

## Structural Change Effect of Ferritin on the Electrode Reaction

Masato Tominaga, Kota Nakao, Isao Taniguchi

*Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami,  
Kumamoto 860-8555, Japan*

*Tel: +81-96-342-3656, Fax: +81-95-342-3656,*

*E-mail: masato@gpo.kumamoto-u.ac.jp*

### Abstract

The biphasic behavior of peak current vs. temperature in cyclic voltammograms of ferritin immobilized onto poly(L-lysine)(PLL)-modified ITO electrodes was observed. The results of CD and fluorescent measurements indicated that the fine phase transition of ferritin structure occurred around 25 °C. The biphasic behavior of peak current of ferritin would be caused by the fine phase transition of ferritin structure induced by temperature.

### Introduction

Ferritin is an iron-storage protein found in most animals and plants. The outside diameter of ferritin is *ca.* 12 nm, and the cavity diameter is *ca.* 8 nm. The iron uptake and release mechanisms of ferritin are caused by the oxidation and reduction of iron ions (Fe(II)/Fe(III)) in the protein cavity. We have been investigating the redox reaction of ferritin immobilized onto a functionalized electrode surface [1,2]. In the present study, we investigated the effect of the structural change on the electrode reaction of ferritin immobilized onto PLL-modified ITO electrode.

### Experimental

Horse spleen ferritin (Sigma) was purified by size exclusion chromatography to remove free iron ions using a Sephadex G-25 column. Ferritin immobilized PLL-modified ITO electrodes were prepared according to previous reports [1]. Electrochemical measurements were carried out in a phosphate buffer solution (pH 7) under argon atmosphere. An Ag/AgCl (saturated KCl) electrode and a platinum electrode were used as the reference and counter electrodes, respectively.

### Results and Discussion

The well-defined a couple of redox peak of ferritin immobilized PLL-modified electrode were observed at temperature region of 5~50 °C. The redox peak currents depended on temperature. The peak currents vs. temperature showed biphasic behaviors around *ca.* 25 °C, as shown in Fig. 1. The decrease tendency in the slope of current increasing was not due to desorption of ferritin from the electrode surface. It was expected that the biphasic behaviors of peak currents would be due to the structural change in ferritin. In fact, the fine structural change in ferritin was detected by CD and fluorescent measurements, although it is known well that the ferritin structure is significantly stable up to *ca.* 80 °C. From the CD measurements, the decrease in the peak corresponding to  $\alpha$ -helix of ferritin with increasing temperature was detected, which showed biphasic behavior around 25 °C. Furthermore, the intensity in the fluorescence emission peak corresponding to tryptophane of amino acid residue of ferritin with increasing temperature was also detected, which also showed biphasic behavior around 25 °C. The results of CD and fluorescent measurements indicated that fine phase transition of ferritin structure occurred around 25 °C.

Taken into account of redox reaction of ferritin, ion follow passing through the ion channels of ferritin would occur due to charge compensate in the ferritin cavity during the redox of ferritin core (Fig. 2) [2]. The iron flow would be rate-determining step of ferritin redox. The fine phase transition of ferritin structure induced by temperature would influence the iron flow through the ion channels of ferritin.

## References

1. M. Tominaga, K. Soejima, M. Matsumoto, I. Taniguchi, *J. Electroanal. Chem.*, **579**, 51 (2005).
2. M. Tominaga, K. Soejima, I. Taniguchi, *J. Electroanal. Chem.*, **617**, 78, (2008).

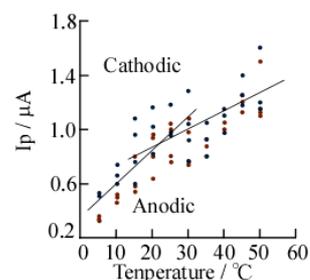


Fig. 1 Anodic and cathodic peak currents obtained from cyclic voltammograms of ferritin immobilized onto PLL-modified ITO electrode as a function of temperature. Potential sweep rate was 50 mV/s. Electrode area was 0.25 cm<sup>2</sup>.

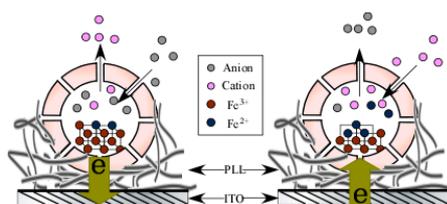


Fig. 2 Schematic representation of ferritin redox reaction on the electrode surface and ion flow during the redox processes.