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Measurement of the surface potential of individual crystal planes of hematite

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Abstract

A device for measuring surface potentials of individual crystal planes was constructed. The surface potentials of the (0 1 2), (1 0 −2), (1 1 3), and (1 1 −3) crystal planes of hematite were measured as a function of pH at different sodium nitrate concentrations. Results of measurement enabled differentiation between the planes, showing agreement with the surface potentials obtained with a single-crystal hematite electrode. At low ionic strength there was no significant difference in potential between the crystal planes, whereas at relatively high ionic strength the difference was noticeable. In the absence of counterion association, but also in the case of their symmetric association taking place, point of zero potential (pH_{pzp}) coincides with other zero points, i.e., with the isolectric point (pH_{iep}) and the point of zero charge (pH_{pzc}). If the counterion affinities toward association are not equal, the pH_{pzp} is shifted in the same directions as the pH_{pzc}. The shift in the point of zero potential to the basic region was more pronounced for the (1 1 −3) plane than for the (1 0 −2) one, indicating a higher affinity of anions for association with oppositely charged surface groups compared to cations. It was demonstrated that measurements of surface potentials of individual crystal planes could help to better understand the equilibrium at solid/liquid interfaces.

Keywords: Surface potential; Surface complexation model; Hematite; Crystal planes; Single-crystal electrodes

1. Introduction

Colloidal particles are often composed of aggregated nano-single crystals [1,2]. Their surface is thus heterogeneous as different crystal planes are exposed to the liquid medium. Apparently, different planes will exhibit different chemical characteristics; the density of active groups will depend on the type of planes, and on their affinity for ionization [3–5]; electrical capacitance of the plane will depend on the density of surface sites [3]. Consequently, the overall interfacial characteristics of colloidal particles will be average, depending on the features of individual planes and on their abundance [6]. The same is true of the colloidal single-crystalline particles which exhibit heterogeneity on a larger scale.

Due to experimental difficulties most of the data published in the literature relate to the colloidal systems and to their "average" properties: adsorption densities, surface charge densities, and electrokinetic potentials.

Use of single-crystals (both natural and synthetic samples) enabled measurements and characterizations of surface properties of individual planes. Among the techniques most frequently used for investigation of individual crystal-face-specific reactivity, i.e., direct information on the pH-charging properties are atomic force microscopy (AFM) [7,8], scanning force microscopy (SFM) [9], and scanning tunneling microscopy (STM) [10]. A diffraction study of hydrated surfaces was also carried out to interpret the reactivity of a model surface in an aqueous environment [11]. Zhanga et al. [12] measured cation adsorption at the (1 1 0) rutile crystal face, applying the X-ray standing-wave technique. Electrokinetic properties, such as electroosmotic behavior [13] and streaming potential [14], of different crystal planes were also examined. Second-harmonic generation (SHG) spectroscopy together with acid–base potentiometric titration served to characterize the crystal surface and to determine the point of zero charge [15].

However, advanced theoretical studies take account of the characteristics of individual planes, and even predict the overall behavior of the system. The relationship among charge distribution, surface hydration, and structure of the metal hydroxide

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interface was analyzed in detail by Hiemstra, Van Riemsdijk et al. [3,4,16]. Rustad et al. [17–19] used molecular statistics calculation to model and identify surface species. Zarzycki et al. applied Monte Carlo simulations to study the acid–base properties of the clays [20] and metal oxide [21,22]/electrolyte interface as well as the influence of surface heterogeneity to adsorption. Sverjensky [23] predicted the pristine point of zero charge from crystal chemistry and solvatation theory. Structural properties of the bulk crystal and crystal surface were calculated by Lazzeri et al. [24].

The bulk of the hematite crystal is composed of alternating layers of iron cations and oxygen anions. The cations occupy two-thirds of the space between the oxygen layers. Each cation is bound to three oxygen atoms from the layer above and to three oxygen atoms from the layer below. The properties of the hematite–electrolyte solution interface were found to depend on the structure of the hematite surface and on surface hydroxyl configuration (SHC) [4]. Several possible faces of the hematite crystal were observed [4,5,17–19,25] having different densities of singly, doubly, and triply coordinated OH groups. Venema et al. [4] introduced the idea that singly and triply coordinated OH groups are reactive groups, whereas doubly coordinated OH groups are not reactive. They calculated proton affinities of individual surface groups of hematite (0 0 1) and (1 1 0) faces and found that those two faces have different pristine point of zero charge [26]. In this article the surface potentials of the (0 1 2), (1 0 −2), (1 1 3), and (1 1 −3) crystal planes of hematite were observed.

Recently, measurement of the surface potential Ψ_0, i.e., of the electrostatic potential of the inner Helmholtz plane, has been introduced. For that purpose single-crystal electrodes (SCrE) have been developed [27,28]. The measured electrode potentials are converted to surface potentials using the isoelectric point (i.e.p.) as an approximation of the point of zero potential (p.z.p.). Such a procedure is correct in the neutral electrolyte medium at relatively low ionic strength. At higher ionic strengths the p.z.p. differs from the i.e.p. so all other potential differences in the measuring circuit need to be determined and subtracted from the measured SCrE values. For that purpose one needs to know the electroneutrality point (the pristine point of zero charge) and to measure the SCrE potential at the isoelectric point [29].

The aim of this work is to describe the construction of a device for measuring surface potentials of individual planes and to present the results obtained with a hematite single crystal.

2. Theoretical

The surface potential Ψ_0 is an important parameter characterizing interfacial properties [30]. According to the surface complexation model (SCM), the surface potential at metal oxide/aqueous interfaces is determined by the pH value. The following reactions may take place at the hematite surface [31]:

$$\equiv\mathrm{FeO}^{-1/2} + \mathrm{H}^+ \rightarrow \equiv\mathrm{FeOH}^{1/2},\quad \text{1-p}K\text{, single-step-protonation mechanism,} \tag{1}$$

$$\equiv\mathrm{FeO}^{-} + \mathrm{H}^+ \rightarrow \equiv\mathrm{FeOH},\quad \text{2-p}K\text{, first-step-protonation mechanism,} \tag{2}$$

$$\equiv\mathrm{FeOH} + \mathrm{H}^+ \rightarrow \equiv\mathrm{FeOH}_2^+,\quad \text{2-p}K\text{, second-step-protonation mechanism.} \tag{3}$$

According to the SCM, the surface potential Ψ_0 is given by

$$\Psi_0 = \frac{RT\ln 10}{F}(\mathrm{pH_{pzp}} - \mathrm{pH}) - \frac{RT}{F}\ln\left(\frac{\{\mathrm{FeOH}^{+1/2}\}}{\{\mathrm{FeOH}^{-1/2}\}}\right),\quad 1-\mathrm{p}K, \tag{4}$$

$$\Psi_0 = \frac{RT\ln 10}{F}(\mathrm{pH_{pzp}} - \mathrm{pH}) - \frac{RT}{2F}\ln\left(\frac{\{\mathrm{FeOH}_2^+\}}{\{\mathrm{FeO}^-\}}\right),\quad 2-\mathrm{p}K, \tag{5}$$

where the curly braces denote surface concentrations of relevant species, while other symbols have their usual meaning. The first term in the r.h.s. of Eqs. (4) and (5) is Nernstian, suggesting the Ψ_0(pH) function slope of, e.g., −59.2 mV at 25 °C. However, the second term indicates that the magnitude of the slope may be significantly lower. The mechanism of the surface charging reaction may be always questioned. However, Eqs. (1)–(5) clearly show that regardless of the assumed reaction mechanism the second term in the Ψ_0(pH) function, being responsible for the lowering of the slope, is determined by the ratio of the surface concentrations of (more) positive to the (more) negative surface groups. The slope will therefore be conditioned by the characteristics of the plane exposed to the liquid medium (charging mechanism, surface density of active sites, and respective thermodynamic protonation equilibrium constants), and also by the liquid medium composition (the type and concentration of electrolyte) owing to the association of counterions and the equilibrium in the diffuse part of the electrical interfacial layer (EIL) [32]. Accordingly, surface potential measurements may be used to distinguish between the physico-chemical properties of crystal planes.

3. Experimental

3.1. Chemicals

All solutions were prepared using distilled, deionized, and decarbonated water; $\mathrm{NaNO_3}$ (p.a., Fluka), NaOH (0.1 mol dm^{-3}, titrival, Fluka), $\mathrm{HNO_3}$ (0.1 mol dm^{-3}, titrival, Fluka).

A hematite single-crystal electrode was constructed using the natural α-$\mathrm{Fe_2O_3}$ mineral from Elba (Italy). The crystal surface was cleaned by extensive rinsing with distilled water. Four planes were examined, two and two symmetrically equivalent ones (0 1 2) and (1 0 −2), and (1 1 3) and (1 1 −3). To characterize the clean sample surface, high-resolution specular X-ray reflectivity data were collected and integrated using CrysAlis (Oxford Diffraction (2003) Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis Software system, Version 1.170). Fig. 1 shows the structures of crystalline planes. According to Barron and Torrent [5] the (0 1 2) hematite crystal faces have singly and triply coordinated OH groups, whereas the (1 1 3) faces have singly, doubly, and triply coordinated OH groups. The (0 1 2)