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$Pt/C_{N\text{-doped}}$ electrocatalysts: Superior electrocatalytic activity for methanol oxidation reaction and mechanistic insight into interfacial enhancement

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ABSTRACT

Nitrogen-doped ordered mesoporous carbon (NOMC) is studied as the support to synthesize a $Pt/C_{N\text{-doped}}$ catalyst for methanol oxidation reaction (MOR). The effects of carbon dimension and metal loading are investigated by nitrogen ad/desorption isotherms, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical methods. Both TEM and XRD results show that platinum nanoparticles (Pt NPs) are highly dispersed on NOMC with a uniform and narrow distribution, while the dimension of NOMC has a considerable effect on the dispersion of Pt. For 10 wt% metal loading, the average diameter of Pt NPs on 2D-NOMC is 1.40 nm; smaller than that on 3D-NOMC (1.90 nm). XPS results reveal that a strong electronic interaction exists between Pt and NOMC, indicating the formation of Pt–N bonds at the interface. Such an interaction gets more pronounced in the case of low Pt loadings and low-dimensional supports; the reason is that the 2D support is more accessible to load Pt and the metal-support interface is better developed at low metal loadings.

The electrochemical results are well correlated with the physiochemical characterizations. 1) The electrochemically active surface area of Pt is higher on the 2D-support than that on the 3D-one, confirming the better dispersion of Pt on NOMC-2D. 2) A positive shift in the potential is observed for the adsorption of oxygen-containing species onto Pt, which is indicative of the charge transfer from Pt to the support and the formation of Pt–N bonds. 3) Both onset and peak potentials are negatively shifted by *ca.* 50 mV for MOR on 10 wt% Pt/NOMC-2D, as compared with the commercial Pt/XC-72. The ratio of forward to backward current, a measure of poisoning tolerance, is 1.1 on Pt/NOMC-2D and 0.80 on Pt/XC-72R. This enhancement can be attributed to the bifunctional mechanism at the $Pt/C_{N\text{-doped}}$ interface. In MOR, CO-like intermediate species on Pt can be effectively stripped off by the adjacent active –OH species on carbon, generated at lower potentials.

1. Introduction

In the last decade, the direct methanol fuel cell (DMFC) has been extensively studied as it shows a promise in electronic applications [1]. The DMFC offers many advantages, such as the fast fuel charging, simple operation, and high energy density; however, there are still a number of issues left to be resolved. First, its cost is too high as the noble metal Pt catalyst is required and its usage is high up to 6 mg cm^{-2} [2–7]. Second, the performance does not meet the

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requirement of practical application due to the slow kinetics of the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) on the current Pt catalyst [8–11]. To address these issues, it is highly desirable to increase the specific activity of Pt and its anti-poisoning ability against CO-like intermediate species in the MOR.

Carbon black powders (like Vulcan XC-72R, BP-2000) are commercially used as the support to increase the dispersion and specific activity of Pt [12,13]. Recently, nanostructured carbons, like carbon nanotube [14–16], carbon nanofiber [17,18], graphene [19], which are featured by either high electronic conductivity or specific surface area, have been explored to support the Pt nanoparticles (Pt NPs) [20]. Among them, ordered mesoporous carbon (OMC) features an extremely high specific surface area and ordered mesoporous pore structure, which favors the dispersion of Pt and the mass transfer in the porous electrode [21–24]. In particular, nitrogen-doped ordered mesoporous carbon (NOMC) has a variety of enriched 'electrochemically active' functional groups on the surface, which is thereby highly promising in the application of the electrochemical energy technologies [25–27]. The doping of nitrogen yields considerable effects on carbon by adjusting the electronic/geometric structure, the basicity and the hydrophilicity. Such an activation of carbon facilitates the nucleation, growth, loading and anchoring of Pt NPs [28,29]. As such, NOMC is expected to be an effective support and capable of highly dispersing and stabilizing the Pt NPs. Besides, the dopant N atoms can denote charge to the adjacent atoms and thus results in strong metal-support interaction (SMSI) at the interface, yielding a considerable effect on both the activity and durability of the catalyst[30–32]. By using the nitrogen-doped carbon support [1,33–35], the Pt/C catalyst shows a significant enhancement in the activity for the oxidation of methanol [36–40] and glycerol [41]. Very recently, it is found that NOMC, as a metal-free electrocatalyst, shows a decent electrocatalytic activity to the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) [42–44].

In terms of the synthesis, NOMC is generally obtained by the nanocasting method, in which the ordered mesoporous silica (OMS), like SBA-15, is used as the hard template. As such, the synthesized NOMC is the reverse replica of the template. It is reported that SBA-15 is in the column-like morphology, of which the diameter is several hundred nanometers and the length is several microns [25,45–52]. It is understandable that both the deposition of Pt NPs and the MOR are not easy to proceed in such long-range mesopores due to the mass transfer issues. Therefore, the above-mentioned morphological features seriously limit NOMC as the support to disperse and anchor the Pt NPs. As a result, the interface of Pt/NOMC is not well developed and, the enriched electrochemically active functional groups on carbon cannot be fully utilized to promote the activity and durability.

To address this issue, a 2D nitrogen-doped ordered mesoporous carbon (NOMC-2D) is developed as the support in this work. The Pt NPs are loaded onto the nitrogen-doped carbon with either 2D- or 3D-morphology for comparison. The physiochemical characterizations reveal that there exists a stronger interaction between the metal and the support in Pt/NOMC-2D than Pt/NOMC-3D, and the metal-support interface is better developed in the former one. The electrochemical result suggests that the nitrogen-doped carbon support indeed improves both the electrocatalytic activity and the anti-poisoning ability of Pt for the MOR than does the carbon black (Vulcan XC-72R). The enhancement can be understood as a result of the bifunctional mechanism at the interface of Pt-$C_{N\text{-doped}}$. That is, the enriched electrochemically active −OH groups on carbon help to strip off the CO-like intermediate species adsorbed on the adjacent Pt atoms. This mechanism is verified by the extensive investigation on both the loading of Pt and the dimension of the carbon support. The 10 wt% Pt/NOMC-2D catalyst yields the lowest overpotential and highest anti-poisoning ability as more bifunctional active sites are generated at the interface.

2. Experimental

2.1. Preparation of NOMC-3D and NOMC-2D

3D nitrogen-doped ordered mesoporous carbon (NOMC-3D) was synthesized by the nanocasting method [25–27], using SBA-15 as the hard template and 1, 10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$) as the precursor. First, the $C_{12}H_8N_2{\cdot}H_2O$ was dissolved into ethanol and mixed with the $FeCl_2{\cdot}4H_2O$ aqueous solution. Second, the SBA-15 template was added in and sonicated at room temperature. Then, the product was filtrated, washed, dried, and then pyrolysed at 900 °C in argon (99.999%). Finally, NOMC-3D was obtained by removing the silica template and iron by successively boiling the powders in 10 M NaOH at 120 °C and 0.10 M $HClO_4$ at 80 °C for 24 h.

2D nitrogen-doped ordered mesoporous carbon (NOMC-2D) was synthesized by the same procedure to NOMC-3D, except the use of a 2D silica template. The synthesis of 2D silica is as follows [53]. i) Graphene oxide (GO) was dispersed in a mixture of 126 ml deionized (DI) water and 20 ml hydrochloric acid (37 wt%), and then P123 was added in as the organic template. ii) 9.2 ml tetraethyl orthosilicate (TEOS) was added in and stirred for 20 h at 35 °C, which was hydrothermally treated at 110 °C for 12 h. iii) The product was filtered and microwave-digested in the mixture of HNO_3 and H_2O_2 to remove the organic template.

2.2. Preparation of Pt/NOMC

Pt nanoparticles (Pt NPs) were loaded on NOMC by the aid of ethylene glycol (EG) reduction method [54]. 250 mg NOMC was suspended in 25 ml EG under ultrasonic stirring for 40 min. A given amount of the H_2PtCl_6/EG solution (Pt: 3.7 mg mL^{-1}) was added in order to obtain Pt/NOMC with two metal loadings: 10 wt% and 30 wt%. Then, the pH of the solution was adjusted to 13 by adding NaOH and heated at 130 °C for 3 h under flowing Ar. After cooling down to the room temperature, the pH of the mixture was adjusted to 2 by adding 1.0 M HCl aqueous solution, which was stirred for another 2 h to ensure that Pt NPs were fully loaded on NOMC. Finally, the powders were filtrated, washed and dried at 80 °C for 8 h in vacuum oven.

2.3. Physicochemical characterization

X-ray diffraction (XRD) measurements were carried out by using a TD-3500 X diffractometer (Tongda Technology, China) with a Cu Kα radiation source operated at 40 keV and at a scan rate of 0.05 s^{-1}. X ray photoelectron spectroscopy (XPS) measurement was carried out with a physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. Transmission electron microscopy (TEM) images were collected on a FEI Tecnai G2 F20 S-TMIN operated at 200 kV. Thermogravimetric analyses (TGA) were made using a TA Instrument SDT 2960. The experiment was performed at 10 °C min^{-1} from room temperature to 800 °C in air at a flow rate of 20 ml min^{-1}. Nitrogen adsorption/desorption isotherms were measured at 77 K using Micromeritics TriStar II 3020 analyzer. The total surface area was analyzed with the well-established Brunauer-Emmer-Teller (BET) method, the microporous (MP) surface area was obtained with the *t*-plot method, and the pore size distribution was analyzed by the Barrett-Joyner-Halenda (BJH) method.