Short communication

Effects of Lewis-acid polymer on the electrochemical properties of alkylphosphate-based non-flammable gel electrolyte

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ABSTRACT

Non-flammable polymer gel electrolytes (NPGE) consisting of $1.0\,mol\,dm^{-3}$ (=M) $LiBF_4$/EC + DEC + TEP (55:25:20 volume ratio) + PVdF-HFP (EC: ethylene carbonate, DEC: diethyl carbonate, TEP: triethylphosphate, PVdF-HFP: poly(vinyledenefluoride-co-hexafluoropropylene)) have been developed for rechargeable lithium batteries. The effects of addition of Lewis-acid polymer (LAP) with different mole ratio in NPGE have been studied. The addition of LAP improved physico-chemical properties of NPGE, viz ionic conductivity and lithium ion transport number, as well as mechanical and thermal properties. The ionic conductivity of the gel electrolyte containing LAP reached that of the base solution electrolyte ($1.0\,M\,LiBF_4$/EC + DEC + TEP (55:25:20)) along with better mechanical properties. Interfacial resistance at Li-metal electrode/NPGE was also improved by introducing LAP in the gel.

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1. Introduction

Safety issue of the conventional organic electrolytes has been a major barrier in the development of lithium-ion batteries (LIBs) with high-energy and high-power densities for electric vehicle (EV) and hybrid electric vehicle (HEV) applications. Different approaches have been proposed to prepare safer electrolytes of LIB. For instance, solid polymer electrolytes, electrolytes based on ionic liquids, and addition of fire retardant co-solvents in liquid electrolytes have widely been investigated [1–11]. In general, however, these electrolytes also have their own drawbacks: solid polymer electrolytes are suffered from low ionic conductivity and poor contact at electrode/electrolyte interface, the most ionic liquids have poor cathodic stability, and organic liquid electrolytes require bulky and heavy enclosures to avoid their leakage.

Polymer gel electrolytes (PGEs) obtained by immobilizing the solution electrolyte in a suitable polymer matrix can be a good candidate for practical use [12–14]. The most of PGEs show high values of ionic conductivity comparable to those of solution electrolytes along with good mechanical strength. However, these electrolytes have safety problems due to the use of flammable organic solvents for their preparation. One of the approaches to solve this problem is the use of fire retardant co-solvents such as trimethyl phosphate (TMP), dimethyl methyl phosphonate (DMMP), ethylene ethyl phosphate (EEP), tris-(4-methoxy phenyl) phosphate

(TMPP) [15–18]. We have also reported NPGEs containing TMP or triethylphosphate (TEP) as a fire retardant co-solvent in the gel electrolytes [19,20], and found that NPGE with TEP shows good electrochemical stability for both cathode and anode without addition of any film forming agent for solid electrolyte interphase (SEI). However, the capacity fading with cycles was observed for graphite/NPGE half cell. The carbonate solvents used in NPGE are Lewis-bases that can interact with cations only and contribute to the ion-pairing in the electrolytes. Thus, the liquid components in the NPGE would affect the ionic conductivity and Li+ transport number of the electrolytes.

In order to improve the ionic conductivity, Li+ transport number, non-flammability and mechanical properties of the gel electrolytes, we have tried to add a Lewis-acid polymer (LAP) in the gel electrolyte. Borane or borate derivatives such as borate esters of glycol, tris(methoxy diethyleneglycol) borate, and polymer electrolyte containing boroxine rings [21–27] generally possess Lewis-acid properties, and have so far been reported to improve the ion transport properties of the polymer electrolytes. Lewis-acid boron and Lewis-base oxygen (provided by glycol) of these derivatives interact with both cations and anions in the electrolytes, which results in an improvement of ionic conductivity and, in some cases, cation transport number. These derivatives can also improve the thermal stability of the electrolytes [28].

In the present work, we have blended an LAP in a non-flammable polymer gel electrolyte system consisting of $LiBF_4$/EC + DEC + TEP (55:25:20) with the polymer matrix, PVdF-HFP, where EC, DEC, TEP and PVdF-HFP denote ethylene carbonate, diethyl carbonate, triethylphosphate and poly(vinyledenefluoride-co-hexafluoropro-

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pylene). Effects of the LAP addition have been investigated on the ionic conductivity, Li$^+$-ion transport number, non-flammability, electrode/electrolyte interface properties, and mechanical properties of the gel electrolyte.

2. Experimental

The component organic solvents, EC (Kishida Chemical; Battery grade), DEC (Kishida Chemical; Battery grade) and TEP (Wako Chemical) were used as received. The electrolytic salt, LiBF$_4$ (Kishida Chemical), was also used as received, but kept in a glove box filled with dry Ar before use. A host polymer, PVdF-HFP (ARKEMA, Kynar 2851) was vacuum-dried at 100 °C prior to use and then stored in the glove box. Boron trioxide (B$_2$O$_3$, Wako), tri(ethylene glycol) monomethylether (TEGMME, Aldrich), poly(ethylene glycol) (PEG, MW: 300, Wako) were used for preparation of LAP. Polymer containing Lewis-acidic boron (termed as Lewis-acid polymer (LAP)) was prepared according to the reported procedure [25]. The reactants B$_2$O$_3$, PEG, and TEGMME in molar ratio of 0.5:1.0:1.03 with a proper amount of solvent toluene were introduced in a two-necked round-bottom flask equipped with reflux condenser and Dean–Stark apparatus. First the mixture was heated to 60 °C to dissolve all the reactants and then refluxed for 4 h under a dry N$_2$ atmosphere. The water formed during the reaction was removed by condensation using Dean–Stark apparatus. The resulting polymer was further dried at 80 °C under a reduced pressure and then stored in the glove box filled with dry Ar.

The solution electrolyte was prepared by dissolving 1.0 mol dm^{-3} (=M) LiBF$_4$ in the ternary solvent system of EC, DEC and TEP, where the mixing ratio of EC and DEC was kept constant, about 2:1 (v/v). The polymer gel electrolyte was prepared by a thermal casting method [29]. An appropriate amount of PVdF-HFP and LAP was dissolved in a mixed ternary solvents (EC + DEC + TEP, typically 55:25:20 (v/v/v)) containing LiBF$_4$. The resulting mixture was stirred for 1 h to form homogeneous solution, and then poured on an Al pan. A transparent flexible film was obtained after heating the solution at 110 °C for 13 min under a reduced pressure (typically at 400 mmHg). These processes were carried out in a dry Ar atmosphere. The mass ratio of the solution component to the host polymer in the resulting gel was about 5:1, which was slightly dependent on the curing condition.

The ionic conductivity of the gel electrolyte was measured by an AC impedance method in a frequency range from 100 kHz to 1 Hz using an impedance response analyzer controlled by a personal computer. A cell with platinum electrodes was used for conductivity measurements of solution electrolyte. The cell constant was determined by using KCl solution (1.0 M). For gel electrolytes, the sample was sandwiched between two stainless-steel electrodes, and the conductivity was measured in an appropriate temperature range. The IR spectra were recorded on JASCO FT/IR-4100 spectrometer with an attenuated total reflection (ATR) attachment with ZnSe crystal in 4000–500 cm^{-1} wavenumber range. The resolution of the spectra was 4 cm^{-1}. Thermal safety analysis of the gel electrolytes was investigated by SYSTAG-Flexy Thermal Safety Calorimeter (TSC) in 30–350 °C temperature range using a RADEX measuring cell. The sample was set in the cell under an Ar atmosphere but no gas was supplied during the measurements.

The positive electrode for the cell test was prepared by coating slurry containing 80 mass% of the active material of LiMn$_2$O$_4$, 10 mass% of acetylene black, 10 mass% of PVdF and N-methylpyrrolidone (NMP) as the solvent. The area and mass of the active material (LiMn$_2$O$_4$) of the working electrode was 0.25 cm^2 and 2.0–2.2 mg, respectively. Charge–discharge characteristics of LiMn$_2$O$_4$ electrode were investigated using a laboratory made three-electrode cell under constant-current charge and discharge conditions with 3.5–4.6 V of cut-off voltage range.
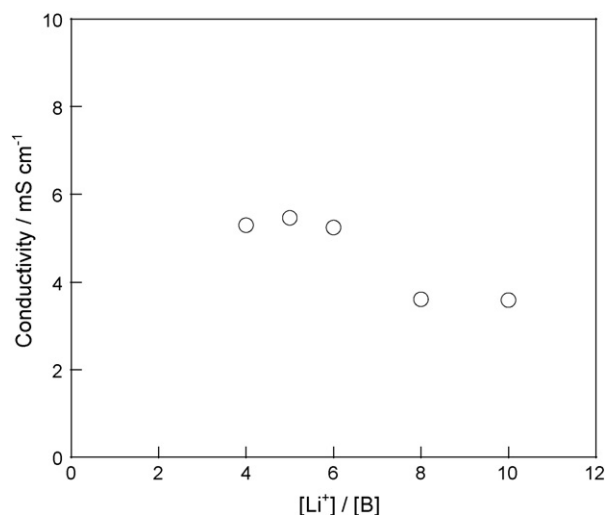

Fig. 1. Variation of the ionic conductivity of NPGE with LAP concentration in the gel.

3. Results and discussion

The effect of addition of LAP on the conductivity of non-flammable polymer gel electrolyte (NPGE): 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20) + PVdF-HFP was investigated for different mole ratio of [LiBF$_4$]/[B] = 10/1, 8/1, 6/1, 5/1 and 4/1 in the electrolytes. The variation of the conductivity of NPGE with concentration of LAP is shown in Fig. 1. The conductivity of the gel electrolyte increases with an increase in LAP concentration (decrease in [LiBF$_4$]/[B] ratio) in the electrolyte. The maximum value of the conductivity, 5.46 mS cm^{-1}, was obtained for [LiBF$_4$]/[B] = 6/1, which is higher than that of the base solution electrolyte (3.82 mS cm^{-1}: 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20)) at 30 °C. The addition of small amount of LAP, [LiBF$_4$]/[B] = 10/1, improved the ionic conductivity and mechanical strength (from visual observation) of the NPGE. However, higher concentrations of LAP deteriorate the mechanical strength of the NPGE. For this reason, NPGE with [LiBF$_4$]/[B] = 10/1 was chosen for the further studies and this composition was designated as NPGE–LAP. The conductivity of the NPGE and NPGE–LAP was measured in the temperature range of −20 to 60 °C. Fig. 2 shows temperature dependence of the ionic conductivity for NPGE, NPGE–LAP and the base solution electrolyte as a reference elec-
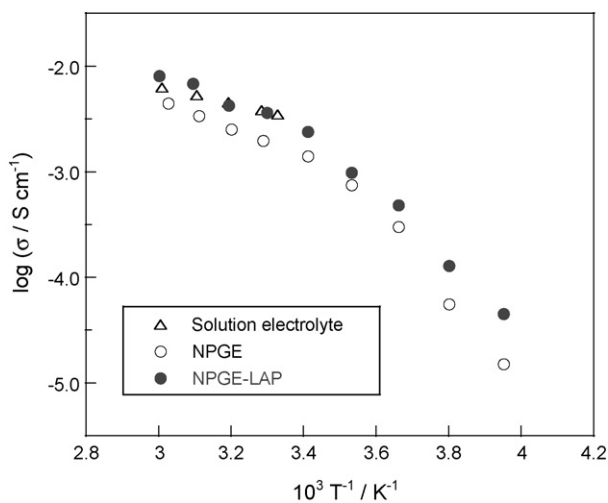

Fig. 2. Temperature dependence of the ionic conductivity of 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20) solution (△), 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20) (NPGE) (○), and 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20) + LAP (NPGE–LAP) (●).
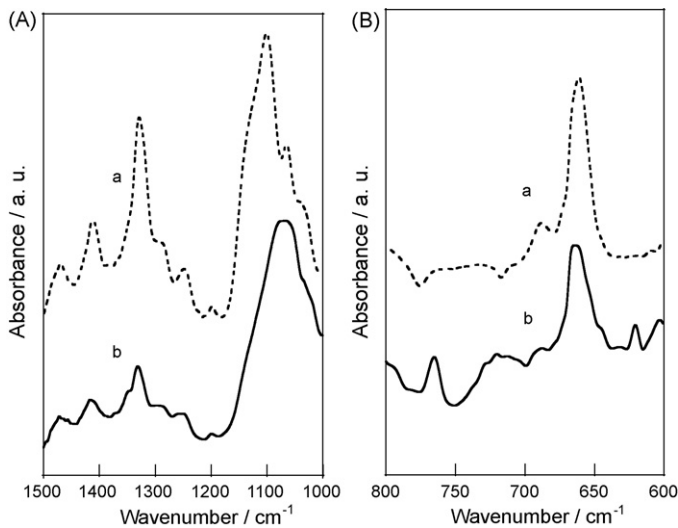
Fig. 3. FTIR spectra of (a) LAP and (b) LAP+LiBF$_4$ in higher wavenumber region (A) and lower wavenumber region (B).

trolyte. The ionic conductivity of NPGE–LAP was higher than that of NPGE over whole temperature range examined and showed almost the same value as that of the solution electrolyte. At lower temperature, NPGE–LAP had reasonably high conductivity of 4.16×10^{-5} S cm^{-1} (at $-20\,^{\circ}$C), which will be sufficient for low temperature operation of the battery.

The improvement in the conductivity of NPGE by adding LAP might be due to interaction between the Lewis-acid boron of LAP and the counter anion BF$_4^-$ of the salt. Fig. 3 shows the IR spectra of the LAP and LAP+LiBF$_4$ ([LiBF$_4$]/[B] = 1/1) in 600–800 and 1000–1500 cm^{-1} regions. The broad absorption peak observed at 662 cm^{-1} is attributed to the B–O units of LAP [25]. The addition of LiBF$_4$ in the polymer results in a small shift of the peak to higher wavenumber due to interaction of the Lewis-acid boron of polymer and the Lewis-base anion of the salt. A peak at 764 cm^{-1} appeared in the spectrum for LAP+LiBF$_4$ is assigned to free BF$_4^-$ [30], while
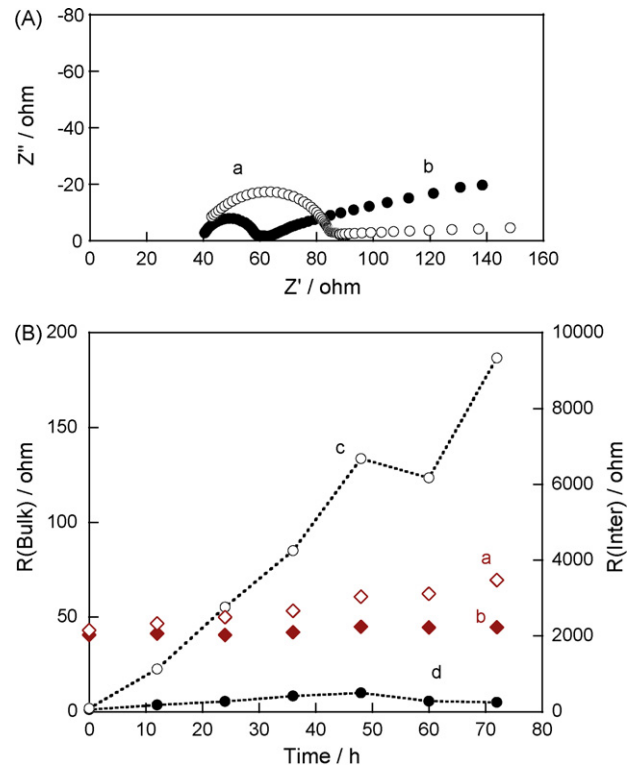

Fig. 4. AC impedance responses of Li/gel (NPGE or NPGE–LAP)/Li cells. (A) Nyquist plot (a: NPGE; b: NPGE–LAP). (B) Time dependence of the bulk resistance (R_{bulk}: a and b) and interfacial resistance (R_{inter}: c and d) (a and c: for NPGE, b and d: for NPGE–LAP).

no peak has been observed for ion pairs. Thus, it shows that LAP helps to dissociate the salt in the electrolyte. The absorption peak at 1329 cm^{-1} in the spectrum of LAP is assigned to asymmetric stretching of ν_{as}(B–O) bond [31]. A shoulder at 1350 cm^{-1} was appeared with the addition of LiBF$_4$ in the polymer which is possibly due to the interaction of B–O with the anion of LiBF$_4$. A strong
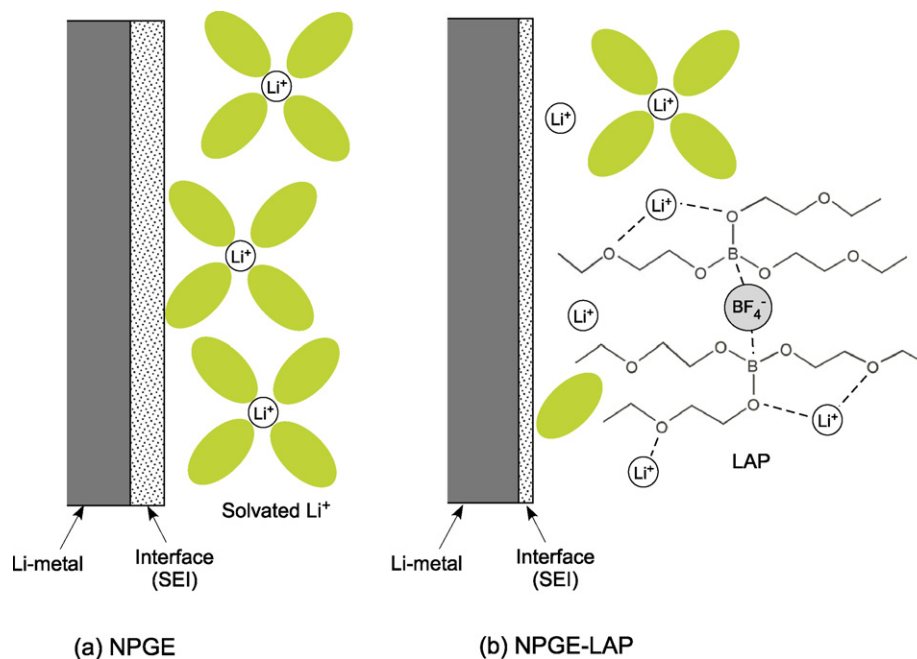

Fig. 5. A model for Li-metal/gel electrolyte interface having interactions between ions and LAP in NPGE. (a) NPGE and (b) NPGE–LAP.

peak was observed at 1103 cm^{-1} for polymer due to the ether bond of C–O–C. The broadening and shift of this peak to lower wavenumber were observed with incorporation of LiBF$_4$ in the polymer. This suggests that a strong interaction should exist between the ether oxygen and Li$^+$ cation. Hence, from the above observation, we can conclude that LAP contributes to the dissociation of ion pairs or undissociated salt in the electrolyte by Lewis-acid/Lewis-base, or ether oxygen/cation interactions.

Ion transport number of Li$^+$ (t_{Li^+}) has been measured for NPGE and NPGE–LAP by a combined AC impedance/dc measurement technique [32,33]. A symmetrical cell with lithium metal non-blocking electrodes, Li/gel (NPGE or NPGE–LAP)/Li, was used for the measurement. For NPGE–LAP, a high value of t_{Li^+} (~0.6) was obtained. A stable interface between Li electrode and gel electrolyte is needed to measure the Li$^+$ transport number for gel electrolytes. As noted later (Fig. 4B), the interfacial resistance between Li and NPGE (without LAP) increases with time and did not find a stable interface, due to which t_{Li^+} for NPGE could not determined.

To examine the effect of addition of LAP in NPGE on the electrode/electrolyte interface, interfacial resistance of Li/gel (NPGE or NPGE–LAP) cell was measured over a period of time. Fig. 4A shows a typical Nyquist plot of the impedance used to calculate the bulk and interface resistance. Variations in the interfacial resistance (R_{int}) and the bulk resistance (R_{bulk}) with storage time are given in Fig. 4B. The interfacial resistance between Li/NPGE increases with the time and shows values ranging from 4000 to 8000 Ω. The decrease in the interfacial resistance by 1–2 folds was observed with the addition of LAP in the NPGE.

From above results, a schematic model has been proposed to understand the effects of LAP on the electrode/electrolyte interface resistance. As lithium metal is highly reactive toward organic substances, it reacts with carbonate molecules that form solvated cation with Li$^+$ at the interface between Li metal and the gel electrolyte, as shown in Fig. 5. The decomposition of solvent molecules by Li metal forms a surface layer on the Li-metal electrode (so-called solid electrolyte interphase (SEI)). The resistance of this interfacial layer influences the movement of Li$^+$ ion at the interface. A thick layer with high resistivity can suppress the fast movement of Li$^+$ ions at the electrode/electrolyte interface, which will deteriorate the working of the Li-metal electrode. Introduction of LAP in the NPGE, leads to trapping of the anions by the Lewis-acid sites (boron atom) and provide free Li$^+$ ions. Hence, the number of Li$^+$ ions solvated by the carbonate molecules decreases at the interface between Li metal and the electrolyte, and a thin interfacial layer
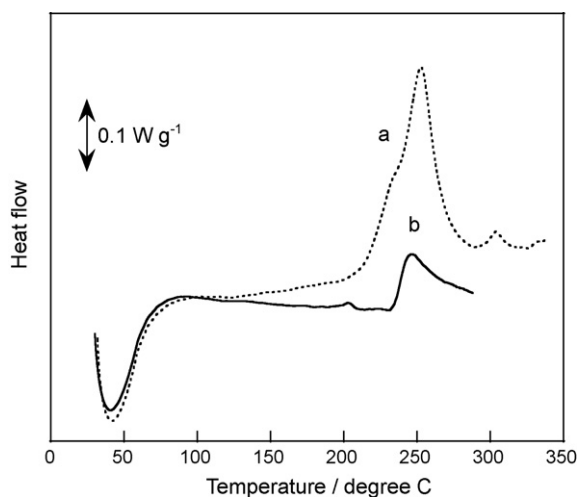
will be formed as compared to NPGE. This phenomenon results in the decrease in the electrode/electrolyte interface resistance.

Fig. 6 compares the thermograms of NPGE and NPGE–LAP measured by TSC. The broad endothermic peak around 50 °C is due to the evaporation of DEC from the gel electrolyte. However, the exothermic peaks observed above 200 °C for NPGE and NPGE with LAP are due to the decomposition of the gel electrolyte. In the previous report [20], it was observed that the addition of fire retardant
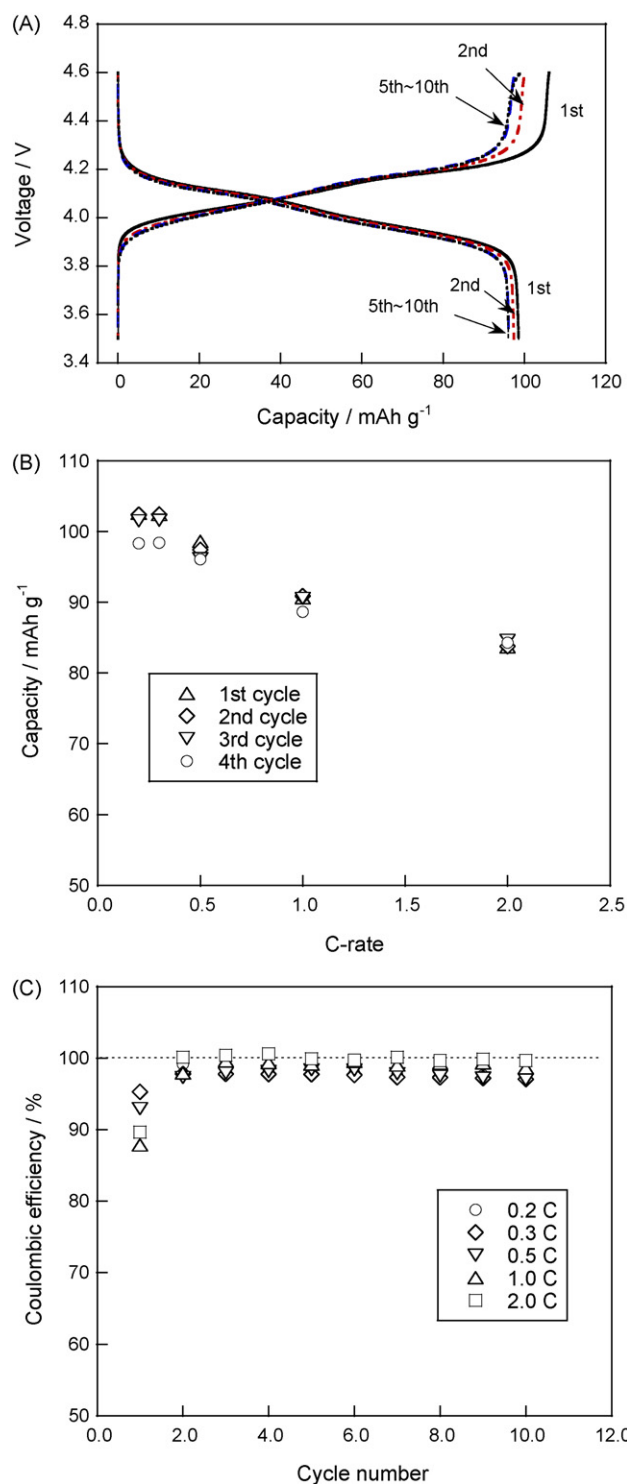
Fig. 7. Charge/discharge characteristics of LiMn$_2$O$_4$/NPGE–LAP half cell. (A) Charge and discharge curves at 0.5 C-rate, (B) variation of discharge capacity with C-rate, and (C) variation of columbic efficiency with cycle number.

Fig. 6. TSC (thermal safety calorimetry) thermograms of (a) NPGE (dotted line) and (b) NPGE–LAP (solid line).

co-solvent TEP suppresses the flammability of the gel electrolyte by suppressing the heat flow above 200 °C. In the present study, further reduction in heat flow has been observed with the addition of LAP in NPGE. The TSC measurement indicates that LAP also helps in the improvement of thermal stability of the present NPGE system.

Charge–discharge characteristics of LiMn$_2$O$_4$ positive electrode in the gel electrolyte, 1.0 M LiBF$_4$/EC + DEC + TEP (55:25:20) + PVdF-HFP + LAP ([LiBF$_4$]/[B] = 10/1) was investigated using a three-electrode cell equipped with Li-metal counter and reference electrodes. Fig. 7A shows typical charge–discharge curves of LiMn$_2$O$_4$. Two different slopes have been observed during charge and discharge process, which are related to the intercalation/de-intercalation of lithium ions in the spinal structure, as commonly observed for LiMn$_2$O$_4$ family. Fig. 7B and C shows the variation of discharge capacity with cycling C-rate and columbic efficiency (discharge capacity/charge capacity) for each cycle, respectively. The discharge capacity decreases with increase in the cycling C-rate. However, the capacity fading from the first to tenth cycles was only 3.6% and 2.2% at 0.2 and 1 C cycling, respectively. The columbic efficiency of the LiMn$_2$O$_4$ electrode was found to be above 97% for 0.2 C and 99% for 2 C. These results indicate that NPGE–LAP can be used for an LIB system with high-power density.

4. Conclusions

The addition of LAP in NPGE improves the ionic conductivity, electrode/electrolyte interface resistance, transport number of Li$^+$ and thermal stability of the gel electrolyte. The Lewis-acid/base interactions between the anion receptor and BF$_4$$^-$ anions of the salt in the electrolyte were confirmed by FTIR spectroscopy. Charge/discharge characteristics of NPGE–LAP for LiMn$_2$O$_4$ shows good performance of the gel electrolyte for cathode at high charge/discharge rates.

Acknowledgement

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