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Dissolution of pure and substituted goethites controlled by the surface reaction under conditions of abrasive stripping voltammetry

Abstract Pure goethites and Al-, Cr-, and Mn-goethites, as synthetic and natural products, were used to establish the conditions for electrochemical reductive dissolution following surface reaction kinetics. In diluted perchloric acid and at reaction rate coefficients of the order of $10^{-4}s^{-1}$, the γ parameters in the kinetic equation $J/N_0 = k(N/N_0)^\gamma$ (where J is the reaction rate and N and N_0 are actual and total molar amounts of a solid reactant) were in the range expected for the shape-preserving dissolution of the particles with a certain size and reactivity distribution function. The same range of γ was found using the dissolution of goethites by a chemical reaction via oxalate-ferrous ion surface complexation. The importance of the charge transfer coefficient to describe the iron oxide reactivities was highlighted as it is sensitive to the synthetic route and also to the substitution of iron.

Key words Abrasive stripping voltammetry · Iron oxides · dissolution

Introduction

Chemical dissolution of iron oxides has been studied for a long time in analysis of natural and synthetic mixtures, material chemistry, and technology [1, 2]. At present, the dissolution kinetics of polydisperse populations of iron oxide particles is further developed [3, 4]. The general reaction order equation [5] is applied

$$J = kN_0 \left(\frac{N}{N_0} \right)^\gamma \tag{1}$$

where $J = dN/dt$ is an overall reaction rate, k is a rate coefficient, N and N_0 are actual and total molar

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amounts of the solid reactant, and γ is a constant. Equation 1 is applicable for the reactions proceeding on the whole free surface of the solid particles. Interpretation of the kinetic data is then much simpler than in the case of nucleation kinetics described, e.g., by the Avrami-Erofeev equation.

Dissolution via a chemical reaction and reductive electrochemical dissolution have already been described. Equation 2 for the rate coefficient of an irreversible electrochemical reaction is then used:

$$k = k_0 \exp(-a\,n\,FE/RT) \tag{2}$$

Iron oxides were originally inserted into carbon paste electrodes (CPEE) [6, 7]. Lately, abrasive stripping voltammetry, AbrSV [8–10] has been utilized [4, 11, 12]. Brainina and Vydrevich [13] introduced the first set of equations for the CPEE peak potential and current based on the first-order reaction and Eq. 2. Mouhandess et al. [7] then highlighted the impact of a particular sample granulometry. The general relationships for linear sweep AbrSV and chronoamperometry on the basis of Eq. 1 have recently been derived [4]. However, a final diffusion rate limits the applicability of Eqs. 1 and 2 and causes the increase of γ with increasing reaction rates. Moreover, the γ values hitherto obtained by AbrSV for iron oxides have been higher than expected for surface reactions of single-phase synthetic samples [11]. It is hence necessary to search for the conditions for obtaining γ that could be discussed in terms of the surface reaction kinetics to simplify the interpretation of the dissolution data and also to understand AbrSV processes.

Because γ for a general particle population is available not directly but by kinetic measurement, an independent dissolution method must be applied to evaluate γ for AbrSV. Relatively fast chemical reductive dissolution of goethite (α-FeOOH), hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) in oxalate catalyzed by ferrous ions [14–16] is suitable for this purpose. The reaction product, $[Fe(C_2O_4)_3]^{3-}$, may be quasireversibly reduced, and hence there is a possibility to adopt the system for

continuously monitoring the dissolution. Al-for-Fe substitution in goethite suppresses its dissolution rate in hydrochloric acid [17], dithionite-citrate-bicarbonate solution [18, 19], and also in oxalate-ferrous ion solution [14]. The effect of Al is of a great interest, especially with respect to common Al-for-Fe substitution in natural iron oxides [2]. The phenomenon has not still been studied under conditions of AbrSV.

The aim of this work is to test the possibility of using AbrSV to dissolve goethite under surface reaction control and to determine the influence of Al-, Cr-, and Mn-for-Fe substitution on the electrochemical dissolution characteristics.

Experimental

Pure goethites were synthesized by aging ferrihydrite at 4°C for 68 days (Sample G1), 40°C for 13 days (Sample G2), or 70°C for 2 days (Sample G3) in alkaline media Sample G4 is a goethite precursor for a maghemite manufacture (producer's number 21, Société Chimique de Provence, France) and was produced by oxidation of ferrous sulfate in acid medium. Sample G5 was prepared by oxidation of ferrous sulfate in slightly acid solution.

Cr-goethite (Cr-G) and Mn-Goethite (Mn-G) were obtained by aging coprecipitates of ferric nitrate with chromium and manganese salts at 70°C for 10 and 45 days, respectively [20]. Cr-G and Mn-G contain 10 mol% of Cr and Mn. Al-goethites were prepared by alkaline aging of Al^{3+}-Fe^{3+} coprecipitates at 25°C for 10 days, producing the following final amounts of Al:3 mol% (Al-G1), 4 mol% (A1-G2), and 6 mol% (A1-G3) [21], or at 155°C for 1 day, producing 10 mol% Al (Al-G4) [22]. Al-goethites A1-G5 and A1-G6, with 10 and 28 mol% A1, were prepared by oxidation of ferrous sulfate in the presence of aluminum salt in acid solutions.

Natural iron oxides were used for comparison with the synthetic samples. N1, N2, and N3 are laterites formed on ultramafic rocks. N1 and N2 were described by Trolard et al. [19] (originally denoted F38 and F40). N3 is a commercially available New Caledonia nickel ore. Laterite N4 was formed on basic rock and was described by Schellmann [23] (originally denoted 12). Phase compositions of the natural samples are summarized in Table 1. N1, N2, and N3 contain a few per cent of a less crystalline, reactive iron oxide fraction which was not found by the phase analysis.

The samples studied were tested by XRD, Mössbauer spectroscopy, and/or TEM (Transmission Electron Microscopy). Ferrihydrite was found in G1, G2, G5, A1-G1, A1-G2, and A1-G3. The specific surface areas were obtained by the N_2-H_2 sorption method (G1 to G5), by BET (A1-G4, Mn-G, Cr-G, N3), and according to [19] (N1 and N2) and [23] (N4).

Table 1 The phase composition, specific surface areas σ, and the molar amount of Al in natural oxides expressed as $x_{Al} = Al/(Al + Fe)$. Data for N1 and N2 are from [19] and for N4 from [23]. In the case of N3, only the total amount of Al and Fe is known. *mh* maghemite, *h* hematite, *g* goethite, *k* kaolinite, *q* quartz

Sample	Phase composition	σ ($m^2\ g^{-1}$)	x_{Al} (mol%)
N1	*mh* (40%), *h* (35%), *g* (20%), *k* (5%)	18	5
N2	*g* (90%), *mh* (5%), *h* (3%), *q* (2%)	70	5
N3	*g*	107	≤ 11
N4	*g* (25%), *h* (11%), *k* (49%) + minor phases	–	20

Abrasive stripping voltammetry was performed as already described [4, 11]. A solution containing 0.1 M $HClO_4$ and 0.4 M $NaClO_4$ was used as the supporting electrolyte. Supporting electrolytes with organic acids have been described in [11]. Voltammetric and chronoamperometric curves were measured by the PA4 polarograph (Laboratory Devices, Prague, Czech Republic). A scan rate of 1 mV · s^{-1} was used for linear sweep voltammetry. Chronoamperometric curves were fitted using transformed Eq. 1 [4, 11]:

$$I = kQ_0 \left(\frac{Q}{Q_0} \right)^{\gamma}$$

where I is a current, and Q and Q_0 are charges corresponding to N and N_0, respectively. The dissolution curves of the samples with a ferrihydrite admixture were processed by the extrapolation method described previously [4].

An alternative dissolution was performed in 20 mM acid ammonium oxalate and 2 mM ammonium ferrous sulfate (Mohr salt) (AAO-Fe^{2+} mixture) under nitrogen atmosphere. The mixture pH = 2.7 is in the range giving the highest dissolution rate of iron oxides [14–16]. The samples were inserted into the AAO-Fe^{2+} mixture as a suspension prepared from approx. 5 mg of a dry sample in 1 ml of water in an agate mortar. The solution was stirred by a magnetic stirrer at 800 rpm with a PTFE-coated stirring bar, 20 mm long, 5 mm in diameter, to avoid any sedimentation of the solid. Fe^{3+} liberated by the reaction was detected by a glassy carbon electrode at −0.5 V vs SCE using the polarograph PA4 and an x-t recorder. The conversion of the reaction $1–N/N_0$ is then

$$1 - N/N_0 = I_D/I_{D,\infty}$$

where I_D and $I_{D,\infty}$ are actual and final currents for $[Fe(C_2O_4)_3]^{3-}$ reduction. The conversion-time curves were derived employing polynomial fitting and transformed into the variables of Eq. 1. For details of polynomial fitting and the estimation of the ferrihydrite admixtures see Appendix A.

Results and discussion

AbrSV of G3 was performed to establish the dependence of γ on measuring conditions. Figure 1 shows the γ values obtained in various supporting electrolytes and under various enforced reaction rates. The rate in AAO-Fe^{2+} was altered by changing the concentration of acid ammonium oxalate and/or ferrous ions. The γ values obtained by AbrSV are close to those obtained in AAO-Fe^{2+} if diluted perchloric acid is used as the supporting electrolyte and rate coefficients are of the order of 10^{-4} s^{-1}. Suitable working electrode potentials were hence chosen for each iron oxide to obtain the γ values discussed below.

The γ values obtained by AbrSV and AAO-Fe^{2+} for 8 synthetic and natural goethites are plotted in Fig. 2. There is no systematic difference between the two methods according to the Student test. The values in the range 0.8–1.1 are also acceptable from the point of view of theory (see Appendix B). We may hence conclude that the electrochemical dissolution of goethites at the rate coefficients of the order of 10^{-4} s^{-1} proceeds as a surface electrochemical reaction. When the rate coefficients are of the order of 10^{-3} s^{-1}, γ exceeds unity, indicating an additional distribution of the solid particle reactivity (see also Fig. 1).
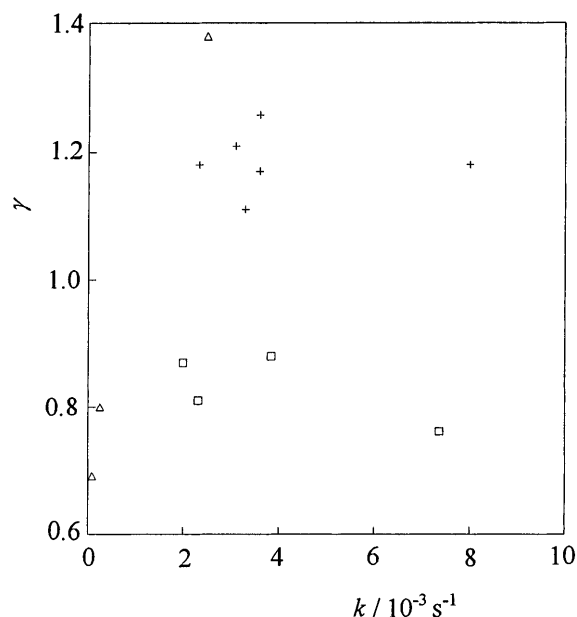
Fig. 1 The dependence of the γ values of the goethite G3 on measuring conditions. AbrSV in supporting electrolytes with organic acids (+) [11] and with perchloric acid (Δ), AAO-Fe^{2+} dissolution ($\square$)
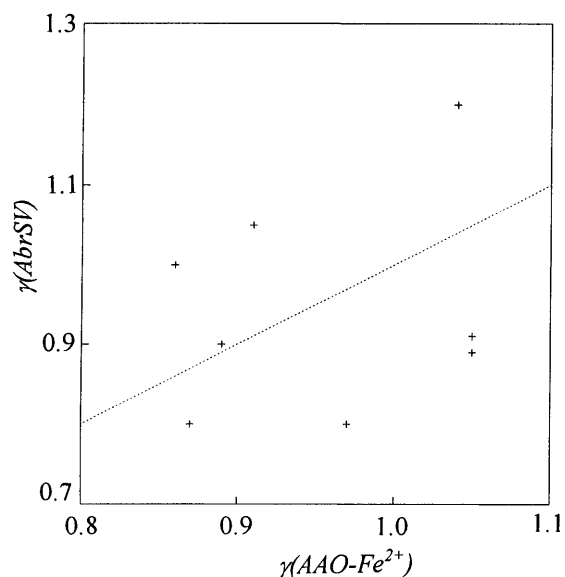

Fig. 2 The plot of γ of goethites obtained by AbrSV and AAO-FE^{2+} dissolution. The *dotted line* represents a theoretical 1:1 line

Up to rate coefficients of the order of 10^{-3} s^{-1}, Eq. 2 is valid, and the charge transfer and reaction rate coefficients at the reference potential may be estimated. From Eq. 2 and the relationship for the peak potential E_P [4, 13], it follows that the rate coefficient at the E_P is proportional to the scan rate v

$$k_P = \alpha n F v / RT$$

If linear sweep voltammetry were to be used to obtain the dissolution kinetic characteristics not affected by the diffusion limit, $v < 10^{-4}$V $\cdot$ s^{-1} ought to be applied.

Because the polarograph used does not allow such low scan rates to be applied, only chronoamperometric curves were processed.

From the definition of the surface reaction kinetics, it follows that

$$J = \frac{dN}{dt} = \frac{\rho}{M} \cdot S \cdot \frac{dr}{dt} = \rho \cdot \sigma \cdot \frac{dr}{dt} N \tag{3}$$

where ρ is the density, M is the weight of the solid yielding one mol of electroactive Fe^{III}, S is the actual surface area of the sample, σ is the specific surface area, and dr/dt is the constant linear rate of the movement of the reaction interface in the direction perpendicular to the surface of the particle. Because the linear dissolution rate dr/dt is independent on the particle geometry, it may be used for the comparison of the studied samples.

Properties of individual samples of pure and substituted geothites differ significantly. They are sensitive both to the method of goethite preparation and to the substitution of iron. The values of α and dr/dt decrease in the order:

pure goethite from Fe^{2+}salt $>$ pure goethite from

ferrihydrite $>$ Al, Cr, and Mn-substituted goethite

A very important feature is a decrease in the electrochemical activity of higher Al-goethites (see Figs. 3 and 4) that is probably caused by the decrease of the charge transfer coefficients. Also, the dissolution rates decrease with an increasing amount of Al and especially Cr. The influence of foreign metal-to-iron substitution is similar for both the dissolving systems studied and even for proton-promoted dissolution [24]. However, in particular, the simultaneous influence of the substitution on α and dr/dt makes AbrSV the most sensitive to the degree

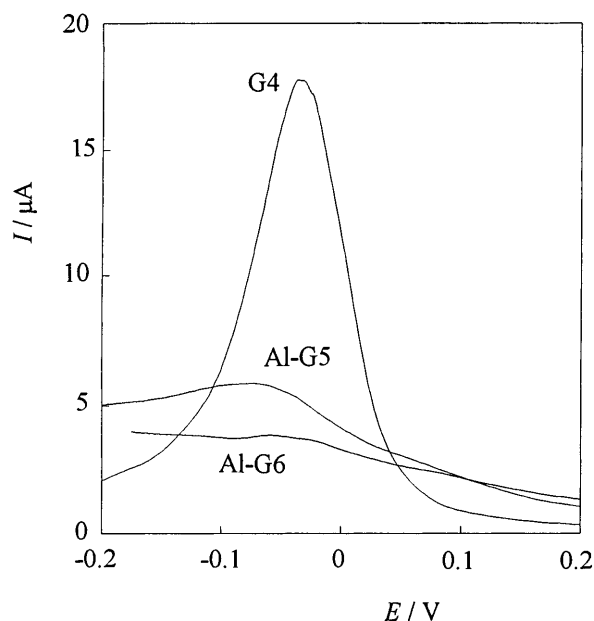**Fig. 3** The AbrSV peaks of Al-goethites. The electrochemical activity decreases with an increasing amount of Al
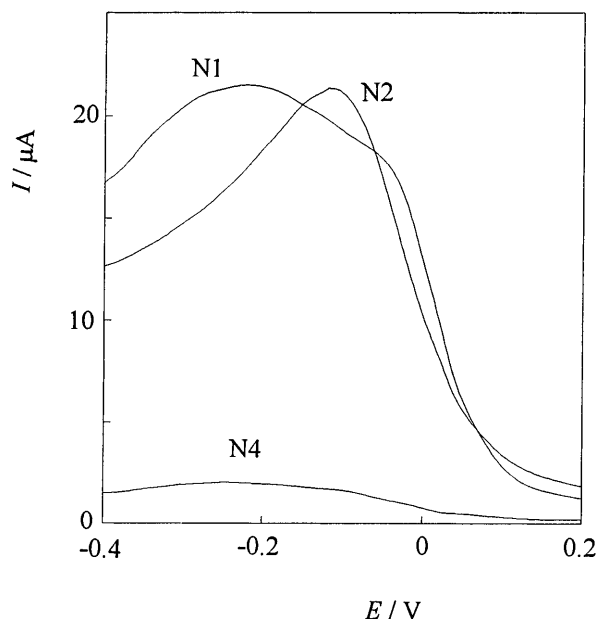
Fig. 4 The AbrSV peaks of natural goethites. A heterogeneous polyphase mixture (*N1*) yields a double peak; the electrochemical activity of N4 is suppressed due to the high Al content of the goethite lattice

propose the additive origin of the reactivity distribution function mentioned in Appendix B.

Another important analytical property obtained by dissolution methods is the amount of less crystalline components, e.g., ferrihydrite, in goethite or hematite. The most common way to evaluate this is by the oxalate extraction procedure [20]. Comparison of the percentage of ferrihydrite according AbrSV and AAO-Fe^{2+} dissolution (see Experimental and Appendix A) was therefore performed. Results are shown in Fig. 5. The linear regression with fixed zero intercept yields the slope non-significantly different from unity (0.91), with standard deviation 0.09. The agreement shows the validity of the fitting procedures used. AbrSV hence offers a simple and sensitive method to test the crystallinity of electroactive metal-oxide particles.
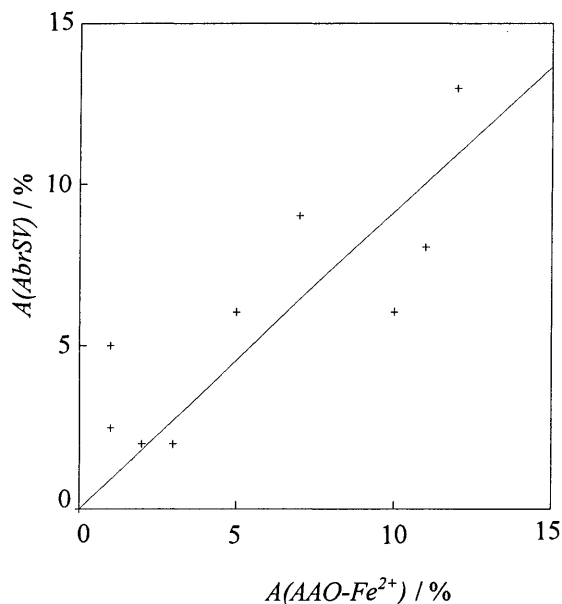
of substitution. If favours, e.g., the peak separation in the voltammetric curve of sample N1 which is composed of low-Al maghemite and a mixture of high-Al goethite and hematite (Fig. 4). Similar double voltammetric peaks were observed even in single-phase goethite assemblages from laterites [25]. The phenomenon is currently being further investigated.

The difference between the dissolution rates under conditions of AbrSV and in AAO-Fe^{2+} (Table 2) cannot be related only to the differences in α and the formal electrochemical potential of the iron oxide surface in AAO-Fe^{2+} solution. Even the orders of the linear dissolution rates of pure goethites are not equivalent despite the similar nature of the two systems. This may be explained by different reactivities of individual crystal planes or by an influence of differences in a goethite bulk structure. Both phenomena lead us to

Fig. 5 The comparison of the estimation of ferrihydrite percentage (**A**) by AbrSV and AAO-Fe^{2+} dissolution

Table 2 The dissolution characteristics of goethites. The linear dissolution rates, dr/dt, were estimated using Eq. 3

Sample	AbrSV			AAO-Fe^{2+}	
	α	$k_0 (10^{-3} s^{-1})$	$(dr/dt)_0 (pm \cdot s^{-1})$	$k(s^{-1})$	$dr/dt (pm \cdot s^{-1})$
G1	0.57	9.2	14	3.85	6.0
G3	0.59	2.5	22	2.0	18
G4	0.90	3.6	41	0.81	9.3
G5	0.74	22	47	2.4	5.5
Al-Gl	0.53	2.7	–	9.3	–
Al-G2	0.31	0.99	–	2.45	–
Al-G4	0.51	0.49	3.0	0.42	2.6
Cr-G	0.41	0.06	0.41	0.045	0.26
Mn-G	0.44	1.6	11	0.25	1.8
N2	0.48	0.74	2.5	0.29	1.0
N3				0.50	1.1

Conclusions

Electrochemical reductive dissolution of iron oxides is controlled by surface reaction kinetics. Assuming that the iron oxide particles are partly immersed in the working electrode surface [9, 10], they must dissolve from the whole free surface exposed to the solution. This enables the dissolution characteristics to be interpreted with respect to the phase purity and the size distribution function of a solid reactant with submicron particles. The sensitivity of both the charge transfer and the rate coefficients to foreign metal-for-iron substitution shows that it is necessary to extend the number of characteristics usually used for the description of iron oxide-reductive dissolution kinetics.

Appendix A: The polynomial fit of conversion-time curves

Eq. 1 may be integrated, yielding

$$1 - \frac{N}{N_0} = [1 - (1-\gamma)kt]^{1/(1-\gamma)} \tag{A1}$$

Equation A1 is not suitable for routine curve fitting because of its exponential form, but a common polynomial regression would facilitate the process. The beginning of the Taylor series of Eq. A1 for $t_0 = 0$ is

$$1 - \frac{N}{N_0} = kt - \frac{\gamma}{2}(kt)^2 + \frac{\gamma}{3}\left(\gamma - \frac{1}{2}\right)(kt)^3$$
$$- \frac{\gamma}{4}\left(\gamma - \frac{1}{2}\right)\left(\gamma - \frac{2}{3}\right)(kt)^4$$
$$+ \frac{\gamma}{5}\left(\gamma - \frac{1}{2}\right)\left(\gamma - \frac{2}{3}\right)\left(\gamma - \frac{3}{4}\right)(kt)^5 - \dots$$

The first three terms may be rewritten

$$1 - \frac{n}{N_0} = at - bt^2 + ct^3 \tag{A2}$$

The contribution of the higher member is less than 5% for $\gamma = 0.8$ up to the conversion 84% and for $\gamma = 0.9$ up to the conversion 72%. The Taylor series offers the possibility to check that Eq. A2 is not any arbitrary polynomial, because we may predict the values of the Z-ratio, defined by Eq. A3 to be close to unity

$$Z = 3a\,c/b^2 \tag{A3}$$

as $Z = 2(2\gamma - 1)/\gamma$ according to the Taylor series. Hence, the problem of mathematical separation of the rapidly dissolved ferrihydrate becomes a search for the conversion range, where ferrihydrite has been consumed (a lower limit), and Eq. A2 with an added constant term is valid (an upper limit of conversion)

$$1 - \frac{N}{N_0} = A + at - bt^2 + ct^3$$

where A is the fraction of ferrihydrite. The Z values from 0.95 to 1.2 were found in the case of AAO-Fe^{2+} dissolution of goethites.

Appendix B: The value of γ for a particle-shape-preserving dissolution

Goethite is composed of acicular crystals [2, 20] with crystal planes of different reactivities [12, 26]. The crystals retained their needle-like shape during dissolution [2]. Hence, unless the dissolution curves are of a sigmoidal shape because of preferential attack on crystal defects, the cube root law is followed [27], i.e., Eq. 1 with $\gamma = 2/3$ is an applicable approximation.

The γ value is exactly equal to 2/3 for monodisperse particles dissolving without shape alterations, but is greater by a few tenths if the particles form a population with a monomodal size distribution function (e.g., normal or log-normal). A distribution of the rate coefficients, e.g., due to dispersed proportions of individual crystal planes or variable levels of Al-for-Fe substitution, would have the same formal impact as the distribution of the sizes. Appropriate computer modeling reveals that the wider the distribution of each individual property and the more contributions that must be taken into account, the larger is the resulting γ.

Exact calculations of γ for the dissolution of goethite crystals are almost impossible because of the complexity of the task. Nevertheless, the following particle populations may approximate to the course of goethite dissolution:

- normal size distribution function (coefficient of variation CV = 30%): $\gamma = 0.76$
- as above with the additive normal distribution of rate coefficients (CV = 20%): $\gamma = 0.83$
- the log-normal size distribution function (CV = 50%): $\gamma = 0.87$
- as above with the additive normal distribution of rate coefficients (CV = 30%): $\gamma = 1.02$

A preference for log-normal size distributions may be expected in the case of iron oxides because of complex formation pathways.

If the electrochemical reaction proceeded only on the ternary interface reactant-electrode-solution [9, 10], the semi-infinite "three-dimensional" size distribution function would change to a planar "two-dimensional" one. The resulting γ should then decrease roughly by $2/3 - 1/2 = 1/6$ (γ is equal to 1/2 for a shrinking circle model). Such a systematic difference would be revealed by the comparison of γ by AbrSV and AAO-Fe^{2+} procedures.

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82

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