

## 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 ( $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) 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/ $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) 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<sup>2</sup>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  $\Omega$  in the 1<sup>st</sup> cycle to 3.78  $\Omega$  in the 35<sup>th</sup> 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  $\Omega$  [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<sub>4</sub>) composites were used for freestanding film [15]. This CA matrix containing [BMIM]BF<sub>4</sub> 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 ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 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 [ $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] 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 ( $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) 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  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was exposed to external water-pressures. Water flux in CA matrix was expressed in L/m<sup>2</sup>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  $\text{Cu}(\text{NO}_3)_2$  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  $\text{Cu}^{2+}$  and  $\text{NO}_3^-$  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/ $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  matrix treated at a water pressure of 8 bar. The pore size and volume of the polymer matrix increased with water pressure, compared with

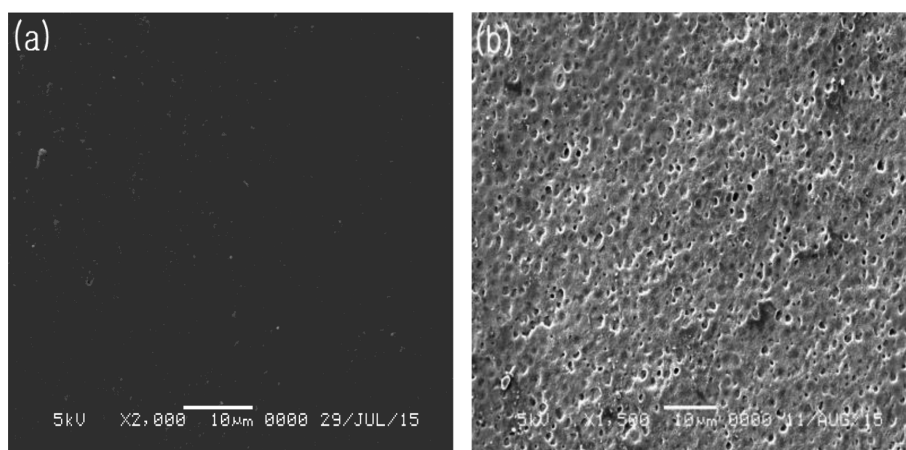


Fig. 1. SEM images: (a) Neat CA polymer and (b) polymer in acetone/water (w/w 8:2).

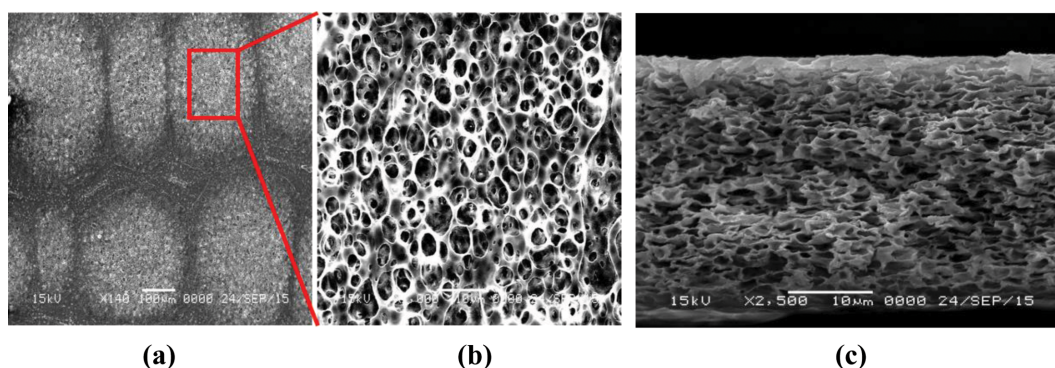


Fig. 2. SEM: (a) Image of 1:0.20 CA/ $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone/water (w/w 8:2) at a water pressure of 0 bar. (b) A magnified view of the square-shaped region marked in (a). (c) Cross-sectional view.

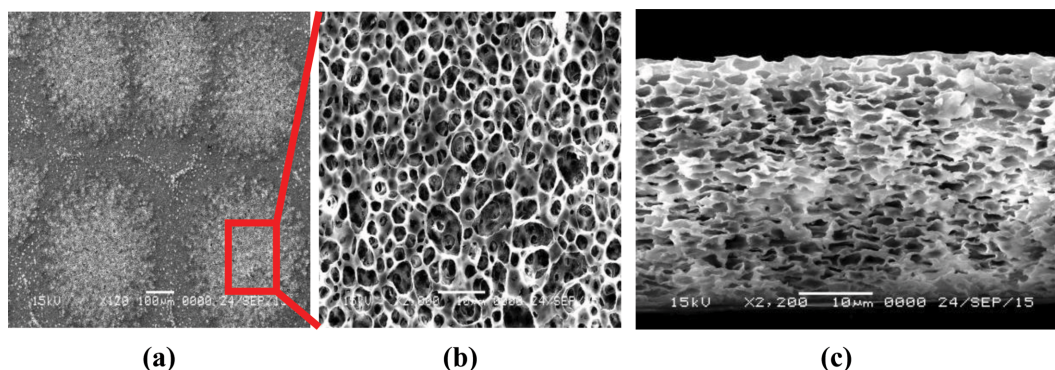


Fig. 3. SEM: (a) Image of pores observed in 1:0.2 CA/ $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone/water (w/w 8:2) under a water pressure of 8 bar. (b) A magnified view of the square-shaped portion marked in (a). (c) Cross-sectional view.

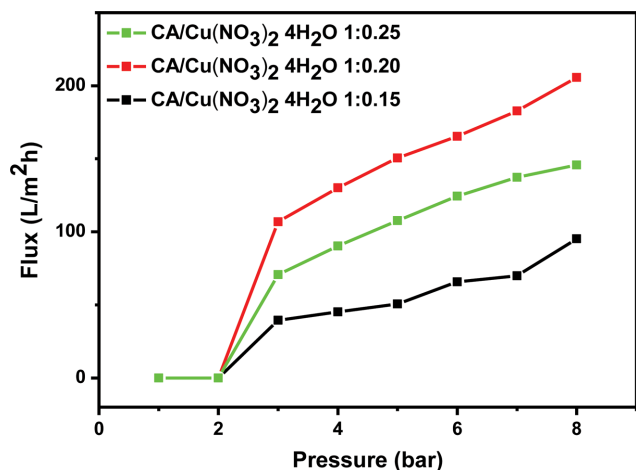


Fig. 4. Flux measured through neat CA and CA with  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at various water pressures.

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  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ .

The water flux for porous CA matrix with various ratios of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  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  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The observed water flux is attributed to the penetration of water through the polymer regions weakened by the solvated  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  aggregates. The water flux through the 1:0.15  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  complex varied from 39.4 to 95.3  $\text{L}/\text{m}^2\text{h}$  when the water pressure was 3–8 bar. For the 1:0.2  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  complex, the water flux increased to 205.75  $\text{L}/\text{m}^2\text{h}$  at 8 bar water pressure. These results show that the 1:0.15  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  complex has small pore sizes, owing to the small size of the solvated  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  molecules. Additionally, we assumed that the increase in the water flux with the

$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  content depended on the number of solvated  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  molecules. A further increase in the  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  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  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  composition. Especially, the reason why Cu salts showed the enhanced water flux than Ni salts reported in previous study was that the abundant free  $\text{NO}_3^-$  ions hydrated by water molecules in  $\text{Cu}(\text{NO}_3)_2$  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  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and 1:0.20  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer matrix at 0 bar and 8 bar water pressures. The peak observed at  $1,743 \text{ cm}^{-1}$  for the neat CA polymer matrix corresponds to the carbonyl group of the CA polymer matrix. When  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was added to the neat CA polymer matrix, the wavenumber decreased, owing to interactions between  $\text{Cu}^{2+}$  ions and carbonyl group of the CA polymer. Furthermore, a peak is observed at  $1,483 \text{ cm}^{-1}$  in the 1:0.20  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer matrix at 0 bar water pressure. However, the observed peak disappears from the FTIR spectra of the 1:0.20  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer matrix subjected to 8 bar water pressure. It was expected that when the  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer matrix was subjected to water pressure, a considerable amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was removed from the matrix and the peak at  $1,483 \text{ cm}^{-1}$  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  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at 8 bar pressure became mostly decomposed at around  $300^\circ\text{C}$ . In contrast, about 85 wt% of  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at 0 bar decomposed between 200 and  $360^\circ\text{C}$  and 15 wt% decomposes between 350 and  $550^\circ\text{C}$ . The boiling point of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was  $170^\circ\text{C}$ . It is estimated that the polymer chains were loosened by the solvated  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in the polymer chains. Thus, the loss of about 85 wt% of the  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer matrix at 0 bar was observed by the degradation of both the solvated  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and loosened polymer chain. The neat CA and CA with the  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  polymer

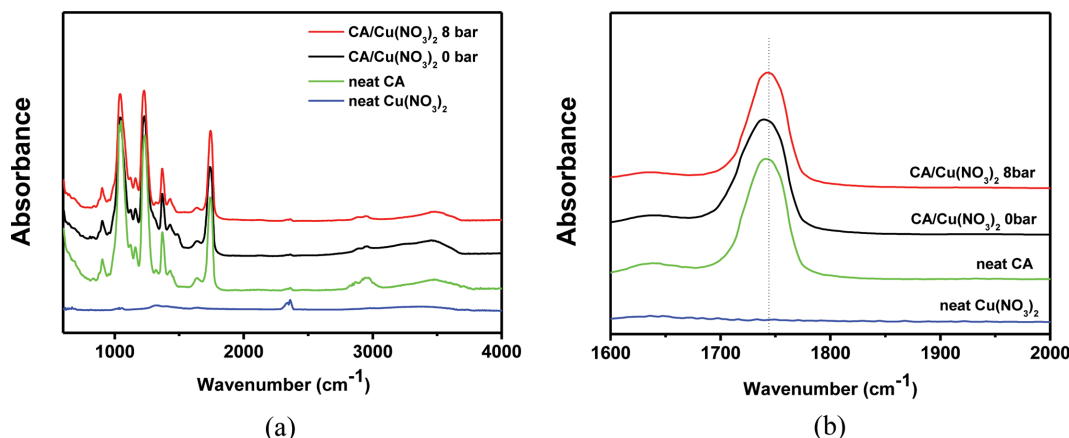


Fig. 5. (a) FTIR spectra of neat CA and 1:0.20  $\text{CA}/\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at 0 bar and 8 bar water pressures, and (b) enlarged spectra at  $1,600\text{--}2,000 \text{ cm}^{-1}$ .

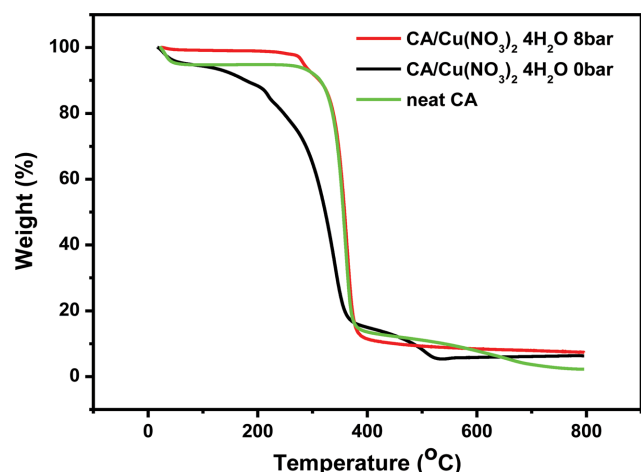


Fig. 6. TGA analyses of neat CA and 1:0.2 CA/Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 0 bar and 8 bar water pressures.

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<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O polymer matrix at 8 bar was easier than in both neat CA and CA with the Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O polymer matrix at 0 bar. Surprisingly, the thermal stability for CA/Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>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<sup>2</sup>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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## REFERENCES

1. H. S. Bang, S. M. Jang, Y. S. Kang and J. Won, *J. Membr. Sci.*, **479**, 77 (2015).
2. I. S. Chae, J. H. Lee, J. Hong, Y. S. Kang and S. W. Kang, *J. Eng. Chem.*, **251**, 343 (2014).
3. I. K. Moideen, A. M. Isloor, A. A. Qaiser, A. F. Ismail and M. S. Abdullah, *Korean J. Chem. Eng.*, **35**, 1281 (2018).
4. J. Albo and T. Tsuru, *J. Ind. Eng. Chem. Res.*, **53**, 8845 (2014).
5. Z. Afsarian and Y. Mansourpanah, *Korean J. Chem. Eng.*, **35**, 1867 (2018).
6. M. Bahrami, J. K. Sabet, A. Hatamnejad, A. Dastbaz and M. A. Moosavian, *Korean J. Chem. Eng.*, **35**, 2255 (2018).
7. K. Xu, *Chem. Rev.*, **104**, 4303 (2004).
8. G. Sung, H. Choe, Y. Choi and J. H. Kim, *Korean J. Chem. Eng.*, **35**, 1045 (2018).
9. L. Pan, H. Wang, C. Wu, C. Liao and L. Li, *ACS. Appl. Mater. Interfaces*, **7**, 16003 (2015).
10. Q. Xu, Q. Kong, Z. Liu, X. Wang, R. Liu, J. Zhang, L. Yue, Y. Duan and G. Cui, *ACS Sustainable Chem. Eng.*, **2**, 194 (2014).
11. W. G. Lee, J. Hwang and S. W. Kang, *Chem. Eng. J.*, **284**, 37 (2016).
12. C. Xie, H. Li, L. Li, S. Yu and F. Liu, *J. Hazard. Mater.*, **151**, 847 (2008).
13. P. K. Singh, B. Bhattacharya, R. M. Mehra and H. W. Rhee, *J. Curr. Appl. Phys.*, **11**, 616 (2011).
14. M. P. Scott, M. Rahman and C. S. Brazel, *J. Eur. Polym.*, **39**, 1947 (2003).
15. W. G. Lee, D. H. Kim, W. C. Jeon, S. K. Kwak, S. J. Kang and S. W. Kang, *Sci. Rep.*, **1287**, 1 (2017).