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Complex electrochemical investigation of ordered mesoporous carbon synthesized by soft-templating method: charge storage and electrocatalytical or Pt-electrocatalyst supporting behavior

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ABSTRACT

Ordered mesoporous carbon (OMC) was synthesized by an evaporation induced self-assembly method, under acidic conditions, with resorcinol as the carbon precursor and Pluronic F127 triblock copolymer ($EO_{106}PO_{70}EO_{106}$) as a structure directing agent. The obtained OMC product was characterized by N_2 sorptometry, X-ray diffractometry and Raman spectroscopy. The mean pore radius of 2 nm and specific surface area of 712 $m^2\,g^{-1}$ were found. The OMC sample was subjected to a complex electrochemical testing in order to check for its applicability in various energy conversion processes. For pure OMC, the charge storage properties and kinetics of oxygen reduction reaction (ORR) in alkaline solution were measured. The OMC sample delivered specific capacitance of 232 $F\,g^{-1}$ at 5 $mV\,s^{-1}$ with 83.6% capacitance retained at 100 $mV\,s^{-1}$. Effective ORR electrocatalysis by OMC in alkaline media was evidenced, with onset potential amounting to −0.10 V *vs.* saturated calomel electrode. A part of the OMC sample was used as a support of Pt nanoparticles, and examined as electrocatalyst for hydrogen evolution reaction (HOR) and ORR in acidic media. Reversible HOR kinetics was observed, while ORR performances were found to be competitive to the ones on other carbon-supported Pt electrocatalysts reported so far. A superb electrochemical behavior was correlated to physico-chemical properties of OMC. Described OMC stands out as a highly versatile material, which can be used to replace carbon materials developed for specific purposes, allowing rationalization of carbon-based technologies aimed for energy conversion purposes.

1. Introduction

Ordered mesoporous carbons (OMCs) belong to a family of porous materials which have drown great attention in recent years, representing a huge challenge for material scientists. Research in this area is based on the tuning of the features of OMCs for specific applications and on elucidation of the mechanisms of their synthesis and physico-chemical interactions with other materials and chemical species.

OMCs are characteristic of hydrophobic surfaces, high surface area, large pore volume, chemical inertness, good thermal and mechanical stability, easy handling and low cost of manufacture [1]. In addition, structure variances, morphology and composition result in a range of potential applications in: catalysis as catalysts and catalyst supports [2,3], separation [4], adsorption [5], energy storage [6], as molecular sieves [7] etc. More interestingly, nanostructured OMC composites which involve wide spectrum of chemical elements, oxides or sulphides exert novel electronic, optical, magnetic, and other properties [8].

Several strategies have been proposed for the synthesis of porous carbons including carbonization of polymer blends [9], organic gels [10], colloidal imprinting [11] and catalytic activation [12]. In general, two approaches have been established. Nanocasting was first developed by Ryoo and Hyoen's research groups independently, as an approach to fabricate ordered mesoporous carbons using a mesoporous silicate as a hard template [13,14]. The idea was based on preparation of adequate silica template, filling of the carbon precursor into the channels of the silica, carbonization of the precursor, and final etching of the template with the aid of acids [15,16]. Since this process is now regarded as being intricate, expensive and time-consuming, direct (soft) templating imposed itself as a promising approach to obtain carbon materials of preferred pore structure. This method includes the self-assembly of resol resin and block copolymer surfactant into periodical mesoscopic structure under controlled conditions followed by precursor cross-linking, subsequent removal of polymer

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framework, and final carbonization of carbonaceous matrix which results in desired mesoporous carbon structure [15]. It may be conducted by employing evaporation-induced self-assembly (EISA) method, dilute aqueous route, macroscopic phase separation and hydrothermal autoclaving [15]. The correlation between structural, mechanical, electrochemical and catalytic properties of OMC will help better understanding of its structure-activity relationship.

Sustainable energy development incites great challenges and opportunities for industrial advancement in the near future. Fuel cells are a clean way of producing electric energy through redox reactions using hydrogen, methanol, ethanol etc. as fuels. The most active electrocatalysts for proton exchange membrane fuel cells (PEMFC) and electrolyzers are based on the Pt-group metals, which have been used to catalyze both anodic reaction (hydrogen oxidation reaction, HOR) and cathodic reaction (oxygen reduction reaction, ORR). Nanoscaling of noble metal particles to more active sites per mass unit is achieved through the use of proper catalytic support. Good support has high surface area, good dispersion of catalyst loadings, suitable pore formation for smooth mass transfer of the fuel, high electrical conductivity for good electron transfer through the electrode, and good electrochemical corrosion resistance [17]. Current status in the field presents carbon-based catalyst as most widely used ones [17]. Moreover, nanosized carbonaceous materials also have purposes in other fields of energy conversion applications. These materials are intensively investigated as ORR catalysts with an attempt to replace noble metal electrocatalysts with cheaper ones. If not doped with some heteroatom (N, P, B), these materials poses high intrinsic activity towards ORR in alkaline media, being attractive in the field of alkaline fuel cells (AFC) and metal-air batteries. In the case of metal-free carbonaceous catalysts appropriate pore structure is necessary for high ORR activity allowing access of O_2 to large fraction surface area where it is reduced to HO_2^- or OH^-, depending on the applied electrode potential and the state of materials surface [18]. Also, carbonaceous materials have been traditionally used as electrode materials for electrochemical capacitors, where its large surface area is utilized to store significant amounts of energy at carbon/solution interface, allowing fast delivery of stored energy when necessary. Nevertheless, in a traditional approach, specific carbon materials are used for different purposes related to energy conversion applications. For example, Vulcan XC-72 is often used as an electrocatalyst support but it has gravimetric capacitance of only 27 F g^{-1} [19] so it is not attractive as electrode material for electrochemical capacitors.

According to the overview provided above, OMC has desirable properties to be applied either as a catalyst support, ORR catalyst in alkaline media or electrode material in electrochemical capacitors. In fact, applicability of different OMCs in some particular fields of energy conversion and storage has been demonstrated so far, as it will be referred later on.

From practical aspect, it is interesting to develop the materials joining a wide range of possible applications in themselves, which would economize synthesis and production costs, in a sense that a material from a single batch can be used in different fields without compromising performances, and OMCs seem to be a satisfactory choice. Regarding energy conversion applications there is an interesting example from automotive applications where different power source systems are used complementary to improve engine performance. In specific, fuel cell powered engine is augmented by electrochemical capacitors to achieve more responsive performance (we avoid to specify the manufacturer as no commercial interest exists in presented work). As presented above, carbon materials have significant role in fuel cell and electrochemical capacitor technologies and an identification of a single material which meets the standards required for both type of applications would have significant impact in the field. To prove the assumption that attractive physico-chemical properties of OMCs provide its wide applicability, in this study we synthesized a sample of OMC by a method known from the literature and subjected it to a complex electrochemical investigation regarding its energy conversion applications. First, pure OMC was examined as electrode material for electrochemical capacitors, and as ORR electrocatalyst in alkaline media. In the second part, OMC was investigated as inert catalyst support for Pt-based electrocatalyst utilized to catalyze HOR and ORR in acidic media. It was demonstrated that the investigated OMC presents itself as a versatile material for a wide range of applications in the field of energy conversion, competitive in performances to the state-of-the-art materials derived for specific applications.

2. Experimental

2.1. Synthesis and physico-chemical charaterization of OMC

OMC was synthesized by EISA method under acidic conditions with resorcinol as the carbon precursor, in a way almost identical to that developed by Zhang group [20]. For this purpose, 1.65 g (0.015 mol) of resorcinol was dissolved in a solution composed of 2.5 g of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) (Sigma-Aldrich) and 20 g of ethanol/water (1/1 vol. %) under stirring at room temperature. After 30 min, 0.2 g of HCl (37 wt. %) was added as a catalyst and stirred for two hours. Afterwards, 2.5 g (0.030 mol, R/F = 1/2) of formaldehyde (37 wt. %) was added dropwise and stirred for another hour. When the mixture turned cloudy and began separating into two layers, it was further kept aging for 96 h. After this time, the upper layer was discarded while the lower polymer-rich phase was stirred overnight until a sticky monolith was formed. Finally, the monolith was cured at 85 °C for 48 h and carbonized under nitrogen atmosphere at 800 °C for 3 h at a ramping rate of 5 °C/min. After cooling down to room temperature, the material was kept in sealed PVC bottle denoted as OMC-SAM-800/3.

Adsorption and desorption of N_2 on OMC-SAM-800/3 was measured at −196 °C using the gravimetric McBain method. From the obtained isotherms, the specific surface area (S_{BET}) pore size distribution, mesopore including external surface area (S_{meso}) and micropore volume (V_{mic}) of the samples were calculated. Pore size distribution was estimated by applying BJH method [21] to the desorption branch of the isotherms. Mesopore surface and micropore volume were estimated using the high-resolution α_s–plot method [22–24]. Micropore surface (S_{mic}) was calculated by subtracting S_{meso} from S_{BET}.

Powders of pure OMC-SAM-800/3 and Pt-OMC-SAM-800/3 were characterized at room temperature by XRPD using Ultima IV Rigaku diffractometer, equipped with Cu Kα1,2 radiation source, using a generator voltage of 40.0 kV and a generator current of 40.0 mA. The range of 10 - 90°2θ was used for all powders in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 2°/min.

Raman spectra excited with a diode pumped solid state high-brightness laser (532 nm) were collected on a DXR Raman microscope (Thermo Scientific, USA) equipped with an Olympus optical microscope and a CCD detector. The powdered sample was placed on X–Y motorized sample stage. The laser beam was focused on the sample using objective magnification 10X. The scattered light was analyzed by the spectrograph with a grating 900 lines mm^{-1}. Laser power was kept at 1 mW.

2.2. Synthesis and physico-chemical characterization of Pt/OMC catalyst

Platinum nanoparticles were deposited on the surface of the OMC-SAM-800/3 by a following procedure. The OMC-SAM-800/3