



Bi-Based Oxide Anodes for Direct Hydrocarbon SOFCs at Intermediate Temperatures

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Doped Bi-based oxides were investigated as potential anode materials for direct hydrocarbon solid oxide fuel cells (SOFCs) at intermediate temperatures. $(\text{Bi}_2\text{O}_3)_{0.85}(\text{Ta}_2\text{O}_5)_{0.15}$ met this criterion most successfully. A fraction of Bi_2O_3 in this material was reduced to BiO and Bi metal under fuel conditions, which yielded high conductivities ($<1 \text{ S cm}^{-1}$) based on oxide ions and electrons above 500°C . Carbon deposition was successfully prevented when butane was used as the fuel below 800°C . The catalytic activities for hydrocarbon oxidation were high enough to promote the complete oxidation of butane during cell operation. These abilities provided an enhanced anode performance with increasing temperature from 600 to 750°C , and the resulting polarization resistance reached $1.4 \Omega \text{ cm}^2$ at 750°C .

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Solid oxide fuel cells (SOFCs) can convert hydrocarbon fuels directly to electrical power with high efficiency, which provides a portable and economical system.^{1,2} However, the most commonly used Ni/yttria-stabilized zirconia (YSZ) cermet anodes are not optimized for small-scale SOFC systems. Such a system must be regularly stopped and restarted for maintenance, which causes a serious volume change upon redox cycling of the Ni component. Moreover, these anodes are not well suited for use with hydrocarbon fuels because these promote their cracking. Recently, LaCrO_3 -based perovskite oxides have been considered alternative anodes.³⁻⁸ These materials are p-type semiconductors in reducing atmospheres and can avoid carbon deposition successfully. Nonetheless, since the LaCrO_3 -based anodes are not as good electrocatalysts as the Ni/YSZ-cermet anodes, the polarization resistances are large, especially at intermediate temperatures, unless catalysts such as Ni are doped into the B-site of LaCrO_3 .

In this study, we attempted to use doped Bi-based oxides as potential anode materials for small-scale SOFC systems. These materials are readily reduced in reducing atmospheres at elevated temperatures,^{9,10} which results in electronic conduction enough to provide the electrical path under fuel conditions. Many doped Bi-based oxides also show high catalytic properties for hydrocarbon oxidation.¹¹ These abilities would offer suitable performance for operation on hydrocarbon fuels. A similar concept was proposed by Steele *et al.* in the 1990s,¹² but still has not been substantiated (although bismuth oxide-based catalysts such as $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $\text{Bi}_3\text{Ru}_3\text{O}_{11}$ have been investigated as cathodes for oxygen sensors).¹³

Experimental

Different doped Bi-based oxides were investigated as anodes (see Table I), where $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) (14 mm diam, 0.75 mm thick), $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (0.5 cm^2 area), and Pt (*ca.* 0.2 cm^2 area) were used as the electrolyte, the counter and reference electrodes, respectively. The preparation and treatment of the latter three materials were described in detail elsewhere.^{14,15} The anodes were synthesized as follows. The desired amounts of Bi_2O_3 and M_xO_y ($\text{M} = \text{Mo}, \text{W}, \text{Ba}, \text{Y}, \text{Yb}, \text{Gd}, \text{Er}, \text{Nb}, \text{V}, \text{Ta}, \text{and Pr}$) were mixed in ethanol with a mortar and a pestle and then heated in air at 800°C for 12 h. Here, the composition of each compound was controlled so as to show the highest ionic conductivity.¹⁶ The compound was ground in terpineol using a planetary ball mill for 14 h. The slurry was painted as thinly as possible with a brush on one side (0.5 cm^2

area) of the GDC pellet and then sintered in air at 900°C for 4 h. A Au mesh (no. 100) and a Au wire were used as the electrical collector and output terminal, respectively.

Two gas chambers were set up by placing the obtained cell between two alumina tubes (9 mm i.d., 13 mm o.d.). Each chamber was sealed by a glass ring gasket at 800°C . The anode was supplied with dry methane, ethane, propane, and butane and wet hydrogen that was saturated with H_2O vapor at room temperature. The flow rate of these gases was 30 mL min^{-1} . The counter and reference electrodes were statically exposed to atmospheric air. The impedance spectrum between the working and reference electrodes at the open-circuit voltage was monitored by an impedance analyzer (Solartron SI-1260) in the frequency range of 0.1 to 10^6 Hz. The separation of the ohmic and polarization losses during cell discharge was made by a current-pulse generator (Nikko Keisoku NCPG-101) with a digital oscilloscope (Yokogawa DL7480). The outlet gas from the anode chamber was analyzed on a dry basis, where it was impossible to measure the amount of steam, by on-line gas chromatography (Varian CP-2002). The analysis precision was $\pm 2\%$ in material balance.

For analysis of the crystalline structure of the doped Bi-based oxides after reduction by hydrogen, the anode was exposed to a hydrogen feed at different temperatures for 2 h and then quenched to room temperature. X-ray diffraction (XRD) analysis was carried out using a diffractometer (Rigaku Rotaflex). For measurement of ac conductivity of the doped Bi-based oxides, the sample was sintered in air at 900°C for 10 h. The conductivity measurement was made by a four-probe technique.

Results and Discussion

The impedance spectra of different doped Bi-based oxide anodes were measured with hydrogen as a typical fuel at 600°C (Table I). Pure Bi_2O_3 showed an ohmic resistance of $2.08 \Omega \text{ cm}^2$, which was larger than a value of $0.82 \Omega \text{ cm}^2$ calculated from the ionic conductivity of the GDC electrolyte at 600°C . The polarization resistance of Bi_2O_3 was also a large value of $7.30 \Omega \text{ cm}^2$. These results were probably due to imperfect reduction of Bi^{3+} to lower valencies, which causes poor electrical collection. Some doped Bi-based oxides, notably $(\text{Bi}_2\text{O}_3)_{0.82}(\text{Ta}_2\text{O}_5)_{0.18}$, showed smaller internal resistances than did Bi_2O_3 . As a result of the optimal Ta_2O_5 content research, both the smallest ohmic and polarization resistances were obtained at 15 mol % Ta_2O_5 : the ohmic resistance was $0.86 \Omega \text{ cm}^2$; the polarization resistance was $1.74 \Omega \text{ cm}^2$. We thus focused on this material (Bi_2O_3 - Ta_2O_5) as the anode in subsequent experiments.

The Bi_2O_3 - Ta_2O_5 anode after the above experiments was partially blackened, which means the reduction of Bi^{3+} to Bi^{2+} or less. The characterizations of this material further clarified this point.

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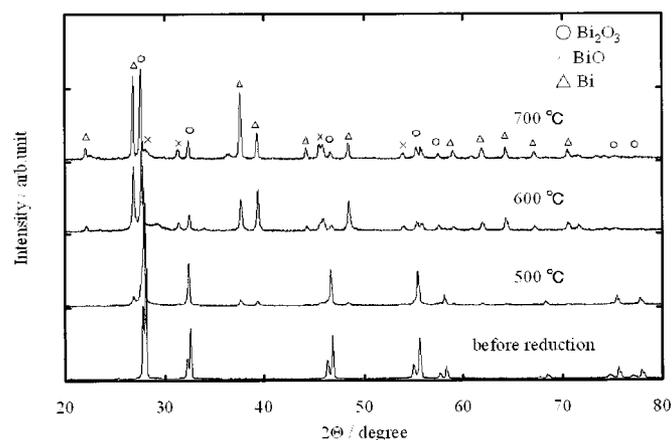
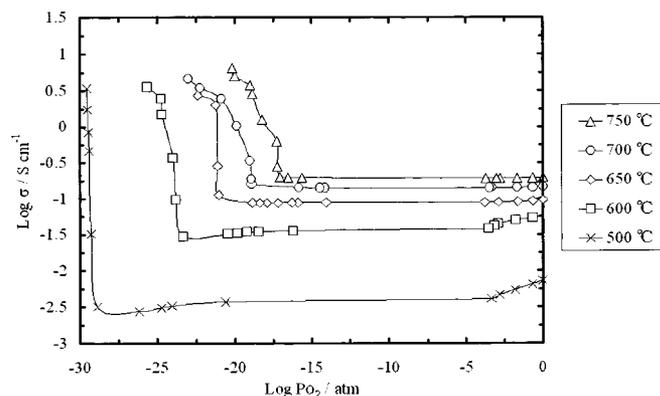
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Table I. Internal resistances of cells between working and reference electrodes with hydrogen at 600°C.

Anode material	Ohmic resistance ($\Omega \text{ cm}^2$)	Polarization resistance ($\Omega \text{ cm}^2$)
Bi_2O_3	2.08	7.30
$(\text{Bi}_2\text{O}_3)_{0.95}(\text{Gd}_2\text{O}_3)_{0.05}$	9.77	158.75
$(\text{Bi}_2\text{O}_3)_{0.85}(\text{Pr}_6\text{O}_{11})_{0.15}$	7.43	86.90
$(\text{Bi}_2\text{O}_3)_{0.73}(\text{Y}_2\text{O}_3)_{0.27}$	6.90	187.86
$(\text{Bi}_2\text{O}_3)_{0.75}(\text{Yb}_2\text{O}_3)_{0.25}$	6.64	110.08
$(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$	5.99	123.34
$(\text{Bi}_2\text{O}_3)_{0.33}(\text{Ba}_2\text{O})_{0.67}$	4.78	88.13
$(\text{Bi}_2\text{O}_3)_{0.78}(\text{W}_2\text{O}_3)_{0.22}$	1.59	2.72
$(\text{Bi}_2\text{O}_3)_{0.85}(\text{Nb}_2\text{O}_5)_{0.15}$	1.14	3.19
$(\text{Bi}_2\text{O}_3)_{0.80}(\text{V}_2\text{O}_5)_{0.20}$	1.13	2.37
$(\text{Bi}_2\text{O}_3)_{0.78}(\text{MoO}_3)_{0.22}$	1.04	3.22
$(\text{Bi}_2\text{O}_3)_{0.82}(\text{Ta}_2\text{O}_5)_{0.18}$	0.97	2.05
$(\text{Bi}_2\text{O}_3)_{0.95}(\text{Ta}_2\text{O}_5)_{0.05}$	0.88	2.13
$(\text{Bi}_2\text{O}_3)_{0.90}(\text{Ta}_2\text{O}_5)_{0.10}$	1.32	1.90
$(\text{Bi}_2\text{O}_3)_{0.85}(\text{Ta}_2\text{O}_5)_{0.15}$	0.86	1.74
$(\text{Bi}_2\text{O}_3)_{0.79}(\text{Ta}_2\text{O}_5)_{0.21}$	0.93	3.12

Figure 1 shows the XRD patterns of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ after reduction by hydrogen at different temperatures. There is no doubt that Bi^{3+} was reduced to Bi^{2+} and Bi metal at all the tested temperatures. This result also suggests that the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode shows good stability to redox cycling because a considerable fraction of Bi_2O_3 remained in the anode even at 700°C. When the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode was alternately supplied with hydrogen and air, it showed no separation from the electrolyte surface. Figure 2 shows the dependence of the overall conductivity of $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ on p_{O_2} at difference temperatures. The conductivities at high p_{O_2} , corresponding to oxide ionic conductivities, were in almost agreement with values reported in the literature.¹⁷ The conductivities at low p_{O_2} were drastically increased up to higher than 1 S cm^{-1} at $p_{\text{O}_2} = 10^{-30}$ to 10^{-15} atm depending on the temperature. It is evident that the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode is a mixed oxide-ionic and electronic conductor under such conditions, which is considered one reason for the smallest ohmic and polarization resistances of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode.

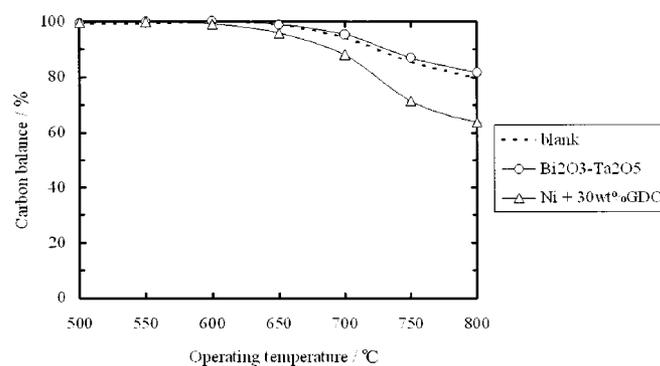
The tolerance of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode to carbon deposition was evaluated with butane as the fuels. Figure 3 shows the carbon balance between the inlet and outlet gases from the anode, which also includes the results for the cells with a Ni-GDC cermet anode (Ni-30 wt % GDC) and without an anode material (blank). While the carbon balance for the Ni-30 wt % GDC anode was by far

**Figure 1.** XRD patterns of $\text{BiO-Ta}_2\text{O}_5$ after reduction by hydrogen at different temperatures.**Figure 2.** Conductivities of $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ as a function of partial pressure of oxygen at different temperatures.

smaller than that for the blank test above 600°C, the carbon balance for the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode showed the excellent agreement with that for the blank test. After experiments, the Ni-30 wt % GDC anode was deposited by a large amount of carbon and was partially shattered by the formation of nickel carbide. In contrast, the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode was perfectly clean, although the walls of the alumina tube were covered with carbon. This high tolerance to carbon deposition may be related to the oxygen species (O_2 , O , O_2^- , O_2^{2-} , O_3^- , O^- , etc.) on the Bi_2O_3 surface,¹¹ which remove the precursors for carbon formation.

The performance of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode was measured with butane as the fuel between 600 and 750°C (Fig. 4). The anodic overpotential decreased with increasing temperature, which reflects the high tolerance to carbon deposition, as described above. As a result, the polarization resistance approached $1.4 \Omega \text{ cm}^2$ at 750°C. Although similar results were obtained with methane, ethane, and propane, the polarization resistance increased in order to butane < propane < ethane < methane: for instance, the resistances of butane, propane, ethane, and methane at 700°C were 2.1, 2.9, 3.6, and $6.0 \Omega \text{ cm}^2$, respectively. It seems that the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode is suitable for use of higher hydrocarbons such as propane and butane.

To better understand the electrode reaction of the hydrocarbons at the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode, the analysis of CO_2 and CO in the outlet gas from the anode was carried out with butane as the fuel at 700°C (Fig. 5). Trace amounts of CO_2 and CO were observed at open-circuit voltage, which indicates that the leak current owing to a mixed conduction was negligible. The dependences of the CO_2 and CO concentration on the current density were roughly linear, where the CO_2 concentration was much higher than the CO concentration at all the current densities. These results demonstrate that the total

**Figure 3.** Carbon balances between inlet and outlet gases from anode with butane fuel between 500 and 800°C.

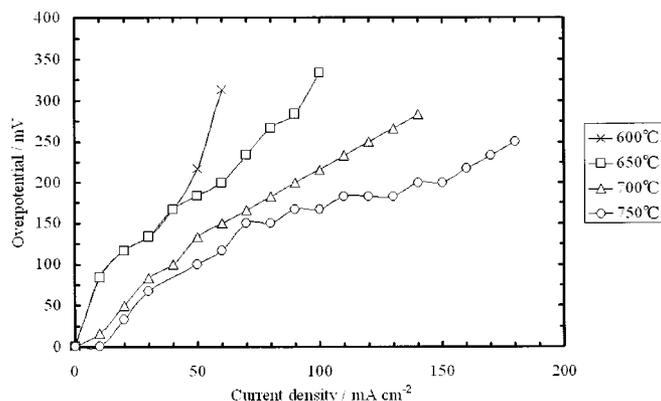


Figure 4. Polarization losses during cell discharge with butane between 600 and 750°C.

electrode reaction is the complete oxidation of butane. However, these results do not mean that this reaction proceeds in one step because the electrochemical oxidation of hydrocarbons is considerably complex.

We finally note information regarding the stability of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode in reducing atmospheres. Bi metal has relatively high vapor pressures at elevated temperatures: for instance, the vapor pressure at 700°C is 7.88×10^{-3} Torr. To clarify the effect of this high vapor pressure on the stability of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode, the long-term stability of this anode was investigated in wet hydrogen at 700°C (Fig. 6). The cell voltage at 40 mA cm^{-2} decreased initially for 10 h, which was usually observed for this anode due to the failed contact of the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode with the Au electrical collector. However, the cell voltage was then stable for at least 180 h. This means either that the vaporization of Bi metal

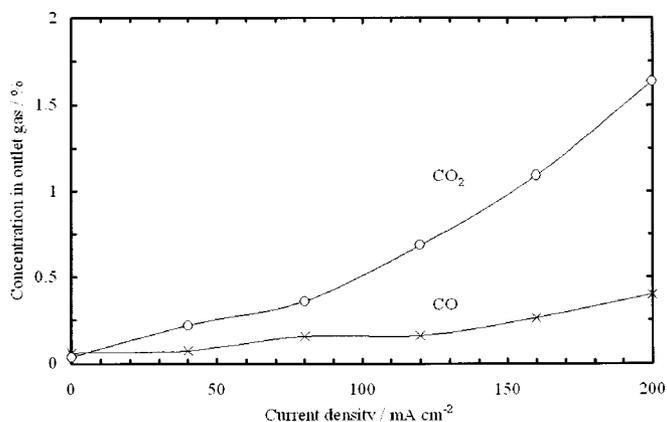


Figure 5. Amounts of CO_2 and CO in outlet gas from anode with butane at 700°C.

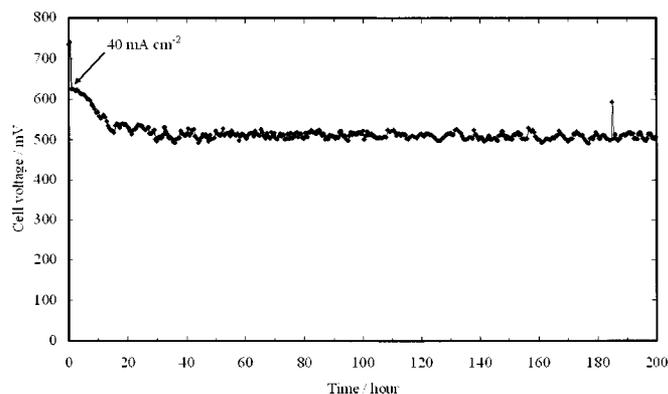


Figure 6. Cell voltage of SOFC at 700°C vs. operating time. The electrolyte thickness was 0.75 mm.

is not significantly serious or that the electrical path in the anode is provided by n-type electronic conduction based on electron hopping between Bi^{3+} and Bi^{2+} .

In conclusion, the present results showed that $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ would be a promising candidate for anodes in the direct hydrocarbon SOFCs. This was achieved by both the high mixed conductivity under fuel conditions and the catalytic properties enough to promote the complete oxidation of hydrocarbons. Furthermore, the $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ anode was stable to both fuel and air and could avoid carbon deposition. The optimization of the anode microstructure is needed to further enhance the position of $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$ as the preferred anode for direct hydrocarbon SOFCs.

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