



Sorption of atmospheric gases by bulk lithium metal



C.A. Hart^a, C.H. Skinner^{b,*}, A.M. Capece^b, B.E. Koel^c

^a Department of Physics, University of Maryland, College Park, MD 20742, USA

^b Princeton Plasma Physics Laboratory, Princeton, NJ 08543, USA

^c Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA

HIGHLIGHTS

- Li in tokamaks will react with air during maintenance and exposure to residual gases in the vacuum vessel.
- The mass gain of Li samples upon exposure to ambient air indicates conversion to Li_2CO_3 .
- Exposure to dry air resulted in a 30 times lower rate of mass gain.
- A rule of thumb for lithium passivation at 26 °C and 45% relative humidity is proposed.

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ABSTRACT

Lithium conditioning of plasma facing components has enhanced the performance of several fusion devices. Elemental lithium will react with air during maintenance activities and with residual gases (H_2O , CO , CO_2) in the vacuum vessel during operations. We have used a mass balance (microgram sensitivity) to measure the mass gain of lithium samples during exposure of a $\sim 1 \text{ cm}^2$ surface to ambient and dry synthetic air. For ambient air, we found an initial mass gain of several mg/h declining to less than 1 mg/h after an hour and decreasing by an order of magnitude after 24 h. A 9 mg sample achieved a final mass gain corresponding to complete conversion to Li_2CO_3 after 5 days. Exposure to dry air resulted in a 30 times lower initial rate of mass gain. The results have implications for the chemical state of lithium plasma facing surfaces and for safe handling of lithium coated components.

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1. Introduction

Lithium conditioning of plasma-facing components has improved plasma performance and reduced recycling on multiple fusion devices [1]. The chemical composition of the lithium surface, which is affected by exposure to ambient air during venting and residual vacuum gases during operation, strongly influences interactions at the plasma–surface interface. Previous studies using X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum (UHV) conditions have shown that lithium metal films were easily oxidized to a depth of at least 10 nm after exposure to 1–2 Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr-s}$) of oxygen or water vapor, corresponding to sticking coefficients of near unity. Exposures to CO_2 or ambient air resulted in an oxidation rate four times smaller than with O_2 or H_2O [2]. The reaction of 7.5-nm lithium films exposed to

O_2 was investigated in a separate study using Auger electron spectroscopy (AES) and ellipsometry and proceeded with an approximately unit reaction probability, though the interpretation of the ellipsometry was complicated by film contraction accompanying the transformation from Li to Li_2O [3]. Oxidation of thicker lithium films exposed to O_2 was investigated by a quartz crystal microbalance and complete conversion to Li_2O occurred within 200 s for films up to 100 nm thick [4]. This work also reported XPS measurements of lithium reactions with water vapor and found the initial formation of one monolayer of oxide followed by the formation of multilayers of hydroxide/oxide mixtures that then converted to oxide over a period of minutes.

In other work, samples of lithium powder with a mass of 0.2 g were exposed to flowing air and its constituent gases at atmospheric pressure and the reactions studied via thermogravimetric analysis (TGA) [5]. In contrast to the thin film results above, no detectable mass gain was observed after exposure to O_2 , CO_2 , and dry air at temperatures from ambient to 250 °C. However, exposure of lithium to circulating air with 50% relative humidity resulted in

* Corresponding author.

E-mail address: cskinner@pppl.gov (C.H. Skinner).

mass gain, and the transformation of lithium into lithium compounds was measured over 24 h.

The fundamental theory of the oxidation of thin metallic films was presented in the classic paper by Cabrera and Mott [6]. This theory describes how the oxidation rate depends on film thickness, electric potentials in the film, lattice parameter differences between the metal and metal oxide, and temperature. If the temperature is low enough, metals exposed to oxygen show an initial rapid growth of oxide, followed by a remarkable slowing down once the film thickness reaches some critical thickness of order 10 nm. Xu et al. [7] have presented a model describing the transition from drift-dominated ionic transport for thin films to diffusion-dominated transport for thick films.

Several factors motivate further investigation of the oxidation of thick lithium samples. Thick lithium films are typically used in tokamaks, and measurements of lithium conditioned tiles from the National Spherical Torus Experiment (NSTX) showed that lithium coverage with a 100–500 nm equivalent thickness was required for effective deuterium retention [8]. Future tokamaks may utilize liquid lithium plasma-facing components that take advantage of the benefits of lithium and avoid the limitations due to radiation damage and erosion lifetime of solid materials [9]. In addition, the formation of lithium compounds, such as lithium oxide, as a result of atmospheric gas exposure, has been shown to influence the reactive wettability of liquid lithium [10]. Finally, knowledge of the rate of oxidation or passivation of macroscopic lithium samples is important for the safe handling of lithium and lithium-coated components.

In the present work, lithium samples up to 1-mm thick were exposed to ambient air and dry synthetic air. A microbalance with 1 μ g resolution was used to probe mass gain of the samples for time periods of up to two weeks. Optical microscopy monitored changes in surface morphology and color during the exposures and was used to estimate the Pilling–Bedworth [11] ratio (volume change upon oxidation). Section 2 presents the experimental setup, techniques of sample preparation, and analysis of experimental uncertainties. Section 3 reports on the optical microscopy and mass measurements during the exposure to ambient air and interprets the data in terms of the formation of Li_2CO_3 . Section 3.2 discusses the results of mass gain after exposure to dry air, and Section 4 summarizes the results.

2. Experimental methods

Lithium sample containers were machined from stainless steel and had an open area of 1 cm^2 and a depth of either 1 mm or 0.3 mm (Fig. 1(A)). The containers were rinsed with water followed by ethanol and then baked at 100 $^\circ\text{C}$ to remove adsorbed water before each sample preparation. Lithium rods were obtained from FMC Corporation [12], and were 12-mm in diameter and 165-mm long with a purity of 99.90% by weight (the largest residual impurities levels were up to 150 wppm of Na, Ca, K, N, and Si). The lithium was stored in an argon glove box with oxygen levels reduced to <0.1 ppm and water vapor levels of <1.0 ppm.

Lithium samples were prepared in the argon glove box in three different ways. In the first method, a 1–2 mm slice of lithium was cut from the lithium rod with a stainless steel knife blade in the argon glove box and placed into the well of the stainless steel container. The lithium-filled well was compressed against a stainless steel plate using a C clamp to extrude excess lithium. The sample was then twisted and lifted from the plate and the excess lithium removed from the edges with a knife. This process filled the well and produced a lustrous lithium surface. However, the surface remained rough because some lithium adhered to the stainless steel plate during separation from the lithium well (Fig. 1(B)). The

second method followed the above procedure, but with the lithium surface compressed against a polytetrafluoroethylene (PTFE) plate. Lithium did not adhere well to PTFE, but a weak chemical reaction between lithium and PTFE left a dull surface (Fig. 1(C)). The reaction product was scraped off with a stainless steel plate and a smooth lustrous surface was recovered (Fig. 1(D)). Earlier work found scraping in UHV produced a lithium surface with greater than 95% purity as measured by XPS [2]. In the third method, a small 9 mg sample of lithium was pressed between a pair of stainless steel tabs. The tabs were then separated to obtain lithium samples with a minimal thickness (Fig. 1(E)). For the dry air exposure experiments, a sample with a smooth surface (Fig. 1(F)) was prepared using the same technique as sample (D). Samples are referenced throughout the text using the lettering assigned in Fig. 1.

The lithium-filled wells were covered with an o-ring sealed enclosure to retain the argon atmosphere during transfer to a separate glove bag for experimental measurements with two mass balances and a digital optical microscope. The lithium-covered stainless steel tab was placed in a sealed plastic container for the same purpose. The primary mass balance, a Sartorius ME-5F, had a precision of 1 μ g and was programmed using LabVIEW for automated data logging every 15 s for periods of up to two weeks. The cover of the Sartorius ME-5F weighing chamber remained partially open (1 cm gap) during gas exposures to help maintain the ambient gas composition in light of potential local depletion of individual gas species near the sample. For samples (C–F), automated mass data collection was initiated at least 5 min before exposure of the sample to air. The mass of sample (B) was recorded manually using a Sartorius BB 211S balance with 0.1-mg precision and no weighing chamber. This second balance enabled the study of two samples simultaneously.

The Sartorius ME-5F balance exhibited a small periodic drift under a constant load. Over a 24-h period (12 a.m.–12 p.m.), the rate of drift would oscillate between positive and negative values, with a net positive drift over the course of a day. The drift was correlated with the on/off cycling of the building air conditioning. The average drift rate, 0.01 mg/h, constituted less than 1% of the initial rates of mass gain for the humid air exposures. To correct for this background drift and estimate the associated uncertainty, an empty sample well was measured for five 24-h periods. The drift rates were averaged and fit to a Fourier sine series [Eq. (1)] using a nonlinear least squares method ($r^2 = 0.997$ using 1440 points) to create a continuous drift rate function.

$$f(x) = \sum_{i=1}^8 a_i \sin(b_i * t - c_i) \quad (1)$$

The resultant function used the following coefficients: $a_1 = 0.0479$, $b_1 = 0.240$, $c_1 = 0.306$; $a_2 = 0.0198$, $b_2 = 0.125$, $c_2 = -0.505$; $a_3 = 0.0198$, $b_3 = 0.7873$, $c_3 = 1.75$; $a_4 = 0.0140$, $b_4 = 0.545$, $c_4 = -2.30$, $b_5 = 0.545$, $c_5 = -2.30$; $a_6 = 0.00982$, $b_6 = 1.31$, $c_6 = -2.32$; $a_7 = 0.00760$, $b_7 = 1.57$, $c_7 = 1.03$; $a_8 = 0.00586$, $b_8 = 2.09$, $c_8 = -2.78$. The cumulative background drift was calculated by integrating the drift rate function over the duration of each exposure, and then subtracting this sum from the sample measurements. 1.96 standard deviations of the mean drift rate were used to estimate the uncertainty in the calculated reaction rates (95% confidence interval). Drift functions 1.96 standard deviations above and below the average drift rate were then generated and integrated with respect to time to calculate the background drift's contribution to the uncertainty for each mass measurement. The error bars shown in Figs. 3 and 7 for the rate of mass gain data indicate the uncertainty in calculated values; which is dominated by the uncertainty in the background drift. Figs. 2, 6 and 8 depict the mass gain of samples with error bars corresponding to the integrated uncertainty described above.

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