BASED ON SU-8 PHOTORESIST OF MEMS SUPERCAPACITOR MANGANESE DIOXIDE（MnO_2） ELECTRODE PREPARATION AND ELECTROCHEMICAL CHARACTERISTICS

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Abstract: Supercapacitor charge storage capacity depends on the size of the electrode surface area and the electrode active material of electrodes. To increase the electrode surface area, carry more electrode active material and enhance the unit area on the bottom electrode of the charge storage capacity, high aspect ratio structures of SU-8 photoresist was fabricated by MEMS technology. this structure was sputtered gold as a collector of current, the galvanostatic current anode deposition method of manganese dioxide (MnO_2) in the electrode structure deposits a thin layer of film electrode activity preparation has been study, and with no corresponding structure of the plane electrode were compared with experiments. Scanning Electron Microscopy(SEM), Energy Dispersive Spectroscopy(EDS), AC impedance spectroscopy, cyclic voltammeter, galvanostatic current charge-discharge was used for testing the characteristic of MnO_2 electrodes. Test results show that, when charge-discharge density 1.5mA/cm^2,the MnO_2 electrode of SU-8 photoresist three-dimensional structure of the unit bottom area of the electrode ratio capacitance is 3.2 mF/cm^2, two-dimensional electrode without structure electrode ratio capacitance is 0.981 mF/cm^2.Inspite of higher charge-discharge density, The electrode ratio capacitance of 3D structure is larger than two-dimensional electrode. The result shows, preparation high aspect ratio structures on the unit area of the electrode floor can effectively increase the electrode surface area, carry more electrode active material to enhance its charge storage capacity and improve the unit bottom area of the electrode capacitance.

Keyword: Supercapacitor, MEMS, Manganese dioxide (MnO_2), SU-8, 3D Micro electrode

1 INTRODUCTION

Supercapacitor become a hot research energy storage devices because of its high capacity, charge and discharge efficiency, high speed, wide temperature range, long cycle life[1-4].With the development of MEMS technology in recent years, miniaturization has become an important direction of development of this kind devices. Micro-devices for power supply system proposed new requirements, super-capacitors preparation by MEMS technology because of it small size, high efficiency, energy storage medium, etc. become a optimization program of micro-devices for the energy, has also some countries and regions research in this area [5-7]. Manganese (Mn) is widespread in nature, it is readily available and inexpensive, while the environmental impact of Mn and its compounds is small, environmentally-friendly, so the MnO_2 produced as a supercapacitor electrode active material has a strong advantage. Ratio capacitance of manganese dioxide is high, the theoretical value of 1233F / g[8-9], but in fact , it can not reach such a high specific capacity, the highest specific capacitance is 600F/g [10]. Ratio capacitance of manganese dioxide can be achieved depends on the carrying amount of the electrode. Manganese dioxide of the electrode equipped in the unit area is limited number, if fabricate three-dimensional structure on the electrode, the effective electrode surface area can increases in the same area on the basis of the bottom, and can carrying more of manganese dioxide, to improve unit bottom area capacitance ratio capacity. The research of manganese oxide performance for of the super capacitors are more [11-13], but the research methods were mainly focused on preparation of manganese dioxide material, the research of direct preparation of manganese dioxide electrode are seldom. This paper studies produce three-dimensional micro-structure by MEMS technology, with the anode electro-deposition method to deposit a layer of micro-structure as the electrode active material of manganese dioxide to prepare MEMS supercapacitor electrodes. Scanning electron microscopy and spectroscopy of the electrode morphology and composition representation, AC impedance spectroscopy, cyclic voltammetry, galvanostatic current charge-discharge methods such as electrochemical properties were tested and characterized. Experimental results show that prepared three-dimensional micro-structure on the floor of electrode can effectively increase the area of the bottom electrode, carry more electrode active material and increase the unit bottom area capacitance of the electrode.

2 EXPERIMENTAL

2.1 SU-8 structure preparation

In this study, 3D micro-electrode structure produced with MEMS UV-LIGA technology. First, standard cleaning base (n-type 100 wafers), spin coating SU-8 photoresist, pre-baked, exposed, developing, post-baked, harden film, sputtering titanium tungsten, as middle layer and sputtering gold as a collector of current .

2.2 Preparation of manganese dioxide electrode

Weigh accurately a certain quality of $MnSO_4 \cdot H_2O$, dissolved into deionized water, configured to 0.2mol / L solution, the platinum electrode is the cathode, with a three-dimensional SU-8 structure of the silicon as anode, with a precision regulated power supply Agilent 6628A galvanostatic current electro-deposition, deposition current density is $6mA/cm^2$, time for 33 seconds.

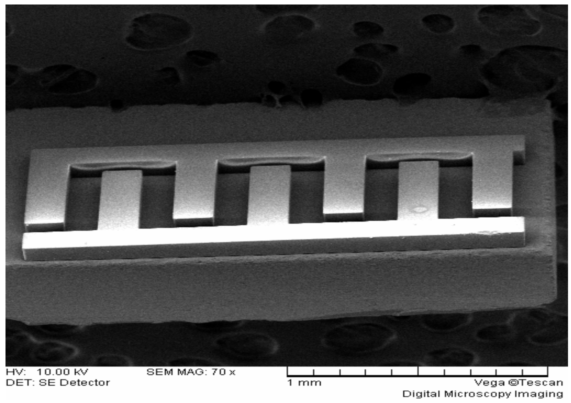
2.3 Electrochemical performance test

The electrode impedance spectroscopy, cyclic voltammetry, galvanostatic current charge-discharge characteristics of the MnO_2 dioxide have been test with versastat v3 electrochemical workstations, the electrolyte for testing is 0.4mol / LNa_2SO_4 solution.

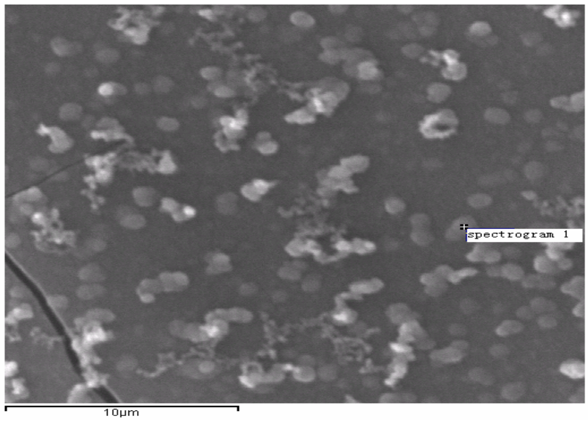
3 RESULT AND DISCUSSION

3.1 The morphology of three-dimensional SU-8 microstructure and Energy Dispersive Spectroscopy of MnO_2 electrode

Surface characterization of SU-8 photoresist three-dimensional structure and deposited manganese dioxide electrode by scanning electron microscopy, the results shown in Figure 1, Figure 1 (a) can be seen, the preparation of three-dimensional micro- structure of neat appearance, no surface holes, burrs, cracking phenomenon, good bond with silicon substrate, without warping, distortion and other situations. Figure 1 (b) shown the material of deposited on the electrode surface was flaky and similar materials on the surface of particles. The deposited material of the electrode surface was testing and analysis by EDS. There are manganese and oxygen exist in the material and similar material of electrode surface, and in a larger proportion of the sample, indicating that the anode material indeed deposited manganese dioxide, the manganese dioxide electrode is prepared dioxide Manganese flake on the surface because of the electrode along the direction parallel to the electrode surface growth, this growth pattern of the manganese dioxide film to be distributed more evenly on the surface, the binding force between layers is weak, too easy to fall off when the film thickness augment. Electrode surface cracks may be due to a stress in the film drying process, there is accumulated to a certain extent led to surface cracking phenomenon.



(a)



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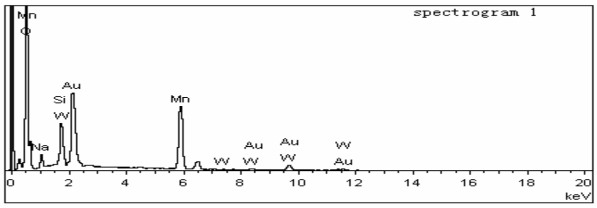

(c)

Fig. 1: Data of super supercapacitor
(a) 3D SU-8 microstructure (b) SEM picture of MnO_2 electrode (c) MnO_2 electrode surface energy spectrogram

3.2 3D micro-elecrtode CV Performance Test

Cyclic voltammetry characteristics of MnO_2 electrode was test with Dual-electrode system in the range of 0V ~ 0.9V, get the curve shown in Figure 2. A broad reduction peak of the Curve can be observed. The reason of the reduction of the generation of manganese dioxide is not stable, continued reduction, release electronic, the formation of trivalent and tetravalent manganese ions. There is an oxidation peak in the oxide zone, showing the Faraday redox properties, which is the curve with the AC impedance characteristics of the front corresponds to a semicircle.

Indication the manganese dioxide electrode redox reactions did occur. With the increase in scanning speed, scanning current is also increased at 0V vicinity, this phenomenon is most obvious, area enclosed by the curve increases, but does not linear change with the scan rate, indicating that manganese dioxide electrode active material as part of scanning speed becomes faster, too late to participate in charge-discharge reaction, so the current is not linear synchronous scanning speed increases, leading to its ratio capacitance increases the scanning speed of decline. Which may be mixed by the electrochemical reaction and diffusion controlled electrode process.

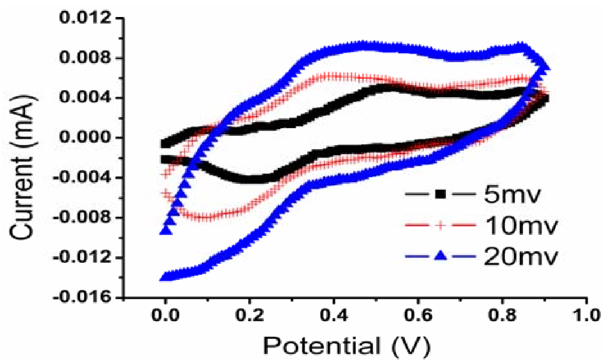

Fig. 2: MnO_2 electrode cyclic voltammetry curve

3.3 3D micro-electrode AC impedance test

As Figure 3 Shown, AC impedance of MnO_2 electrode was tested by 5mV AC signal, 50mHz ~ 100KHz, two-electrode system. From AC impedance curve can be seen in front of the curve there is a small semi-circle, indicating the existence of Faraday impedance, which means the existence of Faraday electrode reaction. Later half of the approximate straight line, and there is a certain slope, the performance characteristics of a capacitor, indicating the presence of double-layer capacitors.

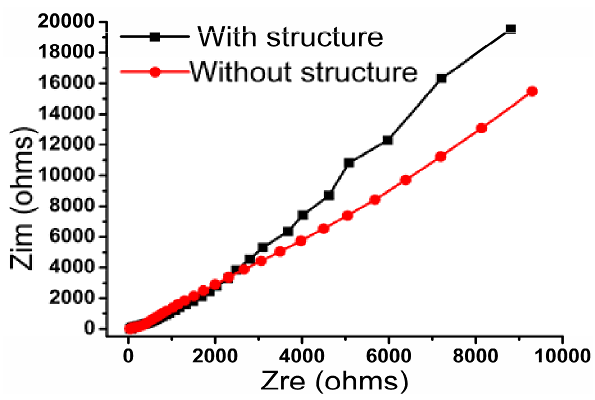

Fig. 3: MnO_2 electrode AC impedance curve

3.4 Galvanostatic current charge- discharge properties test

Preparation of the manganese dioxide electrode has been test by charge-discharge, charge-discharge curve obtained is shown in Figure 4. Charge-discharge changed between 0V~1V, charge-discharge density 1.5mA/cm^2.It can be observed from the chart in the initial stage of the discharge the electrode voltage drops quickly, indicating larger ohms resistance of the electrode, mainly due to deposition of manganese dioxide and the collector contact, unlike the use of nickel foam to suppress the electrode as close contact, so the electrode ohms resistance is large, and the other reason as collector's gold layer thickness only 120nm, there are also there exist great ohms resistance. Manganese dioxide is semiconductor, there is a great ohms resistance exist, so the total ohms resistance become larger.

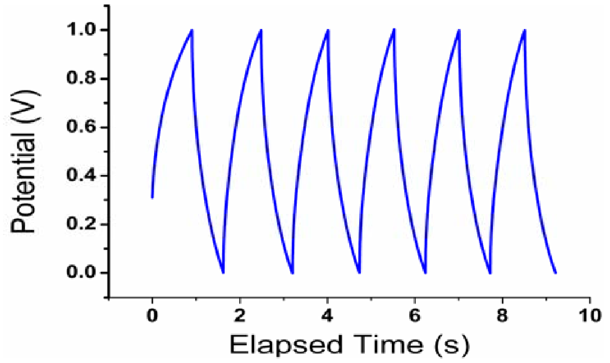

Fig. 4: MnO_2 electrode charge-discharge curve

Manganese dioxide electrode capacitance and the capacitance calculated by the following formula:

$$C = dq/dv = \frac{dq}{dt} * \frac{dt}{dv} = i * \frac{dv}{dt} = i * \frac{\Delta t}{\Delta v} \qquad (1)$$

$$Cs = C/S \qquad (2)$$

Where C is the manganese dioxide electrode capacitance, i is the charge or discharge current, Δt is the discharge time, Δv is the discharge potential difference, Cs is the electrode ratio capacitance.

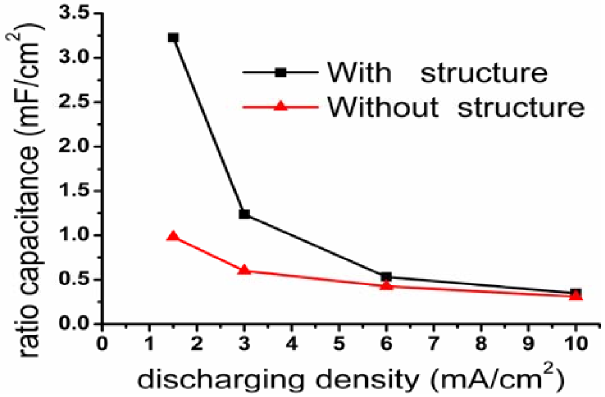

Fig. 5: electrode ratio capacitance comparison chart of with and without structure in different charging - discharging density

When charge-discharge density is 1.5mA/cm^2, With (1) and (2) calculated the MnO_2 electrode has

SU-8 photoresist three-dimensional structure of the unit bottom area of the electrode ratio capacitance is 3.2mF/cm^2, two-dimensional electrode without structure electrode ratio capacitance is 0.981mF/cm^2.

Three-dimensional structure of the unit bottom can augment the electrode ratio capacitance of unit bottom area. Charge-Discharge with different densities of the electrode charge-discharge test results shown in Figure 5. We can found the curve with the higher density discharge, the capacitance of a downward trend, the charge-discharge density raise, but the capacitance of the unit bottom area with three-dimensional structure are greater than the capacitance without three-dimensional structure. Shows produced three-dimensional structure in the same area on the bottom, can helps enlarge the surface area, and effectively boost the unit capacitance of the bottom area.

4 CONCLUSION

Preparation of three-dimensional structure in the same bottom area of the electrode, can effective enlarge electrode surface area and increased carrying more electrode active material on the electrodes, thereby enhancing the charge storage capacity of the electrode to improve electrode unit bottom area capacitance. In some cases the bottom area are limited , such as MEMS systems, preparation of three-dimensional structure of the electrode, can effectively increase its electricity capacity; or in need of electrical capacity in certain circumstances, can reduce the share of the bottom area of the capacitor, the layout make room for other devices, provides the convenience. Preparation of three-dimensional structure of electrodes can improves the unit bottom area capacitance.

Deposited manganese dioxide on the micro-structure of electrode as the electrode active material to direct preparation of MEMS supercapacitor electrode, the preparation process without heating step, re-manganese dioxide together with other substances pressure to prepare the electrode by mechanical, so supercapacitors can be micro-generators and other devices with MEMS integrated on the same silicon chip, tends to reduce the total volume, improve system performance and reduce costs.

REFERENCE

[1] Conway B E 1991 Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage, *Electrochem. Soc*, **138(**6), 1539-1548

[2] Xiao-feng Wang, Dian- bo Ruan, Zhen You 2006 Pseudo-capacitive behavior of cobalt hydroxide/carbon nanotubes composite prepared by cathodic deposition, *Chinese journal of chemical physics*, **19**(6), 499-505

[3] Chunhong Lei, Wilson P., Lekakou C 2011 Effect of poly(3,4-ethylenedioxythiophene) (PEDOT) in carbon-based composite electrodes for electrochemical supercapacitors, *Journal of Power Sources*, **196**(18), 7823-7827

[4] Bose Saswata, Kim Nam Hoon, Kuila Tapas 2011 Electrochemical performance of a graphene-polypyrrole nanocomposite as a supercapacitor electrode, *nanotechnology*, **22**(29), DOI: 10.1088/0957-4484/22/29/295202

[5] Wei Sun, Ruilin Zheng, Xuyuan Chen 2010 Symmetric redox supercapacitor based on micro-fabrication with three-dimensional polypyrrole electrodes, *Journal of Power Sources*, **195**, 7120-7125

[6] Hengxing Ji, Yongfeng Mei, Oliver G. Schmidt 2010 Swiss roll nanomembranes with controlled proton diffusion as redox micro-supercapacitors, *Chem. Commun*, **46**, 3881–3883

[7] David Pech, Magali Brunet, Pierre-Louis Taberna, Patrice Simon,Norbert Fabre, Fabien Mesnilgrente, Véronique Conédéra, Hugo Durou 2009 Elaboration of a microstructured inkjet-printed carbon electrochemical capacitor, *Journal of Power Sources*, **195**,1266-1269

[8] Mathieu Toupin, Thierry Brousse, Daniel Be´langer 2004 Charge Storage Mechanism of MnO_2 Electrode Used in Aqueous Electrochemical Capacitor, *Chem. Mater***,** **16**, 3184-3190

[9] E. Beaudrouet, A. Le Gal La Salle, D. GuyomardToupin 2009 Nanostructured manganese dioxides: Synthesis and properties as supercapacitor electrode materials, *Electrochimica Acta*, **54**: 1240–1248

[10] TIAN Ying, YAN Jing-Wang,LIU Xiao- Xue, XUE Rong, YI Bao-Lian 2010 Electrochemical Capacitance of Composites with MnOx Loaded on the Surface of Activated Carbon Electrodes, *Acta Phys. -Chim. Sin*, **26**(8), 2151-2157

[11] MI Juan, WANG Yu-Ting, GAO Peng-Cheng, LI Wen-Cui 2011 Effects of Thermal Treatment on the Electrochemical Behavior of Manganese Dioxide, Acta Phys.-Chim. Sin, **27**(4), 893-899

[12] Jinho Chang, Sangjin Lee, T. Ganesh, Rajaram S. Mane, Sunki Min, Wonjoo Lee, Sung-Hwan Han. 2008 Viologen-assisted manganese oxide electrode for improved electrochemical supercapacitors, *Journal of Electroanalytical Chemistry*, **624** , 167 – 173

[13] Jeng-Kuei Chang, Chiung-Hui Huang, Ming-Tsung Lee, Wen-Ta Tsai ,Ming-Jay Deng, I-Wen Sun 2009 Physicochemical factors that affect the pseudocapacitance and cyclic stability of Mn oxide electrodes, *Electrochimica Acta*, **54**, 3278–3284