



# Diffusion-restricted electrodeposition of platinum on solid carbon paste for electrocatalytic oxidation of methanol



Wu-Qi Bao, Xiao-Di He, Yan Wang, Jian-Bo He\*

Anhui Key Lab of Controllable Chemical Reaction & Material Chemical Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China

## ARTICLE INFO

### Article history:

Received 10 May 2015

Received in revised form 7 July 2015

Accepted 10 July 2015

Available online 1 August 2015

### Keywords:

Diffusion-restricted electrodeposition

Nucleation and growth

Negative impedance

Negative inductance

Direct methanol fuel cell

## ABSTRACT

Diffusion restriction of precursor ions was applied using filter paper during platinum electrodeposition on a solid carbon paste substrate, in order to uniformize the growth of Pt catalyst particles. An additional 3D nucleation process was then observed in the initial deposition stage, and the growth rate of Pt particles kept constant over whole deposition time. The prepared particles showed a sunflower-head-like morphology with numerous nanoscale “seeds” on the surface. Both the “sunflower-heads” and the “seeds” become more uniform in size, shape and surface distribution due to diffusion restriction, leading to an increase in the electrochemical active area of Pt particles and an enhancement in methanol oxidation kinetics. The analysis of electrochemical impedance spectroscopy by equivalent circuit fitting yields potential-dependent charge-transfer resistances and inductances with the same sign (positive or negative), corresponding to the regeneration or passivation of surface active sites at different potentials. This study offers insight into the role of the diffusion-restricted electrodeposition in preparing the catalyst particles with high catalytic activity.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have the advantages of simple design, low operating temperature, high durability, and using a fuel with high volumetric energy density, easy handling, transport and operation [1,2]. One of the major challenges of DMFCs is how to overcome the sluggish kinetics of methanol oxidation, which is one of the key problems on the way to commercialization. Some noble metals and their alloys (e.g. Pt and Pt–Ru, etc.) have been recognized as the best catalysts for methanol oxidation reaction at the anode of DMFCs. Many efforts have been made to decrease the loadings of noble metals and maximize their catalytic activity to methanol oxidation reaction, by using various strategies to optimize the metal particle size, size distribution, morphology, dispersion and stability [1]. The most used strategy is to develop novel support materials with unique structure, large specific surface area and high electrical conductivity, such as single walled carbon nanotubes [3], graphenes [4,5], graphene-based nanocomposites [6–8], conductive polymers [9,10], and mesoporous carbon [11].

Various strategies to directly mediate the deposition of catalyst particles have been reported, such as the urea-assisted

electrochemical synthesis of flower-like Pt arrays [12], the ampholyte polystyrene spheres self-regulated deposition of noble metal nanoparticles [13], the silver-mediated shape control of Pt [14] and core–shell Ag@Pt nanoparticles [15], the glycine-mediated syntheses of Pt–Cu nanocrystals [16] and Pt concave nanocubes with high-index  $\{hk0\}$  facets [17] and Pt–Ni nanocrystals with high-index facets [18], the seed-mediated synthesis of monodispersed hyperbranched PtRu nanoparticles [19], and the soft template confined growth of ultrathin PtRuFe nanowires [20]. In these methods, at least one substance is introduced into the system as a surfactant, reducing agent, growth directing agent, etched species, seed, or template.

Growth of the metal islands during electrodeposition results in a lasting change of the electrode surface in morphology and homogeneity [21], and thus, we believe, greatly influence the local surface potential and the local diffusion kinetics of the metal ions near the electrode surface. Irregular transient currents are generally observed during potentiostatic deposition of Pt [22], which may be connected with the chaotic growth of Pt particles and the disturbed diffusion of Pt ions. Therefore, a possible protocol aiming to mediate the diffusion of the metal ions near the electrode surface may be worth experimenting, based on use of a suitable solid filtering medium.

In the present work, we attempted to homogenize the diffusion concentration profile of  $\text{PtCl}_6^{2-}$  anions by putting a filter paper on

\* Corresponding author.

E-mail address: [jbhe@hfut.edu.cn](mailto:jbhe@hfut.edu.cn) (J.-B. He).

the surface of electrode, for the purpose of mediating the particle size, uniformity and dispersion of the Pt deposits. The substrate for the deposition is a solid carbon paste electrode (sCPE), which has recently been used to deposit multi-laminated Cu platelets with well-controlled orientation for catalytic oxidation of methanol [23]. It is found that the restriction on the diffusion of  $\text{PtCl}_6^{2-}$  ions led to a stable transient current, and beyond expectation, improved initial nucleation rate of Pt. The resulting Pt particles became uniform in size and shape, with increased electrochemical active area of the deposits and then the catalytic activity to methanol oxidation.

## 2. Experimental

### 2.1. Chemicals and solutions

Spectrograde graphite powders (320 mesh) and spectrograde paraffin wax (solidification point 56–58 °C) were purchased from China-Reagent group for preparing the sCPE.  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  ( $\geq 37.0\%$  Pt) and sulfuric acid (AR) were from Chemical Reagent Company of Shanghai, and were used as received. All other chemicals were of analytical grade from China-Reagent group. High pure  $\text{N}_2$  was used to deaerate the solutions. Doubly-distilled water from an all-glass distillatory apparatus was used as solvent. The solution for electrodeposition of platinum particles composed of  $5.0 \text{ mmol dm}^{-3}$   $\text{H}_2\text{PtCl}_6$  and  $0.5 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ . The electrolyte solutions for methanol oxidation contained  $0.5 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and different concentrations of  $\text{CH}_3\text{OH}$ .

Various filter papers were tried as a diffusion-mediator and eventually a medium-speed quantitative filter paper (No. GB/T1914-2007) was selected (Hangzhou WoHua Filter Paper Co., Ltd.).

### 2.2. Electrode modification

The carbon paste was made from dry graphite powders and paraffin wax (5:2, w/w) [24]. The electrode body was a polystyrene hollow tube with inner diameter of 3.0 mm. The tube was tightly impacted with a copper rod, leaving a cavity of 2 mm depth at one end. The solid wax was heated until molten, and then mixed with the graphite powders in a watch glass with a glass rod until a well-blended paste was obtained. The paste was firmly pressed into the cavity of the electrode body forming a bare sCPE with a geometric area of  $0.0707 \text{ cm}^2$ . This area was used for calculation of current density ( $j$ ).

The bare sCPE was polished successively with 1000 and 4000 grit emery papers followed by ultrasonically cleaning in double distilled water for 5 s. Before use, the cleaned substrates were subjected to repetitive potential cycling between  $-0.4$  and  $1.6 \text{ V}$  at  $0.5 \text{ V s}^{-1}$  in  $1.0 \text{ mol dm}^{-3}$  KCl until the background current was obtained.

Platinum particles were potentiostatically deposited from a  $\text{H}_2\text{PtCl}_6$  solution onto the sCPE substrates, either coated with a filter paper or not. The filter paper was placed close to the substrate surface without a gap between them. The changes of current with time were recorded and integrated over the measured time period to estimate the level of Pt loading. The Pt-loaded electrode prepared by diffusion-restricted deposition is denoted as rPt/sCPE, while the non-restricted one as Pt/sCPE. After the Pt deposition, the electrode was rinsed with distilled water and cleaned in  $0.5 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  by potential cycling between  $-0.3 \text{ V}$  and  $1.3 \text{ V}$  at  $\nu = 50 \text{ mV s}^{-1}$  until a reproducible cyclic voltammogram was obtained.

### 2.3. Apparatus and procedures

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry were performed on the CHI 660C electrochemical workstation (CH Instruments Co., Shanghai,

China). The three-electrode system, which was composed of a Pt-loaded working electrode, a saturated calomel reference electrode (SCE), and a Pt wire counter electrode, was used for all the electrochemical measurements. Two working electrodes, Pt/sCPE and rPt/sCPE, were used for comparison. The  $\text{CH}_3\text{OH}$  solutions were deaerated with high pure  $\text{N}_2$  for about 15 min before experiments. All experiments of  $\text{CH}_3\text{OH}$  oxidation were carried out at room temperatures (approximately 25 °C).

Surface morphologies of the two Pt-loaded electrodes were characterized using an SU8020 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan). The structural properties of the deposited Cu were examined using a D/MAX2500V X-ray diffractometer (XRD, Rigaku, Japan) equipped with Ni filtered  $\text{CuK}\alpha$  as the radiation source. The tube current was 40 mA with a voltage of 40 kV.

## 3. Results and discussion

### 3.1. Electrodeposition of Pt particles

The deposition of Pt was performed on the sCPE substrates coated with a filter paper or not. Potentiostatic and multicycle potentiodynamic methods were comparatively attempted for the Pt deposition, and the former with a constant potential of  $-0.14 \text{ V}$  (vs. SCE) was selected in the following experiments. The deposition time was varied up to 80 min to investigate effect of the Pt loading level on methanol oxidation.

Experimental transients for Pt deposition at  $-0.14 \text{ V}$  on sCPE are shown in Fig. 1A. The current at Pt/sCPE fluctuated irregularly, with a general tendency of increase over the recording time of 60 min. The current transient at rPt/sCPE became extremely stable at a significantly decreased level compared with at Pt/sCPE. The deposition rate of Pt kept constant due to the restricted diffusion through the filter paper, which should be favorable to the uniform growth of Pt particles. This finding indicates that the deposition rate of Pt was completely controlled by the diffusion of the anions through the filter paper. The diffusion flux ( $J$ ) of  $\text{PtCl}_6^{2-}$  ions can be calculated from the current density ( $j$ ),  $J = j/nF = 0.211 \times 10^{-3} \text{ A cm}^{-2} / (4 \times 96,500 \text{ C mol}^{-1}) = 5.47 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ .

Enlarged view of the current transients during the initial 10 s of deposition is also shown in Fig. 1A. After double-layer charging lasting for the first few milliseconds, the transient at Pt/sCPE showed an initial decrease over a time of about 100 s. This current contribution is due to the metal ions adsorbed at the surface defects such as monatomic steps, kink sites and holes, and can be interpreted as an instantaneous nucleation and two-dimensional (2D) growth with surface diffusion control [25,26]. At rPt/sCPE however, a rising transient was observed after the initial decline in current, with a current maximum clearly visible at about 2.8 s. A peak in a chronoamperometric transient generally indicates the occurrence of a nucleation and growth mechanism. This transient trace was compared with the theoretical curves predicted for the different types of nucleation and growth mechanisms (Fig. 1B). The theoretical curves were calculated using the following equations: (1) 2D instantaneous (2Di), (2) 2D progressive (2Dp), (3) 3D instantaneous (3Di) and (4) 3D progressive (3Dp) [27]:

$$\frac{j}{j_m} = \frac{t}{t_m} \exp \left[ -\frac{1}{2} \left( \frac{t}{t_m} \right)^2 - 1 \right] \quad (1)$$

$$\frac{j}{j_m} = \left( \frac{t}{t_m} \right)^2 \exp \left[ -\frac{2}{3} \left( \frac{t}{t_m} \right)^3 - 1 \right] \quad (2)$$

$$\frac{j}{j_m} = \left( \frac{1.9542}{t/t_m} \right)^{1/2} \left\{ 1 - \exp \left[ -1.2564 \left( \frac{t}{t_m} \right) \right] \right\} \quad (3)$$

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