Voltammetric Measurement of the Cu(III)/Cu(II) Ratio and Oxygen Content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Superconductive Materials with a Carbon-Paste Electrode

Juan C. VIDAL[†], Antonio VERA and Juan R. CASTILLO

Analytical Chemistry Department, G.E.A.S., Faculty of Sciences, University of Zaragoza, Pza. San Francisco s/n, E-50009 Zaragoza, Spain

The Cu(III)/Cu(II) content ratio of five $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ high-temperature (T_c , ca. 95 K) superconductive materials prepared under various final heating conditions was determined by differential-pulse voltammetry in an alkaline-supporting electrolyte (0.01 M NaOH). Samples were mixed into a carbon-paste electrode and deposited onto a glassy-carbon surface. A simple calculation method based on voltammetric recordings was used to evaluate the stoichiometric coefficient of oxygen, which is of major interest in the characterization of the physical (conductive and superconductive) properties of these compounds. The thus-obtained results were compared with those provided by classical iodometry. The influence of several instrumental and preparative analytical variables on the voltammograms were studied.

Keywords $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors, oxygen stoichiometry, copper(III)/(II) speciation, carbon paste electrode, differential pulse voltammetry, iodometric titration

Cuprate superconductive materials play a central role in the development of high-temperature superconductors, have opened new prospects and have broadened the scope of applications for this type of material.¹

In particular the superconductive properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBaCuO) are strongly affected by changes in its oxygen content. Thus, it exhibits a metallic behavior, orthorhombic structure and superconductivity at high oxygen contents ($0 < x < 0.5$), but forms tetragonal compounds and acts as an insulator or semiconductor at lower oxygen concentrations ($0.5 < x < 1$). Slight changes in the oxygen stoichiometry have strong effects on the superconducting pairing mechanism, altering the superconductive transition temperature (T_c) and some important physical properties, such as magnetic susceptibility.

Because all of the cations in YBaCuO , except copper, possess a single stable oxidation state, and based on the charge neutrality principle, the oxygen stoichiometry is assumed to affect its valence in the presence of the Cu(III) and Cu(II) oxidation states. Hence, the Cu(III)/Cu(II) concentration ratio is an indirect measure of the oxygen content.

A variety of voltammetric and other electroanalytical methods are usually used to study the electrochemical behavior of cuprate-based superconductors, in order to identify the superconducting properties and to confirm the presence of trivalent copper in superconductive

YBaCuO materials.²⁻¹¹

In addition, some authors have found some of these methods to be suitable for determining the Cu(III)/Cu(II) ratio. By using a rotating ring-disk electrode, Rosamilia *et al.* investigated a YBaCuO superconductor that was placed on a disk in various acidic solutions.¹² Other authors have used cyclic voltammetry to measure the Cu(III) content in highly alkaline aqueous solutions^{13,14} and non-aqueous media.^{15,16} Other electroanalytical methods used for this purpose include chronopotentiometry¹⁷ and coulometric titrations.^{18,19}

The carbon-paste electrode is another useful approach to the problem. Incorporating the sample into the carbon-paste matrix permits a straightforward preparation of an electrode for studying its electrochemical behavior and convenient control as well as renewal of surface coverage. This type of electrode has been used to elucidate the oxidation states of copper in solid YBaCuO ²⁰ and process control of superconducting compounds.²¹

In this work we used differential-pulse voltammetry (DPV) to evaluate the Cu(III)/Cu(II) ratio in YBaCuO superconductive materials by depositing powdered samples mixed with graphite paste onto a glassy-carbon electrode. From the resulting voltammograms, a simple calculation method allow us to obtain its oxygen content and stoichiometry.

[†] To whom correspondence should be addressed.

Experimental

Apparatus

An Inelecsa 1212 three-electrode Potentiostat/Galvanostat interfaced to an Acer 915 computer. All of the electrodes used were from Metrohm. Saturated calomel (SCE) and Pt wire was used as the reference and counter-electrode, respectively. A glassy-carbon electrode (GCE, 3.0 ± 0.05 mm diameter) and a laboratory-made carbon-paste electrode with a PTFE tip and a Pt-wire contact (3.0 ± 0.05 mm active surface diameter) were alternately used as working electrodes.

Samples and reagents

Powdered samples of YBaCuO superconductors were kindly supplied by ICMA (Instituto de Ciencia de Materiales de Aragón). They were prepared by a solid state reaction of Y_2O_3 , $Ba(NO_3)_2$ and CuO by standard ceramic procedures, and annealed under variable conditions.

All of the chemicals were of high-purity and of analytical-reagent grade, and were purchased from Merck. High-purity water was obtained from a Millipore Milli-Q water system. All of the sample vials were rinsed with 0.5 M nitric acid and high-purity water before use.

Preparation of the working electrodes

Two types of carbon-paste electrodes were tested. In both cases, the sample was prepared by mixing with spectroscopic-grade paraffin oil and graphite powder. All of the components were thoroughly mixed in an agate mortar (a typical YBaCuO/graphite/paraffin proportion was 5 mg/25 mg/6 μ l); in the case of the first type they were pressed onto the tip of the carbon paste electrode (CPE, active surface diameter 3.0 ± 0.05 mm).

The second type of electrode was constructed by simply placing successively a small portion of the sample paste onto the active surface of a Metrohm glassy-carbon electrode (GCE, diameter 3.00 ± 0.05 mm). The GCE was polished daily with $\alpha-Al_2O_3$ (alumina) particles of 0.3- μ m particle size for over 60 s, washed thoroughly with water and ethanol between polishings, sonicated in water for 5 min, rinsed again, and finally dried with filter paper before use.

Classical iodometric determination of the Cu(III)/Cu(II) ratio in YBaCuO superconductors

The conventional procedure for determining Cu(III) and Cu(II) in YBaCuO superconductors involves iodometric titration^{22,23} based on the following reactions:

Upon dissolving a superconductor sample containing Cu(III) and Cu(II) in an acidic iodide solution, both cations are reduced to CuI. On the other hand, Cu^{3+} ion

Table 1 Iodometric results for the YBaCuO superconductor samples and oxidation equivalents (OEs $\times 10^4$ g⁻¹)

No. sample	Cu ^{III} , wt%	$x \pm s.d.$ (n=5)	Stoichiometry	OE/ 10 ⁻⁴ g ⁻¹
1	12.00	0.36 ± 0.02	YBa ₂ Cu ₃ O _{6.68}	5.4
2	19.33	0.58 ± 0.03	YBa ₂ Cu ₃ O _{6.79}	8.7
3	18.00	0.54 ± 0.03	YBa ₂ Cu ₃ O _{6.77}	8.2
4	28.00	0.84 ± 0.04	YBa ₂ Cu ₃ O _{6.92}	12.6
5	25.33	0.76 ± 0.04	YBa ₂ Cu ₃ O _{6.88}	11.4

The value of coefficient x (mean $\pm$ s.d.) corresponds to the stoichiometric formula YBa₂Cu^{III} _{x} Cu^{II} _{$3-x$} O _{$6.5+0.5x$} . The percentage of Cu(III) was calculated relative to total copper.

reacts rapidly in slightly acidic media to give Cu(II) in a solution containing no I⁻. A combination of the above-mentioned chemical reactions and subsequent iodometric titration of the released iodine with standard thiosulfate permits the determination of the Cu(III) and Cu(II) concentrations.

Based on the superconductor stoichiometry, *e.g.* YBa₂Cu^{III} _{x} Cu^{II} _{$3-x$} O _{$6.5+0.5x$} , the following ratio held: $X_{Cu(III)}/X_{Cu(II)} = x/(3-x)$; $X_{Cu(III)}$ and $X_{Cu(II)}$ are the fractions of Cu(III) and Cu(II), respectively, in the sample. Each sample was titrated in quintuplicate; the uncertainty in x is given by the standard deviation of the titrations. The results are given in Table 1 for the five samples studied.

Results and Discussion

Preliminary assays: DPV behavior of YBaCuO superconductive materials in alkaline media

The superconductivity of cuprate superconductors is related to the electron deficiency (hole concentration) in the CuO₂-layer, and one common statement is to assign the hole concentration (defect structure of the lattice) to the existence of trivalent copper in its molecule. The use of highly alkaline solutions or non-aqueous solvents increases the stability of Cu(III), and, in some instances, it has allowed the voltammetric behavior of trivalent copper to be studied.^{10,11,13-16,18,20}

Despite the presence of Cu(III) or O(I) in the superconductor, they can act as strong oxidizing species that can be related to defect structure. Accordingly, Cu³⁺ ions have been formally written in the redox reaction with water.

When YBaCuO is used as an electrode it rapidly dissolved in aqueous solutions owing to the instability of Cu(III) and the oxidation of water to O₂. In a general form, the following chemical reactions are produced by a proton attack:

Also, a quick reaction of Cu(III) with the O_2/H_2O coupled at the electrode/solution interface,

which yielded an intermediate oxygen species that remained adsorbed and could be voltammetrically reduced at the paste electrode:

The connection between the adsorption of oxygen (and the corresponding reduction currents) and the defect structure of solid substances was demonstrated before.²⁴ In our experiments, the current involved in this process was found to be proportional to the amount of Cu(III) in the solid superconductor sample.

Figure 1 shows typical cathodic differential pulse voltammograms for a YBaCuO sample. Prior to the cathodic scan, an anodic polarization potential ($E_c = +1$ V) was applied for a time ($t_c = 0.2$ min) in order to pre-condition the electrode. The optimized DPV instrumental settings were: ΔE (step potential) = -10 mV; ΔE_p (pulse potential step) = -20 mV; t_r (step time) = 470 ms; t_p (pulse time) = 30 ms; E_i (initial potential) = $+1000$ mV; E_f (final potential) = -1000 mV; E_e (electrolysis potential) = $+1000$ mV; t_e (electrolysis time) = 12 s; E_{rest} (rest potential) = $+1000$ mV and t_{rest} (rest time) = 2 s; hence, the scan rate was 20 mV s^{-1} .

The cathodic peak (D in Fig. 1) at $E_p = +520$ mV is due to electrodesorption from the porous graphite material of the molecular oxygen evolved under anodic polarization. This peak was observed for both cuprous/cuprate oxide and the superconductive materials, as were others at peak potentials of -560 and -810 mV, due to the reduction of Cu(II) to Cu(I) (peak B) and Cu(I) to Cu(0) (peak A), respectively.

However, the superconductive material in the paste exhibited a new voltammetric peak (C) at $E_p = -10$ mV. The peak only appeared in the first scan (case a of Fig. 1), and was due to evolved oxygen in accordance with Eqs. (1)–(3). Its overall charge was found to be proportional to the Cu(III) content, as suggested by Gruner *et al.*²¹, and hence to the oxygen stoichiometry of the superconductor samples, *i.e.* dependent on the annealing temperature used in their manufacturing.

The oxidizing power of $YBa_2Cu_3O_{7-x}$ was sufficient to give peak C without the need of a more anodic potential, which also appeared when the starting potential was placed at about $+260$ mV (*i.e.* outside peak D evolution). Anodic polarization (E_c , t_c) had no influence on peak C, but was used in order to pre-condition the electrode and to improve the reproducibility of peak C. The statistical results confirmed the good correlation between the iodometry and the areas of the thus-recorded voltammograms.

Because Cu(III) was quickly lost by dissolution, only peak C appeared in the first scan, as shown in Fig. 1, where peak C had disappeared at a second voltammogram (case b) run 5 min after the first.

Fig. 1 Typical DP-ASV voltammograms of a YBaCuO superconductor sample on a GCE: a) first scan; b) second scan, recorded 5 min after first. The instrumental settings are given in the text. Supporting electrolyte, 10^{-2} M NaOH; paste composition, 250 mg of graphite, 50 mg of sample and 60 μ l of paraffin oil.

Fig. 2 Influence of the carbon-paste composition on the voltammograms of a CuO sample. The paste was prepared by mixing 250 mg of graphite and 60 μ l of paraffin oil with: a) 25 mg of CuO, b) 50 mg of CuO and c) 125 mg of CuO. Instrumental settings as in Fig. 1.

The resolution and sensitivity of the voltammograms are strongly dependent on the composition of the paste electrode used. At high YBaCuO/graphite paste (CP) weight ratios (0.5/1 and above) the peaks are broader, and also less sensitive (voltammograms are overly simpler). At lower ratios (YBaCuO/CP weight ratios of 0.1/1 and below) the sample homogeneity is lower, and a number of fairly small peaks are obtained. These irrespective peaks are due to background differences in the sample position in the graphite paste, which results in poor resolution. The best compromise was provided by a 0.2/1 YBaCuO/CP weight ratio. The effect is illustrated in Fig. 2 for a sample of CuO, and was identical with that for the YBaCuO sample under selected conditions.

By comparing the type of electrode used with a given

paste, although the shapes of the voltammograms provided by both electrodes were similar, the reproducibility was better with the GCE than with the CPE (the relative standard deviation of the peak C areas for 5 individual analyses were 11.02% and 21.12%, respectively). This result can be ascribed to the larger volume and higher porosity of the CPE relative to the thin layer of sample deposited over the GCE.

However, the sensitivity was not appreciably influenced by the type of electrode used, since peak areas were similar for the relevant peaks (A, B and C (for example, peak C yielded 109.2 ± 12.0 and $111.4 \pm 23.5 \mu\text{C}$ for the GCE and CPE, respectively)). This suggests that only the electrode surface layer exposed to the solution, which was similar for both electrodes, rather than the overall volume, was responsible for the magnitude of the voltammograms. The optimum YBaCuO/CP weight ratio (0.2/1 (w/w)) was used in all cases.

Obviously, since the supporting electrolyte influenced the stability of Cu(III) in the sample, the electrolyte used was always strongly alkaline in order to minimize the acid attack. Three supporting electrolytes were tested with scan rates of 20, 50 and 100 mV s^{-1} , namely: aqueous 0.01 M NaOH, saturated $\text{Ba}(\text{OH})_2$ and mixtures of the two. All other DP-ASV instrumental settings were as described above (only t_r was adjusted to obtain the desired scan rate), and the paste was placed onto a GCE. Table 2 illustrates the influence of these variables.

Interestingly, the area of peak C decreased linearly with increasing scan rate [$Q_C = K/(\text{scan rate})$, R (coef. of regression) = 0.9999] in all three electrolytes, which is more consistent with an adsorptive process than with a diffusional charge-transfer process [$Q_C = K/(\text{scan rate})^{1/2}$]. The peak areas decreased through a decrease in the time required to record the entire voltammogram, which, in turn, led to a diminished concentration of dissolved species from the sample.

The best sensitivity and reproducibility were provided by a 0.01 M NaOH solution at a scan rate of 20 mV s^{-1} , and were thus adopted for subsequent experiments. The sensitivity achieved with saturated $\text{Ba}(\text{OH})_2$ or mixing of the two supporting electrolytes was worse than that obtained with 0.01 M NaOH, as can be seen from Table 2.

With regard to the gas used to deoxygenate, nitrogen and helium provided similar voltammograms. Nevertheless, a rise in peak D was observed as the deoxygenation time and/or the time that the sample was in contact with the solution. This effect was more marked with nitrogen than with helium, and must be related to the adsorption kinetics between the amount of gas dissolved in the solution (or the ultratraces of oxygen supplied by with each gas) and the porosity of the sample paste. All of the other peaks remained essentially unaltered.

Voltammetric calculation of the superconductor stoichiometry

We showed early the sensitivity achieved to depend on

Table 2 Influence of the scan rate and supporting electrolyte on the area of peak C and A+B (Sample No. 2)

Supporting electrolyte	Scan rate/ mV s^{-1}	$Q_C/\mu\text{C}$ (mean $\pm$ s.d.)	$Q_{A+B}/\mu\text{C}$ (mean $\pm$ s.d.)
10^{-2} M NaOH	20	109.2 ± 12.0	805.3 ± 102.8
	50	42.8 ± 3.4	310.7 ± 37.3
	100	20.1 ± 2.0	143.6 ± 17.2
sat. $\text{Ba}(\text{OH})_2$	20	76.7 ± 10.3	559.1 ± 89.8
	50	30.3 ± 3.6	214.9 ± 32.2
	100	11.6 ± 1.2	81.9 ± 9.2
$10^{-2} \text{ M NaOH} +$ sat. $\text{Ba}(\text{OH})_2$	20	25.6 ± 3.7	185.8 ± 33.4
	50	8.2 ± 1.1	58.1 ± 8.7
	100	4.1 ± 1.0	16.4 ± 2.1

The values are the mean $\pm$ standard deviation for 5 individual voltammograms. The superconductor sample was deposited on a GCE. The values of the instrumental parameters are given in the text.

the experimental conditions used. One other potentially influential variable was the area of the exposed electrode surface, which might have varied slightly between analyses. However, this effect can be cancelled by calculating the stoichiometry from the ratio of the copper species; the latter was always the same, irrespective of the amount of sample transformed (dissolved) during the time that the voltammetric measurement was made.

We assumed the Cu(III)/Cu(II) weight content ratio in the YBaCuO sample to be proportional to the ratio of the charge transferred in the corresponding voltammetric reduction peaks. Since peak C was proportional to the current involved in reducing Cu(III) to Cu(II), *i.e.* to the amount of oxygen produced at the electrode by Cu(III), $Q_C = K \cdot n_1 \cdot [\text{Cu}^{\text{III}}]$. Likewise, $(Q_A + Q_B) = Q_{A+B} = K \cdot n_2 \cdot [\text{Cu}^{\text{II}}]$, *i.e.* $(Q_A + Q_B)$ is proportional to the amount of Cu(II) reduced from the sample to Cu(0). K is the same proportionality constant in both equations, and n_1 and n_2 denote the number of electrons involved in the corresponding electrochemical reactions; Q_A , Q_B and Q_C are the amounts of charge (μC) for peaks A, B and C, respectively; $[\text{Cu}^{\text{III}}]$ and $[\text{Cu}^{\text{II}}]$ are the voltammetrically measured concentrations of Cu(III) and Cu(II) at the electrode/solution interface, respectively, and proportional to the copper content in the YBaCuO sample.

If the same degree of irreversibility is assumed for both electrode reactions, the n_1/n_2 ratio is 0.50, and the following equation holds:

$$[\text{Cu}^{\text{III}}]/[\text{Cu}^{\text{II}}] = 2 \cdot Q_C/(Q_A + Q_B).$$

Since the stoichiometry of the superconductor exclusively depends on this ratio, and can be formulated as $\text{YBa}_2\text{Cu}_{3-2x}\text{Cu}^{\text{II}}_{2x}\text{O}_{8-x}$, we have

$$[\text{Cu}^{\text{III}}]/[\text{Cu}^{\text{II}}] = 2 \cdot Q_C/(Q_A + Q_B) = (3 - 2x)/2x$$

from where the stoichiometric coefficient of oxygen is calculated ($\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$), provided that the charge neutrality holds and the other cations in the molecule

Table 3 Voltammetric results for the stoichiometry of the five YBaCuO superconductor samples studied

Sample	Cu(III), wt%	$x \pm \text{s.d. (n=5)}$	Stoichiometry
1	15.00	1.35 ± 0.10	$\text{YBa}_2\text{Cu}_3\text{O}_{6.65}$
2	21.33	1.18 ± 0.09	$\text{YBa}_2\text{Cu}_3\text{O}_{6.82}$
3	16.67	1.25 ± 0.09	$\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$
4	30.67	1.04 ± 0.07	$\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$
5	28.00	1.08 ± 0.08	$\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$

The value of coefficient x corresponds to the formula $\text{YBa}_2\text{Cu}^{\text{III}}_{3-2x}\text{Cu}^{\text{II}}_{2x}\text{O}_{8-x}$. The percentage of Cu(III) was calculated relative to total copper.

possess their usual valences.

The results of this procedure are summarized in Table 3. The uncertainty in the calculation of x is related to the precision of the voltammetric measurements. The mean oxygen stoichiometric coefficient obtained iodometrically and voltammetrically was not significantly different at the 95% confidence level, as calculated by the statistical paired t-test; thus, the electroanalytical method provides a rapid means for assessing the oxidizing power, stoichiometry and physical properties of YBaCuO.

We also applied the procedure of Gruner *et al.* to our iodometric results.²¹ Gruner calculated the so-called "oxidation capability of the YBaCuO superconductor" as follows. For a generic redox reaction $\text{Ox} + n\text{e}^- \rightleftharpoons \text{H}^+ + \text{Rd}$, the following equality holds:

$$M_{\text{ox}}/(m_{\text{ox}} \cdot n_{\text{ox}}) = M_{\text{rd}}/(m_{\text{rd}} \cdot n_{\text{rd}}),$$

m_{ox} and m_{rd} being the equivalent masses of the oxidized and reduced forms, n the electrons per mole and M the atomic or molecular weight.

Because $m_{\text{ox}} = m_{\text{ox}}\% \cdot m_s / (100 \cdot (m_s - s))$ (m_s is the equivalent mass of the sample and s the sample weight), we can write

$$m_{\text{rd}} \cdot n_{\text{rd}} / (m_s \cdot M_r) = m_{\text{ox}}\% \cdot n_{\text{ox}} / (100 \cdot M_{\text{ox}}) = \text{OE},$$

where OE (the oxidation equivalent) represents the oxidation power of 1 g of YBaCuO, whatever the assumed oxidizing species. From OE, the $m_{\text{ox}}\%$ content of the oxidizing species Ox can be easily calculated, being for both Cu(III) and O(I) $n=1$.

Gruner associates the oxidation equivalents to defect spots or h^+ holes in the superconductor. The number of defect spots can be estimated from the Y(III)/Ba(II)/Cu(II)/O(II) atomic proportion and the charge balance with all elements in their usual valence states in solution. The resulting excess of negative charge represents the defect spots in 1 mol. The OEs, calculated from the iodometric results, are shown in Table 1.

In summary, the proposed differential pulse voltammetric method for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors in an alkaline solution (10^{-2} M NaOH) permits an evaluation

of the Cu(III)/Cu(II) content ratio, and, hence, an indirect calculation of the oxygen stoichiometry. This parameter depends on the annealing temperature used in its production, and greatly influences the conductive and superconductive properties of this type of sample.

This work was financed by DGICYT (Project PB93/306) of the Spanish Ministry of Education and Science.

References

1. J. T. McDevitt, D. R. Riley and S. G. Haupt, *Anal. Chem.*, **65**, 535A (1993).
2. H. Bachtler, W. J. Lorenz, W. Schindler and G. Saemann-Ischenko, *J. Electrochem. Soc.*, **135**, 2284 (1988).
3. K. Ohkawa, I. Kiminori and A. Fujishima, *Bull. Chem. Soc. Jpn.*, **63**, 1287 (1990).
4. D. R. Riley and J. T. McDevitt, *J. Electrochem. Soc.*, **139**, 2340 (1992).
5. G. Tavcar, B. Ogorevc, V. Hudnik and S. Pejovnik, *Physica C*, **175**, 607 (1991).
6. J. M. Rosamilia, B. Miller, L. F. Schneemeyer, J. V. Waszcza and H. M. O'Bryan, *J. Electrochem. Soc.*, **134**, 1863 (1987).
7. M. Bachtler, W. J. Lorenz, W. Schindler and I. Saemann, *J. Electrochem. Soc.*, **135**, 2284 (1988).
8. F. P. Dousek, *Physica C*, **171**, 156 (1990).
9. F. Beck and U. Barsch, *J. Electroanal. Chem.*, **282**, 175 (1990).
10. A. A. Kaplin, N. M. Svishchenko, N. M. Dubova, G. B. Slepchenko, Yu. A. Karbainov and G. F. Ivanov, *Zh. Anal. Khim.*, **46**, 976 (1991).
11. M. Mohammad, A. Y. Khan, M. S. Subhani, A. Naseer and S. Malik, *Bull. Electrochem.*, **5**, 893 (1989).
12. J. M. Rosamilia, *Anal. Chem.*, **61**, 1497 (1989).
13. S. Rochani, D. B. Hibbert, S. X. Dou, A. J. Bourdillon, H. K. Liu, J. P. Zhou and C. C. Sorrel, *J. Electroanal. Chem. Interfacial Electrochem.*, **248**, 461 (1988).
14. U. Barsch and F. Beck, *Electrochim. Acta*, **35**, 759 (1990).
15. B. Viswanathan, N. S. Raman, S. Suchithra, R. P. Viswanath and T. K. Varadarajan, *J. Electrochem. Soc. India*, **37**, 147 (1988).
16. N. S. Raman, B. Viswanathan and T. K. Varadarajan, *Bull. Electrochem.*, **6**, 785 (1990).
17. S. Salkalachen, E. Salkalachen, P. K. John and H. R. Froelich, *Appl. Phys. Lett.*, **53**, 2707 (1988).
18. H. Tengen, H. Xuejie and C. Liguang, *Chin. Phys.*, **11**, 960 (1991).
19. G. Kawamura and M. Hiratani, *J. Electrochem. Soc.*, **238**, 3211 (1987).
20. M. T. San José, A. M. Espinosa, M. L. Tascón, M. D. Vázquez and P. Sánchez-Batanero, *Electrochim. Acta*, **36**, 1209 (1991).
21. W. Gruner and A. Drescher, *Fresenius' Z. Anal. Chem.*, **335**, 304 (1989).
22. P. Lanza and G. Rossi, *Anal. Chim. Acta*, **244**, 253 (1991).
23. E. H. Appelman, L. R. Morss, A. M. Kini, U. Geiser, A. Umezawa, G. W. Crabtree and K. D. Carlson, *Inorg. Chem.*, **26**, 3237 (1987).
24. K. Z. Brainina, *Talanta*, **34**, 41 (1987).

(Received May 1, 1995)

(Accepted November 28, 1995)