Electrochemical studies on hydride ion conducting $caBr_2$-caHBr electrolyte

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Abstract: The solid electrolyte with composition 60 mol% $CaBr_2$-40 mol% CaHBr is used in the electrochemical hydrogen meter which is used to detect the steam leaks in liquid sodium circuits of the fast breeder reactors. AC conductivity and DC polarization experiments were carried out on the solid electrolyte by designing a special cell having cylindrical geometry. The transport number of the hydride ion in this electrolyte was found to be 0.91 at 723 K and 0.88 at 743 K. The activation energy of the ionic conduction is found to be 85 $kJ.mol^{-1}$.

Keywords: Fast breeder reactor, Steam leak, Electrochemical hydrogen meter, electrolyte, hydride ion, transport number, activation energy.

Introduction

Liquid sodium is the coolant of choice in fast breeder reactors to transfer heat from the reactor core due to its favorable physical, chemical, and nuclear properties [1]. The heat energy generated from the nuclear core is transferred to form steam in the steam generator module. In this module liquid sodium and steam are separated by ferritic steel pipes of 2 to 3 mm wall thickness. It is essential to detect any event of leak of high-pressure steam (~150 bar) into the sodium coolant circuit (~3 bar) at the steam generator using reliable sensors to initiate remedial action. As hydrogen is one of the products of steam-sodium reaction and is soluble in sodium, monitoring hydrogen impurity in sodium at ppb levels provides a means of detecting any steam leak at its very inception [2]. Conventional diffusion-based hydrogen meter (CDHM) and electrochemical hydrogen meters (ECHM) are used for monitoring hydrogen concentrations at ppb levels in liquid sodium and to detect any steam leak in the coolant circuits of the fast reactors [3].The CDHM works in dynamic mode, whereas ECHM works in equilibrium mode.

In the CDHM, a 0.25 mm thin-walled nickel membrane separates flowing sodium and the high vacuum side. Under the application of high vacuum in dynamic condition, hydrogen diffuses through the nickel membrane from liquid sodium at high temperature and gets ionized under high voltage applied. The sputter ion pump (SIP) measures the ionic current, and the same is calibrated for hydrogen concentration in sodium [4]. In tandem with the SIP, a quadrupole mass spectrometer is also used to detect the hydrogen concentration. CDHM has complex instrumentation and requires maintenance of high vacuum system.

In the case of ECHM, it is a simple, compact sensor and free of intricate instrumentation. ECHM is an electrochemical concentration cell and can be used to measure the hydrogen partial pressures. The electrochemical cell is represented as,

P^{H}_{2} (sample) || solid electrolyte || P^{H}_{2}(reference)

The electromotive force (E) that develops across the electrolyte is given by the Nernst relation:

$$E = \frac{RT}{2F} \ln \frac{p_{H_2}(\text{ref})}{p_{H_2}(\text{in sodium})} \quad (1)$$

where the reference hydrogen partial pressure, pH_2(ref) is known and fixed by the reference, pH_2(sample) is the hydrogen partial pressure in

sodium, R is the universal gas constant, F is the Faraday constant, and T is the temperature (in Kelvin) of sodium at the sensing position. Basically, dissolved hydrogen concentration is determined from the measurement of the equilibrium hydrogen partial pressure with sodium. Hydrogen partial pressure (pH_2) is related to hydrogen concentration in sodium (C_H) by Sieverts' law [5].

$$\sqrt{[pH_2]} = \frac{[H]_{ppm}}{K_s} \quad (2)$$

Where K_s is the Sieverts' constant, which is found to be almost independent of temperature for this system [6].

Alkali and alkaline earth metal halides and hydrides are the solid electrolytes considered for hydride ion conduction. A solid electrolyte, $CaCl_2$ mixed with CaH_2, which is thermodynamically stable under the operating conditions, was used for this purpose by Smith and in the authors' laboratory [3, 4]. The $CaCl_2$–CaH_2 pseudo-binary system is characterised by a compound, CaHCl, which is a hydride ion conducting phase in the biphasic electrolyte. However, the ionic conductivity of this biphasic solid electrolyte is low (1.0×10^6 S.cm^{-1} at 723 K) and the ionic transport number is only 0.93 [5]. The presence of electronic conduction was due to extrinsic defects in the electrolyte and this led to internal shorting of the cell and polarisation of the electrodes, as reported by these authors. In pursuit of a better electrolyte which has higher hydride ion conductivity than the $CaCl_2$–CaH_2 system that satisfies the other requirements mentioned earlier, a ternary-salt mixture of LiCl, $CaCl_2$ and CaHCl was identified and employed [9]. Later, a biphasic mixture $CaBr_2$-CaHBr as the electrolyte was chosen based on investigations of several alkali and alkaline earth metal halide and hydride systems [10].

Development of ECHM involves identification of suitable (i) hydride ion conducting solid electrolyte, (ii) reference electrode, (iii) addressing of compatibility issues, (iv) design of electrochemical cell and (v) optimisation of various parameters for long-term operation, etc. The efforts on the development and testing of ECHM in the authors' laboratory is summarised in Ref [10] and reflected in the later publications [11, 12, 13].

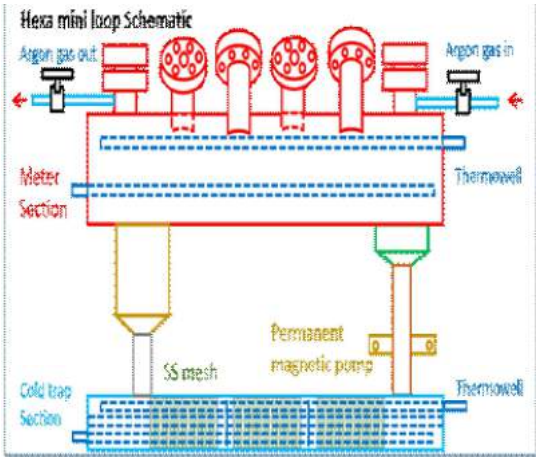
A mixture of 60 mol% $CaBr_2$-40 mol% CaHBr as the solid electrolyte along with a mixture of Ca+Mg+CaH_2 as reference electrode are found to be suitable for the ECHM based on phase diagram investigations [10]. The transport number and activation energy of the hydride ion conduction are important parameters to determine the performance of the sensor. No measurements were carried out so far on these fundamental properties. In this work, impedance spectroscopic measurements were made to determine the total conductivity and a DC polarisation method (Hebb-Wagner blocking electrode method) was used to determine the partial electronic conductivity of the electrolyte as a function of temperature and hydrogen concentration [14, 15]. From the measured electrical conductivity data, the transport number and the activation energy were determined and reported. In order to simulate the conditions in the fast reactor, a bench top sodium loop with dynamic sodium flow was employed for the experiments in the present study.

Experimental

Sodium loop facility

A schematic diagram of mini benchtop sodium loop made of SS 316 L with a sodium inventory of about 10 kg is shown in Fig.1 (a). The sodium loop has two sections namely the meter section and cold trap (CT) section. The meter section compartment has provisions for housing six numbers of ECHMs (Hexamini Sodium Loop). The meter section and cold trap are interconnected using SS pipes at both ends to enable circulation of liquid sodium between them using an electromagnetic pump. The meter section vessel has a dimension of ~400 mm length and ~300 mm inner diameter while the CT vessel has a dimension of ~400 mm length and ~100 mm inner diameter. SS mesh packed inside the CT compartment provides enough surface area for the precipitation of impurities. The loop is filled with liquid sodium up to a height of ~260 mm from the bottom of the meter section vessel and the remaining ~40 mm height from the top of the liquid sodium level is filled with argon cover gas. A photograph of the hexamini sodium loop is shown in Fig.1(b).

The meter section is maintained at 723K and the cold trap section is maintained at 393K using separate temperature controllers and the temperatures were maintained within ±1K. Thermocouples (K-type) were tag welded at different positions in order to measure the temperatures at different places. In order to measure the radial distribution of the temperature in sodium, thermowells were provided at both sections. Continuous temperature scanning of the loop ensures the uninterrupted flow of liquid sodium.



(a)



(b)

Fig. 1 (a) Schematic and (b) photograph of Hexamini sodium loop

Calculated amount of sodium hydroxide was deliberately added into the liquid sodium at the cold trap section of the loop which is a constant source for providing precise concentration of hydrogen and oxygen in liquid sodium. Sodium hydroxide reacts with sodium to form sodium oxide and sodium hydride, which gets deposited over the mesh regions of the cold trap section. The dissolution of the sodium hydride in liquid sodium is a function of temperature. By changing the temperature of the cold trap, the concentration of hydrogen in liquid sodium can be varied and it is governed by solubility data reported by Whittingham [5].

$$\mathrm{Log}[H]_{ppm} = 6.467 - \frac{3203}{T(K)} \qquad (3)$$

All the experiments were performed at the cold trap temperature of 413 K, which accounts for the partial pressure of hydrogen at 6×10^{-7} bar.

Description of the electrochemical cell

The electrolyte materials calcium bromide and CaHBr are highly air and moisture sensitive in nature. The preparation of the solid electrolyte was made by in-situ hydrogenation of the mixture of $CaBr_2$ and calcium metal [10]. The cell was assembled inside an argon atmosphere glove box that is used for handling liquid sodium (oxygen and moisture content < 1 ppm). The schematic of the assembly of the electrochemical cell is shown in Fig. 2. An iron thimble as shown in the figure was fabricated. After decarburization and hydrogen firing of the thimble, it was welded to stainless steel pipe of 20 mm diameter which is attached to a knife edged flange. The reference blocking electrode was made using a decarburized iron rod of 3 mm diameter with and approximate length of 50 mm, tig welded to a SS rod of 3 mm diameter and the straightness was achieved by rolling. Calcium bromide and CaHBr were taken in appropriate amounts inside the cell and the blocking electrode of 3 mm diameter was assembled gastight with the cell using a fitting. The assembly was heated in a furnace for about five days at 1123 K. The cell was cooled to room temperature at a very slow cooling rate of approximately 0.2 K/min. The slow cooling rate was maintained in order to obtain pore free casting of the electrolyte. After the final assembly, the concentricity of the electrodes was examined by radiography. After finalizing the geometry of electrochemical cell arrangement, the cell was installed inside the hexamini sodium loop.

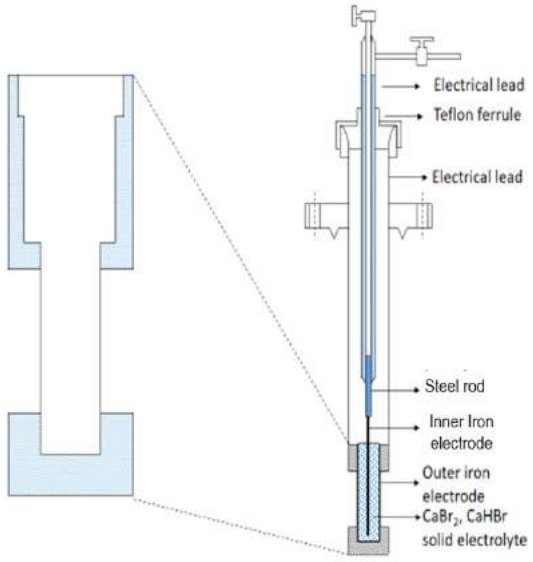


Fig. 2: Schematic of the cell assembly. The thin-walled iron thimble is also shown separately.

Experiments were carried out to measure the transport number and the activation energy of the hydride ion conduction of $CaBr_2$- CaHBr solid electrolyte from 723 K to 743 K and at a hydrogen partial pressure of ~6×10^{-7} bar.

Results and discussion

AC conductivity measurements

AC conductivity measurements are used to derive the total conductivity of the solid electrolyte by measuring the total impedance of the system. The total conductivity is combination of ionic and electronic conductivity represented as equation (4).

$$\sigma_{total} = \sigma_{ion} + \sigma_{electronic} \quad (4)$$

For the cylindrical geometry, the total conductivity is given by the equation (5)

$$\sigma_{total} = \frac{1}{2\,\pi\Omega h}[\ln(b) - \ln(a)] \quad (5)$$

A schematic diagram of the cell depicting cylindrical geometry is shown in Fig. 3. The equation (5) is derived by considering the electrolyte as a dielectric and the system to be behaving as a cylindrical capacitor and considering the Gaussian surface to be a cylinder [1]. Here a and b are the radii of the inner and outer electrodes, respectively. The inner one being the blocking electrode and the outer electrode being the thin-walled iron thimble. Ω is the resistance obtained for the electrolyte at a given temperature, h is the effective height of the electrolyte under study.

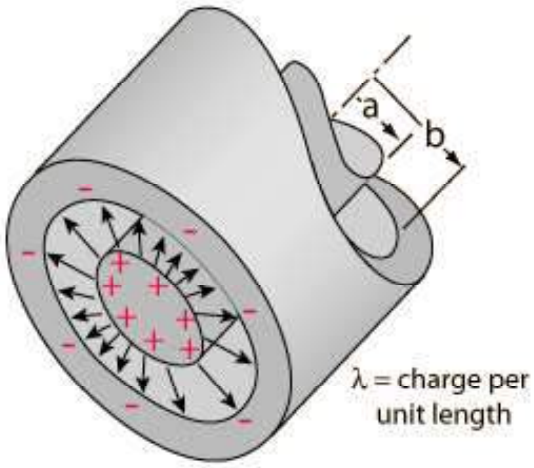


Fig. 3: Schematic depicting the cross section of the cylindrical geometrical assembly of the cell.

All the conductivity measurements were performed using Autolab –Electrochemical Work Station modular Potentiostat / Galvanostat.

A typical impedance plot obtained is shown below in Fig.4. The equivalent circuit for a simple solid electrolyte without grain boundary resistance with blocking electrodes is shown in Fig.5 [2]. The capacitance and resistance due to grains are represented as C_b and R_b, respectively and the electrode-electrolyte double layer capacitance is represented as C. From the Nyquist plot, the obtained bulk impedance of the electrolyte was calculated and the corresponding total conductivity was derived using equation (4). The measured total conductivity values at various temperatures are given in Table 1. It can be seen from the table that the measured total conductivity increases with temperature.

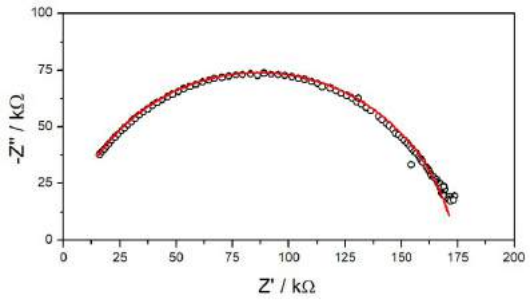


Fig. 4: Representative impedance plot of the electrolyte at 723K.

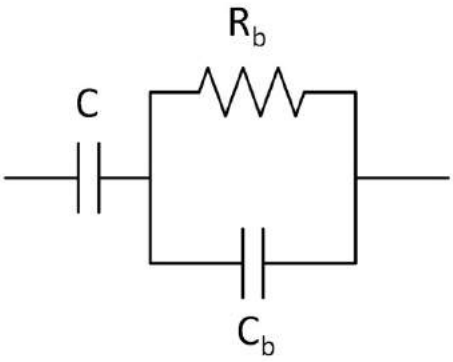


Fig.5: Modelled equivalent circuit for the cell, C_b, R_b: capacitance and resistance due to grains and C: electrode-electrolyte double layer capacitance.

Table 1: Total conductivity of the electrolyte at selected temperatures

S. No.	Cell Temperature (K)	σ (Total) × 10^{-8} (Scm^{-1})
1	673	2.79
2	723	7.79
3	733	9.13
4	743	11.6

DC polarization measurements

A small dc voltage was applied and the resultant current was recorded. The measured current decreases exponentially with time. At the steady state, only residual electronic current was present. The total steady state current I 0is given by,

$$I = I_{Ø}\,(\text{hole}) + I_{\Theta}\,(\text{electron}) \qquad (6)$$

The total electronic conductivity is the combination of the hole and electronic conductivity which is represented by the equations (7) to (9).

$$ó_{\text{electronic}} = \sigma_{Ø} + \sigma_{\Theta} \qquad (7)$$

$$I_{\Theta} = \sigma_{\Theta}\frac{RTA}{LF}\left[1 - e^{-\frac{EF}{RT}}\right] \qquad (8)$$

$$I_{\phi} = \sigma_{\Phi}\frac{RTA}{LF}\left[e^{-\frac{EF}{RT}} - 1\right] \qquad (9)$$

Here E is the applied voltage, F is the Faraday constant, R is the gas constant, and L/A is the cell constant. For the cylindrical geometry the factor $\frac{A}{L}$ shall be replaced by $\frac{1}{2\,\pi h}[\ln(r_2) - \ln(r_1)]$, as $I_{\infty} = I_{Ø} + I_{\Theta}$. The plot of $\frac{I_{\infty}}{1-e^{-\frac{EF}{RT}}}$ which is called the residual current factor Vs $e^{\frac{EF}{RT}}$ which is called the applied potential factor gives a $slope = \frac{RTA}{LF}.\sigma_{Ø}$ gives a measure of the hole conductivity and the $Intercept = \frac{RTA}{LF}.\sigma_{\Theta}$ gives a measure of the electronic conductivity. The plot of Vs at the cell temperature of 743 K with the partial pressure of hydrogen 6.27 x 10^{-7} bar is shown in Fig 6.

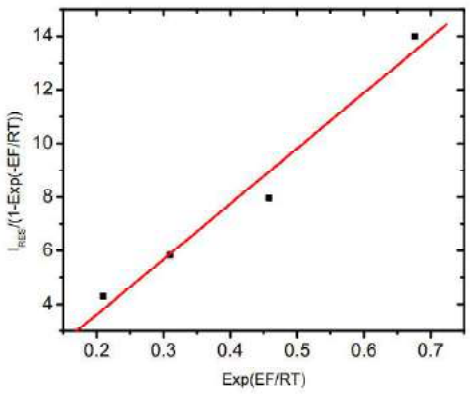


Fig 6: Plot of residual current factor vs applied potential factor to obtain electronic and hole conductivity.

Transport number and activation energy

Based on the conductivity measurements of AC and DC methods, the ionic conductivity was determined by subtracting the electronic conductivity from the total conductivity data. The study revealed that the t_{ion} calculated from these measurements was found to be 0.91 at 723 K and 0.88 at 743 K. It is to be pointed out that the electronic conductivity of the electrolyte is due to both intrinsic defects and extrinsic impurities. As the electrolyte casting is carried out in the compatible iron thimble at high temperatures, introduction of iron impurity is highly probable. The transport number owing to electronic contribution t_e, which arises due to both extrinsic and intrinsic defects, increases with temperature. As a result, the ionic transport number decreases with temperature. Based on the derived data on ionic conductivity as a function of temperature, a plot of $ln\ \sigma_{ion}\ vs\ \frac{1}{T}$ was made (Fig.7). The activation energy for the hydride ion conduction is determined to be 85.0 kJ.mol^{-1}.The obtained value is comparable to that of the activation energy of 96.5 kJ.mol^{-1} reported for $CaCl_2$-CaHCl based solid electrolyte [9].

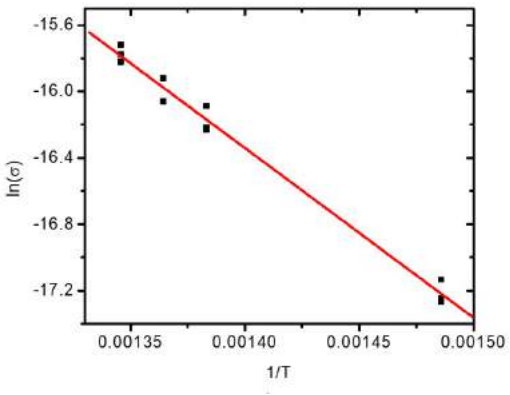


Fig. 7: Plot of ln(σ_{ion}) vs 1/T to obtain the activation energy for the ionic conduction.

Conclusion

The ionic and electronic conductivity of the electrolyte were measured by using AC conductivity and DC polarization blocking electrode techniques. t_{H^-} is calculated from these measurements and found to be 0.91 at 723K and 0.88 at 743K. The temperature (723 K) that showed higher ionic transport number was chosen for the sensor application. The activation energy of the ionic conduction is found to be 85 kJ.mol^{-1}.

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