Numerical and experimental analysis of the effect of pore formers on the processing and properties of solid oxide fuel cell electrode

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Abstract

The fabrication of ceramic components with controlled porosity often requires using pore formers. This paper shows how modeling can help in optimizing pore former quantity and size with respect to sintering behavior and material properties. The case of a mixed ion-electron conductor SOFC cathode is considered. Numerical simulations based on the discrete element method are performed to mimic the sintering of Nd_2NiO_4 ceramic powders processed with various fractions of pore formers (0–40%) and size ratios (1–5 times the size of ceramic particles). From the results of these simulations, the effect of pore former particle size and amount on sintering densification, conductivity and effective surface area is analyzed. Experiments achieved on a Nd_2NiO_4 powder with miscellaneous pore formers confirm simulation outcomes as the minor effect of the pore former particle size ratio on the density and the presence of an optimum of oxygen adsorption for 20 vol.%.
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1. Introduction

Porous ceramic components are key elements in numerous systems used in the fields of energy, chemistry, bioengineering, pharmacy, etc. Typical examples are scaffolds for bone generation, piezoelectrics for ultrasonic transducers, electrodes in solid oxide fuel cells (SOFC), etc. The simplest way of obtaining porous components is partial sintering of a regular green part. However, for a better control of the porosity in terms of size, shape and distribution or for obtaining specific features, as for example a functionally graded microstructure, the use of pore formers may be advantageous. Such pore formers are typically organic powders that are blended with the ceramic powder at the beginning of the forming process. They are eliminated by a thermal or chemical process just before sintering, leaving controlled pores in the microstructure after sintering. A comprehensive analysis of processes using pore formers is available in [1].

Selecting the pore formers characteristics (nature, size, shape and amount) is a major concern. This is because these features may affect strongly the processing route (both forming and sintering) and because they determine the final properties of the component (microstructure, mechanical strength, physical properties, etc.). Since a comprehensive experimental study would be very heavy, modeling tools are useful for guiding this choice. For example, Horri et al. [2] developed an analytical model that provides the porosity of a compact obtained by pressing a ceramic powder mixed with powder formers as function of the applied pressure, the pore former volume fraction and the ceramic–pore former particle size ratio. This model was successfully applied to the processing of solid oxide fuel cell (SOFC) anodes. Also Corbin and Apté [3] analyzed the porous characteristics of ceramic tapes processed from powder suspensions including pyrolyzables particles with the help of a conceptual model that emphasizes the effect of the size distribution of ceramic and pore former particles on the sintered microstructure.

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Advanced modeling techniques involving numerical simulations can be considered for a more realistic description of the microstructure of porous ceramics. The most adapted technique is the discrete element method (DEM) that inherently accounts for the particulate nature of the powder material. This method has already been largely used in the last decade for investigating SOFC electrode performances [4–8]. It is also central in the present paper that analyzes the effect of size and quantity of pore formers on the sintering and properties of a SOFC cathode.

A solid oxide fuel cell consists of a stacking of three layers, an electrolyte enclosed between two electrodes. It is commonly fabricated by powder processing. The electrolyte should be nearly dense to prevent gas leak whereas both electrodes should exhibit a high porosity (typically 30%) to enhance gas transport to reaction sites. The processing of SOFC cells requires several stages, usually including two or three sintering treatments. Simplifying this route by performing a single sintering operation would be a significant progress. However, sintering together these three layers with contradictory requirements in terms of porosity is challenging and certainly requires the use of pore formers to avoid over-densification of the electrodes while ensuring the complete sintering of the electrolyte. Numerous authors considered the use of pore formers to increase the porosity of SOFC electrodes [9–13]. For example Sanson et al. [9] fabricated anodes with 10 vol.% of miscellaneous pore formers. They concluded that carbon black and rice flour were the most adequate due to their low size (5–10 μm). Sanson et al. [9] and Skovgaard et al. [10] discourage the use of graphite because its plate-like shape results in the creation of pores with the same shape, which are mostly perpendicular to gas flow. Mingyi et al. [11] compared the effect of pore formers (5–30 vol.%) made of PMMA balls and rice flour on porosity and electric conductivity of a Ni/YSZ anode. They measured higher conductivity with PMMA, for a given total porosity. Ruiz-Morales et al. [12] significantly increased the efficiency of SOFC by introducing PMMA balls as pore formers in a LSM-YSZ cathode.

The present study considers mixed ion-electron conducting (MIEC) cathode, which has been attracting more and more interest in the past years due to their potential to offer low polarization loss at intermediate temperature [14,15]. Such component should ensure:

– fast gas diffusion in the porosity,
– significant oxygen adsorption on particle surface,
– fast electron and ion transport.

These properties imply that the material exhibits high porosity and large specific surface area together with high conductivity. These requirements are hardly met all together. Numerical simulations based on discrete element method have thus been performed for the optimization of spherical pore former parameters (size and amount) with regard to these requirements. The results of these simulations are compared to experimental data obtained with MIEC Nd_2NiO_4 powder mixed with various types of pore formers.

2. Numerical tools and procedure

In order to fabricate simulated microstructures that are supposed to be representative of the microstructure of porous anodes processed with pore formers, the DEM code dp3D, developed in the SIMAP group at Univ. Grenoble Alpes has been used. Details about dp3D features, in particular for the simulation of sintering, can be found in previous papers [16–18]. The most significant points are summarized in the following. The powder compact is modeled as a 3D random assembly of spherical particles that interact through their contacts with each other. The total force applied on each particle is used to calculate its displacement by enforcing mechanical equilibrium. Interparticle contact forces are given by Bouvard and McMeeking model [19], which considers grain boundary and surface diffusion as mass transport mechanisms for sintering. Periodic conditions are applied to the boundary, as explained in [16]. Relevant material parameters are the surface energy, γ_s, the atomic volume, Ω, and the grain boundary diffusion coefficient, D_b, which is supposed to follow an Arrhenius law:

$$D_b = D_b^0 \exp\left(\frac{-Q_b}{RT}\right) \qquad (1)$$

where D_b^0 is the pre-exponential factor, Q_b is the activation energy, R is the universal gas constant and T is the temperature. Material parameters can be provided by the literature or adjusted by matching simulation results with experimental data. For the present study, as there is no data available for modeling the sintering of Nd_2NiO_4, data corresponding to grain boundary diffusion of alumina ($D_b^0 = 1.3 \times 10^{-8}$ m^3 s^{-1}, $Q_b = 475$ kJ mol^{-1}, $\Omega = 8.47 \times 10^{-30}$ m^3) have been chosen, as in Liu et al. [18]. The value of the surface energy has been set in accordance with experimental results, as described below. Note that grain coarsening is not considered here.

The Nd_2NiO_4 powder used for this study has been provided by Marion Technologies. It exhibits a BET specific surface area of 3.6 m^2/g (or, in another unit, 27 μm^{-1}), which corresponds to a BET equivalent diameter of about 200 nm. In order to decrease its high reactivity, it has been calcinated at 1000 °C for 1 h, leading to a specific surface are of 1.6 m^2/g (or 12 μm^{-1}) and an equivalent diameter of 500 nm. This powder has been compacted in a close die up to 0.49 relative density and sintered in air with the following thermal cycle: 5 °C/min heating up to 1350 °C, 3 h dwell at 1350 °C and air cooling. A relative density of 0.55 was reached at 1285 °C. The final relative density was 0.87.

An assembly of 4000 particles of 500 nm diameter with a relative density of 0.55, matching the relative density obtained experimentally at 1285 °C, has been fabricated with the dp3D standard procedure [9]. A sintering step was imposed to the numerical sample during 3 h and 13 min at 1350 °C. The value of surface energy has been adjusted so that the simulation leads to a relative density of 0.87. A value of 0.4 J/m^2 for γ_s was determined in line with typical values for ceramics [20]. The value of the surface energy, determined for the sample without pore former, was used subsequently for the numerical samples with pore formers.