Journal of Power Sources 221 (2013) 28–34

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Accelerated devitrification of a strontiumlanthanumaluminoborosilicate based intermediate temperature solid oxide fuel cell glass sealant and its effect on thermophysical behaviour of the glass ceramics

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HIGHLIGHTS

- Devitrification of a strontiumlanthanumaluminoborosilicate glass was investigated.
- Change in properties of the glass was correlated with the evolution of phases.
- With evolution of $SrAl_2Si_2O_8$ phase, CTE of the glass ceramics increases.
- With evolution of $La_{10}(SiO_4)_6O_3$ phase, CTE of the glass ceramics decreases.
- Even on 100 h devitrification at 1000 °C the glass ceramics is suitable for SOFC.

ARTICLE INFO

Article history:
Received 30 April 2012
Received in revised form
12 July 2012
Accepted 31 July 2012
Available online 13 August 2012

Keywords:
Glass sealant
Devitrification
Thermochemical stability
Intermediate temperature solid oxide fuel cell (IT-SOFC)

ABSTRACT

A strontiumlanthanumaluminoborosilicate based intermediate temperature solid oxide fuel cell (IT-SOFC) glass sealant has been investigated for isothermal devitrification under accelerated conditions. Sintering of the glass up to 100 h at 1000 °C, results in the formation of two crystalline phases evidenced by X-ray diffraction (XRD) analysis. Hexacelsian phase evolves from the initial hours of sintering; however, lanthanum silicate phase appears at longer hours of sintering. Quantitative XRD of the glass ceramics reveals that hexacelsian occupies majority of the crystalline phases and lanthanum silicate is occupying minor quantity. Formation of crystalline phases has been reconfirmed by microstructure analysis of glass ceramics through Scanning Electron Microscopy (SEM) and elemental analysis of phases by energy dispersive spectroscopy (SEM-EDS). Crystalline phases in the glass ceramics have been quantified by analysis of SEM images through Imagepro plus software. At different stages of sintering, CTE of the glass ceramics has been measured by dilatometer. Correlation of CTE with crystalline phases in the glass ceramics indicates that with formation of hexacelsian phase CTE of the glass ceramics increases, however, formation of lanthanum silicate phase reduces the CTE of the glass ceramics. Phase property correlation indicates that after 100 h of accelerated devitrification at 1000 °C, the glass ceramics attains phase stability therefore the CTE stabilizes and the value remains well within the requirement limit of SOFC sealant.

1. Introduction

In recent years, solid oxide fuel cell (SOFC) has emerged as one of the most challenging energy conversion technology because of its higher efficiency compared to other concurrent technologies, environment friendly nature and fuel flexibility. An SOFC cell has three major components a porous anode, dense electrolyte and a porous cathode. A single cell can generate at most several watt of power; thereby to generate high power output several such cells are stacked together. An SOFC stack can have two basic designs, planar and tubular. Out of which the planar design (pSOFC) provides greater power density compared to a tubular design because of the linear path of current flow [1–6]. Among the planar designs, anode supported planar design has been adopted by most of the leading SOFC developers that can be operated in an intermediate temperature range between 700 and 800 °C (IT-SOFC) [7,8]. Because of a comparatively low temperature operation,

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http://dx.doi.org/10.1016/j.jpowsour.2012.07.110

ceramic interconnect can be replaced by metallic interconnect and other operational costs can be reduced. Moreover, low temperature operation makes it easier to handle the cell component materials and delays the ageing of the materials thereby increases average life span of the cell. Despite all these advantages, a planar IT-SOFC stack requires gas tight sealant to provide edge sealing at SOFC operational temperature. The health of an SOFC stack grossly depends upon the long term thermophysical and thermochemical stability of the sealant in SOFC condition. Hence, selection of a proper sealant material is very important for fuel cell performance. For use in pSOFC, a sealant material should have low leakage of fuel/oxidant gas, optimum viscosity, good wettability, chemical inertness, and thermal expansion matching with adjacent SOFC components. In this regard, researchers have tried out several materials for SOFC sealant and all these materials can be broadly classified into three categories: compressive seals, compliant seals and rigid bonded seals [9–14]. Glass and glass ceramics as rigid bonded seals have advantages over other seals and are therefore preferred for SOFCs. For use in SOFC, a glass sealant should be chemically stable in both oxidizing and wet reducing conditions. CTE should be close to $10 \times 10^{-6}\,^{\circ}C^{-1}$. Glass transition temperature should be less than cell operating temperature and glass softening temperature high enough to maintain viscosity at cell operating temperature. Further, continuous and/or excessive devitrification of the glass should not occur during cell operation temperature.

Thermal stress in pSOFC is commonly observed due to mismatch of coefficient of thermal expansion (CTE) of glass with cell components and temperature gradient during operation. This has been recognized as criteria in selecting the seal materials [15–19]. Some glass systems rarely crystallize at high temperatures so that they overflow due to lowering of viscosity at SOFC operational temperature. Others may partly or completely crystallize during high temperature operation. Crystallization of a glass mainly depends on the glass composition and thermal history of the sample. Crystallization in glass seals is reported to show better physical properties but it causes serious CTE mismatch [9,19,20] which affects the cell performance. For a glass to be used as rigid seal in pSOFC, it must have CTE matching with other SOFC components for a longer period of operation. Thus, flowability and crystallization of glass sealants are two important factors related to thermal stress distribution and mechanical integration in pSOFC stack. The glass sealant should have controlled crystallization and the crystalline phases should be stable so that the sealant can be used for longer time.

Considering all these factors, researchers have tried out several glasses and glass ceramics based on borates, phosphates and silicates and studied their compatibility with both cell components and interconnect [12,21–30]. Out of all these candidate glasses borosilicate glasses with proper B_2O_3/SiO_2 ratio are best suited for SOFC sealing application [23,31,32]. Again, La_2O_3 as a modifier in the glass composition controls the viscosity of the glass sealant at SOFC operational condition [23]. SrO modifies the CTE [33] and Al_2O_3 retards devitrification [34].

Therefore we have selected a group of $SrO–La_2O_3–Al_2O_3–B_2O_3–SiO_2$ based glasses and have investigated their thermal and physical properties to evaluate their suitability as SOFC sealant [35,36]. The research work in this article is an extension of the previous work reported elsewhere [36]. In this work the glass has been investigated for its long term thermochemical and thermophysical stability.

As mentioned in the previous report [36], thermal properties of the glass make it suitable for IT-SOFC application in an operating temperature range 700–800 °C, however, the glass shows two crystallization temperatures under differential scanning calorimetric (DSC) at 807 °C and at 1021 °C. As mentioned previously that devitrification in glass sealant leads to a drastic change in the CTE which is undesired for SOFC application. Therefore in this piece of work, devitrification of the strontiumlanthanumaluminoborosilicate glass has been investigated and corresponding change in the CTE is evaluated. The devitrification in the glass has been carried out at an elevated temperature compared to SOFC operating temperature. The glass has been systematically heat treated at 1000 °C up to 100 h and the phase formation process has been evaluated by XRD and SEM analysis. In each step of devitrification, the CTE of the glass ceramics has been measured through dilatometer. An effort has been made to establish a phase property correlation between the phases formed in the glass ceramics and CTE of it, which highlights the importance of the work.

2. Experimental

A glass with composition SrO (25.7 mol %), La_2O_3 (4.1 mol %), Al_2O_3 (13.1 mol %), B_2O_3 (12.8 mol %) and SiO_2 (44.3 mol %) was heat treated from 700 °C to 1000 °C at an interval of 100 °C. At each temperature the glass was sintered for 15 min. Similarly, the glass was heat treated at 1000 °C for different time up to a maximum of 100 h. At 1000 °C the glass was heat treated for 2 h, 5 h, 10 h, 15 h, 25 h, 50 h and 100 h. In each case the sample was heated from room temperature to the sintering temperature at a heating rate of 5 °C min^{-1}. The sample was hold at the temperature for desired time and was cooled to room temperature by air cooling. All the characterizations of heat treated samples were carried out at room temperature.

Phase analysis of heat treated samples were carried out by powder X-ray diffraction (XRD) using XPert MPD, PAnalytical model, Philips, Netherlands. For phase identification and quantification of phases, semi-quantitative Rietveld method was used.

Scanning Electron Microscopy (SEM) (LEO 1455, UK) was used at room temperature to analyze the microstructures of base glass and heat treated glasses. The compositions of crystalline phases were determined using energy dispersive spectroscopy (SEM-EDS).

SEM images were analyzed through 'Imagepro plus' software for quantitative analysis of phases. Through this software each phase was assigned with a particular color code and was analyzed to get phase details. A calibrated scale was used to obtain grain size, aspect ratio and percentage of crystallinity for each phase. Grain details were obtained from the average data of 50 numbers of grains. Percentage of crystallinity was calculated from area occupied by the crystalline phase with respect to the total area of the glass ceramics.

Coefficients of thermal expansion (CTE) of the heat treated glass samples were measured using a vertical push rod type UNITHERM™ MODEL 1161 Dilatometer System made by Anter Corporation, USA. Through dilatometer, percentage of linear expansion of the sample was measured as a function of temperature. CTE of the sample was calculated using slope of the expansion plot and sample dimension.

3. Results and discussion

In the previous report [36] the glass was thoroughly characterized for its physical and thermal behaviour. In that report, amorphous nature of the glass was evident from X-ray diffraction. Thermal characterization of the glass was carried out by differential scanning calorimetry (DSC). Through DSC it was observed that the glass undergoes glass transition (T_g) at 625 °C and on heat treatment two crystallization phases (T_p) evolve out of the glass matrix at 807 °C and at 1021 °C. Through dilatometric analysis characteristic temperatures were measured for bulk glass and found to be: glass transition temperature (T_g) at 644 °C and glass softening