

Development of a carbon-based lithium microbattery

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Abstract

A conceptual design for a carbon-based rechargeable Li microbattery and the progress in fabricating the electrode microstructures are described in this paper. The microstructures are produced from photoresists that are typically used by the semiconductor industry. The photoresist is spin coated on a silicon wafer, 'patterned' by photolithography and then heated in an inert environment to form carbon microstructures (< 50-micron dimension) which serve as the electrodes. Progress in fabricating the electrode microstructures, lithiation of the carbon negative electrode and electropolymerization of the polypyrrole positive electrode will be discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium microbattery; Carbon electrode; Carbon film; Polypyrrole

1. Introduction / conceptual design

The conventional microbattery is typically formed by depositing thin layers of the positive electrode, negative electrode and solid electrolyte on a substrate material, which contains provisions for current collection. The processing technologies that are used can easily produce thin-layer structures (< 100 μm), and hence very thin batteries. Another approach to fabricating microbatteries based on carbon electrodes is under development in our laboratory. What we are proposing is the application of semiconductor technology to fabricate array elements to serve as the current collector and electrodes in a microbattery. Fig. 1 shows a schematic representation of the arrangement of the positive and negative electrodes, which consist of carbon micropoles that are situated on thin carbon strips that serve as the current collectors. The electrolyte, which could be either a liquid or a polymer, will completely cover the micropoles and the region in between. In the first conceptual design, rows of micropole structures will be fabricated in an interdigitated pattern on the silicon support substrate. The initial demonstration will consider a microbattery consisting of a lithiated carbon negative electrode, a polymer (e.g., polypyrrole) positive electrode and a polymer or gel electrolyte. The micropoles provide additional surface area for electropolymerization

on the positive electrode as well as additional carbon for storing lithium in the negative electrode. In this paper, the preliminary electrochemical results obtained on carbon films are discussed.

Semiconductor processing techniques involving the patterning of carbon electrodes by photolithographic methods will be employed. In this innovative approach, the carbon electrodes are formed from regular photoresist by heat treatment to carbonize and make them electrically conductive. The electrochemically active electrode materials will be selectively deposited on the carbon posts by electrochemical methods, and the electrolyte will be applied on the interdigitated electrodes by spin coating or other techniques. For the proof of concept, we plan to use silicon with an insulating substrate layer for the electrode array in the microbattery.

The goals for the rechargeable Li microbattery are:

- operating cell voltage 3–4 V
- discharge rate 0.1 mA/cm²
- cycle life of at least 200 cycles at 80% depth-of-discharge
- ambient-temperature operation
- diameter of micropoles 5 μm and height 50–100 μm .

Patterned photoresists that are heat-treated (pyrolyzed) at different temperatures in an inert environment are used as a carbonaceous structural material for micro electro mechanical systems (MEMS). This new material permits a variety of interesting new MEMS applications [1] that employ structures having a wide variety of shapes, resistiv-

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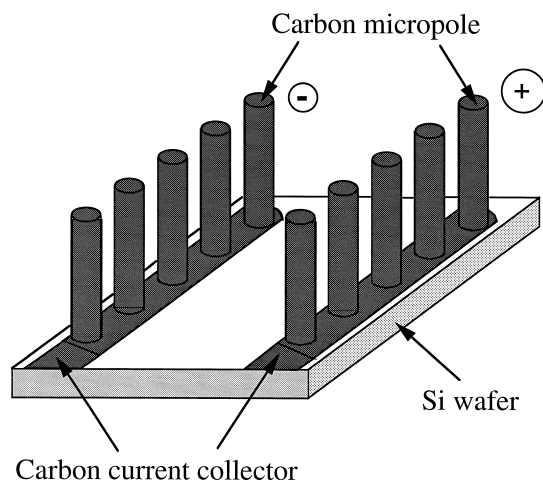


Fig. 1. Schematic representation of the arrangement of carbon electrodes in the microbattery.

ities and mechanical properties. Moreover, carbon surfaces form better electrochemical electrodes and are easier to derivatize with a wide variety of organic molecules than the conventionally used silicon. Potential applications for lithium microbatteries considered here include: (i) memory extension or backup for portable electronic devices, (ii) local power for micromachined actuators, (iii) active cable, battery is embedded in flex cable, (iv) smart battery with integrated circuit, and (v) inventory/access/asset management, radio frequency identification.

2. Experimental

2.1. Preparation and characterization of carbon

Both negative and positive photoresists were used to form conductive carbon films, but to date, most of our experience is with two positive resists, AZ-4330 (Hoechst Celanese) and OCG-825 (Olin). The chemical composition of these types of positive photoresists was not determined, but according to the information (Material Safety Data Sheet) provided by the manufacturers, they are novolak resins. Layers $> 100 \mu\text{m}$ in thickness have been patterned with novolak-type positive photoresist by Lockeh et al. [2], therefore it is anticipated that carbon posts of high aspect ratios (height/diameter) of more than 10 should be achievable. A negative photoresist (SU-8) has also shown good results for producing MEMS structures with high aspect ratio, and Despont et al. [3] reported structures of up to $1200 \mu\text{m}$ in height can be obtained. This negative photoresist is being evaluated in our laboratory.

The initial experiments were directed at determining the feasibility of producing carbon from these photoresists. With this in mind, a thin layer of photoresist was spin coated at 1000 rpm onto 10-cm diameter silicon wafers with OCG-825 or 3000 rpm with AZ-4330. The photoresists were carbonized by heating in nitrogen for 1 h at

600° , 700° , 800° , 900° , 1000° or 1100°C . More details on this procedure are presented elsewhere [4].

The carbon films were characterized by a variety of techniques such as scanning and transmission electron microscopies, atomic force microscopy (AFM), thermal gravimetric analysis and four-point-probe electrical resistivity measurements.

2.2. Fabrication

The processing steps required to form the carbon microstructures were carried out in the Microfabrication Facility in the Electronics Research Laboratory on the campus of the University of California at Berkeley. The processing steps that will be used to fabricate the microelectrode structures are presented in Table 1. In the first step, a thin layer of Si_3N_4 (about 100 nm) is deposited by chemical vapor deposition (CVD), which serves as an insulator to separate the conductive silicon wafer from the carbon structure. Two sequential steps involving spin coating, patterning and pyrolysis of the photoresist are employed to form the final carbon structure. In the first sequence (steps 2–5), the interdigitated arrays are formed, then the process is repeated (steps 6–9), except a different mask is used to pattern the photoresist to form the micropoles. Investigations of several of these steps are underway simultaneously, with the major emphasis so far on producing carbon films from the photoresist. We have previously reported [1,4] on the preparation of carbon films, which can serve as the current collectors, and the electrochemical results on these films. Design and evaluation of the masks for patterning the photoresist are underway. In addition, identifying the appropriate photoresist and determining the optimum procedure to form photoresist layers that will produce microstructures of high aspect ratio (height/diameter ratio of 10–20) are being addressed.

2.3. Electrochemical studies

Cyclic voltammetry was employed to investigate the electrochemical response of the carbon films in both aqueous and nonaqueous electrolytes. The experiments were

Table 1

Processing steps in the fabrication of electrode structures for carbon-based microbattery

Step 1	CVD silicon nitride layer ($\sim 100 \text{ nm}$ thick) on silicon wafer
Step 2	Spin coat photoresist on silicon nitride layer
Step 3	Pattern photoresist by photolithography to form interdigitated arrays
Step 4	Develop and process photoresist
Step 5	Heat treat wafer to carbonize photoresist to form interdigitated current collector arrays
Step 6	Spin coat second layer of photoresist
Step 7	Pattern photoresist by photolithography to form micropoles
Step 8	Develop and process photoresist
Step 9	Heat treat wafer to carbonize photoresist to form micropoles

conducted with a VersaStat™ potentiostat controlled by Model 270/250 software (EG and G Instruments). The electrochemical response of the redox couple ($\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$) in 0.1 M H_2SO_4 was investigated at potential scan rates of typically 60 mV/s. Details on the electrochemical measurements of the carbon films were reported elsewhere [4]. The electrochemical response of the pyrolyzed photoresist in an electrolyte typically used in lithium-ion cells was investigated. The electrolyte selected for these initial measurements was 1 M LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC) (50:50 vol.%). A sealed cell was designed to conduct electrochemical experiments outside of a glove box with the carbon films in nonaqueous electrolytes [5]. A potential scan rate of 5 mV/s or lower was used in nonaqueous electrolyte.

A conventional three-electrode cell was used for electropolymerization studies and electrochemical measurements of polypyrrole (PPy) films. A polypyrrole film was deposited on glassy carbon (Tokai Carbon, GC20S, $18 \times 18 \times 1$ mm) and pyrolyzed negative photoresist (SU-8, 1000°C) at 0.5 mA/cm² in an aqueous solution containing 0.1 M pyrrole and 1.0 M KCl. The surface area of the working electrode was 0.8 cm², and the counter electrode was a gold wire. During deposition, the potential of the working electrode was monitored with respect to an Ag/AgCl (1 M KCl) reference electrode. The film thickness was varied by using different deposition times, and the thickness was estimated by assuming that 1 μm corresponds to 240 mC/cm².

Polypyrrole was also electrodeposited on glassy carbon (Tokai GC20S) substrate (0.28 cm²) in 1 M pyrrole in EC–DMC containing 1 M LiPF_6 by applying a constant current of 100 μA in two 150 s pulses (total 3×10^{-2} coulomb). The potential was measured versus a platinum quasi-reference electrode (QRE) during electropolymerization of pyrrole to polypyrrole. The potential was 0.4 V (vs. QRE) at the beginning of polymerization and it reached 0.7 V at the end of the process. It is estimated that a 450-nm thick film was produced, assuming that 1 μm corresponds to 240 mC/cm².

The electrochemical doping and undoping behavior of PPy films was examined in 1 M KCl, with the pH adjusted to 2.5 by adding 0.1 M HCl. Prior to the measurements, the solution was deaerated by passing nitrogen gas through the solution for 10 min. Cyclic voltammograms were obtained between –0.8 and 0.3 V at different scan rates. Similar experiments were also conducted in EC–DMC containing 1 M LiPF_6 .

3. Results

3.1. Properties of carbon film

Pyrolysis of the photoresist results in a considerable loss of mass and a large volume change, as decomposition

occurs to form volatile products. Thermal analysis indicated that only about 13% of the original mass remains after pyrolysis to 1000°C [4]. The film thickness of the pyrolyzed photoresist (AZ4330) on silicon wafer decreased dramatically after pyrolysis (i.e., shrinkage from 8 μm down to about 2 μm). However, AFM of the carbon film showed that a relatively smooth surface was obtained with an estimated roughness of about 3 nm [1]. This carbon film is believed to be sufficiently smooth to serve as the interdigitated array on which the micropoles will be formed.

The electrical resistivity of the carbon films was measured by the four-point probe method. Fig. 2 shows a plot of the resistivity of pyrolyzed photoresist (AZ4330) as a function of the pyrolysis temperature. It is evident that the resistivity decreases dramatically as the pyrolysis temperature increases above 700°C. The origin of this rapid increase in resistivity is better understood by superimposing in Fig. 2 the data reported by Zheng et al. [6,7] for the hydrogen content (H/C ratio) of pyrolyzed epoxy novolak resin (DEN438, poly(phenyl glycidyl ether)-coformaldehyde, Dow Chemical, Midland, MI). Both the resistivity and H/C ratio show similar changes with the pyrolysis temperature. It is evident that at temperatures > 700°C, these two properties show a comparable response. While we cannot claim that the results obtained by Dahn et al. are directly applicable to the carbon films obtained with pyrolyzed photoresist, the strong correlation suggests that the hydrogen content in the carbon film influences the resistivity. The hydrogen content was not determined in our carbon films because of two factors. First, the carbon film adhered strongly to the silicon, and removing it for hydrogen analysis would be difficult. Second, the thickness of the carbon film (< 10 μm) is considerably less than that of the silicon wafer (about 500 μm), therefore the hydrogen content would be only a small fraction of the total mass of the thin carbon film and silicon.

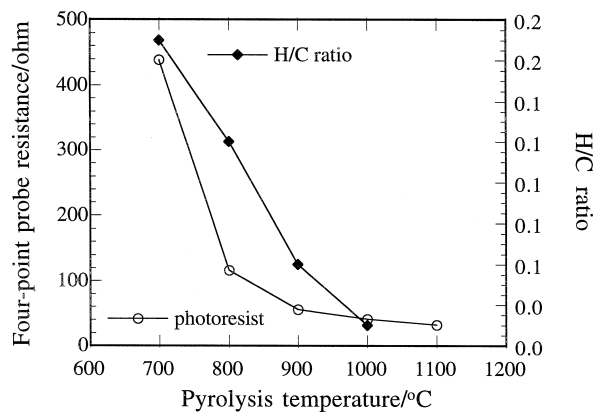


Fig. 2. Changes in the electrical resistance and H/C ratio of novolak resins pyrolyzed at different temperatures. Resistance was measured on pyrolyzed photoresist AZ4330 [1] and the H/C ratio was determined on pyrolyzed DEN438 [7].

3.2. Electrochemical behavior of carbon film

The redox couple ($\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$) was used primarily because it is a well-established reaction to compare the electrochemical properties of pyrolyzed carbon with other carbon electrodes. A comparison of the cyclic voltammogram of a pyrolyzed photoresist AZ4330 and glassy carbon are presented in Fig. 3. It is evident in the cyclic voltammogram that the electrochemical response of the carbon film for the redox reaction is similar to that obtained with glassy carbon. In this regard, the carbon film behaves like a carbon electrode. Preliminary studies of the electrochemical behavior of the carbon films in a non-aqueous electrolyte (1 M $\text{LiPF}_6/\text{EC}-\text{DMC}$) were reported elsewhere [5]. The cyclic voltammogram was similar to that obtained with glassy carbon under comparable conditions.

In this study, pyrrole was electrochemically polymerized on the glassy carbon and carbon film at a constant current density of $0.5 \text{ mA}/\text{cm}^2$ in an aqueous electrolyte. When current was applied, the potential increased rapidly, and then gradually reached a steady state of about 0.65 V with both carbon substrates. This behavior is typical of electrochemical reactions associated with a nucleation process. The ease of nucleation depends on many factors such as flatness, imperfections, surface groups, etc. on of the substrate surface. The glassy carbon had a slightly higher overvoltage (about 20 mV) than the carbon film, which indicates that nucleation is easier on the latter substrate.

AFM studies of the changes in the structure and thickness of polypyrrole on carbon were initiated. The first measurements were conducted on glassy carbon where a polypyrrole film was obtained with a morphology that

consisted of large structures resembling particles, and regions of relative flatness. Potential cycling between 0.3 V (doped state) and -0.8 V (undoped state) revealed that the large particle structures increased by about $0.15 \mu\text{m}$ to $0.20 \mu\text{m}$ upon doping. However, the overall morphology did not change. The thickness of the film present in the flat region is estimated to be $0.25 \mu\text{m}$, and it changed by about 10% (i.e., $0.03 \mu\text{m}$) by doping/undoping. It should be noted that these results were obtained in an aqueous electrolyte. Observations by Otero and de Larreta [8] of polypyrrole films on Pt in nonaqueous electrolyte (0.1 M LiClO_4 in acetonitrile) indicate that a morphology consisting of dendrites and a homogeneous smooth film can be obtained. We are planning to extend our studies to include AFM measurements of electropolymerization of polypyrrole in nonaqueous electrolytes.

Fig. 4(a) shows the cyclic voltammograms for PPy films of the same thickness ($\sim 0.25 \mu\text{m}$) formed on glassy carbon and carbon films in acidic solution. No appreciable difference in doping–undoping behavior was observed between the two carbon substrates. The structure of the PPy film, as observed in the preliminary AFM studies, appears to be quite similar on both carbon substrates. This implies that the properties of the carbon film as a substrate for PPy are very similar to those of glassy carbon. Fig. 4(b) shows the current–potential profiles of the PPy film formed on the carbon film during repetitive cycling for 500 cycles at a potential scan rate of $50 \text{ mV}/\text{s}$. The film showed stable redox current peaks even after 500 cycles, although the peaks shifted slightly to higher potentials and the peak currents decreased a little. The adhesion of the PPy film to the carbon film seems to be very good. These preliminary results suggest that the carbon film should be a good

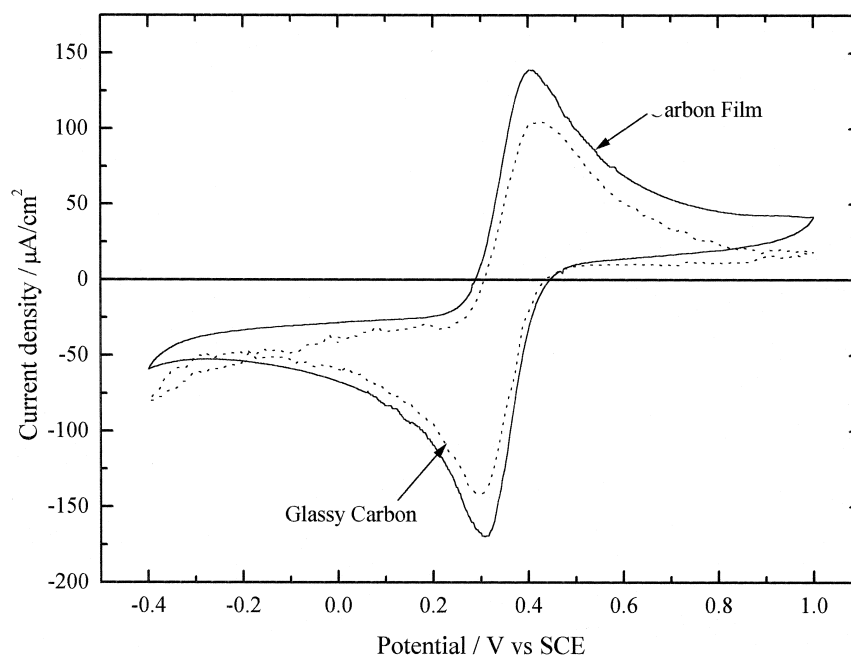


Fig. 3. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ redox couple on pyrolyzed photoresist AZ4330 and glassy carbon.

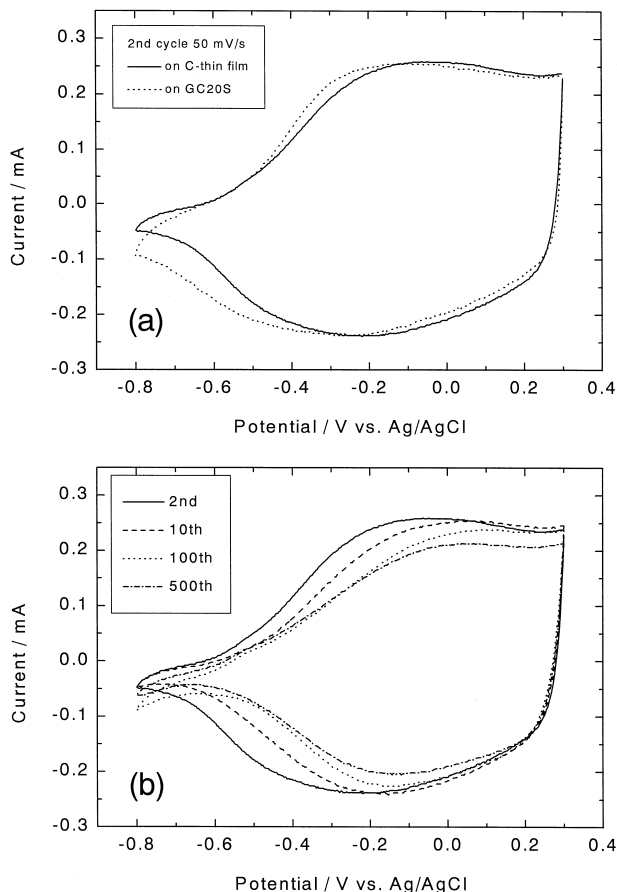


Fig. 4. (a) Cyclic voltammograms of PPY films on glassy carbon and carbon film (AZ4330). (b) Potential cycling of PPY film on carbon film at a scan rate of 50 mV/s in 1 M KCl, pH 2.5.

substrate for PPY electrodes. In addition, Killian et al. [9] have observed that PPY on graphite can be potential cycled in a nonaqueous electrolyte (LiClO_4 in ethylene carbonate/propylene carbonate/acetonitrile), which is an encouraging result for our efforts to develop a carbon-based microbattery. Preliminary results obtained for potential cycling of PPY on glassy carbon in a nonaqueous electrolyte, EC–DMC containing 1 M LiPF_6 , are presented in Fig. 5. The repetitive cyclic voltammograms between 0 V and 0.9 V (vs. Pt QRE), which were obtained at 20 mV/s in an electrolyte containing no pyrrole, clearly show that electroactive species are present on the electrode surface which has the same redox potential as the equilibrium potential observed during constant current chronopotentiometry. The anodic current peak height decreases slightly with cycling but remained relatively constant for a week. This indicates that the PPY film obtained by the above method is stable in the EC:DMC electrolyte.

3.3. Fabrication of interdigitated carbon structures

The fabrication steps outlined in Table 1 require masks to pattern the carbon current collector and micropole elec-

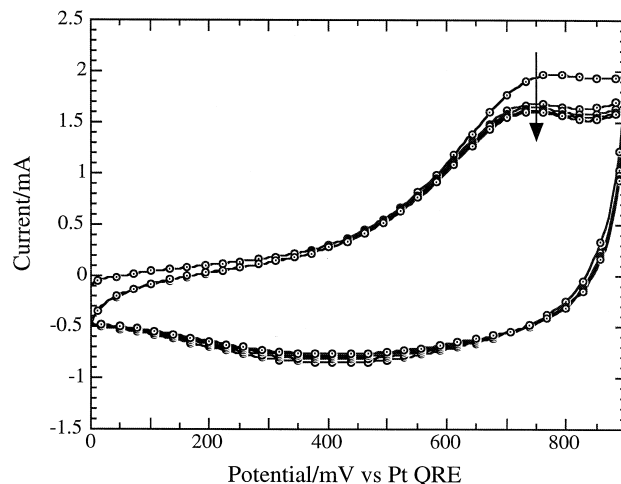


Fig. 5. Cyclic voltammograms of PPY films on glassy carbon in EC–DMC containing 1 M LiPF_6 . Scan rate is 20 mV/s.

trode structures. We are currently considering two arrangements (designated single cell and double cell) for the interdigitated arrays, which are illustrate schematically in Fig. 6, to study the effect of geometry on electrochemical response. Two photomasks are required, one to form the

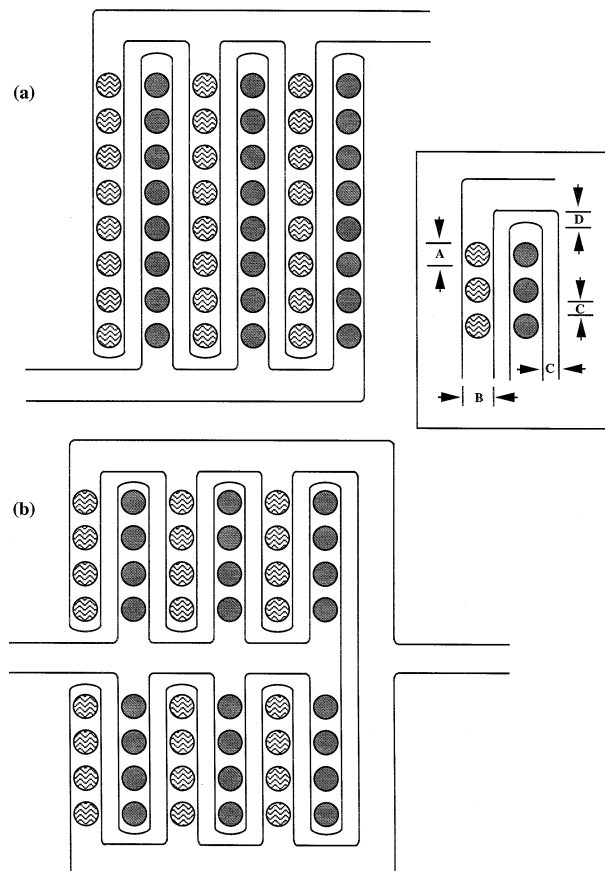


Fig. 6. Schematic representation of interdigitated arrays and micropoles for microbattery. (a) Single cell; (b) double cell.

Table 2
Microbattery dimensions

	A (μm)	B (μm)	C (μm)	D (μm)
Cell 1	5	7	5	1
Cell 2	15	17	5	1
Cell 3	30	34	10	2
Cell 4	50	54	10	2

interdigitated array and the other to produce the micropoles. Table 2 lists the dimensions of the different parts of the array and micropoles (see inset in Fig. 6) for four sizes of cells. Dimensions from 5 μm to 54 μm will be used to form the micropoles and arrays, and distances as small as 1 μm will separate the arrays. The electrode diameter (A) will vary from 5–50 μm , the distance between the carbon micropoles (C) will be either 5 or 10 μm , the width of the current collector (B) will range from 7 to 54 μm , and the separation between the current collector (C, D) will be less than 10 μm . The photomasks are being designed and the carbon patterns that are produced are in the process of evaluation. Preliminary studies are underway using several masks to pattern the interdigitated arrays with both positive and negative photoresists. However, the preliminary studies indicated that better carbon films are obtained from a negative photoresist when the substrate is silicon nitride rather than silicon with a native oxide.

4. Concluding remarks

This study clearly demonstrated that photoresist that is patterned by photolithography and pyrolyzed in inert environment yields carbon films and microstructures on silicon substrates. Furthermore, the carbon films show an electrochemical response that is comparable to that of glassy carbon for selected electrochemical reactions in aqueous and nonaqueous electrolytes. The measurements by Panero et al. [10] with a rocking-chair cell, graphite/(LiClO₄ in

ethylene carbonate/dimethyl carbonate/PPy, indicate that a cell voltage of about 3.0 V and theoretical specific energy of 300 Wh/kg is possible. These results are encouraging for the carbon-based microbattery.

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