Electrical conductivity degradation of metal-ceramic composites

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Abstract — Metal-ceramic composites are of great interest as components for solid oxide fuel cells. One of the main problems of these components is the degradation of the conductivity during their operation at high temperatures. Here a model for sinter processes consisting of metal-ceramic composites with gas pores is described and calculated by Monte-Carlo simulations, which is able to explain the degradation in electrical conductivity in solid oxide fuel cells over time.

Index Terms—Metal-ceramic composites, Monte-Carlo simulation, sintering, conductivity degradation

I. INTRODUCTION

This paper describes random network computer simulations (Monte-Carlo simulations) in order to investigate the influence of different sinter effects on the conductivity of the anode of solid oxide fuel cells during long-term operation. The idea is to randomly setup a cube consisting of metal pieces, ceramic pieces and gas pores with given probabilities. The particles inside the cube are edged on one side by a metal plate with gas channels and on the other side by a ceramic plate. Then the conductivity between these two plates is calculated by the laws of Ohm and Kirchhoff from the linear network analysis. This way the system is treated with real boundary conditions, producing realistic results. Since fuel cells operate with direct current, all imaginary parts of the resistors can be neglected and only the real parts of the resistors are used for the overall admittance of the cube. Each resistor represents the resistance between two single grains in the composite in the presence of pores. For the geometry a face centered cubic structure (FCC) is used, which offers high density of the grains.

II.THE CUBE

The face centered cubic structure (FCC), which is used for the cube, leads to a dense grid. The FCC lattice has twelve neighbors, six in the middle layer and three at the top and bottom layer (see fig. 1). The lattice consists of three different types of particles. Each particle of the lattice can be either a metal particle, a ceramic particle or a gas pore. The density of each type of particle. i.e. its probability, is setup first and then each particle of the lattice is randomly set as one of the three types of particles according to their respective probability. A typical example of such a system is shown in fig. 2. This example shows a cut through an FCC lattice typically used for simulation of solid oxide fuel cells. In order to keep the calculation time of the overall admittance at a reasonable limit, the size of the cube for the Monte-Carlo simulations is set to L=24, W=24 and H=24.

III. ACTIVE TRIPLE PHASE BOUNDARY

For the current production, gas pores are of great significance for solid oxide fuel cells, as they transport the oxygen towards the active boundary and dispatch the reaction product water away from the active boundary. In order for a solid oxide fuel cell to produce current, it needs places, where all three kinds of particles meet as neighbors, and each particle type needs to be connected with its respective channel ([1], [2]). Therefore these places are called active triple phase boundary.

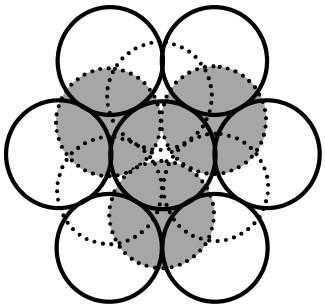

Fig. 1: FCC lattice in three layers with twelve neighbors

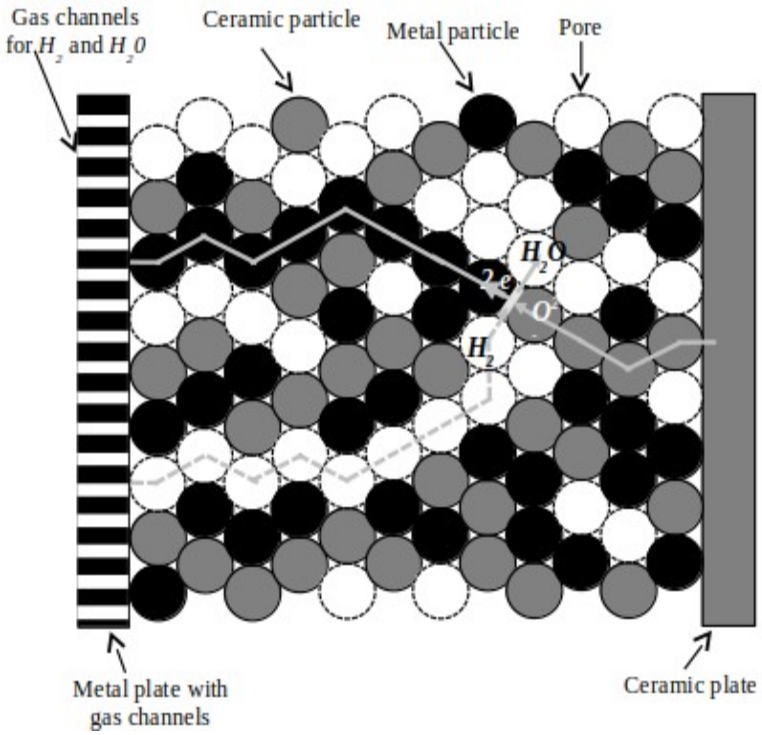

Fig. 2: A cut through an FCC cube for solid oxide fuel cells

For an active triple phase boundary four conditions need to be fulfilled, see fig. 3:

- A metal and a ceramic particle must be connected together with a gas pore.
- The metal particle must be connected either directly or through other metal particles with the
- metal contact plate, forming a continuous channel for the electrons.
- The ceramic particle must be connected either directly or through other ceramic particles with the ceramic contact plate, forming a continuous channel for the ions.
- The gas pore must be connected either directly or through other pores with the metal contact plate with gas channels, forming a continuous gas channel.

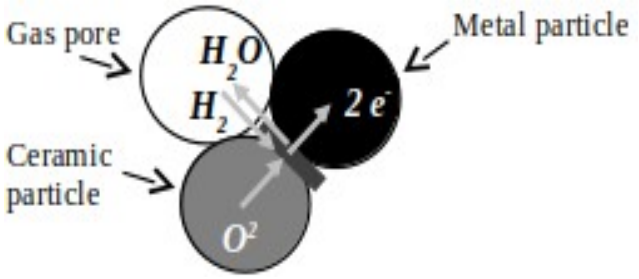

Fig. 3: Active triple phase boundary

IV. EQUIVALENT CIRCUIT DIAGRAMS

Since of the direct current inside the solid oxide fuel cell, capacities can be neglected for all three kind of circuit diagrams. Therefore, all three circuit diagrams are simple ohmic resistors, see fig. 4.

For the simulation, the solid oxide fuel cell has the following requirements:

- Average particle diameter : 5 µm
- Size of the contact surface : 12.5 µm2

- Temperature of the solid oxide fuel cell : 1,000 C
- Metal type : nickel
- Ceramic type : zirconium dioxide

There are three kinds of resistors between metal and ceramic grains. The active triple phase boundary is represented by the third kind.
The resistance $Z_{me\text{-}me}$ reflects the connection between two metal particles from center to center and has a value in the range of 0.2 Ω ([3], [4]).
The resistance $Z_{se\text{-}se}$ depicts the connection between two ceramic particles from center to center and has a value in the range of 40 KΩ ([3], [4]).
The resistance $Z_{me\text{-}se}$ describes the connection between a metal particle and a ceramic particle from center to center of the grains. The value for $Z_{me\text{-}se}$ depends strongly on the reaction conditions at the surface of the metal and ceramic boundary. If the surface is not an active triple phase boundary, the value of $Z_{me\text{-}se}$ is infinite. If the surface is an active triple phase boundary, the value of $Z_{me\text{-}se}$ varies between 40 KΩ up to 400 MΩ ([5]). In the Monte-Carlo simulations a value of 40 MΩ for $Z_{me\text{-}se}$ is used ([1]).

Fig. 4: Circuit diagram for $Z_{me\text{-}me}$, $Z_{se\text{-}se}$ and $Z_{me\text{-}se}$

V. SINTERING

During long-term operation of solid oxide fuel cells, a decrease in the conductance G can be perceived, since of slowly progressing sintering processes of nickel ([1], [6]). Sintering is the fusion of two metal particles into one particle due to adhesion forces to minimize their common surface for thermodynamic reasons, see fig. 5. The operating temperature of the solid oxide fuel cell is typically in the range of 900° C to 1000° C, sufficient for rapid ion transport but below the melting temperature of the metal. However, nickel already shows a distinct plasticity at this temperature, which causes adjacent metal particles to have a tendency to sinter. The sintering of the metal particles leads to a decrease of the active triple phase boundary, as the metal particles loose their contact to the surrounding particles. As a consequence, the overall conductance G is declining.

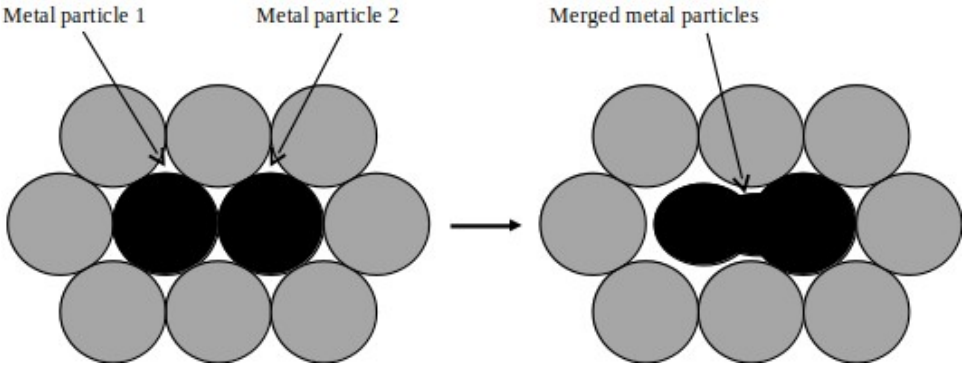

Fig. 5: Sintering of two metal particles

VI. BLOCKING HYPOTHESES

The adhesion force of the metal particles to each other is characterized by the presence of ceramic particles. If a metal particle wants to merge with another metal particle, it must past the adjacent ceramic particles. The more solid electrolyte particles are between the two metal particles, the more difficult and unlikely the sintering becomes. Due to the lattice structure of the FCC lattice there are a total of four particles, which are between two adjacent particles ([7]), see fig. 6.

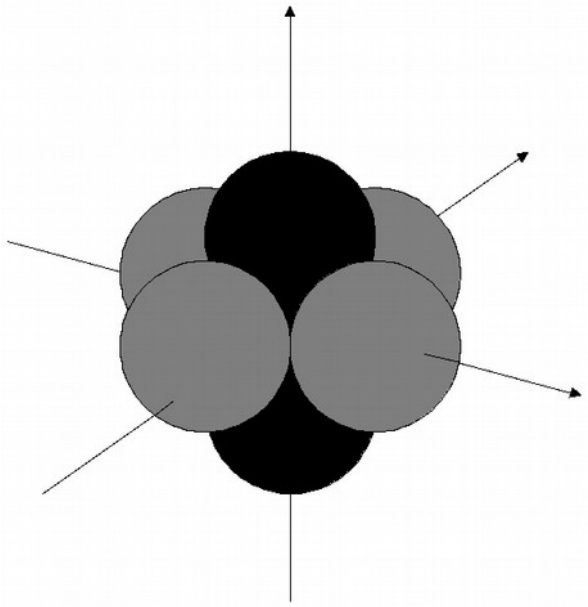

Fig. 6: Two sintering metal particles have four neighboring particles in between

For the simulation of the sintering processes the probability p_{Sinter} is defined, which represents the probability for a metal particle to sinter within one time step t_0 in the simulation, if it has another metal particle as a neighbor. In the Monte-Carlo simulations a value of 0.02 for p_{Sinter} is used ([1]).
To prevent the fusion of a metal particle with an adjacent metal particle, four hypotheses can be distinguished depending on the four kinds of neighbors, see fig. 6:

1. A number of one, two, three or four solid electrolyte particles as neighbors of the two metal particles prevent sintering of the two metal particles, i.e any ceramic particle as a neighbor is blocking the sintering. This is called blocking hypothesis 1 (Blocknummer 1).
2. There must be two, three or four solid electrolyte particles as neighbors between the two metal particles to prevent sintering. This is called blocking hypothesis 2 (Blocknummer 2).
3. Three or four solid electrolyte particles must be present as neighbors to block the sintering process. This is called blocking hypothesis 3 (Blocknummer 4).
4. All four neighbors must be solid electrolyte particles to prevent the sintering process at this point. This is called blocking hypothesis 4 (Blocknummer 4).

VII. SIMULATION RESULTS

For the calculation of the conductance G, the FCC lattice is setup randomly with particles, with equal probabilities for all three kind of particles ($P_{me} = P_{se} = P_{po} = 1/3$) and G is calculated by the bi-conjugated gradient method ([1]). For each time step t_0 in the simulation, the sintering is simulated according to p_{Sinter} and the blocking hypotheses 1 to 4 respectively, i.e. only metal particles which satisfy the respective blocking hypotheses are sintered with a probability of p_{Sinter}. Fig. 7 shows the time dependence of the conductance G during the sintering process for the four blocking hypotheses. It is obvious that the sintering process leads among the blocking hypotheses 2 to 4 after a few time units to a catastrophic decrease of conductance G, so that only a fraction of the fuel can be converted into electrical energy any more. Under the blocking hypothesis 1, the loss is much weaker. Here, only one ceramic particle is enough to successfully inhibit the sintering. Long-term comparisons with real solid oxide fuel cells show that the Voltage drop over time due to the increasing internal resistance of the cell is not as dramatic as the blocking hypotheses 2 to 4 would suggest [8]. The voltage drop of real solid oxide fuel cells is relatively flat, so that the blocking hypothesis 1 comes closest to reality. It is noteworthy that the conductance G drops not completely to 0 in the course of time, but falls to a plateau slightly above zero. The reason for this lies in the model. The metal contact plate is not subject to the sinter process, its metal properties remain constant even during sintering. As a result, active triple phase boundary exists between its surface

and the solid electrolyte particles within the mixture, which is retained throughout the sinter process. However, since the active triple phase boundary at the metal contact plate is limited, this plateau is very low.

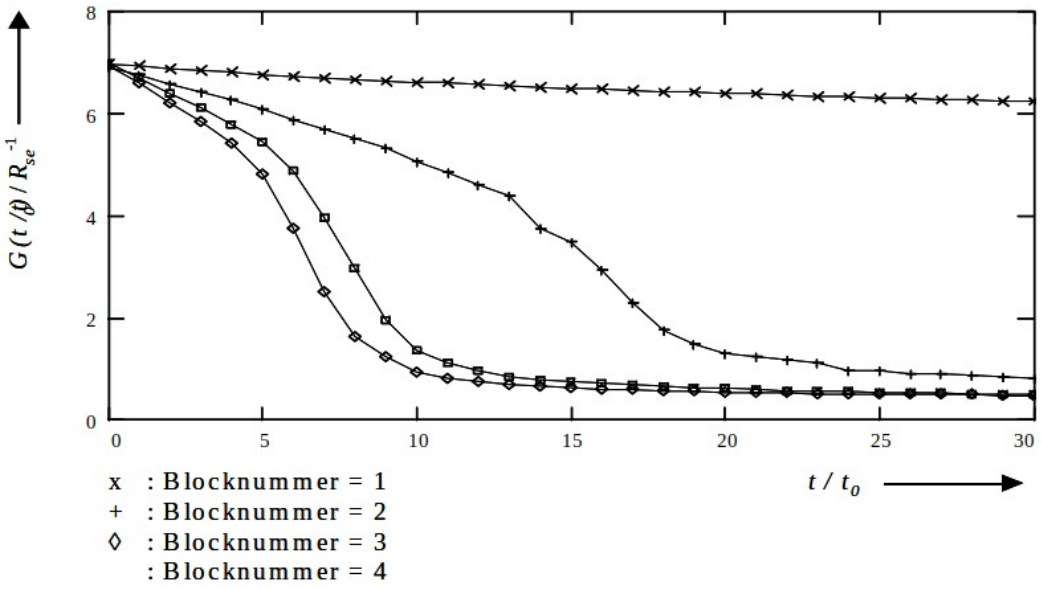

Fig. 7: Time dependence of the conductance $G(t/t_0)$ during sintering

VIII. CONCLUSION

The model presented in this paper makes it possible to explain and investigate the change in conductance of solid oxide fuel cells over time due to the sintering of metal particles. With its help one gets closer to the problems in the long-term operation of solid oxide fuel cells. The presence of even a small amount of solid electrolyte particles on a metal-metal compound is sufficient to significantly reduce the sintering tendency of such compounds. By a uniform and fine distribution of ceramic particles inside the fuel cell, the degradation process can be effectively counteracted. In addition to the examples presented here, the presented network model and its simulation are also useful in other areas, such as the cathode of the solid oxide fuel cell. In addition, due to its equivalent circuit diagrams, it can be further expanded to take into account other aspects of the fuel cell, such as flow and temperature profiles.

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