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Voltammetry of suspended jumbo particles

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Suspended jumbo redox particles are a spherical matrix with a number of redox sites of one or more kinds of redox couples in one particle, such as enzymes, proteins, fullerene, complex cluster metal nanoparticles and colloids. Hence they bring about multielectron transfer reactions. They often show dull electrochemical responses; i.e., broad voltammetric waves, large over-potentials, large irreversibility, and slowly responding current. Possible reasons are chemical complications via a mediator, geometrical blocking of redox sites, sluggish charge propagation within a particle and complicated transport of a particle by aggregation or adsorption. It is not easy to specify a definite reason, because, to our knowledge, there are no data that describe the relation of electrode behavior with size and geometry of large particles. In order to find common feature of electron transfer of jumbo molecules or particles, colloidal particles with simple mass transport have been synthesized, e.g., called redox latex particles. They can take well-stabilized suspensions in a broad range of size with sharp size-distribution (Fig.1), and often have 10 million electrons in one particle. Our idea is to use them as a model to understand how voltammetric electroactivity depends on particle size, particle structure and the chemical species.

Redox latex particles were synthesized by coating near-monodisperse polystyrene latex particles with redox species, or by copolymerizing redox species and styrene. Monodispersion and the size of polystyrene particles were controlled with concentrations of styrene, of potassium persulfate, and of different surfactant as a steric stabilizer. We synthesized seven kinds of latexes with different chemical species, including a core-shell type and a uniformly distributed type. For example, the later was prepared by immobilizing ferrocenylmethanol acrylate into a porous polystyrene latex seed through the emulsion copolymerization reaction (FcMAPS). One of the core-shell types was synthesized by coating hydrophobic cores, polystyrene, with polyaniline shell (PANI-PS). The other was polyallylamine shell on which ferrocenyl carboxylic amide was immobilized (FcCA-PS). The size distribution was determined with the light scattering instrument.

FcCA-PS 2-propanol suspension showed voltammetric redox peaks at 0.63/0.54 V vs. Ag|Ag^+ for the ferrocenyl moiety. FcMAPS aqueous suspensions exhibited stable voltammetric waves at 0.26/0.20 V vs. Ag|AgCl, as shown in Fig.2. A cathodic voltammetric wave was observed in an aqueous suspension of PANI-PS, whereas no anodic wave was detected. It is ascribed to the slow propagation of the conducting zone. This irreversibility was common to particles with eight different diameters ranging from 0.2 to 7.5 μm. The reduction current was controlled by diffusion of dispersed particles.

A common feature of voltammograms for above three kinds of particles is the diffusion-controlled mass transport of the particles, as if the particles were jumbo redox molecules with nearly mega electrons. But they are different from conventional small molecules in voltammetric electroactivity. n_{cv}/n_{uv} was introduced as a measure of the electroactivity. Where n_{cv} is the number of redox sites per particle by the diffused peak current, n_{uv} is that by UV. If all the Fc units react simultaneously at collision with the electrode, n_{cv}/n_{uv} should be close 1. But experimental data point out that all the redox sites of one particle do no react electrochemically as the particle becomes large. Logarithmic variation of n_{cv}/n_{uv} with *a,* radii of particles were plotted in Fig.3. FcMAPS and FcCA-PS showed that n_{cv}/n_{uv} was dependent on *a*, except PANI-PS with n_{cv}/n_{uv} = 0.22. This phenomenon may be ascribed to the thickness of the double layer smaller than the size of particle.

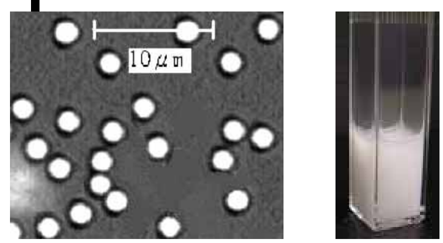

Fig.1. SEM photograph of latex. Optical microscope photograph of latex suspension.

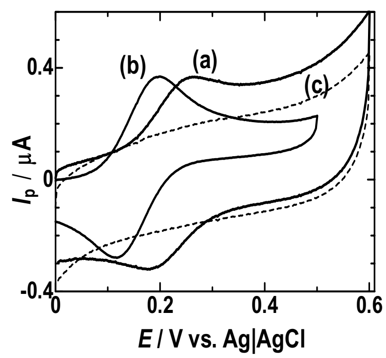

Fig. 2. Cyclic voltammograms of (a) FcMAPS suspension, (b) FcMA, and (c) the supernatant of the suspension by the centrifugation.

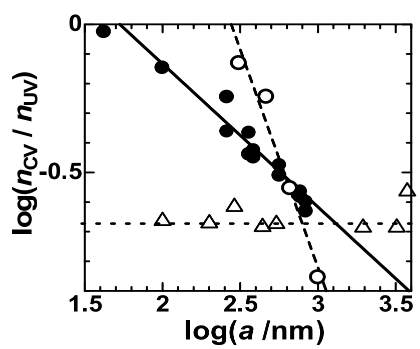

Fig.3. Logarithmic variation of n_{cv}/n_{uv} with *a* for the diffusion-controlled peak currents of latex suspension. filled circles is FcMAPS showed the power -0.47, open circles is FcCA-PS showed the power -1.5 and triangles is PANI-PS showed independent on particle size.