A Rapid Depolarization Charge and Discharge Technique for Lithium Ion Batteries

Yiduo Li[1], Xiaowen Sun[2], Hanbo Wang[1], Haiyan Lu[1, 3, 4, *], Changying Liu[2, *]

[1]College of Chemistry, Jilin University, Changchun 130012, Jilin, China
[2]Jilin Univ, Coll Instrumentat & Elect Engn, Changchun 130021, Peoples R China
[3]Key Laboratory of Physics and Technology for Advanced Batteries of Ministry of Education, Jilin University, Changchun 130012, Jilin, China
[4]Zhuhai Zhongli New Energy Sci-Tech Co., Ltd., Zhuhai 519175, Guangdong, China

Abstract: There is a serious diffusion-polarization effect in the working process of lithium-ion batteries, resulting in a large rebound of battery voltage after charge/discharge. The measurement of the open circuit voltage (OCV) of the battery was interfered by the existence of this polarization, while accuracy of battery state of charge estimating based on open circuit voltage and state of charge (SoC) curve is reduced. At the same time, measurement of AC impedance spectrum was interfered by the fluctuating voltage. In this work battery was rapidly depolarized through pulse charge-discharge in discharging procedure. Compared with the standard depolarization method by reducing the discharge rate (0.05C), the discharge test time was reduced by 72.5% and polarization effect was weakened at low SoC. There was no significant difference in results for this charging technology compared with EIS curve tested after conventional charging and reduced test time by 42%.

Keywords: Lithium ion battery, Depolarization, Experimental technique.

1. Introduction

Low-carbon transportation is an important hot topic in many fields. Fuel-powered vehicles have been gradually replaced by cars powered by hydrogen and electricity in order to reduce traffic carbon emissions, among which electric vehicles have the greatest potential for development[1]. In the past two decades electrochemical devices leaded by lead-acid batteries and lithium-ion batteries have become the main energy sources of electric vehicle. However, the former gradually fades out due to its low specific energy while the latter has been vigorously developed by researchers benefit from its advantages such as high energy density, small memory effect and long cycle life[2].

Lithium-ion battery has good safety performance in general, but sealing of the battery will be damaged once the safety problem occurs then cause a major safety accident. Because of the activity of active substance and electrolyte, lithium-ion battery will react with oxygen after exposure to the air then releasing a lot of heat cause a series of chain reactions and leading to major accidents[3][4]. So battery safety management has been a rapidly growing field in battery application. Many parameters of battery are highly time-varying and cannot be accurately measured by the existing technology, that is, the battery state can be monitored by estimation method[5]. As the two most important indicators in the battery safety management, estimation accuracy of SoC and SoH has always been pursued[6]. Many battery SoC estimation methods are based on OCV-SoC curve and it means that the measurement accuracy of OCV is very important. However, voltage usually rebounds after the end of charging and discharging due to the serious polarization effect of lithium-ion batteries which results in the OCV-SoC curve cannot be measured accurately[7][8]. The polarization is usually eliminated by battery resting method after the low-rate discharge (0.05 C) to measure OCV under different SoC in standard method. However, the resting time is too long if the polarization is completely eliminated, making it difficult to apply to the increasingly rapid detection technology such as electrochemical impedance spectroscopy (EIS) test[9][10]. Because of the advantages of fast and convenient and more importantly reflect the internal working mechanism of the battery, EIS test have become the most commonly used test method for lithium-ion battery state estimation and an indispensable part of battery characteristic test[9]. But EIS test has a quite high requirement for stable voltage namely that a special technique to reduce voltage fluctuation after charging or discharging needs to be developed.

The operating principle of lithium-ion battery is to provide electrons to the external circuit through intercalation/de-intercalation redox reactions between electrode active materials of lithium ion/lithium compound. Lithium ions move in the electrolyte between positive and negative electrodes during the working process, forming a concentration gradient of lithium ions which positively correlated with the SoC of the battery all the time[7][11]. The voltage is constantly reduced when discharge lithium ions migrate to the positive electrode migration because lithium ions diffuse in the electrolyte much faster than diffuse in the membrane. Discharge process is always accompanied by incomplete lithium ion diffusion which caused voltage rebound. The same goes for voltage changes during charging. In this work, the battery is discharged in the form of reciprocating pulse charge-discharge (RPCD), which can weaken the voltage change caused by the lithium ion diffusion in the membrane. So as to accelerate the battery reach equilibrium voltage rapidly. It provides a new method of battery discharge OCV measurement for estimating battery SoC based on OCV-SoC curve method, it also reduces the time for the battery voltage to stabilize for other rapid tests.

2. Experiment

The cell used for experiment is SAMSUNG INR-18650 25R cylindrical cell with following key specifications:

Active materials: Li[Ni0.8Co0.15Al0.05]O2 for cathode and graphite for anode,

Nominal capacity: 2500 mAh,

Maximum discharge current: 20 A (8 C),

End-of-charge voltage: 4.2 V,

End-of-discharge voltage: 2.75 V.

The cell was charged and discharged by Neware 4008T battery cell tester, all discharge test was begun from full charge state. Electrochemical impedance spectrum (EIS) was measured by CHI660E electrochemical workstation with a frequency range from 2000Hz to 0.01Hz and 5mV amplitude. EIS equivalent circuit element was fitted through Zview software.

In order to eliminate the voltage instability caused by the diffusion polarization of lithium ions, RPCD was used for discharging the battery in in the whole range of discharging. The specific steps is as follows (Figure 1):

Determine the discharge capacity.

As shown in the figure1, the first step is the discharge step, each subsequent step is -1/2 of the previous step's charge/discharge capacity (the negative sign represents the current direction) and the total discharge capacity equal to that of step 1.

Repeat Step 3 for an even number of times (6 or 8 times is best).

The battery is discharge and charge 20-30% of the total discharge capacity to eliminate polarization, so that the battery quickly reach voltage stability.

The battery is relaxed for an appropriate amount of time.

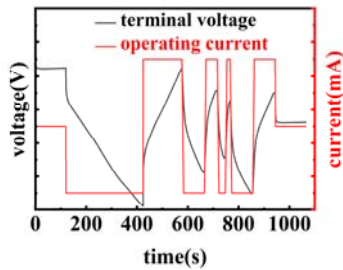RPCD can also be used for charging that just need to reverse all direction of current.

Figure 1. Operating steps of RPCD

The battery HPPC discharge experiment procedure is as follows: 1) The battery is charged with a standard CCCV procedure and relaxed for 30min; 2) The battery is discharged with a constant current of 5000mA(2C) for 30s and then relaxed for 40 s. 3) The battery is charged with a constant current of 3000mA(1.2C) for 10s and then relaxed for 40 s. Steps 2) to 3) are repeated until the battery terminal voltage reaches to 2.75 V. The discharge results are shown in the figure below (Figure 2).
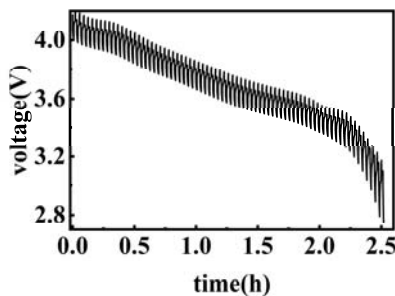

Figure 2. HPPC discharge of battery

3. Results

Using the 1% maximum static capacity (about 25mAh) as discharge capacity reference, the conventional low-rate discharge test and RPCD test were carried out respectively. Demonstrated by discharging curve under two methods, when discharge capacity is 25 mAh, the low-rate discharge method (Figure 3b) still has a large voltage rebound after standing for 30 minutes, while the RPCD method (Figure 3a) almost immediately balances the voltage at the end of the discharge. And the diffusion polarization is completely eliminated within 3 minutes. There was little difference in fitting results between the two OCV-SoC curve measured by the two methods (Figure 4). But low-rate discharge method at low SoC was much lower than that measured by the RPCD method. The reason goes back to the very serious lithium ion diffusion polarization at low SoC, and Li+ balance process in conventional discharge is slower, which leads to the mismeasurement of this method at low SoC. However, RPCD method can still ensure the voltage of rapid equilibrium, there is no obvious difference between the OCV measured by the two methods in other state. OCV-SoC curve measured by RPCD takes about 16.5 h, gives a 72.5% time reduction compared with low-rate discharge which takes 100 h in a same discharge period. Therefore, the RPCD method has advantages over the standard method in the measurement speed and accuracy when measuring the OCV curve of the battery.
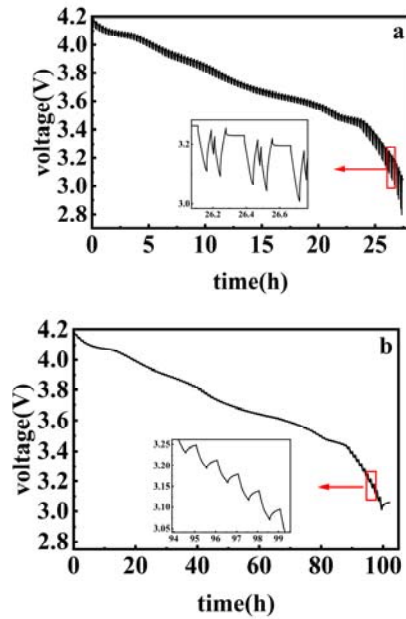

Figure 3. OCV-SoC discharging curve by (a) RPCD and (b) low-rate discharge.
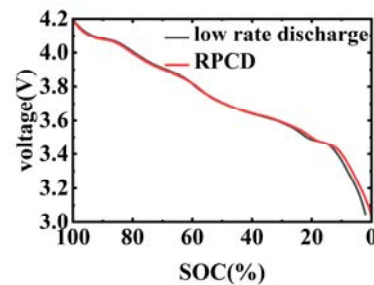

Figure 4. Seventh-order polynomial fitting curve of RPCD and low-rate discharge.

lithium-ion battery could be regarded as a equivalent circuit model (Figure 5) while SoC of battery was estimated. Parameters for each component in the circuit model followed the Kirchhoff's law as below:

$$\begin{cases} \dot{U}_1 = -\dfrac{1}{R_1 C_1} U_1 - \dfrac{1}{C_1} I \\ \dot{U}_2 = -\dfrac{1}{R_2 C_2} U_2 - \dfrac{1}{C_2} I \\ U = U_{OC} - U_1 - U_2 + R_0 I \end{cases} \quad (1)$$
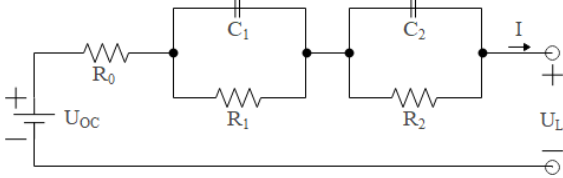

Figure 5. Second-order RC equivalent circuit model.

The formula (1) converted to a frequency domain expression by the Laplace transformation expressed as:

$$U_{oc} = \left(\frac{R_1}{R_1 C_1 s + 1} + \frac{R_2}{R_2 C_2 s + 1} + R_0 \right) I + U_L \quad (2)$$

Where s is the frequency operator.

Let time constant τ_1, τ_2 equals to $R_1 C_1$ and $R_2 C_2$ respectively then above (1) and (2) can be derived as:

$$\tau_1 \tau_2 U_{oc} s^2 + (\tau_1 + \tau_2) U_{oc} s + U_{oc} = \tau_1 \tau_2 (R_0 I + U_L) s^2 + \\ (R_1 \tau_2 + R_2 \tau_1 + R_o(\tau_1 + \tau_2)) I s + (R_o + R_1 + R_2) I + (\tau_1 + \tau_2) U_L s + U_L \quad (3)$$

set following parameter a_1-a_5 for convenience:

$$\begin{cases} a_1 = \dfrac{-(\tau_1 + \tau_2)T - 2(\tau_1 \tau_2)}{T^2 + (\tau_1 + \tau_2)T + \tau_1 \tau_2} \\ a_2 = \dfrac{\tau_1 \tau_2}{T^2 + (\tau_1 + \tau_2)T + \tau_1 \tau_2} \\ a_3 = \dfrac{(R_o + R_1 + R_2)T^2 + (R_1 \tau_2 + R_2 \tau_1 + R_o(\tau_1 + \tau_2))T^2 + \tau_1 \tau_2 R_o}{T^2 + (\tau_1 + \tau_2)T + \tau_1 \tau_2} \\ a_4 = \dfrac{-(R_1 \tau_2 + R_2 \tau_1 + R_o(\tau_1 + \tau_2))T - 2\tau_1 \tau_2 R_o}{T^2 + (\tau_1 + \tau_2)T + \tau_1 \tau_2} \\ a_5 = \dfrac{\tau_1 \tau_2 R_o}{T^2 + (\tau_1 + \tau_2)T + \tau_1 \tau_2} \end{cases} \quad (4)$$

then the difference equation corresponding to second-order RC circuit model can be obtained by the backward difference and used on recursive least squares (RLS) algorithm to identify circuit model parameters:

$$U_{oc}(k) - U_L(k) = a_1[U_L(k-1) - U_{oc}(k-1)] + a_2[U_L(k-2) \\ - U_{oc}(k-2)] + a_3 I(k) + a_4 I(k-1) + a_5 I(k-2) \quad (5)$$

Where T is the sampling interval, $U_{OC}(k)$ and $U_L(k)$ are respectively OCV determined by SOC-OCV curve depended on Ampere integral method and terminal voltage recorded from instrument at the kth sampling instant. $I(k)$ is the operating current at the kth sampling instant.

$$\begin{cases} a_0 = T^2/(a_1 + a_2 - 1) \\ \tau_1 \tau_2 = a_2 a_0 \\ \tau_1 + \tau_2 = -a_0(a_1 + 2a_2)/T \\ R_0 = a_5/a_2 \end{cases} \quad (6)$$

According to Eq. (5), while the forgetting factor introduced and the RLS algorithm based on voltage difference can be derived as below:

$$\begin{cases} \mathbf{K}(k) = \dfrac{\mathbf{P}(k-1)\boldsymbol{\phi}(k)}{\lambda + \boldsymbol{\phi}^T(k)\mathbf{P}(k-1)\boldsymbol{\phi}(k)} \\ \hat{\boldsymbol{\theta}}(k) = \hat{\boldsymbol{\theta}}(k-1) + \mathbf{K}(k)[y(k) - \boldsymbol{\phi}^T(k)\hat{\boldsymbol{\theta}}(k-1)] \\ \mathbf{P}(k) = \dfrac{1}{\lambda}[\mathbf{I} - \mathbf{K}(k)\boldsymbol{\phi}^T(k)]\mathbf{P}(k-1) \\ \lambda(k) = 1 - \dfrac{|y(k) - \phi(k)\hat{\theta}(k)|}{[1 + \phi(k)\mathbf{P}(k-1)\phi^T(k)]\mu} \end{cases} \quad (7)$$

Where,

$$\begin{cases} \boldsymbol{\phi}(k) = [U_L(k-1) - U_{oc}(k-1), U_L(k-2) - U_{oc}(k-1),, I(k), I(k-1), I(k-2)]^T \\ \hat{\boldsymbol{\theta}}(k) = [a_1, a_2, a_3, a_4, a_5]^T \\ y(k) = U_{oc}(k) - U_L(k) \end{cases} \quad (8)$$

In Eq.(8), λ is the variable forgetting factor, μ is an adjustable constant which can be adjusted manually according to the estimated results. λ varies with the residual error to achieve the adaptive adjustment of $\mathbf{P}(k)$ and $\mathbf{K}(k)$ of RLS.

The HPPC working conditions are selected to identify parameters and the parameter identification results estimated by RLS algorithm as shown in the following figure (**Figure 6**). After algorithm convergence, R_0, τ_1, τ_2 are basically stable. R_0 is about 40mΩ, $\tau_1 \tau_2$ are respectively 0.1-1s and 1-10s which is consistent with the identification results of most of the same type 18650 lithium-ion battery in order of magnitude[5][12][13]. Means that RPCD method can be used for OCV-SoC curve calibration and subsequent parameter identification and so on.
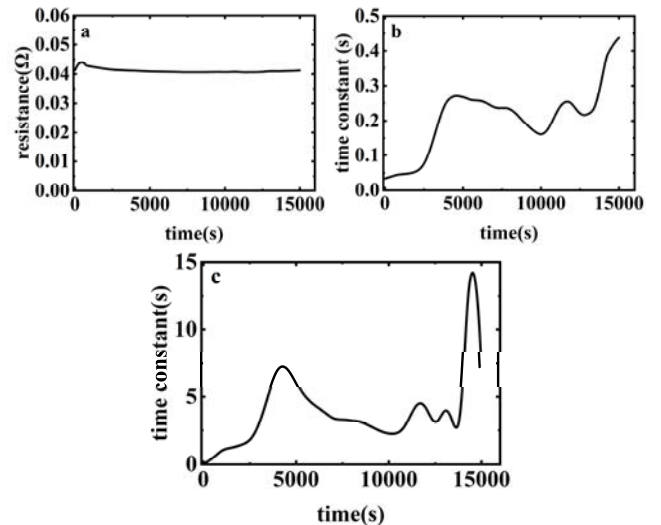

Figure 6. Element of (a)R_0, (b)τ_1, (c)τ_2 parameter

identification results of second-order RC model.

EIS at different SoCs are often measured when it comes to

battery characteristics testing. EIS is usually stimulated with a weak AC amplitude less than 5 mV in 2000s because of lithium-ion batteries' low internal resistance, requires that fluctuation of OCV less than 1mV after lithium-ion battery stop discharging. Since the EIS test of the battery is usually carried out after the static capacity measurement, so charging process was talked about in this work. 10% of the rated capacity of the battery is charged through conventional 1 C (2500 mA) standard-rate constant charge, low-rate charge and RPCD (charge mode). The battery still cannot reach the EIS test requirements 2.3 hours (Figure 7) after 1 C constant charge and it will take at least 1.1 hours (Figure 7) to reach the voltage stable state that can meet the requirements of EIS testing and the voltage is still changing that influence the EIS test with small amplitude. After battery charged by RPCD, battery voltage stabilized to meet the EIS test requirements 5 minutes later (Figure 8), and there was little change in the following 2 hours. RPCD (41min) saved a lot of time of the overall process relative to standard-rate charge (2.4h) and low-rate charge (6.1h).Therefore, RPCD method is very suitable for rapid battery EIS detection.
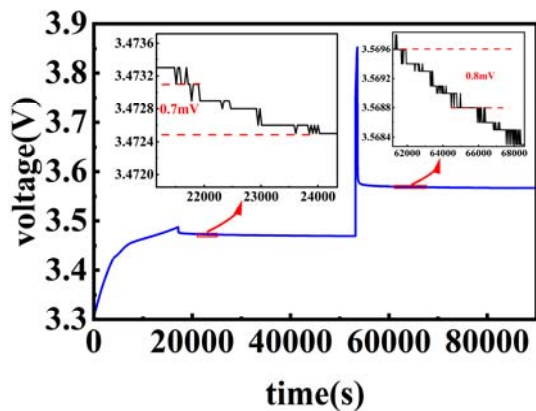
Figure 7. Polarization duration after 10% capacity charged by 0.05C low-rate charge (left) and 1C standard-rate charge (right).
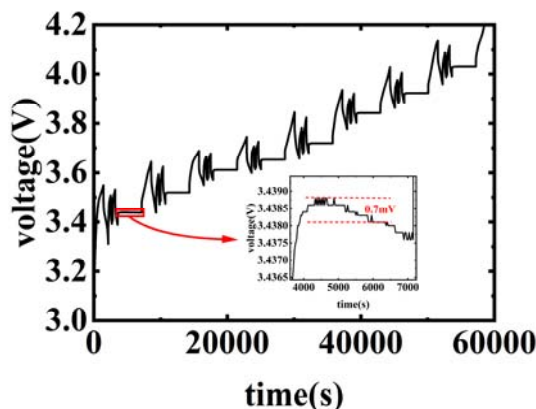
Figure 8. Polarization duration after 10% capacity charged by RPCD.

The EIS test of 18650 lithium-ion batteries under the same SoC after 1C charge and RPCD was performed respectively (Figure 9). The EIS curve fitting results are shown in the table below (Table 1) and it is believed that there is no significant difference of EIS measured under different charge modes within the limits of error.
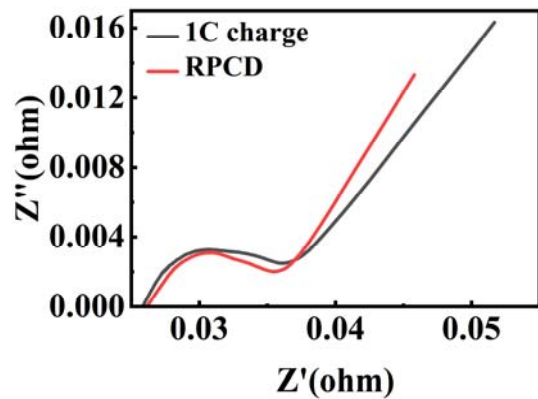
Figure 9. EIS test results after two charging methods.

Table 1. Element value fitted by EIS curve tested after two charging methods.

	R_0(ohm)	τ_1(ms)	τ_2(ms)
1C charge	0.0259	1.98	46.60
RPCD	0.0258	2.08	45.91

4. Conclusion

A convenient method for accelerating lithium ion batteries depolarize was studied in this work. Batteries discharged 1% and 10% capacity would tend to be stable within 2 and 5 minutes. There is a huge advantage in reducing test time overall compared with standard OCV-SoC curve test discharging method while the curves derived from both are almost identical even more accurate measured by RPCD when battery runs low. Battery second-order RC model element parameters was identified through RLS algorithm, results of identification consistent with what most studies have shown in order of magnitude. The results of EIS measured by different discharge methods were fitted and the fitting values of element were almost identical which indicated RPCD fully applicable to the charge and discharge process before EIS test and even can save a lot of time, more suitable for battery rapid detection. Although this method is difficult to perform when the battery is fully charged or empty, RPCD still provides an effective basis for multiple subsequent tests of batteries.

Acknowledgment

References

[1] C. Bauer, J. Hofer, H. J. Althaus, A. Del Duce, and A. Simons, "The environmental performance of current and future passenger vehicles: Life Cycle Assessment based on a novel scenario analysis framework," Appl. Energy, vol. 157, pp. 871–883, 2015, doi: 10.1016/j.apenergy.2015.01.019.

[2] B. Huang, Z. Pan, X. Su, and L. An, "Recycling of lithium-ion batteries: Recent advances and perspectives," J. Power Sources, vol. 399, no. June, pp. 274–286, 2018, doi: 10.1016/j.jpowsour.2018.07.116.

[3] D. Ren et al., "Investigating the relationship between internal short circuit and thermal runaway of lithium-ion batteries under

thermal abuse condition," Energy Storage Mater., vol. 34, no. October 2020, pp. 563–573, 2021, doi: 10.1016/j.ensm.2020.10.020.

[4] W. Huang, X. Feng, X. Han, W. Zhang, and F. Jiang, "Questions and Answers Relating to Lithium-Ion Battery Safety Issues," Cell Reports Phys. Sci., vol. 2, no. 1, p. 100285, 2021, doi: 10.1016/j.xcrp.2020.100285.

[5] Du et al., "An Information Appraisal Procedure: Endows Reliable Online Parameter Identification to Lithium-Ion Battery Model," IEEE Trans. Ind. Electron., vol. 69, no. 6, pp. 5889–5899, 2022, doi: 10.1109/TIE.2021.3091920.

[6] Y. Gao, K. Liu, C. Zhu, X. Zhang, and D. Zhang, "Co-Estimation of State-of-Charge and State-of- Health for Lithium-Ion Batteries Using an Enhanced Electrochemical Model," IEEE Trans. Ind. Electron., vol. 69, no. 3, pp. 2684–2696, 2022, doi: 10.1109/TIE.2021.3066946.

[7] B. Yuan et al., "Study on the Relationship Between Open-Circuit Voltage, Time Constant And Polarization Resistance of Lithium-Ion Batteries," J. Electrochem. Soc., vol. 169, no. 6, p. 060513, 2022, doi: 10.1149/1945-7111/ac7359.

[8] M. Dubarry, V. Svoboda, R. Hwu, and B. Y. Liaw, "Capacity and power fading mechanism identification from a commercial cell evaluation," J. Power Sources, vol. 165, no. 2, pp. 566–572, 2007, doi: 10.1016/j.jpowsour.2006.10.046.

[9] M. Yu et al., "Fractional-order modeling of lithium-ion batteries using additive noise assisted modeling and correlative information criterion," J. Adv. Res., vol. 25, pp. 49–56, 2020, doi: 10.1016/j.jare.2020.06.003.

[10] X. Lai, C. Deng, X. Tang, F. Gao, X. Han, and Y. Zheng, "Soft clustering of retired lithium-ion batteries for the secondary utilization using Gaussian mixture model based on electrochemical impedance spectroscopy," J. Clean. Prod., vol. 339, no. December 2021, p. 130786, 2022, doi: 10.1016/j.jclepro.2022.130786.

[11] S. Peng et al., "Fabrication of spinel one-dimensional architectures by single-spinneret electrospinning for energy storage applications," ACS Nano, vol. 9, no. 2, pp. 1945–1954, 2015, doi: 10.1021/nn506851x.

[12] X. Zheng and Z. Zhang, "State of charge estimation at different temperatures based on dynamic thermal model for lithium-ion batteries," J. Energy Storage, vol. 48, no. August 2021, p. 104011, 2022, doi: 10.1016/j.est.2022.104011.

[13] W. Allafi, K. Uddin, C. Zhang, R. Mazuir Raja Ahsan Sha, and J. Marco, "On-line scheme for parameter estimation of nonlinear lithium ion battery equivalent circuit models using the simplified refined instrumental variable method for a modified Wiener continuous-time model," Appl. Energy, vol. 204, pp. 497–508, 2017, doi: 10.1016/j.apenergy.2017.07.030.