Fundamental study on the wetting property of liquid lithium

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A R T I C L E   I N F O

A B S T R A C T

The wetting behavior of molten liquid lithium is important to many fields of applications, especially to the Li-matrix composite anodes for batteries. Although changing the wettability of matrices has been previously shown through surface-coating, the selection criteria for suitable coating materials and optimal coating thickness and the mechanism of wettability improvement still remain unclear. Here, we study the effects of temperature, surface chemistry and surface topography on the wettability of substrates by molten liquid lithium. We summarize the following guiding principles: 1) Higher temperature decreases the viscosity of molten liquid lithium and produces smaller contact angle. 2) The wettability can be improved by coating the substrates with Li-reactive materials. The negative Gibbs free energy drives the wetting thermodynamically. The solid reaction product (Li_2O) can cause kinetic barriers to wet. The contact angle decreases along with the increase of Li-reactive materials' coating thickness since more materials give more negative Gibbs free energy. Among all the coating materials, gold shows the best wettability due to the large negative Gibbs free energy released by the Li-Au reaction thus providing a strong driving force, and the lack of solid product (Li_2O) formation thus avoiding any spreading resistance of liquid lithium. 3) Substrate morphology also affects the wetting behavior of molten lithium, in way similar to water wetting. Surface roughness can increase drastically the lithiophobicity, resulting in super lithiophobic surface. These findings provide important insights in the design of Li-matrix composites and open up new opportunities for the practical application of lithium.

1. Introduction

The wetting behavior of liquids on solid substrates is a very important aspect of surface chemistry, which plays a key role in addressing many problems related to energy, environment and healthy [1–5]. In the past decades, much effort has been spent on the study of the wetting of water or oil droplets on solid surfaces, including investigations on both fundamental mechanisms and practical applications [6–8]. Recently, increased attention has been focused on the wetting behavior of molten liquid lithium, which has a low melting point, excellent thermal and electrical conductivity and promising application in many fields, such as plasma spraying, tritium production and Li-matrix composite infiltration for batteries [9–13]. Among them, Li-matrix composites which show promise in solving the common problems of lithium metal anodes like dendrite growth, unstable solid electrolyte interphase and infinite relative volume change, have triggered strong scientific and technological interest [14–18]. However, most available matrices cannot be wetted by liquid lithium, thus

hindering the development and practical application of Li-matrix composites.

To address the wetting problem, material-design solutions mainly by surface modification on the matrices have been demonstrated by our group [19,20] and further developed by other researchers [21–28]. The wetting of lithium in carbon and copper was improved by coating with Si [19]. Besides, adding of acetylene black particles [21] or coating with ZnO [20,22], Ge [23], Al [24], Mg [25], Sn [26], Al_2O_3 [27] and Ag [28] have also demonstrated efficacy in improving the wettability of matrices by molten lithium. Despite these great improvements, many issues still remain to be solved: 1) The fundamental mechanism of improving lithium wetting through surface coating needs to be understood. 2) The optimal coating thickness to ensure good wettability while minimizing coating weight should be identified. 3) The effect of other factors such as surface topography and passivation film formation on the wetting of liquid lithium should also be investigated.

Herein, we study the wetting behavior of molten lithium on substrate by changing the temperature, surface chemistry and surface

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topography. The wettability of lithiophobic substrates (lithiophobic indicates a large contact angle, while lithiophilic indicates a low contact angle between liquid lithium and solid surface) (Ti, Ni, Mo, LiF, C, etc.) is improved either by increasing the temperature to decrease the viscosity of liquid lithium, or by coating the lithiophobic substrates with Li-reactive materials (Au, Ag, Al, ZnO, TiO$_2$, Al$_2$O$_3$, etc.). Notably, we found that there's an obvious negative correlation between the contact angle (θ) and the coating thickness of these Li-reactive materials. For the same coating thickness of all materials studied, gold shows the best wettability. This phenomenon results from the strong driving force provided by the large negative Gibbs free energy released by the Li-Au reaction and the low spreading resistance of liquid lithium due to the absence of Li$_2$O formation. In addition, the discontinuous surface topography and trapped inert gas of Ni foam blocks the spreading of liquid lithium, resulting in better wettability of flat Ni foil than Ni foam.

2. Experimental section

2.1. Coating Ti foil with LiF

LiF was deposited onto Ti foil using an evaporator, controlled by SQC-310, deposition controller. The deposition rate is 0.2 nm/s. the deposited thickness is 300 nm.

2.2. Coating Ti foil with Li-reactive materials

Li-reactive materials were deposited onto Ti foil using an AJA International, Inc. ATC ORION sputtering system with a sputter-down configuration. Metals including Au, Ag and Al were deposited via direct current, while metal oxides including ZnO, TiO$_2$ and Al$_2$O$_3$ were deposited via radio frequency magnetron sputtering. For Au, Ag and Al coatings, argon was used as a working gas along with an unbalanced magnetron configuration. All of the deposition power for Au, Ag and Al was 150 W, and the working gas pressure was set at 1.33 Pa. For ZnO, TiO$_2$ and Al$_2$O$_3$ coating, argon and oxygen was used as a working gas, and the ratio of argon to oxygen was 15:1, 10:1 and 10:1, respectively. The deposition power for ZnO, TiO$_2$ and Al$_2$O$_3$ coating was 80, 150 and 200 W, respectively, and all the working gas pressure was set at 0.67 Pa. The thickness of the coated materials is controlled by the coating time.

2.3. Experimental setup for the evaluation of the wettability

To properly investigate the wetting properties of liquid lithium, it is important that the lithium surface should be as clean as possible. Due to the highly reactive nature of lithium with many atmospheric species, the tests were carried out in a glovebox (Both concentrations of H$_2$O and O$_2$ are below 0.1 ppm). The native surface film which is mainly composed of Li$_2$O and Li$_2$CO$_3$ (Fig. S1) on the lithium droplet was removed by scraping gently with a clean stainless steel dipper handle until the lithium droplet looks smooth and shiny with metal luster. Then the freshly scraped lithium droplet was transferred to the testing substrate which is placed on a stainless steel stage. The temperature of the stage can be adjusted via a hotplate situated below the stage (Fig. 1a). We placed a lithium droplet onto the testing substrate and recorded images of the droplet at various temperatures. The still images were then analyzed to determine the contact angle or wettability (Fig. 1b). The photos of the experimental setup and other details for the evaluation of the wettability can be found in Fig. S2. Although the oxidation rate is suppressed in the glovebox, it is still noticeable at the temperatures investigated. To combat this, at set intervals, a new droplet was placed to ensure that the surface of the lithium would be fresh.
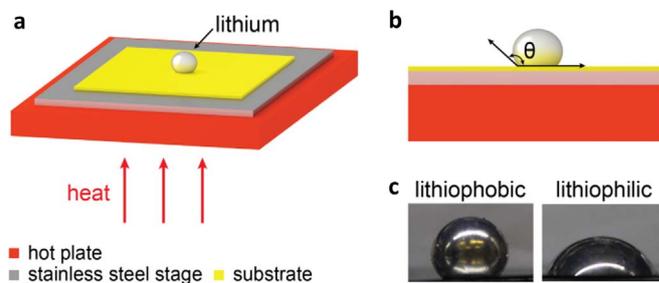

Fig. 1. Schematic for the experimental setup and wettability evaluation by contact angle. (a) Schematic of experimental setup for wettability study. (b) Schematic of the evaluation of contact angle. (c) Optical images of lithium droplet on lithiophobic (left) and lithiophilic (right) substrates.

2.4. Characterization

SEM images were taken using a FEI XL30 Sirion scanning electron microscope at an acceleration voltage of 5 kV. XPS analysis was performed on PHI Versa Probe 5000 (Physical Electronics).

3. Results and discussion

3.1. The effect of temperature

The wetting of liquid lithium on various kinds of substrates including stainless steel, titanium, molybdenum, nickel, lithium fluoride and carbon foil was investigated. All these substrates show a super-lithiophobic (defined as contact angle larger than 120°) behavior at 215 °C (note: to make the lithium droplet transfer more easily, 215 °C is chosen instead of the melting point of lithium (180.5 °C)). And Ti foil exhibits the weakest wettability with the largest contact angle observed of about 146° (Fig. 2), which is possibly due to the native oxide layer. The contact angles for all these substrates decreased when the testing temperature increased. The reason may be that the entropy increases along with the increase of temperature, resulting in the decrease of both the surface tension and the viscosity of liquid lithium [10], thus better wettability at higher temperature.

3.2. The effect of surface chemistry

Besides increasing the temperature, coating substrates with Li-reactive materials, such as Au, Ag, Al, ZnO, TiO$_2$ and Al$_2$O$_3$ can also improve the wettability. As shown in Fig. 3, lithiophobic Ti foil becomes lithiophilic after a thin layer coating of Au, Ag, Al or ZnO (SEM images about the Ti foil after coated with Li-reactive materials can be found in Fig. S3). By increasing the coating thickness of these Li-reactive materials, the contact angle can be reduced. Besides, with the same coating thickness, Au-coated Ti foil shows the smallest contact angle, while the contact angle on the Al$_2$O$_3$-coated Ti foil is the largest ($\theta_{Au} < \theta_{Ag} < \theta_{ZnO} < \theta_{Al} < \theta_{TiO2} < \theta_{Al2O3}$) (Fig. 3). After coated with only 7 nm Au, the lithium affinity of Ti foil improves substantially (146° to 51°, before and after coating).

We propose that the different wettability for these coated materials can be explained mainly by two mechanisms: the thermodynamic driving force provided by the Gibbs free energy of the reactions between Li and coated materials, and the kinetic spreading resistance from the formed Li$_2$O film.

The Gibbs free energy released by the reaction is one of the most important driving force for spreading [29,30]. A more negative Gibbs free energy can provide stronger driving force for the spreading of liquid lithium, thus leading to better wettability. According to previous works [31–34], the contact angle in reactive wetting can be described by the following equation:
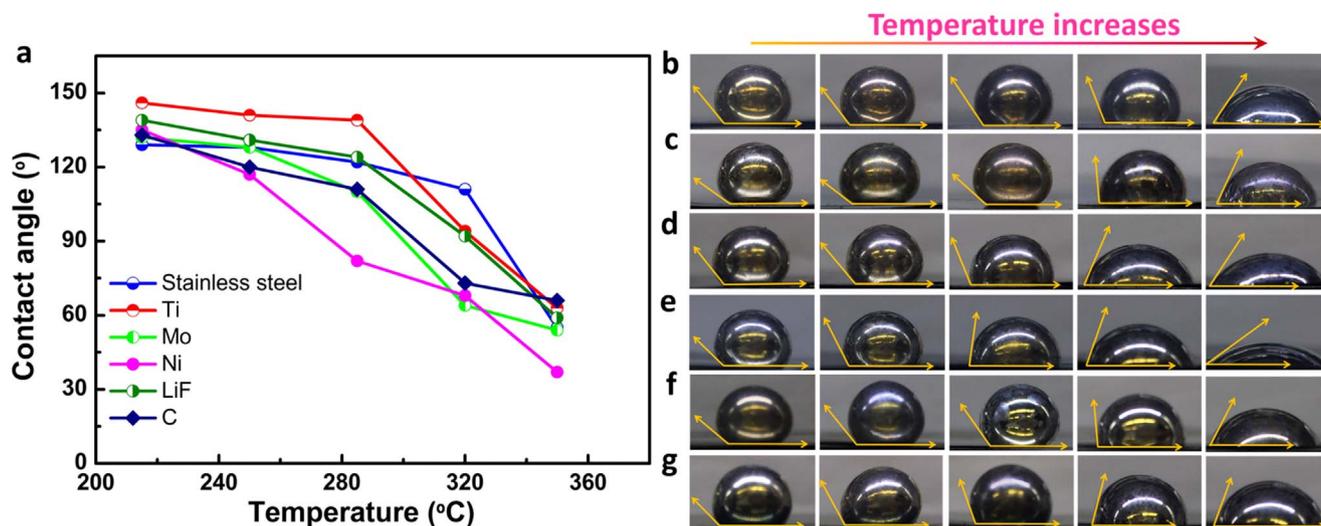
Fig. 2. The effect of temperature on wetting of liquid lithium. (a) Diagram of the contact angle of liquid lithium on various substrates as a function of temperature. (b-g) Optical observation of the contact angle of liquid lithium on (b) stainless steel foil, (c) Ti foil, (d) Mo foil, (e) Ni foil, (f,g) stainless steel coated with (f) LiF and (g) carbon film at different temperatures. Temperature increases from left to right: 215, 250, 285, 320 and 350 °C, respectively.

$$\cos\theta^1 = \cos\theta^0 - \frac{\Delta\gamma_{sl}}{\gamma_{lv}} - \frac{\Delta G}{\gamma_{lv}} \tag{1}$$

Where, γ_{lv} is the liquid-vapor interfacial energy, $\Delta\gamma_{sl}$ is the variation in the γ_{sl} (solid-liquid interfacial energy) due to the change in the physicochemical nature of the interface (such as secondary phase Li-alloy formed in the interface), θ^0 is the contact angle in the absence of reaction, θ^1 is the contact angle after reaction and ΔG is the Gibbs free energy of the reaction. Obviously, both the decrease of the γ_{sl} ($\Delta\gamma_{sl} < 0$) and the negative Gibbs free energy released by the reaction can increase the wettability. Besides, according to Eq. (1), the more negative Gibbs free energy (ΔG) is, the larger the value of $\cos\theta^1$ will be, resulting in a smaller contact angle (θ^1) and better wettability. The specific Gibbs free energy per unit area for the reaction between Li and coated materials was calculated and compared in Table 1 (details of the calculations can be found in Supplementary information). The Gibbs free energy released by the Li-Au reaction is much more negative than that released by other coated materials (except for ZnO), resulting in a better wettability of Au-coated Ti foil.

Table 1

Comparison of the Gibbs free energy released by the reaction between Li and coated Li-reactive materials.

Coated materials	Products	Specific Gibbs energy (10^9 J/m^2)	Critical wetting thickness (nm)
Au	Li$_{15}$Au$_4$	$-15.6 \times t$	7.5
Ag	Li$_9$Ag	$-4.5 \times t$	24.5
Al	Li$_9$Al$_4$	$-4.9 \times t$	35
ZnO	Li$_3$Zn, Li$_2$O	$-20.0 \times t$	34
TiO$_2$	Ti, Li$_2$O	$-8.5 \times t$	$100 < t < 400$
Al$_2$O$_3$	Li$_9$Al$_4$, Li$_2$O	$-9.2 \times t$	$t > 600$

Notes: t indicates the coating thickness; Critical wetting thickness indicates the coating thickness with which the contact angle reaches 45°.

Besides the wetting-assistive effect of Gibbs free energy, one should also consider the hindering effect of Li$_2$O films on wetting by liquid lithium. As Table 1 shows, the critical wetting thickness, i.e., at which a contact angle of 45° was achieved, of ZnO is much larger than that of
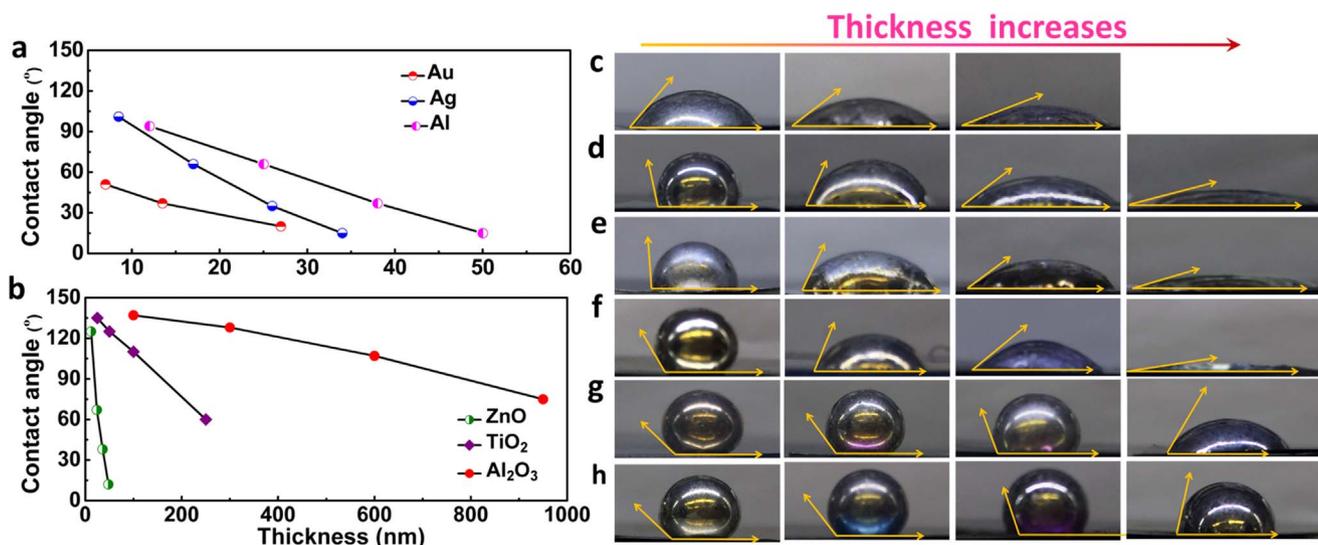

Fig. 3. The effect of surface chemistry on wetting of liquid lithium. (a,b) Diagram of the contact angle of liquid lithium on Ti foil coated with different (a) metals or (b) metal oxides as a function of coating thicknesses. (c-h) Optical observation of the contact angle of liquid lithium on Ti foil coated with (c) Au (the coating thickness is 7, 13.5 and 27 nm from left to right), (d) Ag (8.5, 17, 26 and 34 nm from left to right), (e) Al (12, 25, 38 and 50 nm from left to right), (f) ZnO (12, 24, 36 and 48 nm from left to right), (g) Al$_2$O$_3$ (100, 300, 600, 950 nm respectively) and (h) TiO$_2$ (25, 50, 100, 250 nm from left to right). The test temperature is 215 °C.
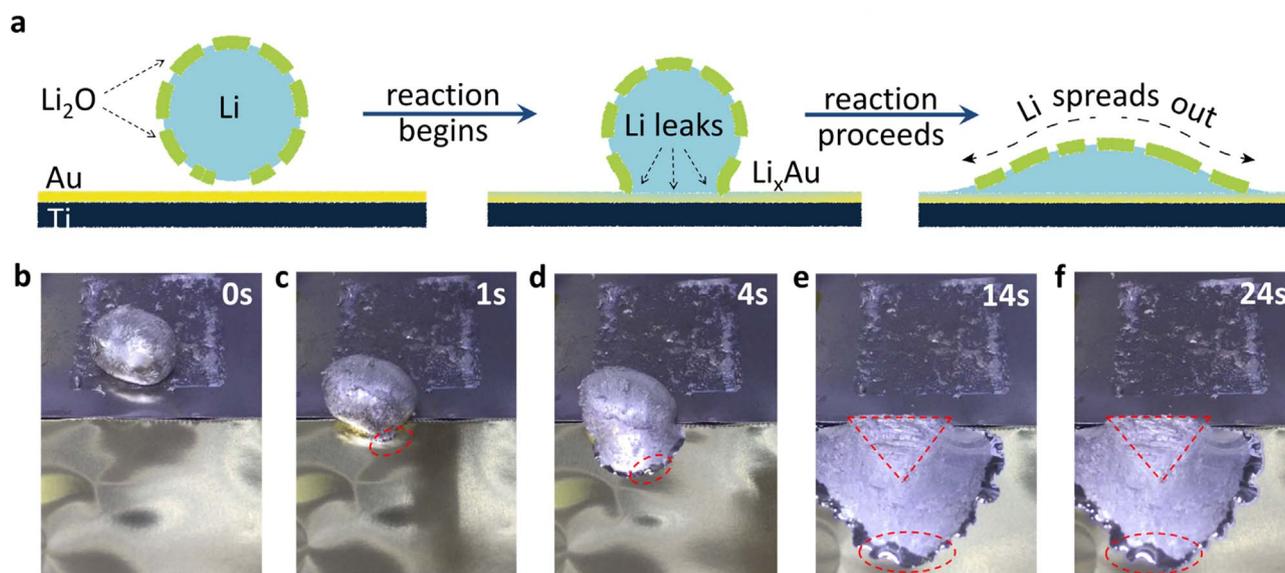
Fig. 4. Surficial Li₂O film hinders the spreading of liquid lithium. (a) Schematic showing the passivation film "breaking effect" of the reaction between Li@Li$_2$O droplet with Au. (b-f) Time lapse images of the reaction between Li@Li$_2$O droplet with 27 nm Au coated Ti foil. Li@Li$_2$O droplet touched with Au for (b) 0 s, (c) 1 s, (d) 4 s, (e) 14 s and (f) 24 s.

Au, although the Gibbs free energy released by the Li-ZnO reaction is more negative than that released by the Li-Au reaction (−20.0 × t × 10⁹ J/cm² vs. −15.6 × t × 10⁹ J/cm², t is the coating thickness). This is due to solid-state Li$_2$O formation at the three-phase contact interface of molten lithium, substrate, inert gas, during the Li-ZnO reaction which can hinder the spreading of liquid lithium, leading to a large contact angle [11,35,36]. Although the specific Gibbs free energy of the Li-Al$_2$O$_3$ reaction is close to that of the Li-TiO$_2$ reaction, the wettability of Al$_2$O$_3$ is actually much weaker than that of TiO$_2$ because more Li$_2$O is formed during the Li-Al$_2$O$_3$ reaction (2 and 3 mol of Li$_2$O are produced by 1 mol TiO$_2$ and Al$_2$O$_3$, respectively), further indicating the hindering effect of the Li$_2$O film. It is also worth mentioning that the poorer wettability of Al as compared to Ag, despite the similar Gibbs free energy for the Li-Ag and Li-Al reactions, is due to the Al$_2$O$_3$ passivation layer at the surface of Al foil which causes the formation of Li$_2$O (Fig. 3e).

To better evaluate the hindering effect of the Li$_2$O film on the spreading of liquid lithium, we performed an *in situ* observation of the reaction between a Li$_2$O-coated lithium droplet (Li@Li$_2$O) with Au (Au was coated on Ti foil, with a coating thickness of 27 nm) (Fig. 4). Fig. 4b-f demonstrate a series of images taken from a movie of the *in situ* reaction of Li@Li$_2$O droplet with Au-coated Ti foil (supplementary movie 1). Fig. 4b (0 s, before touch) shows a lithium droplet coated with a layer of Li$_2$O film with an irregular shape and a rough, wrinkled surface, which is very different from a bare lithium droplet with a round shape and a smooth, shiny surface. Fig. 4c (touch for 1 s) shows that the reaction between Au and Li happens immediately when the Li@Li$_2$O droplet touches the Au-coated Ti foil (Au can reach lithium through some pinholes in the surficial Li$_2$O film, Fig. S4). As a result, the surficial Li$_2$O film breaks, and liquid lithium leaks out from the Li$_2$O 'cage' and spreads on the substrate. Moreover, Li@Li$_2$O foil retains its unbroken shape after melting on bare Ti foil, while the surficial Li$_2$O film breaks and liquid lithium leaks out after melting on Au-coated Ti foil (Fig. S5, supplementary movie 2 and 3), further supporting the passivation film "breaking effect" of the reaction. Fig. 4d-f clearly show that the residual surficial Li$_2$O film floats at the surface of the droplet, while the smooth shiny fresh surface of bare lithium can be observed at the bottom of the droplet. The fresh surface of bare lithium grows bigger as the reaction proceeds and becomes stable after 24 s, indicating that the wetting of liquid lithium has reached equilibrium. Remarkably, a sharp triangle shape can be distinctly observed at the top of the droplet, demonstrating the obvious
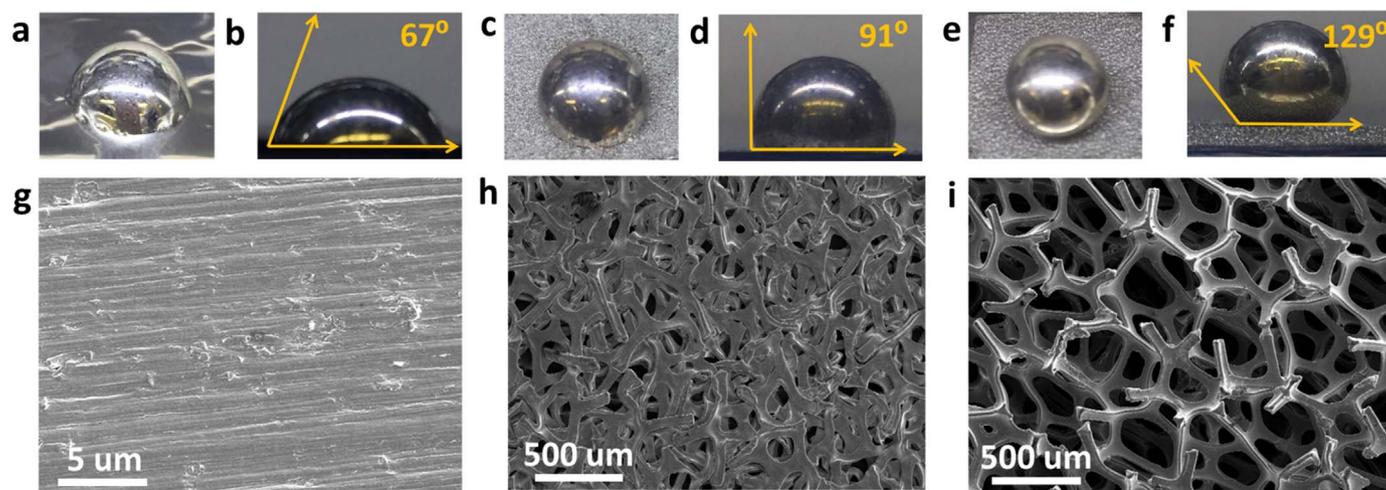

Fig. 5. Effect of surface topography of substrates. Liquid lithium wetting on (a,b) Ni foil, (c,d) pressed Ni foam; (e,f) un-pressed Ni foam. (g,h,i) SEM images of (g) Ni foil, (h) pressed Ni foam and (i) unpressed Ni foam. All the wetting tests were performed at 320 °C.

Table 2
Comparison of the observed contact angles and the calculated values according to the Cassie's equation.

Substrates	Fraction of solid surface (f_s)	Observed contact angle(°)	Calculated contact angle (°)
Ni foil	1.0	67	67
Ni foam	0.30	129	126
Pressed Ni foam	0.77	91	86

hindering effect of the surficial Li_2O film (For a bare lithium droplet, the top looks round and smooth after wetting).

Supplementary material related to this article can be found online at doi:10.1016/j.ensm.2018.05.021.

3.3. The effect of surface topography

Besides the temperature and surface chemistry, the surface topography also plays a key role in the wetting of liquid lithium. As Fig. 5 shows, the wettability of Ni foil is highly superior to Ni foam (the contact angle for Ni foil, Ni foam and pressed Ni foam is 67°, 129° and 91°, respectively; all the tests were carried out at 320 ℃). This can be ascribed to the ability of liquid lithium to easily spread along the smooth surface of Ni foil at a high temperature, while the fractured surface of Ni foam blocks the mobility of lithium. Besides, the gas environment (argon in this case, which is super-lithiophobic) can be trapped underneath the liquid lithium on porous Ni foam (Fig. S6), thus further hindering the wetting of liquid lithium. For this situation, the contact angle could be given mathematically by Cassie's equation [2]:

$$cos\theta_r = -1 + f_s(cos\theta_s + 1) \tag{2}$$

Where, θ_s is the contact angle of liquid droplet on a smooth surface, θ_r is the contact angle of liquid droplet on a rough surface, f_s is the area fraction of the solid on the surface. For the smooth surface of Ni foil, f_s is assumed to be 1, while f_s values of Ni foam before and after being pressed are evaluated to be around 0.30 and 0.77, respectively (Fig. S7). According to Cassie's equation, the calculated contact angles for unpressed and pressed Ni foam are 126° and 86°, respectively, which are close to the observed values (126° vs 129°, 86° vs 91°, Table 2).

3.4. Comparison of the wetting property of liquid sodium to that of liquid lithium

As another alkali metal, sodium shares many properties and applications in common with lithium. Here, the wetting property of liquid sodium is also studied and compared with that of liquid lithium. As shown in Figs. S8 and S9, the wetting of liquid sodium on bare Ti foil is much better than that of liquid lithium, benefited from the lower viscosity of liquid sodium than that of liquid lithium at the same temperature [37]. Interestingly, the wetting of liquid sodium on Au-coated Ti foil is poorer than that of liquid lithium (Figs. S10, S11). The reason may be that the specific Gibbs free energy of the Li-Au reaction is much more negative than that of the Na-Au reaction, resulting in a larger driving force for the spreading of liquid lithium and smaller contact angle with the same coating thickness.

4. Conclusion

In conclusion, we systematically studied the effects of temperature, surface chemistry and surface topography on the wettability of substrates by liquid lithium. Either by increasing the temperature thus decreasing the viscosity of liquid lithium, or by coating the substrates with Li-reactive materials, the wettability of lithiophobic substrates can be greatly improved. Remarkably, an obvious negative correlation was found between the contact angle and the thickness of these coated

materials, wherein gold shows the best wettability with the same coating thickness. After coating with only 7 nm Au, the lithium affinity of Ti foil improves substantially (146°, 51°, before and after coating). The superior wettability of Au-coated Ti foil can be explained by the large negative Gibbs free energy released by the Li-Au reaction which provides a strong thermodynamic driving force for the wetting of lithium, and the absence of Li_2O formation during the reaction thus avoiding kinetic barrier to lithium spreading. In addition, the fractured surface topography and trapped inert gas underneath Ni foam can block the spreading of liquid lithium, resulting in a better wettability of flat Ni foil than Ni foam. Choosing the most suitable coating materials and coating with the optimal thickness can ensure good lithium wettability and minimize coating weight and volume simultaneously. These findings shed new light on the design of Li-matrix structures and open up new opportunities for the practical application of lithium.

Acknowledgements

Declarations of interest

The authors declare no competing financial interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2018.05.021.

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