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Electro-oxidation of CO on Pd black in phosphotungstic acid

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Abstract Electro-oxidation of CO by Pd black in phosphotungstic acid (PWA) has been studied on porous gas-diffusion electrodes. Galvanostatic steady-state polarization data show that the reaction proceeds under strong activation control at low current densities. The current density at 0.5 V_{NHE} is found to be three times higher than that in a H₂SO₄ reference electrolyte. X-ray photoelectron spectroscopic data on various electrochemically tested electrodes show lower oxidized Pd species in PWA than in H₂SO₄. It is conjectured that an increase in the electron density around Pd sites is ameliorated by PWA in relation to H₂SO₄, with a consequent promoting effect of the heteropolyacid towards CO electro-oxidation.

Key words Heteropolyacids · CO electrochemical oxidation · Pd catalyst · Phosphotungstic acid · Gas-diffusion electrodes

Introduction

In the literature, heteropolyacids (HPAs) have been documented as catalysts [1] and surface promoters in electrochemistry [2–8]. Recent studies on HPAs have suggested that these compounds, besides exhibiting appreciable proton conductivities, can also promote methanol electro-oxidation [9, 10] and oxygen electro-reduction in fuel cells [6–8, 11]. Such a flexibility in the characteristics of HPAs is attributed to their unique

structural and chemical properties. HPAs are ionic solids having complex, high molecular weight anions represented by the general formula $[X_xM_mO_y]^{z-}$, with $x \leq m$. One of the important features for the catalytic properties of these compounds is related to the capacity of varying their catalytic functions by changing the elemental composition, while the overall structure is essentially retained.

Electro-oxidation of CO is of particular significance in the electrochemical conversion of hydrogen-rich and carbon-based fuels for energy usage. Besides, CO also acts as a strong deactivating agent for the anode electrocatalyst in low-temperature fuel cells [12–16]. Several studies on the electro-oxidation mechanism of methanol in Direct Methanol Fuel Cells (DMFCs) have pointed out the oxidation of chemisorbed CO-like species as the rate determining step for the reaction [14–16].

Bulk and supported Pd catalysts have been investigated for the low-temperature oxidation of CO, implicating structural effects in the adsorption characteristics of the CO-like poisoning species [17–19]. Moreover, Pd thin films have displayed high resistivity against CO poisoning in the oxidation of formic acid, especially for low-index crystallographic orientations [20]. The catalytic oxidation of CO by palladium-HPAs has also been investigated previously [21, 22]. From these studies, the reaction rate was found to depend on the redox potential of the HPA, determined by its composition; the formation of carbonyl complexes of reduced palladium also appears to enhance the reaction rate. On the basis of these findings, a redox mechanism based on the formation of such Pd complexes and the presence of successively oxidized-reduced forms of heteropolyanions was formulated [21, 22].

The present paper deals with the electro-oxidation of CO by Pd black in the presence of phosphotungstic acid (PWA), which was initially selected to ascertain if its chemical characteristics will be effective in establishing an appropriate electronic structure of the metal-adsorbed CO complex; this appears to be a prerequisite to enhance the electro-oxidation rate [23, 24]. The electrochemical

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behaviour of the reaction in PWA has been compared with that in a sulfuric acid reference electrolyte. The surface properties of the electrodes exposed to both electrolytes have also been investigated by X-ray photoelectron spectroscopy (XPS).

Experimental

A Pd black catalyst was obtained from Johnson Matthey. Porous electrodes were prepared as a Teflon-bonded Pd black catalyst layer deposited onto a wet-proofed carbon paper acting as the diffusion layer. The electrodes were prepared by first mixing the catalyst powder with water at 60 °C in an ultrasonic bath. Subsequently, a suspension of polytetrafluoroethylene (PTFE) was added to the catalyst so as to obtain a 40% PTFE loading in the catalytic layer. The as-obtained paste was spread by the doctor-blade technique over a Toray carbon paper (Toray TGP 90) wet-proofed with a solution of fluoroethylenepropylene polymer (FEP T120, DuPont) up to a FEP loading of 5 mg cm⁻². The electrode was hot-pressed at 70 °C under 15 kg cm⁻² for 30 min, followed by treatment in air at 350 °C for 25 min. The Pd loading in the electrodes was 5 mg cm⁻².

Electrochemical measurements for the electro-oxidation of CO were carried out in PWA and a H₂SO₄ reference electrolyte. The apparatus consisted of a water-thermostated three-electrode cell. The gas-diffusion electrode was mounted into a Teflon holder containing a Pt-ring current collector. The electrode area exposed to the electrolyte was 0.5 cm². A large-area Pt gauze was used as the 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 are 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. Series resistance values were obtained from ac experiments carried out during steady-state galvanostatic measurements.

XPS measurements were performed on the electrochemically tested and untested electrodes after prolonged washing in bidistilled water. Experiments were carried out by using a VSW Scientific Instruments Spectrometer (Manchester, UK); the X-ray source was Mg K_α operating at a power of 150 W. XP spectra were obtained with a pass energy of 90 eV for wide scans and 44 eV per individual elements. The samples were first dried at 100 °C in a low-pressure oven for 1 h. Afterwards, they were introduced into the spectrometer using a separate differentially pumped fast-entry chamber, then into a desorption chamber in ultrahigh vacuum for desorption of highly volatile species adsorbed on the carbon support, and finally into the analyser chamber.

Results and discussion

The cyclic voltammogram of Pd black in PWA for CO oxidation at 70 °C is shown in Fig. 1a. The onset of the oxidation current was observed at 0.74 V_{NHE} followed by an exponential increase of the current density at higher potentials; no peaks related to stripping of strongly adsorbed CO species appear in the voltammogram. The redox behaviour of PWA is observed at low potentials (≈0.17 V_{NHE}), which overlaps with hydrogen adsorption-desorption processes. Accordingly, the acid is not apparently involved in the electro-oxidation of

adsorbed CO since the latter occurs at a much higher potential. However, influence of PWA redox behaviour on the CO chemisorption cannot be ruled out since both the processes occur in the same potential range. Nevertheless, the observed difference between the experimental oxidation onset and the reversible potential for CO oxidation (-0.04 V_{NHE}) suggests that water discharging on the Pd surface, occurring at high potentials, mainly influences the electrochemical behaviour. Accordingly, the mechanism appears to be similar to that widely accepted for Pt catalysts [25]. In the latter case the reaction proceeds through linearly or bridge-bonded CO at Pt sites and, at suitable electrode potentials, water displacement occurs with subsequent formation of adsorbed OH intermediates.

The voltammogram of Pd black in sulfuric acid at 70 °C (Fig. 1b) shows a well defined peak for CO oxidation centred at about 0.94 V_{NHE} with a current density lower than that observed in PWA. The presence of CO considerably depresses the hydrogen chemisorption-desorption processes occurring in the potential region 0–0.4 V_{NHE}. It is noteworthy that both 20% PWA and 0.5 M H₂SO₄ solutions, selected for the present study, have the same Hammett function values ($H_0 = 0.17$) at 60 °C [26], and hence similar characteristics in terms of proton activity.

Figure 2 shows the galvanostatic steady-state polarization data for CO oxidation at 70 °C (10% CO in N₂) on Pd black (5.3 mg Pd cm⁻²) in 20% PWA and in 0.5 M H₂SO₄. The rest potential is slightly lower in PWA (0.27 V_{NHE}) than in H₂SO₄ (0.32 V_{NHE}). The reaction appears to be under strong activation control at low current densities in both the electrolytes but, as the overpotential increases, the polarization behaviour is

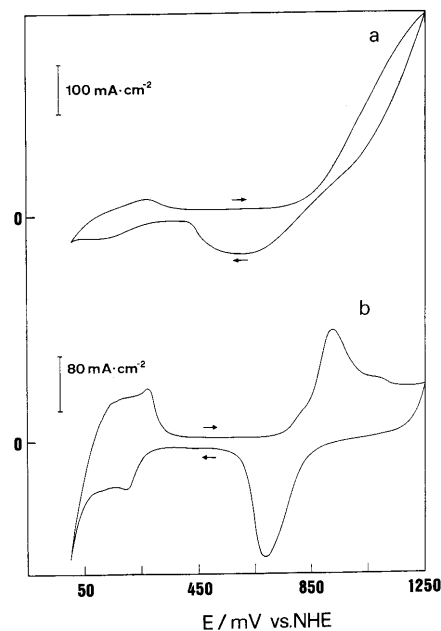


Fig. 1 Cyclic voltammogram of Pd black for CO oxidation at 70 °C in PWA (a) and H₂SO₄ (b). Initial potential 0 V_{NHE}

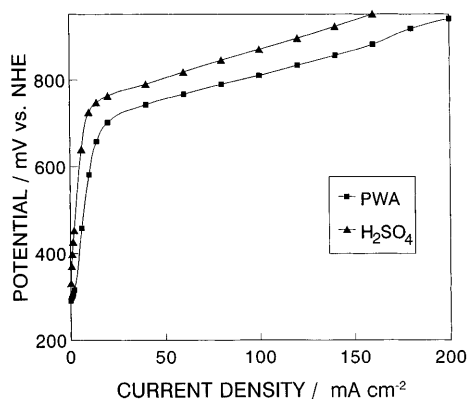


Fig. 2 Galvanostatic steady-state polarization for CO oxidation at 70 °C on Pd black in 20% PWA and 0.5 M H₂SO₄

influenced by ohmic losses and diffusion. A higher overpotential is observed for Pd black in 0.5 M H₂SO₄ in the entire range of current density with respect to the same electrode in PWA. AC impedance experiments showed that this result is not due to ohmic losses, since the uncompensated resistance, in both the cases, is 0.25 ohm cm². Accordingly, the current density for CO oxidation at 0.5 V_{NHE} is about three times higher in PWA compared to that in H₂SO₄. The contribution from possible electrochemical reactions of the electrolyte and corrosion phenomena of Pd has been excluded by conducting similar polarization experiments with nitrogen; negligible steady-state current values (<0.5 mA at 0.8 V_{NHE}) were recorded for all the cases. After repeatedly scanning the cyclic voltammograms (CVs) in presence of CO (2 h), a slight decrease in performance was observed.

The influence of the temperature in the range 25–70 °C for the Pd black-PWA system is shown in Fig. 3. These measurements were carried out after prolonged electrode conditioning by CVs as indicated above; higher overpotentials are recorded at lower temperature, suggesting the temperature-activated nature of the reaction.

Arrhenius plots between 0.40 and 0.95 V_{NHE} (Fig. 4a) show an almost linear behaviour in the overall

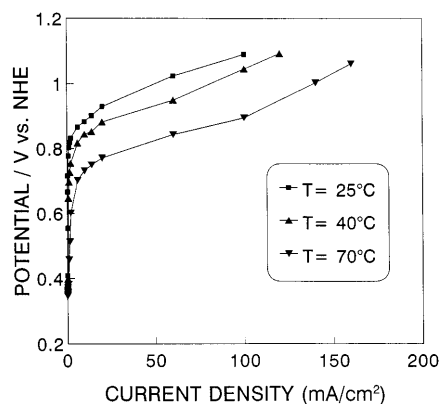
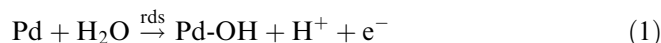


Fig. 3 Galvanostatic steady-state polarization for CO oxidation for the Pd black-PWA system at different temperatures

potential range. Figure 4b shows the corresponding activation energy values as a function of the potential. These appear to increase in the potential region up to 0.7 V_{NHE}, where a strong CO chemisorption occurs. Afterwards, a decrease in activity is due to the prevailing influence of the water displacement reaction.

These results demonstrate that the main drawback for the electrocatalytic CO oxidation by Pd in PWA and H₂SO₄ electrolytes is the sluggishness of water discharge. This occurs at significant rates only at potentials higher than 0.5 V_{NHE}. The surface reaction between adsorbed CO and OH species is thus virtually in equilibrium with respect to water displacement as described below:



In order to gain more insight into the electrode-electrolyte interaction, a surface analysis of the electrodes employed for the reaction, both in PWA and H₂SO₄, was carried out by XPS. The XP spectra (Figs. 5 and 6) were compared with a reference (unused) Pd black electrode.

The survey XP spectra (Fig. 5) show the characteristic electronic features of the PTFE structure in the binding energy (BE) range 600–700 eV, with no evidence of significant differences for the examined electrodes. Accordingly, the F 1s photoelectron peak is located at a BE value of 684.9 eV for the three samples studied here,

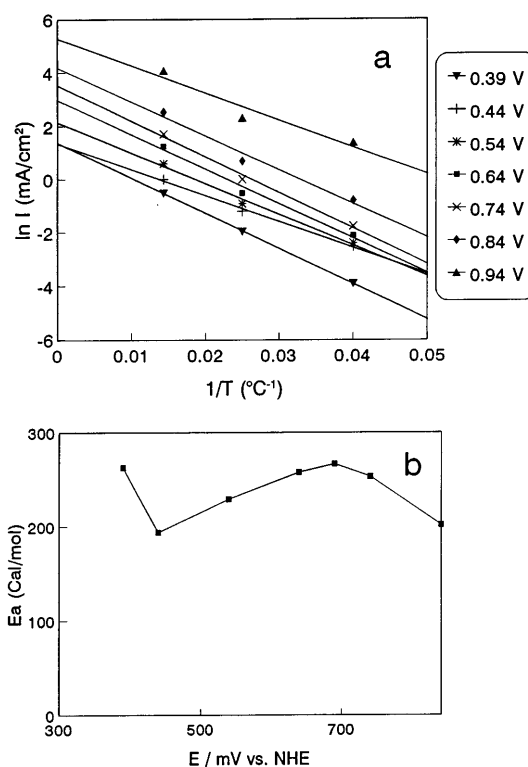
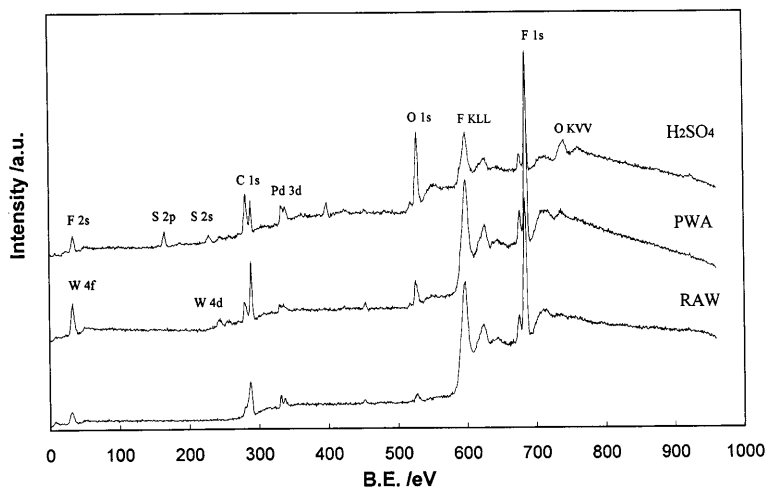


Fig. 4 Arrhenius plots for CO oxidation on Pd black in 20% PWA (a) and corresponding activation energies as a function of the potential (b)

Fig. 5 Survey X-ray photoelectron (XP) spectra of the electrodes in H_2SO_4 and PWA. The spectrum of an unused electrode is shown for comparison



revealing that no PTFE-electrolyte chemical interaction has occurred upon operation in the electrochemical cell.

Contrary to the reference sample, in the XP spectra of the tested electrodes the presence of peaks related to W $4f_{7/2}$ (31 eV), as well as W $4d_{5/2}$ (245 eV), S $2p$ (164 eV) and S $2s$ (235 eV), is observed. This appears to denote a strong electrode-electrolyte interaction accounting for an induced electronic modification of Pd surface atoms.

The Pd $3d$ spectra of the samples are compared in Fig. 6. A significant shift towards higher binding energies of the Pd signal in H_2SO_4 , with respect to the PWA-tested and raw electrodes, is clearly observed. This reflects the presence of a large amount of oxidized Pd^{2+} species in H_2SO_4 , but zero-valent Pd is found prevailing in both untested and PWA-tested electrodes.

Another feature that distinguishes the tested samples from the reference is the larger amount of oxygen (Fig. 5). In particular, the oxygen content of the electrode surface operated in H_2SO_4 is significantly higher than in PWA, as shown by the increase of O_{1s} and O_{KVV} (Auger) signals at BE values of about 532 eV and 745 eV, respectively. A significant fraction of this surface oxygen is most likely due to the uptake of sulfate and heropolyanions, the remainder being derived from

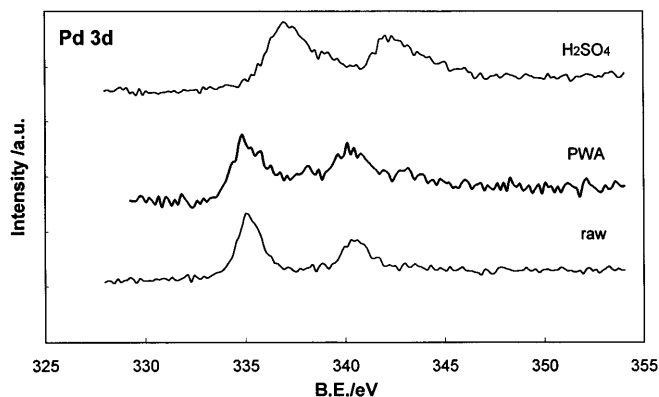


Fig. 6 XP Pd $3d$ spectra of the electrodes (H_2SO_4 , PWA, unused)

Pd oxide species. Accordingly, the amount of oxygen atoms strongly bound to Pd sites is larger in H_2SO_4 . This appears to be a drawback for the water displacement process, as water chemisorption occurs more easily on an oxide-free surface. Furthermore, a surface reaction between chemisorbed CO and OH_{ads} (reaction step 2) generally requires “labile” OH species [16].

On the other hand, it is of interest to elucidate the nature of modifications occurring in consequence of CO chemisorption on Pd surfaces characterized by different oxidation states. The formation of transition metal carbonyl compounds has been widely investigated in the literature. In particular, CO chemisorption on Pd involves the donation of an electron pair from σ^* (anti-bonding) orbitals of CO to the empty $4d$ orbitals of Pd. A back-donation of electrons from the transition metal to CO orbitals further stabilizes this interaction [27]. Accordingly, it is apparent that dative electron donation from CO to Pd is a prerequisite for CO chemisorption. This process occurs irreversibly (high chemisorption energy) on a partially oxidized metal surface whose atoms can allocate CO electrons in their empty orbitals with respect to Pd sites characterized by a high electron density.

The modifications of the electronic environment of transition metals involved in the strong CO chemisorption by alloy formation with additional elements has been studied with particular regard to Pt-alloy systems for methanol electro-oxidation [13], whose reaction rate is strongly affected by the formation of CO-like poisoning residues on the electrode surface. In a previous study of Pt-Sn bimetallic system [28], we observed that a charge-transfer from Sn to Pt, as revealed by a 1.1 eV chemical shift in the X-ray absorption near-edge structure (XANES) spectra, produced a significant increase of the rate of methanol oxidation. More recently, a similar charge-transfer effect was reported to occur on Pt-Ti and Pt-Nb amorphous alloys [29]. Accordingly, these catalysts were found to be active towards the electro-oxidation of methanol. On the other hand, conflicting results have been reported

for the Pt-Ru system. Goodenough et al. [30] observed that a close Pt-Ru interaction produces a significant shift of the Ru 3*p* signal in the XP spectra to higher BE values. This was explained in the light of an electron withdrawing effect exerted by Pt sites towards neighbouring Ru atoms. On the other hand, McBreen and Mukerjee [31] have recently shown, by X-ray absorption spectroscopy, that Pt alloying with Ru causes an increase in the number of Pt *d*-band vacancies. In both the cases a higher activity for methanol oxidation with respect to Pt catalyst was claimed. It is thought that Ru gives rise to a significantly weaker chemical interaction with Pt in comparison with Sn, Ti and Nb, since Pt and Ru have nearly similar electronegativity values of 2.22 and 2.11, respectively [30]. Thus, the catalytic promotion exerted by Ru is more likely attributable to a bifunctional mechanism [32] rather than to an electronic effect.

The present data seem to account for a definite role of PWA in increasing the electron density on Pd sites as compared to H₂SO₄. From a qualitative point of view, the resulting electronic effect is similar to that produced by Sn, Ti and Nb on Pt sites. Accordingly, the electrochemical oxidation of CO and methanol is enhanced under these conditions.

In the light of the present results, however, it appears difficult to attribute the observed promoting behaviour to the PWA electrolyte itself or to the presence of tungsten sites associated with the Pd surface. Our XPS data do not clearly identify phosphorus atoms on the surface which could unambiguously suggest the presence of the whole Keggin structure, PW₁₂O₄₀³⁻. On the other hand, the W/P atomic ratio in the compound could explain, even in the presence of adsorbed heteropolyanions on the surface, the fact that P is not easily detected in the XP spectra. Concerning the possible role of tungsten in determining a promoting effect on the reaction, it should be noted that this element has been claimed to promote Pt in different electrocatalytic reactions, including methanol oxidation and oxygen reduction [5, 33, 34]. However, the increased oxygen content of the PWA-tested sample with respect to the untested electrode, not accompanied by a significant oxidation of the Pd surface or PTFE binder, would suggest that the whole Keggin structure, and not single W atoms, should be present on the electrode surface. It was previously shown [22] that liquid-phase oxidation of CO in HPA is enhanced in presence of partially reduced Pd particles in solution. It is quite likely that the catalytic properties of this system towards CO oxidation are retained during electrochemical operation.

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