

Improvement of the Electrode Performance of Alloy Substrate-type Tubular SOFC

— Development and application of the intermediate layer —

Akihiko Momma, Yasuo Kaga, Takayasu Okuo, Kohji Fujii, Kiminori Hohjyo and Motoi Kanazawa

Anodic and cathodic catalyst layers (intermediate layers) were developed for the purpose of improving the performance of metallic substrate type tubular SOFC that has been being developed in our laboratory. The intermediate layer basically consists of the mixture of the electrode and the electrolyte materials and is inserted between the electrode and the electrolyte and acts as catalyst for the electrode reaction. Anodic intermediate layer was prepared by using nickel powders followed by the plasma spraying of YSZ. The performance of cathodic intermediate layers prepared by three methods were also investigated. Cathodic intermediate layer made by plasma spraying using granulated powder was found to be most effective in reducing the cathodic polarization in the practical tubular cell applications.

§1 Introduction

SOFC has been attracting much attention for its potentially rich possibility to become a major system of conversion of fossil energy resources into useful energy for the coming decades of enforced reduction of CO₂ emission. Because it's not based on thermodynamic cycle, the efficiency is not restricted by Carnot's cycle limitation. Because of its high operational temperatures, SOFC needs no noble catalyst to get substantial driving force for the electrode reaction. The high temperature brings its another alternative of operation; combined system. These features surely became a trigger for the world wide R&D of SOFC as it is today.

One of the outcomes of the decades of world wide R&D of SOFC is the splendid characteristics of the tubular type SOFC⁽¹⁾ that has been developed by Westinghouse Electric Company in U.S. Their cell has passed almost every possible criteria for the practical application but the cost of fabrication. It's well too high. As concerning to the materials, it is the ceramic tubular substrate that occupies almost all the weight of their cell. Our approach⁽²⁾ is to make the tubular substrate using metallic alloy maintaining the mechanical strength that has been achieved with the ceramic tubular

substrate. Less material needed for the purpose is definitely desirable for the suppression of the fabrication cost.

The application of the metallic substrate inevitably sets the operating temperature lower than the nominal operating temperature of the ceramic substrate SOFC. It also restricts the temperatures during the fabrication process. Normal sintering process or firing process which needs temperatures well higher than 1000°C cannot be applied in our manufacturing processes. This is why we set the spraying as a major process for the fabrication of our cells. The idea is to make as many cell elements as possible by the spraying maintaining the fabrication process as simple as possible.

Since lower operating temperature is required, we need electrodes of superior performance. On the other hand, simple spraying of the electrode material on the solid electrolyte would not make an electrode of high efficiency, because of the fact that it is very difficult to control the micro-structure of the deposit by the sprayings. This is the reason why we have come to the idea of the application of the intermediate layer⁽³⁾.

The performance of the cell can be improved by suppressing each polarization included in the cell. The polarizations include some ohmic polarizations and two activation polarizations related to the electrochemical

reactions at the two electrodes. While some of the ohmic contributions are truly determined by the geometrical factors once the materials are given, activation polarizations are considerably dependent on the micro-structure of electrode/electrolyte interface. In other words, the performance of the electrodes is well controllable by modifying the interface, not making any changes in the kind of the materials selected for the electrolyte and for the electrodes.

§2 Experimental

2.1 Sample preparation

2.1.1 Anode catalyst

Schematic of the cross section of the sample is shown in **Fig.1** Planar substrate used for the evaluation of anode catalyst was prepared by die pressing alloy powders and sintering procedures. Two types of alloy substrates were prepared by two different alloys that have almost the same composition but have different particle size. NiCrAlY alloy powders in spherical structure were used. SEM pictures of the sintered alloy surfaces are shown in **Fig.2**.

Ni or Pt catalyst layer was prepared on the substrate by coating the corresponding metal slurry. Ni slurry was prepared by mixing Ni powders ($1\mu\text{m}$, $2-3\mu\text{m}$ Koujundokagaku) and water or iso-propanol alcohol. Commercially available Pt paste (Johnson Matthey Electronics) was used for the Pt slurry. These slurries were painted on the substrate and fired at 1200°C in H_2 for 1 hour. The amount of the catalyst was ca. $20\text{mg}/\text{cm}^2$. Typical SEM picture of the surface with anode catalyst is shown in **Fig.3**. The catalyst was deposited on the substrate in such a way that the catalyst particles flatten the substrate surface.

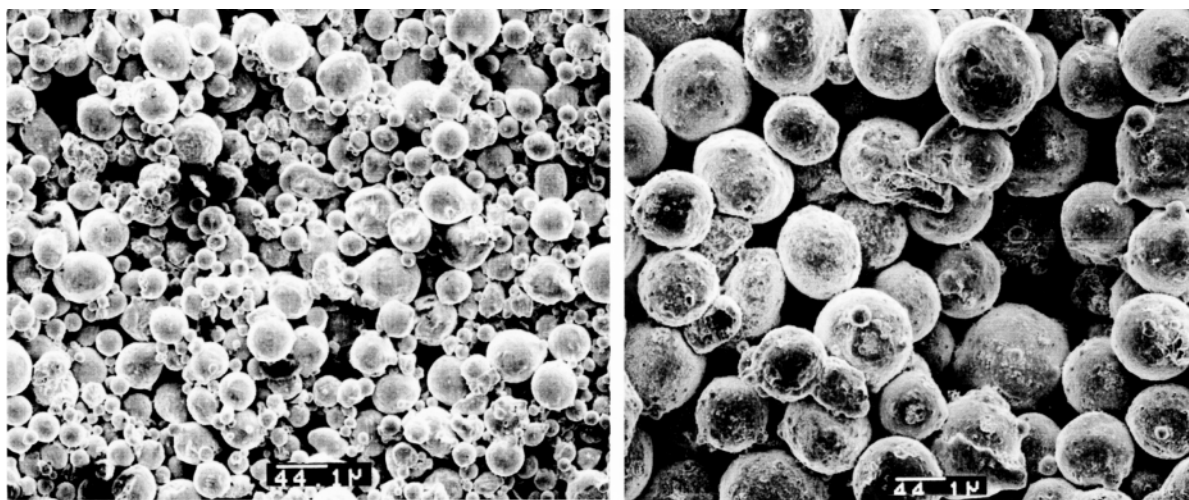


Fig.2 SEM pictures of the surface of two types of porous alloy substrates.

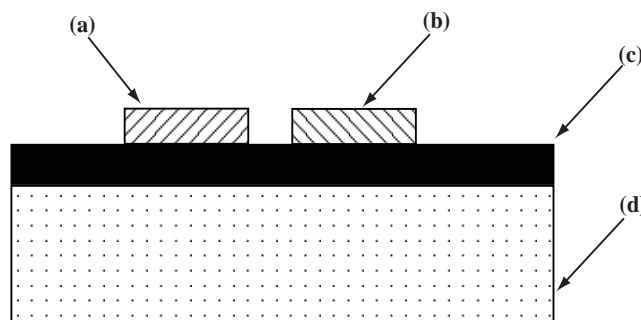


Fig. 1 Schematic of the cross sectional view of the sample used for the anode catalyst evaluations.

(a) air electrode, (b) reference electrode, (c) YSZ, (d) porous metallic substrate

This helped making the succeeding YSZ deposition easier, because YSZ layer is supposed to be as gas tight as possible with minimum thickness. The painted catalyst particles do not necessarily have to form a continuous layer since the underlying substrate works as a current collector.

After the catalyst deposition YSZ electrolyte was deposited by plasma spraying. Thickness of the electrolyte was around $350\mu\text{m}$. And finally, cathode and reference electrodes were deposited by flame spraying using $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ or $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$.

2.1.2 Cathode catalyst

Several methods were tested and evaluated for the deposition of cathode catalysts. These methods tested were also chosen because they were considered to be applicable for our metallic substrate type SOFC, i.e. they don't need any high temperature treatment. Because our cells are based on the alloy substrate, the adoption of the high temperature

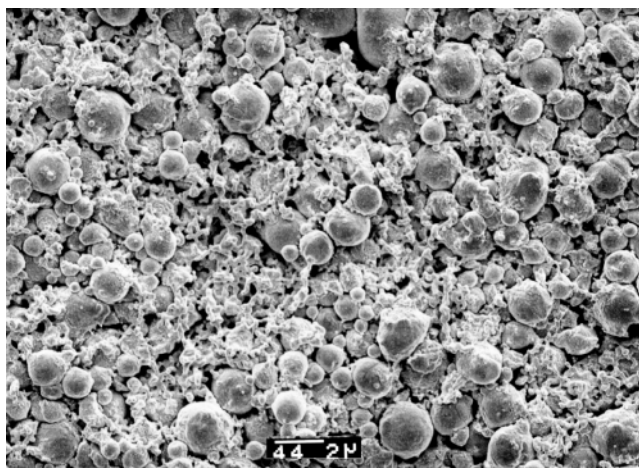


Fig.3 Porous alloy substrate with Ni slurry pasted and sintered.

in the fabrication process is not favorable. The highest temperature that can be possibly included during the preparation process is set to be less than the operational temperature of SOFC at least in oxidizing atmosphere. For this reason, the three methods were applied.

(a) pyrolysis of metalorganic solution

(b) alternate spraying of electrode and electrolyte materials

(c) plasma spraying of granulated mixed powder

The idea in either case is to make a mixed intermediate layer which is consisted of as much electrode and electrolyte material interface as possible in order to secure electrochemical reaction site, i.e. triple phase boundary(tpb).

In the method (a), submicron size LSM powders were mixed with organic solution of Ce and Sm. The obtained solution was then painted on YSZ and was fired at 600°C in air to form an intermediate layer. In the intermediate layer, the submicron size LSM powders are dispersed in SDC electrolyte contributing to the formation of tpb.

Thermal spraying of LSM and plasma spraying of YSZ were alternatively and repeatedly adopted to form an intermediate layer in the method (b). In these spraying, the traverse rate of the spraying guns were maintained at their highest speed and the spraying was conducted only one pass for each material at each time so that the sprayed powders only make non-continuous layer that has an island structure. By repeating the process with LSM and YSZ alternatively, one can obtain a well mixed layer, mingled with flatten sprayed particles, which contains much LSM and YSZ interface. Schematic of the cross section is shown in **Fig.4**.

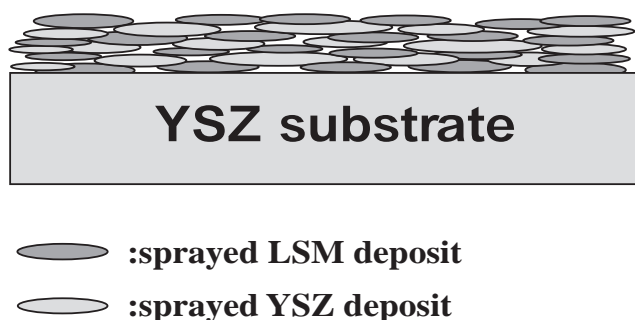


Fig.4 Schematic of the cross sectional view of the intermediate layer prepared by method (b).

Premixed granulated powders are used for the spraying in the method (c). The granulated particles, the secondary particles, have the average particle size of 30μm which is suitable for the spraying. They are consisted of micron size YSZ and LSM primary particles. The SEM picture of the granulated particles is shown in **Fig.5**. The intermediate layer was made by plasma spraying the powder on YSZ.

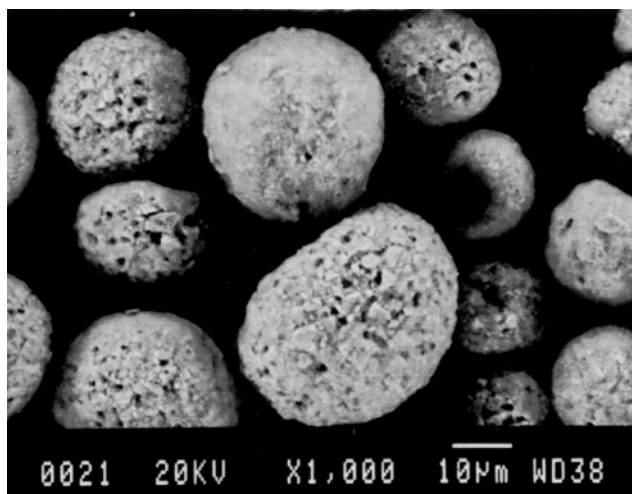
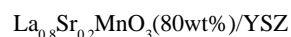


Fig.5 An SEM picture of the granulated particles of YSZ and LSM mixture.



2.2 Measurement

Experimental setup for the electrochemical measurement using planner YSZ substrate on which the cell components are deposited is shown in **Fig.6**. The cell is hold between two Pyrex glass o-rings which make gas sealant at the operational temperature. Platinum mesh is applied on the surface of the electrode for the current collector and the two platinum wires are extended from each electrode, namely the potential probe and the current lead out.

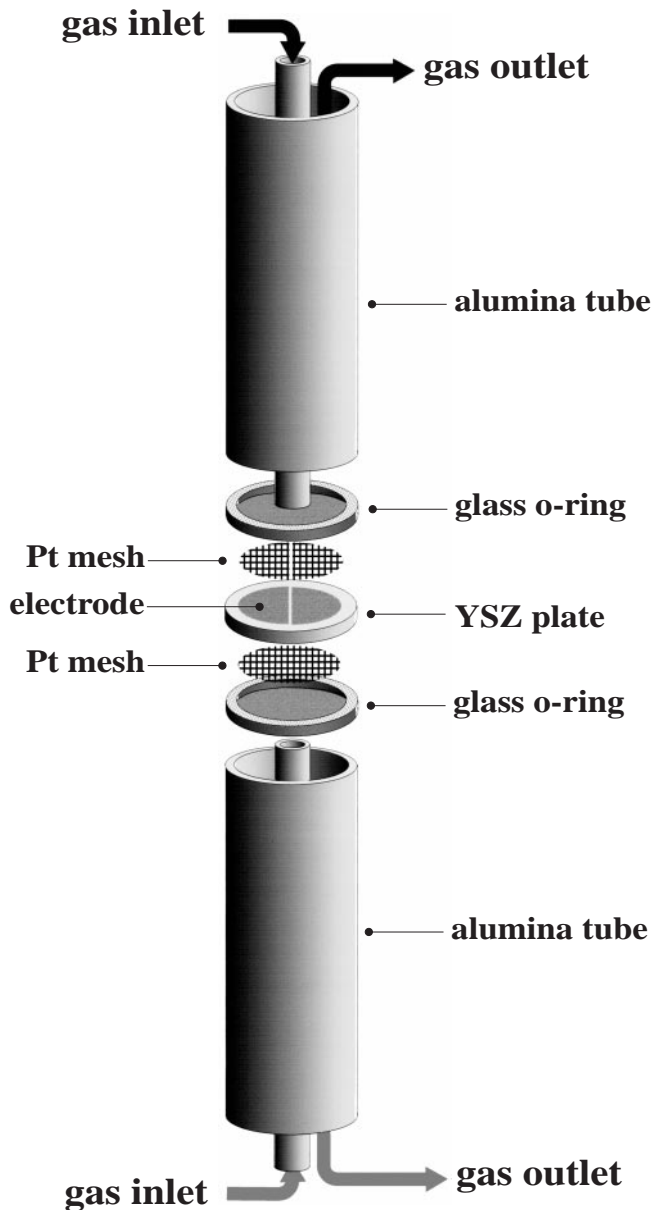


Fig.6 Experimental setup for the electrochemical measurements using a small planar cell.

Oxygen and hydrogen were supplied as cathode and anode gas, respectively. Gasses are fed to the electrode compartments via ceramic tubes at a constant feed rate controlled by gas flow controllers.

The effects of the electrode catalyst layers were also confirmed with the tubular single cells. The structure and the fabrication process of the tubular single cells can be found elsewhere⁽⁴⁾.

As for the electrochemical measurement, ac impedance measurements were carried out using potentiostat (Solartron 1286 or Hokutodenko HA-320) and frequency response

analyzer(Solartron 1260 or NF circuit 5080) at an open circuit voltage. DC voltage if any is canceled out using an electrometer(Hokutodenko-HE104).

In some cases, ohmic losses were separated by current interrupter method using a current pulse generator(Hokutodenko HC-113) and a transient converter(Riken denshi Co. Ltd. TCCQ) of which data were directly sent to a computer.

Current-voltage characteristics curves were obtained using Solartron 1286 built-in sweeper or a function generator(Wavetek model 29) at a sweep rate of 1mV/sec by controlled potential method.

§3 Results and discussion

3.1 Anode catalyst

3.1.1 Investigation by planar cells

Of the cells tested the best anode performance was observed using 1micron Ni powder as anode catalyst. Typical current vs. voltage(i-V) characteristics of the cell is shown in **Fig.7**. In the figure, anodic overvoltage is separately shown. Even though the curve was obtained at 850°C, the anodic overpotential was kept at low value(<60mV) at the practical current density level(200-300mA/cm²). I-V curve of the cell using Pt catalyst layer is shown in **Fig.8**. The overvoltage was kept even lower than that of Ni catalyst suggesting the superiority of Pt as an electrode catalyst.

The cross sectional picture of the interface between electrolyte and metallic substrate is shown in **Fig.9**. Although the picture is that of a sample after fuel cell operation at 900°C, no delamination of the electrolyte was found throughout the surface with SEM observation. Furthermore,

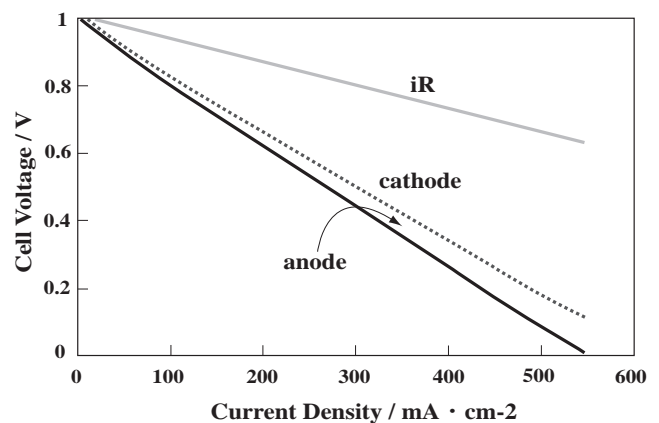


Fig.7 i-V characteristic of the tentative single cell made on porous alloy substrate with Ni catalyst at 850°C.

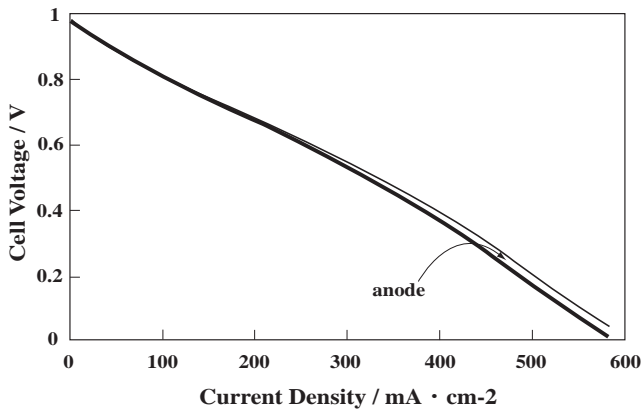


Fig.8 i-V characteristic of the tentative single cell made on porous alloy substrate with Pt catalyst at 850°C.

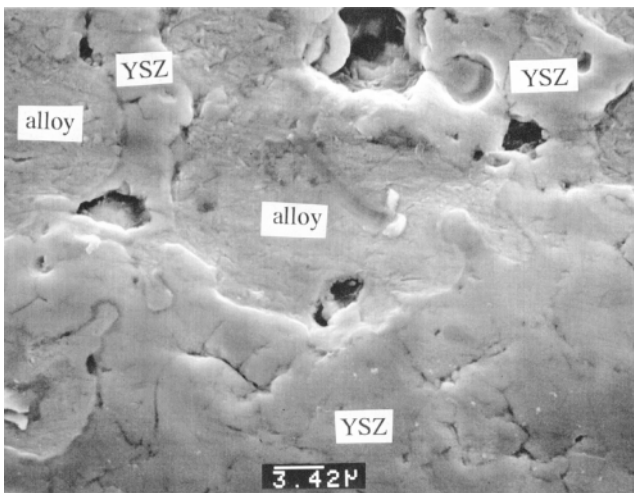


Fig.9 Cross sectional picture of alloy substrate/YSZ interface after fuel cell operation at 900°C.

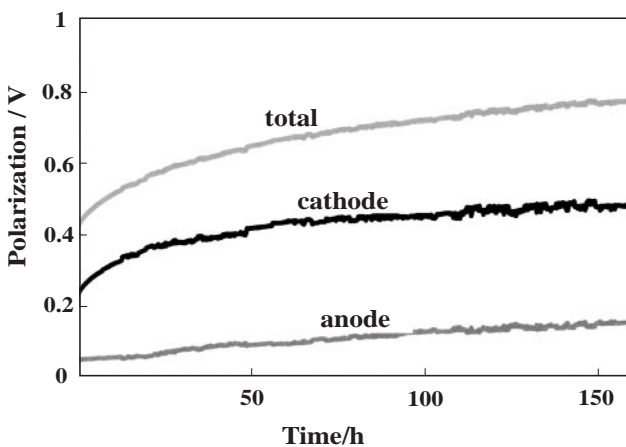


Fig.10 Shift of overvoltage at 200mA/cm² with time. Cathodic and anodic overvoltages are iR free.

on plasma spraying deposition, as the sprayed YSZ particles reach the surface of the substrate with an extremely high speed, it is seen that some of the particles penetrate deep into the substrate. This makes the interface as if it were a cermet, contributing to the formation of much electrode and electrolyte interface. The reason for the good anode characteristics observed here is based on this fact. As will be seen in the cathode catalyst section, the formation of the electrolyte/electrode interface is very important in reducing the polarization at electrode.

The shift of overvoltage with time at a constant current density were shown in **Fig.10**. The overvoltage showed degradation as time elapses with either electrode. This may be attributable to the initiation of the sintering of the alloy substrate which makes the interface unstable in terms of mechanical strength and therefore causes the partial delamination of the anode in the long run.

3.1.2 Application to the practical cell

Although the cell we are developing for the practical application is based on a metallic substrate of quite a different microstructure, the behavior obtained in this study

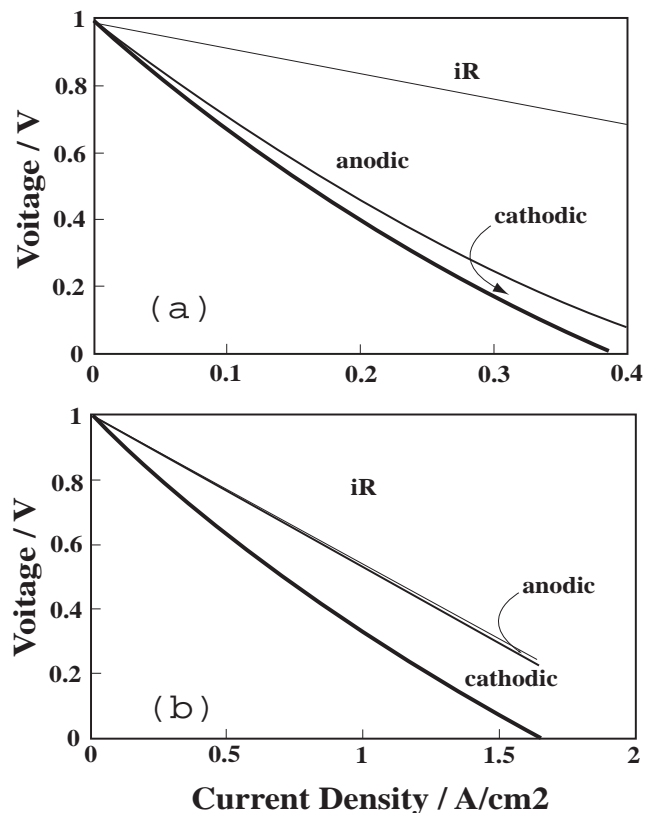


Fig.11 Typical i-V characteristic of the tubular cell with (a) and without (b) an anodic intermediate layer.

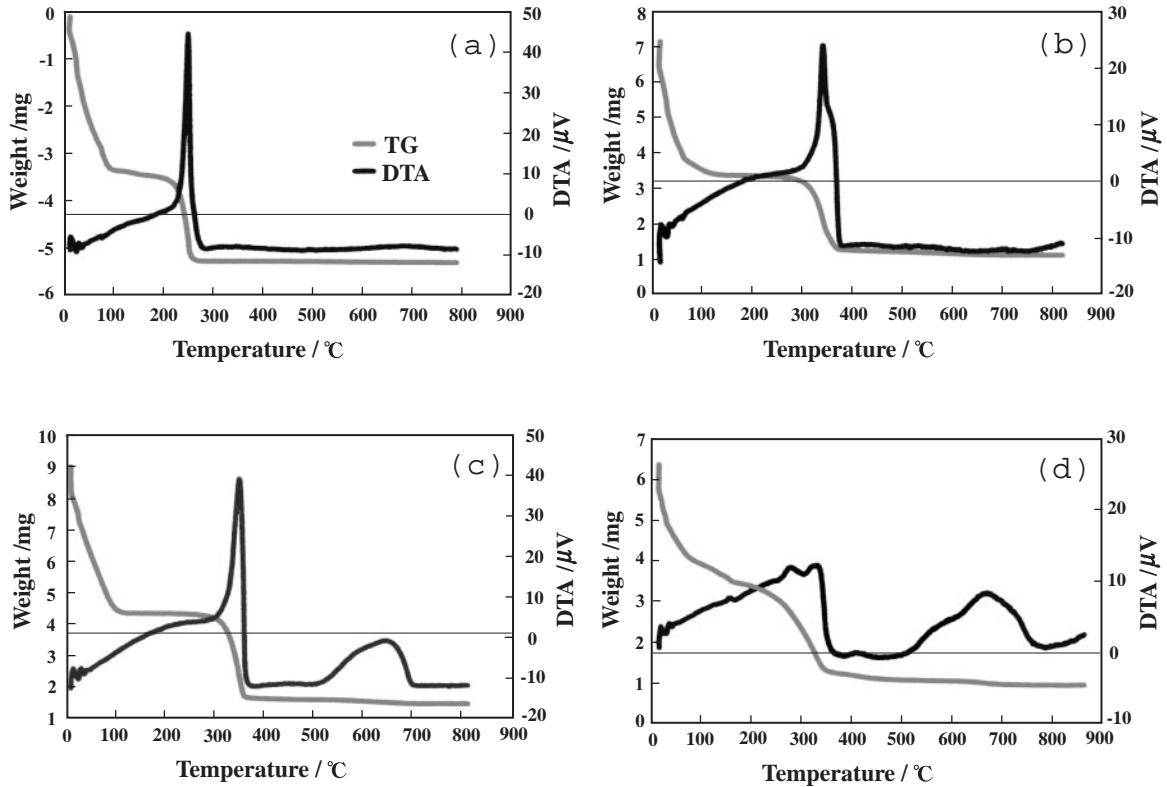


Fig.12 TG and DTA curves of some metal octoates. (a)Ce octoate, (b)Sm octoate, (c)Gd octoate, (d)Y octoate.

can also be considered to be seen in the cell. **Fig.11** shows the i-V characteristics of the tubular single cells in which the substrates were made by the method which is applied for the practical cell fabrication. In the figure i-V curves of the cells with and without the anode intermediate layer are

shown together with each overvoltage contribution. The figure clearly shows the effectiveness of the intermediate layer.

3.2 Cathode catalyst

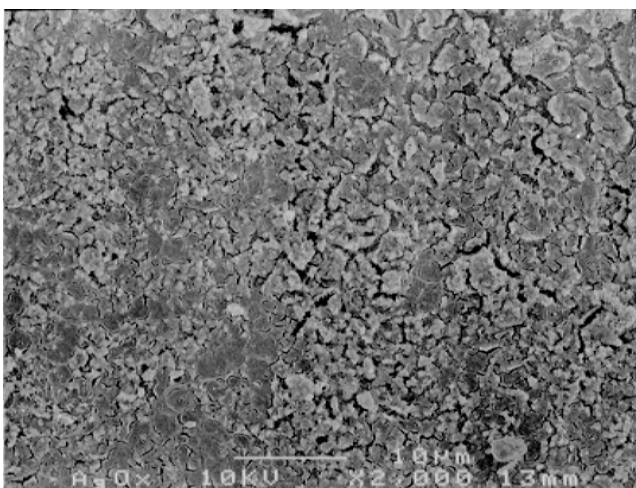


Fig.13 An SEM picture of the surface of cathodic intermediate layer deposited on YSZ substrate by the method (a).

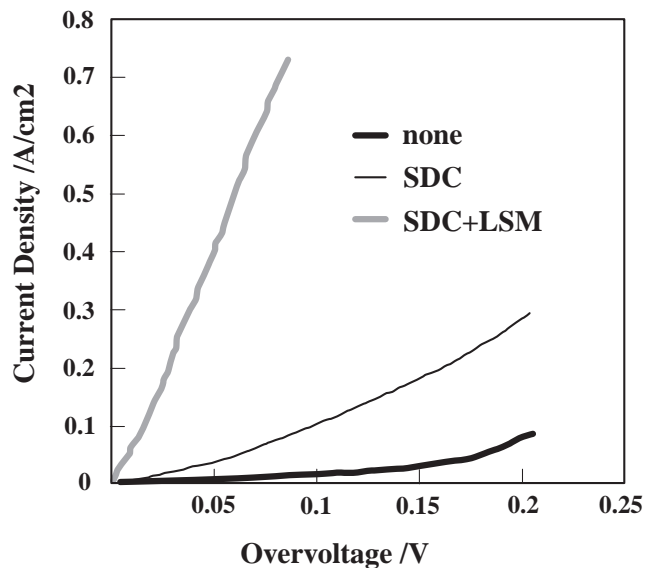


Fig.14 V-i characteristic of the cathode at 1273K with and without a cathodic intermediate layer as indicated in the figure.

3.2.1 Method (a)

Doped ceria was seemed to be promising as a candidate of the electrolyte for the purpose. It has higher oxide ionic conductivity⁽⁵⁾ and is known to be a better electrode catalyst. Some of the TG and DTA curves of metal octoates are shown in Fig.12. In the fabrication process, prior to the deposition of the cathode catalyst layer, the plasma sprayed YSZ is made even impermeable by some treatment in which the cell is heated up to 600°C. In the practical use, the alloy substrate is exposed in the reducing atmosphere. On the other hand, in the process of cathode catalyst layer deposition, the cell is still in production and all the parts of the cell is exposed in the air during the heat treatment in order to make the fabrication process simple and to accelerate the thermal decomposition process of the octoates. For this reason we have selected SDC(samaria(Sm_2O_3) doped ceria(CeO_2)) for the electrolyte of the intermediate layer because other possible dopants have exothermic peaks at temperatures higher than 600°C as can be seen in Fig.12 indicating the incompleteness of the pyrolysis still at the temperature.

The surface picture of the intermediate layer in which submicron size LSM powders are embedded in SDC layer is shown in Fig.13. The electrode material, LSM, was deposited on the surface.

Fig.14 shows the polarization curves of the cathode with and without an intermediate layer made by the method. The electrodes were prepared by sintering the LSM slurry painted on the surface of the intermediate layer. In the figure, the data obtained by using SDC intermediate layer, instead of SDC+LSM mixture are also shown. Although the behavior was drastically improved by the application of the SDC+LSM intermediate layer, it is still shown to be

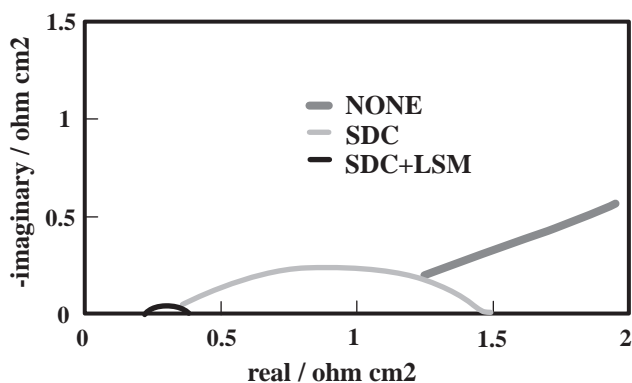


Fig.15 Complex impedance diagram of the corresponding electrode to that of which overvoltage characteristic is shown in Fig.14.

improved by the application of SDC intermediate layer suggesting the additional formation of tpb in either case or the superiority of SDC as a catalyst as compared to YSZ.

Complex impedance plots of the corresponding electrodes are shown in Fig.15. The shift of the intersection at the high frequency side between each curve can be the evidence that the contact resistance is also improved by inserting the intermediate layers between the electrolyte and the electrode, suggesting the improvement of adhesion between them.

The method was also applied to the tubular cell with LSM electrode deposited by the flame spraying. Although the intermediate layer made by this method worked with the electrode made by slurry coating technique, the electrode made on the tubular cell did not stay on the YSZ electrolyte after thermal cycles. Sometimes the electrode came off with itself and sometimes it came off with the intermediate layer, probably because of the insufficient heat treatment on the deposition of the intermediate layer. But we would not have proceeded on making the temperature of the heat treatment higher because of the reason mentioned above and we proceeded to the second alternative.

3.2.2 Method (b)

The cathodic intermediate layer was made by repeating the island structural deposition with electrode and electrolyte materials using flame and plasma spraying, respectively. Fig.16 shows the polarization curves of LSM flame sprayed electrode with and without the intermediate layer. The electrodes were deposited on YSZ disc and the intermediate layer was made by repeating the process twice for each

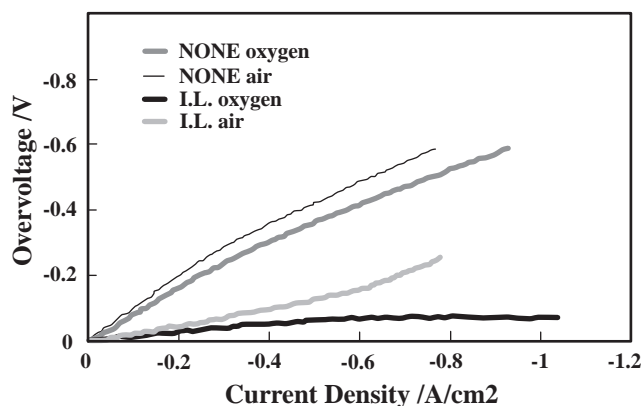


Fig.16 Polarization behavior of the cathode with and without an intermediate layer deposited by the method (b) in air and oxygen atmosphere.

material. As can be seen, the polarization behavior was considerably improved by the application of the intermediate layer, but in the high current region, when measured in air, there appeared concentration polarization in the case of the electrode with the intermediate layer. The phenomena was never observed with the electrode without the intermediate layer. The reason for the observation is that the diffusion path of the reaction species, oxygen, or that of nitrogen which doesn't take part in the reaction scheme was distorted and elongated by the flattened sprayed particles.

The schematic is shown in Fig.4. Since most of the electrode/electrolyte interface which is the candidate of the electrochemical reaction site spreads into the intermediate layer, the oxygen molecules have to diffuse through the sprayed intermediate layer to reach the reaction site, and the nitrogen molecules have to diffuse back to the bulk, dodging their way through the essentially non-porous plasma sprayed YSZ flattened particles. This distorted diffusion path makes the diffusion of these species more difficult and the concentration polarization observed in Fig.16 initiated when current density became large and when oxygen in the cathodic atmosphere was diluted.

The observation clearly tells us that the intermediate layer made by this method is not effective in the high current density region in the practical applications; air is considered to be the oxidant in most of the practical applications. It also suggests that this intermediate layer is not effective even when the current density is not so high under high oxygen utilization rate.

Moreover, the performance of the electrode with this intermediate layer scattered from sample to sample. This is due to the fact that it is very difficult to maintain the feed rate of the powder to the spraying gun at a constant rate. Because in the process of the fabrication of the intermediate layer, the spraying guns pass only once for each material to form an island structure, the maintenance of the feed rate at a constant rate is a key technology to form an intermediate layer of reproducible structure and performance. Note that in the normal spraying process in which certain thickness is supposed to be deposited, the maintenance of the feed rate

at a constant rate is not so important as is the case here. Average feed rate is more important in that case, because the spraying gun passes the substrate over and over to get desired thickness. This is another reason we proceeded to the next method for the intermediate layer deposition; the maintenance of constant feed rate can hardly be achieved.

3.2.3 Method (c)

In the method, relatively small particles of LSM and YSZ were granulated to form mixed powders of which particle size distribution is given in **Table-1**. The powders were then plasma sprayed on YSZ surface followed by LSM flame spraying deposition. The SEM picture and the two dimensional analysis of the cross section of the intermediate layer are shown in **Fig.17** as is the case where platinum was used as current collector instead of LSM. They show the well mixed sprayed intermediate layer in the size of micron level and that the method worked with respect to making much electrode/electrolyte interface.

The intermediate layer was then applied on the tubular single cell of which i-V characteristic is shown in **Fig.18**. The curve is shown with the curve obtained by the tubular single cell without cathode intermediate layer. Considerable improvement seen in the figure clearly suggests the effectiveness of the intermediate layer. The comparison can also be seen in **Fig.19** in terms of ac impedance. The shift of the intersection at high frequency side again, we believe, is the evidence of the improvement also with respect to adhesion between the electrode and the electrolyte as a result of the insertion of the intermediate layer between them.

Air was then used for the oxidant gas and i-V curves were obtained under several constant oxygen utilization (U_{air}) conditions. The curves are shown in **Fig.20**. Although in the case where U_{air} is higher than 20%, there was a sudden deterioration in the performance, there scarcely appeared any sudden increase in overvoltage related to the concentration polarization even at high current region as was seen in Fig.16. The deterioration of the performance under high U_{air} is attributable to the complex structure of the cell mounting we have adopted to the measurement of the tubular single

Table-1 Particle size distribution of the granulated mixture powders

particle size (μm)	63.0	53.0	45.0	38.0	32.0	30.0	20.0	10.0
distribution (%)	0.0	0.0	0.8	15.3	31.9	5.5	35.8	10.7
accumulation (%)	0.0	0.0	0.8	16.1	48.0	53.5	89.3	100.0

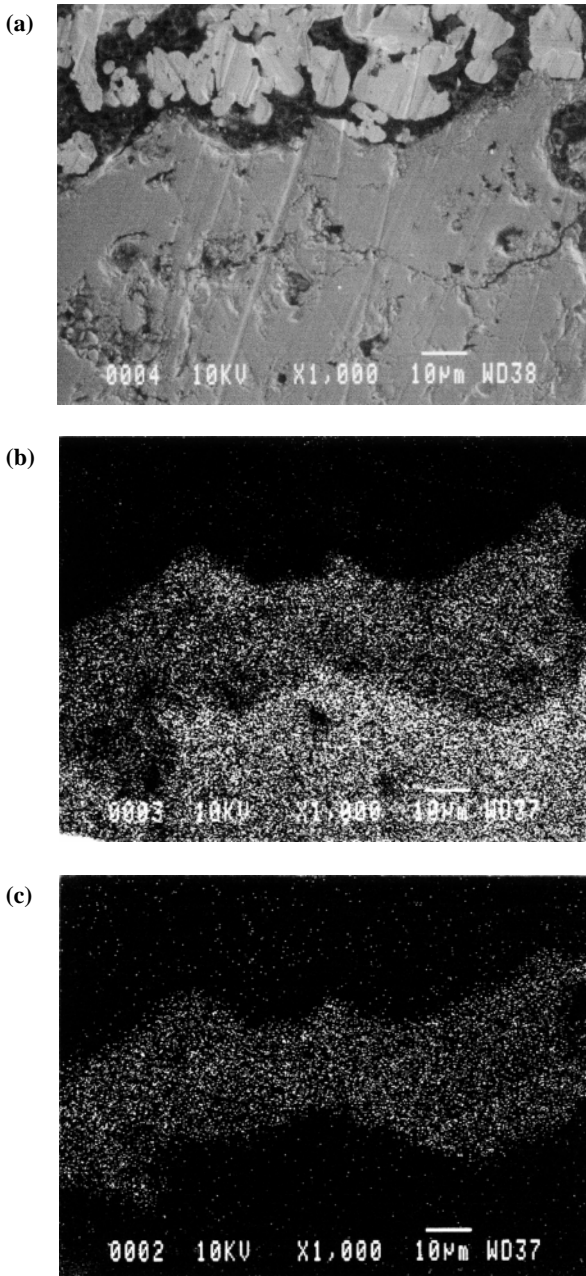


Fig.17 An SEM picture(a) and Zr(b) and La(c) distributions of the cross sectional interface of YSZ/cathodic intermediate layer deposited by the method (c).

cell performance.

Finally, long term performance of the tubular single cell made by the application of the cathode intermediate layer is shown in **Fig.21**. The curve was taken under controlled current condition, including one current step and some interruptions during which i-V characteristics were measured. Although at around 2600 hours of operation, there was a sudden increase in the cell voltage which happened just after an accidental interruption of supply of oxygen, the cell voltage remained fairly stable even under relatively high

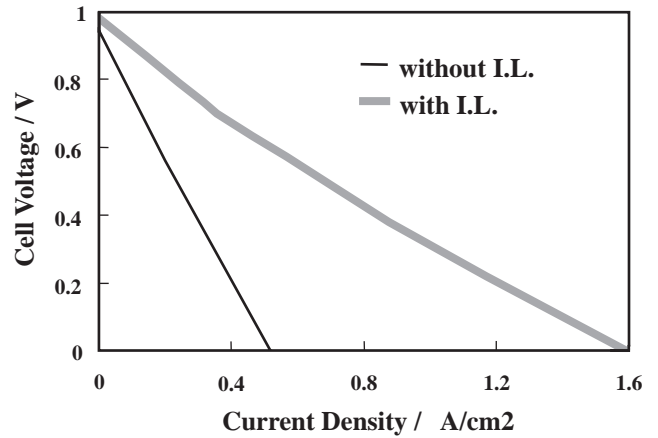


Fig.18 i-V characteristics of the tubular single cell with and without a cathodic intermediate layer deposited by the method (c).

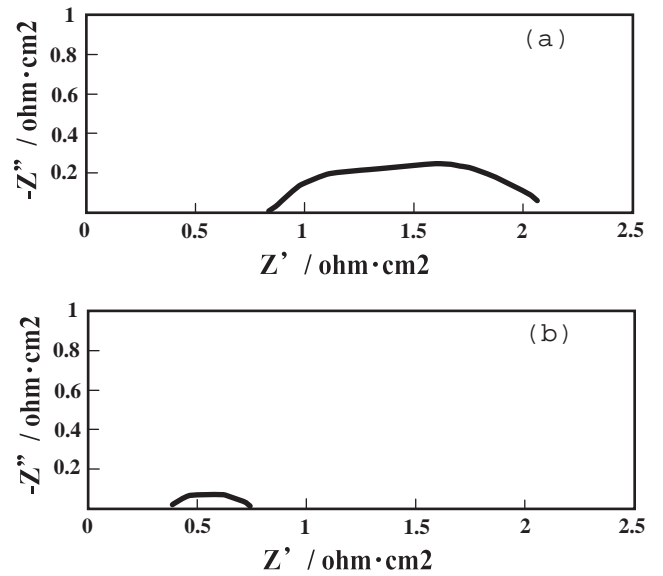


Fig.19 Comparison of the complex impedance diagrams obtained by the electrode with and without a cathodic intermediate layer deposited by the method (c).

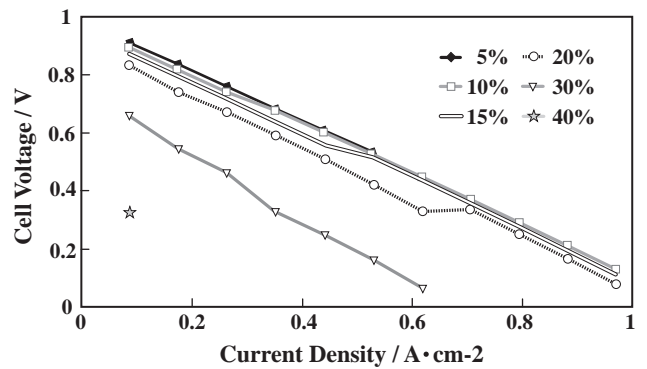


Fig.20 i-V characteristics of the tubular single cell having a cathodic intermediate layer made by the method (c) at several constant air utilization rates indicated by % in the figure.

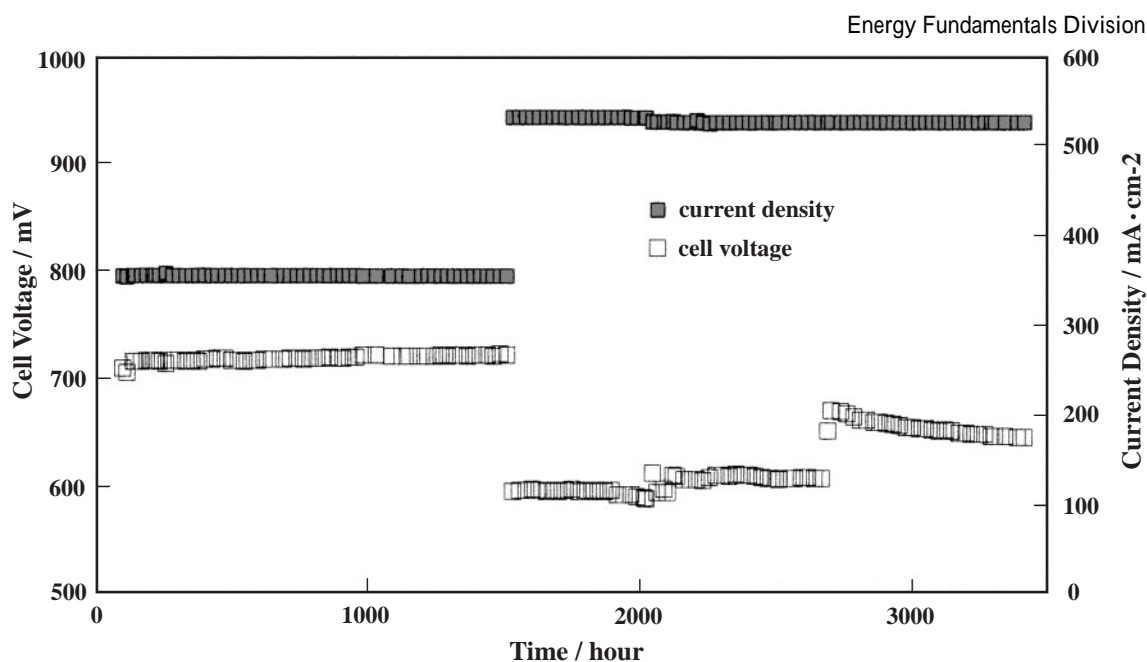


Fig.21 Long term performance of the tubular single cell made by applying the cathodic intermediate layer deposited by the method (c).

current density over 3000 hours of operation. The experiment is still going on and after some heat cycle experiments, optical observation or EPMA analysis will be carried out if any degradation is to be observed.

With regard to the cost of fabrication, since spraying is used in almost all of the other fabrication processes in our cell manufacturing, the method tested here, we believe, will contribute to maintaining the fabrication process simple and therefore to reducing the cost of fabrication⁽⁶⁾.

For the moment, LSM is deposited on the intermediate layer as a current collector, but in the future, we are planning not to use LSM. Instead, highly conductive metallic alloy will be used as a current collector of which long term performance under oxidizing atmosphere at 915°C is now being investigated⁽⁷⁾.

§4 Conclusion

Several types of intermediate layer that should be applied to metallic substrate type tubular SOFC were investigated. The role of the intermediate layer is to increase electrochemical reaction site by inserting mixed layer at electrode/electrolyte interface and consequently to decrease polarization at the electrodes. Although all the method tested showed some good results, some of them were found to be not applicable for the practical cell suggesting the importance of the evaluation of SOFC components from

multiple aspects.

Developed anode intermediate layer showed good performance with the aid of plasma spraying for the YSZ deposition which helped making intricate interface contributing to the formation of tpb.

One of the cathode intermediate layers, despite promising performance with tentative cells, showed delamination after heat cycling when applied to the tubular cell. Another cathode intermediate layer showed concentration polarization at high current density region. The last one using granulated powder showed long term stability as well as satisfactory initial performance. The method can be applied to the practical metallic substrate tubular cell together with the anode catalyst developed.

With the achievements obtained in this work, the development of tubular single cell has almost finished and we have proceeded to the development of the methodology of series connection of single cells: the major feature of the segmented type tubular SOFC.

References

- 1) S.C.Singhal, Proc. 5th Intl. Symp. on SOFC, (1997) 37-50.
- 2) T.Okuo et al., Proc. 1st European Conf. on SOFC, (1994) 909-918.
- 3) Several principles for the improvement of the electrode

are summarized in E.Ivers-Tiffée et al., 4th Intl. Symp. on SOFC, (1995) 1039-1048.

- 4) T.Okuo et al., Denki Kagaku,(1996) 555-561.
- 5) H.Inaba et al., Solid State Ionics, 83(1996) 1-16.
- 6) T.Okuo et al., in preparation
- 7) Y.Kaga et al., to be published in this bulletin.

(Accepted March 5,1999)

Authors



Akihiko Momma

Energy Fundamentals Division. SOFC lab.

E-mail:momma@etl.go.jp

He is working on the improvement of electrode performance in SOFC. His present main interest is the deposition of electrode and electrolyte materials by ultrasonic mist pyrolysis.



Yasuo Kaga

Energy Fundamentals Division. SOFC lab.

E-mail:kaga@etl.go.jp

He is developing electronically conductive high temperature metals for cathode current collector of metallic substrate type tubular SOFC.

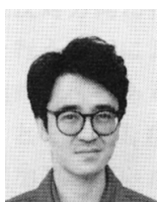


Takayasu Okuo

Energy Fundamentals Division. SOFC lab.

E-mail:okuo@etl.go.jp

He is engaged in the fabrication of tubular SOFC and is responsible for the fabrication of metallic substrate type SOFC as a system.



Kohji Fujii

Nippon Coating Industry Co. Ltd.

He is engaged in the work of spraying of metals and ceramics especially controlling the porosity of sprayed films.



Kiminori Hohjyo

Nippon Coating Industry Co. Ltd.

He is engaged in the work of spraying of metals and ceramics especially controlling the porosity of sprayed films.



Motoi Kanazawa

Nippon Coating Industry Co. Ltd.

He is engaged in the work of spraying of metals and ceramics and in their quality administrations.