

Studies on ionomer stabilized carbon black suspensions by ultrasound scattering techniques with core-shell model

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1. Introduction

The chemical and kinetic stability of the particles in suspension is one of the key factors in controlling the function of the material, e.g., electrode performance in fuel cells. Here, in the case of platinum-loaded carbon black (CB) particles as an electrode catalyst, polyelectrolytes called ionomer are often added to improve dispersibility. Particularly, since the ionomer plays a role of proton conduction, a percolation channel of the ionomers is also important.¹⁾ So far, microstructures of ionomer coated CB particles has been investigated in catalyst ink by light²⁾ and x-ray³⁾ and neutron scattering⁴⁾ methods. Contrast-variation small-angle neutron scattering method allowed one to identify the microstructure of CB core coated with ionomers in the concentrated suspensions.⁴⁾ On the other hand, the structural analysis is limited to about 100 nm at the most due to these wavelength limitations.

In our laboratory, ultrasound scattering methods in the MHz range have been developed to investigate a wide range of hierarchical aggregation structures from nano to micrometers.⁵⁾ However, the analysis of CB coated with ionomer has not been accomplished. Therefore, the purposes of this studies are (1) to examine the ionomer coating using a core-shell model by the ultrasonic spectroscopy method and (2) to obtain dynamic information about coating investigated from particle mobility by applying electric field (Fig. 1).

2. Experimental Section

2.1. Sample preparation

Two types of CB were used: Acetylene black (AB) purchased from Sterm Chemical (USA) and Vulcan XC-72 purchased from Fuel Cell store (USA). Nafion ionomer solution (DE2020) was purchased from Wako Chemical (Japan). 20% Nafion solution was diluted in a mixture of 84% distilled water, 8% ethanol, and 8% 1-propanol. The CB concentration is adjusted 1.0wt%, and the ink was treated by bath sonication for 5 minutes and ultrasonic homogenizer for 30 minutes. The ink was deforming with a spinning/rotating mixer (Awatori Rentaro, Thinky, Japan) at 1000 rpm for 1 minute.

2.2. Ultrasonic spectroscopy (US) method

The ultrasound attenuation coefficient and the phase velocity of the ink was investigated by the US method. A 20 MHz longitudinal transducer (K GK,

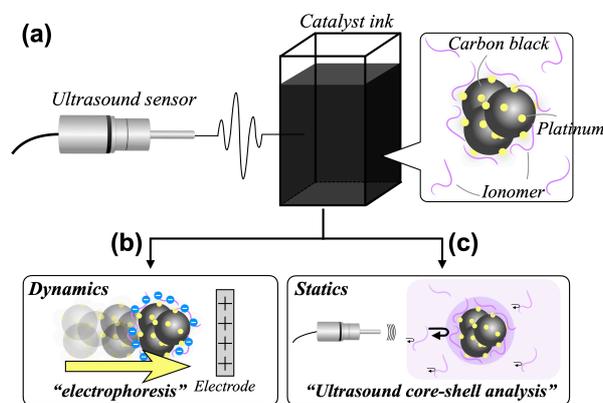


Fig. 1 Schematics of (a) ultrasound scattering analysis of CB particle suspension and (b) electrophoresis of ionomer stabilized CB particles and (c) scattering analysis with a core shell model.

Japan) was excited using spike pulse emitted from a DPR500 pulser (JSR, Japan) or BLP12R remote pulser (iSL, Japan) to generate ultrasonic pulses. A sample cell containing the CB ink was placed between the two ultrasound transducers, and transmitted pulses were recorded with a high-speed digitizer (GaGe, DynamicSignals LLC, Canada) with 200 Ms/s, and 12 bit vertical bit-depth. The voltage waveforms were recorded 5,000 times at a constant time interval of 0.5 ms. The ultrasonic attenuation coefficient and phase velocity were respectively calculated by the amplitudes and phases of the pulses obtained for the sample and pure water.

2.3. Electrophoretic ultrasound scattering (ESS)

The electrophoretic velocities of the CB under electric field were examined by the ESS method. The ESS method is acoustic analogue of electrophoretic light scattering method. A 30 MHz longitudinal transducer was used. The back scattered signals were repetitively recorded 10,000 times at a constant time interval of 10 ms. A sinusoidal or squared AC voltage of 30-50 Vp.p. and the period of 5-20 second depending on the sample characteristics was applied to two platinum electrodes. When the CBs exhibit electrophoresis, the scattered amplitude varies with the observation time. The autocorrelation function was calculated to analyze the electrophoretic velocity.

3. Results

Fig. 2 shows the Nafion concentration dependence of electrophoretic mobility μ of 1wt% CB particles obtained by the ESS measurements. The values of μ increased with the Nafion concentration, followed by decrease regardless of the

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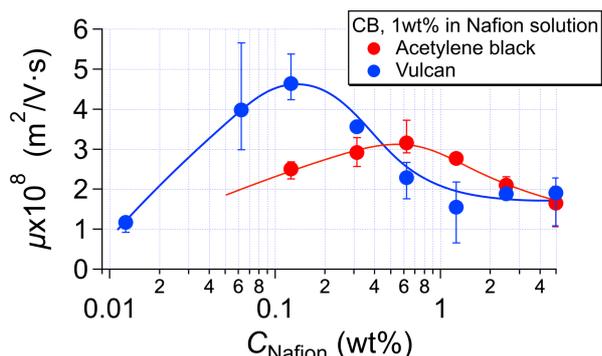


Fig. 2 The Nafion concentration dependences of μ of 1wt% CB particles obtained by the ESS method. The solid lines are guided for eye.

type of the CB. Since Nafion existing in continuous phase screens the charge of particle surface, μ may decrease with the Nafion concentration unless Nafion covers the particles. Conversely, increase in μ implied that the CBs are coated with Nafion. The appearance of a peak in electrophoretic mobility is due to the maximum amount of Nafion that can coat the CB, and any Nafion above this amount is considered to behave as ions in the continuous phase, resulting in a decrease in μ due to the increase in viscosity of the solvent. The peak concentration of AB was higher than that of Vulcan. Although not shown here, a comparison was made between hydrophilic silica particles and hydrophobic polystyrene-based particles, the peak of μ appeared at lower Nafion concentration for the silica particles. Since Nafion is known as a polymer with a fluorinated backbone and ionic side chains, it is likely that this is because the hydrophobic particle surfaces are covered with a greater amount of ionomer. Therefore, the ESS measurement suggests that the ionomer coverage of AB is considered to be higher than that of Vulcan at high Nafion concentrations.

Fig. 3 shows the frequency dependences of the phase velocity, c of the Vulcan suspensions obtained by the US measurement. The solid lines are the prediction by the core-shell model⁶⁾ assuming that the coated Nafion layer exists uniformly surrounding the CB core. As the carbon is coated with ionomer, the Nafion concentration near the CB particle locally increases, and the concentration of Nafion in the continuous phase may decrease. Then, if the sound velocity of the continuous phase can be evaluated, the amount of ionomer coating the CB can be evaluated by comparing it with the sound velocity of the Nafion solution measured in advance. As shown in Fig. 3, the core-shell theoretical analysis, which takes into account the reduced Nafion concentration in continuous phase, confirmed a better agreement with the experimental spectrum than the rigid sphere model. Although not shown here due to space limitation, the concentration of Nafion coated CB

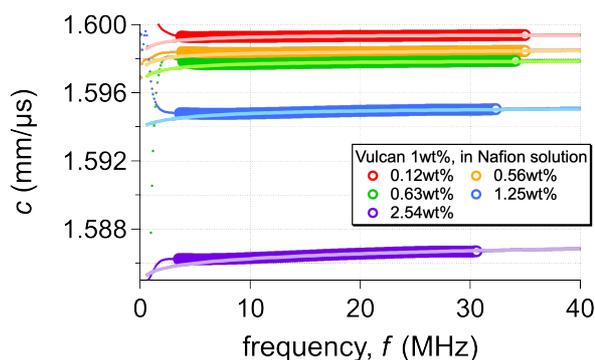


Fig. 3 The frequency dependence of the phase velocity of 1wt% Vulcan suspensions obtained by the US method. The markers are experimental results and the solid lines are theoretical prediction of the core-shell model.⁶⁾

obtained by the core-shell analysis had a trend that Vulcan is coated more effectively with smaller amounts of Nafion compared to AB, and this trend was consistent with the ESS results.

4. Conclusions

The concentration of ionomer coated on the CB particles was determined by ultrasonic spectroscopy (US) method and electrophoretic ultrasound scattering (ESS) method. The electrophoretic mobility, μ of the CB increased with the Nafion concentration, indicating that the CBs were successfully coated with Nafion. The peak concentration of Acetylene black (AB) was higher than that of Vulcan, suggesting that the amount of ionomer coated on AB was higher than that of Vulcan at high Nafion concentrations. The US results of the CB suspensions were compared with the theory of ultrasound scattering with a core-shell model. Considering the decrease in the Nafion concentration in the continuous phase, the concentrations of Nafion coated on CB were determined. There was a consistent trend for Vulcan to coat more effectively with smaller amounts of Nafion compared to AB. Thus, the combination of the US and the ESS methods provided a new insight into more effective ionomer coating of the two types of CBs.

References

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