Short communication

Convection induced by illumination-based metal surface heating increases corrosion potential, corrosion rates

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ABSTRACT

Illumination may increase corrosion rates of important engineering metals. In addition to the well-known photoelectrochemical mechanism which increases dissolution via generation of electron-hole pairs, induced convection via local heating can contribute to increased dissolution. Here, corrosion potential shifts of iron in HCl, aqueous NaCl and NaOH upon illumination with $O(10^2 \, \text{W cm}^{-2})$ white light have been found to be O (10 mV), accompanied by increased corrosion rates. The increase in corrosion potential can be suppressed by stirring. These results are interpreted in the framework of the mixed potential theory. An increase in the diffusion limited current of the O_2 reduction by increased O_2 transport to the surface via induced convection leads to increased corrosion potentials, and thus increased corrosion rates. The induced convection mechanism of increased photocorrosion can be recognised by a delayed onset of corrosion potential shifts. In practice, this mechanism is anticipated to be important mainly in thin film electrolytes under strong illumination.

1. Introduction

The fact that light affects electrochemical reactions is known for almost 2 centuries [1]. There can be absolutely no doubt that in semiconductor films, electron hole pair creation leads to follow up electrochemical processes.

Also corrosion processes may be affected by light. The corrosion rates of zinc, carbon steel, aluminium alloy 6061, copper and silver increased when exposed to UV light [2]. Nickel, titanium, zirconium and 304 stainless steel showed no effect from illumination while brass corroded slower when irradiated [2]. This effect was attributed to electron-hole pair formation in the metal oxide in a semiconductor photoelectrochemistry mechanism [2]. Several works found increased corrosion rates for weathering steels in chloride containing electrolytes when illuminated [3-8]. One result showed a corrosion rate up to $9 \times$ higher when illuminated with UV compared to dark. Such an observation was postulated to be the result of formation of reactive oxygen radicals by holes generated through the interaction of light with iron oxide [4].

Several authors attributed increased corrosion rates under illumination to a semiconductor photoelectrochemical mechanism. Some authors argued that the excited electrons migrate to the oxide/electrolyte interface and facilitate O_2 reduction [5,6]. A key piece of evidence for this hypothesis was an observed quick increase of corrosion

potential E_{corr}, used here synonymously with the open circuit potential, of steel in solution when illuminated with visible light, followed by a slower relaxation for E_{corr} when light shut off [5,6]. A positive photovoltage observed was used to argue that an n-type semiconductor with downward band bending was causing the photo-corrosion [5-8]. This is opposite to an earlier proposition of upward band bending for photocorrosion of n-type semiconductors as oxide on iron [2]. Illumination with visible light affected the type of corrosion products on weathering steels [7,8].

On the other hand, the increased rate of O_2 transfer to steel surfaces, caused by increased convection via local heating, led to an increased corrosion rate of submerged steel [9,10]. The magnitude of the effect was concluded to be too small to affect current consumption on cathodically protected carbon steel structures [10]. In laboratory experiments, inhomogeniety in temperature was shown to affect the electrochemical behaviour because of induced natural convection [11]. Amongst others, voltammetric response is altered [12]. Naturally occurring flow velocities in unstirred solutions were recently reported as $O \, (10^{-4} \, \text{m s}^{-1})$ [11].

The different interpretations encountered for increased corrosion rates of iron under illumination make this topic worth investigating. This paper shall report measurements of E_{corr}, and its response to illumination, of iron in HCl, NaCl and NaOH solutions. The results will discussed in the frame of the mixed potential theory, which is

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typically used to explain E_{corr} developing spontaneously on a submerged metal.

2. Experimental section

ARMCO Pure Iron, grade 4 (99.9% iron; AK Steel), was ground using 320, 800 and 1200 PP paper and then washed with ethanol. An area of $\approx 1 \cdot 1\,cm^2$ was immersed in different electrolytes in a 250 mL beaker that was placed in a dark box. Immersed samples were illuminated using a Navitar fiber optic illuminator with an EKE 21 V 150 W lamp, wavelength range 400–1000 nm. The electrolytes used were 0.2 M NaOH, 3.5 wt% (≈ 0.6 M) NaCl and 0.1 M HCl. All experiments were conducted under ambient, O_2-containing lab atmosphere.

E_{corr} was recorded versus a saturated calomel electrode (SCE) REF401 (Radiometer Analytical), first in the dark to get a baseline. Then the samples were illuminated for 5 min. The effect of light was recorded with the lamp ≈ 4 cm from the sample surface; 100% and 50% output was used, and is referred to as "high intensity" and "low intensity" illumination, respectively. The approximately circular spot covered $\approx 0.8\,cm^2$, which leads to a power density of $O\,(10^2\,W\,cm^{-2})$ in the high intensity case. On the same sample, illumination experiments were repeated up to $10 \times$.

The same type of experiment was conducted with addition of a ≈ 3 cm magnetic stirrer (100 rpm) placed ≈ 10 cm from the sample.

Additionally, E_{corr} was recorded while the electrolyte was quickly heated with a standard laboratory hot plate from ambient temperature up to 70 °C. Iron was immersed in 0.1 M HCl, 0.2 M NaOH and 3.5 wt% NaCl, while E_{corr} was recorded vs. a SCE that was connected to the iron through a salt-bridge. The solution temperature was recorded using a laboratory mercury thermometer.

The temperature increase caused by illumination was measured by fastening a Fluke T-type thermocouple directly on the sample surface, 5 mm and 10 mm from the surface, and recorded with a Fluke 52II B Thermometer.

Electrochemical impedance spectroscopy (EIS) using a standard three electrode setup with a Pt-plate as counter electrode, and a SCE reference electrode was also performed, using a Zahner IM6e potentiostat. A frequency range of 10 kHz to 30 mHz with a 5 mV amplitude was used. Three repeats were conducted, where care has been taken to keep the same pretreatment. Repeatability of the initial E_{corr} served as a quality parameter.

Raw data from this study is available online [13].

3. Results

The effect of illumination on E_{corr} of iron in different electrolytes is shown in Fig. 1. For high intensity experiments, E_{corr} increased with a response time of 10 s by 4, 10 and 16 mV in HCl, NaCl and NaOH, respectively, and started to decrease when the light was turned off. Several samples showed a 1 mV decrease before E_{corr} increased. After the lamp was turned off, E_{corr} decreased again. No increase in E_{corr} was found while stirring even for the case in which the highest shifts were observed in the absence of stirring. When the stirring was switched off, the effect of light was again found (see raw data [13]).

The effect of bulk electrolyte temperature on E_{corr} was recorded by immersing iron and then heating the respective electrolyte (Fig. 2). E_{corr} decreased with increasing temperature for all electrolytes up to $\Delta T \approx$ 20 K.

The temperature at the surface and close to the surface was measured during illumination in solution, with and without stirring (Fig. 3). The temperature increase was low only 10 mm from the surface of the sample, and no effect of illumination was seen at > 10 mm.

EIS was measured with and without illumination (Fig. 4). Results were fitted to the Randles circuit with a constant phase element (Table 1).
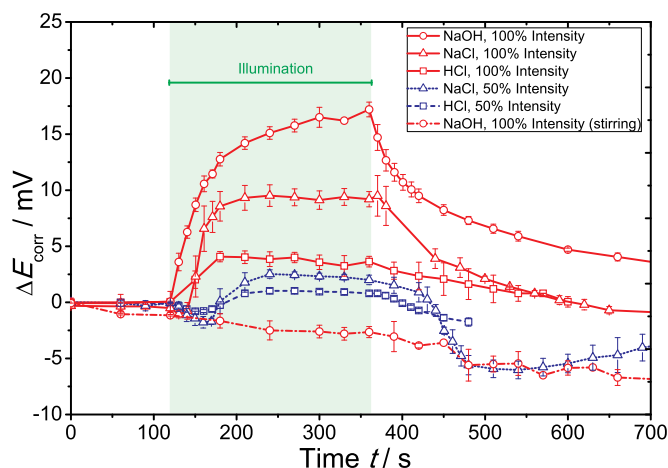

Fig. 1. Effect of illumination on $\Delta E_{corr} = E_{corr}(t) - E_{corr}^{(0)}$ with time t. Initial corrosion potentials $E_{corr}^{(0)}$ were -878 mV (NaCl), -757 mV (HCl) and -511 mV (NaOH), all vs. SHE.
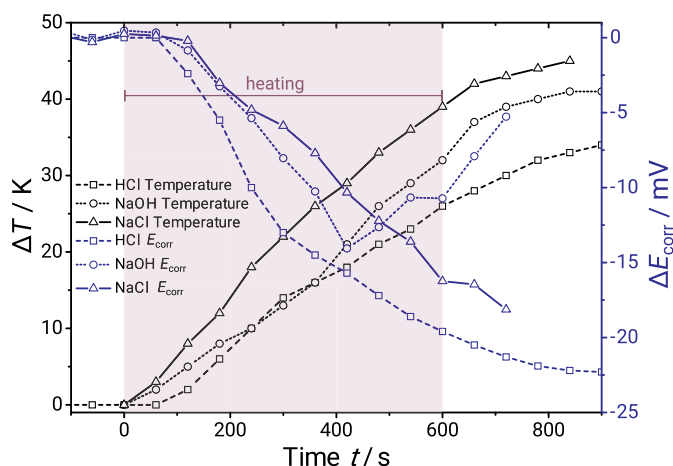

Fig. 2. Effect of temperature measured in solution on E_{corr} of iron in 0.1 M HCl, 0.2 M NaOH and 3.5 wt% NaCl.
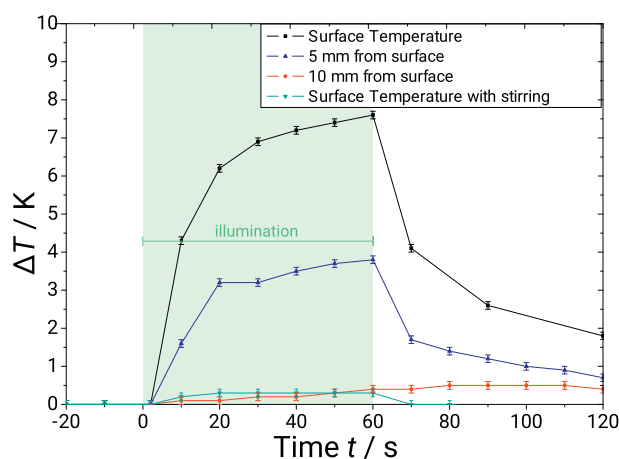

Fig. 3. Temperature at sample surface in 0.2 M NaOH. Solution was unstirred unless indicated otherwise.

4. Discussion

Similar to previous reports [5-8], an increase of E_{corr} during illumination was found without stirring. However, this increase was absent
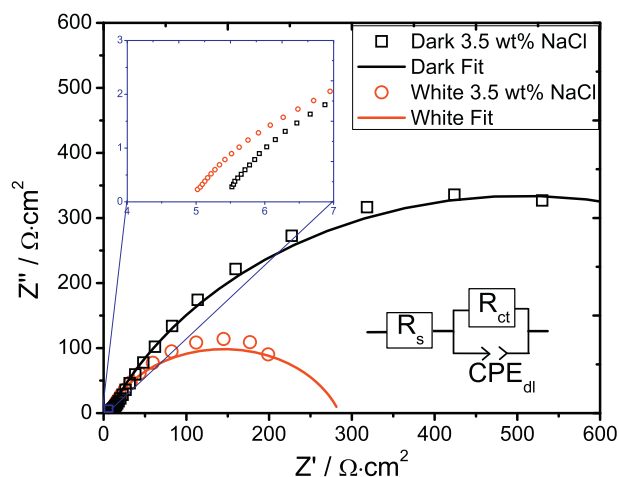
Fig. 4. EIS data for iron in 3.5 wt% NaCl. Illuminated sample was illuminated 10 s before measurement was started and during the entire EIS acquisition. Measurements were conducted without stirring. See Table 1 for fit parameters to equivalent circuit (inset).

Table 1

Solution resistance R_s, charge transfer resistance R_{ct}, double layer constant phase element prefactor Q_{DL} and exponent n obtained from fits to EIS data illuminated (il.) and dark (d.). Corrosion current density i_{corr} was estimated as [14] $i_{corr} = 0.022[V]/R_{ct}$. Uncertainty estimate for the last digit is given in brackets.

		R_s $\Omega\,cm^2$	R_{ct} $k\Omega\,cm^2$	Q_{DL} $mF^{1/n}\,cm^{-2}$	n	i_{corr} $\mu A\,cm^2$
NaOH	il.	7.7 (2)	10.3 (4)	0.305 (5)	0.801 (5)	2.14 (8)
NaOH	d.	9.2 (1)	15.9 (4)	0.219 (9)	0.835 (6)	1.38 (3)
NaCl	il.	4.7 (2)	0.30 (3)	6.9 (7)	0.78 (5)	85 (7)
NaCl	d.	5.3 (7)	0.9 (1)	2.2 (3)	0.72 (5)	27 (4)
HCl	il.	10.7 (2)	0.081 (3)	0.650 (4)	0.75 (1)	317 (12)
HCl	d.	10.8 (3)	0.124 (9)	0.71 (4)	0.74 (2)	207 (16)

while stirring. Consequently, stirring overwhelms the effect of illumination on E_{corr}, already indicating that this effect is not related to a semiconductor process in the surface oxide, but that transport must play an important role. The observed E_{corr} increase may (a) be related to a temperature effect or (b) increased local convection induced by local surface heating.

Bulk heating does, however, decrease E_{corr}, rather than increasing it (Fig. 2). While an initial ≈ 1 mV decrease was observed for low intensity illumination in HCl and NaOH, after < 50 s, E_{corr} started to increase and stabilised above the initial E_{corr}. Consequently, the temperature dependence of E_{corr} alone cannot explain the effect of illumination. Additionally, it is interesting to compare the shape of surface temperature increase and E_{corr} increase. In a photoelectrochemical process, the system reacts on a µs timescale [15], not on the 10 s time scale as observed here.

The combination of initial E_{corr} decrease with a subsequent increase of E_{corr} for the low intensity experiments and the effects of bulk heating and stirring indicates that the iron or the electrolyte at the iron-electrolyte interface was heated. EIS measurements found that R_s slightly decreased when illuminated, which is expected for an ionic conductor at higher temperature.

Consequently, a temperature gradient arises between the iron surface and bulk electrolyte, which creates a local flow, affecting transport of species to and from the electrode surface. We reason here that this locally induced convection is responsible for the E_{corr} increase dominating the experiments in this work.

The rate of iron corrosion in neutral or alkaline electrolytes is typically governed by O_2 transport. Fig. 5 shows the analysis of the
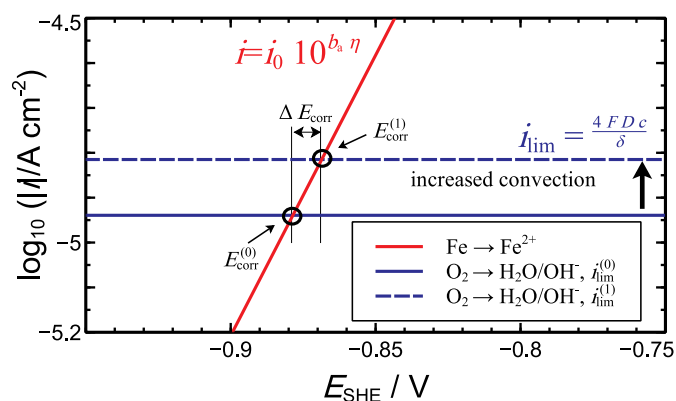

Fig. 5. Effect of increased convection on E_{corr} in mixed potential theory when active corrosion of iron is controlled by transport of O_2, with numbers compatible to experiment in NaCl. Superscripts (0) and (1) indicate the experiment in dark and illuminated, respectively. Iron dissolution is assumed to follow Tafel kinetics with slope 80 mV decade^{-1} [20]. In the dark, $i_{corr} \approx 11\,\mu A\,cm^{-2}$ from a polarisation curve.

dominating partial reactions on the basis of the mixed potential theory. For the situation encountered here, the iron dissolution current density and thus i_{corr} should approximately equal the steady state transport limited current density i_{lim} of the O_2 reduction [14],

$$i_{corr} \approx i_{lim} = \frac{4FDc}{\delta}. \tag{1}$$

Here, F is the Faraday constant, D the diffusion coefficient of O_2 and c the bulk concentration of dissolved O_2. The Nernst diffusion layer thickness δ is determined by the convection around the metal [16]. The measured E_{corr} is at the intersection of the lines denoting the dominating anodic and cathodic partial reactions in Fig. 5. A decreasing δ increases i_{lim}, thus increasing E_{corr} and the dissolution rate. The observed decrease in E_{corr} with increasing bulk temperature originates from the temperature dependence of Dc which was analysed in connection with a different system [17]. Up to ≈ 55 °C, the decreasing O_2 solubility [18] dominates over the increase in D [19], leading to the observed decrease in E_{corr}.

Semiquantitatively, with a Tafel slope b_a of a slowly polarised iron sample in neutral NaCl of 80 mV/decade [20], an increase in E_{corr} of 10 mV corresponds to an increase of i_{corr} by $\approx 1/3$, independent of the original i_{corr}. At the level of approximation presented in Fig. 5, $\Delta(\log_{10} i_{corr}) = 1/b_a \Delta E_{corr}$. Detailed investigations of the induced convection require fluid dynamics simulations [10,11], which are not trivial for ill-defined boundary conditions. In a simple picture, many laminar flow regimes follow a relation in which $\delta \sim u_\infty^{1/2}$, with the flow velocity u_∞ far from the surface, as e.g. in the Blasius or Levich equations. Consequently, the increase in logarithmic corrosion current density with illumination can be approximated as $\Delta(\log_{10} i_{corr}) \simeq 1/2 \Delta \log_{10} u_\infty$,[1] and it is possible to relate the measured ΔE_{corr} to changes in an effective u_∞ as

$$\Delta \log_{10} u_\infty \simeq \frac{2}{b_a} \Delta E_{corr}. \tag{2}$$

The observed ≈ 10 mV shift in E_{corr} thus indicate almost a doubled flow velocity, but no order of magnitude change.

The situation in NaOH is a bit more involved, as the system is passive, indicated by the high E_{corr} and low i_{corr}. Convection increases in this case the rate of O_2 transport and the dissolution products of the (hydr)oxide films. The effect of illumination is highest in this case,

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[1] The equal sign would rely on the very strong assumption that prefactors do not change. As the prefactor contains the viscosity which is strongly temperature dependent, this simple relation is only a first order approximation for small changes.

likely because of the different transport processes involved. In HCl, the slightly higher E_{corr} than in NaCl indicates the expected importance of the hydrogen evolution reaction (HER) as cathodic reaction. In this case, the observed effect of illumination on E_{corr} is lowest, in line with the fact that HER is not strongly affected by transport.

5. Conclusion

Illumination affects the corrosion rate of iron. A convective mechanism is identified as the dominating mechanism that leads to enhanced dissolution under the conditions used in this work. Light absorption in the metal leads to surface heating, induces convection in otherwise unstirred solutions and thus increased transport rates of O_2 to the surface, or of dissolution products from the surface. In potential measurements, the convective mechanism always leads to an increase in E_{corr}. A non-instantaneous photoresponse may serve as indication of the convective mechanism. For a discussion of band alignment, one needs to ensure that natural or induced convection does not affect the measured potentials. In laboratory setups, the often practised approach to control convection is sufficient to control the induced convection. In systems where this is not possible and where strong illumination and fast heating is encountered, such as in the presence of thin electrolyte films on an iron surface, or in the case of metallic photocatalysts, the convective mechanism may contribute to increased corrosion.

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