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CO and CO/H_2 electrooxidation on carbon supported Pt–Ru catalyst in phosphotungstic acid ($H_3PW_{12}O_{40}$) electrolyte*

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An electrode-kinetic study of the oxidation of CO and CO/H_2 mixtures on a Pt–Ru/C catalyst was carried out in phosphotungstic acid (PWA) electrolyte. The influence of temperature, CO partial pressure and proton concentration on the electrochemical oxidation rate was investigated. An apparent activation energy of about 50 kJ mol^{-1} was found for CO oxidation at 0.6 V vs NHE. Fractional reaction orders close to 0.5 and −0.4 with respect to carbon monoxide and proton concentration, respectively, were observed. Tafel slopes were close to 136 mV dec^{-1} at 70 °C for both CO and CO/H_2 oxidation. The PWA electrolyte appeared to promote the methanol electrooxidation by increasing the rate of water discharge at the electrode.

Keywords: *CO electrooxidation*, *Pt–Ru catalyst*, *phosphotungstic acid*, *reaction orders*, *activation energy*, *Tafel slopes*

1. Introduction

The application of heteropolyacids in catalysis and electrochemistry is an important and growing area of technology. Heteropolyacids and isopolyacids have been used as surface promoters in fuel cell cathodes allowing a significant reduction of the Pt loading in the electrodes [1–5]. Phosphotungstic acid (PWA) was recently investigated as a proton conducting electrolyte in low temperature H_2–O_2 fuel cells [6, 7]. It was shown that the electroreduction of oxygen is strongly promoted in the presence of phosphotungstic acid [6] and a performance of about 700 mW cm^{-2} has been obtained with a PWA-based fuel cell at room temperature and atmospheric pressure [7]; furthermore, lifetime experiments on PWA fuel cell showed a stable cell performance for more than 300 h [7].

One of the main drawbacks that limits the practical application of low temperature fuel cells, employing hydrogen derived from reforming of methanol or methane, is the anodic Pt catalyst poisoning by carbon monoxide. The electrochemical oxidation of CO has been widely investigated especially in relation to the poisoning of phosphoric acid fuel cell anodes [8–17]. At present, it is widely accepted that a Pt–Ru alloy with 1:1 atomic ratio is the most active catalytic system for the electrooxidation of carbon monoxide [18]. Yet, the electrochemical activities are still poor at low temperature (70 °C) [19], so that higher temperatures of cell operation (above 200 °C) are mandatory for efficient CO electrooxidation.

In a previous study, we have shown that the electrooxidation of methanol is promoted by a heteropolyacid, that is, silicotungstic acid with respect to sulphuric acid [20]. More recently, other authors [21] have shown that the promoting behaviour of H_3SiWO_{40} towards methanol electro-oxidation is present even when such heteropolyacid is dissolved in small amounts in sulphuric acid. Although methanol electrooxidation on Pt alloys involves some reaction steps which are not present in the oxidation of carbon monoxide [22], in both cases the reaction rate is controlled by the oxidation of strongly chemisorbed carbon monoxide linearly-bonded to Pt, and by the water displacement at low potentials on the alloying element [23].

Previous work [20, 21] carried out on methanol electrooxidation suggests that a parallel strategy to the development of new electrocatalysts would be to employ an electrolyte that, besides having high protonic conductivity, could also ameliorate the oxidation of CO/H_2 mixtures on Pt–Ru surfaces. Phosphotungstic acid is a candidate electrolyte. In the present work, the electrooxidation of CO and CO/H_2 in PWA is investigated on porous Pt–Ru gas-diffusion electrodes of the type commonly employed in low-temperature fuel cells. In order to deconvolute the electrokinetic behaviour of the catalyst from both diffusion and ohmic drop effects, a.c.-impedance analysis during electrode polarization [24] and digital

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* This paper is dedicated to the memory of Professor Nicola Giordano.

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simulation of current potential data [25] were carried out. An evaluation of the contribution of both ionic resistance within the pores and mass transport to the electrode polarization was thus possible. The CO electrooxidation behaviour in PWA is compared with that in sulphuric acid [26] on the same Pt–Ru electrocatalyst.

2. Experimental details

20% Pt–10% Ru/Vulcan XC-72 catalyst was purchased from Electrochem. Inc. (Woburn, MA). The physicochemical properties of this catalyst were described previously [27]. It was observed that the catalyst was mainly composed of Pt–Ru crystallites with face-centred cubic structure. The mean particle size was about 40 Å.

Dual-layer gas diffusion electrodes were prepared according to a procedure previously described [20, 26]. These comprised a Teflon^{TM} (40%) bonded Pt–Ru catalyst layer deposited onto a wet-proofed carbon paper acting as diffusion layer. The platinum loading in the electrodes was 0.5 mg cm^{-2}.

Chemical grade hydrate PWA (water content 10.9%) was supplied by Fluka Chemika. Steady-state galvanostatic measurements and a.c.-impedance experiments were carried out in a water thermostated three-electrode cell at various PWA concentrations, that is, 10, 20, 40, 60 wt % which correspond to 0.04, 0.084, 0.21, 0.45 M, respectively. CO, H_2 as well as premixed CO/N_2 and CO/H_2 mixtures, were employed. The gas diffusion electrodes were mounted into a Teflon holder; the electrode area exposed to the electrolyte was 0.5 cm^2. A large area Pt gauze was used as counter electrode. An AMEL saturated calomel reference electrode (SCE) was placed in an external compartment filled with the same electrolyte and connected to the main body with a Luggin capillary whose tip was placed appropriately close to the working electrode. Electrode potentials in the text were reported with respect to the normal hydrogen electrode (NHE). The electrochemical cell was connected to an EG&G PAR model 273-A potentiostat/galvanostat and a Solartron 1255 frequency response analyser.

3. Results and discussion

3.1. *Effect of protonic concentration on the electrooxidation of CO*

Figure 1 shows the galvanostatic steady-state polarization data at 70 °C for carbon monoxide oxidation (50 kPa CO in N_2) on Pt–Ru/C electrodes at various PWA electrolyte concentrations. The inset shows the polarization data obtained in the absence of carbon monoxide in 20% PWA. The rest potential of the Pt–Ru/C electrode in the presence of carbon monoxide (50 kPa CO) at the same PWA concentration is shifted cathodically by about 0.45 V in relation to the data in the inset. The oxidation of CO is under activation control at low current densities (Fig. 1); as overpotential increases, mixed ohmic losses and diffusion effects influence the polarization behaviour. Series resistances (R_u) were determined by a.c.-impedance spectroscopy experiments (Fig. 2, inset) from the high frequency intercept of the Nyquist plot on the real axis (Z'). Ohmic losses are significant in the presence of 10% PWA concentration (R_u = 0.3 Ω cm^2) with respect to 20% PWA (0.15 Ω cm^2). The oxidation current at a given overpotential decreases as the electrolyte concentration increases in

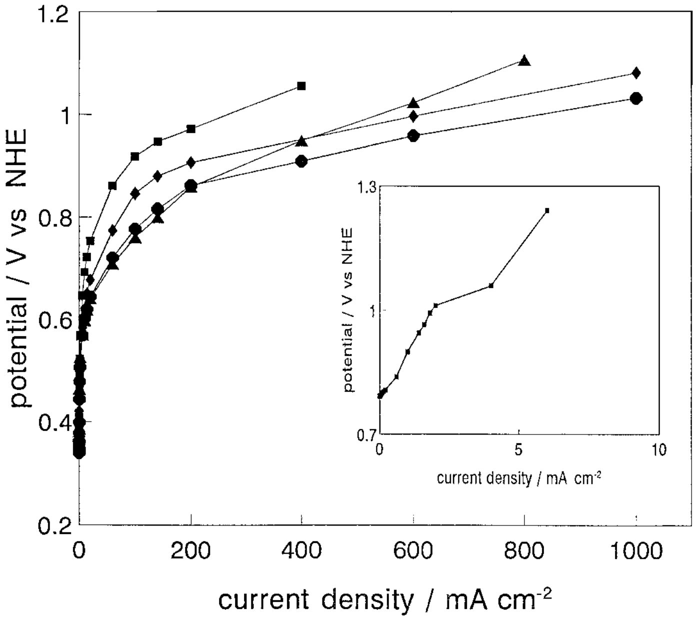

Fig. 1. Galvanostatic polarization curves for carbon monoxide (50 kPa in N_2) oxidation at 70 °C on Pt–Ru/C electrode at various concentrations of PWA. The inset shows the polarization data of Pt–Ru/C in absence of CO in 20% PWA. PWA concentrations: (■) 60%, (◆) 43%, (●) 20% and (▲) 10%.

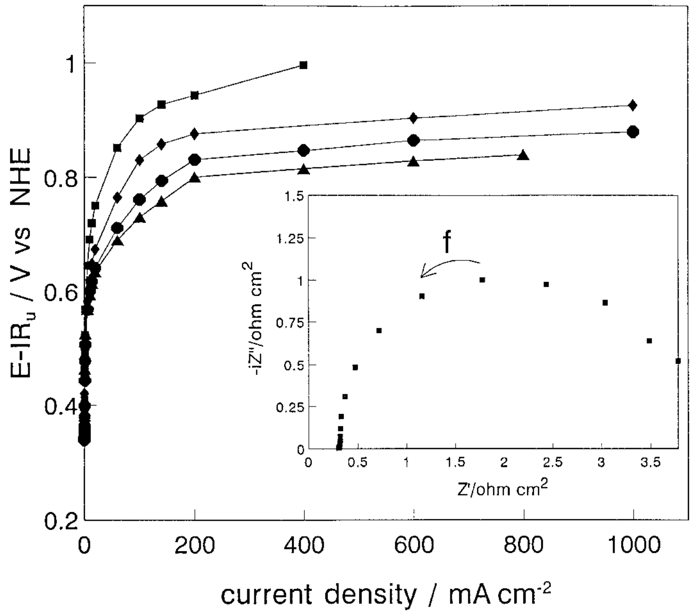

Fig. 2. *IR*-free polarization curves for carbon monoxide (50 kPa in N_2) oxidation at 70 °C on Pt–Ru/C electrode at various concentrations of PWA. The inset shows the a.c.-impedance spectrum obtained in 10% PWA at 0.8 V vs NHE. PWA concentrations: (■) 60%, (◆) 43%, (●) 20% and (▲) 10%.

the region under activation control. Figure 2 shows the oxidation behaviour of carbon monoxide after correction of the potential (E) for ohmic drop effects (IR_u). It is observed that the overpotential increases with increase in proton concentration over the whole range of current densities.

3.2. *Effect of CO partial pressure on the electrooxidation process*

Figure 3 shows the polarization curves obtained at different CO partial pressures (5, 10, 50, 100 kPa). It was observed that the overpotential decreased at the same current density passing from 5 to 50 kPa of CO; it then slightly increased passing from 50 to 100 kPa CO. Although carbon monoxide strongly adsorbs on both Pt and Ru sites [28], the larger affinity of Ru for oxygen species [29] suggests that a significant fraction of Ru sites is involved in the water displacement. This favours the nucleation of oxygen-containing species on the catalyst surface which promotes the oxidation of adsorbed CO, according to a widely accepted bifunctional mechanism [30]. Competition between CO and water molecules for these sites, especially in the

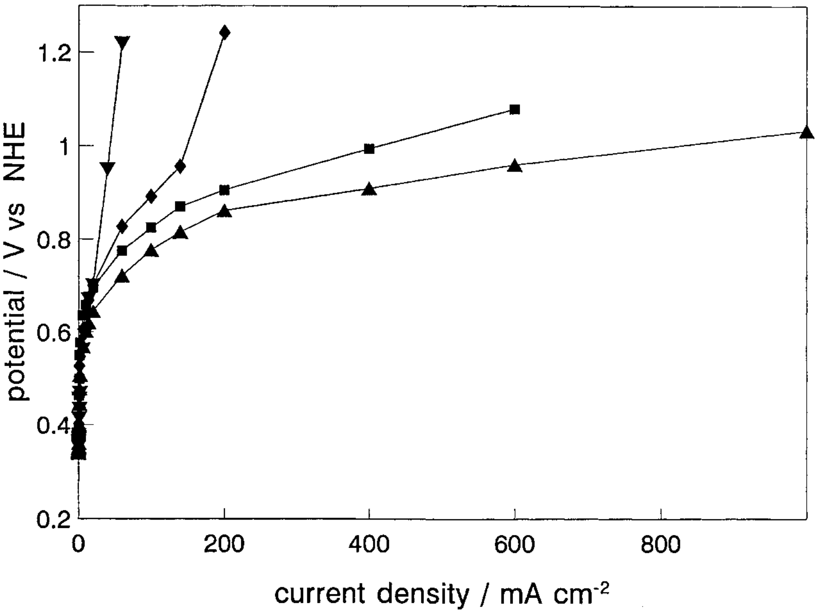

Fig. 3. Galvanostatic polarization curves for carbon monoxide oxidation on Pt–Ru/C electrode at various CO partial pressures in 20% PWA at 70 °C. CO pressures: (■) 100, (▲) 50, (◆) 10 and (▼) 5 kPa.

presence of a strong acidic environment, could decrease the reaction rate in the presence of very high CO partial pressures.

3.3. *Oxidation of H_2/CO mixtures*

The electro-oxidation behaviour of H_2/CO mixtures on Pt–Ru/C catalyst in phosphotungstic acid at 70 °C is compared in Fig. 4 with that of H_2 and CO in the same electrolyte. In general, the performance decreases progressively passing from H_2 to CO/H_2 and CO/N_2 mixtures. The observed linear behaviour for electrooxidation of hydrogen reveals that such a process is under ohmic control. The slope of the polarization curve is very close to the value of the uncompensated resistance, (i.e. $0.15\,\Omega\,cm^2$). Figure 4 shows that, even in presence of small amounts of CO (5 kPa in a hydrogen stream), the rest potential increases from 0 to 0.25 V vs NHE passing from pure H_2 to H_2/CO mixtures. The oxidation reaction for H_2/CO mixtures is under activation control over a wide range of current densities. An increase in overpotential of about 0.6 V at $2\,A\,cm^{-2}$ is recorded passing from pure H_2 to 5 kPa CO in H_2.

The adsorption of carbon monoxide on both Pt and Ru sites at potentials lower than 0.2 V vs NHE impedes the H_2 oxidation in this potential range [28]. Oxidation of H_2 in presence of CO occurs on Pt–Ru alloy only when water displacement on Ru sites allows the oxidation of strongly adsorbed CO. Water discharge commences at potentials above 0.2 V vs NHE on Ru. This probably reduces the steady-state coverage of adsorbed CO molecules providing, at low overpotentials, a small amount of free surface sites for H_2 oxidation. Such behaviour is suggested by the small decrease in rest potential (about 0.1 V) passing from pure CO to CO/H_2 mixtures (compare Fig. 3 and Fig. 4).

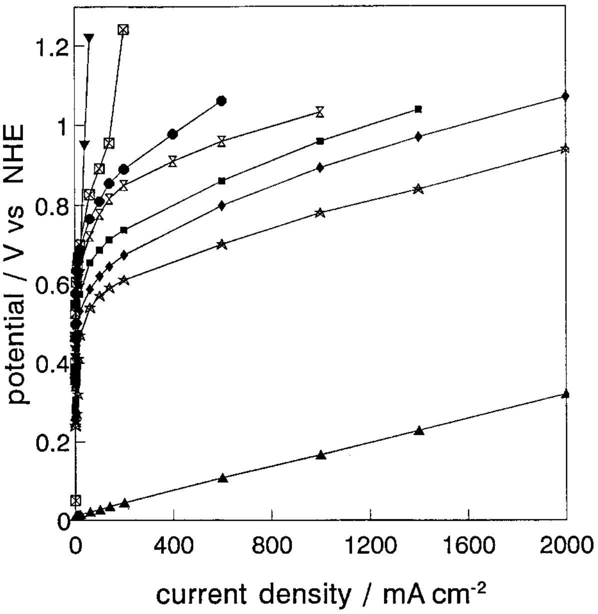

Fig. 4. Comparison of the polarization curves for the oxidation of H_2, CO/H_2, CO/N_2 and CO in 20% PWA on Pt–Ru electrode at 70 °C. Key: (▲) 100 kPa H_2; (☆) 5 kPa CO–95 kPa H_2; (◆) 10 kPa CO–90 kPa H_2; (■) 50 kPa CO–50 kPa H_2; (⧗) 50 kPa CO; (⊠) 10 kPa CO; (▼) 5 kPa CO; (●) 100 kPa CO.

3.4. *Activation energy for the CO electrooxidation*

Polarization curves for 50 kPa CO in N_2 and 10 kPa CO in H_2 mixtures, obtained at various temperatures in 20% PWA, are shown in Fig. 5 (a) and (b). A significant temperature activation is observed in both cases. A typical Arrhenius plot is shown in Fig. 6 for the 10 kPa CO–90 kPa H_2 mixture at the various potentials. The variation of ln I vs $1/T$ is linear with a slope $-E_a/R$, where E_a is the apparent activation energy. Figure 7 shows the variation of activation energy as a function of potential for two oxidation processes, that is, 10 kPa CO–90 kPa H_2 and 50 kPa CO in N_2. The activation energy decreases linearly with increase in overpotential for the H_2/CO mixture, whereas it remains almost constant at around $50\,kJ\,mol^{-1}$ for the CO/N_2 mixture in PWA.

For an electrochemical oxidation reaction, the Arrhenius equation can be written as [17];

$$I = nFCA\exp[-\Delta G^{\#}/RT]\exp[\alpha F\eta/RT] \qquad (1)$$

where $\Delta G^{\#}$ and A are the activation energy and the preexponential factor associated with the intrinsic reaction rate, respectively; C is the solubility of the

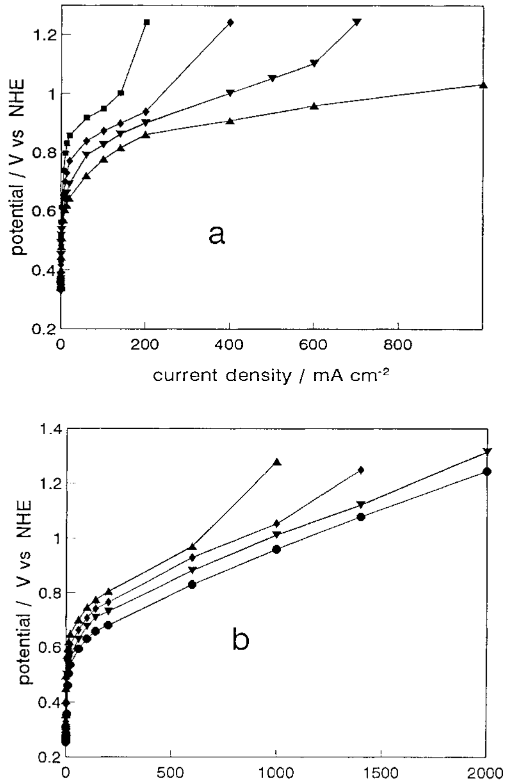

Fig. 5. Galvanostatic polarization curves for oxidation of (a) 50 kPa CO in N_2 and (b) 10 kPa CO in H_2 on Pt–Ru/C electrode at various temperatures in 20% PWA. Temperatures: (▲) 70, (▼) 60, (◆) 50 and (■) 40 °C.

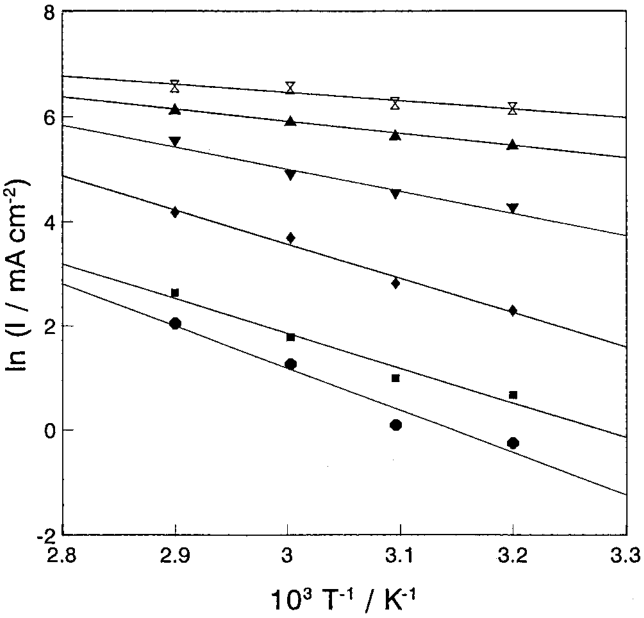

Fig. 6. Arrhenius diagram for the oxidation of 10 kPa CO in H_2 mixture on the Pt–Ru/C electrode at various potentials in 20% PWA. Key: (●) 0.4, (■) 0.5, (◆) 0.6, (▼) 0.7, (▲) 0.8 and (⧗) 0.9 V vs NHE.

electroactive species, α is the product of the number of electrons involved in the rate-determining step by the charge transfer coefficient, η is the overpotential ($\eta = E - E_{\text{rev}}$, E is the measured potential, E_{rev} is the reversible potential) and the other parameters have the usual meaning. Thus, the overall dependence of current density from temperature mainly derives from the contributions of the solubility of the electroactive species, overpotential and intrinsic reaction rate. The observed behaviour for CO/N_2 mixtures may be interpreted by considering that the contribution to the temperature dependence by the intrinsic reaction rate is largely controlling, whereas, in the case of CO/H_2 mixtures such a contribution only prevails at low overpotentials where the poisoning effect of CO is more significant.

3.5. *Tafel analysis for the oxidation of CO and CO/H_2 mixtures*

Mass transfer and ohmic drop corrected Tafel plots for the oxidation of 50 kPa CO in N_2 and 10 kPa CO–90 kPa H_2 in PWA are shown in Fig. 8. A comparison is made in the same diagram with a Tafel curve for 50 kPa CO in N_2 oxidation in 0.5 M sulphuric acid. The limiting current values (I_L) in the diagram were calculated from the I/V polarization curves according to the method described in [25], whereas series resistances were determined from a.c.-impedance spectroscopy [24]. The Tafel curve in H_2SO_4 shows a slope similar to that observed in PWA but is shifted by about 50 mV at higher overpotentials. Accordingly, the reaction rate in PWA at 0.4 V vs NHE is three times higher than in H_2SO_4. It is observed that both solutions of 20% PWA and 0.5 M H_2SO_4 have the same Hammett function values (i.e., $H_0 = 0.17$) [31] and, thus, similar acidity characteristics. Since Tafel plots are corrected for both ohmic drop and mass-transfer effects such a comparison is indicative of the different kinetic behaviour for CO-electrooxidation in the two electrolytes. Tafel slopes of about 137 and 127 mV dec^{-1}, extending to about 3 decades, were observed for the oxidation of 50 kPa CO in N_2 and for 10 kPa CO–90 kPa H_2 mixtures in PWA, respectively. These are close to the theoretical value of 136 mV dec^{-1} at 70 °C. The observed Tafel slope indicates that the rate determining step is a process involving the transfer of one electron in both oxida-

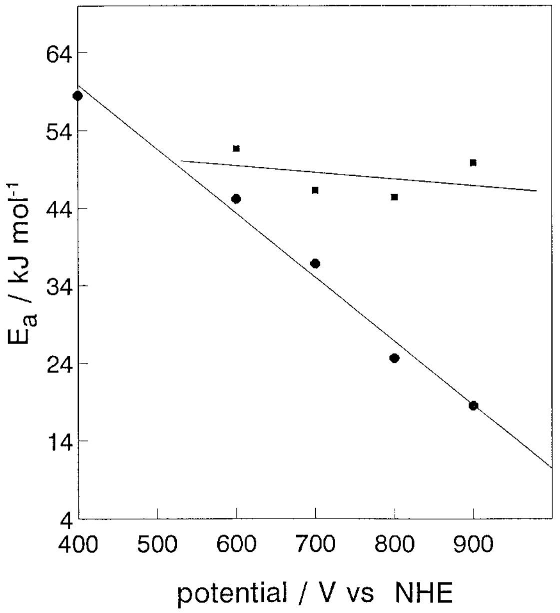

Fig. 7. Variation of the activation energy with the electrode potential for the electroelectrooxidation of 10 kPa CO in N_2 and 10 kPa CO in H_2 mixtures on Pt–Ru electrode in 20% PWA. Key: (●) 10 kPa CO–90 kPa H_2; (■) 10 kPa CO.

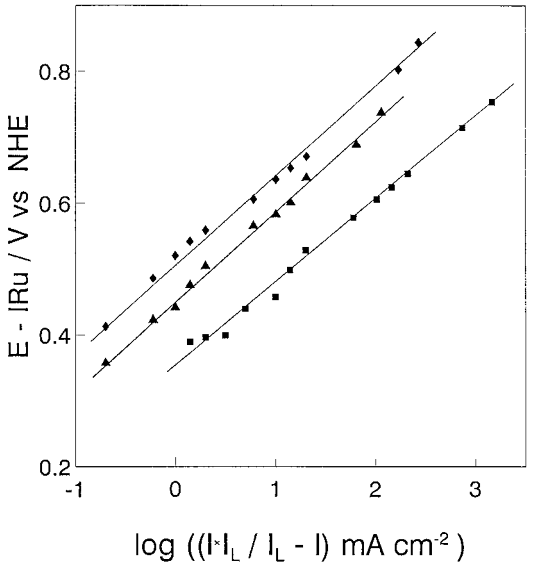

Fig. 8. Ohmic drop and mass transfer corrected Tafel plots for CO and CO/H_2 electrooxidation in 20% PWA and 0.5 M H_2SO_4 at 70 °C. Key: (■) 10 kPa CO in H_2–PWA; (▲) 50 kPa CO in N_2–PWA; (◆) 50 kPa CO in N_2–H_2SO_4.

tion of H_2/CO and CO/N_2 mixtures. In the electrooxidation of carbon monoxide on Pt–Ru, the most likely reaction steps, as indicated by electrochemical and *in situ* spectroscopic analyses [18–32], are described below:

$$H_2O \rightarrow OH_{ads} + H^+ + 1\,e^- \text{ (water displacement)} \qquad (2)$$

$$CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + 1\,e^- \text{ (surface reaction)} \qquad (3)$$

It is argued that the r.d.s. for CO electrooxidation could involve one or more of these steps.

3.6. *Kinetic analysis of the electrocatalytic reaction*

The electrooxidation of carbon monoxide is a bimolecular reaction involving the reaction of CO and water on the electrode surface. The concentration of CO in phosphotungstic acid depends on the CO partial pressure in the gas phase in contact with the electrolyte, whereas, water activity is related to the proton concentration. At constant potential, the coverage of adsorbed species on the electrode surface (θ_{CO} and θ_{OH}) can be related to the activity of the electroactive species in solution by an adsorption isotherm [33, 34]. Thus, the reaction rate (r) for electrooxidation of carbon monoxide which is directly proportional to the current density, may be expressed as

$$r = kP_{CO}^{\lambda}C_{H^+}^{\delta}\exp(\alpha F\eta/RT) \qquad (4)$$

where k is the intrinsic reaction rate constant, P_{CO} is the CO partial pressure in the CO/N_2 stream, C_H^+ the protonic concentration, λ and δ are the reaction orders with respect to CO and H^+, respectively. The reaction order with respect to CO in PWA was determined from: $\lambda = (\partial \ln I/\partial \ln P_{CO})_{E,\theta_{OH}}$ in the region where a linear trend was observed. The plots of ln I vs ln P_{CO} at various electrode potentials and constant proton concentration are shown in Fig. 9. It is observed that the slope of ln I vs ln P_{CO} is close to 0.5 at low overpotentials in the range of partial pressures up to 50 kPa CO. It slightly increases as the overpotential is increased above 0.9 V vs NHE even though no good linearity is observed in such conditions. A negative reaction order is observed at higher CO partial pressures. The present behaviour is similar to that for methanol oxidation on smooth Pt electrodes [34]. A negative reaction order with respect to CO, determined at low overpotentials in H_2SO_4 and extending to a significantly larger range of partial pressures, was observed previously [35].

The plots of ln I vs ln[H^+] at various electrode potentials are shown in Fig. 10. According to the water displacement reaction (Reaction 5), the coverage of OH_{ads} is inversely related to the protonic activity in solution [32]. The observed reaction order with respect to the protonic concentration, $\delta = (\partial \ln I/\partial \ln C_{H^+})_{E,\theta_{co}}$, is close to −0.4, for PWA concentrations lower than 60% at electrode potentials above 0.6 V. At 0.5 V a slightly lower pH dependence was observed.

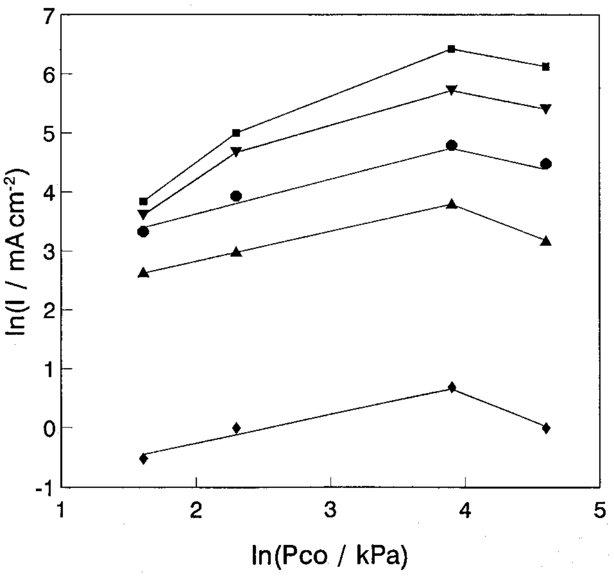

Fig. 9. Dependence of the oxidation current on CO partial pressure at various potentials in 20% PWA at 70 °C. Key: (◆) 0.5, (▲) 0.7, (●) 0.8, (▼) 0.9 and (■) 1 V vs NHE.

The observed reaction order for CO oxidation in PWA with respect to protonic concentration is significantly less negative than that observed in H_2SO_4 (i.e., −1) [26]. This indicates that OH adsorption on the electrode surface is stronger in PWA. Probably, the apparent absence of a dipole momentum in the Keggin structure [36] and the large dimension of the PWA heteropolyanions do not facilitate the orientation of the acid molecules at the electrical double layer at the interface, thus impeding their electrostatic adsorption on the surface. These characteristics likely advantage the water adsorption and its consequent discharge on the electrode in PWA. In contrast, in sulphuric acid the sulphate anions compete with

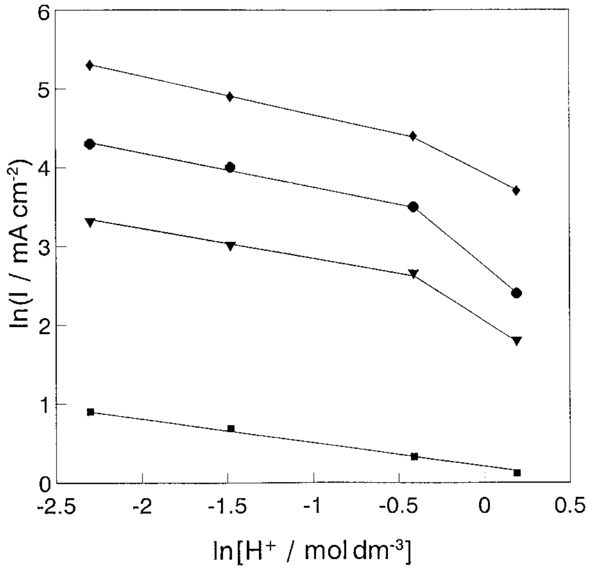

Fig. 10. Dependence of the oxidation current of 50 kPa CO in N_2 mixture on concentration of hydrogen ions at various potentials at 70 °C. Key: (◆) 0.8, (●) 0.7, (▼) 0.65 and (■) 0.5 V vs NHE.

water dipoles for the electrostatic adsorption on the electrode surface [37].

At very high concentrations of PWA most of the water molecules are strongly coordinated by Keggin units and thus they are not completely available for the water displacement process. This probably determines the strong decrease of electrochemical activity towards CO oxidation under such conditions.

In conclusion, the observed reaction orders with respect to CO and H^+ indicate the surface reaction (Equation 3) as the rate determining step at low CO partial pressures. On the other hand, the high coverage of Pt–Ru surface by strongly adsorbed CO species at high CO partial pressures [35] probably impedes the water displacement (Equation 2) determining a negative reaction order with respect to carbon monoxide in these conditions.

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