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Design of electrolyte solutions for Li and Li-ion batteries: a review

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Abstract

This paper reviews approaches to the design of advanced electrolyte solutions for Li and Li-ion batteries. Important challenges are wide electrochemical windows, a wide temperature range of operation, acceptable safety features, and most important, appropriate surface reactions on the electrodes that induce efficient passivation, but not on the account of low impedance. We describe research tools, quick tests, and discuss some selected examples and strategies for R&D of solutions of improved performance.
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1. Introduction

Li-ion batteries are one of the most successes of modern electrochemistry. These batteries, which became a commercial reality about a decade ago, are conquering the markets with increasingly wider applications [1–5]. Present challenges are to extend their use to high power and large size applications (e.g., propulsion, EV) [6–10]. The current systems use graphitic carbons as the anode material, $LiCoO_2$ as the major cathode materials, mixtures of alkyl carbonates including ethylene carbonate (a mandatory component for sufficient negative electrode passivation), dimethyl, diethyl, and ethyl-methyl carbonates (EC, DMC, DEC, EMC, respectively), and $LiPF_6$ as the electrolyte solution [1–10]. The alkyl carbonates were chosen due to their acceptable anodic stability for the 4 V cathodes used in Li-ion batteries, as well as lithiated graphite, together with other properties, such as high polarity (i.e., good conductivity of their solutions), a reasonable temperature range between freezing and boiling points, sufficiently low toxicity, and accept-

able safety features. The $LiPF_6$ salt is, to some extent, also a compromise. Other commercially available Li salts have too many disadvantages: $LiAsF_6$ is poisonous, $LiClO_4$ is explosive, $LiBF_4$ is problematic on the negative side (reactions of the BF_4^- anion on the anode's surface interfere badly with passivation), $LiSO_3CF_3$ forms solutions of too low conductivity, $LiN(SO_2CF_3)_2$ and $LiC(SO_2CF_3)_3$ are problematic on the cathode side—the aluminum current collector currently used for the positive electrodes is not well passivated in the solutions and corrodes [11]. $LiPF_6$, the compromised salt, decomposes to LiF and PF_5, and the latter readily hydrolyzes to form HF and PF_3O [12]. These two hydrolysis products are highly reactive on both the negative and positive sides, and their unavoidable presence in $LiPF_6$ solutions has a detrimental impact on the electrodes' performance [13].

Li-ion battery systems have a very limited performance at elevated temperatures, and their cycle life is also limited, due to surface phenomena on both electrodes that increase their impedance upon cycling [14]. The safety features of commercially produced Li-ion batteries are not sufficient for large size applications [15,16]. Hence, in recent years we have seen intensive efforts to introduce new solvents, salts and additives that may lead to improvements in the performance

of these systems. As examples for new solvents, we should mention organo sulfur compounds, such as propylene sulfite [17], fluorine-substituted compounds (e.g., fluoro alkyl carbonates [18]) and organo phosphorous compounds [19]. As new salts we mention Li bis (oxalato)borate (LiBOB) [20] and $LiPF_3(C_2F_5)_3$ (LiFAP) [21,22]. In addition to these salts, we should mention a wide variety of attempts to introduce new additives to the electrolyte solutions, including organo nitrates [23], sulfates [24], phosphates [25], active gases, such as SO_2 [26] and CO_2 [27], organoboran complexes [28], surface polymerizable agents, such as olefins [29], vinylene carbonate [30], aromatic compounds as over-charge protection agents (by a shuttle mechanism, e.g., biphenyl) [31] and more.

The aim of this paper is to provide some guidelines for R&D of new, improved electrolyte solutions for Li and Li-ion batteries, to suggest quick reliable tests, and to provide some new examples from our recent studies.

2. Experimental

We obtained standard solutions, including EC–DEC–DMC, EC-DMC and EC-DEC with $LiPF_6$ 1 M from Merck (Selectipure series, which could be used as received). LiFAP solutions were obtained from Merck. We used commercial graphitic and $LiCoO_2$ electrodes from LG. Experiments were carried out in glove boxes from VAC and MBrown. The tools for these studies included FTIR (Nicolet-Magna 860, glove box operation, grazing angle reflectance, and diffuse reflectance attachments), XPS (HS-Axis Kratos), ARC (Arthur de Little), DSC (Mettler), NMR (Bruker), XRD (Bruker), and standard electrochemical tools (EIS, SSCV, CV, PITT, galvanostatic cycling) with equipment from Solartron, Eco Chemie, EG&G, Maccor, and Arbin. Measurements were performed in home-made thermostats at a temperature range 25–80 °C. (See references 13, 14, 22, 27, and 30 for details on the experimental aspects).

3. Results and discussion

The present arsenal of solution components that can be produced at high enough purity and reasonable prices includes three families of solvents, namely, ethers, esters, and alkyl carbonates, and salts from the following list: $LiPF_6$, $LiBF_4$, $LiN(SO_2CF_2CF_3)_2$, (LiBETI), $LiBC_4O_8$ (LiBOB), $LiPF_3(CF_2CF_3)_3$ (LiFAP), and $LiN(SO_2CF_3)_2$ (LiTFSI). When selecting electrolyte solutions for battery application, the key features to look at are:

1. Evaluation of transport properties: what influences conductivity and what parameters should be measured in order to evaluate the solvents properly.
2. The electrochemical stability, i.e., the electrochemical window.

3. Temperature range of operation.
4. Safety features.

Evaluation of solution properties related to transport phenomena (conductivity, diffusion) has been dealt with thoroughly in the literature. In general, important parameters that were developed include donor and acceptor numbers, and solvatochromic response (e.g., ET30), in addition to trivial parameters, such as dielectric constant and dipole moment [32] (see detailed discussion in Refs. [33,34]). In general, high solvent polarity usually goes together with strong solvent-solute interactions. This means good solubility, but also high viscosity and high friction for ionic mobility as well. Hence, mixtures of solvents of high polarity and high viscosity with solvents of low polarity and low viscosity may provide optimal conductivity of Li salts (e.g., alkyl carbonates plus ethers or esters) [35]. In this respect, the salt concentration should also be optimized, since too high a salt concentration means a high concentration of charge carriers, but strong solvent–solute and solute–solute interactions that may be detrimental to high conductivity (see discussion and examples in Refs. [33–35]).

The next points for discussion are the electrochemical windows of electrolyte solutions for Li-ion batteries. Fig. 1 shows schematically a summary of EQCM and voltammetric studies of a typical Li-salt/alkyl carbonate solution ($LiClO_4$/PC in this particular case) with a noble metal working electrode (Au in this case) [36]. Major irreversible processes of interest are solvent oxidation of potentials >3.5 V (Li/Li$^+$), trace oxygen reduction (around 2 V versus Li/Li$^+$), trace water reduction (around 1.5 V versus Li/Li$^+$), and gradual, continuous solvent and salt anion reduction at potentials below 1.5 V (Li/Li$^+$). Other reversible processes, such as gold oxidation or Li UPD, which also appear in the scheme, are irrelevant to our discussion.

The study of the electrochemical windows of the Li battery electrolyte solutions by both us and by others can be summarized as follows:

1. The order of oxidation potentials is alkyl carbonates > esters > ethers. The oxidation of the solvents is usually the limiting anodic reaction.
2. In fact, even solvents of apparent relatively high anodic stability, such as alkyl carbonates, undergo slow scale anodic reactions on noble metal (Au, Pt) electrodes at potentials below 4 V versus Li/Li$^+$ [37]. Nevertheless, these solvents are stable with 4 V cathodes ($LiNiO_2$ $LiCoO_2$, $LiMn_2O_4$, etc.), whose charging potentials may reach 4.5 V (Li/Li$^+$), due to passivation phenomena. The commonly used 4 V cathodes react with solution species and become covered by surface films [38]. These surface films seem to inhibit massive solvent oxidation at potentials below 4.5 V. Consequently, alkyl carbonate solutions may be stable with cathode materials at potentials as high as 5 V [39]. Any negative electrode that operates at potentials below 1.5 V (Li/Li$^+$) should react with solution species and become covered by surface films comprising insoluble Li
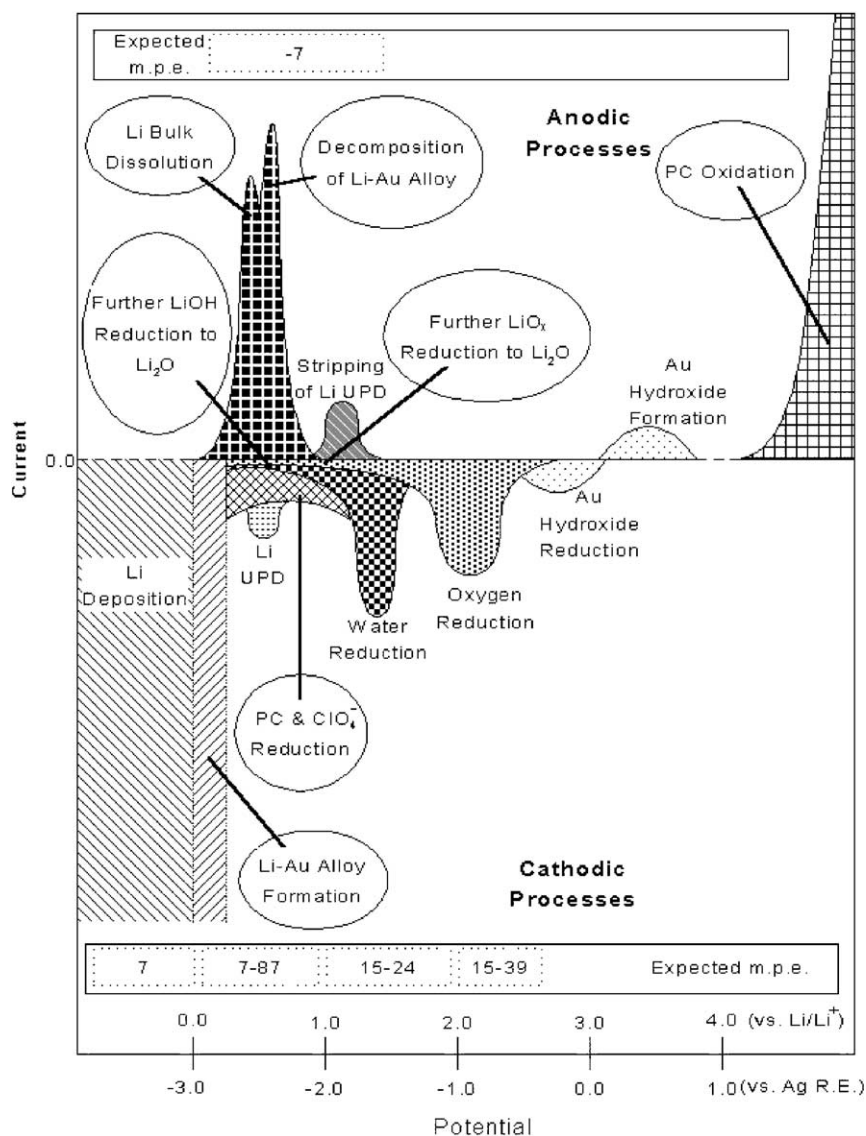
Fig. 1. A schematic presentation of the voltammetric behavior of an alkyl carbonate/Li salt solution with a noble metal electrode, studied by EQCM and spectroscopy [36]. The various processes are sketched as peaks or waves, as they appear in the voltammograms. The m.p.e. numbers listed are the theoretical mass per electron values expected for the various surface film formation processes (EQCM) [36].

salts. Hence, Li or Li–C electrodes are obviously covered by surface films and should be defined as SEI electrodes [40]. Therefore, negative electrodes that operate at potentials >1.5 V (e.g., Li_xTiO_y compounds) [41] may not be controlled by surface films.

3. High oxidation potential requires a high oxidation state of the solvents' atoms are good for cathodes, e.g., alkyl carbonate solvents. However, the high oxidation state of the solvent atoms means high reactivity at the negative side. As a result, with highly reactive anodes, such as Li metal-based systems, low oxidation state solvents/systems (e.g., ethers, PEO derivatives) should be used. This means a penalty on the positive side: with ethers/PEO derivatives one cannot use 4 V cathodes. Thus, with Li metal-based systems cathodes, such as V_2O_5, MV_2O_5 (bronze), 3 V

Li_xMnO_2, etc. should be used, which are compatible with ethers and PEO derivatives.

The next point for discussion relates to electrolyte solutions for Li (metal) electrodes. The behavior of Li electrodes was intensively studied over the years (see for example, Refs. [42,43], and other references therein). Li electrodes are always covered by spontaneously formed surface films comprising insoluble Li salts, which are products of reduction of solution species by the active metal.

Since, the surface films on lithium are comprised of Li salts, they are not sufficiently flexible to accommodate the changes on the active metal surface/volume during Li deposition–dissolution. Moreover, the surface films are very non-uniform on the microscopic and nanoscopic level. The

surface films on Li have a multilayer structure and laterally they are mosaic-like, comprising different clusters of compounds, including Li salts, polymeric species, etc [42]. Hence, there is no way that Li deposition-dissolution can be uniform. In most of the electrolyte solutions, Li deposition is dendritic. Therefore, most of the commonly used electrolyte solutions, i.e., esters, ethers, alkyl carbonates with $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiN(SO_2CF_3)_2$, etc. are not suitable for rechargeable Li batteries with Li metal anodes. There are only a few electrolyte solutions in which Li deposition is not dendritic. One of them is $LiAsF_6$/1-3 dioxolane, stabilized with a tertiary amine [44], in which Li is deposited in a flake-like formation. However, even solutions in which Li deposition is not dendritic, are not suitable for rechargeable Li batteries, because Li passivation can never be hermetic. Hence, if the charging rates of the Li anodes are not very low (C/9–C/12), Li is deposited in small grains, which unavoidably react with solution species due to their high surface area. Consequently, there is a continuous depletion of the electrolyte solutions in practical rechargeable Li batteries whenever operated at practical charging rates (rate > C/3h), due to reactions between the solution components and high surface area Li deposits[44].

Over the years we have worked on Li surface modifications, using Li–Al, Li_3N, Li–Mg, and Li–Ga surface alloys [45]. We also tested additives including alkenes and alkanes, surfactants, polymerizable agents, and active gases (CO_2, SO_2, N_2O). The solvents that we tried included ethers, alkyl carbonates and esters, while the salts included: $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiC(SO_2CF_3)_3$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, LiBr, and LiI. We concluded that there is no future for Li (metal) secondary batteries containing liquid solutions either because of dendrite formation, which means severe safety problems, or because of short cycle life if the charging rates are too high, since the solution disappears by reacting with Li deposits [44].

We foresee the future of rechargeable Li batteries in the use of PEO-based solid electrolytes at elevated temperatures. It should be noted that with gel electrolytes, the surface chemistry of lithium electrodes is dominated by reduction of the solvents (usually alkyl carbonates) that are used as plasticizers [46]. Thereby, similar problems of poor passivation of Li electrodes may be encountered with gels, as is the case with liquid solutions. In the case of PEO-based electrolytes, the Li surface chemistry may be affected mostly by salt anion reduction [47]. However, in spite of the fact that Li attacks ethers and surface ROLi species are formed [47], the Li/PEO-based electrolyte interface is relatively stable and Li electrodes may behave very reversibly when in contact with electrolyte systems based on derivatives of PEO.

The next subject is the effect of temperature. There are three separate issues to be dealt with.

1. The temperature range of operation primarily relates to physical properties, such as freezing, boiling, and conductivity. It should be noted that high boiling points may go together with high polarity, viscosity, and high freezing points (e.g., as with cyclic alkyl carbonates, EC, PC), while low freezing points may go together with high volatility and low boiling points (esters, ethers, linear alkyl carbonates). It appears that relatively high temperature ranges can be obtained with standard alkyl carbonate solutions comprising ternary mixtures, e.g., EC–DEC–DMC [48]. In general, the use of ternary and quaternary mixtures of alkyl carbonates, and alkyl carbonates with esters, allows the attainment of an impressive temperature range of operation and extends the applicability of Li batteries to very low temperatures ($<-30\,^\circ$C) [48].

2. There is a pronounced effect of elevated temperatures on the electrodes' performance. The electrodes' surface chemistry depends on the temperature. At elevated temperatures, the electrodes' passivation may be lost (see later discussion).

3. As the temperature increases, safety issues emerge, i.e., thermal runaway, dangerous electrode-solution interactions, etc. These points are dealt with below.

Safety issues regarding Li and Li-ion battery systems have been intensively dealt with in recent years [49,50]. When dealing with safety there are many subjects to consider, including flammability, short circuit, overcharge and overdischarge, dangerous heat dissipation, thermal runaway due to red–ox reactions of the electrolyte solutions, and thermal runaway/explosion due to electrode/solution interactions at elevated temperatures. The flammability of the commonly used electrolyte solutions was dealt with in recent years, and organophosphorous compounds [19] and fluorinated compounds [18] were suggested as co-solvents in order to decrease flammability. However, when designing any new electrolyte solution for these batteries, one should remember that all electrolyte solutions in Li and Li-ion batteries are reactive with the electrodes. The key factor for battery performance is a surface chemistry that leads to a sufficient passivation with good Li-ion transports at the electrodes' surface. All the other factors should be considered after this first condition is fulfilled. Hence, any introduction of a new co-solvent should involve a rigorous study of its impact on the electrodes surface chemistry, especially at elevated temperatures.

When dealing with safety features, critical issues are possible thermal runaway scenarios for Li-ion batteries. Most of the electrolyte solutions for Li batteries are comprised of red–ox couples, with the solvent as a reductant and the salt as an oxidant. Hence, Li battery electrolyte solutions may undergo self-heating processes in which pressure is developed and heat is liberated. Fig. 2 shows as an example results of thermal studies of $LiPF_6$ and $LiPF_3(C_2F_5)_3$ (Li-FAP) solutions, using accelerating rate calorimetry (ARC) [51]. This figure shows self-heating rates versus the temperature of $LiPF_6$, LiFAP, and $LiPF_6$–LiFAP solutions in EC–DEC–DMC mixtures, measured by ARC. As seen from this figure (upper part), $LiPF_6$ solutions have a relatively low onset for thermal reactions ($<200\,^\circ$C). LiFAP solutions have
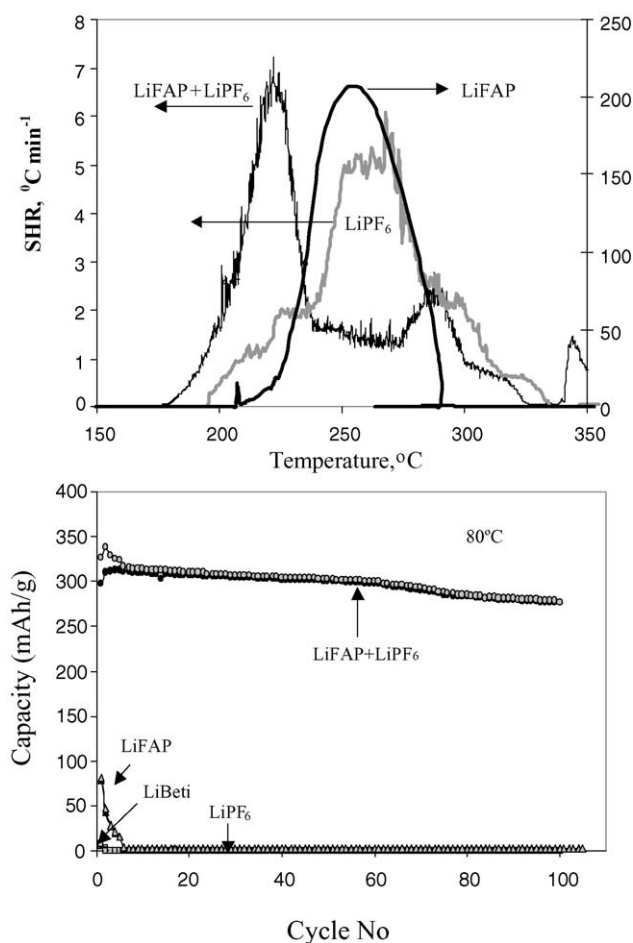
Fig. 2. Self-heating rates of 1 M LiPF$_6$, 1M LiPF$_3$(C$_2$F$_5$)$_3$ (LiFAP) and 0.5 M LiPF$_6$ + 0.5 M LiP(F$_3$C$_2$F$_5$)$_3$ solutions in EC–DEC–DMC (2:1:2) in ARC experiments (upper chart). Specific capacity vs. cycle number measured in galvanostatic processes (C/10) of graphite electrodes (vs. Li electrodes) at 80 °C with LiPF$_6$, LiPF$_3$(C$_2$F$_5$)$_3$, LiN(SO$_2$C$_2$F$_5$)$_2$ (Li Beti), and LiPF$_6$–LiFAP solutions (EC–DEC–DMC, 2:1:2).

a higher onset (>200 °C), but their self-heating rate is very high.

It was interesting to discover that solutions containing both LiFAP and LiPF$_6$ behave differently from the single salt solutions, as can be seen in the figure. It was also interesting to discover that while all the single salt solutions that we tested cannot be suitable for graphite electrodes at elevated temperatures, graphite electrodes behave highly reversibly with LiPF$_6$–LiFAP solutions at elevated temperatures (80 °C), as is also seen in Fig. 2 (lower chart). The special properties of these solutions are currently being investigated. In addition to the red–ox reactions of the solutions, which lead to self-heating phenomena, as demonstrated in Fig. 2, Li salt/alkyl carbonate solutions react vigorously at elevated temperatures with both lithiated graphite and delithiated cathode materials (e.g., Li$_x$CoO$_2$ (x <0.5) [52,53].

At elevated temperatures, the passivation of graphite electrodes is destroyed, and hence the lithium stored in them can react directly with solution species. Delithiated cathodes

can oxidize the alkyl carbonates at elevated temperatures in exothermal reactions. Hence, any R&D of electrolyte solutions for Li batteries has to include calorimetric studies in order to map both the internal thermal red–ox reactions of the solutions (solvent/salt) and their high temperature reactions with the electrodes.

After the above review, the following question arises. How do we optimize solutions for Li-ion batteries? It should be noted that the commonly used solutions (e.g., EC–DEC–DMC, etc. and LiPF$_6$) are a compromise!

The problems with these standard solutions include: HF contamination, which worsens passivation and induces capacity fading (cathodes), the use of DEC in the mixtures for low T conductivity worsens passivation and thermal stability, and the high temperature performance of these solutions is poor (capacity fading). In addition, these solutions are flammable and their electrochemical window may be limited to 4.5 V.

It is difficult to foresee a major revolution in the arsenal of solvents for Li-ion batteries. We do not see any reasonable substitutes for the alkyl carbonate solvents that are currently in use. There are alternatives to LiPF$_6$ that mostly include, LiPF$_3$(C$_2$F$_5$)$_3$ (LiFAP)[22] and LiBC$_4$O$_8$ (LiBOB) [20]. The former is still too expensive, while the latter is still being examined in several laboratories. We should note that the electrode–solution systems in Li-ion batteries are very complicated. By the introduction of a new component, one may gain in one aspect, but lose in another. We emphasize that the surface chemistry of the electrodes in solutions is the critical factor.

We suggest that the cheapest and easiest way to improve the performance of currently used electrolyte solutions for Li-ion batteries is by the use of surface reactive additives (at low concentration in solutions) that can react predominantly on the electrodes' surfaces and form highly protecting surface films, which are stable at elevated temperatures.

During recent years, we have been studying several families of additives that could improve the performance of Li-ion battery systems. These include pyrocarbonates, dicarbonates, strain organic compounds, and organo silicon compounds. A key question here is how to test the impact of additives in the most efficient way. One approach may be to use electrolyte solutions in which graphite or LiCoO$_2$ electrodes show low performance, and to demonstrate how additives improve the electrodes' behavior. We, however, prefer another approach, where the reference solutions are all standard commercial solutions, and the tests are designed to demonstrate how the performance of a standard solution is improved by the use of certain additives. Fig. 3 shows typical results from such testing. Coin-type cells comprised of graphite and LiCoO$_2$ electrodes at the appropriate balance and a standard EC–EMC/1 M LiPF$_6$ solution were cycled at 60 °C. This temperature is too high, and cells containing standard solutions fail very rapidly, as shown in the figure. However, when we added some selected organo silicon compounds (still proprietary, denoted as additives 1 and 2) to the solution at relatively
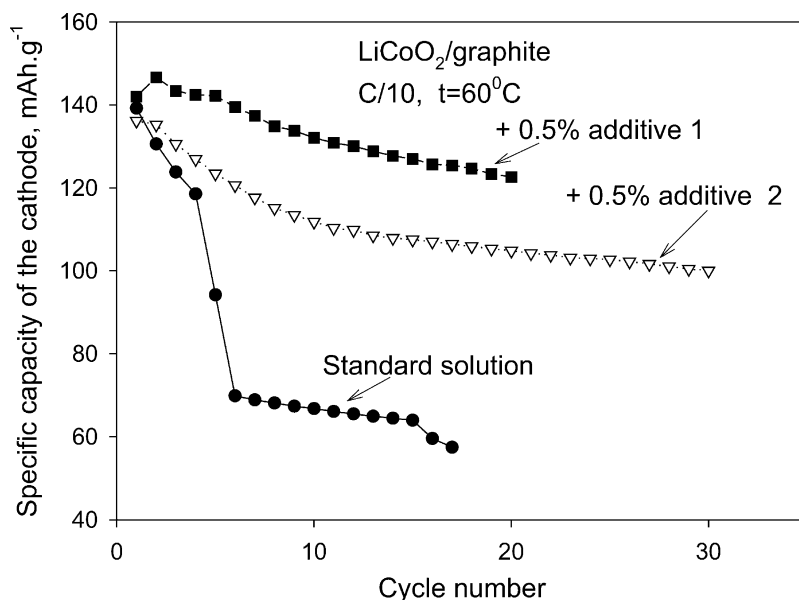
Fig. 3. Specific capacity vs. cycle number measured with coin-type cells containing $LiCoO_2$ and graphite electrodes and EC–EMC/1 M $LiPF_6$ solutions, additive-free and with small amounts (% by weight indicated) of additive 1 from organo siloxane family and of additive 2 from alkoxysilanes (still proprietary), as indicated. 60 °C, galvanostatic cycling at C/10 rates.
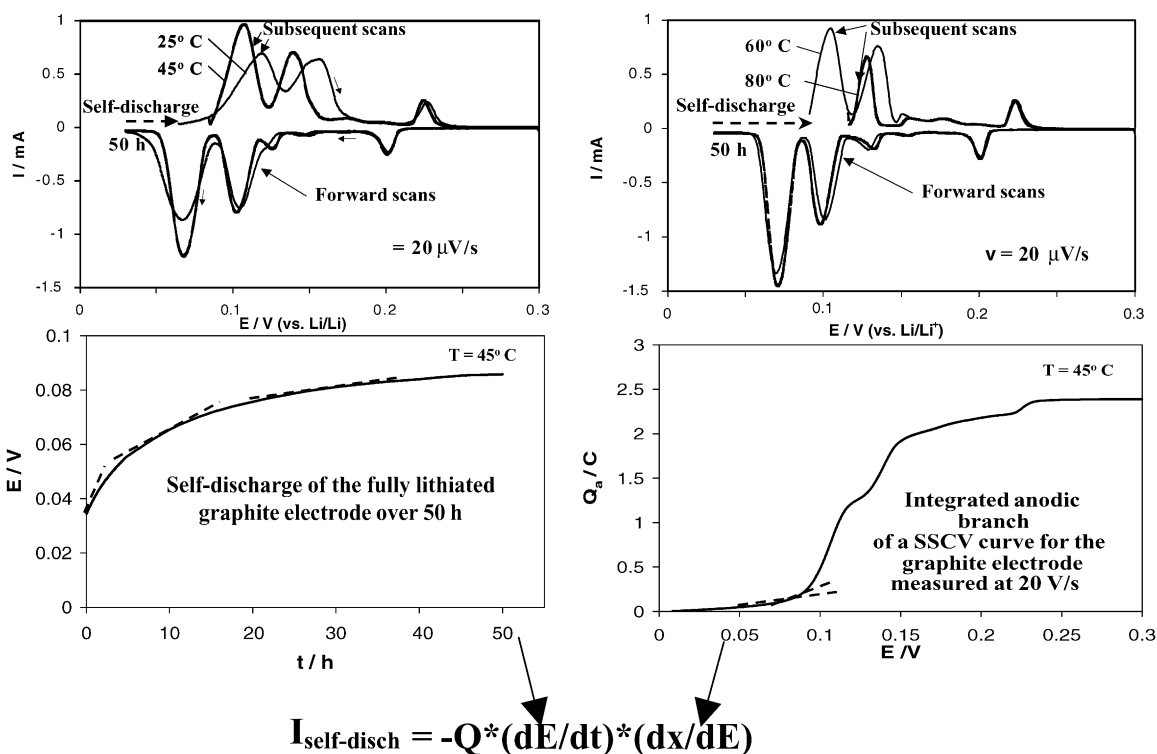

$$I_{\text{self-disch}} = -Q*(dE/dt)*(dx/dE)$$

Fig. 4. Description of self-discharge experiments and calculation of self-discharge currents with graphite electrodes in EC–DMC/$LiPF_6$ solutions at different temperatures (indicated). Graphite electrodes were stabilized and fully lithiated by slow scan rate voltammetry, and were then stored for 50 h at the temperatures indicated, followed by delithiation (by anodic, slow linear potential scan). Upper charts: The relevant cyclic voltammograms of the lithiation–storage–delithiation experiments. Lower charts: A typical plot of OCV vs. t of a graphite electrode upon storage (45 °C) from which dE/dt is calculated, as illustrated (left), and a plot of Q (the electrodes' accumulative charge) during delithiation of the fully lithiated electrode, obtained by integration of the anodic voltammogram (I vs. E, t), from which $Q(dx/dE)$ is calculated.

low percentage (indicated), the performance of the cells improved considerably in terms of both specific capacity and stability, as demonstrated in Fig. 3. It should be noted that the impact of organo silicon compounds is both on the solution bulk (scavengers of problematic contaminants) and on the electrodes' surface. This impact is currently being studied. Hence, we suggest a basic approach in which surface active additives are examined in tests at elevated temperatures, in which the electrodes/cells usually fail. If the additive prevents this failure at high temperature, it provides a relatively quick indication that the modified solution is worth further investigation and optimization.

When using such tests, we recently found that the use of pyrocarbonate and dicarbonate solvents as additives, considerably improves the performance of both graphite and LiCoO$_2$ electrodes at elevated temperatures [54].

The last point dealt with in this paper also relates to significant tests for new solutions that can provide a sufficiently good indication on the performance of modified solutions. We propose a new testing approach that measures long-term impact in terms of self-discharge current. This approach is described in Fig. 4, which provides data of graphite electrodes tested in standard EC–DMC/LiPF$_6$ solutions at different temperatures (three-electrode coin-type cells). This figure shows typical slow scan rate voltammograms of graphite electrodes that were stored for 50 h at a fully lithiated state. The anodic branch of the voltammograms was measured after storage. It is clear from the charts that as the temperature is higher, more stored lithium is lost. The anodic voltammograms measured after storage starts at higher potentials. The self-discharge current is $I_{s.d} = |Q|(dE/dt) \times (dx/dE)$ where $|Q|$ is the total electrode capacity, dE/dt is the derivative of potential with time (measured during storage by the continuous changes in the OCV) and dx/dE is the derivative of the intercalation level ($O < x < 1$, Li$_x$C$_6$) with potential, calculated by integrating the slow scan rate CV curve of the electrode. Both relevant measurements and calculations are also illustrated in the figure. We found that the self-discharge current of graphite electrodes measured during their storage in various solutions at different temperatures can serve as a very good measure for their performance, and can be used as a significant parameter for comparison among different electrolyte solutions.

4. Conclusions

The major challenges in R&D of improved electrolyte solutions for Li-ion batteries are to obtain high anodic stability for 5 V systems, to improve low T conductivity and high T performance with minimal capacity-fading, and to improve safety features, meaning no thermal runaway and no flammability. The key behavior factor is the electrodes' surface chemistry: good passivation at a wide temperature range. We do not foresee a possible revolution with the currently used alkyl carbonate solvents, There are suggestions for new salts, e.g., a combination of LiPF$_6$ + LiPF$_3$(CF$_2$CF$_3$)$_3$ is promising (sur-

face and solution bulk effect), as well as the new LiBOB salt. The easiest, cheapest and most effective route for the improvement of the currently used electrolyte solutions is the use of surface-active additives. However, it is important to carry out reliable tests for new solutions. We suggest tests at elevated temperatures and measurements of self-discharge currents during storage as a suitable basis for the selection of new additives that improve the electrode/solution interactions.

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