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공학석사학위논문

Novel electrolytes in the mixed solvents of
pyrrolinium-based ionic liquid and carbonate
for a Li/LiFePO₄ cell

리튬/아이언포스페이트 셀을 위한 피롤리늄 기반의 이온성액체
와 카보네이트 혼합용매의 새로운 전해질 연구

2013年 8

서울대학교 대학원
화학생물공학부
서상원

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化學生物工學部

徐 祥 源

徐 祥 源 의 工學碩士 學位論文을 認准함

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by
Sangwon Seo

August 2013

Thesis Adviser: Young Gyu Kim

Abstract

Lithium-ion batteries are widely used and have been the one of the most popular batteries as the needs for electrical portable devices increase. The electrolytes used currently are based on the mixture of PC, EC, EMC, DEC, DMC carbonates with a soluble lithium salts. While these solvents are satisfied with required dielectric constants and viscosities, they still remain safety problems such as flammability and volatility. The major concerns of lithium-ion batteries with conventional carbonate electrolytes are that short circuits often lead to overheating and ignition of the organic carbonate solvents, which are part of conventional electrolytes. Carbonate solvents that contribute to the dissociation of lithium salts are volatile and potentially combustible and can lead to the thermal runaway of batteries at any abuse conditions. Recently, an interest in non-flammable materials is greatly becoming high as a mean for improving battery safety. Thus, to solve the problems caused by conventional carbonate solvents, ILs have been picked as a candidate of electrolytes to replace conventional carbonate solvents of lithium-ion batteries.

Ionic liquids(ILs) have come into the spotlight in the field of electrochemistry because of their interesting properties. Due to the ionic nature in bonding, ionic liquids are salts existing in liquid at room

temperature and show unique properties such as non-volatility, non-flammability, low vapor pressure, large electrochemical stability, wide liquid range, high ionic conductivity and high thermal stability. ILs have been issued since it possess high potential to be applicable as components of electrolytes for lithium-ion batteries on account of its unique properties.

Lithium-ion batteries on the basis of ILs are safer than those with conventional electrolytes which are based on organic carbonate solvents. However, there are still some drawbacks as electrolytes of lithium-ion batteries. ILs normally have higher viscosity, high cost and lower conductivity than conventional electrolytes. Another problem is that most ionic liquids have low tendencies to form SEI (solid electrolyte interphase) layers on either anode or cathode. No complete solution to overcome the disadvantages of using ionic liquids has yet been found. To deal with the problems from both ILs and conventional electrolytes, we prepared novel electrolytes in the mixed solvents of pyrrolinium-based ionic liquid and carbonate as advanced electrolytes that could be replacement of conventional electrolytes.

We have been developing ILs that would be competitive and comparable to that of conventional ILs such as imidazolium-based, pyrrolidinium-based, piperidine-based and pyrrolinium-based ILs. Nevertheless, imidazolium-based ILs are well known as one of electrolytes that show good electrochemical properties compared to

conventional ILs for lithium-ion batteries, it still has several defects as electrolytes of lithium-ion batteries. Having an alternative plan for the improvement of all the drawbacks of which is resulting from imidazolium-based ILs such as high viscosity, low conductivity and unstability at low potential, we synthesized several types of pyrrolinium-FSI ionic liquids containing two substituents attached at N-position and C-2 position of pyrrolinium ring and it can remedy defects in imidazolium-based ILs. Among them, three types of selected ILs that are 1-ethyl-2-methoxy-pyrrolinium bis(fluorosulfonyl)imide ([E(OMe)]Pyr1-FSI) (6), 1-propyl-2-methoxy-pyrrolinium bis(fluorosulfonyl)imide ([P(OMe)]Pyr1-FSI) (7) and 1-allyl-2-methoxy-pyrrolinium bis(fluorosulfonyl)imide ([A(OMe)]Pyr1-FSI) (8) showed better cyclability than other pyrrolinium-based ILs with different types of substituents. Therefore, these ILs have been chosen to be treated as a suitable component for preparing novel electrolytes. In addition, we have selected the organic carbonate solvent (EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%)), which is one of commonly used electrolyte for lithium-ion batteries, as the other component of novel electrolytes. We expected that the novel electrolytes we prepared will have positive effect on not only flammability problems set by organic solvent but also cycling efficiency set by forming good SEI layer in Lithium-ion batteries.

LiFePO₄-based half cells were assembled using the novel

electrolytes in the mixed solvents of pyrrolinium-based IL and organic carbonate in different IL contents, and their cycling performances were evaluated. The operating cycling conditions of coin cells containing any electrolytes at 1C-rate have been rarely reported. Thus, we have focused on investigation of cell operation condition with faster C-rate.

In our study, a cell containing the novel electrolyte showed good cycling performance comparable to that of a cell assembled with organic carbonate electrolyte. Especially, the electrolyte consisted of 60% of 1-ethyl-2-methoxy-pyrrolinium bis(fluorosulfonyl)imide ([E(OMe)]Pyr1-FSI) (**6**) and carbonate solvent (EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%)), which have the highest conductivity (13.76 mS cm⁻¹), showed the highest discharge capacity value and capacity retention ratio at 1C-rate (after 100 cycles : 99% and 155 mAh g⁻¹) on the LiFePO₄-based half cells among three types of ILs of which are a part of the novel electrolyte after 100 cycles. Furthermore, as the amount of ILs increases, we were able to confirm reduced flammability of the novel electrolytes after taking a burning test. The novel electrolytes have not caught on fire, especially more than 60 ILs weight percentages.

This study indicates both that safety and cycling performance of the lithium-ion batteries can be improved by using the novel electrolytes consisted of ionic liquid and organic carbonate solvent and it can reduce the cost resulting from the independent use of expensive ILs.

Keywords: lithium-ion battery, ionic liquid, organic carbonate solvent, pyrrolinium, bis(fluorosulfonyl)imide, novel electrolytes

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LIST OF ABBREVIATIONS

[E(OMe)]Pyr1	1-ethyl-2-methoxy-pyrrolinium
[P(OMe)]Pyr1	1-propyl-2-methoxy-pyrrolinium
[A(OMe)]Pyr1	1-allyl-2-methoxy-pyrrolinium
Δ	chemical shift
D	Doublet
Dd	doublet of doublet
DLC	double-layer capacitor
DMC	dimethyl carbonate
DSC	differential scanning calorimetry
H	Viscosity
EC	ethylene carbonate
EMC	ethyl methyl carbonate
[EM]Im	1-ethyl-3-methylimidazolium
EW	electrochemical window
H	hour(s)
Hz	Hertz
IL	ionic liquid
J	coupling constant(s)
LIB	Lithium-ion battery
M	mole(s) per liter

M	Multiplet
ND	not detected
NMR	nuclear magnetic resonance spectroscopy
PC	propylene carbonate
Q	Quartet
quant.	Quantitative
RT	room temperature
RTIL	room temperature ionic liquid
Σ	ionic conductivity
S	Singlet
SEI	solid electrolyte interphase
Sext	Sextet
T	Temperature
<i>T</i>	Time
T	Triplet
T_c	crystallization temperature
T_d	decomposition temperature
FSI	bis(fluorosulfonyl)imide
TGA	thermogravimetric analysis
T_m	melting point
VC	vinyl carbonate

Introduction

1. Lithium-ion batteries

1.1. Introduction of lithium-ion batteries

In recent years, the smart grids functionalized in energy storage devices of renewable energy and electric vehicles have been attracted by the exhaustion of fossil fuels, like petroleum, coal and natural gas, with the purpose of CO₂ reduction, the lithium-ion battery applications such means of energy storage devices has emerged as a candidate.¹

Lithium-ion batteries were first proposed by M.S Whittingham while working for Exxon using titanium(IV) sulfide and lithium metal as the electrodes in the 1970s.² After that, lithium-ion batteries have been continuously investigated and developed until commercial lithium-ion batteries were first released and they still have been widely researched. Lithium-ion batteries are a member of a family of rechargeable battery system in which lithium ions continuously move between two electrodes during charging and discharging. Nowadays, as the demand for portable electrical devices is rapidly increased, lithium-ion batteries have been the one of the most popular types of rechargeable batteries for portable electronics. Beyond consumer electronics, lithium-ion batteries are also growing in popularity for EV, HEV, military and aerospace application because of their outstanding

advantages that are high energy densities(2-3 times), high power densities(5-6 times), no memory effect, much lighter than other conventional energy-equivalent secondary batteries(Ni-Cd and Ni-MH batteries) and a slow loss of charge when not in use.³

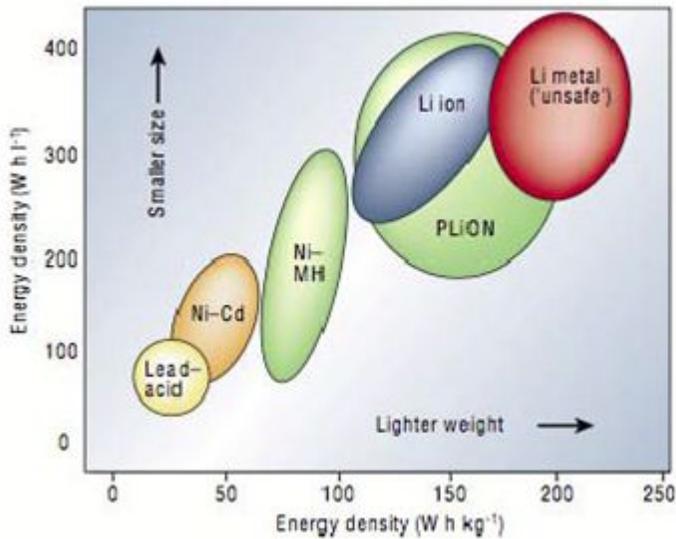


Fig 1-a. Comparison of batteries in terms of volumetric and gravimetric energy density

Lithium-ion batteries are basically consisted of three primary functional components which are a positive electrode, a negative electrode and, a separator/electrolyte. These secondary batteries are energy storage devices which carry on the reversible redox reaction using the electron transport phenomena by electrolytes that show large ionization tendency in between different two electrodes. Lithium-ion batteries are operated by releasing lithium ions from cathode materials to layered carbon-based anode through electrolytes when it discharging, likewise charging process is performed in reverse. That is, the battery-

driven method mentioned above is the representative rechargeable battery technology that makes the batteries possible to use several times using the principle, lithium ions come and go between two electrodes to charge and discharge.^{4, 5c}

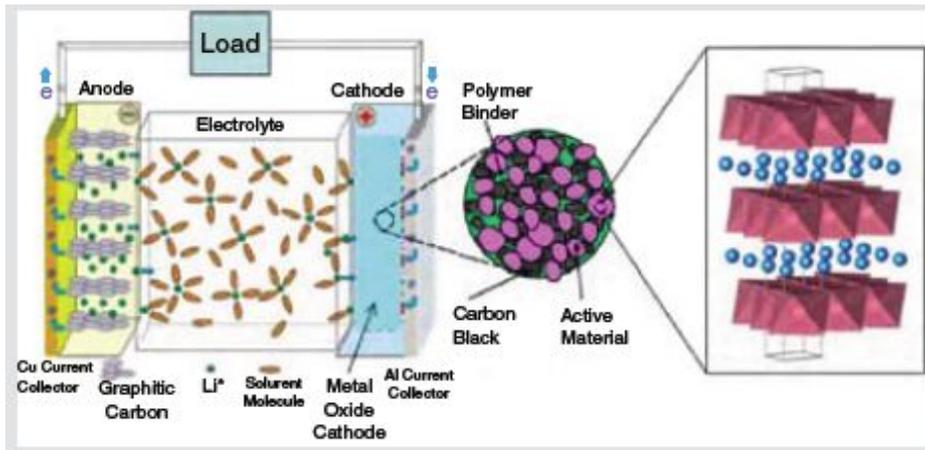


Fig 1-b. Schematics of Lithium-ion battery.

On the basis of the fundamental principle of schematics of lithium-ion battery depicted in Figure 3, lithium-ion batteries are performed with excellent cycle life and can store more energy per volume than any other types of portable rechargeable battery. In addition, it shows higher power, higher energy density, and better charge efficiency than Ni-Cd and nickel metal hydride (NiMH) batteries.¹

However, in spite of these advantages, there are still apparent safety problems which lead to the explosion caused by organic solvents which are parts of the conventional electrolytes in battery system. Since the conventional organic electrolytes including volatile compounds such as propylene carbonate (PC) and dimethyl carbonate (DCM) and so on,

lithium-ion batteries are easily exploded by battery ignition from the spark, causing the fire. The volatile electrolytes spontaneously play a role as a fuel after it has been ignited in lithium-ion battery. That is, these thermally unstable organic electrolytes possibly lead to thermal runaway in danger. In the light of safety standpoint, ILs are able to be alternative materials as the promising electrolyte of lithium-ion batteries due to their properties, both non-volatility and non-flammability. Furthermore, since they show the virtue of wide liquid range, high thermal and electrical stability, and moderate ionic conductivity, there have been many attempts to investigate ILs as an alternative for the electrolytes of lithium-ion batteries.^{5,6}

To conclude, the performance of lithium-ion battery depends on the developments of materials such as two electrodes and electrolytes for the various components of the lithium-ion battery.^{3b-3d} Thus, Lithium-ion batteries have been widely investigated to demonstrate proper mechanism, not clearly, and to improve battery performance toward higher energy density and output density for the EV, HEV than conventional lithium-ion batteries with bettered safety problems.

2. Electrolytes for Lithium-ion batteries

2.1. Species of electrolytes

2.1.1. Organic carbonate solvents

In accordance with the basic requirements for electrolytes, an ideal electrolyte solvent should fulfill the following criteria shown below.

- (1) It should be able to dissolve salts to sufficient concentration. In other words, it should have a high dielectric constant.
- (2) It should have low viscosity, so that facile ion transport can occur.
- (3) It should remain inert to all cell components, especially the charged surfaces of the two electrodes (cathode and anode), when cell operates.
- (4) It should exist in liquid state line in a wide temperature range. In other words, its melting point should be low and its boiling point high.
- (5) It should also be safe (high flash point), nontoxic, eco-friendly, and economical.⁶

Since the beginning of non-aqueous electrolytes, a variety of polar solvents has been investigated, and the majority of them separate out organic esters and ether. The most common used solvents are depicted in Table 1 and Table 2 along with their physicochemical properties respectively.⁷

Table1. Organic Carbonates and Esters as Electrolyte Solvents

Solvent	Structure	M. Wt	T _m / °C	T _b / °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T _f / °C	d/gcm ⁻³ , 25 °C
EC		88	36.4	248	1.90, (40 °C)	89.78	4.61	160	1.321
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
BC		116	-53	240	3.2	53	4.23	97	1.199
γBL		86	-43.5	204	1.73	39	4.23	97	1.199
γVL		100	-31	208	2.0	34	4.29	81	1.057
NMO		101	15	270	2.5	78	4.52	110	1.17
DMC		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC		118	-74.3 ¹	126	0.75	2.805	0.96	31	0.969
EMC		104	-53	110	0.65	2.958	0.89		1.006
EA		88	-84	77	0.45	6.02		-3	0.902
MB		102	-84	102	0.6			11	0.898
EB		116	-93	120	0.71			19	0.878

Table2. Organic Ethers as Electrolyte Solvents

Solvent	Structure	M. Wt	T _m / °C	T _b / °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T _f / °C	d/gcm ⁻³ , 25 °C
DMM		76	-105	41	0.33	2.7	2.41	-17	0.86
DME		90	-58	84	0.46	7.2	1.15	0	0.86
DEE		118	-74	121				20	0.84
THF		72	-109	66	0.46	7.4	1.7	-17	0.88
2-Me-THF		86	-137	80	0.47	6.2	1.6	-11	0.85
1,3-DL		74	-95	78	0.59	7.1	1.25	1	1.06
4-Me-1,3-DL		88	-125	85	0.60	6.8	1.43	-2	0.983
2-Me-1,3-DL		88			0.54	4.39			

As shown on these Tables above, an interesting tendency was observed concerning the physical properties, dependent on the molecular shapes which are cyclic or acyclic compounds. Whereas, all of the ether, cyclic, acyclic show similar moderate dielectric constants and low viscosities, cyclic and acyclic esters show the behavior like entirely different types of compounds in terms of dielectric constant and viscosity. In other words, all cyclic esters are uniformly polar and

rather viscous while all acyclic esters are weakly polar and highly fluid. the origin for the effect of molecular cyclicality on the dielectric constant has been derived from the intramolecular strain of the cyclic structures that brings about the conformation of better alignment of molecular dipoles, while the more flexible and open structure of linear carbonates results in the mutual cancellation of these dipoles.^{6,7}

It has been more than a decade to undertake research in terms of the appropriate electrolytes for lithium-ion battery, since researchers became interested in the electrolytes as a component of Lithium-ion battery. After enormous exploration for a few years, the candidates of the electrolytes that are suitable for lithium-ion battery became narrow toward several types of solvents among all studied electrolytes. To use the electrolyte for lithium-ion battery, it should be mainly composed of two crucial components solvent as the electrolyte and lithium salt as a lithium source. The most common used electrolyte for lithium-ion devices is based on EC as the solvent and LiPF₆ as a lithium salt but, it needs additional linear carbonate, DMC, DEC or EMC, as co-solvents to increase the fluidity and reduce the melting point of the electrolyte.⁶ However, the current electrolyte systems for lithium-ion batteries are too far from perfect. They still have several main problems which have to be solved such as irreversible capacity, temperature limits, safety and hazards, better ion transport.⁸

Speaking of LiPF₆ proposed as a lithium source for lithium-ion

battery in the late 1960s⁹, it obviously shows well-balanced performance in the carbonate solvents mixture than any other reported lithium salt such as LiBF₄, LiAsF₆, LiClO₄, etc.¹⁰ That is, LiPF₆ is the one of most commonly used solute component for commercial lithium-ion devices among the numerous salts. However, at temperatures higher than 60°C, the performance deterioration is permanent, because the reactions between the electrolyte solute and solvents are irreversible. On the other hand, the addition of vinylene carbonate (VC) as additive allow battery systems to have an effect on the formation of the good SEI layers and it improves the cell cycling life with scarcely fading capacity.⁶

Organic carbonate solvents as the electrolytes for lithium-ion batteries are being extensively used and investigated with combination of different types and ratios of organic solvents but it still remains safety defects derived from organic solvents that are parts of electrolytes. Thus, researchers have to challenge to the improved the electrolyte in the field of lithium-ion battery market.

2.1.2. Ionic liquids electrolytes

In general, compound formed by ionic interactions between cations and anions have high melting point above room temperature (298 K) mainly because of its strong ionic interaction in between. Nevertheless, several ionic species exists in the liquid state even at room temperature, having a wide range of liquid. Such ionic species that have melting point below room temperature are called room temperature ionic liquids (RTILs) or molten salts.^{5, 8, 11-13}

The ILs have drawn lots of researcher's interests owing to their unique properties of ILs. Firstly, ILs have low melting point below 100 °C. Therefore, they are possible to be treated as liquids at ambient temperature. One of the remarkable things is that ILs show outstanding designability. Because ILs are normally composed of organic cations and anions, they can be easily synthesized by introducing the combination of various cations and anions. Which means the physic chemical properties can be simply controlled. In addition, ILs have not only high conductivity arising from high concentrations of conducting species but also wide electrochemical stability windows and it shows higher thermal decomposition temperatures over 300 °C. There is an extremely incomparable advantage, it is that they do not burn easily itself compared to the conventional carbonate electrolytes for commercial lithium-ion batteries due to non-flammability. Besides,

negligible vapor pressure can prevent both vaporization and losses from room and high temperature.

Owing to the unique properties mentioned above, ILs have come into spotlights for promising solvent systems, comparable to that of conventional electrolytes in organic synthesis^{11, 12} and electrochemistry, they have rather high melting point and viscosities of them. Above all, non-flammability and volatility of ILs definitely made lots of chemists and engineers have been into focusing on improvement of ILs as the electrolytes for electrochemical devices such as lithium-ion battery although ILs cost a little bit high.^{5, 8, 13}

In the initial period, compounds which have low melting point below room temperature with several types of chloride salts such as AlCl_3 had both corrosiveness and toxicity problems which restrict their applications.¹⁴ In addition, they had entirely faced with troubles in handling because they are very unstable in air- and water-exposed condition. After ILs that are strong at air- and water-condition with a tetrafluoroborate anion were proposed by Wilkes in the early on 1990s¹⁵, ILs began to receive sufficient lots of attention from academia because it was possible that ILs are treated as a potential candidate for advanced electrochemical applications.

Typically, the cations of ILs have a heteroatom such as nitrogen and it can be divided into two categories. The first cyclic ammonium cations: imidazolium, pyrrolinium, piperidinium, pyridinium, etc.

Among these types, imidazolium-based cations are well known and investigated by a number of researchers because of the reason that they have low melting point, low viscosity and high ionic conductivity.^{16, 17} Unfortunately, imidazolium-based cations for lithium-ion battery applications are apparently electrochemically unstable and are easily decomposed due to deprotonation of an acidic proton at the C-2 position of imidazolium ring. There have been lots of attempts to improve the cathodic stability of ILs. One of them is introducing pyrrolidinium and piperidinium as a cation because they show better electrochemical stability than imidazolium-based cations. The acyclic ammonium cations which show good electrochemical stability comparable to that of imidazolium-based ILs have also been studied as cations for ILs. In the recent years, cations having sulfur (S) or phosphine (P) atoms, such as acyclic sulfonium and phosphonium, have been investigated since they show unique properties.

In terms of anions, nowadays perfluorinated anions are the one of which is the most widely used and the most important among the anion candidates owing to the dispersion of anionic character of ILs to make ionic interactions weak. To change anions in ILs play an important role in determining its physicochemical properties. Thus, the development of novel anions and modification studies are active.

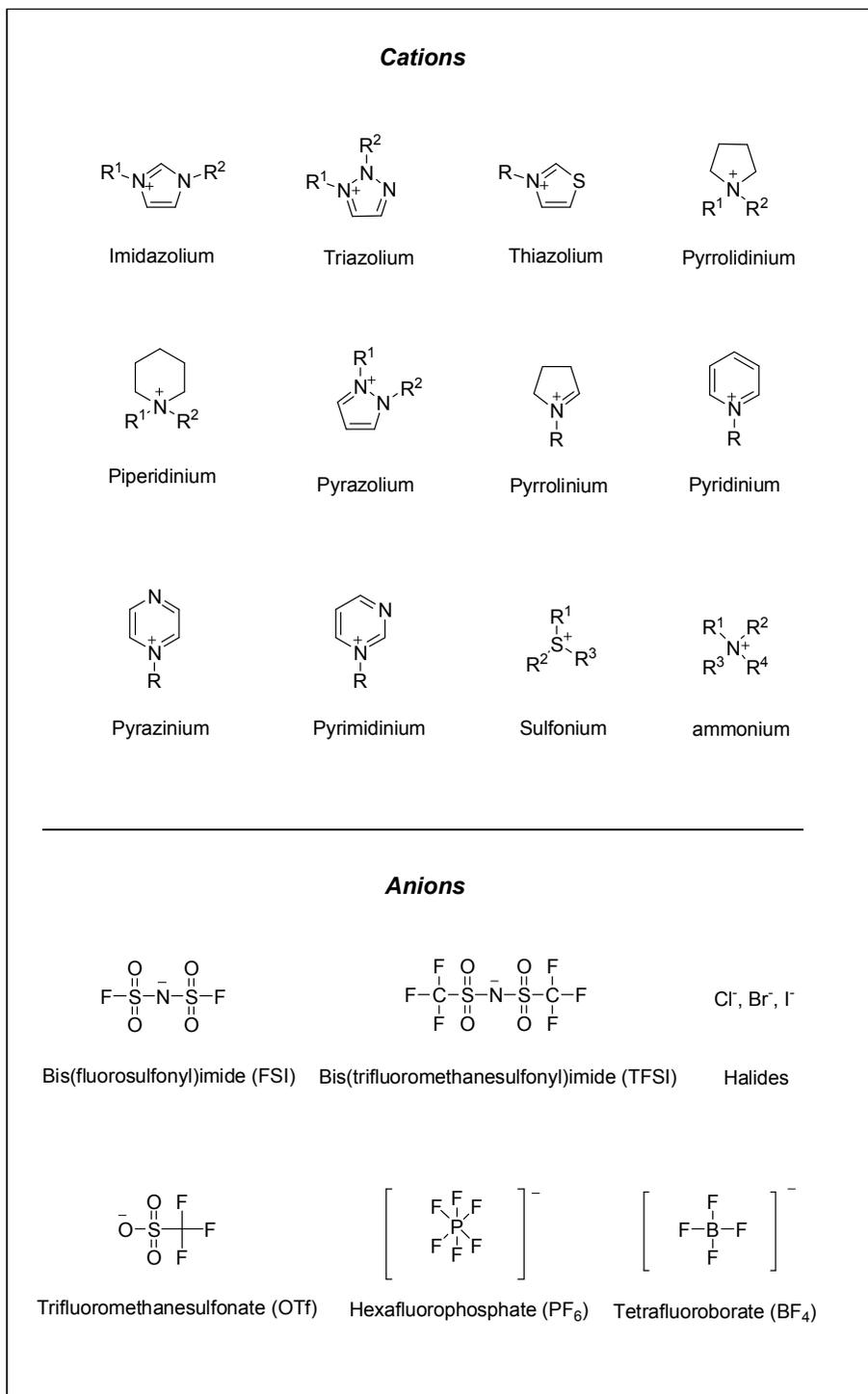


Fig 2. Various species of cations and anions for ILs

Results and Discussion

1. Preparation and Properties of novel electrolytes in the mixed solvents of pyrrolinium-based ionic liquid and carbonate

1.1. Strategy

The organic solvent should be polar solvent not having active proton because the material for organic electrolyte coexists with active cathode/anode substances within cell. Generally what we are using for solvent of electrolyte is mixture of ring-typed ethylene carbonate (EC), chain type dimethyl carbonate (DMC), ethylmethyl (EMC), and diethyl carbonate (DEC). In case of EC, the performance for dissociation is outstanding by removing Coulombic force between positive/negative ions because of having high dielectric constant. The actual moving solvated ion would be formed through the coordination with dissociated Li-ion. On the other hand, the dipole moment within molecular is well formed with EC's high dielectric constant, the interaction from dipole to dipole within EC would be produced. The high viscosity (EC: 1.9 cP at 40 °C) is showed because of large dipole-dipole interaction in EC. Due to the fact that the high viscosity of EC reduces the mobility of dissociated ions then also reduce the ion conductance, DMC and EMC which is able to realize the low viscosity need to be used mixture of chain-type carbonate organic solvent. Although organic carbonates like ethylene carbonate (EC) and linear carbonates such as dimethyl, diethyl

or ethylmethyl carbonate (DMC, DEC or EMC) have been successfully used as key components for lithium-ion batteries, the current electrolyte system has serious problems derived from the use of organic carbonate solvents which are flammable and volatile. To deal with this safety problem, ILs are able to be introduced as an alternative electrolyte for lithium-ion batteries instead. In spite of the fact that the ILs possess several properties that make them an ideal candidates for battery electrolytes, like non-volatile, non-flammable, wide electrochemical windows, high inherent conductivities, and wide thermal operating range, ILs suffer from relatively high viscosity which leads to low conductivity and are high-priced. Another problem is that most ionic liquids have low tendencies to form SEI (solid electrolyte interphase) layers on either anode or cathode. No complete solution to overcome the disadvantages of using ionic liquids has yet been found, but continued research in this field should provide a promising result in the near future. Thus, our study has been focused on decrease in the viscosity, flammability, volatility and forming good SEI layer by preparation of novel electrolytes containing both organic carbonates and ILs in different ratios in between.

In terms of ILs for novel electrolytes, first of all, pyrrolinium-based ionic liquid has been chosen to a component of the electrolytes with organic carbonate solvent by some reasons. There have been many attempts to control the physico- and electrochemical properties of ILs

via the design of their cations and anions. The modification of imidazolium cations is mostly focused due to its lower melting points, lower viscosities, and higher conductivities among the well-known ILs derived from pyridine or tertiary amine. Our group has also investigated several types of ILs imidazolium-based^{18,19}, pyrrolidinium-based, piperidinium-based²⁰ and pyrrolinium-based²¹ ILs to improve and modify their physic- and electrochemical properties. After that, we thought that the cation parts in ILs play a significant role in determining physico- and electrochemical properties.

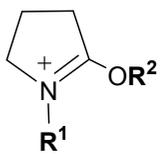
The physicochemical and electrochemical properties of ILs are affected by some factors following below.

- (1) The larger size of cations increases Van Der Waals interactions.^{5, 13, 22}
- (2) Non-planarity of structures of cations does not allow a fairly facile slip between molecules.²³
- (3) Ionic conductivity is proportionate to the number of charge carrier ions and their mobility.

In accordance with factors as mentioned, ILs that are small size of structure of cations and containing oxygen exert influence on electrochemical properties due to their smaller size and rotational freedom. Therefore, for such reasons, we thought that pyrrolinium-based ILs containing oxygen at C-2 position could be not only good solutions to overcome the problems of conventional ILs, but also a

promising candidate of novel electrolytes with organic carbonate solvents due to the fact that pyrrolinium-based ILs do not have any acidic proton which could be reacted with components of battery devices during cells operation and have a relatively planar structure by a double bond between N-1 and C-2 position of the pyrrolinium cation ring. Likewise, Bis(fluorosulfonyl)imide (FSI) anion was selected as a counter anion of pyrrolinium cation because it shows lower melting

Table 3. The strategy of Pyrrolinium-based ionic liquids with alkoxy substituents and selected candidates for preparation of novel electrolytes

Cations	Anions
	$\text{N}^-(\text{SO}_2\text{F})_2$

<i>Pyrrolinium cation</i>	<i>Alkyl substituent (-R¹)</i>
<ul style="list-style-type: none"> - Low viscosity - Easy to design 	<ul style="list-style-type: none"> - To control physicochemical properties - To improve anodic stability
<i>Ether substituent (-OR²)</i>	<i>FSI anion</i>
<ul style="list-style-type: none"> - Enhance cathodic stability - High conductivity 	<ul style="list-style-type: none"> -Low melting point -Low viscosity -water stable

Cations	R ¹	R ²	Anion
[E(OMe)]Pyr1	Ethyl	Methyl	FSI ⁻
[P(OMe)]Pyr1	Propyl	Methyl	
[A(OMe)]Pyr1	Allyl	Methyl	

point, lower viscosity, and higher stability in water and air. After several cycle life tests, only three types of pyrrolinium-FSI were selected as candidates for the novel electrolytes because nothing shows good cyclic performance except for three types of pyrrolinium-FSI ILs.

In a bid to develop novel electrolytes for lithium-ion batteries, EC:EMC=3:7(v/v) as a part of organic solvent of which contains 1M LiPF₆ and vc(3%), pyrrolinium-FSI ([E(OMe)]PyrI-FSI (**6**), [P(OMe)]PyrI-FSI (**7**), [A(OMe)]PyrI-FSI (**8**)) as a part of ILs either were chosen to be treated as components of novel electrolytes. After desired electrolytes were properly mixed, we conducted their cycle life (at 1C-rate) and burning test in different ratios of ILs(wt%).

The main purpose of this study is to prepare novel electrolytes which have all advantages from both carbonate and pyrrolinium-FSI.

A new type of electrolytes	Expected properties
<p style="text-align: center;">R: Ethyl, Propyl, or Allyl</p> <p style="text-align: center;">+ 1M LiPF₆ + vc(3%)</p>	<p>From ILs</p> <ul style="list-style-type: none"> - Non-flammable - Thermally stable electrolyte <p>From carbonates</p> <ul style="list-style-type: none"> - Low viscosity - Reasonable cost

Fig 3.A new type of novel electrolytes

1.2. Preparation

The novel electrolytes in the mixed solvents of pyrrolinium-based IL and carbonate were prepared in different ratios of ILs weight percentage. The organic carbonate solvents which is EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%) were obtained from commercial supplier and the pyrrolinium bis(fluorosulfonyl)imide with alkyl substituents was prepared according to the modified procedure described below.²⁴ Preparation of pyrrolinium-FSI was performed through overall three steps, N-alkylation, O-alkylation and anion exchange. Initially, the reaction was conducted with 2-pyrrolidone and alkylhalide such as 1-iodopropane and allyl bromide to give corresponding 1-propyl-2-pyrrolidone and 1-allyl-2-pyrrolidone respectively. These compounds were synthesized by the reaction between 2-pyrrolidone and 1-iodopropane or allyl bromide in tetrahydrofuran (THF) solvent with sodium hydroxide. After finishing the reaction, the resulting crude mixture of 1-alkyl-2-pyrrolidone was evaporated under reduced pressure and immediately purified by column chromatography (dichloromethane:methanol=10:1) and 1-ethyl-2-pyrrolidone are commercially available.

Properly synthesized 1-alkyl-2-pyrrolidone was reacted with dialkyl sulfate in a neat condition under inert-gas to give corresponding 1-

alkyl-2-alkoxy-pyrrolinium sulfate. When the reaction was finished, the crude mixture of 1-alkyl-2-alkoxy-pyrrolinium sulfate was washed several times with diethyl ether and ethyl acetate to remove organic impurities then was evaporated under a reduced vacuum condition. The resulting 1-alkyl-2-pyrrolinium sulfate is subjected to an anion metathesis reaction with either lithium bis(fluorosulfonyl)imide (LiFSI) or potassium bis(fluorosulfonyl)imide (KFSI) in water at room temperature. After the reaction was completed, distilled water was added to the mixture, and the mixture was extracted with dichloromethane. The desired compound was extracted into dichloromethane layer from water surface. After repeating the extraction several time, the desired 1-alkyl-2-alkoxy-pyrrolinium bis(fluorosulfonyl)imide was obtained in 80- 95% yield.

Scheme 1. Synthesis of 1-alkyl-2-pyrrolidone		
Table 4. Yield of 1-alkyl-2-pyrrolidone		
No.	ILs	1st step - yield (%)
1	1-propyl-2-pyrrolidone	91
2	1-allyl-2-pyrrolidone	93

Scheme 2. Synthesis of 1-alkyl-2-alkoxy-pyrrolinium sulfate

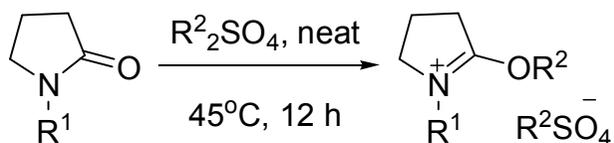


Table 5. Yield of 1-alkyl-2-alkoxy-pyrrolinium sulfate (R^2 : Me)

No.	ILs	2nd step - yield (%)
3	[E(OMe)]Pyr1-MeSO ₄	95
4	[P(OMe)]Pyr1-MeSO ₄	81
5	[A(OMe)]Pyr1-MeSO ₄	87

Scheme 3. Synthesis of 1-alkyl-2-alkoxy-pyrrolinium bis(fluorosulfonyl)imide



Table 6. Yield of Synthesis of 1-alkyl-2-alkoxy-pyrrolinium bis(fluorosulfonyl)imide (R^2 : Me)

No.	ILs	3rd step - yield (%)
6	[E(OMe)]Pyr1-FSI	93
7	[P(OMe)]Pyr1-FSI	80
8	[A(OMe)]Pyr1-FSI	92

After all pyrrolinium-based ILs were synthesized, they were respectively added to organic solvents (EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%)) ,which is one of commonly used electrolyte for Lithium-ion batteries, in different ILs content (20, 40, 60, 80 wt%) to prepare the desired electrolytes. (EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%)-[E(OMe)]PyrI-FSI, **(6)** [P(OMe)]PyrI-FSI **(7)** or [A(OMe)]PyrI-FSI **(8)**). In addition, as for briefly the electrode used in this study, lithium cobalt oxide (LiCoO₂) powders currently used in lithium-ion batteries are hindered by the poor thermal stability, relatively high toxicity, and high cost of them. Recently, lithium iron phosphate (LiFePO₄) powders have become a favorable cathode material for lithium-ion batteries due to their low cost, high discharge potential, large specific capacity (170 mAh/g), good thermal stability, and eco-friendly. As a result, LiFePO₄ powders were selected as a part of cathode material in our study.

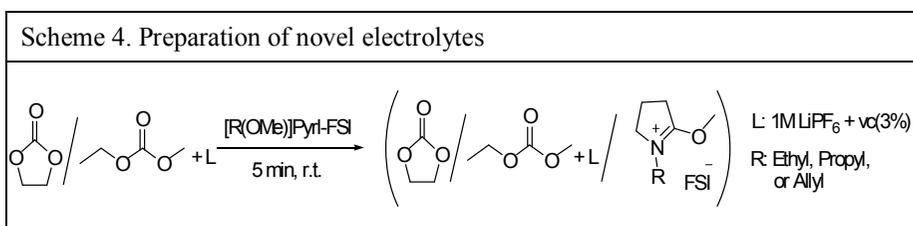
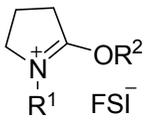


Table 7. Lithium concentration of novel electrolytes

Entry	Carbonate (wt%)	ILs (wt%)	novel electrolyte (wt%)	Li salt (M)
1	20	80	100	0.3
2	40	60	100	0.5
3	60	40	100	0.7
4	80	20	100	0.9

1.3. Thermal behaviors of ILs

Thermal gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were conducted with pyrrolinium-based ILs prepared. The decomposition temperature and melting point are depicted in Table 7 shown below. Among the all pyrrolinium-FSI having different alkyl substituents, [P(OMe)]PyrI-FSI (7) shows the highest decomposition temperature and it melts much higher temperature over 21 °C. As in our previous work, the allyl-group-containing ILs showed less thermal stability than corresponding ILs with propyl group but it still decompose at high temperature.

	No.	ILs	T_m (°C)	T_c (°C)	T_d (°C)
	4	[E(OMe)]PyrI-FSI	8	-15	159
	5	[P(OMe)]PyrI-FSI	21	-31	165
	6	[A(OMe)]PyrI-FSI	4	ND	150

T_d : 1 wt. % loss, R^2 : Me

In comparison to conventional electrolytes such as EC (melting point: 88 °C, boiling point: 248 °C, flash point: 160 °C) and EMC (melting point: -14 °C, boiling point: 107 °C, flash point: 23 °C)⁷, all ILs presented here were thermally more stable.

1.4. Flammability test of novel electrolytes

To demonstrate the safety problems from flammability of electrolytes, burning tests of novel electrolytes in a different weight percentage of ILs were carried out respectively. Figures (4-7) depict the photographs of a direct flame on the electrolytes. As expected, the pure organic solvent (EC/EMC=3/7(v/v)) with 1M LiPF₆ and vc is flammable while the IL-based electrolyte is not. Interestingly, however, the electrolytes containing more than 60% of ILs were found to be non-flammable. The pure organic solvent started to burn itself as soon as it was exposed to flame; in contrast to this behavior, the electrolytes containing more than 60% of ILs did not show any combustion causing thermal runaway even after directly exposing to the flame of a torch more than 5 seconds. As shown in Figures below, all types of novel electrolytes showed a similar tendency toward each other. From these results, this burning test indicates that safety of electrolyte can be improved by using IL mixture.

Table 9. Flammability of novel electrolytes containing three types of ILs

[E(OMe)]Pyr1- FSI wt%	Flammable	[P(OMe)]Pyr1- FSI wt%	Flammable	[A(OMe)]Pyr1- FSI wt%	Flammable
0	Yes	0	Yes	0	Yes
20	Yes	20	Yes	20	Yes
40	Yes	40	Yes	40	Yes
60	No	60	No	60	No
80	No	80	No	80	No
100	No	100	No	100	No

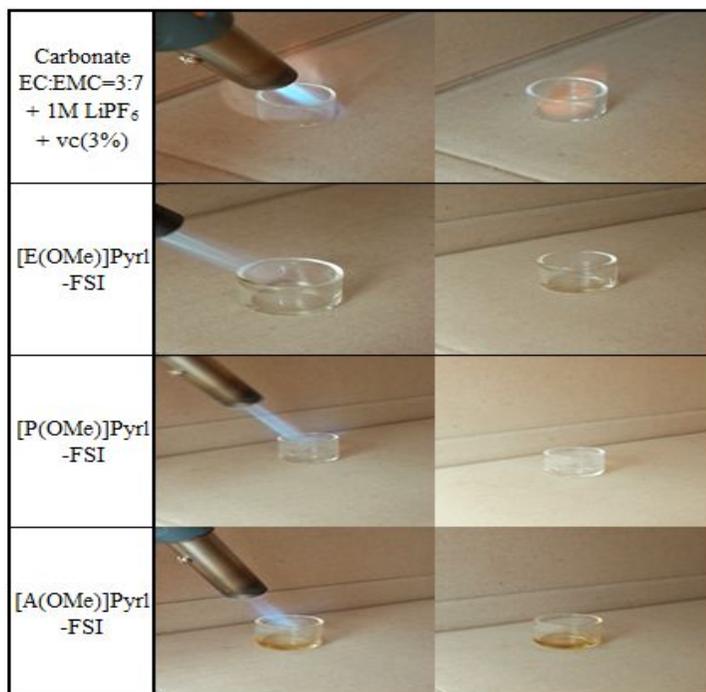


Fig 4. Burnig test of pure electrolytes

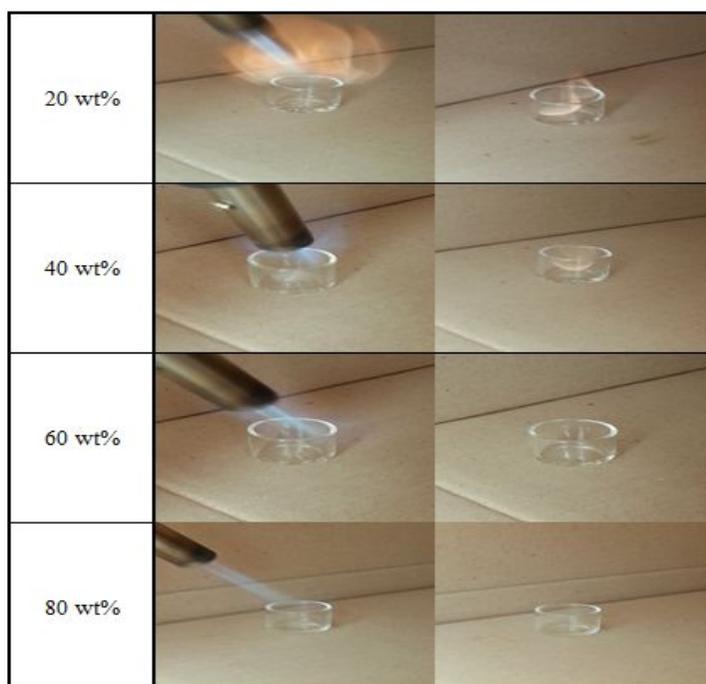


Fig 5. Burning test of novel electrolytes containing [E(OMe)]Pyr1-FSI

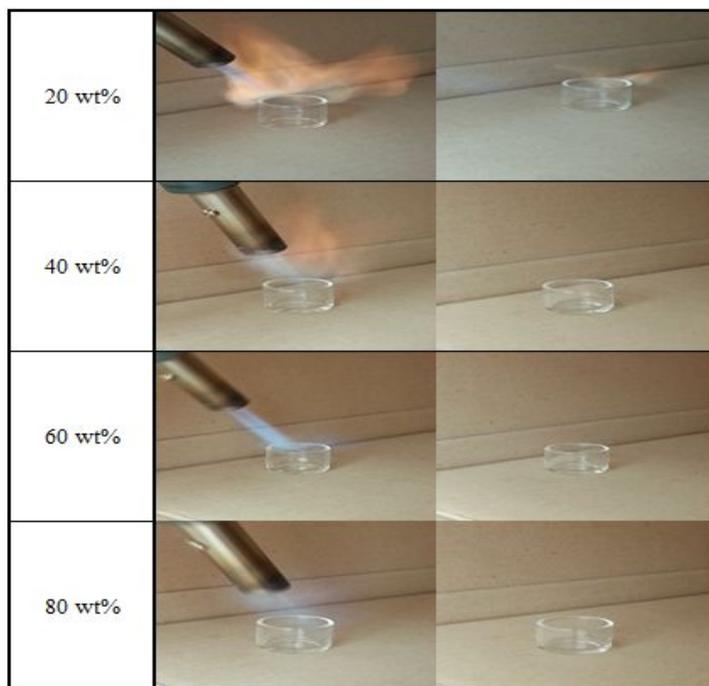


Fig 6. Burning test of novel electrolytes containing [P(OMe)]Pyr1-FSI

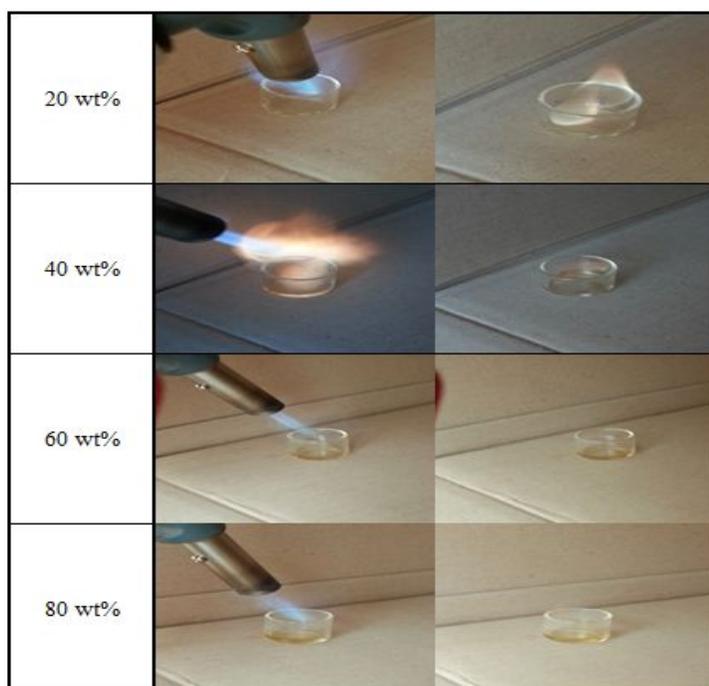
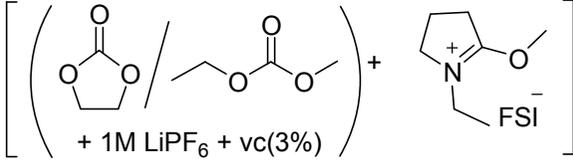


Fig 7. Burning test of novel electrolytes containing [A(OMe)]Pyr1-FSI

1.5. Physical properties

The Tables (9-11) and Figures (8-10) show properties of novel electrolytes respectively, which list conductivity, viscosity and their correlation. The Physical properties of all electrolytes with three types of ILs in different proportion were measured then interesting tendency was presented. In general, the behavior of the liquid is affected by the viscosity dependence. The viscosity dependence is the phenomenon by which viscosity decreases as its temperature increases. Furthermore, the viscosity of liquids is closely connected with their conductivity in inverse proportion. It means that viscosity would invariably increases with decreasing conductivity. However, the unexpected correlation between conductivity and viscosity of the electrolytes was found in this work. That is, the conductivity did not gradually increase when proportion of IL went up to 80%. Besides, in spite of that an electrolyte with [E(OMe)]Pryl-FSI (**6**) or [A(OMe)]Pryl-FSI (**8**) have similar tendency toward relation in between conductivity and viscosity, an electrolyte with [P(OMe)]Pryl-FSI (**7**) is slightly distinct from them. For instance, the highest conductivity in the former ([E(OMe)]Pryl-FSI (**6**) or [A(OMe)]Pryl-FSI (**8**)) is at 60% of ILs while the latter ([A(OMe)]Pryl-FSI (**8**)) shows the maximum at 40% of ILs.

Table 10. Physical properties of novel electrolytes containing [E(OMe)]Pyr1-FSI		
		
Electrolyte	(cP)	(mS cm ⁻¹)
Carbonate with 0 wt% of ILs	3.6	9.44
Carbonate with 20 wt% of ILs	4.9	10.76
Carbonate with 40 wt% of ILs	7.0	11.02
Carbonate with 60 wt% of ILs	10.6	13.76
Carbonate with 80 wt% of ILs	18.0	12.03
^a 100% of ILs	18.3	8.34
Carbonate: EC:EMC=3:7(v/v)+1M LiPF ₆ +vc(3%)		
ILs: [E(OMe)]Pyr1-FSI ^a : without LiPF ₆ and vc		

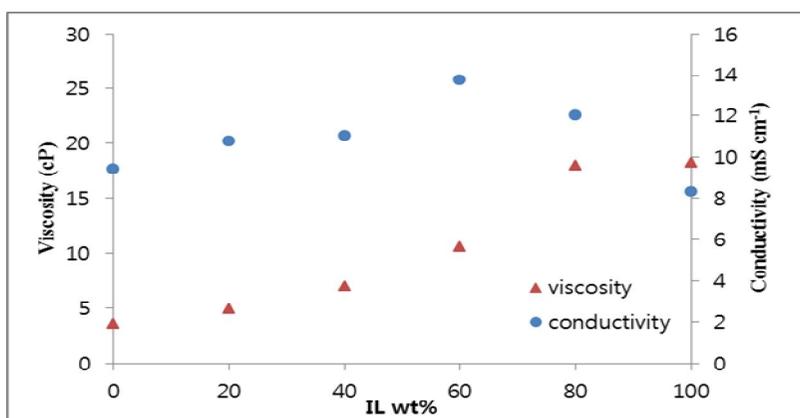


Fig 8. Viscosity and conductivity novel electrolyte with [E(OMe)]Pyr1-FSI

Table 11. Physical properties of novel electrolytes containing [P(OMe)]Pyr1-FSI		
Electrolyte	(cP)	(mS cm ⁻¹)
Carbonate with 0 wt% of ILs	3.6	9.44
Carbonate with 20 wt% of ILs	5.2	9.63
Carbonate with 40 wt% of ILs	7.8	10.26
Carbonate with 60 wt% of ILs	11.7	8.70
Carbonate with 80 wt% of ILs	20.8	8.60
^a 100% of ILs	25.8	6.03
Carbonate: EC:EMC=3:7(v/v)+1M LiPF ₆ +vc(3%)		
ILs: [P(OMe)]Pyr1-FSI ^a : without LiPF ₆ and vc		

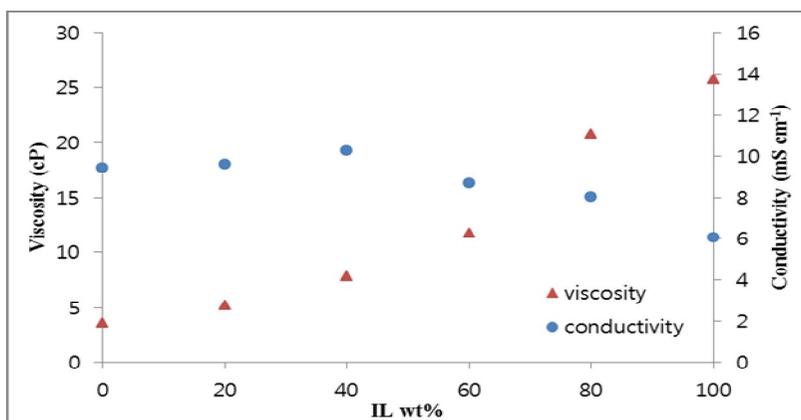


Fig 9. Viscosity and conductivity of novel electrolytes with [P(OMe)]Pyr1-FSI

Table 12. Physical properties of novel electrolytes containing [A(OMe)]Pyr1-FSI		
Electrolyte	(cP)	(mS cm ⁻¹)
Carbonate with 0 wt% of ILs	3.6	9.44
Carbonate with 20 wt% of ILs	4.9	9.69
Carbonate with 40 wt% of ILs	7.0	11.67
Carbonate with 60 wt% of ILs	10.3	12.34
Carbonate with 80 wt% of ILs	16.9	11.69
^a 100% of ILs	17.0	7.88
Carbonate: EC:EMC=3:7(v/v)+1M LiPF ₆ +vc(3%)		
ILs: [A(OMe)]Pyr1-FSI ^a : without LiPF ₆ and vc		

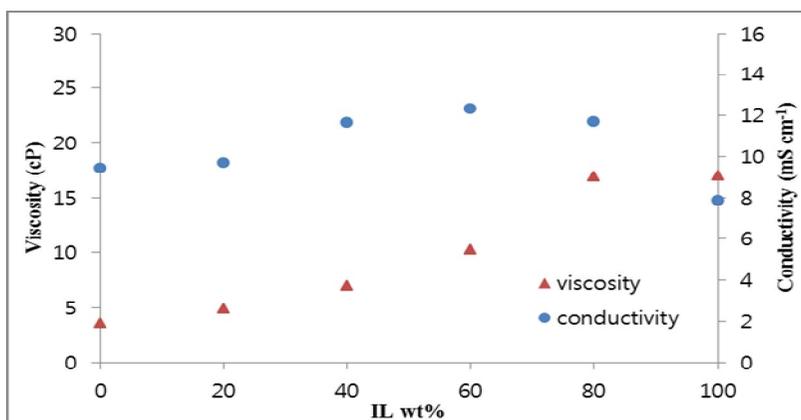


Fig 10. Viscosity and conductivity of novel electrolytes with [A(OMe)]Pyr1-FSI

According to the data of this study, the electrolyte with 60% of [E(OMe)]Pryl-FSI (**6**) show the highest conductivity(12.34 mS cm^{-1}) while the lowest is the electrolyte with 80% of [P(OMe)]Pryl-FSI (**7**) (8.60 mS cm^{-1}). On the whole, viscosity of the electrolytes containing [P(OMe)]Pryl-FSI (**7**) is higher than other mixture of electrolytes in the Tables.

All things considered, we could expect that the improved conductivity of electrolyte by adding ILs would enhance the capacity of cell containing conventional carbonate electrolytes at discharge rate and the optimal cycling performance would be conducted using the electrolyte with 60 wt% of [E(OMe)]Pryl-FSI (**6**) at 1C-rate which has the highest conductivity (12.34 mS cm^{-1}). Besides, the other electrolyte with pyrrolinium-based ILs reported in this work would induce better cycling performance as well.

As the results of this study and burning test, noteworthy optimum composition range has been discovered for promising electrolytes of lithium-ion batteries, when the proportion of IL in novel electrolytes is 60-80% ([E(OMe)]Pryl-FSI (**6**) or [A(OMe)]Pryl-FSI (**8**), which gives desirable properties such as non-flammability, high conductivity and low viscosity.

1.6. Cycle life test

The operating cycling conditions of half-cells containing any electrolytes at 1C-rate have been rarely reported. Generally, high C-rate causes cell's life to be shortened for battery systems, since the electrolyte is decomposed due to its instability and irreversible reaction with electrolyte, decomposed product, lithium salt and it causes fading discharge capacity. As mentioned, our group has been focusing on pyrrolinium-based ionic liquids. Li/LiFePO₄ cells with three types of pyrrolinium-FSI prepared ([E(OMe)]PyrI-FSI (6), [P(OMe)]PyrI-FSI (7), [A(OMe)]PyrI-FSI (8)) with 0.5M LiTFSI were well maintained after 100 cycles at 1C-rate and showed higher discharge capacity retention, even though the initial discharge capacity is lower than the cell with carbonate electrolyte. Especially, as illustrated in Figure 11, [E(OMe)]PyrI-FSI (6) with 0.5M LiTFSI showed the highest discharge capacity retention during 100 cycles among them.

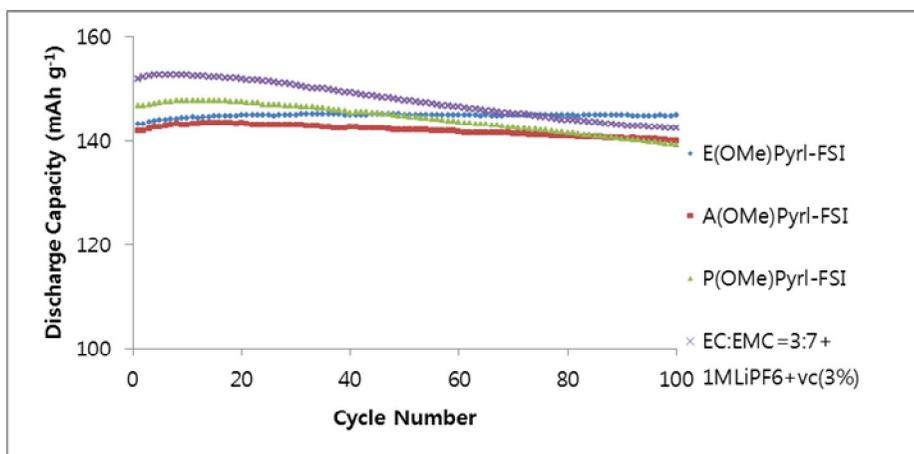


Fig 11. Cycle life test of Li/LiFePO₄ cells with various pure electrolytes at 1C-rate

According to the results that pyrrolinium-based electrolytes are rather stable at 1C-rate, we assumed that ILs can have positive effects on not only flammability but also cyclability of the cells with the electrolyte provided that ILs are added to the carbonate solvent to form electrolytes in the mixed solvents. The cycle life tests were performed with well assembled cells containing the electrolytes in the mixed solvents after they were prepared in different ILs content respectively.

Cycling performances of all Li/LiFePO₄ cells prepared with the electrolytes prepared were evaluated at room temperature. After two preconditioning cycles at low current rate (0.1C-rate), the cells was charged at a constant current (CC) up to the charging cut-off voltage of 4.1V. These were followed by a constant voltage (CV) charge with a decline in the current until a final current of 10% of the charging current was reached. The cells were then discharged down to a cut-off voltage of 2.5V at the same current density (1C-rate).

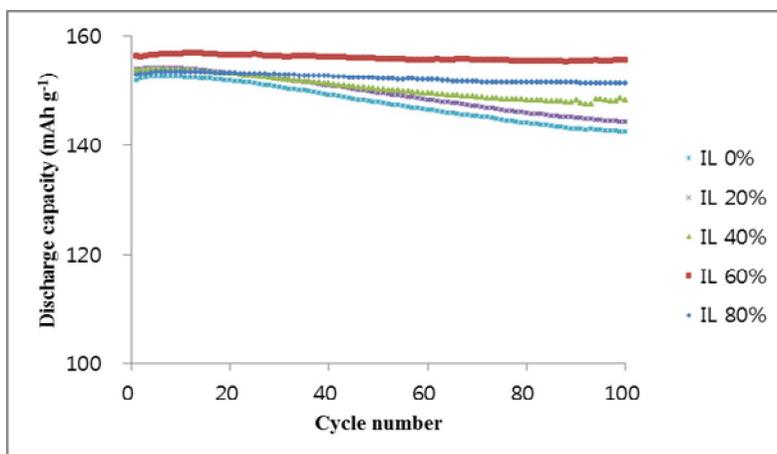


Fig 12. Discharge capacities of Li/LiFePO₄ cells assembled with novel electrolytes containing [E(OMe)]Pyr1-FSI

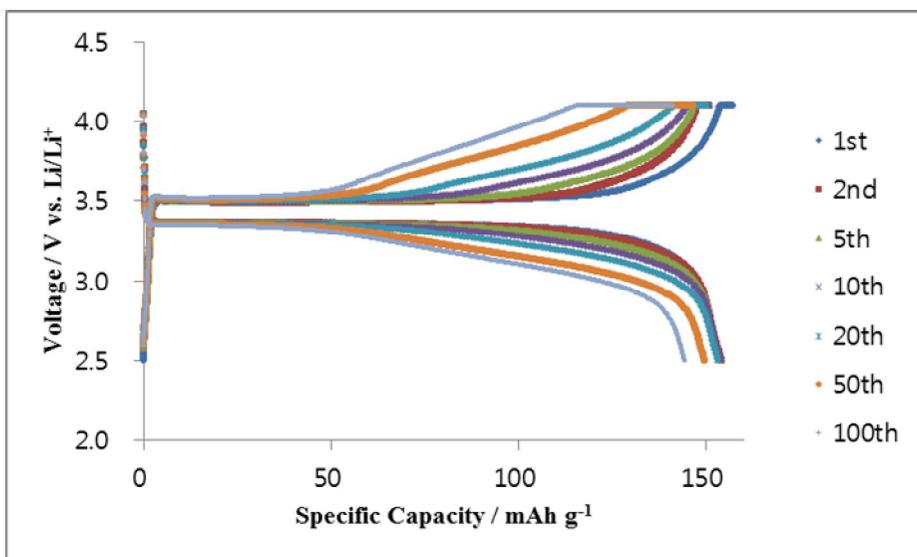


Fig 13. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 20% of [E(OMe)]Pyrl-FSI

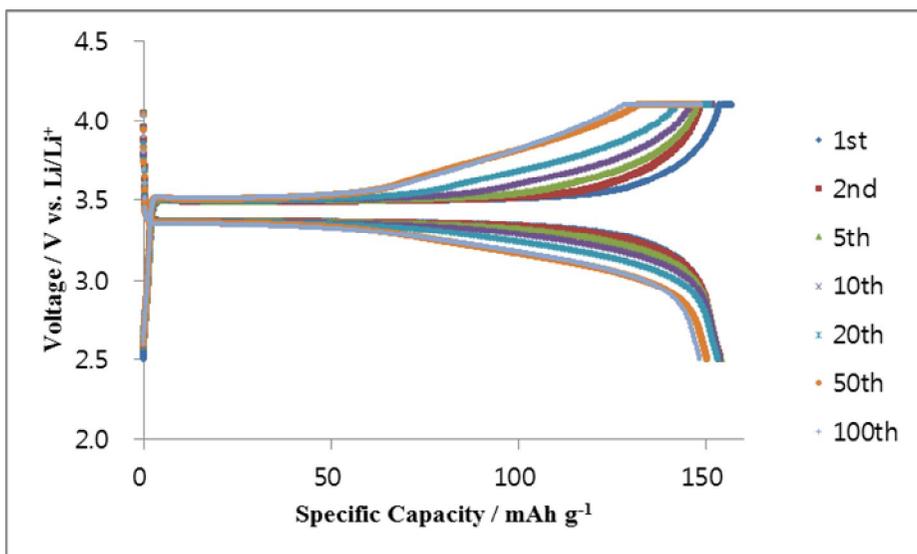


Fig 14. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 40% of [E(OMe)]Pyrl-FSI

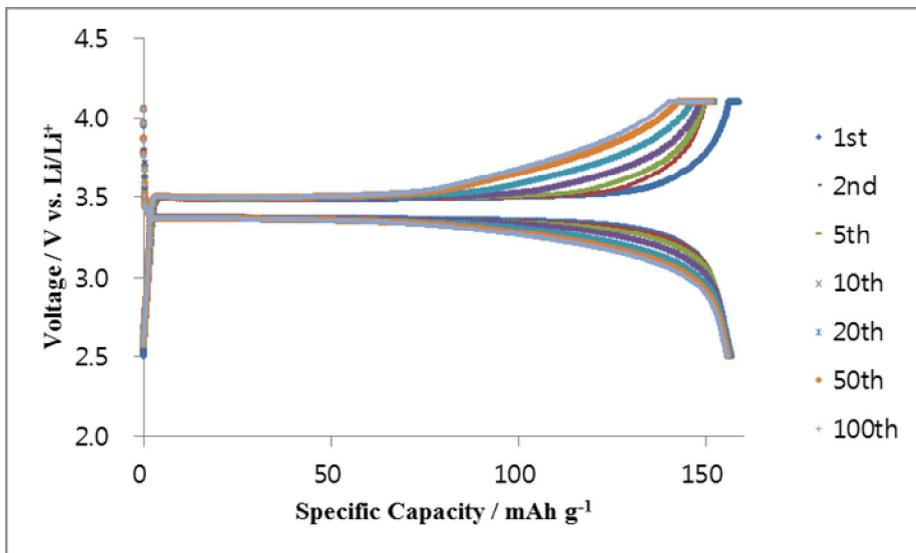


Fig 15. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 60% of [E(OMe)]Pyrl-FSI

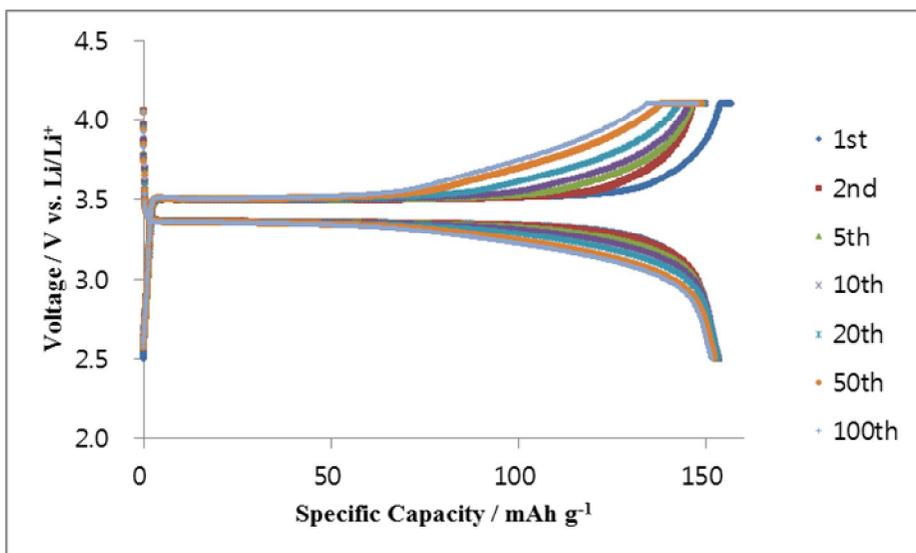


Fig 16. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 80% of [E(OMe)]Pyrl-FSI

Figure 12 shows cycle performance of the Li/LiFePO₄ cells using pure carbonate electrolyte and the electrolytes with different IL weight percent at 1C charge-discharge rate. The cell containing 60 % IL presents higher reversible capacity and coulomb efficiency than other cells which contain not only 20, 40, and 80% of [E(OMe)]Pyr1-FSI (6) respectively but also pure carbonate electrolyte (0% IL) , the cell shows the capacity of 155mAh g⁻¹ even after 100 cycles. In addition, the electrolytes with 20, 40 and 80% of IL show better cycle performance even than pure carbonate solvent. It is attributed to the stabilization of the electrolytes in the mixed solvents during the course of lithium intercalation. Figures (13-16) also show the voltage-capacity plots of Li/LiFePO₄ cells using the electrolytes with [E(OMe)]Pyr1-FSI (6) in different ratios. The sufficient discharge capacities with small irreversible capacity are observed in the each cycle from 1st to 100th.

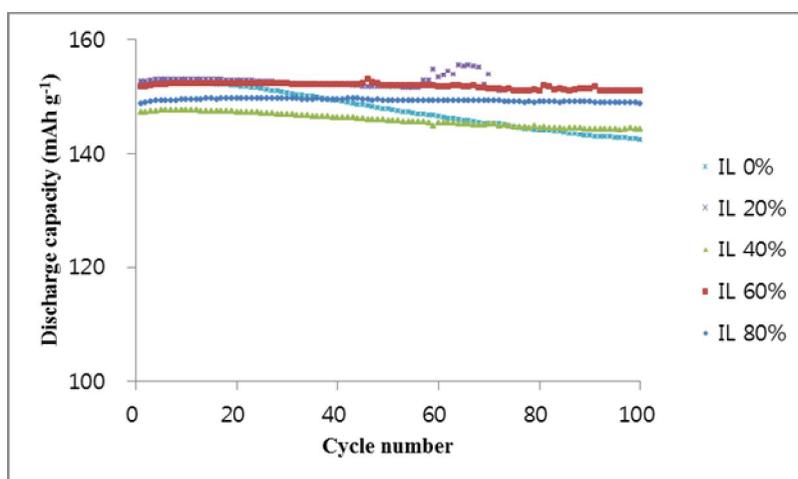


Fig 17. Discharge capacities of Li/LiFePO₄ cells assembled with novel electrolytes containing [P(OMe)]Pyr1-FSI

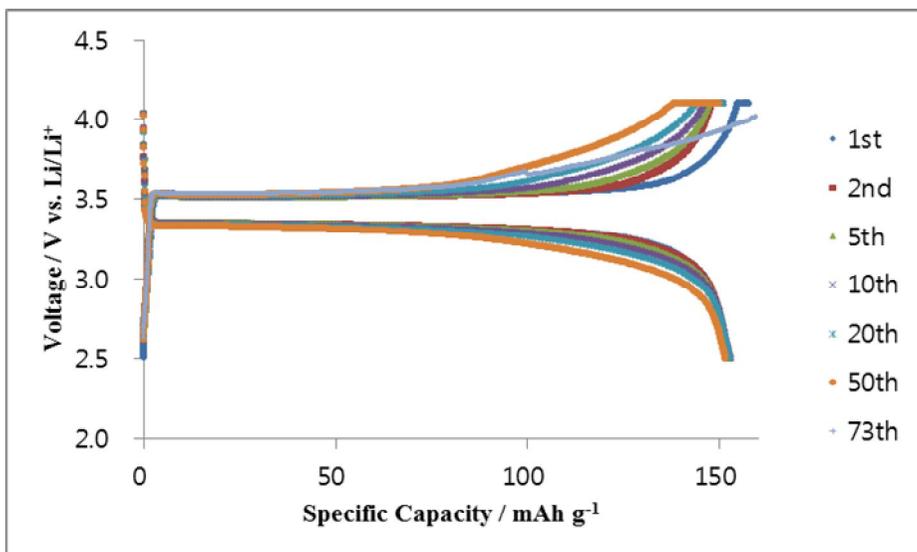


Fig 18. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 20% of [P(OMe)]Pyrl-FSI

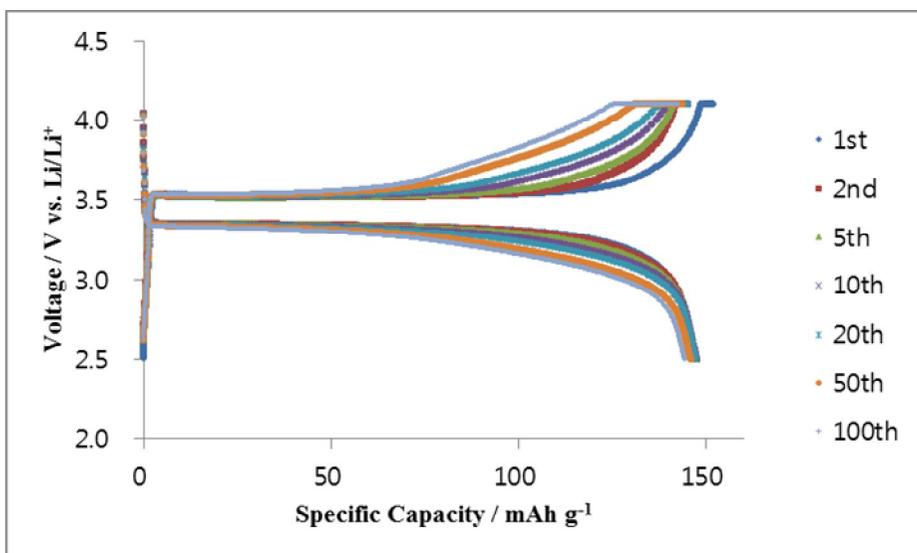


Fig 19. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 40% of [P(OMe)]Pyrl-FSI

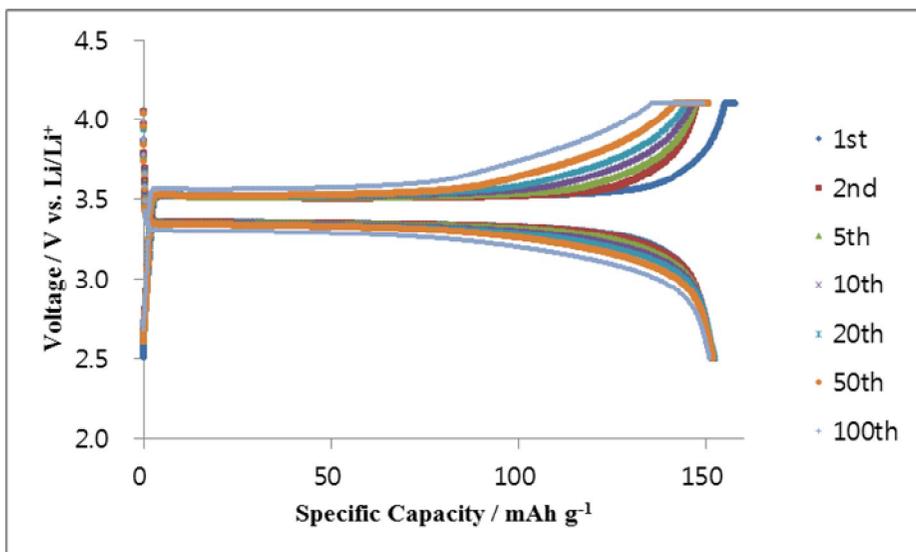


Fig 20. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 60% of [P(OMe)]Pyrl-FSI

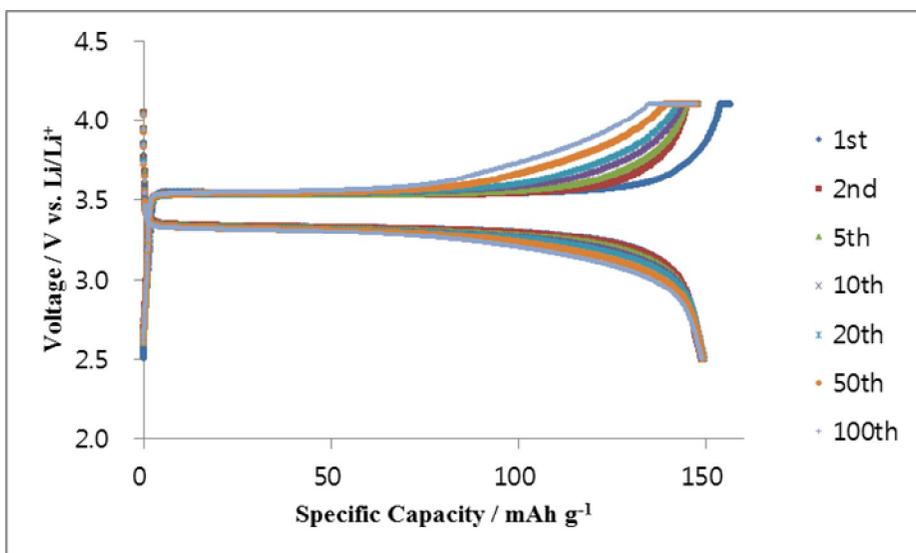


Fig 21. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 80% of [P(OMe)]Pyrl-FSI

Figure 17 illustrated discharge capacity of Li/LiFePO₄ half cells assembled with the electrolytes containing [P(OMe)]PyrI-FSI (7) at a current rate of 1C. It also shows the effect of the [P(OMe)]PyrI-FSI (7) content in the electrolyte on the discharge capacities of the cells, as a function of cycle number. The optimum composition range of IL content for [P(OMe)]PyrI-FSI(7)-based cells is similar to the electrolyte with [E(OMe)]PyrI-FSI (6) which show the best performance in 60% of IL content. The cell shows the capacity of 151mAh g⁻¹ after 100 cycles. On the other hand, the cell containing electrolyte with 20% IL was cut-off after 73th cycles. However, it is still better than pure carbonate in terms of discharge capacity retention ratio until the cell's life was finished. The initial discharge capacity of cells with 40 and 60 IL are slight lower, but the cells were well maintained and more consistent, which has leads to the results been similar and less spread.

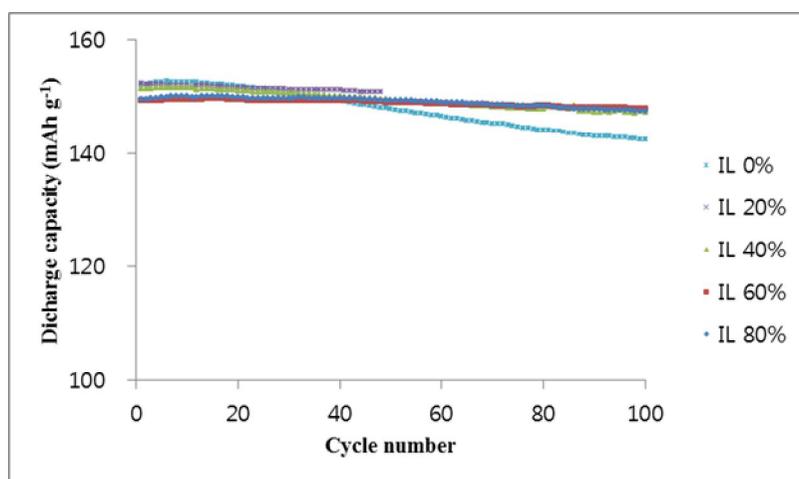


Fig 22. Discharge capacities of Li/LiFePO₄ cells assembled with novel electrolytes containing [A(OMe)]PyrI-FSI

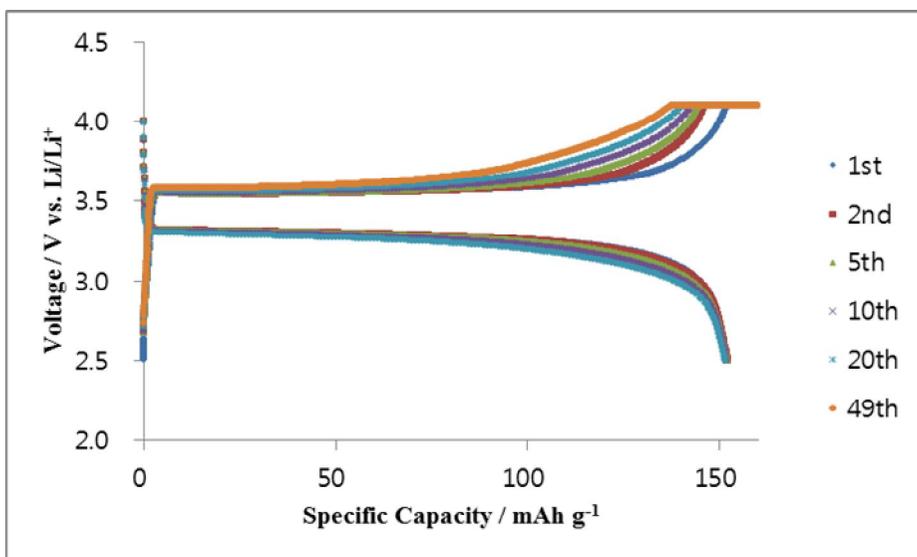


Fig 23. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 20% of [A(OMe)]Pyr1-FSI

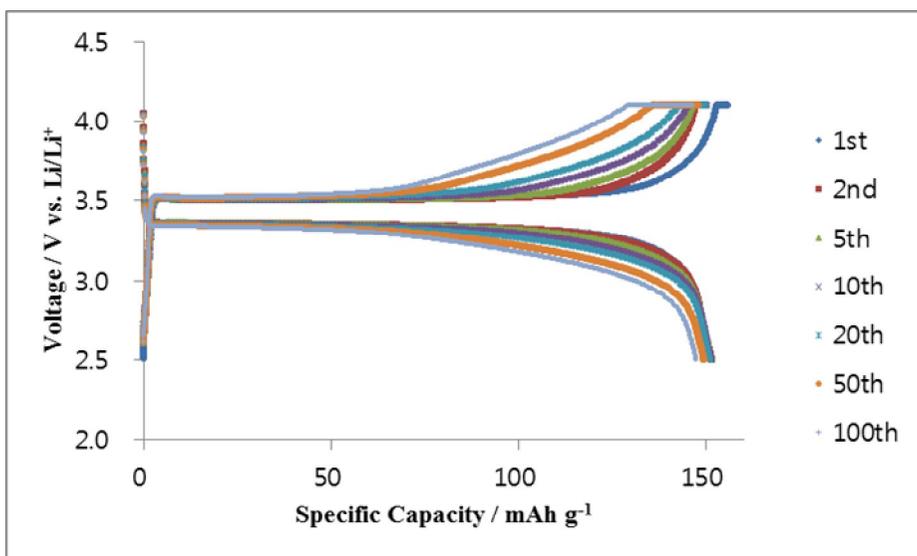


Fig 24. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 40% of [A(OMe)]Pyr1-FSI

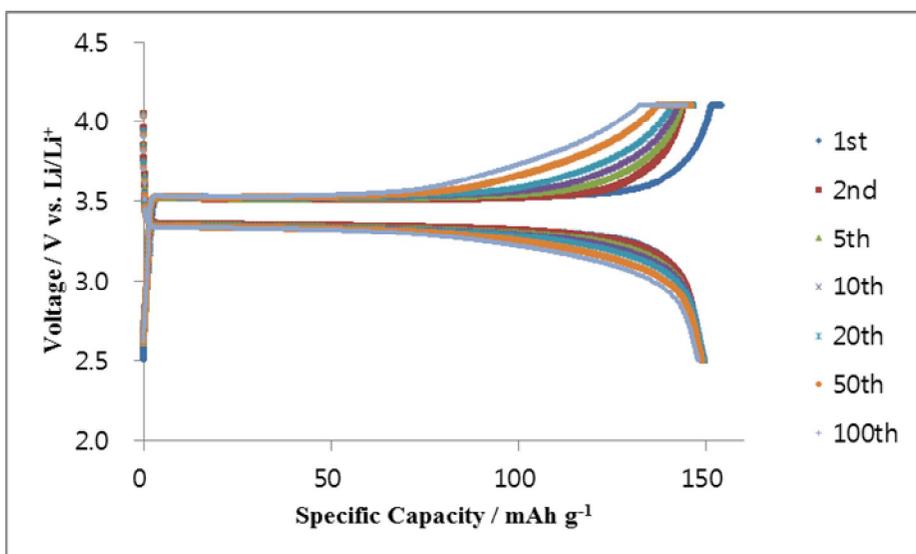


Fig 25. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 60% of [A(OMe)]Pyrl-FSI

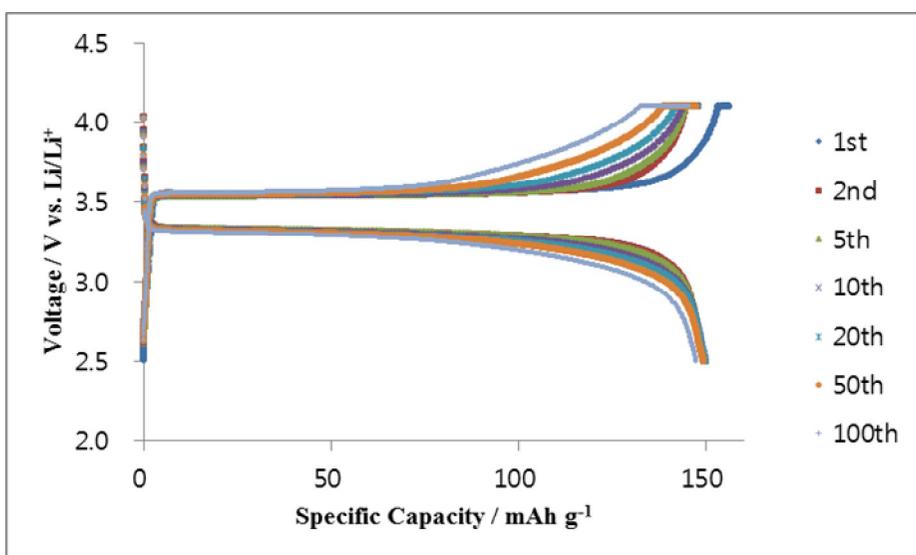


Fig 26. Charge and discharge curves of a Li/LiFePO₄ cell assembled with the electrolyte containing 80% of [A(OMe)]Pyrl-FSI

Figures (22-26) also describe the cycle performance of Li/LiFePO₄ cells assembled with mix electrolytes containing [A(OMe)]PyrI-FSI (**8**) in different ratios. As shown in Figure 22, the electrolyte with IL content of 20% started with slightly higher initial discharge capacity, but it cannot endure until 100cycles with high coulomb efficiency and shows similar behaviors with the electrolyte containing [P(OMe)]PyrI-FSI (**7**) of 20%. Excepting for 20% IL, the other electrolytes have shown good cyclability up to the 100 cycles.

Table 13. Discharge capacity retention ratio of novel electrolytes after 100 cycles

^a Pure carbonate	152 → 142 (94%)				
ILs (wt%) in carbonate	20%	40%	60%	80%	^b 100%
[E(OMe)]PyrI-FSI	154 → 144 (94%)	153 → 148 (97%)	156 → 155 (99%)	153 → 151 (99%)	X
[P(OMe)]PyrI-FSI	152 → 150 (99%) at 73 th	147 → 144 (98%)	152 → 150 (99%)	149 → 148 (99%)	X
[A(OMe)]PyrI-FSI	152 → 150 (99%) at 49 th	151 → 147 (97%)	149 → 147 (99%)	149 → 147 (99%)	X

^a: EC/EMC=3/7(v/v) + 1M LiPF₆ + vc (3%)

^b: pure pyrrolinium-FSI (ILs) with 1M LiPF₆ +vc(3%)

Table 13 shows the discharge capacity retention ratio of novel electrolytes. As shown on the Table 13, the electrolytes with [E(OMe)]PyrI-FSI (**6**) are well performed in any IL content and show better cycle performance than others. Unfortunately, the electrolyte with 20% of [P(OMe)]PyrI-FSI (**7**) or [A(OMe)]PyrI-FSI (**8**) has not

shown good cyclability at 1C-rate. The pure pyrrolinium-FSI (100% ILs) with 1M LiPF₆ +vc(3%) were likewise a failure.

In general, reductive decomposition of electrolytes results in the formation of Solid Electrolyte Interphase (SEI) films. These fabricated SEI films allow Li-ion to intercalate/de-intercalate into electrode and prevent further decomposition of electrolytes by blocking between the electrolytes and the electrodes.^{6,25}

We can reasonably assume that in the case of a cell with the novel electrolytes, the LiFePO₄ electrode is covered by a good SEI film that prevents further decomposition of the electrolyte in the mixed solvents, this allowing an efficient and reproducible cycling response.

1.7. Summary

Novel electrolytes were prepared in different IL content using pyrrolinium-based ionic liquids which were properly synthesized, and carbonates solvents which were purchased from commercial supplier. The physicochemical properties, flammability, and cyclability were measured with the novel electrolytes respectively. Interestingly, the unexpected behavior between conductivity and viscosity was found like that the conductivity did not seem to be affected by the viscosity dependence phenomenon. The electrolyte with 60% of [E(OMe)]Pyr-FSI (**6**) in carbonate solvent, which has higher viscosity, shows the highest conductivity (13.76 mS cm^{-1}) while the electrolyte containing 80% of [P(OMe)]Pyr-FSI (**7**) has the lowest conductivity (8.60 mS cm^{-1}). In addition, the electrolytes containing more than 60% IL content did not show any combustion which allows battery systems to be thermal runaway even after directly exposing to the flame. The discharge capacity of all the electrolytes prepared were maintained after 100 cycles excepting for the electrolyte with 20% of [P(OMe)]Pyr-FSI (**7**) or of [A(OMe)]Pyr-FSI (**8**). The highest discharge capacity after 100 cycles is 155 mAh g^{-1} of the electrolyte with 60% of [E(OMe)]Pyr-FSI (**6**) in a Li/LiFePO₄ half-cell. This enhanced cyclability might be affected by SEI films which prevent further decomposition of the novel electrolytes.

Conclusion

It has been more than decade since the lithium-ion batteries (LIBs) have suffered from the safety problem due to its thermally unstable carbonate-based electrolyte sources which are flammable and volatile. Ionic liquids (ILs) are thought as one of the most promising means to solve this problem owing to their unique properties.

In this work, novel electrolytes are prepared with organic carbonate solvents and pyrrolinium-based ionic liquids with different alkyl substituents to improve both safety problem and cyclability by correlation between two solvents.

The pyrrolinium-FSI ILs with different alkyl substituents were synthesized and added into carbonate solvent with different ratios to prepare the desired electrolytes. In addition, several test and measurement of prepared electrolyte were performed to characterize the physicochemical and electrochemical properties. As expected, viscosity became higher gradually as the IL content increases. However, the unusual correlation, which does not follow viscosity dependence phenomenon, between conductivity and viscosity in terms of novel electrolytes was shown in this work. For instance, the electrolyte containing with 60% of [E(OMe)]PyrI-FSI (**6**) shows the highest conductivity (13.76 mS cm^{-1}) which leads to the good cycle performance among all the electrolytes prepared, despite its rather high

viscosity (10.6 cP) compared to the electrolytes containing less than 40% of ILs.

The electrolytes in the mixed solvents of pyrrolinium-based ionic liquid and carbonate also show the characters of thermal stability and incombustibility, this is significant for improving the safety of lithium-ion batteries which cannot be surpassed by carbonate electrolytes. As expected, in this work, carbonate electrolyte is flammable while the pyrrolinium-based ILs are not. However, for all the electrolytes containing more than 60% of ILs were found to be not flammable. The electrolyte with less than 40% ILs starts to burn itself as soon as it is directly exposed to flame. Considering these results, the mixture containing more than 60% IL appears certainly interesting in terms of safety by showing non-flammability.

This novel electrolyte gave results comparable to the organic electrolyte for LiFePO₄ cathode. From the point of view of a safer Li-ion battery, we evaluated a Li/LiFePO₄ cell with an electrolyte mixture (20, 40, 60, 80% IL) and compared it to the results in the standard organic electrolyte. The novel electrolytes prepared show better cycle performances which are higher discharge capacity retention and discharge capacity value after 100 cycles than pure carbonate solvents or pyrrolinium-based ionic liquids. Overall, Li/LiFePO₄ half cells with the electrolyte containing [E(OMe)]Pyr1-FSI (**6**) are well performed and show better cycle performance than other mixtures at 1C-rate.

Especially, the electrolyte with 60% of [E(OMe)]PyrI-FSI (**6**) shows the highest cycling efficiency and discharge capacity of 155mAh g⁻¹ after 100 cycles at 1C-rate. However, the mixture with 20% of [P(OMe)]PyrI-FSI (**7**) or [A(OMe)]PyrI-FSI (**8**) show unstable tendency of cycle performance at 1C-rate because their cycles are cut-off at 73th and 50th cycles respectively. Nevertheless, the electrolytes with more than 40% of [P(OMe)]PyrI-FSI (**7**) or [A(OMe)]PyrI-FSI (**8**) are well maintained after 100 cycles and show good cyclability. As a result, the presence of more than 40% of ILs in the mixture was able to significantly increase the capacity retention of Li/LiFePO₄ cells due to well-formed SEI layers. In order to make the best choice of the electrolyte composition for use in lithium-ion batteries, we should take into account the flammability, conductivity and viscosity of the electrolyte. According to the results of this work, the electrolytes having the pyrrolinium-based ionic liquid content between 60-80% might approach close to the requirements of electrolytes as an alternative for lithium-ion battery.

Experimental Details

1. General

Materials were prepared from commercial suppliers and were used with further purification by distillation under reduced pressure before their usage. All experimental glassware, syringes, and magnetic bars were oven-dried at 120 °C for at least 4 hours and stored in desiccator until use. Upon workup, solvent was removed with a rotary evaporator and then with a high vacuum pump.

Water contents were determined by Karl Fischer coulometry using a Mettler Toledo DL39 coulometric titrator.

Burning tests were performed using a Kovea TKT-9607 gas torch over 1300 °C, directly exposing on a petri dish.

¹H and ¹³C NMR spectra were obtained using CDCl₃ as a solvent on a Bruker Avance III spectrometer (400 MHz for ¹H and 100 MHz for ¹³C NMR). The ¹H NMR data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm).

Thermal properties were analyzed by DSC and TGA. Crystallization point and melting point were determined by using a TA Instruments Q1000 differential scanning calorimeter under Ar atmosphere. Thermograms were recorded during heating from -50 °C to 110 °C scanning at a heating rate of 10 °C min⁻¹ after cooling to -50 °C scanning at a cooling rate of 10 °C min⁻¹. Thermal decomposition

temperature was recorded by using a SDT Q600 and Mettler TG 50 TA instruments under Ar atmosphere. Heating rate and terminal temperature were set at $10\text{ }^{\circ}\text{C min}^{-1}$ and $500\text{ }^{\circ}\text{C}$, respectively. The temperature of over 1 % loss of its weight was defined as the thermal decomposition temperature.

Viscosity measurements were carried out on a Brookfield DV-II+cone/plate viscometer.

Ionic conductivity was determined using a TOA-DKK CM-30R benchtop conductivity meter at room temperature.

For preparation of a LiFePO_4 -containing composite electrode, a slurry mixture of LiFePO_4 powder, Super-P (as a carbon additive for conductivity enhancement) and poly(vinylidene fluoride) (PVdF, as a binder) (8:1:1 wt. % ratio) was coated on a piece of an Al current collector, which was followed by drying at $120\text{ }^{\circ}\text{C}$. Coin-type half-cells were fabricated with the composite electrode, Li foil as a counter and reference electrode, and glass fiber as a separator. Galvanostatic-charge-discharge cycling was made using a WBCS3000 cycler and the charge-discharge tests on the cells were performed at 4.1-2.5 V of cut-off voltage. The current density is 1C at $25\text{ }^{\circ}\text{C}$ and the cells were fully charged and discharged by constant current/constant voltage (CC/CV) and constant current (CC) modes, respectively.

2. General Procedure for the Preparation of Novel Electrolytes in the Mixed Solvents of Pyrrolidinium-based Ionic Liquid and Carbonate

2.1. General procedure for preparation of 1-alkyl-2-pyrrolidone

The pyrrolinium bis(fluorosulfonyl)imide with alkyl substituents was prepared according to the modified procedure described below.²⁴ Basically, preparation of Pyrrolinium-FSI was conducted through overall three steps, N-alkylation, O-alkylation and anion exchange.

Start with 2-pyrrolidone, 1-alkyl-2-pyrrolidone was synthesized using 2-pyrrolidone with 1-alkylhalide such as 1-iodopropane and allyl bromide. Fortunately, there was no need to synthesize 1-ethyl-2-pyrrolidone because it is commercially available. The 1-propyl and 1-allyl pyrrolidone were synthesized by reaction between 2-pyrrolidone (1 eq, 80mmol) and alkyl halide (1.5 eq, 120 mmol) such as 1-iodopropane or allyl bromide in tetrahydrofuran (THF) (200 ml) solvent with sodium hydroxide (NaOH) (1.5eq, 150 mmol) base under reflux for 12 hours via N-alkylation. The removal of sodium hydroxide (NaOH) and tetrahydrofuran (THF) in a crude mixture by filtration and evaporation which performed under reduced pressure was followed by column chromatography (dichloromethane: methanol=10: 1) purification.

2.2. General procedure for the preparation of the pyrrolinium sulfate

O-alkylation of 1-alkyl-2-pyrrolidone (1 eq, 100mmol) was conducted with appropriate distilled dimethyl sulfate (1.5 eq, 150mmol) in a neat condition at 45 °C for 12 hours to give corresponding 1-alkyl-2-methoxy-pyrrolinium sulfate. The crude mixture of 1-alkyl-2-methoxy-pyrrolinium sulfate was washed with ethyl acetate and ether to remove organic impurities and remained dimethyl sulfate more than three times respectively, after the reaction was finished. The resulting compound was added to dichloromethane (150 ml) and dried over MgSO₄ and NaSO₄ to remove included water in solution. The solution was evaporated to obtain desired resulting pyrrolinium sulfate in high yield.

2.3. General procedure for the anion metathesis-preparation of pyrrolinium bis(fluorosulfonyl)imide

The prepared 1-alkyl-2-methoxy-pyrrolinium sulfate (1 eq, 100 mmol) is subject to an anion metathesis reaction with lithium bis(fluorosulfonyl)imide (LiFSI) (1.5 eq, 150 mmol) or potassium bis(fluorosulfonyl)imide (KFSI) (1.5 eq, 150 mmol) in water at room temperature for 10 minutes (100 ml). After this reaction was completed, distilled water (150 ml) was added to the mixture and the resulting mixture was extracted with dichloromethane (150 ml). The combined

organic layers were washed with distilled water included several times then dried over MgSO_4 and NaSO_4 to remove included water in solution. The organic solution was filtrated and concentrated by the removal of solvent under reduced pressure to afford the desired pyrrolinium bis(fluorosulfonyl)imide in high yield. Completion of all the pyrrolinium-FSI reaction was confirmed by ^1H and ^{13}C NMR.

2.4. General procedure for the preparation of novel electrolytes in the mixed solvents of pyrrolinium-based ionic liquid and carbonate solvent

The resulting prepared pyrrolinium-FSI was added to carbonate solvent (EC:EMC=3:7+1M LiPF_6 +vc(3%)) which is commercially available with different IL ratios respectively(20, 40, 60, and 80wt%) and then stirred for 10 minutes at room temperature to obtain homogeneous solution of the electrolytes in the mixed solvents. The total weight of the each electrolytes prepared was fixed to 1g(100wt%) in this work.

3. Preparation of potassium bis(fluorosulfonyl)imide

Preparation of potassium bis(fluorosulfonyl)imide (KFSI) which is one of anion source of pyrrolinium-FSI was conducted through two steps. Initially, the surfamic acid (154 mmol, 1.2 eq), thionyl chloride (321 mmol, 2.5 eq) and chlorosulfuric acid (108 mmol, 1 eq) were

added to one-pot in order under 0 °C and were reacted in a neat condition for 24 hours at 130 °C. During the first step, a trap which is packed with potassium hydroxide and calcium chloride should be installed to quench released hydrochloric acid gas. After the reaction was done, the next step progressed in situ. The intermediate mixture diluted with 150 ml of dichloromethane was added dropwise to potassium fluoride in dichloromethane solvent at 0 °C and was reacted at 50 °C for 24 hours. Subsequently, the reaction mixture was heated up to 160 °C and maintained at least for 2 hours to remove dichloromethane solvent using dean stark. Then, the reactant with 100 ml of tetrahydrofuran (THF) was ground in a mortar to dissolve desired product in THF solvent which was trapped in reactant. After the filtration of THF solution containing the KFSI and crude product, the evaporation of THF solution under reduced pressure was followed by salting out with dichloromethane (200 ml). Finally, drying under vacuum pump at room temperature gave desired white powder of the KFSI in moderate yield.

1-propyl-2-pyrrolidone (1)

^1H NMR δ 0.88-0.91 (t, $J=7.4$, 3H), 1.49-1.59 (m, 2H), 1.97-2.04 (m, 2H), 2.36-2.40 (t, $J=8.0$, 2H), 3.21-3.25 (t, $J=7.4$, 2H), 3.35-3.38 (t, $J=7.2$, 2H); ^{13}C NMR 11.2, 17.9, 20.5, 31.1, 44.1, 47.0, 174.9.

1-allyl-2-pyrrolidone (2)

^1H NMR δ 1.98-2.06 (m, 2H), 2.39-2.43 (t, $J=8.2$, 2H), 3.33-3.36 (t, $J=7.0$, 2H), 3.88-3.90 (t, $J=6.0$, 2H), 5.15-5.20 (m, 2H), 5.68-5.78 (m, 1H); ^{13}C NMR δ 17.8, 30.9, 45.2, 46.7, 117.7, 132.5, 174.7.

1-ethyl-o-methylpyrrolinium methylsulfate

([E(OMe)]PyrI-MeSO₄) (3)

^1H NMR δ 1.30-1.33 (t, $J=6.0$, 3H), 2.40-2.48 (m, 2H), 3.35-3.39 (t, $J=8.0$, 2H), 3.62-3.68 (m, 2H), 3.72 (s, 3H), 3.97-4.01 (t, $J=7.8$, 2H), 4.37 (s, 3H); ^{13}C NMR δ 11.4, 17.3, 29.8, 41.6, 52.1, 55.1, 62.9, 180.4.

1-propyl-o-methylpyrrolinium methylsulfate

([P(OMe)]PyrI-MeSO₄) (4)

^1H NMR δ 0.94-0.98 (t, $J=7.4$, 3H), 1.66-1.75 (m, 2H), 2.40-2.47 (m, 2H), 3.35-3.39 (t, $J=8.0$, 2H), 3.53-3.57 (t, $J=7.6$, 2H), 3.73 (s, 3H), 3.96-4.00 (t, $J=7.6$, 2H), 4.37 (s, 3H); ^{13}C NMR δ 11.3, 17.5, 19.7, 29.8, 48.3, 52.8, 54.7, 62.9, 180.8.

1-allyl-o-methylpyrrolinium methylsulfate

([A(OMe)]PyrI-MeSO₄) (5)

^1H NMR δ 2.40-2.48 (m, 2H), 3.38-3.42 (t, $J=8.2$, 2H), 3.75 (s, 3H), 3.95-3.98 (t, $J=7.2$, 2H), 4.21-4.22 (d, $J=6.4$, 2H), 4.41 (s, 3H), 5.37-5.42 (m, 2H), 5.79-5.89 (m, 1H); ^{13}C NMR δ 17.3, 29.9, 49.0, 52.4, 54.8, 63.1, 122.2, 128.1, 180.9.

1-ethyl-o-methylpyrrolinium bis(fluorosulfonyl)imide

([E(OMe)]PyrI-FSI) (6)

^1H NMR δ 1.28-1.32 (t, $J=7.4$, 2H), 2.37-2.45 (m, 2H), 3.20-3.24 (t, $J=8.0$, 2H), 3.58-3.64 (q, $J=7.4$, 2H), 3.93-3.96 (t, $J=7.6$, 2H), 4.31 (s, 3H); ^{13}C NMR δ 11.1, 16.9, 29.3, 41.5, 51.9, 62.7, 179.7.

1-propyl-o-methylpyrrolinium bis(fluorosulfonyl)imide

([P(OMe)]PyrI-FSI) (7)

^1H NMR δ 0.95-0.99 (t, $J=7.4$, 2H), 1.66-1.75 (m, 2H), 2.37-2.45 (m, 2H), 3.22-3.26 (t, $J=8.0$, 2H), 3.48-3.52 (t, $J=7.6$, 2H), 3.92-3.96 (t, $J=7.6$, 2H), 4.31 (s, 3H); ^{13}C NMR δ 11.1, 17.0, 19.5, 29.2, 48.1, 52.6, 62.7, 180.1.

1-allyl-o-methylpyrrolinium bis(fluorosulfonyl)imide

([A(OMe)]-PyrI-FSI) (8)

^1H NMR δ 2.38-2.46 (m, 2H), 3.25-3.29 (t, $J=8.0$, 2H), 3.90-3.94 (t, $J=7.6$, 2H), 4.15-4.17 (d, $J=6.8$, 2H), 4.34 (s, 3H), 5.39-5.46 (m, 2H), 5.73-5.83 (m, 1H); ^{13}C NMR δ 17.0, 29.5, 49.0, 52.3, 63.1, 123.0, 127.3, 180.2.

REFERENCES

1. Armand, M. and Tarascon, J. M. *Nature*, **2008**, *451*, 652–657
2. Whittingham, M. S. *Electrical Energy Storage and Intercalation Chemistry*. *Science* **1976**, *192*, 1126
3. (a) Moore, S.; Ehsani, M. *Advances in Electric Vehicle Technology*, SAE, SP-1417 1–8 (**1999**). (b) Whittingham, M. S. *Material challenges facing electrical energy storage*. *MRS Bull.* **2008**, *33*, 411–419. (c) Patil, A.; Patil, V.; Shin, W.D.; Choi, J. W.; Paik, D.S.; Yoon, J. *Issues and challenges facing rechargeable thin film lithium batteries*. *Mater. Res. Bull.* **2008**, *43*, 1913–1942. (d) Shukla, A.K.; Kumar, T.P. *Materials for the next generation lithium ion batteries*. *Curr. Sci.* **2008**, *94*, 314–331
4. (a) *Lithium Batteries Science and Technology* (Eds.: Nazri, G.-A.; Pistoia, G.), Kluwer Academic/Plenum, Boston, **2004**. (b) Whittingham, M. S. *Chem. Rev.* **2004**, *104*, 4271
5. (a) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, *5*, 1106–1120. (b) *Electrochemical Aspects of Ionic liquids*; Ohno, H., ed.; Wiley-Interscience: Hoboken, **2005**; pp 173–223. (c) Webber, A.; Blomgren, G. E. In *Advances in Lithium-Ion Batteries*; van schalkwijk, W. A.; Scrosati, B., Eds.; Kluwer Academic/Plenum Publishers: New York, **2002**; pp 185–232.
6. Xu, K. *Chem. Rev.* **2004**, *104*, 4303–3317.

7. The physical data were extracted and compiled from the following literature sources: (a) Jang, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, **1972**; Vol. 1. (b) Dudley, J. T.; Wilkinson, D. P.; Thomas, G.; LeVae, R.; Woo, S.; Blom, H.; Horvath, C.; Juzkow, M. W.; Denis, B.; Juric, P.; Aghakian, P.; Dahn, J. R. *J. Power Sources* **1991**, *35*, 59. (c) *Aldrich Handbook of Fine Chemicals and Laboratory Equipment*; Aldrich Chemical Co.: **2003-2004**. (d) Ue, M.; Ida, K.; Mori, S. *J. Electrochem. Soc.* **1994**, *141*, 2989. (e) Ding, M. S.; Xu, K.; Zhang, S.; Jow, T. R. *J. Electrochem. Soc.* **2001**, *148*, A299.
8. Lee, J. S. *J. Ind, Eng, chem.*, **2004**, *10*, 1086-1089.
9. Methlie, G. J. U.S. Patent 3,415,687, **1968**.
10. (a) Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336. (b) Tarascon, J. M.; Guyomard, D. *Solid State Ionics* **1994**, *69*, 293. (c) Ue, M. *J. Electrochem. Soc.* **1995**, *142*, 2577. (d) Walker, C. W.; Cox, J. D.; Salomon, M. J. *J. Electrochem. Soc.* **1996**, *143*, L80
11. (a) Walton, T. *Chem. Rev.* **1999**, *99*, 2071-2083. (b) Anthony, J. L.; Brennecke, J. F.; Holbrey, J. D.; Maginn, E. J; Mantz, R. A.; Rogers, R. D.; Trulove, P. C.; Visser, A. E.; Welton, T. In *Ionic Liquids in synthesis*; Wasserscheid, P.; Welton, T., Eds.; Wiley-VCH Verlag: Weinheim, **2003**; pp 41-126.
12. (a) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789. (b) Dyson, P. J. *Transition Met. Chem.* **2002**, *27*, 353-

358.

13. Bonhôte, P.; Dias, A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168-1178.
14. McEwen, A.B.; Chadha, R.; Blackley, T.; Koch, V.R. in: Delnick, F.M. Ingersoll, D. Andrie, X. Naoi, K.(Eds.) *Electrochemical Capacitor II, The Electrochemical Society Proceedings Series*, PV 96-25, Pennington, NJ, **1997**.
15. Wilkes, J. S.; Zaworotko, M J. *J. Chem. Soc., Chem. Commun.* **1992**, 965-967.
16. Sato, T. *Mater. Stage 4*, **2003**, 73.
17. Seddon, K.R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351
18. Min, G.; Yim, T.; Lee, H. Y.; Kim, H.-J.; Mun, J.; Kim, S.; Oh, S. M.; Kim, Y. G. *Bull. Korean Chem. Soc.* **2006**, *27*, 847-852.
19. Min, G.; Yim, T.; Lee, H. Y.; Kim, H.-J.; Mun, J.; Kim, S.; Oh, S. M.; Kim, Y. G. *Bull. Korean Chem. Soc.* **2007**, *28*, 1562-1566.
20. Yim, T.; Choi, C. Y.; Mun, J.; Oh, S. M.; Kim, Y. G. *Molecules* **2009**, *14*, 1840-1851.
21. Kwon, O. M.; Kim, H. T.; Yim, T.; Seo, S.; Oh, S. M.; Kim, Y. G. Master graduation thesis of Seoul National University, **2012**.
22. Sun, J.; MacFarlane, D. R.; Forsynth, M. *Electrochim. Acta* **2003**, *48*, 1707-1711.
23. (a) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221-227. (b)

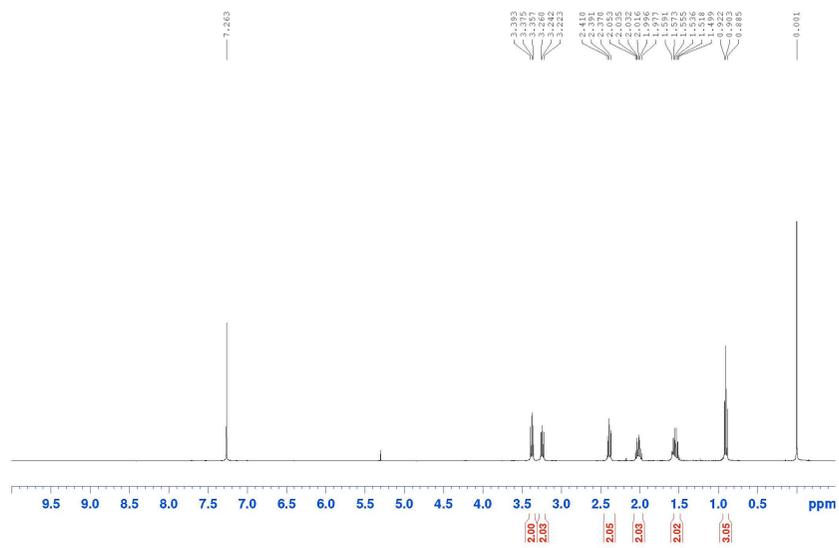
- Nishida, T.; Tashiro, Y.; Yamamoto, M. *J. Fluorine Chem.* **2003**, *120*, 135-141. (c) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133-2139.
24. Yim, T.; Lee, H. Y.; Kim, H. -J.; Mun, J.; Kim, S.; Oh, S. M.; Kim, Y. G. *Bull Korean Chem. Soc.* **2007**, *28*, 1567-1572.
25. Mun, J.; Kim, S.; Yim, T.; Ryu, J. H.; Kim, Y. G.; Oh, S. M. *J. Electrochem. Soc.* **2010**, *157*, A136-A141.

APPENDICES

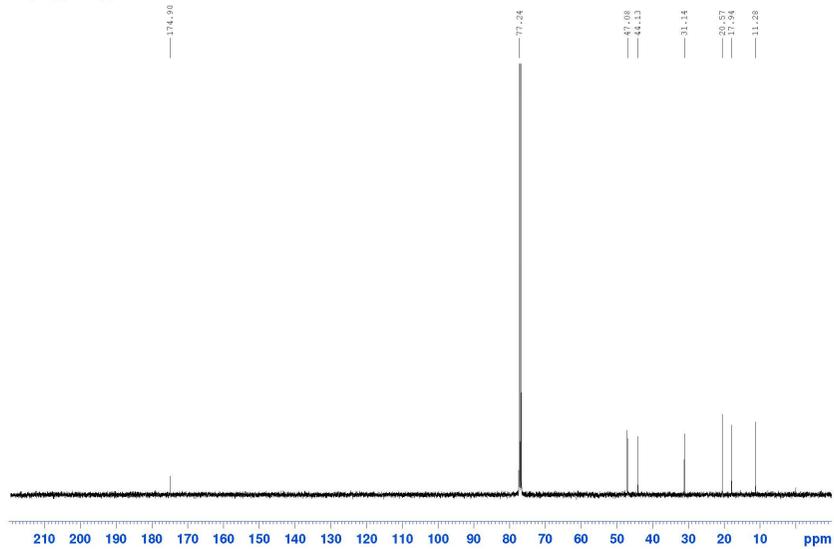
List of ^1H NMR and ^{13}C NMR Spectra of 1-Alkyl-Pyrrolidinone

1. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **1**.....60
2. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **1**.....60
3. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **2**.....61
4. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **2**.....61

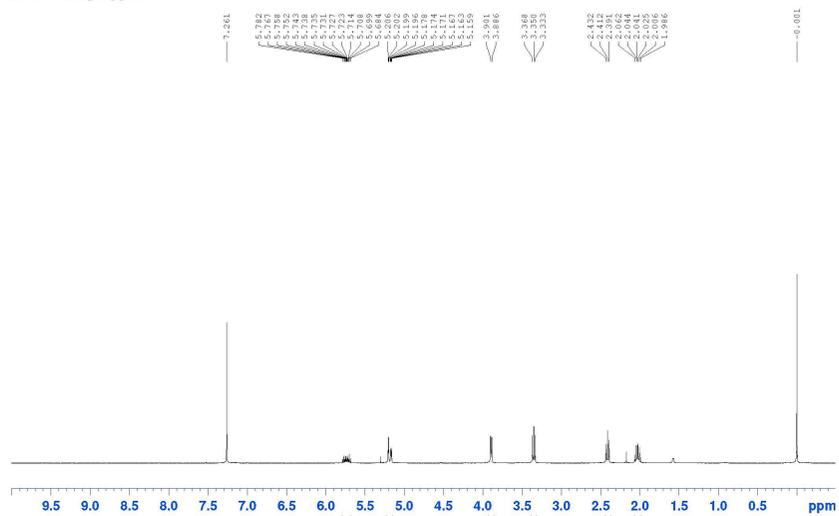
SW-283-Propyl-pyr1



1-propyl-2-pyrrolidone

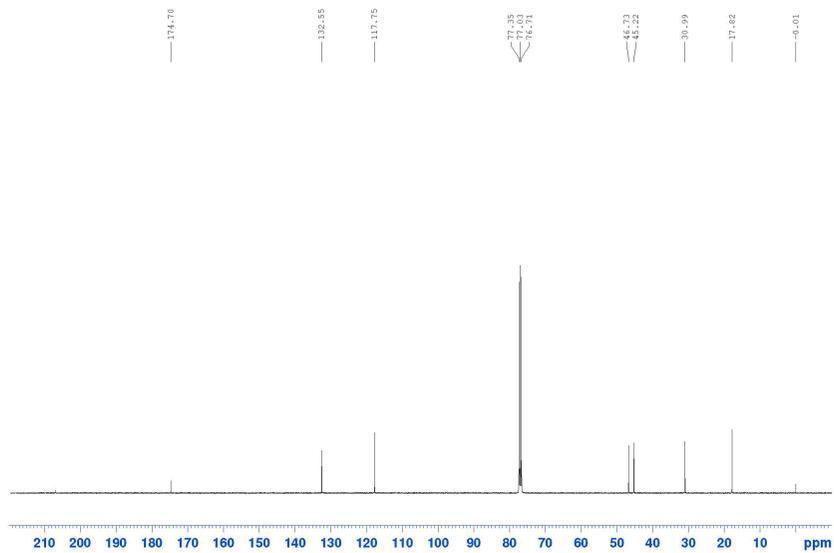


SW-295-Allyl-pyr1



3. 400 MHz ^1H NMR Spectrum (chloroform- d) of compound **2**

SW-286-13C

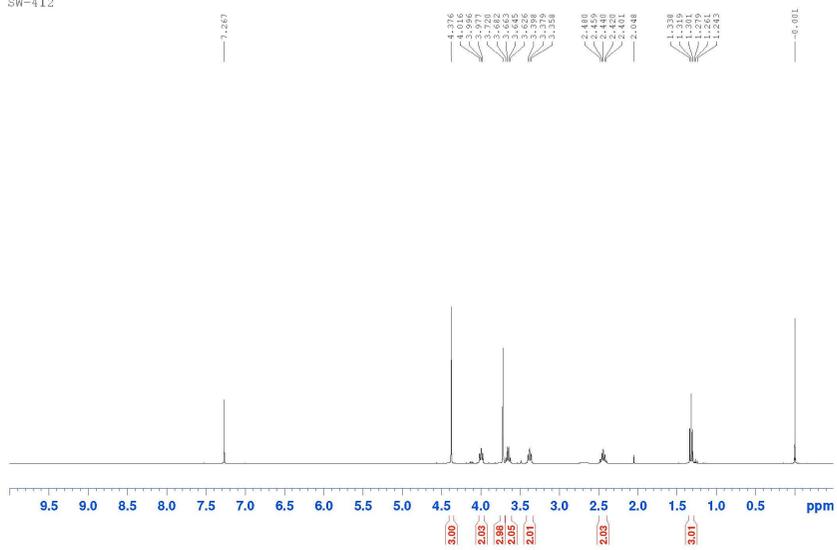


4. 100 MHz ^{13}C NMR Spectrum (chloroform- d) of compound **2**

List of ^1H NMR and ^{13}C NMR Spectra of Pyrrolinium Sulfate

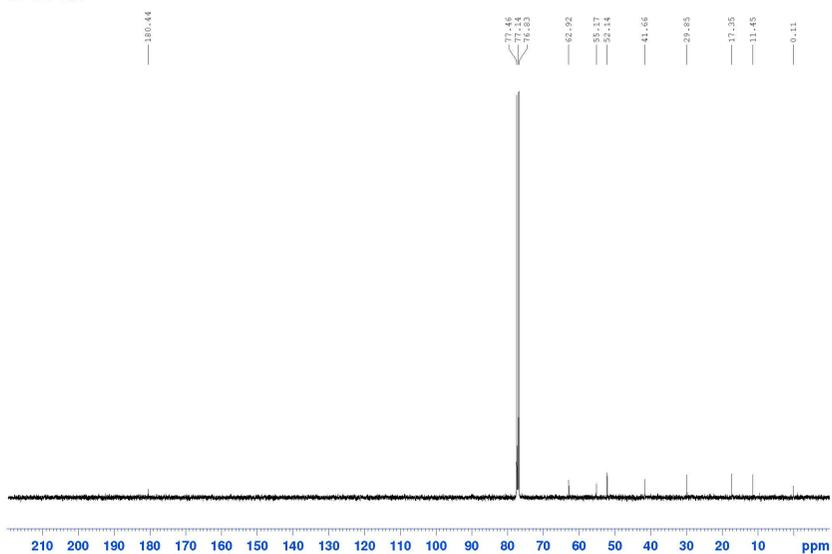
1. 400 MHz ^1H NMR Spectrum (chloroform- <i>d</i>) of compound	
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2. 100 MHz ^{13}C NMR Spectrum (chloroform- <i>d</i>) of compound	
3.....	63.
3. 400 MHz ^1H NMR Spectrum (chloroform- <i>d</i>) of compound	
4.....	64
4. 100 MHz ^{13}C NMR Spectrum (chloroform- <i>d</i>) of compound	
4.....	64
5. 400 MHz ^1H NMR Spectrum (chloroform- <i>d</i>) of compound	
5.....	65
6. 100 MHz ^{13}C NMR Spectrum (chloroform- <i>d</i>) of compound	
5.....	65

SW-412



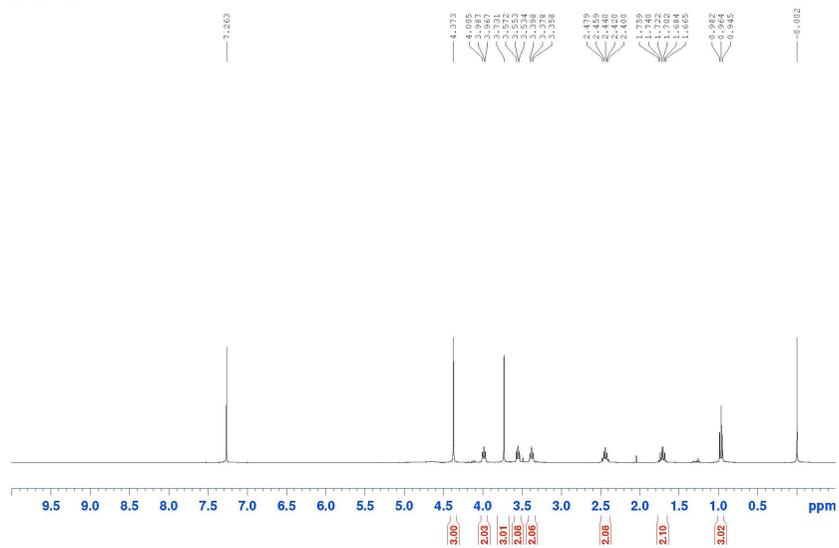
1. 400 MHz ^1H NMR Spectrum (chloroform- d) of compound **3**

SW-413-13C

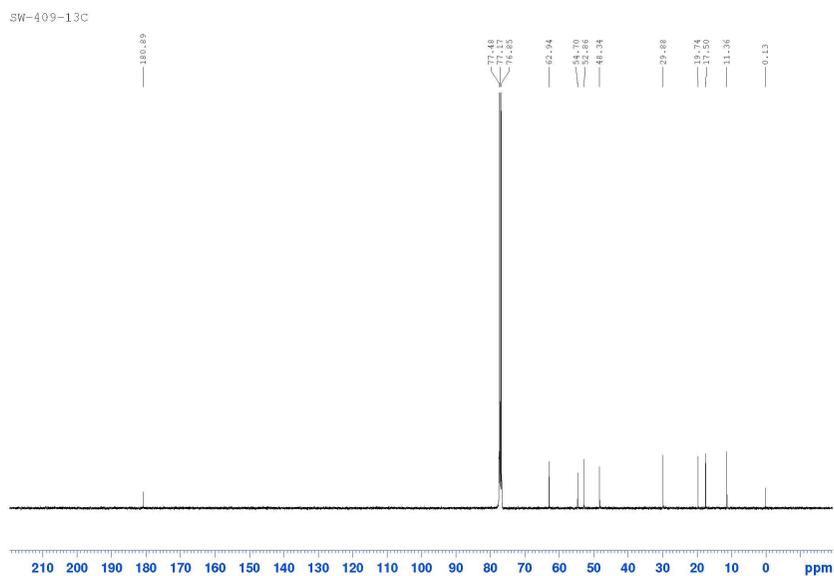


2. 100 MHz ^{13}C NMR Spectrum (chloroform- d) of compound **3**

SW-409-re



3. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **4**

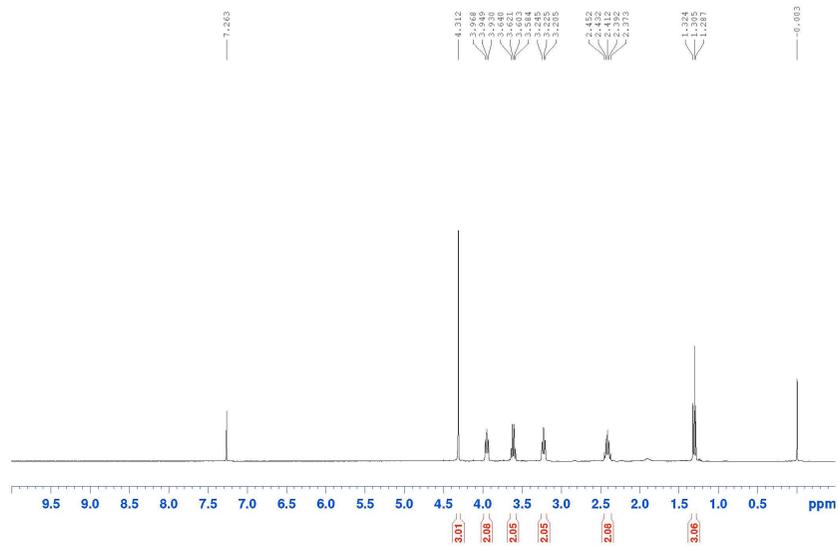


4. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **4**

List of ^1H NMR and ^{13}C NMR Spectra of Pyrrolinium FSI

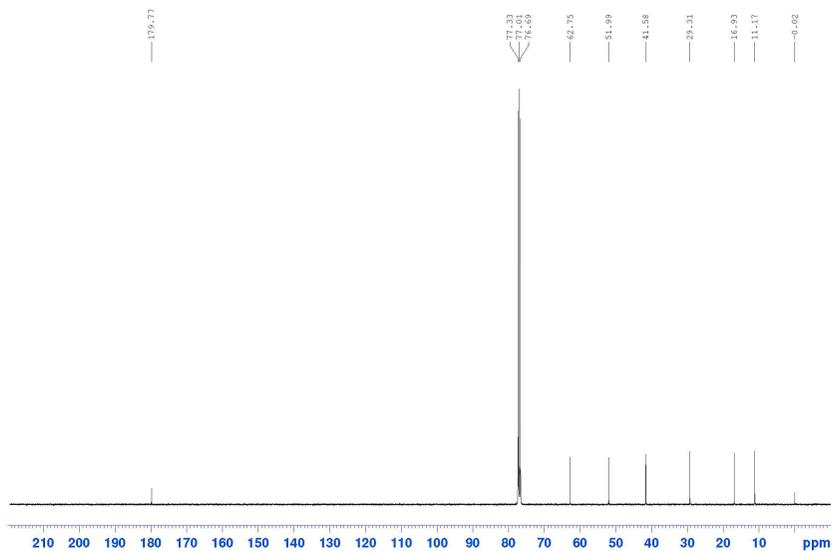
1. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **6**.....67
2. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **6**.....67
3. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **7**.....68
4. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **7**.....68
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6. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **8**.....69

SW-319-E (OMe) Pyr1-FSI



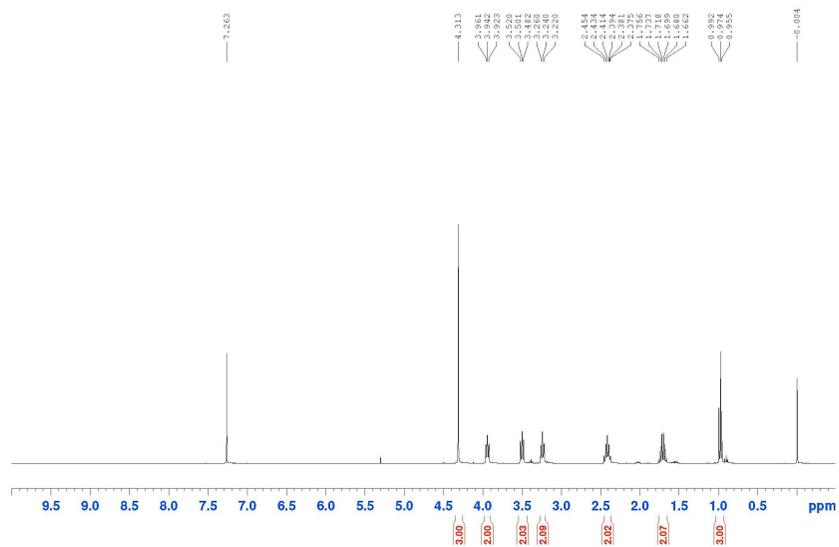
1. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **6**

SW-319-E (OMe) Pyr1-FSI-13C



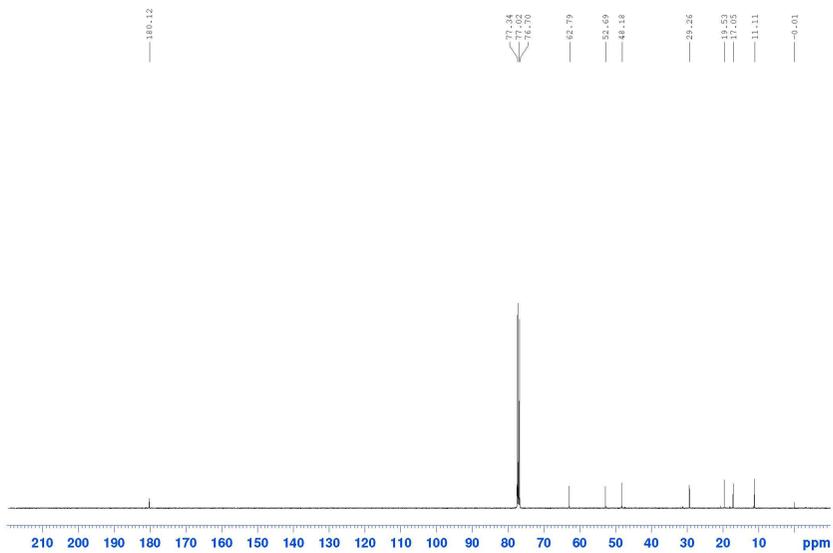
2. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **6**

SW-410



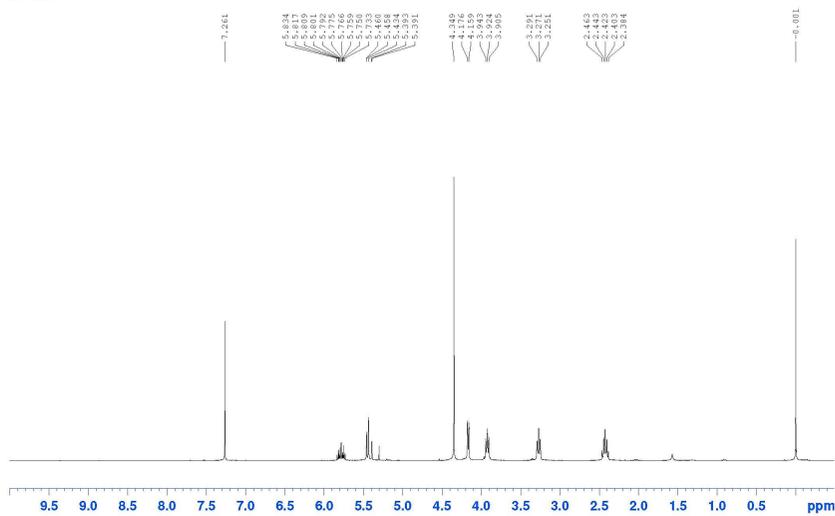
3. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **7**

SW-410-13C



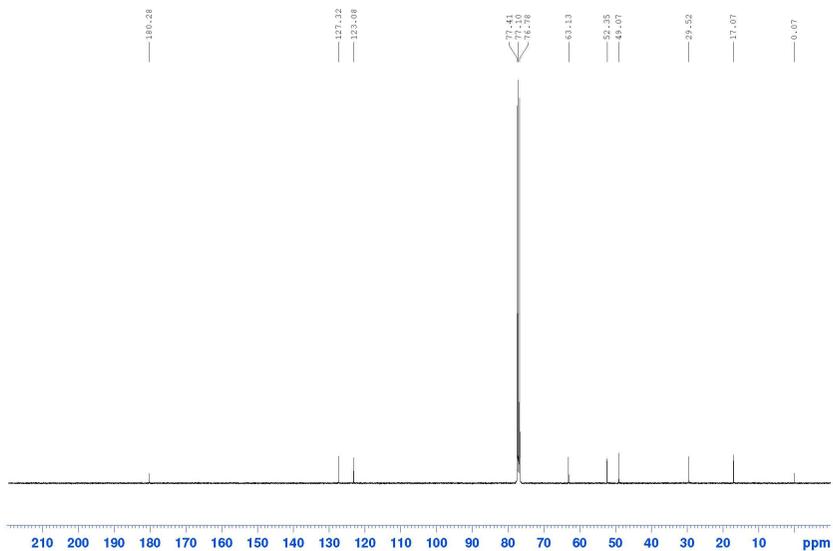
4. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **7**

SW-402



5. 400 MHz ^1H NMR Spectrum (chloroform-*d*) of compound **8**

SW-402-13C



6. 100 MHz ^{13}C NMR Spectrum (chloroform-*d*) of compound **8**

국문 초록

리튬이온 배터리는 현재 가장 많이 사용되고 있고, 늘어나는 휴대용 전기 기기의 수요로 가장 인기 있는 배터리가 되었다. 리튬이온 배터리는 카보네이트 (EC, EMC, DEC, DMC)와 리튬염 을 기본으로 한 전해질을 사용 하고 있는데, 이들은 전해질로서 요구되는 유전상수와 점도에 부합되지만 여전히 가연성, 휘발성으로부터 폭발을 야기 시킬 수 있는 안전 문제가 있다. 이와 같은 문제점을 해결 하기 위하여 이온성 액체가 하나의 대안으로 이야기 되고 있다.

이온성 액체란 이온결합을 통하여 상온에서도 액체상태로 존재하는 물질이다. 이온성 액체는 낮은 증기압, 넓은 전기화학 적 안정성, 넓은 액체범위, 높은 전도도 그리고 높은 열적 안정성과 같은 특성들에 의해 주목을 받고 있다. 특히 이온성 액체는 이가 가지는 불연성, 비휘발성과 같은 특별한 속성들 때문에 폭발과 같은 안전문제를 일으키는 카보네이트 계열의 전해질을 대체 할 수 있는 대체물질로서 높은 잠재력을 가지고 있다.

이온성 액체 전해질을 기반으로 한 리튬 배터리는 카보네이트 전해질을 사용한 것에 비해 안정 적이기는 하지만 높은 점도와 낮은 전도도 그리고 높은 단가와 같은 단점이 있고, 뿐만 아니라 좋은 SEI (solid electrolyte interphase)를 형성함에 있어서도 어려움이 있다. 우리는 카보네이트와 이온성 액

체 양면에서 모두 오는 단점들을 극복하고, 현재 상용화 되어 있지만 안전문제를 가지고 있는 카보네이트 전해질의 대체물질 확보를 위하여 카보네이트와 피롤리늄계 이온성 액체를 기반으로 한 혼합용액을 준비하였다.

우리는 이미다졸리움계, 피롤리디늄계, 피페리디늄계, 피롤리늄계 이온성 액체와 같은 양이온을 연구 개발하고 있다. 잘 알려진 이온성 액체중의 하나인 이미다졸리움계 이온성 액체는 좋은 전기화학적 성질을 보이지만, 이미다졸리움 양이온의 불안정한 C-2 위치의 수소로 인해 환원 불안정성이라는 단점을 가지고 있다. 이를 해결하기 위해 우리는 알콕시 치환기와 환형내 이중결합을 가지며 불안정한 위치의 수소를 가지지 않는 피롤리늄계의 이온성 액체를 합성하였다. 여러 가지 합성된 피로리늄계의 이온성 액체 중에서 하프셀 충-방전테스에서 가장 좋은 결과를 보인 [E(OMe)]Pyr1-FSI (6), [P(OMe)]Pyr1-FSI (7), 그리고 [A(OMe)]Pyr1-FSI (8)를 혼합 전해질의 후보로 선정 한 후, 카보네이트 (EC:EMC=3:7(v/v)+1M LiPF₆+vc(3%)) 용액과 각각의 피롤리늄계 이온성 액체를 다른 비율로(20, 40, 60, 80wt%) 섞어 혼합용액을 준비했다. 그 중에서 [E(OMe)]Pyr1-FSI (6)를 60% 함유하고 있는 혼합용액이 가장 높은 전도도 (13.76 mS cm⁻¹)를 보였고, LiFePO₄ 양극에서 100 사이클 동안 하프셀 충-방전테스트를 한 결과 가장 높은 방전 용량과 초기용량대비 99%의 높은 수준의 가역 용량이 유지되었다

(155 mAh g⁻¹). 또한, 우리는 난연성 확보를 위해 가스 토치를 이용한 버닝 테스트를 진행 하였다. 이 테스트를 통하여 이온성 액체 함유에 의한 감소된 가연성을 확인 하였고, 특히 60%이상의 이온성 액체를 함유한 모든 혼합용액은 불연성을 보였다.

이 연구에서는 피롤리늄기반의 이온성 액체와 카보네이트의 혼합용액을 사용 함으로써 카보네이트 전해질로부터 발생 되는 가연성문제를 개선 하고, 고가의 이온성 액체를 단독 사용하지 않음으로써 가격절감을 할 수 있으며, 높은 충-방전 속도와 100 사이클 이상의 횟수에서도 좀더 안정적이고 높은 효율을 가지는 새로운 혼합 전해질의 가능성을 보여줬다.

주요어 : 리튬이온전지, 이온성 액체, 유기 카보네이트 용액, 피롤리늄, 비스(플루오로설포닐)이미드, 전해질,

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