Journal of Power Sources 361 (2017) 31–38

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Facile synthesis of amorphous $FeOOH/MnO_2$ composites as screen-printed electrode materials for all-printed solid-state flexible supercapacitors

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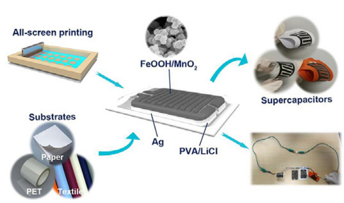
## HIGHLIGHTS

- The amorphous $FeOOH/MnO_2$ composites are prepared by a facile method.
- This material shows 350.2 F $g^{-1}$ and 95.6% capacitance retention after $10^4$ cycles.
- All-printed flexible supercapacitors are fabricated on PET, paper and textile.
- The device is capable to light up a 1.9 V LED, even after bending and stretching.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

Article history:
Received 22 April 2017
Received in revised form
7 June 2017
Accepted 21 June 2017

Keywords:
Flexible energy storage devices
Screen printing technique
All-solid-state supercapacitors
$FeOOH/MnO_2$ composites

## ABSTRACT

More convenience and intelligence life lead by flexible/wearable electronics requires innovation and hommization of power sources. Here, amorphous $FeOOH/MnO_2$ composite as screen-printed electrode materials for supercapacitors (SCs) is synthesized by a facile method, and solid-state flexible SCs with aesthetic design are fabricated by fully screen-printed process on different substrates, including PET, paper and textile. The amorphous $FeOOH/MnO_2$ composite shows a high specific capacitance and a good rate capability (350.2 F $g^{-1}$ at a current density of 0.5 A $g^{-1}$ and 159.5 F $g^{-1}$ at 20 A $g^{-1}$). It also possesses 95.6% capacitance retention even after 10 000 cycles. Moreover, the all-printed solid-state flexible SC device exhibits a high area specific capacitance of 5.7 mF $cm^{-2}$ and 80% capacitance retention even after 2000 cycles. It also shows high mechanical flexibility. Simultaneously, these printed SCs on different substrates in series are capable to light up a 1.9 V yellow light emitting diode (LED), even after bending and stretching.



## 1. Introduction

The rapidly growing of portable electronic devices and flexible/wearable consumer electronics bring convenience and intelligence to our lives, whilst require energy storage devices with excellent electrochemical performance, versatile shape and aesthetic design

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http://dx.doi.org/10.1016/j.jpowsour.2017.06.065

[1–3]. As electrochemical capacitors, SCs are ideally energy storage devices because of their high power density, fast charge/discharge rates, and long cycle life [4,5]. Conventional SCs, which consist of sheet-type electrodes, separators, and liquid electrolytes as the core components, are often fabricated through a rolling and winding or stacking process, and hence show stereotypical forms and lack flexibility. Although a variety of methods have been researched for the fabrication of SCs, such as micro-fabrication [6], photolithography [7], electrochemical deposition [8], laser scribing [9] and so on, which involve a high cost and complicated fabrication process, resulting in hurdles to high-volume and large-areas production. Moreover, these processes are designed for particular electrode materials, and specific chemical treatments or high temperature of them will also limit the selection of substrates, such as low-cost paper or polyethylene terephthalate (PET) flexible substrates [10]. New fabrication processes based on inkjet or screen printing have been suggested as an effective method to tackle the above issues, and provide versatile shape and aesthetic design. Several nanomaterials, such as activated carbon [11,12], carbon fibers [13], graphene [14,15], CNTs [16], Au/polyaniline [17], graphene/polyaniline [18] and $LiCoO_2$ [19], are used to fabricate SCs as electrodes through screen printing or inkjet printing. Nevertheless, the stable and printable inks for inkjet printing is often difficult to prepare, and the micrometer sized particles is not allowed because of the fine diameter of nozzle. As an extensive range of printing method, screen printing techniques possess a wide ink tolerance, which can significant reduce the dependence on expensive manufacturing equipment, and further reduce costs and achieve large-scale production [20]. However, the majority of previous researches are often required to utilized the pre-fabricated collectors, special templates, and liquid encapsulation rather than all-printed methods to achieve the ultimate SCs devices fabrication.

As a key element for screen-printed SCs, the printing ink of electrode materials should not only be stable, low cost, environmentally friendliness and easily printable on various substrates, but also have excellent electrochemical performance. Transition metal oxides have been studied extensively as potential electrode materials [21]. Among various available metal oxides, $MnO_2$ is one of the best options because of its high theoretical specific capacitance (~1370 F $g^{-1}$), low cost, environmental compatibility and low toxicity [22]. However, its lower capacitive performance than theoretical value and low structural stability restrict its practical application [23]. To address these issue, $MnO_2$-based composites with additional metal oxides/hydroxides are developed. Recently, combining the $Co_3O_4$ [24,25], NiO/Ni$(OH)_2$ [26–28], $TiO_2$ [29,30], CuO [31,32], $Fe_2O_3$ [33], and $Fe_3O_4$ [34] with $MnO_2$ and synthesis of $MnO_2$-metal oxide composites become strong candidates to increase the electrochemical performance through the synergistic effect of metal oxides/hydroxides and $MnO_2$. Compared to $MnO_2$-CNTs [35,36], $MnO_2$-graphene [37,38], $MnO_2$-carbon nanofiber [39,40], $MnO_2$-polyaniline [41], $MnO_2$-polypyrrole [42] and $MnO_2$-noble metals [43,44] composites, $MnO_2$-metal oxide/hydroxide shows lower cost and higher electrochemical performance. However, these composites materials are often synthesized by template methods or deposition growth on particular substrates, which are not suitable for using as printable materials. Moreover, recent works demonstrated that amorphous hydroxides show better electrochemical performance than crystalline counterparts. Because moderate structural disorder among the low-crystalline or amorphous phase materials facilitates the formation of irregular surfaces and provides high specific surface area and suitable pore-size distribution, which make the permeation and diffusion of ions easier. And the active sites of amorphous materials are not limited by the crystal structures, that is beneficial to improve the electrical conductivity of the electrode material [45–48]. As a kind of amorphous iron oxides/hydroxides, amorphous FeOOH has been studied as an active material to use for SCs [49–51]. Therefore, it shows great potential to combine with $MnO_2$ as one desirable electrode material for screen-printed SCs.

In this work, amorphous FeOOH/$MnO_2$ composites are successful synthesized through a facile low temperature wet-chemical method, which is easy to realize a large-scale synthesis. By adjusting the mass ratio of amorphous FeOOH and $MnO_2$, amorphous FeOOH/$MnO_2$ composite achieves an excellent performance. Scheme 1 shows the preparation procedure of amorphous FeOOH/$MnO_2$ composites and schematic diagram of SC devices fabrication process through fully screen printing process. The solid-state flexible SCs are successfully fabricated on paper, PET and textile substrates. And these pattern SCs on different flexible substrates in series are evaluated to light up a yellow LED (1.9 V).

## 2. Experimental

### 2.1. Materials and chemicals

$FeCl_3 \cdot 6H_2O$, $NH_4HCO_3$, $KMnO_4$, $MnSO_4 \cdot H_2O$, polyvinyl alcohol (PVA), acetone ($CH_3COCH_3$), HCl and ethanol ($C_2H_5OH$) were purchased from Sinopharm Chemical Reagent Co., Ltd, LiCl was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, n-methyl pyrrolidone (NMP) was purchased from Shanghai Aladdin Reagents Co., Ltd, polyvinylidene fluoride (PVDF) was purchased from Sigma-Aldrich Co., Ltd, Silver (Ag) conductive paste was purchased from KunShan Hisense Electronics Co., Ltd, acetylene black was purchased from Taiyuan Lizhiyuan Battery Co., Ltd, LA133 (a water-based adhesive, polyacrylic latex) was purchased from Chengdu Indigo Power Sources Co., Ltd. The water used in the experiments was ultrapure water (18.2 Ω). All chemical reagents were analytical purity and used without further processing.

### 2.2. Synthesis of the amorphous FeOOH/$MnO_2$ composites

Briefly, 0.5 mmol of $FeCl_3 \cdot 6H_2O$ and 1.5 mmol $NH_4HCO_3$ were dispersed in 10 mL of ethanol, respectively, then $FeCl_3 \cdot 6H_2O$ solution was added into $NH_4HCO_3$ suspension and stirred continuously at room temperature for 10 h. 1 mmol of $KMnO_4$ and 1.5 mmol of $MnSO_4 \cdot H_2O$ were dissolved in 20 mL deionized water, respectively, then certain amount of FeOOH solution was added into $MnSO_4 \cdot H_2O$ solution, and the resulting mixture was mixed into $KMnO_4$ solution at a rate of 1 mL $min^{-1}$ and stirred continuously at room temperature for 10 h. The resulting sample was collected by centrifugation, followed by washing alternately with ethanol and deionized water, and dried at 60 °C in a vacuum overnight.

### 2.3. Preparation of the amorphous FeOOH/$MnO_2$ ink

Here, the FeOOH/$MnO_2$ composites screen printing ink was prepared that containing 75 wt% FeOOH/$MnO_2$ powder, 15 wt% acetylene black, and 10 wt% LA133 solute. LA133 was dissolved in deionized water and stirring 30 min, then FeOOH/$MnO_2$ and acetylene black were added into the LA133 solution under stirring continuously to form a homogeneous ink. The solid content of the FeOOH/$MnO_2$ composites screen printing ink was about 23 wt%.

### 2.4. Fabrication of flexible screen printed multipurpose SCs

There is a simple screen printing method including three steps of current collector printing, electrode printing and electrolyte coating, and three key elements of printing ink, screen plate and printing substrate. First, Ag electrodes were printed by screen printer on the printing substrates including paper, textile, plastic,