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Article

N-doped mesoporous carbon as a bifunctional material for oxygen reduction reaction and supercapacitors

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ABSTRACT

A N-doped mesoporous carbon (NMC-1) has been synthesized at relatively low temperature using chitosan as a nitrogen and carbon source, tetraethoxysilane as a soft template, and nickel nitrate as a catalyst. NMC-1 has a porous structure and heteroatoms such as N and O atoms, indicating that NMC-1 can contribute to electrocatalysis, electric double-layer capacitance, and pseudocapacitance. Hence, NMC-1 was used as a bifunctional material which shows effective activity as an electrocatalyst for oxygen reduction reaction in alkaline solution, and a high specific capacitance as an ultracapacitor (252 F/g at 0.2 A/g). The results demonstrate that the presented NMC-1 has potential applications as a renewable and environmentally friendly material in fuel cells and supercapacitors.

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1. Introduction

Catalysts play a key role in the development of fuel cells, which convert chemical energy directly into electrical energy with less pollution than the direct burning of fuel oils [1,2]. The typical catalysts, Pt or Pt-based catalysts, have hindered the commercialization of fuel cells because of their high cost and inadequacy [3–5]. Recently, many studies have found that N-doped carbon nanostructures such as carbon nanotubes, carbon nanowires, and graphene are active for the oxygen reduction reaction (ORR) [6–9]. However, the practical application of these materials in fuel cells was subject to a complicated synthesis process [10]. Therefore, it is necessary to design an alternative to the above catalysts with a low-cost and simple method.

Supercapacitors, which are regarded as promising energy storage devices [11] for their merits of superior cycle stability

and high power density as well as safety [12–14], have aroused considerable research interest for decades. Ion adsorption or fast surface redox reaction is the means by which supercapacitors store energy [11,15]. To date, carbon materials have been attractive as supercapacitor electrode materials owing to their high surface area, electrical conductivity, good cycle stability, and low cost [16]. Chemical vapor deposition [17], laser elimination [18], electron beam irradiation [19], and arc discharge methods [20] are some of the conventional methods for carbon material synthesis. However, the synthetic conditions used in these methods are very harsh and uneconomical, and have thus become the major barriers to the industrial mass production of carbon materials. Consequently, it is highly important to find an easy and economical approach to prepare excellent carbon materials for supercapacitor electrodes.

Chitin is the second most abundant natural biopolymer af-

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ter cellulose, and is richly found in the vast numbers of waste shells from crustaceans such as shrimps and crabs [21,22]. As the deacetylated product of chitin [22], chitosan is commercially available, plentiful, low-cost, environmentally friendly, and sustainable.

Herein, we provide a simple method for preparing bifunctional N-doped mesoporous carbon (NMC-1) using non-toxic and renewable chitosan as the N-doped carbon precursor, tetraethoxysilane (TEOS) as the template, and $\text{Ni}(\text{NO}_3)_2$ as a catalyst at relatively low carbonization temperature. NMC-1 possesses a promising future as an effective electrocatalyst for oxygen reduction reaction (ORR) in fuel cells and as an electrochemical energy storage material for supercapacitors because of its major advantages of low cost and excellent electrochemical performance.

2. Experimental

2.1. Synthesis of NMC-1

NMC-1 was prepared using chitosan as both a carbon and nitrogen source, TEOS as soft template, and $\text{Ni}(\text{NO}_3)_2$ as a catalyst. Typically, 2.0 g chitosan was dissolved in 17 mL of HCl solution (1.4 mol/L), and then 2.5 mL of $\text{Ni}(\text{NO}_3)_2$ solution (1 mol/L) and 3.25 mL of TEOS was dropped into the system in turns. The system was then covered with plastic wrap and stirred for 2 h at ambient temperature. After this, the mixture underwent a hydrothermal process at 160 °C for 8 h in a Teflon-lined stainless steel autoclave, and was then dried at 100 °C for 4 h in a conventional oven. The resultant product was carbonized under N_2 atmosphere at 800 °C for an optimized time of 1 h at a heating rate of 5 °C/min and then cooled to room temperature at the same rate. The sample, which was denoted as NMC-1, was obtained after immersion in 10% HF solution for 12 h. A comparison material, named C-1, was prepared using the same method without $\text{Ni}(\text{NO}_3)_2$ solution.

2.2. Characterization of NMC-1

The as-prepared samples were characterized using a MSAL-XD2 X-ray diffractometer (XRD; Cu K_α , 40 kV, 20 mA, $\lambda = 0.154056$ nm) to obtain their phase structure. The functional groups of the materials were determined using a Thermo Nicolet-6700 FT-IR. Their morphology was observed using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. N_2 sorption isotherms of the materials were measured by a Micromeritics TriStar 3000 at -196 °C. The specific surface area of the samples was obtained from isotherm analysis of adsorption data, and their pore diameter distribution was calculated using the Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical characterization

2.3.1. Electrocatalysis characterization

The ORR performance of NMC-1 and C-1 was measured in O_2 or N_2 saturated KOH solution (0.1 mol/L) and recorded with

a potentiostat (CH Instruments, China) at a scan rate of 10 mV/s at room temperature in a conventional three-electrode system. A rotating disk electrode (RDE) system (OrigaTrod RDE, France) was used as the working electrode, and the steps of its preparation were as follows: an electrode mixture comprising 2 mg catalyst and 1 mL ethanol solution containing 0.1 mL Nafion (5 wt%) was ultrasonically treated for 30 min. 5 μL or 10 μL of the suspension was spread on the glassy carbon electrode, followed by drying under ambient conditions. Pt foil was used as the counter electrode, while Ag/AgCl (saturated KCl) was used as the reference electrode.

2.3.2. Characterization of electrochemical energy storage

Electrochemical experiments were conducted using KOH electrolyte (6 mol/L) in a conventional three-electrode cell on a CHI 660D electrochemical workstation (CH Instruments, China). A nickel oxyhydroxide electrode and Hg/HgO electrode were used as the auxiliary and reference electrodes, respectively. The working electrode was prepared by dropping a mixture of the active material, acetylene black and PTFE (5%) in a mass ratio of 75: 15: 10 into a foam nickel current collector. 15 mg of NMC-1 or C-1 was used as the active material.

3. Results and discussion

The four diffraction peaks of NMC-1 were observed at 26°, 43°, 54°, and 78°, as shown in Fig. 1(a), which are consistent with the (002), (100), (004), and (110) planes of graphite, respectively. However, the four peaks were not sharp, indicating a partial graphitization of the NMC-1. Compared with that of NMC-1, the XRD pattern of C-1 only shows a wide peak at 24°, suggesting that C-1 was amorphous carbon. Therefore, $\text{Ni}(\text{NO}_3)_2$ acted as a catalyst in the formation of NMC-1. Figure

Fig. 1. The XRD patterns (a) and IR spectra (b) of NMC-1 (1) and C-1 (2).

Fig. 2. TEM images of NMC-1 (a, b) and C-1 (c, d).

1(b) shows that the carbon materials had abundant nitrogen or oxygen functional groups which would provide pseudocapacitance when the heteroatoms were oxidized and reduced. At the same time, such an N-doped carbon material could also act as a metal-free electrocatalyst for ORR in fuel cells.

The degree of crystallization and porous structure of NMC-1 and C-1 were characterized by TEM, as shown in Fig. 2. Both NMC-1 and C-1 were made up of mesoporous carbon microspheres (see Fig. 2(a) and (c)). Compared with that of C-1 in Fig. 2(d), the mesopores and graphitic lattice fringes of NMC-1 can be clearly observed in the HRTEM image shown in Fig 2(b). C-1 mainly exhibited amorphous carbon and worm-like mesopores. The TEM results confirmed that $\text{Ni}(\text{NO}_3)_2$ catalyzed the reaction of amorphous carbon to form the partly-graphitized NMC-1 at the relatively low temperature.

The porous structure of the as-prepared materials was measured using N_2 adsorption-desorption isotherms. Figure 3(a) shows a type IV isotherm for NMC-1, suggesting the

Fig. 3. N_2 sorption isotherms of NMC-1 (1) and C-1 (2).

existence of mesopores. The BET surface area and pore size distribution (PSD) of NMC-1 were $977 \text{ m}^2/\text{g}$ and 4 nm , respectively; while those of C-1 were $651 \text{ m}^2/\text{g}$ and 7.7 nm , respectively. The larger PSD of C-1 resulted in a decreased BET surface area compared with that of NMC-1. The large surface area of NMC-1 will be helpful with charge storage, the graphitic carbon walls will have good electric conductivity, and the suitable mesoporous structure is advantageous to aqueous electrolyte diffusion. NMC-1 was therefore expected to have good electrochemical performance because of these advantages.

To compare the electrocatalytic activity of NMC-1 and C-1 for ORR, the two carbon materials were tested in N_2 -saturated or O_2 -saturated KOH electrolyte (0.1 mol/L) using cyclic voltammetry. As shown in Fig. 4(a), the reduction peak potentials of the ORR for NMC-1 and C-1 were -0.208 V and -0.225 V , respectively, in KOH solution (0.1 mol/L) saturated with O_2 , which indicates that both as-prepared materials show obvious electrocatalytic activity. The ORR performance of NMC-1 and C-1 was further studied by RDE system, and compared with those of commercial Vulcan XC-72 carbon powder and commercial 50% Pt/C catalyst. Figure 4(b) shows that the limit current of NMC-1 reached 0.746 mA , which is 0.048 mA larger than that of C-1

Fig. 4. (a) CV curves in N_2 -saturated (dashed curves) and O_2 -saturated (solid curves) KOH (0.1 mol/L); (b) ORR polarization curves of XC-72 (1), C-1 (2), NMC-1 (3), and 50%Pt/C (4) in O_2 -saturated KOH (0.1 mol/L) at 1600 r/min ; the scan rate is 10 mV/s .

Fig. 5. (a) RDE sweep linear voltammograms of NMC-1 at different rotation rates in KOH solution (0.1 mol/L) saturated with O₂ at a scan rate of 10 mV/s; (b) Koutecky-Levich plots of NMC-1 at different electrode potentials obtained from the RDE data.

(0.698 mA). The onset potential of NMC-1 was observed at -0.094 V, while that of C-1 was -0.105 V. Thus, NMC-1 showed slightly better electrocatalytic activity than C-1. Moreover, the limit current and the onset potential of Vulcan XC-72 carbon are 0.349 mA and -0.227 V, respectively; whereas those of Pt/C catalyst are 0.894 mA and 0.082 V, respectively. Obviously, the performance of the two as-synthesized materials was much better than that of Vulcan XC-72 carbon, whereas they still cannot compete with that of Pt/C catalyst. However, the present N-doped carbon is cheaper than Pt/C.

Sweep linear voltammograms (SLVs) were carried out to explore the possible mechanism of ORR on NMC-1. Figure 5(a) shows the ORR SLV of NMC-1 at different rotation rates (400–2500 r/min). The limit current density of NMC-1 for ORR was gradually enhanced with increasing rotation speed. Furthermore, the corresponding Koutecky-Levich (K-L) plots at different electrode potentials are linear and parallel, suggesting that the first-order kinetic process of ORR on NMC-1 is a dissolved oxygen process. The number of electrons transferred in ORR can be calculated using the K-L equation:

$$J^{-1} = J_L^{-1} + J_K^{-1} = (B\omega^{1/2})^{-1} + J_K^{-1} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

where J (mA/cm²) is the measured current density, related to the Levich current (J_L) and kinetic current (J_K), ω is the RDE rotation speed, n is the ORR electron transfer number, F is the Faraday constant (96486.4 C/mol), C_0 is the bulk concentration of oxygen in air-saturated KOH (0.1 mol/L) (1.21×10^{-6} mol/cm³), ν is the kinematic viscosity of the water (0.01 cm²/s), and D_0 is the diffusion coefficient of oxygen in KOH (0.1 mol/L) (1.9×10^{-5} cm²/s). Figure 5(b) gives the linear plot of J^{-1} versus $\omega^{-1/2}$ possessing a slope of $1/0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$. An n value of 2.5–2.8 is calculated based on equations (1) and (2), demonstrating that ORR on NMC-1 is both a 4-electron reaction and a 2-electron reaction. That is, some O₂ is catalytically reduced to H₂O, while the rest becomes -OOH-.

The cyclic stability of catalysts is extremely vital for practical application. A comparison of the cycle durability of NMC-1 and 50% Pt/C catalyst was conducted by chronopotentiometry. Both catalysts were continually

tested for 2000 s at a potential of -0.4 V and rotation rate of 1600 r/min in O₂-saturated KOH (0.1 mol/L). As shown in Fig. 6, NMC-1 exhibited higher cyclic stability (88.2%) than the 50% Pt/C catalyst (81.6%), which is probably ascribed to the special graphitic structure or the crystal lattice orientation of NMC-1. However, Pt/C catalysts generally use amorphous carbon black as the support. Thus, carbon black is easily corroded under harsh potentials, causing the Pt nanoparticles to come loose from the electrode or aggregate into larger particles. The low-cost and outstanding anti-corrosion property of NMC-1 make it a promising electrocatalyst for alkaline fuel cells.

The electrochemical energy storage ability of NMC-1 was studied by cyclic voltammetry (CV) and galvanostatic charge/discharge in KOH electrolyte (6 mol/L) using a 3-electrode system. The CV behavior shown in Fig. 7(a) exhibited a distorted rectangle compared to typical EDLC because of pseudocapacitance caused by the redox reaction of heteroatoms from nitrogen and oxygen functional groups in NMC-1. The galvanostatic charge/discharge curves of NMC-1 at different current densities indicate that the specific capacitance of NMC-1 reached 252 F/g at 0.2 A/g (see Fig. 7(b)).

The capacitances of NMC-1 and C-1 obtained from gal-

Fig. 6. Current-time (*i-t*) and chronoamperometric responses of the NMC-1 and 50% Pt/C-modified GC electrodes, at -0.4 V in O₂-saturated KOH solution (0.1 mol/L) at a rotation of 1600 r/min.

Fig. 7. (a) Cyclic voltammograms of NMC-1 at different scan rates in KOH electrolyte (6 mol/L); (b) Galvanostatic charge/discharge curves of NMC-1 at different current densities.

vanostatic charge/discharge curves at different current densities are listed in Table 1. The specific capacitance of NMC-1 became more superior to that of C-1 with increasing current density, demonstrating that NMC-1 had better capacitive performance because its BET surface area (977 m²/g) was larger than that of C-1 (651 m²/g). The higher surface area provided for a larger electrolyte/electrode material interface, resulting in higher electric double-layer capacitance.

The cycle stability of NMC-1 was measured by cyclic voltammetry at 100 mV/s. Figure 8 shows that the capacitance retention of NMC-1 was about 105% at the 6000th cycle, implying that NMC-1 is an excellent candidate as a supercapacitors electrode material because of its corrosion resistance, which should be ascribed to the part-graphitic structure of NMC-1. Compared with the initial specific capacitance, the specific capacitance of the 6000th

Table 1

A_{BET} and capacitances of NMC-1 and C-1 obtained from galvanostatic charge/discharge curves at different current densities.

Material	A_{BET} (m ² /g)	C_g /(F/g)				
		0.2 A/g	0.5 A/g	1 A/g	2 A/g	5 A/g
NMC-1	977	252	222	200	183	159
C-1	651	209	185	171	158	149

Fig. 8. Cycle stability of NMC-1 at 100 mV/s over 6000 cycles.

cycle for NMC-1 was slightly increased, corresponding to the fact that some micropores could be utilized to contribute to the capacitance over the long cycle duration [23].

4. Conclusions

In summary, the bifunctional material NMC-1 has been successfully prepared using renewable chitosan as an N-doped carbon source. Moreover, NMC-1 is considerably anti-corrosive and possesses high electrocatalytic activity for ORR as well as good electrochemical energy storage performance. These prominent factors make it promising as an electrocatalyst and supercapacitor electrode material. However, the realization of higher graphitization and nitrogen content, which will improve the efficiency of electron transfer and the rate of ion diffusion, remains to be further studied.

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Graphical Abstract

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N-doped mesoporous carbon as a bifunctional material for oxygen reduction reaction and supercapacitors

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An N-doped mesoporous carbon synthesized from chitosan showed effective activity as an electrocatalyst for the oxygen reduction reaction and high capacitance as an electrochemical energy storage material for ultracapacitors.

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掺氮介孔炭作为双功能材料用于氧还原与超级电容器

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摘要: 以壳聚糖为含氮碳源, 正硅酸乙酯为软模板, 硝酸镍为催化剂, 通过简单的低温水热法及后续炭化, 成功合成出掺氮介孔炭材料(NMC-1)。NMC-1含有多孔结构以及氮氧等杂原子, 能提高其电催化性能、双电层电容与赝电容。由于NMC-1在碱液中表现出显著的催化氧还原反应活性和具有较高的超级电容器比电容(在0.2 A/g时为252 F/g)及好的循环稳定性, 因此, 它有可能作为一种可再生、环保的双功能材料同时应用于燃料电池与超级电容器领域。

关键词: 掺氮介孔炭材料; 壳聚糖; 电催化; 氧还原反应; 超级电容器

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