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Review article

# Pyrolyzable pore-formers for the porous-electrode formation in solid oxide fuel cells: A review

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## ABSTRACT

Porosity is a key property that plays a crucial role in enhancing the performance of solid oxide fuel cell (SOFC) electrodes. The addition of pyrolyzable pore-formers to the electrode materials of SOFCs can generate suitable porous microstructures with the required porosity, pore sizes, and morphology. The present review provides details on the characterization and microstructural analysis, firing profile, electrical conductivity, mechanical strength, and gas permeability of the porous electrodes of SOFCs. A better understanding of these relationships can help to design optimized porous microstructures for generating higher power densities of the cells.

## 1. Introduction

Many researchers have investigated the development of porous electrode microstructures to enhance the performance of solid oxide fuel cells (SOFCs) [1–6]. Controlling porosity can improve the electrode performance by facilitating the gas diffusion and increasing the triple phase boundary for electrochemical reactions. The particle size distribution of the ceramic powder affects the ceramic's porosity, indicating the difficulty in controlling the process of inducing porosity [7].

According to Drozd et al. [8], the trend of research in the use of pore-formers by some researchers is reporting only the final results of material preparation, such as SEM micrographs and pore size distribution data, without considering the mechanism of pore formation. The main purpose of the present review is to compile the important findings from the research on the pyrolyzable pore-formers in the context of solid oxide fuel cells. This review article also gives a comprehensive overview on the characterization and microstructural analysis of porous electrodes; the firing profile for pore-former burnout; and the effect of pore-former amount and particle size on the porosity, electrical conductivity, mechanical strength, and gas permeability of the porous electrodes.

Gas diffusion in the porous electrode has been studied to optimize the electrode microstructure with engineered porosity, pore size, pore distribution, tortuosity, particle size, and permeability [9–11]. He et al. presented a review on recent advances in the gas diffusion models and diffusivity measurement techniques of SOFCs [12]. In SOFC electrodes, the electrochemical reactions proceed at three-phase-boundary (TPB), which is defined as the active sites where the gas phase, the electrolyte,

and the electron conducting phase meet [13–17]. The porous microstructure of SOFC electrodes correlates with the TPB, gas diffusion, and concentration polarization. Thus, the electrode's microstructure affects the performance of SOFC [18–21]. Virkar et al. reached a power density of  $1.9 \text{ W cm}^{-2}$  at  $800^\circ\text{C}$  by adjusting the microstructure of the electrodes and tuning the interface of electrolyte-electrodes [18]. The use of fugitive pore-formers to generate porous electrodes has gained extensive attention and wide use. Pores can be generated through the incorporation of fugitive pore-formers, and the removal of them can be conducted by sublimation [22–25], phase inversion [26,27], chemical leaching [7,28,29], or by burning out the pore-formers [30–32]. The burning-out of pore-formers is capable of generating pores smaller than  $10 \mu\text{m}$  [33]. Sanson et al. [34] investigated the effect of pore-formers on the microstructure of Ni-YSZ anode supports. They pointed out that rice starch and carbon black are the most promising pore-formers for the tape casting of anode supports.

Ohji and Fukushima presented a review on the development of macroporous ceramics and their potential applications [35]. The pores that are derived from the burning-out of the pore-formers correspond closely to the shape and size of original pore-former [28,36]. Schmidt et al. [37] indicated that a more random orientation of the anisometric pores results in higher pore connectivity and gas permeability in porous ceramics. They concluded that the pores' size, shape, and orientation have a significant influence on the gas permeability of tape-casts with constant porosity. Fig. 1 displays the schematic illustration of using a pore-former to obtain a porous electrode. The considerations to select the appropriate pore-former are as following: the morphology of pore-formers (particle size and shape), nature of pore-formers (organic or inorganic) and thermal decomposition/ oxidation profile, capability of

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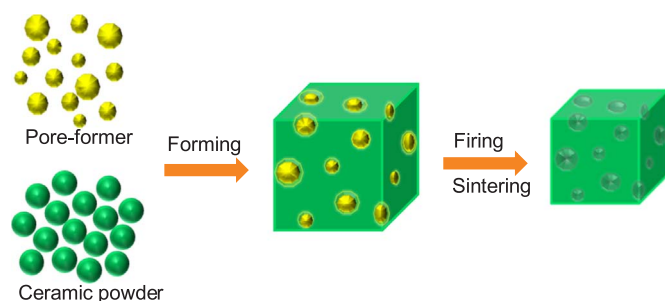


Fig. 1. Schematic illustration of preparing a macroporous microstructure by burning out the pore-former [33].

being burned out completely without any ash residue, compatibility with other materials in the electrode, commercial availability, and low-cost. The selection of the appropriate pore-former also depends on the mode of operation, which can be SOFC or solid oxide electrolysis cell (SOEC). For instance, it is confirmed that both PMMA and potato starch are suitable pore-formers for SOFC cathodes, but PMMA is more suitable than potato starch for using as the pore-former of SOEC cathode [38]. This can be attributed to the fact that an anode of an SOFC will serve as the cathode during operation in an SOEC mode, and the concentration polarization tends to be more critical in SOEC mode due to the larger molecular size of  $H_2O$  versus  $H_2$  [26].

Most of the studies on microstructure modification by pore-formers have focused on the anode electrodes and anode supports [39–43]. Nie et al. [44] reported that, based on the performance characterization, graphite is the most suitable pore-former for the fabrication of cathodes for SOFCs by tape casting. Nie et al. [44] also investigated the effect of using corn starch and graphite pore-formers. They found that corn starch has created open pores to improve the oxygen diffusion in the cathode layer due to the coarse microstructure of the corn starch.

Prestat et al. [45] found that graphite is capable of generating fine microstructure with microscopic pores and large surface area to increase the reactive sites of the cathode layer. Nie et al. [46] reported that the LSCF cathode with 10 wt% graphite for inner-layer and 35 wt% corn starch for outer-layer exhibited the highest cathodic performance based on the interfacial resistance characterization. Li et al. used 10 wt% polyethylene glycol (PEG-4000) for cathode [47], and Han used 10 wt% microcrystalline cellulose for porous substrate support [48]. The binder itself can also act as a pore-former, because increasing the amount of binder would introduce additional porosity after the firing. Normally, 1–2 wt% of dispersant is required and the extra amount of dispersant can be used as pore-former. Up to 6 wt% of fish oil has been used as both dispersant and “soft template” pore-former [49]. In the starch consolidation casting, starch can act as pore-former and at the same time as binder.

## 2. Processing routes

There are significant advantages in the use of aqueous systems for the production of the SOFCs, including the potential for a far wider range of pore-formers that can be used to generate specific pore morphologies and also reduce environmental burdens associated with exhaust handling, operator exposure, and disposal [47]. On the other hand, the organic solvents evaporate much more rapidly than water, and the drying rate is closely tied to fabrication rate [50]. The commonly used method for slip or slurry (thin slip) preparation is mixing the ceramic powders, additives and solvent system in a mill [51]. A slip can be prepared through the simple two step ball milling as follows: (i) dispersion step including the dispersion of desired ceramic powders, dispersant, and pore-former (if any) in the solvent system for 24 h, and (ii) thickening step including the addition of the binder and plasticizers into the dispersed powders and ball-milling for more 24 h [52]. Achieving a homogeneous aqueous dispersion of carbon black is

Table 1  
Traditional forming techniques to fabricate SOFC components.

Process	Components made
Tape-casting	whole cell
Slip-casting	electrodes, electrolyte
Screen-printing	electrodes, electrolyte
Spray-coating	electrodes, electrolyte
Dip-coating	whole cell
Spin-coating	electrodes, electrolyte
Extrusion	electrolyte, support
Dry-pressing	whole cell
Phase inversion	electrolyte, support
Freeze casting	electrodes, support

difficult because of the hydrophobic surface characteristics [41]. Graphite also shows incompatibility in water during ball-milling that leads to the non-homogenous electrode microstructure. Nitric acid treatment was reported to be an efficient method to improve the compatibility and wettability of carbon material in water [53], and the wettability of graphite in water [54].

Two main types of SOFCs have been developed, including planar and tubular SOFCs. The support fabrication is an important step in the manufacturing process, because the support allows the application of functional thin films called anode, electrolyte and cathode layers [55]. One of the fuel cell components could be made thick enough to act as a support. The anode support of a planar SOFC can be fabricated by a simple method like dry-pressing, and the anode functional layer and electrolyte can be applied by a simple technique such as spray-coating, dip-coating, screen-printing, or spin-coating [56]. Planar anode-supported SOFC with double-layered anode can be fabricated by multilayer tape casting and co-firing [57–59]. Extrusion is an appropriate method for the high-rate fabrication of the tubular support [60]. Table 1 presents the traditional forming techniques to fabricate SOFC components. Fig. 2 displays different cell microstructures in relation to the various fabrication techniques. An overview of the fabrication methods of SOFCs is presented in Ref. [33].

## 3. Tuning the electrolyte-electrodes interface

The performance of an SOFC is mainly governed by the micro-interface, especially the length of the TPB [13–17]. An effective approach to enhance the performance of SOFCs is tuning the interface of electrolyte/electrodes to increase the electrochemical active sites [18,65–68]. In this section, different examples of the electrolyte-electrodes interface modification by pore-formers are reviewed:

- (i) The typical tape-cast prepared by the phase inversion method comprises a three-layered structure, including a few micrometers-thick relatively dense layer at the top, a few hundred micrometers-thick highly porous finger-like layer in the middle, and a few ten micrometers-thick relatively dense sponge-like layer at the bottom. These unique structures were intact after firing. Huang et al. [69] used an innovative technique to eliminate the dense bottom layer of the anode using slurry that contained graphite. The graphite slurry and anode slurry were co-tape cast and solidified in a water bath through phase inversion. The pore-forming layer at the bottom was removed by firing at elevated temperatures, leaving a highly porous layer instead of the dense sponge-like layer [69]. Fig. 3 displays the cross-section and bottom surface of the prepared anode substrate after the reduction.
- (ii) Dai et al. [70] modified the electrolyte surface at mesoscale (10–100  $\mu\text{m}$ ) by adding a porous YSZ interlayer onto both sides of the dense YSZ electrolyte. The porous YSZ interlayers were prepared by spraying YSZ slurry containing PMMA pore-former with the mean diameter of 20  $\mu\text{m}$  onto the both sides of electrolyte and

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