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Surface characterization of imidazolium ionic liquids by high-resolution Rutherford backscattering spectroscopy and X-ray photoelectron spectroscopy

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ABSTRACT

The surface composition of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF_6]) and 1-butyl-3-methylimidazolium dicyanamide ([BMIM] [DCA]) are studied by high-resolution Rutherford backscattering spectroscopy. Although [BMIM] [PF_6] is almost stoichiometric up to the topmost molecular layer, considerable deviation from the theoretical stoichiometry is observed for [BMIM] [DCA] in a surface layer of ~1.5 nm thickness. Nitrogen is almost completely depleted in this layer while carbon is enhanced. In addition, there are oxygen impurities of $\sim 3 \times 10^{14}$ atoms/cm^2 in this surface layer. With the help of X-ray photoelectron spectroscopy measurements it is concluded that the surface of [BMIM] [DCA] is covered by $\sim 1.7 \times 10^{14}$ molecules/cm^2 of esters and/or carboxylic acids. These contaminant molecules have a preferred orientation, i.e. the carbonyl groups are on the surface of [BMIM] [DCA] and the alkyl chains are pointing towards vacuum. The origin of the contamination layer could be the surface segregation of bulk impurities.

1. Introduction

Room-temperature ionic liquids (ILs) are thermally stable, nonvolatile, nonflammable solvents. Because of these excellent properties, they are attracting increasing attention. ILs have been studied as alternatives for traditional organic solvents in a wide variety of chemical reactions, separations, and manufacturing processes [1]. Other promising applications, such as electrodeposition [2–4], lithium ion batteries [5,6], capacitors [7,8], fuel cells [9,10], lubricants [11] have been also extensively studied. In these applications, surface and interface properties of ILs are often of prime importance. A variety of analytical techniques were employed to study the surface properties and structures of ILs. Similarly to the study of conventional liquids, X-ray and neutron reflectivity measurement (XR and NR) [12,13], sum frequency generation (SFG) [14–17] and grazing incidence X-ray diffraction [18] have been applied. Because of their extremely low vapor pressures, other surface analytical techniques requiring UHV conditions can also be applied for the study of ILs, such as X-ray photoelectron spectroscopy (XPS) [19–23,26], direct recoil spectroscopy (DRS) [24,25], low-energy ion scattering (LEIS) [20], metastable impact electron spectroscopy (MIES) [26], time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [19,27–29] and high-resolution electron energy loss spectroscopy (HREELS) [30]. As a result of these studies, a general consensus has been established that both cations and anions are sharing the surface almost equally. Concerning the orientation of the ions at the surface, imidazolium-based ILs show preferred orientation at the surface [16,17,21,23]. The aliphatic alkyl chains of the cations tend to protrude toward vacuum. It was also found that in some ILs, such as [EMIM][$EtSO_4$] [19] and [Me(EG) MIM] I [22], the surface was covered by a thin layer of hydrocarbon. The origin of these contamination layers were attributed to the surface segregation of minor impurities in ILs. Because these contamination layers affect seriously the surface properties, detailed information of the contamination layer is very important in the applications of ILs. Nevertheless, the detailed structure of the contamination layer has not been clarified yet. Even the most fundamental information, such as the thickness of the contamination layer, was not known because most of the above mentioned analytical techniques allow only qualitative or, at most, semi-quantitative analyzes.

Rutherford backscattering spectroscopy (RBS) is one of the most widely used technique for surface analysis [31]. It provides composition depth profiles with a depth resolution of ~10 nm. Because the quantification of RBS relies on the simple Rutherford cross section, RBS allows highly quantitative analysis. By employing high-resolution energy analyzer, the depth resolution can be improved up to ~0.2 nm. This technique is called high-resolution Rutherford backscattering spectroscopy (HRBS). Utilizing such an excellent depth resolution, it was demonstrated that single crystal surfaces can be analyzed in layer-by-layer mode [32].

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Recently, we have shown that HRBS can be successfully used to study surface structures of ILs [33,34]. We found that the surface is shared almost equally by the cations and anions and these cations and/or anions have preferred orientation at the surface. These studies demonstrate that HRBS is a useful technique to study the surface structures of ILs. There are, of course, some drawbacks in HRBS and its major drawback is the insensitivity to chemical states. In this respect, XPS could be a good complement to HRBS.

In the present paper, we show that the combination of HRBS and XPS is very powerful to study the surface structures of ILs. We observe the surfaces of two ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF_6]) and 1-butyl-3-methylimidazolium dicyanamide ([BMIM] [DCA]) using HRBS. The observed composition of [BMIM] [PF_6] is almost perfectly stoichiometeric up to the top most molecular layer, while large nitrogen depletion and carbon enrichment are observed at the surface of [BMIM] [DCA]. In addition oxygen impurity of $\sim 3 \times 10^{14}$ atoms/cm^2 is also observed in the sub-surface region of [BMIM] [DCA]. These findings show that the surface of [BMIM] [DCA], as delivered by the supplier, is covered by a thin contamination layer containing carbon and oxygen. With the help of XPS measurements, the structure of the surface contamination layer is discussed.

2. Experimental

The details of the HRBS measurement were described elsewhere [35]. Briefly, He^+ ions are produced by a Penning ion gauge type ion source and accelerated up to 400 keV by a Cockcroft Walton type accelerator. After mass separation by a 90° magnet, the He^+ beam was collimated to 2×2 mm^2 by two sets of 4-jaw slit system and sent to a UHV scattering chamber via a differential pumping system. The base pressure of the UHV chamber was 1×10^{-8} Pa. A typical beam current was about 50 nA and a typical measurement time is about 30 min in the present study.

The [BMIM] [PF_6] and [BMIM] [DCA] were purchased from Kanto Reagent (Japan) and used without further purification. It should be noted that the supplier suggests that there are possible impurities, halogenide (<1000 ppm) and water (<10,000 ppm), in [BMIM] [DCA]. A slowly rotating wheel (diameter 38 mm and rotation rate 6 rpm) was partially immersed in a reservoir of IL. When the wheel emerged from the reservoir the outermost layer of the IL was removed by a skimmer (a razor blade). Thus a thin fresh layer of IL having a clean surface was prepared. It was demonstrated that clean liquid surfaces were actually produced by the same method in the previous pioneering works [36,37]. This wheel system was mounted on a precision goniometer in the UHV scattering chamber. After loading the IL, the UHV chamber was pumped by a turbo-molecular pump. Although the required vacuum for HRBS measurement ($\sim 10^{-6}$ Pa) can be achieved after 1 h of pumping, the HRBS spectra shown in this paper were taken after more than 1 day of pumping (the pressure was better than 10^{-7} Pa) unless otherwise stated.

The wheel covered by IL was irradiated by the He^+ beam. The He ions scattered from IL at an scattering angle θ (50.6° for the measurement of [BMIM] [DCA] and 50.5° for [BMIM] [PF_6]) were energy analyzed by a 90° sector type magnetic spectrometer and detected by a one-dimensional position sensitive detector (1D-PSD) of 100 mm length (the energy window was 25% of the central energy). The non-uniformity of the efficiency of the 1D-PSD was carefully calibrated so that a precise composition analysis can be performed. The energy resolution of the spectrometer was about 0.1% at an acceptance angle of 0.3 msr.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS-165 system with a monochromated Al Kα X-ray source. A disk-shaped sample holder made of stainless steel was filled with ILs and kept for several hours in the UHV XPS chamber before measurements. The energy spectra of photoelectrons were observed at normal emission. The spectrometer pass energy was set to be 80 eV for the survey spectra and 20 eV for high resolution spectra.

3. Results and discussion

Fig. 1 shows an example of the HRBS spectrum of [BMIM] [PF_6] observed at an incident angle, $\theta_i = 44.5°$. The energies of He ions scattered from surface atoms are given by KE_0, where E_0 is the incident energy of He^+ ion and K is the so-called kinematic factor [31].

$$K = \left[\frac{(M_2^2 - M_1^2 \sin^2\theta)^{1/2} + M_1 \cos\theta}{M_1 + M_2}\right]^2, \quad (1)$$

where M_1 and M_2 are masses of the He ion and the target atom, respectively. The calculated energies for ^{31}P, ^{19}F, ^{14}N and ^{12}C are shown by the arrows in Fig. 1. These energies correspond to the surface positions for these elements. Using the stopping power of He

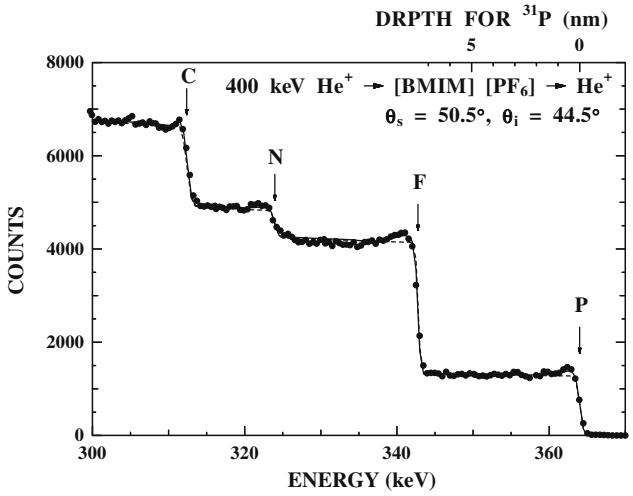

Fig. 1. HRBS spectra of [BMIM] [PF_6] observed at a scattering angle $\theta = 50.5°$. The incident energy was 400 keV and the incident angle was 44.5°. The dashed line shows the calculated spectrum for stoichiometric composition.

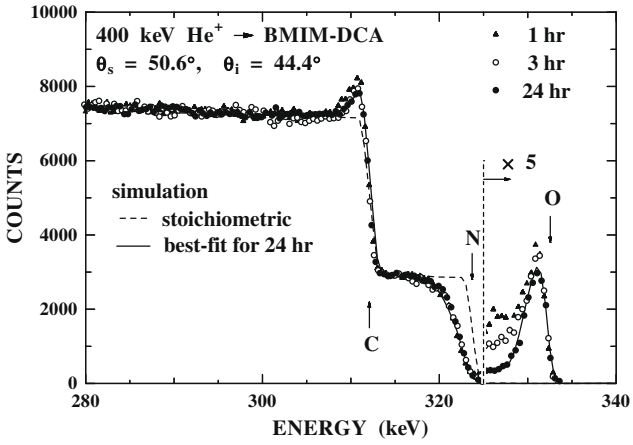

Fig. 2. HRBS spectra of [BMIM] [DCA] observed at a scattering angle $\theta = 50.6°$ after 1 h (solid triangle), 3 h (open circle) and 24 h (solid circle) of pumping. The incident energy was 400 keV and the incident angle was 44.4°. The dashed line shows the calculated spectrum for stoichiometric composition. The solid line shows the best-fit result for the observed spectrum after 24 h of pumping.