Solid Electrolyte Based Electrochemical Sensor for Detecting Hydrogen Gas

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Abstract : Gas phase hydrogen sensing of solid electrolyte $CaBr_2$-CaHBr was explored. Investigations proved the possibility of hydrogen sensing from ppm to percentage level. The study revealed wider electrolytic domain boundaries of the solid electrolyte showing hydride ion conduction at 723 K.

Key words: Electrochemical hydrogen meter, Fast reactor, Electrolytic domain boundary, Solid electrolyte.

Introduction

Electrochemical hydrogen meter (ECHM) is used to detect steam leak in the secondary sodium circuit of sodium cooled fast reactors [1]. Steam at high pressure is separated from liquid sodium by 2.4mm thick ferritic steel in the steam generator of fast reactor. Though strict quality control is ensured at the time of designing and manufacturing of the steam generator liquid sodium can come in contact with of steam in case of material failure due to prolonged operation. The sodium water reaction is exothermic and the reaction products are caustic sodium hydroxide and hydrogen. During normal operating condition of the reactor when sodium temperature is above723 K, hydrogen gets dissolved in sodium because of its higher solubility in sodium. Therefore, monitoring hydrogen level in liquid sodium is adequate to detect steam leak at high reactor operating temperature. However, during the start-up of the reactor or in low power operations, the temperature of the sodium is ~523 K. At this temperature the solubility of the hydrogen is low and most of them would escape to the argon cover gas over surge tank containing sodium[2]. Generally, diffusion-based hydrogen meter based on thermal conductivity (TCD)[3] and tin oxide based sensor[4]are used for this purpose in the argon cover gas in the reactors. In this work, as an alternative approach, an electrochemical sensor for gas phase monitoring of hydrogen has been explored.

Principle of ECHM

The electrochemical hydrogen meter (ECHM) is an electrochemical concentration cell working on potentiometric mode. It has a hydride ion conducting solid electrolyte sandwiched between iron membranes. One side of the iron membrane faces the sample electrode while the other end is in contact with the reference electrode. It uses a biphasic mixture of 60 mol% $CaBr_2$-40 mol% CaHBr as the solid electrolyte. The hydride ion conducting solid electrolyte is stable under operating conditions of 673-773K and at pressure of 0.05 – 5Pa[5]. It has high conductivity for hydride ions. An ideal solid electrolyte has high transport number for the conducting ion[6]. The cell is represented as

$$P_{H_2}(\text{In Mixure}) \,\|\, CaBr_2 - CaHBr \,\|\, P_{H_2}(\text{Ca, Mg, } CaH_2) \quad (1)$$

where, P_{H_2}(reference) is the hydrogen partial pressure in the reference electrode, P_{H_2} (sample) is the hydrogen partial pressure in the sample electrode (argon-hydrogen mixture)

when, P_{H_2}(Sample) < P_{H_2}(reference), the electrode reactions can be written as

At the reference electrode:

$$H_2 + 2\bar{e} \longrightarrow 2H^- \quad (2)$$

At the sample electrode:

$$2H^- \longrightarrow H_2^- + 2e \quad (3)$$

Net reaction is

$$H_2(\text{reference}) \longrightarrow H_2(\text{sample}) \qquad (4)$$

The electromotive force (E) that establishes across the electrolyte can be expressed by the following Nernst expression:

$$E = t_{ion} \frac{RT}{2F} \ln \left(\frac{P_{H_2}(\text{reference})}{P_{H_2}(\text{sample})} \right) \qquad (5)$$

where, F is Faraday constant, R is universal gas constant, T is the operating temperation, is the transport number of H^- ion in the solid electrolyte. The details of ECHM are described in Ref.[5].

A mixture of Ca- 37 mol%, Mg 27 mol %, CaH_2- 36 mol % are employed as the reference electrode which fixes the hydrogen pressure under operating conditions of the ECHM. Hydrogen partial pressure can be directly correlated to the concentration of hydrogen in the cover gas.

Experimental details

A schematic diagram of the electrochemical hydrogen sensor is shown in Fig. 1. The sensor consists of an iron thimble of 16 mm outer dia, 0.5 mm wall thickness and 40 mm height for housing the electrolyte and another one of 8 mm OD, 0.5 mm wall thickness and 25 mm height for holding the reference electrode-materials, were machined from a pure soft iron bar. A knife-edged flange of 70 mm diameter was welded at the top end of the electrolyte compartment as shown in Fig. 1. The reference electrode consisting of Ca, Mg and CaH_2 phase mixtures were encapsulated inside iron thimble and sealed by welding. As the electrolyte and reference electrode materials are air/moisture sensitive, assembly of the electrochemical cell was carried out inside an argon atmosphere glove box that is used for handling liquid sodium (oxygen and moisture content < 1ppm).The details of assembly of the sensor are given elsewhere [6].The knife-edged flange at the top of the probe helped to connect the sensor to the experimental vessel.

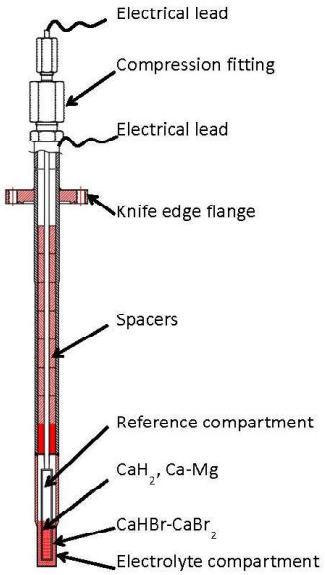


Fig. 1 Schematic diagram of electrochemical hydrogen meter.

Fig.2 depicts a schematic of the experimental set up used for evaluating the response of ECHM for hydrogen in gas phase. ECHM was encased in a steel vessel with a provision of gas inlet and outlet. The meter was fixed to the vessel by a suitable knife edge flange and sealed using a copper gasket. Cooling fans were provided on all sides of the flange portion to prevent overheating of the copper gasket region. Gases from the cylinders were passed through suitable mass flow controllers (MFC)(M/s Alicat Scientific, USA). Range of MFC for both the gases is 0 to 100 ml/min. Percentage levels of hydrogen concentrations were obtained by mixing UHP hydrogen and UHP argon gases. Ppm levels of hydrogen concentrations were obtained by mixing UHP argon gas and pre-mixed calibration gas containing 220 vppm of hydrogen in argon.

The mass flow controllers had digital display and enabled to control the flow from 2.5to 100 ml/min. The gases from MFC then enter a mixing chamber before entering the vessel containing the ECHM. The inlet pipe carrying the gas extended to the bottom of the vessel to ensure thorough mixing of the gases and to ensure that the gases stay near the ECHM sensor portion viz. the thimble portion sufficiently long time for the sensor to sense the gas. Suitable valves

V1 to V6 were provided at suitable locations to control the flow of the gases passed. UHP argon gas, UHP hydrogen gas as well as calibration gas mixtures of hydrogen and argon were used to prepare various concentrations of hydrogen in argon with wide concentration ranges from ppm to percentage levels.

An overall flow of 100 ml/min was maintained throughout the experiment. Prior to the experiment, all the connections were leak tested with soap solution. All the lines were connected after flushing with the desired gas mixtures for sufficient time before their measurements were made. The vessel containing the ECHM was installed in a furnace where it has constant temperature zone at the thimble portion of the meter. The temperature of the ECHM-thimble section was maintained within ± 1K of the set point. Type-K thermocouples were used for both the temperature measurement and controlling the furnace temperature. The output of the ECHM was measured by using a high impedance electrometer (M/s Keithley, USA, model no. 6514). All the data were logged and acquired by a data-logger (M/s Agilent, USA, 34972A, LX1 data acquisition/switch unit). The meter EMF output was recorded for various concentrations of hydrogen gas after allowing sufficient time for equilibration and stable output.

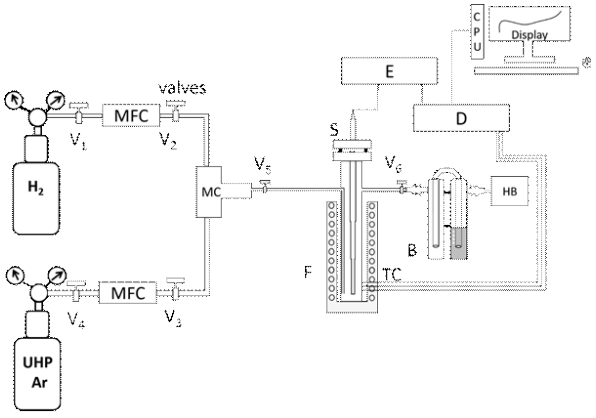


Fig. 2 Schematic of the experimental set up (B: Gas Bubbler, D: Data Acquisition Unit, E: Electrometer, F: Furnace, HB: Hydrogen Burner, MC: Mixing Chamber, MFC: Mass flow controller, S: Sensor, TC: K type Thermocouples, V1 to V6: Valves)

Results and Discussion

The representative response of ECHM for hydrogen concentration variations from percentage levels down to ppm levels at 723K is shown in Fig.3. The standard deviation in the measured emf is ± 0.2 mV. Fig. 3(a) shows the response for change in hydrogen concentration from 20% to 10%. The sensor attains equilibrium in short interval of time ~ 20 seconds.Fig.3 (b) shows typical response of the sensor for hydrogen concentrations 3.2% down to 0.4%.Fig. 3(c) shows the response for change in hydrogen concentrations from 132 ppm to 176ppm. For lower concentrations, the sensor takes relatively more time (~ 40 seconds) to attain equilibrium, which could be due to longer duration for mixing of H_2 in Ar in the entire volume of the vessel. The intent of the present investigations is to evaluate the feasibility of the in-sodium hydrogen sensor towards sensing of hydrogen in gas phase. As the chamber volume is more, homogeneous mixing of gaseous species involves some time, leading to increased response time. Modified design of the chamber would be undertaken and elaborate experiments would be performed to minimize the response time of the sensor in the near future.

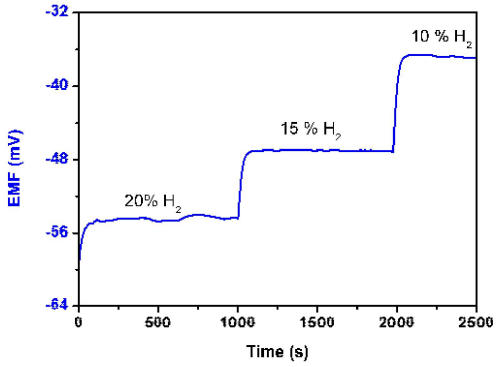


Fig. 3 (a) Typical response of ECHM for hydrogen concentrations – 10,15 and 20% at 723 K

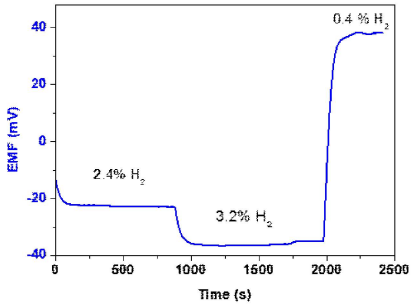


Fig.3(b)Typical response of ECHM for hydrogen concentrations – 0.4, 2.4 and 3.2 % at 723K

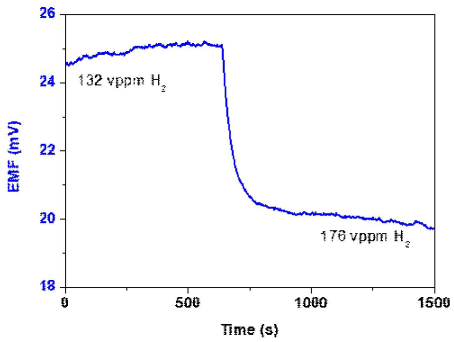


Fig. 3 (c) Typical response of ECHM for hydrogen at 132 and 172 vppm (sensor temperature: 723 K)

Fig. 4 shows the calibration plot of ECHM for hydrogen concentration from ppm to percentage levels. The linear behaviour of measured cell emf over a wide concentration or partial pressure range of hydrogen indicates that the transport number of hydride ion conduction in the electrolyte remains constant. This reflects that the electrolytic domain boundaries of $CaHBr\text{-}CaBr_2$ electrolyte are wider at 723K. In other words, the ionic conduction dominates over a wide concentration / partial pressure range of hydrogen at 723 K falling between the upper and lower electrolytic boundaries of the solid electrolyte. The linear change of emf for logarithmic variation of hydrogen concentration reveals grossly ionic transport of hydride ion through the electrolyte. However, electronic contribution in the electrolyte is required to be elucidated. The current studies revealed the usefulness of ECHM for sensing hydrogen gas from ppm to percentage levels in a dynamic stream.

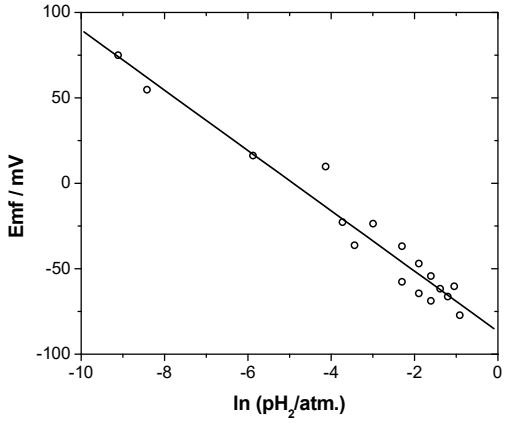


Fig. 4 Calibration plot of ECHM for hydrogen gas concentration variation from ppm to percentage level

Conclusion

Hydrogen in gas phase was measured successfully for the first time using $CaHBr\text{-}CaBr_2$ solid electrolyte based ECHM. The EMF response of the sensor was found to be varying linearly with logarithm of hydrogen concentration. The ECHM sensor could detect from ppm to percentage level of hydrogen in argon hydrogen mixture.

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