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Research Article

Fabrication of size-tunable graphitized carbon spheres with hierarchical surface morphology on *p*-Si (100) by chemical vapour deposition

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ABSTRACT

Graphitized carbon spheres (GCSs) with varied diameters (500 nm to 4.5 μ m) and hierarchical surface morphologies were successfully produced on iron-particles coated silicon (100) substrate at 750°C by chemical vapour deposition (CVD). By varying the mass flow rate of the precursor gasses and the method of catalyst coating on silicon (100), GCSs with varied diameters and differing morphologies were obtained. When the mass flow rate of the precursor gasses was altered, the mean diameter of GCSs increases until it reaches an optimum value (~3.1 μ m) suggesting a size-tunability of GCSs. Changing the catalyst coating method on silicon (100) from dip coating to spin coating produces larger-sized GCSs on silicon (100). Field Emission Scanning Electron Microscopy (FE-SEM) images show that GCSs possess a regular and uniform shape with the formation of a hierarchical surface



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morphology. The analysis of the variation of the surface roughness laterally across the substrate showed that the increased surface roughness resulting in from catalyst spin coating increases the mass transfer rates leading to the formation of larger-sized GCSs on Si (100). Raman spectroscopy and X-ray diffraction spectra obtained from the catalyst spin-coated and dip-coated samples confirmed the presence of graphitized hexagonal carbon networks in CSs. The surface functionality of GCSs was examined using FTIR spectroscopy. Synthesized GCSs were then used to fabricate an anode material in sodium ion rechargeable batteries and the performance of GCSs as an anode material in rechargeable battery system was investigated and the results obtained are also discussed here.

Keywords: graphitized carbon spheres (GCSs), chemical vapour deposition (CVD), dipcoating, hierarchical surface morphology, spin-coating, size tunability, sodium ion rechargeable battery.

1. INTRODUCTION

The inimitable intricacy in the configuration of binding resulting in the ability of carbon to form sp, sp^2 , and sp^3 hybridizations with wide-ranging materials results in an immensely diverse range of structures and morphologies with extensive technical applications. The nano-science and nanotechnology of carbonaceous structures received an exciting further development with the discovery of fullerene¹ and its elongated cousin the carbon nanotube². In recent years, various forms of spheroidal carbon structures have been discovered with extraordinary properties and multidisciplinary applications³. Carbon nano-capsules^{4,5} carbon onions 6 carbon spheres $^{7-9}$ and carbon beads 10,11 are just a few but to name them. Two different schemes have been proposed for the classification of spherical carbonaceous structures: the first such scheme was proposed by Inagaki^{12,13} who classified the spherical carbon structures based on the arrangement of the number of carbon layers. The second approach, made by Serp¹⁴, classifies the spheroidal carbon structures based on their particle size, into fullerene (< 2 nm), carbon onions with closed graphitic layers (2-20 nm), carbon spheres (50 nm-1000 nm), and carbon beads (> 1000 nm). Among these different forms of spherical carbons, carbon spheres (CSs) are unique materials because they can be fabricated with significant characteristics such as adjustable porosity, uniform geometry, surface functionality, flexible particle size distribution, and outstanding chemical and thermal stability ^{15,16} Moreover, CSs have similar properties to fullerenes and graphite. Due to remarkable characteristics, CSs have been used in different fields including, composites material ¹⁷, sodium-ion batteries ¹⁸, adsorbents ¹⁹, and water purification ²⁰. The surface morphology and graphitic structure of CSs are playing a vital role in enhancing the performance of these applications. Therefore, attempts focusing onto produce CSs with tunable surface morphologies (hence size) and more graphitized structures are receiving attention of physicists as well as chemists.

Several approaches have been made in the past to produce CSs which includes chemical vapour deposition (CVD)¹⁴, mixed-valent oxide catalytic carbonization (MVOCC)²¹ highpressure carbonization ^{9,11} and pyrolysis of carbon sources in the presence of transition metals on kaolin support ^{22,23}. However, some of these processes must be operated at high pressure (usually up to 10 MPa). Under high-pressure conditions, the production rate could be enhanced but the purity of the carbon spheres produced decreases. In terms of economy and versatility, chemical vapour deposition (CVD) is the most popular technique to produce carbon spheres (CSs), which can be divided into three types as (i) catalytic CVD ²⁴, (ii) noncatalytic CVD¹², and (iii) template CVD methods²⁵. Although each method has its own advantages and disadvantages, methods capable of producing CSs at relatively low cost and low temperature make their selectivity and suitability in economically viable applications. With this regard, the catalytic CVD method is important as it can produce carbon spheres at temperatures as low as 650 0 C with transition metals as catalysts deposited on a template ²⁴ (in this experiment, the template is p-Si/SiO₂). Jin et al. have reported on the large-scale synthesis and characterization of CSs prepared by the direct pyrolysis of hydrocarbons with two to eight carbon atoms ⁷. Chen et al. have reported on the formation of spherical hydrogenated amorphous carbon particulates generated in a radio frequency plasmaenhanced chemical vapor deposition (rf-PECVD) system ²⁶. Recently, Pol et al. have reported on the high yield one-step synthesis of CSs produced by dissociating individual hydrocarbons at their autogenic pressure and low temperatures ⁹. These techniques are however limited by several factors. For example, in a few cases, the methods are not able to control the size distribution of the CSs and to remove the catalyst encapsulated, which are difficult to separate from the spheres. In the present work, we report the production, characterization and a possible application of size-tunable CSs via CVD by varying the process of catalyst coating on the substrate (which is reported for the first time), the source of catalyst precursor, and the mass flow rate of the precursor gasses at low temperature (750 0 C).

Even though the Lithium-ion batteries (LIBs) are at the peak of their performances as the most popular type of rechargeable batteries, Lithium deposits are depleting rapidly due to the increasing demand for the LIBs. This has made the cost of rechargeable batteries made out with Lithium to be a victim of inflation.²⁷ Due to this reason, researchers are paying their attention in the quest of finding a suitable substitution for LIBs. Sodium shares the same electrochemical properties as Lithium. On the other hand, sodium being more abundant has a great advantage in cost-cutting while in the production process. Hence developing a commercially applicable Sodium-ion battery (SIBs) has taken the interest of modern researchers in the last few decades. The developed Sodium-ion batteries have shared the same rocking chair mechanism as Lithium-ion batteries.²⁸Therefore it is predicted that achieving high capacities with SIBs is also within the reach in near future. The CSs produced in this work therefore were used to fabricate an anode material in sodium-ion rechargeable batteries and the results are also discussed here.

2 MATERIALS AND METHODS

p-type silicon (100) wafer having a diameter 450 mm (18 inches and the surface orientate was confirmed by the XRD) was purchased from international vendors. Subsequently, the wafer was cut into pieces each having an area of $2x2 \text{ cm}^2$. The silicon (100) was prepared for deposition of catalyst as follows. First the silicon substrates were degreased in acetone, and cleaned ultrasonically with deionized water at 40 °C for 10 mins, followed by ultrasonically cleaning with methanol for 5 min, washed again with deionized water, and 100 °C for 2 hours in an oven. Weighted amounts of Iron (III) chloride then dried at (FeCl₃), and iron (III) nitrate nonohydrate (Fe $(NO_3)_3.9H_2O$) were separately dissolved in ethanol (purity 99.99%) to obtain solutions with a concentration of 50 mM. Well cleaned and dried silicon substrates were then gradually slipped into FeCl₃ /ethanol and Fe (NO₃)₃.9H₂O/ethanol solutions, kept for 10 minutes and then were removed from the solutions at a constant speed. Different silicon substrate prepared similarly was spin-coated with catalysts solutions using a spin coater at a rate of 8000 rpm for 60 sec at room temperature. Both types of substrates were subsequently dried in an oven at 100 °C for 2 hrs. The catalyst coated substrates were placed into the quartz tube in the furnace of the CVD and high purity (99.99%) N₂ was introduced at a flow rate of 100 sccm into the tube after heating the tube to a temperature of 750 °C at a rate of 10 °C min⁻¹. The mass flow rate of high purity N_2 was such that the pressure inside the furnace became equal to the atmospheric pressure (one atm). The furnace was kept at this temperature and pressure for 30 mins to form iron particles on the substrates. The production of CSs was then performed by adding a constant mass flow rate of acetylene (*i.e.*, 250 sccm) into the nitrogen flow (mass flow rate was 100 sccm) for another 30 mins. After this step, the supply of acetylene was switched off, and the furnace was kept at a constant flow of N2 (100 sccm) until it cools down to room temperature. The samples were then removed from the furnace and were stored in an airtight container for analysis. CSs were also produced by varying the mass flow rates of the acetylene gas where the ratio of acetylene to nitrogen was 0.4 (*i.e.*, acetylene/nitrogen = 250/100, 500/200, 650/250 and 850/350 sccm). The resulting CSs were then characterized using FE-SEM (ZEISS EVO 40 SE Detector), XRD (The Rigaku Ultima IV X-ray diffractometer equipped with Cu-K α ($\lambda = 0.154056$ nm radiation employing a scanning speed of 4° min⁻¹ and 20 ranges from 10° to 60°), Raman (Thermo Scientific DXR SmartRaman spectrometer), and FTIR (Thermo Scientific Nicolet S10 FT-IR) techniques to probe their structural and surface morphological features. Synthesized CSs were subsequently used in rechargeable sodium ion battery and the performance of CSs as an anode material was investigated. To prepare the CSs anode following method was employed. The CSs, activated carbon, and polyvinylidene fluoride (PVDF) were mixed in the ratios of 85: 8:7 by their mass. The prepared slurry was pasted on a Copperplate using the doctor blade method ²⁹ and dried on a hot plate at about 100 ⁰C. Metallic sodium pressed on an aluminum foil was used as the cathode in the cell. The electrolyte was prepared using 1 mol dm⁻³ NaClO₄ (sodium perchlorate) dissolved in propylene carbonate and a cellulose separator in between the electrodes was soaked with the electrolyte. Cell was fabricated in an argon gas-filled glove box and moved to the cell testing division. In order to investigate the electrochemical properties, charge-discharge cycles were obtained using Potentiostat/Galvanostat HA-15 A, Science Workshop 750 Interface instrument, and Data Lab software. To obtain impedance measurements auto lab instruments and Nova software were employed.

3 RESULTS AND DISCUSSION

3.1 Process of catalyst coating on the formation of GCSs

Fig.1 shows the representatives of the plan view of Field Emission Scanning Electron Microscopy (FE-SEM) images of GCSs grown on silicon. The mass flow rate of the acetylene/nitrogen precursor gas mixture was 250/100 sccm. The left panel in Fig.1 shows

the image of GCSs where the catalyst (FeCl₃) was dip-coated while the right panel in Fig.1 displays the image of GCSs where the catalyst (FeCl₃) was spin coated. It is clearly evidenced from the images that GCSs grown on Si with catalyst dip-coating have smaller sized spheres with variation in their sizes leading to the formation of a hierarchical structure which appears to be emanating from the bottom to upward. The smaller spheres are seemed connected with each other on the surface. Typically the smaller GCSs made by CVD, are found to be connected (accreted) in a 2D strand that can extend well over tens of spheres ³⁰. However, there is a minor amount of deformation and destruction of spheres and the tendency to form larger spheres at the bottom of the hierarchical structure. This nature is more evident in the image shown in the right panel in Fig. 1 where the catalyst was spincoated on Si. In any case, the formation of larger spheres normally happens as discrete carbon structures that can interact with other spheres through van der Waals bonding. Further, if the temperature is high enough, sometimes, the discrete carbon structures can form amalgamated structures *via* sphere coalescence ³⁰. However, in our case, the probability of having former is higher than the latter on the observed morphological differences seen in the images as a relatively low temperature was used in our case. Fig. 2 shows the histogram of the variation of the size distribution of GCSs produced via two different catalyst coating routines. A normal distribution in the variation of the sizes can be observed in Fig 2 (a) where the catalyst was dip-coated on Si.



Fig.1. Representatives of the plan view of FE-SEM image of GCSs grown on (a) catalyst dip coated substrate (b) catalyst spin coated substrate.



Fig.2. Histogram of the size distribution of GCSs grown on silicon (a) with catalyst (FeCl₃) dipcoating (b) with catalyst (FeCl₃) spin-coating

To clarify reasons behind the observations made in FE-SEM of GCSs grown on Si by two different catalyst coating routines, we performed an analysis of FE-SEM images obtained from Si substrate coated with the same catalyst using two different methods (SEM images are not shown here). Open-source software, ImageJ ³¹, designed for image processing and available freely was used for this purpose and the results are shown in Fig 3 (a) and (b). The ImajeJ can be used to display, edit, analyse, process, save and print 8-bit, 16-bit and 32-bit images and read many image formats including TIFF, GIF, JPEG, BMP, DICOM, FITS and "raw". According to ImageJ, the y-axis in these graphs represents Gray Value (roughness) while the x-axis represents the size of the catalyst particles laterally across the selected portion of the image. Higher fluctuations in the y-scale represent lower surface roughness, or in other words, the substrate with catalyst spin-coated has a higher surface roughness (lower fluctuations) than that of with catalyst dip-coated.



Fig.3. Variation of the surface roughness (Gray Value in y-scale) laterally across on Si substrate (a) with catalyst (FeCl₃) dip-coated (b) with catalyst (FeCl₃) spin-coated (smaller the Gray-value in y-direction higher the surface roughness)

Spin-coating and dip-coating are convenient ways of depositing a uniform thin film of liquid for solidification into a coating on a substrate. Of the two methods, spin-coating is a process for rapidly depositing a thin coating from a solution. Here a drop of solution is evenly spread by centrifugal force onto a rotating substrate. In the dip-coating, the substrate is immersed in a solution and is withdrawn from the solution at a constant speed. In both methods, the catalyst particles spread on the substrate tend to agglomerate and result in different surface morphologies (roughness) which affect the yield and the quality of the resulting carbon spheres (CSs). Besides, many parameters influence the quality of the resulting solidified film on the substrate. In particular, in the dip-coating process, the quality of the coated film depends on the viscosity, capillary force (surface tension), density, and gravity of the solution ³², and the catalyst particles tend to coalesce and become a large cluster with multiple layers. Several mechanisms of formation of GCSs from its constituents in the gas phase have been proposed ³⁰ and are appeared to depend on the reaction conditions, carbon source, catalyst, etc. It was confirmed that in all pyrolytic systems as well as in flames, there are three possible routes to the formation of GCSs ³⁰. Following the formation of GCSs in the gas phase, deposition onto the substrate occurs, the rate of which is extremely sensitive to the surface properties of the substrate. If the substrate has higher surface roughness, it could lead to an increase in the energy dissipation rates and kinetic energy ³³. Higher surface roughness can increase the mass transfer rates and it may be a reason for the formation of larger-sized GCSs on the catalyst spin-coated surface.

3.2 Mass flow rate of the precursor gases on the mean diameter of GCSs

As was pointed out earlier ³⁰, the mechanism of formation of GCSs involves the nucleation of pentagonal or heptagonal carbon flakes followed by the formation of spiral shell carbon particles proposed by Kroto and Mckey ³⁰. The growth of the GCSs, *i.e., the addition of added carbon layers to the already formed spiral shell carbon particle*, is due to the deposition of carbon flakes from the gas phase. This growth is influenced by the carbon source and the reaction conditions such as temperature, pressure, mass flow rate, and time in the reactor (feeding time). In CVD synthesis of GCSs, the carbon source will decompose into fragments and radicals and these fragments will provide the building blocks for the formation of flakes. Fig.4 shows the plan view of FE-SEM images recorded from GCS grown on Si by varying the mass flow rate of precursor gasses. Other parameters T (750^oC), P (1 atm) and carbon source (acetylene), feeding time (30 minutes)) were kept unchanged.

The mass flow rate of the precursor gasses was changed (acetylene/nitrogen ratio) from 250/100, 500/200, 650/250, and 850/350 sccm, and the resulting GCSs were labeled as GCS250, GCS500, GCS650, and GCS850. Histogram showing the variation in the size distribution across each SEM image is also shown with the same image. The mean diameter of each sample was obtained by averaging the diameters of GCSs spread over each image. The plot showing the variation of the mean diameter against each sample is shown in Fig.5.



Fig.4. Representative of the plan view of the FE-SEM images of GCSs with differing mass flow rates of the precursor gasses (acetylene/nitrogen) (a) 250/100, (b) 500/200, (c) 650/250, and (d) 850/350 sccm



Fig.5. Variation of the mean diameter of GCSs with changing mass flow rate of the precursor gasses

As can be seen in Fig. 5, when the mass flow rate of acetylene/nitrogen is increased, the mean diameter of the GCSs increases and reaches an optimum value (~3.1 μ m) at the flow rate of 500/200 sccm and then decreases, which shows the size tunability. At a lower flow rate of the precursor gasses, the rate of decomposition of acetylene into fragments is low which affects the nucleation as well as the growth process of GCSs. When the flow rate is increased, the amount of carbon mass available for decomposition and fragmentation becomes higher. The presence of a large number of fragmented radicals that are highly reactive can increase the rate of nucleation followed by the growth of GCSs, as was seen in Fig. 5. In optimum condition, GCS500 maximum mean diameter is achieved (approximately $3.1 \,\mu\text{m}$). Further increase in the mass flow rates of the carbon source decreases the resulting mean diameter of the GCSs, even if higher mass flow rates can increase the number of fragmented radicals available in the gas phase. A similar observation has been made with CSs prepared by direct pyrolysis of hydrocarbons with extended feed time⁷. However, when the mass flow rate exceeds a critical value (500/200), instead of adding carbon flakes to already formed GCSs, the GCSs can act as a catalyst for the formation of a second layer and can continue to do so assembling eventually into a hierarchical structure. The second layer always is observed to have smaller particles, hence smaller mean diameter, than the first layer in a hierarchical structure. Further, the growth of densely packed GCSs at higher mass flow rates seen in Fig. 4 (d) provides corroborative evidence to this explanation.

3.3 Process of catalyst coating on the degree of graphitization of GCSs

Raman spectroscopy is one of the powerful techniques for characterizing carbon materials. The peak in approximately 1592-1600 cm⁻¹ (G band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2 -bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer. ³⁴ The peak in approximately 1308- 1323 cm⁻¹ (D band) is associated with the vibrations of carbon atoms having dangling bonds in-plane terminations of a disordered graphitic network. The intensity ratio of the D and G-bands I_D/I_G is commonly used to characterize the graphitized degree (the degree of graphitization) of carbonaceous materials which is proportional to the number of defects in graphitic carbon within the analyzed spectrum. ³⁵



Fig 6: Raman spectra of CSs a) with catalyst dip-coated, b) with catalyst spin-coated samples and variation of calculated I_D/I_G ratio values with type of sample c) with catalyst dip-coated d) with catalyst spin-coated samples

Intense peaks are seen at 1316 cm⁻¹ and 1592 cm⁻¹ Raman shifts and their shapes agree well with previous observations ³⁵ and are assigned as to originating from typical D band and G band peaks for carbon material. However, when the mass flow rate of the carbon source is increased, the intensity of both peaks diminishes, but only with slight changes to the I_D/I_G ratio. The I_D/I_G ratio manifest the degree of graphitization of GCSs produced in two different catalyst coating methods.

As can be observed in the tabulated data in Table 1, the I_D/I_G ratio of GCSs produced by both methods lies around 1.00 which reflects the presence of somewhat lower degree of graphitization and non-graphitizable carbon (amorphous carbon structure with a high content of lattice edges or defects). However, a slight increase in the graphitization can be observed with samples grown at a flow rate of 500/200 on Si where the catalyst was spin-coated.

Sample	Dip-coated GCSs			Spin-coated GCSs		
	D band (cm ⁻¹)	G Band (cm ⁻¹)	I _D /I _G	D band (cm ⁻¹)	G Band (cm ⁻¹)	I_D/I_G
GCS250	1316	1592	1.08	1323	1600	1.02
GCS500	1314	1597	1.18	1323	1597	0.97
GCS650	1308	1592	1.06	1320	1594	0.99
GCS850	1315	1592	1.03	1315	1592	1.04

Table 1: Tabulated data for the variation of I_D/I_G ratio, D band and G band with different mass flow rates of the precursor gasses under two different processes of catalyst coating.

Figure 7 shows the X-ray diffraction pattern of the as-prepared GCSs samples. Two clear characteristic peaks of the graphite structure at $2\theta=26.2^{\circ}$ (d=3.3985 Å) and $2\theta = 45^{\circ}$ (d=2.0128 Å) can be observed. These peaks are assigned as to originating from typical graphitic (002) and (100) planes, respectively. It has been reported that the presence of the peak at 44.01° gives a good indication of the presence of hexagonal graphite lattice. Besides, minor and major peaks seen at 14.44° and 69.16° are due to Si substrate. The graphite peaks can be indexed to a hexagonal graphite lattice with cell constant a = b = 2.433Å and c = 6.797Å. The deviation was lower than 1.5% compared to the reported values for a = b = 2.470Å and c = 6.790Å³⁶. Peak broadening in the XRD suggests somewhat lower degree

of graphitization and the possible presence of amorphous carbon. The XRD pattern can be used estimate the crystallite size of the GCS by measuring the *full-width half maximum* (FWHM) of the (002) peak and substituting it into Scherer formula ³⁷ with other parameters. Once the corresponding values are submitted into the equation (FWHM of the (002) peak = 5.00531 radians, k = 0.94, λ of incoming X-rays = 1.5406 Å), the crystallite size of GCSs has a value of 16.983 Å which indicates there could be about 5 graphitic layers present in single crystallite.



Fig.7. XRD pattern recorded from CSs

Fourier Transformed Infrared spectral data (FTIR) are used to investigate the functional group of GCSs formed during and after the synthesis process. Both catalyst spin-coated and dip-coated samples were examined and the spectra are shown in Fig.8 (a) and (b). A narrow and intense peak seen at a wavenumber of 3446 cm⁻¹ can be assigned as to originating from the O-H stretching vibration of the adsorbed water.³⁸ The peaks at 2959 and 2851 cm⁻¹ are related to CH₂ asymmetric and CH₃ symmetric stretching vibration, respectively. The band at 1746 cm⁻¹ and 1576 cm⁻¹ can be assigned to the main stretching bands of the carbonyl group (C=O) and carbon–carbon double bonds. This suggests that the CSs are composed of functional groups attached carbon (*sp*³) and graphitized carbon (*sp*²). While stretching bands of the epoxy group (C-O-C) stretching are identified at 1267 cm⁻¹ and C-O stretching is

placed at 1033 and 1639 cm⁻¹.³⁹ The band at 1384 cm⁻¹ can be assigned due to the presence of O-C-O deformation mode carbonyl groups indicating partial oxidation of GCSs after the experimental process.



Fig.8. FTIR spectra recorded from (a) GCS prepared with catalyst dip-coated (b) GCS prepared with catalyst spin-coated

These results indicate that the GCSs on the dip-coated and spin-coated surfaces could be functionalized with hydroxyl, carbonyl, and carboxylic groups and provide a potential avenue to absorb other molecules, ions, and functional groups. However, incorporation of such variety of functional groups during the synthesis process of CSs in our case requires further study using X-ray photoelectron spectroscopy (XPS) where the route cause for the origin of such groups can be properly traced in terms of the binding energy of molecular orbitals.

3.4 GCSs as an anode material in Sodium-ion rechargeable battery

Figures 9 (a) and (b) show typical charging and discharging curves obtained from the cell by using GCSs as the anode. The charging process was carried out using a current of 0.5 mA. The resulting graph shows a steady increment of the voltage until it reaches a voltage of 2.35 V. By observing the curve pattern, it can be predicted that the cell achieves its full charge capacity in this voltage. If the charging time is increased further, the curve shows a decline which indicates that the charging time has exceeded the limit and the cell is unable to retain its capacity any further due to overcharging. The discharging curve of the cell shown

in Fig. 9 (b) was obtained for a discharging current of 0.5 mA. The curve shows a rapid voltage drop starting with around 2.35 V and ending at around 0.25 V. After that, the discharging rate decreases rapidly and retains a steady value until it is fully discharged. The discharge capacity of the cell was calculated to be 107.8 mAh g⁻¹. The high discharging capacity obtained for this cell can be predicted to be arising due to efficient intercalation process involved between sodium ions and the GCSs. The FE-SEM images obtained show that the diameter of the prepared GCSs is in the range of 500 nm ~4.5 μ m. The grinding process can further minimize the particle size of the prepared composite which was used as the active material for the anode. Such porous nanoparticles can increase the contact area between the electrode material and the electrolyte. This process will be resulting in a favourable immersion of the electrolyte leading to high-quality electrochemical performances in the final count⁴⁰. Hence it is evident that the cell capacity can be further increased by reducing the particle size and increasing the porosity of the prepared CSs in future work



Fig.9 Charging (a) and discharging (b) curves of the cell

Figure 10 (a) shows continuous charge-discharge cycles obtained for the prepared cell. This process was carried out using 0.5 mA current (for both charging and discharging) to investigate the cyclability of the prepared cell. There was no significant deviation obtained for either charging or discharging patterns within the tested number of cycles. The starting voltage was around 2.25 V at the beginning which did not show any significant reduction even after seven charge-discharge cycles. The battery has a fairly high reversible capacity within the tested number of cycles without significant drainage. However, it is recommended to test the cell for a much larger number of charge-discharge cycles to get a complete idea

about its cyclability performances. The prepared cell was tested with electrochemical impedance measurements to investigate the sodium-ion migration dynamics. Figure 10 (b) shows the Nyquist plot prepared using the result of the impedance measurements. It consists of a small semi-circle at the high-frequency region, a large semi-circle, and a linear part in the high-frequency region that fits with the inserted circuit. The semi-circle in the high-frequency region indicates the charge transfer resistance and the straight line in the low-frequency region represents the sodium-ion diffusion within the electrode respectively.^{18,41} The linear behaviour of the low-frequency region further illustrates the typical Warburg behaviour associated with the sodium ion conductivity in the electrolyte.⁴² The equitant circuit which entails the values of charge transfer resistances and impedance of constant phase elements is also included in the inserted circuit.



Fig 10. (a) Continuous charging and discharging cycles of the cell (b) Nyquist plot and the equivalent circuit

4. CONCLUSION

In summary, the growth of GCSs was achieved using state-of-the-art CVD technique over an iron-catalyst coated silicon substrate with C_2H_2 as a carbon precursor and N_2 as a carrier gas at 750°C under atmospheric pressure. The method of catalyst coating on Si has an effect on the growth and the formation of GCSs with size-tunable distribution. The carbon spheres produced by CVD have a regular shape with reasonably high yield, and diameters ranging from 500 nm to 4.5µm. Raman, FTIR, and XRD analysis confirmed the presence of graphite hexagonal carbon networks of the products. The results further reveal that the size distribution of the GCSs is dependent on the mass flow rate of the carbon source as well. Further studies are underway to produce graphitized nano carbon spheres (nGCS) which could potentially have interesting physical and chemical properties and wide range of applications due to size confinement in the nanoscale.

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