

Fundamental Thermodynamic Limitations in Wagner's Equation in Solid State Electrochemistry

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Abstract: The use of samarium-doped ceria (SDC) electrolytes in SOFCs (solid oxide fuel cells) lowers the open circuit voltage (OCV) below the Nernst voltage (V_{th}), which is obtained using yttria-stabilized zirconia (YSZ) electrolytes. The OCV is classically calculated with Wagner's equation. However, using SDC electrolytes requires both qualitative and quantitative experimental verification of leakage currents. There are additional limitations to using Wagner's equation with SDC electrolytes due to linear transport theory. A constant voltage loss without leakage currents due to a mixed ionic and electronic conducting (MIEC) dense anode has been proposed, and a local equilibrium can be used to address the transition state during ion hopping. Only carrier species having sufficient energy to overcome the activation energy can contribute to current conduction, which is determined by incorporating a different constant in the definitions of chemical potential and electrical potential. This difference explains the results using dense MIEC anodes. In this study, the fundamental thermodynamic basis of this topic is discussed by considering the Boltzmann distribution.

Keywords: SOFC, Ceria, MIEC, Wagner's equation, The Boltzmann distribution.

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) directly convert the chemical energy of gases, such as hydrogen or methane, into electrical energy. A solid oxide film, usually yttria-stabilized zirconia (YSZ), is used as the electrolyte. Oxygen ions serve as the main carriers in the electrolyte. Lowering the operating temperature (873-1273 K) can extend the lifespan of the cells. Therefore, higher ion-conducting electrolyte materials, such as samarium-doped ceria (SDC), have been studied. However, the open circuit voltage (OCV) of SDC cells is about 0.8 V, which is lower than the Nernst voltage (1.15 V) obtained for YSZ cells. The low OCV value is due to the partial electronic conductivity at the anode under a hydrogen gas atmosphere. Wagner's equation [1-2] also predicts this low value, with the OCV being expressed as

$$OCV = \frac{RT}{4F} \int_{pO_2'}^{pO_2''} t_{ion} d \ln PO_2, \quad (1)$$

where F , R , T , t_{ion} , pO_2' and pO_2'' are Faraday's constant, the gas constant, absolute temperature, the ionic transference number, and oxygen partial pressures at the cathode and anode, respectively. Equation 1 is a classical equation that is still used for modern theoretical calculations [3]. The current-voltage relationship from Equation 1 is calculated based on a constant field approximation [4].

Qualitative [5] and quantitative [6] experimental verification of leakage currents is necessary when using SDC electrolytes. However, there are limitations in using Wagner's equation for SDC electrolytes, because of limits in the linear transport theory. The electric field near the cathode

is large enough to cause a dielectric breakdown; although this has never been reported, the constant field approximation is not rational [7]. Consequently, the low OCV value should be possible without any leakage currents.

Instead of Wagner's equation, a local equilibrium can alternatively be used to describe the transition state during ion hopping, and a constant voltage loss without leakage currents due to the mixed ionic and electronic conducting (MIEC) dense anode has been proposed [8]. From conventional theory [4], the current density I of the charge carrier "k" is

$$I_k = -\frac{\sigma_k}{Z_k F} \text{grad} \eta_k, \quad (2)$$

where σ_k , Z_k , and η_k are the conductivity, charge number, and electrochemical potential, respectively, of the charge carrier k. Examples of k include electrons, holes, and ions. The electrochemical potential η_k is expressed as

$$\eta_k = \mu_k + ZF\phi, \quad (3)$$

where μ_k and ϕ are the chemical potential and electrical potential of the charge carrier k, respectively. Only a carrier species that has sufficient energy to overcome the activation energy can contribute to current conduction. Further transformations are necessary in Equation 3, including

$$\mu_{i_hopping} = \mu_{i_vacancy} + NEa, \quad (4)$$

$$ZF\phi_{hopping} = ZF\phi_{vacancy} - NEa, \quad (5)$$

where N , Ea , and $\mu_{i_hopping}$, $\mu_{i_vacancy}$, $\phi_{hopping}$ and, $\phi_{vacancy}$ are Avogadro's number, the activation energy of the oxygen ions, the chemical potential of the ions at the saddle point in the lattice structure during ion hopping, the chemical potential of the ions in vacancies, the electrical potential of ions at the saddle point in the lattice structure during ion

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hopping and the electrical potential of ions in vacancies, respectively.

From Equation 5, including ($Z = -2$, $N/F = 1/e$),

$$\phi_{\text{hopping}} = \phi_{\text{vacancy}} - NEa/ZF = \phi_{\text{vacancy}} + Ea/2e. \quad (6)$$

Therefore, the value of ϕ_{hopping} is a constant, $Ea/2e$, even near the anode. When the ionic transference number is near unity at the cathodic side and sufficiently small at the anodic side, ϕ_{hopping} is neutralized by enough free electrons in the MIEC dense anode. This energy loss becomes thermal energy and is recycled to activate the ions. Even if the ionic current (I_i) is very small, the OCV can be written as

$$\text{OCV} = V_{\text{th}} - RiI_i - \text{polarization voltage losses} - Ea/2e = V_{\text{th}} - Ea/2e, \quad (7)$$

where R_i is the ionic resistance. Equation 7 was already discovered empirically [9]. As an example, the OCV using SDC electrolytes is 0.8 V at 1073 K ($= 1.15 \text{ V} - 0.7 \text{ eV}/2e$). From Equation 7, the OCV is constant during electrode degradation, which has been experimentally verified [5]. Consequently, the constant voltage loss without leakage currents is supported by both the empirical equation and experimental results.

The modification of the transport equations in solid state ionics is not an isolated topic, but requires significant consideration and investigation [10].

Wagner's equation (Equation 1) is widely accepted as a fundamental equation in solid state electrochemistry. This work discusses limitations in Wagner's equation from a fundamental thermodynamic level and considering separation of the Boltzmann distribution.

2. FUNDAMENTAL THERMODYNAMIC LIMITATIONS IN WAGNER'S EQUATION IN SOLID STATE ELECTROCHEMISTRY

2.1. Separation of the Boltzmann Distribution

Wagner's equation (Equation 1) is widely used as a fundamental equation. However, when there are no leakage currents with SDC electrolytes, there are fundamental limitations with classical thermodynamic models. The voltage loss in the OCV using SDC electrolytes can be explained with fundamental limitations. Wagner's equation is included in the Nernst-Planck equation, which is based on the Boltzmann distribution.

The Boltzmann distribution of oxygen ions at 873 K is shown in Fig. (1). Ions with an energy over the ionic activation energy become carriers that can escape from the electrolyte. Because the Boltzmann distribution cannot be separated using passive filters, a problem known as the "Maxwell's demon," the electrochemical potential should be identical between carriers and non-carriers. Therefore, the average energy of ions should be unchanged by separating the Boltzmann distribution, and is confirmed by the second law of thermodynamics. An incorrect distribution of hopping ions is shown in Fig. (2), and the correct distribution is shown in Fig. (3). The shape of the distribution after separation (Fig. 3) is identical to that before the separation, with the only difference being the scale coefficient. In order to explain the loss of electrochemical potential of hopping

ions in Fig. (4), a different constant is needed in the definitions of chemical potential and electrical potential during hopping. Equations 4 and 5 are explained based on the separation of the Boltzmann distribution, and a schematic view of this explanation is shown in Fig. (5).

The separation of the Boltzmann distribution is not accounted for in Wagner's equation, and the consequences of this are discussed in the following section.

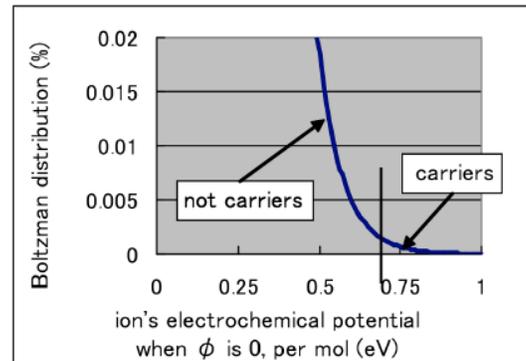


Fig. (1). The Boltzmann distribution.

At 873 K, the percentage of ions with energy above the activation energy (for example, 0.7 eV) is only 0.0092%, and they are carriers that can escape from the electrolytes.

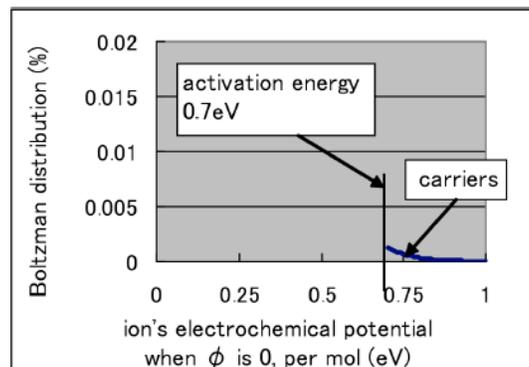


Fig. (2). Incorrect distribution of hopping ions.

This distribution is forbidden by "Maxwell's demon," which can choose ions with larger energy.

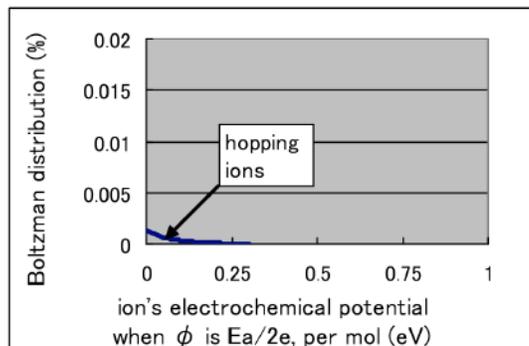


Fig. (3). Correct distribution of hopping ions.

The shape of this distribution is identical to the distribution before separation. The electrochemical potential of the hopping ions ($\eta_{i,\text{hopping}}$) should be the same as the chemical potential of the ions in vacancies ($\eta_{i,\text{vacancy}}$), so there

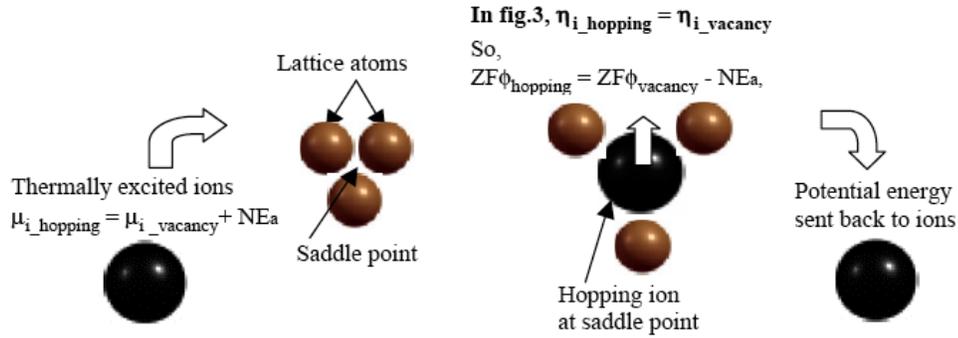


Fig. (4). A schematic view of a different constant in the definitions of chemical potential and electrical potential during hopping.

needs a different constant in the definitions of chemical potential and electrical potential during hopping.

Equations 4 and 5 can be explained based on the separation of the Boltzmann distributions.

2.2. Problems in Separation of the Boltzmann Distribution

2.2.1. The Energy Loss of Hopping Ions

By conventional theory,

$$\eta_{i_hopping} = \eta_{i_vacancy} + NEa \quad (8)$$

Equation 8 is different from the following equation, which was explained in 2.1,

$$\eta_{i_hopping} = \eta_{i_vacancy} \quad (9)$$

By separating the Boltzmann distribution, the electrical potential energy (NEa in Equation 8) should be temporally transferred to the lattice structure during ion hopping and remain entirely with the ions after hopping. Then lattice atoms get potential energy to move from the saddle point during ion hopping. The potential energy of the hopping ions becomes small, even though the total energy of the ions and the lattice structure is not. Consequently, there are no problems with the total energy by separating the Boltzmann distribution.

2.2.2. Energy Loss During Hopping in MIECs

In MIEC electrolytes, the electrical potential of hopping ions is neutralized by free electrons, which get energy from ions and the lattice structure. Therefore, the electrical potential energy cannot be given back to the ions. Even if the ionic current (I_i) is very small, the OCV can be determined, as shown in Equation 7. For example, the OCV using SDC

electrolytes is 0.8 V at 1073 K (= 1.15 V -0.7 eV/2e). A schematic view of the energy loss is shown in Fig. (5).

In MIECs, the energy loss is caused from the separation of the Boltzmann distribution.

2.2.3. Rectification Using Double Layer Electrolytes

At the contact surface between two electrolytes having different activation energies, such as 0.7 eV (electrolyte A) and 1.0 eV (electrolyte B), the distributions of non-carriers are different from each other, as shown in Fig. (6). Ions having energies between 0.7 eV and 1.0 eV can be carriers in electrolyte A, but cannot be carriers in electrolyte B. Therefore, more ions can move as carriers from electrolyte B to electrolyte A at the contact surface. Thus, the direction of rectification can be controlled by the following equation:

$$Ea1 > Ea2, \quad (10)$$

where Ea1 and Ea2 are the activation energies of the different electrolytes that have contact with each other. Equation 10 is important not only for SOFCs, but also for water electrolysis.

The distribution of non-carriers is different in different ionic electrolytes, which explains the rectification.

2.2.4. Describing the Electrical Potential of Hopping Ions in YSZ Electrolytes Under OCV Conditions

The conventional explanation for the electrical potential in YSZ electrolytes under OCV conditions is shown in Fig. (7). For an electrolyte that has an ionic activation energy of 1.0 eV and when the Nernst voltage is 1.15 V, the calculated electrical potential near the cathode is 1.65 V (=1.15 V+1.0 eV/2e), and is greater than the Nernst voltage when $\phi_{vacancy}$ is equal to the Nernst voltage. But there are no problems, since it is impossible to connect hopping ions directly to the

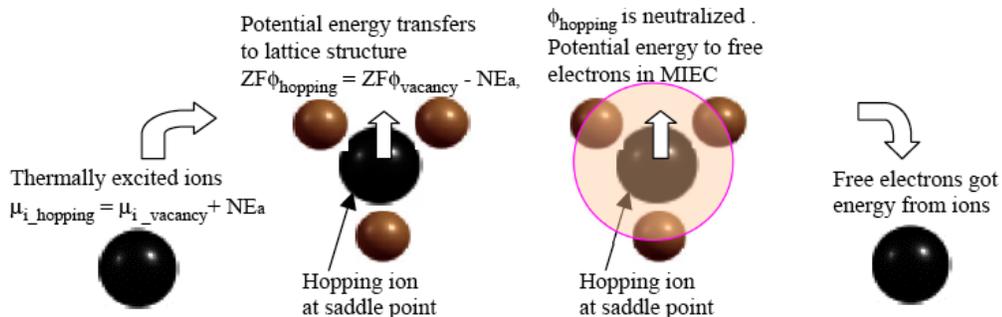


Fig. (5). Energy loss during hopping in MIECs.

electrodes. The electrical potential of hopping ions, which can be carriers in the YSZ electrolyte under OCV conditions, is shown in Fig. (8).

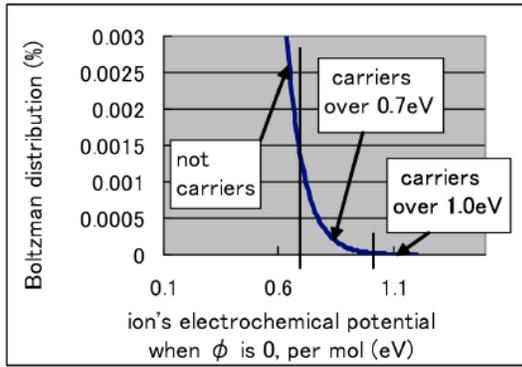


Fig. (6). The direction of rectification.

It is important to make sure that ϕ_{vacancy} is smaller than the Nernst voltage using MIEC dense cathode, since it is possible to connect ϕ_{hopping} to the electrodes.

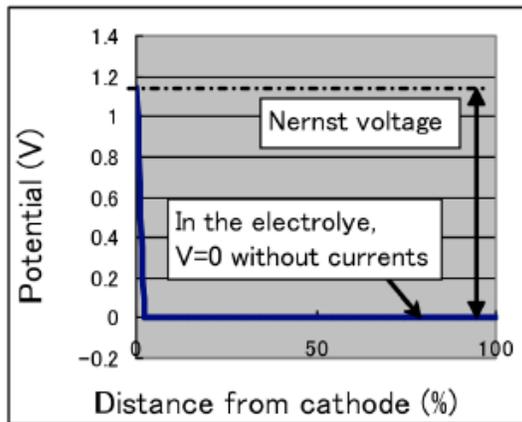


Fig. (7). Conventional electrical potential of ions in YSZ electrolytes under OCV conditions.

In this electrolyte, the electrical potential is zero without any currents.

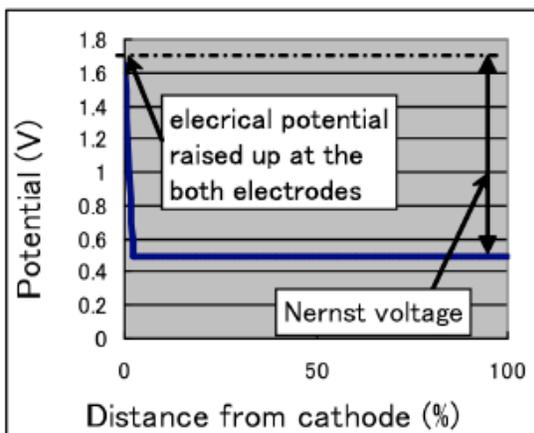


Fig. (8). Electrical potential of hopping ions in YSZ electrolytes under OCV conditions.

It is impossible to connect hopping ions directly to the electrodes using YSZ electrolytes. But it is important to

make sure that ϕ_{vacancy} is smaller than the Nernst voltage using MIEC dense cathode.

2.2.5. Compatibility with Fundamental Equations

Compatibility with fundamental equations is made sure in detail in this section.

2.2.5.1. The First Law of Thermodynamics

Without using MIEC electrolytes, the total energy of ions and the lattice structure is unchanged (written in 2.2.1). So, the first law of thermodynamics is assured. But using MIEC electrolytes, free electrons get energy. Then loss of chemical potential of ions after hopping is equals to NEa . It means that ions can be colder than electrolytes while hopping after traveling the saddle point.

2.2.5.2. The Second Law of Thermodynamics

Without using MIEC electrolytes, hopping process is adiabatic process, since ionic resistance of one hopping is ignorable. It means that the total entropy of ions and the lattice structure should not be changed during hopping. So, the second law of thermodynamics is assured. Since the entropy increase of lattice structure (the thermal energy increase of lattice structure) is enough small during hopping, the decrease of entropy of ions during hopping is ignorable. But using MIEC electrolytes, free electrons get thermal energy. Then the entropy loss of ions (one mol) after hopping is equals to NEa/T . It means that the entropy loss of ions becomes large with lower temperature.

2.2.5.3. Nernst-Planck Equation

Wagner's equation is based on the fundamental Nernst-Planck equation and on the first and second laws of thermodynamics. The Nernst-Planck equation is used not only in the area of solid state electrochemistry, but also in biochemistry, plasma technology and other fields. However, there are not any concepts about the separating the Boltzmann distribution in the Nernst-Planck equation, there.

The separation of the Boltzmann distribution by using a different constant in the definitions of chemical potential and electrical potential should be generalized and added into the Nernst-Planck equation to clarify unknown voltage losses that have previously been ignored as technological problems.

3. SUMMARY

In this study, fundamental thermodynamic limitations in Wagner's equation in solid state electrochemistry were discussed, considering the separation of the Boltzmann distribution. The necessity of a different constant in the definitions of chemical potential and electrical potential was explained.

APPENDIX 1

How to connect or relation between the electrochemical potential (macro description property) and chemical potential of the ions (micro description property) is explained in this Appendix.

The speed of ions at the saddle point should be zero and turned back with the same speed when ions can not through the saddle point, then; the coefficient of restitution is -1. But the loss of the speed of ions is almost nothing when ions can

through the saddle point, since ionic resistance of one hopping is ignorable, then; the coefficient of restitution is 1. So the chemical potential of the ions during hopping (almost same with kinetic energy in micro description property) is larger than ions in vacancies. But the electrochemical potential of ions during hopping (macro description property) should be same with ions in vacancies. Consequently the electrical potential of the ions during hopping (micro and macro description property) is smaller than ions in vacancies.

APPENDIX 2

What is happened when a MIEC electrolyte has more than two kinds of ionic activation energies is explained in this Appendix2.

Some MIEC materials have more than two kinds of ionic activation energies at the same time. The reason is anisotropy or two phase composites. When the ionic transference number is near unity at the cathodic side and sufficiently small at the anodic side,

$$\text{OCV} = V_{\text{th}} - E_{a_small} / 2e \quad (11)$$

$$\text{OCV} = V_{\text{th}} - E_{a_large} / 2e \quad (12)$$

where E_{a_small} and E_{a_large} is smaller ionic activation energy and larger ionic activation energy, respectively, If the main path of ions though the part in which ionic activation energy is E_{a_small} , Equation 1 is right. If the main path of ions though the part in which ionic activation energy is E_{a_large} , Equation 2 is right. So, only observing OCV, we can know the main ionic path. When the OCV is changed abruptly bellow or upper the some temperature, it means that the main path is changed in the electrolyte at this temperature.

APPENDIX 3

About the diffusion of the neutral atoms which do not have electrical potential energies, the role of activation energy of neutral atoms is explained in this Appendix 3.

Electrochemical potential should be same between during hopping and in vacancy. But in this case, electrochemical potential is equal to chemical potential. So, the loss of chemical potential per mol (almost same with kinetic energy in micro description property) during hopping is equal to E_a . Transferring the kinetic energy is easy to be transferring thermal energy which can not be sent back. Maybe the some percentage of E_a is sent back to neutral atom, then; the coefficient of restitution is not 1. This energy loss becomes the increase of thermal energy in the lattice structure and is recycled to activate the neutral atoms.

Consequently, ions transfer potential energy to the lattice structure, but neutral atoms transfer kinetic energy to the lattice structure.

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