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Hydride-Containing Molten Salts and Their Technology Implications

by

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## HYDRIDE-CONTAINING MOLTEN SALTS AND THEIR TECHNOLOGY IMPLICATIONS

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Keywords: alkali hydride, eutectic LiCl-KCl, electrolyte, energy conversion and storage

### ABSTRACT

Hydride-conducting molten salts such as LiH in eutectic LiCl-KCl are attractive electrolyte systems for intermediate-temperature applications. The chemically reducing characteristics of these hydride melts provide a unique method to clean metal surfaces. The high conductivity of these hydride melts makes them the best electrolytes for hydrogen-based energy applications at intermediate temperatures. We will review some earlier work on hydride-conducting molten salts and their potential applications in energy technology. We will also describe some recent work on these hydride-containing molten salts for energy conversion and storage applications, including hydrogen sensing and hydrogen storage, electrochemical characterizations, and thermodynamic and kinetic investigations of metal-hydrogen reactions. More recently, lithium deuteride containing eutectic LiCl-KCl melts have been used for excess heat production by the process of electrolysis to charge deuterium into metal matrix such as Pd and Ti. From these studies we illustrate the prospects of this hydride molten salt technology and its implications for the use in intermediate-temperature electrochemical energy conversion configurations. It will also reveal some interesting electrochemical aspects involved in the processes.

### INTRODUCTION

We reported recently that molten salts containing alkali-hydrides can serve as an effective electrolyte for hydrogen-based electrochemical energy conversion and storage applications over a wide range of operating temperature and potential. Several interesting experiments demonstrated the potential use of these molten salts in chemical sensing [1,2], hydrogen storage [3-5], hydrogen purification, hydrogen transport and electrolytic process [4,6], and more recently, in excess heat generation in metal matrix [7,8].

The most interesting aspect of this technology is the unique hydride reactivity toward metals, particularly refractory base metals such as Ti, Zr, V, Nb, Ta and rare earths. This unique property has been explained by Deublein and Huggins [9], who described an in-situ technique of preparing "hydrogen-transparent" interfaces in the hydride molten salt systems

This molten salt technique offers a unique opportunity for hydrogen-based energy applications, substantially different from other systems that use aqueous solutions or solid electrolytes. Due to increased thermodynamic efficiency, enhanced kinetics, and reduced material problems associated with high-temperature operations, many energy conversion

processes are often operated in the temperature range of 300-700°C. Aqueous electrolytes are useful only at relatively low temperatures, typically below 100°C. Solid electrolytes, on the other hand, are usually operative only at high temperatures because of limited conductivity. For intermediate-temperature operations the hydride molten salt electrolytes seem to offer the utmost potential. The hydride molten salt techniques also show additional benefits that include: relatively simple operation, low cost starting raw materials, high ionic conductivity, good liquid wet contact, and a wide range of composition available for selection of suitable device component and operating condition.

The hydride-containing molten salts can be categorized into: (1) halides, such as eutectic LiCl-KCl with LiH; (2) hydroxides, such as KH in KOH; and (3) metalorganic systems, such as NaH in NaAl(Et)<sub>4</sub>. To select electrode materials and suitable electrolyte for electrochemical applications, thermodynamic considerations such as stability are very important. This aspect has been discussed, for example, by Godshall et al. [10] and by Raistrick and Huggins [11]. Among all three types of molten salts, the halides are more well-studied than the other two. Therefore, we will emphasize the halide-based systems, particularly the eutectic LiCl-KCl that contains excess LiH. The chloride melt has been intensively studied for its potential use in many robust electrochemical applications such as in the iron sulfide-lithium batteries. Our interest in the halide melts containing LiH was favored by the low molecular weight of LiH, the commercial availability of rather pure, inexpensive halide salts; the potential benefits of using low-cost base metals as the electrode materials; and the simplicity of the system.

Our interest in the hydride-containing molten salts also stems from their remarkable properties to prepare "hydrogen-transparent" metal surface by the highly reductive LiH to facilitate a fast metal and hydrogen interaction, which is important for base metals that have surface oxide impeding the metal-hydrogen reactions. The presence of LiH in the melt often eliminates surface metal oxide problems, making the hydride melt ideal for hydrogen energy applications. This unique property also marks a strong distinction from the proton-based liquid or solid electrolytes due to different operating potential regimes — where the hydride melt provides a convenient access to the immunity regime of most metals. The hydride melt also opens a new avenue to environmentally benign hydrogen-based energy technology with markedly improved kinetics, stability, and efficiency for operation.

The hydride-containing molten salts have been proposed for a number of potential energy-related applications since the late 1950s. Early work of the eutectic LiCl-KCl system containing KH, NaH and CaH<sub>2</sub> was reported by Bardwell [12]. He demonstrated that electrolysis of these hydrides in the eutectic chloride melt at low voltages resulted in hydrogen evolution at the anode. The quantity of hydrogen is consistent with that estimated from Faraday's law for hydride oxidation. Later, Shearer and Werner [13], Indig and Snyder [14], and Plambeck, Elder and Laitinen [15] subsequently investigated the eutectic chloride:LiH system because of its potential use in thermally regenerative energy conversion cells proposed by Werner and his co-workers [13,16,17].

Although these hydride-conducting molten salts were promising in energy technology development, some critical technical aspects remain uncharacterized. Among these earlier studies, confusing and inconsistent results have been reported, indicating great complexity in this molten salt system, as noted by Plambeck et al. [15]. For example, Indig and Snyder [14] reported that a current density of 1.55 A cm<sup>-2</sup> can be achieved without appreciable polarization. They also reported a mixed oxidation behavior in the system involving both one- and

two-electron charge transfer reactions; namely,



The two reactions compete with each other, depending on the current density and the nature of electrode surface. This led to the coulombic efficiency varying with current density and resulting in hydrogen gas evolution on both cathode and anode. On the other hand, concentration cell experiments under open circuit conditions showed a Nernstian behavior that agreed with the one-electron charge transfer process. The explanation of this mixed oxidation behavior remains unanswered to date. Recently, a "shuttle mechanism" was proposed to explain this phenomenon [18], but experimental verification remains difficult.

Plambeck et al. [15] focused their investigation on the voltametric behavior of the LiH:eutectic LiCl-KCl system as a function of LiH content. They only found the one-electron charge transfer process. They also found that the electrochemical behavior depends on the electrode materials used.

These earlier works indicated that near the equilibrium condition the electrochemical behavior of the hydride melt does follow what is expected from the thermodynamic considerations. When the LiH concentration became low, however, the electrochemical behavior was less predictable due to the lack of understanding of the effects from electrolyte composition, current density, and electrode materials. In particular, electrode surface property seems to have a significant influence on the charge transfer mechanism and the reaction paths. More characterizations of the phenomenon at low LiH concentrations and at high current densities are therefore desired.

More recent work using molten hydride systems was first reported by Lüdecke, Deublein and Huggins [19] in their study of hydrogen storage in ternary magnesium hydride systems using NaH:NaAl(Et)<sub>4</sub> melts, which have a low melting temperature of about 137°C. They reported the determination of phase diagram of the ternary hydride systems and the associated thermodynamic properties by mapping the compositional dependence of electrochemical potentials using coulometric titration techniques. Although suitable for equilibrium measurements, this melt has relatively low solubility of NaH, resulting in a low conductivity that limits its use in practical applications.

Liaw, Deublein and Huggins [1-6,20] later considered the utilization of the LiH-based eutectic LiCl-KCl molten salts with unique electrochemical cell configurations in several interesting experiments. The LiH-containing chloride melt exhibits an improved conductivity, by far probably the best among all known hydrogen-conducting electrolytes. With carefully selected similar and other types of melt, the operating temperature can easily extend over the range of 300–900°C. We will now discuss in detail the potential applications of this hydride melt.

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## EXPERIMENTAL ASPECTS

The eutectic LiCl-KCl (51.9:47.6 wt%) mixture was made by the Lithium Corporation of America (Lithco). The LiH (98% purity) and LiD (>98% isotope purity) were purchased from the Alfa Products, Johnson Matthey Co. or Aldrich Chemical Co. These materials were used without further purifications. Because of high moisture-sensitivity, the materials were stored in an inert gas-filled glove box station where oxygen, nitrogen, and moisture were constantly removed by a scrubbing system.

Containment of the electrochemical cells are usually made of metals such as Al or steel. We often avoid the use of oxide-based ceramic crucibles like alumina due to the concern of possible oxide contamination, low thermal-shock resistance, high cost, and limited availability in size and shape. Nonetheless, some high quality quartz, graphite or boron nitride crucibles may be considered if desired, although little experience of their use has been reported.

The LiH:LiCl-KCl eutectic molten salt cells have to be operated at elevated temperatures above 350°C. The cell temperature was controlled and maintained by thermocouples, preferably immersed in the melt, and by a resistant heater. Resistant heating elements used were usually nichrome wires or commercially available high-temperature heating tapes wound in a spiral shape on the outer wall of the container and electrically insulated. Stainless steel Dewar flasks and high-density fiberglass kaowool were often used as thermal insulation to minimize heat loss and to provide better control of operating temperature. The thermocouples were protected by a thin-walled stainless steel sheath and were ungrounded, therefore, they can be placed in the melt without much of a degradation problem.

For electrochemical measurements, suitable reference electrodes are essential. Several binary Li- or H-based mixtures are thus useful for this purpose. A good example of the Li-based references is the Al/" $\beta$ -LiAl" couple which gives a constant potential versus Li/Li<sup>+</sup> at constant temperature and pressure. This system has been extensively studied by a few groups, leading to a temperature dependent emf (mV versus Li/Li<sup>+</sup> reference) equal to  $451 - 0.220 \times T$  (K) [21,22]. Other useful systems are the Li<sub>7</sub>Si<sub>3</sub>/Li<sub>13</sub>Si<sub>4</sub> mixture [23] or some other similar binary alloys [24,25]. The H-based references are typically binary metal hydride systems such as Ti/" $\beta$ -TiH<sub>x</sub>" or " $\beta$ -TiH<sub>x</sub>"/" $\delta$ -TiH<sub>y</sub>" two-phase mixtures [1,5]. These references are relatively stable over a long period of time. For easy comparison of experimental results, however, it is more convenient to report the potential versus the H/H<sup>-</sup> or the Li/Li<sup>+</sup> reference. Although the latter was often used in earlier work, we prefer to use the H/H<sup>-</sup> convention for easier, more direct comparison among hydrogen systems than the Li/Li<sup>+</sup> couple. Furthermore, we can always relate these two reference potentials through the decomposition of LiH:



By calculating the corresponding decomposition potential from the free energy of formation of LiH,  $\Delta G_f(\text{LiH})$ ,

$$E_{\text{decomp}} = -\Delta G_f(\text{LiH})/nF, \quad (4)$$

where  $n$  and  $F$  have their usual meanings, we obtained the potential of the H/H<sup>-</sup> versus the Li/Li<sup>+</sup> reference to be 370 mV at 700K.

## ELECTROCHEMICAL CELL CONFIGURATIONS AND EXPERIMENTAL RESULTS

Several electrochemical cell configurations have been utilized to demonstrate this hydride molten-salt technique, in an attempt to evaluate its potential in energy conversion and storage applications. Consistent Nernstian and Faradaic behaviors of the hydride melt were revealed through these experiments.

Figure 1 displays a concentration cell for potentiometric hydrogen sensor application. A close-end Pd tubing was used as a sensing electrode in equilibrium with a  $H_2$ -He gas stream. The open circuit voltage of the Pd sensing electrode versus an Al/" $\beta$ -LiAl" reference was measured as a function of hydrogen partial pressure, showing that correct Nernstian relationship

$$E = (RT/nF) \ln P_{H_2} = (2RT/nF) \ln a_H \quad (5)$$

was obeyed in such a cell.

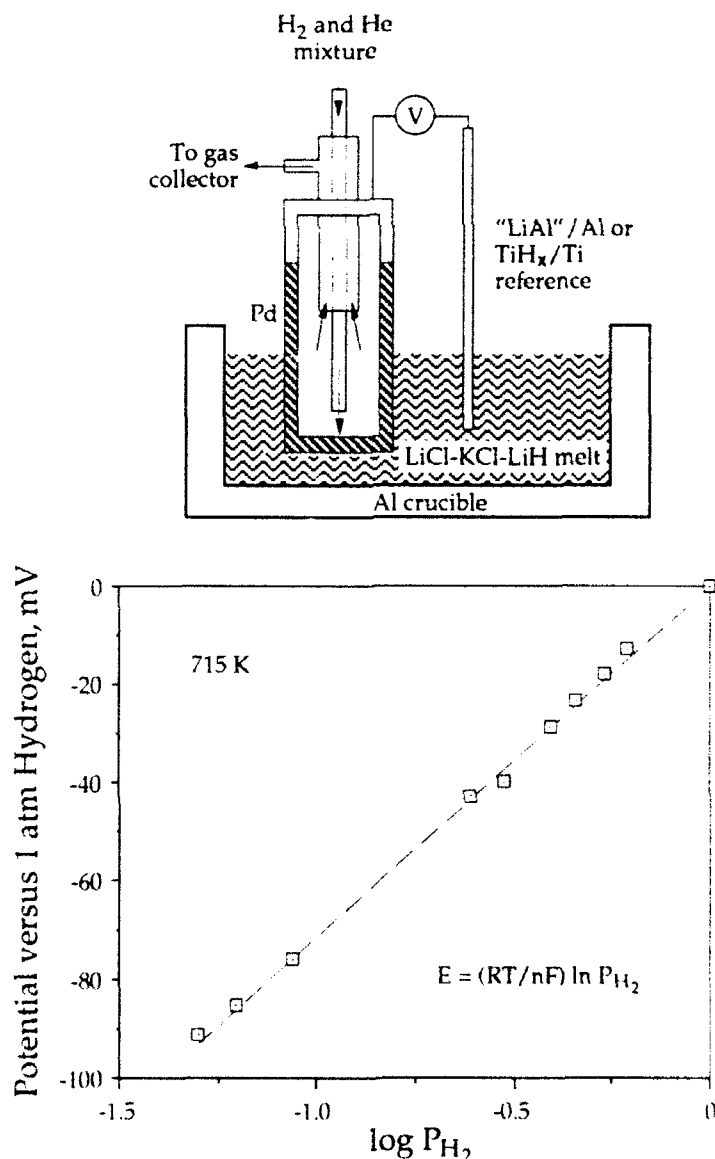


Figure 1. A hydrogen probe showing the correct Nernstian behavior of a Pd electrode in the hydride molten salt environment.

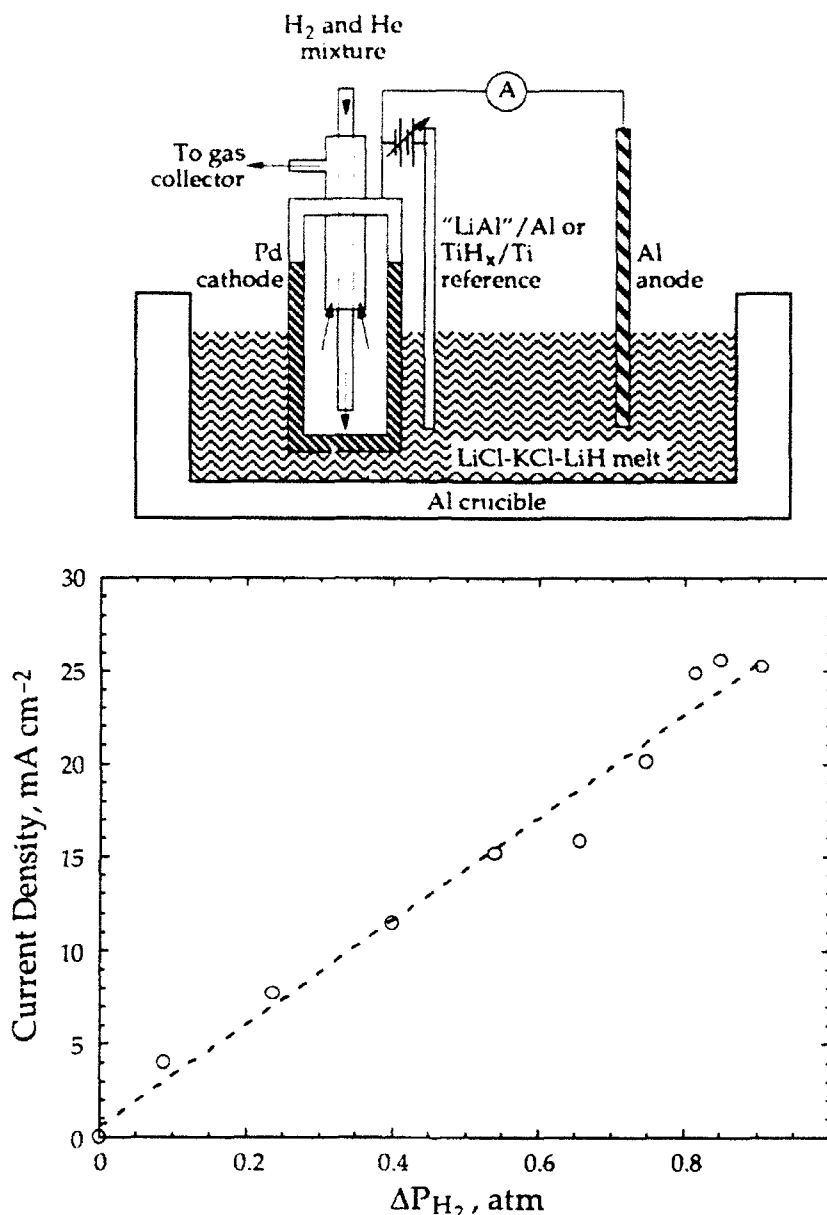


Figure 2. Amperometric mode of measuring steady-state permeation limiting current of the hydrogen probe under a hydrogen concentration gradient.

Figure 2 shows the concentration cell subjected to dc polarization under a constant bias imposed between the Pd tubing and the reference, while a limiting current was measured between the Pd tubing and an Al counter electrode. By varying the bias between the Pd and the reference but maintaining a unity hydrogen partial pressure inside the Pd tubing, we measured a limiting current corresponding to different hydrogen concentration gradient established by the bias. The limiting current showed the hydrogen permeation through the Pd, while hydrogen gas evolution was observed at the Al anode.

A similar experiment was also shown in Figure 3, where a LiCl-KCl:LiH|V|LiCl-KCl:LiH|Pd|H<sub>2</sub>-He mix-stream cell was used to measure the hydrogen permeation currents through the Pd and V membranes. The configuration comprised a hydrogen gas/Pd membrane concentration cell with another cell in which a vanadium foil was used as a hydrogen permeable membrane. This double membrane cell was then subjected to polarization by

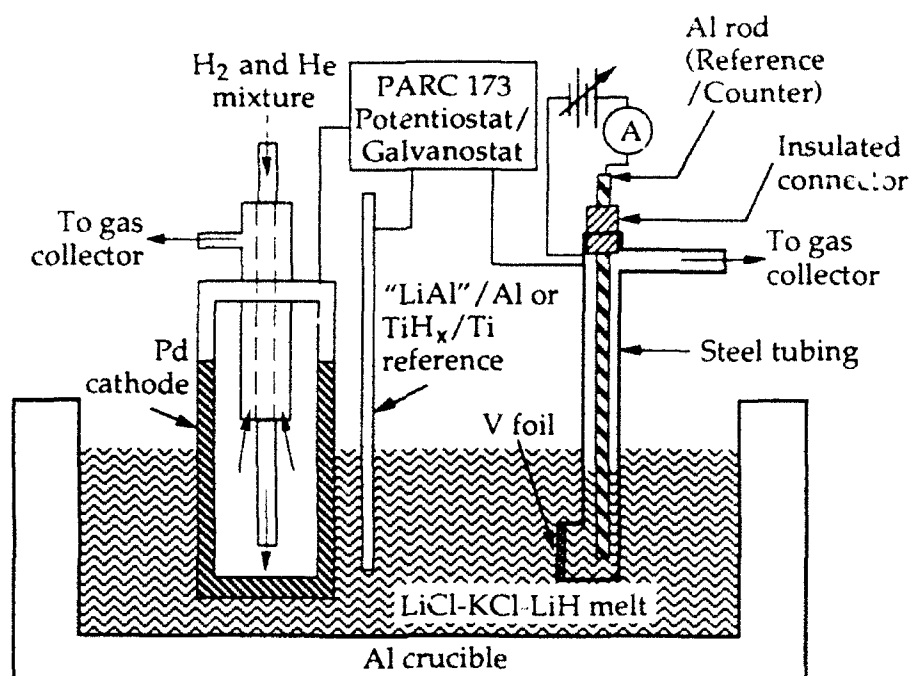


Figure 3. Schematic diagram of a  $\text{LiCl-KCl:LiH} \mid \text{V} \mid \text{LiCl-KCl:LiH} \mid \text{Pd} \mid \text{H}_2\text{-He mix-stream}$  cell working at 718 K.

properly biasing the membranes through separate potentiostats and reference electrodes. In general, the bias was applied to engage very low activities of hydrogen at the interfaces of the Pd backside (short-noted by "b") and the V frontside (short-noted by "f") where the electrolyte contacted. By establishing a concentration gradient electrochemically, we measured the steady-state current passing through both membranes to be the same within instrumental limits (Table 1). This double-membraned three-compartment experiment illustrated the Faradaic behavior of the hydride-containing electrolyte in which hydrogen transport can be controlled quantitatively. The significance of this experiment is the intriguing approach of using two highly hydrogen-conductive metal membranes and the hydride-conducting molten salts as a composite configuration for electrolytic applications. One can take advantage of the metal's solid appearance and its strength combining with molten salt's good conductivity and superb wet contact to employ the composite configuration for hydrogen transport, energy

Table 1. Results of permeation experiments of a  $\text{LiCl-KCl:LiH} \mid \text{V} \mid \text{LiCl-KCl:LiH} \mid \text{Pd} \mid \text{H}_2\text{-He}$  mix-stream configuration at 718 K

| $i(\text{mA})$<br>through Pd | $E(\text{mV})$<br>V(f) vs. Ref | $E(\text{mV})$<br>Pd(b) vs. V(b) | $E(\text{mV})$<br>Pd(b) vs. Ref | $E(\text{mV})$<br>V(b) vs. Ref | $i(\text{mA})$<br>through V |
|------------------------------|--------------------------------|----------------------------------|---------------------------------|--------------------------------|-----------------------------|
| -31.8                        | 22.8                           | 50.3                             | 261.0                           | 210.6                          | -31.5                       |
| -33.8                        | 22.7                           | 40.0                             | 257.9                           | 217.1                          | -34.0                       |
| -31.0                        | 22.6                           | 20.0                             | 256.5                           | 235.7                          | -31.4                       |
| -33.1                        | 22.8                           | 9.28                             | 252.3                           | 242.1                          | -33.1                       |
| -35.5                        | 22.5                           | 0.9                              | 253.4                           | 253.8                          | -35.5                       |
| -109                         | -100.1                         | -101.3                           | 175.3                           | 275.5                          | -120                        |
| -113                         | -100.1                         | -80.5                            | 190                             | 270                            | -112                        |
| -74                          | -98.8                          | -60.4                            | 218.6                           | 277.8                          | -74                         |

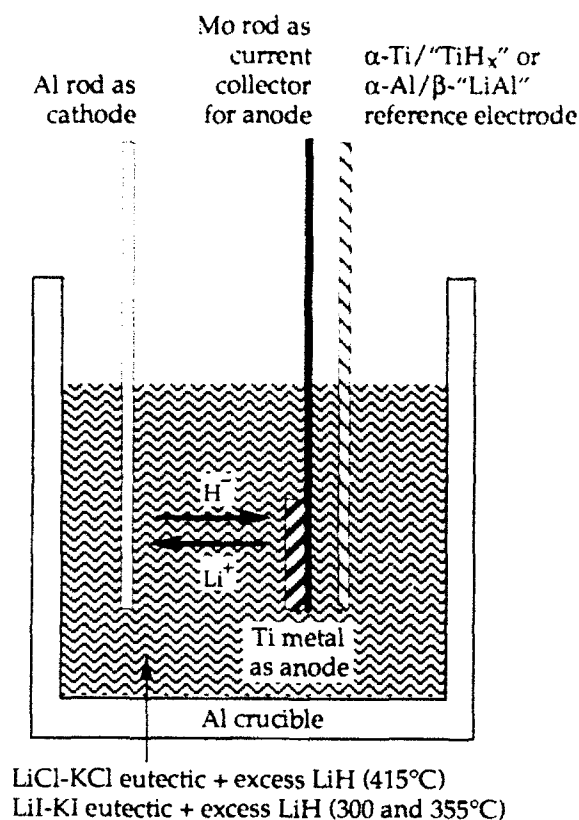
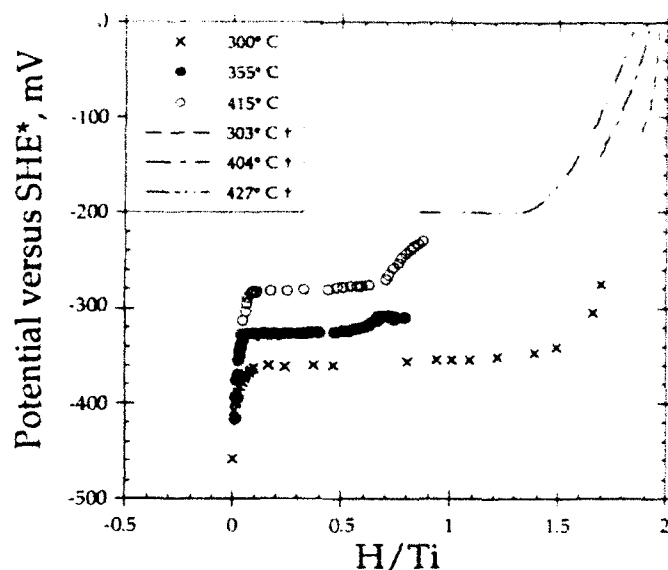


Figure 4. Cell configuration, equilibrium coulometric titration results and the Ti-H binary phase diagram reported by San-Martin and Manchester [26]. The titration results are consistent with the phase diagram and the associated pressure-temperature-composition data, demonstrating the correct application of the hydride molten salt techniques.

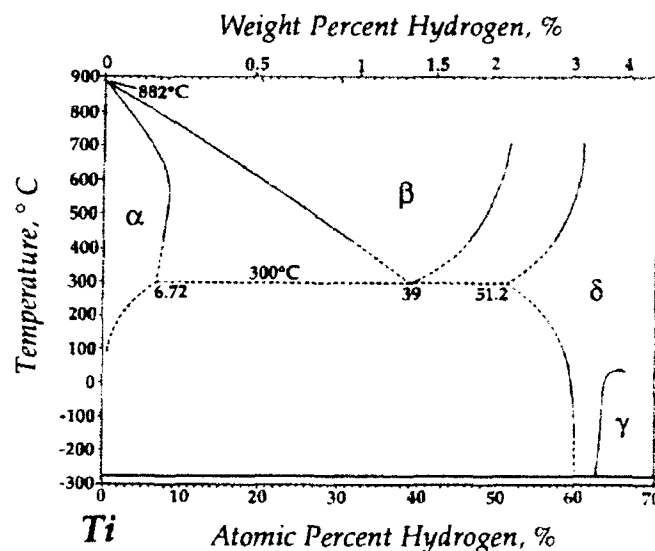
storage, and conversion with a remarkable high rate. The rate of this process seems limited by the permeativity of hydrogen in metals. Therefore, several metals and their alloys that exhibit high hydrogen permeation rates have attractive potential for this approach. Metals such as V and Nb, for example, that have superior permeativity than the better-known Pd may thus be prudent candidates for this application.

Employing the hydride-conducting melts in hydrogen storage and investigations of metal-hydrogen systems is also quite promising. Figure 4 illustrates a cell used in the studies of the thermodynamic properties of the Ti-H system and the equilibrium coulometric titration results. These results are consistent with the reported phase diagram and data obtained by gas volumetric sorption methods [26]. Our electrochemical techniques are, however, more simple



† From: San-Martin and Manchester: Bull. Alloy Phase Diag., 1987, 8, 30

SHE\* refers to the H/H<sup>-</sup> reversible couple.



and applicable in the low hydrogen partial pressure region where the gas sorption method has limited control. Through temperature-dependent titration measurements, we can readily derive many useful thermodynamic data, such as hydrogen solubility in the metal and composition of the hydride phase, equilibrium hydrogen partial pressure as a function of composition, free energy of formation of hydride phase and reaction enthalpy of the hydride formation, Sievert's constant, entropy of hydride formation, etc. [5] By monitoring the transient behavior of the equilibration process using techniques such as the galvanostatic intermittent titration technique, we can also obtain kinetic properties of the metal hydrides [20]. Diffusivity of hydrogen in each hydride phase can be determined as a function of composition.

Figure 5 illustrates an experiment using two Ta membranes in a double-membrane triple-cell configuration to demonstrate the polarization behavior of the hydride melt. We demonstrated with this symmetric cell configuration that the electrolyte can be easily polarized with a small resistance of the order of an ohm. This result agrees with the conductivity measurements made by the ac electrochemical impedance spectroscopy. The conductivity of the melt can reach the order of  $1 \Omega^{-1} \text{ cm}^{-1}$ , which is extremely high compared to those of other liquid systems.

The molten salt techniques have recently been used in the investigation of excess heat generation using the analogous LiD:LiCl-KCl eutectic system. The cell set up was similar to that shown in Figure 4, except that additional calorimetric devices were employed to facilitate the power measurement and calibration. The detailed work was reported in [7,8]. Interesting results were obtained that showed a significant amount of excess power and heat, in the order of more than 600% over the input electrochemical work, were generated in the deuteride system when Pd or Ti were used as the anodes. No excess power and heat were measured in the controlled hydride experiments. This level of excess power cannot be explained easily by any known chemical process. The excess heat phenomenon cannot be explained by any thermochemical origin. Although the actual mechanism is still unknown, some unexpected products were found. The most significant evidence is the detection of excess  $^4\text{He}$  [27-29] and the association of excess heat with a critical high loading of deuterium in metals [30]. Unfortunately, these techniques were difficult to control and thus very irreproducible. The condition for the excess heat generation seems to relate to the energetic formation of deuteron at the anode, while the LiD concentration has to be controlled at a proper level [18]. The difficulty of controlling this process is impeding the progress.

## DISCUSSION

The experiments described illustrate several important characteristics and interesting features of the molten salt technology using hydride-conducting electrolytes. The Nernstian behavior demonstrated by the concentration cell experiments in Figure 1 reveals that the  $\text{H}_2/\text{H}$  equilibrium has been established at the gas | Pd interface, while the  $\text{H}/\text{H}^-$  equilibrium has also been established at the electrolyte | Pd interface, indicating the correct functioning of the hydride-conducting electrolyte and its predominantly ionic transport character. This ionic characteristic has also been verified by an asymmetric polarization experiment that measured the electronic leakage current using ionic blocking electrodes. The electronic leakage current is a function of lithium activity in the melt and is typically well below 1% of the overall current density. Although the transport in the melt is dominated by ionic species, the specific transference number for each ionic species is undetermined so far. This problem possibly

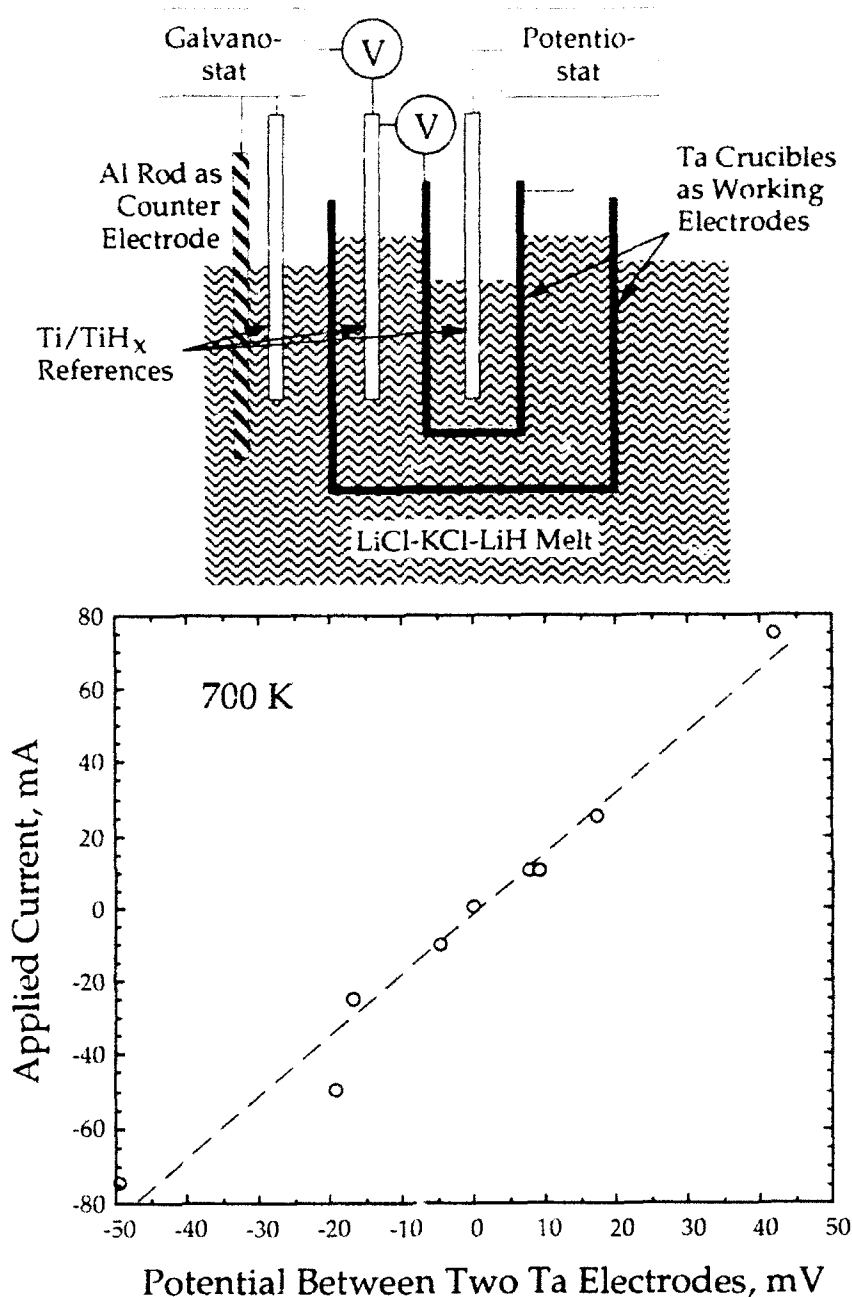


Figure 5. A double-membrane cell configuration demonstrates the small polarization effect of the hydride molten salt system.

caused the confusing results reported by Indig and Snyder [14] in their coulombic efficiency measurements and awaits clarification in future work.

The amperometric measurements (Figure 2) indicate that the permeation current can be measured under a concentration gradient. The current was attributed to the hydrogen permeation through the Pd membrane, which is the rate-limiting step. The rate was not limited by the transport of the electrolyte because the ionic conductivity of the electrolyte was high, as demonstrated by the polarization results in Figure 5. Further evidence is the verification by the electrochemical impedance spectroscopic results reported in [31].

This permeation process is also repeated by the double-membrane experiments (Figure 3). Faradaic behavior is an important aspect of the technology. The superb transport characteristics of the hydride-conducting electrolyte exhibit only small polarization resistivity to the overall kinetics. This implies that the energy consumption in future energy storage and conversion will be small, a great advantage to be considered. Another interesting aspect is the interfacial impedance of metals employed in the experiments has been small too. Hydrogen does become transparent through the electrolyte | metal electrode interfaces, only experiencing little resistance in the overall transport. This property is evidenced by the results that show little change in the permeation current even if the backsides of the Pd and V electrodes are at about the same potential (Figure 3 and Table 1).

The Nernstian and Faradaic behavior of the electrolyte permit the employment of the molten salt techniques in the studies of thermodynamic and kinetic properties of the metal-hydrogen systems. A good example is displayed in Figure 4, in which the Ti-H system was used. Detailed description of the experiment is reported in [5] and will not be repeated here. The significance of this work, however, is that simple molten salt experiments can be used to derive useful thermodynamic and kinetic data that were difficult to obtain by conventional gas-sorption techniques.

If the interesting result of excess heat generation using the molten salt techniques is proven, the significance of its contribution to energy applications will be enormous. High efficiency, superb kinetics and low power consumption will be the benefits from the use of elevated-temperature excess heat generation. Improved understanding of the electrochemical behavior of the hydride-conducting molten salt will facilitate the realization of the technology. Particularly interesting is the control of high current density in the cell configuration to establish a critical deuteride concentration to be sustained for excess heat generation. As evidenced by the previous discussion, this molten salt system seems simple in operation but actually complicated in the electrochemical reaction mechanism. Characterizing the transport property as a function of LiD concentration and current density will help elucidate the mystery of the "uncharacterized" excess heat reaction and its associated charge transfer mechanism. The effect of electrode morphology and impurity poisoning may also play vital roles in achieving a high deuterium loading in metals.

## CONCLUSION

Unique stability regime, impressive kinetics, simple and inexpensive cell configurations constitute great potential for the employment of hydride-conducting molten salt electrolytes in energy storage and conversion technologies. These unique features for electrolytic applications are especially attractive in the intermediate temperature range where no other competitive candidates are available. High power devices have been demonstrated to be feasible in a number of experiments that show a consistent behavior of the molten salts in a Nernstian and Faradaic fashion. More fundamental characterization of the molten salt systems is still urgently needed to improve the performance characteristics.

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