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Master of Engineering

A Study on the Performance of Lithium ion Battery
with Electrode Composition Change

The Graduate School
of the University of Ulsan

Department of Chemical Engineering

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A Study on the Performance of Lithium ion Battery with Electrode Composition Change

Supervisor: Professor Eun-Suok Oh

A Dissertation

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the Graduate School of University of Ulsan
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for the Degree of

Master

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A Study on the Performance of Lithium ion Battery with Electrode Composition Change

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Abstract in Korean

리튬이차전지시장이 소형 IT 기기분야에서 최근 중대형시장으로 급속 성장함에 따라 분야에 따른 전지의 요구 특성이 다양해 졌다. 이에 따라 각 용도에 맞는 전지시스템이 최적화 되어야 한다.

전지시스템이 최적화 되지 않을 경우 전지의 용량이나 수명 등에 영향을 미치게 되며, 이는 전지를 사용하는 기기들의 문제점을 야기 시킨다.

전지시스템의 최적화에는 여러 가지 방법이 있으나, 이번 연구에서는 전극의 조성의 변화, 바인더 및 도전재 종류의 변경 등을 통하여 전지성능을 평가하고자 한다.

우선, 양극전극 2종과 음극전극 2종의 전극을 제작하여 총 4가지 타입의 700mAh급 pouch type full cell을 만들었다. 특히 음극에 사용된 바인더의 경우 수계(CMC/SBR)와 유기계(PVDF)로 나누어 극판을 제작하였으며, 양극의 경우 Graphite계와 Carbon black계의 도전재를 사용함으로써 각각의 소재사용과 조성이 미치는 영향을 전기화학적/물리적 평가를 통해 분석하였다.

평가는 dQdV, 초기용량, 율특성, 수명평가(고온, 상온), 저온방전특성평가, Swelling 평가를 수행하였다.

전지시스템 최적화를 위한 평가결과 고온수명의 경우 인조흑연-유기바인더 기반으로 제작된 음극을 사용한 전지가 더 높은 용량유지율을 보였다. 또한 수계 바인더(CMC/SBR)를 사용한 전지는 모두 고온에서 Swelling 현상이 아주 크게 나타나는 것을 확인 할 수 있었다. 이는 수계바인더의 계면활성제로 사용되는 CMC의 -OH 작용기가 전지내의 전해액과의 반응으로 가스를 발생시켜 부피팽창을 야기시키는 것으로 보인다.

본 전지최적화 평가를 통해 수계바인더를 적용한 음극을 사용시에는 양극에 carbon black계 도전재만을 사용하는 것이 좋은 성능을 나타내는 것을 확인할 수 있었다. 이와 반대로 유기계바인더를 적용한 음극을 사용시에는 carbon black계 도전재와 graphite계 도전재를 혼합하는 것이 더 좋은 성능을 나타냈다.

결과적으로 후보군 1과 후보군 4가 각각의 전지시스템에서 최적의 성능을 나타내었다.

Abstract in English

As the lithium secondary battery market has rapidly grown from the small IT device field to the medium and large market, the demand characteristics of the batteries have been diversified according to the field. Accordingly, the battery system for each application should be optimized.

If the battery system is not optimized, it affects the capacity and cycle of the battery, which causes the problem of the battery-powered devices.

There are many ways to optimize the battery system, but this study aims to evaluate the battery performance by changing the composition of the electrode and the type of binder and conductive material.

First, two types of anode and cathode electrodes each were fabricated to make four types of 700mAh pouch type full cell.

In particular, the binder used for the anode electrode was divided into water-based(CMC/SBR) and organic(PVDF) binder to produce an electrode.

For the cathode electrode, graphite type and carbon black type conductive materials were used to affect the used and composition of each material.

The impact was analyzed through electrochemical/physical evaluation.

As a result of evaluation for the battery system optimization, the battery using the anode electrode manufactured based on artificial graphite-organic binder showed higher capacity retention at high temperature life.

HT(Hot Temperature) storage evaluation, PVDF binder-containing cells have less swell than the CMC/SBR binder-containing electrodes because the hydroxyl groups of the CMC causes to the gas production by the reaction with the electrolyte at HT.

As a result, candidate 1 and candidate 4 battery system are the optimal composition of each.

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1. Introduction

1.1 background of experiments

1.1.1 Importance of Secondary Battery Electrode Fabrication

Lithium secondary batteries are rechargeable batteries that can be used many times and have been widely used in small IT such as mobile phones and laptop, etc.

Recently, environmental regulations have been enacted in the wake of the global environmental issues, demand has also been rising for mid to large sized batteries such as ESS(Energy Storage System) and EV(Electric Vehicle).

In Europe, internal combustion engines will be banned from 2025 and in Germany from 2030 and in Britain and France from 2040. The environmental regulations of each country will be tightened to further accelerate electric vehicle development.

In addition, the needs ESS(Energy Storage System) is increasingly for stabilizing power and preparing for peak power. There is a growing prevalence in home and industries expects to growing by more than 40% over the next 10 years.

As the battery market expands from small IT to medium-large size such as EV(Electric Vehicles) and ESS(Energy Storage System), battery systems for each application should be optimized. In order to satisfy optimization of battery system, electrode formulation of lithium secondary battery and selection of materials are becoming more important.

If during manufacturing of lithium secondary battery not optimized variables conditions such as formulation of electrode, process caused some problems like poor adhesion of the electrode, poor battery performance and bad distribution of the electrodes result in failure to obtain the desired result values. The figure 1-1 shows a problems(bubble occurrence, electrode crack) that can be seen when the electrode manufacturing conditions are not optimized. In other words, if optimization is not achieved in the electrode manufacturing process, which is the basic stage of battery building, it will have a great impact on the performance of the battery.

In this paper, the optimized cell system according to electrode formulation (change the conductive ratio of cathode and kind of anode binder) is studied.



(a)



(b)

Figure 1-1. Electrode Manufacturing Process Conditions Failed Electrode;

(a) fail coating due to bubble in slurry (b) crack of electrode

1.1.2 Characteristics of change conditions(Binder, Active Material, Conductive)

This research is change the electrode formulation(conductive) and kind of binder. The roles and characteristics of the changed conditions are as follows;

Active Material(Anode);

In this study, anodes were fabricated using artificial graphite and natural graphite. In the case of artificial graphite, the specific surface area is small($<1\text{m}^2/\text{g}$) and PVDF binder is used. In case of natural graphite, the specific surface area is large($3\sim 8\text{m}^2/\text{g}$) and CMC/SBR binder is used.

Natural Graphite(NG) is known to perform poorly in some cells, which has in the past been attributed to surface exfoliation and cracking of particles.[1,2,3,4]

Park et al. found spherical natural graphite showed signs of particle swelling and cracking caused by mechanical strain during cycling, which could be suppressed using a carbon coating process.[2,5]

Artificial Graphite(AG) performance reported in the literature appears to outperform natural graphite, however, few direct comparisons of artificial and natural graphite exist in the literature.[5]

Conductive agent;

It is generally accepted that the role of the conducting agent is to enhance the electrode conductivity by filling the free spaces made by the grains of active material to form a continuous network until eventually the electrical conductivity approaches that of the conducting agent. [6] The other important role of the conducting agent is to absorb and retain electrolyte solution, which allows and intimate contact between Li^+ ions and the active material.[7] These carbonaceous conductive agent are different crystallinity, texture, morphology, particle size and purity, depending on their sources and manufacturing processes.[7,8] In this research, use the kind of graphite and kind of carbon black. They are widely used because of their high electrical conductivity and chemical inertness.

Binder;

Binder is an important part of electrode formulation because it can maintain the physical structure of the electrode; without a binder, the electrode would fall apart.[9]

Binder are used as inactive components in composite electrodes to provide mechanical stability and surface adhesion of the coating to the current collector.[10] As well as the ability to form a good electric network between the active material and conductive carbon, to facilitate electron transport and lithium ion diffusion. [9] Poly(vinylidene fluoride)(PVDF) has been a preferred binder for the graphite anode of Li-ion batteries. However, there is currently a trend to replace the PVDF binder in the anode of Li-ion batteries because of its reactivity with lithium metal and lithiated graphite(LiC_6). It has been reported that at elevated temperatures, all fluorinated polymers react with lithium metal and lithiated graphite(Li_xC_6) to form more stable LiF and $>\text{C}=\text{CF}-$ double bonds, and that the presence of liquid electrolyte increases and accelerates the resulting reactions. Furthermore, these reactions are very exothermic, which could cause self-heating thermal runaway. Therefore, safety concerns with Li-ion batteries arise from the use of PVDF in the graphite anode.[6] Another kind of binder that is commonly used in commercial lithium ion batteries is the sodium salt of carboxymethyl cellulose(CMC). The greatest advantage of CMC is that it allows processing of electrode slurries with water solvent rather than with polluting, environmentally unfriendly, volatile organic compound-based solvent. And the CMC is usually used together with styrene-butadiene rubber(SBR). [9] Noted that SBR possesses higher flexibility, stronger binding force, and higher heat resistance than the widely used PVDF. [11]

1.1.3 Lithium ion Battery Market Trends

The lithium secondary battery industry started with small IT devices, but the market for medium-large batteries such as Energy Storage System (ESS) and Electric Vehicle (EV) has grown rapidly due to the recent strengthening of environmental regulations and the fourth industrial revolution.

Thus, next generation lithium ion batteries require higher energy density, longer life, better safety and lower cost.[5]

The global lithium secondary battery market is worth \$18.7 billion in 2017, accounting for 50.3% for xEVs, 46.0% for IT small batteries and 3.7% for ESS. Also, global demand for lithium secondary batteries for electric vehicles is expected to reach 53.4 GWh in 2020, and the market size for 2022 is forecast to surpass demand for IT devices at 94 GWh.

As sales of electric vehicles, which are front-end industries, grow rapidly, it is expected that demand will increase in many secondary battery sectors ranging from small batteries to medium-sized ones in the future.

Accordingly, price fluctuations of raw materials, which are rear-end industries, are also growing, and in the case of Korea, fundamental solutions are needed because the material self-sufficiency rate of the key materials of secondary batteries is low.

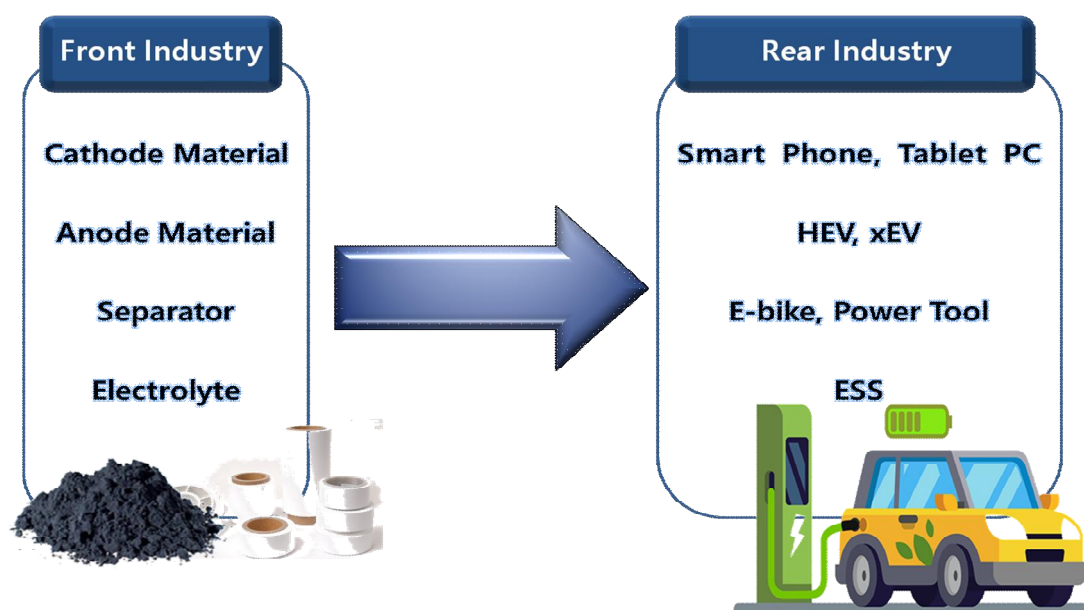


Figure 1-2. Lithium Ion Battery Front & Rear Industry

Energy Storage System (ESS) is also becoming more necessary for the distribution of renewable energy, power stabilization and peak power. In addition, a connected business the ESS market is expected to grow rapidly from 2.3 GWh in 2016 to 15 GWh in 2020 due to the expansion of the supply of new and renewable energy

The Lithium ion secondary battery market is growing at an annual average rate of 10 percent due to steady demand for small IT devices as well as small and medium-large sized ones, and is expected to form the 104 GWh market in 2024.

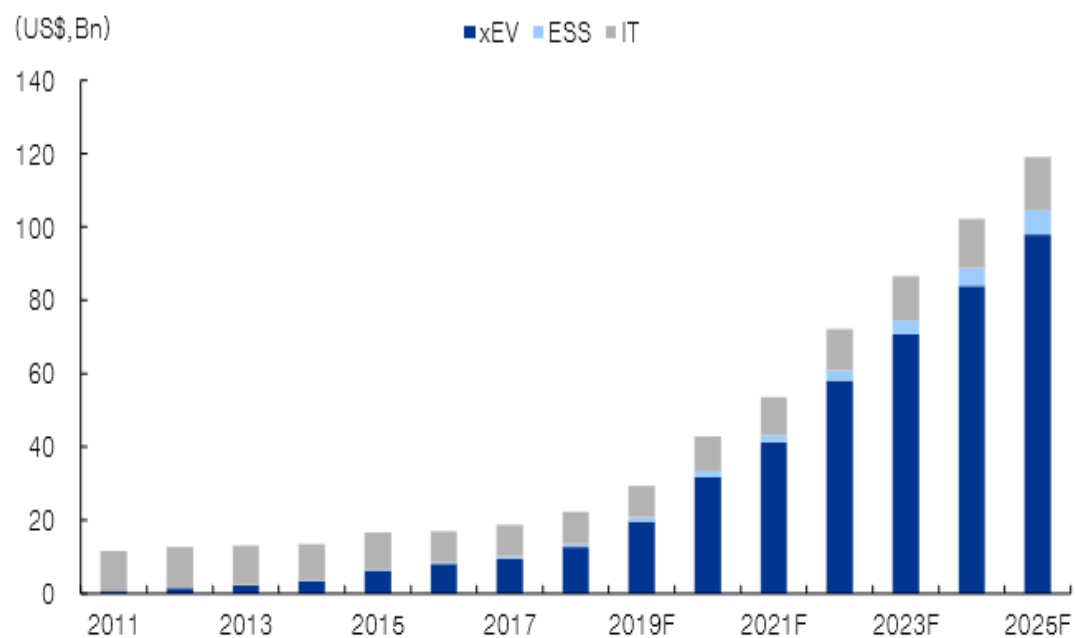


Image: SNE research

Figure 1-3. Global Lithium Ion Battery Market prospect

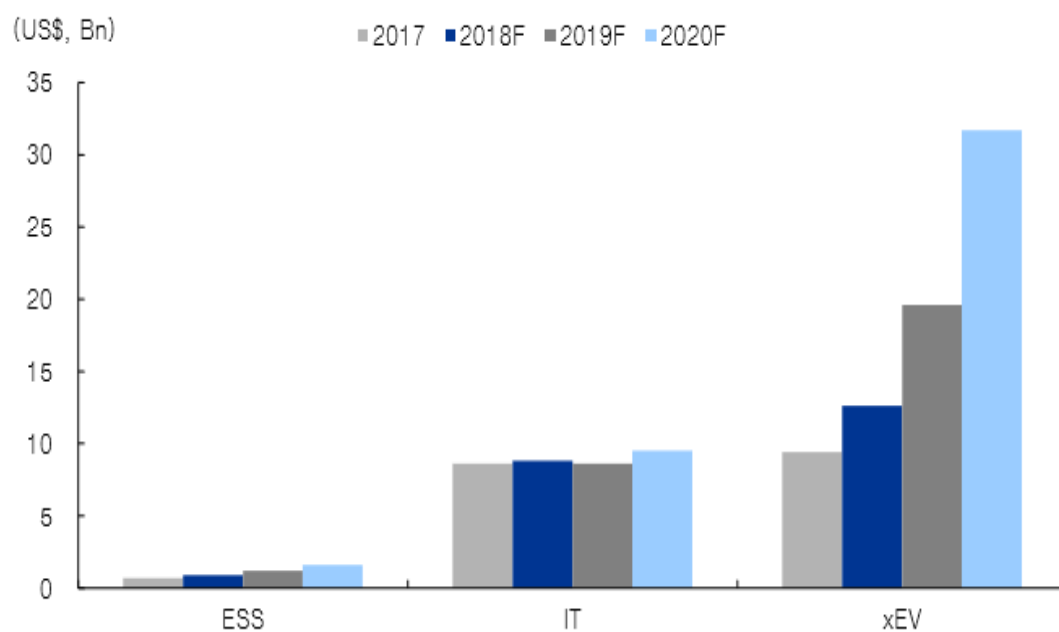


Image: SNE research

Figure 1-4. Annual Sales Forecast by product

1.1.4 Cathode Material Market Trends

Cathode Material is one of the key materials of Lithium ion secondary batteries that provides lithium ion in batteries, and the representative cathode materials are Lithium cobalt oxide(LCO), Lithium nickel manganese cobalt oxide(NCM), Lithium manganese oxide(LMO), Nickel cobalt aluminum(NCA), Lithium iron phosphate(LFP) etc.

Cathode Property	LCO (LiCoO ₂)	NCA (LiNi _{0.80} CO _{0.15} Al _{0.05} O ₂)	NCM (Li(NiCoMn)O ₂)	LMO (LiMn ₂ O ₄)	LFP (LiFePO ₄ /C)
Theoretical capacity (mAh/g)	274	275	285	148	170
Capacity (mAh/g.@4.2V)	145	180	160	100	160
Capacity (mAh/g.@4.3V)	~143	~195	160~170	~120	~150
Voltage(V)	3.7	3.6	3.6	4.0	3.4
Capacity density (mAh/cc)	515	540	490	285	280
Energy density (Wh/cc)	2.06	2	1.86	1.14	0.95
Price	Very High	Medium	Medium	Low	Very low
Synthetic difficulty	~1,000°C, Air Easy	~800°C, O ₂ Difficult	~1,000°C, Air Less difficult	~900°C, Air Less difficult	~700°C, N ₂ Difficult
Eco friendly	Poor	Slightly poor	Slightly poor	Good	Good
Thermal stability	Good	Slightly poor	Good	Very Good	Excellent
Apply field	IT	Medium-large	IT, Medium-large	Medium-large	Medium-large

Table 1. Kind of Cathode Materials

Small Lithium ion secondary batteries such as IT devices use LCO material(greater than 4.5V) because of low price, good discharge ratio and high capacity characteristics. And medium-large sized batteries mainly use NCA and NCM owing to high power.

As mentioned above, cathode materials are reduced cobalt content and increased Ni content in order to improve power, stability, cycle and price as medium-large markets grow, but as increase Ni contents tend to occur problems such as deterioration which leads to poor thermal stability.

So we need to more studied cathode materials continuously.

In case of LFP are not included raw materials that nickel and cobalt, so have lower cost advantages but are less efficient than NCA and NCM.

Cathode materials are expected to grow the most among secondary battery material markets, the explosive demand of cathode materials will increase due to expansion of new application field and growth of medium-large market.

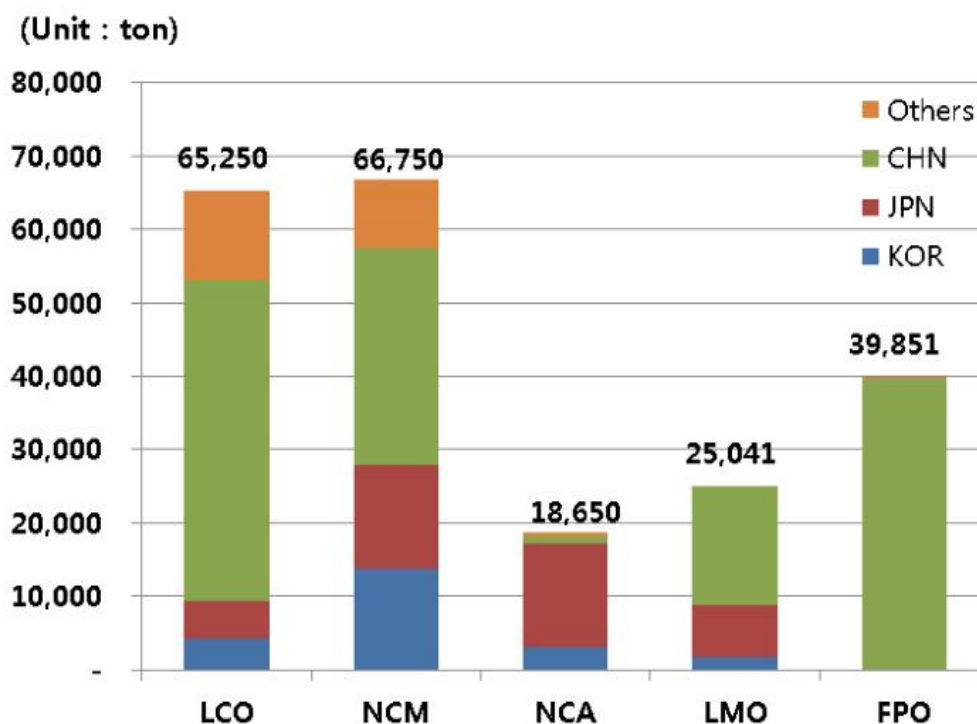


Image: SNE research

Figure 1-5. Country distribution of Cathode Demand Market

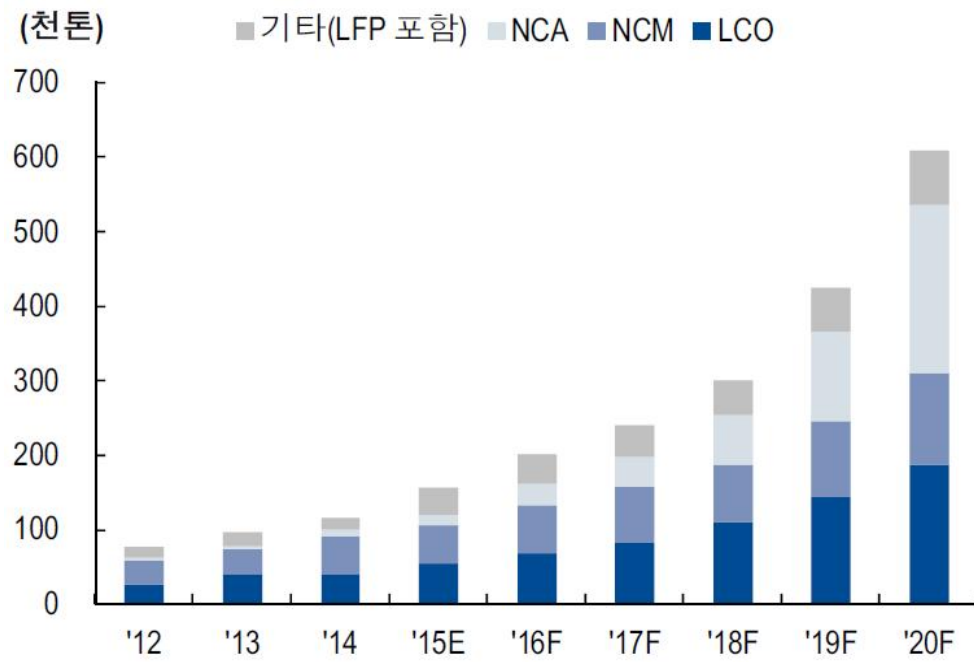


Image: NH research

Figure 1-6. Global Lithium Ion Battery Cathode Market prospect

1.1.5 Anode Material Market Trends

The Anode material role is store the lithium ion that has moved from cathode material when charging lithium ion secondary batteries, anode materials are used such as carbon type, graphite type, si-based type.

As one of the four key materials(Cathode material, Anode material, Separator, Electrolyte) it is the lowest localized.

Anode Property	Artificial Graphite	Natural Graphite	Low temp. Carbon	LTO($\text{Li}_4\text{Ti}_5\text{O}_{12}$)	Si, Sn etc
Capacity (mAh/g.@4.2V)	360	365	235	160	500<
Capacity density (mAh/cc)	553	560	315	230	660<
Energy density (Wh/cc)	1.99	2.02	1.07	0.53	2.13<
Cycle characteristic	High	Medium	Medium		Low
Price	Medium	Low	Very High	Very High	High
Thermal stability	Poor	Poor	Good	Excellent	Poor

Table 2. Kind of Anode Material

Currently commercialized lithium secondary batteries are mostly graphite used, and the theoretical capacity of graphite cannot be used as a battery requiring high capacity, so considered use as an alternative materials Si, Sn, but in the case of silicon, it is difficult to commercialize it because its cycle is poor due to excessive volume expansion and contraction.

These problems are not solved, graphite type and carbon type are mostly used in anode for Lithium ion secondary batteries. Graphite type are used for high capacity, carbon type used for high power applications.



(출처)SNE리서치

Figure 1-7. Market size by Type of Anode

Although natural graphite is widely used as a cathode material at a low price, and in the case of synthetic graphite, it is mainly used for small batteries that require high capacity, but the trend has been increasing as demand for electric vehicles has recently changed from natural graphite to artificial graphite.

For natural graphite often used in ESS for unit price and stability reasons. Natural graphite has a relatively low theoretical capacity and low cycle stability, so LTO is considered as an alternative material, but it has a disadvantage of being low energy capacity and expensive price.

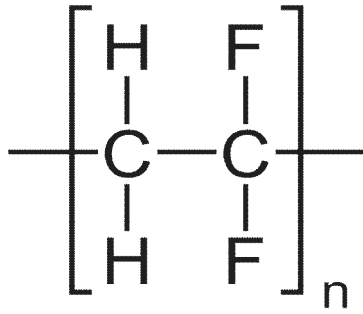
1.1.6 Binder Material Market Trends

In lithium secondary batteries, binders are polymeric materials used to holding active material particles within the electrode (electrode-current collector, active material-conductive agent etc.). Although binders are electrochemically inactive materials, they can have a significant influence on the electrode performance. Binder can be divided two type, organic solvent based and water based. Organic solvent based binder is Poly(vinylidene difluoride)(PVDF) commonly used. Water based binder are Styrene-butadiene rubber(SBR) and Sodium carboxymethyl cellulose(CMC-Na), Poly acrylic acid(PAA) etc.

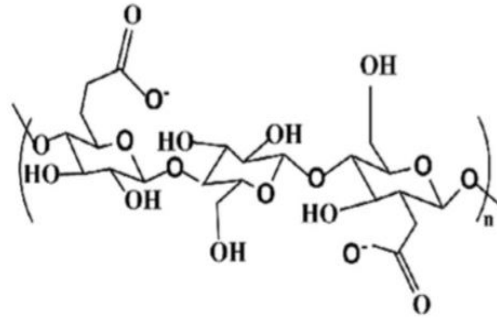
Currently, the organic solvent-based poly(vinylidene difluoride)(PVDF) has been widely used as the binder for both the negative and the positive electrodes in commercial LIBs, as a result of its good electrochemical stability and high adhesion to electrode materials and current collectors. Nonetheless, PVDF binder is expensive, not easily to recycle, and involved the use of volatile organic compounds such as the environmentally harmful and toxic N-methyl-2-pyrrolidone(NMP) for its processing[12,13,14].

Thus, to find cheap, environmentally friendly binders to substitute for the current commercial PVDF binder is important for the improvement of electrochemical performance and for decreasing the manufacturing costs of LIBs. Carboxymethyl groups into natural cellulose, has recently attracted more consideration due to its ability to dissolve much more easily in water and its low cost compared with PVDF binder. Due to both apparent advantages, reports on the application of CMC as the binder for lithium ion batteries have demonstrated its promising characteristics, such as its cycling stability, electrochemical capacity improvement, and environmental friendliness.

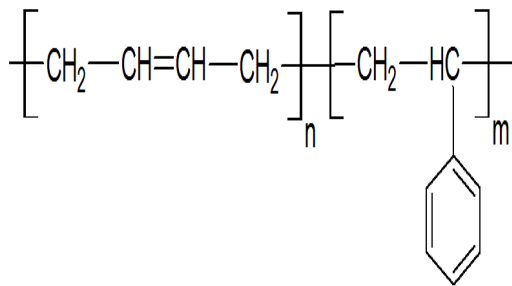
Therefore, the diversity of binders and their advantages for lithium ion batteries can provide more opportunities to improve the energy densities of these batteries for successful commercial applications.[14]



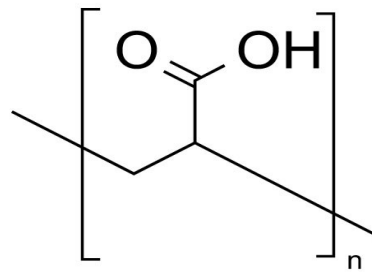
(a)



(b)



(c)



(d)

Figure 1–8. Kind of Binder; (a) PVDF (b) CMC (c) SBR (d) PAA

These days, they are making electrodes using water-based binders that are environmentally friendly and cheap.

In particular, water-based binders exhibit high adhesion even though use small quantities because they have point contact unlike surface contact PVDF.

Using a relatively small amount can increase the proportion of active material, contributing to increased battery capacity.

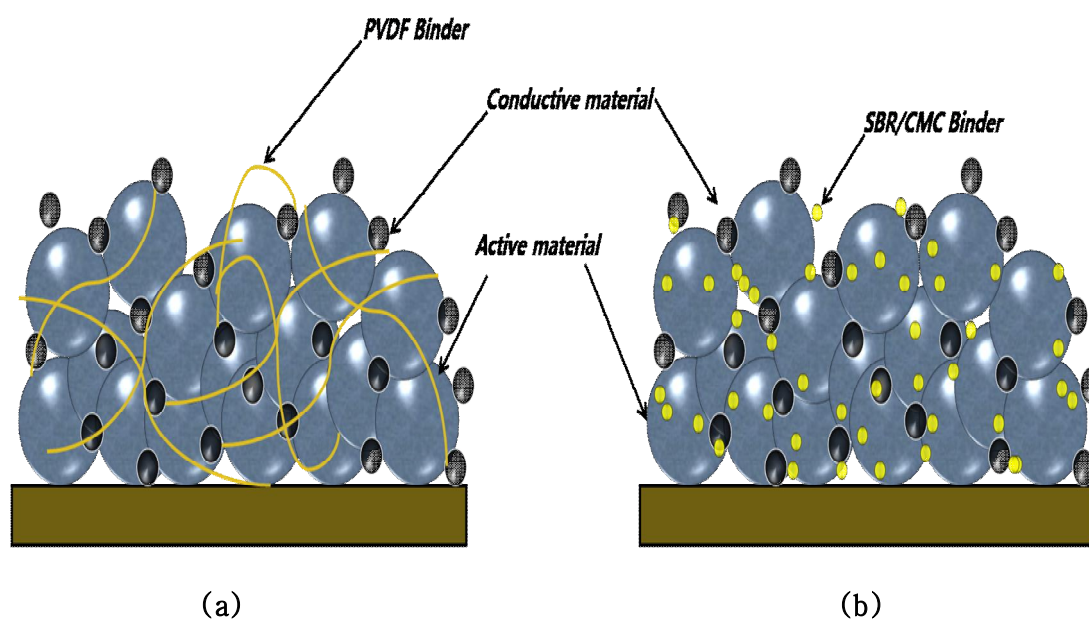


Figure 1-9. Binder Electrode Schematic; (a) PVDF (b) CMC/SBR

In addition, the demand for secondary batteries with high energy density is increasing as medium-large lithium ion secondary battery market has grown rapidly. To obtain high capacity, the charging voltage is increased by 4.4 volts or more, and in such cases, the adhesion of the binder is weakened due to heat inside the battery, causing the battery to deteriorate rapidly.

In order that to solve these problems, binder development is actively research.

2. Experimental

2.1 Preparation of electrodes

2.1.1 Survey of Electrode material

As medium-large lithium ion secondary batteries markets grow, NCM use proportion is increasing. For this experiment NCM was chosen out of various cathode materials.

And conductive agent use two type(Graphite type, Carbon black type) in cathode electrode.

In the case of Anode materials used AG(Artificial Graphite), NG(Natural Graphite). NG is in use today at low unit cost and according to increase medium-large market, AG is growing in demand.

In particular, anode material is divided into two types, and the electrode is produced by applying a binder water-based (SBR/CMC) and an organic-based (PVDF) respectively.

In the case of natural graphite was used CMC and SBR with excellent adhesion because of its large non-surface area.

2.1.2 Design of Cell(Pouch type Full cell)

For manufacture the pouch type cell, by designed 700mAh full cell(NP ratio 1.1). Cathode electrode is used two type conductive agent and one type(NCM) active materials, finally two type cathode electrode was produced.

Anode materials are used NG(Nature Graphite) and AG(Artificial Graphite), each material adapted water-based binder, organic-based binder.

Using this electrode to optimize the battery system.

Manufacturing 700mAh pouch type full cells and their electrochemical evaluation are as follows;

Electrode	Candidate 1	Candidate 2	Candidate 3	Candidate 4
Cathode	NMC424 95 Super-P 2.5 PVDF 2.5		NMC424 95 Super-P 1.5 SGP5 1.5 PVDF 2	
Anode	NG 97.5 SBR 1.5 CMC 1	AG 90 Super-P 2.9 PVDF 7 OA 0.1	NG 97.5 SBR 1.5 CMC 1	AG 90 Super-P 2.9 PVDF 7 OA 0.1

Table 3. Battery candidate according to composition of electrode

2.1.3 Electrode manufacturing

Electrode manufacturing is total 3step process; Mixing, Coating, Pressing. Used the pilot scale M/C(Techland co.) owned by UlsanTechnopark.

Mixing Process;

First, for manufacturing pouch type cell , made the cathode electrode and anode electrode.

This step is make the slurry by mixing active material, binder, conductive agent, solvent etc in planetary&dispersion mixer.

Cathode electrode was used NCM424(BK-723KL, L&F), Super-P(SuperP-Li, Timcal), SGP-5(SGP5, SEC), PVDF Binder(KF1100, KUREHA).

And anode electrode was used NG(918- II, BTR), AG(SCMG-AR, Showadenko), Super-P (SuperP-Li, Timcal), PVDF Bidner(KF9130, KUREHA), SBR(BM-480B, Zeon), CMC(H-1496B, DAI-ICHI), OA(Extra pure, KANTO CHEMICAL). OA(Oxalic Acid) is add a small amount for increase the adhesion with the cu-foil.

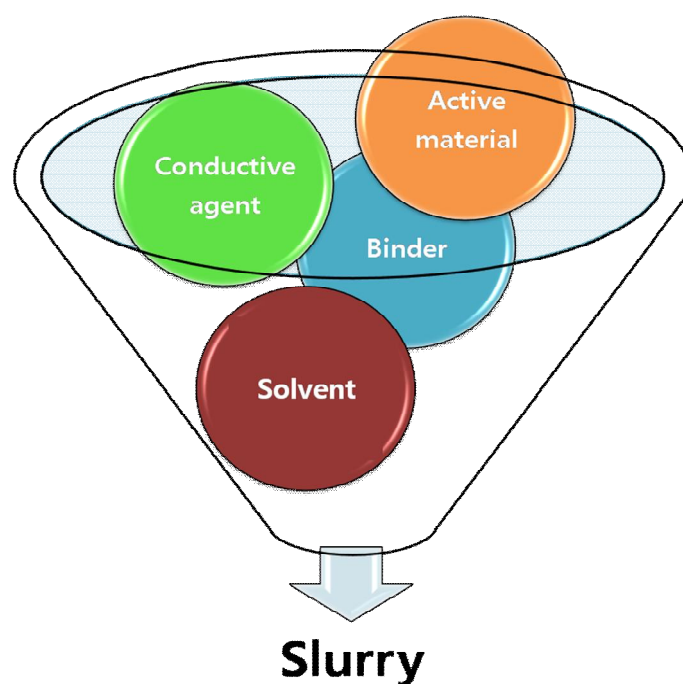


Figure 2-1. Mixing process



Figure 2-2. Manufactured slurry

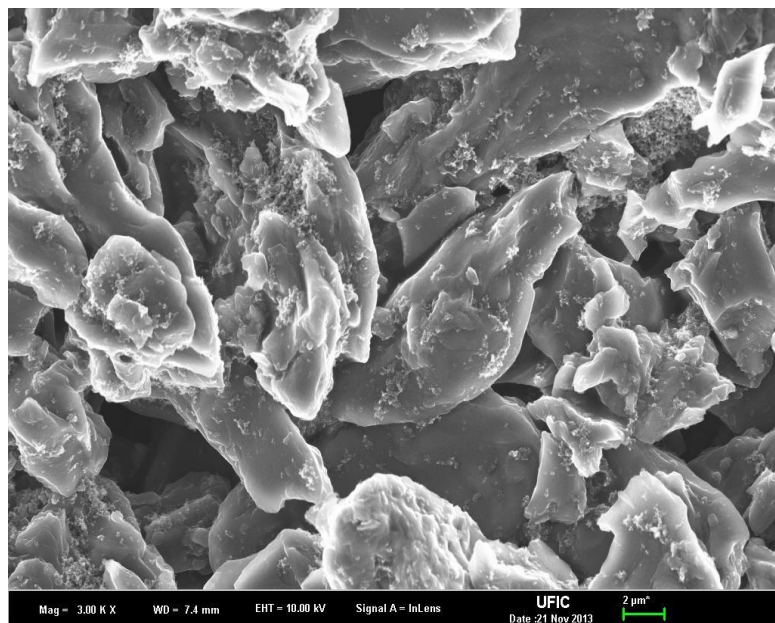
Mixing process is very important step. If the dispersion is not properly performed or the composition of the material is not set properly, performance of the battery is not displayed properly or it can indicate a peel phenomenon in the collector in the coating process. To solve the this problems, planetary&dispersion rpm and mixing time of the mixer were adjusted for dispersion.

Below the SEM image is showing surface of the electrode. On the left hand side(a) image is poor slurry distribution as the conductive agent is one side concentrated, on the other side right image(b) is the surface state of the well-distributed electrode.

If conductive agent are not distributed like concentrated to one side, electrode can cause performance degradation due to bad c-rate characteristics and others.



(a)



(b)

Figure 2-3. Different Surface of Electrode distribution; (a) poor distribution electrode(5k) (b) good distribution electrode(3k)

After the mixing process, transfer the slurry to the slurry storage tank and store it in the 1day vacuum to prevent moisture.

After a day, the air bubble in the slurry disappears while vacuum is removed. If there is a lot of air bubbles inside the slurry, during coating process show the empty space. The charge-discharge process of lithium ion secondary battery is occur by interface reaction between cathode-anode-electrolyte. Empty space by air bubbles becomes a non operated space in the battery which can also cause the capacity of the battery to not be fully appeared.

Coating Process;

Second step is coating process. This step is slurry coating top the current collector. Kind of coating is slot die, comma etc, this coating process used slot die coater because of less deviation of electrode than comma method. And this coating M/C has 2 dry zone.

In the coating process, the operating know-how of operator is important, and the electrode manufacturing was carried out by changing the drying temperature, drying speed according to each materials.

Cathode electrode use Al foil(15um, sam-a company), Anode electrode use Cu foil(10um, LS mtron).

Setting the temperature conditions is important since determined the position of the binder in electrode and fixed the slurry is stable on the current collector during electrode drying.

Dry zone temperature conditions;

Dry Zone(°C)	Cathode Electrode	Anode Electrode (w/ PVDF)	Anode Electrode (w/ SBR, CMC)
Dry Zone 1	105	105	85
Dry Zone 2	125	125	105

Table 4. Coating Temperature condition

When using the water-based binder, the drying temperature setting was lower than the organic-based binder. The migration of water-based binder causes cracks in the electrodes, and the poor adhesion of the electrodes is reduced due to this problem.

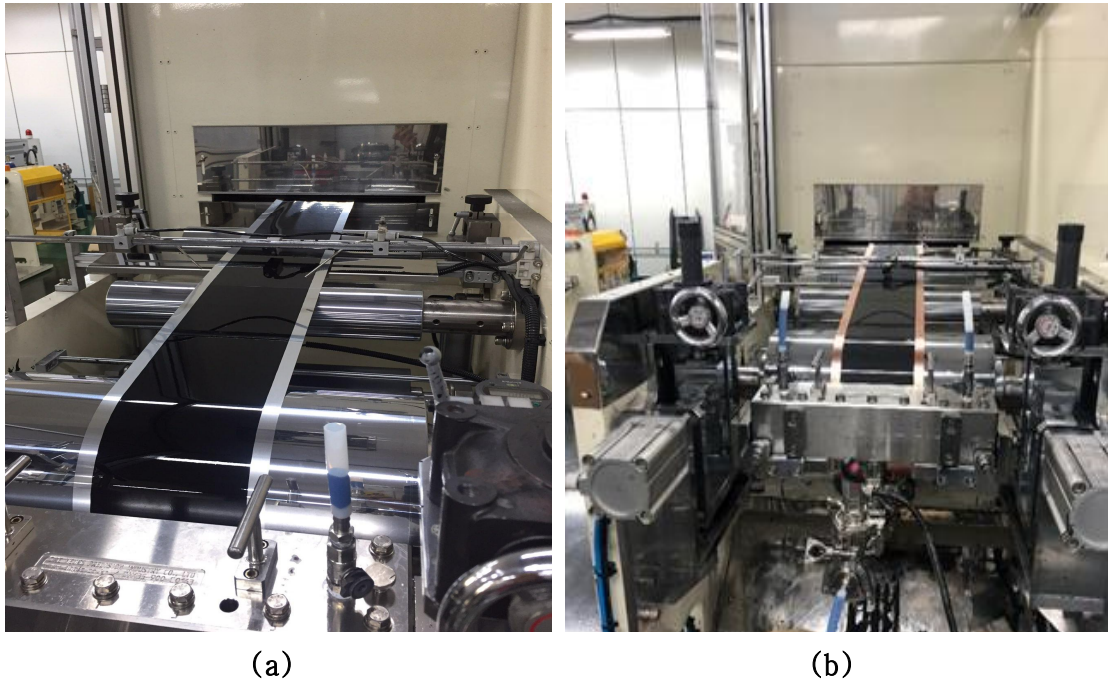


Figure 2-4. Coating process: (a) cathode coating (b) anode coating

Pressing Process:

Third, pressing process is last step of electrode manufacturing process.

The roll pressing process calculates the porosity of the electrode by measuring the true density of the material used in the electrode and increase the current density of the electrode by reducing the thickness. Also increases the adhesion between the electrode and the current collector.

In case of higher composite density is good for increasing energy density. But it is difficult to penetrate electrolyte inside to electrode, which increases the explosion and ignition related when occur inner short.

In particular, if composite density is excessively increase when applied to medium-large size batteries like EV(Electric Vehicle), it cannot respond to stress of the electrode during charging-discharging.

As a result, the amount of electrolyte that enter porosity will be reduced

which lead to rapid depletion of the electrolyte and shorten its life. To solve this problem, should be adapt different of composit density according to materials and appling fields used.

In this study, cathode and anode composite density is each 3.0g/cc, 1.5g/cc and used roll to roll methode.

Also, in case of cathode electrode is pressed at high temperature(60°C) due to spring back and the material was not pressed well, and the anode was pressed at room temperature(25°C).



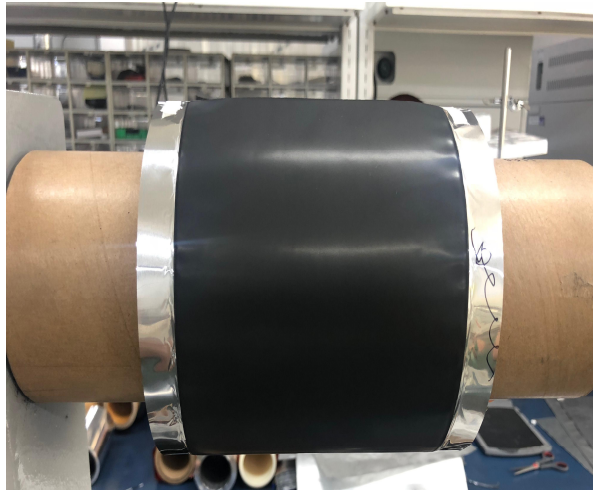
(a)



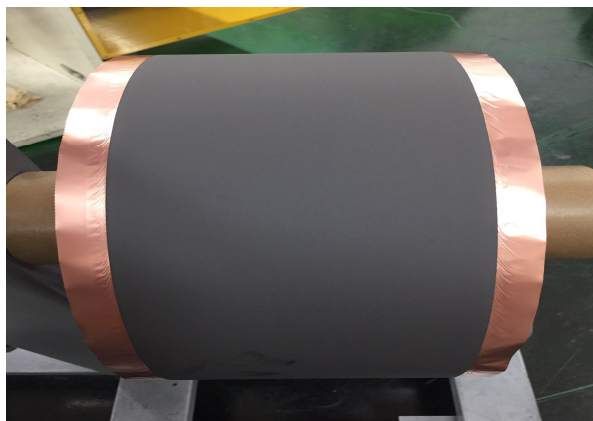
(b)

Figure 2-5. Electrode pressing process: (a) cathode pressing (b) anode pressing

The final electrode that finished electrode manufacturing process are Fig 1-15.



(a)



(b)

Figure 2-6. Final Product of Electrode process;

(a) cathode electrode (b) anode electrode

2.1.4 Fabrication of Pouch cell(700mAh) or Pouch cell assembly

After electrode manufacturing process, electrode were transferred to the dry room for the battery assembly process. The dry room where the battery is assembled is maintained at -60°C below relative humidity.

Cell assembly process is 6 steps: Punching&Cleaning , Z-Stacking, Tab welding, Pouch forming, 3side sealing, EL Injection.

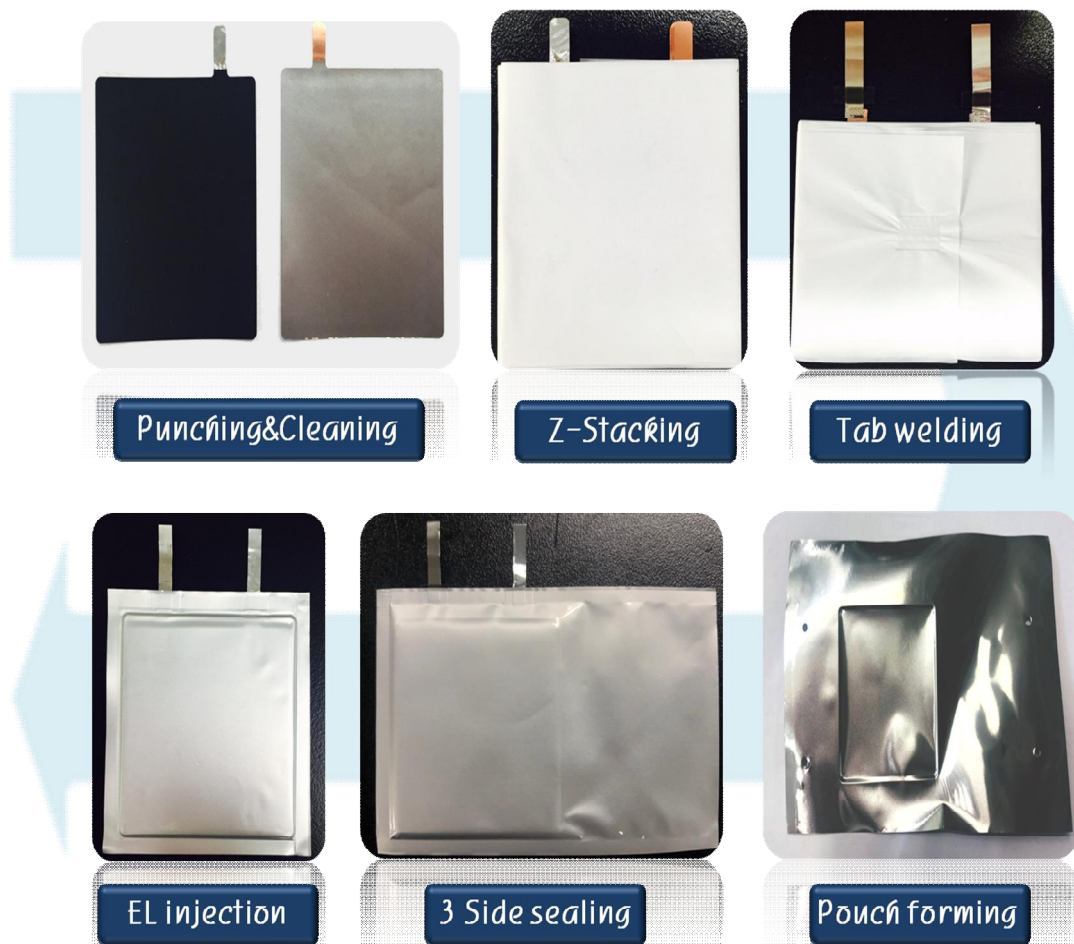


Figure 2-7. Cell assembly process

Punching&Cleaning Process;

Punching process is when finished manufacture electrode is punched with a mold shape. In this case, the bur is cleaned through the brush in the punching M/C to remove the bur from the punching electrode.

If the cleaning is not performed properly, foreign substances or burs in the electrode can pierce the separator and internal short may occur.

After the punching&cleaning process is completed, the electrodes were dried 1day vacuum oven at 100°C to remove moisture. Next day, the moisture content measured by Karl Fischer(Mettler toledo co.) was less than 50ppm.

Z-Stacking Process;

During the Z-Staking process, a separator is placed between the cathode and anode electrodes. In this process, the separator lines must be controlled the electrodes are well inserted in the separator for the cathode and anode do not come into contact with each other. Because the lines do not fit, contact of cathode and anode electrodes caused by internal short, causing problems such as fire of batteries.

In this research, 16um PE separator(F16BME, Tonen) was used.

Tab welding Process;

Tab welding process, external sockets are connected to the battery that has been stacked. Cathode and anode tab were used each Al, Cu and welded by ultrasonic wave. If the position of th tab is not welding to the specified position the battery performance may poor.

Pouch forming Process;

Pouch forming is a process in which press Al pouch by measuring the thickness of a manufactured cell(finished the welding process). The thickness of pouch was prepared not only the thickness of a stacked cell but also the thickness of a gas generated predicting value.

3-Side sealing Process;

Sealing process is put the cell(be completed welding process) into the al pouch, and 3 side sealing. The reason for not sealing all sides is to inject electrolyte into the remaining side.

EL Injection Process:

Assembly final process is EL injection. This process is injection electrolyte in to the finished manufacture cell. For rapid absorption of electrolyte , was used vacuum.

The electrolyte used were 1M LiPF₆ in EC:EMC(1:2 by volume, Soulbrain). Add small amount of additive FEC(solbrain)

2.1.5 Formation process

Battery that have finished injection electrolyte will have a formation process before cell performance test. Formation process is follows;

- 1) 1day aging (RT, room temperature)
- 2) Precharging (0.2C, SOC30%)
- 3) 1day aging (RT, room temperature)
- 4) Shipping charge(0.2C charge-0.2C discharge-0.2C charge(SOC50%))
- 5) Degas & Resealing
- 6) Hot press(80°C)

After the injection was completed, cell kept at RT(Room Temperature) for one day so that the electrolyte could permeate the cell sufficiently.

By activating batteries through the formation process, it forms a solid electrolyte interphase(SEI) on the anode surface and generates gas in the early step by side reaction.

Degassing process is for removing gas generated inside, and after completion of the degas process performed hot press process is press for 3seconds at 80°C.

In hot press process, the battery is a reaction between interface and interface , so it is carried out to improve the contact of between the interface.

Defective cells are excluded from performance test, ordinary defective cell show poor performance such as smaller capacity or bad cycle.

2.2 Electrochemical characteristics

2.2.1 dQdV test & Initial capacity(IC)

The dQdV tests were performed at constant current (0.05 C) in voltage range untill 3.8V at 23 °C, SOC 30% by using a charge/discharge system(ETH).

Initial Capacity tests were CC/CV mode charging(0.2C), CC mode discharging(0.2C) in voltage range of 3.0-4.2V at 23°C.

2.2.2 Room Temperature cycle test

The cycle tests were galvanostatically performed at constant current (1 C) in voltage range of 3.0 - 4.2 V at 23 °C, by using a charge/discharge system(ETH).

2.2.3 High Temperature cycle test

The cycle tests were galvanostatically performed at constant current (1 C) in voltage range of 3.0 - 4.2 V at 60 °C, by using a charge/discharge system(ETH).

2.2.4 Discharging and Charging Characteristics

Discharging characteristics(Li-ion deintercalation) performed 0.2C constant current charging and different current(0.2C, 0.5C, 1C, 3C, 5C) rates discharging in a potential range from 3.0 to 4.2V. Charging characteristics(Li-ion intercalation) different current(0.2C, 0.5C, 1C, 3C, 5C) rates charging and 0.2C constant current discharging a potential range from 3.0 to 4.2V by using a charge/discharge system(ETH).

2.2.5 Low Temperature discharge test

The battery system was tested at low temperature to confirm how much capacity the battery system maintains compared to it initial capacity.

LT discharge test were CC/CV mode charging(0.2C, cut-off 0.05C) at 23°C, CC mode discharging(0.2C) at -20°C in voltage range of 3.0-4.2V.

2.2.6 Electrochemical impedance spectroscopy(EIS)

EIS was measured through fully charged cells resistance. The frequency range was 100kHz to 10mHz by using a potentiostat(VSP, BioLogic.)

2.2.7 Electrode resistance measurement

Electrode resistance was measured 4 point probe(LFA467, DASOL ENG)

2.3 Physical properties

2.3.1 High Temperature Storage

Fully charged cells(700mAh, NCM424/NG, NCM424/AG) Storage at 90°C during 4hr and thickness variations measurement.

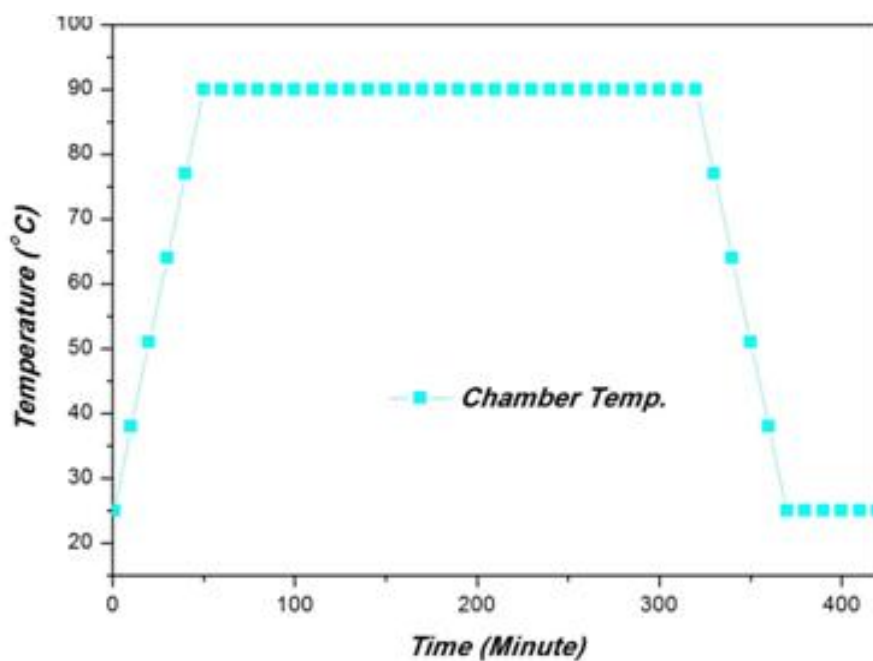


Figure 2-8. Swelling test storage method

3. Results and discussion

3.1 Electrochemical evaluation of battery

3.1.1 Solid Electrolyte Interphase(SEI)

The cycle life of LIBs strongly depends on the passivation of the graphite negative electrode-the formation of the so called solid-electrolyte interphase(SEI). The SEI is formed during the first charge owing to decomposition of the electrolyte components and the formation of insoluble precipitates that prevent further electrolyte-degradation reactions and that render the negative electrode kinetically stable during operation. Volume changes during intercalation produce cracks in the SEI, and this leads to continued electrolyte degradation and loss of lithium inventory.

Improving the stability at the electrode-electrolyte interface is thus paramount to a long cycle life.

Gaberscek and coworkers noted improvements upon using cellulose-based binders and they showed that the proper choice of the polymer and its functional groups could yield more-stable SEI layers.

The above graph shows that the dQdV of a battery with AG(Artificial Graphite) appears at a voltage slightly lower than the dQdV peak of NG(Natural graphite) it resulting in rapid initial SEI generation.

For the candidate 1 and 3 batteries using the water-based binder, a high peak appears in the 2.7V range which is seen as the FEC additive peak.

The dQdV results show that the battery cycle using the AG-PVDF binder in which the SEI was quickly formed will be superior.

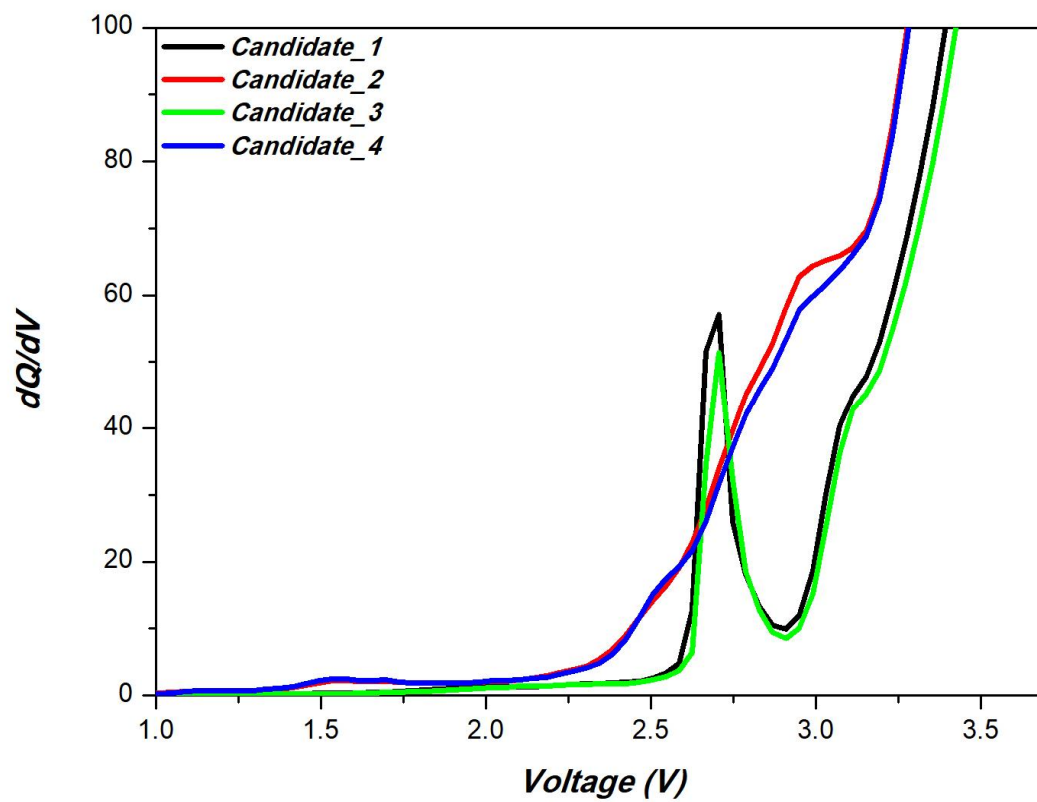


Figure 3-1. dQdV Result data

3.1.2 Initial Capacity(IC)

The initial capacity check of cells was CC/CV mode charge(0.2C, cutoff 0.05C), CC mode discharge(0.2C), voltage range 3.0-4.2V at 23°C.

In this result, i'll divide into two perspectives.

First, change in battery performance according to change the conductive material composition of cathode. Second, battery performance change due to change the binder on the anode.

View 1; Compare the performance of battery according to change the conductive material composition of cathode.

1) candidate 1 and candidate 3, 2) candidate 2 and candidate 4 anode materials were fixed with NG and AG respectively, but the composition of the conductive materials changed.

Both initial capacity of the battery using only carbon black system showed a slightly higher.

In case of 1), the capacity reduction rate was 4.33%, case 2) is 6.22%.

The capacity reduction rate of the battery in which the PVDF binder was applied to the anode was higher.

When using same cathode, the lower the amount of anode conductive material indicated the higher capacity. This means, at low current indicates that does not require a large amount of conductive material when charging-discharging the battery.

View 2; Compare the performance of battery according to change the anode material and binder.

3) candidate 3 and candidate 2, 4) candidate 3 and candidate 4.

The initial capacity is almost no different, but the capacity of the battery with CMC/SBR binder on the anode is slightly higher.

In case of 3), the capacity reduction rate was 1.37%, case 4) is 3.12%.

It can be seen that the capacity reduction rate is generally lower and the initial capacity is higher than the battery that changed the composition of the cathode conductive material in View 1.

As a result, the initial capacity of the battery using CMC/SBR binder is higher than using PVDF binder on the anode when the same cathode is used.

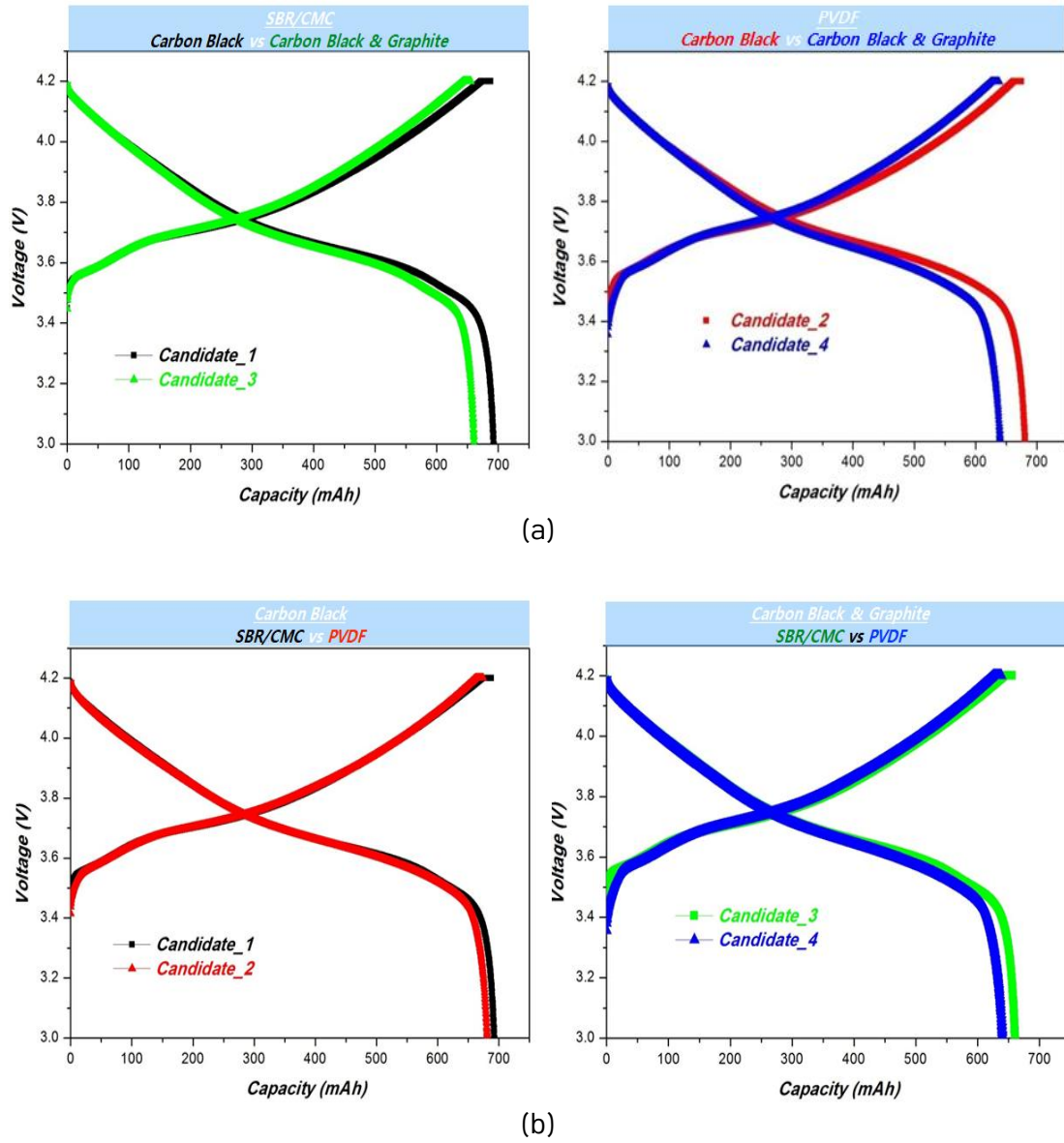


Figure 3-2. The initial capacity performance of battery system according change the composition; (a) View 1, same anode and different conductive composition of cathode (b) View 2, different anode material and binder

In the first charge-discharge, the capacity retention(reversible) is table as follows; Efficiency of all candidates is over 99%.

Candidate	Capacity(mAh)		Efficiency(%)
	Charge	Discharge	
1	692.5	687.3	99.2
2	679.5	673.4	99.1
3	660.7	656.2	99.3
4	639.8	638.4	99.7

Table 5. Capacity retention of batteries

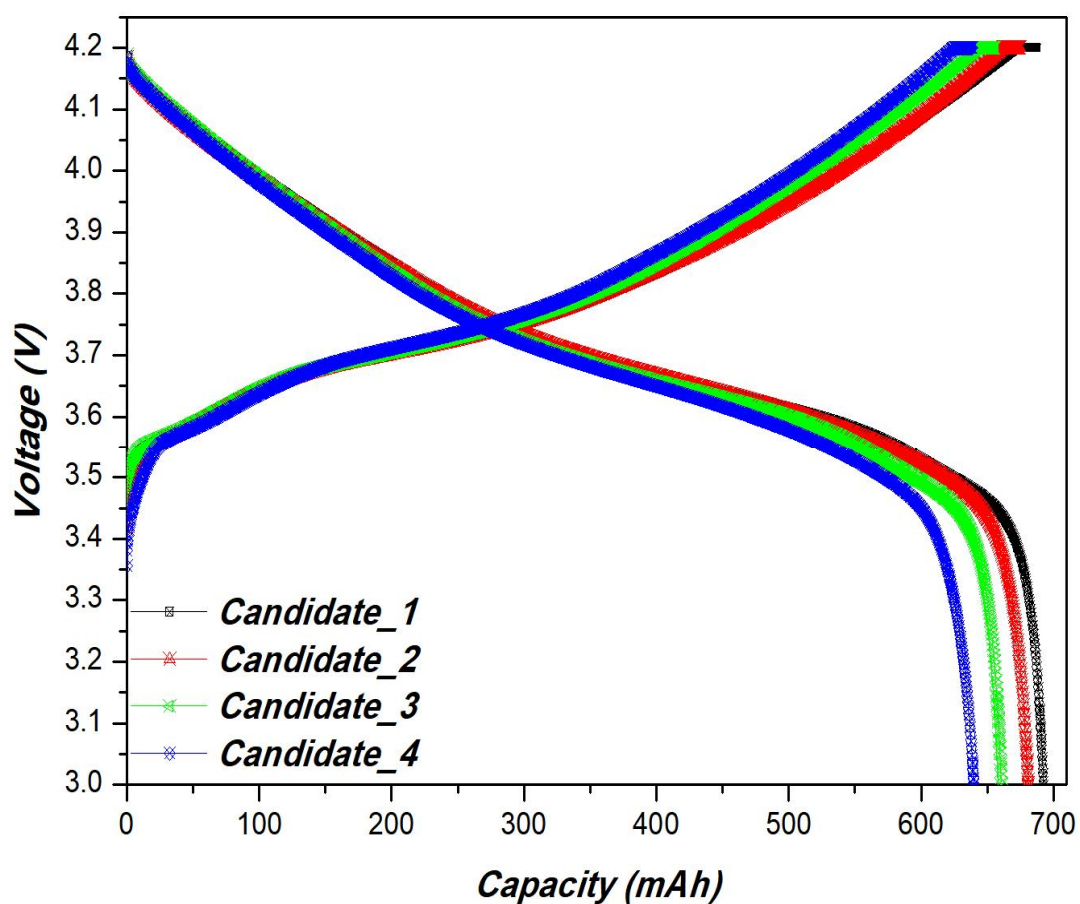
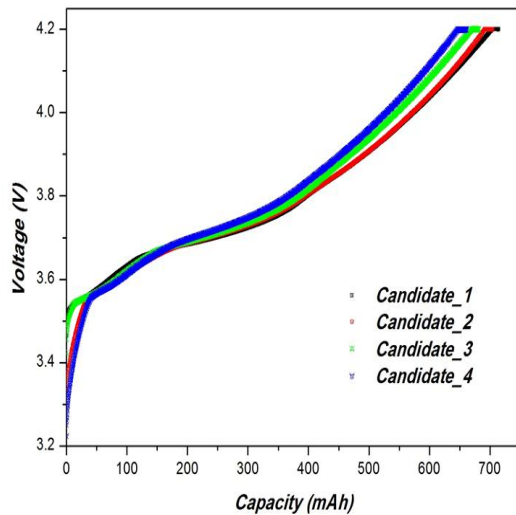


Figure 3-3. Initial capacity of batteries

3.1.3 C-rate(Charge Characteristic)

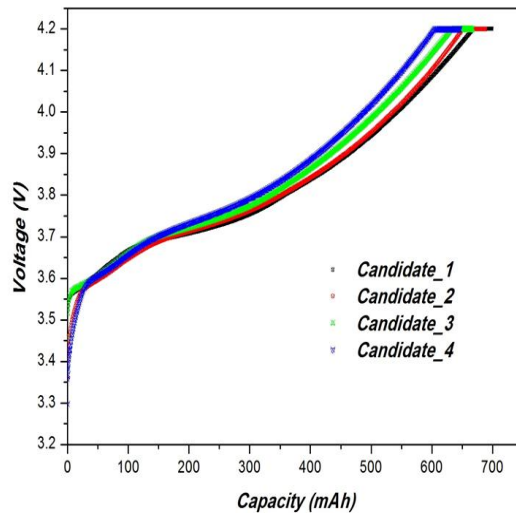
The charge and discharge rate of the current is called c-rate, and the current rate when the battery is discharged in one hour is called 1C.

The discharge capacity was constant at 0.2C, and the charge capacity was changed to 0.2C, 0.5C, 1C, 3C, and 5C.(23°C)



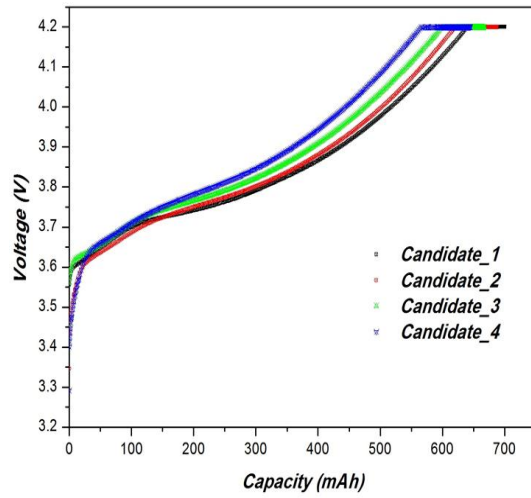
No.	Capacity(mAh)		CC Capacity Proportion(%)
	0.2C	CC	
1	714.1	703.4	98.5
2	704.1	691.7	98.2
3	681.2	669.2	98.2
4	661.1	646.6	97.8

(a)



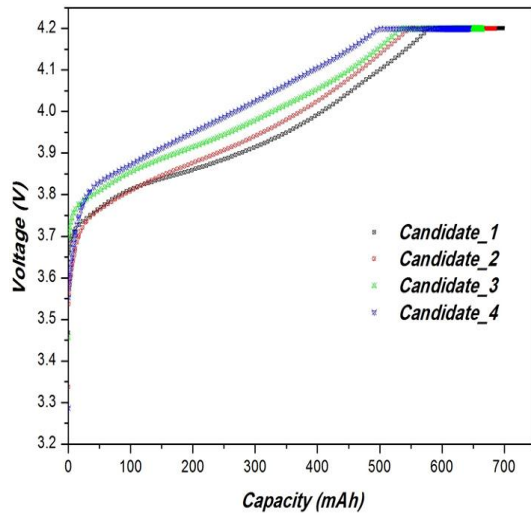
No.	Capacity(mAh)		0.5C/0.2C CC Capacity Proportion(%)
	0.5C	CC	
1	698.8	665.1	$\triangle -5.4\%$
2	688.1	650.6	$\triangle -5.9\%$
3	667.0	632.2	$\triangle -5.5\%$
4	646.3	604.0	$\triangle -6.6\%$

(b)



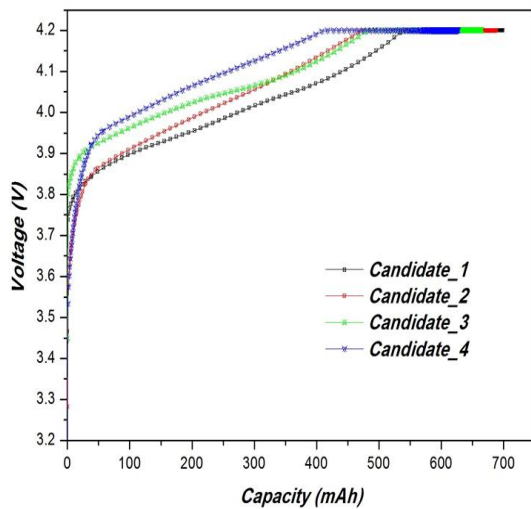
No.	Capacity(mAh)		1C/0.2C CC Capacity Proportion(%)
	1C	CC	
1	699.9	639.8	$\triangle -9\%$
2	687.5	620.4	$\triangle -10.3\%$
3	667.1	599.0	$\triangle -10.5\%$
4	644.8	567.8	$\triangle -12.2\%$

(c)



No.	Capacity(mAh)		3C/0.2CCC Capacity Proportion(%)
	3C	CC	
1	698.2	577.4	$\triangle -17.9\%$
2	685.4	542.4	$\triangle -21.6\%$
3	665.2	530.8	$\triangle -20.7\%$
4	643.7	495.8	$\triangle -23.3\%$

(d)



No.	Capacity(mAh)		5C/0.2C CC Capacity Proportion(%)
	5C	CC	
1	698.7	534.7	$\triangle -24\%$
2	688.5	466.6	$\triangle -32.5\%$
3	664.8	476.3	$\triangle -28.8\%$
4	626.9	408.3	$\triangle -36.9\%$

(e)

Figure 3-4. C-rate result(charge characterisic); (a)0.2C (b)0.5C (c)1C (d)3C (e)5C

As a result of checking the charging capacity according to each rate, candidate groups with a water-based binder (SBR/CMC) showed a higher capacity retention rate than batteries with PVDF.

Due to the point contact of water-based binder, the resistance of the binder for the movement of lithium ions becomes reduced and thus improve the batteries rate characteristic.

C-rate is important to maintain usable capacity even at high current (high C-rate) because it is very important for batteries to be charge-discharge quickly. This requires a lower resistance within the battery.

Material	Super-P	Super-P & SGP5	SBR/CMC	PVDF
Resistivity(Ω-cm)	0.001	- (range over)	0.011	- (range over)

Table 6. Electrode resistance measurement result

Resistivity is the amount of material that goes against the current flow. The inverse of the resistivity is conductivity. So, the smaller the resistivity, the better the current.

Super-p is an amorphous material, and has more contact surfaces with active materials than graphite with crystalline properties. As a result, the conductivity of the electrode containing only super-p is high.

As for the negative electrode, the water-based binder having the point contact has a low specific resistance, so that the charging output characteristic is high.

3.1.4 C-rate(Discharge Characteristic)

To see the discharge characteristics, the charge capacity was constant at 0.2C, and the discharge capacity was changed to 0.2C, 0.5C, 1C, 3C, and 5C.(23°C)

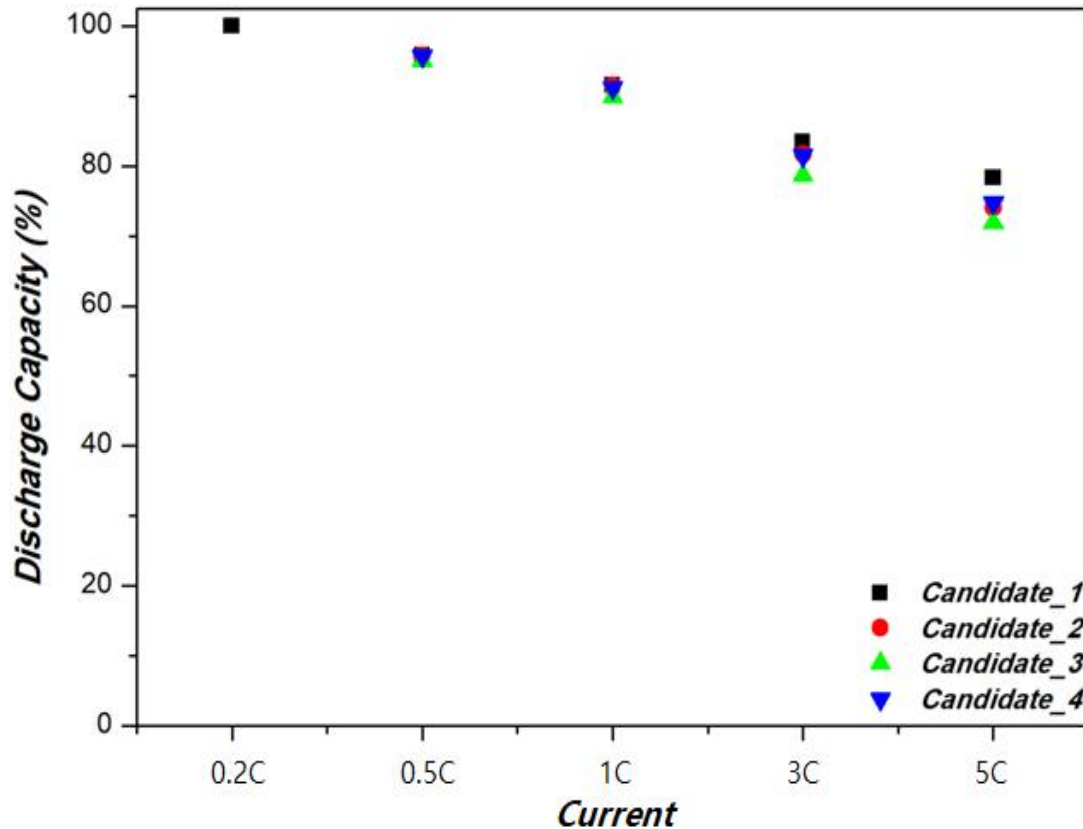


Figure 3-5. C-rate result(Discharge characteristic)

The results show that the discharge characteristic also has the best rate characteristics of a battery using a water-based binder.

On the other hand, batteries that use the same water-based binder but the graphite type of conductive materials(SGP5) can be found to have lower discharge rate than batteries that use PVDF binder.

As a result of slightly opposite charge rate characteristics, batteries with water-based binder all had better rate characteristics than batteries with PVDF, but the discharge rate characteristics were slightly different depending on the type of conductive material in cathode.

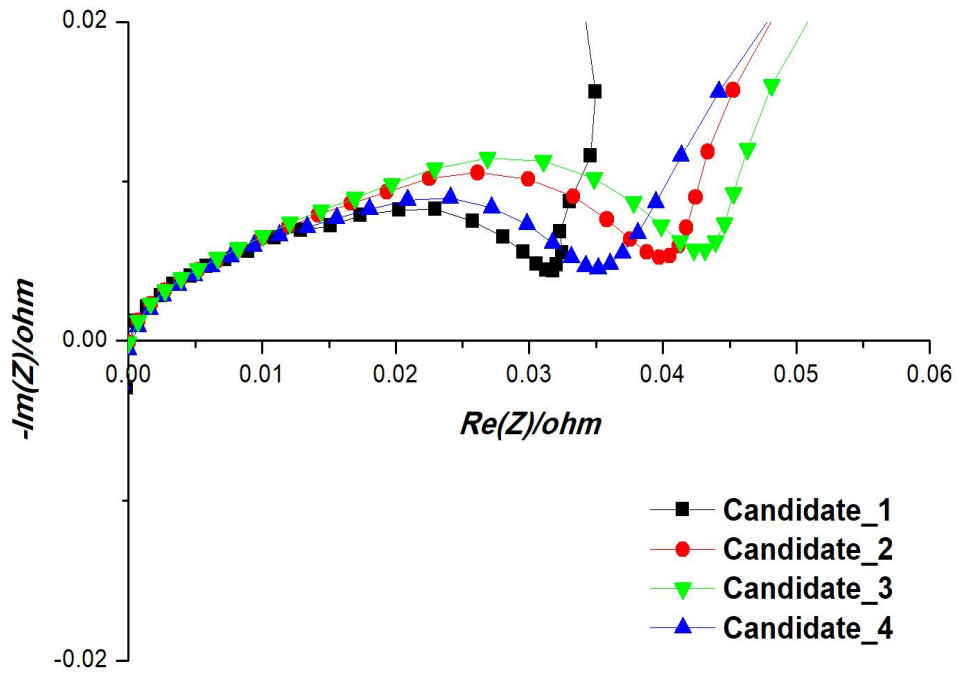


Figure 3-6. EIS

EIS test conducts to analyze the results of discharge characteristic.

Resistance measurement was carried out using a fully charged battery. Discharge is a state in which lithium ion is moved to cathode from anode, and fully charge resistance(SOC 100%) is an important factor.

As a result, the size of resistance was confirmed in the order of candidates 1, 4, 2, and 3. So similar results were obtained from the actual discharge characteristics.

The discharge characteristics are judged to be more important the resistance of the batteries in the state of fully charge than the conductivity of the electrode.

In a battery system that is applied with a water-based binder, batteries that are applied with a graphite type (SGP5) on an anode were shown to have lower discharge rate characteristics than batteries that are used only carbon black (Super-P).

It can be seen that there is a difference in the conductivity of the cathode electrode, and when the carbon black type conductive material(candidate 1) is used alone than the electrode used by mixing the graphite type conductive material and the carbon black conductive material(candidate 3), it shows higher conductivity when the battery is discharged.

On the contrary, battery system that is applied with PVDF binder to anode electrode(Artificial Graphite) has high discharge characteristic of batteries that are mixed with graphite and carbon black system(candidate 4) on an anode. As a result, in case of charging, the change in the composition of the cathode is not visible as the lithium ion is transferred from the cathode to the anode.

3.1.5 Low Temperature discharge test

Recently, secondary batteries are used in various fields, and in particular, low temperature characteristics evaluation are very important because they may need to be used in extreme situations, such as electric vehicles and ess. At low temperatures, mobility decreases when ions move inside the secondary battery electrolyte, which is significantly lower than capacity at room temperature.

In order to solve such a problem, it is necessary to change the composition of the electrode to help power well, or to replace the electrolyte with a material that operates well even at low temperatures.

This evaluation aims to determine whether the battery system manufactured according to each composition works well at low temperatures, and if so, which system performs better.

First, full charging CC/CV mode(0.2C, cut off 0.05C) at RT(23°C). And then discharge at -20°C(CC mode 0.2C), voltage range is 3.0V to 4.2V.

Looking at the discharge characteristics at low temperatures, it can be seen that the initial temperature drops to 60% of the capacity.

At low temperatures, the capacity was almost the same, but candidate 4 cell(using organic binder) showed slightly better capacity retention. In addition, the cell containing the graphite-based conductive material showed the better capacity retention rate as in the discharge rate characteristic test.

In the charging process, lithium ions are transferred from the cathode electrode to the anode electrode, and there is no performance difference according to the change of the positive electrode composition in the charging characteristic. However, in the case of discharge, lithium ions move from the anode to the cathode, and it was confirmed that there is a change in performance depending on the composition of the anode.

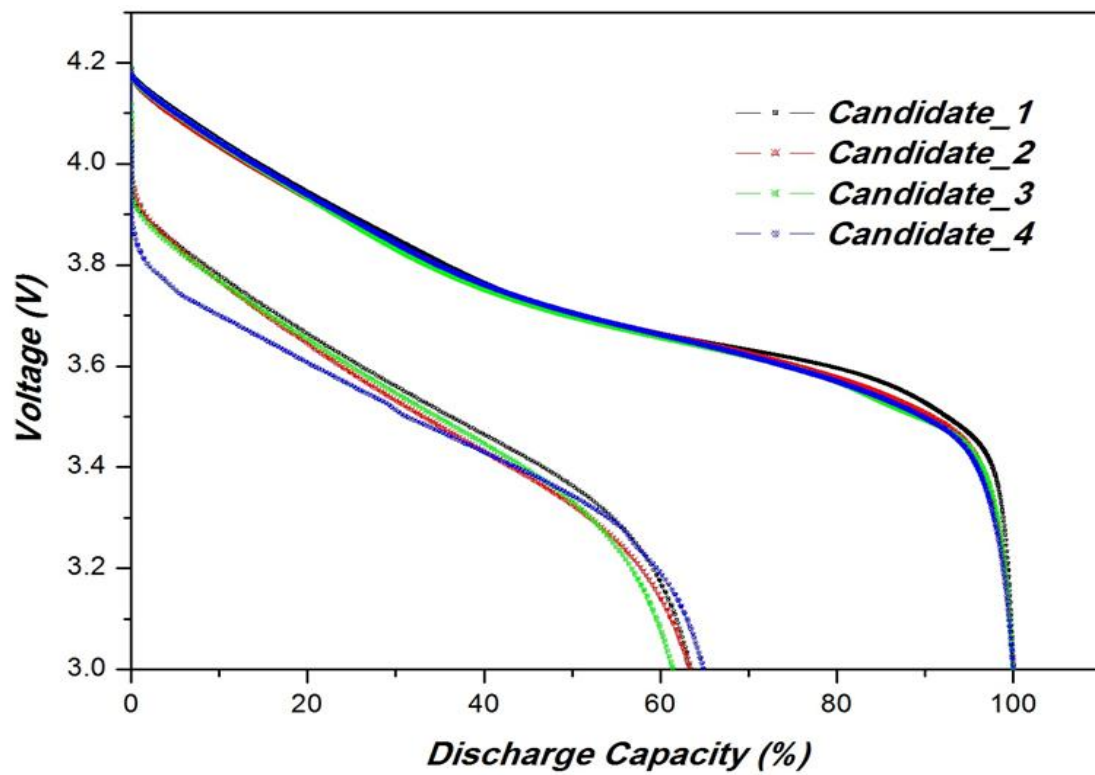


Figure 3-7. Low temperature discharge capacity retention

3.1.6 Room Temperature cycle test

One of the most important things in a battery is how long it can be used. By evaluating the battery cycle according to the electrode composition, the cycle evaluation was conducted at room temperature to confirm how long the performance is maintained.

The cycle test is performed follows; charge - CC/CV mode(1C ,cut off 0.05C), discharge- CC mode(1C), voltage range 3.0-4.2V , 1000cycle at RT.

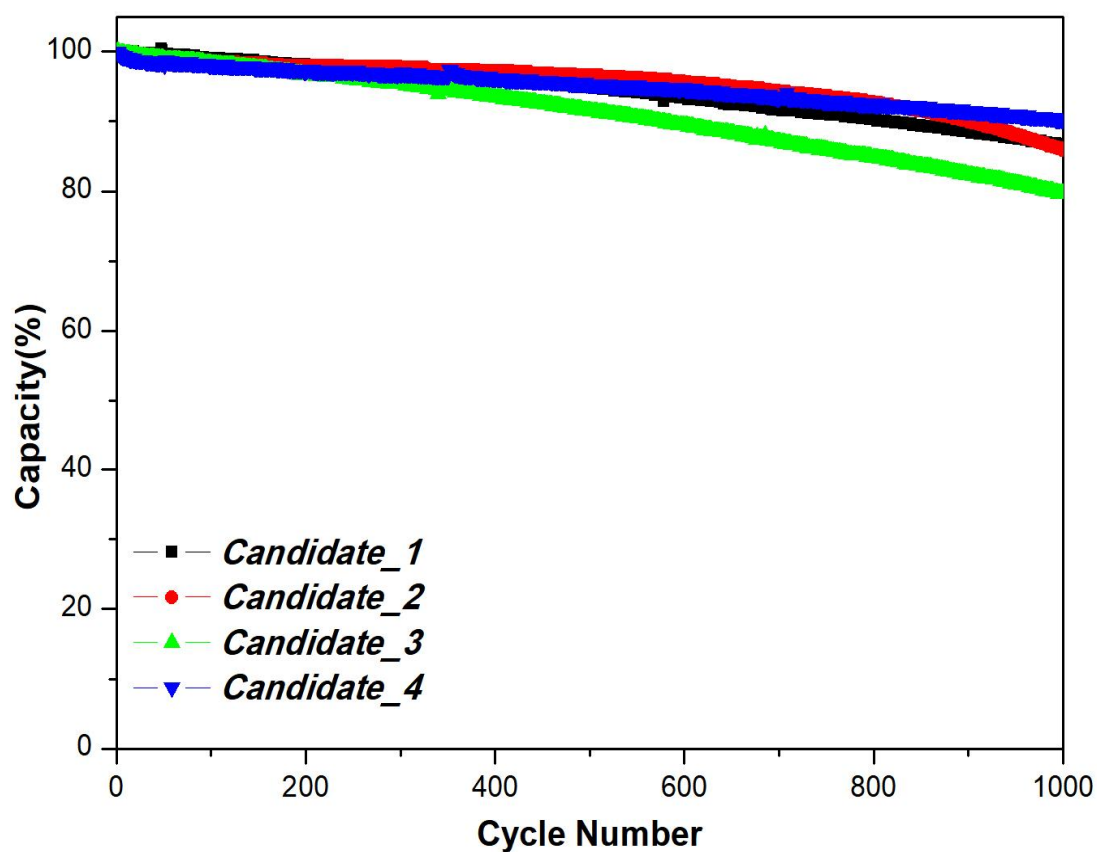


Figure 3-8. RT cycle result

Capacity retention at 1000 cycles at room temperature was more than 80%. The battery(candidate 2, 4) using AG(artificial graphite)-PVDF binder showed high capacity retention even when the composition of the conductive material was changed in the cathode electrode, and the battery(candidate 1, 3) using NG(natural graphite)-water based binder showed relatively low retention. The capacity retention ratio was calculated by dividing the 1000th discharge capacity with the initial capacity. Candidate 1: 86.53% Candidate 2: 85.92% Candidate 3: 80.7% Candidate 4: 90.31%

This difference in the cycle capacity retention seems to be due to the reduction of degradation by the dQdV. The SEI layer of the battery containing PVDF binder may be first formed at 2.5V(very small peak) and thus inhibit direct reaction of the electrolyte and peeling of the carbon layer structure. Finally it improves the cycle performance of the batteries. Faster SEI layer formation means less depletion of electrolyte, resulting in better cycle performance.

In addition, even using the same water-based binder, it can be seen that the cycle capacity retention rate of the battery(candidate 3) used by mixing the graphite-based conductive material(SGP5) in the cathode electrode is low.

In particular, the battery fabricated using PVDF binder-AG(candidate group 4) exhibited a capacity retention rate of more than 90% even in the 1000th life.

This is a retention rate that differs by about 5% from candidate 2, which used the same anode electrode but changed the composition of the conductive material.

In view of this, in the AG-PVDF battery system(candidate 4), a mixture of graphite type conductive materials(SGP5) into the cathode electrode was good for performance. However, in the NG-water based binder battery system(candidate 3), it was confirmed that the graphite type mixture was not good.

3.1.7 High temperature cycle test

As mentioned above, the application of the battery is used in various situations, especially at high temperatures, the capacity of the battery is greatly reduced due to the acceleration of electrolyte depletion, internal chemical reactions, short circuit, etc. makes the battery difficult to use.

Fig. 1-25 below shows the results of the cycle evaluation at high temperature, and the high temperature cycle evaluation is also evaluated at 60 ° C with charge(CC/CV 1C, 4.2V cut off 0.05C) and discharge(CC 1C, cut off 3.0V) proceeded.

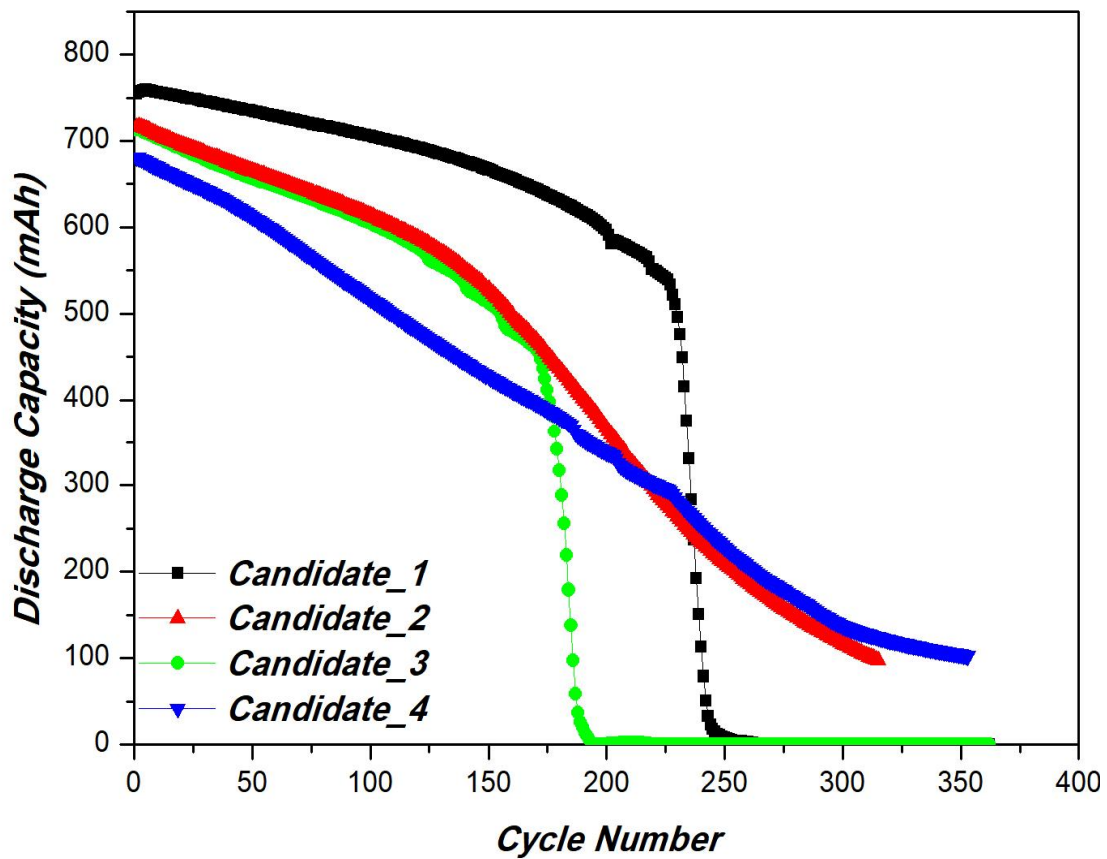


Figure 3-9. HT cycle result

As shown in the figure, the high temperature cycle curves of the batteries of candidates 1 and 3 drop off sharply. This seems to be due to an internal short.

On the other hand, in case of candidate 2 and 4, the capacity decreases gradually, and it can be seen that the performance naturally decreases.

Up to 250 cycles, the battery using the water-based binder(candidate 1) showed a capacity retention of more than 60%, which was much better than the other candidates.

The sudden decrease in capacity of a battery system with a water-based binder(candidate 1, 3) seems to be due to the swelling of the cell as gas is generated inside the cell. As the cell swells, the battery appears to be dying as the cathode and the anode contacts the battery, causing the short.

In addition, as the synthetic is performed at a high temperature in the manufacturing process of the artificial graphite and graphite type conductive material it was confirmed that the high temperature characteristics are higher than the material produced at a relatively low temperature when using the material produced at a high temperature.



Figure 3-10. Appearance of after HT cycle cell; from the left top candidate 1, candidate 2, candidate 3, candidate 4

3.2 Physical evaluation of batteries

3.2.1 Swelling test

Safety issues such as fire and explosion at high temperatures of batteries are becoming more and more important in recent years as they move toward medium and large batteries. Accordingly, it is intended to observe the change in battery thickness generated when the battery is stored at high temperature.

Swelling test is to stored the fully charge cells in 90°C oven during 4hr and to measure the thickness change.

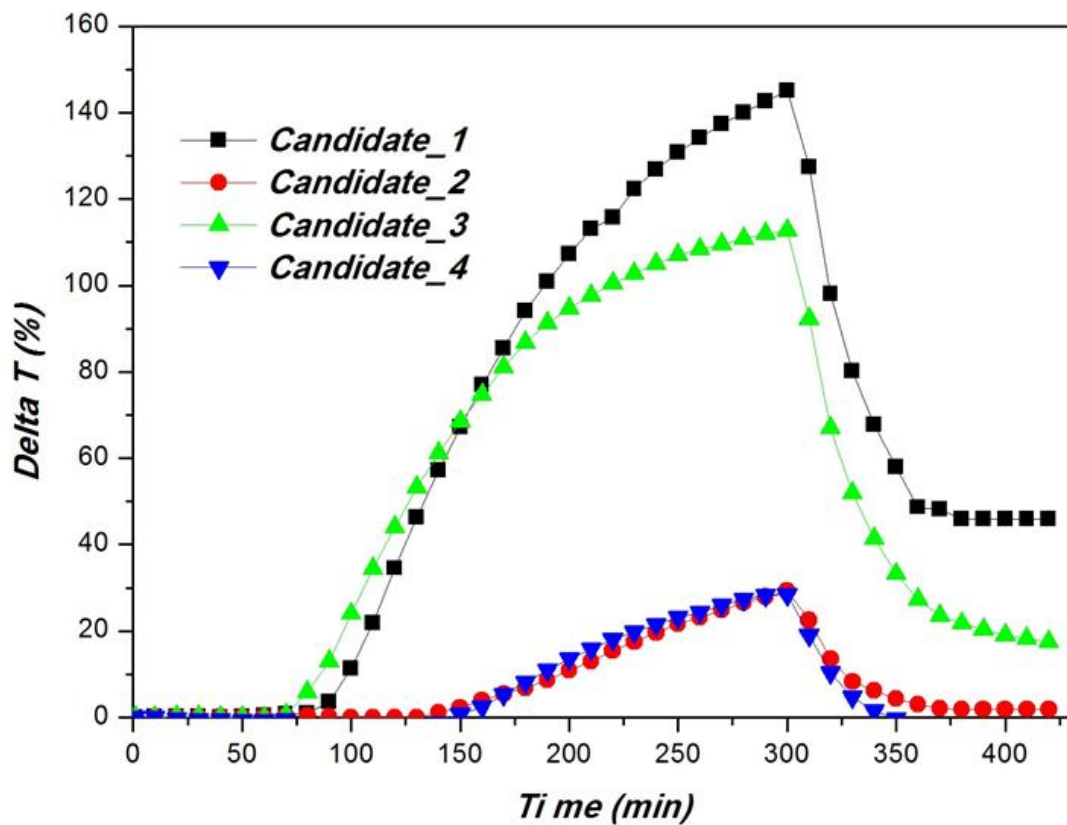


Figure 3-11. Swelling test result

As a result of the evaluation, it can be seen that the thickness of the battery using the water-based binder(candidate 1, 3) increased rapidly.

In contrast, batteries using PVDF binder(candidate 2, 4) can see swelling of about 20%.

Normally, batteries with water-based binders can see about five times the thickness of PVDF binder.

This may be because the -OH group of CMC, which is added as a surfactant(water-based binder), causes gas formation by reaction with the electrolyte.

4. Conclusion

The electrode was fabricated by changing the composition of the electrode (conductive material, kind of anode binder), and for optimized battery system was studied by making four candidate groups.

Currently, small mobile secondary batteries are mainly used in NG(Natural Graphite).

NG(Natural Graphite) has a slightly higher capacity than AG(Artificial Graphite), and together use the water-based binder such as CMC/SBR. Water-based binder can be added a small amount, so that the specific gravity of the anode material in the electrode can be increased. (It means the energy density increases.)

In the case of charge rate characteristics of the battery, it can be seen that the performance of candidate 1, 3 using an water-based binder is better than that of other PVDF binder batteries.

It is thought that the CMC/SBR used in the water-based binder makes the power rate faster by reducing the resistance generated at the interface while making point contact. In addition, through the measurement of the resistivity, candidate 1 using the super-p and the water-based binder has a low resistivity and thus shows good conductivity.

In the case of the discharge characteristics, it was confirmed that the charging characteristics were slightly different.

The resistance of the fully charged battery(SOC 100%) was measured, and the resistance was shown in the order of candidate group $1 < 4 < 2 < 3$. It can be confirmed that this is similar to the tendency of the discharge characteristics. As a result of cycle evaluation at RT, batteries system using AG-PVDF binder (candidate 2, 4) showed high efficiency, and all of them showed more than 80% performance for 1000 cycles.

At high temperatures, the battery(candidate 1, 3) applied with the water-based binder was severely expanded, and it was confirmed that the efficiency dropped rapidly.

Finally, the observation of the thickness change through the storage of the battery at high temperature confirms that the volume of the battery(candidate 1, 3) applied with the water-based binder was expanded five times more than those made of PVDF binder(candidate 2, 4).

In this two high temperature experiments, batteries containing PVDF binder have less expansion than batteries with water based binder. Because the

hydroxyl groups of the CMC causes to the gas production by the reaction with the electrolyte at HT.

When the PVDF binder was applied to the anode during battery manufacturing, used together that the carbon black conductive material and the graphite type cathode(candidate 4) showed better performance than the carbon black alone(candidate 2).

On the contrary, when the water-based binder was applied to the anode, carbon black type conductive material in the cathode showed better performance.

In the case of NG-water based binder, it is better to use amorphous conductive material(candidate 1) for cathode electrode. The contact surface area is different depending on the particle type of the conductive material and the diffusion of lithium ion appears to be affected as well.

As a result, candidate 1 and candidate 4 battery system are the optimal composition of each.

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