Double-layer of the Au(111) electrodes modified by self-assembled monolayers of thiol with carboxyl terminal group: 3-D Poisson-Boltzmann method and Monte Carlo simulation

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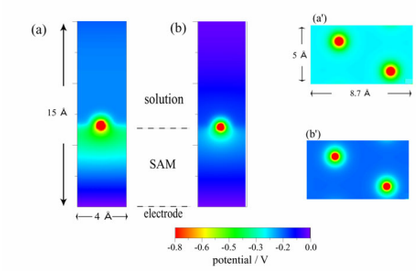
The self-assembled monolayer (SAM) of thiol with carboxyl group terminal on Au(111) has very strong electric double layer when the terminal group is dissociated in alkaline solution. The terminal carboxylate anions of the SAM on Au(111) form the regular periodic array and the surface charge density is ca. 0.74 C m^{-2} if the surface coverage of thiol is one third of the gold surface atoms. This strong double layer changed the capacitance of the system[1], and Finklea et al. reported that the electron transfer rate[2] is increased for the SAM with the dissociated carboxy terminal, and the increase was explained by the electrostatic interaction between the carboxylate anion and the cation redox. Recently we have shown the increase can be explained by the Frumkin effect. To explain the capacitance change and the increase of the electron transfer rate theoretical studies on the three dimensional structure of the double layer may be necessary. In the present study we have carried out the theoretical study on the double layer structure by the three dimensional nonlinear Poisson-Boltzmann(PB) method and the canonical Monte-Calro simulation using the primitive model[3].

In Fig. 1 the double layer structures calculated by the 3-D PB method are shown. From the figure the carboxylate anionis strongly screened by the continuum charge. From the calculated double layer charge and potnetial distribution we have evaluated the electrostatic free energy change by coverage of carboxylate of the SAM on Au(111). From the coverage dependence of the free energy the interaction parameter is determined and we have compared the experimental results of the capacitance change with pH of the solution. The results are shown in Fig.2. It has been found that the agreement is much better than the results by the 1-pKa model we have proposed before[1].

Since the counter ion is approximated by continuum in the PB model, the distribution of the counter cation and co-anion from the SAM electrode with carboxyl terminal may be not accurate. If we consider the electron transfer of the redox such as $Ru(NH_3)_6^{2+/3+}$, this distribution of the electrolyte and the redox itself is crucial. Therefore Monte Calro simulation in the primitive model is applied to this system as shown in Fig.3. We have obtained the thermal averaged ion distribution in the surface normal direction (Fig. 4) and the surface parallel direction (not shown here.) We are now calculating the 3D potential profile from the distribution of electrolyte ion and get the Frumkin effect from this molecular level simulation.

References

[1] T. Kakiuchi et al. Langmuir, **104**, 2000 8862.
[2] H. O. Finklea, *Electroanal. Chem.* (Ed. A. J. Bard, I. Rubinstein) Marcel Dekker. New York, **19**, 207 (1996).
[3] G. M. Torrie and J. P. Valleau, *J. Chem. Phys*., **73**, 5807 (1980).



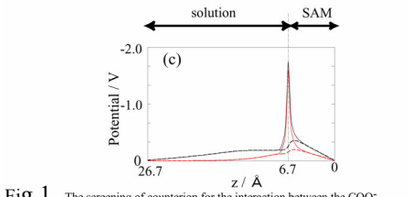


Fig.1 The screening of counterion for the interaction between the COO^- terminals : numerical calculation of the Poisson-Boltzmann equation for three dimensional system.
Electrolyte (1:1) concentration : 0.10 M ((a), (a'), (c: ——)), 1.0 M ((b), (b'), (c: ——))
Electrode potential : 0 mV

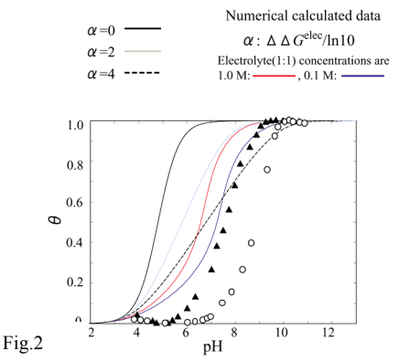


Fig.2 . Comparison of experimental capacitance values with theoretical capacitance titration curves for 3-MPA SAMs as a function of the solution pH. Electrolyte(1:1) concentrations are 1.0 M(▲), 0.1 M(○) $NaClO_4$, respectively.

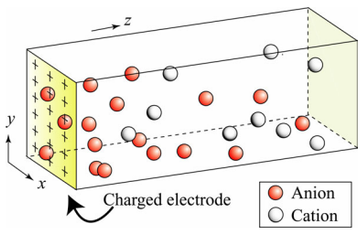


Fig. 3 Schematic drawing of the Monte Carlo cell. The system is extended in the *x* and *y* direction periodically.

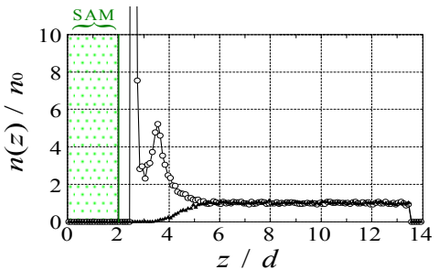


Fig. 4 Reduced density profiles of anion (○) and cation (▲) at charge density of 76 μC cm^{-2}. Electrolyte concentration: 1 M. The *z* coordinate is reduced by the diameter of an ion (*d*). n_0=0.046/(d^2).