

Electro-Active-Paper Actuator Made with LiCl/Cellulose Films: Effect of LiCl Content

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Abstract: The cellulose-based, Electroactive Paper (EAPap) has recently been reported as a smart material with the advantages of lightweight, dry condition, biodegradability, sustainability, large displacement output and low actuation voltage. However, it requires high humidity. This paper introduces an EAPap made with a cellulose solution and lithium chloride (LiCl), which can be actuated in room humidity condition. The fabrication process, performance test and effect of LiCl content of the EAPap actuator are illustrated. The bending displacement of the EAPap actuators was evaluated with actuation voltage, frequency, humidity and LiCl content changes. At a LiCl/cellulose content of 3:10, the displacement output was maximized at a room humidity condition. Even though the displacement output was less than that of a high humidity EAPap actuator, the mechanical power output was not reduced due to the increased resonance frequency, which is promising for developing EAPap actuators that are less sensitive to humidity.

Keywords: cellulose, lithium chloride, *N,N*-dimethylacetamide, electro-active paper (EAPap), bending actuator.

Introduction

Wood pulp remains the most important source in cellulose processing used for papers. Cellulose is considered the most plentiful organic resource on the Earth and is present in various plants as a principal component of cell walls, microorganisms, and animals. It consists of β -D-glucopyranosyl units with a (1-4)- β -D-linkage and forms a linear chain through many inter- and intra-molecular hydrogen bonding. The linearity of cellulose makes it easy for the molecules to produce parallel arrays and cause a high degree of crystallinity.^{1,2} Recently, the potential of cellulose has been emphasized.^{3,4} Cellulose is a versatile framework for supermolecular chemistry, and there is plenty still to discover and celebrate in cellulose. An interesting phenomenon has been discovered in cellulose paper.⁵ When an electric field was applied across the thickness of the paper, it showed a bending deformation. This cellulose paper was termed as electroactive paper (EAPap). This was a discovery of cellulose as a smart material that can be used as sensors and actuators.⁶ In the previous research, the actuation principle was found to be a combination of piezoelectric effect associated with ordered regions of cellulose, and ion migration effect. Cellulose EAPap has merits in terms of lightweight, dryness, biodegradability, abundance, low price, large displacement

output and low actuation voltage. By combining piezoelectricity of cellulose and ionic migration, this oriented EAPap material will enable to develop inexpensive and lightweight bio-mimetic actuators and MEMS devices. Cellulose-based EAPap material is also promising as biosensors since it is biodegradable, biocompatible, sustainable, capable of broad chemical modification and has high mechanical stiffness and strength.

However, the cellulose EAPap actuator requires high humidity to easily allow ion movements in the cellulose. Thus, in this paper, an attempt was made to enhance the performance of EAPap actuators in room humidity condition by customizing the cellulose EAPap. Cellulose EAPap is made by dissolving cellulose, forming a sheet, drying it and coating gold electrodes. In dissolving cellulose, xanthate process (viscous process) has been well known. However, this derivate method results in environmental problems due to the use of carbon disulfide.⁴ As alternate direct processing technologies, it has been suggested that the dissolution and shaping of cellulose could be carried out by *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) or zinc chloride and in aqueous solution with sodium hydroxide (NaOH), or phosphoric acid as a direct solvent.⁴ Among various reported solvents, LiCl/DMAc is advantageous over other solvents due to the following properties: (1) a great level of polymer-solvent interactions and complete dissolution of the polymer, and (2) a negligible reduction of the intrinsic viscosity of the

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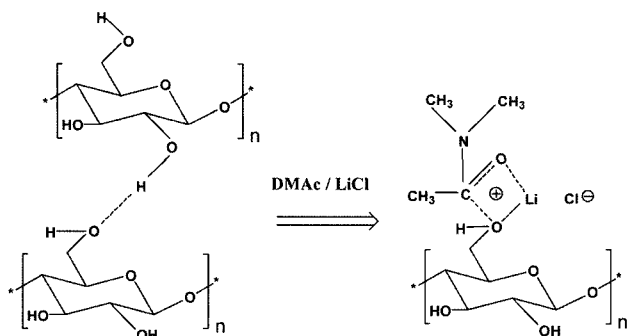


Figure 1. The principle of cellulose resolving in DMAC/LiCl solvent.

polymer solution after a long period of storage.⁷ Dissolution of cellulose in the LiCl/DMAC solvent system is accompanied by interactions as shown in Figure 1. The primary hydroxyl group is expected to be solved better than the secondary hydroxyl groups.⁸ In the present investigation, cellulose/DMAC/LiCl solution was used. Details of the cellulose EAPap fabrication were delineated. The performance of new cellulose EAPap material was tested in terms of bending displacement. The actuation principle was discussed by a Fourier transform infrared spectrometer (FTIR) and nuclear magnetic resonance (NMR).

Experimental

Materials. Cotton cellulose, MVE, DPw 4580, was supplied from Buckeye Technologies Co. (USA). Lithium chloride (LiCl), extra pure, was purchased from Junsei Chemical (Japan). Molecular sieves, 4 A, 4 to 8 mesh, was purchased from Acros organics (New Jersey, USA). *N,N*-Dimethylacetamide (DMAC), anhydrous, 99.8%, was purchased from Sigma-Aldrich (USA). Anhydrous DMAC was carefully dried with molecular sieves for a week before use. Glycerol, Chemical Pure, was purchased from Junsei Chemical Co. (Japan).

Preparing Cellulose/LiCl/DMAC Solution. Cellulose and LiCl were heated under reduced pressure at 110°C for 1 hr. After the LiCl was resolved in the DMAC, the cellulose was mixed with LiCl/DMAC solution according the proportion of cotton cellulose pulp/LiCl/DMAC to 1.5/8.5/90. The mixture was heated at 155°C followed by cooling to 40°C for 2 hrs. After that, Cellulose/LiCl/DMAC solution was obtained.

Preparation of Cellulose Films. The Cellulose/LiCl/DMAC solution (40 g) was cast on the glass plate (10 × 10 mm²) in room temperature and humidity condition for 2 hrs, then immersed into water, resulting in a wet cellulose film. The wet cellulose film was fixed its edges on the glass and washed with flowing tap water for 8 hrs, and then immersed in deionized water for 1 day. After the film was dried in air for 2 hrs, the mixture of lithium chloride, glycerol and water (5 g) was added on the surface of the film. The amount the compounds was listed in Table I. According the molar ratio of lithium chloride and structure unit of cellulose 1:10; 2:10; 3:10; 4:10; 5:10 films were named Li-1; Li-2; Li-3; Li-4; Li-5, respectively. The films were laid in air for 2 days, and then gold electrodes were coated on both sides. For the sake of convenience, the pure cellulose film was named as ‘cellulose,’ while the blend film of cellulose and lithium chloride (without glycerol) as ‘cellulose-LiCl’.

Gold Electrode Coating. Gold electrodes were deposited on both sides of the cellulose paper by using the physical vapor deposition system (SHE-6D-350T, Samhan Vacuum Co. Ltd., Korea). The size of the EAPap sample was 10 × 40 mm². The thickness of the gold electrodes was so thin (0.1 μm) that the gold electrodes do not significantly affect the bending stiffness of the cellulose paper (Figure 2).

Tip Displacement Measurement. To measure the tip displacement of EAPap actuators, a computerized displacement measurement system was made.⁹ An EAPap actuator was supported vertically in air on the room temperature and room humidity condition. Function generator (Agilent 33220A) controlled by computer sent out the excitation ac voltage. The input signal generated from the function generator was applied to the EAPap actuator and it produced a bending deformation. The tip displacement of the EAPap sample

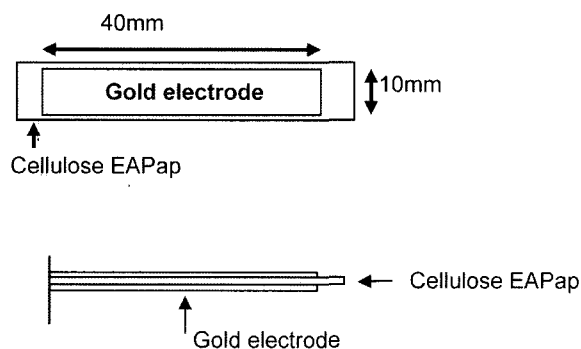


Figure 2. Configuration of cellulose EAPap.

Table I. The Composition of the Blend Cellulose Films

	Li - 1	Li - 2	Li - 3	Li - 4	Li - 5	Cellulose	Cellulose-LiCl
Pure cellulose (g)	0.6	0.6	0.6	0.6	0.6	0.6	0.6
LiCl (g)	0.0161	0.0310	0.0459	0.0601	0.0786	0	0.0786
Glycerol (g)	0.6	0.6	0.6	0.6	0.6	0	0

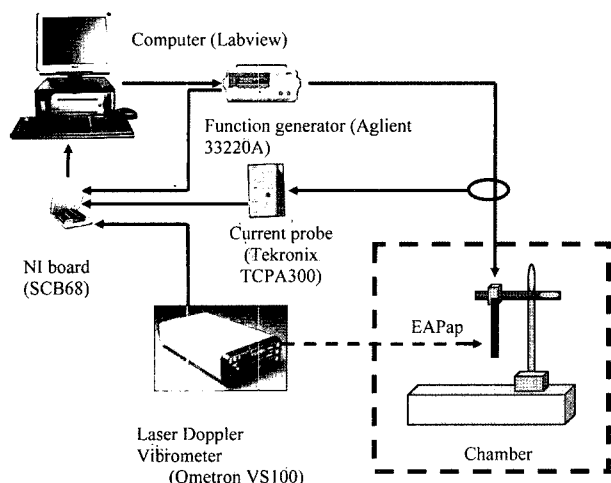


Figure 3. Computerized setup for displacement measurement of EAPap actuator.

was measured by the high precision LDV (Laser Doppler Vibrometer, Ometron VS100) mounted on an optical table and the LDV signal was converted to the displacement through the Labview software. Simultaneously, the current probe (Tektronix TCPA300) measured the input current supplied from the function generator. The measured current signal was also analyzed simultaneously at the computer (Figure 3).

FTIR and NMR. FTIR spectra were obtained using a Perkin-Elmer System 2000 FTIR spectrophotometer. The films were cut into very little particles and characterized by a Fourier transform infrared spectrometer (FTIR) for the evaluation of chemical structures using a KBr pellet. The obtained data were transferred to the PC for the line fitting.

The CP/MAS ^{13}C NMR (nuclear magnetic resonance) measurements were performed at 25°C with a Varian UNITYNOVA 400 spectrometer equipped with a solid-state high-resolution apparatus. The operating frequencies of carbon are 100 MHz, the conventional CP/MAS method was used for high-resolution solid-state ^{13}C measurements. The rotors which contain the cellulose samples about 300 mg spin at ca. 5 kHz, and the 90 pulse, contact time is 2 ms. ^{13}C Chemical shifts were calibrated through the carbonyl carbon resonance of glycine as an external reference at 176.03 ppm and converted to the values from hexamethylbenzene (HMB). The obtained data were transferred to the PC for the line fitting. Nonlinear least-squares methods were engaged for line-fitting with the Lorentz function previously described.

Results and Discussion

Actuation with DC Voltage. At first, the cellulose EAPap actuator was actuated by dc voltage. On the dc voltage (4.5 V), the tip of the sample moved from the vertical position to the cathode (negative electrode). The moving rate was very slow

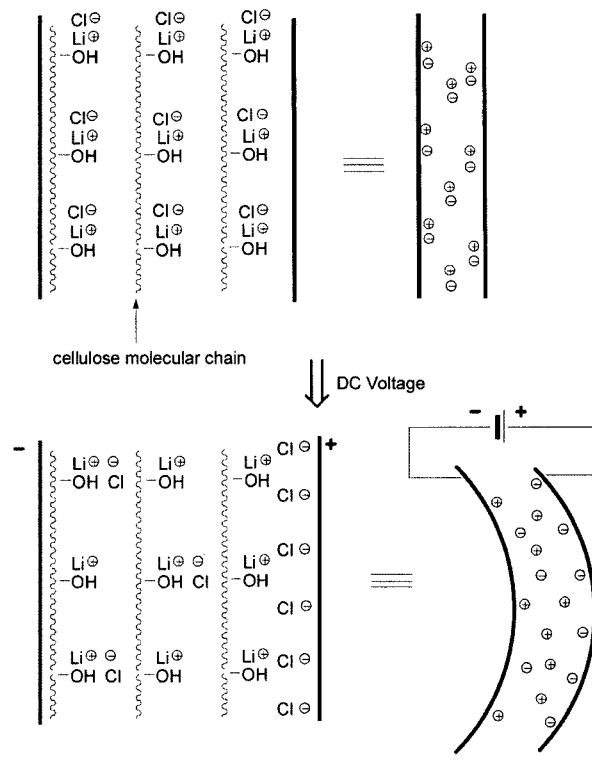


Figure 4. Actuation principle of EAPap actuator under dc voltage.

in the beginning, but with the time increase the moving rate became fast. The actuation principle is shown in Figure 4. Lithium ions are covalently bonded to hydroxyl groups in cellulose molecules, as fixed ions in ion-exchange membranes.¹⁰ On the other hand, the chlorine ions (anion) are counter ions that are conjugated charges to the fixed ions. Chlorine ions can move to positive electrode in the presence of dc voltage. As the chlorine ions assemble at positive electrode, the repelling force between them makes the actuator bend to negative electrode.

To investigate the bonding between lithium ions and hydroxyl groups, FTIR of cellulose and cellulose-LiCl were taken (Figure 5). Free hydroxyl groups, in general, absorb the infrared spectrum in the region of $3650\text{--}3590\text{ cm}^{-1}$.¹¹ Hydrogen bond that exists inter-molecule or intra-molecule shifts the absorbing region to lower wave number and make it broad ($3650\text{--}3200\text{ cm}^{-1}$).¹² Comparing with the spectrum of cellulose, the spectrum of cellulose-LiCl at 3200 cm^{-1} became weak and narrow, which indicates that lithium cations bonded with oxygen atoms of hydroxyl groups in cellulose molecules. Other evidence on this bonding was found from NMR spectra. The NMR spectra of the pure cellulose and cellulose-LiCl are shown in Figure 6. The chemical shifts data are listed in Table II. Comparing with cellulose, the chemical shifts of C1, C4_a, C4_b, and C6 in cellulose-LiCl moved to high, which indicates that the electron cloud density of carbon atom decreased.^{13,14} It was due to the fact that when the lithium

cation was bonded with oxygen atom of hydroxyl group in cellulose molecule, the pair electron of oxygen atom entered into the orbital of lithium. Then, the decrease of the electron

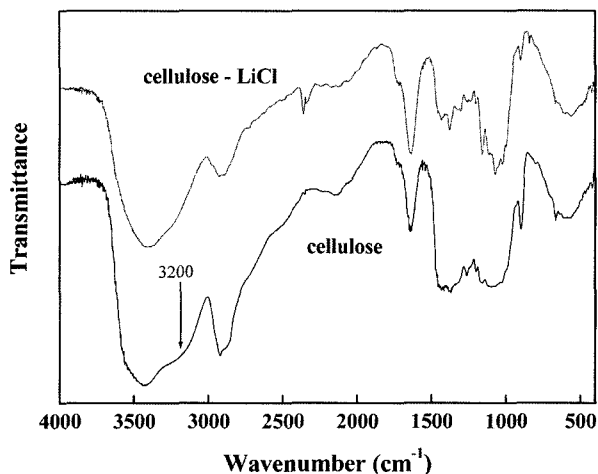


Figure 5. FTIR of cellulose and cellulose-LiCl.

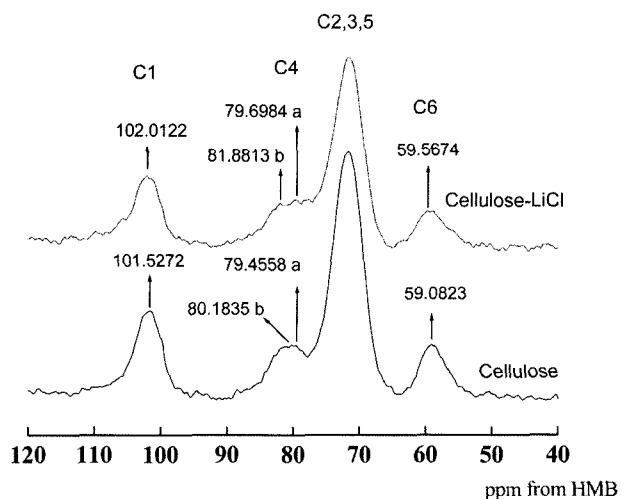


Figure 6. Solid-state ^{13}C NMR spectra of the pure cellulose and cellulose-LiCl.

Table II. ^{13}C Chemical Shift (δ) and Chemical Shift Margin ($\Delta\delta/\text{ppm}$) of the Respective Lines for the ^{13}C NMR Spectra of the Pure Cellulose and Cellulose-LiCl.

Atom	^{13}C Chemical Shifts		
	Cellulose δ/ppm	Cellulose-LiCl δ/ppm	$\Delta\delta/\text{ppm}$
C1	101.5272	102.0122	+ 0.4850
C4 _a	79.4558	79.6984	+ 0.2426
C4 _b	80.1835	81.8813	+ 1.6978
C6	59.0823	59.5674	+ 0.4851

cloud density of oxygen atom resulted in the movement of electron cloud of C-O bond to oxygen atom and the electron cloud density of carbon atom decreased. Thus, the screen of the electron cloud of carbon atom for carbon nucleus decreased and the peaks of ^{13}C chemical shifts removed to high. This result shows a good agreement with the FTIR result.

Effect of Frequency and Voltage. Tip displacements of the actuators were measured with frequency variation. Figure 7 shows the displacements for Li-1 case. Table III represents peak displacement of each sample at the resonance with actuation voltage. From Li-1 to Li-5, all displacements increased as the voltage increased from 1 to 4 V. As the voltage increased, the chlorine anions moved to positive electrode quickly, resulting in the increased repulsive force between chlorine anions on the positive electrode. Consequently, the bending displacement increased. From Li-1 to Li-3 cases, the displacements increased with the amount of LiCl increased, meanwhile the displacements decreased in the cases of Li-3 to Li-5. The displacements of the EAPap actuators depend on not only the amount of LiCl, but also the interaction between lithium cations and hydroxyl groups of cellulose. As the amount of LiCl increases over a certain

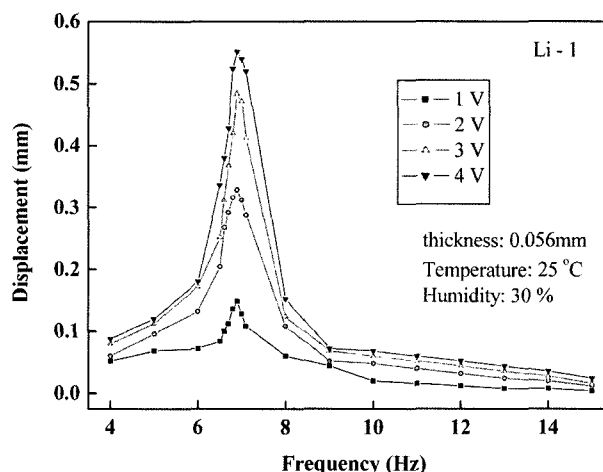


Figure 7. Tip displacement of Li-1 film with frequency variation.

Table III. Compared Maximum Displacements of LiCl/Cellulose Films along with Excited Voltages

Sample	Maximum Displacement [mm]/Resonance Frequency [Hz]			
	1V	2V	3V	4V
Li-1	0.15/6.9	0.33/6.9	0.48/6.9	0.55/6.9
Li-2	0.37/8.5	0.71/8.5	0.91/8.5	1.02/8.5
Li-3	0.74/8.4	1.27/8.4	1.47/8.3	1.64/8.1
Li-4	0.53/9.9	0.9/9.6	1.04/9.5	1.37/9.0
Li-5	0.35/8.6	0.61/8.7	0.74/8.8	0.86/8.5

level, the fixed lithium ions connected to hydroxyl groups of cellulose is saturated, and free lithium ions is getting increased. Once a dc voltage is applied, chlorine counter ions move to positive electrode, while the free lithium ions move to negative electrode, which results in reduced bending displacement. Thus, when the molecular ratio of LiCl and cellulose structure unit is 3:10, the actuator exhibited the maximum bending displacement. Usually, the resonance frequency of the actuator was lowered as the lithium content increased except Li-5 case.

Regarding the actuator performance, EAPap actuators made at this work exhibited the maximum displacement of 1.6 mm at 8 Hz with 4 V. In the previous work, EAPap actuators made with cellophane showed their maximum displacement of 4.2 mm at 4 Hz with 5 V and 90% relative humidity.⁶ The mechanical power output of EAPap actuator is normally proportional to the square of displacement and the cubic of frequency. When these two actuators are compared, although the displacement of this EAPap actuator was reduced by 0.38, the frequency was increased by 2, which states that the mechanical power output of the currently developed actuator was 1.16 times higher than the compared one. Furthermore, the currently developed actuators work at room humidity, which is a big achievement in this work.

Effect of Humidity. Tip displacements of the actuators with humidity variation are shown in Figure 8. As the humidity increased from 30 to 70%, the tip displacements of Li-1, Li-2, and Li-3 cases increased and saturated after the 60% relative humidity level. However, when the lithium content was increased over 4:10 (Li-4 and Li-5 cases), tip displacements showed peak values at 50% relative humidity. The maximum displacement was shown at the Li-3 case when the relative humidity was 60%. This means that increasing the lithium content is not always beneficial to improve the displacement output. When the humidity increases, the water content in the actuator increases and the film becomes

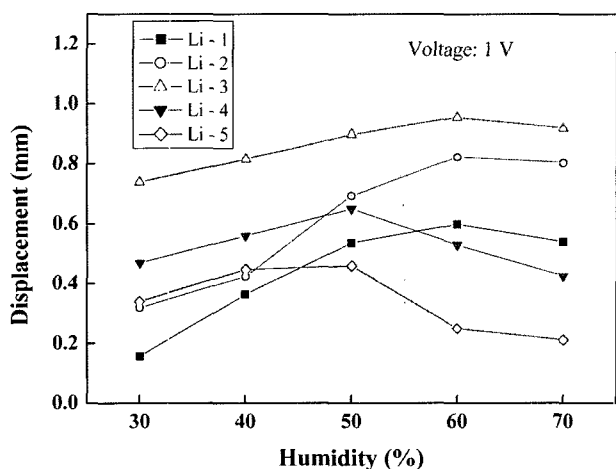


Figure 8. Tip displacement of Li-1 to Li-5 EAPaps with relative humidity levels.

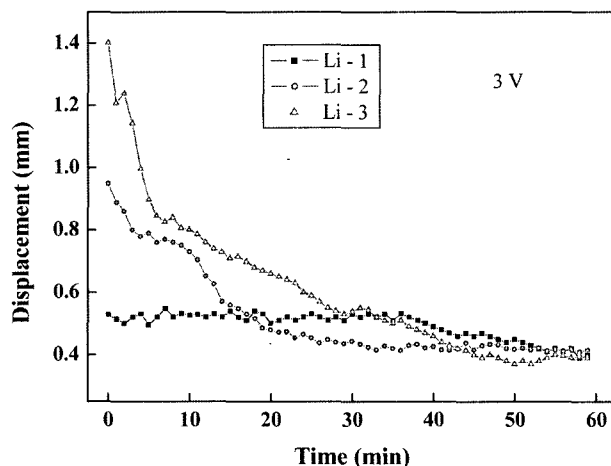


Figure 9. Tip displacement of Li-1, Li-2 and Li-3 EAPaps with time variation (humidity: 30%).

soft. On the other hand, the number of fixed lithium ions decreases and the number of free lithium ions is getting increased. Thus, an optimum lithium content level exists for maximizing the displacement output of the actuator, and Li-3 might be an optimum case.

Effects of Time. Tip displacements of the Li-1, Li-2, and Li-3 on 3 V with time variation are shown in Figure 9. Of course, the high lithium content case (Li-3) showed the maximum displacement output, the displacement decreased very quickly. During the first 8 min, the tip displacement of Li-3 case decreased to the half of initial output, but the decreasing rate became slow after that. Although the initial displacement of Li-1 case was small, the displacement decreasing rate was very slow. Thus, to extend the durability of the EAPap actuator, low voltage or low LiCl content is required. To confirm the suggestion, more investigation on the durability test may be necessary.

Conclusions

Cellulose EAPap actuators were made with cellulose solution and lithium chloride, and their performance was tested. The Cellulose/DMAc/LiCl solution was cast on a glass and immersed water to form the cellulose film, followed by adding glycerol and LiCl aqueous solutions. Different LiCl contents were made in the EAPap samples and its effect was investigated. The actuation test of cellulose EAPap actuators was carried out with frequency, voltage, humidity, and time variations. When the EAPap actuator was activated with ac voltage in a room humidity condition, the tip displacement output increased with voltage increasing. When the LiCl content with respect to the cellulose structure was 3:10, the tip displacement output showed the maximum at 60% relative humidity. As the time increased, the displacement of the EAPap actuators decreased, and the decreasing

rate was decided by the lithium chloride content and voltage. The actuation principle is based upon the chlorine anion migration. Although the displacement output was less than that of a high humidity EAPap actuator, the mechanical power output was not reduced due to the increase of resonance frequency. Thus, the possibility of humidity-less-sensitive EAPap actuator was demonstrated.

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