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New Li-ion electrolytes for low temperature applications

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Abstract

Ethyl acetate and methyl butyrate have been tested as new solvents for Li-ion liquid electrolytes. Specific ternary mixtures have been investigated, containing cyclic carbonate and linear carbonate solvents in addition to the esters. Thanks to their high conductivities, these electrolytes make it possible to obtain very good performances below -30°C , in different LiCoO_2 //graphite cells. Moreover, these electrolyte compositions do not affect cyclability, charge retention of safety of the LiCoO_2 cells, behaving as pure carbonate electrolytes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to allow new application fields for Li-ion batteries, one of the main goals is the increase of the performances at low temperature. The aim of this study is the development of new electrolyte compositions, able to lead to good discharge ability below -20°C , which is presently the limitation with carbonate solvent mixtures. Because of their very low freezing point [1], specific esters have been studied for low temperature applications: methyl acetate (MA; $T_f = -98^{\circ}\text{C}$), ethyl acetate (EA; $T_f = -83^{\circ}\text{C}$) and methyl butyrate (MB; $T_f = -84^{\circ}\text{C}$). EA and MA have already been described in the literature for such properties [2]; nevertheless, because of its low boiling point (57°C), the study on MA has been given up rapidly.

The aim of this study is the electrochemical behaviour of new electrolytes, containing EA or MB, in prismatic LiCoO_2 //graphite cells.

2. Experimental

These new electrolytes have been formulated in ternary mixtures, implying a cyclic carbonate solvent (PC or EC) for their passivating [3] and solvation properties, and a linear carbonate (DEC or DMC) for improving the electrolyte viscosity.

The electrolyte compositions were optimised in terms of conductivity and compared to a EC/DEC/DMC mixture, recently studied at low temperatures [4]. Conductivity was measured on a Tacussel (CDRV62) conductimeter in the range -40 to 40°C .

The electrochemical stability of these new solvents was checked in coin cells by a voltammetry study on both a graphite electrode (reduction, from OCV down to 0 V, at $50 \mu\text{V/s}$) and a LiCoO_2 electrode (oxidation, from OCV up to 5 V); an EGG galvanostat (model 273A) was used for these experiments.

After formulation, vinylene carbonate was added to improve the properties of the negative electrode passivation layer [5].

The selected compositions have been tested in prismatic cells (LiCoO_2 positive electrode and graphite negative electrode) on an Arbin battery test system (BT2043). The following electrochemical tests were conducted.

2.1. Discharge at low temperature

Cells were charged at 4.1 V under a low rate ($C/5$), then put at low temperature during 15 h. A discharge was performed down to 2 V under different rates. Capacities were compared to the results obtained at room temperature ($C/5$ discharge rate).

2.2. Cyclability at room temperature

Between 4.1 and 2.7 V ($C/2$ charge rate, C discharge rate) for LiCoO_2 cells, and from 4.0 to 2.7 V for LiNiO_2 -based cells.

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2.3. Self-discharge tests

Cells were fully charged at low charge rate ($C/5$), then stored 14 days at 60°C ; the irreversible losses were measured by a short cycling at room temperature (RT) after this storage.

2.4. Safety tests

First of all, the reactivity of these mixtures towards both positive and negative electrodes has been studied by differential scanning calorimetry (DSC) experiments under an argon flow between RT and 600°C , with a $10^\circ\text{C}/\text{min}$ temperature rate (DSC50 Shimadzu).

Then, a nail test was performed at 4.0, 4.05 and 4.1 V on prismatic ICP 176065 cells (5.5 Ah: graphite negative electrode).

3. Results

3.1. New solvent properties

EA and MB have very low freezing point ($< -80^\circ\text{C}$). Their viscosity is close to DMC (near 0.6 cP at 20°C), and their dielectric constant is a bit higher (between 5.5 and 6). Moreover, they have good conductivity properties (5.1 mS/cm for pure MB, and 11 mS/cm for pure EA, at 20°C with 1 M LiPF_6).

However, both of them have lower flash points than the different carbonate solvents usually used: 11°C for MB and -3°C for EA, instead of 18°C for DMC or 31°C for DEC. Consequently, one of the aim of this study has also been to check whether the use of these solvents in high amounts in the electrolyte did not affect the safety performances of the cells.

3.2. Conductivity

Binary and ternary mixtures containing EA or MB displayed outstanding conductivity properties under -20°C : up to 7 mS/cm at -20°C and 5 mS/cm at -35°C are being reported, instead of 2 mS/cm (-20°C) for usual electrolytes (Fig. 1). Moreover, no freezing point appears even at -35°C . This property is unusual with carbonate solvent mixtures,

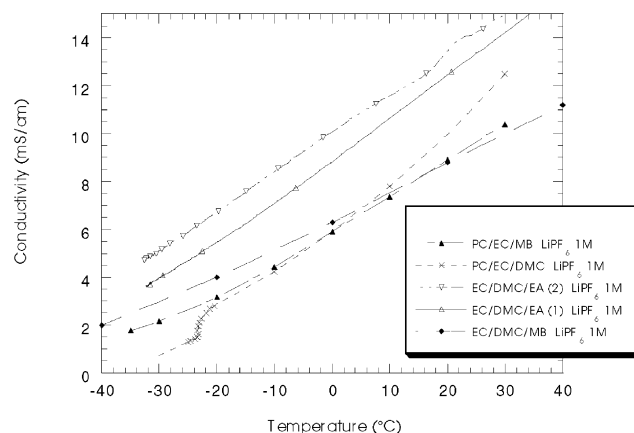


Fig. 1. Conductivity vs. temperature of electrolytes containing EA or MB.

which presents a gelification mechanism near -28°C (Fig. 1). For technical reasons, the real freezing point of the new electrolytes has not been identified.

3.3. Voltammetry

EA and MB present a reduction peak near 0.7 V versus Li^+/Li (at RT) at the same potential as the main carbonates [5]. In oxidation, these solvents seem stable in our test conditions up to 4.85 V versus Li^+/Li (at 60°C).

3.4. First charge and IEC cycles

Electrolytes containing EA or MB induce to a first cycle irreversible capacity, comparative to the one observed with standard carbonate mixtures (Table 1). Moreover, the IEC capacity of the tested prismatic cells are also very similar (Table 1) with, in all cases, a half-discharge voltage of 3.80 V. Consequently, as previously observed by voltammetry in coin cells, no additional polarisation was created by the use of EA or MB solvents.

3.5. Low temperature performances

Table 1 describes the discharge ability at low temperatures of ICP 144350 cells filled with different EA or MB formulations. At -30°C , under a $C/2$ rate, about 85% initial

Table 1

Discharge performances of ICP 144350 cells at low temperatures with EA and MB electrolytes

Electrolyte composition	First-cycle efficiency (%)	Reversible capacity, at RT and $C/5$ rate (Ah)	Discharge capacity ^a				
			-20°C		-30°C		-40°C
			$C/2$ rate (%)	C rate (%)	$C/2$ rate (%)	C rate (%)	$C/2$ rate (%)
EC/DEC/DMC LiPF_6 1 M	83	1.98	96	92	0	0	0
EC/DMC/EA LiPF_6 1 M	92	1.98	90	88	88	87	81
EC/DMC/MB LiPF_6 1 M	78	2.0	91	91	84	90	87
PC/EC/MB LiPF_6 1 M	84	1.96	98	96	95	98	Not tested

^a Percentages were calculated from the discharge capacity at RT under a $C/5$ rate.

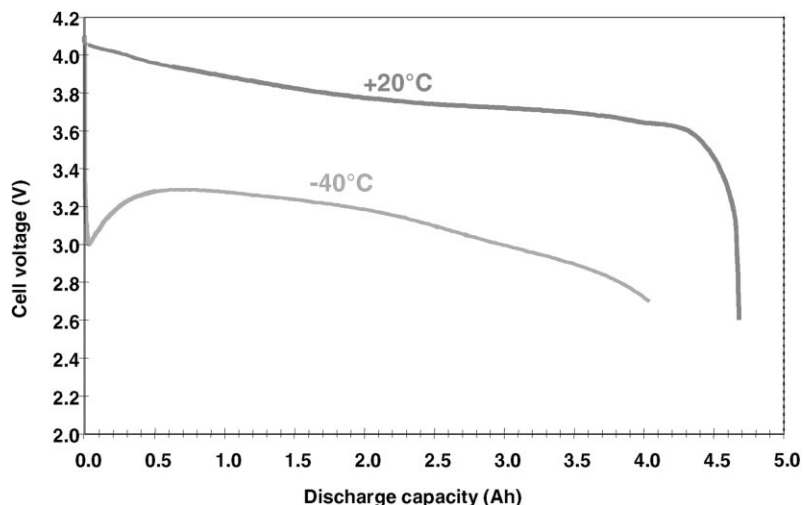


Fig. 2. Discharge characteristics in MP 174865 LiCoO_2 /graphite cells. Electrolyte EC/DMC/EA LiPF_6 1 M; charge 4.1 V at 4.6 A at RT; discharge at 0.92 A ($C/5$) at $+20^\circ\text{C}$ and -40°C .

capacity was recovered with EC/DMC/EA, EC/DMC/MB and PC/EC/MB formulations. Even at -40°C ($C/2$ rate), same mixtures enabled to recover more than 80% initial capacity. Same tests were performed on bigger cells (ICP 174865 and ICP 176065) with different discharge modes (pulsed or constant), allowing more than 80% of the capacity to be recovered (Fig. 2).

Below -30°C , the discharge profile presents a voltage drop in the first seconds of the discharge (as described in Fig. 2). This phenomenon, due to the high internal resistance of the cell at low temperatures, is the main limitation of the cell performance. Because of their high conductivities, EA- and MB-based electrolytes enabled to decrease the impact of this parameter, comparatively to carbonate solvents.

Table 2 gathers this minimum voltage registered at the beginning of the discharge, with different electrolytes, in ICP 176065 cells. It demonstrated obviously the performances of EA and MB mixtures. Moreover, the results in Table 2 also evidenced that this voltage drop is directly related to the lithium salt content; in fact, adding 1.5 M instead of 1 M LiPF_6 in the electrolyte enabled to increase the working range from (-30°C ; $C/2$ rate) to (-40°C ; $C/5$ rate). It exhibits a limitation by the mass transport of lithium ions in the electrolyte.

Moreover, we noticed a slightly positive impact on voltage drop of the VC content in MB electrolytes; the role of such an additive has not been understood yet.

3.6. Cyclability at room temperature

Prismatic cells (ICP 174865) filled with these new electrolyte compositions displayed fading rates at room temperature similar to those observed in carbonate mixtures (Table 3). Even after 200 cycles (C rate), a fading rate between 0.03 and 0.05% per cycle was measured.

3.7. Self-discharge tests

After 14 days at 60°C , full SOC (4.1 V) ICP 174865 cells have a 6% irreversible loss, similar to the one observed in carbonate mixtures (Table 3). These results demonstrate the stability of the passivating layer formed on the graphite surface in the selected electrolytes. Nevertheless, in all these experiments, VC was added in the electrolytes (5%) to improve the passivating layer stability. Without VC, higher irreversible losses were registered, as in the carbonate mixtures.

Table 2

Evolution of the voltage drop (in V) registered at the beginning of the discharge at very low temperatures — impact of the electrolyte composition^a

Electrolyte	Voltage (V)	Discharge at -30°C			Discharge at -40°C	
		D/5	D/2	D	D/5	D/2
EC/DEC/DMC LiPF_6 1 M + 1% VC	U_{\min}	<2	<2	<2	<2	<2
PC/EC/MB LiPF_6 1 M + 1% VC	U_{\min}	2.70	2.35	<2	<2	<2
PC/EC/MB LiPF_6 1.5 M + 1% VC	U_{\min}	2.80	2.45	2.15	2.30	<2
PC/EC/MB LiPF_6 1 M + 5% VC	U_{\min}	2.70	2.50	2.15	2.40	2.05
EC/DMC/EA LiPF_6 1 M + 5% VC	U_{\min}	2.75	2.60	2.25	2.45	2.15

^a ICP 176065 cells; 5.5 Ah; cut-off voltage: 2 V.

Table 3
Impact of the electrolyte composition on cyclability and charge retention

Electrolyte	Cyclability at RT		Self-discharge, irreversible loss (%)
	Fading 50 cycles, C rate (% per cycle)	Fading 200 cycles, C rate (% per cycle)	
EC/DEC/DMC LiPF ₆ 1 M + 5% VC ^a	0.04	0.33	10 ^b
EC/DMC/EA LiPF ₆ 1 M + 5% VC ^a	0.05	0.05	10 ^b
PC/EC/MB LiPF ₆ 1 M + 5% VC ^a	0.05	0.05	7 ^b
PC/EC/DMC LiPF ₆ 1 M + 5% VC ^c	0.09	0.03	1 ^d
EC/DMC/EA LiPF ₆ 1 M + 5% VC ^c	0.09	0.03	1 ^d

^a On ICP 174865 LiCoO₂ cells.

^b Irreversible losses were measured after a 14-day storage at 60°C (100% SOC).

^c On 4 or 5 A LiNi_{1-x}Co_xO₂ cells.

^d Irreversible losses were measured after four successive storages at 40°C (100% SOC, 8 days per storage).

Table 4
Impact of the electrolyte composition on safety

Electrolyte	DSC experiment ^a on LiNi _{1-x-y} Co _x Al _y O ₂ material		Nail test done on ICP 176065 cells (LiCoO ₂ graphite) after IEC cycling (V)
	Temperature peak (°C)	Energy involved during reaction (J/g)	
EC/DEC/DMC LiPF ₆ 1 M	287	1500 (full charge: 187 mAh/g)	4.1
EC/DMC/EA LiPF ₆ 1 M + 5% VC	291	1390 (full charge: 190 mAh/g)	4.05
PC/EC/MB LiPF ₆ 1 M	285	1460 (full charge: 187 mAh/g)	4.1

^a DSC experiments were done on nickel-doped positive electrode after a full charge at 4.1 V; stainless steel crucible; 10°C/min.

3.8. Safety tests

By DSC, the reactivity of these new electrolytes has been tested on a LiNi_{1-x-y}Co_xAl_yO₂ electrode (state of charge: 4.1 V) and a carbonaceous electrode (fully lithiated). On the negative side, no difference was noticed between these new solvents, comparatively to carbonate mixtures. On the cobalt electrode, a slightly higher reactional kinetics was observed with an electrolyte containing a very high amount of ethyl acetate. Nevertheless, this reaction occurs at 290°C, as in the carbonate mixtures, and even the fact that the peak profile seems a bit more sharp, the energy involved by this reaction is close to the one obtained in a EC/DEC/DMC mixture (Table 4).

Consequently, in spite of lower flash points, these new electrolytes do not affect safety. To be sure of that point, nail tests were performed up to 4.1 V on ICP 176065 cells. EA and MB electrolytes present similar results to the one obtained with carbonate electrolytes (Table 4).

4. Discussion

EA and MB ternary mixtures enabled performances at room temperature similar to carbonate mixtures in graphite/LiCoO₂ cells. These results demonstrated that in these cells with an optimised carbonate content, it is possible to use esters as new co-solvents.

Different conclusions have been brought by Hayashi et al. in MA mixtures on Li/LiMn_{1.9}Co_{0.1}O₄ cells [2]. This may be related to the chemical instability of metallic lithium in the esters, which would generate difficulties in the study of these solvents versus metallic lithium.

The described electrochemical characterisation performed in cobalt prismatic cells has not been done with manganese-based materials. Nevertheless, LiNi_{1-x}Co_xO₂ and LiNi_{1-x-y}Co_xAl_yO₂ materials have also been tested in 4 or 5 A cells with EA and MB electrolytes, with the same understanding results. At low temperature, for example, these cells enabled to recover more than 78% of their IEC capacity at -30°C under a C/2 rate. Fading rate and charge retention were also normal (Table 3).

5. Conclusion

At low temperatures, electrolyte compositions containing EA and MB enabled very good performances down to -40°C, even under a C/2 rate. Moreover, in terms of self-discharge, fading rates and even safety, these new electrolytes have very good properties.

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