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(54) **Title**: LEAD ACID BATTERY WITH PROLONGED SERVICE LIFE

(57) **Abstract**: This disclosure relates to improved lead-acid batteries, having a prolonged serviceable life, comprising lead-oxide and carbon-nanotubes formulations. The disclosure further provides a process for operating a lead-acid battery.

LEAD ACID BATTERY WITH PROLONGED SERVICE LIFE

TECHNOLOGICAL FIELD

This invention relates to improved lead-acid batteries, having a prolonged serviceable life.

BACKGROUND OF THE INVENTION

The lead-acid battery has been a successful secondary battery system for over a century and has become the most widely used rechargeable energy-storage system. The advantages of these batteries are their low cost, stable voltage profile, high reliability, and safety. The main disadvantages of such flooded type configuration are a low specific energy and, subsequently, the poor utilization of the positive active-material (PAM). This, in turn, has a significant impact on both the cycle life and the capacity of these batteries.

The low utilization of PAM has been associated with crumbling of the active material, which is caused by sulfation of the active material, i.e. the sulfation process of lead-oxide (PbO_2) to lead-sulfate ($PbSO_4$), which can be described by the following chemical equation:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O$$

Due to physical, morphological and chemical changes ($PbSO_4 \Leftrightarrow PbO_2$) at the positive electrode, the positive electrode is actually mechanically degraded, losing contact and causing short-circuits [1], leading to mechanical stress and crumbling.

$PbSO_4$ crystals are formed during the discharge phase of the battery. These crystals are non-conductive and relatively stable under the battery's operational conditions, such that lead ion oxidation back to the active PbO_2 material is prevented once the $PbSO_4$ crystals reach a stable size (above 1-1.5 micron in diameter). Once reaching a critical size, the formation of $PbSO_4$ crystals can no longer be reversed via the common dissolution/precipitation mechanism, and eventually the non-conductive $PbSO_4$ crystals cause deterioration of the battery's output.

Carbonaceous additives were studied mainly for negative active materials of valve-regulated lead acid (VRLA) cells. Amongst others, their contribution may be associated to the enhancement of the overall conductivity of the active material, and the ability of carbon to act as an electro-osmotic pump that facilitate acid diffusion within the inner volume of the active material, especially at high rates of charge and discharge. Pavlov *et al.* [2] suggested a mechanism for the role of the carbonaceous additives in the negative active material. According to the proposed mechanism, the lead sulfate dissolves and diffuses to conductive sites (i.e. pure lead, extremely thin lead sulfate layer or the carbonaceous additives surface), in which it may be reduced into metallic lead due to its sufficient electrical conductivity. At later stages, due to the mismatch in the crystal lattice parameters, the reduced lead diffuses from the carbon surface, releasing the electro-active sites on the carbonaceous surface to be available for further reduction.

Among the various carbon allotropes, carbon nanotubes (CNTs) seem to be a prominent additive due to their outstanding features, including high mechanical properties, and excellent electric and thermal conductivities [3]. The use of oxidated or polymer-functionalized CNTs has been suggested for improving the negative electrode performance in lead-acid cells [4].

Flooded lead-acid batteries (also known as Start Light Ignition (SLI) batteries), are typically limited for operation in relatively shallow depth of discharge (DOD). Once deeper depths of discharge are used (i.e. 20-30% DOD), the rate of sulfation is significantly increased, thereby shortening the serviceable live of the battery. It is of note, that although there are commercial lead-acid batteries which are designed to operation at high DOD and very prolonged cycle life, these systems, however, require special structure, geometry and complicated and expensive electrodes compositions.

Thus, there is a demand for improved lead-acid batteries, which can operate for a larger number of cycles in deeper depths of discharge, which are relatively simple and cost-effective to produce.

BACKGROUND ART

[1] Ruetschi, P., *J. Power Sources* **1977,** *2* (ACS), 3-24

[2] Pavlov, D.; Rogachev, T.; Nikolov, P.; Petkova, G., *J. Power Sources* **2009,** *191*, 58-75

[3] WO 2013/011516
[4] WO 2014/028856
[5] WO 2014/141279

SUMMARY OF THE INVENTION

The inventors of the invention disclosed herein have developed a lead-acid battery which provides a longer serviceable life by reducing and controlling the formation of $PbSO_4$ crystals during the battery's operation.

In one aspect, the present invention provides a lead-acid battery comprising an electrode assembly (at least one positive electrode (i.e. cathode) and/or at least one negative electrode (i.e. anode)) and sulfuric acid, an electrode of said electrode assembly (e.g., at least one of said positive and negative electrodes) being made of a substrate at least partially coated by a formulation comprising lead oxide particles (PbO_2) and carbon nanotubes (CNTs), the battery being characterized in that lead-sulfate particles having an average size of up to 5 μm are formed onto said electrode assembly (at least one of the positive and negative electrodes) when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30% (e.g. at 25% DOD).

As known in the art, a lead-acid battery is based on a redox reaction occurring when electrons are transferred from the anode to the cathode via an electrolytic medium. The battery may comprise a plurality of anodes and a plurality of cathodes. The battery may further comprise a bus-bar and a suitable housing.

The electrolyte solution is typically a dilute aqueous sulfuric acid solution, comprising 3 to 5M sulfuric acid; the solution provides the sulfate ions necessary for the discharge reactions.

In the batteries of the invention, at least one, at times both, of the anode and the cathode are formed out of substrates that are at least partially coated by a ***formulation*** (i.e. composition of matter) comprising PbO_2 and CNTs. The formulation may be provided initially in the form of a paste, which is pasted (or spread) onto the substrate, and then cured, to subsequently form the electrode. The formulation enables limited and controlled formation of lead-sulfate particles onto the electrodes, such that batteries of the invention are characterized by lead sulfate particles having a size of up to 5 μm

when the battery's output voltage decreases to at least 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

The ***Depth of Discharge*** (DOD) is the percentage of energy discharged from the battery, relative to its full capacity. Namely, DOD of 20% indicates that 20% of the battery's energy have been discharged, relative to its full charged capacity. As a person of skill in the art would appreciate, DOD of at least 17% is considered in the industry as deep discharge.

Typically, when cycled at 25-30% DOD, the battery's open circuit voltage (OCV) is about 12.6V. Thus, a drop of the output voltage below 10.5V is considered to indicate reaching near the end of life point of the battery.

Thus, in some embodiments, the battery is cycled at 25% DOD.

The term ***End of Life***, as known to any person of skill in the art, refers to a drop in the output voltage of the battery which indicates imminent failure of the battery. Thus, batteries of the invention are such in which a significantly larger number of operational cycles may be obtained prior to reaching end of life due to better control of the growth of $PbSO_4$ particles. $PbSO_4$ particles having a size of up to 5 μm, at times up to 1 μm, will still permit operation of the battery in an acceptable performance.

Although end of life is defined, in the context of the present disclosure, under 25% DOD conditions, it is of note that other evaluation protocols may be used. For example, in an SBA cycling protocol (in which the battery is cycled at about 1-15% DOD), the battery typically maintains a service voltage of about 9.5-10.5V at the end of a 300 Amp spike. A significant drop in voltage, e.g. to below about 7.2V, indicates reaching close to the end of life of the battery.

In other embodiments, the positive electrode (cathode) comprises the formulation and the lead-sulfate particles formed onto the cathode have an average size of up to 1 μm when the battery's output voltage decreases below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

In some other embodiments, the negative electrode (anode) comprises the formulation and the lead-sulfate particles formed onto the anode have a size of up to 5 μm when the battery's output voltage decreases below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

In some embodiments, both the positive and negative electrodes comprise lead oxide particles (PbO_2) and carbon nanotubes (CNTs), such that (i) lead-sulfate particles

formed onto the positive electrode have a particle size of up to 1 μm and (ii) lead-sulfate particles formed onto the negative electrode have a particle size of up to 5 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

In batteries of the invention, the lead-sulfate particles may have a substantially homogenous particle size; i.e. in some embodiments, the size distribution of the lead-sulfate particles is substantially monodispersed; namely, $PbSO_4$ crystals formed during operational cycling of the battery grow relatively in a controlled rate, resulting in substantially uniform and narrowly-distributed particle size.

As will be demonstrated hereinbelow, the use of CNTs ensures that in a functioning cell most of the $PbSO_4$ crystals remain below a certain size threshold, which minimizes eventual sulfur concentration (i.e. ***sulfation***). Without wishing to be bound by theory, the CNTs act as "electron sinks", i.e., enabling the creation of oxidation sites which significantly delays failure due to sulfation, resulting in enhanced cycle life of the battery.

As noted above, at least one, at times both, of the anode and the cathode are formed out of substrates that are at least partially coated by a formulation comprising PbO_2 and CNTs. The electrodes' ***substrate*** may be a flexible or rigid structure, which may be substantially two-dimensional (a thin flat substrate) or a three-dimensional, e.g., curved (non-flat) surface. The substrate can be of any smoothness, may be in the form of a plate, a mesh, etc. In most general terms, the substrate is made of an electrically-conductive material.

The surface of the substrate may be coated by the formulation entirely or at a portion thereof to form the electrode anode, cathode, or both). The ***portion*** (region) of the substrate's surface to be coated may be of any size and structure, the portion may be continuous or comprise of several non-continuous sub-regions on the surface.

The ***CNTs*** employed in the products and methods of the invention are carbon nanowires or nanotubes selected in a non-limited fashion from single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), double-walled carbon nanotubes (DWCNTs), and few-walled carbon nanotubes (FWCNTs). In some embodiments, the CNTs are single-walled (SWCNTs) or multiwalled (MWCNTs) CNTs.

In some embodiments, the CNTs have a diameter of between about 1 and 100 nm. In other embodiments, the CNTs may have a diameter of between about 1 and 10 nm.

According to some embodiments, the CNTs have a length of between about 1 and 50 μm. According to other embodiments, the CNTs may have a length of between about 1 and 10 μm.

The ***lead oxide*** is typically in particulate form of any shape and of random or preselected particle size. The term ***particle size*** typically refers to the average diameter of the particles. When the particles are of non-spheroid shape, the term refers to the average equivalent diameter of the particle, namely the diameter of an equivalent spherical particle based on the longest dimension of the particle.

In some embodiments, the lead oxide particle size is between about 0.2 and 10 microns.

In the composite of the invention, the CNTs are substantially not in a preordered contact with each other, namely, they are in the form of a ***discontinuous spatial arrangement*** in the formulation, each being separable from the other by a plurality of lead oxide particles coating and protecting each CNT. In other words, the CNTs form a discontinuous net or a fragmented grid, wherein each CNT is distanced from the other.

The dispersion of CNTs in the lead oxide may be carried out at any method known in the art. An exemplary method for obtaining homogenous dispersions of CNTs in lead oxide pastes is described in [5].

In some embodiments, the concentration of the CNTs in the formulation is between about 0.001% and 5% (wt%) of the total lead oxide weight. In other embodiments, the concentration is between about 0.01% and 2% (wt%) or even between about 0.01% and 0.05% (wt%). In other embodiments, the concentration is between about 0.001% and 0.2% (wt%) or even between about 0.001% and 0.05% (wt%).

As noted above, at least one of the positive and negative electrodes in the lead acid battery may comprise the formulation. In some embodiments, both of the positive and the negative electrodes comprise said formulation; the formulation in each of the positive and the negative electrodes may be the same or different.

According to some embodiments where both of the electrodes comprise the formulation, the CNTs concentration in the formulation is (i) between about 0.001 and

0.05 wt% in the negative electrode and (ii) between about 0.01 and 0.1 wt% in the positive electrode. According to other embodiments, the CNTs concentration in the formulation is (i) between about 0.005 and 0.02 wt% in the negative electrode and (ii) between about 0.02 and 0.07 wt% in the positive electrode.

In order to improve disperseability of CNTs in the lead oxide, it is sometimes required to add a dispersing agent to prevent formation of CNTs bundles, as well as compensate for the mismatch between the surface energies of the PbO_2 and the CNTs. Thus, in such embodiments, the CNTs may be provided as a composition comprising CNT and at least one dispersing agent. In some embodiments, the dispersing agent is selected from carboxymethyl cellulose (CMC), a lignosulfate and mixtures thereof. In such embodiments, the dispersing agent may be carboxymethyl cellulose (CMC).

When a CNT composition is used, the (weight) ratio between CNT and the dispersing agent in the CNT composition may be between about 70:30 and 40:60. In other embodiments, the ratio between CNT and the dispersing agent in the CNT composition may be between about 60:40 and 50:50. In further embodiments, the ratio may be 55:45.

In addition to the dispersing agent, the formulation, by some embodiments, may further comprise at least one additive, optionally selected from modified celluloses; polyethers, such as polyalkylene oxides or polyalkylene glycols; lignosulphonates; polyacrylates; products based on polycarboxylic acids, in particular polyether polycarboxylates or their copolymers; naphthalenesulphonates and their derivatives and their corresponding aqueous solutions, and others.

In some such embodiments, the additive may be carbon black, which may be present in the formulation in an amount of between about 0.1 and 1.5 wt%. In other embodiments, the formulation may comprise carbon black in an amount of between about 0.2 and 0.5 wt%.

In another aspect, there is provided a lead-acid battery comprising at least one cathode, at least one anode and sulfuric acid, at least one of said anode and cathode being made of a substrate at least partially coated by a formulation comprising lead oxide particles (PbO_2), between about 0.01 and 0.2 wt% carbon nanotubes (CNTs), the battery being characterized in that lead-sulfate particles formed onto at least one of the positive and negative electrodes having a size of up to 5 μm when the battery's output

voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

As mentioned herein, the formation of $PbSO_4$ is minimized when using a battery according to the invention, specifically at high Depths of Discharge (DOD). Therefore, in another aspect, the invention provides a process for operating a battery according to the present invention, the process comprising:

- constructing the lead-acid battery of the invention; and

- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation, such that discharging of the battery is carried out at a depth of discharge having a value of between 17.5 and 30%.

In some embodiments, the battery is cycled at a DOD value of at least 25%.

The battery according to the present invention may be utilized in a variety of applications.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 shows charging profiles for 2V lead-acid cells with and without CNT-containing formulation.

Fig. 2 shows the number of cycles for cells cycled at constant capacity (about C/4 rate) corresponding to 30% DOD, and charging at about C/2 rate up to 2.4V: a cathode with 0.02% CNTs vs. a standard cathode (without CNTs). Cell capacity of 60-100mAh.

Fig. 3 shows the number of cycles for cells cycled at constant capacity (about C/4 rate) corresponding to 30% DOD, and charging at about C/2 rate up to 2.4V: an anode with 0.02% CNTs vs. a standard anode (without CNTs). Cell capacity of 60-100mAh.

Fig. 4 show discharge capacity data (**Fig. 4A**) and number of cycles number of cycles at constant capacity (about C/4 rate) corresponding to 30% DOD, and charging at about C/2 rate up to 2.4V (**Fig. 4B**) for 2V lead-acid cells containing 0.01 wt% in both

electrodes (MWCNT), only in the negative electrode (NMWCNT), only in the positive electrode (PSWCNT), and without CNTs (blank).

Fig. 5 shows initial discharge capacity test results for cells with different CNTs loading values at C/20 rate up to 1.75V, compared to a standard cell with CNT-free electrodes. Cells were charged at C/10 rate up to 2.4V and followed by 3h potentiostatic charging.

Fig. 6 shows the number of cycles for industrial scale batteries cycled at 25% DOD: anode and cathode containing 0.01% CNTs vs. a standard anode (without CNTs). Cell capacity of 13.6Ah.

Figs. 7A-7D show SEM micrographs of failed electrodes (i.e. at end of life): anode with CNTs (**7A**), anode without CNTs (**7B**), cathode with CNTs (**7C**) and cathode without CTNs (**7D**).

Fig. 8 shows SEM micrographs of positive and negative electrodes at different stages of cycling with and without CNTs:

Figs. 8A-8C: positive electrode without CNTs: cured material, formed material and cycled materials, respectively;

Figs. 8D-8F: positive electrode with 0.01% wt% CNTs: cured material, formed material and cycled materials, respectively;

Figs. 8G-8I: negative electrode without CNTs: cured material, formed material and cycled materials, respectively;

Figs. 8J-8L: positive electrode with 0.01 wt% CNTs: cured material, formed material and cycled materials, respectively;

Figs. 9A-9B show cycling results of commercial 12.6V batteries at 1.3% DOD at HRPSOC (based on SBA protocol): commercial battery (**9A**), battery with both cathode and anode containing 0.01 wt% CNTs (**9B**).

DETAILED DESCRIPTION OF EMBODIMENTS

Pastes for the preparation of electrodes were manufactures by dry mixing of 23-27 wt% metal lead (Pb), 73-77 wt% PbO_2, and 0.75 wt% of surfactant. 0.2-0.5 wt% of carbon black, as well as 0.1 wt% and 0.2 wt% of glass fibers (Modacrylic) were added to the cathode and the anode formulations, respectively. Then, 9 wt% and 0.85 wt% of water-based CNTs suspension were added water to the cathode and the anode formulations, respectively, to form pastes by homogenous mixing. Next, 9.8 wt% and

8.9 wt% sulfuric acid solution (concentration of 1.325 S/g) were gradually added to the cathode and anode paste mixtures, respectively. Final CNTs concentration in the pastes was 0.01-0.02 wt%.

In all tests detailed below MWCNT CW2-45 from Arkema Inc., having a diameter of 1-10 nm, 1-10 μm (micrometers) long, were used. These CNTs were provided in a mixture with 45% carboxymethyl cellulose (CMC).

As reference, pastes without CNTs were similarly prepared.

The pastes were spread onto lead-antimony (cathode) and lead-calcium (anode) grids and cured at 40°C and 90% relative humidity for 24 hours, and then dried at 60°C for 24 hours.

Cells were then prepared, with sulfuric acid as electrolyte solution, according to the following electrode combinations:

(1) Both cathode and anode without CNTs (reference);

(2) Cathode with CNTs and anode without CNTs;

(3) Cathode without CNTs and anode with CNTs; and

(4) Both cathode and anode with CNTs.

The cells were conditioned prior to testing in a 3-stage charging procedure: charging at 0.1C rate for 3 hours, charging at 0.14C rate for 20-28 hours, and charging further at 0.1C rate for 3 more hours. The 3-stage procedure ensured complete electrolysis of the active mass comprising lead and lead mono-oxide to spongy lead metal anode and lead dioxide cathode. The final step was a full discharge process at a slow rate until the cells reached 1.75V, followed by charging until the cells reached 2.4V. Then, the cells could be continuously cycled.

Cycling included discharge at 25-30% depth of discharge (DOD) at around 0.25C rates. When the charging (at around 0.5C rates) process was completed, the cells usually reached a potential of 2.4V. A drop below 1.75V was considered to indicate failure and reaching end of life of the cell.

Fig. 1 shows the voltage profiles of the reference cell (blank) and the cell with CNTs-containing electrodes (MWCNT) during formation process. Using electrode compositions with CNTs in both electrodes reduced the resistive components in cells as manifested in the formation process. The CNTs-containing cell showed lower voltage plateau compared to the reference cell due to less resistivity.

Fig. 2 shows representative cycling data of standard cells and cells which cathodes contained CNT. Cycling was carried out galvanostatically with a constant capacity, corresponding to 30% DOD. The charging voltage was fixed to 2.4V. Discharging to 30% DOD lowered the cells' voltage to values around 2V. Failure of cells was determined when the discharge potential dropped below 1.75V. Typical voltages at the end of discharge of the cells are plotted as a function of cycle number. The improvement by adding CNTs to the cathode is evident from Fig. 1, showing 2-fold improvement in cycle life for cells with a cathode containing CNTs.

Fig. 3 demonstrates the effect of CNTs addition to the anode. The cells' cycling was limited to 30% DOD of the anodes. The cells having CNTs-containing anodes performed better than reference cells (without CNTs).

Discharge capacity and number of cycles for industry 2V lead-acid cells are shown in **Figs. 4A-4B**, respectively. The cells were cycled at constant capacity (about C/4 rate) corresponding to 30% DOD, and charging at about C/2 rate up to 2.4V. 4 configurations of cells were tested: containing 0.01 wt% in both electrodes (MWCNT), 0.01 wt% only in the negative electrode (NMWCNT), 0.01 wt% only in the positive electrode (PSWCNT), and without CNTs (blank) in the electrodes.

As can be seen from **Fig. 4A**, the discharge capacity of all cells that included CNTs, in either or both of the electrodes, demonstrated better performance compared to the blank cell. The highest capacity was obtained for the MWCNT cell, whereas the NMWCNT cells show better capacity than PSWCNT cells. The discharge voltage plateaus also indicate the resistive behavior of the cells. As evident from **Fig. 4B**, the addition of 0.01 wt% CNTs to either or both of the electrodes increased significantly the number of cycles prior to failure.

The effect of variance in CNTs concentration was also investigated, as presented in **Fig. 5**, which shows the initial discharge capacity testing for cells at C/20 rate up to 1.75V compared to reference cell without CNTs. Cells were charged at C/10 rate up to 2.4V and followed by 3h potentiostatic charging. It is clear that there is a capacity improvement in cells with CNTs compared to blank cells, however the effect of the content of CNTs is less predominant in the tested CNTs concentration range (0.01-0.05 wt%).

The effect of CNTs on industrial scale lead acid batteries was tested for cells having a capacity of 13.6Ah. The amount of CNTs in the industrial size electrodes was 0.01 wt% by weight. **Table 1** summarizes results of tests carried out on industrial size electrodes, including reference batteries (no CNTs), batteries with either CNTs-containing anodes or cathodes, and batteries in which both electrodes contained CNTs. The batteries were cycled to 25% DOD. The indication for failure was the drop of the end-of-discharge voltage below 1.75V. **Fig. 6** shows a graphic comparison of examples 1 and 8 of Table 1.

Table 1: Performance of industrial size batteries

Cell	% CNT		Capacity		Number of cycles to end of life (1.75V)	Improvement of number of cycles (%)
	In cathode	In anode	Measured (Ah/kg)	Effective capacity over 115Ah/kg (%)		
1 (Ref)	0	0	94.8	82	170	-
2	0.01	0	128	112	257	51.1
3	0.01	0	126.5	110	276	62.3
4	0.01	0	124.4	108	298	75.3
5	0.01	0	131.8	114.5	244	43.0
6	0.01	0	128.7	112	276	62.3
7	0.01	0.01	132.2	115	335	97
8	0.01	0.01	136.5	119	387	127.6

A clear improvement in specific capacity and cycle life was observed in all cases were the electrodes (any or both) contained CNTs. Further, addition of CNTs into the formulations of both the cathode and anode doubled the cycle life of practical SLI type lead acid batteries in a relatively high depth of discharge (25% DOD).

The influence of CNTs on the formation of $PbSO_4$ crystals was assessed by post-mortem analysis of cells after their end of life. The $PbSO_4$ particles were characterized from SEM and TEM micrographs (JEOL-JEM 2100 electron microscope with LaB_6 emitter operating at 200kV). Samples for the TEM studies were prepared by scraping material from cycled electrodes, sonicating the powdered samples in ethanol and adding a few drops of the resulting suspension to a copper grid which is used as a substrate for the TEM measurements.

As can clearly be seen from **Figs. 7A-7D**, there are significant differences in the size of $PbSO_4$ crystals obtained at end of life of the cells between electrodes containing CNTs and those devoid of CNTs. $PbSO_4$ crystals in the standard anode significantly exceeded 10μm in size (Fig. 7B), while for an anode containing 0.01 wt% CNTs $PbSO_4$ crystals of well below 10μm in size were observed (Fig. 7A). A similar result was obtained for the cathodes, where in cathodes without CNTs $PbSO_4$ crystals reached a size of about 2-3μm (Fig. 7D), while a cathode with 0.01 wt% CNTs showed PbSO4 crystals of ≤1μm in size.

The effect of the CNTs on the inhibition of $PbSO_4$ crystals growth can also be observed from Figs. 8A-8L, which are micrographs of the positive and negative electrodes, taken at different stages of cycling: as cured materials (i.e. fresh from production), formed materials (i.e. after formation) and cycled materials (end of life). Morphological changes of positive and negative electrodes in the presence or absence of CNTs can clearly be seen. The cured materials have slightly smaller grains in presence of CNTs (0.2-0.3 microns in average) compared to 0.4-0.5 without CNTs, and the presented morphologies suggest that the cured materials are in the form of 3BS needle-like crystals. The formed materials show smaller particles for the compositions containing CNTs compared to standard formed materials. Similar observations are also seen for the cycled materials, but in a larger extent. The smaller particles, as well as higher surface areas maintain improved performance in lead-acid batteries.

Thus, electrodes containing CNTs afford for inhibited $PbSO_4$ growth, without wishing to be bound by theory by facilitating reversible precipitation-decomposition of $PbSO_4$ during cycling, thereby maintaining good electrical integration of the active mass.

Assessment of the performance of electrodes containing CNTs in commercial batteries at low DOD was also carried out. **Figs. 9A-9B** show comparison between commercial 12.6V lead-acid batteries, with and without CNTs, cycled at 1.3% DOD (shallow depth of discharge). As is clearly evident, a 3-folds improvement of the number of cycles was obtained when both the cathode and anode contained 0.01 wt% CNTs, demonstrating that CNTs provide for significant improvement in the serviceable life of the battery also in typical, shallow DODs.

CLAIMS:

1. A lead-acid battery comprising at least one positive electrode, at least one negative electrode and sulfuric acid, at least one of said positive and negative electrodes being made of a substrate at least partially coated by a formulation comprising lead oxide particles (PbO_2) and carbon nanotubes (CNTs), the battery being characterized in that lead-sulfate particles formed onto at least one of the positive and negative electrodes having a size of up to 5 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

2. The lead acid battery of claim 1, wherein the positive electrode comprises said formulation and the lead-sulfate particles formed onto the positive electrode having a size of up to 1 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

3. The lead acid battery of claim 1 or 2, wherein the negative electrode comprises said formulation and the lead-sulfate particles formed onto the negative electrode having a size of up to 5 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

4. The lead acid battery of any one of claims 1 to 3, wherein the battery is cycles at 20% DOD.

5. The lead acid battery of any one of claims 1 to 4, wherein both of the positive and negative electrodes comprise a formulation comprising lead oxide and CNTs.

6. The lead acid battery of any one of claims 1 to 5, wherein the lead-sulfate particles having a substantially homogenous particle size.

7. The lead acid battery of any one of claims 1 to 6, wherein the size distribution of the lead-sulfate particles is substantially monodispersed.

8. The lead acid battery of any one of claims 1 to 7, wherein both the positive and negative electrodes comprise lead oxide particles (PbO_2) and carbon nanotubes (CNTs), such that (i) lead-sulfate particles formed onto the positive electrode have a particle size of up to 1 μm and (ii) lead-sulfate particles formed onto the negative electrode have a particle size of up to 5 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

9. The lead acid battery of any one of claims 1 to 8, wherein said CNTs are in the form of a CNTs composition.

10. The lead acid battery of claim 9, wherein said CNTs composition comprises CNTs and at least one dispersing agent.

11. The lead acid battery of claim 10, wherein the dispersing agent is selected from carboxymethyl cellulose (CMC), a lignosulfate and mixtures thereof.

12. The lead acid battery of claim 11, wherein the dispersing agent is carboxymethyl cellulose (CMC).

13. The lead acid battery of any one of claims 10 to 12, the weight ratio between CNTs and the dispersing agent in the CNT composition is between about 70:30 and 40:60.

14. The lead acid battery of claim 13, wherein said ratio is between about 60:40 and 50:50.

15. The lead acid battery of any one of claims 1 to 14, wherein the CNTs are separated from each other by a plurality of lead oxide particles coating each CNT in the formulation.

16. The lead acid battery of any one of claims 1 to 15, wherein the CNTs form a discontinuous spatial arrangement in the formulation.

17. The lead acid battery of any one of claims 1 to 16, wherein the lead oxide particle size is between about 0.2 and 10 microns.

18. The lead acid battery of any one of claims 1 to 17, wherein the CNTs are selected from single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs), and few-walled carbon nanotubes (FWNTs).

19. The lead acid battery any one of claims 1 to 18, wherein the CNTs having a diameter of between about 1 and 100 nm.

20. The lead acid battery of claim 19, wherein the CNTs having a diameter of between about 1 and 10 nm.

21. The lead acid battery of any one of claims 1 to 20, wherein the CNTs having a length of between about 1 and 50 μm.

22. The lead acid battery of claim 21, wherein the CNTs having a length of between about 1 and 10 μm.

23. The lead acid battery of any one of claims 1 to 22, wherein the concentration of the CNTs in said formulation is between about 0.001% and 5% (wt%) of the total lead oxide weight.

24. The lead acid battery of claim 23, wherein the concentration of the CNTs in said formulation is between about 0.001% and 2% (wt%).

25. The lead acid battery of claim 24, wherein the concentration of the CNTs in said formulation is between about 0.001% and 0.2% (wt%).

26. The lead acid battery of any one of claims 1 to 25, wherein both of the positive and the negative electrodes comprise said formulation.

27. The lead acid battery of claim 26, wherein the CNTs concentration in the formulations in each of the positive and the negative electrodes is the same.

28. The lead acid battery of claim 26, wherein the CNTs concentration in the positive electrode formulation in different from the CNTs concentration in the negative electrode formulation.

29. The lead acid battery of any one of claims 26 to 28, wherein the CNTs concentration in the formulation is (i) between about 0.001 and 0.05 wt% in the negative electrode and (ii) between about 0.01 and 0.1 wt% in the positive electrode.

30. The lead acid battery of any one of claims 1 to 29, wherein said formulation further comprises at least one additive.

31. The lead acid battery of claim 30, wherein said additive is carbon black.

32. The lead acid battery of claim 31, wherein the formulation comprises carbon black in an amount of between about 0.1 and 1.5 wt%.

33. The lead acid battery of claim 32, wherein the formulation comprises carbon black in an amount of between about 0.2 and 0.5 wt%.

34. A lead-acid battery comprising at least one cathode, at least one anode and sulfuric acid, at least one of said anode and cathode being made of a substrate at least partially coated by a formulation comprising lead oxide particles (PbO_2), between about 0.01 and 0.2 wt% carbon nanotubes (CNTs), the battery being characterized in that lead-sulfate particles formed onto at least one of the positive and negative electrodes having a size of up to 5 μm when the battery's output voltage drops below 10.5V when the battery is cycled at a DOD value of between 17.5 and 30%.

35. A process for operating a battery, the process comprising:

- constructing the lead-acid battery of any one of claims 1 to 34; and
- contacting and de-contacting said one or more negative electrode and one or more positive electrode in at least one cycle of operation, such that discharging of the battery is carried out at a depth of discharge having a value of between 17.5 and 30%.

36. The process of claim 35, wherein discharging of the battery is carried out at a depth of discharge of the at least 25%.

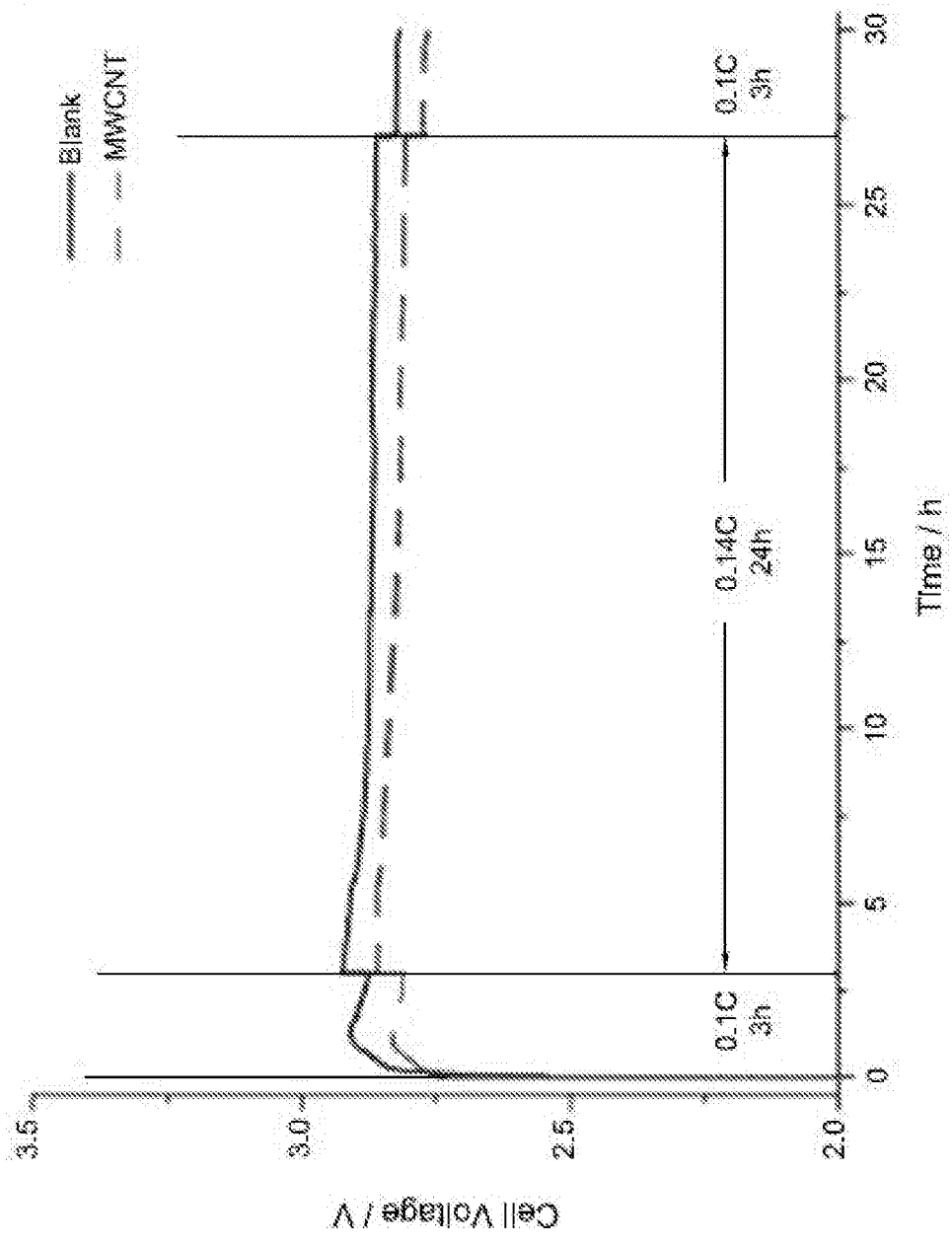
Blank
MWCNT
0.1C
3h
0.14C
24h
0.1C
3h
Time / h
Cell Voltage / V
3.5
3.0
2.5
2.0
0
5
10
15
20
25
30

Fig. 1

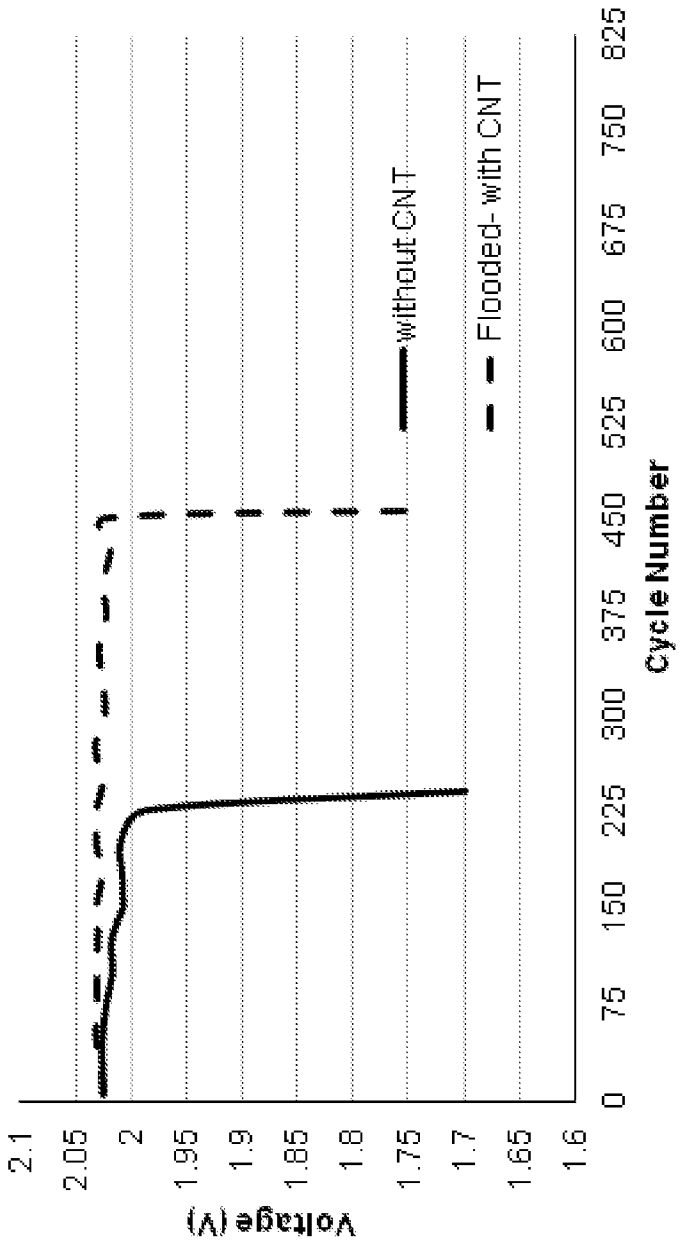
Voltage (V)
2.1
2.05
2
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
0
75
150
225
300
375
450
525
600
675
750
825
Cycle Number
without CNT
Flooded- with CNT

Fig. 2

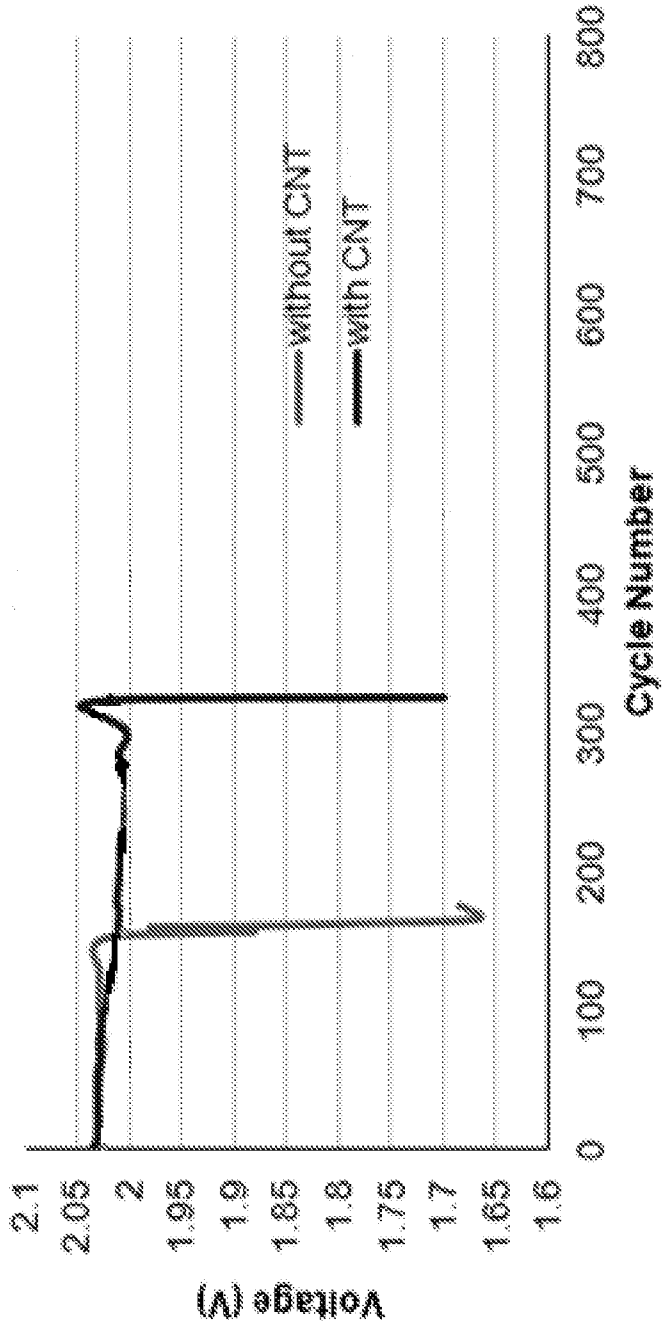
Voltage (V)
2.1
2.05
2
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
0
100
200
300
400
500
600
700
800
Cycle Number
without CNT
with CNT

Fig. 3

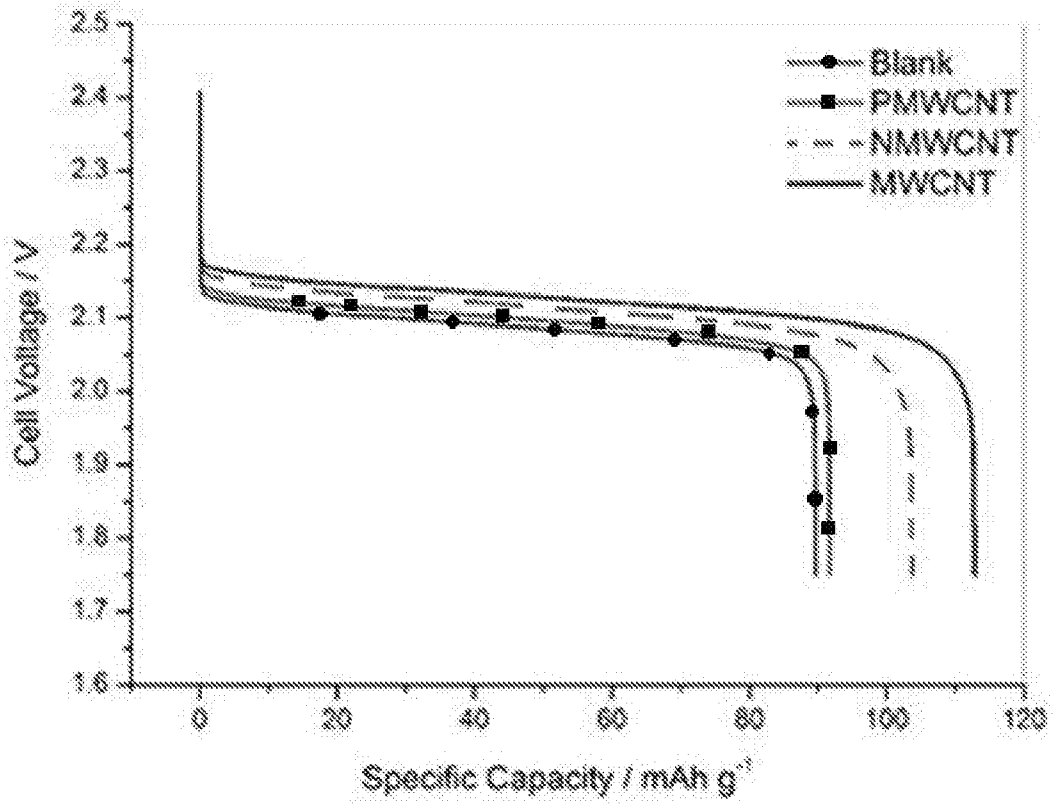
Blank
PMWCNT
NMWCNT
MWCNT
Cell Voltage / V
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
0
20
40
60
80
100
120
Specific Capacity / mAh g-1

Fig. 4A

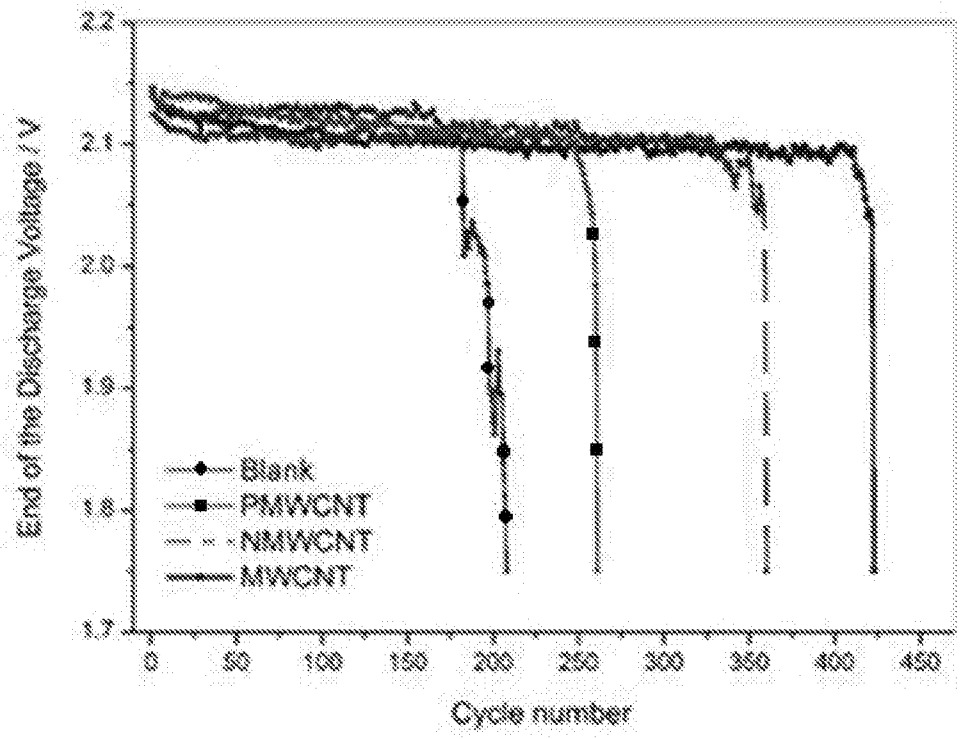
End of the Discharge Voltage / V
2.2
2.1
2.0
1.9
1.8
1.7
0
50
100
150
200
250
300
350
400
450
Cycle number
Blank
PM/WCNT
NM/WCNT
MWCNT

Fig. 4B

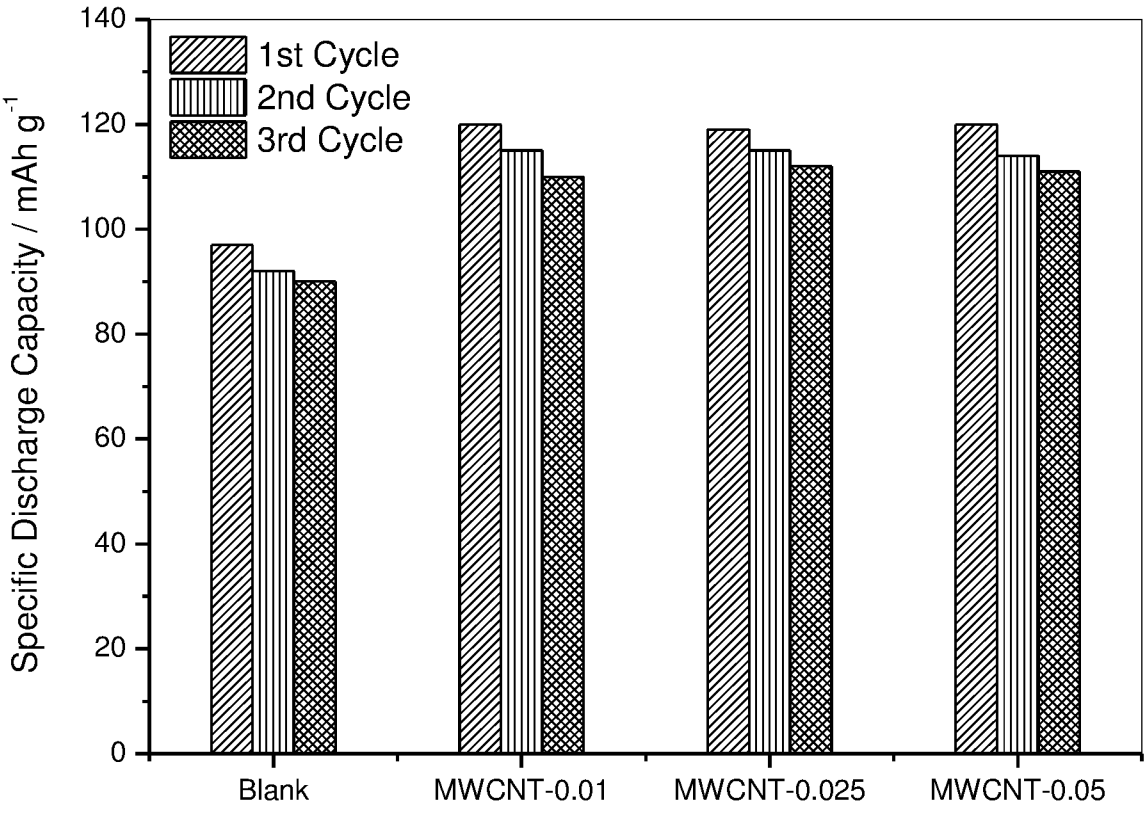
Specific Discharge Capacity / mAh g-1
140
120
100
80
60
40
20
0
1st Cycle
2nd Cycle
3rd Cycle
Blank
MWCNT-0.01
MWCNT-0.025
MWCNT-0.05

Fig. 5

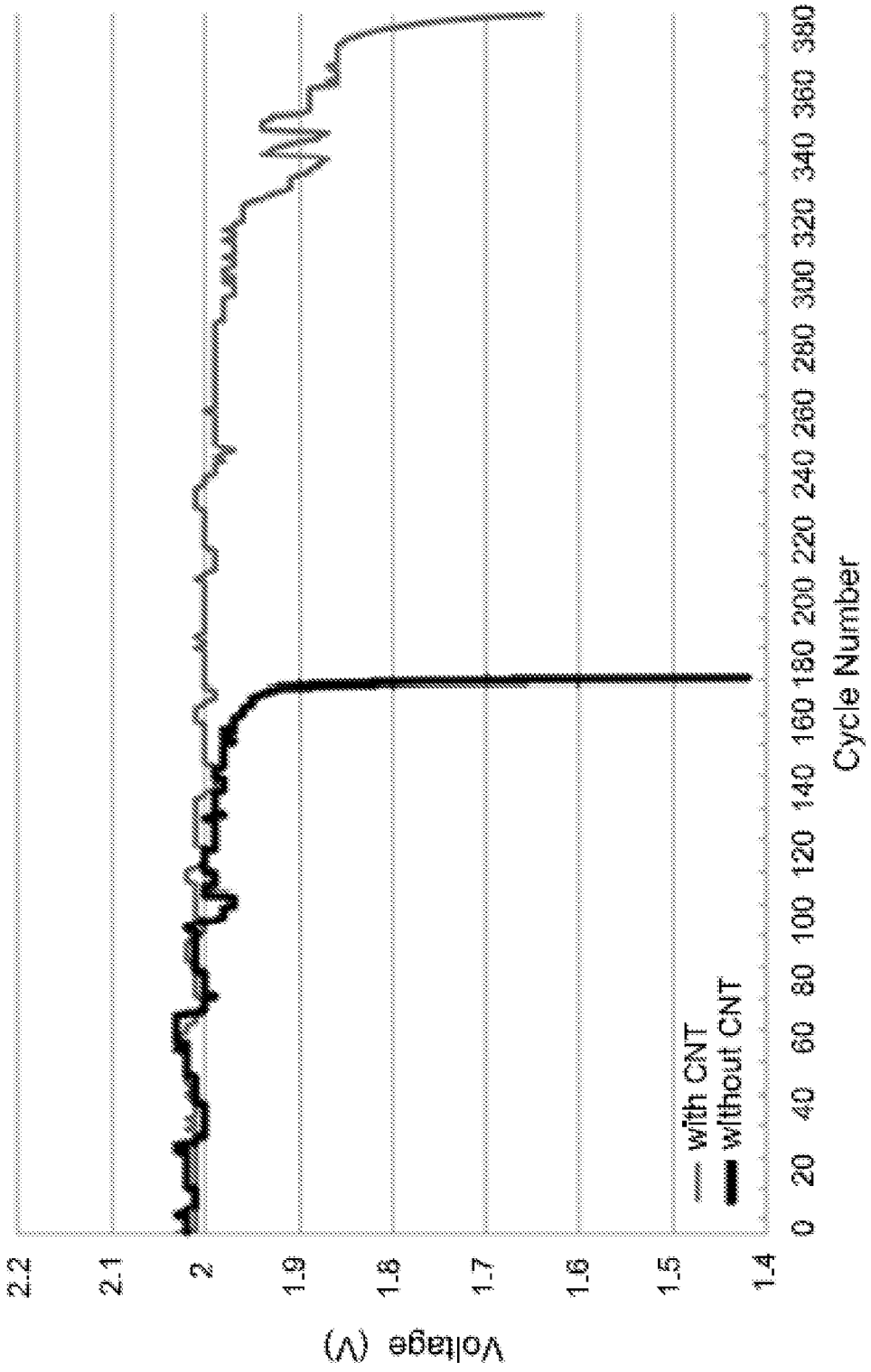
Voltage (V)
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
Cycle Number
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380
with CNT
without CNT

Fig. 6

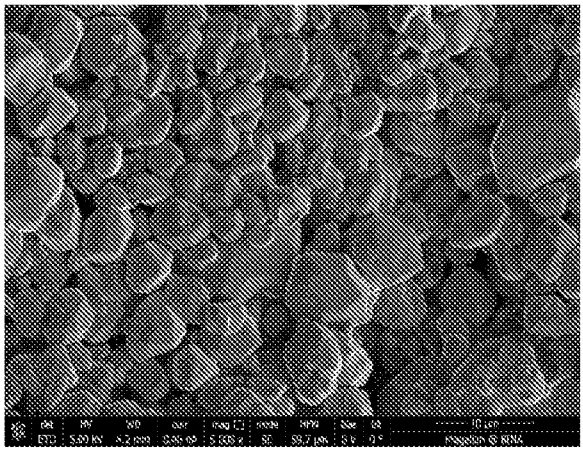

Fig. 7A

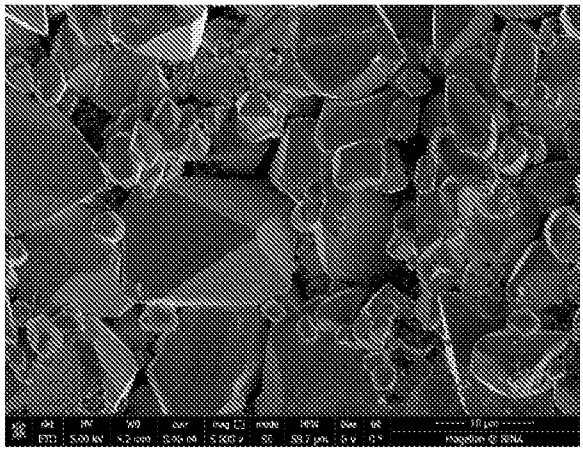

Fig. 7B

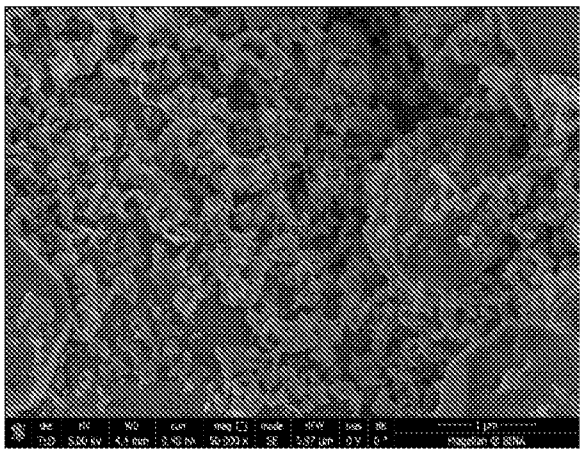

Fig. 7C

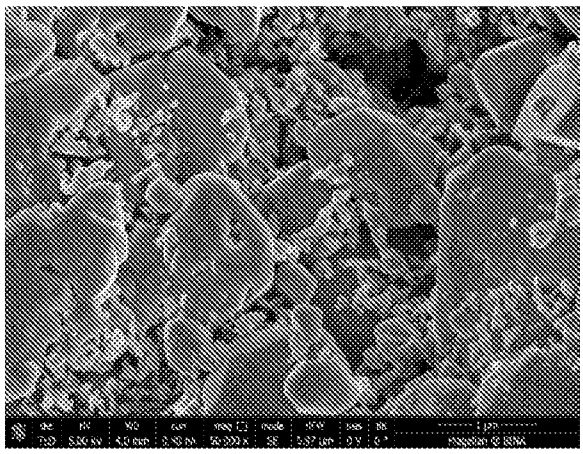

Fig. 7D

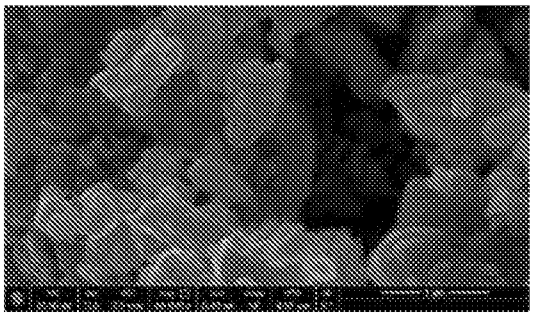

Fig. 8A

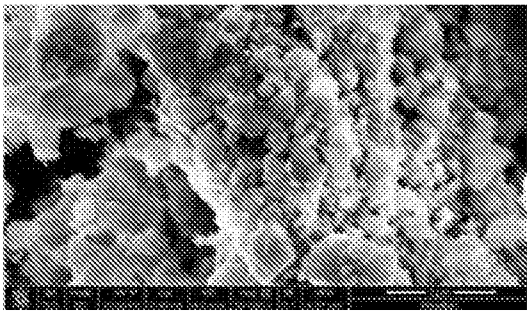

Fig. 8B

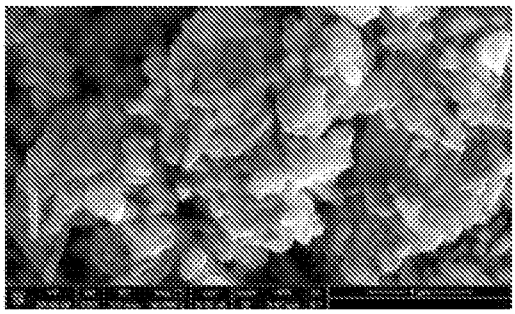

Fig. 8C

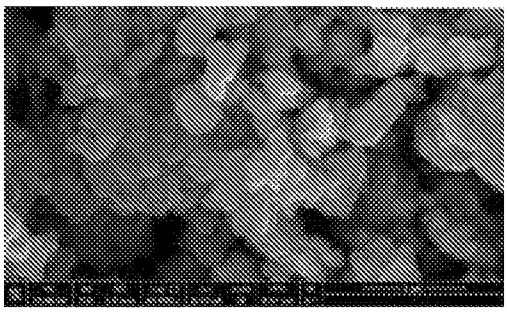

Fig. 8D

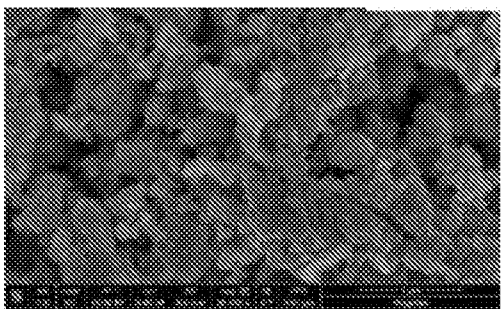

Fig. 8E

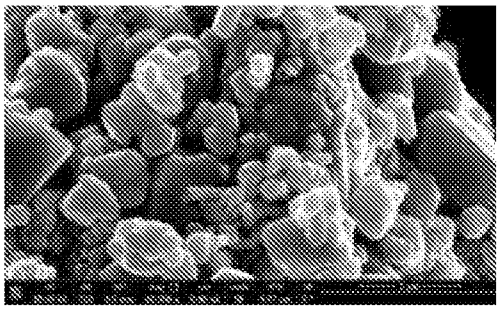

Fig. 8F

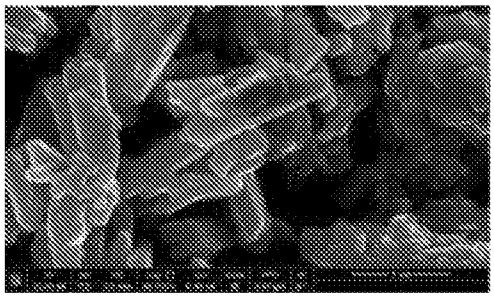

Fig. 8G

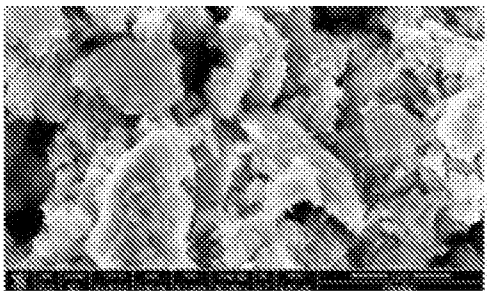

Fig. 8H

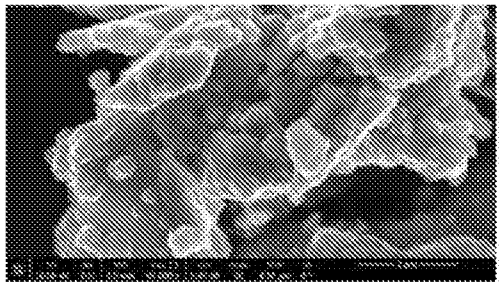

Fig. 8I

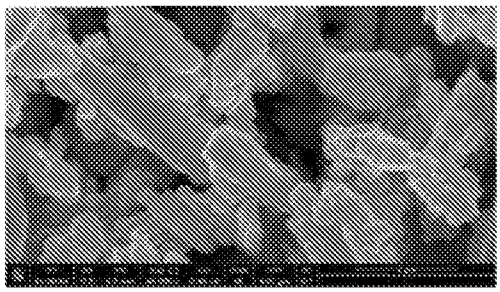

Fig. 8J

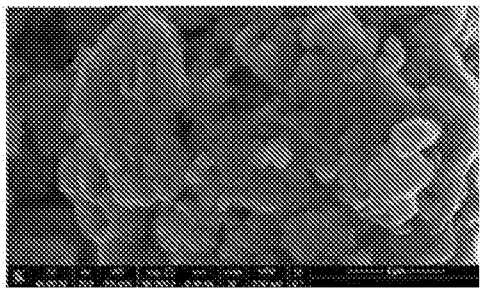

Fig. 8K

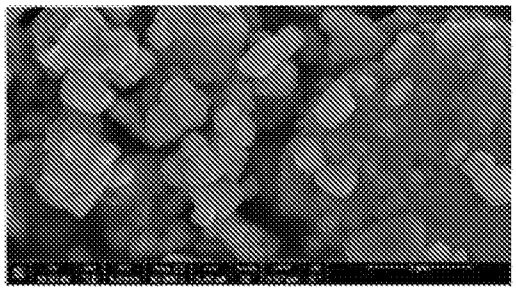

Fig. 8L

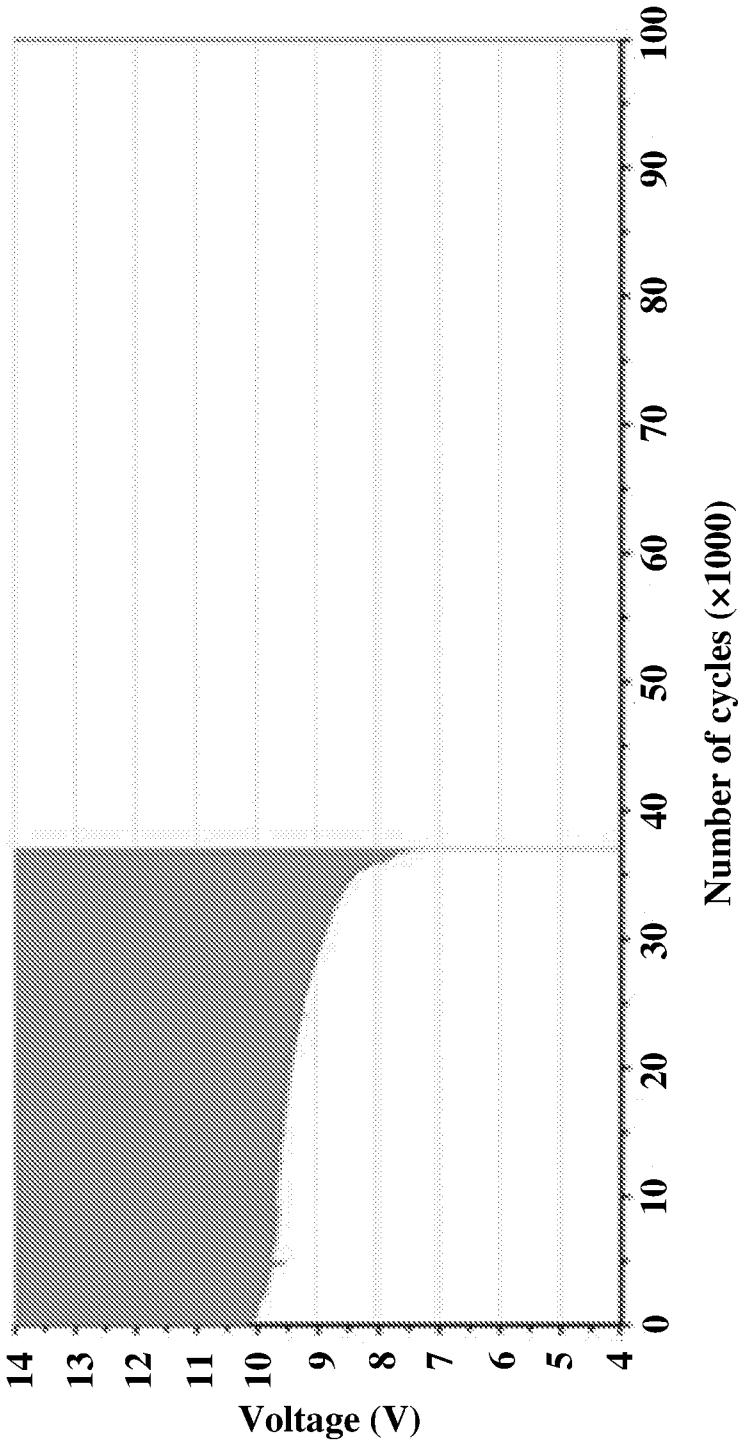
Number of cycles (×1000)
0
10
20
30
40
50
60
70
80
90
100
Voltage (V)
14
13
12
11
10
9
8
7
6
5
4

Fig. 9A

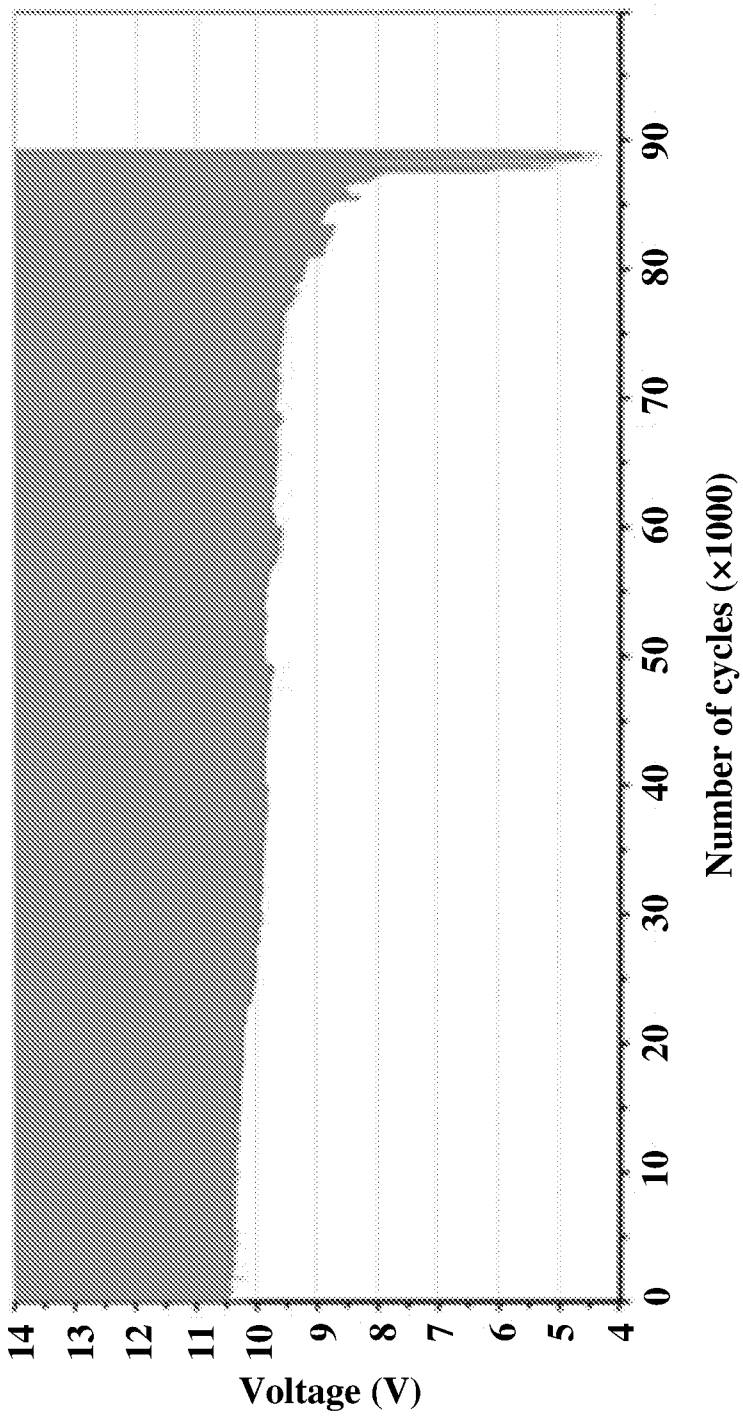
Number of cycles (×1000)
0
10
20
30
40
50
60
70
80
90
Voltage (V)
14
13
12
11
10
9
8
7
6
5
4

Fig. 9B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2016/050460

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2016.01) B82Y 30/00, H01M 10/12, H01M 4/14, H01M 4/68, C01G 21/06

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)

IPC (2016.01) B82Y 30/00, H01M 10/12, H01M 4/14, H01M 4/68, C01G 21/06

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)

Databases consulted: THOMSON INNOVATION, CAPLUS, Google Scholar
Search terms used: lead-acid battery, carbon nanotubes (CNTs)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013011516 A1 VULCAN AUTOMOTIVE INDUSTRIES LTD, ; BAR ILAN UNIVERSITY, ; ZIMRIN, TOMER, ; SHAPIRA, RONI, ; AURBACH, DORON, ; CAHANA, BENI 24 Jan 2013 (2013/01/24) whole document	1-9,13-36
Y	whole document	10-12
Y	Multi-walled carbon nanotubes percolation network enhanced the performance of negative electrode for lead-acid battery. Journal of The Electrochemical Society, 2013, 160.1: A70-A76. SARAVANAN, M., et al. 07 Nov 2012 (2012/11/07) abstract, Page A75	10-12
Y	WO 2014141279 A1 VULCAN AUTOMOTIVE INDUSTRIES LTD, ; BAR ILAN UNIVERSITY 18 Sep 2014 (2014/09/18) abstract, page 6	10-12

☐ Further documents are listed in the continuation of Box C.

☒ 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

"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)

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

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 Jul 2016	10 Jul 2016
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616	Authorized officer BERKOWITZ Tzipora Telephone No. 972-2-5651656

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IL2016/050460

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
WO 2013011516 A1	24 Jan 2013	WO 2013011516 A1	24 Jan 2013
		US 2014162111 A1	12 Jun 2014
WO 2014141279 A1	18 Sep 2014	WO 2014141279 A1	18 Sep 2014
		CN 105051930 A	11 Nov 2015
		EP 2973777 A1	20 Jan 2016
		IL 240697 D0	29 Oct 2015