Characterization of Ferrocene Modified Electrode Using Electrochemical Surface Forces Apparatus

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Chemically modified electrodes have been extensively studied because of broad interests in their applications such as the photovoltaics and the sensors. Microenvironment of the redox molecules adsorbed on the electrodes, such as ion adsorption and solvation, is important for controlling the electrochemical properties of the electrodes. In this study, we performed the forces measurements on interactions between ferrocene (Fc) modified electrode surfaces employing this electrochemical surface forces apparatus (EC-SFA)[1)] for quantitative evaluation of the surface charges of the electrodes and ion-pairing between Fc^+ and various counter anions.

The gold surface was dipped in the 0.5 mM cyclohexane solution of 6-(Ferrocenyl)hexanethiol. Potential of this electrode was controlled by a potentiostat with Ag/AgCl reference electrodes. The forces between this Fc modified electrodes in various 1 mM electrolyte solutions ($KClO_4$, KNO_3, KSO_4^{2-}, and KCF_3SO_3) were measured using EC-SFA (Fig. 1).

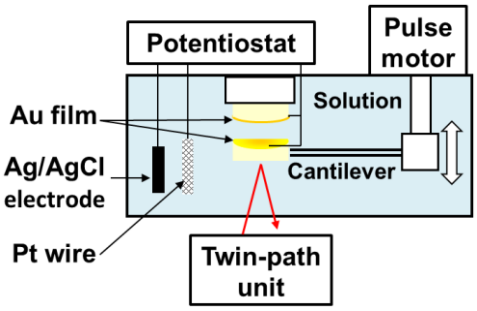

Fig. 1. Schematic illustration of electrochemical surface forces apparatus (EC-SFA).

Fig. 2 shows force profiles of interactions between the ferrocene modified surfaces in 1 mM aqueous $KClO_4$ and KNO_3. Double layer repulsion between the electrodes in 1 mM aqueous $KClO_4$ was increased with oxidation of the Fc when the applied potential was increased from 0 V to 0.8 V vs. Ag/AgCl. In the case of 1 mM aqueous KNO_3, larger double layer repulsion at 0.8 V vs. Ag/AgCl was observed than that in the aqueous $KClO_4$, indicating that ion pairing between counter ions and Fc^+ on the electrode in the aqueous KNO_3 was smaller than that in the aqueous $KClO_4$. The degrees of dissociation (α_D) between Fc^+ and various counter anions were evaluated from the density of Fc^+ and the surface charge on the electrode evaluated from theoretical fits to the Derjaguin-Landau-Verwey-Overbeek (DLVO) forces on the measured force curves. $CF_3SO_3^-$ showed the largest α_D (3.2 %), followed in order by SO_4^{2-}, NO_3^-, ClO_4^-. α_D's of all anions were much smaller than 100 %, indicating that Fc^+ formed the ion pair with counter anions nearly 1:1.

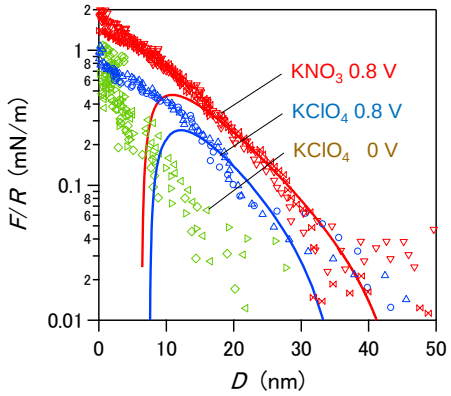

Fig 2. Force profiles between the Fc SAM surfaces in 1 mM aqueous $KClO_4$ and KNO_3 electrolyte solution with various applied potential.

【**Reference**】(1) T. Kamijo, M. Kasuya, M. Mizukami, K. Kurihara, *Chem. Lett.* 2011, **40**, 674.