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Magnetic field effects on the active dissolution of iron

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ABSTRACT

The impact of superimposed magnetic fields on the behavior of iron in 0.05 M H_2SO_4 at low anodic polarization was investigated by means of potentiostatic polarization measurements. Significant magnetic field effects were observed even though the active dissolution reaction in the investigated potential region is formally charge transfer controlled. The current density can be enhanced or reduced dependent on the magnetic field to electrode configuration. The results are discussed in terms of the magnetic field impact on the surface pH value during the anodic dissolution. Our findings are likely to have important consequences for the life-time prediction of ferromagnetic components in electromagnetic devices and for future studies on magneto-electrodeposition processes.

1. Introduction

In the last decades many investigations on the anodic dissolution of Fe in acidic media were performed [1–5]. The partial reaction steps and the electrode kinetics were studied in detail, especially in acidic sulphate electrolytes. A typical current density–potential curve of Fe in 0.05 M H_2SO_4, shown in Fig. 1, identifies the characteristic potential regions at low polarization. In the *cathodic region*, the hydrogen reduction is the dominating reaction. At low anodic polarization, in the so called *active region*, the dissolution reaction of Fe to Fe^{2+} is charge transfer controlled. Therefore, the anodic current density increases logarithmically with increasing potential with a Tafel slope of 40 mV. The anodic current density i_a is independent of the activity of Fe^{2+} and ${SO_4}^{2-}$ ions in the electrolyte, but changes with the pH as given by Eq. (1) [1–5]

$$\frac{\partial \log i_a}{\partial pH} = 1 \qquad (1)$$

At higher anodic potentials the *transition region* is reached where the Fe surface is covered with an adsorbed $Fe(OH)_2$ species. The transition region is characterized by a maximum–minimum behavior in the current density–potential curve due to an inhibiting effect of the layer on the dissolution reaction. The current density level is governed by the decomposition of $Fe(OH)_{2,ads}$. For the local maximum (E_{max1}, i_{max1} in Fig. 1) the pH value dependence is given in Eqs. (2) and (3) [1–3]

$$\frac{\partial E_{max\,1}}{\partial pH} = -\frac{2.303RT}{F} \qquad (2)$$

$$\frac{\partial \log i_{max\,1}}{\partial pH} = -0.5 \qquad (3)$$

In contrast to the frequently reported maximum–minimum behavior in the current density–potential curve, Schweickert et al. [5] observed a plateau of the current density i_{pl} in the same potential region with a pH value dependence according to Eq. (4)

$$\frac{\partial \log i_{pl}}{\partial pH} = -0.6 \pm 0.05 \qquad (4)$$

The authors stated that the maximum–minimum behavior origins from high potential scan rates in the potentiodynamically conducted investigations. At more anodic potentials (not investigated in this study) the transition region is followed by the *prepassive region*. There a new reaction pathway starting from the adsorbed $Fe(OH)_2$ dominates. This potential region is followed by the *passive region* in which the Fe electrode is covered by a protecting oxide layer [2–4].

A superimposed magnetic field can affect the anodic dissolution of Fe by two mechanisms: an impact on the charge transfer step or on the mass transfer in the electrolyte. The magnetic field effects on the mass transfer are the following. First, a superposition of the dissolution current density and the magnetic flux density B results in the Lorentz force F_L

$$F_L = i \times B \qquad (5)$$

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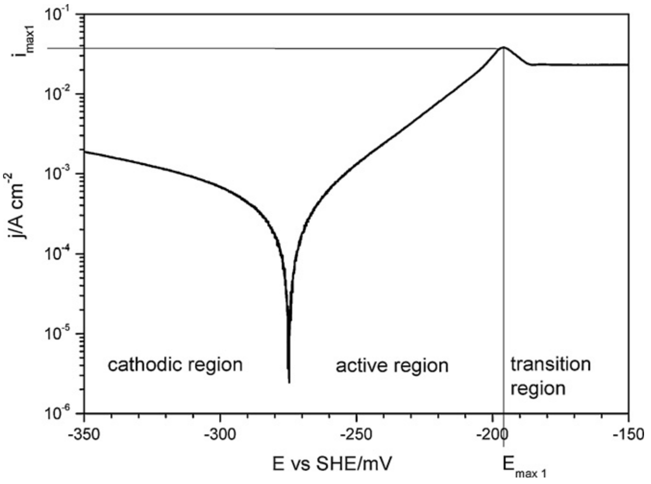

Fig. 1. Current density–potential curve of Fe in 0.05 M H_2SO_4 (scan rate 2 mV/s), subdivision in cathodic region, active region and transition region and the position of the local maximum E_{max1}, i_{max1}.

It enhances the mass transfer by driving a macroscopic convection of the electrolyte [6–10]. Second, due to the ferromagnetic nature of Fe the metal becomes magnetized in the presence of a magnetic field which leads to an inhomogeneous flux density distribution in front of the electrode [15]. In such an inhomogeneous magnetic field, the magnetic field gradient force F_B

$$F_B = \chi_m c \frac{B\nabla B}{\mu_0} \quad \chi_m : \text{molar susceptibility}, \ c : \text{concentration},$$
$$\mu_0 : \text{magnetic permeability of vacuum.} \qquad (6)$$

acts on paramagnetic ions by pulling them into regions of high magnetic flux density [11–14], i.e. into the rim region of the electrode surface [15].

The influence of a superimposed magnetic field on the charge transfer step is discussed more controversially. Kelly [16] reported a shift of the open circuit potential of Ti in H_2SO_4 solution and proposed a modified Buttler–Volmer equation. Aogaki et al. [17] also observed a magnetic field effect in the charge transfer step during Cu deposition in a $CuSO_4$ solution containing 1 M H_2SO_4. On the contrary, Devos et al. [18] as well as Koehler and Bund [19] demonstrated for various redox systems and for the anodic dissolution of Fe [18] that the charge transfer is not significantly affected by superimposed magnetic fields. It was furthermore shown by electrochemical impedance spectroscopy that the double layer capacity is independent of the applied magnetic field.

The anodic behavior of Fe in the active and transition region was stated to be independent of the agitation of the electrolyte [20,21]. Therefore, it was widely accepted in the scientific community that there is no impact of superimposed magnetic fields on the processes related to the charge transfer controlled dissolution of Fe [22–26]. However, all the previous investigations were performed in highly concentrated, i.e. highly conductive electrolytes. In the present manuscript a significant magnetic field effect on the charge transfer controlled anodic dissolution of Fe in low concentrated acidic electrolyte is demonstrated.

2. Theory

At the Fe electrode surface an enhanced Fe^{2+}-ion concentration is present due to the continuous production of ions by the anodic reaction. This accumulation of positively charged Fe^{2+}-ions leads to a migration of cations, such as H^+-ions, away from and of anions towards the electrode surface. Therefore, the surface pH value is enhanced with respect to the bulk electrolyte. Obviously, this effect is stronger pronounced in low concentrated (low conductive) electrolytes, as it was demonstrated by Ateya and Pickering [27]. According to the pH value dependence of the active Fe dissolution (Eqs. (1)–(4), this pH value derivation should affect the anodic current density. Under magnetic field influence the Lorentz force F_L and the magnetic field gradient force F_B introduced above may act on the Fe^{2+}-ion concentration and therefore, on the pH value close to the electrode surface. In consequence, a magnetic field impact on the anodic current density can be expected although the magnetic field does not affect the charge transfer step of the reaction. F_L induces a convective motion in the electrolyte transports Fe^{2+}-ions away from and H^+-ions towards the electrode's surface. Hence, F_L decreases the surface pH value and the anodic current density (see Eq. (1)) compared to the dissolution without applied magnetic field. F_B further accumulates Fe^{2+}-ions at the electrode surface. This accumulation results in a further enhanced pH value and therefore, to enhanced anodic current densities.

Throughout this paper the cross-sectional area of an embedded Fe cylinder will be regarded as the anodically dissolving electrode surface. F_L is maximized when the external magnetic field is applied parallel to the electrode surface (i.e. perpendicular to the dissolution current flow). To separate F_L effects from F_B effects samples with large surface area should be chosen such that the F_B effects are negligible small. Furthermore, high magnetic flux densities result in high F_L effects (linear scaling).

F_L is minimized and F_B is maximized when the external magnetic field is applied perpendicular to the electrode surface (i.e. formally parallel to the dissolution current flow). The ferromagnetic electrode becomes magnetized by the applied magnetic field, which leads to an inhomogeneous magnetic flux density distribution in front of the electrode surface. For a cylindrically shaped electrode high magnetic flux densities and high gradients of the magnetic flux density are present all over the rim of the electrode [15]. However, due to the bent magnetic flux lines at the cylinder rim F_L is minimized, but still present. It drives rotational electrolyte flow along the electrode rim. The velocity of this flow is determined by the equilibrium between F_L and the friction of the electrolyte. Therefore, a small electrode diameter is favourable to investigate the impact of F_B on the anodic current density. This way the surface fraction with high F_B action and hence the ratio F_B/F_L can be maximized. F_B scales linearly with $B\nabla B$. Therefore, the ratio of F_B/F_L is largest when the ferromagnetic electrode is magnetically saturated. According to numerical simulations (not shown) a magnetic flux density of the superimposed magnetic field of 0.3 T is sufficient to magnetically saturate the Fe electrode.

3. Experimental

For the investigation of the F_L impact an in-house produced Fe single crystal of 4 mm diameter and 10 mm length was used as working electrode. To examine the impact of F_B a Fe wire of 1 mm diameter and 10 mm length was used as working electrode. Both samples were embedded in epoxy resin, ground with abrasive paper down to grit 4000, polished with 1 μm diamond suspension and cleaned with water and ethanol. The working electrodes were placed at the bottom of the electrochemical cell with the dissolving surface facing upwards to minimize effects of natural convection (action of gravity on electrolyte volume elements of increased density due to enrichment with Fe^{2+}-ions). For the investigation of the F_L impact on the anodic current density of the Fe dissolution, a homogeneous magnetic field with a magnetic flux density of 0.5 T was applied parallel to the electrode surface using an electromagnet (HV7, Walker Scientific). To investigate the F_B effect a homogeneous magnetic field of 0.3 T was superimposed perpendicular to the electrode surface.