Possible influence of the Kuramoto length in a photo-catalytic water splitting reaction revealed by Poisson–Nernst–Planck equations involving ionization in a weak electrolyte

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ABSTRACT

We studied ion concentration profiles and the charge density gradient caused by electrode reactions in weak electrolytes by using the Poisson–Nernst–Planck equations without assuming charge neutrality. In weak electrolytes, only a small fraction of molecules is ionized in bulk. Ion concentration profiles depend on not only ion transport but also the ionization of molecules. We considered the ionization of molecules and ion association in weak electrolytes and obtained analytical expressions for ion densities, electrostatic potential profiles, and ion currents. We found the case that the total ion density gradient was given by the Kuramoto length which characterized the distance over which an ion diffuses before association. The charge density gradient is characterized by the Debye length for 1:1 weak electrolytes. We discuss the role of these length scales for efficient water splitting reactions using photo-electrocatalytic electrodes.

1. Introduction

The Poisson–Nernst–Planck (PNP) equations have been used to describe a wide range of transport phenomena from electrons and holes in semiconductors to ions in electrolytes [1–9]. The conservation of charge for each ion species and electrostatic interactions among charge carriers are treated by the PNP equations in a self-consistent manner. The PNP equations take into account the drift currents due to the electric fields generated by the distribution of charge carriers. The effect is substantial *e.g.* when electrode reactions generate charge density gradients. The PNP equations can be applied to obtain concentration profiles and an electro-static potential generated by electrode reactions. Although the PNP equations are used for the study of coupled effects between electric fields and charge carrier transports, they are nonlinear and solved mainly by numerical methods. However, for certain cases, approximate analytical solutions have also been obtained for strong electrolytes [2,3,8–13]. Using the PNP equations, it has been shown that the spatial dimensions of concentration gradient can be many orders of magnitude larger than the characteristic length scale of charge density profiles given by the Debye length in strong electrolytes [1–4,13].

In weak electrolytes, only a small fraction of molecules are ionized in bulk. Ion concentration profiles depend on ion transport and the ionization of molecules. It should be noted that depleted ions in the vicinity of the electrode can be replenished by the ionization of molecules and diffusion from the bulk in weak electrolytes. The current at the interface between the electrolyte and electrode can be much larger than that in bulk due to the molecule ionization.

The Nernst-Planck equation is the continuity equation representing the conservation of charge for each ion species, where dissociation and association of ions are not considered. For weak electrolytes, the PNP equations have been extended to describe ionization and recombination of ions [5,14–25]. In the extended PNP (e-PNP) equations, ion concentrations become non-conservative by local dissociation and association of ions in bulk phase.

In this paper, we study charge transport induced by electrode reactions in weak electrolytes using the e-PNP equations without assuming a priori charge neutrality. Photo-electrochemical (PEC) conversion of water can be an example, but the fundamental results apply to other electrode reactions. We show that the gradient of total ion density (the sum of cation and anion concentrations) is characterized by either the Kuramoto length [26–31] or the Debye length depending on the situation, while the gradient of charge density (the difference between cation and anion concentrations) is characterized by the Debye length in binary

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monovalent weak electrolytes. The Kuramoto length characterizes the length scale of local density fluctuations around a uniform concentration state [26–31]. In weak electrolytes, the Kuramoto length is given by the length scale of diffusive migration of ions within its life-time; the life-time is determined by the association rate of ions [26–31]. Our results indicate that the ion density gradients can also be characterized by the Kuramoto length when both cations and anions are discharged at the electrode in binary monovalent weak electrolytes. For this case, ion density drop caused by electrode reactions is recovered by ion density fluctuations localized within the Kuramoto length. We discuss the efficiency of water splitting reactions using photo-electrocatalytic electrodes in terms of the Kuramoto length and the Debye length. We also discuss the over-potential related to a charge density gradient near the electrode and show that it can be reduced when both cations and anions are discharged at the electrode.

2. Theory

As shown in Fig. 1, we considered the thermal motion of cation and anion under Coulombic interactions. The one-dimensional (1D) x-coordinate was introduced by assuming a uniform distribution of ions in the plane parallel to the electrode surface. The origin of the x-coordinate was the electrode surface, and the x-coordinate was normal to the electrode surface. The concentration and diffusion constant of cations are denoted as n_+ and D_+, respectively. The concentration and diffusion constant of anions are denoted as n_- and D_-, respectively, while the electric field is denoted as E. Each species moves by electromigration and diffusion. For simplicity, we consider a binary monovalent electrolyte (1:1 electrolyte). The concentration and the diffusion constant of the undissociated neutral compound are denoted as m and D_m, respectively. At a sufficiently large distance L away from the electrode, the electrolyte is neutral. The external electric field is not applied. We consider ion discharge reaction at the electrode followed by product formation. Products of electrode reactions are assumed to be removed. An example is hydrogen evolution reaction by photo-electrocatalytic (PEC) water splitting [32,33]. For PEC water splitting, cations, anions, and undissociated molecules correspond to H_3O^+, OH^-, and water molecules, respectively. We mainly consider the case that one of the ion species is discharged at the electrode and the other species are inert and reflected at the electrode as described in Fig. 1(a). In Section 6, we consider the special case that both cation and anion species are discharged at the electrode as described in Fig. 1(b). The situation corresponds to overall water splitting into H_2 and O_2 using a single photocatalyst such as GaN-ZnO and ZnGeN$_2$-ZnO under light illumination [34,35]. For simplicity, we assume that reactive sites on the electrode are structureless. In experiments, the electrode can be regarded as

homogeneous when the electrode is modified with molecular or metal complex cocatalyst to realize both oxidation and reduction reactions on the electrode. Some electrodes with nano-particulate photocatalysts could also be regarded as homogeneous.

Ion transport was described by the Nernst–Planck equations and the electric field satisfied the Poisson equation. By taking into account the association and dissociation reactions of ions with diffusion and ion migration under the electric field $E(x)$, the governing equations in the bulk phase are given by [5,14–21,23–25]

$$\frac{\partial}{\partial t}n_+ = \frac{\partial}{\partial x}D_+\left(\frac{\partial n_+}{\partial x} - \frac{eEn_+}{k_BT}\right) + k_dm - k_an_+n_-, \tag{1}$$

$$\frac{\partial}{\partial t}n_- = \frac{\partial}{\partial x}D_-\left(\frac{\partial n_-}{\partial x} + \frac{eEn_-}{k_BT}\right) + k_dm - k_an_+n_-, \tag{2}$$

$$\frac{\partial}{\partial t}m = D_m\frac{\partial^2}{\partial x^2}m - k_dm + k_an_+n_-, \tag{3}$$

$$\frac{\partial}{\partial x}E(x) = \frac{4\pi e}{\epsilon}(n_+ - n_-), \tag{4}$$

where k_d and k_a denote the dissociation rate constant and the association rate constant, respectively. Eq. (4) is the Poisson equation. $-D_+(\partial n_+)/(\partial x)$ and $D_+eEn_+/(k_BT)$ on the right-hand side of Eq. (1) represent the diffusive flux and the ion electro-migration by the electric field E, respectively. $D_+/(k_BT)$ can be regarded as the mobility using the Einstein relation. When the electrostatic potential is controllable by potentiostat operation, Eqs. (1)–(4) may be more conveniently expressed by using the electrostatic potential rather than using the electric field. However, we study the ion currents and the electrostatic potential induced by the ion discharge reactions at the electrode without imposing the external electric field. In this case, the electrostatic potential is not a controllable parameter. To avoid a redundant integration constant associated with the electrostatic potential we express Eqs. (1)–(4) using the electric field.

In the following, we consider steady states. The left-hand sides of Eqs. (1)–(3) are zero in steady states. The electrostatic potential difference relative to the electrostatic potential at L can be defined by

$$V(x) = -\int_L^x dx_1 E(x_1), \tag{5}$$

and can be calculated by solving Eqs. (1)–(4) under proper boundary conditions. The total potential difference between the electrode surface and bulk (overpotential) is $V(0)$.

2.1. Boundary conditions

At a sufficiently large distance away from the electrode surface, the ion concentrations are not affected by surface reactions.
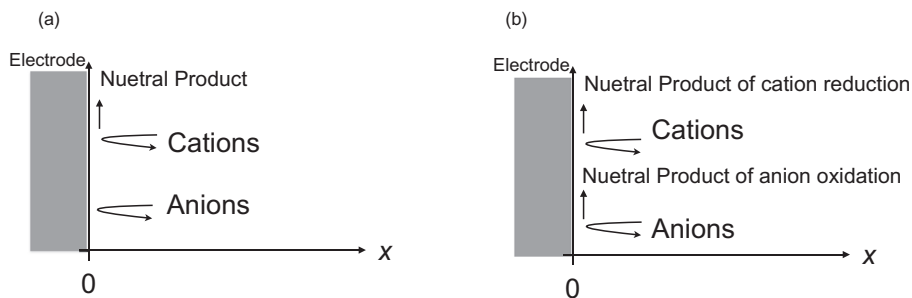

Fig. 1. Sketch of the model of ion discharge reactions at the electrode surface. The distance from the electrode is denoted by x. (a) Cations are reduced at the electrode surface, and the neutral products are dissolved into the solution. Anions are reflected at the electrode surface. (b) Cations are reduced, and anions are oxidized at the electrode surface. The both neutral products are removed from the electrode surface. For photo-electrocatalytic (PEC) water splitting using a single photocatalyst, cations and the neutral products correspond to H_3O^+ and H_2, respectively; anions and the neutral products correspond to OH^- and O_2, respectively.