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ELECTRON TRANSFER CONTROLS CONDUCTIVITY AND REDOX REACTIVITY IN URANIUM DIOXIDE

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The reduction of soluble hexavalent uranium species U(VI) to sparingly soluble tetravalent uranium species U(IV) results in the precipitation of uranium dioxide (UO_2). The mixed-valence iron oxide magnetite (Fe_3O_4) can catalyze this reduction. However, the underlying mechanisms controlling the transformation, particularly the intermediate uranium species and their mineralogic properties, are poorly understood. Uranium oxide nanocrystals (1–5 nm) self-assembled into nanowires extending away from the magnetite surface. A conceptual model proposes that the nanoparticles are U(V)-bearing nanoparticles and that their surface energy is minimized through nanowire formation. Continued reduction ultimately leads to the collapse of the nanowires and to the formation of UO_2 nanoclusters.

The experimental detection of several oxidation states for uranium raises questions about electron transfer (ET) properties of the various uranium-oxide phases involved, particularly their ability to sustain oxidation state changes via solid-state electron transport. Early experimental studies on UO_2 single crystals revealed thermally activated electrical conductivity governed by small-polaron hopping. Despite these foundational investigations, the microscopic mechanisms governing ET in UO_2 under varying redox conditions and defect content remain unresolved. In UO_2, small polarons may correspond to electron- or hole-like charge carriers depending on oxidation extent and defect chemistry. Transport efficiency is governed by thermal activation energy barriers for site-to-site hopping, in turn dependent upon the lattice reorganization energy and the degree of adiabaticity (electronic coupling at the hopping transition state).

To provide a deeper understanding of the mechanisms involved during solid-state ET in UO_2, we use first principles methods to compute these parameters within an ET framework adapted for periodic solids to quantitatively describe U(IV)/U(V) charge exchange. This approach is based on plane-wave electronic structure methods and enables the construction of localized diabatic states within extended supercells. The reaction is modeled as a transition between two charge-localized diabatic states coupled through lattice reorganization associated with small-polaron hopping.

By determining how U(IV)/U(V) ET proceeds, we establish a direct link between microscopic charge exchange and macroscopic conductivity. This framework enables prediction of charge mobility in nonstoichiometric UO_2 under environmentally relevant redox conditions.