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Studies of the oxidation of ethanol on a reticulated nickel rotating cylinder electrode

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Reticulated nickel rotating cylinder electrodes (RRCE) of different porosity grade have been developed and used in the study of the oxidation of ethanol in 1 M KOH. Well-formed waves have been obtained by voltammetry at 2 and 50 mV s^{-1} and the RRCE seems to be a promising tool for electrochemical kinetic studies. As expected for a reaction not controlled by diffusion, the current does not depend on the rotation rate of the electrode.

1. Introduction

Three-dimensional electrodes are used in many electrochemical reactors to increase the rate of conversion and the properties of such electrodes have been extensively reviewed [1, 2]. These electrodes are particularly useful when a low current density must be used, due to a low concentration of the reactant or a slow chemical step.

Recently two research groups [3, 4] have published results on the electrochemical oxidation of an alcohol to the corresponding carboxylic acid on nickel foam. This is a well known reaction of synthetic interest [5–11] but is limited in its application by the low rate of conversion on planar electrodes. On one hand Coeuret *et al.* [3] have not succeeded in observing the formation of NiOOH on a nickel foam by cyclic voltammetry in the presence of diacetone-1-sorbose; on the other hand Pletcher *et al.* [4] had difficulty in identifying the limiting plateaux during the oxidation of ethanol on a nickel foam. The difficulties encountered in displaying this phenomenon were probably due to the insufficiently uniform flow, current and potential-distribution generally observed on three-dimensional electrodes. Generally speaking, it is important to study an electrochemical reaction by voltammetry and other methods on the same electrode as will be used at the preparatory scale. This is especially important in the case of a reaction like the oxidation of alcohol on a nickel oxide layer, which depends strongly on the catalytic activity, the history, the pretreatment and the composition and morphology of the nickel oxide surface. The aim of this paper is to present results of a study of the oxidation of ethanol on a reticulated nickel rotating cylinder electrode (RRCE). The major reasons for the adoption of an RRCE to study this reaction, fully controlled by the surface reaction kinetics, were well-defined flow conditions, known solutions of the transport dependence on rotation speed and a reproducible, known electroactive surface area.

Such rotating cylinder foam electrodes have been used for some time in the field of metal ion analytical work [12–14] and controlled potential coulometry and mass transport studies during metal deposition [15]. The hydrodynamic flow and the mass transport behaviour of the RRCE are under study and will be published later.

2. Experimental details

The RRCE shown on Fig. 1 used a Teflon shaft and was adapted to fit the rotor of a Tacussel (model EDI 101T) instrument. The cylinders of nickel foam (Table 1) were stamped out of a sheet (Resocell foam, Sorapec) with an ultrasonic device to ensure perfect geometry, and were spot-welded onto the nickel rod. A nickel disc (diam.: 4 mm) was also used.

It is well known that pretreatment of the nickel electrodes is essential to ensure a reproducible oxide coating. The disc was polished with 0.3 μm alumina, whereas the foams were used without any physical treatment. Both kinds of electrodes were electrochemically pretreated in 1 M KOH before use; for the cyclic voltammetry study, the potential was cycled between 250 and 600 mV at 50 mV s^{-1} for sufficient time (40–50 min) to obtain stable and reproducible voltammograms, and for potentiostatic measurements after 20 min with a cathodic current of 10 mA cm^{-2} the potential was cycled between 420 and 620 mV at 2 mV s^{-1} for 1 h.

The cylindrical electrochemical cell, represented in Fig. 2 was thermostated at 20° C. The counter electrode was a 50 mm platinum disc; the reference electrode was separated from the electrolyte by a porous glass disc.

Electrochemical experiments were carried out in 200 ml 1 M KOH with different ethanol concentrations, using a PAR scanning potentiostat (model 362). Ohmic drops, determined by the current interruption method, are indicated in Table 2. Cyclic voltammograms were recorded at 50 mV s^{-1}, using

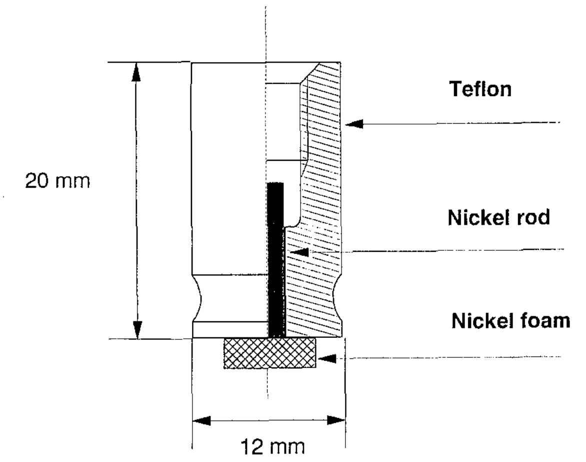

Fig. 1. Schematic view of the reticulated nickel rotating cylinder electrode.

Table 1. Electrode characteristics

Electrode	*Diam.*/cm	*Height*/cm	A_e*/cm^{-1}	*Area*/cm^2
RDE	0.4			0.13
RRCE 45 p.p.i.	0.8	0.2	40	4.0
RRCE 60 p.p.i.	0.8	0.2	55	5.5
RRCE 100 p.p.i.	0.37	0.15	81	1.3

* Indicated by SORAPEC.

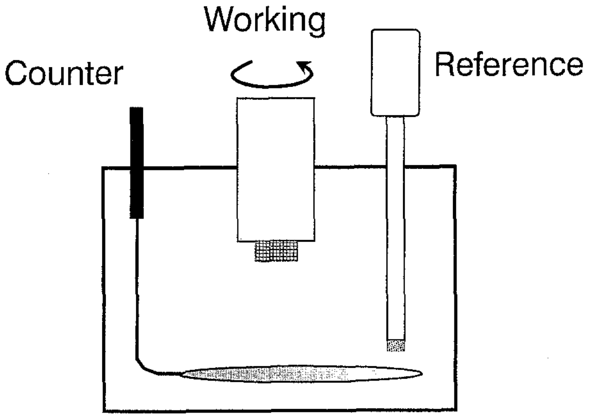

Fig. 2. Schematic view of the cell. Inner diam.: 75 mm; electrolyte volume: 200 ml.

Table 2. Ohmic drop and correction for the different electrodes (ethanol concentration: 0.1 M)

Electrodes	*Ohmic drop*/Ω	*Ohmic drop* correction*/mV
RDE	7	0.1
RRCE 45 p.p.i.	1.6	9.0
RRCE 60 p.p.i.	1.5	16.5
RRCE 100 p.p.i.	3.2	8.3

* At the limiting current.

the ohmic drop correction device of the potentiostat, on a plotting system (Hewlett-Packard 7090A). Current–potential curves at slow potential sweep rate (2 mV s^{-1}) were stored, corrected for ohmic drop (Table 2) and processed with a data acquisition system (ATMIO 16F5 card and Labview software, National Instruments) and recorded on a plotter (Hewlett-Packard 7475A). All potentials in this paper were measured against a Hg/HgO/0.1 M NaOH reference electrode.

3. Results and discussion

3.1. *Cyclic voltammetry*

Figures 3 and 4 show the voltammograms obtained after the pretreatment indicated in the experimental part on a RDE and a RRCE in 1 M KOH. The formation of an oxide film on the nickel is a complex phenomenon; in alkaline solution two oxide layers (β-Ni $(OH)_2$)–(β-NiOOH) and (α-Ni$(OH)_2$)–(γ-NiOOH) are formed, which show distinct reversible potentials [10, 11], and the appearance of the voltammograms depends on the pretreatment of the electrode [16]. In the absence of ethanol, the broader peaks obtained on the RRCE are probably due to the formation of different kinds of nickel oxide, owing to the potential distribution generally observed on three-dimensional electrodes. Cappadonia *et al.* [11] have observed similar behaviour on a two-dimensional electrode at different temperatures.

As expected [6], in the presence of ethanol, the anodic peak is converted into a wave with a significant increase of current, and the cathodic peak on the sweep towards negative potentials is slightly reduced. Owing to the reproducible hydrodynamic conditions in the RRCE, the voltammogram obtained with this electrode is well formed, in comparison to those obtained on a nickel foam in a batch stirred cell [3].

3.2. *Potentiostatic measurements*

The oxidation of alcohol is a reaction not controlled by diffusion [6–8] so that the current should be independent of the rotation speed of the electrode. Figure 5 shows the relatively well formed curves obtained with the RRCE (60 p.p.i.) at 500 r.p.m. with various concentrations of ethanol. As expected the current measured on a given porosity grade of RRCE was almost independent of the rotation rate between 0 and 3000 r.p.m. On the other hand on the RDE the current was higher at 0 r.p.m. than at any rotation rate, and it remains practically the same until 3000 r.p.m. Figure 6 shows five curves, (a)–(e) obtained on the RDE at 500 r.p.m. with various concentrations of ethanol, and two curves, (b′) and (e′), obtained at 0 r.p.m.; the current is significantly higher at 0 r.p.m. than at 500 r.p.m. for the same ethanol concentration. This unexpected behaviour of the RDE is not completely clear; it is generally assumed [6, 7] that the rate determining step of the oxidation is the chemical

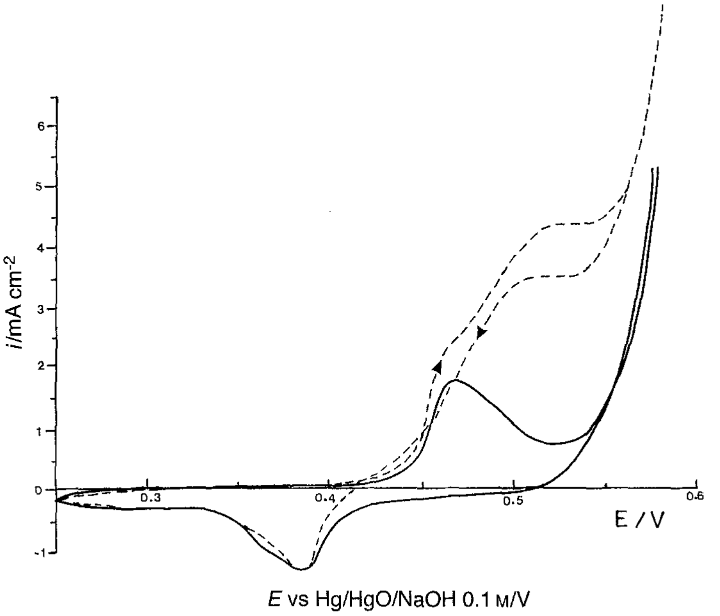

Fig. 3. Voltammograms in 1 M KOH at a polished nickel RDE. Potential scan rate: 50 mV s^{-1}; rotation rate: 500 r.p.m.; ethanol concentration: (——) 0 and (- - -) 0.25 M.

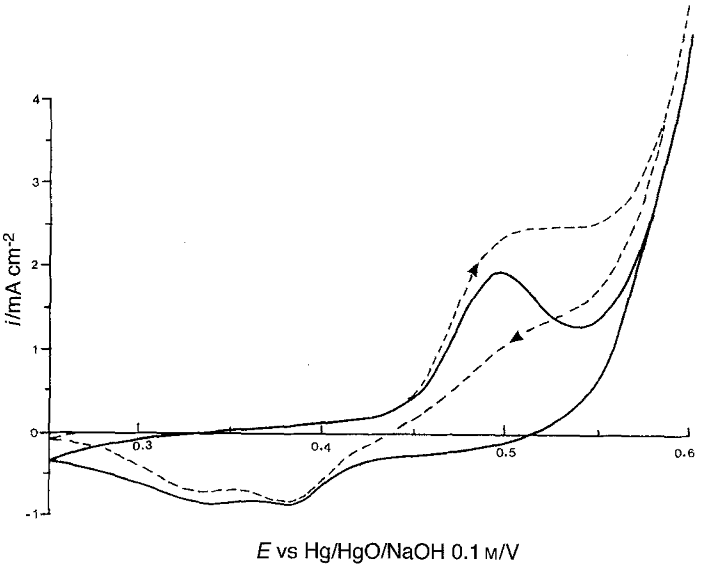

Fig. 4. Voltammograms in 1 M KOH at a nickel RRCE. Potential scan rate: 50 mV s^{-1}; rotation rate: 500 r.p.m.; nickel foam porosity: 45 p.p.i.; ethanol concentration: (——) 0 and (- - -) 0.25 M.

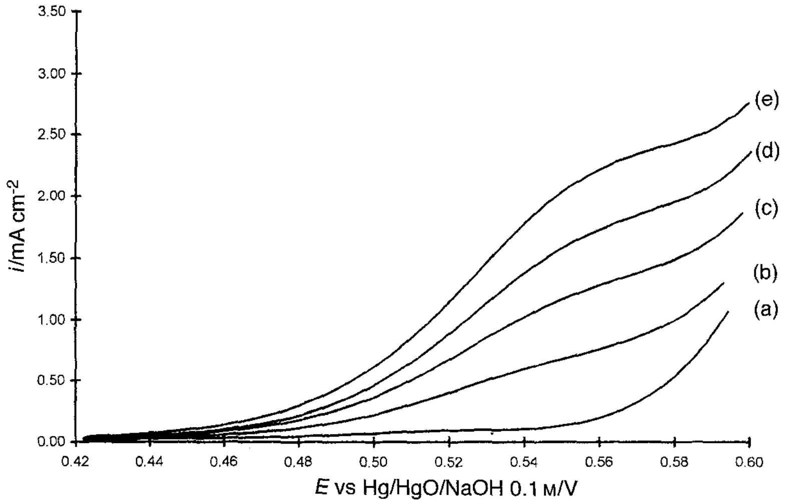

Fig. 5. i/E curves in 1 M KOH at a nickel RRCE. Potential scan rate: 2 mV s^{-1}; rotation rate: 500 r.p.m.; nickel foam porosity: 60 p.p.i.; ethanol concentrations: (a) 0, (b) 0.025, (c) 0.05, (d) 0.075 and (e) 0.1 M.

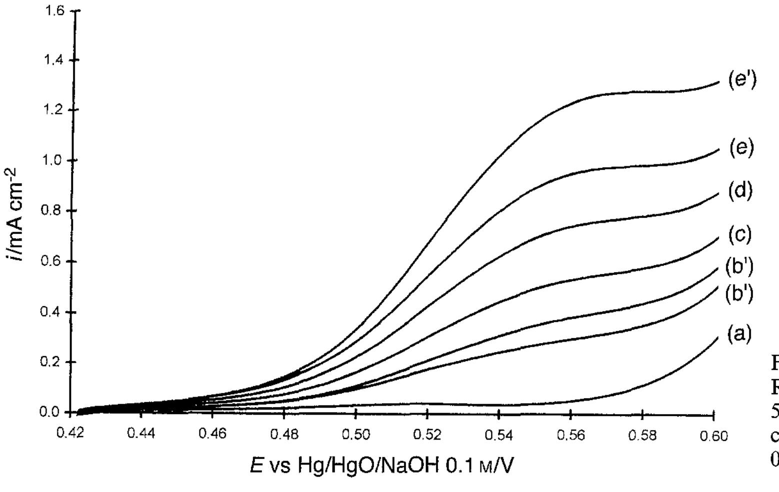

Fig. 6. i/E curves in 1 M KOH at a polished nickel RDE. Potential scan rate: $2\,mV\,s^{-1}$; rotation rate: 500 r.p.m. (0 r.p.m. for curves (b′) and (e′)); ethanol concentrations: (a) 0; (b), (b′) 0.025; (c) 0.05; (d) 0.075; (e), (e′) 0.1 M.

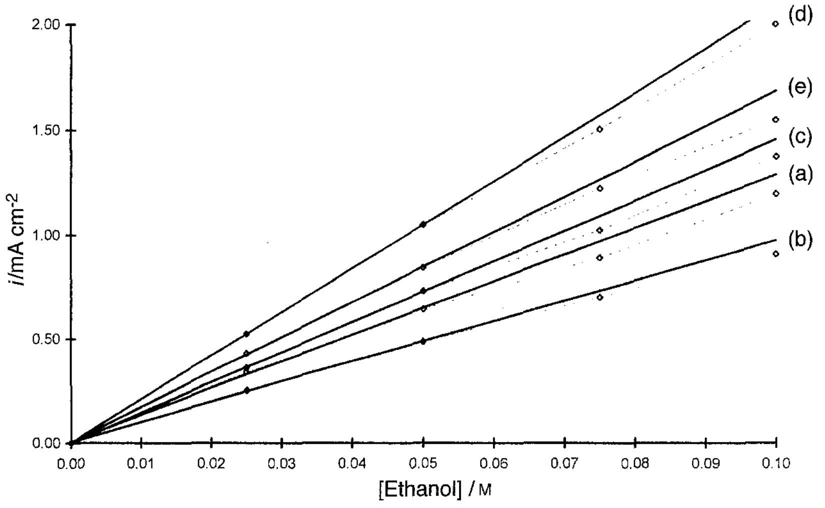

Fig. 7. i_L–ethanol concentration relationship in 1 M KOH (a) disc at 0 r.p.m.; (b) disc at 500 r.p.m.; (c) RRCE 45 p.p.i. at 500 r.p.m.; (d) RRCE 60 p.p.i. at 500 r.p.m.; (e) RRCE 100 p.p.i. at 500 r.p.m. Note: (——) is the linear regression on the three first points.

reaction of the adsorbed ethanol onto the nickel oxide formed anodically on the surface of the nickel, and the current should not depend on the rotation rate of the electrode. The difference in behaviour between the RDE and the RRCE is probably due to the different surface state and hydrodynamic conditions on the electrodes.

Figure 7 shows the relationship between the limiting current density measured on the plateaux at 0.57 V (with allowance for the background current in the absence of ethanol) and the ethanol concentration, for the RDE and the RRCE of different porosity. Good linear correlations were observed up to 0.1 M ethanol, and the slopes of the regression lines between 0 and 0.05 M of ethanol, which are proportional to the overall reaction rate, are indicated in Table 3; all values are of the same order of magnitude. These data are entirely consistent with the result published by Pletcher *et al.* [4], but in cases where well-formed waves were not observed on nickel foam anodes by these authors, the limiting current plateau is more easily identified on the RRCE under the same conditions.

Table 3. Slope of the linear limiting current density against ethanol concentration plots

Electrode	$i_L\,c^{-1}$/mA cm mol^{-1}
RDE 0 r.p.m.	13
RDE 500 r.p.m.	10
RRCE 45 p.p.i.	15
RRCE 60 p.p.i.	21
RRCE 100 p.p.i.	17

4. Conclusion

It has been shown that a reticulated nickel rotating cylinder electrode is useful in the study of an electrochemical reaction, prior to the development of a preparative cell using a three-dimensional electrode. By comparison with measurements on a nickel foam in a stirred cell, well developed voltammograms and potentiostatic curves are readily obtained on a RRCE.

Acknowledgement

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