Observation of Ionic Liquid by Scanning Electron Microscope

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It has been discovered that ionic liquid can be observed by a scanning electron microscope without accumulation of electron charges, allowing SEM observation of insulating specimens wetted with ionic liquid.

Ionic liquid composed solely of ions possesses attractive features such as no vapor pressure, high ionic conductivity, non-combustibility, and capability to dissolve many kinds of substances.[1–4] Such features urge researchers to utilize this material as a new solvent in several fields; environmentally friendly organic synthesis,[5–10] non-volatile electrolyte,[11–22] and so on. In addition to application study with use of commercially available ionic liquids, development of new ionic liquids and search of further abilities are intensively studied. Here, we report shortly the discovery that ionic liquids can be observed by a scanning electron microscope (SEM) without accumulation of electron charges, indicating that the liquid behaves as an electronically conducting material. This finding should allow use of ionic liquid as a material for supplying electronic conductivity to insulating specimens in place of carbon or metal coating.

Observation of ionic liquid by a scanning electron microscope (SEM: Keyence VE-8800) was made using 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6, Aldrich) with a relatively high viscosity. The liquid was heated at 105 °C under vacuum for 3 h prior to use for removing dissolved water. The SEM images taken by electron beam with acceleration voltage of 20 keV are shown in Figure 1. In the picture of Figure 1a, a part of a large drop (lower part) and some small drops are seen. Each drop exhibits bright edge and dark portion in the middle, indicating no accumulation of electron charges in the liquid with emission of secondary electrons. Similar SEM observation was also successfully performed for other ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF_4), trimethyl-*n*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI), BMI-BF_4, EMI-TFSI, and BMI-TFSI. Observation of an insulating oil drop having very low vapor pressure was also attempted but it gave a white image with large noise due to accumulation of electron charges even if the accelerated voltage was reduced to 1 keV.

Electrons in ionic liquid have been studied by fast pulse radiolysis experiments using methyltributylammonium-TFSI.[23] It generates solvated electrons having a lifetime of 300 ns when 8.7 MeV electron pulse were injected. The SEM observation of the ionic liquids were attempted by changing acceleration voltage, and clear images were obtained for all the liquids even when the voltage was decreased to 1 keV, suggesting that such the low energy is sufficient for injecting electrons in the ionic liquids.

It is noteworthy that the middle portion of each drop is darker than the Al sample stage. The secondary electrons are generated by excitation of electrons in atoms on the surface of a specimen. The flux of the electron which determines brightness of the image increases with the atomic weight in the case of solid samples.[24] In the ionic liquid phosphorous has the highest atomic weight (30.97), which is higher than that of Al (26.98). However, the image of the ionic liquid is darker than that of Al. This should be due to the low density of phosphorous in the liquid. High brightness of each liquid drop is due to the effect by inclination of the sample surface.[24] When an angle of electron beam incidence decreases, depth of the area from surface where secondary

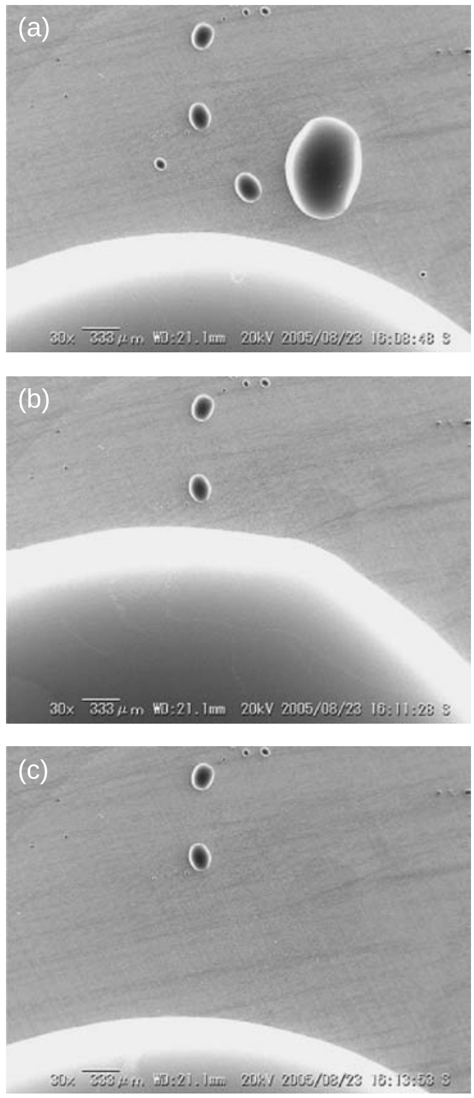

Figure 1. a) SEM image of drops of ionic liquid BMI-PF6. (b) Image after tilting the sample stage at around 10° and (c) after inversely tilting the sample stage to initial position.

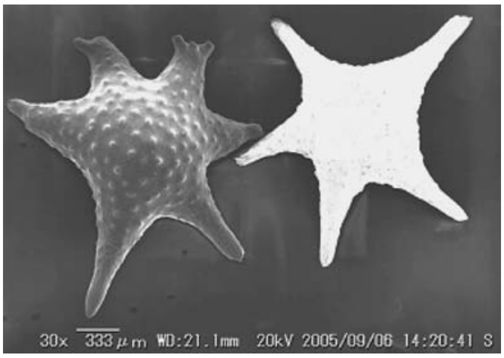

Figure 2. SEM image of two grains of star sand. Left grain was dipped in EMI-TFSI and right one was subject to no treatment before observation.

electrons are generated becomes shallow, causing the increase in the emission of secondary electrons.

Tilting the sample stage at around 10° moved the large drop toward upper of the image, whereas small drops were staying at the same position. As a result, the large drop swallowed up the small drops as shown in Figure 1b. When the sample stage was inversely tilted, swallowed drops were washed away like beach after seawater drawing back, as shown in Figure 1c. The series of images indicates clearly that the ionic liquid keeps liquid state without evaporation under the conditions for SEM observation.

Diffusion of electrons in the ionic liquid has been also confirmed by a transmission electron microscope (TEM). Observation of a carbon-coated microgrid on which ionic liquid was spread gave a clear grid image. However, resolution became low as amount (thickness) of the liquid increased probably due to the scattering of electron beam by the liquid.

The fact that the ionic liquid behaves as an electronically conducting material under the conditions for SEM observation allows us to think of several ideas. One of them is the use of the liquid in place of metal or carbon coating to put conductivity to insulating specimens. Figure 2 shows SEM image of star sands that are shells of a kind of foraminifer. Because the shell is porous, it absorbs ionic liquid of low viscosity. The left star sand in Figure 2 was dipped in EMI-TFSI, followed by removing excess liquid. The right one was subjected to no treatment. They were put on the sample stage using a conducting double-faced adhesive tape. As recognized, the left sand gives clear image in which details of its surface can be recognized, whereas the right one gives white image due to accumulation of electron charges. The difference became distinct by raising magnification.

The results shown in Figure 2 indicate important significance that wet sample can be observed by the electron microscope. There are many materials whose morphology is varied by drying like tissue, living cell, and gel materials. To observe them with wet conditions, some techniques like use of low vacuum SEM are needed with sacrifices of resolution. If replacing water in those materials with one of the ionic liquids did not make significant change in the morphology, we could observe their real figure by an ordinary SEM or TEM with high resolution. Furthermore, it would be possible to observe several chemical reactions including generation and growth of nanomaterials. Investigation of such the application and other utilization is underway.

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