

## Bio-Nanobattery Development and Characterization

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### Abstract

A bio-nanobattery is an electrical energy storage device that utilizes organic materials and processes on an atomic, or nanometer-scale. The bio-nanobattery under development at NASA's Langley Research Center provides new capabilities for electrical power generation, storage, and distribution as compared to conventional power storage systems. Most currently available electronic systems and devices rely on a single, centralized power source to supply electrical power to a specified location in the circuit. As electronic devices and associated components continue to shrink in size towards the nanometer-scale, a single centralized power source becomes impractical. Small systems, such as these, will require distributed power elements to reduce Joule heating, to minimize wiring quantities, and to allow autonomous operation of the various functions performed by the circuit. Our research involves the development and characterization of a bio-nanobattery using ferritins reconstituted with both an iron core (Fe-ferritin) and a cobalt core (Co-ferritin). Synthesis and characterization of the Co-ferritin and Fe-ferritin electrodes were performed, including reducing capability and the half-cell electrical potentials. Electrical output of nearly 0.5 V for the battery cell was measured. Ferritin utilizing other metallic cores were also considered to increase the overall electrical output. Two dimensional ferritin arrays were produced on various substrates to demonstrate the feasibility of a thin-film nano-scaled power storage system for distributed power storage applications. The bio-nanobattery will be ideal for nanometer-scaled electronic applications, due to the small size, high energy density, and flexible thin-film structure. A five-cell demonstration article was produced for concept verification and bio-nanobattery characterization. Challenges to be addressed include the development of a multi-layered thin-film, increasing the energy density, dry-cell bio-nanobattery development, and selection of ferritin core materials to allow the broadest range of applications. The potential applications for the distributed power system include autonomously-operating intelligent chips, flexible thin-film electronic circuits, nanoelectromechanical systems (NEMS), ultra-high density data storage devices, nanoelectromagnetics, quantum electronic devices, biochips, nanorobots for medical applications and mechanical nano-fabrication, etc.

## Introduction

Bio-nanobatteries will function as distributed power sources within an electrical circuit, unlike currently utilized central power storage systems. The bio-nanobattery can be made as a flexible thin film and incorporated into a fabric or made to conform to various applications, even incorporating power harvesting devices for recharging the bio-nanobattery. The ferritin-based bio-nanobattery may also be biocompatible, depending on the core materials. They are lightweight, have a high energy density, and because of their size, can function as a chip scale power source. This characteristic will make possible a smart chip, able to operate autonomously. Bio-nanobatteries will have numerous applications, including flexible thin-film electronic circuits, ultra-high density data storage devices,<sup>4</sup> nanoelectromagnetics,<sup>5</sup> quantum electronic devices,<sup>6</sup> biochips, nanorobots for medical applications and mechanical nano-fabrication, nanomechanical devices, etc.

Ferritins, naturally occurring iron storage proteins, are necessary for the biological mechanisms of humans, animals, and even bacteria, and may contain up to 4,500  $\text{Fe}^{+3}$  atoms. Ferritins consist of 24 monomer subunits arranged in a spherical shell with an outer diameter of about 12.5 nanometers and an inner diameter of around 7.5 nanometers (Figure 1).<sup>7</sup> They form a stable and robust structure able to withstand biologically extremes of high temperature (up to 80 °C) and pH variations (2.0-10.0).<sup>8</sup> Both 3-fold and 4-fold channels in the organic shell allow for the transport of ions and molecules, making electron conduction through the ferritin shell possible. Research conducted at Brigham Young University indicates that naturally occurring HEME groups of bacterioferritins should facilitate electron transport through shell.

Using the reconstitution process of site-specific biomineralization, ferritins may be loaded with different core materials within the protein shell.<sup>8</sup> Core materials are incorporated into the ferritin shell with the addition of an oxidant (see Figure 2). Replacing the naturally occurring iron core using this reversible reaction, ferritins for the bio-nanobattery can be tailored according to redox capability. Ferritins with cobalt and manganese cores have already been made for the bio-nanobattery, as well as ferritins with other core materials for extended applications.

Fe-ferritins and Co-ferritins were used for a unit cell of the bio-nanobattery. In the absence of chelators at pH = 7.0, the  $\text{Fe}(\text{OH})_3$  iron core of ferritins undergoes reversible reduction to produce a stable  $\text{Fe}(\text{OH})_2$  core, while all 4500 iron atoms remain within the ferritin interior. Redox reactions between ferritin with different core materials involve the transfer of an electron from a donor to an acceptor ferritin (Figure 3). We have found that the half-cell potential of Fe-cored ferritins, -400 mV, and the Co-cored ferritins, 1000 mV, indicates that a cell having a 1.4V potential is possible. The charge density per gram exceeds that of both the “D cell” and “button battery.”

Spin coating, dipping, and LangmuirBlodgett deposition were utilized in producing ferritin arrays for incorporating into the bio-nanobattery. Spin coating, a quick and simple process for producing a flat and uniform layer, relies on air drag and centrifugal force, the layer thickness controlled by viscosity and spinning speed. The dipping method also produces a thin ferritin layer by physical adsorption on substrates, the thickness controlled by process time and solution concentration. LangmuirBlodgett deposition is accomplished through monolayer adsorption at the air/water interface.<sup>9,10</sup> With proper surfactant selection, it can form highly ordered ferritin monolayers. The surface pressure of the protein layer controls the film thickness. Figure 4 shows integration of the thin-film bio-nanobattery with a photovoltaic component for high capacity, high efficiency, compact size, and flexible applications.

### **Experimental and Result**

Ferritins were purified through size exclusion chromatography and de-mineralized through a reduction process to make apo-ferritin, ferritins without a core material. Co ferritin was synthesized by adding  $\text{Co}^{2+}$  to apo-ferritin in the presence of  $\text{H}_2\text{O}_2$ .<sup>11</sup> Similarly, ferritins can be reconstituted with other metallic cores. Ferritin arrays were fabricated using cationized Ferritin, enabling a strong electrostatic attraction to the negatively charged Si substrate.

The spin self-assembly (SSA) deposition method<sup>12</sup> was used to produce Ferritin arrays on various substrates. Depositing successive layers of ferritins on silicon substrates formed the arrays, redox charge transfer chains. The total output current and voltage can be tailored by selecting either serial or parallel connection of the pairs. Examination of the layer structure was accomplished using scanning probe microscopy (SPM), while the magnetic properties of the ferritin with metallic cores allowed a magnetic force microscopy (MFM) tip to be used. SPM images show the 2-D ferritin arrays to be smooth and uniform, suggesting that the SSA deposition method will produce fast, reliable arrays for the bio-nanobattery.

Stability tests of Co-ferritin indicate that most of the cobalt(II) remains bound to Co-ferritin (>90%) for extended time periods, demonstrating the stability of the  $\text{Co}(\text{OH})_2$  mineral phase within the ferritin interior. Figure 5 shows the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  in Co-ferritin at 350 nm. The absorbance decreases with the reduction of the cobalt core as ascorbic acid (a 2 electron donor) is added, until it becomes stable when all  $\text{Co}^{3+}$ -ferritin is reduced to  $\text{Co}^{2+}$ -ferritin. This result shows that 1.85  $\text{Co}^{3+}$  are reduced per ascorbic acid added. An electrochemical cell was also used for coulometric reduction measurements, showing that 1.10 e/Co was taken up during the electrolysis of  $\text{Co}^{3+}$ -ferritin. The reduction equilibrium and the reduction kinetics of both Co-ferritin and Mn-ferritin were also examined. Preliminary results showed that an equilibrium condition between the  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  core material was achieved. The reduction kinetics show a reduction of core material with time. Results indicate that the manganese reduces much faster than the cobalt.

The mechanism of electron conduction through the protein shell is a key factor to determine power density, maximum discharge rate, and duty cycle life of bio-nanobattery cell units. Figure 6 illustrates the results of a dynamic redox reaction between Fe<sup>2+</sup>-ferritin and Co<sup>3+</sup>-ferritin. A chelating agent was added to the solution containing ferrous ions. The remaining Fe<sup>2+</sup> is indicated by the decrease in absorbance at 511 nm as the redox reaction takes place, corresponding to the remaining Fe<sup>2+</sup> in the solution. The reaction reached an equilibrium state after 4 min, with the absorbance around 0.07. The initial reaction increased significantly when a piece of gold foil was added to Fe-Co solution, with a corresponding decrease in the absorbance. This result indicates that the presence of gold expedites electron transport from Fe<sup>2+</sup> to Co<sup>3+</sup>, and that the mechanism of electron conduction through the protein shell is a key factor to determine power density, maximum discharge rate, and the duty cycle life of bio-nanobattery cell units.

Two methods may be employed to determine electron transport in ferritins. The first involves conductivity measurement of a single ferritin cell using an AFM tip (Figure 7). A single ferritin cell element is isolated on a positively charged gold substrate. Electrical current applied through the ferritin cell with the AFM tip is then measured. The mechanism of electron transport may be either electrons hopping over the cell surface (electron avalanche?) or electron tunneling through the ferritin cell. The current-voltage (I-V) curves for holo-ferritin (with core material) and apo-ferritin (without core material) indicate that Fowler Nordheim tunneling may be the mechanism of electron transport in the ferritin cell unit. As Figure 8 depicts, the tunneling barrier height is larger for apo than holo ferritin. Note that the apo-ferritin has no current flow when 0.5 volts is applied, while the holo-ferritin begins to conduct electrons. The electron conduction is influenced by the presence of a core material, suggesting that electron tunneling may be the mechanism of electron transport. Another possible method for conductivity measurement involves measuring a DC current through a nonconductive substrate, both with and without a 2-D ferritin array. The number of ferritins sandwiched between electrodes can be approximated to estimate the conductivity of a single ferritin.

### **Summary**

The bio-nanobattery will enable distributed power storage systems, making more flexibility in circuit design. Characterization of Fe-ferritin and Co-ferritin indicate that they would be good candidates for the bio-nanobattery half cell units. Reconstituting ferritins with other metallic core materials having a higher redox potential may improve the power density of the bio-nanobattery. Two-dimensional arrays of ferritins were successfully fabricated on silicon substrates using the spin self-assembly deposition method. Improving the electron transport and using multilayered ferritin arrays and ferritins with other core materials may improve the bio-nanobattery performance.

### **Acknowledgement**

This work was partially supported under NASA grants NCC-1-02005 and NCC-1-02043 to the National Institute of Aerospace and Brigham Young University. Related research

performed under contract to Science and Technology Corporation was also utilized in this work.

## Figures

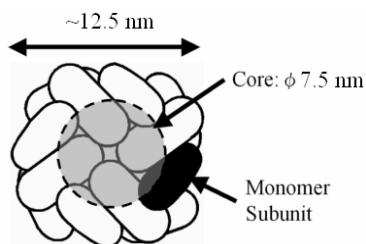


Figure 1. Ferritin protein shell



Figure 2. Ferritin reconstitution

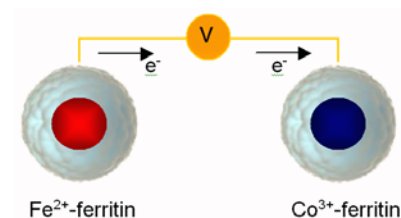


Figure 3. Bio-nanobattery unit cell

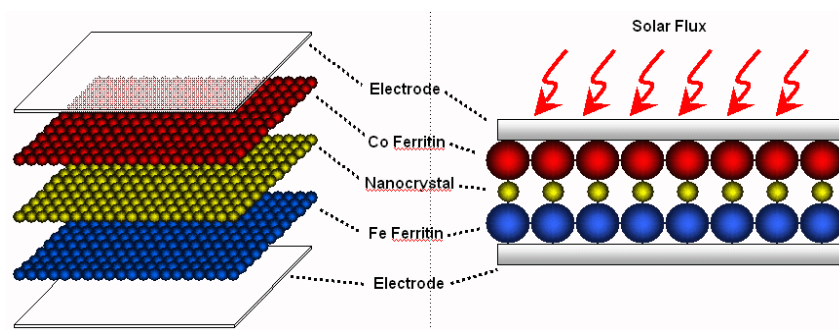


Figure 4. Integration of bio-nanobattery cell

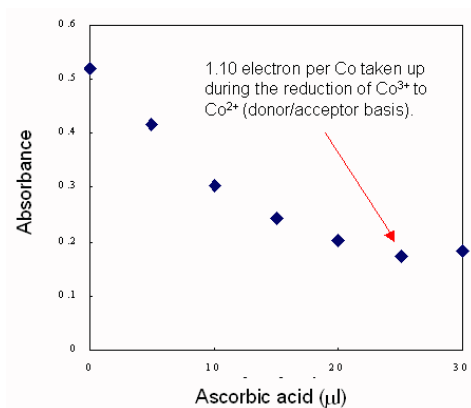


Figure 5. Reducing power of Co-ferritin

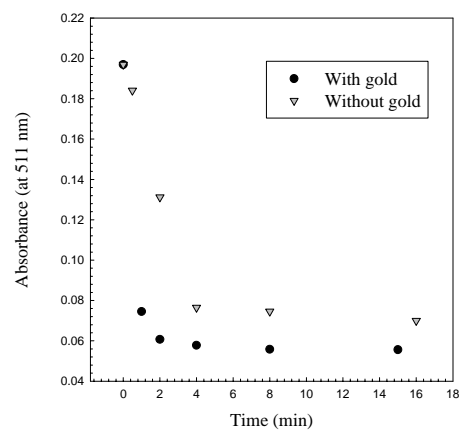


Figure 6. Absorbance change of Fe<sup>2+</sup>-chelates as a function of reaction time.

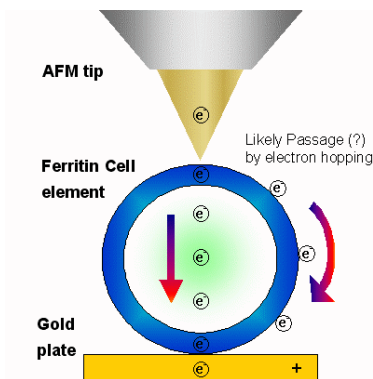


Figure7. Electron transport mechanisms

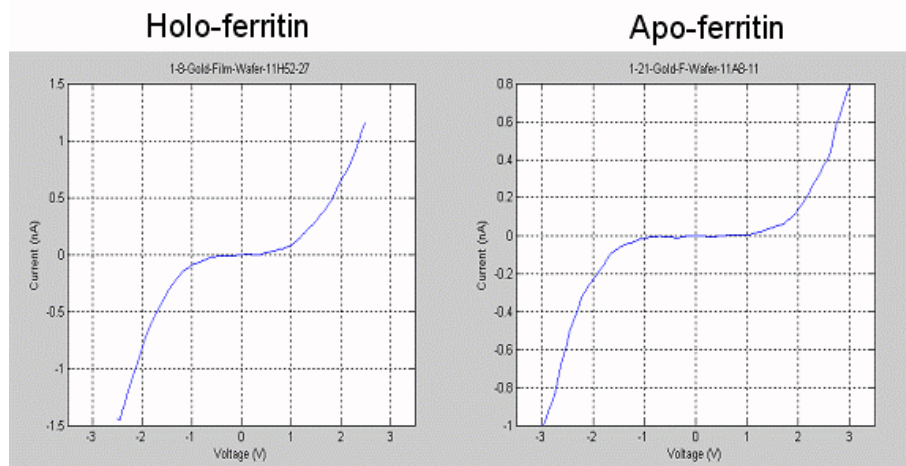


Figure 8. I-V curve for holo and apo-ferritins

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