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Evaluation of the response time of H-concentration probes for tritium sensors in lead–lithium eutectic alloy

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HIGHLIGHTS

- Synthesis and chemical characterization of proton conductor ceramics.
- Qualification of ceramics for hydrogen sensors in molten lithium–lead.
- Ceramics have well-defined grains with a wide distribution of sizes.
- Good agreement with predictions obtained with $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$ ceramic.

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ABSTRACT

Dynamic tritium concentration measurement in lead–lithium eutectic is of major interest for a reliable tritium testing program in ITER TBM and for an experimental proof of tritium self-sufficiency in liquid metal breeding systems. Potentiometric hydrogen sensors using different solid-state electrolytes for molten lead–lithium eutectic have been reported and tested by the Electrochemical Methods Lab at Institut Quimic de Sarria (IQS).

In the present work the following ceramic elements have been synthesized and characterized by X-ray diffraction (XRD) in order to be tested as a Proton Exchange Membranes (PEM) H-probes: $BaCeO_3$, $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$ and $Sr(Ce_{0.9-}Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$. Potentiometric measurements of the synthesized ceramic elements have been performed shifting from a fixed hydrogen partial pressure at the working electrode to high purity argon. In this experimental campaign a fixed and known hydrogen pressure has been used in the reference electrode. The goal of these experiments is to evaluate the sensor response time when the hydrogen concentration in the environment is rapidly changed. All experiments have been done at 500 °C and 600 °C. The sensor constructed using the proton conductor element $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$ exhibited stable output potential and its value was close to the theoretical value calculated with the Nernst equation. In contrast, the sensors constructed using the proton conductor elements $BaCeO_3$ and $Sr(Ce_{0.9-}Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$ showed higher deviations between experimental and theoretical data, and long response times.

1. Introduction

One of the questions that the scientific community should overcome in the ITER project is the tritium generation. ITER will obtain the tritium "fuel" necessary for its expected 20-year lifetime from the global inventory. However, DEMO (the next step on the way to commercial fusion power) will require a larger amount of tritium to produce the estimated 800 MW of electrical power. Since no sufficient external source of tritium exists, the development of tritium breeding systems will be essential for the forthcoming development of the fusion nuclear industry.

Lead–lithium eutectic is one of the candidates to be used for tritium generation in ITER He-Cooled Lead–Lithium Test Blanket Module (HCLL TBM). In order to proof the tritium self-sufficiency in the liquid metal breeding system the on-time and on-board tritium concentration measurement will be of high interest [1,2]. It worth to mention that lead–lithium eutectic can also play the role of a shield, preventing escape of neutrons and γ radiation outside the blanket. Accurate and reliable tritium management is of basic importance for the correct operation conditions of the blanket tritium cycle. Consequently, the determination of the hydrogen

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isotopes concentration in the liquid metal is of high interest for the blanket correct design and operation.

Molten metals provides unique properties on its use in the nuclear industry: excellent heat conduction, reactors can run at extremely high temperatures without generating a great deal of gas pressure, the metal coolant provides negligible moderating effect and a broken coolant pipe in a liquid metal reactor dos not cause a destructive explosion. For example, molten sodium and molten lead or lead–bismuth eutectic have been widely studied for its use in Fast Nuclear Reactors. On the other hand, there are multiple problems related with the use of molten metals: chemical reactivity, materials compatibility, presence of impurities, etc.

Solid-state electrolytes have been used as sensors components for over 40 years. These materials have several advantages in the handling/processing of molten metals: the conductivities of solid electrolytes increase with increasing temperature, the output of solid electrolyte based sensors is determined by the thermodynamic properties of the molten metal/reference electrode and finally, solid electrolytes are generally stable compounds which can withstand the harsh chemical environment in molten metals.

In early 1980s Iwahara et al. [3] demonstrated that acceptor-doped strontium cerate ceramics show proton conductivity at elevated temperatures. Since then, a number of studies on proton conducting solid-state electrolytes have been carried out due to considerable interest for applications in hydrogen gas sensors, hydrogen pumps, solid oxide fuel cells, etc. [4–7].

The crystallographic structure of these compounds (for which almost pure high proton conductivity was reported) was of the perovskite type, where the electrical carriers are positive holes, excess electrons, oxide ion vacancies and interstitial protons which interact with oxide ions. A number of doped perovskites exhibit high proton conductivities and thus have potential as electrolytes in fuel cells [8–11].

From an electrochemical point of view, the sensor is a hydrogen concentration cell, in which the working and the reference systems are separated using a solid-state electrolyte (proton conductor). It can be represented as follows: $H_2(P_1)$||solid-state electrolyte||$H_2(P_2)$. In that equation, P_1 is the hydrogen partial pressure of the reference system whereas P_2 may be an unknown hydrogen pressure. P_1 must be a fixed, known and reproducible parameter in the system. The electrochemical potential of this sensor can be calculated using the Nernst equation:

$$E = -\frac{RT}{nF} \ln \frac{P_1}{P_2} \quad (1)$$

where F is the Faraday constant, T is temperature (K), R is 8.31447 J/mol K, n is the number of electrons involved in the electrochemical reaction, and P_1 and P_2 are the hydrogen partial pressures in the reference and in the working electrodes, respectively.

Potentiometric hydrogen sensors using different solid-state electrolytes have been designed and tested at the Electrochemical Methods Lab at Institut Quimic de Sarria (IQS) [12–14]. The most promising elements have been selected for this work in order to evaluate the sensor response time at different working temperatures. The final goal of this project is to design and develop a high performance and fast response time tritium sensor for molten lithium lead eutectic.

2. Experimental methods

2.1. Proton conductor ceramics synthesis

The sensor design was based on the use of different solid electrolyte proton conductor ceramic materials. Table 1 shows a list of the compounds synthetized and its identifying code.

Table 1
Formulations of the different solid electrolyte proton conductor materials.

Formulation	Identifying code
$BaCeO_3$	BaC
$BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$	BaCeZrY
$Sr(Ce_{0.9}–Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$	SCZYb

The BaC perovskite ($BaCeO_3$) was prepared by coprecipitation method. This was achieved by mixing $BaCO_3$ and $Ce(NH_4)_2{\cdot}(NO_3)_6$ (99.8% and 99.5% from Alfa Aesar) together in the appropriate stoichiometric ratios as described in Ref. [15]. Ammonium oxalate (99.5–101.0% Merck) was used as received.

The BaCeZrY perovskite ($BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$) was prepared also by solid-state reaction. This was achieved by mixing $BaCO_3$, CeO_2, Y_2O_3 and ZrO_2 (99.8%, 99.5%, 99.9% and 99.5% Alfa Aesar) together in the appropriate stoichiometric ratios as described in Ref. [16].

The SCZYb perovskite ($Sr(Ce_{0.9}–Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$) was prepared by citrate method. This was achieved by mixing $Sr(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2$ and $Yb(NO_3)_3$ (99.0%, 99.5%, 99+% and 99% from Alfa Aesar) together in the appropriate stoichiometric ratios as described in Ref. [17]. Acid citric (Panreac ACS) was used as received.

After the synthesis, the ceramics were grounded in order to obtain ultra-fine powders. These powders were then pressed as pellet up to about 30 MPa to attain the compact ceramic samples and finally sintered at 1300 °C. The disk shaped electrolytes (about 1.5 mm in thickness and 13 mm in diameter) coated with Pt ink [Alfa Aesar] and adhered with Pt electrodes (0.5 cm^2) were placed in a Al_2O_3 tube to separate the two compartments. Al_2O_3 cement was used to hold the disk. The tightness of this device was checked. Fig. 1 shows a schematic representation of the electrochemical device. The hydrogen partial pressure in the working compartment was controlled by the continuous gas injection of a gas mixture Ar + 10%H_2 ($P_{H2,WE}$ = 0.1 bar, 200 mL/min) or high purity argon (99.999%). A calibration mixture Ar + 1000 ppm/v H_2 was used as a reference gas in compartment I ($P_{H2,RE}$ = 0.0001 bar, 200 ml/min). Both calibration mixtures were supplied by Abello-Linde.

2.2. Experimental set-up

All tests were performed in an autoclave as described in previous work [12,13]. This experimental set-up allowed working with controlled environments. The temperature of system was measured

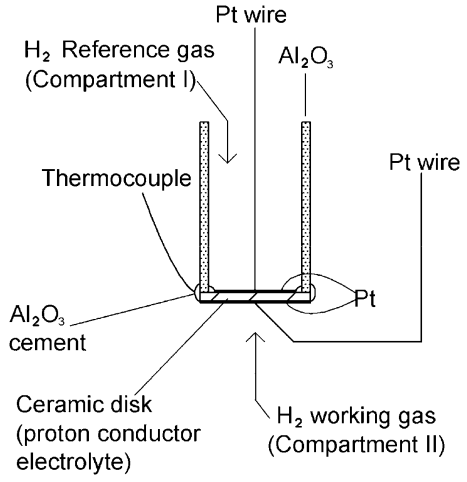

Fig. 1. Schematic representation of the hydrogen sensor.