

Preparation of hollow mesoporous carbon spheres and their performances for electrochemical applications

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Abstract. Hollow carbon materials have received intensive attention for energy storage/conversion applications due to their attractive properties of high conductivity, high surface area, large void and short diffusion pathway. In this work, a novel hollow mesoporous material based on carbide-derived carbon (CDC) is presented. CDC is a new class of carbon material synthesized by the selective extraction of metals from metal carbides. With a two-stage extraction procedure of carbides with chlorine, firstly hybrid core-shell carbon particles were synthesized, i.e. mesoporous/graphitic carbon shells covering microporous/amorphous carbon cores. The amorphous cores were then selectively removed from particles by a careful oxidative treatment utilizing its low thermal characters while the more stable carbon shells remained, thus resulting hollow particles. The characterization methods (e.g. N₂ sorption, Raman spectroscopy, temperature-programmed oxidation and SEM) proved the successful synthesis of the aspired material. In electric double-layer capacitor (EDLC) testing, this novel hollow core material showed a remarkable enhancement of EDLC's rate handling ability (75% at a high scan rate) with respect to an entirely solid-mesoporous material. Furthermore, as a fuel cell catalyst support the material showed higher Pt mass activity (a factor of 1.8) compared to a conventional carbon support for methanol oxidation without noticeably decreasing activity in a long-term testing. Therefore, this carbon nanostructure shows great promises as efficient electrode materials for energy storage and conversion systems.

Keywords: Carbide-derived carbon, Electric-double layer capacitors, Hollow carbon spheres, Methanol oxidation

1. Introduction

Porous carbons play an important role in electrochemical applications. They have been used as electrode material of electric double-layer capacitors (EDLC) and catalyst support for fuel cell electrodes [1]. Hollow carbon spheres are types of structured carbon materials which have received much attention. This is due to their attractive properties of high surface area, large void and short diffusion pathway [2]. A common method to synthesize hollow carbon sphere is templating routes using polymeric materials as carbon precursors [3,4]. Nevertheless, with this method, typically a low degree of carbon ordering results (amorphous structures). Therefore, the produced material features



low electrical conductivity and poor electrochemical stability. These properties, however, are a major drawback in electrochemical devices [5,6]

In this work, hollow-core carbon material based on carbide-derived carbon (CDC) is presented. CDC is a new class of carbon material synthesized by the selective extraction of metals from metal carbides. The special advantage of CDC is its tuneable micro- and pore structures [7–9]. Therefore, it is possible to vary carbon micro- and pore structures within a particle in a core-shell arrangement which is the basis of the successful preparation of hollow core carbon spheres. The hollow core carbon produced was then tested for EDLC electrode and electrocatalysts support for methanol oxidation and the results are discussed.

2. Materials and methods

2.1. Materials

Commercial titanium carbide (TiC, Alfa Aesar) was employed as carbon precursor. Chlorine and hydrogen diluted by helium were used to perform selective extraction of titanium from the carbide matrix (called chlorination process) and subsequent surface annealing. All gases were purchased from Linde AG. In EDLC testing, tetraethylammonium tetrafluoroborate ($\text{NEt}_4\text{-BF}_4$, Sigma Aldrich) in acetonitrile were used as electrolyte. For preparation of catalyst, hydrochloroplatinic acid ($\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$, ABCR GmbH) was used as platinum precursor.

2.2. Material synthesis

Hollow core CDC particles (named as hollow carbon spheres (HCS)) were produced from nonporous commercial TiC particles *via* two-step procedure as shown in **Figure 1** and described as follows.

- i) A two-step chlorine etching to prepare an interim material of mesoporous/graphitic-microporous/amorphous carbon called as Meso-Micro Carbon.
- ii) Amorphous carbon core removal by careful oxidative treatment at 430 °C.

Detail procedures of CDC synthesis are provided in [9,10]. As reference materials, CDC-800 and CDC-1200 were synthesized at fixed Cl_2 etching temperature of 800 °C and 1200 °C, respectively.

For preparation of fuel cell anode catalyst, a wet impregnation method was used to disperse platinum precursor ($\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$) on HCS followed by a hydrogen reduction step at 260 °C

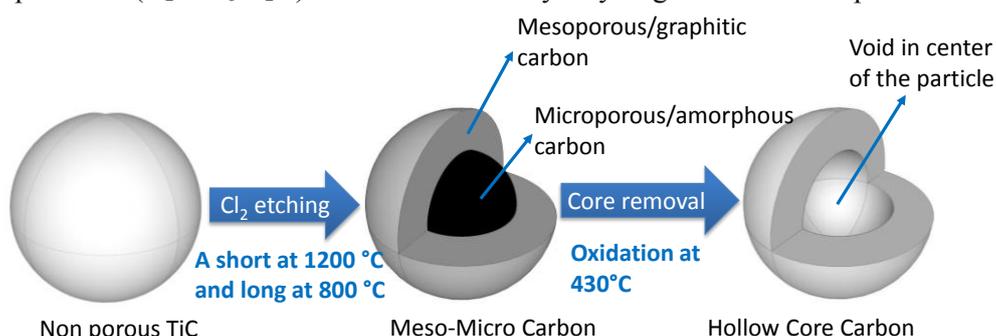


Figure 1. Schematic preparation of hollow core carbon particle from carbide.

2.3. Characterization methods

The properties of materials were characterized using N_2 -sorption (Quantachrome Quadrasorb Si-MP), scanning electron microscopy (SEM, Philips XL 30) and temperature-programmed oxidation (TPO, Netzsch STA 409 PC Luxx).

2.4. Characterization methods

For supercapacitor testing, the working electrode was prepared by mixing carbon particles (95 wt.%) with 5% Nafion binders dispersed in isopropanol. After the mixing process, the ink was then applied onto glassy carbon electrode. Cyclic voltammograms and galvanostatic cycling data of the electrode

were recorded with a PARSTAT 4000. For methanol oxidation, the electrode was prepared by combining catalyst (20% Pt/carbon) with 5% Nafion binders. The three-electrode system was employed to test the catalyst by recording cyclic voltammetry (CV) data. An Ag/AgCl electrode and a Pt wire were used as the reference and counter electrodes, respectively.

3. Results and discussion

3.1. Successful synthesis of hollow core carbon particles

A short reaction of chlorination at 1200 °C yielded the partially extracted carbide particles (carbon/carbide matrix) with 35% conversion. TEM characterization of this material indicated that the carbon shells enveloped the unreacted carbide cores (data not shown). The second conversion step of the unreacted core within chlorination at 800 °C yielded the carbon core. TPO characterization showed that Meso-Micro Carbon featured a bimodal microstructure showing a combination of material properties of CDC-1200 (graphitic) in the shell and CDC-800 (amorphous) in the core.

Selective removal of the amorphous core was carried out by mild oxidation process at 430 °C. The TPO profile of Meso-Micro Carbon was compared to the reference materials (see **Figure 2a**). The figure shows that CDC-800 reference material could be fully oxidized while CDC-1200 exhibits no mass change after 14 hours of the oxidation process. This shows that the shell material has different thermal stabilities compared to the core material which is likely due to different graphitization degree [11]. The oxidation profile of Meso-Micro Carbon shows a mass decrease till 70 wt.% indicating a complete removal of carbon in the core. The final oxidized particles were then mechanically crushed and SEM image was taken. **Figure 2b** shows clearly that carbons shell envelopes a hollow core. With all evidence, we can conclude that the hollow core material was successfully synthesized.

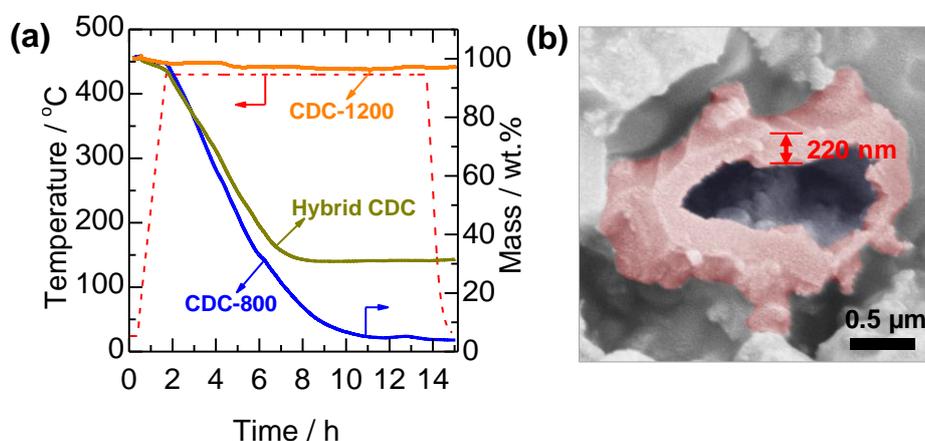


Figure 2. a) TPO profiles of materials. b) SEM image of a cracked carbon particle showing only carbon shell after selective removal of amorphous core. Figure 2B adapted with permission from [5]. Copyright 2015 Elsevier.

3.2. Electrochemical performances

Figure 3a compares the gravimetric capacitance of hollow core material and CDC-1200. At the low scan rate of 5 mV s⁻¹ both materials feature a similar capacitance value (ca. 32 F g⁻¹). With increasing scan rate, the hollow core material exhibits better characteristics to maintain its initial capacitance than the CDC-1200. While only minor decrease in capacitance (30%) is seen for the hollow core material, the entirely solid mesoporous of CDC-1200 shows a huge drop of 62% at the highest scan rate of 5000 mV s⁻¹. Therefore, the hollow core material shows promising application for high rate EDLCs.

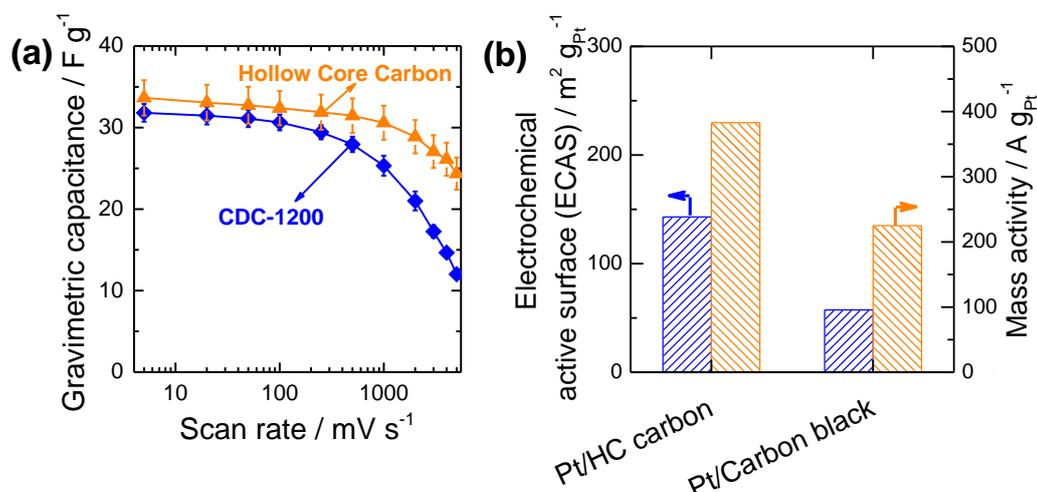


Figure 3. a) Specific capacitance of material evaluated by CV method. b) Active surface and performance of electrocatalysts of hollow core carbon support (Pt/HC carbon) and conventional support material of carbon black (Pt/CB) at 0.6 V.

The hollow core material was employed as catalyst supports. The catalyst characteristics and performances are summarized in **Figure 3b**. Pt/Hollow Carbon Spheres features high electrochemically active surface (ECAS) up to 140 m² g_{Pt}⁻¹. This is remarkably larger than that of the Pt immobilized on a conventional carbon black (60 m² g_{Pt}⁻¹). In the methanol electro-oxidation, Pt/HCS shows a remarkable activity of 390 A g_{Pt}⁻¹@ 0.6 V, which is 1.8 times that of Pt/CB.

4. Conclusions

Hollow core-mesoporous carbon spheres were successfully synthesized based on the CDC method. The novel material showed promising application for electric-double layer capacitor electrode and catalyst support for methanol electro-oxidation.

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