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Electrochemical Performances of NMC811 Lithium-Ion Pouch Cells under Dynamic Conditions

Mahmud TOKUR*[1]

Abstract

Lithium-ion batteries have a wide range of usage areas, from transportation to the defense industry, from daily usage to space applications. The widespread use of consumer electronics day by day also increases the need for this critical strategic technology, which allows us to live at almost every point of our lives without binding factors such as cables. But this technology also has many limitations, which dominate our lives so much that it needs to be overcome. Low cycle life due to poor electrochemical efficiency of electrode materials is one of these limitations. At the same time, energy density constraints are also an obstacle to many technological developments. Therefore, finding new materials with higher capacity and higher cycle life has become inevitable to meet the demands. Moreover, developing novel production techniques suitable for the materials used in the battery is also critical. Cylindrical cells are mostly used commercially in the market due to their easy and fast production technics and relatively safe components. However, the energy density and capacity limit of this architecture pushes the market to use alternative cell designs. There are different cell structures in the lithium-ion battery industry apart from cylindrical cells, such as button type, pouch type, and prismatic type. Among them, pouch cells have rising star geometry due to their unique properties and flexible production style. But many parameters still need to be overcome in pouch cells. In this study, the NMC811 cathode has been selected to investigate some critical parameters in lithium-ion pouch cells. The effects of dynamic conditions such as electrode film thickness, variable temperatures, and current rates on electrochemical performance were analyzed. Finally, a cycle life test was performed on the cell with optimum parameters.

Keywords: Energy storage, lithium-ion battery, pouch cell, NMC cathode

1. INTRODUCTION

The quality of life of living things is becoming poor due to unprecedented ecological degradation depending on many factors such as global warming and pollution. One of the most important reasons for this is the irresistible increase in the use of fossil fuels [1]. Therefore, it has become inevitable to find clean and renewable alternatives to these extremely attractive and harmful energy sources [2]. Over the last two decades, scientists have extensively researched

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batteries as an alternative to fossil fuels. And at this point, the first quarter of this century has been the beginning of an important transition period [3]. In recent years, lithium-ion batteries have been widely used in portable, mobile, and stationary applications, and their designs are being broadened [4, 5]. With the acceleration of technological developments so fast, the demand for electrochemical energy storage systems grew day by day [6]. Increasing energy density, reducing cost, and improving the electrochemical performance of the existing battery technologies are some of the most important efforts to meet the energy needs of commercial electric vehicles [7, 8]. The energy density of the current lithium-ion batteries is changed between 100–265 Wh/kg depending on the cell chemistry, cell type, and cell shape, which are all factors that were chosen for the specific application areas. This performance is still significantly less than that of gasoline. While cell chemistry is responsible for the efficiency of electrochemical reactions, the structure of the cell determines the weight and usage area. Thus, improving both cell chemistry and design is critical to increasing the energy densities of lithium-ion batteries. The elements mentioned above also significantly affect the cost of the cell. The energy sector is trying to reduce the battery costs from $200/kWh to $125/kWh and then $100/kWh, respectively. However, the unfortunate developments, such as the pandemic and Ukraine war between 2020 and 2022, that affect the world negatively, have brought along the increase in raw material prices and production costs, and logistics problems. Therefore, in the shadow of these unexpected developments, battery prices do not look to appear to decrease for a long time. In addition, the unpredictable rapid growth of the electric vehicle industry, and the consequent high demand for batteries, made supply difficult and intensified competition in the market. For all these reasons, it has become a necessity to better understand the current battery technology and to approach the aspects that need improvement more modestly.

In this study, parametric research on the electrochemical performance of commercially available NMC811 cathode in pouch cells has been carried out to understand the key parameters to building better energy storage systems. The most important reason for choosing this pouch type system among geometries such as cylindrical and prismatic is the attractive passion for high energy density. Because pouch cells are lighter than cylindrical and prismatic cells. It is also more likely and possible that they will be adapted to next generation battery operations. This is the first study to compare the electrode thickness, working temperature, and current rates of non-commercial pouch cell prototypes under real conditions. It is believed that this study, which simulates our daily life, will make positive contributions to the literature and the mobility industry.

2. EXPERIMENTAL STUDIES

This study consists of a detailed examination of four main parameters in pouch cells.

(i) Comparison of electrochemical results of the electrodes in different thicknesses in pouch cells, (ii) Investigation of electrochemical performance of pouch cells at different temperatures, (iii) Investigation of the electrochemical performance of the pouch cells at different current rates, (iv) Investigation of electrochemical cycling performance of pouch cells.

A battery consists of some active materials such as an anode, a cathode, and an ion conducting electrolyte. In this paper, the electrolyte is used commercially available 1M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate, diethyl carbonate, and dimethyl carbonate (EC:DEC:DMC) (1:1:1) mixed solution. The anode and cathode electrodes were prepared by the conventional mixing methods using commercial NMC811 and Artificial Graphite (AG) powders.

For the anode preparation process, 94% active material (artificial graphite), 4% binder (Carboxymethylcellulose sodium (Na-

CMC)), and 2% conductive carbon (carbon black (Super-P)) composition was used. To prepare the homogeneous slurry, the CMC binder was first dissolved in deionized water with 4 wt. % concentration in a vacuum mixer and then a selected amount of powders were dry mixed mechanically. Finally, the mixed powders were added into the binder solution and mixed for an additional 2 hours. The obtained slurry was then cast onto 9 μm thick copper foil and coated using a doctor blade (tape casting method). The coating process was applied to both sides of the copper foil. After leaving it for 10 min. in an ambient atmosphere, the drying process was carried out in a tape casting device at 70 °C for 10 h to remove the remaining solvent.

The cathode preparation method is also similar to the anode preparation method. The main difference between the two electrodes is the used materials. For the cathode preparation process, 90% active material (NMC811), 4% binder (Poly(vinylidene fluoride) (PVDF)) and 6% conductive carbon (carbon black (Super-P)) composition was used. To prepare the homogeneous slurry, the PVDF binder was first dissolved in n-methyl-2-pyrrolidone (NMP) with 4 wt. % concentration in a vacuum mixer and then selected amount of powders were dry mixed mechanically. Finally, the mixed powders were added into the binder solution and mixed for an additional 2 hours. The obtained slurry was then cast onto 15 μm thick aluminum foil and coated using a doctor blade (tape casting method). The coating process was applied to both sides of the aluminum foil. After leaving it for 1 h in an ambient atmosphere, the drying process was carried out in a tape casting device at 120 °C for 10 h to remove the remaining solvent. In order to see the differences in electrochemical performances of the cells depending on the cathode thickness, the electrodes were coated as 50 μm, 100 μm, 150 μm, and 200 μm.

The pouch cells were manufactured with the electrodes prepared in the same conditions. The stages of the pouch cell manufacturing process after the electrode preparation step are (i) calendaring to electrodes to decreasing of the porosity, (ii) die cutting of the calendared electrodes in 4,5x5,5 cm dimensions, (iii) vacuum drying of the electrodes to completely remove the remained solvents and humidity, (iv) stacking of the electrodes to separate the anodes and cathodes with an electronic isolator and ion conductive separator (polypropylene (PP)) to prevent physical contact between the anodes and cathodes. They were stacked repetitively in a cycle of anode-separator-cathode-separator-anode with a semi-automatic stacking tool, (v) tab welding using an ultrasonic welding process. Before packaging the pouch cells, copper and aluminum current collectors were contacted with nickel and aluminum cell tabs, (vi) case forming of aluminum laminated film to put stacked electrodes in it, (vii) sealing of the three sides of the aluminum laminated film and electrolyte filling in an argon filled glove box, (vii) vacuum sealing of the electrolyte filled cell to make formation test, (ix) preconditioning and degassing of the cell to teach them the specific electrochemical characteristic. After vacuum sealing, the pouch cells were charged and discharged according to defined current and voltages. Defined charge-discharge potentials are between 2.8V - 4.2V and the current densities are C/20, C/10, and C/5 respectively. The solid electrolyte interface (SEI) layers and gas evaluations form during the first charging and discharging process. The pouch cells were put again in the glove box. The gas was removed from the pouch cells, (x) final sealing, and (xi) aging. For the aging process, the pouch cells were stored at room temperature for up to 3 days before utilizing the battery performance. Digital images of the prepared pouch cells are given in Figure 1. Galvanostatic charging and discharging processes were performed for the parametric electrochemical tests under different conditions of assembled pouch cells.

Figure 1 Digital images of pouch cells

3. RESULTS AND DISCUSSIONS

Undoubtedly, electrode thickness is a very important parameter in determining the amount of active material per unit area. While this parameter directly affects the capacity of the cell, it also indirectly affects the energy density. In other words, as the amount of inactive materials used in the cell increases, the energy density of the cell decreases [9]. Depending on this information, the cathode active materials were cast on both surface areas of the aluminum foil with 50 µm, 100 µm, 150 µm, and 200 µm thicknesses to compare the electrochemical performances by mass loading in approximately 500 mAh capacity pouch cells. These cells were subjected to electrochemical tests under the same conditions and examined from different perspectives.

The electrodes are cast on foils of four different thicknesses. The parameters were analyzed for the cathode (NMC811) parts. The anodes in all the pouch cells used exactly the same conditions. However, the anode side should also be studied, and determined the optimum anode/cathode ratio to get maximum electrochemical efficiency. All the pouch cells are compared in almost equal capacities, that is, approximately 500 mAh. Naturally, some pouch cells had to have more or fewer electrodes. For example, when high-thickness electrodes are used in the cell, the amount of material per unit area increases, and the desired values can be achieved with fewer electrodes. Since this will reduce the amount of inactive materials (current collectors and separators) used, the weight of the cell will decrease and its energy density will increase [10]. Therefore, it is very important to determine the critical coating thickness, especially in applications where weight is very important (such as the aerospace industry).

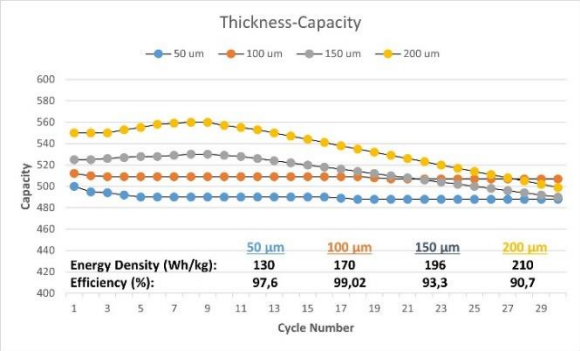

Figure 2 Electrochemical performances of the pouch cells assembled with the electrodes in different thickness

Charge-discharge tests of the pouch cells are performed at C/10 current rate and the capacity efficiencies and energy densities are compared. As shown in Figure 2, the cells were subjected to the charge-discharge test for 30 cycles. The 50 µm electrode exhibited a very stable behavior and showed an efficiency of 97.6%. However, besides this efficiency, the energy density is quite low at 130 Wh/kg. The cell assembled with the 100 µm electrode also showed good stability. At the end of 30 cycles, the cell showed a stable performance of close to 100%, which means almost no capacity loss. The energy density value is at a promising level with 170 Wh/kg. The electrochemical stability of the cell with a thickness of 150 µm electrode decreased when compared to the others. However, the energy density is higher. The 200 µm electrode was performed at the lowest efficiency with approximately 90% stability. However, due to the high coating thickness, the energy density is at the highest level. In fact, the energy densities of the cells were calculated according to their initial capacities.

In other words, the energy density calculation that has been carried out according to the first cycle can be misleading. Therefore, it is even more important to calculate and compare the energy densities of the cells at the end of 30 cycles. In other words, the energy densities of all pouch cells were calculated by multiplying their initial discharge capacity by their nominal voltage, dividing by the total weight of the cell, and compared with the calculated values using the discharge capacities after the 30th cycle. The calculated energy densities of the cells at the end of the 30 cycles are 126.88 Wh/kg, 168.334 Wh/kg, 182.868 Wh/kg, and 190.47 Wh/kg, respectively. According to these calculated values, the electrochemical performance of the cells seems to increase as the coating thickness increases. However, as can be seen from the electrochemical results curves, the gradual decrease in the capacity of the 150 μm and 200 μm electrodes means that it can turn into a disadvantage at high cycle numbers. Therefore, in this study, the optimum coating thickness was found as 100 μm and subsequent analyzes were carried out accordingly. Important note that the key parameter for increasing the energy density of a cell is increasing the ratio of capacity to volume or weight. For this, either a higher capacity should be obtained from a cell of the same volume or weight, or the volume or weight of the cell with the same capacity should be reduced. When it comes to volume and weight, in addition to active materials, the importance of inactive materials that do not contribute to the capacity emerges. Because each component used changes these values. Therefore, in addition to the correct choice of active materials in determining the energy density, the inactive separator, current collector, assembling geometry of the cell, and packaging materials also play an important role.

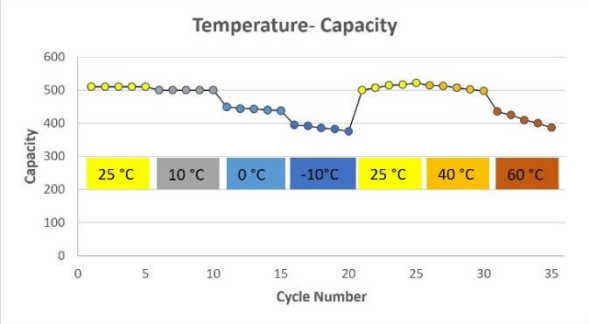

Figure 3 Electrochemical performance of pouch cells at different temperatures

The dynamic conditions mentioned above are also studied in this section. The electrochemical performance differences of the pouch cells in variable seasonal conditions were determined by air-conditioning tests. The electrochemical performances of the pouch cells assembled for this aim were performed at -10 °C, 0 °C, 10 °C, 25 °C, 40 °C, and 60 °C temperatures, assuming room temperature as 25 °C. In fact, the biggest improvements that should be realized in this parameter are on the electrolyte side. Because the main factor affecting the temperature-dependent performance of a cell is the stability of the electrolyte [11]. Nonetheless, the climate tests of the pouch cells are still an important step to see the electrochemical character of the batteries at selected temperatures even if used the same aqueous electrolyte. Because most electronic devices have standard aqueous lithium-ion batteries, they are used in dynamic weather conditions. Figure 3 shows the electrochemical performance results of the pouch cell versus the dynamically changing temperature parameter. The cell assembled with a capacity of approximately 500 mAh/g was subjected to the charge-discharge test at room temperature at a current rate of C/10. Testing intervals vary between -10 and 40 °C depending on the temperature values that are likely to be encountered around the world. However, in some cases, the temperature of the cells may rise abnormally due to the sudden increase in the current rate. Therefore, an additional 60 °C temperature value was added to the electrochemical tests. As expected, when temperatures begin to decrease or increase from standard conditions, variations in the

cell's capacity can be seen. However, depending on the obtained results, it managed to preserve approximately 75% of the cell capacity even under the most adverse conditions, which is a very promising result for safety. However, polymer gel electrolytes or solid electrolytes that can remain more stable at variable temperatures can be developed in order to minimize capacity losses [12].

Another parameter affected by electrolytes is the current density. As it is known, since electronic devices are multifunctional, the power needed from the system changes with the activation of each function. Human beings lead a very dynamic life, which is more attractive and sustainable rather than staying in fixed environments. Similarly, battery-powered electronics are also mostly used dynamically. Therefore, the current rate of the cells plays a very important factor to keep the energy stable in need. For example, when a mobile phone is in standby mode, the current need is minimal, and the battery produces low energy. However, when more than one function is used together in this phone, much more current requirements will occur, and the battery must produce a high amount of energy. Even this situation causes the phone to overheat from time to time as a result of producing high energy by the battery. This issue prevents the standard performance of the battery life and can pull the lifeline down [13]. In order to determine the performance behavior of the cells used in such dynamic conditions, electrochemical tests were analyzed at different current densities in this study. The tests were carried out in variability starting from C/10 current rates and then performed at C/5, C/2, C, 2C, and 5C, respectively. The C value corresponds to the capacity value consumed in 1 hour. In other words, the 1C value in a 1 Ah cell is the 1A current rate. Eventually, the cell will be charged and discharged within 1 hour.

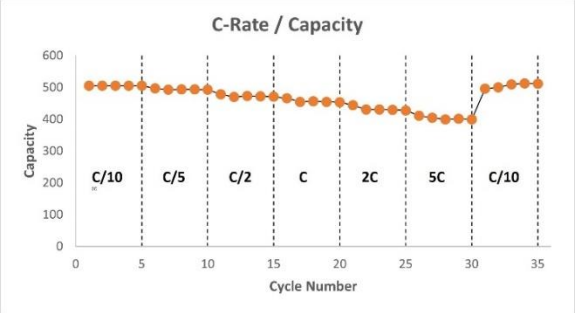

Figure 4 Rate capability of the pouch cell

It is very important to know how the cell behaves at different current densities. Because, depending on the desired features, it would be possible to increase or decrease the capacity that arises. For example, when a 10Ah battery is used for a drone that requires a 10A current, it is a possibility that the drone will stay in the air for approximately 1 hour. However, the activation of the wind during use, frequent maneuvering, or the use of extra features such as a camera will increase the amount of current needed. This time, higher current densities will need to get from the battery. Considering such conditions, current density tests are important in order to estimate how long the battery can be used in different conditions. The electrochemical performance values of a cell cycled at different current densities can be seen in Figure 4.

A cell prepared with a capacity of approximately 500 mAh was subjected to the charge-discharge test at C/10 current rate. For five cycles, the cell showed a stable capacity of 500 mAh. Afterward, the current rate was doubled to C/5 and the test was continued for five more cycles. Despite the doubling of the current rate, there was no significant decrease in the cell's capacity. Subsequently, in the cell, which was subjected to five cycles of charge-discharge tests at C/2, C, 2C, and 5C current rate, respectively, decreases in capacity were observed with the increase in the current rate, as expected naturally, but this decrease is not such a serious degree. In other words, the cell was able to protect 80% of its capacity even at the maximum current rate (5C). Afterward, by reducing the current rate to C/10 again, the capacity of the cell reached

back to about 500 mAh as it was at the beginning.

There is a direct relationship between current density and ionic conductivity in a cell. The higher ionic conductivity in the electrochemical cell leads to able to have a higher current density in the cell. Liquid electrolytes have relatively low ionic conductivity when compared to gel or solid electrolytes. In addition, liquid electrolytes may face some risks such as decomposition and fired in the cases of temperature increases at high current densities. Therefore, polymer or solid electrolytes are generally suggested to use when a high current density is desired. Although polymer electrolytes have been used commercially, the applications of solid electrolytes have not been widely encountered yet. Moreover, the discharge capacity of the cell drops at the higher C-rate. With more passivation of the electrode surfaces at high C-rates the resistance of the cell increases which leads to reaching the discharge cut-off voltage limit earlier, and because of that, the available discharge capacity is lower.

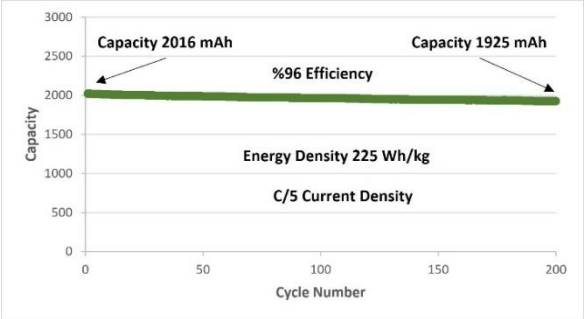

Figure 5 Cycle performance of a pouch cell at C/5 current density for 200 cycles

Considering the parameters optimized so far, 100 μm electrodes were prepared and a pouch cell of approximately 2000 mAh was assembled for a life cycle test. In order to see the capacity loss depending on the number of cycles, charge-discharge tests were carried out at an ambient temperature of 25 °C at a current density of C/5, that is, 400 mA, for 200 cycles. The electrochemical performance values of the cell can be seen in Figure 5. The initial capacity of the pouch cell was determined as 2016 mAh. In addition, the energy density of the pouch cell based on the initial capacity was calculated as 225 Wh/kg, which is quite promising for state of the art lithium ion batteries. A serious decrease in the cell's capacity was not observed depending on the number of cycles. Finally, the cell showed an efficiency of 96% after 200 cycles and was able to maintain its 1925 mAh capacity.

4. CONCLUSIONS

The electrochemical performance of pouch-type cells, which is widely used today and is a suitable geometry for next-generation batteries, was investigated parametrically in this study. The NMC811 cathode, which is described as the most efficient in terms of capacity and energy density, was chosen as a variable parameter in the cell. The analyzes performed were reflected in the study according to the variability of daily life. Indeed, a systematic guide has arisen from intracellular factors, such as comparing the electrodes of different thicknesses, to extracellular factors, such as using the cells at different current rates and different temperatures. It is believed that this study will contribute to the battery optimization of current and future electric vehicle technologies.

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The Declaration of Conflict of Interest/ Common Interest
The author has declared no conflict of interest or common interest.

Authors' Contribution
The author contributed fully to the study.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The author of the paper declare that he comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that he does not make any falsification on the data collected. In addition, he declares that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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