Electrochemical Behavior of Ionic-Liquid/Electrode Interfaces Investigated by FM-AFM with Quartz Tuning Folk Sensors

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Room-temperature molten salts, which are also called "ionic liquids (ILs)", have superior properties compared to water and organic solvent, such as high ionic conductivity, non-volatility, and non-combustibility, and thus, they are expected to be adopted as a new electrolyte in electrochemistry. FM-AFM studies on IL/solid interfaces would provide helpful information for electrochemical reactions using ILs. However, since ILs have high viscosity (typically 100 times higher than that of water), FM-AFM imaging using Si cantilevers is considered to be unstable because of extremely low Q-factor in ILs. Recently, we have developed FM-AFM with a quartz tuning fork sensor for the investigations in ILs, which enables us to investigate IL/solid interfaces on the atomic/molecular resolution [1, 2].

In this study, we newly developed electrochemical FM-AFM (EC-FM-AFM) for investigating electrochemical behavior on IL/electrode interfaces. Figure 1 (a) shows a schematic illustration of the EC-FM-AFM. A qPlus tuning fork [3] was used as a force sensor and just the tip apex was immersed in an IL. The tip-scan system was adopted because the deflection of the sensor can be detected electrically and the sample-holder includes the three electrodes; working electrode (sample), counter electrode (CE), and reference electrode (RE). The electrode potential of the sample was controlled by a potentiostat. Figure 1(b) shows a two-dimensional frequency shift (Δf) vs. distance map obtained on a interface of 1-butyl-1-methylpyrrolidinium tris(tentafluoroethyl)trifluorophosphate (Py1,4-FAP, viscosity: 184 cP) and a Au(111) surface. The electrode potential of the sample was -0.4 V vs. Au-ref. This image clearly shows an oscillation of Δf with a period of approximately 1.0 nm, which indicates the presence of multiple solvation layers on the interface.

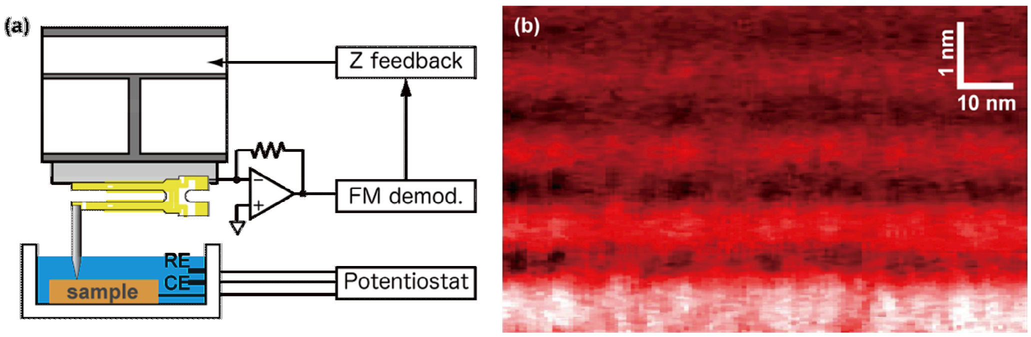

Fig. 1 (a) A schematic illustration of the EC-FM-AFM with a qPlus sensor. (b) 2D Δf map obtaind on a Py1,4-FAP/Au(111) interface. A = 250 pm, E = -0.4V vs. Au-ref.

References

[1] T. Ichii, M. Fujimura, M. Negami, K. Murase, H. Sugimura, Abstract booklet of NC-AFM2011, P1-22
[2] T. Ichii, M. Fujimura, M. Negami, K. Murase, H. Sugimura, submitted to Jpn. J. Appl. Phys.
[3] F. J. Giessibl, Appl. Phys. Lett., **73**, 3956 (1998)