

Study of Monoxide Adsorption/Desorption over Modified Carbon Paper Electrode

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Abstract

The platinum particles were grown directly by electrodeposition process on electrochemically treated carbon paper (CP) for kinetic study of CO desorption carbon monoxide (CO) desorption. The treatments on CP were performed by applying -2 V for cathodic oxidation over 5 min. Treated CP was characterized by (FTIR) for investigating the oxygen surface groups on their surface. CO surface coverage at each temperature was determined by monitoring changes in H_{ad} desorption charge during CO stripping at different desorption time (300 to 1800 s). CO coverage for cathodic electrode is lower than non-treated one in all temperature. Desorption rate constants were calculated for cathodic and non-treated electrodes. From 25 to 85 °C, desorption rate constant calculated and rate constants for cathodic electrode were higher for all temperature. The activation energies for desorption were estimated from data obtained by the experiments is 28480 and 18900 J.mol⁻¹ for non-treatment and cathodic electrode respectively, which shows that CO desorption is easier on the surface of cathodic electrode.

Keywords: Cathodic Treatment; Carbon Paper; CO Poisoning; Kinetics Desorption; PEM Fuel Cell

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1. Introduction

The necessity of reducing the use of petrol derivatives has result in an increasing interest in the development of alternative energy sources. In electrochemistry, a big effort is being made regarding the fuel cell technology, which has become one of the hottest topics in this area. [1]. One problem emerges when using hydrogen containing CO which compete with H₂ for adsorption on Pt surface strongly. There exist several methods to mitigate the effect of CO poisoning which could be considered from two points of view: electrochemical CO oxidation and the equilibrium CO coverage reached through the

adsorption/desorption process. Studies indicate that particle size, exposed crystal faces and oxidation state of carbon supports are important factors influencing on specific activity of the Pt electrocatalyst for CO [2]. In addition to alloying, supporting strategies could dramatically reduce the Pt poisoning. Carbon is widely used as the electrode support for fuel cells. Unfortunately, non-treated carbon is often hydrophobic, so adsorption of catalysts is limited. Therefore, it is of particular interest to carry out treatments on the carbon surface to activate it by additional functional groups. Moreover, according to studies it is expected that the oxidized functional groups on

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carbon supports promote CO electrooxidation [3], [4], [5]. V.M. Jovanovic et al showed that electrochemical treatment of glassy carbon (GC) support, leads to a better distribution of platinum on the substrate and has effect on the activity for methanol electrooxidation [6]. M. Bayati et al. studied the effect of oxidation of the HOPG (highly oriented pyrolytic graphite) [7]. These investigations reveal that oxidation of support has effect on CO and methanol electrooxidations, though as we know, these supports are not real support for fuel cells. Moreover, there is a lack of understanding on the role of oxygen groups on the CO tolerance in point of CO coverage reached through the adsorption/desorption process and its kinetic has rarely been investigated. Sharma et al confirmed the presence of -COOH group provides the most resistance for CO adsorption according to DFT analysis and the CO-Pt binding energy is significantly lower [8]. CP can be utilized as electrode support and diffusion layer, and as catalyst support in some deposition methods for fuel cells [9]. Electrodeposition is one of the method which Platinum can be deposited directly on carbon support. The advantageous of this method is achieving greater selectivity in the placement of the platinum particles into the preformed electrode and controlling the condition for Pt deposition [10]. There are several techniques which able to introduce oxygenated surface compounds via the consecutive formation of hydroxyl, carbonyl, carboxyl and other groups on CP and activate its surface, especially before electrodeposition. One of them is electrochemical oxidation that can be performed by applying anodic and cathodic potential [11]. To the best of our knowledge, and there is no research on cathodic oxidation of CP as catalyst support for enhancing Pt activity for CO tolerance. In our previous study, the effect of the cathode was investigated. In this study, the effect of cathodic treatment on CO tolerance is studied from the point of CO desorption. The Pt was electrodeposited on treated and non-treated CPs and the effect of cathodic treatment for CO tolerance according to kinetic study of desorption was investigated.

1. Materials & methods

0.5*0.5 cm² CP (TGPH-090; Toray) was used as support for electrochemical catalyst preparation. Treatments on CP were performed by applying -2 V for cathodic oxidation during 5 min. Pt was electrodeposited onto the CP by single-pulse chronoamperometry method and adjusting potential profile of 0 V (1 s) and 1.15 V (600 s) (vs. Ag/AgCl(sat)) in deoxygenated 0.2 M H₂SO₄ + 2 mM H₂PtCl₆.6H₂O. Electrodeposition and all of the

electrochemical measurements were performed in a conventional three-compartment electrochemical glass cell at room temperature, using SP-300-Potentiostat – Galvanostat from Bio-Logic Co. and data recorded by EC-Lab V10.22 interface software. A Pt rod and an Ag/AgCl/KCl(sat.) served as the counter and reference electrodes, respectively (AZAR Electrode, IRI). Setup was heated up to the desired temperature using silicon oil bath for CO stripping tests. In this research the coverage of CO was calculated according to equation (1) where Q_H and Q_H' are the quantities of charge for desorption of H_{ad} on the clean electrode and the CO-saturated electrode after desired desorption time, respectively and these quantities can be measured based on CO stripping CV results (Figure 1). Using this method, make it possible to calculating the coverage which is directly related to desorption of CO from Pt sites, conveniently (Figure 1).

$$\theta_{CO} = Q_{CO} / sQ_{CO} = 1 - sQ_H' / sQ_H \quad (1)$$

For CO stripping test, the electrode was exposed to CO in the gas phase for 300 s at room temperature and applying 0 volt for CO adsorption. Immediately the electrode was transferred to the fresh electrolyte that completely purged with nitrogen and is reached the desired temperature, in order to CO_{ads} desorption investigation. The adsorption, desorption and stripping steps were repeated for various desorption times (300, 600, 900 or 1800 s) and temperatures (25, 40, 55, 70 or 85 °C). Desorption rate constants were then estimated by fitting these data to a kinetic model and the respective activation energy was estimated by repeating these procedures at different temperatures.

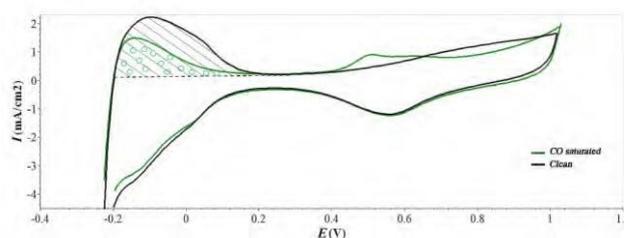


Figure 1. Green circles (Q_H') and black lines (Q_H) in equation (1) for CO coverage calculation

Results and discussion

2.1. FTIR

FTIR is a very useful technique for studying the nature of oxygen surface groups. In this work, cathodic CP was characterized by micro-ATR-FTIR and the finger print regions of the spectra are

shown in Figure 2 and Peak assignments are summarized in Table 1. Despite of non-treated carbon paper FTIR spectra [10], the appearance of distinct species after electrochemical treatment is evident from the FTIR (Figure 2). For cathodic oxidized CP, peaks assigned to oxygen functional groups are clearly observed (Table 1). These result of a high oxidation state of CP during the cathodic oxidation.

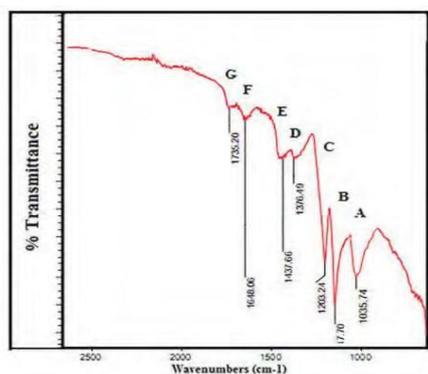


Figure 2. ATR-FTIR spectrum of CP after cathodic electrochemical oxidation Table 1: ATR-FTIR peak assignments for oxidized CP [11,12]

	Wave No.(cm ⁻¹)	Functional Group
A	1040	Primary alcohol
B	1145	Ether
C	1200	Phenol
D	1375	Phenol or tertiary alcohol
E	1435	Carboxylic
F	1650	Quinone and Conjugated ketone
G	1735	Lactone

2.2 SEM

Figure shows the typical SEM micrographs of the electrodeposited Pt on non-treated (Figure .a) and treated CP (Figure). Smaller particles are observed on cathodic electrode compared to non-treated electrode. It shows that oxygen groups apparently influence nucleation and agglomeration of Pt particles deposited on carbon paper.

2.3 CV in H₂SO₄

Typical voltammograms (Figure 4) show an increase in the current when electrodes are treated, compared with non-treated one.

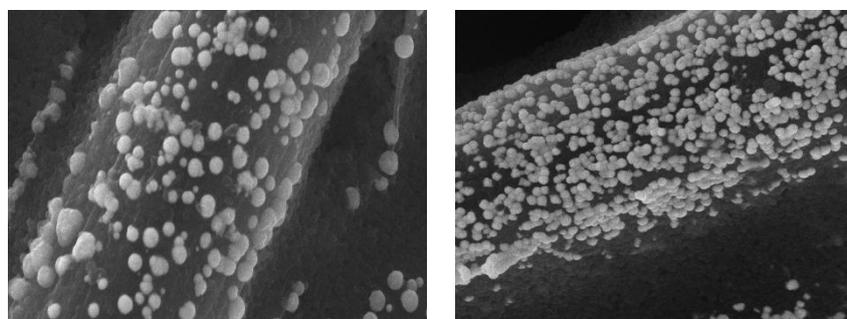


Figure 3. SEM images of Pt particles deposited directly on (a) non-treated and (b) cathodic CP

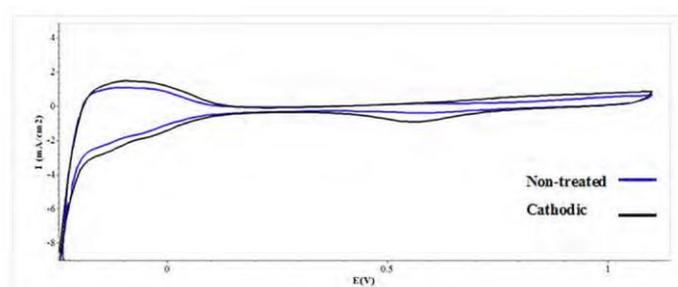


Figure 4. CV curves for treated and non-treated electrodes in 0.5M H₂SO₄ at 25°C and Scan rate of 50 mV/s. The electrochemical active surface area (ECSA) of Pt catalysts is calculated by integrating the charge of hydrogen in adsorption/desorption region of CVs in terms of the metal loading [13]. The ECSA of the electrodes are 11.7 and 13.7 (m².g⁻¹) for non-treated and cathodic electrodes, respectively.

2.4. CO coverage at different temperature

In order to measure coverage, CO stripping CVs at selected desorption time (1800 s) was repeated for all temperatures (25, 40, 55, 70 and 85) for cathodic and non- treated electrodes. As expected, high surface coverage of CO_{ads} decreased with increasing temperature. CO coverages were calculated from the CVs according to equation (1) at selected desorption time (1800 s) and results are shown in **Error! Reference source not found.** This descending linear relationship was reported in other literature [14]. As shown in figure 5, CO coverage for cathodic electrode is lower than non-treated one in all temperature. As a primary result we can declare that CO desorption is more on the electrode surface after cathodic treatment.

2.5 Desorption rate constants

For calculating desorption rate constants which are dependent on CO coverage, desorption rate equation should be considered. Assuming first-order Langmuir desorption kinetics and k_{des} is independent of the surface coverage, the desorption rate constant could be measured

directly from gradient of a plot of $\ln(\theta)$ against t according to equation (2) ⁶. Figure shows $\ln(\theta)$ versus time for both electrodes at different temperature.

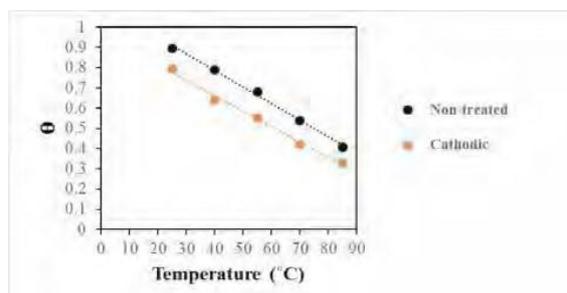


Figure 5. The changes of CO surface coverage with the temperature at the non-treated and cathodic electrode surface, after the initial adsorption of a certain amount of CO at 25 °C.

$$\ln(\theta) = k_{des}t + \ln\theta_0 \quad (2)$$

The linear relation for all experiments in Figure 6 agrees fully with a simple first order model, which was assumed as the simple model rate for CO desorption.

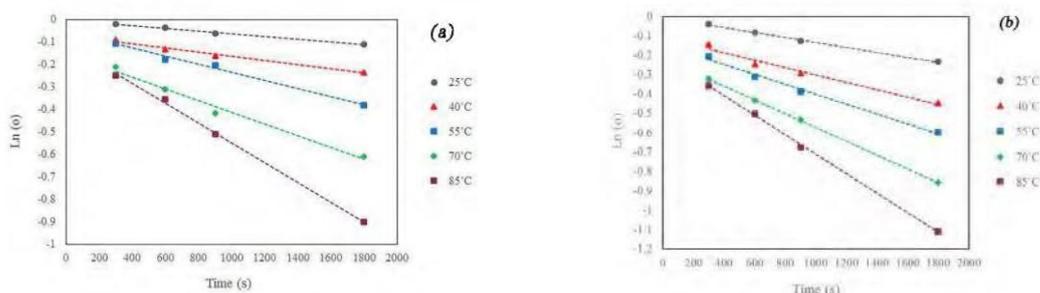


Figure 6. $\ln(\theta)$ versus desorption time at various temperatures (25, 40, 55, 70 and 85 °C) for a) cathodic and b) non-treatment electrodes

According to the correlation in Figure and equation (2) the slope of the plot of natural logarithm of coverage and time is equal to k_{des} . Desorption rate constants are calculated and listed for both electrodes in all temperature in Table . According to these results we can conclude that rate constant for cathodic electrode is higher than non-treated one in this temperature range of experiments.

The temperature dependence of desorption rate constant is given by the Arrhenius equation as shown below [16]:

$$k_{des} = A \cdot \exp\left(-\frac{E_{des}}{RT}\right) \quad (3)$$

Table 2. Desorption rate constants (k_{des}) calculated for CO-saturated condition at various temperatures (25-70) for cathodic and non-treated electrode

Temperature (°C)	Non-treated	Cathodic
	$k_{des}(s^{-1})$	
25	6.1×10^{-5}	1.29×10^{-4}
40	9.3×10^{-5}	1.91×10^{-4}
55	1.79×10^{-4}	2.56×10^{-4}
70	2.6×10^{-4}	3.55×10^{-4}

Where k_{des} is desorption rate constant in s^{-1} , A is the frequency factor in s^{-1} , E_{des} is desorption activation energy in $J mol^{-1}$, R is universal gas constant and T is the temperature in K. The frequency factor can be considered as temperature independent constant.

A natural logarithmic form of equation (3) yields equation (4) :

$\ln(k_{\text{des}}) = \left(-\frac{E_{\text{des}}}{RT}\right) + \ln(A)$	(4)
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Thus, a plot of the logarithmic value of desorption rate constant versus the inverse temperature should provide a linear response. Figure 7 shows the Arrhenius plot, based on natural logarithmic value of desorption rate constant versus the inverse temperature in K.

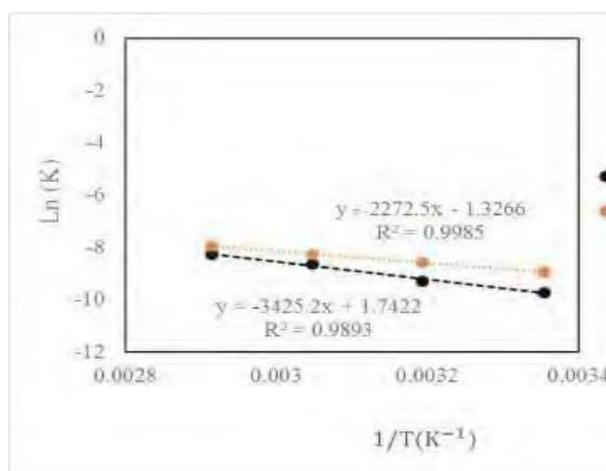


Figure 7. Determination of the apparent Arrhenius parameters, using the Arrhenius plot for cathodic and non-treated electrodes

The activation energy for desorption was estimated from data obtained by the experiments is 28480 and 18900 J.mol⁻¹ for non-treatment and cathodic electrode respectively. The lower activation energy for CO desorption surface of cathodic electrode indicates that the process of desorption could be easier due to oxygen containing groups and the impact of these functional groups in the energy bond between platinum and CO.

2. Conclusion

We found that the presence of oxygen functional groups on carbon paper can play a major role on the desorption of CO species on the Pt sites. Our team have studied the effect of the CP cathodic electrochemical treatment on properties of Pt which was electrodeposited on it for CO desorption. We have revealed cathodic treatment of carbon not

only decrease the surface coverage of CO on its surface at this temperature range but also enhance CO desorption rate in this range. Our results suggest that the oxygenated functional groups can affect the Pt-CO binding energy and facilitate CO desorption. The lower activation energy according to Arrhenius equation for cathodic electrode in compare with non-treated is an evidence for this claim.

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