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Voltammetry of Suspensions of Hollow Particles with Ferrocene-Immobilized Polyallylamine Shells[†]

Jingyuan Chen,* Koichi Aoki, Toyohiko Nishiumi, and Tianbao Li

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

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Redox-active hollow spheres were prepared through extracting a polystyrene core from the latex particle (PSPAAFc) composed of the core and the polyallylamine shell including ferrocenyl carboxylic amide. The suspension of the hollow spheres showed anodic and cathodic voltammetric peaks, which were nearly reversible and diffusion-controlled. The current was 3 times as large as the current for the suspension of the filled PSPAAFc. This value agreed with the theoretical one evaluated from the diameter (1.28 μm), the number of ferrocenyl moieties per particle, 1.2×10^8, by UV spectroscopy, and the diffusion coefficient obtained from the Stokes−Einstein equation. This fact indicates the reaction of the whole loaded charge, in contrast to the partial charge transfer of PSPAAFc. The dynamic flattening motion was observed to support the reaction of the whole charge.

1. Introduction

Electrochemically interesting large molecules or large particles are fullerenes, redox dendrimers, redox polymers, redox proteins, metal nanoparticles, and redox colloids. Their common feature is to contain a number of redox sites of one or more kinds of redox couples in one particle, and hence these particles bring about multielectron transfer reactions. The multielectron transfer of a single redox couple proceeds in general either concomitantly or consecutively as a limiting case.[1] The concomitant electron transfer has not been reported for large particles, to our knowledge, and hence consecutive reactions are predominant. With an increase in the number of electrons, *n*, a single energy level is split into different levels owing to redox interactions.[2] Conducting polymers, which have strong interactions through π conjugation, have distributed energy levels of which the number of electrons is 0.25 for polyaniline,[3] as an example.

The other type of electrochemical complications of a large particle is geometric hindrance experienced when a spherical particle collides with a flat electrode. Because only a small part of the surface of the particle comes in contact with the electrode to participate in the electrode reaction, the current may be smaller than the one predicted from the loaded redox charge. If redox sites are not exposed to the surface or are in an extremely hydrophobic environment, no current is observed.[4] Then the geometrical hindrance can be overcome by using redox species as a mediator, exemplified by the reaction of flavin adenine dinucleotide in enzymes with the help of ferrocenyl moieties.[5] The geometrical hindrance has been quantitatively evaluated for reactions of redox latexes as a loss of current from the predicted diffusion current.[6,7] There are basically three models of geometrical hindrance: (a) the reaction only in the geometrical contact domain,[6a] (b) a given thickness of a reaction layer from the electrode,[6b] and (c) rotational diffusion of the particle near the electrode.[7] The partial charge transfer can obviously be improved by enhancing charge-transport rates within the particle. The enhancement may be realized by making the particle flexible and hydrophilic for the penetration of counterions or by using metal particles with electric percolation.[8]

It is expected that the flexibility is provided by mimicking the structure of vesicles or liposomes,[9] which can be filled with solution and counterions. Redox vesicles can be formed from a core−shell-type latex by dissolving only the cores.[10] If the remaining redox shell is stable, then it may work as a multielectron transfer particle with improved partial charge reactions. Because liposomes and vesicles have been attempted to be used electrochemically for drug delivery techniques,[11] coredissolved particles also have potentiality of working as such as redox liposomes. Although the mass transport of redox species confined in liposomes has been investigated voltammetrically in light of

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* Corresponding author. E-mail: d020111@icpc00.icpc.fukui-u.ac.jp. Fax: +81-776-27-8494.

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flexibility and the release of confined species,[12] no electrochemical report of vesicles having redox activity in a shell has been found to our knowledge. Application of the dissolution technique of the core[10a] to the ferrocene-immobilized latex[7a] is expected to yield hollow redox particles that are dispersed in solution. This article is devoted to dissolving a core from the latex (PSPAAFc) composed of a polystyrene core and the polyallylaminocarboxylic ferrocenyl shell and to investigating the electrochemical efficiency in the context of the flexibility of the shell.

2. Experimental Section

Chemicals. Styrene was purified as previously described.[13] A stabilizer, poly(*n*-vinylpyrrolidone) (PVP) with molar mass of ca. 360 kg mol^{-1}, α-azoisobutyronitrile (AIBN), dimethyl 2,2-azobis-(isobutyrate) (DMAIB), *N*,*N*′-dicyclohexylcarbodiimide (DCC), and 1-hydroxylbenzotriazol (HOBT) were used as received. Commercially available allylamine hydrochloride and ferrocenecarboxylic acid (FcCOOH) (TCI, Tokyo) were stored at 3 °C before use. All of the solvents used were of analytical grade. Aqueous solutions were prepared by the use of ion-exchanged, distilled water. The synthesis process of PSPAAFc was the same as that previously described,[7] with care taken to remove water from the reactor.

Analytical Instruments. The infrared absorption spectra were obtained with a Protege 360 (Nicolet) spectrophotometer by the KBr disk technique. The spectra were corrected against the background spectrum of KBr. UV spectrometry was performed with a UV-570 spectrometer (Jasco, Tokyo).

A digital optical photomicrograph of the latex particles was obtained with a VMS-1900 (Scalar) video microscope and was transferred to a computer. A sample was prepared by spreading a 25 mm^3 drop of a suspension onto a glass plate and was covered with a cover glass.

Elemental analysis was made by EA 1110-CHNS 9726 (AMCO Inc.).

The size distribution of the particles was obtained with a light-scattering instrument (Malvern Zetasizer Nano-S, Sysmex).

Gel-penetration chromatography (TOSOH GPC) was used to determine the average molecular weight of the polymer. The calibration curve was obtained using polystyrene standards (Polym. Lab. Ltd).

A 1.6-mm-diameter platinum disk was used as a voltammetric working electrode. The electrode surface was polished with 0.05 μm alumina powder before each experiment. The platinum wire and the Ag|Ag$_x$O electrode were used as a counter electrode and a reference electrode, respectively. The equilibrium potential at Ag|Ag$_x$O was calibrated with the ferrocene/ferricenium redox couple. Voltammetry measurements were made using a HECS-1112 potentiostat (Fuso, Kawasaki) under computer control.

3. Results and Discussion

Structure of PSPAA Particles. Polystyrene latex coated with polyallylamine (PSPAA) was suspended in 2-propanol. The suspension was turbid and light yellow. It was stable for at least 3 months without appreciable sedimentation. The sizes of the particles in suspension were nearly uniform at 1.28±0.03 μm diameter, as determined by optical microscopy (Figure 1A) and were found to exhibit Brownian motion. When a glass plate was inserted into the suspension, was drawn up vertically into the air and was left until the surface was dried, it was covered with the monoparticle layer into which the PSPAA particles were arranged, as shown in Figure 1B. The arrangement was not destroyed even under a water jet.

The diameter of the particles by SEM was 1.32 ± 0.03 μm. According to our experience of evaluating latex size, diameters of the latex estimated from SEM were always larger than those determined by an optical microscope. Because the observation using the microscope was made in the suspension rather than in a dry environment or in vacuum, the diameter of 1.28 μm was used for evaluating the diffusion coefficient for electrochemical measurements.

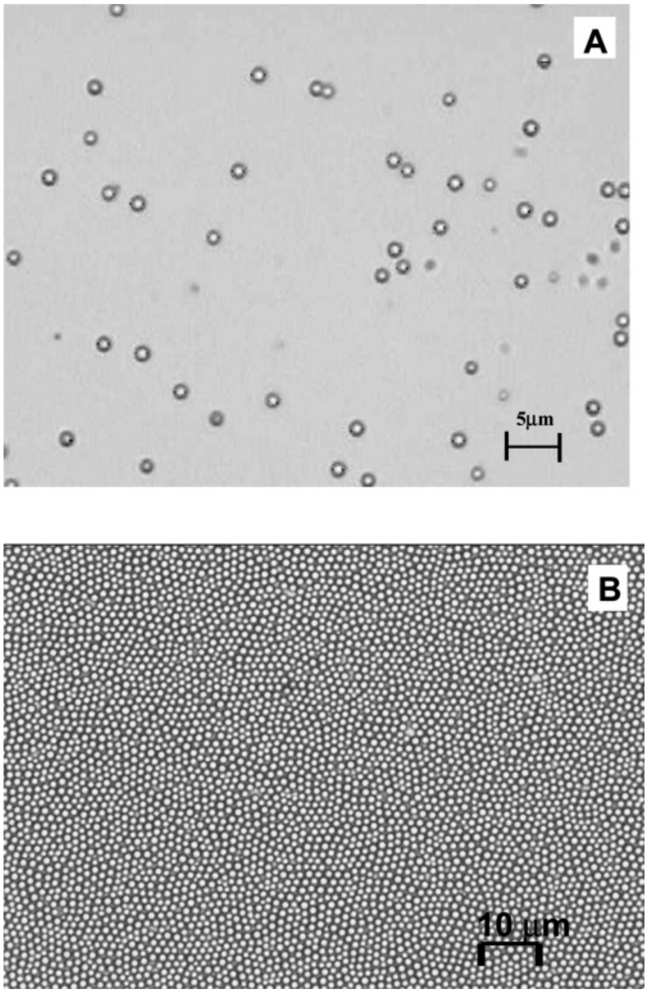

Figure 1. Photographs obtained by the optical microscope (A) of the suspension of PSPAA and (B) dried particles arranged spontaneously on a glass plate.

Structure of PSPAAFc Particles. We attempted to immobilize ferrocenylcarboxylic acid onto PSPAA by the amide bond to yield PSPAAFc particles. The suspension of PSPAAFc in 2-propanol was orange-yellow. The dried PSPAAFc particles was redispersed in 2-propanol to yield a stable suspension. When the suspension containing salt was left in air, it turned green. This variation may be ascribed to the air oxidation of the ferrocenyl moiety to the ferricenyl one. The diameter of PSPAAFc was the same as that of PSPAA, indicating no volumetric contribution by the ferrocenyl moiety. The weight per particle was calculated to be 1.15 pg by use of the diameter of 1.28 μm and the density of polystyrene on the assumption that the shell makes a negligible contribution to the weight. The weight of an aliquot of dried PSPAAFc gives the number of particles.

The FTIR spectra of PSPAAFc did not show any detectable band for the ferrocenyl moiety because of a trace amount of the moiety in comparison with the large amount of core polystyrene. To remove the polystyrene core, we added tetrahydrofuran (THF) to PSPAAFc and collected the insoluble species by filtration, as in the technique of extracting the polyaniline shell.[10a] The insoluble light-yellow species could be dissolved in water,

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methanol, and ethanol. The dissolved PAAFc has been demonstrated not to contain the FcCOO substituent.[7a] The spectrum of the insoluble species was similar to that of the PAAFc in the previous paper.[7] This extraction corresponds to the separation of the hydrophilic PAAFc shell from the hydrophobic polystyrene core. Consequently, the ferrocenyl moiety has been confirmed to be immobilized to the particle in the shell form.

The number of ferrocenyl units per PSPAAFc particle was determined quantitatively with UV spectroscopy.[7] We found that CH_2Cl_2 dissolved the sufficiently dried PSPAAFc without any residue to yield a transparent yellow solution. The UV spectra of this solution showed the band at 447 nm specific to the ferrocenyl moiety.[7] Concentrations of the ferrocenyl moiety were estimated from the comparison of the calibration curve for known concentrations of FcCOOH in CH_2Cl_2. This determination is based on the assumption that the molar absorption coefficient of the ferrocenyl moiety in FcCOOH at 447 nm is the same as that of PAAFc dissolved in CH_2Cl_2. By dividing the number concentration of the ferrocenyl moiety by the number of PSPAAFc particles in the sample, we obtained the number of the ferrocenyl moieties per PSPAAFc particle to be 1.2×10^8, which is denoted by n_{uv}.

The thickness of the shell was estimated to be 29 nm from the density of polyallylamine (1.02 g cm^{-3}) and the weight of the dried shell that was extracted from the core in THF. The elemental analysis of C and N of the dried shell allowed us to evaluate the molar ratio of the ferrocenyl moiety to be 1:9. From the thickness and n_{uv}, the concentration of ferrocenyl moieties in the shell was 1.24 M. This value corresponds to 1.37 nm^3, the volume occupied by one ferrocenyl moiety, suggesting a multilayer of the ferrocenyl moiety in the shell.

We assumed that PSPAAFc ought to be composed of a hydrophobic and a hydrophilic phase. There is, however, another possibility for taking the structure of hydrophilic PAAFc islands in a hydrophobic polystyrene sea. The sea–island structure forms either when allylamine is polymerized predominantly on the foregoing polyallylamine surface onto the polystyrene surface or when allylamine penetrating into pores of polystyrene is polymerized. To examine whether the shell may be generated in a well-defined form, allylamine was polymerized on a polystyrene sheet by the same process as for the generation of PSPAAFc. Figure 2 shows the photograph of the cross sections of the polystyrene sheet with PAAFc, exhibiting two clear phases—the uniform PAAFc layer and the sharp boundary. The composite film was immersed into water to dissolve PAAFc, and the remaining polystyrene sheet was dissolved in THF. The THF solution did not show any UV band or voltammetric wave of ferrocenyl moiety. Therefore, the polystyrene layer is separated specifically from the polyallylamine layer, and hence the core–shell structure should be formed in the PSPAAFc particle.

Voltammetry of PSPAAFc Suspensions. Figure 3 shows voltammograms of the 2-propanol suspension of PSPAAFc including 0.05 M tertabutylammonium perchlorate ($TBAClO_4$). The suspension was electroactive in the potential domain from 0.3 to 0.85 V. The voltammogram at the second and the succeeding scan almost took the common trail, as shown in Figure 3a. The anodic and the cathodic peak potentials did not vary with scan rates of less than 0.1 V s^{-1} (Figure 3b). The difference between the anodic and cathodic peak potentials was 0.10 V when the background current was subtracted. Thus, the voltammetric behavior is close to the reversible process. Voltammograms of the supernatant obtained by centrifuging the suspension did not show any redox wave, as shown in Figure 3 (curve c). Therefore, the voltammogram is not due to a free ferrocenyl moiety decomposed from the latex but is due to the immobilized one. PSPAAFc in the bulk ought to be in the reduced state, as can be seen from the color (yellow) of the suspension. It is confirmed by the zero value of the current (Figure 3) at the forward scan near 0.3 V.

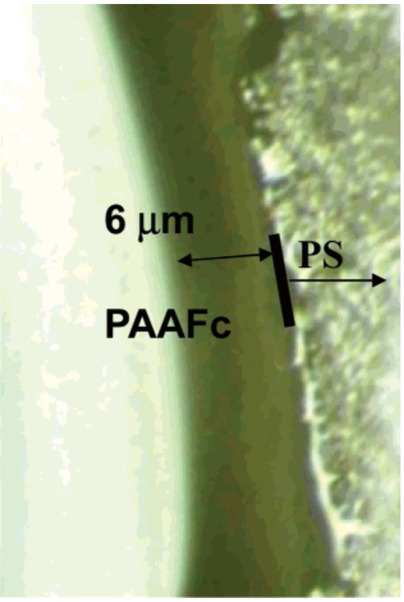

Figure 2. Optical microscope photograph of the cross section of the composite film of the polyallylamine-polymerized polystyrene sheet.

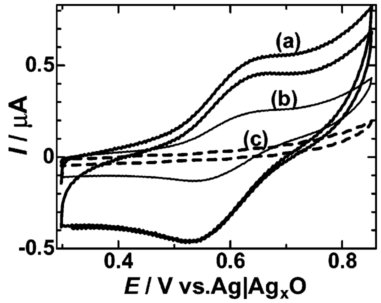

Figure 3. Voltammograms of the suspension including 0.03 g of dried PSPAAFc in 1 cm^3 of a 0.05 M $TBAClO_4$ 2-propanol solution at the Pt disk electrode for scan rates of (a) 100 and (b) 20 mV s^{-1} and (c) of the supernatant of the suspension by centrifugation.

The polyallylamine layer works not only to immobilize the ferrocenyl moiety but also to facilitate the penetration of the counterion (ClO_4^-) into the layer. Because 90% of the amino group is left behind from the amide bond, the polyallylamine layer is thought to be ionic. As the converse data for ionic films, we can cite the ferrocene-adsorbed polystyrene latex suspension in a hydrophobic atmosphere, which showed no voltammetric wave, although the latex was yellow.[4]

Figure 4 shows the variation of the anodic peak currents $I_{p,A}$ with the square root of the potential scan rate, v. The proportionality implies that the anodic current should be controlled by diffusion. A diffusion-controlled peak current of the succeeding n-electron reaction is expressed by[14,10a]

$$I_p = 0.446nF^{3/2}c^*A(Dv/RT)^{1/2} \tag{1}$$

where c^* is the bulk concentration of PSPAAFc, A is the electrode area, and D is the diffusion coefficient of PSPAAFc. It is worth noting that eq 1 includes n rather than $n^{3/2}$.[14] The value of D was

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(14) Aoki, K. *Electroanalysis* **2006**, *17*, 1379–1383.

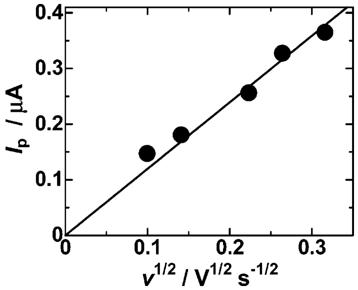

Figure 4. Dependence of the anodic peak current $I_{p,A}$ for a 0.05 M TBAClO$_4$ 2-propanol suspension including 0.03 g of dried PSPAAFc in 1 cm^3 on the square root of the scan rate.

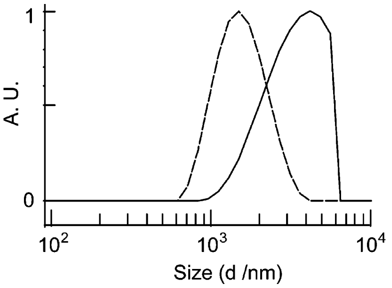

Figure 5. Size distribution of 2-propanol suspensions of PSPAAFc (··) and dichloromethane-dissolved PSPAAFc (−) measured with the light-scattering instrument. The ordinate is the intensity of scattered light.

estimated from the Stokes−Einstein relation, $D = k_BT/6\pi\eta a$[15] on the assumption of a hard sphere model with radius a, where η is the viscosity and k_B is the Boltzmann constant. By use of the viscosity of 2-propanol at 25 °C, 2.04×10^{-3} J m^{-3} s^{-1}, and $a = 0.64$ μm, we obtain $D = 1.67 \times 10^{-9}$ cm^2 s^{-1}. When the known values of $n = n_{UV}$, c^*, A, and D were inserted into eq 1, the calculated value of $I_pv^{-1/2}$ was 3 times larger than the experimental value. It is reported that large redox particles have shown partial charge-transfer reactions in the suspension of polyaniline-coated latex,[10] PSPAAFc,[7] and the vinylferrocene-copolymerized latex.[6] The partial charge-transfer reaction is caused by the

(1) geometrical restriction by the partial area of a spherical particle contacting the flat electrode;[6]

(2) depression of translational diffusion owing to rotational diffusion;[7b] and

(3) slow rate of exchange reactions of a redox couple owing to strong immobilization or hindrance of penetrating counterions within the particle.

If the core of PSPAAFc is replaced by solvent, the restrictions 1 and 3 are expected to be relaxed. The replacement may be realized if only the core of PSPAAFc is dissolved so that hollow latex particles may be stable in suspension form.

Hollow Latex Suspensions. Polystyrene is well dissolved in dichloromethane whereas polyallylamine is not at all. We attempted to dissolve polystyrene in the core of PSPAAFc by adding dichloromethane carefully to the PSPAAFc suspension. The mixture with dichloromethane turned from turbid pale yellow to transparent. The transparency suggests either the possibility of breaking the latex into polymer fragments and solvated polymer chains or forming hollow latex particles by filling the core with dichloromethane. Figure 5 shows the size distributions of PSPAAFc and the dichloromethane-dissolved PSPAAFc. The diameter of the former is 1.3 μm, whereas that of the latter ranges from 3 to 5 μm. It is dangerous to believe the latter value, partly because of the unknown viscosity of the mixed solvent and partly because of the optically complicated structure of the shell for light-scattering measurements. Fortunately, we succeeded in looking at transparent particles in the mixed solvent through the optical microscope by adjusting the direction of irradiation of the light, as is shown in Figure 6. The small particles were the same size (1.28 μm) as PSPAAFc. Larger particles may be formed by the coalescence of some shells. They grew several times larger than the original one within 1 day.

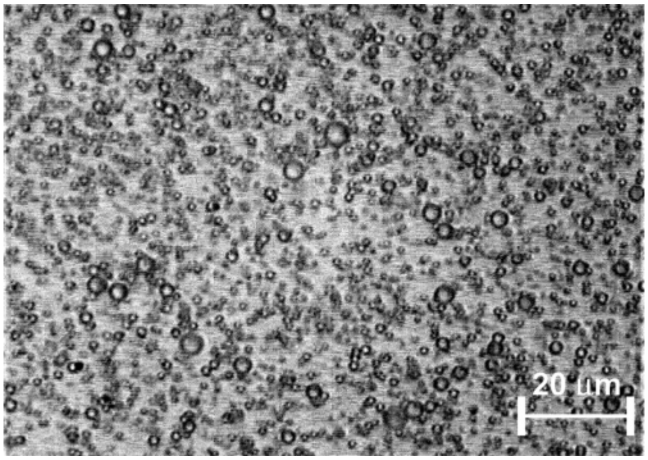

Figure 6. Photograph of dichloromethane-dissolved PSPAAFc by the microscope.

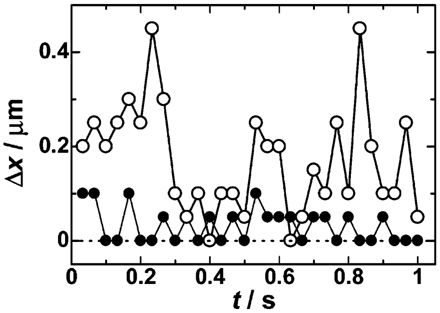

Figure 7. Time variation of the difference between the lengths of the major and the minor axes when an image of (○) a dichloromethane-dissolved PSPAAFc particle or (●) PSPAAFc was regarded as an ellipse by the microscope.

We noticed not only Brownian motion but also a flattening motion of the dissolved particles. We recorded the digital video through the microscope and cut out each panel in a time-sequential manner, from which we obtained time variations of the lengths of the major and minor axes of an elliptic particle. Figure 7 shows the time variation of the difference, Δx, between the lengths of the major and the minor axes at a given particle. The values of Δx for the dissolved particle varied with time almost randomly, whereas the PSPAAFc particle showed only a 0.1 μm deviation in Δx. This is a demonstration of obtaining a solventlike soft core by dissolution. To avoid accidental errors in detecting large variations in Δx, we obtained the frequency of Δx by counting a number of Δx versus t curves, as is shown in Figure 8. Because Δx for PSPAAFc was close to 0.05 μm (Figure 7), the distribution from 0.1 to 0.3 μm can be attributed to the random flattening.

The voltammogram of the transparent solution showed anodic and cathodic peaks, as is shown in Figure 9a. The peak potentials were shifted positively by 0.08 V from those for PSPAAFc in 2-propanol probably because the hydrophobicity of dichloromethane is higher than that of 2-propanol. The negative shift from the wave of FcCOOH (Figure 9b) may be ascribed to the

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[15] Atkins, P. W. *Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, England, 1998; p 749.

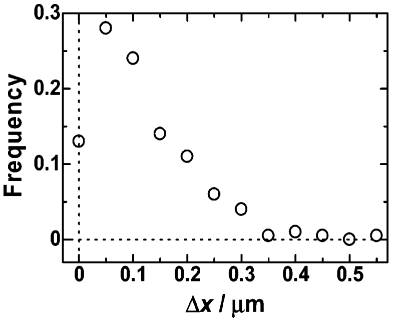

Figure 8. Dependence of the frequency of Δx on Δx for dichloromethane-dissolved PSPAAFc.

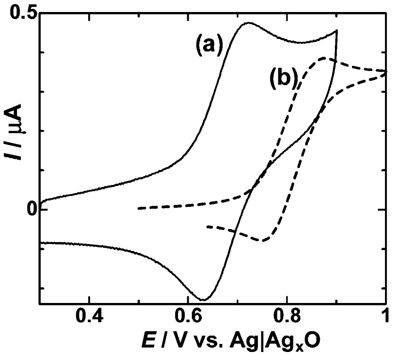

Figure 9. Cyclic voltammograms of (a) 30 mg cm^{-3} of dried PSPAAFc and (b) 0.2 mM FcCOOH in a 0.05 M TBAClO$_4$ dichloromethane solution at v = 10 mV s^{-1}.

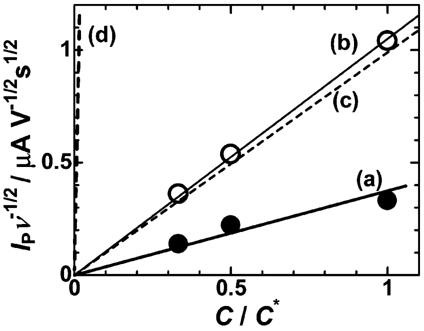

Figure 10. Dependence of the slope of $I_{p,A}$ vs $v^{-1/2}$ on the concentrations of (a) PSPAAFc, (b) dichloromethane-dissolved PSPAAFc, (c) the theoretical (- -) line from eq 1 for $n = n_{UV}$, and (d) the theoretical line from eq 1 when $n = n_{UV}$ and $D = D_{FcCOOH}$. The normalized concentration, c^*, is 0.03 g dried of PSPAAFc in 1 cm^3 of (a) 2-propanol or (b) dichloromethane including 0.05 M TBAClO$_4$.

stabilization of the ferricenium moiety by the amide group. The peak current was proportional to $v^{1/2}$, implying diffusion control. It was also proportional to the concentration, as shown in Figure 10b. Consequently, polyferrocenylcarboxylamide ought to be responsible for the redox reaction. The peak current was 3 times larger than that of the PSPAAFc in 2-propanol (Figure 10a). Even if the latex were to be dissolved uniformly up to molecular fragments, the concentration of the redox charge should not change with the dissolution, being kept constant at nc^*. The factor of 3 increase in the current means that the diffusion coefficient of dissolved PSPAAFc might be 9 times larger than that of PSPAAFc or that the diameter of dissolved PSPAAFc is $^1/_9$ that of PSPAAFc. Nevertheless, the size of the hollow particles is larger than that of PSPAAFc (Figure 6). If the redox moiety were to be decomposed into FcCOOH, the current predicted from eq 1 for $n = n_{UV}$ and $D = 10^{-5}$ cm^2 s^{-1} is 80 times larger (Figure 10d) than the current of PSPAAFc. Consequently, there is no possibility of decomposing PSPAAFc into molecular fragments by the dissolution.

We noticed that the 3 times larger current would be compensated by the ratio ($^1/_3$) for the partial charge-transfer reaction. In other word, the theoretical current value calculated from $n = n_{UV}$ and $D = 1.67 \times 10^{-9}$ cm^2 s^{-1} (Figure 10c) without the partial charge transfer is similar to the observed one. If the hollow particle is flattened at collision with the electrode or if counterion can penetrate from the hollow into the shell, then all of the loaded charge is expected to be oxidized. The former and the latter assumptions correspond to restrictions 1 and 3. They are consistent with the flattening motion in Figures 7 and 8.

Conclusions

PSPAAFc particles had the structure of the polystyrene core and the polyallylamine shell of which one-ninth of the amino molecules were substituted with the amide of ferrocenylcarboxylic acid. They were well dispersed in 2-propanol but dissolved mostly in dichloromethane. They were adsorbed on glass as a one-particle layer in order. The diameter was 1.28 μm, and the loaded charge was 120 mega electrons per particle. The voltammogram of PSPAAFc suspensions showed nearly reversible redox waves of which peak currents were diffusion-controlled. However, only one-third of the loaded charge took part in the charge transfer because of the geometrical hindrance. Except for the partial charge transfer, PSPAAFc can be satisfied with conditions of allowing us potentially to visualize each electrode kinetic process through an optical microscope.

Dichloromethane-dissolved PSPAAFc particles, looking transparent, kept the polyallylamine/ferrocene shell in the suspension. The shell may be stabilized mechanically with the interfacial tension in dichloromethane-like emulsions, although it is coalesced gradually. The dissolved PSPAAFc particle moves randomly not only as translational motion but also as flattening motion, indicating a change to a hollow particle with a solventlike core. The hollow particle exhibited reversible redox waves of which peak currents were diffusion-controlled without partial charge transfer. The reaction of the whole loaded charge may be related to the flattening motion. This point improves the partial charge transfer of PSPAAFc and hence is closer to the ideally visualized redox particles.

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