A team at Hosei University in Japan has tried to fabricate a prototype solid-state battery with a new concept where only the electrolyte solution is gelatinized, utilizing existing manufacturing know-how and equipment. **Shouji Usuda,** a senior member of IEEE and professor at the university reports on the process. He was assisted by **Shunji Hasuo** and **Moh Moh Win Shwe.**

Development of new solid-state battery with gelatinized electrolyte solution containing lithium salt

A lithium-ion battery consists of positive and negative electrode sheets and an organic electrolyte solution. The positive electrode uses $LiCoO_2$ as the active material and the negative electrode uses graphite as the active material.

The electrolyte solution is a mixed organic liquid of EC (ethylene carbonate) and DEC (diethyl carbonate) in a volume ratio of 1:1 or 3:7, with one mole of electrolyte as LiTFSI (lithium bis (trifluoromethane) sulfonimide), LiFSI (lithium bis (fluorosulfonyl) imide), $LiPF_6$ (lithium hexafluorophosphate), etc. dissolved in an organic liquid.

These lithium salts with excellent solution (dissociability) and ionic conductivity are used as the electrolyte. It is known that 1 mol/liter (1 mol/dm³) is the concentration of electrolyte salt at which the ionic conductivity of the electrolyte solution reaches its maximum.

As typical organic electrolyte solutions that have been used in practical applications, 1 mol LiTFSI in EC/DEC (1:1 vol%), 1 mol $LiPF_6$ in EC/DEC (1:1 vol%) and 1 mol $LiPF_6$ in EC/DEC (3:7 vol%), etc. are used in lithium-ion batteries. EC is a high dielectric constant solvent with high dissociability and high lithium ion (Li+) production, while DEC is used as a low viscosity solvent. In particular, EC/DEC (3:7vol%) is designed to increase the mixing ratio of DEC to reduce the viscosity and improve the ionic conductivity of the entire mixed solution.

Considering the dielectric constant of the electrolyte solution, as the viscosity of the solution decreases, the viscous resistance to the migration of ions in the solution also decreases.

One of the key issues in lithium-ion batteries is the control of electrolyte solution leakage. Most of the leakage is caused by misuse of the battery, such as reverse loading, short-circuit, overcharge or over-discharge. There is a need for a battery structure that prevents leakage due to such misuse.

Currently, sulfide solid-state batteries and oxide solid-state batteries are being developed as all-solid-state batteries for the purpose of leakage control.

The former has higher ionic conductivity than the current electrolyte, but requires pressurized molding technology at room temperature in inert gas in the manufacturing process, while the latter has the same ionic conductivity as the current electrolyte solution, but requires sintering technology at high temperature in air.

The latter requires sintering technology at high temperature in the air while maintaining the same level of ionic conductivity as the current electrolyte solution. Both of these require significant development costs and a long development span.

The authors attempted to fabricate a prototype solid-state battery with a new concept in which only the electrolyte solution is gelatinized, utilizing the manufacturing know-how, electrode materials, and equipment that have been cultivated in the research process of lithium-ion batteries.

If activated ions are contained in the gelatinized medium made with polymer gel, which has lost its fluidity, the battery can be configured as a battery cell without worrying about leakage from the cell, which contributes to improved safety.

Gelation test of organic electrolyte solution

The gelation of the organic electrolyte solution requires a gel electrolyte polymer (hereafter referred to as GEP), which has high solubility of Li salt and can be cross-linked by heating, and a radical initiator as a cross-linking accelerator.

The GEP used in this study can be dissolved in many organic solvents and has relatively high heat resistance

Radical initiator	One hour half-life temperature (˚C)	10 hour half-life temperature (˚C)	Curing condition	
			Temperature (˚C)	Time (hour)
Benzoyl peroxide (BPA)	92	73	80	8~12
Nyper BMT-K40[*1]	92	73	80	8~12
Perkadox 16[*2]	64	48	60	1
			80	0.5

[*1] http://www.nof.co.jp   [*2] http://www.nouryon.com

Table1: Half-life of radical initiators and curing conditions

(thermal decomposition temperature is 200°C to 250°C in air). In addition, the water content can be reduced to the 1000 ppm level by vacuum drying at 40°C for 12 hours.

There are several variations of radical initiators depending on their half-life temperature (Table 1). Depending on the half-life temperature of the radical initiator, the curing conditions for gelation will be different. By selecting the curing conditions (temperature and time) in Table 1, sufficient radicals are supplied to the polymer from the radical initiator, and gelation of the electrolyte solution can be expected. In this study, Perkadox 16 was selected as the radical initiator, and the curing conditions were set at a temperature of 60°C and a curing time of one hour.

The electrolyte solution prepared for the gelation test is 1 mol LiTFSI in PC (propylene carbonate). The mixing ratio of this electrolyte solution, GEP, and

Figure 1: Gelation of electrolyte solution (1 mol LiTFSI in PC)

PUTTING IT ALL TOGETHER: CREATION OF A GELLED SOLID STATE BATTERY

Utilizing the knowledge and know-how gained through experience in the production of existing lithium-ion batteries, we attempted to fabricate a prototype of a new concept solid-state battery in which only the electrolyte is gelatinized. The results of this research are summarized as follows.

- Using the gel electrolyte polymer (GEP) specially provided by Japanese chemical manufacturer in Japan and the radical initiator obtained through our own research, the mixing ratio and crosslinking conditions of these gelation agents were studied by trial and error to obtain the optimum mixing conditions for the gelation of the electrolyte.

- As a gelation test of the electrolyte solution, containing 1 mole of electrolytes LiTFSI and LiFSI dissolved in PC (propylene carbonate) was prepared and gelatinized using the gelation mentioned above. As a result of measuring the electrical conductivity before and after gelation, no significant difference in conductivity was observed.

- Gelation of two typical electrolyte solutions used in lithium-ion batteries, 1 mol LiPF6 in EC/DEC (1:1 vol%) and 1 mol LiPF6 in EC/DEC (3:7 vol%), was achieved. The conductivity before and after gelation decreased by about 10%, but no significant difference was observed. It is believed that this is within the range of acceptable conductivity. As a result of measuring the kinematic viscosity of the gelation electrolyte solution, it was confirmed that the viscosity increased significantly when the GEP was dissolved in the electrolyte. Therefore, in consideration of the penetration of the gelation electrolyte solution into the positive and negative electrode materials at the time of injection of the solution, gelation was started in a constant temperature drying equipment after standing for about half a day.

- The lithium-ion battery with a gelation electrolyte solution was called a "gelled solid-state battery". The charge-discharge evaluation of the gelled solid-state battery was carried out. In the charge characteristics, there was a characteristic difference in the current injection over time, which was thought to be due to the difference in bulk resistance between the gelled battery and the non-gelled battery. The battery capacity (mAh) of the gelled solid-state battery estimated from the discharge characteristics was reduced by about half compared to the non-gelled case in both the mixed solution EC/DEC (1:1 vol%) and EC/DEC (3:7 vol%). Specifically, the decrease in battery capacity in the case of EC/DEC (3:7vol%) was from about 280mA to 150mAh, and in the case of EC/DEC (1:1vol%), the decrease was from about 160mAh to 75mAh.

- The process of gas generation in the gelled solid-state battery was observed by using the transparent storage case that was formed. It was confirmed that the amount of gas generation was highest within two to three hours after the start of initial charging.

- Based on the research results obtained so far, the gelation experiment will be continued to investigate the optimal electrolyte solution for gelation by selecting variations in the combination of the electrolyte solutions and mixing ratio with gelation agents. In addition, we would like to investigate the battery shape and the possibility of implementation of small to large-capacity gelled solid-state batteries in electric motorcycles, electric vehicles, and power coordination systems.

(a) Combination ratio

Electrolytic solution	Propylene carbonate (PC)	20g
Electrolyte	LiTFSI	6g
Polymer	Polymers for gel electrolyte	1.355g
Radical initiator	Perkadox 16	0.136g

(b) Calculation example of mixing ratio of PC and LiTFSI

	PC		LiTFSI		
A	1.204 Specific gravity (g/mL)		1.334 Specific gravity (g/mL)		P
B=1000-P	785 mL		287 g/mol		Q
C=A*B	945 g		215 mL/mol		R=Q/P
		LiTFSI:PC=	287	945	
		(Weight ratio)	6	20	

Table 2: Gelation mixing ratio of electrolyte solution PC

radical initiator is shown in Table 2.

The preparation procedure for gelation of electrolyte solution is shown below.

Step 1: Using a precision gravimeter, 20g of electrolyte solution is weighed into a beaker (the amount of electrolyte solution to be weighed is an example).

Step 2: 6g (1 mole) of electrolyte LiTFSI is weighed into 20 g of electrolyte solution, the solution is stirred with a stirrer until LiTFSI is completely dissolved.

Step 3: 1.355g (5%) of GEP is weighed into the PC solution (26 g) in which LiTFSI is dissolved, and the solution is stirred with a stirrer until the GEP is fully dissolved.

Step 4: To the above solution, 0.136g of the radical initiator Perkadox 16 (about 1/10 of GEP) is weighed and thoroughly stirred in a stirrer.

Step 5: The above solution is placed in a constant temperature drying equipment set at 60°C for 1 hour.

Steps 1 through 4 were performed in a glove box purged with argon gas. An example of successful gelation of electrolyte solution 1 mol LiTFSI in PC is shown in Figure 1.

The conductivity of the gel solution was measured before gelation (Table 3). For comparison, the conductivity of the gel solution with electrolyte LiFSI was also measured. The conductivity meter used for the measurement was an EC meter PAL-EC (conductivity 0.00-19.9 mS/cm, resolution 0.01S/cm, measurement accuracy ±0.04 mS/cm) manufactured by ATAGO, a Japanese specialized manufacturer. From the conductivity value of the gel solution, it is presumed that sufficient ionic conductivity is maintained even with the addition of gelation agents (GEP and radical initiator) to the electrolyte solution.

Gelation of electrolyte solution for lithium-ion battery

Gelation was attempted for two electrolytes, 1 mol $LiPF_6$ in EC/DEC (1:1 vol%) and 1 mol $LiPF_6$ in EC/DEC (3:7 vol%), which were used in the assembly of lithium-ion battery cells that have been conducted in our laboratory.

The mixing ratios of the gelation agents (GEP and radical initiator) for gelation of the two electrolytes are shown in Table 4.

The dissolution amount of electrolyte $LiPF_6$ is 1 mole for both electrolyte solutions. The procedure for making the electrolyte solution for gelation is the same as in the case of the electrolyte solution PC gelation test

The gelation of the electrolyte solution of 1 mol $LiPF_6$ in EC/DEC (1:1 vol%) is shown in Figure 2, and the gelation of the electrolyte solution of 1 mol $LiPF_6$ in EC/DEC (3:7 vol%) was confirmed by the same gelation procedure.

Table 5 shows an example of the measurement of conductivity of the two mixed solutions, and Table 6 shows an example of the measurement of kinematic viscosity measured with the Cannon-Fenske viscometer. As a comparison, an example of viscosity measurement of PC solution with dissolved LiFSI, which was tested for gelation, is shown.

There is no significant difference in the conductivity of the electrolyte solution before and after gelation (non-gelation electrolyte solution, which is the electrolyte without dissolving the gelation agents, and the gelation electrolyte solution before gelatinized).

On the other hand, for the kinematic viscosity of the gelation solution, it can be confirmed that the viscosity of the gelation electrolyte solution increases significantly when GEP is dissolved in

(a) The case of LiTFSI

Item	Contents	Conductivity (mS/cm)	Rate of decline (%)	Temperature (°C)
Electrolytic solution	PC	0	-	13.0
Electrolyte	LiTFSI dissolved	4.0	-	14.4
Gelatinized solution	Perkadox 16 injected	3.8	5.0	16.8

(b) The case of LiFSI

Item	Contents	Conductivity (mS/cm)	Rate of decline (%)	Temperature (°C)
Electrolytic solution	PC	0	-	17.0
Electrolyte	LiFSI dissolved	5.7	-	17.9
Gelatinized solution	Perkadox 16 injected	5.5	3.5	18.9

Table 3: Measurement of conductivity of gel solution

Electrolyte solution	EC/DEC (1:1vol%) or EC/DEC 3:7vol%)	20g
Electrolyte	$LiPF_6$	1 mol
Polymer	Polymers for gel electrolyte	1.052g
Radical initiator	Perkadox 16	0.105g

Table 4: Gelation mixing ratio of EC/DEC (1:1 vol%) or (3:7 vol%) dissolved with 1 mole $LiPF_6$

Figure 2: Gelation of electrolyte 1 mol $LiPF_6$ in EC/DEC (1:1 vol%)

the original electrolyte, which is the non-gelation electrolyte solution. The viscosity of the gelation electrolyte solution is considered to affect the penetration of the gelation electrolyte solution into the positive and negative electrode materials when the gelation solution is injected during the process of assembling the battery cell. The mobility of free ions during charging and discharging in the electrolyte solution, which is a normal non-gelation electrolyte solution, is closely related to the viscosity of the electrolyte solution.

Fabrication and charge/ discharge evaluation of cells with gel electrolyte

After assembling the battery cell using the electrode materials of the cobalt-based lithium-ion battery, the electrode body fabricated in the winding process, and the aluminum laminate pouch cell, we attempted to gelatinize the electrolyte solution using the gelation procedure with gelation agents (GEP and radical initiator) as explained above.

We call this cell battery the "gelled solid-state battery". The positive and negative electrode sheets and separators used in the fabrication of the electrode body are shown in Table 6.

The gelation electrolyte solution prepared according to the formula in Table 4 is injected from the bottom of the pouch cell. The injection volume is measured and is roughly 10 milliliters. After the gelation electrolyte solution was injected, the inlet is sealed with a thermos-compression jig. Then, the sealed pouch cell is left in the air for about half a day to accelerate the penetration of the gelation electrolyte solution into the electrode sheet.

After the sealed pouch cell is subjected to static treatment, the pouch cell filled with the gelation electrolyte solution is set in a constant temperature drying equipment and heated under the default gelation conditions (curing temperature: 60°C, curing time: one hour).

At this time, to visually monitor the gelation of electrolyte solution, the gelation electrolyte solution is divided into a beaker and set in the constant temperature drying equipment at the same time as the pouch cell.

In addition, a gelation experiment using a block heater designed and fabricated so that two types of pouch cells of different sizes could be set was tested in anticipation of the future production of gelled solid-state batteries using a pilot line. When Perkadox 16 was used

as the radical initiator, the electrolyte solution can be gelled in a relatively short time, and the workability of the battery fabrication including gelation by the block heater that can be easily introduced into the flow operation was investigated. In the case of the gelation experiment using the block heater, an open pouch cell was prepared after the gelation electrolyte solution was injected as a gelation monitor.

After the gelation electrolyte solution was injected, the sealed pouch cells were set individually in a constant temperature drying equipment and a block heater, and the gelation process was carried out under the same curing conditions. The gelation of the electrolyte solution can be confirmed even when the block heater is used.

The gelled solid-state battery cells were fabricated in this way for two types of electrolytes (1 mol $LiPF_6$ in EC/DEC (1:1 vol%) and 1 mol $LiPF_6$ in EC/DEC (3:7 vol%)), and charge-discharge evaluations were conducted. For comparison, charge-discharge evaluation was also carried out for a conventional type of battery cell using the original electrolyte (non-gelation electrolyte solution).

The measurement results during

(a) The case of EC/DEC (1:1 vol%)

Item	Contents	Conductivity (mS/cm)	Rate of decline (%)	Temperature (°C)
Electrolytic solution	1M $LiPF_6$ in EC/DEC (1:1 vol%)	5.8	-	16.7
Gelatinized solution	With GEP & Perkadox 16	4.9	15.5	16.8

(b) The case of EC/DEC (3:7 vol%)

Item	Contents	Conductivity (mS/cm)	Rate of decline (%)	Temperature (°C)
Electrolytic solution	1M $LiPF_6$ in EC/DEC (3:7 vol%)	5.8	-	24.7
Gelatinized solution	With GEP & Perkadox 16	4.3	25.9	25.8

Table 5: Measurement of conductivity of gelation electrolyte solution of EC/DEC

(a) The case of 1mol $LiPF_6$ in EC/DEC (1:1 vol%)

Solution	Kinematic viscosity (mm²/s) or (cSt)	Temperature (°C)
Electrolytic solution	3.6	24.0
Gelatinized solution	63.6	23.5

(a) The case of 1mol LiTFSI in PC

Solution	Kinematic viscosity (mm²/s) or (cSt)	Temperature (°C)
Electrolytic solution (PC)	2.3	17.5
Electrolytic solution with LiTFSI	6.5	18.0
Gelatinized solution	158.5	18.0

Table 6: Example of kinematic viscosity measurement of 1 mol $LiPF_6$ in EC/DEC (1:1vol%) and 1 mol LiTFSI in PC as a reference

Material	Active material	Active layer thickness* (μm) (Double sided coating)	Electrode density (g/cm³)	Electrode capacity (mAh/cm²)	Current collector (mm)	Length (mm)	Width (mm)
Positive electrode sheet	Lithium cobaltate	140	190	2.7	Aluminium (16μm)	335	22
Negative electrode sheet	Graphite	130	420	2.7	Copper (9μm)	355	23
Separator	Polyolefin	Microporous: 0.1 μm less				840	26

* Total thickness

Table 7: Battery materials used for winding process

charging and discharging are shown in Fig. 3 and Fig. 4.

The charge characteristics were measured using the CCCV method (set voltage 4.2V, set current 50mA), and the discharge characteristics were measured using the constant current method (set current 100mA, discharge end voltage 2.7V).

In the charge characteristics, the charge current injected into the cell was suppressed in both gelation of solution EC/DEC (1:1 vol%) and EC/DEC (3:7 vol%) compared to non-gelation, and the charge voltage tended to reach the set value (4.2V) apparently earlier.

This can be attributed to the fact that the bulk resistance due to gelation is larger than that of the non-gelation solution. This can also be assumed from the conductivity measurement results in Table 5. A decrease in conductivity of 15% to 30% can be confirmed due to gelation.

In terms of the discharge characteristics, it can be confirmed that the battery capacity of the gelled solid-state battery is about 1/2 lower than that of the non-gelation case for both the solution EC/DEC (1:1 vol%) and EC/DEC (3:7 vol%).

In both cases of non-gelation and gelation, the battery capacity of solution EC/DEC (3:7vol%) is about twice as large as that of EC/DEC (1:1vol%).

During the initial charging of the gelled solid-state battery cell, internal gas generation was observed as in conventional non-gelation battery cells. Therefore, a gas pot was installed in the pouch cell to mitigate the swelling of the entire cell.

After the initial charging, the gas was removed using a jig such as a needle. The gas generation during the initial recharging was observed over time using a transparent storage case formed by a 3D printer.

The amount of gas generation was observed to be the largest within two to three hours after the start of charging, and almost no gas generation was observed after the second or subsequent recharging. ■
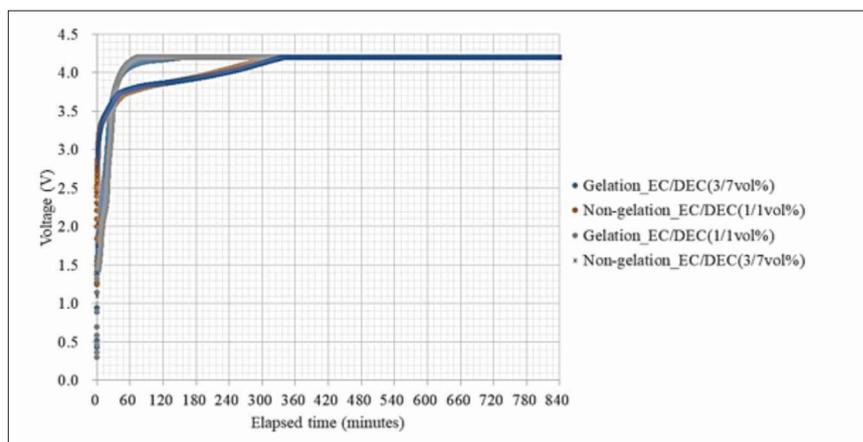
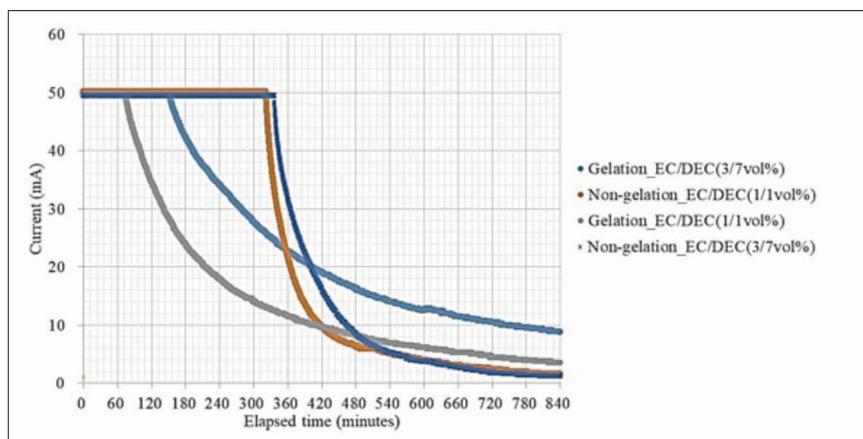**Figure 3-1:** Charge characteristics: (a) Voltage

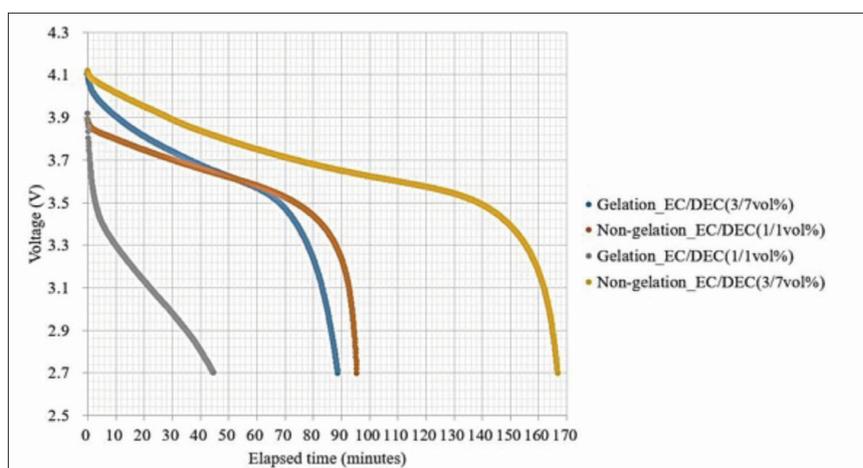**Figure 3-2:** Charge characteristics: (b) Current

Figure 4: Discharge characteristics