Kinetic study of CO desorption from cathodic electrochemically treated carbon paper supported Pt electrodes

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Abstract

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

1. Introduction

The necessity of reducing the use of petrol derivatives has resulted in an increasing interest in the development of alternative energy sources. In electrochemistry, a big effort is being made regarding fuel cell technology, which has become one of the hottest topics in this area [1]. One

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[1]Proton Exchange Membrane

problem emerges when using hydrogen containing CO, it strongly competes with H_2 for adsorption on the Pt surface.There exist several methods to mitigate the effect of CO poisoning which generally fall into two groups: electrochemical CO oxidation and equilibrium CO coverage reached through the adsorption/desorption process. Studies indicate that particle size, exposed crystal faces and the oxidation state of carbon supports are important factors influencing specific activity of the Pt electrocatalyst during CO oxidation and desorption [2]. In addition to alloying, supporting strategies could dramatically reduce 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 carbon supports promote CO electrooxidation 3-5. Jovanovic et al. showed that electrochemical treatment of glassy carbon (GC) support leads to a better distribution of platinum on the substrate and has an effect on the activity for methanol electrooxidation [6]. Bayati et al. studied the effect of oxidation of HOPG (highly oriented pyrolytic graphite) and concluded that oxidation of HOPG has a large influence on methanol electrooxidation [7]. These investigations reveal that oxidation of the support has an effect on CO and methanol electrooxidations. Although, as we know, these supports (HOPG and GC) are not actual support for fuel cells, it is valuable to study the effect of surface oxidation on actual fuel cell supports such as carbon paper, carbon cloth, etc. Moreover, there is a lack of understanding of therole of oxygen groups on CO tolerance, specifically CO coverage reached through the adsorption/desorption process, and its kinetic has rarely been investigated. Sharma et al. confirmed the presence of the -COOH group provides the most resistance for CO adsorption according to DFT analysis and the CO-Pt binding energy reduction [8].

CP can be utilized as an electrode support and diffusion layer, and act as catalyst support in some deposition methods for fuel cells [9]. Electrodeposition is a method in which platinum can be deposited directly on carbon support. The advantages of this method are 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 are able to introduce oxygenated surface compounds via the consecutive formation of hydroxyl, carbonyl, carboxyl and other groups on the CP and activate its surface, especially before electrodeposition. One of these is electrochemical oxidation which can be performed by applying anodic and cathodic potential [8, 11].

To the best of our knowledge there is no research on cathodic oxidation of CP as catalyst support for enhancing Pt activity for CO tolerance and its effect on CO desorption. In our previous study [12], the effect of cathodic oxidation was investigated from the point of view of CO electrooxidation. In this study, the effect of cathodic treatment on CO tolerance is studied from the point of view of CO desorption according to our purposed method [13]. 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 and methods

$0.5*0.5$ cm^2 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 the single-pulse chronoamperometry method and an adjusting potential profile of 0 V (1 s) and 1.15 V (600 s) (vs.Ag/AgCl(sat)) in deoxygenated 0.2 M H_2SO_4 + 2 mM $H_2PtCl_6.6H_2O$. Electrodeposition and all of the electrochemical measurements were performed in a conventional three-compartment electrochemical glass cell at room temperature, using
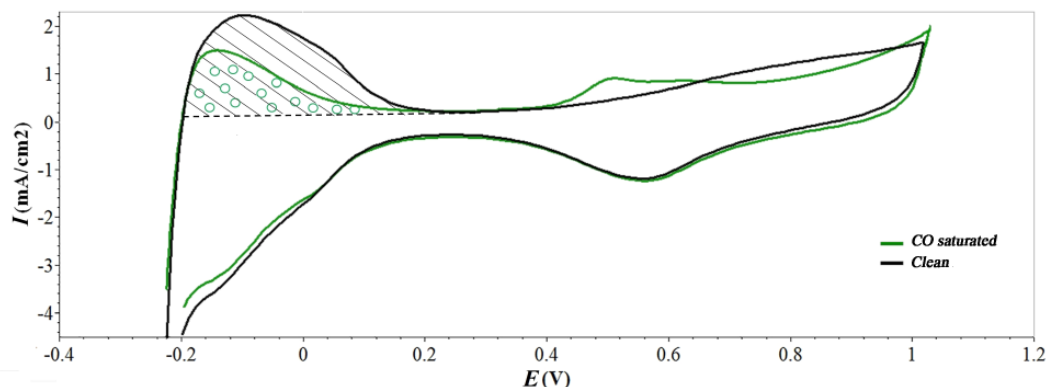
Fig.1. Green circles (Q$_H$') and black lines (Q$_H$) in equation (1) for CO coverage calculation.

a 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 (θ_{CO}) was calculated according to equation (1) where Q$_H$ and Q'$_H$ are the quantities of charge for desorption of Had on the clean electrode and the CO-saturated electrode after desired desorption time, respectively, and these quantities can be measured based on CO stripping cyclic voltammetry (CV) results (Fig. 1).

Using this method makes it possible to conveniently calculate the coverage which is directly related to desorption of CO from Pt sites (Fig. 1).

$$\theta_{co} = {Q_{co}}\Big/{sQ_{co}} = 1 - {}^s{Q'_H}\Big/{}_sQ_H \qquad (1)$$

For the 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. Then the electrode was immediately transferred to a fresh electrolyte that was completely purged with nitrogen until it reached the desired temperaturefor the 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.

2. 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 Fig. 2 and peak assignments are summarized in Table 1. The appearance of distinct species after electrochemical treatment is evident from the FTIR (Fig.2) compare with non-treated carbon paper FTIR spectra [14].

For the cathodic oxidized CP, (Table 1) which show the high oxidation state of CP during cathodic oxidation.

2.2.SEM

Fig. 3 shows typical SEM micrographs of the electrodeposited Pt on non-treated (Fig. 3.a) and treated CP (Fig. 3.b). Smaller particles are observed on the cathodic electrode compare to the non-treated electrode. This shows that oxygen groups apparently

Table 1. ATR-FTIR peak assignments for oxidized CP [16],[17].

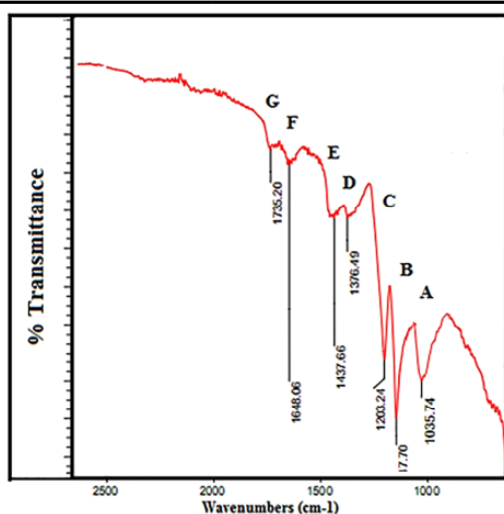|	WAVE NO.(CM^{-1})	FUNCTIONAL GROUP
A	1040	Primary alcohol
B	1145	Ether
C	1200	Phenol
D	1375	Phenol or tertiary alcohol
E	1435	Carboxylic
F	1650	Quinone and Conjugated ketone
G	1735	Lactone

Fig. 2. ATR-FTIR spectrum of CP after cathodic electrochemical oxidation.

influence nucleation and agglomeration of Pt particles deposited on carbon paper.

2.3. CV in H$_2$SO$_4$

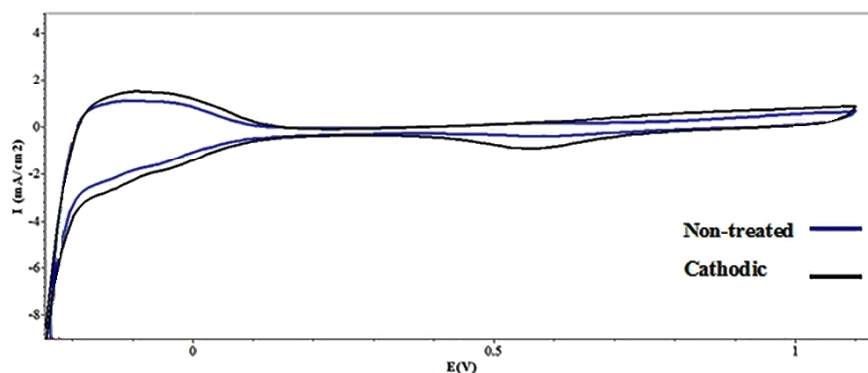Typical voltammograms (Fig. 4) show an increase in the current when electrodes are treated, compared with non-treated one.
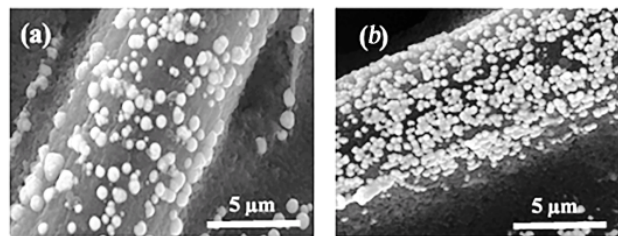

Fig. 3. SEM images of Pt particles deposited directly on a) non-treated and b) cathodic CP.

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 [10]. The ECSA of the electrodes are 11.7 and 13.7 (m^2.g^{-1}) for non-treated and cathodic electrodes, respectively. The higher coulombic charge of the hydrogen adsorption/desorption zone is related to an increase in the ECSA of the catalyst owing to the lower particle size deposited on the cathodic CP.

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 Fig. 5. This descending linear relationship was reported in other literature [14]. As shown in Fig. 5, CO coverage for

Fig. 4. CV curves for treated and non-treated electrodes in 0.5M H$_2$SO$_4$ at 25°C and scan rate of 50 mV/s.
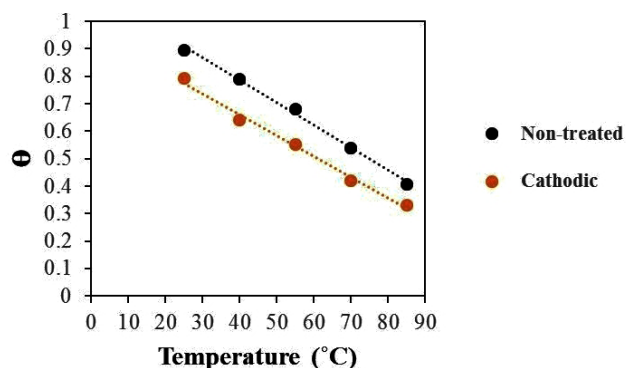
Fig. 5. The changes of CO surface coverage with the temperature on the non-treated and cathodic electrode surface, after the initial adsorption of a certain amount of CO at 25 °C.

the cathodic electrode is lower than the non-treated one at 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

To calculate desorption rate constants which are dependent on CO coverage, a desorption rate equation should be considered. Assuming first-order Langmuir desorption kinetics and that k_{des} is independent of the surface coverage, the desorption rate constant could be measured directly from the gradient of a plot of ln (θ) against t according to equation (2) [18]. Fig.6 shows ln (θ) versus time for both electrodes at different temperatures.

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

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

According to the correlation in Fig. 6 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 at all the temperatures in Table 2. According to these results we can conclude that the rate constant for
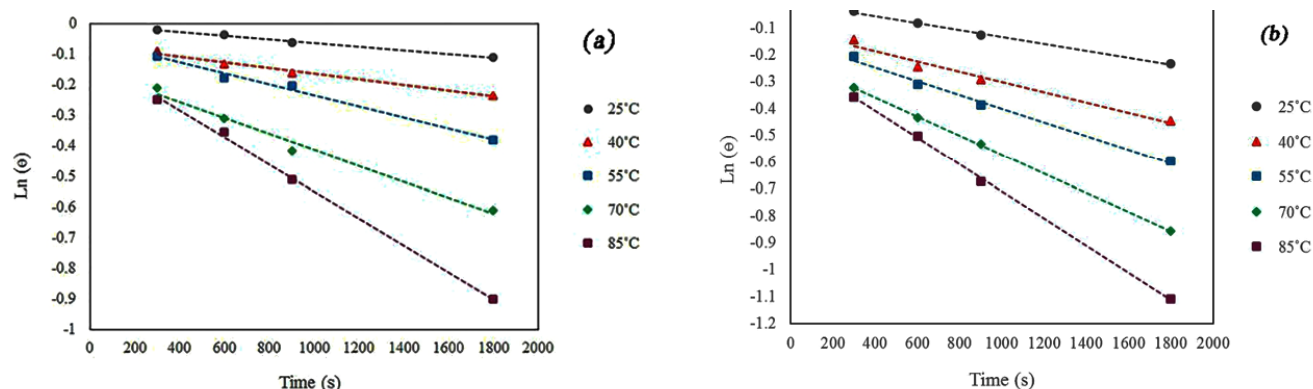

Fig. 6. ln (θ) versus desorption time at various temperatures (25, 40, 55, 70 and 85 °C) for a) cathodic and b)non-treatment electrodes.

Table 2. Desorption rate constants (kdes) calculated for CO-saturated condition at various temperatures (25-85) for cathodic and non-treated electrodes.

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}
85	4.41×10^{-4}	5.02×10^{-4}

the cathodic electrode is higher than the non-treated one in this temperature range of experiments (25-85 ℃).

The temperature dependence of desorption rate constant is given by the Arrhenius equation as shown below [19]:

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

Where k_{des} is the desorption rate constant in s^{-1}, A is the frequency factor in s^{-1}, E_{des} is the desorption activation energy in $J\ mol^{-1}$, R is the universal gas constant, and T is the temperature in K. The frequency factor can be considered as a temperature independent constant. A natural logarithmic form of equation (3) yields equation (4) :

$$\ln(k_{des}) = \left(-\frac{E_{des}}{RT}\right) + \ln(A) \qquad (4)$$

Thus, a plot of the logarithmic value of desorption rate constant versus the inverse temperature should provide a linear response. Fig. 7 shows the Arrhenius plot based on natural logarithmic value of desorption rate constant versus the inverse temperature in K.
The activation energies for desorption estimated from data obtained by the experiments are 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 the effect of oxygen-containing groups and the impact of these functional groups on the energy bond between platinum and CO.

3. Conclusion

Results show 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. The effects on the Pt properties of CO desorption caused by the CP cathodic electrochemical treatment electrodeposited on Pt was studied. Investigation revealed that cathodic treatment of carbon not only decreases the surface coverage of CO on its surface in this temperature range (25-85℃) but also enhances CO desorption rate in this range. Results suggest that oxygenated functional groups can affect the Pt-CO binding energy and facilitate CO desorption. The lower activation energy according to the Arrhenius equation for the cathodic electrode in comparison with the non-treated electrode is evidence of this claim.

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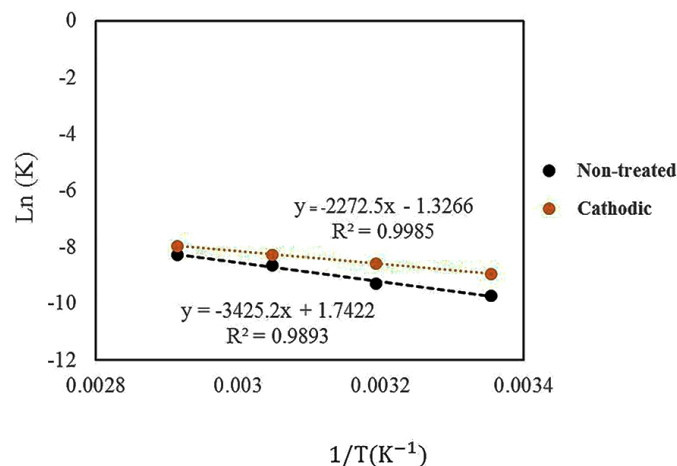

Fig. 7. Determination of the apparent Arrhenius parameters using the Arrhenius plot for cathodic and non-treated electrodes.

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