Acoustic Measurements of Lithium-Ion Battery Electrode Films

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***Abstract*—This research investigates the use of acoustic measurements as an alternative means of non-destructive quality control for Li-ion battery films. The goal of this research is to enable accurate, non-destructive inspection of the battery electrode as it is being manufactured, so that problems can be identified and addressed early on. Here we report on our efforts to distinguish between films with different mechanical properties using acoustic resonances and surface acoustic wave (SAW) velocity. We were able to differentiate between films of various coating thicknesses using resonance measurements. We also used resonance measurements to monitor a material as it dried. SAW velocity measurements need further work for successful implementation.**

I. Introduction

While batteries are vital to space exploration, they also have the potential to cause mission-ending disasters. These failures are costly and potentially deadly in both the short and long terms, as space debris is dangerous to people, spacecraft, and satellites in orbit. From 1957 to 2003, 4.6% of known satellite breakups were caused by battery malfunctions, leading to 12.8% of the satellite debris remaining in orbit [1]. Batteries used in space must pass stringent requirements for operating in harsh conditions and need to be reliable and have a long life [2]. Because of this, it is essential to continue to improve batteries, making them safer and more robust.

Due to their small size, high power density, and ability to recharge, lithium-ion (Li-ion) batteries are ideal for many uses in space, including satellites, rovers, and computers on spacecraft. One important area in improving these batteries is understanding and identifying heterogeneity in the battery electrode properties. Li-ion battery electrode films are essentially a two-layered structure. The bottom layer is the metal current collector, and in the films we used is generally made of aluminum for cathodes and copper for anodes. The top layer coating this metal is either the cathode or anode material that store the energy. In cathodes, this material is a mixture made up of large active material particles, carbon conductivity additive, polymeric binder, and pores. This composition is shown in Fig. 1. In this paper, the top layer will be called the coating, while "film" refers to the entire double-layer structure of the electrode.

Variations in the battery film can create "hot" and "cold" areas on the electrode, which can lead to increasing defects over time as the battery is used. Measuring the mechanical properties of lithium-ion battery films, such as thickness and elasticity, is important for predicting and improving homogeneity of the films and subsequent performance of the battery [3], [4]. It would be advantageous if problems with film heterogeneity could be identified and addressed early on through accurate, non-destructive inspection of the electrode as it is being manufactured. There are several techniques currently used to measure the mechanical characteristics of films, including nanoindentation [5], [6] and laser-induced surface acoustic waves [7]. However, they have not extensively been used for analyzing battery electrodes.

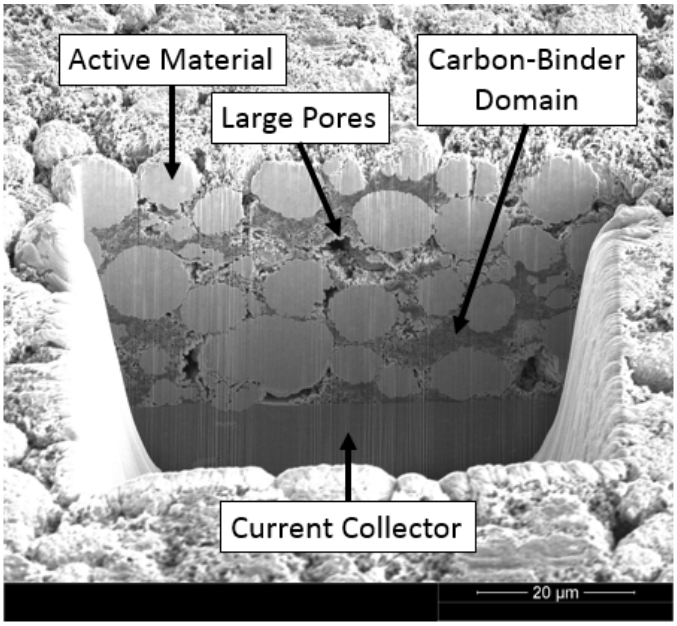

Fig. 1. Scanning electron microscope image of a Li-ion battery film in cross-section. The bottom layer is the current collector, which is often made of aluminum. The top layer is the coating, and is made up of active material (white circles), carbon conductivity additive and polymeric binder (gray filler between active material), and empty pores (dark spaces between active material and binder). The current collector can be seen as the darker material below the coating layer.

This research investigates the use of acoustic measurements as an alternative means of non-destructive quality control that could be adapted for on-line use in battery film manufacturing. Here we report on our efforts to distinguish between films with different mechanical properties using acoustic resonances and surface acoustic wave (SAW) velocity. Our goal is to

enable accurate, non-destructive inspection of the electrode as it is being manufactured, so that problems can be identified and addressed during fabrication. A probe has already been developed to measure conductivity of battery films [8]. To complement these electrical measurements, we have been developing an acoustic probe to detect small changes in the film's local material properties, in particular, density and thickness. As mentioned above, these parameters have been measured before using techniques such as nanoindentation, but the methods are generally not well-suited to use in a manufacturing environment and often require expensive tools and setups [9]. The acoustic probe would be used in conjunction with the conductivity probe to provide better understanding of the electrode properties.

II. Theory

Acoustics have been and are currently being used to make non-destructive measurements of non-battery structures, including concrete bridges [10], nuclear waste storage containers [11], and thin film structures [12]. This research uses some of the same principles to make measurements of battery films by exciting the resonances of the materials and by measuring SAW velocity in the films.

The resonance frequencies of a film are the frequencies at which the film will have the maximum vibration amplitude from a given excitation [13]. When solving for how materials vibrate, thin plates and membranes have similar theory, but membrane theory is somewhat simplified. The only restoring force on a membrane comes from the tension, but a thin plate has a restoring force from its stiffness [13]. These two types of systems are distinguished by the ratio a/h, where a is the length of the material and h is the thickness. Thin plates typically have an a/h ratio ranging from about 8 to 80, while membranes have $a/h > 80$ [14]. The area of the film that we excite is circular, with either a diameter of 1.27 cm or 2.3 cm, so the "element" we are looking at has a minimum dimension of $a = 1.27$ cm. The thickness of the films we tested range from about $20-60$ μm, resulting in an a/h ratio ranging from $210-635$. This means that our films should be considered as membranes rather than thin plates.

The fundamental frequency of a circular, single-layered membrane is given by

$$f_{01} = \frac{\alpha_{01}}{2\pi R}\sqrt{\frac{T}{\rho h}}, \tag{1}$$

where $\alpha_{01} = 2.405$, R is the radius of the membrane, T is the tension, ρ is the density, and h is the thickness [15]. This is not the exact model for our double-layer film, but it gives an approximate prediction for how the resonance frequency changes with thickness. Alternatively, we could model our film as a membrane with an added mass, where the current collector is the membrane and the coating is the added mass. For a circular membrane with an added mass in the middle, the fundamental frequency changes to

$$f_{01} = \sqrt{\frac{T}{2\pi m \ln(\frac{R}{b})}}, \tag{2}$$

where T is the tension, m is the added mass, R is the radius of the membrane, and b is the radius of the added mass [15]. Again, this model does not quite work for our case, as the coating layer (which is considered the added mass) has the same radius as the membrane, resulting in an infinite frequency. However, both of these models can give some intuition about how the resonance frequency will shift when different properties are changed.

Surface acoustic waves (SAWs) are waves generated at the surface of a material. They do not penetrate far into the material, but they can travel along the surface [16]. The velocity of SAWs in a thick material, called the Rayleigh velocity, depends on the elastic properties of the material. On layered materials, the velocity changes with as the excitation frequency changes. This dispersion allows us to find the mechanical properties of the film [12].

III. Apparatus for Measurements

A. Acoustic source

Two types of acoustic sources were used for film excitation. A loudspeaker was used for both resonance and SAW velocity tests, and a piezoelectric element was used for SAW velocity tests. The loudspeaker is connected to a computer through the audio port and controlled via Labview or Python. The piezo is controlled with a Digilent Analog Discovery function generator. Piezo elements have a narrower operating frequency range than a loudspeaker, but they have the benefit of being physically coupled to the film. The efficiency of the sound radiation is therefore much better for a piezo than for a loudspeaker.

B. Resonance measurements

For the resonance measurements, the probe consists of a clamp to confine the vibrating area of the film, the excitation source, and a microphone on the opposite site of the clamp. The acrylic clamp aligns two o-rings in order to securely confine the edges of the film, so that we have a circular film with a clamped boundary. Different boundary conditions, tension, and area will change the resonance response of the material, so we needed to ensure that these were consistent between experiments.

C. SAW velocity measurements

For SAW velocity measurements, the film was stretched across two rollers and weighted on each end in order to provide constant and repeatable tension. When a loudspeaker was used for excitation, it was placed underneath the film. When a piezoelectric element was used for excitation, it was placed on top of the film (to make the required physical contact with the film). We experimented with two types of sensors: microphones and piezoelectric elements. When microphones

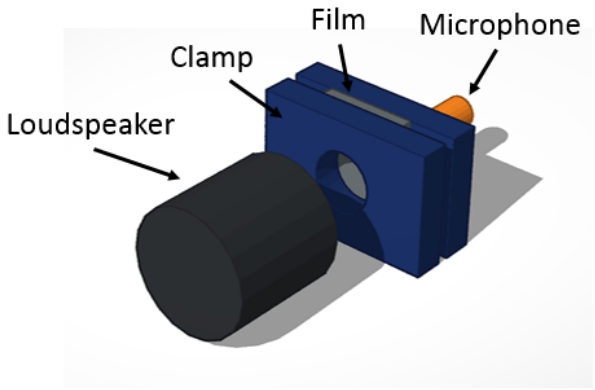

Fig. 2. Illustration of the setup for the resonance measurements using a loudspeaker for excitation. The speaker excites a vibration in the area of the film confined by the clamp. A microphone behind the clamp records the acoustic response of the film.

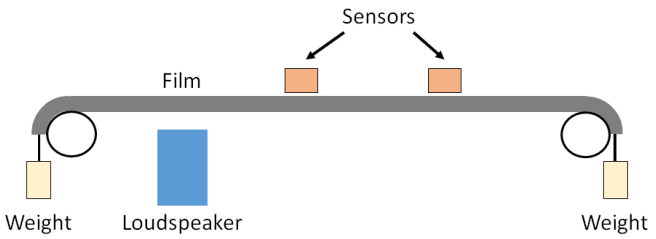

Fig. 3. Illustration of the setup for the SAW velocity measurements using a loudspeaker for excitation and piezoelectric sensors for measuring. The speaker excites a vibration in the area of the film confined by the clamp. Piezo sensors resting on the top of the film record the vibrations. In tests with a piezoelectric source, the source would also be resting on top of the film. In tests with microphones instead of piezoelectric sensors, the microphones would be below the film.

were used, they were placed underneath the film such that they were very close to the film but not touching it. When piezos were used, they were placed on top of the film (as shown in Fig. 3).

IV. Methods

A. Resonance measurements

For resonance measurements, the acoustic probe confines the film using a clamping device so that the vibrating area is limited to a small circular area of the film. This is the only contact portion of the probe. Minimizing contact is ideal as it results in fewer parts that must regularly be replaced and less interference with the battery film. In an on-line process, this clamp could be moved around from location to location in order to get multiple test points. The film is excited using a loudspeaker and the resonances are measured by a microphone on the other side of the film. Resonant response depends on the properties of the film, so differences in thickness, elastic modulus, and density will change the resonance frequencies. The resonance is also dependent on the geometry of the confined area. A smaller confined area will result in a higher resonance frequency than a larger confined area of the same material.

Once we take the resonance data, we analyze the data. If the excitation signal was a sine wave, we take the Fourier Transform of the signal from the microphone or piezo sensors. This gives us the frequency response. From this we are able to find the first resonance frequency of the film. For many of the resonance tests we used a frequency sweep to excite the film. In this case, we need to take a baseline measurement when there is no film in the clamp in order to know what signal the microphone picks up from the source. To analyze the data from the frequency sweeps, we find the power spectrum by summing the squares of the microphone data and dividing by the total number of samples at each frequency.

B. SAW velocity measurements

The other type of acoustic measurement we tried to implement was SAW velocity. Mechanical properties of thin films, including elastic modulus and thickness, have been determined using SAWs [9], [17]. For our experiments, a film under tension is excited to produce a surface acoustic wave. This wave is measured (via microphone or piezoelectric element) at multiple points along the film to determine the speed of the wave. Because wave dispersion is based on properties such as elasticity and density, we can calculate mechanical properties of the film from the wave speed measurements.

Using the data from the two sensors (either microphones or piezos), we find the time delay between when the wave reaches each sensor. With a known distance d between the sensors, we can find the phase velocity c of the wave. Because the SAW velocity will change when the excitation frequency changes, we can get a dispersion curve. This dispersion allows us to use curve fitting to get the mechanical properties of the film.

V. Results

The acoustic sources we used (loudspeaker or piezoelectric transducer) cannot couple a large amount of energy into the film, but they are versatile and allow for good control of the excitation signal. This is because the user can easily control what signal is input by adjusting the function generator, allowing for a variety of signal shapes and frequencies, such as a sine wave or a frequency sweep. When using an acoustic source, the signal detected by the microphone will include the sound generated by the source in addition to the desired resonance. This can be problematic if the two overlap.

A. Resonance measurements

For the resonances, we were able to solve this problem by playing a signal that was near but not at the resonance frequency of the film being tested. When the signal played by the source is close enough in frequency to the peak resonance frequency of the film, it is still able to excite the film's resonance mode. This is shown by the two sets of data in Fig. 4. The resonance at 590 Hz is visibly excited when the excitation signal is 500 Hz or 620 Hz. This enables us to filter out the excitation signal from the final result during

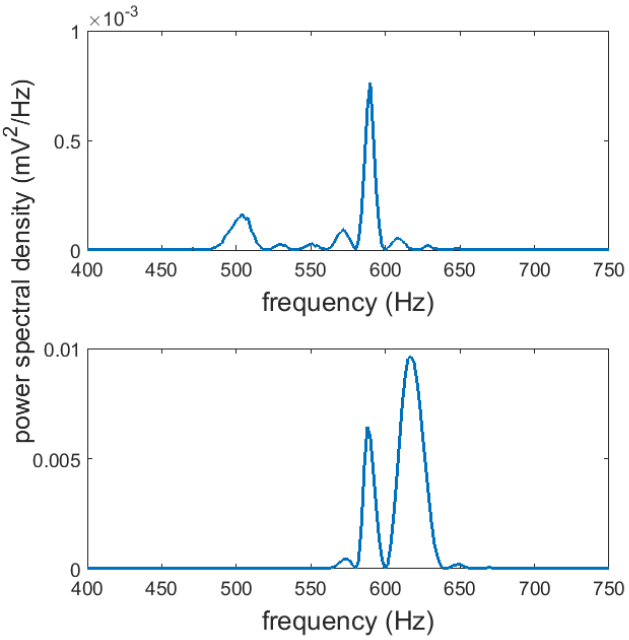

Fig. 4. Acoustic response spectrum for aluminum foil clamped in apparatus shown in Fig. 2. The excitation source is driven by a sinusoidal signal at 500 Hz for the upper plot and 620 Hz for the lower plot. The excited resonance of the clamped foil is visible in both cases at 590 Hz.

post-processing using a bandpass filter around the resonance frequency. With sufficient difference between the excitation and resonance frequencies and proper filter design, filtering should eliminate both room noise and the source signal, leaving only the resonance of the film.

Using a speaker as the excitation source resulted in resonance tests that were able to distinguish between different films. Results from these tests are shown in Fig. 5. The resonances of two cathodes (on an aluminum current collector) and an anode (on copper) are seen to be at different frequencies. Because the current collector affects the frequency response of the film, we would expect the film with copper to have a different resonance than the films with aluminum, and this seems to be the case. The two cathodes had coating layers of different thicknesses (26 μm and 38 μm), and even the 12 μm difference causes a shift in the resonance. From our analytical models in 1 and 2, we would expect the thicker (and more massive) film to have a lower resonance, but this is not the case here. This could be due to inconsistent tension from film to film.

We eventually discovered, however, that our efforts to consistently and securely clamp the edges of the film were causing a calendering effect. The material in the film coating was being compressed by the clamp, resulting in a change in the physical properties. Li-ion films are calendered during the manufacturing process in order to achieve a specific porosity and thickness [18]. This porosity affects the electronic properties of the battery and changes the density of the overall film. When we changed the porosity with our clamping, it did not

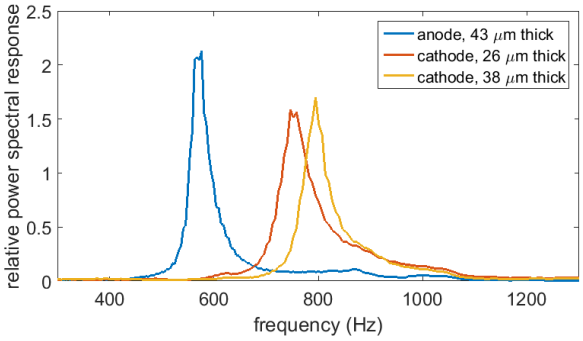

Fig. 5. Acoustic response spectra for various battery films clamped as shown in Fig. 2. The two similar peaks are for two cathode films with different coating thicknesses (26 μm and 38 μm) on aluminum, while the peak at the lowest frequency belongs to an anode film with a coating thickness of 43 μm on a copper current collector.

change the properties of the part of the film that was currently being measured (as that was the area within the confinement), but it meant that we could not repeat measurements in the same place on our film. We are currently experimenting with other techniques for this experiment, including weaker clamping and no clamping.

We also found that the resonance frequency changes with other factors, such as drying. This was tested by putting paint onto aluminum foil while it was in the clamp. By taking resonance tests before, after, and as the paint dried, we were able to see how the frequency changed over time. In Fig. 6, the resonance peaks for the foil without paint and after several paint layer applications. The foil was painted and a resonance test was taken once the paint dried. This process was repeated several times without removing the foil from the clamp. The resonance frequency shifts to lower frequencies as more paint (and therefore more mass) is added to the foil. An interesting effect is seen in Fig. 7. This shows the shift in frequency as the second layer of paint dried. Here the resonance actually increases as the paint dries, even though from Fig. 6 we know that the dry frequency is still lower than the resonance of the foil without paint and the foil with only one layer of dry paint. This could be due to the interplay of mass and stiffness. As the paint dries, it becomes stiffer, and the "composite film" of foil plus paint becomes stiffer overall, causing the resonance to increase. This could have applications for the battery manufacturing process, as it shows that the acoustic response changes as the film dries. This could allow for monitoring of the drying state while they are drying out the slurry that forms the coating on the film [18].

B. SAW velocity measurements

As mentioned before, piezo elements cannot operate at as many frequencies as the loudspeaker (or microphones), but they are much more efficient at radiating or detecting vibrations, due to the fact that they are physically coupled to the film. For this reason, the piezo is a better excitation source for SAWs than the loudspeaker, and picks up vibrations better than our microphones.

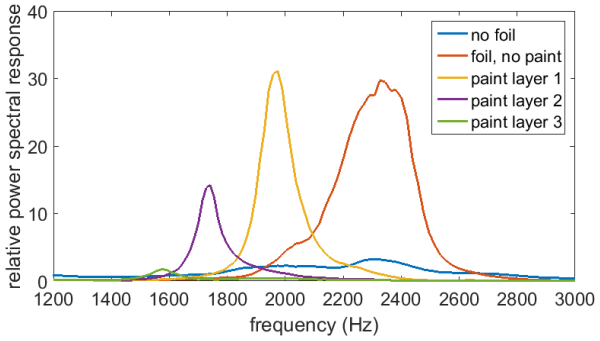

Fig. 6. Acoustic response spectra for aluminum foil with various amounts of paint, clamped as shown in Fig. 2. Different resonance peaks are seen as more paint is added to the foil.

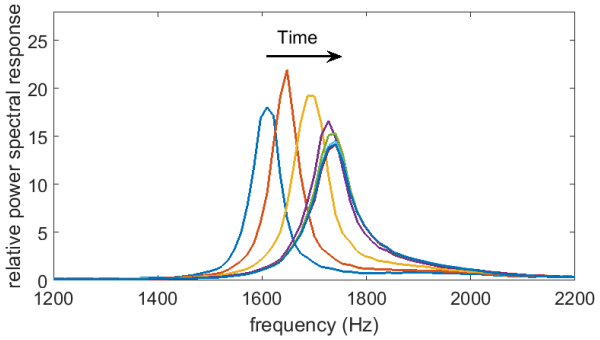

Fig. 7. Acoustic response spectra for aluminum foil with a drying layer of paint, clamped as shown in Fig. 2. Resonance tests were taken every minute as the paint dried. The resonance frequency peaks shift to higher frequencies as the paint dries (direction shown by the arrow).

We attempted to excite SAWs using both types of acoustic sources. However, we eventually concluded that our microphones were not sensitive enough to detect the wave as it traveled through the material. All the microphones picked up was the source sound as it traveled through the air from the acoustic source. Other researchers have successfully made this type of measurement using a laser for detection, rather than microphones [5], [19], [20]. By having a weaker laser (that does not excite SAWs in the material) reflected off the material, small movements on the surface (such as those caused by a SAW) can be detected. The change in the light beam enables detection of the wave as it passes through the material, either by monitoring the location of the reflected beam or by watching for changes in the diffraction pattern between the reflected and original beam. Unfortunately, the coating on battery films is dark and non-reflective, rendering this technique ineffective for our experiments.

We were never able to repeatably pick up the sound from the SAWs as they traveled through our materials. We did the SAW testing with aluminum foil, since we could easily obtain large pieces of it and the current collector on our films is very similar to aluminum foil. The microphones only detected the sound traveling from the source to the microphone through the air. This makes sense, as the signal from the SAW would

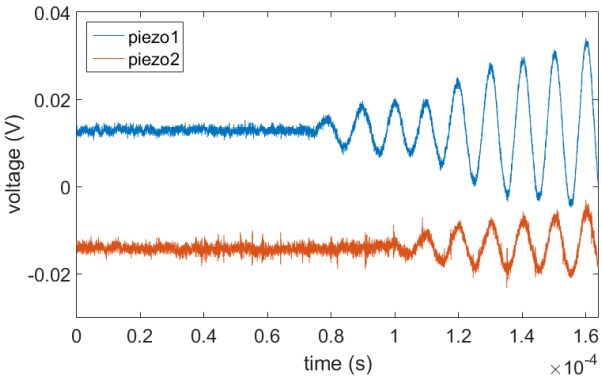

Fig. 8. Data from SAW measurements taken with piezo sensors on aluminum foil, in a setup as shown in Fig. 3, but with a piezo excitation source instead of a loudspeaker. Each piezo has a slightly different "resting" voltage. The signal clearly reaches one piezo before the other, as expected.

likely be very small (only due to the surface moving ever so slightly). A laser diffraction detection system would be better at picking up these small movements from the SAW, but, as mentioned above, the films are not reflective enough for this to work. The piezo sensors were also unable to reliably pick up the vibrations from SAWs, but this may have been due to the source not coupling enough energy to generate large enough SAWs. We were able to pick up vibrations in the foil, but the speed calculated from this data was often much slower than expected. This can be seen in Fig. 8. The data was taken with piezo sensors and piezo excitation on aluminum foil. The sensors clearly pick up a vibration, and there is a definite time delay between when it reaches each sensor. The speed we calculated for this wave, based on a known distance of 14 cm between the piezos and the observed time delay of about 21 μs, is 6580 m/s, which is close to the speed of sound in aluminum, which ranges from 3000-6000 m/s. However, multiple tests yielded wildly differing speeds, some of which were well below the wave speed in aluminum. We believe that some of the signals we detected, which we originally thought were SAWs, were in fact the foil flexing as its resonance is excited. In the future, we may try these measurements again using a high-power pulsed laser for excitation and the piezo sensors for detection. It is likely that a pulsed laser has the capacity to excite larger SAWs, allowing for easier detection with the piezo sensors.

VI. Conclusion

We were able to distinguish between battery films of different coating thicknesses by exciting the acoustic resonances of the clamped films and recording the vibrations. As expected, as thickness (and mass) increases, the resonance frequency decreases. We also found that changes in drying states may be monitored by looking at the shift in the resonance frequency as the material dries. However, more work is needed to successfully implement the SAW velocity measurements on battery films.

Lithium-ion batteries are rechargeable, light, and energy-dense, which makes them an important resource in space applications. Refining the manufacturing process of battery films is crucial to making the batteries both safer and more efficient. Using acoustic resonance to detect changes in the material properties of films could be an inexpensive, non-destructive, and reliable method to optimize the manufacturing process. Since it is independent of the chemistry involved, acoustic testing can be used in many roll-to-roll thin film processes, not just Li-ion battery films, leading to potential applications far beyond those mentioned here. From preventing satellite explosions and dangerous space debris to enhancing the longevity of rovers, improving Li-ion batteries through online measurements during manufacturing will propel us farther into space.

ACKNOWLEDGMENTS

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