

Electrolytes for advanced batteries

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Abstract

The choices of the components of the electrolyte phase for advanced batteries (lithium and lithium ion batteries) are very sensitive to the electrodes which are used. There are also a number of other requirements for the electrolyte phase, which depend on the cell design and the materials chosen for the battery. The difficulty of choice is compounded when the cell is a rechargeable one. This paper looks at each of these requirements and the degree to which they are met for lithium and lithium ion batteries. The discussion is broken into sections on anode or negative electrode stability requirements, cathode or positive electrode stability requirements, conductivity needs, viscosity and wetting requirements. The effects of these properties and interactions on the performance of batteries are also discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Battery; Electrode; Cell design

1. Introduction

The requirements for liquid electrolytes in advanced lithium and lithium ion batteries are many. This paper will present some perspectives on the behavior of the electrolytes in such batteries, what the required properties are for the electrolyte phase and the degree to which such requirements are met. The property discussion will be broken up into sections on anode (negative electrode) stability requirements, cathode (positive electrode) stability requirements, conductivity needs, viscosity and wetting requirements.

2. Anode stability requirements

It has been known for a long time that organic solvents are not intrinsically stable with lithium metal, but have a degree of kinetic stability [1]. This is a reflection of the reducing property of lithium metal and its tendency to form films, which can simultaneously conduct lithium ions and protect the underlying lithium from further reaction with the solvent of choice. The name which has been coined for the type of film which results in this metastability is a Solid Electrolyte Interphase (SEI). The required properties for the SEI have been documented by Peled [2] for lithium electrodes. The reaction to form the SEI on

lithium metal is a very limited one and is barely measurable in lithium primary cells by conventional chemical or electrochemical analysis. The presence of the film is clearly evidenced, however, by the growing impedance of a lithium electrode immersed in an electrolyte [2]. It is also clearly seen in surface analytical techniques such as Fourier Transform Infrared Reflection (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive analysis of X-rays (EDAX) and atomic force microscopy (AFM) [3,4]. For primary batteries, this is most of the story, except that at high currents, the protective film is undercut due to the rapid dissolution of lithium and the impedance is reduced. This effect is responsible for the well-known voltage delay effect in liquid cathode and other primary batteries [5]. In rechargeable lithium cells, however, the film formation reaction tends to accumulate as surface area expands during the cycling of the cells. This is generally described as an inefficiency of the cycling process and results in an exponential decay of the capacity of the lithium electrode, after excess lithium in the electrode has been consumed, when the inefficiency is taken as a constant for each cycle. Fig. 1 shows the type of decay of capacity which is typical for rechargeable lithium metal and lithium–aluminum metal alloy batteries which have been designed with excess lithium metal present in the negative electrode. These cells have the same cathode (LiCoO_2), but the different anodes behave similarly which causes similar cell behavior. Note that the cell with lithium metal shows the exponential

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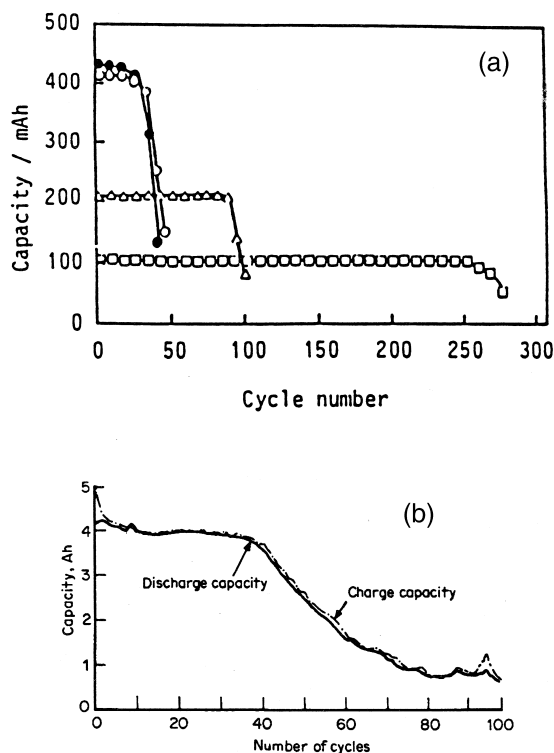


Fig. 1. Capacity vs. cycle number for lithiated cobalt dioxide cells. (a) Li_xAl negative electrode, AA size cell, discharge ○—100% DOD with 2.75 V cut-off at 0.5 C, ●—100% DOD with 2.75 V cut-off at 0.05 C, △—50% DOD at 0.5 C, □—25% DOD at 0.5 C (from T. Nagaura, 5th International Sem. On Lithium Battery Technology, Shawmco, Tulsa, OK, 1991). (b) Li negative electrode, D size cell, charge at 300 mA, 4.3 V cut-off, discharge at 3 A, 3.0 V cut-off (from D. Linden (Ed.), Handbook of Batteries and Fuel Cells, 2nd edn., McGraw Hill, New York, 1995, p. 36.36).

decay quite well after the excess lithium is exhausted. In the alloy case, several depths of discharge show that the excess anode causes a doubling of the flat portion of the capacity when going from 100% depth to 50% depth, as expected. The more than doubling of this portion from 50% to 25% depth may be due to higher anode cycling efficiency at very low depths of discharge.

The reactions which occur on the surface of the lithium electrode are subtle, but have been extensively studied using various methods, particularly by Aurbach et al. [3]. Cyclic ethers such as 2-methyltetrahydrofuran (2MeTHF) tend to react relatively slowly and form very thin films on the surface of lithium metal. The chemical nature of the film is mainly alkoxide ions. The cyclic carbonates, propylene carbonate (PC) and ethylene carbonate (EC), form lithium carbonate and lithium semicarbonates and react quickly on the lithium surface. In fact, these solvents can be used as passivating materials to protect other solvents such as crotonitrile (the nitrile based on the unsaturated crotonic acid) or acetonitrile from reacting with lithium metal to form polymeric substances in lithium primary cells [6]. Of the two cyclic carbonates, PC and EC, the more facile one in reactions with lithium (and other)

surfaces is EC [7]. These rapid surface reactions were not believed to be useful for lithium metal when using PC as sole solvent, for example, apparently because the plated lithium is not easily stripped again on the discharge cycle [8]. However, when EC was used in small amounts (20%) with 2MeTHF by Yamaki et al., a very successful electrolyte with high cycling efficiency resulted [9]. Furthermore, an additional development concerning EC and PC occurred with the use in the MOLICELL (a Li/MoS_2 battery made by Moli Energy) of 1 M LiAsF_6 in a 1:1 PC:EC mixture [10]. This electrolyte was satisfactory for several hundred full depth cycles if the charge and discharge currents were carefully chosen and if sufficient stack pressure was applied to the lithium electrode. This work points out the importance of examining all of the variables in cells when dealing with a property as subtle as rechargeability in battery systems. In fact, it was only with the production of this battery and hence the wide scale testing at high cycle life, that the weakness of the lithium metal system with mobile electrolytes was revealed. Namely, the development of high surface area makes the lithium too sensitive to catastrophic, self-sustaining reaction with electrolyte as revealed by accelerated rate calorimetry [11]. These results led directly to the work with lithiated carbon electrodes in a rocking chair type of battery called the lithium ion cell [12].

The requirements for lithium ion negative electrodes (in particular, lithium intercalated carbon electrodes) have not been as well-studied as lithium, but the general characteristics have been described by Dahn et al. [13]. One of the important differences compared to lithium metal is the need for minimal solvent intercalation into the layers during the intercalation reaction of the lithium ions. The result of solvent intercalation is reaction and exfoliation of the graphite layers, which continually presents fresh surface to the electrolyte for further reaction. Many authors believe that propylene carbonate is prone to intercalation with lithium ions in ordered carbons. Thus, propylene carbonate with graphite in any form (beads, flakes, or fibers) is unsuitable as an electrolyte in a lithium ion cell as the sole passivating liquid. The initial lithium ion work, however, showed that propylene carbonate with disordered carbons, such as petroleum coke [14], or low-temperature hard carbons [15] was quite suitable as a passivating component in the solution, much as it is for lithium metal or alloys. Furthermore, when EC is used as a passivating solvent (even when PC is present in small amounts), excessive reaction does not occur with the various forms of graphite. In fact, the so-called irreversible capacity (the difference between the capacity of the first charge of the carbon and the capacity of subsequent charges and discharges) is relatively small even for graphite and this fact allows cells to be designed which function very efficiently. A plateau in the discharge (or a peak in the derivative discharge or linear sweep potentiogram) of carbon or graphite at about 0.8 V vs. lithium has been ascribed to the

film forming passivation reaction by many authors and has been cited as the explanation for the magnitude of the irreversible capacity [13]. That such a peak appears in the first charge of the carbon and is not observed in subsequent cycling for many carbons is indisputable (Fig. 2). However, the author has recently discovered that this peak does not appear in the initial charge of a powder made from highly annealed pyrolytic graphite (HOPG) in a 1 M LiPF_6 in EC–DMC electrolyte [16]. HOPG is an interesting material because it is made of graphene layers which have a very high degree of planarity. The charge and discharge of the electrode in a lithium half-cell gave the result shown in Fig. 3. The lack of a peak at 0.8 V vs. Li, even though the irreversible capacity was comparable to other forms of graphite, indicated that the analysis of this peak as the explanation for irreversible capacity is incomplete.

Some further observations bear on the electrolyte reactions which occur at the lithiated carbon electrode. A similar loss of the 0.8 V peak was found in an experiment in which a carbon was heated to 1000°C in vacuo to remove oxygen from surface groups in low-temperature carbons. Prior to heating, the carbon gave a substantial peak at 0.8 V [17]. The authors believe that the oxygen is somehow responsible for the presence of the peak. The oxygen is present in a covalently bound state since any adsorbed oxygen-containing species such as oxygen or water would be desorbed at temperatures much lower than 1000°C. The work of Yoshida et al. [18] examined the electrolyte phase by a combination of liquid chromatography–Fourier transform infrared spectroscopy (FTIR) and the generated gases by means of gas chromatography–FTIR. The gases generated were mainly CO and C_2H_4 for all of the electrolytes which included EC, DMC, EMC, DEC, EC + DMC, EC + EMC, EC + DEC and EC + DMC + DEC where DMC, DEC and EMC are dimethyl

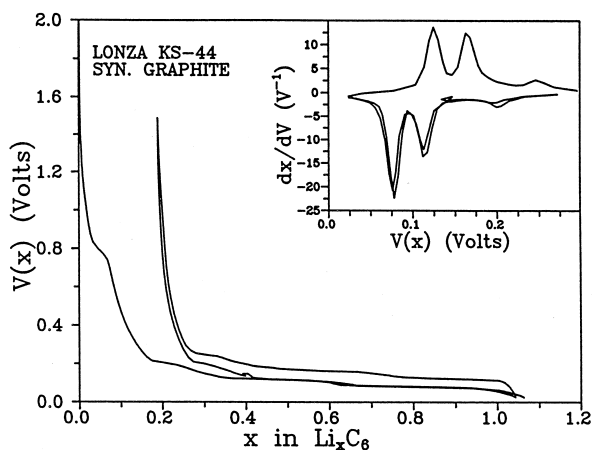


Fig. 2. Capacity vs. x in Li_xC_6 for Lonza (Timcal) KS-44 synthetic graphite in lithium half-cell, first discharge and subsequent cycle at 80-h rate, at 30°C (from Ref. [13]).

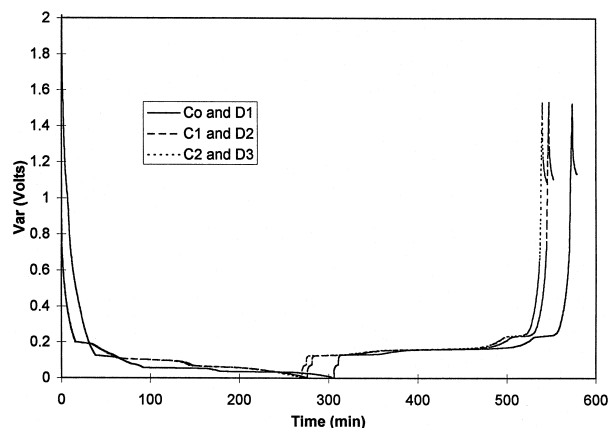


Fig. 3. Charge–discharge voltage as a function of time for HOPG powder electrode in a lithium half cell for initial three cycles.

carbonate, diethyl carbonate and ethyl methyl carbonate, respectively. An exception was for the single component DEC in which continuous gas generation with a high ratio of H_2 and no charging of the cell occurred. The electrolyte studies yielded unequivocal evidence for ester exchange among all of the carbonate esters. The linear esters, DMC and DEC, were readily involved in a *trans*-esterification reaction:



These components established a rapid equilibrium. Further ester exchange reactions were established by the LC–FTIR results, namely:



where DMDOHC, DEDOHC and EMDOHC are the mixed carbonate esters dimethyl-2,5-dioxahexane carboxylate [$\text{CH}_3(\text{OOC}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{COO})\text{CH}_3$], diethyl-2,5-dioxahexane carboxylate [$\text{C}_2\text{H}_5(\text{OOC}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{COO})\text{C}_2\text{H}_5$], and ethylmethyl-2,5-dioxahexane carboxylate [$\text{C}_2\text{H}_5(\text{OOC}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{COO})\text{CH}_3$], respectively. It was also implied that the ester exchange reactions are catalyzed by a lithium alkoxide, which is also formed during initial charge, according to the FTIR information on the surface species. Dr. A. Webber of our laboratory [19] has confirmed the occurrence of these reactions in solution and has identified lithium ethoxide as the main catalyst for the reactions, since it has high solubility in the solution compared to lithium methoxide. The products were identified by GC–mass spectroscopy and found to be in the 2% level, a substantial reaction. Another study by Matsumura et al. [20] showed that while part of the irreversible capacity occurs at voltages more positive than 0.8 V vs. Li, the majority of the irreversible capacity occurs at poten-

tials between 0.5 and 0.01 V with most of that portion occurring from 0.25 to 0.01 V vs. Li for the high temperature coke studied by them. All of these studies point out the complexity of the reactions and that in order to understand the processes in lithium ion cells, it is necessary to study them as a function of potential and to examine both the surface of the carbon and the electrolyte phase.

Examination of the capacity fade of lithium ion cells leads to a realization that the behavior is different from the fade of lithium metal batteries. Since the cells are made in the discharged state, there is no excess of negative electrode material in the cell. In fact, the initial charge determines the maximum capacity of the cell and the irreversible part, which is normally due to losses in the anode as discussed above, diminishes the available capacity. Any continuing reaction on subsequent cycles causes an immediate reduction in capacity which is not recoverable due to the voltage limitation on the charge half cycle. Fig. 4 shows the fade in capacity of a typical lithium ion cell. The loss in capacity is not well-described by an exponential decay as it is for lithium metal cells, but is much better described by a parabolic decay. Thus, the capacity vs. cycle number plot has the functional form:

$$Q = Q_1 - AN^{1/2}, \quad (5)$$

where Q is the discharge capacity at cycle number N , Q_1 is the discharge capacity of cycle 1 and A is a constant which determines the rate of fade. The expression follows directly from regarding a continuing reaction of the anode material with electrolyte as the cause of fade and that this anode reaction occurs with a parabolic rate law as is common for many corrosion reactions (see Appendix A). A similar behavior is seen for the decay of capacity on shelf stand in the charged state, which supports the explanation of anode corrosion as the primary loss mechanism for well-designed lithium ion cells.

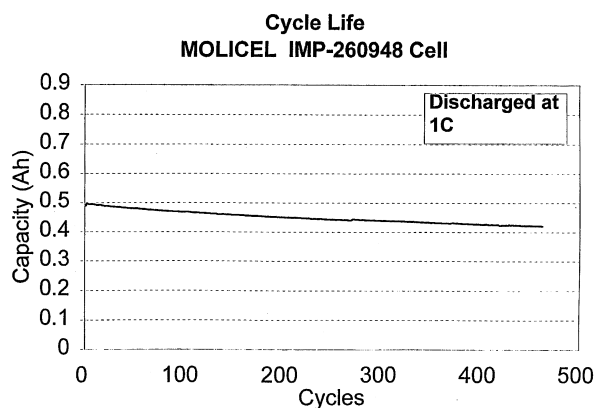


Fig. 4. Cycle life of prismatic lithium ion cell IMP-260948 from Moli Energy showing typical decay in capacity with cycling which is best interpreted by parabolic decay (see text). Curve from product data sheet, Moli Energy.

3. Cathode stability requirements

The cathode (positive electrode) in lithium and lithium ion batteries has a similar problem to that of the negative electrode. That is, the electrolyte reacts with the positive electrode at very positive potentials, a reaction which depends on the solvents as well as the solute in the electrolyte phase. A second problem is evidenced, which depends primarily on the salt which is used in the electrolyte. This problem is corrosion of the substrate metal foil which is used as a carrier for the active material.

The first mechanism of instability at the cathode electrolyte interface, anodic oxidation of the electrolyte, may be studied directly by a potential sweep to very positive potentials and the potential at which a certain small current passes, such as 0.1 mA/cm^2 is taken as the limit of stability towards oxidation for the electrolyte. An inert electrode material such as platinum or glassy carbon is conventionally used for these studies and a slow sweep rate, such as 10 mV/s , is usually used in a linear sweep of the potential. Cathodic sweeps are also often used in the same experiment to test the cathodic stability. A recent compilation of results was presented by Koshina et al. [21]. The results are summarized as follows: cyclic and linear ethers are rather easily oxidized and are generally not suitable for high-voltage cells, such as lithium ion batteries (the most stable are 1,2-dimethoxyethane and diglyme); linear esters are oxidatively stable to over 4.5 V vs. Li, but were found to have a peak in the region of 0.6 V on cathodic sweeps using graphite test electrodes; lactones have quite variable oxidation stability ranging from 3.2 to 5.1 V, but they also have a reduction peak on graphite electrodes, indicating solvent intercalation; carbonic acid esters were very stable to oxidation with potentials of 4.8 V and above, but some of the linear carbonic acid esters have a reduction peak on graphite electrodes similar to that of propylene carbonate, but at slightly more negative potentials; some sulfur-containing solvents like sulfolane and dimethylsulfoxide are very stable on both oxidation and reduction to very high and low potentials, respectively. Sulfolane was found to have the largest electrochemical window, with a range of 6.10 V. These results are consistent with the empirical findings which gave rise to the use of EC–DEC, EC–DMC and EC–EMC in high-voltage lithium ion cells. For lithium metal cells with lower-voltage cathodes, the use of ethers and linear esters, in particular, the cyclic ethers presents no difficulty with the oxidation side and the choice is governed by the stability on freshly plated lithium metal.

The second type of cathodic instability, namely the corrosion of the carrier metal, may also be studied by the use of linear sweep voltammetry at low sweep rates, or stepped potential experiments, but now the working electrode is simply the carrier metal. Iwakura et al. [22] have studied various metal foils as current collectors for positive electrodes in lithium ion cells in this way. They used a

1 M LiPF_6 or 1 M LiClO_4 solution in 1:1 EC:DEC. These workers also used AC impedance measurements to characterize the foils in the solutions. The lowest corrosion currents were found with the LiPF_6 and the purest aluminum (99.99% pure). 304 stainless steel, Cu, and Fe all gave high corrosion currents in the perchlorate solution when the potential exceeded 3.5 V or less depending on the metal. Ti foils gave higher corrosion currents and had a much higher impedance than pure Al foil in perchlorate medium. Likewise, the 304 foil had low corrosion current in hexafluorophosphate solution, but much higher impedance than pure aluminum. As the Al purity decreases, higher corrosion currents were observed in perchlorate solution. These observations led to the conclusion that the Al foil is clearly the best of the metals studied here for lithium ion positive electrodes. The dissolution of the substrate carrier metal would be accompanied in the actual electrode by reduction of active material, leading to very poor cyclability and permanent loss of capacity. LiPF_6 has a serious deficiency in that it is easily hydrolyzed to form HF, which participates in a number of difficult corrosion problems in lithium ion cells and decomposes thermally at quite a low temperature.

Recent studies of aluminum collector foil corrosion have also been carried out using various imide salts by two groups. The lithium bis-trifluoromethylsulfonyl imide salt has a high corrosion current at voltages above 4 V so cannot be used as the electrolyte in conventional lithium ion cells, in spite of high conductivity and excellent hydrolytic and thermal stability. Kita et al. [23] synthesized a series of fluorinated imide salts, $(\text{RSO}_2)(\text{R}'\text{SO}_2)\text{NLi}$, where R, R' may be CF_3 , C_4F_9 , or C_8F_{17} as asymmetric salts, or as the symmetric salts, $(\text{R}''\text{OSO}_2)_2\text{NLi}$, R'' may be CF_3CH_2 , $\text{CF}_3\text{CF}_2\text{CH}_2$, or $(\text{CF}_3)_2\text{CH}$. They found that all of these salts had very high oxidation potentials on platinum (above 5 V) in PC solvent. However, only the butyl, methyl asymmetric salt gave low corrosion current on Al up to 4.8 V, while the symmetric 2-propyl substituted salt gave low corrosion current on aluminum foil to 4.3 V. The symmetric fluorinated methyl imide gave an onset of high corrosion current at 4.0 V. Thus, the asymmetric butyl, methyl salt showed promise as a salt for lithium ion batteries. In similar work, Krause et al. [24] studied $\text{CF}_3\text{SO}_3\text{Li}$, $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{NLi}$ and $(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{NLi}$. These workers showed the thermal stability of the ethyl imide, which is stable to over 300°C, compared to LiPF_6 , which begins to decompose at about 30°C. They also analyzed the corrosion current pitting potentials for the salts as listed above as 1 M solutions in 1:1 EC-PC and found them to be 2.8, 3.6, 4.5 and 4.6 V, respectively. The corrosion currents measured at 4.2 V for 1 M salt in PC were also determined as functions of time and gave steady state currents of more than 10 mA/cm² for the first two salts and only a few $\mu\text{A}/\text{cm}^2$ for the latter two salts, comparable to a solution with LiPF_6 . 1225 coin cells made with the various salts in

1:1 EC-DMC with Conoco XP3 coke as the negative active material and LiCoO_2 as the positive active material and 99.5% pure Al discs as the positive collector material were found to cycle satisfactorily with LiPF_6 and the bis-perfluoroethyl salt, but not at all for the triflate salt or the perfluoromethyl salt.

The conclusion of these kinds of study on the activity of electrolyte at high oxidizing potentials is that the battery chemist must be aware of the reactions of the electrolyte both for direct oxidation and for corrosion of the collector material for the positive electrode.

4. Conductivity, viscosity and wetting

The conductivity and viscosity requirements for electrolytes in high-energy batteries have been discussed extensively [1,25–27]. Therefore, only some of the more recent data on electrolytes will be presented in this paper.

Electrolytes for high-voltage lithium cells were developed by Hayashi et al. [28] which were similar to those developed for lithium ion cells. Specific conductivities were measured for 1.0 M LiPF_6 in PC-DMC and EC-DMC with a range of solvent composition from 50 to 100% of DMC at 20 and 60°C. Broad maxima in the conductivity at 60°C with 40% PC and at 20°C with 30% PC were observed with κ_{max} of about 17 and 10 mS/cm, respectively. In the EC system, the maxima were at 40% EC (60°C) and 30% EC (20°C) with κ_{max} of about 19 and 11 mS/cm, respectively. They also measured solutions with EC-DEC and EC-EMC with variable EC concentration of 0 to 50 vol.% at 20°C. These solutions gave continuously rising conductivities in the composition range and at 50% EC had values of about 9 and 10 mS/cm, respectively. It was interesting that the EC-DMC solutions had very high figure of merit (FOM, defined as the accumulated discharge capacity divided by the sum of lithium metal and lithium in the cathode) values of about 60, which resulted in over 800 cycles in coin cells with excess lithium and $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$ cathodes. The FOM values for other solutions were considerably lower, in the range of 40 for PC-DMC and rising values of 0 to 10 (at 50% EC) for EC-DEC and of 8 to 25 (at 50% EC) for EC-EMC.

Conductivity and viscosity of ternary solvent mixtures of 1 M LiPF_6 solutions with 1:1 EC-DMC and either DME, 2MeTHF or EMC were measured by Sasaki et al. [29] at 25°C. The conductivity of the DME solutions increase from about 11 to 18 mS/cm, while the conductivity decreases for the 2MeTHF mixtures from about 11 to 9 mS/cm and for the EMC solutions from about 11 to 8 mS/cm. The solutions are diluted by the third solvent to a maximum quantity of two times (in moles) the moles of EC:DMC. The viscosity decreases with all of the solvents from 1.19 to 0.7 cP for DME, from 1.19 to 0.75 for 2MeTHF and from 1.19 to 0.95 for EMC. Also the dielec-

tric constant decrease is the least for DME additive (38 to 20), intermediate for 2MeTHF (38 to 19) and the most for EMC (38 to 16). These values are consistent with the conductivity values, since the lowest viscosity values for DME lead to the lowest friction coefficients for the ions and the highest dielectric constant values lead to the lowest ion pair association. The converse applies to EMC.

The conductivity of binary EC mixtures with DMC, EMC and DEC using 1 M LiPF₆ has been measured [30] and is of particular interest for lithium ion batteries. The values are given in Table 1 as a function of composition of the mixture. It should also be noted that these workers noted the ester exchange reaction among DEC, DMC and EMC discussed above. This reaction and the other ester exchange reactions may effect the physical properties of the electrolyte as well as the kinetics of electrode reactions and stability reactions. Further work in this area is obviously desirable.

Another series of measurements of the conductivities and viscosities of binary solvent mixtures with various salts is given in Ref. [31]. The conductivity values from this work are also included in Table 1. There are numerous discrepancies between the two papers, for example with EC:DEC and EC:DMC, so the reader should exercise due caution.

Finally, the topic of wetting will be considered. There are very few measurements of this property in the literature, yet it is of great importance in battery design. The EC:DMC solutions, for example, do not wet separators of the polyolefin type very well. This can have a drastic effect on the operation of the battery. This is true in spite of the fine porosity of the separator, which should give rise

to capillary wetting if the wetting angle is greater than zero. One must conclude that the wetting angle is less than zero in these cases. The cyclic carbonate ester solvents are highly polar liquids which are similar to water in many ways. In fact, PC and water are mutually soluble over the entire range of compositions. In general, one might expect that the solvents, and electrolyte solutions will be attractive to hydrophilic surfaces, such as cathode materials, and repulsive to hydrophobic ones, such as polyolefin separators and carbonaceous anode materials. This behavior is very different from the ether solvents usually used in lithium metal batteries. Simple wetting experiments with each component of the battery and the electrolyte of choice can provide useful information for cell design. The rate of spreading or absorption of electrolyte on the material surface is a good index of the wetting property. Contact angle measurements are very useful, but only if the surface of the bulk material to be measured is identical to the material of interest in the battery. Unfortunately, this is frequently not the case since processing of materials may cause changes in the chemical groups present.

5. Conclusion

The electrolyte phase is a key to the success of an advanced battery. It has been shown that the stability with anode and cathode materials is vital. The subtleties of the stability matters are considerable, however, and all of the methods of instrumental and chemical analysis are necessary to understand these properties. The conductivity and viscosity are also of interest, but do not present the challenge they did at one time, especially as cell design techniques have been devised to make up for deficiencies of organic solvent systems compared to aqueous ones. These techniques deal mainly with the high electrode area construction methods and manufacturing machinery.

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Appendix A

A common type of corrosion behavior is the parabolic type of film growth. This film thickness follows the law:

$$y^2 = kt + A, \quad (A1)$$

where k and A are constants, y is the film thickness and t is the time of exposure to the medium. The rate of film growth, dy/dt is proportional to the corrosion current,

Table 1
Recent values of conductivity for advanced battery electrolytes

Solvent mixture	κ_{\max}	Vol.% EC or PC at κ_{\max}
<i>Conductivity of 1 M LiPF₆ solutions in mS/cm</i>		
From Ref. [30]		
EC–DMC	10.6	33
EC–EMC	8.5	47
EC–DEC	7.6	58
From Ref. [31]		
EC–DMC	12	30
EC–DEC	8	80
EC–DME	19	40
PC–DMC	12	30
PC–DEC	7	70
PC–DME	19	20
<i>Conductivity of 1 M LiCF₃SO₃ solutions in mS/cm</i>		
From Ref. [31]		
EC–DMC	3	50
EC–DEC	3.5	~10
EC–DME	8	40
PC–DMC	2.2	50
PC–DEC	2	0
PC–DME	6	40

I_{corr} . The capacity loss due to the corrosion process is then given by:

$$Q_{\text{corr}} = I_{\text{corr}} t. \quad (\text{A2})$$

From Eq. (A1), the rate is given as:

$$dy/dt = k/2y. \quad (\text{A3})$$

Since the film thickness is equal to 0 at $t = 0$, A is 0 and:

$$dy/dt = k^{1/2}/t^{1/2} \quad (\text{A4})$$

and:

$$Q_{\text{corr}} = k' t^{1/2}. \quad (\text{A5})$$

Finally, since the cycle number, N , is proportional to time, the capacity loss as a function of cycle number is:

$$Q_{\text{corr}} = k'' N^{1/2} \quad (\text{A6})$$

Eq. (A5) explains the capacity loss on shelf as a function of time, while Eq. (A6) explains the capacity loss with cycling as a function of cycle number.

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