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An Experimental Analysis of Entropic Coefficient of a Lithium Titanate Oxide Battery

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Abstract: In order to understand the thermal behaviour of a lithium-ion battery, the heat generation within the cell should be determined. The entropic heat coefficient is necessary to determine for the heat generation calculation. The entropic heat coefficient is one of the most important factors, which affects the magnitude of the reversible heat. The purpose of this research is to analyze and investigate the effect of different parameters on the entropic coefficient of lithium titanate oxide batteries. In this research, a lithium ion pouch cell was examined in both charging and discharging situations. The state of charge levels range was considered from 10% to 90%, and vice versa, in 10% increments. The temperature levels vary from 5 °C to 55 °C and the voltage levels vary from 1.5 V to 2.8 V. The effect of different parameters such as initial temperature, state of charge, thermal cycle, time duration for thermal cycles, and procedure prior to the thermal cycle on the entropic coefficient of lithium titanate oxide batteries were investigated. It was concluded that there is a strong influence of the battery cell state of charge on the entropic heat coefficient compared with other parameters.

Keywords: entropic heat coefficient; lithium titanate oxide batteries

1. Introduction

A battery is an energy storage device. Energy-storing electrochemical batteries are the most important components for mobile and stationary applications. The most prevalent battery on the market for automotive usages is the lithium ion battery. A conventional lithium ion battery cell comprises of an electrolyte, a separator, and a pair of electrodes with current collectors.

Lithium-ion batteries are extensively used for various applications such as laptops, cameras, mobile phones, automotive, and telecommunication. Low self-discharge rate, long cycle life, high open circuit voltage, high specific energy, and no memory effect are some of the advantages of lithium-ion batteries.

Owing to several sustainability concerns such as exhausting greenhouse gases and fossil fuels, there has been raised attentiveness to hybrid electrical vehicles (HEV) and electrical vehicles (EV). Currently, batteries are considered to be the most favourable energy storage system (ESS). Among these, lithium-based batteries have demonstrated high specific power. Consequently, they are considered as main energy storage for the HEV and EVs [1].

Lithium-ion batteries have been extensively employed in many electric appliances, but derisive accidents have happened occasionally. Therefore, it is necessary to understand their heat generation and thermal behaviour. The computation of the heat generation from experimental measurements of the entropic heat coefficient (EHC) and internal resistance can be applied to the thermal models. Consequently, accurate estimation of EHC will contribute to determining a more precise thermal model, which improves the thermal management systems' (TMS) design process [2].

The potentiometric method is one of the main techniques, which is employed to determine the reversible heat, which is generated in a cell. The changes in open circuit voltage (OCV) of a cell divided

into the change in its temperature could be related to the entropy change. In this method, by changing the temperature of the environmental chamber while the SOC is constant in each step, the reversible heat can be estimated. This procedure can be done in an opposite approach by retaining the chamber temperature constant while altering the SOC level of the cell [3].

Temperature and SOC have an intense influence on entropic heat irrespective of the format or specific chemistry of the lithium-ion cell. Unfortunately, cell producers hardly ever provide any details on the amount of this influence on battery behaviour.

The entropic heat coefficient of a lithium-ion battery after and before each cycle was determined by employing the electrochemical thermodynamics measurements tool [4]. Entropic heat coefficient was attributed to the particular electrodes for the battery cell. Lithium intercalation number in positive and negative electrode was compared and determined for the battery after and before each cycle, correspondingly. Outcomes demonstrated that the tendency of entropic heat coefficient with Li-intercalated state after and before each cycle is fundamentally stable, except for the maximum and initial state [4].

Potentiometric measurements of the enthalpy of reaction and entropy as a function of state of charge for different lithium-ion batteries were investigated [5]. Calorimetric measurements were compared to potentiometric measurements of entropy. It was concluded that the potentiometric procedure is most precise for thermally thin cells, whereas calorimetric procedures need big cells to modify the signal-to-noise ratio [5].

A lumped-parameter thermal model for a cylindrical lithium-ion battery was designed [6]. Heat capacity and heat transfer coefficients were determined from simultaneous measurements of the internal temperature and the surface temperature of the battery cell. Heat transfer coefficients outside and inside the battery cell were determined from thermal steady state temperature measurements, while the heat capacity was determined from the transient part. The precision of the model was validated through estimation of internal temperature from surface temperature measurements [6].

A series of experiments were accomplished on a lithium-ion battery under various conditions and the parameters for reaction heat and Joule heat were analyzed and determined [7]. In addition, the influence of current, aging, temperature, and state of charge was considered. The accuracy of heat generation rate was validated using a lumped battery heat transfer model [7].

Heat loss measurement of lithium titanate oxide batteries under fast charging conditions was investigated by using isothermal calorimeter [8]. Thermal and electrochemical behaviour of lithium-ion cells were analysed to achieve a better comprehension of the thermal behaviour of lithium-ion cells [9]. A two dimensional thermal-electrochemical modeling method was used, and the electrical and thermal energy were estimated by simulations [9].

Temperature increase analysis and optimal heat transfer coefficient were determined for a polymer lithium-ion battery under bus-driving cycle's condition [10]. This investigation studied the heat problems, which arise during the working of power batteries, especially high temperature environments. Moreover, a lumped parameter thermal model was constructed to investigate the thermal behaviour of the battery system. The outcomes demonstrated that the heat transfer coefficient is the third power subordinate of the ambient temperature [10].

A battery thermal management system was investigated based on a thermoelectric effect [11].

In addition, an uncomplicated heat generation model for a cooling model and single battery cell were developed. It was concluded that the thermoelectric cooling combined with liquid cooling structure demonstrated better performance [11].

Several publications have appeared in recent years documenting the amount of entropic heat coefficient to analyze and determine thermal behavior and thermal modeling of batteries. A summary of these investigations was described [12,13]. However, most of the previous studies did not take into account different influential parameters on entropic heat coefficient such as state of charge (SOC), charge or discharge process before the thermal cycle, time duration, and thermal cycle. The electrical modeling of this battery was determined [14]. In addition, different thermal behavior and modeling

investigations were accomplished for this battery [15–19]. To analyze the thermal behavior of the battery cell in different way, a comprehensive investigation was accomplished on the entropic heat coefficient of the battery.

2. Open Circuit Potential Experiment

With the intention of determining the heat generation within the battery cell, the entropic heat coefficient could be specified. There are different methods to estimate the entropic heat coefficient. The electrochemical thermodynamics measurement tool is one of the methods, which was used to analyze the capacity fade of a lithium-ion battery [4]. Potentiometry is the most accepted procedure [20]. In this investigation, open circuit potential (OCP), which has the greatest influence on the entropic heat coefficient, was determined as a function of time and the entropic heat coefficient was analyzed using open circuit potential experiments. Entropic heat coefficient can be calculated from the following equation:

$$EHC = \frac{dU_{OCV,avg}}{dT},\tag{1}$$

where

EHC: entropic heat coefficient
T: absolute temperature
U_{OCV}: open circuit potential

It is clear from the above-mentioned equation that voltage has a great influence on entropic heat coefficient. Therefore, to analyze the entropic heat coefficient, it is important to investigate the variation of open circuit potential. With the intention of approximation, the entropic heat coefficient a procedure was used. A least-squares fitting in Matlab was employed. The gradient of the generated surface demonstrates the entropic heat coefficient at a designated state of charge. Following designation of the surface fitting for every state of charge, the entropic heat coefficient was conveniently quantified by the gradient of the surface.

3. The Investigated Lithium-Ion Battery

A 13 Ah lithium titanate oxide battery cell was used in this investigation. Li $(Ni_xMn_yCo_z)O_2$ was used as cathode of the battery cell. Lithium titanate oxide nanocrystals were used on the anode side, which is referred as $Li_4Ti_5O_{12}$. The lithium titanate oxide-based battery has a 13 Ah nominal capacity and 2.26 V nominal voltage. Maximum charging and discharging voltage are 2.8 V and 1.5 V, respectively. Maximum charge and discharge current are 130 A. Calendar life of the battery is 25 years. There is a limitation for storage and operating temperature, which is between −40 °C to +55 °C. These limits are based on manufacturer-imposed restrictions. The lithium-ion battery cell, which was used in this research, is illustrated in Figure 1.
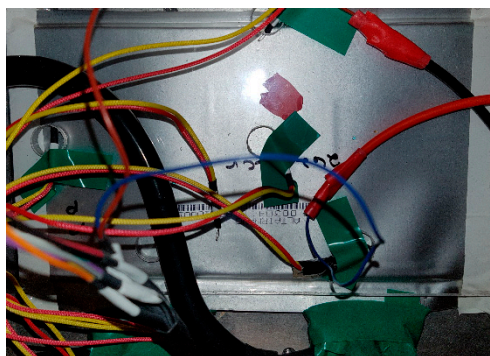

Figure 1. The lithium-ion battery cell.

4. Experimental Setup and Procedure

The Maccor automated test system was used for cycling the battery. The studied battery cell was wired on a test fixture and then was located inside the temperature chamber of the Maccor. The experimental setup, which was used in this experiment, is shown in Figure 2.

Because of safety issues and in order to provide easy connections for the voltage and power cables, the lithium titanate oxide battery was cycled in the battery laboratory by placing the battery cell on a fixture. This fixture will prevent variations in the battery cell volume as a consequence of working with high temperatures and high C-rates.

Preliminary measurements, which consist of a precondition experiment and a relaxation experiment, were applied to the battery cell. The intention of fulfilling a precondition experiment was to take out any achievable passivisation to which the battery cell was exposed to, among the preliminary experiments and the manufacturing time. Furthermore, another objective of this experiment was to scrutinize if the battery voltage, capacity, and temperature are stable.

After a short rest period, the battery was charged with 3.25 A current rate with voltage limitation equal to 2.8 V and end type condition for the current, which was equal to 0.52 A. After a 15-min rest period, the battery cell was discharged with a current rate equal 3.25 A and with voltage limitation less than 1.5 V. This cycle was applied to the battery in order to determine the real capacity of the battery. This capacity was used for determination of the current pulses' step time duration. Then, the battery cell was fully charged with voltage limitation equal to 2.8 V and end type condition for the current, which was equal to 0.52 A. After 15-min rest period, discharge current pulses with ten percent state of charge time duration were applied to the battery. For instance, for the first cycle, the cell's state of charge was decreased by means of a discharging procedure from 100% to 90%, and then the thermal process was accomplished. The mentioned thermal process is described in the following sections and determines the entropic heat coefficient amount for this last-mentioned state of charge. This process was redone until the battery cell was completely discharged for state of charges of 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 10%.
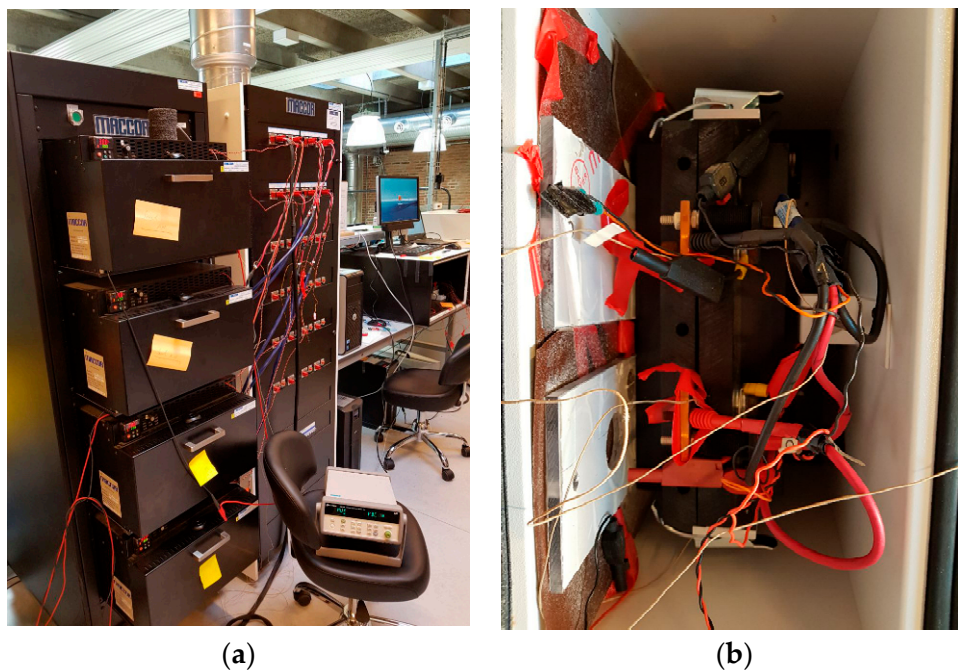

| (a) | (b) |

Figure 2. (**a**) Experimental setup; (**b**) battery inside chamber.

5. Results and Discussion

In order to determine the heat generation, the relationship between SOC and OCV is needed. To analyze the entropic coefficient of the lithium titanate oxide battery, five different cases were considered for the experiments, which are described in the following parts. The nominal capacity and specific energy of the cell are 13.4 Ah and 74 Wh/kg, respectively.

For determining the entropy of reaction by using the potentiometry procedure, the authors in [5] demonstrated that it is more advantageous to adjust the battery cell temperature for a specific state of charge with the purpose of decreasing the fault from self-discharge.

Thermal modeling of the lithium titanate oxide battery during discharge was investigated [21]. A detailed determination of entropic heat coefficient of the lithium titanate oxide battery was described. It was seen that entropic heat coefficient could play an important role in determination of a precise thermal modeling [21].

5.1. Case A

In order to determine the effect of thermal cycle duration on the entropic heat coefficient of the lithium titanate oxide battery, an experiment was accomplished with equal durations for each thermal cycle. In each experiment, the 13 Ah lithium-ion battery cell was charged or discharged to a specific state of charge. For a rest period, it was permitted to relax. After that, a thermal cycle was applied to the battery. The thermal process consist of four hours at 26 °C, four hours at 4 °C, four hours at 14 °C, four hours at 41 °C, four hours at 55 °C, and four hours at 23 °C. This method was repeated for various amounts of state of charge.

5.2. Case B

In order to determine both the effect of thermal cycle and the time duration on the entropic heat coefficient of the lithium titanate oxide battery, case B experiment was repeated by implementing a distinctive thermal cycle (three hours at 27 °C, three hours at 15 °C, three hours at 5 °C, three hours at 20 °C, three hours at 40 °C, and three hours at 15 °C). To assure the results, another distinctive thermal cycle was considered for the lithium titanate oxide battery.

5.3. Case C

In case C experiment, the 13 Ah lithium-ion battery cell was discharged or charged to a specific state of charge. A relaxation process was applied to the battery. The relaxation period was accompanied by a thermal cycle. The thermal process consist of three hours at 26 °C, three hours at 4 °C, three hours at 14 °C, three hours at 41 °C, three hours at 55 °C, and three hours at 23 °C. This method was repeated for various amounts of state of charge. The temperature scope in the thermal procedure was selected according to the temperature range in which the battery cell works safely, as attested by battery cell specification sheets. In this investigation, ten percent state of charge was considered for the current pulse step time duration.

5.4. Case D

In case D experiment, the thermal procedure consists of two hours at 5 °C, two hours at 24 °C, two hours at 10 °C, two hours at 5 °C, two hours at 15 °C, and two hours at 25 °C. A small discrepancy was seen in the results with different thermal cycles (cases A, B, C, and D). Thus, the complete independency of the outcomes with the thermal cycle was not confirmed. Such behavior was expected. Thermal profiles, which were applied to the battery, are shown in Table 1. Figure 3 shows the voltage variations during different SOC levels and experiments for the lithium titanate oxide battery.
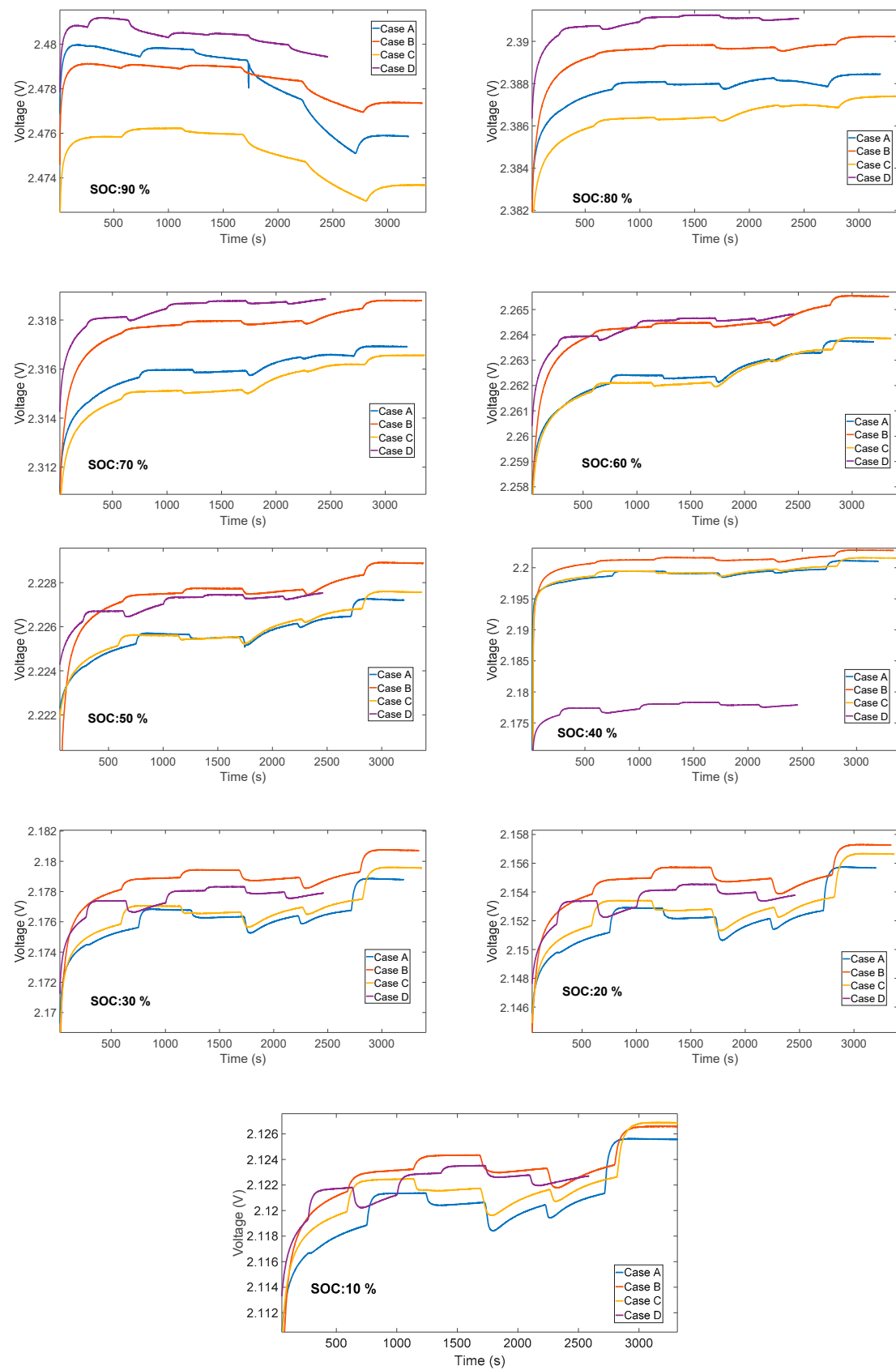
Figure 3. Voltage variations during four cases at various state of charge (SOC).

Table 1. Thermal profiles that were applied to the battery.

Duration				
4 h		**3 h**		**2 h**
Case A	Case B	Case C	Case E	Case D
26 °C	27 °C	26 °C	26 °C	5 °C
4 °C	15 °C	4 °C	4 °C	24 °C
14 °C	5 °C	14 °C	14 °C	10 °C
41 °C	20 °C	41 °C	41 °C	5 °C
55 °C	40 °C	55 °C	55 °C	15 °C
23 °C	15 °C	23 °C	23 °C	25 °C

5.5. Case E

In order to determine the effect of the process before the thermal cycle on the entropic heat coefficient of the lithium titanate oxide battery, experiments were accomplished by both a fully charged and discharged battery cell. After a short rest period, the battery was discharged with 3.25 A current rate with voltage limitation equal and less than to 1.5 V. After a 15-min rest period, the battery cell was charged with 3.25 A current rate with voltage limitation equal to 2.8 V and end type condition for the current, which was equal to 0.52 A. Then, the battery cell was fully discharged with voltage limitation equal and less than to 15 V. After a 15-min rest period, charge current pulses with ten percent state of charge time duration were applied to the battery. For instance, for the first cycle, the cell's state of charge was increased by means of a charging procedure from 10% to 20% and then the thermal process was accomplished, which determined the entropic heat coefficient amount for this last-mentioned state of charge. This process was redone until the battery cell was completely charged for state of charges of 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%.

The thermal process for case E consist of three hours at 26 °C, three hours at 4 °C, three hours at 14 °C, three hours at 41 °C, three hours at 55 °C, and three hours at 23 °C.

Outcomes demonstrated that prior cycling, which consists of charging or discharging cycles, could influence the value of entropic heat coefficient almost the same amount as different thermal cycle. Voltage variations for case E during different SOC levels and experiments are illustrated in Figure 4. It can be seen from the figure that voltage variation for 10% SOC is different compared with others. Entropic heat coefficient at different SOC and cases is shown in Table 2. Entropic heat coefficient of the lithium titanate oxide battery cell as a function of SOC is illustrated in Figure 5. As can be seen from the figure, entropic heat coefficient of the battery demonstrates a similar variation for different cases; in another word, there is a decreasing pattern, which is followed by a decreasing trend for all of them. It is crystal clear from the figure that case E, which is corresponds to the process before the thermal cycle, is much different compared with other cases. Another striking feature for all cases is the great influence of SOC to entropic heat coefficient.

Table 2. Entropic heat coefficient (EHC) (mV/°C) at different state of charge (SOC) and cases.

| SOC (%)	Case A	Case B	Case C	Case D	Case E	Average EHC
10	−0.1115	−0.1098	−0.107	−0.1045	−0.1199	−0.11054
20	−0.0814	−0.0802	−0.0766	−0.0745	−0.0899	−0.08052
30	−0.0562	−0.055	−0.0522	−0.0493	−0.0648	−0.0555
40	−0.0362	−0.0348	−0.0322	−0.0295	−0.0449	−0.03552
50	−0.0234	−0.0217	−0.018	−0.0164	−0.0319	−0.02228
60	−0.0166	−0.0151	−0.0127	−0.0095	−0.0248	−0.01574
70	−0.0184	−0.017	−0.0142	−0.0113	−0.0269	−0.01756
80	−0.0212	−0.0198	−0.016	−0.0145	−0.0298	−0.02026
90	−0.0413	−0.0402	−0.0376	−0.0345	−0.0499	−0.0407
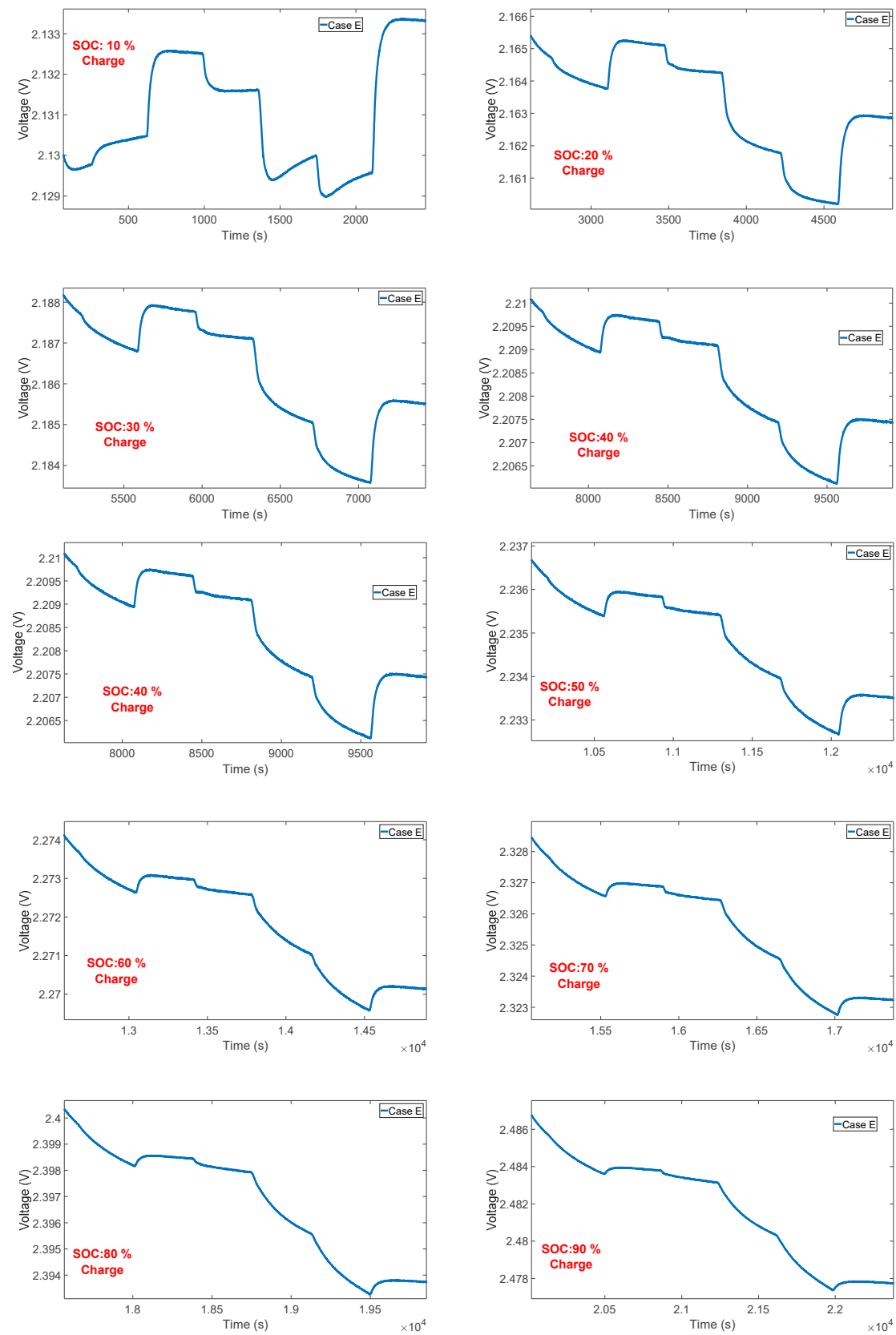
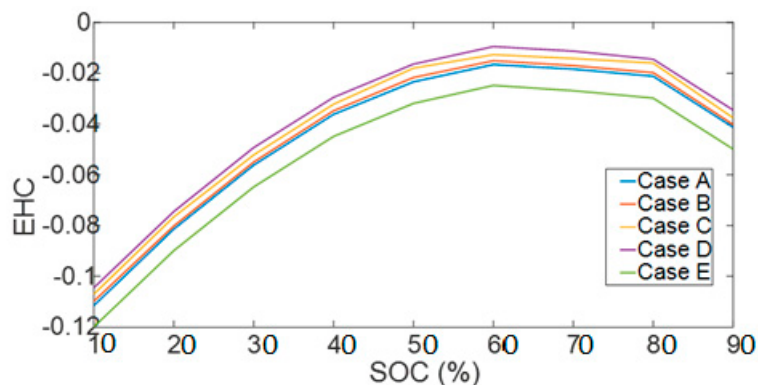**Figure 4.** Voltage variations during case E at various SOC.

Figure 5. Entropic heat coefficient (EHC) (mV/°C) of the battery as a function of state of charge.

6. Conclusions and Future Research

Heat generation inside lithium titanate oxide batteries is a complicated procedure that needs comprehending of how the rates of electrochemical reaction vary with temperature and time. For the researchers, a comprehensive understanding of entropic heat coefficient is essential to construct a precise and practical thermal model. The objective of this research was to analysis entropic coefficient of a lithium ion battery during charging and discharging by employing the potentiometric technique. It was concluded that among different influential parameters, SOC and the process before the thermal cycle have the greatest influence on the entropic coefficient. The thermal cycle and time duration have the lowest influence on entropic coefficient of the battery correspondingly. Thus, the dependence of entropic heat coefficient of the battery cell on the state of charge, thermal cycle, time duration for thermal cycles, and procedure prior to the thermal was confirmed. The collected data will be mapped through curve-fitting to yield the essential equations for future work. In order to relate the entropic coefficient to the voltage, temperature, thermal cycle, and state of charge during charging and discharging, a function will be determined by analyzing the obtained experimental data.

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Conflicts of Interest: The authors declare no conflict of interest.

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