Master's Thesis
석사학위논문

Development of Electrolytes for Improving Electrochemical Performances of High-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

Ye-Seol Nam (남 예 슬 南 藝 瑟)

Department of Energy Systems Engineering
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Co-Advisor : Professor 김 재 현

by

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DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Energy Systems Engineering. The study was conducted in accordance with Code of Research Ethics[1]

12. 07. 2016

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ABSTRACT

Currently there is an urgent need to maximize the energy density of lithium ion batteries (LIBs). LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) is a promising candidate for the high-energy LIBs due to its high operating voltage, low price, and reasonable capacity. However, LNMO suffers from anodic decomposition of the electrolyte under high-voltage operation, leading to severe capacity fading. Here, we examine the effects of linear carbonates (LC: DMC, DEC, and EMC) in 1 M LiPF$_6$ EC/LC (3/7, v/v) on LNMO/graphite, LNMO/Li, and graphite/Li cells. We also investigate LNMO symmetric cell test in cycle at 60 ^{o}C because the use of symmetric cells complementarily suggests that transition metal dissolution is mainly responsible for the LNMO/electrolyte interface degradation. The LNMO cells with EC/DMC show better cyclability and coulombic efficiency at 25 ^{o}C, 55 ^{o}C and 60 ^{o}C than those with EC/EMC and EC/DEC. Also, the cells with EC/DMC exhibit superior self-discharge suppression at 60 ^{o}C to other compositions. The improved performances in the cells with EC/DMC are attributed to diminished HF formation compared to the others, which is evidenced by both HF titration and surface analysis of LNMO using X-ray photoelectron spectroscopy (XPS). Also, through LSV analysis, Oxidation stability of EC/DMC is higher than EC/EMC and EC/DEC.

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Development of Electrolytes for Improving Electrochemical Performances of High-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

1. Introduction

Lithium ion batteries have been widely used in such portable electronic devices as cellular phones and laptop PCs. Also, vehicle electrification has been a rapidly growing trend in the automobile technology landscape. Various types of electric vehicles have come to market during the past several years, including start-stop plug-in hybrid electric vehicles (PHEVs), and pure electric vehicles (EVs). Li-ion batteries have been a great facilitator to enable this movement toward vehicle electrification because of their high energy and power densities compared with other energy-storage devices. [1] After their successful use in consumer electronic devices, Li-ion batteries have been developed in ever larger sizes to support the energy and power requirements needed for electric vehicles. In pursuit of extended driving distances and lowered costs for electric vehicles, extensive research and development efforts have been devoted to finding the next generation of cathode materials for Li-ion batteries. Among these promising new cathodes, LNMO is a promising high voltage cathode candidate in lithium ion battery application due to low cost, being non-toxic, and its high operating potential for high energy demands. However, LNMO suffers from severe electrolyte decomposition

and a manganese dissolution issue at high voltage. As a result, many studies have been investigating

how to improve high voltage lithium ion batteries with variations of electrolyte composition. The

electrolytes of lithium ion battery are divided into linear carbonate (dimethyl carbonate, ethyl-methyl

carbonate and diethyl carbonate) and cyclic carbonate (ethylene carbonate and propylene

carbonate). As shown in table 1, the cyclic carbonates such as propylene carbonate and ethylene

carbonate have more viscosity dielectric constant, and surface energy compared with linear

carbonates. Also, ionic conductivity of linear carbonates is higher than that of cyclic carbonates

because of high viscosity.

Table. 1 HOMO energies and physical properties of single-carbonate solvents.

	HOMO energy(eV)	Density	Dielectric constant	Viscosity(cP)
Propylene carbonate(PC)	-7.70	1.21	65	2.53
Ethylene carbonate(EC)	-7.63	13.32	90	1.92
Dimethyl carbonate(DMC)	-7.80	1.07	3.1	0.625
Ethyl-methyl carbonate(EMC)	-7.30	1.007	2.8	0.665
Diethyl carbonate(DEC)	-7.25	0.975	2.8	0.736

For this reasons, the cyclic and linear carbonates in lithium ion batteries were generally mixed for finding proper composition. Fig. 1 shows the conductivities of ethylene carbonate with a co-solvent. The major factor determining the conductivity of electrolytes is the viscosity of them. [2]　The 1 M LiPF$_6$ ethylene carbonate/dimethyl carbonate (3/7, v/v) exhibits high conductivity compared with diethyl carbonate and ethyl methyl carbonate. This is mainly due to viscosity and dielectric constant of linear carbonates. The choice of co-solvent is an important issue because it greatly affects not only the conductivity, [3] but also performance, such as capacities and efficiencies. Many research groups have reported electrochemical behavior of organic electrolyte solution based on carbonate with different compositions. For example, EC-DMC composition exhibits better cycle performance than EC-EMC and EC-DEC composition for 5 V Li-ion batteries in the paper of Wu et al. [4] However, the paper of Julien Demeaux insists that the 1 M LiPF$_6$ EC/EMC mixture electrolyte has better performance than EC/EMC in case of LNMO/LMMO symmetric cell cycle test and self-discharge test. [5]

Herein, the purpose of this study is to interpret and compare the electrochemical performances with linear carbonates for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) and graphite. To confirm the difference of performance according to linear carbonates, coin cell tests were carried out at room (25℃) and high (55℃) temperatures and then a surface analysis was performed after coin cell tests to investigate the effect of linear carbonates. In particular, electrolyte decomposition and transition metal dissolution are plagued with poor reversibility. So, to better understand electrode/interface,

symmetric cell test was employed. Symmetric cell test show that transition metal ion dissolution is mainly responsible for the $LiNi_{0.4}Mn_{1.6}O_4$/electrolyte interface degradation.
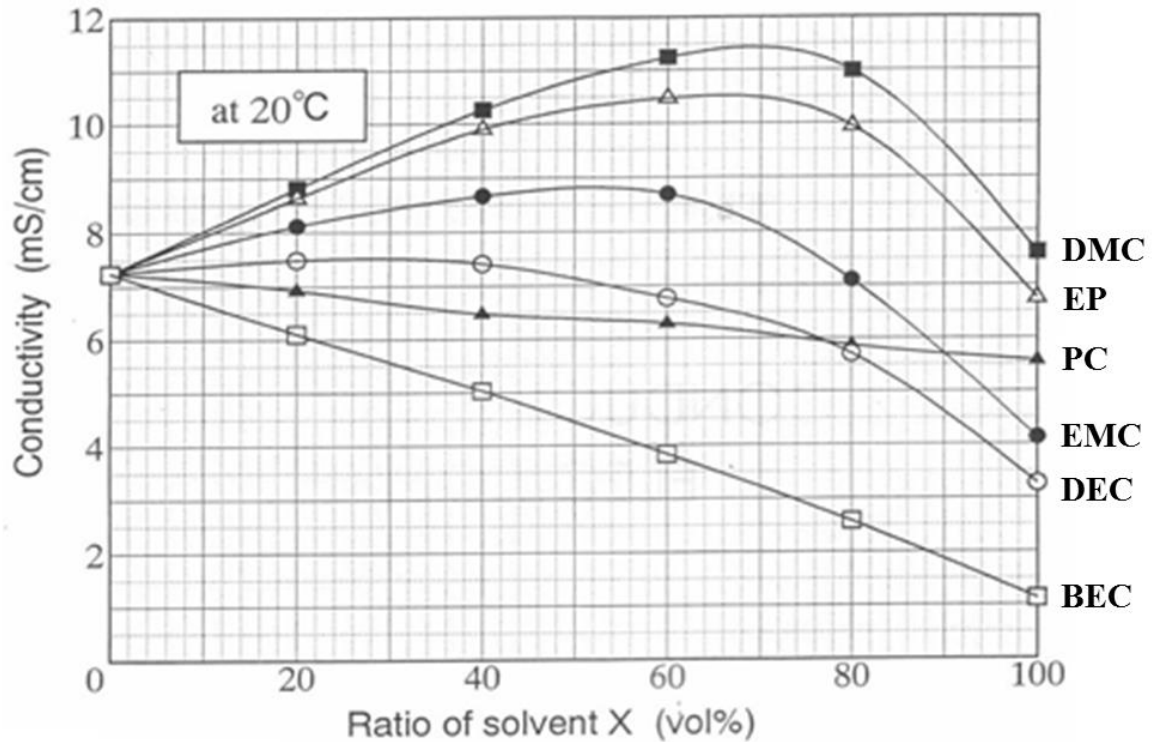
Fig. 1.Conductivity of 1M LiPF$_6$/Ethylene carbonate with a different carbonate at 20 ℃

2. Methods and Materials

2.1 Chemicals and Electrode Preparation.

Battery grade 1 M LiPF$_6$ Ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (EMC) and ethyl-methyl carbonate (EMC) were provided by Panaxetec Co. in South of Korea. The electrolytes were dried overnight using molecular sieves in an Ar-filled glove box. Linear carbonates were mixed with EC (EC/LC ratio: 3/7, v/v). Both The LNMO obtained from LG cathode and The graphite anode obtained from Bexel were consisted of 90 wt% active material, 5 wt% carbon black

and 5 wt% polyvinyldene fluoride(PVDF) binder. The electrodes were cut into pieces 14 mm in diameter.

2.2 Coin-type cell assembly

Coin-type cells are widely recognized as the standard test platform for lithium ion battery electrode research. A coin-type cell (diameter, 20 mm; thickness, 3.2 mm) which consisted of $LiNi_{0.5}Mn_{1.5}O_4$, a separator, graphite and each electrolyte were assembled in an Ar-filled glove box. In order from the bottom of Fig. 2, 150 µl of electrolytes were injected on the bottom of the case. After the electrode was put in place, a separator and a gasket were installed. An anode was inserted on the gasket with a spacer disk and wave spring. Lastly, the coin-type cell was sealed using a clamping machine. After coin-type cell assembly, wetting was initiated for 20 hours at 25 ℃.

2.3 LNMO/LNMO symmetric cell

The cycle tests were performed for LNMO symmetric cell at 60ºC at 0.5 C between -1.5 and 1.5 V. The LNMO/LNMO symmetric cells were fabricated by employing LNMO electrodes with a state-of-charge (SOC) of 50 collected form LNMO/Li cells that had been cycled three times at 0.2 C constant voltage (CV) charge with a cut-off of 1/20 C current and discharging at a constant current of 0.2 C.

2.4 Graphite/Graphite symmetric cell

2032-type coin cells were assembled described above. The graphite/graphite symmetric cells cycle test carried out in cycle tests were at 55 °C and at 60 °C at 0.5 C between -0.5 V and 0.5 V.
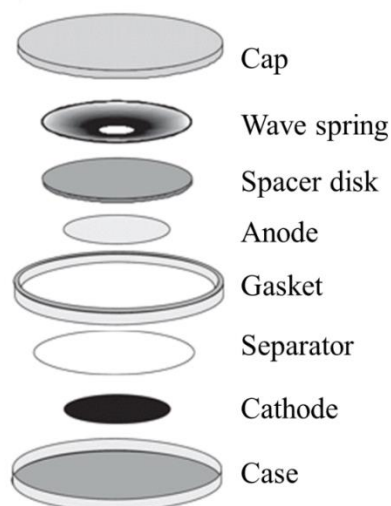
Fig. 2. An illustration of the coin-type cell parts and assembly

2.5 X-ray photoelectron spectroscopy

For the sample preparation, LNMO/lithium coin half cells were cycled 100 times over range 4.8-3 V and the fully discharged cell was disassembled to retrieve the LNMO according to linear carbonates, which were dried in an Ar-filled glove box.

2.6 HF and H$_2$O Content Measurements.

The water and HF content in the electrolytes were analyzed by Karl Fisher and acid-base titration methods, respectively. The water content of electrolytes were less than 20ppm.

2.7 Linear Scanning Voltammetry

The electrochemical oxidation stabilities of binary mixture electrolytes were screened by linear scanning voltammetry carried out with a VSP potentiostat (Biologic). Pt disk, Pt wire and Li metal were used for the working, counter and reference electrodes respectively.

3. Results

To evaluate the effects of the linear carboantes (DMC, DEC, EMC), full cell tests were performed at a room temperature (25 °C) and at a high temperature (60 °C) of as well. All the cells were cycled initially at 25 °C over a 3.0 ~ 4.8 V range three times with a 0.2 C charging current followed by a 4.8 V constant voltage charge (CC/CV) and 0.2 C constant current (CC) discharging to complete the formation process. Cycle test was performed with 0.5 C CC/CV and 0.5 C CC over 3.0 ~ 4.8 V at 25 °C, 55 °C and 60 °C.

3.1 The Effect of the Linear Carbonate on LNMO/Graphite Full cell.

We investigated that LNMO/Graphite full cell test in a variety of conditions.
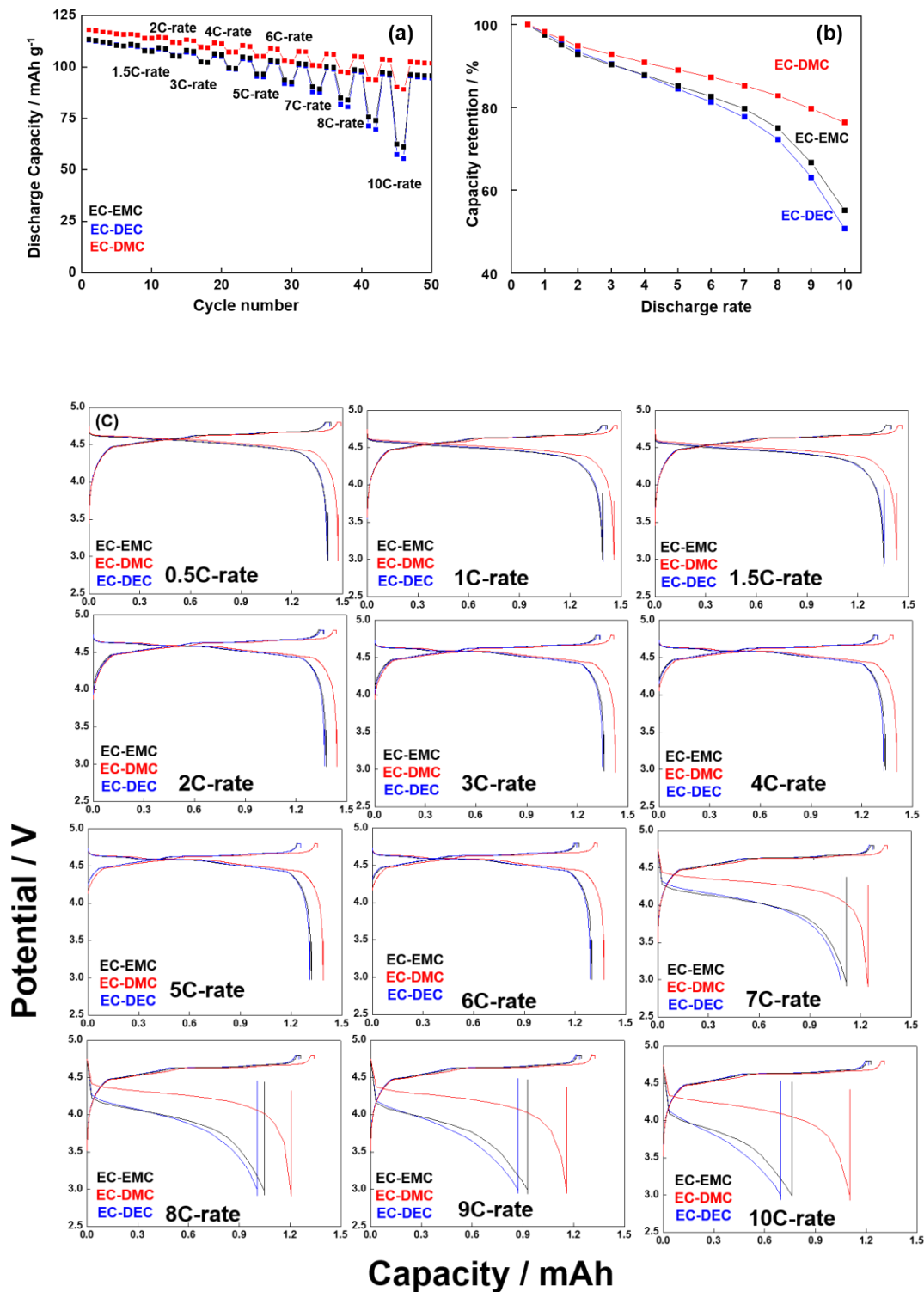
Fig. 3. (a) LNMO/Graphite full-cell C-rate performace at each rate ,(b)capactity retention and
(c) the charging-discharging profiles at 25 °C with linear carbonates arrording to C-rate

Fig. 3. presents the C-rate capability of the LNMO/Graphite cells in each linear carbonate electrolytes. C-rate capability tests were employed in the following order : EC-DMC > EC-EMC > EC-DEC.

Our observation that the EC-DMC cell exhibited superior rate capability to the other cells at higher current densities. Fig. 3. (c) shows the charge-discharge profiles of C-rate with linear carbonates. EC-DMC clearly exhibits a lower over-potential at the high C-rate than EC-DEC and EC-EMC. This result is related to the lower viscosity of EC-DMC compared with EC-EMC and EC-DEC, as shown in table 1.
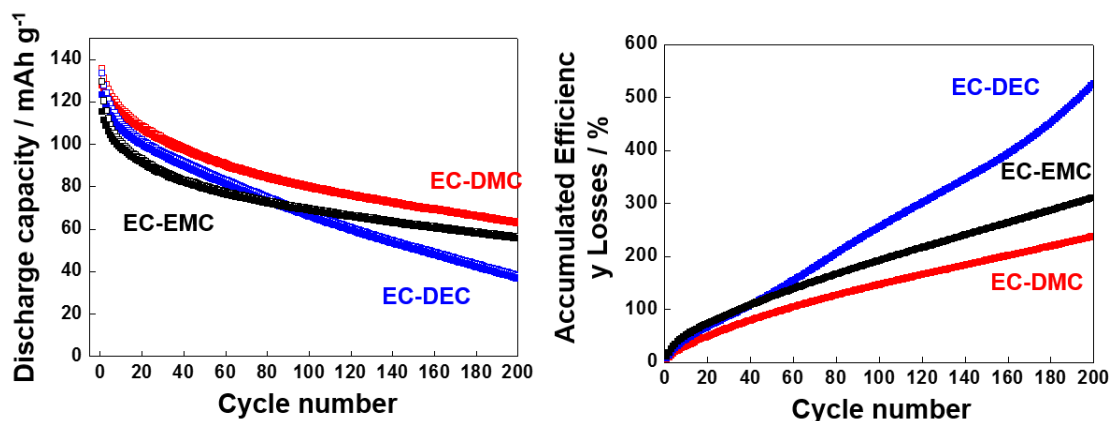
Fig. 4. LNMO/Graphite full-cell performance and accumulated efficeincy losses at 55 °C with linear carbonate

After LNMO/Graphite full cell C-rate capability tests at room temperature, full-cell tests at 55 °C were carried out to evaluate cycle performace with binary imxture electrolytes. As shown as fig. 4, EC-DMC displays great cycle performance and charge-discharge efficiency compared with EC-EMC and EC-DEC at 55 °C.
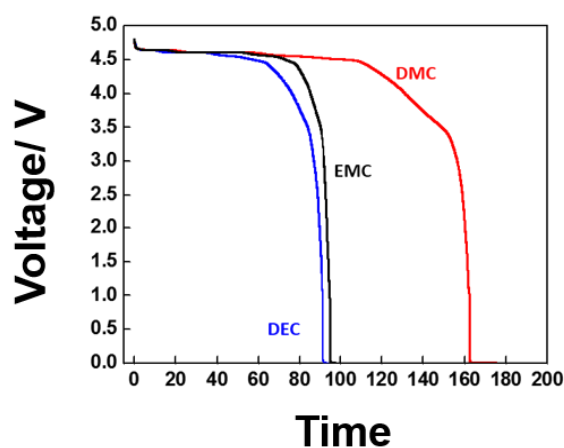
Fig. 5. Open circuit of voltage evolution of LNMO/Graphite full-cell with EC-DMC, EC-EMC and EC-DEC

Table 2. Self-discharge comparison of time to potential of LNMO/graphite full-cells

	EC-DMC	EC-EMC	EC-DEC
Time to 0 V (Self-discharge)	162 h	95 h	91 h
Potential at 160h	4.5 V	0 V	0 V

After cycle test at room and high temperature, we examined that open circuit of voltage (OCV) of

LNMO/Graphite full-cell with the electrolytes at 60 °C. The variation of the OCV is because of a

lithium reinsertion from the electroyte. [6, 7] Fig. 5 presents the self-discharge profiles at a high

temperature of 60 °C. In the EC-DEC, the electrolytes tend to oxidatively decompose on the charged

LNMO, suggesting that it shows the serious potential drop compared with EC-DMC and EC-EMC.

However, EC-DMC displays the best performance during the self-discarhge test. As shown in table

2, the time of the voltage drop to 0 V was 162 hours longer than EC-EMC. This result clearly shows that EC-DMC composition is more stable than EC-DEC and EC-EMC at a high potential range.

3.2 The Effect of the Linear Carbonate on LNMO

 To comfirm the character of beween LNMO and electorlyte interface degredation, we investgated that LNMO/Li half cell cycle tests , LNMO symmetric cell cycle tests and LNMO/Li lithium metal storage tests were carried out at high temperature.
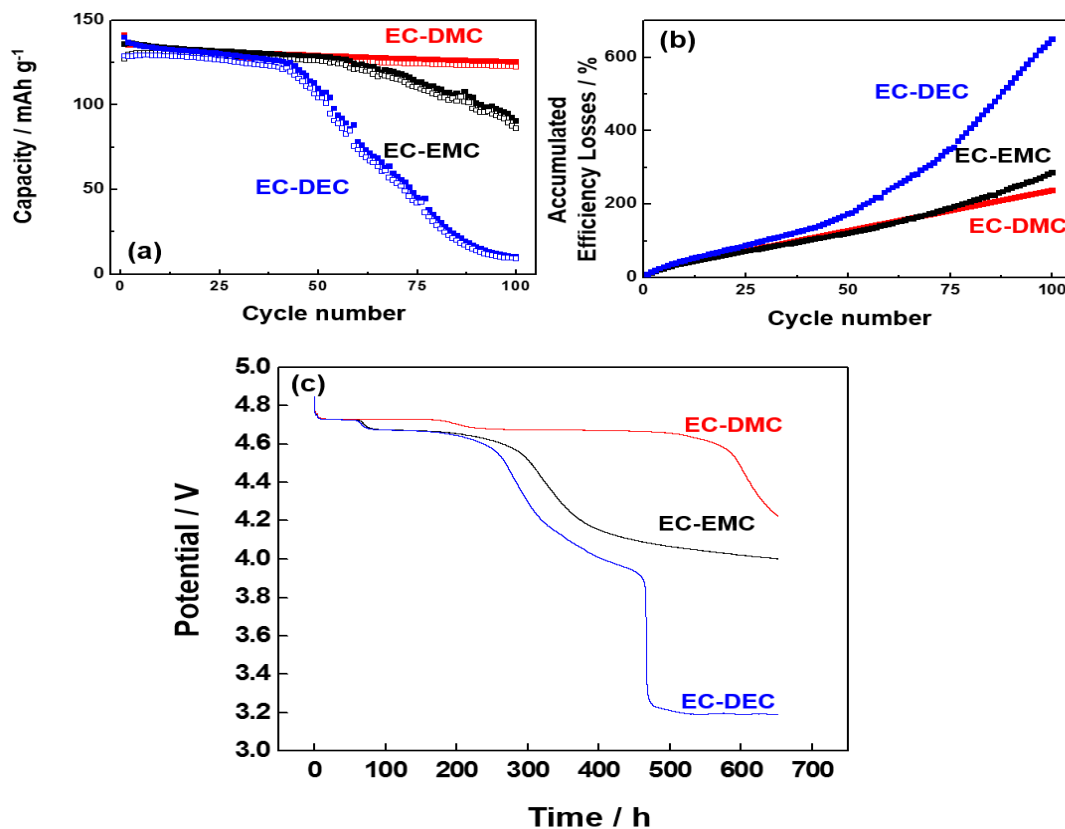
Fig. 6. (a) LNMO/Li metal half-cell performance(0.5C-rate) and (b) accumulated efficiency losses at 55 ℃ and (c) Open circuit of voltage evolution of LNMO/Li metal cell at 60 ℃ with linear carbonates

Table 3. Self-discharge comparison of time to potential of LNMO/Lithium metal half-cells

	EC-DMC	EC-EMC	EC-DEC
Time to 4.2 V (Self-discharge)	650 h	375 h	320 h
Potential at 160 h	4.2 V	4.0 V	3.2 V

Fig. 6. (a) shows cycle performance and accumulatge efficiency losses of LNMO/Li metal cells at 55 ℃. Moreover, EC-DMC exhibits great cycle performance and charge-discharge efficiency compared with EC-EMC and EC-DEC at a high temperature of 55℃, which is consistent with the result at LNMO/Graphite cycle test at 55 ℃.

We also examined that open circuit of voltage(OCV) of LNMO/lithium half-cell with the electrolytes at 60 ℃. Fig.6(c) presents the self-discharge profiles at a high temperature of 60 ℃. As shown in Fig.6(c), the potential of every cell decreased rapidly to 4.73 V. In the EC-DEC, the electrolytes tend to decompose on the charged LNMO, suggesting that it shows the serious potential drop compared with EC-DMC and EC-EMC. However, in case of the EC-DMC, the best performance was observed during the self-discharge test. As shown in the table 2, the time of the voltage drop to 4.2 V was 275 hours longer than EC-EMC. This result clearly shows that EC-DMC composition is more stable than EC-EMC and EC-DEC at a high potential range (~4.85 V).
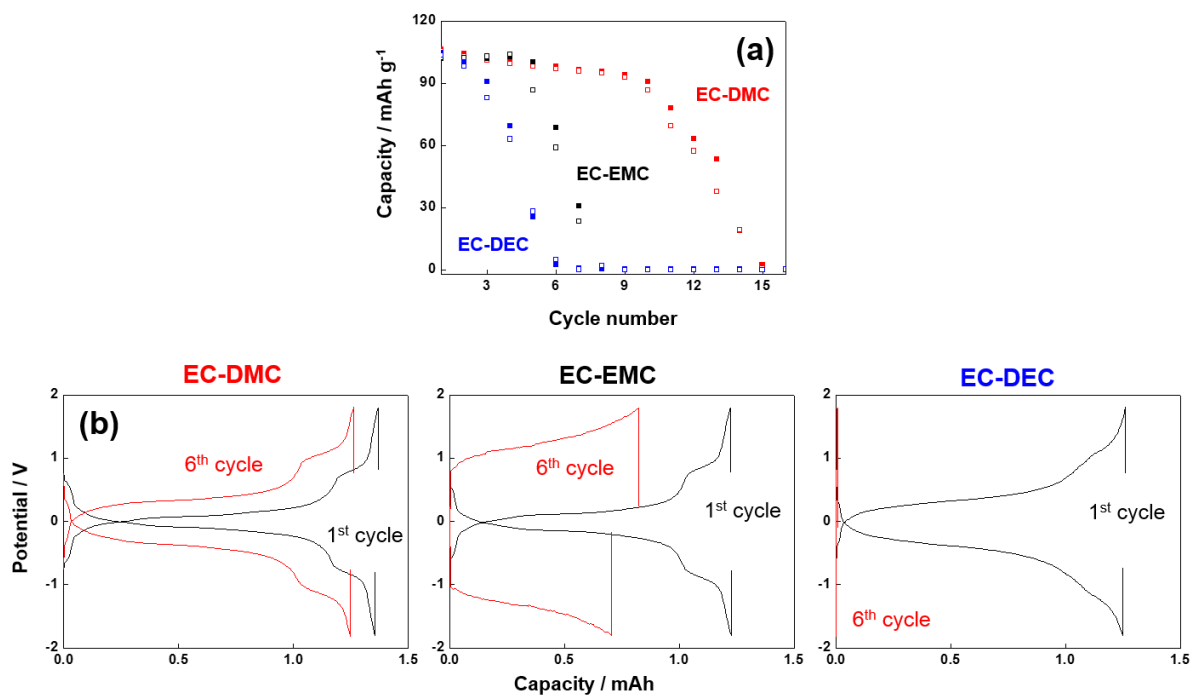
Fig. 7. (a) LNMO SOC 50/LNMO SOC 50 symmetric-cell cycle test (b) the charge-discharge profiles of symmetric cell according to linear carbonates

  After LNMO/Li metal half cell cycle test in high temperature, LNMO symmetric cell tests were

examined at 60 ℃. LNMO symmetric cells are becoming used in lithium ion battery research as a

means to characterize the electrode/electrolyte interface. [8, 9] A symmetric cell was assembled

using two LNMO with state of charge 50. The cyclability of symmetric cell in cycling test at 60℃ for

the binary mixtures follow the order : EC-DMC > EC-EMC > EC-DEC as displayed Fig. 7 (a). Also,

Fig. 7 (b) shows the charge-discharge profiles of C-rate according to linear carbonates. EC-DMC

definetly exhibits a lower over-potential at the high temperauture than EC-DEC and EC-EMC.

3.3 The effect of the linear carbonate on Graphite

To confirm the character of between graphite and electorlyte interface degredation, we examined

that graphite/Li half cell cycle tests and graphite symmetric cell cycle tests were tested at high

temperature.
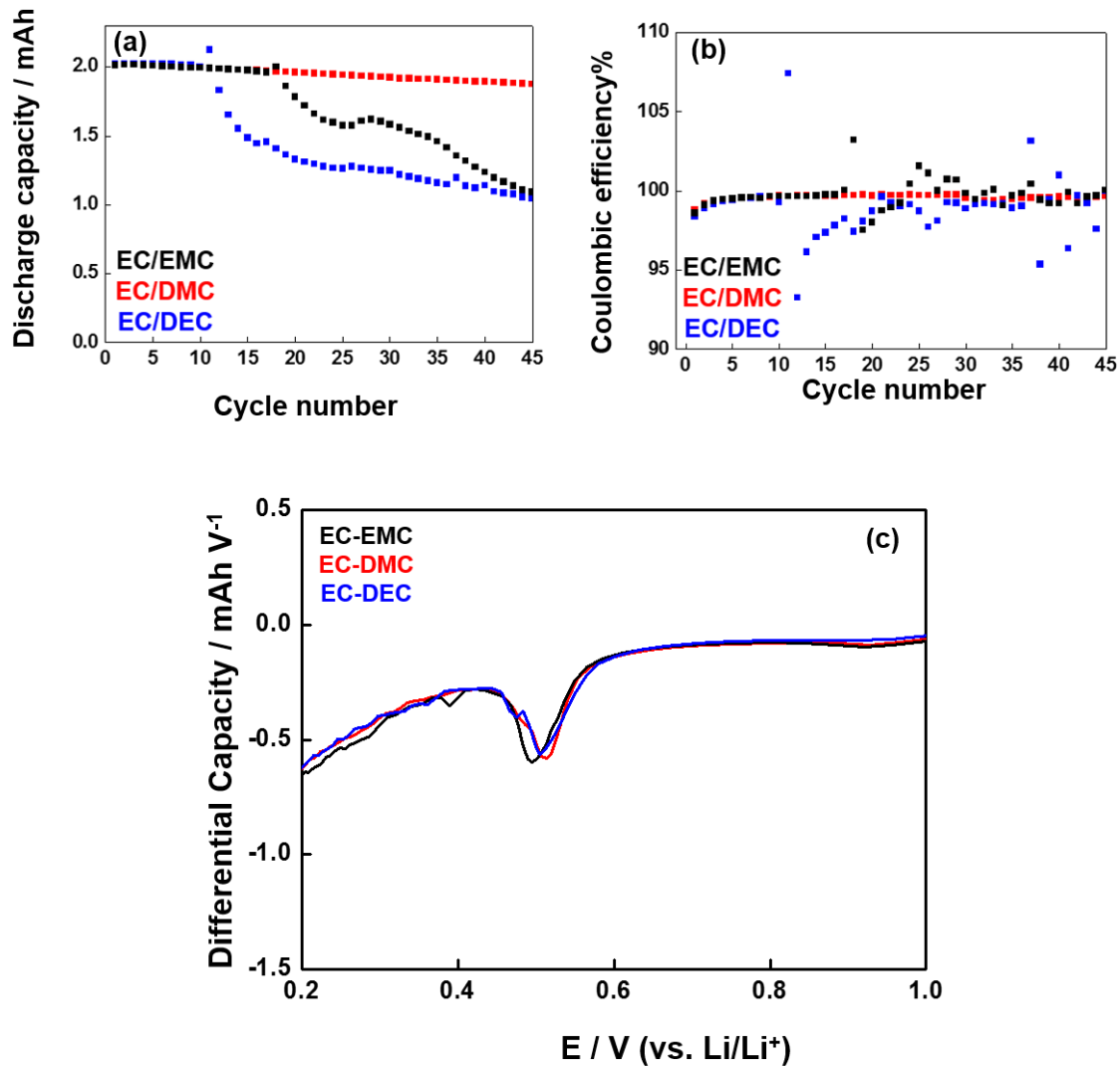
Fig. 8. (a) Graphite/Li metal half-cell performance (0.5 C-rate) and (b) Coulombic efficiency at 55 ℃ with linear carbonates (c) Differential capacity (dQ/dV) curves of the graphite/Li cells with 1M LiPF$_6$ EC/LC (3/7, v/v) electrolytes

Fig. 8. (a) shows cycle performance and accumulatge efficiency losses of graphite/Li metal cells at

55℃. EC-DMC displays great cycle performance and charge-discharge efficiency compared with EC-

EMC and EC-DEC at a high temperautre of 55℃, which is consistent with the result at

LNMO/Graphite cycle test at 55℃. To better understand this results, the effect according to linear carbonate was examined during the first charge (lithiation) and discharge (delithiation). The differential capacity curves (dQ/dV vs V) of the graphite with 1 M LiPF$_6$ EC/LC electrolytes are presented in Fig. 8 (c). During the first lithiation of graphite anodes, the reduction peaks apperaing above 0.4 V are known to be associated with electrolyte reduction which leads to SEI formation. [10] In our results, all of the binary mixture electrolytes showed a same recution peak which was attributed to the reduction of EC. After that, We also investigated graphite symmetric cell test at 55 ℃ and 60 ℃.
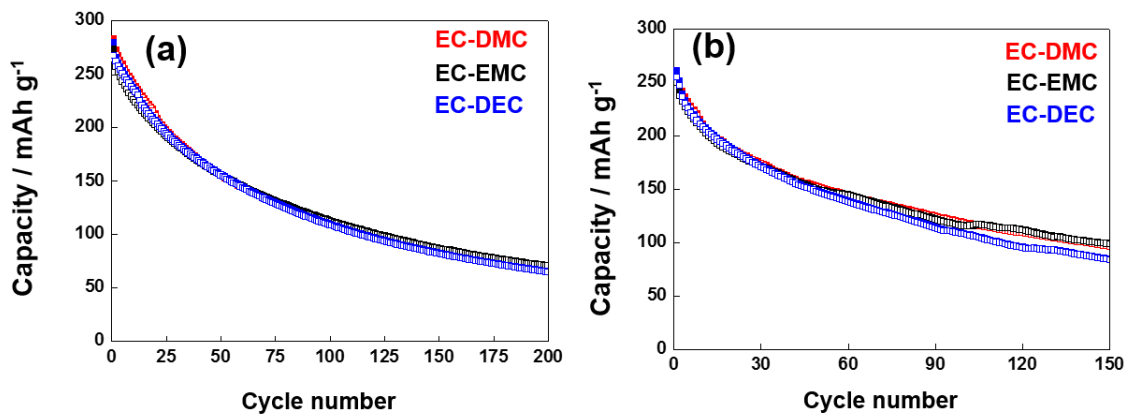
Fig. 9. (a) Graphite SOC 50/Graphite SOC 50 symmetric-cell cycle test at 55 ℃ (b) Graphite SOC 50/Graphite SOC 50 symmetric-cell cycle test at 60 ℃ with the binary mixture electrolytes

Graphite symmetric cell tests were examined at 55 ℃ and 60 ℃. As mentioned earlier, symmetric cells are used because of a means to characterize the electrode/electrolyte interface. A symmetric cell is assembled using two graphite with state of charge 50. As shown at Fig. 9, There is no diffrence according to linear caronates in cycling test at 55 ℃ and 60 ℃.

3.4 The effect of the linear carbonate on Lithium metal

Fig. 10. Electrochemical impedance spectra of Lithium/Lithium symmetric cells in EC-DMC, EC-EMC and EC-DEC electrolyte after 16 performance cycles test at 25 ℃

Besides, We investigated EIS test of lithium symmetirc cell in order to consider the lithium effect.

Internal resistnace values follow the order : EC-DEC > EC-EMC > EC-DMC as displayed in Fig. 10.
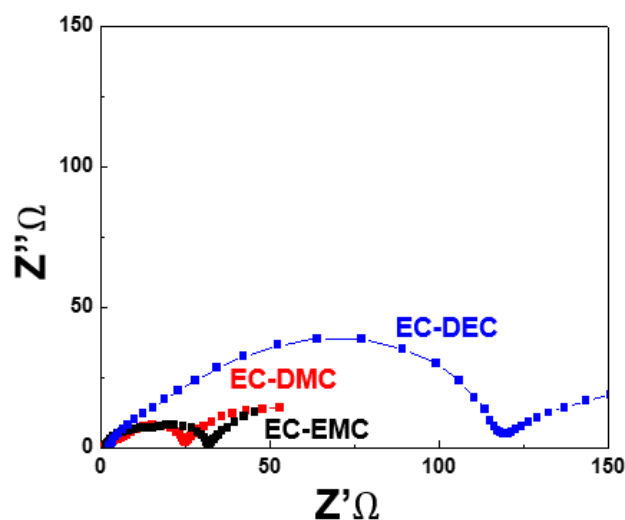
There is no diffrence in graphite symmetric cells (Fig. 9), but lithium metal is the reason for

differences in linear carbonates in graphite half cells (Fig. 8 (a)). So, graphite was not affected by

the type of linear carbonates.

3.5 Surface composition analysis of LNMO with linear carbonates

Lithium metal was also affected according to linear carbonates. However, From the LNMO

symmetric cell results, it can be seen that the high voltage LNMO was affected by the type of linear

carbonate. To better understand the mechanism of linear corbonate on LNMO, the surface

compositions of the LNMO cathode were analyzed by using X-ray photoelectron spectriscopy (XPS)

after 100 cycle at 55 ℃. LNMO/Li metal cells were disassembled and LNMO electrodes were washed

with pure dimethyl carbonate.

Fig. 11. XPS C1 s spectra of the LNMO half cells with EC-DMC,EC-EMC and EC-DEC after 100 performance cycles at 55 ℃

 In the C 1s spectra, the peak located at 284.4 eV is assigned to conductive carbon (Super .P), and

the peaks at 290.3 eV and 285.0 eV correspond to PVDF. [11, 12] C-O and C=O groups are located

at the 286.5 eV and 288.9 eV, respectively. DEC exhibits a C-F peak smaller than DMC and this can

be explained from the electrolyte decomposition and side reaction products on the electrode surface.

[13, 14]

Fig. 12. XPS O1 s spectra of the LNMO half cells with EC-DMC,EC-EMC and EC-DEC after 100 performance cycles at 55 ℃

 The O 1s spectra at 529.4 eV, 531.8 eV and 533.5 eV correspond to metal oxide, Li_2CO_3 and lithium

alkyl carbonates, respectively. [15, 16] Metal Oxide peak of EC/DMC is bigger than other

compositons. The metal oxide peak (529.4 eV) was not detected which is the result of the

decomposition products in the EC-DEC electrolyte.
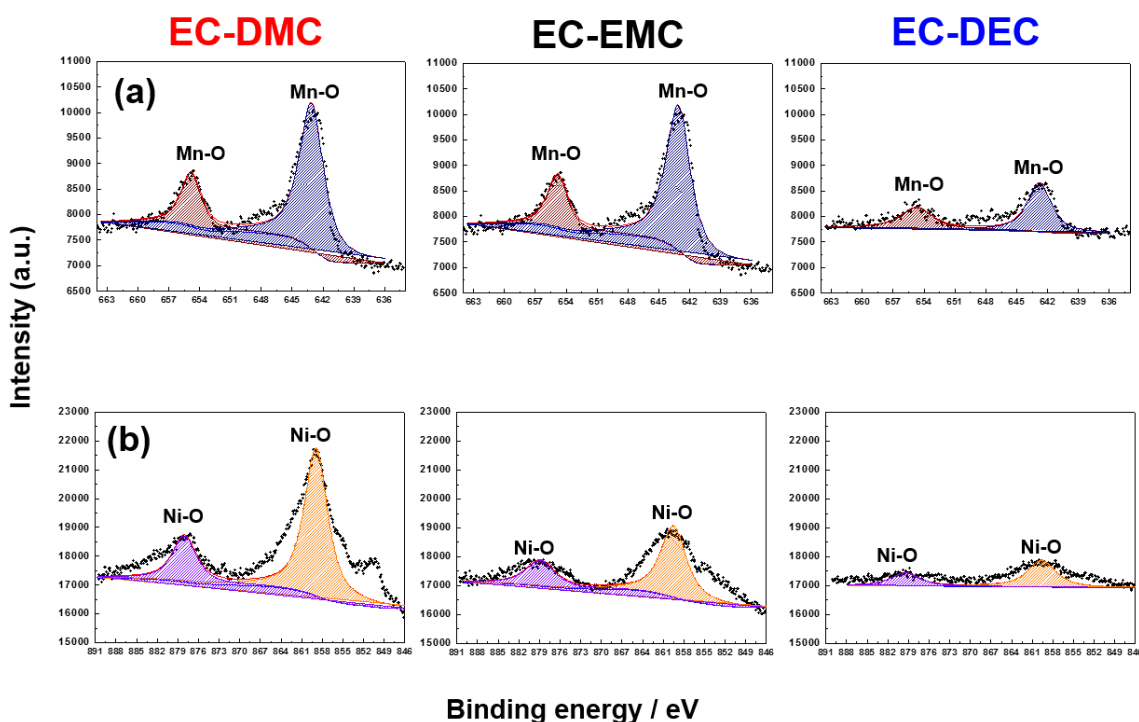
Fig. 13. XPS (a)Mn 2 p$_3$ and (b)Ni 2 p$_3$ spectra of the LNMO half cells with EC-DMC,EC-EMC and EC-DEC after 100 performance cycles at 55 ℃

In Mn 2p spectra, manganese oxide peaks were assigned at 653.6 eV and 641.8 eV ($2p^{3/2}$ and

$2p^{1/2}$). [17] The Mn 2p peaks were stronger for the LNMO electrode in the EC-DMC electrolyte than

the EC-DEC. The Mn 2p spectra contributed much to the electrolyte decomposition products on the

electrode cycled in the EC-DEC electrolyte.

In Ni 2p spectra, Ni 2 p$_3$ 3/2 peaks were assinged at 856.5eV. The amount of nickel follow the

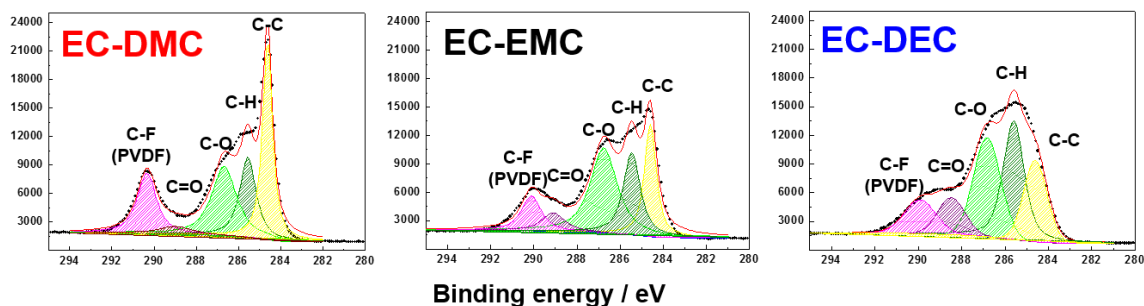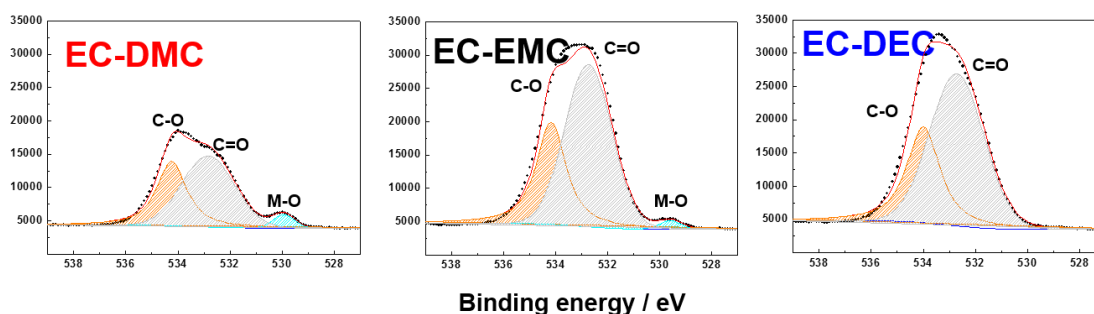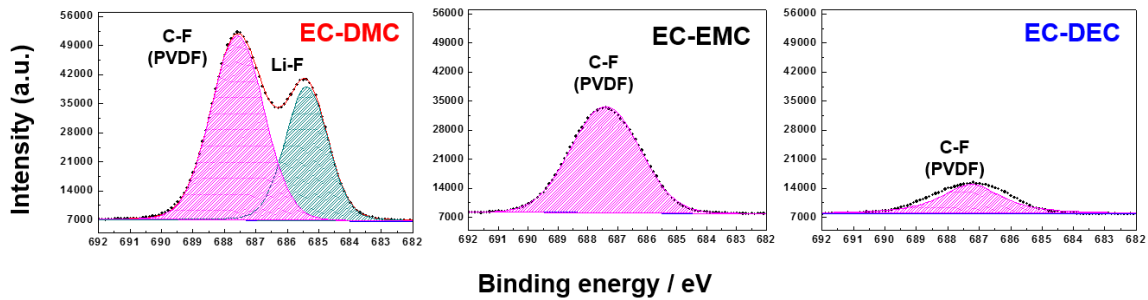order : EC-DMC > EC-EMC > EC-DEC as displayed in Fig. 13(b).[18]

Fig. 14. XPS F1 s spectra of the LNMO half cells with EC-DMC,EC-EMC and EC-DEC after 100 performance cycles at 55 ℃

In the F 1s spectra, the peak located at 687.4 eV was attributed to PVDF and the peak at 684.9 eV was assigned to LiF from the decomposition of the salt in the electrolyte. [19, 20] C-F peak intensity of EC/DMC is largest in binary mixture electrolytes. As shown as Fig. 14, there are only detection of LiF in LNMO using EC/DMC. There are two reasons. First, in the case of EC/EMC and EC/DEC, there are few bare surfaces copmared with EC/DMC. It means that many byproducts are accumulated on the surface of LNMO using EC/EMC and EC/DEC. Second, decomposition of LiPF$_6$ and hydrogen fluoride attack on LNMo have been proposed to be the LiF generation mechanism. Dissolution of LiF by HF or other polar chemical species, which are generated by electrolyte decomposition, has been proposed as the LiF removal mechanism. [21]

Through XPS analysis, transition metal decomposition and electrolyte decompositon of EC/DMC are the least in binary mixture electrlytes.

3.6 Linear carbonate effect of HF formation at high temperature (55 ℃)

To confirm origination of different linear carbonate performance, electrolytes were sotred at 55 ℃ for seven days to check amount of HF.
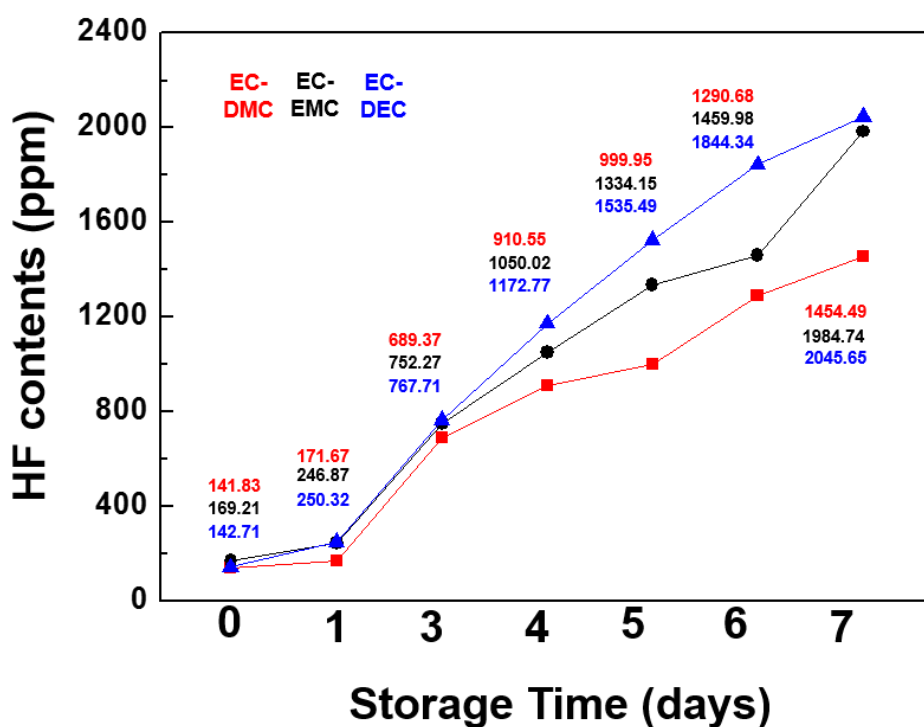
Fig. 15. The concentration of HF and moisture before and after high temperature storage with linear carbonates

Before the storage at 55 ℃, HF contents of EC/DMC, EC/EMC and EC/DEC are 141.83ppm, 169.21ppm and 142.71 ppm repectively. After 7days, the electrolyte that was measured in the highest increase was EC-DEC composition. The next was EC/EMC. This result corresponds to previous study [22] that difference of HF formation from the linear carbonates influence the degradation of LNMO. This factor contributes to electrochemical performance of LNMO.

3.7 Oxidation Potential according to linear carbonates
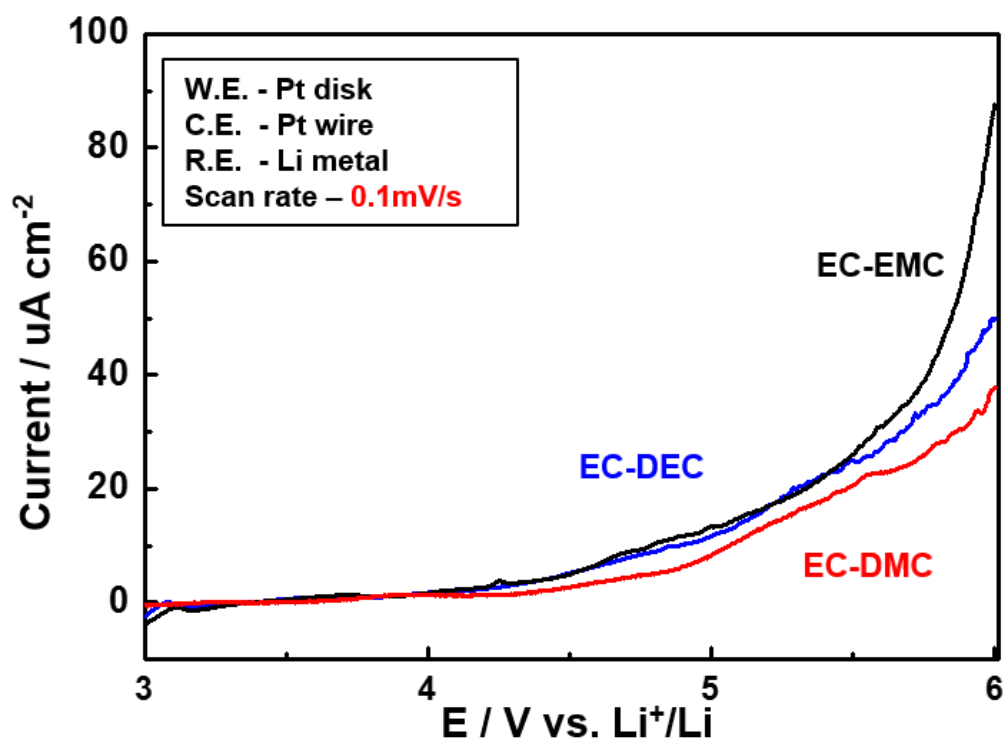
Fig. 16. LSV curves using electrolytes of 1.0 M LiPF$_6$ in binary mixture electrolytes at scan rate 0.1 mV S^{-1}

To evaluate the oxidation potential of alkylcarbonate based electrolytes on the LNMO, LSV was chosen. Scan rate was 0.1 mV/s. The oxidation potential on Pt for the binary-carbonate solvents has the following order : EC/DMC > EC/EMC ≈ EC/DEC same as result of the paper of Wu Xu. [23] Through this result, EC/DMC as binary mixture is the most stable electrolyte toward oxidation in accordance with the oxidation potential.

4. Conclusion

The effects of the type of linear carbonates (LC : DMC, DEC, EMC) in 1M LiPF$_6$ EC/LC (3/7, v/v) were examined. It was found that the electrochemical performances of LNMO cathode were depending on the type of linear carbonate. EC/DMC exhibits superior cyclability and coulombic efficiency at 25 ℃ and 55 ℃ than those EC/EMC and EC/DEC. The cells with EC/DMC also show better self-discharge performance than other compositions. Through LNMO symmetric cell test in cycling at 60 ℃, EC/DMC displays good performance compared other compositions. There are two reasons of the improved electrochemical performances in EC/DMC. First, EC/DMC are attributed to the diminished HF formation compared to the others. This factor affects electrolyte decomposition and manganese dissolution. Second, the oxidation potential of EC/DMC is the highest in EC/LC compositon electrolytes. As a result, the electrochemical stability of LNMO is strongly related to the linear carbonate and EC-DMC composition was found to be most stable.
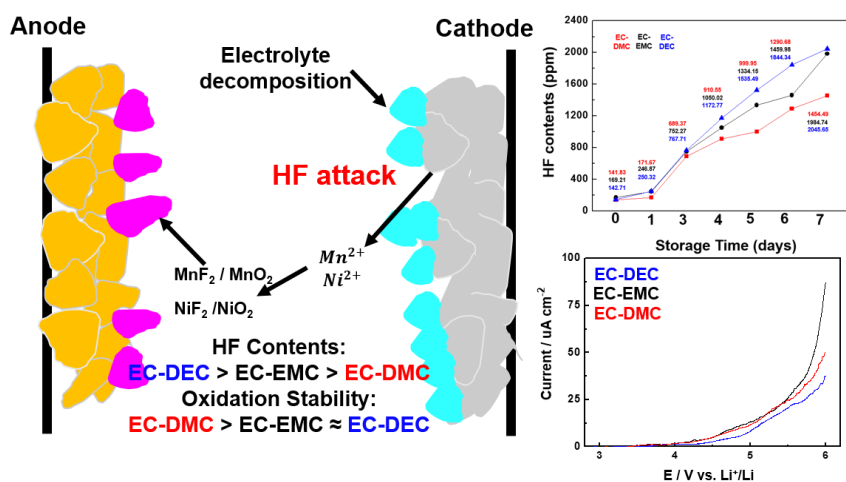

Fig. 17. Schematic of degradation for the manganese and nickel dissolution out of a LNMO

Reference

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요약문

Linear carbonate 종류에 따른 $LiNi_{0.5}Mn_{1.5}O_4$ 양극의 전기화학적 성능에 미치는 영향

리튬 이차전지에서 사용되는 5 V 급 양극재인 $LiNi_{0.5}Mn_{1.5}O_4$ (이하 LNMO)는 높은 구동전압과 낮은 가격, 합리적인 용량으로 인해 $LiCoO_2$ 를 대체 할 양극 물질로 각광받고 있다. 그러나 고전압에서의 전해액분해와 양극 물질로부터 Ni 과 Mn 이온의 용출은 전지의 성능 저하와 수명특성을 감소시키는 문제를 발생시키고, 이러한 문제를 해결하기 위해 다양한 연구들이 진행되어 왔다. 본 논문에서는 LNMO 의 수명특성과 충방전 효율향상을 위해 Linear carbontate 종류에 따른 LNMO 양극의 전기화학적 성능에 관한 연구를 진행하였다.

이 연구에서는 Linear carbonate(LC)에 따른 LNMO 의 수명특성과 충방전 효율을 비교하였다. 전해액 구성은 Ethylene carbonate 와 LC(DMC, DEC, EMC)를 3:7(v/v)로 구성하여, Coin half cell 과 full cell test 를 통해 상온(25℃)과 고온(55, 60℃)에서 수명특성과 효율, C-rate capability 를 확인하였다. C-rate capability(25℃)의 경우 EC-DMC 와 EC-EMC 조합에서 유사한 성능을 보였지만 수명특성과 효율에서는 상온과 고온 모두에서 EC-DMC 가 EC-EMC 와 EC-DEC 에 비해 우수한 성능을 보였으며 자가방전(60℃) test 에서도 coin half cell 과 full cell 모두에서 EC-DMC 가 가장 우수한 성능을 나타냈다. 또한, LNMO symmetric cell 고온 수명특성 결과를 통해, EC/DMC 가 고전압용 LNMO 에 가장 적합한 전해액인 것을 확인 하였다.

이러한 결과는 각 linear carbonate 에 따른 부반응의 차이로부터 기인한 것이라 생각되며, 이를 XPS 표면분석을 통해 확인 할 수 있었다. 또한 각 조성의 전해액을 고온 보존함으로써 보존 전 후의 HF 생성량을 분석한 결과 DEC > EMC > DMC 순으로 HF 생성량이 증가하는 것을 확인할 수 있었으며 LSV 분석을 통해, EC/DMC 가 산화안정성이 가장 높았다. 이는 앞서 언급한 coin-type cell test 결과와도 일치하며 각 linear carbonate 에 따라 생성된 HF 로부터 LNMO 의 열화가 촉진되어 성능 차이에 기인한 것을 확인할 수 있었다.

핵심어: Li-ion batteries, $LiNi_{0.5}Mn_{1.5}O_4$, HF, linear carbonate, oxidation stability.