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Research article

ELECTROOXIDATION OF METHANOL ON PT MODIFIED WITH ADATOMS (NI, CU, PB, CD)

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ABSTRACT: The electro oxidation of methanol has been studied in alkaline medium NaOH 0.1 M and acid medium H_2SO_4 0.5 M on a platinum electrode and a platinum modified by adatom adsorption (Ni, Cu, Pb, and Cd). The influence of different experimental variables (methanol concentration, and temperature) is reported. Preliminary investigations by cyclic voltammetry showed that the catalytic activity of platinum is still too low to be considered as a practical catalyst. Underpotential deposition of lead, nickel, cadmium, or copper adatoms at platinum allowed increasing significantly the current densities.
Keywords: DMFC, methanol, cyclic voltammetry, Electrocatalysis, Adatoms.

INTRODUCTION

Direct methanol fuel cells (DMFC) are the promising power sources for applications such as electric vehicles and electronic portable. Methanol as a fuel has numerous advantages such as low operating temperature, easy transportation and fuel storage, high-energy efficiency, low exhaustion and fast start-up (Andujar et al., 2009; Kamarudin et al., 2009). However, there are some serious technical obstacles to the use of DMFC. One of the most significant barriers for the wide spread commercialization of DMFCs the poisoning of anode catalyst by carbon monoxide from methanol electro oxidation (Jiang et al., 2012). Due to the facile poisoning effect of CO on Pt (Cui et al., 2011), several binary and ternary catalysts has been proposed for methanol oxidation, based on modifications of Pt with one or more other metals. Many research efforts to weaken CO poisoning have been made through using additional elements to platinum. A broad variety of bimetallic systems such as PtRu (Zhiani et al., 2013), PtNi (Habibi et al., 2013), PtSn (Kim et al., 2008) and PtCo (Ahmadi et al., 2012) with improved activity for methanol oxidation have been studied to replace the monometallic Pt catalysts. The addition of a third metal Mo (Teliz et al., 2012), Ru (Arikan et al., 2013), Pb (Chen et al., 2008), or Rh (Soszko et al., 2011), (Farfour et al., 2013a, Farfour et al., 2014b) improves the performance of the electrode.

Another interesting aspect is that in all systems currently investigated, except quaternary PtMnCuX /C (X = Fe, Co, Ni, and Sn) and PtMnMoX /C (X = Fe, Co, Ni, Cu and Sn) (Ammam et al., 2012) are receiving much attention.

In the present work, we discuss results from the study of the electrooxidation of methanol on a Pt electrode modified with adatoms. The utility of the modified electrode for electrocatalytic oxidation of methanol in the alkaline medium and acid medium have been studied by cyclic voltammetry.

EXPERIMENTAL

The solutions were prepared using Double-distilled water, super pure NaOH, H_2SO_4, MeOH, $CuSO_4,5H_2O$ (10^{-5} M), Cd $(NO_3)_2,4H_2O$ (10^{-5} M), $Pd(NO_3)_2$ (5.10^{-5} M) and $NiSO_4,6H_2O$ (10^{-4} M) of analytical grade. A saturated calomel electrode (SCE) was served as reference electrode. Potentials in this paper were reported versus the SCE scale. The solution was deaerated by bubbling pure N_2 gas before experiment, and kept a flux of N_2 over it during measurements to prevent possible interference of oxygen and impurities from the atmosphere. All tests were performed at 25°C. Electrochemical experiments were carried out with a voltalab potentiostat (model PGZ 100) by the general purpose electrochemical systems data processing software (Voltamaster 4). All electrochemical measurements were conducted in a thermo stated three-compartment electrochemical cell with platinum as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum wire electrode was used as the working electrode.

RESULTS AND DISCUSSION

Oxidation of Methanol in basic medium NaOH

Effect of methanol concentration

The dependence of current density on methanol concentration at 50 $mV.s^{-1}$ for Platinum is shown in Figure1. The current density increases sharply from 0.02 M to 2 M, then it grows at a moderate rate. Plots of the logarithm of current densities (log J) vs the logarithm of concentration (log C) give the overall reaction order with respect to the initial concentration of Methanol Figure 2. The reaction orders, derived from the slope of the straight line, are 1.12 and 0.9 for the anodic and cathodic sweeps respectively.

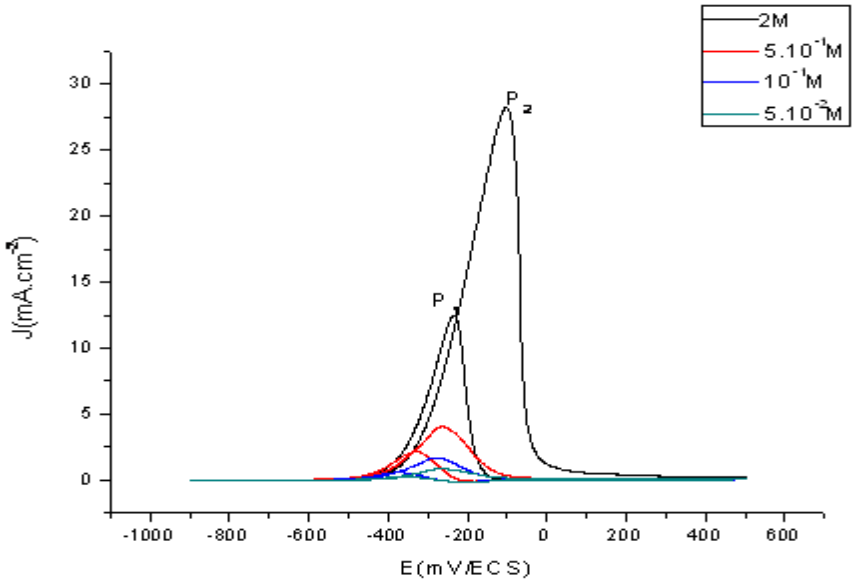

Figure 1: Oxidation current density at 50 $mV.S^{-1}$ versus methanol concentration

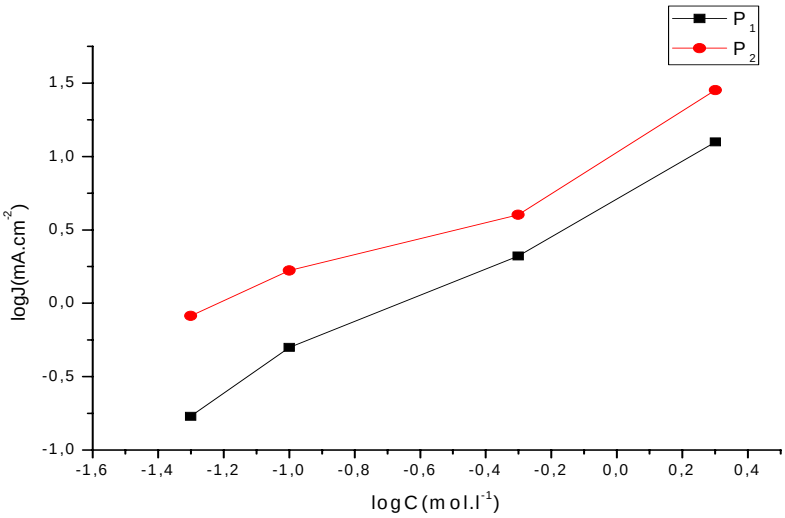

Figure 2: The log of current densities (log J) vs the log of MeOH concentration (log C_{MeOH}) P_1: anodic sweep, P_2: cathodic sweep

Effect of temperature

Cyclic voltammograms of methanol on a Pt electrode at different temperatures of 25°C to 95°C) are shown in Figure 3. Arrhenius plots of logarithm of exchange current density (log J) versus the reciprocal of temperature (T^{-1}) provided the apparent activation energy from the slope of linear fitted as shown in Figure 4. The apparent activation energy of methanol Pt electrode was 22.94 and 16.37 $kJ.mol^{-1}$ for the anodic and cathodic sweeps respectively.

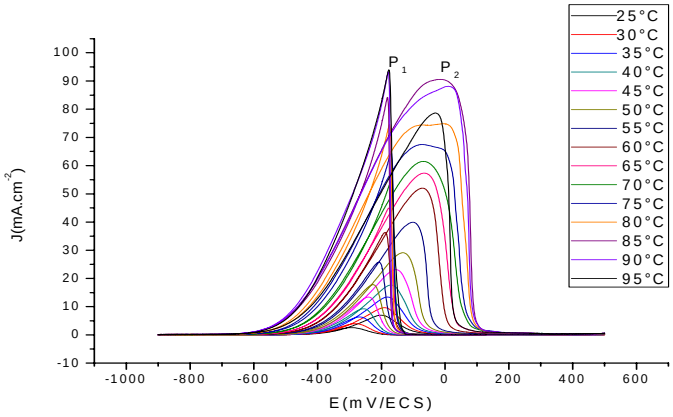

Figure 3: Cyclic voltammograms at different temperatures with Pt electrode in 0.5 M methanol, Scan rate = 50 mV.S^{-1}

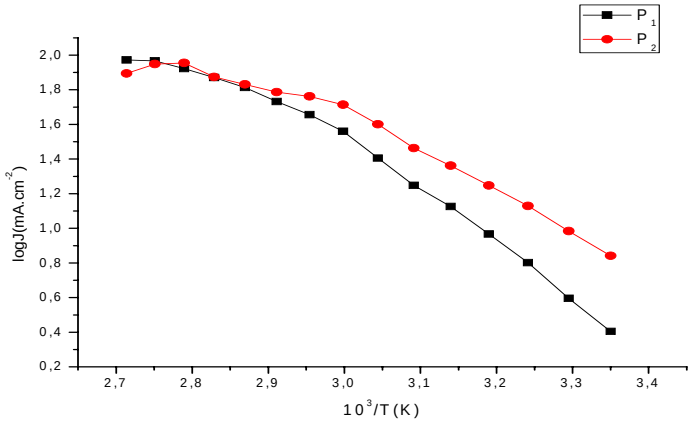

Figure 4: Arrhenius plot for methanol at Pt electrode

Electrocatalytic Effect of Adatoms on the Oxidation of methanol

Figure 5 shows the voltammograms of methanol oxidation on Pt and Pt-adatom (Pb,Cu,Ni and Cd). The catalytic performance closely resembles that of Pt-adatoms catalysed methanol oxidation, where Pt-Pb, Pt-Cu, Pt-Ni and Pt-Cd are reported to be favorable to electrooxidation of methanol, indicating that methanol oxidation is catalysed more easily on Pt- adatom (Pb,Cu,Ni and Cd) than on pure platinum. Pt-Pb displays superior properties to those of Pt-Cu, Pt-Ni and Pt-Cd by exhibiting a higher current maximum.

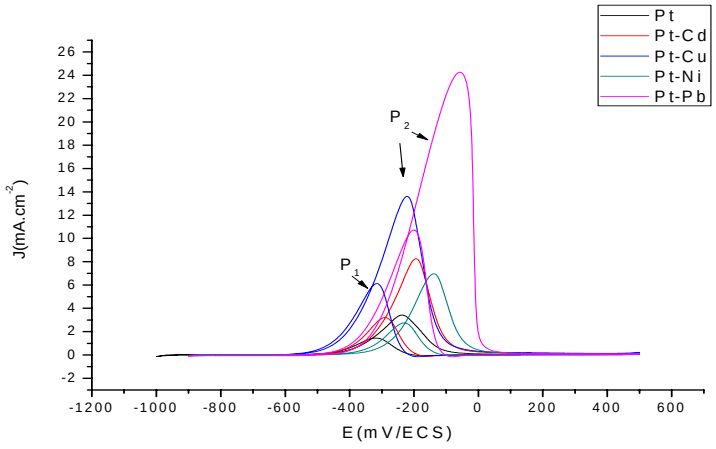

Figure 5: Comparative Study of electrocatalytic oxidation of methanol on platinum modified by adatoms in basic medium NaOH platinum.

Oxidation of Methanol in acid medium H_2SO_4

Effect of methanol concentration

The concentration of Methanol was varied from 5.10^{-2} to 2 M in 0.5 M H_2SO aqueous solutions (Figure 6). With increasing concentration, the current densities of 3 peaks P_1, P_2 and P_3 were increased. Peak P_2 became more intensive when the concentration was greater than 1 M. Plots of the logarithm of current densities (log Jp) vs the logarithm of the concentration of Methanol on the electrode surface are given in Figure 7. The reaction orders, derived from the slope of the straight line, are 1.13, 1.03 and 0.74 for the three peaks.

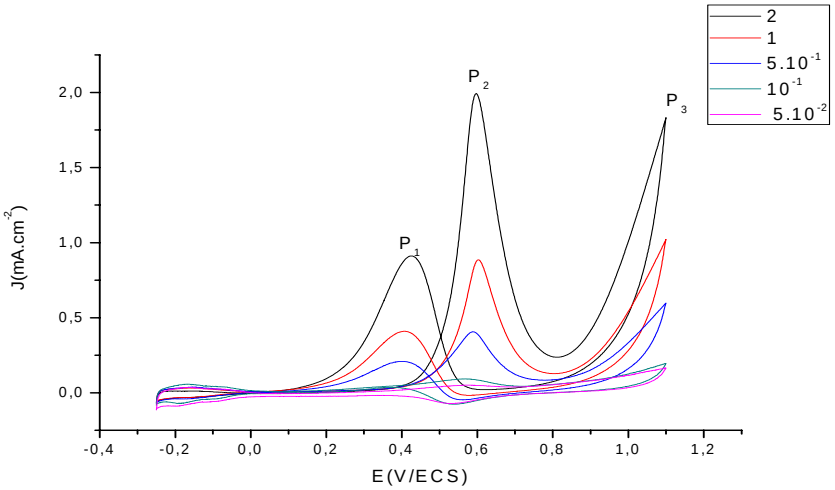

Figure 6: Oxidation current density at 50 mV.S^{-1} versus methanol concentration

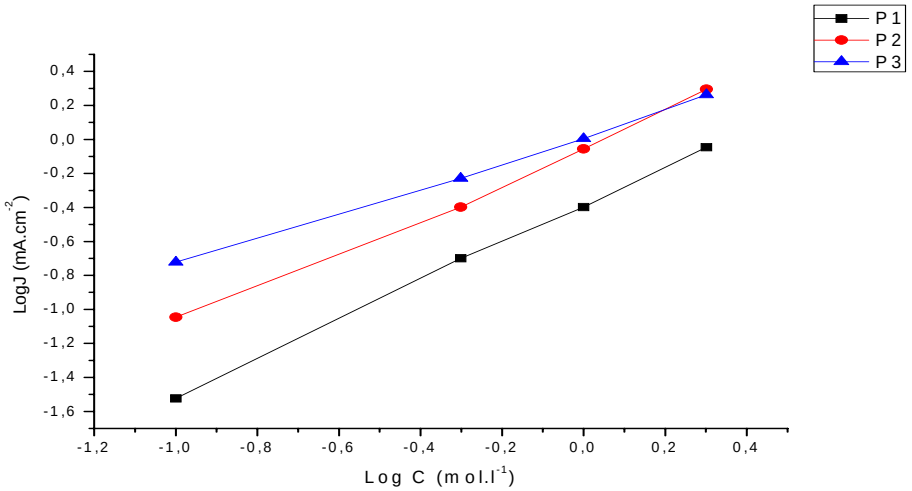

Figure 7: The log of current densities (log J) vs the log of MeOH concentration (log C) P_1: anodic sweep, P_2: cathodic sweep

Effect of temperature

Activation energies were determined by studying the oxidation of Methanol at different temperatures between 28 and 85°C on platinum (Figure 8). Activation energies (E_a) were calculated from the slope of the plots of log J vs 1/T (Figure 9) for certain potential values by the use of the following equation (Yangchuan et al., 2009):

$$slope = \left(\frac{\partial\, logJ}{\partial\, \left(\frac{1}{T}\right)}\right) = -\frac{E_a}{R}$$

The apparent activation energy of methanol Pt electrode was 30.51, 30.29 and 17.54 kJ mol^{-1} for the three peaks P_1, P_2 and P_3 respectively.

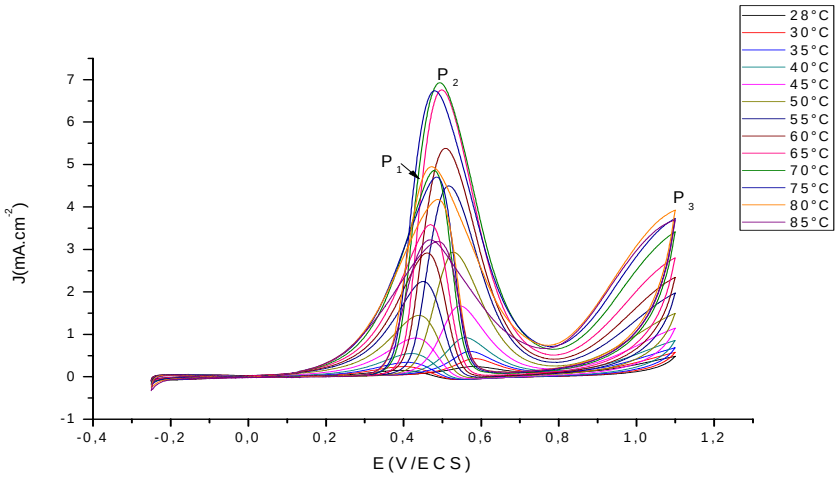

Figure 8: Cyclic voltammograms at different temperatures with Pt electrode in 0.5 M methanol, Scan rate = 50 mV. S^{-1}

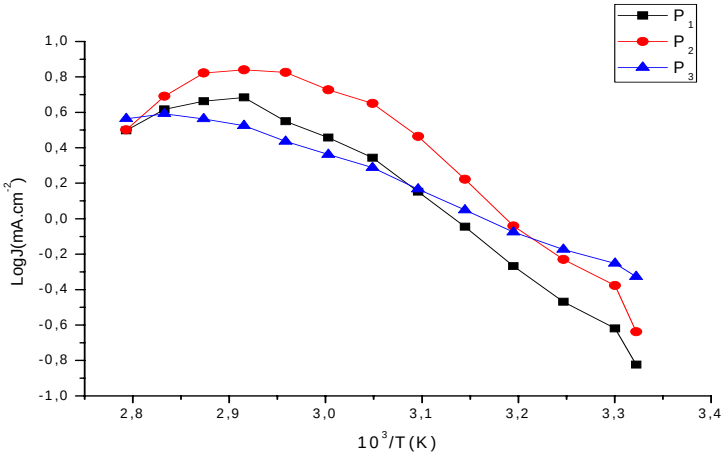

Figure 9: Arrhenius plot for methanol at Pt electrode

Electrocatalytic effect of Adatoms on the oxidation of methanol

The four metal ad-atoms (Pb, Cu, Cd, Ni) studied here have a different effect on the oxidation rate of methanol in alkaline solution. Looking at the voltammograms given in Figure 10, it is obvious that the main effect of the adatoms is a general increase in the current densities. The activity of Pt-Cd for methanol electro oxidation in acid medium is much higher than other catalyst systems.

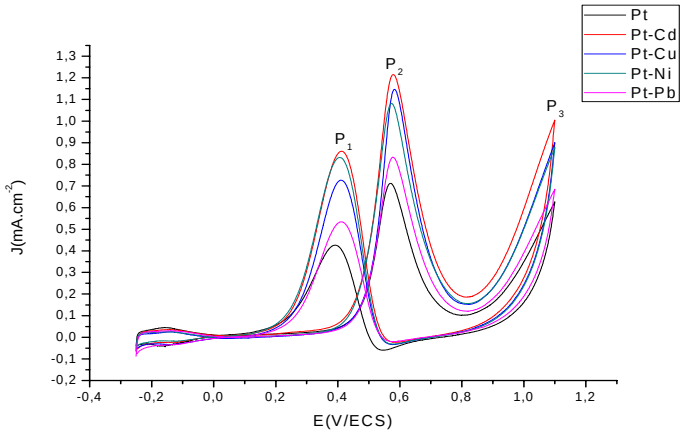

Figure 10: Comparative Study of electrocatalytic oxidation of methanol on platinum modified by adatoms in acid medium H_2SO_4 platinum

The influence of the foreign metal adatoms deposited at under potentials on the oxidation of methanol on platinum was studied in alkaline medium and acid medium. Pronounced catalytic effects caused by under potential of Pb, Ni, Cd and Cu were observed. The methanol oxidation is catalysed more easily on Pt-adatom (Pb,Cu,Ni and Cd) than on pure platinum. Some toxic intermediates, especially carbone monoxyde that produced in the methanol oxidation process will be adsorbed on to the electrode surface of Pt. The primary effect of carbon monoxide adsorption is the blockage of active sites. On the other hand, adatoms are preferentially adsorbed and prevent adsorption of CO on the surface of electrode, which can supply more active sites for methanol oxidation.

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