



Short communication

Dimethyl methyl phosphate: A new nonflammable electrolyte solvent for lithium-ion batteries

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ABSTRACT

A new fire retardant-dimethyl methyl phosphate (DMMP) was tested as a nonflammable electrolyte solvent for Li-ion batteries. It is found that in the addition of chloro-ethylene carbonate (Cl-EC) as an electrolyte additive, the electrochemical reduction of DMMP molecules can be completely suppressed and the graphite anode can be cycled very well with high initial columbic efficiency (~84%) and excellent cycling stability in the DMMP electrolyte. The prismatic C/LiCoO₂ batteries using 1.0 mol L⁻¹ LiClO₄ + 10% Cl-EC + DMMP electrolyte exhibited almost the same charge and discharge performances as those using conventional carbonate electrolytes, suggesting a feasible use of this new electrolyte for constructing nonflammable Li⁺-ion batteries.

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1. Introduction

Safety concern has been a key obstacle for development and applications of large capacity or high power Li-ion batteries. One of the major factors relating to the safety of Li-ion batteries is the use of flammable organic electrolytes in current lithium battery technology. When the internal temperature and pressure increased to cause mechanical damages of the batteries, the volatile electrolyte may vent and ignite, leading to severe safety hazards of the Li-ion batteries [1–13].

To suppress the electrolyte flammability, much work has been done in recent years to develop fire-retardant solvents as either a co-solvent or an electrolyte additive in the organic carbonate electrolytes of Li-ion batteries [14–18]. The fire-retardant compounds explored so far include a variety of organic phosphates [14,15], fluorinated ethers [17] and ionic liquids [18]. Though most of the organic phosphates enable to reduce the flammability of electrolyte, they are difficult for practical use because most of the organic phosphates can decompose electrochemically at quite positive potentials, which cannot form a stable solid electrolyte interface (SEI) film so as to prevent the further decomposition of electrolyte [14,16]. Some of fluorinated esters [17] and ionic liquids [18] were reported to be able to serve as nonflammable solvents; however, these solvents are all very expensive and are also difficult to meet the electrochemical requirements of Li-ion batteries.

Organic phosphates are commonly used as flame-retardants in many aspects of fire prevention [16]. Some of these liquid compounds have very similar physical and chemical properties to the organic carbonates, such as liquidus temperature range, solvating ability and electrochemical stability, seeming to be a good candidate as nonflammable solvents for lithium battery applications. In evaluating the feasibility of organic phosphates as a safe solvent, we found that dimethyl methyl phosphate (DMMP, (CH₃O)₂POCH₃) can be effectively used as a nonflammable solvent for lithium-ion batteries with the help of chloro-ethylene carbonate (Cl-EC, (ClC₂H₃)CO₂) as a SEI film-forming additive. In this paper, we report the electrochemical properties of nonflammable DMMP electrolyte and the performance characteristics of Li-ion batteries using this electrolyte.

2. Experimental

The DMMP reagent used in this work was purchased commercially from Haizheng chem. Ltd., Qingdao, China (99% purity). The phosphate was purified by re-distillation and then dried with molecular sieve 4A and the purified DMMP had a water content <10 ppm determined by the Karl–Fischer method.

Lithium perchlorate (LiClO₄) and Cl-EC were all purchased from Aldrich and used without further purification. All the electrolyte solutions were prepared in the glove box purged with dried argon and had a water content of <10 ppm.

The stable potential regions of the electrolyte solutions were determined by cyclic voltammetry (CV) using a Pt microdisk electrode. The CV responses of the electroactive materials were tested

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by powder microelectrode method using a larger lithium sheet as both counter and reference electrode. The data acquisition and analysis for CV measurements were carried out on a CHI660A electrochemical workstation (Shanghai, China).

The charge–discharge curves of graphite in the DMMP electrolyte were measured with respect to Li anode. The graphite electrode was consisted of 90% graphite powder, 2% acetylene black and 8% PTFE (wt.%). The Li-ion batteries used for evaluating the electrochemical performances of the DMMP electrolyte were prismatic graphite/LiCoO₂ batteries (301564 type, 450 mAh) friendly donated by Fenghua Battery Co. Ltd. (Guangdong, China) and filled with DMMP electrolyte in our laboratory. The charge–discharge measurements were carried out using a computer-controlled programmable battery charger (BTS-0518001 type, Shenzhen, China).

3. Results and discussion

3.1. Electrochemical properties of DMMP solvent

DMMP is a polar liquid compound with very low viscosity ($\eta \sim 1.75$, 25 °C), wide liquidus temperature range (–50 to 181 °C) and strong fire-retardancy (phosphor content: 25%), apparently being a good choice for nonflammable solvent for Li-ion batteries. To evaluate its feasibility for battery applications, we firstly determined the electrochemical window and the ionic conductivity of DMMP-based electrolyte.

Fig. 1 shows the current response of a Pt electrolyte in a wide potential scan from –0.2 to +5.0 V (vs. Li⁺/Li). Except for a pair of redox peaks related to lithium deposition and stripping at –0.25 to 0.25 V, there were almost no detectable oxidation and reduction current in the potential range of 0 to +5.0 V, suggesting that the DMMP electrolyte is quite stable in a sufficiently wide potential range for lithium battery applications.

A qualified electrolyte solvent for Li-ion batteries should also have strong solubility for lithium salts and sufficient Li⁺ conductivity. Fig. 2 shows the room temperature conductivity of the DMMP solution at different molar ratios of LiClO₄ electrolyte. As the conventional carbonate electrolytes, the ionic conductivity of the DMMP electrolyte exhibited a parabolic change with increasing concentration of Li⁺ salt and reached its maximum value of ca. 6 mS cm^{–1} at 0.8 mol L^{–1} LiClO₄, which is comparable to the solution conductivity (about 8–10 mS cm^{–1}) of organic carbonate electrolytes currently used in Li-ion batteries [1,19]. As reported recently [20], the $\log \sigma \sim T^{-1}$ plot of the DMMP electrolyte measured at –20 °C to +90 °C exhibited a straight line in agreement with Arrhenius relation, giving a quite high conductivity of 12 mS cm^{–1}

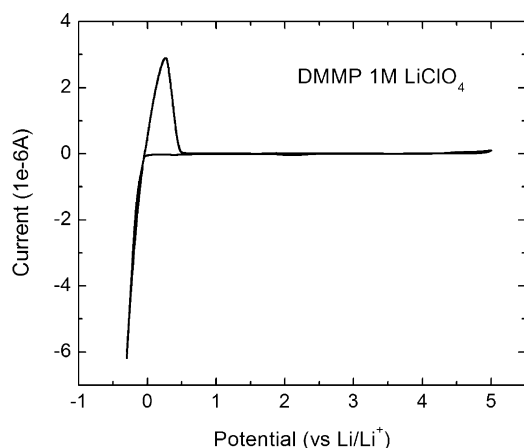


Fig. 1. A cyclic voltammogram of Pt electrode in 1.0 mol L^{–1} LiClO₄ + DMMP electrolyte. Scan rate = 1 mV s^{–1}.

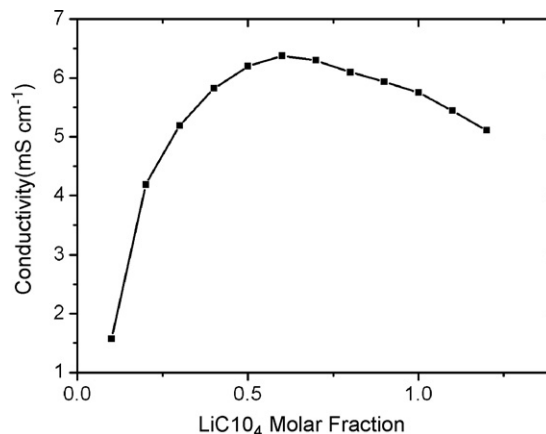


Fig. 2. Ionic conductivity (σ) of the DMMP electrolyte at various molar concentrations of LiClO₄.

at 90 °C and 1.5 mS cm^{–1} at –20 °C.

3.2. Suppressed co-intercalation of DMMP on graphite

Previous studies of phosphate electrolyte additives have revealed that most of phosphates underwent a reductive decomposition continuously on graphite anodes [14–16], causing a low coulombic efficiency and poor cycling stability of Li-ion batteries. This phenomenon appeared also in DMMP-based electrolytes. In the CV measurements of graphite electrodes in DMMP electrolyte, we found that there appeared a series of reduction current peaks in the potential region from 1.7 to 0.5 V, whereas the reversible Li⁺ inserting currents were not observable. These phenomena resemble very much the co-intercalating reactions of propylene carbonate solvent on graphite [21,22], implying that DMMP molecules may participate in electrochemical reduction on the graphite surface, which frustrates the Li⁺ intercalation reaction on the graphite anode.

To solve this problem, we tried to use the film-forming additives in the electrolyte to produce a stable SEI film on the graphite surface before the onset of electroreduction of DMMP solvent and thereby to suppress the direct reduction and co-intercalation of DMMP molecules. By comparison of a number of the film-forming molecules, we found that Cl-EC can function very well for this purpose. Fig. 3 shows the CV curves of a graphite anode in the

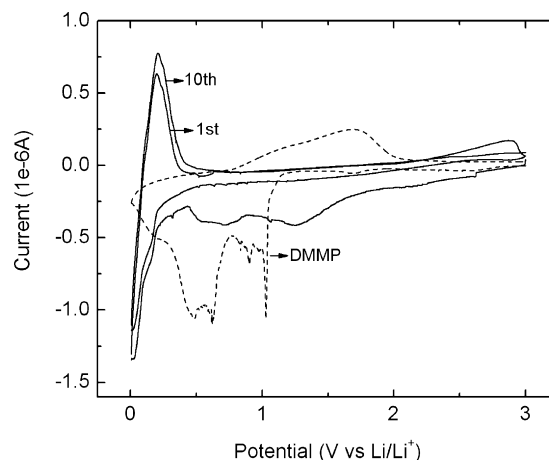


Fig. 3. The CV curve of graphite in 1 mol L^{–1} LiClO₄ + DMMP electrolyte with (solid lines) and without (dashed line) addition of 10% (v/v) Cl-EC. Scan rate = 1 mV s^{–1}.

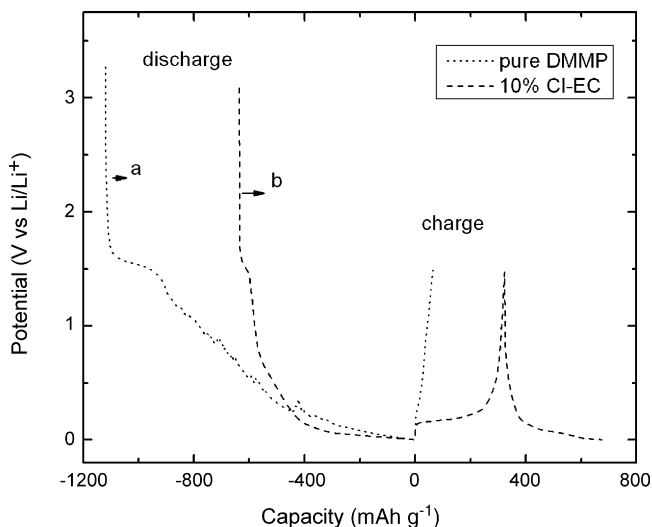


Fig. 4. The charge–discharge curves of graphite in 1 mol L⁻¹ LiClO₄ + DMMP with and without addition of 10% (v/v) Cl-EC, using Li sheet as counter electrode.

DMMP electrolyte containing 10% Cl-EC. At first cathodic scan, a broad irreversible band appeared at ca. +1.7 V, denoting the electrochemical reduction of Cl-EC additive. When the potential scan was swept negatively, the current peaks featuring the decomposition and co-intercalation of DMMP solvent became indiscernible and instead, a pair of redox peaks characteristic of Li⁺ interaction and de-intercalation on graphite appeared reversibly at the potential region of +0.5 to 0 V and became a prominent CV feature since the second scan and afterwards. This CV evidence suggested that Cl-EC reduces to form a stable SEI film on the graphite surface prior to the reductive decomposition of DMMP solvent, which protected the graphite structure from destructive attacking by the co-intercalation of the phosphate molecules. The reason why only Cl-EC can effectively form a protecting film on the graphite anode is simply because the reduction potential of Cl-EC (~1.7 V) is more positive than that of DMMP (~1.3 V) and the electrochemical reduction of Cl-EC is earlier than the decomposition of DMMP molecules. Also, the reductive decomposition of Cl-EC produce CO₂, which is known to be an important component for promoting the formation of a dense and stable SEI film on graphite surface [23–25]. This working mechanism of Cl-EC is very similar to that of vinylene carbonate additive in carbonate-based electrolytes [26].

The strong ability of Cl-EC additive for improving the electrochemical performance of graphite in the DMMP solution can also be seen from the charge–discharge experiments. Fig. 4 compares the charge–discharge curves of graphite in 1 mol L⁻¹ LiClO₄ + DMMP with and without addition of Cl-EC. In the absence of Cl-EC, the charging capacity of the graphite anode was very large (~1200 mAh g⁻¹) and the charging potential showed a plateau at ~1.5 V and then decreased slowly to 0.2 V, suggesting that the charging capacity was mostly consumed in the electrochemical decomposition and co-intercalation of DMMP molecules. Because of this inefficient charging, the graphite electrode gave almost no useful capacity at discharge, showing a rapid rise of the discharging potential. In comparison, the charging potential of the graphite electrode in the presence of Cl-EC additive decreased rapidly from 3 to +0.2 V and then kept stable at +0.2 to +0.05 V, which is characteristic of the formation of LiC_x compound by Li⁺ insertion into the graphite. At discharge, the graphite electrode gave a flat discharge plateau at ~0.25 V and delivered a capacity of ~280 mAh g⁻¹ corresponding to a capacity utilization of ≥85% at the first cycle. This first discharge capacity and coulombic efficiency is very similar to

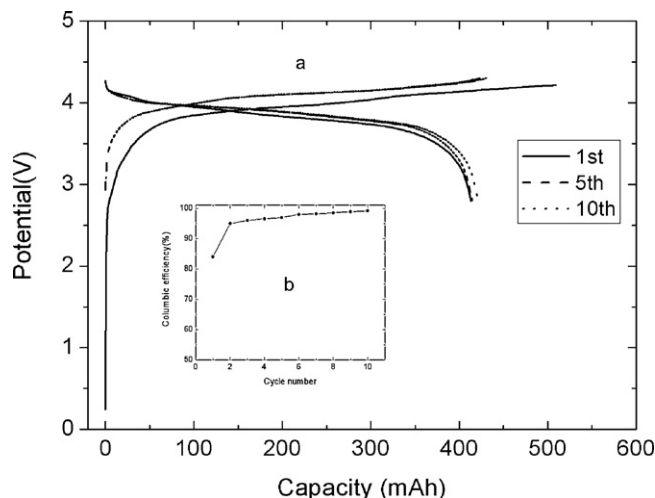


Fig. 5. The charge–discharge (a) and coulombic efficiency–number (b) curves of prismatic C/LiCoO₂ batteries filled with 1.0 mol L⁻¹ LiClO₄ + 10% Cl-EC + DMMP, measured at constant current of 0.2 C and room temperature.

those observed in carbonate electrolytes [1]. From the second cycle, the cycling efficiency of the graphite electrode increased rapidly to ~100% and remained steadily at prolonged cycling. This comparison demonstrates that the graphite electrode can work very well as Li⁺ inserting anodes in the DMMP electrolyte as long as a small amount of Cl-EC additive was added to block off the reductive reactions of DMMP molecules.

3.3. Li⁺-ion battery applications

To evaluate the feasibility of DMMP as a pure electrolyte solvent for commercial battery applications, we assembled the commercial graphite/LiCoO₂ batteries using 1 M LiClO₄ + 10% Cl-EC + DMMP as electrolyte. Fig. 5 shows the charge–discharge curves of these batteries. At first cycle, the batteries can be activated to deliver almost their full capacity of ~450 mAh with a charge–discharge efficiency of ~85%, which is comparable to the initial coulombic efficiencies of the same type batteries using carbonate-based electrolytes. From the second cycle and afterwards, the batteries exhibited a very high current efficiency of ~100% and very stable charge–discharge capacity. This cycling stability is most likely due to the formation of a stable SEI film on the graphite surface during the electrochemical reduction of Cl-EC additive as discussed above. In general, the test batteries using DMMP electrolytes show very similar charge–discharge performances and cycling stability as the batteries using conventional carbonate electrolytes.

4. Conclusions

Dimethyl methyl phosphite (DMMP) is a strong fire-retardant with appropriate physicochemical properties as a nonflammable electrolyte solvent for Li⁺-ion batteries. The major problem of this solvent is its reductive decomposition on graphite surface, which interferes with the normal charge–discharge reactions of the graphite anode.

The electrochemical incompatibility of this solvent with graphite anode can be solved by the use of suitable SEI film-forming additives. We found that in the presence of Cl-EC, the graphite anode can be cycled very well in the DMMP electrolyte with high initial coulombic efficiency (~84%) and excellent cycling stability. The prismatic C/LiCoO₂ batteries using the DMMP electrolyte containing Cl-EC additive exhibited very similar charge and discharge performances to those with conventional carbonate electrolytes,

suggesting that the nonflammable DMMP can be used as a pure electrolyte solvent for constructing safer Li⁺ ion batteries.

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