

Short communication

Enhanced activity of Pt(HY) and Pt–Ru(HY) zeolite catalysts for electrooxidation of methanol in fuel cells

Purnakala V. Samant, Julio B. Fernandes*

Department of Chemistry, Goa University, Taleigao Plateau, Goa 403206, India

Received 4 June 2003; accepted 28 July 2003

Abstract

The investigation describes the synthesis of Pt and Pt–Ru catalysts by a new method using a HY zeolite support. The catalysts are used to study the anodic oxidation of methanol in an acidic medium to investigate their suitability for use in direct methanol fuel cells (DMFCs). The catalysts prepared in a HY zeolite support display significantly enhanced electrocatalytic activity in the order: HY < Pt/C < Pt(HY) < Pt–Ru/C < Pt–Ru(HY). The enhanced electrocatalytic activity is explained on the basis of the formation of specific CO clusters in zeolite cages.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Platinum; Platinum–ruthenium; Methanol oxidation; Electrocatalyst; Tafel plots; Fuel cell

1. Introduction

An effective catalyst for methanol electrooxidation, which will readily decompose partially oxidized species such as adsorbed CO, COH, etc. is not yet available. Direct methanol fuel cells (DMFCs) can make a major contribution to the energy requirements of stationary power supplies and road transportation, if methanol can be decomposed efficiently at fuel cell anodes. Though costly, noble metal catalysts—particularly those containing platinum—are found to be most effective and have therefore been investigated extensively. It is well known that the catalytic activity of platinum for methanol electrooxidation can be enhanced by addition of second element such as tin, ruthenium, etc. [1]. Thus, bimetallic Pt–Sn catalysts are known to have enhanced activity in the low potential region, and Pt–Ru in the higher potential region. Hence, consideration has been given to the development of ternary catalysts of platinum, tin and ruthenium. Unfortunately, ruthenium and tin exhibit poor miscibility and therefore ternary catalysts of the type Pt–Ru–Cr and Pt–Ru–Ni have been prepared and found to be very active [2]. Binary and ternary oxide catalysts such as Pt–WO₃, Pt–Ru–WO₃, Ni–MnO₂, Ni–WO₃ and Ni–Zr, have also been prepared and their enhanced synergistic effect is attributed to the intercalating nature of the oxide components [3–6].

Catalysts are now being developed through combinatorial selection. A quaternary catalyst of optimum composition Pt₄₄Ru₄₁Os₁₀Ir₀₅ has been selected combinatorially and the role of various catalyst components has been specified [7,8]. The current trend is to investigate newer support materials rather than using conventional Vulcan XC carbon or acetylene black. Thus, Pt–Ru supported on a highly oriented pyrolytic graphite (HOPG) or on mesocarbon microbeads have recently been investigated as catalysts for anodic oxidation of methanol and are reported to show lower polarization characteristics than with carbon black [9,10]. Similarly, zeolite A is found to be an efficient support when incorporated with metal groups that consist of Pt, Pd, Ru, Au, Rh, and Ir [11]. The zeolite material contains acidic protonic entities on its surface, which makes it more hydrophilic than carbon, and when used as a catalyst support in fuel cell electrodes, it results in lower resistance and less ohmic power losses than are found in electrodes that employ the use of carbon, exclusively as the support material. Further, these zeolite materials contain an array of channels which allow relatively high gas permeability [12,13]. A special sputtered electrode, which is extremely porous on Zeolite X, has been developed by Surampudi et al. for a DMFC system [13]. The important role for zeolite Y in a copper-based electrocatalyst has recently been reported [14]. The present investigation describes the preparation of platinum and Pt–Ru catalysts in HY zeolite using a simple synthesis procedure and confirms the superior activity of such catalysts as anode material for methanol oxidation.

* Corresponding author. Tel.: +91-832-273-6206;
fax: +91-832-245-2889.
E-mail address: jbfx@rediffmail.com (J.B. Fernandes).

2. Experimental

2.1. Preparation of HY zeolite by ion-exchange process

Zeolite HY was prepared by the twice ion-exchanging of NaY (UCIL India Ltd.) with 5 M NH_4NO_3 to obtain the ammonium form of zeolites. This was calcined at 823 K for 24 h.

2.1.1. Platinization of HY zeolite

Three grams of HY zeolite was washed with 800 cm^3 of de-ionized water and dried at 383 K for 2 days. The zeolite powder was then dispersed in 1000 cm^3 of water and a calculated amount of an aqueous solution of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\cdot\text{H}_2\text{O}$ (0.1 g cm^{-3}) was added drop-wise while stirring so as to obtain a catalyst with the desired metal loading (2 wt.%). The stirring was continued for 10 h. The reduction of the incorporated Pt complex within the zeolite was carried out using 0.1 M NaBH_4 , as suggested elsewhere [15]. After 10 h, the platinized zeolite sample was filtered and dried under flowing nitrogen at 313 K.

2.1.2. Synthesis of Pt–Ru(HY)

Three grams of HY zeolite powder was dispersed in 1000 cm^3 of distilled water and calculated amounts of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\cdot\text{H}_2\text{O}$ and RuCl_3 in a molar ratio (1:1) to yield a metal loading of 2 wt.% were added drop-wise while stirring, followed by reduction with 0.1 M NaBH_4 . The sample was then treated as above to obtain the required product.

2.1.3. Synthesis of Pt/C and Pt–Ru/C catalysts

These catalysts were synthesized in a similar manner as above, except that Vulcan XC 72 carbon was used instead of zeolite HY.

2.2. Fabrication of porous electrodes

One hundred milligrams of the catalysts HY, Pt(HY) or Pt–Ru(HY) were intimately mixed with 100 mg of activated

Vulcan XC carbon by constant mechanical stirring for 3 h to obtain a conductive composite. A 10 wt.% suspension of Teflon was then slowly added with constant stirring over a period of 30 min. A small amount of isopropyl alcohol was added and the resulting slurry was allowed to wet for 2 h. The paste was then spread over a Pt mesh and hot pressed at 343 K and 115 kg cm^{-2} pressure for a period of 5 min. The resulting electrode discs (1 cm^2 , 2.5 mm thickness) were dried in an air oven at 383 K for 1 h and subsequently heated in air at 623 K for 15 min.

2.3. Electrochemical measurements

2.3.1. Polarization studies

The anodic oxidation of methanol was carried out on electrodes made from HY, Pt(HY) and Pt–Ru(HY) electrodes at 333 K in a three-electrode assembly using a mixture of 2.5 mol dm^{-3} H_2SO_4 and 1 mol dm^{-3} CH_3OH as the electrolyte. The working electrode was mounted on a Teflon holder. A saturated calomel electrode (SCE) was employed as the reference electrode with its luggin tip placed appropriately close to the working electrode. The corresponding polarization curves are shown in Fig. 1. The Tafel plots from which Tafel slopes are determined are given in Fig. 2.

2.3.2. Cyclic voltammetric studies

Cyclic voltammograms (CVs) were conducted on the HY, Pt(HY) and Pt–Ru(HY) catalysts by using a 273 PARC potentiostat and a manual recorder. A SCE was used as the reference electrode and platinum foil was used as the counter electrode. The working electrode was prepared by mixing equal amounts of catalyst powder and Vulcan XC 72 carbon. This was followed by addition of 0.3 ml of paraffin to 10 mg of the catalyst/carbon mixture. The resulting paste was applied on to a platinum substrate ($2.5 \text{ mm} \times 2.5 \text{ mm}$) and subsequently dried at 383 K for 10 min. Experiments were carried out at 333 K in a 5 ml mixture of 2.5 mol dm^{-3} H_2SO_4 electrolyte and 1 mol dm^{-3} CH_3OH .

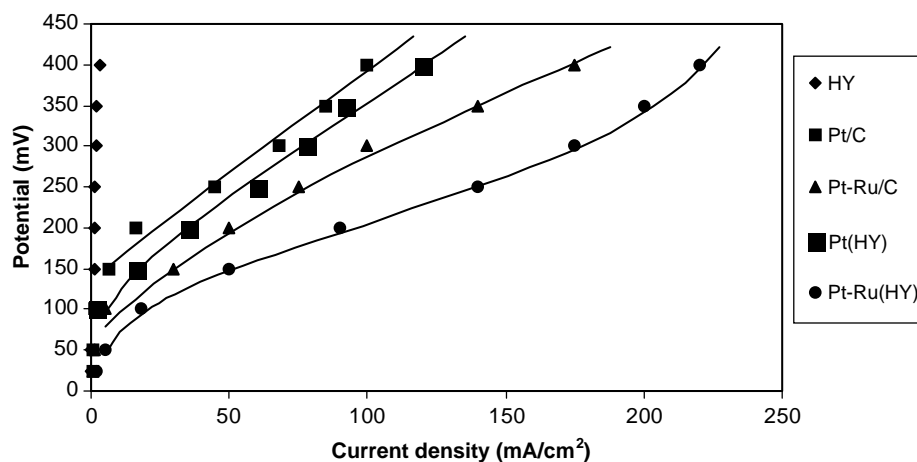


Fig. 1. Polarization curves for oxidation of methanol at 333 K on various electrocatalysts. Electrolyte used: mixture of 2.5 mol dm^{-3} H_2SO_4 and 1 mol dm^{-3} CH_3OH .

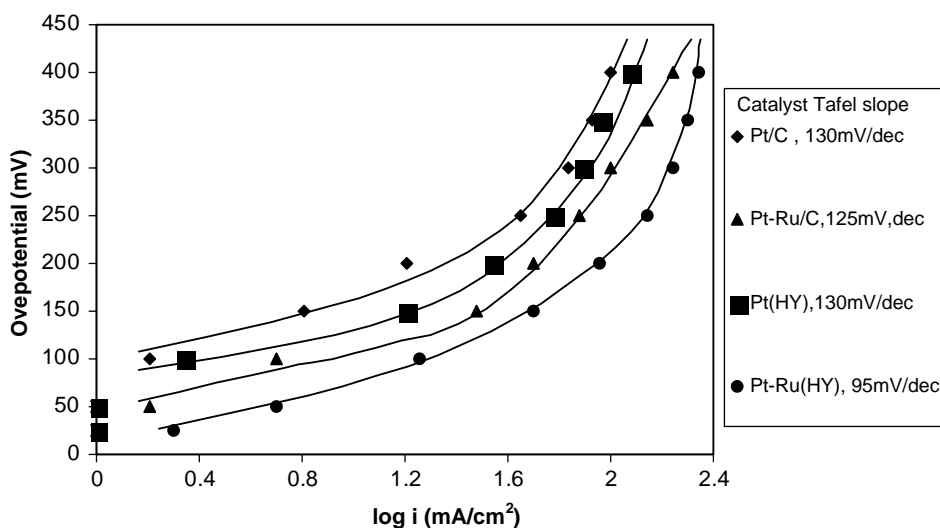


Fig. 2. Tafel plots for methanol oxidation on various electrocatalysts at 333 K. Electrolyte used: mixture of $2.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}$.

The corresponding CVs were recorded at a scan rate of 50 mV s^{-1} and are shown in Fig. 3.

3. Results and discussion

3.1. Electrocatalytic studies

The activity of the electrocatalysts for methanol oxidation may be considered to be a measure of their ability to

decompose methanol to carbon dioxide by preventing the accumulation of partially oxidized intermediates or poisons such as adsorbed CO and/or COH. The current voltage (I - V) curves and Tafel plots (η versus $\log i$) for methanol oxidation on various electrocatalysts are presented in Figs. 1 and 2, respectively. For convenience, the activity of the catalyst may be compared in terms of the current densities produced at some fixed potential. Current densities at a potential of 250 mV (the values are derived from Fig. 1) are listed in Table 1.

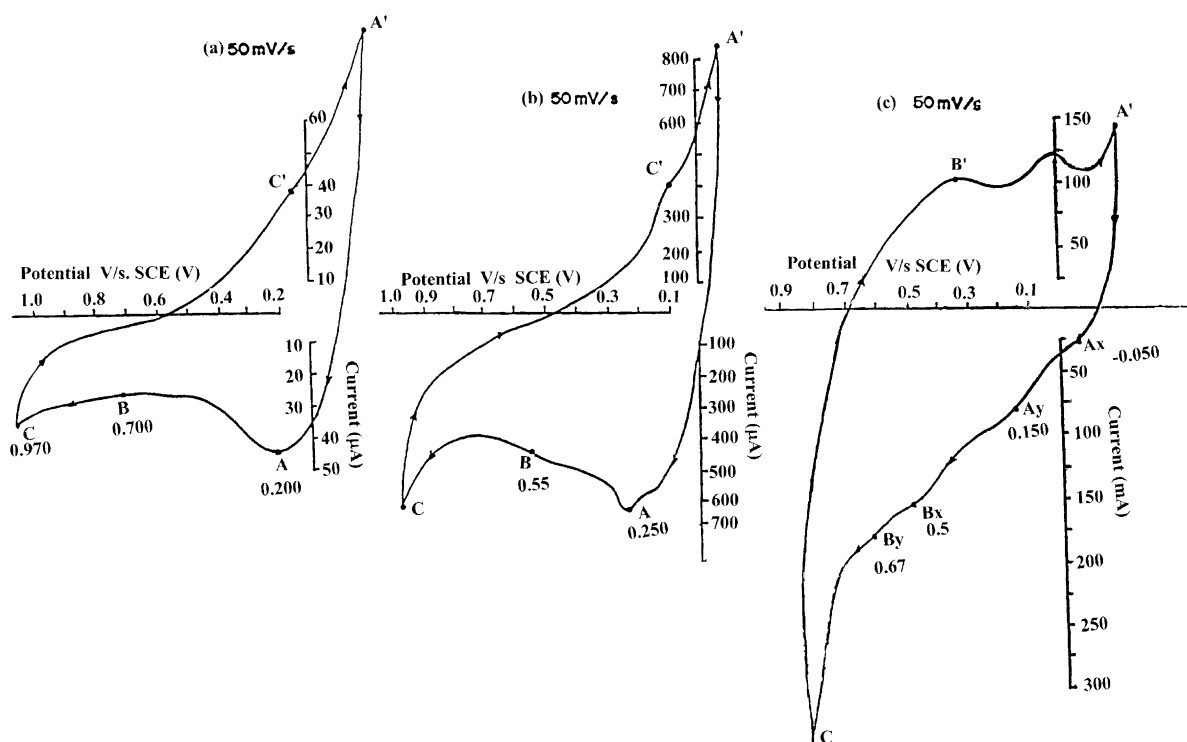


Fig. 3. CVs of the catalysts (a) HY, (b) Pt(HY) and (c) Pt-Ru(HY) recorded at a sweep rate of 50 mV s^{-1} . Electrolyte used: mixture of $2.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}$.

Table 1

Electrochemical activity of test catalysts expressed in terms of current densities at a potential of 250 mV at 333 K in relation to anodic currents obtained from CVs at 50 mV s⁻¹

Catalyst	Metal loading/gram of support (wt.%)	Metal catalyst in electrode composite (mg)	Current density (mA cm ⁻²)	Tafel slope (mV per decade)	Current (mA)		
					Peak A	Peak B	Peak C
HY	–	–	3	–	0.045	0.025	0.035
Pt/C	2	0.52	45	130	–	–	–
Pt(HY)	2	0.52	60	118	0.650	0.450	0.680
Pt–Ru/C	2 (1:1)	0.48	75	125	–	–	–
Pt–Ru(HY)	2 (1:1)	0.48	140	95	25.000	–	49.000

Electrolyte used: mixture of 2.5 mol dm⁻³ H₂SO₄ and 1 mol dm⁻³ CH₃OH.

It is clear from the data in Table 1 that metal catalysts in a zeolite Y matrix markedly enhance the electrocatalytic activity. The small activity for HY zeolites can be considered as background activity following treatment with carbon during electrode fabrication. It may be considered as the activity of HY/carbon, as suggested earlier [14]. Further, the activity of the Pt(HY) catalyst is 60 mA cm⁻² while that of Pt/C is 45 mA cm⁻². Thus, the HY-supported catalyst displays higher activity than the corresponding carbon-supported catalyst, even though the metal loading in the two cases is almost the same.

For methanol electrooxidation, Pt–Ru/C catalysts are well known to be greatly superior to Pt/C catalysts. This trend is also evident in the present investigation as the respective activities are 75 and 45 mA cm⁻². Further, the Tafel slopes of these samples (Table 1) are close to the literature values [16]. It should be noted, however, that the literature reports of Tafel slopes by various investigators are not consistent and are known to be influenced by the type of precursor and the nature of ad-atoms and their bulk and surface composition, as well as the relative proportion of the bimetallics such as Pt–Sn, Pt–Ru, and Pt–WO₃ [17,18].

It is also clear from the data in Table 1 that the Pt–Ru(HY) electrocatalyst exhibits exceptionally high activity (140 mA cm⁻²), while the corresponding Pt–Ru/C carbon gives only about 75 mA cm⁻² under the same conditions. This unusually enhanced activity of the Pt–Ru(HY) catalyst is believed to be due to some form of synergistic effect of the HY support. Further the Tafel slopes with the Pt–Ru(HY) catalyst are significantly different (95 mV per decade), but that of Pt–Ru/C is as expected, namely, 125 mV per decade. This suggests that a different mechanism may operate in the presence of a zeolite support.

3.2. Cyclic voltammetric studies

The CV for HY zeolite (Fig. 3(a)) is a smooth profile with a well-defined anodic peak at +0.15 to +0.2 V due to the oxidation of adsorbed hydrogen on the catalyst surface. The forward scan is continued up to ~+0.96 V which corresponds to growth of an oxide layer on Pt surface. The rapidly rising portion in the negative-going scan from +0.5 to –0.15 V

(point A') is due to hydrogen adsorption/evolution. In the CV profile for Pt(HY) (Fig. 3(b)), three anodic peaks at A, B and C are observed as compared with that of HY. The peak at A at ~+0.2 V. in the profile for HY is now seen to have grown in depth for Pt(HY) and is centered at ~+0.25 V. This is associated with the generation of a much higher current. While the peak for HY is attributed to the oxidation of adsorbed hydrogen in agreement with other work [20], it is quite probable that the new additional effect observed by the deepening of the peak could be due to methanol dehydrogenation. Peak B, which was not seen for HY, is present as a shoulder or a slight depression in the mid-anodic region at ~0.55 V.

In the CV for the Pt–Ru(HY) catalyst (Fig. 3(c)), it is seen that the peaks A and B, which were composite in Pt(HY), have now become distinct and are designated as Ax, Ay and Bx, By. The peaks Ax and Ay can be attributed to hydrogen oxidation and methanol dehydrogenation, respectively. Similarly, peaks Bx and By can be assigned to a two-stage oxidation of the methanolic residue, while peak C is, as before, attributed to the formation of an oxide layer. It is further observed that the onset of all the anodic peaks in the CV for Pt–Ru(HY) catalyst have moved towards lower anodic potentials. This indicates greater activity of this catalyst in comparison with the Pt(HY) catalyst. The anodic currents from CV profiles, which are proportional to the electrocatalytic activity of the samples, are shown separately in Table 1 and correspond with the respective peak potentials. These values demonstrate the higher activity of the Pt–Ru(HY) catalyst compared with Pt(HY) and HY. A similar observation has been reported by Wasmus and Vielstich [2].

3.3. General remarks

The half-cell polarization and cyclic voltammetry studies, as evident from the nature of Tafel slopes and the nature of CV profiles, respectively, particularly for the Pt–Ru(HY) catalyst, imply that the electrocatalytic decomposition of methanol can follow a different mechanism in presence of a zeolite HY support. This could be due to the shape selective or 'cage effect' of HY zeolites. Such an effect is known to operate in presence of carbonyl clusters on noble metal

catalysts [23]. To arrive at an explanation for identifying the role of zeolites HY, it is useful to review the current state of understanding of the mechanism of methanol electrooxidation.

Synergistic increase in the electrocatalytic activity of platinum electrodes by ruthenium in carefully prepared Pt–Ru alloys is well known [21]. Nevertheless, the manner in which ruthenium promotes platinum activity is not clear, namely, whether less CO is generated, or adsorption of CO is decreased, or CO is more readily oxidized anodically [19] on a Pt–Ru catalyst. It has been reported [21,22] that ruthenium does not favour the adsorption of methanol, but favors the nucleation of oxidized species such as Ru–OH, whose exact molecular identity is not clear, but whose formation is possible in an electrochemical environment.

The decomposition of the adsorbed carbonyl is believed to follow the reaction:



No reports are available on the role of zeolite Y in methanol electrooxidation. Recently, however, on the basis of detailed infrared spectral studies of adsorbed CO in pure and cation-exchanged Y zeolites, Gupta and co-workers [23,24] have shown the existence of CO clusters which are not specific to specific zeolite site interactions, but are influenced by a cage effect. Also, the electrostatic zeolites cation field could play an important role in the stabilization of these clusters. They concluded that CO₂ formation could result from strong interaction of CO with framework oxygen sites or surface hydroxyls. These studies, however, were conducted with alkali and alkaline earth metal cation-exchanged zeolite. In the case of methanol oxidation, which precedes methanol adsorption on platinum sites, CO-type adsorbed species will necessarily have to cluster on a metal sites at specific locations within the cages in

zeolites. This assumption is justified, considering recent theoretical studies that CO adsorption is sensitive to the electronic state of platinum in zeolites [23]. It has been found [19] that a synergistic effect for methanol oxidation is observed only on sputtered Pt–Ru alloy and not on its annealed form. It is therefore reasonable to conclude that zeolite Y provides an environment analogous to the formation of sputtered or dispersed Pt–Ru alloy, especially at the low metal loadings (~2 wt.%, Table 1) of the catalyst used in the present work. Also, it is thought that the formation of ruthenium clusters as a nanoelectrode, as in case of annealed alloy within platinum in a zeolite cage, is not desirable. This is because adsorbed OH groups on adjacent ruthenium atoms could undergo mutual dehydration, and be not available for decomposition of adsorbed CO species.

Thus, based on the above discussion, the superior oxidation kinetics in presence of Y zeolites could be due to the preferential formation of CO clusters on platinum that are limited by the steric constraints imposed by the zeolites framework, followed by facile oxidation to CO₂ by interaction with the surface or bridged hydroxyls of the zeolites and/or dispersed RuOH_{ads} species. In fact, this hypothesis is supported by in situ FTIR studies with CO gas on thin self-supporting catalyst wafers, wherein distinct CO₂ formation peaks around 2360 cm⁻¹ are observed only in case of a Pt–Ru(HY) catalyst [25] see Fig. 4.

The enhanced electrocatalytic effect could also be partly due to the following factors which require further investigation: (i) the porous nature of the zeolite support material which provides relatively improved gas permeability and minimizes the disadvantage associated with restricted gas diffusion in the electrode; (ii) the availability of an enhanced electrochemically active surface area by dispersion of the metal catalyst into the zeolite matrix.

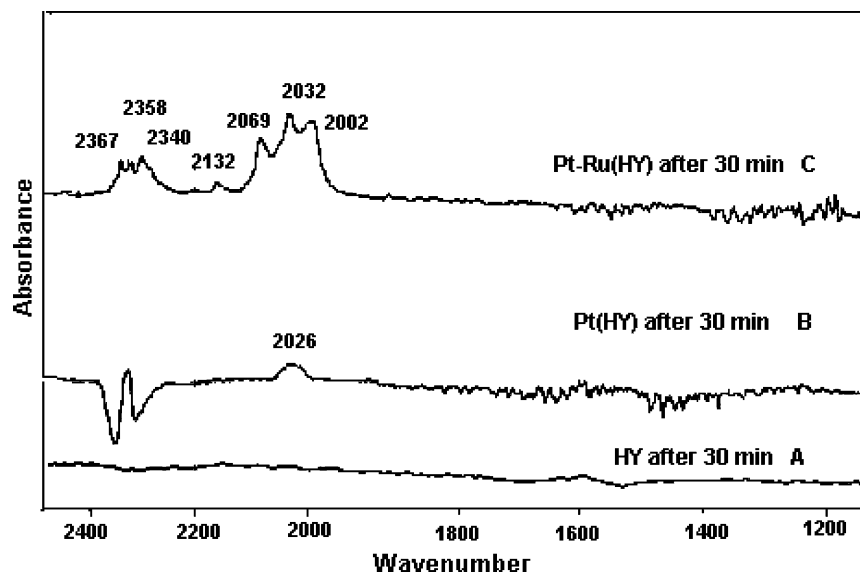


Fig. 4. Overlay of subtraction spectra of CO adsorption on (A) HY, (B) Pt(HY) and (C) Pt–Ru(HY) exposing for 30 min after evacuation.

4. Conclusions

The following conclusions can be drawn from the above investigations:

- (i) The investigation describes the synthesis of Pt and Pt–Ru catalysts by a new method using a HY zeolite support.
- (ii) The catalysts are used to examine the anodic oxidation of methanol with respect to its suitability for use in DMFCs.
- (iii) Catalysts synthesized in a HY zeolite support exhibit significantly enhanced electrocatalytic activity. The activity follows the order:
 $\text{HY} < \text{Pt/C} < \text{Pt(HY)} < \text{Pt–Ru/C} < \text{Pt–Ru(HY)}$.
- (iv) The enhanced electrocatalytic activity is explained on the basis of the formation of CO clusters in zeolite cages.

References

- [1] M.M.P. Janssen, J. Moolhuysen, *Electrochim. Acta* 21 (1976) 869.
- [2] S. Wasmus, W. Vielstich, *J. Appl. Electrochem.* 23 (1993) 220.
- [3] A. Hamnett, B.J. Kennedy, S.A. Weeks, J.B. Goodenough, *J. Appl. Electrochem.* 15 (1995) 323.
- [4] R.S. Babu, S.S. Murthy, B. Viswanathan, *Stud. Surf. Sci. Catal.* 113 (1998) 323.
- [5] P.V. Samant, J.B. Fernandes, *J. Power Sources* 79 (1999) 114.
- [6] C.C. Hays, R. Manoharan, J.B. Goodenough, *J. Power Sources* 45 (1993) 291.
- [7] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangpani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735.
- [8] B. Garau, R. Vishwanathan, R. Liu, T.J. Lafrenz, K.L. Ley, E.S. Somtkin, *J. Phys. Chem. B* 102 (1998) 9997.
- [9] C.H. Lee, C.W. Lee, D. Kim, S. Bae, *Int. J. Hydrogen Energy* 27 (2002) 445.
- [10] Y. Liu, X. Qiu, Y. Huang, W. Zhu, *J. Power Sources* 111 (2002) 160.
- [11] E. Yasumoto, K. Hatoh, T. Gamou, U.S. Patent No. 5,702,838 (December 30, 1997).
- [12] M. Shelef, U.S. Patent No. 6,117,581 (September 12, 2000).
- [13] S. Surampudi, A. Frank, R. Narayanan, W. Chun, B. Jeffries-Nakamura, A. Kindler, G. Halpert, U.S. Patent No. 2,001,005,0230 (December 13, 2001).
- [14] P.V. Samant, S.B. Kakodkar, S.P. Naik, J.B. Fernandes, in: *Proceedings of the 14th Natl. Symp. in Catalysis*. V. Murugesan, B. Arambindo, M. Pal anichamy (Eds.).
- [15] L. Persaud, A. Bard, A. Campion, M.A. Fox, T.E. Mallouk, E.E. Webber, J.M. White, *Inorg. Chem.* 26 (1987) 3825.
- [16] A.S. Arico, H. Kim, M.K. Ravikumar, V. Antonucci, N. Giordano, *Electrochim. Acta* 39 (1994) 691.
- [17] M. Watanabe, M. Uchida, M. Motoo, *J. Electroanal. Chem.* 229 (1987) 395.
- [18] L. She, H. Novinger, W.M.H. Sachtler, *J. Am. Chem. Soc.* 111 (1989) 8125.
- [19] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Crain, *J. Electrochem. Soc.* 141 (1994) 1795.
- [20] J. Prabhuram, R. Manoharan, *J. Power Sources* 74 (1998) 54.
- [21] N. Markovic, H.A. Gasteiger, P.N. Ross Jr., X. Jiang, I. Villegas, *Electrochim. Acta* 40 (1995) 91.
- [22] N. Markovic, H.A. Gasteiger, P.N. Ross Jr., X. Jiang, E.J. Crain, *J. Phys. Chem.* 98 (1994) 617.
- [23] B.S. Shete, V.S. Kamble, N.M. Gupta, V.B. Kartha, *J. Phys. Chem.* 102 (1998) 581.
- [24] N.M. Gupta, *Bull. Cat. Soc. India* 8 (6) 2–13 (1998) 2.
- [25] P.V. Samant, Ph.D. Thesis, Goa University (2000) 110.