



Carbide-derived carbon with hollow core structure and its performance as catalyst support for methanol electro-oxidation



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ABSTRACT

New hollow core particles of mesoporous/graphitic carbon were successfully prepared from carbon core-shell particles, through selective removal of the core. Electrocatalysts prepared by dispersing platinum on these hollow core materials showed remarkably high dispersion. The combination of high dispersion with short pore diffusion length allowed to obtain high mass specific activity in methanol electro-oxidation (ca. 390 A g_{Pt}⁻¹), along with excellent long-term stability. These novel carbon nanostructures show great promise as Pt catalyst support for methanol oxidation.

1. Introduction

Direct methanol fuel cells (DMFCs) featuring high efficiency and low emission to the environment have attracted intensive research interest for over three decades, because of their important roles in the future clean energy solutions. DMFC converts chemical energy to direct usable electrical energy via redox reactions on electrodes [1]. Methanol electro-oxidation takes place at the anode side which is catalyzed typically by Pt supported on carbonaceous materials [2]. A low Pt particle dispersion on carbon supports and Pt poisoning by intermediate substances are major causes for low mass activity and poor long-term stability of anodic catalysts [3,4]. Besides directly engineering the structure of active sites (Pt), architecting catalyst support is an important alternative approach to efficient anodic catalytic systems [5].

Hollow core material could tackle the challenge to provide efficient electrode systems for DMFC systems, due to its outstanding combination of high surface area with thin shells [6]. A high surface area is necessary to provide a large space for immobilizing Pt particles or ions [7], while the thin shell facilitates rapid transports of molecules and/or electrolyte [8,9]. Templating routes employing polymeric carbon precursors are commonly used to synthesize hollow core materials [10–12]. Nevertheless, the carbon shell usually features a low graphitic degree, resulting in poor electrical conductivity and electrochemical stability [13,14]. Both place a major drawback for electrochemical devices. Recently, we reported that core-shell structured carbon materials (Hybrid-CDC in Fig. 1) with mesoporous graphitic shell (CDC-1200) enveloping microporous amorphous core (CDC-800) was synthesized by the reactive extraction of

carbides (carbide-derived carbons, CDC) [14,15]. Inspired by these hybrid materials, herein we made our first attempt to extend this strategy for fabricating hollow core carbon materials. We found that hollow core structured carbon with graphitic mesoporous shell is readily obtained from the core-shell carbon (Hybrid-CDC), by selectively removing the amorphous core through oxidation. Further attempt was also made to explore the electrochemical performance of the as-synthesized hollow core carbon as electrocatalyst support for immobilizing Pt nanoparticles. It is disclosed that for methanol oxidation the hollow carbon based catalysts exhibits both high activities and extraordinary stability for methanol oxidation.

2. Experimental section

2.1. Material preparation

Hybrid-CDC was synthesized by a two-step chlorine etching (a short etching at 1200 °C followed by a long etching until full conversion at 800 °C) of commercial TiC (99.5%, 3 μm average diameter, Alfa Aesar). Hollow core CDC (CDC-HC) was produced by selective oxidation of the carbon core at 430 °C for 10 h. The schematic preparation of CDC-HC is shown in Fig. 1. CDC references were synthesized at fixed Cl₂ etching temperature of 800 °C (CDC-800) and 1200 °C (CDC-1200) [16]. Pt-supported carbons with the target loading of 20 wt% were synthesized by impregnation and subsequent reduction with hydrogen (20 vol% H₂/N₂ at 260 °C) [17]. Commercially available Pt/C catalyst (20 wt%, HiSPEC-3000, Johnson Matthey) was purchased from Alfa Aesar.

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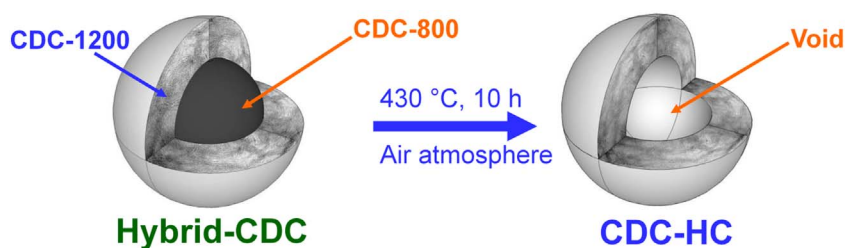


Fig. 1. Scheme of synthesis of a hollow core material based on CDC route.

2.2. Characterization methods

Temperature-programmed oxidation (TPO) was performed on Netzsch STA 409 PC Luxx. The material was heated from room temperature to 800 °C with ramp rate of 2.5 °C min⁻¹ under air flow. The SEM was performed using a Zeiss Gemini Ultra-55 at 2 kV. Pore structure was characterized by N₂ sorption at -196 °C (Quantachrome Quadrasorb Si-MP) and evaluated by Quenched Solid State Density Functional Theory (QSDFT) model assuming slit-shaped pores [18]. A Philips CM300-UT operated at 300 kV was employed for HRTEM. The platinum content was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.3. Electrochemical testing

The working electrode was prepared by mixing 5 mg of catalyst, 0.5 mL of isopropanol, 2 mL of deionized water and 10 μL (5 wt%) of Nafion solution. The mixture was sonicated and the homogenous ink was applied onto a polished glassy carbon electrode (*d* = 0.5 cm). Electrochemical measurements were performed with the three-electrode system connected to PARSTAT 4000. A double-junction Ag/AgCl electrode and a Pt wire were employed as the reference and counter electrodes, respectively. All potentials are reported against the reversible hydrogen electrode (RHE). Methanol oxidation was characterized by cyclic voltammetry (CV) in the potential window of 0.05–1.10 V vs. RHE using 0.5 M CH₃OH in 0.5 M H₂SO₄ electrolyte. The working electrode was firstly pretreated at a scanning rate of 50 mV s⁻¹ in the potential range from -0.1 to 1.2 V vs. RHE for 20 cycles. The chronoamperometry was carried out for up to 3600 s at a constant potential of 0.6 V.

3. Results and discussion

In order to obtain CDC-HC by selectively removing the amorphous core of the Hybrid-CDC, their oxidation characteristics were studied by using TPO. The core-shell material and the reference materials (CDC-800, CDC-1200) were studied. Both reference materials show unimodal curves, with peak centering at 530 °C (Peak I) and 620 °C (Peak II) for CDC-800 and CDC-1200, respectively, indicating a homogenous oxidation behavior due to a homogeneous microstructure. The differences in peak positions stem from the different graphitization degrees. CDC produced at higher reaction temperature shows higher thermal stability [16], i.e., the oxidation onset temperatures are at 375 and 500 °C for CDC-800 (point A) and CDC-1200 (point B of Fig. 2a), respectively. Interestingly, Hybrid-CDC shows an oxidation profile comprising two distinct peaks featuring those of CDC-1200 (shell) and CDC-800 (core), respectively. By integrating the peak area, the portion of graphitic degree of carbon shell was estimated to be 26% of the entire carbon particle.

As stabilities can be overestimated with temperature programmed methods, the isothermal oxidation behavior at 430 °C was studied in more detail. While CDC-1200 displays no mass loss, the amorphous material of CDC-800 shows a linear decrease in mass and is fully oxidized after approx. 10 h (see Fig. 2b). The Hybrid-CDC shows a mass decrease till reaching a plateau at 70 wt% mass loss after 7 h. Since the

carbon shell is thermally stable at this oxidation temperature as CDC-1200, this implies a complete removal of the amorphous carbon core. The remaining mass (30 wt%) is comparable to the graphitic content (Peak II) deduced from Fig. 2a. Moreover, the resultant CDC-HC shows a similar particle size distribution and Sauter diameter (3.0 μm) as Hybrid-CDC (dynamic light scattering data not shown). It suggests that the size/shape of materials remained while the core part was selectively removed from particles. Fig. 2c shows the SEM image of the CDC-HC material after mechanically crushing, displaying a particle with a defect structure. The hollow carbon shell clearly verifies that the hollow core material is successfully synthesized. The textural properties of materials were characterized using N₂-physisorption. The CDC-HC showed the specific surface area of 970 m² g⁻¹, which is the same as that of CDC-1200. This further evidences the complete removal of amorphous core and the remaining shell features CDC-1200 like structure. The pore structures of Hybrid-CDC and CDC-HC are compared in Fig. 2d. Pores in micro-/meso-pore range are featured by Hybrid-CDC centered at ca. 0.8 and ca. 3.2 nm. Pores in CDC-HC show a remarkable decrease in the micropore regime followed by a significant increase in mesopore range due to the selective removal of the microporous/amorphous structure.

CDC-HC and conventional carbon black (CB) were employed as Pt catalyst support and compared for methanol electro-oxidation. The Pt contents in Pt/CB and Pt/CDC-HC determined by ICP-AES are 18.0 wt% and 16.1 wt%, respectively. The Pt loading on the glassy carbon electrode was set to 35 μg cm⁻². To characterize the resulting catalysts, CV curves were recorded in N₂-saturated 0.5 M H₂SO₄ at the scan rate of 20 mV s⁻¹ (see Fig. 3a). The CV curves on both catalysts exhibit characteristic H adsorption/desorption on Pt in the potential region of 0 to 0.25 V, followed by pseudo-capacitive double layer charging regime and surface Pt oxidation beyond 0.6 V. Pt/CDC-HC exhibits a remarkably larger capacitance current than Pt/CB due to the larger surface area of CDC-HC, as reflected by the CV curves on pure carbon (see the inset of Fig. 3a). The electrochemically active surfaces (ECAS) were evaluated from the hydrogen desorption region [19] of CV profiles (after the double layer charging current correction) associated with monolayer coverage of hydrogen on platinum. The reference Pt/CB features an ECAS value of 60 m² g_{Pt}⁻¹ corresponding to a theoretical average Pt size of 4.9 nm. Interestingly, a 2.4-times higher ECAS value (145 m² g_{Pt}⁻¹) is obtained when using the CDC-HC as the support, indicating the higher dispersion of platinum particles with average size of 2 nm. The high specific surface area (ca. 1000 m² g⁻¹) and mesoporous structure of the carbon support (CDC-HC) could be responsible for the higher dispersion of Pt particle [7]. To gain more insight into the particle size and dispersion of Pt on the hollow core material, TEM characterization was carried out. As seen in Fig. 3b, a highly dispersed Pt particle on pores of graphitic carbon support is observed, with a mean diameter of 1.9 nm ± 0.3 nm, corroborating the observation from the electrochemical measurement.

Methanol electro-oxidation properties were studied by recording CV curves in N₂-saturated 0.5 M H₂SO₄ + 0.5 M CH₃OH electrolyte at the scan rate of 20 mV s⁻¹. The two forward peaks (*I*_f and *I*_f') observed in Fig. 3c are associated with the oxidation of methanol, while the one reverse peak (*I*_r) represents the oxidation of methanol on low coordinated platinum atoms present during the reduction of Pt oxides [20–22]. Pt/CDC-HC exhibits a higher value (1.3) of the ratio between

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