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Electrolytic synthesis and properties of potassium oxalatotungstate (V)

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For deposition of thin films of electrochromic WO_3 on NESA glass from an aqueous solution of $K[WO_2(C_2O_4)]\cdot xH_2O$, this compound is needed in a very pure form. The electrolytic reduction of a solution of tungstate(VI) in the presence of oxalate can overcome the disadvantages of the chemical reduction method. In this paper, an improved electrolytic reduction method is described, although a well-crystallized solid could not be obtained. Spectroscopic and conductometric measurements suggest that the chemical deposition proceeds in three steps.

1. Introduction

$K[WO_2(C_2O_4)]\cdot xH_2O$ has been synthesized by chemical reduction of tungstate(VI) with metallic tin in the presence of excess oxalate ions according to the 'Fowles Method' [1]. Since the product thus obtained contains tin(II) and tin(IV) ions, the solution is treated with H_2S gas to remove Sn as SnS. The solution is then poured into excess ethanol with rapid stirring. $K[WO_2(C_2O_4)]\cdot xH_2O$ is precipitated as massive orange crystals. This substance has been a useful intermediate for obtaining other five-valent tungsten compounds.

The aqueous solution of the $K[WO_2(C_2O_4)]\cdot xH_2O$ is unstable and readily decomposes into non-stoichiometric WO_{3-x}, which is deposited onto alumina surfaces as a blue film. This film was found to have electrochromic properties: therefore it may be useful for the construction of electrochromic displays. For this purpose a high purity WO_3 film is desirable, which can be obtained by the vacuum evaporation method. This method is, however, not easy to control and unsuitable for producing large areas. In contrast to the vacuum evaporation method, the process of the decomposition of $K[WO_2(C_2O_4)]\cdot xH_2O$ is very simple and suitable for treatment of large surface areas [2–4].

The purpose of this study is therefore to produce very pure oxalatotungstate(V) complex and to investigate the decomposition of this complex into an electrochromic WO_3 film.

2. Principles of the electrolytic reduction method

The overall reaction during the electrolytic reduction of tungstate(VI) to oxalatotungstate(V) is represented as follows:

$$WO_4^{2-} + 4H^+ + C_2O_4^{2-} + e \longrightarrow [WO_2(C_2O_4)]^- + 2H_2O. \qquad (1)$$

Although the standard redox potential of this reaction is not known, the most probable potential–pH diagram for this system is shown in Fig. 1, where the slope of the H_2 gas evolution and the $[WO_2(C_2O_4)]^-$ formation are calculated to be −0.07 and −0.28 V/decade, respectively, at 80° C. The reduction of WO_4^{2-} should occur preferentially at low pH. On the other hand, the pH value for the complex formation must be maintained at 4 ± 0.5 (region B in Fig. 1), and control of the pH value during the elctrolytic reduction is most important. As the reduction proceeds, hydrogen ions are consumed according to Equation 1 and a supply of hydrogen ions is necessary. To fit this requirement, a special type of two-chambered electrolytic cell separated by an ion exchange membrane was prepared. As the electrolytic reduction proceeds at the cathode, hydrogen ions in the anode chamber migrate through the ion exchange membrane (Nafion-125) into the cathode chamber to compensate for the consumption of hydrogen ions. In this way ideal conditions for electrolytic reduction are maintained.

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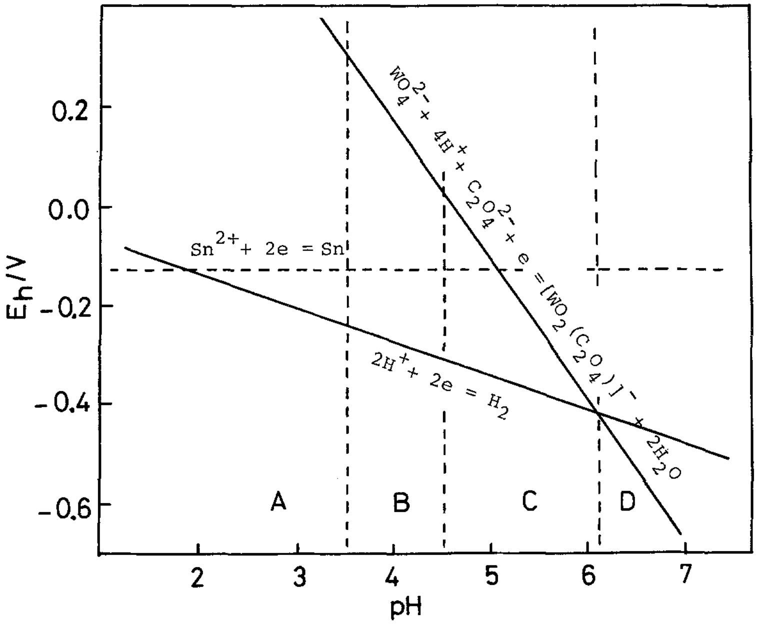

Fig. 1. Potential–pH diagram for the system WO_4^{2-}, $C_2O_4^{2-}$, H^+ and oxalatotungstate(V).

3. Experimental procedure

Guaranteed reagent grade chemicals were used throughout the experiments. The construction of the electrolytic cell is schematically shown in Fig. 2. The volume of the cathode chamber was about 500 cm^3. Several metals were investigated as cathode material and Pb was found to be the best. The temperature of the electrolyte was maintained constant by a thermocouple and a magnetic stirrer was used. The anode was a graphite rod. The cell voltage varied from 10 to 15 V depending upon the current density used and the electrolyte temperature.

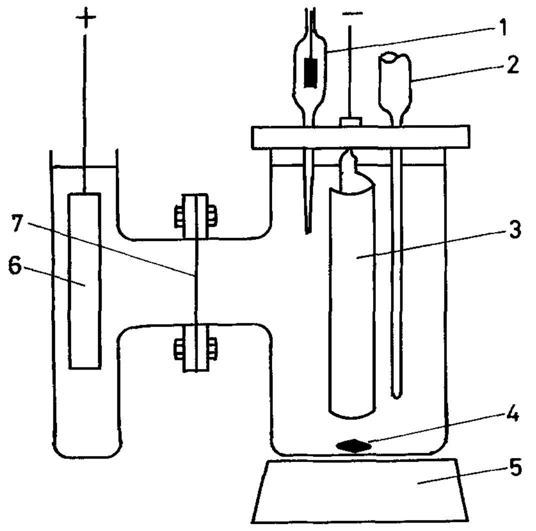

Fig. 2. Experimental apparatus, 1: pH sensor, 2: thermocouple, 3: Pb cathode, 4: magnetic stirrer, 5: thermostat, 6: graphite anode, 7: cation exchange membrane.

The duration of the electrolysis was 1.5 times longer than that estimated from Faraday's Law. When the reduction was completed evolution of appreciable volumes of hydrogen gas was observed.

After electrolysis, the reddish brown aqueous solution containing oxalatotungstate(V) was distilled under reduced pressure at 35° C to concentrate the complex. When the volume of the solution was reduced to one-third of the orginal volume, the concentrated solution was cooled in ice water for several hours. A deep brown powder was slowly deposited, which was successively washed with ice cold water, a water–acetone mixture (1 : 1 vol%) and finally dried in a desiccator over P_4O_{10} (product A).

The remaining reddish brown solution was then mixed with excess acetone. An orange crystalline powder was precipitated, washed with pure acetone and dried in the desiccator (product B). For elementary analysis, the products (A and B) were dried over P_4O_{10} under vacuum at 150° C for 3 h.

Table 1. Experimental conditions for electrolytic reduction of WO_4^{2-} *and yield of oxalatotungstate(V)*

Run No.	K_2WO_4 (g)	$WO_3 \cdot H_2O$ (g)	*KOH* (g)	$H_2C_2O_4 \cdot 2H_2O$ (g)	$K_2C_2O_4 \cdot H_2O$ (g)	*Temperature* (° C)	*Current density* (A dm^{-2})	*Yield A* (%)
1	–	9.5	5.0	15.0	30.0	80	0.6	0
2	–	10.0	5.0	15.0	4.0	80	0.6	65
3	–	10.0	5.0	12.0	0	80	0.6	52
4	13.0	–	–	10.0	7.5	80	0.6	26
5	7.0	–	–	10.0	0	70	0.4	61
6	7.0	–	–	10.0	0	60	0.3	24

4. Results

4.1. *Effect of molar ratio of reactants on the complex formation*

To obtain the purest complex, the stoichiometric molar ratio of oxalate to tungstate should be used, but the pH value of 4.0 could not be attained under these conditions. Therefore excess oxalate ion must be added to control the pH value, or the solution must be neutralized by addition of KOH.

Table 1 shows the conditions for obtaining the complex. Table 2 shows the analytical data. ^{13}C NMR analysis indicated that all the carbon atoms in the complex are in the form of oxalate ligands. No methyl carbon atoms which might have originated from acetone were detected. From these two tables, the best conditions for obtaining the purest oxalatotungstate(V) complex were those of run No. 2.

4.2. *Effect of temperature*

From the view point of the hydrogen overvoltage, low temperature is preferable. On the other hand, the rate of the complex formation will be slow. Therefore, the lowest limit of the temperature was 60° C. The optimum temperature seemed to be 70–80° C, which was in accordance with the method of Fowles.

4.3. *Effect of cathode material on electrolytic reduction*

As expected, reduction of tungstate(VI) was not possible at noble metals, such as Pt or Au. A good reduction yield was obtained with metals having a higher hydrogen overvoltage, e.g., Pb, Zn or Sn. Pb was found to be the best material because of its stability in oxalate solution at 80° C.

4.4. *Effect of pH*

In strongly acid solution (region A in Fig. 1) the colour of the solution became blue and no further change was observed. In region B (pH value 3.5–4.5) reaction proceeded. The colour of the solution changed from blue to green to orange, indicating that the reduction and polymerization of oxalatotungstate anion had occurred.

In region C, reduction of tungstate(VI) hardly occurred, the colour of the solution remaining pale green. In region D, only hydrogen gas was evolved without any change in colour. Figure 3 shows the typical shape of the electronic spectra of the reduced solutions in regions A, B and C in Fig. 1.

Table 2. Analysis of the reaction products

		C (%)	*H (%)*	*W (%)*	*K (%)*
Elemental proportions found	Product A	7.42	0.48	45.9	13.0
	Product B	10.40	1.20	33.5	17.0
Elemental proportions calculated	$K[WO_2(C_2O_4)] \cdot H_2O$	6.62	0.55	50.8	10.8
	$K[WO_2(C_2O_4)] \cdot 2H_2O$	6.31	1.05	48.4	10.3
	$K_6[W_4O_8(C_2O_4)_5(H_2O)_4]$	7.45	0.49	45.6	14.5

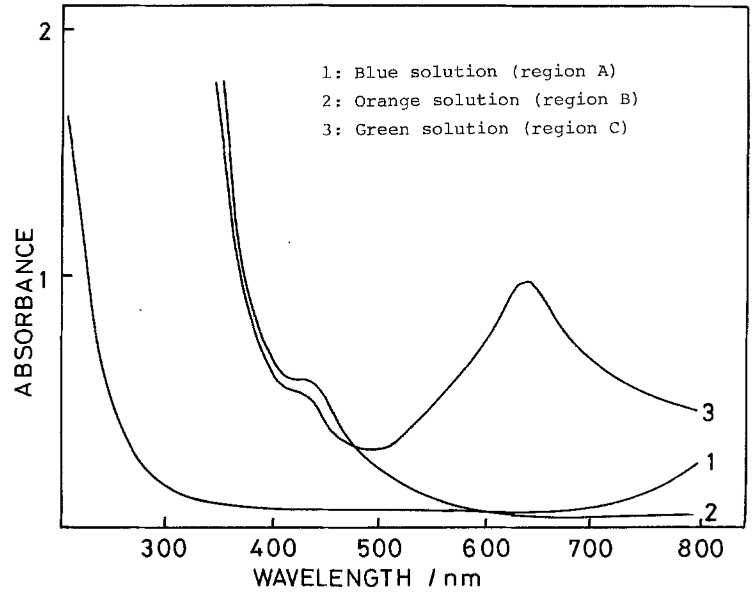

Fig. 3. Electronic spectra of the solutions corresponding to the pH regions A, B and C in Fig. 1.

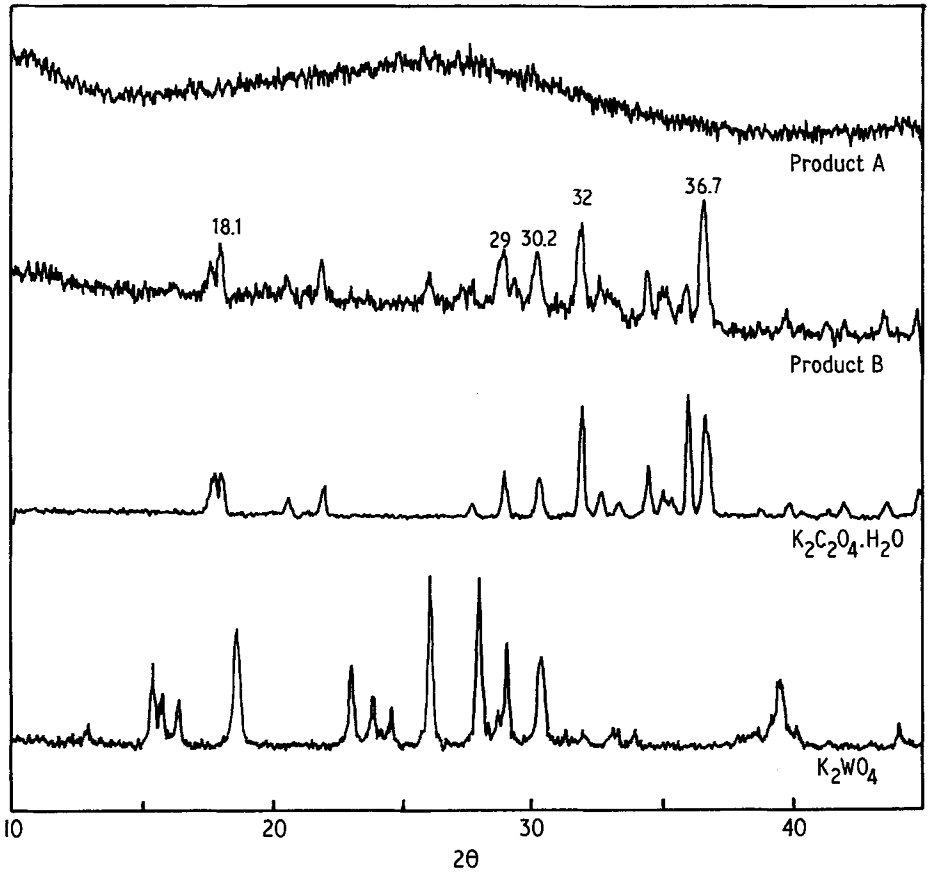

Fig. 4. X-ray powder diffraction patterns of synthesized complexes and reference substances.

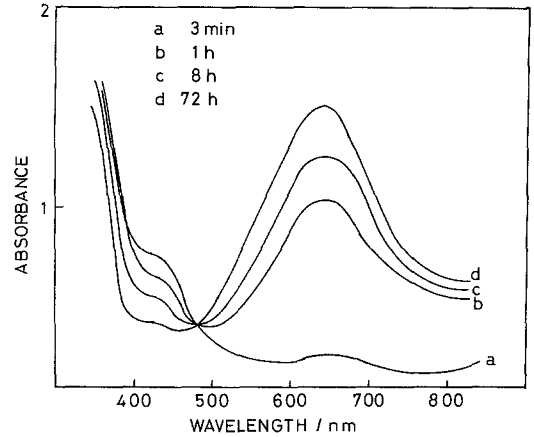

Fig. 5. Change in electronic spectra of the product A under deaerated conditions.

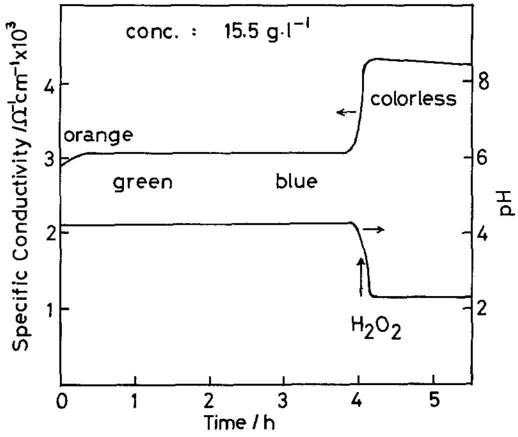

Fig. 7. Time dependence of specific conducitivity and pH of the aqueous solution of the product A.

4.5. *X-ray powder diffraction patterns*

The X-ray diffraction pattern of product A shows it to be almost amorphous (Fig. 4), while that of product B exhibits several diffraction lines which were identified as lines of $K_2C_2O_4 \cdot H_2O$. Both products A and B showed, however, the same electronic spectrum, product B would therefore seem to be a mixture of product A and $K_2C_2O_4 \cdot H_2O$.

It is not clear, whether product A is pure or not, but the elementary analysis suggests that product A is consistent with the formula $K_6[W_4O_8(C_2O_4)_5(H_2O)_4]$.

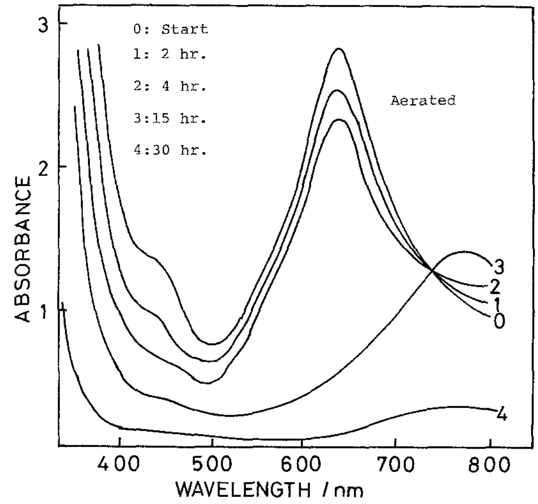

Fig. 6. Change in electronic spectra of the product A under aerated conditions.

Product B nearly corresponds to the formula $K_3[WO_2(C_2O_4)_2]$, which has been proposed by Allen *et al.* [5], but it was not a pure substance as mentioned above.

4.6. *Magnetic susceptibility of the complex salts*

Magnetic susceptibility measurements of products A and B indicated both to be diamagnetic and no ESR signal was observed. According to Cotton *et al.* [6] $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]3H_2O$ was also diamagnetic. They determined its steric conformation and proposed a binuclear complex having a metal–metal bond where the magnetic susceptibility expected from the d^1 electronic structure was missing. In the case of products A and B, spin-paired formation might occur.

4.7. *Decomposition of products A and B in aqueous solution*

Aqueous solutions of product B were stable only when dissolved oxygen had been completely removed from the water prior to dissolution.

When gaseous oxygen or air is introduced into the solution, the complex is slowly oxidized to the six-valent state, thus the solution becomes colourless. By addition of peroxide, it is immediately oxidized. Product A was, on the other hand, less stable in water even when dissolved oxygen gas had been completely removed. The colour of the solution changed slowly from orange to green. Figure 5 shows the change in the electronic spectrum. In the case of the orange solution the absorption peak at 440 nm was predominant. The 440 nm peak decreased with time and a new peak appeared at 635 nm. The iodometric determination of the five-valent tungsten indicated that both the 440 and 635 nm peaks were related to the five-valent tungsten (*d–d* transition). When air was introduced in to the solution, a new peak appeared at 780 nm. This peak first increased and then decreased. The colour of the solution changed to blue and then it became colourless (Fig. 6). Oxidation of product A by air might therefore proceed in at least two steps.

Figure 7 shows the time dependence of the specific conductivity and pH of the aqueous solution of product A under deaerated conditions. The changes in specific conductivity and pH were very slight up to 4 h, although the colour of the solution changed from orange to green to blue. This suggests that the total number of charged particles remains unchanged. Therefore the following decomposition scheme is proposed:

$$6K^+ + [W_4O_8(C_2O_4)_5(H_2O)_4]^{6-} \longrightarrow$$
$$6K^+ + 2[W_2O_4(C_2O_4)_2(H_2O)_2]^{2-} + C_2O_4^{2-}.$$

When peroxide is added to the solution, the solution became colourless and there was a sudden change in specific conductivity and pH value of the solution, as shown in Fig. 7. This indicates that the number of charged particles increased due to generation of hydrogen ions. The decomposition scheme is as follows:

$$[W_2O_4(C_2O_4)_2(H_2O)_2]^{2-} + H_2O_2 \longrightarrow$$
$$[W_2O_6(C_2O_4)(H_2O)_2]^{2-} + C_2O_4^{2-} + 2H^+$$
$$[W_2O_6(C_2O_4)(H_2O)_2]^{2-} \rightarrow 2WO_3 \cdot H_2O + C_2O_4^{2-}.$$

Thus hydrated WO_3 was slowly deposited onto the alumina surface. This is of use in electrochromic displays [2–4].

5. Conclusions

The oxalatotungstate(V) complex salt $K_6[W_4O_8(C_2O_4)_5(H_2O)_4]$ was prepared by an electrolytic reduction method and its properties and decomposition by oxygen were studied by spectroscopic measurements.

This complex salt was not crystalline but was stable in the solid state. The aqueous solution changed colour even under deaerated conditions. In this state the conductivity and pH of the solution remained unchanged.

Under aerated conditions the solution was slowly oxidized to six-valent tungstate and finally, deposited as electrochromic WO_3 in thin films on alumina or NESA glass.

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