The electrochemical dissolution of iron(III) and chromium(III) oxides and ferrites under conditions of abrasive stripping voltammetry

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Abstract

Electrochemical dissolution of iron(III) and chromium(III) oxides can be described as an irreversible reaction of homogeneous, continuous sets of particles or as a mixture of such sets. Each set can be characterized by the rate constant at reference potential, charge-transfer coefficient and heterogeneity factory \( y \) within a certain potential range in which not mass transport but electron transfer controls the overall reaction rate. This condition is easy to maintain in the case of chronoamperometry but not in the case of linear sweep voltammetry at a scan rate of 1 mV s\(^{-1}\) or more. However, the commonly used relationship between the potential of a voltammetric peak and the kinetic characteristics of the charge-transfer is valid. The commonly used exponential shape of chronoamperometric curve is a special case for certain size distributions of particles. The influence of the heterogeneity factor \( y \) on the shape of voltammetric peak is discussed. According to the results obtained, abrasive stripping voltammetry is a more effective tool for studying solid compounds than the carbon paste method, because of negligible disturbance from dissolved species and a correspondingly simpler voltammetric curve, as demonstrated here in the case of \( \text{CuFe}_2\text{O}_4 \).

Keywords: Iron; Chromium; Oxides; Ferrites; Electrochemical reduction

1. Introduction

The reductive or oxidative dissolution reactions of metal oxides are intensively studied in relation to various problems of great practical and theoretical importance, such as the decontamination of primary cooling loops of nuclear reactors and descaling industrial equipment [1-5], Fe and Mn oxide speciation in sediments and soils [6-8], and mineral weathering [9]. Various aspects of these processes can be emphasized, such as the reaction mechanism and influence of a solution composition on the one hand, and the effect of particle shape, size and phase composition on the other. As a consequence, various kinetic equations are used and therefore various solid phase characteristics are obtained. When a reaction mechanism has to be highlighted, the simplest kinetic laws, based on the model of a surface reaction of monodisperse isotropic spheres, are widely used (and a corresponding synthetic route for solid samples must be chosen) [1,2,10-12]. This definition of the problem leads to the so-called inverse-cubic rate law [1,10]

\[
W_0^{1/3} - W^{1/3} = k't
\]

where \( W \) and \( W_0 \) are the weight of undissolved crystals at time \( t \) and at the beginning of the reaction respectively. The observable rate constant \( k' (s^{-1}) \) depends on the particle size, as it is directly proportional to a specific surface area of samples. The overall reaction rate \( J (\text{mol s}^{-1}) \) under the same assumptions [13] can be derived from

\[
J = \frac{dN}{dt} = k'\sigma_0 W_0 \left( \frac{W}{W_0} \right)^{2/3}
\]

where \( N \) is the molar amount and \( \sigma_0 \left( \text{m}^2 \text{ g}^{-1} \right) \) is a specific surface area at the start of the reaction. In the simplest case, a linear time-dependence of the dissolution during its early stages [9,10] is assumed.

In Eqs. (1) and (2), the only characteristics of dissolving particles are the average diameter \( r_0 \) or the specific surface area, and the composition of the solid phase and the solution determine the rate constant \( k' \) or \( k'' \). This simple approach fails even in the case of a mixture of smaller and bigger particles [1], as frequently occurs in some synthetic products, e.g. after high-temperature processing, because of the sintering of single crystals (spinel [2,14], hematite [11,15]). Such a type of polydispersity can cause a double voltammetric peak to appear [11,12,14], and the applicabil-
ity of the kinetic laws (1) or (2) is limited only up to a
certain stage of dissolution [1]. These mixtures could be
considered as a sum of "monodisperse" fractions according
to granulometric measurements [12]. However, a dif-
f erent approach is necessary for mixtures of particles with
continuous distribution of size or reactivity of the surface
unit [8,16–18]. In the case of a pseudo-first-order reaction,
the overall reaction rate of such a continuous mixture is
given by

\[ J = kN_o \left( \frac{N}{N_0} \right) \gamma \]  

(3)

or in terms of the current

\[ I = kQ_o \left( \frac{Q}{Q_0} \right) \gamma \]  

(4)

where \( k \) (\( \text{s}^{-1} \)) is an observable rate constant, \( N_0 \) and \( N \)
are molar amounts of solid at the start and during the
course of the reaction, and \( Q_0 \) and \( Q \) are the correspond-
ing charges. The relationship between \( k \) from Eqs. (3) and
(4) and particle size is the same as for Eq. (1). Eqs. (3) and
(4) allow further separation of composition and geometri-
cal contributions to the change of reactivity in the course
of dissolution. Solid particles are characterized by an
average (initial) rate constant and additional homogeneity
factor \( \gamma \) related to size or composition distribution. An
eventual dissolution anisotropy ought also to affect the
value of \( \gamma \). From comparison of Eqs. (2) and (3) it follows
that the latter type of kinetic law changes to the former one
if \( \gamma = 2/3 \) (for monodisperse spheres and cubes). As far
as we are aware, a simple time dependence of the reaction
rate has not yet been derived on the basis of Eq. (3) or (4),
except for the semiempirical and very flexible equation
reported by Postma [8].

As in the case of irreversible reactions of ions, the
potential of the voltammetric peak is given by the charge-
transfer coefficient \( \alpha \) and the rate constant \( k \) in the case of
solid particles, as derived for a carbon paste electrode with
non-conducting binder [19,20]:

\[ E_p = E_0 = - \frac{RT}{\alpha nF} \ln \left( \frac{\alpha nF}{RT} v \right) + \frac{RT}{\alpha nF} \ln \left( \frac{k_e}{d} \right) \]  

(5)

where \( k_e \) (\( \text{m s}^{-1} \)) is the rate constant of the electrode
reaction at \( E_0 \) and \( d \) is the particle diameter. This equation
was verified for an anodic dissolution of sieved powders at
Co and Ag using carbon paste electrodes. A corresponding
relationship for the peak height [19,20] is

\[ I_p = 0.37 \frac{\alpha nF}{RT} v (nF c_0 d S) \]  

(6)

where \( c_0 \) is the molar concentration of solid and \( S \) the
total surface of the electrode. No attempt has been made so
far to test both equations in the light of Eq. (3) or (4).

Our aim is also to show the ability of abrasive stripping
voltammetry (AbrSV, [21,22]) to easily obtain more infor-
mation on dissolving solid particles. It is well known that
the reductive or oxidative dissolution of metal oxides is
much faster than only a proton promoted one [1–5,9].
Moreover, electrochemical methods are able to bring the
reaction rates even closer to the diffusion-control limit; allowing complete dissolution experiments to be per-
formed in tens of minutes instead of hours, and with a
continuous following of the reaction rate instead of off-line
analysis as in the frequently used chemical dissolution.
Utilization of the simple and quick AbrSV seems to be
particularly promising in this context. Oxidic compounds
of Fe seem to be particularly suitable for testing this
method due to their diversity, sufficient knowledge on
individual phase characteristics, and their practical signifi-
cance as well. This topic was studied previously with
active carbon paste electrodes [11,12,14,23,24]; this offers
a challenging opportunity for comparison of both methods.

2. Experimental

2.1. Apparatus and procedures

A polarograph PA4 and recorders TZ4260 (for
chronoamperometry) and XY4106 (for voltammetry)
(Laboratory Devices, Prague, Czech Republic) were used.
A home-made paraffin-impregnated graphite electrode
[17,21,22] was prepared from spectral graphite rods (5 mm
in diameter) as reported previously [17]. All potentials
mentioned below were referred to a saturated calomel
electrode. Dissolution experiments were carried out in
phosphate buffer (0.05 mol dm\(^{-3}\) H\(_3\)PO\(_4\) and 0.05 mol
dm\(^{-3}\) KH\(_2\)PO\(_4\)); 0.2 mol dm\(^{-3}\) chloroacetate buffer and
0.1 mol dm\(^{-3}\) potassium hydrogen oxalate were also used
for measurement of \( \gamma \) values. Working and reference
electrodes were separated from the Pt sheet counter-elec-
trode by a diaphragm. Samples were fixed on the working
electrode surface by vigorous rubbing of several mil-
ligrams of powder on a strip of filter paper, and weakly
adhered particles were wiped off by a pulp. This procedure
is obvious for AbrSV (see also Refs. [17,21,22,25]).
The surface of the working electrode was cleaned before each
measurement using a mixture of silicon oil and Cr and Si
oxides. A home-made mixture of silica gel with silicone
oil was used before oxidative dissolution of Cr\(_2\)O\(_3\). The
number of dissolving particles was determined by integra-
tion of linear-sweep voltammetric or chronoamperometric
curves. A typical amount of deposited sample was approxi-
mately 1–50 mC (the bigger the particles, the higher the
amount of deposited sample). If the dissolution of a sample
in the course of the voltammetric measurement was incom-
plete, a subsequent chronoamperometric measurement was
conducted. We did not intend to perform time-consuming
complete dissolution in the course of voltammetry, particu-
larly in the case of polydisperse sets of particles [12]. Additionally, the catalytic reduction of H⁺ is suspected to proceed on an oxidic surface at higher negative potential [4].

SOLO and SUPERCALC were used to calculate the kinetic parameters from measured chronoamperometric curves or voltammograms.

2.2. Description of solid samples

Solid samples were synthesized by the usual methods. Hydrothermal processes seem to produce sets of particles with the narrowest size distribution and reasonable phase homogeneity. In general, whenever possible temperatures higher than 500°C were avoided to prevent the sintering of particles.

α-Fe₂O₃ was prepared by a hydrothermal method [26]. Commercially available α-Fe₂O₃ red #130 (Bayer, FRG) and γ-Fe₂O₃ SCP21 for magnetic information storage (Societe Chimique de Provence, France) were also used. BaFe₁₂O₁₉ (barium hexaferrite) was synthesized using the citrate method (final ignition temperature 750°C). α-FeOOH was prepared by aging of ferrihydrite in alkaline media at 70°C [15].

ZnFe₂O₄ was obtained similarly as Fe₃O₄ by the oxidation of Fe²⁺ solution by KNO₃ [15], but in the presence of an appropriate amount of Zn²⁺; the precipitate was then dried and heated for 1 h at 500°C. Neither X-ray diffraction nor Mössbauer spectroscopy found any phase impurities in the resulting ZnFe₂O₄, but in addition to regular cubic particles, small amorphous particles are visible on transmission electron micrographs. The presence of smaller particles was also confirmed by Mössbauer spectroscopy. To analyse their content, a suspended sample was dissolved in a mixture of ammonium hydrogen oxalate (20 mmol dm⁻³) with (NH₄)₂Fe(SO₄)₂·6H₂O (1 mmol dm⁻³). A 5 mg sample in the form of a water suspension (1.3 ml) was injected into 100 ml of deaerated dissolving mixture at the start of the reaction and the limiting diffusing current of Fe(III) oxalate complex formed was continuously measured (glassy carbon electrode, -0.5 V). All procedures were performed under an argon atmosphere. For more details see Ref. [27].

CuFe₂O₄ was obtained by precipitating an equimolar mixture of Fe²⁺, Fe³⁺ and Cu²⁺ with NaOH, followed bubbling of air through the mixture for several hours. The resulting dark precipitate was heated to 800°C. Its X-ray pattern indicated a spinel type with tetragonal symmetry.

The ratio of the metal content in mixed oxides was checked by chelatometric titration or potentiometric stripping analysis (for the determination of Cu). If the X-ray diffraction did not detect the presence of phase impurities, deviations from stoichiometry of up to 5% were accepted.

Chromium(III) oxide (α₂Cr₂O₃) was prepared by heating of an amorphous precipitate of chromium(III) sulphate with urea at 650°C.

X-ray diffraction, Mössbauer spectroscopy and transmission electron microscopy were used to choose synthetic samples with reasonable crystallinity and phase purity.

3. Results and discussion

3.1. Theory and experiment in the case of a homogeneous set of particles

The dissolution of monodisperse single-phase particles as well as of their sets with homogeneous (single-maximum) size distribution function can be easily described using chronoamperometric measurement and Eq. (4), as verified for the variety of Fe(III) oxide phases [17]. The upper limit of the reaction rate that makes it possible to neglect the influence of the final rate of mass transport could be easily detected by checking the validity of

\[ k = k_0 \exp \left( -\frac{αnFE}{RT} \right) \]

for the rate constant of an irreversible process, where \( k_0 (s^{-1}) \) is the rate constant at the potential of the reference electrode. Then, a homogeneous set of particles gives a simple voltammetric peak [11,12,14] and a monotonic \( I-t \) curve [17] (see also Fig. 3 below).

We have found (see Appendix A) that the voltammetric characteristics are determined not only by the \( α \) value and \( k \), as shown previously [19,20], but also by the \( γ \) value, as shown in Figs. 1 and 2 and Table 1. The higher the value of \( γ \), the broader and lower is the peak obtained, and the peak potential does not shift substantially at the same time. Therefore, Eq. (6) for voltammetric peak height has to be modified so as to be valid for a more general shape of

Fig. 1. The influence of the \( γ \) value on the shape of the voltammetric curve. The curves were calculated for \( α = 0.5, k_0 = 1 \times 10^{-2} \text{ s}^{-1} \) and \( ν = 1 \text{ mV s}^{-1} \). The \( γ \) values are given close to the corresponding curves.
Fig. 2. Real voltammograms of hydrothermal α-Fe₂O₃ (curve 1) and BaFe₁₂O₁₉ (curve 2). Note slow decrease of current behind the maximum with respect to Fig. 1.

particle size distribution function. Eq. (A2) and its approximate form

\[
\left( \frac{I_p}{Q_0} \right)_{col} = 0.37 \frac{\alpha n F}{RT} \nu(1 - 0.47 \ln \gamma) \quad (8)
\]

fulfill this requirement.

From the comparison of Eqs. (6) and (8) and from the shape of the chronoamperometric curve for irreversible dissolution in exponential form, \[ I = k Q_o \exp(-k \nu) \quad [19,20] \], it follows that the particle set assumed by Brainina and coworkers, according to Eq. (3) or (4) with \( \gamma = 1 \), is typical for the surface reaction of spherical particles with weight log-normal distribution [18]. Eqs. (8) and (A2) are suitable for a precise description of the course of the dissolution of solid particles by a surface reaction.

It must be pointed out that the description of dissolution by surface reaction requires infinitely fast mass transport (compared with the overall reaction rate). In reality, \( \gamma \) is a non-decreasing function whose value of the rate constant is near the voltammetric maximum (and the rate constant rises only to its diffusion limit at even larger overvoltages). Therefore, real peak heights are usually lower in comparison with Eq. (8). Comparing \( I_p/Q_o \) for five samples of iron(III) oxides (both \( \alpha-\)Fe₂O₃, α-FeOOH, BaFe₁₂O₁₉ and γ-Fe₂O₃) with their \( \alpha \) and \( \gamma \) values (Table 2), we obtained

\[
\left( \frac{I_p}{Q_o} \right)_{meas} = 0.2 \frac{\alpha n F}{RT} \nu(1 - 0.5 \ln \gamma) \quad (9)
\]

\( \gamma \) was measured by chronoamperometry at various potentials and in various acidic solutions at \( k < 2 \times 10^{-3} \) s⁻¹, \( \alpha \) was calculated from Eq. (5) by measuring the dependence of the potential of voltammetric maximum on the scan rate in phosphate buffer. By comparing Eqs. (8) and (9), we can infer that the general effect of heterogeneity of the set of particles on the linear-sweep voltammetric peak height is in acceptable agreement with the theory, but absolute values of the current are somewhat lower than calculated ones. Thus we assume that the validity of Eq. (8) is limited by the final rate of mass transport during the course of voltammetric measurement. The mechanism of this effect is not quite clear, and to explain it we should understand why the \( \gamma \) parameter increases with increasing dissolution rate. The result of such behaviour is clearly visible from the slow decrease of current behind the voltammetric maximum (compare Figs. 1 and 2). This decrease is faster as the acidity of the supporting electrolyte increases in the case of iron(III) oxides, but even in 2 M sulphuric acid or 1 M hydrochloric acid, the peak shape is far from the theoretical one in this region at \( \nu = 1 \) mV s⁻¹. We therefore tried to find another oxidic compound which would behave more closely to the theory. Chromium oxide may be dissolved in dilute acids and the decrease in current behind the voltammetric maximum is much faster, although not theoretically at 1 mV s⁻¹ (if not ignited at too high a temperature).

Table 3 lists the oxidative dissolution characteristics of \( \alpha-Cr₂O₃ \) in dilute sulphuric acid. The growth of \( \gamma \) with \( k \) may be characterized by chronoamperometry, but regression analysis (see Eq. (A1)) of the voltammetric curve yields an “average” value for the potential range described. The “right” value of \( \gamma \) according to Eq. (3) or (4) ought to be constant for the surface reaction, and therefore the formal validity of Eq. (4) with continuously growing \( \gamma \) shows its more general applicability. We can see from the results in Table 3 that the above mentioned theoretical assumptions are compatible with each other, and that the

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha )</th>
<th>( \gamma )</th>
<th>( \alpha n F/Q_o ) 10⁻³</th>
<th>( \nu(1 - 0.5 \ln \gamma) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe₂O₃ (hydrothermal)</td>
<td>0.49</td>
<td>1.18</td>
<td>3.43</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃ (red pigment)</td>
<td>0.25</td>
<td>0.93</td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td>BaFe₁₂O₁₉</td>
<td>0.34</td>
<td>1.48</td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>0.51</td>
<td>0.92</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td>α-FeOOH</td>
<td>0.77</td>
<td>1.27</td>
<td>4.64</td>
<td></td>
</tr>
</tbody>
</table>
observed dependence of $\gamma$ on $k$ is not particular to iron(III) oxides.

The equation

$$E_p = -\frac{RT}{nF} \ln \left( \frac{a_nF}{nF} \right) + \frac{RT}{a_nF} \ln k_0$$

(10)

is valid for the electrode reaction rate constant $k$ defined by Eq. (3) or (4). Because $E_p$ is not affected by the value of $\gamma$ (see Appendix A), the above mentioned unclear behaviour does not limit the validity of Eq. (10).

3.2. ZnFe$_2$O$_4$: a heterogeneous set of particles

Both phase non-uniformity [25] and heterogeneous distribution functions (with more distinct maximums) of the crystal size [11,12,14] can cause the presence of two or more VA maximums. Their separation on the voltammogram can be estimated from Eq. (10). In this case the chronoamperometric curve has a characteristic shape, as demonstrated for the dissolution of zinc ferrite in Fig. 3. For construction of a normalized chronoamperometric curve, Eq. (4) may be simply re-arranged:

$$\ln \left( \frac{I}{k_0} \right) = \gamma \ln \left( \frac{Q}{Q_0} \right)$$

(11)

A homogeneous set of particles (hydrothermal hematite) gives identical straight lines according to Eq. (11), but a heterogeneous set gives a broken line. The curve for the heterogeneous set was obtained as described in Appendix B. From the shape of the normalized chronoamperometric curves, composed of two linear parts, two processes can be easily characterized on the basis of Eqs. (4) and (7), with results listed in Table 4. Comparison of the corresponding calculated linear-sweep voltammetric curve with that found experimentally (see Fig. 4) allows us to suggest that a faster process (Table 4) may result from two hardly distinguishable processes ($C_1$ and $C_2$ on Fig. 4); the potential of peak $C_3$ is close to the value calculated from Eq. (10) using the characteristics of the slower process.

Table 3

<table>
<thead>
<tr>
<th>Method</th>
<th>$k/10^{-3}$ s$^{-1}$</th>
<th>$\gamma$</th>
<th>$k_1/10^{-6}$ s$^{-1}$</th>
<th>$E_p$/V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i-t$, $E = 1.15$ V</td>
<td>0.14</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eq. (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i-t$, $E = 1.20$ V</td>
<td>1.4</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i-t$, $E = 1.25$ V</td>
<td>6.7</td>
<td>1.5</td>
<td>0.62 $^a$</td>
<td>12 $^a$</td>
</tr>
<tr>
<td>$i-t$, $E = 1.30$ V</td>
<td>21</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i-t$, $E = 1.35$ V</td>
<td>58</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i-t$, $E = 1.40$ V</td>
<td>101</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VA, $E_p = f(v)$</td>
<td>$-$</td>
<td>0.57</td>
<td>24</td>
<td>1.30</td>
</tr>
<tr>
<td>Eq. (10) $^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VA, peak fitting</td>
<td>1.7</td>
<td>0.67</td>
<td>8</td>
<td>1.31</td>
</tr>
</tbody>
</table>

$^a$ For $E = 1.2$ to 1.35 V, Eq. (5).
$^b$ For $v = 1, 2.5$ and 10 mV s$^{-1}$.
$^c$ For $E = 1.2$ to 1.32 V.
Table 4
Characteristics of ZnFe$_2$O$_4$ dissolution obtained by chronoamperometry ($I-t$) using Eqs. (4) and (7) (see Appendix B for calculation procedure) and by voltammetry. The chronoamperometric curves were measured at working electrode potentials of 0, 0.05 and 0.1 V and $v = 1$ mV s$^{-1}$, phosphate buffer was a basic electrolyte.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quicker process</th>
<th>Slower process</th>
<th>Procedure used</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0/10^{-3}$ s$^{-1}$</td>
<td>74</td>
<td>2.6</td>
<td>$I-t$, Eqs. (4) and (7)</td>
</tr>
<tr>
<td>Mean value of $\gamma$</td>
<td>1.6</td>
<td>1.3</td>
<td>$I-t$, Eqs. (4)</td>
</tr>
<tr>
<td>Mean value of $\sigma$</td>
<td>0.41</td>
<td>0.37</td>
<td>$I-t$, Eqs. (4) and (7)</td>
</tr>
<tr>
<td>Content/% of $Q_0$</td>
<td>18</td>
<td>78</td>
<td>$I-t$ $^*$</td>
</tr>
<tr>
<td>Corresponding D.c. VA $E_p/V$</td>
<td>0.093</td>
<td>-0.118</td>
<td>Eq. (10)</td>
</tr>
<tr>
<td>Experimentally obtained $E_p/V$</td>
<td>two unseparated peaks, approx. 0.02, 0.12, (denoted C$_1$ and C$_2$)</td>
<td>-0.12 (denoted C$_3$)</td>
<td>voltammetry, see Fig. 4</td>
</tr>
</tbody>
</table>

$^*$ The rest of the sample is formed by much more slowly reacted particles (forming approximately 4% of the total mass of the sample according to the deviations from Eq. (4) at the end of the dissolution).

calculated from Eq. (13) is of intensity approximately double that measured experimentally (see also the discussion of Eqs. (8) and (9)). From Eq. (10) and the estimation of the peak separation of the components C$_1$ and C$_2$ attributed to a faster process (approximately 0.1 V), the ratio of their rate constants, approximately 5:1, can be calculated. According to our experience, such a small difference makes the mathematical resolution of the processes imperfect, particularly with respect to the uncertainty in the approximation of a real, homogeneous set of particles (mean relative deviations are usually less than 10%). This order of differences between the rate constants shifts such heterogeneous sets of particles into the group of those with apparently homogeneous character but a fairly high value of $\gamma$ (1.6). Because ZnFe$_2$O$_4$ is the uniform phase sample, the heterogeneity described can be caused only by particle size heterogeneity.

Dissolution of the sample in a hydrogen oxalate-Fe$^{II}$ mixture (see Experimental section) shows the presence of 7% fast reacted "kinetic impurity" ($k$ at least ten times higher than that of the rest). The amount found is lower than the value obtained by chronoamperometry. Either some side reaction [28] or non-equivalent deposition of the mixture component onto the surface of the working electrode [25] may explain this, as no significant response was found on the bare electrode in the region of C$_1$ and C$_2$. Nevertheless, processes described as C$_1$ and/or C$_2$ are undoubtedly caused by the presence of more reactive smaller particles, whose presence was confirmed by suspension dissolution. The agreement between suspension dissolution and the AbrSV procedure in the case of kinetic impurities in iron(III) oxides is a topic of further study.

3.3. CuFe$_2$O$_4$: comparison of the AbrSV and active paste methods

In order to obtain specific information on dissolved solid particles, the electrode process investigated must be

![Fig. 4](https://example.com/fig4.png)
protected against disturbing ions. If the acidic binder used in the carbon paste electrodes dissolves a part of the sample prior to the voltammetric measurement, the resulting ions contribute to the formation of the electrochemical spectrum even in the case of simple compounds such as α-Fe₂O₃ [11], LiFeO₂ and NaFeO₂ [14], Fe₂O₃, Fe₃O₄ and CuFe₂O₄ [23,24]. Naturally, in the case of the AbrSV, the resulting ions can freely diffuse away into the depth of a solution and therefore they cannot interfere with the dissolution measurement. Fig. 5 shows an example of a cyclic d.c. VA curve of CuFe₂O₄. In contrast to a considerable number of peaks, with those that correspond to the dissolved species dominating, obtained by an active carbon paste electrode with diluted HC₁ as binder [23], the AbrSV gives only two cathodic and one anodic peaks for a solid species. With the aim of finding out the fate of the solid products from the electrode process in the AbrSV open system, we studied the course of the dissolution reaction of CuFe₂O₄ in more detail. We performed a complete dissolution of the ferrite via $\int_{t_0}^{t_1} dt$ measurements (obtaining a total reducing process charge of $Q_\text{c}$), followed by voltammetric measurements of the anodic reaction (obtaining a total anodic oxidation charge $Q_\text{a}$ of Cu). On the basis of the results thus obtained, we propose the following overall reaction scheme, describing the reductive process:

$$\text{CuFe}_2\text{O}_4 + 8\text{H}^+ + (2 + n)e^- \rightarrow 2\text{Fe}^{2+} (aq) + \frac{n}{2}\text{Cu}(s) + \left(1 - \frac{n}{2}\right)\text{Cu}^{2+} (aq)$$ (12)

assuming that the destruction of the crystal lattice of the ferrite requires reduction of all Fe(III) centres (as a result of the irreversibility of the reaction in a non-complexing medium, see also Ref. [4]). The Cu(I) compounds are unstable in the phosphate buffer used, and therefore only Cu²⁺ and Cu⁰ can be present here (this assumption is supported by the existence of a single anodic peak in Fig. 5), and all Cu⁰ formed is deposited on the surface of the working electrode. On the basis of this model, we have found that above $-0.15$ V Cu(II) is evolved from ferrite mostly as Cu²⁺(aq) in the course of the dissolution: $E = -0.15$ V, $n = 0.11$; $E = -0.10$ V, $n = 0.045$; $E = -0.05$ V, $n = 0.016$. But when reduction proceeds at less than $-0.2$ V, experimentally measured $n$ approximates 1 ($Q_\text{a}/Q_\text{c}$ is in the range 0.42 to 0.5).

In the potential range 0 to $-0.15$ V, the chronoamperometric curves adopt a similar shape as in the case of ZnFe₂O₄, apart from the smaller difference between $k_0$ for the faster and slower processes. The $E_p$ corresponding to $k_0$ and $\alpha$ obtained are $-0.14$ and $-0.27$ V. The former value is close to the experimentally found C₁ ($E_\text{c₁} = -0.13$ V). Because of the low $n$ according to Eq. (12), the reaction path can be the same as in the case of any other iron(III) oxide, but the mechanism changes at a more negative potential. The rate constant $k$ (via chronoamperometry) is independent of potential $(8-9) \times 10^{-3}$ s⁻¹ at $E = -0.2$ to $-0.4$ V, and $\gamma$ surprisingly drops from 2 to approximately 1.1, indicating that a slow surface mass transport process of the insoluble species of copper becomes the rate determining step. Thus we suggest that the observed peak C₂ is of quite different essence from C₁. In general, the presence of more than one peak is quite unusual in the case of a uniform phase Fe(III) oxide compound with homogeneous distribution of particle size. As far as we know [17,25], the only exception to this rule is goethite (α-FeO(OH)) at higher scan rates (at least 10 mV s⁻¹), owing to its anisotropic dissolution [10,25].

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Appendix A. A relationship between potentiostatic dissolution characteristics and voltammetric peak potential

From Eqs. (4) and (7) together with $I = \frac{dQ}{dt}$ and linear sweep $E = E_{\text{START}} - \nu t$ it follows that

$$\frac{dQ}{dt} = k_0 Q_o \exp\left(-\frac{\alpha nF(E_{\text{START}} - \nu t)}{RT}\right) \left(\frac{Q}{Q_0}\right)^\gamma$$ (A1)

After separation of variables and solution of the resulting equation, we obtain

$$I = \frac{Q}{Q_0} = \left[1 - (1 - \gamma) \frac{k_0 RT}{\alpha nF} \exp\left(\frac{\alpha nF t}{RT} E_{\text{START}}\right)\right] \times \left[\exp\left(\frac{\alpha nF t}{RT}\right) - 1\right]^{\gamma - 1}$$
The relative deviations of experimentally measured currents and calculated ones can be as small in the case of binary mixtures as in the case of homogeneous sets. For example, the average relative deviation is approximately 7% in the case of ZnFe₂O₄.

A normalized curve in Fig. 3 can be obtained by calculation of the "mean" initial rate constant \( k_{AB} = (k_A Q_{0,A} + k_B Q_{0,B}) / Q_0 \). Eq. (8) can be used with \( k = k_{AB} \) to demonstrate an independence of \( \gamma \) on experimental conditions.

A special iteration program for regression analysis of Eq. (B1) would be more effective for the mathematical treatment of experimental data if it was available (constants A, C, E and function B(t)) would have to be calculated:

\[
l(t) = A \left[ Q(t) - B(t) \right]^c + D \left[ B(t) \right]^e \quad (B1)
\]

Appendix B. The separation of faster and slower processes in the course of chronoamperometric dissolution

We assume for simplicity a mixture of two homogeneous sets of dissolving particles, A and B, with \( k_A > k_B \). Measuring the chronoamperometric curve, we obtain a function \( I(t) \) as a sum \( I(t) = I_A(t) + I_B(t) \), and by integrating the \( I(t) \) curve we get also \( Q_0 = Q_{0,A} + Q_{0,B} \). If the dissolution rates of A and B are sufficiently different, the dependence of \( \ln(I) \) on \( \ln(Q/Q_0) \) has a similar shape as for the example in Fig. 3.

The lack of a simple time dependence of \( I \) on \( t \) in the case of a general homogeneous set of particles (see Eqs. (3) or (4)) complicates the mathematical separation of the processes in the case of heterogeneous sets. The separation of the processes can be carried out only in the event that there is a sufficiently long linear part of the dependence of \( \ln(I) \) on \( \ln(Q/Q_0) \) (according to a linearized form of Eq. (4)) at a later stage of the reaction, or in other words, that the kinetic parameters of the slower process B \( (k_B Q_{0,B} \) and \( \gamma_B \)) can be calculated after complete dissolution of the quickly reacted set A. From that, \( I_A(t) \) for a complete course of dissolution can be calculated by extrapolation; then \( I_A(t) = I(t) - I_B(t) \), and so \( Q_A(t) \) can be calculated and \( k_A \) and \( \gamma_A \) can be obtained from Eq. (4). Because \( Q_{0,B} = Q_0 - Q_{0,A} \), \( k_B \) can be calculated from the previously obtained \( k_B Q_{0,B} \).

References


