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Structure of Bifunctional Planar Micro Supercapacitor and Electrochromic by Screen Printing Technology

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A planar micro-supercapacitor (MSC) has characteristics between a battery and capacitor. MSC sandwich structure's limitation includes a short circuit with two electrodes, electrodes should be loaded with as many active materials as possible to improve the energy storage capacity of the device, both of which will increase the ion transfer impedance, resulting in low power density. On the other hand, the sandwich structure is difficult to integrate into micro electronic devices. In recent years, the cross-fertilization of electrochromic technology with other fields has given rise to a variety of emerging smart devices and technologies by combining supercapacitors, smart energy storage devices, and smart windows. This paper focuses on the hybrid of MSC and electrochromic device structure to verify bifunctional device structure by asymmetric interdigital electrodes. They require the same hydrogel and electrode layer to enhance their performance, which are pursued with the reduction in width, size, power consumption and price in the field of portable, etc. The material of Ag/Carbon/PVA/KCL/PEDOT:PSS (ACPKP) for the new structure will be printed to ensure the device's energy-storage and display. As expected, the micro-supercapacitor based on PET film can deliver areal capacitance up to 6.5 mF/cm^2. Even if, the micro-supercapacitor undergoes continuous 800 cycles, the performance of device can remain nearly 79.4 %. With printing technology, low cost, large area, and green products demonstrate its application in next-generation flexible electronics.

Keywords: MSC, energy storage, asymmetric interdigital electrode, electrochromic.

1. INTRODUCTION

The ion insertion/extraction process in reversible redox reactions during electrochromic reactions is similar to the electrochemical capacitance mechanism of materials. The integration of energy-saving displays and energy storage applications has received widespread attention [1]. Most of the materials used in traditional sandwich type supercapacitors can be used for planar asymmetric supercapacitors, and how to achieve a bifunctional device is the primary challenge. In the means of achieving devices, the main processes among laser assistance, electrochemical deposition, mask method, and printing technology, printing method become more and more popular [2]. Considering the needs of the electronics industry, material options, manufacturing processes, device performance, resolution and application safety have become the most concerned issues for people such as gas sensors, UV-optical sensor and humidity sensor [3]. Planar asymmetric interdigital electrode supercapacitors can meet the needs of modern electronics industry. Although the manufacturing process is relatively complex, the electrochemical characteristics have been greatly improved, and they can effectively solve the risks of short circuits and electrolyte leaks [4]. S.C. Lee, et al. got the pattern with UV and photoresist lithography on PI film and obtained the asymmetric supercapacitors with deposition process by energy density of 0.35 μ W h/cm^2 and a power density of 100.38 μ W/cm^2 [5]. In 2020, J.C. Li et al. used laser lithography to prepare electrode patterns in the shape of forked fingers and sputtered a layer of gold as a current collector. The CuSe/MnOOH/CuSe/FeOOH planar asymmetric supercapacitor achieved an area specific capacitance of 20.47 mF/cm^2 at a current density of 0.11 mA/cm^2 [6].

With the rapid development of green energy technology, the integration of electrochromic devices with other function is expected to solve the energy supply problem by collecting/converting green energy from nature. It can be combined with multiple functional devices, making visual detection/information display receive increasing attention [7]. Wang et al. used PANI nanowires as color changing and energy storage layers to integrate electrochromic and electrochemical energy storage on a flexible device and fabricated an electrochromic supercapacitor with a volumetric capacitance of 400 F cm^{-3}, which can also achieve color changes from yellow green to dark blue [8]. However, the device with PANI nanowires still did not consider the planar structure.

In recent years, to simplify device structure, reduce device size, and achieve lightweight, both electrochromic and supercapacitor devices have developed diaphragm free structures. The typical structure of supercapacitor electrochromic devices adopts a sandwich like stacked structure [9]. Some new structural designs have been proposed to meet emerging application requirements, such as microdevices, thin-film devices, fiber like devices, matrix devices, functionally integrated multi-layer devices, and customizable patterned device designs [10]. According to the different requirements for regulating the transmission path of light, multifunctional electrochromic devices of transmission, reflection, or hybrid types have also been designed. Both electrochromic and supercapacitor devices have developed diaphragm free structures. For example, gel electrolyte is used to realize structural separation of electrodes on both sides [11 – 14]. Essentially, it also uses electrolyte materials with certain mechanical retention to achieve the main function of the diaphragm.

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The most common producing technical methods include photolithography, laser etching, inkjet printing, 3D printing, screen printing, etc. Each method has its advantages and limitations. The appropriate preparation process should be selected based on the properties of the active material, electrolyte, and substrate. According to the production at large market, these methods are substantially complicated and rely on high cost, without green and environmentally friendly, which greatly limits their application in production, P. Zhang et al. used graphene and V_2O_5 as composite electrode materials loaded on the surface of a gold current collector to build interdigital electrode structure supercapacitors with masking method, high lost and complex steps [15]. Screen printing is suitable for large-term production in this paper.

As a representative of organic electrochromic materials, PEDOT: PSS can produce coloring and fading phenomena. PEDOT: PSS is a water-soluble conductive polymer with high coloring efficiency and processability. It has the advantages of good performance and low preparation cost. It is a cathode coloring material that appears transparent blue when in the oxidized state and dark blue when in the reduced state. PEDOT: PSS can show coloring/fading under the action of applied voltage because the injection/extraction of ions and electrons causes the cations in the electrolyte and the structure of PEDOT: PSS to change with electrolyte. In electrochromic devices, the electrolyte layer is the key to affect the color changing performance and stability of devices. According to its composition, it can be divided into liquid electrolyte, gel electrolyte and solid electrolyte. Among them, the liquid electrolyte is easy to leak and is not suitable for flexible devices. The solid electrolyte has poor color changing performance due to low ionic conductivity, so the ionic gel with good stability and high ionic conductivity is the most suitable electrolyte layer for fabric based electrochromic devices. Herein, the PVA/KCL electrolyte is chosen for this experimental.

Micro-supercapacitors with planar interdigital electrodes can be integrated with micro-electronics to work as efficient energy storage micro-devices. Currently, fabrication strategies for asymmetric interdigital electrodes are very limited. However, to hybrid supercapacitor and electrochromic functions together, this paper considers the asymmetric interdigital electrodes new style to analysis to expand the asymmetric interdigital electrodes application specially with screen printing in Fig. 1, better than other processes.

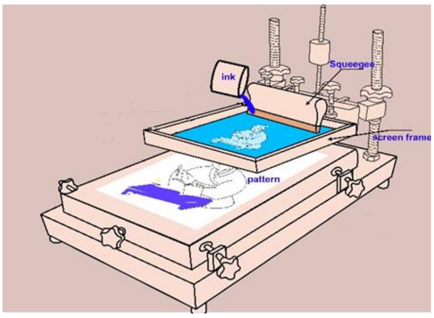


Fig. 1. Screening printing process

2. EXPERIMENTAL

In addition, people are no longer satisfied with the single-color changing function of electrochromic devices (ECD).

In this work, the new design is below in Fig. 2. The material of Ag/Carbon/PVA/KCL/PEDOT:PSS (ACPKP) for new composition will be tested as both of them to ensure the device's energy-storage and electrochromic display. After designed single interdigital electrode as 1.4 × 2.4 cm, with two layers in Adobe Illustrator software, Ag is for the current collector, carbon paste for electrode, PVA/KCL for the electrolyte, and PEDOT:PSS for electrochromic material.

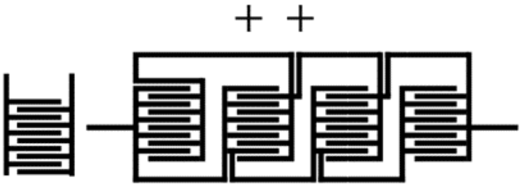


Fig. 2. Designed interdigital electrodes

2.1. Materials preparation

In a typical procedure, Ag paste with a purity of 75 % (GY-180). Carbon paste is bought from JULONGHUINA company. PEDOT: PSS is an organic electrochromic material for interdigital electrode (KV-ECM-pd3100, Zhuhai Kaivo Optoelectronic Technology Co. Ltd) for screening printing. PVA with a purity of 99 + % (31000 – 50000, Sigma-Aldrich). KCL power with a purity of 99.5 % (MACKLIN). Firstly, weigh 0.37 g of potassium chloride and 0.25 g of polyvinyl alcohol (PVA, molecular weight 31000 – 50000) powder separately, and add 5.0 mL of deionized water to ensure that the powder can be fully dissolved. Secondly, add the magnetic stirrer to the beaker, and then put the beaker on the magnetic stirrer. Set the rotating speed to 500 revolutions and the temperature to 90 °C. Heat and stir until a transparent and clear solution is obtained, and finally PVA/KCL hydrogel solution is obtained.

2.2. Printing and characterisations

The whole process was based on screen printing technology (machine type with KV-SP-HY). Firstly, the Ag paste was printed on flexible PE film as current collector by the designed pattern of interdigital electrodes and dried by 150° about 20 minutes. Secondly, the carbon paste was printed half interdigital electrodes on the Ag layer and dried. Thirdly, the PEDOT:PSS was printed on the top of both interdigital electrodes.

The device was evaluated using an electrochemical station of VersaSTAT3 in a voltage window of –1.0 V ~ 1.0 V. The CV curves were measured at different scan rates of 25, 50, 75 and 100 mVs^{-1}. The GCD curves were measured at different densities of 0.1, 0.15, 0.2, and 0.25 $mAcm^{-2}$. The colouring /fading time was measured with the second timer. The transmittance tester of WGT-S is for the film transmittance measurement.

We demonstrated asymmetric interdigital electrodes of flexible in-plane micro supercapacitor and electrochromic function directly on PET film with roll to roll. The result revealed that printed electrodes acquire a superior areal capacitance as high as 6.5 $mFcm^{-2}$ at 0.25 mA, with a coloring/fading time of 3.8 s/6.0 s and a coloring efficiency of 42.1 cm^2/C.

3. RESULTS AND DISCUSSION

Fig. 3 shows a schematic illustration of the technological process of ACPKPs.

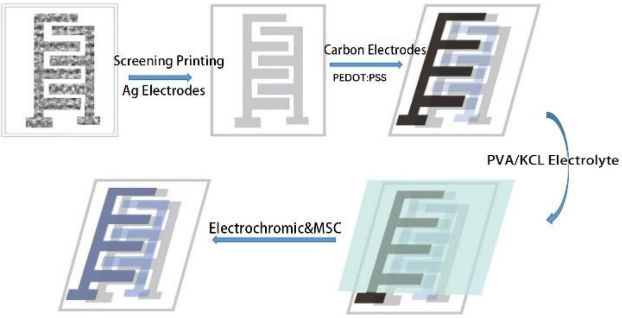


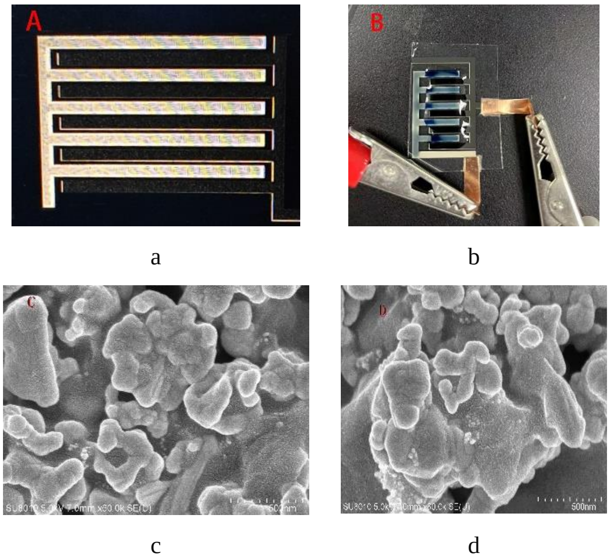
Fig. 3. Schematic diagram of ACPKP structure of bifunctional device

Ag paste and carbon paste were printed on flexible PI film as interdigital electrodes. In this study, electrodes with a sheet resistance of 68 Ohm sq^{-1} were chosen for the following experiments considering the appropriate balance between electrochromic and electrical performance. After printing PEDOT:PSS on the other half electrode, the electrochromic energy-storage electrode was fabricated.

Then, a symmetrical ACPKP was assembled using two electrodes and a KCL/PVA electrolyte. During the PEDOT:PSS coloring/fading process, the formation mechanism could be described as follows, where 0<x<1.

$$PEDTO^{+} \times PSS^{-} + xK^{+} + xe^{-} \rightarrow PEDOT \times PSS^{-} \times Kx^{+}. \tag{1}$$

Fig. 4 shows the representative diagram for the printing technology before and colored after electrolyte. The coloring appearance on the Ag/PEDOT:PSS electrode is lighter than the color on the carbon paste in Fig. 4. That is why the Ag material is used to be transparent electrode, it can keep the transmittance of 69 %, which is higher than 67.7 % and 68.2 % [16, 17]. The phenomena make sure this design could apply on the bifunctional device as a transparent application like biomimetic visualization. The coloring/fading time is 3.8/6.0 s is shorter than 9.9/13.6 s [19]. The whole process with integrated electrodes is better than FECESDs, especially in the feasibility of the producing process.



a b c d

Fig. 4. The coloring process: a – Ag/PEDOT:PSS/Carbon electrodes; b – Ag/PEDOT:PSS/Carbon electrodes with KCL/PVA; c – the Ag/PEDOT:PSS surface morphology and structure of the MSC (SEM image); d – the carbon surface morphology and structure of the MSC (SEM images)

From the microscope studies, the printing result shows the printing technology can ensure overprint accuracy, the PEDOT:PSS layer is 0.5mm thinner than AgNW electrode layer in case the thin PEDOT:PSS material spreads out of the edge during its dryer process. This result shows organic material expansion rate is in control with screen printing roll by roll.

The capacitance calculation is based on the following equation:

$$C = It/\triangle v, \tag{2}$$

where C is the capacitance, mF; I is the charging/discharging current, mA; t is the charging/discharging time, s; $\triangle v$ is the voltage window. And the areal capacitance of the device is calculated according to the following equation:

$$Cs = C/s, \tag{3}$$

where Cs is the areal specific capacitance, $mFcm^{-2}$; s is the area of the whole eletrode, cm^{-2}; C is the capacitance, mF.

The electrochemical performance of the ACPKP structure is analyzed within a potential window from –1.0 V – 1.0 V. Fig. 5 shows the cyclic voltammetry (CV) characterization with different scan rates from 25 mVs^{-1} to 100 mVs^{-1}. The CV shape is well preserved from 25 mVs^{-1} to 100 mVs^{-1}. CV curves with rectangular shapes were observed, suggesting excellent energy-storage behavior of the device. Fig. 6 shows the galvanostatic charging/discharging (GCD) curves at different current densities from 0.1 $mAcm^{-3}$ to 0.25 $mAcm^{-3}$. The device delivered areal capacitance of 2.6, 5.2 and 3.9 $mFcm^{-2}$ at the current density of 0.25, 0.2, and 0.15 0.1 $mAcm^{-2}$ well indicating the high conductivity in this work. The performance of 0.1 $mAcm^{-2}$ is not the best, but we provide a new idea for developing bifunctional and simple ACPKP. The printing process verified areal capacitance with 6.5 mF/cm^{2}, which is higher than 3D printing with ink Mxene and PH1000 with 5 layers M-MSCs structure in [20]. The fewer layers mean a simple structure and extreme cost. These areal capacitances 3.9,5.2 and 6.5 mF/cm^{2} showed high maintance than 3.3 mF/cm^{2} with inkjet printing.

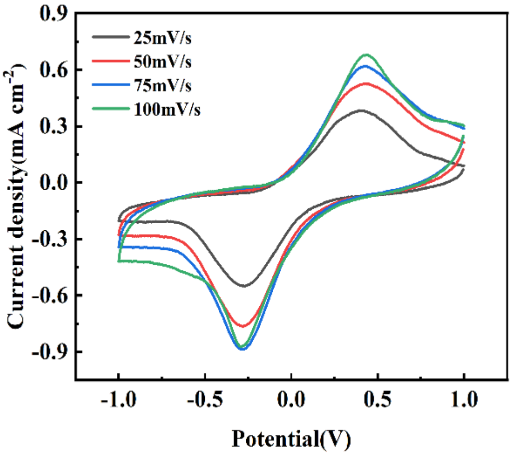


Fig. 5. CV at different scan rates from 25 mVs^{-1} to 100 mVs^{-1}

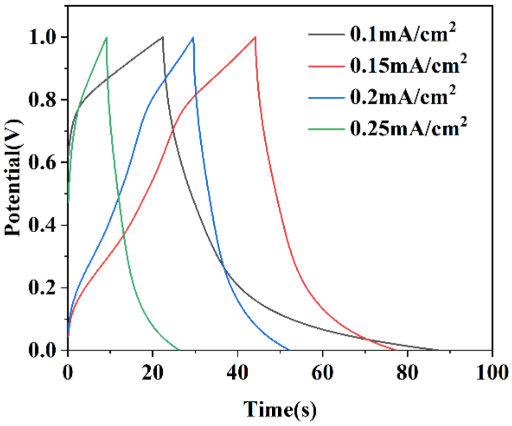


Fig. 6. GCD curves at different current densities from 0.1 to 0.25 $mAcm^{-2}$

Fig. 7 achieves capacitance retention with about 79.4 % after charging/discharging at 0.03 $mAcm^{-2}$ more than 800 cycling. Even though the stability showed a decline less than we thought at the beginning. The reason probably comes from the resistance sharp decline, which caused of water loss from electrolyte heating. Further research will focus on the solid hydrogel electrolyte. However, the rate capability is still above or similar to WO_3/PEDOT nanoarrays [18].

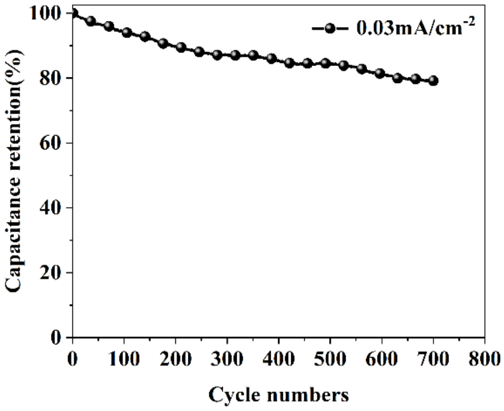


Fig. 7. Cycle life of 1000 times at the current density of 0.03 mAcm^{-2}

4. CONCLUSIONS

In summary, expected electrochromic and energy storage devices were successfully fabricated using the Ag/Carbon/PVA/KCL/PEDOT:PSS(ACPKP) hybrid electrodes with asymmetric interdigital structure. With screen printing technology, Ag electrodes were printed by interdigital structure for the collector current. The widths of electrodes are well done. Carbon paste/PEDOT:PSS is the second layer on the top of Ag electrodes, and the PEDOT:PSS is thinner than the bottom electrode, which verified the overprint accuracy within control by size. In this approach, The PEDOT:PSS layer concurrently served as an electrochromic energy-storage and electrode layer. Furthermore, the Ag network was set to enhance the energy storage and electrochromic performance of the carbon paste/PEDOT:PSS electrode to change the colouring and transmittance of the device. From the electrochemical characteristics, a bifunctional electrochromic and energy-storage device was tested with asymmetric interdigital structure by screen printing, which successfully showed a hybrid electrode top areal capacitance of 6.5 mFcm^{-2}. Moreover, after 800 charging/discharging cycles, the performance of the ACPKP showed stable fluctuation as expected, demonstrating its potential for printed electronics in the further study. Moreover, in this work, we got thin and simple process device, more stable, multifunctional, and cost-effective electrochromic devices will be developed and gradually move towards practical applications and industrialization, bringing more convenience to people's lives.

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