

The Electrochemical Behavior of Nanoscale Cobalt and Iron Mineral Cores in Ferritin Protein Shells

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This paper examines the redox potentials and electron transfer behavior of mineral cores that have been inserted into the hollow interior of ferritin protein molecules. A ferritin containing a mineral core represents a potential building block for nanometer power systems. The feasibility of using such a building block requires an understanding of the electrochemical behavior of the core material and the influence of the protein on that behavior. The present study examines the behavior of cobalt and iron cores which had been inserted into horse spleen ferritin (Fe(III)HoSF).

Ferritins are spherical proteins 12 nm in diameter composed of 24 subunits arranged to enclose a central hollow cavity 8 nm in diameter. Up to 4000 iron atoms can be sequestered inside the cavity as a ferrihydrite (FeOOH) mineral core which is isolated from the external solution by a protein shell 2 nm in thickness. Ferritins function to store excess iron within their cores by an oxidative process ($\text{Fe}^{2+} + \text{oxidant} = \text{FeOOH}$), with O_2 typically used as oxidant, and release iron ($\text{FeOOH} + \text{reductant} = \text{Fe}^{2+}$) by a reductive process to satisfy cellular metabolic requirements. We previously reported [1] that the iron mineral core in horse spleen ferritin can be chemically or electrochemically reduced at pH 7.0 with a reduction potential of -200 mV and a pH dependence of -120 mV per pH unit between 7.0 and 9.0. The reduction reaction forms an all Fe^{2+} mineral core (Fe(II)HoSF) that is stable in the absence of chelators. The synthesis and initial characterization of Co(III)HoSF containing core of up to $\sim 2000 \text{ Co(OH)}_3$ was recently reported [2].

In this study we report additional characterization of Co(III)HoSF and report that it is readily reduced to form Co(II)HoSF that is stable in the absence

of chelators. Our current estimate of the reduction potential is +200 mV, indicating that Co(III)HoSF is a moderately strong oxidant. The reduction potentials of the Fe(II)HoSF and Co(III)HoSF half-cells suggest that the following reaction should occur, if electron transfer occurs through the protein shell.



Because the protein shells isolating the Fe(II) and Co(III) mineral cores are each 2 nm thick, electron exchange through 4 nm of protein requires a facile electron transport pathway through the protein shells. We report results from experiments to examine electron exchange associated with the above reaction, and propose methods to evaluate how electron transfer may occur through the 2.0 nm protein shell.

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REFERENCES

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