



Comparative study of electrolyte additives using electrochemical impedance spectroscopy on symmetric cells



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HIGHLIGHTS

- Impedance spectroscopy on symmetric cells is used to determine which electrodes additives influence most.
- Almost all additives increase the negative electrode impedance.
- Almost all additives decrease the positive electrode impedance.
- Additives studied include VC, FEC, TMOBX, LiTFSI and water and their combinations.
- The impact of these additives on coulombic efficiency was also measured.

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ABSTRACT

The effect of various electrolyte additives and additive combinations added to a 1 M LiPF₆ EC:EMC electrolyte on the positive and negative electrodes surface of 1 year old wound LiCoO₂/graphite cells and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite cells was studied using electrochemical impedance spectroscopy (EIS) on symmetric cells. The additives tested were: vinylene carbonate (VC), trimethoxyboroxine (TMOBX), fluoroethylene carbonate (FEC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and H₂O alone or in combination. In general, compared to control electrolyte, the additives tested reduced the impedance of the positive electrode and increased the impedance of the negative electrode with the exception of LiTFSI in Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite wound cells. Higher charge voltage led to higher positive electrode impedance, with the exception of 2%VC + 2% FEC, and 2% LiTFSI. In some cases, some additives when mixed with another controlled the formation of the SEI at one electrode, and shared the formation of the SEI at one electrode when mixed with a different additive.

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1. Introduction

Li ion batteries have high gravimetric and volumetric energy densities, which make them suitable for transport applications. However parasitic reactions between the electrolyte and the electrodes limit their lifetime. The addition of additives to the electrolyte can in some cases lead to extended lifetime as shown by Broussely et al. [1] and to better rate performances [2,3].

Even if these additives are now widely used in the Li-ion battery industry, the details of how they work are poorly understood. For example, VC was thought to be a good additive for the formation of

an efficient solid electrolyte interface (SEI) at the negative electrode, which has been recently questioned [4,5,6]. It is now believed by some that the major beneficial impact of VC is at the positive electrode.

In an effort to better understand the role of these additives several research groups have dedicated substantial amounts of resources to their study [7–10]. For example, Burns et al. [3,5] used high precision coulometry, automated storage and electrochemical impedance spectroscopy (EIS) to evaluate the effect of additives on the cycling performances of commercial wound LiCoO₂/graphite and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite cells. Amongst other things, they showed that VC reduces the rate of parasitic reactions at the positive electrode, that TMOBX leads to greater parasitic reaction at the positive electrode but lowers the impedance, that the mix of TMOBX and VC leads to a good balance between reduced rate of

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parasitic reactions at the positive electrode and reduced impedance leading to good overall cell performances (rate capability and capacity retention). However, the effect of these additives on the impedance of the positive and negative electrode was not determined.

In order to easily detect the effect of an additive at the positive electrode and negative electrode separately, a method based on electrochemical impedance spectroscopy of symmetric cells developed by Chen et al. [11] was recently introduced [12]. This technique allows one to extract the effect of an additive on the charge transfer resistance (R_{ct}) of the positive electrode and negative electrode. R_{ct} of each electrode can be related to the nature of the SEI on the positive and negative electrode. Comparing the R_{ct} of both electrodes allows the effect of an additive on the positive and negative electrode to be detected (if the products of the reactions are insoluble). This technique proved to be very useful in studying the effect of VC and TMOBX on both electrodes of wound LiCoO₂/graphite cells. Petibon et al. showed that VC greatly reduced R_{ct} of the positive electrode at both 1 wt% and 2 wt%, VC did not strongly affect R_{ct} of the negative electrode at 1 wt%, but greatly increased R_{ct} of the negative electrode at 2 wt%. They also showed that TMOBX does not strongly affect the negative electrode impedance but greatly reduces R_{ct} of the positive electrode when 0.3 wt% of TMOBX is used. Finally, Petibon et al. showed that when 2 wt% VC and 0.3 wt% TMOBX were introduced, the effect of VC at the negative electrode and the effect of TMOBX at the positive electrode were maintained.

In this paper similar studies to those of Petibon et al. [12] are reported for a relatively large set of additives studied over a period of more than two years. The additives, 2 wt% FEC, 2 wt% LiTFSI, 100 ppm H₂O and several pairs of additives in addition to 2 wt% VC and 0.3 wt% TMOBX have been studied to determine their effect on the R_{ct} of the positive and negative electrodes of wound Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]/graphite cells (called NMC cells), and two groups of LiCoO₂/graphite cells charged to different cut-off voltages (called LV-LCO and HV-LCO cells). It is believed that this work will be of interest to scientists trying to improve the lifetime of Li-ion cells.

2. Experimental

Wound prismatic LiCoO₂/graphite and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]/graphite cells with 1 M LiPF₆, EC:EMC (3:7 by weight) were used in this study. The cells studied contained approximately 1.5 g of electrolyte per gram of negative active material. Table 1 lists the additives tested in which cell chemistries. Some combinations were not tested due to unavailability of cells.

Fig. 1 shows the history of the cells used in this study. The cells were first subjected to an automated storage test [7]. This test consists of two discharge–charge cycles between the lower and upper voltage cut-off, followed by an open circuit storage step of 500 h at the top of charge. The two discharge–charge cycles and the open circuit voltage steps are then repeated one more time. The lower and upper voltage cut-offs of the NMC cells were 3.3 V and 4.225 V, respectively. Two groups of LiCoO₂/graphite cells were used. The lower and upper voltage cut-offs of the first group, called LV-LCO cells, were 3.4 V and 4.075 V, respectively. The lower and upper voltage cut-offs of the second group, called HV-LCO cells, were 3.4 V and 4.175 V, respectively. All cells contained the same graphite negative electrode and their negative to positive active material ratio was balanced according to their voltage cut-off. The ratios of the active mass of the positive electrode and the active mass of the negative electrode for the LV-LCO cells, HV-LCO, and NMC cells were 1.6, 1.4, and 1.2 respectively. After the automated storage test the cells were then put away for approximately one year at an open circuit voltage around 3.9 V at room temperature

Table 1

List of additives studied in this work.

Additive	NMC/graphite 4.225 V	LV LCO/graphite 4.075 V	HV LCO/graphite 4.175 V
Control	Yes	Yes	Yes
1%VC (Novolyte)	Yes	Yes	Yes
2% VC (Novolyte)	Yes	Yes	No
0.3% TMOBX (BASF 99.2%)	Yes	Yes	Yes
2% FEC (Novolyte)	Yes	Yes	Yes
2% LiTFSI (3 M, 99.9%)	Yes	Yes	Yes
100 ppm H ₂ O	No	Yes	No
2% VC + 0.3% TMOBX	Yes	Yes	Yes
2% VC + 2% FEC	Yes	Yes	Yes
2% VC + 2% LiTFSI	Yes	Yes	Yes
2% VC + 100 ppm H ₂ O	Yes	No	No
2% VC + 1000 ppm H ₂ O	No	Yes	No
2% VC + 2% LiTFSI	No	Yes	No
+ 100 ppm H ₂ O			
2% VC + 2% LiTFSI	Yes	Yes	No
+ 1000 ppm H ₂ O			
2% VC + 0.3% TMOBX	No	Yes	No
+ 100 ppm H ₂ O			

(19 °C–22 °C). The cells were then cycled for a short period (one full cycle) and stopped at an open circuit voltage of 3.775 V corresponding to approximately 50% state of charge. The electrochemical impedance spectra of the cells were then taken at 10 °C, 20 °C, 30 °C, and 40 °C. Then the cells were taken inside an argon-filled glove box for disassembly and construction of symmetric cells from their electrodes as described in Ref. [12].

The cells were carefully opened in an argon filled glove box. From the long doubled-sided electrodes, 9 coin-cell size (1.54 cm²) positive electrodes and 9 coin-cell size negative electrodes were cut with a precision punch. From the punched (double sided) electrodes, 3 full coin cells, 3 negative symmetric coin cells and 3 positive symmetric coin cells were reassembled using one polypropylene blown microfiber separator (BMF – available from 3M Co. 0.275 mm thickness, 3.2 mg cm⁻²) [13] and the same electrolyte formulation as the parent prismatic wound cells. A full cell is constructed using one positive electrode and one negative electrode, a positive symmetric cell is constructed using 2 positive electrodes, and a negative symmetric cell is constructed using 2 negative electrodes.

The EIS spectra of the reassembled coin cells were then recorded at 10 °C and 30 °C in that order. All EIS spectra were taken using a BioLogic VMP3 equipped with 2 EIS boards. Many EIS spectra were collected over the course of these experiments and in order to automate the process somewhat, the output of one VMP3 EIS board was connected to a Keithley 705 scanner and the output of the other to a Keithley 706 scanner. Each scanner housed two Keithley 7053 10-channel high current scanner cards. In-house software was designed and written so that each scanner could connect up to 16 cells sequentially to have their EIS spectra measured automatically overnight. All impedance spectra were collected at constant temperature by housing the cells in temperature-controlled boxes at 10.0 and 30.0 ± 0.2 °C.

3. Results and discussion

As shown in Ref. [12] the impedance of the positive symmetric cells grows over time, whereas the impedance of the full cells and negative symmetric cells are stable. This indicates the existence of an interaction between the positive and negative electrodes in the full cell that somehow prevents the impedance of the positive electrode from growing. It also suggests the existence of an autocatalytic reaction when the 2 positive electrodes are in the same

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