

On the influence of additives in electrolyte solutions on the electrochemical behavior of carbon/LiCoO₂ cells at elevated temperatures

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Abstract

In this paper, we studied the influence of some organic additives in electrolyte solutions based on alkyl carbonate mixtures and LiPF₆ on the charge–discharge cycling characteristics of Li-ion cells at elevated temperatures (up to 60 °C). These additives were tested in relation to their impact on the electrochemical responses of both lithium–carbon and lithiated cobalt oxide electrodes. The additives chosen belong to organic compounds such as siloxanes, strained olefins, alkoxysilanes, and vinyl ethers. The main findings are as follows: the impedance of carbon and LiCoO₂ electrodes is smaller in solutions containing additive AD1 (hexamethyldisiloxane) from the siloxane family. Both Li/LiCoO₂ and carbon/LiCoO₂ cells exhibited much more stable charge–discharge cycling at 60 °C in the siloxane-containing solutions than in additive-free solutions. XPS analysis of LiCoO₂ electrodes cycled in the solution containing the additives indicated that their surface chemistry is strongly modified by the presence of siloxanes, even at low concentration.

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1. Introduction

One of the simplest ways to further improve the cycling behavior and stability of Li-ion batteries, especially at elevated temperatures, is by the use of inorganic or organic additives in electrolyte solutions. According to their specific impact, these additives can reduce the electrodes' interfacial resistance and better passivate their surfaces. Some additives act as water and HF scavengers, as anion receptors, or as flame-retardants [1–4]. Surface-reactive additives may extend the temperature range of application of Li-ion batteries by improving the electrodes' passivation at high temperatures. A detailed review and analysis of recent advances in using additives in solutions for Li batteries has appeared in a paper by Blomgren [5]. It was emphasized that the high-temperature cycling behavior of Li-ion cells, as well as their storage stability, still remained important problems to be solved. In this respect, suitable reactive ad-

ditives in solutions can stabilize the surface films developed on the electrodes, reduce the irreversible capacity, promote long-term cycling of batteries, and improve their capacity retention upon storage [6–9].

The goal of the present work was to study the influence of some organic additives in electrolyte solutions based on alkyl carbonate mixtures and LiPF₆ on the charge–discharge cycling characteristics of Li-ion cells at elevated temperatures (up to 60 °C). We examined the behavior of several additives belonging to different families of organic compounds. These included siloxanes, strained olefins, alkoxysilanes, and vinyl ethers. The investigation included a vast matrix of voltammetric, chronopotentiometric, and impedance measurements, as well as surface reactions studies of individual electrodes in Li/carbon, Li/LiCoO₂ cells and full cells (carbon/LiCoO₂) at 60 °C. The impact of the presence of these additives on the behavior of Li-graphite and LiCoO₂ electrodes was explored. In this paper, we show the results related to additives in EC-EMC/LiPF₆ solutions. The main focus was on a specific additive denoted as AD1 (hexamethyldisiloxane) from the siloxane family.

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2. Experimental

Electrochemical three-electrode cells consisted of lithiated cobalt oxide LiCoO_2 or composite mesocarbon microbeads MCMB, and mesocarbon fibers MCF (all from LG Chem.) as working electrodes, and Li foil as counter electrodes assembled in a polyethylene rectangular container (flooded cells) [10]. Cells including both LiCoO_2 and Li–C electrodes were also investigated. A lithium chip served as the reference electrode. The electrolyte solution (Li-battery grade, Merck KGaA) was a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC), 1:2 w/w and 1 M LiPF_6 . The concentration of HF in solutions was about 30–50 ppm. We also used three-electrode (LiCoO_2 or Li–C and lithium R.E. and C.E.) and two-electrode (carbon/ LiCoO_2) cells in a coin-type 2325 configuration for electrochemical tests at 60 °C. The active mass of the carbon and the LiCoO_2 electrodes was 13.6 and 27.3 mg/cm^2 , respectively. The accuracy of determination of electrodes' capacity was around 90–95%. Solutions containing organic additives (0.1–1.0%, by weight) were prepared in a glove box (VAC Inc.) filled with purified argon (the oxygen and water levels were less than 5 ppm). All organic additives used in this work are commercially available, non-toxic, and inexpensive. Their purity was not less than 98–99%. Cycling tests of electrochemical cells containing an additive-free solution or solutions with additives were performed several times with each concentration of the additive.

LiCoO_2 electrodes free of carbon black and PVdF binder were prepared by pressing LiCoO_2 powder (average particle size of 8–10 μm) spread on both sides of an aluminum foil (0.15 mm) at 15 000 psi by a hydraulic press. Prior to the electrode preparation, the Al foil was treated with a glass paper, rinsed with pure ethanol and cleaned in an ultrasound bath. The electrodes were dried overnight in vacuum at 100 °C.

Electrochemical experiments included fast and slow scan rate cyclic voltammetry, impedance spectroscopy (multi-channel CellTest system 1470 and frequency response analyzer 1255 from Solartron Analytical driven by the Corware and Zplot software from Scribner Associates), and galvanostatic cycling at a C/10 rate using a Maccor-2000 battery tester. The impedance measurements were performed at OCV potentials after stabilizing the electrodes by several voltammetric cycles. The a.c. frequency range used was 100 kHz to 5 MHz, with 3 mV perturbation. All potentials are given versus Li/Li^+ . X-ray photoelectron spectroscopy (XPS) tests of LiCoO_2 electrodes were performed with the HX Axis system from Kratos, Inc., England.

3. Results and discussion

In Fig. 1a, we present the typical voltammetric behavior of composite MCMB + MCF electrodes at 60 °C in several electrolyte solutions (additive-free solutions and

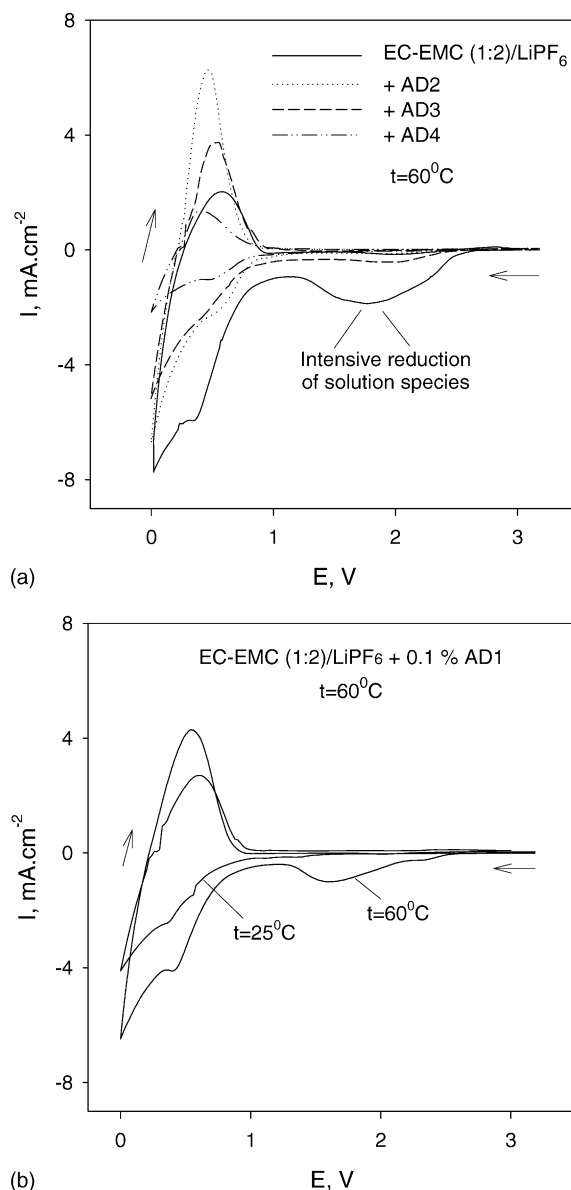


Fig. 1. (a) First cyclic voltammograms obtained at 60 °C from MCMB + MCF electrodes in an additive-free EC-EMC (1:2)/ LiPF_6 solution and in solutions containing 0.1% of AD2 (bicyclo[2.2.1]hepta-2,5-diene), AD3 (tetraethyl orthosilicate), and AD4 (ethylvinyl ether), as indicated. Experiments were performed in flooded cells, and potential scan rate was 2 mV/s. (b) First cyclic voltammograms obtained at 25 and 60 °C from MCMB + MCF electrodes in an EC-EMC (1:2)/ LiPF_6 solution containing 0.1% of AD1 (hexamethyldisiloxane). Flooded cells, potential scan rate 2 mV/s.

those containing some organic additives denoted as AD2 (bicyclo[2.2.1]hepta-2,5-diene), AD3 (tetraethyl orthosilicate), and AD4 (ethylvinyl ether) from the following families: strained olefins, alkoxysilanes, and vinyl ethers, respectively). Fig. 1b represents first cyclic voltammograms obtained from carbon electrodes in a solution containing AD1 (hexamethyldisiloxane) at 25 °C and 60 °C. The charge involved in irreversible reactions at 60 °C in a solution containing this additive is approximately twice as low as that in

an additive-free solution (Fig. 1a). It was established that the carbon electrodes stabilize faster upon repeated initial cycling and demonstrate higher anodic and cathodic capacities during cycling in solutions containing AD1. Typically, in a standard (additive-free) EC-EMC/LiPF₆ solution, the electrode consumes a relatively high amount of charge, which can be attributed to the reduction of all the solution species (EC, EMC, PF₆⁻, traces of HF and H₂O). It was found that at temperatures below 45 °C, stabilization of carbon electrodes in additive-free solutions may be reached within a single voltammetric cycle, but at higher temperatures, it is difficult to passivate the carbon electrode, which can be stabilized only after a number of repeated cycles (potential scan rate in the order of 1 mV/s or less) or by prolonged polarization to 0.0 V (Li/Li⁺) [11]. As follows from the data shown in Fig. 1a and b, the presence of some additives in the electrolyte solutions inhibits massive irreversible processes of the carbon electrodes during the first cycle. In addition, they lead to a better stabilization and improved passivation of these electrodes at elevated temperatures. With the use of some of the additives studied in this work, both inhibition of the reduction of solution species and improved cycling behavior at 60 °C could be obtained. These specific additives belong to siloxanes (AD1) and strained olefins (AD2) families. In contrast, additives from the alkoxy silane family (e.g., AD3, tetraethyl orthosilicate) do not help to stabilize the carbon electrode at 60 °C, as is clearly seen in Fig. 2a. We have found that the charge connected to irreversible reactions was relatively small, and the carbon electrodes stabilized sufficiently quickly when they were cycled at 60 °C in solutions containing vinyl ethers additives (e.g., AD4, ethylvinyl ether), as demonstrated in Fig. 2b. However, in the latter solution, composite MCMB + MCF electrodes develop higher impedance, and the galvanostatic cycling behavior is worse than in an additive-free solution. Note that the results presented in Figs. 1a,b and 2a,b relate to relatively small concentrations (0.1% by weight) of additives in solutions. These results clearly demonstrate that the proper choice of specific additives or their combination should depend upon various electrochemical responses of the electrodes, including the irreversible charge, the quality of passivation (expressed by the level of stability upon storage), the stability upon cycling, and the electrodes' impedance. In addition, the impact of additives on the bulk properties of solution (conductivity, viscosity, etc.) should be taken into account, especially when high concentrations of additives are needed to obtain a considerable impact on the electrodes' surface properties. Hence, one should compromise in order to optimize the characteristics relating to solutions properties, the electrodes' stabilization (protective surface films), their interfacial properties (impedance), and cycling behavior at high temperatures.

Fig. 3 compares slow potential scan rate voltammetric behavior (at 60 °C) of carbon electrodes in an additive-free solution and in solutions containing different amounts of AD1. In additive-containing solutions, the lithium intercala-

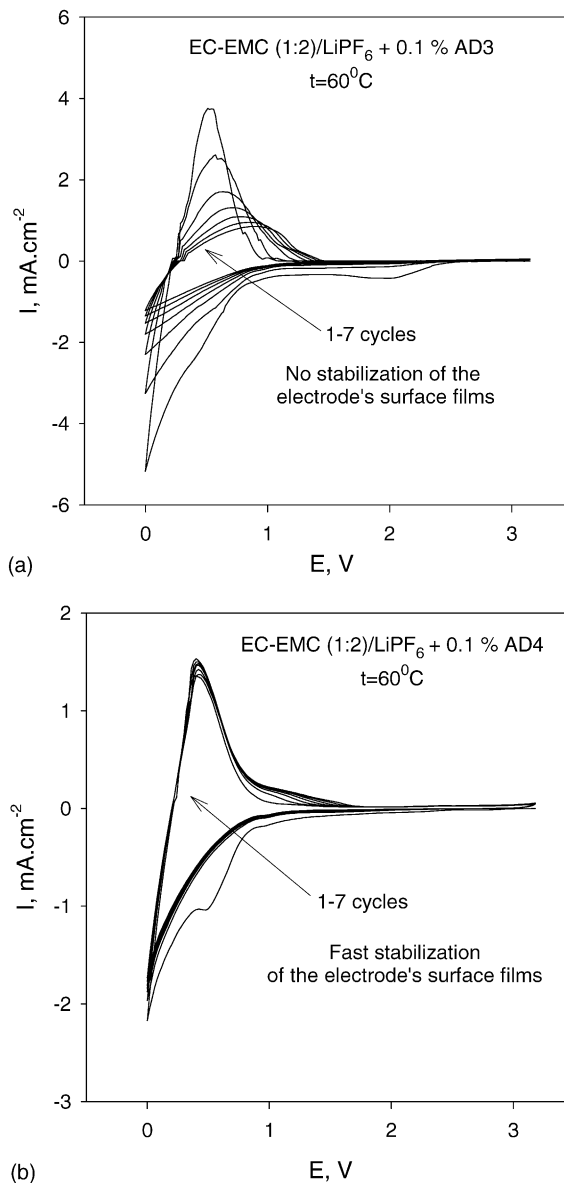


Fig. 2. Sets of first CVs obtained at 60 °C from MCMB + MCF electrodes in solutions containing 0.1% of AD3 (tetraethyl orthosilicate) (a) and 0.1% of AD4 (ethylvinyl ether) (b). Flooded cells, potential scan rate 2 mV/s.

tion potentials are shifted to more positive values indicating the faster kinetics of the insertion process than that in an additive-free solution. We assumed that this could be associated with the lowering of the impedance of MCMB + MCF electrodes in AD1-containing solutions. Indeed, as follows from the impedance spectra of these electrodes (Fig. 4), at AD1 concentrations higher than 0.1% in solution, both the surface film resistance (reflected by the diameter of the high to medium frequency semicircle) and the charge transfer resistance (low frequency semicircle) are substantially smaller than in the additive-free solution. The smallest values of the charge-transfer resistance were measured at low intercalation potentials (80–20 mV) in a solution containing 1% of AD1.

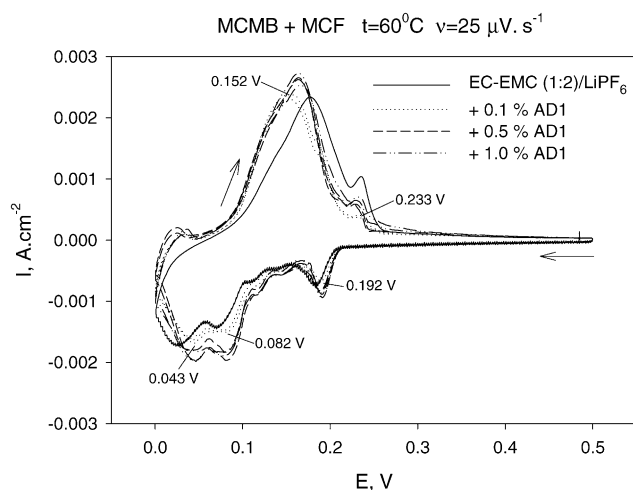


Fig. 3. Slow potential scan rate CVs (0.025 mV/s) recorded at 60 °C from MCMB + MCF electrodes in coin-type cells using an additive-free EC-EMC (1:2)/LiPF₆ solution and solutions containing AD1 (hexamethyl-disiloxane).

Fig. 5 represents a set of consecutive cyclic voltammograms recorded at different temperatures from a LiCoO₂ electrode in a solution containing 0.1% of AD1. A stable electrochemical performance can be obtained with this electrode at temperatures up to 60 °C. In contrast, upon repeated cycling of the LiCoO₂ electrode in an additive-free solution at 60 °C, the electrode's capacity decreases, and at too low a scan rate of 0.05 mV/s it does not show a reversible behavior at all [12]. It was established that at 60 °C, LiCoO₂ electrodes exhibit a much more stable performance during prolonged charge–discharge cycling in solutions containing AD1 or AD3 than that measured in an additive-free solution (Fig. 6). Such behavior may partially relate to special impedance characteristics of LiCoO₂ electrodes in solutions containing the additives. Indeed, as seen in Fig. 7, which represents impedance spectra measured from LiCoO₂ electrodes in an additive-free solution and in solutions contain-

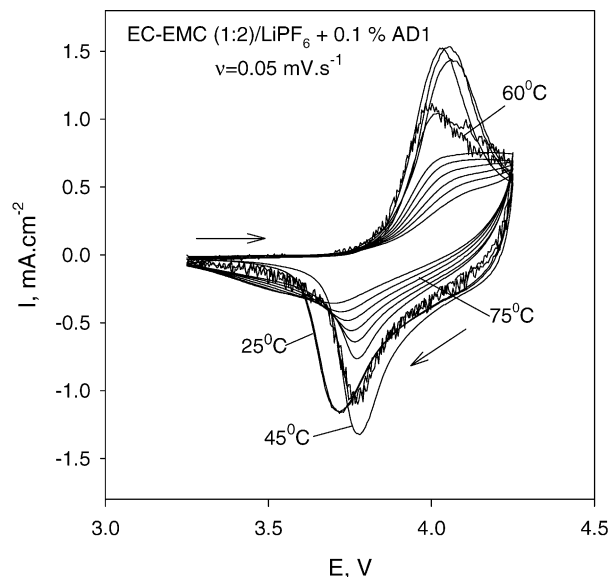


Fig. 5. A set of consecutive cyclic voltammograms of the LiCoO₂ electrode obtained at 25–75 °C in an EC-EMC (1:2)/LiPF₆ solution containing 0.1% of AD1 (hexamethyldisiloxane). Flooded cell, potential scan rate 0.05 mV/s.

ing 0.1, 0.5 or 1.0% of AD1, the impedance of LiCoO₂ electrodes is lower in solutions containing AD1. It is interesting to note that Li–carbon electrodes also show a relatively low impedance in solutions containing AD1 (see Fig. 4). We assume that additives from siloxanes or alkoxy silanes families react rapidly at high temperatures with traces of HF in solution. The fluorinated products interact further with carbon or LiCoO₂ electrodes and are involved in building-up the protective surface films on these electrodes. It was established by XPS analysis (Figs. 8b and 9a) that Si-containing species (binding energy of Si 2s is around 156 eV) are present in surface films developed on LiCoO₂ electrodes cycled in solutions containing AD1. Note that these electrodes were prepared by pressing lithiated cobalt oxide powder on an Al

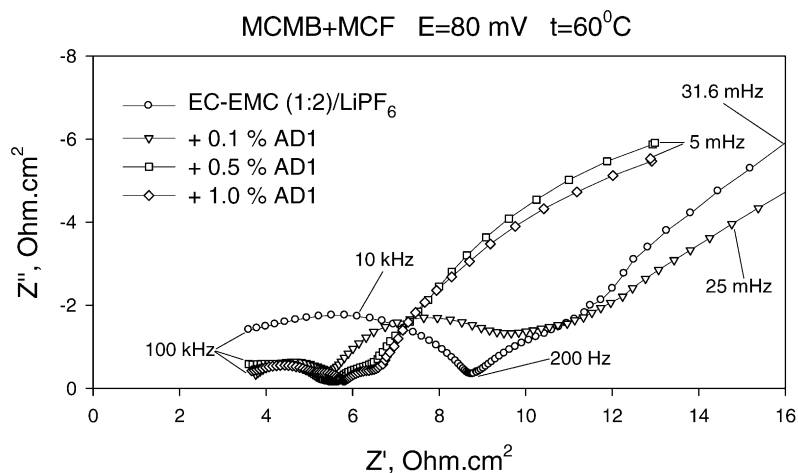


Fig. 4. Impedance spectra of MCMB + MCF electrodes measured during Li intercalation at 60 °C (coin-type cells) in an additive-free solution and in AD1 (hexamethyldisiloxane)-containing solutions. OCV potential was 80 mV.

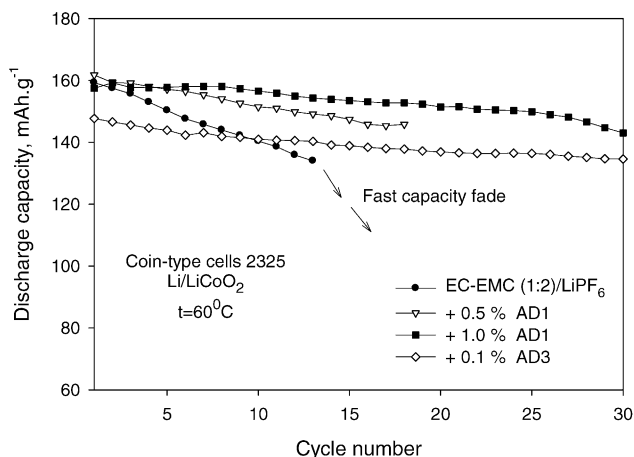


Fig. 6. Cycling behavior of LiCoO₂ electrodes at 60 °C in an additive-free solution and in solutions containing additives AD1 (hexamethyldisiloxane) and AD3 (tetraethyl orthosilicate) as indicated. Charge–discharge rate was C/10 in the potential range of 3.25–4.25 V. The results represent average capacity values from two to three parallel tests with each cell.

foil and they are free of PVdF and carbon black. These electrodes are more suitable for surface studies (in comparison to composite electrodes) due to the elimination of any side effects from the binder and high-specific area carbon black. We assume that surface films on LiCoO₂ electrodes contain fluoro silicate compounds (Fig. 9a) and not, for instance, SiO₂ species (as could be expected), since the corresponding binding energy for SiO₂ is substantially smaller [13]. The surface films developed on these electrodes isolate them from detrimental interactions with solution species, but allow free Li ion transport to the electrodes. By analyzing the intensity of the XPS peaks of silicon and cobalt of LiCoO₂ electrodes cycled in these solutions, one can conclude that the higher the content of AD1 in solution, the thicker are the surface films formed on the LiCoO₂

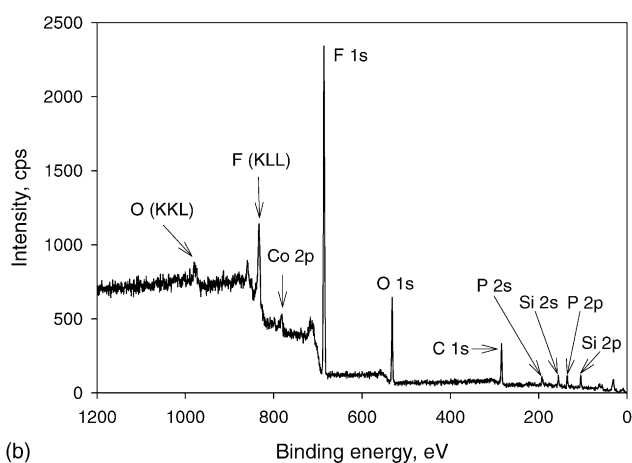
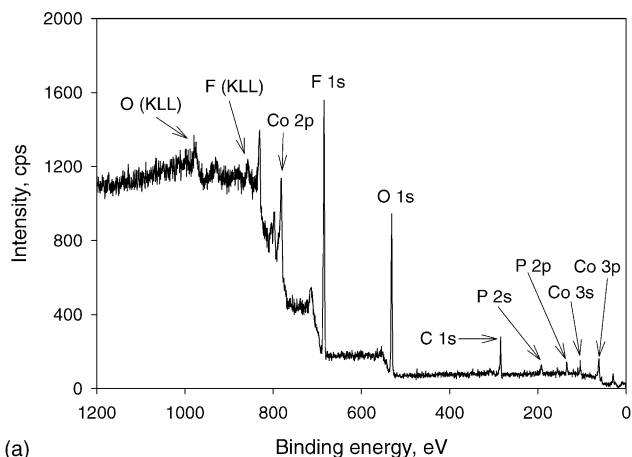


Fig. 8. XPS spectra (general view) of a LiCoO₂ electrode free of PVdF and carbon black cycled at 60 °C in an EC-EMC (1:2)/LiPF₆ solution (a) and a similar electrode cycled at 60 °C in a solution containing 1% of AD1 (hexamethyldisiloxane) (b). After cycling, the electrodes were cathodically polarized to $E = 3.25$ V and kept at this potential for 24 h.

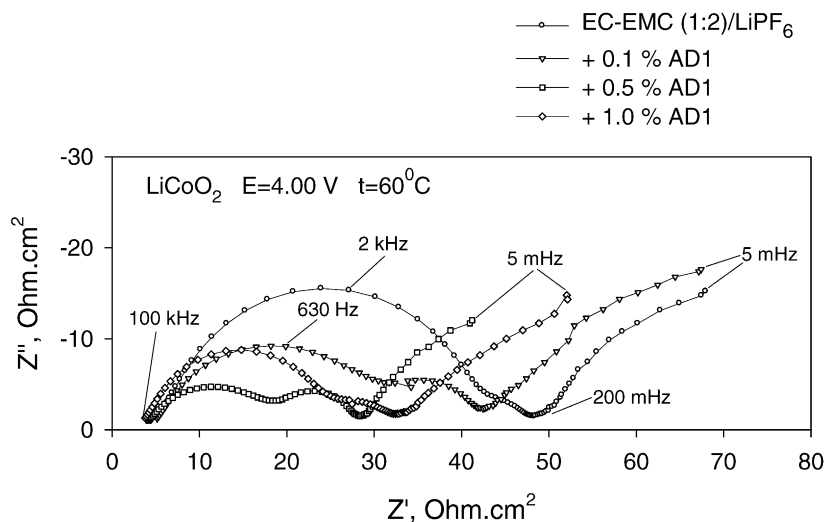


Fig. 7. Impedance spectra of LiCoO₂ electrodes measured during Li deintercalation at 60 °C (coin-type cells) in an additive-free solution and in solutions containing AD1 (hexamethyldisiloxane). OCV potential was 4.00 V.

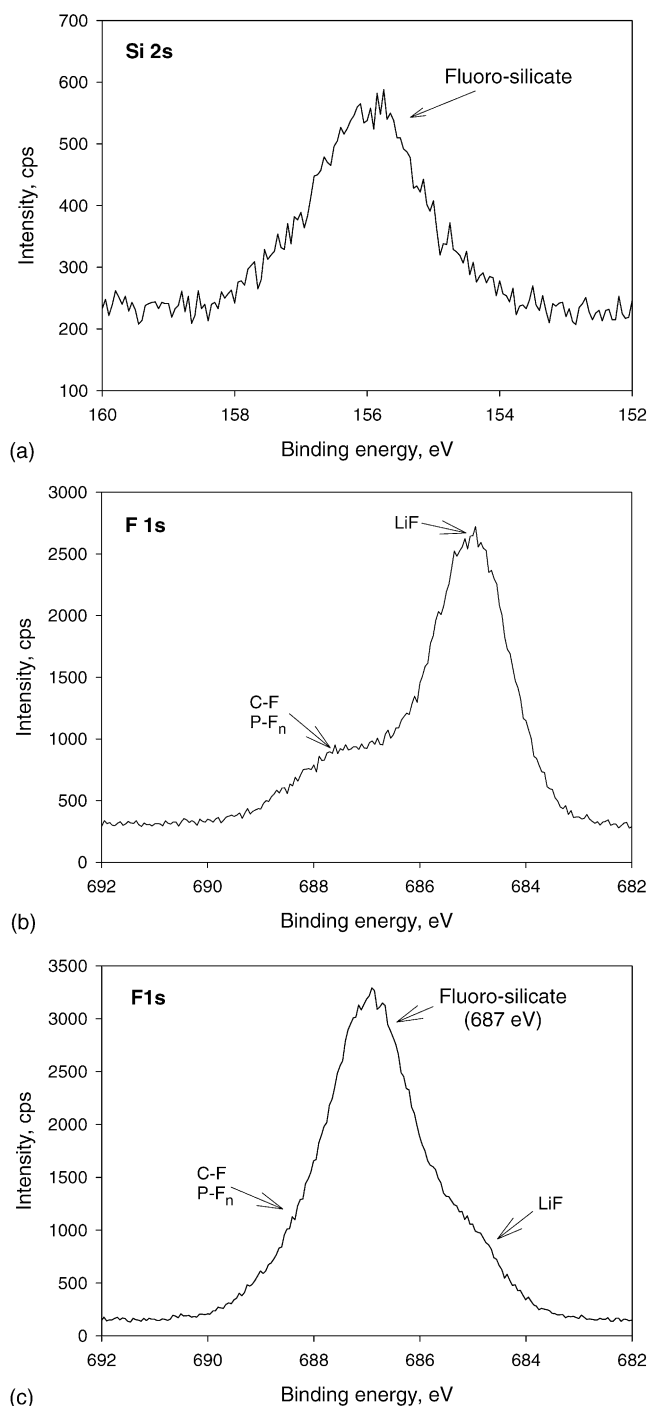


Fig. 9. (a) XPS spectrum of silicone detected on the LiCoO₂ electrode cycled at 60 °C in an EC-EMC (1:2)/LiPF₆ solution containing 1% of AD1 (hexamethyldisiloxane); (b,c) XPS spectra of fluoro compounds detected on LiCoO₂ electrodes cycled at 60 °C in an EC-EMC (1:2)/LiPF₆ solution and in a solution containing 1% of hexamethyldisiloxane (AD1), respectively.

electrodes (higher Si peak intensities, lower Co peak intensities). Fluoro-comprising species are also present on the surface of these electrodes (Fig. 9b and c). In an additive-free solution, surface fluorine compounds may be formed by reactions of HF, PF₆⁻, PF₅, PO₂F₃, etc. Lithium fluoride

species and surface species containing C–F and P–F_n bonds are present in the case of LiCoO₂ electrodes cycled in an additive-free solution (Fig. 9b). In EC-EMC/LiPF₆ solutions containing AD1, the XPS studies indicate the formation of species with Si–F bonds (see the high binding energy of the fluorine peak in Fig. 9c). We assume that siloxanes may react with trace HF to form species with Si–F bonds, and then further react on the electrode's surface.

We have established that in solutions containing 0.1% of AD1 (hexamethyldisiloxane), more stable charge–discharge cycling behavior can be obtained with full carbon/LiCoO₂ cells than in cells containing additive-free solutions. A similar behavior of carbon/LiCoO₂ batteries was also demonstrated in solutions containing 0.5 and 1.0% of AD1, while in an additive-free solution at 60 °C, the cell capacity fades relatively quickly. The results obtained in the galvanostatic cycling of carbon/LiCoO₂ coin-cells clearly demonstrate that AD1 should be considered as a promising additive for Li ion batteries, especially for improving their high temperature behavior.

In order to complete the picture, rigorous studies of the surface chemistry of these systems are needed, and are presently in progress, but beyond the scope of this paper.

4. Conclusions

It was found that some organic additives denoted as AD1 (hexamethyldisiloxane), AD2 (bicyclo[2.2.1]hepta-2,5-diene), and AD4 (ethylvinyl ether), from siloxanes, strained olefins, and vinyl ethers families, respectively, inhibit the irreversible processes of carbon electrodes in solutions comprising alkyl carbonates and LiPF₆. In solutions containing these additives, the electrodes' surface films stabilize faster at higher temperatures (e.g., 60 °C) as compared to the additive-free solution.

The presence of AD1 in EC-DMC/LiPF₆ solutions reduces the impedance of both carbon and LiCoO₂ electrodes at elevated temperatures. It is assumed that AD1 reacts with trace HF in solution, and the reaction products are involved in building-up the surface films on the electrodes. Surface films on LiCoO₂ electrodes in solutions containing AD1 are rich in silicon- and silicon–fluoro-containing species, as detected by XPS. We suggest that detrimental acid–base interactions between the electrolyte solution and LiCoO₂ electrodes are eliminated when the solutions contain siloxanes (AD1, hexamethyldisiloxane) or alkoxysilanes (AD3, tetraethyl orthosilicate), since these additives react with HF.

We have demonstrated that during cycling at 60 °C, the capacity of Li/LiCoO₂ and carbon/LiCoO₂ cells fades quickly in additive-free solutions. Using EC-EMC/LiPF₆ solutions containing additives such as AD1 or AD3 results in much more stable cycling behavior of the above cells at high temperatures, probably due to a better passivation and stabilization of the surface films, which are formed on the electrodes.

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