International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 8 Issue 03 Series. IV || March 2019 || PP 57-64

An Optimized CCCV Protocol for Fast Charging Lithium Ion Batteries

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Abstract: *The aim of this work is to determine the best parameters for constant current, constant voltage (CCCV) to fully charge a lithium ion battery (LIB) in 1 hour. Firstly, LIB cells are tested under different discharge rates following a charge in 3 hours to assess the rate capability. Secondly, a systematic study on the effect on the discharge capacity of the charging current C-rate and on the voltage limit for the constant voltage is carried out. Thirdly, cells are cycled by CCCV charge in 1 hour and 1.5h discharge for 500 cycles. It is found that 1.4C rate and 4.35V voltage limit give the best performances in discharge capacity and cycle life. The cell temperature is monitored during the cycling and found to keep below 40 °C. The capacity loss after 500 cycles is a low 7%. However, when cells are charged again with CCCV in 3 hours and discharged in 1.5 hours, 4% of the capacity is recovered. Such a low capacity loss after 500 cycles suggests that fully charging a lithium ion battery in 1 hour using CCCV is possible by optimized parameters.*
Keywords- *Lithium ion battery, Fast charge, CCCV, temperature, rate capacity.*

Date of Submission: 29-03-2019 Date of acceptance: 09-04-2019

I. INTRODUCTION

Fast charging (FC) of lithium ion batteries (LIB) while insuring long cycle life and excellent safety is one of the most challenging tasks facing the future battery market development [1-5]. FC is in high demand in all LIB application segments, more particularly in electric mobility [5] and in mobile electronics sectors. The driving range of a battery powered electric vehicle (BEV) and the usage time of a portable electronic device (PED) directly relate to the amount of electrical energy stored in the battery system. The latter is the product of the energy density (Wh/kg and Wh/l) times the mass and the volume of the battery system, respectively. The energy density of industrial LIB cells has doubled in ten years until ~2015 to reach ~250 Wh/kg. Since circa 2015 energy density levelled off at ~250-260 Wh/kg and ~700Wh/l mostly due to electrode materials performance limitations in lithium storage capability, operating voltages, cycle life, costs and safety [6].

One possibility to increase the daily driving range of a BEV is by increasing the weight and volume of the battery system. Such an option is not practical due to volume limitation in a mobile system. Another more viable option is FC implementation [7-10]. Ideally, the full recharging time of a BEV (i. e. 100% gain in the state of charge (SOC)) should be similar to the time needed to refill a tank of an internal combustion engine vehicle, which is about 5-10 minutes while insuring a driving range of over 500 km on average. Fully charging a BEV in 5-10 minutes providing 500+ km driving range and ~10 years lifespan is not offered yet. In fact, most of BEV and PED manufacturers recommend charging time in 90-120 minutes at best.

Ultra FC stations in 10-15 min for BEV are claimed by several manufacturers. However, in most cases little is known on the actual SOC gained after charge, on lifespan and on safety [1-4, 11-13]. R&D is in progress to bring to the market efficient FC solutions. Many FC techniques have been proposed such as adaptive charging protocols [6, 11, 16-19], thermal management [1, 3, 12, 20], online monitoring of the source causes of capacity decay [2, 21-23] and thermal runaways including lithium metal plating on the anode surfaces [1, 15]. FC using CCCV and multi-step constant current (MSCC) [2, 12, 17, 24-26], time varying current [2, 26-28], current pulses [9, 29-30] and equivalent circuit modelling [6, 12, 26, 28, 30] have been proposed. Among various FC techniques CCCV and MSCC are the most popular in both BEV and PED. CCCV consists of applying a constant charging current (usually expressed as a C-rate) up to an upper voltage limit V_{lim} followed by applying a constant voltage of V_{lim} till a pre-set capacity or current limit is reached. MSCC is similar to CCCV except it uses several steps of decreasing CC rates. Both CCCV and MSCC work quite well for full charging times above 90 minutes, providing reasonably long life and good safety. However, when the charging time is decreased to 60 minutes and below the

LIB cycle life may be severely affected due to active materials degradation [2, 21-23], temperature rise [1, 3, 12, 14] and lithium metal plating on the anode [1, 15].

Fully charging a BEV and PED in 60 minutes is considered to be an important step towards reducing the charging time. Surprisingly, although CCCV has been used from the inception of LIB there has been no attempt to adapt the CCCV parameters to reduce the charging time from current 90-120 minutes to 60 minutes while keeping long cycle life and good safety.

The CCCV protocol runs in two phases a CC and the CV phase during t_{CC} and t_{CV}, respectively with total charging time to be t_{Ch} =$t_{CC} + t_{CV}$. Both t_{CC} and t_{CV} depend on the CCCV parameters; the constant current C-rate level, the constant voltage limit, V_{lim} and the target gained state of charge, ΔSOC.

In this work we used different C-rate and V_{lim} in order to fully charge LIB cells in 1 hour. For the specific cells used here we found the best performances in terms of capacity and cycle life are achieved with a C-rate of 1.4C and V_{lim} of 4.35V. The cell' temperature during the 500+ cycles achieved did not exceed 40 °C.

II. EXPERIMENTAL

1. LIB cells and conditioning:

Tests are carried out at the ambient temperatures (~27 ±2 °C). Two identical prismatic LIB cells rated 3650 mAh based on the graphite/NMC chemistry are used in this study. Cells were charged and discharged five times using slow rate CCCV with charge current of at 740 mA (~C/5) to V_{lim}=4.4V then CV at 4.4V for 20 minutes followed by a discharge at 740 mA to 2.5 V using a Chen Tech (Taiwan) battery cycler. After completing 5 cycles the discharge capacity stabilized to about 3600 mAh, which is taken here as the cell' nominal capacity.

2. Rate capability profiles/Ragone plots:

Rate capability tests are carried out before FC in order to determine whether cells can sustain high discharge currents. Firstly, cells are charged under CCCV protocol at C/3 rate to 4.4V followed by a discharge at increasing C-rates of C/5, C/2, C, 2C, 2.7C and 3.8C to 2.5V. The discharge capacity Q^{dis} (Ah) and average voltage $< E >$ are then determined. The average discharge voltage $< E >$, the energy density W_d and the power density P_d are computed from the discharge data using Eqs. 1-3:

$$< E > = \frac{\int_0^{Q^{dis}} E(q)dq}{Q^{dis}} \qquad \text{Eq. 1}$$

$$W_d = \frac{Q^{dis} x < E >}{m} \text{ (Wh/kg)} \qquad \text{Eq. 2}$$

, and

$$P_d = \frac{I_d x < E >}{m} \text{ (W/kg)} \qquad \text{Eq. 3}$$

, where $E(q)$ is the discharge profile (V vs. capacity q in Ah), m is the cells' mass (in kg) and I_d the discharge current (A).

3. CCCV 1-hour charging:

Cells are charged with the CCCV protocol in a total time of 1 hour. C-rates of 1.2C, 1.3C and 1.4C and voltage limits V_{lim} of 4.25V, 4.3V, 4.35V and 4.4V are used, respectively. For each C-rate and V_{lim} combination t_{CC} and t_{CV} are recorded. The charge gained during the CC and the CV steps, Q_{CC}^{ch} and Q_{CV}^{ch}, respectively are calculated. Temperature was monitored during all CCCV tests.

4. Cycle capacity

For longer cycling the C-rate and V_{lim} combination which yields the best discharge capacity and lowest capacity fade is selected. After 1h charge the cell is rested for 30 min then cell is discharged at 0.65C-rate (in ~90 min) to 2.5V followed by a 30 min rest time before starting the next cycle. After 500 complete cycles, cells are cycled 10 times with slow CCCV (0.2C-rate to 4.4V) and discharged at ~0.65C rate to 2.5V to assess the irreversible capacity loss.

III. RESULTS AND DISCUSSION

All test data collected on two cells are found highly reproducible. Therefore, only data achieved with one cell are showed here.

1. Rate capability & Ragone plots

Fig. 1a shows voltage-time profiles during the CCCV charge at C/3 rate to V_{lim} =4.4V and during discharge under different C-rates and Fig. 1b displays the voltage-capacity profiles during discharge at different C-rates. The discharge data including the average discharge voltage $< E >$, the discharge capacity Q^{dis}, the power density P_d and energy density W_d for each C-rate are summarized in Table 1. The corresponding Ragone plot is displayed in Fig. 2.

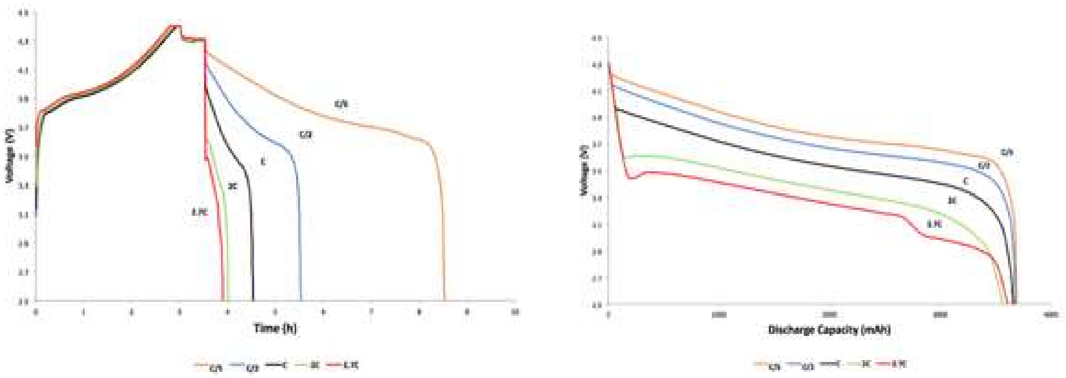

Fig. 1: a) Voltage vs. time profiles during CCCV charge in 3 hours and discharge at different C-rates, b) Voltage vs. discharge capacity profiles at different C-rates

C-rate	C/5	C/2	C	2C	2.7C
$< E > (V)$ % of max	3.8 100	3.7 97.3	3.6 94.7	3.4 89.5	3.3 86.8
Q^{dis} (mAh) % of max	3694 100	3676 99.5	3657 99	3569 96.6	3611 97.7
P_d (W/kg) % of max	51.2 11.6	124.7 20.9	239.1 40.4	452.7 76.5	591.8 100
W_d (Wh/kg) % of max	255.3 100	247.7 97.0	236.3 92.6	218.3 85.5	213.7 83.7

Table 1: Cell performance during discharge at different C-rates

Noteworthy is the excellent performance of the LIB cell in term of energy density, W_d at all discharge rates. As shown in Table 1 starting from ~255 Wh/kg at C/5 rate W_d dropped by ~16% to ~214 Wh/kg at 2.7C rate. Concomitantly, the power density P_d increased ~11.5-time from 51.2 W/kg at C5/ rate to 592 W/kg at 2.7C rate. In fact, the average cell polarization, which is the difference between $< E >$ at C/5 rate and 2.7C rate is as low as 13.2% (100-86.6 % in Table 1). However, when discharged at 3.8C rate after 3h charge the cell's temperature raised above 55 °C and test stopped because of safety limit. The prismatic cells used in this study are designed as high-energy cells. Therefore, they may not able to sustain too high discharge rates. Moreover, the heat dissipation in prismatic cells is less effective than in cylindrical cells, which we used in a previous rate capability study [31].

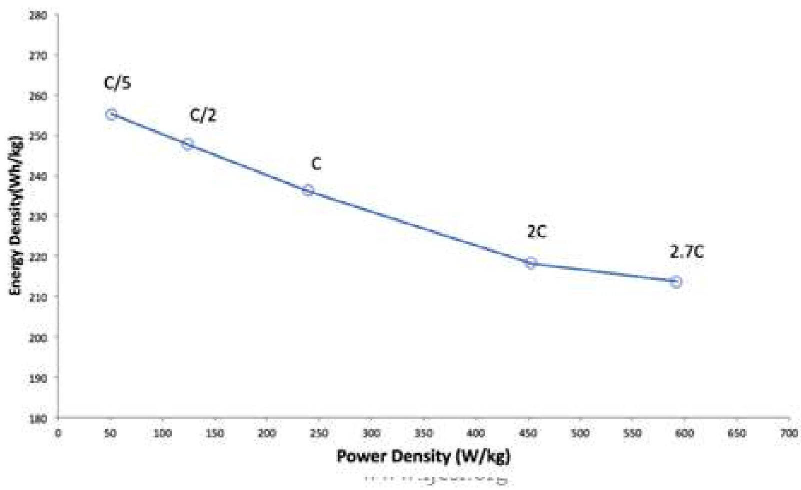

Fig.2: Ragone plot achieved at different discharge C-rate

2. CCCV fast charging

Typical CCCV charge and CC discharge profile is showed in Fig. 3. It illustrates the current and voltage profile during CCCV 1-hour charging followed with 30 minutes rest and a 90 min discharge (C/1.5 rate). Figs 4-a, -b and -c show the charge profiles at 1.2 C, 1.3C and 1.4C rates, respectively with voltage limits of 4.25V, 4.3V. 4.35V and 4.4V, keeping the total charging time t_{Ch} = 60 minutes for all the tests.

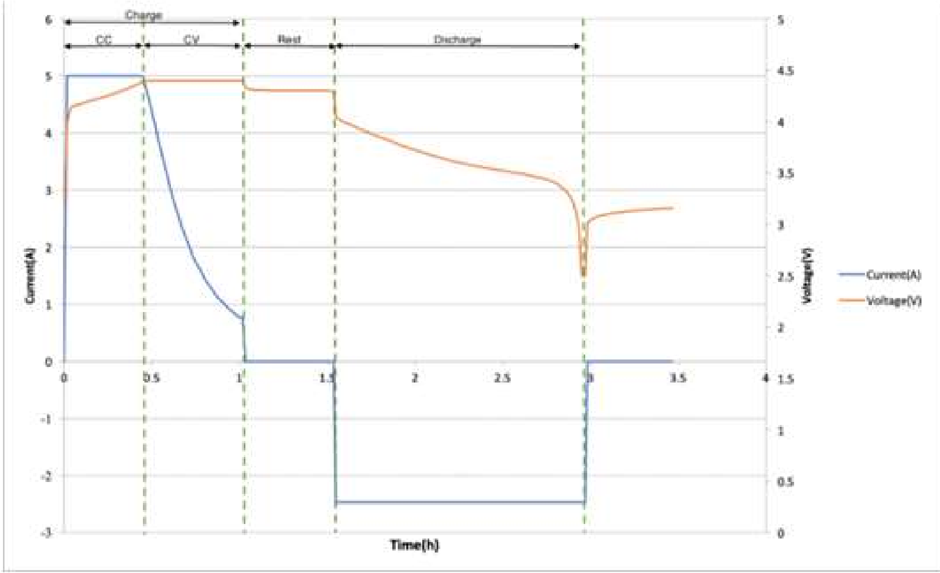

Fig. 3: Typical current and voltage profiles during CCCV charge in 1 hour and discharge in 90 min (30 min rest is applied after each charge and discharge step)

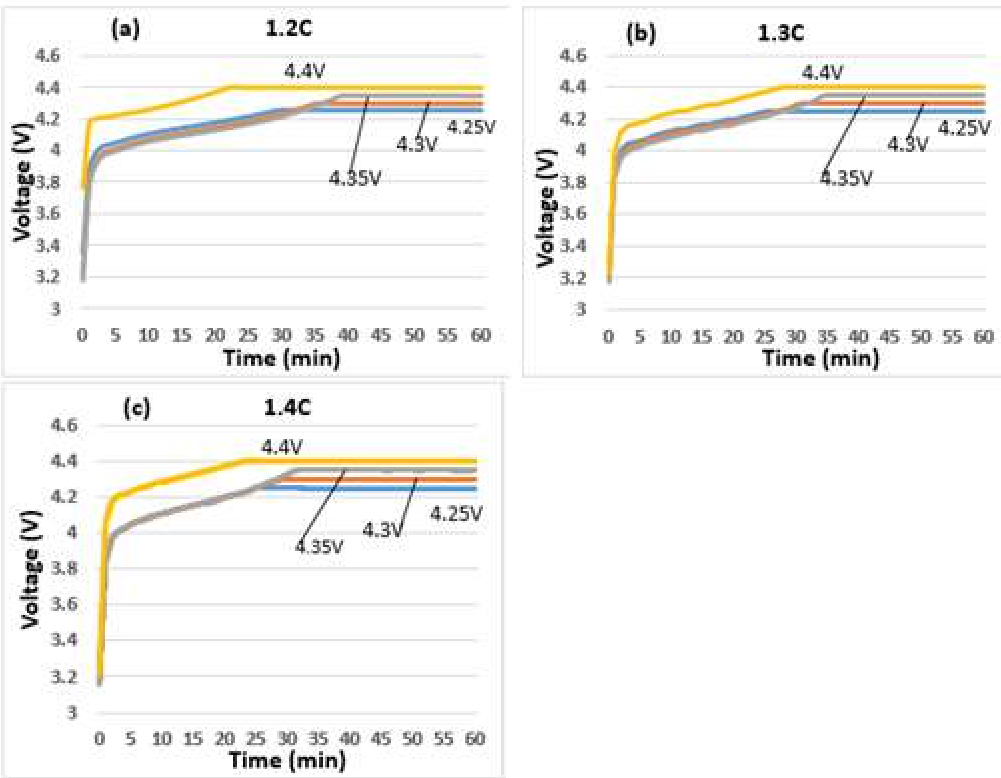

Fig. 4: 1-hour CCCV charge profiles with V_{lim} = 4.25V, 4.30V, 4.35V and 4.4V with different CC rates of a) 1.2C,

b) 1.3C and, c) 1.4C.

Note that when 4.4V is used as the V_{lim} the cell polarization is much higher at any C-rate. Higher cell polarization generates more heat and promote electrode and electrolyte materials degradation. Therefore, V_{lim} values lower than 4.4V should be used for long cycle life tests.

Table 2 details the CCCV charge and CC discharge data, including CC and CV duration and associated capacity in absolute and relative (ΔSOC) values together with the total charge and discharge capacity. Fig. 5 is a 3D plot showing the effects of C-rate and V_{lim} on the discharge capacity (%). The maximum capacity is reached at 4.4V for 1.2C-rate and at 4.35V for 1.3C and 1.4C rates. Noteworthy is the CC contribution to the total charge capacity is maximum at 4.35V for all C-rates.

C-Rate			1.2				1.3				1.4			
V_{lim} of CV (V)			4.25	4.3	4.35	4.4	4.25	4.3	4.35	4.4	4.25	4.3	4.35	4.4
Charge	CC	t_{cc} (min)	30	35	39	22	26	31	35	28	25	29	32	24
		Q_{cc}^{ch} (mAh)	2118	2472	2754	1550	1989	2372	2678	2137	2060	2389	2635	1972
		% of nominal	66.2	73.1	78.1	55.4	61.1	69.3	74.9	61.2	62.1	68.8	73.1	56.0
	CV	t_{cv} (min)	30	25	21	38	34	29	25	32	35	31	28	36
		Q_{cv}^{ch} (mAh)	1083	908	773	1249	1265	1049	899	1355	1259	1082	971	1552
		% of $Q_{□}^{ch}$	33.8	26.9	21.9	44.6	38.9	30.7	25.1	38.8	37.9	31.2	26.9	44.0
	Total	$Q_{□}^{ch}$ (mAh)	3201	3380	3527	2799	3254	3421	3577	3492	3319	3471	3606	3524
		% of nominal	88.8	93.7	97.8	77.6	90.2	94.9	99.2	96.8	92.0	96.3	100.0	97.7
Discharge	$Q_{□}^{dis}$(mAh)		3215	3379	3523	3661	3252	3421	3572	3493	3316	3467	3600	3526
	% of nominal		87.8	92.3	96.2	100.0	88.8	93.4	97.6	95.4	90.6	94.7	98.3	96.3

Table 2: Charge and discharge performance during 1-hour CCCV charge and 0.6C-rate discharge

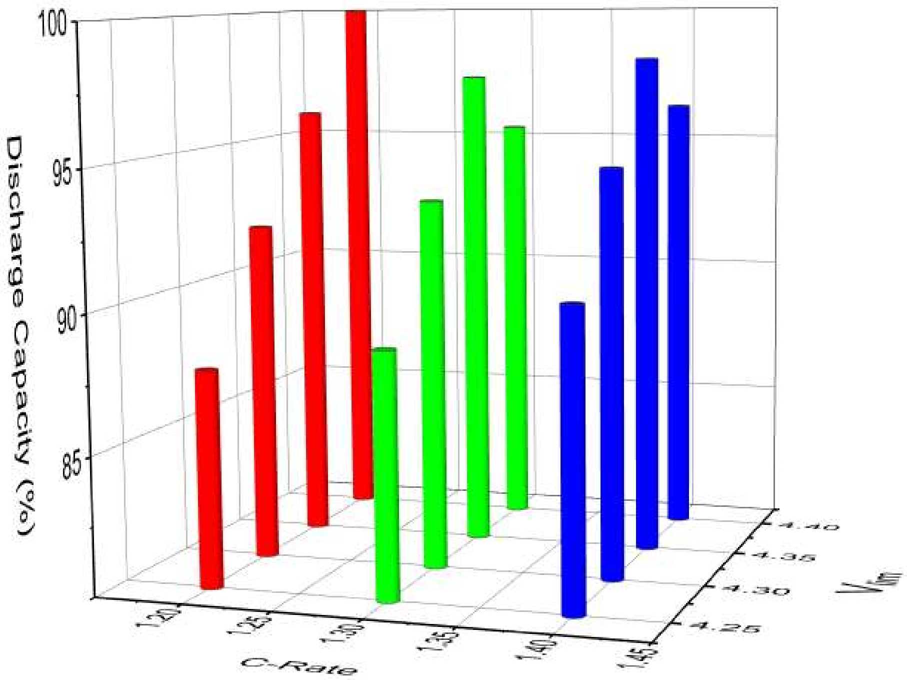

Fig. 5: 3D plot of {C-rate, V_{lim}, discharge capacity (%)} during 1h CCCV charging.

3. Cycle capacity

Our preliminary cycle life tests show that when 4.4V was used as the V_{lim} the capacity fading rate during cycling was high as compared to when 4.35V is used. This finding is in good agreement with our earlier studies on the effect of V_{lim} on the cell's performance degradation rate [32]. Accordingly, we selected 1.4C-rate and V_{lim} =4.35 V for the long cycle test because it provides a good trade-off between high capacity (98.3% as in Table 2) and lower cell' polarization for longer life.

The cycle capacity profile is displayed in Fig. 6. After 500 complete cycles, the capacity dropped by about 7%. This is followed with a few slow rate CCCV cycles (0.2C, 4.4V) which show over 97% initial capacity is recovered. Accordingly, our optimized CCCV conditions for 1h-charging allowed irreversible capacity loss below 3% to be achieved after 500 cycles This suggests no significant lithium plating and electrode and electrolyte degradation has occurred during the 1h CCCV charging and ~1.5h discharging for over 500 cycles.

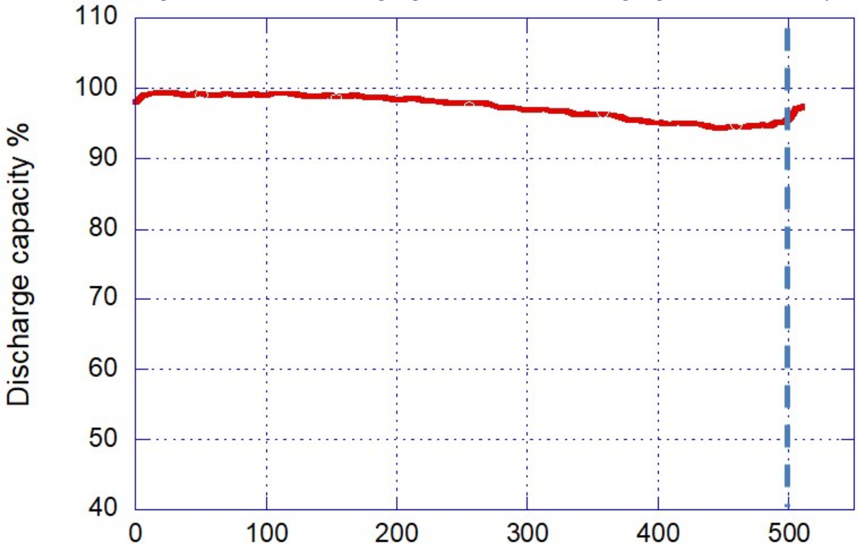

Fig. 6: Discharge capacity vs. cycle # profile during CCCV charge in 1h for the first 500 cycles and during CCCV in 5h for cycles # 501 to 510. Note the capacity recovery during slow CCCV charge after 500 cycles

4. Temperature profile

Cells temperature is recorded during the 500 cycles as described above. Figs 7 a-c show the temperature and the current profiles during cycles # 1, 250 and 500, respectively. It is interesting to notice that during the CCCV charging, temperature increases during the CC phase then it decreased during the CV and rest phases. A maximum temperature of 38 °C is reached at the end of the CC phase during cycle # 250. However, for whole 500 cycles test temperature never exceeded 40 °C. During 0.6C rate discharge temperature increased without exceeding 35 °C then it decreased again in the 25-30 °C range during the rest phase. The temperature profile during the CCCV charge suggests the cell heats mostly due to the Joule effect, which is proportional to I_{Ch}^2. Because the charge in the 25-30 °C range during the rest phase. The temperature profile during the CCCV charge suggests the cell heats mostly due to the Joule effect, which is proportional to I_{Ch}^2. Because the charge current I_{Ch} sharply decreases during the CV step so does temperature as the Joule effect is lower. Another interesting feature is the fundamentally different temperature profile during 1.4 C-rate CC charge and 0.6 CC-rate discharge. During the CC charge temperature increased monotonously with negative curvature ($\frac{\partial^2 T}{\partial^2 t}$, T=temperature, t=time), whereas the curvature during discharge changes sign about half-way discharge to be negative in the first half and positive in the second one. The fact that the cell temperature kept below 40 °C should be behind its excellent cycle capacity performance of the cell. Higher temperatures may have accelerated the electrode and electrolyte materials degradation leading to discharge capacity and voltage fading [1,14, 22].

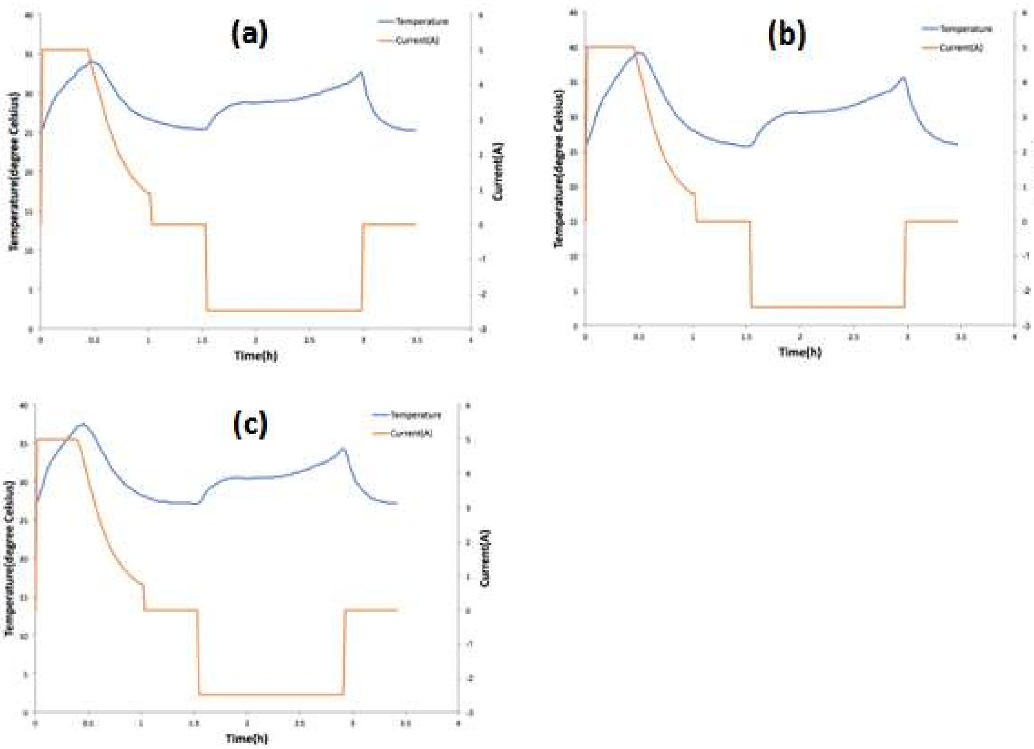

Fig. 7: Current and temperature profiles during CCCV charge in 1h and discharge in 90 min at cycles # 1 (a), 250, (b) and 500 (c).

IV. CONCLUSION

CCCV protocol with controlled charging time of 1h has been achieved by optimized C-rate and voltage limit, V_{lim}, values during the CC and CV steps, respectively. In the specific case of our cells based on the graphite/NMC chemistry, the best combination is achieved at 1.4C-rate and 4.35V CV. After 500 complete cycles 7% and 3% of the initial capacity is lost after 1h and 5h CCCV charge, respectively and 0.6C discharge. Fully charging a LIB cell is 1h while keeping high cycle capacity of 500 cycles is a significant leap in reducing the charging time from the BEV and PED manufacturers best recommended time of 90-120 minutes. Such a significant achievement is allowed because the high quality of the cells tested here, as demonstrated by rate capacity test together with a low temperature increase during the 1h CCCV charge.

Our ongoing tests performed on different origin LIB cells show that the optimized combination of C-rate and V_{lim} for full charge in 1 hour is cell's chemistry and design dependent. In order to implement the 1h CCCV charging it is suggested to adapt the best C-rate and V_{lim} combination first to achieve the highest discharge capacity with lowest V_{lim}. It is also suggested to check whether the cell sustain high discharge rates while keeping temperature below 50 °C. Adapted CCCV conditions are specific to the cell chemistry and design and perhaps to the electrode capacity balance in the cell.

FC tests should be carried out to determine whether the charging time under CCCV can be reduced below 1h to meet the US-DOE 2020 target of 80% ΔSOC gained in 15 min [33].

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Rachid Yazami" An Optimized CCCV Protocol for Fast Charging Lithium Ion Batteries"International Journal of Engineering Science Invention (IJESI), Vol. 08, No. 03, 2019, PP 57-64