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ҚАЙЫРЫМДЫЛЫҚ ҚОРЫ
HALYK
CHARITY FOUNDATION

«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ
«ХАЛЫҚ» ЖҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ АКАДЕМИИ
НАУК РЕСПУБЛИКИ КАЗАХСТАН»
ЧФ «Халық»

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ЧФ «ХАЛЫҚ»

В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект Ozgeris powered by Halyk Fund – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz.

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

С уважением,
Благотворительный Фонд «Халык»

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A REVIEW ON ELECTROLYTIC SYSTEMS FOR LITHIUM-ION BATTERIES

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Abstract. *Introduction*. Lithium-ion batteries have been the dominant energy storage technology over the past decades, and demand is expected to grow tenfold over the next decade. To meet the future demand for such batteries, alternative technologies will be required to provide extended cell life and increase the overall capacity of these batteries. The development of electrolytic systems with the proper structure and composition will increase the development of lithium-ion batteries. It is imperative to consider that electrolytic systems include components, such as additives, solvents, salts, and there are two types: liquid and solid. They have a very important role in creating electrolytic systems capable of forming passivation layers. Currently, the most urgent problem of lithium power sources is safety. The main way to solve the safety problem is to replace the liquid organic electrolyte with a solid electrolyte, as well as doping liquid electrolytes with various additives. *The purpose* of this review is to analyze publications on electrolytes and their various additives used in lithium-ion batteries. *Objects of research*: liquid and solid electrolytes for lithium power sources. *Conclusion*: research in the field of electrolytic systems for lithium-ion batteries is promising and relevant. Modern studies show that doping of both liquid and solid electrolytes with additives, the use of new salts and solvents make it possible to improve the characteristics of LIB.

Keywords: lithium-ion batteries, solid-state batteries, solid electrolytes, interface, NASICON, Garnet, Perovskite type solid-state electrolytes, LLZO

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ЛИТИЙ-ИОНДЫ АККУМУЛЯТОРЛАРҒА АРНАЛҒАН ЭЛЕКТРОЛИТТІК ЖҮЙЕЛЕРГЕ ШОЛУ

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Аннотация. Кіріспе. Литий-ионды аккумуляторлар соңғы онжылдықта энергия сақтаудың басым технологиясы болып табылады және алдағы уақытта осы құрылғыларға сұраныс он есе өседі деп күтілуде. Литий тоқ көздеріне болашақ сұранысты қанағаттандыру үшін ұяшықтардың қызмет ету мерзімін ұзартатын және олардың жалпы сыйымдылығын арттыратын балама технологиялар қажет болады. Литий-ионды батареялардың табысты дамуы электролиттік жүйелердің дамуына тікелей байланысты болып келеді, олардың құрылымы мен құрамы таңдалған электродтық материалдарға қатысты олардың тұрақтылығына байланысты айтарлықтай өзгеруі мүмкін. Литий-ионды аккумуляторларда электролит заряд-разряд процестері кезінде электродтар арасында литий иондарын тасымалдау үшін орта ретінде қызмет етеді. Бұл себеппен электролиттер осы құрылғылардың жұмысы үшін өте маңызды болып табылады. Электролиттік жүйелерге қоспалар, еріткіштер, тұздар сияқты компоненттер кіретінін ескеру қажет, және өз кезегінде электролиттер екі түрлі болып келеді: сұйық және қатты. Электролиттердің екі түрінің де артықшылықтары мен кемшіліктері бар. Олар алюминий ток жинағыштарында пассивтеуші қабаттарды қалыптастыруға қабілетті электролиттік жүйелерді құруда өте маңызды рөл атқарады. Бұл қабат жанама реакциялардың пайда болуына және осылайша электродтың деградациясына жол бермейді. Қазіргі уақытта литий қуат көздеріне қатысты ең өзекті мәселе қауіпсіздік болып табылады. Қауіпсіздік мәселесін шешудің негізгі жолы сұйық органикалық электролиттерді қатты электролитке ауыстыру, сонымен қатар сұйық электролиттерді әртүрлі қоспалармен легирлеу болып табылады. Бұл мақаланың мақсаты негізгі сұйық және қатты электролиттердің маңызды түрлеріне, сондай-ақ олардың модификацияларына жан-жақты шолу жасау болып табылады. Зерттеу объектілері: литий-ионды аккумуляторларға арналған сұйық және қатты электролиттік жүйелер. Қорытынды: бүгінгі таңда литий-ионды аккумуляторларға арналған электролиттік жүйелер саласындағы зерттеулер маңызды және өзекті болып табылады. Заманауи зерттеулер сұйық және қатты электролиттердң жаңа түрлерін зерттеу, олардың модификациясы, сондай-ақ, жаңа тұздар мен еріткіштерді пайдалану осы құрылғылардың электрохимиялық көрстекіштеріне тікелей әсер ететінін көрсетеді.

Түйін сөздер: литий-ионды аккумуляторлар, қатты электролиттер, NASIKON қатты электролиттер, гранат типті электролиттер, перовскит, LLZO

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ОБЗОР НА ЭЛЕКТРОЛИТНЫЕ СИСТЕМЫ ДЛЯ ЛИТИЙ-ИОННЫХ АККУМУЛЯТОРОВ

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Аннотация. Литий-ионные аккумуляторы являются доминирующей технологией хранения энергии в течение последних десятилетий, и ожидается, что спрос на них вырастет в десять раз в течение следующего десятилетия. С целью удовлетворения будущего спроса на данный тип накопителей энергии потребуются альтернативные технологии, обеспечивающие продление срока службы элементов и увеличение их общей емкости. Успешное развитие литий-ионных аккумуляторов зависит от разработки электролитических систем, структура и состав которых могут существенно различаться в зависимости от их стабильности по отношению к выбранным электродным материалам. В литий-ионных аккумуляторах электролит действует как среда для переноса ионов лития между электродами во время процессов заряда-разряда. По этой причине этот компонент необходим для работы этих устройств. Необходимо обязательно учитывать, что электролитические системы включают такие компоненты, как добавки, растворители, соли, а так же, электролиты бывают двух видов: жидкие и твердые. Оба типа электролитов имеют свои преимущества и недостатки. Они играют очень важную роль в создании электролитических систем, способных образовывать пассивирующие слои на алюминиевых токосъемниках. Этот слой препятствует возникновению побочных реакций, и таким образом, деградации электрода. В настоящее время наиболее актуальной проблемой литиевых источников питания является безопасность. Основным путем решения проблемы безопасности является замена жидкого органического электролита твердым электролитом, а также легирование жидких электролитов различными добавками. *Цель* данной статьи – это предоставить всесторонний обзор некоторых основных, а также новых жидких и твердых электролитов и их модификаций. *Объекты исследования:* жидкие и твердые электролитические системы для литиевых источников питания. *Заключение*: на сегодняшний день исследования в области электролитических систем для литий-ионных аккумуляторов перспективны и актуальны. Современные исследования показывают, что легирование как жидких, так и твердых электролитов добавками, использование новых солей и растворителей позволяют улучшить характеристики литий-ионных аккумуляторов.

Ключевые слова: литий-ионные аккумуляторы, твердотельные электролиты, твердотельные электролиты NASIKON, перовскит, ЛЛЗО

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Introduction

With the ever-increasing variety of devices from portable to powerful electric vehicles, the demand for safe and long-lasting energy storage systems is increasing. The most popular and frequently used storage systems are Lithium-ion batteries (LIB). They are playing an progressively critical part in our daily lives. Batteries not only power our portable devices (such as phones, laptops and cameras), but also power vehicles (such as electric cars and hybrid EVs, and even serve as temporary storage systems for excess energy supplied by renewable energy sources such as solar, wind, nuclear and hydroelectric power. However, as the use of Li-ion batteries increases each year, the demands on their properties, and their power density, are increasing. Obviously, improvements in these characteristics depend on technical advances in the main battery components: positive/negative electrodes and electrolytes.

The electrolyte acts as an important "connecting bridge" in LIBs for the transport of ions between two opposite electrodes during cycling processes. Electrolytes for lithium chemical power sources should have the following features (Duan, 2020):

1. Favorable layered structure for rapid transfer of lithium ions.
2. High electrical conductivity (10^{-3} to 10^{-7} S*cm^{-1}) and electrochemical stability.
3. Low melting point (from -50C) and high boiling point (up to +70C), to provide a wide operating temperature.
4. The low pressure of emitted vapors is necessary to reduce the fire hazard.

With insufficient reversibility of electrodes and electrical conductivity of lithium electrolytes (regardless of their nature), there are many factors limiting the elaboration of chemical current sources with a lithium anode. The reason why this problem is important is that the value of the current source's internal resistance directly affects its main performance characteristics, such as power and charge current.

There are two main types of electrolytes, namely liquid-phase and solid state electrolytes. Liquid electrolytes are used for a long time in commercial chemical energy storages, as they have key properties, such as, ionic conductivity approximately 10^{-3}-10^{-2} cm^{-1} and good electrode interface. Nevertheless, traditional electrolytes have drawbacks. They are the risk of electrolyte leakage, which leads to burning, another problem is increase of dendrites, caused by the uneven charging current of porous separators, especially chemical power sources with a metallic lithium electrode.

This problem also occurs with solid electrolytes. In 2023, was proposed a physical model of lithium coating and dendritic formation in LIB (Sahu, 2023). A side effect of fast charging is the formation of lithium metal, which leads to degradation. Model made of metallic lithium sharpened in the pores of the interfacial phase of a solid electrolyte. The model was validated by experimental studies and demonstrated the trends being more prevalent at increased C-rate and/or decreased temperature. To improve the performance of lithium ion batteries, electrolytes play a significant role in development of lithium-ion batteries, as well as researches in this area are ongoing at the moment, and this review is devoted to electrolytes used in modern lithium-ion batteries.

Electrolytes solutions for lithium-ion batteries

Due to recent achievements in solid-state batteries many safety problems with LIBs were solved, most LIB applications require capabilities. Thus, it rather difficult to eliminate LEs for commercial applications because they are still more effective at transporting lithium-ion than their solid-state analogues. There are many factors to consider when selecting the electrolyte composition. First, it is imperative to consider the environmental impact reported in a study by Flamme et al. which studied the relative environmental impact of conventional organic solvents (Flamme, 2017). Requirements for the electrolyte are ionic conductivity and chemical inertness at the electrode/

electrolyte interface. Another critical factor is the electrochemical stability window in which the electrolyte must be stable to a wide range of battery operation (0–5 V) (Flamme, 2017). Solution of lithium salt, such as $LiPF_6$, LiDFOB, $LiClO_4$ dissolved in a mixture of solvents, such as vinylene, carbonate, ethylene carbonate, and e.t.c and additives is the electrolyte used in the LIB. Layered graphite anodes are widely used anodes in lithium batteries. In order to introduce/lead lithium ions between multiple graphite layers, a passive layer called the interfacial solid electrolyte (SEI) is required. In fact, if there is no SEI on the graphite surface, peeling processes occur, leading to degradation of the material itself and then the battery. The SEI layer consists mainly of electrolytes, which means that it has a significant impact on the charging characteristics of the electrolyte. In addition, the secondary reactions resulting from rapid charging can also decrease the stability of the electrolyte. Even worse, the generation of internal heat or growth of lithium dendrites will degrade the conductivity of the electrolyte, causing an exothermic reaction. In some cases, the high concentration of lithium ions produced at high current densities can limit battery capacity. Therefore, the use of a safe electrolyte is of high importance.

Solvents. Traditionally, liquid organic solvents are used in electrolytes for LIBs. Solvents must satisfy following criteria: to have high chemical, thermal and electrochemical stability towards to two electrodes in the working range of potentials; the ability to dissolve electrolytic salts and non-electrolytes; high conductivity in a wide temperature range. High dielectric permittivity provides lithium salt dissociation, while low rates provide ionic pair formation. Solvents with a high dielectric constant dissolve a large amount of electrolyte salts.

Low viscosity advances ion mobility. This negates the previous requirement since high-dielectric permittivity solvents are too as a high-viscosity solvents. This contrarily influences the transport of ions inside the electrolyte, specifically its ionic conductivity. As a rule, well-balanced mixtures with high dielectric constant and low viscosity solvent are preferred for such applications.

Last, the solvent must provide suitable interfacial properties, i.e., promote the formation of a stable, electron-insulating but highly ionic conductive SEI at both electrodes, especially at the anode.

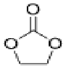
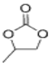
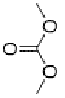
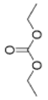
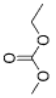
The mixture of cyclic carbonates and linear carbonates are usually used as electrolyte solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC). Since all solvents have different electrochemical and chemical properties, for optimal performance of LIB, their mixture is used, they compensate each other. Solvents with low viscosity promote suitable ionic conductivity by reducing the general viscosity of the mixture. Since EC and PC solvents have a high viscosity, the electrolyte based on them (1:1) demonstrates low conductivity at any temperature. The lower the temperature, the conductivity decreases due to thickening of the binary solvent. Electrolyte with composition EC-DMC (1:1) shows better conductivity.

Many LIBs use the fluorinated solvent N,N-dimethyltrifluoroacetamide (DTA) (Moller, 2001). Due to its high boiling temperature, flash point and low viscosity, DTA is able to replace low viscosity solvents such as dimethyl carbonate, diethyl carbonate. Due to its film-forming properties, it is possible to use DTA with PC in an amount of 10 %, as these solvents have a freezing point below -40°C, their mixture is used as a low temperature electrolyte.

The massive demand for lithium-ion batteries is drawing particular attention to their safety, the main reason is the flammable component - liquid electrolyte. In this paper (Gebert, 2023) represented promising non-flammable liquid electrolytes - based on phosphate derivatives and fluorinated hydrocarbons - are chosen from the literature and tested in industrial high-voltage connections under conditions. The studies were carried out on $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$|graphite cells and on inert electrodes, as a result, electrochemical determinations of electrolytes were obtained. Each electrolyte was evaluated using long-term cycling and rate testing experiments, and cell resistance was monitored during aging. It has been determined that electrolytes containing phosphate and phosphonate based solvents generally perform very poorly compared to non-phosphorus fluorinated solvents; the latter resulted in an average of doubling capacity retention after 500 cycles of the former. A strong correlation was observed between long-term cycling performance, speed properties and cell resistance.

Researchers proved that many non-flammable liquid electrolytes have improved speed and cyclic stability compared to conventional flammable liquid electrolytes.

Table 1 - Some properties of electrolyte solvents for LIBs

Properties	EC	PC	DMC	DEC	EMC
Structure					
Chemical formula	$(CH_2O)_2CO$	$CH_3C_2H_3O_2CO$	$OC(OCH_3)_2$	$(C_2H_5O)_2CO$	$C_4H_8O_3$
Dielectric constant	high	high	low	low	low
Viscosity	high	high	low	low	low
Contribution to SEI	high	low	low	low	low
Anodic stability	high	high	medium	medium	medium

According to table 1, it is shown that EC is suitable compound for LIB, as well as it is able to form film.

Salts. Inorganic lithium salts, such as $LiPF_6$, $LiAsPF_6$, $LiBF_4$, $LiClO_4$, $LiNO_3$, Li_2SO_4 and LiOH are the most used lithium salts in electrolytes for LIB.

During the development of LIB, various salts were used until a compromise was found in the form of $LiPF_6$. There are many kinds of organic salts to choose from. However, only a few have been tested for LIB applications. The most traditional among them is $LiPF_6$, but the most successful one is LiTFSI. Viscosity and conductivity of salts LiTFSI- and $LiPF_6$- in EC/DMC (1/1, v/v) were compared at different temperatures from 20°C to 80°C. The authors used Waldenrul's method. The authors showed that LiTFSI 1 M in EC/DMC is more ionic than $LiPF_6$ 1 M in the identical binary solvent. Based on physicochemical and electrochemical measurements, data were obtained that the specific capacity of activated carbon improved with increasing ionicity of the LiTFSI salt in binary EC/DMC. LiTFSI can also be used in aqueous solutions, which makes it even more promising (Xiao, 2022).

Any salt used in the LIB should promote the formation of a passivating surface film that is inert to the current collector and thermally stable.

Additives. Existing electrolyte systems for lithium-ion batteries have disadvantages, such as non-reversible capacity, thermal limitations, safety concerns. One method of minimizing these problems is to incorporate small quantities of other components into the system to modify the certain properties of the electrolyte while maintaining its bulk properties. Many of the problems associated with surface phenomena can be solved by the applying of additives in electrolytes. This method is the most economical and effective. Additives in lithium-ion systems improve not only the properties of the interfacial layer on the electrode surface, but also safety and the ionic conductivity. Additives ought to diminish irreversible capacitance and outgassing, make strides the thermal stability of the lithium salts against organic electrolyte solvents, and protect the positive electrode material from dissolution and overcharge. Thus, improving battery performance by stabilizing the SEI is the main focus of research devoted to additives. These additives include unsaturated organic compounds (double or triple bonds, cyclic structures, phenyl, etc.), organic phosphorus/nitrides/fluoride/sulfide, new type lithium salts, etc. (Figure 1).

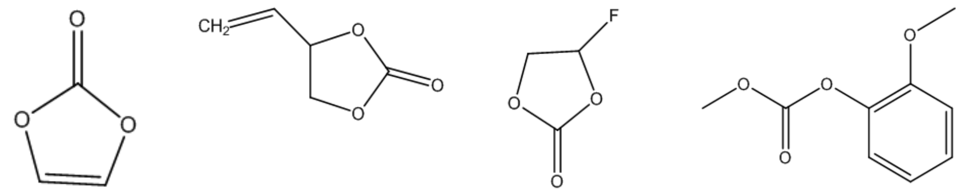
Several types of electrolyte additives, nitrogen-containing, fluorine-containing, phosphorus-containing additives are presented in this review.

Phosphorus-containing organic compounds are widely known and find practical application as flammability-suppressing materials of liquid electrolytes. The first additives investigated are trimethylphosphate and triethylphosphate with high phosphorus content. Their instability to the low reducing potential on the anode surface was solved by replacing the alkyl groups with aryl (phenyl) groups. This approach improved the reductive and thermal instability. Fluorine-containing additives are also attractive due to property to form strong and protective layers at the electrode boundary.

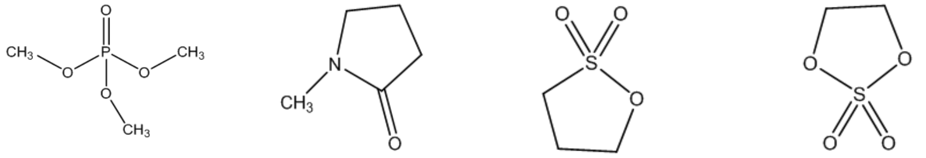
Nitrogen-containing additives mainly include nitriles which have a 7 V (Li^+ /Li) electrochemical stability window. This type of additives can suppress the risk of fire due to the strong interaction between the functional group of the nitrile (-CN) and transition metal ions of the cathode material. Nitrogen-containing heterocyclic compounds can also be applied as additives. They can prevent overcharge. Heterocyclic compounds polymerize at high voltages and form an insulating polymer layer sufficient for protection.

Fluoroethylene carbonate (FEC) has been used as an additive to the electrolyte in a large number of studies. Like other additives, fluoride-containing additives are capable of forming a negative electrode film and also inhibit side reactions.

When fluorine-containing additives are used in the electrolyte, FEC molecules can bond another fluorine-containing chemical bond to the base of the EC molecules, and quantum-chemical calculations have shown that FEC in the electrolyte is reduced so much that a SEI layer with good characteristics can be formed on the negative electrode surface. Not only FEC, but also other fluorine-containing 1,2-divofluoroethylene carbonate (DiFEC) is involved in film formation at the negative electrode surface.



Vinylene carbonate | Vinylene ethylene carbonate | Fluoroethylene carbonate | Carbonic acid (2-methoxy-phenyl ester)-methyl ester



Trimethyl phosphate | 1-methyl 2-pyrrolidinone | 1,3-Propanesultone | 1,3,2-Dioxathiolane 2,2-dioxide

Figure 1 – Chemical composition of some electrolyte additives

As an additive in the electrolyte Bis(di-tert-butyl)-4-dimethylaminophenylphosphine (Bis-4TMPA) is used. In work (Zhuang, 2023) Bis-4TMPA was added to improve the performance of cathode material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The phosphine group in this molecule can react with the oxygen species released from the cathode surface, which protects electrolytes from oxidative decomposition.

For advanced lithium-ion bateries, pyrazole-based additives are used, namely 1-methyl-3,5-bis(trifluoromethyl)-1H-pyrazole (MBTFMP). It was first synthesized and characterized in work (Aspern, 2020). To compare the characteristics, the functional additive 3,5-bis(trifluoromethyl)-1H-pyrazole (BTFMP) was chosen and various studies were carried out, such as constant current cycling, cyclic voltammetry, etc. As a result of the research, the reductive and oxidative abilities of MBTFMP and BTFMP functional molecules and reactivity with a surface cathode were revealed. Both the reduction and oxidation of BTFMP molecules were accompanied by intermolecular H-transfer, which narrowed the electrochemical stability window of the electrolyte containing BTFMP, compared with the functional additive MBTFMP. Functional groups in molecule of additives can significantly affect the important physicochemical properties of LIB.

Solid State Electrolytes

Key useful properties of SSEs utilized in solid state lithium batteries (SSLBs) ought to incorporate:

- high overall bulk and grain boundary conductivities of Li^+ ions in a wide range of temperature about (10^{-4} $S \cdot cm^{-1}$),
- a wide electrochemical window for bonding with lithium metal anode and high voltage cathode,
- chemically and mechanically consistent anode and cathode interfaces,
- chemically steady within the environment,
- low interfacial resistance to protection electrodes,
- Low cost.

Inorganic solid electrolytes are more suitable for high temperatures or aggressive environments, and a wide range of inorganic electrolytes have been developed, due to their amorphous and crystalline structures.

Although solid state electrolytes have numerous appealing properties, particularly from a safety point of view, a customized SSE with comprehensive functions has not yet been developed. Various solid electrolytes face various problems that ruin their practical application. First, most solid electrolytes, counting those based on oxides and solid polymer electrolytes (SPEs), have moderately low ionic conductivity compared to their liquid analog at room temperature. For example, a polyethylene oxide-based solid polymer electrolyte (eg, a complex of polyethylene oxide with a lithium salt) has an conductivity of about 10^{-7} - 10^{-5} S/cm at 25°C. Solid electrolytes such as NASICON (e.g. $Li_{1x}Al_xTi2\ x(PO_4)_3$ (LATP)) and $Li_{1x}Al_xGe_2\ x(PO_4)_3$ (LAGP)), lithium-filled garnet material ($Li_7La_3Zr2O_{12}$, (LLZO)) and perovskite ($Li_3xLa_{(2/3)}\ xTiO_3$, (LLTO) (Kwon, 2017) have an ionic conductivity of about 10^{-5} -10^{-3} S/cm, electrodes also limits their practical application.

The popular oxide-based SSEs for SSLIB are: NASICON, perovskite, and garnet-type electrolytes, owing to their high ionic conductivity and stability. Classified according to different structures, solid electrolytes based on oxides have various ionic conductivity and chemical properties and occur with contacts when exposed to LIB. Typical examples are shown below in this review.

NASICON – type electrolytes. The name of solid state electrolyte NASICON was originally given to the sodium superionic conductor with formula $NaM_2(PO_4)_3$ (where, M might be Ge, Ti, Zr Crystalline NASICON framework (symmetry group R-3c, a = 8.804 Å, c = 22.758 Å), composed of BO_4 tetrahedra connected at vertices with AO_6-octahedra. The basis of the structure is three-dimensional macromolecular structure of discrete AO_6 – octahedrons and single BO_4-tetrahedra. In combining polyhedra of different types into a single structural motif involved all oxygen atoms, i.e. each octahedra is connected to six tetrahedra, and each tetrahedron has four octahedra. M^+ ions occupy 2 positions: the M(1) ions are located in distorted MO_6 (M = Ge, Ti, Zr) octahedra, and the M(2) ions are in framework voids formed by 10 oxygen atoms. Na^+ ions, which in interstices are transported around the axis (Kumar, 2009). The NASICON solid electrolyte becomes a conductor of Li^+ ions without changes in the NASICON crystal structure when Na^+ ions are replaced by Li^+ ions.

To date, are $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) and $Li_{1+x}Al_xGe_{2-\ x}(PO_4)_3$ (LAGP) are the most popular NASICON solid electrolytes, they are formed by partial substitution of Al with Ge in $LiGe_2(PO_4)_3$ or for Ti in $LiTi_2(PO_4)_3$. 10^{-3}–10^{-2} S/cm is considered the highest ionic conductivity of NASICON solid electrolyte at room temperature (Kumar, 2009), which is not inferior to liquid electrolytes. However, the harsh nature of the NASICON electrolyte makes it difficult to achieve good contact with the electrodes. Another problem is that Ti-containing LATP can attack lithium metal and polysulfides, which greatly limits its practical application.

The garnet-type electrolytes. The garnet-type solid state electrolyte has the general chemical formula $A_3B_2(XO_4)_3$, (A = Ca, Mg, Y, La, etc. B = Al, Fe, Ga, Ge, Mn, Ni, or

V; X = Si, Ge, Al). A, B, and X may have 8, 6, 4 oxygen-coordinated cation sites in the crystal face-central-cubic structure. Studies of this type of solid electrolyte include studies of Li_3-type $Li_3Ln_3Te_2O_{12}$ (where Ln might be Y, Nd, Sm-Lu), Li_5-type $Li_5La_3M_2O_{12}$ (where M might be Nb, Ta), Li_6-type $Li_6ALa_2M_2O_{12}$ (A = Mg, Ca, Sr, Ba) and Li_7-type $Li_7La_3X_2O_{12}$ (X = Zr, Sn, Ta) (Kwon, 2017). The first three garnet-type electrolytes have a relatively low ionic conductivity at room temperature (~10^5 S/cm), while $Li_7La_3Zr_2O_{12}$ (LLZO) has a relatively high ionic conductivity (10^{-4}–10^{-3} S/cm), especially high conductivity at the grain boundary. In the LLZO structure, ZrO_6 octahedra and LaO_8 dodecahedra are combined into a structure, while Li^+ ions and Li vacancies are located in the invasive position of tetrahedral and octahedral regions. The Li^+ ions are in the tetrahedral position 24d, and the other is in the octahedral position 96d. For this reason, modern studies are mainly devoted to LLZO and its derivatives with various elemental additives (Rettenwander, 2016). Garnet-type SESs have a wide electrochemical window and they are chemically resistant to lithium metal compared to NASICON oxide-based SSEs such as LATP ($Li_{1.7}Al_{0.3}Ti_{1.7}(PO_4)_3$ and LAGP ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$). For example, LAGP has an ionic conductivity comparable to LLZO SEs but exhibits mechanical/thermal failures as a result of chemical reaction with lithium metal. As a result, garnet LLZO SEs were found to be the most suitable SEs for SSLIBs, as a solid state cell with LLZO can use Li metal as an anode. Thus, they have achieved high energy densities.

The LLZO exists as two polymorphic phases: a cubic phase (c-LLZO) and a tetragonal phase (t-LLZO). At room temperature, the cubic phase has 100 times higher ionic conductivity (~ 10^{-4} S/cm) than the tetrahedral phase (~ 10^{-6} S/cm), this is explained by the uniform movement of Li^+ ions in the x, y and z, while t-LLZO has low conductivity, since Li^+ ions move only in the x and y directions (Chen, 2018).

Also, problems such as poor wettability of lithium and poor ionic conductivity can be caused by the formation of Li_2CO_3 on the surface of LLZO, due to the exchange of Li^+/H^+ ions under the influence of moisture. Although LLZO has high ionic conductivity and is resistant to lithium metal anodes, the problem of lithium dendrites (Porz, 2017) and the problem of interfacial mismatch due to hard properties remain difficult for garnet-pod solid state batteries.

The ionic conductivity of garnet-type SEs can be increased in several ways: by doping and by increasing the density of the granules. The increase in ionic conductivity in LLZO SEs is to increase the grain density through the use of sintering agents, they reduce the sintering temperature and the number of grain boundaries. For example, Shin et al. In order to increase the conductivity of LLZOs, LI_3BO_3 (LBO) was considered as a sintering agent at a lower temperature than the typical sintering temperature of LLZO SEs, 1100-1250°C. When LLZO SEs are sintered below the sintering temperature, they acquire a high porosity or tetrahedral phase, as well as low grain density, and low Li ionic conductivity. However, when LLZO is sintered with LBO above the melting temperature of LBO (~850°C) but below the sintering temperature of LLZO, liquid-phase sintering occurs and therefore LLZO can achieve high grain density, resulting in high ionic conductivity. Low temperature sintering of LLZO helps suppress Li evaporation and reduce chemical reactivity between SEs and active materials in composite electrodes.

Perovskite-type electrolytes. Solid electrolytes in the form of perovskite-type with the structure ABO_3 (A = Ca, Sr, La; B = Al, Ti) were first described as a conductor of oxygen ions (Shin, 2016).

Naguma et al. (Naguma, 1993) were the first to present perovskite-type solid electrolytes $Li_{3x}La_{2/3-x}TiO_3$ (LLTO), which showed a bulk ionic conductivity of 1×10^{-3} S/cm and a total ionic conductivity above 2×10^{-5} S/cm at room temperature for $Li_{0.34(1)}La_{0.51(1)}TiO_{2.94(2)}$. Unfortunately, high grain boundary resistance, high interfacial resistance, and poor compatibility of Ti^{4+} with lithium metal anode limit their wide application. In general, SSEs based on oxides have a relatively high ionic conductivity and chemical stability in the environment. Oxide-based SSEs have the highest Young's modulus among all types of SSEs. The Young's moduli for LATP, LLZO, garnet-type and perovskite-type SSEs are 115 GPa, 150 GPa and 203 GPa, respectively. This harsh property can be useful for suppressing lithium dendrites if designed correctly, but leads to the problem of electrode mismatch. There is a mismatch problem between the NASICON type electrolyte and the electrodes when there is a large gap at the interface.

An interfacial problem has been reported due to side reactions or diffusion of elements at the interface between the oxide-based SSE and the cathode (Shell, 2017). At the $LiCoO_2$/LLZO interface, interdiffusion of Co with Zr and La occurs, forming an interface with low ionic conductivity (i.e., high interfacial resistance). Another common problem is the incompatibility of the lithium anode and the SSE based on titanium oxide. Ti^{4+} in LATP or LLTO can be easily reduced with a lithium metal anode, resulting in a SSE phase change that reduces ionic conductivity but increases electronic conductivity. This type of interphase with high electronic conductivity is especially prone to enhanced growth of lithium dendrites (Song, 2019). Thus, interfacial mismatch and side reactions between oxide based SSE and electrodes are key issues in the application of oxide based SSE and more research is required. The interfacial issues include:

- solidifying lithium in a melting state on the SSE to ensure close contact,
- co-sintering active materials and SSE with a sintering agent,
- creating an SSE with a porous structure to increase the area of contact between the electrode materials and the SSE,
- use of a cover layer to prevent side reactions.

It is believed that the development of a high ionic conductivity soft layer interface between the SSE and the electrodes may be a good strategy to address the issues associated with SSLB with oxide-based SSE.

Sulfide-based electrolytes. SSEs are classified as amorphous, crystalline, and glass-ceramic sulfide SSCs. Typical solid electrolytes based on amorphous sulfides include $xLi_2S\cdot(1-x)P_2S_5$ and $xLi_2S\cdot(1-x)SiS_2$ systems. Both systems have an ionic conductivity at room temperature above 10^{-4} S cm^{-1}. Crystalline sulfide based solid electrolyte Li_3PS_4 was first described by Tachez et al. Later, Kanno's group reported a thio-LISICON type SSE obtained by replacing O^{2-} of the LISICON family $[Li_{14}Zn(GeO_4)_4]$ with S^{2-} (Kanno,2000). The substitution results in higher ionic conductivity at RT because S^{2-} has a larger ionic radius, higher polarizability, and lower electronegativity than O^{2-}. The replacement of O^{2-} by S^{2-} reduces the binding of Li^+ in the crystal framework and expands the ion transport channel, thereby increasing the ionic conductivity. Most of the known SSEs based on crystalline sulfides have an ionic conductivity more than 10^{-4} S/cm at RT. Glass-ceramic ESE are obtained by crystallization of glassy SSEs. Glass-ceramic SSCs based on xLi_2S-$(1-x)P_2S_5$ have attracted great attention from researchers, especially after the discovery of the $Li_{10}GeP_2S_{12}$ (LGPS) families and their derivatives, such as $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, both of which exhibit ionic conductivity greater than 10^{-2} S/cm at room temperature (Kato, 2016).

As solid electrolytes, amorphous systems based on glasses with increased lithium conductivity are used. Among amorphous electrolytes, electrolytes based on lithium metaphosphate, as well as glasses formed in systems Li_2O-B_2O_3-P_2O_5, Li_2O_3-P_2O_5-Ta_2O_5, Li_2O-P_2O_5-MoO_3. In the form of thin films, amorphous lithium conductors of the composition $LiPO_3$-Li_3N (LIPON) and $LiNbO_3$ with ionic conductivityb above 10^{-6} S/cm at 25°C.

Moreover, the highest lithium conductivity at 25°C is exhibited by sulfide glasses Li_2S-SiS_2, Li_2S-LiI-SiS_2 and Li_2S-LiI-SiS_2-P_2S_2 obtained by quenching from the melt or by mechanical activation of the initial components. Amorphous systems have a number of advantages: the complete absence of grain boundaries, high density and impermeability of the material for gas or liquid phases. The common disadvantages of amorphous electrolytes include their thermodynamic instability, as well as the difficulty of obtaining a reliable interfacial contact at the electrolyte verge with an electrode that changes volume during charge-discharge processes.

Due to the high ionic conductivity and the relative physical and mechanical characteristics of SSEs based on sulfides, they are used in solid states lithium ion batteries. Such batteries can be fabricated by cold pressing without high temperature exchange sintering manufactured. However, sulfide-based SSEs exhibit sensitivity to lithium metal anode sensitivity and significant cathode material, which may be due to their practical application in SSLB. The behavior of side reactions between electrodes and SSE based on sulfides attracts a lot of attention. The electrochemical stability window of various types of sulfide-based SSEs has been evaluated through theoretical calculations and experimental characterizations, where they measure that sulfide-based SSEs have a narrow electrochemical stability window. In work (Aki, 2019) was described obtaining solid electrolyte based on LGPS, having a certain crystal structure containing Li, P and S. The method for obtaining solid electrolyte based on LGPS is characterized by the presence of a stage at which a mixture of Li_3PS_4 crystals having a peak on the Raman spectrum at 420±10 cm^{-1} and Li_4MS_4 crystals (M is selected from a group consisting of Ge, Si and Sn) is subjected to heat treatment at 300-700°C; the presence of a stage at which Li_3PS_4 crystals having a peak on the Raman spectrum at 420±10 cm^{-1}, Li_2S crystals and sulfide crystals represented by the MS_2 structure (M is selected from the group consisting of Ge, Si and Sn) are mixed, while preserving crystals and synthesizing a precursor; and a stage at which the precursor is subjected to heat treatment at 300-700°C. Technical results are high performance, stable characteristics and reduction in the formation of by-products.

The use of solid electrolytes based on sulfides is not widespread due to electrochemical and chemical instability and the formation of a space charge layer (SCL) at the interface between the solid electrolyte and the electrode. An instability problem was identified by transmission electron microscopy at the interface of a solid electrolyte based on sulfides and a positive electrode based on $LiCoO_2$, this is the formation of by-products Li_2S, CoS_3 and $Co(PO_3)_2$. As a result of the difference in chemical potentials, a SCL is formed at the electrolyte/electrode interface, which reduces performance of SSLIB. Usually, SCR is formed at the interface between sulfide-based SSEs and electrode based $LiCoO_2$ due to the difference in chemical potentials between them (Wang, 2018).

Conclusion

As a result research, the development of electrolytic systems for lithium-ion batteries has made a great progress. Liquid electrolytes with different compositions and additives affect the stability and structure of the electrodes during the cycling process, as well as affect the overall electrochemical performance of lithium-ion batteries. All liquid and solid state electrolytes have various advantages and disadvantages. Solid polymer electrolytes are famous for their flexibility and softness, due to their low interfacial resistance towards to electrodes, especially oxide-based SSEs towards to lithium metal anode, however their practical application is limited. This is explained by the low ionic conductivity at room temperature and the relatively narrow window of electrochemical stability, furthermore, contact with electrodes is very difficult due to their rigid structure. Sensible combinations of liquid electrolytes with additives, solid electrolyte doping are promising methodologies to maximize the benefits of each component, thereby increasing the electrochemical performance of lithium-ion batteries.

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