Starch-*g*-PAN 고분자 전해질막 합성 및 플렉서블 고체 슈퍼 캐퍼시터 응용

민 효 준 · 정 주 환 · 강 미 소 · 김 종 학[†]

연세대학교 화공생명공학과
(2019년 6월 22일 접수, 2019년 6월 26일 수정, 2019년 6월 26일 채택)

Synthesis of Starch-*g*-PAN Polymer Electrolyte Membrane and Its Application to Flexible Solid Supercapacitors

Hyo Jun Min, Joo Hwan Jung, Miso Kang, and Jong Hak Kim[†]

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea

요   약: 본 연구에서는 녹말(starch)과 poly(acrylonitrile) (PAN)으로 이루어진 가지형 공중합체 기반의 슈퍼 캐퍼시터용 전해질막을 손쉽게 제조하는 방법을 제시하였다. 가지형 공중합체(starch-*g*-PAN)는 세륨 이온에 의해 개시된 자유 라디칼 중합을 통해 합성되었다. 실온에서 어떠한 유기용매 없이 Starch-*g*-PAN 고분자를 이온성 액체, 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA)에 용해하였으며 1시간 동안 100℃의 고온을 가해줌으로써 손쉽게 고분자 막을 만들었다. 제조된 막은 유연하여 플렉서블 고체 슈퍼 캐퍼시터의 전해질에 적용되었다. Starch-*g*-PAN 기반의 고분자 전해질막을 사용한 슈퍼 캐퍼시터는 0.5 A/g의 전류 밀도에서 약 21 F/g의 정전용량을 가졌으며 10,000 사이클 동안 86%의 유지율을 보이며 높은 주기 안정성을 보였다. 본 연구를 통해 starch-*g*-PAN 기반의 고분자 전해질막이 우수한 성능을 가진 플렉서블 고체 슈퍼 캐퍼시터에 응용될 수 있음을 확인하였다.

Abstract: In this work, we demonstrate a facile process to prepare an electrolyte membrane for the supercapacitor based on a graft copolymer consisting of starch and poly(acrylonitrile) (PAN). The graft copolymer (starch-*g*-PAN) was synthesized via free radical polymerization initiated by ceric ions. The starch-*g*-PAN was dissolved in ionic liquid, i.e. 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA) without any organic solvents at room temperature. The gelation of polymer electrolyte membranes occurred by applying high temperature, i.e. 100℃ for 1 hour. The resultant electrolyte membrane was flexible and thus applied to flexible solid supercapacitors. The performance of the supercapacitor based on starch-*g*-PAN graft copolymer electrolyte reached 21 F/g at a current density of 0.5 A/g. The cell also showed high cyclic stability with 86% of retention rate within 10,000 cycles. The preparation of starch-*g*-PAN based polymer electrolyte membrane provides opportunities for facile fabrication of flexible solid supercapacitors with good performance.

Keywords: polymer electrolyte membrane, flexible supercapacitor, graft copolymer

1. Introduction

Flexible supercapacitors have been reported as a new generation of flexible energy storage devices due to their high power density and various applications[1-6].

Many researches have been carried out to improve the energy density by enhancing the performance of the electrolyte. Gel polymer electrolytes are attracting much attention as a new alternative to liquid electrolytes due to their high stability and good mechanical properties

---

[7-9]. Gel polymer electrolyte membrane is composite of a polymer network and a liquid electrolyte formed by gelation within plasticizer, copolymerization or heat induction[10]. Polymer electrolyte membranes based on poly(vinyl alcohol) (PVA) with potassium hydroxide or phosphoric acid aqueous electrolytes have been commonly used as gel polymer electrolytes for supercapacitors[11-14]. However, supercapacitors based on aqueous electrolytes suffer from narrow potential windows which leads to low energy densities. Also, most of the gel polymer electrolyte membranes require the use of organic solvents in the process, which results in difficulties in scale up or increase of production cost[15].

Starch is a low cost and biodegradable polymer [16,17]. One of the methods to chemically modify starch is graft polymerization[16]. Starch can be grafted with vinyl monomers via free radical polymerization [18,19]. Cerium salts are widely used as initiators graft polymerization of starch[20,21]. In this work, a hydrophobic acrylonitrile monomer was grafted onto a hydrophilic starch to prepare amphiphilic graft copolymers.

An ionic liquid is an organic salt that has a low melting point and exists in liquid state at room temperature. Their high conductivity, large heat and electrochemical stability, small volatility are well known to be used as electrolyte in batteries and supercapacitors[7,22-25]. Ionic liquids are known as good solvent for starch and cellulose such as 1-buthyl-3-methylimidazolium chloride (BMIM Cl) or 1-buthyl-3-methylimidazolium dicyanamide BMIM DCA[6,26,27]. The Kadokawa group reported that cellulose in some ionic liquids forms gelation by increasing temperature[28,29]. 1-Ethyl-3-methylimidazolium dicyanamide (EMIM DCA) is another ionic liquid that has a high conductivity and is a solvent for starch. Due to the low viscosity, ion size, EMIM DCA-based supercapacitors showed a high specific capacitance and low resistance[30]. We have chosen EMIM DCA as an electrolyte salt to increase the ionic conductivity of electrolyte, expecting high interactions between ions and polymer chains.

Here, we examined an organic solvent-free, simple process to prepare an electrolyte membrane for the su-

percapacitors based on a graft copolymer consisting of starch and PAN synthesized via free radical polymerization. The gel polymer electrolyte membrane was fabricated by dissolving in ionic liquid (EMIM DCA) and increasing temperature. Flexible electrostatic double-layer capacitors (EDLCs) were prepared using carbon-based electrode consisting of carbon clothes as substrates and polymer electrolyte membranes consisting of starch-*g*-PAN graft copolymer and EMIM DCA. We have examined the structural properties of the graft copolymer and electrolyte membranes based on the copolymer through Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) analysis. The electrochemical properties of the supercapacitors based on starch-*g*-PAN polymer electrolyte membranes have been investigated by cyclic voltammetry (CV) and constant current charge/discharge (GCD) and cycling tests.

2. Experimental Section

2.1. Materials

Starch from wheat, acrylonitrile ($\geq$ 99%, contains 35~45 ppm monomethyl ether hydroquinone as inhibitor), ammonium cerium(IV) nitrate (ACN, $\geq$ 98.5%), nitric acid (HNO_3, 70%), 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA, 98.0%), activated carbon (DARCO, ~100 mesh particle size), poly(vinylidene fluoride) (PVDF, M_w = ~534,000) were purchased from Sigma Aldrich. Carbon black (Super P) was purchased from Alfa Aesar. Methanol (MeOH, 99.9%), N-methyl-2-pyrrolidone (NMP) were obtained from J. T. Baker. Carbon cloth was purchased from CNL Energy. All solvents and chemicals were reagent grade and were used as received without any treatment.

2.2. Synthesis of starch-*g*-PAN graft copolymer

Starch-*g*-PAN was synthesized via free radical polymerization. Briefly, 2 g of starch was completely dissolved in 30 mL of deionized water. The solution was preheated at 80°C for 1 h for gelatinization. Then 0.12 g of ACN dissolved in HNO_3 and 10 mL of acryloni-
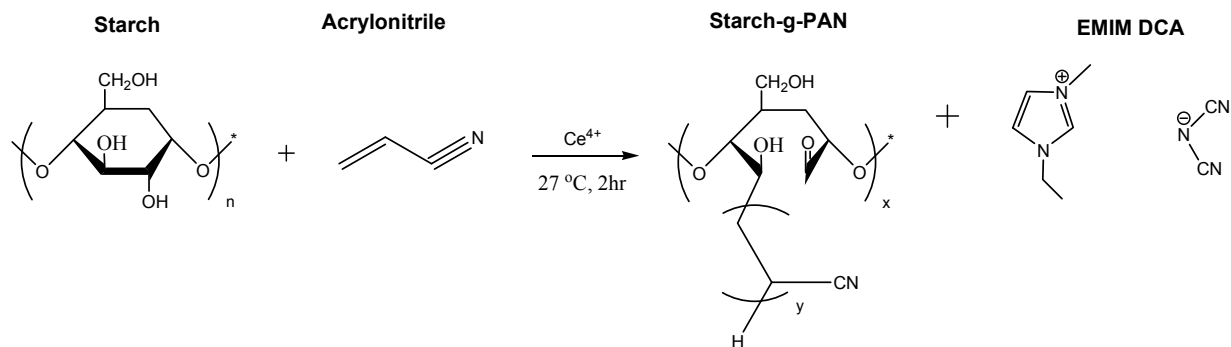
Scheme 1. Synthesis of starch-*g*-PAN graft copolymer and chemical structure of ionic liquid.

trile were added to the solution, followed by purging with N_2 gas. After placed at 27°C for 2 hours for polymerization, MeOH was added into the solution and the polymer was obtained by vacuum filtration. To purify the synthesized copolymer, the filtration process was repeated thrice.

2.3. Preparation of electrodes

First, the mixture of activated carbon, Super P, PVDF binder with the ratio of 16 : 3 : 1 was dissolved in NMP. Homogeneous solution was obtained by stirring overnight. The solution was casted on carbon cloth with an active area of 1 cm × 4 cm. Then, carbon clothes were placed in a drying oven at 80°C to evaporate the solvent overnight. About 5 mg of electrode materials were casted on carbon cloth.

2.4. Fabrication of supercapacitors

First, different amounts (0.05, 0.2 and 0.5 g) of starch-*g*-PAN graft copolymers were dissolved in 1 mL of EMIM DCA, denoted as SPAN-IL1, SPAN-IL2, SPAN-IL3, respectively, without using any organic solvents. EMIM DCA was casted onto the electrode to enable the electrode to have better contact with the electrolyte membrane. Then, the prepared graft copolymer electrolyte solution was casted onto the electrode and sandwiched together to fabricate EDLC. The fabricated cells were placed in the oven at 100°C for 1 hour to proceed the gelation of the solution. After gelation, the cell was washed with MeOH to prepare supercapacitors based on starch-*g*-PAN graft copolymer

membrane.

2.5. Characterization

FT-IR spectra of the synthesized copolymer was obtained in the frequency range from 4,000 to 500 cm^{-1} to confirm the successful graft copolymerization with an Excalibur series FT-IR instrument (DIGLAB CO., Hannover, Germany). The structures of the polymer and electrolyte membranes were observed with TEM (JEM-F200, JEOL Ltd., Japan) and XRD spectrometer (SmartLab, RIGAKU, Japan). The electrochemical properties of supercapacitor based on starch-*g*-PAN graft copolymer electrolyte membrane were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) experiments.

3. Results and Discussion

3.1. Synthesis of starch-*g*-PAN and characterization of electrolyte membranes

The starch-*g*-PAN graft copolymer was synthesized via a one-step free radical polymerization using ceric ion as the initiator at 27°C, as shown in Scheme 1. This is a low-cost facile reaction based on water solvent and mild reaction conditions which are suitable for scale up[31]. The EMIM DCA ionic liquid consists of EMIM$^+$ cations and DCA$^-$ anions. The DCA$^-$ ions contain cyanide groups and their molecular weight is relatively low compared to other EMIM-based ionic liquids[30], providing higher ionic conductivity.

Fig. 1 shows the preparation of electrolyte membranes

Fig. 1. Digital photos of (a) SPAN-IL solution in Teflon dish, (b) SPAN-IL electrolyte membrane after gelation process and (c) flexibility of SPAN-IL electrolyte membrane.

based on starch-*g*-PAN graft copolymer. The starch-*g*-PAN graft copolymer was dissolved in EMIM DCA (SPAN-IL) as shown in Fig. 1(a). The gelation of the solution was easily proceeded by placing the solution in the oven at 100°C in Fig. 1(b). The SPAN-IL graft copolymer electrolyte membrane was highly transparent and maintained good mechanical strength. It also showed high flexibility, indicating that the SPAN-IL electrolyte membrane is suitable for flexible solid supercapacitors as shown in Fig. 1(c).

FT-IR spectra were obtained to confirm the successful synthesis of starch-*g*-PAN graft copolymer. The FT-IR spectra of neat starch backbone, acrylonitrile monomer and synthesized starch-*g*-PAN graft copolymer are shown in Fig. 2(a). The absorption band at 1,614 cm^{-1} for acrylonitrile was assigned to the stretching vibrations of the C=C double bond. After graft copolymerization, the band completely disappeared in starch-*g*-PAN, indicating that polymerization was completed and no residual monomers were remained. Acrylonitrile and starch-*g*-PAN showed an absorption band near 2,240 cm^{-1}, which was assigned to the C≡N triple bond. The absorption band of starch-*g*-PAN due to the C≡N triple bond at 2,243 cm^{-1} differed from that of acrylonitrile (2,230 cm^{-1}), indicating the formation of cyanide functional group of PAN. Also, the band shift between neat starch and starch-*g*-PAN was observed, which indicates that the starch-*g*-PAN graft copolymer was successfully synthesized which is in good agreement with previous researches[21].

The interaction between the graft copolymer and ionic liquid was characterized by FT-IR as shown in Fig.
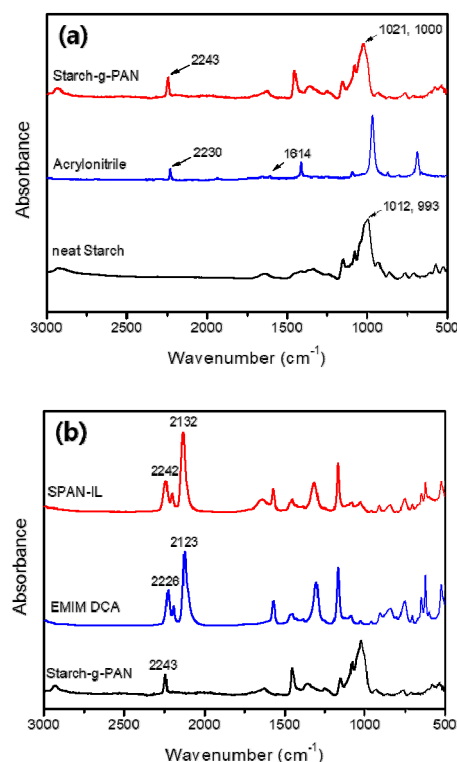

Fig. 2. FT-IR spectra of (a) starch, acrylonitrile and starch-*g*-PAN and (b) starch-*g*-PAN, EMIM DCA and SPAN-IL.

2(b). The nitrile absorption band at 2,123 cm^{-1} in EMIM DCA was shifted to a higher wavenumber at 2,132 cm^{-1}. In addition, the absorption band of cyanide group of EMIM DCA was shifted from 2,226 to 2,242 cm^{-1} in SPAN-IL, indicating that the starch-*g*-PAN graft copolymer interacted with EMIM DCA. To be specific, the hydrophilic EMIM DCA interacted with the hydrophilic starch chains of starch-*g*-PAN matrix because of their good miscibility between the ionic liquid and the
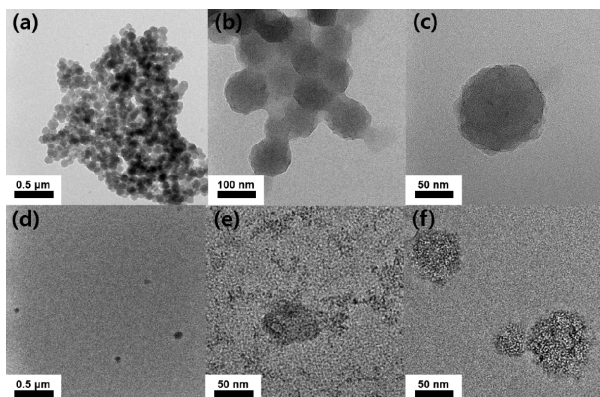
Fig. 3. TEM images of ((a)~(c)) starch-*g*-PAN and ((d)~(f)) SPAN-IL.

Fig. 4. XRD profiles of (a) starch-*g*-PAN and (b) gel polymer electrolyte membrane based on SPAN-IL.

starch.

TEM was used to observe the morphologies of the starch-*g*-PAN graft copolymer and the SPAN-IL electrolyte membrane, as shown in Fig. 3. In the TEM images, it appears dark in the high electron density regions and bright in the low regions. The starch-*g*-PAN showed some aggregations of nanospheres with a diameter of approximately 100 nm (Fig. 3(a)). The formation of nanosphere structure might be due to emulsion polymerization process constructing the micelle structure of synthesized graft copolymer. The nanosphere of polymer showed uniform brightness where no phase separation is observed (Fig. 3(c)). However, the TEM images of SPAN-IL (Fig. 3(d)) showed no aggregation of nanospheres of the copolymer, indicating that ionic liquid worked as good solvent to disperse the polymer. In Fig. 3(e) and (f), the microphase-separated structures were observed consisting of bright and dark regions. The bright region represents the PAN chains while the dark region represents the ionic liquid with high electron density, which interacted with the hydrophilic starch, consistent with the FT-IR results. EMIM DCA not only worked as the solvent of the graft copolymer but also penetrated into the polymer to induce microphase-separation. The microphase-separated structure could facilitate the transport of ions inducing the increase of electrochemical performance as an electrolyte[13,32].

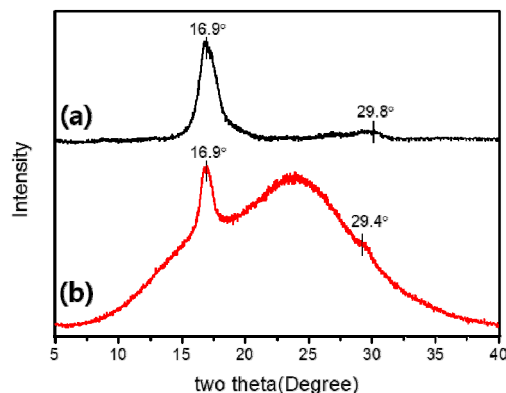XRD analysis was conducted to analyze the crystal-linity of the starch-*g*-PAN copolymer and gel polymer electrolyte membrane based on SPAN-IL. In the XRD profile of the starch-*g*-PAN, the crystalline peaks were observed at 16.9° and 29.8° (Fig. 4(a)). These peaks are assigned to PAN chains of the graft copolymer. In Fig. 4(b), the membrane based on SPAN-IL shows broad curves with crystalline peak at 16.9° same with the polymer. However, shoulder peak was observed at 29.4° which is lower than peak of starch-*g*-PAN at 29.8°. When analyzing the XRD results, lower 2θ means a higher *d*-spacing by Bragg relationship. The *d*-spacing of PAN chains of membrane based on SPAN-IL has slightly increased compared to starch-*g*-PAN copolymer. This might be because hydrophilic ionic liquid penetrated into the polymer and had high interaction with hydrophilic starch. The penetration of ionic liquid into the polymer induced the increase of *d*-spacing of hydrophobic PAN chains, consistent with the previous results.

3.2. Electrochemical properties of supercapacitors

CV measurements were conducted to investigate the capacitance of the supercapacitors. Fig. 5 shows the CV curves of supercapacitors based on SPAN-IL1, SPAN-IL2 and SPAN-IL3 polymer electrolyte membranes in 0~0.8 V potential window at a scan rate of 100 mV/s. Among the supercapacitors, SPAN-IL3 based cell showed the largest area of curve which corresponds to the highest capacitance. The capacitance of SPAN-IL3
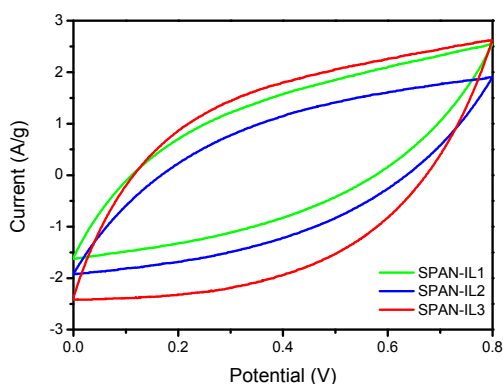
Fig. 5. CV curves of supercapacitors based on SPAN-IL1, SPAN-IL2 and SPAN-IL3 graft copolymer electrolyte membranes.
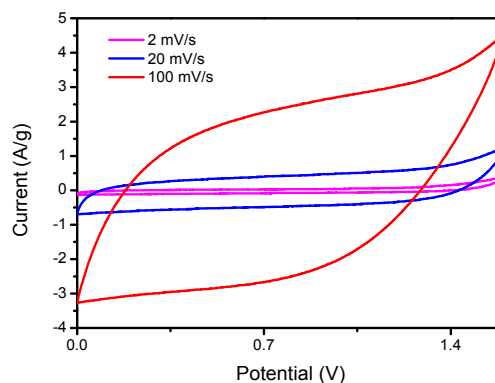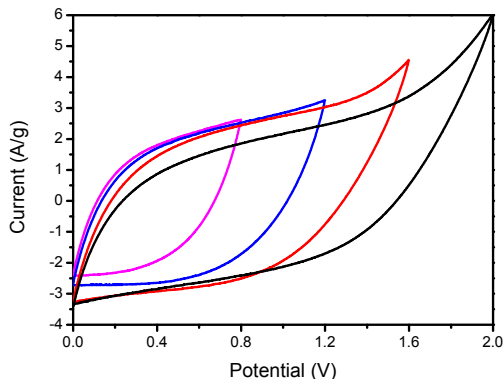

Fig. 6. CV curves of the supercapacitor based on SPAN-IL3 graft copolymer electrolyte membrane in various potential windows.

Fig. 7. CV curves of the supercapacitor based on SPAN-IL3 graft copolymer electrolyte membrane at different scan rates.

within different potential windows from 0~2.0 V. As shown in Fig. 6, the rectangular shape of the CV curve maintained until the potential windows of 1.6 V. The CV curve of potential window within 2.0 V was slightly deviated from the rectangular shape. This result shows that the potential window increased by the use of ionic liquid which has high potential windows. The cell showed higher potential window than that of conventional aqueous electrolyte membrane based supercapacitors inducing the increase of energy density. In Fig. 7, the CV curves of SPAN-IL3 electrolyte membrane within various scan rates from 2 mV/s to 100 mV/s were investigated. As the scan rate decreased, the area of CV curve became smaller and changed to more like rectangular shape. At the scan rate of 2 mV/s, the capacitance of the cell was 37.5 F/g while it exhibited 23.3 F/g of capacitance at the scan rate of 100 mV/s, showing 62% of capacitance retention.

GCD method was applied to examine the specific electrochemical properties of the supercapacitor based on SPAN-IL3 graft copolymer electrolyte membrane. The GCD curves at different current densities are shown in Fig. 8. At the current density of 0.5 A/g, the capacitance of the cell was 21 F/g. The IR drops were observed in general GCD graphs, which corresponded to the contact resistance of the cells. The cell in this work showed a low value of IR drops (145 mV) at the current density of 0.5 A/g. This result indicates that the SPAN-IL based membranes are effective for flexi-

based cell was 16.9 F/g whereas the SPAN-IL1 and SPAN-IL2 based supercapacitors showed capacitance of 12.5 F/g and 11.7 F/g, respectively. Lower concentration of starch-*g*-PAN in ionic liquid showed lower performance, indicating that graft copolymer matrix in the ionic liquid enhanced the ion mobility because the polymer matrix acted as the pathways for ion transport.

Aqueous electrolyte membranes have narrow potential windows due to the decomposition of water at around 1.23 V. Oxygen evolution occurs at a potential of around 1.23 V, which leads to the decrease in stability of the cell. The polymer electrolyte membranes based on ionic liquids are expected to have more broad potential windows. Fig. 6 shows the CV curves of the device based on the SPAN-IL3 electrolyte membrane
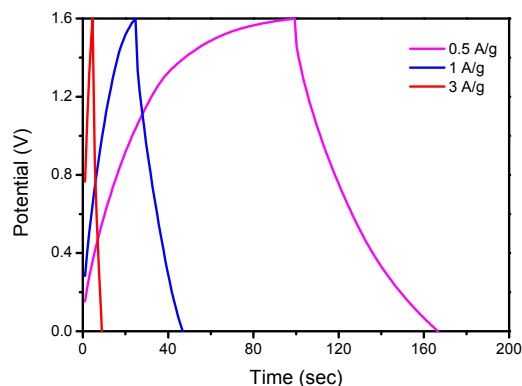
Fig. 8. GCD curves of the supercapacitor based on SPAN-IL3 graft copolymer electrolyte membrane at different current densities.
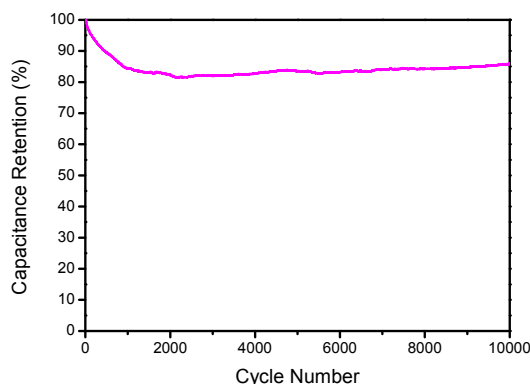

Fig. 9. Cyclic stability of the supercapacitor based on SPAN-IL3 graft copolymer electrolyte membrane.

ble solid supercapcitors with polymer electrolytes. The cyclic stability of supercapacitor based on SPAN-IL3 electrolyte membrane was also investigated by using GCD method at a current density of 3 A/g as shown in Fig. 9. After 10,000 cycles, SPAN-IL3 based supercapacitor exhibited a great performance with 86% of capacitance retention. No significant failure or aging of electrolyte was observed during the cycle tests.

4. Conclusions

We fabricated solid electrolyte membranes for flexible solid supercapacitors based on starch-*g*-PAN graft copolymer. The starch-*g*-PAN graft copolymer was synthesized via free radical polymerization initiated by

ceric ion in mild reaction conditions. The electrolyte membrane was prepared by dissolving starch-*g*-PAN in ionic liquid without using any organic solvents and by increasing the temperature. The microphase-separated structures were observed by TEM images. The hydrophilic EMIM DCA penetrated into the starch-*g*-PAN graft copolymer, indicating good affinity with the hydrophilic starch chains. Microphase-separation of structure was formed due to the separation of hydrophobic chains of PAN chains and the hydrophilic part of ionic liquid and starch regions, confirmed by XRD results. As a result, the polymer matrix was well dispersed in the ionic liquid and worked as a pathway for facile transport of ions. The specific capacitance of the supercapacitor based on starch-*g*-PAN electrolyte membrane reached 21 F/g at a current density of 0.5 A/g. The supercapacitor showed a potential window within 0~2.0 V which is higher than that of aqueous electrolyte membrane based supercapacitors due to high potential window of the ionic liquid. In addition, the device exhibited excellent cyclic stability of 86% of capacitance retention rate even after 10,000 cycles. This work suggests that the starch-*g*-PAN based electrolyte membrane can be one of the candidates for the facile preparation of flexible solid supercapacitors.

Acknowledgements

Reference

1. H. S. Kim, M. S. Kang, and W. C. Yoo, "Boost-up electrochemical performance of MOFs via confined synthesis within nanoporous carbon matrices for supercapacitor and oxygen reduction reaction applications", *J. Mater. Chem. A*, **7**, 5561 (2019).

2. Y. Liu, N. Liu, L. Yu, X. Jiang, and X. Yan,

"Design and synthesis of mint leaf-like polyacrylonitrile and carbon nanosheets for flexible all-solid-state asymmetric supercapacitors", *Chem. Eng. J.*, **362**, 600 (2019).

3. R. Na, Y. Liu, N. Lu, S. Zhang, F. Liu, and G. Wang, "Mechanically robust hydrophobic association hydrogel electrolyte with efficient ionic transport for flexible supercapacitors", *Chem. Eng. J.*, **374**, 738 (2019).

4. X. Zhao, B. M. Sánchez, P. J. Dobson, and P. S. Grant, "The role of nanomaterials in redox-based supercapacitors for next generation energy storage devices", *Nanoscale*, **3**, 839 (2011).

5. Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, and E. Xie, "Freestanding three-dimensional graphene/MnO$_2$ composite networks as ultralight and flexible supercapacitor electrodes", *ACS nano*, **7**, 174 (2012).

6. D. Zhao, C. Chen, Q. Zhang, W. Chen, S. Liu, Q. Wang, Y. Liu, J. Li, and H. Yu, "High performance, flexible, solid-state supercapacitors based on a renewable and biodegradable mesoporous cellulose membrane", *Adv. Energy Mater.*, **7**, 1700739 (2017).

7. C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, and J. Zhang, "A review of electrolyte materials and compositions for electrochemical supercapacitors", *Chem. Soc. Rev.*, **44**, 7484 (2015).

8. S. A. Alexandre, G. G. Silva, R. Santamaría, J. P. C. Trigueiro, and R. L. Lavall, "A highly adhesive PIL/IL gel polymer electrolyte for use in flexible solid state supercapacitors", *Electrochim. Acta*, **299**, 789 (2019).

9. G. Pandey, A. Rastogi, and C. R. Westgate, "All-solid-state supercapacitors with poly (3,4-ethylenedioxythiophene)-coated carbon fiber paper electrodes and ionic liquid gel polymer electrolyte", *J. Power Sources*, **245**, 857 (2014).

10. J. H. Lee, C. H. Park, C. S. Lee, and J. H. Kim, "Review on polymer electrolyte membranes for dye-sensitized solar cells", *Membr. J.*, **29**, 80 (2019).

11. C.-C. Yang, S.-T. Hsu, and W.-C. Chien, "All solid-state electric double-layer capacitors based on alkaline polyvinyl alcohol polymer electrolytes", *J. Power Sources*, **152**, 303 (2005).

12. H. Yu, J. Wu, L. Fan, K. Xu, X. Zhong, Y. Lin, and J. Lin, "Improvement of the performance for quasi-solid-state supercapacitor by using PVA-KOH-KI polymer gel electrolyte", *Electrochim. Acta*, **56**, 6881 (2011).

13. J. Y. Lim, J. K. Kim, J. M. Lee, D. Y. Ryu, and J. H. Kim, "An amphiphilic block-graft copolymer electrolyte: Synthesis, nanostructure, and use in solid-state flexible supercapacitors", *J. Mater. Chem. A*, **4**, 7848 (2016).

14. J. H. Lee, C. H. Park, M. S. Park, and J. H. Kim, "Poly(vinyl alcohol)-based polymer electrolyte membrane for solid-state supercapacitor", *Membr. J.*, **29**, 30 (2019).

15. G. Zheng, L. Hu, H. Wu, X. Xie, and Y. Cui, "Paper supercapacitors by a solvent-free drawing method", *Energy Environ. Sci.*, **4**, 3368 (2011).

16. Q. Chen, H. Yu, L. Wang, Z. ul Abdin, Y. Chen, J. Wang, W. Zhou, X. Yang, R. U. Khan, H. Zhang, and X. Chen, "Recent progress in chemical modification of starch and its applications", *RSC Adv.*, **5**, 67459 (2015).

17. M. O. S. Lobregas and D. H. Camacho, "Gel polymer electrolyte system based on starch grafted with ionic liquid: Synthesis, characterization and its application in dye-sensitized solar cell", *Electrochim. Acta*, **298**, 219 (2019).

18. M. Çelik and M. Saçak, "Synthesis and characterization of starch-poly(methyl methacrylate) graft copolymers", *J. Appl. Polym. Sci.*, **86**, 53 (2002).

19. L. O. Ekebafe, D. E. Ogbeifun, and F. E. Okieimen, "Effect of native cassava starch-poly (Sodium Acrylate-co-Acrylamide) hydrogel on the growth performance of maize (Zea may) seedlings", *Am. J. Poly. Sci.*, **1**, 6 (2012).

20. M. Rakesh and R. Bengt, "Graft copolymerization onto starch. 111. Grafting of acrylonitrile to gelatinized potato starch by manganic pyrophosphate initiation", *J. Appl. Polym. Sci.*, **22**, 2991 (1978).

21. D. Apopei, M. Dinu, and E. Dragan, "Graft copolymerization of acrylonitrile onto potatoes starch by ceric ion", *Dig. J. Nanomater. Bios.*, **7**, 707 (2012).

22. A. Balducci, R. Dugas, P.-L. Taberna, P. Simon, D. Plee, M. Mastragostino, and S. Passerini, "High temperature carbon-carbon supercapacitor using ionic liquid as electrolyte", *J. Power Sources*, **165**, 922 (2007).

23. A. Balducci, U. Bardi, S. Caporali, M. Mastragostino, and F. Soavi, "Ionic liquids for hybrid supercapacitors", *Electrochem. Commun.*, **6**, 566 (2004).

24. K. W. Yoon and S. W. Kang, "1-Butyl-3-methyl-imidazolium tetrafluoroborate/Al_2O_3 composite membrane for CO_2 separation", *Membr. J.*, **27**, 226 (2017).

25. D. A. Kang, K. Kim, and J. H. Kim, "Highly-permeable mixed matrix membranes based on SBS-*g*-POEM copolymer, ZIF-8 and ionic liquid", *Membr. J.*, **29**, 44 (2019).

26. J. Gao, Z. G. Luo, and F. X. Luo, "Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts", *Carbohydr. Polym.*, **89**, 1215 (2012).

27. M. Isik, H. Sardon, and D. Mecerreyes, "Ionic liquids and cellulose: Dissolution, chemical modification and preparation of new cellulosic materials", *Int. J. Mol. Sci.*, **15**, 11922 (2014).

28. J. Kadokawa, M. A. Murakami, and Y. Kaneko, "A facile preparation of gel materials from a solution of cellulose in ionic liquid", *Carbohydr. Res.*, **343**, 769 (2008).

29. J.-i. Kadokawa, M.-a. Murakami, A. Takegawa, and Y. Kaneko, "Preparation of cellulose-starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid", *Carbohydr. Polym.*, **75**, 180 (2009).

30. M. Shi, S. Kou, and X. Yan, "Engineering the electrochemical capacitive properties of graphene sheets in ionic-liquid electrolytes by correct selection of anions", *ChemSusChem*, **7**, 3053 (2014).

31. U. M. Lindstrom, "Organic reactions in water: Principles, strategies and applications", John Wiley & Sons (2008).

32. S. Y. Lee, H.-J. Kim, S. Y. Nam, and C. H. Park, "Synthetic strategies for high performance hydrocarbon polymer electrolyte membranes (PEMs) for fuel cells", *Membr. J.*, **26**, 1 (2016).