Theory of Stable Formation of Ionic Vacancy in a Liquid Solution

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The stable formation of ionic vacancy in a liquid solution was theoretically examined by means of a mean-field approximation based on Debye-Hückel’s framework. As the process of the vacancy formation, metal deposition from electrolyte solution was adopted, where anions associated with metallic ions adsorbed at electrical double layer were transcribed to the inner wall of the vacancy during the reaction. Then, it was concluded that since the formation energy of the vacancy is cancelled out by the electric work between the charged inner wall and its ionic atmosphere, the vacancy is stably self-organized. In copper deposition from potassium chloride solution and sulfuric acid solution, by measuring the partial molar volumes of the vacancies with gravity electrode, the radius of the vacancy theoretically predicted was experimentally validated.

Key Words: Vacancy, Ionic Solution, Electrolyte Solution, Gravity Electrode, Nano-bubble

1 Introduction

When an electrolyte dissolves in a solution, it dissociates into cations and anions, yielding solvated ions. In a solid solution, vacancies of atoms and ions are simultaneously formed. However, in a liquid solution, because of the random thermal motion of solutes and solvents, it has been thought that such vacancies, even if possible, do not stably exist.

Electrodeposition is, in a sense, a reaction extracting metallic ions from a solution phase, and depositing them on a metallic phase. Such a reaction takes place at the inner Helmholtz plane (IHP) in electric double layer, transferring electrons from the metallic phase to the ions. At the IHP, except for solvent molecules, only metallic ions and counter anions such as chloride ion specifically adsorb, associating with each other. Counter anions with non-specific adsorption property can adsorb at the outer Helmholtz plane (OHP), also associated with the metallic ions. Whether the anions specifically adsorb or not, electrodeposition adiabatically occurs with electron transfer, extracting the metallic ions from the IHP. As a result, due to electrostatic repulsion, some of the counter anions left behind contribute to the self-organization of the vacancy in liquid phase.

Vacancy formation by adding impurities to a solid crystal is generally measured by the variation in its volume. To detect vacancies formed in electrode reactions, a special electrode system called gravity electrode has been developed. This system is composed of a set of rotor and electrode cell. The cell revolves around the rotor, receiving a centrifugal force. Because of the small scale of the cell, one-directional acceleration just like natural gravity can be applied to its electrode surfaces. Depending on the direction of the applied gravitational acceleration, two kinds of gravity modes are usable: one is vertical mode, where the acceleration is applied vertically to electrode surfaces, and the other is parallel mode with the acceleration parallel to electrode surfaces. In each mode, characteristic convection takes place enhancing the mass transfer of reaction species. The equations of limiting-diffusion currents were theoretically derived. Then, it was verified that the equations precisely describe experimental results. Moreover, using gravity electrode, the dendritic growth of silver crystals and copper electrodeless plating under high gravity fields were examined. As a result, it was clarified that gravitational convection suppresses the dendritic and three-dimensional growth of deposits, which is convenient for measuring kinetic parameters such as exchanging current density. The electrode system easily detects the buoyancy force arising from the change in the partial molar volume between reactant and product during electrode reaction, which was applied to the analysis of iron-pitting corrosion. Therefore, using gravity electrode, it is possible to determine the vacancy size from the change in volume accompanying the vacancy formation.

In the present paper, based on a mean-field approximation, firstly vacancy formation energy is generally formulated. Then, as a compensating work for the vacancy formation, using Debye-Hückel’s formulation, an electric work for forming ionic atmospheres around the vacancies is calculated. Finally, in copper deposition from potassium chloride solution and sulfuric acid solution, the radii of the vacancies are determined by theoretical and experimental examination.

2 Theory

2.1 Vacancy formation energy

Figure 1 exhibits the formation mechanism of a vacancy during electrodeposition; when transferring electrons to a metallic ion at the IHP and extracting it from solution side, due to electrostatic repulsion, some of the counter anions left behind form a vacancy, being transcribed to its inner wall, which yields an electrically
charged layer. A principal method to analyze the problems of interfacial effects discussed here rests upon the assumption that liquid containing ions can be described by a continuum mean-field approximation or mean molecular field, wherein it is assumed possible to define an element of the liquid that is small compared to the range of the intermolecular force but large enough to contain a sufficient number of molecules. This approximation adopted by Debye and Huckel implies that on average the attractive force on any molecule in the liquid is the same in all directions, giving to the liquid its fluid characteristics. Then, counter ions attracted by a central ion are incessantly moving; on average, their distribution can be expressed as if forming an ionic cloud called ionic atmosphere.

Figure 2 shows a vacancy structure based on the mean field approximation, which is separated by two parts; one is the electrically charged layer of the inner wall contributed by the anion of the supporting electrolyte and water molecules, and the other is the outer ionic atmosphere adjacent to the charged layer, where the cations of the supporting electrolyte together with the anions and water molecules are also contained. \( R^* \) is the inner radius of the vacancy, and the charged layer exists between \( r = R^* \) and \( r = R^* + \Delta R^* \) (infinitesimal increment from \( R^* \)), of which the total electric charge \( q_v \) is expressed by

\[ q_v = -\alpha z_m e \]  

where \( z_m \) is the charge number of the metallic ion including sign and \( e \) is the elementary electric charge, 1.60210 × 10⁻¹⁹ C. \( \alpha \) is the transcription coefficient of the anion, which is introduced since the minus charges opposite to the metallic ion \( -z_m e \) is not always transcribed to the inner wall; that is, \( \alpha = 1.0 \) means that complete transcription occurs, \( \alpha = 0.5 \) means that a half of \( -z_m e \) is transcribed, and \( \alpha = 0.0 \) corresponds to no transcription.

The partial molar volume of the vacancy \( V_w \) gives the radius of the vacancy as follows,

\[ V_w = \frac{4}{3} \pi R^*^3 N_A \]  

where \( N_A \) is Avogadro’s constant. Since the electrolyte solution is incompressible, the chemical potential of the vacancy \( \mu_v \) is given by

\[ d\mu_v = V_w d\rho \]  

where \( \rho \) is the pressure applied to the vacancy.

Then, the surface tension is related to the pressure difference across the inner wall, which is referred to as the Young-Laplace equation.¹⁰ From a calculation of the \( p-V \) work required to expand a curved surface and to change its surface area, in the special case of a spherical vacancy, it is relatively straightforward to show that this equation is

\[ p_r - p_o = \frac{2\sigma}{R^*} \]  

where \( p_r \) is the internal pressure, which is zero due to a free space inside the vacancy, and \( p_o \) is the external pressure outside the vacancy. \( \sigma \) is the surface tension of the inner wall. By integrating Eq. (3) from \( R^* = R^* \) to \( R^* = \infty \), then inserting the pressure difference from Eq. (4) into the resulting equation, and finally using Eq. (2), the chemical potential for the vacancy formation is given by

\[ \mu_v (R^*) - \mu_v (\infty) = \frac{8\pi}{3} N_A \sigma R^*^2 \]  

where \( \mu_v (R^*) \) and \( \mu_v (\infty) \) are the chemical potential of the vacancy and that at the bulk of the solution, respectively. It should be noted that though within the mean-field approximation, Eq. (5) is the rigorous equation for the vacancy formation. Therefore, measuring the radius of the vacancy, we can calculate the exact formation energy of the vacancy.

Although according to Gibbs’s adsorption isotherm, the surface excess of the anion emerges at the inner wall, as elucidated in Appendix A, the surface tension of the inner wall is not affected by the adsorption of the anions, so that the surface tension is equal to that of the electrolyte solution without adsorption. As for electrolyte solutions, the amount of electrolyte hardly changes the value of the surface tension. In the case of 1 mole dm⁻³ NaCl solution, the value slightly increases from that of pure water by 2.7%, where the effect of air can be negligible.¹¹ Therefore, in the present case, the following relationship

\[ \begin{align*}
\text{Fig. 1} & \quad \text{Vacancy formation process in electrodeposition.} \ 
\end{align*} \]

\[ \text{Fig. 2} & \quad \text{Structure of a vacancy based on a mean-field approximation. The area of minus sign is the electrically charged inner wall, and the area of plus sign expresses the ionic atmosphere.} \ 
\]
\[ \sigma = \sigma_w \]  
\[ \text{can be adequately used, where } \sigma_w \text{ is the surface tension of pure water.} \]

2. 2 Compensation of vacancy formation energy by electrostatic interaction

Equation (5) indicates that the vacancy formation requires a certain extra work, so that the vacancies are not self-organized. However, the electrically charged inner wall attracts ions of opposite charge and repels ions of like sign. Random thermal motion of the ions and the solvent molecules (i.e., water molecules) tends to counteract this electric effect and promote a random distribution of ions, forming an ionic atmosphere around a vacancy. The balance of these competing effects of ionic species in the ionic atmosphere can be expressed by a Boltzmann distribution of ionic concentrations:

\[ C_i = C_i (\infty) \exp \left( \frac{-z_i F \Phi}{RT} \right) \]  
\[ \text{where } z_i \text{ is the charge number of the ionic species } i \text{ including sign, and } R \text{ and } T \text{ are the universal gas constant and the absolute temperature, respectively. } C_i (\infty) \text{ is the average concentration (bulk concentration) of the species } i. \text{ Far from the inner wall, the potential } \Phi \text{ approaches zero and consequently, } C_i \text{ approaches } C_i (\infty). \]

The chemical potential variation for the vacancy formation, as will be discussed, can decrease as a result of the electrostatic interaction between the charged inner wall and the ionic atmosphere. Though only the coulombic electrical force is considered here, other contributions to the interaction energy are also possible. Therefore, all the non-ideality of ionic solution accompanying the interaction would be cancelled out by the vacancy formation, and as is discussed in Appendix A, this is the reason why the charged inner wall does not change the surface tension. It can be also said that the vacancy solely acts as an ideal ion with the activity coefficient of unity.

For the actual calculation of the electrostatic interaction, it is necessary to find the eventual distribution of the ionic atmosphere and the electric work to add electric charges to the vacancies. The electrostatic potential results not only from the charged inner wall but also from the other ions that are attracted toward or repell from the origin. In the present case, because a spherical ionic atmosphere is considered, the following simplified Poisson’s equation in spherical coordinates can be employed to calculate the potential distribution.

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Phi}{dr} \right) = -\frac{\rho_e}{\epsilon} \]  
\[ \text{where } \epsilon \text{ is the dielectric constant of pure solvent (i.e., pure water). } \rho_e \text{ is the electric charge density at the distance from the center of the vacancy } r, \text{ expressed by} \]

\[ \rho_e = F \Sigma z_i C_i \]

Equation (8) describes the potential distribution around the inner wall in terms of the known average concentration \( C_i (\infty) \). According to the conventional Debye and Hückel approximation, the average molar energy of the electrostatic interaction is assumed to be smaller than the average thermal molar energy \( RT \), so that the following relationship can be utilized.

\[ \exp \left( -\frac{z_i F \Phi}{RT} \right) = 1 - \frac{z_i F \Phi}{RT} \]  
\[ \text{Substituting Eq. (10) into Eq. (7) and using the resultant equation, we can rewrite Eq. (9) as} \]

\[ \rho_e = -\frac{e \Phi}{\lambda^2} \]
\[ \text{where } \lambda \text{ is the Debye length given by} \]

\[ \lambda = \left( \frac{e RT}{F \Sigma z_i C_i (\infty)} \right)^{1/2} \]

\[ \text{where } \Sigma z_i C_i (\infty) = 0 \text{ is used for the electroneutrality. The inner walls of other vacancies as well as the centers of other ions are supposed to be precluded from approaching within a distance } R^* \text{ of the radius of the vacancy because of the short-range repulsive force of the adsorbed anions at the inner wall (Born repulsive force).} \]

Equation (8) can be applied for \( r > R^* \), so that the boundary condition at \( r = R^* \) can be found by applying Gauss’s law to the region within \( r = R^* \), i.e.,

\[ 4\pi r^2 \left( -\frac{d\Phi}{dr} \right) = q_e \]  
\[ \text{for } r = R^* \]

\[ \text{where } q_e \text{ is the electric charge of the anions at the inner wall shown in Eq. (1). Since the inside of the inner wall is a free space, } \epsilon_0 \text{ is the dielectric constant of free space. Equation (13) together with the other boundary condition} \]

\[ \Phi = 0 \quad \text{for } r = \infty \]

allows us to solve Eq. (8), i.e.,

\[ \Phi (r) = -\frac{\alpha z_m e}{4\pi \epsilon_0 r} e^{-r^2/\lambda^2} + \Phi_0 \]

\[ \text{where as elucidated in Eq. (1), } z_m \text{ is the charge number of the metallic ion, } e \text{ is the elementary charge, and } \alpha \text{ is the transcription coefficient of the anion. The potential due to the charged inner wall alone would be } -\frac{\alpha z_m e}{4\pi \epsilon_0 r}. \text{ Equation (15) therefore reveals that the other ions attracted toward the origin of the vacancy, being of opposite sign to the inner wall, lower the magnitude of the potential and cause it to vanish rapidly at large distances from the vacancy. Thus, ions at the same distance are shielded from the charge of the inner wall by these other ions.} \]

Then, using Eq. (15), we can calculate the electric
work required for making ionic atmospheres around the inner walls. The reversible electric work per unit mole of species at constant temperature and constant volume is equal to its molar Helmholtz free energy. From Appendix B, the contribution \( \mu_{vd} \) to the chemical potential of the vacancy \( \mu_v \) is thus expressed by

\[
\mu_{vd} = \frac{\alpha e^2 \varepsilon_0 \varepsilon}{8 \pi \varepsilon_0 \lambda} \frac{1}{1 + R^*/\lambda}.
\]

(B4)

2.3 Determination of the radius of the vacancy

Since the formation work of the vacancy is compensated with the formation work of the ionic atmosphere, the total change in the chemical potential of the vacancy for both of the contributions is kept equal to zero, i.e., from Eqs. (5) and (B4),

\[
\mu_v(R^*) - \mu_v(\infty) + \mu_{vd} = 0
\]

(16)

First of all, the approximated equation of \( R^* \) is derived under the condition where \( R^* \) is much smaller than the Debye length

\[
R^*/\lambda, \ll 1
\]

Equation (B 4) is thus simplified as

\[
\mu_{vd} = \frac{\alpha e^2 \varepsilon_0 \varepsilon}{8 \pi \varepsilon_0 \lambda}
\]

(18)

Substituting Eqs. (5) and (18) into Eq. (16), and using Eq. (6), we obtain the approximated equation,

\[
R_{\text{app}}^* = \frac{\alpha e^2 \varepsilon_0 \varepsilon}{8 \pi \varepsilon_0 \lambda} \left[ \frac{3}{e \sigma v \lambda} \right]^{1/2}
\]

(19)

For convenience, suppose that the supporting electrolyte is only a majority salt, so the Debye length is given by

\[
\lambda = \frac{1}{F} \left[ \frac{e^2 RT}{2 z_e^2} \right]^{1/2} C_i(\infty)^{-1/2}
\]

(20)

where \( C_i(\infty) \) is the average concentration of the supporting electrolyte, \( z_e \) and \( z_\lambda \) being the numbers of the electric charges of the cation and anion including signs. Substitution for \( \lambda \) from Eq. (20) in Eq. (19) leads to

\[
R_{\text{app}}^* = \frac{\alpha e^2 \varepsilon_0 \varepsilon}{8 \pi \varepsilon_0 \lambda} \left[ \frac{3F}{e \sigma v \lambda} \right]^{1/2} \frac{z_e^2 + z_\lambda^2}{z_e^2} \left[ \frac{e^2 RT}{2 z_e^2} \right]^{1/4} C_i(\infty)^{1/4}
\]

(21)

Then, substituting Eqs. (5) and (B4) into Eq. (16), we derive the following equation for rigorous solutions.

\[
\alpha_1 R^* + \alpha_2 R^* - \alpha_3 = 0
\]

(22)

where

\[
\alpha_1 = \frac{8 \pi}{3} N_i \sigma
\]

(23)

3 Calculation and Experiments

Theoretical calculation and its experimental validation were performed for copper deposition from two kinds of electrolyte solutions, KCl and \( \text{H}_2\text{SO}_4 \) solutions; the former contains well-known \( \text{Cl}^- \) anions of specific adsorption, and the latter does not contain such ions. In view of the vacancy formation, the reaction is expressed by

\[
\text{Cu}^{2+} \text{(solution)} + 2e^- \text{ (metal)} \rightarrow \text{Cu} \text{ (metal)} + \text{V}_{\text{Cu}^{2+}} \text{(solution)},
\]

(26)

where \( \text{V}_{\text{Cu}^{2+}} \) implies a vacancy made from \( \text{Cu}^{2+} \) ion. The theoretical calculation was done by computer, using the following data; for KCl solutions were used \( \alpha = 0.5 \) or 1.0, \( z_e = 2 \), \( z_\lambda = 1 \), \( z_\kappa = -1 \), \( F = 96500 \text{ C mol}^{-1} \), \( R = 8.312 \text{ J deg}^{-1} \text{ mol}^{-1} \), \( T = 298 \text{ K} \), \( N_i = 6.0221 \times 10^{23} \text{ mol}^{-1} \), \( e = 1.6021 \times 10^{-19} \), \( \varepsilon = 6.954 \times 10^{-10} \), \( \varepsilon_0 = 7.2 \times 10^{-2} \text{ N m}^{-1} \), \( C_i(\infty) = 100 \) or 250 mol m\(^{-3}\). For \( \text{H}_2\text{SO}_4 \) solutions, the same data except for \( z_\lambda = -2 \) were used. For the case of \( \alpha = 0.0 \), for both solutions, an explicit solution \( R^* = 0.0 \) was mathematically derived from Eq. (22).

To verify the theoretical prediction, we measured the change in the partial molar volume during copper deposition from both electrolyte solutions. In view of equilibrium measurement, the partial molar volume of \( \text{Cu}^{2+} \) (solution) in each electrolyte solution was first measured by using pycnometer. Then, the change in the partial molar volume during the reaction was measured by gravity electrode (GE-02, Nikko Keisoku Co.). Both of the methods have been newly established for these experiments, of which full papers will be published in quite near future. Prior to experiments, dissolved oxygen was removed by bubbling argon gas. The temperature of the solutions were kept at 27 + 2°C. The working electrode was a platinum plate for KCl solution and a copper plate for \( \text{H}_2\text{SO}_4 \) solution, and the counter electrode was a copper plate with the same circular surface of 5 mm in diameter, which were polished mechanically. The reference electrode was a platinum rod with 1 mm in diameter.

As for the experiments in KCl solutions, small amounts of \( \text{CuCl}_2 \) were added to the solutions of 100 and 250 mol m\(^{-3}\) KCl. For gravity electrode, after observing cyclic voltammograms at various gravitational accelerations, limiting-diffusion currents were measured at the overpotential of -0.6 V. As for the experiments in \( \text{H}_2\text{SO}_4 \) solutions, small amounts of \( \text{CuSO}_4 \) were also added to 100 mol m\(^{-3}\) \( \text{H}_2\text{SO}_4 \) solution, and limiting-diffusion currents were measured at the overpotential of -0.4 V. After finishing the experiments, the deposited surfaces were observed by scanning microscope (SEM). Consequently, it was ascertained that the deposited surface remained
flat without any enlargement.

4 Results and Discussion

In Figure 3, theoretically obtained radii of the vacancies are plotted against the concentrations of the supporting electrolyte of KCl. Curve a is obtained for the case of the absence of the electric charge of the vacancy, so that the radius is equal to zero. Curves b and c correspond to the cases of the charge numbers of −1 and −2, respectively, where the radius increases with the charge number.

Figure 4 exhibits the experimental results for the copper deposition from 100 mol m⁻³ potassium chloride solution. The obtained radii of the vacancies are plotted against the concentrations of cupric ion. For comparison, the theoretical values of the radii for the charge numbers, 0 (line a), −1 (line b) and −2 (line c) are also plotted. As a result, the line b is in the best agreement with the experimental data. This means that for the deposition of cupric ion, the vacancies with the charge number of −1 are yielded in potassium chloride solutions.

Then, in Fig. 5, the same kind of plotting is performed for 250 mol m⁻³ potassium chloride solution. For comparison, the theoretical radii for the charge numbers of 0 (line a), −1 (line b), and −2 (line c) are drawn. In this case, the line b is also in the best agreement with the experimental data. Even in higher concentration like this, the agreement between the experiment and the theory is as good as that in the 100 mol m⁻³ solution shown in Fig. 4. Though the electric work calculated by the Debye-Hückel theory is, as will be discussed below, adequate only in dilute solutions, this may be because the expression of the vacancy formation energy in Fig. 5 has sufficient accuracy.

For copper deposition from sulfuric acid solution without anion of specific adsorption, as shown in Fig. 6, the average radii are in good agreement with line c (i.e., the charge number is −2), which means that the transcription of the electric charge by anions is indifferent to specific adsorption, and the charge number of the vacancy depends on both charge numbers of the metallic ion and

![Graph](image1)

**Fig. 3** Theoretical calculation of the radius of the vacancy against the concentration of supporting electrolyte. Curve a corresponds to the electric charge number of 0, curve b to the electric charge number of −1, and curve c to the electric charge number of −2. \( R^* \) is the radius of the vacancy, and \( C_i (\infty) \) is the bulk concentration of KCl. Other calculation data are as follows: \( \alpha = 0.5 \) or 1.0, \( z_m = 2 \), \( z_e = 1 \), \( z = -1 \), \( F = 96500 \) C mol⁻¹, \( R = 8.312 \) J deg⁻¹ mol⁻¹, \( T = 298 \) K, \( N_A = 6.0221 \times 10^{23} \) mol⁻¹, \( \epsilon = 1.6021 \times 10^{-19} \) C, \( \varepsilon = 6.954 \times 10^{-10} \) F m⁻¹, \( \alpha_e = 7.2 \times 10^{-8} \) N m⁻¹.

![Graph](image2)

**Fig. 4** Comparison between theoretical and experimental data of the radius of the vacancy in 100 mole m⁻³ KCl solution. ●: Experimental data. Line a corresponds to the electric charge number of 0, line b to the electric charge number of −1, and line c to the electric charge number of −2. The theoretical data for line b and line c come from those of Fig. 3. \( R^* \) is the radius of the vacancy, and \( C_m (\infty) \) is the bulk concentration of Cu²⁺ ion.

![Graph](image3)

**Fig. 5** Comparison between theoretical and experimental data of the radius of vacancy in 250 mole m⁻³ KCl solution. ●: Experimental data. Line a corresponds to the electric charge number of 0, line b to the electric charge number of −1, and line c to the electric charge number of −2. \( R^* \) is the radius of the vacancy, and \( C_m (\infty) \) is the bulk concentration of Cu²⁺ ion.
Fig. 6 Comparison between theoretical and experimental data of the radius of vacancy in 100 mole m\(^{-3}\) \(\text{H}_{2}\text{SO}_{4}\) solution.

\(\bullet\): Experimental data. Line \(a\) corresponds to the electric charge number of 0, line \(b\) to the electric charge number of \(-1\), and line \(c\) to the electric charge number of \(-2\). \(R^*\) is the radius of the vacancy, and \(C_m(\infty)\) is the bulk concentration of \(\text{Cu}^{2+}\) ion. The calculation data of line \(b\) and line \(c\) are the same as those of Fig. 3 except for \(z = -2\).

the counter anion.

As has been elucidated, within a mean-field approximation, Eq. (5) exactly describes the work required for the vacancy formation in ionic solution. On the other hand, the expression of Debye and Hückel used here for calculating the work to form the ionic atmosphere is valid only in dilute solutions. This restricted range of validity mainly comes from the short-range interaction neglected in the calculation and from the mathematical approximation in Eq. (10). At higher concentrations, ion-solvent interactions and short-range interactions between ions become important. Equation (10) is the only significant mathematical approximation introduced by Debye and Hückel. Its validity depends on the magnitude of \(zF\Phi/RT\) being small compared to unity. However, this ratio is larger than unity. Fortunately, as Newman discussed,\(^{20}\) the Debye-Hückel limiting law can be validated. Interpreting his discussion in the present case, we can say that this is because the potential at \(r = R^*\) in Eqs. (10) and (B4) comes not directly from the vacancy but indirectly from the ionic atmosphere. For extremely dilute solutions, the Debye length becomes very large. This means that most of the ions comprising the ionic atmosphere are at a considerable distance from the vacancy, where the potential due to the vacancy is greatly reduced, and the approximation in Eq. (10) is valid. Consequently, a valid approximation to the concentration distributions in Eq. (10) is obtained in the region where most of the counterbalancing charge is found, and this, in turn, yields a correct value for the potential at \(r = R^*\) due to the ionic atmosphere. This result is obtained even though there is always a region near the vacancy where the approximation is not valid.

It should be also noted that whatever the work of the

Fig. 7 Vacancy formation energy vs. radius of vacancy. Curve (1) was obtained from the calculation for the charge number \(-1\) (\(\alpha = 0.5\)) in 100 mol m\(^{-3}\) \(\text{KCl}\) solution in Fig. 4. Curve (2) was obtained from the calculation for the charge number \(-2\) (\(\alpha = 1.0\)) in 100 mol m\(^{-3}\) \(\text{H}_{2}\text{SO}_{4}\) solution in Fig. 6.

formation of ionic atmosphere may be, it would be exactly cancelled out by the work of the vacancy formation. Therefore, we can exactly determine the formation energy from the experimental data of the vacancy radius. In Fig. 7, as an example, the formation energies against the vacancy radii are plotted.

5 Conclusion

Ionic vacancy is stably formed even in a liquid solution. As the formation mechanism, not only the present process via. electrodeposition but also other processes should be possible. However, the framework for the vacancy formation explained here is always correct, that is, the work of the vacancy formation is compensated by the work of the formation of the ionic atmosphere.

As have been established in solid-state physics and chemistry, vacancies are quasi-particles behaving in the same way as other particles, i.e., molecules and ions.\(^2\) It can be also said that the vacancy in liquid solution is an ideal anion with the activity coefficient of unity. As for other physical quantities, some specific properties in reaction and transportation are now being studied.

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Appendix A Effect of the adsorption of anions on the surface tension of the inner wall

Let us first suppose a solution containing negligibly small amounts of metallic ions and vacancies and a large amount of a single salt (i.e., supporting electrolyte), of which the equation in dissociation equilibrium is written as

\[ C_{\text{c}} A_{\text{c}} \rightleftharpoons v_{\text{c}} C_{\text{c}}^{z_{\text{c}}} + v_{A} A_{\text{c}}^{z_{A}} \tag{A1} \]

where \( C_{\text{c}} \) and \( A_{\text{c}} \) denote the cation and anion of the salt, and \( z_{\text{c}} \) and \( z_{A} \) are the charge numbers of the cation and anion including signs, respectively. The \( v \)'s indicate the numbers of moles of the cation and anion per formula weight of the salt.

In Eq. (A1), the following stoichiometric relationship is derived from the electroneutrality,

\[ v_{\text{c}} z_{\text{c}} + v_{A} z_{A} = 0 \tag{A2} \]

Here, it can be thought that at the inner wall of a vacancy, due to the transcription of anions, a kind of Helmholtz layer of electrical double layer is formed. Therefore, the surface tension of the inner wall would be changed by the adsorption of the ions of the supporting electrolyte. This effect is assessed by means of the following thought experiment: as shown in Fig. A1, it expeditiously starts with regarding the spherical inner wall as a flat surface, of which area is composed of the charged inner wall and adjacent ionic atmosphere corresponding to the two parts of electric double layer, i.e., Helmholtz and diffuse layers, respectively.

For the variations in the surface tension of the inner wall at constant temperature and constant pressure, Gibbs adsorption isotherm becomes

\[ d\sigma = -\Gamma_{-} d\mu_{-} - \Gamma_{+} d\mu_{+} \tag{A3} \]

where \( \mu_{-} \) and \( \mu_{+} \) are the chemical potentials of the cation and anion at the average concentrations (i.e., in the bulk of the solution). \( \Gamma_{-} \) and \( \Gamma_{+} \) are the relative surface excesses of the cation and anion, consisting of two portions, i.e.,

\[ \Gamma_{-} = \Gamma_{-1} + \Gamma_{-2} \tag{A4} \]

\[ \Gamma_{+} = \Gamma_{+2} \tag{A5} \]

where the subscripts 1 and 2 mean the adsorbed layer of the inner wall and the ionic atmosphere, respectively, to be composed of the cations and anions of the supporting electrolyte and water molecules. According to Gibbs’s convention, the water molecules are taken as the reference surface excess, so that the Gibbs surface is chosen such that \( \Gamma_{R,0} = 0 \) and identified with the inner wall. We emphasize that the interface as a whole is electrically neutral.

\[ v_{\text{c}} z_{\text{c}} \Gamma_{-} + v_{A} z_{A} \Gamma_{+} = 0 \tag{A6} \]

Substituting Eqs. (A2) and (A6) into Eq. (A3), we

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**Fig. A1** Schematic structure of a vacancy expressed in the form of plane. IW, inner wall; IA, ionic atmosphere; BS, bulk solution; \( \Gamma_{-} \), surface excess of anion at the inner wall. \( \Gamma_{-2} \) and \( \Gamma_{+2} \) are surface excesses of anion and cation at the ionic atmosphere, respectively.
obtain

$$d\sigma = - \frac{1}{v_{\mu-}} d\mu_{\mu-}$$  \hspace{1cm} (A7)

where $\mu_-$ is the chemical potential of the supporting electrolyte, i.e.,

$$\mu_-=v_+ \mu_+ + v_- \mu_-$$  \hspace{1cm} (A8)

Now imagine the surface of the electrolyte solution without the adsorption of electric charges and let them add to the surface. The anions are now to be transferred reversibly at constant volume from the bulk to the given volume of the inner wall. As a whole, the work involved in this process is an ideal contribution to the change in the chemical potential of the supporting electrolyte. The change in the $\mu_-$ required to bring an element of charge $dq$ from infinity to the distance $r=R^*$ of the inner wall is expressed by

$$d\mu_{\mu-} = \left(\frac{\partial \mu_{\mu-}}{\partial q}\right)_{\mu} dq$$  \hspace{1cm} (A9)

where the subscript $\mu'$ implies that all the components except for $q$, temperature and volume are kept constant. From Eqs. (A7) and (A9), the charging process is given by the following integral.

$$\sigma - \sigma_{i} = - \frac{1}{v_{\mu-}} \int_{-\infty}^{0} \left(\frac{\partial \mu_{\mu-}}{\partial q}\right)_{\mu} dq$$  \hspace{1cm} (A10)

where $q_{i}$ is the electric charge at the inner wall shown in Eq. (1) and $\sigma_{0}$ is the surface tension of the electrolyte solution without the adsorption of ions.

However, as is discussed in this paper, the electric work of the inner wall is completely cancelled out by the work of the vacancy formation. This means that the chemical potential of the supporting electrolyte in the bulk of the solution does not change for the charging; i.e.,

$$\left(\frac{\partial \mu_{\mu-}}{\partial q}\right)_{\mu} = 0$$  \hspace{1cm} (A11)

Namely, it is concluded that the excess charge of the anion at the inner wall does not affect the surface tension of the same wall. From Eqs. (A10) and (A11),

$$\sigma = \sigma_{0}$$  \hspace{1cm} (A12)

is derived. In spite of the charged inner wall, the surface tension remains at the value without adsorption.

**Appendix B Electric work for the ionic atmosphere formation**

The chemical potential of a species can be obtained by the suitable differentiation of the Helmholtz free energy $A$.

$$\mu_i = \frac{\partial A}{\partial n_i} = \frac{\partial A}{\partial C_i} \left(\frac{\partial C_i}{\partial n_i}\right)_{T, \lambda} = \frac{1}{V} \frac{\partial A}{\partial C_i}$$  \hspace{1cm} (B1)

where $V$ is the volume, and $n_i$ is the number of moles of the species $i$. Equation (B1) shows that the chemical potential of the species $i$ is equal to the reversible work of transferring, at constant temperature and constant volume, one mole of the species to a large volume of the solution. The electrical contribution $\mu_{\nu \mu}$ to the $\mu_i$ then comes from an electric work charging one ion or a mole of ions in a solution in which all the other ions are already charged, i.e., forming an ionic atmosphere.

For a vacancy surrounded by its ionic atmosphere, it is necessary to find the electric work to charge up the vacancy. Prior to calculation, it is also required to find the potential at the position of the vacancy formed by the ionic atmosphere, i.e.,

$$\Phi_{\text{atmos}} (r=R^*) = \Phi (r=R^*) - \Phi_i (r=R^*)$$  \hspace{1cm} (B2)

where $\Phi (r=R^*)$ and $\Phi_i (r=R^*)$ are the total potential and the potential formed by the vacancy itself.

Let $\xi$ denote the fraction of the final charge carried by any ion at any time during the charging process. Then, the charge on a vacancy is $-\alpha \xi \mu_e$, and the variation of the charge is $dq = -\alpha \xi \mu_e d\xi$. $\xi$ varies from 0 to 1 during the charging process, and we have

$$\mu_{\nu \mu} = N_i \alpha \xi \Phi_{\text{atmos}} (r=R^*) dq$$  \hspace{1cm} (B3)

and then

$$\mu_{\nu \mu} = \frac{\alpha \xi \mu_e F}{8 \pi \epsilon \kappa} \left(\frac{1}{1 + R^*/\kappa}\right)$$  \hspace{1cm} (B4)

where $F = N_i \mu_e$ is used.