JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 509–512

Anodic oxidation of cyanide on a reticulated three-dimensional electrode

P. TISSOT, M. FRAGNIÈRE

Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, 30 Quai E. Ansermet, CH-1211 Geneva 4, Switzerland

Received 21 June 1993; revised 10 November 1993

The preparation of a three-dimensional electrode suitable for the oxidation of dilute solutions of cyanide, by the electrodeposition of PbO_2 on a reticulated vitreous carbon substrate is described. The electrode obtained (RVC–PbO_2) is corrosion resistant and allows the oxidation of less than 5 p.p.m. of CN^- with a faradaic yield estimated at 50%. The mass transfer coefficient for the oxidation of the potassium ferrocyanide and the specific surface area of the RVC–PbO_2 electrode has been determined.

List of symbols

n	number of electrons
v	linear velocity of the electrolyte ($m\,s^{-1}$)
i_L	limiting current (A)
Q_v	volumetric flow ($m^3\,s^{-1}$)
C_e	concentration ($mol\,m^{-3}$)
A_e	specific surface area of the electrode (m^{-1})
L	length of the electrode (m)

1. Introduction

Several industries, including ore extraction, chemical synthetic manufacturing and metal finishing, produce cyanide waste streams. Detoxification, generally achieved by the oxidation of cyanide to the nontoxic cyanate, is based on chemical methods like alkaline chlorination, ozonation, hydrogen peroxide or air oxidation, sulphur-based technologies, etc. [1].

The electrochemical oxidation of cyanide represents an attractive alternative, since it obviates the use of dangerous chemicals and the formation of toxic volatile compounds containing chlorine, which may be formed during the alkaline chlorination.

The direct electrochemical oxidation of cyanide has been the subject of several reviews and publications [2–9]; the detailed mechanism of the reaction is still controversial, but it has been generally accepted that the first step of the electrochemical oxidation of cyanide is

$$CN^- + 2OH^- = CNO^- + H_2O + 2e^- \qquad (1)$$

This reaction is slow on platinum and graphite, and more active anodes like stainless steel, magnetite or lead present a lack of corrosion resistance. Electrodeposited lead dioxide on titanium [4, 10] or stainless steel [11] seems to be a good compromise between a good efficiency and acceptable corrosion.

To increase the specific surface area, several authors have used packed or fluidised bed anodes [12–18]. The purpose of this study is the development and the application of a reticulated vitreous carbon–lead dioxide (RVC–PbO_2) electrode. For the oxidation of cyanide, the main advantages of this anode are a good kinetic activity, a high specific surface area and a good corrosion resistance.

2. Experimental details

2.1. *Preparation of the RVC–PbO_2 electrode*

All the experiments were made with 6 mm thick plates of reticulated vitreous carbon (Energy Research and Generation, Oakland); the specific surface area, A_e, of the chosen porosity (30 p.p.i.) is $1700\,m^{-1}$. In order to increase the adhesion of the deposit, the RVC was treated anodically before coating for 3 min at $100\,A\,m^{-2}$ in 10% NaOH at room temperature. It is generally agreed that in strong acidic media, a relatively large number of small nuclei continue to grow and form a compact beta-PbO_2 phase [19]. The following conditions gave the best results. Electrolyte: $Pb(NO_3)_2$ 0.25 M; $Cu(NO_3)_2$ $3H_2O$ 0.041 M; HNO_3 1 M. Temperature: 20° C. Magnetic stirring. Anodic current density: $100\,A\,m^{-2}$. Duration: 75 min. Two stainless steel cathodes.

During PbO_2 deposition, significant dissolution of the RVC was observed at the air–electrolyte interface. To avoid this dissolution, the upper part of the RVC was sandwiched between two platinized titanium grids to ensure electrical contact, and the air–electrolyte interface was maintained at the level of the platinized titanium grids, so that the RVC was completely immersed.

With the above conditions, a regular coating was obtained over the whole electrode surface; the mean quantity of PbO_2 deposited was $43\,mg\,cm^{-2}$, which correspond to a faradaic yield of 76%. Such RVC–PbO_2 electrodes are suitable for cyanide oxidation. They have very good mechanical and chemical

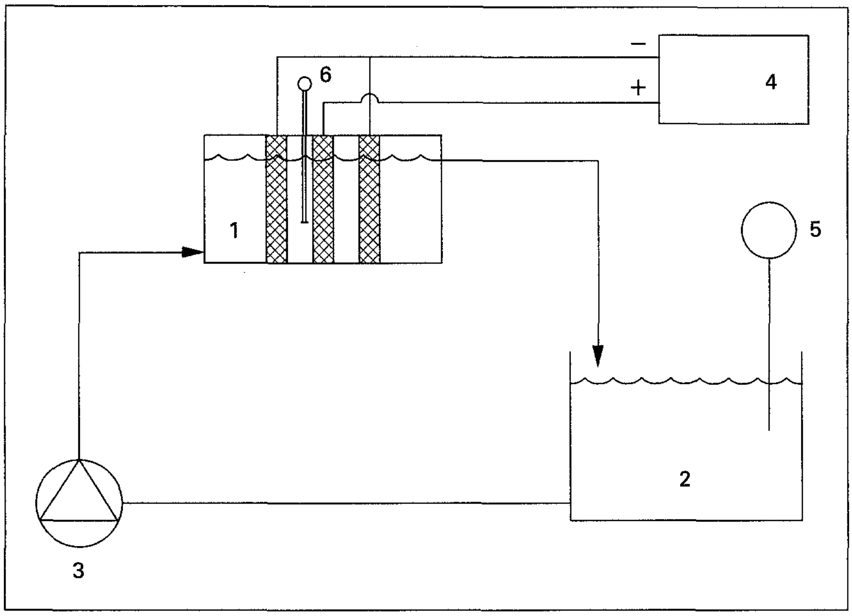

Fig. 1. Schematic diagram of the apparatus. (1) Electrochemical cell (length: 7×10^{-2} m; width: 3.3×10^{-2} m; electrolyte depth: 4×10^{-2} m; (2) thermostated tank; (3) pump (Ismatec MV7); (4) controlled DC unit (Witmer elektronic); (5) Ag/AgI specific electrode with data storage device (Wavetek 52); and (6) reference electrode (SCE).

stability in alkaline conditions and a large specific surface area of 2500 m^{-1} [20].

2.2. *Electrooxidation of cyanide*

The electrooxidation of cyanide was studied with the apparatus shown in Fig. 1. The parallelepipedic cell, made of Plexiglass, comprised two cathodes (RVC 30 p.p.i.; surface area: $2.7 \times 10^{-2}\,m^2$) and one anode (RVC–PbO_2; surface area: $2 \times 10^{-2}\,m^2$). The total volume of the electrolyte ($NaHCO_3$ 0.064 M; Na_2CO_3 0.036 M; CN^- 100 p.p.m.) was 500 ml. The temperature was maintained at 20° C at pH 10. The anode potential was measured during electrolysis with a saturated calomel reference electrode, corrected for ohmic drop, and expressed versus normal hydrogen electrode.

The Ag/AgI electrode was prepared according to the method described by Harzdorf [21]. It reacts with CN^- as indicated in Reaction 2:

$$AgI + 2CN^- = [Ag(CN)_2]^- + I^- \qquad (2)$$

and tends to dissolve in the electrolyte; however its life was more than 50 h with the cyanide concentration used in this study. The response time of the electrode was determined by the addition of 50 ml of water to 50 ml of a solution containing the electrode equilibrated with a known concentration of cyanide $[CN^-]^O$, and the measure of the time necessary to recover equilibrium. The results are given in Fig. 2. For concentrations higher than 1 p.p.m., the response time was less than 3 min, which allows the decay of CN^- during the electrolysis to be followed.

3. Results and discussion

3.1. *Determination of the mass transfer coefficient, K_d*

The limiting current for the anodic oxidation of $Fe(CN)_6^{4-}$ on the RVC–PbO_2 electrode was measured at different electrolyte velocities in the cell shown in Fig. 1. The experimental procedure has already been described [20]. The results are shown in

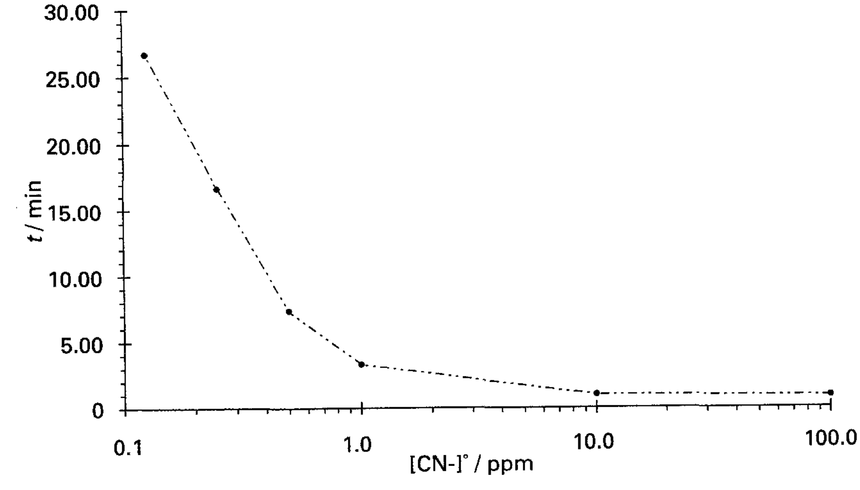

Fig. 2. Response time of the Ag/AgI electrode for 50% dilution of CN^-. ($[CN^-]^O$ is the concentration before dilution).

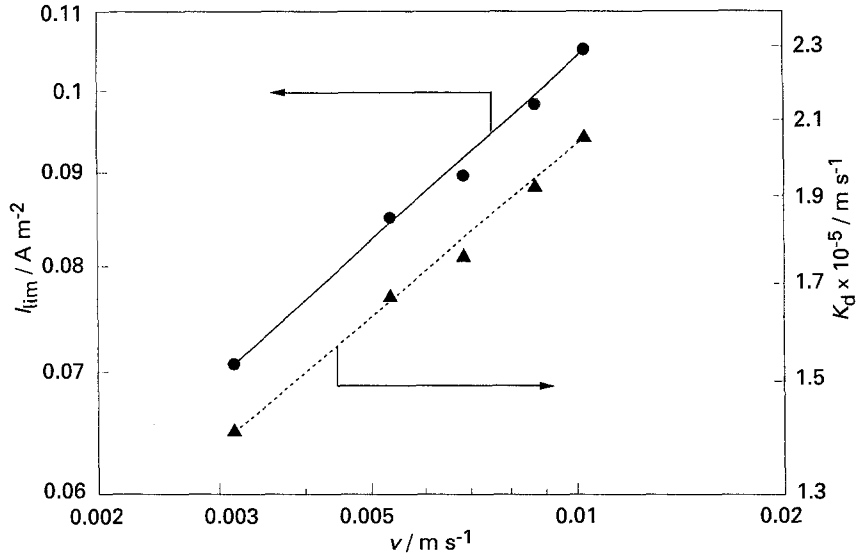

Fig. 3. Limiting current and mass-transfer coefficient as a function of the electrolyte velocity. Anode: RVC–PbO_2; temperature: 25° C; electrolyte: NaOH 2 M, $[Fe(CN)_6]K_3$ 5 × 10^{-2} M, $[Fe(CN)_6]K_4$ 5 × 10^{-3} M.

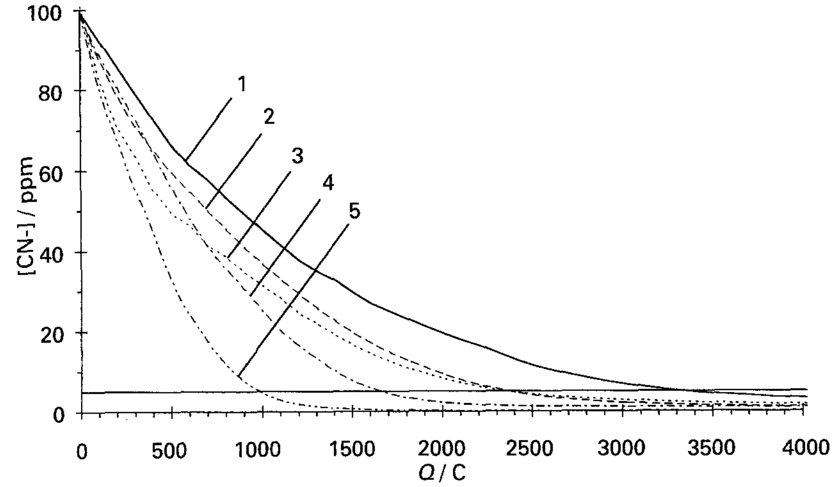

Fig. 4. Cyanide concentration as a function of the charge passed for different flow rates ($m^3 s^{-1}$) and current densities ($A m^{-2}$): (a) 6.6 × 10^{-6}, 17; (b) 6.6 × 10^{-6}, 8.5; (c) 6.6 × 10^{-6}, 4.25; (d) 10 × 10^{-6}, 17; (e) 3.3 × 10^{-6}, 17.

Fig. 3. Sioda [22] and later Coeuret [23] have shown that, in the case of a laminar flow in a porous electrode, the limiting current is proportional to v^a, where v is the fluid velocity and a is a constant between 0.32 and 0.42. The slope measured on Fig. 3 ($a = 0.33$) is in good agreement with the results proposed by these authors.

From the limiting current, the mass transfer coefficient can be calculated according to the Equation 3 [24]:

$$K_d = \frac{-\ln(1 - i_L/nFQ_vC_e)v}{A_eL} \tag{3}$$

The transfer coefficients (Fig. 3) are very close to those obtained for the same velocities with a nickel foam electrode of the same porosity [25]. Obviously the result depends greatly on the procedure of the preparation of the RVC–PbO_2 electrode. To obtain reproducible limiting current and mass transfer coefficient, the current density, the stirring and the duration must be strictly controlled during the PbO_2 electrodepostion.

Table 1. *Electrolyte flow rates*

Flow rate $/m^3 s^{-1}$	*Linear velocity* $/m s^{-1}$	*Residence time* /s	*Turnover of electrolyte* $/s^{-1}$
3.3 × 10^{-6}	0.0025	10	0.007
6.6 × 10^{-6}	0.0051	5	0.013
10.0 × 10^{-6}	0.0077	3.3	0.020

3.2. *Oxidation of cyanide*

Table 1 indicates the experimental conditions used for

Table 2. Results of cyanide oxidation

Run	*Current density* $/A m^{-2}$	*Flow rate* $/m^3 s^{-1}$	*Time** /s	*Charge** /C
1	17	3.3 × 10^{-6}	9900	3380
2	17	6.6 × 10^{-6}	7100	2380
3	17	10.0 × 10^{-6}	7100	2380
4	8.5	6.6 × 10^{-6}	9900	1690
5	4.25	6.6 × 10^{-6}	11800	990

* Values to reach 5 p.p.m.

the electrolyte flow; the residence time was calculated from the velocity and the length between the two cathodes (0.024 m).

During the electrolysis, the decay of the CN^- concentration with time was followed with a Ag/AgI electrode. The results obtained for several anodic current densities are shown in Fig. 4 and Table 2.

The straight line on Fig. 4 corresponds to a concentration of 5 p.p.m.; this concentration was chosen to compare the time and the quantity of electricity for the different experimental conditions.

It was not possible to calculate a faradaic yield, because the number of electrons involved in the process is not known. At the electrode potential measured during electrolysis (1.64 V vs NHE at 17 $A\,m^{-2}$), oxidation reactions (Reactions 4 and 5) are thermodynamically possible in addition to Reaction 1:

$$CNO^- + 2H_2O = HCO_3^- + \frac{1}{2}N_2 + 3H^+ + 3e^- \quad (4)$$

$$\frac{1}{2}N_2 + 3H_2O = NO_3^- + 6H^+ + 5e^- \quad (5)$$

The concentration of CNO^- was determined by spectroscopy at 680 nm of the complex $Cu(C_2H_5N)_2(OCN)_2$, according to the method described by Martin and McClelland [26]. At the end of each run, the main part (80 to 90%) of CNO^- formed by Reaction 1 was oxidized to HCO_3^- and probably NO_3^- (the presence of nitrate was not determined in this study). Comparison of runs 1, 2 and 3 of Table 2 shows that the results do not change when the flow rate is higher than $6.6 \times 10^{-6}\,m^3\,s^{-1}$; this means that the mass transfer is not the limiting phenomenon above this flow rate. By comparison of runs 2, 4 and 5, carried out at the same flow rate but at a decreasing current density, it is seen that a compromise must be found between a low consumption of electricity and a short electrolysis time.

4. Conclusion

RVC–PbO_2 is a suitable anode material for the oxidation of cyanide in dilute alkaline solutions. The stability of this electrode is excellent; no weight loss occured over more than 120 h of use, and lead concentration measured by atomic absorption in the electrolyte after each run was less than 0.1 p.p.m. Due to the high activity and specific area, the RVC–PbO_2 electrode produced an acceptable faradaic yield even when the cyanide concentration was less than 5 p.p.m. This yield can be estimated at 50% on the basis of the consumption of 6 faraday per mole.

Acknowledgement

We thank the Swiss National Science Foundation (Grant 21.31273.91) for financial support of this research.

References

[1] S. Palmet, M. A. Breton, T. J. Nunno, D. M. Sullivan and N. F. Surprenant, 'Metal/Cyanide Containing Wastes: Treatment Technologies', Noyes Data Corporation, Park Ridge (1988).
[2] J. P. Randin, *in* 'Encyclopedia of Electrochemistry of the Elements', Vol 8, (edited by A. J. Bard), Marcel Dekker, New York (1976) pp. 206.
[3] T. Arikado, C. Iwakura, H. Yoneyama and H. Tamura, *Electrochim. Acta* **21** (1976) 1021.
[4] F. Hine, M. Yasuda, T. Iida, Y. Ogata, *ibid.* **31** (1986) 1389.
[5] A. S. Hinman, R. A. Kydd, R. P. Cooney, *J. Chem. Soc., Faraday Trans. 1* **82** (1986) 3225.
[6] S. Yoshimura, A. Katagiri, Y. Deguchi and S. Yoshizawa, *Bull. Chem. Soc. Jpn* **53** (1980) 2434 and 2437.
[7] J. P. Wiaux and T. Nguyen, *Oberfläche-Surface* **31** (1990) 20.
[8] B. Wels and D. C. Johnson, *J. Electrochem. Soc.* **137** (1990) 2785.
[9] G. H. Kelsall, S. Savage and D. Brandt, *ibid.* **138** (1991) 117.
[10] T. C. Wen, *Plat. Surf. Finish.* **77** (1990) 54.
[11] J. Feng and D. C. Johnson, *J. Appl. Electrochem.* **20** (1990) 116.
[12] E. A. El-Ghaoui, R. E. W. Jansson and C. Moreland, *J. Appl. Electrochem.* **12** (1982) 69.
[13] E. A. El-Ghaoui and R. E. W. Jansson, *ibid.* **12** (1982) 75.
[14] J. P. Wiaux, *Oberfläche-Surface* **30** (1989) 25.
[15] M. Yasuda, A. Ohkawa, M. Tonsho and S. Yasukawa, *Denki Kagaku* **57** (1989) 682.
[16] R. Ochmann, B. Kastening, *Chem.-Ing.-Tech.* **61** (1989) 830.
[17] R. M. Sabarathinam, C. A. Basha, R. Vijayavalli, *Bull. Electrochem.* **1** (1985) 143, 207.
[18] M. L. Lin, Y. Y. Wang and C. C. Wan, *J. Appl. Electrochem.* **22** (1992) 1197.
[19] D. Velayutham and M. Noël, *Electrochim. Acta* **36** (1991) 2031.
[20] R. Alvarez, M. Fragnière, A. Lecoultre, F. Pasquini and P. Tissot, *Chimia* **46** (1992) 152.
[21] C. Harzdorf, *Anal. Chem.* **86** (1976) 103.
[22] R. E. Sioda, *Electrochim. Acta* **15** (1970) 783.
[23] F. Coeuret, J. M. Marracino and S. Langlois, *ibid.* **32** (1987) 1303.
[24] F. Coeuret and A. Storck, (Eds), Elements de Génie Électrochimique, Lavoisier, Paris (1984).
[25] S. Langlois and F. Coeuret, *J. Appl. Electrochem.* **19** (1989) 51.
[26] E. L. Martin and J. McClelland, *Anal. Chem.* **7** (1964) 304.