

Preparation and catalytic efficiency of mixed noble metal catalysts on electrochemically activated carbon fibre supports

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Mixed noble metal catalytic systems were prepared on electrochemically activated PAN-based carbon fibre supports through a procedure of repetitive cation exchange between the acidic ($-\text{COOH}$ and $-\text{OH}$) groups of the electrooxidized carbon surface and noble metal salts and subsequent cathodic reduction of the exchanged noble metal ions to the metallic state.

The whole investigation was carried out for the binary system Ag–Pd. The catalytic efficiency of palladium deposited on silver is more pronounced compared to a Pd-deposition obtained after only one Pd^{2+} -exchange procedure and subsequent cathodic reduction, whereas an inhibition of the catalytic activity of palladium is noticed when it is covered by silver deposition. The catalytic efficiency of the obtained mixed noble metal catalysts was studied by means of hydrogen-adsorption and absorption profiles in H_2SO_4 , the electroreduction of nitrobenzene in aqueous methanolic H_2SO_4 solutions and the hydrogenation reaction of nitrobenzene to aniline in methanolic solutions. The study was completed by impedance spectroscopic measurements at the potential of hydrogen evolution in H_2SO_4 solutions.

Mixed Ag–Pd systems are even more stable than double Pd–Pd depositions on activated carbon fibre supports, as shown by the fact that they retain their mechanical stability and catalytic activity even after prolonged storage in aqueous or methanolic solutions, as well as after ultrasonic treatment.

1. Introduction

Recently the ion-exchange properties of activated carbon have been the object of significant interest, both theoretical and practical [1, 2]. Compared to many other ion-exchanging materials, both synthetic and mineral, activated carbons exhibit a number of advantages. Their specific ion-exchange properties may be readily tailored in the desired direction and their ion-exchange capacity may also be controlled. Additionally, activated carbon shows high chemical resistance to aggressive solutions. To create the ion-exchange properties, as well as to develop them in the desired direction, the carbon surface is usually chemically modified. This treatment consists in incorporating different heteroatoms into the surface with simultaneous chemical bonding of these atoms onto the carbon lattice. Carbon with oxygen-containing functional groups are of particular importance. For technological and economic reasons oxidation of carbon with nitric acid, sodium hypochlorite, hydrogen peroxide or air is usually recommended. In this way a carbon of ion-exchange capacity of 2–3 meq g^{-1} is usually obtained.

The use of each of the above oxidants is associated, however, with certain disadvantages. Oxidation with nitric acid, for instance, gives a suitably rigorous surface oxidation, but also produces a large concentra-

tion of humins on the oxidized carbon surface. These substances are also formed in the case of other oxidants, but usually in smaller amounts. The removal of these substances (which may contaminate the solutions during the use of the carbon as an ion exchanger) from carbon usually requires a complex treatment.

Very satisfactory results for ion-exchange are obtained by electrochemical oxidation of carbons, especially of highly oriented carbon fibres.

The anodic oxidation of graphitic materials in aqueous solutions creates surface oxides and also three-dimensional defect oxides, consisting mainly of carboxylic ($-\text{COOH}$) and phenolic ($-\text{OH}$) groups [3–8].

Carbon fibres are characterized by favourable mechanical properties and a high surface area; graphite-like highly oriented fibres are, in addition, good electronic conductors. It has been demonstrated that custom-tailored surface groups of acidic character ($-\text{COOH}$ and $-\text{OH}$) on carbon fibres can be electrochemically obtained by choice of potential–current profiles and electrolytic solutions. The total amount of $-\text{COOH}$ and $-\text{OH}$ groups, as well as the partial quantities of the groups, can be determined by a combination of simple chemical and electrochemical reactions. For these determinations very small quantities of carbon fibres are required [9].

These hydrophilic surface functional groups play an important role in the preparation and stabilization of highly dispersed metals on carbon fibres. By careful control of the electrochemical oxidation process and, most effectively, by discontinuous repetitive anodic oxidation and cathodic reduction of highly crystalline fibres in selected electrolytic solutions, layers of an activated carbon-like material can be obtained on a 'backbone' of still unreacted 'fibre core'. These fibres supply excellent mechanical stability and electronic conductivity. The electrochemical surface oxidation should be carefully controlled to avoid oxidation, i.e. damage to the fibre core.

Fibre damage is a serious problem when thick layers of oxides are required on highly oriented fibres, i.e. on fibres that are able to undergo intercalation reactions. Moreover, surface oxidation of polyacrylonitrile (PAN)-based highly oriented fibres requires fairly drastic conditions because of the 'onion peel' morphology basal planes that have to be attacked.

Surface oxides prepared by anodic oxidation of carbon fibres in dilute neutral aqueous media are characterized by a high cation exchange capacity of about 2.5 meq g^{-1} [10]. Graphite fibre-based cation exchangers have the additional advantage of considerable electronic conductivity.

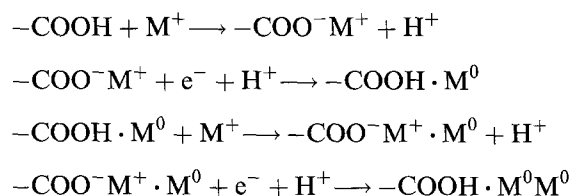
It is the combination of these properties which offers a unique range of potential applications. In particular, surface-oxidized graphite fibres are an interesting basis for all sorts of further chemically modified electrodes [11, 12].

The cation exchange capacity of surface oxides on graphite-like highly oriented PAN-based carbon fibres is a very important property for their suitability as catalyst supports. Loading of electrochemically activated carbon layers with noble metal cations via ion-exchange followed by an electrochemical reduction yields noble metal clusters on the carbon support. Control of the electrochemical reduction current density allows the rates of nucleation and crystal growth and, hence, the catalytic activity of the noble metal to be influenced. Pulse reduction at high current density yields many small metal clusters, whereas reduction at low current density yields fewer, but larger, crystals.

The spatial distribution, the number and the size of noble metal clusters can be adjusted within wide limits by the thickness of the activated carbon layer, by the concentration of the noble metal cations offered for exchange and by the conditions of the electrochemical reduction process, respectively. In particular, noble metal cluster 'peels' of controlled thickness can be fabricated on the surface of the carbon fibres, thus avoiding noble metal wastage at sites which are not easily accessible by reactants.

A further chance to control the distribution of noble metals on carbon fibres is given by the fact that the cation-exchange can be repeated after electrochemical reduction, i.e. the cation-exchanger can be reactivated by electrochemical reduction according

to the scheme:



By repeated exchange and electrochemical reduction very thin but compact catalytic layers can be prepared.

As the cation exchange capacity of the oxide layer is the most important property for its suitability as a catalyst support, the amount of Ag^+ taken up under standard conditions is used as a 'quality criterion'. Ag^+ was chosen as a model ion because it has very high cation-exchange selectivity for electrochemically activated PAN-based carbon fibres (high value of $\text{Ag}^+ - \text{H}^+$ exchange constant) and because it can be easily detected by various instrumental and analytical techniques.

The amount of exchanged Ag^+ can be also estimated from the peak area of the cathodic (reduction) peak. This peak is not an 'ordinary' diffusion-controlled peak, where the peak current increases with the square root of the sweep rate. It is a quantitative reduction of a surface component and, hence, the peak current increases linearly with the sweep

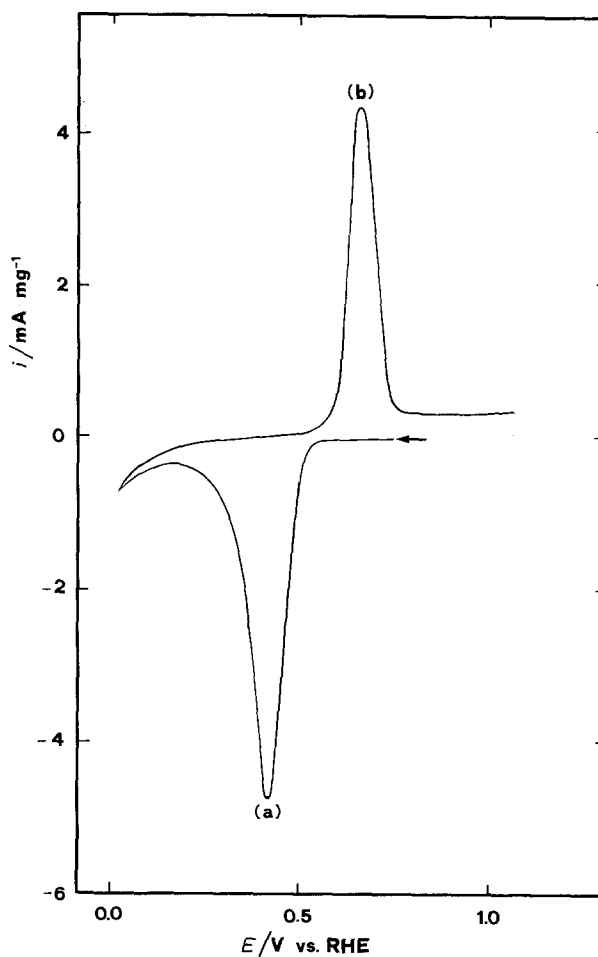


Fig. 1. Cyclic voltammogram ($u = 10 \text{ mV s}^{-1}$) of Ag^+ -loaded electrochemically activated carbon fibres in $0.5 \text{ M H}_2\text{SO}_4$.

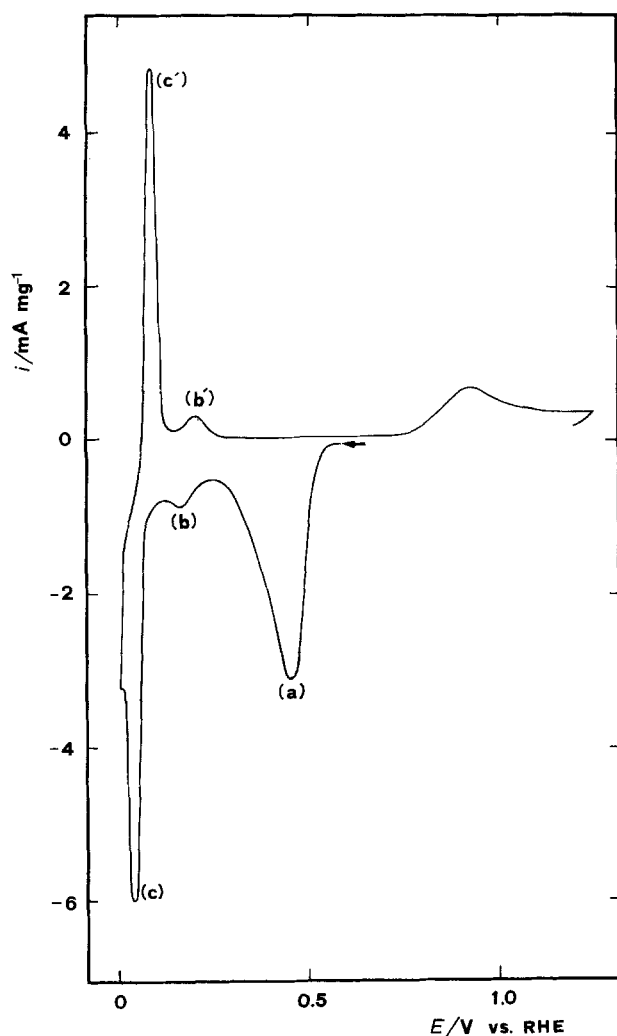
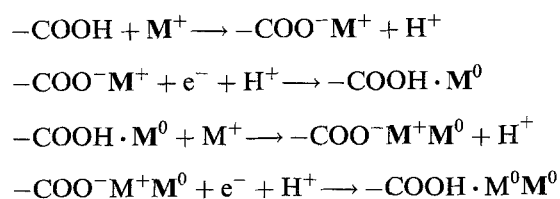


Fig. 2. Cyclic voltammogram ($u = 10 \text{ mV s}^{-1}$) of Pd^{2+} -loaded electrochemically activated carbon fibres in $0.5 \text{ M H}_2\text{SO}_4$

rate. The peak area corresponds to the electrochemically reducible fraction of exchanged Ag^+ and hence must be regarded as the lower limit of the total Ag^+ uptake. The cathodic current peak of the reduction of Ag^+ to metallic silver (Ag^0) is followed by the reduction peak of the oxide layer. In the anodic half cycle, the metallic silver is reoxidized to Ag^+ , from which metallic silver (Ag^0) can be redeposited, but at $\sim 150 \text{ mV}$ more positive potential than in the first cathodic half cycle. This potential difference is caused by the stabilization of the Ag^+ complexed by the cation exchanger ($-\text{COO}^- \text{Ag}^+$) in comparison to free Ag^+ (in the interfacial region), which is predominant in the second and following cycles [7].

In this paper we describe the possibility of preparing mixed metal catalysts on electrochemically activated carbon fibre supports, according to the scheme:



The investigation was carried out mainly for the binary system Ag-Pd. The catalytic efficiency of the

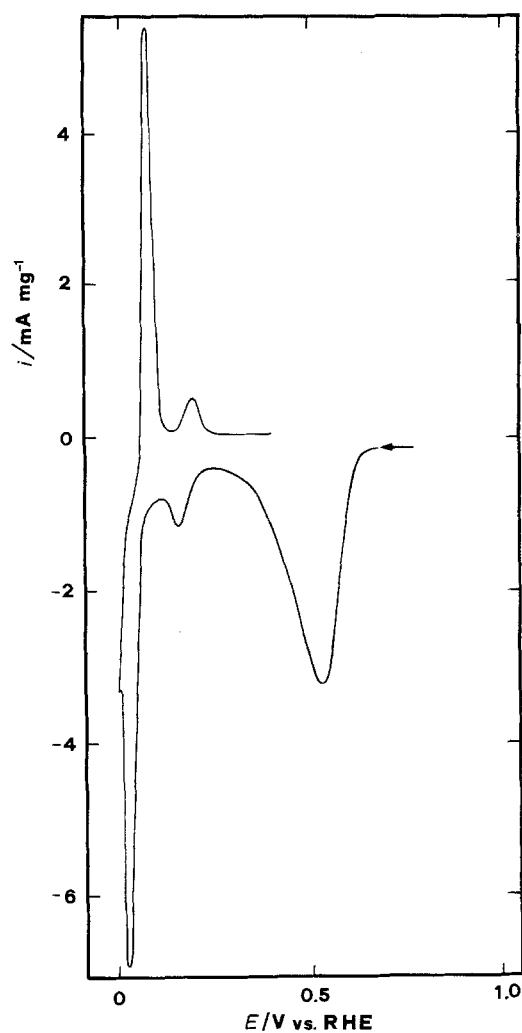


Fig. 3. Cyclic voltammogram ($u = 10 \text{ mV s}^{-1}$) of a Ag-Pd system on electrochemically activated carbon fibres in $0.5 \text{ M H}_2\text{SO}_4$.

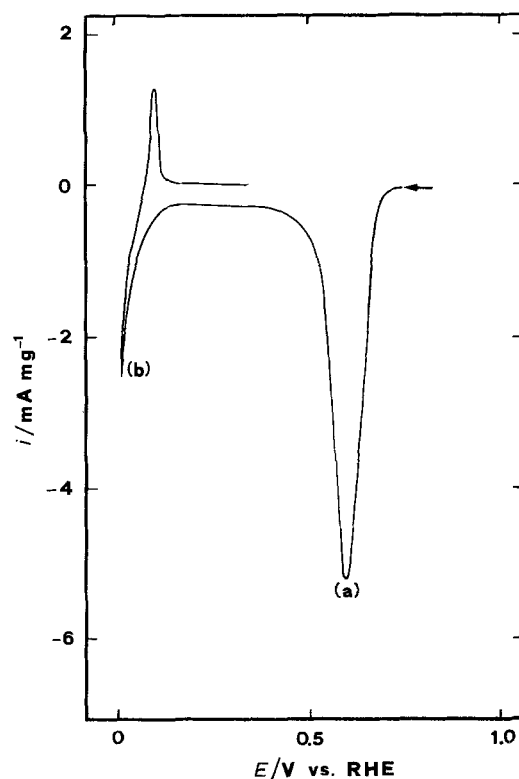


Fig. 4. Cyclic voltammogram ($u = 10 \text{ mV s}^{-1}$) of a Pd-Ag system on electrochemically activated carbon fibres in $0.5 \text{ M H}_2\text{SO}_4$.

mixed noble metal catalysts was studied by means of H-adsorption and absorption profiles, the electroreduction of nitrobenzene and the hydrogenation of nitrobenzene to aniline in methanolic solutions.

2. Experimental details

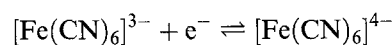
The PAN-based carbon fibres (Celion GY-70) used in this study were the product of BASF-Celanese Corporation (USA). The fibres were pretreated with methanol in an ultrasonic bath for 1 min. Electrochemical activation of the carbon fibres was performed by potentiostatic double pulse application in 0.5 M Na₂SO₄, with $E_{\text{ox}} = 2.3$ V vs SCE, $E_{\text{red}} = -0.3$ V, $t_{\text{ox}} = 4.5$ min, $t_{\text{red}} = 0.75$ min, $t_{\text{total}} = 6$ min.

Potentiostatic square wave pulses were applied through a double pulse control generator from Bank-Elektronik, extended by a Biomation waveform recorder model 805 and a VC 6025 digital storage oscilloscope from Hitachi.

Cyclic voltammetric experiments were carried out with a setup from Bank-Elektronik, consisting of a Wenking standard potentiostat model ST 72 and a Wenking voltage scan generator model VSG 72. Current-potential curves were obtained on a Servogor X-Y 733 recorder from BBC Goerz.

Current densities are expressed per mg of bundles of carbon fibres (bundle length 2.5 cm, about 400 fibres with a diameter of 7 μm). The effective electrode area of 1 mg bare or electrochemically activated car-

bon fibres was determined on the basis of the peak currents of the reversible reaction



and was found to be 1.7 cm² and 6.8 cm², respectively.

Impedance measurements were performed with a system consisting of a potentiostat (Jaissle IMP 80, 10 ± 10 v, 0.5 A) and a lock-in amplifier (EG&G Parc model 5210), connected to a computer (AT Acer 910). Frequency sweeps extended from 10⁵ Hz to 0.5 Hz using a sinusoidal perturbation signal of 7 mV peak to peak. High frequency measurements were obtained using a resistor of known value placed in series with the counter electrode.

Cation-exchange was performed by dipping the electrochemically activated carbon fibres in 0.3 M aqueous AgNO₃ or Pd(NO₃)₂ solutions for 1 h and subsequent washing with water.

All electrochemical measurements were carried out at 25°C.

3. Results and discussion

Figure 1 shows a typical cyclic voltammogram of Ag⁺-loaded activated carbon fibres in a 0.5 M H₂SO₄ solution. Peak 'a' is due to the reduction of Ag⁺ to Ag⁰, while in peak 'b' Ag⁰ is reoxidized to Ag⁺.

In Fig. 2 the cyclic voltammogram of the Pd²⁺-exchanged electrooxidized carbon fibres is illustrated also in 0.5 M H₂SO₄ solution. After the cathodic

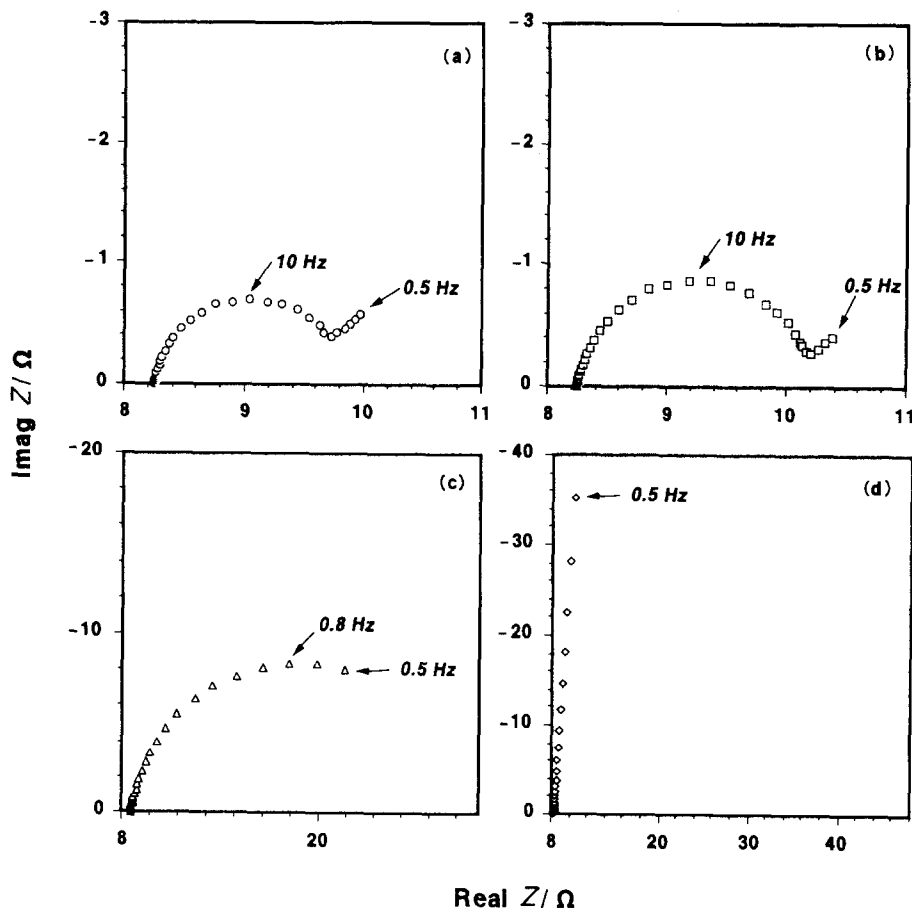


Fig. 5. Impedance spectra of noble metal systems on electrochemically activated carbon fibres (1 mg) at -50 mV vs RHE in 0.5 M H₂SO₄. (a) Pd-Pd, (b) Ag-Pd, (c) Pd-Ag and (d) Ag-Ag.

peak a, corresponding to the reduction of Pd^{2+} to Pd^0 , the characteristic reversible peaks for H-adsorption (b, b') and H-absorption (c, c') appear.

In order to obtain a mixed Ag–Pd catalytic system, Ag^+ was first exchanged on the activated carbon fibres and then cathodically reduced by stopping the potential scanning at 0.1 V vs RHE (Fig. 1). On such Ag-modified carbon fibres, Pd^{2+} was introduced by ion-exchange. The cyclic voltammogram of the obtained binary system is given in Fig. 3. As it is shown in this figure, the characteristic behaviour of palladium in H_2SO_4 solutions is observed on the mixed Ag–Pd system, while the H-adsorption and absorption peaks are even more pronounced than on the simple Pd-modified electrodes.

When palladium is first deposited on the oxidized carbon fibres, by ion-exchange and subsequent cathodic reduction through potential scanning till 0.25 V vs RHE (Fig. 2), and the Ag^+ -exchange follows, the obtained system shows the characteristic reduction peak of Ag^+ to Ag^0 (Fig. 4, peak a), which is followed by a hydrogen-evolution current (Fig. 4, peak b), but the characteristic H-adsorption and absorption profiles of the Pd-sublayer are not observed. This means that the deposition of Ag on Pd inhibits the appearance of the characteristic palladium behaviour.

After the electrodisolution of Ag^0 to Ag^+ on the mixed Pd–Ag systems, the H-adsorption and absorption peaks appear again and are even more pronounced than those on the simple Pd-modified electrodes, indicating a reactivation of the Pd-sublayer.

The inhibition of the catalytic activity of palladium on the mixed Pd–Ag systems is not only obvious from the absence of the H-adsorption and absorption profiles, but also from the fact that several electrochemical reactions, which take place on Pd-modified carbon fibre electrodes, are not performed on the Pd–Ag-modified carbon fibre electrodes, e.g. the electro-oxidation of formic acid.

The catalytic efficiency of palladium deposited on silver as well as the inhibition of the catalytic activity of palladium by silver coverage were investigated by means of impedance spectroscopy.

In order to receive comparable impedance spectroscopic data, the behaviour of double Ag–Ag and Pd–Pd depositions and of mixed Ag–Pd and Pd–Ag depositions on activated carbon fibres was studied in 0.5 M H_2SO_4 solutions at -50 mV vs RHE, i.e. at a potential where hydrogen evolution takes place on palladium electrodes. As shown in Fig. 5, slightly depressed semicircles were obtained for Pd-containing electrodes, where a faradaic process (i.e. hydrogen evolution) occurs, whereas in the case of the silver electrodes, on which such a process is absent, a simple capacitive behaviour was observed.

From the impedance data the values of R_{sol} , α , Q , C_0 and R_{ct} (charge transfer resistance) were estimated according to the following equation [13]:

$$Z = Z' + iZ'' \quad (1)$$

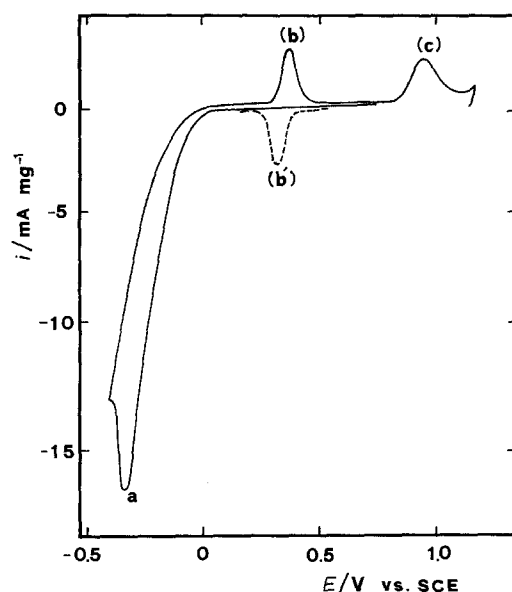


Fig. 6. Cyclic voltammogram ($u = 10 \text{ mV s}^{-1}$) of $\text{C}_6\text{H}_5\text{NO}_2$ ($c = 4 \times 10^{-2} \text{ M}$) on Ag–Pd modified carbon fibre electrodes in 1.5 M H_2SO_4 (MeOH 30% v/v).

where

$$Z' = R_{\text{sol}} + \frac{R_{\text{ct}}[1 + R_{\text{ct}}Q^{-1}\omega^{(1-\alpha)}\sin(\alpha\pi/2)]}{1 + [R_{\text{ct}}Q^{-1}\omega^{(1-\alpha)}]^2 + 2R_{\text{ct}}Q^{-1}\omega^{(1-\alpha)}\sin(\alpha\pi/2)} \quad (2)$$

and

$$Z'' = -\frac{R_{\text{ct}}^2Q^{-1}\omega^{(1-\alpha)}\cos(\alpha\pi/2)}{1 + [R_{\text{ct}}Q^{-1}\omega^{(1-\alpha)}]^2 + 2R_{\text{ct}}Q^{-1}\omega^{(1-\alpha)}\sin(\alpha\pi/2)} \quad (3)$$

and the equation

$$Q^{-1} = C_0^{1-\alpha}[R_{\text{sol}}^{-1} + R_{\text{ct}}^{-1}]^\alpha \quad (4)$$

The values obtained are listed in Table 1.

The small values of the charge transfer resistance for the Pd–Pd and Ag–Pd systems indicate the strong electrocatalytic activity of these electrodes toward the hydrogen evolution reaction (h.e.r.).

The catalytic effectiveness of the prepared mixed noble metal systems was then tested for the electrochemical reduction of nitrobenzene in relatively concentrated H_2SO_4 solutions. Nitrobenzene is not reduced on the Pd–Ag systems up to the potential of hydrogen evolution, whereas its electrochemical

Table 1. Results obtained from analysis of impedance data for noble metal-catalysts on electrochemically activated carbon fibres ($m = 1 \text{ mg}$)

System	Pd–Pd	Ag–Pd	Pd–Ag	Ag–Ag
R_{sol}/Ω	8.25	8.25	8.55	8.50
α	0.09	0.095	0.11	0.04
$Q/\Omega \text{ s}^{-(1-\alpha)}$	67.83	78.25	80.58	105.8
C_0/mF	10	8.5	9	8.5
R_{ct}/Ω	1.6	2	20	–

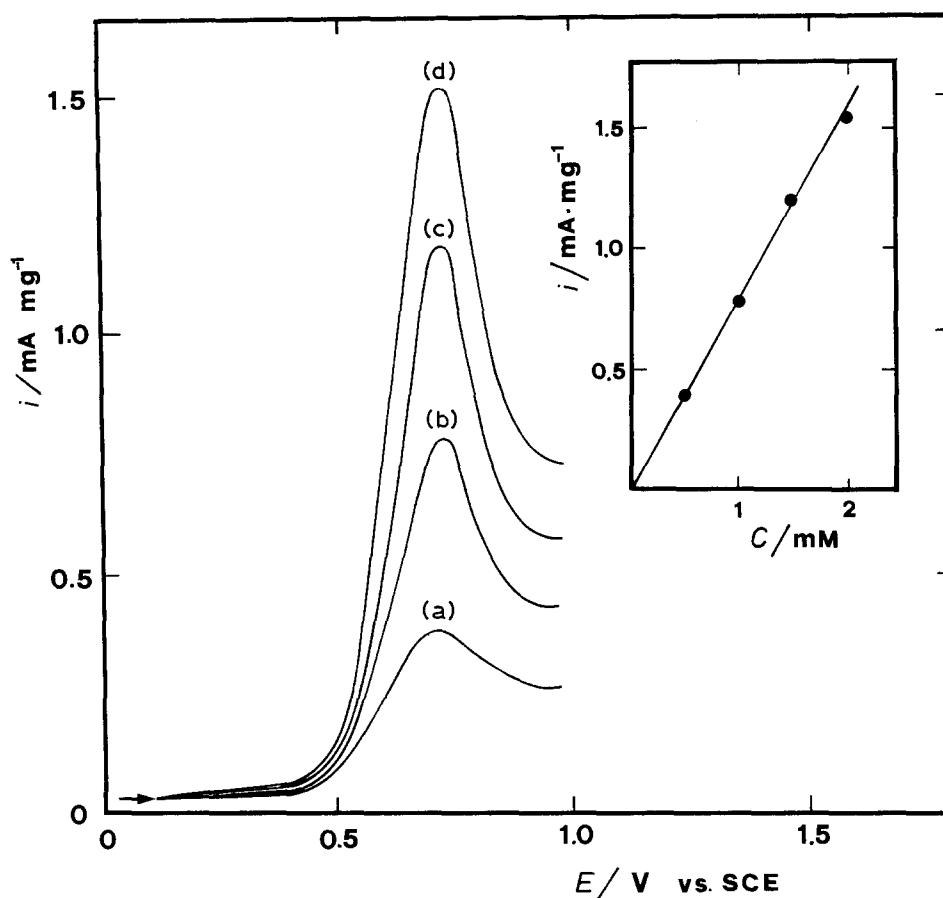
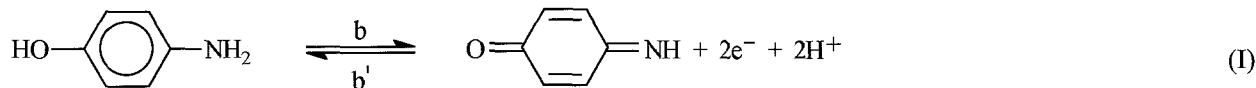


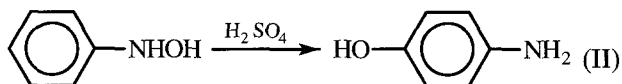
Fig. 7. Anodic parts of the cyclic voltammograms ($u = 100 \text{ mV s}^{-1}$) of aniline on pristine carbon fibre electrodes in 20% v/v MeOH–H₂O solution with pH 7. c_{aniline} : (a) $5 \times 10^{-4} \text{ M}$, (b) $1 \times 10^{-3} \text{ M}$, (c) $1.5 \times 10^{-3} \text{ M}$, (d) $2 \times 10^{-3} \text{ M}$. Inset: dependence of i_p on C .

behaviour on the Ag–Pd systems was found to be similar to that on simple Pd-modified fibres [14] and is illustrated in Fig. 6.

Peak a in Fig. 6 is attributed to the reduction of nitrobenzene and the simultaneous reduction of the carbon surface oxide layer. Two reduction products are formed, as indicated from the appearance of two oxidation peaks (b and c) in the reverse potential scan. The first oxidation peak (b) is reversible and corresponds to the oxidation of *p*-aminophenol according to the following scheme:



p-Aminophenol is formed in the H₂SO₄ solution by conversion of the first reduction product of nitrobenzene, i.e. of phenylhydroxylamine:



Increase in the H₂SO₄-concentration favours the above reaction. The attribution of the peak pair b, b' to the oxidation and rereduction of *p*-aminophenol was confirmed by obtaining the cyclic voltammogram of this compound in the same solution.

The second oxidation peak, c, is due to the oxidation of aniline, i.e. the second reduction product of nitrobenzene, as verified by cyclic voltammetry for

this compound under the same experimental conditions.

Owing to its well known ability to adsorb hydrogen, palladium is a good hydrogenation catalyst. Hence, the prepared mixed noble metal systems were also examined as catalysts for hydrogenation of nitrobenzene in methanolic solutions. This reaction took place in a hydrogenation apparatus (Parr, Gerhardt). Nitrobenzene ($c = 0.3 \text{ M}$) was stirred in 500 ml methanol in the presence of 50 mg modified carbon fibres, at 75° C and at a hydrogen pressure of 7 atm for 6 h.

Under these conditions, 60% of the initial nitrobenzene was converted to aniline on the mixed Ag–Pd modified carbon fibre electrodes. A similar result was obtained with the use of double Pd–Pd depositions on the carbon fibre supports, whereas on mixed Pd–Ag systems, aniline was formed only to a very small extent.

The amount of aniline produced was followed on the basis of its electrooxidation in neutral aqueous-methanolic solutions. Aniline was electrooxidized to polyaniline at about 0.8 V vs SCE on pristine carbon fibres in pH 7 aqueous-methanolic solutions (30% v/v MeOH) and the height of the electrooxidation peak for relatively dilute solutions depended linearly on the aniline concentration (Fig. 7).

Although the catalytic efficiency of the double Pd–Pd-depositions is similar to that of the mixed Ag–Pd systems, the latter electrodes have the advantage of a higher mechanical stability. The catalytic activity of these mixed systems remains unchanged, even after prolonged storage in aqueous or methanolic solutions as well as after ultrasonic treatment.

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