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Investigations on the phase equilibria of some hydride ion conducting electrolyte systems and their application for hydrogen monitoring in sodium coolant

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Abstract

Electrochemical meters for measuring hydrogen levels in liquid sodium need thermodynamically stable hydride ion conducting electrolytes. In order to identify electrolytes that have high hydride ion conductivity, phase diagram of systems consisting of low melting compounds such as $CaCl_2$–LiCl, $SrBr_2$–LiBr, $SrBr_2$–SrHBr and $CaBr_2$–CaHBr were investigated by differential scanning calorimetry and their phase diagrams established. Using these information and supplementary information on effects of addition of alkaline earth hydride to these systems, potential electrolytes were tested for their use in electrochemical meters. Meters were constructed using electrolytes with (i) 22mol%$SrCl_2$–12.2mol%$CaCl_2$–54.5mol%LiCl–11.3mol%CaHCl, (ii) 70mol%LiCl–16mol%CaHCl–14mol%$CaCl_2$ and (iii) 40mol%-CaHBr–60mol%$CaBr_2$ compositions. Output of meters that had Li ions in liquid phase electrolyte showed non-linearity at low hydrogen levels. Output of meters using $CaBr_2$–40mol%CaHBr solid showed linearity in the concentration range of 50–250 ppb in sodium.

1. Introduction

Liquid sodium coolant is used to transfer the heat produced in a fast reactor core into a steam generator. Any leakage of steam into sodium at the steam generator, even at micro levels, would result in sodium–water reaction with consequent undesirable effects. It is essential to detect this steam leak at its inception itself and initiate remedial steps [1]. The occurrence of steam leaks can be detected by continuous monitoring of hydrogen levels in sodium coolant since sodium–water reaction releases hydrogen [2]. This involves measurement of the hydrogen partial pressure in equilibrium with the dissolved hydrogen in sodium. Hydrogen partial pressure (p_{H_2}) is correlated to hydrogen concentration in sodium (C_H) by Sievert's law [3]:

$$(p_{H_2})^{1/2} = C_H/k, \tag{1}$$

where k is the Sievert's constant for this system, which is found to be almost temperature independent [3,4]. The method that is widely used for monitoring hydrogen in sodium involves measurement of hydrogen flux diffusing through a metallic membrane exposed to hot sodium on

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one side and with vacuum maintained on the other side [5]. Using an electrochemical meter that works on principles of concentration cell is an alternate method to measure the hydrogen pressures. The electrochemical cell can be represented as

$$p_{H_2}(\text{sample})\|\text{electrolyte}\|p_{H_2}(\text{reference}).$$

The electrolyte used in such meters must have good ionic conductivity for hydrogen (proton or hydride ions) and thermodynamic stability under the operating conditions. The design of Indian fast reactors such as Fast Breeder Test Reactor and Prototype Fast Breeder Reactor requires hydrogen meters that can operate at 450 °C and at hydrogen pressures as low as 0.03 Pa in sodium circuits. Proton conducting electrolytes require humid conditions for their conductivity and hence cannot be used in liquid sodium [6,7]. A solid electrolyte, $CaCl_2$ mixed with CaHCl was used for this purpose [8,9]. The $CaCl_2$–CaH_2 pseudo-binary system is characterised by a compound CaHCl which is the hydride ion conducting phase in the biphasic electrolyte. However, the electrolyte possessed an ionic conductivity of $\sim 1 \times 10^{-6}$ S cm^{-1} only and showed appreciable electronic conductivity ($t_{\text{ion}} = \sim 0.93$) at 450 °C and at low hydrogen pressures (in the range of 0.05 Pa–5 Pa) [10]. Hence, investigation on systems that can provide electrolytes in molten or solid state with high hydride ion conductivity and thermodynamic stability at the operating conditions was made. Electrolyte systems that possess eutectic temperatures close to but above the meter operating temperature could be expected to show high ionic conductivity in the solid state as the crystal structure becomes less rigid near eutectic temperatures. Considering the melting points of pure salts and the stability of hydrides, mixtures of alkaline earth and alkali halides containing CaH_2 or SrH_2 were explored. For this purpose, binary systems of chlorides and bromides such as $CaCl_2$–LiCl, $SrBr_2$–LiBr, $SrBr_2$–SrH_2 and $CaBr_2$–CaH_2 were investigated by Differential Scanning Calorimetry. Iodide salts were not considered because of their easy oxidation even during their dehydration and purification processes. In this paper, results of these studies and testing of hydrogen meters that were constructed by using different electrolytes are discussed.

2. Experimental

2.1. Chemicals

Chlorides of lithium (AR Grade, M/s Alfa Products) and calcium (99.9% pure, M/s Alfa Products) were purified by heating them up to their melting points under dry HCl–argon gas mixture and followed by cooling [11]. Bromides of lithium (99.9% pure, M/s Aldrich) and strontium (99.9% pure, M/s Riedel) were purified in the same way under dry HBr–argon gas mixture [12]. $CaBr_2$ was prepared by reacting $CaCO_3$ (M/s Sigma–Aldrich, 99.95% pure) with HBr and drying the products at 150 °C. The dried $CaBr_2$ salt was also further purified under Ar–HBr gas stream. The purified salts were stored and handled in an argon atmosphere glove box used for liquid sodium work [13]. CaH_2 and SrH_2 were prepared by reacting known amounts of pure calcium metal (99.5% pure, M/s Alfa products) and strontium metal (98% pure, M/s Johnson & Matthey) at 550 °C with hydrogen that diffused through an iron membrane.

2.2. DSC experiments

Calculated amounts of purified halides were mixed and intimately ground to prepare samples of various compositions for DSC experiments in the inert atmosphere glove box. The details of the compositions prepared for studying LiCl–$CaCl_2$ and LiBr–$SrBr_2$ systems are reported elsewhere [11,12]. Similarly, the compositions studied in $CaBr_2$–CaH_2 and $SrBr_2$–SrH_2 systems are given elsewhere [14,15]. Approximately 30 mg of these samples were taken in one end closed, 2.5 mm dia and ∼15 mm long thin-walled iron capsules (∼700 mg) and the ends of the capsules were hermetically sealed by pulsed-arc welding inside an argon atmosphere glove box. The capsules were brought out of the glove box and heated at 800 °C and cooled under argon −1% hydrogen-mixture prior to DSC runs. This was carried out to ensure complete equilibration of the sample components and also to check leak-tightness of the welded iron capsules. DSC (model 111, M/s SETARAM, France) experiments were carried out with samples of different compositions. An empty iron capsule was used as reference and a heating rate of 2 K/min was employed in all of the experiments. Argon–1% hydrogen flowing at a rate of 1 l/h was used as gas ambient. Temperature calibration of the DSC was done by fixed melting point method by using In, Sn, Zn and Al standards. The uncertainty in the temperature measurement was ±0.5 °C.

2.3. Construction and testing of the meter

A schematic diagram of the electrochemical hydrogen meter constructed and tested in this work is shown in Fig. 1. The meter consists of an iron thimble of 16.5 mm outer dia, 0.5 mm wall thickness and 35 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. They were machined from stocks of high purity soft iron bars. These pieces were then welded to stainless steel pipes

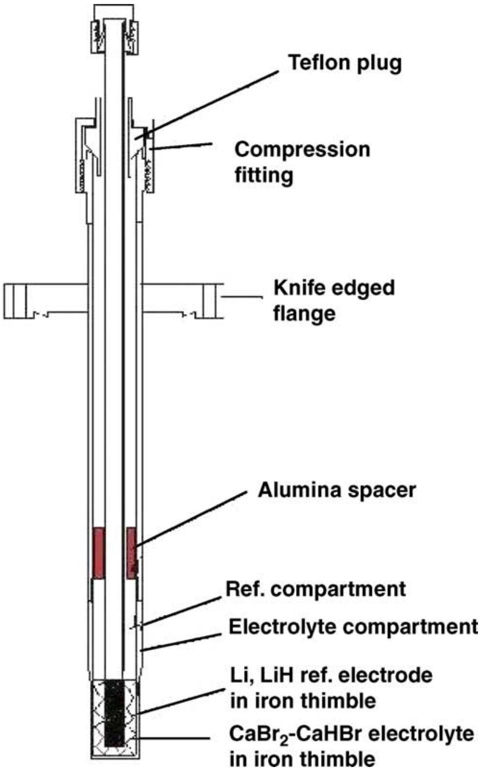

Fig. 1. Schematic diagram of electrochemical hydrogen meter.

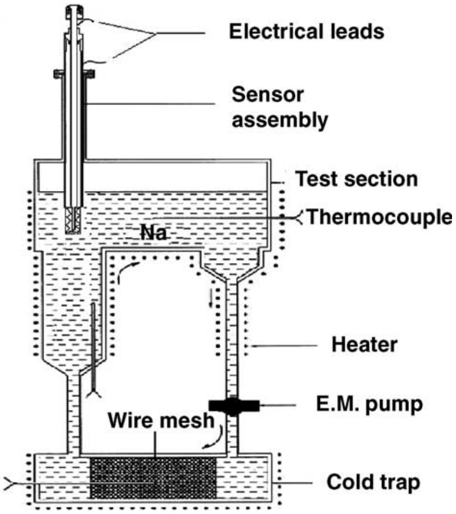

Fig. 2. Schematic diagram of mini sodium loop.

with a knife-edged flange of 70 mm diameter and a swagelok-type compression fitting as shown in figure. Li–LiH mixture was loaded in the reference electrode compartment and used as reference electrode. Meters were assembled with (i) 22mol%$SrCl_2$–12.2mol%$CaCl_2$–54.5mol%LiCl–11.3mol%CaHCl, (ii) 70mol%LiCl–16mol%CaHCl–14mol%$CaCl_2$ and (iii) $CaBr_2$–20mol% CaH_2 electrolytes. For constructing these meters, an appropriate mixture of halide salts of alkali and alkaline earth metals were taken inside the iron thimble of the electrolyte compartment along with required amount of calcium metal shots. Reference electrode was kept secured in position by the compression fitting at the top of electrolyte compartment. The calcium in the electrolyte compartment was then hydrided at 550 °C for several days to form CaH_2. In case of electrolytes with no liquid phase, CaHCl (or CaHBr) phase is formed in situ by reaction between $CaCl_2$ (or $CaBr_2$) and CaH_2. The reference compartment was later inserted into molten electrolyte and the entire assembly was cooled slowly to room temperature. A mini sodium loop, the schematic of which is shown in Fig. 2, was used to maintain different hydrogen concentrations in sodium during the calibration of the meters. Sodium circulating in the loop by means of an electromagnetic pump experiences the lowest temperature in cold trap. The hydrogen concentration in sodium (C_H), is dictated by the cold trap temperature and can be calculated using the solubility data reported in literature [16]:

$$\log(C_H/\mathrm{ppm}) = 4.825 - 2398/(T/\mathrm{K}). \tag{2}$$

3. Results and discussion

Phase diagrams of LiBr–$SrBr_2$ and $CaCl_2$–LiCl systems established from DSC experiments are shown in Figs. 3 and 4, respectively [12,11]. LiBr–$SrBr_2$ system has a compound $LiSr_2Br_5$ which exhibits a eutectic reaction with LiBr at 434 °C and has a eutectic composition of 35mol%$SrBr_2$–65mol%LiBr. $CaCl_2$–LiCl also has a compound, $LiCaCl_3$ that is stable above 439 °C. The

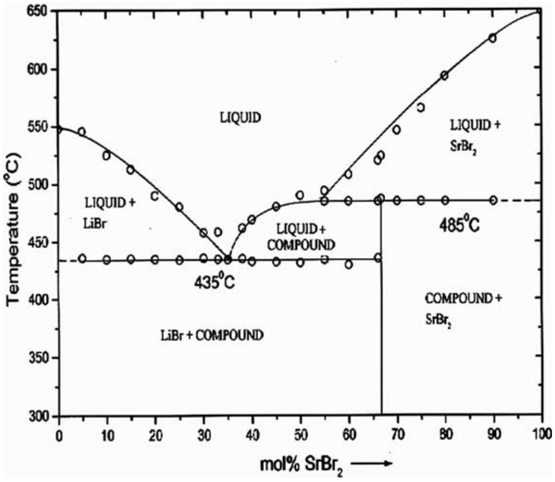

Fig. 3. Phase diagram of LiBr–$SrBr_2$.

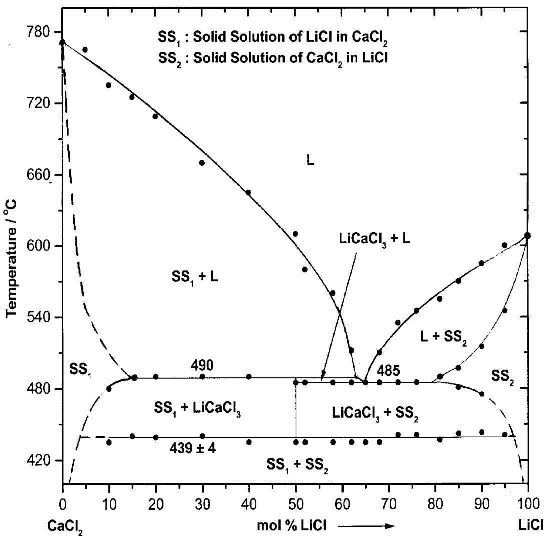

Fig. 4. Phase diagram of $CaCl_2$–LiCl.

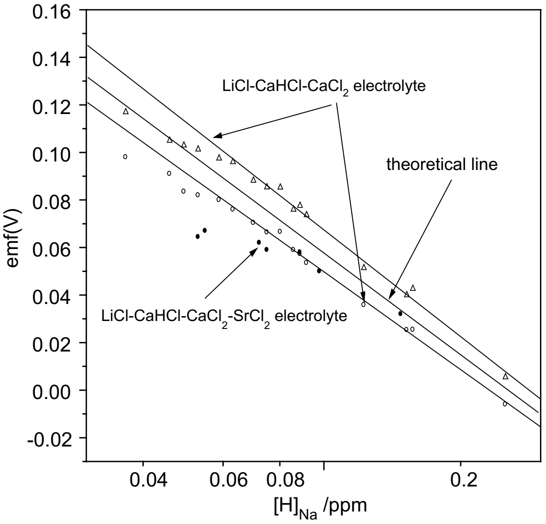

Fig. 5. Electrochemical hydrogen meter output with various electrolytes.

system shows a eutectic reaction between this compound and LiCl rich phase at 485 °C and has a eutectic composition of 35mol%$CaCl_2$–65mol%LiCl. Based on thermochemical calculations, Chartrand and Pelton [17] reported the phase diagram of LiCl–$CaCl_2$–$SrCl_2$ system. They had reported the ternary eutectic temperature and eutectic composition as ~450 °C and ≈20 mol% $SrCl_2$: 24.5 mol% $CaCl_2$ and 55.5 mol% LiCl, respectively. The electrolyte with a composition of 22mol%$SrCl_2$–12.2mol%$CaCl_2$–54.5mol%LiCl–11.3 mol%CaHCl would have a major liquid phase at the operating temperature of 450 °C. Typical output of one such meter for different hydrogen concentrations is shown in Fig. 5. Using relations (1) and (2) and the data given in Ref. [18], an expression of the form, $E = A + B \log C_H$ can be obtained and theoretically expected emf values (E) as a function of C_H can be calculated. Fig. 5 shows that the meter response is lower than the theoretical values below 135 ppb of hydrogen in sodium. This linear relation between E and $\log[H]_{Na}$ is valid when the electrolyte is thermodynamically stable at hydrogen pressures established at the two electrodes of the cell. The molten salt electrolyte of the sensor consists of Li^+, Sr^{2+} and Ca^{2+} cations, and H^- and Cl^- anions. During the operation of the sensor in the sodium loop, if the hydrogen pressure in liquid sodium is below that of Li/LiH system, hydrogen will be evolved from the melt releasing metallic lithium. This process could occur when dissolved hydrogen concentration in sodium are low (for example, at a dissolved hydrogen concentration of 135 ppb, equilibrium hydrogen pressure in sodium would be ~0.29 Pa compared to ~1 Pa of Li/LiH, [18]). Lithium metal would dissolve in the molten salt and introduce electronic conduction in the electrolyte. Due to this electronic conduction, emf generated would be less than theoretically expected values. This observation indicates that use of lithium salts in molten electrolyte systems would be undesirable. Electrolyte systems based on SrH_2–$SrBr_2$–LiBr also would not be useful since LiBr–$SrBr_2$ has an eutectic temperature of 434 °C and the ternary system would also be based on a molten electrolyte at the operating temperature of the meter. DSC results of 70mol%LiCl–16mol%CaHCl–14mol%-$CaCl_2$ showed that upon addition of CaH_2 to the binary $CaCl_2$–LiCl system, the eutectic temperature is brought down to ~452 °C and this electrolyte showed conductivity that is four orders higher than that of the binary electrolyte, namely $CaCl_2$–20mol%CaHCl [19]. Electrochemical meters showed satisfactory performance down to ca. 60 ppb of hydrogen in sodium [19]. But at still lower hydrogen concentrations, output of these meters deviated from linearity as shown in Fig. 5. It could not be ascertained whether this is due to any unidentified impurity present in the electrolyte at ppm levels or due to instability of H^- ions caused by the possible appearance of pockets of molten phase regions within the electrolyte at the meter operating temperature (since the eutectic temperature for this system was ~452 °C only).

Partial phase diagrams of CaH_2–$CaBr_2$ and SrH_2–$SrBr_2$ systems constructed from the results of DSC experiments are shown in Figs. 6 and 7. Phase diagram of $CaBr_2$–CaH_2 system shows the existence of solid solutions between $CaBr_2$ and CaH_2 up to 30 mol% CaH_2 at ~575 °C and a eutectic reaction between $CaBr_2$ rich phase and CaHBr at ~580 °C. The eutectic has a composition of ~65mol%$CaBr_2$–35mol%CaH_2. $SrBr_2$–SrH_2 system shows a eutectic reaction between $SrBr_2$ and a

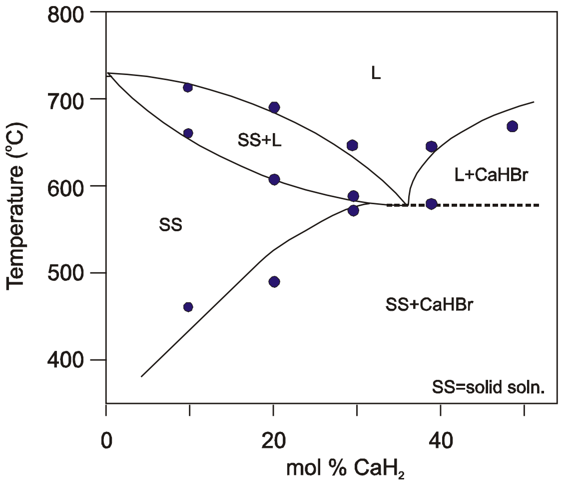

Fig. 6. Partial phase diagram of $CaBr_2$–CaH_2 system.

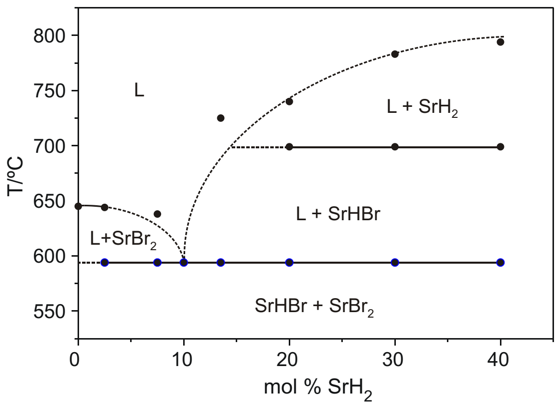

Fig. 7. Partial phase diagram of $SrBr_2$–SrH_2 system.

compound SrHBr at ~594 °C and the eutectic has a composition of ~90mol%$SrBr_2$–10mol%SrH_2. Lower eutectic temperature and significant solid solution of the conducting phase (CaHBr) in $CaBr_2$ at the meter operating temperature are favourable factors for selecting $CaBr_2$–CaH_2 as electrolyte than $SrBr_2$–SrH_2. A composition of 20mol%CaH_2–80mol%$CaBr_2$ was chosen as electrolyte for use in hydrogen meters.

A typical calibration graph of the meter that employs the electrolyte of 20mol%CaH_2–80mol%$CaBr_2$ composition is shown in Fig. 8. It is seen that the meter output is linear with respect to logarithm of hydrogen concentration in sodium (C_H) from 50 to 250 ppb. The expression obtained by least square analysis of the data is given below:

$$E(\pm 2\ \mathrm{mV}) = -51.9 - 29.8 \ln C_H. \tag{3}$$

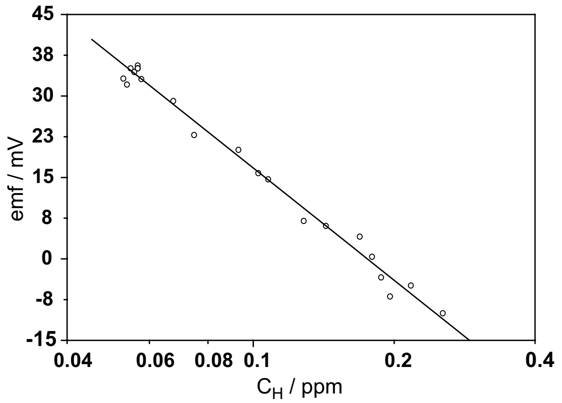

Fig. 8. Calibration plot of hydrogen meter with CaHBr–$CaBr_2$ as electrolyte.

Though cell output could be measured with an accuracy of ±0.5 mV, the uncertainty in the fitted expression is ±2 mV. This arises mainly from the error in measuring the temperatures of coldest point in cold trap.

The resolution of the meter for hydrogen detection (which can be obtained by differentiating the expressions (3)) is dependent on hydrogen concentration as shown below:

$$\mathrm{d}E/\mathrm{d}C_H = -29.8/C_H. \tag{4}$$

Taking the required signal to noise ratio as 4 for a reliable detection of an event, changes in hydrogen concentration that result in a change of 8 mV in meter output was calculated. This corresponds to 13 ppb change at a background level of 50 ppb of hydrogen in sodium.

4. Conclusion

A biphasic electrolyte of 80 mol% $CaBr_2$ and 40 mol% CaHBr composition has been identified as a suitable electrolyte for use in the electrochemical meter for measuring hydrogen in sodium based on the results of phase diagram investigations on potential binary alkali/alkaline earth metal hydride/halide systems. Output of the electrochemical meters that were constructed by using this electrolyte showed the capability to detect reliably a change of 13 ppb $[H]_{Na}$ at a background level of 50 ppb hydrogen in sodium.

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