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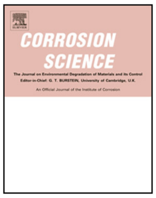

Full Length Article

Effect of air humidity on microstructure and phase composition of lithium deuteride corrosion products

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ABSTRACT

Lithium deuteride (LiD) was exposed to air for 600 min to determine the effect of air humidity on its microstructure and phase composition. XRD and XPS results revealed that LiOH and Li_2CO_3 formed at relative humidity values of >30%, whereas only LiOH formed at values <20%. SEM and EDS images showed a clear LiOH layer; Li_2CO_3 was confined to the surface of this layer. The schematic illustration revealed that the concentration gradient of H_2O across the LiOH layer resulted in little Li_2CO_3 formed in the layer. This work will contribute to increase understanding of LiD corrosion in air.

1. Introduction

Metal deuteride has primarily been the focus of deuterium storage and energy storage material [1,2]. As an good deuterium storage material, lithium deuteride (LiD) consists of low atomic number elements, and has a simple electronic structure [3,4], low density, high deuterium content, high melting point, and good thermal stability in both vacuum and inert gases [5]. LiD plays an important role in thermonuclear reaction [4,6]. With the application of LiD from military fields to civil fields, LiD would have significant potential for use as a raw material or catalysis of organic deuterides, deuterated solvent and deuterated polymer.

However, pure LiD is extremely sensitive to water owning to its strong reducibility. Air is everywhere during the process of preparation, machining, packaging, transporting, and storing. It consists of various components (such as N_2, H_2O, O_2 and CO_2) and, hence, the reaction between LiD and water vapor may lead to complex surface corrosion. The corrosion process occurs in two stages namely physical absorption and chemical reaction; the adsorbance is correlated with the state and nature of the solid.

Much similar research has been conducted on the surface corrosion of metal Li [7], LiH [8–11], $LiBH_4$ [12] and CaH_2 [13]. The corrosion of LiD by H_2O has also been studied [14]. However, LiD corrosion in air has scarcely been investigated. Although LiD is an isotopic molecule of LiH, LiD is 12.66% heavier than LiH. These materials differ significantly owing to the large isotopic effect, which may influence the thermal, elastic, and dynamic properties of crystals [6,15–17]. LiD and LiH are different types of chemical compounds. As such, these materials have different atomic structure, molecular weight, electron distribution, lattice parameters [6,18], thermodynamic properties [18], cohesive energy [2], dielectric constants [2], surface energy, and adsorbability to air. Therefore, it is essential to investigate LiD corrosion products and corrosion process in air, which contributes to the understanding and prevention of LiD corrosion.

The effect of air humidity on the microstructure and phase composition of LiD corrosion products was determined in this study. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to determine the phase and composition of the corrosion products formed during exposure to air with different relative humidity (RH). Furthermore, the microstructural evolution and corrosion process were evaluated via scanning electron microscopy (SEM) characterization of the surface morphology. The composition was examined in further detail via energy disperse spectroscopy (EDS), which yielded the element distribution of the samples. In addition, Fourier transform infrared (FTIR) spectroscopy was used to further investigate the compositional changes that occur during the corrosion process. Moreover, a schematic illustration of the LiD corrosion process describing the microstruc-

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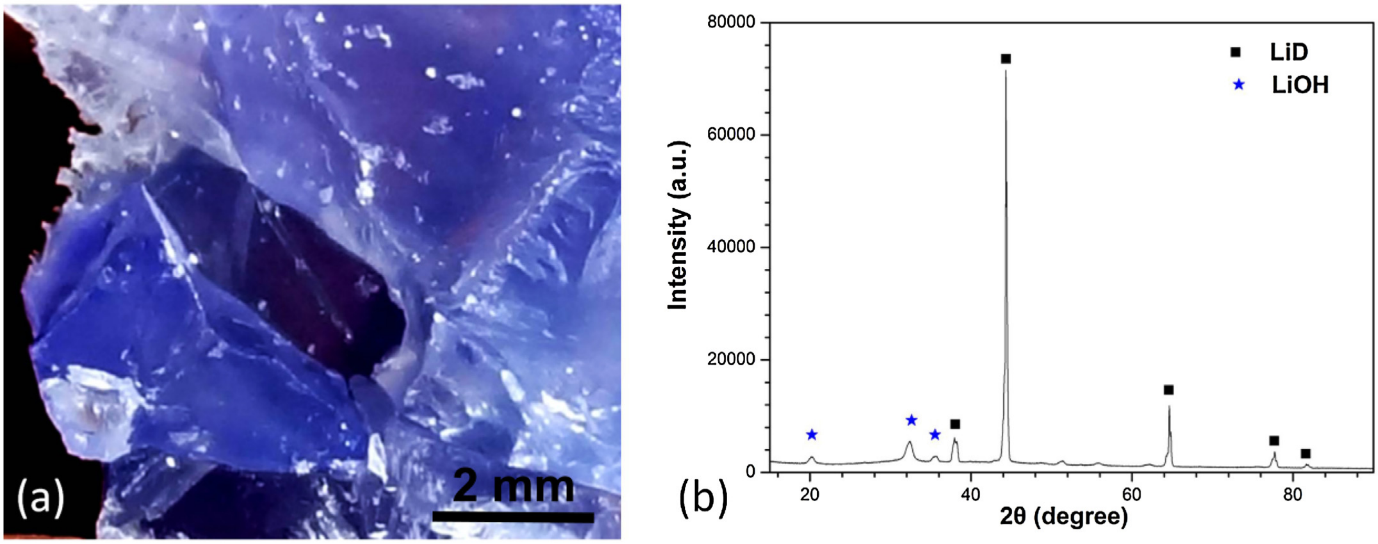

Fig. 1. Photograph of pure LiD blue transparent crystal (a), and XRD patterns of pure LiD particles (b) containing only a little LiOH.

tural evolution, compositional changes and concentration gradient of H_2O, was provided.

2. Experimental procedure

The LiD (99.99% purity) was prepared by heating lithium metal (99.99% purity) in an atmosphere of D_2 (99.999% purity). The lithium metal was placed in an airtight crucible in an argon-atmosphere glovebox. This crucible was then placed in a horizontal furnace equipped with a gas inlet, gas outlet, vacuum port, heating equipment, thermocouple, and vacuum meter. Afterwards, the inlet valve was opened and the horizontal furnace was filled with argon. The airtight crucible was then opened and the horizontal furnace was closed. The argon was subsequently replaced with deuterium, and the furnace was heated to 700 °C for 5 h, and the D_2 was maintained at ambient pressure during the experiment. After natural cooling to ambient temperature, the D_2 was replaced with argon. The argon atmosphere was maintained until the crucible was sealed, and the prepared LiD was subsequently moved to the glovebox.

The blue transparent LiD crystal is shown in Fig. 1a. LiD particles (99.9% purity, average particle size: 1 mm) were prepared by grinding in a pestle in an argon-atmosphere glovebox equipped with a recirculation system and oxygen/humidity sensors where oxygen and water levels were kept below 1 ppm during all operations. Even though, a small amount of LiOH formed, as shown in Fig. 1b, because pure LiD is extremely sensitive to trace water.

The LiD particles were placed, for 600 min, in air with a constant RH of 20, 30, 40, 50, and 60%, respectively, at 20 °C.

The phase and composition of samples were determined via XRD (Bruker D8-advance diffractometer equipped with a LynxEye detector, Cu Kα radiation source, $\lambda = 1.54056$ Å). In addition, the surface composition of corroded LiD samples was determined via XPS, (PHI Quantera, Japan). The binding energy was calibrated using C1s = 284.8 eV as the reference. The surface morphology and elemental composition of the corroded LiD samples were evaluated by using a SEM, (Hitachi S-4800, Japan) equipped with EDS capabilities, and with an operating voltage of 15 kV. Moreover, FTIR (Bruker tensor27, Germany) was employed to investigate time-dependent changes in the corrosion products.

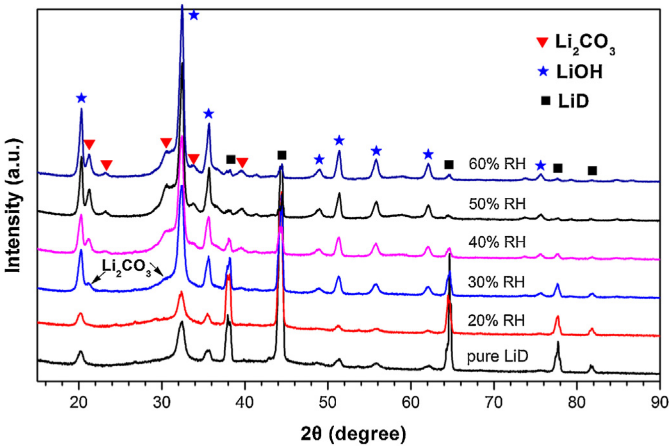

Fig. 2. XRD patterns of LiD samples corroded, for 600 min, by air with an RH of 20, 30, 40, 50, and 60%, respectively. LiOH and Li_2CO_3 formed at 30%–60% RH, whereas only LiOH formed at <20% RH.

3. Results

3.1. XRD and XPS

To investigate the effect of air humidity on the phase composition of corrosion products, LiD particles were corroded, for 600 min, in air with RH of 20, 30, 40, 50, and 60%, respectively. The phase compositions of the corroded samples were then determined via XRD and XPS.

As Fig. 2 shows, LiD, LiOH, and Li_2CO_3 were clearly identified, whereas $LiOH{\cdot}H_2O$ and Li_2O were absent. This indicates that, in contrast to the corrosion behavior of LiH [19,20], LiD reacts with air, thereby forming LiOH and Li_2CO_3, rather than $LiOH{\cdot}H_2O$ and Li_2O, during the corrosion process. LiD persists even after for 600 min of corrosion in 60% RH air, indicating that the corrosion reaction was incomplete and relatively slow. In addition, the amount of LiOH and Li_2CO_3 increases gradually with increasing relative humidity, confirming that the humidity has a significant effect on the corrosion reaction. Furthermore, below 20% RH, the absent characteristic peak of Li_2CO_3 occurs in contrast to the sharp characteristic peak of LiOH, confirming that Li_2CO_3 was not synthesized.