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Uneven Discharge of Metallic Lithium Causes Increased Voltage Noise in Li/MnO₂ Primary Batteries upon Shorting

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The voltage noise of primary batteries with Li/MnO₂ chemistry increases when the battery suffers a short circuit. This noise level is measurable only after a proper offsetting scheme that involves a battery that has undergone the same history is employed. In the current work, we are showing that the increased voltage noise is due to the metallic lithium anode and the heterogeneous discharge thereof. Periods of short circuit causes the lithium to get depleted from points of lowest resistance, which eventually causes uneven depletion and the current collector to be partially exposed. This is similar in nature to pitting corrosion of metals and their protective films, a phenomenon which is also routinely characterized by electrochemical noise signals.
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The contemporary importance of batteries in devices and applications ranging from portable electronics to large scale storage is self-evident.¹ The recognition of the work of Goodenough, Wittingham and Yoshino with a Nobel Prize is also testament to this importance.² As such, non-destructive, non-invasive and preferably non-perturbing battery diagnosis and characterization methods attract both scientific and industrial attention.^{3,4,5} Non-invasive and non-perturbing analysis methods, in particular, enable observations under operational conditions without any disturbance.

The need for noninvasive real-time monitoring is exacerbated by the necessity of employing materials with higher energy and power densities.⁶ Materials such as lithium metal provide substantial advantages regarding the energy and power density both in the volumetric and the gravimetric sense, however, they also create enormous challenges regarding safety and performance. On the safety front, high energy density combined with the ability to quickly discharge creates a potential for discharging in an unsafe manner.⁷ On the performance front, cells that employ lithium metal anodes are more prone to dendrite formation and mossy structures that may lead to capacity loss and internal shorting.⁸

State-of the art techniques use either external excitations of various forms or postmortem materials analysis. The postmortem analyses are extensively reported and reviewed recently by Waldmann et al.⁹ Chemical analyses are invaluable especially when performed with proper control experiments. Electrical testing involves applying a known waveform of current or potential as a function of time to measure the corresponding potential or current respectively. Through analysis of the response of the battery, chemical information regarding the components of the battery can be inferred. PITT/GITT,¹⁰ pulse testing,¹¹ voltage decay¹² are all methods that probe components of the battery through current voltage relationships.

Chief among the electrical are methods based on sinusoidal excitations and their subsequent equivalent circuit analysis that constitutes electrochemical impedance spectroscopy (EIS). EIS is used to gather information about the subcomponents of batteries in a non-destructive manner. The applied symmetric excitation going between charge and discharge makes sure that the state of the battery is unchanged and the small amplitude necessary for linearity ensures that the battery never ventures far from the equilibrium state.¹³ Though a mature literature exists around battery diagnosis through EIS, its application to primary chemistries is problematic, both due to stability and linearity issues.¹⁴ Indeed, our group recently achieved the linear and stable EIS measurement of a primary

chemistry, Li-SOCl₂, by ensuring the battery is always under a discharge load. The constant discharge necessary in the method, however, irreversibly depletes the battery and causes the otherwise non-invasive EIS technique to become invasive for the case of primary chemistries.

Diagnosis of primary batteries through non-invasive methods is, thus an open question. Several attempts have been made in the literature to employ electrochemical noise as a tool to non-invasively extract information regarding batteries.^{15,16} As natural extensions of the stochastic corrosion noise measurements, the electrochemical noise of traditional aqueous electrolyte batteries such as lead-acid and nickel metal hydride chemistries were investigated to demonstrate bubble formation due to electrolysis of the electrolyte when exposed to high overpotentials.^{17,18,19} Though attempts at extending these measurements to new generation energy storage devices such as supercapacitors, Li and Li-ion batteries were demonstrated,^{19–23} they either suffer from ill-defined experimental parameters (such as bandwidth and cut-off frequency) or analysis methods. This casts doubt upon the extracted noise related information. There are two significant problems in noise analyses for batteries: voltage drift and large background levels. Both problems are related in the sense that the large background needs to be corrected through a mechanism that also adapts to the drifting voltage. Commonly used offset correction schemes that are electronically designed are mostly problematic in that they tend to add extra noise of the voltage reference components. This causes the measurement and the subsequent data analysis to be especially challenging.

We have recently introduced a new offset reduction scheme²⁰ that involves the use of two batteries that are kept in parallel for equilibration. Making sure that the offset reduction is achieved by a completely symmetric system, the noise measurements reflect the sample with a minimum of measurement related artefacts. Using the scheme that we developed, we showed that shorting a primary Li/MnO₂ battery measurably increases the voltage noise exhibited. Having demonstrated the plausibility of voltage noise measurements as a diagnostic tool in this primary chemistry, herein we support our findings by materials analysis to elucidate the origins of the electrochemical noise in primary batteries.

Electrochemical noise is a well-established technique in the corrosion literature where the voltage or current swings around the equilibrium of a corroding metal sample or couple of metals is regularly used to determine the mode of corrosion.²⁴ Early examples in literature showed the three common modes of corrosion (uniform, pit formation and crevice) to be distinguishable using their unique electrochemical noise signatures (or lack thereof for uniform corrosion) both in the time domain²⁵ and the frequency domain.²⁶ Even though disagreements exist in the interpretation, the correlation between the noise data and the mode of corrosion was only possible

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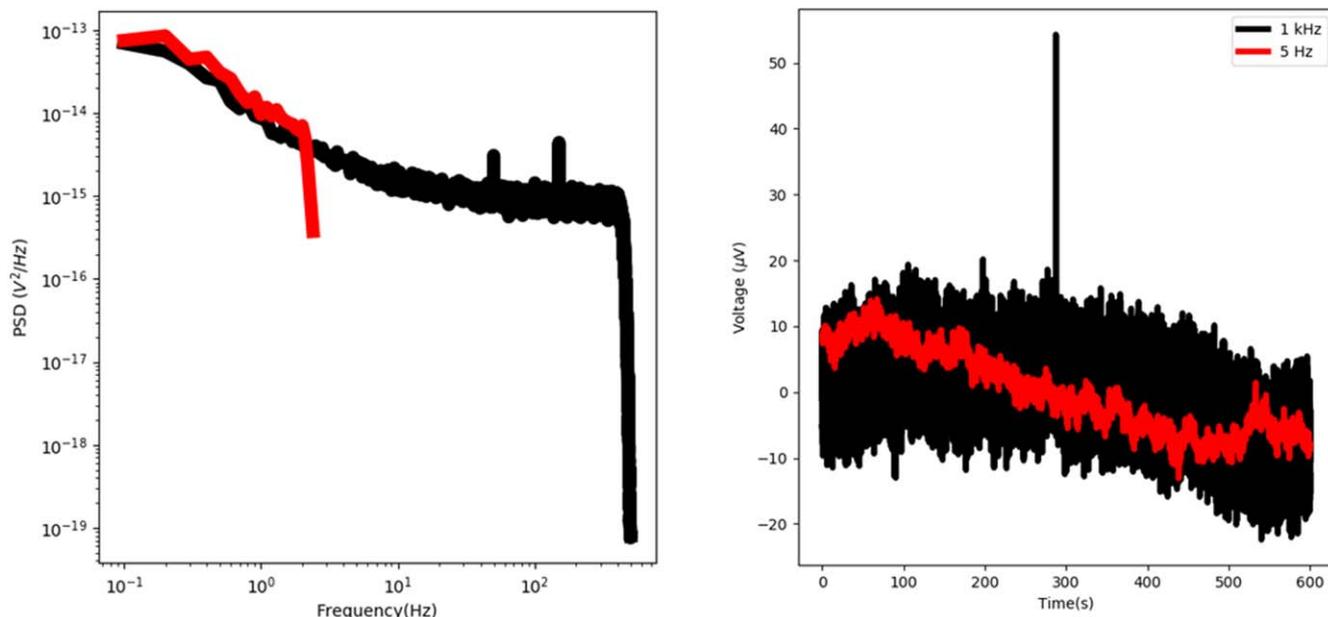


Figure 1. The noise measurement of CR2032 with 1 kHz (black) and 5 Hz (red) low pass filters in frequency domain (averaged with 10 s-long segments) (left) and time domain (right).

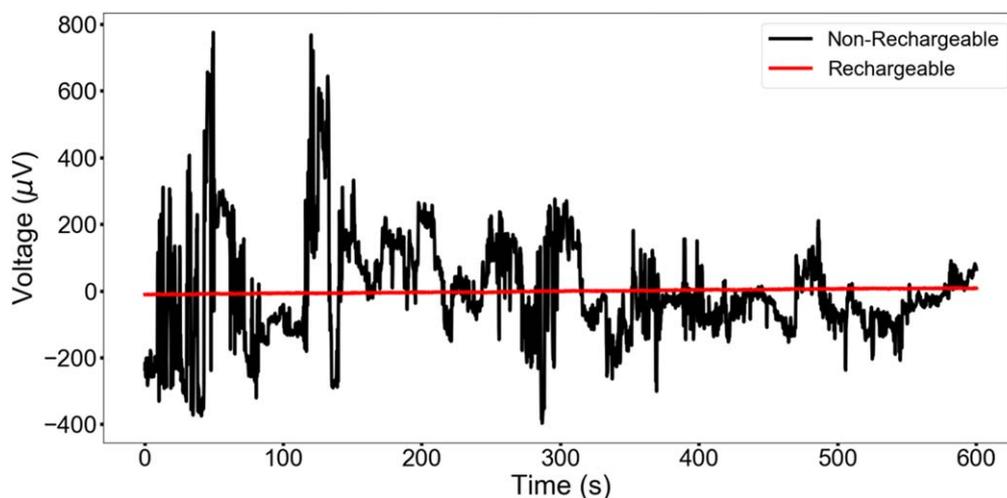


Figure 2. Noise measurements of non-rechargeable and rechargeable CR2032 in anti-serial connection after suffering 3 d shorting.

after a visual analysis of the sample after the measurement. In the same vein, the only way to correlate features of the noise signal to the underlying phenomenon is a postmortem inspection of the battery components. Data obtained from noise studies for corrosion detection have been inspected by various mathematical analysis methods over the past couple decades. However, there is no consensus in the literature regarding the analysis method.^{27,28} For electrochemical noise of batteries, no such consensus exists for data collection methods precluding a discussion on analysis. In the current manuscript, the data is mostly presented as is along with the variance, to convey the existence or absence of measurable noise.

As mentioned before, efforts in extending noise measurements to batteries are complicated by the comparatively low noise amplitudes (μV) that need to be resolved over the already high battery voltage (>1.5 V). Nature of the observed noise signal derives from the various stochastic events that cause movement of charges at the battery electrodes. For a given amount of charge movement, a large voltage swing can only occur if the capacitance of the electrode is

small. Common battery electrodes have high capacitances and therefore batteries are known to have extremely low noise. The high open circuit voltage of the battery (~ 3 V for the present study) also introduces another challenge in battery noise measurements. Instrument manufacturers routinely subtract the DC portion of the signal from the total to improve the voltage resolution at low amplitudes by increasing the gain after the DC background is subtracted. These offset correction schemes, however, were shown to introduce noise artifacts stemming from the offset correction method of choice and the background level. Indeed, in our investigations of noise in pristine CR2032 li-MnO₂ coin cell batteries no measurable noise stemming from the coin-cells was measured in amplitudes as low as 1 μV (from DC to 5 Hz), a resolution only achieved through a novel offsetting scheme.²⁰

Only when the batteries were disturbed through shorting, noise events with amplitudes over 5 μV were resolved.²⁰ To fully develop electrochemical noise as a non-invasive diagnostics tool for primary batteries, chemical events/changes taking place that cause the

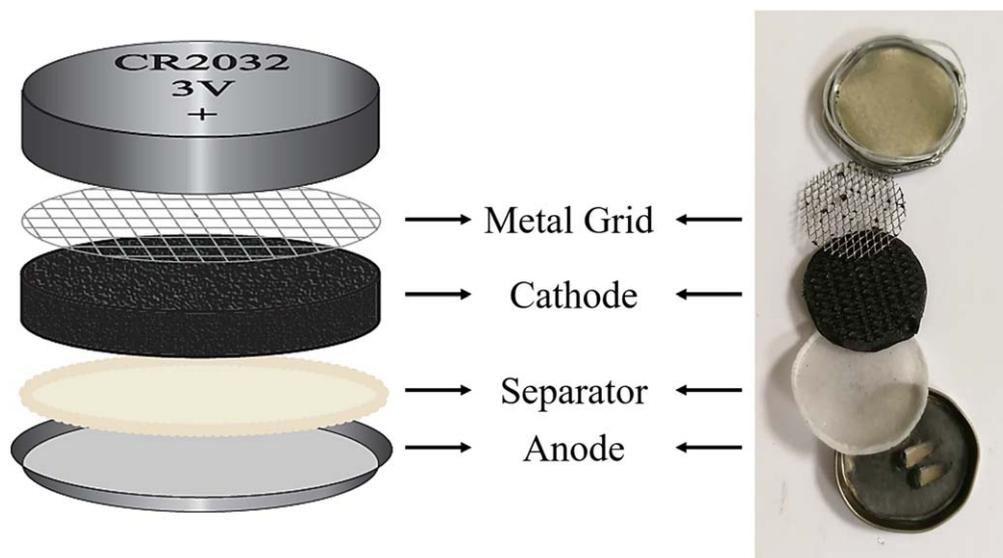


Figure 3. Schematic of the cell components. From top to bottom: Metal grid, cathode, separator and anode.

measured noise profile needs to be detailed, similar to the phenomena that constitute the noise profile for corroding metal surfaces. As mentioned above, insights regarding the types of corrosion and their association with certain noise profiles derive from detailed microscopic and macroscopic investigations of the metal surface after it is thoroughly corroded. Thus, drawing inspiration from the corrosion literature, the origins of the noise events in batteries were investigated systematically through post-mortem investigations of the electrodes. We show that the noise measured in shorted batteries are the results of uneven Li depletion across the anode surface compared to the even depletion when the batteries are properly-discharged. Our findings prove that the information content in the noise profile is mainly from the anode side/the lithium metal of the battery cell, rather than the changes on the other battery components. We corroborate our findings through control experiments on a rechargeable battery of similar chemistry and construction that uses a lithium/aluminum alloy as the anode.

Experimental

CR2032 coin cells from Maxell were procured from local suppliers. Primary LiMnO_2 chemistry is used in these batteries and noise analysis on this chemistry was studied previously.²⁰

Noise measurements.—Noise measurements were done using a Gamry Interface 5000 potentiostat after comparing different instruments as outlined in an earlier publication.²⁰ Electrochemical Signal Analyzer (ESA 410) version 7.0.4 software from Gamry Instruments was used to adjust analog parameters of the instrument. The cut-off frequency of the measurement, the sampling rate and low pass filters were all set to 5 Hz. Since the time domain will provide the necessary information (whether the battery is shorted or not) it is important to filter the output and subsequently choose the suitable low pass filter. The bandwidth was selected based on our previous experiments on the same battery regarding where most of the electrochemical information resides in the noise spectrum.²⁰ Figure 1 clearly indicated that important features can be extracted from the measurement that has been done with 5 Hz.

An acquisition time of 10 min was used. To reduce the effects of voltage drift on our measurements, a voltage stability criterion of $\sim 100 \mu\text{V min}^{-1}$ was selected, meaning over a 10-min period the change in voltage never exceeded 1 mV. In cases of severely abused batteries, this criterion was relaxed as the noise profile is easily distinguished from drift by visual inspection.

As described elsewhere, offset correction is an important consideration to obtain noise measurements without instrumental artifacts.²⁰ We recently developed a scheme that achieves offset correction without introducing any artifacts by using two identical energy storage devices connected in anti-serial (i.e. connected in series but the same sign poles facing towards each other). This connection allows the overall voltage measured by the instrument to be at 0 V thus removing the need for instrumental offset correction. To ensure this identity, batteries of the same batch were put through

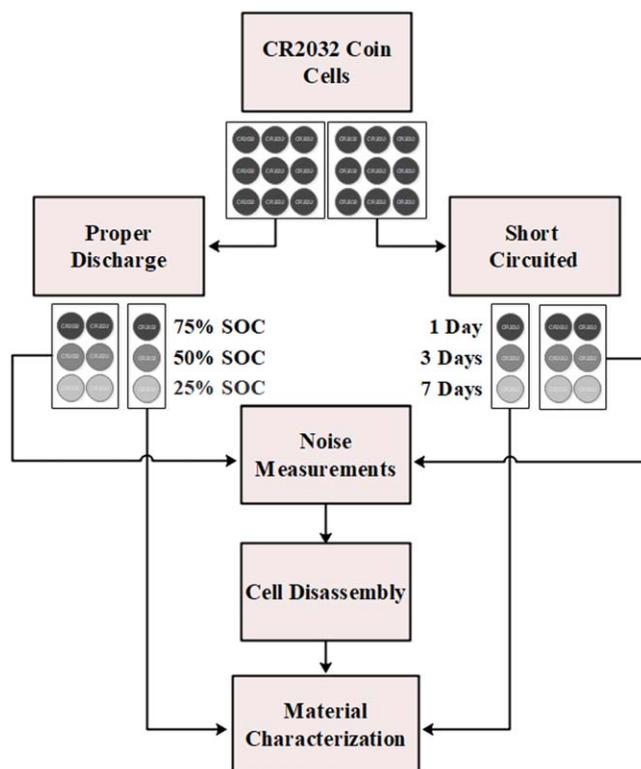


Figure 4. The flow chart of our study process. Noise measurement and material characterization in batteries that are divided into two sets as they are properly discharged and short circuited.

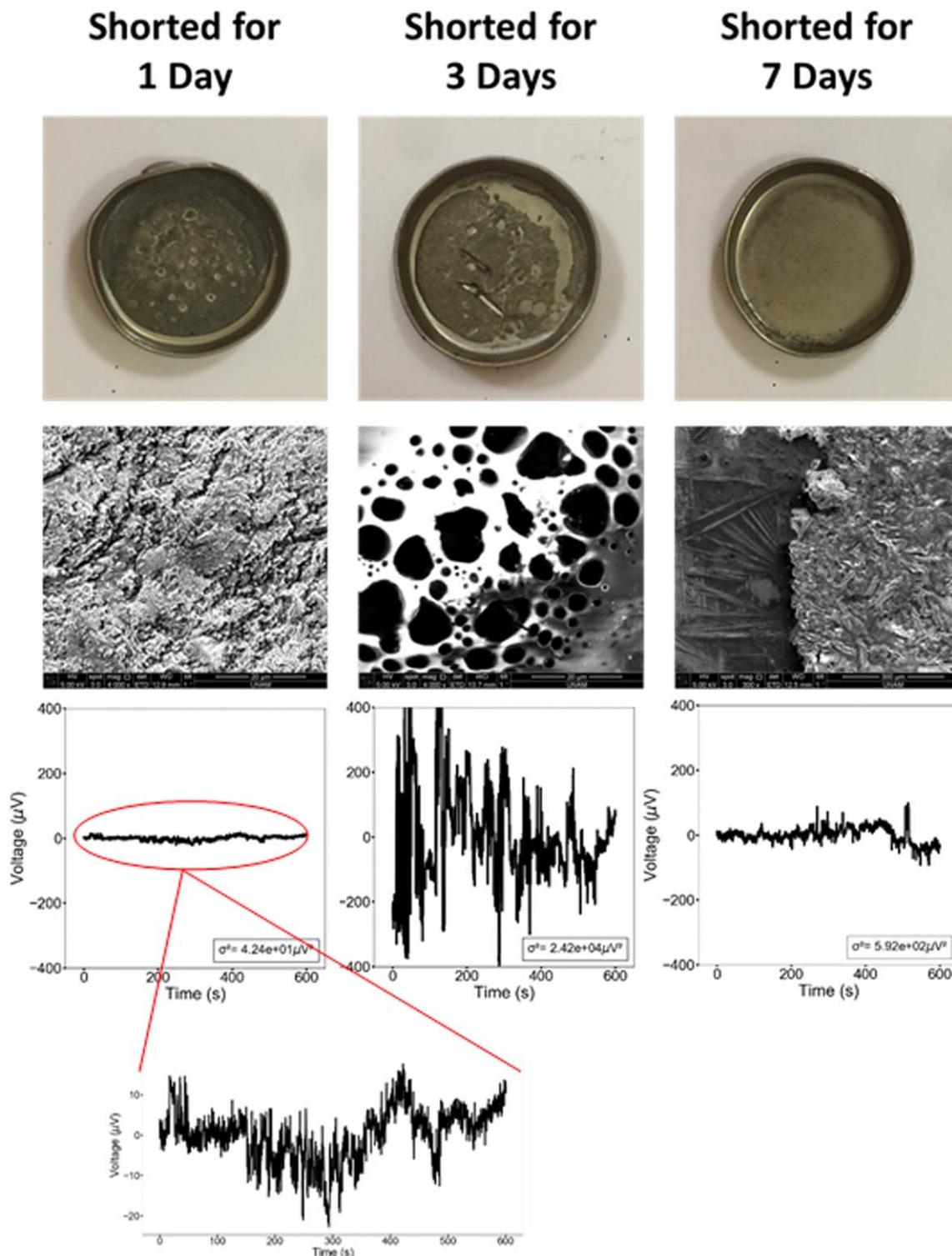


Figure 5. Photograph, SEM image and noise data of Lithium anode of shorted CR2032 batteries at various stages of abuse durations (1 d, 3 d and 7 d).

either shorting or proper discharge for equal periods of time in pairs. Prior to noise measurement, these pairs were left to equilibrate in a parallel connection so that any slight difference in their voltage can be removed and that drift is avoided when measuring the noise. The details of the process can be found elsewhere.²⁰ The drift correction was slightly modified from the reported method. Instead of employing a piecewise linear subtraction, the entire dataset was

detrended with a simple linear fit. This ensures that no artefacts are introduced.

Battery disassembly.—To ensure that the materials under study do not undergo degradation due to the presence of O_2 and H_2O , batteries were disassembled under an inert atmosphere. Further, to separate each component of the coin cell with minimal deformations,

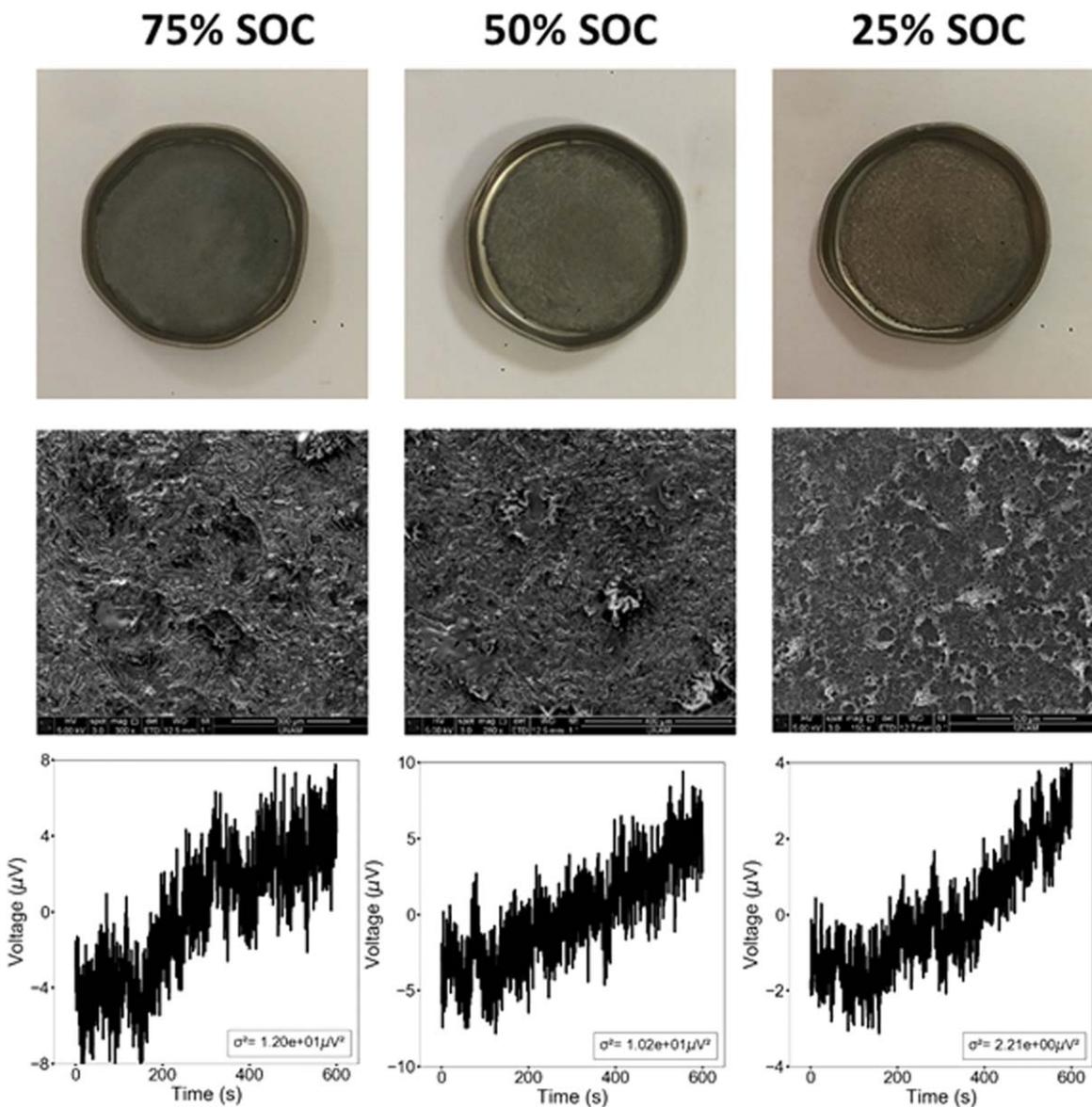


Figure 6. Photograph, SEM image and noise data of Lithium anode of discharged CR2032 batteries at different states of charge (75% SOC, 50% SOC and 25% SOC).

the cells were held with medical pliers with the tips wrapped by cloth. Small cuts were performed along the perimeter of the positive terminal. Once the full perimeter of the positive terminal was cut, the cell can simply be pulled apart revealing all the components of the battery with minimal deformations.

SEM analysis.—FEI Quanta 200 F scanning electron microscope was used for Scanning electron microscopy (SEM) images. Samples were placed on aluminum sample holders.

Results and Discussion

In our previous work, it was shown that the voltage noise of the CR2032 coin cells with the primary Li/MnO_2 chemistry was increased when the cells were shorted for set periods of time. As the first control, shown in Fig. 2, the noise profile of rechargeable Li/MnO_2 batteries of the same geometry was shown to have no increase in the noise upon shorting. The difference between the non-rechargeable and rechargeable cells is the composition of the anode material. While pure lithium metal is used as the anode material in

non-rechargeable Li/MnO_2 batteries, lithium aluminum alloy is used as the anode material in rechargeable Li/MnO_2 batteries.²⁹ The striking difference in the noise levels of primary and secondary chemistries warrants a closer examination of the anode in the primary cells and its relation to noise measurements.

In Fig. 3, coin cell components are shown as a schematic. The coin cell contains a current collector mesh, cathode active material, polymeric separator and Lithium foil as the anode respectively from top to bottom. Drawing inspirations from electrochemical noise studies in corrosion, visual inspection and chemical and physical analyses on the components of the battery were carried out to identify the phenomenological reason behind the increased noise.

In order to investigate the differences in a controlled manner, two major experimental routes were followed to systematically study the effects of abuse on the outlined battery components. These involved comparisons between shorted and properly-discharged^a batteries both in terms of their noise profiles and their chemical properties as outlined in Fig. 4. Pristine batteries as well as properly-discharged

^aWe define proper discharge per the CR2032 spec sheet which specifies a continuous constant current discharge at 0.2 mA for 50 d.

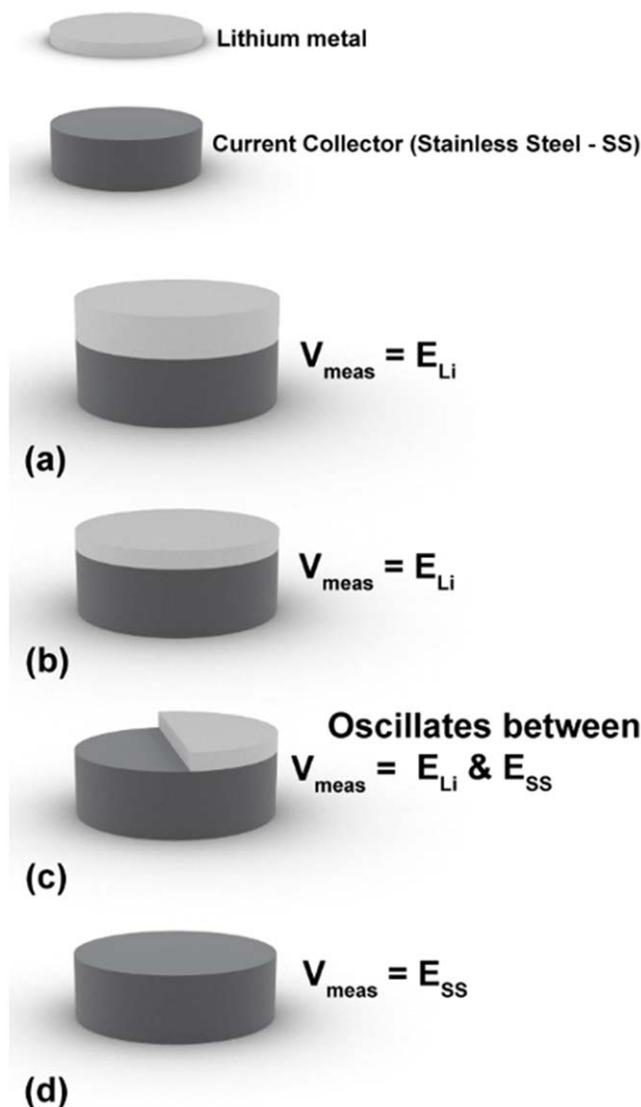


Figure 7. Schematic description of a current collector (black) and lithium active material (gray) Pristine battery (a), properly discharged battery (b), 3-d shorted battery (c), 7-d shorted battery (d) (E_{Li} : Open Circuit Potential for the Li Metal, E_{SS} : Open Circuit Potential for the Stainless Steel, V_{meas} : Measured Voltage).

batteries were used as controls to make sure that the changes could unequivocally be correlated with the increased noise.

Postmortem analysis reveals that upon shorting, the appearance and the texture of the Lithium anode changes. Non-uniform depletion of the Lithium foil is clearly observed in the first row of Fig. 5. As the duration of shorting time increases, non-uniform depletion of Lithium foil also increases. At the end of 7 d of shorting, it is clearly observed that no anode active material is visible. The SEM images in the second row of Fig. 5 prove that the depletion of Lithium in the anode is non-homogeneous. In the last row, there are noise measurements for each battery after the short circuit exposure. As photos also suggest, when after short circuit exposure, noise levels increase up to $\sim 100 \mu V$ and this can be attributed to the non-homogeneous depletion of metallic Lithium in the anode. Without the need for any additional analysis, simple inspection of the noise level yields information about the homogeneity of the discharge.²⁸

Following up on these two observations, we investigated the anode side and showed that depletion mechanism is different compared to shorted and properly-discharged batteries. For the properly-discharged batteries, the lithium on the anode side gets depleted homogeneously throughout discharge as shown in Fig. 6.

During this depletion, no appreciable noise is measured at the relevant amplitudes ($\sim 10 \mu V$), while the morphology of the anode shows uniform thinning of the lithium coating.

Another interesting observation can be made on the voltage noise level of primary batteries as the length of shorting increases. The voltage noise level increases when the battery first suffers a short that lasts 1 d or 3 d. However, when the battery is shorted for a full week, the measured voltage noise decreases drastically back to levels that are still above the pristine battery (limited by the instrument) yet much lower compared to a battery that is shorted for three days. This result sheds some more light into the phenomenon behind the voltage oscillations. It appears that the measured voltage noise is larger when the exposed surfaces of stainless steel and lithium are comparable in area. In contrast, the signal is quieter when only the lithium metal, or only the stainless steel is exposed. We speculate that the noise measured is fundamentally due to the voltage measurement mechanism choosing the dominant surface when one exists and is effectively bi-stable when both surfaces are roughly equally available. Measurement of voltage, by definition is done via a small DC current passing through the device under test.^{30 b} This

^bIrrespective of the method used, there is a small current, either the current on the needle, or the input bias current on the comparator.

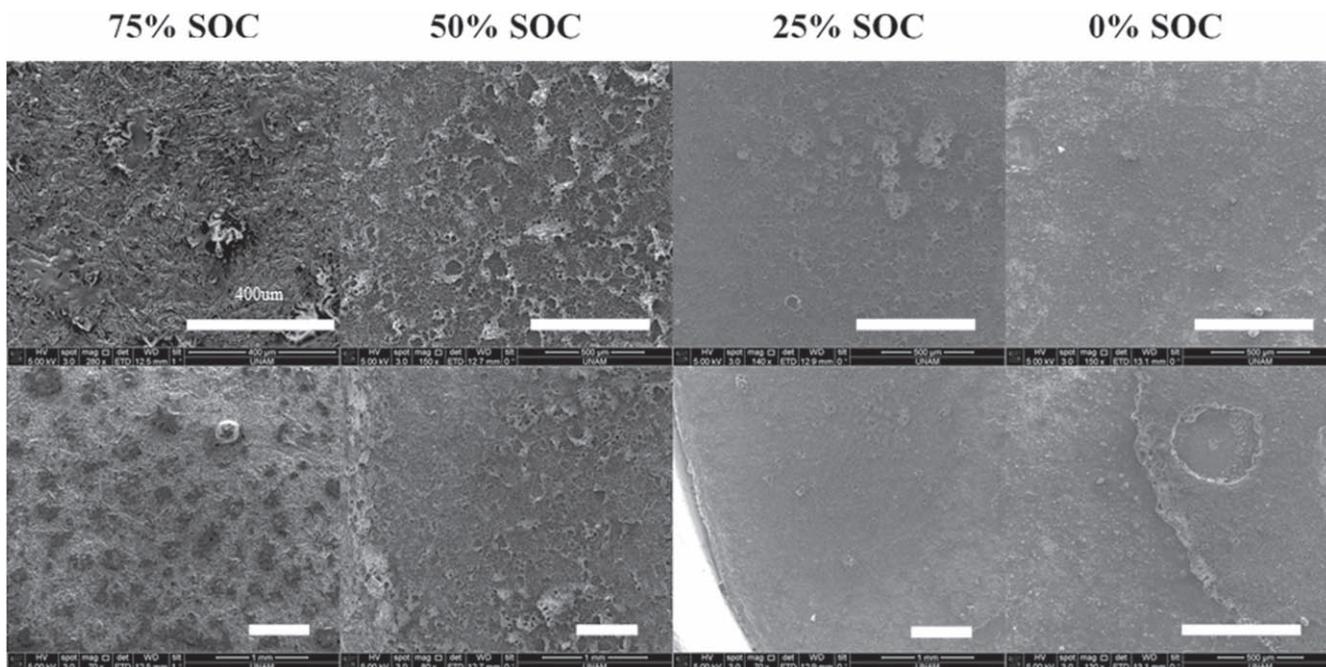


Figure 8. SEM images of anode of discharged CR2032 batteries at different states of charge. The SEM images were taken at different spots with different magnifications. All the scale bars are 400 μm .

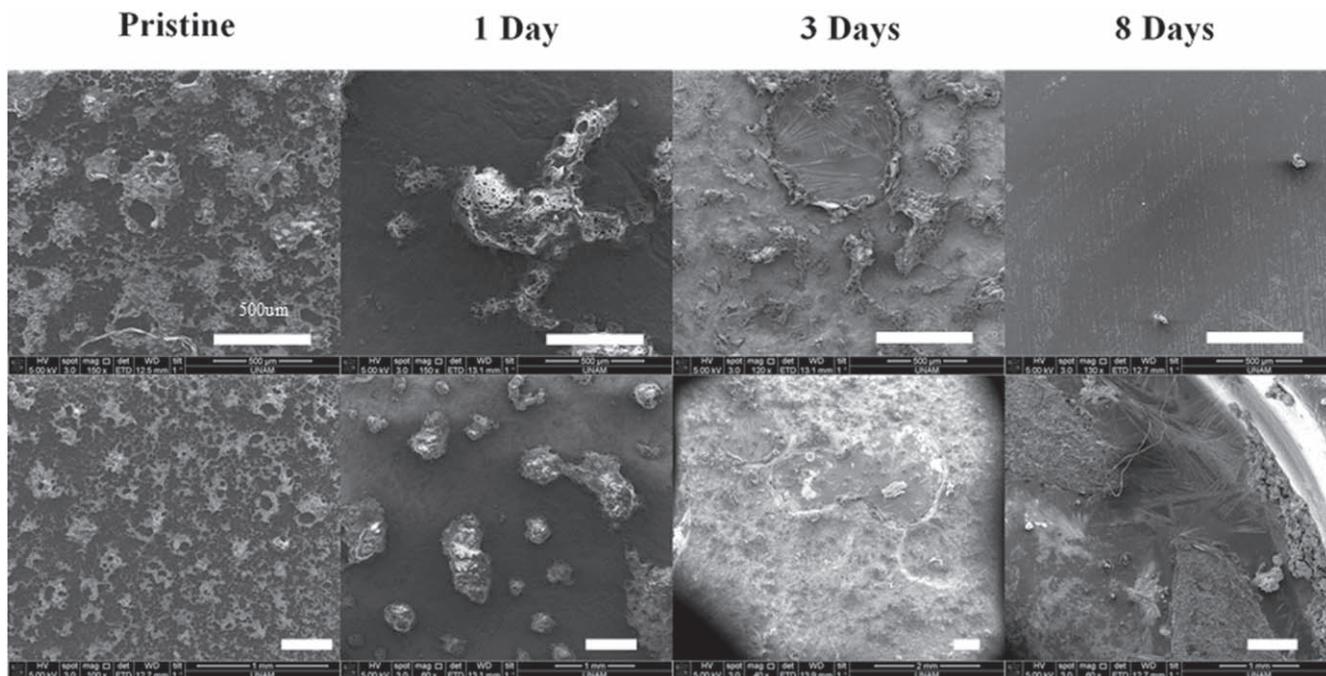


Figure 9. SEM images of anode of shorted CR2032 batteries after different shorting durations. The SEM images were taken at different spots with different magnifications. All the scale bars are 400 μm .

current will pass through the path of least resistance, in the case where multiple paths exist. As illustrated on Fig. 7, the only time voltage would be noisier is when the electrode surface has two severely different options for the current as shown on Fig. 7c.

We further investigated the status of the Lithium anodes via SEM. The analysis reveals that as the battery is discharged either through a slow discharge or a short, the initially porous Li metal on the anode side is consumed as expected. The severity and the mechanism of consumption, however, depends on the mode of

discharge. Batteries that are properly-discharged are shown to keep the initial porous anode structure until 50% SoC which is also followed by a uniform depletion of the layer as shown in Fig. 8. Large deposits on the sides of the anode cap can be observed at the 0% SoC level which stem from the inhomogeneous contact pressure of the battery package. This, in turn, causes slight changes in the rate of depletion at regions of lower contact pressure. When the batteries are shorted, however, the porous structure is seen to collapse to localized networks of severe depletion even for relatively brief

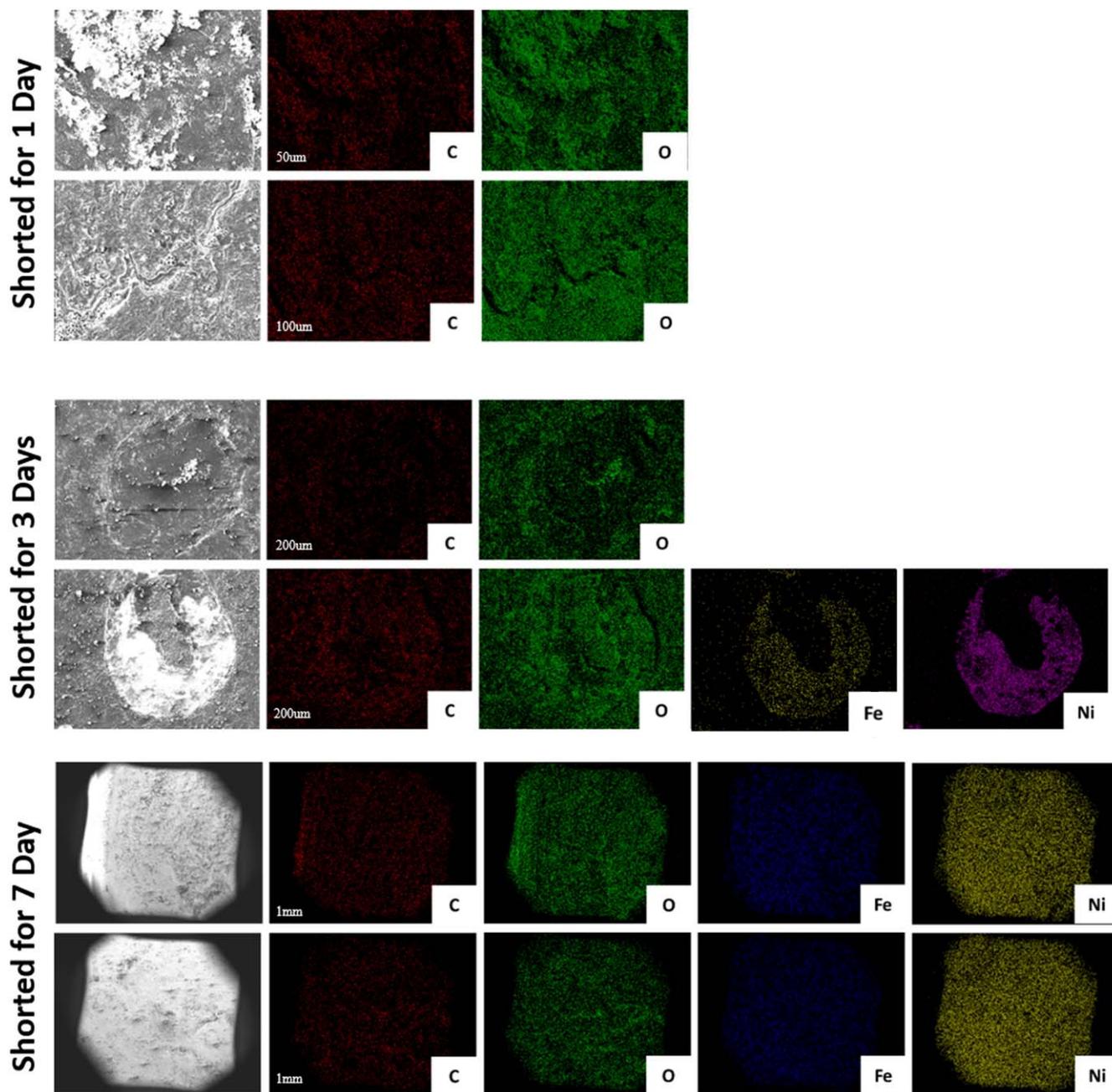


Figure 10. EDX mapping of anode of shorted CR2032 batteries after different shorting durations (1 d, 3 d and 7 d). The width of the field of view is given as a text inset on the C image.

shorting durations which is then followed by the formation of clear circular regions that either have relatively very thin layers of Li or none at all as seen in Fig. 9. Though indirect, a method to follow the presence of a Li overlayer on the anode cap is EDX. EDX is not easily sensitive to small nuclei such as Li,³¹ however the presence of Li on top of the cap can be followed by the absence of the signature signals of the stainless-steel anode cap (Fe and Ni). For instance, EDX signal measured on the pristine battery anode only consists of C and O due to various impurities. This is seen as evidence of perfect covering with Lithium as no signals regarding the underlying stainless steel is visible. As Lithium is depleted by shorting or discharging, in the EDX signal measured on the flat regions in the anode, a significant Ni peak can be measured which originates from the stainless steel (Figs. 10 and 11). Further, in SEM images of the

anodes of shorted batteries, a mechanism for depletion of Li can be deduced that is different compared to the properly-discharged batteries. When shorted, due to the rapid discharge, large amounts of lithium ions need to quickly move which start either at defect sites or points of lower electrolyte resistance. Since these points constitute the path of least resistance, once uneven depletion occurs due to shorting, it continues from these points and further extends until the lithium metal is depleted.

In summary, we have shown that increased noise of primary Lithium batteries is due to the heterogeneous oxidative dissolution of the Lithium anode. We have two significant experiments that lead to this conclusion. First, when the shorting experiment is repeated using a rechargeable battery with almost the same composition (except the anode material), the noise is not present. Second, when

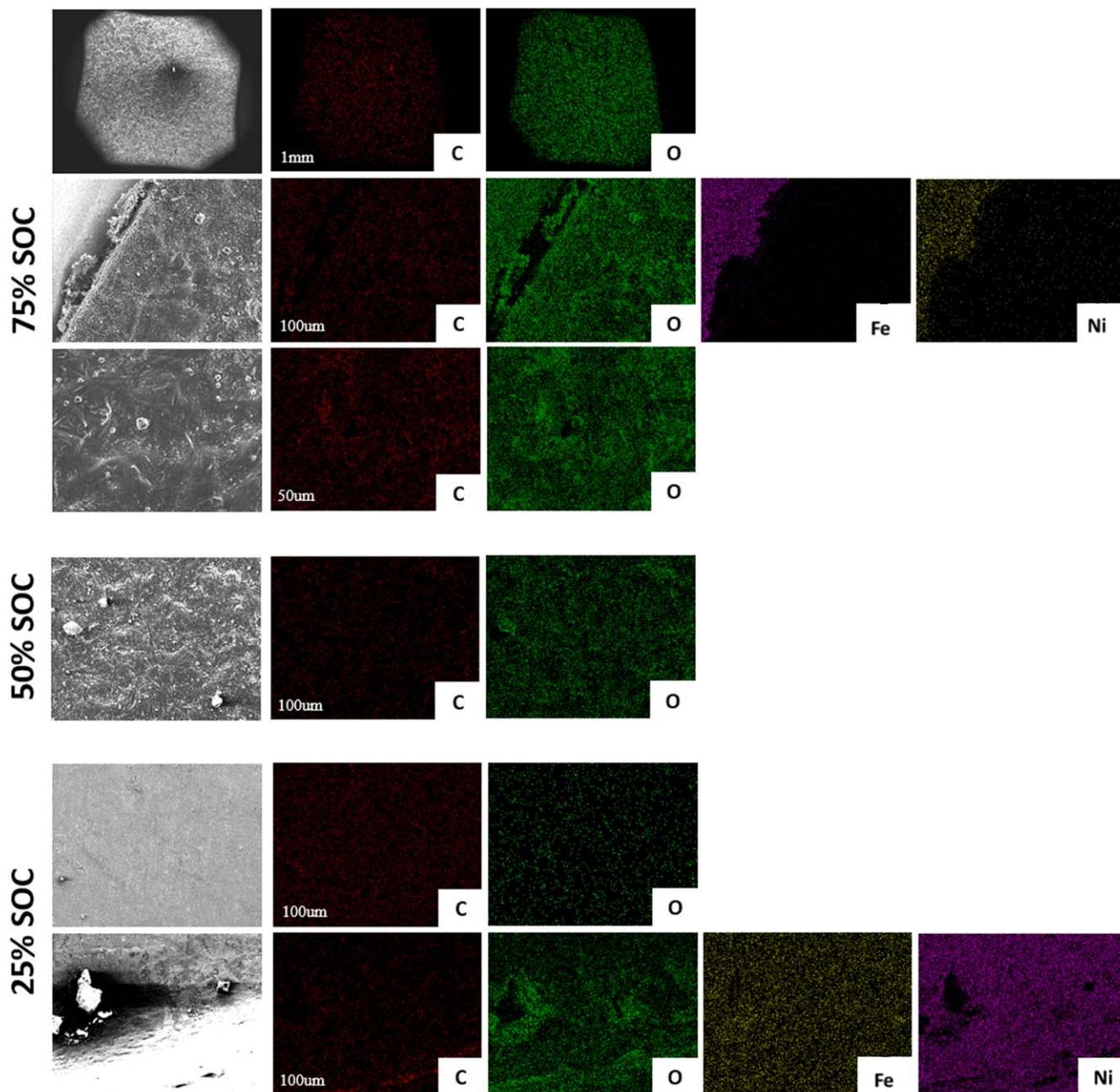


Figure 11. EDX mapping of anode of discharged CR2032 batteries at different states of charge (75% SOC, 50% SOC and 25% SOC). The width of the field of view is given as a text inset on the C image.

the discharge is carried out with a low current (homogeneous dissolution), the noise is not present. This is summarized in Fig. 12.

This noise is similar in nature to pitting corrosion where electrochemical noise measurements are routinely used. Localized oxidative discharge of the anode eventually exposes parts of the underlying stainless-steel substrate. This causes the open circuit to be noisier, akin to the voltage noise increasing when pitting corrosion occurs. Increased noise can be attributed to various competing electrochemical processes on different parts of the electrode surface.

Conclusions

Voltage noise in LiMnO_2 primary batteries was shown to be due to the localized discharge of metallic lithium anode. The localized discharge eventually exposing the underlying stainless-steel substrate causes the open circuit to be noisier, akin to the voltage noise increasing when pitting corrosion occurs. The increased noise can be attributed to the various competing electrochemical processes on different parts of the electrode surface.

	Primary Batteries (Li Anode)	Rechargeable Batteries (Li-Al Anode)
Fast Discharge	Noise	No Noise
	Non-Homogenous	Homogenous
Slow Discharge	No Noise	No Noise
	Homogenous	Homogenous

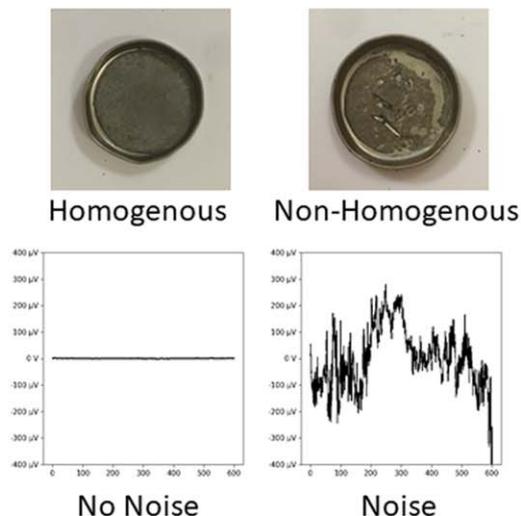


Figure 12. Short summary of the findings and the conclusion of the article.

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Appendix

XRD.—XRD analysis.—XRD characterization was done on the anode and the cathode materials to follow apparent changes in the crystallinity upon abuse (shorting). Once the coin cell was disassembled under inert atmosphere, the cathode material composed mainly of Li-MnO₂, was fixed on a microscope slide using Kapton tape (<http://www.panalytical.com/Application-notes/Sample-holders-for-air-sensitive-materials.htm>). Kapton serves to protect the material from the reactive atmosphere while the sample is transferred to the XRD instrument. The added Kapton on the top creates problems with the height of the overall sample. This creates problems with the accuracy of the angles measured due to the positioning of the goniometer which decreases the overall reproducibility of the patterns.

The XRD results for the anode and cathode active materials are shown in Fig. A-1. Within experimental reproducibility, there is no significant difference in the diffraction patterns in of the materials collected from the shorted batteries and the pristine ones. Similar

analyses were performed for other parts of the cell, as well as the properly discharged ones to confirm that there were no significant differences.

In corrosion literature, both voltage and current noise measurements are routinely used. In this study, we only considered voltage noise because the current noise measurement involves controlling the potential. In doing so, the noise due to the control electronics on the potential gets translated into the measured current noise. In Fig. A-2, the applied bias voltage and its current response is shown for a battery. The data clearly shows that the current noise obtained progresses following the trends of potential applied. There is undoubtedly some information in the current noise pertaining to the battery, however, it is practically impossible to extract the part of the current noise that is not related to the voltage control circuitry. For this reason, when studying batteries, we investigate voltage noise and not current noise.

As shown in Fig. A-3, control experiment was performed to observe the minimum shorting duration that leads to increased voltage noise. Significant increase in noise levels starts after just 1 h of shorting. However, more harsh conditions were studied in this paper: batteries were shorted for longer times (such as 1 d, 3d and 7d) in order to see some visual changes inside the battery in order to help finding correlations between the chemistry and the noise.

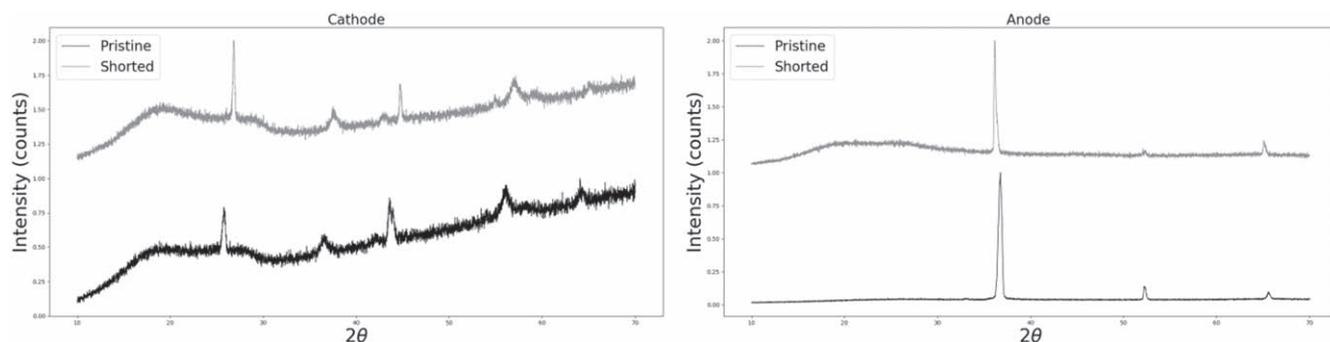


Figure A-1. XRD measurement of pristine and shorted CR2032 batteries for cathode and anode sides.

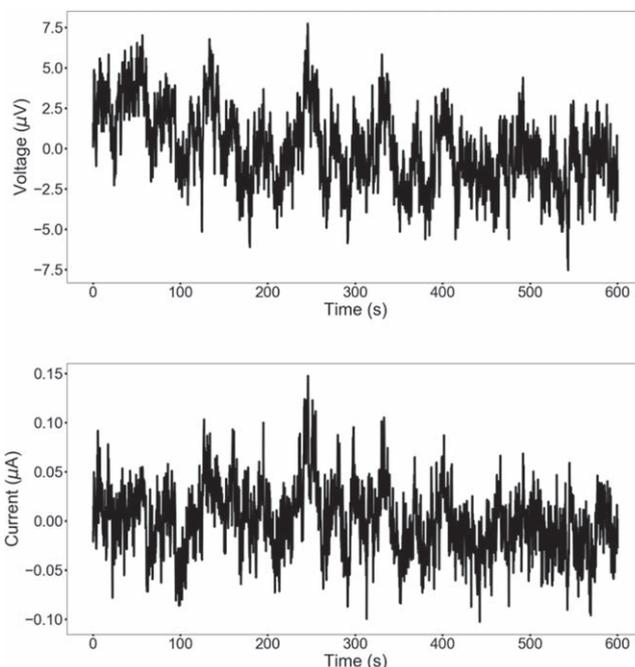


Figure A-2. Current noise measurement of CR2032 battery, applied voltage (top) and its current noise (bottom).

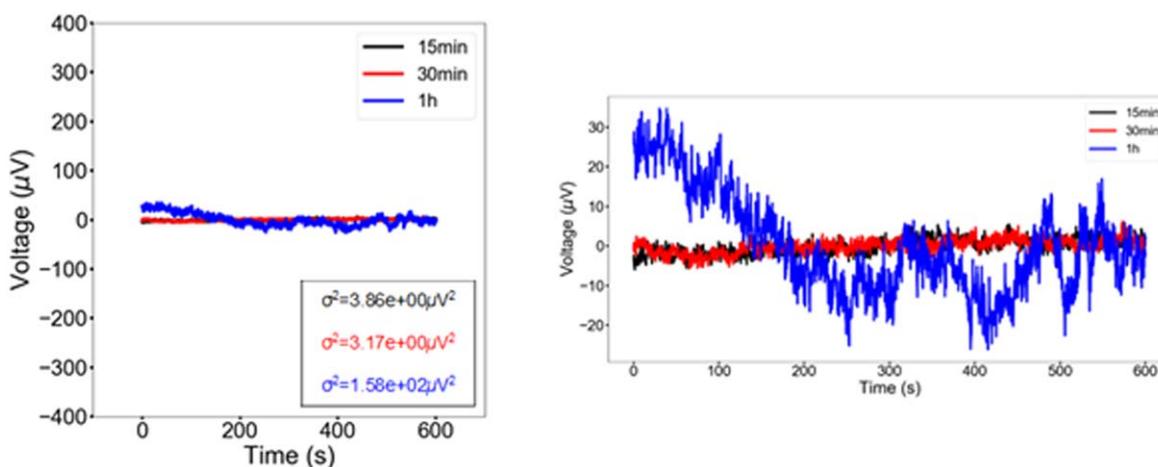


Figure A-3. Noise measurement of CR2032 after 15 min (black), 30 min (red) and 1 h (blue) shorting.

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