

Short communication

## Flexible micro-supercapacitors

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### Abstract

Flexible micro-supercapacitors are fabricated by photolithography and an electrochemical polymerization technique. They are made solely from polymeric materials, including the electrodes. The cell has an active electrode area of roughly  $2\text{ mm} \times 2\text{ mm}$ , and the pattern size can be arbitrarily reduced to a micron scale. Rectangular capacitive behaviour is observed at relatively low scan rates of up to  $100\text{ mV s}^{-1}$  using cyclic voltammetry. The electrochemical performance remains without any deterioration and cell failure, even when the cell is bent and rolled up.

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### 1. Introduction

Miniaturized electronic devices, such as micro-electro-mechanical systems, (MEMS), microrobots and implantable medical devices, require micropower sources with small dimensions and high power density. Conventional thin-film batteries cannot satisfy these requirements. Electrochemical capacitors – also known as supercapacitors – have power densities far superior to those of batteries, so that they can be used when high power is required or a discharge time greater than that given by batteries is necessary [1]. If electrochemical capacitors were miniaturized to a microscopic scale, they could satisfy a variety of micropower demands [2]. A miniaturized electrochemical capacitor based on conducting polymers was first proposed by Wrighton et al. [3]. Full cell configurations for practical operations have been developed recently by using photolithography and an electrochemical polymerization technique [4,5].

In this study, the fabrication of flexible micro-supercapacitors is reported, together with their electrochemical properties. Since this novel device is made solely of polymeric materials, the flexibility is superior to that of devices based on inorganic materials (for example, Power paper<sup>®</sup> and Power Fab<sup>™</sup>) [6–8]. The technology is expected to be widely applicable to flexible electronic devices such as e-papers, smart cards and plastic electronic devices.

### 2. Experimental

The fabrication procedure for the flexible micro-supercapacitors is presented in Fig. 1. Gold microelectrode arrays were fabricated on a silicon substrate by UV photolithography and a wet etching method. Details of the preparation of the gold microelectrode are described elsewhere [4].

Polypyrrole (PPy) was potentiostatically synthesized on the gold microelectrode arrays. A three-electrode assembly was employed. The working electrode was the gold microelectrode, the counter electrode was a platinum plate, and the reference electrode was Ag/AgCl, saturated KCl against which all potentials are reported. All electrochemical experiments were performed with an EG&G model 273A potentiostat/galvanostat connected to a personal computer. Prior to PPy synthesis, dry nitrogen was bubbled through the electrolyte solution for 30 min,

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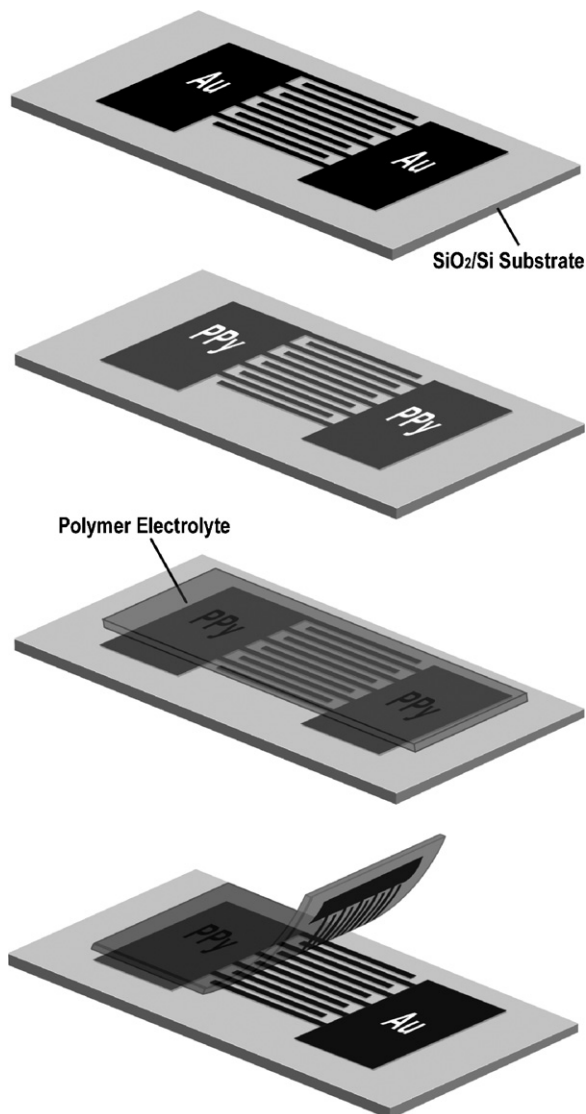


Fig. 1. Fabrication procedure of flexible micro-supercapacitors.

and the PPy synthesis was performed under a dry nitrogen atmosphere. The PPy was electro synthesized on the gold microelectrode array at 0.65 V versus Ag/AgCl in a 0.1 M pyrrole (Aldrich Chem. Co.) aqueous solution using 0.1 M  $\text{H}_3\text{PO}_4$  (85%, Kanto Chem. Co. Ind.) as a supporting electrolyte at 25 °C until desired synthesis charges were reached. After synthesis, the PPy electrodes were kept in a doped state (as prepared) because in this state PPy is stable in air.

A polyvinyl alcohol (PVA) electrolyte was synthesized by means of the solution casting method. To achieve this, PVA powder (Aldrich Chem. Co.) was added to de-ionized water, followed by subsequent heating to 95 °C with vigorous stirring. After the solution became transparent, it was cooled to room temperature and  $\text{H}_3\text{PO}_4$  was added. The solution was mixed for 12 h to ensure homogeneity and then poured into a Petri dish to allow evaporation of excess water. After becoming solidified in an elastomeric state, the product was cut into the required sizes and attached firmly to the PPy microelectrode arrays. The flexible micro-supercapacitor cell was completed

by detaching the polymer electrolyte layer from the silicon substrate.

### 3. Results and discussions

The procedure for the preparation of the flexible micro-supercapacitor is presented in Fig. 1. The adhesion between the PPy electrodes and the PVA film is stronger than that between the PPy electrodes and the gold surface. Therefore, the PPy microelectrode pattern can be transferred from the gold microelectrode surface to the PVA electrolyte film by peeling off the PVA film from the silicon substrate. A potentially destructive method such as hot pressing can be avoided by using this method. The method proposed here has an additional advantage in that the gold pattern can be used repeatedly for multiple cell fabrication. The PPy-removed gold pattern has a fresh surface, though some cleaning process is necessary. Re-use of gold patterns would considerably lower the fabrication cost and time because photolithography is an expensive and time-consuming process.

A flexible micro-supercapacitor cell made according to the process described above is shown in Fig. 2. The size of the patterns and the whole cell can be arbitrarily reduced to the micron scale because a photolithography technique is employed. There is no restriction on the shape of the pattern and the cell. The cell in Fig. 2 has an active electrode area of roughly 2 mm × 2 mm. It can be rolled up and freely deformed without deterioration of the electrochemical properties. Even when the cell is completely folded, the cell performance is little affected. To the author's knowledge, such flexibility has not been demonstrated for other flexible batteries or supercapacitors.

Fig. 3(a and b) are optical microscopic images of PPy electrode patterns transferred to the PVA film. Here, the PVA film can play the role of an electrolyte as well as a substrate for the flexible micro-supercapacitor cell. These micrographs clearly show the serpentine patterns of the PPy electrodes on the PVA film. Scanning electron micrographs confirm that the PPy patterns are well aligned without any conspicuous defects and cuts, see Fig. 3(c). The interface between the PPy electrode and the PVA is sharp, as shown in Fig. 3(d). The pattern transfer technique can be applied to various polymer substrates (e.g., polystyrene, polyethylene and polyethylene terephthalate), though not presented here. Hard polymer substrates, however, require a different procedure such as hot pressing or solution casting. Hot pressing requires the heating of a polymer above its glass transi-

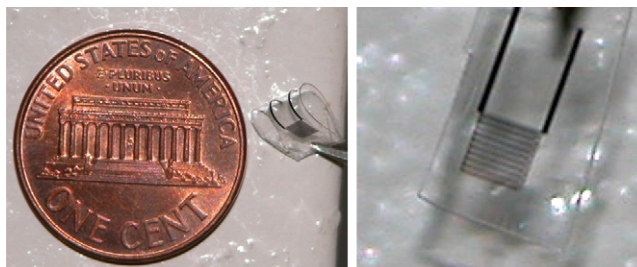


Fig. 2. The flexible micro-supercapacitor. The all-polymeric cell can have any shape: bending and even folding have little effect on cell performance.

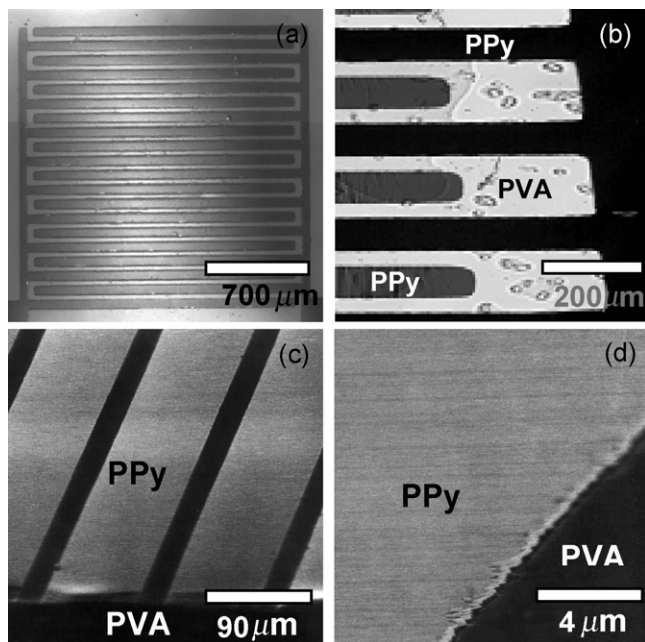


Fig. 3. Serpentine patterns of flexible micro-supercapacitor: (a and b) are optical microscopic images, and (c and d) are scanning electron images. The dimensions of the transferred PPy patterns are almost identical with those of original ones.

tion temperature ( $T_g$ ) and pressurizing for the pattern transfer. It is found that the pattern becomes wider than its original size with hot pressing. On the other hand, prerequisites for the solution casting method include a good solvent for the polymer and easy evaporation of the solvent. Thus, the method for pattern transfer should be chosen according to the properties of the polymer substrate.

Cyclic voltammograms for the flexible micro-supercapacitor cell are presented in Fig. 4. Rectangular capacitive behaviour is observed at relatively low scan rates up to  $100 \text{ mV s}^{-1}$ , while the voltammogram becomes resistor-like at a much higher scan rates of  $500 \text{ mV s}^{-1}$ . This type of transition in the cyclic voltammogram is due to the existence of cell resistance, and it is more or less a general phenomenon for all capacitors. The total resistance of a cell is composed of a series of component resistances [5]. The flexible micro-supercapacitor cell is made of polymeric

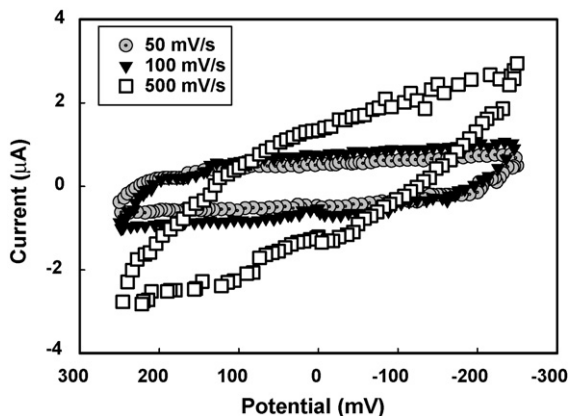


Fig. 4. Electrochemical property of flexible micro-supercapacitor cell.

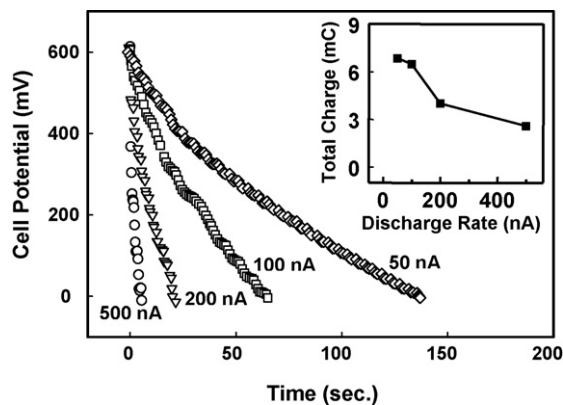


Fig. 5. Constant-current discharge behaviour of micro-supercapacitor cell.

materials only, including the electrode materials. Although these polymers are conductive, in most cases their electrical properties are close to that of a semiconductor. As the cell developed here does not have any metal current-collector, the polymer electrodes act both as an electroactive material and a current-collector. Therefore, the cell becomes resistor-like at a modest scan rate of  $500 \text{ mV s}^{-1}$ .

The cyclic voltammogram signals contain some noise, which indicates an unstable doping–dedoping process. It appears that PPy electrodes have high resistance, and their energy state becomes non-uniformly distributed. The non-uniform distribution gives rise to the locally irregular doping energy states.

Fig. 5 shows the discharge behaviour of the flexible micro-supercapacitor cell. A significant initial potential drop is observed at a high discharge current of  $500 \text{ nA}$  due to the high cell resistance. This drop becomes progressively smaller with decreasing discharge current. Accordingly, the total amount of discharged energy decreases with increasing discharge rate (inset).

Ideally, the current should decrease with a constant slope during the extraction of energy from a capacitor. The voltage of a real capacitor, however, rapidly drops at the early stage of discharge, then decreases with a smaller slope. The area under the potential curve corresponds to the amount of energy actually delivered to a load, thus really utilized. It is obvious that the reduction of the initial voltage drop is the key to the efficient extraction of the stored energy. The sources of the initial voltage drop include the internal resistances of the electrode material and the electrolyte, and the contact resistances between the electrode and the electrolyte or between the electrode and the current-collector. Addition of conductive fillers such as carbon blacks or carbon nanotubes would be helpful in reducing the resistance of conducting polymer electrodes [9].

In conclusion, a flexible micro-supercapacitor cell has been fabricated. The cell is small, lightweight and flexible and it is solely composed of polymeric materials. Such characteristics enable the cell to take any shape without limitations, thus to be integrated into any space. The fabrication process has a cost-advantage due to the repeated use of gold patterns. The flexible micro-supercapacitors developed here are expected to be integrated into the flexible, mobile microelectronic devices in the years to come.

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