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Pt/Mo_2C/C-cp as a highly active and stable catalyst for ethanol electrooxidation

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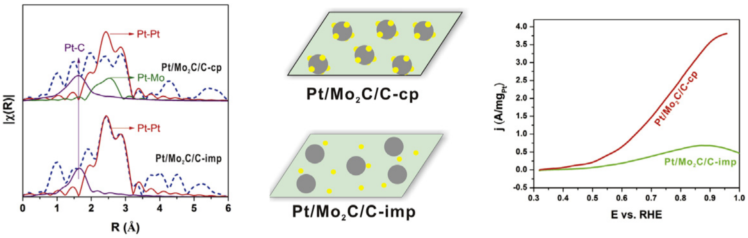
HIGHLIGHTS

- Pt and Mo_2C forms direct chemical bonding in the Pt/Mo_2C/C-cp catalyst.
- The Pt–Mo_2C chemical bonding is responsible for the enhanced EOR performance.
- The Pt/Mo_2C/C-cp catalyst exhibits significantly low onset CO oxidation potential.
- The Pt/Mo_2C/C-cp catalyst shows anti-poisoning ability to carbonyl-containing species.

GRAPHICAL ABSTRACT



Closer Interaction, Better Performance !

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ABSTRACT

A Pt/Mo_2C/C-cp electrocatalyst with optimized Pt–Mo_2C chemical bonding is synthesized and evaluated for the ethanol oxidation reaction (EOR). The chemical bonding of Mo_2C to Pt particles renders exceptional EOR activity at low potentials, which is 15 and 2.5 times higher than Pt/C and commercial 40% PtRu/C, respectively, at 0.6 V (vs. RHE). The stability of the Pt/Mo_2C/C-cp electrocatalyst is comparable to the commercial 40% PtRu/C catalyst. CO stripping test demonstrates the existence of highly active sites for CO oxidation on the Pt/Mo_2C/C-cp catalyst. *In-situ* infrared spectroscopic studies of EOR reveal that the excellent anti-poisoning ability of the Pt/Mo_2C/C-cp catalyst is related to the relatively weak binding of carbonyl intermediates over the Pt/Mo_2C/C-cp catalysts.

1. Introduction

Direct alcohol fuel cells (DAFCs) have attracted extensive research interests due to their potential utilization in portable, residential and transportation applications. Benefiting from the liquid phase character, alcohols have high volumetric energy density and can be stored and transported safely and conveniently with traditional fuel infrastructure [1–3]. Ethanol is one of the most attractive sources of alcohols as it has several important advantages, including nontoxicity and high energy density [4]. In particular, ethanol can be widely obtained from fermentation of renewable cellulose-containing biomass, which is considered as a CO_2 neutral process [5]. However, one of the major limitations for the application of direct ethanol fuel cells is the slow anodic kinetics of the ethanol oxidation reaction (EOR) at low potentials, such as below 0.7 V (vs RHE) [6]. The carbonyl intermediates

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(CH_3CO^*) or carbon monoxide (CO) generated from the partial oxidation of ethanol tend to strongly adsorb on the electrode surface and poison the active sites of the electrocatalysts at low anodic potentials, resulting in poor activity and rapid deactivation, especially for platinum, the most frequently used anodic material in DAFCs [7,8].

It is commonly accepted that oxygen containing groups (OH or O) can accelerate the removal of the adsorbed intermediates from the active sites by promoting the electrooxidation of the CH_3CO^* and CO intermediates into acetic acid and CO_2, respectively [9–12]. Due to the inability of generating OH or O over Pt at low potential ($Pt + H_2O{=}Pt{-}OH + H^+ + e$, $E > 0.6$ V vs. reversible hydrogen electrode (RHE) [13,14]), the EOR performance of Pt-based electrocatalysts can be significantly enhanced by introducing a second metal component (typically Ru, In, Sn, etc.), which is considered to increase the density of hydroxyls or oxygen in the vicinity of the Pt sites at lower potential [15]. As alternatives to metal promoters, transition metal carbides (TMCs) also exhibit similar surface properties. The formation of adsorbed hydroxyl and oxygen over TMC surfaces has been proven to be thermodynamically favored both by experiments and theoretical prediction [16–18]. Furthermore, the TMC promoters have relatively strong electron-affinity, which could effectively reduce the electron density of Pt centers. This special electronic property should weaken the binding of poisonous intermediates and accelerate their desorption [19].

Our previous surface science studies employing well-defined thin films suggest that the formation of Pt monolayer over the carbide substrate is able to improve the catalytic performance for alcohol electrooxidation [20,21]. Other studies have also reported that the deposition of Pt on pre-synthesized Mo_2C/C substrate renders a considerable enhancement (compared with Pt/C) on the activity and stability of alcohol electrooxidation [22–24]. However, in the traditional powder catalyst preparation, Pt is randomly dispersed over the carbide and active carbon support. Furthermore, it remains unclear how Pt and Mo_2C interact with each other and how the Pt–Mo_2C interaction influences the catalytic performance. To solve this problem, we develop a control synthetic method that can maximize the contact between Pt and Mo_2C on active carbon (AC). X-ray absorption fine structure (XAFS) studies demonstrate that the chemical bonding between Pt and molybdenum carbide is greatly promoted after a high temperature carburization process. This catalyst shows high EOR activity at relatively low potentials and has comparable anti-poisoning ability to the commercial 40% PtRu/C catalyst. The very low onset potential (0.33 V vs RHE) in CO-stripping and the relatively weak chemical bonding of poisonous intermediates shown in the *in-situ* IR spectra suggests that the direct Pt–Mo_2C chemical bonding accelerates the conversion and/or desorption of poisonous intermediates during ethanol electrooxidation.

2. Experimental methods

2.1. Catalyst synthesis

Pt/Mo₂C/C-cp catalysts were synthesized by adding the appropriate amount of chloroplatinic acid ($H_2PtCl_6{\bullet}xH_2O$, sigma-aldrich, 99.995%) solution (3.72 mg/mL in water) into an ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, sigma-aldrich, 99.98%) solution (0.635 mg/ml) and kept under vigorous magnetic stir for 2 h. Then, 0.2 g Vulcan XC 72 active carbon (AC, Cabot Corp.) was poured into the above solution followed by 15 min sonication. The suspension was stirred at room temperature for another 2 h, and then heated to 50 °C to evaporate the solvent. The catalyst powder was transferred into a container and dried at 100 °C for 6 h. The sample was carburized in 40 ml/min H_2 using the same carbon-thermal hydrogen reduction method reported elsewhere [25,26]. After cooled down to the room temperature, the catalyst was passivated with a flow of CO_2 to protect the carburized Mo_2C-based material from the pyrophoric oxidation when contacted with air. The CO_2 flow mildly oxidizes the surface of the molybdenum carbide, which could prevent the bulk phase Mo_2C from being fully oxidized. The catalyst is denoted as Pt/Mo_2C/C-cp(1:x), with x representing the relative molar ratio of Mo to Pt. For catalysts with different Pt/Mo ratios, the Pt loading is kept at 7 wt% of the active carbon support.

Pt/Mo₂C/C-imp catalysts were synthesized according to a reported method [23]. Firstly, the precursor of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O/C$ was obtained using the wet impregnation method by depositing $(NH_4)_6Mo_7O_{24}$ over active carbon. Then the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O/C$ was carburized into Mo_2C/C using temperature program carburization and the carburization procedure was similar to the synthesis of Pt/Mo_2C/C-cp described above. Appropriate amount of H_2PtCl_6 precursors were deposited on the Mo_2C/C support to obtain the precursor $H_2PtCl_6/Mo_2C/C$, which was loaded in a quartz tube and reduced by 40 ml/min H_2 at 550 °C for 2 h, then passivated at room temperature for 3 h by 20 ml/min CO_2 flow before use to prevent pyrophoric oxidation of the carburized Mo_2C-based and reduced Pt. The catalyst is denoted as Pt/Mo_2C/C-imp (1:x), with x representing the relative molar ratio of Mo to Pt.

Pt/C catalysts were synthesized by depositing appropriate amount of H_2PtCl_6 over the Vulcan XC 72 active carbon using similar impregnation method as the Pt/Mo_2C/C-imp catalyst. In order to reduce the Pt and remove the Cl^- ion, the H_2PtCl_6/C precursor was treated with H_2 (40 ml/min) at 550 °C for 2 h. After cooling down, the sample was passivated with 20 ml/min CO_2 for 3 h to prevent pyrophoric oxidation of the reduced Pt.

2.2. Electrode preparation

The glassy carbon disk electrodes used in this study were 5 mm in diameter (pine instrument). The electrode was polished with 0.05 μm alumina powders, and then sonicated for 10 s, washed with deionized water and dried with air. The catalyst powder was dispersed in deionized water with a concentration of 1 mg/ml and sonicated for 15 min. The electrode was made by dropping 20 μL catalyst ink onto the glassy carbon and slowly dried overnight. 15 μL Nafion (0.01% in water) was added on top to fix the catalysts onto the glassy carbon.

2.3. Electrooxidation measurements

The EOR was carried out in a three-electrode electrochemical cell in 0.05 M H_2SO_4 containing 1 M ethanol. The counter electrode was a Pt wire. The reference electrode was a Saturated Calomel Electrode (SCE). Unless explicitly stated, all reported potentials were referred to the reversible hydrogen electrode (RHE), which was calibrated by performing hydrogen oxidation/evolution experiments on a Pt disk electrode in 0.05 M H_2SO_4. The electrolyte was purged by Argon (Ar) for 15 min before the sample surface was immersed in the electrolyte. The activity of the electrode was evaluated by cyclic voltammetry at a sweep rate of 50 mV/s. Each electrode was pretreated with CV cycles from 0.318 to 0.118 V in the electrolyte until the steady state was reached.

The steady-state activity and stability of the Pt/Mo_2C/C-cp, Pt/Mo_2C/C-imp, Pt/C and 40% PtRu/C commercial catalysts for EOR were compared by chronoamperometric measurements at 0.6 V vs RHE.

For CO stripping voltammetry, CO was adsorbed at 0.1 V vs RHE for 10 min, and then the electrolyte was purged with pure Ar for 50 min. The CV measurements for CO oxidation were recorded at