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Substrate effect on oxygen reduction electrocatalysis

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ABSTRACT

The oxygen reduction reaction (ORR) was investigated on carbon (XC-72) supported platinum nanoparticles, generated via the carbonyl chemical route and on oxide composites supported platinum generated via the UV-photo-deposition technique in sulfuric acid medium. The behavior of Pt/C was examined using a careful dosing of the catalyst loading spanning the range from 4.3 to 131 $\mu g\,cm^{-2}$. The ORR electrochemical response of Pt/C (in line with recent literature data) is put into contrast with the Pt/oxide-composite systems. Our results point out that it is possible to use smaller amounts of catalyst for the ORR when platinum atoms interact with the oxide (anatase) surface of the substrate composite. Evidence of the incipient metal–substrate interaction is discussed in the light of the results of XRD experiments.

1. Introduction

The tailoring *per se* of efficient and selective cathode catalysts in the nano-scale domain is interesting and still challenging for the oxygen reduction reaction (ORR) process. Moreover, some significant progress has been achieved in the search of nanometer scale range cluster-like mono-, bi-metallic and chalcogenides catalysts [1–4]. For the low temperature fuel cell system, the sluggish kinetics and high overpotentials associated with ORR are currently important issues. Platinum is still the best one-metal center catalyst, and alloying with *3d* transition metals has constituted one strategy to improve the ORR electrochemical kinetics [5–10]. Another way to improve the ORR activity, the tolerance and the stability is to modify the carbon supporting substrate [11–21] or develop novel substrates using metal oxides, e.g., MnO_x [22], TiO_x [22–28], SiO_2 [29], WO_x [30,31], and NbO_2 [32]. The support substrate plays an important role on catalysts [33], i.e., enhancing catalyst dispersion preventing aggregation [34]; reducing the required loading of catalyst [29]; and improving catalytic activity as a co-catalyst [35]. To date, carbon, e.g., Vulcan XC-72 carbon black with high surface area is the most used support substrate due to its reasonable electric conductivity and chemical stability in acid or alkaline medium. Electrochemical corrosion of carbon [36,37], as catalyst support in fuel cell operation potential window causes aggregation/dissolution of nanocatalysts (e.g., Pt) and is certainly one important factor that contributes to reduce the performance and the durability of fuel cells [38], and increase the surface hydrophobicity to influence the gas transport in electrodes [39,40]. Therefore, it is important to develop novel catalyst support for fuel cell systems.

Another interesting and important goal is to diminish the utilization of electrocatalysts as much as possible. Some recent investigations, however, show that there exists a limit of mass catalyst loading for Pt/C [41–44], Fe–N–C [45,46], Ru_xSe/C [47] and $CoSe_2/C$ [48] to attain high ORR activity. When the mass catalyst loading is lower than this limit, the catalyst will show lower ORR activity, e.g., lower current density, fewer electrons transfer leading to higher H_2O_2 production. These results mean that we cannot reduce the catalysts' mass any further. A higher mass limit for a kind of catalyst material implies that the ORR kinetics is limited by the number of catalytic sites. When 5% H_2O_2 production at 0.4 V vs. RHE (reference hydrogen electrode) was detected at the ring electrode, for example, the mass catalyst at the disk electrode was 28.3 $\mu g\,cm^{-2}$ for 20 wt.% Pt/C [41], 10 $\mu g\,cm^{-2}$ for Pt/NSTF (nanostructured thin films substrate) [44], 800 $\mu g\,cm^{-2}$ for Fe–N–C [45], and 92 $\mu g\,cm^{-2}$ for 20 wt.% Ru/Se/C [47]. Therefore, the catalytic activity decreases in the order: Pt/NSTF > 20 wt.% Pt/C > 20 wt.% Ru–Se/C $\gg$ Fe–N–C. Even for 20 wt.% Pt/C, a mass catalyst of 5.7 $\mu g\,cm^{-2}$ produced 22% H_2O_2 at 0.4 V vs. RHE, which is much higher than the requirement for polymer electrolyte membrane fuel cells, i.e., below 5% H_2O_2 production. In all these works, the Pt mass loading was adjusted

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by varying the concentration of catalyst ink or the volume of ink dropped on the disk electrode, using the same catalyst formulation. Therefore, we asked ourselves if it is possible to reduce this mass limit by modifying the nature of the catalyst's substrate. Recently, we investigated the in situ photo-deposition of Pt nanoparticles on the surface of TiO_2 in TiO_2/C composites and their corresponding catalytic activity towards ORR [49].

In this paper, we will give a further insight of the chemically and photochemically deposited platinum nanoparticles onto carbon and onto oxide–carbon composites by means of XRD, as well as the complex interplay between catalyst mass density with the electrochemical pathways of the ORR process in 0.5 M H_2SO_4 by rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques.

2. Experimental

2.1. Synthesis of Pt/TiO_2/C by in situ photo-deposition method

2.1.1. Synthesis of TiO_2/C composites

Four TiO_2/C composites with different anatase loading nanoparticles were prepared by mixing carbon (Vulcan XC-72) with titanium isopropoxide in isopropanol solvent [49]. In short, to produce 5 wt.% TiO_2/C composite, 200 mg carbon, prior heat treated at 400 °C under nitrogen for 4 h, was ultrasonically dispersed in isopropanol for 2 h at room temperature. 39 μL titanium isopropoxide was added in the resulting suspension and mixed for another 1 h. Milli-Q ultrapure water (1 mL) was added to produce TiO_2 nanoparticles and then stirred for another 24 h at room temperature. The obtained composite powder was collected on a Millipore filter membrane (dia. 0.22 μm pore size), washed with water and dried in vacuum at room temperature. Following the same procedure, another 1.5, 3 and 10 wt.% TiO_2/C composites were prepared by adjusting the volume addition of titanium isopropoxide to 11.3, 22.9, and 82.4 μL, respectively. Carbon substrate (200 mg) and water (1 mL) were used in the same amount for all four TiO_2/C composites.

2.1.2. Synthesis of Pt/TiO_2/C

The synthesized TiO_2/C composites, as support substrate, were used to deposit platinum particles. For example, to prepare 8 wt.% Pt/5 wt.% TiO_2/C catalysts, the obtained 5 wt.% TiO_2/C (52.6 mg) was dispersed in argon-saturated water in a photo-reactor with an optical quartz window. An isopropanol solution containing 34.9 mg $H_2PtCl_6{\cdot}6H_2O$ (Pt^{4+}), as platinum precursor, was added into the cell and stirred for 3 h, under illumination with an UV lamp (Xe lamp, 159 W). Visible and infrared light was cut off via a filter (hot mirror UV, Silica). The electron–hole pairs, photogenerated via UV-irradiation on TiO_2 (anatase, energy gap of 3.2 eV) in the composites, reduced Pt^{4+} to platinum (Pt^0) [50]. The deposition of Pt nanoparticles occurred essentially onto the TiO_2 surface. In the same way, other Pt/TiO_2/C catalysts were prepared with different platinum loadings ranging from 1.5 to 20 wt.%.

2.1.3. Synthesis of Pt/C catalysts in carbonyl route

For a comparison Pt/C catalysts with different Pt loadings were synthesized via a carbonyl chemical route [51]. For instance, to produce 8 wt.% Pt/C via this route, platinum carbonyl $[Pt_3(CO)_6]_5{}^{2-}$ was prepared by mixing 50.12 mg $Na_2PtCl_6{\cdot}6H_2O$ with 44.24 mg sodium acetate (mol ratio of NaAc/Pt = 6) in methanol solution under CO atmosphere for 24 h. Subsequently, 200 mg activated carbon (Vulcan XC-72) was added to the above solution and stirred for another 12 h under nitrogen atmosphere. The final product (Pt/C) was collected on a Millipore filter membrane (dia. 0.22 μm pore size), washed with water and dried in vacuum at room temperature. Other Pt/C catalysts were prepared with different Pt loadings of 1.5, 3, 5, 8, 10, 15, 20, 30, and 40 wt.% by adjusting the amount of Pt precursor, respectively. Carbon support was kept constant at 200 mg for all synthesis of the Pt/C catalysts.

2.2. Electrochemical measurement

All the electrochemical measurements were carried out at 25 °C in a thermostated three-compartment electrochemical cell. All the potentials in this paper were related to a reference hydrogen electrode (RHE) in a 0.5 M H_2SO_4 aqueous solution electrolyte. The rotating disk electrode (RDE) measurements were performed using a Potentiostat (Autolab PGSTAT 30). The working electrode was a glassy carbon disk with a 3 mm diameter (geometric surface area, 0.071 cm^2) and polished with Al_2O_3 (5 A) powder before catalyst deposition. The catalyst ink was prepared by dispersing 10 mg of catalysts, e.g., 8 wt.% Pt/C and 8 wt.% Pt/5 wt.% TiO_2/C, in 250 μL Nafion® (5 wt.% in water/aliphatic alcohol solution, Aldrich) and 1250 μL ultra pure water (18 mΩ cm) in an ultrasound bath for 1 h. A drop of 3.0 μL catalyst ink was deposited onto the working electrode surface and dried under nitrogen. Glassy carbon and home-made reference hydrogen electrodes were used as the counter and the reference electrode, respectively. The reference electrode was separated from the working electrode compartment by an electrolyte bridge with a Luggin capillary. Before the ORR measurements, cyclic voltammetry, in nitrogen-saturated electrolyte, was performed to clean the electrode surface from 0.05 to 1.2 V at 50 mV s^{-1}. 20 cycles were necessary to stabilize the current–potential signal. Linear current–potential curves were recorded from 1.0 to 0.2 V in oxygen-saturated electrolyte at a different rotating speed from 400 to 2500 rpm, respectively.

The rotating ring-disk electrode (RRDE) measurements were conducted on an interchangeable ring-disk setup with a bi-potentiostat (Autolab PGSTAT30) and a rotation control system (Pine Instruments). The Pt ring electrode (0.152 cm^2) was potentiostated at 1.2 V for the detection of hydrogen peroxide. The disk electrode (0.162 cm^2) was glassy carbon. The counter and the reference electrodes were the same as in the RDE measurements. The mol fraction (%) of H_2O_2 formation during ORR can be evaluated from the molar flux of O_2 and H_2O_2 according to Eq. (1) [52], based on the detected ring (I_R) and disk (I_D) currents and the collection efficiency (N, 0.21).

$$H_2O_2\ (\%) = \frac{200 \times I_R/N}{I_D + I_R/N} \tag{1}$$

2.3. Physical characterization

Transmission Electron Microscopy (TEM) graphs were recorded on a JEOL JEM-2001 LaB_6 microscope with an accelerating voltage of 200 kV and a resolution of ca. 0.19 nm.

X-ray patterns were obtained with a Guinier powder diffractometer (HUBER), set at the 45° transmission position. A Johansson type Ge monochromator produces a focused monochromatic Cu-$K_{\alpha 1}$ primary beam ($\lambda = 0.15406$ nm). The powder sample was slightly pressed and fixed between two 3 μm polyethylene foils and measured immediately in ambient conditions. Scans of the pure Vulcan XC-72R, as well as of the oxide-composite supports, were used for the background correction. The background-corrected patterns were subjected to the usual angular correction for absorption, polarization and geometrical factors, and plotted vs. the reciprocal scattering length $b = 2\sin\theta/\lambda$ (θ, Bragg angle; λ, wavelength).