A nanoindentation study of the viscoplastic behavior of pure lithium

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Abstract

Applying mechanical stresses is a possible approach to suppress dendrite and mossy lithium (Li) in Li metal electrodes. We conducted, in this work, nanoindentation tests on pure Li metal in an argon-filled glove box to study its viscoplastic behavior at room temperature. Both load-controlled and strain rate-controlled nanoindentations showed clear viscoplastic characteristics of Li. Based on an iterative finite element (FE) modeling approach, we determined a viscoplastic constitutive law for Li. In addition, we demonstrated by FE modeling that elastic modulus, on the order of GPas, has a negligible influence on the nanoindentation response of Li at ambient temperature.

Keywords: Lithium; nanoindentation; plasticity; finite element analysis

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With its high theoretical specific capacity (3862mAh/g), lowest negative reduction potential (-3.040 V vs. the standard hydrogen electrode) and low density, Li metal has been considered to be a desirable negative electrode; thus triggered worldwide interest in the rechargeable Li metal batteries, such as Li-O₂ and Li-S batteries [1, 2]. However, uncontrollable Li dendrites could penetrate through the separator and even the electrolyte, leading to short-circuit inside batteries. Mechanical suppression through polymer or solid state electrolytes (SSE) [3-5] and artificial stiffer solid electrolyte interphase (SEI) [6] has been proposed as an economical and promising solution for this problem. Based on the elastic deformation assumption, the theoretical work by Monroe *et al.* [3] indicated that SSE with a shear modulus twice of Li could inhibit Li dendrites. However, since the yield strength of Li is low, the stress generated at the separator/Li interface could cause plastic deformation of Li at a yield strength fraction of the modulus value [5, 7, 8]. Continued plastic deformation during repeated charging/discharging may cause Li redistribution, leading to shape change of Li at the anode/separator interface, and hence posing a threat to the safety and reliability of Li metal batteries [7, 8]. A comprehensive understanding of the mechanical properties, especially the plastic flow behavior, of Li is necessary.

The mechanical test of Li metal is challenging because Li is extremely reactive with oxygen, nitrogen, water vapor, and carbon dioxide. Sample preparation and mechanical tests must be conducted in a protective environment. However, the few reported tensile [9], compression [10], and resonance tests [11] were not carried out in a protective atmosphere. Thus, it is unsurprising that the reported elastic modulus (E) ranges from 1.84 to 7.8 GPa, and the yield strength from 0.48 to 1.10 MPa [9-11]. Similar to other soft metals and alloys, such as Sn-alloys [12, 13], indium [14] and lead [15], the

deformation behavior of Li exhibits low yield strength and viscoplasticity. Because of the importance of viscoplastic behavior, we report, in this letter, nanoindentation measurements of Li performed in an argon-fill glove box. Combining FE modeling with nanoindentation measurements, we determined a constitutive law for viscoplastic deformation of Li during indentation loading. The influence of E on viscoplastic deformation was also studied.

High purity polycrystalline Li foils (99.9%, with thickness of 750 μm , Alfa Aesar) were used for nanoindentation measurements. Nanoindentation tests were conducted using the Nanoindenter G200 (Agilent) positioned inside an argon-filled glove box (both oxygen and moisture <0.1 ppm, MBRAUN) at 2.1 mbar (Fig. 1(a)). Load-controlled tests were carried out using a diamond Berkovich indenter (tip radius 200 nm) with loading rates, $\dot{F}$, ranging from 0.196 to 3.92 mN/s to the maximum load, F , of 5.88 mN. The holding periods were set to be 1s. Constant strain rate-controlled tests were conducted with constant $\dot{F}/F$ values ranging from 0.1 to 1.0 s^{-1} . After nanoindentation measurements, the indents were examined by scanning electron microscope (SEM, FEI Quanta 250), as shown in Fig. 1(b). Since the maximum depth in each test was larger than 4500 nm, reproducible nanoindentation data were obtained despite of the slight surface roughness.

As shown in Fig. 1(c) and (d), the load-displacement (L-D) curves of Li exhibit obvious rate-dependent characteristics, i.e., the higher the loading rates, $\dot{F}$, the larger the load, F , is needed to reach the same indentation depth. For constant strain rate-controlled nanoindentation tests, the load corresponding to the same depth increases with the value of $\dot{F}/F$. The creep penetration depth during the holding period increases with the loading

rate. Similar to viscoelastic materials [16], “noses” appeared at the initial part of the unloading curves. The elastic recovery during the unloading is only few tens of nanometers. Therefore, the indentation deformation is mainly plastic. In the following analysis, we focus on the loading part as our interest is the constitutive law of viscoplasticity.

The rate-dependent plasticity, or viscoplasticity, of Li during the indentation loading may originate from two mechanisms. First, the thermally activated diffusion and viscous flow [17], such as Nabarro-Herring creep, Coble creep and dislocation climb, are expected to occur since the homologous temperature, T_{rm}/T_{melt} , is 0.66 at room temperature for Li. Second, the stable crystal structure of Li is body centered cubic (BCC) at room temperature [18]. The plastic deformation of BCC metals and alloys is governed by the motion of screw dislocations via kink pairs which require thermal activation [19, 20]. Therefore, the viscoplasticity of Li is likely the result of those multiple physical mechanisms. Although a mechanism-based model would have been more reliable in describing the viscoplastic behavior of Li, such a model would require detailed information at the atomic scale (e.g., dislocation structure and diffusion coefficient) that is generally unavailable. Instead, several empirical or phenomenological constitutive models, such as Anand model [21, 22], Johnson-Cook model [23], and Perzyna model [24, 25], have been developed based on somewhat different assumptions to describe viscoplastic deformation of soft metals and alloys [13, 14, 26, 27]. Anand model does not have an explicit yield condition or loading/unloading criterion, such that plastic strain can take place under any nonzero stress. This model is preferred for the steady-state creep under constant load or stress [13, 14]. Johnson-Cook model has been widely used for

various materials over a wide range of temperature and strain rate, especially for high strain rate deformation. But consistent parameters could not be obtained for Li with Johnson-Cook model (see Fig. S1 and Table SI in the Supplementary Material). The one-dimension Perzyna model and Cowper-Symonds model [28] have the equivalent functional form. Cowper-Symonds model was derived for high rate impact tests of cantilever beams, and thus suitable for high strain rate deformation; while Perzyna model was derived for general elastic-viscoplastic solids under general stress states [24, 25]. It has a yield surface with a strain rate-hardening mechanism activated only after yielding. Perzyna model has been successfully used to describe the rate-dependent flow behavior of many soft metallic materials (such as Sn-based solder alloys [26, 27]). Considering both the elasticity and viscoplasticity, we assume Li as a Perzyna elastic-viscoplastic solid with work hardening. The flow stress after yielding follows a constitutive law in the form of,

$$\sigma_f = k \varepsilon_p^n \left[1 + \left(\frac{\dot{\varepsilon}_p}{\gamma} \right)^m \right] \quad (1)$$

where σ_f is the flow stress, k is the strength coefficient, ε_p is the plastic strain, n is the work hardening exponent, $\dot{\varepsilon}_p$ is the plastic strain rate, γ is the material viscosity parameter, and m is the strain rate sensitivity. This overstress constitutive law was assumed for the indentation loading part. It is not likely to be applicable to the holding and unloading parts because the deformation mechanisms of overstress yielding and creep (under static stress) may be different [29, 30].

There exists a representative strain, ε_r (physically uniaxial or equi-biaxial plastic strain [31, 32]), for self-similar Berkovich indenter [31-34]. For power law work

hardening materials, ε_r only relates to the half apex angle (α) of the indenter ($\alpha = 70.3^\circ$ for Berkovich indenter), and does not depend on the work hardening exponent [31-34]. If the rate-dependent part of Eq. (1) is treated as a constant (i.e., constant strain-rate indentation tests), the constitutive law can be rewritten as the power law work hardening for a representative strain (ε_r) of nanoindentation. A representative stress is then given by,

$$\sigma_r = k\varepsilon_r^n \quad (2)$$

Then, Eq. (1) is readily reduced to the power law creep model as,

$$\sigma_{ef} = \sigma_f - \sigma_r = \sigma_r \left(\frac{\dot{\varepsilon}_p}{\gamma} \right)^m \quad (3)$$

where σ_{ef} is here defined as the effective flow stress. There is an effective indentation strain rate, $\dot{\varepsilon}_{ef}$, for power-law creep materials [35, 36],

$$\dot{\varepsilon}_{ef} = 0.12 \frac{\dot{h}}{h} \quad (4)$$

where $\dot{h}$ is the penetration rate, h is the indentation depth. Since the nanoindentation deformation of Li is mainly plastic, $\dot{\varepsilon}_p$ is assumed to be the same as $\dot{\varepsilon}_{ef}$. From the dimensional analysis [37, 38], the flow stress during the nanoindentation by an ideally sharp self-similar cone indenter is proportional to the ratio of the indentation load to the square of indentation depth,

$$\sigma_f = C \frac{F}{h^2} \quad (5)$$

where C is a constant for a given indenter geometry and a material subject to the indentation test (i.e., Li in the present case). Under the above assumptions, Eq. (1) can be rewritten as,

$$\frac{F}{h^2} = \frac{k\varepsilon_p^n}{C} \left[1 + \left(\frac{\dot{\varepsilon}_{ef}}{\gamma} \right)^m \right] \quad (6)$$

Both γ and m can be obtained from the F/h^2 vs. $\dot{\varepsilon}_{ef}$ curves. Constant effective strain rate $\dot{F}/F$ nanoindentation result was obtained only after 3500nm, as shown in Fig. 2(a). Three sets of F/h^2 vs. $\dot{\varepsilon}_{ef}$ corresponding to 4000, 5000, and 6000 nm were extracted. Both averaged F/h^2 and $\dot{\varepsilon}_{ef}$ were used here, as indicated by the error bars in Fig. 2(b). Fitted with Eq. (6), the obtained values of γ and m are quite consistent, as shown in Fig. 2(b) and Table I. The average values of γ and m are taken for the constitutive law.

FE modeling using the commercial software ABAQUS was carried out to determine k and n . As illustrated in Fig. 3(a), an axisymmetric isotropic model with 26244 elements was used with the mesh size finer around the contact area and gradually coarser away from the indent. The Berkovich indenter was represented by a rigid cone with a half apex angle of 70.3° because this conical indenter has the same depth-contact area relationship as the Berkovich [39]. The tip radius was set to be 200 nm, which is the same as the tip radius of the Berkovich indenter in experiments. In this study, the influence of tip radius, in the range of 50 to 400 nm, is negligible since the ratio of tip radius to the contact radius is small (less than 10%, see Fig. S2 in the Supplementary Material). The friction coefficient between the indenter and Li foil was set to be 0.1, which is a typical value for nanoindentation analysis [33]. For nanoindentation with constant value of $\dot{F}/F$, $\dot{h}/h \approx 0.5\dot{F}/F$ [35]. Since the effective strain rate before 3500 nm indentation depth is scattered

to some extent, as shown in Fig. 2(a), FE modeling was conducted with load-controlled mode. The independent parameters in the FE modeling are the loading rate and the maximum load, both of which were set to be the same values as those in the indentation measurements. For FEM input, the elastic modulus was assumed to be 3.5 GPa (in the reported range of 1.84 to 7.8 GPa) and Poisson's ratio was taken as 0.3. Later in this paper, we show that E , on the order of GPas, has little influence on L-D curves.

As shown in Fig. 3(c) and (d), the indentation load increases with increasing k and n . A larger k means higher flow stress, leading to larger indentation loads. The parameter n (usually $n < 1$) reflects the non-linearity of flow stress. To determine k and n , an iterative FEM procedure, shown in Fig. 3(b), was performed. The main idea is to iteratively compare the L-D curves from FEM and experimental, and refine the values of k and n until satisfactory match between the two was achieved. The averaged experimental L-D curves are used for this comparison. With this iterative method, k and n are determined to be 0.0042 and 0.23, respectively. Fig. 4(a) and (b) show the good agreement between the averaged experimental L-D curves and FEM L-D curves with different loading rates. Therefore, it is reasonable to conclude that the viscoplastic behavior of Li could be described by the following constitutive law,

$$\sigma_f = 0.0042 \varepsilon_p^{0.23} \left[1 + \left(\frac{\dot{\varepsilon}_p}{0.30} \right)^{0.54} \right] \quad (7)$$

Cheng and Cheng [40] showed that multiple stress-strain relationships of power law work hardening materials could lead to nearly identical L-D curves. In this study, the iterative FEM approach with 4 different loading rates would reduce the choices of k and n .

Although the uniqueness of k and n is not proven mathematically, alternative sets of k and n were not found by our iterative FEM approach.

In the above FEM analysis, $E=3.5$ GPa was assumed. The reported value of E ranges from 1.84 to 7.8 GPa [9-11]. While one might expect a clear influence of E on the viscoplastic deformation behavior, our FE result shows that E within this range has negligible influence on the indentation response, as shown in Fig. 4(c). This can be explained by the very low yield strength (σ_y) of Li. For the continuity of the constitutive law, $\sigma_y = \sqrt[n]{k/E^n} \approx 0.56$ MPa for static deformation. The ratio of σ_y/E is about 1.6×10^{-4} , which is on the same order of magnitude as indium (0.8×10^{-4}) [41], tin (2.4×10^{-4}) [42, 43] and many tin-based solder alloys [44]. Since the homologous temperature, $T_{rm}/T_{melt} = 0.66$, of Li is relative high at room temperature, the thermal diffusion activated creep would make significant contributions to the total deformation [17]. As a results, the elastic deformation is much less than the viscoplastic deformation. The variation of elastic modulus on the order of GPas only causes relatively small change of the overall deformation. Therefore, the elastic modulus may not be as important as the viscoplastic properties of Li in the mechanical design of Li metal electrodes.

In summary, the nanoindentation response of Li is dominated by viscoplastic deformation at room temperature. Combining nanoindentation measurements with an iterative FE modeling approach, we determined a constitutive law for the viscoplasticity of Li during nanoindentation. The FE modeling results show that the elastic modulus (on the order of GPas) has negligible influence on the indentation response of Li. Attention should therefore be paid to the viscoplastic deformation rather than the elastic deformation in designing Li metal electrodes operating at or near room temperature. The

method used in this study to determine the viscoplastic constitutive law may also be applied to other viscoplastic metals and alloys.

Acknowledgements

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Table

Table I. Fitting results of the F/h^2 vs. $\dot{\varepsilon}_{ef}$ curves with Eq. (6)

Depth(nm)	Fitting results			
	$k\varepsilon_p^n/C$	γ	m	R^2
4000	249.98	0.31	0.59	0.96
5000	220.76	0.29	0.42	1.00
6000	233.87	0.30	0.60	0.99
Average value		0.30	0.54	

Figures

Fig. 1. (a) The G200 nanoindentation system in the Ar-filled glove box; (b) a typical SEM image of the indent on the Li foil; (c) typical L-D curves with different values of $\dot{F}/F$; and (d) typical L-D curves with different loading rates.

Fig. 2. (a) The variation of effective indentation strain rate ($0.12 \dot{h}/h$) and $\dot{F}/F$ with indentation depth ($\dot{F}/F$ is 0.75s^{-1} in the experimental). Prior to 3500 nm, the distribution of strain rate is scattering. The effective strain rate trends to be a constant value only after 3500 nm. (b) The F/h^2 vs. $\dot{\epsilon}_{ef}$ relationship corresponding to different indentation depths. The averaged values of F/h^2 and the effective strain rates ($0.12 \dot{h}/h$) were used here.

Fig. 3. (a) The FE model for nanoindentation; (b) the flow chart for determining k and n from an iterative FE modeling, and the effect of n (c) and k (d) on loading curves from FE modeling.

Fig. 4. Comparisons of averaged experimental loading curves with FE modeling results with different loading rates. (a) 3.92mN/s and 0.49mN/s; and (b) 1.96mN/s and 0.196mN/s. (c) The effect of elastic modulus on the L-D curves. The L-D curves with $E \geq 3.5$ GPa almost overlap with each other.

Graphical abstract