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(54) **SOLID OXIDE FUEL CELL AND MANUFACTURING METHOD OF THE SAME**

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(56)               **References Cited**  
  
U.S. PATENT DOCUMENTS  
  
4,767,680 A     8/1988   Hijikata ..... 429/456  
5,670,270 A     9/1997   Wallin ..... 429/496  
6,146,780 A     11/2000   Cisar ..... 429/435  
2002/0048699 A1   4/2002   Steele et al. .... 429/30  
2004/0043272 A1\*   3/2004   Gorte ..... H01M 4/8885 429/488  
  
(Continued)  
  
FOREIGN PATENT DOCUMENTS  
  
CN               1897337 A     \*   1/2007  
CN               103765647 A   4/2014  
  
(Continued)  
  
OTHER PUBLICATIONS  
  
Fabbri, Emiliana, et al. "Electrode materials: a challenge for the exploitation of protonic solid oxide fuel cells." Science and technology of advanced materials (2010) (Year: 2010).\*  
  
(Continued)  
  
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(57)               **ABSTRACT**  
  
A solid oxide fuel cell includes a support of which a main component is a metal, and an anode supported by the support, wherein the anode includes a first oxide having electron conductivity, wherein the first oxide is perovskite type oxide expressed as a composition formula ABO<sub>3</sub>, wherein "A" of the composition formula includes at least one of Ca, Sr, Ba and La, wherein "B" of the composition formula includes at least Cr.

**12 Claims, 3 Drawing Sheets**



(56)

## References Cited

## U.S. PATENT DOCUMENTS

2004/0247978	A1	12/2004	Shimamune	428/685
2005/0019642	A1	1/2005	Hishitani	429/465
2005/0266297	A1	12/2005	Irvine et al.	429/40
2006/0113034	A1 *	6/2006	Seabaugh	H01M 8/1246 156/308.2
2006/0127749	A1	6/2006	Christie	427/126.3
2006/0286433	A1	12/2006	Rakowski	429/455
2007/0269701	A1	11/2007	Larsen et al.	429/33
2007/0275292	A1	11/2007	Sin Xicola	429/495
2008/0090127	A1	4/2008	Gorte	429/535
2009/0061279	A1	3/2009	Larsen	429/410
2010/0028757	A1	2/2010	Fu et al.	429/40
2010/0178589	A1	7/2010	Kwon	429/535
2012/0003565	A1	1/2012	Son	429/496
2012/0082920	A1	4/2012	Mukerjee	429/495
2012/0129039	A1	5/2012	Drenckhahn	429/223
2013/0157166	A1	6/2013	Tsai	429/481
2013/0224628	A1 *	8/2013	Moon	H01M 4/8657 429/479
2013/0295489	A1 *	11/2013	Kim	H01M 4/8605 264/105
2014/0072836	A1 *	3/2014	Mills	H01M 14/00 429/422
2014/0170529	A1	6/2014	Jain	252/518.1
2014/0170532	A1	6/2014	Ohtani et al.	429/534
2014/0242858	A1	8/2014	Ochiai et al.	440/88 M
2014/0287342	A1	9/2014	Jabbar et al.	429/482
2015/0064596	A1	3/2015	Leah	429/465
2015/0194682	A1	7/2015	Ashary	429/468
2017/0273769	A1	9/2017	Dengler	A61C 17/3472
2018/0019493	A1	1/2018	Jakus	
2018/0323443	A1	11/2018	Tucker et al.	H01M 4/8882
2019/0081331	A1	3/2019	Bauer	
2019/0088969	A1	3/2019	Koizumi et al.	H01M 8/1226
2019/0140287	A1	5/2019	Liu et al.	H01M 4/8882
2019/0296385	A1	9/2019	Sugihara	
2022/0200033	A1	6/2022	Seno et al.	H01M 8/1213

## FOREIGN PATENT DOCUMENTS

CN	107994234	A *	5/2018	B82Y 30/00
JP	H 04-075262		7/1990	
JP	H 07-249412	A	9/1995	
JP	H 09-027330	A	1/1997	
JP	2004512651	A	4/2004	
JP	2005-535084	A	11/2005	
JP	2008502113	A	1/2008	
JP	2009-541955	A	11/2009	
JP	2012-033418	A	2/2012	
JP	2012190746	A	10/2012	
JP	2013012473	A	1/2013	
JP	2014163286	A	9/2014	
JP	2015-153467	A	8/2015	
JP	2016039099	A	3/2016	
JP	2016-115506	A	6/2016	
JP	2017033799	A	2/2017	
JP	2017525431	A	9/2017	
JP	2018-055946	A	4/2018	
JP	2020087792	A	11/2018	
JP	2019517098	A	6/2019	
JP	WO 2019/159276	A1	8/2019	
JP	2012-074307	A	4/2021	
WO	WO 98/49738	A1	11/1998	
WO	WO 2014/046196	A1	3/2014	
WO	WO 2018042476	A1	3/2018	
WO	WO 2020/218431	A1	10/2020	

## OTHER PUBLICATIONS

Ju, Young-Wan, et al. "New buffer layer material La (Pr) CrO<sub>3</sub> for intermediate temperature solid oxide fuel cell using LaGaO<sub>3</sub>-based electrolyte film." *Journal of Materials Research* 27 (2012): 1906-1914 (Year: 2012).\*

Vert, Vicente B., et al. "Redox stability and electrochemical study of nickel doped chromites as anodes for H<sub>2</sub>/CH<sub>4</sub>-fueled solid oxide fuel cells." *Applied Catalysis B: Environmental* 115 (2012): 346-356. (Year: 2012).\*

Oh, Tae-Sik, et al. "Infiltrated lanthanum strontium chromite anodes for solid oxide fuel cells: Structural and catalytic aspects." *Journal of Power Sources* 262 (2014): 207-212 (Year: 2014).\*

Yan, Yan, et al. "Fabrication of reactive element oxide coatings on porous ferritic stainless steel for use in metal-supported solid oxide fuel cells." *Surface and Coatings Technology* 272 (2015): 415-427 (Year: 2015).\*

Huang, B., et al. "Characterization of a Cu—La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>-CeO<sub>2</sub>/La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>-YSZ/Ni—ScSZ three-layer structure anode in thin film solid oxide fuel cell running on methane fuel." *Fuel Cells* 15 (2015): 398-407. (Year: 2015).\*

Wasilewski, Eric, et al. "Cu/LaCrO<sub>3</sub> joining by local melt infiltration through laser cladding." *Journal of the American Ceramic Society* 101 (2018): 4472-4479. (Year: 2018).\*

Gupta, Sapna, Manoj K. Mahapatra, and Prabhakar Singh. "Lanthanum chromite based perovskites for oxygen transport membrane." *Materials Science and Engineering: R: Reports* 90 (2015): 1-36 (Year: 2015).\*

Gao, Zhan, et al. "A perspective on low-temperature solid oxide fuel cells." *Energy & Environmental Science* 9.5 (2016): 1602-1644 (Year: 2016).\*

Fan, W., et al. "Improved properties of scandia and yttria co-doped zirconia as a potential thermal barrier material for high temperature applications." *Journal of the European Ceramic Society* 38.13 (2018): 4502-4511 (Year: 2018).\*

WO2019159276A1, Shibata, et al., "Metal Supported Cell", machine English translation retrieved from <https://worldwide.espacenet.com/> on Dec. 8, 2022 (Year: 2019).\*

CN1897337A, Gao Jianfeng Meng, "Solid oxide fuel battery anode and its production", machine English translation retrieved from <https://worldwide.espacenet.com/> Date: Aug. 2, 2023 (Year: 2007).\*

Jiang, San Ping, et al. "Electrical conductivity and performance of doped LaCrO<sub>3</sub> perovskite oxides for solid oxide fuel cells." *Journal of Power Sources* 176.1 (2008): 82-89 (Year: 2008).\*

Teocoli, Francesca, et al. "Effects of co-sintering in self-standing CGO/YSZ and CGO/ScYSZ dense bi-layers." *Journal of Materials Science* 49 (2014): 5324-5333 (Year: 2014).\*

CN107994234A, Fan, "Ceramic fuel cell and fabrication method thereof", machine English translation retrieved from <https://worldwide.espacenet.com/> Date: Dec. 12, 2023 (Year: 2018).\*

Irvine, John Thomas Sirr. "Perovskite oxide anodes for SOFCs." *Perovskite oxide for solid oxide fuel cells* (2009): 167-182 (Year: 2009).\*

"What is Spark Plasma Sintering" California Nanotechnologies—Intro to Spark Plasma Sintering, <https://www.calnanocorp.com/what-is-spark-plasma-sintering> accessed Aug. 1, 2024 (Year: 2023).\*

Notice of Reasons for Refusal issued on May 9, 2023, in related Japanese Patent Application No. 2019-157789.

Notice of Reasons for Refusal issued on Jul. 25, 2023 in related Japanese Patent Application No. 2019-184725.

Notification of First Office Action dated Oct. 26, 2023, issued by the China National Intellectual Property Administration in corresponding application CN 202011030776.X.

Peter Blennow et al., "Development of Planar Metal Supported SOFC with Novel Cermet Anode", *ECS Transactions*, 25 (2) 701-710 (2009).

Office Action issued on Oct. 19, 2023, in a counterpart Chinese Patent Application No. 202110245145.8.

A Notice of Reasons for Refusal issued by the Japanese Patent Office, mailed Dec. 6, 2022, for Japanese counterpart application No. 2018-222503. (3 pages).

A Notice of Reasons for Refusal issued by the Japanese Patent Office, mailed Sep. 6, 2022, for Japanese counterpart application No. 2018-222503. (5 pages).

Notice of Reasons for Refusal issued on Jan. 23, 2024 in a counterpart Japanese Patent Application No. 2020-040846.

Office Action issued on Dec. 20, 2023 in a related Chinese Patent Application No. 202010884982.0.

(56)

**References Cited**

OTHER PUBLICATIONS

Chinese Office Action issued on Jun. 24, 2024 in a related Chinese  
Patent Application No. 202010884982.0.

\* cited by examiner

FIG. 1

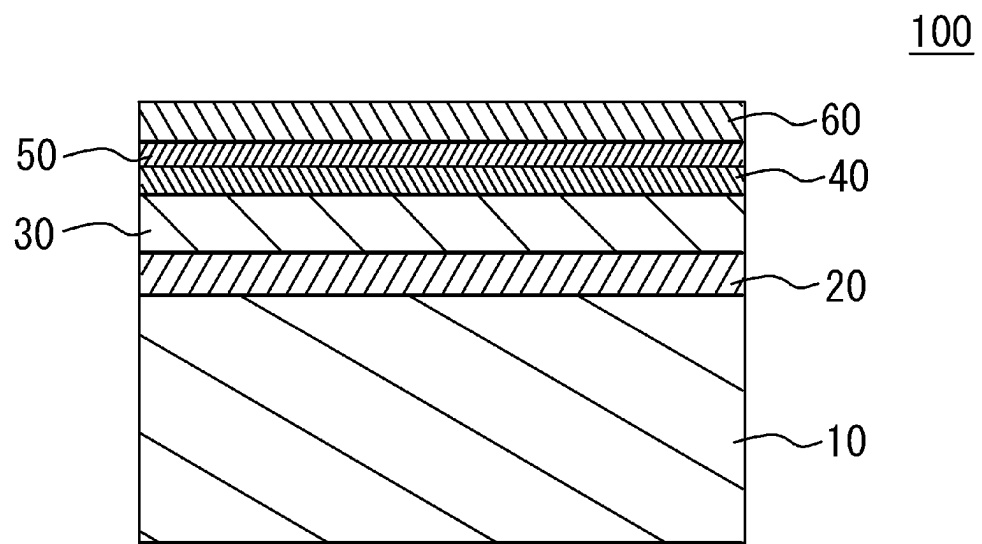


FIG. 2

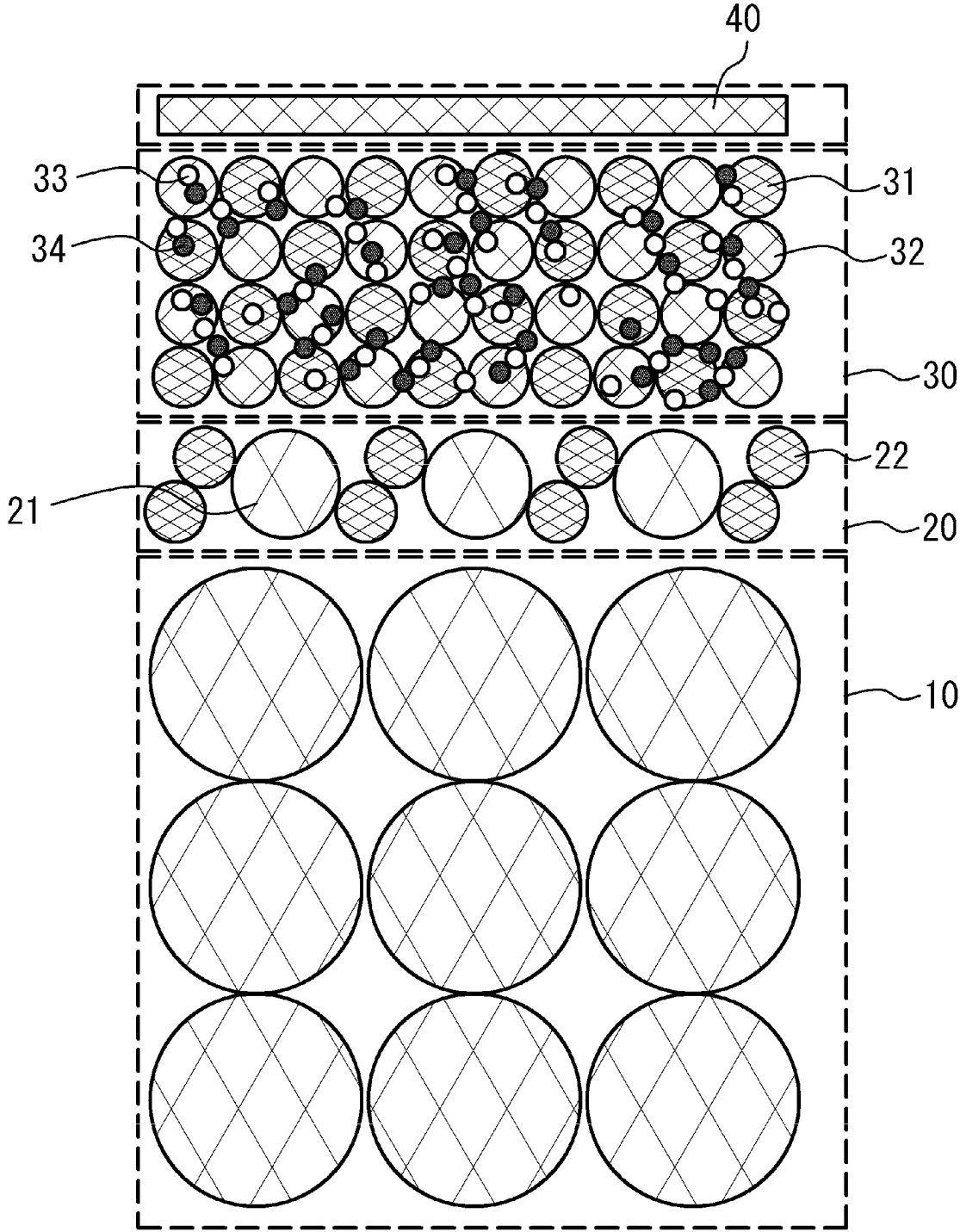
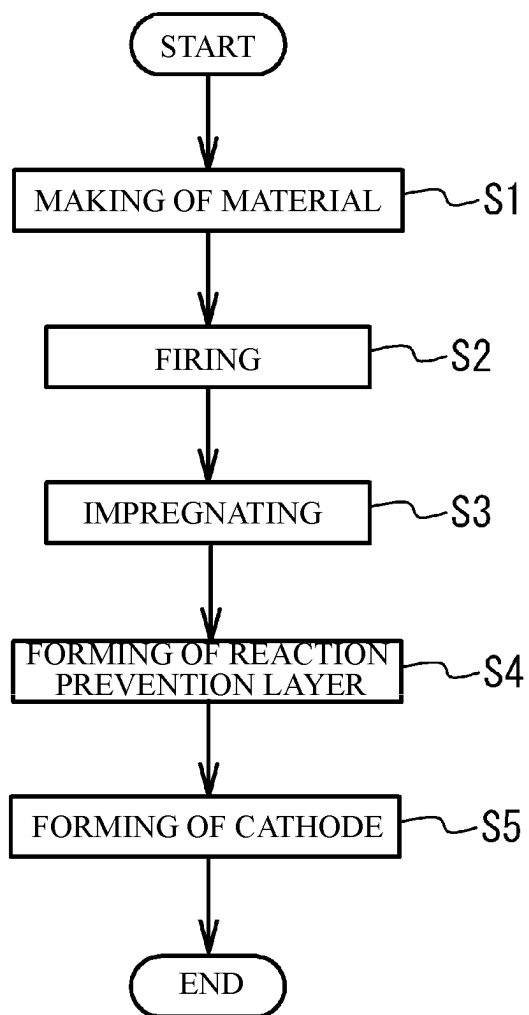


FIG. 3



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# SOLID OXIDE FUEL CELL AND MANUFACTURING METHOD OF THE SAME

## CROSS-REFERENCE TO RELATED APPLICATION

This application is based upon and claims the benefit of priority of the prior Japanese Patent Application No. 2019-184725, filed on Oct. 7, 2019, the entire contents of which are incorporated herein by reference.

## FIELD

A certain aspect of the present embodiments relates to a solid oxide fuel cell and a manufacturing method of the same.

## BACKGROUND

The solid oxide fuel cell includes a solid oxide electrolyte layer having oxygen ion conductivity, an anode, and a cathode. At the anode, oxygen ions passing through the solid oxide electrolyte layer from the cathode react with hydrogen contained in a fuel gas. This reaction generates electrical power. It is necessary for the anode to have electron conductivity. And so, there is disclosed a technology in which an anode includes LaTiO<sub>3</sub>-based material having the electron conductivity (see Japanese Patent Application Publication No. 2012-33418 and Japanese Patent Application Publication No. 2009-541955).

## SUMMARY

There is a problem that solid oxide fuel cells made of ceramics are susceptible to thermal shock or mechanical shock. And so, it is thought that the fuel cells are supported by a metal member so as to high resistance against vibration, shock or rapid rate of rising and falling temperature. However, a metallic support is fired in strong reductive atmosphere in order to suppress oxidation of the metallic support. And so, developing of an anode which can be fired in the strong reductive atmosphere is requested.

According to a first aspect of the present embodiments, there is provided a solid oxide fuel cell including: a support of which a main component is a metal; and an anode supported by the support, wherein the anode includes a first oxide having electron conductivity, wherein the first oxide is perovskite type oxide expressed as a composition formula ABO<sub>3</sub>, wherein "A" of the composition formula includes at least one of Ca, Sr, Ba and La, wherein "B" of the composition formula includes at least Cr.

According to a second aspect of the present embodiments, there is provided a manufacturing method of a solid oxide fuel cell, the manufacturing method including: preparing a multilayer structure in which a support green sheet and an anode green sheet are stacked, the support green sheet including metal material powder, the anode green sheet including perovskite type oxide as ceramic material powder, the perovskite type oxide being expressed by a composition formula ABO<sub>3</sub> in which "A" of the composition formula includes at least one of Ca, Sr, Ba and La and "B" of the composition formula includes at least Cr, firing the multilayer structure in reductive atmosphere.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of a multilayer structure of a fuel cell;

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FIG. 2 is an enlarged cross-sectional view of details of a support, a mixed layer, and an anode; and

FIG. 3 is a flowchart of the manufacturing method of a fuel cell.

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## DETAILED DESCRIPTION

Hereinafter, an embodiment will be described with reference to the accompanying drawings.

FIG. 1 is a schematic cross-sectional view of a stacking structure of a solid oxide fuel cell 100. As illustrated in FIG. 1, the fuel cell 100 has, as an example, a structure in which a mixed layer 20, an anode 30, an electrolyte layer 40, a reaction prevention layer 50, and a cathode 60 are stacked on a support 10 in this order. A plurality of the fuel cells 100 may be stacked to structure a fuel cell stack.

The electrolyte layer 40 is a dense layer that is mainly composed of solid oxide having oxygen ion conductivity and has gas impermeability. The electrolyte layer 40 is preferably mainly composed of scandia yttria stabilized zirconium oxide (ScYSZ). The oxygen ion conductivity is the highest when the concentration of Y<sub>2</sub>O<sub>3</sub>+Sc<sub>2</sub>O<sub>3</sub> is 6 mol % to 15 mol %. Thus, use of a material having this composition is preferable. The thickness of the electrolyte layer 40 is preferably 20 μm or less, further preferably 10 μm or less. The thinner electrolyte layer is better. However, to prevent gas at the upper face side and gas at the lower face side from leaking, the thickness is preferably 1 μm or greater.

The cathode 60 is an electrode having electrode activity as a cathode, and has electron conductivity and oxygen ion conductivity. For example, the cathode 60 is lanthanum strontium cobaltite (LSC) having electron conductivity and oxygen ion conductivity. LSC is LaCoO<sub>3</sub> doped with strontium (Sr).

The reaction prevention layer 50 is mainly composed of a component that prevents reaction between the electrolyte layer 40 and the cathode 60. For example, the reaction prevention layer 50 is mainly composed of Gd-doped ceria (GDC) that is CeO<sub>2</sub> doped with gadolinium (Gd). As an example, when the electrolyte layer 40 contains ScYSZ and the cathode 60 contains LSC, the reaction prevention layer 50 prevents the following reactions.

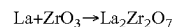
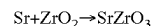


FIG. 2 is an enlarged cross-sectional view illustrating details of the support 10, the mixed layer 20, and the anode 30. As illustrated in FIG. 2, the support 10 is a member that has gas permeability and is able to support the mixed layer 20, the anode 30, the electrolyte layer 40, the reaction prevention layer 50, and the cathode 60. The support 10 is a porous metallic material, and is, for example, a porous material of Fe—Cr alloys.

The anode 30 is an electrode having electrode activity as an anode, and has an electrode bone structure made of a ceramic material. The electrode bone structure contains no metallic component. In this configuration, decrease in the porosity in the anode due to coarsening of a metallic component is inhibited during firing in a high-temperature reductive atmosphere. Additionally, alloying with a metallic component of the support 10 is inhibited, and deterioration of the catalyst function is inhibited.

The electrode bone structure of the anode 30 preferably has electron conductivity and oxygen ion conductivity. The anode 30 preferably contains a first oxide 31 as an electron

conductive material. The first oxide **31** can be a perovskite-type oxide expressed by the composition formula of  $ABO_3$  where the A site is at least one selected from a group consisting of Ca, Sr, Ba, and La, and the B site includes at least Cr. The perovskite-type oxide has favorable electron conductivity. The mole fraction of the B site may be equal to or greater than the mole fraction of the A site ( $B \geq A$ ). More specifically, the first oxide **31** can be a  $LaCrO_3$ -based material. The B site of the perovskite-type oxide included in the first oxide **31** may include another element such as Ti, in addition to Cr. For example, when the  $LaCrO_3$ -based material is expressed by  $LaCr_xTi_{1-x}O_3$  because the B site includes both Ti and Cr, x is 0.5 or more and 1 or less.

When the amount of  $CrO_3$  generated by decomposition of the first oxide **31** is large in the anode **30**, the anode **30** may not necessarily achieve favorable electron conductivity. And so, it is preferable that the amount of  $CrO_3$  has a lower limit. For example, when the cross section of the anode **30** is observed, it is preferable that {the area of  $CrO_3$ /(the area of  $CrO_3$  and the area of the first oxide **31**)} is 10% or less. It is more preferable that {the area of  $CrO_3$ /(the area of  $CrO_3$  and the area of the first oxide **31**)} is 5% or less. It is still more preferable that {the area of  $CrO_3$ /(the area of  $CrO_3$  and the area of the first oxide **30**)} is 1% or less. It is possible to measure the area of the perovskite oxide and the area of  $CrO_3$ , by SEM-EDS mapping of the cross section.

The electrode bone structure of the anode **30** preferably contains a second oxide **32** as an oxygen ion conductive material. The second oxide **32** is ScYSZ or the like. For example, it is preferable to use ScYSZ having the following composition range. Scandia ( $Sc_2O_3$ ) is 5 mol % to 16 mol %, and yttria ( $Y_2O_3$ ) is 1 mol % to 3 mol %. It is more preferable to use ScYSZ of which the total additive amount of scandia and yttria is 6 mol % to 15 mol %. This is because the highest oxygen ion conductivity is obtained in this composition range. The oxygen ion conductive material is, for example, a material with a transference number of oxygen ion of 99% or greater. GDC may be used as the second oxide **32**. In the example of FIG. 2, a solid oxide identical to the solid oxide contained in the electrolyte layer **40** is used as the second oxide **32**.

As illustrated in FIG. 2, in the anode **30**, for example, the first oxide **31** and the second oxide **32** form the electrode bone structure. This electrode bone structure forms a plurality of pores. A catalyst is carried on the surface exposed to the pore of the electrode bone structure. Thus, in the spatially continuously formed electrode bone structure, a plurality of catalysts is spatially dispersed. A composite catalyst is preferably used as the catalyst. For example, a third oxide **33** having oxygen ion conductivity and a catalyst metal **34** are preferably carried, as a composite catalyst, on the surface of the electrode bone structure. The third oxide **33** may be, for example,  $BaCe_{1-x}Zr_xO_3$  doped with Y (BCZY,  $x=0$  to 1),  $SrCe_{1-x}Zr_xO_3$  doped with Y (SCZY,  $x=0$  to 1),  $LaScO_3$  doped with Sr (LSS), or GDC. Ni or the like may be used as the catalyst metal **34**. The third oxide **33** may have a composition identical to that of the second oxide **32**, or may have a composition different from that of the second oxide **32**. A metal acting as the catalyst metal **34** may be in a form of compound when electric power is not generated. For example, Ni may be in a form of a nickel oxide (NiO). These compounds are reduced with a reductive fuel gas supplied to the anode **30**, and becomes in a form of metal acting as an anode catalyst.

From a viewpoint of favorable power generation performance of the fuel cell **100**, it is preferable that the area of the electron conductive path, the area of the ion conductive path,

and the area of the pore are appropriately balanced. For example, in the cross section of the anode **30**, it is preferable that each of the area of the first oxide **31**, the area of the second oxide **32** and the area of the pore is 20% or more and 60% or less. For example, in the cross section of the anode **30**, the area ratio of the first oxide **31** is 60%, the area ratio of the second oxide **32** is 20%, and the area ratio of the pore is 20%. Alternatively, in the cross section of the anode **30**, it is preferable that each of the area ratio of the first oxide **31**, the area ratio of the second oxide **32**, and the area ratio of the pore is 33%.

The mixed layer **20** contains a metallic material **21** and a ceramic material **22**. In the mixed layer **20**, the metallic material **21** and the ceramic material **22** are randomly mixed. Thus, a structure in which a layer of the metallic material **21** and a layer of the ceramic material **22** are stacked is not formed. Also in the mixed layer **20**, a plurality of pores is formed. The metallic material **21** is not particularly limited as long as the metallic material **21** is a metal. In the example of FIG. 2, a metallic material identical to the metallic material of the support **10** is used as the metallic material **21**. The first oxide **31** or the second oxide **32** can be used as the ceramic material **22**. For example, ScYSZ, GDC, a  $LaTiO_3$ -based material, or a  $LaCrO_3$ -based material can be used as the ceramic material **22**. Since the  $LaTiO_3$ -based material and the  $LaCrO_3$ -based material have high electron conductivity, the ohmic resistance in the mixed layer **20** can be reduced. It is preferable that the same oxide of the first oxide **31** is used as the ceramic material **22**.

The fuel cell **100** generates power by the following actions. An oxidant gas containing oxygen, such as air, is supplied to the cathode **60**. At the cathode **60**, oxygen reaching the cathode **60** reacts with electrons supplied from an external electric circuit to become oxygen ions. The oxygen ions conduct through the electrolyte layer **40** to move to the anode **30** side. On the other hand, a fuel gas containing hydrogen, such as a hydrogen gas or a reformed gas, is supplied to the support **10**. The fuel gas reaches the anode **30** through the support **10** and the mixed layer **20**. Hydrogen reaching the anode **30** release electrons at the anode **30** and reacts with oxygen ions conducting through the electrolyte layer **40** from the cathode **60** side to become water ( $H_2O$ ). The released electrons are drawn out to the outside by the external electric circuit. The electrons drawn out to the outside are supplied to the cathode **60** after doing electric work. Through the above-described actions, electric power is generated.

In the above-described power generation reaction, the catalyst metal **34** acts as a catalyst in the reaction between hydrogen and oxygen ions. The first oxide **31** conducts electrons obtained by the reaction between hydrogen and oxygen ions. The second oxide **32** conducts oxygen ions reaching the anode **30** from the electrolyte layer **40**.

The fuel cell **100** of the embodiment has the support **10** of which the main component is a metal. Therefore, the fuel cell **100** has resistance against thermal shock, mechanical shock and so on. The support **10** can be fired in strong reductive atmosphere because the main component of the support **10** is a metal. The first oxide **31** is the perovskite type oxide of which the composition formula is expressed as  $ABO_3$ . The A site includes at least one of Ca, Sr, Ba, and La. The B site includes at least Cr. It is possible to fire the anode **30** in the strong reductive atmosphere. It is therefore possible to fire the support **10** together with the anode **30**. And it is possible to make the fuel cell **100**. The first oxide **31** has favorable electron conductivity. Therefore, the fuel cell **100** can achieve favorable power generation performance.



In the fuel cell 100 according to the present embodiment, the support 10 is mainly composed of a metal, and the electrode bone structure of the anode 30 is composed of ceramic. In the aforementioned structure, when firing is performed such that the support 10 and the anode 30 are in contact with each other, the difference in material properties between metal and ceramic may cause interlayer peeling between the support 10 and the anode 30. In particular, ceramic fired in a strong reductive atmosphere has poor adhesiveness with metal. In contrast, it is preferable that the fuel cell 100 according to the present embodiment includes the mixed layer 20 interposed between the support 10 and the anode 30. Since the mixed layer 20 contains the metallic material 21 and the ceramic material 22, the mixed layer 20 has material properties of metal and material properties of ceramic. Thus, the mixed layer 20 has high adhesiveness with the support 10 and high adhesiveness with the anode 30. Therefore, interlayer peeling between the support 10 and the anode 30 can be inhibited.

Additionally, in the fuel cell 100 according to the present embodiment, the third oxide 33 is carried on the electrode skeleton of the anode 30. This structure allows to first form the electrode bone structure by firing, and then, impregnate the electrode bone structure with the third oxide 33 and fire the electrode bone structure at low temperature. Thus, even when the second oxide 32 and the third oxide 33 do not have the same composition, reaction between oxides is inhibited. Therefore, the degree of freedom to select, as the third oxide 33, an oxide appropriate to the composite catalyst is increased.

Additionally, the porosity in the support 10, the porosity in the mixed layer 20, and the porosity in the anode 30 preferably have a relationship of the porosity in the support 10>the porosity in the mixed layer 20>the porosity in the anode 30. This relationship allows the support 10 to have sufficient gas permeability. Since the anode 30 has a comparatively low porosity, the anode 30 obtains high electron conductivity and high oxygen ion conductivity while maintaining gas permeability. The mixed layer 20 obtains gas permeability and the contact area with the support 10 is obtained. Thus, the mixed layer 20 obtains the adhesion with the support 10. The porosity is calculated from the ratio of the estimated area of the pores to the entire area based on an SEM image of the cross-section of a sample.

Hereinafter, a manufacturing method of the fuel cell 100 will be described. FIG. 3 is a flowchart of the manufacturing method of the fuel cell 100.

#### Making Process of Material for Support

Metallic powder having a particle size of, for example, 10  $\mu\text{m}$  to 100  $\mu\text{m}$ , a plasticizer, a solvent, a vanishing material, and a binder are mixed to make slurry as a material for support. The amount of the plasticizer is adjusted to, for example, 1 wt % to 6 wt % to adjust the adhesiveness of the sheet. The solvent is toluene, 2-propanol (IPA), 1-butanol, terpineol, butyl acetate, ethanol, or the like. The amount of the solvent is 20 wt % to 30 wt % depending on the viscosity or the like. The vanishing material is an organic substance. The binder is PVB, acrylic resin, ethyl cellulose, or the like. The material for support is used as a material for forming the support 10. The ratio of the volume of the organic components (the vanishing material, the solid component of the binder, and the plasticizer) to the volume of the metallic powder is within a range of, for example, 1:1 to 20:1. The amount of the organic components is adjusted depending on the porosity.

#### Making Process of Material for Mixed Layer

Ceramic material powder, which is the raw material of the ceramic material 22, metallic material powder having a small particle size, which is the raw material of the metallic material 21, a solvent, a plasticizer, and a binder are mixed to make slurry as a material for mixed layer. The ceramic material powder has a particle size of, for example, 100 nm to 10  $\mu\text{m}$ . The metallic material powder has a particle size of, for example, 1  $\mu\text{m}$  to 10  $\mu\text{m}$ . The solvent is toluene, 2-propanol (IPA), 1-butanol, terpineol, butyl acetate, ethanol, or the like. The amount of the solvent is 20 wt % to 30 wt % depending on the viscosity. The amount of the plasticizer is adjusted to 1 wt % to 6 wt % to adjust the adhesiveness of the sheet. The vanishing material is an organic substance. The binder is PVB, acrylic resin, ethyl cellulose, or the like. The ratio of the volume of the organic components (the vanishing material, the solid component of the binder, and the plasticizer) to the volume of the ceramic material powder and the metallic material powder is within a range of, for example, 1:1 to 5:1. The amount of the organic components is adjusted depending on the porosity. The diameter of the pore is controlled by adjusting the particle size of the vanishing material. The ceramic material powder may contain powder of an electron conductive material and powder of an oxide-ion conductive material. In this case, the ratio of the volume of the powder of the electron conductive material to the volume of the powder of the oxide-ion conductive material is preferably within a range of, for example, 1:9 to 9:1. Use of an electrolyte material such as ScYSZ, GDC, or the like instead of the electron conductive material also prevents the peeling of the boundary face and enables the manufacture of the cell. However, to reduce the ohmic resistance, it is preferable to mix an electron conductive material and metallic powder.

#### Making Process of Material for Anode

Ceramic material powder structuring the electrode bone structure, a solvent, a plasticizer, a vanishing material, and a binder are mixed to make slurry as a material for anode. The solvent is toluene, 2-propanol (IPA), 1-butanol, terpineol, butyl acetate, ethanol, or the like. The amount of the solvent is 20 wt % to 30 wt % depending on the viscosity. The amount of the plasticizer is adjusted to, for example, 1 wt % to 6 wt % to adjust the adhesiveness of the sheet. The vanishing material is an organic substance. The binder is PVB, acrylic resin, ethyl cellulose, or the like. Powder of the electron conductive material that is the raw material of the first oxide 31 and has a particle size of, for example, 100 nm to 10  $\mu\text{m}$  and powder of the oxygen ion conductive material that is the raw material of the second oxide 32 and has a particle size of, for example, 100 nm to 10  $\mu\text{m}$  may be used as the ceramic material powder structuring the electrode bone structure. The ratio of the volume of the organic components (the vanishing material, the solid component of the binder, and the plasticizer) to the volume of the powder of the electron conductive material is within a range of, for example, 1:1 to 5:1, and the amount of the organic components is adjusted depending on the porosity. Additionally, the diameter of the pore is controlled by adjusting the particle size of the vanishing material. The ratio of the volume of the powder of the electron conductive material to the volume of the powder of the oxygen ion conductive material is within a range of, for example, 3:7 to 7:3.

#### Making Process of Material for Electrolyte Layer

Powder of an oxygen-ion conductive material, a solvent, a plasticizer, and a binder are mixed to make slurry as a material for electrolyte layer. The powder of the oxygen-ion conductive material is, for example, ScYSZ, YSZ, GDC, or

the like, and has a particle size of 10 nm to 1000 nm. The solvent is toluene, 2-propanol (IPA), 1-butanol, terpineol, butyl acetate, ethanol, or the like. The amount of the solvent is 20 wt % to 30 wt % depending on the viscosity. The amount of the plasticizer is adjusted to 1 wt % to 6 wt % to adjust the adhesiveness of the sheet. The binder is PVB, acrylic resin, ethyl cellulose, or the like. The ratio of the volume of the organic components (the solid component of the binder and the plasticizer) to the volume of the powder of the oxygen ion conductive material is within a range of, for example, 6:4 to 3:4.

#### Making Process of Material for Cathode

Powder of lanthanum strontium cobaltite (LSC:  $\text{LaSr-CoO}_3$ ), a solvent, a plasticizer, and a binder are mixed to make slurry as a material for cathode. The solvent is toluene, 2-propanol (IPA), 1-butanol, terpineol, butyl acetate, ethanol, or the like, and the amount of the solvent is 20 wt % to 30 wt % depending on the viscosity. The plasticizer is adjusted to 1 wt % to 6 wt % to adjust the adhesiveness of the sheet. The binder is PVB, acrylic resin, ethyl cellulose, or the like. The ratio of the volume of the organic components (the solid component of the binder, the plasticizer) to the volume of LSC powder is within a range of, for example, 6:4 to 1:4.

#### Firing Process

A support green sheet is made by applying the material for support on a polyethylene terephthalate (PET) film. A mixed layer green sheet is made by applying the material for mixed layer on another PET film. An anode green sheet is made by applying the material for anode on yet another PET film. An electrolyte layer green sheet is made by applying the material for electrolyte layer on yet another PET film. For example, several support green sheets, one mixed layer green sheet, one anode green sheet, and one electrolyte layer green sheet are stacked in this order, cut into a predetermined size, and fired within a temperature range of approximately 1100° C. to 1300° C. in a reductive atmosphere with an oxygen partial pressure of  $10^{-16}$  atm or less. Through the above process, a half cell including the support **10**, the mixed layer **20**, the electrode bone structure of the anode **30**, and the electrolyte layer **40** is obtained. The reductive gas flown into the furnace may be a gas in which  $\text{H}_2$  (hydrogen) is diluted with non-flammable gas (Ar (argon), He (helium),  $\text{N}_2$  (nitrogen) or the like). 100% of the reductive gas may be  $\text{H}_2$ . From a view point of safety such as explosion limit, it is preferable that the concentration of  $\text{H}_2$  has an upper limit. For example, it is preferable that the concentration of  $\text{H}_2$  is 4 volume % or less, when the reductive atmosphere is a mixed gas of  $\text{H}_2$  and Ar.

#### Impregnating Process

Next, the electrode bone structure of the anode **30** is impregnated with the raw materials of the third oxide **33** and the catalyst metal **34**. For example, the following process is repeated as many times as needed such that Gd-doped ceria or Sc, Y-doped zirconia and Ni are generated when the cell is fired in a reductive atmosphere at a predetermined temperature. Nitrate or chloride of Zr, Y, Sc, Ce, Gd, or Ni is dissolved in water or alcohol (ethanol, 2-propanol, methanol or the like). A half cell is impregnated with the resulting solution, and dried. The resulting half cell is subjected to heat treatment.

#### Forming Process of Reaction Preventing Layer

As the reaction prevention layer **50**,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$  is formed so as to have a thickness of 1  $\mu\text{m}$  by, for example, PVD.

#### Forming Process of Cathode

Next, the material for cathode is applied on the reaction prevention layer **50** by screen printing and is then dried. Then, a cathode is sintered by heat treatment. Through the above process, the fuel cell **100** can be fabricated.

In the manufacturing method of the embodiment, the first oxide **31** is the perovskite type oxide of which the composition formula is expressed as  $\text{ABO}_3$ . The A site includes at least one of Ca, Sr, Ba, and La. The B site includes at least Cr. It is possible to stably fire the anode **30** in the strong reductive atmosphere. It is therefore possible to fire the support **10** together with the anode **30**. And it is possible to make the fuel cell **100**. The main component of the support **10** is a metal. Therefore, the fuel cell **100** has resistance against thermal shock, mechanical shock and so on. The first oxide **31** has favorable electron conductivity. Therefore, the fuel cell **100** can achieve favorable power generation performance.

When the oxygen partial pressure in the firing atmosphere is  $10^{16}$  atm or less, it is possible to suppress the generation of  $\text{CrO}_3$  caused by the decomposition of the first oxide **31**. Therefore, the first oxide **31** achieves favorable electron conductivity. From a view point of suppression of the generation of  $\text{CrO}_3$ , it is preferable that the oxygen partial pressure in the firing atmosphere is  $10^{-20}$  atm or less. It is more preferable that the oxygen partial pressure is  $10^{-22}$  atm or less.

Since the material for mixed layer contains the metallic material powder and the ceramic material powder, the mixed layer **20** after the firing the metallic material **21** and the ceramic material **22**. Therefore, the mixed layer **20** has material properties of the metallic material **21** and the ceramic material **22**. Therefore, interlayer peeling between the support **10** and the anode **30** can be inhibited.

Additionally, the amount of the vanishing material in the material for support, the amount of the vanishing material in the material for mixed layer, the amount of the vanishing material in the material for anode are preferably adjusted such that the porosity in the support **10**, the porosity in the mixed layer **20**, and the porosity in the anode **30** have a relationship of the porosity in the support **10** > the porosity in the mixed layer **20** > the porosity in the anode **30**. This relationship allows the support **10** to have sufficient gas permeability. The anode **30** becomes dense, and obtains high oxygen ion conductivity. The mixed layer **20** obtains gas permeability, and also obtains the contact area with the support **10**, thereby obtaining adhesion with the support **10**.

In the manufacturing method according to the present embodiment, the electrode bone structure is first formed by firing. Then, the electrode bone structure is impregnated with the composite catalyst and fired at low temperature (for example, 850° C. or less). Thus, even when the second oxide **32** and the third oxide **33** do not have the same composition, the reaction between oxides is inhibited. Therefore, the degree of freedom to select, as the third oxide **33**, an oxide appropriate to the composite catalyst is increased.

#### EXAMPLES

The fuel cell **100** was fabricated according to the manufacturing method in accordance with the above embodiment.

#### Example 1

SUS (stainless) powder was used as the material for support. ScYSZ was used as the electrolyte layer **40**. A  $\text{LaCrO}_3$ -based material was used for the first oxide **31** of the

anode **30**, and ScYSZ was used for the second oxide **32**. GDC was used for the third oxide **33**, and Ni was used for the catalyst metal **34**. The electrode bone structure was formed of the first oxide **31** and the second oxide **32**. A  $\text{LaCrO}_3$ -based material was used for the ceramic material **22** of the mixed layer **20**. Stainless steel (SUS) was used for the metallic material **21** of the mixed layer **20**. The cell after stacking was fired under a reductive atmosphere with an oxygen partial pressure of  $10^{-16}$  atm or less. Additionally, the resulting cell was impregnated with the composite catalyst, and was then fired under an air atmosphere at a temperature of  $850^\circ\text{C}$ . or less.

#### Example 2

ScYSZ was used as the electrolyte layer **40**. A  $\text{LaCr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ -based material was used for the first oxide **31** of the anode **30**, and ScYSZ was used for the second oxide **32**. GDC was used for the third oxide **33**, and Ni was used for the catalyst metal **34**. The electrode bone structure was formed of the first oxide **31** and the second oxide **32**. A  $\text{LaCrO}_3$ -based material was used for the ceramic material **22** of the mixed layer **20**. SUS was used for the metallic material **21** of the mixed layer **20**. The cell after stacking was fired under a reductive atmosphere with an oxygen partial pressure of  $10^{-16}$  atm or less. Additionally, the resulting cell was impregnated with the composite catalyst, and was then fired under air atmosphere at a temperature of  $850^\circ\text{C}$ . or less.

#### Comparative Example 1

A  $\text{LaTiO}_3$ -based material was used for the first oxide **31** of the anode **30**. A  $\text{LaTiO}_3$ -based material was used for the ceramic material **22** of the mixed layer **20**. Other conditions were the same as those of the example 1.

#### Comparative Example 2

A  $\text{LaCrO}_3$ -based material was used for the material for support. No mixed layer **20** was provided. The cell after the stacking was fired under normal atmosphere. Other conditions were the same as those of example 1.

Table 1 shows the manufacturing conditions of the examples 1 and 2, and the comparative examples 1 and 2.

TABLE 1

	ELECTROLYTE	ANODE BONE STRUCTURE		MIXED LAYER			OHMIC RESISTANCE ( $\Omega \cdot \text{cm}^2$ )	REACTION RESISTANCE ( $\Omega \cdot \text{cm}^2$ )
		FIRST OXIDE	SECOND OXIDE	OXIDE	METAL	SUPPORT		
EXAMPLE 1	ScYSZ	$\text{LaCrO}_3$	ScYSZ	$\text{LaCrO}_3$	SUS	SUS	0.25	0.28
EXAMPLE 2	ScYSZ	$\text{LaCr}_{0.9}\text{Ti}_{0.1}\text{O}_3$	ScYSZ	$\text{LaCrO}_3$	SUS	SUS	0.26	0.28
COMPARATIVE EXAMPLE 1	ScYSZ	$\text{LaTiO}_3$	ScYSZ	$\text{LaTiO}_3$	SUS	POWDER	0.25	0.4
COMPARATIVE EXAMPLE 2	ScYSZ	$\text{LaCrO}_3$	ScYSZ	—	—	$\text{LaCrO}_3$	0.31	0.78

#### Evaluation of Electrical Power Generation

Impedance of each of the fuel cells of the examples 1 and 2 and the comparative examples 1 and 2 was measured to separate the resistance value to measure the ohmic resistance of the fuel cell as a whole and the reaction resistance of the

anode **30**. In the example 1, the ohmic resistance was  $0.25 \Omega \cdot \text{cm}^2$ , and the reaction resistance of the anode **30** was  $0.28 \Omega \cdot \text{cm}^2$ . In the example 2, the ohmic resistance was  $0.26 \Omega \cdot \text{cm}^2$ , and the reaction resistance of the anode **30** was  $0.28 \Omega \cdot \text{cm}^2$ .

From the results of the examples 1 and 2, it is thought that the anode **30** was stably fired in the strong reductive atmosphere, the first oxide **31** achieved favorable electron conductivity, and the ohmic resistance was favorable, because the first oxide **31** of the anode **30** was the perovskite type oxide expressed as the composition formula  $\text{ABO}_3$  in which the A site included at least one of Ca, Sr, Ba and La, and the B site included at least Cr. From the result of the example 2, it is understood that the anode **30** achieves favorable electron conductivity even if another element such as Ti is added to the B site of the perovskite type oxide of the first oxide **31** in addition to Cr.

The cross section of the cell of the example 1 after the firing was observed by the SEM-EDS. {the area of  $\text{CrO}_3$ /the area of  $\text{CrO}_3$  and the area of the first oxide **31**} in the anode **30** was 5% or less. It is thought that this was because the anode **30** was fired in the strong reductive atmosphere and the flocculation of  $\text{CrO}_3$  was suppressed. The area ratio of the first oxide **31** in the cross section of the anode **30** was 27%. The area ratio of the second oxide **32** was 27%. The area ratio of the pores was 46%. Interlayer peeling did not occur in the examples 1 and 2. It is thought that this was because the mixed layer **20** was provided.

In the comparative example 1, the ohmic resistance was  $0.25 \Omega \cdot \text{cm}^2$ , and the reaction resistance of the anode was  $0.40 \Omega \cdot \text{cm}^2$ . In this manner, the electrical power generation performance of the comparative example 1 was less than that of the examples 1 and 2. In the strong reductive atmosphere, resistance of the  $\text{LaTiO}_3$ -based material against reductive force is small, and oxygen defects occur because of reduction of Ti. In this case, grain growth tends to be promoted. The anode becomes dense more easily than the  $\text{LaCrO}_3$ -based material of the examples 1 and 2. It is thought that the porosity of the anode after the firing was reduced, and the electrical power generation performance gets worse. The cross section of the anode was observed by the SEM-EDS. The area of the pores in the anode using the  $\text{LaTiO}_3$ -based material was 30% or less in the whole of the anode. It is thought that this was because gas diffusion became

worse, and the high performance of the electrical power generation of the example 1 was not achieved.

In the comparative example 2, the ohmic resistance was  $0.31 \Omega \cdot \text{cm}^2$ , and the reaction resistance of the anode was  $0.78 \Omega \cdot \text{cm}^2$ . In this manner, the electrical power generation

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performance of the comparative example 2 was less than that of the examples 1 and 2. It is thought that this was because the resistance value of the ceramic support was larger than that of the metallic support. Moreover, the anode was fired in the normal atmosphere, the LaCrO<sub>3</sub>-based material of the first oxide **31** was decomposed, and a large amount of CrO<sub>3</sub> was generated. The cross section of the cell of the comparative example 2 after the firing was observed by the SEM-EDS. {the area of CrO<sub>3</sub>/(the area of CrO<sub>3</sub> and the area of the first oxide **31**)} in the anode was approximately 30%.

Although the embodiments of the present invention have been described in detail, the present invention is not limited to such a specific embodiment, and it is to be understood that the various change, substitutions, and alterations could be made hereto without departing from the spirit and scope of the invention.

What is claimed is:

1. A solid oxide fuel cell comprising:

a support of which a main component is a metal;

an anode supported by the support; and

a mixed layer provided between the support and the anode,

wherein the anode includes a first oxide which is LaCrO<sub>3</sub>-based perovskite of which an A site is only La and of which a B site is only Cr and Ti and a second oxide having oxygen ion conductivity,

wherein the support, the mixed layer and the anode are sintered bodies which are obtained by arranging a powder material of a LaCrO<sub>3</sub>-based material and a powder metal material for the mixed layer mixed together with a width in a stacking direction, on a powder metal material for the support, and arranging a powder material including the first oxide on the powder material of a LaCrO<sub>3</sub>-based material and a powder metal material for the mixed layer, and sintering the powder metal material for the support, the powder material of a LaCrO<sub>3</sub>-based material and the powder metal material for the mixed layer, and the powder material including the first oxide,

wherein the LaCrO<sub>3</sub>-based material of the mixed layer is LaCrO<sub>3</sub>-based perovskite of which an A site is only La and of which a B site is only Cr or only Cr and Ti,

wherein the anode forms an electrode bone structure with the first oxide and the second oxide having oxygen ion conductivity,

wherein the bone structure contains no metallic component, is spatially continuously formed, and includes pores and catalysts, and

wherein each of the catalysts is carried on a surface exposed to each of the pores,

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wherein an ohmic resistance of the solid oxide fuel cell as a whole is 0.26 Ω·cm<sup>2</sup> or less, and wherein a reaction resistance of the anode is 0.28 Ω·cm<sup>2</sup> or less.

2. The solid oxide fuel cell as claimed in claim 1, wherein {an area of CrO<sub>3</sub>/(the area of CrO<sub>3</sub> and an area of the first oxide)} is 10% or less, in a cross section of the anode.

3. The solid oxide fuel cell as claimed in claim 1, wherein an area ratio of a total of the first oxide/a total of (the first oxide+the second oxide+the pores) in the cross section of the anode is 20% or more and 60% or less,

wherein an area ratio of a total of the second oxide/the total of (the first oxide+the second oxide+the pores) in the cross section of the anode is 20% or more and 60% or less, and

wherein an area ratio of a total of the pores/the total of (the first oxide+the second oxide+the pores) in the cross section of the anode is 20% or more and 60% or less.

4. The solid oxide fuel cell as claimed in claim 1,

wherein a porosity in the support, a porosity in the mixed layer, and a porosity in the anode have a relationship of the porosity in the support>the porosity in the mixed layer>the porosity in the anode.

5. The solid oxide fuel cell as claimed in claim 1, wherein each of the catalysts includes a catalyst metal and a third oxide having oxygen ion conductivity.

6. The solid oxide fuel cell as claimed in claim 1, wherein the second oxide is scandia yttria stabilized zirconium oxide.

7. The solid oxide fuel cell as claimed in claim 1,

wherein {an area of CrO<sub>3</sub>/(the area of CrO<sub>3</sub> and an area of the first oxide)} is 5% or less, in a cross section of the anode.

8. The solid oxide fuel cell as claimed in claim 1,

wherein the second oxide of the anode is scandia yttria stabilized zirconium oxide; and

wherein the catalysts are Gd-doped ceria and Ni.

9. The solid oxide fuel cell as claimed in claim 1,

wherein the LaCrO<sub>3</sub>-based material of the mixed layer is LaCr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> and x is 0.5 or more and less than 1.

10. The solid oxide fuel cell as claimed in claim 1,

wherein an A site of the LaCrO<sub>3</sub>-based material of the mixed layer is only La, and

wherein a B site of the LaCrO<sub>3</sub>-based material of the mixed layer is only Cr and Ti.

11. The solid oxide fuel cell as claimed in claim 1,

wherein the first oxide is LaCr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> and x is 0.5 or more and less than 1.

12. The solid oxide fuel cell as claimed in claim 1,

wherein a ratio of the reaction resistance to the ohmic resistance is 1.12 or less.

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