METAL-CORED CARBON MICROPOSTS FOR THREE-DIMENSIONAL Li^+ MICROBATTERY

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ABSTRACT

We have designed, fabricated and tested a novel carbon electrode for three-dimensional (3D) lithium-ion microbattery applications. This structure consists of an array of high-aspect-ratio carbon posts ($> 15:1$) with nickel metal embedded in their core. Carbon was prepared by pyrolyzing parylene precursor in an inert environment at high temperature. Proper reversible capacity was observed during charge and discharge of lithium ion in a half-cell battery setup. The initial results suggest that this half cell battery can be post-processed to form a full 3D lithium ion battery with high energy density at high discharge rates.

INTRODUCTION

Microbatteries based on 3D architecture offer the opportunity to overcome the energy and power deficiencies of conventional thin-film batteries when limited to small foot-print areas [1,2]. Different types of 3-D architectures including nano-scale aerogel electrodes and micron size post electrodes have recently been reviewed [2]. Full secondary (rechargeable) 3D nickel-zinc [3] as well as lithium-ion [4] microbatteries have already been demonstrated. Lithium ion batteries have drawn serious attractions in the past few years due to their high energy densities. Different types of carbonaceous materials have been extensively used as anodes in commercial lithium ion batteries [5]. Recently, electrode post arrays of carbon have been fabricated by molding them in silicon template [6] or by pyrolysis of photoresist [7,8] to be used as the anode electrode in 3D Li-ion batteries. The main drawback of these carbon rods, however, is the loss of energy density at high discharge rates [2,7] due to the semi-conducting behavior of the carbon and high ohmic potential losses along the length of the post. The novel electrode structure that we introduce here circumvents this effect by placing a metal core (nickel in this report) inside the active carbon material (Fig. 1).

DESIGN

To provide enough active carbon and increase the energy density of the electrode on a given footprint area, it is necessary to increase the aspect ratio of the post structure. On the other hand, this high energy is inaccessible at high discharge rates due to the excessive ohmic losses in the high aspect ratio post array [2]. Our 3D electrode structure presented here is designed in a way that minimizes the overall internal resistance of the carbon post structures. Fig. 2a schematically depicts the previously introduced carbon post [7], and Fig. 2b is the structure introduced here for the first time. The nickel post inside each rod effectively extends the current collector into the carbon. Any point on the high surface area anode directly communicates to the nickel current collector without having to go through a large volume of the carbon and minimizes the overall ohmic potential drop at high discharge rates. Parylene has been previously used as the precursor for making carbon and the mechanical and

electrical properties of pyrolyzed parylene have been measured [9]. The intercalation and deintercalation of lithium ion in pyrolyzed parylene is investigated in this report for the first time. Its benzene rich structure and conformal deposition on surfaces with high topographical variations makes it a suitable choice of polymer precursor to fabricated carbon for our design.

Fig. 1 Schematic of carbon post electrode array with metal in its core. (a): overall, (b): cross-section of a post

Fig. 2 Schematic of deintercalation of Li-ion in carbon post anode during discharge. (a): Previously reported carbon post suffers from the high potential drop along the slender carbon post at high discharge rates. (b): Our design of carbon post has minimized potential drop through its metal core, while maintaining the carbon as the anodic material

FABRICATION

Two types of samples were fabricated. The first type was flat and representing a conventional 2D thin film carbon electrode. Thermal oxide was first grown on silicon substrate as the passivation layer. Parylene-C was then deposited on the sample using CVD and pyrolyzed at 1000°C in the furnace during argon gas

flow to form the carbon. The second type of the samples was fabricated by conformal deposition of parylene over nickel post array and subsequent pyrolysis to form carbon. Fig. 3 shows the detailed fabrication process. Silicon was etched in step 1, using the method of either DRIE or photo-assisted anodic etching, to form an array of high-aspect-ratio holes as the electroplating mold [6]. In step 2 the backside was etched using RIE to make the through holes. It was followed by thermal oxidation to passivate the silicon for the following metallization steps.

Fig. 3 Fabrication of carbon-coated nickel micropost array

In step 3, Ti/Ni (100/1000Å) seed layer was evaporated. Ni was electroplated at 10mAh/cm^2 in step 4 using nickel sulfate electroplating solution to seal the holes at the top side of the substrate. In step 5, nickel was electroplated in the holes using the top-side nickel as the seed layer. Nickel was electroplated at constant current density of 5 mA/cm^2 . Photoresist was applied to passivate the top side from being electroplated during this step. In step 6, the oxide and silicon were etched away using BOE and XeF_2 , respectively, to expose the nickel post array. In step 7, parylene-C was conformally deposited on the nickel posts using CVD. As the final step it was pyrolyzed into carbon in the furnace and during argon gas flow at 1000°C . Temperature increase and cooling down rate was set to 1°C/min .

Fig. 4 is the SEM image of a silicon mold fabricated by anodic etching of n-type silicon in 5% HF during backside illumination. Fig. 5 corresponds to step 6 of the process, showing the nickel posts before parylene deposition. The nickel posts are $10\text{ }\mu\text{m}$ in diameter and $170\text{ }\mu\text{m}$ tall. $5\text{ }\mu\text{m}$ of parylene-C was conformally deposited on the nickel posts. Fig. 6 is the SEM image of the final carbon posts. The thickness of the carbon is $1\text{ }\mu\text{m}$. Fig. 7 is the SEM image of a sample prepared by using DRIE etched mold. $11.5\text{ }\mu\text{m}$ of parylene was deposited on the nickel posts. The diameter of each post is $60\text{ }\mu\text{m}$ and the height is $400\text{ }\mu\text{m}$. The parylene pyrolyzed to $3.2\text{ }\mu\text{m}$ of carbon.

Fig. 4 Array of high aspect ratio holes in silicon, fabricated by anodic etching in HF during backside illumination

Fig. 5 Nickel post array before parylene deposition, corresponding to step 6 of the process

Fig. 6 Fabricated sample using anodic-etched silicon mold. Nickel posts are 10 μm in diameter and 170 μm tall, covered with 1 μm carbon

Fig. 7 Fabricated sample using DRIE-etched silicon mold. Nickel posts are 60 μm in diameter and 400 μm tall, covered with 3.2 μm carbon

EXPERIMENT

Resistivity of parylene-pyrolyzed carbon was measured at 0.015 $\Omega\text{-cm}$ on the flat sample using four-point probe. Electrochemical measurements were carried out for both type of flat and post array electrode. The electrolyte was 1 M LiClO_4 in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Two different types of cyclic voltammetry and galvanostatic charge-discharge tests were performed on the samples in an argon-filled glove box. Three-electrode system setup with lithium metals as the counter and reference electrodes was used for testing. As the first step, lithium ion was intercalated at 0.1 mA/cm^2 in a flat sheet of carbonized parylene. The thickness and area of the sample were 1 μm and 1 cm^2 , respectively. The sample was electrically connected using an alligator clip at one corner. The results exhibited reversible intercalation/deintercalation of lithium with an areal capacity of 0.047 mAh/cm^2 . This translates to gravimetric capacity of 235 mAh/g , which is in the range of reversible capacities reported for pyrolyzed SU-8 [7]. The micropost structures were tested in the subsequent experiments. Fig. 8 is the cyclic voltammetry of post array of Fig. 6, with 10 μm diameter and 170 μm high on 0.5 cm^2 footprint area. The electrode was cycled at 1 mV/s between 0.01 V and 2 V. The graph shows proper intercalation/deintercalation of lithium. Charge-discharge behavior of this structure was tested during galvanostatic test at

two different discharge rates. Fig. 9 shows the galvanostatic charge-discharge measurements at 0.1 mA/cm^2 (the first cycle is not shown here due to its irreversible capacity). The lithium capacity of 0.75 mAh/cm^2 was observed at this discharge rate. Fig. 10 is the galvanostatic charge-discharge at 1 mA/cm^2 for the same structure. At this higher discharge rate a lower capacity of 0.16 mAh/cm^2 was observed. The lower aspect ratio structure of Fig. 7 was also tested for charge-discharge behavior. Fig. 11 shows the expected irreversible capacity loss on the first discharge. For the second and succeeding three cycles, the lithium capacity of 0.55 mAh/cm^2 was observed at discharge rate of 0.1 mA/cm^2 .

Fig. 8 Cyclic voltammetry scan curves at 1 mV/s for carbon post array of Fig. 6

Fig. 9 Galvanostatic charge-discharge curves at 0.1 mA/cm^2 for carbon post array of Fig. 6

Fig. 10 Galvanostatic charge-discharge curves at 1 mA/cm^2 for carbon post array of Fig. 6

Fig. 11 Galvanostatic charge-discharge curves at 0.1 mA/cm^2 for carbon post array of Fig. 7

DISCUSSIONS

It was observed that pyrolyzed parylene reversibly intercalates lithium ion and can be used as the anode material for rechargeable batteries. Comparing the lithium capacities for the flat sample and the post structure, high increase of stored energy was observed for the post structures. This is due to the increase in the surface area and the large volume of the active carbon material. The effect of the discharge rate on the lithium capacity was also tested for the post structures. By increasing the discharge rate from 0.1 mA/cm^2 to 1 mA/cm^2 , only 1/5 of the capacity was accessed. This is suspected to be due the geometrical configuration of the half cell testing setup and not the ohmic potential losses. During our measurements, the 3D carbon electrode was placed in the electrolyte in front of a lithium sheet counter electrode, causing a high electric field concentration at the tip of the posts and much lower field at the bottom area of the posts. Due to this effect most of the insertion of lithium ions takes place at tip area, and lowers the active volume of the carbon. This effect will be eliminated when a full battery is made out of this half cell, by conformal deposition of thin electrolyte and the counter electrode. In this case, the electric field will be more uniform along the long post and high energy density lithium battery may be fabricated.

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