Specific Redox Properties of Ferrocenyl-thiol SAM in Ionic Liquids <u>Takahiro ASAI</u>, Shodai AOYAMA, Atsushi KITADA,Takashi ICHII, Hiroyuki SUGIMURA and Kuniaki MURASE Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan asai.takahiro.23x@st.kyoto-u.ac.jp

Electrochemically active self-assembled monolayers (SAM) of ferrocene (Fc)-terminated alkanethiols on gold surface have been expected for application to sensors and molecular electronic devices. Redox and reductive desorption behaviors of SAM have been well studied in aqueous solutions such as HClO₄ aq [1]. However, there are less reports on the electrochemical behavior of SAM in ionic liquid (IL) electrolytes than in aqueous ones. Previously some of the authors reported the redox behaviors of 11-ferrocenyl-1-undecanethiol (FUT) SAM on Au(111) in IL electrolytes. The results suggested that only part of the FUT molecules is involved in the redox reaction. This implies the steric effect by large anions, because they could not assemble around the oxidated Fc⁺ groups to compensate charges completely. At that time, however, it was not excluded that trace water in the electrolytes may shield the positive charge of Fc groups and affect redox behaviors. In this study, we examined the redox behaviors of the FUT SAM with controlling the water content in ILs. We also checked the adsorption and desorption of anions associated with redox of Fc groups using an electrochemical QCM (EQCM).

FUT SAM was prepared by coadsorption method as reported in ref. 2. QCM substrate was ultrasonically cleaned in ultrapure water and then immersed for 24 h in ethanol solutions of FUT with thiol concentration of 1 mM. The redox behaviors for Fc groups were examined by CV and EQCM. Electrochemical measurements were performed in 0.1 M HClO₄ aqueous solution with Ag/AgCl (3 M NaCl) as reference and several ILs (TMHA-Tf₂N, EMI-Tf₂N and EMI-BF₄) with Pt/EMI-Tf₂N as references, respectively.

Figure 1 shows the CV for FUT SAM in 0.1 M HClO₄ aq and ILs. The peak splitting of the CV curve in HClO₄ aq was observed. The redox potential of FUT SAM is known to depend on the interaction between the molecules [3]. This is because, when one FUT molecule oxidated or positively charged, the oxidation of the neighbor molecules become harder due to coulomb repulsion between the charged moieties, requiring a higher potential. Similarly, the shoulder peak in EMI-BF₄ was observed. By contrast, at higher potentials the peak disappeared in TMHA-Tf₂N and EMI-Tf₂N. This indicates that the interaction between FUT molecules in the Tf₂N-based ILs is reduced because of a steric hindrance of large IL anion. The CV for TMHA-Tf2N and EMI-Tf₂N gave smaller (about 80%) peak area than that in $HClO_4$ and EMI-BF₄, suggesting that less molecules were electrochemically active in the Tf₂N-based ILs, possibly because of the steric effect. The estimated amount of electroactive FUT was listed in Table 1, similar to the previous report [2]. Notably, the difference in the peak area of redox by the water content of ILs was not observed. Figure 2 demonstrates the EQCM results in an aqueous and an IL electrolytes, where we observed frequency changes corresponding to potential changes. The EQCM for $HClO_4$ gave periodic changes in frequency, while the freq. changes in IL was not constant. Consequently, it was not able to take quantitative for ionic liquid electrolyte, likely reflecting the slow relaxation rate of the ionic liquid.

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Figure 1. Cyclic voltammograms for FUT SAM in (a) 0.1 M HClO₄ aq and (b) ILs with scan rate of 100 mV s⁻¹.

Table 1. Amount of FUT involved in redox reaction.

Electrolyte (water content)	Amount of $FUT/10^{14} \text{ cm}^{-2}$
0.1 M HClO ₄ aq	2.79
EMI-BF ₄ (1000ppm)	2.75
EMI-BF ₄ (10000ppm)	2.82
EMI–Tf ₂ N (200ppm)	2.25
EMI-Tf ₂ N (10000ppm)	2.27
TMHA–Tf ₂ N (50ppm)	2.19
TMHA–Tf ₂ N (10000ppm)	2.29



Figure 2. Frequency changes for the EQCM coated with FUT SAM in (a) 0.1 M HClO_4 aq and (b) EMI–Tf₂N.