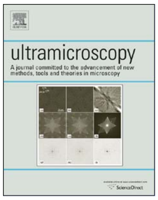
ARTICLE IN PRESS

Ultramicroscopy #vol# (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



Full lenght article

Fabrication of thin TEM sample of ionic liquid for high-resolution ELNES measurements

Tomohiro Miyata*, Teruyasu Mizoguchi

Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

ARTICLE INFO

Keywords:
Liquid
ELNES
Specimen preparation
STEM
Theoretical calculation
Ionic liquid

ABSTRACT

Investigation of the local structure, ionic and molecular behavior, and chemical reactions at high spatial resolutions in liquids has become increasingly important. Improvements in these areas help to develop efficient batteries and improve organic syntheses. Transmission electron microscopy (TEM) and scanning-TEM (STEM) have excellent spatial resolution, and the electron energy-loss near edge structure (ELNES) measured by the accompanied electron energy-loss spectroscopy (EELS) is effective to analyze the liquid local structure owing to reflecting the electronic density of states. In this study, we fabricate a liquid-layer-only sample with thickness of single to tens nanometers using an ionic liquid. Because the liquid film has a thickness much less than the inelastic mean free path (IMFP) of the electron beam, the fine structure of the C-K edge electron energy loss near edge structure (ELNES) can be measured with sufficient resolution to allow meaningful analysis. The ELNES spectrum from the thin liquid film has been interpreted using first principles ELNES calculations.

1. Introduction

Liquids are widely used in industrial activities as chemical reaction fields and transport carriers. Liquid contains many types of local structures, such as electric double layers and nano-sized heterogeneous structures, from single nanometer or smaller [1–7]. The macroscopic properties of liquids are heavily affected by these local structures. Thus, to develop efficient liquid-phase reactions/transportation and, consequently, new liquid devices, liquid analysis at high spatial resolution is required. In response to this demand, some methods have been developed, such as scanning probe microscopy, surface-enhanced Raman spectroscopy, and tip-enhanced Raman spectroscopy. These techniques reaches not only nano-structural but also single-molecular sensitivity [1,3,8–10]; however, they are limited to surface analysis and do not allow for elemental selectivity. Therefore, complementary high-resolution techniques that can catch both chemical and bonding information must be used to obtain a better understanding of liquid nanostructures.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) both have high spatial resolution (less than 0.1 nm). These techniques are powerful tools for atomic scale analyses of solid materials [11,12]. Furthermore, local elemental and electronic/vibrational state analyses in TEM/STEM is possible using energy-dispersive X-Ray spectrometry (EDS) and electron energy-loss spectroscopy (EELS) [13]. Because of the potential of these techniques, the applications of TEM/STEM have gradually expanded to the study of liquids [14–21].

In order to observe the atomic/molecular structure and detailed EEL spectrum of liquid molecules or materials in the liquid phase using TEM/STEM, we have to prepare the sample that has ultra-thin liquid layers of around 10 nm thickness. Besides, easy handling and not having solid films are preferable. Accordingly, we focused on ionic liquid, which is composed of only cationic and anionic molecules [22]. Owing to the strong coulombic interaction, it doesn't evaporate even under ultrahigh vacuum, and thus thin liquid-layer-only sample can be fabricated for TEM observation. The property of the ionic liquid including hydrophilicity is controllable by designing the molecular structure, ionic liquid is, thus, used in extensive fields, such as liquid capacitors, extraction solvents and electrolyte of lithium ion batteries. Because some ionic liquids have been reported to have nano-domain structures [7,23,24] and they contributes to the property such as ionic/thermal conductivity and solubility, investigating local environment is essential for ionic liquid application.

In this study, we fabricate a thin liquid-layer-only samples of an ionic liquid C_2mim-TFSI in a very easy manner. Then, we evaluate the liquid film thickness by EELS. Moreover, to demonstrate the advantages of our method, we measured electron energy loss near edge structure (ELNES) spectra from the thin liquid film and investigated the origins of the peaks in the ELNES spectrum using a first principles calculation.

---

* Corresponding author.
E-mail addresses: tomo-m@iis.u-tokyo.ac.jp (T. Miyata), teru@iis.u-tokyo.ac.jp (T. Mizoguchi).

http://dx.doi.org/10.1016/j.ultramic.2016.10.009
Received 27 November 2015; Received in revised form 25 September 2016; Accepted 18 October 2016

Please cite this article as: miyata, t., Ultramicroscopy (2016), http://dx.doi.org/10.1016/j.ultramic.2016.10.009

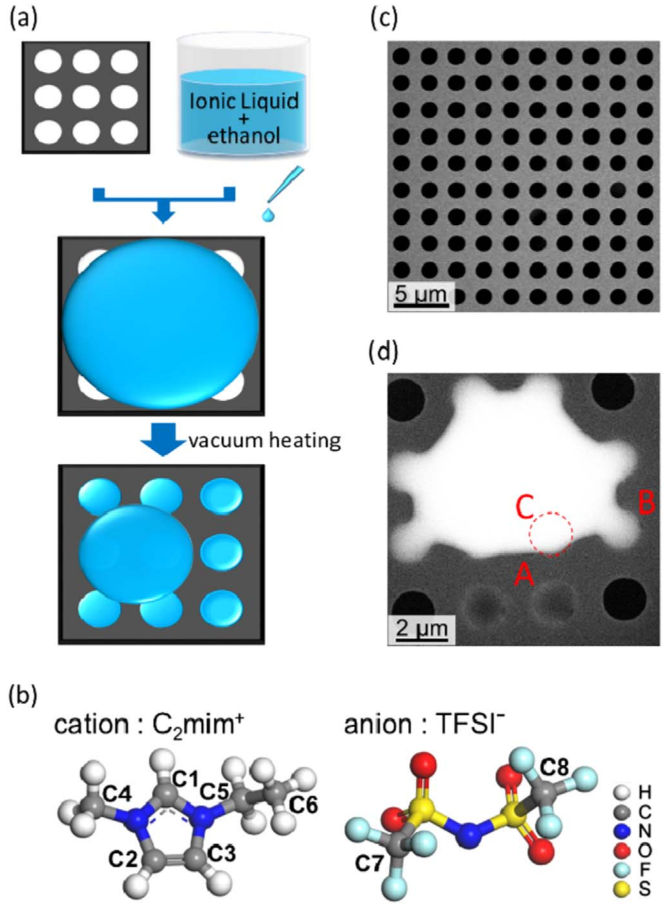


Fig. 1. (a) Fabrication method of thin liquid-film samples. (b) Molecular structure of ionic liquid C_2mim-TFSI, which has 8 carbon atoms C1 ~ C8 in a molecule. (c) SEM image of holey-carbon film Quantifoil R1.2/1.3. (d) HAADF-STEM image of a C_2mim-TFSI liquid sample. Region A is thin and separated from the droplet. Region B is thicker than A and partly connected to the droplet. Region C is very thick and contained in the droplet.

2. Methods

Fig. 1(a) shows the fabrication process of the liquid film sample. Firstly, the ionic liquid and ethanol were mixed at a ratio of 1:10. Next, this solution (2 µl) was dropped onto a thin holey solid film using a micropipette. Then, the ethanol was evaporated by vacuum heating (~1 Pa, 100 °C) for 20 min to form pure ionic liquid droplets; liquid films are formed inside the holes due to surface tension.

In this study, the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide (C_2mim-TFSI) was used as the sample liquid. This ionic liquid is composed of a cation C_2mim^+ and an anion $TFSI^-$ as shown in Fig. 1(b). Holey carbon film Quantifoil R1.2/1.3 (Quantifoil GmbH, Germany) was used for the holey solid film. Fig. 1(c) shows a scanning electron microscopy (SEM) image of a Quantifoil R1.2/1.3, which is composed of an amorphous carbon film with periodic holes. Fig. 1(d) shows a high-angle annular dark-field (HAADF)-STEM image of an area around a liquid droplet.

For image and spectrum measurement, an STEM (JEM-ARM200CF, JEOL Ltd., Japan) equipped with a probe aberration corrector (CEOS GmbH, Germany) and a cold-type field-emission gun was used. EEL spectrum was measured by Enfinium spectrometer (Gatan Inc., USA). The accelerating voltage was set to 200 kV, and the probe size was approximately 0.8 Å. The beam current was ~20 pA. The full width at half maximum (FWHM) of a zero-loss peak without sample (energy resolution) was about 0.7 eV. To prevent the irradiation damage, the EEL spectrum of the liquid film was obtained with scanning an area of 100×100 nm with ~30 nm thickness. The dose rate was estimated to be ~0.1 e/Å^2 s. The acquisition time was 27.5 s, and the energy dispersion of the spectrometer was set to 0.1 eV/pix. The HAADF-STEM collection semi-angle was set to 68–280 mrad.

The absolute thicknesses were estimated from low-loss spectra of EELS by the Log-Ratio method, which has the following relationship [25].

$$\frac{t}{\lambda_i}=\ln\left(\frac{I_t}{I_0}\right)$$

t is the thickness, λ_i is the mean free path of the inelastic scattered electrons (IMFP), and I_O and I_t are the zero-loss peak and the total spectrum intensity, respectively. This equation shows that the absolute thickness t can be estimated from an experimental EEL spectrum and the IMFP. The IMFP of amorphous carbon at the accelerating voltage of 200 kV is 160 nm [26]. In contrast, the IMFP of C_2mim-TFSI can be obtained by the following equation [25].

$$\lambda_i=\frac{106\gamma\,(E_0/E_m)}{\ln\left(\frac{2\beta E_0}{E_m}\right)}$$

$$E_m=7.\,6Z_{eff}^{\,0.36}$$

E_O is the accelerating voltage (kV) and β is the collection semi-angle (mrad).

The effective atomic number Z_{eff}, and relativistic correction factor γ are expressed as follows.

$$Z_{eff}\ =\ \frac{\sum f_n Z_n^{\,1.3}}{\sum f_n Z_n^{\,0.3}}$$

$$\gamma=\frac{T}{E_0}=\frac{m_0v^2}{2E_0}=\frac{1\,+\,(E_0/1022)}{(1\,+\,(E_0/511))^2}$$

Here, n is the elemental species, f_n is the ratio of element n in the material, and γ=0.6176 at E_O=200 kV. Because semi-angle β was more than 10 mrad at E_O=200 kV, the IMFP was approximated to be β=15 mrad as mentioned in ref. [24]. The formula of C_2mim-TFSI is $C_8H_{11}N_3O_4F_6S_2$; therefore, the effective atomic number, Z_{eff}, is 6.857. Eventually, at E_O=200 kV and $\beta > 10$ mrad, the IMFP of C_2mimTFSI is estimated to be 144 nm [27]. The absolute thicknesses in Fig. 2(c) and (f) were calculated using the IMFP 160 and 144 nm, respectively. The error in thickness is generally less than 15% [26,28].

For the comparison, we also measured EEL spectrum from a droplet on a silicon nitride (SiN) film. The thickness of the SiN film was ~100 nm. The spectrum was measured from an area of 100×100 nm at the edge of the droplet (thickness: ~30 nm), and the acquisition time was 90 s. The multiple scattering effect was eliminated by deconvolving the core-loss spectrum by the low-loss spectrum with Maximum-Entropy Algorithm using DeConvEELS code [29].

To interpret the ELNES spectrum of C_2mim-TFSI, we performed the C-K edge ELNES calculations using first principles plane wave basis pseudopotential method (CASTEP code) on a structure that has a structure-optimized cation-anion pair of C_2mim-TFSI in a 1.50 nm cubic supercell (single-molecule model) [30–33]. The structure is shown in Fig. 5(a). The distance between the cation and anion molecules was estimated from the distance between the carbon atom C1 in the cation and the nitrogen atom N in the anion, which takes 0.306 nm in the most stable structure. Moreover, to understand the relationship between the structures and ELNES profiles, the C-K edges were also calculated from the structures with different cation-anion distances, ranging from 0.245 to 0.612 nm. Furthermore, we also calculated a liquid structure with 8 C_2mim-TFSI molecules in a 1.49 nm cubic supercell (8-molecular liquid model), which is shown in Fig. 6(a). The liquid model was constructed by molecular dynamics (MD) simulation. The charge of each atom was estimated by the separately performed first principles numerical-basis molecular orbital