

# Potential shifts of ferrocene-derivatives at ultra-small microelectrodes

Akihoko Mori, Jingyuan Chen\*

Department of Applied Physics, University of Fukui, 3-9-1  
Bunkyo, Fukui-shi, 910-8507 Japan

## 1. Introduction

An electrochemical tool of searching nanometer domains is a nanometer-sized electrode such as in the scanning electrochemical microscope. Since a nanometer-sized electrode takes also nano-structure, it may exhibit itself some behavior different from the bulk properties. Thus, it is crucial to understand properties of nanometer-sized electrodes. Techniques of fabricating ultramicroelectrodes have been gradually developed, and now allow us to conveniently use nanometer-sized electrodes with few artifacts use nanometer-sized electrodes. An interesting behavior at nano-scaled electrodes is an increase in standard rate constants with a decrease in the electrode size. This subject has still been in debate partly because of technical problems of the fabrication. The problem may be solved if we could get voltammetric data for redox species with large and small charge transfer rate constants at wide-ranged microelectrodes.

## 2. Experimental

Nanometer-sized electrodes (Fig.1) was fabricated by etching electrochemically a Pt wire 20  $\mu\text{m}$  in diameter and then coating the Pt tip with anodic electrophoretic paint (PPG, ZQ84-3225) including polyacrylic acid. A dc potential of +2.1 V was applied between the Pt wire and the Pt coil to initiate the oxidation of water. Then, the coating began from the support of the Pt wire toward the tip. The electrode was put in an oven, kept at 200  $^{\circ}\text{C}$  for 7 minutes to harden the paint. Then the oven was cooled to 100  $^{\circ}\text{C}$ . The electrode was kept in the oven for 24 hours and cooled for 48 hours at room temperature in order to stabilize the cured paint.

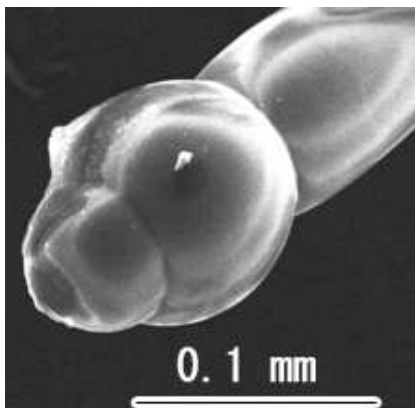


Fig.1  
SEM of the  
polymer-coated  
Pt tip electrode.

## 3. Results and Discussion

Voltammograms of ferrocenylmethyltrimethyl ammonium (FcTMA) in 0.1 M KCl aqueous solution showed steady a state wave at these electrodes. From the diffusion-controlled limiting current of FcTMA, we evaluated radii,  $r$ , of the electrode through

$$I_d = 4Fc^*Dr$$

on the assumption that the an exposed electrode might be disk shape. The smallest electrode was 6 nm in radius. The half-wave potential was plotted against logarithm of the radii in Fig.2, showing the slightly positive shift with a

decrease in the radii. The shift is ascribed to the exhibition of the charge transfer rate over the diffusion-control.

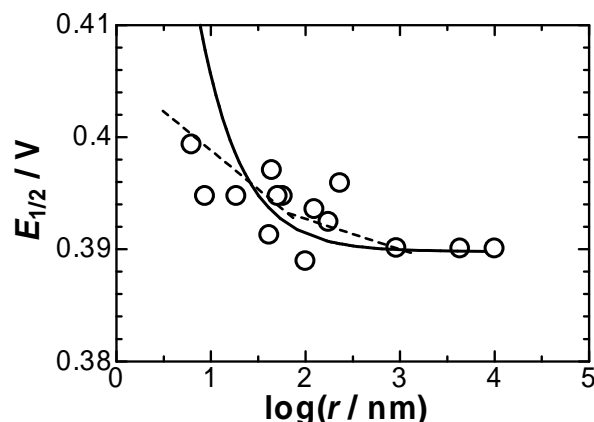


Fig.2 Variation of the half-wave potential against logarithm of the radii in 2 mM FcTMA aqueous solution including 2 mM KCl.

According to the theory of mass transfer associated with the simple charge transfer kinetics at a hemi-sphere electrode, the relation among the half-wave potential, the radius, the diffusion coefficient,  $D$ , the charge transfer rate constant,  $k^0$ , and the transfer coefficient,  $\alpha$ , under the steady-state condition is expressed by

$$e^{(1-\alpha)\zeta'}(1 - e^{-\zeta'}) = D/k^0r \quad (\zeta' = (E_{1/2} - E^0)F/RT)$$

The curve (solid) calculated for  $\alpha=0.5$ ,  $k^0 = 10 \text{ cm/s}$  is deviated upward from the experimental points, probably because of nanometer-effects. The data have not such quality that detailed discussion cannot be made.

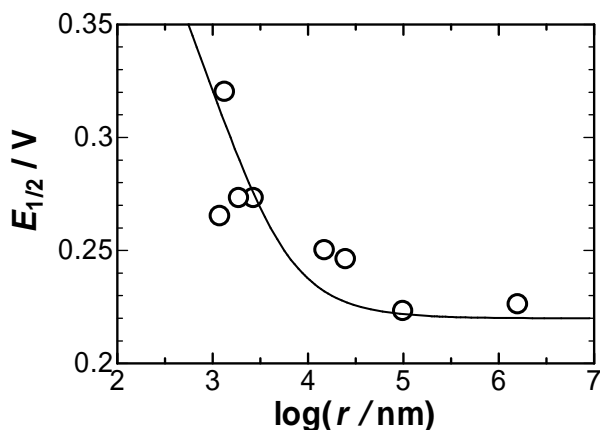


Fig.3 Variation of the half-wave potential against logarithm of the radii in 0.2 mM ferrocene of  $\text{CH}_2\text{Cl}_2$  including 0.1M tetrabutylammonium perfluorate.

We obtained more basic data by use of ferrocene in  $\text{CH}_2\text{Cl}_2$  solution, in which ferrocene shows slow charge transfer rate constant.

The potential shift was much larger than that in Fig.2 (vertical scale is 6 times larger). The curve fitted for  $k^0 = 0.009 \text{ cm/s}$  by use of the above equation is better than the scattering in Fig.2. The deviation in Fig.2 is caused by nano-size effects.

\* Corresponding author. Tel: +81-776-27-8753, fax: +81-776-27-8494  
e-mail: d020111@icpc00.icpc.fukui-u.ac.jp.