



Short communication

Effect of O₂ concentration on performance of solid oxide fuel cells with V₂O₅ or Cu added (LaSr)(CoFe)O₃–(Ce,Gd)O_{2–x} cathode with and without NO

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ARTICLE INFO

Article history:

Received 2 March 2009

Received in revised form 30 March 2009

Accepted 10 April 2009

Available online 18 April 2009

Keywords:

Open circuit voltage

Mass transfer

Pore diffusion

Flow rate

Oxygen concentration

Solid oxide fuel cell

ABSTRACT

A solid oxide fuel cell unit is constructed with Ni-(Ce,Gd)O_{2–x} (GDC) as the anode, yttria-stabilized zirconia as the electrolyte, and V₂O₅ or Cu added (LaSr)(CoFe)O₃–GDC as the cathode. The effect of the O₂ concentration on the open circuit voltage (OCV) is studied and a mass-transfer limited OCV is observed. The power density with Cu addition can be much higher than that with V₂O₅ addition but the effect of the O₂ concentration with Cu addition is larger than that with V₂O₅ addition. Without the presence of NO, both the power density and the OCV decrease with decreasing O₂ concentration. The OCV variation can be substantial with the variation of the flow rate, the O₂ concentration and the NO concentration. The presence of CO₂ can increase the OCV while that of NO can decrease the OCV; however, a synergistic effect can occur on the OCV when NO is present at a very low O₂ concentration which results in a sudden drop of the OCV.

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1. Introduction

The removal of nitric oxide (NO) from industrial flue gas in stationary sources is traditionally performed by the selective catalytic reduction (SCR) process, in which NO in the flue gas reacts with ammonia to produce nitrogen and water [1]. This SCR process has to use a reducing gas, usually ammonia, while residual ammonia needs additional treatment. Thus, the electrochemical NO reduction without a reducing gas has been studied extensively [2–6]. However, this process of electrochemical NO reduction is performed with an applied current and the current efficiency is generally only a few percent; additionally, the reduction of O₂ occurs simultaneously to consume a substantial amount of the electrical current [5]. Therefore, simultaneous NO reduction and electricity generation in a solid oxide fuel cell (SOFC) should be an attractive process; the feasibility of such a process has been confirmed in the SOFCs with either V₂O₅ or Cu added La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3–δ} (LSCF)–Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) cathodes [7]. The use of V₂O₅ or Cu added LSCF–GDC cathodes is based on the fact that V₂O₅ is the catalytic component of the commercial SCR catalyst [8], Cu is effective for direct electrochemical NO reduction [5], and LSCF–GDC composite exhibits good cathode performance [9].

A process of simultaneous NO reduction and electricity generation means that the SOFC operation is performed with the flue gas

passing the cathode side; thus, the O₂ concentration would be much lower than the normal 20%. For the flue gas of the power plants or the nitric acid plants, the O₂ concentration is usually 4–6% and the NO concentration can be 1000–5000 ppm or higher. This may have some effect on the open circuit voltage (OCV); notably, Zha et al. [10] have reported that the OCV is greatly influenced by gaseous composition over the anode; thus, the OCV may also be affected by the gaseous composition over the cathode. Additionally, the gaseous composition can vary in a porous structure, such as the cathode layer, due to the effect of mass transfer, i.e. the pore diffusion [11]. However, there is no report on the effect of mass transfer on the OCV of the SOFCs, as far as the authors know.

In this work, the effect of the O₂ concentration on the SOFC performance with and without NO simulating the flue gas was investigated over either V₂O₅ or Cu added LSCF–GDC cathode. The results show that the OCV can vary substantially with the variation of the flow rate, the O₂ concentration and the NO concentration. Mass-transfer limited OCV is observed and discussed.

2. Experimental

2.1. Material preparation

LSCF of this work is La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3–δ}. LSCF was prepared by glycine–nitrate process. Appropriate amounts of reagent-grade (Showa, Japan) metal nitrates La(NO₃)₃·6H₂O, Sr(NO₃)₂, Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in de-ionized water. Glycine (Sigma, USA) was also dissolved in de-ionized water.

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Then, these two solutions were mixed with glycine to NO_3 ratio of 1:0.8. The mixture was heated under stirring at 110°C until combustion occurred. The product was ground to powders and then calcined by heating to 500°C and held for 2 h, then to 900°C and held for 4 h. The heating was always done in air at 5°C min^{-1} .

Gadolinia-doped ceria (GDC) of this work is $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$. GDC was prepared by co-precipitation. The details of the method have been presented elsewhere [12]. The GDC powders were calcined by heating to 500°C and held for 2 h, and then to 1000°C and held for 2 h before cooling.

The LSCF–GDC composite was prepared by mixing the above-prepared LSCF and GDC powders at LSCF:GDC = 100:50 in weight. The mixture was ground for 24 h, then calcined by heating to 500°C and held for 2 h, and then to 900°C , held for 10 h.

LSCF–GDC– V_2O_5 was prepared by mixing V_2O_5 powder (Showa, Japan) with LSCF–GDC powder in de-ionized water. Cu adding to LSCF–GDC was done by impregnation with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Showa, Japan) solution. After drying, the powders were calcined by heating to 500°C and held for 2 h, and then to 800°C and held for 2 h. The V_2O_5 and Cu loading of LSCF–GDC– V_2O_5 and LSCF–GDC–Cu, respectively, was 2 wt% with respect to LSCF.

2.2. Current–voltage measurement in SOFC unit cell

A disk was cut from yttria-stabilized zirconia (YSZ) tape (156 μm thickness, Jiuhow, Taiwan) to make an electrolyte-supported cell. One side of the YSZ disk was spin-coated with Ni–GDC paste, with Ni:GDC = 60:100 in weight [13]. The other side of the YSZ disk was spin-coated with LSCF–GDC–Cu powders to make the cathode layer. The details of the construction of the SOFC unit cell have been presented elsewhere [13]. The SOFC has an anode area of 1 cm^2 , an anode thickness of $30\text{ }\mu\text{m}$, an electrolyte thickness of $156\text{ }\mu\text{m}$, a cathode area of 1 cm^2 , and a cathode thickness of $10\text{ }\mu\text{m}$. These thicknesses were measured from a scanning electron micrograph of the cross-section of the cell.

The current–voltage measurements were performed at 800°C with pure hydrogen flowing on the anode side. The cathode-side gas was various oxygen or oxygen plus NO mixture, all balanced by argon. Oxygen, NO and argon were added via mass flow meters, respectively, into a mixer. The flow rate was $150\text{ cm}^3\text{ min}^{-1}$ if not indicated otherwise. The flow measurement was done by a gas bubble meter at the outlet of the experimental setup. With the same cathode materials, the current–voltage measurements were all performed with the same SOFC unit cell in the same experimental setup. To check whether there is possible leak in the experimental setup, a series of measurements started with 20% O_2 and then the oxygen concentration was reduced to 1% before increasing stepwise until 20%. These two 20% O_2 measurements showed exactly the same results with an OCV close to the theoretical one; this assured that there is no leak in the experimental setup.

3. Results and discussion

3.1. Effect of O_2 concentration on SOFC performance

The variations of voltage–current and power–current profiles with 2–20% O_2 but without the presence of NO are shown in Fig. 1(a) and (b) with LSCF–GDC– V_2O_5 and LSCF–GDC–Cu as the cathode, respectively. As the O_2 concentration decreases, the power density decreases; the extent of this decrease of the power density increases with increasing current density. This is attributed to the effect of mass diffusion, which increases with increasing current density [14]; notably, an increasing current density is associated with an increasing rate of the electrochemical reaction. The reaction rate can increase with increasing mass flux, which is a function of the reactant concentration according to the Fick's law [11].

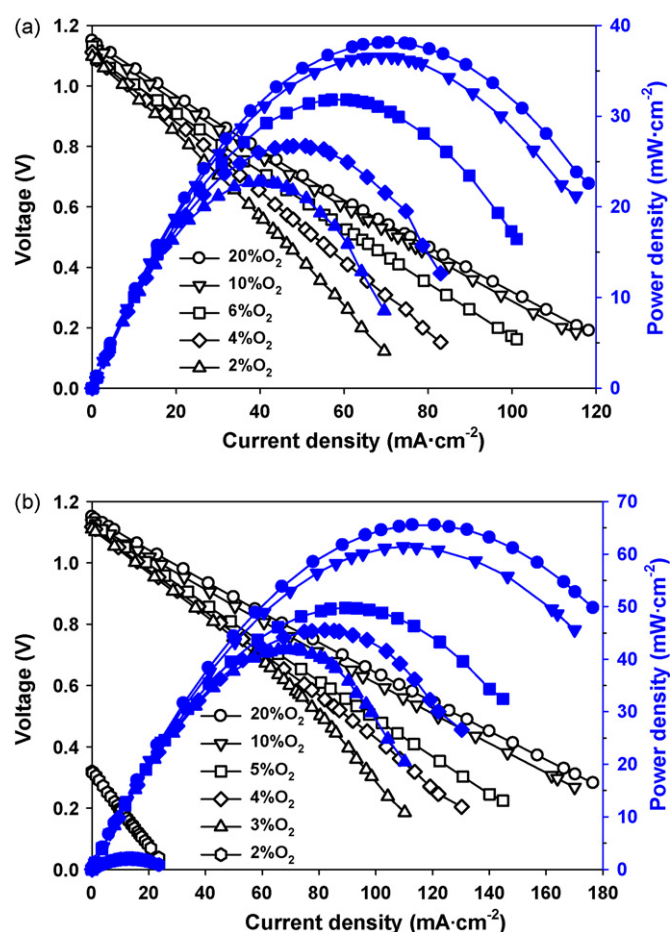


Fig. 1. Variation of voltage–current and power–current profiles with O_2 concentration (in argon) at 800°C . (a) LSCF–GDC– V_2O_5 cathode; (b) LSCF–GDC–Cu cathode. Open symbol: voltage; filled symbol: power density.

A comparison between Fig. 1(a) and (b) shows that the power density with LSCF–GDC–Cu as the cathode can be much higher than that with LSCF–GDC– V_2O_5 . However, the effect of O_2 concentration on the power density with LSCF–GDC–Cu as the cathode is stronger than that with LSCF–GDC– V_2O_5 , as shown in Fig. 2. When LSCF–GDC–Cu is used as the cathode, there is a sudden drop of the SOFC performance, in terms of both the maximum power density and the OCV, as the O_2 concentration decreases from 3 to 2%; there

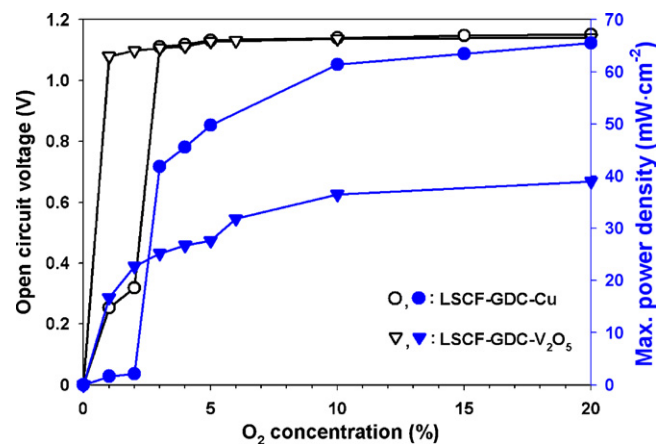


Fig. 2. Effect of O_2 concentration (in argon) on open circuit voltage and maximum power density at 800°C . Open symbol: open circuit voltage; filled symbol: maximum power density.

is no such sudden drop of the SOFC performance occurring with LSCF–GDC–V₂O₅. Consequently, at 2% O₂, the power density with LSCF–GDC–Cu as the cathode can be much lower than that with LSCF–GDC–V₂O₅, as also shown by a comparison between Fig. 1(a) and (b).

Fig. 2 shows that, as the O₂ concentration decreases from 20 to 1% over the LSCF–GDC–V₂O₅ cathode, the OCV decreases only very slightly while the maximum power density decreases although considerably but gradually. However, as the O₂ concentration decreases from 20 to 3% over the LSCF–GDC–Cu cathode, the OCV is about the same as that with LSCF–GDC–V₂O₅ as the cathode. A further decrease of the O₂ concentration from 3 to 2% causes a sudden drop of the OCV for SOFCs with LSCF–GDC–Cu as the cathode but not with LSCF–GDC–V₂O₅. As the O₂ concentration decreases from 20 to 3% over LSCF–GDC–Cu, the maximum power density decreases also gradually but with a higher extent than that with LSCF–GDC–V₂O₅; a further decrease of the O₂ concentration from 3 to 2% also causes a sudden drop of the maximum power density only with LSCF–GDC–Cu as the cathode. Notably, the OCV is a characteristic for ideal operating voltage and an evaluation of drop of this voltage may provide information on the extent of improving energy efficiency of a fuel cell [15]. Thus, the sudden drop of both the OCV and the maximum power density for SOFCs with LSCF–GDC–Cu as the cathode but not with LSCF–GDC–V₂O₅ is attributed to the much higher power density which can be achieved with LSCF–GDC–Cu than with LSCF–GDC–V₂O₅. Notably, also, when LSCF–GDC–Cu is used as the cathode, the sudden drop of the OCV occurs at the same time as that of the maximum power density. This indicates that the OCV could affect the maximum power density, similar to the case in the field of catalysis that the activation energy determines the reaction rate, which is according to the Arrhenius relationship.

Fig. 3 shows that, with 20% O₂, the performance of the SOFC with LSCF–GDC–V₂O₅ as the cathode is not affected by a variation of the flow rate. This again assured that there is no leak in the experimental setup of this work; notably, the experimental procedure for Fig. 3 was 1% O₂ at 150–100 cm³ min⁻¹ and then 20% O₂ at 150–100 cm³ min⁻¹. However, with 1% O₂ at a flow rate of 150 cm³ min⁻¹, although the OCV decreases only slightly but the maximum power density decreases considerably from that with 20% O₂, as also shown in Table 1. As the flow rate of this mixture of 1% O₂ in argon decreases from 150 to 125 cm³ min⁻¹, the OCV decreases considerably and the maximum power density decreases dramatically; a further decrease of the flow rate causes the further decrease of both the OCV and the maximum power density. This indicates that not only the maximum power density but also

Table 1

Effect of flow rate in association with O₂ concentration on open circuit voltage and maximum power density with LSCF–GDC–V₂O₅ cathode.

Cathode gas	Flow rate (cm ³ min ⁻¹)	Open circuit voltage (V)	Maximum power density (mW cm ⁻²)
20% O ₂	150	1.150	38.99
20% O ₂	125	1.148	38.73
20% O ₂	100	1.145	38.48
1% O ₂	150	1.080	16.68
1% O ₂	125	0.552	1.55
1% O ₂	100	0.247	0.574

the OCV depend on the rate of O₂ supply. This rate of O₂ supply is associated with the rate of oxygen mass transfer to the cathode three-phase boundary; notably, the rate of interface mass transfer depends on the flow rate [16]. Thus, the OCV is mass-transfer limited. Since the mass-transfer limited activation energy is termed an apparent one [17], the mass-transfer limited OCV can be termed an apparent OCV; this apparent OCV is not the true OCV just as that the apparent activation energy is not the true one [17].

The true OCV, the ideal operational voltage, is calculated from the thermodynamic activities of the chemical species via the Nernst equation [18]. However, since the SOFCs are operated under flow condition, the electrochemical potential of oxygen at the cathode TPB (three-phase boundary) is sometimes not at the thermodynamic value due to the flow condition and the cathode microstructure, both being associated to the effect of mass transfer. This leads to the observation that the mass-transfer limited OCV does not equal the true OCV. Notably, the mass-transfer limitation in this work can also be considered as the pore diffusion limitation; the microstructure of the porous layer of the LSCF–GDC cathode, before V₂O₅ or Cu addition, is revealed in the SEM image as shown in Fig. 4. Additionally, with catalysts of low activity, the mass-transfer limitation is minor; the same is considered to be true with SOFCs of low performance. Therefore, the occurrence of mass-transfer limited OCV in this work with relatively low SOFC performance, due to the use of an electrolyte-supported cell, makes it more significant than its occurrence in SOFCs with relatively high performance.

3.2. Effect of NO concentration on SOFC performance

Table 2 shows that, with LSCF–GDC–V₂O₅ as the cathode, adding 1000–5000 ppm NO into 1–6% O₂, respectively, does not change the

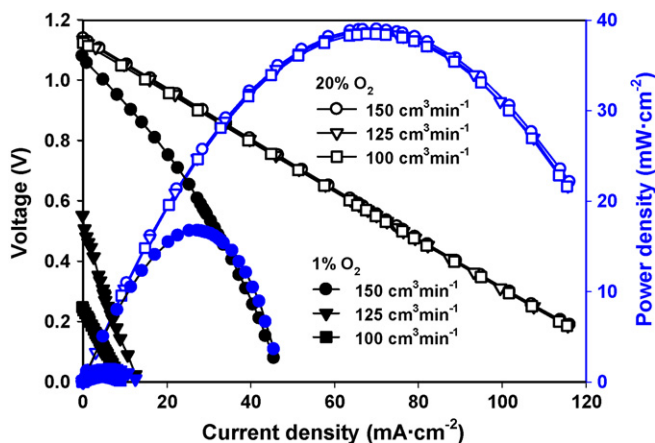


Fig. 3. Variation of voltage–current and power–current profiles with flow rate and O₂ concentration (in argon) over LSCF–GDC–V₂O₅ cathode at 800 °C.

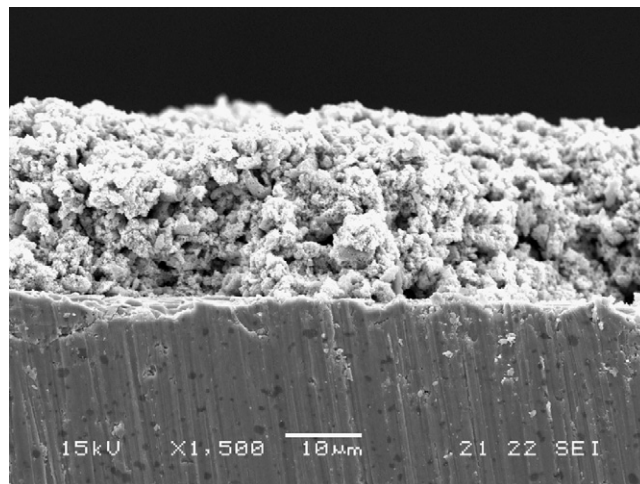


Fig. 4. SEM image of LSCF–GDC cathode (the porous layer) and YSZ electrolyte (the dense layer).

Table 2

Variation of open circuit voltage with O₂ concentration, plus 1000–5000 ppm NO, with LSCF–GDC–V₂O₅ cathode.

Cathode gas	Open circuit voltage (V)
6% O ₂	1.130
6% O ₂ + 5000 ppm NO	1.129
6% O ₂ + 3000 ppm NO	1.130
6% O ₂ + 1000 ppm NO	1.130
5% O ₂	1.128
5% O ₂ + 5000 ppm NO	1.127
5% O ₂ + 3000 ppm NO	1.127
5% O ₂ + 1000 ppm NO	1.128
4% O ₂	1.112
4% O ₂ + 5000 ppm NO	1.110
4% O ₂ + 3000 ppm NO	1.110
4% O ₂ + 1000 ppm NO	1.112
3% O ₂	1.106
3% O ₂ + 5000 ppm NO	1.106
3% O ₂ + 3000 ppm NO	1.106
3% O ₂ + 1000 ppm NO	1.106
2% O ₂	1.098
2% O ₂ + 5000 ppm NO	1.097
2% O ₂ + 3000 ppm NO	1.098
2% O ₂ + 1000 ppm NO	1.098
1% O ₂	1.079
1% O ₂ + 5000 ppm NO	1.077
1% O ₂ + 3000 ppm NO	1.078
1% O ₂ + 1000 ppm NO	1.079

Table 3

Variation of open circuit voltage with O₂ concentration, plus 0.1–3% NO or plus 7000 ppm NO and 10% CO₂, with LSCF–GDC–Cu cathode.

Cathode gases	Open circuit voltage (V)
5% O ₂	1.133
5% O ₂ + 3% NO	1.123
5% O ₂ + 2% NO	1.125
5% O ₂ + 1% NO	1.128
5% O ₂ + 7000 ppm NO + 10% CO ₂	1.132
5% O ₂ + 7000 ppm NO	1.132
5% O ₂ + 4500 ppm NO	1.132
5% O ₂ + 1000 ppm NO	1.132
4% O ₂	1.118
4% O ₂ + 3% NO	1.113
4% O ₂ + 2% NO	1.113
4% O ₂ + 1% NO	1.117
4% O ₂ + 7000 ppm NO + 10% CO ₂	1.117
4% O ₂ + 7000 ppm NO	1.117
4% O ₂ + 4500 ppm NO	1.117
4% O ₂ + 1000 ppm NO	1.118
3% O ₂	1.111
3% O ₂ + 3% NO	1.096
3% O ₂ + 2% NO	1.104
3% O ₂ + 1% NO	1.107
3% O ₂ + 7000 ppm NO + 10% CO ₂	1.110
3% O ₂ + 7000 ppm NO	1.109
3% O ₂ + 4500 ppm NO	1.110
3% O ₂ + 1000 ppm NO	1.110
2% O ₂	0.319
2% O ₂ + 3% NO	0.709
2% O ₂ + 2% NO	0.675
2% O ₂ + 1% NO	0.466
2% O ₂ + 7000 ppm NO + 10% CO ₂	0.476
2% O ₂ + 7000 ppm NO	0.388
2% O ₂ + 4500 ppm NO	0.383
2% O ₂ + 1000 ppm NO	0.326
2% NO	0.184

OCV or decreases it only slightly; this decreased extent is higher with higher NO concentration. When LSCF–GDC–Cu is used as the cathode, Table 3 shows that, for the O₂ concentration of 3% or higher, adding NO into O₂ also does not change the OCV or decreases it only slightly; however, as the O₂ concentration comes down to 2%, adding NO into O₂ increases the OCV instead. This increased extent is higher with higher NO concentration and becomes dramatic with adding 2% NO.

Fig. 5 shows that, with 2% O₂, the power density increases with increasing NO concentration. This increased extent is higher with higher NO concentration and becomes dramatic when the added NO is 2% or higher. When 3% NO is added into 2% O₂, the maximum power density becomes four times and the OCV is over 2.2 times that with 2% O₂. Since a synergistic effect between NO and O₂ has been shown to occur for the maximum power density [7], such a synergistic effect may also occur for the OCV. Table 3 shows

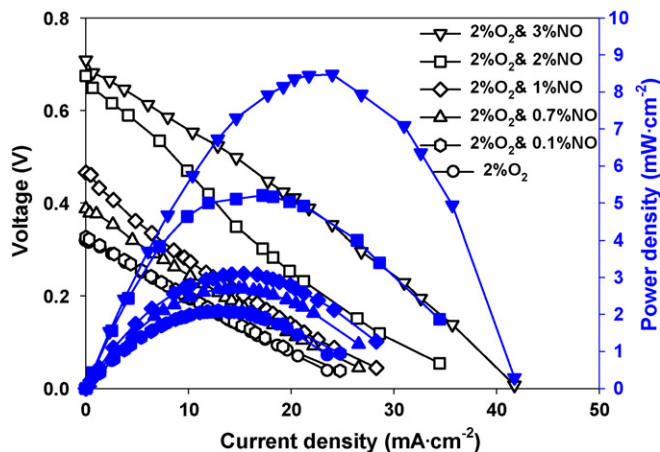


Fig. 5. Variation of voltage–current and power–current profiles with 2% O₂ plus NO with various concentrations (in argon) over LSCF–GDC–Cu cathode at 800°C. Open symbol: voltage; filled symbol: power density.

that adding 2% NO into 2% O₂ resulted in an OCV which is larger than the sum of the OCV with 2% O₂ plus that with 2% NO. This indicates a synergistic effect on the OCV. However, this synergistic effect between NO and O₂ can occur on the OCV only when NO is associated with a very low O₂ concentration which results in a sudden drop of the OCV.

3.3. Effect of CO₂

The exhaust gas usually contains carbon dioxide and water. Tofan et al. [19] has reported that, on studying NO decomposition over perovskites, both CO₂ and water inhibit NO decomposition but the inhibition effect by CO₂ is considerably stronger. Thus, the effect of CO₂ on the SOFC performance in terms of the OCV was investigated in this work.

Table 3 also shows that, with cathode-side gas mixture containing 10% CO₂ plus 7000 ppm NO, the OCV is the same as that without CO₂ or even increases with the presence of CO₂. This increased extent is considerable at 2% O₂. In any case, the presence of CO₂ results in either no effect or a beneficial effect on the OCV.

4. Conclusions

- (1) The power density with LSCF–GDC–Cu as the cathode can be much higher than that with LSCF–GDC–V₂O₅.
- (2) The effect of the O₂ concentration on the power density with LSCF–GDC–Cu as the cathode is larger than that with LSCF–GDC–V₂O₅ and the power density of the former can become much lower than that of the latter at very low O₂ concentrations.

- (3) Without the presence of NO, both the power density and the OCV can decrease with decreasing O₂ concentration.
- (4) The OCV variation can be substantial with the variation of the flow rate, the O₂ concentration and the NO concentration.
- (5) The OCV is mass-transfer limited.
- (6) The presence of CO₂ can increase the OCV while that of NO can decrease the OCV; however, a synergistic effect can occur on the OCV when NO is present at a very low O₂ concentration which results in a sudden drop of the OCV.

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