Recent Progress on Cold Fusion Research Using Molten Salt Techniques

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A novel elevated-temperature molten salt technique has been demonstrated for generating high-level excess heat. More than 4 MJ mol\(^{-1}\) D\(_2\) of excess heat, at least 600% over the input power, was measured in two incidents using a torched Pd anode and an Al alloy cathode in a eutectic LiCl-KCl mixture saturated with excess LiD above 350° C. No thermochemical explanation can account for this excess heat. Measurements on the hydrogen-based system showed the expected endothermic behavior.

The Pd samples were later examined for their morphology and for helium analysis. A porous microstructure of the samples was found. The electrolysis and deuteriding processes changed the morphology substantially. Enhancement of α-particles in the deuterided sample was detected, while the hydrided sample showed an opposite effect. The amount of the α-particles in the sample, however, was not commensurate with the measured excess heat.

Reproducibility of the experiments has been poor to date.

INTRODUCTION

The origin of excess heat found in the Pd-D electrolysis system at ambient temperatures, as reported by Fleischmann \textit{et al.} [1], has not yet been conclusively identified. Despite the confusion over whether it was nuclear in nature, this phenomenon offered a potentially inexhaustible, clean, source of energy.

A novel molten salt approach [2], using a Pd | eutectic LiCl-KCl molten salt saturated with excess LiD | Al electrochemical cell, has recently been demonstrated
to generate excess heat above 350°C. This approach offers considerable merits, such as high-grade heat, faster rates, high efficiencies, and a strong reducing environment permitting use of less expensive materials for utility applications.

The high deuterium activity at high loading seems critical to reproducing excess heat, as suggested by Fleischmann et al. [1] and reported by others [3]. The molten salt approach can achieve high deuterium activities at a much lower loading at elevated temperatures, as depicted in the Pd-H phase diagram [4].

Using molten salt techniques to study metal-hydrogen reactions has been reported [5-8], and the principles were explicitly described by Deublein and Huggins [9]. Liaw et al. [10] employed a eutectic LiCl-KCl mixture saturated with excess LiH to study the thermodynamic and kinetic aspects of the Ti-H system. A similar approach using LiD to generate excess heat in the Pd-D system is the focus of this work. Due to the similar chemical properties between deuterium and hydrogen, we often describe the deuterium system with no distinction from its hydrogen analog in this context, except the anomaly in excess heat.

**ELECTROCHEMICAL BEHAVIORS**

Hydrogen-transparent metal surfaces can be prepared in situ using a eutectic LiCl-KCl molten salt saturated with LiH [9]. In Figure 1, the stability window of some base metals, such as Ti or V, is shown to explain their immunity to corrosion in the molten salt environment. The presence of excess alkali hydride imposes a very strongly reducing environment of extremely low oxygen and water activities, as Figure 2 shows. Thus, most metal oxides are unstable and can be readily removed from metal surfaces, facilitating deuterium reaction with metals in a controllable fashion in electrochemical cells.

Dissociation of the alkali hydride in the electrolyte results in an alkali cation and a hydride anion, which can be readily transported, exhibiting a conductivity

![Figure 1. Immunity of Ti and V in the chloride melt at 700 K](image1)

![Figure 2. Ternary phase diagram of the Li-O-H system](image2)
typically of $10^{-1} \text{ cm}^{-1}$ [7]. Therefore, the excess heat effect can be tested using a cell, as described previously [2] (Figure 3). The cell half reactions are:

\[ \text{LiD} = \text{Li}^+ + \text{D}^- \]  
\[ \text{At the anode:} \quad \text{Pd} + x \text{D}^- = \text{PdD}_x + x \text{e}^- \]  
\[ \text{At the cathode:} \quad \text{Al} + \text{Li}^+ + \text{e}^- = \text{"LiAl"} \]

which give the total cell reaction:

\[ \text{Pd} + x \text{Al} + x \text{LiD} = \text{PdD}_x + x \text{"LiAl"} \]

with an endothermic reaction enthalpy, $\Delta H_r$, approximately 3 kJ mol\(^{-1}\) at 700 K [11]. At this temperature, the palladium hydride and deuteride are above the $\alpha$-$\beta$ two-phase immiscibility regime [4]. The reaction of Li with Al in similar molten salts is very fast and the phase transformation proceeds at high rates [12-14].

The $\Delta G_f$ for LiH is -40.25 kJ mol\(^{-1}\) at 648 K (375 °C) [15]. This corresponds to the reverse reaction of:

\[ \text{LiH} = \text{Li} + 1/2 \text{H}_2 \]

with an electrochemical stability window of 417.1 mV. A standard hydrogen reversible electrode (SHE) in the hydride electrolyte environment is thus 417.1 mV above a standard reversible lithium electrode (SLE). The "LiAl" | Al mixture has a constant potential, 308.4 mV above the SLE [13], over a wide composition range (Li=5.7-45.2 at.% [14]) at 375 °C, and can be used as a reference electrode. The hydrogen evolution reaction therefore occurs at 108.7 mV above the reference electrode, which is the reversible cell potential for a PdH\(_x\) (at $a_H = 1$) | eutectic LiCl-KCl with excess LiH | "LiAl" | Al cell. The potential for the deuterium system should be slightly higher, as shown in Figure 4, where a cyclic voltammetry was performed on a Mo | D\(_{2(9)}\) | eutectic LiCl-KCl with excess LiD | "LiAl" | Al cell.

Figure 3. Schematic drawing of the molten salt cell

Figure 4. Polarization behavior of a Mo | D\(_{2(9)}\) | eutectic LiCl-KCl w/excess LiD | "LiAl" | Al cell at 375 °C
EXPERIMENTAL ASPECTS

Experimental details regarding this experiment were described previously [2] and will not be elaborated here. Figure 5 shows some modifications of the recent cell design. This configuration allows on-line gas collection for quantitative analysis. Stainless steel dewar flasks show less degradation and are easier to handle than glass. Boron nitride can withstand the melt’s reducing vapor and provide good electrical insulation. Inserted into the cathode holder were thermocouples to assure consistent readings without local hot spots. The use of steel crucibles avoids the shape changes found with Al crucibles. However, Li activity is less controllable and may cause excessive electronic leakage and reactions with anode or current leads.

The heat balance of the cell was periodically monitored by thermocouples in an isoperibol-like calorimeter [2]. Calibration was conducted with an internal heater adapted from a standard Pt-resistance temperature detector from Omega Engineering, Inc., with its heating zone dimensions similar to the anode.

He analysis was performed by Rockwell International Corp. using a high-sensitivity mass spectrometer system that operates in the static mode and can measure as low as $10^{-11}$ atom fraction of $^4$He and $^3$He in solid metals.

RESULTS

Figure 6 shows the power excursions of a PdD$_x$ eutectic LiCl-KCl molten salt saturated with excess LiD | Al cell when subjected to high-current-density charging conditions. Significant excess power was measured above the input
power. Table 1 lists experimental variables and interpretations, in which excess heat is calculated under a pseudo-steady-state condition of a constant deuterium consumption rate. Figure 7 provides the calibration data for temperature-power conversion in Figure 6 and illustrates the marked power-temperature deviations in excess heat events. In this figure, other experimental data are also shown.

Integration of the difference between the two power curves in Figure 6 yields an excess energy of 5.02 MJ for this particular experiment, which was limited by the amount of LiD present in the melt. The charge applied to the cell during the charging period corresponded to 0.801 moles of D₂ gas. Thus, an excess heat of 6.26 MJ mol⁻¹ D₂, or 1096 MJ mol⁻¹ Pd, was obtained, similar to those shown in Table 1. In a particular case, where the charging current was 692 mA cm⁻², the resulting excess power gain was 1512%, in the range of 627 W cm⁻³ Pd.

Preliminary experiments based on LiH have been performed and no excess heat has been measured to date. A calorimetry result from the Pd-H system is shown in Figure 8, which agrees with thermochemical reactions, illustrating the correct response from the calorimetry technique.

The surface morphologies of the Pd samples are shown in Figures 9a and 9b.

Table 1. Experimental parameters and interpretation of data in excess heat events

<table>
<thead>
<tr>
<th>Cell voltage V</th>
<th>Current density mA cm⁻²</th>
<th>Heater power W</th>
<th>Electrochem. power W</th>
<th>Total input W</th>
<th>Output measured W</th>
<th>Excess power W</th>
<th>Gain %</th>
<th>Excess heat MJ mol⁻¹ D₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.230</td>
<td>606</td>
<td>71.91</td>
<td>1.94</td>
<td>73.85</td>
<td>86.76</td>
<td>12.91</td>
<td>665</td>
<td>- 4.15</td>
</tr>
<tr>
<td>2.188</td>
<td>290</td>
<td>69.25</td>
<td>0.63</td>
<td>69.88</td>
<td>79.24</td>
<td>9.36</td>
<td>1486</td>
<td>- 6.27</td>
</tr>
<tr>
<td>2.270</td>
<td>420</td>
<td>69.30</td>
<td>0.94</td>
<td>70.24</td>
<td>82.81</td>
<td>12.57</td>
<td>1337</td>
<td>- 5.83</td>
</tr>
<tr>
<td>2.453</td>
<td>692</td>
<td>69.25</td>
<td>1.68</td>
<td>70.93</td>
<td>96.34</td>
<td>25.41</td>
<td>1512</td>
<td>- 7.16</td>
</tr>
</tbody>
</table>
EDX results on the deuterided sample showed Fe and Zn contamination (Figure 10b) in contrast to the blank (Figure 10a).

The polarization of a Mo eutectic LiCl-KCl molten salt with excess LiD | Al cell at 375°C (Figure 4) shows a reversible Li deposition reaction occurred at -300 mV and a deuterium gas evolution at ~200 mV versus a "LiAl" | Al reference.

Figures 11a and 11b show the ⁴He analysis results for the deuteride and hydride systems, respectively. The enhancement of ⁴He in all four deuteride specimens, in one case 12 σ, is shown above the background level. By contrast, the hydrogen specimens show a decrease in ⁴He content after electrolysis, as severe cracking and embrittlement were observed in the hydride sample.

DISCUSSION

Thermochemical Aspects

Most thermodynamic data, such as enthalpies that represent heat associated with the reactions in the system, can be found in the literature (e.g., [15]). Table 2 lists possible chemical reactions and their corresponding enthalpies. All enthalpies are positive, indicating these reactions are endothermic in nature and should not contribute to any excess power or heat measured. This is verified by the work performed on the hydrogen system, as shown in Figure 8. Thus, the results from the deuterium system strongly suggest that the anomaly effect is non-chemical. The origin of the excess heat generation can only be attributed to a nuclear process or, perhaps, several processes that have yet to be identified.

Nuclear Evidence

The He analysis results indicate ⁴He was enriched in the deuteride sample. An opposite effect was observed in the hydride sample. Bush et al. [17] recently
Figure 9a. SEM micrograph shows surface morphology of the as-prepared blank sample

Figure 9b. SEM micrograph of the deuteride sample surface

Figure 10a. EDX elemental analysis of the blank

Figure 10b. EDX analysis of the deuteride sample

Figure 11a. $^4$He analysis for the deuteride system. Four specimens all show signals above background level.

Figure 11b. $^4$He analysis for the hydride system. Electrolysis reduced the $^4$He content.
Table 2. Enthalpies of reaction in the Pd-H(D)/molten salt systems

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \Delta H ), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{0.56}) LiH + Pd + (^{0.56}) Al = (^{0.56}) &quot;LiAl&quot; + PdH(^{0.56})</td>
<td>12.13</td>
</tr>
<tr>
<td>(hydride formation)</td>
<td></td>
</tr>
<tr>
<td>(^{0.56}) LiD + Pd + (^{0.56}) Al = (^{0.56}) &quot;LiAl&quot; + PdD(^{0.56})</td>
<td>13.68</td>
</tr>
<tr>
<td>(deuteride formation)</td>
<td></td>
</tr>
<tr>
<td>(^{8}) LiH + PdH(^{x}) + (^{8}) Al = (^{8}) &quot;LiAl&quot; + PdH(^{x+\delta})</td>
<td>23.05 2.13 (x=0.35)</td>
</tr>
<tr>
<td>(hydrogen dissolution)</td>
<td>29.74 (x=0.65)</td>
</tr>
<tr>
<td>LiH + Al = &quot;LiAl&quot; + 1/2 ( \text{H}_2 )</td>
<td>41.66</td>
</tr>
<tr>
<td>LiD + Al = &quot;LiAl&quot; + 1/2 ( \text{D}_2 )</td>
<td>41.95</td>
</tr>
<tr>
<td>2 LiCl + PdH + 2 Al = 2 &quot;LiAl&quot; + PdCl(_2) + 1/2 ( \text{H}_2 )</td>
<td>556.55</td>
</tr>
<tr>
<td>2 LiCl + PdD + 2 Al = 2 &quot;LiAl&quot; + PdCl(_2) + 1/2 ( \text{D}_2 )</td>
<td>555.17</td>
</tr>
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</table>

reported the detection of \(^4\)He in the effluent gas from electrolysis cells producing excess heat. This evidence suggested a nuclear scenario with \(^4\)He being the major product of the excess heat. The majority of \(^4\)He was not retained in the electrode but escaped to the effluent gas, possibly through microcracks or pore channels. This suggests the \(^4\)He was most likely produced near the surface region.

The mechanism of the \(^4\)He production has yet to be identified. While a large amount of heat was expected to be released, energetic nuclear debris or secondary reaction products have not been detected to date, which is difficult to explain by the conventional theory. The d-d\((^4\)He, \(\gamma\)) channel is less favorable than the \((^3\)He, n) and \((^3\)H, p) branches in conventional plasma fusion. No 23.8 MeV \(\gamma\)-ray has ever been reported, implying that \(^4\)He production, if any, is untraditional. The to-be-released 23.8 MeV energy represents the difference between the excited \(^4\)He* and \(^4\)He ground state. An explanation of heat release through interactions with the lattice (phonons) or electrons seems to lack of a plausible theoretical justification.

Assuming the 23.8 MeV was released by a pair of deuterium to \(^4\)He reaction, 6 MJ of excess heat combined from two experiments should result in \(1.6 \times 10^{18}\) \(^4\)He atoms. The \(^4\)He remaining in the electrode was estimated to be \(2.9 \times 10^{10}\) atoms, indicating that only \(1.8 \times 10^9\) of the \(^4\)He atoms produced by the reaction were retained in the electrode. Accordingly, the excess heat reaction consumed \(1.6 \times 10^{18}\) \(\text{D}_2\) molecules. Compared to the total 1.036 moles, or \(6.24 \times 10^{23}\) \(\text{D}_2\) molecules used, the excess heat episode occurred every \(2.6 \times 10^6\) events – indeed a small fraction. However, the fusion rate, if the assumption is true, was \(8 \times 10^{12}\) sec\(^{-1}\) d-d pair\(^{-1}\) – many orders of magnitude above that calculated by the conventional coulomb-barrier model.