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Carbon-MEMS based Rectangular Channel Microarrays Embedded Pencil Trace for High Rate and High-Performance Lithium-ion Battery Application

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Abstract

The miniaturization of a lithium-ion battery has aspired in portable electronic devices and the possible way of implementation is by changing electrode configuration from the 2D system to 3D. Carbon microelectromechanical system is a plausible execution of lithium-ion storage from 2D carbon films to 3D structures. However, the usage of semiconducting silicon as a substrate for 3D structures and dendrite formation are hurdles. The present work describes a noble way-out fabrication of 3D carbon rectangular channels on pencil traced stainless steel current collector and its utilization as anode in the lithium-ion battery. The detailed physical and electrochemical studies demonstrate the advantage of this electrode in terms of reversible storage capacity and establishment of a low resistance path for electrochemical reaction. The cell exhibits an extraordinary capacity of 2000 mAh g⁻¹ at 150 mA g⁻¹ and retained a capacity of ~400 mAh g⁻¹ even at 10,000 mA g⁻¹ after 1750 cycles. Also, the full cell prototype further proves the potency of this electrode. Additionally, time-dependent Li-ion concentration gradient across the 3D carbon rectangular channels is estimated using a diffusion-limited model. These simulation studies clearly
suggest that the Li-ion diffusion is more favorable in 3D carbon rectangular channels compared to 2D films.

**Keywords:** C-MEMS 3D carbon rectangular channels; lithium-ion battery; high rate anode; full cell, photolithography;
1. Introduction

Miniaturization of portable electronic devices is demanding for high storage capacity compact batteries\(^1\). In this regard, the replacement of conventional planar geometry of the electrode with three-dimensional (3D) microarrays can be a remedial approach\(^2-4\). The carbon microelectromechanical system (CMEMS) opens a new avenue for various three-dimensional carbon geometries on a substrate. Marc Madou et al. introduced the concept of CMEMS and reported different 3D geometries on a silicon substrate\(^5,6\). These carbon structures were explored in various electrochemical applications such as batteries, supercapacitors, fuel cells, sensors, and solar cells\(^2,7-14\). Wang et al. derived high aspect ratio carbon posts by the pyrolysis of negative photoresist and verified the aptness of these carbon structures for reversible lithium-ion intercalation/deintercalation process\(^2\).

Further, F. Galobardes et al. investigated the formation of a solid electrolyte interface (SEI) on the CMEMS anode and its attribution to the large irreversible capacity and charge transfer resistance\(^15\). Hong Soek Min et al. extended the CMEMS fabrication by creating positive electrode arrays of dodecylbenzene sulfonate doped polypyrrole (PPYDBS) on carbon posts using electrochemical deposition technique. Their group successfully fabricated a prototype of a 3D C/PPYDBS full cell on a silicon substrate with a capacity of 10.6 µAh cm\(^{-2}\). However, its operation was limited due to electrical short \(^4\). Another turning was the fabrication of cross-shaped CMEMS arrays, and the realization of its advantage over conventional carbon posts and the group proposed that cross-shaped CMEMS with thinner features are more favorable for better utilization of carbon\(^14\).

The concept of 3D carbon structures has been explored in many ways rather than building only pyrolyzed SU-8 carbon posts on a silicon substrate. Different types of carbon structures are integrated with the SU-8 carbon posts and RF gel derived carbon posts. Sharma et.al reported RF
gel derived 3D cross-shaped and cylindrical shaped geometry and suspended SU-8 carbon nanofiber over carbon posts by a simple and efficient electrospinning method. Other reports show carbon nanowire integrated CMEMS; binder-free advanced matrixes nanostructured electrodes; the integration of SWNT/MWNT on carbon posts. Some reports show thin film deposition on the carbon posts by a sputtering method. However, the growth of the 3D carbon structures on a semiconducting silicon substrate is an issue for the faster electron conduction in the electrochemical storage devices. Therefore, our group optimized the parameters for the growth of high aspect ratio 3D carbon posts on stainless steel (SS) substrate instead of the silicon substrate. From our previous study, we observed a dramatic increment in the capacity with cycle number without stabilization, resulting in a fall of coulombic efficiency of the battery. We scrutinized the electrochemical behavior of these batteries and summed up the possible reasons that are: (i) Lithium ions reversibility in the high aspect ratio 3D carbon posts in vertical alignment are not efficient; (ii) There can be a direct contact of lithium ions with the substrate material, that can lead to malfunctioning of the battery, and (iii) Inefficient utilization of the 3D carbon posts for the reversible lithium-ion storage. To address these issues, in the present work, we fabricated an electrode with horizontally aligned high aspect ratio rectangular carbon channels on pencil traced (graphite coated) stainless-steel current collector (of 2032 coin cell) for the feasible lithium-ion storage. These rectangular channels can be more advantageous than cylindrical carbon posts geometry due to the direct interaction of lithium ions with the larger surface area of the electrode with the shortest diffusion path. Moreover, we found that the pencil trace graphite layer avoids the direct contact of lithium ions with the stainless steel (SS) substrate through the embedded space between each channel. In this way, this thin layer of pencil trace graphite simultaneously acts as a barricade for dendrite formation and a reversible storage material for lithium ions. Therefore, as
fabricated lithium-ion battery using this 3D rectangular channel geometry as anode material exhibited excellent electrochemical performance in the half cell as well as in full cell prototype. In half cell configuration, the cell delivered an extraordinary capacity of around 2000 mAh g\(^{-1}\) and 600 mAh g\(^{-1}\) at current density of 150 and 10,000 mA g\(^{-1}\) respectively. After the rate capability (at various current densities of 150, 200, 500, 1000, 2000, 5000, 10000 mA g\(^{-1}\)) and stability test for 1750 cycles (at current density of 10,000 mA g\(^{-1}\)) the cell retained 80% of its initial capacity. To the best of our knowledge, this is the only 3D based anode that exhibited a high capacity of 114 \(\mu\)Ah cm\(^{-2}\) and that too at high current density in the full cell prototype. Finite element-based COMSOL Multiphysics simulations are performed to analyse and establish the ease of Li-ion diffusion in 3D carbon rectangular channels.

2. Experimental section

An array of horizontally aligned high aspect ratio 3D rectangular channels of carbon has been designed to fabricate on a pencil traced (graphite coated) stainless steel substrate. For that 2032-coin cell, stainless steel current collector of 12 mm diameter has been chosen as a substrate. Further, the surface of the steel substrate was deliberately coarsened with emery paper (paper no: 120) and washed thoroughly with DI water and alcohol to remove the impurities. The coarsened surface of the steel substrate was penciled with graphite lead to obtain a uniform graphite layer over it; later it was named as pencil trace modified stainless steel substrate (PTSS). An epoxy-based negative photoresist, SU-8 2015 (purchased from Microchem Corp., USA) was spin-coated on PTSS at 3000 rpm speed for 30 sec followed by pre-baking at 95 °C for 2 min and 30 s to remove excess solvent. We have used a mask-less photo-lithography approach to fabricate 3D rectangular patterns of photo-resist. To attain the 3D patterned structures, photo-lithography tool
equipped with UV light source (with a wavelength of 365 nm) and in-built optical grating set-up
(Intelligent Micro patterning, LLC Model no: SF-100 Xpress) has been used. Pre-baked photoresist
coated PTSS substrate was subjected to UV exposure (selective exposure) for 25 s to allow the
epoxy to endure polymerization through the cross-linking process. This exposed sample was baked
at 95 °C for 3 min and washed carefully with a commercially available developer solution for 1
min and 30 sec. During this washing process, UV unexposed areas will be solubilized to the
solution and left with only 3D rectangular microchannels. The patterned sample was further hard-
baked at 150 °C for 5 min and loaded into the horizontal tubular furnace for pyrolysis. This
fabrication procedure is schematically depicted in Fig. 1(a). Before the heating process, the
furnace chamber was purged with nitrogen gas at 75 lph for 30 min and further maintained a flow
rate of 20 lph throughout the pyrolysis process. We followed the two-step pyrolysis approach.
Initially, the sample was stabilized at 350 °C (heating rate of 2 °C/min) for a dwell time of 30 min.
For the carbonization, later, the temperature of the furnace was increased to 900 °C at 5 °C/min
ramp rate and maintained the sample at this temperature for 1 h. The sample was collected once
the furnace cooled down to room temperature and labeled as 3D rectangular carbon channels on
PTSS (3DRC-PTSS). Without any further treatment, the as-prepared 3DRC-PTSS was used as an
anode during cell fabrication. The active material mass loading of 3D carbon anode was measured
to be 0.26 mg cm². To make sure the feasibility of the electrode fabrication, further we fabricated
the electrode with UV flood exposure photolithography technique using chrome mask instead of
maskless photolithography.

2.1 Structural characterization

Morphological features of the pre-pyrolyzed and post-pyrolyzed patterned samples were studied
using an optical microscope (Zeiss AxioCam) and a scanning electron microscope (Phenom ProX,
operated at 5 kV). 3D optical profiler (NanoMap-D) was used to measure the height distribution of as-fabricated microchannel arrays. Raman spectra of 3DRC-PTSS were obtained by WiTec Raman spectroscopy with green laser excitation (532 nm, excitation energy of 2.33 eV).

2.2 Electrochemical studies

2032-coin cells were assembled inside the glove box (O₂ < 0.1 ppm, H₂O < 0.1 ppm) using 3DRC-PTSS as the working electrode and lithium foil as the counter/reference electrode while for the full cell fabrication, LiFePO₄ was used as the cathode. The Whatman glass fiber filter paper was used as a separator and 1M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1(v/v%) was used as an electrolyte in the half cell/full cell assembly (a small video clip has been given in the supplementary to show the electrolyte absorption to the anode electrode). Further electrochemical tests, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance analysis (EIS) were conducted on these assembled cells using Biologic VSP 300 electrochemical work station. The GCD was performed in the potential window of 0.01 V to 3V for half-cell and 2.5 to 3.9 V for the full cell. The EIS measurement was carried out in the frequency range 0.1 Hz to 1 MHz by applying a perturbation of 10 mV.

3. Results and discussion

3.1 Fabrication of 3D rectangular channels on pencil traced SS

For the growth of the 3D rectangular channels, a conventional silicon wafer substrate has been replaced by a pencil traced (graphite coated) stainless steel current collector (PTSS). The surface of the steel substrate was deliberately coarsened with emery paper to provide good adhesion to the thin layer of coated graphite. This graphite coating can reduce the contact resistance between the active material and SS substrate while cycling the cell and also can contribute as a storage material.
(detailed description has been given in electrochemical studies). The spacing of the rectangular channels is important in determining the total active surface area on the substrate. This directly influences electrochemical performance. If the spacing is larger, then the number of 3D channels is less, which further reduces the areal capacity of the electrode. On the other hand, the minimum spacing between the rectangular channels is determined by the experimental limitations. Considering the above all, the spacing is determined as 20 µm for 3D rectangular channels array.

To understand the influence of these 3D rectangular channels on pencil traced SS substrate over conventional 3D carbon posts on a silicon wafer, the physical and electrochemical properties of this material have been scrutinized.

3.2 Profilometry: Inspection of the empty spaces between the 3D rectangular structures when compared to cylindrical posts

The substrate (current collector) exposure to the electrolyte has to be controlled to avail maximum material surface (3D surface) for electrochemical reaction. Therefore, the 3D structures must be tightly packed with minimum substrate exposure, thereby the direct contact of lithium-ion with the substrate can be avoided. Fig.1(b) depicts the three-dimensional profilometry of the equally spaced rectangular geometry of the fabricated 3D channels. The structure exhibited uniformity with straight walls and an excellent edge profile. The average height of the channel in 3D RC-PTSS is 15 ± 2 µm and width and spacing between the rectangular channel are 20 ± 5µm. The importance of this geometry is that the 3D rectangular channel reduces the substrate (current collector) exposure to electrolyte when compared to carbon posts. The maximum area of the circular substrate is covered by this 3D geometry and the remaining exposed area is graphite coated. Therefore, the direct exposure of the SS substrate area to the electrolyte is eliminated when
compared to the cylindrical carbon posts geometry on SS/Silicon substrate Fig.1(c) schematically represents the reduction in substrate exposure.

3.3 SEM and Optical imaging

Optical microscope and SEM images as shown in Fig.2(a, b) provide the panoramic view of the 3D RC-PTSS. It shows an array of uniform 3D channel structures with consistency in channel width and spacing between channels. The width and spacing between the 3D channels are labeled in Fig.2(a). The color contrast in the optical image (Fig 2a) and SEM image (inset of Fig 2b) verifies the 3D projection of the rectangular channels on the substrate. The obtained 3D pattern without any distortion points out that the penciled graphite layer could provide a good adhesive surface for the growth of the 3D structures. SEM and optical images provide a clear visualization of the grown 3DRC-PTSS. After the cycling, the cell was dissembled and the electrode was examined under SEM to verify the structural integrity of the 3D rectangular channels. Fig. S1 reveals that the 3D rectangular channel structure is stable and only a minor distortion was noticed.

3.4 Raman spectroscopic analysis: scrutiny on substrate carbon and SU-8 derived carbon

To identify the nature of SU-8 derived carbon and pencil traced carbon on SS substrate, Raman spectra are collected from PTSS (graphite coated area) and the top surface of the 3D RC-PTSS respectively (Fig. 2c). The top surface of 3D RC-PTSS (SU-8 derived carbon) exhibits two characteristic peaks at ~1330 cm\(^{-1}\) and ~1590 cm\(^{-1}\) representing A\(_{1g}\) symmetry of disordered graphite and E\(_{2g}\) symmetry mode associated with the in-plane stretching of the sp\(^2\) bonded carbon atoms, respectively\(^{22,23}\). This partially superimposed D and G bands with I\(_D\)/I\(_G\) ratio ~1 indicate the degree of disorder with glassy carbon nature\(^{11}\). While, Raman spectrum of penciled carbon (graphite coated surface) shows a well-defined D, G as well as 2D bands at ~1350 cm\(^{-1}\), ~1590 cm\(^{-1}\), and ~2590 cm\(^{-1}\) respectively which are the characteristic peaks of the graphitic carbon. I\(_D\)/I\(_G\)
ratio ~0.79 also indicates the more graphitic nature of pencil trace carbon. Therefore, we can say that the fabricated anode (3D-RCPTSS) is the combination of glassy carbon as well as graphitic carbon.

3.5 Electrochemical properties

We identified the possible issues of a conventional 3D cylindrical carbon posts electrode on the SS/silicon substrate (current collector) related to the electrochemical performance of the cell. The main issues are 1) Irreversible capacity \(^2\) 2) Limited lithium-ion storage 3) Inefficient utilization of carbon pillars, and 4) Lithium-ion substrate interaction (Schematically represented in Fig.3a and 3b). Due to these severe setbacks, the cell miserably ended up in short circuit or malfunctioning (falling of cumbic efficiency of the cell). Therefore, fabricating 3D rectangular channels over PTSS instead of 3D cylindrical carbon posts aids the utilization of these 3D structures to their full potential as anode material. The detailed electrochemical studies of 3D RC-PTSS as described below address all the issues related to conventional 3D pillars on Silicon/SS substrate.

3.5.1 Reversible lithium-ion storage in 3D RC-PTSS

To understand the reversible lithium-ion storage capability of 3D glassy carbon rectangular channels on pencil traced SS current collector as anode material, coin cells were assembled using LiPF\(_6\) as electrolyte and lithium foil as a counter/reference electrode. Cyclic voltammetry measurement has been employed on the assembled cell in the potential window of 0.01 to 3V vs. Li/Li\(^+\) at a scan rate of 0.1 mV s\(^{-1}\). The anodic and cathodic peaks are observed at 0.15, 0.23, and 0.05 V respectively (Fig.4(a)). The large hysteresis of the first cycle CV (Fig. 4(a)) attributes to the formation of a passive SEI layer\(^2\). This SEI layer is formed at the electrode-electrolyte interface by electrolyte decomposition. This passive layer stabilizes the electrode in subsequent
cycles by further preventing any solvent molecules from co-intercalation into the carbon structures\textsuperscript{26,27}. The repeatability of these anodic and cathodic peaks in all cycles without hysteresis loss in further cycles represents a stable reversible lithium-ion storage capacity of the anode.

Moreover, the distinct peak positions and its repeatability in the anodic scan represent the lithium-ion storage in the pencil lead graphite by the intercalation/de-intercalation method. These peaks are due to stage transformation of lithium-graphite intercalation compound of LiC\textsubscript{24}, LiC\textsubscript{12}, and LiC\textsubscript{6} at PTSS base of 3DRC-PTSS respectively\textsuperscript{28–30}. This is further clarified by the CV of the cell with only PTSS (graphite coated SS) as anode presented in Fig.S2. The CV analysis shows that 3D RC-PTSS has a larger electrochemical surface area than that of only PTSS, this emphasizes the lithium-ion storage in the glassy carbon. It is also proof of reversible lithium-ion storage in penciled graphite as well as 3D glassy carbon rectangular channels in 3DRC-PTSS. This result is evident for the direct interaction of lithium ions with the substrate material through embedded space in between the 3D structures. In other words, if the SS substrate (current collector) is not pencil traced with graphite, there will be a direct interaction of lithium ions with SS substrate (current collector) that can cause dendrite formation and ultimately shortage of the battery.

**3.5.2 Substrate (current collector) modification prevents the malfunctioning of the battery**

The other serious concern is the proper functioning of the battery without diminishing coulombic efficiency. This will be possible only when the electrode material shows a high level of reversibility in the lithium-ion transfer. Therefore, it is necessary to grow the 3D structures with minimum substrate exposure, and also exposed substrate area should be a reversible lithium-ion storage material to access high electrode surface area for reversible electrochemical reaction. This is one of the important findings in the present work which we could not find in the reported literature, i.e., utilization of substrate (current collector) exposed area to the electrolyte, for
reversible lithium-ion storage to avoid the malfunctioning of the battery or shortage of the battery. Herein due to pencil traced graphite layer modification, the direct interaction of lithium ions with the SS substrate is prevented. Moreover, it plays a vital role to enhance the capacity of the battery along with compact rectangular channels. Further, the wettability of electrodes with the electrolyte is also studied as discussed in the supplementary data. The reversibility of pencil lead graphite in composite on lithium-ion storage was recently reported from our group.31 Any way to prove our point further, GCD has been conducted only on PTSS (graphite coated SS) as the anode (Fig.53). Cell stability and capacity retention are the important criteria to understand the proper functioning of the battery without any malfunctioning or shortage of battery due to large irreversible capacity and lithium dendrite formation. In this aspect, for vivid confirmation, the cell is cycled at different current densities ranging from 150 mA g⁻¹ to as high as 10,000 mA g⁻¹ (Fig.4(b)). The charging and discharging of the battery at a low current rate provide information regarding the maximum utilization of the anode material as well as the efficiency of the battery to deliver current to the load. The cell cycled at different current densities 150, 200, 500, 1000, 2000, 5000 and 10,000 mA g⁻¹ exhibited capacities of 2000, 1750, 1645, 1451, 1183, 746 and 484 mAh g⁻¹ respectively. The capacity retention of 2034 mAh g⁻¹ at 150 mA g⁻¹ after cycling at 10,000 mA g⁻¹ shows the applicability of the cell at a low current rate as well as the high current rate (Fig.4(c)). This electrochemical response shows that there is no malfunctioning of the battery neither at high nor at low current densities due to the substrate protection from lithium plating by pencil lead graphite coating.

3.5.3 Capacity enhancement due to 3D rectangular structures on PTSS

Fig.5(a) demonstrates the capacity enhancement of 3DRC-PTSS in comparison with only PTSS(graphite coated SS), and the results are compared with carbon posts on SS, and conventional
carbon posts and other 3D geometries on a silicon wafer\textsuperscript{11,14,32,33} (Table 1). 3DRC-PTSS exhibited a capacity of 2000 and 484 mAh g\(^{-1}\) at 150 and 10000 mA g\(^{-1}\) respectively, whereas PTSS shows a capacity of 1080 and 228 mAh g\(^{-1}\) respectively. Besides, Fig. 5(b) depicts that when the current increases from 150 to 10000 mA g\(^{-1}\) (almost \(\sim 67\) times increment in current density), the cell could retain 25\% of its capacity. This observation undeniably proves the role of 3D RC structures in the fast-reversible lithium-ion storage mechanism. Further compared to the reported capacity values and cycle life (550 mAh g\(^{-1}\) at 0.1C (100 cycles)\textsuperscript{32}, 220 mAh g\(^{-1}\) at 0.5828 mA (9 cycles)\textsuperscript{33}, \(\sim 200\) mAh g\(^{-1}\) at 76.4 uA cm\(^{-2}\) (6 cycles)\textsuperscript{14}, 596 mAh g\(^{-1}\) at 37.2 mA g\(^{-1}\) (160 cycles)\textsuperscript{11}, and the cylindrical 3D structures on penciled SS reported a capacity of 538 mAh g\(^{-1}\) at 500 mA g\(^{-1}\) (100 cycles)\textsuperscript{34}). For further confirmation, cylindrical carbon structures are fabricated on SS and penciled SS and the electrochemical data have been given in Fig. S5a and S5b respectively. The cell exhibited a capacity of 100 and 900 mAh g\(^{-1}\) respectively. When compared to previous report\textsuperscript{11} as well as carbon posts on SS and penciled SS, we observed that 3DRC-PTSS showed its supremacy both in capacity and capacity retention. This can be due to the large surface area that is accessible for lithium-ion storage with the shortest diffusion path while cycling the cell.

The rate capability test signifies the ability of 3DRC-PTSS to work equally well in a higher current density range. Therefore the stability test of the cell is performed at 1000, 5000, and 10000 mA g\(^{-1}\) for 150, 250, and 1750 cycles respectively (Fig. 5(c)). The cell could deliver a capacity of \(\sim 400\) mAh g\(^{-1}\) at 10000 mA g\(^{-1}\) (after 1750 cycles), 700 mAh g\(^{-1}\) at 5000 mA g\(^{-1}\) (after 250 cycles), and 1400 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\) (after 150 cycles) respectively. The long cyclic life of the battery at different current densities range without shortage and malfunctioning substantiates the potential of 3DRC-PTSS as anode material.

3.5.4 Electrochemical impedance as a supporting study for the storage mechanism
To further examine the electrochemical properties of the cell in terms of electrochemical impedance, EIS measurement was carried out on the same cell after stability testing. **Fig. 6 (a)** represents the EIS profile of 3DRC-PTSS, the obtained EIS data fitted by an equivalent circuit shown in **Fig. S4**. The equivalent circuit consists of series and parallel combinations of resistors and constant phase elements. $R_E$ is the equivalent series resistance that indicates the resistance involved in the electrolyte, and the obtained $R_E$ value is 5.4 $\Omega$ after fitting.

Similarly, $R_{SEI}$ and CPE$_{SEI}$ indicate the impedance due to SEI layer formation and $R_{CT}$, and CPE$_{CT}$ measures the impedance involved in the charge transfer reaction$^{35-37}$. The calculated $R_{SEI}$, $R_{CT}$ values are 19 $\Omega$ and 4.5$\Omega$ respectively, which, implies that the cell provides minimum resistance for charge transfer. The SEI layer resistance is higher than the charge transfer resistance. This may be due to the resistance involved due to layer formation on the glassy carbon channels and penciled graphite. These impedance values are negligibly small when compared to the reported impedance values in the range of hundreds and thousands of ohms and clearly shows the advantage of the 3DRC-PTSS electrode over conventional silicon substrate is grown 3D structures$^{14,15}$. The faster reaction kinetics of the cell with capacity retention reveals that SEI acts as a good passivation layer for lithium ions. The appearance of a small diffusion line represented by a constant phase element (semi-infinite diffusion) further proves the lithium-ion diffusion process is reasonably good.

### 3.5.5 Full cell study reveals the proficiency of 3DRC-PTSS as anode for commercial batteries

The ultimate goal of developing an anode material is to check the efficiency of the material in the full cell. Therefore, to evaluate the material a prototype full-cell has been fabricated using carbon-coated LiFePO$_4$ as a cathode material and 3DRC-PTSS as an anode. To avoid lithium deficiency while cycling the cell, the weight of the cathode material is balanced according to the anode material. The cyclic voltammetry and galvanostatic charge-discharge measurements were
performed in the potential window 2.5 to 3.9 V (Fig. 6(b&c)). The cell showed an oxidation peak at 3.67 V and reduction peak at 3.18 V, the difference between the oxidation and reduction peak is 0.49 V shows the good reversibility of the cell. The cell delivered an initial capacity of 122 mAh g\(^{-1}\) (114 µAh cm\(^{-2}\)) at a current 100 µA with columbic efficiency of 94.6%. After cycling the cell for 100 cycles the cell retained a discharge capacity of 110 mAh g\(^{-1}\) (107.6 µAh cm\(^{-2}\)). These values are almost eleven times higher than the reported 3D carbon posts based on full cell (10.6 µAh cm\(^{-2}\)) \(^4\). The capacity of ~107 µAh at 100 µA after 100 cycles shows the potency of this material in the practical usage (Fig. 6(d)).

### 3.6 Li-ion diffusion model

The finite element method (FEM) based diffusion model on the COMSOL simulation platform is carried out to examine the variation of Li-ion concentration across the 3D carbon rectangular channels with respect to the time. To perform the Li-ion diffusion studies, we have considered two cases namely i) 3D morphology of rectangular channels ii) the equivalent volume of flat (2D) electrodes. Further, a comprehensive comparative study for both cases is done to investigate the concentration gradients as depicted in Fig. 7. In this study, we have modeled the Lithium ion diffusion across the electrode by using Fick's Second Law of diffusion as described in equation (1)\(^{38}\). Here, the preliminary assumption is that the change in Li-ion concentration is mainly due to concentration gradient and other term (migration and source reaction) is negligible.

\[
\frac{\partial C_{Li}}{\partial t} = \nabla \cdot (D_{Li} \nabla C_{Li}) \quad \text{......... (1)}
\]

In the equation (1), \(D_{Li}\) is Li-ion diffusivity (m\(^2\) s\(^{-1}\)) and \(C_{Li}\) represents the concentration of Li-ions (mol m\(^{-3}\)) at time \(t\).

In order to have more closer condition of simulation study with the experimental, the following measures are taken. (i) A more accurate replica of model geometry is constructed (Fig. 7a) based
on optical profiler data (Fig. 1b) of the real system. (ii) The experimental current density is used to calculate the flux boundary condition as given in equation 2\textsuperscript{39,40}.

\[ D_{Li} \frac{\partial c_{Li}}{\partial x} = \frac{i_{app}}{nF} \quad (2) \]

where \(i_{app}\) denotes the applied current density (A m\(^{-2}\)) at the cell level, F is Faraday constant, and \(n\) is the number of electrons involved in the electrochemical reaction.

The effective diffusion coefficient of 3D carbon rectangular channels is calculated using EIS data as discussed in the literature \textsuperscript{41,42}. The calculated diffusion coefficient for the 3D carbon rectangular channels electrode is 1.44×10\(^{-8}\) m\(^2\) s\(^{-1}\). Figure 7b shows the Li-ion concentration (0.026 mol m\(^{-3}\)) in a 3D carbon rectangular channels after 0.1 sec and its increase to 6120 mol m\(^{-3}\) after 60 min (Fig. 7c). The change in Li-ion concentration of 2D flat electrode with equivalent volume of 3D carbon rectangular channels is also model as shown in (Fig. 7d). After 60min, Li-ion concentration in a 2D flat electrode increase from 0.013 mol m\(^{-3}\) (Fig. 7e) to 3500 mol m\(^{-3}\) (Fig. 7f). The maximum Li-ion concentration after 60 min in bothe cases is found to be 6120 mol m\(^{-3}\) and 3500 mol m\(^{-3}\) for 3D rectangular channels and 2D flat electrode morphology, respectively. This clear indicates that the 3D carbon rectangular channels enabled effective Li-ion diffusion over the 2D flat electrode.

4. Conclusions

We introduced a unique three-dimensional rectangular channel geometry on pencil traced stainless steel current collector to avoid the malfunctioning of the battery due to direct contact of lithium-ion with SS substrate as well as to maximize the capacity with minimum lithium-ion diffusion path length and minimum substrate exposure. We observed a successful growth of the 3D structures on pencil traced SS due to excellent adhesion of SU-8 polymer with the graphite layer which after...
pyrolysis yielded into 3D carbon rectangular channels without any structural damage. These rectangular geometries provided a larger surface area for the electrochemical reaction by decreasing the direct substrate exposure to the electrolyte and therefore, showed its advantages over cylindrical carbon posts on the substrate which are typically shown as 3D electrodes in literature. From a battery perspective, 3DRC-PTSS exhibited outstanding electrochemical performance in the half cell as well as in full cell configurations. The cell showed excellent lithium-ion storage characteristics, more importantly, in lower as well as higher current densities. At 150 mA g$^{-1}$, the cell exhibited a reversible capacity of 2000 mAh g$^{-1}$ and ~400 mAh g$^{-1}$ at as high as 10 A g$^{-1}$ current density. This can be due to the synergetic effect of pencil trace graphite along with the 3D carbon structures. Also, the full cell study proves its potential to work at a high current by retaining the capacity of 110 mAh g$^{-1}$ (107.6 µAh cm$^{-2}$) at 100µA. The outcome of this work shows the plausible usage of this anode material for the development of next-generation lithium-ion batteries.

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Figures

(a) Schematic representation of fabrication of 3D-RCPTSS (b) 3D profiler image of 3D-RCPTSS (c) Comparison of substrate exposure area of 3D cylindrical structure and 3D rectangular channel
Fig. 2 (a) Optical image of 3D-RCPTSS (b) SEM image of 3D-RCPTSS and inset is 3D constructed SEM image (c) Raman spectra of 3D-RCPTSS
Fig. 3 (a) Schematic representation of the issues related to conventional cylindrical carbon post electrode, (b) 3D microelectrodes channels advantages over planar electrodes.
Fig. 4 (a) Cyclic voltammetry of 3DRC-PTSS at scan rate of 0.1 mVs$^{-1}$ in the voltage window of 0.01 to 3V (b) GCD of 3DRC-PTSS at different current rates (c) rate capability of 3DRC-PTSS at different current rates 150, 200, 500, 1000, 2000, 5000 and 10,000 mA g$^{-1}$
Fig. 5 (a) Comparison of 3DRC-PTSS with only PTSS (b) Capacity retention of 3DRC-PTSS at high current density (c) stability test of 3DRC-PTSS at different current rates 1000, 5000 and 10,000 mA g\(^{-1}\)
Fig. 6 (a) EIS analysis of 3DRC-PTSS in the frequency range 0.1 Hz to 1 MHz (b) cyclic voltammetry on the full cell prototype in the potential window 2.5 to 4.2 V at 0.1 mVs$^{-1}$. (c) GCD of the full cell (d) stability test of the full cell at 100 µA in the potential window 2.5 to 3.9 V.
Fig. 7 Li diffusion model (a) 3D microelectrode geometry used to construct the FEM model. (b) Li-ion distribution (mol m$^{-3}$) in a 3D carbon rectangular channels after 0.1 sec. (c) Li-ion distribution (mol m$^{-3}$) in a 3D carbon rectangular channels after 60 min. (d) Model geometry for flat electrode used to construct the FEM model. (e) Li-ion distribution (mol m$^{-3}$) in a flat electrode morphology after 0.1 sec. (f) Li-ion distribution (mol m$^{-3}$) in a flat electrode morphology after 60 min.