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Microbalance study of the corrosion kinetics of lithium hydride by water

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Abstract

The corrosion kinetics of commercial LiH powder (~100 μm, Alfa Aesar) by gaseous water in a humidified nitrogen stream was found to be constant in time and first order in gas phase water (<1% relative humidity). Data obtained using a customized microbalance system equipped with a precision water saturator, dew point analyzer, and magnetic sectoring mass spectrometer were used to derive a rough empirical rate expression for the corrosion of the powder by water at low (0.1–0.9%) RH values. The present data are consistent with two models: (i) the tri-layer model [J. Phillips, J. Tanski, Int. Mater. Rev. 50 (2005) 265], and (ii) rate control by diffusion through a barrier layer.

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1. Introduction

A recent review of the corrosion of lithium compounds in the literature due to interactions with atmospheric gases contain novel and simple models to explain both LiH corrosion by water and the thermal decomposition of the corrosion layer [1]. Although the models presented were shown to be consistent with the present body of literature, the existing data base is insufficient to buttress unequivocally all key aspects of the proposed models. There is a need for additional experimentation designed to directly test various aspects of the models. There is also a need for reliable kinetic data for input into quantitative corrosion models.

Aspects of the new model (Fig. 1) that relate to the structure and mechanism of growth of the corrosion layer that forms upon the exposure of LiH to water are central to the present work. In brief, it is postulated that initially H_2O interacts with LiH to form a thin (ca. 100 Å) layer of Li_2O, with the release of hydrogen. Once Li_2O reaches its ultimate thickness, water continues to interact at the Li_2O/gas interface to form LiOH with no release of hydrogen. The mechanism then changes to one in which some of the adsorbed water diffuses through the LiOH layer to react with Li_2O at the Li_2O/LiOH interface and produces more LiOH. Some of the H_2O diffuses even further to react with LiH at the Li_2O/LiH interface to form fresh Li_2O and release hydrogen. The net result of this postulated process is that the Li_2O layer is reacted away/recreated at an equal rate such that the Li_2O layer quickly reaches a steady thickness. This reaction will also lead to a steady rate of hydrogen production. Moreover, this layer effectively ‘sinks’ below a steadily growing LiOH layer. Key predictions that follow from the model include: (i) for water reaction on a truly clean LiH surface, the ratio of hydrogen evolution/water reacted will drop quickly by a factor of two and then become constant, (ii) the corrosion rate will increase with increasing water concentration and (iii) the temperature dependence will be quite complex, even possibly displaying a negative activation energy. It is surprising to find that there is ambiguity in the data regarding all of these simple

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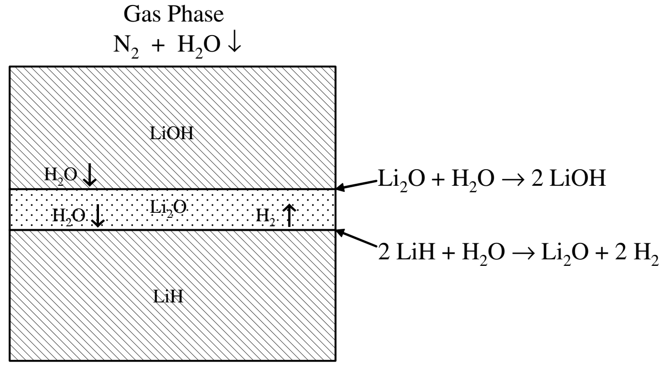

Fig. 1. Tri-layer model. Simple cartoon of the tri-layer model and the chemical equations postulated for the production of the different layers.

expectations in the current literature on lithium compound corrosion.

The present work was designed to fill some of the voids in the literature. Quantitative data was collected with the intent of testing key postulates of the model regarding the nature of LiH corrosion by water. The data collected also fill a need for empirical rate data for LiH reaction with water as a function of temperature and water concentration, as well as kinetics of hydrogen evolution as a function of the same parameters.

The key instrument employed was a microbalance system, equipped both with a custom gas feed system to precisely control relative humidity of gases passing through the sample chamber, and a magnetic sectoring mass spectrometer for determination of relative hydrogen concentration in the exit stream. The rate of weight change, recorded as a function of temperature, and with a measure of water concentration in a flow stream, empirical rate parameters can be easily calculated. These data also confirmed key, and apparently unintuitive suggestions contained in the recent review/model including the suggestions the net corrosion rate is a very weak function of temperature and almost unaffected by the thickness of the corrosion layer. While predicted by the model, an initial change in the ratio of hydrogen produced per water molecule reacted was not detected. This disconnect may simply reflect the fact that the LiH powders studied were slightly corroded prior to start of the experiment.

2. Experimental

The microbalance system (VTI, Hialeah, Fl USA) shown in Fig. 2 has several custom elements that allow rapid collection of reliable data on rates of reaction of water with hygroscopic materials. The microbalance is fully contained in a glove box (Fig. 2(G)) so that sample loading can be done without exposure to air or water. The concentration of water in the stream flowing through the microbalance sample chamber is precisely controlled. This control is accomplished by passing the gas stream (generally nitrogen) through a water-porous material (e.g. tygon tubing) placed in a water bath held at a controlled temperature (Fig. 2(B)). A steady water concentration can be selected by controlling one or all of the following factors: (i) the type of 'water porous' tubing in the water bath, (ii) the length of tubing inside the water bath, (iii) the temperature of the water bath or (iv) the gas flow rate through the tubing. In this work, only the temperature was changed.

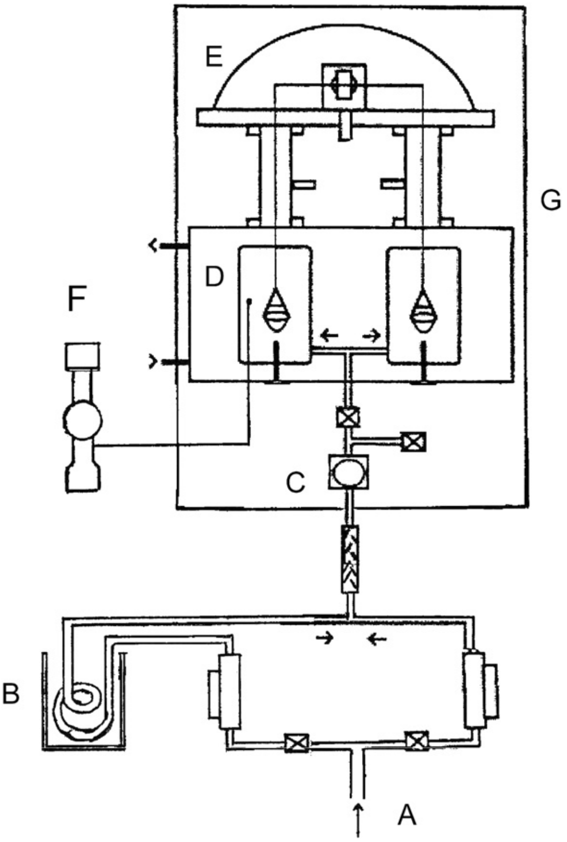

Fig. 2. Schematic of microbalance system: (A) gas inlet/mass flow controllers; (B) chiller/saturator; (C) dew point analyzer; (D) sample controlled temperature zone and sample chamber; (E) balance electronics section with independent gas purge; (F) magnetic sectoring mass spectrometer; (G) glove box.

The system is equipped with a dew point mirror analyzer that reports the dew point and water concentration in the input stream at all times. As shown in the data the dewpoint and water concentrations were remarkably steady once set. Thus, it was possible to calibrate the system. In this work the total gas rate was kept constant, and the system calibrated simply by changing the bath temperature and obtaining the humidity from the chilled mirror analyzer. The sample chamber temperature can be precisely set over a range from 25 to 80 °C (Fig. 2(D)). Evolved gases are collected just above the sample (Fig. 2(D)) with a capillary tube and 'pumped through' a magnetic sectoring mass spectrometer (Fig. 2(F), Vacuum Technologies, Inc. Oak Ridge, TN). This type of spectrometer was selected because they are superior for quantitative analysis of low

Z gases, particularly hydrogen and helium, relative to quadrupole mass spectrometers.

A Hitachi S-4200 field emission scanning electron microscope (SEM) was used for all SEM images. All images were collected at a low 1 kV acceleration voltage to minimize surface charging. The samples were placed on an SEM stub inside the glove box and then placed inside a sample vial. The sample vial was removed from the glove box and quickly transported to the SEM lab. The sample stub was removed from the vial under a dry nitrogen stream and inserted into the SEM. Sample exposure outside of the glove box was less than 15 s. The samples were 99.4% (metals basis) LiH powder obtained from Alpha Aesar (Catalog #41596, Lot #K30P09) with an average particle size of approximately 100 micrometers.

3. Results

The following conclusions can be made from the microbalance data presented in Fig. 3: (i) the weight increase, assuming both constant temperature and water concentration, is very close to linear with time, (ii) the corrosion layer growth rate increases with increasing water concentration, (iii) growth rate increases very slowly with increasing temperature, (iv) the relative concentration of hydrogen in the effluent stream is nearly constant until sample weight gain is greater than 100% and (v) the hydrogen concentration in the gas phase only decreases after the weight increases on the order of 100%.

In Fig. 3 weight gain vs. time is plotted for nine experiments, all run at the same temperature, but with different concentrations of water vapor. In some cases there appears to be a brief 'initiation' period, but within minutes a steady linear increase in weight is observed in all cases.

The data in Fig. 3 can be used to determine the rate and reaction order as a function of relative humidity (RH) at 25 °C. This is done in Fig. 4. The process is first order with respect to relative humidity. The normalized rate at 25 °C and 0.75 atmosphere pressure for this powdered material is given in Eq. (1a):

$$\begin{aligned}\% \text{ increase in weight/min} &= \text{normalized rate}\\ &= \text{RH}\ (\%_{\text{H}_2\text{O}}) * 6.4\\ &\quad \times 10^{-3} \left(\%_{\text{wt}}\ \text{min}^{-1}\ \%_{\text{H}_2\text{O}}^{-1}\right).\end{aligned} \tag{1a}$$

This can also be expressed in terms of water concentration (ppmv) at 25 °C:

$$\begin{aligned}\% \text{ increase in weight/min} &= [\text{H}_2\text{O}] * 1.6\\ &\quad \times 10^{-5}\ (\%_{\text{wt}}\ \text{min}^{-1}\ \text{ppmv}^{-1}),\end{aligned} \tag{1b}$$

where $[\text{H}_2\text{O}]$ is the concentration of water in ppmv. In developing this latter expression Eq. (1b) the relationship

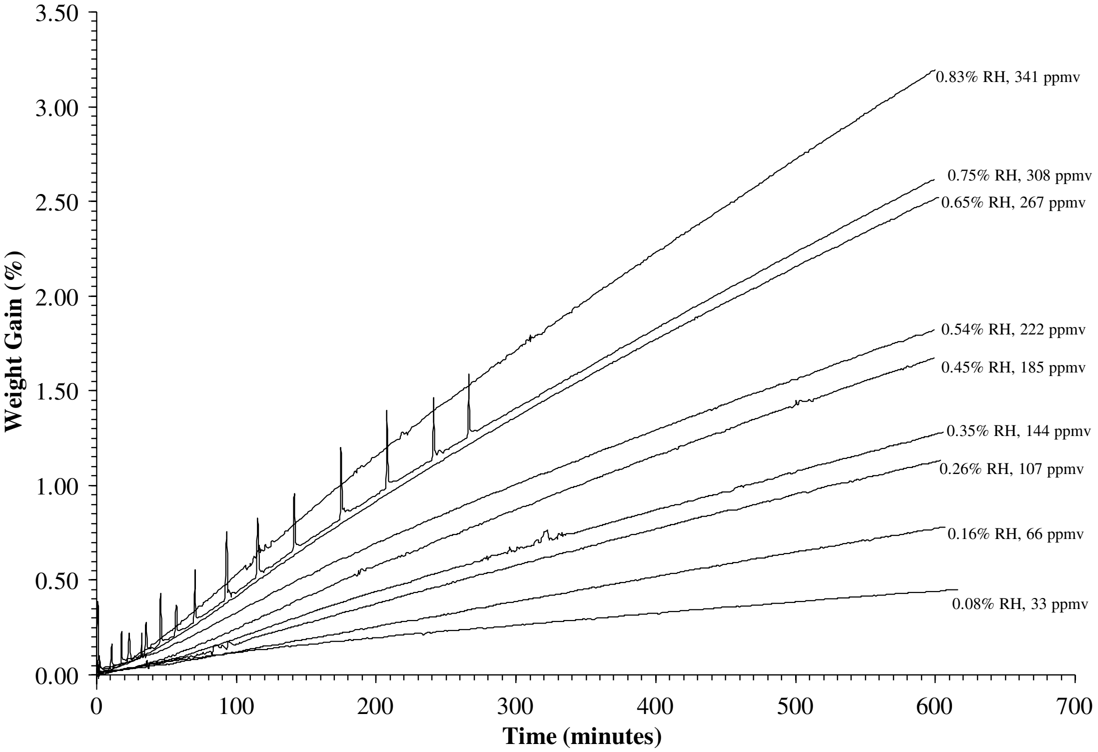

Fig. 3. Weight gain vs. time. The plot shows that the corrosion rate/weight gain is linear with time and increases monotonically with relative humidity for at least one order of magnitude of relative humidity values at 25 °C.

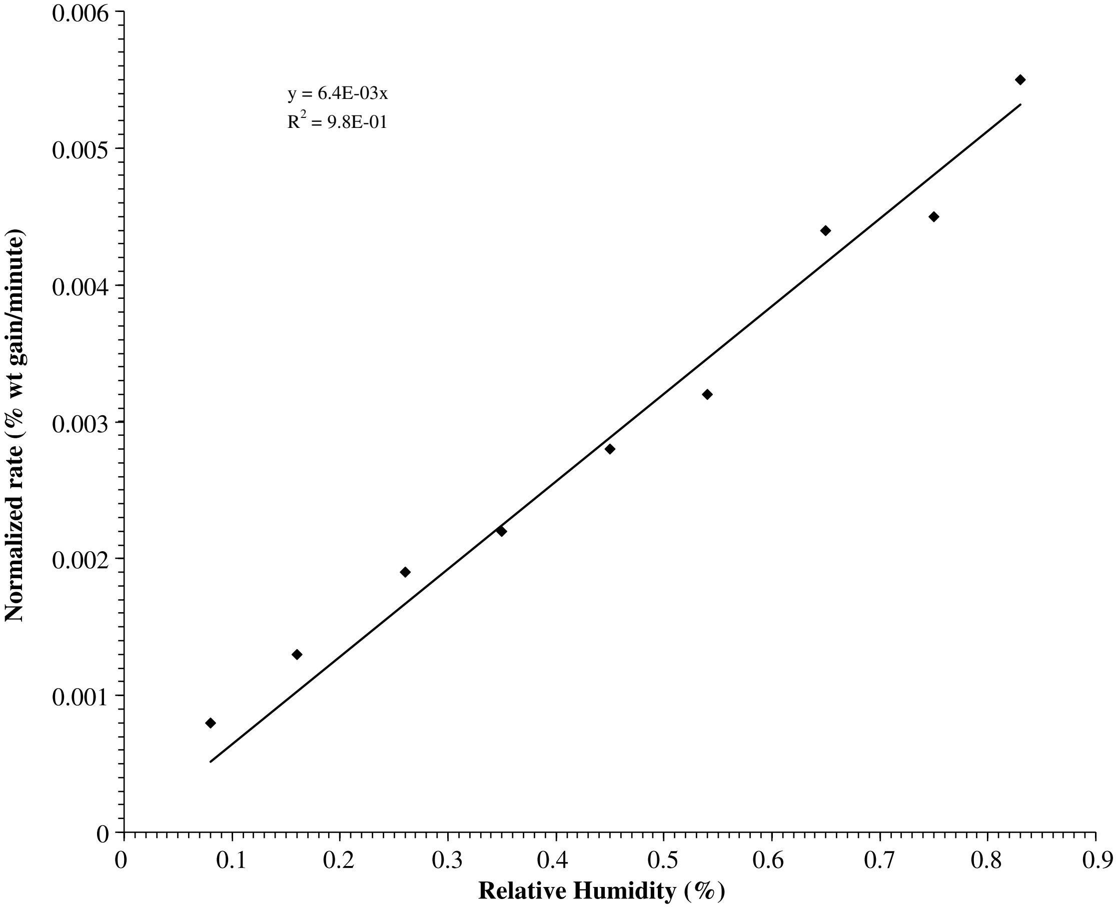

Fig. 4. Rate at 25 °C as a function of relative humidity (RH). This figure shows that the rate is linearly proportional (first order) to the relative humidity.

between RH and ppmv was corrected for the sub-atmospheric pressure conditions (approximately 0.75 atm) existing at Los Alamos, New Mexico USA (approximately 7500' above sea level). It should be noted that the initial measured rate (ca. first 10 min) is perhaps 25% slower than that given in the expressions. This deviation may reflect artifacts in the instrument (see Fig. 2). One of which may be that the sample chamber needs a few minutes to reach the RH levels measured for the input stream.

Assuming that the rate is proportional to the surface area, these equations must be converted to a rate per unit surface area, specifically the rate gain per m^2 of surface area. Analysis of SEM images (Fig. 5) suggests an average diameter grain size of 30 μm. A rough calculation based on the micrograph translates into a surface area, given an LiH specific gravity of 0.8, of approximately 0.2 m^2/g. Since this number does not take into account surface roughness or effective porosity, we employed the surface area determined on the unreacted surface using the BET method, 3.3 m^2/g. This leads to these expressions for rate:

$$\text{Rate (g/min)} = S\ (\text{m}^2) * \text{RH}\ (\%_{\text{H}_2\text{O}}) * 2.0 \times 10^{-5}\ \left(\text{g min}^{-1}\ \%^{-1}_{\text{H}_2\text{O}}\ \text{m}^{-2}\right), \tag{1c}$$

where S is the (BET measured) total surface area (m^2) of the material in question.Or we have:

$$\text{Rate (g/min)} = S\ (\text{m}^2) * [\text{H}_2\text{O}]\ (\text{ppmv})\ 4.8 \times 10^{-8}\ (\text{g min}^{-1}\ \text{ppmv}^{-1}\ \text{m}^{-2}). \tag{1d}$$

Moreover, the rate of weight gain is remarkably steady until there has been a very large weight gain suggesting that no kinetic factors change over time. There is a reduction in rate at high conversions (ca. >50%), probably due to the 'shrinking' of the reactive interface. Certainly the above expressions can be used with confidence in any modeling efforts for fractional conversions of less than half conversion. The data suggests that above 50% conversion the rate expressions (1a)–(1d) are reasonable estimates, and in fact represent 'upper bounds' on the rates.

The fact that the rate of growth increases with increasing temperature is seen in Fig. 6. All parameters except temperature were kept constant. The impact of temperature on the growth rate is very small. The activation energy is approximately 13.8 kJ/mole, a rate so low it is comparable to diffusion values (Fig. 7). Could water diffusion to the particle surfaces be the rate limiting step? This was tested by conducting a study of NaH (similar BET surface area, 2.2 m^2/g) corrosion in the same apparatus. At 25 °C and

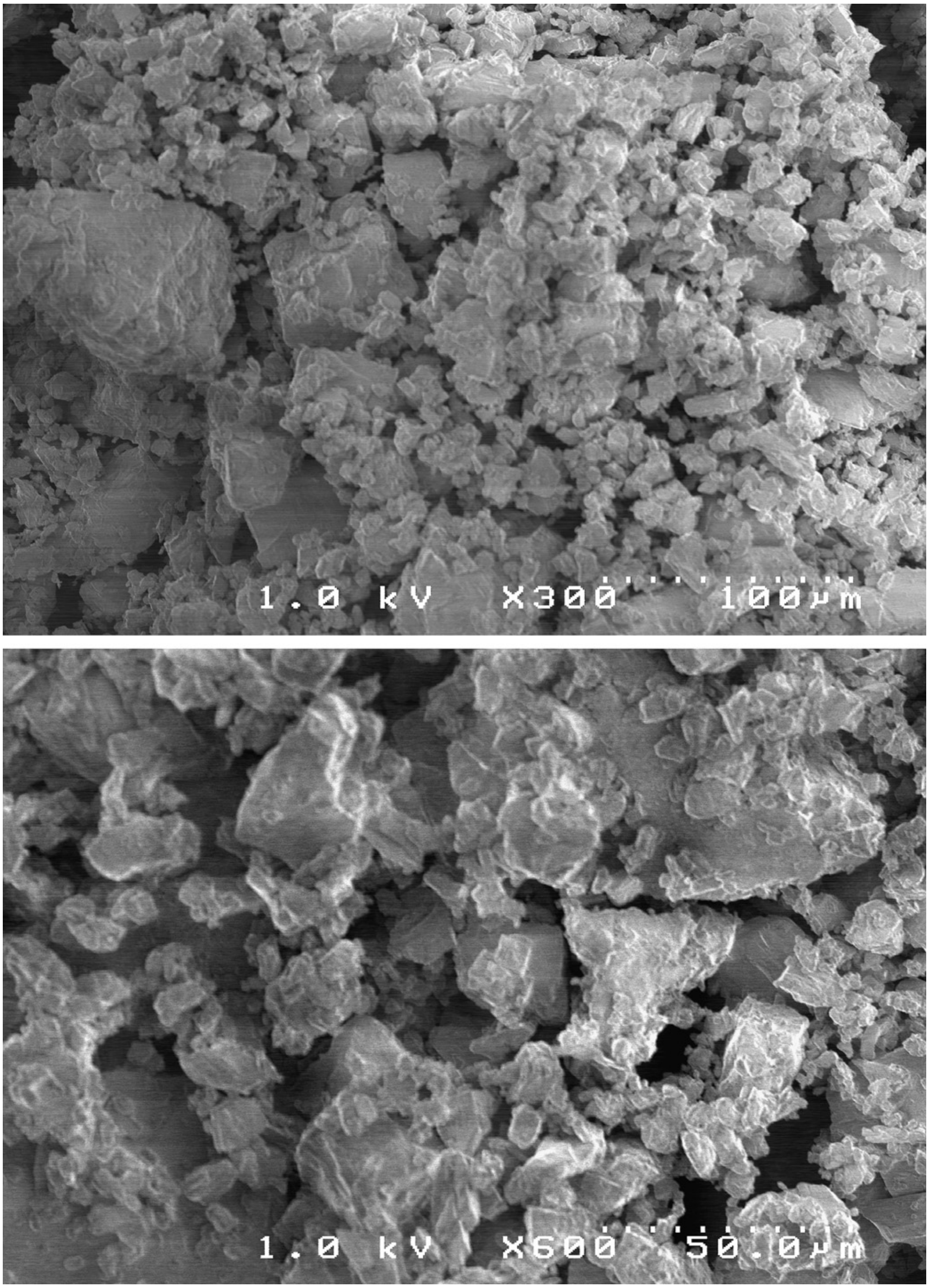

Fig. 5. SEM images of LiH. Both images show powdered LiH (Alfa Aesar) prior to reacting with water.

0.5% relative humidity, NaH corroded linearly with time and more than 3 times faster than LiH under the same conditions. Water diffusion through the gas to the particle surfaces is not rate limiting. This suggests that complex processes are at work, such as the model of 'tri-layer' corrosion developed by Phillips and Tanski [1]. It also implies that a 'flat' reacting surface model can be employed. That is, if gas diffusion is not rate limiting then the RH of water at all particle surfaces in the bed is the same. The flat reacting surface model is also consistent with the micrographs. The SEM work establishes that the pore spaces between particles are roughly of the same magnitude as the characteristic dimensions of the particles (>10 μm). Such large pores are consistent with rapid gas diffusion to all particle surfaces in the shallow bed (ca. <500 μm).

In the tri-layer model, the effective rate at any temperature is a complex function of temperature, relative humidity, diffusion rates and equilibrium concentrations of water in both Li_2O and LiOH. Still, it may prove useful to have an 'approximate' model of the process. A simple

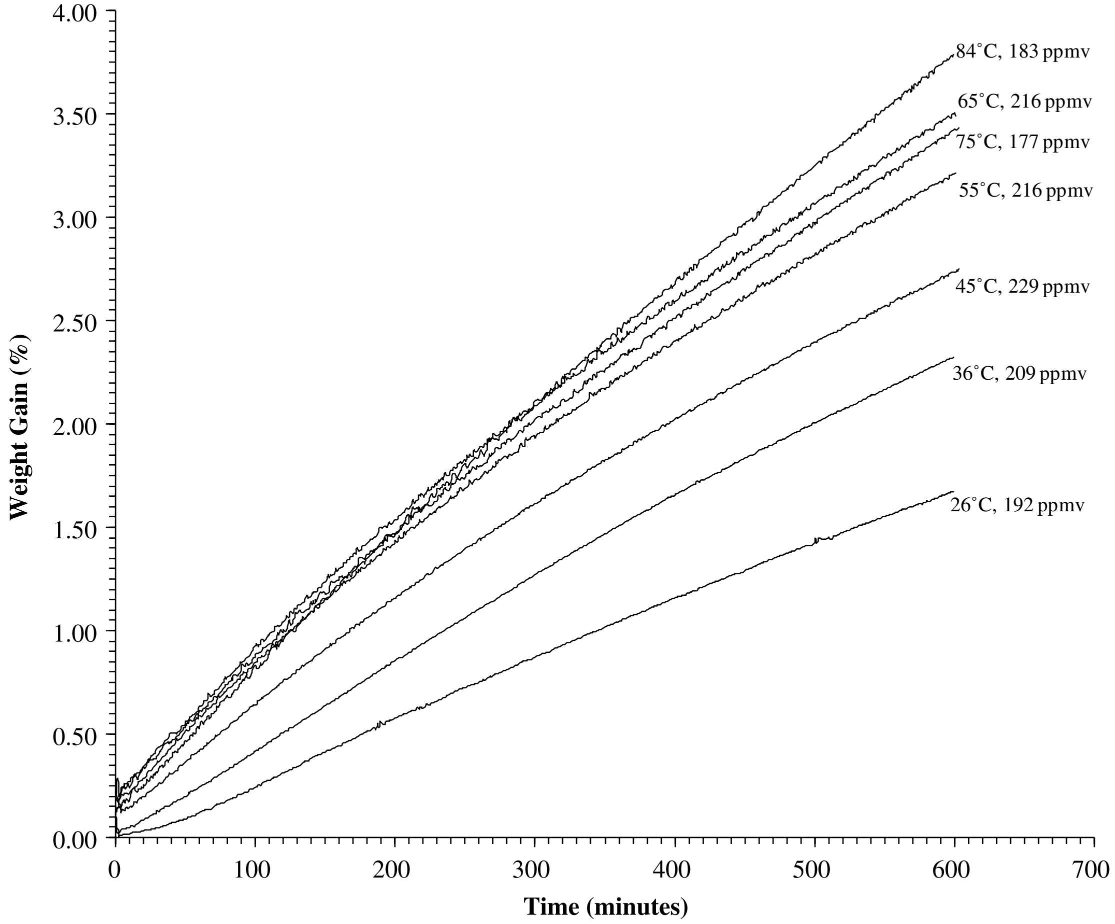

Fig. 6. Normalized rate as a function of temperature. Rates were measured over a range of temperatures at nearly constant ppm values of water (200 ± 20 ppmv). The rate goes up very slowly, if at all, between 55 and 85 °C.

relationship, approximately valid over the temperature range studied, is given below:

$$\text{Normalized rate } (\%/\text{min}) = (3.82 \times 10^{-3}\%\ \text{min}^{-1}\ \text{ppmv}^{-1}) * [H_2O]\ (\text{ppmv}) * (e^{((-13.8\ \text{kJ/mol})/RT)}). \tag{2a}$$

Similarly, incorporating the dependence on surface area into Eq. (2a), we have

$$\text{Normalized rate } (\%/\text{min}) = (3.35 * 10^{-2}\%\ \text{min}^{-1}\ \text{ppmv}^{-1}\ \text{m}^{-2}) * (S\ \text{m}^2) * [H_2O\ (\text{ppmv})] * (e^{((-13.8\ \text{kJ/mol})/RT)}). \tag{2b}$$

The apparatus did not lend itself to determinations of absolute concentrations of hydrogen in the effluent gas stream. However, for testing the model, it is sufficient to measure changes in the relative concentration of hydrogen in the effluent and this data is readily available. As shown in Fig. 8 the apparatus yields very constant data, indicating gas composition stability (including H_2O) over long periods of time. Indeed, the only concentration that changes is the hydrogen concentration, and that only changes significantly when the weight change due to corrosion is large, on the order of 100%.

Other raw data is provided in order to establish the quality of the data. Fig. 9, for example, shows that qualitatively the hydrogen evolution rate is 'flat', until the fractional conversion of the sample is more than 50% (at approximately 950 min – see Fig. 10). At that point, the reduction in the surface area of the unreacted core (assumes surface reaction rate controlling) will begin to slow the reaction rate in an observable fashion. In any event, this data shows that the hydrogen evolution data can be considered qualitatively indicative of trends in the process. There is no significant lag between the reaction of water and the evolution of hydrogen. There is also an apparent 'time constant' of about 4 min (Fig. 11) for changes in both weight gain and hydrogen evolution data once the water is shut off. This is consistent with a mean residence time of about 2.3 min for gases in the chamber surrounding the sample.

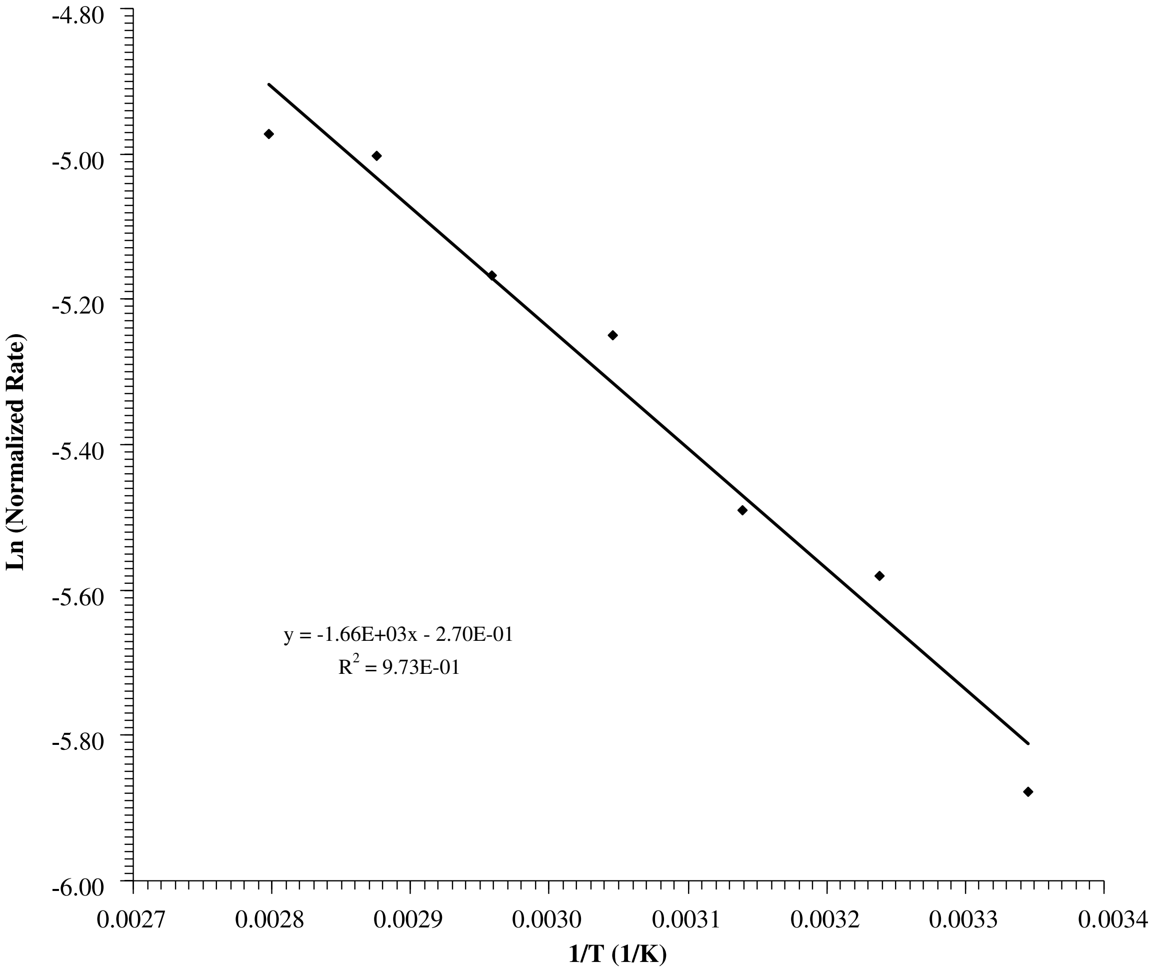

Fig. 7. Boltzmann rate plot. The data fits an activation energy/Boltzmann description.

4. Discussion

The value of the data collected for this study is fourfold. The primary value is that, it makes available for the first time reliable kinetic information regarding the rate of corrosion of LiH powder in low concentrations of water. This data can be employed empirically to predict corrosion behavior in complex systems including for example lithium based engines [1–4] and nuclear reactors [5]. In fact, (see Eqs. (1) and (2)) the data can be used to create empirically approximate models of corrosion. That is, the data can be used to create simple algebraic expressions relating corrosion rate to water concentration, and temperature to extent of corrosion as well as rate of hydrogen evolution, without reference to the mechanism. The equations can be used to directly model corrosion in any LiH system for which the surface area is known. Second, the model provides an additional test of the unusual findings reported elsewhere [1,6–10] that the process is only weakly a function of temperature or in fact has a negative activation energy for this process. In moderate contrast to earlier studies, activation energy was found to be very small, but positive. This difference may be a reflection of the different samples and methods employed. In this study a powder was used whereas in earlier studies a variety of sample types and apparatus were employed [10]. This could create differences in net diffusion rates large enough to produce a small positive activation energy in this case and a negative activation energy in the other system. Third, it provides qualitative data on hydrogen evolution consistent with the tri-layer model. Finally, it provides information that suggests the simple tri-layer model, that is corrosion occurs at a steady rate at sinking internal interfaces on either side of a very thin (ca. 100 Å) Li_2O layer is valid, after correction for ‘shrinking core’ effects. The shrinking core corrected model explains the constant weight gain at low (<50%) conversions and the gradual flattening of the weight gain curve at higher conversions.

The claim made above that the simple first order rate expression provided here is the simplest and easiest to apply for any modeling work, particularly for systems with a known surface area, may appear surprising. A review of the literature, however, shows this to be true. Most of the earlier kinetic work is reviewed elsewhere [1], but a review of some of the more important work is summarized below in order to more directly make the point that the present

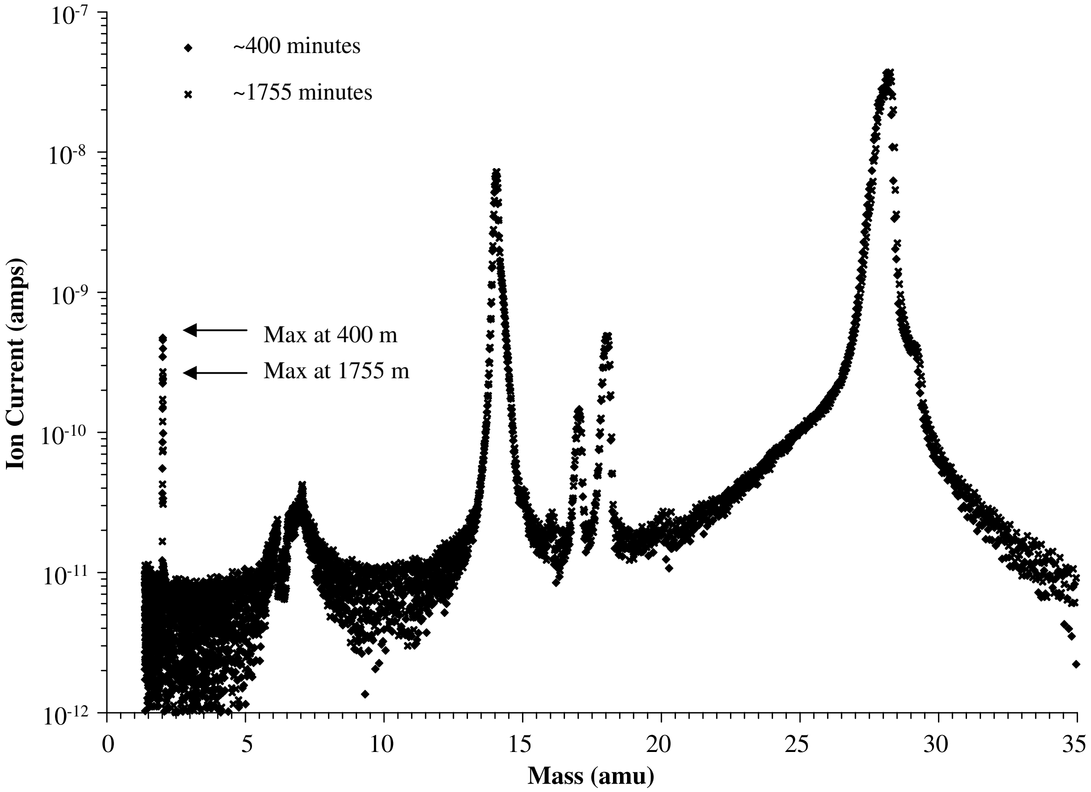

Fig. 8. Typical magnetic sectoring mass spectrometry data. The data show that all the mass peaks, except for hydrogen, are virtually constant over many hours. Only the peak at 2 amu (H_2) is changing with time. In this case the higher peak, taken after 400 min of water exposure is about twice the height of the signal taken after 1755 min. This corresponds to a slowing reaction rate, as seen in a decrease in weight gain rate as well (Fig. 10).

work provides rate expressions of unprecedented simplicity.

The earliest work on LiH/water reactions was that of Machin and Tompkins [11]. Very complex rate expressions were developed with multiple 'constants' that were reported to be 'constants' in name only as the constants were a function of the extent of reaction. There is some even earlier work but it regards kinetics of 'allied' systems, particularly water reaction with lithium metal [12,13]. For example, Deal and Svec [14,15] studied rates of growth of corrosion layers on lithium metal, but only at very high RH values. They concluded that the growth rates were logarithmic with time. It could be argued, however, in retrospect, that the data is linear once correction for 'shrinking core' effects is included. Moreover, those investigations included odd observations. For example below a specific, and relatively high RH value, the corrosion rate was reportedly independent of RH.

There are also a few papers that report rate expressions for LiH reactions with liquid phases. Rozenband [16] reported expressions for rates based on heat evolution data obtained from liquids containing more than 50% water by volume reacting with solid LiH. It was concluded that the LiH/water reaction rate is first order in water concentration; however, the reported activation energies were far higher than those obtained in the present work. Leckey et al. also developed rate expressions for liquid water reacting directly with solid LiH [6].

There is recent work containing kinetic data on water vapor reaction with LiH, but surprisingly none includes unambiguous kinetic expressions. Some of the best kinetic data is from Broughton [7,17]. In one case Broughton, using a very limited set of data, interpreted with the fractional life method, obtained a reaction order with respect to water, but no overall rate expression was presented [7]. Dinh and collaborators published a number of kinetic papers on LiH/water reactions, but none include a clear rate expression [9,18,19]. A recent report by Haertling et al. [20] contains data on the kinetics of the LiH/water reaction that does not include a rate expression. Moreover, some parameters of clear value in developing rate expressions are reported in inappropriate units in that work. At low RH values in the experiments water is reported as a flow rate, not a concentration. Perhaps the study which comes closest to developing a full rate expression is that of Kong et al. [21,22]. They developed a rate expression that can be employed in the event that water is not a limiting reactant. That is, the rate expression developed contains no water concentration term and is assumed to be valid only at very high RH values or in cases in which, due to low temperature or rapid delivery, water concentration is constant and 'high' at the reacting surfaces. Indeed,

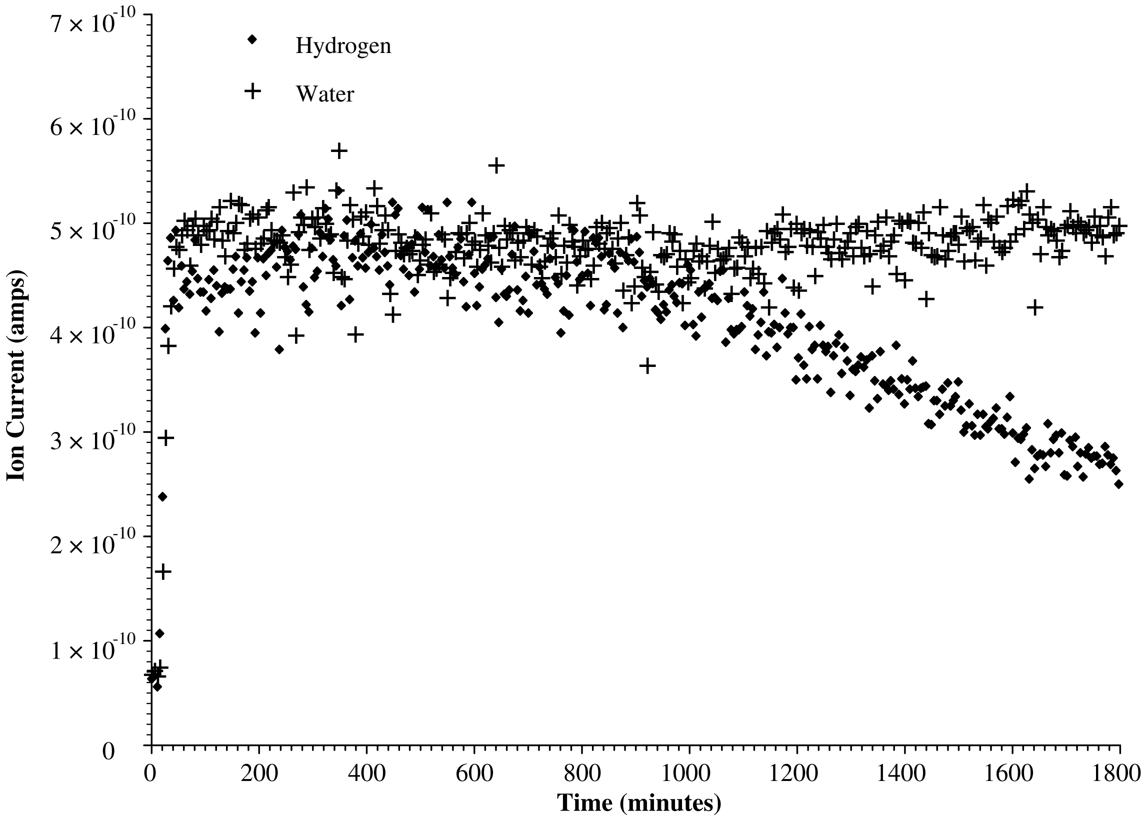

Fig. 9. Relative H_2 and H_2O vs. time. Gas containing water (2% RH, 60 °C) was only added after 20 min. The vapor phase water concentration (peak max values shown) is steady over many hours and significant corrosion (final weight gain was 160% of initial weight). Moreover, the evolved hydrogen rate is also steady until the unreacted core begins to shrink significantly (see Fig. 10). The absolute maximum signal strengths are not meaningful, only relative value is considered meaningful.

the goal of the work was to develop an expression for the maximum rate of hydrogen evolution due to the reaction of water with LiH. One difficulty they faced was the lack of reliable humidity control and independent determination of humidity. Still, these workers did reach two conclusions consistent with the main findings of the present study: First that the reaction rate is first order in water and second that there is only a very weak temperature dependence.

It is clear that on a simple empirical basis the kinetic expressions developed can be used in modeling. It is also interesting to determine if the data supports the tri-layer model and the earlier postulated mechanism of rate control, not by diffusion, but by reaction rate at interior surfaces [1]. In particular, three aspects of the data require some comment: (i) Is the data consistent with a shrinking core of unreacted LiH as required by the model? (ii) Why is the hydrogen evolution rate essentially flat from the start? Does not the model require a hydrogen evolution burst initially? (iii) Is the data consistent with an entirely different model, one in which there is a thin diffusion layer, possibly a carbonate, that effectively controls the rate of water transfer from the gas to the reacting 'tri-layer' structure?

An examination of the shrinking core model [23] does show that the data is consistent with that model. As shown in Fig. 10, the weight gain, even for a sample treated for more than 30 h, is consistent with the shrinking core model for a system in which the reaction rate at the surface of the unreacted core is rate determining. (The data is not consistent with the rate predictions in the event that the rate controlling step is diffusion of reactant through the corrosion layer.)

The second unresolved issue is the relative rate of hydrogen evolution initially, vs. the steady value, for perfect LiH. The tri-layer model indicates that the first 50 Å of corrosion of LiH should be only Li_2O. This thickness of the oxide (Li_2O) layer is consistent with both surface science [1] and calorimetric data [2,3]. Later, a net increase in LiOH is anticipated, via a process in which Li_2O is both consumed at the LiOH/Li_2O interface (no hydrogen) and produced at the same rate at the LiH/Li_2O interface (hydrogen). The initial process in which only Li_2O is produced should yield twice the hydrogen of the latter process per water molecule reacted (or unit weight gained), as in the latter process only half the water reacted produces free hydrogen. In this study, the tri-layer model predicted 'spike' in H_2 production at the start of the process was not detected. This may result from partial conversion of the LiH prior to the start of the measurement. The samples obtained were only 99.4% purity. The primary impurity

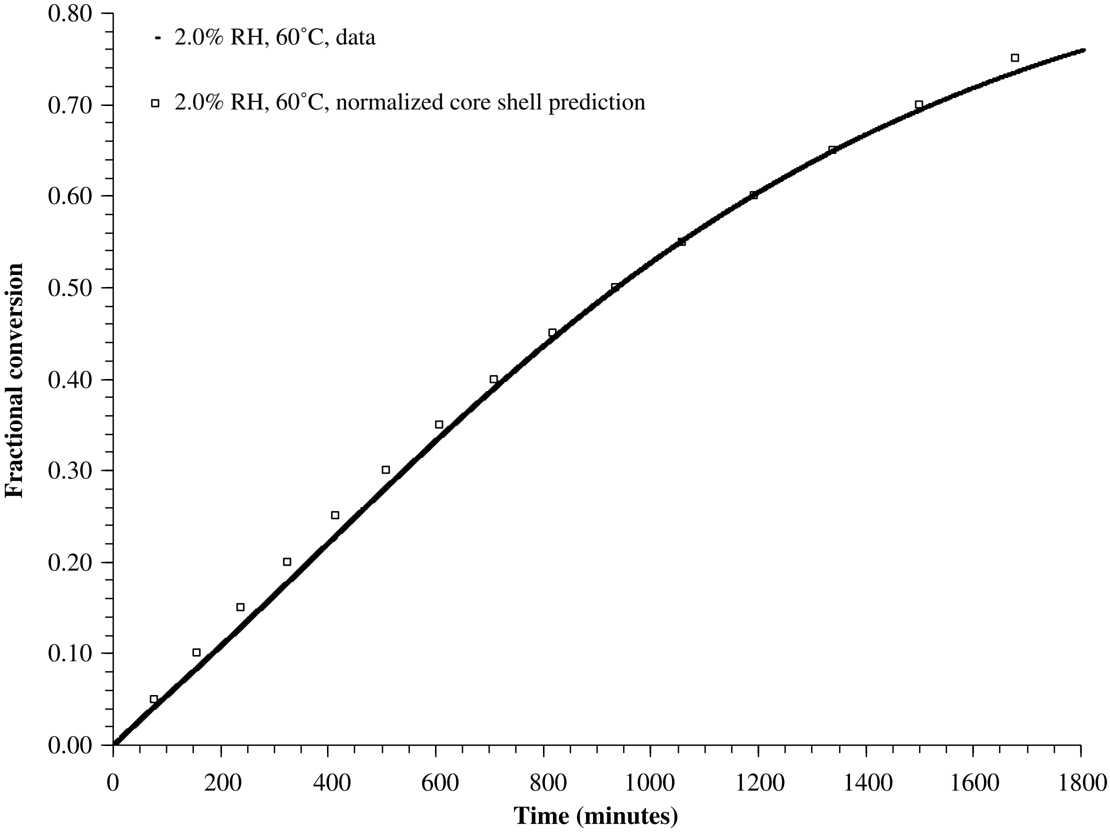

Fig. 10. Shrinking core model fits data. Data collected at 60 °C, 2% RH, was collected for 30 h (see Fig. 9 as well) to determine if the 'core shell' model in which the rate determining step was assumed to be reaction (e.g. $2LiH + H_2O \rightarrow Li_2O + 2H_2$) at the unreacted core (LiH) surface.

was oxygen, consistent with a partial conversion of the sample surface to Li_2O prior to placement in the microbalance. Also, the simple act of storing the LiH may have allowed a small amount of reaction between water vapor and LiH to occur, enough to create the initial Li_2O layer. In this case the generation of hydrogen should be steady with time until some of the grains in the powder are completely converted.

Can 'time averaging' of the hydrogen signal hide a spike? The flow rate is such that the mean residence time in the chamber above the sample is approximately 2.3 min. Some 'time averaging' necessarily takes place. This time averaging effect will 'hide' any oxide formation. Indeed, it is clear that even at the lowest RH values employed the rate of corrosion is sufficient to convert one layer in less than 5 s. Thus, approximately 25 layers, the entire thickness of the oxide will form, even in the lowest RH case, in less than 3 min. At most one hydrogen data point in the lowest RH case could show excess hydrogen. Moreover, as shown in prior studies, it is likely that the oxide layer was partially or fully formed prior to the deliberate input of water.

Another significant issue is the possibility that the observed kinetics are not fundamental chemical kinetics, but rather the 'kinetics of diffusion'. That is, a thin, but effective diffusion barrier could account for all data. Specifically, all data are consistent with a 'quad-layer' model in which on top of the tri-layer structure described above there is thin lithium carbonate layer. How? There is already data that supports the postulate that carbonate is a water diffusion barrier [1]. Moreover, if the reaction rate at the tri-layer interfaces is far faster than the rate of diffusion to the tri-layer, then a low activation energy would be expected (e.g. Eqs. (2)), and the reaction order with respect to water concentration in the gas phase would be first order. That is, the diffusion rate would be proportional to the reactive species concentration gradient in the constant thickness diffusion layer, and assuming the free water concentration in the tri-layer structure is near zero, would be proportional to the gas phase water concentration. Hence, the quad-layer hypothesis cannot be rejected on the basis of the available data. Future studies should focus on determining if there is carbonate on LiH samples and the effect of the thickness of such a layer on observed kinetics.

One final question: is the data consistent with the formation of a monohydrate layer on top of the LiOH, as suggested by others [5,12]? In those studies the formation of monohydrate was associated with an increase in the rate of weight gain, not observed herein. Also, for constant weight gain, observed here for conversion <50% monohydrate formation would reduce the rate of hydrogen produc-

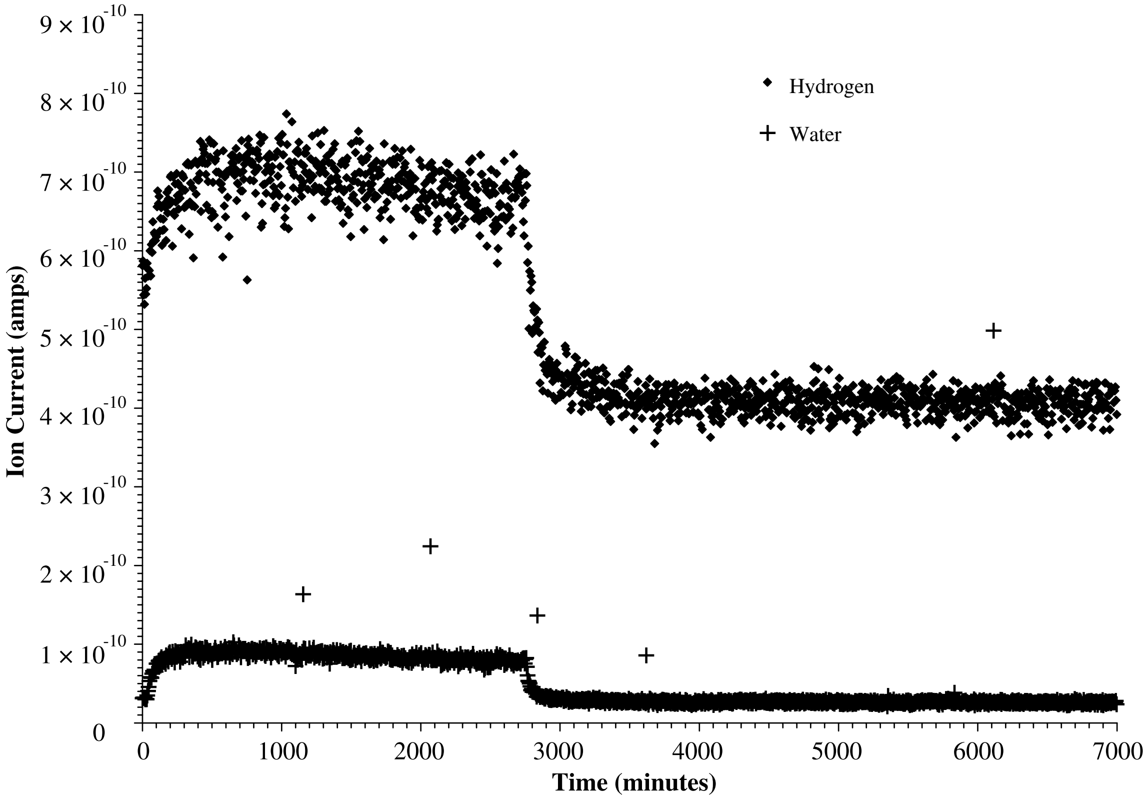

Fig. 11. Hydrogen tracks water. The relative hydrogen signal strength tracks the water concentration (2% RH, 25 °C) in the input stream. The system does not show evidence of hydrogen evolution during the period in which no water is input to the system ($t > 2900$ min).

ing reactions, hence hydrogen production would drop. This is not observed. Even at high conversions (>50%) hydrogen production rate declines at the same rate as weight increase declines. The failure to form monohydrate may reflect the very low RH values, and hence slow reaction rates, employed in this study.

5. Conclusions

Using a controlled temperature/atmosphere microbalance setup we generated data showing the effects of change in water concentration and temperature on the reaction of lithium hydride and water. From the data we generated kinetic expressions incorporating the temperature, water concentration, and surface area dependence on the rate of reaction. We also determined an activation energy for the reaction of lithium hydride with water from the temperature variation data. The technique and equations can be used over a wide range of temperature and water concentrations, and the generated rate tracks the data fairly well. The data show that the reaction is not diffusion limited, and fits well to a 'shrinking core' model.

Future work should focus on a number of issues. First, there is a need to unequivocally establish that the rate is proportional to BET surface area. This can be done by employing the same methods, but to samples with a wide range of BET surface areas. Second, there is still a need to determine if on truly unreacted materials there is a spike in initial hydrogen production. Earlier work with a microcalorimeter did produce the postulated hydrogen spike [2], but simultaneous observation of the spike and weight gain would confirm that earlier observation. Third, the existence of a carbonate diffusion layer, as well as its impact on corrosion, on powder samples should be studied in detail.

Acknowledgements

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