

Unusual Voltammetric Behaviour of an Electrochemically Synthesized Conducting Platinum Cluster Compound $K_{1.64}[Pt(C_2O_4)_2]$

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The compound $K_{1.64}[Pt(C_2O_4)_2]$ was electrochemically synthesized on a glassy carbon electrode using both single-potential step and cyclic voltammetry techniques; voltammetric behaviour of the working electrode was changed dramatically with deposition of the conducting material on the surface of the electrode.

For some time now, much attention has been paid to one-dimensional conducting platinum cluster compounds.^{1–3} Various methods, including X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), X-ray diffuse scattering (XDS) and neutron diffuse scattering (NDS) *etc.*, were employed to characterize the structures. The crystal structures of these compounds reveal square-planar monomers stacked together to form a linear chain of Pt atoms. Structural and chemical observations reveal that the platinum atoms are crystallographically identical, indicating that structure does not contain discrete Pt^{2+} and Pt^{4+} sites, hence, they are in a single partial oxidation state. The high, possibly metallic, conductivity exhibited by these mixed-valence materials is attributed to electron delocalization along partially filled, overlapping platinum d_{z^2} orbitals.^{5–8} However, little research has been carried out to investigate the electrochemical properties of these one-dimensional inorganic conducting salts. Their unusual properties such as anisotropic conductivity, linear crystal morphology and partial oxidation state aroused our interest in the course of our study of inorganic one-dimensional conducting materials which have potential applications as electrochemical catalyst, single-crystal ultramicroelectrodes or ultramicroelectrode arrays.

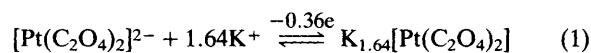
In the present study, $K_{1.64}[Pt(C_2O_4)_2]$ was electrochemically synthesized. This compound is a typical member among the class of inorganic one-dimensional conducting salts, in which the platinum atoms are co-ordinated in a square-planar array to two oxalate ligands.⁴ Potassium tetrachloroplatinate was used as the starting material, and $K_2[Pt(C_2O_4)_2]$ was chemically synthesized by ligand-exchange between $PtCl_4^{2-}$ and $C_2O_4^{2-}$ according to the method of Krogmann.^{8,9} Reaction conditions were adjusted to minimize the solubility of $K_{1.64}[Pt(C_2O_4)_2]$ by addition of K_2SO_4 as a co-ion. Also, K_2SO_4 plays the role of supporting electrolyte during the electrochemical measurements. An excess of $K_2C_2O_4$ was used in order to obtain complete ligand exchange between $C_2O_4^{2-}$ and $PtCl_4^{2-}$, and the concentration ratio of $K_2C_2O_4$ to K_2PtCl_4 was usually $>10:1$.

The precursor, $K_2[Pt(C_2O_4)_2]$, which is moderately soluble in water, can be transformed into the conducting salt $K_{1.64}[Pt(C_2O_4)_2]$ upon oxidation either in the presence of an oxidizing agent⁹ or *via* anodic electrogeneration.¹⁰ The product $K_{1.64}[Pt(C_2O_4)_2]$ is reported to be sparingly soluble in water whereas $K_2[Pt(C_2O_4)_2]$ is moderately soluble.² This feature was exploited in our electrochemical preparation and all experiments were conducted in aqueous medium. The concentrations of $K_2[Pt(C_2O_4)_2]$ typically in the range of *ca.* 10^{-3} mol dm⁻³ was varied to control the amount of conducting material formed on the electrode. For the electrochemical measurements performed in this study, glassy carbon (GC) was used as the working electrode, platinum wire as the counter-electrode and saturated calomel electrode (SCE) as the reference electrode. All potentials were recorded with respect to SCE.

Chronoamperometry was performed with an initial potential of +0.2 V where no Faradaic processes occur and a final potential of +0.7 V. The current response to this single potential step is shown in Fig. 1. The current initially decays owing to depletion, and then, in marked contrast to what is

usually observed, the electrolytic current increases dramatically; at the same time, clearly visible fibrous material,[†] is produced on the surface of working electrode (Fig. 2). The current increase is attributed to the formation of conducting material on the surface of working electrode, which results in an increase of the effective electrode area and also in the change of diffusion behaviour.

Cyclic voltammetry was employed to study the formation of the cluster compound $K_{1.64}[Pt(C_2O_4)_2]$. The electrochemical behaviour of the working electrode is altered upon formation of the conducting material on its surface. Typical voltammograms are shown in Fig. 3(a). Upon cycling the potential between +0.2 and +0.9 V, the anodic peak at +0.58 V diminishes gradually and is replaced, starting with the fourth cycle, by a plateau-shaped anodic response which increases steadily with cycling. The onset of this irreversible electrode behaviour can be accounted for by the depletion of $[Pt(C_2O_4)_2]^{2-}$ eqn. (1).



The conducting fibres, which form on the electrode, can be

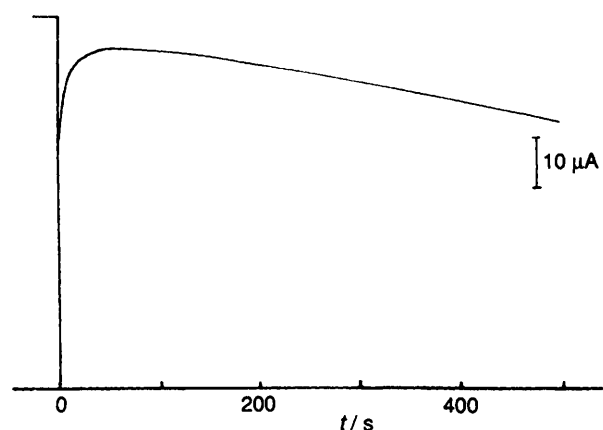


Fig. 1 Current-time response upon application of a single potential step: $K_2[Pt(C_2O_4)_2]$, 5.0×10^{-3} mol dm⁻³; supporting electrolyte, 0.1 mol dm⁻³ K_2SO_4 ; pH 4.0; electrode area, 7.1 mm²; initial potential +0.2 V, final potential +0.7 V

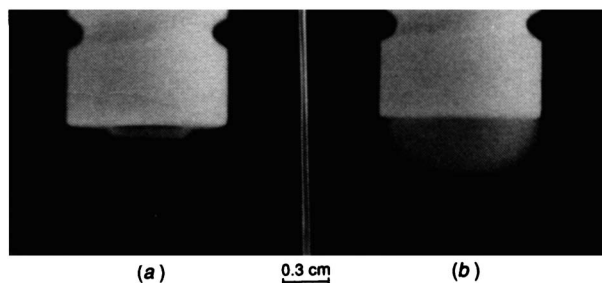


Fig. 2 Photographs taken during the potential step: (a) after 5 s and (b) 50 s. The reference electrode was positioned just behind the working electrode.

regarded as forming an ultramicro-disk electrode, considering its anisotropic conductivity.¹ The branch-style growth of the conducting fibres results in an increase of the plateau-shaped current response during the cyclic potential scanning. A current plateau was observed at scan rates even as high as 100 mV s⁻¹. Although the electrode is covered with conducting fibres, significant charging current was observed. It should be noted that the shape of cyclic voltammograms were influenced by several factors including scan rate, pretreatment of the glassy carbon electrode, the concentration of [Pt(C₂O₄)₂]²⁻ and also the concentration of supporting electrolyte K₂SO₄. Voltammograms obtained at relatively slow scan rates are shown in Fig. 3(b). Typical diffusion steady-state behaviour was observed upon formation of the conducting fibrous material on the surface of electrode. Charging current, as compared with the case under high scan rate, was minimized.

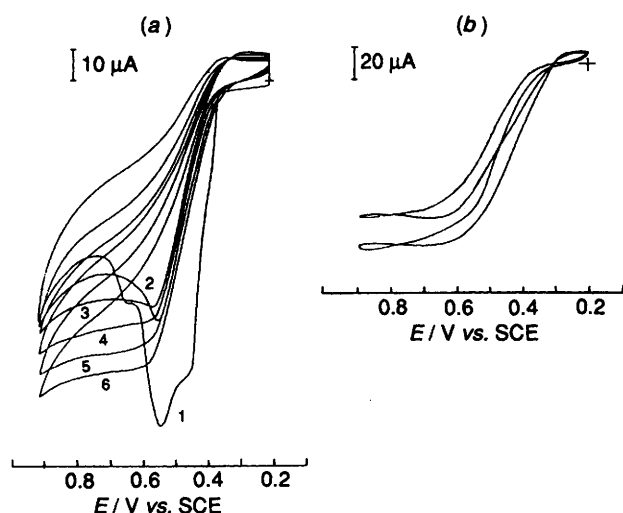


Fig. 3 (a) Cyclic voltammograms of $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_2\text{Pt}(\text{C}_2\text{O}_4)_2$ solution with $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$ as supporting electrolyte. Scan rate: 100 mV s^{-1} . Number on the curves indicates the corresponding cycle. (b) Cyclic voltammograms of the same system with conduction fibres on the electrode surface and at scan rate of 10 mV s^{-1} .

In conclusion, these excellent conductivity of the fibrous material was demonstrated by its unusual voltammetric properties described above and suggests its potential application in ultramicroelectrodes.¹¹ The diffusion steady-state conditions observed during the cyclic voltammetry reflects the stability of the conducting material over the potential range investigated. In addition, the conducting fibres have been proven responsive to the electro-active species in solution since the plateau current appeared at the same potential as that of the initial current peak. Detailed studies are required to investigate the kinetics of the electrocrystallization, which will be helpful in determining the factors which control the formation of the conducting material on the electrode.

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Footnote

† Elemental analysis of $\text{K}_{1.64}[\text{Pt}(\text{C}_2\text{O}_4)_2]$ (Found: C, 11.70; K 13.80; O, 27.65. $\text{C}_4\text{K}_{1.64}\text{O}_8 \text{ Pt}$ requires C, 11.05; K, 14.75; O, 29.40%).

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