

Anode Oxidation of Sulphite and Thiosulphate Ions on Porous Electrodes Made of Carbon Fibres

A. G. BELOBABA, D. V. SUKHORUKOV, A. I. MASLIY and A. A. GUSEV

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 6300128 (Russia)

E-mail: belobaba@ngs.ru

(Received July 29, 2008; revised November 6, 2008)

Abstract

Dynamics of the anode oxidation of sulphite and thiosulphate solutions (concentration: 10 g/L) on carbon felt VNG-30 and Karbopon V-22 under different electrolysis conditions was studied. It was established that these materials are rather stable under the anode polarization up to $\phi = 1.7$ V (s.c.e.) and can be used for the anode oxidation of sulphite and thiosulphate ions. It was shown that the rate of oxidation increases with an increase in the anode polarization, especially with a decrease in the concentration of the anions to be oxidized. It was shown that the addition of KBr (up to 10 g/L) into the solution causes substantial acceleration of the oxidation of both sulphite and thiosulphate.

Key words: porous electrode, carbon fibres, anode oxidation, sulphite, thiosulphate

INTRODUCTION

Industry related solutions containing sulphur compounds, such as sulphite and thiosulphate, are among the widespread sources of environmental pollution. They include, for instance, waste water from paper industry, textile works and tannery where sulphite is used as reducing agent, and worked out (in particular, fixing) solutions. They contain such dangerous toxicants as silver (2–15 g/L), sulphite anions (10–15 g/L) and thiosulphate anions (120–200 g/L) [1]. The latter are characterized by the high chemical and biological oxygen demand (COD and BOD, respectively) and intensively decompose in open water bodies with the release of toxic sulphur-containing compounds. In this connection, in the majority of countries there are rather rigid requirements to the purification of worked out fixing solutions, so that the residual COD and BOD values should be decreased by several ten times.

Taking into account the scale of ecological consequences of the disposal of worked out fix-

ing solutions containing sulphite and thiosulphate into the environment, it is urgent to solve the problem of their utilization. We demonstrated previously [2] that the use of flow porous electrodes (FPE) made of fibrous carbon materials and the optimal choice of pH of solution and the potential of deposition allow one to achieve a decrease in the residual silver content down to 0.5–1 mg/L, thus fulfilling one of the above-mentioned ecological requirements.

The goal of the present work was to study the kinetic features of the anode oxidation of sulphite and thiosulphate anions on FPE made of fibrous carbon materials.

EXPERIMENTAL

The anode oxidation of sulphite and thiosulphate ions was carried out using a flat graphite electrode and a FPE made of carbon felt VNG-30 [3] and Karbopon V-22 (Svetlogorsk Production Association “Khimvolokno”, Belarus). The overall area of anodes was 0.3 dm³.

The circulation mode of FPR operation and potentiostatic mode of electrolysis without membrane separation of electrode spaces were involved. The objects of investigation were aqueous solutions of Na_2SO_4 (10 g/L) and $\text{Na}_2\text{S}_2\text{O}_3$ (10 g/L), the background solution was 1 M Na_2SO_4 . If necessary, KBr (10 g/L) was added to the solution 0.5 L in volume under treatment. The solution flow rate was $0.3 \text{ cm}^3/\text{s}$ per 1 cm^2 of the overall area of the anode.

The scheme of the experimental electrochemical set-up was presented in [4]. Experiments on the anode oxidation were carried out at pH 10–12, that is, under the conditions when the cathode reduction of sulphite is strongly hindered [2]. To choose the conditions of the oxidation of sulphite and thiosulphate and the conditions of voltammetric determination of SO_3^{2-} concentration, we used a measuring unit based on the sensor with mechanically renewed graphite epoxy electrode [5] and the IPC-compact potentiostat. It is established preliminarily that the height of the peak of anode oxidation of sulphite (0.5 V, pH 13) is linearly dependent on its concentration within the range 0.2–15 g/L. The values of potential in this work are reported with respect to the silver chloride reference electrode (s.c.e.). The concentration of thiosulphate was monitored using the iodometric method [6].

RESULTS AND DISCUSSION

Anode stability of graphite

Efficient oxidation of sulphite and thiosulphate on the anode made of graphite fibres is possible only in the region of the potentials of fibre stability; under definite conditions, the fibres can undergo oxidation. Using the graphite epoxy electrode (2 mm in diameter), it was established preliminarily that in the anode voltammograms in the background solution in the region of potential ϕ up to 1.7 V the current strength is practically equal to zero, only in strongly alkaline medium (pH 13) the polarization curve exhibits an additional peak of current, which is likely connected with the oxidation of the surface groups of graphite [7]. The evolution of oxygen and the anode destruction of graphite, accompanied by dark-

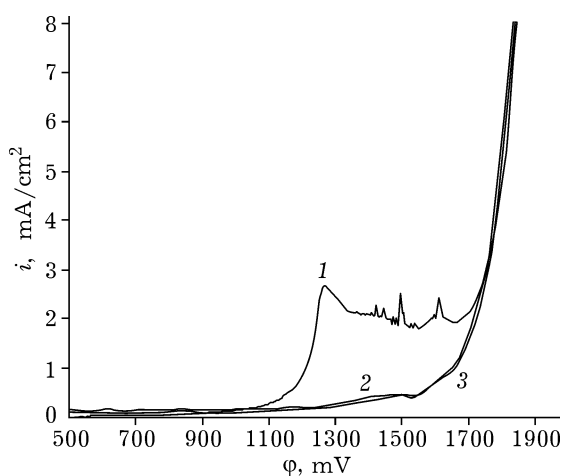


Fig. 1. Effect of pH value on the anode voltammograms of the background solution 1 M Na_2SO_4 (graphite electrode, $S = 0.03 \text{ cm}^2$; rate of potential sweep 1 mV/s; temperature 25 °C). pH: 13.0 (1), 10.0 (2), 3.0 (3).

ening of the solution, is observed only in the region $\phi > 1.8 \text{ V}$ (Fig. 1).

Potentiostatic tests of the samples of carbon felt VNG-30 and Karbopon V-22 in the background solution 1 M Na_2SO_4 (pH 12) under the anode polarization $\phi = 1.7 \text{ V}$ for 1 h showed that the mass remains almost unchanged; no darkening of the solution as a result of the destruction of carbon fibres occurs. This is the evidence of the stability of these carbon fibrous materials and the possibility to use them as anodes in this potential range. A similar conclusion was made previously by the authors of [8] who stress a weak effect of the anode polarization on the electric conductivity and mass of graphitized materials even under the current density of $50\text{--}100 \text{ mA}/\text{cm}^2$ in the solution of 0.01 M NaOH.

Anode oxidation of sulphite

The process of the anode oxidation of SO_3^{2-} ions, similarly to the cathode reduction of sulphite [2], is strongly dependent on the acidity of solution. The anode voltammograms (Fig. 2) show two oxidation waves with the maxima at $\phi_{\text{I}} \sim 0.5$ and $\phi_{\text{II}} \sim 0.9 \text{ V}$. In this situation, the first wave prevails in strongly alkaline solutions (pH ≥ 13), while the second one dominates in acidic solutions (pH < 4). A similar picture was previously observed with the ano-

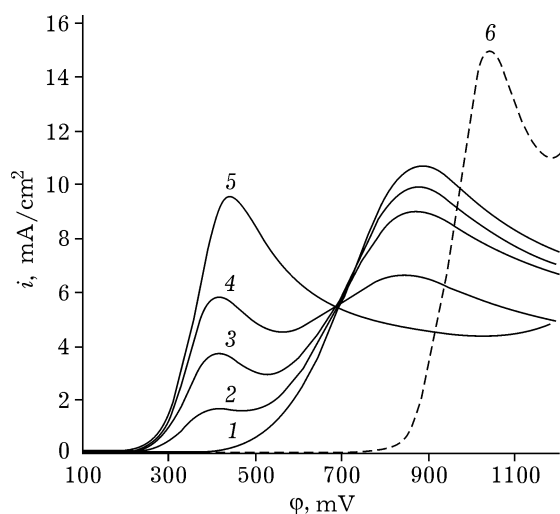


Fig. 2. Anode voltammograms of the oxidation of sulphite (1-5) and bromide ions (6) depending on pH (graphite electrode, $S = 0.03 \text{ cm}^2$; rate of potential sweep 20 mV/s; temperature 25 °C): 1-5 - 10 g/L $\text{Na}_2\text{SO}_3 + 1 \text{ M Na}_2\text{SO}_4$; 6 - 10 g/L $\text{KBr} + 1 \text{ M Na}_2\text{SO}_4$; pH: 3.5 (1), 6.6 (2), 7.6 (3), 12.0 (4), 13.0 (5), 6.5 (6).

des made of natural and impregnated graphite [9]. Such an effect of pH value is connected with the prevalence of different sulphite forms and with different possible mechanism of their anode oxidation. For instance, SO_3^{2-} ions prevail in alkaline media, while SO_2 form dominates in strongly acidic solutions [9-12].

In acidic solutions, the process of sulphite ion oxidation on graphite anode runs in one stage with the formation of sulphate ion [12]:

$$\text{SO}_2 + 2\text{H}_2\text{O} - 2\bar{e} = \text{SO}_4^{2-} + 4\text{H}^+ \quad (1)$$

In alkaline solutions, sulphite oxidation follows a more complicated route. Along with its oxidation into sulphite according to reaction



the oxidation of sulphite with the formation of dithionate as the intermediate product is also possible according to reaction



However, dithionate is very unstable in solution and disproportionates rapidly with the formation of sulphite and sulphite ions. As a result, according to the data reported by the authors of [12], the concentration of dithionate does not exceed 3 % at pH 7.0.

In our experiments, too it was established that a substance (presumably dithionate) ap-

pears in solution in course of the anode oxidation of sulphite; the peak of the cathode current of its reduction is in the region of -0.3 V . The concentration of this substance is insignificant, and the substance itself is very unstable because the height of the cathode peak of current at $\varphi_1 = -0.3 \text{ V}$ sharply decreases during the repeated recording of curves.

The data on changes of sulphite content in circulating solution for different versions of electrolysis are shown in Fig. 3. One can see that at the initial stage of electrolysis, that is, with the high Na_2SO_3 concentration (7-10 g/L), the oxidation rate is weakly dependent on the potential and even on the type of anode. In other words, in this case FPE works as almost flat electrode. However, on flat graphite, the rate of oxidation remains almost constant with time, while for the FPE it increases substantially, especially with an increase in the anode potential and a decrease in the concentration of sulphite ions. This is connected with the fact that the efficiency of FPE operation increases with decreased concentration of the electroactive component [13]; this once again proves the efficiency of FPE for processing diluted solutions [14].

The process of sulphite oxidation on graphite flow electrodes takes place with the high current yield reaching 120-125 %, calculated

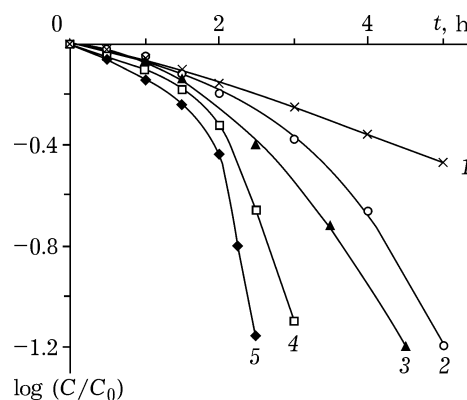
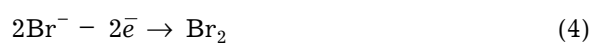


Fig. 3. Dynamics of changes of relative concentration of sulphite in the circulating solution during the anode oxidation under different electrolysis conditions: 1, 2, 4 - 10 g/L $\text{Na}_2\text{SO}_3 + 1 \text{ M Na}_2\text{SO}_4$; 3, 5 - 10 g/L $\text{Na}_2\text{SO}_3 + 1 \text{ M Na}_2\text{SO}_4 + 10 \text{ g/L KBr}$; 1-5 - anodes (1 - flat graphite, 2-5 - one layer of carbon felt VNG-30); anode potential, V: 1.5 (1), 1.2 (2, 3), 1.7 (4, 5); C_0 , C - initial and current sulphite concentration, respectively.

for the two-electron oxidation process (see eq. (2)). Such an excess of the current yield may be due to the additional chemical oxidation of sulphite by dissolved oxygen, especially in the case of its low concentration. It follows from the data shown in Fig. 3 that the rate of sulphite oxidation increases substantially with an increase in the anode potential. For example, at $\phi = 1.2$ V, to achieve the degree of sulphite oxidation 92–93 %, 5 h was necessary, while at $\phi = 1.7$ V this value was achieved within about 3 h. The process of sulphite oxidation on a flat graphite anode takes place with much lower rate: at $\phi = 1.5$ V the oxidation degree was only 64 % after 5 h.

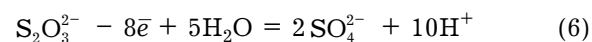
Additional noticeable positive effect on the process of anode oxidation of sulphite is produced by Br^- ions that are almost always present in real fixing solutions. This effect is due to the parallel anode oxidation of Br^- into Br_2 at $\phi = 1$ V (see Fig. 2, curve 6), followed by the chemical oxidation of sulphite with bromine and regeneration of Br^- :



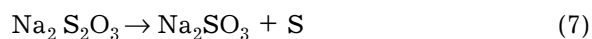
It also follows from the data shown in Fig. 3 that the maximal effect of the addition of Br^- ions is observed exactly for the diluted sulphite solutions.

Anode oxidation of thiosulphate

Unlike for sulphite, the anode oxidation of thiosulphate requires much larger number of electrons and is accompanied by the formation of the large number of H^+ ions [15]:



This leads to the fact that the pH of solution of the initially alkaline electrolyte rapidly decreases during the electrolysis with the separation of electrode spaces and reaches $\text{pH} < 4$, then chemical decomposition of thiosulphate with the formation of sulphite and sulphur starts with the noticeable rate [9]:



In this connection, to avoid rapid acidifying of the anolyte and chemical decomposition of thio-

sulphate, its anode oxidation should be carried out without the separation of electrode spaces.

In addition, thiosulphate differs from sulphite by the fact that the rate of the anode oxidation of the former is weakly dependent on pH (Fig. 4). Within a broad pH range, two processes are observed on the anode polarization curve: the first one ($\phi \geq 0.5$ V) is due to the oxidation of thiosulphate into tetrathionate, while the second one ($\phi \geq 1.1$ V) with the oxidation of sulphate ions [15]. One can also see from the data shown in Fig. 4 that, though much higher anode potential is necessary to provide deep oxidation of thiosulphate into sulphate, these anode potential values are within the region of the anode stability of fibrous carbon material ($\phi = 1.7$ V).

During the electrolysis of initially alkaline solutions without the separation of electrode spaces, the acidity in the solution volume changes insignificantly during the electrolysis. Nevertheless, slight opacification of solution is observed with time; while inside the FPE, especially from the side where the solution is fed, small (micrometer-sized) solid white-coloured particles are detected. Figure 5 shows the diffraction patterns of carbon felt VNG-30 before the process of thiosulphate oxidation (curve 1) and after it (curve 2). New reflec-

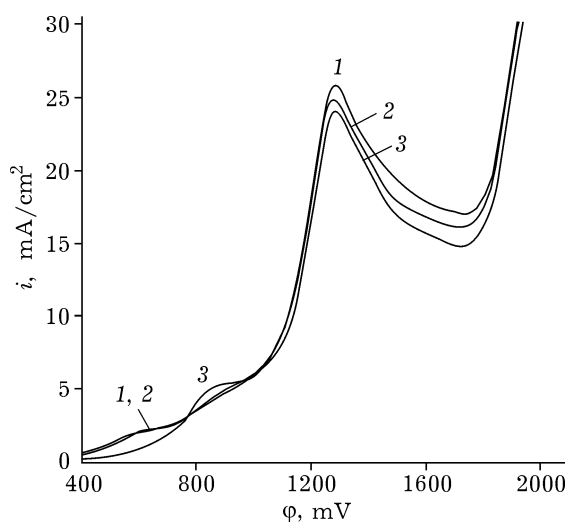


Fig. 4. Anode voltammograms of the oxidation of thiosulphate (10 g/L $\text{Na}_2\text{S}_2\text{O}_3$ + 1 M Na_2SO_4) depending on pH (graphite electrode, $S = 0.03$ cm²; rate of potential sweep 30 mV/s; temperature 25 °C). pH value: 4.4 (1), 7.2 (2), 12.0 (3).

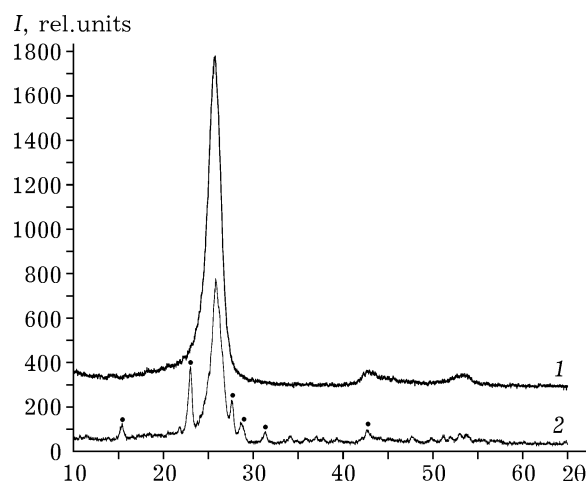


Fig. 5. Diffraction patterns of graphitized carbon felt BNG-30 before (1) and after oxidation of thiosulphate solution at $\varphi = 1.5$ V for 6 h (2). * Major reflections from the orthorhombic modification of sulphur.

tions observed in the X-ray diffraction patterns after electrolysis corresponds to elemental sulphur with orthorhombic modification. The formation of sulphur inside the porous electrode is likely to be connected with strong local acidifying of the near-anode layer of solution (see eq. (6)) and partial progress of thiosulphate decomposition reaction in it (see eq. (7)).

One can see in Fig. 6 that the rate of the anode oxidation of thiosulphate on FPE increases noticeably with an increase in the anode

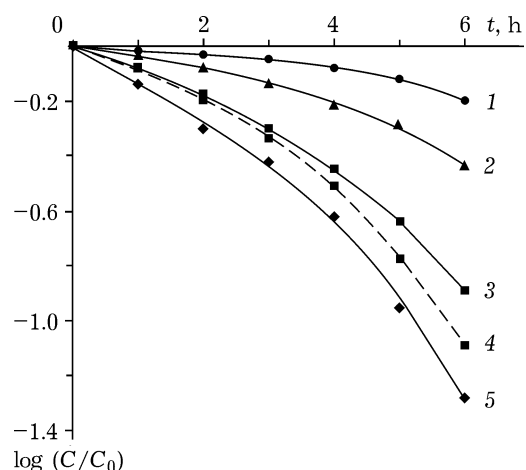


Fig. 6. Dynamics of changes of the relative concentration of thiosulphate during the anode oxidation of solution: 10 g/L $\text{Na}_2\text{S}_2\text{O}_3$ + 1 M Na_2SO_4 on VNG-30 depending on potential (1-3, 5) and the effect of bromide (10 g/L KBr) on the rate of thiosulphate oxidation (4). Potential, V: 1.2 (1), 1.5 (2), 1.7 (3, 4), 2.0 (5).

potential, especially in the region $\varphi = 1.5$ –1.7 V, and with a decrease in the concentration of thiosulphate in solution. Similarly to sulphite, the current yield calculated for the oxidation of thiosulphate according to eq. (6) slightly exceeds 100 %. This may be in part due to the additional oxidation of thiosulphate by dissolved oxygen, which accounts for 3–5 % as the blank experiment (without current) under the conditions of intense contact of solution with the air for 2.5 h showed. This value is much smaller than the observed excess for the yield as a function of current. Therefore, the most probable reasons of this excess are partial oxidation of thiosulphate to tetrathionate and the decomposition of thiosulphate in the near-surface layer at the anode due to local acidifying (see reaction (7)).

Similarly to sulphite oxidation, the addition of KBr into thiosulphate solution noticeably accelerates its anode oxidation, especially in the region of low concentrations (see Fig. 6, curve 4).

We also tested a new carbon material Karbopon V-22 in the anode oxidation of thiosulphate. In comparison with carbon felt VNG-30, it possesses much higher electric conductivity and larger specific surface but its porosity is somewhat lower. It was established that under similar conditions this material provides much higher rate of thiosulphate oxidation (Fig. 7). For example, at $\varphi = 1.5$ V, the degree of thio-

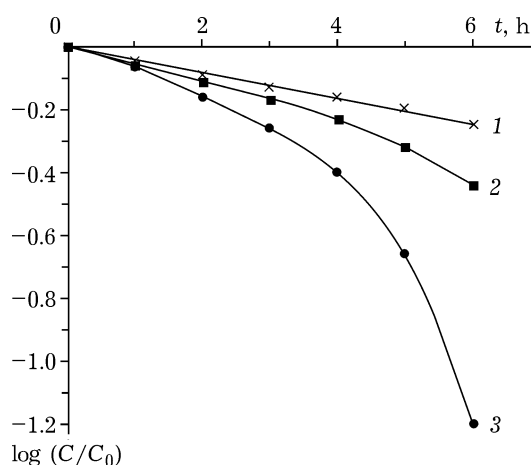


Fig. 7. Anode oxidation of thiosulphate on different carbon materials in the potentiostatic mode ($\varphi = 1.5$ V, solution: 10 g/L $\text{Na}_2\text{S}_2\text{O}_3$ + 1 M Na_2SO_4 ; pH 12.0): 1 - flat graphite; 2 - carbon felt VNG-30; 3 - Karbopon V-22.

sulphate oxidation after electrolysis for 6 h on a flat graphite electrode is 45 %, on carbon felt VNG-30 64 %, while on Karbopon V-22 94 % with the average current yield of 124 %.

So, investigation showed that the fibrous carbon materials VNG-30 and Karbopon V-22 possess sufficient stability for their use as flow porous anodes for the oxidation of sulphite and thiosulphate anions. Taking into account previously obtained results concerning the possibility of deep purification of fixing solutions from silver ions [2], it may be concluded that the use of the electrodes made of carbon fibre materials is promising for solving the problem of complete utilization of fixing solutions.

CONCLUSIONS

1. The dynamics of the anode oxidation of sodium sulphite (10 g/L) and sodium thiosulphate (10 g/L) solutions on carbon felt VNG-30 and Karbopon V-22 was studied. It was shown that both materials are rather stable under the anode polarization up to $\phi = 1.7$ V (s.c.e.) and can be used for the anode oxidation of both sulphite and thiosulphate.

2. It was established that the rate of sulphite and thiosulphate oxidation increases with an increase in anode polarization, especially with a decrease in the concentration of the

ions to be oxidized. The addition of KBr (up to 10 g/L) causes substantial increase in the rate of oxidation of these anions.

REFERENCES

- 1 A. V. Red'ko, *Osnovy Chernykh i Tsvetnykh Fotoprotsessov*, Iskusstvo, Moscow, 1990.
- 2 A. G. Belobaba, A. I. Masliy, D. V. Sukhorukov, Li Gann, *Chem. Sust. Dev.*, 15 (2007) 317.
URL: <http://www.sibran.ru/English/csde.htm>
- 3 V. K. Varentsov, A. F. Zhrebilov, M. D. Maley, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 17 (1984) 120.
- 4 A. G. Belobaba, A. I. Masliy, G. R. Bochkarev, G. I. Pushkareva, *Galvanotekhn. Obrab. Pov-sti*, 12 (2004) 30.
- 5 Yu. B. Kletenik, L. Yu. Polyakin, V. A. Tarasova, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 6 (1985) 63.
- 6 W. J. Williams, *Handbook of Anion Determination*, Butterworths, London, 1979.
- 7 M. R. Tarasevich, *Elektrokhimiya Uglerodnykh Materialov*, Nauka, Moscow, 1984.
- 8 V. K. Varentsov, V. I. Varentsova, *Khim. Ust. Razv.*, 8 (2000) 353.
- 9 T. Hunger, F. Lapique and A. Storck, *J. Appl. Electrochem.*, 21 (1991) 588.
- 10 B. V. Nekrasov, *Osnovy Obshchey Khimii, Khimiya*, Moscow, 1965.
- 11 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York, 1990.
- 12 J. Lu, D. B. Dreisinger and W. C. Cooper, *J. Appl. Electrochem.*, 29 (1999) 1161.
- 13 A. I. Masliy, N. P. Poddubny, A. V. Panasenko, *Elektrokhim.*, 33 (1997) 94.
- 14 R. Yu. Bek, *Izv. SO AN SSSR. Ser. Khim. Nauk*, 4 (1977) 11.
- 15 J. Feng, D. C. Johnson and S. N. Lowery, *J. Electrochem. Soc.*, 8 (1995) 2618.