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Preparation of High Catalytic Activity and Low Platinum Loading Catalyst for Methanol Oxidation

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In this paper, low platinum loading catalysts for methanol oxidation was fabricated by impregnation and reduction of inductively coupled plasma (ICP). The Pt-based supported on RGO catalysts (Pt/RGO-2) was finally obtained, which was of well dispersion, uniform sizes distribution, a stable adhesion of Pt nanoparticles with GO and suitable platinum crystal structure. Compared with commercial Pt/C catalysts, the catalysts Pt/RGO-2 was exhibited an improved and stable electrocatalytic activity and good tolerance towards CO poisoning for methanol oxidation via cyclic voltammetry (CV) and chronoamperometry in acid medium. The electrochemically active surface area (ESCA) of the achieved catalysts reached to 1026 cm²·mg⁻¹, attributing to the large surface area of graphene for Pt nanoparticles anchoring. The forward peak anodic current density (I_f) and the backward peak anodic current density (I_f) of Pt/RGO-2 were measured to be 59 mA·mg⁻¹ and 54 mA·mg⁻¹, respectively. The ratio of the forward current to the backward current (I_f / I_b) was calculated to be 1.09.

Keywords: Pt-based catalyst; Graphene; Electrocatalyst; Methanol oxidation reaction

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) using renewable and liquid methanol as fuel is considered to be a favorable option, according to available raw materials, low price, facile store and portable fashion [1-5]. The catalyst for DMFCs is asked for a high electrochemical activity, resistance of CO poisoning, and the inexpensive cost, et al. Till now, noble metals such as platinum are still the best option for fuel cells catalysts. However, noble metal catalysts have restricted commercial applications in DMFCs due to their poor durability, unstable activity of catalytic, and high cost [6,7]. Therefore, current studies of DMFCs catalysts are mainly focused on the supported catalysts with a low level of noble metal loaded, particularly platinum. The Pt-based electrocatalysts should minimize the use of platinum and maximize the performance of DMFCs. The support materials play an important role in improving the electrocativity of Pt-based catalysts, attributing to their effects on the size distribution of

platinum nanoparticles, nanoparticles dispersion and the interactions with the other activity groups. Generally, the support materials are asked for unique electrical properties, large specific surface area and corrosion resistance in the surrounding of acid or alkali. Currently, the supported electrocatalysts for methanol oxidation are based on carbon materials, e.g. carbon black, carbon nanofibers, single-walled carbon nanotubes, mesoporous carbon and graphene [8-10]. Graphene, which behaves large theoretical surface area, high conductivity, unique graphitized basal plane structure, durability and thermal stability has been regarded as an efficient support material for Pt-based catalyst [11-14]. The active surface and defects functional groups of the graphene can anchor the platinum nanoparticles steady. The related researches were reported successively by many scholars worldwide, including synthesis methods, characterization and electrocatalytic performance, et al [12, 15-21].

Graphene oxide (GO) is the oxidation production and ramification of graphene, which is single atomic layer as similar as graphene. There are some differences with graphene that certain oxygencontaining functional group was introduced to graphene oxide, such as OH, C-O-C, C=O and COOH, et al., which promotes the dispersion of GO in aqueous solution and anchors metal precursors by electrostatic interactions and chelate [22]. Metal ions can be bounded with these groups. Therefore, the performance of metal ions sorption on GO would be excellent, especially polyvalent metal ions. Meanwhile, the size distribution and dispersion of Pt (IV) can be improved with graphene oxide support. The reduction graphene oxide (RGO) reduced via reduction reaction can avoid the Pt nanoparticles moving and dissolving in the electrolyte solution for Pt supported on RGO catalysts [21]. In the past research, the sorption performance of Pt (IV) on GO was mentioned rarely, which determined the practical Pt loading of the Pt/RGO catalyst.

Herein, the electroactivity of low Pt loading catalysts prepared via our method for methanol oxidation was investigated. This study was trying to investigate: (1) The sorption of Pt (IV) from aqueous solution by GO was studied by using batch sorption experiments; (2) Two catalyst materials were synthesized by impregnation denoted as Pt/RGO-1 and Pt/RGO-2, both the total Pt content of Pt/RGO-1 and Pt/RGO-2 were closed to 10%. The GO and Pt precursors were both reduced by inductively coupled plasma(ICP); (3) The crystal size and dispersion of platinum nanoparticles supported on RGO of Pt/RGO-1 and Pt/RGO-2 were compared with each other according to characterization of the XRD and FESEM diagnostic results. (4) The performance of the Pt/RGO-1 and Pt/RGO-2 catalysts for MOR were studied via cyclic voltammetry (CV) and chronoamperometry in acid medium, and the electrocatalytic activities were comparatively investigated with 10 wt.% commercial Pt/C catalysts.

2. EXPERIMENTAL

2.1. Materials

Pt (IV) stock solution (6 g/L) was prepared by dissolving appropriate amounts of analytical reagent grade chloroplatinic acid (J&K chemical Co., Beijing, China). Graphene oxide (XF-NANO Materials, Nanjing, China) was synthesized via modified Hummers method. The GO stock solution (1 $g \cdot mL^{-1}$) prepared by sonication was applied as adsorbents to support active material and remove them from stock solutions. Color developing reagents stannous chloride and xylenol orange were both purchased

from the same suppliers (Sinopharm Chemical Reagent, Beijing, China). Unless otherwise stated, all other reagents used are of analytical reagent grade. *2.2. Batch sorption experiments*

Batch sorption experiments in 10 mL polyethylene centrifuge tubes were used to investigate the adsorption of Pt (IV) on GO. In order to achieve a desired concentration, the stock dispersions of GO adsorbent (0.30 g/L, 1 mL), KCl (0.01 mol/L, 1 mL), and Pt (IV) stock solution (1 mL) were added. The mixture solution was adjusted to the desired pH value with 0.1, 0.01 and 0.001 mol L^{-1} HCl or NaOH, and then gently shaken for 24 h to obtain sorption equilibrium after diluting it to 6 mL. The Pt (IV) concentration was analyzed by the stannous chloride spectrophotometric technique at the wavelength of 402 nm.

The adsorption capacity $(q_e = (C_0 - C_e) \times V/m_{GO})$ of Pt (IV) on GO and the Pt loading (*Pt wt.%*) were calculated from the subtraction of the initial concentration (C_0) and the equilibrium one (C_e) in the solution supernatant. The effects of pH, GO content, Pt (IV) initial concentrations and the temperature on Pt (IV) sorption by GO were investigated.

2.3. Catalysts synthesis

In this experiment, two catalyst materials were synthesized denoted as Pt/RGO-1 and Pt/RGO-2. Both of total Pt content of Pt/RGO-1 and Pt/RGO-2 were about 10%. The amount of GO and Pt (IV) inventory was according to the results of the sorption performance of Pt(IV) on GO.

The catalyst Pt/RGO-1 was synthesized as followed: $H_2PtCl_6 \cdot 6H_2O$ aqueous solution (0.2 mL, 6 g·mL⁻¹) and the graphene oxide aqueous solution (10.8 mL, 1g·mL⁻¹) were added to a 100 ml measuring flask, and then diluted to 100ml with distilled water. The mixture which was adjusted to the desired pH by adding 0.1 mol/L HCl or NaOH with negligible volumes was stirred magnetically for 4 h at 333 K and dried under vacuum at 213 K by freeze-drying.

The synthesis of catalyst Pt/RGO-2 was different from the synthesis of Pt/RGO-1. More Pt (IV) aqueous solution (0.6 mL, 6 $g \cdot mL^{-1}$) was added to the system, then follow the same process. Instead of drying directly, the mixture was concentrated to 20 ml at 333 K first. After that the solid of the concentrates, which was centrifuged at the rotation rate of 8000 r/min by a high-speed centrifuge, was collected and dried under vacuum at 213 K.

The above resultant mixtures Pt/GO-1 and Pt/GO-2 were treated with a home-made hydrogen (99.999%) inductively coupled plasma (ICP) generator (1 Pa, 100 W) for 60 min under continuous stirring *[23]*. The ICP plasma was used to reduce GO and Pt (IV) to synthesize the Pt/RGO-1 and Pt/RGO-2 catalysts.

2.4. Characterization and Electrochemical measurement

X-ray diffraction (XRD) patterns were recorded by X-ray diffractometer (X'Pert Pro MPD, Panalytical, Netherlands) using a Cu Ka radiation (Cu $\lambda_{K\alpha I}$ =0.15418 nm) operating at 40 kV and 40

mA. The morphology, crystal structure of RGO and Pt nanoparticles were analyzed by using a transmission electron microscopy (TEM) (JEM-2010, JEOL, Japan) operating at 100 kV.

The catalysts aqueous dispersion was prepared by mixing 0.5mL of deionized water, 0.5mL of ethanol, and 5 mg of the synthesized Pt catalysts powders. Electrocatalytic measurements were carried out by coating the prepared catalysts on glassy carbon electrode. For this aim, catalysts aqueous dispersion with volume of about 20 µL was uniformly spread on the glassy carbon electrode with a polished surface and dried under nitrogen stream, and then 2 µL of 5 wt.% liquid Nafion was coated and dried under nitrogen stream *[12, 19]*. The electrochemical performance of the catalysts was studied by cyclic voltammetry, chronoamperometry using an electro chemical workstation (CHI660e, Chenhua, Shanghai) in a standard three-electrode cell including catalysts with glassy carbon electrode coated, Ag/AgCl standard electrode and Pt wire which were used as the working, reference and counter electrodes, respectively. The preparation of 10 wt. % commercial Pt/C electrodes and the electrochemical measurements were operated in the same way. From the hydrogen electro-sorption peaks of the CV curves recorded within range of -0.3~1.2 V in an argon purged 0.5 M H₂SO₄ solution, we calculated the electrochemically active surface area (ECSA) of the Pt nanoparticles. By using cyclic voltammetry within range of 0~ 1.0 V, we measured the methanol electro-oxidation activity of the catalysts in an argon purged 1 M CH₃OH and 0.5 M H₂SO₄ aqueous solution *[24]*.

3. RESULTS AND DISCUSSION

3.1. Performance of Pt (IV) sorption on GO



Figure 1. Effect of pH on Pt (IV) sorption on GO. $T=293\pm 1K$, $m_{GO}/V=0.05g/L$, [KCl]=0.01M, (a) initial [Pt (IV)] =0.2g/L

Fig.1 shows the Pt (IV) sorption on GO as a function of pH. The Pt (IV) sorption increases visibly within range of 3–5 and decreases since pH > 5. Therefore, the solution pH value plays an important part in Pt (IV) adsorption on GO. Within the range of pH 3~5, the adsorption capacity of Pt (IV) on GO decreases due to the weak dissociation of the functional groups on GO and the competition

between H^+ and metal ions for the same sorption site on GO [25, 26]. At pH 5, it is beneficial for the ionization of functional groups with the oxygen containing on the surface of GO, causing to combine with Pt (IV).

The negative charges rpoduced on the GO surface can enhance the GO cationexchange capacity. And the electrostatic attraction becomes more important simultaneously [27]. The decrease of adsorption capacity of Pt (IV) on GO at pH 5–7 can be explained by the formation of hydroxide complexes. At high pH values, the predominant Pt (IV) species is Pt $(OH)_3^-$, which is difficult to be adsorbed on GO due to the negative surface charge of GO [28]. The next adsorption experiments were performed at pH = 5 by taking into consideration the high adsorption of Pt (IV) from aqueous solution and to prevent precipitation of metal hydroxides. Under these conditions, the adsorption of Pt (IV) was determined by an intensive surface complexation of Pt (IV) with the oxygen-containing groups on the GO surface.

The sorption of Pt (IV) on GO as a function of contact time is shown in Fig. 2. The adsorption of Pt (IV) was remarkable at the contact time of about 1 h, then proceeded at a slow increasing rate and finally reached almost saturation after contact time of about 4 h. Therefore, the contact time in the following experiments was fixed more than 4 h to ensure the sorption saturation. To simulate the kinetic sorption, a pseudo-second-order rate equation was used [29]:

$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{k} \cdot \mathrm{q}_{\mathrm{e}}^{2}} + \frac{\mathrm{t}}{\mathrm{q}_{\mathrm{e}}} \qquad (1-1)$$

Where $k (g/(mg \cdot h))$ is the pseudo-second-order rate



Figure 2. Sorption kinetics of Pt (IV) on GO. T=293 \pm 1K, mGO/V=0.05g/L, [KCl]=0.01M, (a)initial[Pt(IV)] =0.2g/L

To test the proper ratio of Pt (IV) on GO sorption The effect of GO concentration on Pt (IV) sorption is It is appropriate that the Q_{max} and q_e is 255 mg and



Figure 3. Effect of different initial GO concentrations on the sorption of Pt (IV); $T=293\pm 1K$, $_0=0.2g/L$, [KCl]=0.01M, $pH=5.0\pm 1$.

The sorption isotherms of Pt (IV) on GO was shown

The equation (1-2) is expressed in linear form:

where $Cs \pmod{g}$, $C_{smax} \pmod{g}$ and $b \pmod{d}$ is the The Freundlich isotherm model is used to describe

The equation (1-4) can be reorganized in a linear

 $Log C_s = log K_F + n Log C (1-5)$

 $C_{s} = \frac{bC_{smax}C_{e}}{1+bC_{e}} \quad (1-2)$

 $C_{s} = K_{F}C_{e}^{n}$ (1-4)

 $\frac{C_{e}}{C_{s}} = \frac{1}{bC_{smax}} + \frac{C_{e}}{C_{smax}} \quad (1-3)$

Where $K_F (\text{mol}^{1-n} L^n/g)$ is the Freundlich sorption coefficient related to the sorption capacity and *n* is an indicator of isotherms nonlinearity corresponding to the sorption intensity.

Isotherms parameters are obtained by fitting the adsorption equilibrium data to the isotherms models, and listed in Table 1. From the correlation coefficients, one can see that the Langmuir isotherms model fits the experimental data much better than the Freundlich isotherms model, which means that the sorption of the Pt (IV) on GOs was monolayer coverage.



Figure 4. Sorption isotherms of Pt (IV) on graphene oxides; mGO/V=0.05g/L, [KCl]=0.01M, $pH=5.0\pm1$.

Table 1. Parameters for Freundlich and Langmuir sorption isotherms of Pt (IV) on GO at 293 K.

		Langmuir				Freundlich			
Mode	el	Isotherms	Cm	b	R^2	Isotherms	K	п	R^2
simulation		1.50000000000	(mmol/g) (L/mol)				(mol/g)		
293 <i>K</i>	C _e /	$C_s = 0.681C_e + 0.176$	2.667	7.212	0.9953	$logC_s=0.294logC_e$ -	0.991	0.294	0.7959
						0.0038			

The effect of temperature on the distribution coefficient, defined as $\ln K_d$, was shown in Fig.5 at different initial concentrations. The constant of thermodynamic equilibrium K_d (L/g) is the ratio of the sorption capacity q_e and the equilibrium concentration C_e . The values of $\ln K_d$ and 1/T are liner correction as shown in equation (1-6). The values of enthalpy (ΔH°) and entropy (ΔS°) are calculated from the slope and intercept of the relation [32, 33].

$$ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} (1-6)$$

The change of Gibbs free energy (ΔG°) is calculated from the equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} (1-7)$$

Where R (8.314 J/mol•K) is the constant for perfect gas, and T is the temperature in Kelvin. The thermodynamic data calculated by equation (1-6) and (1-7) are listed in Table 2. The positive enthalpy change (ΔH°) implies that the sorption process of Pt (IV) is endothermic. The original structural of Pt (IV) needs to be destroyed before being absorpted on GO surface. Energy is needed in this process, and high temperature would be favorable. The exothermicity of cations can attach to the GO surface as the energy exceeds the threshold.



Figure 5. Dependence of temperature on the Pt (IV) sorption distribution coefficient at different initial concentrations. mGO/V=0.05 g/L, [KCl]=0.01 M, pH=5.0±1.

$$ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

C ₀		$\Delta G^{\circ}(kJ/mol)$		ΔH°	$\Delta \mathrm{S}^{\circ}$	
(mol/L)	293K 313K		333K	(kJ/mol)	(J/mol·K)	
0.05	-4.29	-8.13	-12.87	58.40	213.51	
0.25	-3.25	-4.67	-6.50	20.50	80.86	
0.51	-1.63	-2.84	-4.30	17.92	66.58	
1.02	-0.03	-1.21	-2.35	16.92	57.88	
2.04	1.23	-0.05	-0.42	13.50	42.32	
3.07	1.94	0.85	0.50	12.57	36.65	
4.09	2.56	1.55	1.15	12.94	35.74	

Table 2. Thermodynamic parameter of Pt (IV) sorption on GO.

The change of Gibbs free energy (ΔG°) is negative at the Pt (IV) concentration ranging from 0 to 1 mol/L as expected, and positive since 1 mol/L, which indicates that the adsorption reaction can not be occurred spontaneously at the standard state due to the agglomeration of graphene oxide at high concentrations of Pt (IV) [34]. At a high temperature the Pt (IV) is easy to be adsorbed, and with increasing temperature the value of ΔG° becomes more negative, which shows that the Pt (IV) sorption would be more efficient at higher temperature. The positive value of the change of entropy (ΔS°) implies that some structural changes appear in Pt (IV) and GO for a sorption. The values of ΔH° and ΔS° decreased with increasing initial Pt (IV) concentrations. Initially the sorption occurs on the most

active available sites due to the high interaction energies. The attractive force between Pt (IV) and sorption sites of GO is different. At lower concentration, Pt (IV) sorption is easy to proceed because of the cooperative and non-cooperative ability at higher binding energy for metal ions. When the Pt (IV) solution with a higher concentration was used as one of the starting materials, Pt nanoparticles were partly aggregated because of their high number density. It is indicated that Pt (IV) sorption on the GO increased at low solution concentrations as compared to that at high concentrations.

3.2. Morphological and electrocatalytic characterizations

XRD patterns of Pt/RGO-1, Pt/RGO-2 and 10 wt.% commercial Pt/C catalysts were shown in Fig.6. The diffraction peaks of Pt/RGO-1, Pt/RGO-2 and 10 wt.% commercial Pt/C at 40.0°, 46.2° and 67.5° corresponded to Pt (111), Pt (200), and Pt (220) planes of face center cubic structure (FCC) of Pt (JCPDS No.4–802), respectively, which further supported the successful formation of platinum nanoparticles on graphene sheets. Pt (111) plane has the lowest surface energy for Pt based catalysts. Therefore, it was often observed in the spherical shape [12, 35, 36].

The diffraction peaks at around 2θ = 26.2° of the Pt/C and Pt/RGO-1 catalysts can be indexed to C (002) reflection of the carbon hexagonal structure, implying that the composite has few-layer graphene sheets. The peak C (002) of the Pt/RGO-2 was almost disappeared, which indicated a successful reduction of GO to RGO by plasma treatment. There were several unapparent peaks of Pt/RGO-2 at 42.3°, 44.5°, 54.6°, 59.8° and 77.4° corresponding to C (100), C (101), C (004), C (103), C (110), respectively, indicating a low graphite crystalline of the catalysts [36, 37].

The relatively large FWHM of the diffraction peaks indicated a smaller size of the Pt nanoparticles. The diffraction peak for Pt (220) was used to estimate the Pt crystallite size since there was no interference from other diffraction peaks. The sizes of Pt nanoparticles calculated upon Scherrer formula (2-1) were 4.3 nm, 7.8 nm and 2.8 nm, respectively. The average Pt nanoparticle sizes of 10 wt.% commercial Pt/C, Pt/RGO-1, and Pt/RGO-2 were 5.54 nm, 6.67 nm and 3.31 nm which were listed in Table 3. These values were in a good agreement with the FESEM results and those of the Pt/graphene composites reported previously [37].

$$L = \frac{0.9\lambda_{Kal}}{B_{(2\theta)}Cos\theta_{max}} (2-1)$$

Where L (nm), $\lambda_{K\alpha l}$ (Cu $\lambda_{K\alpha l}$ =0.15418 nm), θ_{max} (rad),



Figure 6. X-ray diffraction patterns of Pt/RGO-1, Pt/RGO-2 and Pt/C catalysts



Figure 7. TEM image of GO (a), Pt/RGO-1 (b) and Pt/RGO-2 (c); HRTEM image (d) released from Pt/RGO-2. Image (e) is a high-resolution image of a Pt nanoparticle shows the Pt nanoparticle revealing the (111) plane of Pt. The distribution diagram (f) of Pt nanoparticles on RGO surface. (a2, b2, c2) electrodes

TEM images of GO, Pt/RGO-1 and Pt/RGO-2 were From Fig.7 (b), both the size and shape of Pt In order to find out the ECSA of the Pt/RGO, cyclic

Where
$$q_H$$
 is the adsorption charge density of a

Where
$$d, \rho$$
 were the mean Pt particle size in nm (from





Figure 8. Cyclic voltammogram of Pt /RGO-1, Pt/RGO-2 and Pt -C in Ar saturated 0.5 M H2SO4aqueous solution at a scanning rate of 50 mV/s.



Figure 9. Cyclic voltammogram of Pt /RGO-1, Pt/RGO-2 and Pt/C in Ar saturated aqueous solution of 0.5 M H₂SO₄ and 1 M CH₃OH mixture, at a scanning rate of 10 mV/s.

As shown in Table 3, the ECSA of 10 wt.% commercial Pt/C catalysts obtained by using the above equation was 47.49 cm²·mg⁻¹. The ECSA of Pt/RGO-1 and Pt/RGO-2 was found to be $139 \text{cm}^2 \cdot \text{mg}^{-1}$ and $1026 \text{cm}^2 \cdot \text{mg}^{-1}$, respectively, which showed a larger surface area provided by RGO of Pt/RGO-2 catalyst for anchoring more Pt nanoparticles. The large ECSA could be due to the good electrocatalytic activity of the catalysts towards methanol oxidation process. The utilization efficiency of Pt for methanol oxidation of the Pt/RGO-2 was 89.12% which is higher than the others.

The CV curves (versus saturated Ag/AgCl) of Pt/RGO-1, Pt/RGO-2 and 10 wt.% commercial Pt/C catalysts for methanol oxidation reaction (MOR) were shown in Fig.9. The cyclic voltammetry was utilized to investigate the methanol oxidation in argon saturated 0.5 mol/L H_2SO_4 and 1 mol/L CH₃OH aqueous solution. The hydrogen adsorption-desorption peaks observed in 0.5 M H_2SO_4 was suppressed in 1 M CH₃OH and 0.5 M H_2SO_4 solution due to the adsorption of CO.

Catalysts	Pt /C	Pt /RGO-1	Pt /RGO-2	Pt/RGO [12]	Pt/TMPyP-g[39]	Pt/graphene[39]
Pt Loaded (wt.%)	10%	10%	8.6%	20%	13.09%	10.08%
NPs Size (nm)	5.54	6.67	3. 31	2.67	3.3	4.2
SCA $(cm^2 \cdot mg^{-1})$	513.70	425.96	1152.24	_	_	_
ECSA $(cm^2 \cdot mg^{-1})$	47.49	139.13	1026.89	521.6	1262	801
n (%)	9.24%	32.66%	89.12%	_	—	—
$I_f \pmod{mA \cdot mg^{-1}}$	20	31	59	_	_	_
$I_b (\mathrm{mA} \cdot \mathrm{mg}^{-1})$	20	22	54	_	_	_
I_{f}/I_{b}	1.00	0.91	1.05	1.36	1.08	1.07

Table 3. Comparisons of morphological and electrochemical data of Pt/RGO-1, Pt/RGO-2, Pt/TMPyP-g, Pt/grapheme, and Pt/C electrode.

The peak observed at around 680 mV in the forward scan was characteristic of the methanol oxidation. Whereas, the peaks at around 490mV in the reverse scan was primarily associated with the removal of the residual carbon species formed in the forward scan. The forward anodic peak current density (I_f) of Pt/RGO-2 was measured to be 59 mA·mg⁻¹, nearly 3 times that of Pt/RGO-1(I_f =20 mA·mg⁻¹) and Pt/C catalyst (I_f =20 mA·mg⁻¹). The small changes in backward anodic peak current density (I_b) led to a negligible potential shift of the backward anodic waves, indicating that the Pt/RGO-2 catalyst enhanced the electro-oxidation of methanol and the stability of the catalyst. The peak in the reverse scanning corresponded to the residual carbonaceous species oxidation formed during the forward scan. The peak current density of Pt/RGO-1, Pt/RGO-2 and Pt/C are 22, 54 and 20 mA·mg⁻¹, receptively, after 50 cycles at around a potential of 490 mV versus Ag-AgCl.

The ratios of the forward to the backward current were the way of exploring the electrocatalyst performance towards the poisoning of CO. The I_f/I_b ratio, for Pt/RGO, calculated after 50 cycles was 1.09 which was almost 1.2 times of the Pt/RGO-1 electrocatalyst ($I_f/I_b = 0.91$), and 1.1 times of the Pt/C electrocatalyst ($I_f/I_b = 1.0$). After 50 cycles, the I_f/I_b ratio of Pt/RGO-2 remained almost the same stability towards the poisoning of CO. It was considered that the strong interaction between the Pt nanoparticles and the RGO sheets has improved the CO tolerance of Pt/RGO-2. The results demonstrated a better tolerance of the Pt/RGO-2 electrocatalyst towards CO poisoning and better electrocatalytic performance, which were in accordance with the electrochemical active surface area, revealing that the actual loading amount of Pt nanoparticles played an important role in Pt/RGO catalysts with Pt loaded about 20%. The ECSA for the Pt/RGO was only about 521.6 cm²·mg⁻¹. However, the I_f/I_b ratio was about 1.36 which meant a better tolerance towards CO poisoning which may attribute to the smaller nanoparticles size and the RGO sheets. In reference 39, similar experimental results were presented with the Pt loading of about 13.09% and 10.08% for prepared Pt/ TMPyP-g and

Pt/graphene, respectively. The I_{f}/I_{b} ratios were 1.08 and 1.07 for the prepared Pt/ TMPyP-g and Pt/graphene catalysts which has a nanoparticles size of about 3.3 nm and 4.2 nm, respectively, while the ECSA for the catalysts were 1262 cm²·mg⁻¹ and 801 cm²·mg⁻¹. The results indicated that the nanoparticles size would be the more important factor determining the tolerance towards CO poisoning compared with the ECSA of catalysts.

As shown in Fig.10, the stability of the electrocatalyst was further confirmed by chronoamperometry at 0.4 V. The current decreased rapidly for Pt/RGO-1, Pt/RGO-2 and Pt/C catalysts at the initial stage due to the formation of intermediate species during methanol oxidation reaction [15]. However, the electrocatalytic performance of the Pt/RGO-2 catalyst for the methanol oxidation reaction was higher than that of the Pt/RGO-1 and Pt/C, which was accordance with the result of the ratio of the forward current to the backward current.



Figure 10. Chronoamperometric curves for Pt/RGO-1, Pt/RGO-2 and Pt-C in argon saturated0.5 M H₂SO₄and 1 M CH₃OH mixture aqueous solution at a potential of 0.4 V vs saturated Ag/AgCl.

From the above results, higher activity and long-term stability of the Pt/RGO-2 catalyst can be attributed to the synergetic effects of the Pt nanoparticles and the graphene sheets, such as a good dispersion which enhanced the charge transfer rate, uniform sizes distribution, and a stable adhesion of Pt nanoparticles with GO.

4. CONCLUSION

In order to confirm that the Pt sorption activity on graphene is the actual Pt loading, the control condition of Pt loading on GO was explored by batches of sorption experiments. The ICP plasma was used to reduce the Pt (IV) and graphene oxidation. Both of the total Pt content of Pt/RGO-1 and the actual Pt loading of Pt/RGO-2 which were synthesised by impregnation were approximately about 10 wt.%. The Pt/RGO-2 catalyst was proved that it improved catalytic activity for methanol oxidation because Pt nanoparticles distributed more uniform on graphene sheets. The increase in performance of

Pt/RGO-2 electrocatalyst such as an increase in the number of catalytic reaction sites was caused by a good dispersion which enhanced the charge transfer rate, uniform sizes distribution, and a stable adhesion of Pt nanoparticles with GO. The catalytic activity of the Pt/RGO for methanol oxidation can be further improved by exploring better reaction parameters of the ICP plasma technology.

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