Anodic oxidation of sodium formate and methanol on Pd and Pt electrodes in alkali: a comparative study

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Abstract. Formate and methanol oxidation reaction (FOR and MOR)s are compared at room temperature on Pd and Pt electrodes in alkali. The onset potential and tafel slope for FOR on Pd are less by 0.203 V and 0.481 Vdec⁻¹ than these on Pt electrode. The peak current densities on Pd are 15.8 and 144 times greater than that on Pt in MOR and FOR respectively. The greater catalytic activity of Pd in FOR is supported by the greater formation of carbonate as obtained from IR spectroscopic and chromatographic investigation of products. The equilibrium exchange current density on Pd for FOR and MOR are 52.3 and 2.3 times of the corresponding data on Pt electrode. Despite methanol provides greater steady current than formate, the latter is better fuel particularly on Pd electrode in respect to formation of carbonate and power development.

1. Introduction
The use of formate as a fuel is an alternate to methanol in fuel cell reaction. Formate fuel cell produces an overall theoretical $E_\text{cell}^\circ$ of 1.45 V which is 0.24 V greater than the alkaline methanol fuel cell [1] (DMFC) respectively. In addition, the formate salts have low toxicity, high solubility in water to form liquid fuel, food additive and air plane road de-icing agents [2], non-flammable property, renewable fuel. The anodic oxidation of formate and methanol in alkali is a two and six electron transfer reaction respectively on complete oxidation as given by
\begin{align}
\text{HCOO}^- + 3 \text{OH}^- & \rightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \quad (1) \\
\text{CH}_3\text{OH} + 8 \text{OH}^- & \rightarrow \text{CO}_3^{2-} + 6\text{H}_2\text{O} + 6\text{e}^- \quad (2)
\end{align}
The differences in mechanisms for Pt and Pd anodes in both MOR and FOR are not completely established. Moreover, most of the works of such oxidation have been done on modified Pt and Pd electrodes [1,3-5], the study on pure Pt and Pd electrodes is very rare particularly as a comparative study, involving product analysis, order determination and mechanistic information, etc. of the reactions.

2. Experimental
2.1. Electrochemical measurement
All electrochemical measurements were carried out using AUTOLAB electrochemical workstation. The working electrodes were platinum (99.99%), palladium (99.97%) wires (Arora Matthey) with a geometrical area of 0.457 and 0.112 cm² respectively. A platinum foil (3.00 cm² area) and Hg/HgO/OH⁻ (1M) electrode (MMO) were used as counter and reference electrodes respectively. Following our previous studies [1,3,5], FTIR study (Perkin Elmer, SN 74514 Spectrum RX1, Resolution 4 cm⁻¹) and Chromatographic determination of products of FOR and MOR was executed using a high performance liquid chromatography (HPLC) (Shimadzu Corporation, Japan).

3. Results and Discussion
3.1. Cyclic Voltammetry study
The steady cycle of formate oxidation on Pt and Pd electrode (Fig.1a) reveal that the observed peak-current which occurs mainly at lower potential, is much greater on Pd than that on Pt electrode and the adsorption of formate on Pd electrode is too large to form Pd-OH or PdO. Table 1 reveals that the peak current densities on Pd are 15.8 (22.23/1.41) and 144 time (10.57 / 0.073) greater than that of Pt in MOR and FOR respectively. The reduction of the onset potential of 200 mV (-0.6027 V + 0.8052 V) indicates significant improvement of catalytic activity of Pd electrode (than Pt) for direct formate fuel cells. Figs. 1b and 1c exhibit the forward peak current density of methanol (1.41 mA cm⁻² at ca -0.175 V) is ~20 times higher than the anodic peak current density of formate (0.073 mA cm⁻² at ca -0.073 V) for Pt electrode. It indicates that methanol is a better current providing fuel than formate on Pt electrode.

![Figure 1](image1.png)

Figure 1. (a) Cyclic voltammograms of steady cycle for Pt and Pd electrodes in 1M HCOONa in 1M NaOH at scan rate 50 mV s⁻¹. Top inset represents steady cycle of HCOONa on Pt in a different scale. Comparative study of cyclic voltammograms of 1M HCOONa and 1M CH₃OH in 1M NaOH solution for (b) Pt and (c) Pd electrodes.

In the forward scan of potential, Pd electrode exhibits current density of 22.23 mA cm⁻² at -0.073 V for MOR with which is only ~2 times higher than the corresponding peak of formate. Significant improvement of peak potential is found in selecting HCOONa as fuel instead of CH₃OH for both Pt and Pd electrodes. These are -0.224 V (-0.399 V + 0.175 V) and -0.222V (-0.295 V + 0.073 V) for Pt and Pd electrodes respectively. So, for the same change of fuel from methanol to formate, the changes in apparent power density ($\Delta(I_f \times E_f)$ in mW cm⁻²) at the respective peak potentials are 1.50 (3.118-1.623) for Pd and -0.218 (0.029-0.247) for Pt.

![Figure 2](image2.png)

Figure 2. Tafel plots ($E$ or $V$ vs log of current density) for Pt and Pd electrodes in aqueous alkaline (1M) solution of 1M (a) sodium formate (b) methanol (c) Comparative studies of chronoamperometry of 1M HCOONa and 1M CH₃OH in 1M NaOH on Pt electrode at -0.3 V.
It means that power density increases 92% for Pd and decreases 88% for Pt for changing the fuel from methanol to formate. So, the choice of formate instead of methanol as fuel is beneficial in alkaline fuel cell particularly when Pd is used as anode.

Tafel plots were obtained using potentiodynamic measurement by application of 0.001 Vs\(^{-1}\) scan rate of Pt and Pd in alkaline methanol and formate (Figs. 2a and 2b) Equilibrium exchange current density \(i_0\) is calculated [3] and found to be greater on Pd (1.151 mA cm\(^{-2}\)) than that on Pt (0.022 mA cm\(^{-2}\)) indicating that the former is a better electrode catalyst than the latter in the near equilibrium region.

### 3.2. Chronoamperometric studies

| Fuel       | Electrode | Onset potential \(E_o\) (V) | Forward peak potential \(E_f\) (V) | Backward peak potential \(E_b\) (V) | Forward peak current density \(I_f\) (mA cm\(^{-2}\)) | Backward peak current density \(I_b\) (mA cm\(^{-2}\)) | Tafel slope \((V\ dec^{-1})\) | Exchange current density \(I_0\) (mA cm\(^{-2}\)) |
|------------|-----------|----------------------------|----------------------------------|-----------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------|-----------------------------------------------|
| Methanol   | Pt        | -0.5028                    | -0.175                           | -0.117                            | 1.41                                          | 0.058                                          | 0.061                                      | 1.16×10\(^{-9}\)                  |
|            | Pd        | -0.4326                    | -0.073                           | -0.047                            | 22.23                                         | 8.816                                         | 0.057                                      | 2.63×10\(^{-9}\)                  |
| Formate    | Pt        | -0.6027                    | -0.399                           | -0.409                            | 0.073                                         | 0.064                                         | 0.9750                                    | 0.022                                          |
|            | Pd        | -0.8052                    | -0.295                           | -0.181                            | 10.57                                         | 26.96                                         | 0.4940                                    | 1.151                                           |

The analysis of Figs. 2c and 3a reveal that the steady current density for methanol oxidation is 3 times greater than that for oxidation of formate on Pt electrode but ~5 times on Pd electrodes. The steady current density on the Pd electrode (alike corresponding cyclic-voltammetric peak current density) is greater using methanol signifying relatively less blocking of electrode surface during MOR than FOR.

**Table 1.** Comparison of electrochemical- performances of formate and methanol as fuel on Pd and Pt electrodes immersed in alkali. Hg/HgO/OH\(_2\)- (MMO) is used as reference electrode.

![Figure 3](image_url)  
(a) Comparative studies of chronoamperometry of 1M HCOONa and 1M CH\(_3\)OH in 1M NaOH on Pd electrode at -0.3 V. FTIR spectra of the concentrated residue after electro-catalytic oxidation of 1M HCOONa in 1M NaOH using (b) Pt and (c) Pd anodes respectively.

### 3.3. FTIR study of the products
Figs. 3b and 3c indicate the presence of the bifurcated bands (M1 and M2) at 1594 and 1386 cm$^{-1}$ due to C-O stretching for formate and weak peaks (N1 and N2) around 884 and 762 cm$^{-1}$ for carbonate on analysis of solution of anode-chamber where FOR occurs on Pd electrode. It is observed that absorbance ratio corresponding to carbonate : formate (N1: M1 and N2: M2) are 0.587 and 0.462 for Pd electrode and similar ratios are 0.435 and 0.372 for Pt electrode respectively. These indicate that formation of carbonate occurs more on Pd electrode compare to that on Pt electrode.

3.4. Order with respect to formate in FOR

The order with respect to any species k is determined at various potential using the following equation:

$$\beta_k = \frac{d \log I}{d \log [C_k]}$$

The order with respect to formate ion in FOR (Fig. 4a) is greater for Pd than Pt indicating adsorbed formate ion is more susceptible to oxidation on Pd surface. The decrease of order for Pd is due to the lack of surface-sites for formate and more adsorption of OH$^-$ ions at higher potential. Above a certain potential, the increase of order for Pt is due to removal of poisonous intermediate at higher potential.

3.5. Chromatography Study

The HPLC profiles (Figs. 4b and 4c) exhibits retention time of 5.01 min, 6.62 min and 9.44 min correspond to the evolution of peaks and detection of pure formaldehyde, sodium carbonate and sodium formate solutions respectively [3]. The ratio of absorbances of the peaks of carbonates obtained as product in FOR using Pd and Pt electrodes is found to be 1.63 (12945 / 7905) indicating Pd is better electrode than Pt in respect to FOR. The a small peak of carbonate is observed for the solution of the products of MOR on Pt electrode reveals that methanol oxidation does not pass through formate as an intermediate on Pt electrode and Pd electrode is unable to oxidise methanol completely.

3.6. Mechanism of FOR and MOR

The oxidation of formate ion follows three paths on Pd and Pt electrodes as shown in Scheme 1.
Scheme 1. Mechanism of Formate.

At higher potential path II is followed particularly for Pt and path III is for Pd. For methanol oxidation (scheme 2), two different paths: path (1) may be dominated at lower potential with the formation of adsorbed intermediate, (a). At higher potential MOR passes through the second path.

Scheme 2. Mechanism of methanol oxidation.

4. Conclusions
Pd is more beneficial than Pt as anode for oxidation of both formate and methanol in alkali. The equilibrium exchange current density increases 52.3 times and power density 107 times at peak potential of CV, for replacing Pt by Pd in FOR. The power density at the peak potential of CV is increased by ~6.57 times for replacing Pt by Pd as anode catalyst for oxidation of methanol. For MOR the ratio of exchange current density is 184 times higher with Pt compare to Pd. The experimental results conform to the probable mechanism of the reaction as presented by scheme 1. Formate is easily oxidised at lower potential but the reaction is retarded at higher potential due to blockage of the electrode surface. Methanol is not easily and not at all oxidised to CO$_3^{2-}$ on the bulk Pt and Pd electrode because the product formate is not oxidised to carbonate at higher potential. Adsorption and oxidation of formate at lower potential is substantially high on Pd electrode than these on Pt in FOR.

Reference
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