitric acid is of concentration from about 0.5M to about 1.5M, preferably about 1M.

11. The method of preparation of substrate integrated lead dioxide as claimed in claim 8, the sulphuric acid is concentrated in the range from about 4M to about 7M, preferably about 6M.

12. The method of preparation of substrate integrated lead dioxide as claimed in claim 8, wherein the perchloric acid is concentrated in the range from about 0.05M to about 0.2M, preferably about 0.1M.

13. The method of preparation of substrate-integrated lead dioxide as claimed in claim 8, wherein the oxidation of lead sulphate to lead dioxide is by using the lead sulphate as an anode in an electrochemical cell.

14. 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) in a container (6) with separator(4) soaked in an electrolyte (5) in-between the substrate-integrated lead dioxide and the carbon electrode to manufacture the energy storage device.

15. The method as claimed in claim 14, wherein the container (6) is made of material selected from a group comprising porous glass and porous polymer, preferably porous glass.

16. A method of using energy-storage device (1 or 7), said method comprising act of conjugating said energy-storage device with electrical device for generating electrical energy to devices in need thereof for working.
DC Power supply

Pb anodes

Pb metal sheet of 0.3mm as cathode for forming PbO$_2$

Electrolyte: 6M H$_2$SO$_4$ + 0.1M HClO$_4$

Figure – 3

Figure – 4
Figure – 5

Figure – 6
Figure – 7

Figure – 8
Figure – 9

Figure – 10
INTERNATIONAL SEARCH REPORT

International application No.
PCT /IN20 10/000439

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.
H01G 9/155 (2006.01) H01M 4/14 (2006.01) H01M 10/12 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI, EPDOC, TXTE (H01G, +capacitor+, lead dioxide, lead sulphate, acid, sulphuric, perchloric, activated carbon, etch, oxid+ and like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>WO 2009/052 124 A1 (AXION POWER INTERNATIONAL, INC.[US]) 23 April 2009 Abstract, page 1, page 3 lines 3-20, page 10, page 11 lines 4-33, page 13 lines 15-17 figures 11, 12</td>
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<td>X</td>
<td>WO2007/00 1202 A1 (UNIVERSAL SUPERCAPACITORS LLC [US]) 4 January 2007 Abstract, page 4 lines 1-22, figure 4, page 12 line 18 to page 13 line 29, claims 20, 23, 26, 27</td>
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<td>WO 2007/00 1201 A1 (UNIVERSAL SUPERCAPACITORS LLC [US]) 4 January 2007 Abstract, see page 12 lines 17 to page 13 line 8</td>
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<td>A</td>
<td>Page 16 lines 10-20</td>
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<td>X</td>
<td>US 2007/0 128472 A1 (TIERNEY et al.) 7 June 2007 Abstract, paragraphs 2, 8, 15, 25, 43, 72-77, 96 claims, figures 6, 11, 12</td>
<td>1-4, 7, 14, 15</td>
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[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance,

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search: 16 December 2010

Date of mailing of the international search report: 22 December 2010

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Form PCT/ISA/2 10 (second sheet) (July 2009)
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<td>Whole document, esp. pages 1-4, page 10 line 18 to page 11 line 2, page 12 lines 3-19, page 18 lines 13-16, page 23 line 32 to page 24 line 20, Examples on pages 22-29, claim 22</td>
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<td>WO 2003/098648 A1 (C AND T COMPANY, INC.) 27 November 2003</td>
<td>1, 3, 14, 15</td>
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<td>see example 1 paragraph bridging pages 6 and 7, example 2 paragraph bridging pages 7 and 8, claims 1, 60-72</td>
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<td>PELL, W.G., et al., &quot;Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes&quot; Journal of Power Sources</td>
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<td>Volume 136, Issue 2, 1 October 2004, Pages 334-345, Section 7</td>
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<td>RAGHEB, A., et al., &quot;Effect of current density and perchloric acid concentration on the formation of lead anodes in sulphuric acid baths&quot;, Materials and Corrosion, 23: 105-1 09, 30 February 1972</td>
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<td>Whole document, esp. Sections entitled Experimental, Results and Discussion (Effects of Perchloric acid) and Summary</td>
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<td>Abstract, column 2 lines 42-63, column 14 line 62 to column 15 line 7, col. 20 lines 59, 60, col. 23 lines 32-38, col. 24 lines 12-15</td>
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<td>US 43260 17 A (WILL) 20 April 1982</td>
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<td>US 6129822 A (FERDMAN) 10 October 2000</td>
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<td>Abstract, column 1, column 4 lines 41-50</td>
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Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

- Claims 1-7, 14, 15, 16 are directed to an energy storage device with a particular combination of electrodes and a separator. It is considered that using the particular choice of separator between the two particular known electrodes comprises a first distinguishing feature.

- Claims 8-13 are directed at a method of making a substrate integrated lead dioxide electrode. It is considered that the method steps; for preparing the substrate integrated lead dioxide electrode comprises a second distinguishing feature.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

Each of the abovementioned groups of claims has a different distinguishing feature and they do not share any feature which could satisfy the requirement for being a special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention a priori.

Note: without further defining features it is considered that lead dioxide electrodes per se are already known and hence this feature on its own does not make a contribution over the prior art and does not fit the above definition for a special technical feature. Therefore the lead dioxide electrode on its own cannot provide unity amongst the two groups of claims listed above.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ 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 claims Nos.:

**Remark on Protest**

- ☑ Additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

- ☒ No protest accompanied the payment of additional search fees.
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX