

Short communication

Hexamethylphosphoramide as a flame retarding additive for lithium-ion battery electrolytes

Suzette Izquierdo-Gonzales, Wentao Li, Brett L. Lucht*

Department of Chemistry, University of Rhode Island, Kingston, RI 02881, USA

Received 30 March 2004; accepted 20 April 2004

Available online 3 July 2004

Abstract

Hexamethylphosphoramide (HMPA) was investigated as a flame retarding additive for lithium-ion batteries. The flammability, electrochemical stability, conductivity, and cycling performance of electrolytes containing HMPA were studied. The addition of HMPA to electrolytes comprising solutions of LiPF_6 in organic carbonates provided a significant reduction in the flammability of the electrolyte. However, the HMPA caused a slight decrease in the conductivity and electrochemical stability window of the electrolyte. Cycling performance of coin cells containing HMPA modified electrolytes was diminished.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Flame retardants; Lithium-ion rechargeable batteries; Electrolyte

1. Introduction

Lithium-ion rechargeable batteries contain electrolyte solutions composed of Li salts dissolved in single or blended organic solvents, typically organic carbonates. Almost all of these solutions are flammable and may be ignited when hot solvents expelled from the cells come in contact with oxygen under abusive conditions such as overcharge [1]. In extreme cases of abuse lithium-ion batteries have been reported to combust and explode.

One of the ways to reduce electrolyte flammability is to replace liquid electrolytes with solid electrolytes. Many polymer and polymer-gel electrolytes have been investigated and are expected to have improved flame resistance [2]. However, the improved flame retardancy was accompanied by reduced battery performance including significantly lower conductivity, especially at low temperature. Due to the inherent low conductivity, solid electrolytes are not practical for many applications where high power and low temperature performance are required.

The combustion of organic solvents is largely vapor phase oxidations, involving active H, OH, and O radicals [3]. Species that trap these active radicals and produce less active radicals result in flame inhibition. When compounds con-

tain more than one element that retards burning, the effect is synergistic [4].

Initial investigations into flame retarding additives for lithium-ion batteries have focused on organophosphorus compounds, in particular, on trialkylphosphates such as trimethyl phosphate [5] (TMP), triethyl phosphate [6] (TEP), tris(2,2,2-trifluoroethyl)phosphate [7] (TFP), and bis(2,2,2-trifluoroethyl)methyl phosphate [8] (BMP), and cyclophosphazenes such as hexamethoxycyclophosphazene (HMPN) [6,10]. However, none of these materials have functioned ideally. Trialkylphosphates-containing cells have problems associated with their reduction on the cell anode. HMPN has good electrochemical stability towards the electrodes but the high concentration required for reduction in flammability results in capacity loss during the cell cycling [6]. The best flame-retarding additives currently reported are the fluorinated phosphates TFP and BMP [8,9]. While phosphorus (V) compounds are some of the most widely investigated flame-retardants, materials containing other elements such as halogens or nitrogen have also been studied for various applications [3,4].

Since the high content of flame retardants in many cases worsens the cells performance, it is important to develop additives that prevent flammability at low additive concentrations. Therefore, we have investigated additives containing both nitrogen and phosphorus to take advantage of the synergistic effect of flame inhibition. The addition of nitrogen to organophosphorus flame-retardants allows the same flame

* Corresponding author. Tel.: +1 401 789 8348;

fax: +1 401 874 5072.

E-mail address: blucht@chm.uri.edu (B.L. Lucht).

retarding capacity with lower phosphorus content. Additives containing both phosphorus and nitrogen should allow non-flammable electrolyte at a lower concentration of additive. The P-N linkage in phosphoramides and phosphazenes reportedly promotes phosphorylation over other decomposition mechanisms that produce combustible gases providing additional flame retardance [11]. The only reported P-N containing flame retardant investigated for use in lithium-ion batteries is HMPN, which was found to be compatible with the electrodes but problematic in electrolytes that contain enough HMPN to retard flammability [6,10]. In general, P-N containing flame retardants are superior to the corresponding P-O containing flame retardants.

We report an investigation of a commercially available P-N containing flame retarding additive, hexamethylphosphoramide, HMPA. We have determined the conductivity, electrochemical properties, and flame retarding behavior of lithium-ion battery electrolytes composed of LiPF_6 dissolved in solvent mixtures derived from ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) with added HMPA. In addition to the flame retarding properties, the Lewis basicity of HMPA makes it an interesting thermal stabilizing additive for lithium-ion batteries [12].

2. Experimental

HMPA was purchased from Aldrich and purified by repeated fractionation under high vacuum and its purity was analyzed by ^1H , ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy and gas chromatography with mass selective detection (GC-MS). HMPA is a suspect carcinogen and should be handled with caution. Battery grade

carbonate solvents were purchased from EM Sciences and used as received. The solvents are stored in an argon glove box. LiPF_6 was purchased from Tomiyama was used as received. A solution of 1.0 M LiPF_6 in EC/EMC (1/3 mass ratio) was prepared in an argon glove box and used as a standard electrolyte.

We analyzed the self-extinguishing time (SET) of electrolyte versus the mass percent of the flame-retarding additive as described previously by Xu and co workers [6,7]. A micropipet was used to transfer 100 μL of electrolyte, with a mass of approximately 125 mg. The electrolyte was adsorbed into a cotton ball-wick (~ 0.5 cm diameter) in a glass dish and placed in a fume hood with a face velocity of 100 ft/s. The ball-wick was ignited. The burning time was followed with a stop watch and the SET was obtained by normalizing the flame burning time against the electrolyte mass. For each sample, the experiment was repeated eight times to provide an average value and standard deviation.

The conductivity measurements were performed with a Metrohm 712 conductivity meter using ThermoOrion conductivity cells. The cell constant is 1 cm^{-1} . The conductivity cells were enclosed in airtight glass tubes by means of Ace-Thred Teflon adapter and FETFE or Chemraz O-ring. The use of these conductivity cells makes it possible to take the cell outside of the glove box and perform conductivity measurements without atmospheric contamination. The temperature was controlled within about $\pm 0.1^\circ\text{C}$ with a Tenney Environmental chamber.

The electrochemical stability of the electrolyte (electrochemical window) was determined by means of cyclic voltammetry (CV) on platinum electrode (EG&G, 2 mm diameter) using a Solartron 1460 MultiStat potentiostat. A three-electrode cell (AG&G) with both lithium counter and reference electrodes was employed. The experiments

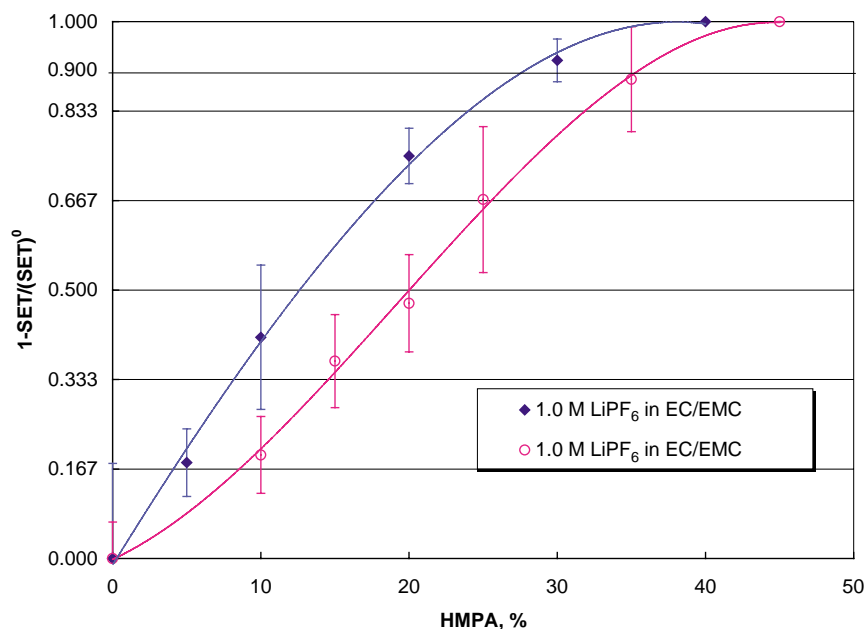


Fig. 1. Relative flame retardancy determined by self-extinguishing time (SET).

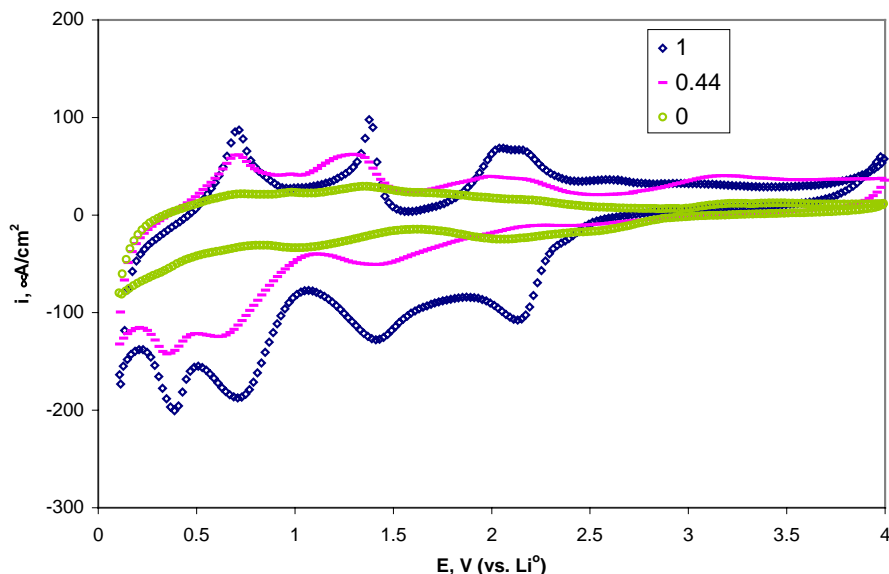


Fig. 2. CVA of 1.0 M LiPF₆ in EC/EMC/HMPA (1/3/X), where X = 0, 0.44, 1 (platinum electrode, 10 mV/s).

were performed in an argon-filled glove box at room temperature.

The effect of flame retardant on the cell performance was tested in coin cells. The electrodes of 1.27 cm diameter have been blanked from one-side coated aluminum or copper foil with lithium–nickel–cobalt oxide (cathode) and graphite (anode), respectively. The composition of cathode was 89% of LiNi_{0.8}Co_{0.2}O₂, 6% of carbon conductive diluents, and 5% of PVDF binder; the composition of the anode was 87% of carbon MCMB, 3% of carbon black, and 10% of binder PVDF. Polyethylene separator having 20 μm thickness was used. The cell contained 60 μl of electrolyte. The coin cells were tested on an Arbin Instrument cycler at room temperature. The profile followed by the cells was five cycles at constant current of 250/250 μA charge/discharge

from 3.0 to 4.1 V with taper charge at constant voltage of 4.1 V.

3. Results and discussion

Previous work showed that longer self-extinguishing times (SETs) are consistent with a greater flammability of the liquid solutions [6,7]. We define an electrolyte with 67%-reduced flammability as a *flame retarded* electrolyte, and that with 90%-reduced flammability as a *non-flammable* electrolyte. The relative values of $[1 - \text{SET}/(\text{SET})_0]$ where $(\text{SET})_0$ is the SET of the solution without HMPA is presented in Fig. 1. For the presented solutions, $(\text{SET})_0 \approx 40$ s. Addition of HMPA to solutions of either EC/EMC

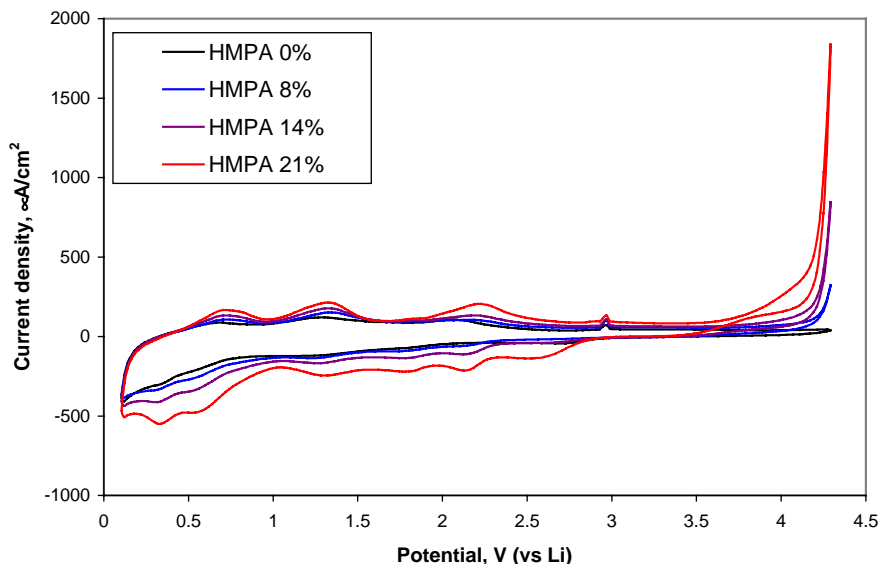


Fig. 3. CV of 1.0 M LiPF₆ in 1/3 EC/EMC containing HMPA, at 50 mV/s.

(1/3) or EC/EMC (1/1) provides a gradual loss of electrolyte flammability (Fig. 1). The addition of between 20 and 25% (by wt.) of HMPA results in the generation of a flame retarded electrolyte while addition of approximately 25–35% (by wt.) converts the electrolyte to non-flammable. These results suggest that HMPA is a better flame retarding agent than TMP and TEP and comparable to TFP [6,7]. The flammability tests suggest the incorporation of at least 10% (by wt.) HMPA to afford a significant (i.e.; about 20–30%) reduction in the flammability of LiPF_6 /carbonate electrolytes. Therefore, further investigations of electrolytes with reduced flammability focused on samples containing 10–40% (wt.) HMPA.

In order to determine the viability of HMPA incorporation into lithium-ion batteries, evaluation of the electrochemical stability of HMPA on the anode and cathode surfaces was conducted on samples with 10 and 20% (wt.) of HMPA. The results are presented in Fig. 2, where the cyclic voltammogram of HMPA containing electrolytes are compared to those without HMPA. The electrolyte solution was 1.0 M LiPF_6 in EC/EMC/HMPA (1/3/0, 1/3/0.444, and 1/3/1). A number of oxidation/reduction peaks are observed over the entire potential area. The height of the peaks is dependent upon the concentration of added HMPA, the scan rate, and the number of cycles suggesting that their appearance may be due to the presence of impurities of the HMPA. The amplitude of the peaks at 0.6, 1.3, and 2.2 V decrease with increasing cycles consistent with a decreasing concentration of impurities upon electrochemical decomposition during each cycle.

A similar trend was found upon addition of small amounts of HMPA to 1.0 M LiPF_6 in EC/EMC (1/3) (Fig. 3). Cyclic voltammetry clearly shows the same small oxidation and reduction peaks present in electrolyte at low concentration of HMPA. In addition the presence of HMPA makes the

electrochemical window slightly narrower, the current increase is exhibited at approximately 4.2 V versus 4.4 V in an HMPA-free solution.

The conductivity of electrolytes of 1.0 M LiPF_6 in 1:3 EC/EMC with several concentrations (in wt.%) of HMPA at various temperatures is presented in Fig. 4. In general, HMPA modestly decreases the conductivity of the original solution, by approximately 2% per 10% of the HMPA content at all temperatures investigated. Previous work showed that the solutions in binary solvent systems of EC with methyl acetate (MA) have exceptionally high conductivity, up to 13–14 mS/cm at 25 °C, compared to 7–8 mS/cm in a ternary electrolyte 1.0 M LiPF_6 in EC/DEC/DMC (1/1/1 mass) at 25 °C [13,14]. In Fig. 5, the conductivity of 1.0 M LiPF_6 solutions in MA with different mass content of HMPA is presented. Here, the conductivity of the solution containing even 50% of HMPA is still higher than that of the baseline electrolyte so that the addition of MA can compensate the conductivity decrease due to the presence of flame retardant. To verify the resulting effect of HMPA and MA on conductivity, the electrolytes containing both carbonates and esters were also examined. Fig. 6 shows that increasing the concentration of HMPA and MA in 1.0 M LiPF_6 (EC/EMC, 1/3) results in an overall increase in conductivity. This suggests that the conductivity enhancements of MA outweigh the conductivity reduction of HMPA. An increase of the HMPA content to 33% results in solubility problems and precipitation within the electrolyte solution. NMR spectroscopy suggests that the solubility problem in the solution may be due to the formation of an equilibrium complex between HMPA and LiPF_6 [12].

Coin cells were used to test the stability of HMPA under charge/discharge cycling. The cells were made with 1.0 M LiPF_6 solutions containing different solvent ratios namely EC/EMC (1/3) (as a baseline cell), EC/EMC/MA

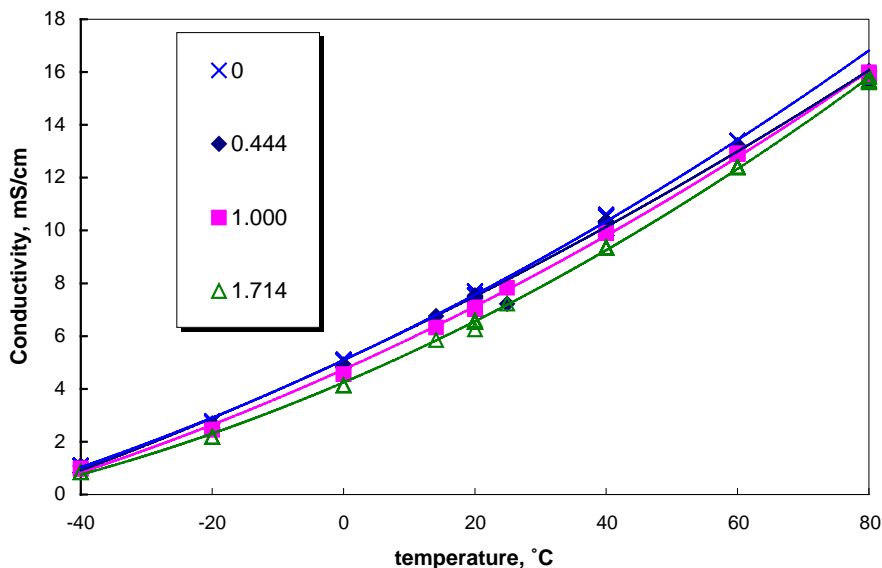


Fig. 4. Conductivity test of 1.0 M LiPF_6 EC/EMC/HMPA (1/3/X), where X = 0, 0.44, 1.0, 1.714.

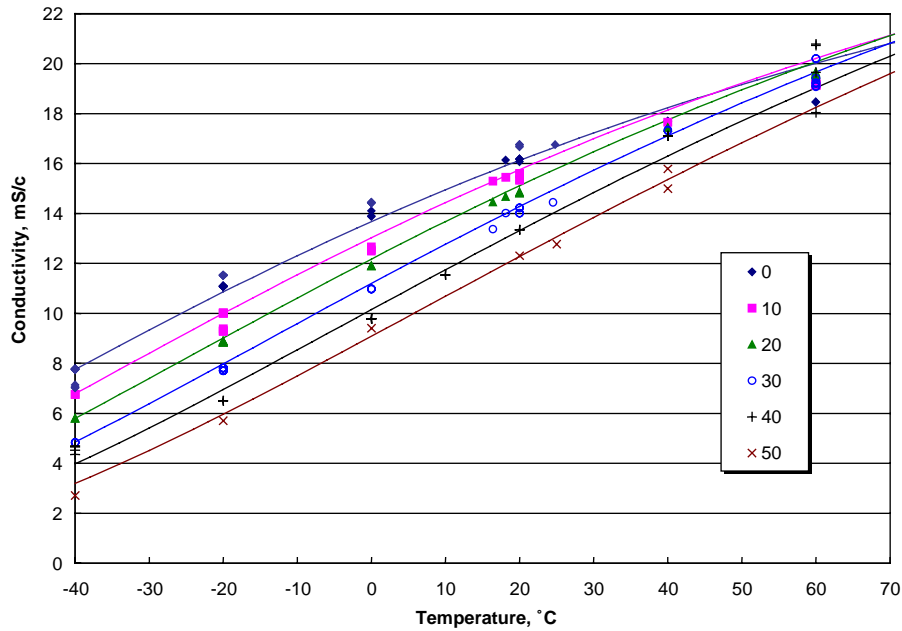


Fig. 5. Conductivity of 1.0 M LiPF₆ in MA with X% HMPA; X is in the inset.

(1/3/1), EC/EMC/MA/HMPA (1/1/1/1) and EC/EMC/HMPA (1/3/1). The cells were cycled within the voltage range from 3.0 to 4.1 V (versus Li/Li⁺). Fig. 7 shows the results of the first few charge/discharge cycles of these cells. As observed, the discharge capacity for baseline cells and the cells containing 1.0 M LiPF₆ in EC/EMC/MA (1/3/1) do not change upon repeated cycling. Addition of flame retarding additive HMPA to liquid electrolytes (1.0 M LiPF₆ EC/EMC/HMPA (1/3/1)) resulted in a decrease in the battery's performance.

The addition of MA to the flame retarded electrolyte does not improve the performance. Approximately 45% irreversible capacity at 250 μ A was observed on the first cycle, and the discharge capacity gradually decreases upon increasing cycles. The continued degradation of the discharge capacity is consistent with electrolyte degradation in the cells. The discharge capacity of cells containing HMPA is consistent with instability of the electrolyte at high positive potentials (Fig. 3).

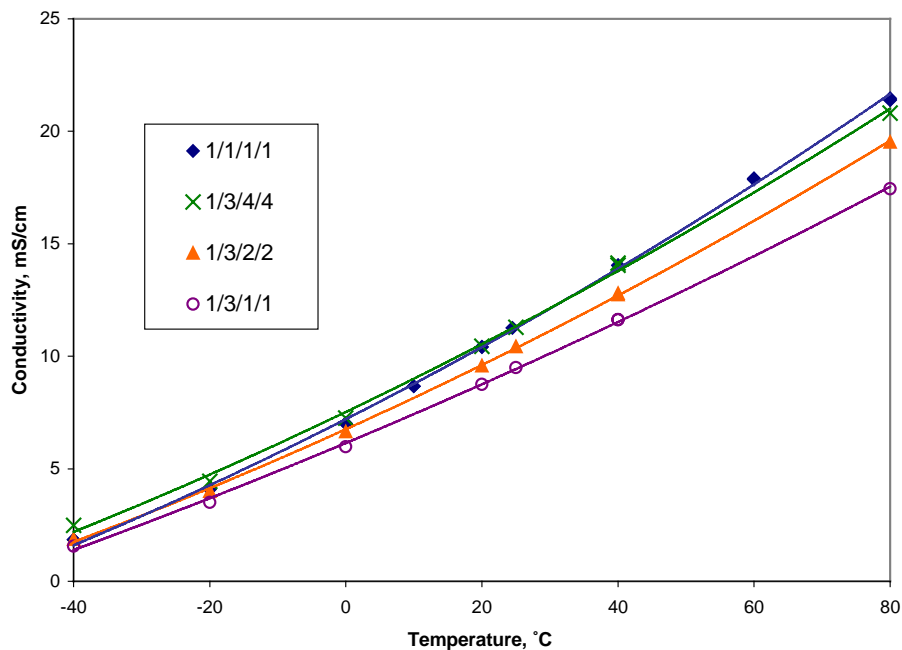


Fig. 6. Conductivity test of 1.0 M LiPF₆ EC/EMC/MA/HMPA at various ratios (in inset).

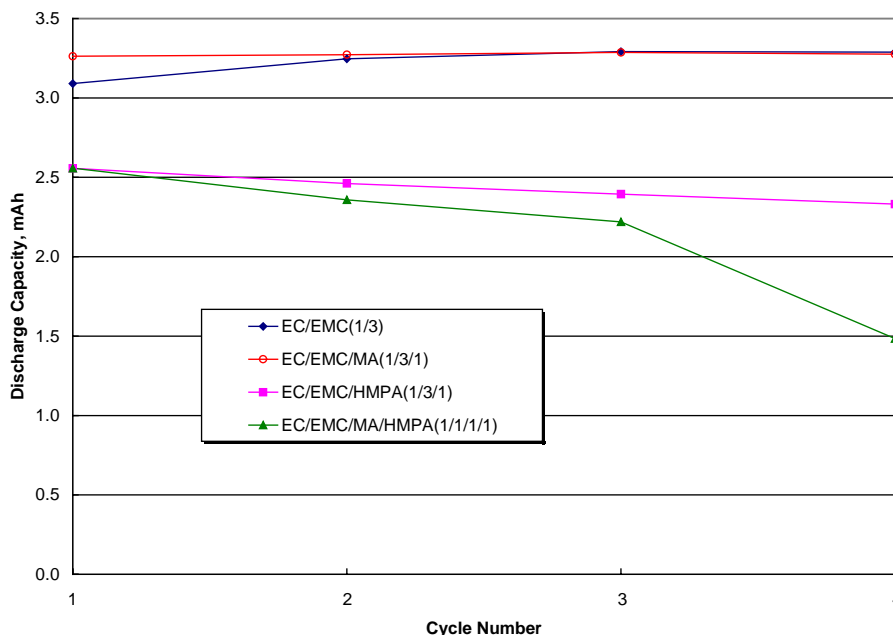


Fig. 7. Cycling performance of lithium-ion coin cells containing different solvent of various ratios (in inset) at room temperature.

4. Conclusions

The work confirmed that commercially available hexamethylphosphoramide acts as a flame retarding additive for lithium-ion batteries. We suggest that it is the P-N bond that provides improved flame retardance of electrolyte. However the presence of HMPA narrows the electrochemical window of the electrolyte. In addition, the high concentrations of HMPA results in the formation of precipitate from the electrolyte. The incorporation of HMPA to lithium-ion battery electrolyte is accompanied by decreased performance. Therefore, future investigations will focus on the discovery of flame retarding additives that are more stable to electrochemical oxidation while retaining stability with respect to reduction.

References

- [1] J.S. Hong, H. Maleki, S. Al Hallaj, L. Redey, J.R. Selman, *J. Electrochem. Soc.* 145 (1998).
- [2] F.B. Dias, L. Plomp, J.B. Veldhuis, *J. Power Sources* 88 (2000) 169.
- [3] S.L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley Interscience, New York, 1964.
- [4] J.W. Lyons, *The Chemistry and Uses of Flame Retardants*, Wiley, New York, 1970.
- [5] X. Wang, E. Yasukawa, S. Kasuya, *J. Electrochem. Soc.* 148 (2001) A1058.
- [6] K. Xu, M.S. Ding, S. Zhang, J.L. Allen, T.R. Jow, *J. Electrochem. Soc.* 149 (2002) A622.
- [7] K. Xu, S. Zhang, J.L. Allen, T.R. Jow, *J. Electrochem. Soc.* 149 (2002) A1079.
- [8] K. Xu, M.S. Dind, S. Zhang, J.L. Allen, T.R. Jow, *J. Electrochem. Soc.* 150 (2003) A161.
- [9] K. Xu, S. Zhang, J.A. Allen, T.R. Jow, *J. Electrochem. Soc.* 150 (2003) A170.
- [10] C.W. Lee, R. Venkatachalapathy, J. Prakash, *Electrochem. Solid-State Lett.* 3 (2000) 63.
- [11] C.J. Hilado (Ed.), *Flame Retardants, Part II*, Technomic Publishing Co., Westport, CT, 1976.
- [12] C. Campion, W. Li, W.B. Euler, B.L. Lucht, B. Ravdel, J. Dicarolo, R. Gitzendanner, K.M. Abraham, *Electrochem. Solid-State Lett.* 7 (2004) A194.
- [13] K.M. Abraham, D.M. Pasquariello, E.M. Willstaedt, *J. Electrochem. Soc.* 145 (1998) 462.
- [14] M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, K.B. Chin, S. Surampudi, H. Croft, D. Tice, R. Staniewicz, *J. Power Sources* 119–121 (2003) 349.