Experimental Research on the LiNi_{x}Co_{y}Mn_{z}O_{2} Lithium-ion Battery Characteristics for Model Modification of SOC Estimation

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Abstract: The Kalman Filter (KF) known as an optimum adaptive algorithm based on recursive estimation, has been widely used to estimate the State Of Charge (SOC) of the lithium-ion batteries. To improve the performance of SOC estimation, the parameters of battery model in the KF method should be chosen correctly. Nevertheless, the battery parameters, such as the OCV-SOC, capacity and resistance are significantly depended on the battery SOC, temperature, current and ageing. In this study, these dependencies and their variation over the temperature, current and ageing are investigated on a Samsung ICR18650-22P-typed lithium-ion battery with LiNi_{x}Co_{y}Mn_{z}O_{2} cathode which offers guidance to model modification of SOC estimation. The experimental results show that the OCV-SOC relationship are strong consistent under the conditions of 0–60°C but it varies when the temperature remains below zero degrees Celsius. The capacity varies considerably with the temperature and cycles and slightly with the current of below 3C. The Ohmic resistance varies slightly with charge current but considerably with discharge current and SOC. Based on the experimental results, some suggestion for model modification of SOC estimation is put forward.

Key words: Lithium-ion battery, state of charge, battery characteristics, model modification

INTRODUCTION

With the soaring energy shortage and environment deterioration, Electric Vehicles (EVs) have been rapidly developed in recent years (Gong et al., 2013; Tian et al., 2013). As the main part of energy carrier and power source, power battery affects both the economic and driving performance of the EVs. Lithium-ion battery is widely used for its high performance in energy density, power density, life cycle and so on (Cho et al., 2012). The performance of lithium-ion battery is seriously affected by the cathode material, such as LiFePO_{4}, LiCoO_{2}, LiMn_{2}O_{4}, and LiNi_{x}Co_{y}Mn_{z}O_{2} (x+y+z = 1). Compared with other material, LiNi_{x}Co_{y}Mn_{z}O_{2} has the advantages of high energy density, excellent consistency, mild thermal stability, low cost and low toxicity (Guo et al., 2009; Pan et al., 2013). Due to these characteristics, LiNi_{x}Co_{y}Mn_{z}O_{2} lithium-ion battery has a promising widespread application on EVs. In order to improve the safety and capability of the battery, a Battery Management System (BMS) is required. As one of the most important functions, SOC estimation should be included to prevent the battery from being over-charged and over-discharged and to manage the energy flows of the EVs. Several methods, such as Ampere-hour (Ah) counting (Lu et al., 2013), Open-Circuit Voltage (OCV) (Lee et al., 2008), Artificial Neural Network (ANN) (Charkhgard and Farrokhi, 2010; Capizzi et al., 2011; Kang et al., 2014) and Kalman Filter (KF) (Lee et al., 2007; He et al., 2011; Dai et al., 2012; He et al., 2013; Xiong et al., 2014; Sepasi et al., 2014; Xing et al., 2014) have been proposed to estimate the battery SOC. The KF algorithm has been widely employed for online SOC estimation due to its high performance under dynamic driving conditions. KF is a model-based method (Song et al., 2012; Ma et al., 2013) and as a result, the model parameters should be chosen correctly to improve the estimation performance. However, the parameters of the battery model, such as the OCV-SOC, capacity and resistance are significantly depended on the battery SOC, temperature, current and ageing.

There have been some efforts to resolve these problems. The various OCV-SOC relationships caused by the difference in capacity among cells were discussed (Lee et al., 2008). The difference in internal resistance among cells was dealt with by choosing the internal resistance as a state-variable (He et al., 2013). The different equilibrium potentials during charge and discharge process at the same SOC were considered and the OCV was defined as the average value of the equilibrium potentials of charge and discharge process to simplify the model (He et al., 2011). In this study, it can
be seen that only a single parameter variation was taken into consideration, besides, the parameter variations with temperature and ageing are often neglected.

In order to obtain more accurate SOC estimation by modification of the battery model, in this study, aforementioned dependencies and their variation over the battery SOC, temperature, current and ageing are investigated on an ICR18650-22P-typed lithium-ion battery with LiNi_{x}Co_{y}Mn_{z}O_{2} cathode produced by Samsung. Several experiments are implemented to obtain the battery characteristics. Based on the experimental results, several correction factors and suggestion for modification of the battery model are put forward.

**BATTERY MODEL AND SOC ESTIMATION**

A battery model is crucial to SOC estimation using the KP algorithm. Various models have been proposed to simulate the electrochemical characteristics of a lithium-ion battery. The equivalent circuit model, consisting of resistor, capacitor and inductor performs well in describing the dynamic characteristics and as a result, it is usually used in battery SOC estimation (Hu et al., 2012, Li et al., 2013). A simple equivalent circuit model is shown in Fig. 1, where, OCV, L, R, and V, represent the open-circuit voltage, current, Ohmic resistance and terminal voltage of the battery, respectively and OCV varies with SOC.

Based on Fig. 1, the space-state functions of the battery model can be derived as shown in Eq. 1 and 2:

\[
\text{SOC}(k) = \text{SOC}(k-1) - \frac{I(k-1) \times \Delta t}{Q_b} \quad (1)
\]

\[
V_i(k) = \text{OCV}(\text{SOC}(k-1)) - R_s \times I(k-1) \quad (2)
\]

where, \(Q_b\) is the normal capacity of the battery.

Usually, \(Q_b\) and \(R_s\) are selected as constant which results in large model error due to the fact that they are significantly depended on the battery SOC, temperature, current and ageing. These dependencies will be studied in the following part of this study.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Experimental configurations:** The LiNi_{x}Co_{y}Mn_{z}O_{2} lithium-ion batteries used in the experiments are Samsung ICR18650-22P type with a normal capacity of 2200 mAh (0.2°C discharge at temperature of 25±5°C), a minimum capacity of 2150 mAh (0.2°C discharge at temperature of 25±5°C), a normal voltage of 3.6 V, a charging voltage of 4.2 V and a discharge cut-off voltage of 2.75 V. The experimental equipment is consisted of a power supply, an electric load, a constant temperature and humidity chamber, an Electrochemical Impedance Spectroscopy (EIS) instrument, a control board and a Personal Computer (PC), as shown in Fig. 2.

In the experiments, the temperature was set in the range of -20° to +60°C which is the storage temperature suggested by the battery specification.

**Voltage SOC characteristics**

**Terminal voltage variation with different capacity test:** At the temperature of 25±2°C, the battery was charged with a constant current of 100 mA until the charging voltage of 4.20 V and the terminal voltage was recorded simultaneously. Then the battery was rest for 2 h to reach the steady state. Afterwards, the battery was discharged with the same constant current of 100 mA until the cut-off voltage of 2.75 V. The measured terminal voltage variations with the charge and discharge capacity (Q) are shown in Fig. 3.

It can be seen that the terminal voltage variation at the charge process is similar to that at the discharge process. However, they have different values at the same SOC or rather the terminal voltage at the charge process is higher than at the discharge process. This difference in terminal voltage is the reason that the different OCV-SOC relationship during the charge and discharge process. And this difference should be taken into account when a battery model is built. For example, the OCV is redefined as the average value of the charging and discharging equilibrium potentials to improve the SOC estimation accuracy and simplify the battery model, meanwhile, the OCV measured as a function of the SOC was obtained by the quadratic curve fitting method (He et al., 2011).

**OCV-SOC variation with temperature test:** At the temperature of 25±2°C, the battery was firstly charged to the charge voltage of 4.2 V and was rest for 3 h to reach the steady state. Afterwards, it was discharged with a
Fig. 2: Experimental equipment

Fig. 3: Relationship between terminal voltage and capacity

constant current of 0.3C A from the fully charged state to 98% of the actual capacity which will be introduced in the following part of this study. Then, it was left in the open-circuit condition and the terminal voltage was measured after 3 h. The measured terminal voltage is chosen to be the OCV as the charge of the terminal voltage is negligible and the battery is assumed to already reach the steady state. Then, the battery was continuously discharged by a further 95, 90, 80, 70, 60, 50, 40, 30, 20, 10, 8, 5, 3, 2, 1 and 0% of the actual capacity with the same current and the OCV was measured after 3 h, respectively.

These steps were repeated under the same charge temperature of 25±2°C and different discharge temperature of [-20, 0, 10, 40, 60°C], respectively. The measured OCV at different SOC and different temperature are shown in Table 1. Furthermore, the corresponding OCV-SOC curves are shown in Fig. 4.

From Fig. 4, it can be found that at the different temperature of [0, 10, 25, 40, 60°C], the OCV-SOC curves have a similar trend. However, the situation becomes obviously different under the temperature of -20°C. Based on these facts, it is suggested that to improve the accuracy of the battery model, different OCV-SOC functions should be used under the condition of high temperature and that of low temperature, respectively.
Moreover, it can be seen that there is no voltage platform that exists on the OCV-SOC curve for a LiFePO₄ lithium-ion battery, as shown in Fig. 5 (Huria et al., 2014; Sepasi et al., 2014). As a result, some empirical models used for other kinds of lithium-ion batteries are no longer suitable for LiNi₀.₅Co₀.₅Mn₂O₄ battery. From Fig. 4, it is clear that a high-order polynomial should be able to describe the nonlinear relationship between the OCV and the SOC of a LiNi₀.₅Co₀.₅Mn₂O₄ battery. However, this will increase the complexity of the stability and computation cost of the SOC estimator. To solve this problem, segmented linear functions (Habiballah et al., 2014; Chen et al., 2014) have been proposed and each of them can be described as shown in Eq. 3:

\[
OCV = f(SOC) = b_0 + b_1SOC
\]

**Capacity characteristics**

**Discharge capacity variation with temperature test:** At the temperature of [-20, -10, 0, 10, 25, 40, 60]°C, the battery was discharged with a constant current of 0.3C A from the fully charged state to the cut-off voltage, respectively and the terminal voltage as well as the discharge capacity calculated by Ah method were recorded simultaneously. The recorded terminal voltage and discharge capacity are shown in Fig. 6.

From Fig. 6, it can be seen that the discharge capacity decreases as the temperature decreases. The decline becomes significant when the temperature decreases to under 0°C. At the temperature of -20°C, the discharge capacity is reduced to about 70% of the normal value. The discharge characteristic at the temperature of 45°C is very close to that at the temperature of 60°C. It is shown that under the condition of high temperature, the potential discharge capacity is larger. However, high temperature is bad for both the life cycle and safety usage of the battery. Therefore, avoiding of working at high temperature is still essential to the battery.

To compensate the model error caused by capacity variation with temperature, a correction factor marked as \( K_T \) is introduced which is defined as:

\[
K_T = \frac{\text{Capacity at the temperature of } T_x \degree C}{\text{Capacity at the temperature of } 25 \degree C}
\]

The relationship between \( K_T \) and temperature \( T \) is shown in Fig. 7, where, the blue-circles are the measured data and the red-line is obtained according to a fitting formula as shown in Eq. 4. It is clear that the introduced formula can describe the battery capacity variation with temperature very well. Thus, such a method can be used to online correct the model error caused by the ambient temperature variation to improve the SOC estimation accuracy.

\[
K_T = -5.063 \times 10^{-5} \times T^2 + 0.00518T + 0.904
\]

Fig. 4: OCV-SOC curves at different temperature

Fig. 5: OCV-SOC curve of a typical LiFePO₄ battery

Fig. 6: Voltage-Q curves at different temperature
Capacity variation with discharge rate: At the temperature of 25±2°C, the battery was firstly charged to the charge voltage of 4.2 V and was rest for 10 min. Afterwards, it was discharged with a constant current of 0.3C A until the cut-off voltage and the discharge capacity calculated by Ah method was recorded.

At the same temperature, the foregoing procedure was repeated with different discharge current of [1C, 2C, 3C, 10] A, respectively. The results are shown in Fig. 8. It can be seen that the potential capacity decreases with the increase of the discharge current. An obvious decrease turns up at the max discharge current of 10 A. Hence discharging with a high current is endeavored to avoid in practical application to increase the discharge capacity of a battery.

To compensate the model error caused by capacity variation with discharge rate, a correction factor marked as \( K_i \) is introduced which is defined as:

\[
K_i = \frac{\text{Capacity under different discharge rate}}{\text{Nominal capacity}}
\]

The relationship between \( K_i \) and discharge current is shown in Fig. 9, where, the blue-triangles are the measured data and the read-line is obtained according to the fitting formula as shown in Eq. 5. It is clear that this formula can describe the battery capacity variation with operating current very well. Thus, such a method can be used to online correct the model error caused by the operating current variation to improve the SOC estimation accuracy.

\[
K_i = -7.571 \times 10^{-3} \times I^3 + 9.897 \times 10^{-7} \times I^5 - 4.198 \times 10^{-10} \times I^7 + 1.035
\]

Capacity variation with ageing: At the temperature of 25±2°C, the battery was charged with a constant current of 0.5C A to the voltage of 4.1 V. After rest for 10 min, the battery was discharged with a current of 1C A to the voltage of 3 V and then rest for 10 min. It should be indicated that discharging the battery from 3-4.1 V represents 80% DOD (Depth Of Discharge). After this forego cycle repeated for 50 times, the battery was then charged with a constant current of 0.5C A to 4.2 V and rest for 10 min. Then the battery was discharged with a current of 1C A to 2.75 V (100% DOD).

The foregoing procedure was repeated for 900 times to investigate the capacity variation with aging and the results are shown in Fig. 10, where the red-circles and blue-line represent the capacity of 100% DOD and that of 80% DOD, respectively.

From Fig. 10, it can be seen that the capacity loss resists during the charging and discharging process. Nevertheless the distinction of capacity loss is not obvious between that under 100% DOD and that under 80% DOD. After 900 cycles, about 15% of the original capacity has been lost. Thus actual capacity reduction should be considered to improve the accuracy of SOC estimation.
To compensate the model error caused by ageing, a correction factor marked as $K_a$ is introduced which is defined as:

$$K_a = \frac{\text{Capacity at the cycles of } a}{\text{Initial capacity}}$$

The relationship between $K_a$ and the cycles $a$ is shown in Fig. 11, where the blue-circles represent the measured capacity of 100% DOD and the red-line is obtained according to a fitting formula as shown in Eq. 6. Obviously, the introduced formula can describe the battery capacity variation with aging very well. Thus, such a method can be used to online correct the model error caused by the aging variation to improve the SOC estimation accuracy.

$$K_a = -1.225 \times 10^{2} \times a^{4} + 2.726 \times 10^{-3} \times a^{3} - 1.980 \times 10^{-6} \times a^{2} + 3.610 \times 10^{-4} \times a + 0.942$$  \hspace{1cm} (6)$$

**Ohmic resistance characteristics**

**Ohmic resistance variation with SOC test:** The battery was discharged with a constant current of 0.5C A until the cut-off voltage at the temperature of 25±2°C. After a rest of 10 min, it was charged with the same constant current of 0.5C A till the SOC reaches 5% and the Ohmic resistance was measured after a rest of 3 h. Then, the battery was charged to 20, 50, 80 and 100% of the normal capacity, respectively and the corresponding ohmic resistance was measured after a rest of 3 h. At the same temperature, the procedure above was repeated with different charge current of 1C A. The results are shown in Table 2 and Fig. 12.

From Fig. 12, it can be seen that with the current of 0.5C A, the difference between the highest and the lowest ohmic resistance is 0.013 Ω and the value is 0.0135 Ω under the current of 1C A. The highest difference between the ohmic resistance under 0.5C A and 1C A is 0.0021 Ω. Therefore, a conclusion can be drawn that the charge current has not obviously effect on the ohmic resistance at the same SOC and SOC is the main factor that leads ohmic resistance variation as shown in Eq. 6. Moreover, the Ohmic resistance variation with SOC performs as V-shape and the highest values appear when the battery is fully charged.

At the temperature of 25°C, the battery was charged with a constant current of 0.3C A till the charge voltage of 4.2V and the ohmic resistance was measured after a rest of 3 h. Then it was discharged to the 80, 50 and 20% of the normal capacity, respectively and the ohmic resistance was measured after the same rest time. At the same temperature, the procedure above was repeated with different discharge current of 1C and 2C A, respectively. The results are shown in Table 3 and Fig. 13.
Fig. 13: Discharge ohmic resistance

Table 3: Discharge ohmic resistance (Ω)

<table>
<thead>
<tr>
<th>Current (C)</th>
<th>SOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0350</td>
</tr>
<tr>
<td>1</td>
<td>0.0406</td>
</tr>
<tr>
<td>2</td>
<td>0.0426</td>
</tr>
</tbody>
</table>

From Fig. 12, it can be found that the ohmic resistance increases as the discharge current increases at the same SOC. Under the condition of different discharge rate, the biggest difference between the ohmic resistances is 0.0049 Ω. And the current rate has more obvious effect on the discharge ohmic resistance than that on the charge ohmic resistance. The variation of ohmic resistance with SOC also performs as V shape and the highest values appear when the battery is fully discharged. The variation is gentle under a low rate.

From Fig. 12 and 13, it is indicated that the ohmic resistance of battery is not a constant but varies with current, SOC, etc. Therefore, large error of SOC estimation is almost resulted by battery model with a constant ohmic resistance. To resolve this problem, ohmic resistance is also selected as a state-variable and estimated in real-time (He et al., 2013). Unfortunately, it increases the computation cost obviously. Thus, more efforts have to be made to improve the model accuracy.

**SOLUTIONS FOR ACCURATE SOC ESTIMATION**

Based on the experimental results of this study, it is suggested that two solutions can be used to improve the accuracy of SOC estimation. The first one is to update the parameters of battery model, e.g., normal capacity, internal resistance, etc., based on its operating conditions, including SOC, temperature, current and ageing. This method is called static correction method in this study. For instance, the SOC updating function in Eq. 1 can be rewritten as in Eq. 7 by using the static correction method. Furthermore, defining the SOC in term of energy balance can be more accurate as the energy loss due to the internal resistance is not ignorable under the condition of high current discharging or charging. And the definition of SOC can be expressed as in Eq. 8 according to Fig. 1, where, $E_b$ is the average equilibrium potential of battery:

$$SOCA(k) = SOCA(k-1) - \frac{(k-1) \times \Delta t}{(K_K, K_F) E_b}$$  

$$SOCA(k) = SOCA(k-1) - \frac{(V_h + R_h \times (k-1) \times (k-1) \times \Delta t)}{(K_K, K_F, Q_h) \times E_b}$$

The second one is called as dynamic correction method in this study. It is to employ intelligent algorithms with superior estimation performance, such as Kalman filtering, sliding mode observer and their modified method, etc. Although this method has been widely used in recently years and reported in many literatures. It has some drawbacks such as dependency on model accuracy, high requirement for hardware, high computation cost, etc. Therefore, algorithms with more superior performance are still required to improve the SOC estimation accuracy under the conditions of model error, measurement error and operating condition variation.

**CONCLUSION**

In order to improve the model accuracy of SOC estimation, this study based on the characteristics of Samsung ICR18650-22P-typed lithium-ion battery with LiNi$_x$Co$_{y}$Mn$_{1-x-y}$O$_2$ cathode that is being applied more and more in electric vehicles for its excellent performance. Several experiments have been implemented to obtain the dependency of OCV-SOC relationship, capacity and ohmic resistance on the battery SOC, temperature, current and ageing. The experimental results can be concluded as follows:

- The terminal voltage variation at the charge process is similar to that at the discharge process. However, they have different values at the same SOC which is the reason that the different OCV-SOC relationship during the charge and discharge process. And this difference should be taken into account when a battery model is built.
- At the different temperature of [0, 10, 25, 40 and 60]°C, the battery OCV-SOC relationship has a similar trend and the cut-off voltage decreases as the temperature rises. However, the situation becomes obviously different at the temperature of -20°C. Thus, it is suggested that different OCV-SOC functions should be used under the condition of high temperature and that of low temperature, respectively.
On the OCV-SOC curve of LiNi$_2$Co$_x$Mn$_{2-x}$O$_4$ battery, there is no voltage platform that exits on the curve for a LiFePO$_4$ battery. Therefore, some empirical model used for other kinds of battery is not suitable for LiNi$_2$Co$_x$Mn$_{2-x}$O$_4$ battery.

- The discharge capacity decreases as the temperature decreases. At the temperature of -20°C, the capacity is even reduced to about 70% of the normal value.

- The potential capacity decreases with the increase of discharge current. Hence, it is suggested that a battery should be prevented from discharging with a high current to increase the discharge capacity.

- The actual capacity fades with ageing. After 900 cycles of charging and discharging, about 15% of the original capacity has been lost. This fading should be taken into account when estimating the SOC of a long-term used battery.

- The ohmic resistance of battery is not a constant but varies with current, SOC, etc. and its variation with SOC performs as V shape. Therefore, large error of SOC estimation is almost resulted by battery model with a constant ohmic resistance.

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