



Electrochemical Evaluation of Suspensions of Lithium-Ion Battery Active Materials as an Indicator of Rate Capability

Zhaoxiang Qi and Gary M. Koenig Jr.^{*,z}

Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22904-4741, USA

A variety of physical and electrochemical properties are used to characterize lithium-ion battery active materials, both in the academic literature to understand the fundamental structure-property relationships of materials and in a manufacturing setting to provide quality control during battery material production. One important metric of battery performance is the ability to retain capacity at increasing rates of discharge, or rate capability; however, it can be influenced by a number of factors related to different electrode components and preparations and also requires time consuming cell fabrication and testing. Herein, we describe a relatively fast test that relies on electrochemical evaluation of battery active material particles in a suspension undergoing collisions with a current collector. While this technique does not provide a full rate capability characterization for a material, these results will demonstrate that the measured resistance provides the relative rate capability of the active materials without the potential interference of other composite electrode components.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0681702jes] All rights reserved.



Manuscript submitted October 18, 2016; revised manuscript received November 18, 2016. Published December 15, 2016.

High performance battery active materials are a key enabler in the development and improvement of plug-in hybrid and battery electric vehicles, and lithium-ion (Li-ion) battery chemistry is the predominant battery technology within these applications.^{1,2} Among many physical and electrochemical evaluations conducted on Li-ion electrode active materials as part of material characterization and validation protocols, rate capability is an important metric in applications that require fast charge and/or high power output.^{3,4} Rate capability is the ability of active materials to retain electrochemical capacity at high cycling rates, i.e. high currents.^{5,6} It is highly dependent on the overpotential while discharging the cell, which is especially large at high rates of charge/discharge.^{5,7-9} This overpotential is dependent on many factors at the cell level that are not specific to the active material, including electrode contact to the current collector, pressure applied to the electrode and/or calendaring, connectivity of cell components, homogeneity of electrode slurry, conductive carbon loading, binder integrity, and other factors.¹⁰ For the active material itself, rate capability can be dependent on additional attributes including material stoichiometry, crystal structure, particle size, and crystallinity;^{3,5,6,8,9,11} therefore, there is value in evaluating the electrochemical properties of active materials independent of the influences of other cell components or fabrication practices. Obtaining such material properties is important both from a research perspective to compare the electrochemical properties between candidate materials and from a quality control perspective of validating batch to batch variability between battery active materials in a manufacturing process.

Electrochemical evaluation of active materials is frequently reported in the literature by casting the material into thin film composite electrodes from slurries and then fabricating coin cells to undergo various electrochemical testing.^{3,8,11} Including battery and electrode fabrication steps and charge/discharge cycling at multiple rates, electrochemical measurements such as rate capability on an active material can take weeks.^{3,8,11} While these analyses are time consuming, they are important to quantify the rate capability of an active material and are thus frequently reported in the literature.¹²⁻¹⁷ Another method to compare the rate capability of materials was reported recently by Gaberscek, et al.¹⁸ The authors' extracted the potential of coin cells at the same state of charge at increasing cycling rates and demonstrated a linear relationship between current (per mass) and overpotential.¹⁸ The slope of the regression line (defined as mass electrode resistance, or R_m in the report, units of $\Omega\text{-g}$) is a single parameter that correlates with the rate capability of active materials because it shows the dependence of the overpotential on discharge current for a given

material.¹⁸ While this method is valuable for comparison between materials, especially of the same chemistry, it still requires electrode and cell fabrication. In this report we will demonstrate preliminary results for a simple resistance measurement that correlates to rate capability, much like R_m , but without electrode fabrication or coin cell assembly, resulting in faster material analysis.

An additional challenge in the coin cell electrochemical evaluation described above is that the resistance not only reflects the active material properties but also reflects the resistance from other cell components and the interaction between those components. For example, increasing and decreasing the pressure on a lithium-ion battery electrode results in reversible decreases and increases in the resistance as measured using electrochemical impedance spectroscopy.¹⁰ While such measurements provide insights into the improvements in electrode performance for common manufacturing steps such as electrode calendaring, they also highlight that electrochemical measurements on coin cells reflect more than the active material properties.¹⁰ One way that such a challenge has been addressed in the literature is through electrochemical evaluation of individual lithium-ion battery particles.^{19,20} These measurements provide direct evaluation of the battery active material, however, they require relatively complex fabrication and are specific to the particle under evaluation, meaning that many individual particles would need to be assessed to provide information on the electrochemical properties of an ensemble average over a powder of many particles that will be processed into a composite electrode.

In this paper, we will describe initial results for a method that 1) quickly provides a resistance measurement associated with the electrochemical charge/discharge of a lithium-ion battery material without electrode or coin cell fabrication and 2) provides this measurement that represents an average over an ensemble of many particles randomly distributed from a lithium-ion battery active material powder. This method to evaluate active material particles was adapted from a collision-based dispersion flow battery redox couple previously reported by our group.^{21,22} Within the flow battery redox couple system, battery active material was dispersed in electrolyte and either pumped or stirred to force the active material into collisions with a current collector. There are no conductive carbon additives in this system, and thus only active material in contact with the current collector contributes to the observed electrochemical activity. The measurement process in this report follows similar methodology and requires three steps: 1) disperse the active material in the electrolyte; 2) flow the suspension into the customized cell and take measurements of voltage using sequential constant currents; 3) flow the suspension out. This method is fast and can accommodate multiple measurements performed in succession. Although the measurements do not give full rate capability in terms of the percentage of capacity at different

*Electrochemical Society Member.

^zE-mail: gary.koenig@virginia.edu

rates, they result in a single resistance parameter which we demonstrate correlates to the relative rate capability for the three materials used to demonstrate the proof-of-concept in this report. This fast and simple technique specifically interrogates the active material without other composite electrode components and should enable fast screening and qualification of battery active materials, though validation across many more battery material samples will be needed to fully demonstrate the limits of this technique.

Experimental

Material synthesis and characterization.—The lithium-ion battery active material used to demonstrate the method in this report was the anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). LTO was chosen because it is a well characterized lithium-ion battery anode material with high rate capability, and the rate capability has previously been demonstrated to vary significantly across LTO material produced using different methods.^{9,14} The flat discharge potential of LTO is beneficial for measuring a stable potential when using constant current testing.^{9,14,21,23} Three LTO materials from either different suppliers or synthesized in lab were first characterized in conventional coin cells using existing methods to measure the capacity retention at increased rates of discharge and the mass electrode resistance.^{12–18} Three LTO materials were used in this study, which we refer to as LTO-1, LTO-2, and LTO-3. LTO-1 and LTO-3 were obtained from battery material vendors. LTO-2 material was synthesized following a solid state calcination method previously published in the literature.^{9,24,25} A mixture of anatase titanium oxide (Acros Organics) and lithium hydroxide (Fisher Scientific, 4% excess than stoichiometric amount) was calcined in a Carbolite CWF 1300 box furnace in an air atmosphere by heating at an incremental rate of 3°C min^{-1} up to 800°C and then holding at this temperature for 20 hours before turning off the furnace and allowing cooling down to ambient temperature without control over the cooling rate. To characterize the morphologies of the materials, scanning electron microscope (SEM) images were taken for all three LTO materials with a Quanta 650 SEM (see Supplementary Material, Figure S1). A Panalytical X'pert diffractometer with $\text{Cu K}\alpha$ radiation was used to obtain the X-ray diffraction (XRD) patterns of the materials (see Supplementary Material, Figure S2). Tap densities were measured with a tap density analyzer (Quantachrome Instruments). The focus of this manuscript is demonstrating the electrochemical evaluation of flowing particle dispersions and the correlation of the method to material rate capability, and thus the physical property characterization of the three LTO powders including SEM, XRD, and tap density can be found in the Supplementary Material.

Coin cell fabrication and electrochemical characterization.—Electrochemical characterizations were carried out using CR2032-type coin cells with LTO electrode as the working electrode and lithium foil as the counter and reference electrode, separated by a polypropylene/polyethylene/polypropylene trilayer membrane. LTO electrodes were prepared by first mixing 80 wt% LTO powder with 10 wt% carbon and 10 wt% polyvinylidene difluoride (PVDF) binder, which was dissolved in *N*-methylpyrrolidone (NMP, Sigma-Aldrich). The mixtures were pasted on aluminum foil using a doctor blade. Electrodes were then dried in the oven at 70°C overnight followed by further drying in a vacuum oven at 70°C for three hours. Electrode disks of 1.6 cm^2 were prepared using a punch, and the loading of LTO active material in the electrodes for all samples was $\sim 10\text{ mg}$. The electrolyte used was 1.2 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with EC/EMC = 3:7 by volume ratio (BASF Corporation). The cells were assembled in an argon-filled glove box (with concentrations of both O_2 and $\text{H}_2\text{O} < 1\text{ ppm}$) at room temperature. The galvanostatic charge-discharge tests of coin cells were performed with a Maccor battery cycler. For experimental results where the C rate is given, 1 C was assumed to be 175 mA g^{-1} LTO active material, with the rate scaled

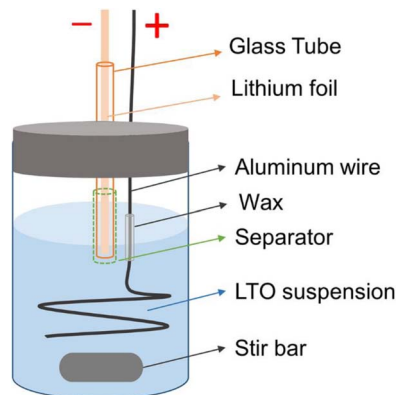


Figure 1. Cartoon illustration of the customized electrochemical cell with aluminum wire as the cathode current collector immersed in an LTO suspension and lithium foil as the anode.

by the amount of active material loaded into each individual electrode. The cycling window for LTO cells was 1.0 to 2.5 V (vs. Li/Li^+).

Active material suspensions electrochemical evaluation.—LTO suspensions were prepared by dispersing the LTO powder in the electrolyte (using agitation provided by a magnetic stir bar at 400 rpm). Three different loadings of LTO suspensions (0.5 vol%, 1 vol% and 2 vol%) were prepared for each LTO material. Loadings were kept low to minimize the formation of larger particle floculates. A customized cell was designed and assembled to characterize the suspensions. As shown in Figure 1, the cathode current collector was an aluminum wire (9.4 cm^2 total surface area immersed in the suspension, Fisher Scientific) surrounded by the LTO suspension, which was agitated by a stir bar. The active surface area of the aluminum wire was controlled by coating wax at the liquid-gas interface, creating an inert surface on the wire even if the interface underwent fluctuations due to the agitation of the suspension. The anode (and reference electrode) was a piece of lithium foil. The cathode and anode were separated by a glass tube and a polypropylene/polyethylene/polypropylene trilayer membrane. The cell was assembled and tested in the argon-filled glove box. All electrochemical tests on this customized device were performed with a Biologic SP-150.

Results and Discussion

Electrochemical testing on conventional cells.—The LTO materials were electrochemically tested in conventional coin cells to determine the rate capability for benchmarking. Both the discharge profiles and the discharge capacities at increasing rates of discharge (cells were cycled between 0.1 C and 10 C) are shown in Figure 2. All three LTO electrodes had flat discharge curves at $\sim 1.5\text{ V}$ at low cycling rates, which is consistent with other reports on LTO materials in the literature.^{9,14–16,26} Discharge capacities for all three LTO materials decreased with increasing rates, which is typical because of increasing overpotential at increasing discharge currents. At each C-rate, the capacity retention (in terms of the percentage of the discharge capacity relative to the capacity at 0.1 C) follows the ranking order of $\text{LTO-1} > \text{LTO-2} > \text{LTO-3}$. This difference became more pronounced as the rate of discharge was increased. LTO-3 lost almost all discharge capacity when cycled at 10 C. However, LTO-1 still maintained $\sim 50\%$ of the capacity at this rate. This test was highly reproducible and the standard deviation of capacity retention for three coin cells of each LTO material was below 1% for most rates tested (see Supplementary Material Table S1 for standard deviation of capacity retentions at different C rates). We do note that while the low-rate capacities (0.1 C) for LTO-1 and LTO-3 were very close ($\sim 165\text{ mAh g}^{-1}$), LTO-2 had a significantly lower capacity ($\sim 148\text{ mAh g}^{-1}$) which we attribute to significant rutile TiO_2 impurity phase in this material (see Supplementary Material). This electrochemical testing was primarily done to establish the baseline order of rate capability between the materials

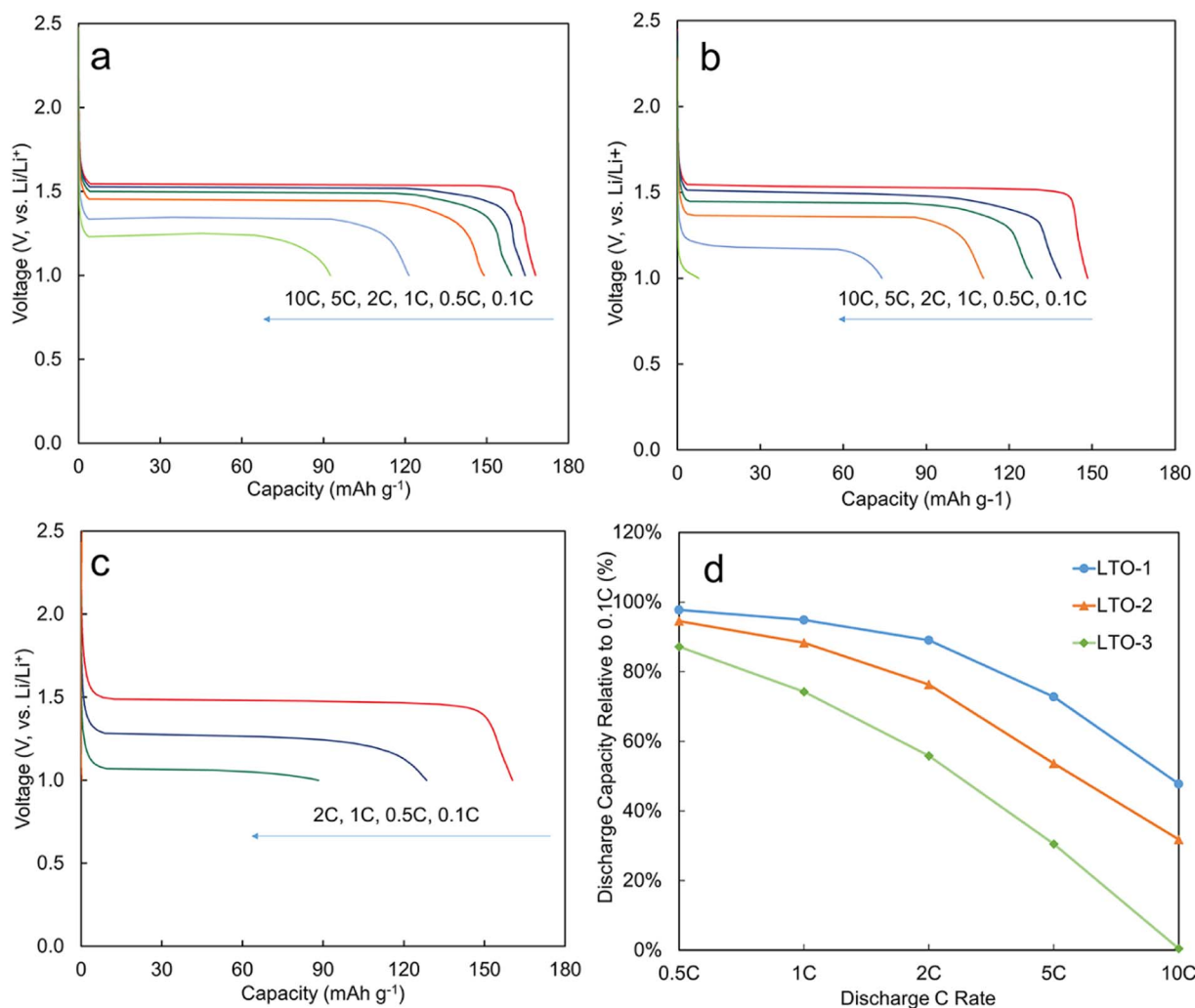


Figure 2. Constant current discharge profiles at increasing C-rates for (a) LTO-1, (b) LTO-2, and (c) LTO-3; (d) discharge capacity of all three materials (blue circles: LTO-1; orange triangles: LTO-2; green diamonds: LTO-3) at different C-rates relative to the capacities at 0.1 C (lines in (d) added to guide the eye).

with LTO-1 having the highest rate capability and LTO-3 having the lowest rate capability.

Using the discharge profiles at various discharge currents in Figures 2a–2c, the potential at 25 mAh g⁻¹ (the same state of charge) was extracted to determine the mass electrode resistance (or R_m , units of Ω -g) using methods previously reported in the literature.¹⁸ The potential as a function of the current (divided by the mass of active materials) displayed a linear relationship, with a representative example shown for LTO-3 in Figure 3. We note that for each current in Figure 3 there are four separate data points representing the potential measured for four successive discharge cycles under the same conditions, but that the high reproducibility of the measured potentials results in difficulty in distinguishing the four individual data points in the figure. A linear fit of data such as that displayed in Figure 3 provides a slope which is the parameter previously referred to as the R_m .¹⁸ We measured the R_m values for LTO-1, 2, and 3 to be 0.693, 0.847, and 2.357 Ω -g, respectively. Increasing values of R_m correlated with decreasing rate capability of the LTO materials, consistent with previous reports on other lithium-ion battery electrode materials.¹⁸ R_m is particularly useful in comparing between materials because it normalizes the effects of material loading on the resistance of the electrode and rate capability.¹⁸ R_m provides a single straightforward parameter that can be used to compare the discharge resistance among different active electrode materials, and because lower resistance results in lower overpotential lower R_m materials have higher rate capabilities as long as everything else regarding the cells has been held equivalent.

Although R_m is a valuable parameter to use that correlates to the rate capability of active materials, it still requires electrode and cell

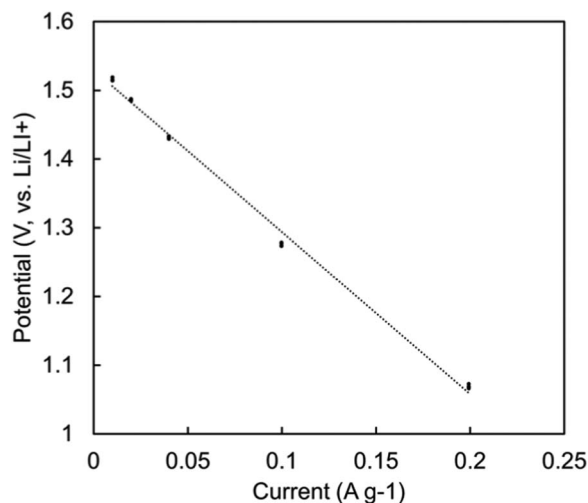


Figure 3. Potential at a capacity of 25 mAh g⁻¹ at increasing current per mass of active material for LTO-3. Black dots are measured data points and the dashed line is the linear fit. The slope of the line is 2.357 Ω -g.

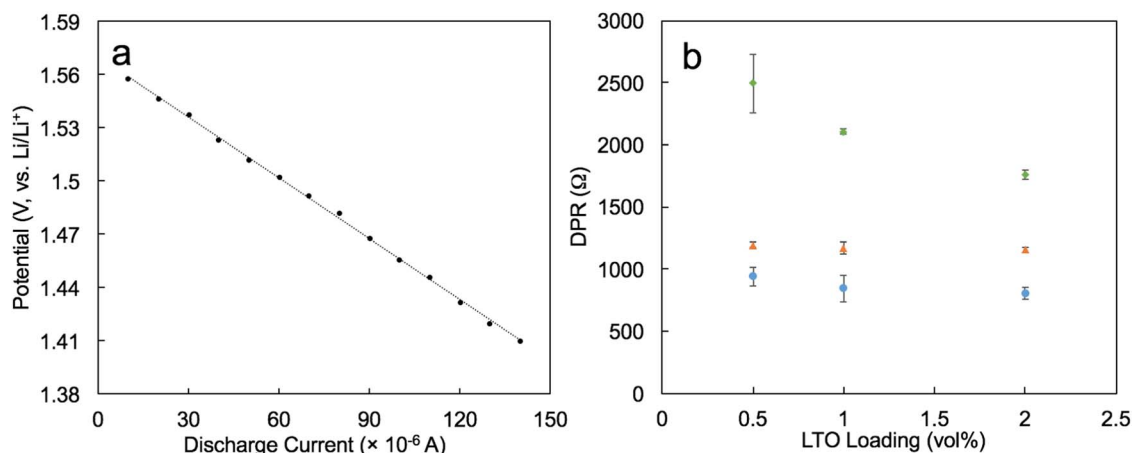


Figure 4. (a) Example of the average potentials after reaching a steady plateau in the measured potential at increasing CP discharge currents for a 2 vol% suspension of LTO-2 dispersed in electrolyte. Dashed line is a line plotted using parameters from a linear regression of the data. (b) The dispersed particle resistance (DPR) values determined from the slopes of all fitted lines for three LTO materials at three different loadings (blue circles: LTO-1; orange triangles: LTO-2; green diamonds: LTO-3; error bars show the standard deviations of a series of three measurements).

fabrication and many charge/discharge cycles at different rates which take significant time. Also, while R_m in many cases is dominated by the resistance of the active material itself, it is also influenced by other factors in the electrode, such as the particle “wiring”.^{10,27} Also, the influence of active material loading is compensated by the mass term in R_m only within a particular range of loading.²⁷ The electrode microstructure still influences the R_m value measured, and thus a method to interrogate the active material without electrode microstructure effects would be desirable. A technique that does not involve electrode fabrication to electrochemically probe the active materials could in principle remove the contributions from electrode microstructure and non-active material components.

LTO Suspension testing and rate capability correlation.—A customized electrochemical cell was designed (shown in Figure 1) to characterize LTO active material suspensions. After dispersing the powder in the electrolyte, a series of chronopotentiometry (CP) tests at systematically increasing discharge currents were performed. An example of a sequence of CP tests can be found in Figure S3, though this example has relatively few current steps compared to most of the measurements discussed below. The potential quickly stabilized after an initial drop in potential due to the capacitance of the electric double layer.^{1,28,29} After reaching a stable plateau, the average potential of the final 20 seconds at a given current was determined. These average potentials have a linear decrease as the discharge current is increased (see Figure 4a as an example for LTO-2 with 2 vol% loading). Data such as that found in Figure 4a was used for a linear fit (dashed line, $R^2 = 0.999$) and the slope was extracted from this fit. We call this slope the dispersed particle resistance (DPR), which has units of Ω . DPR measures the increasing rate of overpotential over increasing current for the particles contacting the electrode in the dispersions. A higher DPR means a faster increase of overpotential while increasing the discharge current, which we hypothesized would indicate a material has a lower rate capability. Importantly, this technique provides a significant measured current from only the active material particles when the particles are actively colliding with the current collector (see Figure S4 in the Supplementary Material for control experiment without LTO particles in electrolyte and Reference 21 for demonstration that our experimental setup only provides electrochemical response when particles are actively agitated and colliding with the current collector). Thus, the DPR technique is probing a resistance that is the sum of many resistances in the system, including the resistance of the active material particles, ohmic resistance from the circuit, and resistance from the electrolyte. The combined value of these later two resistances was consistently found to be between 125 Ω and 140 Ω from the high frequency intercept of electrochemical impedance spec-

troscopy measurements, which was always less than 20% of DPR and can be subtracted from the measured resistance for normalizing between measurements. Thus, DPR was most sensitive to the active material particles and the variability due to electrolyte/cell resistance is low. The primary contribution to DPR is from the active material particles, which consists of resistance due to the particle electronic and ionic conductivity as well as activation resistance. Each of these factors are challenging to measure individually and vary across multiple orders of magnitude with different methods.³⁰ The DPR approach measures the sum of all of these factors and so only when one can be significantly assumed to dominate can an explicit electrochemical parameter be extracted; however, DPR does provide a collective measure that indicates the overall average resistance from an ensemble of the active material particles.

To confirm the relative correlation between DPR and rate capability, we performed DPR measurements on all three LTO materials at 0.5, 1, and 2 vol% LTO loading in electrolyte and the results are shown in Figure 4b. The DPR across all suspension loadings went in the order of LTO-3 > LTO-2 > LTO-1. Notably, this is the same order as the R_m measurements and has the same general trend that a greater DPR value correlates with a lower rate capability of the active material. Figure 4b also shows that DPR decreased as the loading increased for each material. This increase of active material loading results in an increase in the particles in contact with the current collector on average, which increases the effective active material surface area and hence decreases the resistance. A similar effect has been shown previously for conventional coin cells in the literature. Atebamba et al. has shown that both contact resistance and lithium insertion resistance decrease as the mass loading of active materials increases.¹⁰ Gallagher et al. and Dees et al. also have previously demonstrated that the area specific impedance (ASI) of the electrode is lower with thicker electrodes (corresponding to higher active material loading per unit area) below a critical thickness using both experimental analysis and computations.^{31,32} In the DPR system, a higher active material loading in the suspension increases the areal density of particles in the fluid contacting the current collector, which should result in more total active material particles in contact with the current collector and contributing to the electrochemical reactions at any given time. Thus, the total electroactive material area in contact with the current collector is increased, similar to increasing the active material loading or thickness in a conventional coin cell as was the case in the studies mentioned above that measured and predicted decreased resistance under such conditions. These results demonstrated the sensitivity of the DPR technique both to the properties and the amount of electroactive material within the suspension. The DPR measurements and the previous literature discussed above lead us to expect that the

measured DPR will decrease with increased active material loading in the electrolyte, decrease with an increase in the ionic and electronic conductivities of the active material, and increase with an increase in particle size. Detailed measurements with independent verification of each of these parameters being explicitly verified are the subject of ongoing and future experiments.

Discussion.—A major benefit of the DPR method is that the measurement can be made in a convenient way without electrode fabrication, and thus is relatively fast and does not have contributions from other electrode components or the electrode microstructure and connectivity.²¹ Additionally, because the suspension is agitated and there are many different particles that are coming into contact with the electrolyte, the measured resistance is an average of contributions from the ensemble of particles in the powder. Thus the technique is representative of the polydisperse particle population of interest, as opposed to single particles selected from within that population.^{19–22} While more materials need to be tested to more generally affirm the DPR technique limits and reliability, these three materials show that a quick DPR measurement provides insights into the relative rate capabilities of the active materials. Most of the DPR measurements took less than 30 minutes total in sample preparation and CP testing.

While the DPR technique is fast and has the advantages of probing the active material more explicitly than when it is within a composite electrode, the technique still has some limitations that will be the subject of future investigations. One limitation is that the technique is only probing the pristine dispersed particle resistance, and not the resistance at a set of state of charge as was used for R_m measurements. During the course of DPR measurements the total capacity discharged is <0.1% of the discharge capacity of the particles in the system. While this provides confidence that the particles are all in an effectively undischarged state when contacting the current collector, the technique would be challenging to implement after formation cycling on the material or at various states of charge because the current densities are very limited in dispersion redox couple experiments.^{21,22} Another limitation is that this technique would be challenging to interpret when using active materials outside of the electrolyte stability window. The resistance determined when using active materials outside of the electrolyte stability window would be complicated to interpret because the electrochemical current would be a combination of the active material intercalation reactions and electrolyte decomposition.³³ Thus, for some cathode and anode active materials the electrolyte would need to be changed such that stability window of the electrolyte contained the intercalation potential of the active material to be evaluated. Also, we do not have an independent verification of the average mass of active material in contact with the current collector. As can be seen in Figure 4b, as the volume fraction is increased the DPR decreases for all samples. Other methods will need to be developed to independently estimate the mass of active material contacting the current collector and account for this effect. Finally, the measured resistance correlates to the active material rate capability but does not necessarily provide a means to diagnose the root cause of the rate capability differences. Other techniques will be needed in combination to diagnose the material qualities resulting in the measured resistances such as particle size, crystallinity, and other factors.^{6,7,13,15,18,34–37} The R_m method can be used to provide an estimate of the active material conductivity,¹⁸ and the DPR method should provide similar insights if the average mass of particles contacting the current collector can be reliably and independently determined.

Conclusions

Three LTO lithium-ion battery active materials were electrochemically evaluated in particular with regards to rate capability and mass electrode resistance using conventional coin cells. Consistent with previous reports, materials with higher mass electrode resistance had lower rate capability. A new method to quantify the resistance of the active material, dispersed particle resistance, was demonstrated and also has a relationship of lower resistance correlating with increas-

ing rate capability when the material is cycled in battery cells. The dispersed particle resistance measurements were conducted without fabricating electrodes and under conditions with flowing dispersions colliding with a current collector, providing a fast method to electrochemically evaluate ensembles of particles without the time commitments of electrode fabrication, cell fabrication, and rate capability testing. This simple technique demonstrates a platform to quickly provide one parameter to contribute to the electrochemical evaluation of battery active materials.

Acknowledgment

This research was supported by the National Science Foundation through award ECCS-1405134.

References

1. N. Omar, M. Daowd, P. van den Bossche, O. Hegazy, J. Smekens, T. Coosemans, and J. van Mierlo, *Energies*, **5**(8), 2952 (2012).
2. B. Dunn, H. Kamath, and J. M. Tarascon, *Science*, **334**(6058), 928 (2011).
3. T. Liu, L. Zhao, D. Wang, J. Zhu, B. Wang, and C. Guo, *RSC Adv.*, **4**, 9 (2014).
4. S.-H. Kang, W. Lu, K. G. Gallagher, S.-H. Park, and V. G. Pol, *Journal of The Electrochemical Society*, **158**(8), A936 (2011).
5. K. S. Kang, Y. S. Meng, J. Breger, C. P. Grey, and G. Ceder, *Science*, **311**(5763), 977 (2006).
6. M. Kunduraci and G. G. Amatucci, *Electrochim Acta*, **53**(12), 4193 (2008).
7. X. Bai, T. Li, C. Wei, Y.-K. Sun, Y.-X. Qi, H.-L. Zhu, N. Lun, and Y.-J. Bai, *Electrochim Acta*, **155**, 132 (2015).
8. W. Wang, B. Jiang, W. Xiong, Z. Wang, and S. Jiao, *Electrochim Acta*, **114**, 198 (2013).
9. T.-F. Yi, S.-Y. Yang, M. Tao, Y. Xie, Y.-R. Zhu, and R.-S. Zhu, *Electrochim Acta*, **134**, 377 (2014).
10. J.-M. Atebamba, J. Moskon, S. Pejovnik, and M. Gaberscek, *Journal of The Electrochemical Society*, **157**(11), A1218 (2010).
11. J. Liu, K. Song, P. A. van Aken, J. Maier, and Y. Yu, *Nano letters*, **14**(5), 2597 (2014).
12. C. T. Hsieh, Y. F. Chen, C. T. Pai, and C. Y. Mo, *Journal of Power Sources*, **269**, 31 (2014).
13. W. Tang, L. L. Liu, S. Tian, L. Li, Y. B. Yue, Y. P. Wu, S. Y. Guan, and K. Zhu, *Electrochem. Commun.*, **12**(11), 1524 (2010).
14. H. Ge, T. Hao, B. Zhang, L. Chen, L. Cui, and X.-M. Song, *Electrochim Acta*, **211**, 119 (2016).
15. S. Zhao, O. Ka, X. Xian, L. Sun, and J. Wang, *Electrochim Acta*, **206**, 17 (2016).
16. C. F. Lin, X. Y. Fan, Y. L. Xin, F. Q. Cheng, M. O. Lai, H. H. Zhou, and L. Lu, *Nanoscale*, **6**(12), 6651 (2014).
17. Z. Qi and G. M. K. Jr., *ChemistrySelect*, **1**(13), 3992 (2016).
18. M. Gaberscek, R. Dominko, and J. Jamnik, *Electrochem. Commun.*, **9**(12), 2778 (2007).
19. K. Dokko, M. Mohamedi, Y. Fujita, T. Itoh, M. Nishizawa, M. Umeda, and I. Uchida, *Journal of The Electrochemical Society*, **148**(5), A422 (2001).
20. N. Takami, H. Inagaki, T. Kishi, Y. Harada, Y. Fujita, and K. Hoshina, *Journal of The Electrochemical Society*, **156**(2), A128 (2009).
21. Z. Qi and G. M. Koenig, *J. Power Sources*, **323**, 97 (2016).
22. Z. Qi and G. M. K. Jr., *Electrochim. Acta*, submitted, (2016).
23. M. S. Song, A. Benayad, Y. M. Choi, and K. S. Park, *Chem Commun.*, **48**(4), 516 (2012).
24. T. Ohzuku, A. Ueda, and N. Yamamoto, *J. Electrochem. Soc.*, **142**(5), (1995).
25. I. Belharouak, G. M. Koenig, and K. Amine, *J. Power Sources*, **196**(23), 10344 (2011).
26. Z. He, Z. Wang, F. Wu, H. Guo, X. Li, and X. Xiong, *J. Alloy Compd.*, **540**, 39 (2012).
27. M. Gaberscek, *Acta Chim. Slov.*, **61**, 480 (2014).
28. R. Kotz and M. Carlen, *Electrochim Acta*, **45**(15–16), 2483 (2000).
29. C. R. Dennison, Y. Gogotsi, and E. C. Kumbur, *Phys Chem Chem Phys*, **16**(34), 18241 (2014).
30. M. Park, X. Zhang, M. Chung, G. B. Less, and A. M. Sastry, *J. Power Sources*, **195**(24), 7904 (2010).
31. K. G. Gallagher, P. A. Nelson, and D. W. Dees, *Journal of Power Sources*, **196**(4), 2289 (2011).
32. D. Dees, E. Gunen, D. Abraham, A. Jansen, and J. Prakash, *Journal of The Electrochemical Society*, **155**(8), A603 (2008).
33. K. Xu, *Chem. Rev. (Washington, DC, U. S.)*, **114**, 11503 (2014).
34. L. Madec, M. Youssry, M. Cerbelaud, P. Soudan, D. Guyomard, and B. Lestriez, *Journal of The Electrochemical Society*, **161**(5), A693 (2014).
35. J. Li, Y. Zhu, L. Wang, and C. Cao, *ACS applied materials & interfaces*, **6**(21), 18742 (2014).
36. I. D. Scott, Y. S. Jung, A. S. Cavanagh, Y. F. An, A. C. Dillon, S. M. George, and S. H. Lee, *Nano Lett.*, **11**(2), 414 (2011).
37. M. C. Lin, M. Gong, B. Lu, Y. Wu, D. Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B. J. Hwang, and H. Dai, *Nature*, **520** (7547), 325 (2015).