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Journal of Nuclear Materials 312 (2003) 10–15

journal of
nuclear
materials

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An electrochemical hydrogen meter for measuring hydrogen in sodium using a ternary electrolyte mixture

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Received 15 January 2002; accepted 8 October 2002

Abstract

An electrochemical sensor for measuring hydrogen concentration in liquid sodium that is based on a ternary mixture of LiCl, $CaCl_2$ and CaHCl as the electrolyte has been developed. DSC experiments showed the eutectic temperature of this ternary system to be ~725 K. Impedance spectroscopic analysis of the electrolyte indicated ionic conduction through a molten phase at ~725 K. Two electrochemical hydrogen sensors were constructed using the ternary electrolyte of composition 70 mol% LiCl:16 mol% CaHCl:14 mol% $CaCl_2$ and tested at 723 K in a mini sodium loop and at hydrogen levels of 60–250 ppb in sodium. The sensors show linear response in this concentration range and are capable of detecting a change of 10 ppb hydrogen in sodium over a background level of 60 ppb. Identification of this electrolyte system and its use in a sensor for measuring hydrogen in sodium are described in this paper.

PACS: 89.20.Bb

1. Introduction

Fast reactors use liquid sodium metal to transfer the heat generated in a reactor vessel to a steam generator in order to produce steam. Any leakage of steam into sodium at the steam generator, even at micro levels, would result in sodium–water reaction. It is essential to detect this steam leak at its very beginning and take immediate corrective action to avoid explosion and costly shut down of the reactor [1]. The occurrence of seam leaks can be detected by monitoring the sodium coolant for hydrogen. A great deal of effort has gone towards the development of a sensitive and fast sensor for hydrogen in sodium. Hydrogen detection in sodium involves measurement of the hydrogen partial pressure in equilibrium with the dissolved hydrogen in sodium [2]. Hydrogen partial pressure (p_{H_2}) is correlated to concentration of hydrogen in sodium (C_H) by Sieverts' law:

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

where k is the Sievert's constant for this system, which is found to be almost independent of temperature [3,4]. A method that is widely used for detecting hydrogen in sodium involves measurement of hydrogen flux diffusing through a metallic membrane exposed to sodium on one side and vacuum on the other [5]. Alternately an electrochemical sensor based on a concentration cell can be used to measure the hydrogen pressures:

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

The electrolyte used in the above cell must have characteristics that satisfy conditions such as compatibility with liquid sodium, good conductivity for hydrogen ions (proton or hydride ions) and thermodynamic stability under the operating conditions (0.05–5 Pa of hydrogen pressures). The sensors need to function in the temperature range of 673–773 K in sodium for detecting any steam leak effectively [6].

Proton conducting electrolytes such as hydrogen uranyl phosphate (HUP), $SrCeO_3$ etc. require humid conditions for exhibiting proton conductivity and hence

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0022-3115/03/$ - see front matter
PII: S0022-3115(02)01550-7

are not suitable for use in liquid sodium [7,8]. HUP is also thermally unstable at high operating temperatures. The choice is thus restricted to hydride ion conducting electrolytes. In the first electrochemical measurement of hydrogen in sodium by Newcombe and Thompson [9], alumino-silicate glass was used as the electrolyte, which was attacked by sodium. Holden and Fuhrman [10] employed concentration cells that used a eutectic melt of LiCl–KCl containing 0.2–2 mol% of either LiH or KH or CaH_2 as electrolyte. The hydride ion conducting melt was contained in a thin iron membrane, which prevented direct contact between electrolyte and sodium and thus avoided any chemical attack by sodium. Iron membrane is permeable to hydrogen and facilitates electrochemical equilibrium of hydrogen at the electrodes. However, the dissociation of the less stable KH in the eutectic caused the presence of free metal in the electrolyte and hence the electrolyte had significant electronic conductivity. A solid electrolyte, $CaCl_2$ mixed with CaH_2, which is thermodynamically stable under the operating conditions, was therefore used for this purpose by Smith and in our laboratory [11,12]. The $CaCl_2$–CaH_2 pseudo-binary system is characterised by a compound, CaHCI, which is the hydride ion conducting phase in the biphasic electrolyte. However, the ionic conductivity of this biphasic solid electrolyte is low (1.0×10^{-6} $\mathrm{S\,cm^{-1}}$ at 723 K) and the ionic transport number is only ~0.93 [13]. 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.

Hence, there is need to develop an electrolyte which has higher hydride ion conductivity than $CaCl_2$–CaH_2 system and satisfies the other requirements mentioned earlier. A ternary-salt mixture of LiCl, $CaCl_2$ and CaHCl was identified as the electrolyte, by considering the melting points of pure salts, the stability of hydrides and high ionic conductivity of the electrolyte at the operating conditions. A sensor based on this ternary electrolyte was constructed and the results of the testing of the new hydrogen sensor are discussed in this paper.

2. Choice of the ternary-salt electrolyte

$CaCl_2$–CaHCl, binary system provides a thermodynamically stable electrolyte at high temperatures and low hydrogen pressures of interest in sodium coolant circuits even though it has poor ionic conductivity [13]. Our recent studies showed that LiCl and $CaCl_2$ system has an eutectic temperature of 758 K [14] and the eutectic composition is ~65 mol% LiCl. It could be expected that by adding another component, such as CaH_2, to this binary system, the eutectic temperature could be brought down further. This would beget an electrolyte system that would exhibit high hydride ion conduction if the ternary eutectic temperature lies below or closer to the operating temperature of the electrolyte.

3. Experiments

3.1. Chemicals used

Chemicals used for the experiments were purified from Puratronic grade $CaCl_2$ (99.9% pure, M/s. Alfa Products) and AR grade LiCl (M/s. Alfa Products). They were further purified by heating them upto their melting points under dry HCl–argon gas mixture. The purified salt was stored and handled in a pure argon atmosphere glove box [15].

High purity CaHCl needed for carrying out DSC experiments were prepared by reacting CaH_2 and $CaCl_2$ at elevated temperatures. CaH_2 needed for this was prepared by hydriding known amounts of pure calcium metal shots (99.5% pure, M/s. Johnson & Matthey). This was carried out in the electrolyte compartment of the meter (described in Section 3.3 and shown in Fig. 1). Calcium was taken in an iron cup and placed inside the iron thimble of the electrolyte compartment. The

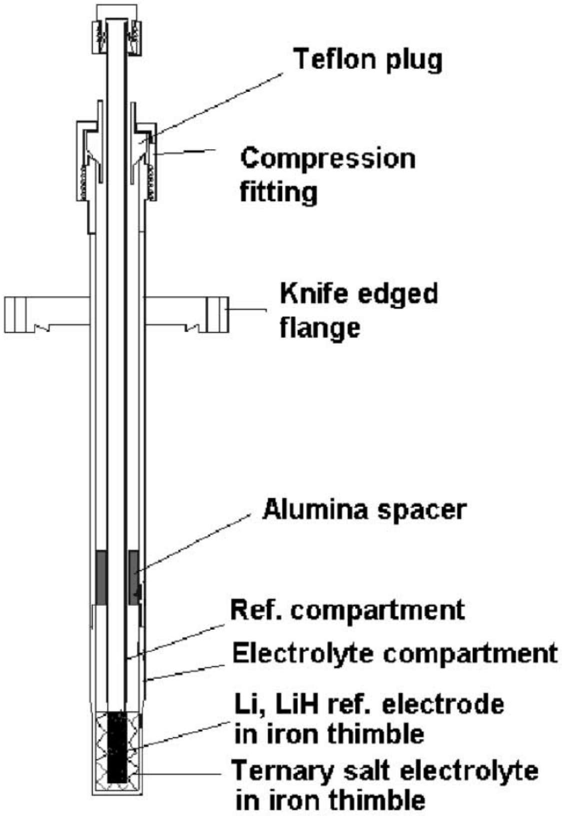

Fig. 1. Schematic diagram of electrochemical hydrogen meter.

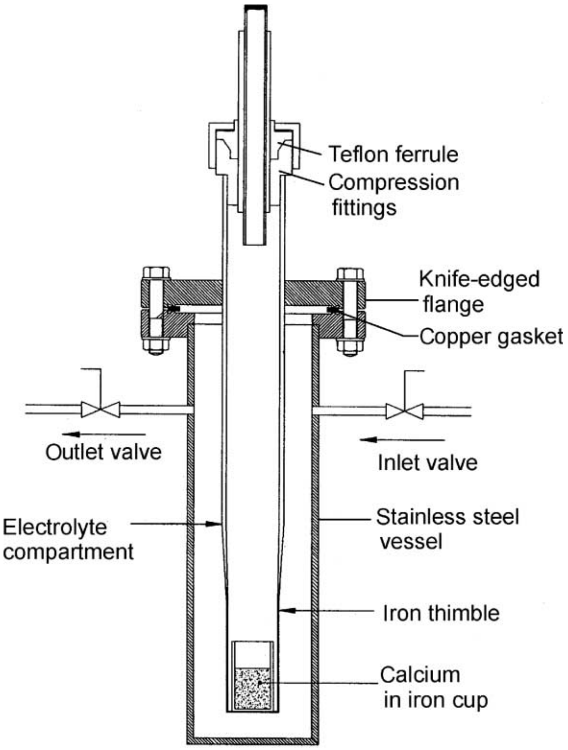

Fig. 2. Schematic diagram of hydriding vessel.

electrolyte compartment was closed leak-tight by means of compression fittings at the top. This arrangement was connected to a stainless steel vessel by a mating flange as shown in Fig. 2. The stainless steel vessel had inlet and outlets for passing hydrogen gas. The calcium metal was hydrided at 973 K for 4–5 days using this vessel to form CaH_2. This procedure enabled diffusion of only hydrogen through iron membrane and its reaction with the metal to yield pure hydride and avoided the reaction of impurities in the gas to form oxide, nitride and hydroxide. CaHCl was prepared by reacting calculated amounts of $CaCl_2$ and CaH_2 in sealed iron capsules at ~1073 K under hydrogen atmosphere inside the hydriding vessel mentioned above.

3.2. DSC experiments

Electrolyte mixtures containing a major proportion of LiCl (~70 mol%), were chosen for investigation because (i) LiCl has the lowest melting point among the components of the mixture and (ii) LiCl–$CaCl_2$ binary system has an eutectic composition of 65 mol% LiCl and eutectic temperature at 758 K. Two salt mixtures of compositions viz. (a) 69 mol% LiCl:31 mol% CaHCl and (b) 70 mol% LiCl:13 mol% CaHCl:17 mol% $CaCl_2$ were studied by differential scanning calorimetry. These investigations were undertaken to determine the eutectic temperature of ternary LiCl–$CaCl_2$–CaHCl system and the eutectic temperature of the binary LiCl–CaHCl system.

Calculated amounts of purified LiCl, $CaCl_2$ and CaHCl were mixed to prepare samples for DSC experiments. Approximately 30 mg of these samples were taken in 2.5 mm dia and ~15 mm long thin-walled iron capsules (~700 mg) and hermetically sealed by weld-closing the ends of the capsules by a pulsed-arc welding unit inside an argon glove box. The iron capsules were then brought out and heated up to 1073 K and cooled in an atmosphere of 2% hydrogen–argon mixture prior to DSC runs. This was done to ensure complete equilibration of the sample components and also to check leak-tightness of the welded iron capsules. The sample and empty reference iron capsules were then introduced into the heating compartment of a DSC equipment (model: M/s. SETARAM, France). Argon–2% hydrogen was used at a flow rate of 1 l/h during the experiment. The samples were generally heated at a scan rate of 2 °C/min. Temperature calibration of the DSC was done using standard samples of In, Sn, Zn and Al. The uncertainty in the temperature measurement is ±0.5 °C.

3.3. Construction and testing of the meter

A schematic diagram of the electrochemical hydrogen sensor is shown in Fig. 1. The sensor was constructed by the following procedure: an iron thimble of 16 mm outer dia, 0.25 mm wall thickness and 40 mm height for housing the electrolyte and another one of 8 mm OD, 0.25 mm wall thickness and 25 mm height for holding the reference electrode-materials, were machined from a pure soft iron bar. These pieces were decarburised in sodium saturated with calcium at 973 K for 72 h. They were then welded to stainless steel pipes as shown in Fig. 1.

A knife-edged flange of 70 mm dia was welded at the top end of the electrolyte compartment and a swagelok fitting was welded at the top of the pipe to hold the reference compartment. The knife-edged flange at the top of the probe helped to connect the meter to the bench-top loops containing sodium. A copper gasket pressed between the knife-edges of the flanges was used as a seal between the meter and its housing.

Li–LiH mixture is used as the reference electrode [12]. LiH was prepared by hydriding lithium metal (99.5% pure) with hydrogen gas by adopting a procedure similar to that used for preparing CaH_2. A known amount of lithium was taken in the iron thimble of reference compartment which was connected leak-tight to the hydriding vessel as shown in Fig. 2. Hydrogen was passed through this vessel at ~823 K for 3 days. The product obtained was characterised by XRD analysis. Equal amount of lithium (by volume) was added to the reference electrode. A similar procedure was used to prepare electrolyte mixture of high purity. Purified mixture of $CaCl_2$ and LiCl were taken along with 99.5% pure calcium shots inside the iron thimble of the electrolyte compartment. It was sealed at the top with gas tight compression fittings. This arrangement was connected to the hydriding vessel as mentioned earlier. The calcium in the salt mixture was hydrided at 823 K for 4–5 days to form CaH_2 in situ. This process ensured the formation of CaHCl phase by reaction between $CaCl_2$ and CaH_2.

After the in situ hydriding at ~823 K, the electrolyte compartment was cooled and the reference compartment containing Li and LiH was inserted into the electrolyte compartment and positioned above the electrolyte level by means of compression fittings. The assembly was then heated to ~823 K, the reference compartment was further inserted into molten electrolyte and the entire assembly was cooled slowly to room temperature.

A mini sodium loop, the schematics of which is shown in Fig. 3, was used to maintain different hydrogen concentrations in sodium during the calibration of the sensors. This loop consists of a meter test section (into which the cell assembly is inserted), a cold-trap vessel (in which the sodium experiences the lowest temperature in the entire sodium loop) and connecting pipes to close the loop. Thermowells were provided in the meter test section and the cold trap to measure and control temperatures in these regions within ±1 °C. Sodium in the loop was circulated employing electromagnetic principles by using a permanent magnet and a DC power supply. The hydrogen level in the sodium was maintained at any particular concentration (C_H) by controlling the cold-trap temperature, T and is given by the relation [16]

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

The corresponding hydrogen partial pressure is given by the Sievert's relation mentioned earlier. The cold-trap vessel is a part of the dynamic sodium loop and hot sodium continuously enters into it at one end and leaves it at the other end at a colder temperature. Hence, a small temperature gradient always exists within the cold-trap vessel and this is dependent on operating parameters of the loop. The uncertainty in the cold-trap temperature, due to this temperature gradient is observed to be ±2 °C.

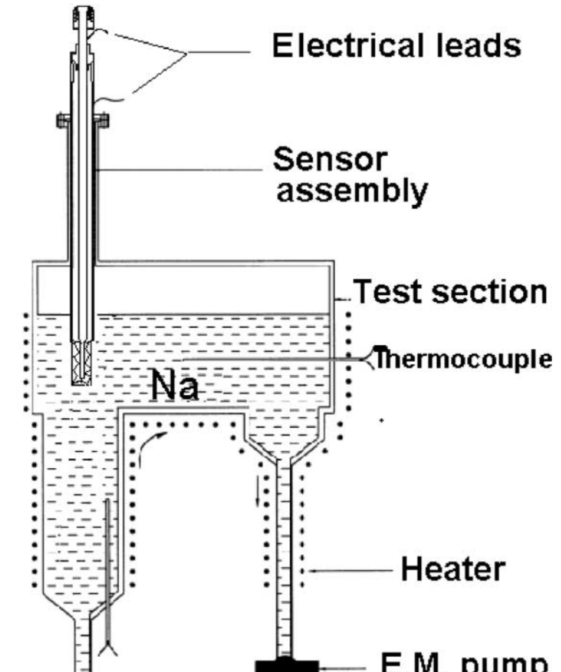

Fig. 3. Schematic diagram of mini sodium loop.

3.4. Impedance spectroscopic analysis

A Solartron model SI 1255 HF frequency response analyser along with a Solartron model 1286 electrochemical interface was used to measure the total resistance of the electrolyte. The electrolyte – electrode configuration used for these experiments is the same as that used in meters made for hydrogen measurement in sodium (refer Fig. 1) except that (i) the reference electrode compartment was not filled with Li, LiH reference electrode and was kept empty and (ii) hydrogen gas pressure of 1 atm was maintained on both electrode compartments by attaching the cell to a stainless steel vessel similar to the one used for hydriding. The outer iron membrane and the central iron tube were used as the electrodes during the impedance measurements. The measurements were made in the temperature range of 673–773 K. The frequency range of measurement was from 100 mHz to 100 kHz.

4. Results and discussion

The DSC results obtained for samples with compositions (a) 69 mol% LiCl:31 mol% CaHCl and (b) 70 mol% LiCl:16 mol% CaHCl:14 mol% $CaCl_2$ are shown in Figs. 4(a) and (b) respectively. The DSC pattern of sample (a) does not show any thermal event up to ~757 K. It shows an endothermic peak at ~757 K which is broad and reaches the base line at ~813 K. This pattern is typical of a binary system that exhibits a simple

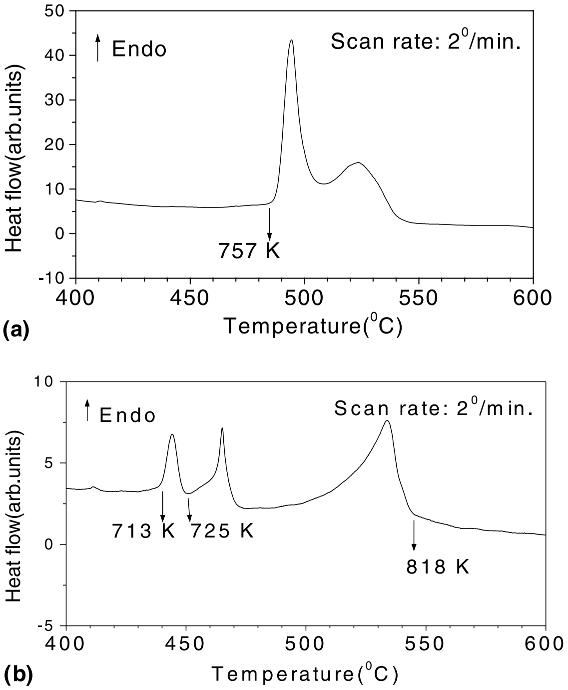

Fig. 4. DSC curves obtained for samples of compositions: (a) 69 mol% LiCl:31 mol% CaHCl and (b) 70 mol% LiCl:16 mol% CaHCl:14 mol% $CaCl_2$.

eutectic reaction followed by the continuous dissolution of the second solid phase up to the liquidus temperature. XRD analysis of the products obtained after equilibration of a sample of this composition at ~725 K showed the presence of LiCl and CaHCl only. This indicates that CaHCl coexists with LiCl up to the eutectic temperature of this binary system, ~757 K. The DSC pattern of sample (b) shows an endothermic peak at ~713 K. LiCl–$CaCl_2$ system exhibits a reversible solid state reaction between $CaCl_2$ and LiCl to form a compound, $LiCl \cdot CaCl_2$ at 712 ± 4 K [14]. As the sample contained excess $CaCl_2$ (14 mol%), the endothermic peak at ~713 K in Fig. 4(b) is attributed to the solid state reaction between the solid phases $CaCl_2$ and LiCl to form $CaCl_2 \cdot LiCl$. The DSC pattern shows that the next endothermic event starts at ~725 K. The XRD of the samples of these compositions which were equilibrated at ~698 K, showed the presence of three phases, $CaCl_2$(s), CaHCl(s) and LiCl(s). Hence the endothermic peak that starts at ~725 K could be representing (i) either a ternary eutectic reaction between $CaCl_2 \cdot LiCl$ (formed at ~713 K), CaHCl and LiCl or (ii) a solid state reaction or (iii) phase transition, involving any one or more of these phases. From our earlier reports [12,13] it has been established that other binary systems, namely, $CaCl_2$–CaHCl and $CaCl_2$–LiCl do not exhibit any solid state reaction or phase transition at ~725 K. Since eutectic reaction between LiCl and CaHCl also is not observed at this temperature, the endothermic peak that begins at ~725 K in Fig. 4(b) must be representing a ternary eutectic reaction between LiCl, CaHCl and $LiCl \cdot CaCl_2$. This system would then possess a liquid phase at temperatures >725 K. It would facilitate high H^- ion conduction in the electrolyte, if the operating temperature is closer to this ternary eutectic temperature.

The impedance plots obtained for the samples with composition, 70 mol% LiCl:16 mol% CaHCl:14 mol% $CaCl_2$ in the temperature range 693–738 K are shown in Fig. 5. These plots show that the electrolyte system undergoes a phenomenal change with respect to its ionic conductivity upon heating. When the cell is heated, up to ~713 K, a semi-circle type of plot could be obtained when $Z_{imaginary}$ is plotted against Z_{real} as a function of frequency. The decrease in the electrolyte resistance with increasing temperature is indicated by the decreasing size of the semi-circle plots up to ~713 K. The impedance plots obtained at ~728 K and above show a different pattern. The impedance plots show only a straight-line at lower frequencies and no semi-circles at higher frequencies. This indicates that ionic conduction through a molten phase of the electrolyte appears at ~728 K. This is in agreement with the DSC results which showed an endothermic peak beginning at ~725 K for the appearance of liquid phase by eutectic reaction. From the results of impedance measurements and the geometry of the electrolyte, the ionic conductivity of the electrolyte is estimated to be $\sim 3.5 \times 10^{-3}$ S cm^{-1} at ~728 K. This electrolyte system has a conductivity that is nearly 10^3 times higher than $CaCl_2$–CaHCl solid electrolyte. Therefore, an electrolyte having a composition of 70 mol% LiCl:16 mol% $CaCl_2$:14 mol% CaHCl was used for constructing an electrochemical hydrogen

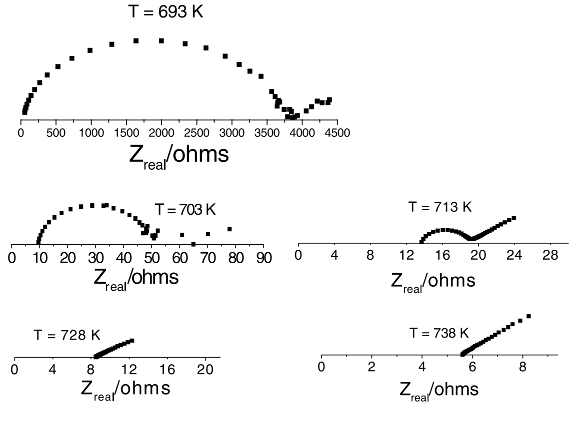

Fig. 5. Impedance plots of ternary-salt based electrolyte at temperatures between 693 and 738 K.

meter so that the electrolyte possesses very good H^- ion conductivity while operating the meter at 723 K.

Two sensors (echm-1 and echm-2) were constructed using this new electrolyte. The output of these sensors at 723 K as a function of hydrogen concentration in sodium (C_H) are shown in Fig. 6. The output is found to be linear with respect to logarithm of hydrogen concentration in sodium (C_H) from 250 to 60 ppb (Fig. 6). The expressions obtained by least square analysis are given below:

$$E\ (\pm 2.6\ \text{mV}) = -86.7 - 136.8 \log C_H \quad \text{(echm-1)}, \qquad (3)$$

$$E\ (\pm 1.8\ \text{mV}) = -81.6 - 149.3 \log C_H \quad \text{(echm-2)}. \qquad (4)$$

Though cell output could be measured with an accuracy of ±0.5 mV, the uncertainty in the fitted expressions for echm-1 and echm-2 are 2.6 and 1.8 mV respectively. This arises mainly from the error in measuring the temperatures of coldest point in cold trap as mentioned in Section 3.3. This sensor, which uses a ternary-salt electrolyte, does not show the problems of electronic conduction at low hydrogen pressures (equivalent to hydrogen concentration of 60–250 ppb in sodium) due to its inherent high hydride ion conduction.

The resolution of the meters for hydrogen detection (which can be obtained by differentiating the expressions (3) and (4)) are dependent on hydrogen concentration as shown below:

$$\mathrm{d}E/\mathrm{d}C_H = -59.4/C_H \quad \text{(echm-1)}, \qquad (5)$$

$$\mathrm{d}E/\mathrm{d}C_H = -64.8/C_H \quad \text{(echm-2)}. \qquad (6)$$

Taking the required signal to noise ratio as 4 for a reliable detection of an event, changes in hydrogen concentration which result in 10.4 mV for echm-1 and 7.2 mV for echm-2 can be easily detected. These correspond to 0.11 ppm change for echm-1 and 0.07 ppm for echm-2 at a background level of 0.60 ppm of hydrogen in sodium. At 0.060 ppm background level the sensitivity is 0.011 ppm for echm-1 and 0.007 ppm for echm-2.

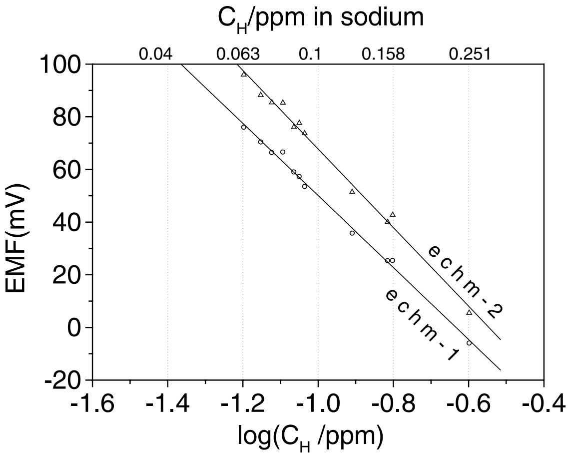

Fig. 6. Output vs C_H in sodium of electrochemical hydrogen sensors.

5. Conclusion

A ternary-salt mixture of 70 mol% LiCl, 16 mol% CaHCl and 14 mol% $CaCl_2$ has been identified as a suitable electrolyte for use in a sensor for measuring hydrogen in sodium. The electrolyte has a high ionic conductivity of $\sim 3.5 \times 10^{-3}\ \mathrm{S\,cm^{-1}}$ at 723 K as it is very close to the ternary eutectic temperature of the electrolyte system. Electrochemical sensors which are constructed using this electrolyte, are capable of detecting a change of ~10 ppb $[H]_{Na}$ at a background level of 60 ppb hydrogen in sodium reliably.

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