Carbon microelectromechanical systems (C-MEMS) based microsupercapacitors

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ABSTRACT

The rapid development in miniaturized electronic devices has led to an ever increasing demand for high-performance rechargeable micropower sources. Microsupercapacitors in particular have gained much attention in recent years owing to their ability to provide high pulse power while maintaining long cycle lives. Carbon microelectromechanical systems (C-MEMS) is a powerful approach to fabricate high aspect ratio carbon microelectrode arrays, which has been proved to hold great promise as a platform for energy storage. C-MEMS is a versatile technique to create carbon structures by pyrolyzing a patterned photoresist. Furthermore, different active materials can be loaded onto these microelectrode platforms for further enhancement of the electrochemical performance of the C-MEMS platform. In this article, different techniques and methods in order to enhance C-MEMS based various electrochemical capacitor systems have been discussed, including electrochemical activation of C-MEMS structures for miniaturized supercapacitor applications, integration of carbon nanostructures like carbon nanotubes onto C-MEMS structures and also integration of pseudocapacitive materials such as polypyrrole onto C-MEMS structures.

Keywords: Carbon microelectromechanical systems (C-MEMS), electrochemical capacitors, microsupercapacitors, carbon nanotubes, polypyrrole, electrostatic spray deposition, microfabrication

1. INTRODUCTION

With the ever changing technology, reliable energy storage has become a prerequisite. Given the plethora of applications ranging from microelectronics to electric vehicles to large stationary applications, the demand for electrochemical energy becomes very device specific. With the recent boom in the development of miniaturized electronic systems such as wireless sensors, smart cards, implantable devices, etc. the demand for miniaturized power supplies is an all-time high. Micro-energy storage systems including microbatteries and micro fuel cells and energy harvesters are expected to be next generation energy sources for such systems. However, quite similar to their larger counterparts, microbatteries and micro-fuel cells suffer from low power densities and short cycle lives. On the other hand, energy harvesters require

an energy storage device in conjunction to store their excess energy. Electrochemical capacitors (ECs), also colloquially referred to as supercapacitors and ultracapacitors, are known for their exceptional power handling capabilities coupled with phenomenal cycle lives. Charge is stored at the electrode/electrolyte interface and depending upon the charge storage mechanism, ECs are subdivided into i) electrochemical double layer capacitors (EDLCs) and ii) pseudocapacitors. A third category of ECs known as the “hybrid capacitor” essentially combines the latter two charge storage mechanisms. However, it should be noted that the term “hybrid” is quite generic and can refer to a system that uses an EC electrode in tandem with a secondary battery electrode or even fuel cell electrodes. EDLCs, also known as double layer capacitors, quite similar to electrolytic capacitors, store energy in an electrostatic manner; charges are stored at the electrode/electrolyte interface and the capacitance is governed by the thickness of the double layer also known as the Helmholtz double layer and hence the name. EDLCs have capacitances larger than one or two orders of magnitude higher than electrolytic capacitors and very long cycle lives (10^5 - 10^6 cycles). EDLC materials include carbon based materials including activated carbon (AC), carbon aerogels, carbon nanotubes (CNTs), onion like carbons (OLCs), carbon nanowires (CNWs), carbon nanorods, carbon nanofibers (CNFs), fullerenes and graphene [1]. In pseudocapacitors, on the other hand, capacitance arises from the charge transfer between the electrode and the electrolyte and therefore the charge storage is redox and hence the prefix “pseudo”. However, the charge storage is very fast and highly reversible, which lends such devices capacitive charging-discharging characteristics. Typically, pseudocapacitors have much larger capacities as compared to their EDLC counterparts but given the redox charge storage mechanism, such capacitors suffer from poor cycling. Pseudocapacitive materials include metal oxides and hydroxides mostly ruthenium oxide, nickel hydroxide, manganese oxide, p- or n- dopable conducting polymers such as polyaniline (PANI), polypyrrole (PPY), and polythiophenes (PTH) [2].

Miniaturized supercapacitors also known as microsupercapacitors have gained considerable attention in recent years; applications of these capacitors include implantable biomedical devices, sensors and personal electronics equipment that require power in the order of microwatts. Depending upon the power and energy requirements, microsupercapacitors can be connected in series or parallel in order to meet the energy requirements. Typically the footprint area of the microsupercapacitors is in the millimeter or centimeter range and such capacitors consist of either thin film electrodes with thicknesses smaller than 10 μm or arrays of microelectrodes of micron scale sizes which can either be 2D or 3D. For larger supercapacitors, the electrochemical performance measures such as specific capacitance and specific power are usually expressed in “gravimetric terms” meaning that quantities are normalized with the mass of the active material. However for microsupercapacitors, the mass of the active materials is almost negligible and therefore gravimetric parameters are rendered almost inappropriate for reporting the electrochemical performance of such devices. The more appropriate measure for such capacitors is the “footprint area” and therefore power and energy normalized in terms of area is more appropriate [3]. The first supercapacitors followed a planar 2D architecture consisting of two electrodes and a separator soaked in an electrolyte. However a more recent design comprising “interdigitated” electrodes offers several advantages over the conventional 2D design including facile electronic and ionic transport given the small distances between the electrodes and also facile fabrication given the electrodes are within the same plane.

Carbon microelectromechanical systems, also known as carbon MEMS or simply C-MEMS, is a popular microfabrication technique, which involves the pyrolysis of a patterned photoresist into carbonaceous structures. The applications of C-MEMS based structures include lithium-ion batteries, fuel cells, biosensors, electrochemical sensors and supercapacitors. Until 2004, the synthesis of pyrolyzed carbon from polymeric photoresists was limited to two-dimensional architectures, when Wang and Madou et al[4] were able to fabricate C-MEMS structures with aspect ratios greater than 10. Since then, a variety of complex architectures have been synthesized using C-MEMS including high-aspect pillars, suspended bridges, plates and networks [5, 6]. Using a photoresist as the initial choice of material comes along with several benefits that include: i) the wider electrochemical stability window of carbon in comparison to gold and platinum; ii) the ease with which photoresists can be patterned using photolithography and their ability to produce much finer features than carbon-ink silk screening; iii) the accuracy with which carbon electrodes can be reproduced using C-MEMS allowing for flexibility in the complexity of geometries; iv) difference in processing parameters such as temperature and curing conditions allow to tailor mechanical and electrochemical properties of the C-MEMS structures; v) the consistency of material properties for a given temperature range; vi) the flexibility of the C-MEMS structures to be integrated with additive materials such as carbon nanotubes or conducting polymers to further enhance the electrochemical and mechanical properties.

2. FABRICATION PROCESSES

2.1. Carbon microelectromechanical systems (C-MEMS)

Typical C-MEMS fabrication process has been illustrated in Figure 1a. Detailed C-MEMS techniques are subjects of other works [4-7]. Briefly, first an SU-8 photoresist is spincoated onto a silicon oxide wafer using a photoresist spinner after which the photoresist is baked. After the baking process, the photoresist is patterned by a mercury lamp using an OAI contact aligner. Post exposure bake is carried out after the patterning process. The exposed samples are then developed using an SU-8 developer in order to wash away the unexposed photoresist, followed by rinsing and drying. The carbonization process is then carried out in an alumina tube furnace with a constant flow of 500 sccm of forming gas (5% H₂ + 95% N₂). Finally, the three-dimensional carbon micropillars are obtained by heating the polymer micropillars from room temperature to 350°C at a ramp of 5°C/min with 40 min hold time followed by a ramp to 1000°C at 5°C/min for 60 min before it cools down to room temperature.

2.2. Electrostatic spray deposition (ESD)

Electrostatic spray deposition (ESD) is a versatile technique that has been used for the successful integration of nanostructures such as carbon nanotubes, graphene and different metal oxides onto the C-MEMS architectures. In the ESD process, the precursor solution is atomized into aerosol by the application of a high electric potential between the spray nozzle and the preheated substrate [8, 9]. The deposited film is a function of several parameters including flow rate, temperature of the substrate, applied potential, nozzle geometry and the composition of the precursor solution [9]. ESD is particularly attractive owing to the high deposition rate, good uniformity and its ability to deposit varied functional materials as compared to other deposition techniques such as atomic layer deposition (ALD), electrodeposition and spincoating [7]. Figure 1b illustrates a schematic of the ESD process [10].

Figure 1 a) C-MEMS process flow; b) schematic of electrostatic spray deposition (ESD) [10]

3. C-MEMS BASED MICROSUPERCAPACITORS

3.1. Electrochemically activated C-MEMS based microsupercapacitors

In this study [11], first the interdigitated microelectrode arrays were fabricated using C-MEMS and then in order to enhance the capacitive performance of the microsupercapacitor, electrochemical activation was carried out. Figure 2a and 2b show the morphology of the SU-8 structures and the pyrolyzed C-MEMS structures, respectively. The activation was carried out by connecting the two C-MEMS electrodes with a silver wire. The silver wire and the contact pads were then covered with epoxy resin to prevent them from electrolyte exposure. The activation was performed using a three-electrode setup in a 0.5M H₂SO₄ electrolyte by applying a potential of 1.9V. After the activation process, the electrodes were negatively polarized at -0.3V for 10 min. Figure 3a displays the cyclic voltammograms of both the non-activated C-MEMS sample and the sample activated for 30 min. The area under the CV curve for the activated sample is clearly much larger than that of the non-activated sample, which indicates that the activated sample has much higher capacity than the non-activated sample. The geometric capacitance of the 30 min activated sample was 75 mF cm⁻² as compared to the very low capacitance of 0.07 mF cm⁻² of the non-activated C-MEMS sample, when measured at 5 mVs⁻¹. Moreover for the cyclability tests conducted for the 30 min activated electrodes, only a 12.3% capacitance fade was noted after 1000 cycles. Figure 3b displays the charge-discharge curves of the 30 min activated C-MEMS electrodes for different current densities between a potential of 0 and 1V. The charge-discharge curves are typical of a capacitor with nearly triangular curves and small iR drops. Slight deviation from the ideal capacitor is attributed to the introduction of pseudocapacitance from the redox active surface functional groups and as expected, the iR drop increases with higher current densities. The superior electrochemical characteristics of the activated samples to that of the non-activated samples can be attributed to the introduction of pseudocapacitance imparted from the oxygen-containing functional groups during the activation process and also the increase in the surface area from the electrochemical treatment.

3.2. Carbon nanotubes integrated C-MEMS based microsupercapacitors

Carbon nanotubes (CNTs) are one-dimensional carbon allotropes that owing to their exceptional mechanical strength, electrical and thermal conductivities have been widely used both in pristine and composite forms for enhancement of mechanical [12] and electrochemical properties of materials. In this study [13], CNTs were integrated onto C-MEMS structures using chemical vapor deposition (CVD). First the iron catalyst particles were coated onto the C-MEMS electrodes using ESD and then CNTs were synthesized using CVD. For the catalyst particles deposition time of 90 min, the CNTs were the most uniform. Figure 2c and 2d show the low magnification SEM images of the C-MEMS and CNT/C-MEMS composites produced at the optimum deposition time of 90 min. Figure 3c shows the CV curves of bare C-MEMS and CNT/C-MEMS structures with different deposition times. The CV curves are rectangular as expected for capacitive behavior. As opposed to the measly capacitance of 1.6 Fg⁻¹ exhibited by the bare C-MEMS electrodes, the CNT/C-MEMS composites deposited for 90 min, exhibit a capacitance of 33 Fg⁻¹ (8.3 Fcm⁻² footprint), which is more than twenty times larger. The CNT/C-MEMS composites were further treated with oxygen plasma in order to introduce oxygen-containing functional groups. Figure 3d shows the galvanostatic charge-discharge curves of the CNT/C-MEMS composites obtained for pre- and post-oxygen plasma treatment. Post plasma treatment, the specific capacitance of the composites was doubled to about 61 Fg⁻¹ for the first cycle. However, the increase in the capacitance came at the expense of cycling; only 71% of the capacitance was retained after 1000 cycles as opposed to 97.3% retention in the CNT/C-MEMS structures without oxygen treatment.

3.3. C-MEMS/polypyrrole (PPy) based microsupercapacitors

In this work [14] symmetric microsupercapacitors with 3D interdigitated electrode structures were first fabricated using C-MEMS and then PPy films were conformally coated onto the C-MEMS structures. The C-MEMS electrodes were fabricated using the standard procedure, while the PPy film was deposited electrochemically onto the C-MEMS structures. For electropolymerization of the PPy film, first the C-MEMS electrodes were connected externally and the device served as the working electrode in a three-electrode setup, with an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. The polymerization process was then carried out using an electrolyte solution containing 0.1M pyrrole monomer and 0.5M LiClO₄ supporting salt at a constant current density of 1 mAcm⁻² for durations of 5-15 min. Figure 2e shows the SEM micrograph of the as-pyrolyzed C-MEMS electrodes while Figure 2f shows the morphology of the PPy film; the morphology is granular raspberry-like which is typical of perchlorate doped PPy. Figure 3e shows the CV curves of the symmetric microsupercapacitors between a potential of -0.8 to 0.8V.

The CV curves are rectangular which is typical for capacitors. The symmetric microsupercapacitor polymerized for 15 min exhibited an average specific capacitance of $78.35 \pm 5.67 \text{ mF cm}^{-2}$ at a scan rate of 20 mVs^{-1} . Fig 3f shows the galvanostatic charge-discharge curves of the symmetric PPy/C-MEMS microsupercapacitor. The highly symmetric triangular curves are indicative of almost ideal capacitive behavior of the C-MEMS/PPy supercapacitors.

Figure 2: SEM images of a) SU-8 structures [11] and b) carbonized structures [11]; c) C-MEMS [13] and d) CNT/C-MEMS structures produced at optimum deposition time of 90 min [13]; e) as-pyrolyzed C-MEMS electrodes [14] and f) nanostructure of the PPy film [14].

Figure 3: a) CV curves of the non-activated C-MEMS samples and the samples activated for 30 min [11]; b) galvanostatic charge/discharge curves at different discharge rates [11]; c) CV curves of bare C-MEMS and CNT/C-MEMS composites deposited for different deposition times [13]; d) galvanostatic charge/discharge curves for pre-and post-oxygen plasma treated CNT/C-MEMS composites [13]; e) CV curves for PPY/C-MEMS symmetric microsupercapacitors [14]; f) galvanostatic charge/discharge curves of the symmetric PPY/C-MEMS microsupercapacitors [14]

4. CONCLUSIONS

The results from our research indicate that the C-MEMS based structures are promising platforms for 3D microsupercapacitors. Despite the fact that bare C-MEMS are glassy carbon substrates, they can be further integrated with nanostructures such as CNTs and conducting polymers such as polypyrrole to enhance their electrochemical

performance. Furthermore, C-MEMS structures can be activated electrochemically in order to impart oxygen-containing functional groups that lend pseudocapacitive effects to the C-MEMS electrodes and enhance the overall electrochemical performance. We anticipate that further improvement in the performance of micro-supercapacitors can be achieved through the optimization of the microelectrode design, the composition of the electrode materials and ESD conditions.

5. REFERENCES

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