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Apatite type lanthanum silicate and composite anode half cells

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ABSTRACT

Apatite type rare earth silicates are being extensively studied as electrolyte material for intermediate temperature solid oxide fuel cells (SOFC). In this paper we presents results on synthesis of Al and/or Fe-doped ATLS, the design of compatible anode materials, thermal expansion properties and co-sintering of half-cells from expansion matched materials using the advanced pulsed electric current sintering (PECS) technique. The issues related to the co-sintering of half cells have been addressed successfully by the combined use of nano powders and PECS.

1. Introduction

Solid electrolytes having good oxygen ion conductivity over a wide range of temperature region are constantly investigated for development of new electrolyte materials. Oxy-apatites are one such alternate electrolyte material of interest for SOFCs operating at intermediate temperature region (500 °C–800 °C). The structure of the oxy-apatites is isostructural with the well-known apatite minerals like fluro-apatite and hydroxyapatite biomaterials. When considering the general formula $M_{10}(XO_4)_6O_{2\pm y}$, M site can be any rare earth and X site can be Si or Ge but majority of work in literature focus on the La (M site) and Si (X site) containing system, $La_{9.33+x}(SiO_4)_6O_{2+3x/2}$, (referred to ATLS further in this paper) due to the higher conductivities of this system in comparison to samples containing smaller rare earths [1,2].The ionic conductivity of ATLS with cation dopants or anion excess are better than that of yttria stabilized zirconia in the intermediate temperature range establishing themselves as potential electrolyte material for intermediate temperature SOFCs [3–6]. Though there have been lot of reports on the possible use of these electrolytes as an alternative electrolyte for SOFCs, but, only few studies concerning possible suitable electrodes and on the processing of half and or full cells [7–14]. The processing of half cells having ATLS as the electrolyte is challenging due the high sintering temperature demanded by these electrolytes. The sintering temperatures reported for this type of materials are >1600 °C with dwell times greater than 10 hours for powders synthesized via solid state route [5,15–17]. At these high temperatures maintaining the porosity of the anode is a major problem. The sintering temperature can be reduced to a certain extent by use of electrolyte powders prepared by sol gel or similar low temperature process which produce nanometer powders. But the co-sintering of materials with different sintering behaviour will continue to remain as a challenge.

In this paper we report the synthesis of different electrolyte powders and composite anode using modified sol–gel process. The thermal expansion co-efficient (TEC) of the different electrolyte powders were measured and the electrolyte powder whose TEC matched closely that of anode was used for preparing half cells. Half cells were co-sintered by using an advance sintering technique namely PECS. By adopting this technique it was possible to co-sinter dense (electrolyte)/porous (anode) half cell for the first time at temperatures as low as 1200 °C (60MPa) and with dwell times as low as 2 min.

2. Experimental

2.1. Electrolyte powder preparation

Electrolyte powders having aluminium or iron on the silicon site, namely, $La_{9.83}Al_{1.5}Si_{4.5}O_{26}$ (LASO), $La_{9.83}Fe_{1.5}Si_{4.5}O_{26}$ (LFSO) and

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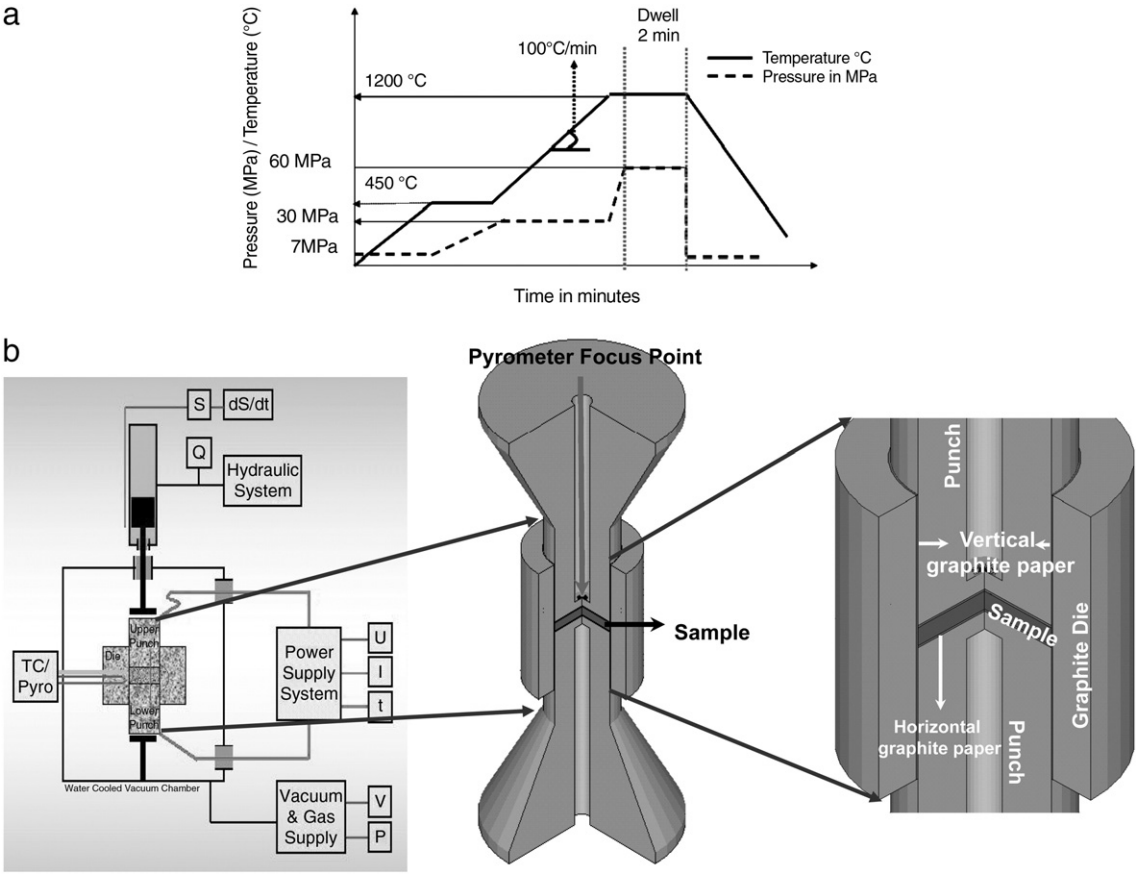

Fig. 1. (a): Sintering cycle used in PECS for sintering electrolyte and half cells. (b): Schematic set-up of die with powder loading as used in PECS.

$La_{9.83}Al_{1.0}Fe_{0.5}Si_{4.5}O_{26}$ (LAFSO) were considered in this study. All of them were synthesized using a modified sol–gel process [18]. The metal nitrates and tetraethyl orthosilane were used as the starting material. Ethylene glycol and citric acid were used as gelling agents. The clear solution transforms to gel after few hours at 70 °C. The gel is then calcined at 900 °C for 8 h in air.

Two different anode compositions were considered in this study. The first one is the conventional mixture of the electrolyte (LASO) with coarse nickel oxide powders (Acros reagent grade 97%). The fine electrolyte powder (crystallite size <70 nm—60%) was mixed with nickel oxide (particle size >10 μm—40%) in the multidirectional mixer for 24 h. The second anode composition considered was a composite system containing 15%Ni (NiO)–15%$La_{0.1}Sr_{0.9}TiO_3$–10%$La_{0.8}Sr_{0.2}Mn_{0.8}$-$Cr_{0.2}O_3$–$La_9SrSi_6O_{26}$. This composite anode was prepared using Pechini method as this was best suited with respect to the anode microstructure and improved anode activity [19].

2.2. Sintering

The electrolyte, anode powders and half cells were sintered in the PECS equipment (HP D 25, FCT System, Rauenstein, Germany). The powders were loaded without any pressure or sintering aids in graphite die (30 mm diameter) and punch unit. During the sintering process the pressure is increased to 60 MPa while reaching maximal temperature (1200 °C). The actual sintering cycle applied is given in Fig 1(a) and the sintering set-up with the die dimensions is given in Fig 1(b). The heating rate was at 100 °C/min; the dwelling time was 2 min.

2.3. Characterization

XRD analysis of the powders, sintered electrolyte, anode and half cells was carried out on a Seifert-3003 equipment in order to determine the phase purity and crystal structure. Θ–θ measurements were performed using Cu-Kα radiation (40 kV–40 mA) using a step size of 0.02º 2θ and an acquisition time of 2 s. Microstructures of the powder and sintered pellets were examined by scanning electron microscopy (SEM, XL30-FEG, Philips, Eindhoven), equipped with an energy dispersive analysis system (EDS, EDAX) for compositional analysis. Thermal expansion co-efficient studies of the electrolyte and anode composition were carried out on sintered cylindrical pellets of dimension 10*10 mm. The measurements were carried out in air up to 1000 °C using Dilatometer (DIL 402C/7 Netzsch) with a heating and cooling rate of 5 °C/min. The densities of sintered samples were measured using the Archimedes principle.

3. Result and discussion

3.1. Powder preparation

Electrolyte powders having aluminium and or iron on the silicon site (LASO, LFSO and LAFSO) were considered in the studies. It is known that substitution of aluminium increases the conductivity compared to the undoped ALTS [2,4] whereas the addition of iron helps in reducing the sintering temperature [5] and a novel

Table 1
Thermal expansion co-efficient of all the electrolyte and anode compositions investigated.

Composition	Alpha*10^{-6}/°C (100–1000/°C)	Composition	Alpha*10^{-6}/°C (100–1000 °C)
BIC-Anode	10.3	LASO	6.7
NiO-LASO	12.5	LAFSO	7.3
Cathode	13.3	LAFSO	9.5