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Electrocatalytic oxidation of methanol to soluble products on polycrystalline platinum: Application of convolution potential sweep voltammetry in the estimation of kinetic parameters

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ABSTRACT

Irreversible oxidation of methanol on polycrystalline platinum leading to soluble products has been carried out by fast scan voltammetry, and the reaction has been studied under diffusion controlled process. The conventional analysis of current–potential data, viz. dependence of peak potential on scan rate and peak width measurements, resulted in the estimation of apparent diffusion coefficient of methanol and the anodic transfer coefficient of the electrode reaction. However, from the convolution potential sweep voltammetry, a more accurate and reliable kinetic data were obtained. Under the above conditions, methanol oxidation follows Butler–Volmer rate law with a linear variation of logarithmic heterogeneous rate constant with electrode potential. A constant apparent anodic transfer coefficient independent of electrode potential was observed pointing to the fact that the standard potential of the reaction cannot be determined from the voltammetric experiments. The experimental current–potential curve was compared with a theoretical voltammogram and further oxidation of products at the electrode surface has also been analyzed using limiting convolution current.

1. Introduction

The electrocatalytic oxidation of methanol over platinum has been studied well by various electrochemical and spectroscopic techniques [1–13]. Over the past decades, a majority of the studies on electrocatalytic decomposition of methanol has been focused on engineering new electrocatalysts on various support materials that are poison-tolerant, yet cost-effective for practical applications [14–24]. Much effort has also been devoted on the mechanistic aspects as well as on the detection of various intermediates and their dependence on potential and time coordinates [2,5,7,10]. However, only a few studies have focused on the estimation of the kinetic parameters of the heterogeneous electron transfer process of methanol oxidation on platinum [8,25], which knowledge is important for a complete understanding of the reaction and improving the performance of the new electrocatalysts being developed.

The underlying reason to this effect can be traced to the following limitations: (i) the kinetics of electrocatalytic oxidation of methanol is complicated involving multi-step electrode reactions and parallel pathways and (ii) formation of partial oxidation intermediates like $–CH_3O$, $–CH_2O$, $–CHO$ and unwanted parallel reactions yielding poisonous carbon monoxide (CO) [2,26]. The above limitations preclude the application of mathematical models developed for simple heterogeneous electron transfer reactions [27]. However, it was shown by Xu et al. [8] that by applying potential pulses (>0.52 vs. RHE) of short-time potentiostatic electrolysis (<30 ms) and with larger waiting periods between successive pulses, the total electrooxidation of methanol on a polycrystalline platinum can be simplified to the reaction,

$$CH_3OH + H_2O \rightarrow\ HCOOH + 4H^+ + 4e^- \quad (1)$$

That has a rate determining step of initial dissociative adsorption of methanol from solution with the concomitant electron transfer,

$$CH_3OH_{sol} \rightarrow CH_2OH_{ad} +\ H^+ + e^- \quad (2)$$

The characteristic feature of short-time methanol decomposition on platinum surface is that no significant CO formation is observed. In the absence of surface poisons, mathematical models developed for simple electron transfer process at the electrode surface can be applied to the above reaction (1) wherein the number of electrons involved in the rate determining step is one while four electrons are transferred overall.

The same simplification of methanol oxidation process (reaction (1)) can be realized by employing fast scan voltammetry [10]. Lu et al. [10] reported that at sufficiently fast potential scan

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($35\,\mathrm{V\,s^{-1}}$), no surface CO is observed and the methanol oxidation occurs in the potential range between hydrogen desorption and platinum surface oxide potential regions [10]. In this paper, we apply convolution analysis of fast scan voltammetric technique to simplified methanol oxidation on polycrystalline platinum (reaction (1)) with the rate determining step of initial dissociative adsorption of methanol with concomitant charge transfer (reaction (2)). Convolution potential sweep voltammetry (CPSV) is one of the most powerful electrochemical methods for analyzing the subtle details of heterogeneous electron transfer process and is independent of a particular electrochemical method employed. The convolution method of analyzing cyclic voltammograms was developed independently by Oldham [28–30], who termed it as semi-integral analysis, and Saveant and co-workers [31–35] as convolution potential sweep voltammetry. The convolution current I is related to the actual current i and time t through the convolution integral [29]

$$I = \frac{1}{\sqrt{\pi}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \tag{3}$$

In this study, the heterogeneous electron transfer kinetics of methanol oxidation under fast scan condition is analyzed without defining *a priori* the electron transfer rate law (for example Butler–Volmer), and the same is obtained as a result of convolution analysis. Furthermore, unlike conventional voltammetric analysis, all the experimental current–potential data are employed in CPSV and hence more accurate kinetic parameters are obtained. From the combination of fast scan voltammetry and convolution analysis, true diffusion controlled reaction was observed at high scan rates and the apparent heterogeneous rate constant (k_H) was obtained as a function of electrode potential. The apparent anodic transfer coefficient β was also estimated from the derivative of $\ln k_\mathrm{H}$ vs. potential (E) plot and is in agreement with the one obtained from the conventional analysis of the voltammetric wave. The resulting kinetic parameters are substituted in the current equation for irreversible electrode reactions and compared with the experimental voltammetric wave.

2. Experimental

Voltammetric experiments were carried out with a CH Instruments electrochemical workstation in a three-electrode single compartment cell. The working electrode was a polycrystalline platinum disc of 2 mm diameter (active area = $0.0343\,\mathrm{cm^2}$; CH Instruments) and was polished successively with finer grades of alumina and sonicated for 3 min with high purity water. The electrochemical pretreatment rendered the electrodes highly reproducible. The electrode was scanned between 20 and 1200 mV (vs. RHE) for 20 times at such a scan rate ($20\,\mathrm{mV\,s^{-1}}$) where a good reversible but not exactly mirror images of hydrogen adsorption/desorption peaks appeared [36]. A mercury/mercury sulphate electrode standardized with hydrogen electrode (pH 0.3) served as the reference electrode and potentials were referred subsequently with respect to RHE. A platinum wire was used as a counter electrode. ACS certified methanol (Fischer Scientific), ultra high pure sulphuric acid (Fischer Scientific), and Millipore water (18 MΩ cm) were used in the experiments. Solutions were purged with high purity nitrogen for 10 min before the experiments. All experiments were conducted at ambient temperature.

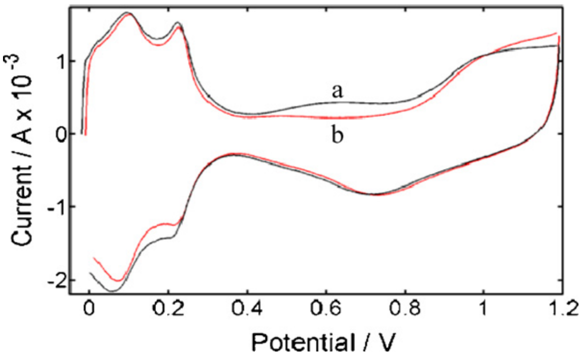

Fig. 1. Cyclic voltammograms recorded on polycrystalline platinum disc electrodes in (a) methanol (1 M) + H_2SO_4 (0.5 M) and (b) H_2SO_4 (0.5 M). Scan rate = $35\,\mathrm{V\,s^{-1}}$ and temperature = 298 K.

The properties of the interfacial region affect both the magnitude and shape of the current–potential curves especially at high scan rates. For example, uncompensated solution resistance tends to shift peak potentials of oxidation waves in a positive direction while the charging currents have deleterious effects both on the quality and magnitude of the voltammograms [37,38]. The positive feed back function of the potentiostat was employed to measure and compensate the *iR* drop without getting the circuit into oscillatory modes. Furthermore, without assuming that the charging current to be a linear function of potential, experimental charging current was estimated from the voltammogram measured under identical conditions but methanol. The current data obtained from the potentiostat were subsequently transferred to Matlab workspace for convolution analysis. The algorithm (Eq. (4)) used to evaluate the semi-integral from the experimental data was from Lawson and Maloy [39] and was applied to the current–potential data free of background current,

$$I = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{j=k} \frac{i(j\Delta t)\Delta t}{\sqrt{k\Delta t - j\Delta t + 0.5\Delta t}} \tag{4}$$

3. Results and discussion

There are several literature studies conforming to the fact that at short-time potentiostatic electrolysis of methanol above 0.5 V on smooth polycrystalline platinum in sulphuric acid only the soluble products other than CO and CO_2 are formed [8–10]. A maximum production of formaldehyde was observed near 0.5 V in perchloric acid [40]. The faster potentiodynamic electrolysis is advantageous since all the thermodynamic/kinetic information of the interested reaction is obtained in a single scan of short time. Formate was found to be an active and main product in the non-CO reaction pathway of methanol oxidation in a study based on in situ surface enhanced IR absorption spectroscopy (SEIRAS), and the other reaction intermediates proposed for this reaction pathway were not detected [41].

Fig. 1 shows fast scan voltammograms at smooth polycrystalline platinum disc electrode in 0.5 M sulphuric acid with and without methanol (1 M). No significant modifications of voltammogram in the hydrogen desorption/adsorption and surface oxide regions were observed due to the presence of methanol. While in the double layer region, an irreversible oxidation wave exists in the case of the voltammogram with methanol. Increase in current after 1 V in the positive going scan in the case of background voltammogram could be because of oxidation of organic impurity. Similar results were obtained by Lu et al. [10] with fast scan voltammetry wherein at higher scan rates methanol oxidation does not involve CO formation pathway and soluble products proceeds actively. Moreover, methanol oxidation peak current depends on the isotopic composition indicating that a C–H bond cleavage (reaction (2)) is involved in the rate determining step [10,42]. Voltammograms were measured at various scan rates as shown in Fig. 2. According to the current equation for irreversible diffusion controlled electrode reaction