

# Dynamics of Polymer-coated Microparticles in Suspension Probed by Electrophoretic Dynamic Ultrasound Scattering Techniques

電気泳動的超音波散乱法による懸濁溶液中のポリマー被覆粒子のダイナミクス

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## 1. Introduction

Carbon black dispersed in an ionomer solution can be a good candidate to be employed in fuel cell applications. Since optical techniques are not suitable for optically turbid systems such as metal pastes and carbon slurries, we have developed ultrasound scattering techniques to investigate the structures and dynamics of microparticles. In our previous studies, the hierarchical structures and dynamics of the ionomer coated carbon black particles was investigated<sup>[1]</sup>. Electrophoresis of the particles was also explored recently.

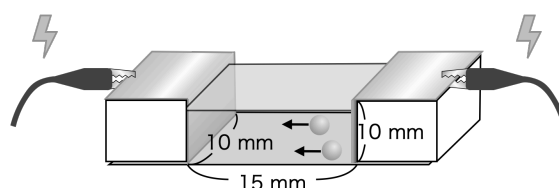
Carbon particles do not exist as independent nanoparticles but as aggregates in water or alcohol solution even in the presence of ionomer. Therefore, the role of ionomer on the dynamics was not clear because of the complicated structure. In this study, we investigated the dependence of the electrophoretic dynamics on the concentration of ionomer using simple model systems by the Electrophoretic dynamic ultraSound Scattering (ESS) technique.

## 2. Experimental section

### 2.1 Sample

Polydivinylbenzene (PDVB) with the diameter 5  $\mu\text{m}$  was purchased from Sekisui Chemical Co., Ltd., Japan. Silica particle 2.5  $\mu\text{m}$  was purchased from Nippon Shokubai Co., Ltd., Japan. The surface of silica particle was chemically modified by a silane-coupling reaction using methoxytrimethylsilane to obtain the partially hydrophobic surface<sup>[2]</sup>. These particles were dispersed in an aqueous solution of Nafion, DE2020 purchased from Wako Chemical (Japan). The concentration of particles was 1wt% and Nafion concentration was varied in range 0.0001 - 4wt%. These suspensions were sonicated for 30 seconds to disperse uniformly.

### 2.2 Electrophoretic dynamic ultrasound scattering (ESS)

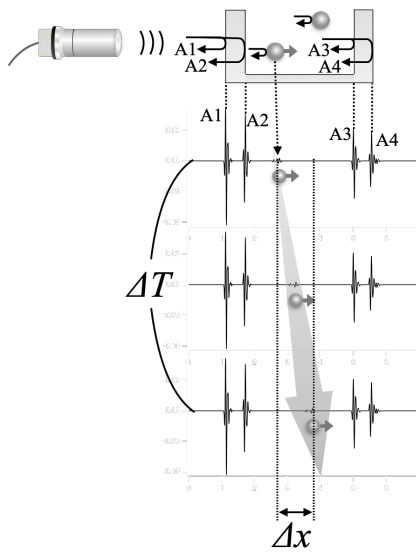


**Fig. 1** Schematic illustration of the sample cell of the ESS measurement.

A spike pulse emitted from BLP12R remote pulser (iSL, Japan) was transferred to a 20 MHz longitudinal plane wave transducer (KKG, Japan) immersed in a water bath to generate ultrasound pulses. The back scattered signals were received by the same transducer, followed by successive recording with a CSE1622 high-speed digitizer (Gage, DynamicSignals LLC, Canada). Such scattering signals were repetitively recorded 10,000 times at a constant time interval (10 ms) of during the particle motion. **Fig. 1** shows the schematic illustration of the sample cell of the ESS measurement with the dimension  $15 \times 10 \times 10 \text{ mm}^3$ . Two platinum electrodes were fixed parallel to the cell wall. Arbitrary wave generator (Keysight Technologies, 33500B) produced a sine waveform with an amplitude of 1 V and a period of two seconds. This sinusoidal waveform was amplified 50 times by a high-speed high-voltage amplifier (9100A, Tabor, Israel) to produce 50 V of the applied voltage.

When the ultrasound pulse wave is irradiated onto the sample cell, four reflected echoes from the cell wall were observed (**Fig.2**). For particle suspensions, scattering signals are observed between A2 and A3. The position,  $x$  of the particles in the suspension is obtained by the ultrasound scattering analysis as a function of the observation time,  $T$ . Then, the electrophoretic velocity of particles,  $V$  can be calculated from  $\Delta x$  and  $\Delta T$  by repetitively emitting ultrasound pulse<sup>[3]</sup>. The electrophoretic mobility,  $\mu$  is expressed as follows:

$$\mu \equiv \frac{V}{E} \quad (1)$$



**Fig. 2** Schematic illustration of the four reflected echoes observed by ultrasound measurement.

where  $E$  is the applied electric field.

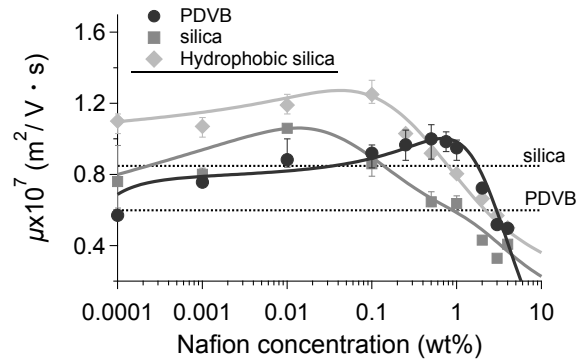
Particles coated with a layer of polyelectrolytes are called soft particles and the theory of electrophoresis was developed by Ohshima<sup>[4]</sup>. According to this theory,  $\mu$  is given by,

$$\mu = \frac{\epsilon_r \epsilon_0 \psi_0 / \kappa_m + \psi_{\text{DON}} / \lambda}{\eta (1/\kappa_m + 1/\lambda)} + \frac{ZeN}{\eta \lambda^2}. \quad (2)$$

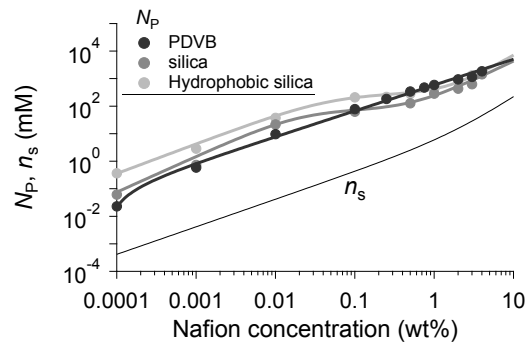
The readers should refer to the detail of the theory as well as the definition of symbols. The important parameters used in this study are the viscosity  $\eta$  and number density of polyelectrolyte  $N$ . In order to evaluate the concentration of ionomer surrounding the particle, the parameter  $N$  was determined from  $\mu$  obtained by the ESS measurement.

### 3. Results

**Fig. 3** shows the Nafion concentration dependences of  $\mu$ .  $\mu$  increased with the Nafion concentration, followed by decrease regardless of the type of particle. However, the peak concentrations differed depending on the hydrophobicity of particle. The Nafion concentration dependences of  $N_p$  calculated by the theory were shown in **Fig. 4**. Here,  $N_p (= N/1000N_A, N_A : \text{Avogadro constant})$  is the concentration of polyelectrolyte surrounding the particle. In addition, the salt concentration of solvent,  $n_s$  obtained by the conductivity measurements was plotted in the figure. While  $\mu$  exhibited a peak,  $N_p$  systematically increased. The level-off of  $N_p$  and decrease in  $\mu$  occurred simultaneously at the specific Nafion concentration. These results suggest that the decrease in  $\mu$  is due to increase in the viscosity of solvent and increase in  $n_s$ . The maximum locations of the Nafion concentration of the silica particle were much lower than that of the PDVB particle. This suggests that the amount of Nafion surrounding the



**Fig. 3** The Nafion concentration dependences of  $\mu$  obtained for the PDVB and silica particles (markers). The solid and dashed lines respectively indicate the theoretical curve and the experimental data without Nafion.



**Fig. 4** The Nafion concentration dependences of the  $N_p$  and  $n_s$  obtained for PDVB and silica particles.

particle was on the order PDVB > hydrophobic silica > Silica.

### 4. Conclusions

The electrophoretic mobility of the silica and the PDVB particles in the presence of Nafion was investigated by the ESS method. It was found that the  $\mu$  increased with the Nafion concentration due to adsorption, followed by decrease due to the viscosity and the electrostatic screening. The peak location was found to be depended on the hydrophobicity of the particle.

### References

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