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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.

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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]:

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

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