



# Hydrogenotitanates nanotubes supported platinum anode for direct methanol fuel cell



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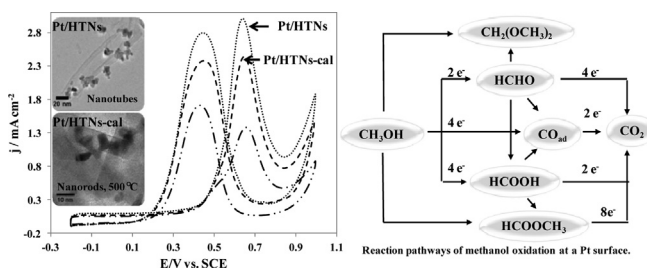
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## HIGHLIGHTS

- HTNs as a support for catalysts.
- In situ infrared reflectance spectroscopy measurements of different catalysts.
- For methanol oxidation, Pt/HTNs have high current density.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Hydrogenotitanates nanotubes (HTNs) are prepared from TiO<sub>2</sub> powder via hydrothermal processing in 11.25 M NaOH aq. The reaction temperature is 130 °C for 20 h. Afterward a heat treatment is done during 2 h at 500 °C in air, to obtain calcined HTNs (HTNs-cal). The structural change on the molecular TiO<sub>2</sub> during the hydrothermal treatment is investigated in detail by various analytic techniques such as XRD and TEM, which reveal that the crystal structure of the HTNs materials is similar to that of H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O nanotubes with 160 nm in length and 10 nm in diameter. Nitrogen adsorption–desorption isotherms indicate that synthesized solids are mesoporous materials with a multiwalled nanotubular structure and high specific surface area. Platinum nanoparticles are deposited on the HTNs by the impregnation method for a total noble metal loading of 10 wt%. The electrocatalytic activity of these electrocatalysts is evaluated by cyclic voltammetry in acid medium. Typical CO stripping voltammetry in acidic solutions is investigated. The results demonstrate that the HTNs can greatly enhance the catalytic activity of Pt for methanol oxidation. The CO stripping test shows that the Pt/HTNs can shift the CO oxidation potential to lower direction than Pt/C (XC72) and Pt/HTNs-cal catalysts.

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## 1. Introduction

Direct methanol fuel cell (DMFC) has received extensive studies in the two past decades because of its great application potential as an alternative power source. DMFCs can operate at low

temperatures, have a high energy density, a long lifetime and are lightweight with a simple system design [1–6]. As far as the methanol oxidation reaction (MOR) is concerned at the anode, major challenges receiving particular attention are for minimizing the Pt catalyst loading and keeping higher electrocatalytic activities with a better tolerance against the adsorbed CO poisoning effect formed during methanol dissociative adsorption. The widely adopted method to improve the electrocatalytic mass activity of the Pt catalyst toward MOR is to disperse Pt nanoparticles on a large

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surface area support [7–9]. On the other hand, to improve the CO<sub>ads</sub> tolerance, numerous studies used Pt-based binary or ternary catalysts (as Pt–Ru, Pt–Sn) to enhance CO<sub>ads</sub> electro-oxidation via the bifunctional mechanism and the so-called electronic effect [10–12].

Usually, carbon powder is used as support for these electrocatalysts. However, during the long-term operation of these electrocatalysts, a corrosion phenomenon was observed leading to a decrease of their activity and a deterioration of the system performance. Effort was made for improving the stability of carbon or to find an alternative stable material as support. In previous studies, nanocrystalline metal-oxide semiconductors have been widely employed in photocatalytic or photoelectrochemical systems because of the large area of the solid–solution interface, where the interactions between the photon-induced charge carriers and the active species in the solution [13,14]. Among these semiconductors, TiO<sub>2</sub> has drawn much attention, and numerous efforts have been devoted to the synthesis of nanosized TiO<sub>2</sub>. Kasuga et al. [15] reported that the thermal treatment of TiO<sub>2</sub> particles in NaOH resulted in the formation of anatase TiO<sub>2</sub> nanotubes with large surface areas. Apart from the crystalline structure of anatase TiO<sub>2</sub> nanotubes, some titanate structures, such as A<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O [16], A<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> [17,18], H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>·H<sub>2</sub>O [19], and lepidocrocite titanates [20], have been assigned as nanotubes constituents (A = Na and/or H). Studies carried out on commercial Pt/C catalysts mixed with titanium dioxide nanotubes for direct alcohol fuel cells have shown that the presence of titanium dioxide nanotubes improved the catalytic performance of Pt/C [21,22].

In this study, the hydrogenotitanates nanotubes (HTNs) were synthesized through the dissolution of TiO<sub>2</sub> powders in high concentrated NaOH solution at a high reaction temperature and then treated with hydrochloric acid or water. Their tubular structure showed a larger surface area and a higher degree of porosity than that of hydrogenotitanates nanotubes calcinated at 500 °C, and an improvement of the electrochemical activity was evidenced. Furthermore, a strong interaction has been reported in the case of platinum catalysts dispersed on hydrogenotitanates nanotubes leading to an improvement of the electrocatalytic activity of platinum when compared with platinum dispersed on other substrates.

In this paper, we will present recent progress made in the understanding of the mechanisms of the methanol oxidation reaction at Pt/HTNs catalyst by in situ infrared reflectance spectroscopy. The catalysts were characterized by Nitrogen adsorption–desorption isotherms (N<sub>2</sub> adsorption–desorption), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Their electrocatalytic activities were evaluated through the methanol oxidation by cyclic voltammetry and in situ reflectance infrared spectro-electrochemical measurements (FTIR).

## 2. Experimental

### 2.1. Preparation of hydrogenotitanates nanotubes by hydrothermal process

Hydrogenotitanates nanotubes were prepared by hydrothermal method similar to that described by Kasuga et al. [15]. In a typical procedure, 0.5 g of TiO<sub>2</sub> (Degussa P25) were dispersed in an aqueous solution of 11.25 M NaOH (15 mL) and placed in a Teflon-lined stainless-steel autoclave. The autoclave was statically heated at 130 °C for 20 h. After the hydrothermal treatment, one proceeded to the first filtration with one liter of distilled water (at approximately 80 °C) and to a neutralization with 0.1 M of a hydrochloric acid solution (HCl) until pH = 7. After this neutralization, a second washing with 0.5 L ebullient water was carried out, followed by a filtration and finally by a drying at 80 °C for 24 h. HTNs were obtained. Finally, HTNs were calcinated at 500 °C under air for 2 h (HTNs-cal).

### 2.2. Preparation of Pt nanoparticles

The platinum nanoparticles were synthesized using the impregnation method. In order to produce 10 wt% Pt/substrate catalysts, 0.5 g of substrate (carbon Vulcan XC72, HTNs or HTNs-cal) was mixed with 6.25 mL of hexachloroplatinic acid solution (20 g L<sup>-1</sup>). The mixture was ultrasonically treated for 30 min and stirred for 2 h. Then 200 mL of 0.4 M NaBH<sub>4</sub> at 80 °C was added to the mixture under vigorous stirring. The catalytic powder was then filtered and washed with a large amount of water and dried under vacuum at 110 °C for 4 h.

### 2.3. Characterization of catalysts

The morphology of the prepared catalyst was investigated by transmission electron microscopy (TEM). The sample specimens for TEM experiment were prepared by dispersing the catalyst powder in ethanol by ultrasonic treatment for 15 min, dropping onto a carbon film supported by a copper grid. TEM images were obtained using instrument a JEOL JEM-2001 LaB<sub>6</sub> microscope with an accelerating voltage of 200 kV and a resolution of ca. 0.19 nm. X-ray diffraction (XRD) analysis was performed using a “Philips analytical” X-ray diffractometer with Cu K $\alpha$  radiation. The  $2\theta$  angular regions between 2° and 70° were explored at a scan rate of 6° min<sup>-1</sup> with step of 0.02°.

The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area ( $S_{\text{BET}}$ ). Mean pore diameter ( $d_p$ ) was obtained using the Barrett–Joyner–Halenda (BJH) model in the range of mesopores. Pore distribution of the HTNs and  $S_{\text{BET}}$  were calculated from nitrogen adsorption and desorption isotherms at 77 K using a “Micromeritics ASAP 2000” instrument. 100 mg of HTNs sample was sealed in the reactor equipped with a temperature control unit. The adsorption isotherm was measured at 25 °C using a standard sequence, with a 30 min time out for each point.

Atomic absorption spectroscopy was performed to determine the platinum loading on the supports. An A Analyst 200 atomic absorption Spectrometer (Perkin Elmer) with platinum hollow cathode lamp ( $\lambda = 265$  nm) was used. The catalytic powder was previously mineralized in a hydrofluoric, hydrochloric and nitric acid solution under microwave activation for 40 min. The excess of hydrofluoric acid is then removed by the addition of H<sub>3</sub>BO<sub>3</sub>.

The cyclic voltammetry and CO stripping measurements were obtained using an Autolab potentiostat–galvanostat. All the electrochemical measurements were carried out at 25 °C in a thermostated three electrodes cell. All the potentials in this work were related to a reference saturated calomel electrode (SCE). A solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> Suprapur sulfuric acid (Merck) was used as the supporting electrolyte and to prepare the methanol solution (1 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) for the oxidation activity test. The working electrode was a glassy carbon disk with a 3 mm diameter (geometric surface area, 0.071 cm<sup>2</sup>). It was polished with Al<sub>2</sub>O<sub>3</sub> powder and washed carefully before the catalyst deposition. Platinum based working electrodes were prepared from Pt/C (Vulcan XC72), Pt/HTNs or Pt/HTNs-cal catalysts. An ink was prepared by ultrasonically dispersing 5 mg catalytic powder with 5 mg of carbon Vulcan XC72 in 0.5 mL 5% wt. Nafion<sup>®</sup> solution (from Aldrich). The 5 mg of carbon Vulcan XC72 powder were added to Pt/HTNs and Pt/HTNs-cal in order to ensure a good electronic conductivity of the catalytic layer. A drop of 3.0  $\mu$ L catalyst ink was deposited onto the working electrode surface. Glassy carbon was used as the counter electrode. The reference electrode was separated from the working electrode compartment by an electrolyte bridge. Before the cyclic voltammetry measurements, nitrogen was bubbled in the supporting electrolyte for 30 min at room temperature. Recorded at

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