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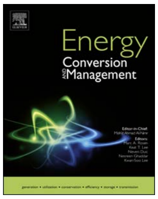

Effect of pulse electrodeposition parameters on electrocatalytic the activity of methanol oxidation and morphology of Pt/C catalyst for direct methanol fuel cells

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ABSTRACT

The electrodeposition technique for preparing direct methanol fuel cell electrodes has been developed to increase the Pt utilization and lower the Pt loading. The performance of the Pt/C electrode for methanol oxidation reaction (MOR) was optimized by adjusting the electrodeposition parameters such as applied electrical signal types, ratios of t_{on}/t_{off}, deposition temperatures, and electrolyte concentrations, systematically. Furthermore, the effects of two kinds of additives, i.e. polyethylene glycol (PEG) and sodium dodecyl sulfonate (SDS), on the catalytic performance and morphology of Pt catalyst were investigated for MOR by SEM, XRD, cyclic voltammetry and linear sweep voltammetry. The results show that the optimal Pt catalyst has been prepared by the square wave current method with t_{on}/t_{off} of 1 s/5 s at 30 °C in a $1.0\,\text{mmol}\,L^{-1}$ H_2PtCl_6 solution with a $10^{-4}\,\text{mmol}\,L^{-1}$ PEG additive. Moreover, the effect of the additive type and amount on the formation mechanism of the Pt crystallite morphology has also been discussed. From the results, introducing additives into the deposition solution in the pulse electrodeposition process is useful for designing and fabricating electrocatalytic electrodes for direct methanol fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs) have been the subject of great interest, because the direct-fed liquid fuel cell is perfect in potential portable power source applications such as electric vehicles and mobile electronic devices [1]. However, the high cost of the Pt catalysts is a critical problem which impedes the wide commercialization of DMFCs [2]. Therefore, one of effective ways is, under the premise of enough high catalytic activity of the Pt catalyst, to decrease the Pt loading. This is to say, it is urgently necessary to enlarge the effective surface area of Pt.

To achieve high catalytic performance and utilization efficiency, a lot of efforts have been devoted to the development of various catalysts via many new synthesis methods for producing small-sized and highly dispersed Pt particles [3]. The commonly used approaches for preparing DMFC electrocatalytic electrodes include chemical reduction [4], chemical vapor depositing [5], spraying [6], brushing the prepared carbon supported catalyst (e.g. Pt/C and PtRu/C) ink [7] and deposition Pt nanowires into the Nafion membrane [8]. However, the Pt utilization in such conventional electrodes is still low, because Pt particles are easy to agglomerate [9]. Ideally, the Pt particles should be located in the three-phase reaction zone with effective gas and water diffusion, proton transport and electron transport [10]. That is to say, the Pt particles should be exposed to the reactant, electron and proton, simultaneously [11]. When the catalyst agglomeration exists, the catalyst particles inside the agglomerates are not in good contact with the electrolyte phase, so the catalyst cannot be fully utilized [12].

The electrodeposition method has been proved to be very useful for improving the utilization of new types of metal nanostructures [13]. By using the electrodeposition method, Pt catalysts can be selectively deposited on desirable three-phase locations of the electrode. So the electrodeposition method has been considered as a very promising technique to increase the Pt utilization [14]. Till now, some types of electrodeposition methods with different applying current signals have

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been reported, such as square wave current, square wave potential, cyclic voltammetry, and constant current pulse electrodeposition. However, most of the works have focused on the catalyst preparation via only an individual method. Few reports are available on comparison of the effect of the above-mentioned different four applied electrical signals on the electrocatalytic performance of the deposited Pt catalyst.

On the other hand, recently, polyethylene glycol (PEG) used as a nonionic surfactant has been added in the electrolytic baths to affect the crystal growth and change the morphology of ZnO or Cu [15]. The polymer compound has been widely applied in the electrodeposition of Cu and Zn as a nonionic surfactant additive due to its selective adsorption [16]. In catalyst synthesis, the surfactant agents have been habitually used to prevent the agglomeration of nano-sized catalyst particles, e.g., sodium dodecyl sulfonate (SDS) used as film for preparation of Pt-Cu bimetallic nanoparticles [17]. However, the electrodeposition of Pt nanoparticles has been studied systemically without adding surfactant additives [18]. As a useful technique, this strategy can be extended to prepare Pt nanoscale materials by the electrodeposition method with introducing surfactant agents. However, there are limited reports available on introducing different surfactants (nonionic and ionic) in the direct electrochemical growth of Pt to further control the particle size and crystallite morphology.

Herein, in the present study, an electrodeposition process with the optimized parameters such as four applied electrical signal types, deposition temperature, electrolyte concentration, has been systemically investigated. Based on the best electrical signal, the effect of different operating conditions on the catalytic performance was investigated. In addition, the effect of adding additives in the deposition solution was studied. The prepared catalysts were characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The performance of the prepared Pt/C electrocatalysts for methanol oxidation was investigated. Furthermore, the effect of the two different additives on the formation mechanism of the Pt crystallite morphology was also discussed.

2. Experimental

2.1. Fabrication of Pt/C graphite electrodes by electrodeposition

The preparation process of the Pt/C graphite electrode via the electrodeposition method includes two steps. The first step was to make the graphite electrode as a substrate for Pt catalyst electrodeposition. And the second step was the pulse deposition of Pt catalyst on the carbon-based substrate.

In the first step, the electrode slurry was obtained by mixing 30 mg carbon black (Vulcan XC-72), 120 μl Nafion® solution (5 wt%) and 6 mL ethanol thoroughly in a supersonic bath. Then, 100 μl prepared slurry was pipetted on a graphite electrode ($\Phi = 8$ mm) that was polished to mirror-like state and cleaned by ethanol and ultrapure water previously. After that, the electrode was dried at 60 °C for 5 h in a vacuum oven to vaporize the ethanol. The resulting carbon graphite electrode was served as the substrate for depositing the Pt catalyst. The total charge density and the deposition current density were normalized to the geometric area of the carbon-based substrate ($S = 0.5\,\text{cm}^2$).

In the second step, the Pt/C graphite electrodes were fabricated by four different applied electric signal methods. Based on the best electric signal, the effect of the operating the parameters was investigated. In addition, the effect of adding additives (PEG or SDS) in the deposition solution was also studied. All electrodes were rinsed thoroughly with de-ionized water and dried at 60 °C in a vacuum oven immediately.

In the following, the electrode are noted as PEG-1, PEG-2, PEG-3, SDS-1, SDS-2 and SDS-3. As a contrast, an electrode without adding additives (named as A) was prepared by the same procedure. Detailed operating parameters for the different electrodes are listed in Table 1.

Table 1
Preparation parameters for various Pt catalysts on the carbon substrate.

No. of the electrode	Additive	Concentration of additives/ mmol L^{-1}	Total charge density/ C cm^{-2}	Deposition current density/mA cm^{-2}	On-time (t_{on})/ s	Off-time (t_{off})/ s
A	/	0	1.0	6.0	1	5
SDS-1	SDS	10^{-5}	1.0	6.0	1	5
SDS-2	SDS	10^{-4}	1.0	6.0	1	5
SDS-3	SDS	10^{-3}	1.0	6.0	1	5
PEG-1	PEG	10^{-5}	1.0	6.0	1	5
PEG-2	PEG	10^{-4}	1.0	6.0	1	5
PEG-3	PEG	10^{-3}	1.0	6.0	1	5

2.2. Electrochemical measurements

All the electrochemical experiments were performed by using the Potentiostat of Princeton Applied Research Model VMP2 at 30 °C and a conventional three-electrode-cell. Pt sheet and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. All potentials in this paper were quoted with reference to the SCE [19].

Cyclic voltammetry (CV) in 0.5 mol L^{-1} H_2SO_4 with the scan range of -0.25 to 1.1 V and the scan rate of 100 mV s^{-1} was carried out to determine the electrochemically active surface area of the Pt catalysts [20]. CV with scan window of 0–0.85 V at 10 mV s^{-1} in the mixed solution consisting of 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} CH_3OH solution was recorded to study the MOR activity of the Pt catalysts. Prior to the CV experiments, pure argon gas was passed through the electrolyte solution to remove oxygen in it. The CVs were continuously performed until a reproductive curve was acquired.

Besides, linear sweep (under a negative sweep mode) voltammetry in an O_2-saturated 0.5 mol L^{-1} H_2SO_4 solution was used to evaluate the electrocatalytic activity of the samples for the oxygen reduction reaction (ORR). The linear sweep voltammetry, sweeping from 1.0 to 0.0 V at 10 mV s^{-1}, was performed until a reproductive curve was acquired.

2.3. Physical characterizations

The physical characterizations of the catalysts were investigated through the Scanning electron microscopy (SEM) and the X-ray diffraction (XRD) measurements. The SEM observations were carried out in the ZEISS and LEO-1530 FESEM instruments, while the X-ray diffraction (XRD) measurements were carried out in the MXP21 VAHF system (Cu Kα/35 kV/200 mA) from 30° to 90°.

3. Results and discussion

3.1. Electrodes deposited by different applied electrical signals

It is known that the current waveform has a significant effect on the electrodeposition results of Pt particles [21]. At present, the potentiostatic method is mainly used to electrodeposit Pt. In addition, the electrodeposition of Pt can be carried out by 4 electrical signal types: square wave current, square wave potential, cyclic voltammetry and constant current pulse method. The common characteristic of these four kinds of current signal types is that, the positive and negative currents are alternately applied on the working electrode. On the one hand, the positive current urges metal ions to accumulate and remove adsorbed H. On the other hand, the negative current plays a role in deposition to produce uniform metal nanoparticles.

In this paper, the deposition of Pt was performed on the carbon substrate in the solution with 0.5 mol L^{-1} H_2SO_4 and 1.0 mmol L^{-1} H_2PtCl_6 at 30 °C with the total charge of 2C and four different electrical signal types as shown in Figs. 1–4: the square wave current (Fig. 1), the