Comparison of Voltammograms at the Polymer-coated Nano-electrode with Those at the Glass Sealed One

Jingyuan Chen, Koichi Aoki
Department of Applied Physics, University of Fukui
3-9-1 Bunkyo, Fukui-shi, 910-8507 Japan
jchen@u-fukui.ac.jp

Using metal electrodes of nanometer dimensions is of fundamental interest in interpretation of electron-transfer kinetics and mass-transport mechanisms in nanoscale domains. Metal electrodes with characteristic dimensions with 1 nm or less have been reported during the past 25 years, and applied in a wide range of studies including investigations of the influence of the electrical double layer on molecular transport and kinetics. Unfortunately, the electron transfer rate constants of ferrocenyl compounds determined at nano-electrodes have varied from researchers to researchers.

The wide variation of the rate constants may be ascribed to instability or an irreproducibility of nano-electrodes. Fabricating techniques of exposed electrode surface can be divided into the two types: coating a metal with insulating films [1,2] and sealing a metal with glass [3]. The former have a number of inherent disadvantages, such as poor reproducibility, temperature- and moisture-dependence, fragility as we have often experienced damage of electrodes by low degree of swelling and chemical proof. The glass sealed electrodes have a long life. But it is not easy to control polishing a glass-sealed tip until predicted nano-size.

The polymer-coated electrodes were fabricated by coating the Pt tip with insulating films [4]. Standard rate constants of hexacyanoferrate were evaluated from a plot of half-wave potentials of the steady-state voltammograms against logarithms of radii of ultramicroelectrodes. The smaller is the radius, the more positively shifts the anodic voltammogram and the more negatively does the cathodic wave.

The glass-encased platinum nano-electrodes were fabricated at the success rate 76 %. Thus fabricated electrodes had diameters ranging from 1 nm to 5μm, estimated from the steady-state current of diffusion-controlled current of ferrocene in acetonitrile and ferrocenyl derivative in aqueous solution. They exhibited reproducible and stable voltammograms without hysteresis, withstanding 6 hours' continuous use and 15 hours' iterative processes of heat and voltammetry. Not only the halfwave potentials but also slopes of the log-plots were independent of radii of the electrodes. No kinetic effect was revealed in the steady-state voltammograms.

Here, we report nano-electrode voltammograms by two type electrodes. The aim is to discuss why the value of electron transfer rate constants have largely deviation from normal.

[1] J.L. Conyers, Jr., H.S. White *Anal. Chem.* **72** (2000), p. 4441.
[2] C.J. Slevin, N.J. Gray, J.V. Macpherson, M.A. Webb, P.R. Unwin *Electrochem. Commun.* **1** (1999), p. 282.
[3] G. Wang, A. K. Bohaty, I. Zharov, H. S. White, *J. Am. Chem. Soc.* **128** (2006) 13553.
[4] J. Chen, K. Aoki, *Electrochem. Commun*., **4** (2002) 24.