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Electromechanical Probing of Li/Li_2CO_3 Core/Shell Particles in a TEM

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We provide a detailed electromechanical study of individual core/shell structure – Li metal/Li_2CO_3 particles by utilizing an in-situ probing technique in the transmission electron microscope (TEM). This technique allows us to concurrently monitor the mechanical and electrical response of single Li/Li_2CO_3 core/shell structures in real time. The pressure on the Li/Li_2CO_3 core/shell particle was measured to be ~15 MPa at the initiation of fracture and the conductivity of the Li_2CO_3 shell is estimated to be ~10^-3 S/cm. To simulate the application of the core-shell particles in a real battery, we assembled coin cells with Li metal as a counter electrode. Prior to the cell assembly, the electrode was compressed in order to break the Li_2CO_3 shells to expose the fresh lithium metal to the graphite. When the electrolyte is added to wet the electrode, an electrochemical reaction spontaneously occurs between the exposed Li and graphite particles to produce a partially lithiated graphite anode. This lithiation occurs prior to the initial charging process, therefore compensating for the irreversible capacity loss due to the lithium consumption events during standard formation.1–3 Our results demonstrate a new pathway for the utilization of non-lithiated cathode material in future Li-ion batteries.

Figure 1. (a) Low magnification SEM image of the Li/Li_2CO_3 core/shell particles. (b) High magnification SEM image of the Li/Li_2CO_3 core/shell particles. (c) TEM image of single Li/Li_2CO_3 core/shell particle. The dark contrast at the edge represents the Li_2CO_3 shell (~350 nm).

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In a lithium battery cell, using lithium metal as the anode provides the most electropositive conductor (~3.04 V versus standard hydrogen electrode) and is the lightest possible material out of all the metallic elements.4 However, lithium metal is also highly reactive with moisture, oxygen and nitrogen,5 requiring that the battery cell fabrication and assembly processes occur in inert gaseous atmospheres. Using core-shell composite structures is one way to alleviate complications such as this since the different properties of the core and shell material can be used in the same system.6 In this paper, we use lithium in the form of a Li/Li_2CO_3 core/shell particle where the Li metal is sealed inside the Li_2CO_3 shell, therefore protecting the pure Li metal from being directly exposed to the environment. This approach has great potential for reducing handling costs in the lithium battery industry. In Li-ion batteries an insoluble layer forms at the solid-electrolyte interface (SEI) during the passivation of the negative electrode that stops the further chemical attack on the electrode from the solution.7 However, this SEI formation process results in the reduction of the cycle-able lithium in the cell, leading to irreversible capacity loss in the subsequent cycle (contributing to first-cycle loss).8 However, in the case of the Li-ion battery system using Li/Li_2CO_3 particles, also known as Stabilized Lithium Metal Powder (SLMP)9 the core/shell structure particles are mixed with graphite to form the anode of a cell. After applying pressure on the electrodes to crush the Li_2CO_3 shells, the fresh lithium metal is exposed and incorporated into the graphite anode material. When the electrolyte is added to wet the electrode, an electrochemical reaction takes place spontaneously between the exposed Li and graphite particles to produce a partially lithiated graphite anode. This lithiation happens prior to the cell charging process, therefore minimizing the irreversible capacity loss due to the lithium consumption events during formation.

The mechanical breakdown of the Li_2CO_3 shell layer exposes fresh lithium to the anode graphite particles and is a critical step for the SLMP to transfer Li material to the graphite particles. The process of breaking the shell is integral to the use of the SLMP, and thus measuring the local pressure on the particles needed to break the Li_2CO_3 shell and the electrical properties of the individual particles are of interest for understanding this technology. Here, we have utilized a Hysitron, Inc. nanoscale Electrical Contact Resistance (nanoECR) system for performing coupled electromechanical tests of individual Li/Li_2CO_3 core/shell structure particles in situ in a transmission electron microscope (TEM). The nanoECR provides an electrical path from the conductive boron-doped diamond tip, through the sample and to the signal acquisition and measurement hardware. The nanoECR nanocompression technique10 therefore enables us to directly observe the Li/Li_2CO_3 particle fracture events and quantify both the mechanical force and the electrical resistivity during compression in the TEM. The initial yield pressure calculated in this paper enables us to predict the failure behavior of the core/shell Li/Li_2CO_3 particles and assist in optimization of the material design.

As shown in Fig. 1a, the scanning electron microscope (SEM) image at low magnification shows that the Li/Li_2CO_3 core/shell particles have varying diameters ranging from ~5 µm to ~50 µm. The coating is continuous and no obvious cracks are observed on the surface of Li/Li_2CO_3 core/shell particles as shown in Fig. 1b. The higher magnification TEM image in Fig. 1c shows the core/shell structure of the particle where the lithium metal is sealed by a continuous Li_2CO_3 shell. During the carbonation process, the lithium metal particle reacts with CO_2 then forms a Li_2CO_3 layer at the surface.11 The thickness
of the Li$_2$CO$_3$ layer can be estimated from the TEM images as shown in Fig. 1c.

In considering future battery applications that would incorporate the Li/Li$_2$CO$_3$ core/shell particles, the mechanical behavior of the particles is critical to the processing routine. To investigate the ultimate strength and deformability of the particles, compression-failure tests were carried out. The Li/Li$_2$CO$_3$ core/shell particles were transferred onto a tungsten flat punch (~200 μm in diameter), and then the sample was brought into contact with a Pt substrate as demonstrated schematically in Fig. 2a. The particle could then be compressed in situ in the TEM by employing the coarse screw-driven motion of the indenter and fine positioning of the piezo drives. The Li/Li$_2$CO$_3$ core/shell

Figure 2. (a) Schematic diagram of an in-situ compression test of a single Li/Li$_2$CO$_3$ core/shell particle. (b) Load-displacement plot of a single particle measured under displacement control. (c-f) Selected frames from supplementary movie S1 demonstrate the deformation behavior and fracture event of the Li/Li$_2$CO$_3$ core/shell particle corresponding to the labels on the plot of load-displacement in (b). (g) The pressure versus% compression curve of the test shown in Fig. 2(b). A red arrow on the plot indicates that the pressure at yield is ~15 MPa.
structure particle was compressed between the tungsten flat punch and Pt plate by a displacement control test, and the fracture events were in-situ monitored in the TEM. As reported by Shan et al., the percent compression (or effective strain) is defined as the tungsten flat punch displacement after initial contact between the particle and the Pt substrate, divided by the initial outer diameter of the particle. The load versus displacement curve for one in situ test is shown in Fig. 2b. Selected frames (c-f) of a video (S1) show the deformation behavior at different loading regimes (c-f) as noted in Fig. 2b. Fig. 2c shows no deformation before the particle contacts the Pt plate. During the initial loading regime from c to d shown in Fig. 2b, the particle deforms elastically as shown in Fig. 2d, reaching 5.6% compression. A plateau in the load from d to e as shown in Fig. 2b indicates plasticity. At this point a kink feature can be observed along the contact area as marked by a green dotted ellipse shown in Fig. 2c, indicating flattening and possible fracture. Prior to the regime f, the particle was taken to about 8.5% total compression. At the loading apex f, because of the imperfect loading of the particle, tangential forces lead to large compressive stresses on one side and equally large tensile stresses on the other, which nucleates a crack down the contact area between the substrate and particle as highlighted by another green dotted ellipse shown in Fig. 2f. With an increase in displacement, the crack begins to extend outwards (supplementary Movie S1).

During the initial loading regime from c to d shown in Fig. 2b, the compression of the Li/Li2CO3 core/shell structure particles as they deform in real time and the particle fracture toughness during the compression process. In the case of a compressed particle between two rigid platens, the area supporting the compressive load can be estimated as the contact area between the particle and platens. This contact radius \( r_{cyl} \) is

\[
 r_{cyl} = \left( \frac{4R}{3(2R - b)} \right)^{1/2} \tag{1}
\]

Where \( R \) is the radius of the particle and \( b \) is the total displacement measured by the nanoindenter. Assuming a rigid flat punch and substrate, the pressure versus% compression curve is plotted in Fig. 2g. The distinct changes in the slope of the loading curve correspond to plastic events (including initiation and growth of cracks). Indicated by a red arrow in Fig. 2g, we achieve a value of the pressure at initial fracture of \( \sim 15 \) MPa, which enables us to benchmark the failure of the core/shell structure particle subjected to an applied pressure for future battery applications.

Our in-situ TEM electromechanical testing technique also enables us to simultaneously study the electrical and mechanical properties of the Li/Li2CO3 core/shell structure particles as they deform in real time in the TEM. In order to take more accurate electrical measurements, a point contact is advantageous to a cylindrical contact. Thus, we also probed the particles with a sharp conductive indenter. As shown in Fig. 3a, a particle on a Pt plate was indented by utilizing a conductive diamond sharp tip (\( \sim 100 \) nm in tip radius). During the test a constant 10 V was applied between the tip and the Pt plate to monitor the current change in the system. Figure 3b shows the current-tip displacement and load-tip displacement curves recorded during the test. The current curve (in red) measured during the compression process shows the nonconductive trait of Li2CO3 shell (\( \sim 220 \) nm in thickness) upon initial loading. At the load regime I as shown in the load-displacement curve (in green color), a fracture event was induced by the sharp tip indentation and the tip penetrated into the core/shell structure. The occurrence of the contact between the tip and the Li core switched the system from a high-resistance state to a low-resistance state, which is revealed as a “step” behavior indicated on the plot by a blue “up” arrow. The initial high resistance state is not only from the resistance at the contact area between the sharp tip and the Li2CO3 shell, but also from the resistance at the contact area between the Li2CO3 shell and the Pt plate, while the low resistance state is mostly from the resistance at the contact area between the Li2CO3 shell and Pt plate, since the Li core is highly conductive. The low resistance state still includes the resistance of one side of the particle in contact with the Pt plate. From the current plot in Fig. 3b, we estimated the electrical conductivity of the Li2CO3 shell to be a value of \( \sim 10^{-6} \) S/cm (see details of calculation in Methods). After the tip was retracted from the particle, the measured current value dropped to zero as demonstrated by a blue “down” arrow shown on the current curve. This in-situ mechanical and electrical test was also recorded in real time at a rate of 30 frames per second in the TEM. Selected frames from Supplementary Movie S2 are shown in Fig. 3c-3f. After the fracture event occurred in the Li2CO3 shell, the sharp tip reached the Li core as shown in Fig. 3d. Due to the ductile property of the Li material, when we retracted the tip from the particle, there was a gap generated between the sharp tip and the Li core as marked by green dotted lines in Fig. 3e. Both the load and the measured current immediately dropped to zero when the contact between the sharp tip and the particle was lost.

In order to demonstrate the improvement in the battery performance due to the Li/Li2CO3 core/shell structures, we assembled test coin cells for electrochemical cycling. CGP-G8 graphite was used as the base anode material. We fabricated cells mixed both with and without Li/Li2CO3 core/shell particles. Both electrodes were manually compressed to reduce the porosity and break the Li2CO3 shells in the electrode containing the particles. Details of the fabrication process can be found in the Methods section. The coin cell performance was evaluated in a thermal chamber at 30°C with a Maccor Battery Test system by going through ten cycles at C/20 between the voltage of 1.0 V and 0.01 V with a lithium counter electrode. Voltage profiles of the coin cells with and without the particles were plotted in the Fig. 4. The discharge capacities for both coin cells were more than 300 mAh/g and the two discharge curves are quite similar in shape. A 7% capacity loss is observed in the CGP-G8 coin cell without the SLMP at the first full cycle as marked in the charge-discharge plots. The first cycle capacity loss of the CGP-G8 graphite based anode is very typical due to the passivation of the graphite via the formation of electrically insulating and ionic conducting layers, the SEI. The consumption of the Li ions species for the formation of SEI is responsible for the capacity loss at the first full cycle. However, in the CGP-G8 coin cell with the use of the SLMP particles, the capacity loss was removed through the pre-lithiation process as shown in the charge-discharge curves. Prior to the start of the first cycle in this cell, after the shell fracture events induced by the crushing procedure during the cell assembly, the exposed fresh lithium metal from the core/shell particles reacts efficiently with the graphite at anode to form a partially lithiated anode. Through the control of the pre-lithiation process, we are able to compensate for the capacity loss due to the loss of lithium ions during the formation process.

In summary, our in-situ TEM technique provides direct observations and measurements of the fracture events of the core/shell structure Li/Li2CO3 particles. By using the in-situ electrical measurements in the TEM, we have confirmed that the particle structure is composed of a highly conductive core and nonconductive shell. The electrical conductivity of the Li2CO3 shell could be directly measured from the in-situ electrical measurement. The in-situ mechanical and electrical measurements suggest that the lithium is well sealed by the insulating Li2CO3 shell that has a conductivity of \( \sim 10^{-5} \) S/cm. Compared with the standard Li-ion battery unit cell performance curve, the pre-lithiated Li-graphite alloys induced by the Li/Li2CO3 particle fracture events provide sufficient charges for the subsequent cycles and minimize the capacity loss through the use of the core/shell structure particles in the battery unit cell.

Through a pre-lithiation procedure, this promising core/shell structure configuration provides a method to compensate for the Li-ion battery capacity loss due to the loss of lithium species during the SEI formation process. The degree of pre-lithiation can be controlled by adjusting the amount of SLMP powder. Therefore, the core/shell structure particles are confirmed as excellent potential candidates for a new and important class of materials to be considered for advanced Li-ion batteries to enable effective pre-lithiation in a Li ion battery.
Methods

In situ TEM tests.— The Li/Li$_2$CO$_3$ particles were sprayed onto an edge of platinum plate (∼1 mm in thickness) using a nebulizer. The mechanical test was run under displacement control with a loading rate of 60 nm per second. The mechanical and electrical measurement process in the TEM is recorded at a rate of 30 frames per second.

Battery materials.— Battery-grade acetylene black (AB) with an average particle size of 40 nm and a material density of 1.95 g/cm$^3$ was acquired from Denka Singapore Private Limited. Polyvinylidene difluoride (PVDF) no. 1100 binder with a material density of 1.78 g/cm$^3$ was supplied by Kureha, Japan. CGP-G8 graphite was provided by Conoco Phillips. Anhydrous N-methylpyrrolidone (NMP) was purchased from Aldrich Chemical Company.

Electrode casting.— The anode mixture (3% AB/15% PVDF/82% CGP-G8) was homogenized using Polytron PT10-35 homogenizer at 3000 rpm until viscous slurry was acquired. The anode laminates for coin-cell testing were cast on 12-μm thick battery-grade Cu sheet using a Mitutoyo doctor blade and a Yoshimitsu Seiki vacuum drawdown coater. The laminates were dried at 130°C under 10$^{-2}$ Torr.

Frames selected from movie
pressure for 16 h. The laminate thickness was measured with a Mitutoyo micrometer with an accuracy of 1 μm. The typical thickness of AB/Binder/CGP-G8 film is ∼60 μm with an initial porosity of ∼52%. The electrodes were compressed to 35% porosity before coin cell assembly using a rolling mill with a continuously adjustable gap from International Rolling Mill. The gap between the rollers was set at the targeted thickness. The electrode laminate was fed through the gap to compress the electrode to the thickness corresponding to 35% overall porosity.

Li/Li$_2$CO$_3$ particles compression.— A 9/16 inch diam disk was punched out from the anode laminate for use in the coin cell assembly. 10% Li/Li$_2$CO$_3$ particles were spread out evenly on top of the anode disk. Then the anode disk with Li/Li$_2$CO$_3$ particles was covered with polypropylene separator from Celgard. The Li/Li$_2$CO$_3$ particles were crushed by calendar to expose the Li out from Li/Li$_2$CO$_3$ core/shell particles.

Coin cell fabrication and testing.— Coin cell assembly was prepared in standard 2325 coin cell hardware with CGP-G8 graphite as the active anode material. The lithium metal was cut to 11/16 inch diam disk both as the reference and counter electrodes, which are larger than the anode to prevent lithium deposition at high charge rate. The anode electrode was placed in the center of the outer shell of the coin cell assembly and 50 μL of 1 M LiPF$_6$ in EC:DEC (1:1 weight ratio) electrolyte were added to wet the electrode. A 2 cm diam of Celgard 2400 porous polyethylene separator was placed on top of the anode electrode. The counter electrode was placed on the top of separator. Special care was taken to align the counter electrode symmetrically above the anode. A stainless steel spacer and a Belleville spring were placed on top of the counter electrode. A plastic grommet was placed on top of the outer edge of the electrode assembly and crimped closed with a custom-built hydraulic crimping machine manufactured by National Research Council of Canada. The entire cell fabrication procedure was done in an argon-filled glove box at oxygen level below 0.5 ppm and dew point below −80 °C. The coin cell performance was evaluated in a thermal chamber at 30 °C with a Maccor Battery Test system. The cell was formed by going through ten cycles at C/20 between the voltage of 1.0 V and 0.01 V.

Li$_2$CO$_3$ conductivity estimation.— Fig. S1 (a) is the schematic of the in-situ electrical measurement in TEM. During the electrical measurement, the particle was switched from a high resistant state $R_{L}$ to a low resistant state $R_{S}$ as labeled in the Fig. S1 (b) plot. A fracture event occurred on a portion of the Li$_2$CO$_3$ shell and was responsible for the total particle resistance change. Before the fracture event occurred, the total particle resistance $R_{\text{particle}}$ was mainly from the resistance $R_{\text{plate}}$ between the shell and the tip, and the resistance $R_{\text{plate}}$ between the shell and the Pt plate. After the fracture event, the conductive tip contacted the Li metal, then the total particle resistance $R_{\text{particle}}$ was mainly from the resistance $R_{\text{plate}}$. By using the equation $S1$,

$$V = \frac{1}{\sigma} \frac{l}{s} \quad [S1]$$

we are able to estimate the Li$_2$CO$_3$ shell conductivity $\sigma$. $l$ is the thickness of the Li$_2$CO$_3$ shell. The average contact area $s$ can be calculated from the equation 1. Our estimated Li$_2$CO$_3$ shell conductivity $\sigma$ has a value of $\sim 10^{-6}$ S/cm.

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