

Full paper

Insights into morphological evolution and cycling behaviour of lithium metal anode under mechanical pressure

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ABSTRACT

Dendritic Li formation is one of the critical reasons for the failure of Li batteries. In order to improve the lithium metal anode performance, a better understanding of the growth mechanisms of Li dendrites is necessary. Due to the malleable nature of lithium metal, mechanical pressure should play an important role in determining the morphology and cycling behaviour of Li anode. Here we investigated the effect of an applied external pressure on the electrochemical deposition of lithium metal. Instead of a highly porous, wire-like Li growth in the absence of pressure, a much more compact Li deposition can be achieved when a pressure is applied to the batteries in the charge/discharge processes. The improved Li deposition/stripping behaviour in the pressed cells yields a 5% higher Coulombic efficiency (~90%) and more than 5-fold longer cycling life than the cells without pressure at a current density of 2 mA/cm². The use of pressure in shaping Li metal is an effective approach to address the Li metal problem and advance Li technologies in the future.

1. Introduction

Li metal anode, with the highest theoretical capacity of 3860 mA h/g among lithium anode materials, has a great potential to improve the energy density of Li-based batteries. Successful application of lithium anode will not only improve the performance of existing lithium ion batteries (by replacing the graphite anode), but will also enable a wide range of high capacity cathodes (such as sulfur and oxygen cathode) to be practical. Despite the superior capacity, Li metal batteries have suffered from safety risks and cycling performance degradation since its first introduction in 1970s [1–3]. Recent research efforts have shed new light on the Li metal chemistry and provided possible attempts to modify Li anode [4–6]. It has been widely accepted that the root cause of Li metal problem comes from the inherent formation of highly porous structures, i.e. dendritic or mossy Li [7–9]. The internal short circuit caused by Li dendrite penetration results in safety issues, and the high surface area structure leads to accumulation of dead Li and depletion of electrolyte. Several strategies have been proposed to suppress the porous Li formation [4]. One approach is to introduce strong and stable solid electrolyte interphase (SEI) layers through electrolyte modification or artificial SEI formation [10–20]. Another is to confine Li metal

growth in specially designed anode frameworks or using solid state electrolyte [21–32]. Due to the malleable nature of lithium, the presence of a mechanically strong and confined structure can suppress lithium dendrites growth. Therefore, a thorough understanding of Li deposition and dissolution under pressure during electrochemical cycling will provide insight into the Li metal issue.

Although there are several works about the pressure effect on lithium batteries performance, most of these works were conducted in a specific type of battery system and the results from different reports are sometimes contradicting. Wilkison et al. demonstrated an increased cycling efficiency by enhancing electrode stack pressure in a Li-Li_xMoS₂ cell [33]. Hirai et al. reported varied dependences of Li cycling efficiency on external pressure in Li-V₂O₅-P₂O₅ cells using different electrolytes [34]. Gireaud et al. found an improved efficiency of Li-Cr₂O₃ cells with increasing pressure [35]. Besides, positive influence of pressure on the cyclability of a Li-S battery was reported by Mikhaylik et al. [36]. On the other hand, pressure was also reported to reduce the specific capacity of Li-S batteries [37], due to reduced battery kinetics of the pressed cathode. The added complexity caused by the cathode materials results in ambiguous understandings of the genuine response

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of Li metal to external pressures. Considering the significance of pressure in lithium batteries and the fact that there lacks a clear understanding of Li deposition and dissolution under pressure, it is worthy of an exploration of the relationship between pressure and morphological evolution of Li metal as well as its cycling performances.

Here, we present a comprehensive study on the deposition and dissolution behaviour of Li metal under mechanical pressure. Our theoretical simulation predicted distinctive morphological characteristics of Li growth caused by a pressure-induced deformation. The anticipated wire-like growth of Li without pressure and the compact deposition with pressure were observed experimentally in a step-by-step Li plating/stripping test. The more efficient Li stripping under pressure also leads to less Li residue than the case without pressure. Such microstructural variation accumulates during prolonged cycles, and consequently, generates a much thicker and more porous Li layer in the cell without pressure. The morphological changes of Li metal with and without pressure bring about notable differences in their electrochemical performances in terms of coulombic efficiency and cycling life. The clear correlation between structural changes and electrochemical performances of Li metal with respect to mechanical pressure reveals the fundamental role of pressure in suppressing porous Li formation. It may also inspire pathways to an effective Li anode design for high performance Li metal batteries in the future.

2. Experimental section

2.1. Numerical analysis

The effect of pressure on lithium growth was simulated by commercial FEM analysis software (COMSOL Multiphysics, COMSOL Inc.). Physical parameters of pure Li metal were used, i.e. thermal conductivity of 84.8 W/(m K), coefficient of thermal expansion of 46 $\mu\text{m}/(\text{m K})$, heat capacity of 24.86 J/(mol K), density of 0.534 g/cm³, Young's modulus of 4.9 GPa and Poisson's ratio of 0.36. Two conditions, one with a restricted top boundary and the other with a free top boundary, were modelled to represent the cases with and without pressure, respectively. It should be noted that an anisotropic growth nature of Li metal was employed in the simulation according to experimental observations [38–41].

2.2. Cell assembling

The effect of pressure on Li growth was studied using an apparatus shown in Fig. S1. A pouch cell was placed between a pair of stainless steel (SS) plates. Various pressures were applied through a set of compression springs by adjusting their lengths according to Hook's law. The configuration of pouch cells was shown in Fig. 1. The size of components in each cell was standardized. The pouch was made of Al laminated film with a size of 55 mm \times 70 mm. Two Ni lugs bonded with SS spacers (ϕ 15.5 mm \times 1 mm) served as the current collectors.

The two electrodes placed between SS spacers were a Li disk (ϕ 12.5 mm \times 0.6 mm) and a Cu foil (25 mm \times 25 mm). A commercial LiNiCoMnO₂ (NCM with Ni: Co: Mn = 5: 2: 3, MTI Corporation) cathode was used to construct a practical cell. A Celgard separator (35 mm \times 35 mm) was inserted between the electrodes to insure electrical insulation. 120 μL electrolyte (1.0 M LiPF₆ in EC: DEC = 1: 1, Sigma Aldrich) was added in each cell in an Ar filled glovebox (MBRAUN, Labmaster 200) and the pouch was sealed by a vacuum sealer (HENKELMAN, Jumbo 35).

2.3. Electrochemical testing

Galvanostatic charge-discharge cycling tests of the cells were carried out in a multi-channel battery tester (Arbin Instrument) with various current densities of 0.5 mA/cm², 1.0 mA/cm² and 2.0 mA/cm². Each cycle was consisted of Li metal deposition (1 mAh/cm²) on Cu foil and Li stripping from Cu foil to 0.5 V. The coulombic efficiency was determined by dividing the amount of stripped Li over the deposited Li in each cycle. Pressure dependent cycling test was performed with a pressure of 0 MPa, 0.5 MPa, 0.8 MPa, 1.1 MPa, 1.6 MPa and 2.2 MPa at a current density of 1 mA/cm² (see Fig. S10). Electrochemical impedance spectroscopy (EIS) and potentiostatic measurements were conducted using an electrochemical working station (Biologic SP-300). It should be noted that each test has been repeated several times for a reliable data.

2.4. Material characterization

The morphology of Li metal on Cu foil and Li disk after deposition and stripping was characterized by a field-emission scanning electron microscopy (FESEM) (JEOL, JSM 6700F). The SEM samples were raised in dimethyl carbonate (95%, Sigma Aldrich) to remove residual electrolyte. To minimize the exposure to air, the sample was sealed in an Ar filled vessel before transferring into the SEM chamber.

3. Results and discussion

The effects of pressure on Li metal were studied by using pouch cells and the cell configuration is shown in Fig. 1 and S1. The pouch was made of Al laminated film with a size of 55 mm \times 70 mm. Two Ni taps bonded with stainless steel (SS) spacers (ϕ 15.5 mm \times 1 mm) served as the current collectors. The two electrodes are consisted of a Li disk (ϕ 12.5 mm \times 0.6 mm) and a Cu foil (25 mm \times 25 mm). A Celgard film (35 mm \times 35 mm) and 120 μL 1.0 M LiPF₆ in EC: DEC = 1: 1 were added as separator and electrolyte. The pouch cell was placed between two SS plates in a specially designed apparatus shown in Fig. S1. Variable pressures were applied through a pair of compression springs by adjusting their lengths according to Hook's law.

A step-by-step comparative study of Li plating and stripping was carried out and presented in Fig. 2. Li metal on the Cu foil (Fig. 2d and e) and the Li disk (Fig. 2g-i) in two types of cells, one with a pressure of

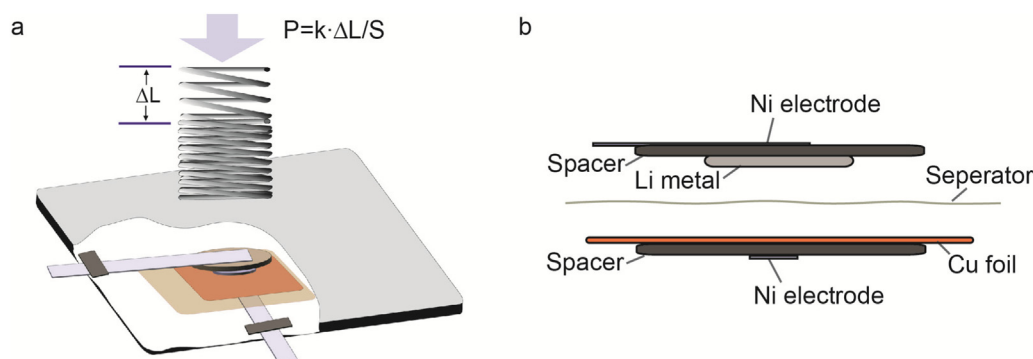


Fig. 1. Schematic illustrations of device assembling. (a) Pouch cell assembling configuration. (b) Stacking layers in the pouch.

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