

Platinum Surface Modification For The Electrochemical Oxidation Of Methanol In Potassium Hydroxide Solutions

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Abstract—This work deals with the modification of mechanically polished platinum surface in aqueous dilute potassium hydroxide solutions as an alkaline media. Modification was accomplished by the repetitive cyclic polarization. The electrolytic formation of surface hydrated platinum oxide is shown to be a highly irreversible reaction. This hydrated oxide film catalyze the electro-oxidation of methanol in potassium hydroxide solutions. The electro-oxidation properties of methanol which is promising candidates for direct alcohol fuel cells were studied on this electro-catalyst. Testing was undertaken by tracing the cyclic voltammograms under different experimental conditions. The mechanism of the oxidation process was reported. Kinetic equations representing the electro-oxidation of methanol are given.

Keywords—methanol electro-oxidation; electro-catalysis; modified platinum

1. INTRODUCTION

Fuel cells show promise to provide environmentally friendly energy converters at high efficiency and power density. Direct alkaline alcohol fuel cells (DAAFCs) have attracted increasing interest over the past decade because of their favorable reaction kinetics, higher energy densities achievement and the easy handling of the liquid fuels. A lot of work has been done to study the electro-oxidation of methanol and ethanol with various catalysts. Platinum and platinum-based are commonly used catalysts in acid medium [1,2]. Under alkaline conditions, the reaction mechanism and kinetics of alcohol oxidation are significantly improved [3–6]. A problem with alkaline fuel cells is the carbonation of the solution due to CO₂ production of the fuel oxidation and from air. This can cause solid precipitation of carbonate salts on the porous electrode and a pH decrease in the alkaline electrolyte solution [7]. Consequently, it leads to a reduction in reactivity for fuel oxidation in the system [8].

The oxygen reduction reaction (ORR) overpotential causes a loss in efficiency in alkaline fuel cells (AFCs) and in alkaline membrane fuel cells (AMFCs). It is

very similar to that occurring in (polymer electrolyte membrane fuel cells) PEMFCs, i.e., the cathode overpotential loss remains the major factor limiting the overall energy conversion efficiency and performance of AFCs [9] and AMFCs [10]. The ambiguity in the measurement of the hydrogen oxidation reaction (HOR)/hydrogen evolution reaction (HER) kinetics in acid can be related to the fact that it is experimentally very challenging to eliminate hydrogen mass-transport resistances in rotating disk electrode measurements. Most often, the quantification of kinetic constants for the HOR/HER is not an easy task. Hence in this study we use stationary electrode with three dimensions surface film; a common feature of hydrated surface oxide films.

2. EXPERIMENTAL

As working electrode, pure platinum (0.4 cm² as a sheet, Aldrich, thermocouple quality) was used. This working electrode was polished with decreasing grades of fine emery papers, degreased with acetone and washed with running distilled water, before its immersion in the test solution. A three compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode were used. The electrode potential was controlled by a voltage scan generator, an automatically-controlled electronic Wenking Laboratory Potentiostat (LB 75). D C voltammograms were recorded using Allen, Model 1000 X-Y recorder.

Each experiment was carried out in a freshly prepared solution and with a newly polished electrode surface. After cyclization for a definite time (number of cycles), the electrolyte was replaced by pure 0.05 M or 0.1 M KOH free or containing methanol.

3. RESULTS AND DISCUSSION

3.1. Platinum modification process

It is of interest that the excellent synergistic effect of O_{ad} layer generates some novel catalytic properties different from those of monometallic platinum catalysts. It can significantly enhance electro-catalytic activity of platinum as anode in the alcohol electrooxidation. In alkaline media and because of the presence of oxide, OH_{ads} (adsorbed OH species) can

be formed at lower potentials, which can transform the CO-like poisoning species adsorbed on catalyst surfaces to CO_2 , releasing the active sites for electrochemical reactions. The kinetics of growth of thin anodic oxide films at platinum electrodes was studied in alkaline solutions of different pH's [11].

The electrochemical behavior of modified platinum electrode was studied by the cyclic voltammetry technique. The cyclic voltammogram (CV) of the platinum electrode in 0.1 M KOH, is shown in Fig. (1). It is found the CV changes gradually which indicate that the morphology of the structure has not drastically changes that confirm the stability of the structure in alkaline medium. The change in the features of the voltammogram is due to roughness of the surface and increase of the thickness of the formed hydrated oxide film.

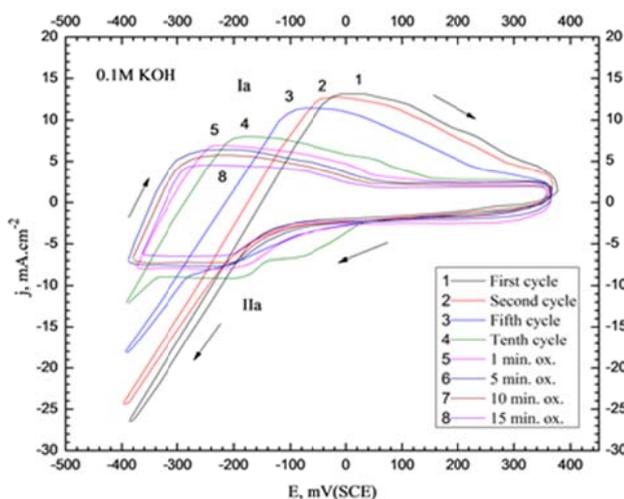


Figure 1. Cyclic voltammogram of Pt electrode in 0.1 M KOH at 2000 mV s^{-1} , for different times at 25°C .

For anodic peak (I_a), during $0 \leq t \leq 15$ min (t is time of cyclization), the O-electrodesorption current peak at about -0.006 to -0.25 V is shifted toward negative values as t grows and is well defined, Fig. 2(a). Also, for cathodic peak (II_c), during $0.1 \leq t \leq 15$ min, the current peak in the range from -0.18 to -0.23 V is shifted towards the negative direction as t grows, Fig. 2(b), the purpose of this experiment was to determine how long it takes the surface coverage to reach a steady state.

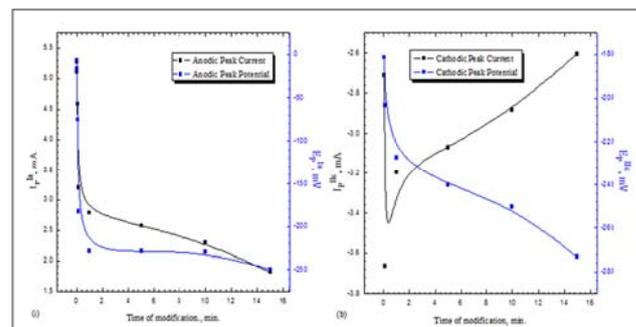


Figure 2. The relation between time of modification on Pt electrode in 0.1 M KOH with (a) the anodic peak current (I_p) and peak potential (E_p) of oxidation peak (I_a); (b) the cathodic peak current (I_p) and peak potential (E_p) of reduction peak (II_c).

The charge densities (in milli coulomb per square centimeter) with the number of cycles were determined and are given in table (1), for both anodic peak and cathodic peak reactions. Charge associated with a cyclic voltammetry could be determined by manual technique of cutting and weighing the peaks and then taking the ratio of the peak weight to that of a rectangle of a known area and weight [12]. A comparison of the anodic and cathodic charge densities shows that their ratio changes with number of cycles. The difference is due to a difference in reaction rates. A comparison of the charge curves also shows that the cathodic charge densities indicate that the electricity which used to reduce the oxide is increased. This indicates that the initial adsorption rate grows with time increase as expected [13], due to activation of the surface by cyclization which enhances reduction of dissolved oxygen. In contrast for the anodic charges which decreased with the modification time indicating that the less electricity required for oxide formation, i.e., the oxide become easily formed.

Table 1. Charge densities of both anodic and cathodic peaks for different number of cycles.

Number of cycles	Charge Density Q_d (mC.cm^{-2})	
	I_a	II_c
1	2.38	0.95
2	2.25	1
5	2.03	1.03
10	1.83	1.05
48	1.68	1.08
240	1.6	1.13
480	1.58	1.15
720	1.4	1.21

The conditions for complete monolayer oxide formation on platinum surfaces are important from a practical viewpoint as it forms the basis of a useful method for determining the true surface area (or roughness value) of the metal surface [14]. Roughness factor of oxide-supported platinum

electrode as determined from the charge corresponding to the hydrogen adsorption peak is around 4.

3.2. Methanol electro-oxidation in 0.1 M KOH

The cyclic voltammetric behavior reported during the electro-oxidation of methanol on a modified platinum electrode surface in 0.1 M KOH is shown in Fig. (3). The potential sweeps are after 15 minutes of modification in 0.1 M KOH solution in absence and presence of different concentrations of methanol over the range from 0.1 to 0.5 M. The CVs were performed between -400 and 400 mV at a scan rate of 50 mV s^{-1} , at room temperature. As can be seen, in the potential range from -400 to 400 mV, there are no peaks in 0.1 M KOH solution in absence of methanol but in the presence of methanol an anodic peak (I_a) appears with a broad shoulder in the potential region of about 200 mV vs. SCE and a backward anodic peak (II_a) exists in the potential range from 100 to 50 mV. Thus, a single oxidation peak, centered at 200 mV vs. SCE appears during the anodic sweep; however, when the CV sweep is reversed towards the H_2 reversible potential, another oxidation peak (centered at 75 mV) emerges in the voltammetric profile.

Comparison of these curves demonstrates that the current density is higher in the presence of methanol and increase by increasing its concentration. For methanol oxidation, both liquid products formaldehyde and formate can be formed [15].

The most obvious voltammetric characteristic of the methanol oxidation process at the modified platinum electrode is that the CVs recorded display a large oxidation peak (primary oxidation peak) at 200 mV in the forward anodic scan and another oxidation peak (secondary oxidation peak) around 75 mV in the backward cathodic scan, Fig. (3). Plots of the logarithm of current densities ($\log j_p$) vs. the logarithm of the concentrations of methanol for each anodic and reverse anodic peak on the modified platinum electrode surface are given in Fig. (4).

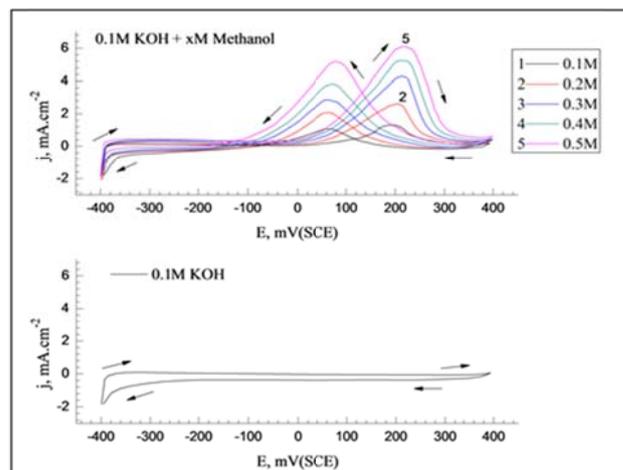


Figure 3. Cyclic voltammograms of platinum at different concentrations of methanol, at 25°C (15 min. modification), at the sweep rate of 50 mV s^{-1} in 0.1 M KOH.

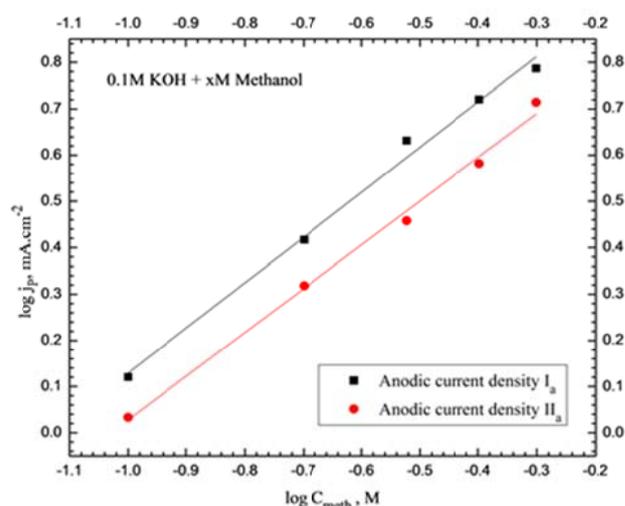


Figure 4. Plots of the logarithm of current densities ($\log j_p$) vs. the logarithm of the concentrations of methanol for each anodic and reverse anodic peak on the modified platinum electrode in 0.1 M KOH after 15 minutes of platinum modification, at 25°C .

3.3. Methanol electro-oxidation in 0.05 M KOH

The effect of concentration of methanol in the range from 0.05 to 0.2 M on its oxidation on the modified platinum electrode in 0.05 M KOH is investigated by CVs, Fig. (5), this figure shows the CVs for the potential range from -400 to 400 mV; the peak potential has a continuous negative shift with an increase in the methanol concentration. Furthermore, the peak current is observed to increase as the methanol concentration increases from 0.05 to 0.2 M, i.e., the oxidation current increases as the methanol concentration increases. Comparing the results in 0.1 M KOH with those in 0.05 M reveal that the later is more efficient possibly due to the competitive adsorption between the hydroxide ions and methanol molecules [16]. Furthermore, the peak potential has a continuous negative shift with the increasing of

methanol concentration. Figure (6), shows the relation between the logarithm of current densities ($\log j_p$) vs. the logarithm of the concentration of methanol for each anodic and reverse anodic peak on the modified platinum electrode surface at the same conditions. It is found that the oxidation current density of methanol increases with the increase of its concentration.

The negative shift of the peak potential suggests that the dilution of KOH has a favorable effect on the oxidation of methanol in addition to methanol concentration. It is an indication that at first the alcohol oxidation reaction on the modified platinum electrode can be accelerated at lower OH^- concentrations that lead to an increase in the anodic peak current, but at higher KOH concentrations, the adsorption of hydroxyl ions may be dominant on the modified platinum electrode which blocks the adsorption of alcohol on the electrode. Such imbalances lead to a decrease in the anodic peak current [16].

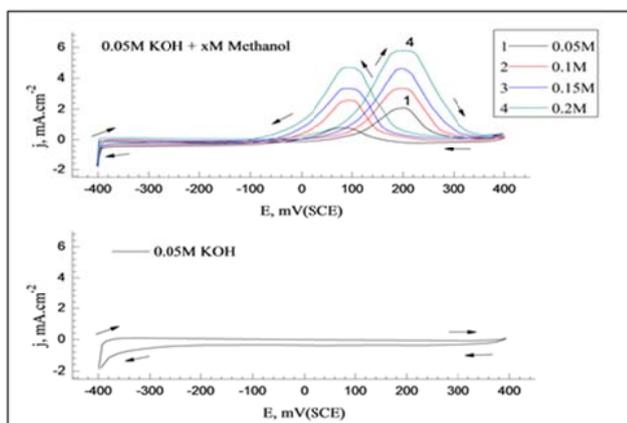


Figure 5. Cyclic voltammograms of platinum at different concentrations of methanol, at 25°C (15 min. modification), at the sweep rate of 50 mV s^{-1} in 0.05 M KOH.

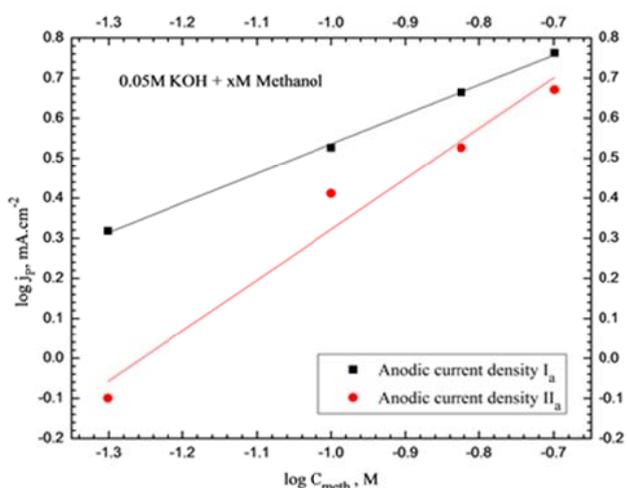


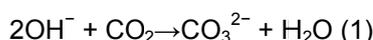
Figure 6. Plots of the logarithm of current densities ($\log j_p$) vs. the logarithm of the concentrations of methanol for each anodic and reversible anodic peak on the modified Pt electrode in 0.05 M KOH after 15 minutes of Pt modification, at 25°C.

3.4. Electro-oxidation mechanism

The oxidation mechanisms of methanol have been widely studied in alkaline media with cyclic voltammetry [17,18]. The oxidation products observed at platinum are formaldehyde and formate [15]. Electro-oxidation of methanol is relatively simple compared to other alcohols. However, two major obstacles have restrained the more rapid development and applications of DAFCs, even for methanol systems:

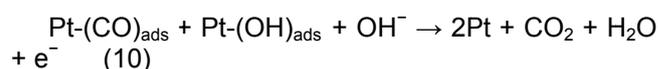
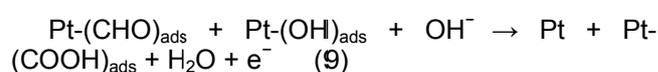
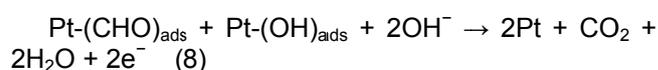
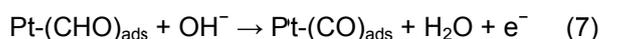
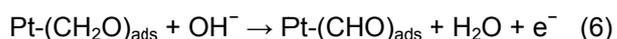
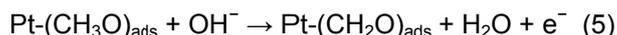
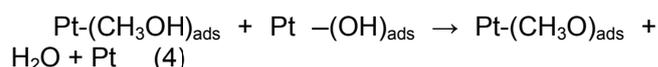
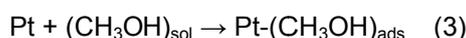
- Alcohol crossover from the anode to the cathode.
- The relatively low activity and complex reaction mechanism of most alcohols.

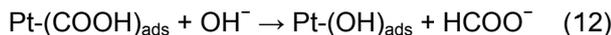
It is known that for many reactions, electro-catalysts perform better in alkaline electrolyte except the carbonation of the solution due to CO_2 production of the fuel oxidation and from air [7]:



However, the disadvantage of purely electrochemical methods is that no information on the adsorbents or the oxidation products is obtained. Therefore, several spectroscopic methods, such as Fourier Transform Infrared Spectroscopy (FTIRS) [19,20], Surface Enhanced Raman Spectroscopy [21] and Differential Electrochemical Mass Spectrometry [22], have been applied to probe reaction intermediates and mechanisms. With these methods (volatile) reaction products and/or adsorbed species can be probed. The results of these investigations indicated that carbon dioxide is the main product as no further carbon cleavage is required.

The mechanism of electrochemical oxidation of methanol on platinum in alkaline systems involves formation of adsorbed methanolic species and hydroxyl species on the platinum surface. The oxidation takes place through a series of reaction steps involving successive electron transfer, i.e. partial oxidation, to form adsorbed species. These react with adsorbed species to form carbon dioxide. The reaction mechanism has been given as follows [23, 24]:





The rate-determining step is most likely reaction 6.

The ratio of the forward anodic peak current (I_f) to the reverse anodic peak current (I_b), I_f/I_b , may be used to evaluate the tolerance of catalyst to carbonaceous species accumulation. The higher the I_f/I_b ratio, the stronger the catalyst tolerance to catalyst poisons [25]. The relative high I_f/I_b ratio ($\square 1.2-1.5$) indicates good tolerance of the modified platinum as a catalyst to CO-like intermediate species in 0.1 M KOH and it raises for modified Pt in 0.05 M KOH to be ($\square 1.3-2.2$).

3.5. Quantity of electricity consumed:

The charge densities Q deduced from the anodic peak (I_a) of CV curves are presented in Fig. (7), for different methanol concentrations over the range 0.1–0.5 M after 15 minutes of platinum modification in 0.1 M KOH. It was found that the charge density is dependent of the methanol concentration. The increase in concentration of methanol increases the charge corresponding to methanol oxidation at the modified platinum electrode. Also, the same calculations are made for methanol concentrations over the range 0.05–0.2 M in 0.05 M KOH after 15 minutes of platinum modification, Fig. (8). In case of 0.05 M KOH, the charge density found to be 2 times higher than that of 0.1 M KOH which confirm the more feasible oxidation of methanol in 0.05 M KOH possibly due to the competitive adsorption between OH^- ions and methanol molecules.

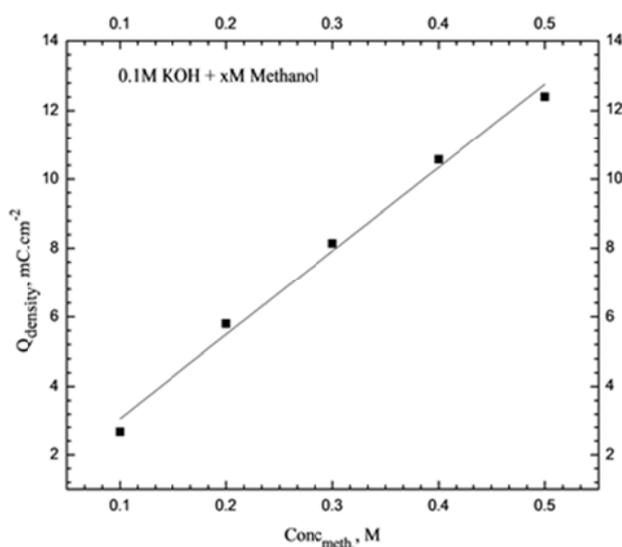


Figure 7. Charge densities vs. methanol concentration in 0.1 M KOH for peak (I_a), after 15 minutes of Pt modification.

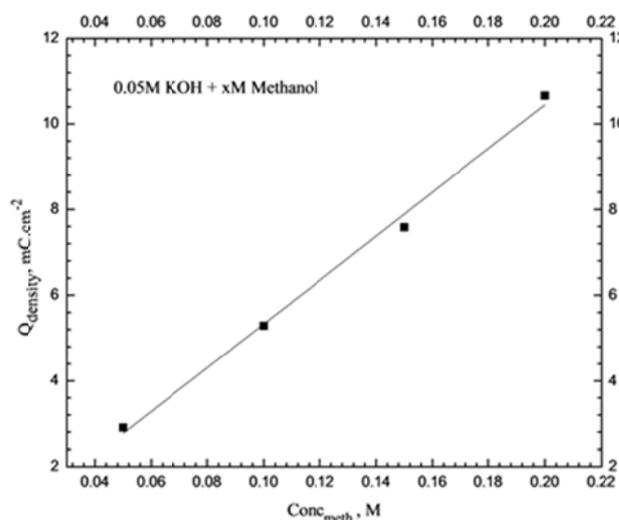


Figure 8. Charge densities vs. methanol concentration in 0.05 M KOH for peak (I_a), after 15 minutes of platinum modification.

4. CONCLUSIONS

This study demonstrates the feasibility of applying modified platinum surface for methanol electro-oxidation. Modification has been undertaken by repetitive cyclic polarization in aqueous potassium hydroxide solutions. This process produces active O_{ad} and hydroxyl species readily for electro-oxidation of methanol in these media.

The electro-active O_{ad} films were used in electro-oxidation of methanol in both 0.1 and 0.05 M KOH. The onset potential decreases and the current density increases for electro-oxidation of methanol with increase of its concentration. This effect is more pronounced in 0.05 M KOH as compared to that in 0.1 M KOH.

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