Charge transfer rate constants

at electrodes of nanometer dimensions

Name

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Chemical characteristics in a nanoscale domain are frequently different from bulk properties, as is seen in specific catalysis at nano-materials [1]. An electrochemical tool of searching nanometer domains is a nanometer-sized electrode [2]. Since a nanometer-sized electrode takes also nano-structure, it may exhibit itself some behavior different from the bulk properties [3,4].The goals of our experiments are to estimate the accuracy of using steady-state voltammetric limiting currents (ilim) in determining the true electrode area, and to understand properties of nanometer dimensions electrodes.

Techniques of fabricating Pt electrodes of nanometer dimensions prepared by electrophoretic coating of etched Pt wires with polyacrylic acid, is described, and gave electrodes in radii ranging from 1 to 1000 nm. Steady-state voltammograms of ferrocene (Fc), ferrocenylmethyltrimethylammonium hexafluorophosphate (FcTMA$^+$), and hexacyanoferrate $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ were obtained. With a decrease in the radii, the voltammogram showed a gentler slope at the halfwave potentials, and shifted slightly in the positive and the negative directions. The shift is ascribed to the increase in the current density, which alters the diffusion-control into the charge transfer control. However, the amount of the shift was smaller than that predicted from the conventional theory for kinetic mass transport at ultramicroelectrodes. Consequently, the standard rate constant was overestimated by three times. A possible reason of the smaller shift is a non-negligible length of the mean free path of the diffusing redox particle in comparison

with the electrode size. A stochastic diffusion model is proposed, in which a particle walks by random distances of which average is of the order of the electrode diameter. Monte Carlo simulation for this model showed that the concentration profiles were smoother than the conventional profile, and hence the overpotential is observed to be apparently smaller. The standard rate constant of Fc, $FcTMA^+$ and Fe^{2+}/Fe^{3+} were estimated to be 40, 0.7 and 0.2 cm s^{-1}, respectively.
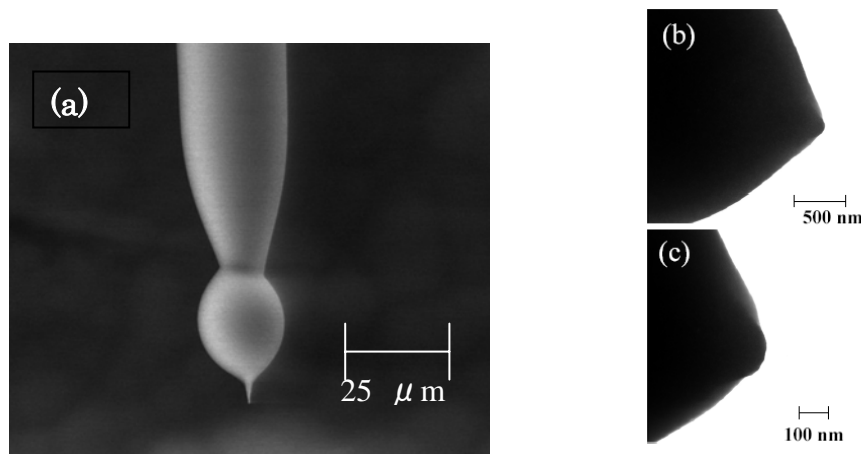

Fig.1a shows a nanometer-sized electrode that was fabricated by etching electrochemically a Pt wire 20 μm in diameter and then coating the Pt tip with anodic electrophoretic paint (PPG, ZQ84-3225) including polyacrylic acid. The exposed portion of the Pt wire tip was immersed into a dilute aqueous paint solution (50:1) and positioned in the center of a Pt coil (1 cm diameter). 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 °C for 7 minutes to harden the paint. Then the oven was cooled to 100 °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. In this process, the paint can cover only the junction between the insulating glass and the Pt wire, keeping the tip exposed to the air, because the paint shrank during the heating. In order to coat the tip except a small portion with an area less than 0.01 μm², iterative coating processes were required. Fig.1b and Fig.1 c are TEM images of the same electrode at (b) 10,000x and (c) 100,000x magnification.
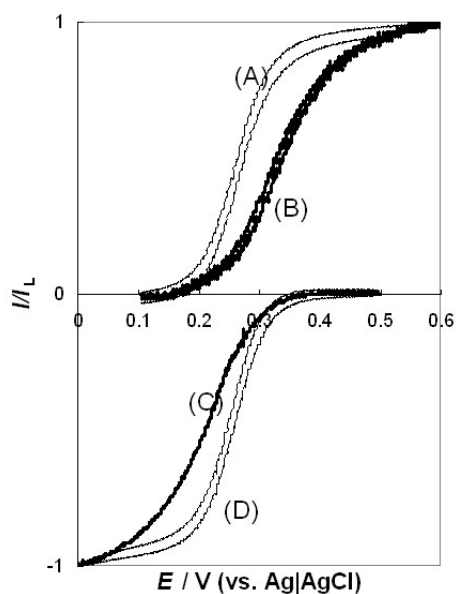
Steady-state voltammograms of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ in 1 M KCl solution were obtained at nanometer- and micrometer-scaled electrodes, as are shown in Fig.2, where current values are normalized. With a decrease in the radii, the voltammogram showed a gentler slope at the halfwave potential, $E_{1/2}$, and shifted slightly in the positive and the negative directions, respectively, for the positive and the negative currents.
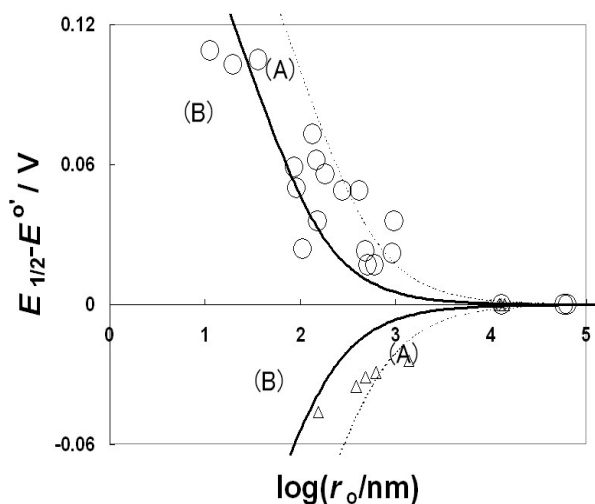

Figure 3 shows the plot of the halfwave potentials, $E_{1/2}$, for $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ against logarithm of the radii. Values of $E_{1/2}$ are shifted in the positive and the negative direction, respectively, for the oxidation of $[Fe(CN)_6]^{4-}$ and the reduction of $[Fe(CN)_6]^{3-}$ although points are widely scattered. Reported values of k^o for hexacyanoferrate are 0.08 [5] and 0.09 [6] cm s^{-1} in 1 M KCl at Pt electrodes. Curves of $E_{1/2}$ vs. log(r_o) were computed for $k^o =$ for 0.09 cm s^{-1} at $\alpha_c = \alpha_a = 0.5$, $D_O = 0.76 \times 10^{-5}$cm^2 s^{-1} and $D_R = 0.63 \times 10^{-5}$cm^2 s^{-1} [7] from

Eq(4), and were drawn in Fig.3 (solid curve). Points for $\log(r_0 / \text{nm}) > 2.5$ are distributed around the calculated curve, whereas those for $\log(r_0 / \text{nm}) < 2.5$ are shifted toward $E^{b'}$. The value of k^0 at which $E_{1/2}$ values for $10 < r_0 < 300$ nm fit Eq. (2) is three times overestimated.

Conclusion

According to the conventional mass-transport theory, anodic waves shift positively with a decrease in r_0, especially showing a linear relation with $\log(r_0)$ for the totally irreversible case. However, the halfwave potentials of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ did not shift so much from the theoretical values. In other words, voltammograms were observed to be more reversible, or the standard rate constant was estimated to be larger than the constant obtained at conventional electrodes. The shift toward a reversible system may be a hint of understanding the enhancement of catalytic activities of nano-meter scaled particles.

[1] G. Gonzalez-Moraga, Cluster Chemistry, Springer-Verlag, Berlin, 1993, p. 202-277.
[2] R. J. Forster, Chem. Soc. Rev., (1994) 289.
[3] J. L. Conyers Jr., H. S. White, Anal. Chem., 72 (2000) 4441.
[4] J.Chen, K.Aoki, Electrochem. Commun., 4, 24-29 (2002).
[5] J. Jordan, R. A. Javick, Electrochim. Acta, 6 (1962) 22.
[6] J. E. B. Randles, K. W. Somerton, Trans. Faraday Soc., 48 (1952) 937.
[7] M. von Stackelberg, M. Pilgram, W. Toom, Z. Elektrochem., 57 (1953) 342.