High Ionic Conducting Polymer with Polysaccharide and its Applications

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Polysaccharide polymers such as cyanoethylpullulan, cyanoethylcellulose, and acetylcellulose were examined for use as matrix polymers in gel-electrolytes (ionic conducting polymers). Using cyanoethylpullulan matrix polymer, an excellent gel-electrolyte which provided a high ionic conductivity of up to 2.4 $\times$ 10^{-3} S/cm at ambient temperature and good mechanical strength was obtained. In one of our applications of the newly developed gel-electrolyte, we used it to fabricate rechargeable lithium ion polymer batteries. These batteries showed good electrochemical properties, for example, a high charge/discharge efficiency and high discharge current density.

1. Introduction

In recent years, much attention has been paid to the use of high ionic conductivity polymer electrolytes in advanced electrochemical devices such as lithium polymer batteries and electrochemical sensors. Various liquid electrolytes, including polyether-Li salt complexes (e.g., polyethylene oxide-$LiClO_4$) and gel-electrolytes that use polyacrylonitrile as a gel matrix polymer, have been investigated for applications in lithium polymer batteries.[1)-4)] However, these materials have not yet been used as solid electrolytes in lithium polymer batteries because they have a very low ionic conductivity (< 10^{-4} S/cm) and are mechanically too weak for use as battery separators. Polysaccharides, on the other hand, are attractive because they have a rigid backbone structure, which can improve the strength of a gel composition. Therefore, to obtain a composition with sufficient ionic conductivity and mechanical strength, we studied gel-electrolytes having matrix polymers made of polysaccharides such as cyanoethylpullulan, cyanoethylcellulose, and acetylcellulose. (We did not find any reports on polysaccharide polymer electrolytes that would help us in these studies.) This paper describes the excellent solubility, gelation properties, electrochemical stability, and ionic conductivity of a new gel composition we developed and the method used for its polymerization. This paper also describes how we used the new gel-electrolyte as the electrolyte in Li ion polymer batteries.

2. Experiments

2.1 Preparation of gel-electrolyte

Cyanoethylpullulan (CRS, Shin-etsu Chemical), cyanoethylcellulose (Polysciences), acethylcellulose (Kanto Chemicals), and carboxymethylcellulose (Wako Pure Chemicals) were dried at 100°C in a vacuum and examined for use as the matrix polymers of gel-electrolytes. An ethylenecarbonate-diethlycarbonate (EC-DEC) mixture containing 1.0 mol/dm^3 $LiBF_4$ was used as a liquid electrolyte. Diacrylated-polyethylenoxide (DA-PEO, Mw = 400, Shinnakamura Chemicals) was used as a gelation reagent and dried with molecular sieves. Gel-electrolytes were prepared by UV or thermal polymerization.5) Benzoyl peroxide (BPO) and riboflavin (B2), 2,2'-azobis-isobutyronitlile (AIBN) were used as a photo initiator and thermal polymerization initiator, respectively. Gel-electrolytes were prepared as follows: one of the polysaccharide polymers and the DA-PEO monomer were dissolved together in an EC-DEC solution at several wt%. Then, initiator was added to the mixture at the rate of 0.1 wt% of the amount of DA-PEO. The mixture was cast onto glass cells (ø 12 mm, 1.2 mm thick) and either heated at 90°C for 5 minutes or irradiated with UV light for 2 minutes at an energy density of 10 mJ/cm^2. The UV light was obtained from a high-pressure Hg lamp.

2.2 Mechanical strength measurement

The mechanical strength was determined from the yield stress of compressed gel-electrolytes. The compressing stress-strain measurement system that was used is shown in **Figure 1**. A linear actuator was used to compress the gel-electrolytes with a graphite plate (ø 5 mm), and a pressure sensor (Aiko Engineering, Model-9550, 50 kgf/cm^2 maximum range, 0.01 kgf resolution) was used to measure the compressing stress. A displacement sensor (KEYENCE, LB-1000/LB-040, 2 µm maximum resolution) was used for the strain measurements.

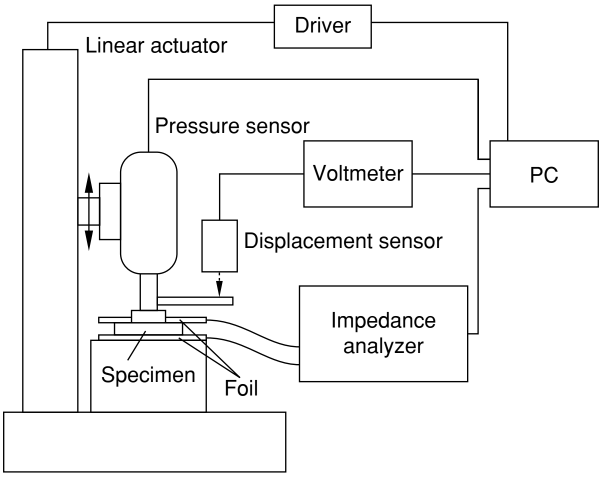


Figure 1
Measurement system.

2.3 Conductivity measurement

The conductivities of the gel-electrolytes were determined from complex impedance measurements utilizing a potentiostat (Hokuto Denko, HA501G) coupled with a frequency response analyzer (NF Electronic Instruments, S-5720C). Impedance measurements were done using Li/gel-electrolyte/Li sandwich cells (ø 1.2 mm, 1.1 mm thick) over the frequency range of 0.1 Hz to 10 kHz.6),7)

2.4 Cyclic voltammetry

Cyclic voltammetry was done over the potential range from 0 to 3.6 V vs. Li/Li$^+$ at a scan rate of 50 mV/s. An Ni electrode (1 cm^2) was used as the working electrode. Li foils were used as a counter electrode and a reference electrode. All the electrochemical experiments were run in an Ar atmosphere in a glove box at ambient temperature.

2.5 Battery fabrication

The gel-electrolytes that provided the highest ionic conductivity were selected. $LiCoO_2$ was used as a cathode active material. The cathode mixture was prepared by mixing $LiCoO_2$, acethylene black, and poly(vinylidene fluoride) (PVdF) binder in N-methyl-2-Pyroridone until a uniform slurry was obtained. Graphite was used as an anode active material. The anode mixture was prepared with graphite and PVdF binder in N-methyl-2-Pyroridone. These mixtures were spread onto the current collector and dried at 120°C in a vacuum. Cathode and anode current collectors were used with Al and Cu, respectively. The cathode seat, gel-electrolyte, and an anode seat were stacked together and sealed with aluminum laminate films.

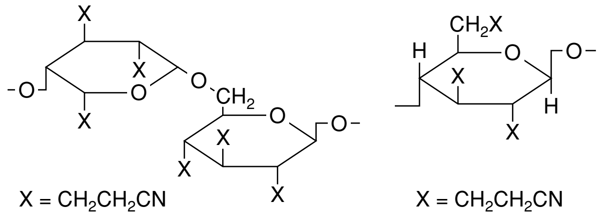
3. Results and discussion

3.1 Gelation properties

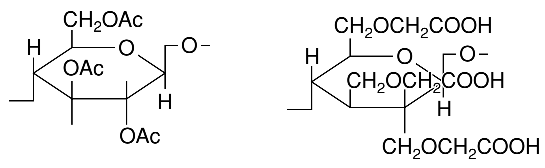
We studied the solubility of polysachharide polymers into EC-DEC solvents and their gelation by UV polymerization; the results are shown in **Table 1**. The structures of these polymers are shown in **Figure 2**. Cyanoethylpullulan has a solubility of up to 15 wt%. The solubility of cyanoethylcellulose and acethylcellulose is less than 5 wt%. Carboxymethylcellulose hardly dissolves into EC-DEC. We found that the solubility of these polyscahharides is affected not only by the high dielectric constants of their side chains, but also by their polymer chain structures. When the DA-PEO concentration is higher than 6 wt%, gel polymers based on cyanoethylpullulan were obtained. On the other hand, no gel-electrolytes based on cyanoethylcellulose or acethylcellulose were obtained whenever any DA-PEO was added. These results suggest that cyanoethylpullulan is an excellent gel-electrolyte because of the rigidity of its polymer chains and the affinity between EC-DEC solvents and cycanoethyl groups, which have high dielectric constants. We therefore decided to use cyanoethylpullulan as a matrix polymer and look for a suitable polymerization method.

Table 1
Gelation properties.

Sample	Solubility	Gelation properties
Cyanoethylpullan	< 15 wt%	Excellent
Cyanoethylcellulose	< 5 wt%	None
Acethylcellulose	< 5 wt%	None
Carboxymethylcellulose	< 1 wt%	None



(a) Cyanoethylpullulan (b) Cyanoethylcellulose



(c) Acethylcellulose (d) Carboxymethylcellulose

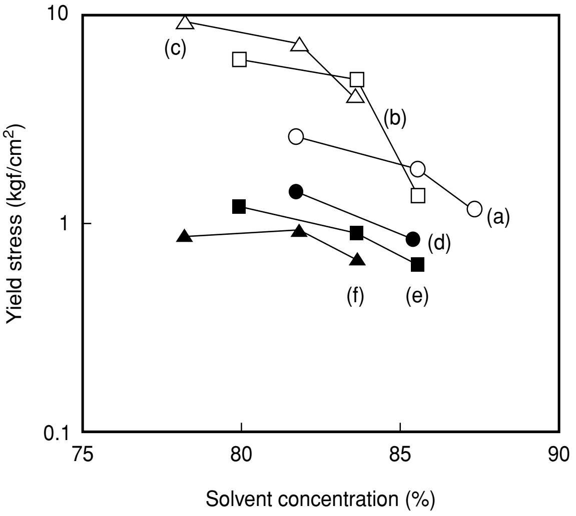
Figure 2
Polymer structures of polysachharide.

3.2 Gelation method

To obtain gel-electrolytes having both a high ionic conductivity and good mechanical strength, we examined UV and thermal polymerization methods.

3.2.1 Mechanical strength

We measured the compressed stress-strain curves of gel-electrolytes prepared by UV and thermal polymerization. **Figure 3** shows the yield stress as a function of the EC-DEC solvent concentration in the gel-electrolytes. The figure shows that the thermally polymerized samples were mostly stronger than the UV-polymerized samples and had a wider range of strengths. The figure also shows a large dependence of strength on the polymer content and therefore a large



(a), (b), and (c) were prepared with thermal polymerization.
(d), (e), and (f) were prepared with UV polymerization.
(a) and (d): CRS6%, (b) and (e): CRS8%, (c) and (f): CRS10%

Figure 3
Dependence of yield stress on solvent concentration.

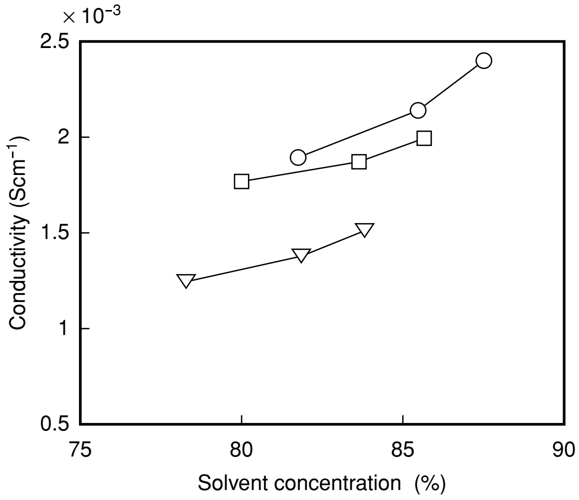
dependence on the cyanoethylpullulan content. The difference in the strengths of the two sets of samples derives from the homogeneity of gel-electrolytes. When precursor solutions of gel-electrolytes were irradiated with UV light, the gelation rate at the top of the precursor solution was different from that at the bottom because of differences in UV irradiation intensity. Therefore, gel-electrolytes prepared by UV light are heterogeneous and crack easily. On the other hand, we found that gel-electrolytes prepared using thermal polymerization were homogeneous and accept as much as 87 wt% of solvent in their gel matrixes. In the vacuum process of battery manufacturing, a gel-electrolyte must have a mechanical strength of more than 1 kgf/cm^2. To obtain this level of strength when the UV polymerization method is used, the solvent concentration must be below 84 wt%.

3.2.2 Ionic conductivity

Figures 4 and **5** show the ionic conductivities of gel-electrolytes at various solvent concentrations. When the solvent concentration was below 84 wt%, the maximum ionic conductivity among the gel-electrolytes was 1.8×10^{-3} S/cm. For thermal polymerization, since the gel-electrolyte showed good mechanical strength even though the solvent concentration was higher, we were able to obtain an excellent gel-electrolyte at a solvent concentration of 87% that showed both a high ionic conductivity of up to 2.4×10^{-3} S/cm and good mechanical strength. These gel properties came from the gel-electrolyte's excellent homogeneity, which enables it to contain a large amount of solvent but still have a satisfactory mechanical strength.

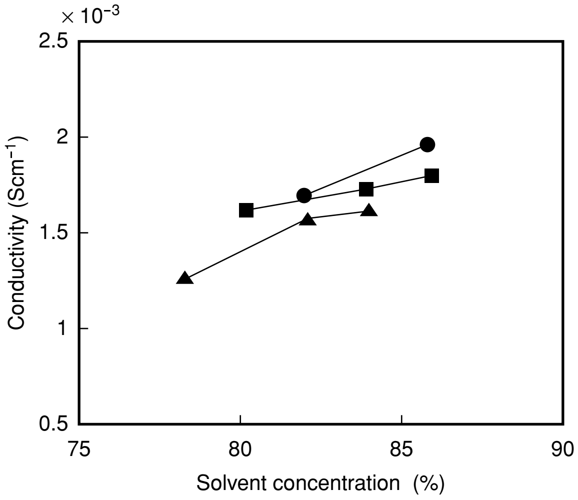
3.3 Cyclic voltammetry

Gel-electrolytes for battery applications must have an electrochemical stability within the potential range from 0 to 3.6 V vs. Li/Li$^+$. The cyclic voltammograms of the EC-DEC solvent, gel precursor solution, and gel-electrolyte are shown in **Figures 6** to **8**, respectively. Figure 6 shows that EC-DEC has reversible peaks. Although the reduction current of EC-DEC increased in Figures 7 and 8, no new peaks were observed. Therefore, we concluded that a gel-electrolyte with cyanoethylpullulan was electrochemically stable



○: CRS6%, □: CRS8%, △: CRS10%.

Figure 4
Dependence of gel conductivity on solvent concentration in thermally polymerized compositions.



●: CRS6%, ■: CRS8%, ▲: CRS10%.

Figure 5
Dependence of gel conductivity on solvent concentration in UV polymerized compositions.

for Li polymer battery applications.

3.4 Battery fabrication

We fabricated several Li ion polymer battery cells using the thermally polymerized gel-electrolyte composition that showed the highest conductivity and also a good mechanical strength in the experiments. The charge/discharge curve and the current density dependence of the capacity of these cells are shown in **Figures 9** and **10**, respectively. The charge/discharge efficiency was almost 100%, and an 80% discharge capacity was obtained at a discharge current of 2 mA/cm^2. The battery cells operated stably and gave good performance, even at a high discharge rate. These results were achieved because the ionic conductivity was high and therefore the voltage drop was low. These results show that a gel-electrolyte with cyanoethylpullulan using thermal polymerization is suitable for use as the electrolyte in Li ion polymer batteries.[8),9)]

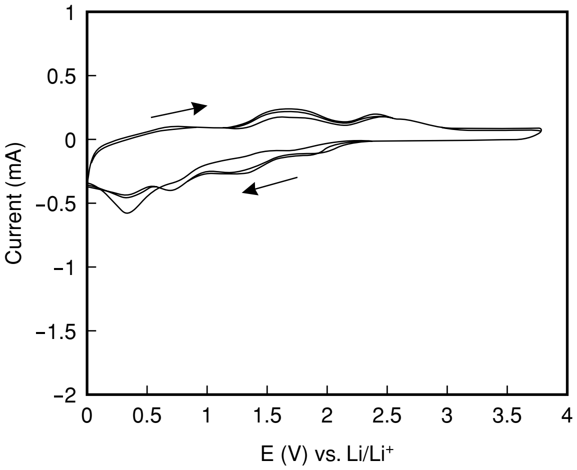


Figure 6
Cyclic voltammogram of EC-DEC/LiBF$_4$.

4. Conclusion

This paper described a new polysaccharide-based gel-electrolyte that is prepared by thermal polymerization with cyanoethylpullulan. The new gel-electrolyte shows an enhanced ionic conductivity of up to 2.4×10^{-3} S/cm and improved mechanical strength compared to optically polymerized gel-electrolytes. The good mechanical strength is due to the rigidity of the cyanoethylpullulan polymer chain and the use of thermal polymerization to achieve homogeneity in the gel-electrolyte. The high ionic conductivity is due to the large solvent concentration in the gel matrix. We fabricated Li ion polymer battery cells using our newly developed gel-electrolyte. These batteries showed a high charge/discharge efficiency and a high capacity at the high discharge rate of 2 mA/cm^2. Polysaccharide-based gel-electrolytes

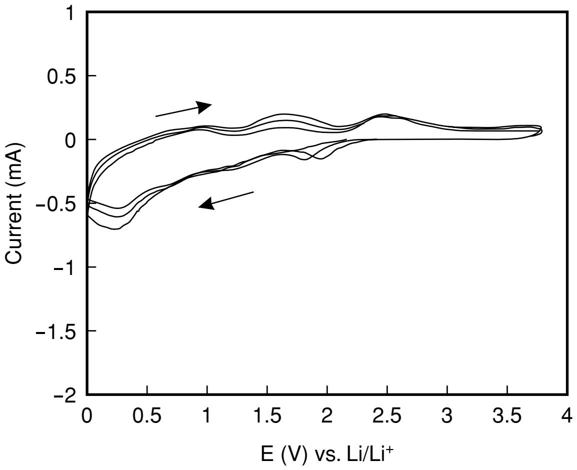


Figure 7
Cyclic voltammogram of gel precusor solution.

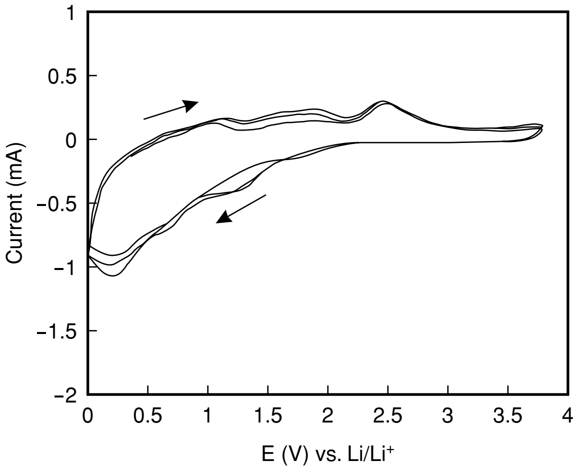
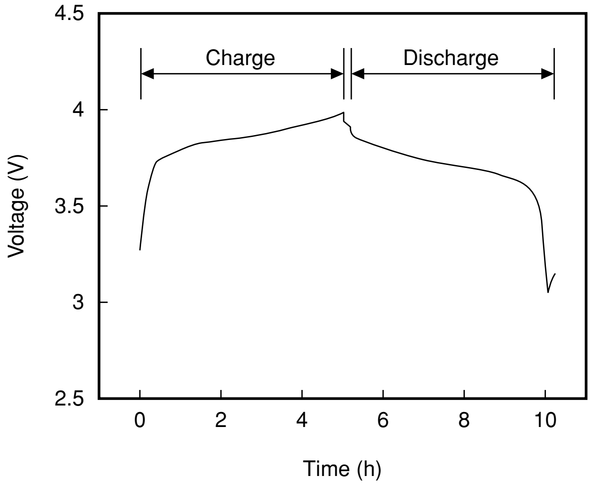


Figure 8
Cyclic voltammogram of gel-electrolyte.



Current density: 0.4 mA/cm^2

Figure 9
Charge/discharge curve of polymer battery.

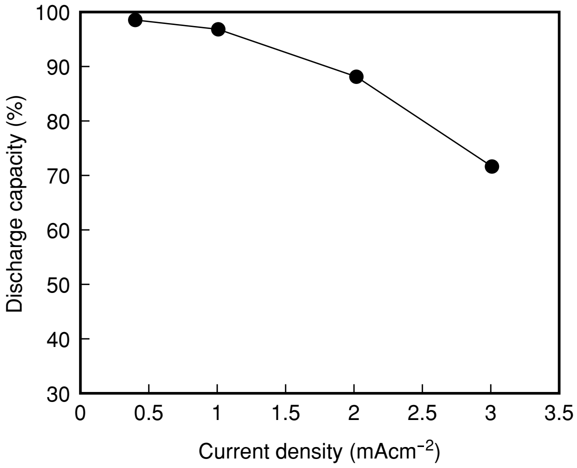


Figure 10
Dependence of discharge capacity on current density.

will be widely used in high-capacity energy devices in the future. The electrical and mechanical advantages of batteries containing these new electrolytes will enable many new technology applications.

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