Lithium Metal–Gas Reactions

Interaction of Lithium Metal with Air and its Component Gases

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BECAUSE OF increasing use of lithium as the elemental material (*17*), it is important to know the nature of the interaction between lithium metal and its gaseous environment. Inasmuch as air represents the most common gaseous atmosphere, the present study relates to the corrosion of lithium metal by air and by its component gases (N_2, O_2, CO_2, H_2O, and Ar). This study attempts to resolve the reactions occurring when lithium is exposed to air and to determine the significant role of water vapor in the deterioration of lithium.

The present work confirms the frequency cited similarities between lithium and the alkaline earth metals, particularly magnesium (*4*). This is reflected in the ready exothermic formation of lithium nitride when lithium metal is exposed to moist air or to dry nitrogen at elevated temperatures. Lithium, unlike the other alkali metals, forms a stable nitride of considerable ionic character (*27*). The parallelism between the behavior of lithium and magnesium is heightened by the higher rates of nitridation of these metals compared to their rates of oxidation at moderate temperatures (*3, 18, 33, 36*).

Much of existing knowledge of lithium metal-gas interactions was accumulated at the turn of the century. The early studies were performed at a time when pure lithium was virtually unknown and when dry-box protective atmosphere techniques were in crude stages of application, if used at all. As a result, the literature is not consistent about the phenomena accompanying lithium-gas reactions. A recent work (*34*) sums up the interaction of lithium and air as simply "(Lithium metal) develops a black nitride tarnish when exposed to air." Although the present work demonstrates that lithium nitride is formed on exposing the metal to damp air, it also demonstrates that a number of other reactions occur simultaneously and sequentially, and that the black film observed need not necessarily be lithium nitride.

EQUIPMENT AND PROCEDURE

A 100 to 125-mesh metal dispersion was prepared from pure, bulk lithium metal (99.95% Li min., 0.005% Na max., 0.01% K max., 0.01% Cl max., 0.004% N max., Foote Mineral Co.) by deagglomeration at 200° C. in a purified hydrocarbon solvent (Amsco 450, American Mineral Spirits Co., New York, N. Y.); no emulsifying agent was used. After cooling, the dispersion was washed with lithium-treated hexane and dried in a steam of argon. All handling and manipulation of the lithium metal were performed in a glove box under a dry, flowing argon atmosphere.

HUMIDITY CHAMBER STUDIES

To determine the course of the reactions between lithium and air, individual samples (0.2 of a gram) of the dry metal dispersion were exposed for varying periods of time to circulating air at 50% relative humidity (±1%) and 27° (±1°) in a controlled temperature-humidity chamber (Vapor-Temp. Model VP-100, Blue M Electric Co., Blue Island, Ill.). All exposed samples, individually covered, were stored in a desiccator for several days prior to x-ray or chemical analysis.

X-ray examination of a set of metal samples maintained in the chamber showed that products formed early in the corrosion process were primarily anhydrous lithium hydroxide and lithium nitride, and that subsequently anhydrous and hydrated lithium hydroxide formed with a concomitant diminution of the lithium nitride content. Contrary to early reports, the lithium nitride produced at these low temperatures is not amorphous (*6*). A General Electric Co. XRD-5 x-ray diffractometer with nickel-filtered copper-K_α radiation was used for these studies. Before x-ray identification, each sample was mixed with lithium-treated vaseline to prevent further atmospheric attack. This procedure was satisfactory because pure lithium metal dispersions mixed with the vaseline showed no diffraction lines due to products of air oxidation.

The quantities of reaction products in the various air-exposed samples were determined by chemical analyses. Each sample, after weighing and applying a correction to account for the density difference between argon and air, was hydrolyzed overnight in a flowing wet (100% relative humidity at room temperature) argon atmosphere using the apparatus shown in Figure 1. The sample-containing reaction kettle was maintained at 40° to 50° C. during hydrolysis. Such slow hydrolysis is necessary because direct reaction with liquid water of even a partially corroded dispersion is very violent. Any ammonia formed by hydrolysis of the nitride, viz., $Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$ was absorbed in the receiving flask containing excess standardized 0.1*N* hydrochloric acid solution. Upon essential completion of the hydrolysis, 250 ml. of boiled, distilled water was added to the kettle through the separatory funnel. The contents of the flask were then boiled and about 150 ml. of distillate was collected in the absorption flask. The long vertical connecting tube between the reaction kettle and the condenser served as an effective spray

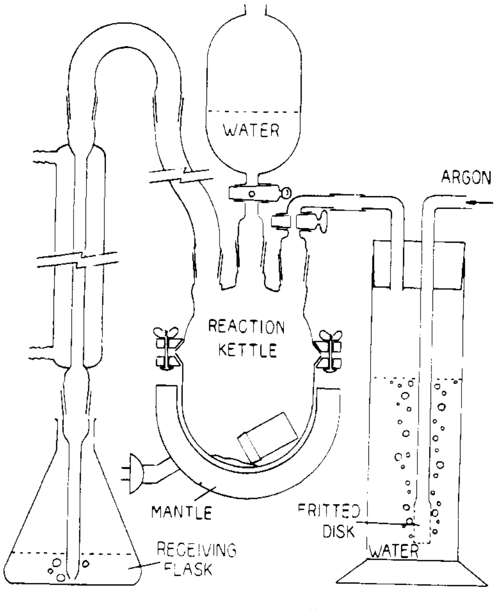

Figure 1. Hydrolysis and distillation apparatus

trap. A continuous slow stream of argon during the distillation prevented any suck-back of liquid from the receiver. Titration of the contents of the latter with 0.1N sodium hydroxide solution to a mixed bromocresol green–methyl red end point permitted independent determination of the lithium nitride portion of the sample. The ice-cooled solution in the reaction kettle was titrated with 0.5N hydrochloric acid to the phenolphthalein end point to yield ultimately the contents of [Li + LiOH] and ½[Li_2CO_3] or of [LiOH + LiOH·H_2O] and ½[Li_2CO_3], and then after addition of excess acid and boiling, the cooled solution was titrated back to the modified methyl orange end point to give ½[Li_2CO_3]. These data, combined with the weight gain results, allowed computation of the product pair contents of [Li + LiOH] or [LiOH + LiOH·H_2O]. The results of these analyses are presented in Figure 2 (center). After completion of each set of differential titrations, the residual solution was treated with Nessler's reagent to ascertain complete removal of ammonia. All such tests indicated the absence of any undistilled ammonia.

Figure 2 (bottom) contains a temperature-time profile of a typical lithium metal dispersion (0.2 gram) maintained, as the previous samples, in the constant humidity chamber. To obtain this plot, a thermocouple in a thin copper ring was placed under the reacting sample, and the e.m.f. was continuously recorded. The temperature rise during the early period of atmospheric attack is noteworthy.

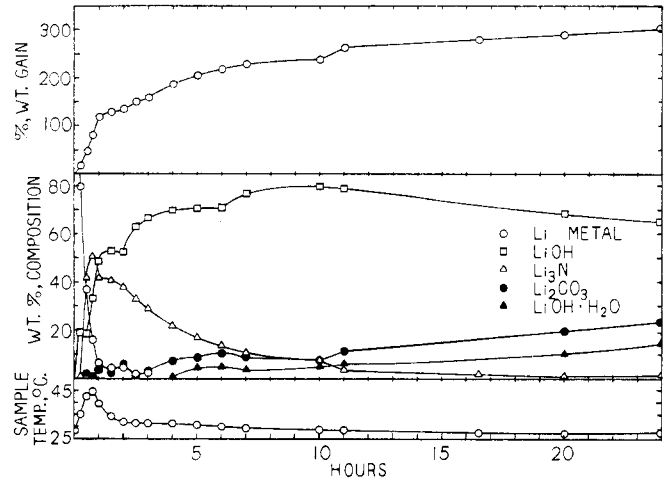

Figure 2. Reaction profiles of samples of 100–125 mesh lithium metal exposed to circulating air at 50% relative humidity and 27° C.

TGA STUDIES

The large relative weight gains shown by the reacting lithium samples (Figure 2, top) make the lithium metal-gas reactions particularly convenient to study by thermogravimetric analysis (TGA). Accordingly, a series of experiments was performed using the TGA equipment previously described (*22*) in combination with a motorized variable transformer (*25*) and a vertical tube furnace (*24*). A heating rate of 0.67° per minute was uniformly used in all the TGA runs. The heating chamber arrangement and temperature corrections applied to all the TGA data are depicted in Figure 3. With the indicated chamber, the lithium dispersion samples were held in small quartz cups and subjected to various dynamic gaseous atmospheres (flow rate of 150 ml. per minute at ambient conditions). All gases were of high purity (99.9% min.) and were dried by passage through a column of anhydrous magnesium perchlorate. The argon gas was further purified by passage through a tube containing calcium turnings kept at 500°. When wet gases were desired, the gases were dispersed through a saturated solution of sodium dichromate dihydrate to provide approximately 50% relative humidity at room temperature (p_{H_2O} = 9.03 mm. Hg at 20°). Experiments were performed with wet and dry flowing gases (Figure 4).

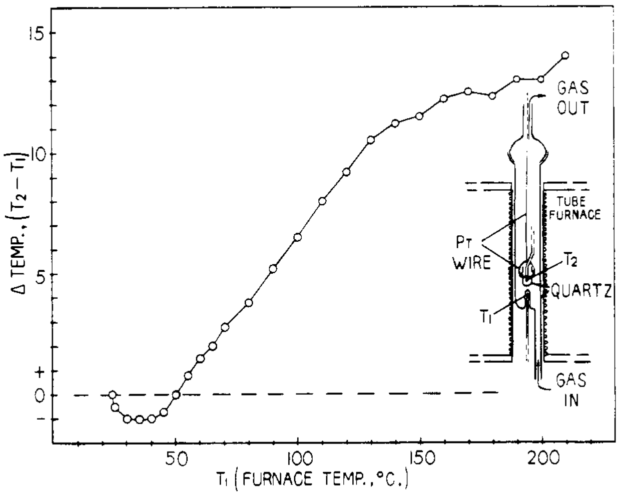

Figure 3. TGA heating chamber and temperature correction plot

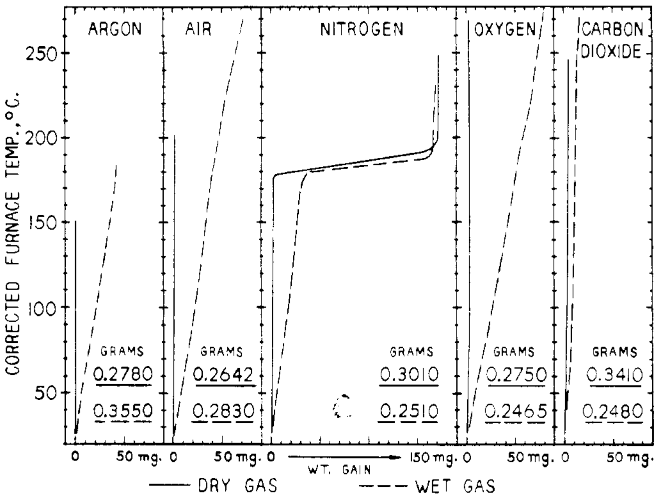

Figure 4. TGA results of lithium metal dispersions exposed to various gases

DTA STUDIES

It was anticipated that as in the case of the magnesium-oxygen reaction (*23*) the TGA results for lithium in a nitrogen atmosphere would not reflect the true sample temperature in the region of rapid metal-gas interaction. The formation of lithium nitride is exothermic (*30*),

$$\Delta H^0_{25} = -47.2 \text{ kcal./mole } Li_3N$$

Thus, rapid conversion of lithium to lithium nitride might result in considerable deviation of the sample temperature from the furnace temperature. To ascertain the existence and magnitude of this effect, differential thermal analyses (DTA) were performed on lithium metal dispersions in dynamic nitrogen atmospheres at a heating rate of 5° per minute. The sample holder of Figure 5 was used. The bottom portion of the sample tube is a disposable test tube, thus permitting repetitive re-use of the more elaborate,

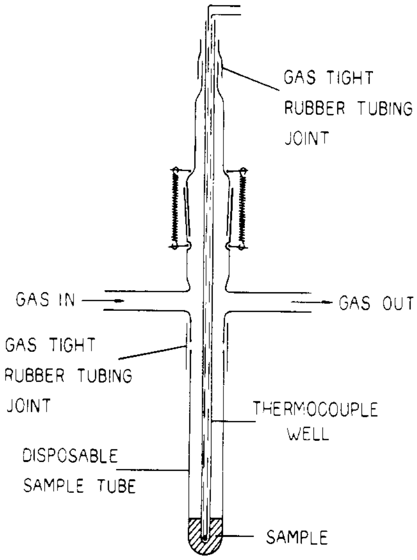

Figure 5. Sample holder for variable atmosphere DTA studies

upper part of the assembly. Because lithium and lithium nitride are exceedinly corrosive to glass at elevated temperatures, these DTA runs were made using an additional inner sample test tube holder in the configuration of Figure 5. A typical DTA plot is shown in Figure 6. The instrumentation and open furnace assembly have been described (*20*). To avoid the possibility of suck-back during the interval of rapid reaction, the effluent nitrogen gas was passed through a shallow mercury bubbler.

RESULTS

Humidity Chamber Studies. Figure 2 (center) shows that no significant amount of lithium nitride appeared during the first 15 minutes of air exposure; rather, appreciable quantities (18.6 weight %) of anhydrous lithium hydroxide were formed. Beyond this initial stage, the formation of lithium nitride was rapid. At any time following the first formation of the hydroxide, the accumulation of the nitride must be due to the resultant of two reactions: the formation of nitride (rapid)

$$6Li + N_2 \rightarrow 2Li_3N$$

and the disappearance of nitride by hydrolysis (slow)

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Later, as the monohydrate content increases, it can also react with the nitride

$$Li_3N + 3LiOH \cdot H_2O \rightarrow 6LiOH + NH_3$$

Within about 1 hour, the lithium metal content dropped to only 6.3 weight %. During these periods, the samples removed from the humidity chamber smelled strongly of ammonia.

The equilibrium $LiOH + H_2O \rightleftarrows LiOH \cdot H_2O$ provides a means for diffusing water to reach the hydrolyzeable nitride through the reaction sequence:

$$H_2O(\text{gas, atm.}) + LiOH\ (\text{surface}) \rightarrow LiOH \cdot H_2O\ (\text{surface}),$$

$$LiOH \cdot H_2O\ (\text{surface} + LiOH\ (\text{interior}) \rightarrow LiOH\ (\text{surface}) + LiOH \cdot H_2O\ (\text{interior}),$$

$$3LiOH \cdot H_2O\ (\text{interior}) + Li_3N\ (\text{interior}) \rightarrow 6LiOH\ (\text{interior}) + NH_3(\text{gas, interior, and atm.})$$

As expected, there was a continuous build-up of lithium carbonate in these air-exposed residues. The use of lithium hydroxide as a carbon dioxide absorbent for atmosphere purification is well established (*28*). The present results thus demonstrate that the ultimate fate of lithium metal exposed to moist air is lithium carbonate.

The temperature increases observed during the early stages of corrosion are probably due to the sequential occurrence of the reactions: $Li\ (\text{solid}) + H_2O\ (\text{gas}) \rightarrow LiOH\ (\text{solid}) + \frac{1}{2}H_2\ (\text{gas}),\ \Delta H^0_{25} = -58.7$ kcal., and $6Li\ (\text{solid}) + N_2\ (\text{gas}) \rightarrow 2Li_3N\ (\text{solid}),\ \Delta H^0_{25} = -94.4$ kcal. The subsequent lower but still elevated temperatures can be maintained by the more slowly occurring but also exothermic reactions:

$$Li_3N\ (\text{solid}) + 3H_2O\ (\text{gas}) \rightarrow 3LiOH\ (\text{solid}) + NH_3\ (\text{gas}),\quad \Delta H^0_{25} = -139.9\ \text{kcal.}$$

$$3LiOH \cdot H_2O\ (\text{solid}) + Li_3N\ (\text{solid}) \rightarrow 6LiOH\ (\text{solid}) + NH_3\ (\text{gas}), \Delta H^0_{25} = -96.4\ \text{kcal.}$$

$$2LiOH\ (\text{solid}) + CO_2\ (\text{gas}) \rightarrow Li_2CO_3\ (\text{solid}) + H_2O\ (\text{gas}),\quad \Delta H^0_{25} = -21.2\ \text{kcal.}$$

$$LiOH\ (\text{solid}) + H_2O\ (\text{gas}) \rightarrow LiOH \cdot H_2O\ (\text{solid}),\quad \Delta H^0_{25} = -14.5\ \text{kcal.}$$

The reaction following, on the other hand, is slightly endothermic: $2LiOH \cdot H_2O\ (\text{solid}) + CO_2\ (\text{gas}) \rightarrow Li_2CO_3\ (\text{solid}) + 3H_2O\ (\text{gas}),\ \Delta H^0_{25} = +7.8$ kcal.

The use of a lithium metal dispersion characterized by a high available reaction surface area tends to exaggerate the rate of corrosion because of the minimization of possible rate-controlling diffusion effects. Thus, the sequence of events is unchanged in nature but accelerated in time. Additional studies are in order with the aim of elucidating area-volume effects in lithium metal-gas reactions.

TGA Studies. The TGA curves depicted in Figure 4 clearly show the deleterios effects of water vapor-containing gases on lithium dispersions. All the anhydrous gases including nitrogen (up to about 160°) appear inert with respect to lithium metal. However, with the presence of a partial pressure of water vapor in each gas, continuous and significant weight gains are observed over the heating period. Of especial interest is the absence of any detectable reaction between lithium and dry oxygen, dry carbon dioxide, and dry air over the temperature range covered (ambient to about 250°). These results are consistent with the observed high ignition temperatures (630°–870°) of lithium in oxygen (*36*) and the reported relative stability of lithium metal in dry air even (*16*) at fusion temperatures (m.p., 180.5°). Apparently the oxidation of lithium by carbon dioxide requires higher temperatures than those encountered in the present investigation (*14*).

During this program it was found that lithium metal dispersions (0.2 gram) exposed to flowing dry air or to flowing dry nitrogen at room temperature for periods up to a week showed no significant weight changes (within ±0.0005 gram). No ammonia was obtained upon hydrolysis of the nitrogen-treated samples. Clearly water vapor must play a decisive role in promoting the formation of lithium nitride when the metal is exposed to air.

The low temperature conversion of lithium to lithium nitride had been reported by Deslandres (*8*) but Guntz (*12*) had pointed out that this occurred only with wet nitrogen. Dafert and Miklauz (*6*) had claimed the preparation of lithium nitride at room temperature with dry nitrogen, but also reported that the reaction was not always reproducible. These contrary observations can be reconciled by the realization that the nucleation of lithium nitride is ordinarily a very slow step (*15, 21*). Thus, impure lithium already containing some lithium nitride is highly suspectible to further nitridation even at low temperatures; pure metal lacking such nuclei is apparently resistant to nitridation, as seen in the present work. However, the constant humidity chamber studies and collateral evidence (*21*), show that the formation of lithium nitride is also hastened by the presence of a lithium hydroxide film on the surface of the metal. As a result, the hydroxide also represents an impurity rendering lithium metal susceptible to low temperature nitridation.

The presence of oxygen or hydrogen in nitrogen tends to diminish or even to inhibit completely the formation of lithium nitride at low temperatures (*6, 10*). Apparently, there is a preferential absorption of these gases over the reactant nitrogen within the voids of the porous nitride product layer, so that the diffusion of the nitrogen gas to the unreacted lithium is prevented. However, this inhibitory effect appears operative only for bulk lithium metal—i.e., low ratio of surface-to-volume—where reactant diffusion through a contiguous product layer becomes important. The present dispersion-air studies support the relative unimportance of inhibition of nitrogen diffusion for this high available surface area material as exposed in the constant humidity chamber.

Comparison of the results from the wet air TGA studies with those from the humidity chamber indicates an apparent discrepancy. The rate of weight gain found for the TGA sample is much less than that observed in the chamber experiment. Except for the instance of carbon dioxide (rate of weight gain = 0.065 mg./° C.), the rates of weight pickup by the lithium samples in the TGA experiments using the wet gases argon (0.265 mg./° C.), air (0.294 mg./° C.), oxygen (0.320 mg./° C.), and nitrogen (0.207 mg./° C., up to about 160°) are rather similar despite the differences in sample weight and gaseous environment. This can be traced back to the fact that in the constant humidity chamber the samples were contained in a cylinder of approximately 5.7 sq. cm. cross-sectional area, whereas in the TGA runs, the samples were held in cylinders of only about 0.9 sq. cm. of cross-sectional area. Thus, for the TGA runs, reactant diffusion beyond the initial surface layers of lithium appeared to be a limiting factor; in a narrow, cylindrical sample configuration the rates would tend to be about the same. The primary reaction occurring in the presence of these wet gases is

$$\text{Li (solid)} + H_2O \text{ (gas)} \rightarrow \text{LiOH (solid)} + \tfrac{1}{2}H_2 \text{ (gas)}$$

This problem of diffusion of gaseous reactants through a packed bed of small granular particles must be considered as a common occurrence in most atmosphere-dependent TGA studies. The packing of the sample determines the effective surface area available for reaction. The effect is further evidenced when in some TGA experiments carried out in otherwise reactive atmospheres, the center or bottom portions of the lithium samples were found to be molten below a layer of reaction product. Clearly, a sample holder of large diameter would be desirable in this type of TGA work..

The conversion of lithium to lithium nitride in the TGA run using dry nitrogen was only about 85% of theoretical on the basis of the observed weight gain. This incomplete conversion may be accounted for by inclusion of unreacted lithium in the lithium nitride, partial volatilization of the metal due to its high vapor pressure at elevated reaction temperatures (*14*), and reaction of the lithium or lithium nitride with the quartz sample holder (*11*).

DTA Studies. That high temperatures do occur during the rapid nitridation of lithium may be seen from Figure 6. Upon ignition in nitrogen, a temperature of about 600° is reached in less than a minute with a 0.26 gram sample of lithium dispersion.

The DTA curve departs significantly in the exothermic direction from the base line at anout 150°, whereas the TGA results indicate the onset of rapid nitridation at about 170°. The latter temperature is more indicative of rapid nitridation than the former. The departure of the DTA curve from the steady-state temperature rise at 150° is probably due to a rapid influx of heat from the outer reacting core of the sample, rather than from reaction of that portion of the sample immediately surrounding the thermocouple. As a result, there is usually a tendency to interpret this first deviation of the base line as the temperature of rapid reaction in DTA work. However, the distinction between rapid heat transfer from the peripheral layers and the exothermic reaction of the center segment of the sample cannot be readily made in the usual DTA experiment. In the TGA experiments, this ambiguity does not exist; as in the present case with a low heating rate, the correlation between onset of rapid reaction and sample temperature at that point is much more clearly defined.

The shape of the DTA curve of Figure 6 during the period of rapid reaction is unique and merits some comment. The intersection of the cooling portion of the exotherm with the heating portion is in contrast to the usual type of DTA exotherm (*26*). With the exotherm in Figure 6, at any given sample temperature within the region of the closed loop, the ΔT value is greater during the sample cooling than during heat generation within the sample. In the more customary exotherm the converse is true with ΔT, at any given temperature, during the cooling of the sample being less than the corresponding ΔT during the internal heating sequence. It appears that the crossover in Figure 6 is due to a decrease in ΔT at the time of reaction because of heat transfer through the heating block from the high temperature of the sample to the much lower temperature of the alumina reference. Once the heat-producing step subsides, and the sample and reference start to return to the normal furnace conditions, this diminution in ΔT is no longer operative. This DTA behavior observed for the lithium-nitrogen reaction is probably characteristic of many highly exothermic reactions which are studied in equipment allowing some heat transfer at high temperature differences between the sample and the reference. To observe this effect appropriate application of voltage divider networks is necessary, so as to keep the T and ΔT variables on the scale of the usual low-range millivolt potentiometric x-y recorder.

Both the TGA and DTA experiments demonstrate that the reaction between lithium and pure, dry nitrogen is rapid and exothermic at about 170°, making kinetic rate measurements impossible. Under the experimental conditions employed here, the ignition with nitrogen apparently

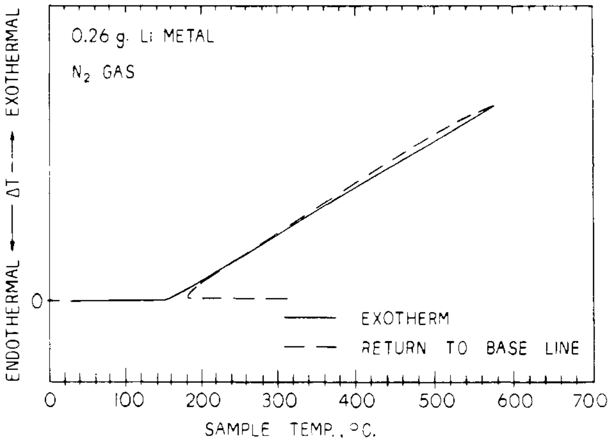

Figure 6. DTA plot of lithium metal dispersion in a flowing nitrogen atmosphere

occurred without fusion and coalescence of the metal, so that rapid diffusion of the reactant nitrogen through a bed of porous, solid lithium and lithium nitride is possible. With a compact mass of liquid lithium, nitridation can actually be slower because the reaction can become diffusion controlled. Furthermore, the exothermicity of the nitridation can lead to nonisothermal conditions. Accordingly, the divergencies among different workers become understandable. Such studies have resulted in linear (*1*), parabolic (*18*), and exponential (*3*) rate laws for the nitridation of liquid lithium over comparable temperature ranges.

DISCUSSION OF RESULTS

As seen from the TGA studies, lithium metal does not appear to be reactive with dry carbon dioxide up to about 250°, despite the potential for reaction. Similarly, lithium nitride does not appear to reduce carbon dioxide at low temperatures by the reported reaction (*11*):

$$4Li_3N + 9CO_2 \rightarrow 6Li_2CO_3 + 3C + 2N_2$$

because all the samples from the humidity chamber runs were found to be completely water-soluble, indicating the absence of elemental carbon. The attack of lithium metal by wet carbon dioxide is small compared with the other wet gases. Lithium carbonate, probably formed by the over-all reaction,

$$2Li + H_2O + CO_2 \rightarrow Li_2CO_3 + H_2$$

yields a protective coating on the surface of the metal. On the basis of the Pilling-Bedworth rule (*29*), which stipulates for a protective coating a value greater than one for the ratio (molar volume of corrosion product)/(atomic volume of metal) (number of gram-atoms of metal in one mole of corrosion product), lithium carbonate would be expected to exert an allaying effect on further corrosion. Lithium carbonate is unique in this respect (Table I) among all the alkali metal carbonates for which appropriate data are available. In addition, anhydrous, and hydrated lithium hydroxide would be expected to act as protective coatings. However, the monohydrate itself is capable of reacting with lithium, and the anhydrous base could participate in the transfer of water by the mechanism discussed earlier involving the anhydrous base-monohydrate-water vapor equilibrium. Thus, the possible protective effects of anhydrous lithium hydroxide are diminished, particularly if the monohydrate phase can be easily nucleated. It is also possible that a coating of lithium hydroxide on lithium metal can become defective by virtue of strains set up by the hydrogen gas formed in reaction between the hydrate and the free metal.

Table I. Pilling-Bedworth Ratios for Some Alkali Metal Compounds

Compound	Pilling-Bedworth Ratio
Li_2CO_3	1.34
Na_2CO_3	0.89
K_2CO_3	0.63
Li_3N	0.64
LiOH	1.26
$LiOH \cdot H_2O$	2.13
NaOH	0.83
KOH	0.60
RbOH	0.42
CsOH	0.60

It is almost axiomatic in the phenomenology of lithium metal that when it is exposed to ambient air, the metal surface turns black (*2, 34, 35*). X-ray studies of these black reaction films formed after exposure of the metal to water vapor (*2, 7*), moist argon and moist oxygen (*15*), moist nitrogen (*2, 15*), and moist air (*2*) have shown the coating to be anhydrous lithium hydroxide. Similar results have been reported from use of the electron-diffraction technique which permited identification of the presence of lithium oxide as well in the black coating (*37*). As seen in Figure 7, a black aspect is even assumed by oil-coated lithium metal in flowing moist air (50% relative humidity) and in moist argon at room temperature; the sample exposed to flowing dry air is unaffected.

The foregoing information leads to two conclusions: A black coating on lithium metal does not necessarily signify that the film consists of black lithium nitride because a black coating is clearly also obtained with wet argon as well as with wet air. Identification of the nature of the surface film has been consistently made by the use of techniques primarily detecting ordered, crystalline, atomic arrays. Thus, the presence of amorphous materials would not be as clearly observed by these diffraction methods as crystalline materials. Ordinarily, lithium hydroxide appears transparent within the visible spectral range, so that its occurrence as a complete absorber and nonreflector of visible light is difficult to comprehend.

Consideration of these points leads to the suggestion that the black coating on lithium metal as formed during short exposures to damp atmospheres (even carbon dioxide, as determined in the present study), is really amorphous lithium metal as viewed through a thin, transparent coating of lithium hydroxide. Prolonged exposure of lithium metal to damp atmospheres produces a white coating of lithium hydroxide with a bluish underlying appearance. Apparently, water vapor is able to facilitate the destruction of the normal body-centered cubic structure of lithium metal to yield a nonreflective, amorphous metal coating. The existence of such a coating would produce a layer of lithium of high surface free energy. This layer would be expected to be exceedingly reactive and would thus account for the ready formation of lithium nitride in moist air. Alternately, it has been proposed that the black coating is an anion-deficient form of lithium hydroxide (*19*).

The possible presence of lithium oxide as part of the composite coating could be explained through the partial occurrence of the reactions:

$$2Li\ (solid) + H_2O\ (gas) \rightarrow Li_2O\ (solid) + H_2\ (gas) \qquad \Delta F^0_{25} = -79.2\ kcal.$$

$$LiOH\ (solid) + Li\ (solid) \rightarrow Li_2O\ (solid) + \tfrac{1}{2}H_2\ (gas) \qquad \Delta F^0_{25} = -27.7\ kcal.$$

Appreciable quantities of lithium oxide would not be expected among the corrosion products of lithium at high humidities or prolonged contact times because of the reaction

$$Li_2O\ (solid) + H_2O\ (gas) \rightarrow 2LiOH\ (solid)$$

The effect of water vapor in producing a black coating on lithium appears to be peculiar to this gas. Thus, it was found that partial pressures of absolute methanol or ethanol vapors in argon or nitrogen streams did not produce black coatings on lithium; rather white, easily flasked scales were formed within a very short period of exposure.

Consideration of the very high heat of atomization of molecular nitrogen (225.8 kcal./mole at 25°) (*5*) makes the formation of lithium nitride under the mild conditions reported here a rather remarkable phenomenon. Indeed, of all the alkali metals lithium is the only one to form a stable nitride. The nitrides of the other alkali metals are poorly

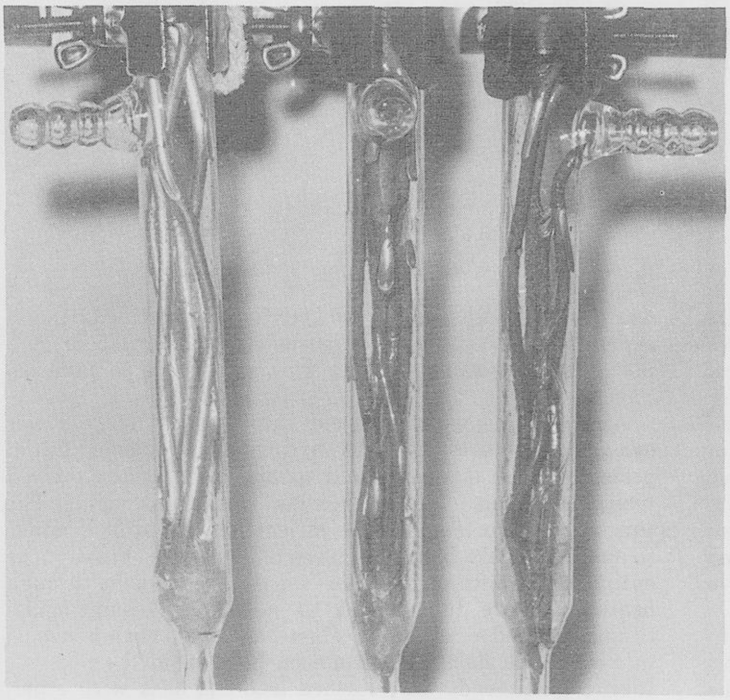

Figure 7. Oil-covered lithium metal after 30-minute exposure to flowing dry air (left), flowing moist air (center), and flowing moist argon (right)

characterized, extremely unstable substances which are formed only as transients in the thermal decompositions of the alkali metal azides or by reaction of the free alkali metal with activated or atomic nitrogen in electric discharges (*31*). The ready formation of a nitride is but another reflection of the ability of lithium to form stable compounds of considerable ionic character with relatively small atoms of intermediate electronegativities—e.g., C, H, S, B, Si, Se, Te, P, etc. This tendency can be ultimately related to the high lattice energies of such compounds which promote favorable contributions of exothermic values of the enthalpies of formation to the free energies of formation (*13*).

The low temperature formation of lithium nitride in moist air and the subsequent hydrolysis to produce ammonia gas is an interesting example of readily achievable atmospheric nitrogen fixation. Along similar lines, lithium nitride has been proposed as an intermediate in ammonia production by alternate hydrogenation and nitridation steps (*9*, *32*).

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RECEIVED for review February 27, 1962. Accepted July 10, 1962. Portions of this article were presented at the Fourth Delaware Valley Regional Meeting of the Am. Chem. Soc., Jan. 25–6, 1962, Phila., Pa.