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Mechanism of cathodic $PtCl_6^{2-}$ reduction to platinum clusters on electrodes coated with polyvinylpyridinium films

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The electrochemical reduction of $PtCl_6^{2-}$/HCl to Pt^0 is investigated on electrodes coated with anion exchange polymer films. The first step is the cathodic reduction to $PtCl_4^{2-}$. Three possible routes for the reaction $PtCl_4^{2-}$ to Pt^0 are discussed: (i) a second electrochemical step; (ii) $PtCl_4^{2-}$ disproportionation; (iii) reduction by cathodically produced H_2. It is demonstrated that route (i) is normally dominant. The Pt^0 produced has a large surface area. Individual microparticles ('clusters') can be conveniently formed. As expected from the electrochemical mechanism the Pt^0 produced is located at the electrode–coating interface.

1. Introduction

Dispersions of small platinum particles in polymeric matrices are of considerable interest in the field of catalysis. It has been shown, for example, that platinum particles embedded in membranes retain their high activity much longer than platinized platinum [1]. Such dispersions can be prepared by mixing the dispersed metal with the dissolved polymer or by reduction of platinum complexes with $NaBH_4$, N_2H_4, etc. [2]. It has been demonstrated recently that platinum clusters can also be produced in polymer films by electrochemical reduction of platinum complexes. Wrighton and co-workers [3, 4] and Tourillon and Garnier [5] found that in the case of electronically conductive films the platinum clusters are located inside the polymer coatings. This can easily be recognized because the polymer fibres are electronically conducting so that the nucleation process can begin simultaneously throughout the bulk of the polymer. For non-conductive materials, however, nucleation on the conductive support (e.g. glassy carbon, GC) followed by the growth of platinum particles can be expected [6, 7]. This mechanism has been confirmed by Itaya *et al.* [8] for Nafion films on GC electrodes.

The electrodeposition of platinum microparticles into films of poly(vinylpyridine) (PVP) has been described [9, 10]. It was observed that the platinum microparticles are electrodeposited in a three-dimensional array in the polymer matrix. This platinum formation mechanism is remarkable because PVP is an electronic insulator. Electrochemical reduction could proceed inside the membrane if, for instance, dendrite-type platinum fibres grew into the film which makes the electrical contact. Alternatively, the reduction could proceed by a chemical step. It is the purpose of this work to study the reduction of $PtCl_6^{2-}$ on PVP-coated electrodes to obtain a more detailed understanding of these processes.

The reaction considered is the four-electron reduction of $PtCl_6^{2-}$ to Pt^0:

$$PtCl_6^{2-} + 4e \rightarrow Pt^0 + 6Cl^- \qquad (1)$$

This can proceed by either of the following mechanisms:

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(A) Two consecutive electrochemical steps

$$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2Cl^-$$

$$E_0 = 0.68\,V \text{ vs NHE} \qquad (2)$$

$$PtCl_4^{2-} + 2e = Pt^0 + 4Cl^-$$

$$E_0 = 0.73\,V \text{ vs NHE} \qquad (3)$$

(B) An electrochemical two-electron step followed by a disproportionation reaction

$$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2e \qquad (2)$$

$$2PtCl_4^{2-} = PtCl_6^{2-} + Pt^0 + 2Cl^- \qquad (4)$$

(C) An electrochemical step followed by a chemical reaction

$$2H^+ + 2e = H_2 \qquad (5)$$

$$2H_2 + PtCl_6^{2-} = Pt^0 + 4HCl + 2Cl^- \qquad (6)$$

The effect of the concentration of the chloride ions on the reduction of $PtCl_6^{2-}$ was studied by Hubbard and Anson [11]. As expected, an increase in the chloride concentration inhibits Equation 3 in which $4Cl^-$ ions are produced much more strongly than Equation 2 in which only $2Cl^-$ ions are formed. The platinum produced has been shown [12, 13] to consist of conglomerates of small particles. The disproportionation reaction (Equation 4) has been found to proceed at a low rate [14], even at elevated temperatures, suggesting that its contribution should be negligible under the experimental condition of this work.

2. Experimental details: preparation of polymer films

Glassy carbon (Sigri, Meitingen) or platinum cylinders were used to provide a conducting support. The discs of 0.5 cm^2 surface area embedded in Teflon were polished down to 3 μm with a diamond paste. The pyridine groups of poly[(4-vinyl-pyridine)$_{0.83}$-co-(styrene)$_{0.17}$] were quaternized to 55 mol % with *p*-toluene-sulphonic acid methyl ester. The quaternized polymer and 1,3-bis(brommethyl)benzene were dissolved separately in methanol, and the solutions were mixed and then spin-coated onto the glassy carbon disc electrode. The electrode was then heated at 60° C for 1 h for the process of cross-linking to occur. Eventually the remaining free pyridine groups were quaternized with *p*-toluene sulphonic acid methyl ester in water-free methanol at 60° C. This last step was omitted for some of the electrodes, with little noticeable consequence. More details of the experimental procedure were reported recently [7]. In the following the abbreviation PVP is used for the quarternized polymer.

3. Results and discussion

3.1. *Electrochemical reduction of $PtCl_6^{2-}$*

Cyclic voltammograms summarizing the typical behaviour of platinum and GC electrodes are represented in Figs 1 and 2A–C. Starting at positive potentials, a first cathodic current peak is observed at potentials between 0.15 and −0.1 V, depending on the electrode material and the electrolyte. This is not associated with formation of Pt^0. In agreement with Hubbard and Anson [11] we conclude that this cathodic current flow corresponds to the reduction of Pt(IV) to Pt(II) according to Equation 2.

In the absence of the coating this current peak, at the given solution concentration of $PtCl_6^{2-}$ and the given sweep rate, would be $i_p = 30\,\mu A\,cm^{-2}$. The observed Pt(IV) to Pt(II) peak thus corresponds mainly to $PtCl_6^{2-}$ incorporated in the film. Since even 1 M HCl does not replace the $PtCl_6^{2-}$ from the film it may be concluded that specific interactions are effective between the quaternized pyridine groups and the redox anions. This is in agreement with the known properties of soluble pyridinium compounds which act as precipitating agents for platinum complexes [15].

Because of the strong partitioning of the redox ions into the film we cannot predict the effective concentration of Cl^- ions in the films. However, at 1 M HCl the Donnan exclusion principle must have broken down, i.e. the Cl^- concentration should be of the same order of magnitude as in solution. At this concentration one may conclude that the overvoltage of the Pt(IV) to Pt(II) reduction according to Equation 2 is ≈ 0.50 V. With decreasing HCl concentration this current peak shifts to more positive potentials indicating that the cathodic reaction

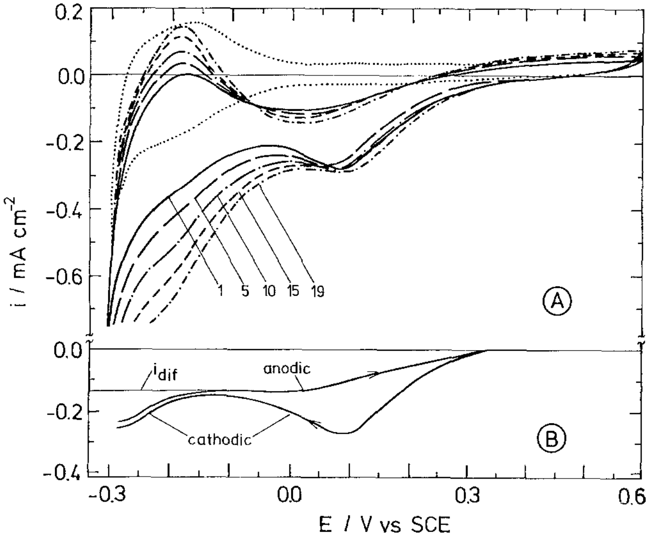

Fig. 1. (A) Selected cyclic voltammograms (numbers 1, 5, 10, . . .) on platinum electrodes coated with PVP films of thickness 0.5 μm. Sweep rate, 0.01 V s^{-1}; electrodes rotated at ω = 73 rad s^{-1}. Electrolyte, 0.1 M HCl + 2 × 10^{-4} M K_2PtCl_6; dotted curve represents absence of the platinate, at the beginning of the experiment. (B) Difference between the curves in the presence (first sweep) and absence of the redox system; i_{dif} is the stationary $PtCl_6^{2-}$ to $PtCl_4^{2-}$ reduction current.

order of chloride differs from zero, as it does with uncoated electrodes [11]. An exact determination of this reaction order would require an accurate knowledge of the Cl^- concentration prevailing in the film.

Note that the position of the Pt(IV to II) peak at a given HCl concentration is not stable. There are several reasons for this. On platinum (Fig. 1A) the overvoltage rises after the first sweep because of the increased Cl^- concentration associated with the reaction (Equation 2) proceeding at the electrode–polymer interface. Eventually, this effect is overcompensated by the increase in the microscopic surface area, leading to an effective reduction of the overvoltage (cf. sweep 19, Fig. 1A). With the glassy carbon electrodes the Pt(IV to II) peaks shift during the experiment by up to 0.3 V to values constituting smaller overvoltages. It turns out that the final stationary current peak position resembles the platinum value in the same electrolyte. Apparently, the overvoltage of the reaction (Equation 2) is smaller on platinum than on GC. The large peak potential shift corresponds to progressive coverage of the GC surface with platinum. This conclusion is in agreement with electron microscopic investigations of the coated electrodes.

When the potential scan is extended to more negative potentials, Pt^0 is formed. As expected from the stoichiometry the rate of Pt^0 formation is again a function of the Cl^- concentration. This is borne out qualitatively by electron micrographs (Fig. 2A–C), in which the platinum particles within the films can be observed as light areas.* Note that, particularly at the larger HCl concentrations, remarkably homogeneously distributed particles of similar size and shape are formed. The reduction of Pt(II) to Pt^0 proceeds at potentials where electrosorption of H on platinum occurs. In all experiments the systematic increase of the cathodic current can be associated with increasing amounts of H adsorbed, i.e. with increasing platinum surface area. As shown in Fig. 1, this parallel process can be analysed independently by omitting the redox ions from the electrolyte.

3.2. *Characterization of the Pt^0 produced*

It turns out that the polymer coating does not reduce the H adsorption charge of a platinum electrode by more than 10–20% (cf. Fig. 1). It may thus be employed to measure the surface of the Pt^0 produced. The evaluation (cf. Table 1) was based on a value of 0.18 mC adsorption charge, Q_H, per 1 cm^2 platinum surface under the PVP film [16]. After subtracting the H adsorption–desorption current from the total current the faradaic process can be isolated, as demon-

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* The platinum particles are located within the organic coatings. Their electron microscopic pictures could still be obtained by using primary electrons of high kinetic energy (10 keV). The pictures appear somewhat blurred, probably because of scattering of the electrons by the organic matrix.

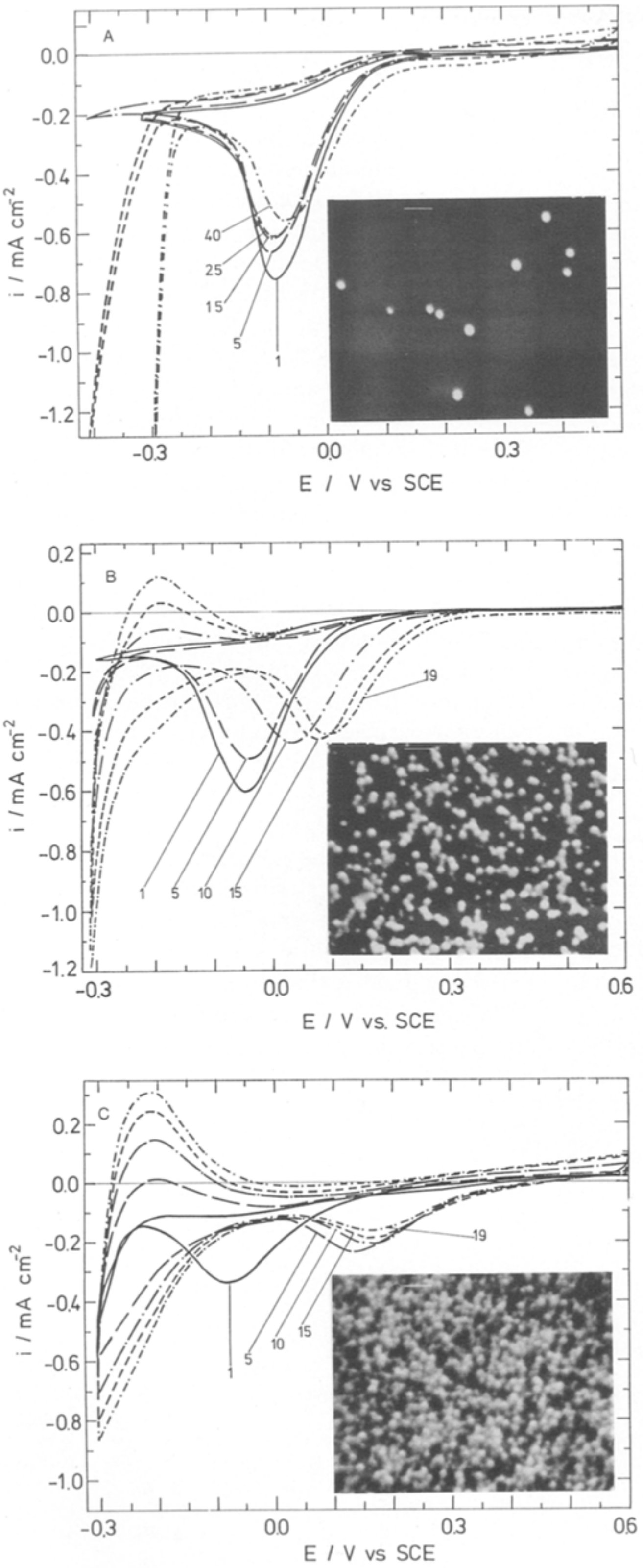

Fig. 2. Selected cyclic voltammograms as in Fig. 1, but on coated glassy carbon electrodes. Background electrolyte: (A) 1 M HCl; (B) 0.1 M HCl; (C) 0.01 M HCl. The photographs were each taken after the 19th sweep. In experiment (A) the sweep was extended to more negative potentials after the 14th sweep. Scale bar in photographs corresponds to 1 μm.

Table 1. Pt^0 formation in 19 cyclic potential scans

C_{HCl} *(mol l^{-1})*	m_{Pt} *(μg cm^{-2})*	A_{Pt} *(from Q_H)*	θ_{Pt} *(from SEM)*
1	3	0.36	7×10^{-3}
0.1	55	20	1×10^{-1}
0.01	110	49	2×10^{-1}

A_{Pt} is the platinum surface area in cm^2 per 1 cm^2 electrode area (glassy carbon).

strated in Figs 1B and 3. This shows more clearly the two current regimes associated with the two reduction steps and the diffusion current, I_{dif}, associated with a stationary flux of $PtCl_6^{2-}$ across the film. The areas under the Pt IV → Pt(II) peaks in Fig. 3 decrease with the HCl concentration because of incomplete ion exchange $PtCl_4^{2-}/PtCl_6^{2-}$ at the positive potentials.

For each potential sweep an amount of Pt^0 characterized by the current integrals $2Q_3 + Q_4$ is formed (cf. Fig. 3C). The total charge used for Pt^0 formation during the cyclic voltammetry experiment is given by

$$Q_{Pt} = \sum_{i=1}^{N} (2Q_{3,i} + Q_{4,i}) \qquad (7)$$

This can be evaluated for each sweep separately which makes the experiment difficult. A constancy of the values of $(2Q_{3,i} + Q_{4,i})$ was assumed, however, for consecutive reduction cycles ($i = 1, 2, 3, \ldots, N$) which enables us to calculate Q_{Pt} by using the value obtained for the last sweep (N). Thus the expression for Q_{Pt} can be written as

$$Q_{Pt} = N(2Q_{3,N} + Q_{4,N}) \qquad (8)$$

Typical values of platinum masses, m_{Pt}, obtained by this method, are included in Table 1 for different HCl concentrations. This table also contains the H adsorption results and results of the analyses of the electron micrographs. One can estimate the 'coverage', θ_{Pt}, of the GC surface from the ratio of the white area to the total area. In some cases the number of particles per unit area can be estimated together with their diameter. A number of conclusions can be derived from these results:

(a) Taking into account m_{Pt} and θ_{Pt} and assuming that the produced Pt^0 forms prisms or cylinders the height of these structures can be estimated. The values are 0.2, 0.25 and 0.25 μm for 1, 0.1, and 0.01 M HCl, respectively. These results are somewhat high because Q_3 and Q_4 tend to increase with increasing sweep number (Equation 7). One may thus conclude that the platinum particles produced are spherical with diameters up to ≈ 0.3 μm. This is in agreement with the observation by SEM at various angles.

(b) For these particles formed in 1 HCl one can estimate the geometrical surface area, assuming a spherical shape. This area can be compared with the area calculated from Q_H. This latter value turns out to be larger than the geometrical surface area by a factor of 10 to 20. Clearly, these particles (Fig. 2A, electron micrograph) are porous. Formation of highly

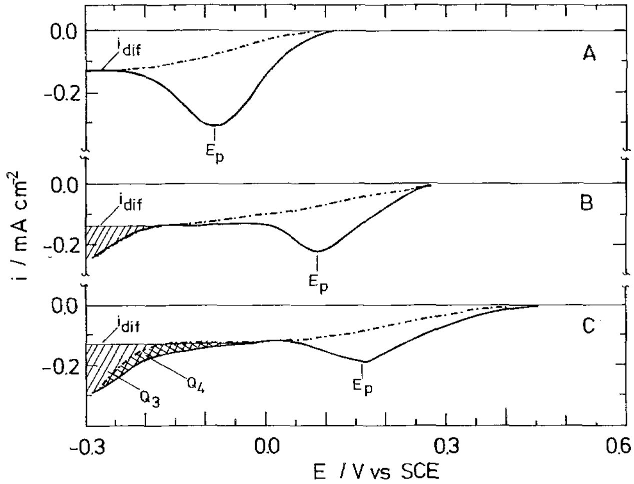

Fig. 3. Differences between the currents of Fig. 2A–C, 19th cycle, and the corresponding currents in the absence of the redox system (cf. Fig. 1B). (A) 1 M HCl + 2×10^{-4} M K_2PtCl_6; (B) 0.1 M HCl + 2×10^{-4} M K_2PtCl_6; (C) 0.01 M HCl + 2×10^{-4} M K_2PtCl_6. Dashed traces, anodic sweeps; full lines, cathodic sweeps.

porous Pt^0 is also indicated by the linear rise of Q_H with the number of cycles in the case of the platinum substrate (Fig. 1), and with the glassy carbon electrodes in the case of larger coverages. All this indicates that the platinum produced has a platinum black-type structure as obtained in the absence of the coating [12, 13]. Comparing A_{Pt} and m_{Pt} (Table 1) the specific surface area of the Pt^0 produced in 1, 0.1 and 0.01 M HCl is 0.12, 0.36 and $0.45\,cm^2\,\mu g^{-1}$, respectively.

3.3. *Contribution of $PtCl_4^{2-}$ disproportionation to Pt^0 formation*

The disproportionation reaction, Equation 4, is of particular interest for the system under consideration because it could lead to particle formation inside the insulating PVP matrix. To determine the rate of this process the GC electrode coated with a PVP film was saturated with $PtCl_4^{2-}$ ions in 0.01 M HCl + 2×10^{-4} M K_2PtCl_4. It was first potentiostatically polarized from open circuit potential to $E = -0.3$ V at a sweep rate of $0.01\,V\,s^{-1}$. Thus platinum nuclei were produced. Then the potentiostat was switched to the open circuit potential measurement mode. The electrode was kept for 24 h in the same solution of $PtCl_4^{2-}$ ions stirred with N_2 bubbles. Finally, the electrode coating was washed carefully, the Q_H was measured for the supporting electrolyte solution and the electrode surface was inspected by SEM.

Using the value of Q^0_{Pt} from the nucleation sweep, the mass of the platinum nuclei, m^0_{Pt}, was estimated. The mass of platinum metal, m^d_{Pt}, formed in the experiment over 24 h was calculated from SEM photographs on the assumption that the platinum clusters are spheres. Knowing the values of m^d_{Pt} and m^0_{Pt} the ratio $\Delta m/\Delta t$, where $\Delta m = m^d_{Pt} - m^0_{Pt}$, was found to be in the range 0.1–$0.4\,\mu g\,cm^{-2}\,h^{-1}$. It may be concluded that the contribution of $PtCl_4^{2-}$ disproportionation to Pt^0 formation in the electrochemical experiments (Figs 1, 2) is less than 1%.

3.4. *Location of the Pt^0 produced on the coated electrode*

All the results and considerations point to the electrochemical reduction mechanism Pt(IV) to Pt(II) to Pt(0) (Equations 2 and 3) as dominating in the process. It is hard to see that the Pt^0 produced would be located anywhere but at the interface between the conducting substrate and the coating. This location in the film was confirmed by ESCA measurements. The ESCA spectra recorded for the electrodes withdrawn from the platinate solution after 19 reduction cycles show only the presence of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ ions on the film surface. The Pt^0 $4f_{7/2}$ peak with a binding energy of 70.9 eV was not detected (Fig. 4).

If the electrode is immersed in 1 M HCl for 15 min and then analysed by ESCA, spectra, as represented in Fig. 5, are obtained. These indicate that $PtCl_6^{2-}$ is extracted more easily than $PtCl_4^{2-}$ from the organic matrix.

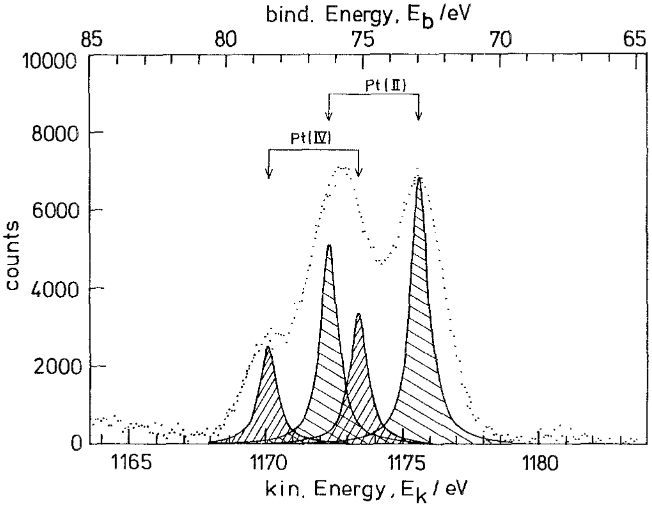

Fig. 4. Typical ESCA results obtained with the electrode of Fig. 2B withdrawn from the electrolyte. The analysis (Lorentz fits) suggests an excess of $PtCl_4^{2-}$ in the film and absence of Pt^0 (E_b = 70.9 eV) near the polymer surface.

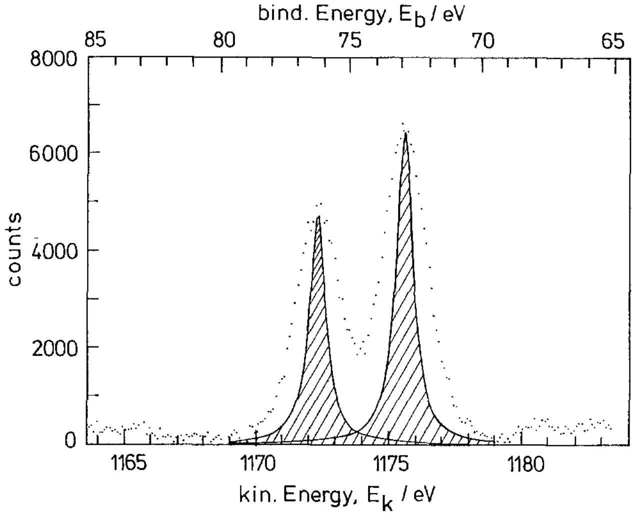

Fig. 5. ESCA spectrum as in Fig. 4, but after washing in 1 M HCl for 15 min. The Lorentz fit indicates that the peaks correspond exclusively to $PtCl_4^{2-}$.

4. Conclusions

Taking into account the above data, the following can be concluded.

1. $PtCl_6^{2-}$ is partitioned strongly into the PVP matrix, even in the presence of 1 M HCl in the electrolyte. It is thus available to the electrochemical reaction at the electrode–polymer interface.
2. Pt^0 formation occurs inside the PVP film; the growth of platinum particles begins at the GC surface.
3. The reduction of $PtCl_6^{2-}$/HCl proceeds in two consecutive electrochemical steps, as on uncoated electrodes. The intermediate, $PtCl_4^{2-}$, is attached more strongly to the PVP matrix than $PtCl_6^{2-}$. There are indications that $PtCl_4^{2-}$ binds particularly strongly to pyridine groups which are not quaternized.
4. The rate of Pt^0 formation increases with the dilution of HCl solution.
5. The true surface area, determined by H adsorption–desorption, is larger than the geometrical surface of the Pt^0 produced. Even individual particles of diameters 0.1–0.3 μm, as characterized by electron microscopy, are found to have roughness factors of 10 to 20.
6. The electrode potential established on platinum in the presence of H_2 is negative enough for the $PtCl_6^{2-}$ to Pt^0 reduction to proceed effectively. Thus, when platinum nuclei are available Equations 5 and 6 can contribute to the Pt^0 formation. We have found that Pt^0 forms when the electrolyte is saturated with H_2 and the electrode is kept at an open circuit. The platinum particles obtained in these preliminary experiments constituted larger aggregates located mainly at the polymer surface. It would appear plausible that, by choosing the right experimental conditions, they could be formed inside the insulating matrix. Our conclusion is, therefore, that the Pt^0 formation observed by Kao *et al.* [9, 10] (see above) proceeds by chemical platinate reduction.

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