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Colossal Reversible Volume Changes in Lithium Alloys

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It is uncommon to consider strains in a stiff solid approaching or exceeding 100% even though some materials exhibit large volume changes during chemical reactions. We used *in situ* atomic force and optical microscopy to study, for the first time, the colossal volume changes that occur as lithium is electrochemically added and removed from lithium alloy films. When lithium is first added to alloy films on rigid substrates, the films expand perpendicular to the substrate. When lithium is removed, the films shrink both perpendicular and parallel to the substrates, leading to crack patterns similar to those found in dried mud. Subsequently, the formed particles expand and contract reversibly without further cracking as lithium is added and removed from the alloy. Time lapsed "movies" of this process can be found at www.physics.dal.ca/~dahn/ECS_Letters.html

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Some of the largest and best-known expansions in solids are those that occur when hydrogen is absorbed within metal hydrides.[1,2] The reversible expansion is characterized by the so-called hydrogen-induced volume change which has been shown to be about 2.8 ± 0.2 Å^3 per incorporated hydrogen atom in most d-band metal hydrides.[2] Typical metal-hydride systems like H_xPd and H_xTi can react to a level of $x = 1$ and $x = 2$, respectively, leading to overall volume expansions of about 20 and 32%, respectively.[2] Such expansions, which have been observed by various microscopy techniques, lead to particle fracture that can have important consequences for hydrogen storage alloys in fuel cell applications and for nickel/metal hydride battery electrodes.[3]

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There has recently been significant interest in alloy-type electrodes for lithium-ion batteries[4-6] but their application in practical devices has not yet occurred. This is primarily because the volume expansion in Li alloys is an order of magnitude larger than for hydrogen in metals. For example, Table I shows that the "lithium induced volume change" for several lithium-tin and lithium-silicon alloys is about 14 or 15 Å^3 per lithium atom.[7] Furthermore, the maximum lithium concentration in Li_xSn and Li_xSi is $x = 4.4$,[8] so that the volume expansions that occur when lithium reacts with Si or Sn are 310 and 260%, respectively [calculated as 100% × (final volume-initial volume)/(initial volume)].

The reader is cautioned, however, that such volume changes due to chemical reaction cannot be thought of in the same way as volume changes due to an external dilating force. There is no such force applied in the present example of the reaction of lithium with thin films on rigid substrates. The only external force to be considered is that from the constraining substrate, which acts to restrict the in-plane dimensional change due to the chemical reaction. Bearing that in mind, lithium alloys are model systems to study the mechanical characteristics of large volume changes in solids that are due to a change in composition, and are larger than those studied to date. Lithium can be titrated electrochemically into the alloys in a controlled manner and the volume changes of bulk pieces of material can be studied using an appropriate probe. Using novel methods of *in situ* atomic force microscopy (AFM) and optical microscopy, we have studied the reversible volume changes and cracking when lithium is added to and removed from lithium alloy films.[9] One astounding result that we report here (and illustrate with time lapsed AFM and optical "movies" available on the internet) is that 30 μm wide flakes of 1-8 μm thick films can reversibly expand and contract by up to 100% without noticeable damage.

The cell used for *in situ* optical microscopy consisted of a glass chamber with a thin glass cover-plate. A 7.5 μm sputtered film on a 130 μm disk of copper foil was mounted as the working electrode in a two-electrode cell with lithium metal as the counter and reference electrode. The holes used for leads and for injecting the electrolyte (1 M $LiPF_6$ dissolved in equal volumes of ethylene carbonate and diethyl carbonate) were sealed with polypropylene hot melt glue. A Sony charge coupled device (CCD) color video camera DXC-151AP mounted on the microscope was used to collect images of the sample magnified by either a 10× or 20× objective and a 0.55× eyepiece. Digital images of the film surface were stored at 5 min intervals during the discharge/charge cycles. A constant current was applied such that each cycle lasted 5 h.

Figure 1 shows a schematic diagram of the experimental apparatus used for the *in situ* AFM studies. The sample consisted of an electrochemically active layer deposited on an inactive layer, which in turn was deposited on a substrate. For this experiment, the film thickness is limited by the finite range of the piezoceramic in the AFM scanner. Therefore, 1 μm thick SiSn films were sputter deposited on highly polished stainless steel (430 series) disk 1 cm in diam and 2 mm thick. The mass of the sputtered film was determined to be 0.38 ± 0.04 mg. To improve the adhesion between the stainless steel substrates and the SiSn film, an intermediate 4 μm thick layer of Cu was applied by sputter deposition to the substrate. The sample was mounted as the working (or active) electrode in a two-electrode lithium cell. The cell is open from the top so that the sample can be

Table I. Lithium-induced volume change in Li_xM materials ($M = Si$ or Sn).

Phase	Volume of the solid per M atom (Å^3)	Volume change of the solid induced per Li atom (Å^3)	Percent expansion for $x = 1$ in Li_xM 100% x (molar volume Li_xM-molar volume M)/(molar volume M)	Ref.
Li[a]	-	21.6		10
Si	20.01	-		
Li_7Si_2	67.3	13.5	67.5	10
$Li_{22}Si_5$	82.4	14.2	70.8	10
Sn	27.0	-		
LiSn	41.1	14.1	51.9	10
$Li_{22}Sn_5$	96.7	15.8	58.6	10

[a] For lithium metal, the volume per Li atom is given.

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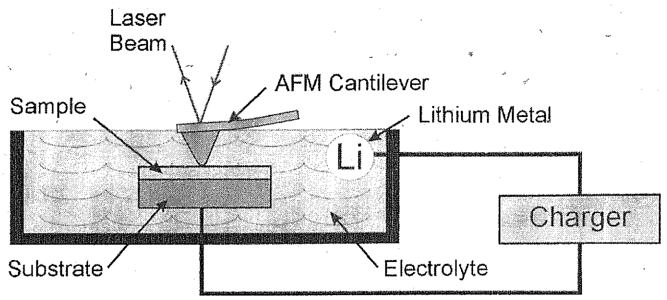

Figure 1. Schematic diagram of the *in situ* AFM apparatus. (Not to scale.)

imaged in electrolyte with a Molecular Imaging (Phoenix, AZ) Picoscan AFM equipped with a 37 μm range scanner. The entire AFM and cell are housed within a Vacuum Atmospheres (Hawthorne, CA) double glove box with water and oxygen levels below 1 ppm. The AFM is mounted on a 70 kg granite slab suspended from the ceiling of the glove box by springs and bungee cords. A low vapor pressure electrolyte, 1 M $LiPF_6$ dissolved in equal volumes of ethylene carbonate and propylene carbonate, was used so that the electrolyte evaporation from the open cell would not be a concern. AFM topographic images of the film surface were recorded continuously as the discharge (adding lithium to the film) and charge (removing lithium from the film) proceeded. Each AFM image took about 9 min to collect. One discharge/charge cycle lasted for 1 day.

Current was supplied to the AFM cell by a computer controlled Keithley 236 source-measure unit and to the optical microscopy cell by a Maccor cycling unit. The films studied are described in detail in Ref. 9. Briefly, they were co-sputtered $Si_{1-x}Sn_x$ films. The amount of lithium added to the film was determined coulometrically from the film mass, the current, and the time of current flow.

Figure 2 shows the results of an *in situ* optical microscopy experiment designed to determine the degree of in-plane strain induced during the addition of lithium to the film. The grid-lines are razor blade marks made prior to assembling the cell. Three interruptions were made during the first discharge (adding lithium to the film) to determine whether the metal film on the copper foil would expand in-plane over time. A careful analysis of the grid-lines from the sample in its initial state (Fig. 2a) and in its discharged state (Fig. 2b) showed that no measurable lateral expansion occurred despite the fact that x in Li_xM reached 1.98, for which at least a doubling of volume is expected. We conclude that the metal expanded solely in the out-of-plane direction as it alloyed with lithium the first time. After about 1 h during the first charge (removing lithium) the film shrinks and cracks (Fig. 2c). At this magnification it is impossible to judge whether the cracks form all at once. Now the particles of metal film delimited by the crack edges shrink until almost all of the lithium has been removed (Fig. 2d). This crack pattern is similar to the crack pattern observed by *ex situ* scanning electron microscope (SEM) studies performed by Brousse *et al.* on SnO_2 thin films.[10] However in their case, the particles formed by the cracking were on the order of 100 nm while those shown here in Fig. 2d, f, and g are on the order of 100 μm. Figure 2e shows that once the particles have alloyed with lithium again to the level of Fig. 2b, the cracks become too small to observe. The particle shape is almost perfectly preserved, causing the cracks in the film to seemingly disappear. Indistinguishable twin views at higher magnification (Fig. 2f and g) of the fully charged film show clearly that the particles maintain their shape. The gaps between these particles were measured to be 18% of the particle diameters on average, which is very close to that expected (21%) for an isotropic reduction in the particles' volume. The last image shows that even on this fine scale the cracks seem to disappear. A time lapsed "movie" of this experiment can be viewed at www.physics.dal.ca/~dahn/ECS_Letters.html

It appeared from this optical microscopy experiment that fracture occurs once during the first charge (removing lithium), after which the particles shrink and expand reversibly without further cracking. The AFM experiment allowed us to determine whether the fracture occurs on a scale finer than that perceptible with optical microscopy.

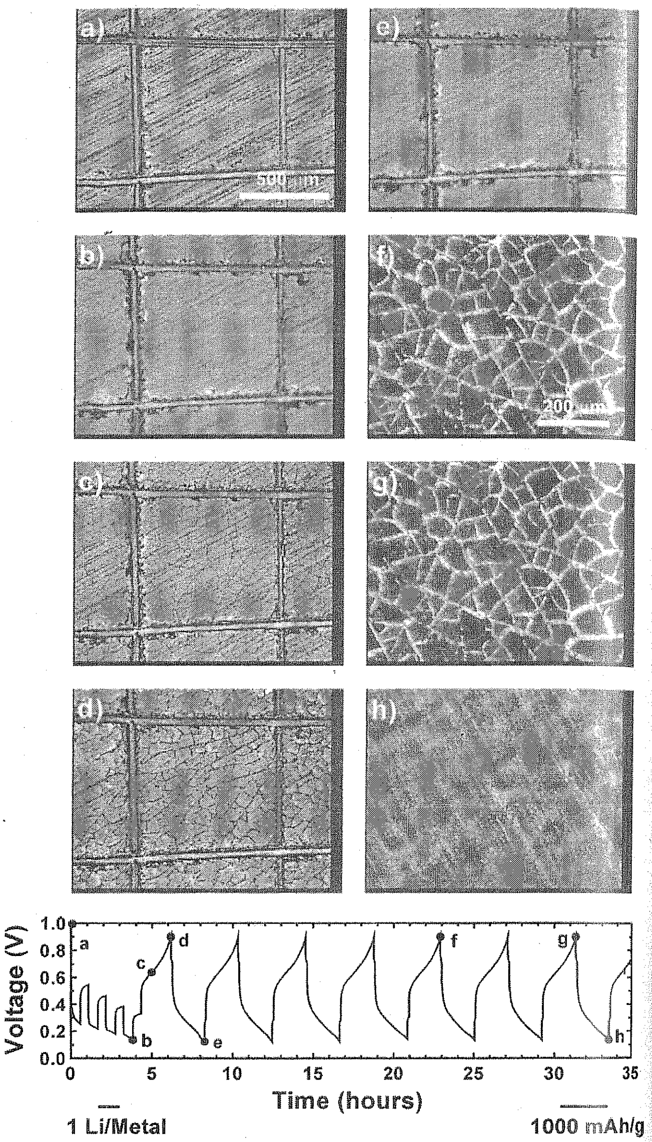

Figure 2. Selected micrographs corresponding to points labeled in the voltage curve below. Where the voltage decreases with time (discharging), lithium is being added to the film, and where the voltage increases with time (charging), lithium is being removed from the film. A scale bar displays the length of time that corresponds to a charge transfer of 3.5 mol of lithium per mole of metal in the original film. Figures a through e are at the same lower magnification, and figures f through h are at higher magnification.

Figure 3 shows the results of a typical AFM experiment. The open-circuit voltage of the freshly assembled cell was 2.0 V. The cell was discharged to 0.5 V, and then the experiment began. Figure 3a shows the AFM image collected after this initial discharge to 0.5 V. The vertical distance corresponding to maximum contrast (white to black) and the lateral scan range are given in Table II. Figure 3b shows an image of the same region of the film after all available lithium has been removed from the film. A crack can be seen in the lower right corner of the image. Figure 3c shows the same region of the film after lithium had been added again to the same level as in Fig. 3a, demonstrating that the crack closed as the segments of the film expanded to their previous size.

The scan range was then increased to 37 μm to view more of the crack pattern, and selected to include the region previously scanned

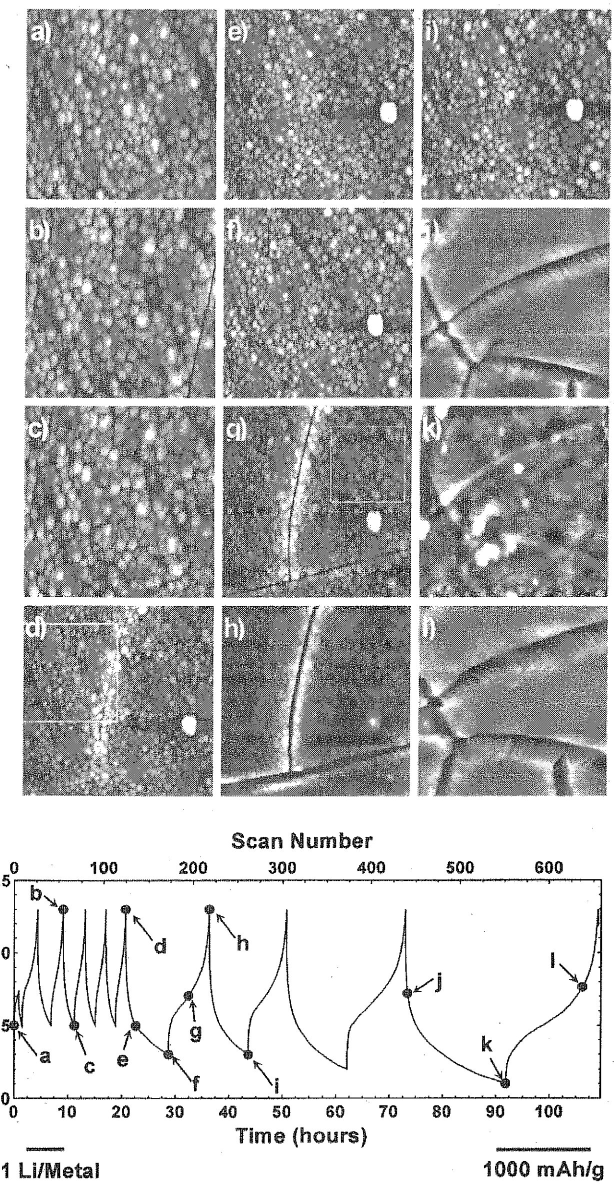

Figure 3. Selected AFM images with scan ranges and contrasts given in Table II. The images a-l were collected at the corresponding points indicated in the voltage-time curve. A scale bar displays the length of time that corresponds to a charge transfer of 1000 mAh/g and another scale bar displays the time that corresponds to the reaction of 1 mol Li per mole M.

Table II. Description of the images displayed in Fig. 3.

Image in Fig. 3	Lithium content in the film corresponding to the indicated image, measured as x in Li_xM	Lateral image size (μm)	Vertical distance corresponding to maximum contrast (white to black) (nm)[a]
a	0.3	19	150
b	0	19	138
c	0.3	19	140
d	0	37	185
e	0.3	37	150
f	1.0	37	185
g	0.5	37	270
h	0	37	440
i	1.0	37	175
j	0.06	37	1040
k	2.5	37	290
l	0.4	37	1900

[a] Image was flattened to remove gross tilt.

(indicated by the white square in Fig. 3d). Figure 3d shows the AFM image (lithium removed) after 5 discharge/charge cycles between 1.3 and 0.5 V with two cracks present. The cracks closed as lithium was inserted to 0.5 V (Fig. 3c) as shown in Fig. 3e. Up to this point only about 0.3 Li per M had been added and removed and the volume changes (estimated to be about 16% based on Table I) were completely reversible. Then, further lithium (about 1 more Li per M) was added to 0.3 V (Fig. 3f). No cracking or peeling occurred, suggesting that all volume expansion takes place in the vertical direction. When lithium was subsequently removed, as shown in Fig. 3g and h, the original cracks (see Fig. 3d) opened to a much wider extent but no further cracking was observed. In addition, the particles curled substantially near their edges, where they had detached from the substrate. Note the vertical distance corresponding to maximum contrast changed dramatically as the edges curled (see Table II). Finally, Fig. 3i shows that the cracks closed and the film flattened again when lithium was added once again to 0.3 V. Figure 4 shows three-dimensional views of the film corresponding to Fig. 3h and i.

The cell was cycled a few more times and a different region of the film was selected for imaging. Figure 3j shows the image when almost all the Li was removed. Lithium was then added to a level of 2.5 Li per metal at 0.1 V (Fig. 3k). The cracks closed and the curling of the edges was eliminated. Note that the cracks first closed at 0.3 V (not shown), so between 0.3 and 0.1 V, all of the expansion of the film must have been in the vertical direction. Finally (Fig. 3l) almost all the Li was removed and larger cracks between more curled particles, but in the same places as those initiated before, were observed. Most of the scan sequence (about 400 images) described here is available for viewing as a time lapsed "movie." It can be either viewed or downloaded at www.physics.dal.ca/~dahn/ECS_Letters.html

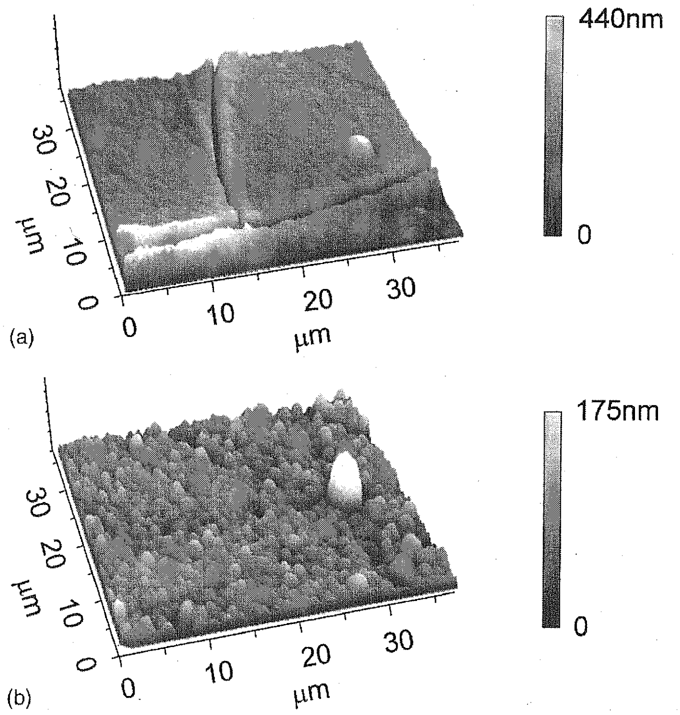

Figure 4. Three dimensional views of (a) image 2h and (b) image 2i. The out-of-plane distance is shown using the contrast scale given to the right of each image.

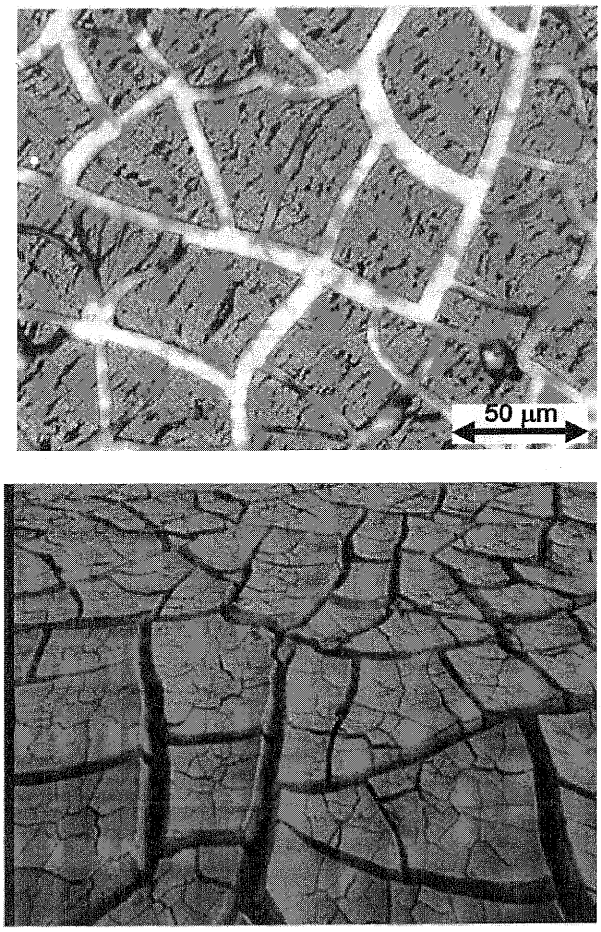

Figure 5. The resemblance of an optical micrograph of a Li-alloy film after expansion and contraction (top) to cracked mud in a dry lake bed (bottom).

The sequence of events shown in Fig. 2 and 3 can be qualitatively understood by considering the desiccation of mud. As an example, Fig. 5 compares an optical image of a film after a discharge/charge cycle with a photograph of dried mud. The similarities are clear. There have been a number of experimental and theoretical investigations of mud drying[11,12] that are useful to our experiments. Groisman and Kaplan[11] show that when the volume of a mud layer in a glass dish is reduced by drying, cracks that extend to the base of the dish form at approximately the same time, separating the mud film into separate "cells." Further volume reduction is accomplished by the shrinking of these cells without further cracking. Kitsunezaki[12] shows that during this shrinking, the edges of the cells slide with respect to the stationary dish, while a "patch" at the center of the cell remains fixed with respect to the dish. This is clearly shown in Fig. 7c in Ref. 12.

The same sequence of events that occurs during the drying of mud also occurs here as lithium is removed from the alloy film. First, a series of cracks form, creating separate flakelike particles. The edges of the particles move with respect to the substrate as shrinking occurs and the particle centers appear to remain firmly attached. It is fortunate that the particle centers do remain attached, for the electrical connection to the substrate is necessary for the transfer of the needed electrons to complete the electrochemical reaction. Once the particles are formed, they are able to expand and contract reversibly over a remarkable range as Li is added and removed. If enough Li is added to cause the particles to touch, and then if further Li is added, the particles must expand in thickness or buckle away from the substrate. We have seen evidence for both events in our studies, but have not shown examples of particles buckling away here.

These studies have shown that the electrochemical reaction of lithium with alloys provides a unique opportunity to study colossal volume changes in solids. Metallurgists normally work in regions where metals undergo only a few percent of reversible strain at large applied stress. In the lithium alloys studied here, enormous strain can be caused with zero applied stress. The strain is caused by the incorporation of interstitial Li atoms between the existing M atoms of the alloys. It is our opinion that the theories of elasticity in solids are not suited to describe the colossal volume changes described here. We invite theorists to take up the challenge to describe these phenomena.

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