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Cathode performance and oxygen-ion transport mechanism of copper oxide for solid-oxide fuel cells

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Abstract Various copper oxide cathode materials were studied over a YSZ tube at 800 °C and an oxygen partial pressure of 0.21 atm. It was found that the cathode performance of CuO may be improved by doping Ag metal into it. However, an optimal doping content exists and is around 50 mol% Ag. It was also found that copper oxide itself possess enough oxygen vacancies needed for the role of a mixed conductor. The activation energy for the lattice-oxygen reduction and migration has been calculated to be 55.4 kJ/mol. By the use of electrochemical measurements over Ag-YSZ/CuO electrodes, models for the two-layer electrode have been proposed and justified for oxygen-ion transport mechanisms at low and high overpotentials, respectively; thus, the roles of CuO on the cathode behavior of the electron and oxygen-ion conductivities were well identified.

Keywords Solid-oxide fuel cell · Cathode performance · Copper oxide · Oxygen-ion transport

Introduction

Solid oxide fuel cells (SOFCs) have several advantages over other types of fuel cell systems. The use of a solid electrolyte eliminates most problems of corrosion and liquid management [1]. Moreover, the high operating temperature facilitates rapid electrode kinetics without expensive noble metal electro-catalysts such as Pt for phosphoric acid fuel cells.

At present, perovskite-type mixed conductors such as LaSrMO_3 ($M = \text{Co, Fe, Mn}$) are the most widely used and studied materials for SOFC cathodes [1, 2, 3, 4]. An important advantage of using mixed-conductor

electrodes in SOFCs is to spread the triple-phase boundaries, such as $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ employed as the cathode material in our previous investigation [5]. However, these complicated oxide compounds are difficult to prepare, and their cathode properties are very sensitive to their structures, including the stoichiometric ratio of elements. In this work, we extended our earlier investigation of CuO cathodes, which are easy to prepare [6].

On the other hand, it has been demonstrated [6] that the rate-limiting steps for oxygen reduction on CuO electrodes are adsorption and charge transfer at high and low overpotentials, respectively. However, the roles of CuO on the cathode behavior of the electron and oxygen-ion conductivities are still not well identified. In the present study, models for the oxygen-ion transport mechanism over Ag-YSZ/CuO electrodes at low and high overpotentials, respectively, are proposed and justified; thus, the roles of CuO on the cathode behavior of the electron and oxygen-ion conductivities were well identified.

Experimental

Cathode materials

For doping Ag in CuO, the copper oxide powder was impregnated with an aqueous solution of AgNO_3 for 24 h, and then dried for 24 h at 100 °C. Additionally, for investigating the oxygen-vacancy effect on CuO, oxygen-ion conducting materials such as YSZ (yttria-stabilized zirconia) were impregnated with an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ for 24 h and dried for 24 h. These materials were then mixed with glycerol to form pastes for use as cathode materials. It is found that doping YSZ by directly mixing YSZ powder with CuO powder causes uniformity and boundary problems.

Electrode preparation

The cathode material was painted on the inner bottom surface of a YSZ tube. The tube was then calcined at 850 °C for 90 min. In addition, platinum paste was painted on the outer bottom surface of the YSZ tube as the anode and the reference electrode. It was then calcined at 850 °C for 90 min.

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The polarization experiments were performed using a three-electrode cell. The experimental apparatus was the same as that in our previous investigation [5]. A potentiostat (Pine RDE4) was used to control the working potential. The working potential and the current through the cell were measured by a digital multimeter (HP34401A) with a high input resistance of 10 G Ω .

Results and discussion

Effect of doping metal on cathode performance

The effect of doping silver metal on the cathode behavior of the CuO electrode is shown in Fig. 1. It is seen that the current-overpotential curves of the Ag and the 80 mol% Ag-CuO electrodes are the same. The 50 mol% Ag-CuO electrode exhibits the best cathode performance and this indicates that an optimal doping content of Ag in CuO exists and is about 50 mol%.

A lack of good electron conductivity is a potential issue for pure CuO used as the cathode material. This is because the conductivity of a mixed-conductor material, and thus its cathode performance, is due to both electron and oxygen-ion transport. In our former study [6], where Ag was deposited over the CuO electrode, the oxygen adsorption process was proven to be the rate-limiting step at high overpotential; in addition, the performance of the CuO electrode had observable improvement by doping 15 mol% Ag in CuO. As also shown in Fig. 1, the 10 mol% Ag-CuO electrode has much better cathode performance than that of the CuO electrode.

However, the effect of doping silver metal on the performance of the CuO cathode is not always positive when the Ag content increases; as seen in Fig. 1, the cathode performance approaches an optimum with the electrode contains about 50 mol% Ag doping, and then decreases with increasing Ag doping.

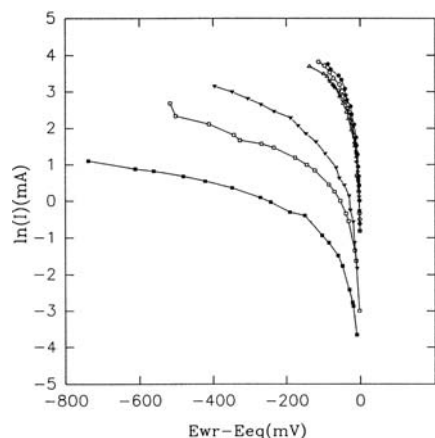


Fig. 1 Current-overpotential curves for Ag-CuO electrodes at 800 °C and $P_{O_2}=0.21$ atm. Open down triangles: Ag; open up triangles: 80 mol% Ag-CuO; open circles and solid circles: 50 mol% Ag-CuO; down solid triangles: 30 mol% Ag-CuO; open squares: 10 mol% Ag-CuO; solid squares: CuO

The optimal cathode performance is proposed for the material with a ratio of electron to oxygen-ion conductivity being able to maintain a maximum quantity of the electrochemical reaction sites for carrying out the charge-transfer reaction, e.g. at the triple-phase boundary of gas, electrode, and electrolyte. For a mixed-conductor cathode material, the triple-phase boundary is delocalized from the electrode-electrolyte interface to the whole electrode surface [3, 4, 5, 7]. Thus, in the case of a mixed conductor, the electrochemical reaction sites can be over the whole cathode surface where the adsorbed oxygen species can meet electrons to form oxygen ions, and then the oxygen ion can meet an oxygen vacancy for its transport through the electrode and/or the electrolyte. Therefore, since excess Ag doping is adverse to the oxygen-ion conductivity of a CuO cathode, an optimal doping of Ag in CuO exists and gives an optimal ratio of electron to oxygen-ion conductivity, which leads to the optimal cathode performance. This also indicates that CuO should be a material capable of oxygen ion transport.

Effect of doping YSZ on cathode performance

Figure 2 shows the effect of doping YSZ, an oxygen-ion conducting material, on the cathode behavior of CuO. It is seen that the CuO cathode with YSZ doping shows a worse I - V performance compared to that of pure CuO. This may be due to the fact that CuO has poor electron conductivity; thus, the doping of YSZ, a pure oxygen-ion conducting material without any electron conductivity, will only cause the problem of poor electron conductivity of CuO to get worse, and, as a consequence, the cathode performance becomes worse. This also indicates that the conduction of oxygen ions is not a problem for CuO as a cathode material.

Additionally, as shown in Fig. 3, doping 10 mol% Bi_2O_3 in CuO, or mixing 10 mol% YSZ or TiO_2 with

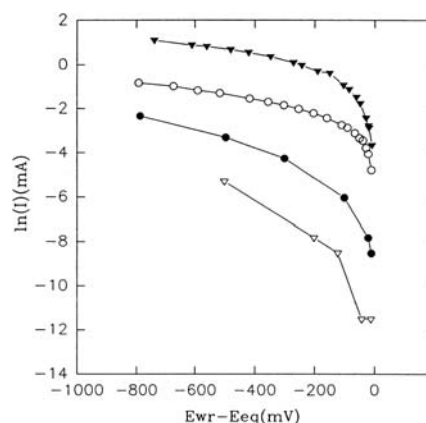


Fig. 2 Current-overpotential curves for CuO-YSZ electrodes at 800 °C and $P_{O_2}=0.21$ atm. Solid down triangles: CuO; open circles: 65 mol% CuO-YSZ; solid circles: 35 mol% CuO-YSZ; open down triangles: 8 mol% CuO-YSZ

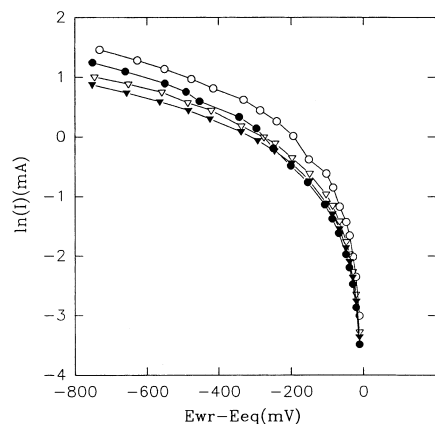


Fig. 3 Current-overpotential curves at 800 °C and $P_{O_2}=0.21$ atm for CuO electrodes doped or mixed with oxygen-ion conducting materials. *Open circles*: CuO; *solid circles*: 10 mol% $\text{Bi}_2\text{O}_3\text{-CuO}$; *open down triangles*: 10 mol% YSZ+CuO; *solid down triangles*: 10 mol% $\text{TiO}_2\text{+CuO}$. The + sign means powder mixing

CuO, is not beneficial to the performance of the CuO electrode. Note that both Bi_2O_3 and TiO_2 have the capability of conducting oxygen ions [8]. Besides, according to the results of Fig. 4, the CuO electrode doped with 50 mol% Ag has a better cathode performance than that of the 50 mol% Ag-doped YSZ electrode, although YSZ is well known as an oxygen-ion conductor. Therefore, it is proposed that CuO itself should have enough oxygen-ion conductivity to satisfy the requirement of the triple-phase boundary for the transport of the oxygen ions; what is needed for the improvement of its cathode performance is an improvement in its electron conductivity.

Oxygen-ion transport mechanism in CuO

In order to clarify the mechanism of oxygen-ion transport in CuO, the current-overpotential characteristics of a 50 mol% Ag-doped YSZ electrode is

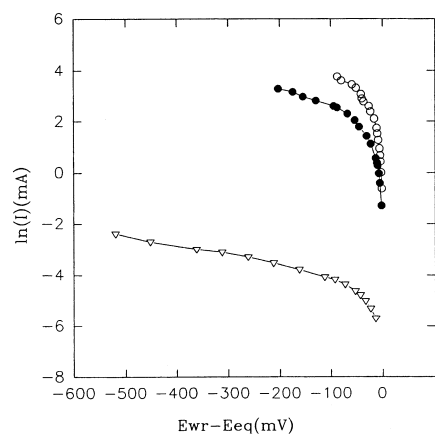


Fig. 4 Current-overpotential curves at 800°C and $P_{O_2}=0.21$ atm for electrodes doped with 50 mol% Ag. *Open circles*: Ag-CuO; *solid circles*: Ag-YSZ; *open down triangles*: Ag- CeO_2

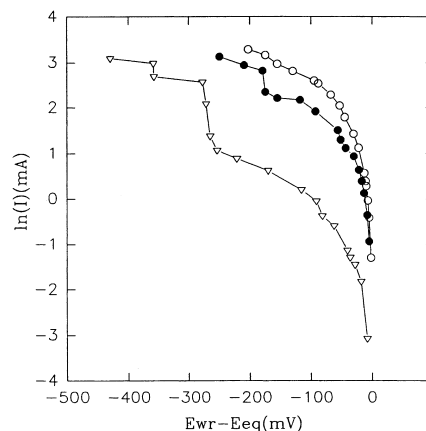


Fig. 5 Current-overpotential curves for 50 mol% Ag-YSZ electrodes with an under-layer of CuO, at 800 °C and $P_{O_2}=0.21$ atm. *Open circles*: Ag-YSZ; *solid circles*: Ag-YSZ/CuO with CuO = 0.004 g; *open down triangles*: Ag-YSZ/CuO with CuO = 0.008 g

compared to those with an under-layer of CuO, as shown in Fig. 5. Because the Ag-doped YSZ material is a mixed conductor, oxygen ions can migrate and penetrate through the electrode along the triple-phase boundary. According to the model shown in Fig. 6a, oxygen will migrate in the form of an ion through the Ag-YSZ layer or diffuse over its surface. If CuO is not conducting the oxygen ions, the oxygen species have to diffuse over the surface to reach the interface of the CuO and electrolyte, and then complete the reduction process.

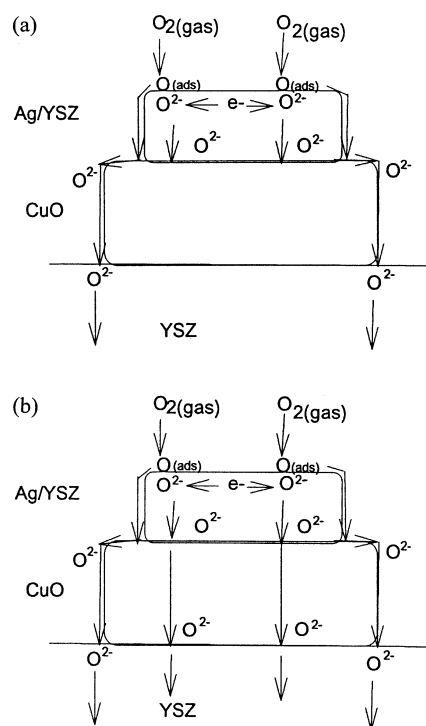


Fig. 6 Models for oxygen-ion transport mechanism over Ag-YSZ/CuO electrodes: (a) at low overpotential; (b) at high overpotential

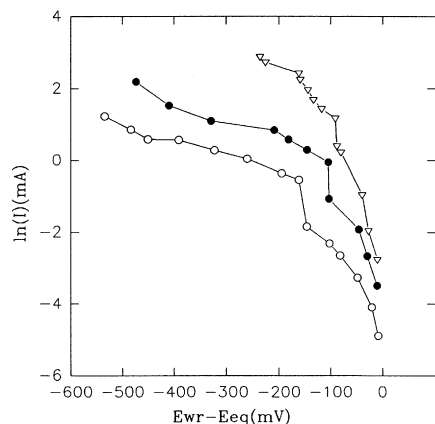


Fig. 7 Current-overpotential curves for a 50 mol% Ag-YSZ/CuO electrode at $P_{O_2}=0.21$ atm. Open circles: 700 °C; solid circles: 750 °C; down open triangles: 800 °C

As also shown in Fig. 5, in the overpotential range of -100 to -200 mV, the 50 mol% Ag-doped YSZ electrode displays a much better performance than that with an under-layer of CuO. The mechanism of oxygen-ion transport may be described by the model shown in Fig. 6a. However, the behavior of the I - V curve for the electrode with a CuO under-layer has an abrupt shift (jump) when the overpotential reaches a value around -200 mV, as shown in Fig. 5. This behavior is attributed to a dramatic change of the path of oxygen-ion transport, and may be described by the mechanism such as that of Fig. 6b. This is due to part of the oxygen species migrating directly through the CuO under-layer in the form of ions. Therefore, an enormous amount of oxygen vacancies should have been created in CuO at the overpotential around -200 mV to cause the dramatic change of the cathode behavior.

The mechanism to create oxygen vacancies in CuO is supposed to be the lattice-oxygen reduction and migration when the lattice oxygen overcomes the energy barrier by a specific electrical field. When a certain energy barrier of the lattice-oxygen migration in CuO is overcome, the triple-phase boundary may be extended to the whole bulk of CuO so that the oxygen-ion transport rate and thus the cathode reaction rate increase greatly.

The above-proposed mechanism of creating oxygen vacancies is further supported by the results of doubling the thickness of the CuO under-layer, as shown in Fig. 5, where an increase of the thickness of the CuO under-layer causes the dramatic change (shift) of the cathode behavior to occur at a higher overpotential due to the increase of the energy barrier of the lattice-oxygen migration in this CuO layer.

On the other hand, as shown in Fig. 7, the shift point of the potential depends on the operating temperature.

This is an indication that the reduction and migration of the lattice oxygen in CuO has to do with temperature. According to the Arrhenius law, the activation energy of the lattice-oxygen reduction and migration can be calculated by plotting the log values of the overpotentials at the shift points relative to $1/T$. The calculated activation energy is 55.4 kJ/mol, which is close to the value of 100 kJ/mol for the lattice oxygen migration in Cu₂O [9]. Therefore, it is concluded that CuO has great potential for conducting oxygen ions, not only by the intrinsic oxygen vacancies promoted by adding metal, but also by the extrinsic oxygen vacancies created by an electrical field.

Conclusions

From the above results and discussion, it is seen that the cathode performance of CuO may be improved by doping Ag metal in it. It is also seen that an optimal doping content exists and is around 50 mol% Ag.

It is also found that copper oxide itself possess enough oxygen vacancies needed for the role of a mixed conductor because doping an oxygen-ion conducting material such as YSZ does not improve the cathode performance of CuO.

The activation energy for the lattice-oxygen reduction and migration has been calculated to be 55.4 kJ/mol according to the results of the overpotential shift.

By the electrochemical measurements over the Ag-YSZ/CuO electrodes, models for the two-layer electrode have been proposed and justified for an oxygen-ion transport mechanism at low and high overpotentials, respectively; thus, the roles of CuO on the cathode behavior of the electron and oxygen-ion conductivities are well identified.

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