

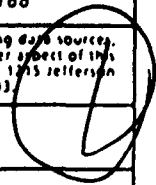
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**Molten Salt Techniques for Excess Heat Production
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Bor Yann Liaw

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MOLTEN SALT TECHNIQUES FOR EXCESS HEAT PRODUCTION AND THE LOADING ISSUE

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ABSTRACT

An interesting molten salt technique for elevated-temperature excess heat production has recently been reported, promising great potential for commercial applications. This technique shows improved efficiency due to a high-temperature operation, high-grade heat production and fast kinetics in metal-hydrogen reactions. This paper gives an overview of our work in molten salt electrolysis experiments using Ti and Pd as anodes in deuteride melts, in which substantial excess heat was found. This paper also presents some preliminary results using Ni and steel as anodes for electrolysis in hydride melts. Because the deuterium loading in Pd is considered a critical parameter for excess heat production, this paper will discuss this aspect and extend to elevated-temperature conditions.

THE MOLTEN SALT TECHNIQUES

Deuteride-Based Systems

Since the announcement of the Fleischmann-Pons effect in 1989, a team led by Liebert and Liaw has been working on a project using the molten salt techniques to verify such an effect. Earlier experiments in 1989 involved the electrolysis of Ti and Pd anodes in LiD-containing melts [1,2], in which commercially available Al alloys were used as the cathode. Operating at about 400°C, these molten salt cells produced excess power, ranging from 30% in the Ti-D system to more than 600% in the Pd-D system. No excess power or heat has ever been measured in analogous experiments using LiH-containing melts. However, replication of the excess heat effect in the Pd-D system has been difficult due to several problems, including chloride formations involving various electrodes and lead materials under a starving LiH(D) condition in the melts and severe cracking and disintegration from uncontrollable sample preparations and uneven charging conditions associated with the Pd electrodes.

Molten salt techniques provide an interesting alternative to the aqueous electrolysis methods for excess heat production, although the degree of control of these techniques need to be improved. Typical molten salt electrolytes used in our experiments are eutectic LiCl-KCl melts saturated with excess LiH(D). This electrolyte system has a melting point of 350°C and has a very high ionic conductivity of the order of $1 \Omega^{-1} \text{cm}^{-1}$, higher than any other proton-based conductors at these temperatures. The presence of LiH(D) in the melts introduces a very reducing environment, in which most transition metal oxides become unstable. This unique property provides an effective method of removing metal surface oxides in situ, resulting in "hydrogen-transparent"

ent" metal surfaces which facilitate the metal-hydrogen reactions. This technique is particularly useful for transition metals such as Ti, Zr, V, Ta, and their alloys, whose potential for excess heat production might be attractive due to their high solubility of hydrogen and deuterium.

The molten salt techniques are based on the electrolysis of LiH(D) through hydrogen-transparent surfaces to charge H or D into metal anodes and produce excess heat with enhanced kinetics and efficiency. Several interesting results were found in our successful excess-heat-producing Pd-D experiments:

- The excess power level, of the order of 9-25 W, was 6-15 times, or 600-1,500%, larger than the input electrochemical power ($\sim 0.6-1.7$ W, depending on current density) with no consideration of thermoneutral potentials. The excess power was a linear function of current density. The excess heat was of the order of $6-7$ MJ mol⁻¹ D₂, significantly larger than any known chemical reaction enthalpies. Figure 1 shows the input and output power excursion profiles at different current densities in this particular experiment.
- The total excess heat was of the order of 5 MJ, at a rate of about 9-25 W for 4 days. This magnitude of excess power is difficult to be explained by any storage mechanisms, contaminations or other artifacts.
- Four specimens from the spent Pd electrode have been analyzed by high-precision mass spectroscopy to quantify their residual He-4 content. All of them have shown enhanced He-4 content above the level of the background or a control Pd blank [3]. Although the amount of excess He-4 was not commensurate with the magnitude of excess heat, the increased He-4 content was a surprise to us since a similar H-based experiment showed an opposite result. Figure 2 shows the He-4 enhancement in the Pd specimens versus those of the background and the virgin electrode used as a control.

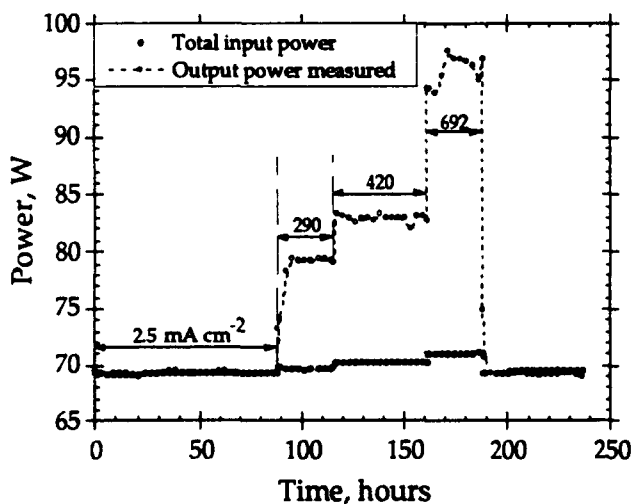


Figure 1. The power excursion curves of the inputs and outputs during a charging experiment using a Pd anode and an Al alloy cathode in a D-melt. Charging current densities are indicated. For detailed experimental parameters, please refer to refs. 1 and 2.

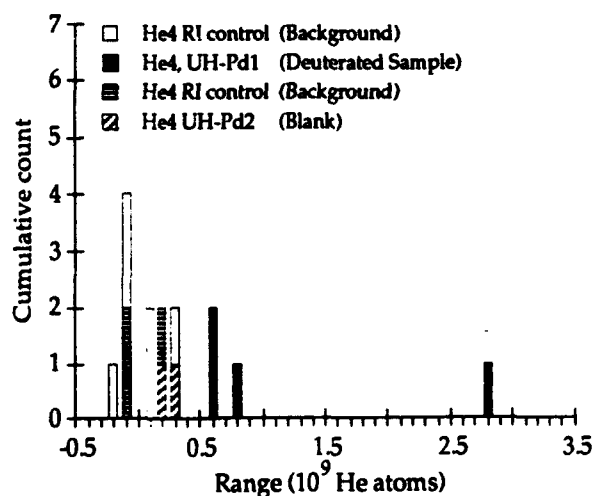


Figure 2. He-4 analysis results of the spent Pd anode and a control sample. All four specimens of the anode show increased He-4 content, although the amount was not commensurate with the excess heat measured.

Electrochemical Characterization

Because of the irreproducibility of the molten salt techniques, substantial effort has been made to study the electrochemical behavior of the electrodes in the molten salt system. Cyclic voltammetry technique and polarization studies [4,5] were conducted in the H-containing melts using various anode materials, including Pd, W, Mo, Al and Ni. These studies have led to the understanding of the effect from impurities such as Si, which acts as an inhibitor to the hydrogen evolution reaction. The results also indicate the LiH concentration can alter electrochemical behaviors and reaction paths. When LiH concentration is low, increased chloride activity can promote the metal chloride formation that corrodes the electrode and the lead, leading to the failure of cell operation. It is important to control the type of impurity present in the melt and its concentration to facilitate the Pd-hydride formation, thus enhancing the loading.

Hydride-Based Systems

These electrochemical studies also led to a more recent calorimetric investigation of the Ni-H system in the molten salt [6], in which excess power was measured, similar to those reported by several groups using carbonate-electrolyte light-water electrolysis and Ni cathodes at ambient temperature. Preliminary results showed that some low level of excess power was measured during the galvanostatic charging process with different current densities. The excess power (~0.5 W) was of the order of 30-100% of the input power. If we take the thermoneutral potential from various possible cell reactions into consideration, the gain of the excess power was even higher, of the order of several hundred per cent. Although the Ni-H experiments seem quite reproducible, the magnitude of the excess power however is low, unlike the Pd-D results. The origin of the excess power in this Ni-H case is unknown and may be caused by side reactions or other artifacts, which need to be investigated further. However, in a similar electrolysis using steel as the anode showed no excess power.

THE LOADING ISSUE

It has been demonstrated in low-temperature heavy-water electrolysis experiments [7,8] that a threshold loading ratio of about 0.84 is essential for excess heat production. In all molten salt experiments so far, we have not been able to report the loading ratio related to the calorimetric measurements. It is inherently difficult in our elevated-temperature experiments, particularly in situ, to measure the loading ratio. The resistivity ratio (R/R^0) and gas volumetric techniques are two methods often used to measure the loading ratio in ambient-temperature experiments. The gas volumetric technique has recently been adopted by Okamoto and Nezu [9] at the IMRA Material R&D, Japan, to measure the loading ratio of H in Pd in the molten salt environments. They reported a very shallow loading, similar to what would be expected from the equilibrium phase diagram, in their Pd samples from electrochemical charging. Their cyclic voltammetry results, however, showed a series of anodic and cathodic peaks, quite different from what we have reported [3,4], indicating a very complicated environment in their electrolyte systems. According to the phase diagram reported by Levine and Weale [10] and the overpotentials often measured in our cells (~0.6-1.0 V), we can estimate the fugacity of the Pd anode to be about 10^{10} - 10^{15} atm. The relationship of pressure and fugacity reported by Baranowski and Wisniewski [11] can then be used to extrapolate the loading ratio during an effective charging. A range of $D/Pd > 0.7$ is thus obtained, which is quite different from those reported by Okamoto and Nezu.

The gas volumetric technique is less sensitive than the R/R° technique for time-dependent loading measurements in a dynamic charging situation. Nevertheless, reliable data between the R/R° and the loading ratio at elevated temperatures have not been established experimentally. The R/R° technique is difficult to be used in the molten salt environment due to the lack of a suitable insulating material in order to confine the cell geometry. In addition, the high conductivity of the melt makes the parasitic resistance of the electrolyte comparable to that of the electrode hence increases the difficulty of an accurate measurement. Despite these problems, the loading ratio is still an important parameter to be characterized for better control of the excess heat effect.

The issue of the threshold loading for observing anomalous excess heat effect is an interesting open question for both ambient and elevated temperatures. Although the necessity of such a threshold loading at elevated temperatures has not yet been demonstrated or verified experimentally, there is a consensus in this field that such a threshold loading should exist.

The underlying mechanism dictating how the threshold loading control the excess heat effect has not been revealed yet. The meaning of R/R° and its relationship to this threshold loading have not been discussed in great details, either. On the other hand, experimental evidence shows that R/R° could vary with the state of the electrode to some extent associated with the electrode preparation, heat treatment, history, and other metallurgical and material aspects such as microstructure and morphology, defect type and concentration, magnification and interaction of defects, stress state and distribution, etc. However, how well are these factors related to the origin of the excess heat should provide important clues to our understanding of the excess heat phenomenon. To seek such links, we have to carefully investigate these factors and their effect on the loading issue.

The threshold loading of $D/Pd=0.84$ at room temperature did not coincide with the crystallographically-ideal, saturated composition of $D/Pd=1$, of which deuterium will occupy all the octahedral sites in the lattice. This threshold loading did not coincide with the maximum of the R/R° curve at $D/Pd=0.72$, either. More recently, the possibility of a new γ -hydride phase was proposed. The structure of this phase has not been reported yet. It could be associated with tetrahedral-site occupancy. It could also be associated with a lattice distortion in which octahedral sites were distorted into a different symmetry due to partial site occupancy of deuterium. It could also come from a disordered-ordered lattice transition with preferred site occupancy. If the structure is anisotropic, it could exhibit a Jahn-Teller effect. This phase, if it exists, should be considered metastable, to only occur under certain extreme, non-equilibrium conditions.

In the case of elevated temperatures such as 400°C , according to the phase diagram of the Pd-H(D) system, it is difficult to conceive how a loading ratio of over 0.8 can be achieved through gas loading unless an extremely high hydrogen pressure was applied. The pressure-concentration-temperature (p-c-T) curves of the system indicate that the H(D) concentration in Pd decreases with temperature under an isobaric condition. The equilibrium H(D) concentration in Pd is rather low (<0.1) at low ambient pressures (<30 atm) and high operating temperatures such as 400°C . On the other hand, electrolysis is a dynamic situation which could be different from the equilibrium condition significantly. It is generally believed that electrochemically charging can achieve conditions beyond those from gas loading. If we believe the threshold loading is related to excess heat production through some crystal structure changes and/or defect interactions, it would be beneficial to consider the loading from a thermodynamic point of view to reveal more insightful aspects of the defect chemistry involved.

It is well known that crystal defect structure and interaction strongly affect the p-c-T characteristics. Wagner [12] has shown, from thermodynamic principles, the significance of the curvature of the p-c-T curves, or, in electrochemical sense, the coulometric titration curves in terms of stoichiometry of a solid compound, which is readily attainable from the following analysis:

Consider the compound $\text{PdH}_{\beta+\delta}$ involving H atoms in interstitial sites (H_i) of the Pd lattice and their vacancies (V_H) as the essential point defects, as described by a Frenkel disorder model. The excess H is the difference between the mole fractions of H_i and V_H ,

$$\delta = X(\text{H}_i) - X(\text{V}_H), \quad (1)$$

where $X(\text{H}_i)$ equals to the loading ratio, and PdH_β is presumably the stoichiometric composition of the hydride phase at a particular temperature. When the defect concentrations are low, interaction among defects may be neglected. We can then assume that

$$X(\text{H}_i) \approx a_H, \text{ and} \quad (2)$$

$$X(\text{V}_H) \approx a_H^{-1} \quad (3)$$

For the stoichiometric composition PdH_β , where $\delta = 0$,

$$X^\circ(\text{H}_i) = X^\circ(\text{V}_H). \quad (4)$$

We can rewrite

$$X(\text{H}_i) = X^\circ(\text{H}_i)(a_H/a^\circ_H), \text{ and} \quad (5)$$

$$X(\text{V}_H) = X^\circ(\text{H}_i)(a_H/a^\circ_H)^{-1}. \quad (6)$$

Substituting (5) and (6) in (1), we obtain

$$\delta = X^\circ(\text{H}_i)[(a_H/a^\circ_H) - (a_H/a^\circ_H)^{-1}] = 2X^\circ(\text{H}_i)\sinh[\ln(a_H/a^\circ_H)]. \quad (7)$$

A plot of $\ln(a_H/a^\circ_H)$ versus δ yields an antisymmetric curve with an inflection point at the ideal stoichiometric composition. We can thus determine the stoichiometric point for a solid phase at the inflection point of the coulometric titration curve. This behavior applies to the p-c-T curves of the Pd-H system at high temperatures above the 300°C critical point, and, indeed, distinct inflection points are identifiable. Thus, at 400°C, the stoichiometric point is at about H/Pd=0.38, according to the p-c-T curves reported by Levine and Weale [10].

Below the critical point, where the α - β miscibility gap presents, the p-c-T curve in the β -phase region is concave above the phase boundary (H/Pd>0.59 at 25°C) [13]. Neutron diffraction measurement, however, indicated that the hydrogen occupies the octahedral sites in Pd, thus leading to the belief that, at saturation, H/Pd=1 is the stoichiometric composition of the β -phase. There is no indication if the p-c-T curve turns convex and an inflection point exists that represents the stoichiometry as described above. Therefore, it seems that the defect chemistry may be different at low and high temperatures. Despite the difference, how the defect chemistry play the role to the maximum (H/Pd=0.72) of the R/R° versus loading ratio curve and the threshold loading (D/Pd=0.84) for the anomalous excess heat effect is an intriguing subject for future studies.

CONCLUSION

The molten salt technique is a unique approach to excess heat production at elevated temperatures, promising high grade heat and improved efficiency. Both the Pd-D and Ni-H systems were investigated, and excess power was observed, although the origin of these anomalies were not identified. The electrochemical behavior of the molten salt system is complicated by the presence of impurities. Control of the electrode material property and the impurities are critical for reproducibility. Although demonstration of a threshold loading to the excess heat effect in elevated-temperature electrolysis is lacking, the importance of this parameter is speculated. We are interested in investigating the temperature-dependent relationships among the stoichiometric composition of the hydride phase, the loading of the maximum R/R^0 value and the threshold loading of the excess heat effect. The correlation of these three loading values with the underlying defect chemistry may reveal some important crystal structure variations and associated defect interactions that may be related to the excess heat phenomenon.

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