Short communication

A new phosphate-based nonflammable electrolyte solvent for Li-ion batteries

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ABSTRACT

A new fire-retardant—dimethyl(2-methoxyethoxy)methylphosphonate (DMMEMP) has been synthesized and evaluated as a high safe electrolyte solvent for lithium-ion batteries. This report summarizes the physical and electrochemical properties of the new compound. It is found that, this nonflammable phosphonate has a moderate viscosity, a high dielectric constant and a good thermal stability. It can provide a wide electrochemical stability window of 0–5.5 V (vs. Li$^+$/Li), a high conductivity of 2.0 mS cm^{-1} at 20 °C with 1 M LiTFSI. The electrochemical performance investigated with the Li/LiFePO$_4$ half-cells shows a good capacity of 148.1 mAh g^{-1} and a coulombic efficiency close to 100% at the 10th cycle.

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1. Introduction

Safety concern has been a key obstacle for development and applications of Li-ion batteries, especially for high-power battery packs designed for electric vehicle (EV) or hybrid electric vehicle (HEV) applications [1]. The safety hazard is the apparent result of the combination of the highly reactive electrode material and the highly flammable components in the electrolyte [2–4]. When used under abusive conditions, lithium-ion batteries may undergo thermal runaway that generates a sharp rise in temperature and then results in serious hazards of fire and explosion [4,5]. Therefore, it becomes very important to find an effective approach to retard the fire and explosion.

Much effort has been devoted in recent years to reform the electrolytes by using a flame-retarding additive or co-solvent, with the goal that its presence, kept at a minimum, could result in nonflammability or at least retarded flammability of the whole electrolyte [6–20]. So far, varieties of fire-retardant compounds have been investigated, including organophosphorus compounds [6–15], fluorinated ethers [16] or esters [17], fluorinated sulfones [18] and ionic liquids [19,20]. Because of their poor electrochemical compatibility with lithium battery electrodes, most of the organophosphorus compounds have to be used in low concentrations, usually no more than 20% either by weight or by volume. The reduction in flammability has to be realized at an expense of the other performances such as ionic conductivity of the electrolyte, capacity of the cell and so on.

It was reported that some of fluorinated esters [16] or esters [17], fluorinated sulfones [18] and ionic liquids [19,20] could 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 [21,22].

PEO-poly(ethylene oxide) has been studied extensively for using as polymer electrolytes due to its ability of forming complexes with a wide variety of lithium salts [23]. The present work reported a new EO-containing phosphate-dimethyl(2-methoxyethoxy)methylphosphonate (DMMEMP) with the advantages of moderate viscosity, high boiling point and nonflammability. So far as we know, little has been published about the use of organic phosphates as a single electrolyte solvent for lithium batteries [24]. Taking its properties mentioned above into account, DMMEMP seems to be a good candidate as nonflammable solvent for lithium batteries. In this paper, we evaluated the feasibility of DMMEMP-based electrolyte as a single electrolyte solvent for lithium-ion battery. Besides the thermal safety characteristics, the electrochemical properties and the performance in the Li/LiFePO$_4$ half-cells were also investigated and discussed.

2. Experimental

2-Methoxyethanol, phosphorus oxychloride and trimethylphosphite (Sancaitang Chemical Industry and Technology Co. Ltd., China) were directly distilled prior to use. LiFePO$_4$ was synthesized by high temperature solid state method according to the literature [25]. Paraformaldehyde, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Aldrich) and other chemicals were used as received.
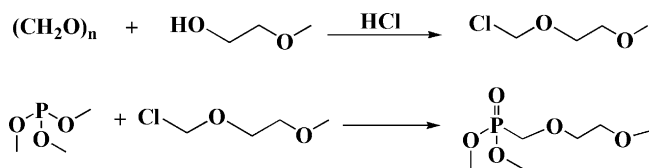

Fig. 1. The synthetic route of DMMEMP.

MEMCl (1-(chloromethoxy)-2-methoxyethane) was prepared following the method proposed in the literature [26].

DMMEMP can be synthesized through the schematic reaction procedures outlined in Fig. 1. A mixture of 12.46 g (10 mmol) of MEMCl and 18.28 g (11 mmol) of trimethylphosphite was heated at 130 °C in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser, until there was no gas ceased. The mixture was then distilled under the reduced pressure and 17.07 g product was got (86.2%). b.p.: 118–119 °C/8–9 mmHg. ^{1}H NMR (CDCl$_3$) δ: 3.36 (s, 3H, −OCH$_3$), 3.55 (t, 2H, −OCH$_2$CH$_2$OCH$_3$), 3.75 (t, 2H, −OCH$_2$CH$_2$OCH$_3$), 3.80 (d, 6H, −P(OCH$_3$)$_2$), 3.90 (d, 2H, −P−CH$_2$−); ^{13}C NMR (CDCl$_3$) δ: 53.1–53.2, 59.1, 63.7, 65.8, 71.9–72.7; ^{31}P NMR (CDCl$_3$) δ: 24.7; ESI HRMS for C$_6$H$_{15}$O$_5$P[M+H]$^+$: found 199.0732, calcd. 199.1553.

The viscosity of DMMEMP was measured at 25 °C on a Cannon–Ubbelohde dilution viscometer, using water as the standard substance.

The dielectric constant was determined by the PGM-II dielectric constant Electronic Equipment (Nanjing Sangli Electronic Equipment Factory) at 15 °C, using cyclohexane to calibrate the constant.

Thermogravimetric analysis was carried out from room temperature to 500 °C at 10 °C min^{-1} under an atmosphere of dry argon.

Most of the existing flammability tests used in the fire-proofing industry is mainly for solid materials and few of them can be directly applied to liquid electrolyte samples. Here we adopt the modified test reported by Wang et al. [8]. Thus a ball of glass wick was first immersed in the electrolyte for a sufficient interval, and then set vertically on a stainless steel stand. An alcohol lamp was then brought to burn the wick holding the electrolyte. The electrolyte was judged to be nonflammable as that the electrolyte never ignited during the testing, or the ignition of electrolyte ceased within 1 s after the flame was removed.

The liquid electrolyte was prepared by dissolving LiTFSI in the above-synthesized solvent at 1 M concentration. The ionic conductivity of thus-prepared electrolyte was determined by AC impedance measurement (frequency range: 10^6 Hz to 10^2 Hz, 5 mV s^{-1}) on a two-electrode electrochemical cell in which two stainless steel blocking electrodes were separated by electrolyte-soaked membrane (Celgard 2300).

The electrochemical stability of the tested electrolyte was investigated by cyclic voltammetry over a 0–6 V range on a three-electrode cell, where stainless steel acts as the working electrode (1.0 cm in diameter) and lithium foil as the counter and reference ones.

The compatibility of the electrolyte to the lithium anode was also examined by impedance measurement on a three-electrode cell in which the electrolyte-soaked Celgard 2300 separator was sandwiched between two lithium electrodes, and lithium foil is used as the reference electrode. The test was carried out using the Li with native film and the naked Li without native film, respectively. The Li with native film was set in the cell by using commercially
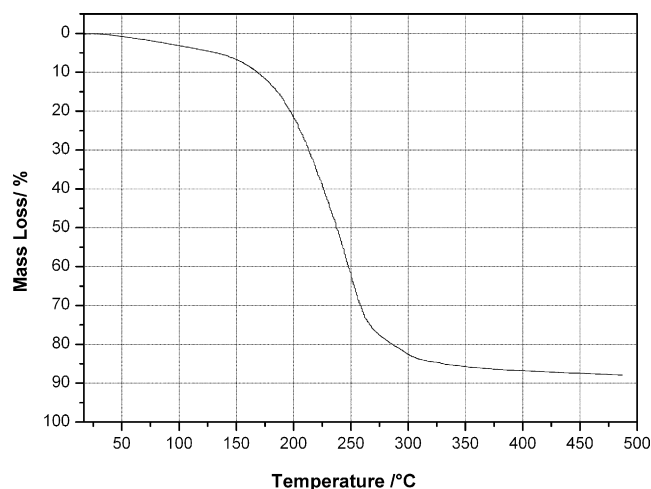

Fig. 2. Thermogravimetric curves of DMMEMP/1.0 M LITFSI electrolyte.

available Li foil, and the naked Li was polished off the native film in a glove box under argon atmosphere containing less than 1 ppm (w/w) H$_2$O and O$_2$. All the above electrochemical measurements were conducted using Autolab PGSTAT302.

The cycling performance tests were carried out on 2016 coin cells with an LAND Battery Testing system at 30 °C. The cathode was fabricated with LiFePO$_4$ (75 wt.%), acetylene black (20 wt.%) and polytetrafluoroethylene (PTFE) (5 wt.%) binder following the literature [25]. Thus-obtained cathode was separated from lithium foil anode by a Celgard 2300 membrane, which was soaked in the DMMEMP-based electrolyte under vacuum. The cell was assembled in an argon-filled glove box at room temperature.

3. Results and discussion

Table 1 lists the physical parameter of DMMEMP-based electrolyte with a 1.0 M LITFSI salt concentration. Other lithium salts, such as LiPF$_6$, LiClO$_4$, etc. also easily dissolve in this solvent to form liquid electrolytes. The moderate viscosity enables good flowability of electrolyte solution to enhance the performance of the battery. The dielectric constant of the solvent was outside the capacitance superior limit of measurement by the dielectric constant electronic equipment, which meant that this solvent had a high dielectric constant exceeding 77. Comparing with the conventional electrolytes (such as EC, PC, and DMC), which could be easily ignited and continued burning, the new electrolyte exhibited significant nonflammability that it was hard to be ignited and the flame was automatically extinguished within 1 s after the burner was removed.

Fig. 2 shows the thermogravimetry (TG) curves of DMMEMP-based electrolyte with a 1.0 M LITFSI salt concentration. As can be seen, the sample presents a mass loss of about 10% up to 165 °C. The initial mass loss of 10% may be caused by the slight volatilization of solvent and water. The mass loss stage of the electrolyte starts at about 220 °C. The result clearly demonstrates that the DMMEMP/1.0 M LITFSI electrolyte has a good thermal stability up to 165 °C and may provide good safety characteristics.

Table 1
The physical parameter of DMMEMP-based electrolyte.

Compound	Boiling point (°C, 760 mmHg)	Viscosity (cP, 25 °C)	Dielectric constant	Conductivity of 1.0 M LITFSI (mS cm^{-1}, 20 °C)	Flammability
DMMEMP	280–283	4.85	>77	2.0	Nonflammable
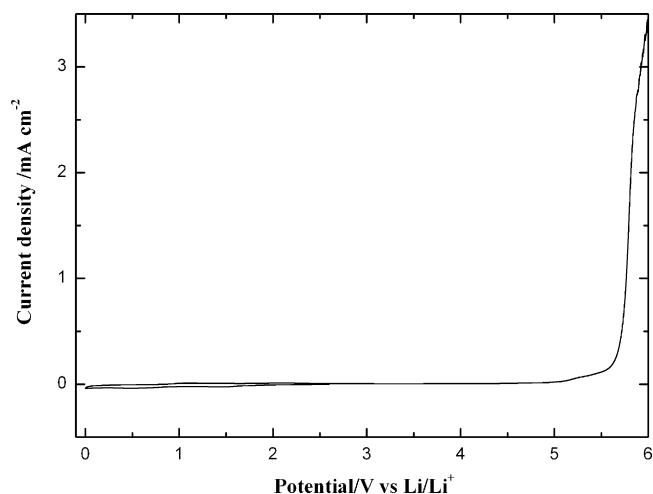
Fig. 3. A CV curve of Li/1 M LiTFSI in DMMEMP/stainless steel (20 °C, scan rate: 1 mV s^{-1}).

The result of ionic conductivity shows that the electrolyte of 1 M LiTFSI in DMMEMP has a high ionic conductivity of 2.0 mS cm^{-1} at 20 °C and thus approaches that of conventional organic carbonate-based electrolytes. With the temperature decreasing, its ionic conductivity decreases accordingly and the conductivity is kept at 0.9 mS cm^{-1} at 10 °C and 0.6 mS cm^{-1} at 0 °C, respectively.

The CV curve of the solvent is shown in Fig. 3. As it can be seen, there is no obvious oxidation and reduction current in the potential range of 0–5.5 V (vs. Li$^+$/Li), indicating a sufficiently wide electrochemical stability window. Theoretically, from the point of view of the potential window, the new electrolyte is quite stable in a sufficiently wide potential range for lithium battery applications.

The solid electrolyte interphase (SEI) film established between the lithium electrode and the electrolyte was investigated by impedance measurement. Fig. 4 shows the evolution of the AC impedance spectra of Li/1 M LiTFSI in DMMEMP/Li cells. The semi-circle extends obviously accompanying the prolonged duration of storage, which indicates the increased interfacial resistance. It is also found that the exhibited semicircles in the impedance spectrum are kept nearly unchanged after 24 h-storage in Fig. 4(a) and 48 h-storage in Fig. 4(b), respectively, which suggest the formation of stable SEI films on the electrode surfaces. Comparing with the Li foil with native film, it takes much more time for the naked pure Li to form the stable SEI film. One possible reason of such difference is that the presence of native film stabilizes the interface, while the naked pure Li without native film is more active to react with
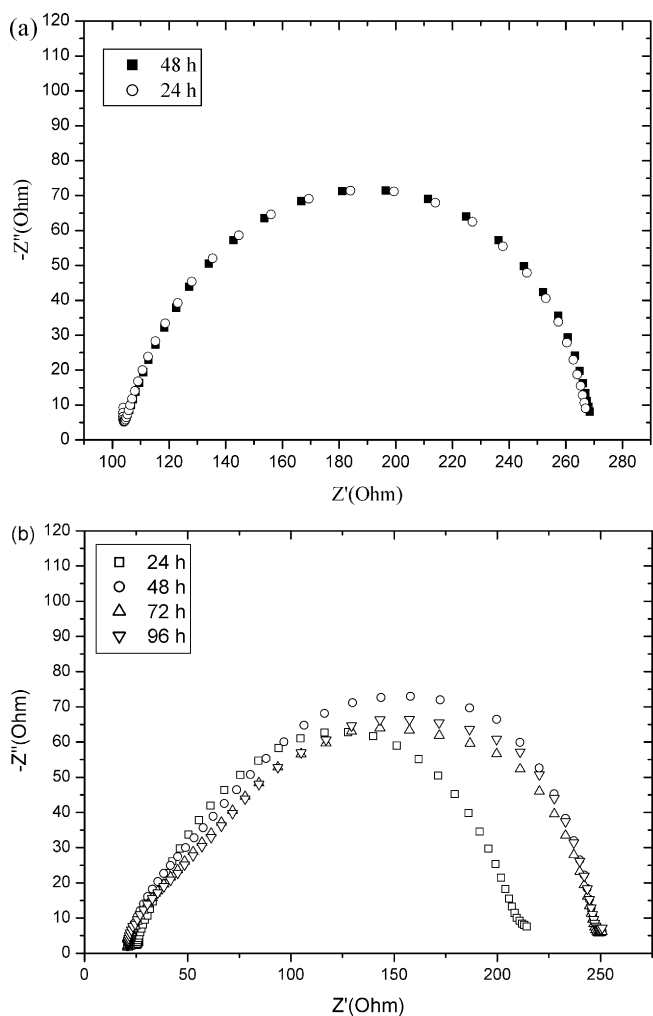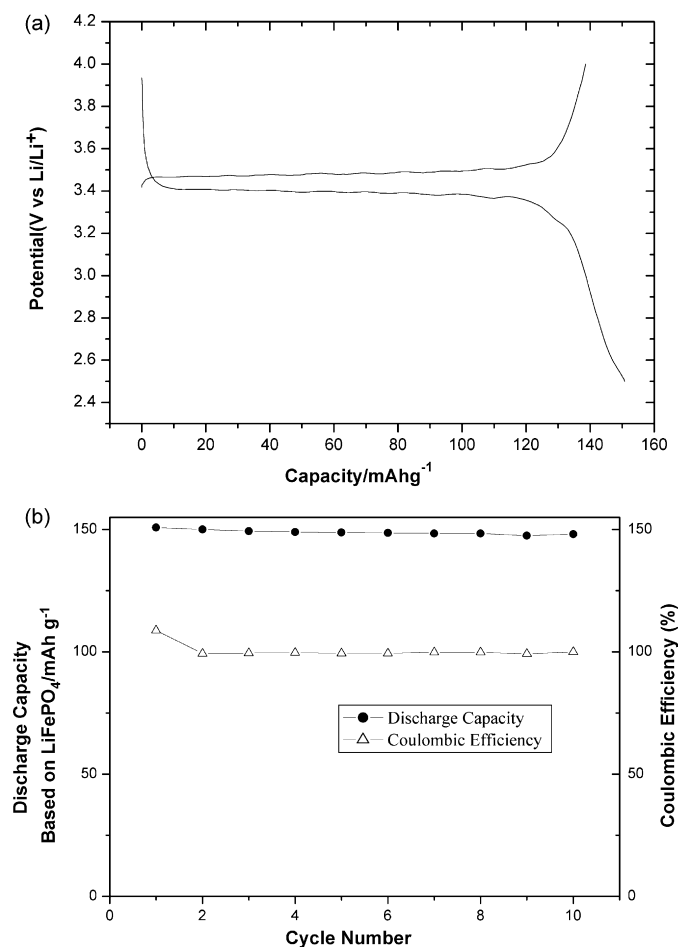

Fig. 4. Evolution of the AC impedance spectra of (a) Li (with native film)/1 M LiTFSI in DMMEMP/Li (with native film) cell and (b) Li (without native film)/1 M LiTFSI in DMMEMP/Li (without native film) cell at 20 °C (electrode area: 0.785 cm², frequency range: 10⁴ Hz to 1 Hz scan rate: 5 mV s^{-1}).

Fig. 5. The initial charge–discharge profiles (a) and cycling performances (b) of Li/1 M LiTFSI in DMMEMP/LiFePO$_4$ half-cells at 30 °C. Charge–discharge current density: 0.1 C; cutoff: 4.0 to 2.5 V.

the electrolytes, and therefore increases the time of the formation of passivation film. A careful surface analysis on the composition of the electrodes may give more hints about this, which will be investigated by our further experiments.

The electrochemical performance of the Li/LiFePO$_4$ half-cells was examined with DMMEMP/1.0 M LITFSI electrolyte. Fig. 5(a) shows the initial charge and discharge curves at 0.1 C between 4.0 and 2.5 V at 30 °C. A high capacity of 150.8 mAh g^{-1} was obtained. Fig. 5(b) presents the first 10 cycles of this Li/LiFePO$_4$ cell. The capacity of 148.1 mAh g^{-1} and the coulombic efficiency close to 100% were obtained at the 10th cycle, implying an electrochemical stability of Li and LiFePO$_4$ electrode in the DMMEMP electrolyte.

Finally, it must be pointed out that the cycling results shown in Fig. 5 are preliminary, and that further extensive investigations are still in progress, including the testing of its performance with higher voltage cathode materials, the effect of its stability on the much longer cycle life of the Li-ion cells, the impact of its viscosity on rate capability of Li-ion battery at lower and higher temperatures, and the performances of its serving as co-solvents with the commercial carbonate-based or ether-based electrolytes, etc.

4. Conclusions

A modified phosphate containing EO unit was synthesized and evaluated as a high safety electrolyte solvent for lithium-ion batteries. It is found that, this nonflammable electrolyte solvent with a good thermal stability can provide an electrochemical stability window in excess of 5.5 V, a high conductivity of 2.0 mS cm^{-1} at 20 °C with 1 M LiTFSI and a good compatibility with the lithium electrode. The cycling tests of Li/LiTFSI in DMMEMP/LiFePO$_4$ cell indicate that the first discharge capacity is 150.8 mAh g^{-1}. In brief, the nonflammable DMMEMP-based electrolyte provides us with a promising approach to the high safety lithium-ion batteries.

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