



# The enhancement effect of MoO<sub>x</sub> on Pd/C catalyst for the electrooxidation of formic acid

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## ABSTRACT

Molybdenum oxide (MoO<sub>x</sub>) was added to a Pd/C catalyst using a novel two-step procedure. The enhancement effect of MoO<sub>x</sub> on Pd/C catalyst for the electrooxidation of formic acid was verified by electrochemical experiments. Compared to the Pd/C catalyst, the experimental results showed that the addition of MoO<sub>x</sub> could significantly enhance the electrocatalytic performances for the electrooxidation of formic acid. Significant improvements in electrocatalytic activity and stability were primarily ascribed to the effect of MoO<sub>x</sub> on the Pd catalyst. In addition to the large specific surface area, the hydrogen spillover effect is speculated to have accelerated the electrooxidation rate of formic acid in the direct pathway.

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## 1. Introduction

Significant attention has been directed to direct formic acid fuel cells (DFAFCs) due to their many advantages, such as low toxicity, limited fuel crossover and high practical power densities at low temperatures [1,2]. Pt-based and Pd-based anode catalysts have also been studied extensively [2,3]. However, Pt-based catalysts used for the electrooxidation of formic acid are severely poisoned by the adsorbed CO intermediate during the reaction. The same effects are seen in the best-known catalysts such as Pt–Ru [4] and Pt–Pd [5,6] alloys, which only diminish the CO poisoning effect slightly. In recent years, the Pd-based catalysts have shown higher catalytic activity for the electrooxidation of formic acid than the Pt-based catalysts because they can overcome the CO poisoning effect [7–10]. However, the activity and stability of the Pd-based catalysts still need further improvements for the electrooxidation of formic acid.

The addition of transition metal oxides to noble metals for use as electrocatalytic materials have performed well because the inorganic oxides can modify the electronic structure of the noble metals, which affects their catalytic properties [11–14]. MoO<sub>x</sub> is one of the most important transition metal oxides; it can improve the CO-tolerance properties and shows high activity for methanol

oxidation. These traits can be attributed to the high electronic conductivity, relative stability in acidic solution and synergistic effect with noble metals [15–18]. To our knowledge, the use of MoO<sub>x</sub> as a co-catalyst material in the DFAFC has seldom been reported. Pickup and co-workers evaluated Pt black catalysts and PtRu black catalysts modified with Mo oxide as anodes in fuel cells, which significantly improved their catalytic activities in DFAFCs [19]. It is accepted that the electrooxidation of formic acid on Pd-based catalysts occurs primarily through the direct dehydrogenation pathway. During formic acid oxidation, a significant amount of hydrogen is produced. Interestingly, Pd is an excellent material that can adsorb the hydrogen [20,21]. Therefore, it can be inferred that the hydrogen produced by formic acid dehydrogenation may be easily adsorbed onto the Pd surface, and the adsorbed hydrogen would hinder the adsorption of formic acid molecules on the Pd active sites. As a result, the adsorbed hydrogen on Pd surface could decrease the formic acid oxidation rate and lead to low catalytic activity. It has been proposed that the hydrogen spillover effect of WO<sub>x</sub> and MoO<sub>x</sub> combined with Pt or Pd catalysts can promote the electrooxidation of small organic molecules [22–24]. In-situ hydrogen spillover from a catalyst to the substrate during electrocatalytic oxidation of methanol was observed using electrochromism on a Pt–WO<sub>x</sub> catalyst [25]. Because of the hydrogen spillover effect [26], during the introduction of MoO<sub>x</sub>, the adsorbed hydrogen from formic acid dehydrogenation on the Pd surface transferred onto the MoO<sub>x</sub> surface and more active sites of Pd were released for formic acid adsorption and oxidation. As a result, the high catalytic activity for formic acid oxidation could be maintained. The preparation

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methods and the existent state of  $\text{MoO}_x$  can affect the catalytic activity of the catalyst. Phosphomolybdic acid (PMA) was strongly adsorbed onto various active carbons; it was not desorbed when washed with hot water or hot methanol [27–29]. Based on this property, the well dispersed  $\text{MoO}_x/\text{C}$  support could be obtained by thermal decomposition of the adsorbed PMA on the Vulcan XC-72R carbon.

It can be inferred that the addition of  $\text{MoO}_x$  to a Pd catalyst should greatly increase the performance of the electrooxidation of formic acid, and it is of interest to develop a novel applicable catalyst for DFAFC. In the work presented here, a Pd– $\text{MoO}_x/\text{C}$  catalyst was designed to obtain high catalytic activity for the electrooxidation of formic acid; the enhancement effect of  $\text{MoO}_x$  on Pd catalysts is also discussed. The Pd– $\text{MoO}_x/\text{C}$  catalyst was prepared by a new two-step procedure. In the first step, a  $\text{MoO}_x/\text{C}$  support was prepared by thermal decomposition of the adsorbed PMA on a carbon surface. In the second step, the palladium catalyst was directly reduced onto the hybrid support. The obtained Pd– $\text{MoO}_x/\text{C}$  composite catalyst was investigated for the electrooxidation of formic acid. The results indicated that the catalyst had excellent catalytic activity and stability for the electrooxidation of formic acid.

## 2. Experimental

### 2.1. Catalyst preparation

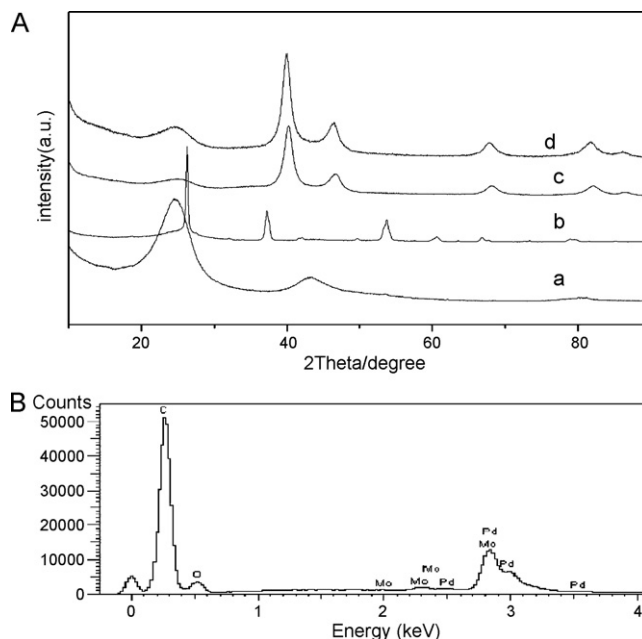
Firstly, the  $\text{MoO}_x/\text{C}$  hybrid support was prepared. A given amount of Vulcan XC-72 carbon was added into an aqueous solution of  $10 \text{ mg ml}^{-1}$  PMA, and maintained at room temperature ( $20^\circ\text{C}$ ) for 72 h under vigorous agitation. Subsequently, the suspension was filtered and the solid was transferred to a tubular oven at  $550^\circ\text{C}$  for 6 h to obtain a stable  $\text{MoO}_x/\text{C}$  support under the protection of nitrogen.

In the second step, the Pd– $\text{MoO}_x/\text{C}$  catalyst was synthesized according to the following procedure: first, a given amount of  $\text{MoO}_x/\text{C}$  hybrid support was ultrasonically dispersed in 50 ml of deionized water and second, an appropriate amount of  $\text{H}_2\text{PdCl}_4$  solution was added to the above suspension under agitation. After thoroughly mixing, the pH value of the suspension was adjusted with a 5% NaOH solution to ca. 7. After stirring for 30 min, an excess of freshly prepared  $\text{NaBH}_4$  solution was added dropwise into the above suspension in the pH range 7–8.5. Subsequently, an additional 4 h of stirring was performed to complete the reaction. Finally, the suspension was filtered, washed and dried overnight at  $80^\circ\text{C}$  in a vacuum oven. For comparison, the Pd/C catalyst using Vulcan XC-72 carbon as support was prepared with the above method. The nominal content of Pd in the catalysts was 20 wt.%. All solutions were prepared using Millipore-MiliQ water and analytical-grade reagents.

### 2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) as a radiation source operating at 40 kV and 200 mA. The composition of the catalysts was determined by energy dispersive X-ray analysis (EDX) on a JEOL JAX-840 scanning electron microscope operating at 20 kV. The transmission electron microscope (TEM) images were obtained using a JEOL 2010 microscope operating at 200 kV.

The electrochemical measurements were performed with an EG&G Par potentiostat/galvanostat (Model 273A Princeton Applied Research Co., USA) and a conventional three-compartment electrochemical cell. A Pt plate and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials were



**Fig. 1.** (A) XRD patterns of Vulcan XC-72R carbon (a), hybrid support  $\text{MoO}_x/\text{C}$  (b), Pd– $\text{MoO}_x/\text{C}$  catalyst (c) and Pd/C catalyst (d); (B) EDX spectra of the Pd– $\text{MoO}_x/\text{C}$  catalyst.

quoted against the reference Ag/AgCl electrode. All electrochemical measurements were carried out in a 0.5 M  $\text{H}_2\text{SO}_4$  solution with or without 0.5 M  $\text{HCOOH}$  deaerated by pure nitrogen for 15 min before experimentation. The preparation of the working electrode and electrochemical CO stripping voltammetry were carried out according to literature [30]. In this report, the current density was normalized to the geometric surface area ( $0.07 \text{ cm}^2$ ) of the vitreous carbon, unless otherwise noted.

## 3. Results and discussion

Fig. 1A shows XRD patterns of the Pd– $\text{MoO}_x/\text{C}$  and Pd/C catalysts, as well as the hybrid support  $\text{MoO}_x/\text{C}$  and the Vulcan XC-72R carbon. In the XRD pattern of Vulcan XC-72R carbon (a), the characteristic diffraction peaks of graphitic carbon with two broadened peaks were observed at about  $25^\circ$  and  $45^\circ$ . In the XRD pattern of the hybrid support  $\text{MoO}_x/\text{C}$  (b), the diffraction peak at ca.  $27^\circ$  corresponded to the mixture of Vulcan XC-72 carbon and  $\text{MoO}_x$ , while the other peaks were assigned to the reflection of  $\text{MoO}_x$  (such as  $\text{MoO}_2$  or  $\text{MoO}_3$ ) and some were very small [31,32]. The diffraction peaks at ca.  $39^\circ$ ,  $46^\circ$ ,  $67^\circ$  and  $81^\circ$  observed in the Pd– $\text{MoO}_x/\text{C}$  (c) and Pd/C (d) pattern corresponded to the typical face-centered cubic phase of Pd. There were no obvious signals for  $\text{MoO}_x$  in the XRD patterns of the Pd– $\text{MoO}_x/\text{C}$  catalyst. However, the existence of  $\text{MoO}_x$  cannot be discarded; the  $\text{MoO}_x$  phase is likely amorphous during the reduction process of the impregnated Pd precursor or the content is very low [33]. The position shift of Pd characteristic peaks towards higher Bragg angles was observed with respect to the Pd/C catalyst, indicating that the crystal structure of Pd was changed by the effect of the  $\text{MoO}_x$ . This characteristic confirmed the existence of  $\text{MoO}_x$  in the Pd– $\text{MoO}_x/\text{C}$  catalyst.

Fig. 1B displays a typical EDX spectrum of the Pd– $\text{MoO}_x/\text{C}$  catalyst. The obvious Mo peaks appeared in the EDX spectrum, which further confirmed the existence of Mo oxide inside the bulk phase of the Pd– $\text{MoO}_x/\text{C}$  catalyst, and the content of Mo was approximately 3.7 wt.%. The absence of a chlorine peak indicated that the chlorine ions were completely removed during the filtration. The TEM observation results of the Pd/C and Pd– $\text{MoO}_x/\text{C}$  catalysts are shown

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