



## Comparative study of methanol adsorption and electro-oxidation on carbon-supported platinum in acidic and alkaline electrolytes

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### ABSTRACT

Methanol electro-oxidation reaction over carbon-supported platinum nanoparticles, including methanol adsorption, apparent reaction order and activation energy, in acidic and alkaline media was investigated comparatively. The results show that the rate constant for methanol adsorption in 1 M NaOH is significantly higher than that in 0.5 M H<sub>2</sub>SO<sub>4</sub> at the relatively low potential and the CO<sub>ad</sub> removal in alkaline media is easier, due to the availability of oxygen-containing species, than in acidic media at the same potential. The apparent activation energy for the MOR in alkaline media is 25.3–14.6 kJ mol<sup>-1</sup>, significantly lower than that in acidic media (34.9–28.5 kJ mol<sup>-1</sup>). The better MOR activity of Pt/C in alkaline media is attributed to the faster methanol adsorption and the availability of oxygen-containing species.

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### 1. Introduction

Direct methanol fuel cells (DMFCs), as a potential alternative power source for transportation and portable devices, is attracting more and more interests nowadays due to the advantages over other power sources, such as high power density, environmental benign and compact system [1,2]. The practical output power density of DMFCs is significantly influenced by the kinetics of electrodes, especially by the anodic methanol oxidation reaction (MOR). In the past decades, great efforts were made including to understand the MOR mechanism and to improve the MOR kinetics by seeking suitable electrocatalysts [3,4]. From 1950s to 1970s, most studies on the electro-oxidation of methanol and other small organic molecules were taken on smooth metal electrodes. It was found that Pt is more active than other metals toward the MOR [5]. In 1980s, the cyclic voltammogram corresponding to a well-ordered Pt (111) surface in sulfuric acid was reported for the first time by Clavilier [6]. After that, the studies focused on the influences from metal single crystals with different facets on methanol adsorption and electro-oxidation. With the fast development of the characterization techniques combined with electrochemistry, such as: FTIR (Fourier Transform Infrared spectroscopy), DEMS (Differential Electrochemical Mass Spectroscopy) and isotope studies identification of reaction intermediates, product yields, the pathway and the kinetics of the MOR became clearer. However, as above-mentioned, most of the work was carried out on signal crystals or polycrystalline platinum electrode, so-called ‘model

electrodes’, which are different from the carbon-supported nanoparticle catalysts under realistic fuel cells relevant conditions [7,8]. Due to the complex of the structure of nanocatalysts and the difficulty in sampling, it is difficult to study the MOR kinetics for such catalysts. Since 1990s, the study on MOR over carbon-supported nanocatalysts has been mainly concentrated in acidic media with the prosperity of proton-exchange membrane fuel cell. Recently, MOR in alkaline media has attracted increasing interest with the development of anion-exchange membrane fuel cells. A typical study on MOR over Pt/C and Pt<sub>2</sub>Ru<sub>3</sub>/C in both acidic and alkaline medium was done by Tripkovic and co-workers [9–11], however, the methanol adsorption behavior on the carbon-supported Pt catalysts and the kinetic parameters are not systematically studied yet.

In this paper, by virtue of a flow cell, the methanol adsorption and electro-oxidation over Pt/C (E-TEK, 20%) in both acidic and alkaline media were systematically studied and compared, including the influence of pH on (i) formation of oxygen-containing species, (ii) dissociative adsorption of methanol (adsorption isotherm, adsorption rate), (iii) the oxidation of methanol (apparent reaction order and activation energy). The results are expected to provide basic information on understanding the MOR process over carbon-supported nanocatalysts.

### 2. Material and method

#### 2.1. Reagents

Methanol (>99.9% Xilong Chem. Com.), sulfuric acid (95–98%, Beijing Chem. Factory) and sodium hydroxide (>98%, Tianjin Dalu

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Chem. Reag. Com.) were used. Liquid electrolyte was prepared with ultrapure water. Carbon-supported Pt catalyst was purchased from E-TEK (20 wt.% Pt). The Pt particle size of the Pt/C is about 2.3 nm [12], as shown in the TEM image (Fig. 1).

## 2.2. Preparation of thin-film electrodes

The preparation of the thin-film electrode follows the method in Ref. [13]. In brief, the catalyst powder was dispersed ultrasonically in deionized (DI) water to form ink with a concentration of  $2 \text{ mg}_{\text{Pt}} \text{ ml}^{-1}$  for at least 30 min in an ice bath. Before each measurement the catalyst ink was again ultrasonically dispersed for 10 min or more. 20  $\mu\text{L}$  of the Pt/C catalyst ink was deposited on a cleaned glassy carbon electrode (GCE) disk, dried in nitrogen at room temperature. The commercial Nafion™ solution was diluted 40 times with DI water and 12  $\mu\text{L}$  of the diluted Nafion™ solutions were deposited on the GCE disk with a dried catalyst film. For all measurements, the catalyst loading is  $41 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ .

## 2.3. Electrochemical measurements

The thin-film Pt/C electrode was mounted into a dual thin-layer flow cell [14,15] and pressed against a ca. 100  $\mu\text{m}$  thick spacer. A three-electrode electrochemical cell with undivided compartments for the working and auxiliary electrodes was utilized. A reference electrode (saturated calomel electrode (SCE) in acid electrolyte and mercury/mercuric oxide electrode (MMO) in alkaline electrolyte), separated by an electrolytic bridge from the working electrode compartment was used in each experiment. However, all potentials in this paper are converted to the reversible hydrogen electrode (RHE). Ametek parstat 2273 controlled by a computer was employed to record the Current–Potential curves. The temperature of electrolyte contained in the jacket-bottle was controlled by cycling the water in jacket with a Yuguang thermostat of an accuracy of  $\pm 1$  °C. The cell temperature was calibrated by inserting a thermocouple into the center of the cell.

## 3. Results and discussion

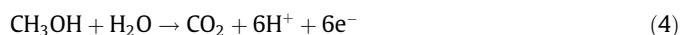
It is generally accepted that the anodic oxidation of methanol over Pt is a very complicated multi-step process. In acidic media, a simplified process is expressed as Reactions (1)–(3) [16]:



Reaction (1) is the dissociative adsorption of methanol; Reaction (2) is the formation of oxygen-containing from water dissociation and Reaction (3) stands for interaction of the adsorbed intermediates and oxygen-containing species to produce  $\text{CO}_2$ . The isotope studies [17,18] suggested that, in addition to  $\text{CO}_{\text{ad}}$  as intermediate (Reaction (1)), other intermediates expressed in Reactions ((1') [16], (1'') [19], (1''') [19]) are also possible:

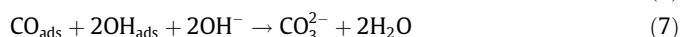
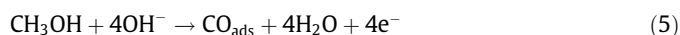


The consecutive and parallel combination of Reactions (1)–(3) gives the overall Reaction (4):

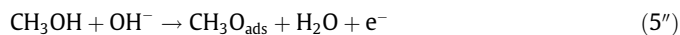
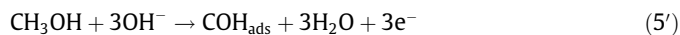


$$E^0 = 0.016 \text{ V vs. SHE @ pH} = 0$$

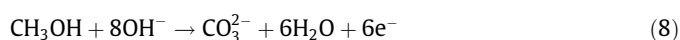
In alkaline media, a simplified process includes Reactions (5)–(7) [3]:



Same as the reactions in acid media, other intermediates expressed in Reactions ((5') [3], (5'') [3], (5''') [3]) are also possible:



The consecutive and parallel combination of Reactions (5)–(7) gives the overall Reaction (8):



$$E^0 = -0.810 \text{ V vs. SHE @ pH} = 14$$

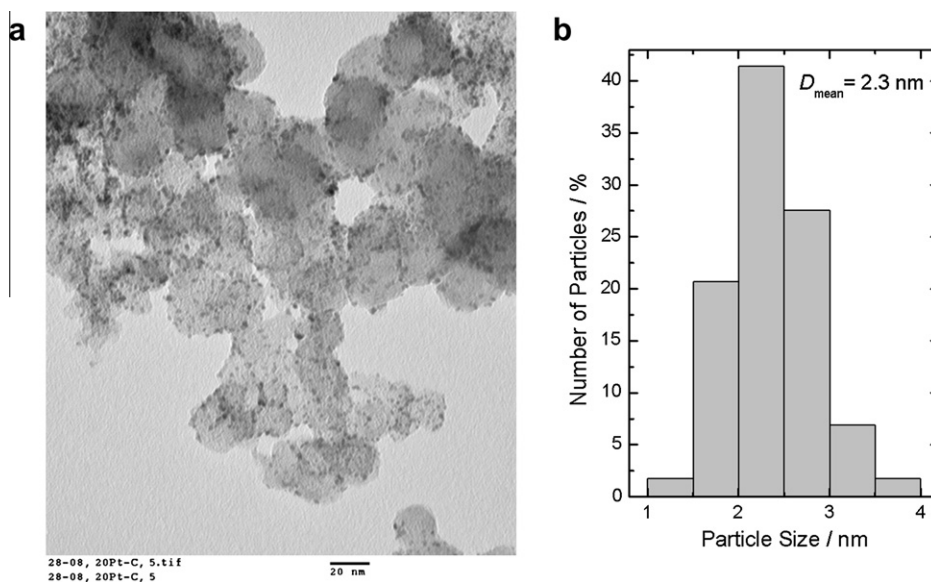


Fig. 1. TEM image of Pt/C (a) and the histograms of the corresponding mean particle size distribution (b).

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