Development of a Bio-nanobattery for Distributed Power Storage Systems

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ABSTRACT

Currently available power storage systems, such as those used to supply power to microelectronic devices, typically consist of a single centralized canister and a series of wires to supply electrical power to where it is needed in a circuit. As the size of electrical circuits and components become smaller, there exists a need for a distributed power system to reduce Joule heating, wiring, and to allow autonomous operation of the various functions performed by the circuit. Our research is being conducted to develop a bio-nanobattery[1,2,3] using ferritins reconstituted with both an iron core (Fe-ferritin) and a cobalt core (Co-ferritin). Both Co-ferritin and Fe-ferritin were synthesized and characterized as candidates for the bio-nanobattery. The reducing capability was determined as well as the half-cell electrical potentials, indicating an electrical output of nearly 0.5 V for the battery cell. Ferritins having other metallic cores are also being investigated, in order to increase the overall electrical output. Two dimensional ferritin arrays were also produced on various substrates, demonstrating the necessary building blocks for the bio-nanobattery. The bio-nanobattery will play a key role in moving to a distributed power storage system for electronic applications.

Keywords: ferritin, bio-nanobattery, battery, power, storage, cell, electronic

1. INTRODUCTION

1.1 Bio-nanobattery characteristics

Unlike conventional power storage systems, the bio-nanobattery will make distributed power sources within an electrical circuit practical. The bio-nanobattery can be made as a flexible thin film, therefore, it can be incorporated into a fabric or made to conform to various applications. Additionally, the thin film configuration allows easy embodiment with power harvesting devices, making the bio-nanobattery rechargeable. 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. The development of the bio-nanobattery for distributed power storage will have numerous applications, including flexible thin-film electronic circuits, ultra-high density data storage devices,[4] nanoelectromagnetics,[5] quantum electronic devices,[6] biochips, nanorobots for medical applications and mechanical nano-fabrication, nanomechanical devices, etc.

1.2 The ferritin protein

Ferritins are naturally occurring iron storage proteins in biological mechanisms of humans, animals, and even bacteria, and may contain up to 4,500 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).[7] 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).[8] Both 3-fold and 4-fold channels in the organic shell allow for the transport of ions and molecules, making electron conduction

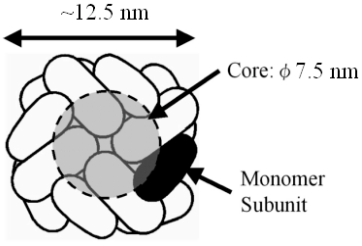


Figure 1. Ferritin protein shell

through ferritin shell possible. Research conducted at Brigham Young University indicates that naturally occurring HEME groups of bacterioferritins should facilitate electron transport through shell.

2. METHODOLOGY

2.1. Biomineralization and reconstitution of cores

By the reconstitution process of site-specific biomineralization within the protein shell, ferritins are loaded with different core materials,[8] each with a different redox capability. Core materials are incorporated into the ferritin shell with the addition of an oxidant (see Figure 2). Using this reversible reaction, various core materials can be incorporated in the ferritin shell, in place of the naturally occurring iron core. Cobalt and manganese cores have been made for the bio-nanobattery, as well CdS, CdSe. Magnetite-maghemite cores for ferromagnetic applications and trimethylamine-N-oxide cores for superparamagnetic applications are also also envisioned. The following discussion will focus on the Fe and Co-core ferritins for incorporation into the bio-nanobattery.

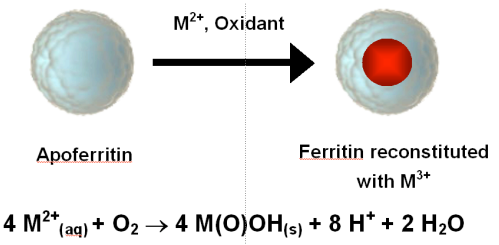


Figure 2. Ferritin reconstitution

2.2. Bio-nanobattery concept

Fe-ferritins and Co-ferritins are used for a unit cell of the bio-nanobattery. In the absence of chelators at pH = 7.0, the $Fe(OH)_3$ iron core of ferritins undergoes reversible reduction to produce a stable $Fe(OH)_2$ core, while all 4500 iron atoms remains within the ferritin interior. The redox reactions between each ferritin with different core materials involve the transfer of an electron from a donor to an acceptor ferritin (Figure 3). Our research has 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."

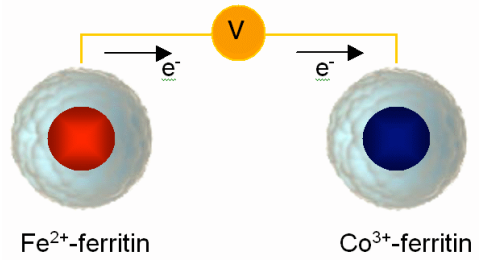


Figure 3. Bio-nanobattery unit cell

2.3. Ferritin arrays

Three methods were utilized in producing ferritin arrays for incorporating into the bio-nanobattery: spin coating, dipping, and LangmuirBlodgett deposition. Spin coating is a quick and simple process for producing a flat and uniform layer. A robust structure is formed by 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.[9,10] 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 for high capacity, high efficiency, compact size, and flexible applications. It also shows an energy harvesting scheme with a photovoltaic component.

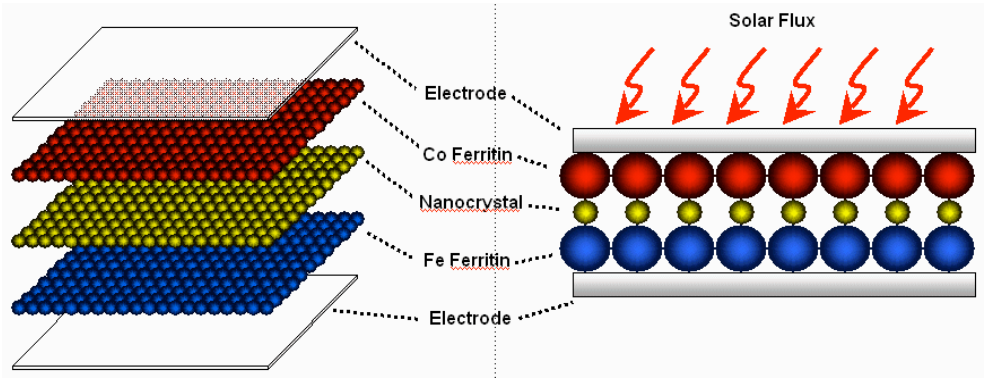


Figure 4. Integration of bio-nanobattery cell

3. EXPERIMENTAL

3.1 Materials

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 Co^{2+} to apo-ferritin in the presence of H_2O_2.[11] 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.

3.2 Spin Self-Assembly method

The spin self-assembly (SSA) deposition method[12] was used to produce Ferritin arrays on various substrates. SSA deposition quickly produces thin films that are highly ordered, flat, and stable. Electrostatic force holds the ferritin particles on the surface during the spin-coating process, while centrifugal force and air drag force remove loosely attached ferritin particles and strengthen the protein binding. Repeating the process, the second layer of a ferritin array is built on the top of the first layer to form a redox charge transfer chain. The total output current and voltage are determined by the connection of the pairs, either in a serial or parallel mode. Scanning probe microscopy (SPM) was used to image the ferritin arrays on the Si substrate (see Figure 5). The magnetic properties of the ferritin with metallic cores allowed a magnetic force microscopy (MFM) tip to be used for imaging the ferritin arrays. The 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.

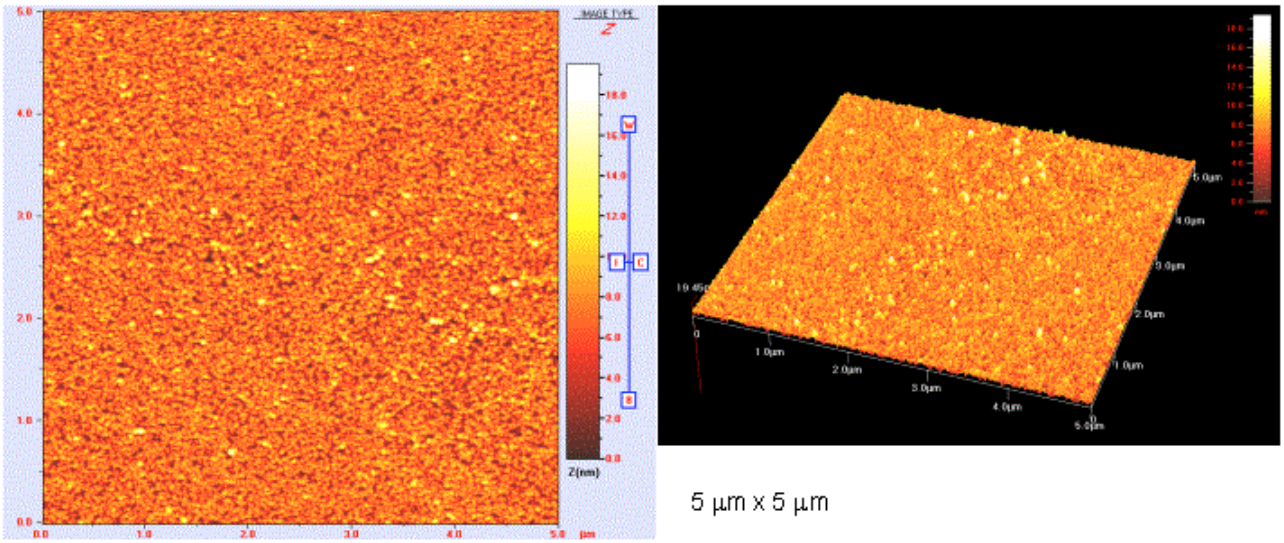


Figure 5. Cationized ferritin on Si substrate

4. RESULTS

4.1 Ferritin characterization

A stability test of Co-ferritin indicated that most of cobalt(II) remained bound to Co-ferritin (>90%), demonstrating the stability of the $Co(OH)_2$ mineral phase within the ferritin interior for extended time periods. Figure 6 shows the reduction of Co^{3+} to 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 Co^{3+}-ferritin is reduced to Co^{2+}-ferritin. This result shows that 1.85 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 Co^{3+}-ferritin. Figure 7 shows

the reduction equilibrium and the reduction kinetics of both Co-ferritin and Mn-ferritin. Preliminary results showed that an equilibrium condition between the M^{II} and M^{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.

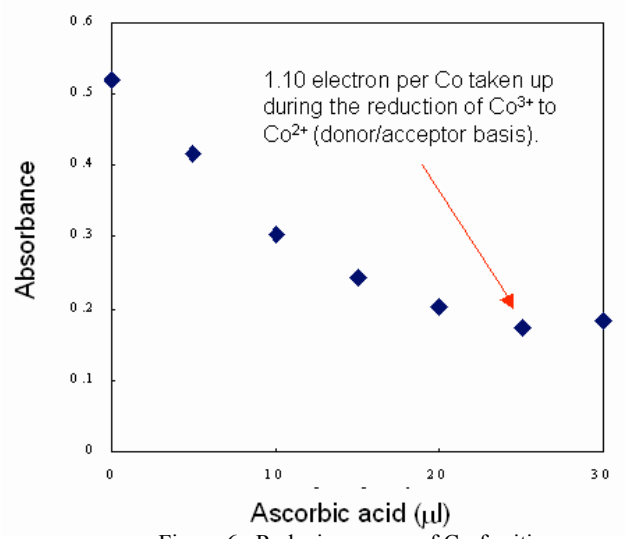
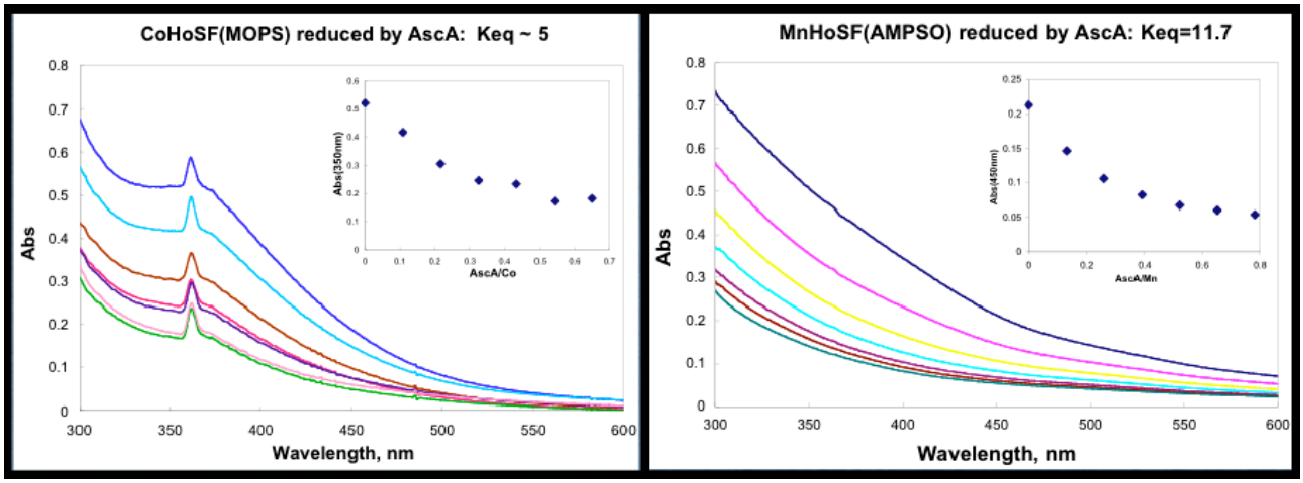
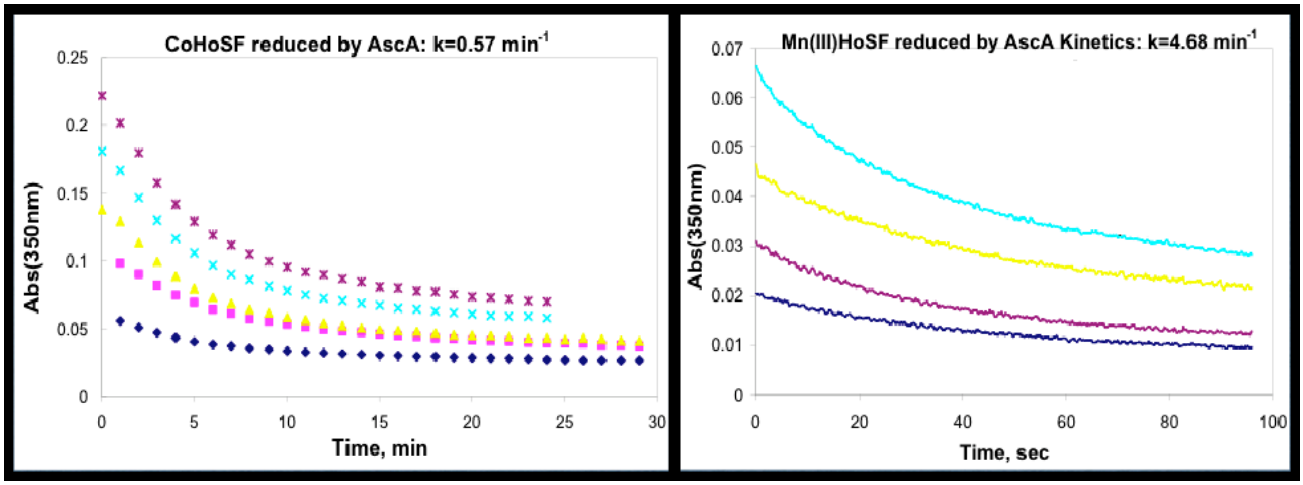


Figure 6. Reducing power of Co-ferritin



a) Absorbance for various wavelengths. Inset: Absorbance at fixed wavelength for increasing ascorbic acid percentage



b) Absorbance at 350nm with time.

Figure 7. Reduction equilibrium (a) and reduction kinetics (b) of Co-ferritin and Mn-ferritin

4.2 Electron transport in the bio-nanobattery

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 8 illustrates the results of a dynamic redox reaction between Fe^{2+}-ferritin and Co^{3+}-ferritin. A chelating agent was added to the solution containing ferrous ions. The remaining Fe^{2+} is indicated by the decrease in absorbance at 511 nm as the redox reaction takes place, corresponding to the remaining Fe^{2+} 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^{2+} to Co^{3+}, and that the mechanism of electron conduction through the protein shell is a key factor to determine power density, max. discharge rate, and duty cycle life of bio-nanobattery cell units.

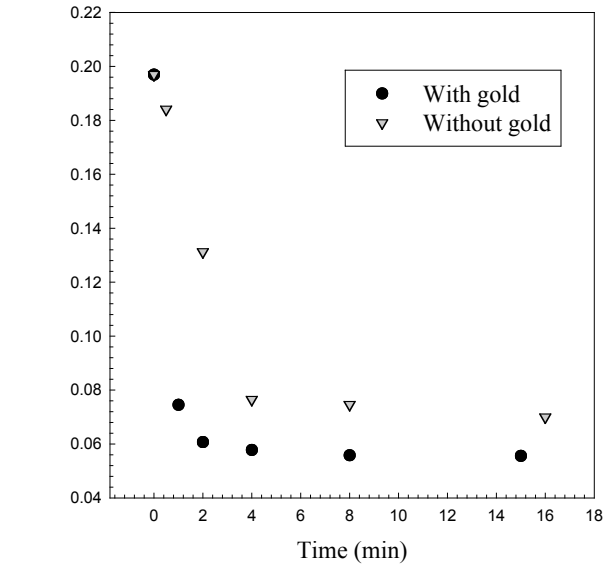


Figure 8. Absorbance change of Fe^{2+}-chelates as a function of reaction time.

4.3 Ferritin conduction

Two methods are employed to determine the electron transport in ferritins. The first involves conductivity measurement using an AFM tip (Figure 9). 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.

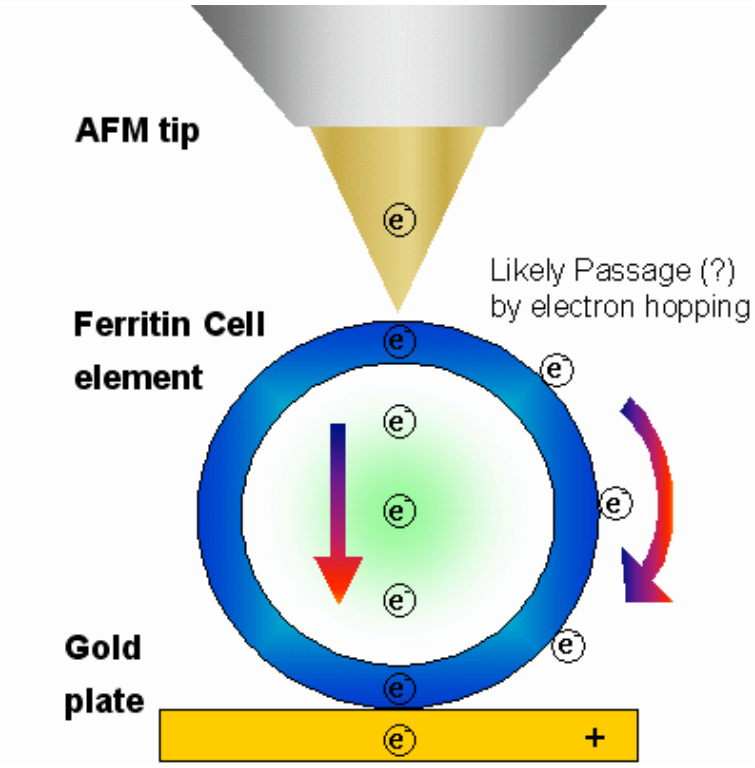


Figure 9. Electron transport mechanisms

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 10 depicts, the tunneling barrier height is larger for apo than holo ferritin.

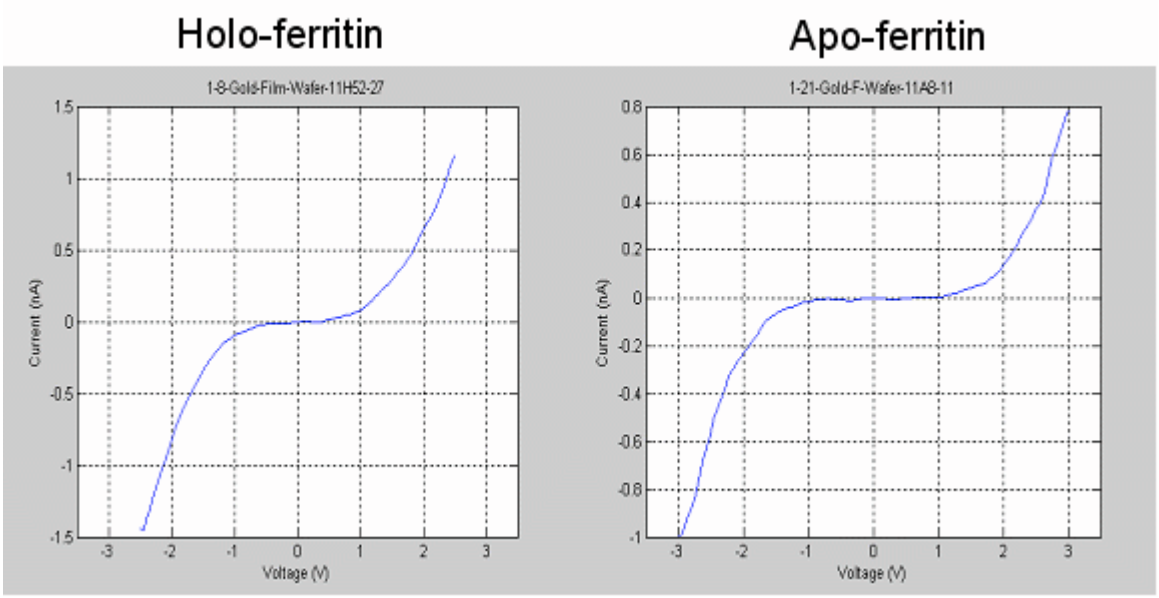


Figure 10. I-V curve for holo and apo-ferritins

Note that the apo-ferritin has no current flow when at 0.5 voltage is applied, while the holo-ferritin begins to conduct electrons. The results show that the conduction is dependent on the presence of a core material, suggesting that electron tunneling may be the mechanism of electron transport.

Another method for conductivity measurement, shown in Figure 11, involves testing conduction through 2-D ferritin arrays. A DC current is monitored with and without a ferritin layer on a nonconductive substrate to determine the conductivity of the ferritin layer. The number of ferritins sandwiched between electrodes is approximated to estimate the conductivity of a single ferritin.

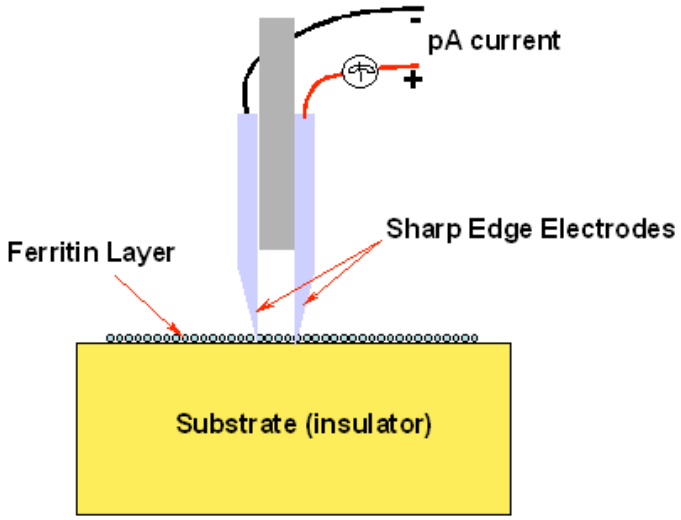


Figure 11. Alternate conductivity measurement method

5. CONCLUSIONS

The bio-nanobattery will enable a shift from central power storage systems to 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.

ACKNOWLEDGEMENTS

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