

Calculation of the structure of the electric double layer on polyelectrolyte gel-electrode interfaces

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電解質ゲルと接合された電極界面の電気二重層のデバイ長と、電位分布、イオン分布、ゲルの弾性変形、界面応力分布を計算し、浸透圧、Maxwell 応力、カウンターイオンの排除体積の各々の寄与のゲルの組成との相関について理論モデルと実験との両面から議論したい。Nafion の電解質ゲルに金電極をメッキした界面の場合、界面応力の実験結果は電極に充電されるイオンの数密度に比例し、その比例係数はイオンの Stokes 半径の 2 乗に比例することを示す。ここでは、Nafion のような低含水率で高イオン濃度の系で効いてくる界面応力へのイオンサイズ依存性のモデルの導入を行う。

1 Introduction

We have calculated the structure of the electric double layer on the polyelectrolyte gel-electrode interfaces. using the mechanical balance based on three fluids model . The results include the effects of hydration volume of counterion, osmotic pressure of ionic gels and Maxwell stress in electric double layer. We discuss the relation of the structure of the electric double layer, such as Debye length, network deformation and amount of charge, and the type of gels, such as pore size, water content and ion density, e.t.c., and compare with the experimental results.

2 Experiment

When a constant voltage is applied to the polyelectrolyte gel actuator of Nafion117 plated with gold electrodes, the gel remains to deform at the equilibrium state. To investigate the mechanism of this deformation, the displacement and the total charge under a constant voltage were measured. The result is that if the gel has large counterions, the equilibrium displacement d is large while the charge Q is small, and that the displacement is proportional to the square of the Stokes radius of the counterion a_i and inversely proportional to the valence of that Z : $d \propto a_i^2 Q / Z$. Under a voltage, cations gather at the gel-cathode interface and repulsive

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each other because they have volume defined by the Stokes radius. The result means that the equilibrium deformation is caused by this repulsion.

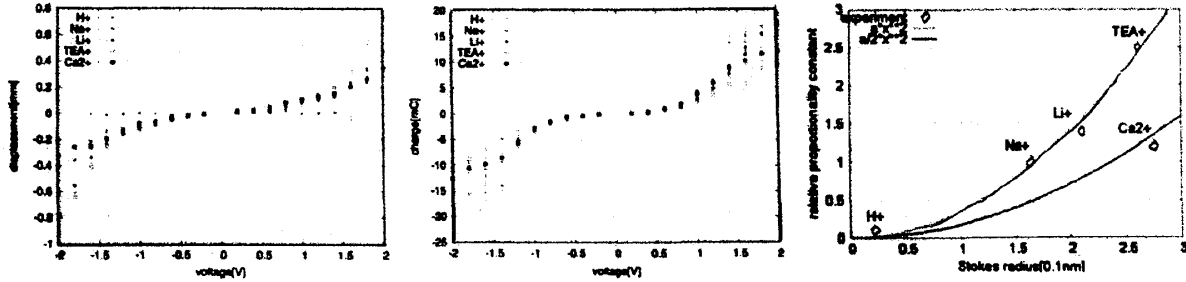


図 1: Left : the displacement and the applied voltage. Center : the amount of charge on interface and the applied voltage. Right : the ion radius dependency of the displacement per an ion.

3 Theoretical Model

The basic equations to calculate the equilibrium counter ion distribution and the elastic deformation of gel networks in the electric double layer on the flat electrodes are described on the three fluids model [1] as follows.

$$\rho = \frac{q_p}{w_p} \phi + \sum_i C_i q_i \quad (1)$$

$$0 = -C_i q_i \nabla \Psi - k_B T \nabla C_i \quad (2)$$

$$0 = -\frac{q_p}{w_p} \phi \nabla \Psi + \nabla \cdot \sigma, \quad (3)$$

where ρ denotes the charge density, q_p the charge on a monomer of gels, q_i the charge on a i -kind counter ion, w_p the volume of a monomer of gels, ϕ the polymer volume fraction, C_i the density of i -kind counter ion, Ψ the electric potential, σ the stress tensor of gel networks. These equations lead the Poisson-Boltzmann eq. and the mechanical balance eq. of gels in one-dimensional model.

$$\nabla_x^2 \Psi(x) = -\frac{1}{\epsilon} \left\{ \frac{q_p}{w_p} \phi(x) + \sum_i C_{bi} q_i \exp \left(-\frac{q_i}{k_B T} \Psi(x) \right) \right\} \quad (4)$$

$$1 - \frac{\phi(x)}{\phi_b} = \left(K + \frac{4}{3} G \right)^{-1} \left[\frac{q_p}{w_p} \int_{bulk}^x dx' \phi(x') \frac{\partial \Psi(x')}{\partial x'} + \Delta \Pi(\{C_i(x)\}) \right], \quad (5)$$

where C_{bi} denotes the i -kind counter ion density in the bulk region, ϕ_b the polymer volume fraction in the bulk region, K and G the bulk and shear moduli of gel networks, $\Delta \Pi$ is the stress change of gel networks by the redistribution of counter ions under electric field. Here, we discuss the model of free energy and $\Delta \Pi$ for electrolyte gels having large counter ions.

References

- 1) T.Yamaue, H. Mukai, K. Asaka and M.Do, Macromolecules 38 (2005) 1349.