

# Electrochemical investigations of the Ce(III)/Ce(IV) couple related to a Ce(IV)-assisted process for SO<sub>2</sub>/NO<sub>x</sub> abatement

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This paper presents the results of electrochemical investigations of the Ce(III)/Ce(IV) couple, for use in a SO<sub>2</sub>/NO<sub>x</sub> abatement process. A voltammetric study was conducted at a platinum rotating disc electrode for the conditions corresponding to the gas scrubbing processes. The charge transfer coefficients were weakly affected by increasing the concentration of sulfuric acid up to 5 M. Conversely, the diffusion coefficients and the rate constants were decreasing functions of the concentration of sulfuric acid. The electrochemical regeneration of Ce(IV) was also studied at a platinized titanium surface and the oxidation appeared to be linked to other oxidative processes such as O<sub>2</sub> formation. Batch experiments, carried out in a filter press cell, showed good faradaic yields even in the potential domain corresponding to significant background current attributable to the supporting electrolyte.

## List of symbols

$C$	concentration (M or mol m <sup>-3</sup> )
$D$	diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
$E$	electrode potential (V)
$F$	Faraday constant (96 487 A s mol <sup>-1</sup> )
$i$	current density (A m <sup>-2</sup> )
$i_k$	kinetically limited current density (A m <sup>-2</sup> )
$i_L$	limiting current density (A m <sup>-2</sup> )
$k_0^0$	standard rate constant (m s <sup>-1</sup> )
$k_d$	mass transfer coefficient (m s <sup>-1</sup> )
$R$	gas constant (J K <sup>-1</sup> mol <sup>-1</sup> )
$T$	temperature (K)

## Greek letters

$\alpha$	charge transfer coefficient
$\eta$	overpotential (V)
$\mu$	dynamic viscosity (Pa s)
$\nu$	kinematic viscosity (m <sup>2</sup> s <sup>-1</sup> )
$\nu_e$	number of electrons involved
$\omega$	rotation rate (rad s <sup>-1</sup> )

## Subscripts

a	Anode
c	Cathode

## 1. Introduction

The Ce(III)/Ce(IV) redox couple has often been selected as a mediator in indirect electrooxidation because of its excellent selectivity for partial oxidation of organic compounds [1–5]. Because of its oxidizing properties, Ce(IV) has also been used in the treatment of waste biological material [6] as well as in processes for the removal of SO<sub>2</sub> and NO<sub>x</sub> from waste gases [7, 8]. In particular, we recently proposed a process in which the gas is continuously scrubbed in a gas–liquid column, the liquid solutions circulating in a loop through the column and an outer cell for the regeneration of Ce(IV) [9, 10]. Continuous oxidation of sulfur dioxide results in a regular increase in sulfuric acid concentration. Comprehensive design and development of the process require the investigation of the oxidant regeneration in the outer cell. Electrochemical methods can also yield physicochemical data, such as diffusion coefficients for use in the modelling of gas absorption with chemical reaction [11].

The electrochemistry of this couple has been

investigated for several decades on various surfaces, for example, noble metals or substrates coated with either noble metals or metal oxides. Most electrochemical data reported in the relevant literature are for 0.5 or 1 M sulfuric solutions and the case of more concentrated media has been scarcely considered. Regeneration of ceric species is often conducted for high concentration of cerium salts in various configurations: divided cells [3, 4, 12], undivided cells with very different areas of cathode and anode [13], or with *in situ* extraction of the Ce(IV) produced [2, 14].

The purpose of the present study is to investigate the electrochemistry of the Ce(III)/Ce(IV) couple for the conditions of the scrubbing process for SO<sub>2</sub> treatment: the electrode reaction was studied at a platinum layer, the concentration of cerium species was restricted below 20 mol m<sup>-3</sup> whereas the sulfuric acid concentration was varied from 0.1 to 5 M. A voltammetric study of the couple at a platinum RDE led to diffusion coefficients and to kinetic parameters of both the Ce(IV) reduction and Ce(III) oxidation. Then, the electrochemical regeneration of ceric

species was carried out at the platinized titanium (Pt/Ti) anode of a filter-press cell.

### 1.1. Reaction kinetics of Ce(III)/Ce(IV) couple

Oxidation of Ce(III) takes place at high potential and may be associated with oxygen formation, depending on the electrode material. Conducted at a platinum surface, the electrochemical reactions involving the couple are strongly governed by the platinum surface state and the complexation of both species, when dissolved in sulfuric media. Because of these phenomena, the couple does not exhibit Nernstian behaviour and the rest potential is affected by the nature and the concentration of the supporting electrolyte.

The presence of platinum oxides, of  $\alpha$  or  $\beta$  type, has been shown to govern the kinetics of both oxidation and reduction [15]. The recognition of this fact led to several methods being proposed for the surface pretreatment: potentiostatic operations [16–19], cyclic voltammetry [20], or a well-defined potential programme for the creation of a stable and reproducible oxide layer [21, 22].

### 1.2. Complexation of Ce(III) and Ce(IV) species in sulfuric acid media

Tetravalent cerium dissolved in sulfuric solution is strongly complexed by sulfate species [23] and, according to most authors (e.g. [3]) the species  $\text{Ce}(\text{SO}_4)_3^{2-}$  predominates in Ce(IV)-containing sulfuric solutions.

Complexation of trivalent cerium was indicated using spectrophotometric techniques by Newton and Arcand [24]; the dissociation quotient of the  $\text{CeSO}_4^+$  complex was reported to depend on the ionic strength of the sulfate solution through a Debye–Hückel law for ionic strengths in the range 0.2 to  $2 \text{ mol kg}^{-1}$ . The extent of complexation of cerous species was estimated through a thermodynamic approach for sulfuric media containing Ce(III), depending on the concentration of sulfuric acid and initial  $[\text{Ce}^{3+}]$  [25]. The dissociation of  $\text{CeSO}_4^+$  was assumed to obey the law reported in [24] and the non-ideal behaviour of dissolved matter was expressed by Pitzer's model for the  $\text{H}^+$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  ions [26]. The complexed form was shown to be of minor significance with a mole fraction below 4%, in the range of  $\text{H}_2\text{SO}_4$  concentration 0.1–5 M and Ce(III) concentration below  $200 \text{ mol m}^{-3}$ . Therefore  $\text{Ce}^{3+}$  is the predominant Ce(III) species, and physicochemical data obtained by electrochemical techniques can be considered to be those for  $\text{Ce}^{3+}$  ions.

## 2. Electrochemistry at a platinum surface

### 2.1. Experimental section

Reduction and oxidation at a platinum surface were investigated separately. The medium was a sulfuric acid solution containing either Ce(III) species at  $20 \text{ mol m}^{-3}$  for the oxidation, or  $10 \text{ mol m}^{-3}$  Ce(IV) for

the reduction. All chemical products, sulfuric acid, cerous sulfate, in the form of  $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , and ceric sulfate,  $\text{Ce}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  were of analytical grade (Pro-labo, France). Fresh solutions of Ce(IV) were titrated potentiometrically using ammonium-iron(II) sulfate solution with ferroine as an indicator. The electrical conductivities and the kinematic viscosities of all the solutions used were measured.

Voltammetric curves were recorded using a platinum disc electrode (diam. 2 mm). All potentials were referred to the saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode (0.658 V vs NHE at 25 °C) and a platinum cylindrical sheet acted as the counter-electrode. The electrodes were inserted in a laboratory glass cell provided with a water jacket and the temperature was fixed at  $25 \pm 0.2$  °C for all experiments. Oxygen was removed by blanketing the solution with a nitrogen flow.

The platinum electrode was chemically cleaned with a  $\text{H}_2\text{SO}_4$ – $\text{HNO}_3$  solution. Prior to voltammetric experiments for a given sulfuric acid concentration, the platinum surface was prepared by cycling the potential at  $100 \text{ mV s}^{-1}$  in a cerium-free solution of the same acid concentration. Both durations and potential ranges were selected to enable reproducible Ce(III)/Ce(IV) voltammograms to be recorded. These were, namely, (i) Ce(III) oxidation within the range  $-0.2$  to  $+1.2$  V for 30 min and (ii) Ce(IV) reduction within the range  $-0.7$  to  $+0.2$  V for 20 min.

For the reduction, attempts to activate the platinum electrode up to  $+0.7$  V or more, did not enable reproducible  $i/E$  curves of Ce(IV) reduction to be obtained. In addition, for the oxidation, the potential of the activation procedure was kept below 1.2 V to avoid formation of platinum oxides which could inhibit the electrochemical reactions. These potentials have to be compared with the rest potential of the couple, near 0.77 V, and its standard potential, 0.78 V in a 0.5 M sulfuric medium. Voltammetric curves of the Ce(III)/Ce(IV) system were recorded at  $5 \text{ mV s}^{-1}$  and the rotation rate was varied from 100 to 3000 rpm. Electrode pretreatment was repeated after each voltammetric curve.

### 2.2. Interpretation procedure

The electrode potential was corrected for ohmic drop by applying the term for the total primary distribution together with the electrical conductivity of the solution used [27]. The overpotential was deduced from the corrected potential and the rest potential measured for each ( $i/E$ ) curve.

$i/E$  curves exhibited well-defined plateaus and the residual current was negligible for the reduction and the oxidation below 1.0 V; above this value, this current was subtracted from the overall current. Voltammetric curves recorded for separate reactions were interpreted using a classical model describing electrochemical reaction together with diffusion phenomena at the rotating surface:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.621 \nu_e F C D^{2/3} \nu^{-1/6} \omega^{1/2}} \quad (1)$$

where  $D$  represents the diffusion coefficient for Ce(III) or Ce(IV) species. The effect of migration phenomena was neglected since supporting electrolyte was in excess concentration.  $i_k$  is the current density in the absence of mass transfer control;  $i_k$  was expressed considering the irreversible reaction at the surface. In addition, as shown by Randle and Kuhn [21] for the cerium concentrations considered, oxidation and reduction were postulated to be first-order processes with respect to Ce(III) and Ce(IV), respectively:

$$i_k = \nu_e F k_{0a}^0 [\text{Ce(III)}] \exp\left(\alpha_a \frac{\nu_e F \eta}{RT}\right) \quad \text{for Ce(III) oxidation} \quad (2a)$$

$$i_k = \nu_e F k_{0c}^0 [\text{Ce(IV)}] \exp\left(-\alpha_c \frac{\nu_e F \eta}{RT}\right) \quad \text{for Ce(IV) reduction} \quad (2b)$$

If both reactions were simple electron transfers, coefficients  $\alpha_a$  and  $\alpha_c$  would add to one and the standard rate constants would be identical. The values of the parameters—diffusion coefficient, charge transfer coefficient and standard rate constant—were deduced by numerical fitting of the experimental ( $i/E$ ) variations.

### 2.3. Diffusion coefficient

The diffusion coefficient of Ce(IV) species varies from  $4.5 \times 10^{-10}$  to  $1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in the concentration range 0.1–5 M (Fig. 1): this coefficient is fairly constant in dilute sulfuric solution at  $4.5 \pm 0.12 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , then strongly decreases for concentrations between 0.7 and 1.5 M. Increasing the sulfuric acid concentration further results in a smoother and more regular decay of the diffusion coefficient. Values in dilute solution are consistent with published data: values varying from  $3.4 \times 10^{-10}$  to  $6.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in a 0.5 M solution [16–21] or  $(3.4\text{--}3.7) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  given by Kiekens *et al.* [28] in a molar H<sub>2</sub>SO<sub>4</sub> solution.

The decreasing variation of the diffusivity is linked to the change in the viscosity,  $\mu$ , of the solution. The

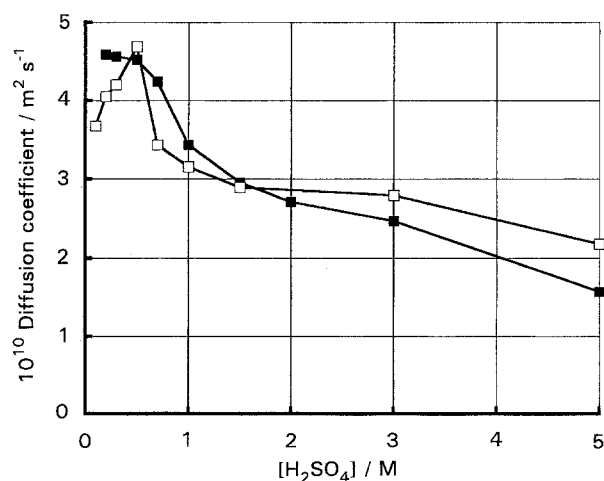


Fig. 1. Variation of the diffusion coefficient of Ce(III), (□), and of Ce(IV), (■), with the concentration of sulfuric acid at 25 °C.

most classic relationship is the Stokes–Einstein equation:

$$\frac{D\mu}{T} = \text{constant} \quad (3)$$

and its derived expressions, even though these laws allow a poor description of the interactions between the various species dissolved in electrolyte solutions. At 25 °C, the product ( $D\mu$ ) is slightly affected by the concentration of sulfuric acid: ( $D\mu$ ) is equal to  $4.40 \pm 0.20 \times 10^{-13} \text{ Pa m}^2$  below 1 M, and in the range  $(3.7\text{--}3.8) \times 10^{-13} \text{ Pa m}^2$  in more concentrated media.

The diffusion coefficient of Ce(III) is observed to increase with the acid concentration and a well-defined maximum appears near 0.5 M (Fig. 1): the value obtained,  $4.82 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , is in a good agreement with literature data ( $4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  according to Vetter [29] and  $5.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  after reference [21]). The presence of this maximum was confirmed by additional experiments. A sharp decrease is observed for intermediate concentrations and the variation becomes more regular over 1 M. Applying Stokes' law does not result in constant values of the product ( $D\mu$ ): in particular, the maximum in  $D$  seems to contradict this law, since the viscosity is an increasing function of the acid concentration in the investigated range.

### 2.4. Kinetic parameters

The charge transfer coefficient of Ce(III) oxidation,  $\alpha_a$ , is roughly constant at 0.29 within 0.03 and the effect of the sulfuric acid concentration is very weak (Fig. 2). On the other hand, the reduction transfer coefficient,  $\alpha_c$ , is an increasing function of the acid concentration in the range 0.1–1 M, then remains fairly stable near  $0.32 \pm 0.01$  in more concentrated media. The sum of the two charge transfer coefficients is not equal to one because of the complexation phenomena and the likely involvement of sulfate species in the redox process. Both sets of values are consistent with the

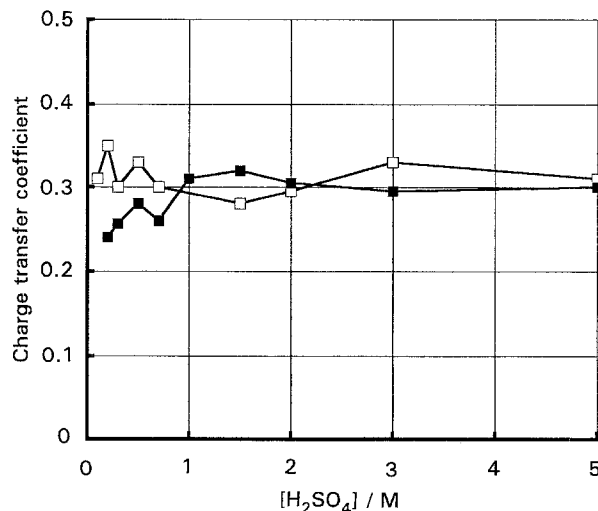


Fig. 2. Charge transfer coefficient for Ce(III) oxidation,  $\alpha_a$  (□), and Ce(IV) reduction,  $\alpha_c$  (■), as a function of the concentration of sulfuric acid at 25 °C.

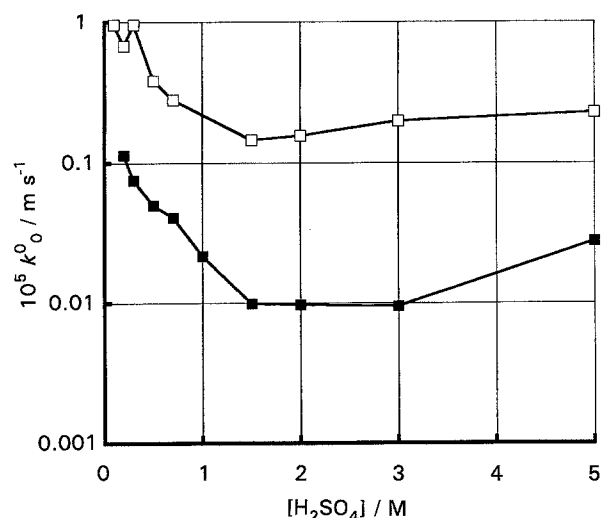


Fig. 3. Standard rate constant for Ce(III) oxidation,  $k_{\text{Ox}}^0$  ( $\square$ ), and Ce(IV) reduction,  $k_{\text{Red}}^0$  ( $\blacksquare$ ), as a function of the concentration of sulfuric acid at 25°C.

available data related to dilute solutions [15, 17, 19, 28].

The standard rate constants of both reduction and oxidation decrease strongly with increasing sulfuric acid concentration, which appears to inhibit the charge transfer over a large range of concentration (Fig. 3). The rates of both processes pass through very flat minima near 1.5 M and  $k_0^0$  values are slightly greater over 2 M, especially for the Ce(IV) reduction. In spite of similar tendencies, reduction and oxidation are processes of different rate constant: Ce(IV) reduction seems to occur with a constant an order of magnitude below that of Ce(III) oxidation. For instance,  $k_0^0$  in a 0.5 M sulfuric solution is found to be  $3.8 \times 10^{-6} \text{ m s}^{-1}$  for the oxidation and  $5.0 \times 10^{-7} \text{ m s}^{-1}$  for the reduction. Both series of data are consistent with published data which vary typically from some  $10^{-7} \text{ m s}^{-1}$  to some  $10^{-5} \text{ m s}^{-1}$  [15–22, 29].

The different rates obtained for the two reactions suggest that Ce(III)/Ce(IV) is not a simple electron transfer couple. In addition, this difference seems to

contradict the results obtained from redox voltammograms [21, 22]. The reaction constant rates depend on the electrode surface, and thus on the pretreatment, and it is likely that potential cycling results in a platinum surface which is different from that produced using Randle and Kuhn's potential programme.

### 3. Regeneration in a filter-press cell

#### 3.1. Experimental section

Ce(III)-containing solutions were submitted to anodic oxidation in a laboratory filter-press cell described in a previous paper [30]. The reactor is provided with an Ionac™ membrane. In both compartments, the electrode was a stack of three sheets of expanded platinumized titanium (Oxy-Metal Industries, France) with a platinum thickness of  $2.5 \mu\text{m}$ . External dimensions of one sheet were  $40 \text{ mm} \times 70 \text{ mm}$  and the wetted area of the 3D electrode was estimated to  $0.012 \text{ m}^2$ . The device consisted in a batch recirculating system provided with pumps, flowmeters and storage tanks. Moreover, a heat exchanger allowed the temperature of the anodic solution to be kept to  $25 \pm 1^\circ\text{C}$ .

All experiments were carried out with one litre of sulfuric solution containing  $20 \text{ mol m}^{-3}$  Ce(III) in the anodic circuit. A sulfuric acid solution was introduced into the counter compartment and hydrogen was formed at the cathode. Electrode potential, referred to the saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode was kept constant and the cell current was continuously recorded. The conversion of Ce(III) was followed by potentiometric titration of the fractions sampled.

The superficial velocity of the solution was fixed at  $0.236 \text{ m s}^{-1}$  and the mass transfer rate at the electrode was deduced from previous measurements [30] with the NaOH-potassium hexacyanoferrate system, taking into account the changes in diffusion coefficient and kinematic viscosity. The limiting current density in a 0.5 M sulfuric cerous solution was therefore estimated to be  $66.4 \text{ A m}^{-2}$ . The effects of the

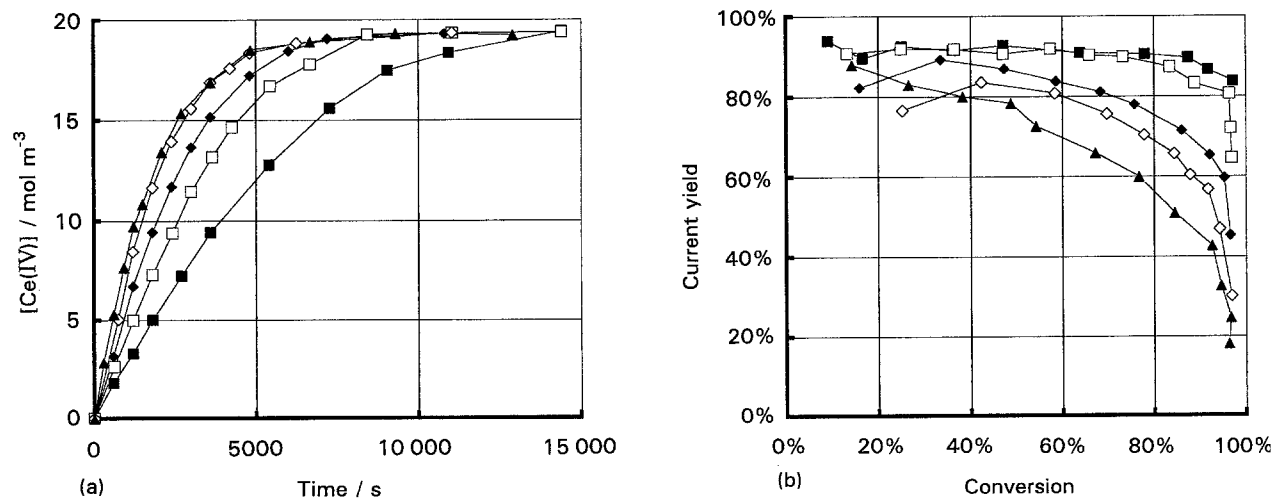


Fig. 4. Batch oxidation of one litre of  $20 \text{ mol m}^{-3}$  Ce(III) solution in the filter-press cell (electrode area:  $0.012 \text{ m}^2$ , superficial velocity:  $0.24 \text{ m s}^{-1}$ ), for various values of the electrode potential referred to Hg/Hg<sub>2</sub>SO<sub>4</sub> system; concentration of sulfuric acid: 0.5 M. (a) Time variation of Ce(IV) concentration; (b) variation of the current yield with the extent of conversion. Key: ( $\blacksquare$ ) 1.15, ( $\square$ ) 1.25, ( $\blacklozenge$ ) 1.35, ( $\diamond$ ) 1.45 and ( $\blacktriangle$ ) 1.55 V.

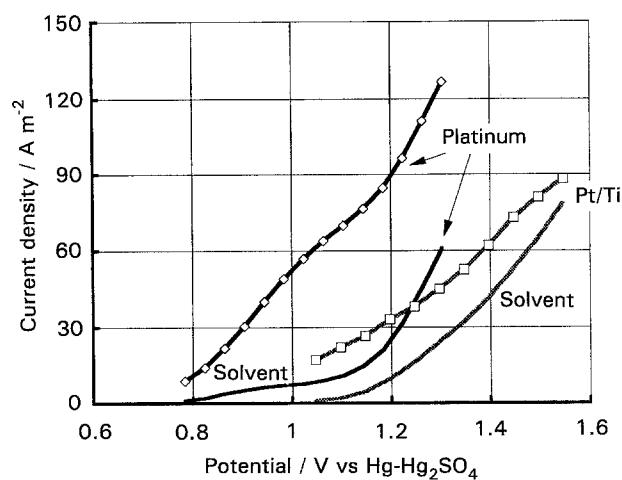


Fig. 5.  $i/E$  curves at the filter-press anode of the ground electrolyte ( $\text{H}_2\text{SO}_4$  0.5 M) or with  $20 \text{ mol m}^{-3}$  Ce(III); comparison of the experimental curves recorded at the Pt/Ti anode (in grey) with the voltammetric curves at platinum surface (in black) which were obtained at a Pt RDE for the ground electrolyte, and by calculation for the overall current, as explained in the text.

electrode potential and the sulfuric acid concentration on both the conversion rate and the current yield, were observed.

### 3.2. Effect of electrode potential

Batch runs were carried out using a 0.5 M sulfuric acid solution of cerous salt and the potential ranged between 1.15 V and 1.55 V; the corresponding current density at  $t = 0$  was in the range  $26\text{--}89 \text{ A m}^{-2}$ . The conversion was almost complete within four hours, as shown in Fig. 4(a). Increasing the potential up to 1.40 V allowed faster oxidation, the rate of which remained unchanged over 1.40 V. The raw data were expressed in terms of current efficiency and conversion: Fig. 4(b) shows that the oxidation can be achieved with current yield over 80% for the lowest potentials; conversely, increasing the electrode up to 1.45 V resulted in lower yields and significant side-formation of oxygen was observed. Potentials in the range 1.20–1.40 V allowed fair current yields,

in the range 60–80%, with satisfactory production rates.

Voltammetric curves were recorded in the cell to interpret the effect of the electrode potential on the cell performance. Firstly, as regards the ground electrolyte, comparison of the  $i/E$  curve recorded at the platinum disc electrode with that obtained on the Pt/Ti surface showed the significant effect of the electrode material (Fig. 5). Moreover, the oxidation of cerous salts at the expanded Pt/Ti electrode resulted in an  $i/E$  curve parallel to that for the ground electrolyte (Fig. 5): in contrast to the behaviour observed with the platinum electrode, the so-called residual current cannot be subtracted from the overall current. The electrochemical behaviour of an expanded platinum electrode was simulated taking into account the limiting current density in the filter-press cell and the kinetic parameter values given in Section 2.4; residual current at a Pt disc electrode was added to the current obtained. This enabled comparison of both electrode materials for Ce(III) oxidation, as shown in Fig. 5: the oxidation of cerous salts appeared to be a slower process at a Pt/Ti electrode than at a pure platinum surface. Whereas the oxidation could be conducted under diffusion control between 1.1 and 1.2 V at a pure platinum surface, higher potentials were required for fair production rates at a platinized surface. The electrochemical oxidation of Ce(III) species seems to be partly linked to other oxidative processes at the electrode; for example, formation of platinum oxides and oxygen evolution, for higher potential values. Further investigations are required to confirm this observation.

### 3.3. Effect of sulfuric acid concentration

The effect was followed for an electrode potential of 1.35 V, allowing high current yields and good conversions to be obtained. The cell current recorded for the run was observed to be reduced by a rise in acid concentration. Both the diffusion coefficient

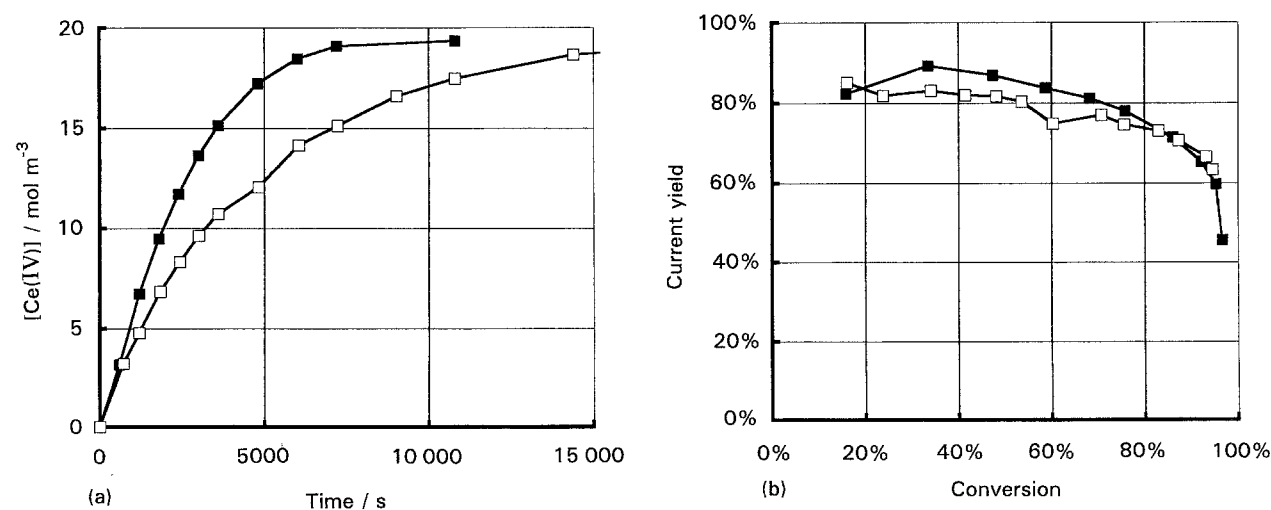


Fig. 6. Batch oxidation of one litre of  $20 \text{ mol m}^{-3}$  Ce(III) solution in the filter-press cell (electrode area:  $0.012 \text{ m}^2$ , superficial velocity:  $0.24 \text{ m s}^{-1}$ ), at 1.35 V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>; influence of the concentration of sulfuric acid: 0.5 M, (■) and 5 M, (□); (a) Time variation of Ce(IV) concentration; (b) variation of the current yield with the extent of conversion.

and the standard rate constant were much lower in a 5 M medium than in a 0.5 M solution, as shown above. In the early stages of the batch run, the conversion rate in a 5 M medium was twice lower than in a 0.5 M solution, as shown in Fig. 6(a). However, calculated current yields were not affected significantly by changing the concentration of sulfuric acid and the deviations did not exceed a few percent (Fig. 6(b)). In both solutions, current yields of 80 and 60% were obtained for conversions of 70 and 95%, respectively.

#### 4. Conclusion

Investigation of Ce(III) oxidation and Ce(IV) reduction by linear voltammetry at a platinum disc electrode yielded values for the diffusivities, the charge transfer coefficients and the rate constants, over a large domain of sulfuric acid concentration. The diffusion coefficients of both species decreased regularly with the sulfuric acid concentration: the values obtained were used for modelling the absorption of sulfur dioxide into Ce(IV)-containing solutions and for the determination of the kinetic constants of the liquid phase oxidation of SO<sub>2</sub> [10].

Whereas the charge transfer coefficients remain roughly constant near 0.30, the rate constants of both reactions are decreasing functions of the acid concentration in the range 0.1–2 M. When conducted at Pt/Ti surface, the oxidation appears to be linked to oxidative phenomena occurring with the ground electrolyte, and the process of Ce(IV) formation at this surface may differ from that on a pure platinum electrode. In addition, dilute solutions of Ce(IV) can be regenerated at a Ti/Pt electrode with high current yields, whatever the concentration of sulfuric acid.

These encouraging results have been confirmed at larger scale using a 0.80 m<sup>2</sup> Prod-Cell<sup>TM</sup> (Electro-Cell AB, Sweden) in series with a gas-liquid absorption column for the continuous treatment of 50 m<sup>3</sup> h<sup>-1</sup> of SO<sub>2</sub> containing waste gas [31]. Preliminary results obtained with a pilot device suggest that, regardless of the investment cost, the electrochemical regeneration of the Ce(IV) consumed for the removal of 1 kg SO<sub>2</sub>, was in the range 0.10–0.25 Ecu, depending on the operating conditions.

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