

Short communication

Possible use of non-flammable phosphonate ethers as pure electrolyte solvent for lithium batteries

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Abstract

Dimethyl methyl phosphonate (DMMP) was selected and tested as a non-flammable solvent for primary and secondary lithium batteries, because of its non-flammability, good solvency of lithium salts and appropriate liquidus properties. Experimental results demonstrated that DMMP can solvate considerable amount of commonly used lithium salts to form non-flammable and Li^+ -conducting electrolyte, which has very wide electrochemical window ($>5\text{ V}$ vs. Li) and excellent electrochemical compatibility with metallic lithium anode and oxide cathodes. Primary Li– MnO_2 cells using DMMP-based electrolyte showed almost the same discharge performances as those using organic carbonate electrolytes, and also, Li– LiMn_2O_4 cells using DMMP electrolyte exhibited greatly improved cycleability and dischargeability, suggesting a feasible application of this new electrolyte for constructing high performance and non-flammable lithium batteries.

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1. Introduction

Safety is a problem of prime concern for development of large size lithium batteries, which are greatly needed in many applications such as electric tools and electric vehicles. Although a number of factors can induce the unsafe behaviors of lithium batteries, one of major sources for safety hazards comes from the oxidation reactions of electrolyte solvent on charged cathodes, which release excessive amount of heat and cause thermal runaway of the cells. As a consequence, the cells may appear to vent and burn due to the ignition of flammable electrolyte leaked at high temperature [1–13]. Thus, it is expected that the firing and burning of electrolyte solution could be avoided if the electrolyte are non-flammable or fire retardant.

In recent years, much work has been done to use fire-retardant solvents as either a co-solvent or an electrolyte additive for lowering the combustibility of conventional organic carbonate electrolytes [14–36]. These fire-retardant compounds reported so far include trimethyl phosphate (TMP) [16–20], triphenyl phosphate (TPP) and tributyl phosphate (TBP) [33],

ethylene ethyl phosphate (EEP) [34] and fluorinated phosphate/phosphates [16] and so on. Usually, these fire-retardant liquids cannot be used as a pure solvent or as a co-solvent at high content, due to its poor electrochemical compatibility with lithium battery electrodes [1,14–19]. When used in low concentrations, the electrolyte additives cannot function very well and can only provide a limited fire-retardant action. Though some of fluorinated ethers or esters and ionic liquids [37–46] were reported to be able to serve as non-flammable solvents, these solvents are all very expensive and also have the problem of electrochemical incompatibility.

Organic phosphates are known as commonly used fire-retardant liquids. Compared with alkyl carbonates, some of these liquid compounds have similar liquidus temperature range, solvating ability and electrochemical stability, seeming to be a good candidate as non-flammable solvents for lithium batteries. To our knowledge, however, there has been no report on the use of organic phosphates as a single electrolyte solvent for lithium batteries. In evaluating the feasibility of organic phosphates as a safe solvent, we found that some liquid phosphates exhibited suitable electrochemical properties for battery applications. In this paper, we report a high electrochemical performance and non-flammable electrolyte solution using dimethyl methyl phosphonate (DMMP) as pure solvent and describe the performance

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Table 1
Physical property of some typical phosphate ethers and alkyl carbonates

Name	mp (°C)	bp (°C)	Viscosity (cP, 25°C)	Flash point (open cup, °C)	Phosphor content (%)	d (g cm ⁻³)
PC	-48	242	2.53	132	0	1.21
TMP	-46	197	1.3	148	18	1.21
DMMP	-50	181	1.75	104	25	1.16

characteristics of this electrolyte used for primary and secondary lithium batteries.

2. Experimental

All the phosphate ethers used in this work were purchased commercially. The phosphate ethers were all purified by re-distillation and then dried with molecular Sieves 4A. Lithium perchlorate (LiClO₄) were purchased from Aldrich and used without further purification, and lithium bis(oxalato)borate (LiBOB) were synthesized according to the method described in Ref. [47], which has a purity of >99% measured from elemental analysis. All the electrolyte solutions were prepared in the glove box purged with dried argon and had a water content <10 ppm.

The electrochemical windows of the electrolyte solutions were examined by cyclic voltammetry (CV) using a Pt microdisk electrode as working electrode. The CV behaviors of the electroactive materials were tested by power microelectrode method using a larger lithium sheet as both counter and reference electrode. The data acquisition and analysis were carried out on a CHI660A electrochemical workstation (Shanghai, China). The CV scan was always starting from open circuit potential to positive potential limit (+5 V) and then cycled to negative limit (-0.3 V vs. Li/Li⁺).

The charge–discharge experiments were carried out using simulated Li–MnO₂ and Li–LiMn₂O₄ cells of a three-electrode design. The positive electrode was consisted of 80% MnO₂ (or LiMn₂O₄) powder, 12% acetylene black and 8% PTFE (wt.%) and prepared by roll-pressing the mixed paste into an electrode film and then pressing the electrode film onto an aluminum net. The positive electrode and negative electrode were separated by a Celgard 2400 porous film and a small piece of lithium foil contacted with electrolyte was served as a reference electrode. The charge–discharge measurements were carried out using a computer-controlled programmable battery charger (BTS-0518001 type, Shenzhen, China).

The conductivity of the electrolyte was measured using a conductivity measurement (DDS-307, Shanghai, China) and calibrated with reference to the conductivity of standard 0.1 M KCl solution.

3. Results and discussion

DMMP is a polar liquid compound of low viscosity (cP ~1.75, 25 °C), strong solvating ability and wide liquidus temperature range (-50 to 181 °C). Particularly, this compound is incombustible and is now used as a strong fire-retardant in many aspects of fire protections [48,49].

Table 1 compares the physical properties of DMMP with other two types of organic solvents: widely used PC and frequently reported TMP solvent. Except for flammability, PC possesses all the physicochemical properties, such as wide temperature range, low viscosity and high dielectric coefficient, which are required for lithium battery applications. TMP have been suggested as a fire-retardant electrolyte additive for Li ion batteries [16–20], but this compound is electrochemically unstable and may decompose at charged cathode and anode [31,34]. In comparison with PC and TMP molecules, DMMP has almost the same liquidus temperature range as PC and higher molecular polarity than TMP, which implies possible use of DMMP as electrolyte solvent for lithium batteries. Besides, DMMP has a strong flame-retardancy, low cost and low toxicity, particularly suitable for electrolyte applications.

3.1. Electrochemical properties

For most lithium batteries, the electrolyte solvents should have at least a stable potential window of 0–4.5 V (vs. Li) to avoid the electrochemical interference of the electrolyte in the normal charge–discharge of lithium storage anodes and oxide cathodes. Fig. 1 shows the cyclic voltammograms of a number of lithium battery electrode materials in 0.8 mol L⁻¹ LiBOB + DMMP electrolyte. As it can be seen, the CV curve from a Pt working electrode in the DMMP electrolyte showed negligible background current in the potential region from 4.5 to 0 V and gave only a pair of lithium deposition and strip-

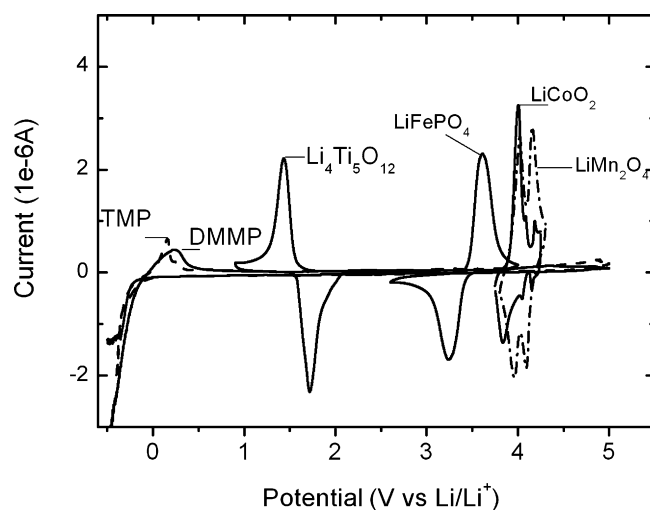


Fig. 1. Cyclic voltammograms of a number of electrode materials (as labeled at each curve) in DMMP containing 0.8 mol L⁻¹ LiBOB. Scan rate = 1 mV s⁻¹. A CV curve of Pt in 0.8 mol L⁻¹ LiBOB + TMP electrolyte is also given for comparison.

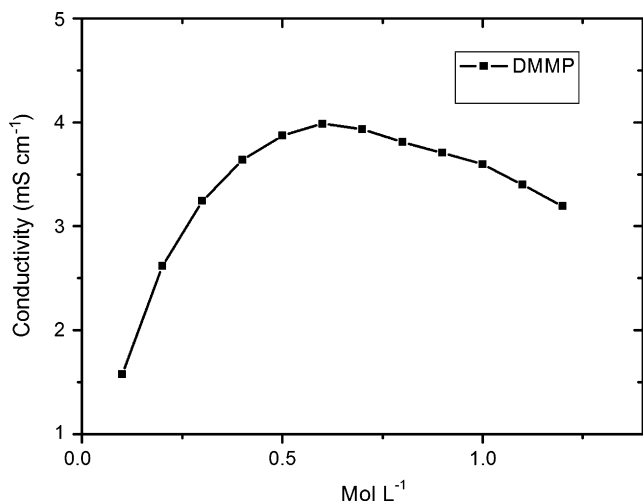


Fig. 2. Plot of the ionic conductivity of DMMP electrolyte vs. molar ratio of LiBOB salt at 298 K.

ping peaks once potential was scanned to -0.5 V. At more positive potentials than 4.5 V, a small oxidation current was observed due to the oxidative decomposition of LiBOB [50]. This suggests that DMMP is very stable in the potential range of 4.5 – 0 V and is also workable for electrochemical deposition and dissolution of lithium. Similarly, all the cathode materials LiMn_2O_4 , LiCoO_2 , LiFePO_4 and anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the DMMP electrolyte exhibited their perfect CV bands, identical to those observed in commercial organic carbonate electrolytes [1], demonstrating that electrochemical activities of these electrode materials are unaffected in the DMMP electrolyte.

Another important property of an electrolyte solvent for lithium batteries is its ability to dissolve sufficient amount of lithium salt. In our experiment, DMMP solvent can dissolve more than 2 mol L^{-1} of LiBOB, LiPF_6 or LiClO_4 salt, forming considerably conductive electrolyte solutions. Fig. 2 gives the change in the room temperature conductivity of DMMP electrolyte with molar concentration of LiBOB salt. It is shown in the figure that the ionic conductivity of the DMMP solution can reach a considerable high value of $>3 \text{ mS cm}^{-1}$ at a wide concentration range of 0.3 – 1.2 mol L^{-1} LiBOB electrolyte with its maximum conductivity of 4 mS cm^{-1} at 0.6 mol L^{-1} LiBOB. Though the conductivity is not as high as those reported in organic carbonate electrolytes (6 – 7 mS cm^{-1}) [1], it is higher than gel electrolyte (1 – 3 mS cm^{-1}) used in lithium batteries. Fig. 3 shows the temperature dependence of the ionic conductivity of 0.8 mol L^{-1} $\text{LiBOB}(\text{LiClO}_4)$ in DMMP. Like organic carbonates-based electrolytes, the conductivity of the DMMP electrolyte varies with temperatures in accord with Arrhenius relation. In comparison, the ionic conductivity of the DMMP-based electrolyte is even higher than the PC-based electrolyte at the same concentration of LiClO_4 salt.

3.2. Test in primary Li–MnO₂ cells

Among primary lithium batteries, Li–MnO₂ system possesses a dominant share in consumer electronic market. The

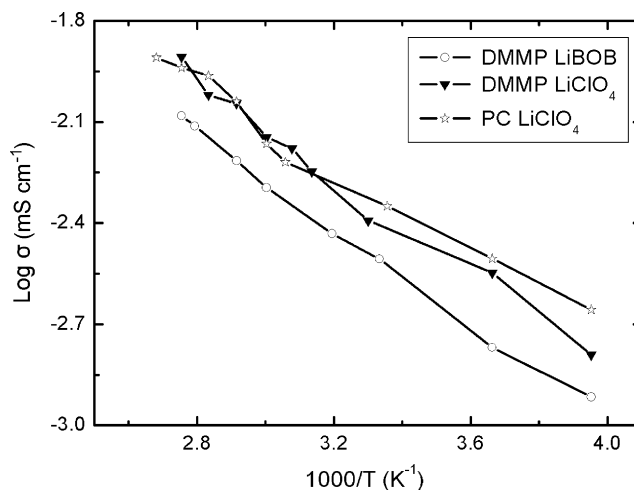


Fig. 3. $\lg\sigma$ – $1/T$ plot for some DMMP and PC-based electrolytes.

organic electrolyte for Li–MnO₂ batteries is now based on highly flammable alkyl carbonate solvents, which imposes a potential unsafe factor on the batteries and limits Li–MnO₂ cells to be made in small sizes. If non-flammable DMMP solvent can be used to replace the organic carbonate solvents, it may greatly enhance the safety of Li–MnO₂ batteries in storage, usage and transportation.

Fig. 4 shows the discharge behaviors of Li–MnO₂ cells using DMMP and PC-based electrolytes at different temperatures. At room temperature, Li–MnO₂ cells using conventional PC electrolyte delivered only a discharge capacity of 140 mAh g^{-1} with an average voltage plateau of 2.70 V, while the same cells using DMMP electrolyte can give a capacity of 150 mAh g^{-1} and a greatly enhanced voltage of 2.85 V, demonstrating a feasible use of DMMP as a single electrolyte solvent for primary Li–MnO₂ batteries. Also, even measured at quite low temperature of -20°C , the Li–MnO₂ cells can yield 100 mAh g^{-1} , about 66% of its capacity delivered at room temperature. This low temperature performance of the DMMP-based

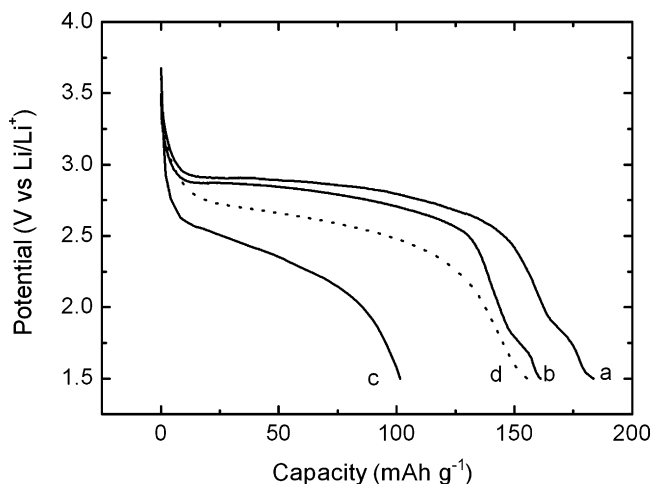


Fig. 4. The discharge curves of laboratory Li–MnO₂ cells at 30 mA g^{-1} in 0.8 mol L^{-1} LiClO_4 in DMMP at temperature of 40°C (a), 20°C (b), -20°C (c) and in 0.8 M LiClO_4 in PC at 20°C (d).

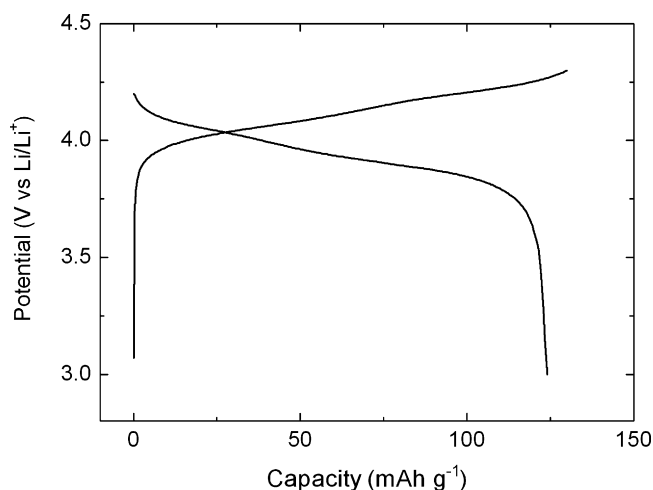


Fig. 5. The initial charge and discharge profiles of a Li–LiMn₂O₄ cell at constant current density of 50 mA g⁻¹ LiMn₂O₄ using 0.8 mol L⁻¹ LiBOB + DMMP electrolyte.

Li–MnO₂ cells is comparable to those reported for PC-based batteries.

3.3. Test in secondary Li–LiMn₂O₄ cells

Fig. 5 shows the initial charge and discharge curves of a Li–LiMn₂O₄ cell using 0.8 mol L⁻¹ LiBOB + DMMP electrolyte. Both the capacities and voltage profiles in Fig. 5 are very similar to those observed in EC-based electrolytes [1], suggesting that DMMP do not affect the normal charge–discharge reaction.

Fig. 6 shows the capacity retention of Li–LiMn₂O₄ cells cycled in DMMP electrolyte and in TMP electrolyte. As it can be seen in Fig. 6, the cells using DMMP electrolyte can be cycled very well with only 5% capacity loss during 50 cycles, while the cells using TMP electrolyte showed rapidly declined capacity after a few cycles, implying an electrochemical stability of

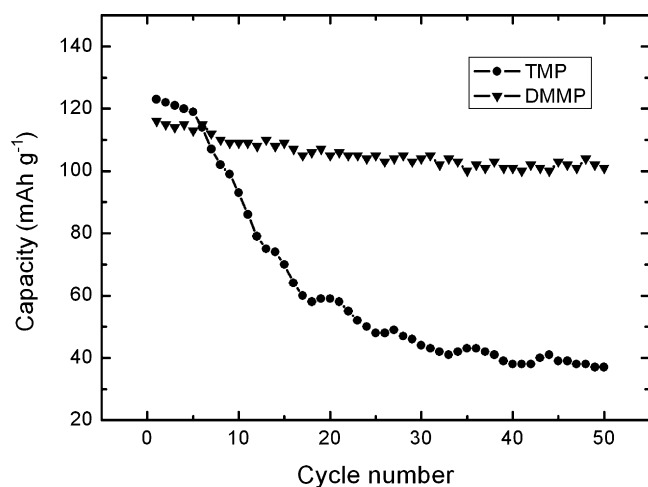


Fig. 6. Changes in the discharge capacity of Li–LiMn₂O₄ cells cycled in 0.8 mol L⁻¹ LiBOB + DMMP electrolyte and compared with the same cells cycled in 0.8 mol L⁻¹ LiBOB + TMP electrolyte. The charge–discharge rate is 0.5C (50 mA g⁻¹).

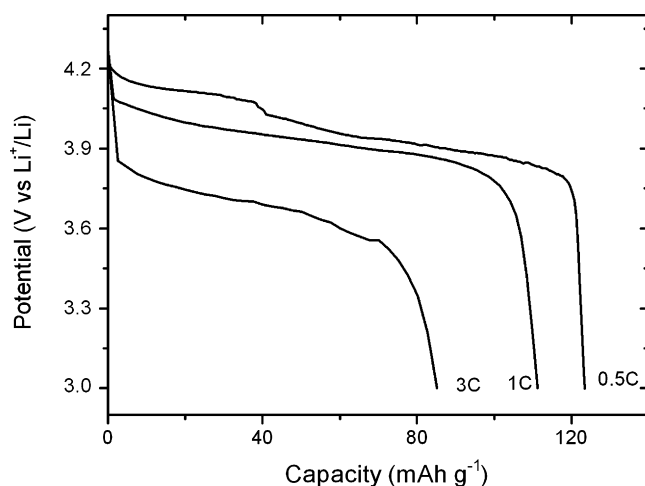


Fig. 7. Discharge curves of Li–LiMn₂O₄ cells in 0.8 mol L⁻¹ LiBOB DMMP electrolyte at different rate of 0.5C (50 mA g⁻¹), 1C and 3C.

Li and LiMn₂O₄ electrode in the DMMP electrolyte. In previous work [31,35], it has been revealed that since the SEI film formed on the cathode surface in TMP electrolyte is not stable, TMP molecules can react continuously with the oxidized cathode to result in continuous degradation of the cathode material. In contrast, DMMP exhibited considerable electrochemical stability at the charged cathodes as shown from the CV evidence in Fig. 1, and it is therefore expected that the cycleability of Li–LiMn₂O₄ cells may be greatly improved by use of DMMP electrolyte.

A good rate capability of the Li–LiMn₂O₄ cells using 0.8 mol L⁻¹ LiBOB DMMP electrolyte can also be seen from Fig. 7. At a moderate rate of 0.5C (50 mA g⁻¹), the discharge capacity of LiMn₂O₄ cathode can reach 125 mAh g⁻¹, ca.85% of its theoretical capacity (148 mAh g⁻¹). Even when the current was increased to 1C rate and 3C, the LiMn₂O₄ cathode can still deliver a discharge capacity of 110 and 85 mAh g⁻¹, respectively. This rate capability of Li–LiMn₂O₄ cells discharged in DMMP electrolyte is comparable to those discharged in carbonate-based electrolyte.

Finally, it should be mentioned that the graphite anode used in Li-ion batteries do not work well in DMMP electrolyte, showing large potential polarization during charge and discharge. To explain this phenomenon, further work is needed to get a deeper understanding of the interfacial reactions of DMMP molecules at graphite surface. Nevertheless, the results given above do suggest the possibility of using DMMP as pure electrolyte solvent for constructing non-flammable lithium batteries.

4. Summary

DMMP and TMP were comparatively tested for possible use as pure electrolyte solvent for lithium batteries. It is found in this work that DMMP can solvate considerable amount of lithium salts to form non-flammable and Li⁺-conducting electrolyte. This type of electrolyte has very wide electrochemical window and excellent electrochemical compatibility with

metallic lithium anode and oxide cathodes, showing a great prospect for application in constructing high performance and non-flammable lithium batteries.

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