Beam-assisted large elongation of \textit{in situ} formed Li$_2$O nanowires

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As an important component of the solid electrolyte interface in lithium ion batteries and an effective blanket breeding material in fusion reactor, the mechanical property of Li$_2$O is of great interest but is not well understood. Here we show that the polycrystalline Li$_2$O nanowires were formed \textit{in situ} by touching and pulling lithium hydroxide under electron beam (e-beam) illumination. The Li$_2$O nanowires sustained an enhanced elongation (from 80% to 176%) under low dose e-beam irradiation near room temperature as compared with that (from 51% to 57%) without e-beam irradiation. The extremely high deformability could be understood by the fast Li$_2$O diffusion under e-beam irradiation and tensile stress condition. The large elongation without e-beam irradiation implies that nano-structured Li$_2$O is ductile near room temperature.

As one of the simplest ionic oxides, lithium oxide (Li$_2$O) is an important component of a solid electrolyte interface (SEI) layer in the anodes of lithium-ion batteries$^1$ and an effective promoter for hydrogen storage materials$^2$. The electrical and mechanical properties of the SEI layer determines performance and cycle lifetime of lithium ion batteries. Meanwhile, Li$_2$O is the major product of the lithiated metal oxide anodes$^3,4$. After lithiation, the pristine metal oxide electrodes will evolve to metal or lithium-metal alloy particles dispersed in Li$_2$O matrix. As such, the mechanical properties of Li$_2$O are critical for the integrity of the electrodes and will have impact on the cyclability of lithium-ion batteries.

More attractively, its high melting temperature (1711 K) and tritium breeding properties have made Li$_2$Oa demanding blanket breeding material in fusion reactor$^5$, serving as a possible future energy resource for human beings. Nonetheless, how to utilize the nuclear energy safely has posed a challenge for the engineers in terms of designing appropriate materials working under the radiation environment, where the mechanical behavior was found to differ from the counterpart without radiation. For instance, Kiener \textit{et al.} indicated that the yielding strength of neutron-irradiated copper nano-pillars was affected by the interactions of dislocations with irradiation-induced defects$^6$. In this light, a fundamental understanding of mechanical properties of Li$_2$O with and without high-energy radiation is of significant value.

Besides, the perspective to reduce the critical feature sizes of modern electronic and mechanical devices has nourished the extensive investigation of nano-scale materials. As the sample dimension scales down to the nanometer range, the mechanical behavior might be quite different as compared with that of bulk counterpart. For instance, recent work has revealed that the silicon$^7$ and germanium$^8$ nanowires (NWs) are indeed ductile while their bulk counterparts are usually brittle. Regarding the nano-scale oxides, the electron beam (e-beam) was shown to be a useful tool to effectively tune the mechanical properties. To be specific, the ductility of the SiO$_2$ NWs can be greatly enhanced by low-intensity e-beam irradiation$^9$. Furthermore, the e-beam irradiation may increase the Young’s modulus of the zinc tin oxide NWs$^{10}$. Nonetheless, the mechanical response of nanostructured Li$_2$O, which would be meaningful for developing the nano-electrolytes and nano-electrodes for lithium ion batteries$^{11}$, was rarely discussed. In this letter, we report a simple approach for fabricating the fresh polycrystalline Li$_2$O NWs inside the transmission electron microscope. The corresponding mechanical behavior with and without e-beam irradiation has been investigated at room temperature.

\textbf{Results}

We found that the Li$_2$O nano-structures could be synthesized by e-beam irradiation of lithium hydroxide (LiOH), confirming the previous experimental results$^{12}$. The polycrystalline Li$_2$O NWs were successfully fabricated by touching the LiOH surface followed by pulling with a gold tip (Fig. 1a). The NWs were fabricated as a result of the
Li₂O diffusion from the substrate to the gold tip as induced by the e-beam irradiation. Selected area electron diffraction (SAED) patterns indicate the substrate is a polycrystalline phase of LiOH (JCPDS 76-0911, Tetragonal, a = 0.355 nm, c = 0.433 nm) (Fig. 1b) and the extracted NW is Li₂O (JCPDS 77-2144, Cubic, a = 0.462 nm) (Fig. 1c, see also Fig. S1). Figure 1d shows the electron energy loss spectroscopy (EELS) spectra of Li-K edge and O-K edge in LiOH (red curve) and Li₂O (black curve). In LiOH, the Li-K edge peaks rise at 58.2, 62.7 and 75 eV, and the O-K edge peaks rise at 529.4 and 535.1 eV; while in Li₂O, the Li-K edge peaks appear at 58.2 and 62.7 eV, and the O-K edge peaks appear at 526.1, 532.4 and 545.9 eV. The different near-edge fine structures of Li and O-K edges indicate the different electronic environment in LiOH and Li₂O. Subsequently, we conducted in situ tensile loading test of individual NWs with the whole deformation process directly recorded by video streaming.

During the tensile loading tests, we intentionally decreased the beam current density to suppress the mass transport from the substrate to the NW root. Figures 2a–2e show a typical tensile loading test of a Li₂O NW (see Supplementary Movies S1–S4 online) with the current density of 1.83 x 10⁻³ A/cm². The initial length of the NW was estimated to be 5010 nm as shown in Fig. 2a. As we pulled, the segment between the two surface notches (pointed out by the arrowheads in Figs. 2b–2e), which exhibits a uniform diameter of around 323 nm, elongated significantly until a NW length of 13816 nm (Fig. 2e) was finally formed without breaking! Due to the limited range of the manipulator, we could not pull the NW any further. Hence, the elongation of ~176% is the lower bound. In addition, the necking process which reduced the diameter from the initial 323 nm (Fig. 2b) to 190 nm (Fig. 2e) was directly visualized. The strong diffraction contrast, which appeared and vanished quickly, was frequently observed during the necking process (pointed out by arrows in Figs. 2c and 2d), indicative of the massive dislocation activities during the NW elongation. In nanostructure materials, the grain boundaries (GB) and free surface might serve as the nucleation as well as the annihilation site of the dislocations, as demonstrated by both theoretical and experimental work. Meanwhile, Figures. S2–S4 show three more examples signifying the large elongation of Li₂O NWs under the e-beam irradiation with the strain rate of 4.1 x 10⁻³, 4.3 x 10⁻³ and 1.4 x 10⁻³ s⁻¹, respectively. The total elongations are ~80% (Fig. S2), ~105% (Fig. S3) and ~110% (Fig. S4), respectively. During these tests, we have intentionally decreased the current density to the order of 10⁻⁴ A/cm², which further suppressed...
the atomic diffusion process and thus lead to the smaller elongation as compared with that (176%) indicated in Fig. 2. The gradual necking process, which is a typical phenomenon during the tensile loading of ductile materials, continued until the fracture of NWs (Figs. 3a–3c). Another tensile test showing the elongation of ~57% in Li$_2$O NW without e-beam irradiation is illustrated in Fig. S5.

**Discussion**

It is clearly seen the e-beam irradiation could effectively enhance the elongation of Li$_2$O polycrystalline NWs. Without the e-beam irradiation, the plasticity of NWs could be mediated by the nucleation and subsequent annihilation of the dislocations at GB and free surfaces. Under the e-beam irradiation, besides the dislocation activities, the plasticity could be assisted by the fast atomic diffusion, promoted by dynamic displacements of the constituent atoms. The basic idea is that the incoming electrons can be deflected by the Coulomb field of each atomic nucleus. The energy transferred from the incident electron to the atomic nucleus is given by:

$$E = E_{\text{max}} \sin^2(\theta/2)$$

where $\theta$ being the deflected angle of the electron in the field of atom nucleus, $E_{\text{max}}$ being the maximum energy that might be transferred, $E_e$ being the incident electron energy (in eV), and $A$ being the atomic mass number. Once the transferred energy exceeds the energy required for the displacement of the constituent atoms, the atom displacement may occur. In the current case, the maximum energy transferred from the 100 keV electron beam to lithium and oxygen are 80 and 15 eV, respectively. Since lithium and oxygen are both light elements, it is believed that such high energies are able to create atomic displacement and thus mass transport. This is actually the mechanism through which the fresh NWs were fabricated (the diffusion of the Li$_2$O from the substrate to the gold tip). The fast diffusion assisted the annihilation of defects such as cracks nucleated during the mechanical loading and thus contributed to the plasticity.

Simultaneously, the current density applied to take the TEM images ranged from $3.2 \times 10^{-4}$ to 0.1 A/cm$^2$, several orders of magnitude lower than those employed previously in nano-engineering field. Besides, the gold tip is a material with high thermal conductivity (300 W/mK) and is therefore able to conduct heat away quickly. The maximum temperature rise in Li$_2$O NWs is thus expected to be less than 10 K (See the Methods for detailed information). As compared with its high melting point (1711 K), such small temperature rise would have little effect on its mechanical behavior. Moreover, the creep deformation, which may become noticeable at high temperature, is thus not expected to be dominant during the current tensile tests.

It is worth noting that former works have demonstrated the formation of metallic lithium colloids in Li$_2$O crystal irradiated by 1 MeV e-beam. To clarify the possible e-beam effect on the structure of Li$_2$O NW, we have recorded *in situ* SAED patterns of single NW under long period e-beam irradiation (see Supplementary Movie S3 online). The patterns can be consistently indexed based upon pure Li$_2$O polycrystalline phase (Fig. S1) as shown in Fig. 1c, implying that the Li colloids were not created under the low energy e-beam irradiation (i.e., 100 keV).

In summary, it has been found that the e-beam irradiation greatly enhances the ductility in polycrystalline Li$_2$O NWs during the tensile loading which can be well understood by the fast diffusion caused by the e-beam irradiation under tensile stress. The large elongation (51% and 57%) without e-beam irradiation indicates that Li$_2$O NWs is ductile, and can sustain large mechanical stress, implying that the lithiated metal oxide nano-anodes in a lithium-ion battery...
might not be easily fractured during cycling. Our results have important implications for the application of Li₂O nanostructures in nuclear environment and illustrate that e-beam irradiation can be an outstanding approach in nano-engineering field by means of tailoring the mechanical property in materials.

Methods

The experiments were carried out inside a FEI Tecnai F30 field emission gun transmission electron microscope (TEM) operated at 100 kV, with the Nanofactory TEM – scanning tunneling microscopy (STM) platform. The LiOH crystals were attached to a gold rod by using electrically conductive, silver-filled epoxy-resin-based adhesive, CW2400 Circuit Works by ITW Chemtronics. Subsequently, the gold rod was inserted into one end of the TEM-STM platform. To successfully prepare a fresh Li₂O NW inside the TEM, we firstly aligned the gold tip to touch the LiOH substrate. Subsequently, the contact area was irradiated by an e-beam with sizes ranging from 200 to 1000 nm (the corresponding current density spans from 0.5 to 12 A/cm²) to form the Li₂O crystals in the substrate. The irradiation time is dependent on the current intensity. The higher current intensity, the less time required to nucleate the Li₂O phase. Typically, for a current density of 12 A/cm², the Li₂O will be formed after 10 seconds e-beam irradiation. By slightly compressing the STM tip against the substrate, some of the Li₂O crystals attached onto the STM tip. Finally, the tip was retracted back to form a Li₂O NW which was subjected to further tensile loading (Fig. 1a).

The temperature rise under irradiation can be calculated by the Fisher’s model:

$$\Delta T = \frac{1}{\rho} \left( \frac{\Delta E}{d} \right) \ln \left( \frac{I}{I_b} \right)$$

where $I$ is the beam current, $\kappa$ is the thermal conductivity, $\epsilon$ is the electron charge ($1.6 \times 10^{-19}$ C), $b$ is the sample radius, $r_0$ is the beam radius, and $\Delta E$ is the total energy loss per electron in a sample of thickness $d$. Since the energy loss in the sample is small compared with the initial energy which is 100 keV, the term $\Delta E/d$ is equal to the stopping power for electrons $dE/dx$ which can be calculated from the Bethe-Bloch equation:

$$\frac{dE}{dx} = \frac{2\pi Z \rho (e^2/q \mu)^2}{\rho^3} \ln \left[ \frac{E (E + me^2/2\mu)^2}{2\beta E_r} \right] + (1 - \beta^2)$$

$$- \left( 1 - \sqrt{1 - \beta^2} + \beta^2 \right) \ln \left( 2 + \frac{1}{\beta} \left( 1 - \sqrt{1 - \beta^2} \right)^2 \right)$$

in which $Z$ is the atomic number of the target element, $\rho$ is atomic density, $c_0$ is the dielectric constant (8.85 $\times 10^{-12}$ F/m), $m$ is the electron rest mass (9.33 $\times 10^{-31}$ kg), $\nu$ is the electron velocity, $c$ is the speed of light (3 $\times 10^8$ m/s), $E$ is the electron energy, $I_b$ is the average excitation energy for electrons in the target and $\beta = \nu/c$.

Currently, the acceleration voltage is 100 kV, thus, $\beta = 0.548$ and $v = 1.64 \times 10^8$ m/s. For LiO₂, $\rho = 4.04 \times 10^{-3}$ m$^3$ (mass density 1313 kg/m$^3$), melting point 1711 K, thermal conductivity $\kappa = 7$ W/mK. The maximum temperature rise is estimated to be around 1K with $I = 3.7$ nA, $b = 1.5$ mm, $r_0 = 4$ μm.

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Author contributions

J.W. carried out the TEM experiments and wrote the paper. H.Z. and S.M. contributed to the data analysis. J.Y.H. and J.W. revised the paper. The project was designed by J.W. and J.Y.H.

Additional information

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