# Necessity of verification of leakage currents using Sm doped Ceria electrolytes in SOFCs

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Low open circuit voltage (OCV) has been explained by the theory of transport equations [1–4]. According to this theory (Riess's model), even if there is no external current, there are ionic ($I_i$) and electronic currents ($I_e$). Here, the sum of $I_i$ and $I_e$ is zero. Electron conductivity is derived from the contact of reduced Sm doped Ceria (SDC) electrolytes with hydrogen gas. By ohmic loss caused by $I$i, OCV becomes lower than Nernst voltage (Vth). At the same time, polarization voltage losses (on the cathode and anode) are caused by $I$i. The equation for OCV using SDC electrolytes is expressed as:

$$\text{OCV} = \text{V}_{\text{th}} - R_i I_i - \text{polarization voltage losses.} \quad (1)$$

Here ionic resistance ($R_i$) is constant, but polarization voltage losses should be changed with time, because every electrode worsens with time. Consequently, the value of OCV using SDC electrolytes should be changed. The mathematical proof is shown in the appendix. But, since there are no reports about the changing of OCV with time using SDC electrolytes, using rapidly aggregating anodes, the time dependence of OCV using SDC electrolytes in SOFCs was investigated.

The SDC electrolyte was 25 mm in diameter and 600 $\mu$m thick. Porous Pt electrode (10 mm in diameter) was attached as a cathode electrode. Ni-YSZ (5:5 using volume ratio) cermet was used as an anode electrode. Ni particle size was 580 $\mu$m. Yttria stabilized Zirconia (YSZ) was 80 $\mu$m and sintered at 1400 °C for 5 hrs. Oxygen gas was fed to the cathode, and hydrogen gas with 3% steam, was supplied to the anode as the fuel gas. The operating temperature was 1073 K. The I–V characteristics of the cells were measured with four probes and automatically recorded. The time dependence of the output voltage was measured with 200 mA extra current (current density 255 mA/cm$_2$) from the galvanostat in 2 hrs. During measurement, this current was stopped in 20 min. When the external current was 200 mA, output voltage was decreased during the measuring time. When the external current was stopped, output voltage (= OCV) was constant, as shown in Fig. 1.

One considerable problem in this experiment is whether the internal short-circuit ionic current under open circuit conditions would be large enough to cause the anode polarization voltage loss. From Equation 1, V$_{\text{th}}$ was 1.15 V (determined by components of fuel gas and operating temperature). $R_i$ was 0.76 ohm (= 0.06 cm/0.785 cm$^2$/0.1 S cm). Since $I_i$ could not be measured, it was estimated. The Butler-Volmer type polarization voltage losses in Equation 1 were caused by $I_i$. They strongly depend on electrode conditions. Since these voltage losses could not be measured, they were estimated. Because Ni contacts with reduced SDC electrolytes on the anode side, which has very high electronic conductivity, ion capacitance between Ni and reduced SDC electrolytes could not be measured. When the value of polarization voltage losses was estimated to be 0.2 V, $R_i$-drop was 0.2 V (= 1.15 V − 0.75 V − 0.2 V). Then $I_i$ was 263 mA (= 0.2 V/0.76 ohm), which was large enough compared with the extra current 200 mA. These estimations were valid. Therefore, in this experiment the above problem did not occur.

The same type of procedure could be done in any other experiment. OCV was constant in every experiment. These results explain why there are no reports about the changing of OCV with time, using SDC electrolytes.

From transport equations [1], OCV cannot be constant while the anode is degrading with time when there are internal short-circuit currents in SDC electrolytes. But experimentally, OCV was constant with rapidly aggregating anode, so there is a contradiction between the theory and experimental results. Leakage currents using doped Ceria electrolytes must be completely verified.

## Appendix

From transport equations [1], OCV cannot be constant while the anode is degrading with time when there are internal short circuit-currents in SDC electrolytes. The mathematical proof is shown in this appendix. The symbol list is shown next. These symbols are the same as in reference [1].

DOI: 10.1007/s10853-006-6371-8

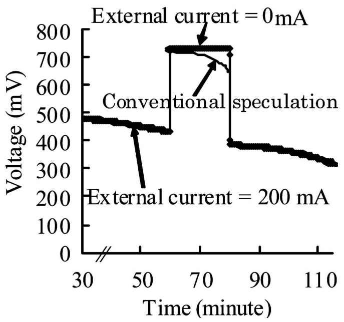

*Figure 1* OCV was 0.75 V constant with rapidly aggregating anode that differed from theoretical results.

## List of symbols

| | |
|---|---|
| $I_\mathrm{i}$ | ionic current |
| $I_\mathrm{e}$ | electronic current |
| $S$ | electrode cross-section |
| $L$ | cell thickness |
| $q$ | elementary charge |
| $k$ | Boltzmann constant |
| $T$ | temperature |
| $\beta$ | 1/kT |
| $R_\mathrm{i}$ | ionic resistance |
| $\sigma_\mathrm{e}$ | electronic conductivity |
| $V_\mathrm{th,app}$ | Nernst voltage |
| $V_\mathrm{cell}$ | cell voltage |
| $\delta V_\mathrm{th,C}$ | cathode polarization voltage loss |
| $\delta V_\mathrm{th,A}$ | anode polarization voltage loss |
| $P_{\mathrm{O}_2}^\mathrm{high}$ | oxygen partial pressure at cathode side |
| $P_{\mathrm{O}_2}^L$ | oxygen partial pressure at anode side |
| $P_{\mathrm{H}_2}^\mathrm{ext}$ | hydrogen partial pressure at anode side |
| $P_{\mathrm{H}_2\mathrm{O}}^\mathrm{ext}$ | water vapor pressure at anode side |
| $A_1$ | molecular hydrogen |
| $A_n$ | molecular hydrogen ($n=1$), atomic hydrogen ($n=2$) |
| $\alpha_\mathrm{A}$ | anode charge transfer coefficient |
| $I_{0,\mathrm{A}}$ | anode exchange current density |

From Equation 1, the partial ionic and electronic currents are the following:

$$I_\mathrm{i} = \frac{V_\mathrm{th,app} - V_\mathrm{cell} - \delta V_\mathrm{th,C} - \delta V_\mathrm{th,A}}{R_\mathrm{i}} \tag{2}$$

$$I_\mathrm{e} = -\frac{S}{L}(V_\mathrm{th,app} - V_\mathrm{cell} - \delta V_\mathrm{th,C} - \delta V_\mathrm{th,A}) \times \sigma_\mathrm{e}\left(P_{\mathrm{O}_2}^\mathrm{high}\right) \times \left(\frac{P_{\mathrm{O}_2}^L}{P_{\mathrm{O}_2}^\mathrm{high}}\right)^{-1/4} \frac{e^{\beta q V_\mathrm{cell}} - 1}{1 - e^{-\beta q (V_\mathrm{th,app} - V_\mathrm{cell} - \delta V_\mathrm{th,C} - \delta V_\mathrm{th,A})}}. \tag{3}$$

Under open-circuit conditions, $Ii + Ie = 0$. So,

$$\frac{1}{R_\mathrm{i}} = \frac{S}{L}\sigma_\mathrm{e}\left(P_{\mathrm{O}_2}^\mathrm{high}\right)\left(\frac{P_{\mathrm{O}_2}^L}{P_{\mathrm{O}_2}^\mathrm{high}}\right)^{-1/4} \times \frac{e^{\beta q V_\mathrm{cell}} - 1}{1 - e^{-\beta q (V_\mathrm{th,app} - V_\mathrm{celll} - \delta V_\mathrm{th,C} - \delta V_\mathrm{th,A})}}. \tag{4}$$

So,

$$\frac{1 - e^{-\beta q (V_\mathrm{th,app} - V_\mathrm{cell} - \delta V_\mathrm{th,C} - \delta V_\mathrm{th,A})}}{e^{\beta q V_\mathrm{cell}} - 1} = \frac{R_\mathrm{i} S}{L}\sigma_e\left(P_{\mathrm{O}_2}^\mathrm{high}\right)\left(\frac{P_{\mathrm{O}_2}^L}{P_{\mathrm{O}_2}^\mathrm{high}}\right)^{-1/4}. \tag{5}$$

Next, using Equations 6, 7, and 8 ($C$ in 6 is constant and positive),

$$\sigma_\mathrm{e} C = \frac{R_\mathrm{i} S}{L}\sigma_\mathrm{e}\left(P_{\mathrm{O}_2}^\mathrm{high}\right)\left(\frac{P_{\mathrm{O}_2}^L}{P_{\mathrm{O}_2}^\mathrm{high}}\right)^{-1/4}. \tag{6}$$

$$x = e^{\beta q V_\mathrm{cell}} \tag{7}$$

$$y = e^{\beta q \delta V_\mathrm{th,A}} \tag{8}$$

Then Equation 5 can be rewritten as:

$$x = \frac{1 + \sigma_\mathrm{e} C}{e^{-\beta q (V_\mathrm{th,app} - \delta V_\mathrm{th,C})} y + \sigma_\mathrm{e} C} \tag{9}$$

$$\frac{\partial x}{\partial y} = \frac{-e^{-\beta q (V_\mathrm{th,app} - \delta V_\mathrm{th,C})}(1 + \sigma_\mathrm{e} C)}{\left(e^{-\beta q (V_\mathrm{th,app} - \delta V_\mathrm{th,C})} y + \sigma_\mathrm{e} C\right)^2} < 0 \tag{10}$$

From Equation 10, the value of $x$ decreases with an increase in the value of $y$. So from Equations 7 and 8, the value of$V_\mathrm{cell}$ decreases with an increase in the value of $\delta V_\mathrm{th,A}$. Therefore, $\delta V_\mathrm{th,A}$ should be constant when $V_\mathrm{cell}$ is constant. Next, for example, $\delta V_\mathrm{th,A}$ is written as:

$$\delta V_\mathrm{th,A} = \frac{kT}{4q}\ln\left(\frac{P_{\mathrm{H}_2\mathrm{O}}^\mathrm{ext} + A_1 I_\mathrm{i}}{P_{\mathrm{H}_2\mathrm{O}}^\mathrm{ext}}\right) + \frac{kT}{2q}\ln\left(\frac{P_{\mathrm{H}_2}^\mathrm{ext}}{\left(\left(P_{\mathrm{H}_2}^\mathrm{ext}\right)^{1/n} - A_n I_\mathrm{i}\right)^n}\right) + \frac{kT}{2q\alpha_\mathrm{A}} ar\ \sin\mathrm{h}\left(\frac{I_i}{2I_{0,\mathrm{A}}}\right). \tag{11}$$

In Equation 11, $\alpha_\mathrm{A}$ and $I_{0,\mathrm{A}}$ are determined by the anode electrode situation and are independent of each other. So $\delta V_\mathrm{th,A}$ cannot be constant while the anode is degrading with time. Consequently, OCV cannot be constant while the anode is degrading with time when there are internal short-circuit currents in SDC electrolytes.

## References

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*Received 24 February*
*and accepted 29 August 2005*