The Pennsylvania State University

The Graduate School

# EXPERIMENTAL STUDY OF LITHIUM-ION CELLS WITH HIGH LOADING NMC622 CATHODE AND NMP-FREE PROCESS

A Thesis in

Mechanical Engineering

by

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Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science

August 2019

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#### ABSTRACT

A set of lithium-ion pouch cells consisting of thick NMC622 cathodes with high loading (~21.65 mg/cm<sup>2</sup>) and graphite anodes (~12.1 mg/cm<sup>2</sup>) were tested under C/3 and 1C cycling. Three different cathode coatings utilized binder with NMP-free process is developed. The aim of this study is to investigate the cycling performance of such cathodes compared to the baseline cathode with NMP-PVDF binder. NMP-free and NMP-PVDF based cells have discharge capacity retention of 87.9% and 88.7% after 600 cycles, respectively. The cycle life for both groups is expected to reach more than 1000 cycles at C/3 cycling. Fresh and aged cells were characterized by various techniques, including C-rate test, electrochemical impedance spectroscopy (EIS), direct current resistance (DCR) test. The NMP-free cells were found to have larger resistance than the NMP-PVDF cells, and the significant increase of resistance on the cathode side of which also found from the EIS measurement. Moreover, it is found that the rate capability became poor after 600 cycles, especially for cells with NMP-free binder at higher C-rate. Further improvement is required for a high loading lithium-ion battery with the NMP-free binder, focusing on getting high energy density with good rate capability and longer cycle life of LIB.

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# **ACKNOWLEDGEMENTS**

I would first express my sincerest thanks to my advisor, Dr. Chao-Yang Wang, for giving me the opportunity to work on this project. I am grateful for his support and patience throughout the thesis process. His leadership and insights toward research have helped me learn much more than I've ever imagined. I would also like to thank Dr. Donghai Wang for agreeing to be my thesis reader. I gratefully acknowledge the financial support from PPG for this work.

Secondly, I would like to thank our group members in Electrochemical Engine Center: Shanhai, Yongjun, Ryan, Teng, Jianan and Jinyong. They have given me insightful advices and help throughout the time I work in ECEC. I would also like to thank my friends in State College for their help and support.

Last but not least, I would like to thank my parents and my brother for their support, encouragement and love during my master's program at Pennsylvania State University.

# Chapter 1

# Introduction

Since the first Li-ion battery was launched in the market by Sony in 1991, the rechargeable Li-ion battery (LIB) has become one of the most utilized electrochemical storage devices in our daily life. Li-ion batteries have been applied in a wide variety of division from the small portable electronics to automotive applications. As the electronic devices gets smaller, such as cell phones, tablets and laptops, LIB has become an ideal candidate in these portable devices due to its lightweight and high energy density. On the other hand, as the environment issues are noticed by more and more countries around the globe, reducing the greenhouse gas (GHG) emission, carbon dioxide (CO<sub>2</sub>), has become one of the important consensuses to slow down the global warming effect. A large portion of pollution sources come from the transportation sector. The conventional gas-powered car burns fossil fuel, resulting in large amount of GHG emit into the atmosphere. In order to gradually reduce our demand on fossil fuel in transportation sector, much more people nowadays move their attention to electric vehicles industry and see it as the sustainable solution for our environment around the world.

With the high demand for sustainable environment and the development of Li-ion battery, researchers have delved into the electric vehicle application for the past decade, from hybrid electric vehicles (HEV) and plug-in electric vehicle (PHEV) to the electric vehicles nowadays (EV). One of the most common battery types applied in today's EV is Li-ion battery, and thus the growth in EV demand has led the Li-ion battery to a greater potential in the market. This automotive application is feasible because of its high energy density and good service life. Moreover, the cost-effectiveness of electric vehicle is expected to improve significantly in the near future [1].

#### 1.1 Background to LIB

Over the past decade, the Li-ion battery has become the dominant electrochemical energy storage in commercialized electric vehicles due to their numerous benefits, such as light weight, high energy content, low self-discharge rates. Thus, in the current industry, most of the companies choose to use the Li-ion battery for manufacturing their electric vehicle, from BMW, Tesla, Honda, to Toyota, etc.

LIBs are composed of three main parts: positive electrode (aluminum foil as current collector), negative electrode (copper foil as current collector) and the electrolyte. In between the positive and negative electrode, there is a separator to prevent the short circuit occurred in the cell. Different configurations such as cylindrical, prismatic and pouch cells are designed for various uses. In a battery system, a single cell is used, or several cells are connected in series or in parallel. In addition, it is often equipped with a battery management system for controlling purposes.

Unlike other conventional electrochemical rechargeable batteries, the electrochemical mechanism in a LIB is called intercalation, which means the lithium-ion migrates back and forth between the electrodes during charging and discharging and are intercalated into the active materials. In the reduced state, the lithium-ions are stored in between layers of electrodes. Upon oxidation, the lithium ions are transported into the electrolyte and migrate to the electrode on the other side, where the reduction process reinserts lithium ion between the electrode layers [2].



Figure 1-1: The intercalation mechanism in a Li-ion battery (shown in the discharging process) [2]

The traditional positive electrode material of a LIB is lithium cobalt oxide, LiCoO<sub>2</sub>, with a layered structure. It has been used in small portable electronics for many years. However, due to the high cost of cobalt and safety concern [3], efforts are put into the development of alternative electrode materials for future EV application. Table **1-1** gives several commercial cathode materials for LIB. Among them, the nickel manganese cobalt oxide (NMC) has become one of the most promising class of cathode active materials. Nowadays, the commercial NMC111 is continuously altered toward high nickel content for reducing cost and acquiring higher capacity.

Table 1-1: Several alternatives for cobalt oxide in market

Compound	Abbreviation	Chemical Structure
Manganese Oxide	LMO	LiMn <sub>2</sub> O <sub>4</sub>
Nickel manganese cobalt oxide	NMC	LiMi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub>
Nickel cobalt aluminum oxide	NCA	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Iron phosphate	LFP	LiFePO <sub>4</sub>

Lithium metal is used as anode initially with its high specific capacity (3860mAh/g) and large negative potential. However, it is only used in coin cell nowadays, since the lithium can be deposited as dendrite, which will grow through the separator and then lead to short circuit in the cell. Today, the most common active material of anode is graphite carbon, which is a lithium interaction material. During charging the lithium ions are intercalated into graphite between its layers while during discharging lithium ions go to the opposite direction [2].

In addition to the active material on the electrode, binder is required to hold the active material adhesive with the current collector. In the conventional Li-ion battery manufacturing process, the use of polyvinylidene fluoride (PVDF) binder with N-methyl-2-pyrrolidone (NMP) solvent is the most common technique, especially in cathode. However, the NMP solvent is toxic, so alternatives are developed to eliminate the use of solvent by a water-soluble binder, such as styrene-butadiene rubber (SBR) or new fabrication method. On the other hand, for the anode, it is found that styrene-butadiene rubber/carboxymethylcellulose (SBR/CMC) binder system performs better than PVDF binder on anode [4].

LIB use nonaqueous organic solvent as their electrolyte. Unlike other rechargeable batteries, Li-ion cannot use aqueous electrolytes since its operation will be well outside the decomposition potential of water. Instead, carbonates are used. Propylene carbonates (PC) is initially applied in the LIB. By far, the use of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) is more common in the industry.

#### **1.2 Study Objective**

In this study, pouch cells with high loading electrode that utilize graphite and NMC622 as active material for anode and cathode are fabricated and tested. This study will focus the discussion on the performance of different cathode coating types. The baseline cathode with NMP-PVDF binder, is compared with several cathode coating with NMP-free binder. These cells are characterized under several tests to evaluate their performance. The main obstacle for the cell performance and cycle life is believed to be the resistance and transportation of ions due to thick cathode. The expecting performance and overall goal for this study is to acquire capacity retention above 85% of its initial C/3 capacity after 300 cycles at C/3 rate cycling. The 80% retention can be seen as standard cutoff line for an effective cell. The testing data will be analyzed and provide an insight for the future research on high loading electrode.

## **1.3 Thesis Outline**

The thesis begins with the introduction of lithium-ion battery, followed by the literature review of the previous studies, regarding the nickel-rich NMC cathode, high loading electrode, and the aging mechanism of the battery. Next, the experiment facility and testing procedure is presented. Then, the results are discussed, followed by the final conclusion of the study.

#### Chapter 2

# **Literature Review**

This chapter will discuss about the previous studies regarding the nickel rich cathode material in LIB, then the studies in high loading cell, and last, the aging mechanism of the lithium ion battery.

## 2.1 Nickel-rich NMC Cathode

The layered lithium nickel-rich manganese and cobalt-containing oxides, usually termed NMC, have been widely used as cathode active material for EV batteries nowadays. Great effort has been made toward on the synthesis of NMC materials [5][6]. Among these layer structured materials,  $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$  (NMC111) has already been commercialized for automotive application. However, NMC111 will not meet the requirement for next generation EV applications, since its specific capacity of ~155 mAh/g is quite low [7]. In addition, reducing the Co content in the electrode is preferable, since Ni is much more cost-effective than scarce Co material.

Thus, in order to supply the increasing EV applications demand and lower the cost, new materials of nickel-rich NMC (Li(Ni<sub>X</sub> Mn<sub>y</sub> Co<sub>Z</sub>)O<sub>2</sub>) (x+y+z = 1,  $x\geq 0.5$ ) is developed. Among them, Li(Ni0.6Mn0.2Co0.2)O<sub>2</sub> (NMC622) and Li(Ni0.8Mn0.1Co0.1)O<sub>2</sub> (NMC811) are the most common candidate for Ni-rich cathode recently. It delivers higher capacity than NMC111 due to the higher nickel content which is the main active redox species (Ni<sup>2+</sup>  $\leftrightarrows$  Ni<sup>4+</sup>) in the host structure [8].

However, there is a trade-off between capacity and thermal stability of NMC cathodes. Noh et al. [9] reported that a linear decrease in the thermal stability is found when the discharge capacity is raised as the Ni content increases. In addition, the capacity retention is reported to have poor performance as the Ni content increases, as higher surface reactivity result in shorter cycle life. Moreover, the rate capability of Ni-rich cathode is reported to have worse performance when compared to structure similar NMC111 [10], which is due to lower electronic conductivity from less Co content in the Ni-rich NMC cathode.

#### 2.2 Development of Thick Electrode

Increasing electrode thickness is an effective way to achieve high energy densities for a LIB. In addition, the use of thick electrode gives the possibility to reduce the production cost [12]. Several studies have reported the effect of thick electrode. Zheng et al. [11] studied the cell with NMC111 cathode and LFP anode of different active material loading. They observed that enhanced energy densities from increasing the thickness of electrode is accompanied by a significant loss of power density. Singh et al. [12] prepared single-sided 70µm and 320 µm NMC 111 and graphite anode cells. The pouch cell with thicker electrodes show 19% higher volumetric energy density at C/5 in comparison to thin electrode. In addition, thick electrode only shows good performance at medium to small C-rate.

Danner et al. [13] modeled the experimental study from Singh et al. [12] with 3D microstructure resolved simulations, and it showed good agreement, which provided an insight into limiting factors for thick electrode cells. They found at high C-rate the limitation of lithium ion transport is attributed to significant loss in capacity. Small inhomogeneities in carbon black distribution did not affect the performance of electrode. Another numerical modelling was conducted from Du et al. [14] to study the energy-power density relationship. The energy density was found to have a maximum point versus electrode thickness (critical thickness) at given discharging C-rates. Also, cell polarization and active material underutilization were found to offset the advantage of high-volume ratio of active materials in thick electrodes.

Lee et al. [15] studied the rate limitation for high loading electrode > 25g/cm<sup>2</sup> under C/3 and 1C.They found the galvanostatic charge/discharge behaviors at high rate and the cycling performance at C/3 rate are more closely related to the electronic conductivity than the ion conductivity. Heubner et al. [16] investigated the effect of thickness and porosity for NMC622 cathode for high energy cell. Batteries with thicker electrode increase specific ohmic, charge transfer and contact resistance while reducing the effective Li-ion diffusivity in the electrolyte. Reducing the porosity increases the specific ohmic and charge transfer resistance while reducing the contact resistance and the effective Li-ion diffusivity in the electrolyte.

## 2.3 Cell Aging Mechanisms

Battery aging, increasing cell impedance, capacity decay and power fade comes from multiple and complex mechanism, and it is also strongly dependent on the operating conditions. For carbon electrode, ageing effect is mainly attributed to changes at electrode/electrolyte surface, which is the solid electrolyte interphase (SEI) formation and growth [17]. In the first few cycles for cycling, there is a large irreversible capacity loss due to SEI layer formation, resulting in a decrease in initial capacity. The SEI layer continue to grow during the long-term cycling, which usually consume not only electrolyte, but also active, cyclable lithium, thus leading to capacity fade for the LIB [18].

As the long-term cycling proceed, lithium plating and lithium dendrite tends to form and eventually result in malfunction of the batteries. The lithium metal will deposit on the SEI surface of the anode during charging, which is often occur in low temperature (below 25 °C) and high charging rate. When the lithium deposit and dendrite continue to grow between the anode and separator, a short circuit create and eventually result in thermal runaway and battery failure [17][19].

Several studies have utilized model-based analysis to simulate battery ageing processes [20] [21] [22]. Yang et al. [23] modeled the aged cell induced by SEI and lithium plating by a transition model from linear to non-linear. Cell aging is found to be linear with the cycle number at the early stage of cycling, meaning the capacity loss linearly with a slightly resistance increase. In addition, SEI is found to be the dominant ageing mechanism in this early stage. As the cycling proceed, lithium plating is triggered and the cell ageing transit from linear to highly nonlinear. The dramatic increase in lithium plating rate result in rapid loss of lithium inventory and significantly rise in resistance at the later stage of LIB cycle life.

Moreover, for the cycle life performance for NMC cathodes, Zheng et al. [11] reported the long-term cycling performance for thick NMC111 and found that the performance is largely deteriorated, which is attributed to the high internal resistance and poor mechanical integrity of thicker electrode. Ma et al. [24] investigated the rollover failure of cycling NMC532/graphite pouch cell. They found the impedance growth after rollover completely originated from the positive side while the negative side did not change at all. Also, by lowering the electrode loading can delay the occurrence of rollover. Jung el at. [25] studied the aging phenomena and of NMC111, NMC622 and NMC811. The capacity fades of these cells are found to be due to significant increase in the polarization of NMC cathode while the polarization of anode remained rather constant. In addition, the highest specific energy of ~650mWh/g<sub>NMC</sub> with a stable cycling at 1C was obtained at a high voltage of NMC622-graphite cell cycled up to 4.4V.

# 2.4 Motivation of this Study

As the demand for electric vehicle is getting higher for the next decade, higher energy densities and more environmentally friendly lithium-ion battery need to be developed. Therefore, in this study, a set of pouch cells that utilized cathode of high loading NMC622 as active material with NMP-free binder are prepared and compared with the performance of baseline cells that use NMP-PVDF binder.

# Chapter 3

# **Experimental Design and Method**

# 3.1 Cell Design

A total of 21 pouch cells were prepared for performance evaluation. These cells were made from combinations of different types of cathode and anode. There are five types of NMC622 cathode and three types of graphite anode to be used in the pouch cell fabrication. Table **3-1** shows the properties of the positive electrodes, and Table **3-2** shows the properties of the negative electrodes. The total thickness for double-sided electrodes (including Al and Cu foil) is  $175\sim180 \ \mu m$  and  $195 \ \mu m$ , for positive and negative electrodes, respectively. Note that the thickness of MU anode is only  $130 \ \mu m$ .

Cathode Name	Active Material Loading (mg/cm <sup>2</sup> )	Approximate areal capacity (mAh/cm <sup>2</sup> )	Binder System	Formula (AM:CA:B)
P1	21.6	3.69	NMP-PVDF	93:03:04
P10	21.1	3.61	NMP-free	93:03:04
P11	20.8	3.55	NMP-free	93:03:04
P25	19.5	3.33	NMP-free	93:03:04

Table 3-1: The detailed properties of positive electrode design

Table **3-2:** The detailed properties of negative electrode design

Anode Name	Active Material Loading (mg/cm <sup>2</sup> )	Approximate areal capacity (mAh/cm <sup>2</sup> )	Binder System	Formula (AM:CA:B)	
M1	12.1	4.24	CMC/SBR	96.5:0.5:3	
M6	12.1	4.24	CMC/SBR	97:00:03	
MU	11.1	3.89	CMC/SBR	N/A	

The active material loading is the prescribed value and the approximate areal capacity is determined based on measurement of the total area-specific mass of electrode multiplied by the mass fraction in the electrode formula, then convert it to areal capacity by applying a specific capacity of 171 mAh/g for NMC622 and 350 mAh/g for graphite. Besides from P1 cathode utilized NMP-PVDF binder, other cathode binders used the NMP-free process instead. As for the anode binder, SBR/CMC binder is utilized, and the SBR/CMC ratio is maintained at 1:2. Note that graphite anode M1 and graphite anode M6 are very similar, with only a slightly difference in the formula, thus, in this study, it is seen as the same type of anode.

Six cell types were fabricated from these different types of positive and negative electrodes. The separator is 25  $\mu m$  in thickness, and the electrolyte is 1.0 M lithium hexafluorophsphate (LiPF6) dissolved in ethylene carbonate (EC): ethylmethyl carbonate (EMC) (3:7 by wt. with 2% vinylene carbonate). The design discharge capacity are approximately 2.57 Ah and 2.29 Ah for the cells with 9 cathode layers and 8 cathode layers, respectively. The calculation of design capacity for 9 cathode layers is shown as Equation **3-1**.

$$Q_{\text{design}} = 9 \text{ layers } \times \frac{2 \text{ sides}}{1 \text{ layer}} \times \frac{40.56 \text{ cm}^2}{1 \text{ side}} \times 20.65 \frac{\text{mg}_{\text{NMC622}}}{\text{cm}^2} \times 171 \frac{\text{mAh}}{\text{g}} = 2.57 \text{ Ah}$$
 (3-1)

The approximate N/P ratio (where "N" is the negative electrode, or anode during cell discharging and "P" is the positive electrode, or cathode during cell discharging) in Table **3-3** is calculated from the areal capacity in Table **3-1** and Table **3-2**. Using the value of areal capacity of negative electrode divided by the corresponding value of the positive electrode. All N/P ratios in Table **3-3** are above 1.1, which aids to prevent the lithium plating at the graphite anode [26], except P1-MU cell has only 1.05 N/P ratio, the impact of this low ratio will further be discussed in the following chapter.

Cell Type	Electrode (positive-negative)	Cell Count	Design Capacity (Ah)	N/P ratio
Type 1	P1-M1	2	2.57	1.15
Type 2	P1-MU	4	2.29	1.05
Type 3	P10-M1	2	2.57	1.17
Type 4	P11-M1	3	2.57	1.19
Type 5	P25-M6	3	2.29	1.27
Туре 6	P25-MU	4	2.29	1.17

Table 3-3: Pouch cell names and its properties

# **3.2 Experiment Facility**

The fabricated pouch cells were connected to testing station as Figure **3-1**(a), cell holders were used as the base plate in order to prevent the short circuit during operating. An environmental chamber was used to maintain the testing condition at 30 °C at all times, see Figure **3-1**(b). Then a multichannel Arbin battery testing system (Model: BT 2000 with 32 channels, Arbin Instrument, USA) was used as show in Figure **3-3**. In addition, the Solartron Modulab XM ECS, Figure **3-4**, was utilized for measuring the impedance of the pouch cells.



Figure **3-1:** (a) The connection of the pouch cells on the cell holders. (b) The environmental chamber



Figure **3.2:** The Arbin testing station with 32 channels used in this study.



Figure **3-3**: (a)The Solartron Modulab XM ECS testing machine (b) the connection with testing pouch cell

#### **3.3 Testing Procedures**

Formation cycles were made before starting to characterize the cell. The purpose of which is to format a protection layer on the graphite anode, which is called a solid electrolyte interphase (SEI) layer. The SEI layer is found to be essential for the system performance, especially for the long-term cycling [27]. SEI can preserve the structure of the cell assuring their high capacity and good cycling ability.

#### 3.3.1 Characterization Test

The following three characterizing test were performed for the fresh pouch cells and then repeated for each 200-cycle increment. They are C-rate test, electrochemical impedance spectroscopy (EIS), and direct current resistance characterization (DCR).

For C-Rate testing, the cell was charged to 100% SoC using constant current/constant voltage (CCCV) standard charging protocol. The charging rate was C/3 until the upper voltage of 4.2V was reached, then held at voltage of 4.2V until the cutoff current C/20 was measured. After resting for 30 minutes, the cell was discharged at a given C-rate until reached down to a cutoff voltage of 2.8V. The cell was rested for another 30 minutes to start the next charging C/3 cycle. The discharge C-rates were applied in the following order for each testing cycle: C/10, C/5, C/3, 1C, 2C and 3C, as shown in Figure **3-4**. This test was conducted at 30 °C in an environmental chamber.



Figure 3-4: The current and voltage profile for c-rate test.

Next, the cell was connected to the Solartron machine to measure the EIS impedance. Before making measurement, the cell with 90% state of charge (SOC) rested for an hour. The frequency was swept from 0.01 Hz to 50k Hz with a 5mV AC perturbation, which is a wide range enough to cover pertinent time step scales associated with various transport and charge transfer process in the cell. All EIS tests were conducted at 25 °C.

EIS is an effective technique to study the dynamics and properties of materials and electrochemical systems such as batteries and fuel cell [28]. Impedance is a measure of the ability of a circuit to resist the flow of electrical current. By applying a small sinusoidal current of fixed frequency, a response is measured and compute the impedance. Repeat for a wide range of frequencies. The measured impedance is calculated from Equation **3-1** at each frequency.

$$Z_{\omega} = E_{\omega}/I_{\omega}$$
(3-1)

where  $E_{\omega}$  is the frequency-dependent potential and  $I_{\omega}$  is the frequency-dependent current.

A Nyquist plot of EIS test example is shown as Figure **3-5** with frequency range from 0.01 Hz to 50k Hz and 90% SOC of a Li-ion pouch cell. The low frequency area close to a straight line represents the diffusion phenomenon in the cell. A semi-circle in the middle frequency typically represents the charge transfer resistance at the electrode surfaces. In the high frequency region, typically is above 1kHz, there is a curve intersect with abscissa axes, which reflects the battery inductance and ohmic resistance from current collector and wire.



Figure 3-5: The Nyquist impedance plot for a LIB,  $Z_{total} = Z'+Z''$ .

EIS data is usually fitted by equivalent circuit model, which can be compared with the actual EIS measurement of the LIB. One of the most widely used equivalent circuit model for LIB is Randles circuit [30], the simplified circuit is shown in Figure **3.6** (a). However, in real system, these idealized circuit elements are inadequate to model electrochemical charge transfer and double layer capacitance due to the spatial distribution of these processes [28]. Thus, a constant phase element (CPE), which is independent of frequency, is usually used to replace  $C_{dl}$  for a Li-ion cell. Table **3-4** presents the commonly used circuit element in the model. For CPE

impedance, where Q is a constant,  $\omega$  is the radian frequency and  $\alpha$  is usually range from  $0\sim1$ , (if n=1, an ideal capacitor, if n = 1, a resistor)



Figure **3-6**: (a) The simplified Randles circuit [29], (b) The modified circuit with CPE [30].

Tab	le <b>3-4</b> :	The	element	used	in t	he circuit.	
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<b>Equivalent Element</b>	Impedance
R	R
С	1/j@C
L	jωL
Q (CPE)	$1/Q(j\omega)^n$

The last characterization is the direct current resistance test (DCR), the cell was discharge to 50% SoC and then rest for 1 hour. A pulse discharge rate of 5C was applied for 10 seconds followed by a 40 seconds rest and then a pulse charge rate of 3.75C was applied for 10 seconds. Charge and discharge rate were calculated using Ohm's law as Equation **3-2**.

$$R = \frac{V_{\text{final}} - V_{\text{initial}}}{I}$$
(3-2)

where the  $V_{\text{final}}$  denotes the cell voltage at the end of current pulse, and  $V_{\text{initial}}$  denotes the cell voltage before the current passed through the cell. The current I represent the given pulse current applies to the cell and the discharge current is in negative sign. All pouch cells were tested at 30 °C in the environmental chamber.

# 3.3.2 Long-Term Cycling Test

After the characterization part, the fresh cell started to do the cycle test. For each type of cells, 1~2 cells were subjected to cycle at the rate of C/3, while the rest of the cells were cycling at rate of 1C for a quicker overview of the cell performance. The standard protocol is used as follows: CCCV at rate of C/3 or 1C with the upper cutoff voltage of 4.2V and cutoff current of C/20. The cell then rested for 5 minutes. Next, discharge at a rate of C/3 or 1C until the cutoff voltage at 2.8 V followed by a rest for 10 minutes. This accounts for one cycle, and the whole procedure was repeated until the next characterization test scheduled at next 200-cycle increment. Note that only cells cycling at C/3 were taken to do the characterization test. In addition, since the C/3 capacity represents the "true" discharge capacity of a cell, a C/3 cycle is performed to the 1C cycled cells at every 200 cycles.

## **Chapter 4**

# **Results and Discussion**

#### 4.1 Initial characterization of fresh cells

A set of 22 NMC622/graphite high loading pouch cells were prepared and screened in this study. This chapter will present and discuss the result from the experimental method that described in the previous section. In order to get the early stage evaluation of each cell types, three characterization methods were applied to the pouch cells.

# 4.1.1 Initial C-rate characterization

The c-rate testing result for 6 types of pouch cell is shown in Figure **4.1** with the discharge capacity that normalized by C/10 value as the vertical axis because of the different layers used of cathode between types, with the corresponding discharge c-rate as the horizontal axis.



Figure **4-1**: The beginning-of-life (BOL) performance of 6 types of pouch cells based on different C-rate discharging from C/10, C/5, C/3, 1C, 2C, and 3C.

Туре	Electrode (cathode binder system)	Discharge Capacity (mAh/g)	C/5	C/3	1C	2C	<b>3</b> C
1	P1-M1 (NMP-PVDF)	177.23	0.982	0.960	0.874	0.777	0.466
2	P1-MU (NMP-PVDF)	149.23	0.951	0.891	0.727	0.530	0.404
3	P10-M1(NMP-free)	168.21	0.985	0.974	0.894	0.672	0.363
4	P11-M1(NMP-free)	179.61	0.995	0.982	0.928	0.744	0.423
5	P25-M6(NMP-free)	156.64	0.990	0.978	0.923	0.697	0.449
6	P25-MU(NMP-free)	149.41	0.935	0.876	0.711	0.536	0.411

Table **4-1** The C-rate result all cells type at BOL.

The normalized discharge capacity on the y axis in Figure **4-1** is calculated by using the discharge capacity at a certain c-rate divided by the discharge capacity at C/10, the discharge capacity with normalized data are shown in Table **4-1**. The results show that there are two distinct groups of trend at low c-rates, from C/5 to C/3, the discharge capacity of P1-M1, P10-M1, P11-M1and P25-M6 have similar performance (>96%), whereas P25-MU and P1-MU performs worse and retains only ~87% (C/3 rate) of their C/10 discharge capacity. Thus, P25 and P1 with MU anode show a relatively poor performance than usual. On the other hand, for the high c-rate performance, larger difference can be found between each type. Among them, P1-M1 have the best performance at high C-rate, with 77.7% and 46.6% at 2C and 3C, respectively.

However, based on the standard effective capacity retention of 80%, one can find that all of these thick electrode cells have poor performance when running at high c-rate (>2C), which may be limited by ion diffusion in the electrolyte. At high C-rate, the limitation of lithium ion transport is attributed to significant loss in capacity.

#### 4.1.2 Initial EIS characterization



Figure 4-2: The beginning-of-life (BOL) impedance from EIS testing results for 6 types of pouch cells.

Next, looking into the EIS testing for fresh cells, the measured impedance results for all fresh cells at 90% SoC are shown in Figure **4-2** with a Nyquist plot, both axes are normalized with electrode area. The intersection of the data with the abscissa corresponds to the pure ohmic resistance and the inductive area of impedance spectrum. If there is a single arc, it is simply attributes to the lumped charge transfer resistance. When there are two arcs, the first arc is said to represent the resistance due to the passivated film that develop on the cathode active materials, while the second arc represent charge-transfer resistance from both electrodes, mainly cathode. Moreover, it is found that, the impedance largely come from the cathode, since the kinetics on the cathode is more sluggish than the graphite anode [10]. In particular, two arcs were observed in Type 3: P10-M1, Type 4: P11-M1, and Type 6: P25-MU, whereas the other types only show one arc. It potentially indicates that these cathodes have already developed or already possessed an

additional barrier to transport on the cathode. In addition, it is observed that the cell with P1 cathode with NMP-PVDF binder possesses a lower ohmic and charge-transfer resistance, with a single arc exist. Unlike P10- and P11- based cells, which have larger ohmic resistance and charge transfer resistance.

# 4.1.3 Initial DCR testing

The pouch cells were then discharge to 50% SOC prior to the DCR testing. The result for the internal resistance for the fresh cell is shown in Table **4-2**. Again, the DCR results are also normalized with the electrode area.

Туре	Electrode (cathode binder system)	Discharge Resistance (Ωcm²)	Charge Resistance (Ωcm²)	Initial C/3 discharge capacity (Ah)
1	P1-M1 (NMP-PVDF)	26.78	27.79	2.67
2	P1-MU(NMP-PVDF)	28.17	27.19	1.78
3	P10-M1(NMP-free)	64.94	55.29	2.56
4	P11-M1(NMP-free)	62.67	53.14	2.47
5	P25-M6(NMP-free)	44.63	40.19	2.07
6	P25-MU(NMP-free)	50.2	45.65	1.72

Table **4-2:** The discharge and charge resistance from initial DCR testing and the initial C/3 discharge capacity for 6 cell types.

From the Table **4-2**, the initial internal resistances of all cell types tested by direct current are shown. It can be found that that Type 3 and Type 4 both have higher resistance in discharge and charge process, which is consistent with EIS result that there were two arcs already developed at fresh cell stage.

Cycling was started after the initial characterization; all cells were run under C/3 rate at the first cycle. The initial C/3 discharge capacity is shown in Table **4-2**. While the initial C/3 discharge capacity of P1-M1, P10-M1 and P11-M1 are close to (>96.1%) of design capacity(2.57Ah), and for P25-M6 shows relative low capacity (90.1%) than the design value of 2.29Ah. However, for P1-MU and P25-MU, they only have about 77.8% and 75.1% of design capacity, respectively. The low initial capacity for Type 2 and 6 is considered to be noncompetitive for cycling among all other the cells. This may mainly due to the Li-ion lose occurring in the first few cycles; lithium ions extracted from the oxide during initial charge are not fully re-inserted into the cathode, leading to loss of available capacity [31].



Figure 4-3: The discharge capacity retention for all types of (a)at C/3 rate for 100 cycles(b)with 1C rate for 200 cycles.

The initial first 100 cycles are shown in figure **4-3**, it is observed the P1-MU have poor performance even in C/3 capacity retention, it reaches down to 90% capacity retention after 100 cycles, while the other still retain above 95% at 100 cycles. Among the cells cycled in C/3 rate, P1-M1 and P10-M1 and P11-M1 have relatively excellent retention at the early stage of cycling. On the other hand, for the 1C cycling, all cells show the much lower retention compared to the

C/3 cycling performance. Especially for P25-MU, a discrete slope appeared after 100 cycles, showing a non-stable cycling performance in the early stage.

From the initial evaluation for all cell types, regarding all the factors from resistance and cycling, a decision point can be made that Type 2 (P1-MU) and Type 6(P25-MU) are both have poor performance and thus not suitable for the following cycling test. It is found that both types have relatively bad performance on rate capability based on the c-rate test, this may due to anode used in these two types. Finally, after these two types were cycled about 100 and 200 cycles at C/3 and 1C, respectively, the poor performance further proved that these two types with MU graphite anode is not able to be a good candidate to meet the study objective. The reason for the bad performance of MU-based cell is mainly believed to be the low porosity of this anode. From Equation **4-1**, the approximate porosity can be obtained.

$$\epsilon = 1 - \frac{V_{solid}}{V_{total}} = 1 - \frac{m''}{l + \sum_{i} m f_i \rho_i} \quad (i = AM, CA, B)$$
(4-1)

where m'' is the mass of solid material per unit area of electrode, l is the thickness of the electrode excluding the metal foil,  $mf_i$  is the mass fraction of the i<sup>th</sup> component of the mixture, and  $\rho_i$  is the density of the i<sup>th</sup> species of the mixture. Here, AM, CA and B stands for the active material, conductive additive, and binder. This calculation can provide a good approximation of the range in which the porosity falls. A low porosity of ~16% is obtained from the calculation for MU anode, which is well below the typical porosity of electrode ~35%. Thus, the observed initial and cycling capacity retention for these MU-based cells is expected. In addition, it is noticed during the fabrication process that this MU graphite anode surface is shiny instead of a matte surface, which typically indicates excessive calendaring of the electrode. Therefore, 2 cell types were stopped testing and will not be included in the further discussion.

Based on the BOL initial screen, upon utilized the same anode, cathode P10, P11, and P25 with NMP-free binder are found to have similar c-rate performance. However, these cathodes perform worse at the higher c-rate, indicating that they don't have good rate capability even in the fresh status. This is expected for such high electrode loading due to poor kinetics inside the cell. In addition, this can be further proved by the EIS and DCR result, both tests show that P10, P11 and P25 NMP-free cathode have larger resistance than P1 cathode. Thus, the utilization of NMP-free process coating for P10, P11 and P25 cathode is the reason to cause a larger resistance than NMP-PVDF based cathode in this study.

#### 4.2 Cell Aging

#### 4.2.1 Capacity Fade

The primary metric for success in this study is defined by cycle life, the results for capacity evolution is extremely important. Figure **4.4** shows the cycling result at C/3 rate and 1C rate, respectively. For C/3 cells on the left, they were stopped at each 200-cycle increment and then characterized for c-rate, EIS and DCR test after 200 cycles; whereas for 1C cells, they were continued cycling with 1C rate and run a C/3 characterization at each 200-cycle increment, since the C/3 discharge capacity can be seen as the true capacity of each cell.



Figure 4-4: The discharge capacity retention for all types of (a) at C/3 rate for 600 cycles (# 5 for 400 cycles), (b) with 1C rate for 1400 cycles (#5 for 600 cycles), the peak at each 200-cycle interval denotes a C/3-cycle characterization.

The C/3 capacity evolution for all 4 cell types demonstrates a similar rate of capacity fade. For the Type 1, P1-M1 with NMP-PVDF binder, has the most stable and the best retention rate of 91.4% and 88.7 % at 400 and 600 cycles, respectively. As for Type 3, P10-M1 with the

NMP-free binder, has discharge capacity retentions of 90.2% and 87% at 400 and 600 cycles, respectively. And Type 4, P11-M1 with the NMP-free binder, has a discharge capacity retention of 91% and 87.9% at 400 and 600 cycles, respectively. And the last P25-M6, has a capacity retention of 88.9% at 400 cycles. Thus, from the above result, the cycling performance for four cell types until 400 cycles is: Type 1> Type 4>Type 3>Type 5. Further, the cycling performance for three cell types until 600 cycles is: Type1> Type 4>Type 3. Since the anode used (M1 and M6) in these cells are very similar, the cycling performance of cathode is evaluated to be: P1 > P11>P10>P25.



Figure 4-5: The fitting result (blue line) for four cell types cycled at C/3 and the fitted trend upon 1000 cycles.

In order to further understand the capacity fade along the cycling process. The capacity fade is fitted as the capacity retention as a function of cycle number. The four curves are reported in the following as Equation **4-2(a-d)**:

$$CR\%(Type 1) = 100 - 0.2197\sqrt{N} - 0.0111N$$
 (4-2a)

$$CR\%(Type 3) = 100 - 0.2210\sqrt{N} - 0.0130N$$
 (4-2b)

$$CR\%(Type 4) = 100 - 0.1633\sqrt{N} - 0.140N$$
 (4-2c)

$$CR\%(Type 5) = 100 - 0.3084\sqrt{N} - 0.0120N$$
 (4-2d)

As can be seen from the figure **4-5**, there are relative large capacity loss occur in the first 200 cycles for all cell types, which may be due to the loss of lithium inventory by the quick growth of solid-electrolyte interphase (SEI) layer on the graphite negative electrode [31].

Thus, the discharge capacity retention at the initial stage is dominated by parabolic behavior ( $\sqrt{N}$ ), then the trend gradually transits to linear (N) as the cycling proceeds. From the fitting extrapolating, it is expected that three cell types can proceed to 1000 cycles without lowering than 80% capacity retention. If no lithium plating or gas release, the approximate cycle life of Type 1, Type 3, Type 4 and Type 5 is expected to have: 1200, 1000, 1100, 900 cycles. Therefore, it is found that even this kind of high loading cathode with NMP-free binder can be cycling until more than 1000 cycles, especially for P11-based cathode, which have an excellent cycle performance at C/3 rate.



Figure 4-6: The discharge capacity retention % for 1C at every 200 cycles.

For the 1C cycling performance, Figure **4-6** shows the characterized C/3 discharge capacity for 1C cycling cell at each 200-cycle increment. It demonstrates the strong rate-dependence of cell aging, as the capacity decreases significantly faster for cells cycled at 1C as compared to cell cycled at C/3. For Type 1, 3 and 4, they reached below 80% after 600 cycles, while for Type 5, its capacity loss is so large that it already reached down to 80% at around 200 cycles. Compared to C/3 cycling performance, 1C cycling shows much more capacity fade rate. This is an expected result for electrodes of such high loading, which possess more significant transport losses that produce conditions more favorable for loss of lithium inventory. Moreover, the higher resistances observed for cells from EIS and DCR test with NMP-free cathodes potentially exacerbate this issue by lowering the anode potential further, which is again more favorable for aging, such as lithium plating.

#### 4.2.2 Power Fade

While the capacity is the main objective of this study, power fade is also an indicator of long term cycling as well as an instantaneous power availability in the system. Figure **4-7** shows the power evolution for four cell types.



Figure 4-7: The voltage and specific capacity profile at 1st, 200th, 400th and 600th cycles (a) type1, (b)type3, (c) type4 and (d) type 5.

Units: V	Type 1: P1-M1 (PVDF-NMP)	Type 3: P10-M1 (NMP-free)	Type 4: P11-M1 (NMP-free)	Type 5: P25-M6 (NMP-free)
1 cycle	3.635	3.593	3.606	3.615
200 cycles	3.616	3.546	3.564	3.581
400 cycles	3.611	3.521	3.545	3.563
600 cycles	3.607	3.513	3.538	N/A

Table 4-3: The cell voltage for four cell types from fresh to aged stage.

From the Figure 4-7, it can be observed that at the first 200-cycle increment for all cell types have relatively larger power fade than the later 200-increment. For type 1, the power fade from 200 to 600 cycles is relatively small. On the other hand, for type 3,4 and 5, the power fade after 200 cycles is relatively larger than type 1. In addition, voltage decrease can be observed through the aging process in the Figure 4-7, which may be due to the increase internal resistance. Thus, Table 4-3 is made to demonstrate the decrease trend of average voltage for all cell types. For type 1, the full cell voltage decreased by 24 mV and 28mV after 400 cycles and 600 cycles, respectively. For type 3, the full cell voltage decreased by 72mV and 80mV, respectively. For Type 4, the full cell voltage decreased by 61mV and 69 mV after 400 and 600 cycles, respectively. Finally, for type 6, the full cell voltage decreased by 52 mV after 400 cycles.

According to Leng et al. [10] work on the three electrodes analysis, it is found that the average voltage decreases mainly come from the positive electrode for this kind of thick electrode pouch cell, when means the power performance for cathodes are worsen. Among all types, type 1 have the best power performance, while type 3 and type 4 seems to have worse power capability after 600 cycling. Therefore, the cell with the conventional binder, PVDF-NMP, is found to act better in power and capacity retention rate.

# 4.2.3 Impedance Rise

It is reported that the power fade is directly related to the impedance of the cell [10][12][33]. Thus, it is important to look into the impedance evolution in this study. The impedance spectrum is measured at 90SOC. Figure **4-8** shows impedance measured at fresh, 200, 400, and 600 cycles for four cell types, respectively. As can be observed from the Figure **4-8**, the first arch for cells with NMP-free binder increase significantly as the cycling proceed, while type 1 cell with NMP-PVDF binder only shows little change as the cycling test proceed. It means that the internal resistance for P10, P11 and P25 based cell increase significantly. Moreover, it can be observed that the second arch does not show much increase in the process for all types. We can first evaluate that P10 based cell has largest impedance along the way, while P1 based cell has the smallest impedance.





Figure 4-8: The EIS spectrum for 4 cell types (a) fresh (b) 200 cycles (c) 400 cycles (d) 600 cycles.



Figure 4-9: The equivalent circuit model used for fitting experimental EIS data.

To get a further understanding of the EIS data, an equivalent circuit model is used to fit the EIS spectrum. The equivalent circuit is show in circuit Figure **4-9**. The inductance Li shows the effect in the high frequencies, it mainly due to the cell wires or the potentiostat connections. The pure ohm resistance, Rohm is from the electrode, electrolyte, and separator and contact between component inside the cell. R1and CPE1 represent the behavior for the first arch in the system, which mainly represent the surface film and electronic transport on the cathode side. As for R2 and CPE2, which are used to fit the second arch, representing the charge-transfer resistance on the electrode [10]. A constant phase element is used to model the depressed semicircle, which is used to get a better fit quality than a capacitor [32]. Note that the Warburg diffusion part (the 45° straight line in Nyquist plot) is excluded for fitting in this study.



Figure **4-10**: The fitting result for EIS at 200-cycle increment (a) type1: P1-M1, (b)type 3: P10-M1, (c) type 4: P11-M1 and (d) type 5: P25-M6.

Figure **4-10** is the fitting result for experimental measured impedance. The fitting model shows a good agreement with the experimental data. Except type 1 at 400 and 600 cycles that did not show good fitting, and thus the equivalent model is added an extra R3 and CPE3 to get a better fitting result. Figure **4-11** shows the total R<sub>tot</sub> values for the fresh and aged cells, which is calculated by adding Rohm, R1 and R2 (plus R3 for type1) together. The resistance increased significantly after 200 cycles of ageing for type 3,4 and 5 with NMP-free binder, with is consistent with the power fade observed in Figure **4-7**. The impedance then gradually increased until 600 cycles. Whereas for type 1, the total resistance remained nearly constant until 600 cycles. The detailed fitting data are included in Appendix.



Figure 4-11: The total resistance ( $R_{tot}$ ) value (a) type 1 (b) type 3 (c) type 4 (d) type 5.

Looking into the impedance rise for each section of resistance. As Figure 4-12, the ohmic resistance (Rohm) and the charge transfer resistance only increase slightly when compared to the R1 increase until 600 cycles. The tiny change of ohmic resistance at high frequency area reflecting the stability of electrolyte solution. On the other hand, R1 significantly rise with the cycle number, indicating the passivated film continuously growing on the cathode active material and the electronic transport in the cathode are attributed for impedance rise for this kind of thick electrode cells. The contribution to the total resistance is R1 > R2 > Rohm.



Figure 4-12: The impedance evolution for type 4.

## 4.2.4 C-rate and DCR test

C-rate and direct current were tested at each 200-cycle increment to characterize the cell status. The testing result is shown in Figure **4-13**. The c-rate is normalized by the C/10 discharge capacity, and DCR is normalized with the electrode area.



Figure **4-13**: The C-rate test after (a) 200 cycles (b) 400 cycles (c) 600 cycles. The DCR test (d) discharge resistance (e) charge resistance.

Poor rate performance can be found after 600 cycles. For 2C discharge rate of type 3 and type 4, only about 30% capacity is acquired, which is only a half of type 1 with NMP-PVDF binder. Moreover, extremely poor performance is found in type 3 and type 4 at 3C rate, which reached cutoff voltage of 2.8V in a few minutes. This is due to the large resistance found in the cell as in Figure **4-13**(d)(e). The resistance measured from direct current for type 3 and type 4 is

3~4 time larger than type 1. Also, the rate of resistance rise for type 1 relatively slower than other cell types, and this also reflecting on each incremental c-rate test. Thus, poor rate performance for a high energy cell is related to high internal resistance for ion transport within thick electrodes.

## Chapter 5

# Conclusion

In this study, 2.5Ah and 2.2Ah NMC622/graphite pouch cells were cycled at C/3 and 1C rate. A combination of incremental capacity analysis, resistance measurements, and impedance spectroscopy were used to evaluate and compare each cell type. The study objective of reaching 300 cycles at C/3 rate above 80% capacity retention is achieved for 4 cell types. After C/3 cycling for 600 cycles, capacity retention of 87.9% and 88.7% is found for cells with NMP-free binder and NMP-PVDF binder, respectively. Cycle life of these high loading cells is expected to have about 1200 cycles at C/3 rate. The capacity fade is suggested to be due to SEI layer growth on the anode and the polarization of NMC cathode. On the other hand, the anode with low porosity is found to have worse performance.

In addition, the resistance rise is found relatively large for the NMP-free based cells when compared cells with NMP-PVDF based cells, which result in poor rate capability at higher C-rate. This can be reflected by the worse capacity retention at 1C cycling than C/3 cycling in this study. The significant loss in capacity at high C-rate is suggested to be the limitation of lithium ion transport. According to the fitted impedance result of fresh and aged cells, the ohmic resistance and charge-transfer reaction are found to have tiny change. In fact, the large impedance rise comes from the cathode side. This is suggested to be due to the passivated film gradually grow on cathode active material and electronic transport in the cathode.

Some drawbacks of thick electrodes and binders are considered to cause poor performance in this study. Thick electrodes are hard to be penetrated by lithium ions and thus lead to underutilization of active materials. Cathode with NMP-free process may have bad adhesion with current collector and insufficient mechanical integrity which lead to relatively worse performance than NMP-PVDF based cell.

While the cycling performance for three types of cathode coatings with NMP-free binder reach the study target, further improvements need to be made regarding the large internal resistance rise as the cycling proceeds.

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# Appendix

# Fitting Result for Experimental EIS Measurement

a)

)				
P1-M1	Fresh	200 cycles	400 cycles	600 cycles
$L (H cm^2)$	0.000251	0.0005	7.89E-05	9.36E-05
Rohm ( $\Omega$ cm <sup>2</sup> )	8.058	8.338	5.881	5.704
R1 ( $\Omega$ cm <sup>2</sup> )	20.94	23.12	14.98	13.39
$CPE1A1(F \text{ cm}^{-2})$	0.001245	0.003596	1.25E-05	2.02E-05
n1	0.72866	0.70853	0.79666	0.75407
R2 ( $\Omega$ cm <sup>2</sup> )	8.328	11.06	10.72	11.9
CPEA2 (F cm <sup>-2</sup> )	0.000366	0.01986	0.002171	0.0019276
n2	0.68151	0.902	0.5683	0.58892
R3 ( $\Omega$ cm <sup>2</sup> )			13.94	14.87
CPE3A3 (F cm <sup>-2</sup> )			0.0148	1.51E-02
n3			0.85947	0.85025
(b)				
P10-M1	Fresh	200 cycles	400 cycles	600 cycles
$L (H cm^2)$	0.000347	0.000522	9.88E-05	8.51E-05
Rohm ( $\Omega$ cm <sup>2</sup> )	6.92	6.822	7.351	7.589
R1 ( $\Omega$ cm <sup>2</sup> )	24.73	56.68	64.76	71.65
CPE1A1(F cm <sup>-2</sup> )	2.21E-06	2.72E-06	2.00E-06	2.23E-06
nl	0.96622	0.92565	0.95669	0.94152
R2 ( $\Omega$ cm <sup>2</sup> )	26.26	28.23	29.73	30.66
CPE2A2 (F cm <sup>-2</sup> )	0.00138	0.005254	0.006013	0.007817
n2	0.5689	0.49016	0.47319	0.4686
(c)				
P11-M1	Fresh	200 cycles	400 cycles	600 cycles
$L (H cm^2)$	0.000299	0.000727	0.000572	0.000105
Rohm ( $\Omega$ cm <sup>2</sup> )	7.288	7.533	7.412	7.636
R1 ( $\Omega$ cm <sup>2</sup> )	24.5	53.31	62.23	65.18
$CPE1A1(F cm^{-2})$	2.14E-06	2.68E-06	2.65E-06	2.21E-06
nl	0.97057	0.93038	0.92594	0.94641
R2 ( $\Omega$ cm <sup>2</sup> )	22.47	28.45	30.85	31.57
CPE2A2 (F cm <sup>-2</sup> )	0.001506	0.005863	0.00749	0.009993
n2	0.57779	0.48095	0.48	0.41207

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P25-M1	Fresh	200 cycles	400 cycles
$L (H cm^2)$	0.000474	8.81E-05	8.34E-05
Rohm ( $\Omega$ cm <sup>2</sup> )	6.813	6.175	6.992
R1 ( $\Omega$ cm <sup>2</sup> )	13.89	33.73	39.88
CPE1A1(F cm <sup>-2</sup> )	2.44E-06	2.96E-06	2.25E-06
n1	0.99629	0.93264	0.95165
R2 ( $\Omega$ cm <sup>2</sup> )	23.79	26.64	30.97
CPE2A2 (F $cm^{-2}$ )	0.001508	0.010634	0.011336
n2	0.47225	0.38125	0.39832