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Electro-oxidation of methanol on SnO_2-promoted Pd/MWCNTs catalysts in alkaline solution

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ABSTRACT

The methanol electro-oxidation (MEO) on Pd–SnO_2/MWCNTs catalysts prepared by microwave-assisted polyol reduction method has been investigated. The structure, morphology and electro-catalytic performances of the catalysts were characterized with XRD, TEM and cyclic voltammetry (CV). The results showed that the highly dispersed Pd nano-particles (PdNPs) with a narrow size distribution on MWCNTs were successfully synthesized. The catalytic activity of Pd–SnO_2/MWCNTs for MEO was up to 778.8 mA/mg Pd in 0.1 M KOH solution containing 1 M methanol, which was significant higher than that of Pd/C (414.2 mA/mg Pd) or Pd–SnO_2/C (566.7 mA/mg Pd). Moreover, the MEO on Pd–SnO_2/MWCNTs electrode displayed an irreversible behavior under a diffusion control giving an exchange current density (j^0) of 3.76×10^{-4} A cm^{-2} and a Tafel slope of 149 mV dec^{-1} ($\alpha = 0.56$) at 25 °C, which indicates that Pd–SnO_2/MWCNTs catalyst has a high electro-catalytic performance for the MEO in alkaline media.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention in recent years due to its high energy efficiency, convenient transportation and storage of the methanol fuel, as well as environment friendly etc [1]. It is considered as a promising power source for portable electronic devices and electric vehicles [2]. However, it is difficult for widespread application due to several technical barriers such as the relatively low kinetics of methanol electro-oxidation (MEO) on the anode and the poisoning of anode catalyst etc [3]. Hence, considerable efforts must be made in order to enhance the catalytic efficiency of the electrode catalysts for the MEO [4,5].

Generally, Pt-based metals are the most promising electrode catalysts for the MEO in acid media [3,4]. However, Pt catalysts have limitations for widespread applications due to its limited resource, high cost and terrible adsorbed carbon monoxide type intermediates tolerance [6]. On the contrary, Pd is more widespread in the earth crust. Replacing Pt with Pd would reduce the cost of the electrodes [7]. In addition, Pd-based catalysts exhibit better CO-type intermediates tolerance comparing to Pt-based catalysts in alkaline media [8,9].

It is well known that the electro-catalytic activity of noble metal or noble metal alloy catalysts is also dependent on the carbon supports [10]. Recently, multiwalled carbon nanotubes (MWCNTs) used as potential supports for electro-catalysts have been extensively investigated. It has been demonstrated that MWCNTs decorated with the catalytically active noble metal nano-particles, displayed high catalytic performances [11–14].

The catalytic activity of the electro-catalyst gradually decreases with the generation of adsorbed carbon monoxide type intermediates from the oxidation of methanol [15]. One

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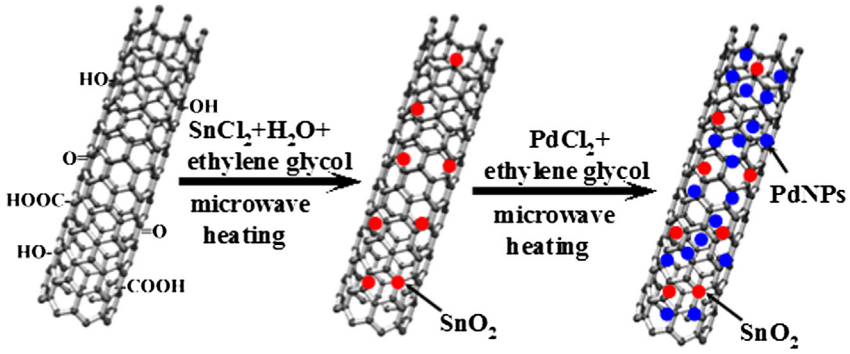

Fig. 1 – Schematic diagram of the synthesis procedure of the Pd–SnO_2/MWCNTs catalysts.

attractive approach to enhance the removal of CO-type intermediates is to introduce active materials into the single electrode catalyst to take the advantage of the introduced components thorough the assisted catalysis effect [12], resulting in enhanced catalytic performances [16–18]. In recent years, great attention has been focused on the carbon supported Pt or Pd-based electro-catalysts modified by active transition metal or their oxidations for the MEO. The composite electro-catalysts such as Pt–SnO_2/MWCNTs [12], Pt–Sn/C [19], PtRhSnO_2/C [20], Pt–NiO/C [21], Pt–TiO_2/ITO [22], Pd–CeO_2/C, Pd–Co_3O_4/C, Pd–Mn_3O_4/C and Pd–NiO/C [23] have been successfully prepared and pronounced results have been demonstrated for the electro-oxidation of methanol.

To the best of our knowledge, an application of Pd–SnO_2/MWCNTs to fuel cells anode catalysts for the MEO has not been previously reported. Therefore, Pd/MWCNTs promoted with SnO_2 catalysts were prepared by using a simple microwave-assisted polyol method in this research. The polyol reduction process has been extensively applied to prepared noble metal and metallic oxide at a nanoscale particles deposited on carbon supports [23,24]. As a comparison, Pd/C and Pd–SnO_2/C catalysts were also prepared by the same method. In the following section the catalytic performances of Pd/C, Pd–SnO_2/C and Pd–SnO_2/MWCNTs for the MEO were discussed in detail, and the Tafel slope and kinetic parameter (j^0) for the MEO on Pd–SnO_2/MWCNTs electrode were analyzed.

2. Experimental section

2.1. Synthesis of SnO_2/MWCNTs and SnO_2/C

MWCNTs (50 nm in outer diameter and 2–5 μm in length) were purchased from Chengdu Organic Chemicals Co. Ltd., The detailed treated procedure of MWCNTs was referred to the literature [12]. Carbon black (Vulcan XC-72R, Cabot Corp., USA) and ethylene glycol (EG) were used as received. $SnCl_2$ and $PdCl_2$ solutions were prepared with deionized water.

To prepare the SnO_2/MWCNTs nano-composites, the microwave-assisted synthesis method was developed. Briefly, 100 mg pretreated MWCNTs and appropriate amount of $SnCl_2$ precursors (100 mM in ethylene glycol) for designed SnO_2 weight ratios of 5% were added into the mixture (200 mL) of EG and water with the volume ratio of H_2O/EG = 0.1. The solution was then placed in a domestic microwave oven (800 W) with heating for 2 min, and then rested for 2 min, followed by another 2 min. Finally, the as-synthesized products were filtrated and washed, dried in a vacuum oven at 80 °C for 12 h. 5 wt.% loading of SnO_2 deposited on carbon black were also obtained by the same preparation method.

2.2. Pd loading on SnO_2/MWCNTs

Pd–SnO_2/MWCNTs with 20 wt.% Pd loading were prepared by microwave-assisted polyol process in polyol solution with $PdCl_2$ as a precursor salt. Briefly, as-prepared SnO_2/MWCNTs was firstly impregnated into 1 mL of 0.0565 M $PdCl_2$, The pH value of the ink was adjusted to 9 by adding 1 M NaOH–EG solution drop by drop, after ultrasonic treatment for 30 min, the beaker was placed in the center of the domestic microwave oven (800 W) for 20 s. After cooling down to ambient temperature, the dispersed ink was added into the above solution with stirring overnight. The slurry was allowed to continuous stir at ambient temperature, and then 0.1 mol/L HNO_3 was introduced into the cooled mixture to adjust pH value of the solution to about 4. The mixture was kept stirring for 3 h and then filtrated and washed. The as-prepared Pd–SnO_2/MWCNTs catalyst was dried for 12 h at 80 °C. Pd/C and Pd–SnO_2/C were also synthesized in the same manner for comparison [25].

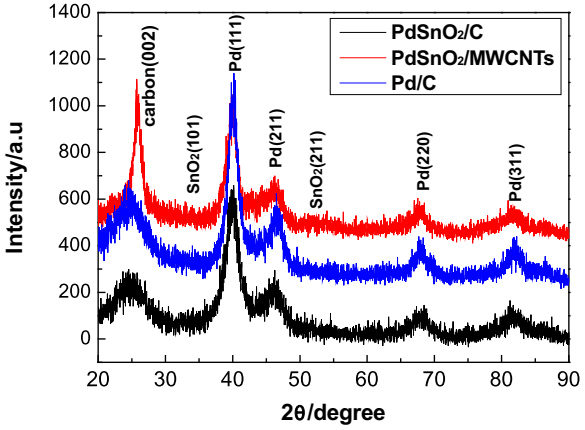

Fig. 2 – XRD patterns of Pd/C, Pd–SnO_2/C and Pd–SnO_2/MWCNTs.