Liquid electrolytes for lithium and lithium-ion batteries

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Abstract

A number of advances in electrolytes have occurred in the past 4 years, which have contributed to increased safety, wider temperature range of operation, better cycling and other enhancements to lithium-ion batteries. The changes to basic electrolyte solutions that have occurred to accomplish these advances are discussed in detail. The solvent components that have led to better low-temperature operation are also considered. Also, additives that have resulted in better structure of the solid electrolyte interphase (SEI) are presented as well as proposed methods of operation of these additives. Other additives that have lessened the flammability of the electrolyte when exposed to air and also caused lowering of the heat of reaction with the oxidized positive electrode are discussed. Finally, additives that act to open current-interrupter devices by releasing a gas under overcharge conditions and those that act to cycle between electrodes to alleviate overcharging are presented. As a class, these new electrolytes are often called "functional electrolytes". Possibilities for further progress in this most important area are presented.

Another area of active work in the recent past has been the reemergence of ambient-temperature molten salt electrolytes applied to alkali metal and lithium-ion batteries. This revival of an older field is due to the discovery of new salt types that have a higher voltage window (particularly to positive potentials) and also have greatly increased hydrolytic stability compared to previous ionic liquids. While practical batteries have not yet emerged from these studies, the increase in the number of active researchers and publications in the area demonstrates the interest and potentialities of the field. Progress in the field is briefly reviewed.

Finally, recent results on the mechanisms for capacity loss on shelf and cycling in lithium-ion cells are reviewed. Progress towards further market penetration by lithium-ion cells hinges on improved understanding of the failure mechanisms of the cells, so that crucial problems can be addressed.

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1. Introduction

The author reviewed the progress in electrolytes for lithium and lithium-ion batteries at the 9th International Meeting on Lithium Batteries [1]. Since that time, a number of new approaches and advances have occurred that have led to important improvements particularly in lithium-ion batteries. In this paper, improvements in extended temperature operation, and the effect of additives in improving storage stability, lowering flammability and activating current interrupter devices during overcharge are all considered. The effects of tailored SEI layers for lithium metal systems and the relation to the electrolyte phase is also discussed as well as work done on lithium alloy systems. An indication of the increased interest in ionic liquids for lithium and lithium-ion (as well as sodium) batteries is the greatly increased level of publication using these electrolytes [2]. Perspectives in this area are given. Finally, the losses and failure mechanisms in lithium-ion cells and the cycle life and calendar life issues resulting are discussed. The view is a personal one and no

effort has been made to be comprehensive in coverage, but only to highlight what the author feels are the most important advances in the last 4 years.

2. Extended temperature operation for lithium-ion battery electrolytes

Much electrolyte work of the past several years has been devoted to extend the temperature range of battery operation. In particular, the limitations of commercial cells to low temperature operation have hampered the application to aerospace and military uses for these batteries. Many of the recent studies for low temperature aerospace uses have come from the US Jet Propulsion Lab. A recent paper highlights the state of the art for these electrolytes [3]. An electrolyte with 1.0 M $LiPF_6$ salt in 1:1:1 ethylene carbonate (EC); diethyl carbonate (DEC): dimethyl carbonate (DMC) gives good performance at $-20\,°C$ as well as good stability and performance at room temperature. Attempts to improve the performance to -30 and

40 °C, however, with addition of linear carboxylic acid esters, such as methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP) and ethyl butyrate (EB) were not highly successful. The lower molecular weight esters, EA and MA, give films on the negative electrode that are too resistive and insufficiently protective. The EP and EB gave more promising results as far as film impedance and SEI protection are concerned. However, their long chain structure gives poorer impedance behavior at 25 °C due to higher electrolyte viscosity and lower conductivity. This work is still in progress, but it should be noted that the starting composition is modified after the first cycle due to ester exchange reactions, and the properties must also be expected to change [1]. This fact severely complicates the interpretation of results on full cells of this type of work. The US Army has also carried out work on extending the temperature range of electrolytes. A recent paper has measured the conductivity for EC: ethylmethyl carbonate (EMC) of different compositions and different salt concentrations for a temperature range of −30 to +60 °C [4], which is the range of temperature interest for military applications. The same group has also made lithium-ion cells for low temperature studies that show the carbon electrode to be the limiting factor at low temperature. The impedance of the solid electrolyte interphase (SEI) is high and continues to grow during cell operation, possibly due to lithium deposition [5].

High-temperature operation has also been found to be a problem for lithium-ion cells. A Telcordia group has found that the SEI is unstable at temperatures as low as 70 °C in actual cells [6]. The SEI can reform, but is found to cause irreversible losses in the cell. Subsequent studies, for example by Andersson and Edstrom, have verified these findings and further analyzed the SEI film on graphite at elevated temperature [7]. Clearly, further work needs to be done to determine cell effects as well as better understanding of the SEI in the region of 70–80 °C.

3. SEI properties

The SEI plays the crucial role in all high-voltage batteries of providing a protective barrier against continued reaction of the electrolyte with the charged active material. Extensive studies have continued on the reactions of the negative electrode to form the SEI in addition to those mentioned above. Quantitative monitoring of the growth of the SEI by an NMR method was reported by Wang et al. [8]. An interesting study of the potential dependence of the growth of the SEI was made by Zhang et al. [9] using electrochemical methods (impedance and voltammetric studies) that showed the growth of the SEI occurred in two potential regions, above 0.25 V and between 0.25 and 0.04 V. The reduction of organic carbonates on inert electrodes was studied by electrochemical, infrared and atomic force microscopy [10]. The reduction potentials do not correspond to those found on graphite, but high quality infrared spectra were obtained from the reflective electrode surfaces that

should be useful for comparison to results on graphite. Very little work on alloy electrodes was found in the literature, and this lack of understanding may be part of the problem in development of this otherwise promising area.

The positive electrode is also understood now to form a "passivation" layer of the SEI type which allows electrochemical redox reactions of the active material to occur without further extensive participation of the electrolyte indirect reaction with the charged positive after the initial film formation. ^{7}Li NMR studies [8] and soft X-ray absorption studies [11] have confirmed the development of lithiated materials on the surface of the active material of the positive electrode. LiF was shown to be at least part of the film, while the latter study suggested that iron contamination of the positive electrode also occurred. The formation of anion intercalants has been known for many years in the ionic liquid field (where passivating films are unlikely to be formed) and with non-passivating solvents like nitromethane [12]. The absence of these intercalants in organic solvent systems strongly suggests that the layer forms on graphite conductor as well as the active material and also protects this surface.

4. New salts

LiPF$_6$ has been the standard salt from the onset of lithium-ion battery work. Unfortunately, this salt has very limited stability, even in totally nonaqueous systems, due to its spontaneous thermal degradation (see [13] for recent work on salt stability in lithium-ion electrolytes). Several new chelating boronate salts have been developed in recent years by the Barthel–Gores group in Germany, utilizing 6 and 7 member rings on either side of the boron atom [14]. The stability of these compounds has been validated recently by Sasaki et al. [15]. Another type of boronate salt with five member rings has been synthesized independently by Xu and Angell [16] and Lishka et al. [17]. These anions are all very weak Lewis bases which allows a very low degree of association of their salts even in moderately low dielectric solvents. Solution conductivities are therefore relatively high (of the order of 10^{-2} S/cm) in spite of the high molecular weight of the anion. The unsubstituted five member ring salt, given the name "LiBOB" by Xu and Angell, was tested in lithium-ion batteries and found to have good high temperature stability [18] as cells operated without electrolyte decomposition at 60 °C. At this point, the salt is relatively difficult to prepare and purify, but LiPF$_6$ was also difficult to purify in early work. This area of new salts may yield a new generation of more stable lithium-ion batteries.

5. Electrolyte additives

The field of electrolyte additives has been very active in the last several years. Additives have been sought to lower the flammability of electrolyte solutions under cell venting;

to limit the effects of overcharge by shuttling back and forth as a redox couple in the cell or by evolving gas to activate the current interrupter device (CID) and shutting off the cell current; and to improve the SEI. Each of these types will be considered in turn.

Another term for "low flammability" is "flame retarding". In effect, it is very difficult to find electrolyte soluble materials that can completely repress the development of flames in the presence of heat and spark or externally applied flame. The goal is rather to find materials that do not support continued combustion when the source of heat, spark or flame is withdrawn. This effect is generally accompanied by lowering the heat of reaction of the electrolyte with the charged negative and/or positive active materials. This is an important result in that a self-sustaining cell reaction may not occur under accidental heating due to external short circuiting or hot box conditions. Because flames generally require the presence of a chain reaction to be self-sustaining, the majority of workers have sought materials that are known chain breakers. This is also the search strategy of other flame retardant studies in industry and materials have been selected for the battery work that have already been found effective in other applications. Trimethyl phosphate (TMP) has been widely studied and recent work at Mitsubishi Chemical has given important results using this material. TMP has the tendency to cointercalate with lithium-ion into graphite, but the tendency can be minimized by using low levels of TMP [19] or by using disordered carbon negative active material [20]. A solution 1 M $LiPF_6$ in 30:30:20:20 EC:PC:DEC:TMP gave fairly good cycling with amorphous carbon negative electrode, low heat of reaction with charged material and performance at $-40\,°C$ as an unexpected benefit [20]. Prakash and his coworkers at IIT have found that hexamethoxycylcotriphosphazene (HMPN) has flame retardant behavior in solutions [21]. Recent work by Xu et al. [22] surveyed the effects of TMP, HMPN and triethyl phosphate (TEP), which is also a common flame retardant. They found that the TEP and HMPN do not tend to cointercalate and react with graphite and therefore give much better cycling in 1:1 EC:EMC solvent mixtures, especially when kept to lower levels. Cycling with HMPN can even be carried out at 70 °C. Because of high viscosity, however, a penalty in power capability was paid and the capacity utilization was not as high under normal cycling conditions as with the base electrolyte. Arai et al. have investigated trifluoropropylene carbonate as a flame retardant additive with some success [23].

Additives to deal with overcharging problems are of two types. The first type is the redox shuttle mentioned above. The material is generally oxidized to form a radical cation at the high voltage of the positive electrode, diffuses to the negative electrode where it is reduced to the neutral molecule and shuttles back to the positive electrode. Yoshino has described several of these materials patented in Japan, including veratrole (Sony), difluoroanisole (LG Chemical), bipyridyl (Sanyo) and biphenyl carbonate (Sanyo and Ube) [24]. Unfortunately, these materials are mainly useful at lower charge currents due to the limitations of solubility and material flux. Additives which cause activation of the CID by evolving gas on overcharge are more useful. According to Yoshino, cyclohexylbenzene (Ube patent) evolves hydrogen and has been in use in Japan for 2 years [25]. Biphenyl (Moli/NEC) and pyrocarbonate (SONY—evolves CO_2) have also been patented in Japan for this purpose [24].

Additives to improve the SEI include vinylene carbonate (SAFT and Sanyo), one of the most effective additives, and methyl cinnamate (NEC) [24,25].

6. Ionic liquids

Room temperature ionic liquids have been studied for a great many years, even in the attempted use of active metal anodes such as lithium or lithium alloys as well as lithiated carbon. The difficulty has been in the past to find examples of electrolytes with enough lithium-ion to allow high flux of lithium-ion through the electrolyte. A review of the recent literature by Webber and the author, in which such electrolytes are discussed, is now available [26]. A central problem which remains was alluded to above. The liquids are not prone to forming SEI layers on either the positive or negative electrode. Therefore, the systems are stable only at lower voltages (such as with aluminum negative electrodes) or with some kind of additive which can form protective films. No complete solution to this problem has yet been found, but only a few of the many possibilities from the organic solvent literature have been applied. It is likely that with continued work in the field, satisfactory solutions will be found. The ionic liquids are likely to be very good flame retardants and are likely to have very low heat of reaction with active materials resulting in enhanced safety. They also have very high ion concentrations, which should result in low concentration polarization.

7. Fade and calendar life

This area was discussed in the author's paper in IMLB9 [1] and models for lithium metal and lithium-ion capacity fade during cycling were presented. Lithium metal fade behaves with an exponential decay of capacity as a function of cycle life, but only after the metal excess has been exhausted. For lithium-ion cells, the capacity loss behaves predominantly with a square root behavior as a function of time (shelf decay) or cycle number (fade). The Saft group has developed this idea substantially (see [26]) and verified the corrosion mechanism (film growth) of the negative electrode as an important aspect of the capacity degradation. A factor discussed above, however, which is difficult to account for, is the effect of the growth of impedance due to failure of the positive electrode SEI. It is likely that this
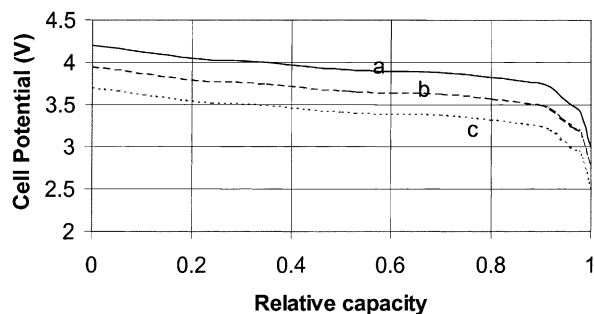
Fig. 1. Schematic discharge curve showing potential vs. relative capacity for initial discharge (a), after *N* cycles (b) and after 2*N* cycles (c). If the cut-off potential is 3 V, the loss of relative capacity after *N* cycles is less than half that of the loss after 2*N* cycles due to the downward curvature of the discharge curve.

factor is accelerating and only comes into play at longer cycle number. Fig. 1 shows schematically how the impedance growth can operate. The author has found that the mid-life potential decays in an approximately linear fashion with cycle life in many lithium-ion batteries. In this case, we can view the three curves in Fig. 1 as being initial (a), after a number of cycles, *N* (b), and after twice as many cycles, 2*N* (c). Note that the effect at cycle *N*, the middle curve, is rather small, while that at cycle 2*N* is much greater. Thus the effect is an accelerating one, which would not be noticed at lower cycle numbers. A functional form to describe the discharge curve is needed to carry this idea to the quantitative stage, but the qualitative behavior is exactly what is observed in many cells. Thus, a parabolic decay is the main initial feature in early cycling while later cycling an accelerating loss of capacity occurs with cycling that is not described at all by the parabolic law. This is particularly apparent in systems for which the presence of impurities aggravates the growth of impedance in the positive electrode by catalyzing electrolyte decomposition.

8. Conclusions

The electrolyte phase continues to occupy a central role in lithium-ion battery performance and stability. New salts and solvents are constantly under investigation and a number of new possibilities have been introduced in the last 4 years that may improve safety and performance. The role of additives to make up for the shortcomings of the electrolyte phase, particularly for problems with protective films at the positive and negative electrodes, is expanding rapidly and showing some success already. Continued study of interfaces and the effects of the electrolyte with and without additives is likely to result in superior lithium-ion batteries in the future.

Theoretical studies of degradation mechanisms will also play a significant role in improving the behavior of lithium-ion cells.

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