Modelling of the Electrochemical Performance of Functionally Graded Fuel Cell Electrodes by Discrete Simulations

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Abstract

Solid Oxide Fuel Cell technology uses powder processes to produce electrodes with residual porosity by partially sintering a mixture of electronically and ionically conducting particles. We model porous fuel cell electrodes with 3D packings of monosized spherical particles. These packings are created by numerical sintering. Each particle-particle contact is characteristic for an ionic, electronic or electrochemical resistance. The numerical packing is then discretized into a resistor network which is solved by using Kirchhoff's current law to evaluate the electrode's electrochemical performance. We investigate in particular percolation effects in functionally graded electrodes as compared to other types of electrodes.

Keywords : discrete modelling, numerical sintering, resistor network, fuel cell, percolation

1. Introduction

The electrochemical reaction of Solid Oxide Fuel Cells (SOFC) takes place in the anode and cathode at the Triple Phase Boundarys (TPB). The TPB are the zones where electronic and ionic particles, and the gas phase meet. The electrode needs to be sufficiently porous to enable gas diffusion while a higher density is beneficial for increasing ohmic conductivity and optimizing the number of TPB (nTPB). The composite electrode consisting of electronically conducting electrocatalyst and ionically conducting electrolyte particles allows spreading of the electroactive zone into the electrode. This increases the fuel cell performance. Additionally, composite electrodes help thermal mismatch stresses at fuel cell component interfaces to be reduced.

The partially sintered electrode is a porous material that has kept a particulate nature and can be modelled advantage- ously as such using discrete simulations. The objective of this work is to investigate how electrical, electrochemical and microstructural parameters interact to influence the overall electrochemical electrode performance.

2. Discrete modelling

The porous composite electrode is modelled as a 3D packing of spherical particles. The packing is created by numerical sintering to 0.75 relative density using the Discrete Element Method (DEM) code dp3D [1-2]. The sintering model allows the evolution of microstructural features such as contact size, coordination number and particle position to be obtained for packings that consist of electronic and ionic particles, typically 40 000 in total.

The TBP are only active if the electrocatalyst particle is connected to an electronically conducting network which is in contact with the current collector, and the electrolyte particle is connected to an ionically conducting network in contact with the electrolyte membrane. We define these type of networks or particles as percolating. We refer to non-percolating particles and particle clusters as being isolated.

Fig. 1 (a) shows a functionally graded electrode (FG-electrode) where the volume fraction of ionic conducting particles Φ_{io} decreases linearly from 100% at the electrolyte side to 0% at the current collector. The effective microstructure, i.e. the one obtained after removing isolated particles is shown in Fig. 1 (b). As soon as the composition reaches either the ionic or the electronic percolation threshold a large number of isolated particles is removed. For this type of grading the most electroactive zone is in the centre of the electrode and is much more limited than expected from observing Fig. 1 (a).

The effective conductivity of the electrode depends on the intrinsic conductivity of the solid particles, the charge transfer resistance, the geometry of the contact zone, and the microstructure of the packing. The particle packing is discretized into a resistance network where each contact in the packing is replaced by a bond resistance which is characteristic of the two contacting particles [3]. The resistance network is solved using Kirchhoff's current law to determine K_{eff} which is the electrode area specific conductivity. K_{eff} includes the effect of intrinsic electronic, ionic and electrochemical charge transfer conductivities. For all the simulations shown here we use values typical for the

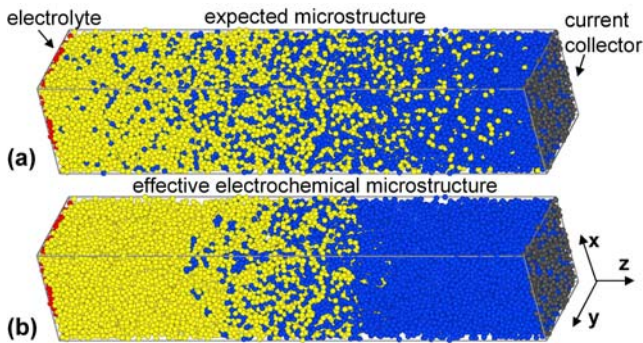anode [3]. Error bars relate to simulations on five packings created by different random seeds.

Fig. 1 FG-electrode (a) before and (b) after removal of isolated particles.

3. Results

Fig. 2 shows K_{eff} as a function of the slope of the compositional decrease (FGS) from the electrolyte towards the current-collector. We refer to the inital composition at the electrolyte site as FGC. The results at FGS = 0% represent the uniformly randomly mixed electrode (UR-electrode) where FGC = Φ_{io}.
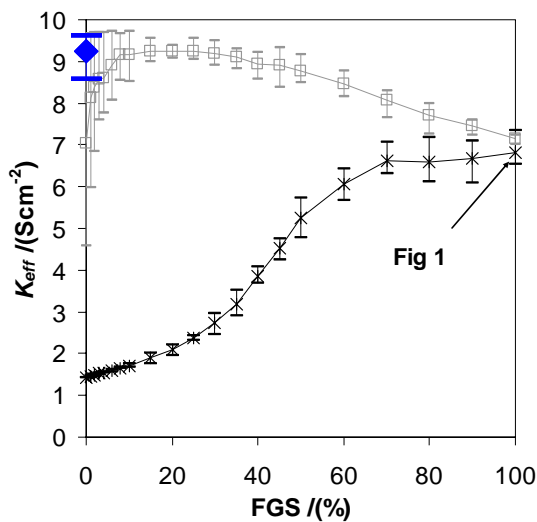

Fig. 2 Performance of graded electrodes with FGC of 65 % (□) and 100 % (∗) as compared to a UR-electrode with FGC = Φ_{io} = 60 % (◆).

The mean values of the UR-electrode with FGC = Φ_{io} = 60% (FGS=0%) and the FG-electrode with FGC = 65% and FGS = 20% are similar. Scatter for the FG-electrode is however reduced indicating better percolation which makes the FG-electrode the better design. Grading electrodes always reduces the nTPB but improves percolation. This allows strengthening the ionic network by increasing Φ_{io} even further keeping the electronic network percolating.

Fig. 3 compares the UR-electrode with an electrode for which percolation of electronically conducting particles is enforced by creating electronically conducting particle chains (PC-electrode). The space between the chains is occupied by ionic particles which are not shown in Fig. 3.
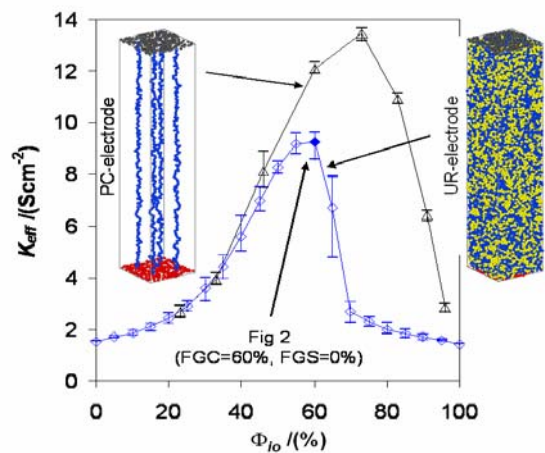

Fig. 3 Electrochemical performance of UR- (◇) and PC-electrode (△).

The PC-electrode performs much better compared to the UR-electrode demonstrating the importance of percolation. A general rule for electrode optimization is to increase Φ_{io} as closely as possible to the electronic percolation threshold to improve the conductivity of the poorly conducting ionic network. The PC-electrode provides a useful example of a design that optimizes percolation limits. The use of elongated or fiber-like electronically conducting particles can thus improve the effective conductivity of the electrode.

4. References

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