

SHORT COMMUNICATION

Use of Zr/ZrO₂ as a counter electrode for the minimization of loss reactions in single compartment electrolysis cells

Y. MALHERBE, Ch. COMNINELLIS*

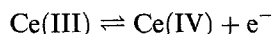
Institute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Received 7 June 1993; revised 22 September 1993

1. Introduction

It is generally recognized that electrosynthetic processes have a better chance of commercial exploitation if they can be performed in a diaphragm-less electrolysis cell. Unfortunately, the use of these simpler electrolysis cells is only possible when the feedstock and product are inactive at the counter electrode. When this is not the case other measures must be taken to minimize the rate of material loss at the counter electrode.

For example consider the electrochemical oxidation of Ce(III) to Ce(IV), which is a reversible electrochemical reaction



The maximum degree of conversion of Ce(III) in a single compartment cell with geometrically identical working and counter electrodes and uniform stirring will be 50%.

The situation may be improved in various ways, for example: by reducing the size of the counter electrode relative to the working electrode [1, 2], or by *in situ* formation of a selective film at the counter electrode. This last technique is used in the electrosynthesis of chlorate in which chromate (which is introduced in the feed solution) is reduced at the cathode to an ion selective film which inhibits the cathodic reduction of ClO₃⁻ [3]. Although functional, these methods are not entirely satisfactory. In the first instance a more complex electrode design is necessary and in the second instance the solution is contaminated with chromate.

In this work new possibilities for the minimization of the rate of material loss at the cathode (counter-electrode) are presented using valve metal oxide cathodes (TiO₂, ZrO₂, Ta₂O₅,...). These oxides can be formed directly on the valve metal using different techniques (thermal treatment, anodic oxidation, chemical oxidation,...) or can be prepared on a conductive substrate using the thermal decomposition technique [4].

The present paper is a preliminary study of the cathodic properties (reduction of Ce(IV) and hydrogen evolution) of ZrO₂ layer formed on zirconium

by thermal treatment at high temperature. Zirconium was chosen as base metal due to the fact that this valve metal is stable under conditions of hydrogen evolution.

2. Experimental details

2.1. Thermal treatment of zirconium

The zirconium plates of 2 mm thickness (Signer Titanium, quality: ZR 702) were sand blasted, washed with water and then thermally treated in air at 550 °C for three hours (Solo furnace type 111-13). Thermogravimetric measurements for metallic zirconium have shown that, at this temperature, a layer of ZrO₂ is formed at the zirconium surface [4]. For this reason the thermally treated zirconium is designated as Zr/ZrO₂.

2.2. Preparative trials, current-potential curves and analysis

To study the influence of the thermal treatment of zirconium on the cathodic rate of Ce(IV) reduction a two-compartment and a single-compartment cell were used. In the two-compartment cell (160 cm³ capacity) the test cathode was a platinum or zirconium (thermally treated or not) cylinder (30 cm² area), and the anode was a platinum spiral enclosed in a 10 cm³ porous porcelain pot; stirring was provided by a magnetic bar. The catholyte was 0.2 M Ce(SO₄)₂ solution in 1 M H₂SO₄ and the anolyte 1 M H₂SO₄. The electrolysis was carried out at constant current density (50 mA cm⁻²) and temperature (50 °C).

The single-compartment cell contained two parallel plates (10 cm² area each), the anode (platinum), and the test cathode (zirconium or thermally treated zirconium). The electrolyte was 0.2 M Ce₂(SO₄)₃ solution in 1 M H₂SO₄ and the electrolysis conditions were identical to the two-compartment cell.

The current-potential (*I/V*) curves were obtained after *IR* drop correction using the current interruption technique. Current densities were based on the geometrical area of the test cathode and Hg/Hg₂SO₄ · K₂SO₄ (sat.) was used as a reference electrode.

* Author to whom correspondence should be addressed.

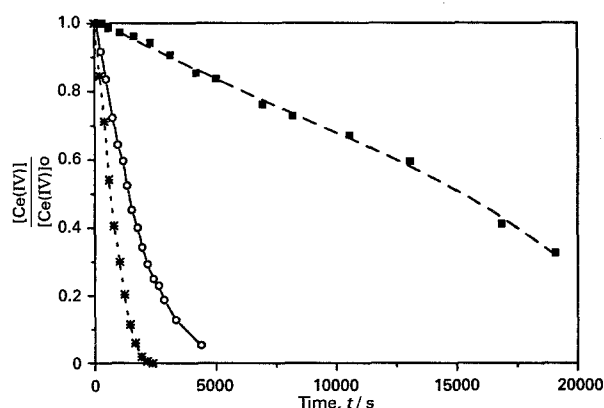


Fig. 1. Decrease of Ce(IV) concentration (relative to the initial value) during the electrochemical reduction of 0.2M Ce(SO₄)₂ in a two-compartment cell using Pt (*), Zr (O), and Zr/ZrO₂ (■) cathodes. Electrolyte: 1 M H₂SO₄, $i = 50 \text{ mA cm}^{-2}$, $T = 50^\circ \text{C}$.

The Ce(IV) concentration change during electrolysis was determined by iodometric titration.

3. Results

3.1. Preparative electrolysis

Figure 1 shows the decrease of Ce(IV) concentration (relative to the initial value) during the electrochemical reduction of 0.2M Ce(SO₄)₂ solution in the two-compartment cell using Pt, Zr, and Zr/ZrO₂ cathodes. The thermally treated zirconium (Zr/ZrO₂ cathode) results in a considerable decrease in the rate of Ce(IV) reduction.

The results obtained in a single compartment cell with geometrically identical anode (Pt) and cathode (Zr or Zr/ZrO₂) show that for the zirconium cathode the maximum degree of conversion of Ce(III) is about 0.5 (Fig. 2). This is due to the fact that at this conversion the flux of Ce(III) to the anode is equal to the flux of Ce(IV) to the cathode (the latter resulting in a loss of current efficiency). The situation is completely different for the Zr/ZrO₂ cathode for which, not only the rate of attainment of equilibrium is decreased, but the maximum degree of conversion is considerably increased (~ 0.9).

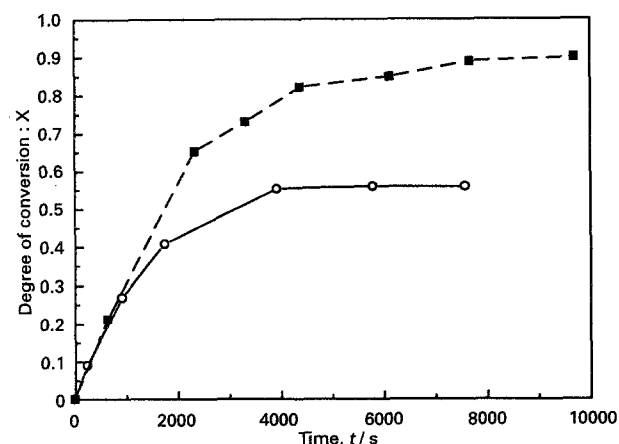


Fig. 2. Degree of conversion (X) of Ce(III) to Ce(IV) during electrolysis of 0.2M Ce₂(SO₄)₃ solution in 1M H₂SO₄ using Zr (O) and Zr/ZrO₂ (■) cathodes. $i = 50 \text{ mA cm}^{-2}$, $T = 50^\circ \text{C}$.

To quantify this behaviour we consider that the reduction of Ce(IV) (in a two-compartment cell) is a first order reaction.

$$\frac{d[\text{Ce(IV)}]}{dt} = -\frac{k_i A}{V} [\text{Ce(IV)}] \quad (1)$$

where

k_i rate constant of Ce(IV) reduction at a given cathode (m s^{-1})

A geometrical cathode area (m^2)

V electrolyte volume (m^3)

t time of electrolysis (s)

Integrating Relation 1, considering that at $t = 0$ $[\text{Ce(IV)}] = [\text{Ce(IV)}]_0$ we obtain

$$\ln \frac{[\text{Ce(IV)}]}{[\text{Ce(IV)}]_0} = -\frac{k_i A}{V} t \quad (2)$$

Thus a plot of $\ln\{[\text{Ce(IV)}]/[\text{Ce(IV)}]_0\}$ against t for different cathodes give a straight line having a slope $-k_i A/V$ (Fig. 3).

Table 1 gives the rate constants (determined from Fig. 3) for the reduction of Ce(IV) using Pt, Zr, and Zr/ZrO₂ cathodes; in the same table the decrease in rate constants for zirconium and Zr/ZrO₂ relative to platinum cathodes, defined as the factor γ (eq. 3), are given.

$$\begin{aligned} \gamma &= \frac{\text{rate constant for Ce(IV) reduction at Zr or ZrO}_2}{\text{rate constant for Ce(IV) reduction at Pt}} \\ &= \frac{k_i}{k_{\text{Pt}}} \end{aligned} \quad (3)$$

This table clearly shows the drastic reduction in the reaction rate constant for Ce(III) reduction obtained with thermally treated zirconium (Zr/ZrO₂).

3.2. Electrochemical measurements

Figure 4 shows the current-potential (I/V) curves (with IR drop correction) for Zr and Zr/ZrO₂ cathodes in 1M H₂SO₄ in the presence and absence of Ce(IV). The main characteristics of these curves are:

(i) At the zirconium cathode and in the presence of Ce(IV) (curve II) there is a shift of the I/V curve to more negative values indicating that the reduction of Ce(IV) at the zirconium cathode occurs before hydrogen evolution (curve I).

(ii) The Zr/ZrO₂ cathode (curve III) has higher hydrogen evolution overpotential than zirconium (curve I), and the presence of Ce(IV) (curve IV) slightly modifies the I/V curve (curve IV) indicating that the overpotential for Ce(IV) reduction is strongly increased at the Zr/ZrO₂ cathode.

Thus the current-potential curves confirm the preparative electrolysis results: the Zr/ZrO₂ cathode strongly decreases the rate of Ce(IV) reduction.

4. Discussion

The observed effect of a decrease in the rate of Ce(IV)

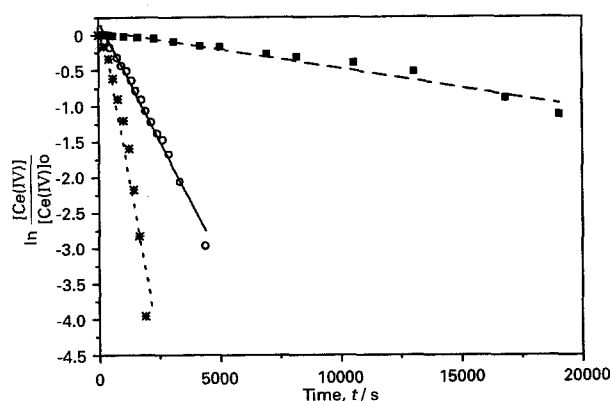


Fig. 3. Determination of the rate constant of Ce(IV) reduction at a Pt (*), Zr(O) and Zr/ZrO₂ (■) cathode using Relation 2. Conditions: as in Fig. 1.

reduction (and consequently increase of the rate of hydrogen evolution) on Zr/ZrO₂ cathodes may be explained by two different models.

(a) The kinetic model in which a selective increase in overpotential for the Ce(IV) reduction process occurs at the Zr/ZrO₂ cathode without a commensurate increase in the hydrogen evolution overpotential.

(b) The diaphragm model in which the cathodic reduction of Ce(IV) (which in H₂SO₄ solution is present in the form of the Ce(SO₄)₃²⁻ anion [5]) is suppressed by the adverse potential gradient generated

Table 1. Rate constant k_1 and the factor γ for Ce(IV) reduction at different cathodes*

Electrodes	k_1 /m/s	$\gamma = k_1/k_{Pt}$
Pt	4.8×10^{-5}	1.00
Zr	3.1×10^{-5}	0.62
Zr/ZrO ₂	2.5×10^{-6}	0.16

* Conditions: as in Fig. 1

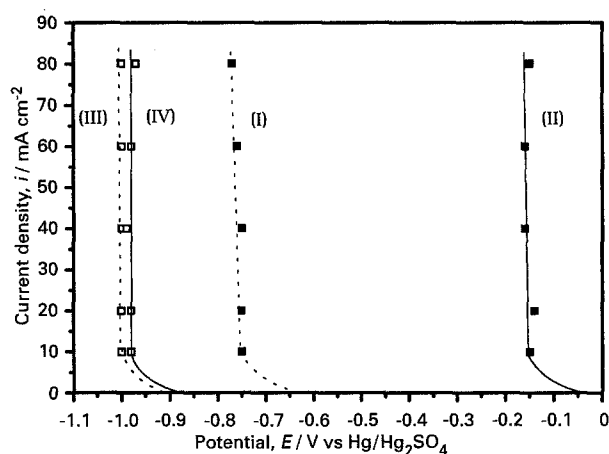


Fig. 4. Current-potential curves for Zr (■) and Zr/ZrO₂ (□) cathodes with (—) or without (-----) Ce(IV) in 1 M H₂SO₄.

by the ZrO₂ film, whereas the cathodic reduction of protons (cation) is unhindered under the same conditions [6].

The current-potential curves confirm the first model, in which the increase in overpotential for Ce(IV) reduction on Zr/ZrO₂ is much higher than that for hydrogen evolution. Work is now in progress to clarify the mechanism of hydrogen evolution and Ce(IV) reduction on Zr/ZrO₂. Long time stability tests of the Zr/ZrO₂ cathodes are also under investigation.

References

- [1] Carus Chem. Co., *US Patent 2 843 537* (1958).
- [2] Carus Chem. Co., *US Patent 2 980 620* (1959).
- [3] E. Müller and P. Ekwall, *Z. Electrochem.* **35** (1929) 84.
- [4] G. P. Vercesi, J. Rolewicz, and Ch. Comninellis, *Thermochim. Acta* **176** (1991) 31.
- [5] T. J. Hardwick and E. Robertson, *Canad. J. Chem.* **29** (1951) 828.
- [6] C. Wagner, *J. Electrochem. Soc.* **101** (1954) 181.