Perfect Composition Depth Profiling of Ionic Liquid Surfaces Using High-resolution RBS/ERDA

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In order to reveal the surface structures of large molecular ionic liquids (ILs), the near-surface elemental depth distributions of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([CnC1Im][Tf2N], n = 2, 6, 10) were studied using high-resolution Rutherford backscattering spectroscopy (HRBS) in combination with high-resolution elastic recoil detection analysis (HR-ERDA). The elemental depth profiles of all constituent elements, including hydrogen, were derived from HR-ERDA/HRBS measurements, so that the profiles would reproduce both HR-ERDA and HRBS spectra simultaneously. The derived elemental depth profiles agree with state-of-the-art molecular dynamics simulations, indicating the feasibility of this method. A controversy concerning the preferential orientation of [C2C1Im] at the surface has been resolved by this new combination analysis; namely, the [C2C1Im] cation has a preferential orientation with the ethyl chain pointing towards the vacuum in the topmost molecular layer.

Keywords Surface structure, ionic liquid, hydrogen, ERDA, RBS

(Received June 9, 2016; Accepted July 6, 2016; Published October 10, 2016)

Introduction

Although hydrogen is the most abundant element in the universe, most of the conventional analytical techniques cannot detect hydrogen at all. Only a limited number of techniques, such as secondary ion mass spectrometry (SIMS), nuclear reaction analysis (NRA), elastic recoil detection analysis (ERDA), can analyze hydrogen. However, even if these techniques are employed, precise hydrogen analysis is still difficult. It is known that the quantification of SIMS is problematic due to a lack of knowledge concerning ionization probability. SIMS also suffers from the so-called surface transient effect, which makes precise surface analysis difficult. Although NRA and ERDA can analyze hydrogen quantitatively, the typical depth resolution of NRA and conventional ERDA is not better than a few nm. The depth resolution of ERDA can be improved to sub nm by employing a high-resolution energy spectrometer, which is called high-resolution ERDA (HR-ERDA). As shown below, however, information concerning other elements is necessary for precise hydrogen analysis in ERDA. Figure 1 shows a simulated ERDA spectrum for Au(1.7 nm)/Si containing hydrogen of 0.1 at.% through the whole sample, i.e. both the Au layer and the Si substrate contain 0.1 at.% hydrogen. Although the hydrogen concentration is constant throughout the whole sample, there is a step-like structure at the Au/Si interface (at ~98 keV) due to differences in stopping power (S) and atomic density (N) between Au and Si. The height of the ERDA spectrum is roughly proportional to N/S. Because N/S for Au is about two-thirds of that for Si in the present case, there appears to be a step-like structure at the Au/Si interface (at ~98 keV), although the hydrogen concentration is constant through the whole sample. This clearly demonstrates that precise hydrogen depth profiles cannot be derived solely from ERDA.
measurements unless the depth profiles of other elements, which determine the stopping power, are known. In this respect, ERDA should be combined with other techniques that can analyze other elements than hydrogen.

There is a complementary technique, high-resolution Rutherford backscattering spectroscopy (HRBS), that allows quantitative analysis of the surface composition, except for hydrogen with a sub nm depth resolution. Properly speaking, precise elemental depth profiles cannot be obtained solely by HRBS, even for the elements other than hydrogen. This is because information concerning hydrogen profile is needed to accurately calculate the stopping power. This is a similar situation in that HR-ERDA cannot provide precise hydrogen profile without information about other elements. In this respect, HR-ERDA and HRBS are really complementary techniques. By combining these two techniques (HR-ERDA and HRBS), the quantitative analysis of all elements can be performed with high precision. It is noteworthy that both HR-ERDA and HRBS can be performed with the same equipment, which is an additional advantage of this combination analysis.

In the present paper, the feasibility of this novel combination analysis is examined by analyzing the surface compositions of typical ionic liquids (ILs), 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([CₙC₃Im][Tf₂N], n = 2, 6, 10, see Fig. 2). ILs are promising materials for a wide range of applications, such as electrolytes for energy-storage devices,7 heterogeneous catalysis8 and gas capture/separation media.9,10 In these applications, the measurement and control of the surface adsorption sites is crucial. In this respect, hydrogen is a key element because of its important role in hydrogen bonding. There have been a number of studies on the surface structures of ILs containing [CₙC₃Im] cations,11,12 A consensus has now been established that the alkyl chains of [CₙC₃Im] cations are pointing towards the vacuum in the topmost molecular layer for n ≥ 4.11,12 Concerning the shorter alkyl chains, however, there is still a controversy. While molecular dynamics (MD) simulations13 and sum-frequency generation (SFG) spectroscopy14 have shown that [CₙC₃Im] cations have a preferential orientation with the ethyl chain pointing towards the vacuum, angle resolved x-ray photoelectron spectroscopy (AR-XPS) has shown that there is no preferential orientation.22 The present combination analysis provides a useful insight into the surface structure of these ILs, and may resolve this controversy.

Experimental

The ILs used in this study were purchased from Kanto Reagent (Japan) and measured using HRBS and HR-ERDA without further purification. The surface of the IL was prepared by a rotating wheel system (diameter, 38 mm) installed in an ultrahigh vacuum (UHV) chamber.23 This system continuously provides a clean surface that allows for damage-free measurements. The details concerning the equipment of HRBS were described elsewhere.6,23 We also used the same equipment for HR-ERDA. In HR-ERDA measurements, a beam of 200 keV He⁺ ions was produced by a Cockcroft Walton type accelerator. The produced ion beam was mass analyzed by a dipole magnet. The selected He⁺ beam was collimated to 2 × 2 mm² by two sets of a rectangular-shaped slit system, and sent to the UHV scattering chamber via a differential pumping system. The typical beam current was about 30 nA and the base pressure of the UHV chamber was 1 × 10⁻⁹ Pa. The H⁺ ions recoiled from the sample at 25° were measured by a magnetic spectrometer.

The same ionic liquids were measured by HRBS using a 400-keV He⁺ ion beam. The results of HRBS measurements were already published in our previous papers.17,24 In the present paper, we re-analyze the HRBS spectra together with the HR-ERDA spectra.

Results and Discussion

Figure 3 shows the HR-ERDA spectra of [C₆C₃Im][Tf₂N] observed at incident angles θ₁ = 20° (open circles) and 22° (closed circles). The depth scale for θ₁ = 20° and 22° were calculated using a bulk density, and are shown in the upper abscissa and in the lower part, respectively. The dashed lines show the simulated spectra for a uniform and stoichiometric composition. The solid lines show the spectra simulated with the elemental depth profiles derived through the combination analysis.
be converted to the depth scale using the stopping powers. The stopping powers were estimated by the SRIM code using the bulk densities (1.52, 1.37 and 1.28 g/cm³ for [C₆C₆Im][Tf₂N], [C₆C₆Im][Tf₂N] and [C₆C₆Im][Tf₂N], respectively). The converted depth scales for θ = 20° and 22° are shown in the upper abscissa and in the lower part of Fig. 3, respectively. Because these two measurements were done at grazing exit angles (5° and 3° measured from the surface plane), the converted depth scales and the signal intensities of these two spectra greatly differ from each other. Note that these depth scales may not be accurate because the actual stopping power depends on the composition, which may deviate from the bulk composition in the surface region. The spectra simulated for a uniform stoichiometric composition are shown by dashed lines.

In the spectrum simulation, the trajectories of the incident He ions and the recoiled hydrogen ions are assumed to be straight lines, and the energy loss straggling of both ions are calculated using a semi-empirical formula given by Yang et al. Although the simulated spectra have no structure, the measured spectra have a peak at ~105.2 keV, which corresponds to ~0.3 nm. This suggests that the hydrogen concentration is enhanced near the surface. However, such a surface peak might result from a non-uniform distribution of other elements, as discussed above.

The same sample, [C₆C₆Im][Tf₂N], was characterized by HRBS. The observed HRBS spectrum is shown by black circles in Fig. 4. Note that the scattering angle, larger than 90°, is usually used in the conventional RBS to achieve better separation of constituent elements in the observed spectrum. In HRBS, however, a large scattering angle is not necessary for better elemental separation because of its excellent energy resolution. Therefore, we chose a scattering angle of 50°, which allows for a short measurement time due to larger scattering cross sections, while keeping a reasonably good separation of the elements. The dashed line shows the HRBS spectrum simulated for a uniform stoichiometric composition. Although the simulated spectrum roughly reproduces the observed spectrum, there are some discrepancies at the leading edges of the elements. This indicates that the elemental depth profiles deviate from the uniform stoichiometric composition at the surface. Such deviations might lead to an artificial hydrogen peak at the surface in the ERDA spectrum. In order to see if the observed hydrogen peak is artificial or not, the elemental depth profiles were derived from the HR-ERDA and HRBS spectra so that the profiles would reproduce both the HR-ERDA and HRBS spectra in parallel. The result is shown by the histograms in Fig. 5. It should be noted that both RBS and ERDA analysis provide the depth scale in units of the areal density of atoms (e.g. atoms/cm²). This depth scale can be converted into “nm” using a bulk density of IL, as is shown in the upper abscissa. This scale in nm is just a rough estimate because the atomic density might be different from the bulk density in the surface region. The spectra simulated with the determined depth profiles are shown by solid lines in Figs. 3 and 4. The agreement between the simulated and observed spectra is very good for both HR-ERDA and HRBS, indicating the consistency of the derived depth profiles.

The surface structure of [C₆C₆Im][Tf₂N] has also been studied by MD simulations. The elemental depth profiles calculated by the MD simulations were convoluted with a Gauss function that represents the effect of capillary waves. The convoluted profiles are shown by thick solid lines in Fig. 5. The agreement with the depth profiles derived by the present combination analysis is almost perfect. This further confirms the reliability of the present combination analysis. The present result shows a surface enrichment of carbon and a surface depletion of nitrogen. Because carbon is one of the representative elements of the hexyl chain and nitrogen is that of the imidazolium ring, these observations indicate that the [C₆C₆Im] cation has a preferential orientation with a hexyl chain pointing towards the vacuum. Although this was already pointed out in our previous HRBS study, the preferential orientation of [C₆C₆Im] can be concluded with confidence by considering the hydrogen profile. The ratio of the hydrogen-to-carbon concentration is shown by a dashed line in Fig. 5. The H/C ratio is ~1.8 at the surface, and decreases to ~1.6 with depth. Considering that the H/C ratio in the hexyl chain is 2.17 (~13/6) and the average H/C ratio in the whole IL is 1.58 (~19/12),
the present result clearly indicates that the hexyl chains are enriched in the surface region. This preferential orientation was also observed using various experimental techniques, such as SFG,14 AR-XPS15,16 and neutral impact collision ion scattering spectroscopy (NICISS)18 as well as MD simulations.20

Similar combination analyses were also performed for \([C_2C_1Im][Tf_2N]\) and \([C_{10}C_1Im][Tf_2N]\). The observed HR-ERDA spectra are shown in Figs. 6 and 7 for \([C_2C_1Im][Tf_2N]\) and \([C_{10}C_1Im][Tf_2N]\), respectively. The spectra simulated for uniform stoichiometric compositions are shown by dashed lines. Although the simulated spectra have no structure, the measured spectra have a surface peak similarly to \([C_6C_1Im][Tf_2N]\). The observed surface hydrogen peak for \([C_2C_1Im][Tf_2N]\) is very small, while the surface peak for \([C_{10}C_1Im][Tf_2N]\) is much pronounced, and there is a dip at a depth \(\sim 1.3\) nm. The observed HRBS spectra are shown by red triangles and blue squares for \([C_2C_1Im][Tf_2N]\) and \([C_{10}C_1Im][Tf_2N]\), respectively, in Fig. 4. The dashed lines show the HRBS spectra simulated for uniform stoichiometric compositions. The agreement is roughly good, but again there are discrepancies at the leading edges of the elements, indicating that the elemental depth profiles deviate from the uniform stoichiometric composition at the surface. The elemental depth profiles were derived from the HR-ERDA and HRBS spectra, so that the profiles reproduce both HR-ERDA and HRBS spectra. The results are shown by histograms in Figs. 8 and 9 for \([C_2C_1Im][Tf_2N]\) and \([C_{10}C_1Im][Tf_2N]\), respectively. The spectra simulated with the determined depth profiles are shown by solid lines in Figs. 4, 6 and 7. The agreement between the simulated and observed spectra is very good for both HR-ERDA and HRBS, indicating that the derived depth profiles are accurate.

The preferential orientation of \([C_{10}C_1Im]\) cations can be deduced from the derived elemental depth profiles (Fig. 9). Both hydrogen and carbon profiles have a surface peak and a shallow dip at \(\sim 1.2\) nm. On the other hand, there is surface depletion of nitrogen, and the nitrogen profile has a peak at \(\sim 1.1\) nm. These results indicate that the decyl chains protrude to the vacuum. The surface enrichment is more clearly seen in the hydrogen profile compared to the carbon profile. This is because the decyl chain contains 78% of hydrogen in this IL while it contains only 63% of carbon. This demonstrates that the hydrogen profile is more useful for the determination of the preferential orientation of \([C_{10}C_1Im]\).

Concerning \([C_6C_1Im][Tf_2N]\), the fluorine profile has a large peak at the surface and a dip at \(\sim 0.5\) nm, while the sulfur, oxygen and nitrogen profiles show surface depletion and a weak...
broad peak at ~0.5 nm (see Fig. 8). This indicates that the [Tf$_2$N] anion has a preferential orientation with the CF$_3$ moieties pointing toward the vacuum. On the other hand, the carbon profile has a broad peak at ~0.4 nm, where the nitrogen profile also has a broad peak. This suggests that the [C$_6$C$_1$Im] cation has no preferential orientation. A close inspection, however, shows that the hydrogen profile has a peak at the surface. Because hydrogen is a good representative element of the ethyl chain (45% of hydrogen atoms are in the ethyl chains), this surface hydrogen peak indicates that the ethyl chains protrude into the vacuum.

In order to confirm this conclusion we performed MD simulations on [C$_6$C$_1$Im][Tf$_2$N] in contact with a vacuum using the program DL_POLY 2.20 with a force field having the CHARMM functional form and with the partial charges based on quantum calculations for isolated ion pairs. The total charge on cations and anions is around +0.96 e and ~0.96 e, respectively, which somewhat mimics the anion to cation charge transfer and many-body effects. The details of the MD simulation are described elsewhere. We used 512 ion pairs and a simulation box of $5.98 \times 5.98 \times 16$ nm$^3$. The elemental depth profiles calculated by the MD simulation were convoluted with a Gauss function to take account of the effect of capillary waves; the results are shown by thick lines in Fig. 8. The MD simulation reproduces the observed profiles very well, especially the small structures seen in the hydrogen and carbon profiles. From the trajectories of MD simulations for [C$_6$C$_1$Im][Tf$_2$N], we evaluated the density variations of the ring center-of-mass (COM) and terminal C atom of the ethyl chain as a function of the position from the surface (Fig. 10a). The orientation of the ethyl chain was also evaluated, and is shown in Fig. 10b. Figures 10a and 10b also display the analogous results for [C$_6$C$_1$Im] for the sake of comparison. The orientation of the alkyl chains was characterized by the tilt angle $\theta$ between the surface normal and vector pointing from the ring nitrogen to terminal C atom of the chain as shown in the inset of Fig. 10b. As can be seen in Fig. 10a, the outermost peak in the density of the terminal C atom occurs further in the vacuum with respect to the outermost peak in the density of the ring COM, indicating the cation chains point into the vacuum. From Fig. 10b, it is evident that the alkyl chains are pointing towards the vacuum in the topmost molecular layer ($<\cos \theta> \sim 0.7$), and that there is no preferential orientation on the deeper layers. Thus, the MD simulation confirms the preferential orientation of the [C$_6$C$_1$Im] cation determined by the present combination analysis.

It should be noted that there was a MD simulation study about the surface structure of [C$_6$C$_1$Im][NO$_3$], and it was already concluded that the ethyl chains protrude to the vacuum. However, it is known that the orientation of the alkyl chains is affected by the size of the anion. The larger anions reduce the degree of the preferential orientation of alkyl chains. Because the degree of the preferential orientation of shorter alkyl chains is weaker than those of longer alkyl chains the orientation of shorter alkyl chains are more seriously affected by the size of anion. Therefore, we performed a new MD simulation on [C$_6$C$_1$Im][Tf$_2$N] to support the present combination analysis. Although the preferential orientation of [C$_6$C$_1$Im] derived in this work is in agreement with the previous MD simulations and SFG measurements, AR-XPS has shown no preferential orientation. This may be attributed to the relatively poor depth resolution of AR-XPS. A typical escape depth of photoelectrons in ILs is several nm, which is several times larger than the thickness of the molecular layer. Thus, AR-XPS measurements at grazing emission angles are necessary in order to obtain the information of the topmost molecular layer. At grazing emission angles, however, photoelectrons suffer from the effect of elastic scattering and the quantitative analysis is rather difficult in
Finally, we address other useful information obtained by the present combination analysis. Figure 11 shows the surface concentration of each element determined by the present combination analysis. Because these concentrations correspond to the topmost atomic layer, this is a measure of the probability of incoming gas-phase molecules hitting the particular element. Such information is important to understand the reactions of all constituent elements including hydrogen were derived from the concentration of each element determined by the present combination analysis. Figure 11 shows the surface profiles were compared with the MD simulations, and almost perfect agreement was found. This demonstrates the feasibility of the proposed combination analysis of HR-ERDA/HRBS. It was also found that the $[\text{C}_6\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ cation has a preferential orientation with the ethyl chain pointing towards the vacuum in the topmost molecular layer. The present combination analysis provides useful insights into the surface structures of ILs.

Conclusions

We have proposed a novel combination analysis of HR-ERDA and HRBS. The feasibility of this combination analysis was examined by measuring the surface structures of $[\text{C}_6\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ and $[\text{C}_5\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ the incoming molecules hit mainly hydrogen, carbon and fluorine with an almost equal probability, while one-third of them hit carbon and the rest of them hit almost exclusively hydrogen in the case of $[\text{C}_6\text{C}_1\text{Im}][\text{TF}_2\text{N}]$. Similar information may also be obtained by LEIS. However, due to a lack of information concerning hydrogen in LEIS, the obtained probability is a relative probability, even for elements other than hydrogen.

Acknowledgements

This research was partly supported by the Czech Science Foundation (Grant P208-16-12291S).

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