

Electronic Supplementary Information (ESI)

**Mechanisms of Microexplosion-accelerated Pyrolysis and Oxidation of Lithium-containing
Droplets: An Atomistic Perspective**

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1. Effect of ambient gas on droplet behaviours and formation of lithium clusters

To better identify the impact of ambient gas, a comparative study is conducted using three simulation systems under vacuum, nitrogen gas and oxygen gas conditions, respectively. In these cases, the Nosé–Hoover thermostat³² is utilized to raise the droplet temperature from 373 K during the heating up period (before 10 ps) and maintain constant temperature of 1500 K for the whole simulation system. Selecting the relatively low temperature of 1500 K is to achieve a comprehensive understanding of the mechanisms of evaporation and chemical reactions with low evaporation and reaction rates. The ambient pressure under both nitrogen and oxygen gas conditions remains constant at 1.0 MPa. Figs. S1(a), S1(b) and S1(c) illustrate a series of snapshots showing the dynamics of a lithium nitrate droplet under vacuum, oxygen and nitrogen ambient gas conditions, respectively. Figs. S2(a), S2(b) and S2(c) depict the effect of ambient gas on the droplet behaviours and the formation of lithium clusters, as indicated by the normalized droplet diameter squared, probability distribution of the number of lithium atoms in a molecule, and proportion of synthesized lithium compounds after droplet microexplosion, respectively.

At the initial stage (before 100 ps), the droplet undergoes a relatively slow evaporation process, and the trends of droplet diameter in all simulation environments are similar. As depicted in Fig. S2(a), the normalized droplet diameter squared initially increases, implying a volume expansion due to a rise in droplet temperature, and then gradually diminishes over time. Nevertheless, compared to the cases with ambient gas present, the volume expansion of droplet is observed to be more pronounced with a larger droplet size under vacuum condition. Meanwhile, a core-shell structure, where lithium atoms agglomerate in the inner region, while other atoms distribute in the outer layer, is formed at 42 ps under both vacuum and ambient nitrogen conditions, as displayed in Figs. S1(a) and S1(c). Conversely, the core-shell structure cannot be captured throughout the entire droplet lifetime under oxygen condition; instead, a more homogenous distribution of lithium atoms is observed within the droplet. This is caused by the heat transfer from the high pressure ambient to the droplet after the initial heating up period (no heat transfer occurs from the vacuum environment to the droplet), which leads to the accelerated atom motions and ultimately the more homogenous distribution of lithium atoms within the droplet.

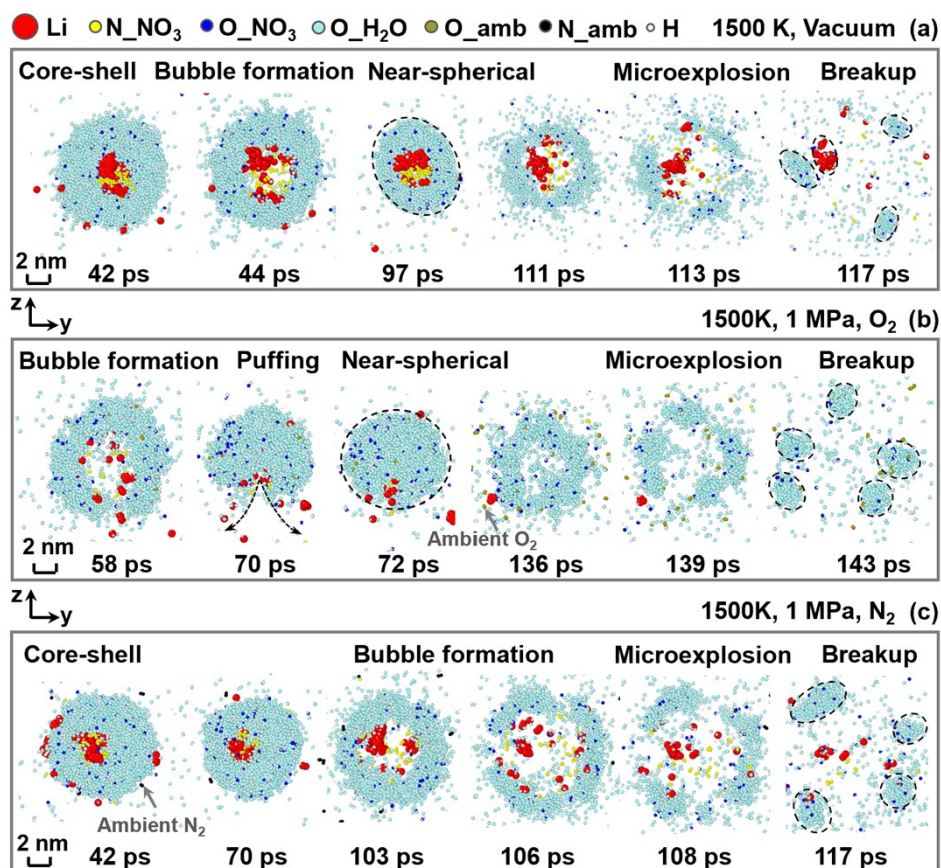


Fig. S1 Snapshots (slice view) of dynamics of an LNT droplet under (a) vacuum condition (b) O₂ condition with ambient pressure of 1.0 MPa (c) N₂ condition with ambient pressure of 1.0 MPa, $T_a = 1500$ K. ‘N_NO₃’ and ‘O_NO₃’ denote the nitrogen and oxygen atoms from nitrate, respectively; ‘O_H₂O’ represents the oxygen atom from water, while ‘O_amb’ and ‘N_amb’ refer to the oxygen and nitrate atoms from the ambient, respectively.

It should be noted that droplet microexplosion occurs, accompanied by a rapid change in droplet size in all studied simulation systems, as seen in Figs. S1(a)–(c) and S2(a). This confirms the occurrence of droplet microexplosion under the relatively low temperature conditions. It is found that the presence of ambient gas influences the size and composition of synthesized lithium clusters. Compared to vacuum condition, the presence of ambient oxygen and nitrogen gases leads to an increased normalized number of LiX (clusters containing a single lithium atom) and correspondingly reduced normalized number of Li_nX (clusters containing more than a single lithium atom), as depicted in Fig. S2(b). This is mainly caused by the elevated heat transfer rate from the ambient to the droplet, which

accelerates the atom motions within the droplet, as discussed above. Regarding the difference in the role of ambient oxygen and nitrogen gases, it is found to significantly alter the composition and size of reaction products after the droplet microexplosion by influencing the reaction pathways of precursor. Compared to the nitrogen gas condition, the existence of oxygen gas in the environment further facilitates the formation of small-sized lithium clusters, as indicated by the increased normalized number of Li_nX and reduced normalized number of Li_nX in Fig. S2(b). Besides, the presence of ambient oxygen leads to the variations in lithium compounds; for example, the proportion of Li_xO_y is elevated from 14% to 36% compared to the nitrogen condition, as illustrated in Fig. S2(c). In general, the presence of ambient gas impacts the dynamics of LNT droplets and the formation of lithium clusters.

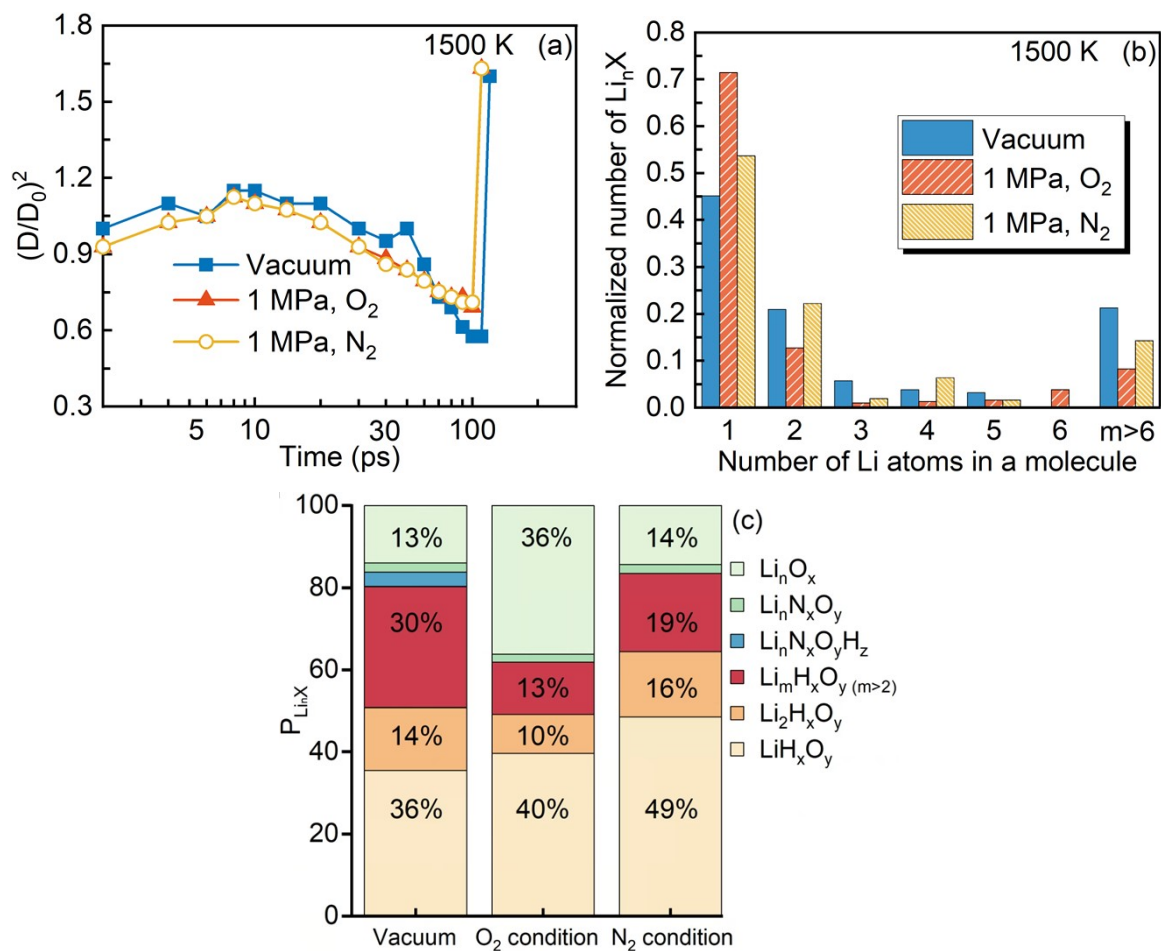


Fig. S2 Ambient gas effect on droplet behaviours and lithium cluster formation, as indicated by (a) temporal evolution of normalized diameter squared of an isolated lithium nitrate droplet, and (b) probability distribution of the number of lithium atoms in a molecule at the

time when droplet disrupts, and (c) proportion of lithium compounds at the time when droplet disrupts. $(D/D_0)^2$ refers to the normalized droplet diameter squared.