The surface structure of $\alpha$-Fe$_2$O$_3$ (001) by scanning tunneling microscopy: Implications for interfacial electron transfer reactions

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ABSTRACT

STM images of hematite ($\alpha$-Fe$_2$O$_3$) (001) surfaces taken under a wider variety of conditions than in previous studies are presented. The results strongly suggest that only Fe sites contribute to the tunneling current. Specifically, corrugated unit-cell structures expected of the Fe sublattice are observed under both occupied- and unoccupied-states imaging conditions. A pattern of apparent vacancies was observed under conditions previously attributed to oxygen states; this is most simply interpreted either as Fe vacancies, or Fe sites whose electronic structure has been altered by a (unknown) coordinating anion, but difficult to explain as the oxygen sublattice. For unoccupied states imaging, decreasing the tip-sample distance (increasing the tunneling current) results in an image change from only one site per unit cell to three sites per unit cell. This is also relatively easy to explain using the Fe sublattice, but difficult to explain using the oxygen sublattice. These results are modeled using resonant tunneling theory, which shows that changes in bias voltage, tunneling medium, and tip-sample distance can have the observed effects only if Fe atoms are being imaged. The results have implications for modeling electron transfer across mineral-water interfaces more generally because they provide a framework for understanding site-specific electron transfer kinetic parameters.

INTRODUCTION


Studies of Al and Fe oxide surfaces by low energy electron diffraction (LEED) and photoelectron spectroscopy revealed complex surface reconstructions and non-stoichiometry (see Eggleston and Hochella 1992; Henrich and Cox 1994; Kim et al. 1997 and references therein). The sputter-anneal cycles used to prepare clean, well-defined surfaces of single-element metals and other materials (e.g., Si, Au, Ge) were problematic for Fe, Al, and other oxides. For example, Condon et al. (1995) showed that an unusual phenomenon they called “biphase ordering,” most likely a product of particular sample preparation conditions, is probably the cause of complex LEED patterns observed in earlier work. Recent work by Gao and Chambers (1997), Gao et al. (1997a, 1997b), and Kim et al. (1997) on growth of well-defined thin films of $\alpha$-Fe$_2$O$_3$ is providing well-defined iron oxide surfaces for study by surface science methods.

Scanning tunneling microscopy (STM) has been applied to several iron oxides; here, only studies of hematite ($\alpha$-Fe$_2$O$_3$) are discussed. Hochella et al. (1989) produced topographic images, and Heil et al. (1989) tentatively interpreted their image as showing oxygen positions. Eggleston and Hochella (1992) concluded that images showed the oxygen sublattice at negative (sample-to-tip; occupied states) bias and the uppermost Fe sublattice at positive (tip-to-sample, unoccupied states) bias. Condon et al. (1995, 1998) imaged $\alpha$-Fe$_2$O$_3$ (001) in vacuum; the surface had been partly reduced to FeO (111) in the cleaning process, and they found biphase ordering in which areas of FeO (111)-like surface alternated in a periodic pattern (unit-cell size, $3.5 \pm 0.3$ nm) with areas of $\alpha$-Fe$_3$O$_4$(001)-like surface. They interpreted the $\alpha$-Fe$_3$O$_4$(001)-like areas as consistent with oxygen atoms, but could not rule out a contribution from Fe atoms. Wang et al. (1998) found two distinct surface domains in STM images of the (001) surface in vacuum, and proposed that they represent coexisting oxygen-terminated and iron-terminated (001) surface structures.

In the $\alpha$-Fe$_2$O$_3$ (001) surface structure, each type of Fe site has a different height relative to a (001) surface plane (Fig. 1). The uppermost (“A”) Fe layer should relax significantly (50–60%) toward the surface in vacuum (Becker et al. 1996; Wang et al. 1998), but this effect is likely to be mitigated in aqueous solution or humid air where Fe coordination (tetrahedral and octahedral coordination have both been proposed; Wasserman...