

Fabrication of SU-8 derived Three-dimensional Carbon Microelectrodes as High Capacity Anodes for Lithium-Ion Batteries

Suresh Mamidi^a, Manohar Kakunuri^b, Chandra S. Sharma^{a,*}

^a Creative & Advanced Research Based on Nanomaterials (CARBON) Laboratory,
Department of Chemical Engineering,

^b Department of Materials Science and Metallurgical Engineering,
Indian Institute of Technology, Hyderabad, Kandi-502285, Telangana, India.

E-mail: cssharma@iith.ac.in

It has been shown earlier that three-dimensional (3-D) electrode architecture facilitates higher energy and power density than the planar thin film based electrodes. In the present study, we fabricated SU-8 photoresist derived micro-patterned three-dimensional carbon-based electrodes using photolithography on stainless steel (SS) wafer used as a current collector. The preference of SS wafer over conventionally used silicon (Si) wafer is based on our previous study where use of SS wafer as a current collector enhanced the reversible capacity of thin carbon films to almost double as compared to the thin films prepared on Si wafer. As-fabricated 3-D carbon electrodes were then investigated for their electrochemical performance. At 0.1 C-rate, Li-ion reversible capacity was found to be nearly 600 mAh/g after 165 continuous charge/discharge cycles. Nearly 100% coulombic efficiency and excellent cyclic stability confirms the potential use of such 3-D micro-patterned carbon electrodes for next generation Li-ion batteries.

Introduction

Carbon materials have been synthesized with controllable physiochemical properties and morphologies like nanofibers, nanoparticles, nanotubes, fullerenes and carbon nanotubes and therefore find their use in wide ranging applications due to their exceptional mechanical and electrical properties (1-4). One such major applications of carbon materials is as anode material for Li-ion batteries and supercapacitors. To achieve higher energy density and specific capacity, nanostructured carbon materials are well studied in literature with an aim to reduce the Li-ion diffusion length and therefore to facilitate faster intercalation reversibly. However excess surface area and porous structure of carbon nanomaterials also add to high irreversible capacity losses and cause significant capacity fade during cycling. Another approach to achieve high energy density Li-ion batteries is to alternate the electrode configuration from planar thin films to three-dimensional (3-D) electrodes (5-11). In 3-D electrode more amount of active electrode material can be accommodated in the same footprint area along with minimized transport losses.

SU-8 is an epoxy based negative photoresist which is widely used in microelectronics and can be easily patterned into 3-D structures using photolithography (8,9,11,12). Upon pyrolysis, SU-8 also yields glassy carbon which can be reversibly intercalated by lithium ions. SU-8 derived

carbon has been successfully tested for its anodic performance in Li-ion batteries in the form of thin films, nanofibers and also as 3-D microelectrode arrays (8, 9, 11-15). However in earlier studies (8, 9, 11, 12), SU-8 derived carbon thin films and 3-D microelectrode arrays were prepared on silicon wafer as a substrate. Recently our group has studied the effect of substrate (used as a current collector for electrochemical measurements) in detail and shown that SU-8 thin films prepared on stainless steel (SS) wafer resulted in almost double reversible capacity (~ 400 mAh/g) as compared to SU-8 carbon thin films on Si wafer (~ 220 mAh/g) (13, 15). Considering these results, we hereby extend the use of SS wafer for preparing the 3-D carbon microelectrode arrays to be used as electrode. Interestingly in real applications also, it is either SS foil or copper foil which is used as current collector rather than Si wafer due to better electronic conductivity and stability in wide range of potentials. However as similar to thin films, it is a great challenge to prepare SU-8 based 3-D microstructures on SS wafer due to relatively poor adhesion of SU-8 with SS substrate. More challenging task is to further retain the 3-D morphology during pyrolysis.

In this work, we have optimized various pre-baking, post-baking conditions along with UV exposure time to successfully fabricate SU-8 based 3D carbon microstructures on SS wafer which were then pyrolyzed in a controlled manner to yield 3-D carbon microelectrode arrays. As-fabricated SU-8 derived 3-D carbon microelectrode arrays have then been tested for their electrochemical performance.

Experimental Section

Materials and Methods

A single side polished 1 inch SS wafer (Make: MTI Corporation, CA, USA) was dehydrated on a hotplate at $150\text{ }^{\circ}\text{C}$ for 5 minutes to remove moisture. SU-8 2050 photoresist (Make: Microchem Corporation, MA, USA) was spin-coated at 3000 rpm for 30 s in a dust-free yellow room. These SU-8 thin films were soft-baked at $65\text{ }^{\circ}\text{C}$ and $95\text{ }^{\circ}\text{C}$ for 2 and 5 minutes respectively to remove any excess solvent. After cooling to room temperature, the films were exposed to UV light through the chrome mask (25 μm diameter cylinders with 30 μm spacing) (Make: Front Range Photomask, CO, USA) for optimized exposure time to promote polymerization reaction through the cross-linkage process. Then these SU-8 films were post-baked at $65\text{ }^{\circ}\text{C}$ and $95\text{ }^{\circ}\text{C}$ for 1 and 6 minutes respectively to enhance the rate of reaction. Later these SU-8 thin film samples were developed in commercially available developer solution (Make: Microchem Corp., MA) with mild agitation for 20 seconds where unexposed parts were solubilized in the solution. As-fabricated SU-8 3D microstructures were then finally hard baked at $150\text{ }^{\circ}\text{C}$ for 10 min before pyrolysis.

A controlled two step pyrolysis at final temperature of $900\text{ }^{\circ}\text{C}$ in the nitrogen atmosphere was carried out in an alumina tube furnace (Make: Nabertherm GmbH). SU-8 based 3-D Samples were kept in the furnace at room temperature. Initially furnace tube was purged at 75 lph N_2 flow rate for 30 min and then maintained constant at 20 lph to obtain the inert atmosphere inside the furnace tube. In two-step pyrolysis process, the furnace temperature was first raised from room temperature to $350\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C}/\text{min}$ and samples were maintained at the same temperature for 30 min. Then the temperature was further ramped up at $5\text{ }^{\circ}\text{C}/\text{min}$ to $900\text{ }^{\circ}\text{C}$ and dwelled there for 60 min. followed by cooling to room temperature in the presence of nitrogen gas atmosphere. The major challenges involved in preparing these 3-D carbon structure on SS wafer were roughness of the substrate, dissolved gas evolution during pyrolysis and thermal stresses engaged due to

thermal coefficient differences in film and substrate. We have successfully overcome the challenges and fabricated carbon 3D microstructures on SS wafer.

Structural Characterization

X-ray diffraction (XRD) pattern for SU-8 photoresist derived carbon was obtained over a 2θ range from 10 to 80° using a PANalytical X-ray diffractometer with the $\text{CuK}\alpha$ radiation source. The Raman spectrum was recorded using a Bruker Raman microscope spectrometer equipped with a 532 nm laser. Optical and surface profiler (Make: Aep-technologies Model: NANOMAP-D (Dual mode)) was used to measure the surface profile.

Electrochemical Testing

For electrochemical performance testing, as-prepared binder free SU-8 derived carbon 3D microstructures on SS wafers were used as a working electrode in Swagelok cell assembly. The weight of active carbon material was measured to be 1.1 mg. The galvanostat potentiostat (Make: Biologic Science Instruments, Model: VSP) was used to carry out experiments for electrochemical testing. Lithium foil (99.9% pure, Sigma Aldrich) was used as counter electrode in 1 M solution of LiPF_6 in a 1:1 v/v mixture of ethylene carbonate and dimethyl carbonate was used as an electrolyte. The glass microfiber filters (Make: Whatman Filters) were used as a separator. The Swagelok cell assembly was packed entirely inside an argon-filled glove box. The soaking time of 6 hours provided to reach equilibrium voltage followed by galvanostatic cycling at a 0.1C rate.

Results and discussion

XRD Analysis

As shown in Figure 1, two broad diffraction peaks, (002) and (100) imply the presence of small domains of parallel stacked graphene layers as in a typical glassy carbon materials. The $d_{(002)}$ spacing was found to be 0.35nm, which is slightly higher than that of $d_{(002)}$ of graphite (0.345 nm). However, it was known that this larger interlayer distance favors capacity retention during Li-ion insertion and de-insertion process (16).

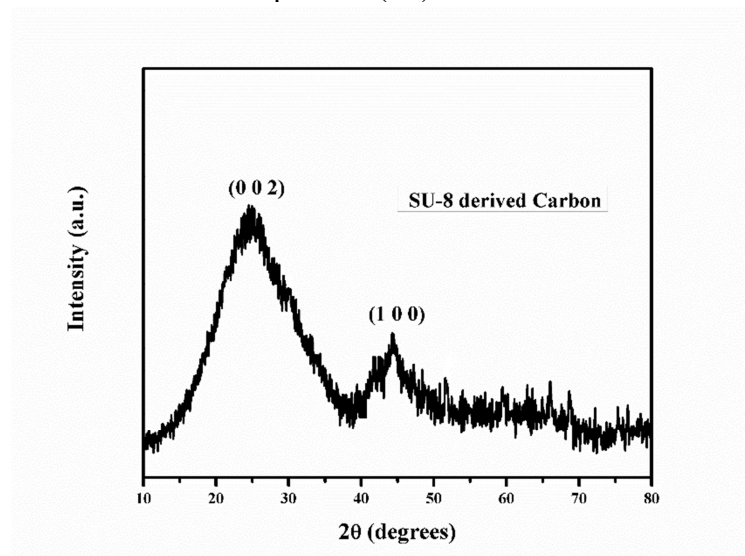


Figure 1: X-Ray diffraction pattern for SU 8 derived 3-D carbon microstructures

Raman Spectroscopy Analysis

Raman Spectrum for SU-8 derived carbon 3D microstructures displays the characteristic bands around 1353 cm^{-1} and 1597 cm^{-1} for D band and G band respectively. The D band signifies the nongraphitic carbon content, which corresponds to A_{1g} breathing vibration mode. Another characteristic G band signifies the presence of graphitic content which corresponds to E_{2g} vibrational mode (17). The empirical formula $L_a=4.4(I_G/I_D)$ was used to calculate the in-planar crystallite thickness (17) which was found to be 4.3 nm for SU-8 derived carbon 3D microstructures. The ratio ($I_D/I_G = 1.02$) also confirms the glass nature of SU-8 derived 3-D carbon microstructures.

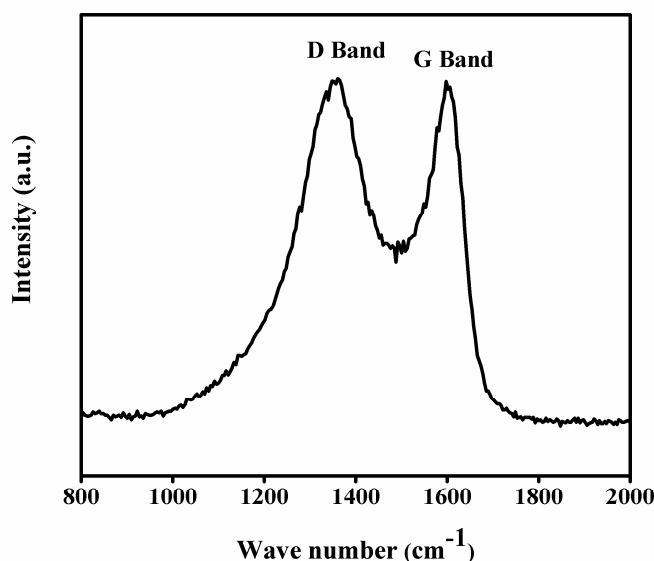


Figure 2: Raman spectrum for SU 8 derived 3-D carbon microstructures

Surface Profile and Morphology

Optical profiler was used to check the morphology of as-fabricated 3-D SU-8 and its derived carbon microstructure while optical microscope was used to observe top planar view of the same. Figure 3a and 3c shows the SU-8 3D structures with 50 μm height, 25 μm diameter, and 30 μm spacing. Upon pyrolysis, 3-D morphology was well retained as observed in Figure 3b and 3d. However there was almost 45% shrinkage but nearly isotropic. SU-8 derived 3-D carbon microstructures were obtained with the following dimensions: 27 μm height, 15 μm diameter, and 40 μm spacing. Aspect ratio of 3-D carbon microstructures was changed to 1.8 from 2 upon pyrolysis.

Electrochemical Testing

Galvanostatic charge-discharge experiments were carried out at 37.2 mA/g current density (0.1 C-rate) for SU-8 derived 3-D carbon microstructures fabricated on SS wafer (used as a current collector also) in half cell configuration. Although initial reversible capacity was observed as 127 mAhg^{-1} , it started increasing continuously with increased number of cycles. Coulombic efficiency was found to be greater than 100% up to 60 cycles (Figure 4a). After 130 continuous cycles of charge/discharge, reversible capacity showed stabilizing trend. After 165 cycles, reversible capacity was found to be 596 mAhg^{-1} at a 0.1C rate (Figure 4a). This

impressive reversible capacity and excellent cyclic stability was way higher than carbon 3D microstructures on Si wafer (5) and also to carbon thin films on SS wafer as reported earlier (13,15). These higher capacity values can be attributed to two major factors: first, decrease in electrical resistance of the current collector by replacing it with SS wafer and secondly due to increased electrode-electrolyte interface surface in case of 3-D electrode configuration as compared to planar 2-D thin films (5).

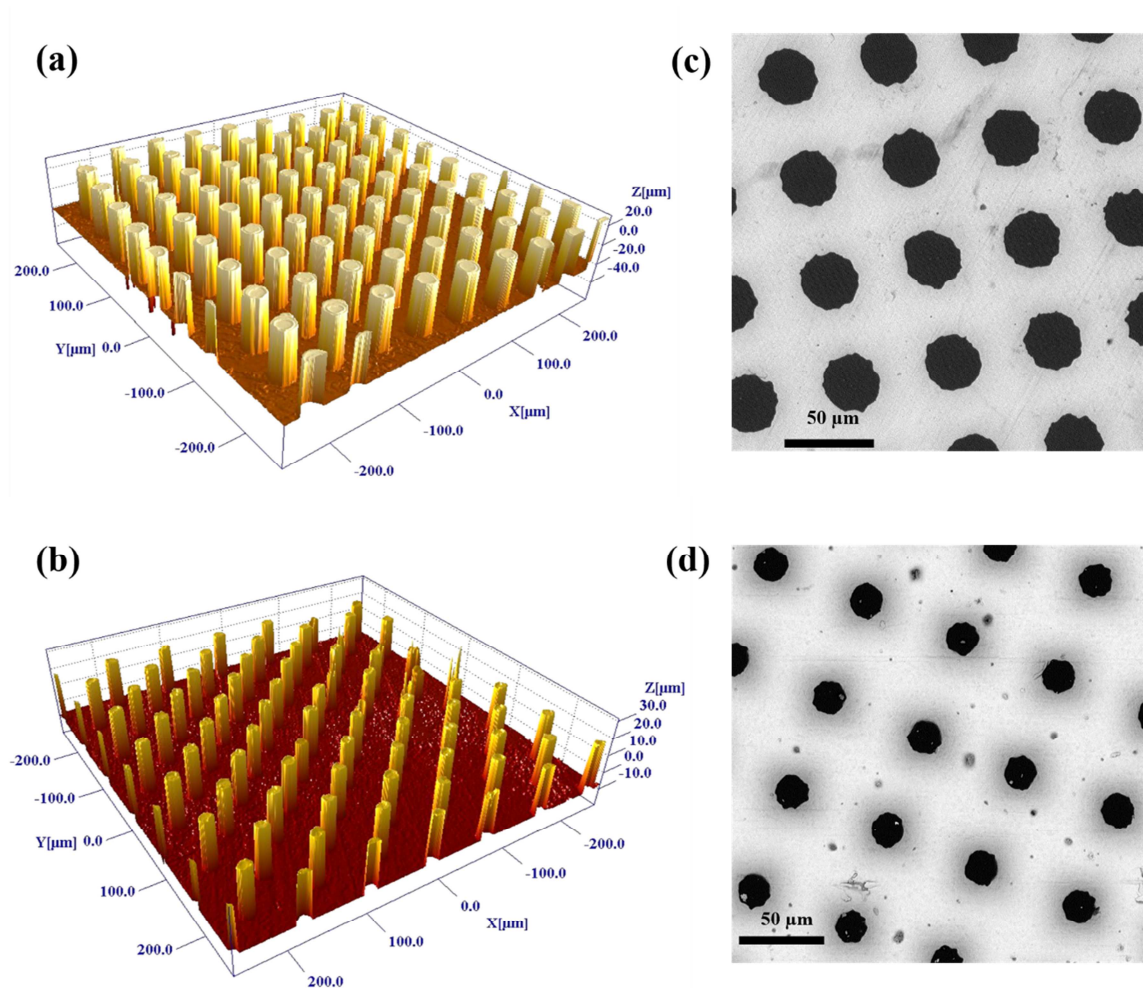


Figure 3: Three-dimensional optical profiler image of (a) SU-8 3-D microstructures; (b) SU-8 derived carbon microstructures. Optical microscopy image of planar top view of (c) SU-8 3-D microstructures; (d) SU-8 derived carbon microstructures.

From the charge/discharge profiles as shown in Figure 4b, we observed that the specific discharge capacity of the first cycle is large (320 mAh/g) because of the formation of solid electrolyte interphase (SEI) layer (18). It was also evident with a plateau at 0.5 V in Figure 4b for the 1st cycle. The increase in capacity with number of cycles may be attributed to the improved access of Li ions into the inner parts of 3D carbon microelectrode upon cycling, which leads to

an increased accommodation behavior for Li-ions, and this behavior is in line with some studies in the literature (19-21).

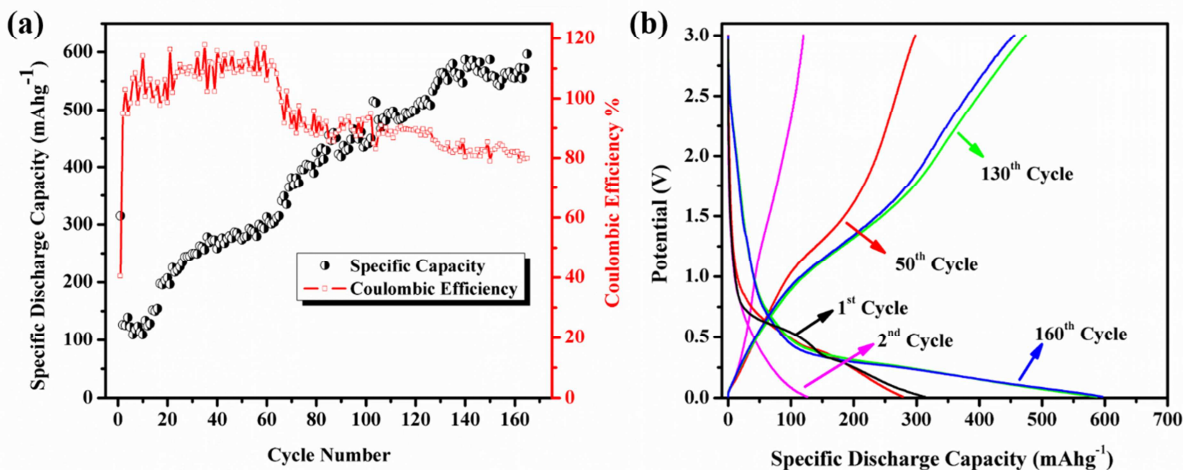


Figure 4: (a) Cyclic performance and (b) charge/discharge profiles of SU-8 derived 3-D carbon microstructures at 37.2 mA/g current density.

Conclusions

To the best of our knowledge, we have first time successfully micro-patterned SU-8 to fabricate 3-D microstructures on SS wafer. To this, baking conditions and UV exposure time conditions were tuned. Further pyrolysis conditions were also optimized to retain and yield 3-D microstructures in carbon. Although there was a 45% shrinkage, but aspect ratio of these 3-D structures remains almost unchanged. As fabricated array of SU-8 derived 3-D carbon microelectrodes was then tested for its anodic performance in half-cell configuration. An impressive reversible capacity of 596 mAhg⁻¹ was achieved at the 0.1 C-rate even after 165 continuous charge/discharge cycles. Excellent cyclic stability with large reversible capacity of as-fabricated 3-D carbon electrodes suggest an alternative route to achieve high performance Li-ion batteries, rather than focusing on controlling the microstructural properties of carbon materials. There is as cope of further improvement in the performance the 3D carbon microstructures by fabricating hierarchical hybrid electrode materials for next-generation Li-ion batteries.

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References

1. S. Iijima, *Nature*, **354**, 6348,(1991).
2. R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, *Science*, **297**, 5582, (2002).

3. W. Ruland, *Adv. Mater.*, **2**, 11, (1990).
4. S. Mamidi, M. Kakunuri, and C. S. Sharma, *ECS Trans.*, **77**, 11, (2017).
5. G. T. Teixidor, R. B. Zaouk, B. Y. Park and M. J. Madou, *J. Power Sources*, **183**, 730 (2008).
6. R. E. Garcia, Y. M. Chiang, W. C. Carter, P. Limthongkul and C. M. Bishop, *J. Electrochem. Soc.*, **152**, A255 (2005).
7. R. W. Hart, H. S. White, B. Dunn and D. R. Rolison, *Electrochem. Commu.*, **5**, 120 (2003).
8. J. W. Long, B. Dunn, D. R. Rolison and H. S. White, *Chem. Rev.*, **104**, 4463 (2004).
9. C. Wang, L. Taherabadi, G. Jia, M. Madou, Y. Yeh, and B. Dunn, *Electrochem. Solid-State Lett.*, **7**, A435 (2004).
10. R. E. Garcia and Y-M. Chiang, *J. Electrochem. Soc.*, **154**, A856 (2007).
11. C. Wang and M. Madou, *Biosensors and Bioelectronics*, **20**, 2181 (2005).
12. C. Wang, G. Jia, L. H. Taherabadi and M. Madou, *J. MEMS.*, **14**, 348 (2005).
13. M. Kakunuri and C. S. Sharma, *ECS Trans.*, **61**, 7, (2014).
14. M. Kakunuri, S. Kaushik, A. Saini, and C. S. Sharma, *Bull. Mater. Sci.*, **40**,3, (2017).
15. M. Kakunuri, and C. S. Sharma, *ECS J. Solid state Sci. Tech.*, **6**(6), M3001, (2017).
16. Z. Yi, Y. Liang, X. Lei, C. Wang, and J. Sun, *Mater. Lett.*, **61**, 19, (2007).
17. J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, and S. r p Silva, *J. Appl. Phys.*, **80**, 1, (1996).
18. P. Verma, P. Maire, and P. Novak, *Electrochim. Acta*, **55**, 22, (2010).
19. W. Ai, L. Xie, Z. Du, Z. Zeng, J. Liu, H. Zhang, Y. Huang, W. Huang, and T. Yu, *Sci.Rep.*, **3**, (2013).
20. L. Qie, W. M. Chen, Z. H. Wang, Q. G. Shao, X. Li, L. X. Yuan, X. L. Hu, W. X. Zhang, and Y. H. Huang, *Adv. Mater.*, **24**, 15, (2012).
21. W. Ai, Z. Luo, J. Jiang, J. Zhu, Z. Du, Z. Fan, L. Xie, H. Zhang, W. Huang, and T. Yu, *Adv. Mater.*, **26**, 35, (2014).