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복합막 기반 바나듐 레독스 흐름 전지의 최근 발전

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Recent Advance on Composite Membrane Based Vanadium Redox Flow Battery

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요 약: VRFB에 사용되는 막의 수송 능력은 배터리 성능에 필수적인 요소이다. 탁월한 배터리 성능을 위해서는 높은 양성자 전도도와 낮은 바나듐 이온 투과도가 달성되어야 한다. 하지만 양성자 전도도와 바나듐 이온 투과도 사이에는 상충관계가 존재한다. 따라서 이 상충관계를 해결하는 것이 VRFB의 발전에 필수적이다. 또한 높은 쿨롱 효율, 전압 효율 및 에너지 효율을 유지하는 것이 고성능 VRFB를 위해 필수적이다. 최근 복합막과 SPEEK 막을 중심으로 나피온 막의 기존 한계를 극복하기 위한 다양한 시도가 이루어지고 있다. VRFB은 이 논문에서 검토하는 복합막에서 충전식 배터리의 필수 등급이다.

Abstract: The transport properties of membranes used in vanadium redox flow batteries (VRFB) are fundamental in battery performance. High proton conductivity and low vanadium ion permeability must be achieved to achieve high battery performance. However, there is a trade-off relationship between proton conductivity and vanadium ion permeability. So, solving this trade-off relationship is crucial in VRFB development. Also, maintaining high coulombic efficiency, voltage efficiency, and energy efficiency is essential for high-performing VRFB. Recently, various attempts have been made, primarily on composite membranes and SPEEK membranes, to overcome the existing limit of Nafion membranes. VRFB is an essential class of rechargeable battery in composite membranes reviewed here.

Keywords: *membrane, VRFB, battery, proton conductivity*

1. Introduction

Renewable energy, such as solar energy and wind energy, is attracting significant attention due to severe environmental pollution and depletion of natural resources. Because of renewable energy's fluctuating and intermittent nature, highly stable and efficient energy storage technology is required for sound power output[1,2]. So far, many battery technologies have been developed. Still, among them, VRFB is considered as perfect candidate due to its high chemical stability, high efficiency, long life cycle, and environmental friendliness. VRFB comprises liquid electrolytes, two electrodes, and an ion-conductive membrane. Ion conductive membrane separates two redox couples which are VO^{2+}/VO^{2+} and V^{3+}/V^{2+}, in the catholyte and anolyte[3-5].

An ideal ion conductive membrane should show the property of high proton conductivity while maintaining

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low vanadium ion permeability. Nafion membrane is commonly used as an ion conductive membrane as it offers good chemical stability and high proton conductivity. However, due to the high price, high vanadium ion permeability, and high water migration, there is a limit to the development of VRFB using the Nafion membrane[6,7]. To overcome these problems, many attempts are being made by modifying the structure of the Nafion membrane or synthesizing other components to the Nafion membrane. Some shots were successful, but an alternative is still needed because of the high price of the Nafion membrane[8,9]. Some composite membranes and SPEEK membranes showed outstanding performance when used in VRFB[10]. In this review we discuss the composite membrane based on various sulfonated membrane.

2. Composite Membrane

Sizov *et al*. demonstrated Celgard films that are covered with PIM-1 to be used in VRFB[11]. To compare with original Celgard film (iCel), two different membranes with different loading of PIM-1 were built. One is Celgard with deposition of 0.2 mg/cm^2 PIM which is Cel_PIM_1 and the other is Celgard with deposition of 0.4 mg/cm^2 PIM which is Cel_PIM_2. Compared to the original Celgard membrane, newly built membranes showed smaller pore diameter because when the PIM-1 is deposited, it creates a sleek layer on the outer surface of Celgard and also permeates into the porous matrix. For Cel_PIM_1, the surface area of pores significantly decreased from 21.4% to 9.5% and their Feret diameter decreased from 121nm to 90 nm. Cel_PIM_2 showed more dramatic reduction in both properties. So, there was significant change in transport properties of the demonstrated membranes compared to the original membrane. The nanoporous structure allowed reduced vanadium ion permeability by size-screening of H_3O^+/hydrated vanadium ions. So, the high ion selectivity was observed while maintaining high proton conductivity.

Thong *et al*. created an advanced coupled layer membrane, which involves applying an ultra-thin ionomer coating comprised of perfluorosulfonic acid (PFSA) polymer and functionalized alkoxysilane (FAS) onto one surface of porous polyethylene substrate[12]. This membrane was produced easily using automatic control coater. When the membrane was observed at both sides of the coupled layer, it showed low diffusion coefficient. Even after the unit cell cycling, it showed good cycling performance and the morphology of the membrane remained constant. Also, chemical stability was greatly improved because of the dense and stable PFSA layer.

Yang *et al*. demonstrated anomalously high elastic modulus of a poly(ethylene oxide)-based composite polymer electrolyte (CPE) by using a method of synthesizing materials that involves crosslinking poly(ethylene oxide) (xPEO) in the exsistence of woven glass fiber (GF)[13]. This trial was to achieve high ionic conductivity and mechanical strength simultaneously. It showed good mechanical strength because interaction of xPEO and GF created much more hydrogen and ionic bondings. The addition of a plasticizer, such as tetraglyme, led to the attainment of good ionic conductivity. The trifluoromethanesulfonate anions attached to the xPEO matrix, facilitating good transport of Li+ cations through interaction with the plasticizer. And when tested through galvanostatic cycling, CPE showed stable cycling for more than 3000 h in a Li-metal symmetric cell.

3. PVA Based Composite Membrane

Yu *et al*. demonstrated sulfonated polyimide (SPI) / polyvinyl alcohol (PVA) composite membrane[14]. Due to the good barrier and high hydrophilicity of PVA, the newly built membrane showed better hydrolysis stability and vanadium ion resistance compared to original SPI membrane. Also compared to the Nafion membrane, new membrane presented property of lower self-discharge rate along with higher coulombic efficiency, and higher energy efficiency. This is because of the high proton selectivity of composite membrane.

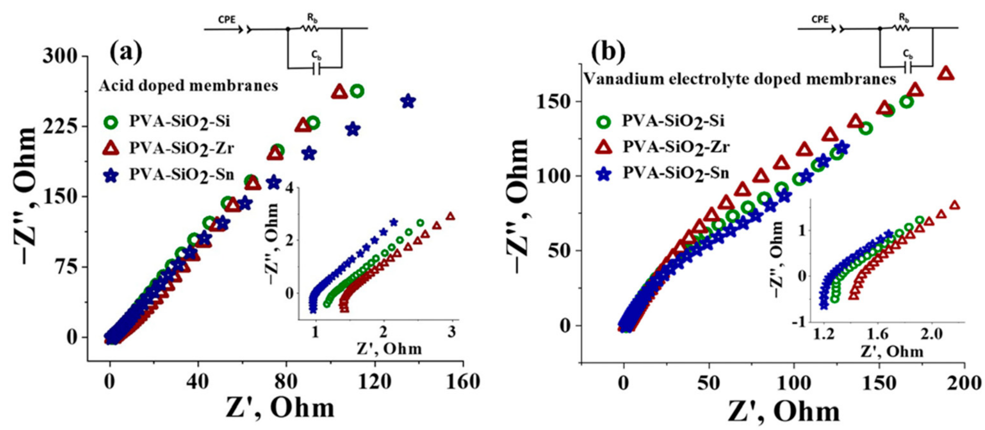

Fig. 1. Impedance spectra of surface-modified PVA-SiO_2 membranes, (a) acid-doped membranes and (b) vanadium-electrolyte-doped membranes (Reproduced with permission from Sreenath *et al.*[15], Copyright 2023, MDPI).

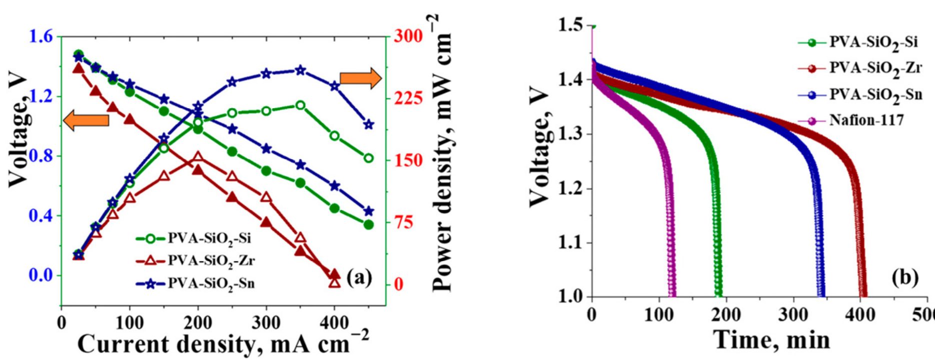

Fig. 2. (a) Polarization curves and (b) self-discharge of VRFB assembled with PVA-SiO_2-Si, PVA-SiO_2-Zr and PVA-SiO_2-Sn (Reproduced with permission from Sreenath *et al.*[15], Copyright 2023, MDPI).

Furthermore, new membrane showed good performance continuously up to 100 cycles without notable decrease in energy efficiency.

Sreenath *et al.* prepared a composite membrane of PVA with silicon oxide (SiO_2) for application in VRFB[15]. When these membranes are coated with silicon (Si), zirconium (Zr) or tin (Sn) then it has excellent stability of VO_2^+ in sulfuric acid. These membranes have good conductivity and usually better columbic efficiency then commercial Nafion-117 membrane. Among them PVA-SiO_2-Sn has highest power density of 260 mW cm^{-2}. Performance of different membranes in VRFB are presented in Fig. 1 and 2.

Zhang *et al*. fabricated ultrathin composite membrane through the zwitterionic interface engineering between conductive polybenzimidazole (PBI) and porous polyethylene (PE) substrate[16]. In this process, covalent reaction happens between polydopamine and zwitterionic sulfonated 3-dimethylaminopropylamine (DMAPAPS) which leads to building new membrane thickness up to 10 μm. Newly built membrane showed good mechanical properties, high dimensional stability, low vanadium ion permeability and high proton conductivity. And the ion selectivity was maintained three times greater. These properties were derived from the unique functioning of zwitterionic interface engineering. Firstly, zwitterionic interface engineering makes the membrane structure more compact and stronger which is the result of strong electrostatic interaction between sulfonic groups of DMAPAPS and imidazole groups of PBI. Secondly, zwitterionic interface engineering prevent permeation of vanadium ions through the Donnan

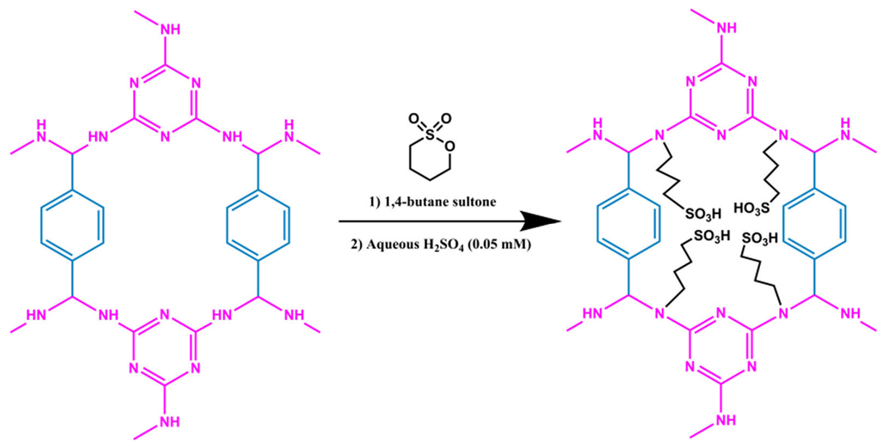

Fig. 3. Synthesis of SSNW-1 (Reproduced with permission from Li *et al.*[19], Copyright 2022, American Chemical Society).

exclusion effect. This is due to the positively charged amino groups in DMAPAPS. Thirdly, zwitterionic interface engineering enables more protons to migrate through "acid-base" pair.

4. Sulfonated Poly (ether ether ketone) Based Composite Membrane

Afzal *et al.* demonstrated oxidized black phosphorous nanosheet (O-bPn) to improve ion selectivity of sulfonated poly (ether ether ketone) (SPEEK) membrane[17]. O-bPn can block vanadium ion effectively because of its distinctive 2D puckered lattice. And the incorporation of O-bPn into the SPEEK matrix promoted proton conductivity. It is because the oxygen-incorporating groups on O-bPn produced more proton carriers which are strong acid and made hydrogen bonds with $-SO_3H$ in polymer matrix. So, compared to original SPEEK membraned, newly built membrane showed greater ion selectivity. Also compared to the Nafion membrane, it showed 7% higher coulombic efficiency, 10% higher energy efficiency and higher capacity after 100 cycles.

Chola *et al.* proposed SPEEK with covalent organic frameworks (COF)[18]. The sulfonated COF (SCOF) blended membrane was prepared with 10%, 15% and 20% loading. Because of the higher ionic conductivity and hydrophilicity after SCOF loading, new membranes showed improved capacity about 36% compared to the original SPEEK membrane. When it comes to achieving the best possible battery performance, a loading exceeding 15% wasn't advisable. This is because such a high loading could contribute to dendrite growth on the membrane surface.

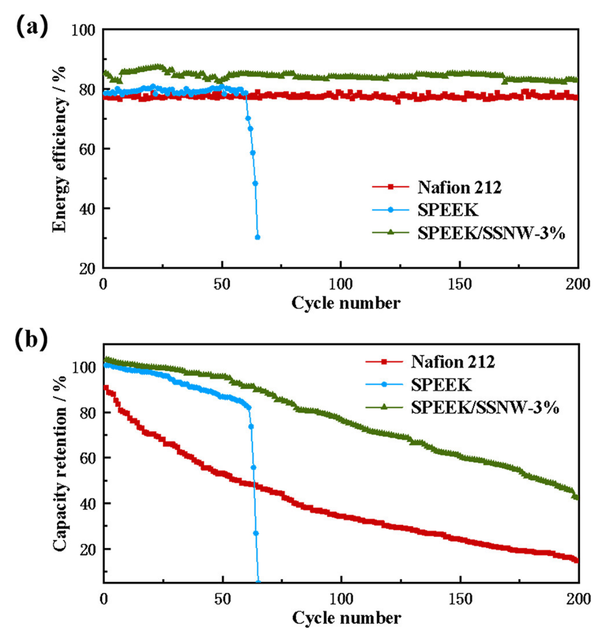

Fig. 4. (a) Cycle performance and (b) discharge capacity retention of VRFBs equipped with SPEEK/SSNW-3%, SPEEK, and Nafion 212 at 80 mA cm^{-2} (Reproduced with permission from Li *et al.*[19], Copyright 2022, American Chemical Society).

Li *et al.* prepared SPEEK based ionic exchange membrane by incorporating sulfonated Schiff base network-type (SSNW-1) covalent organic frameworks[19].

Due to the size screening of SSNW-1, new membrane showed lower vanadium permeability compared to the original SPEEK membrane and Nafion 212 membranes. Also, it showed advanced thermal stability, mechanical properties. For the Coulombic efficiency (CE), new membrane showed 99.8% whereas original SPEEK membrane and Nafion 212 membranes showed 95.4% and 90.4% respectively. For voltage efficiency (VE), new membrane showed 85.9% whereas original SPEEK membrane and Nafion 212 membranes showed 82.6% and 85.0% respectively.

Qian *et al*. demonstrated the amphoteric composite membrane made of SPEEK membrane containing imidazole chains (SPEEK-IM) and polyethersulfone with sulfonated side chain which has covalently cross-linked perfluoroalkyl chains (CSPF)[20]. The imidazole and sulfonic acid groups in the CSPF regulated the local semi interpenetrating network. So, the many channels that can transport protons were constructed. Compared to Nafion 212 membrane, SPEEK-IM/CSPF membrane showed higher proton conductivity and ion selectivity. This is because of the interaction between ionic imidazole-sulfonic acid and covalently linked perfluoroalkyl chain of CSPF offered balance between conduction of proton and ion selectivity. Also, it showed high energy efficiency up to 87.5%.

Qian *et al*. demonstrated SPEEK based membrane which contains amphoteric functionalized nanofibrous network (SP@f) having three-dimensional interlaced structure[21]. This new membrane is called S/SP@f-10. Due to the large specific surface area and aspect ratio of nanofibers, S/SP@f-10 showed high concentration of proton carriers and enough hydrogen bonds to transfer proton. So, it showed better proton conductivity compared to the original SPEEK membrane and Nafion 212 membrane. Also, because of the acid-base interaction and interconnected network structure of SP@f, S/SP@f-10 showed improved ion selectivity and chemical stability compared to original SPEEK membrane and Nafion 212 membrane. Moreover, voltage efficiency (up to 93%) and energy efficiency (up to 87.5%) of S/SP@f-10 were both higher than original SPEEK membrane and Nafion 212 membrane.

Qian *et al*. developed novel type of composite membrane by the insertion of various proportions of sulfonated poly(aryl ether sulfone) (SPAES), which contains sulfoalkylamine chains. This innovative material is known as SPEEK-based composite membrane[22]. The new membrane is called SPEEK/SPAES-15. By the formation of synergistic proton transport channel provoked by the sulfoalkyl groups of SPAES, trade off relationship between proton conductivity and permeability was solved. SPEEK/SPAES-15 showed ion selectivity of 28.8×10^3 S min cm^{-3} which is 7 times higher than original SPEEK membrane. Also, SPEEK/SPAES-15 showed higher energy efficiency and coulombic efficiency compared to original SPEEK membrane, Nafion 117 membrane and Nafion 212 membrane. Even after 600-time charge-discharge cycles, it maintained good structural stability and durability.

5. Conclusions

Due to the technical limitation and high price of the Nafion membrane, the need for a new membrane for VRFB has emerged. Many attempts have been made in composite membranes and SPEEK membranes. Some successfully broke down the trade-off relationship between proton conductivity and vanadium ion permeability while maintaining high coulombic efficiency, voltage efficiency, and energy efficiency. Especially ultrathin composite membrane through the zwitterionic interface engineering between conductive polybenzimidazole (PBI) and porous polyethylene (PE) substrate seemed successful. Engineered zwitterionic interfacial successfully induced three types of effects simultaneously. Strong electrostatic interaction made membrane structure more compact and robust, the Donnan exclusion effect restricted vanadium ion permeability, and “acid-base” pairs formed more proton channels. So, it can be the most promising way to improve the VRFB performance. This review discusses a sulfonated membrane based on different membranes for redox flow batteries.

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