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The Reaction of LiD with Water Vapor: Thermogravimetric and Scanning Electron Microscopy Studies

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The reaction of LiD with water vapor: Thermogravimetric and scanning electron microscopy studies

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Abstract

The kinetics of hydroxide film growth on LiD have been studied by the thermogravimetric method in nitrogen saturated with water vapor and by scanning electron microscopy (SEM) of samples that have been exposed to air with 50% relative humidity. The reaction probability is estimated to be $4x10^{-7}$ for LiD exposed to ambient air with 50 % relative humidity, suggesting that the diffusion through the hydroxide film is not the limiting step on the overall process at high moisture levels. The rate of growth is drastically reduced when the temperature is increased to 60 C.

Introduction

Low atomic number elements such as hydrogen, lithium and beryllium are essential parts of materials for neutron shielding applications. In ground-based reactors, water or hydrogen-containing materials are used since the weight of shielding materials is relatively unimportant. However, for applications that are weight sensitive, such as mobile nuclear reactor, lithium hydride is an ideal material to be used for neutron shield. The unique properties of this material include: high hydrogen content, high melting point, low dissociation pressure and low density.[1] Lithium hydride, unfortunately, has high affinity for water which, in turn, converts lithium hydride to lithium hydroxide and release hydrogen.

The interaction of LiH salt with water is strong. Depending on the partial pressure of water and the temperature of the salt, LiOH or $LiOH.H_2O$ film is formed. Due to a change in density, the film would be under stress. In addition, the film interacts with the underlying substrate to convert to Li_2O and releases hydrogen. More than two decades ago Myers[2] studied the LiOH/LiH interaction to release hydrogen, using ion-backscattering technique. Since then very little fundamental studies have been reported in the literature.

In the present work, using SEM and microgravimetric techniques, the interaction kinetics of water with salt at high concentration of water is examined.

Experimental

I. SEM studies

A single crystal of LiD is cleaved to obtain two perpendicular {100} surfaces for SEM studies. As a result of exposure to air with 50% relative humidity, the hydroxide starts to grow on salt surfaces. Since the hydroxide has a larger volume, tensile stress builds up as the hydroxide grows. At the yield point, the corner fractures to relieve the stress. The lines which develop on the hydroxide as it grows are the indication of the thickness at which point fracture takes place (Fig. 1). The observed growth, χ , by SEM is not the actual thickness of the hydroxide. SEM measures the thickness with respect to the starting corner. A portion of the hydroxide growth is obscured by the hydroxide growth perpendicular to axis of SEM as shown in figure 1. However, since the density of LiOH and LiD are known, the actual hydroxide thickness, X, can be easily calculated. The time evolution of observable hydroxide growth, χ , at 50 % relative humidity as monitored by SEM *in situ* is shown in figure 2. The calculated hydroxide thickness, X, as a function of exposure is shown in figure 3. The thickness varies linearly with exposure for films having thickness of the order of many microns or more. This suggests that unlike thin hydroxide films, the growth of thick ones are no longer controlled by the diffusion through the hydroxide film. The absence of a diffusion limitation does not necessarily imply that the lattice diffusion is rapid. The extensive microcracking observed during exposure offers a possible pathway for water migration to LiD/LiOH interface. The reaction probability, is defined here as the number of LiOH molecules divided by the number of water molecules striking at the surface, is estimated to be around $4x10^{-7}$. This value is six orders of magnitude lower than the reaction probability obtained on bare LiD surface.

II. Thermogravimetric studies

The weight gain in time as a function of temperature in nitrogen atmosphere saturated with water is shown in figure 4. The sample is LiD single crystal slab ($1cm^2$, 0.1 cm thick) cleaved and immediately pumped prior to the experiment. The measured weight gain rate is about 7.5 mg /hr at room temperature. This implies an oxygen uptake of $7.6x10^{16}$ atoms per second. The number of collision of water to the faces of the sample can be obtained from kinetic theory of gasses:

$$n = \frac{3.5x10^{22}\,P(Torr)}{\sqrt{M_{H_2O}T(K)}}\,A(cm^2) \qquad (1)$$

For saturated water the number of collisions is estimated as $1.7x10^{22}$. Therefore the reaction probability is about $4.5x10^{-7}$, in good agreement with SEM studies. It is interesting to note that the rate reduces by almost an order of magnitude as the temperature increases to 60 C. From then on the reduction in rate becomes small.

Summary and Discussion

The overall reaction rate consists of adsoption /desorption of water on the surface, transport through hydroxide film to the LiD and hydroxide interface and the reaction with salts at interface. Using modulated molecular beam mass spectrometry we have previously

examined the interaction of water with pure LiD at low dosage (about 10^{-7} Torr equivalent pressure). The results suggest that the reaction probability of water with salt is about 0.1 and is independent of temperature. However, as the oxygen concentration increases, the reaction probability decreases. At full coverage, the probability is estimated to be 0.007. As thin multilayer film grows on salt, an appreciable phase lag is observed on desorbed hydrogen suggesting that the reaction is controlled by diffusion through the film. However the stress is built up as the thickness of the film increases. Approaching yield stress, the film fractures to provide less resistance pathway for transporting water to the LiD/LiOH interface.

At thickness on the order of many microns and high water vapor pressure studied here (e.g. 50 to 100% humidity in air) the reaction probability is further reduced to $4x10^{-7}$. The rate of growth is linear with time as observed by SEM and thermogravimetric methods. This implies that the diffusion does not play an important role in the overall process for high levels of moisture exposure. This is may be due to the fact that the film is probably $LiOH.H_2O$ at room temperature as predicted by thermodynamics. Thermodynamics calculations suggest a phase transition to occur between LiOH and $LiOH.H_2O$ at around 50 C and at relative humidity above 15 %. A change in sticking probability associated with a transition from LiOH to $LiOH.H_2O$ explains the reduction of reaction probability. Further work to confirm this assumption is in progress.

The rate of hydride growth drastically reduces as the temperature is increased to 50 C. The increase in the desorption rate of water can account for the reduction in weight gain rate at such elevated temperature. This finding may assist in handling the material in some stages of salt manufacturing.

References

1. F. H. Welch, Nuclear Eng. Design 26, 444(1974).
2. S. M. Myers, J. Appl. Phys. 45, 4320(1974)

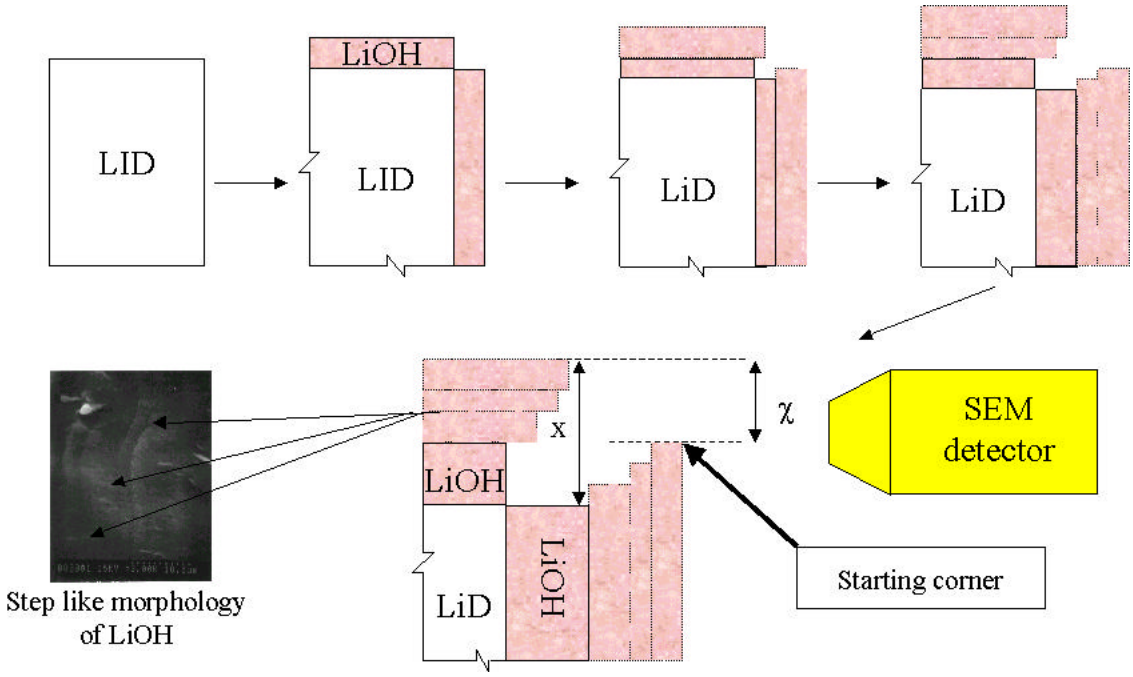

Figure 1. The growth of LiOH on the edge of a cleaved LiD single crystal is observed by a SEM

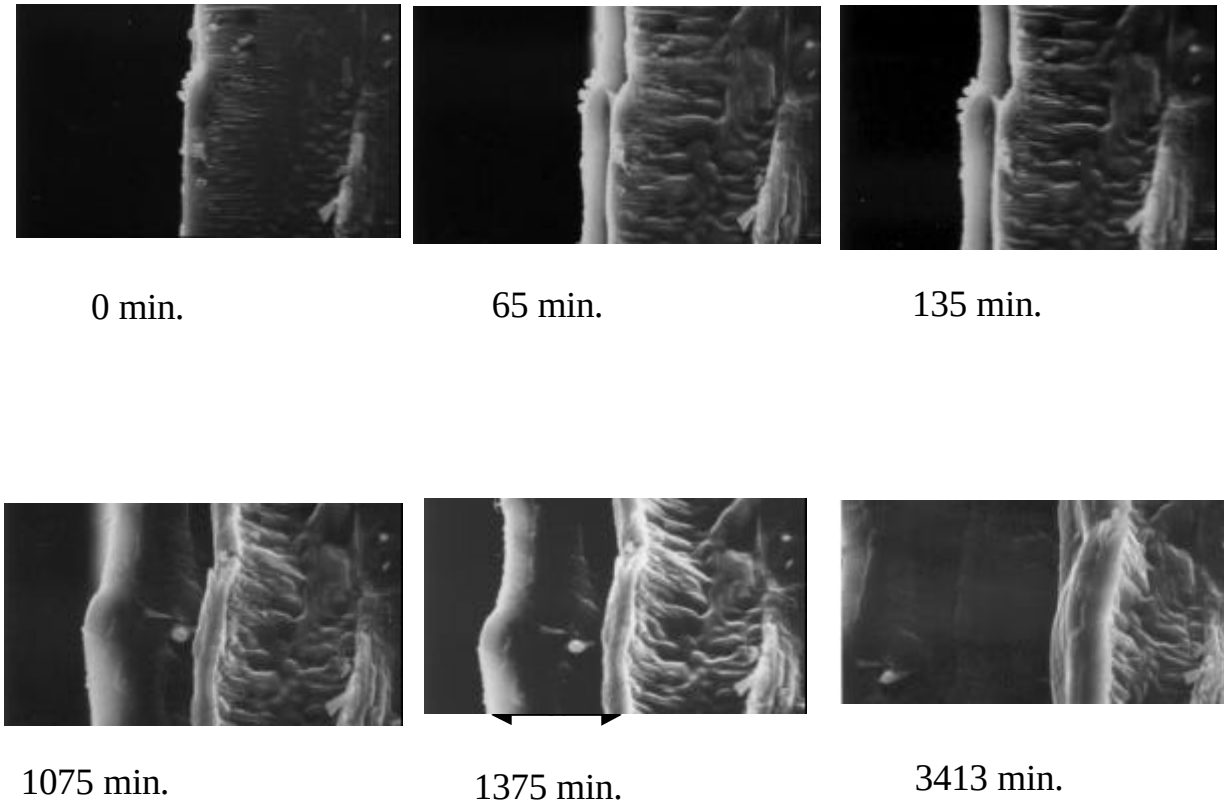

Figure 2. The growth of LiOH on LiH as observed by a SEM is rapid

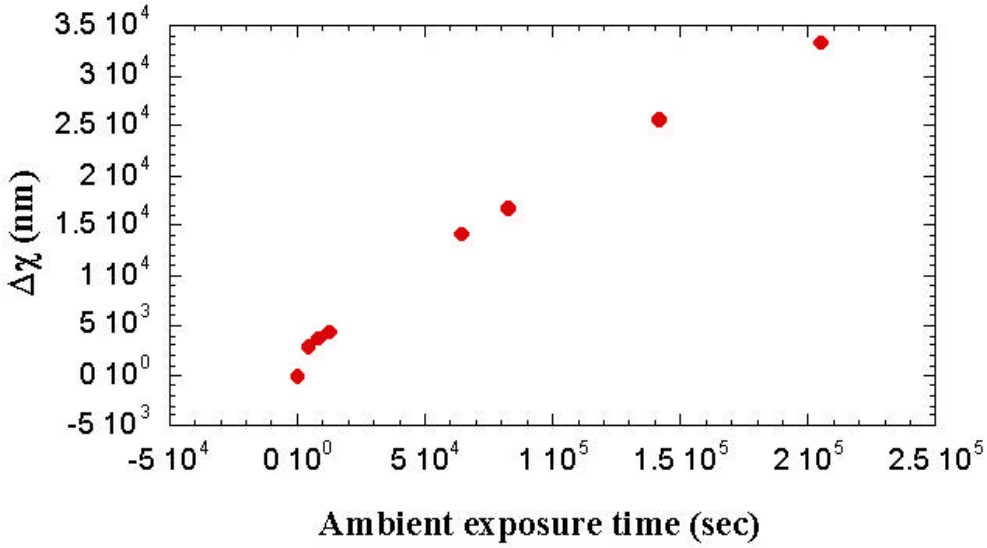

Figure 3. Lithium hydroxide growth as a function of temperature

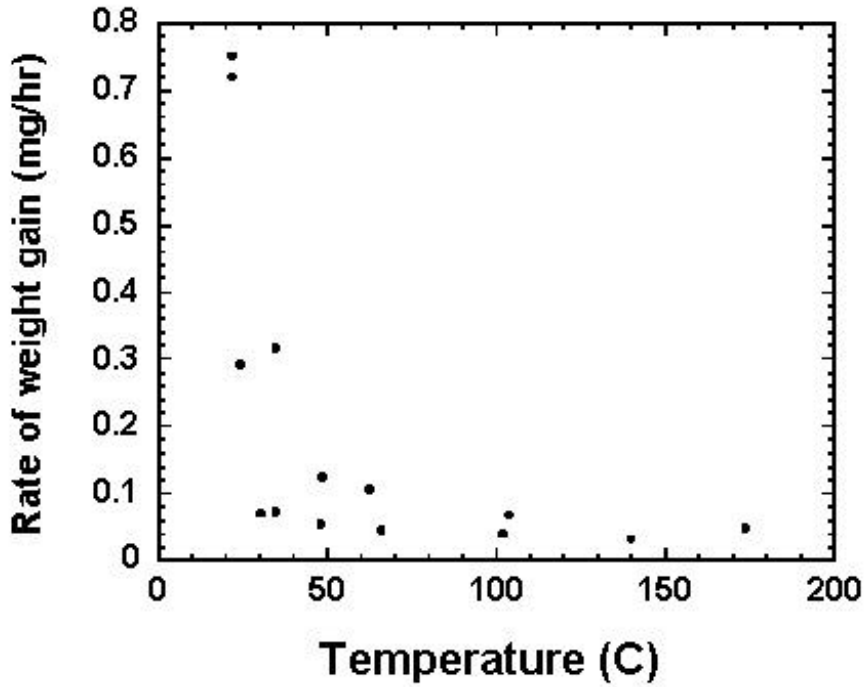

Figure.4. Temperature dependence of LiD weight gain as exposed to 100% humidity.