

Recent developments in the electrolyte for LiC₆/ electrolyte/ cathode battery

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Abstract : We present a reviewed the development and status of electrolyte for LiC₆/ electrolyte/ cathode battery. The effect of the salt , solvent , additive and impurity on the conductivity of the electrolyte , formation of the solid-electrolyte-interphase (SEI) and cycle life of the battery were described.

Key words : electrolyte ; lithium-ion Battery ; SEI ; conductivity

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1 Introduction

As an important part of the Li-ion battery , electrolyte plays a critical role on the working temperature , cycle stability , high rate discharge capability and the safety. Since industrial considerations relative to safety and cycling behavior lead to the replacement of lithium by carbonaceous materials (Li_xC₆) as the anodes for lithium batteries , it is also necessary to consider the compatibility of the electrolyte to the anode^[1]. In addition , the trace impurity in the electrolyte greatly influence the battery performance^[2]. In this paper , it is reported the effect of salt , solvent , additive and impurity on the electrolyte conductivity and battery 's cycle life.

2 On the conductivity

2.1 freezing point , viscosity , dielectric constant and donating number (DN) of the solvent

For lithium ion rechargeable batteries , since the mean charge or discharge voltage remains

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beyond 3 V ranges, the aqueous electrolyte cannot be used as it would decompose. Hence, inorganic salts (for example, LiClO_4) dissolved in organic solvent with a large stability window have been considered as candidacy electrolytes. Electrolytes based on organic carbonate mixtures have become the standard for lithium ion batteries. To be a good electrolyte, such a non-protonic electrolyte must have good ionic conductivity, high chemical stability, assure safety and be cost-effective. With the development of commercial lithium ion battery, it is more and more important to obtain a electrolyte which can be operated at a wider temperature range, especially the lower temperature^[3,4]. It is well known that the low-temperature performance of the battery is closely related to the ionic conductivity of Li^+ in the electrolyte. The ionic conductivity of Li^+ is proportional to its mobility and the number of mobile ions.

In order to obtain low-temperature electrolyte, it is very necessary to consider all kinds of physics constant of the solvents such as freezing point, boiling point, vapor pressure, viscosity, dielectric constant and donating number. Although cyclic carbonic acid esters (carbonate) like PC and EC have high dielectric constants, their viscosity values are high due to the interaction between molecules, which results in deviation of the electric charge of the molecule. Lower viscosity is more desirable for easier movement of the lithium ion. It is common practice to mix two or more solvents so as to obtain a desired set of properties which are suitable for high performance batteries. The main developments recently have been investigations of the different mixtures of propylene, ethylene, diethyl, dimethyl and ethyl methyl carbonated to obtain the optimal low temperature performance. Performance down to about -20°C is possible with various mixtures of the above compounds^[3].

It is reported^[5] that the molar conductivity of the EC-DMC-DME ternary solvent electrolytes gradually increased with the addition of DME. However, the molar conductivities of the EC-DMC-2-MeTHF and EC-DMC-EMC ternary solvent electrolytes gradually decreased with the addition of the 2-MeTHF and EMC. The decrease of the molar conductivity for these solutions is attributed to a decrease of the dissociation degree for electrolytes versus a decrease of the dielectric constant rather than that of the viscosity of the EC-DMC-2-MeTHF and EC-DMC-EMC ternary solvent mixtures. The further discussion is based, however, on the donor ability of the solvents. The value of the donor number (DN) and the dielectric constant are strongly related but not necessarily always in parallel. The molar conductivities of EC-DMC-DME ternary solvent electrolytes depend on the increase of the dissociation degree for LiPF_6 and LiClO_4 . Since the EC or DMC molecules of the solvent shell for the Li^+ ion are selectively substituted by the DME molecule with a higher DN of EC (DN = 16.4) or DMC molecule (it is assumed that the DN of DMC is smaller than that of DME, although that value of DMC is unknown at present). On the contrary, it is considered for the EC-DMC-2-MeTHF and EC-DMC-EMC ternary solvent electrolytes that the dissociation degree for LiPF_6 and LiClO_4 becomes small by a decrease of the dielectric constant for these ternary solvent mixtures because of the difficulty of substitution of EC or DMC for

2-MeTHF and EMC with smaller DN compared with that DME (the DN of EMC similarly to DMC, also seems to be smaller than that of DME).

To get lower temperature performance (which is needed for some military applications) with organic electrolyte systems, other organic compounds, such as acetates, need to be added to the carbonate mixtures^[6].

The conductivity of the electrolyte with different composition mixture is also closely related to the variety of the lithium salt and the solvent. It is illustrated in Table 1 the conductivity of mixtures of EC with other solvents^[7]. These mixtures presented here show around 10 mS/cm of conductivity. The conductivity of electrolytes based on mixed carbonate solvents is generally about one half that of electrolytes with DMC as the co-solvent, although this depends on the type of lithium salt which was dissolved in it.

Tab.1 Conductivity of EC-based electrolytes (EC: co-solvent, 1:1 by volume) at 25

Electrolytic salt (1 mol/dm ³)	Co-solvent	Specific conductivity (mS/cm)
Li(CF ₃ SO ₂) ₂ N	DME	13.3
	DMC	9.2
	DEC	6.5
	MP	10.8
LiCF ₃ SO ₃	DMC	8.3
	DME	3.1
	DEC	2.1
	MP	3.7
LiPF ₆	DME	16.6
	DMC	11.2
	DEC	7.8
	MP	13.3

2.2 Lewis acid and Lewis base theory

All non-aqueous lithium battery electrolytes are Lewis bases that interact with cations^[8]. Unlike water, they do not interact with anions, the result is a closely ion pairing and the formation of triplets and higher aggregates. Then the conductivity and the lithium ion transference will reduce, and results in polarization losses in batteries.

Approaches that have been used to increase ion dissociation in (PEO)-based electrolytes are the introduce of salts with low lattice energy, the addition of polar plasticizers to the polymer, and the addition of cation complexing agents such as crown ethers or cryptands. Crown ether or cryptands were considered effective complexing agents to alkali metal ions, and the 12-crown-4,

the most effective complexing agents to Li^+ ^[8].

Complexing of the anions is a more promising approach, since it should increase both ion dissociation and the lithium transference. It has been synthesized of two new families of neutral anion complexing agents, each based on Lewis acid centers^[9]. One is based on electron deficient nitrogen sites on substituted aza-ethers, wherein the hydrogen on the nitrogen is replaced by electron withdrawing groups such as CF_3SO_3^- . The other is based on electron deficient boron sites on borane or borated compounds with various fluorinated aryl or alkyl groups. Some of the borane-based anion receptors can promote the dissolution of LiF in several solvents. Several of these compounds, when added in equivalent amounts, will form 1.2 mol/L LiF solutions in DME. An increase in solubility of LiF by six orders of magnitude. Some of these LiF electrolytes have conductivities as high as $6 \times 10^{-3} \text{ S cm}^{-1}$. The LiF electrolytes with borane anion acceptors in PC EC DEC solvents have excellent electrochemical stability.

3 On the solid electrolyte interface (SEI)

It is well known that the carbon is very sensitive (especially the more ordered carbon which is graphite-like) to the composition of electrolyte solution in terms of stability (cycle life) and degree of intercalation^[10,11]. The main cause of the instability of Li-graphite anodes upon cycling is probably cointercalation of solvent molecules together with the Li ions into the graphite structure. This process, which may be accompanied by the reduction of the solvent molecules, is detrimental to graphite stability and destroys its structure (exfoliation of the graphite and thereby a physical and electrical disconnection of anode particles from the bulk occurs). The compact surface films (SEI) act as a screen, allowing Li^+ migration into the carbon, but preventing penetration of the solvating molecules^[12].

A condition for their protecting effect is that these passivating surface films will be fully developed and compact before the electrode reaches the intercalation stage (when the electrode is first charged with Li in solutions). Therefore, in the case of Li-C anodes, using a reactive solvent may be an advantage as its reduction may occur at potentials much higher (2-1 V vs. Li/Li^+) than that of the intercalation stages (0.5-0 V vs. Li/Li^+). This can lead, therefore, to the passivating surface films being fully developed when the electrode reaches the potential of intercalation during its first charging in solutions. It is possible to modify the Li-C anode surface chemistry by using active additives in solutions, whose reduction may form highly compact insoluble films. It is summarized the several improvement techniques as following:

3.1 PC-based electrolyte

PC presents interesting properties since it is able to dissolve and dissociate lithium salts leading to highly conducting electrolytes even at low temperatures. Moreover, electrolytes containing PC as a unique solvent are stable against oxidation to $\sim 5 \text{ V}$ ^[13]. Unfortunately, during the reduction of graphite, PC is decomposed at a potential lower than that corresponding to the intercala-

tion of solvated lithium ions^[14,15]. The ternary intercalation compounds obtained in such conditions are unstable and intercalated solvent molecules decompose into propylene between the graphite sheets. This results in the exfoliation of graphite and in the formation of small particles of exfoliated graphite which are electrically disconnected, leading consequently to a loss of the reversible capacity of the graphite electrode^[16].

Firstly, in order to improve the cycleability of graphite electrodes in the presence of PC, It is reported^[17] that the additives of the nonaqueous solvent with S-O bond and the new halogenated additives are beneficial to the formation of stable protective film before the intercalation of Li^+ , so the decomposition of electrolyte is controlled and the intercalation and deintercalation of Li^+ are assured. The use of additives of cosolvents added to PC and taking part into the formation of the SEI allows graphite to be cycled reversibly^[18].

Another way to form the passivating layer in the presence of PC-based electrolyte, is to impregnate the composite electrode with a wetting solvent able to decompose or to reduce at potentials higher than those corresponding to graphite exfoliation. Such a method allows to use very lower amounts of added solvent. A. Naji et al^[19] immersed graphite electrode in Cl-EC or Br-BI for ~ 2 min. Such a treated electrode can then be transferred in a cell containing PC/LiX as electrolyte. The reversible capacity is significantly higher than that obtained in commercial electrolytes based on EC.

In addition, the solvent cointercalation is closely related to the steric structure and the kinds of the bond in the solvent. The former determined the steric hindrances for solvent hindrance, the later is related to the LUMO level^[20]. In order to decrease the solvent co-intercalation, it is reported^[21] that the new cyclic carbonate *trans-2, 3-butylene carbonate* is useful for lithium ion batteries with graphite carbon anode. Although it is structurally very similar to propylene carbonate, it is much less reactive toward graphite than propylene carbonate. The decrease in the reactivity can be explained in terms of its unique geometry that hinders its co-intercalation into the layer spacing of graphite structure. It is demonstrated that electrolytes containing this solvent exhibit a satisfactory initial efficiency and discharge performance at low temperature.

3.2 the influence of CO_2

Another effective method to form highly compact insoluble films is CO_2 , which leads to the formation of surface Li_2CO_3 films. As expected, CO_2 has a pronounced effect on the electrodes' performance in terms of both the degree of the intercalation and the electrodes' cycle life (stability)^[22].

3.3 the charge condition for the first cycle

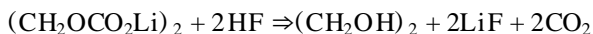
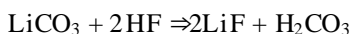
The influence of solvent on the cycle life of battery is closely related to the charge condition for the first time. For example, the reduction potential of Me-ClF in Me-ClF + PC/LiClO₄ is a little higher than the solvent cointercalation potential in PC/LiClO₄, both the reversible and irre-

versible capacity are higher using the charge current $7 \mu\text{A mg}^{-1}$ than the charge current $20 \mu\text{A mg}^{-1}$, which is showed the lower charge current is beneficial to the formation of more compact effective film^[22].

The another method to improve the performance of Li-C anodes in electrolyte solutions is to perform the first charging step of a freshly prepared graphite electrode at low temperature^[11]. It is possible to conclude that by lowering the temperature the kinetics of salt reduction on the carbon surface is more pronouncedly slowed down than solvent (such as MF or CO_2) reduction, therefore, at low temperature precipitation of salt reduction products (mostly Li halides) does not interfere with the sedimentation of compact films of Li formate or Li formate- LiCO_3 (when CO_2 is present). Therefore, the charge involved in their formation is smaller and their ability to prevent detrimental solvent cointercalation is better.

4 The influence of protic impurities

The quality of electrolyte for lithium battery is a major topic in science and battery industries. The solvent and lithium salts should be of highest purity. Therefore, during preparation and handling of electrolyte solutions, the contamination level has to be minimized and the quality during packaging, storage and transportation has to be guaranteed. The impurities in the electrolyte solution have a great effect on the performance of the battery. Especially, protic impurities are found to be very critical for LiPF_6 -based electrolytes. It is reported that the influence of water is reported to be tremendous, and there is the following reaction: $\text{LiPF}_6 + \text{H}_2\text{O} \Rightarrow 2\text{HF} + \text{POF}_3 + \text{LiF}$. Also other protic impurities like alcohols are considerable to play an important role in the electrolyte quality. The reaction of the protic impurities with LiPF_6 leads to the formation of HF which further reacts with cathode active materials (e. g., spinel) and the passivating films of the cathode and anode. Aurbach et al^[22] reported the reaction of HF with the solid electrolyte interface (SEI):



That leads to a rapid capacity loss and poor cycle life of the battery.

It is reported^[24] that when the 334 ppm glycol and 84 ppm water was doped in 1 mol/L $\text{LiPF}_6/\text{EC}:\text{DMC}(50:50 \text{ wt. } \%)$ electrolyte, the composition analysis showed that the content of glycol and water were decreased and the content of HF increased gradually during the first 4 days in room temperature. Other protic impurities such as methanol and ethanol also influence the contents of HF. Although the trace water has a great effect on the cycle and stability of the cathode and anode^[22, 25]. It is reported that, in some electrolytes, certain content water (300 ~ 700 ppm) can improve the battery performance^[22]. Due to the reaction of trace water with the ROCO_2Li formed by the reduction of solvent to produce Li_2CO_3 , CO_2 and ROH ^[26, 27], the formed Li_2CO_3 is beneficial to the SEI film, where the water plays a role like CO_2 in the literature^[28, 29].

It is generally accepted that this charge loss occurring during first charging of the carbon electrodes^[30] is mainly due to reductive decomposition of the electrolyte on the negative electrodes^[31]. herein, it is studied the effect of H₂O on the SEI information based on EC and DMC.

$$CL = [(C_{\text{int}} - C_{\text{de-int}}) / C_{\text{int}}] \times 100 \%,$$

where CL: charge loss, C_{int}: charge of the intercalation reaction including SEI formation, C_{de-int}: charge of the de-incalation reaction. It was illustrated that the irreversible charge loss increased gradually with increasing water content, and it can not conclude that electrolytes containing several hundred ppm of water have an improved cycling stability over dry electrolytes, as was suggested in the literature^[22] for the electrolyte 1 M LiAsF₆ in DMC + EC. It was showed that the higher the trace water content of the electrolyte solution, the more hydrogen gas is detected during the first cycle. Hydrogen evolution starts at about 1.3 V vs Li/Li⁺ during the first intercalation and is explained by water reduction. The observation agrees with the results of cycling experiments in which additional charge was consumed during the first cycle, probably due to additional water decomposition. The observation that the amount of evolved ethylene decreases with increasing water content implies that the SEI is built up differently depending on the amount of water present. The SEI probably contains more lithium salts, when the water content is high. On the other hand, if the content of water is low, the SEI film contains more decomposition products of the organic carbonates. However, the cycling experiments revealed no clear correlation between the fading of the capacity and the water content. It is very necessary to study the influence of water in different electrolytes on the battery properties.

5 Conclusions

The electrolyte plays an important role on the battery performance. The conductivity of the electrolyte and the cycle life of the battery are closely related to the solvent, additive and the purity of the electrolyte.

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锂离子电池电解液的研究进展

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摘要: 综述现今锂离子电池电解液的研究进展. 评估了电解液中锂盐、溶剂、添加剂以及杂质等对电解液的电导、固体电解质相界面(SEI)的形成、电池循环寿命等的影响.

关键词: 电解液; 锂离子电池; 固体电解质相界面(SEI); 电导