Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 8, No. 1, 2023

Review of SPEEK Amphoteric Proton Exchange Membranes in All Vanadium Flow Batteries

Tianyuan Han, Ying Bi, Ming Song, and Penghua Qian*

School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou, 221018, China
* Corresponding author

Abstract: Sulfonated polyether ether ketone (SPEEK) membranes have been widely used in the field of all vanadium flow batteries (VFRB) due to their simple structure, convenient preparation, good thermal and mechanical stability, low cost, and easy modification. However, its membrane performance largely depends on the degree of sulfonation. As the degree of sulfonation increases, the proton conductivity increases, but it also increases water uptake, leading to excessive swelling and vanadium ion penetration, thereby reducing the stability of the membrane and the performance of the battery. The introduction of alkaline functional groups can serve as proton acceptors to promote proton transport through the Grotthus mechanism, and on the other hand, they can form acid-base pairs with sulfonic acid groups. The resulting hydrogen bonds, acid-base interactions, ion bonds, and other interface interactions are beneficial for reducing the swelling rate of SPEEK membranes, and can also adjust the size of proton transport channels, constructing efficient proton transport channels that are both conducive to proton transport and can hinder the passage of vanadium ions, Improve the ion selectivity of membranes. Therefore, this article reviews the basic research and practical development status of SPEEK amphoteric membranes in VRFB, including the latest progress in various modification strategies. And evaluated the challenges and potential future research directions faced by the development of SPEEK membranes.

Keywords: Proton exchange membrane; SPEEK; Amphoteric membranes; All vanadium flow batteries.

1. Introduction

As a large-scale energy storage device, all vanadium flow battery (VRFB) has attracted widespread attention due to its controllable capacity, low environmental impact, long service life, and convenient maintenance. Its development and application in the field of new energy are becoming increasingly mature [1]. Proton exchange membrane (PEM) is one of the key components in the composition of VRFB, and its performance and cost determine the life and ultimate performance of batteries. PEM not only needs to prevent the cross pentration of vanadium ions with different valence states, avoiding the phenomenon of short circuit, but also allows the directional movement of protons to form a current circuit [2,3]. The active groups of PEMs mainly include sulfonic acid groups (-SO_3H), carboxyl groups (-COOH), phosphate groups (-PO_3H_2), phosphite groups (-PO_2H_2), etc. These acidic groups can dissociate H^+ and exchange with H^+ in the electrolyte to conduct current [4]. Excellent proton conductivity, low vanadium ion permeability, good chemical stability, outstanding mechanical properties and low price are the ideal proton exchange membrane required [5]. At present, the most widely used PEMs are DuPont's Nafion series membranes, which contain polytetrafluoroethylene main-chain (superhydrophobic) and perfluorosulfonic acid group side-chain (superhydrophilic), and will form large-scale microphase separation domains. Although Nafion membranes have good chemical stability and high proton conductivity, their high cost and serious vanadium ion permeability make it difficult to develop VRFB on a large scale [6,7]. Therefore, the research on non-fluorinated PEMs with both high performance and low cost has become a worthwhile topic to delve into.

At present, sulfonated aromatic polymers with aromatic ring structures have become a research hotspot in non-fluorosulfonic acid PEMs due to their simple preparation, stable structure, low price, and high mechanical strength. Generally, sulfonic acid groups are introduced into aromatic polymer structures through the use of sulfonated monomers or post-sulfonation, thereby possessing the potential for the application of PEM [8]. Widely used sulfonated aromatic polymers mainly include sulfonated polyimide (SPI) [9], sulfonated polysulfone (SPF) [10], sulfonated polybenzimidazole (SPBI) [11] and sulfonated polyether ether ketone (SPEEK) [12]. Among them, SPEEK is considered the most promising high-performance membrane material to replace Nafion membranes. The main-chain of PEEK is composed of ether bond (-O-), ketone group, and aromatic ring. In which, the aromatic ring has strong rigidity, providing excellent dimensional stability for PEEK, while the ether bond provides good flexibility and thermal oxidation resistance stability for the molecular chain [13]. After sulfonation, SPEEK retains most of its advantages, and the introduction of -SO_3H groups endows it with the ability to conduct protons. The high proton conductivity of SPEEK membranes depends on their high degree of sulfonation (DS), but it also leads to a decline in mechanical and vanadium penetration resistance due to an increase in water uptake [14]. Studies have shown that anion exchange membranes (AEMs), containing alkaline or cation functional groups, have lower vanadium ion permeability due to the Donnan effect (the repulsion effect between the alkaline or cation functional groups of AEM and vanadium ions) [15]. Therefore, introducing alkaline groups into SPEEK membranes to prepare amphoteric PEM is expected to reduce vanadium ion permeability and improve ion selectivity.

Amphoteric ion exchange membranes (AIEMs) contain both cationic and anionic groups. Due to the fact that cationic groups can act as proton acceptors and form acid-base interactions with sulfonic acid groups (proton donors) to promote proton transport, and the Donnan effect between vanadium ions, AIEM not only shows high proton conductivity but also low vanadium ion permeability, making it promising in VRFB applications [16]. Amphoteric functional modified SPEEK membranes have high proton conductivity and excellent vanadium penetration resistance, which has become an effective way to prepare high-performance ideal PEM [17]. For SPEEK membranes, the main methods of introducing cationic groups include covalent modification of SPEEK (introducing side-chains containing cationic groups) and blending modification with materials containing cationic groups. Different preparation methods, structural characteristics, and interface interactions play different roles in improving the performance of SPEEK membranes. Therefore, this paper summarizes the amphoteric PEEK proton exchange membranes prepared by the above two methods, analyzes their structure-activity relationship and application in VRFB, and discusses their present situation and future development.

2. Modification of SPEEK

2.1. Covalent Modification

Covalent modification is one of the important methods to modify polymer materials by changing the organizational structure of polymer materials with the help of chemical reactions. The amphoteric covalent modification of SPEEK is mainly achieved by grafting side-chains containing basic groups. By adjusting the chain structure mi to analyze the structure-activity relationship and introducing different alkaline groups to optimize the proton transport microenvironment within the membrane, the modified amphoteric membrane exhibits improved mechanical properties and increased ion selectivity, which is conducive to large-scale promotion and application.

A series of amphoteric SPEEK PEMs were prepared by inducing the reaction of the $-SO_3H$ groups on the SPEEK with the -NH_2 or imidazole groups of the modifier using 1,1 '-carbonyl diimidazole (CDI) as initiator (Fig. 1a and c) [18,19]. Li et al. [20] prepared amphoteric SPEEK membrane named TA-x and IM-x (x is the alkaline groups content) by introduced tertiary amine and imidazole groups into SPEEK, as shown in Fig. 1 b. In which, $-SO_3H$ groups and alkaline groups were used to construct acid-base pairs, which reduced the water uptake and swelling rate of the membrane, and thus improved its mechanical properties. Gong et al. [21] grafted alkyl side-chains containing quaternary cationic groups onto the SPEEK main-chain (S-DMEAx-BPT) used the same method, and further anchored phosphoric acid (PA) utilized alkaline quaternary cationic groups on the side-chains, promoting rapid proton transfer between PA molecules or between PA and quaternary cationic groups (Fig. 1d). Compared with conventional PA-doped PBI membrane (PA molecules fixed on rigid main-chains), PA fixed on flexible alkyl side-chains can transport protons faster, resulting in excellent proton conductivity (> 223 mS cm^{-1}). In addition, with the help of abundant acid-base ion cross-linking, the membrane exhibited excellent mechanical properties.

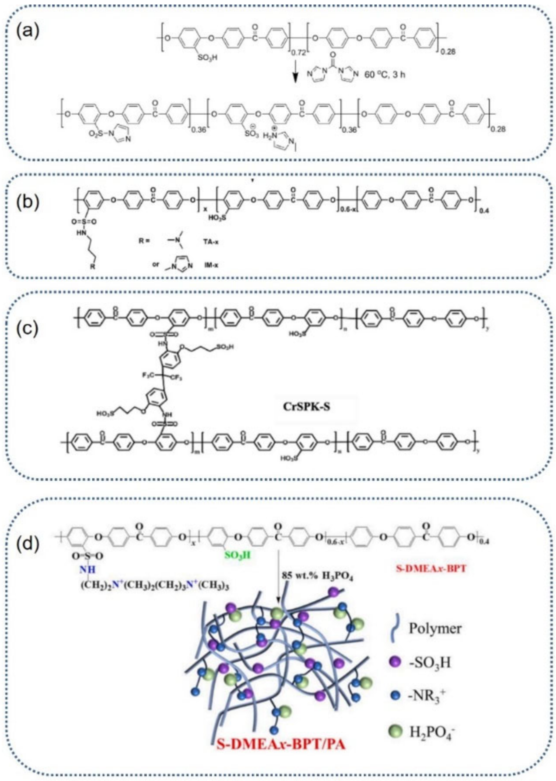

Figure 1. (a) The reaction between the $-SO_3H$ groups of SPEEK with CDI to form a sulfonamide linkage [18]. (b) The structural formula of TA-x and IM-x [20]. (c) The structural formula of CrSPK-x [19]. (d) The fabrication of S-DMEAx-BPT/PA membranes [21].

Polymer modification followed by membrane casting has achieved certain results in promoting proton transport. However, it is inevitable that the random distribution of conductive functional groups in the membrane makes it difficult to achieve substantial breakthroughs in proton conductivity. Pokprasert et al. [22] grafted polyacrylic acid (poly (AA) and/or poly (benzimidazole acrylamide) (poly (BImAm)) onto SPEEK through surface initiated polymerization. The graft of the proton donor (AA) and proton acceptor (BImAm) in the form of a polymer brush allows the SPEEK surface to efficiently accept protons charged from the anode and provide continuous proton transfer. The proton conductivity of membrane with proton acceptor brush (SPEEK-poly (BImAm)) was 1.5 times and 2.9 times higher than that of pristine SPEEK at 170 ºC. While the conductivity of SPEEK-Poly(AA63-stat-BImAm26) membrane grafted with proton acceptor and proton donor was 48.4 times and 7.5 × 10^3 times higher than that of pristine SPEEK in anhydrous (170 ºC) and aqueous (90 ºC) states, respectively. It is proved that proton conducting substances such as carboxylic acids and imidazole groups can be grafted on the surface of SPEEK membrane in the form of polymer brushes to construct proton transfer channels, in which the proton transfer mechanism mainly depends on the proton jumping on the brush, that is, the Grotthuss mechanism.

2.2. Non-covalent Modification

It is difficult to balance the high proton conductivity and low vanadium ion permeability of single component SPEEK membrane. To further improve the comprehensive performance of SPEEK proton exchange membrane, the blending method were used to prepare a high-performance

SPEEK amphoteric composite membrane. The so-called SPEEK amphoteric composite membrane is prepared by introducing a filler containing cationic groups into the pristine SPEEK matrix. Wherein, the filling materials can be organic or inorganic. By introducing filler materials, it is possible to reconstruct the hydrophilic/hydrophobic microphase separation structure within the membrane and induce the formation of proton transport channels at the interface. Simultaneously the dimensional stability, thermal stability and chemical stability are enhanced by the acid-base interaction between the filling material and SPEEK polymer, thus extending the service life of the composite SPEEK amphoteric proton exchange membrane.

2.2.1. Blending with Inorganic Materials

The swelling rate and vanadium ion permeability of SPEEK mmembranes can be effectively reduced by introducing inorganic fillers into the polymer matrix. Interfacial interactions such as hydrogen bond, acid-alkali interaction and ionic bond between alkaline inorganic fillers and SPEEK polymer matrix are conducive to reducing the swelling rate of SPEEK mmembranes. At the same time, interface interactions can also be used to adjust the size of proton transport channels, constructing efficient proton transport channels that are both conducive to proton transport and can hinder the passage of vanadium ions, thereby improving the ion selectivity of composite membranes. In addition, the high mechanical strength and corrosion resistance of inorganic fillers are also helpful to improve the mechanical properties and chemical stability of SPEEK-based amphoteric composite membranes.

Esmaeilzadeh et al. [23] coated polydopamine (PDA) on the surface of multi-walled carbon nanotubes (MWCNT-COOH) to obtain nanofillers containing alkaline groups (P@MWCNTs), and prepared amphoteric composite membrane (SPEEK/P@MWCNT) after incorporated them into SPEEK matrix in different contents. The results indicate that the dimensional stability of composite membrane was improved by 32% compared to pristine SPEEK due to the decrease in water absorption (Fig. 2a). In addition, the proton conductivity of SPEEK/P@MWCNT is significantly increased to 0.064 S cm−1 with the addition of 3.5 wt% P@MWCNTs. Based on the interface energy, the contribution of SPEEK/P@MWCNT interface to proton conduction was investigated. The increased interfacial energy between P@MWCNTs and SPEEK polymer chains indicates that protons can be transferred along the interfacial region between the nanofiller and the matrix.

Sheng et al. [24] grafted 3-(1-vinyl-3-imidazole) propane sulfonate (VIPS) onto graphene oxide (GO) sheets and prepared SPEEK-based hybrid membrane (S/GO-VIPS) by solution blending method. GO-VIPS nanosheets played a physical barrier role to vanadium ions and contain amphoteric acid-base functional groups, which play a good regulatory role in improving proton conductivity and reducing vanadium ion permeability of S/GO-VIPS membrane. Compared with SPEEK and Nafion 117 membrane, S/GO-VIPS-5 had the highest ion selectivity of 24.4 × 103 S min cm-3 indicates that the amphoteric GO-VIPS nanosheets have superior vanadium ion resistance and proton conductivity. Correspondingly, at a current density of 100-200 mA cm-2, S/GO-VIPS-5 exhibits excellent coulombic efficiency (97.4-99.0%), energy efficiency (78.9-66.3%), and self-discharge time (78 hours).

An ideal PEM urgently needs to break through the trade-off between proton conductivity and ion selectivity. The proton channel is one of the keys to control ion screening and proton conductivity. Zhang et al. [25] prepared IM-UIO-66-AS/SPEEK hybrid membrane by introducing imidazole-functionalized MOF fillers (IM-UIO-66-AS) into SPEEK matrix, and reconstructed two proton channels in the hybrid membrane. As shown in Fig. 2b, the internal proton channels of IM-UIO-66-AS and the interfacial proton channels constructed by IM-UIO-66-AS imidazole groups and SPEEK sulfonic acid groups. The proton conductivity of IM-UIO-66-AS/SPEEK hybrid membrane was greatly improved. More importantly, the two reconstructed proton channels blocked the penetration of vanadium ions according to size screening and Donnan repulsion effect respectively, and realized the enhancement of ion selectivity. The energy efficiency was as high as 79.6% at 200 mA cm^2, and significant cycle stability has been maintained in 300 long-term cycle tests.

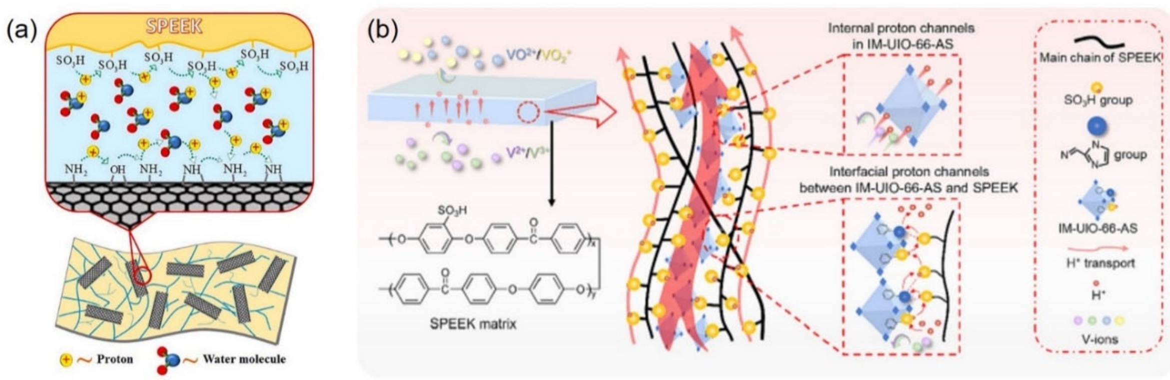

Figure 2. Schematic illustration of the interface proton conduction mechanism in (a) the P@MWCNT/SPEEK membrane [23] and (b) the IM-UIO-66-AS/SPEEK hybrid membrane [25].

2.2.2. Blending with Organic Materials

Blending SPEEK with other organic polymers containing alkaline groups is also an economical and effective method for preparing SPEEK amphoteric membranes. The interfacial acid-base interaction is formed by ion crosslinking to inhibit the movement of molecular chain, which narrows the whole ion channel and reduces the permeability of vanadium ions. For example, converting H^+-SPEEK into Na^+-SPEEK can improve the compatibility of hydrophilic SPEEK with polybenzimidazole (PBI). Due to the internal cross-linking network caused by acid-base interaction, a good balance between ion selectivity and proton conductivity of the amphoteric composite membrane based on SPEEK and PBI has been achieved. At a current density of 80 mA cm^{-2}, a coulombic efficiency of 98.5 % and an energy efficiency of 89.8 % were achieved [26].

Zhang et al. [27] prepared a novel amphoteric PEM by blending three tertiary amine grafted polyphenylene ether (PPO-TTA) with SPEEK. The acid-base pair structure was formed by the tertiary amine group and the sulfonic acid group, in which the hydrogen bond cross-linking network reduced the size of the hydrophilic ion transport channel in the membrane, and effectively reduced the penetration of vanadium ions (Fig. 3a). Meanwhile, the efficient hydrogen bond network structure promoted proton transport. The tertiary amine without acid-base pair was positively charged with protons in acidic environment, which further promoted the construction of hydrogen bond network, enhanced the conduction of protons, and hindered the penetration of vanadium ions through Donnan effect. As the content of tertiary amine groups increases, the coulombic efficiency and energy efficiency of VRFB single cells assembled with SPEEK/PPO-TTA amphoteric membranes were significantly improved due to the establishment of high-performance hydrophilic proton transport channels based on acid-base pair structures and efficient hydrogen bonding networks.

Qian et al. [28] reported a method for developing high-performance PEMs with ideal physical and chemical properties by regulating the main/side-chain proton transport channels of SPEEK matrix through amphoteric side-chain polymers (SPAES). Under the influence of the sulfonyl side-chain of SPAES and the main-chain sulfonic acid of SPEEK, an enhanced synergistic proton transport channel is formed, exhibiting a balance between proton conductivity and permeability (Fig. 3b). The SPEEK/SPAES-15 membrane showed the highest ion selectivity (28.8× 10^3 S min cm^{-3}) against pristine SPEEK (3.9× 10^3 S min cm^{-3}), Nafion 117 (4.0× 10^3 S min cm^{-3}) and Nafion 212 (3.0× 10^3 S min cm^{-3}).

Although the ion selectivity can be improved by the acid-base interaction within SPEEK, the predictability of the channel structure within the membrane is poor. In addition, the microphase structure of polymers is not only affected by internal factors such as segment polarity and distribution, but also by external factors such as solvents and treatment conditions. These influencing factors are complex, making it difficult to accurately construct ordered ion channels in membranes. Therefore, it is necessary to find new channel construction methods, such as the use of ordered nanopore structures or nanofiber long-range ordered structures to enhance the designability and regulability of ion channels in membranes, and improve the order, continuity and stability of channel structures.

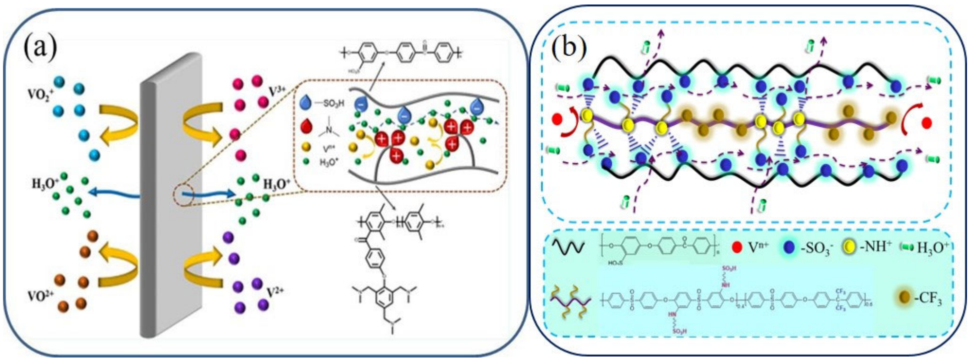

Figure 3. Proton conduction mechanism of (a) the SPEEK/PPO-TTA amphoteric membrane [27] and (b) the SPEEK/SPAES membrane [28].

3. Summary

As a type of non-fluorosulfonated aromatic PEM materials, sulfonated aromatic polymers have attracted much attention in recent years. As a representative of sulfonated aromatic polymer, SPEEK has a simple synthesis process and low cost, which is easy to meet the requirements of large-scale industrial production, and has great application prospects as a PEM material. At high degree of sulfonation, SPEEK membrane has a hydrophilic/hydrophobic phase separation structure similar to Nafion membrane, but followed a high water uptake capacity and excessive swelling behavior or even dissolve, resulting in a significant decline in dimensional and mechanical stability and serious vanadium ion penetration. However, the proton transport channel in SPEEK membrane with low sulfonation degree is narrow, and there are many forks and many dead ends, which hinder the transmission of protons in the membrane, resulting in low proton conduction capacity of SPEEK membrane, and cannot meet the requirements of VRFB. Therefore, the most challenging problem of SPEEK membranes in VRFB applications is that the trade-off between high proton conductivity and low vanadium ion permeability, which is also a common problem in sulfonated aromatic polymer PEMs. The introduction of acid-base functional groups can promote the ion selectivity in SPEEK membrane to a certain extent. This work compares and analyzes the structure and performance of several different SPEEK amphoteric PEMs to balance the relationship between proton conductivity and vanadium ion permeability. The covalent modification of SPEEK was through the adjustment of membrane structure, while the non-covalent modification was through the interfacial acid-base interaction to achieve the improvement of proton conductivity and the reduction of vanadium ion permeability in the membrane. The acid-base pair structure was formed by the alkaline groups and sulfonic acid groups, and the hydrogen bond cross-linking network reduced the size of the hydrophilic ion transport channel in the membrane, effectively reduced the penetration of vanadium ions, and obtained high performance SPEEK amphoteric membrane. The further development and research of SPEEK membrane should focus on but not be limited to the construction of directional proton transport channels.

Acknowledgment

This work was supported by the Jiangsu Province 2023 College Student Innovation and Entrepreneurship Training Program Project [202311998048Y].

References

[1] Messaggi, M.;Canzi, P.;Mereu, R.; et al. Analysis of flow field design on vanadium redox flow battery performance: Development of 3D computational fluid dynamic model and experimental validation. Appl. Energy. Vol. 228 (2018), p. 1057–1070.

[2] Dai, L.; Jiang, Y.; Meng, W.; et al. Improving the electrocatalytic performance of carbon nanotubes for VO2+/VO2+ redox reaction by KOH activation. Applied Surface Science. 2017, Vol. 401 (2017), p. 106–113,

[3] Jiang, B.;Yu, L.;Wu, L.; et al. Insights into the impact of the nafion membrane pretreatment process on vanadium flow battery performance. ACS applied materials & interfaces. Vol. 8 (2016) No. 19, p.12228–12238.

[4] Shi Y, Eze C, Xiong B, et al. Recent development of membrane for vanadium redox flow battery applications: A review. Applied Energy, Vol. 238 (2019), p. 202-224.

[5] Zhang, D.; Xu, Z.; Zhang, X.; et al. Oriented proton-conductive nanochannels boosting a highly conductive proton-exchange membrane for a vanadium redox flow battery. ACS applied materials & interfaces. Vol. 13 (2021) No. 3, p, 4051−4061.

[6] BAZRGAR B. M, MOUSAVI S A. Effect of casting solvent on the characteristics of Nafion/TiO2 nanocomposite membranes for microbial fuel cell application. International Journal of Hydrogen Energy, Vol. 41 (2016) No. 41, p. 476-482.

[7] Sun C, Chen J, Zhang H, et al. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. Journal of Power Sources, Vol. 195 (2010) No. 3, p. 890-897.

[8] Rozi R. J, Jones D J. Non-fluorinated polymer materials for proton exchange membrane fuel cells. Annual Review of Materials Research, Vol. 33 (2003) No. 1, p. 503-555.

[9] Wang N, Yu J, Zhou Z, et al. SPPEK/TPA composite membrane as a separator of vanadium redox flow battery. Journal of Membrane Science, Vol. 437 (2013) No. 12, p. 114-121.

[10] Krathumkhet N, Vongjitpimol K, Chuesutham T, et al. Preparation of sulfonated zeolite ZSM-5/sulfonated polysulfone composite membranes as PEM for direct methanol fuel cell application. Solid State Ionics, Vol. 319 (2018), p. 278-284.

[11] Lee Y, Kim S, Maljusch A, et al. Polybenzimidazole membranes functionalised with 1-methyl-2-mesitylbenzimidazolium ions via a hexyl linker for use in vanadium flow batteries. Polymer, Vol. 174 (2019), p. 210-217.

[12] Ding M, Ling X, Yuan D, et al. SPEEK membrane of ultrahigh stability enhanced by functionalized carbon nanotubes for vanadium redox flow battery. Front Chem, Vol. 6 (2018), p. 286.

[13] Wang F, Wang G, Zhang J, et al. Novel sulfonated poly(ether ether ketone)/oxidized g-C3N4 composite membrane for vanadium redox flow battery applications. Journal of Electroanalytical Chemistry, Vol. 797 (2017), p. 107-112.

[14] Ji Y, Tay Z Y, Li S F Y. Highly selective sulfonated poly(ether ether ketone)/titanium oxide composite membranes for vanadium redox flow batteries. Journal of Membrane Science, Vol. 539 (2017), p. 197-205.

[15] Xiaobin Y.; Linlin Y.; Feitian R.; et al. Interface-confined surface engineering constructing water-unidirectional Janus membrane. Journal of Membrane Science. Vol.576 (2019), p. 9–16.

[16] Ran J.; Wu L.; He Y.; et al. Ion exchange membranes: New developments and applications. Journal of Membrane Science. Vol. 522 (2017), p. 267–291.

[17] Chien-Hong L.; Ming-Chien. Y.; Hwa-Jou W. Amino-silica modified Nafion membrane for vanadium redox flow battery. Journal of Power Sources. Vol. 282 (2015), p. 562–571.

[18] Bhushan, M.; Kumar, S.; Singh, A. K.; et al. High-performance membrane for vanadium redox flow batteries: Cross-linked poly (ether ether ketone) grafted with sulfonic acid groups via the spacer. Journal of Membrane Science. Vol. 583 (2019), p. 1−8.

[19] Lei, L.; Zhu, X.; Xu, J.; et al. Highly stable ionic-covalent cross-linked sulfonated poly (ether ether ketone) for direct methanol fuel cells. Journal of Power Sources. Vol. 350 (2017), p. 41−48.

[20] Xu, Z.; Tang, H.; Li, N. Enhanced proton/iron permselectivity of sulfonated poly (ether ether ketone) membrane functionalized with basic pendant groups during electrodialysis. Journal of Membrane Science. Vol. 610 (2020), p. 118227.

[21] Juan W.; Fei W.; Xiangjian F.; et al. Phosphoric acid-doped Gemini quaternary ammonium-grafted SPEEK membranes with superhigh proton conductivity and mechanical strength for direct methanol fuel cells, Journal of Membrane Science. Vol. 672 (2023), p. 121431.

[22] Adisak P.; Patrick T.; Suwabun C. Proton donor/acceptor copolymer brushes on sulfonated poly(ether ether ketone) membrane: An approach to construct efficient proton transfer pathway in polymer electrolyte membrane fuel cell. Polymer. Vol. 240 (2022), p. 124523.

[23] Zahra E.; Mohammad K.; Ahmad M. S.; et al. Linking interfacial energies with proton conductivity in sulfonated poly (ether ether ketone) nanocomposite. Polymer. Vol. 230 (2021), p. 124067.

[24] Jiaxuan S.;, Lang L.; Haixia W.; et al. An ultrahigh conductivity and efficiency of SPEEK-based hybrid proton exchange membrane containing amphoteric GO-VIPS nanofillers for vanadium flow battery. Journal of Membrane Science. Vol. 669 (2023), p. 121326.

[25] Denghua Z.; Wenjie Y.; Yue Z.; et al. Reconstructing proton channels via Zr-MOFs realizes highly ion selective and proton-conductive SPEEK-based hybrid membrane for vanadium flow battery. Journal of Energy Chemistry. Vol. 75 (2022), p. 448–456.

[26] Dongju C.; Xiaoli C.; Lifang D.; et al. Advanced acid-base blend ion exchange membranes with high performance for vanadium flow battery application. Journal of Membrane Science. Vol. 553 (2018), p. 25-31.

[27] Zhang, H.; Yan, X.; Gao ,L. et al. Novel triple tertiary amine polymer-based hydrogen bond network inducing highly efficient proton-conducting channels of amphoteric membranes for high-performance vanadium redox flow battery. ACS applied materials & interfaces. Vol. 11 (2019) No. 5, p. 5003−5014.

[28] Penghua Q.; Haixia W.; Lei Z.; et al. An enhanced stability and efficiency of SPEEK-based composite membrane influenced by amphoteric side-chain polymer for vanadium redox flow battery. Journal of Membrane Science. Vol. 643 (2022), p. 120011.