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# Preparation and characterization of porous cellulose acetate with copper (II) nitrate additives for separator applications

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**Abstract**−We succeeded in generating nanopores in a cellulose acetate (CA) matrix under water pressure using copper nitrate ($Cu(NO_3)_2 \cdot 4H_2O$) as the additive. The nanopores were produced when the polymer matrix was subjected to isostatic water pressure adding copper(II) nitrate into the CA membrane. The polymer chains were weakened by the plasticization effect of copper(II) nitrate present in the CA membrane. We confirmed that the pore properties were readily changed by water pressure as external physical forces with additive content. The water flux of the CA composite (CA/$Cu(NO_3)_2 \cdot 4H_2O$) membrane improved with increasing water pressure and additive content. For the CA membrane without the additive, the water flux was not measured from 1 to 8 bar water pressure. In contrast, the water flow of the polymer film with the additive varied from 95.3 to 205.75 L/m$^2$h, depending on the water pressure and additive content.

Keywords: Cellulose Acetate, Copper (II) Nitrate, Pore, Separator

## INTRODUCTION

The nanoporous polymer membrane finds application in various fields, such as water treatment, gas separation, electrolyte and separator in batteries, and ion selective membranes [1-6]. Currently, microporous polyolefin films have been utilized as commercial separators in batteries due to high mechanical strength, good electrochemical and chemical stability, low cost, and thermal shutdown property [7,8]. Li et al. reported that battery performance could be improved by using tannic acid-coated polypropylene (TA-PP) [9]. The coulombic efficiency of TA-PP was 99.11% after 200 cycles. The high specific-capacity retention in cells with the TA-coated PP separator was observed as 0.5 C to 9 C with 53% retention of the discharge capacity. Furthermore, the interfacial resistance of the TA-PP separator increased from 2.67 Ω in the 1st cycle to 3.78 Ω in the 35th cycle [9]. In lithium cobalt oxide/graphite battery with a separator based on cellulose/polysulfonamide (PSA) composite, high capacity retention was recorded [10]. Furthermore, the resistance of the prepared composite membrane was 200 Ω [10]. Recently, we reported a nanoporous polymer matrix using an ionic liquid and cellulose acetate for application as a separator [11]. The ionic liquid acted as plasticizing agent for polymer chains and supported the free volume increase [12-14]. Considering these properties, our group suggested a method for generating nanopores in a polymer matrix with ionic liquid under water pressure. The cellulose acetate (CA)/1-butyl-3-methylimidazolium tetrafluoroborate (BMIM $BF_4$) composites were used for freestanding film [15]. This CA matrix containing [BMIM]$BF_4$ was exposed to external physical forces such as water-pressure. The water flux of the matrix gradually increased with increasing water pressure. However, the use of ionic liquid reduced the pore volume. To overcome such drawbacks, our group reported that an inorganic complex could be used instead, which solvated better than the ionic liquid [15]. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), an inorganic complex, showed good dissolution in water or acetone, and it could be applied to CA dissolved in an acetone/water (w/w 8 : 2) solution [15]. As a result, both the pore properties such as porosity and size of the CA matrix remarkably increased with uniformly distributed pores [15]. Therefore, we confirmed that a nitrate salt such as nickel(II) nitrate could be used for generating nanopores in a polymer matrix. In this study, we suggest a new method for generating a straight-forward porous CA membrane by utilizing hydrated copper(II) nitrate [($Cu(NO_3)_2 \cdot 4H_2O$)] as an additive for generating various pore size.

## EXPERIMENTAL

CA (10 wt% solution) was prepared in an acetone/water (w/w 8 : 2) mixture. The amount of copper(II) nitrate hydrate ($Cu(NO_3)_2 \cdot 4H_2O$) added to the polymer matrix was determined based on the mole ratio of the Cu ion to the monomeric unit of CA. Then, the solution was cast after stirring as freestanding film on the plate and dried at atmosphere for 2 h. The dried CA matrix with $Cu(NO_3)_2 \cdot 4H_2O$ was exposed to external water- pressures. Water flux in CA matrix was expressed in L/m$^2$h.

Fourier-transform infrared (FTIR) spectra were observed by Varian FTS-3100. Thermogravimetric analysis was performed with Mettler Toledo) at rate of 10 °C/min. The scanning electron microscopy (SEM) was observed with JEOL JSM-5600LV and the pore properties in the CA matrix were measured by a mercury porosimeter (AutoPore IV 9500, Micromeritics Inc.)

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## RESULTS AND DISCUSSION

Fig. 1 shows the pores generated in neat CA polymer matrices dissolved in pure acetone and acetone/water (w/w 8 : 2). When the polymer matrix was dissolved in acetone, no pores were generated (Fig. 1(a)). In contrast, small pores were generated when the polymer matrix was dissolved in the acetone/water cosolvent (Fig. 1(b)). Subsequently, when $Cu(NO_3)_2$ salt was utilized for the CA dissolved in acetone/water, the pore properties, such as porosity and size of the polymer matrix, increased as shown in Fig. 2. When $Cu^{2+}$ and $NO_3^-$ ions were solvated by water molecules, the radius of the solvated aggregates increased. Phase separation between the polymer chains and solvated aggregates initiated the pore formation. Fig. 3 shows the porosity generated in a 1 : 0.20 CA/$Cu(NO_3)_2 \cdot 4H_2O$ matrix treated at a water pressure of 8 bar. The pore size and volume of the polymer matrix increased with water pressure, compared with

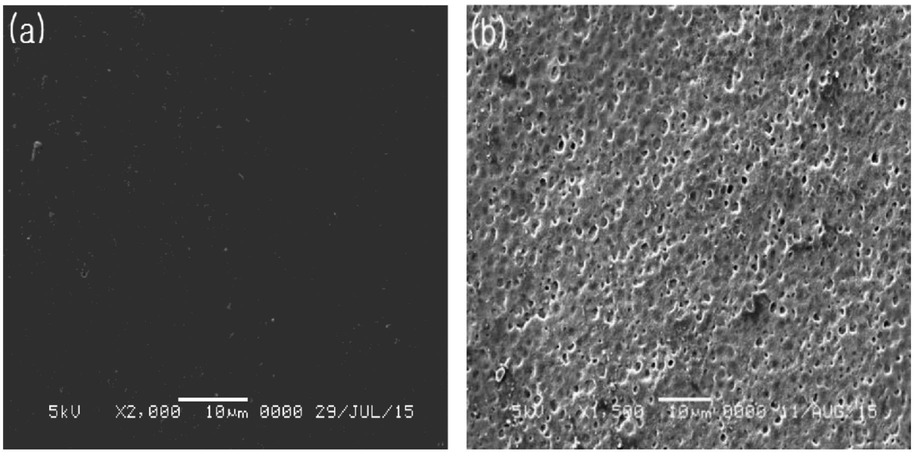
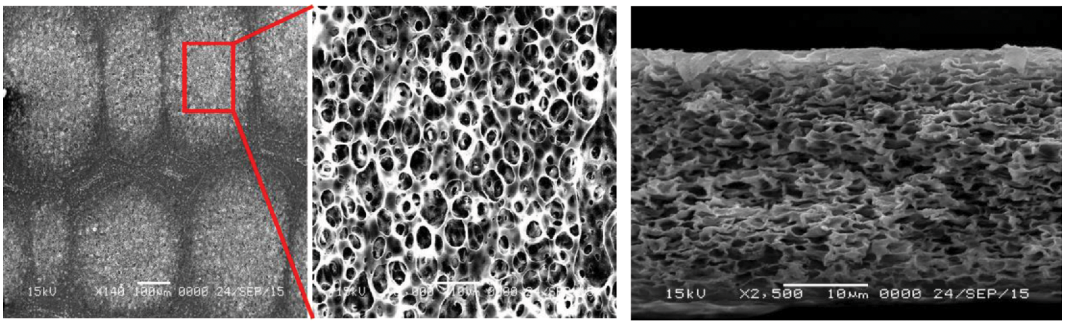
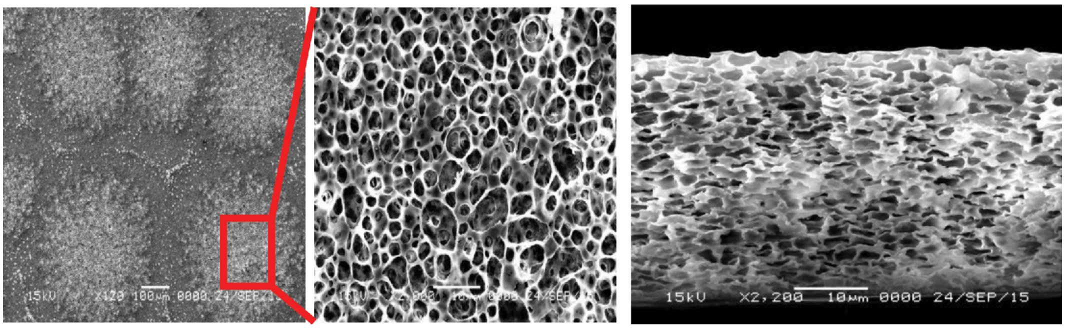


**Fig. 1. SEM images: (a) Neat CA polymer and (b) polymer in acetone/water (w/w 8 : 2).**



(a) (b) (c)

**Fig. 2. SEM: (a) Image of 1 : 0.20 CA/$Cu(NO_3)_2 \cdot 4H_2O$ in acetone/water (w/w 8 : 2) at a water pressure of 0 bar. (b) A magnified view of the square-shaped region marked in (a). (c) Cross-sectional view.**



(a) (b) (c)

**Fig. 3. SEM: (a) Image of pores observed in 1 : 0.2 CA/$Cu(NO_3)_2 \cdot 4H_2O$ in acetone/water (w/w 8 : 2) under a water pressure of 8 bar. (b) A magnified view of the square-shaped portion marked in (a). (c) Cross-sectional view.**

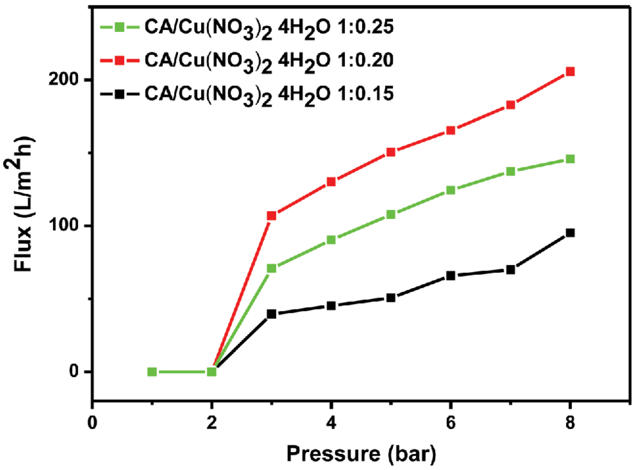


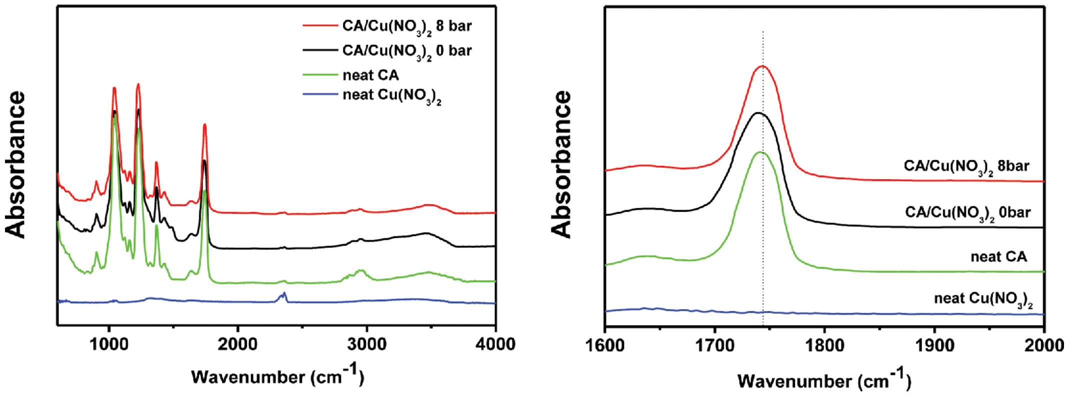
**Fig. 4. Flux measured through neat CA and CA with $Cu(NO_3)_2\cdot 4H_2O$ at various water pressures.**

those without water treatment. A comparison of the cross-sectional views in Fig. 2(c) and 3(c) shows an increase in pore size with water pressure. This indicates that water pressure generated the interconnected pores into the weakened polymer chains through plasticized region by addition of $Cu(NO_3)_2\cdot 4H_2O$.

The water flux for porous CA matrix with various ratios of $Cu(NO_3)_2\cdot 4H_2O$ is shown in Fig. 4. Up to 2 bar pressure, no change is observed in the water flux for different additive concentrations. However, when the pressure increases above 3 bar, increased water flux is observed for all CA/$Cu(NO_3)_2\cdot 4H_2O$. The observed water flux is attributed to the penetration of water through the polymer regions weakened by the solvated $Cu(NO_3)_2\cdot 4H_2O$ aggregates. The water flux through the 1 : 0.15 CA/$Cu(NO_3)_2\cdot 4H_2O$ complex varied from 39.4 to 95.3 L/m$^2$h when the water pressure was 3-8 bar. For the 1 : 0.2 CA/$Cu(NO_3)_2\cdot 4H_2O$ complex, the water flux increased to 205.75 L/m$^2$h at 8 bar water pressure. These results show that the 1 : 0.15 CA/$Cu(NO_3)_2\cdot 4H_2O$ complex has small pore sizes, owing to the small size of the solvated $Cu(NO_3)_2\cdot 4H_2O$ molecules. Additionally, we assumed that the increase in the water flux with the $Cu(NO_3)_2\cdot 4H_2O$ content depended on the number of solvated $Cu(NO_3)_2\cdot 4H_2O$ molecules. A further increase in the $Cu(NO_3)_2\cdot 4H_2O$ content decreased the flux because of the strengthening of interactions between polymer chains by crosslinking but not plasticization. Therefore, a polymer matrix to show the best performance and easily controllable pores was obtained for the 1 : 0.20 CA/$Cu(NO_3)_2\cdot 4H_2O$ composition. Especially, the reason why Cu salts showed the enhanced water flux than Ni salts reported in previous study was that the abundant free $NO_3^-$ ions hydrated by water molecules in $Cu(NO_3)_2$ caused the polymer chains to be more plasticized, resulting in the easy control of pore size for CA.

Fig. 5 shows the FTIR spectra of neat CA, neat $Cu(NO_3)_2\cdot 4H_2O$, and 1 : 0.20 CA/$Cu(NO_3)_2\cdot 4H_2O$ polymer matrix at 0 bar and 8 bar water pressures. The peak observed at 1,743 cm$^{-1}$ for the neat CA polymer matrix corresponds to the carbonyl group of the CA polymer matrix. When $Cu(NO_3)_2\cdot 4H_2O$ was added to the neat CA polymer matrix, the wavenumber decreased, owing to interactions between $Cu^{2+}$ ions and carbonyl group of the CA polymer. Furthermore, a peak is observed at 1,483 cm$^{-1}$ in the 1 : 0.20 CA/$Cu(NO_3)_2\cdot 4H_2O$ polymer matrix at 0 bar water pressure. However, the observed peak disappears from the FTIR spectra of the 1 : 0.20 CA/$Cu(NO_3)_2\cdot 4H_2O$ polymer matrix subjected to 8 bar water pressure. It was expected that when the CA/$Cu(NO_3)_2\cdot 4H_2O$ polymer matrix was subjected to water pressure, a considerable amount of $Cu(NO_3)_2\cdot 4H_2O$ was removed from the matrix and the peak at 1,483 cm$^{-1}$ disappeared.

TGA was carried out to confirm the remaining salts by observing the change of thermal properties for CA. Fig. 6 shows that both neat CA and CA incorporated with $Cu(NO_3)_2\cdot 4H_2O$ at 8 bar pressure became mostly decomposed at around 300 °C. In contrast, about 85 wt% of CA/$Cu(NO_3)_2\cdot 4H_2O$ at 0 bar decomposed between 200 and 360 °C and 15 wt% decomposes between 350 and 550 °C. The boiling point of $Cu(NO_3)_2\cdot 4H_2O$ was 170 °C. It is estimated that the polymer chains were loosened by the solvated $Cu(NO_3)_2\cdot 4H_2O$ in the polymer chains. Thus, the loss of about 85 wt% of the CA/$Cu(NO_3)_2\cdot 4H_2O$ polymer matrix at 0 bar was observed by the degradation of both the solvated $Cu(NO_3)_2\cdot 4H_2O$ and loosened polymer chain. The neat CA and CA with the $Cu(NO_3)_2\cdot 4H_2O$ polymer



(a) (b)

**Fig. 5. (a) FTIR spectra of neat CA and 1 : 0.20 CA/$Cu(NO_3)_2\cdot 4H_2O$ at 0 bar and 8 bar water pressures, and (b) enlarged spectra at 1,600-2,000 cm$^{-1}$.**

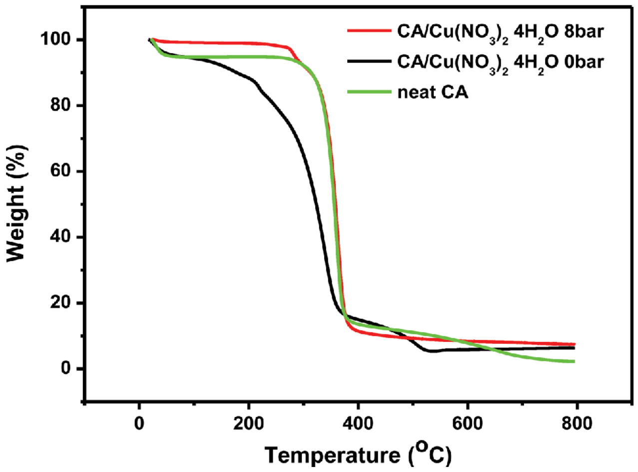


**Fig. 6. TGA analyses of neat CA and 1 : 0.2 CA/Cu(NO$_3$)$_2$·6H$_2$O at 0 bar and 8 bar water pressures.**

matrix at 0 bar decompose at around 70 °C. The decomposition was correlated with the degradation of solvent. From these results, it was thought that the vaporization of water in the CA/Cu(NO$_3$)$_2$·4H$_2$O polymer matrix at 8 bar was easier than in both neat CA and CA with the Cu(NO$_3$)$_2$·4H$_2$O polymer matrix at 0 bar. Surprisingly, the thermal stability for CA/Cu(NO$_3$)$_2$·4H$_2$O at 8 bar was recovered as observed in neat CA. These similar decomposition patterns with neat CA indicate that most of additives (Cu salts) were removed by external water-pressure. Thus, the generated porous CA materials were expected to be utilized as separator in battery and water-treatment membranes.

## CONCLUSIONS

A method to generate nanopores in a CA matrix using water pressure and copper(II) nitrate as an additive was suggested. The nanopores were generated when the polymer matrix was subjected to isostatic water pressure after copper(II) nitrate was added into the CA polymer matrix. These results indicated that the polymer chains were weakened by the plasticization effect of copper(II) nitrate present in the CA polymer matrix. Thus, water molecules were removed from the CA polymer matrix when exposed to high water pressure. The water flux increased with water pressure, indicating that pore properties such as porosity and size could be controlled by external water pressure and the additive content. The water flux of the additive-substituted CA polymer varied from 95.3 to 205.75 L/m$^2$h, depending on the water pressure and the additive content. Furthermore, it was demonstrated that the contained additives were removed by high water pressure, which was confirmed by FTIR and TGA studies. Thus, we could suggest a method to fabricate the porous CA polymer by using water pressure and copper(II) nitrate additive for applications to separators in batteries.

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