IMPROVEMENT OF THE ELECTRONIC CONTACT BETWEEN THE BIPOLAR PLATE AND CATHODE OF A SOFC: MODEL EXPERIMENTS AND SCREENING OF INTERFACIAL COATINGS

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ABSTRACT

Ceramic coatings applied to the metallic bipolar plate of a SOFC are able to considerably lower the contact resistance between the bipolar plate and cathode down to the target value of 10 mΩ cm². The layers are made from powders similar to those used for the sintered cathode. A screening of different coating materials and coating techniques was performed under typical operating conditions. A special experimental set up was used to model the contact between the bipolar plate and the cathode.

1. INTRODUCTION

A typical component in the flat plate design of a solid oxide fuel cell (SOFC) stack is the bipolar plate (BIP). The purpose a BIP has to serve can be described as follows:
- gas tight separation of anode and cathode compartments of piled cell levels within the stack,
- homogeneous distribution of reaction gas across the electrode area,
- electrical series connection between the anode and cathode side of stacked cell levels.

To meet these tasks the electronically conducting BIP is usually structured in a way that channels for gas distribution are formed. The ridges separating the channels are in contact with the electrode and thus serve to collect the current.

As long as the bulk resistance of the BIP can be neglected, two effects dominate on the additional contribution of interconnection to the overall resistance of a stack level (fig. 1):
- the sheet resistance of an electrode leads to a voltage drop as electronic current flows towards the contact from electrochemical reaction sites located in its surrounding;
- the actual contact resistance, leading to a voltage drop while electronic current passes from the electrode side of the contact to the BIP side.

The following article deals with this last mentioned effect. First it is shown what problems have to be solved to get a low contact resistance and which target value has to be achieved. A model experiment is described to measure values of contact resistance, and results are reported for different types of interfacial coatings applied to the contact between a metallic BIP and the perovskitic cathode of a SOFC.

2. FUNDAMENTAL CONSIDERATIONS

If a difference of electrical potential in the range of 10 mV is imposed on two electronically conducting solids under mechanical contact, electrons will flow only across those regions of their surfaces where these are separated by distances of 0.1 nm. Especially in the case of the contact between the metal surface of a BIP and the porous ceramic cathode of a SOFC, individual regions of electrical contact, as described, are rare and quite small. In any case, the sum of the areas of these regions is always lower by orders of magnitude than the area intended for the contact, for instance, the surface of a contact ridge on the BIP. This is mainly due to the rigidness of the two materials in contact and to the unavoidable residual corrugation of their surfaces. In case of the electrode surface of a Siemens SOFC single cell, this corrugation of some 10 µm is caused by a slight undulation of the underlying electrolyte. This means, that the surface roughness due to the desired porosity of the electrode (in the 1 µm range) is negligible in comparison.

To enlarge the current carrying regions within an "intended contact zone", one may thus apply a 50 µm thick coating of any cathode powder on such areas of the BIP before assembling the stack. When heating the stack to operating temperature under moderate mechanical pressure (< 1 bar), the interfacial coating can adjust to the local variations of mechanical pressure, thus compensating for the described corrugation of the adjacent surfaces. So the current carrying area of a contact can be enlarged considerably.

Apart from this mainly geometrical effect, additionally applied interfacial layers have an influence on the chemical composition within the contact zone: the formation of an oxidation scale on the BIP and the interdiffusion of elements of BIP and electrode are modified. In any case the resulting structure should show low values of specific resistivity and the electrochemical activity of the neighbouring electrode area should not be reduced.

To get a target value of the contact resistance related to the intended contact area (only this quantity is experimentally well defined), one can argue as follows: the
overall resistance of a stack level should not exceed 1 Ω cm². At most 10 % of this value may be induced by contact resistivity between BIP and one electrode. As the percentage of intended contact zone related to active electrode area is assumed to be again 10 %, the value of contact resistance related to the intended contact area should be in the range of 0.01 Ω cm². Obviously this is only a first rough approximation and the given value may change with the details of the stack design and the state of the overall stack optimization.

3. EXPERIMENTAL SET UP FOR SIMULATION AND MEASUREMENT OF CONTACT RESISTANCES IN A SOFC STACK

The typical width of a contact ridge on the metallic BIP in the Siemens design of a SOFC stack is 1 mm and the length 40 mm. The intended contact area corresponding to one contact ridge would thus be 40 mm². To get a lower limiting value for the contact resistance a much smaller pair of model contacts is used: two cylinders of the material of the BIP are pressed against both sides of a sintered sheet of porous cathode by means of a sample holder (fig. 2). The operating conditions are 950 °C and air as ambient gas. The porous cathode foil, 50 μm in thickness, serves as a model electrode. Diameter and height of the metal cylinders are 2 mm each. The additional interfacial coating is applied to the corresponding ground surface of each of the metal cylinders. Each cylinder is spot welded to separate current and voltage leads made of Pt. The sample holder allows the two cylinders to slightly tilt with respect to one another, so realizing a maximum of contact area even in the case of a wedge shaped sheet of electrode foil. The value of contact resistance related to the intended contact area is calculated by multiplying the measured resistivity and the ground surface of the metal cylinder (3.14 mm²). As the model setup gives the resistance value of two contacts in series, it has to be divided by two when comparing with the above mentioned target value of 0.01 Ω cm². Values of contact resistance measured in this way will give a lower limit to the contact resistance attainable in a stack. The small surfaces of the cylinders can adjust more easily to both surfaces of the model electrode than can a 40 mm long contact ridge rigidly fixed to the BIP.

In order to measure the resistivity of the contact, a constant current of 0.1 A is applied. This corresponds to a current density of 3 A/cm² with respect to the intended contact area of 3 mm². This value for the current density is based on a mean value of 0.3 A/cm² in the SOFC, which is multiplied by the assumed ratio of electrode area to intended area of contact. Additionally, the resulting voltage drop across the contact is limited to 0.1 V to avoid electrochemically caused changes within the contact. On the other hand a contact related voltage loss in this range would not be acceptable in a stack level.
As the results of measurements of contact resistance always scatter, the sample holder was constructed in such a way that four equally prepared samples could be measured simultaneously under identical conditions. A view of the final set up is shown in fig. 3.

4. EXPERIMENTAL RESULTS

Two types of metals for the BIP were investigated: the commercially available Ni based alloy Haynes 230 and a self-developed Cr-based alloy. Both materials showed a low corrosive attack in long term experiments under anode or cathode gas mixtures at 1000 °C (1). In addition the thermal expansion coefficient of the Cr alloy fits well to that of YSZ thus minimising the danger of cracks under thermal cycling in a rigidly joint stack structure. The same chemical composition of a Sr-doped Lanthanum manganite was used as a model cathode in all cases. Coating materials similar in chemical composition to typical SOFC cathodes were applied to the metals as painted, plasma sprayed, sputtered or screen-printed layers. The time dependence of the contact resistance was recorded over 100 h for a first screening.

Fig. 4 shows the results for Haynes 230 as a bipolar material. Without any additional coating the resistance is around 250 mΩ cm² and fairly constant. With coating a pronounced decrease of the resistance to values below 50 mΩ cm² is observed. The exact numbers depend on chemical compositions and coating techniques applied. Obviously only one type of coating was able to realize the target value of 20 mΩ cm². In any case, the measured resistances were decreasing with time or at least constant.

The results of the Cr alloy are given in fig. 5. The values of 300 to 400 mΩ cm² realized without coating drop to below 100 mΩ cm² with an additional interfacial layer. The lowest value, 30 mΩ cm², was observed for the same kind of coating that has already minimized the resistance of the HA 230 contacts. Though the result is slightly beyond the target value it seems to be still acceptable.

To get a first idea about the long term stability of the resistance in the case of the above mentioned optimum coating, a 400 h run was performed with both kinds of alloys. The curves in fig. 6 satisfactorily reproduce the values reported for the short term behaviour in figs. 4 and 5. On long terms the resistance of the Cr alloy samples obviously tends to increase with time, whereas the decreasing curve of the HA 230 finally becomes constant.

All results reported so far showed the time dependence of the mean values of the resistance measured simultaneously on four identically prepared samples under identical conditions. When comparing the values among the individual samples they
scatter by a factor of 2 to 3 within the maximum and minimum limits. This is illustrated by fig. 7 for the case of the optimum coating applied to HA 230. This scattering of data is of no influence as long as the mean value is in the range of the target value. Otherwise those areas of the cell are not able to contribute to the overall current, which are adjacent to a high resistance contact between BIP and one electrode.

The optimized coatings of the two above mentioned alloys on the cathode side were tested in stacks of varying size. Current densities up to 0.4 A/cm$^2$ at 0.7 V were thus realized, whereas without additional coatings only some 10 mA/cm$^2$ could be measured. Besides further screening experiments, tests over at least 10000 h have to be carried out in future to further assure the long term applicability of the described method for SOFC stacks.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Ivers-Tiffée and Mr. Schießl of Siemens Corporate Research and Development in Munich for fruitful discussions and preparation of powders.

REFERENCES

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Fig. 2: Details of the experimental setup used to measure contact resistances.

Fig. 3: View of the sample holder for the simultaneous measurement of four resistances.
Fig. 4: Time dependence of the contact resistance when HA 230 is used as a bipolar material:
- without additionally applied interfacial coating;
- other curves: effect of a number of differently prepared interfacial coatings.

Fig. 5: Time dependence of the contact resistance when the Cr alloy is used as a bipolar material:
- without additionally applied interfacial coating;
- other curves: effect of a number of differently prepared interfacial coatings.
Fig. 6: Long time dependence of the contact resistance when the optimum interfacial coating is used on
- Cr alloy;
- HA 230.

Fig. 7: Time dependence of the contact resistance of four identically prepared samples (optimum coating on HA 230) measured simultaneously under identical conditions.