Flooded homogeneous model for composite cathode of SOFC.

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One approach to improving the performance of the cathode in SOFC is to use a composite electrode that typically consist in a two phase porous mixture of a solid electrolyte (YSZ) and an electrocatalytic material. Theoretical calculations[1] and experimental results[2, 3] have clearly demonstrated that a composite electrode should exhibit lower activation polarisation than a pure electrode by spreading the electrochemically active area into the electrode's bulk. The effect of electrode microstructure on charge transfer in composite electrode was theoretically analysed by Taner et al[1]. In this model, the electrochemical reaction was described by an activation polarisation and assumed to be ohmic.

The present modelling has been performed in order to give a complete description of the electrode structure as well as the process occurring therein. A one-dimension flooded homogenous model was used. In our approach the cathode was assumed to be composed of spherical particles of both YSZ and electrocatalytic material M.

The structure of the cathode and the gas partial pressure at electrode/current collector interface were regarded as uniform.

The mass transport processes considered are the following :

i. the gas phase diffusion of oxygen which is predominantly of Knudsen type for pore size of 1μm and the diffusion coefficient D_k was defined as a function of the pore diameter, d_{pore}.

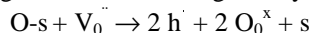ii. the migration of oxygen ions in the porous electrode layer.

The reduction of oxygen is governed by :

i. the dissociative oxygen adsorption according to :

$$O_{2\,(gas)} + 2\,s \rightarrow 2\,O\text{-}s$$
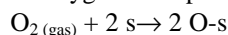
this reaction is assumed to occur on the particle surface. The reaction rate is given by classical chemical kinetic law.

ii. the charge transfer reaction given by :

$$O\text{-}s + V_0^{''} \rightarrow 2\,h^{'} + 2\,O_0^x + s$$

this step occurs at the triple phase boundary. The corresponding reaction rate is expressed by a Butler-Volmer equation.

The geometrical parameters are : the diameter of the particles ($d_{YSZ} = d_M = d$), the porosity (ε), the specific adsorption area (av_{ads}), the specific reduction area (av_{tpb}), and the pore diameter (d_{pore}).

The mixture of spherical particles was described as a cubic face centred lattice (CFC) to study the relationship between d_{pore}, ε and d. The porosity was assumed to result from the existence of void on the lattice site in addition to the intrinsic porosity of CFC lattice. The specific areas were also related to the porosity and the particle diameter. Accordingly, our approach included only two independent geometrical parameters that were ε and d.

The dc behaviour was simulated for a cathode with d = 10 μm and ε = 0.3. At low overpotentials, a Tafel like behaviour was observed (activation polarisation). A limiting current due to oxygen adsorption at high overpotentials was obtained. The gas diffusion was found to decrease the current density.

The dependence of the polarisation curve on geometrical parameters was studied by keeping one of the geometric parameter constant and varying the other one. For instance, the porosity was fixed at 0.3 and the particle size was decreased from 10 μm to 0.1 μm. The increase of current by decreasing the particle size was demonstrated. The change from a Tafel behaviour to a current limited type polarisation curve was evidenced.

In another simulation, the particle size was fixed at d=10 μm and the porosity was decreased from 0.3 to 0.05. The current was shown to first increase as a function of ε down to 0.1 and a further decrease due a Knudsen type gas phase diffusion was determined. The sensitivity to porosity variation was less important than to pore variation.

References
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