A Smart Information Storage Equipment with High-Capacity and Energy Level-Indicating Functionality

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Abstract. The tendency that the neonatal smart storage devices are integrated with energy storage and electrochromism functions have captured enormous attentions, showing potential applications in energy conservation, emission reduction and environmental protection. Here, we demonstrate a new approach to improve the capacity (170 mAhg-1), which is almost three times larger than that the recently reported approach simply through by enlarging voltage range (0.3-2.5 V). The improved capacity may come from complicated structure and valence state variation of Prussian blue, which facilitate the two pair redox reactions. Metal aluminum was used to reduce Prussian blue (PB) to Prussian white (PW) then to Berlin green (BG) in potassium chloride electrolyte and vice versa. That is, there are two charging/discharging processes in our battery (Smart Information Storage Equipment) providing a higher capacity than that provided by only one. Additionally, the device we designed would provide a convenient user-device interface based on a three-colored human-readable output.

Keywords: Smart Information Storage Equipment, Electrochromic Information Storage Equipment, High-Capacity.

1. Introduction

Batteries, parts of the most widespread energy storage devices have been intensively investigated, playing an important role in modern human life [1-3]. The application of batteries are also positive solutions for energy shortage and global warming that the world is currently facing to promote the environmental sustainability. Previous work is committed to solve the conventional problems of batteries, such as low capacity, unsatisfied cycle life span, and so on [4-7]. While current efforts have been made to the smart applications required along with an improved demand of the flexibe, fiber devices and smart applications with convenient user-device interface based on a friendly human-readable output [8-10]. In our previous work, an smart energy storage approach was proposed, in which a pattern of “SINANO” indicating the energy storage at different levels through the colors change of electrodes driven by the external bias was demonstrated [8]. Recently, Sun's group has reported a typical smart device of potential application in the future, who used electrochromic Prussian blue as the electrode material with the operating voltage for of 1.26 V and the optimal discharge capacity of 72.2 $mAhg^{-1}$ [4]. Obviously, they provided a bi-functional device: self-powered electrochromic window and self-rechargeable transparent battery. Additionally, the energy storage state can be directly observed by the color change of the electrode. The concept of such equipment is extremely innovative and will possibly open the door for the development of novel multi-functionalized battery. The newly exploited field of smart batteries, however, still leaves a crucial problem to be addressed, that is the specific capacity (72.2 $mAhg^{-1}$) of such electrochromic battery delivers is still too low to meet the requirements of practical application.

2. Methodology

It is well known that electrochromic materials, previously explored to exhibit battery characteristics, are able to store and release ions at switching biases. PB is an impotant clan of traditional electrochromic materials and pioneered by Neff et al [11-15]. There are two transformation modes of valence state, among which PB can act either as an oxidant to accept one electron transforming into reduced PW or as a reductant to lose one electron turning into BG at different potential intervals. Therefore, we select PB and aluminum (Al) as anode and cathode materials for the cell fabrication respectively. The measured open circuit voltage of the cell is 1.2 V with 1Mpotassium chloride (KCl) electrolyte. In order to seek the appropriate battery voltage range, applied biases are first set between -0.4 and 1.45 V to focus on the redox reactions using a three-electrode system with PB, Al and Ag/AgCl as the working, counter and reference electrodes, respectively (Figure S1). Then, with regard to the two-electrode Al/PB cell, the cyclic voltammetry configuration is monitored from 0.3 V to 2.6 V, which is calculated from the potential difference of Al versus Ag/AgCl (about -0.9 V) by electrochemical workstation (Figure 1a).

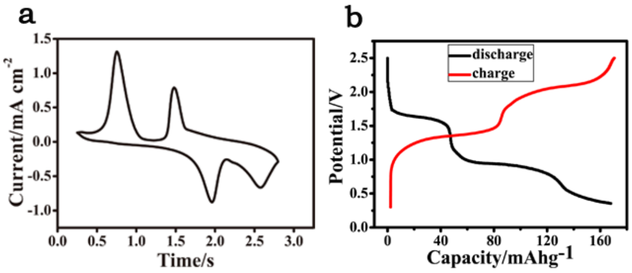

Fig. 1 Electrochemical characterization of Al-PB battery: (a) The cyclic voltammetry curve at the scan rate of 5 mV s-1 employing two-electrode system; (b) The lines of galvanostatic charge and discharge capacity measured at a current density of 1400 mAg-1, the red and black solid lines represented the charge and discharge process, respectively.

There are two pair of redox peaks appearing with electrode material at the potentials (V) of (0.75, 1.9V) and (1.48, 2.5V), respectively, the first pair of peaks can be attributed to the redox reactions between PB and PW along with K+ and one compensated electron inserted or extracted into/from the lattice of electrode materials. While the reason for another pair of peaks is the reversible transformation between PW and BG with the insertion or extraction of K+ together with another one compensating electron. In line with the CV result, two platforms can be observed in the galvano-static charge and discharge processes as shown in the Figure 1b. For charge curve, the first platform is consistent with the results previous reported by Sun's group, which occurs at 1.25V in accordance with reaction (1). And the second one appears at 1.75 V corresponding to the reaction (2). For discharge line, the first platform occurs at 1.75 V and the second one appears at 1 V, corresponding to the reaction (3) and (4), respectively. The discharge and charge capacity are calculated to be 168mAhg-1 and 170.33mAhg-1, respectively, which are extremely higher than that reported by the Sun's group. The discharge capacity is very close to the charge capacity, indicating a perfect reversibility in the discharging and charging of our battery.

$$K_2Fe^{II}[Fe^{II}(CN)_6](PW)- K^{+}- e^{-}= KFe^{III}[Fe^{II}(CN)_6](PB) \qquad (1)$$

$$KFe^{III}[Fe^{II}(CN)_6]\ (PB)- K^{+}- e^{-}= Fe^{III}[Fe^{III}(CN)_6]\ (BG) \qquad (2)$$

$$Fe^{III}[Fe^{III}(CN)_6]\ (BG)+ K^{+}+ e^{-}=KFe^{III}[Fe^{II}(CN)_6]\ (PB) \qquad (3)$$

$$KFe^{III}[Fe^{II}(CN)_6](PB)+K^{+}+e^{-}=K2Fe^{II}[Fe^{II}(CN)_6](PW) \qquad (4)$$

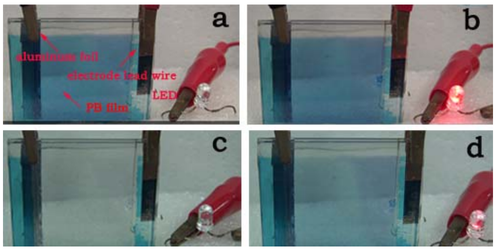

Fig.2 Visual photos of the electrochemical Al-PB battery: (a) The initial state is blue in color, implying a full power state with disconnection of the both electrodes; (b) The LED is lightened at the brightest when one connects the two electrodes together; (c) The Al-PB battery remains a transparent state and the LED cannot be lightened indicating that the electric power storage of the

device has been exhausted; (d) The Al-PB battery spontaneously recovers to thirsty blue and the LED can be lightened again after 24 h in air, indicating that the device is self-charged but not completely.

Another meaningful function of the as-prepared cell is the human-readable color output that is to say we can recognize the energy storage states through the different color states. We can catch sight of the initial state of the electrochromic battery in Figure 2a. And the chromic states of Al-PB battery can also be monitored in the whole visible range (400-800 nm) under differently self-charged condition by in situ UV-vis spectroscopy as shown in Figure 3b. The transmittance of the device is kept at 10% as the self-charged time increased from 5 to 40 min in air. The initial state of Al-PB battery under full charged condition typically manifests much lower light transmittance than that of the exhausted Al-PB battery as shown in Figure 3a, and the maximal optical modulation (60%) is definitely high enough to be observed even after the penetration from two FTO (SnO2: F) glasses and electrolyte. The original battery exhibits a blue color, which means a situation of full power. At the meantime, the light emitting diode (LED) is lightened at its brightest when the positive and negative electrodes were connected together by the metal wires to make a circuit (Figure 2b). As the discharged battery showing a transparent appearance, the LED cannot be lighted up (Figure 2c), demonstrating that the energy of the battery is used up. As shown in Figure 2d, by simply disconnecting the Al and PB electrodes, the device can be self-charged after exposure to air for 24 h due to oxidization of PW by O_2 in the air. At this time, the LED is lightened again but with dim brightness which signifies the materials is not activated completely.

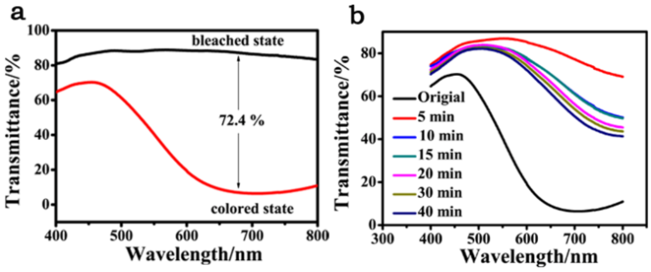

Fig.3 The characterization of the transmittance of the Al-PB battery transmittance: (a) The transmittance of bleached and colored state is monitored by in situ UV-vis spectroscopy. The maximum optical modulation is 72.4% at 670 nm; (b) The transmittance spectra of our battery is measured at various recovery times at 0 min, 5 min, 10 min, 15 min, 20 min, 30 min and 40 minby in situ UV-vis spectroscopy.

It deserves to be mentioned that the as-prepared Al/PB battery can also serve as electrochromic windows that can operates with no external driving force. The window can keep in blue and protect the house from hurting by the strong ultraviolet ray, when one keeps the Al and PB electrodes disconnecting, while the window can be changed into transparent to improve the visible transparency at any time by simply connecting the Al and PB electrodes. The bleaching and coloring processes correspond to the charging and discharging processes, respectively. For our battery, there are two approaches that could be chosen to charge the exhausted battery: (1) charged by the external bias, such as electrochemical workstation and mobile power; (2) charged by oxygen in the open. If external bias is used to drive our battery, it will tremendously accelerate the coloration rate by quick insertion and removal of the ions, the reversible change between high and low transmittance means a good reversibility, as shown in Figure S_2. The initial discharge capacity of our Al-PB electrochromic battery accurately monitored at -2 V for 60 s is 200 mAhg-1 by the electrochemical workstation as shown in Figure 4a.The charge capacity of the recovered Al-PB electrochromic battery recharged at 2.5 V for 60 s is 200 mAhg-1 and the electrochromic battery after spontaneous recovery via exposure to air for 24h is 80 mAhg-1. The first discharge capacity is approximately equal to 100% of the first dischargeable amount of the battery, compared with the only 40% by recovery storage in air in Figure4b. At last, the Al-PB electrochromic battery is experienced 20 cycles to evaluate its endurance

(Figure 4b).The charging and discharging capacity at constant voltage are almost equal to the capacity of galvano static charging and discharging, indicating a good reversibility again for the Al-PB electrochromic battery.

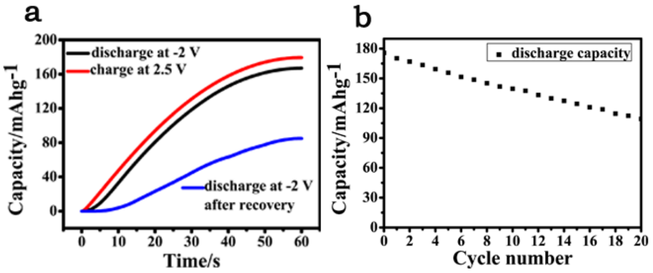

Fig.4 Specific capacities of the electrochemical Al-PB battery. (a) The battery is charged at 2.5 V; (b) The battery discharges at -2 V; (c) The battery is charged for 24 h in air.

3. Summary

In summary, we have successfully manufactured an electrochromic battery that possesses very high capacity and exhibits energy storage indication in color at different charged/discharged states. We employ the multi-valence state redox reaction of PB as electrode material to enlarge the voltage gap and largely improve the capacity of the electrochromic battery of Al/PB. The devices we have fabricated deliver an amazingly high discharge capacity of 429 $mAhg^{-1}$, which is approximately three times higher than the best capacity reported in previous literatures for the electrochromic batteries. Our advanced results may come from the following aspects: the intricate combination of structure and multi-valence state change of PB.

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