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Calorimetric studies of the thermal stability of electrolyte solutions based on alkyl carbonates and the effect of the contact with lithium

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Abstract

The thermal stability of different electrolytes—$LiPF_6$, $LiPF_3(C_2F_5)_3$ (LiFAP), LiFAP solutions containing 5% vinylene carbonate, and LiFAP solutions containing 1% Li bisalicylato borate—in a mixture of (2:1:2 v/v/v) EC, DEC and DMC is investigated. The results of a comprehensive study of the thermal behavior of these solutions in contact with Li metal and lithiated graphite electrodes (synthetic flakes) using both accelerating rate (ARC) and differential scanning (DSC) calorimetry, are reported herein. The surface films formed at room temperature on Li and lithiated graphite surfaces in all the solutions studied are not stable at elevated temperatures. The main exothermic reactions of the solution thermal decomposition in contact with Li metal occur at temperatures lower than the Li melting point (180 °C). The highest onset (at 165 °C) for the thermal decomposition in the presence of Li, was observed for solutions containing both LiFAP and VC. $LiPF_6$ solutions showed the lowest onset for thermal reaction (at 132 °C).

Keywords: Thermal stability; ARC; DSC; $LiPF_6$; LiFAP; Li metal

1. Introduction

During the past three decades, lithium ion batteries have become a dominant rechargeable power source for portable electronic devices. The thermal stability and safety concerns of lithium ion batteries are related mainly to the intrinsic thermal reactivity of the materials in the cells [1,6]. Events such as short circuit, overcharge, over discharge and heating may lead to thermal ran away which means development of high pressure and explosions. The thermal stability of $LiPF_6$ solutions in organic carbonates in the presence of metallic Li was investigated using DSC calorimetry at a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$ by Pasquier et al. [1], Kawamura et al. [2], Katayama et al. [3] and Sato etel. [4] They showed that the main exothermic reactions of the solution thermal decomposition occur at temperatures higher then that of Li melting point. Dahn and co-workers [6] studied thermal stability of 1 M $LiPF_6$ in EC–DEC solutions in the presence of lithiated graphite using ARC calorimetry.

We studied the thermal stability of electrolyte solutions based on alkyl carbonates by ARC and DSC calorimetry. The intrinsic thermal behavior was studied (bulk solutions) as well as the thermal behavior of these solutions in contact with Li metal and lithiated graphite electrodes (KS35).

2. Experimental

An accelerating rate calorimeter (ARC) from Arthur D. Little Inc., Model 2000 and a differential scanning calorimeter (DSC) from Mettler Toledo Inc., Model DSC 822 were used. Four following solutions were studied: 1 M $LiPF_6$/EC:DEC:DMC, 2:1:2; 1 M $LiPF_3(C_2F_5)_3$ (LiFAP) EC:DEC:DMC, 2:1:2; 1 M LiFAP/EC:DEC:DMC, 2:1:2 containing 5% vinylene carbonate; 1 M LiFAP/EC:DEC:DMC, 2:1:2 containing 1% Li bisalicylato borate (Merck's AD25).

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In the ARC tests, 1.0 ml of solution and 6 mg of Li metal in thin foils with an estimated exposed surface area of 140 mm^2 were placed in a titanium bomb (8.2 ml volume) within the ARC calorimeter and were heated from 40 to 350 °C with 5 °C increments at the rate of 2 $^\circ\mathrm{C\,min}^{-1}$ in the search for self-heating at a sensitivity threshold of 0.02 $^\circ\mathrm{C\,min}^{-1}$. The controller was programmed to wait 15 min for the sample and the calorimeter temperatures to equilibrate, and then to search during 20 min for a temperature increase of 0.02 $^\circ\mathrm{C\,min}^{-1}$. In tests with lithiated graphite, the weight of graphite samples (LiC_{12}) was about 90 mg, and solution volume was 1.5 ml.

DSC tests were conducted in high pressure, gold-plated stainless crucibles 30 μl in volume at a temperature range of 30–400 °C. The crucibles were filled by 3 μl of solution and 0.6 mg Li metal with estimated 14 mm^2 surface area exposed to the solution, and then sealed in a glove box under argon atmosphere. The heating rates were 0.5, 1, 2 and 5 $^\circ\mathrm{C\,min}^{-1}$.

3. Results and discussion

3.1. The thermal stability of the surface films in the absence of solution

We checked the thermal stability of the surface films on the lithium in solution absence. Li metal was stored in 1 M $LiPF_6$ solutions. The lithium after being passivated by surface films was rinsed by pure THF or DMC. The dried Li samples heated in the DSC to temperature of 350 °C. The results are shown in Fig. 1. With Li washed by THF the onset of the exothermic reaction is >300 °C and with Li washed by DMC there was no reaction at all. It can be suggested that part of possible reactive surface species are dissolved by rinsing in THF and DMC. No process is observed below the lithium melting point (180 °C).

3.2. The thermal stability of the electrolyte solutions in contact with Li metal and with lithiated graphite electrodes

Figs. 2 and 3, show the thermal behavior of 1 M $LiPF_6$ solutions without and with Li or lithiated graphite in DSC and ARC testing. A new exothermic process (an onset near 120 °C for Li presence, and near 60 °C in the presence of lithiated graphite) is seen in the ARC tests (Fig. 2). Dahn and co-workers [6] studied lithiated graphite in 1 M $LiPF_6$ in EC–DEC solutions and observed exotherms with onsets at temperatures 70–80 °C. They suggested that the conversion of metastable organic components of the surface films to stable inorganic species takes place in this temperature range. The higher uniformity of Li metal surfaces compared to Li–graphite increases the thermal stability of the surface layer on Li compared to the highly heterogeneous surface films on graphite particles. We suggest that the surface films formed at room temperature, do not passivate well the Li and graphite surfaces at elevated temperature because of dissolution of surface species (according to results in Fig. 1) and (or) mechanical separation.

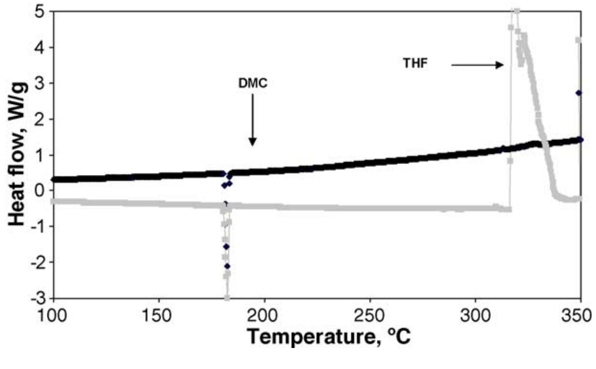

Fig. 1. DSC tests of lithium metal dry after heating on which surface films were formed in a $LiPF_6$ solution, rinsed with DMC or THF.

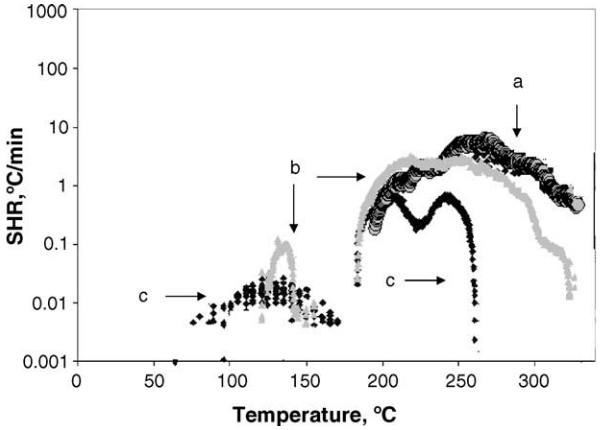

Fig. 2. ARC tests with 1 M $LiPF_6$ in EC:DEC:DMC (2:1:2, v/v/v) solution: (a) solution only, (b) solution with lithium metal and (c) solution with lithiated graphite.

The onsets of exotherms in DSC studies depended on the heating rate (Fig. 3). The slower is the heating rate, the lower and closer to ARC data is the exotherm onset. As it can be seen in Fig. 3 at heating rate of 0.5 °C, the main exothermic reactions of the solution thermal decomposition occur at temperatures lower then Li melting point. This phenomenon

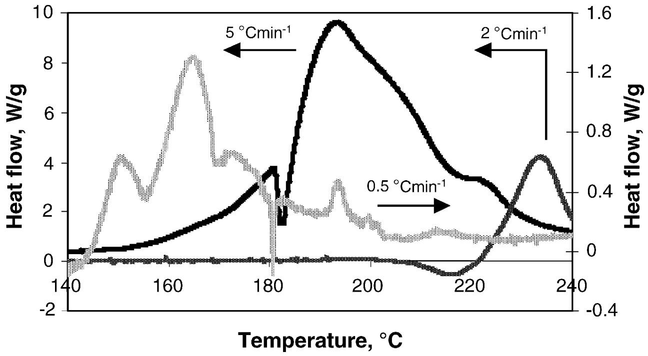

Fig. 3. DSC tests of 1 M $LiPF_6$ solution with lithium metal, at the scan rates of 0.5 and 5 $^\circ\mathrm{C\,min}^{-1}$ and a test with 1 M $LiPF_6$ solution (no lithium) at the scan rates of 2 $^\circ\mathrm{C\,min}^{-1}$.

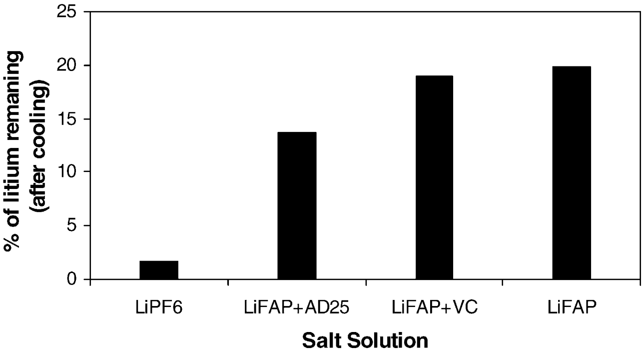

Fig. 4. The amount of Li remained after reactions between solutions and lithium estimated according to the Li solidification in DSC tests upon cooling.

contradicts with [1–4] results. The surface films formed at room temperature on Li or graphite surfaces in the solutions studied, do not protect the electrode from reactions with solution species at elevated temperatures.

According to Figs. 2 and 3 the reactions at temperature >80–120 °C (ARC tests) and >140 °C (DSC tests), are between fresh electrode surfaces and the solution. The thermal decomposition of the solution in the presence of electrodes (onset at 180 °C in Fig. 2) looks similar to decomposition of own solution, due to reactions between the solvents molecules and F^- anions (formed by decomposition of $LiPF_6$ [5]).

Heat effect of decomposition process with presence of Li is near two times higher than with lithiated graphite (Fig. 2). Such a result correlates well with a small, near 4 mg, amount of Li in the graphite sample in comparison to 6 mg of lithium metal.

Li consumed by the reactions with solutions species, and lithium stability in different solutions was estimated by remaining amount of Li, which crystallized upon cooling (DSC tests, Fig. 4). Fig. 4 shows the highest reactivity for $LiPF_6$ solutions and the lowest reactivity for LiFAP solutions. Thermal and spectroscopic studies of $LiPF_6$ and LiFAP solutions indicate higher thermal stability of the P–F bonds of LiFAP than the P–F bonds of $LiPF_6$ in the same solvent mixtures solutions. DSC measurements (Fig. 4 and Table 1) correlate well with these studies showing higher thermal stability of LiFAP solutions than of $LiPF_6$ solutions. The fluoride anions are the most reactive species in thermal reactions at those systems, but in the Li presence thermal stability of all solution reduces.

Table 1
Onsets and heat of reactions of the salt solutions

Solution	Onset (°C)		Heat reaction ($J\,g^{-1}$)	
	Without Li	With Li	Without Li	With Li
$LiPF_6$	190	132	583	1950
LiFAP	240	137	453	748
LiFAP + VC	195	165	248	1829
LiFAP + ad25	218	155	236	1936

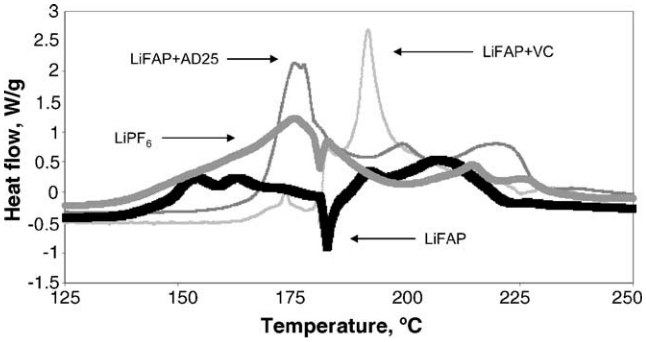

Fig. 5. DSC tests of 1 M $LiPF_6$, $LiPF_3(CF_2CF_3)$ (LiFAP), LiFAP + VC and LiFAP + AD25 with Li metal.

3.3. The influence of additives on the thermal stability of the electrolyte solutions

The influence of additives such as vinylene carbonate (VC) and Li bisalicylato borate (Merck's AD25) on thermal behavior of solutions was studied. Additives increase the thermal stability of the solutions in the presence of Li (Table 1; Fig. 5), in addition to their positive effect on the performance of Li ion batteries at R.T. (in terms of cycle life, reversibility, low impedance). These additives are very reactive due to their chemical structure, so they react with the Li surface thus forming very stable surface films. LiFAP solutions show an onset of exothermic reactions at 137 °C at heating rate of 2 °C min^{-1} that is similar to that of $LiPF_6$ solutions 132 °C (Table 1). The surface films formed on Li or Li–graphite due to the reduction of AD25 are less thermally stable than the surface films formed on the same electrodes due to the reduction of VC. Therefore, mixtures comprising LiFAP + VC solutions and electrodes, show the highest onset for thermal decomposition, at about 165 °C.

4. Conclusion

The surface films formed at room temperature on Li and lithiated graphite surfaces in all the solutions studied do not protect the active metal from exothermic reactions at elevated temperature.

The highest onset (at 165 °C) of thermal decomposition in a presence of Li was observed for LiFAP + VC solution. $LiPF_6$ solution showed the lowest thermal stability onset (at 132 °C). The highest amount of remaining Li after thermal reactions in solution was measured in LiFAP solutions and the lowest amount in the $LiPF_6$ solutions.

The additives increase the thermal stability of the LiFAP solutions.

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