

Comparison of isoelectric points of single-crystal and polycrystalline α -Al₂O₃ and α -Fe₂O₃ surfaces

YINGGE WANG¹, PER PERSSON², F. MARC MICHEL^{1,3,†}, AND GORDON E. BROWN, JR.^{1,3,*}

¹Surface and Aqueous Geochemistry Group, Department of Geological Sciences, School of Earth, Energy, and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

²Centre for Environmental and Climate Research and Department of Biology, Lund University, SE-22362, Lund, Sweden

³Department of Photon Science and Stanford Synchrotron Radiation Lightsources, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, MS 69, Menlo Park, California 94025, U.S.A.

ABSTRACT

The surface charging behavior as a function of pH and isoelectric points (IEPs) of single-crystal α -Al₂O₃ (0001) and (1 $\bar{1}$ 02) and α -Fe₂O₃ (0001) was determined by streaming potential measurements using an electrokinetic analyzer. The IEPs of α -Al₂O₃ (0001) and (1 $\bar{1}$ 02) and α -Fe₂O₃ (0001) were found to be 4.5, 5.1, and 6.5, respectively. These IEP values for oriented single crystals of α -Al₂O₃ are in good agreement with literature values, whereas the new IEP value for α -Fe₂O₃ (0001) is significantly lower than four reported values (IEP = 8–8.5) for single-crystal α -Fe₂O₃ (0001) (Eggleston and Jordan 1998; Zarzycki et al. 2011; Chatman et al. 2013; Lützenkirchen et al. 2013) and significantly higher than one (IEP = 4) recently measured by Lützenkirchen et al. (2015) on a fresh α -Fe₂O₃ (0001) surface. Most of the single-crystal IEP values measured recently are lower than IEP values reported for polycrystalline α -Al₂O₃ and α -Fe₂O₃, which are generally in the pH range of 8 to 10. Calculations of the IEP values based on estimated K_a values of α -Fe₂O₃ and α -Al₂O₃ surfaces in contact with water as a function of defect type and concentration suggest that highly reactive surface defect sites (primarily singly coordinated aquo groups) on the Fe- and Al-oxide powders are possibly a major source of the surface charge differences between polycrystalline samples and their oriented single-crystal counterparts studied here. The results of this study provide a better understanding of the surface charging behavior of Fe and Al-oxides, which is essential for predicting complex processes such as metal-ion sorption occurring at mineral/water interfaces.

Keywords: Isoelectric point (IEP), pH point of zero charge (pH_{pzc}), Fe- and Al-oxides, single crystal, polycrystalline, surface, defects