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# Constructing a uniform lithium iodide layer for stabilizing lithium metal anode

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# ABSTRACT

The metallic lithium (Li) is the ultimate option in the development of anodes for high-energy secondary batteries. Unfortunately, inferior cycling reversibility and Li dendrites growth of Li metal as anode enormously impede its commercialization. Here, a uniform Lil protective layer is constructed on Li metal anode via a facile and direct solid–gas reaction of Li metal with iodine vapor. The pre-constructed Lil layer possesses more steadily and faster Li ion transport than the conventional SEI layer and contributes to a steady interface for the Li metal anode, which affords a smooth Li deposition morphology without Li dendrites formation. The symmetrical cell with the Li metal anode protected by Lil layer exhibits a longer cycling lifetime of over 700 h at a current density of 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>. Moreover, the Lil layer protected Li metal anode can still remain high capacity retention of 74.6% after 500 cycles in the full cell paired with NCM523 cathode. The work proposes an easy and effective method to fabricate a uniform and stable protective layer on the Li metal anode and offers a practicable thinking for the commercial implementation of Li metal batteries.

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### 1. Introduction

Since Sony Corporation had successfully launched the first commercial lithium-ion batteries (LIB) in 1991, LIB have been generally applied in portable electronics, electric vehicles (EV) and high-end communication terminal [1,2]. However, the rapid development of industries such as EV, high-end communication terminals, and large-scale energy storage stations urgently require developing novel secondary batteries with much higher energy density to satisfy the growing energy demand in such new application scenarios [3–5]. Li-S (2600 Wh kg<sup>-1</sup>) and Li-O<sub>2</sub> (3500 Wh kg<sup>-1</sup>) batteries using Li metal as the anodes are considered to be very promising high-energy battery systems and have attracted widespread attention [6]. Li metal anode with superhigh theoretical specific capacity (3860 mAh g<sup>-1</sup>) and ultralow reduction potential (-3.045 V vs. standard hydrogen electrode) has become extremely attractive anode candidate in the high-energy secondary battery [7,8].

Unfortunately, the commercial implementations of Li metal anodes are still greatly impeded by safety hazards and inferior Coulombic efficiency, mainly originating from uncontrollable growth of Li dendrites and unstable formation of solid electrolyte interface (SEI) during cycling. Li metal has high activity and reacts with the components of electrolyte to generate SEI on Li metal anodes, thus preventing further reactions between metallic Li and the electrolyte [9–11]. However, the naturally formed SEI is unstable and fragile, and it is prone to cracks owing to volume expansion during repeated Li plating/stripping. The fracture of SEI causes uneven Li ion flux, which accelerates Li dendrites growth that eventually may penetrate through the separator, leading to cell short circuit and safety problems such as thermal runaway and explosion [12-14]. In addition, the repeated breakage and regeneration of SEI and the emergence of "dead" Li increase the continuous loss of electrolyte and active metallic Li, resulting in a low Coulombic efficiency [15,16]. Therefore, unstable electrode/electrolyte interface and growth of dendritic Li seriously deteriorate cycling lifespan and security of Li metal anode and its application in the high-energy storage system.

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In recent years, to solve these problems, a large number of effective approaches have been taken to enhance the electrochemical cycling performance of Li metal anodes. An effective method is to designing 3D conductive matrix for Li metal. For example, 3D porous Cu foil [17], graphitized carbon fibers (GCF) [18], vapor grown carbon fiber (VGCF) [19], and reduced graphene oxide (rGO) [20] have been widely investigated. A conductive current collector with multi-dimensional network structure could act as the deposition substrate, which can not only greatly decrease the current density through enlarging the deposition surface area and thus delaying the onset of Li dendrites, but also provide a fixed host for Li deposition and decrease the damage caused by volume during repeated charging/discharging process expansion [11,21,22]. However, Li metal is still exposed and reacts with the electrolyte to generate a fragile SEI. At the same time, the increased specific surface area causes more parasitic reaction, accelerating the consumption of chemical active Li metal and electrolyte. In such a context, constructing a steady and uniform SEI layer on the Li metal anode is regarded as the most fundamental and promising strategy for stabilizing Li deposition. An ideal SEI should possesses at least homogeneous and fast Li ion transport property for promoting uniform electrochemical Li conduction and deposition as well as electronic insulation to prevent parasitic reactions between chemical active Li metals and electrolyte [10,23,24]. Liguid electrolyte additives such as LiNO<sub>3</sub> [25,26], vinylene carbonate (VC) [27], vinyl ethylene carbonate (VEC) [28] and fluoroethylene carbonate (FEC) [29,30] can be applied to regulate the composition of SEI to obtain more stable SEI. Localized high concentrated electrolytes can be applied to enhance the stability of SEI and improve Coulombic efficiency [31]. Constructing polymer coating layers, such as polyvinylidene fluoride (PVDF) [32], polyacrylonitrile (PAN) [33] and polypyrrole (PPy) [34], which act as physical barrier to inhibit growth of Li dendrites were also attempted. Another approach is to construct Li alloy layers (for example Li-Al [35], Li-In [36], Li-Zn [37] and Li-Si [38]) to enhance electrochemical kinetics and mitigate Li dendrites formation. In addition, the Lihalide SEI lavers (such as LiF or LiI) are formed by soaking Li metal in solution containing halogen ions, which is beneficial to Li deposition without dendrite morphology because its faster ion transport than Li<sub>2</sub>CO<sub>3</sub> that is the most common component in native SEI [39–41]. However, the SEI obtained by the common solution soaking method is uneven and rough, due to the solid-liquid reaction usually combined with the decomposition of electrolyte thus made the composition and structure of the SEI more complex which is not conducive to homogeneous Li-ion flux and deposition. Hence, based on the above considerations, a new method is needed to prepare a steady and even SEI to promote uniform Li deposition and ameliorate the cycling performance of Li metal anodes.

Inspired by the reaction of Li metal with iodine in Li-I<sub>2</sub> batteries to form LiI as a solid electrolyte film, we reports a simple solid-gas reaction method to fabricate a uniform LiI layer in situ on Li metal anode surface as a protective layer via using Li metal react with iodine vapor, which enables high uniformity of LiI layer and avoids by-products from the side reactions between metallic Li and organic solvent in the common solution soaking method. The asobtained LiI layer shows faster Li ion transport than the conventional fragile SEI layer, which regulates Li deposition behavior and effectively inhibits the formation of dendritic Li. In addition, the uniform Lil layer formed by this simple solid-gas reaction could keep the integrity throughout the repeated cycles and effectively prevent the contact and side reactions between Li metal anodes and the electrolyte, providing a steady electrode/electrolyte interface for the Li<sup>+</sup>/Li plating/stripping process. These features of the Lil layer render the Li metal anode with good stability in the electrolyte and dendrite-free morphology during cycling. Consequently, in the symmetrical cell, the Li metal anode protected

by Lil layer exhibits a distinct improvement in the cycling stability and can be stably cycled for over 700 h at 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>. In full cells paired with NCM523 cathode, the Li metal anode protected by Lil layer shows a higher capacity retention of 74.6% after 500 cycles at a charge–discharge rate of 2 °C (1.056 mA cm<sup>-2</sup>), which is superior to the bare Li anode. In this work, we demonstrate an easy and effective method to restrain Li dendrites growth and ameliorate the cycling lifespan of Li metal anodes.

#### 2. Experimental

# 2.1. Synthesis of Li metal foil with Lil layer

The Li metal foil (12 mm in diameter and 1 mm in thickness) was scraped and polished by means of a sharp blade. After polishing, the Li metal foil and iodine powder (I<sub>2</sub>, Aladdin, 99.8%) were placed in a quartz reactor (200 mL), and then the quartz reactor was sealed and heated at 140 °C for 4 h to induce the solid–gas reaction and the LiI layer on the Li metal foil (LiI-Li). All of these procedures were carried out in a glove box filled Ar.

### 2.2. Material characterization

The surface morphologies of the Li metal foil were characterized by scanning electronic microscopy (SEM, Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo Scientific K-Alpha+ spectrometer with Al  $K\alpha$  radiation source.

#### 2.3. Electrochemical measurements

Symmetric cells (both LiI-Li foils and bare Li foils were applied as working and counter electrodes) were assembled as CR2032 coin cells in a glove box filled Ar (both H<sub>2</sub>O and O<sub>2</sub> concentrations below 0.5 ppm). Li plating/stripping cycling and electrochemical impedance spectroscopy (EIS) tests were conducted by assembling symmetric cells. In the symmetric cells, 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in ethylene carbonate (EC) and diethyl carbonate (DEC) (v/v = 1/1) without other additives was applied as the electrolyte, and the electrolyte added into each cell was controlled at 60 µL. The Celgard 2400 was applied as the separator. Li plating/ stripping measurements were performed on a NEWARE multichannel battery testing system at 25 °C. The EIS tests were carred out on a Solartron electrochemical workstation in the frequency range of  $10^{-1}$  Hz.

The  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  (NCM523) and  $LiFePO_4$  were used as the cathode materials for the assembly of full cells (CR2032). To prepare the NCM523 electrodes, the NCM523 powder, poly(vinyl difluoride) (PVDF), acetylene black were mixed in N-methyl pyrrolidone (NMP) at a weight ratio of 8:1:1, stirred for few hours and evenly coated on the aluminum foil, then placed in vacuum oven at 80 °C and dried for 24 h. The laminate was cut into discs (diameter 11 mm). The areal mass loading of active material on NCM523 electrode was ~3.3 mg cm<sup>-2</sup>. The LiFePO<sub>4</sub> electrodes were prepared by mixing the LiFePO<sub>4</sub> powder, acetylene black, PVDF in NMP at a weight ratio of 8:1:1. The areal mass loading of active material on LiFePO<sub>4</sub> electrode was ~5.3 mg cm<sup>-2</sup>. The electrolyte applied to the full cell was 1 M LiPF<sub>6</sub> (EC/DEC, v/v = 1/1) (the electrolyte added into each full cell was controlled at 80 µL), and the Celgard 2400 was applied as the separator. The full cells tests were conducted on a NEWARE multichannel battery testing system at 25 °C. The NCM523/Li cells were worked in the voltage range of 2.8–4.3 V. The LiFePO<sub>4</sub>/Li cells were worked in the voltage range of 2.5-4.0 V.

### 3. Results and discussion

A uniform LiI protective laver is fabricated on the Li metal foil surface via a facile and direct solid-gas reaction. As displayed in Fig. 1(a), polished Li metal foil and iodine powder were placed in a quartz reactor and heated to 140 °C. Iodine powder was heated to generate iodine vapor to react with fresh Li metal foil at the solid-gas interphase, thereby forming an even LiI protective layer on Li metal foil (LiI-Li). After reacting with iodine vapor, the color of Li metal foil changes obviously (Fig. S1). The elevated temperature facilitates the conversion of iodine powder into iodine vapor, which reacts with the polished Li metal foil and promotes the construction of a uniform and mechanically robust LiI layer. Compared with other methods to construct an artificial SEI, the solid-vapor reaction method has following advantages: Firstly, in an atmosphere filled with iodine vapor, enabling high uniformity of LiI layer formation and avoiding by-products from side reactions between metallic Li and organic solvent in the common solid-liquid method; Secondly, the method of heating the Li foil providing assistance of the thermodynamic conditions for the reaction of Li metal with iodine vapor to form LiI; Thirdly, easily applying for practical large-scale manufacturing. The schematic illustration of Li deposition behavior with and without LiI laver protection is illustrated in Fig. 1(b). For the bare Li electrode, the uneven and fragile SEI results in inhomogeneous Li-ion flux and growth of dendritic Li. By contrast, the uniform composition with high purity of Lil and fast Li-ion transporting in this in situ constructed protective layer not only causes the homogeneous distribution of Li-ion flux near the interface but also contributes to a steady electrode/electrolyte interface for the Li metal electrode in the electrolyte, resulting in uniform Li deposition and suppression of Li dendrites.

The element content and valence on the surface of LiI-Li electrode are analyzed using X-ray photoelectron spectroscopy (XPS). Li 1s, O 1s, C 1s, I 3d are clearly seen in the spectrum shown in Fig. 2(a). I 3d spectrum in Fig. 2(b) exhibits that two obvious XPS peaks of I element at 618.90 eV and 630.40 eV, which belong to the electrons from the I  $3d_{5/2}$  and I  $3d_{3/2}$  level of LiI, respectively. The morphologies of LiI-Li and bare Li electrodes are observed by scanning electron microscopy (SEM). As displayed in Fig. 2(c), the bare Li electrode shows a smooth surface with a few scratches. After treatment of the Li metal with iodine vapor, the resulting LiI-Li electrode has a uniform and smooth surface without cracks (Fig. 2d, e). This even LiI layer which was in-situ constructed directly on the Li metal electrode can not only prevent the contact between Li metal electrodes and the electrolyte, but also contribute to the uniform distribution of current density. From the cross-sectional SEM image of LiI-Li electrode, it can be observed that the thickness of LiI protective layer is around 500 nm (Fig. 2f), which is thinner than the protective layer obtained by the solution soaking method and thus could reduce the transport resistance of Li ion at the interface. These results could confirm a uniform Lil protective layer with high purity was successfully formed on the Li metal foil surface via a reaction of metallic Li with iodine vapor. Moreover, the in-situ constructed protective layer by solid-gas reaction shows compact structure without any pores or crack formation which is quite common in solid-liquid reaction due to the introduction of electrolyte.

The EIS measurements of the symmetric cells at different standing time were performed to investigate the interfacial stability of LiI-Li and bare Li electrodes in the carbonate-based electrolyte. As displayed in Fig. 3(a), the interfacial impedance ( $R_i$ ) of the bare Li electrode shows a significant increase from 237  $\Omega$  to 798  $\Omega$  after 96 h, revealing that the ion-insulating passivation layer is gradually getting thicker by continuous side reactions between metallic Li and the electrolyte and the interfacial impedance is increased.



**Fig. 1.** (a) The schematic illustration of preparation of Lil-Li electrode. (b) The schematic illustration of Li deposition behavior with or without Lil layer protection.

What is worse, the R<sub>i</sub> is still increasing means that the electrode/electrolyte interface on the bare Li electrode in the electrolyte is still unstable even after quite a long time. This uncontrollable side reaction could induce continuous electrolyte consumption and low Coulombic efficiency. While in comparison, the R<sub>i</sub> value of the LiI-Li electrode increases to 325  $\Omega$  after 24 h and then remains stable (Fig. 3b). The increase of the  $R_i$  value after 24 h may be attributed to the fact that LiI is an inorganic crystal particle with tiny gaps between particles. The  $R_i$  value of the LiI-Li electrode stabilizes at a lesser value after a shorter standing time compared to that of the bare Li electrode, indicating that the side reactions between the LiI layer protected Li metal electrode and the electrolyte have been availably suppressed and the electrode/electrolyte interface is very stable. The stable interface could be attributed to the uniform Lil layer without cracks constructed by the solid-vapor reaction process, preventing the contact between Li metal electrodes and the electrolyte. Furthermore, the LiI-Li electrode shows a smaller initial R<sub>i</sub> value compared with the bare Li electrode, which indicates that the Lil layer possesses better Li ion transport capability than the conventional SEI layer formed on the bare Li electrode. The reason could be that LiI laver is an ionic conductor and reduces the formation of ion-insulating reduction species on Li metal electrode surface in the electrolyte. As a result, constructing a uniform Lil protective layer in situ on Li metal electrode surface is benefit to form a stable and low resistive electrode/electrolyte interface in the carbonate-based electrolyte.

To evaluate the cycling stability of the Lil-Li electrode, the symmetric cells of the Lil-Li and bare Li electrodes were assembled using carbonate-based electrolyte without any additive for galvanostatic cycling tests at different current densities. As shown in Fig. 4(a), when cycling at 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>, the cell with bare Li electrode shows an increasing hysteresis voltage after 260 h, even cell short circuit after 386 h. As a comparison, the cell with Lil-Li electrode can be stably cycled to 700 h with only slightly increased hysteresis voltage and subsequent without cell short circuit, indicating that the cycling stability of Li metal electrode is improved by the Lil layer on Li metal surface. Fig. 4(b-d) shows local more detailed comparison of cycling plateaus corresponding to Fig. 4(a). The bare Li electrode (85 mV) exhibits a larger hysteresis voltage than the



Fig. 2. (a) XPS spectrum of Lil-Li electrode. (b) I 3d XPS spectrum of Lil-Li electrode. SEM images of (c) bare Li electrode and (d, e) Lil-Li electrode. (f) Cross-sectional SEM image of Lil-Li electrode.



Fig. 3. EIS diagrams of the symmetric cells with (a) bare Li electrode and (b) Lil-Li electrode as a function of standing time at room temperature.

Lil-Li electrode (63 mV) at 100 h (Fig. 4b). This reason is that the Lil Layer possesses better Li ion transport capability than the conventional SEI layer, decreasing the overpotential of Li deposition. With the repeated charge–discharge cycling, the conventional SEI layer repeatedly ruptures and repairs and more Li dendrites form and break, leading to the appearance of interfacial layer containing thick SEI and "dead" Li and the continuous consumption of the electrolyte. The hysteresis voltage of bare Li electrode increases to 109 mV and 245 mV at 280 h and 374 h, respectively (Fig. 4c,d). By contrast, the Lil-Li electrode does not exhibit a significant fluctuating voltage profile, which is because of the keeping stable interfacial impedance resulting from the stable

interface of the LiI-Li electrode. When cycling at 2 mA cm<sup>-2</sup>, both bare Li electrode and LiI-Li electrode show an increase in hysteresis voltage (Fig. 4e). The cell with bare Li electrode shows greatly increased hysteresis voltage after 125 h and short circuit at about 179 h, while the cell with LiI-Li electrode can stably cycle for more than 250 h without cell failure. The regularity of local more detailed comparison of cycling plateaus is the same as that of the cell cycling at 1 mA cm<sup>-2</sup> (Fig. S2). These results well reflects that the uniform LiI protective layer can availably ameliorate the cycling stability and cycling lifespan of the Li metal electrodes via providing a stable and low resistive electrode/electrolyte interface for the Li metal electrodes.



**Fig. 4.** Comparison of the cycling stability of the symmetric cells for bare Li (black) electrode and Lil-Li (red) electrode. (a) Voltage profiles at 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>. (b–d) Magnified voltage curves of 100–120 h, 280–300 h, 374–394 h at 1 mA cm<sup>-2</sup>. (e) Voltage profiles at 2 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>.

To further confirm the stability of LiI-Li electrode, the interfacial impedance of the bare Li electrode and the LiI-Li electrode at different cycles was investigated by performing EIS measurements of the symmetric cells. Fig. 5(a) shows the interfacial resistance of the bare Li electrode is around 120  $\Omega$  after 50 cycles and decreases obviously to around 61  $\Omega$  after 100 cycles. This could be because uneven Li deposition leads to rough and dendritic Li on surface of Li metal electrode during cycling, which expands the contact area between fresh Li metal and the electrolyte. Nevertheless, the bare Li electrode exhibits an obviously increased interfacial resistance after 150 cycles, which is because of the continuous consumption of the electrolyte and the generation of interfacial layer containing thick SEI and "dead" Li mainly originating from the repeated breakage and regeneration of SEI and the fracture of Li dendrites. By contrast, the LiI-Li electrode shows lower and indistinctively fluctuant interfacial resistances after 50, 100 and 150 cycles, with around 69  $\Omega$ , 61  $\Omega$  and 58  $\Omega$  respectively owing to fast Li ion transport and lack of accumulative "dead" Li layer, which nicely verifies its excellent stability (Fig. 5b).

To judge the effect of Lil layer on the morphology of Li deposition, SEM was applied to characterize the surface morphologies of the Lil-Li electrode and bare Li electrode after 100 cycles (Fig. 6). The cycled bare Li electrode shows a broken and uneven surface with remarkable formation of Li dendrites after 100 cycles (Fig. 6a-c). This is because the conventional SEI layer easily breaks up during repeated Li plating/stripping, resulting in Li-ions preferentially deposited near the cracks and consequently Li dendrites form. On the contrary, as display in Fig. 6(d-f), the LiI-Li electrode exhibits more smooth and uniform surface without obvious dendritic structure after 100 cycles. Fig. S3(a) is the cross-sectional SEM image of the bare Li electrode after 100 cycles, which shows the accumulated layer of Li dendrites and dead Li with a thickness of about 159 µm. In comparison, the cross-sectional SEM image of the LiI-Li electrode displays a uniform and dense morphology of Li deposition under the protective layer after the same plating/stripping cycling (Fig. S3b). This result suggests that the uniform LiI protective layer conduces to a homogeneous distribution of Liion flux near the interface of the Li metal electrode, resulting in uniform Li deposition and no Li dendrites growth. As shown in Fig. S4, the I 3*d* spectrum of the LiI-Li electrode after cycling still exhibits that two obvious XPS peaks from the I  $3d_{5/2}$  and I  $3d_{3/2}$ level of LiI, respectively, which indicates partly that the LiI layer could keep the integrity during the repeated plating/stripping cycling.

The galvanostatic cycling tests of full cells were performed to further analyze the cycling performance of the LiI-Li anodes. NCM523 cathodes were used to match the LiI-Li and bare Li anodes to assemble full cells (Fig. 7). As shown in Fig. 7(a), both full cells exhibits a similar initial discharging capacity of around 157 mAh  $g^{-1}$ . The full cell with the LiI-Li anode still remains discharging



Fig. 5. EIS diagrams of the symmetric cells of (a) bare Li electrode and (b) LiI-Li electrode at different cycles under 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>.



Fig. 6. SEM images of (a-c) bare Li electrode and (d-f) LiI-Li electrode in symmetric cells after 100 cycles at 1 mA cm<sup>-2</sup> with Li plating capacity of 1 mAh cm<sup>-2</sup>.



Fig. 7. (a) Cycling performance of NCM523 full cells with Lil-Li anode and bare Li anode at a charge-discharge rate of 2 °C (1.056 mA cm<sup>-2</sup>). NCM523 cathode area specific capacity is around 0.528 mAh cm<sup>-2</sup>. Voltage profiles of NCM523 full cells with (b) bare Li anode and (c) Lil-Li anode at different cycles.

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capacity of 117.2 mAh g<sup>-1</sup> and corresponding capacity retention of 74.6% after 500 cycles under a charge-discharge rate of 2 C  $(1.056 \text{ mA cm}^{-2})$ . By contrast, the full cell with the bare Li anode exhibits a sharp decreased discharging capacity after 180 cycles, and only remains discharging capacity of 70.7 mAh g<sup>-1</sup> and corresponding capacity retention of 45.0% when the cycle number reaches to 500. The voltage profiles of NCM523 full cells with the bare Li and LiI-Li anodes at different cycles are illustrated in Fig. 7(b and c). The voltage profiles of the full cell with the bare Li anode exhibits that the polarization voltage increases sharply with cycling and thus rapidly deteriorating the cell. The reason could be that the generation of interfacial layer containing thick SEI and "dead" Li and the continuous consumption of the electrolyte decrease ion transport, leading to an increased interfacial resistance. By contrast, the voltage profiles of the full cell with the LiI-Li anode displays a tiny increase in polarization voltage with cycling, which profits from a stable electrode/electrolyte interface provided by the uniform LiI protective layer. In addition, the LiFePO<sub>4</sub> full cells were assembled to perform galvanostatic charging/discharging measurements (Fig. S5). The cell with the LiI-Li anode (67.5%) shows higher capacity retention than the bare Li anode (31.6%) after 400 cycles at a charge-discharge rate of 2 C (1.59 mA cm<sup>-2</sup>) (Fig. S5a). The full cell with the bare Li anode exhibits a rapid increased polarization voltage with cycling, while the full cell with the LiI-Li anode shows a relatively slow increase in polarization voltage with cycling (Fig. S5b and c). These results reveal that the homogeneous and fast Li-ion transporting LiI protective layer can effectively ameliorate the cycling performance of Li metal anodes for the implementation of Li metal batteries.

#### 4. Conclusions

In conclusion, a uniform LiI layer as a protective layer is successfully fabricated on the Li metal foil by a facile and novel solid-gas reaction. The LiI layer protected Li metal anode exhibits a better stability in the electrolyte compared with the bare Li metal anode and realizes a smooth and uniform surface without dendrite morphology during cycling. The LiI layer possesses faster Li ion transport than the conventional SEI layer, favoring uniform Li deposition. Moreover, the uniform Lil layer can effectively prevent the contact and side reactions between Li metal anodes and the electrolyte, which provides a steady electrode/electrolyte interface for the Li metal anode in the electrolyte. Consequently, the symmetrical cell with the Li metal anode protected by Lil layer exhibits a notable improvement in cycling stability and can be cycled steadily for over 700 h at 1 mA  $cm^{-2}$  with Li plating capacity of 1 mAh cm<sup>-2</sup>. In the full cells with NCM523 as cathode, the LiI layer protected Li metal anode shows higher discharging capacity of 117.2 mAh g<sup>-1</sup> and capacity retention of 74.6% after 500 cycles under a charge–discharge rate of 2 C (1.056 mA  $cm^{-2}$ ), which is obviously superior to the bare Li anode. This work displays an easy and useful strategy to inhibit Li dendrites formation and promote the electrochemical performance of Li metal anodes by forming a uniform and stable protective layer on Li metal anode through a direct solid-gas reaction and proposes a practicable idea for the commercialization of Li metal batteries.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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