

SHORT COMMUNICATION

ELECTRODESORPTION SPECTRA OF RESIDUES FORMED ON ELECTROCHEMICALLY MODIFIED POLYCRYSTALLINE PLATINUM FROM CARBON DIOXIDE, FORMIC ACID, METHANOL AND ETHYLENE GLYCOL ADSORPTION*

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Reduced carbon dioxide has been reported as either an intermediate or a poison in electrooxidation reactions of various organic fuels. Two different adsorbed intermediates were postulated to account for the voltammetric multiplicity of reduced carbon dioxide [1], formic acid [2], methanol [3, 4] and ethylene glycol [5, 6] electrooxidation reactions on polycrystalline platinum both in acid and base electrolyte. The characteristics of these reactions depend considerably on the electrolyte composition and on the parameters determining the potential perturbation program. Despite data previously reported the influence of the crystallographic plane on the kinetic of these reactions was investigated only for methanol [7] and formic acid electrooxidation [8] in acid electrolyte. These results however, were obtained under organic fuel readsorption from the bulk of the solution masking the true electrodesorption spectra of the adsorbed residues.

This preliminary report attempts to correlate the electrodesorption characteristics of adsorbed residues from those substances resulting on electrochemically modified polycrystalline platinum electrodes from acid and base solution, without interference of readsorption of the initial reactant from the electrolyte solution. This was accomplished by using the micro flux cell electrochemical technique [3]. The modifications of polycrystalline platinum imply reconstruction and faceting processes yielding two different types of electrode surface topographies [9]. These electrodes were recently tested in the electrooxidation of adsorbed CO in both acid and base electrolyte [10].

The electrochemically modified polycrystalline platinum electrodes, denoted either as Type I or Type II electrodes, respectively, were prepared from polycrystalline platinum wires (J. Matthey Chem. Co., 0.12 cm² apparent area) immersed in either 1 M H₂SO₄ or 1 M HClO₄ by applying a symmetric repetitive square wave potential program (period 0.2 ms) during 5 min between 0.75 and 1.45 V (*vs rhe*) following the technique recently described [11]. Electrodes of Type II were prepared by using the same

potential perturbation program during 10 min in the 0.1–1.45 V range [11]. In both cases, the changes of the platinum polycrystalline surface were accomplished with the minimum change in charge compatible with the corresponding surface atom rearrangements.

The voltammograms run with Type I electrodes at 0.1 V s⁻¹ both in 1 M H₂SO₄ and 0.05 M HClO₄ in the potential range of the electroadsorption/electrodesorption of H-adatoms are very similar to those reported for a Pt(111) single crystal surface after it has been cycled at a relatively low scan rate a few times through the anodic oxide region [12, 13]. Similar voltammetric profiles run with Type II electrodes exhibit closely the characteristics described in the literature for Pt(100) single crystal electrodes [12–15]. The characteristics and stability of Type I and Type II electrodes were tested by checking systematically the H-adatom electroadsorption/electrodesorption voltammograms in acid on different electrodes before and after the residue electrooxidation reactions. Type I and Type II electrodes also exhibit different electrodesorption spectra of *upd* copper (Fig. 1). The corresponding

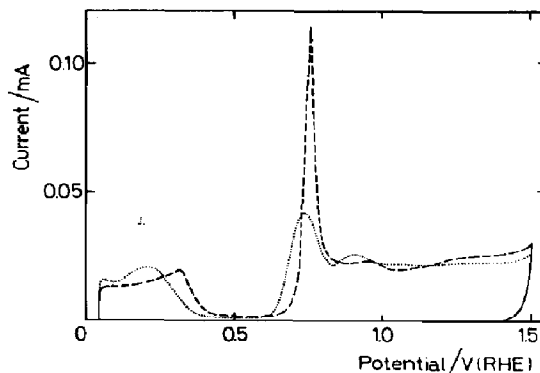


Fig. 1. Voltammograms corresponding to *upd* of copper on Type I (---) and Type II (···) platinum electrodes. Adsorption potential $E_{ad} = 0.05$ V, adsorption time 10 s, sweep rate $v = 0.1$ V s⁻¹; 0.05 M HClO₄ + 10⁻⁴ M Cu(ClO₄)₂; 30°C.

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voltammograms depend not only on the type of electrode surface but also to a large extent on the solution composition, adsorption potential and adsorption time. This makes difficult the direct comparison of data shown in Fig. 1 with those already reported in the literature [14-17].

Electrolyte solutions were chosen either to minimize (0.05 M HClO₄) or to enhance (1 M H₂SO₄) the anion adsorption influence. Experiments were also made in 1 M KOH. Runs were made in the 0-70°C range.

Carbon dioxide is the reaction product from the electrooxidation of the different residues in acid electrolyte. The electrodesorption of the residue produced in the adsorption of CO₂ on both Type I and Type II electrodes (Fig. 2) depends on the electrolyte composition and platinum surface structure. For a constant composition (0.05 M HClO₄) and adsorption conditions, the electrooxidation reaction at Type II

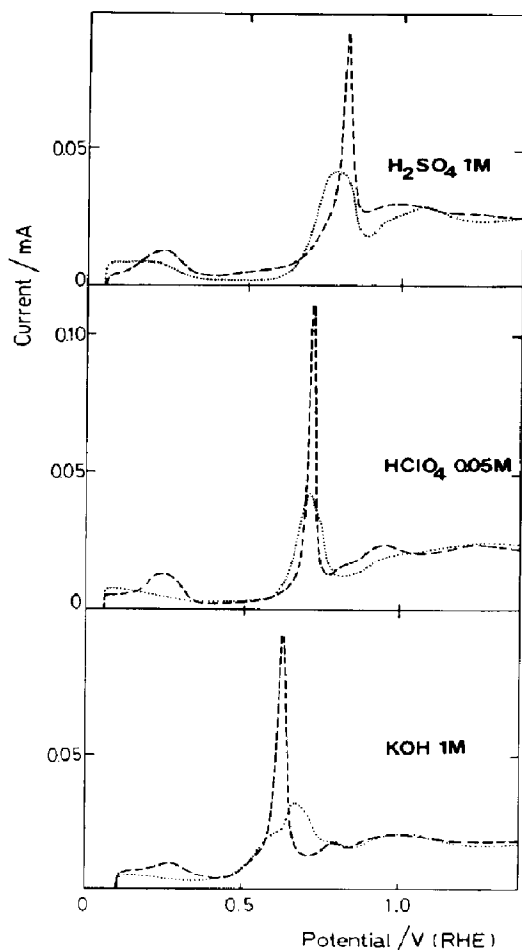


Fig. 2. Voltammograms of reduced CO₂ electrooxidation in different electrolytes on Type I (---) and Type II (···) platinum electrodes. $E_{ad} = 0.05$ V; $t_{ad} = 120$ s; $v = 0.1$ V s⁻¹; 25°C.

electrodes occurs at potentials lower than at Type I electrodes. The reaction in the latter exhibits an anodic peak sharper than in the former case. The corresponding current peak multiplicity in polycrystalline platinum involves a considerable contribution of the different faces. The same conclusion is arrived at 1 M H₂SO₄, where the strong influence of HSO₄⁻ ion adsorption is evident by producing equally in Type II and Type I electrodes a broadening of peak currents and a shift of the overall processes towards more positive potential values (Fig. 2). In any case, the charge involved is nearly the same for Type I, Type II and polycrystalline electrodes, and nearly independent of the solution composition, provided that comparable switching potentials and potential sweep rates (v) are chosen.

The voltammograms obtained for the electrooxidation of residues adsorbed on platinum from ethylene glycol, methanol and formic acid in the absence of readsorption (Fig. 3) are nearly the same. This indicates that independently of the initial reactant, closely similar residues are poisoning the electrode surface on both Type I and Type II electrodes. Similarly, the existence of the adsorbed residues on platinum is compatible with an appreciable surface coverage degree by H-adatoms. Both in Type I and Type II electrodes, however, the presence of the electroadsorbed residue changes the H-electrodesorption spectra to a single broad peak that is shifted towards lower potentials for Type I electrodes, and in the opposite direction for Type II electrodes. This can be interpreted as a tendency to homogenize the H-adatom metal surface bond caused by the organic residue, probably by inducing a surface rearrangement. In principle, the peak multiplicity resulting from electrodesorption of residues adsorbed on platinum from CO₂, methanol, formic acid and ethylene glycol can be attributed to the contribution of different faces of the polycrystalline platinum electrodes. These contributions, however, are influenced by anion adsorption. The common features of the electrodesorption spectra, observed in the 0-70°C range, support the idea that the same kind of adsorbed residue is formed at the platinum surface from either reduced CO₂, formic acid, methanol or ethylene glycol, as suggested in previous works [1, 4, 6, 18].

Distinguishable electrodesorption spectra of the various residues on both Type I and Type II electrodes are also observed in 1 M KOH (Fig. 4). The product of the overall reaction is CO₃²⁻ ion from methanol and formic acid, and oxalate ion from ethylene glycol. In base electrolyte, the current peak potential at the Type I electrode becomes lower than that of the Type II electrode.

The multiplicity of peaks can be produced either by the occurrence of different adsorbed species, as it is the case of bridge and linear adsorbed CO on platinum already proposed for CO electrooxidation in acid [19, 20], or by contributions of different crystallographic planes remaining both in the Type I and Type II electrodes. The number of electrons per adsorption sites obtained from the different electrodesorption spectra reported in this work as well as that from CO electroadsorption is comprised between 1.8 and 2.0. It suggests that different stable-bonded CO-type species are predominantly involved in these processes [21-23].

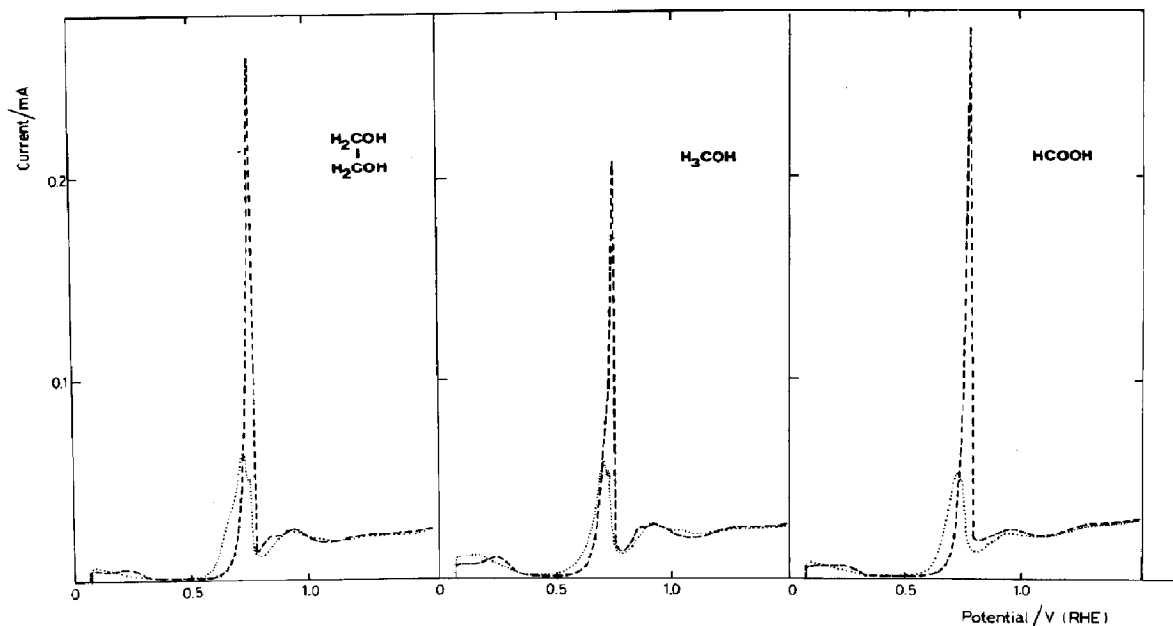


Fig. 3. Voltammograms for the electrooxidation in 0.05 M HClO_4 of residues adsorbed on platinum from different substances. Type I (---) and Type II (···) platinum electrodes. ($E_{\text{ad}}^{\text{ethylene glycol}} = 0.450$ V, ($E_{\text{ad}}^{\text{methanol}} = 0.525$ V and ($E_{\text{ad}}^{\text{formic acid}} = 0.3$ V; $t_{\text{ad}} = 1$ min; $v = 0.1$ V s^{-1} ; 25°C).

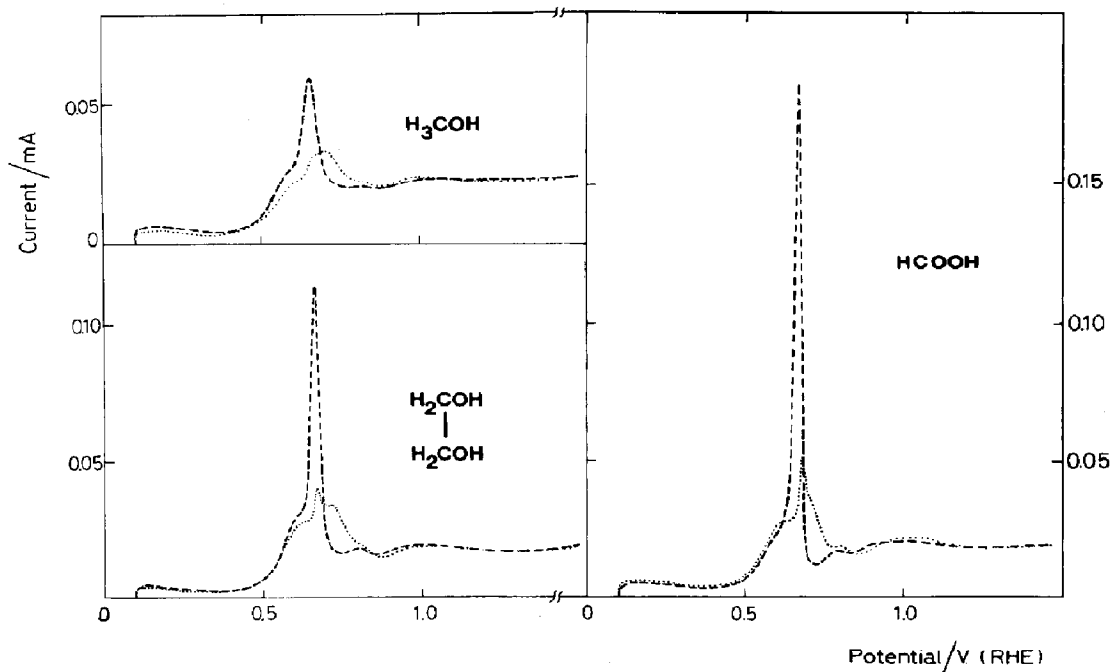


Fig. 4. Voltammograms for the electrooxidation in 1 M KOH of residues adsorbed on platinum from different substances. Type I (---) and Type II (···) platinum electrodes. ($E_{\text{ad}}^{\text{formic acid}} = 0.3$ V; $t_{\text{ad}} = 1$ min. Residue adsorption was previously made in 0.05 M HClO_4 (flux cell); 25°C).

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