Research and Development of Thermally Durable Electrolyte for Lithium Ion Battery
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ABSTRACT
For ensuring safety of lithium ion batteries (LIBs), we have extensively investigated the quasi-solid electrolyte where lithium ion conductive liquid is quasi-solidified at silica surfaces as thermally durable electrolyte, and applied it to high capacity and high energy density LIB. For the liquid phase, a solvate ionic liquid, which is an equimolar complex of lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) and tetraethylene glycol dimethyl ether (G4), Li(G4)TFSI, was used. For enhancing discharge capability at a higher rate, Li(G4)TFSI was diluted by low viscos solvent such as propylene carbonate (PC). The developed electrolyte possessed a favorable volatilization temperature higher than 373 K. A 100-Wh-class laminated LIB with energy density of 363 Wh L−1 was fabricated by employing the electrolyte to graphite-LiNi0.5Mn1.5O4 cathode chemistry, and it generated neither fire nor smoke in a nail-penetration test. The result suggest that the developed LIB has high safety compared to a LIB comprised of a conventional organic liquid electrolyte. In addition, to enhance the cycle life of the LIB, the formation and growth mechanism of a solid-electrolyte interphase on a graphite-based negative electrode was investigated. Nuclear magnetic resonance and hard x-ray photoelectron spectroscopy revealed that the decompositions of LiTFSI, PC, and G4 contributed to the SEI formation at the initial charge, and that continuous decompositions of G4 and PC were a major reason for the SEI growth during charge-discharge cycles. Based on these analysis, we have substituted a highly concentrated sulfolane based liquid which exhibits a high Li ion conductivity with less amount of the low viscosos solvent, for the G4 based liquid. The modification effectively improved the electrochemical durability of the electrolyte, leading to a higher capacity retention after charge-discharge cycle test.

Keywords : Thermally Durable Electrolyte, Lithium Ion Battery, High-energy Battery, Quasi-solid-state Electrolyte

1. Introduction
Lithium-ion batteries (LIBs) are currently used in a broad range of applications, including portable devices and automobiles, because of their high energy density. One of the emerging issues that needs to be addressed is ensuring the safety of LIBs, which is currently problematic from the viewpoint of applications. In general, organic liquid solvents have high vapor pressure and are inflammable; thereby, current LIBs using organic liquid solvents have a risk of catching fire and exploding upon unexpected accidents. Hence, for large-scale applications, including vehicles, current rechargeable LIB systems require a safety system and a cooling space, which do not directly contribute to energy storage. If the safety of LIBs were improved, the energy-storage system could be simplified, and that simplification would be advantageous in terms of enhancing energy density and cost competitiveness of the systems. Therefore, a design principle for LIBs that meets the requirement of essential safety is urgently required. A promising approach is the application of thermally durable electrolyte with a high flash point, a volatilization temperature, and a superior resistance against the chemical reaction between anode/cathode materials under the elevated temperature.

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We have been investigating the research and development of the thermally stable electrolyte for LIBs, and will report recent progress on them in this article.

An all-solid-state battery with a solid-state electrolyte would be a possible approach to ensure battery safety. Materials that possess sufficient lithium-ion conductivity as well as electrochemical stability in the voltage range for battery operation are limited to several in number. In addition, to reduce internal resistance and enhance cycle life, it is necessary to develop technologies that allow for a smooth charge-transfer reaction and hinder mutual diffusion of constituent elements across the electrode active material and electrolyte particles in the composite electrode layers.

Another approach is to use a room-temperature ionic-liquid (RTIL) electrolyte, which has negligible vapor pressure and non-flammability, and high safety of this class of materials (RTIL) is suggested by ignition tests. As another aspect, RTILs are quasi-solidified owing to a strong interaction between the oxide surface and RTILs. It was reported that that the viscosity of RTILs is enhanced just beneath the silica substrate surface by approximately three orders of magnitude compared to that in the bulk, and that it relaxes within approximately 10 nm from the substrate surface. A quasi-solid-state electrolyte (QSE), which is the result of mixing RTILs with oxide nanoparticles, exhibits liquid-like high ionic conductivity as well as solid-like mechanical toughness. On the basis of a design principle exploiting this electrolyte, electrochemical devices such as fuel cells, dye-sensitized solar cells, electric double-layer capacitors, and LIBs have been developed. Since a liquid-phase electrolyte is quasi-solidified by mixing with oxide particles, a QSE is expected to hinder leakage of the liquid phase from the electrolyte layer. We have focused on the unique features of the electrolyte, and attempted to apply it to the highly safe LIB, as shown in Fig. 1, which will exhibit a high capacity and energy density. In this article, we will firstly introduce the material concept of the QSE to adjust the large capacity LIB greater than 100 Wh, and then report the synthesis demonstration of the laminated cell, and the of the QSE to adjust the large capacity LIB greater than 100 Wh, and the double-layer capacitors, and LIBs.

Figure 1. Schematic illustration of quasi-solid electrolyte LIB.

Figure 2. Molecular and ionic structures of (a) Li(G4)⁺, (b) TFSA⁻, (c) PC, (d) VC, (e) TBA⁺, and (f) PF6⁻. © The Electrochemical Society. Reproduced with permission. All rights reserved.

An equimolar mixture of lithium bis(trifluoromethanesulfonyl)amide, LiTFSA, and tetraethylene glycol dimethyl ether (or tetrglyme), G4, namely Li(G4)TFSA, was used as a typical example of a SIL. Repeated operation of a LIB that uses quasi-solid-state Li(G4)TFSA has been demonstrated. For LIBs that use SILs, intrinsically high concentration of Li-salt in the electrolyte enhances the viscosity of the SILs; thereby, ionic conductivity is suppressed. In addition, high concentration of Li-salt causes high internal resistance owing to concentration polarization under current flow. To solve this problem, Li(G4)TFSA was diluted with a wide range of solvents. To ensure both rate capability and safety of a LIB, Li(G4)TFSA must be diluted with a solvent that has comparatively low vapor pressure and high flash point. In the current study, propylene carbonate (PC) was chosen as a low-viscosity diluting solvent (Fig. 2(c)), and the resultant mixture, i.e., Li(G4)TFSA-PC, was quasi-solidified with silica particles. Although mixing of Li(G4)TFSA with PC might cause ligand exchange, interaction between PC and Li-ions is pronounced; thereby, PC solvent is expected to be less vaporized from the QSE than PC itself. In addition, PC has a high flash point of approximately 403 K (in comparison, 414 K for G4, and 293–303 K for conventional organic liquid electrolytes containing linear carbonates (such as LiPF6) in ethylene carbonate:ethyl methyl carbonate (EC : EMC)86,87. For preparing the QSE containing the above chemical, G4 (Merck KGaA, ≥99 %) and PC (Kishida Chemical Co., Ltd., 99.5 %) were used as received. LiTFSA was purchased from 3 M, Inc. and purified by annealing at 393 K for 2 h in vacuum for removing residual water. The moisture content in the resultant LiTFSA powder was only 40 ppm in the nuclear magnetic resonance (NMR, ECA-500, JEOL, Japan) analysis where the powder containing moisture and trifluorotoluene as internal standard material were dissolved by deuterated chloroform. G4 and LiTFSA were mixed in a molar ratio of 1 : 1, forming Li(G4)TFSA. Li(G4)TFSA was further mixed with PC in the desired weight.
ratios. It is denoted as Li(G4)TFSA-\(x\)%PC hereafter, where \(x\) represents wt\%.

Viscosity of the Li(G4)TFSA-\(x\)%PC mixture was evaluated by a digital viscometer (VISCOMATE VM-100A, SEKONIC Corp.).

A self-standing QSE sheet was prepared and used for evaluating ionic conductivity of the QSE. The starting materials, namely, fumed silica powder (Merck KGaK) and Li(G4)TFSA, were mixed at 20 : 80 volume ratio. Then, the mixture was dispersed in methanol, stirred, and dried at 333 K to remove the methanol. The resultant QSE powder was further mixed with polytetrafluoroethylene (PTFE) powder (Teflon-J, Du Pont-Mitsui Fluorchemicals Co., Ltd.) at a weight ratio of 95 : 5, and pressed to form a transparent sheet with thickness of 200 \(\mu\)m. To prevent corrosion of the aluminum current collector, TBAPF\(_6\) (Figs. 2(e) and 2(f)) was utilized as an additive for the formation of a passivation layer on the aluminum surface.

The QSE comprised of a desired liquid phase was prepared by a liquid phase exchange. First, the desired ratio of TBAPF\(_6\) was added to the Li(G4)TFSA-PC mixture and then mixed. The QSE sheet, comprised initially of Li(G4)TFSA as the liquid phase, was soaked in an excess volume of Li(G4)TFSA-PC-TBAPF\(_6\) mixture several times to alter the liquid phase composition. Then, a QSE sheet with the desired liquid phase was obtained.

2.2 Characterization of quasi-solid-state electrolyte

Self-diffusion coefficients of the constituent species in Li(G4)TFSA-\(x\)%PC (\(x = 0\) and 44.5) were measured by pulse-gradient spin-echo NMR (PGSE-NMR) at 298 K. A Bruker Avance 400 spectrometer (Bruker BIOSPIN), equipped with a Diff60 diffusion probe (Bruker BIOSPIN), at a magnetic field of 9.4 T was used for the NMR measurements, as described elsewhere.\(^{32}\) The self-diffusion coefficients were determined by Hahn’s spin-echo pulse sequence based on the Stejskal-Tanner relation,\(^{38}\)

\[
\frac{S}{S_0} = \exp \left[-\gamma^2 g^2 \Delta^2 D \left(\frac{\Delta}{2} - \frac{\delta}{2}\right)\right]
\]

where \(S, \delta, \gamma, \) and \(\Delta\) are the spin-echo signal intensity, the length of the gradient pulse, the duration of the field gradient with magnitude, \(g,\) the gyromagnetic ratio, and the interval between the two gradient pulses, respectively. Flash points of Li(G4)TFSA and Li(G4)TFSA-44.5%PC were measured according to the JIS 2265 K-based self-di\(_S\) point test (aco-8, Tanaka Scientific, Ltd.).

For measuring the ionic conductivity of the QSE, the fabricated QSE sheet was sandwiched by Li-foils (as electrodes) and placed in a 2032-type coin cell. To evaluate electrolyte resistance, \(R,\) ac impedance spectra were taken in the frequency range of 1 M to 2032 kHz with an input-voltage perturbation of 10 mV. \(R\) was then converted to ionic conductivity, \(\sigma,\) according to the relationship \(\sigma = \frac{1}{2L A},\) where \(L\) and \(A\) are respectively QSE thickness and electrode area. To evaluate conductivity of the QSE sheet containing PC, the liquid phase in the QSE, i.e., Li(G4)TFSA, was exchanged by Li(G4)TFSA-\(x\)%PC. Composition of the liquid phase in the QSE after the liquid-phase exchange was analyzed by NMR, the result of which confirmed that the resultant QSE contained the desired composition of Li(G4)TFSA-\(x\)%PC.

2.3 Battery assembly and performance evaluation

Li[Ni,Co,Mn]O\(_2\), pseudo-ternary oxide (denoted by NCM hereafter) was used for the active material of the positive electrode. For the active material of the negative electrode, graphite was used. A positive-electrode slurry was prepared by mixing NCM with a conductive additive, binder, and N-methylpyrrolidone (NMP) at the desired ratios. The prepared slurries were coated on both surfaces of an aluminum current collector and a copper current collector to form positive and negative electrodes, respectively. The formed electrodes were then dried, pressed, and used for the composite positive and negative electrode layers, respectively.

To reduce QSE thickness and subsequently reduce electrolyte resistance of the assembled cells, the QSE slurries containing silica, binder, and NMP were coated on both the positive and negative electrodes. Cross-sectional microstructures of the layered QSE and electrodes were observed by field-emission scanning electron microscopy. During stacking of the layered QSE and electrodes to form a cell, a short circuit sometimes occurred owing to fracture of cut surfaces and bending. To prevent that short circuit, a separator was placed between the QSE layers of the positive and negative electrodes. The stacked cell (with size of 21 \(\times\) 25 cm), containing 26 negative electrodes and 25 positive electrodes, was placed in an aluminum laminate. A 100-Wh-class laminated cell was formed by injecting the mixed liquids, namely, Li(G4)TFSA-44.5%PC containing the additives such as VC and TBAPF\(_6\), into the stacked LIB and sealing it.

The above-described 100 Wh-class laminated cell was initially charged at a charge rate (c-rate) of 0.005 C for 10 h and subsequently charged in constant-current (CC) mode at 0.05 C up to an upper cut-off voltage of 4.2 V. At that voltage, charge was continued in constant-voltage (CV) mode until the current decreased to 0.005 C. The cell was then discharged in CC mode at 0.05 C to a lower cut-off voltage of 2.7 V. Discharge-rate capability of the cell was then evaluated after the initial charge and discharge. After that, the cell was charged in CC mode at 0.2 C up to the upper cut-off voltage of 4.2 V, at which, it was further charged in CV mode until the current decreased to 0.005 V. The retention ratio of discharge capacity was defined by taking the ratio of discharge capacity at 0.05 C in each cycle to that of initial discharge capacity in the first cycle.

2.4 Nail-penetration test

The safety of the 100-Wh-class laminated cell assembled with the QSE was evaluated with a nail-penetration test. The cell in fully charged state was sandwiched between two Bakelite plates to ensure thermal insulation. A hole with a 5-mm diameter was drilled at the center of the upper Bakelite plate, and a stainless-steel nail (with a 3-mm diameter and a thermocouple inside its tip) was penetrated into the cell at a rate of 40 mm s\(^{-1}\). Another thermocouple was placed at the laminated cell surface and fixed by the Bakelite plate. To examine how the electrolyte composition affects battery safety, the fully charged 100-Wh-class laminated cell using the conventional organic liquid electrolyte, i.e., 1 M LiPF\(_6\) in EC : EMC (33.3 : 66.7 vol\%), was prepared and also used for the nail penetration test. For the nail-penetration test on this cell, instead of being placed between the QSE layers, the separator was sandwiched by the positive and negative electrodes.

2.5 Analysis of interphase between electrolyte and electrode

Composition variations of the liquid phase in the QSE by the battery operation were evaluated by a nuclear magnetic resonance (NMR) measurement (ECA-500 FT-NMR, JEOL Ltd.) with a magnetic field strength of 11.747 T. The LIBs after the charge and discharge operation were disassembled in an Ar-filled glove box. The electrodes were separated and soaked in 250-µL deuterated chloroform, and the resultant liquid was transferred into an NMR sample tube. The extraction of the liquid from the electrodes was carried out three times. A certain amount of trifluorotoluene was added as an internal standard, and then \(^1\)H- and \(^{19}\)F-NMR spectra were collected. The detailed condition was described in the previous report.\(^{39}\)

Hard X-ray photoelectron spectroscopy (HXPES) was applied to investigate the elemental compositions and thickness of the SEI, since the probing depth was as deep as 50 nm.\(^{39}\) HXPES was performed at BL28XU, SPring-8, Japan. The detailed condition was described in the previous reports.\(^{38,39}\)
Figure 3. Ionic conductivity of the quasi-solid-state electrolyte containing Li(G4)TFSA-x%PC and inverse of viscosity of Li(G4)TFSA-x%PC as a function of PC concentration, x.

3. Results and Discussion

3.1 Characterization of quasi-solid-state electrolyte

3.1.1 Application of low viscos solvent to enhance ionic conductivity

Since Li(G4)TFSA contains a high concentration of a LiTFSA, its viscosity is high (i.e., 140 cP) at room temperature; it thereby compromises lithium-ion transport under current flow and rate capability. Hence, adding a lower-viscosity solvent including PC effectively lowers the viscosity of Li(G4)TFSA and enhances its ion transport.33,34 Figure 3 shows ionic conductivity, \( \sigma \), of the QSE containing Li(G4)TFSA-x%PC and inverse of viscosity of the Li(G4)TFSA-x%PC mixture as plotted as a function of PC concentration, x. The inverse of viscosity increases monotonically with increasing x, meaning that PC with a small viscosity of 2.5 cP at 298 K lowers the viscosity of Li(G4)TFSA. The value of ionic conductivity exhibits a maximum around x = 60. The conductivity is a function of both the diffusion coefficient of the charged species and carrier concentration.40-42 Hence, in the region where PC concentration is lower than 60% weight ratio, conductivity increases with increasing x, owing to the enhanced diffusivity of charged species by lowering the viscosity. In contrast, due to the decreased carrier concentration accompanied by dilution of the Li-salt, conductivity started to decrease with further addition of PC when x exceeds 60%. In the region where 40 \( \leq x \leq 75 \), \( \sigma \) exceeded 2 mS cm\(^{-1}\). Hence, x = 44.5 was set for the following evaluations of ion dynamics and battery tests.

To investigate the coordination arrangement of the solvents contained in Li(G4)TFSA-x%PC, the self-diffusion coefficients of the diffusing species were evaluated by using NMR. Table 1 lists the self-diffusion coefficients of G4, PC, TFSA, and Li, represented by \( D_{G4}, D_{PC}, D_{TF}, \) and \( D_{Li} \), respectively, viscosity of the Li(G4)TFSA-x%PC \((x = 0 \) and 44.5% mixture), and ionic conductivity of the QSE containing Li(G4)TFSA-x%PC. For \( x = 0 \), log\( (D_{G4}/m^2s^{-1}) \), log\( (D_{PC}/m^2s^{-1}) \), and log\( (D_{Li}/m^2s^{-1}) \) are −11.1 at 298 K, which is consistent with values in the literature.30,31 The ratio of the self-diffusion coefficient of G4 to that of Li, \( D_{G4}/D_{Li} \), is 0.97, suggesting that G4 is essentially coordinated with Li ions, forming Li(G4)TFSA, and a very low concentration of free G4 stays.33,34 For \( x = 44.5 \), ionic conductivity of the QSE as well as the self-diffusion coefficients of G4, F, and Li are enhanced by the addition of lower-viscosity PC. log\( (D_{G4}/m^2s^{-1}) \), log\( (D_{PC}/m^2s^{-1}) \), and log\( (D_{Li}/m^2s^{-1}) \) are similarly, −10.0. And \( D_{G4}/D_{Li} \) is 1.17, suggesting that free G4 is formed by a ligand exchange with PC in the Li(G4)TFSA-x%PC mixture, as discussed elsewhere.22,33 PC solvent promotes co-intercalation of the solvated species into the graphite negative electrode and its reduction during battery operation.53 In addition, excess glyme solvent contained in SILs promotes co-intercalation.44 These co-intercalations can interfere with repeated battery operation. In fact, our preliminary half-cell test on the graphite negative electrode, comprised of Li(G4)TFSA-44.5%PC, revealed remarkable capacity fading within a few dozen cycles. Considering these results, we decided to introduce VC in this study as an SEI former at the graphite surface in order to ensure repeated battery operation.45 The charge-discharge profile evaluation of the 2032-type coin cell using the QSE revealed that the addition of VC with optimal concentration (~3%) suppressed the unfavorable side-reaction caused by the intercalation of G4 and PC.5 After optimizing VC concentration, we used the QSE containing the Li(G4)TFSA-PC mixture for assembling the 100-Wh-class laminated cell.

3.1.2 Investigation of TBAPF6 concentration for passivation layer formation at aluminum current collector

In an electrolyte containing LiTFSA salt, the aluminum positive electrode current collector is known to corrode at high voltage.46-48 Hence, we added TBAPF6 to the QSE to form a fluorine-based passivation layer at the aluminum surface and then evaluated the dependence of the durability of the positive electrode on its concentration.

Figure 4(a) shows linear sweep voltammetry (LSV) profiles of the asymmetric Al || Li cells using the QSE without TBAPF6 and with TBAPF6, where the concentration was varied from 1 to 20 wt%. The voltage was swept from OCV to a higher voltage. For the cell without TBAPF6, the oxidation current of 0.5 nA cm\(^{-2}\), considered to stem from the corrosion of the aluminum current collector, flowed at 4.17 V. The aluminum corrosion voltage became higher by the introduction of TBAPF6. For example, the aluminum corrosion voltage was 4.33 V when the TBAPF6 concentration in the QSE was 2.5 wt%. Although inorganics (including Al(Tf)3,67 and AlF3) are possible constituents here, the detailed mechanism of the passivation layer formation remains unclear. We conjecture that oxidative decomposition of the TBAPF6 during cathodic sweep, which corresponds to the charge in the cell, might allow for the fluorine-based passivation layer formation at the aluminum surface.

Figure 4(b) shows the effect of the TBAPF6 concentration on the ionic conductivity values of the QSE comprised of Li(G4)TFSA-44.5%PC-TBAPF6 and the inverse of viscosity of the Li(G4)TFSA-44.5%PC-TBAPF6 solution. Both the conductivity and inverse of viscosity reached maximum values when the TBAPF6 concentration was 2.5 wt%, and they decreased with the increase of the concentration, namely, when the concentration was higher than 2.5 wt%. These results indicate that the enhanced conductivity of the QSE with 2.5 wt% of TBAPF6 is caused by the lowering of its viscosity.

Figure 4(c) shows the effect of the TBAPF6 concentration on the ionic conductivity values of the QSE and the aluminum corrosion voltage obtained in the LSV measurement. The aluminum corrosion voltage monotonously increased with an increase of the TBAPF6.

Table 1. Summary of ionic conductivity of the quasi-solid-state electrolyte containing Li(G4)TFSA-x%PC, \( \sigma \), viscosity, \( \eta \), and self-diffusion coefficients of G4, D_{G4}, PC, D_{PC}, F, D_{F}, and Li, D_{Li} at 298 K.

| \( x \) | \( \log(D_{G4}/m^2s^{-1}) \) | \( \log(D_{PC}/m^2s^{-1}) \) | \( \log(D_{F}/m^2s^{-1}) \) | \( \log(D_{Li}/m^2s^{-1}) \) | \( \sigma/mS cm^{-1} \) | \( \eta/cP \) |
|---|---|---|---|---|---|---|
| 0 | −11.1 | — | −11.1 | −11.1 | 0.5 | 140 |
| 44.5 | −10.0 | −9.7 | −10.0 | −10.0 | 1.9 | 11.2 |
concentration, which suggests that the aluminum current collector is covered with a more robust passivation layer containing a concentrated fluorine element by adding a higher concentration of TBAPF6. On the other hand, the ionic conductivity and aluminum corrosion voltage are in a trade-off relationship in Fig. 4(c). On the basis of these results, we determine the desirable concentration to be 2.5 wt%, where the ionic conductivity reached maximum and the aluminum corrosion voltage of 4.33 V was sufficient for the cell operated from 2.7 to 4.2 V.

In addition to TBAPF6, we investigated other additives—LiPF6, LiBF4, tetrabutylammonium tetrafluoroborate (TBABF4), 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIPF6), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF6)—for suppressing the aluminum corrosion. In the performance measurement of the cell with the QSE, the TBAPF6 additive exhibited the best effect for enlarging the charge-discharge cycle lifetime.

### 3.2 Performance of 100 Wh-class laminated cell

Figure 5 shows schematic illustration of the laminated cell structure and photographs of the fabricated 100 Wh-class laminated cell. After optimizing the QSE slurry, compositions, and coating conditions, we formed a uniform QSE layer with 20-µm thickness at the non-uniform surfaces of both the composite positive and negative electrodes. As for the liquid phase, Li(G4)TFSA-44.5% PC with additives (3 wt% of VC and 2.5 wt% of TBAPF6). The cell recorded initial charge capacity of 42 Ah and initial discharge capacity of 32 Ah, and its coulombic efficiency was high (76%). Since average reaction voltage is 3.67 V, discharge energy was calculated to be 115 Wh. Then, based on the cell geometry, energy density of the cell was calculated to be 363 Wh L⁻¹ and 135 Wh kg⁻¹. The rate capability test of the 100-Wh-class laminated cell revealed that discharge capacity is greater than 30 Ah and almost independent of discharge rate and that the cell still exhibited discharge capacity of 26 Ah at 2 C. This high discharge-rate performance is a result of mixing PC with Li(G4)TFSA. That is, decreasing viscosity enhanced lithium-ion diffusivity in the QSE.

### 3.3 Safety demonstration in nail penetration test

When a metallic nail penetrates a LIB under charged state, a short circuit occurs via the nail, and joule heat is generated. The generated joule heat triggers oxygen release from the positive electrode, and that oxygen feeds continuous combustion of the electrolyte, so called “thermal runaway”. For the fully charged 100-Wh-class laminated cell containing the conventional organic liquid electrolyte, i.e., 1 M LiPF6 in EC : EMC (33.3 : 66.7 vol%), typical thermal runaway took place as shown in the photograph in Fig. 6(a). Namely, joule heat was generated after the nail penetrated the cell and, subsequently, fire and smoke appeared. Soon after the nail penetration, the temperatures of the tip of the nail and in the cell were increased to 747 K and 817 K, respectively (Fig. 6(c)). Accompanied by this temperature increase, cell voltage dropped to 0 V, as shown by the temperature and voltage profiles. On the other hand, when the fully charged 100-Wh-class laminated cell using the QSE, comprised of Li(G4)TFSA-44.5% PC, was subjected to the same test, fire and smoke were not generated, as shown in Fig. 6(b).
and the temperatures of a tip of the nail and the cell remained low, i.e., 365 K and 324 K, respectively, as shown in Fig. 6(d). Despite the short circuit via the nail, cell voltage remained high, i.e., 4.03 V (compared with 4.2 V before the nail-penetration test). These results suggest that the temperature increase and voltage drop due to the short circuit are very limited in the case of the newly developed LIB. This result implies that although some joule heat was generated, subsequent combustion was hindered by the QSE layers; thereby, thermal runaway did not take place.

Our high-energy 100 Wh-class LIB with energy density of 363 Wh L⁻¹ using the QSE demonstrated higher level of safety compared to the cell using the conventional organic-liquid electrolyte at least for a nail-penetration test. One of the possible reasons for passing the nail-penetration test, as shown in Fig. 6(b), is the high flash point of the liquid phase; namely, organic-liquid electrolyte, LiPF₆ in EC : EMC, has a flash point of 293–303 K, while Li(G4)TFSA–44.5 %PC has one of 415 K. That result agrees with that revealed by ignition tests showing the safety of a mixture of room-temperature ionic liquid and solvents.¹⁷,¹⁸ Another possible reason is the existence of the QSE layer formed by oxide particles and binder, which can exist and avoid a direct contact between the nail and electrodes during the nail penetration,⁵⁰ and thereby the voltage drop during the test is mitigated, as the voltage profile shown in Fig. 6(d). In that case, the quantity of joule heat generated by the nail penetration, which triggers thermal runaway, should be affected by the microstructure and composition of the QSE layer existing between the positive and negative electrodes. Hence, optimizing not only the liquid phase but also the QSE layer would be advantageous for further ensuring the safety of a LIB. Specifically, it has been reported that rate of joule-heat generation by a short circuit is faster (on a logarithmic scale) than that of the combustion reaction of the electrolyte, and the combustion of the electrolyte is triggered by the joule-heat generation.⁵⁰ When the quantity of joule-heat generation is lowered by the LIB materials and modifications to the microstructure of the QSE layer, it is possible to avoid occurrence of the subsequent combustion reaction and, thereby, thermal runaway is hindered.

Figure 6. (a)(b) Nail-penetration-test results: 100-Wh-class laminated cell using (a) conventional organic liquid electrolyte, 1 M LiPF₆ in EC : EMC (33.3 : 66.7 vol%), and (b) QSE comprised of Li(G4)TFSA–44.5 %PC. (c)(d) Temperature and voltage profiles after the nail-penetration tests for the 100-Wh-class laminated cell using: (c) conventional organic liquid electrolyte and (d) the QSE.⁶

A battery pack built with the developed 100-Wh-class laminated cells could be a power source of an electric vehicle (EV). A module was configured with six cells in parallel, and a battery pack containing 14 of those modules in series was then built. Eighty-four cells were used for building the battery pack, so the resulting battery pack had an energy of 10 kWh. Then, the 10-kWh battery pack was installed in a commercially available compact EV, instead of its original battery pack. A controlling unit for regenerative braking energy was also developed and used in the battery pack. The EV containing the battery pack allowed for driving in areas of our company property, with a maximum speed of 35 km h⁻¹. During this driving, maximum charge current reached to 78 A (corresponding to 0.4 C) and discharge current was 123 A (0.6 C). Owing to the enhanced LIB volumetric energy density and optimized battery-pack design, we could reduce total volume of the battery pack by two-thirds. This result suggests that ensuring battery safety is crucial and beneficial for enhancing energy density of the battery pack.

In addition, we developed a high capacity, high energy density and high power bezel-less LIB with the QSE by focusing on the high volatilization temperature of the QSE. The bezel-less LIB eliminates the extra space needed for casing, as shown in Figs. 7(a) and 7(b). The idea of the bezel-less structure comes from the smartphone displays with extremely narrow casing, which gives users an impression that the product does not have the bezel part.⁵¹ By switching from the conventional aluminum laminate to the bezel-less structure as shown in Figs. 7(c) and 7(d), we reduced the LIB cell volume by 16 %. By combining a Ni-rich high capacity positive electrode, a graphite negative electrode and the QSE, the proposed structure has successfully demonstrated high energy density of 600 Wh L⁻¹ (256 Wh kg⁻¹ defined by the LIB volume) and high capacity of 132 Wh, where an output power of 1160 W L⁻¹. High safety of the bezel-less LIB was successfully demonstrated by overcharge and collapse tests, which are parts of the International
Electrotechnical Commission (IEC) standards, IEC62660-3. These results suggest that a combined use of the bezel-less concept and the QSE may enhance the energy density of the LIB and the LIB pack for large-scale applications such as EVs and stationary uses.

3.4 Cycle performance and its correlation with SEI formation and growth on graphite surface

To evaluate the durability of the LIB containing the QSE, the charge-discharge cycle test was conducted for the coin-type LIB. Figure 8 shows the discharge capacity and coulombic efficiency of the cell with the QSE composed of Li(G4)TFSA-44.5%PC-3 wt%VC-2.5 wt%TBAPF6, depending on the square root of the cycle number. The retention ratio of the discharge capacity was 59% at the 520th cycle. Although the coulombic efficiency was approximately 80% at the initial cycle, the values rose to as high as 99.7 to 99.8%, except in the charge-discharge cycle for confirming capacity, indicating stable charge and discharge with less side reaction.

To clarify the degradation mechanism of the QSE constituents, we have analyzed the variation in the chemical composition in the cell by using an NMR. We measured NMR spectra for the electrolyte solution as prepared and for those extracted from the cell with the QSE after the initial and 520th cycles, respectively. The chemical composition was evaluated using the molar ratios of G4, PC, and LiTFSA, since the total amount of the extracted solution was different in each sample. Table 2 shows the molar ratios for G4 and PC normalized by LiTFSA in the samples. The measured values of G4/LiTFS and PC/LiTFS for the as-prepared sample were 1 and 4, respectively, which is the same as the designed ones. In the sample after the initial cycle, the G4/LiTFS ratio increased to 1.13 and the PC/LiTFS ratio decreased to 3.31. These results suggest that the LiTFSA was consumed prior to G4 in the SEI formation.

| Samples                  | G4/LiTFS | PC/LiTFS |
|--------------------------|----------|----------|
| As-prepared QSE          | 1.00     | 4.00     |
| QSE after initial cycle   | 1.13     | 3.31     |
| QSE after 520th cycle     | 0.87     | 2.96     |

Table 2. Molar ratios of G4/LiTFS and PC/LiTFS summarized for the liquid phase of as-prepared QSE and after initial and 520th cycles (obtained by NMR measurement).  
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reaction at the initial charge, and that PC was more easily decomposed in the side reaction compared to G4. On the other hand, the ratios of both the G4/LiTfS and PC/LiTfS decreased after the 520th cycle, meaning that the consumption of LiTfS occurred only at the initial cycle but that G4 and PC decomposed successively in the cycle test. In particular, the PC/LiTfS ratio significantly decreased, which suggests that PC decomposed more easily than G4 during the cycle test.

We also performed NMR measurements to evaluate the composition variation of the additives (e.g., VC and TBAPF6) during the initial cycle. The molar ratio of VC/G4 was 0.320 in the as-prepared sample and decreased to 0.046 after the initial cycle, revealing that almost all of the VC was decomposed for the SEI formation during the initial charge. In contrast, the molar ratio of TBAPF6/G4 was changed from 0.059 to 0.029, meaning that half of the TBAPF6 remained after the initial cycle. As shown in Fig. 4(c), the aluminum corrosion voltage monotonously increased with an increase in the TBAPF6 concentration. These results indicate that the formation rate of the fluorine-containing passivation layer on the aluminum current collector was low, and the formation of the passivation layer continued after the second cycle.

For qualitative and quantitative analysis of the SEI formation on the graphite surface, HXPE spectra for three negative electrodes—namely, those as prepared, after the initial cycle, and after the 520th cycle—were measured. Figures 9(a)–9(c) shows narrow HXPE spectra originating from C1s, O1s, and F1s, respectively. Each spectrum was similar to that obtained in previous reports on a cell spectra originating from C1s, O1s, and F1s, respectively. Each

Table 3. Atomic concentrations of C, O, F, S, and Si in SEI at the negative electrode surface.

| Samples                                | C  | O  | F  | S  | Si |
|---------------------------------------|----|----|----|----|----|
| As-prepared graphite negative electrode | 50.1| 0.0| 49.7| 0.0| 0.2|
| Negative electrode after initial cycle | 39.8| 19.6| 37.7| 2.4| 0.4|
| Negative electrode after 520th cycle  | 37.2| 39.1| 20.1| 0.7| 2.9|
due to the difference in VC additive concentration in the electrolyte; the optimal concentration of VC was 3 wt% for the QSE, whereas that for the conventional cell is approximately 1 wt%. In the cell with the QSE, a larger amount of VC was electrochemically decomposed on the graphite surface at the initial charging process, resulting in the thicker SEI. As for the growth rate of the SEI, we assume that the SEI thickness grew in proportion to the square root of the cycle number, since the capacity retention and square root of the cycle number showed a linear relationship in Fig. 8. The slope of the line for the QSE is slightly steep compared with that of the conventional cell, probably because the QSE constituents contributed to the SEI growth—namely, not only a large amount of VC but also PC and G4, as observed in the NMR measurements (Table 2).

Figure 10 summarizes the mechanism underlying the SEI formation and growth on the graphite surface of the LIB containing Li(G4)TFSA-based QSE, which were estimated on the basis of the results of NMR and HXPS analyses. In the initial charge (the 1st cycle), not only VC but also LiTFSA, PC, and G4 were decomposed on the bare surface of graphite, which contributed the formation of thick SEI where C, O, F, and S elements were contained. During the charge-discharge cycles, the decomposition of LiTFSA was suppressed by the SEI as a passivation layer, while G4 and PC were successively decomposed. The successive decomposition resulted in the SEI growth, which mainly consisted of C and O originating from the decomposition of G4 and PC.

### 3.5 Application of highly concentrated sulfolane based electrolyte to QSE

The analysis of the SEI at the interphase between the negative electrode and the QSE revealed that the decompositions of LiTFSA, PC, and G4 contributed to the SEI formation at the initial charge, and that continuous decompositions of G4 and PC were a major reason for the SEI growth that deteriorated the capacity during charge-discharge cycles. Although a reduction of the amount of G4 and PC would seem effective to suppress the SEI growth, it would lower the rate properties due to degraded ionic conductivity of the QSE. Therefore, a new type of electrolyte needs to be developed for obtaining a high output property with a low amount of PC as a low-viscosity liquid.

We have focused on using a highly concentrated sulfolane (SL)-based solution (here, Li(SL)3TFSA) as an electrolyte to achieve high safety, a high output property, and sufficient durability in charge-discharge cycle. In the Li(G4)TFSA-based electrolyte, Li ion is transported via a vehicle mechanism, where the Li ion moves together with the translational movement of the solvent molecules. Since the Li⁺ transport number estimated by potentiostatic polarization method is quite low, the result is a high polarization resistance in the high rate charge-discharge reaction and subsequently a low rate property. As an alternative, a sulfolane-based electrolyte has been intensively investigated due to its high Li⁺ transport number originating from the Li ion hopping conduction. As a low-viscosity solvent, we utilized propylene carbonate (PC) and butylene carbonate (BC) with respective boiling points of 315 and 523 K, both of which are higher than HFE (328 K). Figure 11 summarizes the molecular structure, volatile, and capacity retention after 100 cycle of charge-discharge operation. Our TG-DTA and DSC measurements indicated that the volatilization temperature of Li(SL)3TFSA-20% PC and BC was ca. 413 K, which is higher than that of Li(G4)TFSA-44.5% PC. Also, they revealed that the heat generated by the thermal oxidative decomposition on the positive electrode, which was determined as the peak area between 250–350 °C, was less than that of the organic electrolyte solution and Li(G4)TFSA-45% PC. This result means that the SL-based electrolyte exhibited a higher stability against oxidative decomposition, which is a promising feature in terms of the longer lifetime of the cell.

Figure 12 shows the relationship between the discharge capacity ratio (defined as the ratio of discharge capacity at 0.5 C to that of 0.05 C (Q(0.5 C)/Q(0.05 C) × 100)) and the inverse of the electrolyte viscosity for the for the coin cells comprised of Li(SL)3TFSA-(PC, BC) and Li(G4)TFSA-PC. The weight concentrations of PC to Li(G4)TFSA in Fig. 12 were 0 and 45 wt%, and the ionic conductivity of the electrolyte was monotonously increased with an increase of the PC concentration. The discharge capacity ratio was also increased by increasing the PC concentration, indicating that the enhancement of ionic conductivity due to the low-viscosity solvent improved the rate performance. In contrast, the dependence of the discharge capacity ratio on the viscosity for Li(SL)3TFSA-x% (PC, BC) was apparently different from the case of Li(G4)TFSA: the discharge capacity ratio of Li(SL)3TFSA-x% (PC, BC) was higher than that of Li(G4)TFSA-x% PC at the low viscosity region, meaning that a superior rate performance was obtained even for the cell in which electrolyte solution viscosity was high and ionic conductivity was low. For example, while the viscosity of the Li(SL)3TFSA-20% PC solution was 63 eP, which is six times higher than that of Li(G4)TFSA-45% PC(11.2 eP), the discharge capacity ratios of the coin cells were almost the same.
LiBC) was not due to low viscosity but rather to the reduction of the ionic conductivity and high energy density of LIB, and the highly safe LIB could be implemented into the EV. Also, the modification of the constituents based on the degradation mechanism investigation effectively improved the durability in the charge-discharge test. On the basis of the results, we can conclude that QSE is one of the promising candidates to realize highly safe LIB system exhibiting superior battery performance.

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