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Hybrid Energy Storage Devices Combining Carbon-Nanotube/Polyaniline Supercapacitor with Lead-Acid Battery Assembled through a “Directly-Inserted” Method

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In this work, we used a new method to assemble hybrid energy storage devices combining electrochemical capacitor with lead-acid battery. The ultrathin, flexible and low-weight carbon-nanotube/polyaniline (CNT/PANI) composite films used as supercapacitor electrodes were “directly-inserted” into lead-acid battery in series or parallel. This quite simple and effective method is promising for large-scale industrialization with less increase of production process complexity. The assembled hybrid devices showed notably improved properties including higher specific capacity by 19%, higher specific energy by 21% or higher specific power by 6% than the conventional independent lead-acid batteries, which can be attributed to the synergic effect of batteries and supercapacitors.

Introduction

With the approaching fossil energy source crisis and the exacerbating environmental pollution, the use of clean energy such as electrical energy has been urgently needed. Electrical energy storage devices with high stability and excellent efficiency are needed to collect the unstable electrical energy generated from wind or solar power systems and to supply power for portable electronic equipment or electric vehicles. As the most common electrical energy storage devices, rechargeable batteries can supply high specific capacity and specific energy, but their low specific power and short cycle-life limits some special applications such as high current charge-discharge[1]. Compared with rechargeable batteries, supercapacitors can provide higher specific power and more outstanding cycle stability, but their specific energy is much lower[2-7]. Therefore, the hybrids of rechargeable battery and supercapacitor have been investigated to achieve electrical energy storage devices having both high specific energy and specific power[8].

Some routes to hybrid rechargeable battery with supercapacitor have been tried on conventional batteries, including nickel metal hydride battery[9], lithium ion battery[10-13], lithium sulfur battery[14], biofuel cell[15], etc, which show remarkable improvements of battery properties. Compared with above batteries, lead-acid battery, a classical battery, has shown merits of safety, reliability and mature manufacture technology, which usually serves as uninterruptible power supply (UPS) and power supply of various electrical equipments[16]. Moreover, Pb is a much cheaper, more abundant and more easily recycled source than most metal used in other batteries, which enables wider application potentials of lead-acid battery such as supporting electrical energy for hybrid-electric vehicles (HEVs). However, the comparable low specific energy and power of lead-acid battery than other new-generation batteries limited its applications with larger power need. Therefore, further studies on hybrids of supercapacitor and lead-acid battery in one cell have been operated to improve the electrochemical performances of classical lead-acid batteries. The hybrid methods can be classified to the following two types.

First, there have been trials on combining supercapacitor and lead-acid battery in new electrode configurations. As Lam *et al.*[17] reported, PbO_2 was used as the common positive plates, and carbon-based supercapacitor electrode was connected internally with the sponge Pb in parallel to be common negative plates. A hybrid energy-storage device combining an asymmetric supercapacitor and lead-acid battery in one unit cell was achieved showing a higher discharging-charging power and longer cycle-life than the conventional lead-acid batteries. Yu *et al.*[18] designed a hybrid supercapacitor with PbO_2 as positive electrode and activated carbon as negative electrode, which exhibited larger specific capacitance, higher power and more stable cycle performance than the lead-acid battery.

Second, hybrids of supercapacitor and lead-acid battery also have been achieved by adding capacitive carbon materials to the battery plates. When HEVs work under high rates and partial state-of-charge (HRPSoC) mode, $PbSO_4$ will be generated on the surface of Pb negative plates , that is also called sulfation, leading to the reducing of electrode effective surface-area, battery charging-discharging efficiency and cycle-life. Carbon materials such as activated carbons, carbon blacks and graphite have been added to the negative active material to form a capacitive carbon system combined with an electrochemical Pb system, which enhances electroconductivity of negative plates and improves the charge–discharge characteristics of batteries[19-23]. Shapira *et al.*[24] improved the cycle life of lead-acid batteries through adding properly oxidized carbon nanotubes (CNTs) to the positive active material of lead-acid batteries. Consisted of CNTs conformably coated with Pb salts, a stable conductive grid was formed to enable the delivery of current to all the active material, which avoids the sulfation of lead-acid batteries plates.

From above works, the electrode configuration designing of devices and the choice of added capacitive carbon materials are identified as the two key points of methods to assemble hybrid energy storage devices combining supercapacitors with lead-acid batteries.

Flexible film supercapacitors based on CNT, graphene or other carbon nanoporous materials have recently attracted interests because of their application potentials in wearable electronics[25-30]. The superaligned CNTs fabricated in our laboratory have the merits of great aspect ratio, large special surface-area and excellent electric conductivity[31,32], which have been used as flexible film supercapacitor electrodes showing high specific capacitance[33-35]. Polyaniline (PANI), a conventional conducting polymer, shows larger pseudo capacitance than the electric double-layer capacitance of CNTs, but has worse cycle-life and mechanical properties. By coating PANI on freestanding super-aligned CNT networks, CNT/PANI composite film have been fabricated in our laboratory as supercapacitor electrodes showing ultra-thinness, outstanding light-weight, perfect flexibility and enhanced electrochemical properties[36,37]. This composite film is a good choice for supercapacitor electrodes used to hybrid with lead-acid batteries.

In this work, we tried to assemble hybrid energy storage devices combining CNT/PANI composite film supercapacitor with lead-acid battery through a much easier method that supercapacitor electrodes were "directly-inserted" into lead-acid battery, which have never been reported previously. These new hybrid devices showed higher specific capacity, specific energy and specific power than the conventional independent lead-acid battery.

Experimental

Fabrication of CNT/PANI composite film electrodes.

Superaligned CNTs used in this work were fabricated by chemical vapor deposition (CVD) on silicon wafers with iron as the catalyst and acetylene as the precursor. A uniform suspension of CNTs was obtained by ultrasonication (800 W, 10 minutes) of superaligned CNTs in ethanol. After filtration of CNTs suspension through a microporous membrane with the aid of vacuum, CNT networks was formed and dried at 80 °C for 12 h in a vacuum oven to be peeled off from the microporous membrane. The as-prepared CNT networks were immersed in 40 ml aqueous solution containing 0.04 mol L^{-1} HCL and 0.002 mol L^{-1} aniline monomers (purity $\geq$ 99.5%) for ten minutes of complete infiltration. As oxidant for polymerization, 40 ml precooled aqueous solution containing 0.002 mol L^{-1} ammonium persulfate was dropped slowly in the above solution. The mixed solution was put at 0 °C for 24 h to react completely resulting in the PANI coated uniformly on the CNT networks. The obtained CNT/PANI composite film was picked out from reacted solution, cleaned with deionized water, acetone and ethanol and dried at 80 °C in a vacuum oven for 12 h.

Fabrication of Pb negative plates and PbO_2 positive plates.

We disassembled a commercial Valve regulated lead-acid (VRLA) battery (6V 1.3Ah, Jiangsu Jiuhua Energy Technology Co., Ltd., China) and directly use the negative and positive plates to assemble new devices.

Assembling of batteries.

The CNT/PANI composite film electrodes and the disassembled battery plates were cut into rectangles with the same size of 1.2 cm × 1.4 cm. Then, we sealed the structures constructed by electrodes and plates by plastic film, with glass fiber cross wall (also called AGM) as separator and 5 mol L^{-1} H_2SO_4 aqueous solutions as electrolyte.

Characterization.

The microstructures of the CNT/PANI composite films were characterized by scanning electron microscopy (SEM) (Sirion 200, resolution 1.0 nm, FEI, USA). The electrochemical performances were tested through Galvanostatic charging-discharging experiments (Land Battery Testing System, China).

Results and discussion

First, we fabricated CNT/PANI composite film through an in situ chemical solution method reported before in our laboratory. As Fig. 1a-d demonstrates, the composite film as thin as a piece of printing paper (about 100 μm) can be easily folded and bended. Combining flexibility and thinness, it shows great potential to match up with battery plates with various shapes. Fig. 1e shows the scanning electron microscopy (SEM) image of the CNT/PANI composite film. CNTs are connected with each other to form nanoporous networks with pore size in about 100 nanometers, where PANI is coated uniformly on the CNTs.

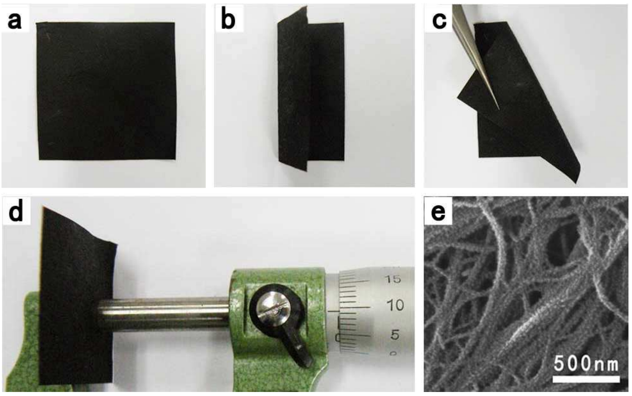

Fig. 1 Photographs of CNT/PANI film in (a) flat, (b) folded and (c) bended state, respectively. (d) The thinness of CNT/PANI composite film shown with measurement by micrometer caliper. (e) SEM image of the microstructures of CNT/PANI composite film.

Second, we disassembled a commercial VRLA, and got the positive plate and negative plate. As Fig. 2a illustrates, the positive plate (thickness, 3.17 mm) and negative plate (thickness, 2.49 mm) in this battery are constructed of the current collector made of a thick grid of lead's alloys with calcium, which are coated with positive and negative paste materials of lead oxide and lead, respectively. Compared with these battery plates, the fabricated CNT/PANI composite films are ultrathin and low-weight.

Finally, we directly inserted CNT/PANI film electrodes into a cell of the disassembled VRLA in the following three different ways:

1. Positive-Plate//CNT/PANI//Separator//CNT/PANI//Negative-Plate,

also called Lead-acid Battery + Supercapacitor in series inside;

2. CNT/PANI//Positive-Plate//Separator//Negative-Plate//CNT/PANI,

   also called Lead-acid Battery + Supercapacitor in series outside;

3. Positive-Plate//Separator//Negative-Plate in parallel with CNT/PANI//Separator//CNT/PANI,

   also called Lead-acid Battery + Supercapacitor in parallel.

Fig. 2b-d demonstrates above structures.

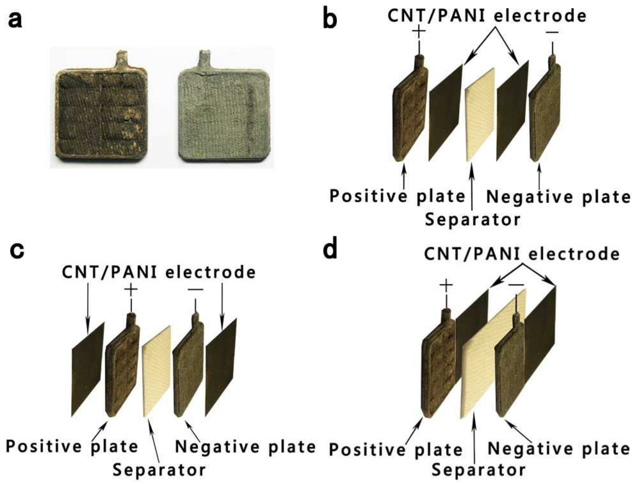

Fig. 2 (a) Photographs of the positive plate (left) and negative plate (right) disassembled from a commercial VRLA. The schematic structures of the three hybrid energy storage devices: (b) Lead-acid Battery + Supercapacitor in series inside; (c) Lead-acid Battery + Supercapacitor in series outside; (d) Lead-acid Battery + Supercapacitor in parallel.

For comparison, we also manufactured an independent symmetric supercapacitor with CNT/PANI as electrodes and an independent lead-acid battery in the following ways:

1, CNT/PANI//Separator//CNT/PANI;

2, Positive-Plate//Separator//Negative-Plate.

All above devices were assembled in the same condition, including supercapacitor electrodes and lead-acid battery plates with the same mass and size, the same electrolyte, separator, current collector and packaging method.

To compare the electrochemical performances of the independent lead-acid battery and three hybrid energy storage devices at high rate charge-discharge state, galvanostatic charging-discharging experiments were performed as the following steps:

1, charged at the same current of 60 mA (the rate of about 1.2 C) for 1 hour from the initial window potential of 1.6 V;

2, discharged at the same current of 60 mA to the potential of 1.6 V.

As the charge-discharge curve in Fig. 3 displays, all the devices get the same charge capacity of 60 mAh, while the Lead-acid Battery + Supercapacitor in series outside displays a longer discharging time than the other two types of hybrids and the independent lead-acid battery, which indicates that this device has the largest discharge capacity among all above devices.

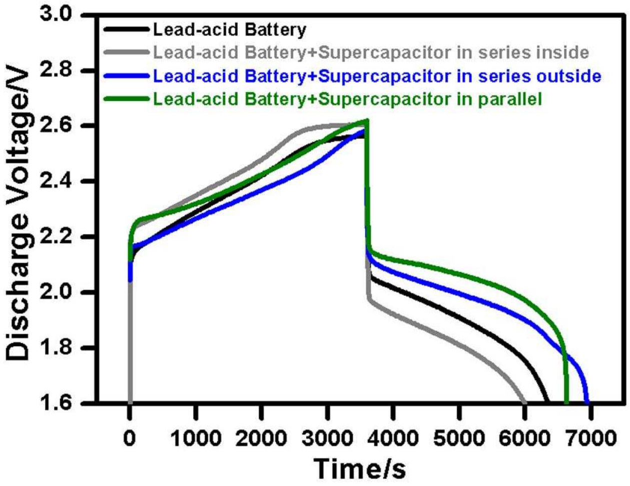

Fig. 3 The galvanostatic charging-discharging curves of the independent lead-acid battery, three types of hybrid energy storage devices tested as the following steps: 1, charge at the same current of 60 mA for 1 hour from the initial potential of 1.6V; 2, discharge at the same current of 60 mA to the potential of 1.6V.

To study the high rate charge-discharge performance of the independent supercapacitor, a galvanostatic charging-discharging experiment was carried out at the current of 60 mA in the potential window of 0-0.8 V (this potential window is adaptable to the pseudo capacitance of PANI). Fig. 4 shows the charge-discharge curve of the supercapacitor. The discharging time (24 seconds) of the supercapacitor is much shorter than the lead-acid battery (2736 seconds) demonstrating that the supercapacitor owns the enhanced ability for rapid charge and discharge.

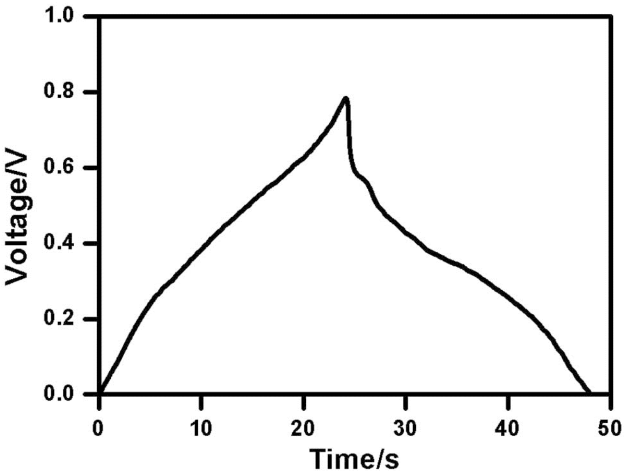

Fig. 4 The constant current charging-discharging curves of the independent supercapacitor at the current of 60 mA in the potential window of 0-0.8 V.

By calculating results obtained from above experiments, we achieved some characters of the three hybrid devices, lead-acid batteries and supercapacitors, including the mass of all electrodes in one cell (M), specific capacity (C_s), specific energy (E_s) and specific power (P_s) in the discharge process. The specific capacity is calculated according to

$$C_s=I\times\Delta t/M \quad (1)$$

where I is the discharging current, Δt is the discharging time. The specific energy is calculated according to

$$E_s=\int U\times Idt/M \quad (2)$$

where U is the discharging voltage. The specific power is calculated according to

$$P_s=E_s/\Delta t \quad (3)$$

Table 1 Characterizations of the devices.

Device	M (g)	C_s (mAh g^{-1})	E_s (Wh kg^{-1})	P_s (W kg^{-1})
Supercapacitor	0.017	23.8	7.2	1095.0
Lead-acid Battery	5.500	8.4	15.9	20.7
Lead-acid Battery + Supercapacitor in series inside	5.517	7.1	12.9	19.6
Lead-acid Battery + Supercapacitor in series outside	5.517	10.0	19.3	20.9
Lead-acid Battery + Supercapacitor in parallel	5.517	9.1	18.5	22.0

As Table 1 demonstrates, the independent supercapacitor shows a higher specific capacity (23.8 mAh g^{-1}) of 2.8 times of the lead-acid battery (8.4 mAh g^{-1}) and an extra higher specific power (1095.0 W kg^{-1}) of 52.9 times of the lead-acid battery (20.7 W kg^{-1}), but its specific energy (7.2 Wh kg^{-1}) is much lower than the lead-acid battery (15.9 Wh kg^{-1}).

The Lead-acid Battery + Supercapacitor in series outside shows a higher specific capacity (10.0 mAh g^{-1}) of 19% improvement over the lead-acid battery (8.4 mAh g^{-1}), a higher specific energy (19.3 Wh kg^{-1}) of 21% improvement over the lead-acid battery (15.9 Wh kg^{-1}), and a similar specific power (20.9 W kg^{-1}) with the lead-acid battery (20.7 W kg^{-1}). The Lead-acid Battery + Supercapacitor in parallel shows a higher specific capacity (9.1 mAh g^{-1}) of 8% improvement over the lead-acid battery (8.4 mAh g^{-1}), a higher specific energy (18.5 Wh kg^{-1}) of 16% improvement over the lead-acid battery (15.9 Wh kg^{-1}), and a higher specific power (22.0 W kg^{-1}) of 6% improvement over the lead-acid battery (20.7 W kg^{-1}). However, the mass of all electrodes of hybrid device (5.517 g) is only 0.3% higher than the lead-acid battery (5.500 g), indicating that the adding of low-weight supercapacitive electrode can markedly enhance the electrochemical performance of the lead-acid battery. The lead-acid batteries and the hybrid energy storage devices here are manual assembled in the laboratory. Their electrochemical properties can be further optimized by using industrialized skills in producing batteries. However, the obtained results do not affect relative comparison among the assembled devices. The Lead-acid Battery+Supercapacitor in series inside show the worst performance among all the hybrid devices and the independent lead-acid battery.

The enhanced electrochemical performances of the hybrid energy storage devices: 1, Lead-acid Battery+Supercapacitor in series outside; 2, Lead-acid Battery+Supercapacitor in parallel can be attributed to the synergistic effect of lead-acid battery and supercapacitor. The hybrid approach improves the overall utilization of all electrode materials. In the high current discharging process of the hybrid device, the supercapacitor shares the large percent of the whole current for its higher power ability than the lead-acid battery so that the lead-acid battery discharged in a lower current than the whole current. Because of electrode polarization in high current discharge, the discharge capacity of the same battery will decrease with the increase of discharge current. As the lead-acid battery partial in the hybrid device is discharged in a lower current than the independent lead-acid battery, the former can supply higher capacity than the latter. Meanwhile, the mass of all electrodes of hybrid device is only a little higher than the independent lead-acid battery. Therefore, the hybrid device shows higher specific capacity than the independent lead-acid battery. The discharge specific energy can be calculated according to

$$E_s=U_p\times C_s \quad (4)$$

where U_p is the discharge voltage platform. It is shown in Fig. 3 that the hybrid device combined in series outside and in parallel has a higher discharge voltage platform than the independent lead-acid battery. Hence, the specific energy of the hybrid device is also higher than the independent lead-acid battery. Nevertheless, the specific mechanism of the enhanced electrochemical performances for these new hybrids of supercapacitor and lead-acid battery needs further investigation.

Conclusions

In summary, we have used a quite simple and effective method to assemble new hybrid energy storage devices combining supercapacitor with lead-acid battery in one cell. The ultrathin, flexible and low-weight CNT/PANI composite film supercapacitor electrodes are "directly-inserted" between lead-acid battery plates, which had never been reported previously. Compared with the independent lead-acid battery, the hybrid device combined in series outside shows a 19% higher specific capacity and a 21% higher specific energy, and the hybrid device combined in parallel shows a 6% higher specific power. The improvement of electrochemical properties of hybrid devices can be attributed to the synergic effect of lead-acid battery and supercapacitor.

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