Synthesis of Graphitic Ordered Macroporous Carbon with a Three-Dimensional Interconnected Pore Structure for Electrochemical Applications

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In this study, ordered macroporous carbon with a three-dimensional (3D) interconnected pore structure and a graphitic pore wall was prepared by chemical vapor deposition (CVD) of benzene using inverse silica opal as the template. Field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman spectrometry, nitrogen adsorption, and thermogravimetric analysis techniques were used to characterize the carbon samples. The electrochemical properties of the carbon materials as a carbon-based anode for lithium-ion batteries and as a Pt catalyst support for room-temperature methanol electrochemical oxidation were examined. It was observed that the CVD method is a simple route to fabrication of desired carbon nanostructures, affording a carbon with graphitic pore walls and uniform pores. The graphitic nature of the carbon enhances the rate performance and cyclability in lithium-ion batteries. The specific capacity was found to be further improved when SnO₂ nanoparticles were supported on the carbon. The specific activity of Pt catalyst supported on the carbon materials for room-temperature methanol electrochemical oxidation was observed to be higher than that of a commercial Pt catalyst (E-TEK).

1. Introduction

The demands for advanced energy conversion and storage devices such as fuel cells, lithium-ion batteries, and supercapacitors have resulted in many recent studies on nanostructured electrode materials.¹ Carbon materials such as carbon black, graphite, and highly ordered pyrolytic graphite have been used as the working electrode materials.² Recently, the preparation of nanoporous carbons with different structural properties by using a hard template has been described.^{3–6} Such carbon materials are technologically significant in catalysis, adsorption, and templating matrixes for fabricating nanomaterials. The template approach allows one to obtain a desired carbon pore structure, thus offering new opportunities to realize nanostructured carbon-based electrode materials for electrochemical applications.^{7–14}

As a promising anode in lithium-ion batteries, $SnO_2/carbon$ nanostructured composite is attracting a great deal of interest. It is well-known that SnO_2 possesses a higher theoretical capacity (800 (mA h)/g) than that of graphite (372 (mA h)/g).^{15–18} However, its practical application is hampered by the poor cyclability due to the large volume change (expansion and contraction) during the lithium intercalation/deintercalation process, which causes a fast capacity fading. Additionally, the agglomeration of primitive SnO_2 particles drastically reduces the total entrance/exit sites available for lithium ions (i.e., reduction in surface-to-volume ratio).¹⁷ SnO_2 nanoparticles supported on a porous material may overcome these problems. It has been observed that porous carbon can act as a barrier to

avoid the aggregation of SnO_2 particles because of the confinement of SnO_2 nanoparticles in the pores,¹² as well as the strong interactions between the nanoparticles and the support.¹⁸ Moreover, the nanopores of the carbon provide a void space when SnO_2 nanoparticles experience a volume change.¹² On the other hand, a well-developed porous carbon structure with a 3D connectivity enhances the ionic conductivity of electrolyte and the movability of lithium ions, thus improving the rate performance of lithium-ion secondary batteries.¹⁵ Therefore, SnO_2 /carbon nanostructured anode composite is believed to display a better cycle life than SnO_2 alone and a higher capacity than graphitic carbon itself.

For the direct-methanol fuel cell (DMFC) application, recent studies have shown that the characteristics of a carbon support for Pt catalyst have a significant impact on the electrochemical properties. A highly accessible surface area enables a high dispersion of Pt nanoparticles, thus enhancing the catalytic activity of the Pt/carbon catalyst.¹⁹ A graphitic nature enables rapid electron transfer.²⁰ A 3D interconnected pore system facilitates the transport of reactants and products during electrochemical oxidation reaction.^{7,21}

In this paper, ordered graphitic macroporous carbons with a 3D interconnected pore structure were fabricated using the chemical vapor deposition (CVD) method with inverse silica opal as the template following a surface-templating route.²² The fabrication involves the preparation of an inverse silica template, carbon deposition on the template surface using the CVD method with benzene vapor as the carbon source, and removal of the template using HF solution. The electrochemical properties of the prepared carbon materials as carbon-based anode materials in lithium-ion battery and as Pt catalyst supports for methanol electrochemical oxidation in DMFCs were examined.

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2. Experimental Section

2.1. Synthesis of Carbon Materials. The carbon preparation procedure in this work is described as follows. First, monodisperse polystyrene (PS) spheres synthesized according to Shim and co-workers²³ were fabricated into colloidal crystals using a flow-controlled vertical deposition method.²⁴ Second, the interstices between the PS spheres were infiltrated with a silica sol, which was prepared by mixing tetraethyl orthosilicate (98%, Acros Organics), ethanol, and 0.1 M HCl solution with a volume ratio of 1:3:0.1. After hydrolysis and condensation of the silica sol, the PS spheres were removed by calcination in air at 700 °C for 5 h, yielding a 3D macroporous inverse silica opal, which was employed as the template. Third, deposition of carbon on the surface of the inverse silica opal was carried out using a CVD method with the benzene vapor as the carbon precursor. In detail, a 0.5 g inverse silica template in quartz tube was placed into a furnace and heated to 900 °C with a heating rate of 5 $^{\circ}$ C/min under highly pure N₂ flow (30 cm³/min). Subsequently, nitrogen gas containing 10 wt % benzene vapor at a flow rate of 30 cm³/min was introduced into the quartz tube for 2 h. Then, carbon/silica composite was cooled in pure nitrogen gas and dissolved in 20% HF solution to remove the silica. The obtained carbon was named as GMC900, where GMC means graphitic macroporous carbon and 900 refers to the CVD temperature. Another sample named GMC1000 was prepared at the CVD temperature of 1000 °C for 2 h. The experimental results demonstrated that when the CVD temperature is lower than 900 °C, there is no deposition of graphitic carbon on the surface of the macroporous silica template. In contrast, at the temperature higher than 1100 °C, the 3D structure of the silica template is partially destroyed.

2.2. Characterization. The microscopic features of the samples were observed with a field-emission scanning electron microscope (FESEM; JSM-6700F, JEOL Japan) operated at 10 kV and transmission electron microscopy (TEM; JEM 2010F, JEOL, Japan) operated at 200 kV. Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer TGA 2050 (Thermal Analysis Instruments, USA) in air with a flow rate of 100 cm³/min and a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 (Japan) with Cu K α radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 30 mA. The pore structural properties were investigated by nitrogen adsorption at -196 °C on an automatic volumetric sorption analyzer (Quantachrome, NOVA1200). Prior to measurements, the samples were degassed at 200 °C for 5 h. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method in the relative pressure of 0.05-0.2. The micropore volume was calculated from the Dubinin-Radushkevich (DR) equation.

2.3. Preparation and Electrochemical Measurements of Carbon-Based Anode Materials for Lithium-Ion Batteries. The SnO₂/carbon composite was prepared by the microwave-assisted hydrolysis method.¹⁸ Briefly, in a 100 mL glass vessel, 0.2 M urea (Aldrich, 98%) was dissolved in 0.1 M SnCl₄ (Riedel-de Haen, 99%) aqueous solution to a mole ratio of urea to SnCl₄ of 4:1. A calculated amount of GMC1000 with two different SnO₂ loadings was added to the solution and sonicated for 0.5 h. The glass vessel was then placed in the cavity of a 300 W CEM Discover microwave reactor. The temperature was ramped from room temperature to 85 °C in 10 s and kept for 3 min under stirring. The resulting suspension, after cooling in an ice bath, was centrifuged at 8000 rpm for 30 min to precipitate the nanocomposites. After washing with a copious amount of distilled water, the precipitate was dried in a vacuum

at 130 °C overnight and heated in a tube furnace at 350 °C for 3 h. The exact amounts of SnO_2 in the composites (74.5 and 18.6 wt %; designated as SnO₂/GMC1000) were determined by the inductively coupled plasma (ICP) spectroscopy. The synthesized GMC1000 and SnO₂/GMC1000 composites with different loadings of SnO2 were used as the active anode materials. The working electrode consisted of 90 wt % active material, 5 wt % conductivity agent (Carbon Black, Super-P), and 5 wt % binder (poly(vinylidene difluoride), PVDF, Aldrich). A lithium foil was used as negative electrodes. The electrolyte was 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The room-temperature electrode activities were measured by a Maccor Series 2000 battery tester (with anode Li⁺/Li). Cells were tested at the constant currents 40, 200, 600, and 1000 mA/g and a fixed voltage limit (5 mV to 2 V).

2.4. Preparation and Evaluation of Pt/Carbon Catalysts for Methanol Electrochemical Oxidation. Pt catalysts supported on carbon samples GMC900 and GMC1000, designed as Pt/GMC900 and Pt/GMC1000, respectively, were prepared for room-temperature methanol oxidation using the established borohydride reduction method.²⁵ An appropriate amount of 0.05 M chloroplatinic acid (H₂PtCl₆•6H₂O, Aldrich) solution was added in distilled water containing carbon powder under stirring. Then, a stoichiometric excess of 0.5 M NaBH₄ (Aldrich) solution was used to initiate deposition of Pt nanoparticles. After stirring for 12 h, the solid was recovered by centrifugation, extensively washed with distilled water, and vacuum-dried at room temperature overnight. The Pt loading in each catalyst was kept at 20 wt % to allow a comparison with a commercial E-TEK Pt/C catalyst (Pt supported on carbon black Vulcan XC-72; Pt loading, 20 wt %). A conventional three-compartment electrochemical cell was used to evaluate the electrochemical performance by cyclic voltammetry. An Autolab PGSTAT12 was employed as the potentiostat/galvansotat. The working electrode with a Pt loading of 100 μ g/cm² was fabricated by casting Nafion-impregnated catalyst ink onto a 5 mm diameter vitreous glassy carbon disk electrode, which was cleaned with ethanol and dried before use. The catalyst ink is prepared by ultrasonically dispersing 10 mg of Pt catalyst into a mixture of 0.1 mL of Nafion (5 wt % solution from Aldrich) and 0.9 mL of ethanol. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively, while 1 M CH₃OH in 0.5 M H₂SO₄ was the electrolyte. All reported potentials were referenced to the SCE. The catalysts were electrochemically cleaned by continuous cycling until a stable response was obtained before the cyclic voltammograms were recorded.

3. Results and Discussion

3.1. Pore Structures of GMCs. Figure 1a shows the crosssection FESEM image of the inverse silica opal template. The spherical voids with a diameter of about 220 nm packed in a face-centered cubic (fcc) structure are seen. Each air void is interconnected with spherical windows of about 50 nm in size. Parts b and c of Figure 1 show the FESEM images of carbons GMC900 and GMC1000 replicated from the macroporous silica template. A 3D ordered structure with a fcc arrangement of spherical voids is also seen, indicating that the long-range order of the GMCs inherited from the inverse silica opal template. It is also seen that the GMCs contain quasi-spherical cavities of around 200 nm in diameter with smaller quasi-cylindrical pore channels. Figure 1d is a higher magnification image of the GMC1000 sample. The crack highlighted with a black circle reveals the hollow carbon framework, demonstrating that the



Figure 1. FESEM images: (a) inverse silica template; (b) GMC900; (c, d) GMC1000.



Figure 2. TEM image: (a, b) GMC900 with different magnifications; (c) GMC1000; (d) lattice-fringe image of GMC1000 framework.

macroporous carbon was replicated from the inverse silica template via a surface-templating mechanism.²² From the broken edge, it can be estimated that the carbon wall thickness is about 20-30 nm. It should be noted that the obtained macroporous carbons are not highly perfect in pore structure due to some fractures and defects, which may stem from structural collapses of the inverse silica template during the calcination or template removal process.

Shown in Figure 2 are the TEM images of the GMCs. It can be seen that GMC900 substantially consists of hollow carbon spheres with a diameter of around 200 nm, showing a highly periodic carbon structure. Figure 2b further shows a homogeneous 3D interconnected pore structure with an average carbon wall thickness of 20 nm. Similarly, carbon GMC1000 also displays a 3D pore structure, but with a thicker carbon wall of around 30 nm. The high-resolution TEM image of Figure 2d taken from the carbon wall of Figure 2c reveals the presence of imperfect graphene sheets, which are packed tightly. As a result, significant lattice distortions and defects are observed. These graphene layers are parallel to the surface of the carbon wall. The microscopic features clearly indicate the low crystallinity of the carbon walls.

The nitrogen adsorption/desorption isotherms of GMC900 and GMC1000 reveal a type-II isotherm with a type-H3 hysteresis



Figure 3. XRD patterns of synthesized GMC900, GMC1000, carbon black XC-72, and amorphous carbon C1000-2.



Figure 4. Raman spectra of the GMC1000, GMC900, and carbon black XC-72.

(not shown here), characteristic of a macroporous material. The Brunauer–Emmett–Teller (BET) surface areas of carbons GMC900 and GMC1000 were measured to be 94 and 43 m^2/g , respectively. The micropore volumes of both carbon samples estimated using the DR method are negligible, implying a dense packing of graphene layers.

3.2. Graphitic Nature of GMCs. Compared in Figure 3 are the XRD patterns of different carbons. It can be seen that GMC1000, GMC900, and XC-72 possess a broad diffraction peak at around 25°, which is assigned to the (002) diffraction of graphitic carbon, showing the presence of graphitic carbon. GMC1000 has the strongest intensity of this peak at 25.3°, indicating the highest degree of graphitization among the carbon samples. The peak at about 43° corresponds to (101) diffraction of solid carbon materials. The intensity of the (002) peak of carbon GMC900 is comparable to that of carbon black XC-72. In contrast, carbon C1000-2 synthesized at 1000 °C using zeolite Y as the template and furfuryl alcohol as the carbon precursor²⁶ is amorphous in nature because no peak at around 25° is seen. The interlayer distance values between graphene planes (d_{002}) together with the crystalline size (L_c) can be determined from the (002) peak using the Bragg's law and Scherrer equation, respectively. The broad width and lower position of the (002) peak than the typical peak of graphite ($d_{002} = 0.335$ nm) indicate the low crystalline nature of GMC1000 ($d_{002} = 0.352$ nm, L_c = 3.8 nm), in agreement with the data revealed by the TEM lattice-fringe images.

Figure 4 shows the Raman spectra of the carbon samples. The strong peak at around 1590 cm⁻¹ (G band) is attributed to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice, namely, the stretching modes of C=C bonds of typical graphite, while the weak peak at about 1350 cm⁻¹ (D band) is associated with the vibration of carbon atoms with dangling bonds in plane terminations of the disordered graphite and is also related to the defects and disorders of carbon materials. It should be noted that the G band peaks of all three samples (for GMC1000 at 1585 cm⁻¹, GMC900 at 1596 cm⁻¹, and XC-72 at 1593 cm⁻¹) are shifted to higher wavelength numbers in comparison with that of graphite single crystals



Figure 5. Thermogravimetric analysis of synthesized GMC1000, GMC900, carbon black XC-72, and amorphous carbon C1000-2.

 TABLE 1: Specific Capacities of GMC1000 at Various

 Specific Currents

specific current (mA/g)	specific capacity ((mA h)/g)	specific current (mA/g)	specific capacity ((mA h)/g)
40	327	1000	260
200	320	15^{a}	300^{a}
600	303	150^{a}	150^{a}

^{*a*} From ref 13.

(1580 cm⁻¹), suggesting a structural imperfection of the graphene sheets of the three samples.²⁷ The relative intensities of the two peaks (G and D bands) reflect the graphitization degree. The observed low intensity of the broad D band peak and the high intensity of the G band narrow peak indicate that the carbons are composed of small graphene sheets with a low graphitization degree.²⁷ Additionally, the large Raman $\Delta \nu_{\rm G}$ value (full width at the half-maximum (fwhm)) of the G band, which is closely related to the structure regularity,²⁸ also indicates a low graphitization degree. The $\Delta \nu_{\rm G}$ values of GMC1000, GMC900, and XC-72 are 72, 79, and 78 cm⁻¹, respectively. Therefore, the G-band peak position, the relative intensity of the two peaks, and the Raman $\Delta \nu_{\rm G}$ values suggest the highest graphitization degree of carbon GMC1000, in agreement with the XRD data presented in Figure 3.

The thermogravimetric (TG) curves of the GMC carbons prepared in this work are compared with that of carbon black XC-72 and an amorphous carbon in Figure 5. The TG curves of carbons GMC900 and GMC1000 clearly show that the silica template had been completely removed by aqueous HF solution because of the negligible residue at the temperature above 800 °C. The temperature range of weight loss was observed to be between 500 and 600 °C for amorphous carbon C1000-2, between 530 and 720 °C for carbon black XC-72 and carbon GMC900 and between 580 and 800 °C for carbon GMC1000. It has been reported that the oxidation reaction of carbon materials first occurs on the graphene layer edge defects or disordered graphene layers.²⁹ In general, pure graphite with less defects and a good organization of graphene layers has a much higher oxidation temperature than amorphous carbon. In this work, the sequence of oxidation temperature range of the carbons in air follows the graphitization degree as characterized by the XRD and the Raman spectrum data. It is also worthy to note that in comparison with liquid carbon precursors, such as divinylbenzene,7 resorcinol-formaldehyde,13 sucrose,30 phenolformaldehyde,31 and polyacrylonitrile,32 the aromatic hydrocarbon precursor, benzene, used in this study allows the formation of graphitic nature except for the treatment of mesophase pitch at a higher temperature (2500 °C).33

3.3. Electrochemical Properties of Carbon-Based Anode Materials for Lithium-Ion Batteries. Table 1 shows the specific capacities of GMC1000 at various specific currents, together with the results of an amorphous 3D macroporous



Figure 6. (a) FESEM image of SnO₂/GMC1000 (74.5 wt %); (b) TEM image of SnO₂/GMC1000 (74.5 wt %); (c) FESEM image of SnO₂/GMC1000 (18.6 wt %); (d) XRD patterns of SnO₂/GMC1000 composite (18.6 wt %).

carbon for comparison purpose. It can be seen that the specific capacity of GMC1000 was 326 (mA h)/g at a specific current of 40 mA/g. When the current was increased from 40 to 600 mA/g, only a slight decrease in capacities from 326 to 303 (mA h)/g was observed. Instead, the 3D amorphous carbon with a similar macroporous structure to carbon GMC1000 prepared in this study displayed a lower specific capacity at a similar current,13 indicating a substantial improvement of rate performance in the present work and a great application potential of our carbon materials. In lithium-ion batteries, the electrochemical behaviors largely depend on the chemical and physical properties of the carbon material, such as crystallinity, surface chemistry, pore structure, and micromorphology.¹⁵ Extremely high surface area creates excessive side reactions with the electrolyte, forming a solid-electrolyte interface (SEI) to inhibit reversible faradaic reaction, giving rise to a poor cyclic stability. On the other hand, a carbon with a very low surface area cannot provide sufficient electrochemical active sites for the charge-discharge process. The GMC1000 carbon with an appropriate surface area (around 42 m²/g) and an interconnected pore structure consists of graphitic carbon walls with a thickness of around 30 nm, as shown in Figure 2c. The stacked graphene layers as shown in Figure 2d, together with the unique structure, not only improve the electronic transport for electrochemical reaction but also promote the lithium ion diffusion, leading to a good electrochemical performance as an anode material.

The FESEM image shown in Figure 6a and the TEM image shown in Figure 6b of the $SnO_2/GMC1000$ composite with a SnO_2 loading of 74.5 wt % all demonstrate the existence of a large number of uniform SnO_2 nanoparticles of around 5 nm in diameter. The FESEM image of another $SnO_2/GMC1000$ composite with a SnO_2 loading of 18.6 wt % shown in Figure 6c indicates sparsely dispersed SnO_2 nanoparticles of around 5 nm in size on the surface of GMC1000. The XRD pattern of sample $SnO_2/GMC1000$ with a SnO_2 loading of 18.6 wt % in Figure 6d exhibits four peaks of (110), (101), (200), and (211) reflections of the rutile-like SnO_2 .³⁴ The (002) reflection peak



Figure 7. Cycling performances of GMC1000 and different $SnO_2/GMC1000$ composites (discharge potential limits, 5 mV to 2.0 V; constant current, 0.1 C).

of graphitic carbon of GMC1000, shown in Figure 3, overlaps with the (110) reflection peak of SnO_2 . The particle size calculated using the Scherrer equation is consistent with that estimated from the TEM or FESEM data.

Figure 7 compares the cycling performance of pure carbon GMC1000 with that of the SnO₂/GMC1000 composite materials of different loadings of SnO2. It can be seen that carbon GMC1000 displays a very stable cyclability (specific capacity, 320 (mA h)/g after 60 cycles; 98% retention), which is better than other template-synthesized carbon materials.^{10,13} After it was coated with SnO₂ nanoparticles, higher initial capacities $(415 \text{ (mA h)/g for } 18.6 \text{ wt \% SnO}_2 \text{ loading and } 645 \text{ (mA h)/g}$ for 74.5 wt % loading) were observed in the first cycle. However, after 12 cycles, the specific capacity of composite SnO₂/GMC1000 with a higher loading of SnO₂ was found to be lower than that of the composite with a lower loading of SnO₂. In addition, the lower loading composite retained about 90.5% of its initial specific capacity after 60 cycles, indicating a better cycle performance than the higher loading composite anode, which showed a dramatically faster capacity fading (25% retention after 30 cycles). The average capacity fading of $SnO_2/$ GMC1000 (18.6 wt % loading) is around 0.16%/cycle, which is much better than that of previously reported 3D macroporous carbon coated with SnO₂ nanoparticles,¹³ hollow carbon spheres encapsulated with Sn particles,35 and ordered mesoporous carbon deposited with tin-based oxide nanoparticles.12 The enhancement



Figure 8. (a) FETEM images of Pt/GMC1000 catalyst; (b) FETEM image Pt/C E-TEK catalyst; (c) XRD patterns of Pt/GMC900, Pt/GMC1000, and Pt/C E-TEK.

of cycle performance is presumably related to the relatively good graphitic crystallinity of carbon GMC1000 and the appropriate particle size of SnO_2 , which was prepared by the microwave-assisted hydrolysis method.¹⁸

3.4. Electrochemical Oxidation of Methanol on Pt/Carbon Catalysts. The electrochemical properties of Pt catalyst supported on GMCs were experimentally compared with that of commercial catalyst E-TEK Pt/C, which is a Pt catalyst supported on Vulcan XC-72 carbon. The FETEM images of catalysts Pt/GMC1000 and E-TEK Pt/C shown in Figure 8a,b reveal the presence of a large number of Pt nanoparticles. The Pt particle sizes are about 4 nm for catalyst E-TEK Pt/C and around 6 nm for catalyst Pt/GMC1000. Figure 8c shows the XRD patterns of the three Pt catalysts. The peak at 25.3° is due to the (002) diffraction of the graphitic structure of the carbon supports. The strong diffraction peaks at the Bragg angles of 39.8, 46.3, 67.5, and 81.3° are assigned to the diffractions of the (111), (200), (220), and (311) facets of Pt nanocrystals with a fcc lattice structure. Using the Debye-Scherrer equation, the average Pt nanoparticle sizes of catalysts Pt/C, Pt/GMC1000, and Pt/GMC900 were estimated to be about 3.7, 5.3, and 5.9 nm, respectively, consistent with the observations from the FETEM images shown in Figure 7. The difference of Pt particle sizes may be due to the different surface areas accessible for Pt nanoparticles or different surface chemistries of the carbon supports.36-37



Figure 9. Cyclic voltammograms of Pt/GMC1000, Pt/GMC900, and E-TEK Pt/C catalysts measured at a scan rate of 20 mV/s at room temperature in the electrolyte of $1 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$. (Forward scan, 0-1 V; reverse scan, 1-0 V).

Figure 9 compares the cyclic voltammograms of the three catalysts measured in 0.5 M $H_2SO_4 + 1$ M CH₃OH at room temperature. The current density, which reflects the specific activity and represents the intrinsic activity of the Pt active sites, was normalized to the electrochemically active surface area of the corresponding catalysts according to the standard technique.38 The peak at around 0.66 V is attributed to electrooxidation of methanol in the forward scan, while the peak at around 0.53 V is due to the reactivation of Pt-oxides in the reverse scan.³⁹ The specific activities of catalyst Pt/GMC1000 (0.98 mA/ cm²) evaluated from the peak at 0.66 V in the forward scan are significantly higher than that of Pt/GMC900 (0.66 mA/cm²) and E-TEK Pt/C (0.57 mA/cm²). This is probably attributed to the 3D interconnected macroporous structure of the GMC supports, which facilitates the transport of reactant methanol and product CO₂ as compared with carbon black XC-72.^{7,21} The highest degree of the graphitic nature of GMC1000 also accounts for the highest specific activity of catalyst Pt/GMC1000 because of its high electrical conductivity.^{19,20}

4. Conclusions

In summary, the synthesis of ordered macroporous carbon with three-dimensional periodicity was demonstrated by using inverse silica opal as the template and benzene as the carbon precursor. This simple CVD route based on a surface-templating mechanism can be applied to fabricate 3D macroporous carbons with a controllable thickness of pore walls and a tunable degree of graphitic crystallinity. A high specific capacity (around 326 (mA h)/g), good rate performance, and good cyclability (98% retention per cycle within 60 cycles) of the 3D graphitic macroporous carbon prepared in this work as a carbon anode material in lithium-ion batteries were noted. The SnO₂/carbon nanocomposite anode with a loading of 18.6 wt % also displays a significant improvement in initial capacity (415 mAh/g) and cyclic stability (90.5% retention over 60 cycles). The specific activity of Pt catalyst supported on the synthesized carbon for methanol electrochemical oxidation was found to be better than that of a commercial catalyst E-TEK Pt/C with the same Pt loading. The enhancement of these electrochemical characteristics is presumably related to the graphitic nature and the 3D interconnected open pore structures of the carbon materials. It is anticipated that the nanostructured carbon can be used as the novel anode material for electrochemical energy conversion and storage devices.

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