

New design for a safe lithium-ion gel polymer battery

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Abstract

We present a new design of a lithium-ion gel polymer battery which is fabricated using a semi-interpenetrating network (semi-IPN) type gel polymer and LiCoO_2 , covered by an ion conductive polyurethane. A 7 wt.% solution of a semi-IPN gel polymer, composed of a fully cyanoethylated cellulose derivative and multifunctional poly(oxyethylene)methacrylate has an ionic conductivity of $2.7 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , and has a higher degree of control of liquid electrolyte evaporation when compared with conventional fluoride polymer gels. Another ion conductive polymer, a caprolactone segmented polyurethane, arranged on the surface of the cathode active material in order to increase the start temperature of the thermal runaway reaction worked as planned, raising the exothermic decomposition temperature by 50°C . A large (2500 mAh) cell showed good discharge performance and improved safety characteristics as judged by a nail penetration test. Furthermore, this battery system exhibited a unique phenomenon, that of preventing overcharging. The new design of this lithium-ion gel polymer battery could be promising for large batteries that must be inherently safe, such as batteries for mobile applications.

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1. Introduction

Recently developed lithium-ion (Li-ion) gel polymer battery systems, consisting of graphite-based anodes, lithium metal oxide-based cathodes and polymer electrolytes that contain polar liquid organic solvents, have several advantages. These include a high operating voltage, a high energy density, good cycle durability, no leakage of electrolyte, and thin, prismatic cell design [1,2]. Many kinds of polymer materials for gel electrolytes, such as poly(ethylene oxide) (PEO) [3,4], polyacrylonitrile (PAN) [5] and poly(methylmethacrylate) (PMMA) [6] have been studied in the last decade. In particular, much practical research exists on poly(vinylidene fluoride) (PVdF) [7] and poly(vinylidene fluoride-co-hexafluoro-propylene) (PVdF-HFP) [8] because these compounds have a relatively high ionic conductivity and good mechanical properties.

However, the applications of these Li-ion gel polymer cells presently include only those for which a small capacity cell suffices, since the flammable electrolytes in such polymers and the highly reactive charged materials that they contain still raise safety concerns. Indeed, electrolyte flammability is an important safety issue in various systems, not only in a liquid electrolyte battery system. However, investigations into protective mechanisms against the thermal runaway of charged active materials in this type of battery are very scarce.

We have found that Li-ion PVdF-gel polymer cells operated at high temperatures undergo a thermal runaway reaction, producing very high cell temperatures, smoke and fire [9]. When a metal nail penetrated a fully charged battery, the internal electrical short-circuit resulted in a high internal temperature and the battery caught fire. Zhang et al. [10] have reported that commonly used charged cathode materials such as Li_xCoO_2 , Li_xNiO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ with $x \leq 0.5$ showed a significant exothermic reaction at high temperatures. Materials with $0.5 \leq x < 1$ are in a charged state, whereas those with $x < 0.5$ are overcharged and are liable to decompose with the liberation of O_2 . Both Li_xCoO_2 and Li_xNiO_2 exhibited a

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strong reactivity with onset temperatures in the 200–230 °C range as x was decreased.

To develop a large, truly safe Li-ion gel polymer battery suitable for electric or hybrid vehicles, we much achieve control of thermal runaway reactions and effectively prevent heated and evaporating liquid electrolyte from generating inflammable gas.

In this study, we present a new conceptual design to ensure the safety of the Li-ion battery. Two different gel polymer electrolytes were tested for the cells. The first polymer, which had a semi-interpenetrating polymer network (semi-IPN) system, was used as the gel electrolyte, with a porous separator membrane, between the positive and negative electrodes. This semi-IPN system consisted of cyanoethylated dihydroxypropyl cellulose and poly(ethylene glycol) dimethacrylate; it had good mechanical properties and the capability to prevent the evaporation of the liquid electrolyte from the polymer gel. The second polymer, polyurethane (PU), had a poly-caprolactone segment in the polymer chain, and was used as an ion-conductive binder polymer in the positive electrode. This PU polymer was specially arranged on the cathode active material surface in order to raise the starting temperature of a thermal runaway reaction. Here, we discuss the performance of this newly designed Li-ion gel polymer battery using both polymer electrolytes, and present the results of a nail penetration test of a large cell.

2. Experimental

2.1. Polymer materials and other chemicals

We used the semi-IPN polymerization system, which consists of a cross-linkable monomer material and non-reactive polymer materials, for the gel polymer electrolyte. As the cross-linkable monomers, we used three type of methacrylate compounds purchased from Shin-Nakamura Chemical Co. Ltd.: trimethylol propane triacrylate (as a three-functional monomer, NK-ester TMPT), poly(ethylene glycol) dimethacrylate (as a two-functional monomer, NK-ester 9G, average molecular weight (M_w) of polyethylene glycol; ca. 400), and methoxy diethylene glycol methacrylate (as a mono-functional monomer, NK-ester M20G) without further purification.

The compound O-(2,3-dihydroxypropyl)cellulose (DHPC) is a polyhydroxy cellulose derivative produced by reacting cellulose with 2,3-epoxypropanol (glycidol). Fully cyanoethylated DHPC (CN-DHPC) was used as a non-reactive polymer for the semi-IPN system. The molecular characteristics and thermal properties of CN-DHPC are: number-average degree of polymerization (DP), 210; M_w by GPC measurement, 45,000; molecular substitution of dihydroxypropyl group for anhydro glucose unit (MS), ca. 4; glass transition temperature (T_g), -42 °C; dielectric constant (ϵ') at 25 °C, 31. Details and preparation methods were described in our previous paper [11,12]. Since CN-DHPC

has a relatively rigid backbone and a high dielectric constant, it could be formed into a physically strong and highly ionic conductive semi-IPN polymer gel.

Electrochemical device grade ethylene carbonate (EC), diethylene carbonate (DEC), propylene carbonate (PC), vinylene carbonate (VC) and other chemicals were purchased from Kishida Chemical Co. and used without further purification. As the liquid electrolyte solution for the gel polymer electrolyte, 1 M LiPF₆ in EC/DEC/PC/VC (35:55:10:1, v/v) was used. A mixture of methacrylate monomers (three-functional/two-functional/mono-functional monomer = 2:10:10, w/w) and the CN-DHPC were dissolved in a liquid electrolyte solution composed of 6 wt.% of methacrylate monomers, and 1 wt.% of cellulose derivatives. We dried this solution (the pre-polymer solution) to a moisture content (w/w) of less than 10 ppm in vacuum at room temperature. The semi-IPN gel polymer electrolyte was prepared by a radical initiated polymerization reaction of methacrylate monomers in a pre-polymer solution. The compound 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, Wako Pure Chemical Industries Ltd.) was used as the radical initiator at a concentration of 1 wt.% with respect to methacrylates in the pre-polymer solution. The polymerization reaction was performed in an aluminum laminated battery bag at 55–80 °C.

Another polymer electrolyte material, polyurethane (PU), which has a poly-caprolactone segment, constituted the ionic conductive polymer binder for the cathode materials. This PU was prepared by the poly-condensation reaction of poly-caprolactone diol (Pracel 220N, M_w ; 2000, Daicel Chemical Industries Ltd.) and 4,4'-diphenylmethane diisocyanate. The prepared PU, with a M_w of 1.7×10^5 , had a sticky rubber-like consistency with a T_g of -40 °C. This PU absorbed 320% per weight of 1 M LiPF₆ liquid electrolyte at 25 °C, and its ionic conductivity was 3.9×10^{-3} S cm⁻¹. Detailed preparation methods, and physicochemical and electrochemical properties are described in our patent [13].

2.2. Fabrication of Li-ion gel polymer cells

In order to coat the cathode material with polymer, 1820 g of LiCoO₂ (Seido Chemical Corp.), 60 g of Ketjen black (EC, Kao Corp.), and 857 g of 7 wt.% PU in *N*-methyl-2-pyrrolidone solution (NMP, Wako Pure Chemical Industries) were mixed in a specially designed mixer (Fig. 1) for 24 h at room temperature [14]. Next, 500 g of 12 wt.% poly(vinylidene)fluoride (PVdF; average M_w ca. 71,000, purchased from Sigma-Aldrich Fine Chemicals Co. Ltd.) in NMP was added and mixed to make a homogeneous ink. To prepare the cathode, we spread the ink on an aluminum foil using a knife blade designed to maintain a fixed distance from the aluminum foil. We coated both sides of the aluminum foil, then dried the foil at 140 °C for 72 h in vacuum to remove NMP and moisture, pressed it with a roll press at 30 MPa, and dried it again at 120 °C in vacuum for 15 h. The electrode thus obtained, which was composed of 91 wt.% of

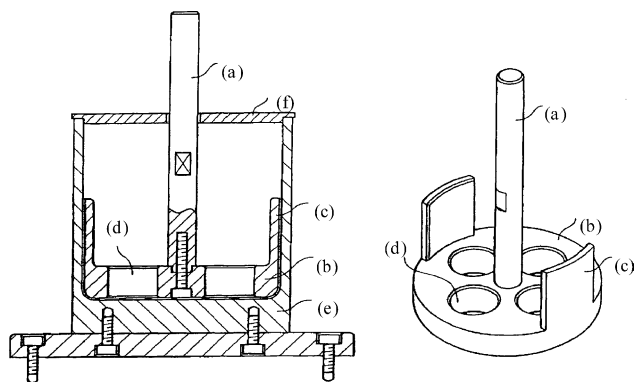


Fig. 1. Schematic view of press-rolling mixer: (a) rotating axle connecting directly to the motor; (b) press-rolling blade with mortar-like shape; (c) scraper; (d) holes supplying the electrolyte mixture to below; (e) container with a mortar-like base; (f) lid.

LiCoO₂, 3 wt.% ketjen black, 3 wt.% of PU and 3 wt.% of PVdF, was $128 \pm 2 \mu\text{m}$ thick. The typical mass loading of the electrodes corresponded to an electrode capacity of ca 2.7 mAh cm^{-2} . We prepared the anode in the same manner, except that instead of aluminum foil, we used copper foil as a current collector, and PVdF alone as a binder. The anode, composed of 92 wt.% of synthetic graphite (MCMB- #6–28; Osaka Gas Chemical Co. Ltd.), and 8 wt.% of PVdF, was $133 \pm 3 \mu\text{m}$ thick.

We rolled up the electrodes, arranged with two paper separators ($35 \mu\text{m}$ thick, Nihon Kodoshi Corporation), sandwiched them, and welded a nickel tab onto them. After pressing the resultant rolls of electrodes and fixing them onto a tape, we inserted the electrode assembly into a bag made of thermoplastic film laminated to an aluminum sheet. We allowed the pre-polymer solution to penetrate the electrode assembly in the bag by keeping them under reduced pressure for 8 h; afterward, we sealed the bag by hot pressing under reduced pressure. Then, the assembled cell was heated to 55°C for 2 h and 80°C for 20 min. We performed all of this fabrication process in a dry atmosphere (dew point of air $< -45^\circ\text{C}$). The prepared 600 and 2500 mAh cells weighed, respectively, 15 and 74 g, and were $50 \text{ mm} \times 76 \text{ mm} \times 3.5 \text{ mm}$ (width \times length \times thickness) and $104 \text{ mm} \times 112 \text{ mm} \times 4.4 \text{ mm}$ in size.

To form a solid electrolyte interface on the graphite in the negative electrode, we used the following procedure. First, we charged the assembled cell at quite small constant currents of 0.01 and 0.1 C to 3.2 and 4.0 V, respectively, and then discharged the cell to 3.0 V at 0.1 C. Next, we charged it a second time to 4.2 V at 0.1 C, and discharged it to 2.75 V at the same current at 25°C . The nominal operating voltage of the cells prepared in this way ranged from 2.75 to 4.2 V.

2.3. Measurements

The T_g of the polymer materials and the thermal runaway temperature of the charged cathode materials were obtained

by differential scanning calorimetry (DSC) measurements in a sealed aluminum pan (prepared in a dry box), with a heating rate of 1°C min^{-1} for the T_g and $10^\circ\text{C min}^{-1}$ for the thermal runaway temperature; the instrument used was a EXSTAR 6000, Seiko Instruments Inc. The DSC measurements for charged cathode material were performed by methods described in the literature [10]. The ionic conductivity measurements of polymer electrolyte were performed as described in our previous papers [15,16].

Weight changes due to solvent evaporation from samples of the semi-IPN polymer gel and the PVdF-gel (prepared as described in our patent [17]) with the same surface area and containing the same liquid electrolyte (1 M LiPF₆ in EC/DEC = 1:1, v/v) were separately determined under the same atmosphere (25°C in air, dew point of air $< -80^\circ\text{C}$). The weight change was measured for each experimental run, and, for comparison, the data for a liquid electrolyte without polymer materials was also recorded.

To carry out the gel polymer cell testing, we used a charge–discharging system (Hokuto Denko Co. Ltd.). We calculated the specific capacity of the cell from the result of the 0.1 C charge–discharge process. The cells cycled through the 0.1 C charge–discharge cycles at 25°C ; the cut-off limit voltages were 4.2 and 4.1 V for the charge and 2.75 V for the discharge.

The thermal stability of the fully charged 2500 mAh gel polymer cell under rapid and extreme temperature changes was checked by a metal nail penetration test. The 2 mm diameter metal nail penetrated the fully charged cell at a speed of 10 mm s^{-1} at 25°C .

To perform the overcharge test, we cycled the freshly prepared cells five times between 2.75 and 4.2 V at room temperature at a 1 C rate. The test cell was charged in separate experiments by 1 and 3 C to a charge of 300% at 25°C . The cell temperature and voltage was recorded, and, for comparison, a conventional Li-ion cell using the same liquid electrolyte, but without the polymer materials, was overcharged.

3. Results and discussion

3.1. Selection of polymer material and its arrangement inside a battery

In our selection of polymer materials, and design of the cell, we considered the following points:

- (1) We chose a polymer material that could form a physically strong gel, and could prevent the evaporation of high polarity liquids in gel, even when added in small amounts.
- (2) Our design ensured that a thermal runaway reaction of the Li-ion cell at a high temperature might be prevented by covering the surface of the cathode material by ion conductive polymer materials. In addition, we selected as a covering material a suitable polymer which would not degrade cell performance even in a low temperature

discharge. We realized that easy and effective covering methods needed to be developed.

3.2. Semi-IPN gel polymer electrolyte

There are many investigations of gel polymer electrolytes prepared by in situ polymerization of monomers in liquid electrolyte. A gel polymer electrolyte prepared from monomers and a low molecular weight cross-linking agent often has high Young's modulus but, low breaking strength, especially, at more than 20 wt.% of the cross-linking agent content in the liquids [18,19]. However, this type of gel polymer is often brittle, because of the low molecular weight between the cross linking points in the gel structure.

In order to obtain a gel polymer electrolyte with high mechanical strength, we prepared a semi-IPN gel polymer by in situ polymerization of a cross-linkable monomer and non-reactive polymer materials. The monomer materials react with each other in the liquid electrolyte to form a three-dimensional polymer network, within which the non-reactive polymer is entrapped. The semi-IPN gel polymer in this study that combined cellulose derivatives with a relatively rigid backbone with cross linkable monomers is capable of considerable mechanical strength, even at a polymer concentration of 7 wt.%. Finally, a monofunctional monomer was added in order to increase the molecular weight between the cross linking points, so that the gel had a flexible character.

The CN-DHPC that we used in the semi-IPN gel polymer formation also has the capability to dissolve lithium salts independent of the liquid electrolyte. In an X-ray scattering analysis of CN-DHPC which contained a 1 M concentration of dissolved lithium salt, we did not observe the peak indicating the existence of a crystal. Thus, there must have been a complete dissociation of the lithium salt in the polymer matrix. At room temperature, the specific conductivities of the CN-DHPC and the semi-IPN gel polymer electrolyte (7 wt.% polymer concentrations) that contained a 1 M concentration of LiClO_4 are, respectively, 1.6×10^{-4} and $2.7 \times 10^{-3} \text{ S cm}^{-1}$. The temperature dependences of these conductivities are illustrated in Fig. 2. The CN-DHPC with the lithium salts showed a relatively high conductivity even in an all-polymer electrolyte; it could potentially serve as an all-polymer electrolyte at temperatures over 50°C . The Arrhenius activation energies for conduction ($\kappa = A e^{-E_a/RT}$) in the linear region are, respectively, 23 and 73 kJ mol^{-1} for the semi-IPN gel polymer and CN-DHPC. In the case of the all-polymer electrolyte, the linear temperature dependence in the Arrhenius plot suggested that the lithium ion dissolved mainly in the oxyalkylene side chain of the CN-DHPC. Since the selected polymer materials remain mobile, and do not interfere with the solubility of the lithium ion, the semi-IPN gel polymer exhibits a practical high ionic conductivity level over a wide temperature range.

The results of our measurement of the weight loss of the liquid electrolyte in the gels through evaporation are shown in Fig. 3. The liquid evaporation profiles of the semi-IPN gel

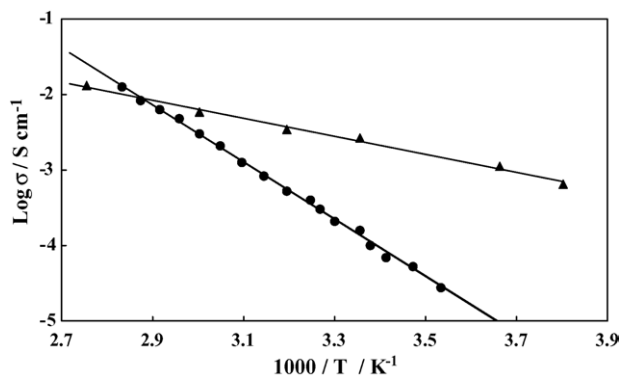


Fig. 2. Temperature dependences of conductivity of polymer electrolyte without liquids and semi-IPN gel polymer electrolyte: (●) CN-DHPC including 1 M LiClO_4 ; (▲) semi-IPN gel polymer including 1 M LiClO_4 in EC/DEC 1:1 (v/v) (7 wt.% concentration of polymer compounds).

polymer and the solvent differed, and the evaporation speed of the semi-IPN was slower compared to that of the solvent only. The high-polarity polymer matrix that included a cellulose derivative with a high dielectric constant interacted with the liquid electrolyte, and probably prevented electrolyte evaporation in the gel. At higher temperatures, such liquid electrolyte evaporation is also prevented by the formation of a polymer gel. The liquid electrolyte in the PVdF-gel with microporous structure evaporated the quickest. In addition, the evaporation profile of the PVdF-gel resembled that of a liquid electrolyte. Evidently, the PVdF did not interact extensively with the solvent.

3.3. Cathode material covered by ion conductive polymer

In a thermal runaway reaction, the charged active materials cause a significant exothermic reaction and oxygen liberation

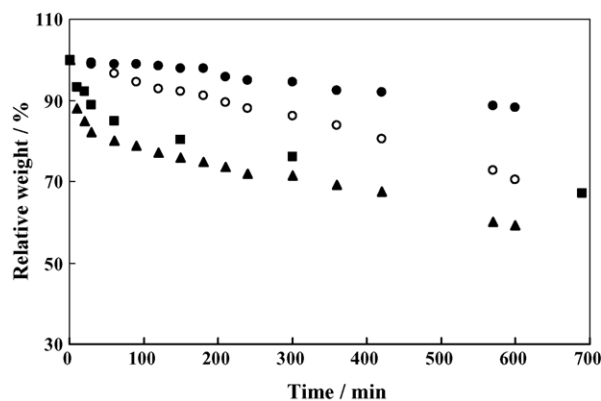


Fig. 3. Relative weight loss of gel polymer electrolyte with time in a dry atmosphere: (●) semi-IPN gel polymer including 1 M LiClO_4 in EC/DEC 1:1 (v/v) (50 wt.% concentration of polymer compounds); (○) semi-IPN gel polymer including 1 M LiClO_4 in EC/DEC 1:1 (v/v) (7 wt.% concentration of polymer compounds); (▲) PVdF-gel including 1 M LiClO_4 in EC/DEC 1:1 (v/v) (ca. 40 wt.% concentration of polymer compounds); (■) liquid electrolyte only, 1 M LiClO_4 in EC/DEC 1:1 (v/v).

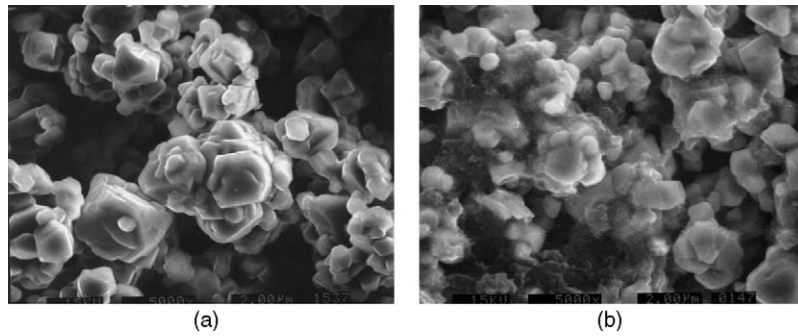


Fig. 4. Scanning electronic micrographs of LiCoO_2 covered with the polyurethane ionic conductive polymer: (a) untreated LiCoO_2 ; (b) covered LiCoO_2 .

at temperatures over 200°C . Such a reaction ignites the liquid electrolyte, and, consequently, the battery catches fire. By covering the active materials' surface with an ion conductive polymer which did not interfere with the movement of the lithium ion, we hoped to control a thermal runaway reaction. By choosing in particular a polymer with a low glass transition temperature, we thought it would be possible to minimize low temperature performance degradation. Thus, for the polymer cover compounds, we selected a polycaprolactone polyurethane with a T_g of -40°C , whose ionic conductivity in the gel state was approximately $4 \times 10^{-3} \text{ S cm}^{-1}$, and with adhesive, rubbery characteristics. A SEM image of the polymer-coated powders is shown in Fig. 4.

Fig. 5 shows the DSC curves of the $\text{Li}_{0.5}\text{CoO}_2$ /electrolyte combination. For the active material with a conventional PVdF binder, the onset temperature of the first major exothermic peak was about 250°C . This result was similar to that of Zhang et al. [10]. However, in the case of the cathode covered with polyurethane, the first major exothermic peak shifted to 302 , about 50°C higher than that for the PVdF. This special

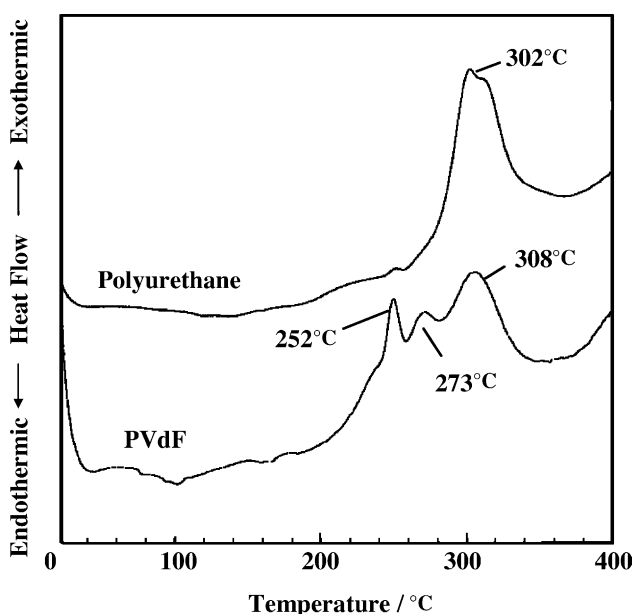


Fig. 5. DSC curves from charged positive electrodes containing $\text{Li}_{0.5}\text{CoO}_2$.

coating may be able to shift the start of a thermal runaway reaction to a higher temperature. As we will describe later, the combination of this covering method with the use of a semi-IPN gel polymer can improve the safety of large batteries.

3.4. Cell performance

The semi-IPN gel polymer has a relatively high ionic conductivity even at low temperatures, $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at 0°C . This high conductivity probably results from the low concentration of polymer materials used to form the gel electrolyte; additionally, these materials do not reduce lithium-ion solubility, and thus, the ionic conductivity itself. Therefore, this Li-ion gel polymer battery demonstrated a high level of performance. Figs. 6 and 7, respectively, present the rate capability of the 600 and 2500 mAh cells at 25°C . The capacity at 2 and 3 C discharge was approximately 96% and 65%, levels comparable to the 0.1 C discharge of the 600 mAh cell. Thus, a large current discharge at 2.5 A is possible for a large battery; our cell had a capacity loss of only 1.4% compared to the loss at a 250 mAh (0.1 C) discharge. The 600 and 2500 mAh cells exhibited 151 and 127 Wh kg^{-1} , respectively, of the energy density at 0.1 C charge.

The results in discharge operation at low temperature are shown in Fig. 8. The capacities of the cell at 1 C discharge were 609, 424, and 66 mAh for temperatures of 25, 0 and -15°C , respectively. Such results might indicate that the polymer gel battery had a relatively good discharge capacity

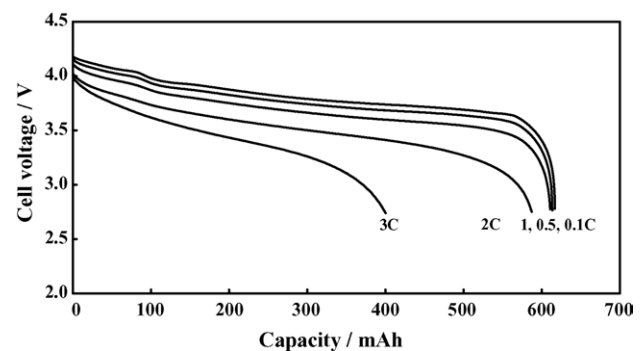


Fig. 6. Discharge curves of the Li-ion semi-IPN gel polymer cell (600 mAh) at various current densities at 25°C .

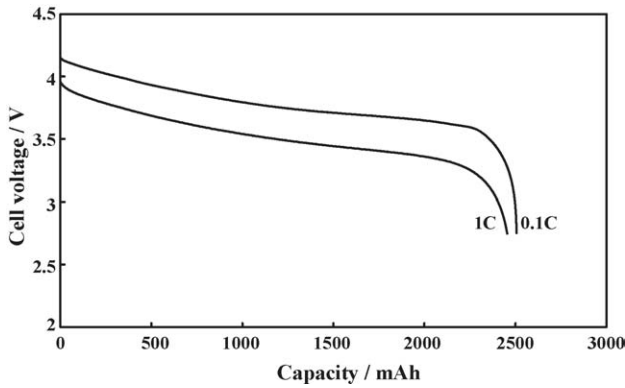


Fig. 7. Discharge curves of the Li-ion semi-IPN gel polymer cell (2500 mAh) at 0.1 and 1 C of current density at 25 °C.

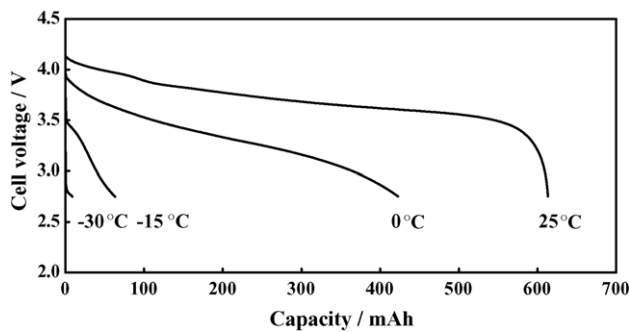


Fig. 8. Discharge curves with 1 C current density of the Li-ion semi-IPN gel polymer cell (600 mAh) at various temperatures.

at low temperatures; however, it did not discharge at -30°C because of a remarkable increase of internal resistance.

The cycling behavior of the cells is plotted in Fig. 9. The battery using the liquid electrolyte without the IPN polymer materials showed good cycle durability. The relative capacity maintenance at 500 cycles was about 92%. In the case of

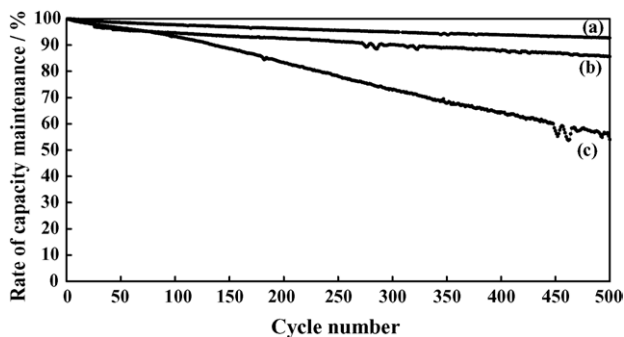


Fig. 9. Cycle life of the Li-ion and the semi-IPN gel polymer cell (600 mAh) at 25 °C. The charge–discharge process was performed at 0.1 C constant current: (a) the Li-ion cell using a liquid electrolyte, without the presence of semi-IPN gel polymer material in the cell; (b) and (c) the Li-ion semi-IPN gel polymer cell with 7 wt.% of polymer materials in the liquid electrolyte. The electrolyte of all cells was based on the 1 M LiPF_6 in EC/DEC/PC/VC (35:55:10:1, v/v). The cut-off limit voltages were 4.2 V for (a) and (c) and 4.1 V for (b) for the charge, and 2.75 V for the discharge, respectively. The electrode materials and other cell components were the same in all the cells.

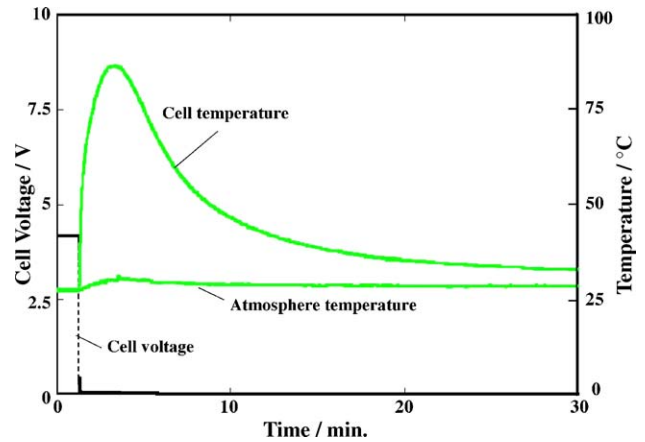


Fig. 10. Cell temperature and voltage profiles of the nail penetration test for the large size (2500 mAh) Li-ion semi-IPN gel polymer cell.

the Li-ion semi-IPN gel polymer battery, the relative maintenance was less than 60% at 500 cycles, a result inadequate for practical cycle durability. However, the cycle durability of the cell improved dramatically, 87% at 500 cycles, when we decreased the cut-off charging voltage. It may be that an electrochemical reaction to the polymer materials occurred at voltages above 4.1 V. To resolve this issue, a detailed electrochemical investigation is required.

3.5. Safety performance of the newly designed semi-IPN gel polymer cell

In Figs. 10 and 11, we present, respectively, a plot of the change in the cell temperature and voltage after its penetration by a metal nail, and a photograph showing the appearance of the cell after penetration. In tests of 15 very large 2500 mAh batteries, we observed no ignition, smoke emissions, or cell expansions. The voltage of the battery went to zero immediately after inserting the nail; the internal electric short generated enough heat to raise the battery surface temperature to 80°C . We suspect that the internal temperature might have



Fig. 11. Photograph of a Li-ion semi-IPN gel polymer (2500 mAh) cell after a nail penetration test.

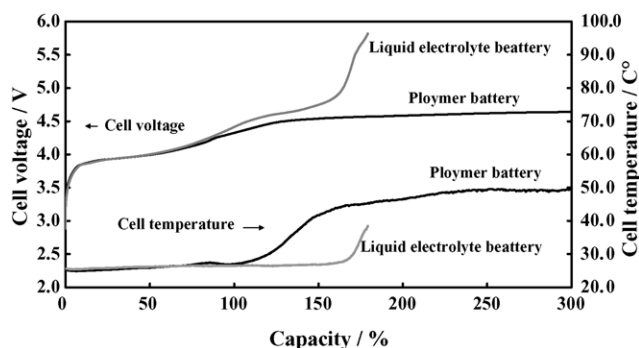


Fig. 12. Cell potentials vs. charged capacity during an overcharge for cells with Li-ion semi-IPN gel polymer and a liquid electrolyte Li-ion cell without semi-IPN materials. Charge current: 600 mA, charge temperature: 25 °C.

risen to over 200 °C, but after that, it gradually cooled down. In contrast, a cell of the same capacity, but missing the PU and semi-IPN gel polymer suffered a surface temperature rise to 300 °C, burned violently, and emitted a remarkable amount of smoke. It is clear that the newly designed Li-ion semi-IPN gel polymer battery has a high safety potential.

An unexpected and unique overcharge tolerance phenomenon was observed when we examined the overcharge behavior of our gel polymer battery. Fig. 12 shows the potential and temperature profiles of the Li-ion and the semi-IPN gel polymer cell during an overcharge. The charging current was 600 mA, and upon charging, the cell potential reached 4.2 V in 1 h at 25 °C. With additional charging, in the semi-IPN gel polymer battery, the cell voltage and temperature reached 4.5 V and 43 °C at 150% overcharge. Furthermore, even if the overcharge continued to 300%, the battery voltage and cell temperature remained at a plateau. At the end of the overcharge period, 3 h, the cell voltage and temperature values were 4.6 V and 50 °C. The total charge capacity was three-fold that of the nominal capacity. During the overcharge, we saw no fire, no smoke, and only a slight swelling caused by a very small amount of gas generation. The discharge capacity immediately after the overcharge was slightly larger than the nominal capacity (Fig. 13). This phenomenon

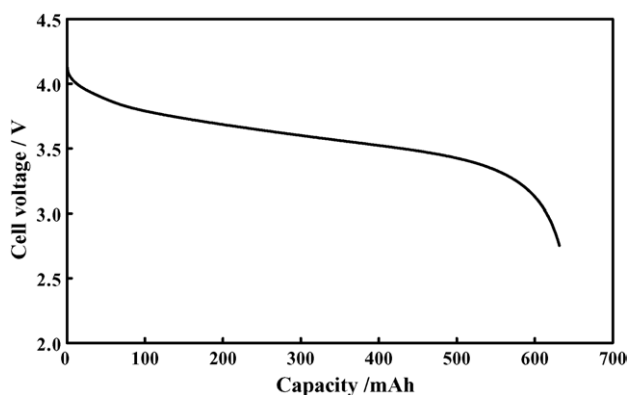


Fig. 13. A discharge curve of the 300% overcharged Li-ion semi-IPN gel polymer cell. Discharge current: 600 mA, discharge temperature: 25 °C.

was observed in all of 12 cells examined. In the case of overcharging at a 3 C rate, the plateau potential and temperature were raised a little compared to those obtained at an overcharging rate of 1 C. On the other hand, a regular 600 mAh Li-ion battery ignited when it reached the point of a 170% overcharge.

When semi-IPN gel polymer batteries that had been charged to various levels of 100, 200 and 300%, were transferred to an argon box and opened, no lithium metal dendrites were observed on either the negative and positive electrode surfaces or even in the separator. Xing [20] reported similar phenomenon in other types of gelled polymer lithium cells, also finding no dendrites and no oxidation–reduction shuttle species in the battery. However, the overcharge tolerance phenomenon we have observed only in the Li-ion semi-IPN gel polymer battery. It is possible that the oxidation–reduction shuttle species are generated from polymer compounds in the voltage region greater than 4.1 V. Further investigations are needed to elucidate the overcharge tolerance mechanism.

4. Conclusions

A novel gel polymer electrolyte consisting of high polarity cellulose derivatives and several kinds of multifunctional poly(oxyethylene) methacrylates had a practical level of output, high ionic conductivity and the ability to prevent evaporation of the liquid electrolyte. Furthermore, the start temperature of the thermal runaway reaction of the charged cathode active material was increased by about 50 °C by a new design where the cathode material was covered with ion conductive polyurethane. A Li-ion gel polymer battery using a semi-IPN gel polymer and a polyurethane covered cathode material showed good performance even in a low temperature discharge. Large batteries of this type were stable, and did not catch fire even in response to the exothermic heat generated by the penetration of a metal nail. The new design of this battery significantly improves the safety performance of the Li-ion gel polymer battery.

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