

A Potential Shuttle Mechanism for Charging Hydrogen Species into Metals in Hydride-Containing Molten Salt Systems

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ABSTRACT

This paper proposes a "shuttle mechanism" in the hydride-containing molten salts under severe charging conditions. Our previous work reported that the use of elevated-temperature deuteride-containing molten salts promises great potential for charging deuterium into metals for excess heat generation. Substantial excess heat was measured occasionally but was difficult to reproduce, which reduced the prospect of this technology. We believe an understanding of the reaction mechanism is critical for reproducibility.

The proposed "shuttle mechanism" is based on the interpretation of the polarization behavior for various cell operating conditions. An attempt has been made to understand the reaction(s) responsible for the excess heat generation in spite of the complexity of the electrochemistry of this molten-salt system compared to heavy-water electrolysis. We examined the oxidation potentials reported in the literature and compared with results obtained from polarization techniques.

1. Introduction

The reducing environment of the eutectic LiCl-KCl system incorporated with excess LiH has been proposed [2] for preparing "hydrogen-transparent" interfaces to enhance metal-hydrogen interactions without interference from surface oxides. It is particularly important for base metals, e.g. Ti, V, Nb, and Zr, that usually have oxides. The narrow stability of LiH at very reducing potentials is shown in Fig. 1. This narrow stability window of LiH, on the other hand, provides an additional potential range suitable for imposing a high hydrogen activity on metals, as the shaded areas in the figure show. We call this regime the "Window of Opportunity for Excess Heat (WOEH)." The lower limit of the WOEH starts from the reversible D^-/D_2 potential where the hydrogen partial pressure is 1 atm at the particular temperature. The upper limit is constrained typically by the chlorination of the specific metal.

The redox potential for metals in the eutectic LiCl-KCl system has been reported in the literature [6,7,9]. This information, although for equilibrium conditions, is useful for interpreting reactions during the

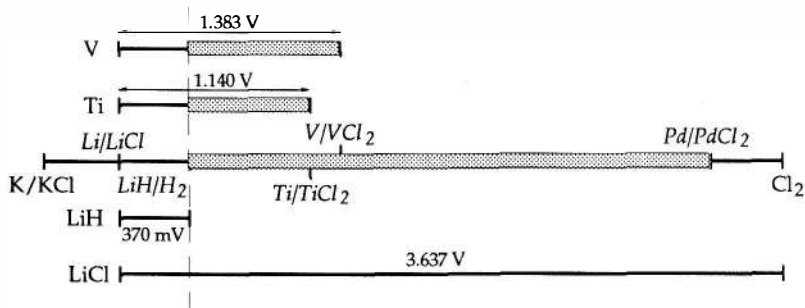


Figure 1. Immunity of V, Ti, and Pd in the molten salt melt at 700 K. The shaded areas represent the "Window of Opportunity for Excess Heat" (WOEH) for V, Ti, and Pd, respectively.

charging conditions and for selecting materials for molten salt cells. Pd exhibits a wide range of stability and thus has an optimal WOEH.

We reported two intriguing events of excess heat production using molten salt techniques [3-5]. Thermochemical considerations cannot explain the excess heat anomaly. ^4He enrichment found in the deuteride sample [3] seems to support the results reported by Bush et al. [1]. However, the complexity of the molten salt system causes difficulty in reproducing excess heat on demand. We believe a understanding of the electrochemical behavior of the molten salt system will help us achieve reproducible excess heat generation.

2. Methods

A typical molten salt cell comprises:

"LiAl"/Al | LiCl-KCl eutectic, excess LiD(H) | M; M=Pd or Mo.

The "LiAl"/Al mixture services as a secondary reference electrode as well as a Li reservoir, while the choice of Pd or Mo depends on the need for D(H) absorption. The cell was operated in a controlled argon atmosphere with minimal oxygen and moisture content. Voltammetry was conducted using a PARC 173 potentiostat with a PARC 175 Universal Programmer or a HP-3325B Synthesizer/Function Generator.

3. Results

Fig. 2 is a cyclic voltammogram which displays a concentration dependence of the polarization behavior in a semi-quantitative manner. The relative concentration was calculated from the charge (by integrating the current over the time) involved during the polarization cycles. This result demonstrated that a continuous cycle has a noticeable effect on the polarization behavior at high potentials as LiD became depleted in the melt. Table 1 lists a series of possible reactions and their potentials obtained from the thermodynamic data [4].

4. Discussion

As we considered a number of possible reactions we found that:

1) Pd tends to evolve, rather than absorb, hydrogen, according to the reversible cell potentials. However, under a low-current-density charging, the absorption and hydride formation dominate, attributing to

overpotentials associated with each process.

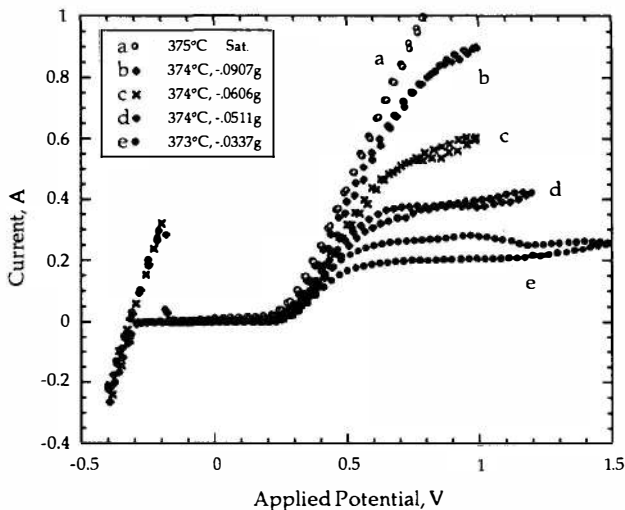
2) The cyclic voltammogram (Fig. 2, curve a) displays two distinct peaks: one located at -307.7 mV and the other at about 150 mV vs. an "LiAl"/Al reference. The peak at -307.7 mV is assigned to the reversible Li^+/Li reaction, similar to that reported by Wen et al. [8]. The peak at about 150 mV is assigned to deuterium gas evolution (expected at 106.7 mV at 648 K). The gas evolution is almost irreversible, as expected, since no reverse peak is found. The curve also exhibits curvatures for activation and transport-limiting regimes, respectively.

3) According to the redox-potential series, we assume the cell reactions varied with LiD concentration in the melt, resulting in various chloride formations. The formation of LiAlCl_4 was expected at about 1.1 V. We detected Al deposition on Pd using the SEM/EDX technique. Al seems to result from a further oxidation of AlCl_4^- at the anode. ZnCl_2 formation was next to follow, as Zn was also detected on the Pd surface by SEM/EDX. The Zn deposition might follow a similar route as ZnCl_4^{2-} being oxidized to Zn on the Pd anode at potentials higher than 1.73 V.

4) The FeCl_2 formation occurs at about 2.02 V, while the FeCl_3 formation is at a higher potential of about 3.10 V. Fe was an impurity introduced by the current leads. The two reactions exemplify the corrosion of leads in the melt, which often caused failure of the cell.

5) Finally, an interesting shuttle reaction depicts the conversion of deuteride into deuteron at a potential higher than 2.148 V. The presence of the deuteron under the charging condition could lead to an intriguing consequence at the anode. This situation suggests that a substantial polarization could result in a high concentration of D^+ at the anode and D^- at the cathode. The influx of D^- accelerated by the strong electric field to impact the concentrated D^+ at the anode might have an unpredictable but significant effect on the excess heat production. One may also consider a dynamic shuttle process of which deuteride was stripped into deuteron at the anode and subsequently converted back to deuteride at the cathode.

From our reported polarization behavior in the excess heat events [4,5], we identified a possible scenario that corresponds to the excess



heat process. Due to a similar cell resistance as to what a LiD-saturated cell exhibits, we conclude that the transport property of the cell after a long charging remained similar to the original; however, the reversible cell potential changed to about 1.995 V.

Figure 2. Polarization curves of an Al|LiCl-KCl eutectic, excess LiD|Mo cell.

Table 1. Free Energy and Enthalpy of Reactions in the Molten salt Pd-D System at 700 K

Reaction	ΔG , kJ mol ⁻¹	Potential, V
1. $x \text{ LiD} + \text{Pd} + x \text{ Al}$ = $x \text{ "LiAl"} + \text{PdD}_{x x \rightarrow 0}$	26.363	0.273
2. $x \text{ LiD} + \text{PdD}_{0.5} + x \text{ Al}$ = $x \text{ "LiAl"} + \text{PdD}_{0.5+x x \rightarrow 0}$	12.41	0.129
3. $\text{LiD} + \text{Al} = \text{"LiAl"} + 0.5 \text{ D}_2$	7.00	0.073
4. $2 \text{ LiCl} + \text{PdD}_{0.5} + 2 \text{ Al}$ = $2 \text{ "LiAl"} + \text{PdCl}_2 + 0.25 \text{ D}_2$	606.637	3.143
5. $2 \text{ LiCl} + \text{Fe} + 2 \text{ Al}$ = $2 \text{ "LiAl"} + \text{FeCl}_2$	390.123	2.021
6. $3 \text{ LiCl} + \text{Fe} + 3 \text{ Al}$ = $3 \text{ "LiAl"} + \text{FeCl}_3$	898.839	3.105
7. $4 \text{ LiCl} + 4 \text{ Al}$ = $3 \text{ "LiAl"} + \text{LiAlCl}_4$	425.181	1.102
8. $2 \text{ LiCl} + 2 \text{ Al} + \text{Zn}$ = $2 \text{ "LiAl"} + \text{ZnCl}_2$	333.856	1.730
9. $0.5 \text{ LiCl} + \text{PdD}_{0.5} + 0.5 \text{ Al}$ = $0.5 \text{ "LiAl"} + 0.5 \text{ DCl} + \text{Pd}$	103.652	2.148

This potential seems related to FeCl_2 and/or D^+ formation. We further excluded the FeCl_2 formation to be solely responsible for excess heat based on the arguments of thermochemical data and mass balance. Therefore, it is most likely that the D^+ and D^- transport contributes to the current passing through the cell. Without an impeding surface layer, the high potential implies a high deuterium activity and loading in Pd.

5. Conclusions

- 1) D^+ formation may occur during high-current charging at over 2V, enhancing the deuterium loading for excess heat generation.
- 2) The Fe/FeCl_2 redox can help stabilize the D^+ formation.
- 3) The D^+/D^- shuttle process could maintain a high current at high potentials without exhausting LiD in the melt.
- 4) The control of the relative concentration of Li^+ , Fe^{2+} , D^+ , D^- and Cl^- in the melt seems crucial for the excess heat effect.

6. References

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