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APPLICATION OF MORPHOLOGICAL EVALUATION BY OPTICAL AND ULTRASONICAL TECHNIQUE TO V_2O_5 SOL

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We newly developed an evaluation method for colloid particle morphology based on the fluid dynamics, in which the translational diffusion constant D was measured by the dynamic light scattering technique. In addition, the solution is composed of anisotropic particles and shows birefringence Δn under the propagation of the ultrasonic wave. The temporal decay curve of the ultrasonic birefringence $\Delta n(t)$ is measured and related to their orientational relaxation time τ. The size and shape was uniquely evaluated using D and τ on the basis of Perrin's theory. It was directly confirmed that prolate particles, which spreads about 1-10μm in the lateral size at the concentration of 0.01-0.2M (Vanadium), disperse in the sol and grows up with increasing sol concentration. The capacity of the cells including the cathodes is found to increase with the decrease in the colloidal particle size of the V_2O_5 sol.
Key words: dynamic light scattering, ultrasonic birefringence, colloid, V_2O_5 sol

1. INTRODUCTION

Recently, we developed a new soft solution process for fabricating cathodes of a supercapacitor coated with V_2O_5/carbon composite [1, 2]. Since the cathode is formed in the sol mixture, the morphological property of the colloidal particles seriously influences the electrochemical performance of the cell. By investigating the relationship between the morphology of colloidal particles and the electrochemical property of the cathode surface, we could improve the ability of the supercapacitor.

The colloidal particles fabricated in the soft solution process are generally very fragile and its higher order structure is easily broken when they are exposed to the atmosphere. The *in situ* measurement is, therefore, quite important to characterize the colloidal particles assembled by weak physical interaction. For the purpose, we applied the ultrasonic birefringence and the dynamic light scattering techniques to characterize the structure of the fragile colloidal particles in a non-destructive and non-contact manner.

First, we assumed that the particle shape is spherical and investigated the relationship between the electrochemical performance and the particle size. We found that the cathode fabricated from solution containing smaller V_2O_5 particles shows superior electrochemical performance.

Next, we assumed the hard anisotropic particles with the uniaxial elliptical shape and its fluid dynamic behaviour consisting of translational motion and rotational motion. The shape is characterized only by two parameters, the length of the particle into the uniaxial direction and the radius of the cross section. In other words, the typical length and anisotropy uniquely represent the shape of the particle. The dynamic light scattering measurement gives information on the translational diffusion behavior, while the ultrasonic birefringence technique yields that on the rotational motion of the particle. Therefore, we can uniquely determine the anisotropic shape of the particle with these two techniques. The experiment was carried out first for the colloid of anisotropic TiO_2 particles whose shape could be observed directly by SEM, and then applied to the fragile V_2O_5 sol with unknown particle shape.

2. EXPERIMENTAL

2.1 Cathode fabrication

Figure 1 outlines the fabrication process used in this study. A dark brown hydrosol containing vanadium of about 16 g/l is prepared by reacting metal vanadium powder (Mitsuwa Chemicals Co., Ltd., 325 mesh) of 1.0 gram with hydrogen peroxide of 100 ml (Wako Pure Chemicals Industries, Ltd., 30wt%) [3]. Water and acetone are added to the sol at a volume fraction of 1:1:1 (0.0725 mol/l-vanadium), 1:0.3:1 (0.0948 mol/l-vanadium) or 1:0.1:1 (0.104 mol/l-vanadium). Carbon powder are then added to the solution and mixed sufficiently at a carbon/V_2O_5 ratio of 130wt%. After stirring for 1 hour, a homogeneous suspension of a V_2O_5/carbon composite was obtained. In this case, acetylene black was employed as the carbon powder whose diameter is 10-100 nm [4]. We tested other carbons, however there was no difference in performance. The addition of acetone is essential to promote dispersion of the carbon powder in the mixture. Finally, a $10\times20\times1.0$ mm^3 macroporous nickel substrate was soaked in the mixture, dried, and then heated at 120°C for 5 hours. Here, nickel formed metal (Sumitomo Electric Industries, Ltd.) with average

pore diameter of 20 μm and density of 0.42g/cm^3 was used as the nickel substrate.

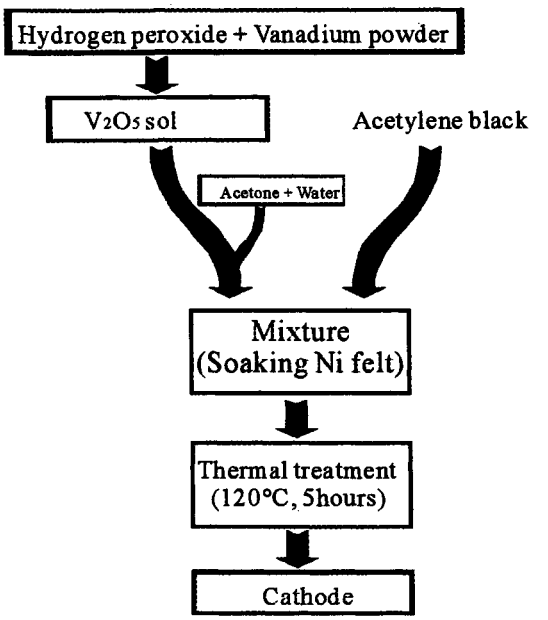

Figure 1. Preparation process of V_2O_5/carbon composite cathodes.

2.2 Characterization of cathodes

A three-electrode cell was used to evaluate the electrochemical properties of the cathode. Lithium plates were employed as reference and counter electrodes, and a 1.0 mol/l $LiClO_4$/propylene carbonate solution was used as the electrolyte. Charge/discharge cycle tests were carried out ranging from 2.0 to 3.7 volts (vs. Li) at room temperature using an automatic polarization system (Hokuto Denko, HZ-3000). Because of enough high voltage compared with lithium insertion potential into carbon layer, which is below 1.5 volt (vs. Li), lithium ion isn't intercalated into the carbon layer in the discharge/charge voltage range. Thus, the carbon particle agglomerates just work as electrical paths between the V_2O_5 layer and the Ni substrate, but don't work as lithium intercalation host.

2.3 Evaluation of size and shape of colloidal particle

The dynamic light scattering measurement was carried out with a He-Ne laser of 35mW output as the light source in the range of the scattering angle of 18°-51°, which corresponds to the scattering wave number of k = 3.09×10^6-8.04×10^6m^{-1}. The temporal decay constant Γ of the correlation function is well described in terms of the diffusional behavior of $\Gamma = 2Dk^2$, where D is the translational diffusion constant. When the particles is approximated as spherical particles with radius a, D is

$$D=\frac{k_BT}{6\pi\eta_0 a}, \qquad (1)$$

where η_0 is the viscosity of solvent.

The measurement system of the ultrasonic birefringence was set up following ref [5]. The anisotropic particles in liquid are oriented by the radiation force of the ultrasound into the direction of the ultrasonic propagation, and the resultant optical birefringence is measured by the ellipsometric analysis.

Next, we assumed an ellipsoid shape of the particle, where a and b are the large and small radii, respectively, and the aspect ratio p is defined as a/b. Both the translational and rotational motions of ellipsoids in sol depend only on its shape and the solvent viscosity η_0. The translational diffusion constant D of the elliptical particle is thus given by [6, 7],

$$D=\frac{k_BT}{6\pi\eta_0 a}t(p)p^{\frac{2}{3}},$$

$$\text{where } t(p)=\frac{p^{1/3}\ln(p+\sqrt{p^2-1})}{\sqrt{p^2-1}}. \qquad (2)$$

On the other hand, the orientational relaxation time τ is given by,

$$\tau = 3\frac{\eta_0 V}{k_B T r(p)},$$

where

$$r(p)=\frac{3}{2}\frac{p^2}{P^4-1}\left\{-1+\frac{2p^2-1}{2p\sqrt{p^2-1}}\ln\frac{p+\sqrt{p^2-1}}{p-\sqrt{p^2-1}}\right\}. \qquad (3)$$

Here V is volume of the particle ($V = 4\pi ab^2/3$), k_B is the Boltzmann constant and T is the temperature.

As described previously, two characteristic parameters, D and τ are obtained by the dynamic light scattering and the ultrasonic birefringence measurements, respectively. By solving eqs. (2) and (3) with the experimental values, we can, in principle, determine a and b, thus the complete shape of the ellipsoid particles.

3. RESULTS AND DISCUSSION

3.1 Relationship between particle size and electrochemical property

Figure 2 shows the relationship between current density and lithium insertion for cathodes prepared at various concentrations of sols. Three lines show data for cathodes made from mixtures containing V_2O_5 sol of various particle sizes based on the spherical approximation using eq. (1). Although there is no remarkable variation between the cathodes at below 60 C (39 A/g-Vanadium), the cathodes made from more dilute sol solutions have higher insertions above 80 C (53 A/g-Vanadium). As mentioned above, the colloidal particles in the dilute sol are smaller than those in the dense sol. Hence, cathodes made from solutions containing smaller colloidal particles have higher insertion at high discharge rates exceeding 80 C (53 A/g-Vanadium). We conclude that the V_2O_5/carbon composite structure in the cathodes depends on the sol concentration. If we require current density above 80 C (53 A/g-Vanadium) in the future,

morphological control of the sol concentration will be important in the fabrication of cathodes.

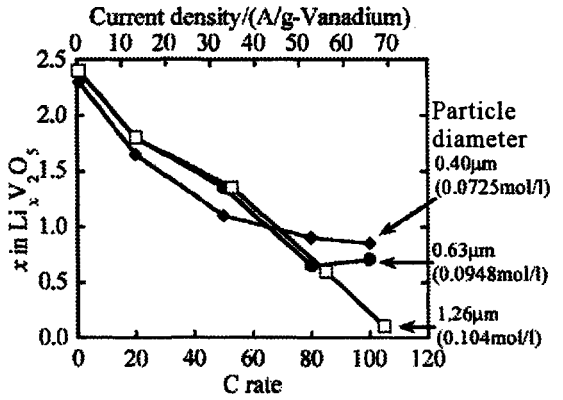

Figure 2. Particle size dependence of V_2O_5 on Li insertion based on the spherical approximation.

3.2 Shape evaluation

The accuracy of the present method of morphological evaluation was confirmed for the colloidal sample of titanium oxide particles whose size and aspect ratio are known. Four kinds of titanium oxide purchased powder from Ishihara Techno Corporation were dispersed in pure water. The catalogue data for each sample is given in Table I. Figure 3 shows the typical example of the self-correlation function of the dynamic light scattering signal obtained for one of the prepared sample (FT-2000). The translational diffusion constant D is calculated to $8.77\times10^{-13}m^2/s$ with the scattering wavenumber k = $8.04\times10^{6}m^{-1}$. Figure 4 shows the ultrasonic birefringence signal of FT-2000 obtained under the radiation of the ultrasonic pulse at 3.1MHz gated into the rectangular envelope. The relaxation time τ of 0.428sec was obtained from the exponential decay tail of the observed birefringence signal. The experimental values of D and τ provide particle length $2a$ = 2.44μm and aspect ratio p = 33.8 through of eqs. (2) and (3). To visibly compare the catalogue and the experimentally determined values, the shapes of the particles are schematically illustrated for each sample in figure 5. As shown in the figure, the experimental results could reproduce the actual particle shape, which is directly observed by the electron microscope in advance. We, therefore, confirmed that the simultaneous measurement of the dynamic light scattering and the ultrasonic birefringence could give quantitative estimation of the anisotropic micro particles in sol, as far as they have a hard ellipsoid structure.

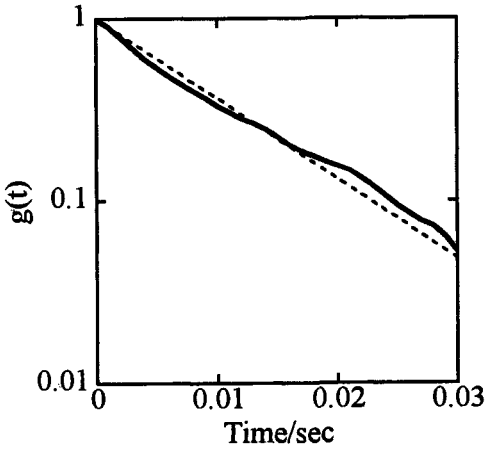

Figure 3. A typical example of the auto-correlation function of the light scattering signal obtained for FT-2000. The dashed line shows the signal exponential decay best fitted to the datum.

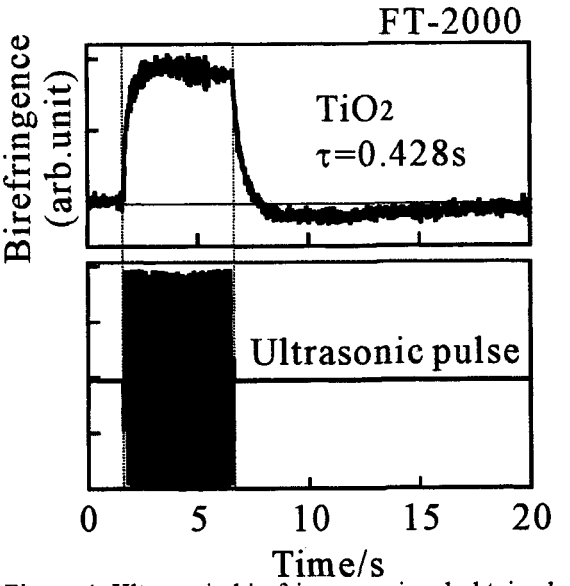

Figure 4. Ultrasonic birefringence signal obtained fro FT2000.

Table I Comparison between catalogue and measurement values for titanium oxide particles

Sample	Catalogue value		Measurement value	
	Length $2a$/μm	Aspect ratio p	Length $2a$/μm	Aspect ratio p
FS-10P	1.00	20.0	1.47	10.4
FT-1000	1.68	12.9	2.58	85.4
FT-2000	2.86	13.6	2.44	33.8
FT-3000	5.00	25	4.6	28.15

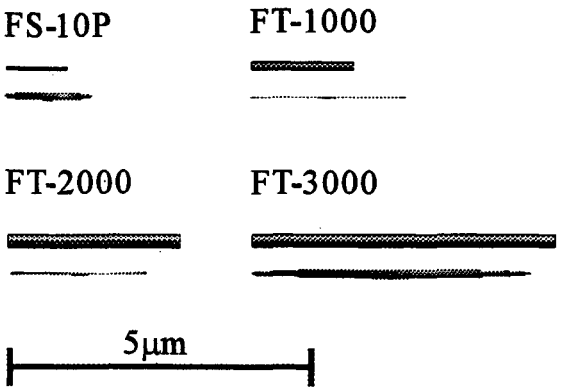

Figure 5. Schematic view of the colloidal particles of TiO_2 in sol (upper: catalogue, lower: experimental result).

We then tried to evaluate the unknown structure of the V_2O_5 colloidal particles in sol (0.03 mol/l-vanadium) prepared by our ordinal method especially developed for the fabrication of the supercapacitor electrode. The translational diffusion constant obtained by the dynamic light scattering measurement is $D = 1.59\times10^{-12}m^2/s$. The ultrasonic birefringence measurement was also carried out and we found, as shown in figure 6, the V_2O_5 sol also shows large optical anisotropy under the ultrasonic radiation suggesting that the V_2O_5 particles have anisotropic shape. The relaxation time of the birefringence signal is obtained to τ = 2.61sec. Note here, that the diffusion constant of V_2O_5 is about twice as large as that of FT-2000, while the rotational relaxation is about 6 times larger. As expected from eq. (2), the translational diffusion constant is inversely proportional to the hydrodynamic radius of the particle, and the experimental result shows that the roughly estimated largeness of V_2O_5 particle is smaller that that of FT-2000. On the other hand, the rotational relaxation time depends on the particle anisotropy as well as the particle volume; larger anisotropy requires longer relaxation time. To summarize these conditions, V_2O_5 particles should be extremely anisotropic. By mechanically substituting the experimental values to eqs. (2) and (3), we obtain the particle length of $2a$ = 8.56μm and the aspect ratio of $p = 2.2\times10^{11}$, which is by far large and seems physically meaningless. The result indicates that the ellipsoid model could no longer be applied for the V_2O_5 sol.

One of the possible morphology of our V_2O_5 sol is a ribbon-like shape. The model is reasonable from the viewpoint of the electro-chemistry. The electrode actually coated by the present V_2O_5 sample has a large capacity of anion, which suggests very fine, complicated and thin structure of the electrode surface in nano-meter size. Simple ellipsoids obviously cannot make such a complex surface layer. While Yasuda et al. have come to a conclusion that V_2O_5 colloidal particle's shape is tactoid in the concentration range from 0.004 to 0.02 mol/l (vanadium) using ultrasonic induced birefringence technique and sol viscosity measurement [8], Livage reported that some V_2O_5 colloidal particles have ribbonlike structure [9]. Since their synthesis-processes are different in between, the difference in morphologies also might appear. We would like to examine the present results using the physical model based on the dynamics of soft strings in liquid.

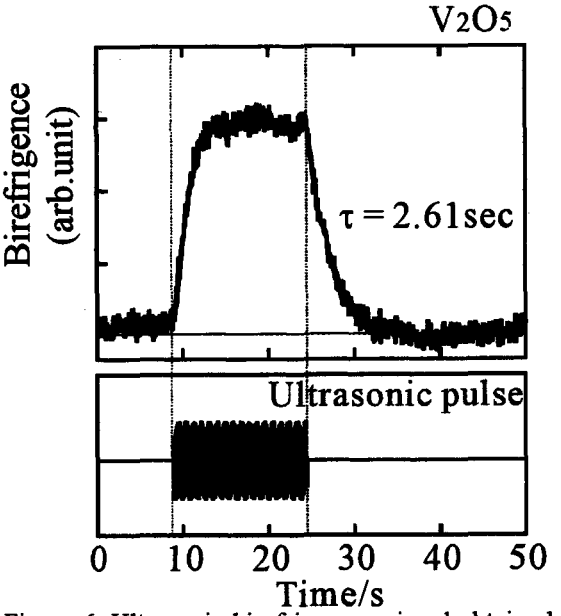

Figure 6. Ultrasonic birefringence signal obtained for V_2O_5 sol at 0.03mol/l.

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