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Development of biomaterial-based membranes for sustainable redox flow batteries

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ABSTRACT

As the key component in the redox flow battery (RFB) systems, the ion exchange membrane (IEM), which facilitates proton transport while preventing electrolyte crossover, plays an important role in determining the overall system performance. However, up till now, the common commercial Nafion membranes still face the challenges raised from high cost and environmental concerns. There is an urgent demand for the development of novel membranes with low cost, high performance, and environmental friendliness. Recently, there has been growing interest in bio-sourced materials such as lignin, cellulose, and chitosan for membrane fabrication. These renewable materials offer low-cost and sustainable alternatives, providing opportunities to improve the economic viability of RFB technology while meeting environmental regulations. This review focuses on the progress of biomaterial-based membranes developed for RFBs. The potentials and limitations of various bio-sourced materials as membrane matrices and additives are evaluated and discussed. Furthermore, future research directions are suggested to provide insights for the development of next-generation membranes that meet the stringent requirements of sustainable long-term energy storage solutions.

Introduction

The reliance on fossil fuels has led to profound environmental crises such as global warming and air pollution [1,2]. It has become an urgent need to pursue the transition to renewable energy [3]. As the key to the utilization of renewable energy sources, reliable energy storage solutions are essential for effectively ensuring consistent power supply and enhancing grid stability. In recent years, redox flow batteries (RFBs) have been considered the promising electrochemical technologies for clean and sustainable energy storage [4,5]. They have many advantages, such as long cycle life, environmental friendliness, room temperature operation, high safety, high discharge capacity, fast response and high efficiency for long-term application. As one of the most critical components in RFBs, the ion exchange membrane (IEM) separates the positive and negative electrode compartments in the battery, allowing proton transport to complete the circuit while preventing electrolyte crossover [6]. Therefore, the properties of the IEM play a large role in affecting the overall performance of the RFBs. Ideally, the IEM is expected to possess high ion selectivity, high proton conductivity, good mechanical properties and dimensional stability. At the same time, the membrane must also have excellent chemical stability and maintain a long cycle life under the strong oxidative and acidic conditions of the RFB electrolytes [7]. Currently, the most widely used IEMs in RFBs is the Nafion series of perfluorosulfonic acid (PFSA) membranes produced by DuPont Company [10,8,9]. These cation exchange membranes (CEMs) were proven to have high proton conductivity and ion selectivity. Meanwhile, they demonstrated good chemical stability in harsh electrolyte environments, making them suitable for the wide range of RFB types. However, one major challenge of the Nafion series membranes is their high capital cost of ~ $ 500–800 m^{-2}, which can account for over 40 % of the total cost of RFB systems [11]. In addition, the production complexity and environmental issues caused by the formation of fluorinated compounds and toxic intermediates also limit the wide application of these membranes, especially under the current tightening environmental regulations. Therefore, effective strategies must be developed to reduce the cost of conventional membranes while

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maintaining their superior performance.

In the past two decades, bio-sourced materials such as lignin and celluloses have gained significant attention for their potential in energy storage technologies [12,13]. As the candidates to replace conventional petroleum-based materials, these materials derived from renewable resources have low-cost and abundant natural availability [14]. Thereby, they are believed to possess great promise for cost-effective and sustainable membranes for the RFB systems (Fig. 1) [15,16]. This review explores the application of various bio-sourced materials in the development of membranes for RFB technologies, both as membrane matrices and additives. The effects of the materials on membrane-level and battery-level performance are evaluated. The potential of these sustainable materials to enhance membrane performance while reducing costs and addressing environmental concerns are highlighted.

Bio-sourced material as membrane matrix

Biomass-derived cellulose fibers are promising materials for matrices fabrication of the IEM due to its numerous advantageous properties [17,18]. As a naturally renewable material, it is abundant, cost-effective, and exhibits exceptional mechanical performance. Furthermore, cellulose can form networks across a wide range of dimensions, making it versatile for various applications. Its biopolymeric nature is characterized by polymers chains that are rich in hydroxyl (-OH) groups, facilitating extensive chemical modification [19]. This inherent reactivity allows for the introduction of cationic or anionic functional groups, enabling the tailored optimization of cellulose to meet specific requirements in diverse applications. Yang et al. reported the use of cellulose nanofibrils (CNFs) membrane made from wood-derived carboxymethylated nanocellulose (NC) [20,21]. The CNFs are usually produced by mechanical grinding process to release the stacked nanofibrils from bulk cellulose. The obtained CNFs can be formed into thin films at a reasonable cost by simple solution casting or filtration processes. The author applied 1,2,3,4-butanetetracarboxylic acid (BTCA) as the cross-linking agent to fabricate the CNFs membrane (Fig. 2(a)). The cross-linked structure restricts the swelling of the fibril entanglement network and thereby enhances the size exclusion for redox molecules. Meanwhile, the cross-link between cellulose and BTCA introduces unreacted carboxyl groups with negative charges, which can promote proton transport and improve ion selectivity due to stronger Donnan exclusion effects. The authors examined the effect of cross-linking agent content on the membrane performance [21]. When the content of BTCA increased, the density of negative charges increase and thereby promote cation transport, but excessive cross-linkers destroyed the ordered membrane structure and expanded the size of the nanochannels. However, the NC membrane was found to have relatively lower proton conductivity and higher electrical resistance than Nafion membrane, which lead to limited voltage efficiency (VE) and energy efficiency (EE) of the RFB. In 2021, Jiang et al. utilized NC as the matrix material and sulfonated polyethersulfone (SPES) as the filler material to prepare a core-shell structure NC reinforced SPES hybrid membrane (CNC-SPES) [22]. The hydrophilic NC fibers led to higher water absorption rate of the composite membrane than the Nafion 212 membrane. Meanwhile, the strong hydrogen bonds inside the NC network provide enhanced mechanical strength for the composite membrane. To further improve the chemical stability of NC fibers and inhibit the penetration of vanadium ions, the authors applied the in-situ sol-gel method to covalently synthesize a dense silica layer on the surface of NC fibers. The fabricated composite membrane demonstrated better low vanadium permeability of 3.67×10^{-7} cm^2 min^{-1} due to the blocking effect of silica-coated NCs, while the proton conductivity was impaired (Fig. 2(b)). In the full battery tests, the VRFB equipped with the composite membrane showed comparable efficiencies to the Nafion 212 membrane. In 2022, Crispin et al. reported a membrane made from wood-derived oxidized sulfonated nano-fibrillated cellulose [23]. The fabrication process began with the selective oxidation and sulfonation of the bleached fibers, which incorporated aldehyde and sulfonic acid (-SO_3H) groups into the cellulose structure. The modified fibers were then processed into nanofiber gel form by high pressure homogenization and formed into membranes by vacuum filtration. In this process, hemiacetals were formed from aldehyde groups to achieve inter- and intramolecular crosslinks. The fabricated sulfonated cellulose membrane contains abundant -OH and -SO_3H groups and possesses small pore size, therefore enabling more efficient proton transport than other cations. However, since the density of negatively charged groups in the sulfonated cellulose membrane is less than that of Nafion 115, it exhibits weaker cation selectivity. The performance of the fabricated membrane was examined in an acidic aqueous organic RFB with alizarin red S and tiron solutions as negative and positive electrolytes, respectively. At a charge-discharge current density of 4.0 mA cm^{-2}, the RFB assembled with sulfonated cellulose-based membrane showed higher capacity retention of 63 % than the Nafion-based battery (5 %) after 90 cycles (Fig. 2(c)). The authors explained that it was because the high water content in the cellulose-based membrane suppressed the electroosmotic drag, thereby alleviating the crossover of alizarin red S. Kheawhom et al. reported the application of carboxymethyl cellulose (CMC) in membrane fabrication for the zinc-iodine RFB [24]. The CMC is a cellulose derivative with good film-forming capabilities which generally formed from the plant cell walls. However, it possesses insufficient mechanical strength and conductivity, which can be enhanced by blending with other salts or polymers. In this work, the author incorporated polyvinyl alcohol (PVA) containing rich -OH groups to synthesize the CMC/PVA membranes via the casting process. The effects of CMC/PVA ratios on the membrane properties were examined. The increased PVA can enhance the ionic conductivity of the composite membranes due to more hydrogen bond between PVA and CMC (Fig. 2(d)). However, too high PVA content would result in more serious cross-contamination of iodine and polyiodide. Consequently, the composite membrane with a higher CMC content demonstrated elevated overpotential in battery, yet exhibited greater stability during long-term cycling tests.

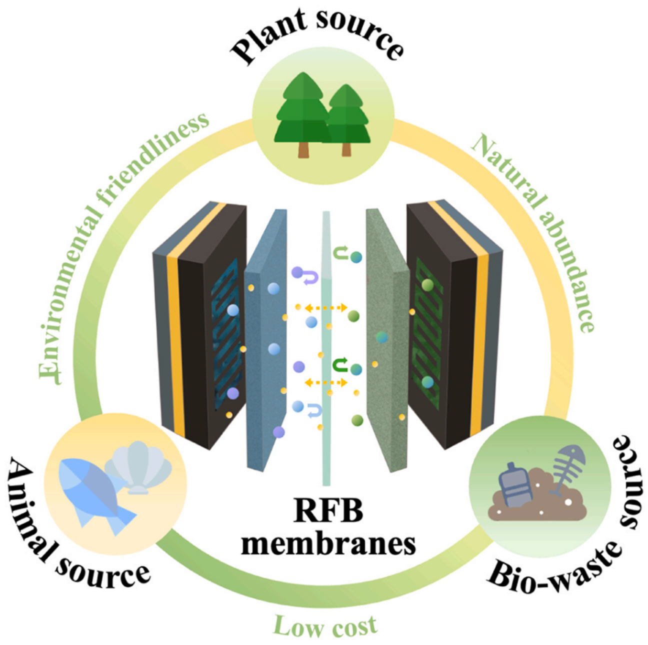

Fig. 1. Development of sustainable membranes for RFBs through bio-sourced materials.

In addition, the application of bacterial cellulose (BC) was also reported [25]. The BC is commonly synthesized through the microbial fermentation process of Acetobacter xylinum and Gluconacetobacter hansenii bacteria on industrial scale [26,27]. It contains the coherent hydrophilic three-dimensional network, which not only provides porous

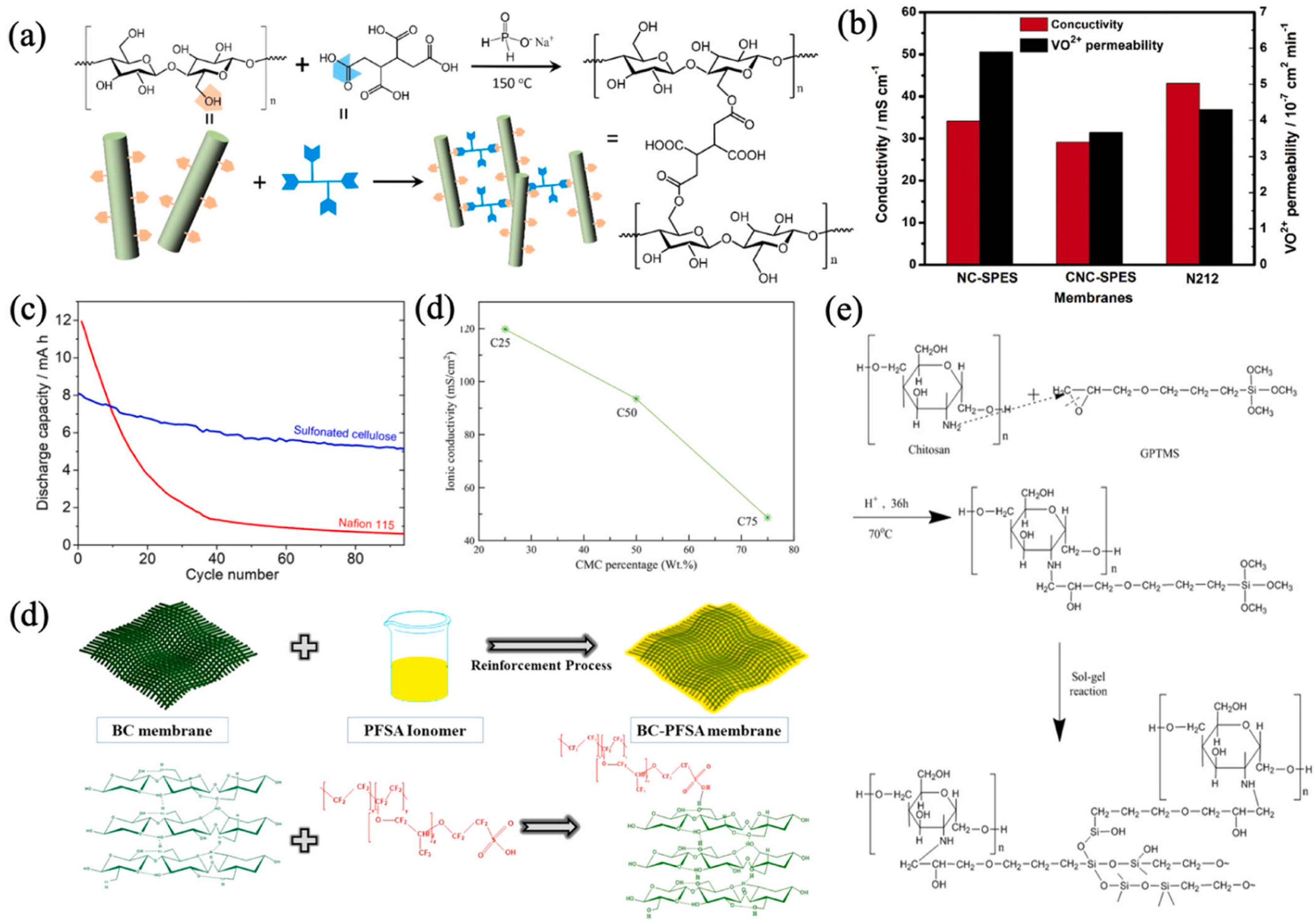

Fig. 2. (a) Crosslinking effect on ion transport in NC-based membranes. Reproduced with permission from [20]. (b) Ion conductivity and vanadium permeability of the NC-SPES hybrid membrane, silica-encapsulated CNC-SPES hybrid membrane and Nafion 212 membrane. Reproduced with permission from [22]. (c) Cycling performance of the chemical modified CNF membrane. Reproduced with permission from [23] (d) Variation of membrane conductivity with CMC/PVA ratio for the composite membrane. Reproduced with permission from [24]. (e) Preparation process of the BC-PFSA membrane. Reproduced with permission from [28]. (f) Preparation process of the chitosan-silica membrane. Reproduced with permission from [32].

geometry with high surface area but also good mechanical properties. In 2020, Jung et al. reported the use of BC-based membrane in VRFB with PFSA ionomer reinforcement[28]. The preparation process involves immersing the biocellulose membrane in the PFSA solution and performing a rolling process to introduce PFSA (Fig. 2(e)). After reinforcement, the PFSA was uniformly incorporated into the pores among the cellulose fibrils, which inhibiting the water adsorption of membrane. Compared with the unmodified BC membrane, the water update rate of the BC-PFSA membrane decreased from 126.8 % to 126.8 %. Meanwhile, as the introduced -SO_3H groups from PFSA improved the proton conductivity of the modified membrane from 5 mS cm^{-1} to 60.5 mS cm^{-1}, which was comparable to commercial Nafion membrane. While, the BC-PFSA membrane still demonstrated slightly higher vanadium ion permeabilities compared with the Nafion membrane. Overall, the battery assembled with BC-PFSA membrane showed relatively inferior cycling stability and efficiencies compared with the battery with Nafion membrane. In another study by Zhu et al., the authors prepared BC aerogel through freeze-drying of BC membrane, and subsequently immersed it in poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) solution to obtain a BC/PVDF-HFP membrane [29]. Since the BC possess highly hydrophilic network with abundant -OH groups which can facilitate proton transport, the BC/PVDF-HFP membrane exhibited high proton conductivity from 9.5 to 10.8 mS cm^{-1} at 25–45 °C, which exceeds that of Nafion 115. The performance of fabricated BC/PVDF-HFP membrane was evaluated in the VRFB. It was found that the battery assembled with BC/PVDF-HFP membrane achieved a lower area-specific resistance than that assembled with Nafion 115 membrane due to higher water uptake of membrane. During the rate performance test from 40 to 150 mA cm^{-2}, the battery with BC/PVDF-HFP demonstrated higher coulombic efficiency (CE) than the battery with Nafion 115. The authors attributed the reason to the fact that the hydrophobic PVDF-HFP filled the pores in the BC matrices lead to a lower vanadium permeability.

Furthermore, the application of chitosan has also been reported. Chitosan is a low-cost polymer obtained from chitin, which can be extracted from biological resources such as shellfish and mushrooms [30]. Chitosan contains rich -OH and amino (-NH_2) groups, making it prone to absorb water in acidic environment and leading to inferior structural stability [31]. To improve its mechanical properties and acid resistance, some studies have introduced crosslink agents to stabilize the chitosan. Lin et al. used (3-glycidyloxypropyl)trimethoxysilane (GPTMS) to react with chitosan main chain and fabricated a chitosan-silica anion exchange membrane through nucleophilic substitution reaction and sol-gel process (Fig. 2(f)) [32]. With the increasing content of GPTMS, the water uptake ratio and vanadium ion permeability of the chitosan-silica membrane both decreased. As the GPTMS ratio reached 75 wt%, the composite membrane exhibited comparable permeability with the comparable Nafion 117 membrane. While, the membrane resistance was found to elevate due to the addition of hydrophobic GPTMS groups. The VRFB battery assembled with the composite membrane with different GPTMS content from 25 to 75 wt% all demonstrated improved CE, VE and EE at 20 mA cm^{-2}.

In overall, cellulose materials from various sources have been regarded as promising candidates for fabrication of membrane matrices (Table 1). The internal hydrogen bonds in cellulose can construct rigid networks to enhance the mechanical properties of the membrane. Meanwhile, the abundant -OH groups allow introduction of various functional groups via flexible chemical modifications. In addition, chitosan has also been studied as potential matrix to fabricate membrane with high water uptake. However, its structural instability in acidic environments requires further improved by crosslinking with other materials. Currently, compared to commercial membranes such as Nafion, the biomaterial-based membranes still face the challenges associated with insufficient proton conductivity, relatively high resistance, and limited chemical and mechanical stability. Furthermore, while offering potential economic and environmental benefits, many reported membranes have yet to achieve exceeding performance in RFBs than commercial membranes, which may affect the overall cost-effectiveness of the membranes. Therefore, future improvements should focus on improving chemical resistance and mechanical properties through advanced modification techniques, exploring new bio-sourced matrix materials, and conducting comprehensive economic evaluations to ensure cost-effectiveness and sustainability. In addition, in terms of future scalability, maintaining consistent quality and performance of membranes with biomaterial-based matrix can be challenging due to variations in raw material sources. Ensuring the consistent properties of the raw materials and the development of scalable manufacturing processes are essential.

Bio-sourced material as membrane additives

Another application of bio-sourced materials is to be incorporated as additives into the pristine polymer matrix to form the composite membranes (Table 2). In the past few years, various efforts have been made to explore the potential of bio-sourced fillers for fabricating high-performance composite IEMs via simple and environmentally friendly modification/fabrication methods. In 2019, Zhu et al. demonstrated the use of cellulose nanocrystals (CNCs) as membrane fillers for VRFB [33]. The CNCs are rigid, rod-shaped crystalline particles with high aspect ratio, which are typically derived from wood cellulose fibers or the coats of molluscs. They possess unique structure with both -OH richen hydrophilic surface and hydrophobic surface. They can create rigid networks through strong hydrogen bonding with neighboring nanocrystals or hydrophilic polymer matrices to improve the mechanical properties of the composites. The authors extracted CNCs from naturally occurring cellulose fibers in trees through the acid hydrolysis process. The prepared CNCs with superhydrophilicity feature were introduced into the hydrophobic PVDF-HFP matrix to prepare a CNC/PVDF-HFP composite membrane (Fig. 3(a)). The obtained membrane possesses better shape stability and higher tensile strength. However, the high rigidity and increased crystallinity also lead to the loss in ductility. Compared with Nafion membrane, the CNC/PVDF-HFP membranes showed better selectivity. When tested in the VRFB with corrosive, acidic, and oxidative environments, the membrane exhibited good stability and achieved operation for over 650 cycles.

In addition to the cellulosic materials, the application of lignin as filter was also widely reported [34]. Lignin is a complex organic polymer found primarily in the cell walls of plants, which is a byproduct of the pulp and paper industry [35,36]. The abundant source, low cost, excellent dispersibility and high availability of lignin make it an attractive material for diverse applications [37,38]. When being used as membrane additives, the rich -OH groups in lignin can form hydrogen-bond interactions with the -SO$_3$H groups in the polymer matrix, which can improve the mechanical strength and enhance its hydrophilicity of the membrane. In addition, the addition of lignin restricts size of water channels within the membrane, which minimizes the permeability of ions with larger Stokes radius and leads to enhanced ion selectivity. In 2019, Ye et al. fabricated a composite membrane with low-cost sulfonated poly(ether ether ketone) (SPEEK) as polymer matrix and lignin as filler by solution blending and casting method for VRFB [39,40]. It was found that the increased lignin content led to enhanced hydrophilicity but lower ion exchange capacity due to the reducing -SO$_3$H groups. Compared to the commercial Nafion 212 membrane, the composite membrane demonstrated lower vanadium ion permeability. However, the area-specific resistance (ASR) was found to increased, which might be due to the reduction in water channel size and elongation of ion transport paths in thicker membranes. The VRFB assembly with optimal composite SPEEK/lignin membrane exhibited an improved

Table 1
Reported membranes with biomaterial-derived matrices in the literature.

System	Ref	Membrane	Matrix	Thickness (μm)	Water uptake	IEC (meq g^{-1})	Permeability (cm^2 min^{-1})	Ion conductivity (mS cm^{-1})
Zn/I$_2$ RFB	[24]	CMC/PVA C25 wt%	CMC	/	/	/	/	119.8
		CMC/PVA C50 wt%		/	/	/	/	93.5
		CMC/PVA C75 wt%		/	/	/	/	48.7
VRFB	[32]	CG−1 (25 wt% GTMS)	Chitosan	150	85 %	0.71	8.17×10^{-6}	11.28
		CG−2 (37.5 wt% GPTMS)		150	64 %	0.42	7.53×10^{-6}	10.87
		CG−3 (50 wt% GPTMS)		150	41 %	0.35	6.38×10^{-6}	9.8
		CG−4 (75 wt% GPTMS)		150	28 %	0.34	3.13×10^{-6}	7.58
		LB*	/	175	25 %	0.65	3.9×10^{-6}	12.91
		Nafion 117*	/	195	21 %	0.99	8.82×10^{-6}	41.05
	[29]	BC/PVDF-HFP	BC	200 mm	~16 % (25°C)	/	/	9.5 (25°C)
		Nafion 115*	/	127	~12.5 % (25°C)	/	/	5.8 (25°C)
	[28]	BC	BC	/	126.80 %	0.129	4.84×10^{-5}	5
		BC-PFSA		/	36 %	0.869	0.0855×10^{-5}	6.05
		Nafion*	/	/	24.49 %	/	/	7.161
BQDS/ARS RFB	[21]	Nanocellulose	Nanocellulose	50	21.9 ± 1.7 %	/	0.275×10^{-7}	19.4
		Nafion 115*	/	127	19.6 ± 2.2 %	/	2.1×10^{-7}	2.13
Tiron/ARS RFB	[23]	Sulfonated cellulose	Sulfonated cellulose	20	200 %	/	/	5.2 ± 1.2 (in 0.1 M H$_2$SO$_4$)
		Nafion 115*	/	127	25 %	/	/	23.5 (in 0.1 M H$_2$SO$_4$) 11.9 (in 0.5 M KCl)

[*] Commercial membrane for comparison.

Table 2
Bio-sourced material as membrane additives.

System	Ref	Membrane	Substrate	Additives	Thickness (μm)	Water uptake	Swelling ratio	IEC (meq g^{-1})	Permeability (cm^2 min^{-1})	Conductivity (mS cm^{-1})	Tensile strength (MPa)
VRFB	[41]	rNafion/L5	Nafion	Lignin	~39	~4.5 %	4.71 %	/	0.85×10^{-7}	15.8	/
		rNafion/L8			~42	~6 %	/	/	0.82×10^{-7}	12.7	/
		Nafion 212[*]	/		50	~10.88 %	6.00 %	/	2.01×10^{-7}	17.3	/
	[39]	SPEEK/L15	SPEEK	Lignin	81	29.62 %	/	1.11	0.17×10^{-7}	29.56	61
		SPEEK[*]	/		71	23.58 %	/	1.37	/	/	46.03
		Nafion 212[*]	/		50	15.24 %	/	/	1.981×10^{-7}	32.26	22.28
	[46]	CM1	pTAP copolymers	Chitosan	70	16.3 %	9.10 %	/	10.65×10^{-7}	4.7 (20°C) 6.52 (50°C)	/
		CM2			70	31.9 %	13.30 %	/	10.31×10^{-7}	17.39 (50°C)	/
		CM3			70	26.1 %	11.30 %	/	9.89×10^{-7}	4.89 (20°C) 13.33 (50°C)	/
	[40]	SPEEK41/L15	SPEEK	Lignin	81	23.62 %	6.60 %	/	$\sim 0.23 \times 10^{-7}$	7.7	/
		SPEEK50/L15			81	27.61 %	8.25 %	/	$\sim 0.25 \times 10^{-7}$	13.3	/
		SPEEK59/L15			81	30.07 %	10.28 %	/	$\sim 0.28 \times 10^{-7}$	17.6	/
		SPEEK72/L15			81	42.63 %	12.47 %	/	$\sim 0.36 \times 10^{-7}$	19.9	/
		Nafion 212[*]	/		50	/	/	/	$\sim 1.6 \times 10^{-7}$	20.4	/
	[43]	SPI/CS	SPI	Chitosan	50	28.66 %	6.66 %	1.65	1.12×10^{-7}	39.4	/
		SPI[*]	/		45	41.40 %	4.80 %	1.61	1.89×10^{-7}	30.2	/
		Nafion 117[*]	/		175	18.6 %	10.90 %	1.14	15.41×10^{-7}	64.1	/
	[45]	Nafion_216	Nafion	Chitosan	/	/	/	/	17×10^{-7}	85.0 ± 1.3	/
	[33]	45-C–CNC/PVDF-HFP	PVDF-HFP	Cellulose nanocrystals	~50	~	/	/	/	~13	34.68
Inorganic VRFB	[16]	C/U film	Celgard	Chitosan, urushi	29	75 %	8 %	/	83.1×10^{-7}	568	109.05
		Celgard[*]	/		25	37.5 %	/	/	1455×10^{-7}	551	148.28
Zn/I$_2$ RFB	[42]	NanoSL 5 %	PVOH	NanoSL	50	/	/	1.26	/	30.2	22.1
		Nafion 112[*]	/		50.8	38 %	/	0.98	/	83	27.1
		Fumasep F–1050[*]	/		45	25 %	/	0.95	/	65 – 91	31–49

[*] Commercial membrane for comparison.

self-discharge performance (Fig. 3(b)) and achieved stable operation at 120 mA cm^{-2} for 350 cycles with a capacity retention of ~65 % at the 350th cycle. Later on, the group reported a Nafion/lignin composite membrane [41]. With the increased lignin mass loading, the swelling ratio of the composite membrane was decreased, which may be due to the hydrogen bonds between lignin and -SO_3H and the rigid benzyl ring structure within lignin. However, a too high lignin content above 30 % would lead to lignin aggregation in the composite films and deteriorate the mechanical properties of the membrane. The assembled battery with optimal membrane composition achieved high CE of ~97.4 % and EE of ~82.7 % at 120 mA cm^{-2}. Meanwhile, the battery exhibited slower capacity decay rate of ~0.047 % per cycle for 1000 cycles (Fig. 3(c)). The capital cost of the composite membrane was calculated to be ~72 % of the commercial Nafion 212 membrane. In 2024, Foster's group reported another biomaterial-based PEM with sulfonated lignin nanoparticles (NanoSL) using polyvinyl alcohol (PVOH) polymer matrix [42]. The NanoSL was synthesized by the solvent-antisolvent precipitation method, and was found to possess high surface area, chemical and morphological uniformities, improved miscibility and dispersibility. The zinc-iodine RFB equipped with the NanoSL/PVOH membrane contains 5 % NanoSL content achieved a capacitance of 1.75 Ah L^{-1}, which is comparable to the commercial Nafion, Fumasep and Daramic membrane (Fig. 3(d)). However, it was found that, due to the low cross-linking density of PVOH, the fabricated membrane could not effectively prevent the crossover phenomenon. In addition, the high hydrophilicity of PVOH caused the membrane to absorb water and become brittle during long-term testing. The water absorption also affected the uniformity of the membrane, thereby increasing its internal resistance.

Chitosan has also been reported as hydrophilic additive in membranes for RFBs. This species contains abundant -OH groups, which can facilitate its dispersion in the ionomer matrix. Chitosan contains abundant -OH groups, which can promote its dispersion in the ionomer matrix and effectively improve the water absorption and ionic conductivity of the membrane. In 2012, Yue et al. introduced chitosan as the environmentally friendly acid-base polymer precursor into the sulfonated polyimide (SPI) membrane to improve its oxidative stability [43]. The composite SPI-chiosan membrane fabricated via the immersion and self-assembly method was found to possess sandwich structure with one SPI central layer and two thin chitosan layers at both sides. The cross-linking of chitosan and sulfuric acid provides more rigid and compact membrane structure, resulting in a lower vanadium ion permeability of 1.89×10^{-7} cm^2 min^{-1} compared with Nation117 membrane (15.41×10^{-7} cm^2 min^{-1}). However, the addition of hydrophilic chitosan groups led to inferior dimensional stability of the SPI/CS membrane to pristine SPI membrane. In 2021, Gallyamov et al. impregnated the commercial polyolefin matrix Celgard 2512 membrane with the hydrophilic chitosan polymer to increase membrane hydrophilicity and control the pore size [44]. A layer of chitosan was deposited from the carbonic acid aqueous solution onto the polyolefin membrane under high pressure. The chitosan coating increased the affinity of the composite membrane for water while suppressing vanadium permeability by reducing the pore size of the membrane. With the prolonged deposition time, the higher water update and ion selectivity can be achieved. However, the proton conductivity would decrease under too long deposition time, which indicated that the chitosan can also block the permeability of protons (Fig. 3(e)). Later on, the group performed the similar method on Nafion membrane [45]. The deposited chitosan matrix was protonated into polycationic state under acidic media, which created a barrier that hindered the transport of vanadium ions while allowing protons passage. Compared to pristine Nafion membrane, the chitosan-modified membrane exhibited reduced vanadium ion permeability from 3.0 to 1.7×10^{-6} cm^2 min^{-1}. Concurrently,

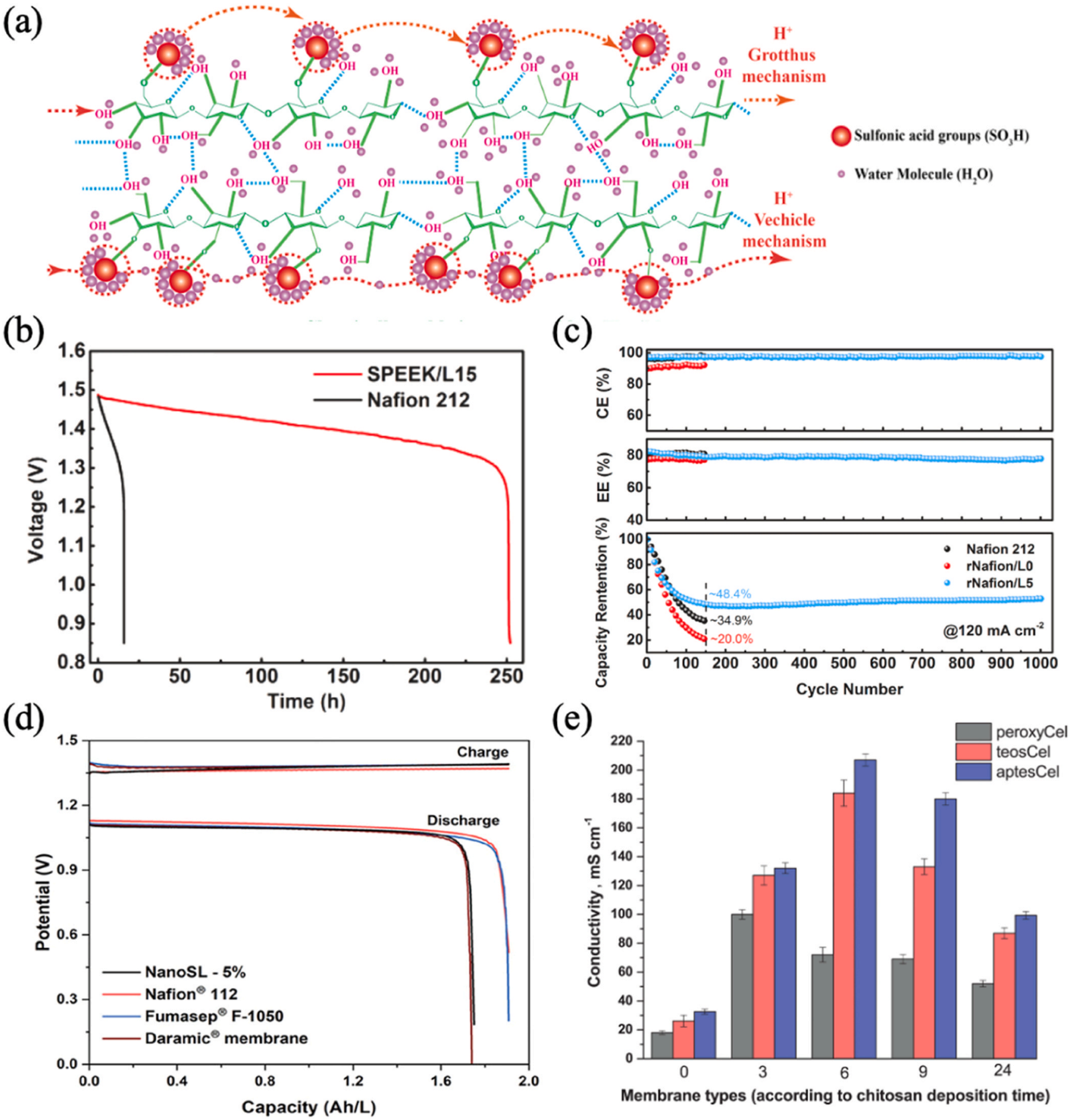

Fig. 3. (a) Structure and transport mechanism of the CNC/PVDF-HFP composite membrane. Reproduced with permission from [33]. (b) Self-discharge behavior of the SPEEK/lignin composite membrane and Nafion 212. Reproduced with permission from [40]. (c) The cycling performance of the VRFBs with the modified membranes (0wt.% and 5wt.% lignin content) and Nafion 212. Reproduced with permission from [41]. (d) Charge-discharge behavior of the NanoSL/PVOH membrane compared with commercial membranes in zinc-iodine RFB. Reproduced with permission from [42]. (e) Effect of chitosan coatings deposition time on proton conductivity of Celgard membrane (peroxyCel) and two different silica pretreated membrane (teosCel and aptesCel). Reproduced with permission from [44].

the proton conductivity was also slightly declined from 90.4 to 85.0 mS cm^{-1}. The CE and EE of battery assembled with the modified membrane were improved within the current density range of 40–100 mA cm^{-2}. Additionally, Aïssa et al. blended chitosan with synthesized various tetraarylpolyphosphonium (pTAP)-based copolymers and polyvinylidene fluoride (PVDF) to fabricate the AEM [46]. The hydrophilicity of chitosan enhanced the miscibility between the two polymers and pTAP copolymers, resulting in a smooth surface for the membrane. Meanwhile, the rigid segments of PVDF limit the excessive water absorption of hydrophilic chitosan, which can improve the mechanical strength and dimensional stability of the composite films especially under high temperature or swelling conditions. The composite membrane demonstrated reasonable alkaline stability, indicating that it may be suitable for alkaline RFBs applications in the future. At the same time, when used in acidic VRFB, the composite membrane exhibited a lower vanadium ion permeability than Nafion 212, which may be because that the less hydrophilic ionomers and hydrophobic domains in the composite membrane limited the size of ion channels. However, the cycle stability of the VRFB equipped with the composite membrane still needs to be enhanced.

For other potential materials, Won et al. explored the application of urushi, which is a natural polymeric film derived from lacquer tree with high durability, mechanical robustness and corrosion resistance [47]. The groups fabricated a semi-interpenetrating network (semi-IPN) photo polymerization of urushiol in the presence of poly(diallyldimethylammonium chloride) (PDDA). The fabricated selective layer was coated on Celgard membrane. The developed membrane was utilized in non-aqueous vanadium acetylacetonate ($V(acac)_3$) RFB. Due to the introduction of selective semi-IPN layer, the vanadium crossover was inhibited compared with the pristine Celgard membrane. However, the ion conductivity of the modified membrane was obviously decreased. Meanwhile, the interfacial interaction between the semi-IPN layer and the Celgard was found to be low, which may affect the long-term stability of the membrane in RFBs. Additionally, the PDDA may affect the oxidation stability of the composite membrane, leading to decay in mechanical properties. Later on, the author designed an anion exchange pseudo-interpenetrating polymer network (IPN) structure composed of chitosan and chemically stable crosslinked urushi and coated the selective layer on a commercial Celgard microporous membrane [16]. Similarly, the modified membrane with pseudo-IPN selective coating exhibits reduced $V(acac)_3$ permeability and achieved higher CE and EE in the RFBs. While the mechanical strength of the modified membrane was reduced due to the presence of chitosan.

Overall, there have been significant efforts to introduce bio-sourced resources as membrane additives, particularly for lignin and chitosan. Lignin possesses natural abundance, low cost, and ability to enhance mechanical strength and ion selectivity. Improper management of lignin content also may lead to aggregation and reduce membrane integrity. Chitosan has been used as the hydrophilic additive to improve the water uptake and ion selectivity of the membrane. However, though it effectively reduces reactant crossover by encapsulating the original fibrous materials, it may also decrease proton conductivity. Cellulose materials have also been studied as potential candidate for improving the mechanical properties of membrane by constructing rigid networks through hydrogen bonding with the polymer matrix. While these materials show promise, challenges remain in optimizing membrane composition to balance the mechanical properties, proton conductivity and permeability. In addition, membranes made from cellulose, lignin, and chitosan could be susceptible to chemical degradation when exposed to strong oxidative and acidic conditions, which can lead to the breakdown of polymer chains and result in reduced mechanical strength and increased permeability. Therefore, future directions could focus on developing new materials which can effectively combine with the polymer matrices and improve membrane stability during battery cycling through chemical modification or structural design.

Discussion and outlook

In recent decades, the exploration of various bio-sourced materials such as cellulose, lignin, and chitosan has shown promising advancements as both matrices and additives for membrane fabrication in RFBs. These materials offer several advantages, including low cost, natural abundance, and environmental friendliness, making them attractive alternatives to conventional petroleum-based membranes. Despite certain progress, the reported biomaterial-based composite membranes still face limitations compared to commercial membranes such as Nafion. Though many reported composite membranes possess lower permeability than commercial membranes, achieving a balance between ion selectivity and proton conductivity remains a key challenge. Meanwhile, the long-term stability under operational conditions remains a critical challenge for their application in RFBs since the biomaterial-based membranes may experience degradation due to oxidative and acidic conditions, the improper material ratios in membrane can lead to structural inhomogeneity and cause mechanical instability and further affect the stability in RFBs. In addition, the high temperature stability issues such as material degradation and increased swelling still need to be addressed. The improvement strategies, such as the introduction of chemical cross-linking agents, inorganic nanofillers, and functional groups can be further adopted. Furthermore, the required precise control over membrane thickness and uniformity during scaled manufacturing may also lead to increased complexity and cost. Although many studies claim that their membranes offer economic advantages, the overall cost-effectiveness of the membranes must be evaluated. This includes considering the costs associated with raw materials, processing, and any additional treatments or modifications required to enhance performance. To better assess the economic viability of the developed membranes, the comprehensive techno-economic assessment analyses between the biomaterial-based membranes and commercial petroleum-based membranes are of great significance. Overall, to develop next-generation membranes that meet the demanding requirements of long-term energy storage, future research should focus on the advanced modification and functionalization of the biomaterial-based membrane to further improve the mechanical and chemical properties. Potential strategies to mitigate membrane crossover including adding functional additives that enhance ion selectivity, using nanostructured fillers to reduce ion pore size, applying surface modifications or coatings to introduce selective barriers also required further investigation. Meanwhile, it is suggested to explore the potentials of other alternative bio-sourced materials and conduct detailed economic evaluations for the biomaterial-based membrane. By overcoming these challenges, it is believed that the low-cost, naturally abundant and environmentally friendly bio-sourced materials could play a crucial role in the development of future sustainable energy storage technologies.

CRediT authorship contribution statement

Liang An: Writing – review & editing, Supervision, Funding acquisition. **Yikai Zeng:** Supervision, Funding acquisition. **Xingyi Shi:** Writing – review & editing. **Xiaoyu Huo:** Writing – original draft, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

No data was used for the research described in the article.

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