In-situ EC-AFM observation on Au(100) electrode in room temperature ionic liquid ($EMImBF_4$)

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Room temperature ionic liquids have attracted a recent growing interest as novel electrolytes for electrodeposition, batteries, electrochemical capacitors, and so on. The understanding of these ionic liquids/ electrodes interfaces is very important to increase the possibility of these novel electrolytes. Electrochemical scanning tunneling microscope and electrochemical atomic force microscope (EC-AFM) are powerful tools which can observe electrode surfaces in electrolytes. High resolution images observed by these microscopes have provided considerable knowledge of metal surface in contact with aqueous solutions [1, 2]. There have been also a few electrochemical STM observations [3, 4], however, no images with atomic resolution have been reported.

1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) [5] is an air- and moisture-stable ionic liquid at room temperature and has a wide electrochemical window of over 4V. It is expected to be used for any kinds of applications, such as, ester synthesis [6], electrochemical capacitors with polymer electrolytes [7], dye-sensitized solar cells [8], and so on. In this work, in-situ EC-AFM images of Au(100) with atomic resolution in $EMImBF_4$ under potential control, as well as decay of multiayered islands on Au(100) in $EMImBF_4$ are shown.

The electrode used here was an Au(100) disk with 12 mm diameter and 2mm thickness. The preparation of the electrode surface was almost the same as that used for the EC-AFM observation in aqueous solutions [9, 10]. The electrolyte used here was $EMImBF_4$, supplied by Kanto Chemical Co., Inc. In order to remove the water as far as possible from the electrolyte, it was dried under vacuum at 100ºC for more than 24 hrs before use. After the drying, it was handled in a glove box filled with dried argon gas. All of the experiments were performed at room temperature in a glove box filled with dried argon gas. The microscope used was a Nanoscope IIIa (Digital Instruments Inc.), which was combined with a potentiostat to control the electrode potential. The EC-AFM cell was almost the same as that used for the EC-AFM observation in aqueous solutions, except the reference electrode. The reference electrode used here was a silver electrode immersed in a 100mM $AgBF_4$-$EMImBF_4$ solution (Ag/Ag^+), to which all the potentials shown here were referred.

Fig. 1 shows a cyclic voltammogram (CV) for glassy carbon in $EMImBF_4$ from -3.0 to 1.3V at a sweep rate of 50 mVs^{-1}, indicating an electrochemical potential window of over 4V. Fig. 2(a) shows a CV for Au(100) in $EMImBF_4$ from -2.1 to 0.3V at a sweep rate of 50 mVs^{-1}. As shown in fig. 2(b), a topographic EC-AFM image of Au(100) surface was obtained in $EMImBF_4$ at -0.6V. On the terrace of the surface, a high resolution EC-AFM image obtained on the terraces of Au(100) as shown in fig.1(c). In a filtered image of image (c) (fig.2(d)), the bright spots characterized by four-fold symmetry with interatomic distance of 0.30 ±0.02 nm can be seen. This observed structure is consistent well with a bare and unreconstructed Au(100)-(1×1) structure.

We have also succeeded in the observation of the decay of multilayered islands located on Au(100) electrode in $EMImBF_4$, as shown in figs.3. The observed dacay is quite similar to that observed in aqueous solution [9]. The points of similarity and difference of the dacay in $EMImBF_4$ compared with that in aqueous solution will be presented in the meeting.

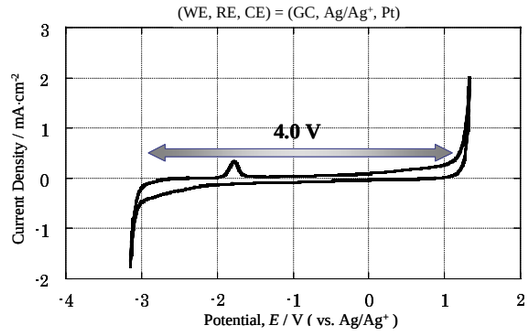

Fig.1 Cyclic voltammogram for glassy carbon in $EMImBF_4$ from -3.0 to 1.3V at a sweep rate of 50 mVs^{-1}.

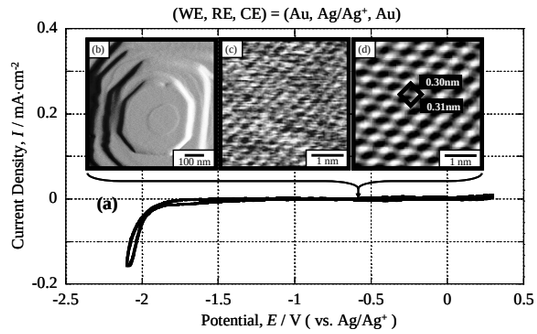

Fig.2 (a) Cyclic voltammogram for Au(100) in $EMImBF_4$ from -2.1 to 0.3V at a sweep rate of 50 mVs^{-1}. (b) Topographic EC-AFM image of Au(100) surface obtained at -0.6V (c) High resolution EC-AFM image on an terraces of Au(100) obtained at -0.6V. (d) Filtered image of image (c).

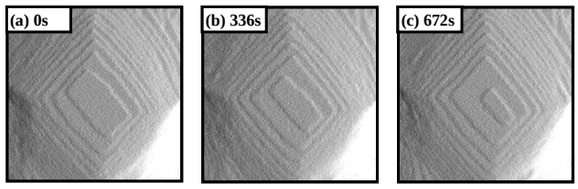

Fig. 3 In-situ EC-AFM images (600nm×600nm) showing the dacay of the multilayered island on Au(100) in $EMImBF_4$ when keeping the potential at -0.6V.

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