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# 고체 산화물 연료전지 음극에서 개질 가스의 경쟁적 전기화학 반응

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# Competitive electrochemical oxidation of reformate gas in SOFCs

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**Key words** : Solid oxide fuel cell (고체 산화물 연료전지), Reformate gas (개질가스), Electrochemical oxidation (전기화학적 산화)

**Abstract** : SOFC (Solid oxide fuel cell) has an advantage in the term of fuel flexibility, comparing with other kinds of fuel cells. In SOFC and fuel reformer cooperation system, the reformate gas with the various $H_2$/CO ratios is delivered into the anode of SOFC. In this situation, electrochemical oxidation reactions of the reformate gas in the anode are complex and competitive. In this paper, the effects of the composition of $H_2$ and CO on the overall electrochemical oxidation at Ni-YSZ anode are studied by testing the open circuit voltage (OCV) and current-voltage characteristics of single cells.

## Nomenclature

E : Reversible open circuit voltage (V)
R : Universal gas constant (J/mol/K)
T : Temperature (K)
F : Faraday constant (C/mol)
P : Pressure (Pa)

## Subscript

E : Reversible open circuit voltage (V)

## 1. Introduction

The flexibility in the choice of fuels is one of most important advantages of the solid oxide fuel cell (SOFC), comparing with other kinds of fuel cells.[1] In the fuel reformer and SOFC cooperation system, the reformate gas including $H_2$ and CO in various composition ratios from the external reformer is delivered into the anode of SOFC. Through the electrochemical oxidation of the reformate, the electricity can be generated from the SOFC. In this situation, electrochemical oxidation reactions of the reformate gas in the anode are complex and competitive.

When the electric current is not equal to zero, the oxygen reduction reaction, Eq. (1) is occurred irreversibly in the three-phase boundary (TPB) of the cathode.

$$1/2\,O_2 + 2e^- \rightarrow O^{2-} \quad (1)$$

In the TPB of the anode, $H_2$ and CO oxidation reactions, Eq. (2) and (3) can occur in parallel.

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3)$$

Additionally, the water gas shift reaction, the Boudouard reaction and the catalytic cracking reaction, shown in Eq. (4), (5) and (6) respectively, can happen actively on Ni-YSZ cermet, the widely used anode material.

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$$CO + H_2O \rightarrow CO_2 + H_2O \quad (4)$$

$$2CO \rightarrow CO_2 + C \quad (5)$$

$$2CO \rightarrow 2C + O_2 \quad (6)$$

The pyrolytic carbon at the TPB of the anode, generated from Eq. (5) and (6) can be used possibly as a fuel through the following reactions.[2)]

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (7)$$

$$C + O^{2-} \rightarrow CO + 2e^- \quad (8)$$

As explained above, comparing to the case where $H_2$ is only used as a fuel, if CO is used supplementarily, many electrochemical and reforming reactions can arise additionally. Electrode potentials of five electrochemical reactions are shown in Fig. 1. The difference between the standard oxidation potential of the anode (solid lines) and that of the cathode (dot line) is the reversible open circuit voltage (OCV) at standard pressure of the SOFC.

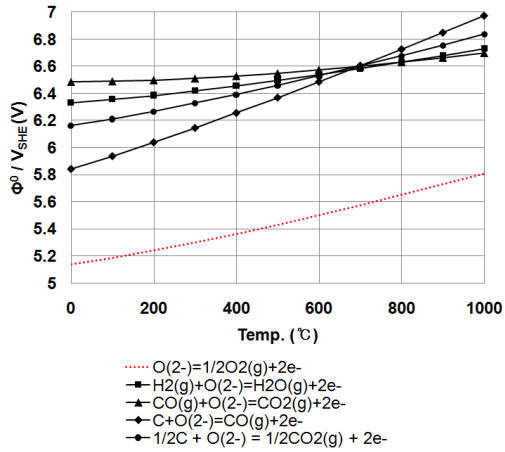


**Fig. 1 Oxidation potentials of five possible electrochemical reactions occurring in the SOFC**

According to the reaction frequencies of at least five electrochemical reactions and the circumstance of the anode composed of activities of reactants and products and temperature, the overall electrochemical reaction is changed. However, the methods to investigate the reaction frequencies still are limited and consequently understanding the overall electrochemical reaction is difficult.

Another reason why the overall electrochemical reaction in the anode is veiled is that electrochemical reactions happen dependently. Fig. 2 shows that if the oxidations of CO and $H_2$ occur simultaneously, the total electrode potential of the anode is somewhere in the middle of that of CO and $H_2$, because of the interaction between the electrochemical reactions of $H_2$ and CO. This anode can be called as a mixed electrode.[3)]

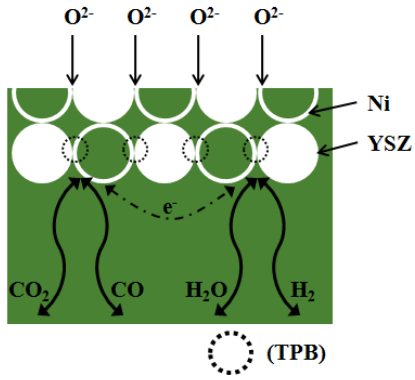


**Fig. 2 Schematic of the anode, where CO and $H_2$ are both used in the electrochemical oxidation reaction**

The aim of this work is to elucidate the effects of the composition of $H_2$ and CO on the overall electrochemical oxidation at Ni-YSZ anode by testing single cells. The circumstance in the anode is predicted by analyzing the OCV and current-voltage characteristics.

## 2. Materials and Methods

### 2.1 Single Cell Preparation

Anode-supported SOFCs were prepared: Ni-YSZ/YSZ/LSM82. The anode supports, composed of NiO and YSZ (Tosoh TZ-8Y) in the ratio of 60:40 wt% with 15wt% of Poly-methyl-methacrylate (PMMA) as the poreformer were pre-sintered at 1200℃. Then, a 15㎛ dense YSZ electrolyte layer was coated on the support by the dip-coating method. The anode/electrolyte bi-layers were fired at 1500℃ for 2h. As a cathode, a 15㎛ $La_{0.8}Sr_{0.2}Mn_{3-\delta}$ (LSM82) was coated on the YSZ layer by the screen printing method and sintered at 1000℃ for 1h. The apparent active area of the cathode is 0.785cm$^2$.

### 2.2 Single Cell Testing

A single cell testing step was prepared. Air was supplied to the cathode in 100 sccm with 3 mol% water. $H_2$ and CO were supplied to the anode as various $H_2$ and CO ratios, 100:0, 80:20, 60:40, 20:80 and 0:100. 50 sccm of $N_2$ was supplied additionally to decrease the carbon deposition rate and fix the operating condition during each case. The furnace temperature is 800℃. The open circuit voltage (OCV) and current-voltage characteristic of the single cell was measured and electrochemical impedance spectroscopy (EIS) was carried out in zero current state.

## 3. Results and Discussion

### 3.1 Open circuit voltage

The OCVs for $H_2$ and CO are defined as Nernst equations, Eq. (9) and (10), respectively.[4)]

$$E^{H_2} = E_0^{H_2} + \frac{RT}{2F}\ln\frac{a_{H_2}a_{O_2}^{1/2}}{a_{H_2O}} \quad (9)$$

$$E^{CO} = E_0^{CO} + \frac{RT}{2F}\ln\frac{a_{CO}a_{O_2}^{1/2}}{a_{CO_2}} \quad (10)$$

The activity is usually assumed to be partial pressure of the gas in the gas flow channel divided by the standard pressure.[4)]

$$a_i = \frac{P_i}{P_0} \quad (11)$$

E. Achenbach proposed one approach to determine the overall OCV that if the water gas shift reaction is regarded to be at equilibrium, the OCV of CO is equal to that of $H_2$.[5)] Still, previous approaches to determine the activities and the effect of the OCVs of $H_2$ and CO on the overall OCV are far away from the real anode situation.

To determine the OCV when the $H_2$ and CO are both supplied into the anode is difficult because the activities of reactants and products and the reaction frequencies are hard to be examined. In the real situation, the gases from the gas flow channel diffuse into the anode with different effective diffusivities. The compositions of gases are changed and byproducts such as carbon are generated in the pathway to the TPB, because of various chemical reactions. The gases reaching to the TPB should be absorbed on the active site to be electrochemically oxidized. Although the adsorption strengths of CO and $H_2$ are different according to the surrounding condition, the heat of adsorption of CO is higher than that of $H_2$ in general.[6)] Throughout these processes, the activities of $H_2$, CO, $H_2O$ and $CO_2$ near the TPB of the anode are determined and seem to be quite different from Eq. (11).

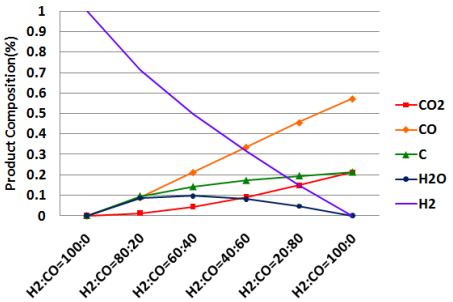


**Fig. 3 Thermodynamic equilibrium at 1073 K as the $H_2$/CO ratio is changed**

In this paper, the OCVs of various $H_2$ and CO ratios are simulated, assuming that the activity of each gas is the partial pressure of the gas in thermodynamic equilibrium at 1073K, as shown in Fig. 3, divided by the standard pressure where the anode side is regarded as a continuous stirred-tank reactor (CSTR). Also, the adsorption strengths of gases are assumed to be all same. Additionally, the pyrolytic carbon is excluded from the OCV calculation.

The CO ratio, $r_{CO}$ and the $H_2$ ratio, $r_{CO}$ are defined as Eq. (12) and (13) respectively. They can be considered as values which are in proportion to the frequencies of CO and $H_2$ oxidation reaction. The total OCV is defined as Eq. (14) used for the simulation.

$$r_{CO} = \frac{P_{CO@Eq.1073K}}{P_{H_2@Eq.1073K} + P_{CO@Eq.1073K}} \quad (12)$$

$$r_{H_2} = \frac{P_{H_2@Eq.1073K}}{P_{H_2@Eq.1073K} + P_{CO@Eq.1073K}} \quad (13)$$

$$E_{totol} = r_{CO}E^{CO} + r_{H_2}E^{H_2} \quad (14)$$

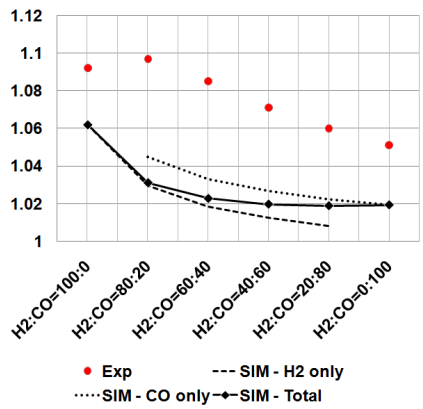


**Fig. 4 OCVs according to the various $H_2$/CO ratios**

Fig. 4 shows that experimental and simulated OCVs from for various $H_2$ and CO compositions. Although the OCV increases slightly from $H_2$/CO=100:0 to 80:20 in the experimental result, the OCV decreases as the amount of CO increase in both experiment and simulated result. The difference between experimental and predicted values is clearly due to too simplified model excluding the difference of the adsorptions strengths and diffusivities of gases. More precise model to predict the OCV is needed to be developed. The interesting point is that as the amount of CO increases, the OCV decreases constantly. It might be caused by the coke formation inside of the anode. However, as shown in Fig. 1, the OCV of carbon is higher than that of $H_2$ if it can be electrochemically oxidized. Therefore, it can be concluded that in Ni-YSZ anodic system, the generated carbon at the TPB is hardly used as a fuel and decrease the activities of $H_2$ and CO by occupying the active sites.

### 3.2 I-V and Impedance Characteristics

According to the previous report, when the amount of CO in the reformate gas increases, the I-V characteristic is deteriorated.[7] Fig. 5 shows the similar result. One of the reasons of the deterioration is the rate of CO oxidation is 2-3 times less than that of $H_2$ oxidation over the entire range of overpotential.[8] Also, the diffusional limitation is increased by the decrease of the pore size caused by the coke formation. As shown in Fig. 3, except when $H_2$ is only a fuel, the carbon generation is thermodynamically favourable. As precedent literatures suggest, the following conclusion can be derived from the results. Although $H_2$ and CO can be used as fuel, $H_2$ is oxidized more dominantly when $H_2$ and CO is mixed together. Because it has high diffusivity and faster oxidation rate without leaving any hazardous byproducts like carbon, because of its high diffusivity and faster oxidation

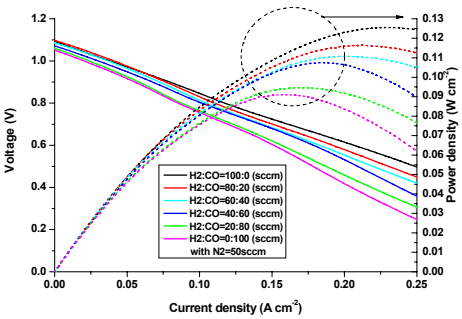


**Fig. 5 I-V characteristic at various $H_2$/CO**

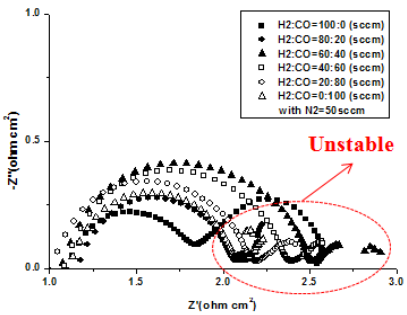


**Fig. 6 Impedance characteristic at various $H_2$/CO**

Fig. 6 shows that if the amount of CO increases, the low frequency impedance characteristic is quite unstable. The reason is that the circumstance in the anode is not at the equilibrium but still change. Although the oxidation of $H_2$ is faster than that of CO, if the amount of CO increases, the dominance of the electrochemical oxidation is shifted from $H_2$ to CO. When the amount of CO is dominant, the circumstance on the anode is complex and competitive and it is hard to converge to the equilibrium.

## 4. Conclusion

Throughout this paper, the effects of the various $H_2$/CO ratios on the overall electrochemical oxidation at Ni-YSZ are discussed by analyzing the OCV and current-voltage characteristics.

Although $H_2$, CO and carbon originated form CO can be all used in electrochemical oxidation reactions of the SOFC, the oxidation reaction of $H_2$ is dominant up to the certain boundary. However the amount of CO gets higher, the dominance of the oxidation reaction is shifted from $H_2$ and the situation inside of the anode gets complex and competitive. To investigate this situation deeply, additional experiment needs to be conducted.

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