Correlation between the Ion Permeation and Free Volume Property in Ethyl Cellulose Film during the Acid Treatment

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Characterization Method

The infrared spectra were obtained with a Fourier Transform Infrared (FTIR) spectrometer (Nicolet 6700).

A Netzsch STA 449F3 differential scanning calorimeter with nitrogen as the purge gas was used. Samples with 3 mg were analyzed at a heating rate of 10 K/min.

Results

The Nyquist plots of the samples treated for different time were shown in Figure S1. It can be clearly found that the semicircle in Nyquist plot of the untreated sample is much larger than immersed ones. That means the ions can hardly permeate through the EC film. When EC was treated by acid, more tunnels would be formed.

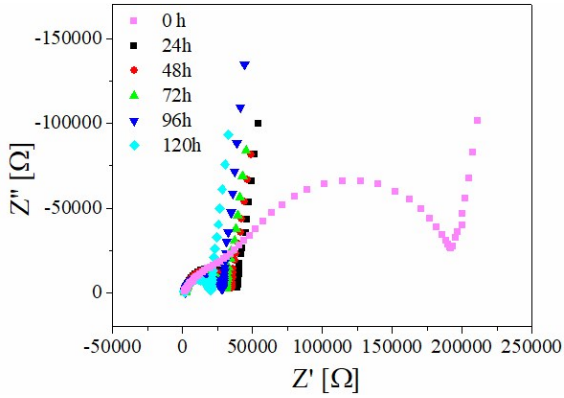

Figure S1 The Nyquist plots of the samples immersing in acid for different time

And the change of hole structure should be owing to the rearrangement of chain

segment in EC during the acid treatment, accompanying with chain scission or crosslink. In this case, FTIR was employed to detect the variation of chemical groups in EC film, and the spectra were presented in Figure S2. An absorption peak around 3300 cm^{-1} belongs to-OH stretching vibration, while the peaks around 2950, 2930 and 2860 cm^{-1} can be identified as the asymmetric, symmetric CH_2 stretching and the CH stretching bands, respectively. It is obviously found that the peak position shifts to higher wave number with the sample immersing in the acid. The absorbance of –OH could be decomposed into different components according to their contribution. For instance, "free" (nonhydrogen bonded) and hydrogen bonded –OH groups [1]. Therefore, the variation in –OH stretching vibration might be attributed to the esterification of EC in the presence of acid [2]. Moreover, the peak around 2930cm^{-1} weakened during the acid treatment. The schematic figure of the probable reaction was shown in Figure S3.The ether linkage in EC would be cleaved during the acid treatment. Therefore, the results suggested that the chain scission may be happened during the acid treatment, and this could be the reason for the expansion of the pores in the EC film detected by EIS and positron annihilation technique.

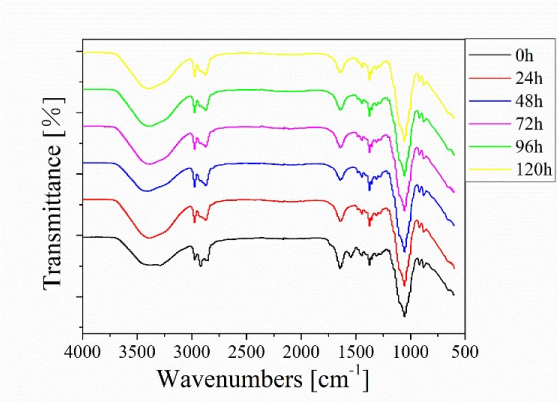

Figure S2 The FTIR spectra of EC film immersing in hydrochloric acid for 0h, 24h,

72h, 96h and 120h

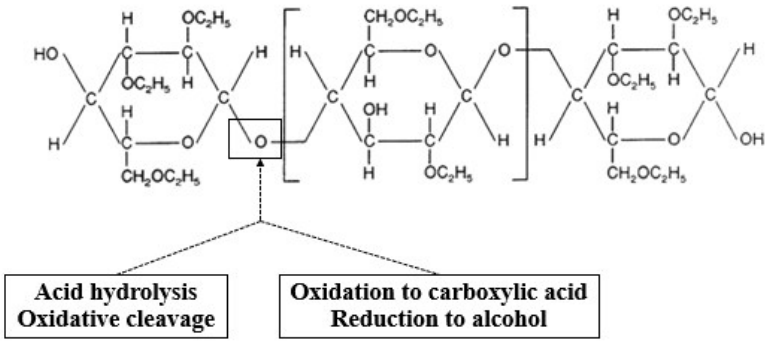

Figure S3 Acid-catalyzed cleavage of ether linkage

The DSC results were presented in Figure S4. There is no obviouse peak in the figure, implying EC treated in acid is an amorphous polymer. Many previous studies have proved that EC is a typical amorphous polymer [3-5]. The DSC results evidenced the same conclusion.

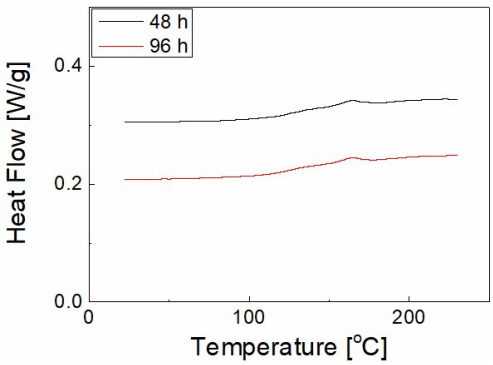

Figure S4 The DSC results of EC film immersing in acid for 48 h and 96 h

References:

[1] Chen Z, Huang W, Fang PF, Yu W, Wang SJ, Xiong J, Xu YS. The hydrogen bond and free volume property of poly(ether-urethane) irradiated by neutron. J. Polym. Sci. Pol. Phys., 2010, 48, 381-388.

[2] Lee S, Ko KH, Shin J, Kim NK, Kim YW, Kim JS. Effects of the addition of dimeracid alkyl esters on the properties of ethyl cellulose, Carbohyd. Polym., 2015,

121, 284-294.

[3] Zuo XX, Ma XD, Wu JH, Deng X, Xiao X, Liu JS, Nan J. Self-supporting ethyl cellulose/ poly(vinylidene fluoride) blended gel polymer electrolyte for 5 V high-voltage lithium-ion batteries. *Electrochim. Acta*, 2018, 271, 582-590.

[4] Shi XJ, Hu SF, Song SJ, Ding ZJ, Sheng XX. Selective crystallization of agomelatine from molton state induced by polymer. *J. Drug Deliv. Sci. Tec.*, 2019, 49, 448-454.

[5] Lin YX, Zhu CQ, Alva G, Fang GY. Microencapsulation and thermal properties of myristic acid with ethyl cellulose shell for thermal energy storage. *Appl. Energ.*, 2018, 231, 494-501.