The influence of temperature and charge-discharge rate on open circuit voltage hysteresis of an LFP Li-ion battery

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***Abstract*- Open circuit voltage (OCV) is a crucial parameter in an equivalent circuit model (ECM). The path dependence of OCV is a distinctive characteristic of a Li-ion battery; this is known as OCV hysteresis. In this manuscript the influence of temperature and charge/discharge rate on OCV hysteresis has been identified. OCV hysteresis was found to be 13mV higher at 0°C while remaining unchanged at 45°C compared to the 25°C result. In general, OCV hysteresis was found to be less dependent on charge/discharge rate than temperature. The potential explanations of these results have been reported.**

I. INTRODUCTION

Equivalent circuit models (ECM) are commonly used by a battery management system (BMS) to estimate the power and energy performance of the battery pack in real operating scenarios [1-3]. Open circuit voltage (OCV), the thermodynamic equilibrium potential of a battery, is a key input parameter for an ECM, which is essential from the simplest form of ECM to the very complex form [4]. An accurate measure of OCV is therefore vital for BMS operation.

A common method to measure OCV is to discharge/charge a cell with very low current (e.g. C/25) and record the cell voltage [5-7]. It is assumed that the low current will reduce the diffusion limitation and the cell voltage will represent OCV. In reality, the cell will experience kinetic contributions even at low current, which will be more pronounced at the beginning and end of charge/discharge. To avoid the kinetic contributions in OCV measurement a methodology has been proposed in [8], which employs charging/discharging in steps, and allow intermediate rest steps. The shorter the step size, longer the test duration (due to rest period) and higher the resolution of OCV plot. Therefore, selecting a step size (Δz) is important to balance the test duration and the requirement of OCV plot resolution.

However, the OCV is path dependent, which is known as OCV hysteresis [9, 10]. The presence of OCV hysteresis in different Li-ion battery chemistries has been shown previously [8, 9, 11]. This path dependency implies that the OCV with respect to state-of-charge (SoC) may depend on experimental parameters such as the SoC step size, the charge-discharge rate ($I\_\Delta z$) and temperature (T). In [8] the influence of Δz when evaluating the magnitude of hysteresis is shown to be insignificant. The influence of very high current (10C) at a particular SoC (50%) has been shown previously in [12]. However the influence of a range of nominal operating currents, $I\_\Delta z$, and temperature, T on the magnitude of hysteresis over the entire SoC range is not known.

It was previously shown that inclusion of OCV hysteresis can considerably improve the SoC estimation accuracy of a BMS [8]. Therefore, it is important to know how OCV hysteresis changes with the operating conditions (temperature and current) of an electric vehicle (EV) battery pack. This manuscript presents experimental evidence of the influence of temperature and current amplitude on the magnitude of hysteresis, and provide potential explanations. In Section II, experimental procedures are outlined. Results and analysis of the results are presented in Section III. Finally, Section IV summarises the key findings.

II. EXPERIMENTAL PROCEDURE

Charge-discharge OCV tests were carried out on six commercially available 20 Ah Li-ion cells. The cell has a LiC_6 anode and $LiFePO_4$ (LFP) cathode, with a nominal voltage of 3.2 V and maximum 10 second discharge capability of 15C.

The test procedures are similar to that outlined in [8]. The cells were initially fully charged at 25°C via a constant current constant voltage (CC-CV) procedure, using a 1C constant current for the CC part and 3.6 Volts for the CV part with a charge cut-off current of C/20. Following full charge, the cells were allowed to rest for 4 hours prior to any further testing. To study the effect of temperature on the magnitude of hysteresis the cells were discharged at three different temperatures 0°C, 25°C and 45°C with a 4 % step size and 1C for discharge until the manufacture specified cell minimum voltage (V_{min}) was reached. The test temperatures of 0°C, 25°C and 45°C were selected as being representative of the low, nominal and high operating temperatures of an EV battery pack. After every SoC decrement a 4 hour rest was allowed and the battery terminal voltage was subsequently recorded as the corresponding discharge OCV at that particular SoC. The 4 hour rest period was used to allow the cells to reach electrochemical equilibrium [13], thus the voltage recorded can be considered as OCV. Following the 4 hr rest period upon reaching V_{min}, the cells were charged with 4 % step size and 1C current at the same temperature until the maximum voltage (V_{max}) was reached. Similar to the discharge procedure, after each SoC increment and a 4 hr rest the battery terminal voltage was recorded as the charge OCV at that corresponding SoC. The difference in charge/discharge OCV provides the magnitude of the OCV hysteresis.

To study the effect of charge-discharge rate, the test procedure was repeated at 25°C, with 4 % step size but at two different discharge rates of 0.2C and 3C. These two C rates represent low and high continuous current demand to the EV battery pack.

All the tests were performed within a Weiss Gallenkamp Votsch VC3 4060 environmental chamber to control test temperature. The charge-discharge cycling and data recording was completed using a Bitrode cell cycler (MCV 16-100-5).

III. RESULTS

As mentioned in Section II, OCV hysteresis was calculated as the difference of charge and discharge OCVs. Battery capacity varies with temperature and charge/discharge rates. Therefore, to allow a direct comparison between temperature and charge/discharge rate, capacity values are represented as SoC by considering that the total capacity charged/discharged represents 100 % SoC for that particular temperature and rate.

A. *Temperature Dependency Of Hysteresis*

The OCV hysteresis magnitudes obtained from the tests at different temperatures are shown in Fig. 1. In general, the shape of the hysteresis voltage vs SoC curve is found to be similar irrespective of temperature, except around 70 % SoC. At 25°C and 45°C the OCV hysteresis magnitude is identical within 3 mV maximum variation. However, the hysteresis increases by 13 mV at 0°C almost across the entire SoC range.

The change of OCV hysteresis can be further understood by analysing charge-discharge OCV at different temperatures, which is presented in Fig. 2. The discharge OCV at 25°C and 45°C are identical (except at the beginning of discharge). However, at 0°C OCV is lower over the entire discharge region. On the other hand, the charge OCV is identical at all three temperatures. Therefore, the difference of OCV hysteresis between 0°C and other temperatures is purely from discharge OCV difference.

As explained by Dreyer et al [10] several apparent equilibrium potentials exist in a lithium-ion battery, which causes OCV hysteresis. The interconnectedness of many particles with a non-monotonic chemical potential function as

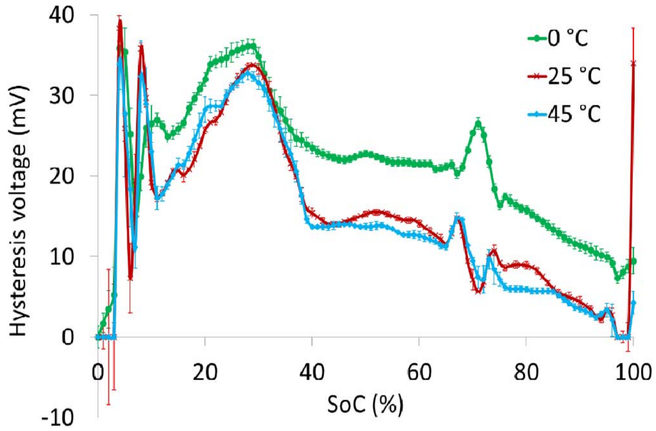

Fig. 1. Change in OCV hysteresis with temperature. Cell to cell variation (from 6 cells) is shown as the error bar.

suggested by *Dreyer et al* are the root cause of the existence of several equilibrium potential. Based on the result presented in this manuscript it can be said that this mechanism as suggested by *Dreyer et al* [10] is affected by low temperature compared to 25°C. More specifically, the process in which one particle distributes lithium ions to neighbouring particles and decreases its chemical potential can be affected at lower temperature after complete discharge. Another interesting observation is near 70 % SoC the hysteresis has a downward hump at 25°C and 45°C, while it is upward at 0°C indicating greater hysteresis at lower temperature. While this phenomenon is interesting, an in depth explanation only can

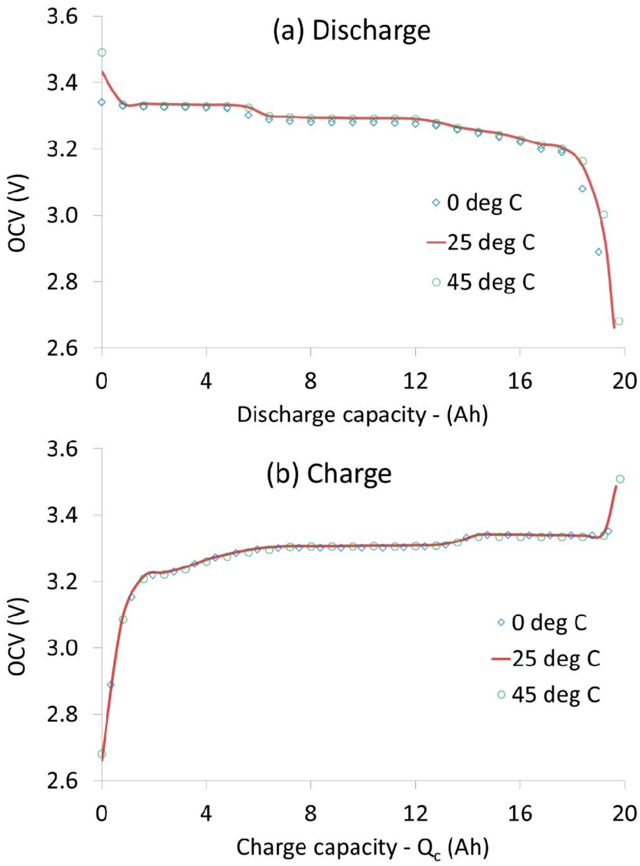

Fig. 2. (a) Charge and (b) discharge OCV of the cell at different temperature.

be provided through further research.

B. Charge-Discharge Rate Dependency Of Hysteresis

The levels of the OCV hysteresis obtained from the tests with different charge/discharge rates are shown in Fig. 3. In general, the hysteresis voltage vs SoC curve remains similar irrespective of rates which exception between 15-30 % SoC and around 70 % SoC. Only a 4mV increase in hysteresis was found with 0.2C between 15-30 % SoC compared to 1C and 3C rates. Similar to temperature dependency, near 70 % SoC the 1C test showed a 10 mV lower hysteresis compared to 3C and 0.2C test. Again, this phenomenon requires further investigation. In general, OCV hysteresis is found to be less dependent on rate than temperature. This result is in contrast to the previously reported results by Roscher et al [12] where it was suggested that OCV hysteresis is rate dependent. However, according to the electrochemical origin of OCV, when cells are allowed to reach electrochemical equilibrium following a charge/discharge event, the OCV will be same irrespective of the charge/discharge rate if allowed to relax significantly. One possible reason why Roscher et al saw the change can be due to the use of the high discharge rate used by Roscher et al (discharged to 50 % SoC from 100 % SoC using 0.5C and 10C). 10C discharge current is commonly considered as very high current which can make reversible and irreversible change within the cell [14, 15], which potentially explains the 8 mV difference of hysteresis found by Roscher et al.

From Fig. 2 it can be seen that the OCV change is small with capacity (and thus SoC), for example from 6 Ah to 12 Ah (from 30 % to 60 % SoC approximately, depending on temperature) the OCV changes by only 7 mV. In the same range OCV hysteresis increases by 13 mV at 0°C compared to 25°C. Therefore, when BMS uses OCV and OCV hysteresis for its functionality (e.g. SoC estimation) it needs to account for change of OCV hysteresis.

IV. CONCLUSION

In this work the hysteresis magnitude of an LFP Li-ion battery is evaluated with regards to temperature and charge-discharge rates. Hysteresis increases by 13mV at 0°C compared to 25°C; however it remains unchanged when temperature is increased from 25°C to 45°C. At 0.2C rate there is a small change (4mV) in hysteresis magnitude between 10-30 % SoC, although for remaining SoC and rates (1C and 3C) this hysteresis magnitude remains mostly unchanged. The inclusion of hysteresis voltage at different temperature and rate as a function of SoC in a BMS will therefore improve OCV estimation accuracy by BMS and thus the performance of BMS.

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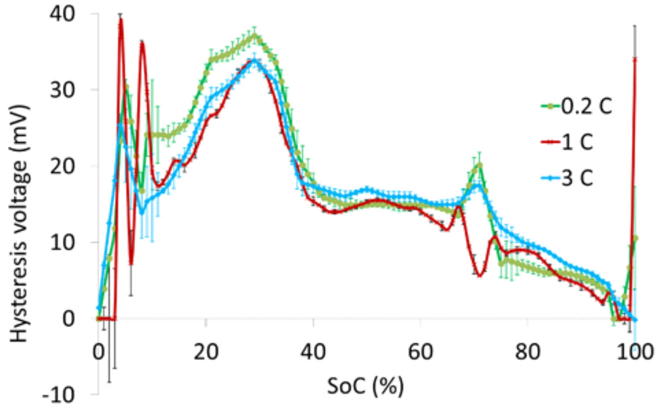

Fig. 3. Change in OCV hysteresis with charge-discharge rate. Cell to cell variation (from 6 cells) is shown as the error bar.

REFERENCES

[1] J. Gomez, R. Nelson, E. E. Kalu, M. H. Weatherspoon, and J. P. Zheng, "Equivalent circuit model parameters of a high-power Li-ion battery: Thermal and state of charge effects," Journal of Power Sources, vol. 196, pp. 4826-4831, 5/15/ 2011.

[2] S. Rodrigues, N. Munichandraiah, and A. K. Shukla, "AC impedance and state-of-charge analysis of a sealed lithium-ion rechargeable battery," Journal of Solid State Electrochemistry, vol. 3, pp. 397-405, 1999/09/01 1999.

[3] V. Sauvant-Moynot, J. Bernard, R. Mingant, A. Delaille, F. Mattera, S. Mailley, et al., "ALIDISSI, a Research Program to Evaluate Electrochemical Impedance Spectroscopy as a SoC and SoH Diagnosis Tool for Li-ion Batteries," Oil Gas Sci. Technol. – Rev. IFP, vol. 65, pp. 79-89, 2010.

[4] H. L. Chan and S. D., "A new battery model for use with battery energy storage systems and electric vehicles power systems," in Power Engineering Society Winter Meeting, 2000. IEEE, 2000, pp. 470-475 vol.1.

[5] G. L. Plett, "Extended Kalman filtering for battery management systems of LiPB-based HEV battery packs: Part 2. Modeling and identification," Journal of Power Sources, vol. 134, pp. 262-276, 8/12/ 2004.

[6] B. Pattipati, B. Balasingam, G. V. Avvari, K. R. Pattipati, and Y. Bar-Shalom, "Open circuit voltage characterization of lithium-ion batteries," Journal of Power Sources, vol. 269, pp. 317-333, 12/10/ 2014.

[7] V. Pop, H. J. Bergveld, J. H. G. Op het Veld, P. P. L. Regtien, D. Danilov, and P. H. L. Notten, "Modeling Battery Behavior for Accurate State-of-Charge Indication," Journal of The Electrochemical Society, vol. 153, pp. A2013-A2022, November 1, 2006 2006.

[8] A. Barai, W. D. Widanage, J. Marco, A. McGordon, and P. Jennings, "A study of the open circuit voltage characterization technique and hysteresis assessment of lithium-ion cells," Journal of Power Sources, vol. 295, pp. 99-107, 11/1/ 2015.

[9] V. Srinivasan and J. Newman, "Existence of Path-Dependence in the LiFePO4 Electrode," Electrochemical and Solid-State Letters, vol. 9, pp. A110-A114, March 1, 2006 2006.

[10] W. Dreyer, J. Jamnik, C. Guhlke, R. Huth, J. Moskon, and M. Gaberscek, "The thermodynamic origin of hysteresis in insertion batteries," Nat Mater, vol. 9, pp. 448-453, 05//print 2010.
[11] T. Huria, G. Ludovici, and G. Lutzemberger, "State of charge estimation of high power lithium iron phosphate cells," Journal of Power Sources, vol. 249, pp. 92-102, 3/1/ 2014.
[12] M. A. Roscher, O. Bohlen, and J. Vetter, "OCV Hysteresis in Li-Ion Batteries including Two-Phase Transition Materials," International Journal of Electrochemistry, vol. 2011, 2011.
[13] A. Barai, G. H. Chouchelamane, Y. Guo, A. McGordon, and P. Jennings, "A study on the impact of lithium-ion cell relaxation on electrochemical impedance spectroscopy," Journal of Power Sources, vol. 280, pp. 74-80, 4/15/ 2015.
[14] M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, et al., "Main aging mechanisms in Li ion batteries," Journal of Power Sources, vol. 146, pp. 90-96, 8/26/ 2005.
[15] D. Aurbach, E. Zinigrad, Y. Cohen, and H. Teller, "A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions," Solid State Ionics, vol. 148, pp. 405-416, 6/2/ 2002.