

Surfactant effects on methanol oxidation at Pt–Ru/C coated glassy carbon electrode

N. Karthikeyan · V. V. Giridhar · D. Vasudevan

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Abstract The role of surfactants, cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and Triton X-100 (in the catalyst), on methanol oxidation at commercial 50:50 Pt–Ru/C catalyst-coated glassy carbon has been studied using cyclic voltammetry, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Surfactant containing catalysts showed a considerable reduction in the methanol oxidation potential. In terms of oxidation potential, better results (lower methanol oxidation potential) were observed in the order SDS>Triton X-100>CTAB>no surfactant. SEM studies on the catalyst ink showed better homogeneity in the sample prepared using surfactant. This indicates better Pt–Pt contact, which is likely to favour methanol adsorption and its oxidation. Hence, lowering of oxidation potentials for methanol oxidation could be seen with use of surfactants. Results of FT-IR on the catalyst ink showed definite changes in the frequencies in the case of Pt–Ru/C containing surfactants indicating definite interaction between catalyst and surfactant. Catalysts, with and without surfactants, yielded linear plots of concentration vs peak currents for methanol oxidation (0–2 M). With surfactant containing catalysts, reduction in methanol oxidation current was observed, and the order followed was the reverse of the above.

Keywords Electro oxidation · Methanol · Surfactant modified Pt–Ru/C catalyst · SEM

Introduction

The nature and structure of the electrocatalyst plays a crucial role in alcohol adsorption and its electrooxidation. Depending on the preparation procedure, the nature and structure of the catalyst vary. The search for alternative routes to produce carbon-supported metal nanoparticle by a simple methodology is a goal in this area. The metallic nanoparticles are comparatively less stable for the normal environment. For this reason, surfactants have been used as stabilising agent to form stable nanoparticles and later destroyed by annealing the catalysts at high temperature in a flow of N₂ or H₂, followed by the treatment with ethanol while preparing the electrodes [1–9]. Heat treatment of samples disturbs the core level structure of its individual atoms. A trace amount of surfactant still remains after heat treatment and has been detected by X-ray diffraction [10]. Catalysts prepared with surfactants have shown better activity than those prepared without surfactants. The chain length, degree of branching, presence of charged functional group, and packing density of the surfactants and the core size of the micelles are found to affect the size of the metal nanoparticles [10].

The hydrophilicity/hydrophobicity ratio of the surfactant is indicated by hydrophilic–lipophilic balance (HLB). The HLB values of Triton X-100, cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) are 13.5, 21.4 and 40, respectively. Increase in current values has also been reported with the use of CTAB [11] (for hydrogen oxidation) and Triton X-100 [12] (for methanol oxidation). The former was expected to improve the wettability of carbon support as well as the dispersion of Pt nanoparticles.

The aim of the present work is to explore the influence of trace amount of cationic, anionic, and nonionic surfac-

N. Karthikeyan · V. V. Giridhar · D. Vasudevan (✉)
Electrodes and Electrocatalysis division,
Central Electrochemical Research Institute,
Karaikudi 630006, India
e-mail: vasudevand@rediffmail.com

tants in the electrocatalyst on methanol oxidation. Scanning electron microscopy (SEM) studies have been made to see the structure of the catalyst inks prepared and Fourier transform infrared spectroscopy (FT-IR) studies made to see the effect of any interactions if any between the catalyst and the surfactant. Hitherto, no such studies related to quantitative measure of various surfactant actions towards methanol electrooxidation have been made.

Experimental

Chemicals

Commercial 50:50 Pt–Ru/C catalyst (Alfa Aesar) contains 60% (w/w) alloy and 40% (w/w) of carbon. Nafion-117 (5% solution, Fluka), methanol (SRL, Mumbai), sulphuric acid (AR, Merck) and the surfactants CTAB (Merck), SDS (CDH) and Triton X-100 (Acros) were all used as purchased.

Electrochemical instrumentation and characterization of electrocatalysts

Cyclic voltammetry studies were carried out using EG & G PARC (M 273A) in conjunction with a computer with built in software model 270/250 Research Electrochemistry Software 4.23.

Cyclic voltammograms were recorded using a three-electrode system, with the catalyst modified glassy carbon (apparent surface area, 0.1256 cm^2) as the working electrode, Hg/Hg₂SO₄, 0.5 M H₂SO₄ as the reference electrode [0.68 V vs reversible hydrogen electrode (RHE)] and a platinum foil (1 cm^2) as the counter electrode. All potentials are reported vs RHE. Sweep rate employed was 20 mV s^{-1} .

A stock solution of 0.5 M H₂SO₄ was prepared with Millipore water. Standard addition of methanol was made to have a concentration in the range of 0–2 M. The solution was stirred using a magnetic stirrer. The mixture of catalyst, surfactant and nafion prepared as dispersion in Millipore water, was ultrasonicated using fast clean Ultrasonicator (EnerTech Electronics Pvt Ltd, India). The catalyst coating on GC was done using nafion, which was mixed with the catalyst and coated on GC. It was also ensured that the nafion catalyst ratio ($1 \mu\text{l}$ to 3.5 mg) was the same in all the cases.

The catalyst ink was prepared using 3.5 mg of Pt–Ru/C, $1 \mu\text{l}$ of 5% nafion, 2 ml of Milli Q Water and 2 ml of 2-propanol. For surfactant modified catalyst inks, in addition, $1 \mu\text{l}$ of 0.00001% (w/v) CTAB, 0.00001% (v/v) Triton X-100 or 0.00001% (w/v) SDS were used, as the case may be. From the prepared ink, $10 \mu\text{l}$ portions are coated over GC. The amount of surfactant present in the catalyst ink is found to be 2.5 ppb.

The particle morphology was studied by using scanning electron microscope (Hitachi, Japan, model no.S3000H).

FT-IR spectra of the products were recorded using a Perkin Elmer FTIR spectrophotometer (Model Paragon 500, OK).

Results and discussion

Cyclic voltammetry studies

Cyclic voltammograms for oxidation of 1 M methanol at Pt–Ru/C containing no surfactant and with CTAB in 0.5 M H₂SO₄ are displayed in Fig. 1. It is evident from the figure that the potential for methanol oxidation decreases with increase in CTAB concentration. The decrease is in the range of 5–30 mV depending on the surfactant concentration. With Pt–Ru/C containing 0.1% CTAB, interestingly, no reverse oxidation peak is seen in the whole concentration range of methanol oxidation studied. As the methanol oxidation current values also decreased with increase in concentration of CTAB, the lowest surfactant concentration was chosen for methanol oxidation studies with catalysts containing other surfactants.

Cyclic voltammetric response for methanol oxidation (1 M) at Pt–Ru/C without surfactant and with CTAB, Triton X and SDS in 0.5 M H₂SO₄ is shown in Fig. 2. The observation that surfactant containing catalyst lowers methanol oxidation potential in comparison to the catalyst without surfactant can be made from the figure. The peak current value is also reduced in presence of surfactants.

The plot of anodic peak potential vs concentration of methanol for methanol oxidation at Pt–Ru/C with and without surfactants is shown in Fig. 3. A clear reduction of potential values for methanol oxidation is evident from the figure.

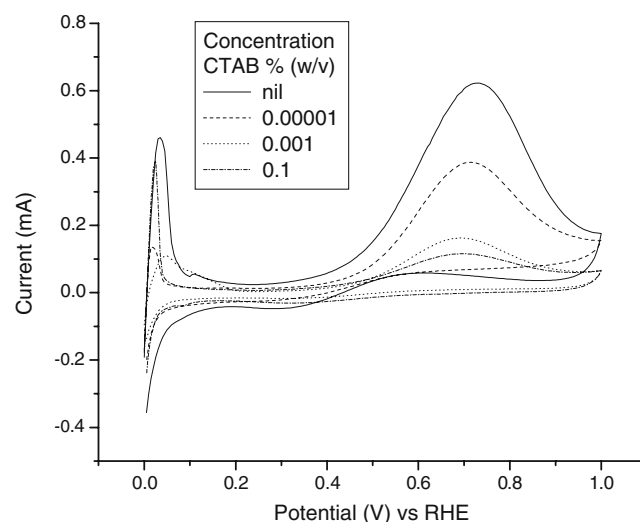


Fig. 1 Cyclic voltammetric response for methanol (1 M) oxidation at Pt–Ru/C containing no surfactant and with different concentrations of CTAB in 0.5 M H₂SO₄

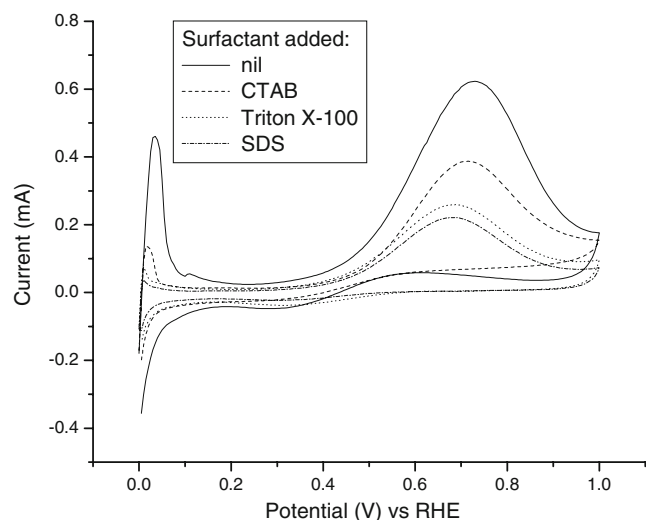


Fig. 2 Cyclic voltammetric response for methanol (1 M) oxidation at Pt–Ru/C containing no surfactant, 0.00001% (w/v) CTAB, 0.00001% (v/v) Triton X-100 and 0.00001% (w/v) SDS in 0.5 M H₂SO₄

Cyclic voltammetric data obtained for methanol oxidation at Pt–Ru/C with and without surfactants are presented in Table 1. Better results are obtained (lesser oxidation potential for methanol) in the order SDS>Triton X-100>CTAB>unmodified Pt–Ru/C. This means that an anionic surfactant is more effective than a neutral one, which is more effective than the cationic surfactant in reducing the methanol oxidation potential. It is likely that the anion adsorption from the anionic surfactant aids methanol oxidation.

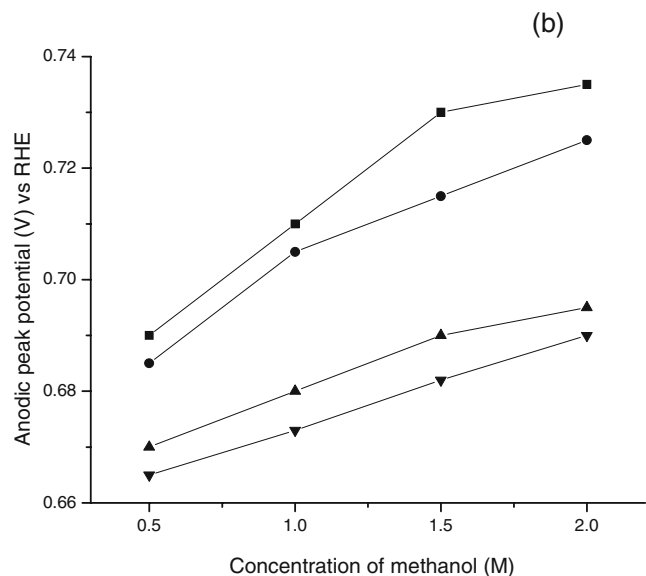


Fig. 3 Concentration vs anodic peak potential plot for methanol oxidation at Pt–Ru/C containing no surfactant (square), CTAB (circle), Triton X-100 (triangle) and SDS (inverted triangle)

Table 1 Cyclic voltammetry data on methanol oxidation at Pt–Ru/C containing no surfactant and with surfactant

Pt–Ru/C				
Concentration of aqueous methanol (M)	Anodic peak potential ^a (V)	Reverse oxidation potential ^a (V)	Methanol oxidation current ^b (mA)	<i>I_p/I_b</i>
0.5	0.690	–	0.287	–
1.0	0.710	0.630	0.471	17.82
1.5	0.730	0.610	0.592	10.56
2.0	0.735	0.605	0.676	8.78
Pt–Ru/C with 0.00001% v/v Triton X-100:				
0.5	0.670	–	0.112	–
1.0	0.680	0.641	0.188	49.75
1.5	0.690	0.630	0.247	28.78
2.0	0.695	0.615	0.299	20.00
Pt–Ru/C with 0.00001% w/v CTAB				
0.5	0.685	–	0.270	–
1.0	0.705	0.555	0.285	12.20
1.5	0.715	0.545	0.364	7.44
2.0	0.725	0.529	0.428	6.63
Pt–Ru/C with 0.00001% w/v SDS				
0.5	0.665	–	0.112	–
1.0	0.673	0.645	0.177	61.33
1.5	0.682	0.615	0.209	44.20
2.0	0.690	0.575	0.249	23.91

^a ±0.001 V

^b ±0.001 mA

It is likely that due to their negative charge on the surface of the catalyst, they tend to favour loss of electron by methanol more easily, thereby lowering the potential. However, the neutral and cationic surfactants as well lower the potential, which suggest that surfactants tend to alter the catalyst structure in a positive way which tends to lower the potential for methanol oxidation.

Another explanation could be made from the HLB values [13]. SDS is most hydrophilic, while Triton X-100 is most hydrophobic amongst the three surfactants. A higher HLB ratio for SDS may favour adsorption of the hydrophilic substrate methanol over the catalyst and hence cause reduction in its oxidation potential value.

A slight lowering in current density values is seen with CTAB, whereas the current densities are decreased to a greater extent with Triton X and SDS, as compared to the current density values in the absence of any surfactant. Current density values at Pt–Ru/C with or without surfactants decrease in the order: no surfactant>CTAB>Triton X-100>SDS. The plots are nearly linear in the concentration range of 0.5–2.0 M methanol. This lowering of the current values in the presence of surfactants is understandable since they seem to be blocking some of the

catalyst sites, thus reducing methanol electrooxidation current.

The performance of a catalyst is influenced by the I_f/I_b ratio, where I_f and I_b refer to the currents in the forward and reverse scans, respectively [10]. High I_f/I_b ratio indicates good methanol oxidation to carbon dioxide during anodic scan and low accumulation of carbonaceous residues like CO and CHO on the surface of catalyst [10]. The I_f/I_b ratio increases for methanol oxidation at Pt–Ru/C containing Triton X-100 and SDS and decreases at that containing CTAB as compared to oxidation at Pt–Ru/C having no surfactant. Hence, in terms of the catalyst performance based on the ratio, the order followed is SDS>Triton X-100>no surfactant>CTAB.

SEM and FT-IR studies

SEM images of catalyst ink with and without surfactants are shown in Fig. 4.

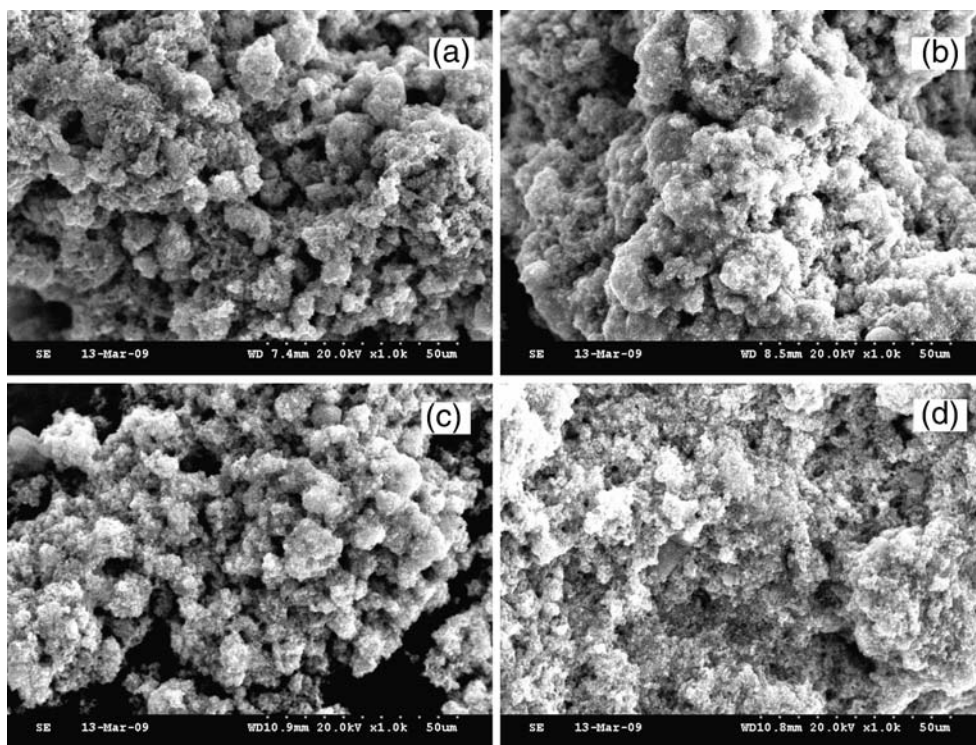
It can be seen from the SEM images that studies on the catalyst ink showed better homogeneity in the sample prepared using surfactant, especially those prepared using Triton X-100 and SDS. This indicates better Pt Pt contact in the catalyst ink, which is likely to favour methanol adsorption and its oxidation. Hence, lowering of oxidation potentials for methanol oxidation could be seen with use of surfactants, especially Triton X-100 and SDS.

Results of FT-IR on the catalyst ink showed one or two peaks corresponding to the surfactant (in case of surfactant containing catalysts) apart from peaks due to carbon and nafion, whose frequencies were altered in presence of surfactants.

The C–O stretch of –COOH in Vulcan XC 72 observed at frequency (per centimetre) of 1,019 was changed to values of 1,062, 1,035 and 1,022, respectively, in Pt–Ru/C containing Triton X-100, CTAB, and SDS. The quinone-stretching frequency (per centimetre) observed at 1,629 in nafion was observed at values of 1,629, 1,591.5, 1,629 and 1,629, respectively, in Pt–Ru/C containing no surfactant, Triton X-100, CTAB- and SDS. The O–H stretch of –COOH observed at frequency (per centimetre) of 2,376 in Pt–Ru/C containing no catalyst was found at 2,374, 2,364 and 2,362, respectively, at Pt–Ru/C containing Triton X-100, CTAB and SDS. In addition, the –CH₂CH₃ stretch observed at frequency (per centimetre) of 2,923 was observed at 2,923, 2,925 and 2,923, respectively, at Pt–Ru/C containing Triton X-100, CTAB, and SDS. Some of the frequencies in the above cases have been altered in the presence of surfactants, indicating a definite interaction of surfactant with the catalyst. However, it is complex to exactly envisage the actual interaction though the effects of interaction are seen in terms of SEM images and performance in terms of methanol oxidation potentials.

Catalysts, with and without surfactants, yielded linear plots of concentration vs peak currents for methanol

Fig. 4 SEM images of catalyst ink containing **a** no surfactant, **b** Triton X-100, **c** CTAB, **d** SDS



oxidation (0– 2 M). With surfactant containing catalysts, reduction in methanol oxidation current was observed and the order followed was the reverse of the above.

Conclusion

The anodic oxidation of methanol occurred at lesser oxidation potentials at surfactant modified Pt–Ru/C as compared to that at unmodified Pt–Ru/C. Methanol oxidation occurs more easily in the order: SDS>Triton X-100>CTAB>unmodified. Surfactant gave rise to homogeneity and more ordered and closer Pt Pt contact as could be seen from the SEM figures, which was essential for better performance in terms of methanol oxidation. The HLB values, the peak current ratios and the SEM images point towards catalysts with SDS and Triton X-100 performing better than catalyst without surfactant or with CTAB as surfactant. FT-IR studies indicate some changes in the absorption frequencies for Pt–Ru/C containing surfactants, indicating definite interaction between surfactant and the catalyst. In a typically operating direct-methanol fuel cell, Pt–Ru/C-containing surfactants could be favourable due to a decrease in oxidation potential of methanol as compared to that without surfactant.

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