



Multi-modal porous microstructure for high temperature fuel cell application



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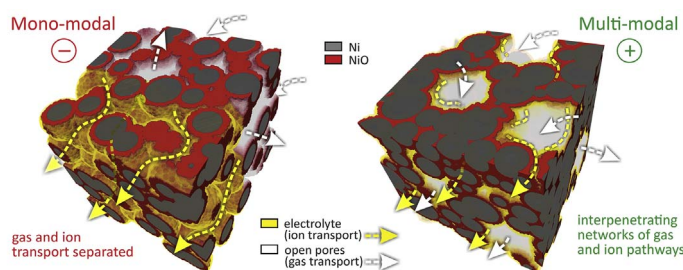
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HIGHLIGHTS

- Molten carbonate fuel cell cathodes with various microstructures are fabricated.
- Materials are extensively characterized before and after operation.
- The evolution of pore space due to oxidation and infiltration is described.
- Multi-modal microstructure results in doubling the power density of the fuel cell.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the effect of microstructure of porous nickel electrode on the performance of high temperature fuel cell is investigated and presented based on a molten carbonate fuel cell (MCFC) cathode. The cathode materials are fabricated from slurry consisting of nickel powder and polymeric binder/solvent mixture, using the tape casting method. The final pore structure is shaped through modifying the slurry composition - with or without the addition of porogen(s). The manufactured materials are extensively characterized by various techniques involving: micro-computed tomography (micro-XCT), scanning electron microscopy (SEM), mercury porosimetry, BET and Archimedes method. Tomographic images are also analyzed and quantified to reveal the evolution of pore space due to nickel *in situ* oxidation to NiO, and infiltration by the electrolyte. Single-cell performance tests are carried out under MCFC operation conditions to estimate the performance of the manufactured materials. It is found that the multi-modal microstructure of MCFC cathode results in a significant enhancement of the power density generated by the reference cell. To give greater insight into the understanding of the effect of microstructure on the properties of the cathode, a model based on 3D tomography image transformation is proposed.

1. Introduction

High temperature fuel cells are emerging energy technologies

developed for stationary power generation from unconventional sources, and accord with current trends in development of energy-related catalytic processes for sustainable society [1,2]. The high power

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density and efficiency achievable can compensate for the demanding requirements of high-temperature catalysts, mainly in terms of their stability during fuel cell operation.

Their high fuel-to-energy conversion efficiency, fuel flexibility and low environmental impact make high temperature fuel cells [3] (MCFCs [4–12] and SOFCs [13–19]) attractive for the power market, particularly in the field of distributed generation of clean electricity [20–23]. MCFC stacks are assemblies of single cells, where each single cell is comprised of porous components *i.e.* electrodes (cathode and anode) and a matrix which separates electrodes, and holds molten (Li/K)₂CO₃ or (Li/Na)₂CO₃ electrolyte [24–26].

The electrodes in *operando* are fed with reactant gases and convert their chemical energy into electricity. Finally, the MCFC is capable of producing electricity through the electrochemical conversion of hydrocarbons- and oxygen-containing gases [25]. Following successful commercialization in industry, much effort is being devoted to improving the performance and lifetime of MCFC technology, especially the electrodes [27].

The cathode – oxygen electrode – is a crucial component as regards determining the overall performance of MCFC, since it promotes complex chemistry between carbon dioxide and oxidant (oxygen, air) in the formation of carbonate ions (CO₃²⁻) [28]:



which are transported via liquid electrolyte [29] to the anode. At the elevated operating temperature of 650 °C, and in the presence of molten alkali carbonates, the MCFC cathode is exposed to a highly aggressive environment causing its degradation, due to NiO dissolution, which is reflected in increasing potential losses and Ni deposition in the matrix that may lead to short circuiting between electrodes [29].

Generally, the performance and lifetime of high-temperature catalysts for fuel cell applications are contingent to a great extent on materials issues related to the chemical composition and microstructure of their components. Most of the published literature to date in the field of MCFC cathode has addressed modifications to the chemical composition of nickel based materials as opposed to microstructure design. Chemical composition determines in particular corrosion resistance (chemical and thermal stability) as well as catalytic activity in respect of electrodes. The MCFC operating temperature is high enough to provide sufficient catalytic activity of NiO towards promoting a cathode reaction and incorporation of Li⁺ ions coming from the electrolyte into the NiO lattice (lithiation), but also inducing degradation at the same time. The evident need to enhance the protection of NiO cathodes against dissolution was achieved through modifying their materials [30,31] or applying coatings [32–34], at the expense however of fuel cell performance. The microstructure, in turn, should compromise sufficient mass transport of gaseous reactants in the pore space with the highest possible specific surface area for catalytic transformations into products [35,36]. Open-porous components are featured to facilitate the transport of reactant gases, removal of desorbed products, and simultaneously offer a large geometric area for chemical reactions to take place. On the other hand, specific surface area makes a contribution to adequate contact between the electrode catalyst and the electrolyte, which vary depending on the fuel cell type. This is of great importance since the triple phase boundary (TPB) is formed in regions where catalyst surface (electronic conductor), electrolyte (ionic conductor) and pore space (with reactants) combine [37]. In accordance with the theoretical concept, half-cell electrochemical reactions in a molten carbonate fuel cell occur in the presence of these three phases at TPB. The vicinity of the TPB perimeter is an active site compromising expected individual steps of the cathode reaction mechanism: adsorption of O₂ and CO₂ molecules, surface diffusion, activation of adsorbed species driven by charge transfer from the catalyst surface, formation of the carbonate ion and its desorption/transport to electrolyte melt. Therefore, access of the gas phase to both electronically and ionically

conductive phases at the interface between the electrode and electrolyte, together with the total length of TPB within the material, should be optimized [38,39] to maximize the active area for electrode reactions taking place in the fuel cell. To this end, the design of the internal architecture of electrodes is of major concern.

The microstructure of the MCFC cathode is mostly characterized by porosity and mean pore size. The literature reports cathode porosity in the range of 60 ÷ 80% and mean pore size of 10 ÷ 12 μm before oxidation, and 40 ÷ 60%, 7 ÷ 10 μm respectively after oxidation. It is noticed that the porosity can be significantly reduced, by up to 20%, due to *in situ* formation of an NiO layer during fuel cell start-up and operation [25,27,40,41]. Porosity and pore size after oxidation should remain sufficient to facilitate mass transport and infiltration with the electrolyte. Molten carbonate electrolyte infiltrates the cathode through pores of single micrometers in size as a result of wettability and capillary action [42,43]. From the viewpoint of operating conditions, the optimal electrolyte content in an MCFC cathode is in the range 15 ÷ 30% [44,45]. Therefore, variation in pore size should be introduced in the cathode material in a way that provides advantageous features, namely: 1) a fraction of small pores which, after oxidation, are responsible for capillary action and infiltration by the electrolyte, and 2) an extended internal area of pores (specific surface area). Pore size variation has a measurable reflection in the properties of open-porous materials, particularly related to mass transport, as we reported in our previous papers [46–48]. Moreover, non-monomodal structures, hierarchical in terms of pore size variation, are broadly developed for heterogeneous catalysis applications [49].

In the present work, we scrutinized the realization of pore size variation in MCFC cathode materials manufactured by the tape casting technique. To this end, two granular porogens: starch and PVB particles, were added to a slurry. The addition of porogen particles opens up the possibility of shaping the internal architecture of porous MCFC cathodes in terms of porosity, pore size distribution and specific surface area.

2. Materials and methods

2.1. Materials fabrication

MCFC cathode samples were manufactured by means of tape casting and a subsequent firing process (see Fig. 1). Initially, the slurry was obtained by mixing the nickel powder with solvent (water), binder (carboxymethyl cellulose) and other additives, which provide the desired viscosity (*i.e.* defoamer, dispersant).

In order to control the porous structure of samples, two types of porogen were added to the slurries: fine starch and larger polyvinyl butyral (PVB), hereafter denoted as P1 and P2 respectively. The size distribution of nickel and porogen particles was measured by laser diffraction analysis [50] equipped with an ultrasonic source (HORIBA LA-950). The results together with corresponding SEM images can be found in Fig. 1. Four different cathodes were manufactured: with no porogens addition (Ref), only with porogen 1 (P1), only with porogen 2 (P2) and with both porogens mixed (P1 + P2). The composition of the slurries is listed in Table 1. Our previous studies have shown that using electrodes with a porosity in the range of 50 ÷ 60% and mean pore diameter 5 ÷ 15 μm assures a relatively high specific surface area [51]. These materials provide a good compromise between gas transport (porosity) and catalytic reaction phenomena (specific surface area). It should be noted that due to a technological barrier, where the larger addition of porogen P1 (starch) resulted in brittleness of the tape, we decided to keep the maximum fraction of P1 in all the samples at 7.5 wt %.

The slurries were cast through the gap in a doctor blade on the glass surface with velocity 0.5 mm s⁻¹. The tapes obtained were dried for 24 h at room temperature. Afterwards, the three-step heat treatment presented in Fig. 2f was conducted in a reducing atmosphere of a N₂/

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