

Loss of Gibbs Energy Using Sm-Doped Ceria Electrolytes in SOFCs Considering Local Equilibrium while Ion Hopping

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Abstract: Using Sm-doped Ceria electrolytes (SDC) in SOFCs (solid oxide fuel cell), the open circuit voltage (OCV) becomes lower than the Nernst voltage (V_{th}), which is obtained using Ytria-stabilized Zirconia (YSZ) electrolytes. Classically, OCV is calculated with Wagner's equation. However, experimental verification of leakage currents using SDC electrolytes is necessary, both qualitatively and quantitatively. Furthermore, there are limitations in Wagner's equation using SDC electrolytes, from the limits of linear transport theory. Consequently, the voltage loss in OCV cannot be explained by the conventional transport equations with leakage currents, in which the system as being close to equilibrium. In this report, the constant voltage loss without leakage currents due to mixed ionic and electronic conducting (MIEC) dense anode is proposed, considering the local equilibrium to deal with the transition state while ion hopping. Thus, the effective Gibbs energy is smaller than the theoretical Gibbs energy.

Keywords: SOFC, Ceria, OCV, Wagner's equation, local equilibrium, ion hopping.

1. INTRODUCTION

SOFCs directly convert the chemical energy of fuel gases like hydrogen or methane to electrical energy. Solid oxide film is used as an electrolyte. In the electrolyte, oxygen ions serve as the main carriers. Usually, in these cells, YSZ is used as electrolyte material. If the operating temperature (873-1273 K) could be lowered, the life span of cells could be extended. By lowering the temperature, the use of higher ion-conducting electrolyte materials such as SDC has been studied. But the OCV using SDC cell is about 0.8 V and is lower than the Nernst voltage (1.15 V) using the YSZ cell. The low value in the OCV is due to partial electronic conductivity under a hydrogen gas atmosphere at the anode. The energy conversion efficiency of SOFCs is determined by the ratio of the operated voltage to the theoretical voltage. Consequently, the investigation of voltage loss in OCV is very important. The low value of OCV is explained by Wagner's equation [1], expressed as:

$$OCV = \frac{1}{4F} \int_{\mu_{O_2}'}^{\mu_{O_2}''} t_{ion} d\mu_{O_2} \quad (1)$$

where F , μ'_{O_2} and μ''_{O_2} are Faraday's constant and the chemical potentials of oxygen on the cathodic and anodic sides of the electrolyte, respectively. The oxygen chemical potential is given by:

$$\mu_{O_2} = \mu_{O_2}^0 + RT \ln\left(\frac{p_{O_2}}{p_{O_2}^0}\right) \quad (2)$$

where R is the gas constant and T is the absolute temperature in Kelvin. The standard oxygen chemical potential and the

standard oxygen pressure are represented as $\mu_{O_2}^0$ and $p_{O_2}^0$ are, respectively. Combining Equations 1 and 2 gives [2]:

$$OCV = \frac{RT}{4F} \int_{p_{O_2}'}^{p_{O_2}''} t_{ion} d \ln p_{O_2} \quad (3)$$

where p_{O_2}' and p_{O_2}'' are the oxygen partial pressures at the cathode and anode, respectively. Equation 3 is a classical equation that is still used for modern theoretical calculations [3], which is within the limits of linear transport theory. The current-voltage relation from Equation 3 was calculated from the constant field approximation [4].

However, experimental verification of leakage currents using SDC electrolytes is necessary, both qualitatively [5] and quantitatively [6]. Furthermore, there are limitations in Wagner's equation using SDC electrolytes, coming from the limits of linear transport theory. The electric field near the cathode is large enough to lead to a dielectric breakdown which has never been reported, and the constant field approximation is not rational [7].

Considering the local equilibrium to deal with the transition state while ion hopping, the constant voltage loss without leakage currents is explained in the next section.

2. CONSTANT VOLTAGE LOSS WITHOUT LEAKAGE CURRENTS WHILE ION HOPPING

From the conventional theory [4], the current density I of the charge carrier "k" is:

$$I_k = -\frac{\sigma_k}{Z_k F} \text{grad} \eta_k \quad (4)$$

where F , σ_k , Z_k , and η_k are the Faraday's constant, the conductivity, the charge number and the electrochemical potential, respectively, of the charge carrier k. Examples of k

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include electrons, holes and ions. Z_k should be nonzero to avoid problems with Equation 4. The electrochemical potential η_k is expressed as;

$$\eta_k = \mu_k + ZF\phi \tag{5}$$

where μ_k and ϕ are the chemical potential and the electrical potential of the charge carrier k , respectively.

Using Kröger-Vink notation, the simplest local equilibrium while ion hopping is represented by Anti-Frenkel disorder;



For ions, the following problems exist with Equation 5. Only the carrier species O_i'' (hopping ions) which has sufficient energy to overcome activation energy can contribute to current conducting. But conventional theory ignores the concept of effective carriers hopping in ionic conduction, since the hopping time is very small. Consequently, the difference between O_o^x and O_i'' is ignored in Equation 5.

The chemical potential energy of the carriers (O_i'') is larger than that of non-carriers (O_o^x). This is because the hopping ions are thermally excited and have greater-than-ionic activation energy (for example, 0.7 eV). But the electrical potential energy of O_i'' is smaller than that of O_o^x . Ions move from vacancies to any other vacancies through the saddle point in the lattice structure. The kinetic energy of ions equals the ionic activation energy (0.7 eV). So the speed of ions is 2.9 km/sec. If the speed of ions is smaller than 2.9 km/sec, the ions cannot travel through the saddle point. At the saddle point, the speed of the ions should be zero, it means that electrochemical potential energy should be same between O_i'' and O_o^x . However, the loss of kinetic energy is on the order of 0.003 eV and ignorable, which can be calculated from ionic resistance. Consequently, the electrochemical potential of O_i'' should be decreased by the electrical potential made by lattice atoms that should be moved by hopping ions. So the electrical potential energy should be smaller than O_o^x . The situation is shown in Fig. (1).

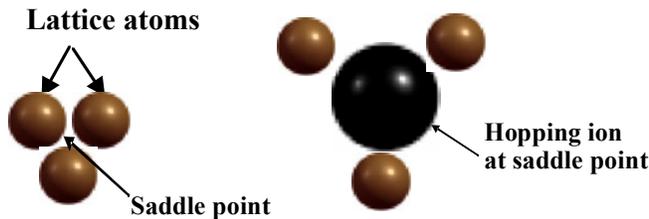


Fig. (1). The situation of hopping ion at saddle point.

The electrochemical potential energy of hopping ions should be decreased by the electrical potential made by the lattice atoms which are moved by hopping ions.

From the above arguments considering the local equilibrium to deal with the transition state while ion hopping, in Equation 5, subsequent transformations are

necessary. Here, ϕ does not exist at the vacancies, but exist at the saddle point in the lattice structure during ion hopping:



where N , Ea , μ_i are Avogadro's number, the activation energy of oxygen ions and the chemical potential of the ions, respectively. These transformations show that compared to conventional values, $ZF\phi$ becomes small, the electrochemical potential does not change, and μ_i is increased in the electrolytes.

From Equation 7, including ($Z = -2$, $N/F = 1/e$), we see:

$$\phi \rightarrow \phi + NEa / ZF \rightarrow \phi - Ea/2e \tag{9}$$

Therefore, the value of ϕ 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 is neutralized by enough free electrons in the MIEC dense anode. This voltage loss becomes thermal energy and is recycled to activate ions. The situation is shown in Fig. (2). Even if ionic current (I_i) is very small, the OCV is written as:

$$OCV = V_{th} - R_i I_i - \text{polarization voltage losses} - Ea/2e = V_{th} - Ea/2e \tag{10}$$

where R_i is ionic resistance. Equation 10 was already discovered empirically [8]. For example, OCV using SDC electrolytes is 0.8V at 1073K ($= 1.15V - 0.7eV/2e$). From Equation 10, the OCV is constant during electrode degradation, which was made sure, experimentally [5]. Consequently, the constant voltage loss without leakage currents is supported by the empirical equation and experimental results. Consequently, the loss of Gibbs energy can be explained without leakage currents.

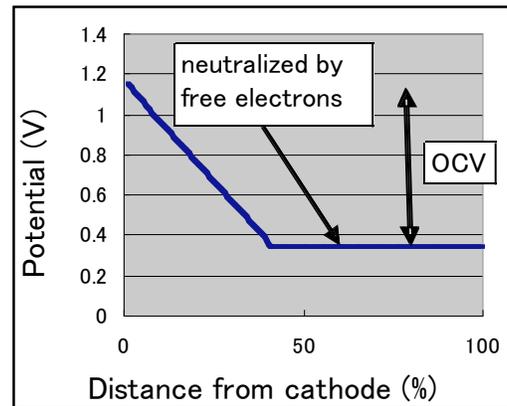


Fig. (2). Relationship between potential made by ions and distance from cathode.

Electrical potential in the electrolyte is different from the anode surface (0 V). If there are enough free electrons, this potential should be neutralized by free electrons.

Experimentally, there are no observable effects in Equation 7 and 8 when the MIEC dense anode is not used. The reason is that the neutralization requires a sufficient number of free electrons from the dense MIEC anode. In the most of other cases such as YSZ electrolytes having only ionic conduction or Ni electrodes having only electronic conduction, there are no contradictions in the typical results of standard and experiment. Furthermore, unexplained

phenomena can be elucidated. Until the anode polarization voltage loss is over than $E_a/2e$ ($=0.35$ V), this voltage loss is masked by the loss of the OCV. So,

$$\text{Cell voltage} = \text{OCV} - R_i I_{\text{ext}} - \text{cathode polarization voltage loss} \quad (11)$$

where I_{ext} is external current. Equation 11 has already been used for cube-type SOFCs [9].

3. DISCUSSIONS

Using SDC electrolytes in SOFCs, the OCV becomes lower than Nernst voltage, which is obtained using YSZ electrolytes. Classically, the OCV is calculated with Wagner's equation. However, experimental verification of leakage currents using SDC electrolytes is necessary, both qualitatively and quantitatively. Furthermore, there are limitations in Wagner's equation using SDC electrolytes, which result from the limits of linear transport theory.

In this report, the constant voltage loss without leakage currents due to MIEC dense anode is proposed considering the local equilibrium to deal with the transition state while ion hopping. Transformations (Equation 7 and 8) during hopping are necessary. The value of ϕ is a constant, $E_a/2e$, even near the anode, which is neutralized by free electrons. The voltage loss is constant and equals $E_a/2e$. Then, the OCV is expressed by Equation 10, which was already discovered empirically. From Equation 10, the OCV is constant during electrode degradation, which was made sure experimentally. Consequently, the constant voltage loss without leakage currents is supported by the empirical equation and by experimental results, and thus the effective Gibbs energy is smaller than the theoretical Gibbs energy.

In the voltage loss without leakage currents, the compatibility with the second law of thermodynamics should be made sure. At 873 K, the Boltzmann distribution is shown in Fig. (3). The number of ions over 0.7 eV is only 0.0092%, and they become carriers which can escape from electrolyte. Since we cannot separate the Boltzmann distribution using passive filters which is well known as "Maxell's demon", the electrochemical potential should be same between carriers and non-carriers, and the electrical potential energy of the carriers is smaller than that of non-carriers. Consequently, transformations (Equation 7 and 8) during hopping are supported by the second law of thermodynamics. The

generalization of the effective Gibbs energy will be discussed in the next report.

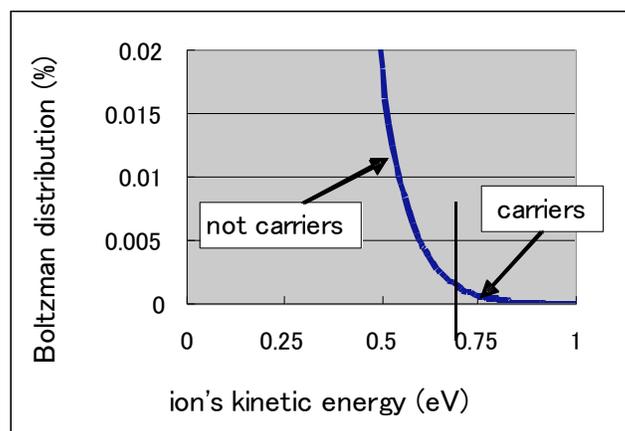


Fig. (3). Boltzmann's distribution and "Maxell's demon".

At 873 K, the number of ions over 0.7 eV is only 0.0092%, and they become carriers that can escape from the electrolytes. We cannot separate the Boltzmann distribution using passive filters.

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