ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–11

Available online at www.sciencedirect.com

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# A novel electrolyte-electrode interface structure with directional micro-channel fabricated by freeze casting: A minireview

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ARTICLE INFO

*Article history:*
Received 14 January 2017
Received in revised form
1 June 2017
Accepted 29 June 2017
Available online xxx

*Keywords:*
Solid oxide cell
Freeze casting
Yttria stabilized zirconia
Micro-channel structure

ABSTRACT

Freeze casting, a near net shaping technique to fabricate porous materials with directional microstructures, has a very good development prospect. This review elaborates the applications of freeze casting technology on the preparation of robust YSZ (yttria stabilized zirconia) scaffolds in solid oxide electrolysis cells (SOECs), with the goal of reducing the polarization resistance caused by gas diffusion. In this article, the freeze casting process of YSZ support and its solidification principles are summarized. Meanwhile, the critical factors influencing the pore morphology and distribution, such as the dispersion mediums, additives, freezing conditions, and solid content, are included and discussed. The further development, application and prospect of freeze casting technology are proposed.


## Introduction

The increasing severe environmental pollution and energy crisis exert an exceeding negative impact on the economic and social developments. Every main country of the world attaches great importance to develop efficient, clean and secure energy technologies for meeting the ever-increasing energy demands. Recently, as a novel, clean and efficient energy conversion device, solid oxide cell (SOC) has captured worldwide attention [1–4]. SOC has two reversible operating modes: solid oxide fuel cells (SOFC) [5–10] and solid oxide electrolysis cell (SOEC) [11–14]. It can achieve the high-effective convert between electricity energy and chemical fuels, which provides a potential pathway for renewable electricity storage [8,13,15–23]. Generally, there are two designs for SOC: electrolyte supported and electrode supported SOCs. Compared with the former, the later can effectively reduce the thickness of electrolyte, which can effectively lower the ohmic resistance [24,25]. Recently, as a novel near net shaping technique, freeze casting has been proposed and widely used for fabricating electrode supports with directional graded micro-channel structures [26–28]. Through freeze casting, tree-like scaffold with large pore size (5–100 μm), high porosity and appropriate mechanical strength can be obtained [29,30]. The graded directional channels with high connectivity will lower the polarization resistance caused by the gas diffusion. As a result, the cell performance can be improved significantly. In the early days, freeze casting materials are

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http://dx.doi.org/10.1016/j.ijhydene.2017.06.224

considered as promising candidates in bionic domain, such as tooth and bone on account of excellent mechanical strength [31–33] (e.g. 145 MPa at 47% porosity and 65 MPa at 56% porosity). In 2007, NASA [28] and Sofie et al. [26] firstly adopted freeze-casting technology to synthesize Ni-YSZ hydrogen electrode supports with graded and continuous micro-channels structures.

The traditional methods for synthesizing supports includes dry-pressing [34–37] and tape-casting [38,39]. However, the porosity, TPBs (three-phase boundaries) and connectivity of these supports are unideal, therefore, the polarization resistance may increase significantly. Regarding to the supports prepared through freeze casting method [27,40], the micro-channels structure gives rise to high porosity [29] and extended TPBs, thus more effective electrochemical reaction sites can be generated. In addition, there is a dense layer on the bottom of support which will effectively reduce the thickness of electrolyte and thereby reduce the ohmic resistance. Furthermore, if the support's material is in accord with electrolyte (typically yttria stabilized zirconia, YSZ [41,42]), it will enable to effectively avoid the delamination between electrode and electrolyte, which is caused by unmatched coefficient of thermal expansion (CTE) at high-temperature [43–48] (e.g. the CTE of Sr-doped $LaCoO_3$ (LSC) is $20.5 \times 10^{-6}$ $K^{-1}$ (30–1000 °C) [49] while the CTE of YSZ only is $10.5 \times 10^{-6}$ $K^{-1}$ (25–1000 °C)) [50].

As a novel promising fabrication method, although the freeze casting is widely used for synthesizing porous materials, it is still limited to just medicine and bionic fields so far [51–58]. The applications of this useful and effective method have rarely been studied and developed in other areas such as chemical industry [28,59]. Additionally, there is almost no published review article related to this freeze-casting method, especially for the fabrication of YSZ electrode supports. To facilitate research and development of fabrication for electrode materials, we have organized this comprehensive review to specifically focus on the novel YSZ electrode supports with directional graded micro-channel structure fabricated by freeze casting method. The fabrication processes and the solidification principle of freeze casting are summarized. Meanwhile, the critical factors influencing the micro-channels size, tortuosity, morphology and distribution, such as the dispersion mediums, additives, freezing temperature, freezing rate and solid content are investigated and discussed in detail. The further development, application and prospect of freeze casting technology are proposed.

## The process and critical factors of freeze casting

The process of freeze-casting approach including freezing and vacuum drying. The critical factors such as dispersion mediums, additives, freezing temperature, freezing rate and solid content are summarized and discussed in this section.

### *The process of freeze casting*

The process of freeze casting is presented in Fig. 1. Firstly, preparing the YSZ slurry by sufficiently mixing YSZ powders, various solvents (such as water and camphene) [60–62] and additives (such as glycerol and polyvinyl alcohol) [30,63](Fig. 1a). Secondly, pouring the well-dispersed YSZ slurry into the mold [64–66] and then freezing below zero (Fig. 1b). Under the supercooling condition, the solvent solidifying and crystallizing, then the ice crystals growing and rejecting the YSZ particles, consequently forming the graded laminar morphologies [67]. Thereafter, shifting the frozen samples to the vacuum drier (Fig. 1c). A porous scaffold with micro-channels structure is obtained after sublimating the ices, where pore is a replica of the crystal. In the end, sintering the scaffold at high temperatures in order to gain the appropriate mechanical strength (Fig. 1d).

### *Effect of dispersion medium*

In general, the common dispersion mediums are water [68], camphene [60–62] and tert-butyl alcohol [69,70]. Among them, water is the most commonly used solvent for the advantages of environmental-friendly, splendid reserve and low cost. Extensive works have been carried out to investigate the relations between ice nucleation and crystal growth [71–75]. The ice crystals can form needle, columnar, layered to branched morphologies under the different freezing condition. Fig. 2a [29] shows the common ice molecule structure. When the freezing temperature gradually decreases from the room temperature to subzero, the whole solution system could be considered in thermal equilibrium. In this case, ices firstly nucleate on the slurry surface and grow downward along the temperature gradient direction (a-axis). As a result, homogeneous freezing leads to homogeneous columnar crystals. However, if the slurry is controlled under a supercool condition, the ices initially grow with large anisotropy due to high freeze rate. Then, with the freeze rate declining and reaching a steady-state, it is easier for crystals to grow along the a-axis than the c-axis, and finally form vertical lamellar morphology (Fig. 2b). It is reported that the ice growth rate parallel to a-axis is $10^2$-$10^3$ times faster than that of c axis, on account of the horizontal c axis have a higher chemical potential [76].

The premise behind the formation of pore structures is satisfied with thermodynamic and dynamic criterions in the same time. Thermodynamically, the interfacial energy between YSZ particles and solidification front $\delta_{PS}$ should be greater than the sum of interfacial energies of particle–liquid $\delta_{PL}$ and solid–liquid $\delta_{SL}$, as shown in Equation (1) [77] :

$$\delta_{PS} > \delta_{PL} + \delta_{SL} \tag{1}$$

From a dynamic view, the YSZ particles in the slurry are loaded by the repulsive force $F_\delta$ and the attractive drag force $F_\eta$, which are expressed as Equations (2) and (3) [77]. When the resultant force is dominated by the former, the YSZ particles will be rejected from the solidification front:

$$F_\delta = 2\pi \Delta\delta_0 \left(\frac{a_0}{d}\right)^n \tag{2}$$

$$F_\eta = \frac{6\pi\eta v R^2}{d} \tag{3}$$

where R is the particle radius, $a_0$ refers to the average intermolecular distance, $d$ refers to the distance between particle