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Oxygen Reduction on Mild Steel and Stainless Steel in Alkaline Solutions

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ABSTRACT

The cathodic polarisation curve of steel in alkaline solutions always shows three regions: (1) oxygen reduction with a Tafel behaviour at potentials cathodic to the open circuit potential followed by (2) a diffusion limited current of oxygen reduction at more negative potentials and (3) hydrogen evolution at very negative potentials. The diffusion limited region of the cathodic current density is controlled both by the oxygen concentration in solution and the flow rate whereas in the Tafel region (charge transfer) the temperature and the pretreatment of the sample determine the intensity of the current density and the slope of the Tafel line. On stainless steels the cathodic reduction currents are lower then on mild steel. It can be concluded that under usual corrosion conditions for steel in concrete the cathodic oxygen reduction is not diffusion limited but charge transfer controlled.

1. Introduction

The corrosion reaction, i.e. the anodic dissolution of steel in concrete, has to be sustained by a corresponding cathodic reaction: in general, this is the reaction of oxygen with water producing hydroxyl ions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$
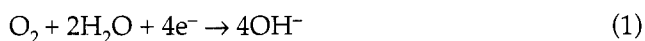
The availability of oxygen at the steel surface and the reaction kinetics of oxygen reduction are thus key factors in the corrosion of steel in concrete. Quite often the reduction of oxygen at the steel surface in alkaline environments is called diffusion limited although only a few papers report results on kinetics and mechanism of oxygen reduction on passive iron or steel in alkaline solutions [1,2]. The influence of oxygen on corrosion of steel in concrete has been studied [3–5]. In this work, the influence of oxygen content, temperature and ageing of the passive film on the oxygen reduction reaction on normal and stainless steel in alkaline solutions has been studied. The results are discussed with respect to the mechanism of oxygen reduction and the importance for corrosion of steel in concrete.

2. Experimental

Potentiodynamic polarisation curves (scan rate 1 mVs^{-1}) were recorded in an electrochemical flow cell (Fig.1) at defined temperatures and hydrodynamic conditions. The flow velocity was regulated by the flux of solution, 1 mLs^{-1} corresponds to a flow velocity of *ca.* 1.4 mms^{-1}. The counter electrode was a platinum wire spiral and the reference electrode was a saturated calomel electrode. The materials tested (working electrode) were mild steel and DIN 1.4301 stainless steel cylinders with a diameter of 8 mm, embedded in resin and mounted in the flow cell. For each experiment the samples were freshly ground with 180 grit emery paper in water, cleaned with ethanol in an ultrasonic bath, rinsed with deionised water and immersed for 24 h in the alkaline test solution open to air to form the passive film. As electrolytes 0.1M NaOH and synthetic pore solution (Table 1) were used. The temperature (5–47°C), oxygen concentration (open to air or saturated) and flow velocity (stagnant or 1 mLs^{-1}) were varied; in addition, experiments with prolonged immersion times (ageing of the passive film up to 4 months) of the samples were performed.
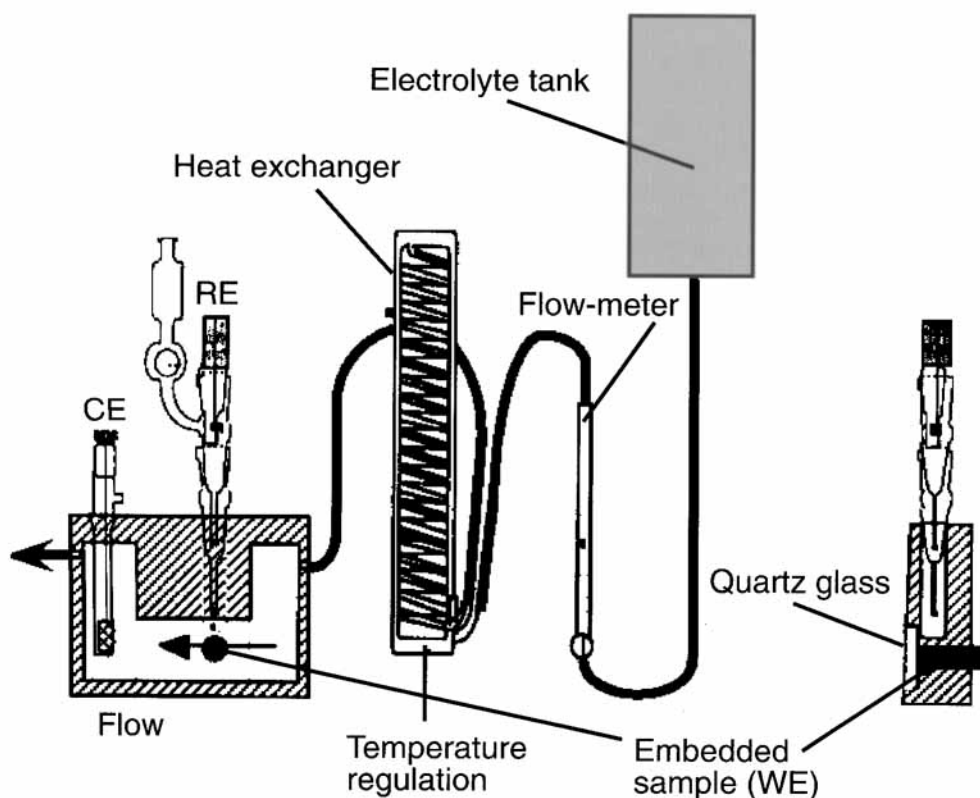

Fig. 1 *Schematic representation of the electrochemical flow-cell that allows the registration of cathodic polarisation curves under controlled temperature, potential and oxygen content.*

Table 1. *Composition of the synthetic concrete pore solution*

Concrete pore solution	Ca(OH)$_2$	KOH	Na$_2$SO$_4$	NaOH
mgL^{-1}	9.6	13967.8	3121.6	616.8

3. Results

The cathodic polarisation curves, starting from the open circuit potential, in solutions of 0.1M NaOH with different oxygen contents (open to air, saturated) are shown in Fig. 2(a). The diffusion limited current density increases by a factor of about two in O$_2$ saturated conditions. The slope of the Tafel region of the curve remains constant at *ca.* 250 mV per decade, although the higher oxygen content results in a slightly higher cathodic current density in the Tafel region. The influence of flow velocity at constant oxygen content (solution open to air) is shown in Fig. 2(b). As expected, the diffusion limited current density, i_{O_2D}, increases with higher flow velocity, the current densities of oxygen reduction in the Tafel region of the polarisation curve are not influenced by the flow velocity.

The influence of temperature on the cathodic polarisation curves of oxygen reduction was studied in more detail in synthetic pore solution, with solutions open to air and flow velocity 0.1 mLs^{-1}. As is shown in Fig. 3, the diffusion limited current
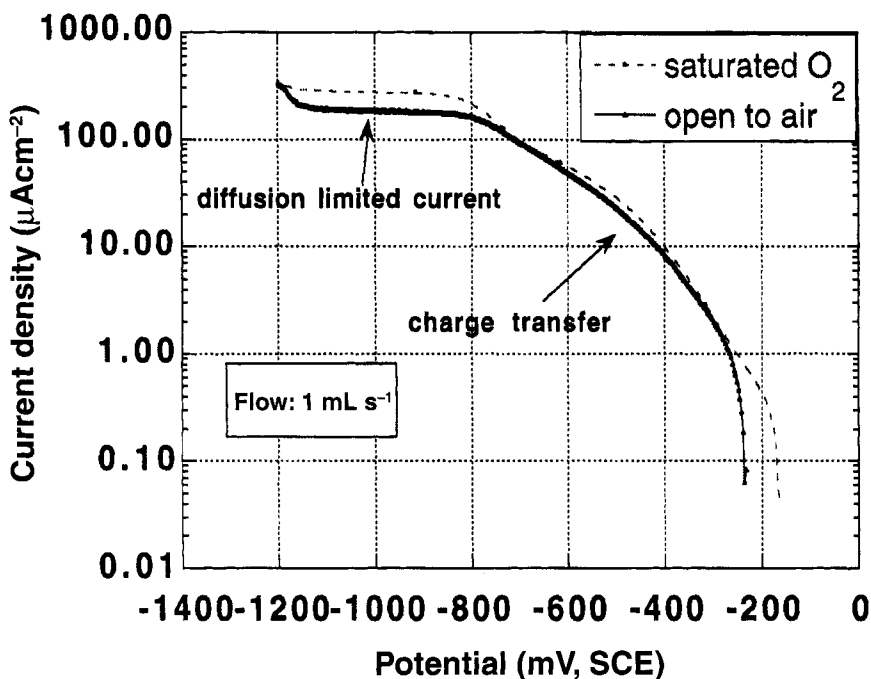

Fig. 2(a) *Typical cathodic polarisation curves of mild steel in 0.1M NaOH solutions as a function of oxygen content. Flow rate 1 mLs^{-1}.*
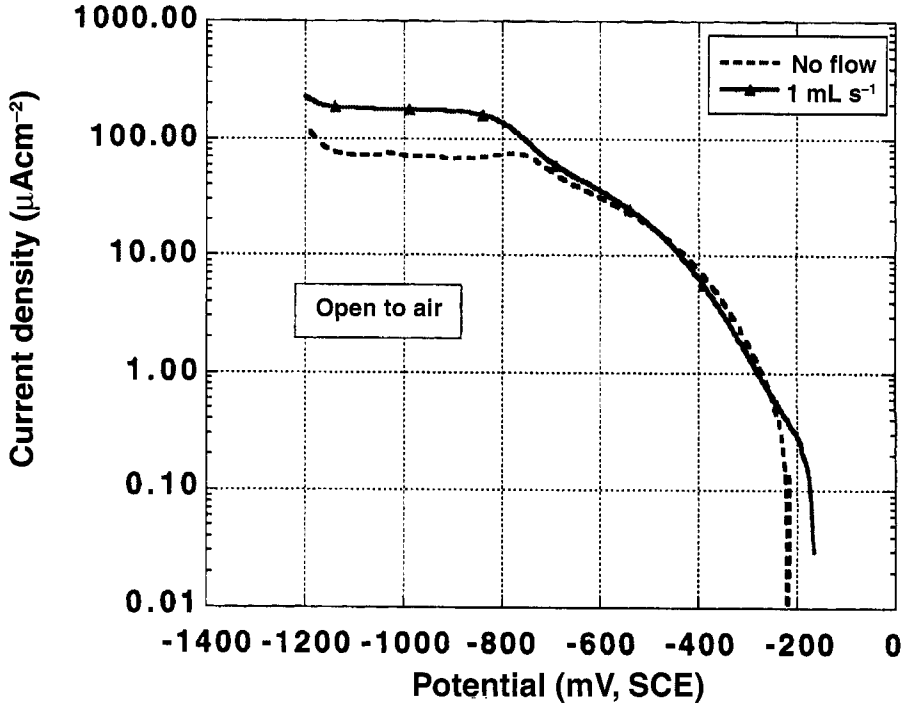
Fig. 2(b) Typical cathodic polarisation curves of mild steel in 0.1M NaOH solutions as a function of solution flow rate. Solutions open to air.
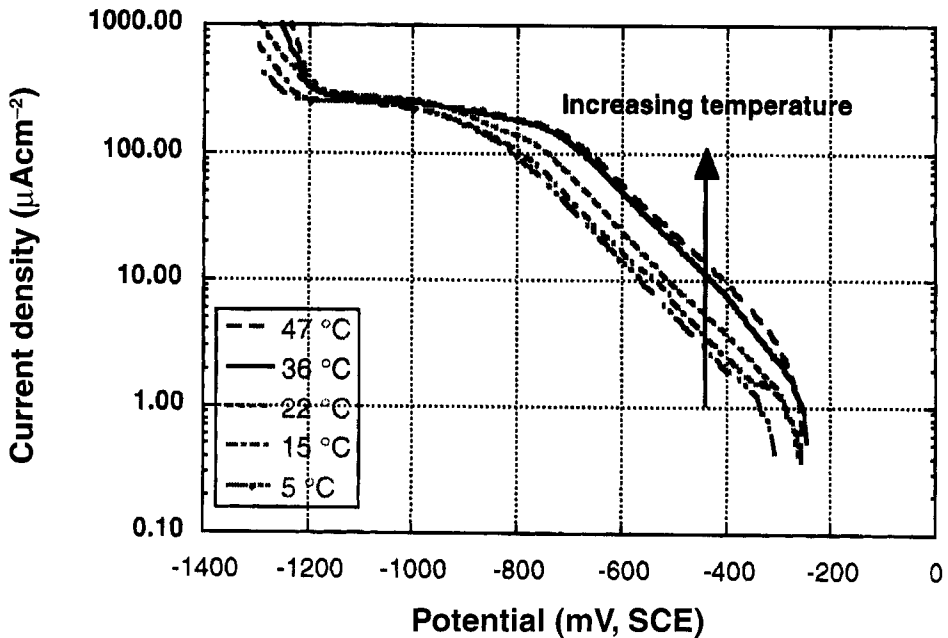

Fig. 3 Cathodic polarisation curves of mild steel in synthetic pore solution (pH 13.4) at different temperatures, flow rate 1 mLs⁻¹, open to air.

density, $i_{O_2,D}$, remains practically constant. The Tafel region of the polarisation curve is slightly shifted to more negative potentials, the slope of the Tafel region increases slightly with increasing temperature (Table 2).

Prolonged exposure to the test solution (ageing of the passive film) showed the most pronounced effect on the cathodic polarisation curves (Fig. 4). An increase of this pre-passivation time results in a marked increase of the slope of the Tafel region, the diffusion limited current density remaining unchanged. Finally, as can be seen from Fig. 5, the electrode material influences the cathodic polarisation curve: with the same surface preparation the cathodic current density of DIN 1.4301 stainless steel is about 4 times lower compared to mild steel. Platinum shows practically uninhibited oxygen reduction with a Tafel slope of –60 mV.

4. Discussion

4.1. Kinetics of the Cathodic Oxygen Reduction

As it is well known from literature, cathodic oxygen reduction (e.g. Fig. 2) shows a Tafel line at low overpotentials and a diffusion limiting current density at high overpotentials (more negative potentials). The thermodynamic equilibrium potential E_{O_2} corresponding to eqn (1) depends, according to the Nernst equation,

$$E_{O_2} = +1.27 - 2.3RT/F \, \text{pH} + 2.3RT/4F \, \log p_{O_2} \qquad (2)$$

on pH, oxygen content and temperature of the solution and $E_{O_2} \approx +0.23$ V SCE would result theoretically. On platinum, a potential E_{O_2} of –0.05 V SCE was measured. On passive steel in alkaline solutions, the equilibrium potential E_{O_2} cannot be measured; since due to the interaction with the anodic dissolution of the passive film mixed open circuit potentials around –0.2 V SCE are found which influenced by the magnitude of the cathodic current densities and the passive film dissolution rates (e.g. Fig. 5).

Table 2. Cathodic Tafel slopes b_c, charge transfer coefficient α and exchange current densities for the oxygen reduction on passive mild steel in synthetic pore solutions at different temperatures

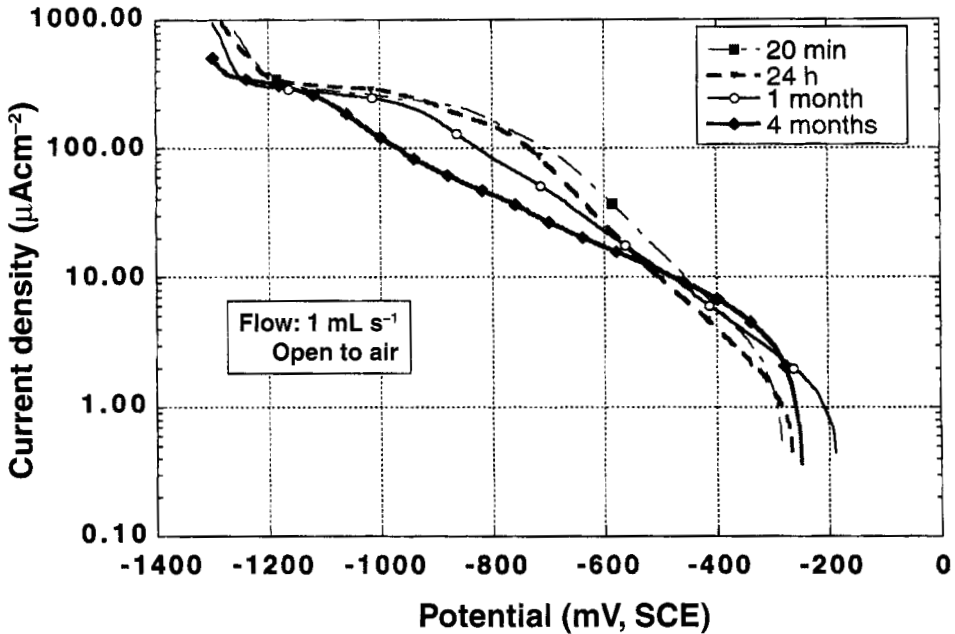| Temperature (°C)	b_c (mV/dec)	2.3 RT/F (mV)	α	i_o (μAcm⁻²)
5	238	55.1	0.77 ± 0.01	0.006
15	222	57.1	0.74 ± 0.02	0.008
22	233	58.6	0.75 ± 0.03	0.011
36	235	61.2	0.74 ± 0.01	0.013
47	239	63.4	0.73 ± 0.02	0.015

Fig. 4 *Influence of the ageing time of the passive film in synthetic pore solution on cathodic polarisation curves (flow rate 1 mLs^{-1}, open to air).*

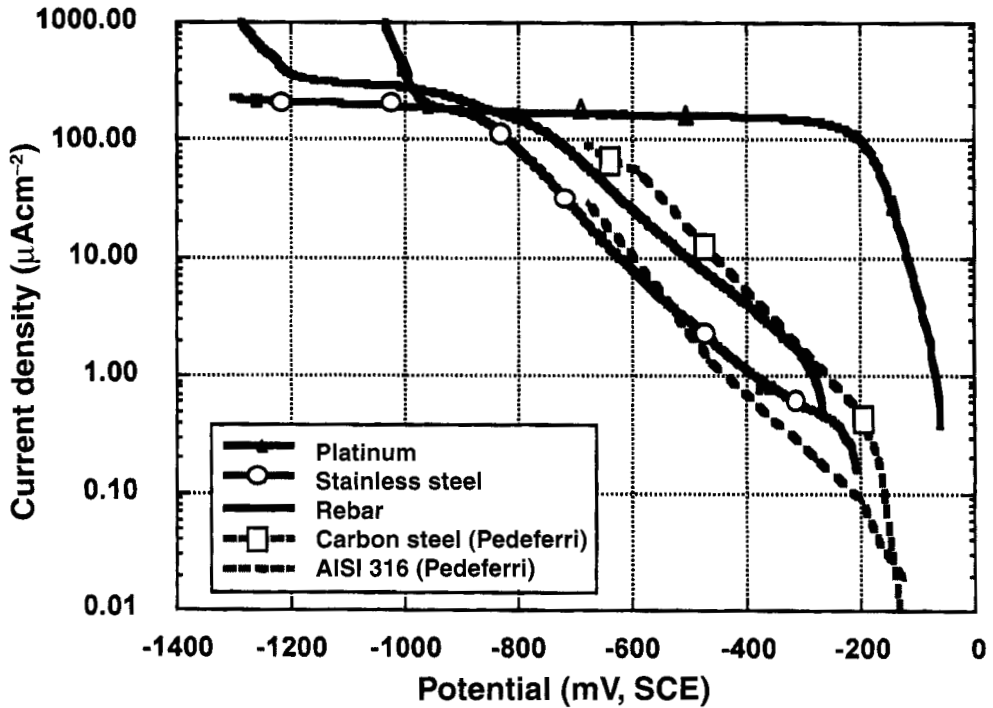**Fig. 5** *Cathodic polarisation curves of mild steel, 1.4301 stainless steel and platinum in synthetic pore solution at flow velocity of 1 mLs^{-1} compared to results of Pedeferri [6].*

On increasing the overpotential in the cathodic direction a Tafel behaviour is found corresponding to the charge transfer controlled region of oxygen reduction. In the experiments on passive metals, this Tafel line could be observed only at $E \ll E_{ocp}$ (Figs 4, 5). The current densities in this charge transfer controlled region do not change with flow velocity (Fig. 2b) as observed also in studies with rotating disk electrodes [1,2]. Assuming that in this potential region oxygen transport does not influence the overall reaction rate, the cathodic polarisation curve can be written as

$$i_{O_2} = i_{0'O_2} \exp\left[-(E - E_{O_2}) / b_c\right] \tag{3}$$

with E_{O_2} = equilibrium potential, $i_{0'O_2}$ = exchange current density at E_{O_2} and the cathodic Tafel slope $b_c = RT/F\,(1-\alpha)$, α being the charge transfer coefficient and R, T, and F have their usual meanings. Curve fitting of the experimentally measured cathodic polarisation curves (Fig. 3) with eqn (3) allows these parameters to be determined (Table 2).

Whereas on platinum a steep Tafel line (slope 60 mV / decade) is observed, on passive metals (both mild steel and stainless steel) the cathodic reduction of oxygen is inhibited. This inhibition might cease once the steels start to corrode. The lower cathodic current densities observed on 1.4301 stainless steel, reported also by Bertolini *et al.* [6], correspond to a lower exchange current density $i_{0'O_2}$. Thus stainless steel in alkaline solutions is a less effective cathode compared to mild steel (Fig. 5), this can be important when considering repair of reinforced concrete structures.

The observed influence of temperature (Fig. 3) on the charge transfer reaction rate (eqn (3)) can be explained by the factor RT/F in the Tafel slope, the charge transfer coefficient α remaining constant (Table 2). A marked increase in the exchange current density (factor of 3 between 5 and 47°C) can be observed, the calculated activation energy is $\Delta E = 16$ kJmol^{-1}.

At very high overpotentials the overall reaction rate is limited by oxygen transport to the electrode surface. In this potential region a diffusion limited current density, $i_{O_2,D}$, is observed. According to

$$i_{O_2,D} = -4F\,D_{O_2}\,C_{O_2} / \delta \tag{4}$$

the oxygen concentration, C_{O_2}, the oxygen diffusion coefficient D_{O_2} and the thickness of the diffusion layer, δ, determine the limiting current density. Despite increasing temperatures $i_{O_2,D}$ remains practically constant (Fig. 3), thus the higher diffusion coefficient is compensated by the lower oxygen solubility at higher temperatures.

The kinetics of oxygen reduction as discussed above can be considered valid also for the cathodic reaction on steel in mortar or concrete — with two additional features: the oxygen content and the water content in the porous cementitious materials will vary strongly with humidity. According to eqn (1) both the oxygen content and free water may influence the reaction kinetics of oxygen reduction.

4.2. Corrosion of Steel in Concrete

The results of this laboratory study on the cathodic reduction of oxygen in alkaline solutions have several implications in the field of corrosion of steel in concrete. First, the progressive inhibition of the oxygen reduction (Fig. 4) with prolonged ageing of the passive steel (long time in the alkaline pore solution, mortar or concrete) will lead — for otherwise constant conditions — to lower corrosion rates of steel in concrete because the cathode efficiency decreases. This means that in constant environmental conditions — as frequently established in laboratory experiments — the corrosion rate of steel in concrete will decrease with time. Similar results have been reported by Yalcyn *et al.* [9]. Regarding the rate controlling reaction of corrosion of steel in concrete, these results from solutions indicate that a true diffusion limited corrosion current is found only for fully immersed conditions which is in agreement with the experiments of Raupach [3,4]. Under more usual environmental conditions, i.e. not completely water-saturated, the cathodic reaction is oxygen reduction under charge transfer control as has been confirmed by numerical simulations [10].

Not only the cathodic but also the anodic reaction (pitting corrosion of steel in chloride-containing media) is strongly influenced by the ageing of the passive film: as is shown in Fig. 6, prolonged immersion in alkaline solution shifts the pitting potential to much more positive values. Similar results have been reported in a surface analytical study on the ageing of passive films on stainless steels [11]. This fact has to be considered in studying pitting corrosion of steel in concrete.

4.3. Measuring Oxygen Content

Cathodic polarisation at a constant potential and recording the resulting reduction current is used to determine the oxygen content *in situ* (on structures or on laboratory samples) [5,12]. The results of this work indicate that the choice of the electrode material (mild steel, stainless steel, platinum) and of the cathodic polarisation potential may strongly affect the results: with increasing duration of the experiment, i.e. with ageing of the passive film, lower oxygen reduction currents will be measured at potentials in the charge transfer region (e.g. –0.7 V SCE (Fig. 4)) even if the oxygen content effectively remains constant. Only at potentials in the limiting current density region has this ageing effect not been observed [5]. The limiting diffusion current densities of steel embedded in mortar or concrete have not been determined in this work but it is expected that they will be lower than in solution [5,8]. Further results will be reported [13].

4.4. Beneficial Influence of Stainless Steel

The DIN 1.4301 stainless steel shows much lower oxygen reduction currents compared to normal mild steel (Fig. 5) and this has also been reported by Pedeferri *et al.* [6,7]. This will reduce the corrosion of an actively corroding steel part in a macrocell and thus it is beneficial to use stainless steels in new and repaired structures not only because of a much higher pitting potential but also because of the reduced macrocell corrosion activity [6,7,13]. Care has to be taken because this effect can get lost when the stainless steel has been cold-deformed or welded [6,7].
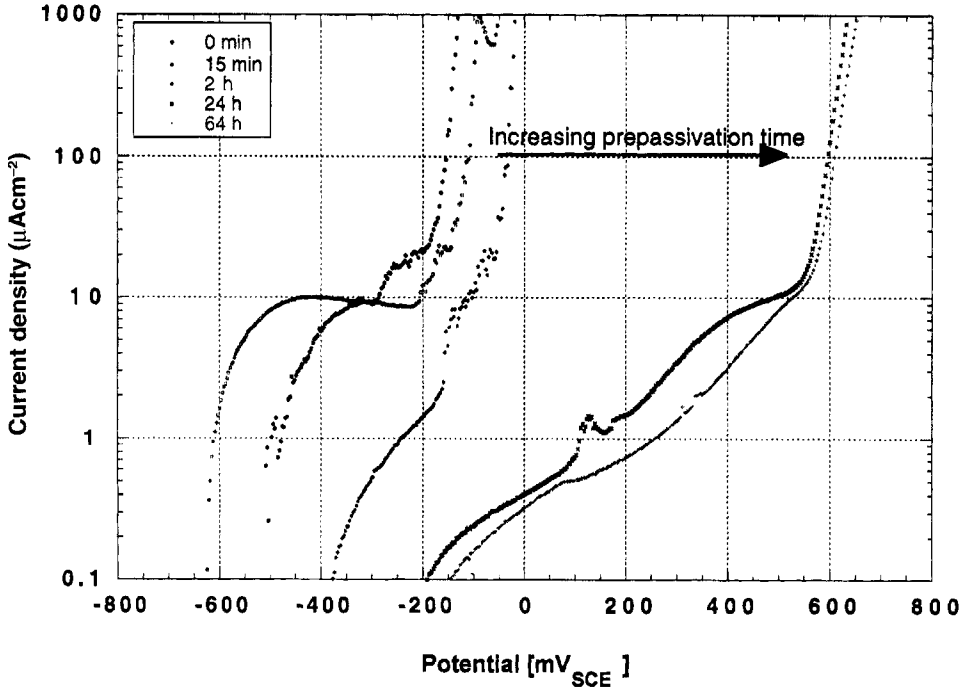
Fig. 6 *Influence of the ageing of the passive film on mild steel in synthetic pore solution on the anodic polarisation curves (positive currents) and on the pitting potential* E_p *(chloride concentration 1 molL^{-1}).*

5. Conclusions

From this laboratory study on the reduction of oxygen on mild steel and stainless steel in alkaline solutions it can be concluded that

- the oxygen reduction on passive mild steel and even more on stainless steel in alkaline solutions is strongly inhibited compared to that on platinum. This inhibition increases with prolonged ageing of the passive film;

- the oxygen reduction current density increases with temperature, this is mainly the result of higher exchange current densities; and

- experiments to monitor the oxygen content in mortar or concrete should be performed only in the limiting current density region.

Further experiments in mortar and concrete are ongoing to establish the potential region of the diffusion controlled limiting current density region.