



On the thermal behavior of model Li–Li_xCoO₂ systems containing ionic liquids in standard electrolyte solutions

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ABSTRACT

We report herein on the possibility of using ionic liquids (ILs) as additives to conventional electrolyte solutions, based on alkyl carbonates and LiPF₆ for attenuating thermal reactions in Li battery systems. As a model, a Li–Li_{0.5}CoO₂ system was used. The ionic liquids chosen included cations based on derivatives of pyrrolidinium and imidazolium, and the anions bioxalato borate (C₄O₈B[−], BOB), (CH₃SO₂)₂N[−] (TFSI), and PF₃(C₂S₅)₃[−] (FAP). The thermal behavior of solutions alone, solutions with Li metal, Li_{0.5}CoO₂ and Li metal + Li_{0.5}CoO₂ was studied. It was found that the presence of 10% of ILs, with derivatives of pyrrolidinium cations and FAP or TFSI anions in standard EC–DMC/LiPF₆ solutions, improves considerably the thermal stability of Li_{0.5}CoO₂ in electrolyte solutions. The onset temperatures of the thermal reactions of Li_{0.5}CoO₂ with solution species are higher and their heat evolution is considerably lower, when they contain these ionic liquids as additives. This finding opens the door for further studies and optimization of the use of selected ILs as additives that may improve the safety features of Li-ion batteries.

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1. Introduction

The main challenge for rechargeable Li-ion batteries is their possible use as the main electric vehicle (EV) batteries. Only Li-ion batteries seem to be able to provide the high energy density required for EV application. Many hundreds of R&D groups throughout the world are struggling to advance Li-ion battery technology in terms of energy density, high rates and prolonged cycle life. Not less important are the safety features. The higher the energy density, the more severe are the problems of thermal runaway in cases of local heating, due to the poor dispersion of heat in operating batteries and abuse cases such as over charging and short circuiting. Uncontrolled thermal reactions in high-energy density Li batteries may obviously lead to dangerous explosions and fire. Hence, in the development of novel Li-ion battery systems, we may face disappointing compromises between energy density and acceptable safety features. In recent years we have seen a intensive efforts to develop additives that improve safety by overcharge protection (via shuttle mechanisms) [1,2], co-solvents that may act as fire retardants [3,4] and non-flammable components to standard electrolyte solutions [5,6].

When examining carefully the many publications that have appeared on these subjects in recent years, one can find that in most cases the use of such additives in Li-ion battery systems was on the account of performance. Electrolyte solutions that may be highly interesting and important for improving safety features of Li batteries are those based on ionic liquids (ILs, namely, low-temperature molten salts). Ionic liquids have become increasingly important in nonaqueous electrochemistry over the past years. They are highly polar and conductive systems which are usually non-volatile and may demonstrate wide electrochemical windows [7,8]. In recent years we have seen an increasing number of publications describing the application of ILs in Li-ion batteries [9–13] and super (EDL) capacitors [14]. We have demonstrated the stability and compatibility of some families of ILs for 4.8 V cathode materials such as LiMn_{1.5}Ni_{0.5}O₄ spinel [15] and anodes such as Li silicon [16] and Li-graphite [17]. The advantage of the use of ILs in terms of safety is still questionable [18] and in fact there is no generalization here. Each system has to be explored separately and rigorously. Most ILs may suffer from two main disadvantages:

1. Their viscosity may be too high, resulting in problems of wetting the electrodes active mass and poor rate capability, especially at low temperatures.
2. Most of the relevant IL systems are (still) very expensive.

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It is possible that the use of ILs as additives to standard solutions may be beneficial. The presence of ILs in standard electrolyte solutions may contribute to increased electrochemical and thermal stability and to the reduction of the overall flammability of electrolyte solutions. However, there is no *a priori* knowledge regarding which IL systems may be relevant and suitable. In order to advance the possible beneficial use of ILs as additives, a great deal of screening work is required in which large matrices of combinations should be studied electrochemically and thermally.

The work described herein is aimed at initiating such screening studies, in which the possible use of ILs as additives for improving the safety features of Li battery systems is examined. We composed a matrix of mixtures of ILs based on derivatives of imidazolium, pyrrolidinium cations, BC_4O_8^- (BOB, bioxalato borate), $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (TFSI), and $\text{PF}_3(\text{C}_2\text{F}_5)_3^-$ (FAP) anions, with standard electrolyte solutions based on EC–DMC and LiPF_6 . We studied the thermal behavior of these solutions as neat systems and in contact with Li metal samples, $\text{Li}_{0.5}\text{CoO}_2$ (delithiated LiCoO_2) powder and $\text{Li}_{0.5}\text{CoO}_2 + \text{Li}$ samples, using differential scanning calorimetry (DSC). It was possible to identify families of ILs whose presence in standard electrolyte solutions (10% by volume) improves the thermal stability of $\text{Li}_{0.5}\text{CoO}_2$. These results justify the further optimization and screening work with ILs and other electrode materials for Li-ion batteries, work which is in progress.

2. Experimental

The electrochemical windows of the standard electrolyte solutions, 1 M LiPF_6 in EC–DMC 1:1, contained 10% of different ILs were determined in T-type cells made of Teflon as described elsewhere [15], with glassy carbon working electrodes (0.2 cm^2), freshly polished before every anodic and cathodic scan. Li wire and Li foils served as reference and counter electrodes, respectively. These measurements were carried out in a glove box (argon atmosphere) using an Autolab potentiostat from Eco-Chemie Inc.

The thermal behavior of standard electrolyte solutions that contains a 10% by weight different ionic liquids in the presence of metallic Li and delithiated LiCoO_2 electrodes, in the temperature range of 40–350 °C, was studied by DSC method. A differential scanning calorimeter from Mettler Toledo Inc., Model DSC 822, was used.

The ILs used were obtained from Merck KGaA, and are listed below:

- 1-Hexyl-3-methylimidazolium–tris(pentafluoroethyl)trifluorophosphat (HMI–FAP).
- 1-Butyl-1-methylpyrrolidinium–tris(pentafluoroethyl)trifluorophosphat (BMP–FAP).
- 1-(2-Methoxyethyl)-11-methylpyrrolidinium–tris(pentafluoroethyl)trifluorophosphat (MEMP–FAP).
- N*-Ethoxyl-*N,N*-dimethyl-2-methoxyethylammonium–tris(pentafluoroethyl)trifluorophosphat (EDME–FAP).
- 1-Hexyl-3-methylimidazolium–bis(trifluoromethylsulfonyl)imide (HMI–TFSI).
- N*-Ethyl-*N,N*-dimethyl-2-methoxyethylammonium–bis(trifluoromethylsulfonyl)imide (EDME–TFSI).
- 1-Butyl-1-methylpyrrolidinium–bis(trifluoromethylsulfonyl)imide (BMP–TFSI).
- 1-(2-Methoxyethyl)-3-methylimidazolium–bis(trifluoromethylsulfonyl)imide (MEMI–TFSI).
- 1-Butyl-1-methylpyrrolidinium–bis(oxalato-borate) (BMP–BOB).
- Ethyl-3-methylimidazolium–bis(oxalato-borate) (EMI–BOB).

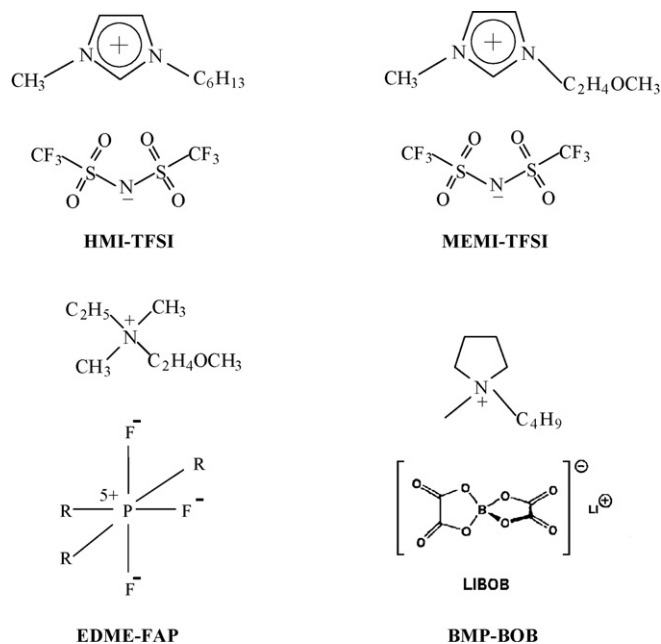


Fig. 1. Representative structural formulae of the ILs used in this study.

11. 1-2-(Methoxyethyl)-11-methylpyrrolidinium–bis(oxalato-borate) (MEMP–BOB).
12. *N*-Ethoxyl-*N,N*-dimethyl-2-methoxyethylammonium–bis(oxalato-borate) (EDME–BOB).
13. Ethyl-3-methylimidazolium– PF_6 (EMI– PF_6).

All of these ILs dissolve easily in standard electrolyte solutions. We also studied EC–DMC/1 M LiBOB for comparison (this salt was obtained from Cemetal Inc.). Structural formulae of selected ILs used herein, are presented in Fig. 1.

Li foils (0.3-mm thick) were mechanically cleaned in an argon-filled glove box in order to remove native surface films resulting from Li reactions with the atmospheric components, and were then smoothed by rolling on them a glass rod. Lithium disks of 3 mm in diameter and 0.6 mg in weight, with a total surface area of 0.17 cm^2 , were cut and placed in standard high-pressure gold-plated stainless steel crucibles, 30 μl in volume (Mettler Toledo Inc.) in a glove box (VAC, Inc.) under highly pure argon atmosphere. The crucibles were filled with 3 μl of solution, and then sealed.

For studies with $\text{Li}_{0.5}\text{CoO}_2$ we prepared composite LiCoO_2 electrodes comprising 80% active mass (from OMG Inc.), 10% carbon black and 10% PVdF binder on Al foil current collectors. Delithiation of LiCoO_2 electrodes was carried out electrochemically in coin-type cells, Model 2325, NRC, Canada, using 14-mm diameter cathodes, a lithium foil counter electrodes, a polypropylene separator (Cellgard), and a 1 M $\text{LiPF}_6/\text{EC–DMC}$ (1:1 v/v) electrolyte from Merck. All the preparation was carried out in an argon-filled glove box (VAC, Inc.). The cells were charged to 4.2 V vs. Li, with a current density of 0.6 mA cm^{-2} and then potentiostatically stabilized at this potential for 10 h using a multi-channel battery tester from Maccor, Model 2000. The cells were then disassembled and the delithiated LiCoO_2 electrodes were taken out, rinsed with DMC in order to remove the original electrolyte solution from the electrode and dried under vacuum. Finally, power scraped from the electrodes was used for the thermal analysis (comprising $\text{Li}_{0.5}\text{CoO}_2$, carbon black and PVdF 8:1:1) The DSC crucibles were filled with 1–2 mg of powder and 3 μl of solution, and then sealed. All the tests were carried out at a heating/cooling rate of $1 \text{ }^\circ\text{C min}^{-1}$. The specific heats generated during the DSC tests are calculated per gram of the sample or per

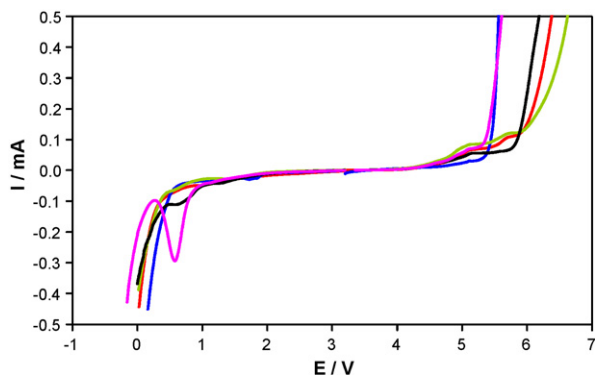


Fig. 2. Typical linear sweep voltammograms of the following electrolyte solutions measured with freshly polished glassy carbon electrodes, 25 °C, 20 mV s⁻¹: red line—1 M LiPF₆ EC-DMC, blue line—1 M LiPF₆ EC-DMC:BMP-BOB 9:1, green line—1 M LiPF₆ EC-DMC:BMP-FAP 9:1, black line—1 M LiPF₆ EC-DMC:BMP-TFSI 9:1, pink line—1 M LiPF₆ + EC-DMC:HMI-TFSI 9:1.

gram of Li_{0.5}CoO₂ in the case when solutions are in contact with Li_{0.5}CoO₂.

3. Results and discussion

3.1. A short electrochemical overview

Fig. 2 shows typical linear sweep voltammograms of glassy carbon electrodes in selected mixtures of ILs with standard electrolyte solution, EC-DMC/LiPF₆ (1:9 w/w). Thus electrodes were prepared fresh for each linear sweep voltammetric measurement. The most important subject to deal with is the effect of the IL additives on the electrochemical windows of these solutions, compared to the additive free, standard solution. Voltammetric studies of these solutions show the following trends:

- The presence of ILs based on derivatives of imidazolium, limits the electrochemical windows. Note that because of the presence of the Li salt, reduction of solution species (mostly alkyl carbonates) leads to passivation of the electrodes which can be reached during their first cathodic polarization. Thereby, all of these systems demonstrate apparent cathodic stability upon repeated voltammetric cycling. Nevertheless, the pronounced cathodic reactivity of the imidazolium derivative is well demonstrated in the relevant voltammogram in Fig. 2. The presence of these types of ILs limits also the anodic stability of the mixtures.
- The presence of BOB anions in solutions limits pronouncedly their anodic stability, due to the relatively low oxidation potential of these ions.
- The presence of ILs based on derivatives of pyrrolidinium and FAP or TFSI ions does not shorten the electrochemical windows of these solutions. It does not decrease the anodic and cathodic stabilities of the mixtures. It seems that the presence of BMP-TFSI slightly increases the anodic stability of the mixture.
- Some differences in the anodic behavior of solutions containing BMP-based ILs, which result from the different type of anions used, can be observed. The order of related anodic stability is FAP > PF₆⁻ > TFSI (see the pronounced anodic currents at potentials >5.5 V vs. Li/Li⁺).

3.2. Thermal behavior of the solutions (no electrode materials)

Fig. 3 shows DSC curves of the standard solution (EC-DMC/1 M LiPF₆) and solutions containing ionic liquids based on the BMP cation with different anions (10% by volume). A typical DSC of

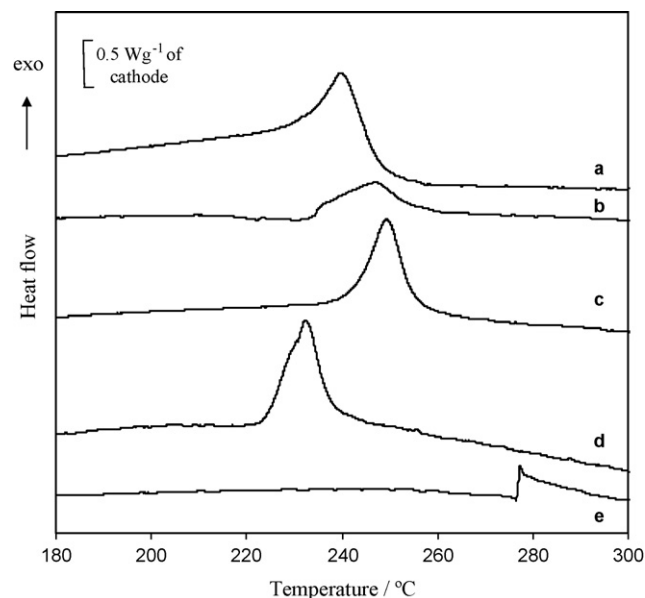


Fig. 3. DSC curves obtained by heating different EC-DMC/1 M LiPF₆ solutions containing 10% IL in EC-DMC/1 M LiPF₆: (a) BMP-FAP, (b) BMP-BOB, (c) BMP-TFSI and IL free, EC-DMC solutions of 1 M LiPF₆ and 1 M LiBOB ((d) and (e), respectively). A heating rate of 1 °C min⁻¹.

a EC-DMC/1 M LiBOB solution is also presented for comparison. All the LiPF₆ solutions exhibit a main exothermic process in the temperature range of 220–270 °C. It is identified as the solutions' irreversible thermal decomposition, since the DSC cooling curves did not show any peaks. Such behavior is typical for all the solutions. In contrast, the onset temperatures of the exothermic decomposition of 1 M LiBOB EC-DMC solutions are around 275 °C. The results of 15 different DSC tests at a heating rate of 1 °C min⁻¹ are summarized in Table 1. The onset temperature of the redox thermal decomposition of the solutions with different ILs is higher than that in standard 1 M LiPF₆ EC-DMC solutions, and varies from about 220 to 240 °C. A standard solution with TFSI anion shows the best thermal stability (Fig. 3 and Table 1). The heat of the solution decomposition is lower when the anions are TFSI and BOB compared to solutions containing PF₆⁻ and FAP anions (Table 1). These

Table 1

Parameters related to decomposition of EC-DMC/LiPF₆ solutions with different ILs (indicated) obtained by DSC measurements at a heating rate of 1 °C min⁻¹. The parameters related to a standard EC-DMC/1 M LiPF₆ solution and EC-DMC/1 M LiBOB are presented as well.

No.	ILs additive	Weight of solution (mg)	Onset temperature (°C)	ΔU of decomposing of solution (J g ⁻¹)
1	HMI-FAP	5.15	226	145
2	BMP-FAP	3.77	222	200
3	MEMP-FAP	4.02	216	200
4	EDME-FAP	4.14	228	150
5	EMI-BOB	4.39	227	160
6	BMP-BOB	4.76	228	105
7	MEMP-BOB	4.14	230	170
8	EDME-BOB	4.62	231	130
9	HMI-TFSI	4.57	235	140
10	BMP-TFSI	4.41	232	160
11	MEMI-TFSI	3.88	236	150
12	EDME-TFSI	4.53	239	115
13	EMI-PF ₆	7.12	231	150
14	IL free	2.27	224	200
15	1 M LiBOB	4.31	245	-21
			275	5

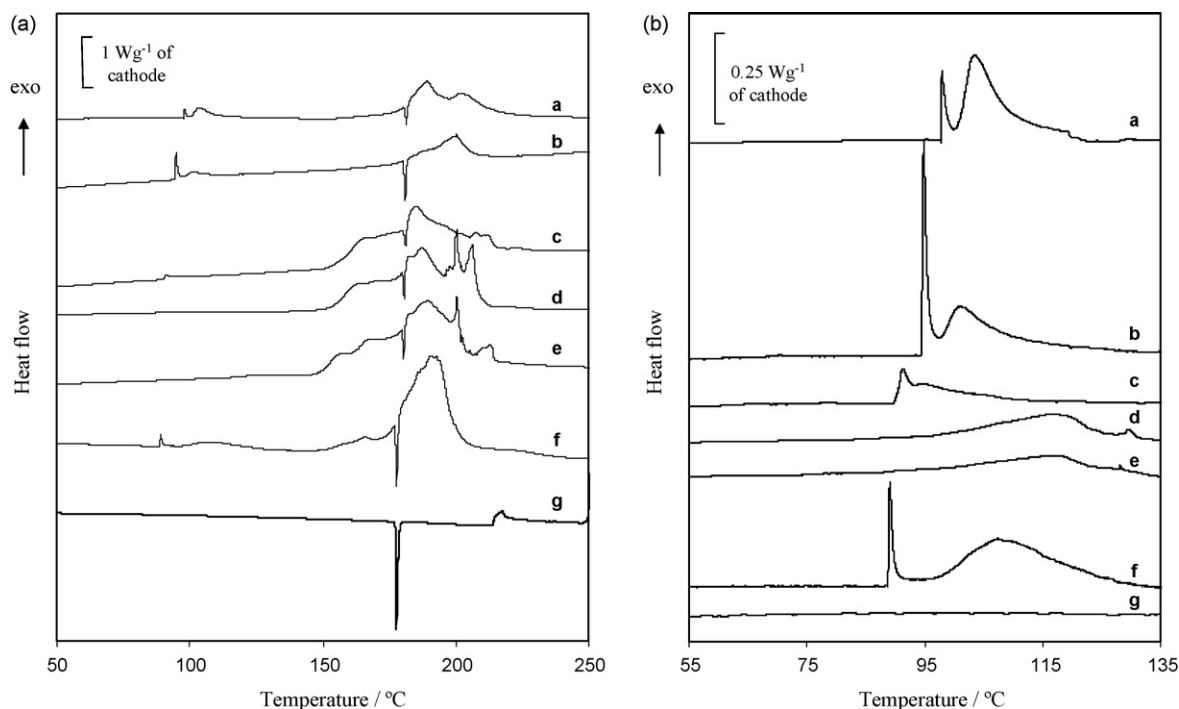


Fig. 4. (A) DSC curves obtained by heating different IL containing solutions (10%) in contact with Li metal: (a) HMI-FAP, (b) EDME-FAP, (c) EMI-PF₆, (d) HMI-TFSI, (e) EDME-TFSI, (f) standard IL free EC-DMC/LiPF₆ and (g) EC-DMC/LiBOB. A heating rate of 1 °C min⁻¹. (B) Same as (A), a narrower temperature range for clarification.

results are in line with our previous studies that showed that the phosphorous at an oxidation state of 5+, is a strong oxidizer for the alkyl carbonate solvents at elevated temperatures [19].

3.3. Solutions with Li metal

Typical DSC curves of Li samples in contact with IL containing EC-DMC/LiPF₆ solutions and with 1 M LiPF₆ and 1 M LiBOB EC-DMC solutions are presented in Fig. 4A. Fig. 4B presents some of these curves as indicated, at a narrower temperature range. The curve related to the standard (IL free) LiPF₆ solution shows two consequent exothermic peaks in the 80–120 °C range (Fig. 4B). These peaks belong to irreversible processes, as proven by DSC measurements during cooling at the end of the heating process (reverse direction). It is assumed that the two exothermic processes between 80 and 120 °C relate to the surface films. They reflect a serial conversion of the meta-stable surface species formed at RT to more stable compounds upon heating [20]. However, the passivating films which are formed on Li in LiBOB/EC-DMC solutions are stable and protect Li metal even above the Li melting temperature around 180 °C. In the 80–120 °C range there are no peaks corresponding to the thermal decomposition of the surface films formed on Li in the LiBOB solution (Fig. 4B).

The thermal behavior of the surface films formed on metallic Li surfaces in the mixed electrolyte solutions depends on the identity of the IL additive. The identity of both the cation and the anion is important in this respect. As expected, the solutions containing BOB anions demonstrate the stability of the surface films on lithium in the 80–120 °C range. In contrast, in solutions containing 10% by volume HMI-FAP, EDME-FAP, EMI-PF₆, HMI-TFSI, and EDME-TFSI additives, the surface films formed on lithium are very active in the temperatures range of 80–120 °C. When the mixtures containing Li samples and solutions are heated during the DSC measurements further (beyond 120 °C), multiple exothermic peaks are observed at temperatures above 170 °C (Fig. 4A and Table 2). These exothermic processes relate to the solution reactions with Li

metal (solid and then liquid after melting). None of the solutions exhibit a thermal stability, equal to that of EC-DMC/LiBOB solutions, whose reactions with Li occur at temperatures higher than 210 °C. Hence, the passivation of lithium in LiBOB solutions is so effective that it even protects liquid lithium. Moreover, the specific heat of the exothermic reactions of LiBOB EC-DMC solutions is lower by 1000 J g⁻¹ compared to those of LiPF₆ solutions. For the solutions containing FAP- and TFSI-based ILs (Fig. 4A), the onset of the exothermic reactions is lower than the endothermic peak of Li melting (around 180 °C), as is the case for the 1 M LiPF₆ EC/DMC standard electrolyte solution (Fig. 4A and Table 2). The onset temperature of the exotherms in these solutions varies from about 135 to 155 °C. The presence of BOB anions ensures the formation of more thermally stable surface films on the Li surface (Fig. 4A and Table 2) as expected [21]. However, the specific heat of the exothermic reac-

Table 2

Parameters related to the thermal reactions of Li metal and the various LiPF₆ solutions containing 10% ILs as indicated and IL free solution, measured by DSC at a heating rate of 1 °C min⁻¹.

No.	ILs additive	Weight of sample (mg)	Onset temperature (°C)	ΔU of thermal reactions (J g ⁻¹)
1	HMI-FAP	4.97	147	1250
2	BMP-FAP	5.18	145	2810
3	MEMP-FAP	4.79	145	2220
4	EDME-FAP	4.79	157	2190
5	EMI-BOB	5.39	158	1990
6	BMP-BOB	5.90	171	2650
7	MEMP-BOB	5.47	166	2760
8	EDME-BOB	5.02	168	1390
9	HMI-TFSI	5.02	136	2800
10	BMP-TFSI	5.19	142	2180
11	MEMI-TFSI	4.92	146	3100
12	EDME-TFSI	4.94	141	2936
13	EMI-PF ₆	4.71	146	2380
14	IL free	5.34	145	2590
15	1 M LiBOB	4.13	247	1730

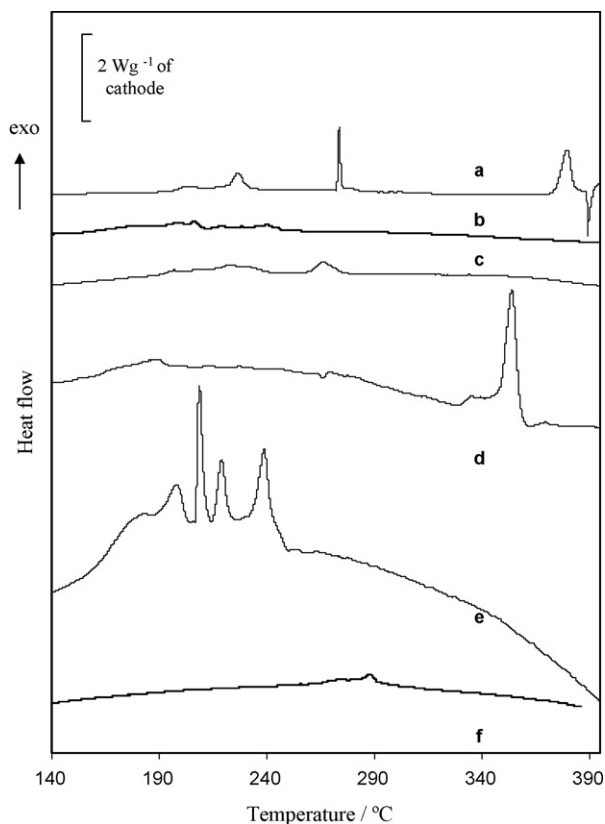


Fig. 5. DSC curves obtained by heating different IL containing EC–DMC/1 M LiPF₆ solutions (10%) in contact with Li_{0.5}CoO₂: (a) BMP–FAP, (b) BMP–BOB, (c) BMP–TFSI, (d) 1 M LiBOB in EC–DMC 1:1, (e) standard, IL free, EC–DMC/1 M LiPF₆ and (f) neat Li_{0.5}CoO₂ (no solution). A heating rate of 1 °C min⁻¹.

tions between Li and solutions containing ILs with BOB anions, is similar to that measured in the other solutions. In any event, LiBOB solutions and standard electrolyte solutions containing ILs with BOB anions are not too important, because the presence of the BOB anion in solutions limits considerably the anodic stability of the electrolyte solution (below 4.5 V vs. Li/Li⁺) as demonstrated in Fig. 2 and the related discussion in Section 3.1. This limitation excludes the use of these solutions for advanced cathode materials such as LiNi_{0.5}Mn_{1.5}O₄ spinel (4.8 V vs. Li/Li⁺), and layered materials such as Li[MnNi]O₂ and Li[MnNiCo]O₂, whose capacity can be pushed to

Table 3

Parameters related to the thermal reactions of Li_{0.5}CoO₂ in contact with various LiPF₆ solutions containing 10% ILs as indicated, with an IL free solution, and 1 M EC–DMC/LiBOB solution, measured by DSC at a heating rate of 1 °C min⁻¹. Parameters related to DSC measurements of Li_{0.5}CoO₂ powder (no solution) are presented as well. Values of the thermal effect are based on the weight of cathodes.

No.	ILs additive	Weight of cathode (mg)	Weight of solution (mg)	Onset temperature (°C)	ΔU of thermal reactions (J g ⁻¹)
1	HMI–FAP	2.72	4.42	185	810
2	BMP–FAP	3.07	4.64	179	910
3	MEMP–FAP	3.79	4.23	183	830
4	EDME–FAP	2.37	5.02	177	710
5	EMI–BOB	2.54	4.55	152	520
6	BMP–BOB	5.37	3.2	155	680
7	MEMP–BOB	3.10	4.12	150	1350
8	EDME–BOB	2.58	4.21	148	1290
9	HMI–TFSI	2.67	4.68	214	250
10	BMP–TFSI	2.57	4.40	173	490
11	MEMI–TFSI	2.38	3.97	190	360
12	EDME–TFSI	1.75	4.95	185	650
13	EMI–PF ₆	2.29	4.83	189	390
14	1 M LiPF ₆	2.77	2.97	157	1370
15	1 M LiBOB	1.19	4.74	158	460
	LiBOB			328	1350
16	Neat Li _{0.5} CoO ₂	2.29	–	254	330

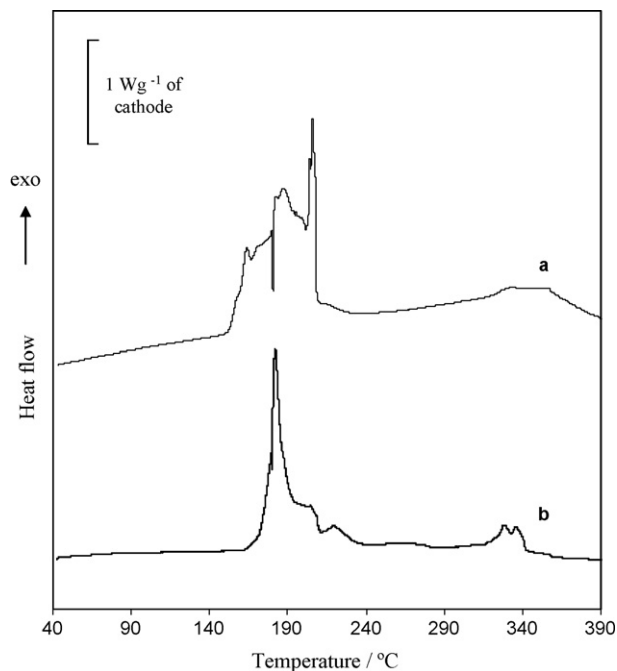


Fig. 6. DSC curves obtained by heating EC–DMC/LiPF₆–BMP–TFSI (10%) solution in contact with either both Li metal and Li_{0.5}CoO₂ or with Li metal alone: (a) EC–DMC/LiPF₆–BMP–TFSI (10%) with Li (without Li_{0.5}CoO₂) and (b) EC–DMC/LiPF₆–BMP–TFSI (10%) with Li and Li_{0.5}CoO₂. A heating rate of 1 °C min⁻¹.

200 and 170 mAh g⁻¹, respectively, if the charging potential can be as high as 4.6 V (Li/Li⁺).

3.4. Mixtures of solutions in contact with Li_{0.5}CoO₂ cathode material

Delithiated Li_{0.5}CoO₂ powder, rinsed in DMC and then heated as a neat, dry powder in closed crucibles under argon atmosphere exhibits exothermic decomposition starting at about 260 °C (Fig. 5). Two exothermic peaks between 260 and 280 °C are observed. The overall specific heat generation under these peaks is about 200 J g⁻¹. The thermal decomposition of Li_{0.5}CoO₂ undergoes the following stages [22–24]:

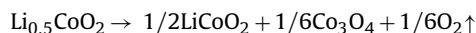
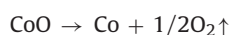


Table 4
Parameters related to the thermal reactions of mixtures containing Li metal and $\text{Li}_{0.5}\text{CoO}_2$ in contact with various LiPF_6 solutions containing 10% ILs as indicated, with an IL free solution, and 1 M EC–DMC/LiBOB solution, measured by DSC at a heating rate of 1°C min^{-1} . Values of the thermal effect are based on the total weight of samples.

No.	ILs additive	Weight of cathode (mg)	Weight of solution (mg)	Onset temperature ($^\circ\text{C}$)	ΔU of thermal reactions (J g^{-1})
1	HMI–FAP	3.53	4.23	146	1550
2	BMP–FAP	1.62	5.15	155	1660
3	MEMP–FAP	1.8	5.04	158	1090
4	EDME–FAP	1.93	4.76	150	1320
5	EMI–BOB	4.44	4.98	156	1530
6	BMP–BOB	4.58	4.43	156	1340
7	MEMP–BOB	3.13	4.41	155	1310
8	EDME–BOB	3.29	4.14	157	1290
9	HMI–TFSI	2.0	4.91	164	1510
10	BMP–TFSI	1.03	4.99	152	2100
11	MEMI–TFSI	2.55	4.86	152	1810
12	EDME–TFSI	1.57	5.01	158	1420
13	EMI– PF_6	1.97	5.46	143	1560
				326	400
14	1 M Li PF_6	0.86	4.38	137	3020
				326	380
15	1 M LiBOB	2.25	3.48	258	3260
				328	2370



The oxygen thus released, can react at the high temperatures vigorously with the alkyl carbonate solvents in highly exothermic reactions. Hence, upon heating systems containing both the partially lithiated cobalt oxide and solution, the presence of the latter component accelerates decomposition of $\text{Li}_{0.5}\text{CoO}_2$.

In our measurements of $\text{Li}_{0.5}\text{CoO}_2$ powder in contact with solutions (thus having in the mixtures sufficient amount of the EC/DMC solvents) the DSC response shows four superimposed exothermic peaks (Fig. 5), which probably reflect well the above thermal reactions. The thermal reactivity of $\text{Li}_{0.5}\text{CoO}_2$ with standard electrolyte solutions is indeed affected by the presence of ILs. The overall specific heat generation by the thermal reactions of $\text{Li}_{0.5}\text{CoO}_2$ and solution species is reduced and the onset temperature increases by about 25°C when the solutions contain ILs, compared to reactions with the IL free standard solution. It is spectacular in Fig. 5 and clearly demonstrated in Table 3 that the thermal stability of $\text{Li}_{0.5}\text{CoO}_2$ /solution mixtures considerably improves due to the presence of all the ILs. It is important that a pronounced improvement in the thermal stability of these systems is obtained by the presence of ILs such as BMP–TFSI and BMP–FAP which are also advantageous in terms of the electrochemical windows of these systems and good cathodic and anodic stability of the solutions (see Section 3.1).

3.5. Mixtures containing solutions and both Li and $\text{Li}_{0.5}\text{CoO}_2$ cathodes

Fig. 6 demonstrates the thermal behavior of mixtures containing different solutions and both Li metal and $\text{Li}_{0.5}\text{CoO}_2$. Two groups of superimposed exothermic peaks around 140 and 320°C correspond to the interaction of both Li and $\text{Li}_{0.5}\text{CoO}_2$ with solution species. The specific heat of the exothermic processes thus presented in the DSC curves does not vary noticeably as a function of the composition of the investigated solutions (Table 4). It is interesting to note that thermal stability of Li in the presence of $\text{Li}_{0.5}\text{CoO}_2$ improves in standard solutions containing ILs with TFSI anions (Fig. 6 and Table 4). The onset temperatures of the exothermic reactions are higher by about 20°C in mixtures containing both Li and $\text{Li}_{0.5}\text{CoO}_2$, compared to mixtures of solutions with Li only. The suppression of Li reactivity when both Li and $\text{Li}_{0.5}\text{CoO}_2$ are present in solutions can be

caused by the presence of Co ions in the solution. The phenomenon of Co dissolution from LiCoO_2 cathodes was detected at elevated and ambient temperatures [25–27]. Co^{2+} ion dissolution is connected to the first above-mentioned thermal reaction of $\text{Li}_{0.5}\text{CoO}_2$, which forms LiCoO_2 , O_2 and Co_3O_4 . The latter compound contains both Co^{2+} and Co^{3+} ions. LiCoO_2 itself can also disproportionate to CoO_2 , Li_2O and Co_3O_4 . Co^{2+} ions from Co_3O_4 dissolve to the solution. These ions are readily reduced by lithium to form metallic cobalt. The reduction process is known to increase the overall impedance of Li and Li graphite electrodes in standard solutions. It was reported that the presence of cobalt ions in solutions improved the behavior of graphite electrodes [28,29]. Hence, it is possible that the formation of Co clusters on Li surfaces attenuates the reactivity of the active metal at elevated temperatures. These results show that thermal studies of solution/single electrode material mixtures alone do not provide the entire thermal picture. It is always important to study entire systems: mixtures containing solutions and both anode and cathode materials, because the reflection between the electrode materials can affect strongly the behavior of the entire systems.

4. Conclusions

1. The thermal behavior of standard solutions alone is not changed noticeably in the presence of IL additives.
2. The addition of BOB-based ILs to standard solutions distinctly improves their thermal stability in the presence of Li metal. However, it does not make sense to use BOB-based ILs as additives, because the much cheaper LiBOB can be used as an additive for that purpose. The use of additives containing BOB ions limits considerably the anodic stability of the electrolyte solutions, and hence, is irrelevant for many advanced, high voltage cathodes such as spinel $\text{Li}[\text{MnNi}]_2\text{O}_4$ and layered $\text{Li}[\text{MnNi}]\text{O}_2$ and $\text{Li}[\text{MnNiCo}]\text{O}_2$.
3. The thermal stability of $\text{Li}_{0.5}\text{CoO}_2$ in standard electrolyte solutions can be improved markedly by the presence of ILs additives, comprising derivatives of pyrrolidinium as cations, TFSI and FAP as anions. This finding is important because such ionic liquids have a very wide electrochemical window ($>5.5\text{V}$) and hence, their presence in solutions contribute also to the electrochemical stability of the systems.
4. The thermal stability of mixtures containing metallic lithium, $\text{Li}_{0.5}\text{CoO}_2$ and solution is improved in standard solutions containing TFSI-based ILs, compared to mixture containing ILs free

standard solutions. It appears that the presence of both Li and $\text{Li}_{0.5}\text{CoO}_2$ in the mixture, attenuates the reactivity of Li towards the solutions. We attribute this phenomenon to possible deposition of cobalt (by reduction of Co ions in solution) on Li, which reduces its surface reactivity.

5. The studies described herein are of course preliminary. The 10% presence of ILs in solutions chosen for this work is not necessarily optimal. However, the results presented in this paper definitely show a real direction for judicious use of ILs in Li ion batteries, namely, in mixtures with standard solutions. In such mixtures the presence of ILs contributes to safety and anodic stability while the presence of polar-aprotic solvents provide low enough viscosity, good wetting of the electrodes' active mass and reasonable conductivity at low temperatures.

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