

Comparison of Characteristic for Lithium-ion Batteries

W Wiputgasemsuk^{1,*}, W Kobsiriphat², P Karin¹ and S Tsushima³

¹ International College, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

² National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand

³ Department of Mechanical and Control Engineering, Tokyo Institute of Technology, Tokyo 152-8550, Japan

*Corresponding Author: Email: Terng34@hotmail.com, Tel: +66-85-143-9193

Abstract

In this study, the behavior of lithium-ion batteries with four cathode chemistries was studied for battery electric vehicle (BEV) application. Individual cell properties such as energy density, power density and heating behavior of commercial cylindrical cell with LiMn_2O_4 , LiCoO_2 , $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ and LiFePO_4 cathodes were compared. The characterization test was adapted from enhance test methodology to be fit with the BEV application. The test results show the energy density varied from 90-235 Wh/kg, while power density was between 650 and 1200 W/kg. Cell temperature increase varied from 7 to 40 °C. Test results indicated that the individual cell behavior is strongly related to the cathode material properties. Finally, the cell performances were discussed and compared with the requirements for battery electric vehicle.

Keywords: Lithium-ion Battery, Electric Vehicle, Characterization, Electrochemical

1. Introduction

Due to the recent intense efforts to reduce CO_2 emission and dependency on fossil fuels, the use of electric vehicles (EV) like plug-in hybrid (PHEV) or battery electric vehicles (BEV) is increasing. By 2020, it is expected that more than half of new vehicle sales will likely be EV. The key and enabling technology to this revolutionary change is battery [1]. Lithium-ion batteries are considered to be the key technology for the mass market of BEV over the next decade. The performance of lithium-ion batteries depend on the material properties of the various battery components. Lithium-ion batteries generally comprise of a positive electrode (cathode),

electrolyte and a negative electrode (anode). The cathode material is usually the most expensive with highest weight in the battery, which justifies the intense research focus on this electrode [2]. Many research and development studies on cathode material with varying compositions and microstructures have been reported [3-5]. Meng [2] reviewed the recent research progress of different cathode material in terms of structural category and modification of morphology. Mulder [6] evaluated the behavior of lithium-ion cells of several chemistries for automotive application like PHEV and BEV.

In this work, the commercial cylindrical cells with four cathode chemistries were evaluated for

BEV application. Cell chemistry was selected based on those currently used in electric vehicles [7]: lithium manganese oxide (LMO), lithium cobalt oxide (LCO), Lithium nickel cobalt aluminium oxide (NCA) and lithium iron phosphate (LFP). The characterization tests were adapted from the enhanced test methodology [8] to fit with the BEV application.

2. Experimental

The properties of the commercial cylindrical cell with different cathode chemistries are given in Table.1. Two samples per chemistry were tested with a MACCOR 4000 battery testing unit. Thermocouples were attached on the cell surfaces to measure the cell temperature. The tests were thermally controlled at 32 ± 1 °C. The characterization methods consist of four techniques as described in the following:

2.1 Pre-Conditioning Test

This test verifies whether the capacity of a new cell is stable. It consists of a series of 0.33 C charge and discharge rate according to manufacturers. Charge and discharge conditions are given in Table. 1. The cell is considered to be pre-conditioned when the change in capacity between two consecutive discharges is $\leq 3\%$. The capacity of the last discharge is considered 1C capacity for the subsequent tests.

Table. 1 Battery specification.

Manufacturer Information				Test Condition			
Cathode Chemistry	Rated Capacity (AH)	Max charging C rate (C)	Max discharging C rate (C)	Measured Capacity (Ah)	Charge Voltage (V)	Charge Current Cutoff (C)	Discharge Voltage Cutoff (V)
LiCoO ₂	2.4	0.3	-	2.44	4.2	0.02	2.7
LiMn ₂ O ₄	1.6	2.8	10	1.02	4.2	0.02	2.7
LiNiCoAlO ₂	3.1	0.3	-	2.95	4.2	0.02	2.7
LiFePO ₄	2.3	4	30	2.17	3.6	0.02	2.2

2.2 Capacity Test

The test gives information on the effect of discharge rate on battery performance. Tests were performed at three discharge rates, 0.33 C, 1 C, and 2 C and a single charge rate of 0.33 C was used. Rest time between charge and discharge process is one hour. After the discharge process, the cell was allowed to rest until the cell temperature reached ambient temperature before the next test was started.

2.3 Internal Resistance Measurement

In this work, the internal resistance was determined by intermittent discharge current in 10-s durations. The measurement was performed at eight state-of-charge (SOC) levels: 100%, 90%, 80%, 65%, 50%, 35%, 20% and 10%. After the battery was fully charged, it was then discharged to the desired SOC. The resistance was determined by dividing the voltage drop during intermittent discharge by the discharge current.

2.4 Power test

In order to characterize the power capabilities of the batteries, a charge/discharge pulse train was performed on each cell. It consisted of a series of four charge and discharge pulses that are executed at five SOC levels: 80%, 65%, 50%, 35%, and 20%, as shown in Fig. 1. The power capability was calculated according to PNGV HPPC method [9] using the following Eqs. (1)-(2).

$$\text{Discharge power capability} = V_{\min} \cdot I_{\max} \quad (1)$$

$$I_{\max} = (V_{\text{ocv}} - V_{\min}) / R_{\text{discharge}} \quad (2)$$

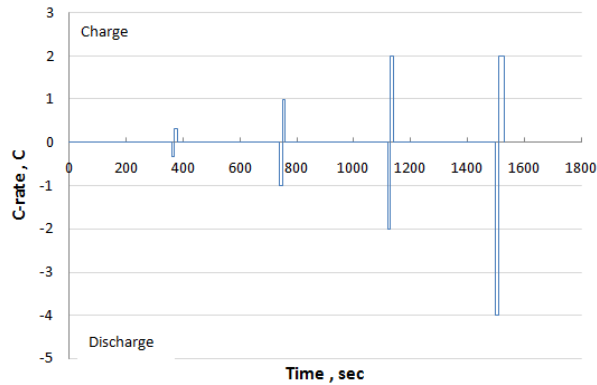


Fig. 1 Pulse train consisting of 4 pulses.

3. Result

3.1 Pre-conditioning Test

The discharge capacity from the last cycle of the pre-conditioning test for each cell is shown in Table. 1. Cell capacity ranges between 1 and 3 Ah. Most cells have a capacity difference from the value declared by the manufacturer of around 2 -

6%, except LMO cells have a large difference of approximately 37%. This may be due to the long storage time prior to being shipped. The storage time affects capacity of lithium-ion cells, especially those with LMO cathode, where the dissolution of manganese in electrolyte can cause capacity loss [10].

3.2 Capacity Test

Figure 2 shows the discharge profile of the cells at discharge rates of 0.33 C, 1 C and 2 C. The capacity decreased with higher discharge rate. At 1 C, all chemistry have capacity drop less than 0.5%. At 2 C, capacity drop around 1.5-2%, with the exception of LFP, where the capacity drop was <0.5%. Goodenough [11] indicated that at a high discharge or charge rate, the capacity is limited by the diffusion of Li insertion into the electrode. This capacity loss is recovered when discharge rate is decrease.

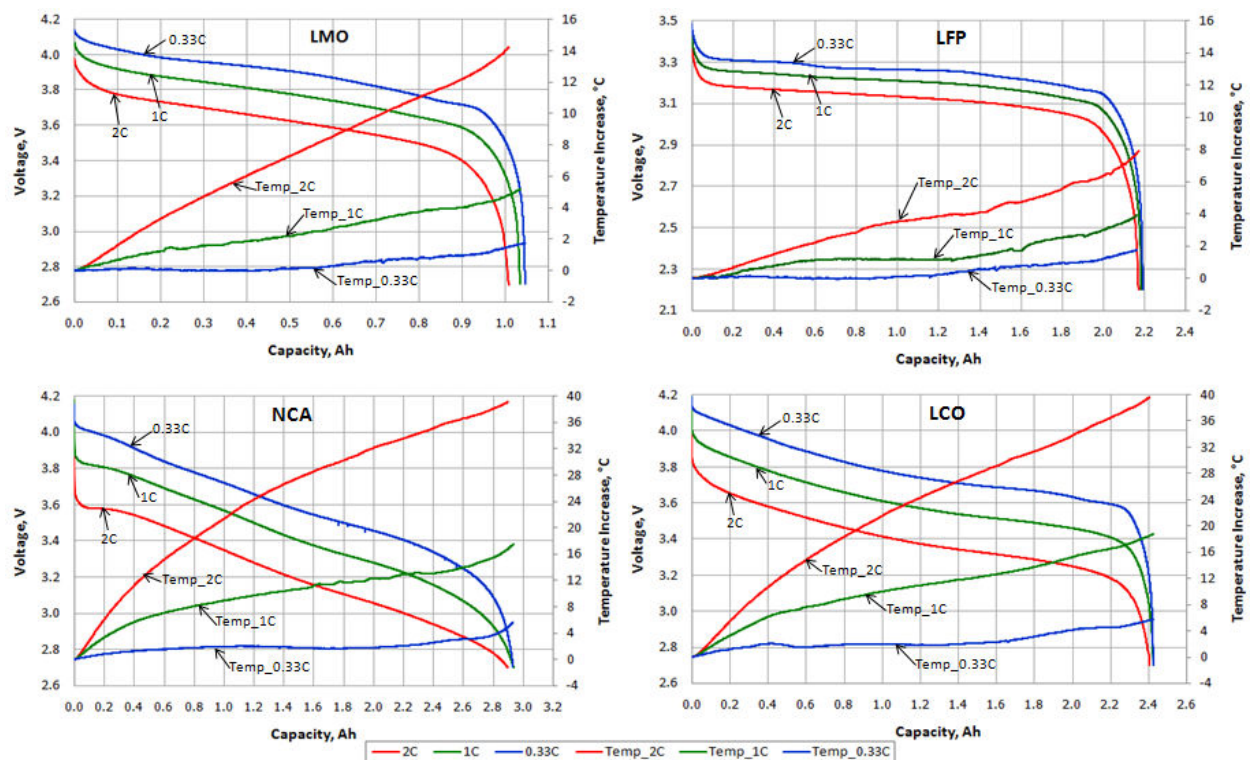


Fig. 2 Discharge profile at different discharge rate.

3.3 Cell Voltage Profile

A comparison of discharge voltage profile of cells with different cathode chemistries is shown in Fig. 2. LMO-cathode cells show small linear slope and offer the highest average voltage, 3.86 V. LFP cells gave the lowest average voltage, 3.23 V, and show a small, nearly flat curve. A flat output voltage is reported to be characteristic of the two phase reaction between LiFePO_4 and FePO_4 [11]. LCO and NCA cells yield intermediate average voltage, 3.76 V and 3.58 V, respectively, and show higher linear slope when compared to LFP and LMO cells. The percent of cell voltage drop between 0.33 C and 2 C are around 10% for NCA and LCO, 7% for LMO and 4% for LFP.

3.4 Energy density and efficiency

Energy density is the product of voltage and capacity per unit weight. Energy density and efficiency at different discharge rates are shown in Fig. 3. At 0.33 C, NCA cells have the highest energy density of 235 Wh/kg and efficiency, 94%. LFP cells have an energy density of 96 Wh/kg and the highest efficiency, 98%. LMO cells have an energy density and efficiency comparable to LFP cells. Energy density and efficiency decreased when discharge rate was increased. The energy density and efficiency decrease between 0.33 C and 2 C for NCA and LCO cells were around 11% while for LMO and LFP cells, the decrease were around 9% and 5%, respectively. The percentage decrease in energy density and efficiency correspond with the cell voltage drop as stated in the previous section. The energy density of each cathode is consistent with its specific capacity and cell voltage as shown in Table. 2 [12]. The combination of high specific capacity and high cell voltage of NCA

cells resulted in superior energy density compared to cells with other cathode chemistries. Low specific capacity of LMO cells and low voltage of LFP cells resulted in their lower energy density.

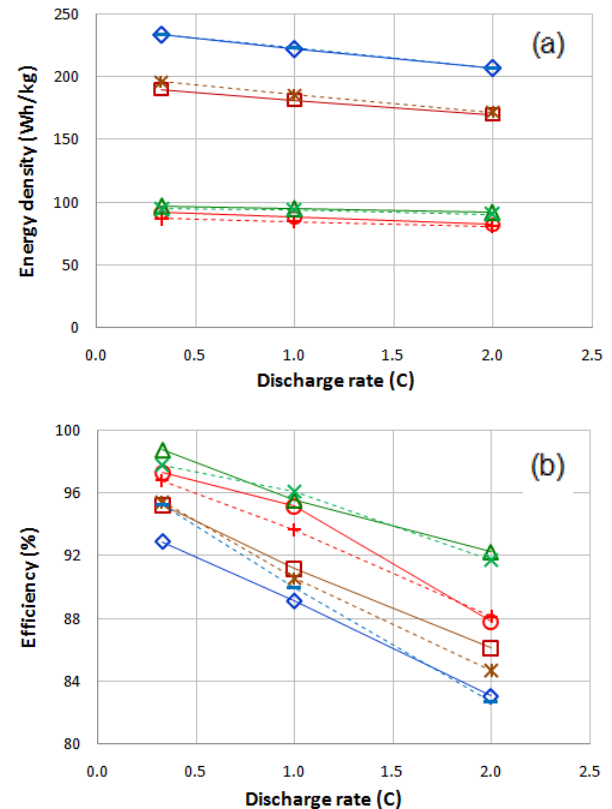


Fig. 3(a) Energy density and (b) efficiency at different discharge rate.

Table. 2 Characteristic of some positive electrode material [12].

Material	Specific capacity mAh/g	Midpoint V vs. Li at C/20
LiCoO_2 (LCO)	155	3.9
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)	140-180	3.73
LiMn_2O_4 (LMO)	100-120	4.05
LiFePO_4 (LFP)	160	3.45

3.5 Power Test

The power capability of the batteries at different SOC is shown in Fig. 4. LFP cells

showed the highest power density, up to 1340 W/kg (50% SOC), compared to 900 W/kg for LMO and $\cong 970$ W/kg for LCO and NCA cells. The decrease in power density of NCA cells occurred at a higher rate than that found in others. At 20% SOC, power density of NCA drop rapidly to 660 W/kg. Fig. 5 shows the Ragone plot of the energy density and the power density. It is clear that LFP cells have the highest power density by 42% compared to that with the lowest (NCA). NCA have the highest energy density by 60% compared to that with the lowest (LMO). The maximum C-rate corresponding to the power density is included in Fig. 5.

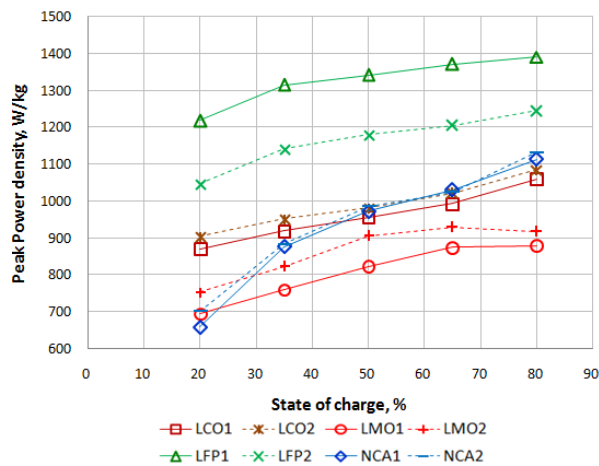


Fig. 4 Power density as function of SOC.

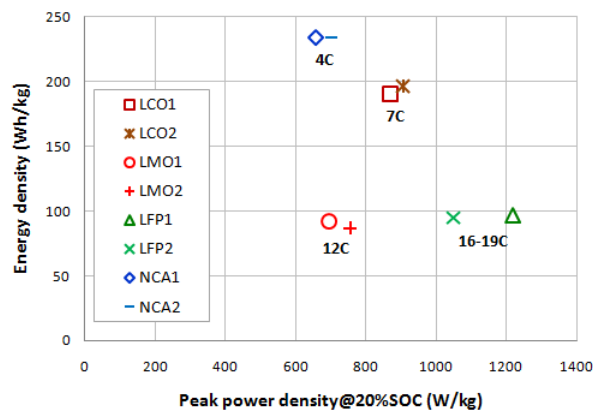


Fig. 5 Ragone plot of the energy density and the power density.

3.6 Temperature Increase and Resistance

The temperature increase at different discharge rates is shown in Fig. 2. At 0.33 C, the temperature increase of LFP and LMO cells is around 2 °C. For NCR and LCO cells, this value was 6-8 °C. At 2 C, NCR and LCO cells reached a temperature increase of 39 °C, while temperature increase of LMO and LFP cells is around 8 and 14 °C respectively.

The temperature increase in batteries results from heat generation, which is mainly caused by two factors: (1) the overpotential resistance and (2) the electrochemical reaction heat [13]. The overpotential resistance includes ohmic, activation and diffusion polarization resistance. Heat from electrochemical reaction corresponds to thermodynamic properties (entropy change) of the cathode and anode materials. The electrochemical reaction heat has been reported as only a small contribution to total heat generation and decreases as discharge rate is increased [14]. Fig. 6 shows the resistance for each cell type at different SOC levels.

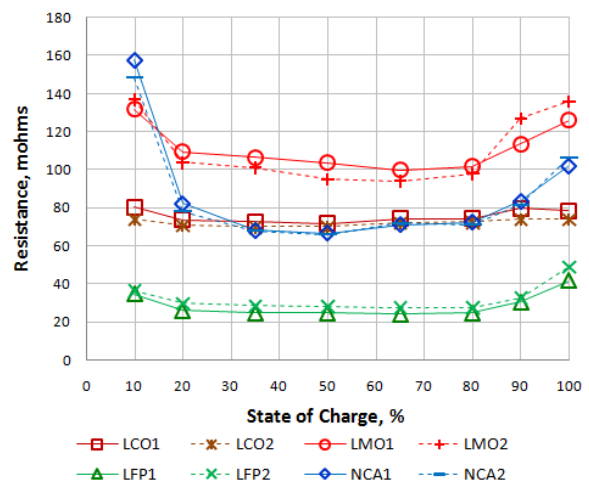


Fig. 6 Resistance as function of SOC.

As shown in Fig. 6, the resistance is dependent upon the SOC and the values are high at either of the extreme SOC levels. This is the reason why temperature rise fast during the beginning and end time of discharge. Mulder [6] noted that the relationship between resistance and cell capacity is inversely proportional. In order to compare cell with different capacity values, the resistance values were multiplied by cell capacity to obtain capacity-normalized resistance. The relationship between normalized-resistance with temperature is shown in Fig. 7(a). Higher normalized resistance results in a higher temperature increase. However, it has a notice that NCA have normalized resistance higher than LCO but the temperature increase of NCA result in lower than LCO. This is possibly because LCO has a much larger contribution from electrochemical reaction heat as reported in literature [14]. The relationship between normalized resistance with efficiency loss and maximum discharge rate is apparent in Fig. 7(b) – 7(c). The results in Fig. 7 show that resistance is significantly affects efficiency and discharge rate capability. The cell with less normalized resistance yields higher efficiency and discharge rate capability.

4. Discussion

A comparison was performed between our results and the requirements for batteries in electric vehicles. United States Advanced Batteries Consortium (USABC) specifies the requirement for energy density in minimum goal at 150 Wh/kg, long term goal at 200 Wh/kg, a normal recharge time of 6 hours and a high-rate

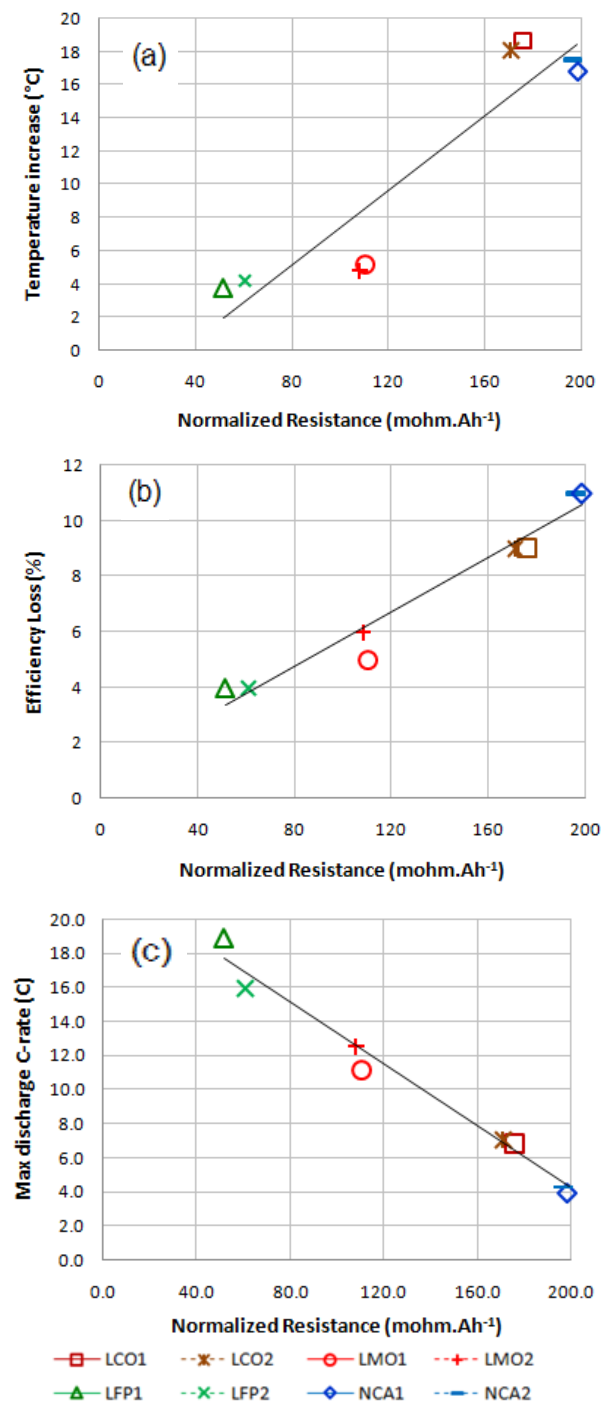


Fig. 7(a) Temperature, (b) Efficiency loss and (c) Max C-rate relationship with resistance.

charge in less than 30 minutes [15]. Comparing the results in this study with USABC requirements, only NCA cells fulfill the energy density requirement. Even though LCO cells have energy density values that exceed the minimum

requirement, it is likely that this type of chemistry may fail the requirements if the weight of cooling, connection and packing were taken into account. Based on the maximum charge rate specified by the manufacturers, all cells meet the requirement for normal recharge time of 6 hours. Only LFP and LMO cells meet the requirement of high-rate charge. In the case of power requirements, the evaluation based on the actual discharge rate of realistic vehicles, as reported by Whitacre [16]: that the absolute values of C-rate exceed 1 only 20% of the time and that the maximum C-rate value be around 2.85 C. By comparing with the result in this study, all cells meet those requirements of discharge rate. Finally, it can be concluded that only NCA chemistry cells have the possibility to fulfill the requirements of USABC goal and the actual discharge rate for battery electric vehicle. It must be noted, however, that this study did not take into account safety requirements, which is a major issue that must be taken into consideration for electric vehicle batteries.

5. Conclusion

In this paper, lithium-ion batteries with four cathode chemistries have been evaluated: lithium manganese oxide (LMO), lithium cobalt oxide (LCO), lithium nickel cobalt aluminium oxide (NCA) and lithium iron phosphate (LFP). The results show that NCA and LCO have high energy density, which is a crucial performance measure for batteries in electric vehicles. However, these cell chemistries have poor performance in terms of charge/discharge rate capabilities. LMO and LFP cells have high discharge rate capabilities and energy efficiency.

However, the low energy density can be a limiting factor for BEV application. In addition, cell performances were compared with the requirement for battery electric vehicle. Based on overall performance, and pending safety tests, NCA chemistry appears to be the best candidate for batteries in electric vehicles.

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7. References

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