Materials Research Bulletin 44 (2009) 1879–1888

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

# Usefulness of gel-casting method in the fabrication of nonstoichiometric $CaZrO_3$-based electrolytes for high temperature application

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ARTICLE INFO

*Article history:*
Received 22 March 2009
Received in revised form 30 April 2009
Accepted 21 May 2009
Available online 29 May 2009

*Keywords:*
A. Ceramics
B. Chemical synthesis
C. Electrochemical measurements
D. Ionic conductivity
D. Thermodynamic properties

ABSTRACT

Hydrogels obtained from lower toxicity monomers of *N*-(hydroxymethyl)acrylamide and *N*,*N*′-methylenebisacrylamide were applied to form nonstoichiometric $CaZrO_3$-based electrolytes. A coprecipitation-calcination method with $((NH_4)_2C_2O_4)$ in concentrated $NH_3$ aqueous solution was used to synthesise $CaZrO_3$ involving 51 mol.% CaO (CZ-51) powder. The gas-tight $CaZrO_3$-based rods were prepared by the gel-casting method with 45 vol.% suspension and then sintered at 1500 °C–2 h. It was found that in low oxygen partial pressure, the nonstoichiometric $CaZrO_3$ obtained by gel-casting method were pure oxide ion conductors. These samples exhibited comparable electrical conductivity values to isostatically compressed pellets starting from the same powder. The results of experiments on thermochemical stability of CZ-51 gel-cast shapes at high temperatures in air or gas mixtures involving 2–50 vol.% $H_2$, as well as the corrosion resistance in exhaust gases from a self-ignition engine were also presented and discussed. The thermal resistance of $CaZrO_3$ obtained rods against molten nickel or iron was also examined. Based upon these investigations, it is evident that only in hydrogen-rich gas atmospheres can the stability of $CaZrO_3$ shapes be limited due to the presence of CaO precipitation as a second phase. The nonstoichiometric $CaZrO_3$ (CZ-51) gel-cast materials were also tested in solid galvanic cells, designed to study thermodynamic properties of oxide materials, important for SOFC and energy technology devices. In this way, the Gibbs energy of $NiM_2O_4$, M = Cr, Fe, at 650–1000 °C was determined. The $CaZrO_3$ involving 51 mol.% CaO gel-cast sintered shapes seems to be promising solid electrolytes for electrochemical oxygen probes in control of metal processing and thermodynamic studies of materials important for the development of the energy industry.

## 1. Introduction

There is growing interest in $CaZrO_3$-based electrolytes for high temperature application. Ceramic membranes involving $CaZr_{0.9}M_{0.1}O_3$, where M = In, Gd, due to their sufficiently high protonic conductivity in hydrogen-containing atmospheres combined with high chemical stability and good mechanical properties are good candidates for possible application as proton-conducting electrolytes in electrochemical sensors to control dissolved hydrogen in molten metals [1–3].

Janke et al. reported that $CaZrO_3$ with calcia or zirconia excess, exhibited extremely high chemical stability and practically pure oxygen ionic conduction and was successfully tested as solid electrolytes in electrochemical probes to determine oxygen activity in molten steel [4,5]. It was found that the electrical properties of $CaZrO_3$ are strictly connected with its stoichiometry [6,7]. The introduction of excess CaO or $ZrO_2$ excess led to a significant improvement of ionic conductivity of $CaZrO_3$-based materials compared to stoichiometric $CaZrO_3$. The analysis of electrical conductivity values for $CaZrO_3$-doped CaO samples, with the formula $(CaO)_x(ZrO_2)_{1-x}$, indicated that the total ionic conductivity reached a maximum value for composition $x = 51$–52 mol.%, which are close to solubility limit CaO in $CaZrO_3$. Further increase in calcia content caused the occurrence of CaO as a second phase and led to a decrease of ionic conductivity for investigated materials [8,9].

The improvement of electrical conductivity in the $CaZrO_3$ with excess $ZrO_2$ samples, where $30 < x < 49$ mol.%, was also noticed. In this case, an appearance as cubic calcia solid solution as better conductive phase than orthorombic $CaZrO_3$ phase led to the enhancement of ionic conductivity compared to monophase $CaZrO_3$ samples [10].

The main advantage of nonstoichiometric $CaZrO_3$ compared to cubic calcia solid solution (CSZ) is lower electronic conduction, which occurred in ceramic electrolytes at high temperatures (above 1200 °C and low oxygen partial pressure) in such applications. The electrolytic domain of nonstoichiometric $CaZrO_3$ is close to thoria or hafania-solid solution, considered to be the most adequate oxide electrolytes for high temperature application. The costs of producing $CaZrO_3$-based electrolytes are also lower than $MO_2$, M = Th, Hf-solid solutions [11,12]. Our previous research on this subject showed that nonstoichiometric $CaZrO_3$ also seems

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doi:10.1016/j.materresbull.2009.05.008

to be promising solid oxide electrolytes for solid galvanic cells designed to study thermodynamic properties of oxide systems with low equilibrium oxygen partial pressure [13].

Due to the interest in nonstoichiometric $CaZrO_3$-based materials for electrochemical oxygen sensors application, the technology for manufacturing ceramic gas-tight shapes from electrolytic materials is in progress. The former paper [14] showed that isostatically pressed CZ-51 cylindrical samples from powders synthesised by citrate or coprecipitation methods and then sintered at 1500 °C for 2 h in air, exhibited significantly better electrical properties than samples densified in hot-pressing processes.

Gel-casting could also be an attractive forming process for manufacturing high-quality, complex-shaped ceramic parts from electrolytic materials. The process consists of casting a suspension of ceramic particles and gelformer in a mould, followed by in situ gelation of a binder. After solidification, the gelled part can be removed from the mould and sintered in the conventional way. Distinct advantages of the gel-casting process over the conventional ceramic forming processes such as dry pressing, slip casting, tape casting, and injection molding, are near net shape forming, high green density, low levels of organic additives, and mach inability in the green statue due to a high strength [15,16].

Nowadays, the gel-casting method of forming ceramic materials seems to be very useful for the development of intermediate solid fuel cells technology (IT-SOFC), especially for producing thin electrolytes on porous anode support. This method has been successfully applied to obtain thin electrolytic films involving; zirconia stabilized yttria (8YSZ), ceria-doped, samaria (SDC) or gadolina (GDC) on anode supported solid oxide fuel [17–21].

At present, most ceramic electrolytes are formed by gel-casting processes involving monofunctional acrylamide $CH_2{=}CHCONH_2$ and difunctional *N*,*N*′-methylenebisacrylamide $(CH_2{=}CHCONH_2)_2CH_2$ as the reactive organic monomers. The main disadvantage of this gelling system is that acrylamide is a neurotoxin [22]. Therefore, many new gel formers, especially those consisting of monomers of low toxicity or environmentally friendly biopolymers are extensively studied [23,24]. Contrary to $MO_2$-based electrolytes (M = Ce, Zr) there is no information about the possibility of forming gas-tight $CaZrO_3$-based electrolytes by the gel-casting method for application in electrochemical devices.

The aim of this paper is to examine the possibility of forming ceramic shapes from nonstoichiometric $CaZrO_3$ (51 mol.% CaO) electrolytic material by gel-casting method using monomers with lower toxicity and investigate the properties of sintered samples, which are crucial for application in electrochemical gas sensors.

## 2. Experimental

Nonstoichiometric $CaZrO_3$ powder (51 mol.% CaO), denoted in whole text as CZ-51 was prepared by a coprecipitation-calcination method. All reagents applied for the CZ-51 powder synthesis were of 99.99% purity and supplied by the Aldrich company. The zirconyl nitrate (1.2 mol $dm^{-3}$) solution was used as a starting material. An appropriate amount of $CaCO_3$ was added to the solution. Common solution was dropwise introduced into saturated solution of $(NH_4)_2C_2O_4$ in concentrated $NH_3$ solution. The final pH in the precipitating slurry was 9.5. The resulting gels without washing were dried to a constant weight at 100 °C for 12 h. The dried $CaZrO_3$-precusror was calcinated at 1050 °C for 2 h to obtain pure $CaZrO_3$ phase. The details of this synthesis method were included in the former paper [14].

The CZ-51 obtained powder was rotary–vibratory milled in dry ethanol with zirconia grinding-media and grounded powder was used in the gel-casting process. Specific surface area of the $CaZrO_3$ was calculated using the BET method from $N_2$ adsorption isotherm obtained in a Sorpty 1760 analyser. Before BET measurement, the samples were degassed at 150 °C in a vacuum. The morphology of grounded CZ-51 powder was observed using transmission electron microscopy (TEM) (Philips CM 200).

The suspension vehicle was an aqueous solution containing 15 wt.% of *N*-(hydroxymethyl)acrylamide (Aldrich, Germany) and *N*,*N*′-methylenebisacrylamide (Aldrich, Germany) monomers in 24/1 weight ratio. $CaZrO_3$ was slowly added to the solution with dispersant (Darvan C, R.T. Vanderbilt Company Inc., U.S.A.) to prepare the suspension at 45 vol.% of solids. All the slips components were further homogenised for 6 h by ball-milling using zirconia grinding media. After homogenisation the slips were degassed and accelerator and initiator were added to induce polymerisation in the ceramic suspension. The redox pair consisted of ammonium persulfate (APS) (Aldrich Germany) as the initiator and *N*,*N*,*N*′*N*′-tetramethylethylene diamine (TEMED) (Fluka Switzerland) as the accelerator was used. The concentration of initiator was 0.2 wt.% of the monomers. A weight ratio of APS to TEMED was 1:1. Next, the slip was poured to polyethylene moulds and allowed to gel in $N_2$ atmosphere at 60 °C. The gel-cast ceramics bodies were dried in a controlled climate box with 95% relative humidity, next in a less humid atmosphere. The last stage of drying was performed in an oven at 80 °C. The procedure was similar to described in papers [25,26].

The rods were sintered at 1500 °C for 2 h with heating rate of 2°/min and cooling rate 5°/min to 1000 °C and later naturally with a furnace to room temperature. The sintered nonstoichiometric $CaZrO_3$ gel-cast full rods were cut on diamond sieve to small cylindrical samples (~diameter 10 mm and ~3 mm height) to investigate electrical, electrochemical and mechanical properties.

The phase composition of CZ-51 powder and the sintered samples were evaluated by X-ray diffraction analysis. XRD measurements were done at 25 °C using $CuK_\alpha$ monochromated radiation (Philips X'Pert) within the $2\Theta$ range 10–90° with a scan rate of 0.01°. The lattice parameters were calculated using X'Pert+ (Philips) software according to the Rietveld method. The Scherrer formula using the full width at half maximum of the (2 1 1) diffraction peak of $CaZrO_3$ adjusted by a pseudo-Voigt function, enabled evaluation of the crystallite size $d_{(h\ k\ l)}$. Apparent density of CZ-51 gel-cast sintered samples was determined by Archimedes method.

In order to verify the thermochemical stability of CZ-51 gel-cast materials during long-term operation at a temperature close to metal processing conditions, the $CaZrO_3$ gel-casted samples were additionally heated within a temperature range 1000–1200 °C for 100 h. The stability of $CaZrO_3$-based ceramic shapes was also tested in gas atmospheres involving hydrogen from 2 to 50% $H_2$ in Ar at 1000 °C for 48 h.

The corrosion resistance of the CZ-51 gel-cast to exhaust gases from Diesel engine was also investigated according to the European Test Standard (ESC) in an engine test bed. The selected chemical composition of gases during performed research varied from 1.9 to 10.5% for $CO_2$, 150 to 620 ppm for $NO_x$, 0 to 56 ppm for $SO_2$ and 251 to 720 ppm for CO. The procedure was similar to the one described in the previous paper [27].

Hardness HV, and fracture toughness $K_{Ic}$ of CZ-51 gel-cast sintered samples was determined on polished surfaces by Vickers' indentation. A loading force of 29.43 N imposed by 10 s was applied. The Palmqvist crack model [28] was applied to calculate $K_{Ic}$.

To test the thermal resistance of $CaZrO_3$-based materials to molten melts involving copper, nickel and iron, the samples were subject to rapid cooling. Scanning electron microscopy (JEOL JSM-5400) equipped with EDX analysis was used to observe the microstructures of starting CZ-51 gel-cast sintered samples as well as after additional stability tests. The electrical conductivity of CZ-51 sintered samples was determined by d.c. four probe method in air,