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Electro oxidation study of isopropanol in surfactant media

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ABSTRACT

Isopropanol electro-oxidations on to Pt surface in surfactant environment have been reported. Analysis of the cyclic voltammetry results shows that isopropanol solution containing surfactants show a remarkable depression of all the peak current as compared to pure isopropanol solution. It is observed that in the presence of SDS (sodium dodecyl sulfate) the oxidation current of 2-PrOH is reduced to a small extent but it is reduced to a large extent in the presence of CTAB (cetyl trimethyl ammonium bromide). It is also revealed from the study that both oxidation potential and the peak current are function of surfactant concentration.

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KEYWORDS

Isopropanol;
Surfactant;
Cyclic voltammetry;
Electro-oxidation;
Diffusion.

INTRODUCTION

Direct alcohol fuel cells (DAFCs) attract attention as power sources in numerous applications at low operating temperature^[1]. Different types of alcohols can be used in DAFC. Electro-oxidation of long chain carbon atom alcohols involves more intermediates and products than that of methanol electro-oxidation and thus more efficient electro-catalysts are needed at low temperature. Platinum is the best choice as an electro-catalyst for alcohol fuel cell^[2-3].

The electro-oxidation kinetics of organic molecules is of fundamental importance in electro catalysis, and is also a vital factor in the application of the oxidation as anodic process in direct fuel cells.

Alcohol electro-oxidation mechanism on to plati-

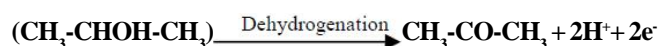
num surface has been studied widely for long time. Many mechanisms for alcohol oxidation have been proposed. Although a breakthrough in the understanding of the alcohol electro oxidation mechanism was obtained by techniques like in situ infrared reflectance spectroscopy, in situ IR reflection-absorption spectroscopy, in situ surface-enhanced IR absorption spectroscopy etc.^[4-5].

Electrooxidation mechanism of isopropanol is very complex in nature. Recently isopropanol (2-PrOH) electro-oxidation studies show that it is a promising fuel because it shows a lower over potential and higher performance than methanol.

Therefore, the investigations of reaction mechanisms are very important. The reaction mechanism of 2-PrOH electro-oxidation has also been investigated by means of electrochemical and spectroscopic techniques (in situ

infrared spectroscopy), on line mass spectroscopy. According to these studies, it is found that acetone is the main electro-oxidation product of 2-PrOH. Acetone plays both the role of product and intermediate, and that the formation of a further oxidized product, CO₂, was also observed. Sun and Lin carefully examined the electro-oxidation of 2-PrOH on platinum surface^[6-7]. The electro-oxidation of 2-PrOH on three basal planes ((111), (110) and (100)) and two stepped surfaces ((610) and (211)) of platinum single crystals has been studied by using in situ FTIR spectroscopy^[7]. The results showed that the oxidation of 2-PrOH obeys the same reaction mechanism on the basal planes as well as on the stepped surfaces. It was determined that acetone (characterized by IR bands around 1698, 1430, 1368, 1238 and 1157 cm⁻¹) and carbon dioxide (depicted by an IR band near 2345 cm⁻¹) are the main product species involved in isopropanol electro-oxidation. The production rate of acetone and carbon dioxide in isopropanol electro-oxidation at different potentials and on different Pt single crystal electrodes has been evaluated quantitatively from in situ time-resolved FTIR spectroscopic data.

Two potential regions are characterised for the production of acetone in isopropanol oxidation, one between 0.20 and 0.80 V/SCE and the other from 0.80 to 1.20 V. The activity of the Pt single crystal electrodes in the first potential region is Pt (100)>Pt (610)>Pt (211)>Pt (111)>Pt (110), and in the second potential region it is Pt (110)>Pt (111)>Pt (211)>Pt (100)>Pt (610). This study provides new data to describe quantitatively the kinetics of isopropanol oxidation on Pt single crystal electrodes, and contributes to the understanding of the structural effects of the Pt surface atomic arrangement in the electrocatalysis of irreversible reactions. They showed quantitatively that acetone forms through the dehydrogenation of 2-PrOH as a main reaction path, and also that the oxidation of adsorbed 2-PrOH proceeds further to yield CO₂ in parallel. From the study it was concluded that dehydrogenation of isopropanol is the main reaction,



In the present study, we like to add more light on the proposed mechanism using cationic and anionic surfactant as probe molecules. It is expected that in sur-

factant medium the diffusion of alcohol molecules will be sluggish. Again cationic and anionic surfactants are expected to behave oppositely towards dehydrogenation step. It should be mentioned that electrode kinetic studies for large number reactions using surfactant have been reported earlier^[8-10]. In almost all the cases it has been found that surfactants can markedly affect the redox reactions on the electrode surface. These may be due to i) changing the double layer structure ii) changing the rate of electron transfer by both acceleration or inhibition iii) changing the E_{1/2} value of an electro active species. It is expected that the present study will help understanding the mechanism of 2-PrOH oxidation.

EXPERIMENTAL

Sulfuric acid (Merck), cetyl trimethyl ammonium bromide, CTAB (Aldrich) and sodium dodecyl sulfate, SDS (Himedia Lab.Limited, Mumbai) were used as supplied. Isopropanol (Merck) was distilled under nitrogen atmosphere. A three electrode set up was constructed for this study, where bare Pt foil was the working electrode; the counter electrode was the Pt foil, while a saturated calomel electrode (SCE) served as reference electrode. The supporting electrolyte was 1M H₂SO₄ solution. For surfactants, the concentration below and above CMC were investigated. The isopropanol oxidation was measured by cyclic voltammetry at different scan rates. All the experiments were carried out at room temperature, 25°C. Electrochemical measurements were performed using a Potentiostat-galvanostat (VersaStat™ II, Princeton Applied Research).

RESULTS AND DISCUSSION

Figure 1 represents the cyclic voltammograms of 2-PrOH in 1M H₂SO₄ medium at 30 mVs⁻¹ scan rate in the presence of different surfactants. Cyclic voltammogram of pure isopropanol solution shows that three oxidation peaks are observed at about 0.271 V and at about 1.041 V in the forward scan and in the reverse scan at about 0.3 V.

But the cyclic voltammogram of alcohol solution containing surfactant show that the first oxidation peak prac-

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tically negligible and the second oxidation peak decreases. From the figure, it is seen that in the presence of SDS the oxidation current of 2-PrOH i.e. I_p (second oxidation peak) is reduced to a small extent but it is reduced to a large extent in the presence of CTAB. But E_p values change to a small extent in both the surfactants. It is also observed that E_p and I_p both are function of SDS concentration (figure 2.) Above the CMC, the oxidation rate still decreases for the anionic surfactant systems, which was not observed for the cationic one and at high concentration of CTAB, the voltammograms are entirely changed and is due to the bromide oxidation.

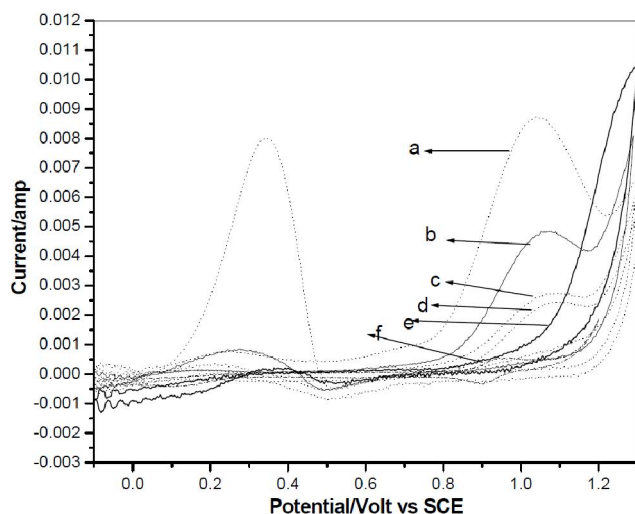


Figure 1 : Isopropanol oxidation in surfactant environment (a) pure 2-PrOH solution (b) in 3 mM SDS (c) in 8.1mM SDS (d) in 11mM SDS (e) in 0.2mM CTAB (f) in .95mM CTAB.

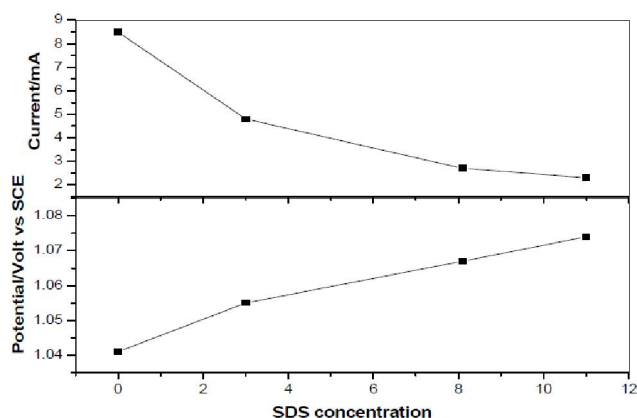


Figure 2 : Variation of peak current and peak potential with SDS concentration

We assumed that the dehydrogenation step is the rate determining step. The cationic and anionic surfactants behave oppositely towards the dehydrogenation

step. SDS accelerates the dehydrogenation of 2-PrOH but CTAB retards the dehydrogenation. The positively charged CTAB layer retards the deprotonation at the electrode surface via electrostatic repulsion. The negatively charged layers of SDS may favor the accumulation of H^+ ion near the electrode because of electrostatic interaction. The observed behaviors of two surfactants established the proposed rate determining step of oxidation of 2-PrOH.

The currents I_p of peak2 increase with the square root of scan rate. Plots of the anodic peak currents of 2-PrOH oxidation (I_p) versus scan rates (V) ranging from 30 to 50 $mV s^{-1}$ gave straight lines (figure 3) and thus obeys the following relationship.

$$I_p = 2.985 \cdot 10^5 n [(1-\alpha)n_e]^{-1/2} A D^{1/2} C V^{1/2} \quad (1)$$

Where I_{p_a} is the anodic peak current (mA), n is the number of electrons involved in the oxidation, A is the area of electrode (cm^2), V is the scan rate (Vs^{-1}), C is the concentration of the electro active species in bulk solution ($mol cm^{-3}$). Thus 2-PrOH electro-oxidation is an irreversible one. As the equation contains D (diffusion coefficient), so from the slope of the curves it is seen that diffusion coefficient decreases with increasing surfactant concentration. The cyclic voltammograms of 2-PrOH solution containing SDS show a remarkable depression of all the peak current as compared to only 2-PrOH solution. These observations may be explained by changes of the diffusion coefficients (D) of the electro active species. The diffusion coefficient value (D) is a

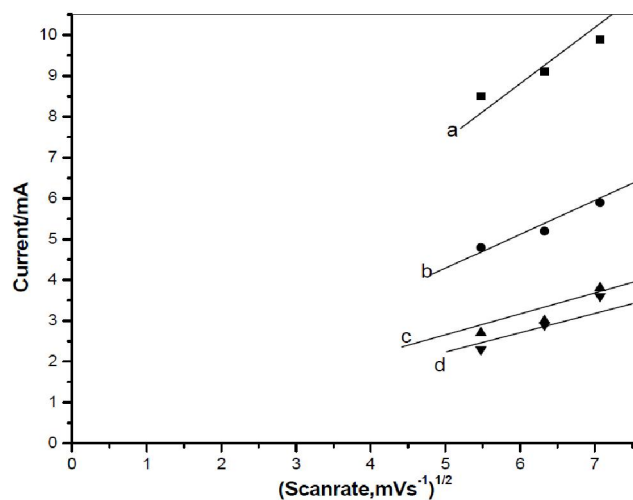


Figure 3 : Scan rate dependence of the anodic peak current for (a) only 2-PrOH (b) in 3mM SDS (c) in 8.1mM SDS (d) in 11 mM SDS solution

measurement of the charge transport rate within the liquid film near the electrode surface. The diffusion coefficient decreases with the increase of surfactant concentration. This may be due to the fact that the surfactant molecules are adsorbed on the electrode surface and simply serves as a wall to prevent the 2-PrOH molecules for electrodic reaction.

At the same time, the growing thickness of adsorption layer moves the plane of electron transfer away from the electrode surface. The diffusion of electroactive substance i.e, 2-PrOH through the compact adsorbed layer of surfactant is much slower and this leads to the increase of the oxidation potential.

CONCLUSION

A general conclusion emerging from our investigation is that the dehydrogenation is the vital step for the 2-PrOH oxidation. It is also seen that the dehydrogenation of 2-PrOH is much facile in SDS environment compared to CTAB. The positively charged CTAB layer retards the dehydrogenation and the negatively charged layers of SDS may favor the accumulation of H^+ . It is also observed from the study that the values of diffusion coefficients are gradually decreases with increasing SDS. Thus the surfactant molecules control the diffusion of 2-PrOH molecules towards the electrode, which leads to decrease the rate of 2-PrOH oxidation.

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