

# Theoretical Verification Necessity of Leakage Currents Using Sm Doped Ceria Electrolytes in SOFCs

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**Abstract:** Numerous approaches have been made to solve the basic transport equation that describes a solid oxide fuel cell (SOFC) with mixed conduction. Classically, the open circuit voltage (OCV) is calculated with Wagner's equation, which is right within the limits of linear transport theory. In order to generalize Wagner's equation, many models have been proposed to describe the current-voltage relation in mixed ionic electronic solid conductors (MIEC) using constant field approximation to calculate an electronic current. However, experimental verification necessity of leakage currents in SOFCs using Sm doped Ceria electrolytes has already been pointed out both qualitatively and in quantities. Using the constant field approximation, the limits of linear transport theory can not be clear. In this report, a new model is expressed without using the constant field approximation. This model follows from Wagner's equation and continuity. The calculated electronic current for doped Ceria electrolyte matches the values calculated using conventional models. But the electrical field near the cathode is large enough to cause dielectric breakdown which has never been reported. Continuity is not deniable, so there are limitations in Wagner's equation, coming from the limits of linear transport theory.

**Keywords:** SOFC, Ceria, Wagner's equation, Constant field approximation, Riess's model.

## 1. INTRODUCTION

The Nernst voltage ( $V_{th}$ ) is expressed as:

$$V_{th} = \frac{RT}{4F} \ln\left(\frac{pO_2'}{pO_2''}\right) \quad (1)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature in Kelvin.  $F$  is the Faraday's constant.  $pO_2'$  and  $pO_2''$  are the oxygen partial pressures at cathode and anode, respectively. With mixed conducting electrolytes, there are ionic ( $I_i$ ) and electronic currents ( $I_e$ ), even in the absence of an external current. When  $t_{ion}$  (ionic transference number) is constant,

$$I_i = \frac{V_{th} - OCV}{R_i} \quad (2)$$

$$I_e = -\frac{OCV}{R_e} \quad (3)$$

where  $R_i$  and  $R_e$  are ionic resistance and electronic resistance of the electrolyte, respectively. Here, the sum of  $I_i$  and  $I_e$  is zero. Thus,

$$OCV = \frac{R_e}{R_i + R_e} V_{th} \quad (4)$$

Wagner's equation is expressed as [1]:

$$t_{ion} = \frac{R_e}{R_i + R_e} \quad (5)$$

$$OCV = t_{ion} \times \frac{RT}{4F} \ln\left(\frac{pO_2'}{pO_2''}\right) \quad (6)$$

In Equation 6, the constant field approximation in equation 6 is justified because  $R_i$  and  $R_e$  are constant. When  $t_{ion}$  is not constant in the electrolyte, Wagner's equation is expressed as [1]:

$$OCV = \frac{1}{4F} \int_{\mu O_2''}^{\mu O_2'} t_{ion} d\mu O_2 \quad (7)$$

where  $\mu' O_2$  and  $\mu'' O_2$  are the chemical potentials of oxygen on the cathode and anode side of the electrolyte, respectively. The oxygen chemical potential given by,

$$\mu O_2 = \mu O_2^0 + RT \ln\left(\frac{pO_2}{pO_2^0}\right) \quad (8)$$

where  $\mu O_2^0$  and  $pO_2^0$  are the standard oxygen chemical potential and the standard oxygen pressure, respectively. Thus, combining equations 7 and 8 gives [2],

$$OCV = \frac{RT}{4F} \int_{pO_2''}^{pO_2'} t_{ion} d \ln pO_2 \quad (9)$$

When  $t_{ion}$  is constant in the electrolyte, Equation 9 and Equation 6 are identical. Equation 9 is a classical equation that is still used for modern theoretical calculations [3], which is right within the limits of linear transport theory.

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The generalized form of equation 9 allows for  $I_e$  to be calculated from the constant field approximation [4].

However, experimental verification necessity of leakage currents using Sm doped Ceria electrolytes in SOFCs was already made sure qualitatively [5] and in quantities [6].

## 2. CURRENT-VOLTAGE RELATION IN MIXED IONIC ELECTRONIC SOLID CONDUCTORS

In order to calculate the current-voltage relation in MIEC, we consider the following:

$$I_e = -k \times I_i \quad (10)$$

where  $k$  is constant in the electrolyte, from Equation 2 and Equation 3,

$$I_i = \frac{V_{th} - V_{cell}}{R_i} \quad (11)$$

$$I_e = -\frac{V_{cell}}{R_e} \quad (12)$$

$$I_{ext} = I_i + I_e = (1-k) \times I_i = (1-k) \times \frac{V_{th} - V_{cell}}{R_i} \quad (13)$$

where  $V_{cell}$  and  $I_{ext}$  are the cell voltage and output current, respectively. From Equations 10, 11 and 12,

$$V_{cell} = \frac{k \times R_e}{R_i + kR_e} V_{th} \quad (14)$$

$$f(k) = \frac{k \times R_e}{R_i + k \times R_e} = \frac{k \times t_{ion}}{(k-1) \times t_{ion} + 1} \quad (15)$$

where  $f(k)$  is solely a function of  $k$ . If  $t_{ion}$  is not constant for the electrolytes, then  $f(k)$  is not constant. Under these conditions, the electrolyte is treated as a collection of series meshes. The voltage is calculated by summing the voltages for each mesh, given their local oxygen pressure in the electrolyte. This scenario is graphically depicted in Fig. (1). In Fig. (1), Considering continuity,  $I_i$  and  $I_e$  should be same value in every mesh. Equation 14 and Equation 15 are applied for each mesh, therefore,

$$V_{cell} = \frac{RT}{4F} \int_{p_{O_2}}^{p_{O_2}^{O''2}} f(k) d \ln p_{O_2} \quad (16)$$

Equation 16 is a generalized version of Wagner's equation. When  $k$  equals to 1,  $V_{cell}$  equals to OCV, so Equation 16 and Equation 9 are identical. For doped Ceria electrolytes,  $t_{ion}$  is expressed as [3]:

$$t_{ion} = \frac{1}{1 + \left(\frac{p_{O_2}}{p_{O_2}^*}\right)^{-\frac{1}{4}}} \quad (17)$$

where  $p_{O_2}^*$  corresponds to an oxygen partial pressure at which the ionic transference number is 0.5. Unfortunately,

Equation 16 and 17 cannot be integrated mathematically, and must be solved numerically. By continuity, the thickness of each mesh is:

$$l_{mesh} = l_{average} \left( \frac{1 - f_{mesh}(k)}{1 - f_{average}(k)} \right) \quad (18)$$

where  $f_{average}(k)$  comes from Equation 14 and  $l_{average}$  is the calculated thickness of the mesh using  $f_{average}(k)$ .  $f_{mesh}(k)$  and  $l_{mesh}$  represent  $f(k)$  and actual mesh thickness, respectively. A mathematical proof for Equation 18 is given in Appendix 1. Equation 18 shows that the oxygen partial pressure in the electrolyte is determined by continuity and Wagner's equation.

Calculations were done using 500 mesh elements in Microsoft Excel, without a numerical solver. The temperature was 873K. 100% Oxygen gas (1atm) was fed to the cathode, and hydrogen gas with 3% steam was supplied to the anode as the fuel gas ( $8.3 \times 10^{-28}$  atm). At 873K,  $p_{O_2}^*$  is  $2 \times 10^{-25}$  atm [6]. The  $R_i$  was 1 ohm. Conductivity is 0.02 S/cm. Using 1cm<sup>2</sup> electrodes, thickness is 0.02cm (=0.02/1). A 30 meshes calculation example is shown in Appendix 2.

$V_{th}$  is 1.174 V. When  $k$  is 1,  $t_{ion}$  is 0.898. The corresponding OCV is 1.054V (= 1.174V × 0.898), which also agrees with previous work [7]. The calculations for the relationship between  $t_{ion}$  and  $\log(p_{O_2})$  are shown in Fig. (2). These results agree with previous reports [6].

The ionic current-voltage relation, electronic current-voltage relation, external current-voltage relation and external current-power output relation are shown in Figs. (3-6), respectively.

From Reiss's model [4],  $I_e$  is;

$$I_e = \frac{V_{th} - V}{R_{e\_cathode}} \times \frac{e^{-\beta q(V_{th}-V)} - e^{-\beta q V_{th}}}{1 - e^{-\beta q(V_{th}-V)}} \quad (19)$$

where  $\beta$ ,  $q$  and  $R_{e\_cathode}$  are the reciprocal of the multiplication of Boltzmann constant and absolute temperature, elementary charge and electronic resistance near the cathode. The  $R_{e\_cathode}$  was 3.94 ohm at OCV condition. This value is much less than the resistance of air, 1.3 M ohm, when  $R_i$  is 1 ohm, which has been explained by the high mobility of electrons. The calculated electronic current matches the values predicted by Reiss' model. Theoretical explanation is shown in Appendix 3.

The calculated relationship between the distance from the cathode and voltage,  $\log(p_{O_2})$ ,  $\log(\text{electrical field})$  are shown in Figs. (7-9), respectively. As seen in Figs. (7, 8), in the absence of a large external current, voltage and  $\log(p_{O_2})$  change abruptly near the cathode. Without large external currents, large voltage losses are observed in the 0.02% thickness of electrolytes near the cathode. With 0.02cm thick electrolytes, this distance is 40nm. The lattice constant is 0.54nm, which means that there are only 74 lattices within the 40nm distance. Therefore, the constant field approximation cannot be used in this case. As seen in Fig. (9), a problem is discovered in our calculation. Even for an electrolyte 0.02cm thick, the electrical field near the cathode

is greater than 880MV/m. This value is large enough to cause dielectric breakdown which has never been reported.

Consequently, continuity is not deniable, so there are limitations in Wagner's equation, coming from the limits of linear transport theory. Leakage currents in SOFCs using doped Ceria electrolytes must be completely verified theoretically.

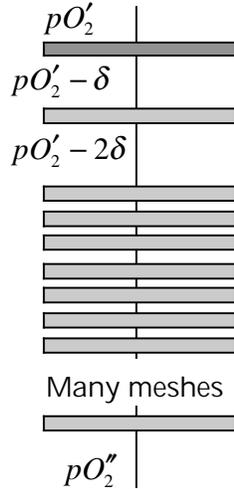


Fig. (1). Graphical depiction of Eq. 16. Considering continuity,  $I_i$  and  $I_e$  should be same value in every mesh. Equation 14 and Equation 15 are applied for each mesh.

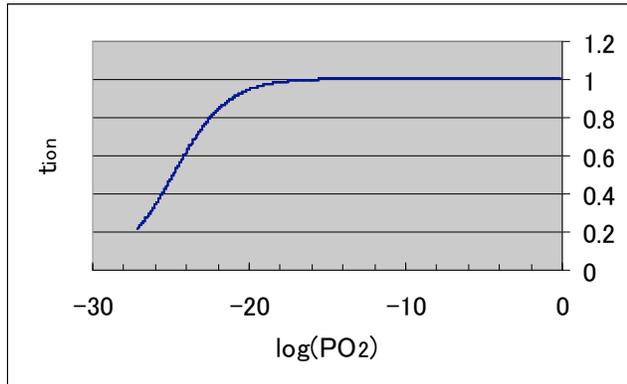


Fig. (2). Relationship between  $\log(pO_2)$  and  $t_{ion}$ . These results agree with previously reported experimental results.

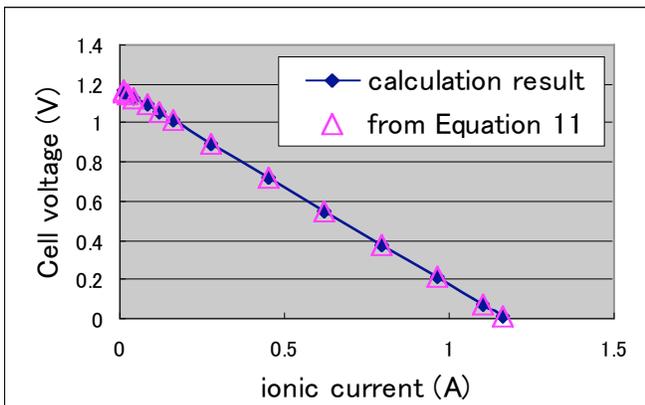


Fig. (3). Ionic current-voltage relation. The calculation results agree with Eq. 11.

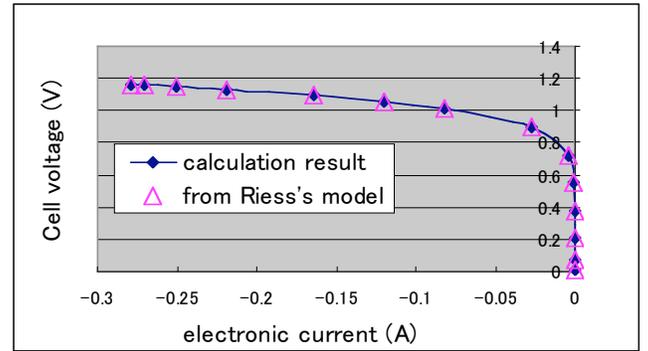


Fig. (4). Electronic current-voltage relation. The calculated electronic current matches the values predicted by Riess' model.

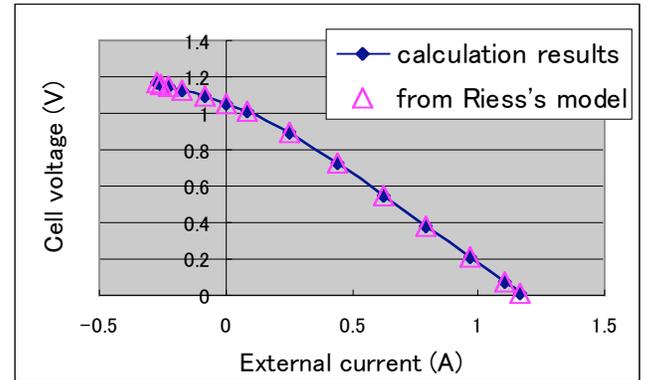


Fig. (5). External current-voltage relation. The calculated external current matches the values predicted by Riess' model.

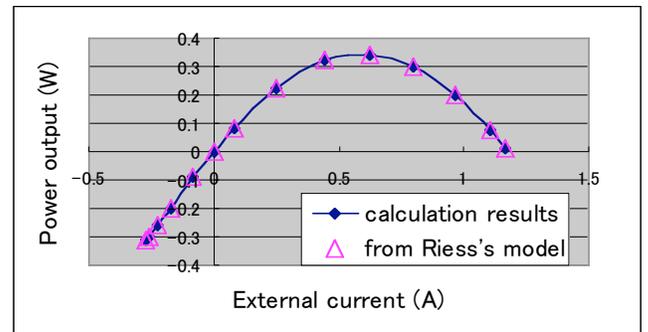


Fig. (6). External current-power output relation. The calculated power output matches the values predicted by Riess' model.

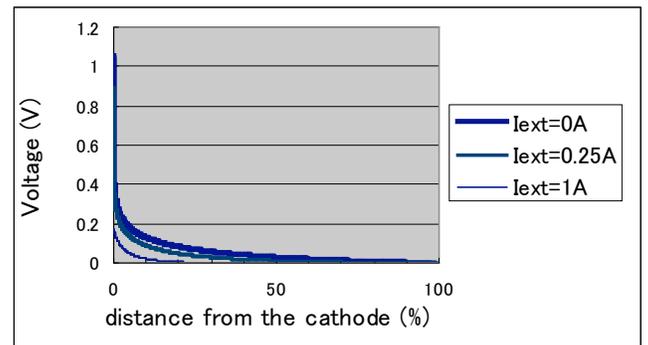
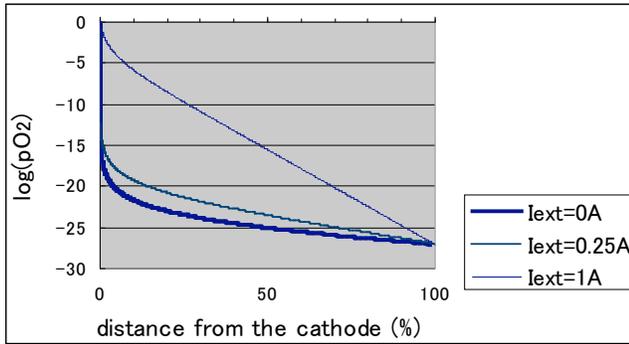
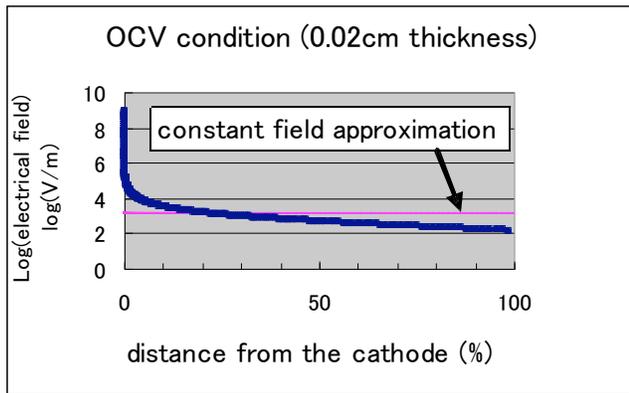


Fig. (7). Relationship between distance from the cathode and voltage. Without large external current, voltage abruptly changes near the cathode.



**Fig. (8).** Relationship between the distance from the cathode and  $\log(pO_2)$ . Without large external current,  $\log(pO_2)$  abruptly changes near the cathode.



**Fig. (9).** Relationship between the distance from the cathode and  $\log(\text{electrical field})$ . Even for an electrolyte 0.02cm thick, the electrical field near the cathode is greater than 880MV/m.

### 3. SUMMARY

Numerous approaches have been made to solve the basic transport equation that describes SOFCs with mixed conduction. Classically, OCV is calculated with Wagner's equation, which is right within the limits of linear transport theory. In order to generalize Wagner's equation, many models have been proposed to describe the current-voltage relation in MIEC using constant field approximation to calculate an electronic current. Experimental verification necessity of leakage currents in SOFCs using Sm doped Ceria electrolytes has already been pointed out both qualitatively and in quantities. But these experimental results were ignored by the reason of no theoretical descriptions for the necessity. Using the constant field approximation, the limits of linear transport theory cannot be clear.

In this report, a new model is expressed without using the constant field approximation. This model follows from Wagner's equation and continuity. The calculated electronic current for doped Ceria electrolyte matches the values calculated using conventional models.

But the constant field approximation cannot be used in this case. Without large external currents, large voltage losses are observed in the 0.02cm thickness of electrolytes near the cathode. With 0.02cm thick electrolytes, this distance is 40nm. The lattice constant is 0.54nm, which means that there are only 74 lattices within the 40nm distance. Furthermore, the electrical field near the cathode is large enough to cause dielectric breakdown which has never been reported.

Continuity is not deniable, so there are limitations in Wagner's equation, coming from the limits of linear transport theory. Leakage currents in SOFCs using doped Ceria electrolytes must be completely verified theoretically.

## APPENDIX 1

A mathematical proof for Equation 18 is given in this appendix.

**Table 1. Symbol List**

Symbol	Explanation	Status
N	the number of meshes	constant
$pO_2'$	Oxygen partial pressures at the cathode	constant
$pO_2''$	Oxygen partial pressures at the anode	constant
$V_{th}$	Nernst voltage of the cell	determined
$V_{cell}$	the cell voltage	variable of cell
$V_{th\_mesh}$	Nernst voltage of mesh	determined
$V_{mesh}$	the voltage across each mesh	variable of mesh
$f_{average}(k)$	$V_{cell}/V_{th}$	variable of cell
$f_{mesh}(k)$	$V_{mesh}/V_{th\_mesh}$	variable of mesh
L	thickness of the electrolyte	constant
$l_{mesh}$	thickness of the mesh	variable of mesh
$l_{average}$	thickness of mesh when $f_{mesh}(k)$ is equal to $f_{average}(k)$	determined
$R_i$	ionic resistance of the electrolyte	constant
$r_i$	ionic resistance of the mesh	variable of mesh

$$V_{cell} = f_{average}(k) \times V_{th} \quad (20)$$

The difference in  $\ln(pO_2)$  between cathode and anode side of mesh is  $\frac{\ln(pO_2') - \ln(pO_2'')}{N}$ .

$$l_{average} = \frac{L}{N} \quad (21)$$

$$V_{th\_mesh} = \frac{V_{th}}{N} \quad (22)$$

$$V_{cell} = \sum_1^N V_{mesh} = \sum_1^N (f_{mesh}(k) \times V_{th\_mesh}) = \frac{V_{th}}{N} \sum_1^N f_{mesh}(k) \quad (23)$$

Thus, from Equation 20 and Equation 23,

$$\frac{1}{N} \sum_1^N f_{mesh}(k) = f_{average}(k) \quad (24)$$

From Equation 18,

$$\sum_1^N l_{mesh} = \sum_1^N l_{average} \left( \frac{1 - f_{mesh}(k)}{1 - f_{average}(k)} \right) = \frac{N \times l_{average}}{1 - f_{average}(k)} \times \frac{1}{N} \sum_1^N (1 - f_{mesh}(k)) \quad (25)$$

Therefore, from Equation 24 and Equation 25,

$$\sum_1^N l_{mesh} = \frac{L}{1 - f_{average}(k)} (1 - f_{average}(k)) = L \quad (26)$$

Consequently, when Equation 24 is satisfied, the cell voltage and the thickness of electrolyte become the real value. Next, from Equation 10, Equation 11 and Equation 12,

$$I_e = -k \times I_i = \frac{k \times (V_{cell} - V_{th})}{R_i} = k(f_{average}(k) - 1) \times \frac{V_{th}}{R_i} \quad (27)$$

For each mesh,

$$I_e = -k \times I_i = k(f_{mesh}(k) - 1) \times \frac{V_{th}}{N} \times \frac{1}{r_i} \quad (28)$$

Here, the ionic conductivity is constant. Thus,

$$\frac{r_i}{l_{mesh}} = \frac{R_i}{N \times l_{average}} \quad (29)$$

From Equation 29,

$$\frac{1}{N \times r_i} = \frac{l_{average}}{R_i \times l_{mesh}} \quad (30)$$

From Equation 28 and Equation 30,

$$I_e = k(f_{mesh}(k) - 1) \times \frac{l_{average} \times V_{th}}{l_{mesh} \times R_i} \quad (31)$$

Considering continuity, from Equation 27 and Equation 31,

$$l_{mesh} = l_{average} \left( \frac{1 - f_{mesh}(k)}{1 - f_{average}(k)} \right) \quad (32)$$

Consequently, the cell voltage, thickness and continuity is reflected in Equation 18. Equation 24 is the only necessary condition. The electrical field (E) is expressed as,

$$E = \frac{V_{mesh}}{l_{mesh}} = \frac{V_{th} \times f_{mesh}(k)}{L} \times \left( \frac{1 - f_{average}(k)}{1 - f_{mesh}(k)} \right) \quad (33)$$

The value of E increases with an increase in  $f_{mesh}(k)$ . Consequently, E cannot be constant. This means that the constant field approximation cannot be justified solely by Wagner's equation and continuity.

## APPENDIX 2

In this report, 500 meshes are used for the calculation from Equation 18. Here, a 30 meshes calculation example is shown. Calculating  $f_{mesh}(k)$ , Equation 34 was inserted into Equation 17.

$$pO_2 = \frac{pO'_{2\_mesh} + pO''_{2\_mesh}}{2} \quad (34)$$

where  $pO'_{2\_mesh}$  and  $pO''_{2\_mesh}$  are the oxygen pressure of the cathode and anode side of each mesh, respectively.

**Table 2-1. 30 Meshes Calculation Example (k=0.1)**

Mesh No.	log(pO <sub>2</sub> )	f <sub>mesh</sub> (k)	l <sub>mesh</sub>	Distance from the Cathode	V <sub>mesh</sub>	Potential	Electrical Field
Cathode	0		(%)	(%)	(Volt)	(volt)	(Volt/m)
1	-0.9027	0.999992278	1.12E-04	1.12E-04	0.039138	0.904079	1.75E+08
2	-1.80539	0.999987017	1.88E-04	3.00E-04	0.039137	0.864941	1.04E+08
3	-2.70809	0.99997817	3.16E-04	6.16E-04	0.039137	0.825804	6.19E+07
4	-3.61079	0.999963295	5.32E-04	1.15E-03	0.039136	0.786667	3.68E+07
5	-4.51349	0.999938286	8.94E-04	2.04E-03	0.039135	0.747531	2.19E+07
6	-5.41618	0.999896237	1.50E-03	3.55E-03	0.039134	0.708395	1.30E+07
7	-6.31888	0.999825544	2.53E-03	6.07E-03	0.039131	0.669261	7.74E+06
8	-7.22158	0.999706702	4.25E-03	1.03E-02	0.039126	0.63013	4.60E+06
9	-8.12428	0.999506944	7.15E-03	1.75E-02	0.039119	0.591004	2.74E+06
10	-9.02697	0.999171247	1.20E-02	2.95E-02	0.039105	0.551886	1.63E+06
11	-9.92967	0.998607311	2.02E-02	4.97E-02	0.039083	0.51278	9.68E+05
12	-10.8324	0.997660535	3.39E-02	8.36E-02	0.039046	0.473697	5.76E+05
13	-11.7351	0.996072654	5.69E-02	1.40E-01	0.038984	0.434651	3.42E+05
14	-12.6378	0.993414135	9.54E-02	2.36E-01	0.03888	0.395666	2.04E+05
15	-13.5405	0.988975915	1.60E-01	3.96E-01	0.038706	0.356786	1.21E+05
16	-14.4432	0.981602166	2.67E-01	6.62E-01	0.038418	0.31808	7.20E+04
17	-15.3459	0.969448653	4.43E-01	1.11E+00	0.037942	0.279662	4.28E+04
18	-16.2486	0.949678178	7.29E-01	1.83E+00	0.037168	0.24172	2.55E+04
19	-17.1513	0.918193388	1.19E+00	3.02E+00	0.035936	0.204552	1.52E+04
20	-18.0539	0.869712094	1.89E+00	4.91E+00	0.034039	0.168616	9.01E+03
21	-18.9566	0.798795181	2.92E+00	7.82E+00	0.031263	0.134577	5.36E+03
22	-19.8593	0.702482363	4.31E+00	1.21E+01	0.027494	0.103314	3.19E+03
23	-20.762	0.584072073	6.03E+00	1.82E+01	0.022859	0.07582	1.90E+03
24	-21.6647	0.455090854	7.90E+00	2.61E+01	0.017811	0.052961	1.13E+03
25	-22.5674	0.331866241	9.68E+00	3.57E+01	0.012989	0.03515	6.71E+02
26	-23.4701	0.228043679	1.12E+01	4.69E+01	0.008925	0.022161	3.99E+02
27	-24.3728	0.149436798	1.23E+01	5.93E+01	0.005849	0.013236	2.37E+02
28	-25.2755	0.094605121	1.31E+01	7.24E+01	0.003703	0.007387	1.41E+02
29	-26.1782	0.058508462	1.36E+01	8.60E+01	0.00229	0.003685	8.39E+01
30	-27.0809	0.035642327	1.40E+01	1.00E+02	0.001395	0.001395	4.99E+01
		0.769995795			0.904079		
		↑Σf(k)/30 =f <sub>average</sub> (k)			↑ΣV <sub>mesh</sub> =V <sub>cell</sub>		

Table 2-2. The Calculation of  $I_{ext}$  when  $R_i$  is 1 ohm

k	$V_{th}$ (Volt)	$f_{average}(k)$	$V_{cell}$ (Volt) = $V_{th} \times f_{average}(k)$	$I_i$ (A) = $(V_{th} - V_{cell})/1$	$I_e$ (A) = $-k \times I_i$	$I_{ext}$ (A) = $I_i + I_e$
0.1	1.174135	0.769996	0.904079	0.270056	-0.02701	0.24305

## APPENDIX 3

The calculated electronic current without constant field approximation matches the values predicted by Reiss' model. Theoretical explanation is given in this Appendix.

One goal of this paper is to develop a simple numerical method to solve the relevant equations in the current system without making any assumptions. Equation 16 and 17 cannot be integrated mathematically, and must be solved numerically. Using a numerical method, the analytical results from the Reiss's model is verified. Reiss's model is compatible with a generalized version of Wagner's equation. So the close match between the current data and Reiss's model is not surprising at all. But continuity is not included in Equation 16 and 17.

The assumption of constant ionic conductivity will lead to the constant field when there is no chemical potential gradient. In appendix 1, the assumption of constant ionic conductivity is used. But Fig. 8 shows the chemical potential gradient. Therefore, the constant field approximation can not be used in this case. Reiss's model is not compatible with a generalized version of Wagner's equation and continuity.

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