

Real-time observation of lithium fibers growth inside a nanoscale lithium-ion battery

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Formation of lithium dendrite/fibers during charging-discharging cycles not only causes short circuit but is also known as a major safety issue. In this work, an electrochemical cell was constructed inside a transmission electron microscope to observe the real-time nucleation and growth of the lithium fibers inside a nanoscale Li-ion battery. Our results show that during the lithiation process, the lithium ions nucleate at the interface of anode and electrolyte and then grow into fibers. These fibers grew parallel to the direction of the applied electric field. Such observations can assist the nanoscale design of better electrodes and electrolyte materials needed for safe and high power Li-ion batteries. © 2011 American Institute of Physics. [doi:10.1063/1.3643035]

Lithium-ion batteries are of great interest due to their high energy density, however, various safety issues such as lithium dendrite formation limit their practical application.^{1,2} The formation of the lithium dendrite³ or accumulation of mossy lithium⁴ on the anode electrode can create short-circuit after several lithiation-delithiation cycles, causing high-rate discharge. In a severe case, when a high rate of overcharging is applied to the cell, it can catch fire or even explode.⁵ It was found that there is a direct relationship between the current density and dendrite formation using scanning electron microscopy.¹ While more than two decades ago,^{6,7} polymer electrolytes were proposed as a solution, their application remains limited because of the high working temperature need to achieve ionic conductivity of the polymer.⁸

Ionic liquids (ILs), discovered by Wilkes *et al.*,⁹ are liquid-like salts that are composed solely of ions and have high ion conductivity with no structural variations. Due to their physicochemical properties, many applications are possible.^{10,11} One is the electrolyte of the lithium-ion batteries, where high ionic conductivity and zero electrical conductivity are needed.¹² However, despite the improved cycling performance compared to the traditional electrolytes, the formation of lithium dendrite still occurs at practical current density.¹³ Therefore, it is crucial to understand the mechanism of the formation of lithium fibers to enable the safe and secure use of lithium-ion batteries in mobile applications.

To understand the Li fiber growth in ionic-liquid based batteries, we performed *in-situ* lithiation experiments using Si nanorods (NRs) as the anode, LiCoO₂ as the cathode, and 1-butyl-3-methylimidazolium (BMIMCl) ILs as the electrolyte. The lithiation process was conducted inside a transmission electron microscope (TEM) and the formation of Li fibers was observed. During the *in-situ* experiments, the beam was expanded and condenser lens apertures were used to minimize the beam intensity and radiation.

Aligned silicon nanorods were grown on the Cu substrate using a glancing angle deposition technique. The details of nanorod fabrication were reported in our previous publication.¹⁴ LiCoO₂ powder, purchased from Sigma-Aldrich, was used as cathode materials. A small amount of the cathode powders was glued on a gold wire, and the anode material was glued to the scanning tunneling microscope (STM) side (NanofactoryTM STM sample holder). The gold wire with cathode and ILs was then placed on a hat, which sits on the sapphire ball of the sample holder. The applied bias voltage introduces surface tension to the IL stream on the NR, which breaks the stream into droplets according to the Plateau-Rayleigh instability phenomenon.¹⁵ Here, we biased the cathode -3.5 V in relationship to the anode materials to initiate the releasing of the Li⁺.

Figure 1(a) represents a schematic of the *in-situ* experiment set-up inside the TEM. As can be seen, the cathode is mounted on the gold wire and the Si NRs are placed on the STM electrode. Figure 1(b) represents a typical configuration of a nano-battery where the anode and ILs are in contact. Figure 1(c) shows that a thin layer of the IL is formed due to the stream of the ILs in the presence of the applied voltage. Figure 1(d) depicts a typical amorphous NR after 1 h of the lithiation process, where arrows indicate the formation of Li₂₂Si₅ phase with their electron diffraction pattern (EDP) shown in the inset.

The growth of Li fibers was investigated by focusing on the evolution of IL-Si NR interface. Figure 2(a) shows an IL droplet just before the lithiation process begins, while the diffraction image in the inset shows a fuzzy pattern that indicates no crystalline ordering presents. After the lithiation experiment took place, the formation of small islands was observed on the IL (Figure 2(b)). The diffraction pattern in the inset of Figure 2(b) confirms that these islands have a crystalline order similar to Li metals.

A snapshot series of the formation of Li islands in the IL is shown in Figures 2(c)–2(g). The black arrow in Figures 2(c)–2(f) follows the evolution of IL during the lithiation process (see movie in Fig. 2). The movie in Fig. 2 was

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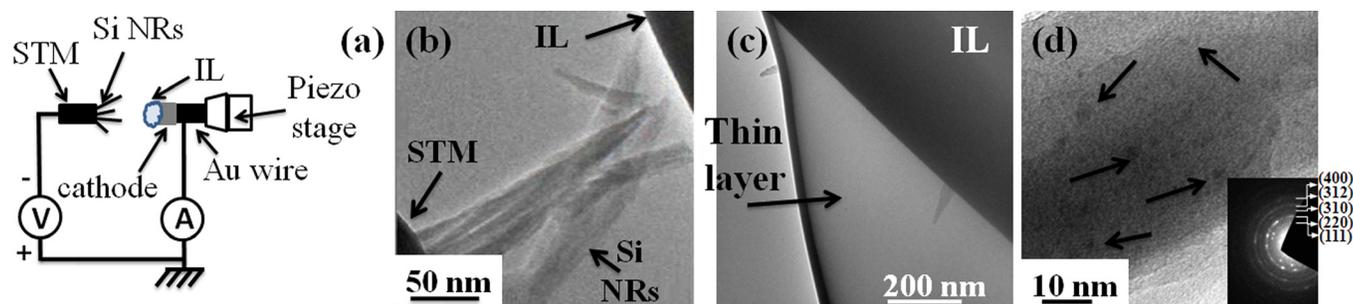


FIG. 1. (Color online) (a) A schematic of the *in-situ* lithiation setup is shown where the anode is placed on the STM and the IL is placed on the cathode. (b) The TEM image shows a nano-battery configuration in which the Si NRs are in contact with the ILs prior to the lithiation experiment. (c) The formation of a thin layer of ILs on the surface of ILs (the darker region) is shown. (d) The TEM image of Si NR structure after 1 h of lithiation. Arrows indicate the $\text{Li}_{22}\text{Si}_5$ particles that are formed. Inset represents a diffraction pattern of the lithiated Si NR indicating the presence of the $\text{Li}_{22}\text{Si}_5$ phase.

captured from the early stage of lithiation process, when the nucleation of Li islands took place inside the IL. One can see that behind the movement of the IL, small islands of Li remain (shown by the red arrows). The islands appear to have random distribution. The inset in Figure 2(g) shows the EDP of the islands that confirms the formation of the crystalline lithium islands. Note the ILs have a low tendency to crystallize due to flexibility (anions) and dissymmetry (cations);¹² hence, the EDP spots can only be correlated to the lithium contents. Also, one should note that the Li islands, once they formed, are pretty much stable and do not move during the lithiation process. The reason behind this is unclear for the authors and needs further studies on thermodynamics and kinetics of these islands.

Wang *et al.*¹⁶ reported the changes in the distributions of anion and cations under high electric field. His simulation study showed that, by increasing the externally applied electric field, the ILs structure changed from spatially heterogeneous to spatially homogenous and then to nematic-like. On the other hand, when the external electric field is comparable to the electro-

static interactions between the cations and anions, the system acts like a simple liquid with more freely moved ions. Moreover, one should note that the effect of electron beam radiation on the formation of these Li islands needs further investigation. Particularly, the e-beam may cause the knockout of ions in the ionic liquid and forms vacancy. The vacancy formation can mediate the short-range diffusion of Li ions and, therefore, assists the segregation of the Li islands.

Figure 3 shows the subsequent stages of Li islands growth. Figure 3(a) shows a Si NR that is dipped into ILs from both sides. After almost 30 min of the lithiation process, one can see the formation of lithium fibers as indicated with white arrows in Figure 3(b). As one expects, the growth of the Li fibers is in the same direction as that of the applied electric field. Figures 3(c) and 3(d) represent the growth of lithium fibers toward the cathode (see movie in Fig. 3). This is in agreement with the previous report that shows that lithium fibers form on the surface of the anode material and grow toward the cathode, inside the electrolyte, due to the presence of an electric field.^{3,17,18}

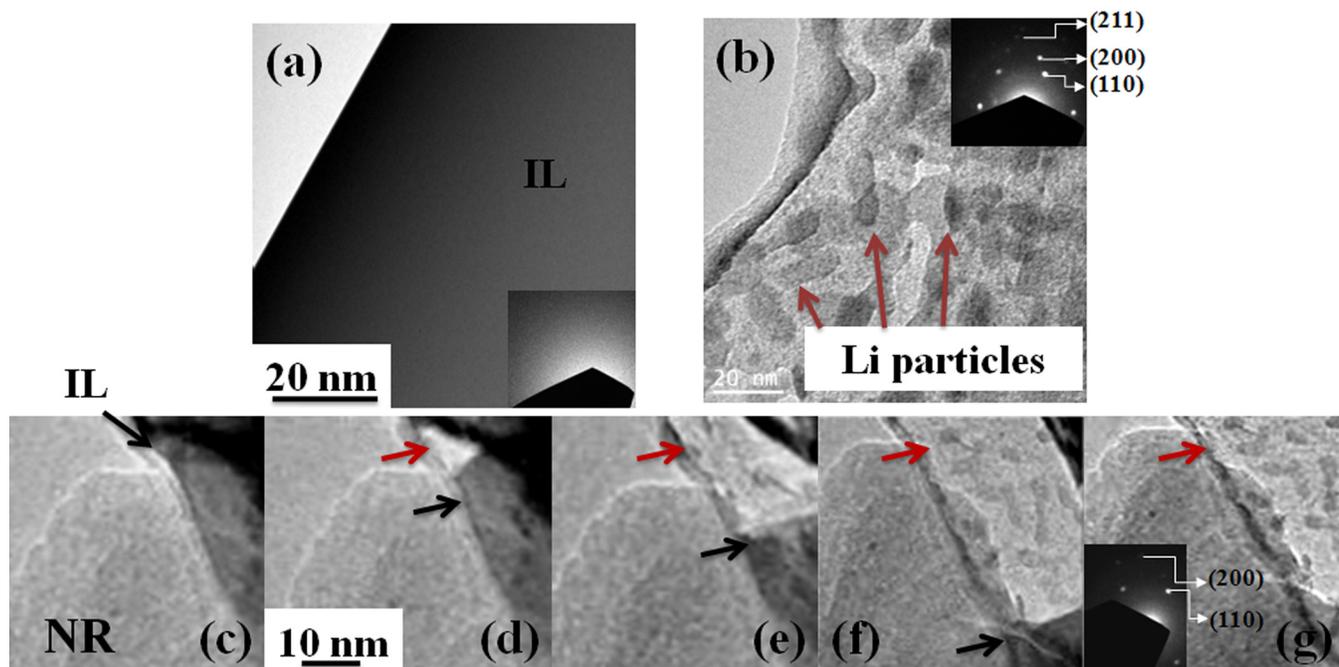


FIG. 2. (Color online) (a) Represents a typical surface of ILs prior to the lithiation process; the EDP in the inset shows no crystalline ordering can be found within the IL. (b) The nucleation of Li fibers during the lithiation process. The EDP in the inset indicates the crystalline ordering within the IL. (c)-(g) Series of snapshots taken from the real-time video indicate the appearance of the Li fibers at various stages. The inset shows that the newly formed fibers have crystalline orders (enhanced online) [URL: <http://dx.doi.org/10.1063/1.3643035.1>].

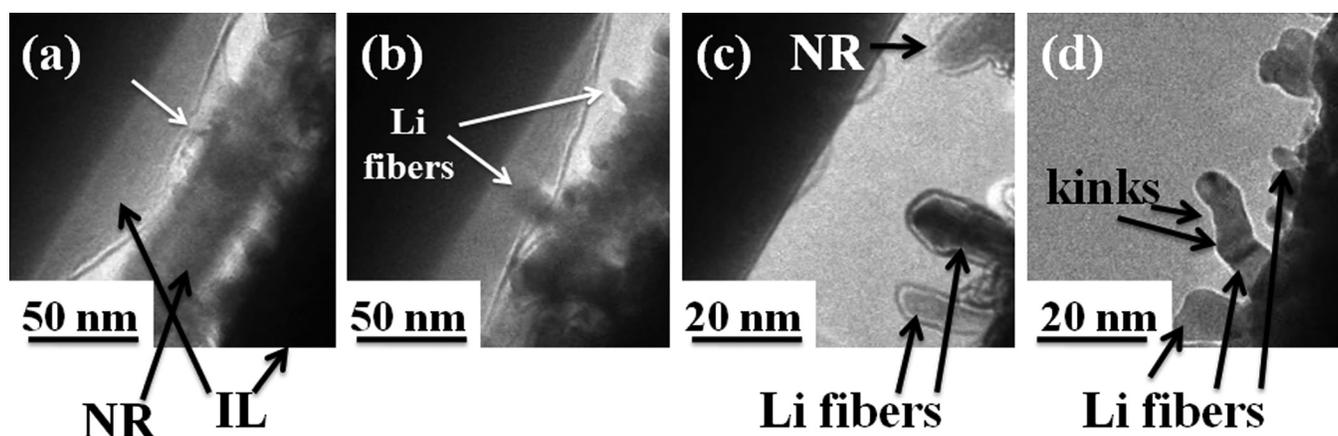


FIG. 3. (a) Black arrows indicate an individual NR surrounded by IL. (b) Arrows indicate the formation of Li islands on the NR. (c) Represents the growth of Li fibers. (d) The formation of kinks and growth of Li fibers are marked by black arrows (enhanced online) [URL: <http://dx.doi.org/10.1063/1.3643035.2>].

The movie in Fig. 3 represents the final stage of Li growth in the form of fibers on the surface of the anode. One can observe that each of the fibers grows rapidly to a certain length and then slows or even stops, and another fiber starts to grow. As the fibers grow, it seems that their length increases but the diameter remains constant. The formation of kinks on the fibers during the growth stage was also observed (as marked in Figure 3(d)). These observations are in good agreement with the reported SEM observations.¹⁹ It was first reported²⁰ that lithium deposits on the anode as needle-like during lithiation. Upon delithiation process, if the dissolution current is larger than deposition current, then they detach from the anode surface and float into the electrolyte. These so-called “dead-Li” are electrochemically inactive but chemically active due to their large surface area and responsible for the loss of cycling performance of the battery.

Runaway reactions can take place between the cathode and anode, risking explosion and fire.²¹ Therefore, from a practical point of view, it is necessary to prevent unwanted reactions and phenomenon due to the growth of lithium fibers. A number of methods have been proposed to increase the safety of Li-ion batteries including the replacement of the organic electrolyte with ionic liquids. However, the results of this study shows that the Li fibers can nucleate and grow in such ionic liquid electrolytes. Therefore, further studies should be pursued to design the electrolytes that prevent the growth of Li fibers.

A nanoscale Li-ion battery was constructed inside a transmission electron microscope to study the formation of lithium fibers during the lithiation process. The ionic liquids served as the electrolyte to enable the observation of electrochemistry process. Interestingly, it was observed that, in addition to the lithiation of Si NRs, some Li islands formed inside the IL. These islands continued to grow as Li fibers toward the counter electrode parallel to the applied electric field. The formation of Li fibers can induce possible short circuit and compromise the safety of the Li-ion battery. The experiments shown in this study can elucidate understanding of the formation and growth mechanism of the lithium fibers using different electrolytes to diagnose the safety issue toward the next generation of high performance Li-ion batteries.

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