

Surface modified Pt/C as a methanol tolerant oxygen reduction catalyst for direct methanol fuel cells

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Abstract

A new procedure has been successfully developed by which PtN_x/C is synthesized to enhance methanol tolerance while maintaining a high catalytic activity for the oxygen-reduction reaction (ORR). The nitrogen-modified Pt surface, which is prepared using a chelating agent followed by heat treatment, exhibits considerable selectivity toward the ORR in the presence of methanol. The high methanol tolerance could be attributed to the suppression of methanol adsorption resulting from the modification of the Pt surface with nitrogen. A direct methanol fuel-cell (DMFC) test showed that a power density of up to 120 m W cm⁻² was generated when PtN_x/C was used as the cathode catalyst (1 mg cm⁻²) in 6 M methanol and oxygen at 70 °C.

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1. Introduction

One of the main technical obstacles to the commercialization of direct methanol fuel cells (DMFCs) is methanol crossover from the anode to the cathode through polymer electrolyte membranes [1–3]. The methanol transported to the cathode as a result of the concentration gradients and electro-osmotic drag adsorbs on the catalysts and gives rise to a mixed potential, which results from oxygen-reduction and methanol oxidation reactions occurring simultaneously. These events lead to a negative shift in the cathode potential, which results in a significant decrease in the performance and durability of the DMFCs [4,5]. To solve this problem, many researchers have focused on developing proton-conductor electrolyte membranes with low methanol permeability [6–8]. An alternative approach to attack this problem lays in the development of oxygen-reduction-reaction (ORR) selective electrocatalysts that are tolerant to methanol oxidation.

Several types of methanol tolerant oxygen reduction catalysts have been reported in the literature. Transition-metal macrocycles with N-based ligands, such as porphyrins and phthalocyanines, are known to be very active toward oxygen reduction and insensitive to methanol oxidation [9,10]. Another approach is to use chalcogenide compounds based on Chevrel-type materials, which are characterized by a central octahedral metal cluster (i.e., M₆X₈, where M is a high valent transition metal and X is a chalcogen, e.g., S, Se, Te) [11–13]. These materials are prepared by decarbonylation of metal-carbonyl clusters under an inert-gas atmosphere at low temperatures. Although chalcogenide compounds show a higher selectivity—compared to that of Pt for oxygen reduction in an acid medium containing methanol, their intrinsic catalytic activity toward ORR is lower and their durability under fuel-cell operating conditions is not as good as that of Pt-based catalysts. Therefore, Pt-group-based compounds are still considered efficient candidates to be used as DMFC cathode catalysts. However, research has been mainly restricted to Pt alloys with transition metals, such as Co, Ni, and Fe to increase the methanol tolerance [14–16].

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In this study, Pt/C catalysts were endowed with a methanol tolerance ability, which was achieved by modifying their surface with the aid of a chelating agent followed by heat treatment at elevated temperature. Popov et al. reported that the carbon-supported Co-ethylenediamine complex showed an improved activity towards the four-electron reduction of molecular oxygen [17]. The aims of the present work were to verify the ORR activity and the selectivity of the chelate-modified Pt/C catalysts toward methanol oxidation in an acid medium containing methanol and to demonstrate the feasibility of using these catalysts as cathode materials in DMFCs. The electrochemical performance was evaluated by using a rotating ring-disk electrode (RRDE).

2. Experimental

2.1. Preparation of the catalysts

Platinum (IV) chloride (PtCl₄, Alfa Aesar) was dissolved in 100 mL of deionized water. The solution was stirred for 20 min, and then the chelating agent 1, 3-propylendiamine was added dropwise under stirring—whereupon the color of the solution changed from clear to cloudy yellow. The calculated amount of carbon (Ketjen Black 300J) was added to the prepared Pt-chelate solution under vigorous stirring to form a 40 wt% metal-loading solution. The mixture was refluxed at room temperature overnight, and then the carbon impregnated with the platinum-chelating complex was dried in a rotary evaporator at 50 °C under vacuum. The dried powder was then collected and heat-treated for three hours at 700 °C under a continuous flow of Ar gas.

2.2. Electrochemical and physical characterization

The electrochemical measurements were performed in a three-electrode electrochemical cell, using 0.5 M H₂SO₄ as the electrolyte, in the presence and absence of methanol; the experiments were carried out on a bi-potentiostat (CH Instrument) at room temperature. The working electrode was an RRDE (Pine Instrument) composed of a glassy-carbon (GC) disk (4.57 mm O.D.) and a Pt ring (4.93 mm I.D. and 5.38 mm O.D.). A Pt wire was used as the counter electrode and Hg/HgSO₄ was used as the reference electrode. All the potentials reported herein, however, refer to that of the reversible hydrogen electrode (RHE). To prepare the electrodes for the electrochemical evaluation, the catalyst powder was mixed with a solution of Nafion® (5 wt.%), isopropyl alcohol and water in an ultrasonic bath for 15 min. The suspension (12 μL) was dropped onto the GC electrode and dried in a nitrogen chamber. X-ray photoelectron spectroscopy (XPS, Sigma probe UK) was performed to analyze the surface characteristics of the catalysts. In the fuel-cell tests, commercial PtRu black (E-TEK, 4 mg cm⁻²) was used as the anode. For the cathode material, either the prepared PtN_x/C or the commer-

cial Pt/C (E-TEK, 40 wt%) catalysts were deployed. The pretreated Nafion 112 and the electrodes were hot-pressed for three minutes at 120 °C and a pressure of three metric tons to form a piece of the membrane electrode assembly (MEA). The performance of the cell was evaluated by measuring the current density versus the cell voltage with a commercial fuel-cell test system (Wonatech). The polarization curves were conducted at 70 °C by circulating 6 M methanol through the anode at a rate of 1 mL min⁻¹ and feeding humidified oxygen gas to the cathode at a pressure of 1 atm.

3. Results and discussion

XPS analysis of the chelated PtN_x/C catalyst, pyrolyzed at 700 °C, was carried out to determine the type of chemical bonding between nitrogen and platinum. The N 1s spectra as shown in Fig. 1 is resolved into two components: a peak at 398.8 eV and a shoulder at 400.7 eV, which are assigned to two types of nitrogen on a carbon matrix, namely pyridinic and pyrrolic nitrogen, respectively [18]. It is known that the pyridinic nitrogen is capable of coordinating metal ions [19–21]. According to an XPS study carried out on a PtN_x thin film prepared by reactive laser ablation in a molecular-nitrogen ambient, the existence of an N 1s binding energy of 398.4 eV can be used to support the existence of chemisorbed nitrogen [22]. Consequently, the peak in the N 1s spectrum is believed to reveal the interaction between N and Pt, which is related to the formation of platinum nitride.

Fig. 2 shows a comparison between the cyclic voltammograms of the PtN_x/C and the commercial Pt/C catalysts in 0.5 M H₂SO₄ saturated with N₂ at a scan rate of 5 mV s⁻¹. The effective surface area of the catalysts was calculated from the area of the hydrogen-desorption peak after subtracting the contribution from double-layer charging. This area was then converted into the effective active surface area by using the factor 210 μC cm⁻² for a monolayer of hydrogen adsorbed on polycrystalline Pt. It is assumed that hydrogen could adsorb only on free Pt sur-

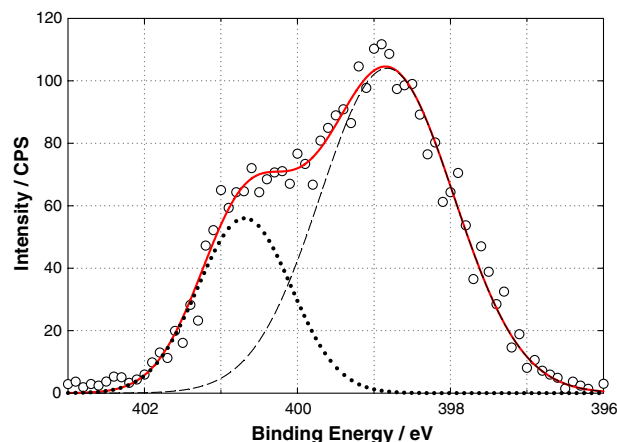


Fig. 1. XPS spectra of the PtN_x/C catalyst in the N 1s region.

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