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Membranes in non-aqueous redox flow battery: A review

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- The first review article on the state-ofthe-art membranes in NARFBs.
- Ion transfer mechanism and mathematical models are summarized.
- Strategies to improve the performance of membrane in NARFBs are proposed.



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ABSTRACT

Redox flow battery (RFB) is promising in grid-scale energy storage, and potentially applicable for facilitating the harvest of the intermittent renewable power sources, like wind and solar, and stabilizing the power grid. Early RFBs are based on aqueous electrolytes and the all-vanadium as well as Zn/Br systems have been demonstrated in close commercial scale. Non-aqueous RFBs (NARFBs) are the second-generation flow batteries based on organic solvent which have potentially much wider electrochemical window, and thus possible much higher energy density, and temperature window than those of the aqueous systems. As a crucial component of NARFBs, the membrane serves to prevent the crossover of the positive and negative active species whilst facilitating the transfer of the supporting electrolyte ions. However, the membranes utilized in the state-of-the-art publications still need great improvements in performance. In this article, the fundamentals, classifications, and performances of the membranes are summarized. A perspective on the near future developments of NARFB membranes are presented. The composite membranes are likely the promising direction to forward the development of the NARFB technologies.

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1. Introduction

With the ever-growing global population and the economy, the demand of humanity for energy is fast increasing. To relieve the concerns of the environmental damage and energy crises caused by the utilization of fossil-based fuels, the proportion of renewable energy in the overall energy consumption has been developing worldwide. In 2018, renewable energy capacity of 181 GW was newly installed on global, grew to around 2378 GW in total [1]. Solar photovoltaics accounted for 55% of the renewable capacity additions, followed by wind power (28%) [1]. The International Energy Outlook 2019 predicts that driven by the growth of electricity demand and the development of economy and society, the worldwide renewable energy consumption will increase by 3% per year between 2018 and 2050 and will become the leading sources of primary energy by 2050 [2]. However, both the solar and wind energies are intermittent in nature, the power generated from both the two sources cannot be incorporated directly by the existing grid, otherwise, it brings instability and shutdowns [3]. In addition, the electric power grid needs to balance with the supply and the consumption. When the consumption is low, the unused electric energy needs to be stored, and when the supply is not enough, the stored energy must be returned to the system, for stabilizing the grid. Therefore, the development of large-scale energy storage technology is an urgent task to ensure the integrity and compatibility of the renewable power generation with the existing grid.

Energy storage technology has a long history and already has a flexible selection, including flywheel energy storage, pumped water energy storage, compressed air energy storage, and electrochemical energy storage, suitable to different scales. In practice, water reservoirs have been utilized to serve as the buffer of the grids in many countries. However, the economic and environmental impacts have arisen concerns of the mechanical energy storage technologies, like water pumping reservoirs. Electrochemical energy storage technologies, e.g., lead-acid batteries, lithium-ion batteries, sodium-sulfur batteries, redox flow batteries (RFBs) and etc., possess environmentally benign operation, high efficiency, rapid response and low need of maintenance [4]. Among the various electrochemical energy storage technologies, RFBs, firstly proposed by Posner in 1955 [5], and firstly practiced by Thaller in 1974 [6], stand out as the most promising ones for grid scale electricity storage owing to its decoupled capacities of power and energy, flexible modular design and excellent scalability, long cycle life and rapid response. As the name implies, RFBs take the advantages of an electrochemical flow reactor and the chemical energy is stored in the active materials dissolved in the anolyte and catholyte electrolytes, circulating between the reservoirs and the cell compartments by pumps. The total energy output depends on the volume of the reservoirs, which implies that the capacity is unlimited, nevertheless, high-energy density and high-power density are always needed [7]. Therefore, RFBs are widely recognized easy for scale up and suitable for large-scale energy storage applications.

Aqueous, i.e. with water as the solvent, RFBs and non-aqueous RFBs (NARFBs) are both under intensive development in every continent. Early RFBs are based on aqueous electrolytes and the all-vanadium system, which was firstly invented by Skyllas-Kazacos et al. [8–10] in 1980s, has been commercially demonstrated [3]. In the development history of the aqueous RFBs, the performance of the batteries has been significantly improved with the optimization of the electrolytes, electrodes, and the membrane. However, the operation voltage window inherited from the water electrolysis redox potential, i.e. 1.23 V under standard conditions, restricts the energy density of the aqueous RFBs [11]. The energy density depends mainly on the cell voltage, the number of charges delivered by a unit mass of the molecule in the battery redox reaction, and the concentration of the active species. Higher cell voltage also reduces the number of cells in series needed to achieve a target output, which can further reduce system complexity and cost.

as the active species of the electrolytes in acetonitrile solvent by Matsuda et al., in 1988 [12]. Since then, numerous NARFBs based on organometallic compounds have been investigated. For instance, Liu et al. [13] reported a non-noble metal complex, vanadium acetylacetonate (V(acac)₃), as the active material in a NARFB in 2009 and obtained promising performance. However, the relatively low solubility of the organometallic compounds and the decomposition of ligands during charge/discharge remain to be unsolved problems up to now. To get rid of the issues of the organometallic complexes, the metal-free organic molecules as the active species of RFBs were proposed [14] in 2011. Since then, many organic molecules have been designed and examined [15–19]. Organic solvents permit a much wider electrochemical window and enable a much higher energy density for the RFBs [20,21]. For instance, acetonitrile has an electrochemical window as wide as ~6.1 V at 25 °C [22], which provides the possibility to design a high voltage RFB. In addition, electrolytes based on organic solvents may also allow a working temperature window much larger than that of the water-based electrolytes, which is highly demanded by the energy storage in the areas with cold winter.

NARFBs are typically composed of two electrolytes, often distinctly divided as anolyte and catholyte, two electrodes, and one membrane. Application of non-aqueous electrolyte provides a wide selection of solvents, thus, more flexible design of the device, although NARFB works on the similar principles as the aqueous RFBs. A general scheme for the NARFBs can be illustrated as Fig. 1a, where Aⁿ and B^m represent the negative and positive active species, respectively. During the charge/discharge processes, the active materials flow through the electrode chambers and undergo redox reactions. The supporting electrolyte (its anion and/or cation) transfers through the membrane to achieve the charge balance.

The cathode and anode are the location for the surface electrochemical reactions to take place [23]. For a real NARFB, all the three components, electrolytes, electrodes, and membrane jointly determine the electrochemical performance and the long-term stability of the NARFB [24,25]. For the innovation and optimization of the electrolytes, the configuration and the surface reaction steps happening on the electrodes have been dynamic research topics and many excellent review articles have been published already, thus these topics are out of the scope of this review article except the contents closely linked to the membrane in the NARFBS [21,26–28].

Based on the structure of the batteries and the status of the active materials, most of NARFBs can be divided into three categories, i.e. conventional, hybrid, and redox-targeting NARFBs (Fig. 1b–d). The conventional NARFBs are those in which both positive and negative active materials are dissolved in the solvents and circulated between tanks and cell chambers. Most NARFB researches are based on this configuration. For hybrid NARFBs, one of the redox couples is based on a metal, i.e. redox between the metal and one of its ions, with which phase transition and thus metal deposition happens during cycling such as in a lithium NARFB [29]. For the redox-targeting NARFBs, solid active materials are immobile and fixed in the reservoirs, but two pairs of redox mediators dissolved in the electrolyte are circulated. The charge/discharge electrochemical steps are completed by target redox reactions [30].

As the development of the membrane for NARFBs lags far behind the redox active species, it is important in the near future for non-aqueous systems to provide a suitable membrane that has good electrochemical and physical properties. In this article, the development of the membranes used in the three types of NARFBs are summarized. The purpose is to provide a comprehensive overview of the fundamentals, classification, and performance of the membranes applied in NARFBs. A perspective on the future development of membranes for NARFB technologies are also proposed.

Non-aqueous RFBs (NARFBs) was firstly reported with Ru-complex



Fig. 1. (a) Schematic of NARFB. Schematic illustration of three different types of NARFBs: (b) conventional NARFBs, (c) hybrid NARFBs, (d) redox-targeting NARFBs.

2. Membranes in non-aqueous redox flow battery

2.1. Requirement and classification

The membrane, viz. separator, serves as preventing the crossover of the positive and negative active species whilst facilitating the transport of the supporting electrolyte ions, is crucial to achieve a high performance and a long-term stability for an RFB [31,32]. An ideal membrane in NARFBs should have high ionic conductivity and selectivity, low swellability, low-cost, and high stability, both mechanical and chemical, in the organic solvent (Fig. 2) [33-35]. Table 1 summarizes the general targets that should be considered for NARFB membranes. Membranes must be chemically and electrochemically stable to the electrolyte in NARFBs. They should be stable under strong oxidizing and reducing conditions during long-term cycling. The mechanical properties of separators are characterized by the tensile strength and puncture strength in the machine direction. For a battery membrane of 25 μ m thick, the minimum tensile strength measured according to ASTM D882 and D638 is 98.06 MPa [36]. The ionic conductivity and selectivity are different when using different electrolytes, which affects the operating current



Fig. 2. The requirements of NARFB applications to the ideal membranes.

Table 1

General targets for membranes used in NARFBs.

Chemical stabilityStable for a long period of timeMechanical stability>1000 kg cm^{-2} (98.06 MPa)^aIonic conductivity 10^{-2} S cm^{-1b}Ionic selectivityNo crossoverSwellabilityNo swelling	Parameter	Targets					
	Chemical stability Mechanical stability Ionic conductivity Ionic selectivity Swellability	Stable for a long period of time $>1000 \text{ kg cm}^{-2} (98.06 \text{ MPa})^{8}$ $10^{-2} \text{ S cm}^{-1b}$ No crossover No swelling					

^a For 25 µm-thick membranes.

^b Requirement for lithium batteries.

density and efficiencies of the battery. There are no existing standards and guidelines of ionic conductivity yet for NARFBs. The generally ionic conductivity of lithium batteries is the order of 10^{-2} S cm⁻¹ at room temperature [37], which might be considered as a reference value for flow batteries. An ideal membrane can help reach a Coulombic efficiency (CE) close to 100%, as well as a high current density (aqueous RFBs are currently peaking over 200 mA cm⁻² [38]).

Intensive effort has been devoted to the development of membranes to satisfy the above-mentioned requirements. These membranes up to date used in NARFBs can be classified into two categories: dense and porous. Dense membranes are usually thin layers of dense materials. In contrast, porous membranes consist of a solid matrix with defined pores. Dense membranes, mainly including dense ceramic and ion exchange membranes (IEMs), are also often referred to as ion conducting membranes. Different membrane has been shown to exhibit different performance when assembled in a NARFB.

2.2. Ion transfer through membrane in flow battery

2.2.1. Description of ion transfer

The membrane in an RFB is indispensable for the performance of the RFB, with the function of separating the positive and negative electrolytes to avoid short-circuit and cross-contamination, while allowing the supporting electrolyte ions to pass through to maintain the charge balance [24].

IEMs often have setting in negatively or positively ionic functional groups in the transfer path. Therefore, they selectively allow the passage of only one kind of ions while rejecting the opposite ones. The ideal membrane should selectively allow only one kind of ion to transfer through it, however, this is not always the case in real world [39]. Both cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are useful in RFBs. The ionic functional groups are sometimes capable of dissociating ions when soaked in a solution [40]. For instance, in the Nafion CEM structure, cations transfer in three modes [41]: 1. Grotthus mechanism, ions transfer via the "passing" of protons from one solvent molecule to the next with the formation and dissociation of hydrogen bonds. 2. Vehicular mechanism, ions transfer as solvated species through the membrane. 3. The bonding ability of the counter anion group ($-SO_3^-$) enables a third mode for cation transportation, viz. the surface mechanism, in which cations are believed to be transported among counter anion groups. When the membrane is immersed in electrolyte, the ions transfer by Grotthus mechanism and vehicular mechanism is facilitated [42].

Dense ceramic membranes are one of the categories of the feasible membrane materials for NARFBs. For instance, In the NASICON-type structure, Li^+ ion selective transfer was achieved with the aid of a ceramic membrane with three dimensionally connected cavities [43]. Li^+ occupies two interstitial positions: one (M1) is coordinated by a trigonal antiprism of oxygen atoms, and another (M2) has a distorted eightfold coordination. Long-range ion conduction is enabled through Li^+ hoping between the M1 and M2 sites [44]. The ionic conductivity is positively correlated with the vacancy concentration of lithium ions in the lattice.

Porous membranes are also often called as porous separators. The selective ionic transfer and electrolyte separation is achieved by the size effect, i.e. allowing smaller sized ions to pass and blocking the bigger sized ions. The size of the supporting electrolyte ions is often smaller than that of the active species, which allows the transfer of the supporting electrolyte ions and limits the crossing of the active species through the membrane.

2.2.2. Mathematical models

In RFBs operation, due to the presence of electrochemical potential, Fick's diffusion law is no more suitable for the description of the ionic transfer in the membrane. In this case, the transfer of ions through the membrane is represented with the Nernst-Planck equation, which describes the motion of charged particles [45–48].

The molar flux density of ion *i* across the membrane, *J_i*, consisting of diffusion and migration, is described by the Nernst-Planck equation as [48]:

$$J_i = -D_i \nabla c_i^m - z_i D_j f c_i^m \nabla \varphi^m \tag{1}$$

where f = F/RT, the term D_i represents the effective diffusion coefficient in the membrane of ionic species i, c_i^m the concentration of ionic species iin the membrane, z_i the charge number of ionic species i, F Faraday's constant, φ^m the electric potential across the membrane, R the universal gas constant and T is the temperature. Note: In this section, all the concentration terms should be the activity of the ionic species i in organic solvent, which is calculated by $c_i = \gamma x_i$, where γ is activity coefficient and x_i is the molar concentration of ionic species i.

In the absence of concentration changes and convective flow, an ionic species of charge number z_i under the influence of an electric field \vec{E} moves with respect to the solvent with an average velocity,

$$v_i = u_i z_i F \vec{E} \tag{2}$$

where u_i is the ionic mobility of ionic species *i*. The flux density is

$$J_i = c_i v_i = c_i u_i z_i F \vec{E} = -c_i u_i z_i F \nabla \varphi^m$$
(3)

compare with the migration term in eq. (1). The ionic mobility, u_i must satisfy the Nernst-Einstein relation,

$$u_i = \frac{D_i}{RT} \tag{4}$$

The Nernst-Planck approach is based on the principle of

independence of the ionic fluxes. The main approximations behind this approach are as follows:

- 1) There are no short-range interactions among different ions.
- 2) Deviations from the Nernst–Einstein relation (e.g. electrophoretic contributions) are neglected, i.e. the electrical and the diffusion mobilities, u_i and D_i/RT , are the same.
- 3) The gradient of the activity coefficient is neglected (i.e. the activity coefficient is independent of concentration).
- 4) They all can be accepted as reasonable approximations for dilute solutions. Accordingly, the coefficients D_i usually gives the constant values corresponding to infinite dilution, which do not depend on the other ions present in solution.

The further quantifications of the ion transfer through dense ceramic membrane, IEM and porous membrane are different.

For dense ceramic membrane, the spatial and temporal variations in defect concentrations are governed by the conservation equation as [47]:

$$\frac{\partial c_i^m}{\partial t} + \nabla J_i = 0 \tag{5}$$

where c_i^m equals to defect concentrations. At steady state,

$$\nabla J_i = \nabla \left(D_i \nabla c_i^m \right) + \nabla \left(z_i D_j f c_i^m \nabla \varphi^m \right) = 0 \tag{6}$$

The electric potential φ^m across the membrane can be related to the charge density ρ_e by the Gauss law as [49]:

$$\nabla(\varepsilon \nabla \varphi^m) = -\rho_e = -F \sum_{i=1}^k z_i c_i^m \tag{7}$$

where ϵ is the permittivity, *k* the number of the types of defect.

Defect diffusion is assumed to provide an approach to establish equilibrium defect concentrations at the two surfaces of dense ceramic membrane. In addition to equilibrium defect concentrations, boundary conditions associated with the electric potentials φ^m are needed. Defined the potential of one surface is reference potential, i.e. $\varphi = 0$ V, the other side of the membrane should be at a different potential, i.e. $\varphi > 0$ V. There must be a balance between the electrical current density *i* through an external circuit and the current density associated with charged-defect flux within the membrane,

$$i = -F \sum_{i=1}^{k} z_i J_i \tag{8}$$

Once boundary conditions are specified, the combination of eqs. (6) and (7) is commonly used as the governing equations to describe the transport of ions in the dense ceramic membrane.

For a steady-state transport across IEMs, the polymer nature, the presence of fixed-charged groups and internal structure influence the membrane transport property and make it different from that in the external solution. Here, we consider the transport of a electrolyte $A_{\nu_1}C_{\nu_2}$, which dissociates into ν_1 ions A^{z_1} and ν_2 ions C^{z_2} . The charge numbers z_1 and z_2 satisfy the stoichiometric relationship,

$$z_1 v_1 + z_2 v_2 = 0 \tag{9}$$

the flux density of electrolyte can be obtained by Fick's first law for the electrolyte diffusion of Donnan equilibrium [50],

$$i_{AC} = \frac{t_2^M}{v_1} j_A + \frac{t_1^M}{v_2} = -D_{AC}^M \nabla c_{AC}$$
(10)

$$D_{AC}^{M} = t_{2}^{M} D_{A}^{M} + t_{1}^{M} D_{c}^{M}$$
(11)

where t_1^M and t_2^M are the transport numbers of ions A^{z_1} and C^{z_2} , respectively. D_A^M and D_c^M are the values of the ion diffusion coefficients, and D_{AC}^M

is the overall diffusion coefficients of the electrolyte in the membrane. Although the ionic diffusion coefficients may take, in practice, different values inside the membrane (D_i^M) and in the solution (D_i^S) , we neglect here such a difference because we want to concentrate on the effect of the composition of the membrane phase on its transport properties, i.e. $D_i = D_i^M = D_i^S$.

The Nernst-Planck equation is based on the principle of independence of the ionic fluxes. In fact, the motions of all charged species in IEM may have interactions, the flux density of ionic species *i* is written in terms of the electric current density *I* and the electrolyte flux density j_{AC} under closed-circuit conditions, i.e. $I \neq 0$,

$$j_{i} = j_{AC} + \frac{t_{i}^{M}I}{z_{i}F} = -D_{AC}^{M}\nabla c_{i} + \frac{t_{i}^{M}I}{z_{i}F}$$
(12)

when describing the transport of a binary electrolyte across a strongly charged membrane, the concentration gradient of the Donnan electrolyte inside the membrane is $\nabla c_{AC} = \nabla c_A = \nabla c_C$. Eq. (12) is the diffusion and migration flux equation for a symmetric and binary electrolyte inside an IEM. The ionic transport numbers t_i^M is obtained,

$$t_{i}^{M} = \frac{z_{i}^{2} D_{i} c_{i}^{M}}{\sum_{j} z_{j}^{2} D_{j} c_{j}^{M}}$$
(13)

combined with eq. (11), the overall electrolyte diffusion coefficient D_{AC}^{M} is obtained.

$$D_{AC}^{M} = \frac{D_{A}D_{C}\left(z_{1}^{2}c_{A}^{M} + z_{2}^{2}c_{C}^{M}\right)}{z_{1}^{2}D_{A}c_{A}^{M} + z_{2}^{2}D_{C}c_{C}^{M}}$$
(14)

In membranes with high solvent content, it can be assumed that the activity coefficients and the standard chemical potentials are the same in both phases, and therefore the distribution equilibrium is described by the simpler equations [50],

$$c_i^M = c_i^S e^{-z_i f \Delta \varphi^D} \tag{15}$$

where $\Delta \varphi^D = \varphi^M - \varphi^S$ is the Donnan potential, φ^S the electric potential of the solution, c_i^S the concentration of ionic species *i* in the external solution. In the external solution, this concentration is related to the stoichiometric concentration,

$$c_{AC}^{s} = \frac{c_{A}^{s}}{v_{1}} = \frac{c_{C}^{s}}{v_{2}} \tag{16}$$

Since the ion-exchange groups $-R^{z_M}$ participate in the ionic distribution equilibrium, the solution filling the membrane can be considered to be composed of two binary electrolytes with a common ion, the counter ion A^{z_1} . The stoichiometric concentration of the electrolyte in the membrane is

$$c_{AC}^{M} = \frac{c_{C}^{M}}{v_2} \tag{17}$$

The local electroneutrality condition inside the membrane,

$$z_1 c_A^M + z_2 c_C^M + z_M c_M = 0 (18)$$

where z_M and c_M are the charge number and the molar concentration of ion which dissociated by IEM, respectively. Combined with eqs. (15) and (16), the following equation is achieved,

$$X = \frac{z_M c_M}{z_2} = v_2 c_{AC}^S \left(e^{-z_1 f \Delta \varphi^D} - e^{-z_2 f \Delta \varphi^D} \right)$$
(19)

In the case of symmetric electrolytes, eq. (18) simplifies to

$$c_A^M = c_C^M + X \tag{20}$$

The ionic concentration of ionic species C^{z_2} in the membrane phase c_C^M is equal to c_{AC}^M , from eqs (19) and (20), the stoichiometric electrolyte concentration in the membrane phase can be evaluated as [50],

$$c_{AC}^{M} = -\left(X/2\right) + \left[\left(X/2\right)^{2} + \left(c_{AC}^{s}\right)^{2}\right]^{1/2}$$
 (21)

It is important to observe that D_{AC}^{M} and t_{i}^{M} are functions of the local ionic concentrations, therefore, they are position dependent under transport conditions. This makes the exact analytical integration of eq. (12) across the membrane difficult.

Approximate solutions can be obtained, however, when the external electrolyte concentrations in two cells are very similar to each other. The transport coefficients in a binary symmetric electrolyte can then be approximated by the equilibrium values.

$$\frac{D_{AC}^{M} \approx \overline{D_{AC}^{M}} = D_{A} D_{C} \left(\overline{c_{A}^{M}} + \overline{c_{C}^{M}} \right)}{D_{A} \overline{c_{A}^{M}} + D_{C} \overline{c_{C}^{M}}}$$
(22)

where the average ionic concentrations are given by

$$\overline{c_A^M} = \overline{c_C^M} + X = \left(X \middle/ 2\right) + \left[\left(X/2\right)^2 + \left(\overline{c_{AC}^S}\right)^2 \right]^{1/2}$$
(23)

For porous membrane, the ions transfer through the membrane is governed by mass conservation eq. (5), which is the same with the dense ceramic membrane. Here, we describe different aspects of the one-dimensional transport processes. According to the Nernst-Planck equation (eq. (1)), The molar flux density of ionic species *i* across the membrane is given by.

$$J_i = -D_i \left(\frac{dc_i^m}{dx} + z_i f c_i^m \frac{d\varphi^m}{dx} \right)$$
(24)

For the cases in which migration enhances the ionic species *i* in the positive *x* direction, which requires that $z_i f \frac{d\varphi^m}{dx} < 0$. For the sake of simplicity, the Goldman constant-field assumption is used, $d\varphi/dx = \Delta \varphi/L$. *L* is the thickness of the porous membrane. Since the steady-state flux density is independent of position, then eq. (24) becomes a first-order, linear, ordinary differential equation that can be integrated over the membrane. This leads to an exponential concentration profile of ion concentration inside the membrane [50],

$$c_i^m = c_i^{S2} + \left(c_i^{S1} - c_i^{S2}\right) \frac{e^{-z_i f \Delta \varphi} - e^{-z_i f \Delta \varphi x/h}}{e^{-z_i f \Delta \varphi} - 1}$$
(25)

where c_i^{S1} and c_i^{S2} are the concentrations of ionic species *i* in external solutions on both sides of the porous membrane, $c_i^{S1} > c_i^{S2}$. Combining with eq. (24), the Goldman equation for the flux density J_i is obtained,

$$J_{i} = -\frac{D_{i}}{L} \frac{z_{i} f \Delta \varphi}{e^{z_{i} f \Delta \varphi} - 1} \left(c_{i}^{S2} e^{z_{i} f \Delta \varphi} - c_{i}^{S1} \right) = \frac{D_{i}}{L} E \left(c_{i}^{S1} - c_{i}^{S2} e^{z_{i} f \Delta \varphi} \right)$$
(26)

where iontophoretic enhancement factor, $E = \frac{z_i f \Delta \varphi}{e^{z_i f \Delta \psi} - 1}$, reflects the migration contribution to the steady-state solute flux density across the porous membrane.

2.3. Solvent effects

Compared with the membranes applied in aqueous system, the most fundamental requirement to the membranes applied in non-aqueous system is the stability in the organic solvent. The properties of the organic solvent are totally different from water, which leads to the stability of the membranes in organic solvent is different from that in water. The stability of the membranes in organic solvent depends on the interaction between membrane materials and organic solvent molecules. It is well known that many membranes will swell when contacting organic solvents, such as the polymer membrane and the twodimensional (2D) material-based membrane. The interaction between membrane materials and solvent molecule will influence the swelling ratio of the membrane. The stronger the force, the higher the swelling rate. The membrane will decompose when the force is strong enough.

Basically, the interaction of organic solvent molecules with the membrane material follow the rule of "like dissolves like", meaning that polar solvents tend to dissolve polar components of the membrane, while non-polar solvents tend to dissolve non-polar components. Thus, we need to know the physical properties of organic solvents before examining the stability of the membrane in an organic solvent. Table 2 summarizes the physical properties of the reported organic solvents applied in NARFBs. Among the several physical properties, permittivity ε is the most important parameter, which relate to the polarity of the solvent molecular. The solvents with relative permittivity greater than 3.6 are polar solvents, in the range of 2.8–3.6 are weakly polar solvents, and less than 2.8 are non-polar solvents. As shown in Table 2, the solvents, such as acetonitrile ($\varepsilon = 35.90$), dimethyl sulfoxide ($\varepsilon = 46.50$), dimethylformamide ($\varepsilon = 36.70$), ethylene carbonate ($\varepsilon = 89.80$), and propylene carbonate ($\varepsilon = 64.92$), possess high permittivity and thus will relatively easily to dissolve the polar components in the membrane, which lead to the instability of the membrane. Similarly, weakly polar solvents, like diethyl carbonate ($\varepsilon = 2.84$), dimethyl carbonate ($\varepsilon =$ 3.13), ethyl methyl carbonate ($\varepsilon = 2.93$) will easily dissolve the weakly polar components in the membrane relatively. For 2D material-based membrane, weather the interlamellar spaces remain unchanged or pop-open depends on the interaction between the material and the solvent molecules. If the force between them is strong, a colloidal solution will be formed and keep stable over a long time when 2D materials disperse in the solvent, and the interlamellar spaces of the layer of the membrane will pop-open when contacting the solvent; otherwise, a deposition will happen and the space remains unchanged. Thus, we can use this rule to judge the stability of the membrane materials in the solvent preliminarily.

For further understand the stability of the membrane in a solvent, Amorphous Cell Module in Materials Studio can be used to simulate the binding states. It is well known that this module is a comprehensive model building tool for creating amorphous materials, which has been extensively used in the previous work [38]. The structure of polymer was further accurately optimized by the first-principle method. We can simulate the swelling ratio of the membrane with the aid of the software.

2.4. Performance description

Parameters used to characterize the membranes are ionic selectivity, ionic conductivity, swelling, stability of chemical and mechanical properties, and cycling performance in an RFB. These parameters are equally useful for aqueous RFBs and now are also commonly used in

Physical properties of organic solvents [51].									
Solvents	Density (g cm ⁻³)	Viscosity (mPa s)	Permittivity (C ² N ⁻¹ M ⁻²)	Dipole moment (D)					
Acetonitrile	0.776	0.34	35.90	3.53					
Dichloroethane	1.253	0.73	10.37	1.86					
Dichloromethane	1.327	0.39	8.93	1.55					
Diethyl carbonate	0.975	0.75 [52]	2.84 [53]	1.07					
Dimethoxyethane	0.868	0.46	7.20	1.71					
Dimethyl carbonate	1.069	0.58 [52]	3.13 [53]	0.93					
Dimethyl sulfoxide	1.100	1.99	46.50	4.06					
Dimethylformamide	0.948	0.80	36.70	3.24					
Dioxolane	1.060	0.59 [52]	7.13	1.50					
Ethyl acetate	0.902	0.43	6.02	1.82					
Ethyl methyl carbonate	1.006	0.65 [54]	2.93 [54]	0.51 [55]					
Ethylene carbonate	1.321	1.90	89.80	4.90					
Methyl acetate	0.932	0.36	6.68	1.72					
Propylene carbonate	1.205	2.53	64.92	4.94					
Tetraethylene glycol dimethyl ether	1.009	4.01	7.68 [56]	1.92 [57]					
Tetrahydrofuran	0.888	0.46	7.58	1.75					

NARFBs.

2.4.1. Ionic permeability and selectivity

The non-selective diffusion of the active materials across the membrane causes self-discharge of the battery, thus should be prevented. The selectivity of ion transfer is characterized by the permeability of the preferred ion divided by the overall permeance of all the ions. Generally, the permeabilities of the ions of both the active species and supporting electrolyte can be measured individually with using a H-type diffusioncell, in which one half-cell is filled with active species and supporting electrolyte solution while the other side is filled with a solution of only supporting electrolyte [58–60]. The solutions in both half cells are vigorously stirred to avoid the concentration gradient. The concentration of the active species is monitored with a UV–Vis spectrometer. The permeability is calculated according to the equation:

$$V\frac{dC_t}{dt} = A\frac{P}{L}(C_0 - C_t)$$
⁽²⁷⁾

where V is the volume of the solution in the active species compartment, C_t the concentration of the active species in the same side as a function of time, A the effective area, L the thickness and P the permeability of the membrane and C_0 is the concentration of active species in the other half-cell.

The measurement H-type diffusion-cell can also be configured as that, one half-cell is filled with one solution of active species or supporting electrolyte, while the other side is filled with pure solvent. The solutions in both half cells are also under vigorously stirring to mitigate concentration polarization. The concentration of the active species is monitored by UV–Vis spectrometer and that of the supporting electrolyte is determined by conductivity measurement with a conductivity meter. The permeabilities of active species and supporting electrolyte are calculated according to eq. (27). Usually, the ionic selectivity of the membrane in a NARFB is defined as the ratio of the permeability of the supporting electrolyte ion to that of the active species [61]:

$$Ionic \ selectivity = \frac{P_s}{P_a} \tag{28}$$

where P_s is the permeability of the supporting electrolyte ion, P_a is the permeability of the active species.

2.4.2. Ionic conductivity

The ionic conductivity of the membranes is measured via electrochemical impedance spectroscopy (EIS) from high frequency $(10^5 - 10^6)$ Hz) to low frequency (0.1–0.01 Hz) with an AC impedance using an Hcell [58,62]. The membrane is immersed in the electrolyte at least for 24 h, prior to the measurements. The intercept of EIS with the real axis at the highest frequency is dominated by the ohmic resistance. The resistance of the conductivity cell with and without the membrane can be obtained at high frequency. The ionic conductivity (σ) is determined by using the following equations:

$$\sigma = \frac{d}{R} \tag{29}$$

$$R = A \times (r_1 - r_2) \tag{30}$$

where *R* is the membrane resistance, *d* the thickness, *A* the effective area of the membrane, r_1 and r_2 are the electric resistances of the test cell with and without membrane, respectively.

2.4.3. Swelling, chemical and mechanical stability

The swelling ratio is determined with measuring a dimension, such as the length, change of the membrane before and after immersing in the electrolyte for a specific time period [59,63], or the electrolyte-uptake as a ratio is used to evaluate the compatibility between the electrolyte and the membrane [64]. The excess electrolyte on the membrane surface is

removed by absorbent paper. The membrane is weighed, or the size of the membrane is measured before and after absorption of the electrolyte. The electrolyte uptake is

Electrolyte uptake (%) =
$$\frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$
 (31)

where W_{wet} and W_{dry} are the weight of the membrane under wet and dry conditions, respectively. The swelling ratio is calculated by the difference in length between the dry (L_d) and solution saturated states (L_w) of the membrane.

Swelling ratio(%) =
$$\frac{L_w - L_d}{L_w} \times 100\%$$
 (32)

Note, that the swelling behavior of the membranes is not always isotropic, it is also meaningful to analyze the swelling by the changes of the thickness and area of the membrane.

To evaluate the chemical stability of the membrane, scanning electron microscopy, infrared, X-ray diffraction and X-ray photoelectron spectroscopies are often utilized to compare the chemical and structural properties of the membrane before and after cycling [31,61].

The mechanical strength of the membrane is often determined with the tensile strength measurement with a tensile test machine at room temperature [58,63]. The stress-strain curve demonstrates the maximum tensile stress of the membranes.

2.4.4. Cycling performance

Cycling performance of the membrane in an RFB is the most important characterization, but only can be measured with the battery assembly. The retentions of the capacities, rates and the efficiencies along with the testing time of the NARFB are all dependent factors of the membrane. CE is the ratio of charge and discharge capacities, so that CE reflects the extent of active species crossover. Voltage efficiency (VE) is the ratio of charge and discharge voltages, and mainly determined by the resistances of ion transfer through the membrane, as well as the concentration polarization of the redox reactions. Energy efficiency (EE) is the product of CE and VE.

During the operation of a NARFB, the undesirable transport of active species through the membrane always happens in an extent, and is referred to as crossover, leading to unexpected self-discharge and lowing the CE. The electrolyte crossover through the membrane is often the main reason for the capacity loss, so that an ideal membrane should have a negligible permeability of active species [65]. Although VE mainly depends on the resistances of ion transfer through the membrane, ohmic resistance sometimes can be a decisive factor.

3. Commercial membranes

In 1988, Matsuda et al. [12] reported the first NARFB. Comparing the performance of the cell assembled with Neocepta ACH-45T AEM with the cells assembled with two porous membranes (MF-2508 and YS-UE02-4B), respectively. The results showed that the characteristics of the membrane influenced the cell performance remarkably. Relatively high efficiencies were obtained when the membrane with a small pore size or selective permeability, and the authors stressed the concept of selective permeability. Since then, many commercial membranes were tested in NARFBs to achieve high performance of the cell. A recent literature search result for the usage of membranes are 42% (some works used both).

3.1. Dense membrane

3.1.1. Ion exchange membrane

IEMs are generally made of organic polymer with ionic side groups thus selectively allow the passage of only one kind of ions while rejecting the opposite ones [39]. They normally have high ionic selectivity and good mechanical stability. As mentioned, IEMs consist of AEMs and CEMs. Table 2 summarizes the reported commercial IEMs in NARFBs.

3.1.1.1. Cation exchange membrane. CEMs, such as Nafion series, are the most often employed membranes in all-vanadium aqueous RFBs, which possess high chemical stability and ionic selectivity in aqueous media. As shown in Table 3, Nafion CEMs are new also used in NARFBs based on both organometallic and metal-free organic active species, and can transfer the cation of the supporting electrolyte after an ion exchange procedure, often with Li⁺, tetraethylammonium (TEA⁺), and tetrabutylammonium (TBA⁺) etc. Original Nafion CEMs only transfer proton, thus the membrane should be pretreated to convert the H⁺-form to the Li^+ , TEA^+ or TBA^+ -forms before use. The H⁺-form membranes are soaked in supporting electrolyte for the transformation. In addition, the low chemical stability and high swellability of Nafion membranes in organic solvents limit their application in NARFBs [66,67]. The morphological change of the membrane in organic solvents also often dictates species crossover [67]. CMI-7000 CEM has been often applied as an ion exchanger in water treatment, and has been recently used as the membrane in NARFBs [68]. CMI-7000 is considerably more cost-effective than Nafion membranes [69], but its ionic conductivity is much lower than Nafion based ones, which leads to extremely low current density [70,71]. Otherwise, Nepem-117 and Fumapem F-14100 CEMs were also used in NARFBs.

3.1.1.2. Anion exchange membrane. AEMs, such as Neosepta [72–74] and Fumasep [74–77], have been often used in NARFBs (Table 3). As well, they have originally been used for desalination of sea and brackish water, as well as in the treatment of industrial polluted water [39]. They also show low ionic conductivity, high swellability and low chemical stability in organic electrolytes [78]. AMI-7001 AEM, similar with CMI-7000 CEM, has been often applied as an ion exchanger in water treatment, however, showing a quite low ionic conductivity when used as the membrane in NARFBs. In contrast, a kind of Fumasep, i.e. FAP-375-PP AEM, was designed for RFBs and showed relatively good performance in NARFBs [79]. However, the morphology of the FAP-375-PP membrane changed after cycling in acetonitrile solvent, and the same membrane even decomposed in ether solvents, such as dimethoxyethane (DME).

IEMs are superior with ionic selectivity, but still only low rate performance up to now are achieved with them [78]. Furthermore, a high degree of swelling in organic solvents leads to dimensional distortion, which results in the crossover of active redox species, and thus decreases the EE. The long-term stability of most commercial IEMs in NARFBs is still not satisfactory. As reported in literature, most NARFBs using Nafion, Nepem and Neosepta IEMs were only tested within 30 cycles [14,72,80-85]. The chemical stability of those membranes in organic electrolytes needs further enhancement. Some NARFBs using Nafion 117 [86], Neosepta AHA [73], and AMI-7001 [71] AEMs showed relatively good long-term stability, which have been tested under 100 cycles, but their extremely low ionic conductivities lead to extremely low current densities (lower than 1 mA cm⁻²). In comparison, Fumasep FAP-375-PP AEMs showed good long-term stability among these IEMs, albeit its morphology still changed after cycling [79]. Therefore, the development of IEMs for NARFBs with high ionic conductivity and low swellability by using chemically stable materials for NARFBs under harsh operating conditions is demanded.

3.1.2. Ceramic membrane

The first application of dense ceramic membrane in batteries was reported in 1972, in which β -alumina was used in high-temperature sodium-sulfur battery [96]. β -alumina is a selective conductor of sodium ion. However, it was called as a solid electrolyte in batteries. Its

Table 3

Commercial IEMs used in NARFBs.

IEMs	Commercial name	Conductivity (mS cm ⁻¹)	Permeability (\times $10^{-9}~m^2~s^{-1})$	Active species	Supporting electrolyte	Solvent	CE (%)	VE (%)	EE (%)	Current density (mA cm ⁻²)	Ref.
CEMs	CMI-7000	1.5 ^{aq}	-	Fc + TEMPO/[Co (Cp) ₂]PE ₄ +MePh	TBAPF ₆	MeCN	~94	-	-	0.1	[68]
	Nepem-117	58.7 ^{aq} [67]	_	TEMPO/MePh	NaClO ₄	MeCN	90	_	_	0.35	[14]
	Fumapem F- 14100	65 ^{aq}	-	$Fe(bpy)_3(BF_4)_2/Co$ (bpy)_3(BF_4)_2	TEABF ₄	PC	~87	~92	~81	2.2	[87]
	Nafion 1035	10.7	_	V(acac) ₃	TEABF ₄	MeCN	91	-	80	1	[72]
	Nafion 212	3.75	77.8	Fe(BiPy) ₃ (BF ₄) ₂ /Ni (BiPy) ₃ (BF ₄) ₂	TEABF ₄	PC	~80	~87	~69	1	[78]
	Nafion 115	5.9 [<mark>67</mark>]	-	V(acac) ₃	TEABF ₄	MeCN	~95 [67]	~93 [67]	~88 [67]	10 [67]	[67, 88]
	Nafion 117	10 [89]	88 [90]	BCF3EPT/TMeQ	LiBF ₄	PC	~92	-	-	0.14	[86]
				DBBB/TMQ	LiBF ₄	PC	~70	-	~37	0.0625	[80]
				Ni(aneS ₄)[TFSI] ₂	LiPF ₆	EC/PC	~ 83	~ 57	~47	0.005	[<mark>91</mark>]
				FcPI	TBABF ₄	DOL	97.3	-	-	$2 C^{b}$	[92]
AEMs	AMI-7001	1.1^{aq}	-	V(acac) ₃	TEABF ₄	MeCN	~50 [13]	-	-	0.14/0.014	[13, 93]
				[Fe(phen) ₃](PF ₆) ₂ / [Co(phen) ₃](PF ₆) ₂	TEAPF ₆	MeCN	80	48	39	0.25	[94]
				TEMPO/BP	TEAPF ₆	MeCN	81	53	42	0.5	[70]
				DBB/DMBP	TEAPF ₆	MeCN	72	47	-	1	[71]
				Fc + TEMPO/[Co (Cp) ₂]PF ₆ +MePh	TBAPF ₆	MeCN	~97	-	-	0.1	[68]
	Neosepta AFX	0.33	-	Fe(BiPy) ₃ (BF ₄) ₂ /Ni (BiPy) ₃ (BF ₄) ₂	TEABF ₄	PC	-	-	-	-	[74]
	Neosepta AFN	0.18 ^{aq}	-	V(acac) ₃	TEDABF ₄ / TEDAPF ₆	MeCN	-	-	-	-	[85]
	Neosepta AHA	0.21 [74]	8.5 [95]	Fe(BiPy) ₃ (BF ₄) ₂ /Ni (BiPy) ₃ (BF ₄) ₂	TEABF ₄	PC	-	-	-	-	[74]
				[PPN] ₃ [V(P ₃ O ₉) ₂]/ [PPN] ₄ [Co(P ₃ O ₉) ₂]	TBAPF ₆	MeCN	~90	-	-	0.4/0.1 C ^b	[73]
		0.48 [72]		V(acac) ₃	TEABF ₄	MeCN	~95 [81]	-	~27 [81]	0.3 [81]	[72, 81,82, 84]
				Cr(acac) ₃	TEABF ₄	MeCN	~55	-	~20	0.14/0.014	[83]
	Fumasep FAP- PK	0.29	-	Fe(BiPy) ₃ (BF ₄) ₂ /Ni (BiPy) ₃ (BF ₄) ₂	TEABF ₄	PC	94	82	-	2	[74]
	Fumasep FAP- 450	0.5	6.13 [78]	Fe(BiPy) ₃ (BF ₄) ₂ /Ni (BiPy) ₃ (BF ₄) ₂	TEABF ₄	PC	90	87	-	2	[74]
		0.35 [78]		Cobalt(II) complexes	TBAPF ₆	MeCN	~95	~76	~72	0.0044	[76]
	Fumasep FAP- 375-PP	15 ^{aq}	-	4-Oxo TEMPO/ Camphorquinone	TEABF ₄	PC	80.3	88.8	71.3	1	[75]
				2-Me ⁺ /N- alkylphthalimide 6	TBAPF ₆	MeCN	>83	>74	>70	10	[77]
				Fc1N112-TFSI/Fe (acac) ₃	TEATFSI	MeCN	98.7	84.5	83.4	10	[79]

Note: ^{aq}: data collected from aqueous solution. ^b: C here is not converted to mA cm⁻². Fc: ferrocene; TEMPO: 2.2.6,6-tetramethylpiperidinyl-N-oxyl; MePh: N-Methylphthalimide; [Co(Cp)₂]PF₆: cobaltocenium hexafluorophosphate; TBAPF₆: tetrabutylammonium hexafluorophosphate; MeCN: Acetonitrile; TEABF₄: tetraethylammonium tetrafluoroborate: PC: propylene carbonate: EC: ethylene carbonate: FcPI: N-ferrocenylphthalimide: Fe(bpy)₃(BF₄)₃: tris(2.2'-bipyridine)iron tetrafluoroborate; Co(bpy)₃(BF₄)₂: tris(2,2'-bipyridine)cobalt tetrafluoroborate; BCF3EPT: 3,7-bis(trifluoromethyl)-N-ethylphenothiazine; TMeQ: 2,3,6-trimethyl DBBB: 2,5-Di-tert-butyl-1,4-bis(2-methoxyethoxy)benzene; TMQ: 2,3,6-trimethylquinoxaline; Ni(aneS₄)[TFSI]₂: quinoxaline: nickel(II)-1.4.8.11tetrathiacyclotetradecane bis(trifluoromethane) sulfonamide; [Fe(phen)₃](PF₆)₂: 1,10-phenanthrolineiron(II) hexafluorophosphate; [Co(phen)₃](PF₆)₂: 1,10-phenanthrolineiron(II) hexafluorophosphate; [Co(phen)₃](PF₆)₃](PF₆)₃](PF₆)₃| hexafluorophos throlinecobalt(II) hexafluorophosphate; BP: benzophenone; DBB: 2,5-ditert-butyl-1,4-dimethoxybenzene; DMBP: 4,40-dimethylbenzophenone; Fe(BiPy)₃(BF₄)₂: iron tris(2,2'-bypyridine) tetrafluoroborate; Ni(BiPy)₃(BF₄)₂: nickel tris(2,2'-bypyridine) tetrafluoroborate; TEDABF₄: 1-butyltriethylamine tetrafluoroborate or 1-ethyltriethamine tetrafluoroborate; TEDAPF₆: 1-buthyltriethamine hexafluorophosphate or 1-ethyltriethamine hexafluorophosphate; [PPN]₃[V(P₃O₉)₂]: bis(triphenylphosphine)iminium vanadium bistrimetaphosphate; [PPN]₄[Co(P₃O₉)₂]: bis(triphenylphosphine)iminium cobalt bistrimetaphosphate; Cr(acac)₃: chromium acetylacetonate; 4-Oxo TEMPO: 4-Oxo 2,2,6,6-tetramethyl-1-piperidinyloxy; 2-Me+: thioether-substituted cyclopropenium derivative; Fc1N112-TFSI: N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium bis (trifluoromethane-sulfonyl) imide; Fe(acac)₃: iron acetylacetonate.

function is the same as the membrane in RFBs, i.e., preventing the self-discharge of the battery. Muthuraman et al. [97] recently employed Na- β -Al₂O₃ as the separator in the V(acac)₃ NARFBs with sodium salt, NaClO₄, as the supporting electrolyte in acetonitrile. No obvious dimensional change of the Na- β -Al₂O₃ membrane was observed, so that the authors postulated good stability of the material towards long term operation. However, they obtained only 16% VE and 11% CE at current densities for charge and discharge of 0.01 and 0.0015 mA cm⁻², respectively.

Lithium ion conductive ceramics, which have been widely applied in lithium batteries due to their high Li⁺ conductivity [98], and also shown

a great potential in NARFBs [44,99–101]. Zhang et al. [101] reported a Li-based hybrid NARFB using *N*-Benzylphthalimide (BenPh) as active species with lithium bis(trifluoromethane)sulfonimide (LiTFSI) as supporting electrolyte and dimethylformamide/dichloroethane (volume ratio 3:1) as solvent, using Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP) as the separator. Their battery showed impressive performance during the cycling, exhibited a 99% CE and maintained 90% of the initial capacity after 50 cycles at a current density (*j*) of 0.2 mA cm⁻² (Fig. 3a). The potential–capacity profile shows that the NARFB maintains the stable charge and discharge potentials during the cycling (inset of Fig. 3a). However, the LAGP is unstable with the existence of lithium metal and exhibits low



Fig. 3. (a) Cycling performance of Li/BenPh cell at 0.2 M with j = 0.2 mA cm⁻². (b) Cycling performance and (c) charge-discharge profiles of an all-metallocenebased NARFB. Reproduced with permission [100,101].

chemical stability in reductive electrolyte [96,102]. Upon contacting with Li metal, Ge^{4+} would be reduced to Ge^{2+} and Ge^{0} . Therefore, replacing Ge⁴⁺ ions with Ti⁴⁺ ions in the material to make LATP would enhance the stability of lithium ion conductive membrane. Ding et al. [100] reported an all-metallocene-based NARFB with ferrocene and cobaltocene as the active materials, lithium hexafluorophosphate $(LiPF_6)$ as the supporting electrolyte in dioxolane (DOL) by using $Li_{1+x+3z}Al_xTi_{2-x}Si_{3z}P_{3-z}O_{12}$ (LATP) as the separator, which showed a CE of >95% and an EE of >85% at current of 0.4C (Fig. 3b, also note, as the original article did not give the volume of the electrolyte, C here is not converted to mA cm^{-2}). With a LATP separator, the crossover of the active species was limited to the low extent. As shown in Fig. 3c, the potential-time profile shows that the NARFB maintains the potential at 1.7 V during discharging and 1.8 V during charging. The steady voltage profile over time demonstrates not only the reversibility and stability of the metallocene redox species, but also the stability of the LATP separator during the electrochemical process.

Although dense ceramic membranes exhibit excellent ionic selectivity, the low ionic conductivity, leading to a limited current density [103], fragile nature and high cost limits their application [24,44,104].

3.2. Porous membrane

Commercial porous membranes applied in NARFBs are also usually made from organic polymers. Porous membranes achieve ion sieving with the size effect, without the function of ionic selectivity. They generally show high chemical and mechanical stability and lower area resistance if compared to the IEMs and thus make it possible to achieve charge/discharge cycling at high current density, but the ionic selectivity has been an issue which lowers the CE and EE [105,106].

Most of the commercial porous membranes applied in NARFBs are in two categories: Daramic and Celgard, which are produced by two companies. Compared to the IEMs, the porous membranes show higher ionic conductivity and dimensional stability in NARFBs. Table 4 lists the thickness, pore size and porosity parameters of several commercial

porous membranes applied in the NARFBs. Daramic membranes have different thicknesses with the same polyethylene/silica composite formulation and pore structures. Wei et al. [105] evaluated three Daramic membranes for the effect of thickness on cell resistance and crossover by assembling the cell with 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB) and N-Methylphthalimide (MePh) as active materials, LiTFSI as supporting electrolyte in DME solvent. The area-specific resistivity of the cell decreases, which is reflected by greatly improved VEs of corresponding NARFB, when the membrane thickness decreases (Fig. 4a and c). Meanwhile, the thicker separator yields less crossover of active species and self-discharge rate, as demonstrated by the higher CEs at the same testing current density (Fig. 4b). EE is the product of CE and VE, thus, we can obtain a highest value in the range of the tested current densities. Wei et al. [105] further demonstrated that the pore size of a porous membrane is another important parameter that decides the membrane performance. As shown in Fig. 4a and c, even 7-fold thinner than Daramic 175 membrane, the much smaller pore size (28 nm) of Celgard 2325 membrane still lead to a slightly higher cell area-specific resistivity (5.1 Ω cm²) and lower VEs in the same testing current density range $(5-60 \text{ mA cm}^{-2})$. It is well known that small pore size limits the crossover of the active species more effectively and leads to high CE in cell, however, the CEs of Daramic 175 memrbane are higher than that of Celgard 2325 membrane at the same testing current density (Fig. 4b). Here, the thickness of Daramic 175 membrane make a major contribution in CE. Zhen et al. [79] further demonstrated that a cell based on iron acetylacetonate (Fe(acac)₃) anolyte and N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium bis (trifluoromethane-sulfonyl) imide (Fc1N112-TFSI) catholyte with Daramic 250 membrane exhibited a low CE of 88.3% compared that of FAP 375-PP AEM (98.7%) at j = 10 mA cm⁻², which is associated with a more severe crossover effect.

To summarize, VE increases with the decrease of thickness and the increase of the pore size whereas CE shows a reverse correlation due to the increased crossover. Thus, there indeed exists a trade-off in the thickness and pore size of porous membranes, which should be balanced

Table 4

Commercial porous membranes used in NARFBs.

Commercial name	Thickness (μm)	Pore size (µm)	Porosity (%)	Conductivity (mS cm ⁻¹)	Permeability ($\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$)	Active species	Supporting electrolyte	Solvent	CE (%)	VE (%)	EE (%)	Current density (mA cm ⁻²)	Ref.
Daramic	-	0.15	57	-	-	DBMMB/FL	TEATFSI	MeCN	86	83	71	15	[19]
						PTIO	TBAPF ₆	MeCN	~96	~74	~ 71	20	[109]
Daramic 175	175	0.15	57	4.6 [105]	-	DBMMB/MePh	LiTFSI	DME	90	77	69	35	[105]
						DMFc/BuPh	TBABF ₄	MeCN	93	-	51	60	[110]
						BD1	KPF ₆	MeCN	-	-	-	40	[17]
						Fc1N112BF ₄ /Fe (bpy) ₃ (BF ₄) ₂	TBABF ₄	MeCN	81	91	-	5	[111]
						AcNH-TEMPO	LiBF ₄	PC	-	-	-	20	[112]
				17.2 [72]		V(acac) ₃	TEABF ₄	MeCN	73	-	68	1	[72]
Daramic 250	250	0.15	57	6.1 [108]	-	DBMMB/ BzNSN	TEATFSI	MeCN	85.7	94.0	80.6	20	[108]
						DBMMB/2-MBP	TEAPF ₆	MeCN	95	73	70	7.5	[113]
						DBMMB/3-MBP	TEAPF ₆	MeCN	94	70	66	7.5	[114]
						Fc1N112-TFSI/ Fe(acac) ₃	TEATFSI	MeCN	88.3	91.8	81.1	10	[79]
Daramic 450	450	0.15	57	~5 [105]	-	DBMMB/MePh	LiTFSI	DME	-	-	-	-	[105]
Daramic 800	800	0.15	57	4.4 [105]	-	DBMMB/MePh	LiTFSI	DME	-	-	-	-	[105]
						DBMMB/ BzNSN	LiTFSI	MeCN	94	77	72	10	[106]
						PT3/AQ4	TEABF ₄	MeCN	91	89	81	10	[115]
Celgard	25	0.028	39	0.49 [105]	0.48 [116]	DBMMB/MePh	LiTFSI	DME	-	-	-	-	[105]
2325						FeCp ₂ PPh ₂ RCN + Fc/Li	LiPF ₆	EC/ PC/ EMC	98	-	72	20	[117]
Celgard	25	0.043	41	1.0	_	Fe	LiPF6	EC/	_	_	_	_	[74]
2400						(BiPy) ₃ (BF ₄) ₂ / Ni(BiPy) ₃ (BF ₄) ₂	0	EMC					
					2.43	V(acac) ₃	TEABF ₄	MeCN	49	_	32.4	1	[63]
Celgard 2500	25	0.064	55	0.1 [74]	-	Fe (BiPy) ₃ (BF ₄) ₂ /	TEABF ₄	РС	-	-	-	-	[74]
						M^{2+} [DE] M	ND11 DE	MoCN	00			10	[110]
Colgord	25	0.064	55			EalN112 TESI	INDU4PF6	FC /	99	-	- 07	2 5	[110]
3501	23	0.004	55	-	-	Li	LIIFSI	PC/ EMC	99	00	87	5.5	[29]
Celgard	110	0.064	55	3.2 [105]	_	DBMMB/MePh	LITESI	DME	_	_	_	_	[105]
4560				8.5 [106]		DBMMB/ BzNSN	LiTFSI	MeCN	~90	-	~60	40	[106]
						BMEPZ/FL	LITESI	MeCN	~96	_	~70	20	[119]
						DBPZ/FL	LITESI	MeCN	~90	78	~70	20	[120]
						Cr(acac) ₃	TEABF ₄	MeCN	55	-	25	0.39/	[121]

Note: FL: 9-fluorenone; PTIO: 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; DMFc: 1,1-dimethylferrocene; BuPh: *N*-butylphthalimide; BD1: 4-benzoylpyridinium derivative 1; BzNSN: 2,1,3-benzothiadiazole; Fc1N112BF4: ferrocenylmethyl dimethyl ethyl ammonium tetrafluoroborate; Fe(byy)₃(BF4)₂: ferrocenylmethyl dimethyl ethyl ammonium tetrafluoroborate; AcNH-TEMPO: 4-acetamido-2,2,6,6tetramethylpiperidine-1-oxyl; 2-MBP: 2-methylbenzophenone; 3-MBP: 3-methylbenzophenone; PT3: phenothiazine derivative; AQ4: anthraquinone derivative; FeCp₂PPh₂RCN: *N*-(pyridine-2-ylmethylene)-1-(2-(diphenylphosphino) ferrocenyl) ethanamine; Fe(BiPy)₃(BF₄)₂: iron tris(2,2'-bypyridine) tetrafluoroborate; Ni(BiPy)₃(BF₄)₂: nickel tris(2,2'-bypyridine) tetrafluoroborate; M: bis(dimethylamino) derivative of diquat; BMEPZ: 5,10-bis(2-methoxyethyl)-5,10-dihydrophenazine; DBPZ: 5,10-dihydro-5,10-dimethyl phenazine; EC: ethylene carbonate; EMC: ethyl methyl carbonate; NBu₄PF₆: Tetrabutylammonium hexafluorophosphate.

and optimized [107,108].

4. Effort in improving the membrane

As discussed above, the fragile nature, and high cost limits the application of dense ceramic membranes. Most of the IEMs exhibit high swelling, low chemical stability and ionic conductivity. The commercial porous membranes exhibit low ionic selectivity. Therefore, several schemes to improve the performance of dense and porous membranes in NARFBs have been proposed.

4.1. Intrinsic dense membrane

Over the last decade, several preparation techniques have been practiced in academic labs to overcome the issues of commercial AEMs. Most of them employed a solution-casting method with preparing the polymer solution in an appropriate ratio of monomer and solvent, stirring to obtain a viscous solution, and then casting on a glass plate. After phase-transformation, the membrane is peeled off from the plate. Maurya et al. [59] reported a single step process for the synthesis of an AEM with simultaneous polymerization and quaternization. Their membrane exhibited good dimensional and chemical stability in V (acac)₃/acetonitrile solution and an ionic conductivity of 0.105 mS cm^{-1} with a vanadium permeability of $1.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Their battery achieved CE 91.7%, VE 95.7% and EE 87.7% for 20 cycles at i = 0.1 mA cm⁻². The membrane has a lower swelling ratio, tunable still with monitoring the crosslinking degree, than that of the commercial membranes available. Nonetheless, 3% of swelling ratio was observed which was still not acceptable for the practical need of the dimensional stability. Li et al. [62] prepared an AEM with benzovl peroxide as the monomer and with brominating and crosslinking. Their membrane showed good thermal and chemical stability in acetonitrile solvent and utilized in a NARFB with tetrakis(acetonitrile)copper(I) bis(trifluoromethylsulfonyl)imide material as an active and



Fig. 4. Electrochemical performance of the flow batteries with different commercial porous membranes: (a) flow cell area-specific resistivity before cycling; (b) CE; (c) VE; and (d) EE. Reproduced with permission [105].

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as the supporting electrolyte in acetonitrile, yielding a CE 89%, VE 61% and EE 54% during 10 cycles at i = 7.5 mA cm⁻². However, the swelling ratio was still in the range of 2%–6% in the electrolyte and pure acetonitrile solvent. McCormack et al. [89] reported a method to functionalize polyphenylene oxide backbone with phenoxyaniline trisulfonate, and to show an ionic conductivity of $0.015-0.06 \text{ mS cm}^{-1}$ with low ferrocene permeability in dimethyl carbonate solvent. The membranes appear to be dimensionally stable over a period of at least four months in the non-aqueous electrolyte. However, they did not give the battery performance data. Recently, Kwon et al. [122] reported an AEM consists of polyarylene ether ketone (PAEK) and crosslinked with alkyl chains containing quaternary ammonium ions for transporting anions and utilized the membrane in a NARFB with V(acac)₃ in tetraethylammonium tetrafluoroborate (TEABF₄)/acetonitrile electrolyte. The crosslinked PAEK membrane enhanced the chemical/mechanical stability and BF₄ conductivity for operating NARFBs. Their battery exhibited CE 92%, VE 90%, EE 81%, which are higher than Neosepta AHA AEM (54%, 69% and 37%, respectively) at j = 1 mA cm⁻².

4.2. Intrinsic porous membrane

Doris et al. [123] reported intrinsic microporous polymer (IMP) membranes with pore sizes in the range of 0.4–0.8 nm, synthesized from 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol and 2,3,5,6-tetrafluoroterephthalonitrile, and confirmed that active species crossover is mitigated by reducing the pore size to that of molecular dimensions. However, their IMP membrane has high swellability in the acetonitrile solvent, thus, 2,6-bis(4-azidobenzylidene) cyclohexanone, as cross-linking agent, was mixed into the monomer solution before polymerization. After cross-linking, the degree of swelling of the IMP is lowered, and the pore size is further constricted. In another work, Hendriks et al. [124] tested the cross-linked IMP membrane, in the stack of a cross-linked IMP membrane sandwiched in between two layers of

Celgard 2500 membranes, with using tris(dialkylamino) cyclopropenium-derived tetramer as an active material in LiPF₆/acetonitrile and achieved CE 95% and EE 79% at j = 2.5 mA cm⁻² over 6 days of cycling.

4.3. Composite membrane

4.3.1. Intrinsic composite membrane

Intrinsic composite membrane has been often prepared with the solution casting technique which was used also in the preparation of intrinsic IEMs. Jia et al. [30] reported a polymeric Nafion/polyvinylidene difluoride (PVDF) composite membrane. Nafion has exchangeable cations thus can be used as an ion selective material. PVDF used as a rigid framework to control the swelling and consequently eliminate the crossover. After lithiation, the composite membrane was assembled in a redox-targeting NARFBs using ferrocene and cobaltocene as the active materials in the catholyte and anolyte for the redox targeting reactions with LiFePO₄ and TiO₂, respectively, LiTFSI as a supporting electrolyte and tetraethylene glycol dimethyl ether (TEGDME) as solvent. The membrane showed an excellent capability to block the crossover of redox molecules, i.e. ferrocene and cobaltocene. Their cell achieved a CE ~90% at j = 0.05 mA cm⁻². Meanwhile, the Nafion and PVDF components in the composite membrane retained uniform dispersion without appreciable phase separation and chemical degradation after 47 cycles. However, the poor conductivity of the Nafion/PVDF membrane only allowed an extremely low current density (0.05 mA cm⁻²) during the cycling.

Shin et al. [60] reported an organic-inorganic composite membrane with PVDF as a supporting polymer matrix for improving the chemical and thermal stability of the organic-inorganic composite membranes, and introduce silica nanoparticles into the membranes to ensure the low crossover of active species. The fabrication of semi-interpenetrating polymer network through the addition of glycidyl methacrylate, 4-vinyl-pyridine, or *N*-vinylcarbazole enables control of the membrane

structure. Their membrane ensured a low V(acac)₃ crossover, CE was measured as ~99% and EE was 82.4% at j = 3 mA cm⁻² in a NARFB using V(acac)₃ as the active material in TEABF₄/acetonitrile electrolyte, but the authors did not give the cycling data.

4.3.2. Modified composite membrane

Two preparation methods, i.e. surface coating and pore filling methods, have been adopted in synthesizing modified composite membranes.

4.3.2.1. Surface coating. Surface-coating method has been applied to



Fig. 5. Composite membrane of a (a) chitosan/urushi layer, (b) PDDA/urushi semi-interpenetrating polymer network layer, (c) polyDDA/urushi charged-porous and PDDA/urushi thin-layered coated on a porous support. (d) CE, VE, and EE of non-aqueous Fe–Ni RFBs with a polyDDA/urushi charged-porous composite membrane, PDDA/urushi thin-layered composite membrane, and commercial FAP 450 membrane. (e) Tensile strength of several membranes as a function of the immersion time (a: polyDDA/urushi charged-porous membrane; b: Celgard 2400 membrane; c: PDDA/urushi thin-layered membrane; d: FAP-450 membrane; e: Nafion 212 membrane). Reproduced with permission [58,78,95].

modify the surface of a porous substrate, with incorporation of ionic selective function. Won and his coworkers [58,78,95] reported three surface-modified Celgard membranes with coating a polymer layer. Three polymers were employed as the surface modifiers, i.e. urushi, a natural polymer, which was shown to have high chemical and mechanical stability, chitosan and polydiallyldimethylammonium chloride (PDDA) as anion exchange polymers. The structures are illustrated in Fig. 5a-c. As shown in Fig. 5a, a free-standing chitosan/urushi (C/U) pseudo-interpenetrating polymer network (IPN) film was prepared under a humidifier, where the urushi networks were formed by laccase-catalysed polymerization and an autoxidation reaction on the unsaturated side chain, and the free-standing C/U pseudo-IPN film was prepared with different amounts of chitosan. The modified composite membranes by C/U pseudo-IPN with 17% chitosan coated on the surface of Celgard 2400 membrane, tested with a NARFB using V(acac)₃ as the active material in TEABF₄/acetonitrile electrolyte. The CE value of the V (acac)₃ NARFB was 66% which was higher than Celgard 2400 and Neosepta AHA membranes (38% and 52%, respectively) at i = 1.39 mA cm⁻². The PDDA/urushi (P/U) semi-IPN free-standing film was prepared by a solution-casting method, i.e. an appropriate amount of PDDA was mixed with the urushiol paste and casted onto the surface of the Celgard support, followed by using a doctor blade (50 mm) technique and crosslinking initiated with the UV-irradiation. Afterwards, the membrane was turned over, the back side of the Celgard membrane was coated with the same process as the formation of the top layer (Fig. 5b). The CE and EE of V(acac)₃ NARFB increase with increasing the amounts of PDDA in the P/U semi-IPN layer. For one of the composite membranes containing 40 wt% of PDDA, the CE and EE values reached 69.5% and 42.5% at j = 0.5 mA cm⁻², respectively, which are higher than those of both the Neosepta AHA and Celgard 2400 membranes. Kim et al. [78] synthesized the PDDA-urushi/Celgard composite membrane by the similar method (Fig. 5c). The iron tris(2,2'-bypyridine) tetrafluoroborate (Fe(BiPy)₃(BF₄)₂)/nickel tris(2,2'-bypyridine) tetrafluoroborate (Ni(BiPy)3(BF4)2) NARFB assembled with thin-layer PDDA-urushi/Celgard composite membrane obtained a CE 79.0% and EE 68.7% at j = 0.5 mA cm⁻², all were higher than those obtained with the commercial FAP-450 AEM (Fig. 5d). The presence of the chemically stable urushi in the composite membrane maintains the chemical and mechanical stability in acetonitrile and the anion exchange polymeric component further mitigates the crossover issue. However, the authors only gave 10 cycles data for the battery performance. The mechanical strength of the thin-layered composite membrane was 1356 kg cm^{-2} , mainly attributed to the strength of the Celgard 2400 membrane (1581 kg cm⁻²), which was much higher than that of the FAP 450 and Nafion 212 membranes (Fig. 5e).

Jung et al. [125] tested a cross-linked ladder-like structured polysilsesquioxanes (L-PSQ)/Celgard composite membrane with thermal initiation of the crosslinking reaction of L-PSQ after dip-coating, and utilized the membrane in a NARFB with V(acac)₃ in TEABF₄/acetonitrile electrolyte. The L-PSQ layer with anion exchange site took the role of selecting ionic transfer mitigating the V(acac)₃ crossover. The composite membranes showed high ionic conductivity (0.14–0.32 S cm⁻¹) that were of the same order of magnitude as that of the Celgard 2400 support (0.37 S cm⁻¹). The charged nanopores formed by the ladder-like polyelectrolyte that permitted a high ion transport across the membrane while blocking the crossover of the active species. However, their battery exhibited low CE 62.7%, EE 43.7% at j = 1.39 mA cm⁻².

Surface modification of porous substrate with coating a material achieving ionic sieving by size effect, without the function of ionic selectivity, also enhances the performance of the composite membrane. Bang et al. [63] presented a porous composite membrane with surface-modification of Celgard 2400 membrane using electrospun Nafion/polyvinyl alcohol (PVA) fiber as an overlayer. Their modified membrane showed a lower swelling ratio than that of the Nafion 212 membrane due to the hydrophobic nature of Celgard 2400 membrane, and a lower V(acac)₃ permeability than that of the Celgard 2400

membrane due to the permselective nanofiber woven on the surface of the Celgard 2400 membrane. They achieved a CE 69% and an EE 50% at i = 1.39 mA cm⁻².

Xi et al. [126] reported a carbon coated composite membrane used in the Li/Br hybrid NARFB, which is based on Br_2/Br^- and Li⁺/Li as active redox pairs, LiTFSI as supporting electrolyte, and DOL and DME (volumetric ratio of 1:1) as the solvent. Expanded graphite and activated carbon were mixed with Nafion isopropanol solution, then the solution was sprayed onto the surface of the Daramic HP-200 support to form carbon coated composite membrane. Due to the higher surface area of the carbon phases, the charge transfer resistance of the battery was reduced, from 418.9 to 35.6 Ω cm². Their battery displayed a CE 90% and an EE 80% at current density of 1.0 mA cm⁻² after continuously cycling for more than 1000 times.

Metal-organic framework (MOF), assembled with inorganic central metallic atoms and organic ligands, possesses regular micropores and high porosity [127], and has been applied for many separation purposes. Yuan et al. [116] reported a 2D MOF nanosheets-modified Celgard membrane via a simple infiltration method, i.e. the ultrathin Ni-MOF nanosheets dispersion, which was synthesized by sonication exfoliation, were filtrated on the surface of Celgard 2325 support. Most active species are blocked by the MOF layer; a small portion can go through the stacked layer via the zigzag paths between the MOF nanosheets. The supporting electrolyte ions can not only pass through the MOF interlayer spaces formed by the nanosheets assembling, but also the intracrystalline MOF pores, i.e., via the shorter transport channels. The NARFB based on Fe(acac)₃ and Fc1N112-TFSI in tetraethylammonium bis(trifluoromethylsulfonyl) imide/acetonitrile constructed with their composite membrane exhibited much higher CE (91.0% vs 82.9%) without much compromise on VE (93.7% vs 94.2%), at a larger average discharge capacity (1.30 vs 0.86 Ah L^{-1}) compared with the pristine Celgard membrane at $j = 4 \text{ mA cm}^{-2}$. The NARFB used the same electrolytes but used a Daramic 250 membrane exhibited a CE of 88.3% [79].

Ma et al. [128] reported a Y-zeolite with a microporous PVDF composite membrane, prepared with spray coating Y-zeolite on both sides of the PVDF substrate, and made a NARFB using with 5,10,15, 20-tetraphenylporphyrin (H₂TPP) as the active species, tetrabutylammonium perchlorate/dichloromethane as supporting electrolyte in acetonitrile, and tested the performance in a wide temperature range between -40 and 20 °C, see Fig. 6. The pore size of the Y-zeolite (0.74 nm) is between the calculated diameters of H₂TPP (1.141 nm) and one of the supporting-electrolyte ions (ClO_4^- , 0.547 nm). Thus, the Y-PVDF ion-selective membrane retains H₂TPP and permits ClO₄⁻ to transport owing to the pore size exclusion effect. The prepared Y-zeolite/PVDF ion-selective membrane has a surface covered by Y-zeolite particles and a clear sandwich cross-section structure with Y-zeolite layers (the optimized thickness is 7-8 mm) attached on each side (Fig. 6b). As shown in Fig. 6c, their NARFB delivered an impressive CE >99% and exceptional capacity retention ratio (>99.98% per cycle) during the cycling at j = 1mA cm⁻². However, their EE was as low as <50%, most probably due to the low ionic transfer rate.

4.3.2.2. Pore filling. As the name implies, pore-filling is realized by filling an ion selective functional component, possible both with inorganic and organic materials into the pores of a porous substrate, thus improves the ionic selectivity. As aforementioned, Kim et al. [78] have further improved their membrane with letting diallyl dimethyl ammonium chloride (DDA)/urushi viscous solution penetrates into the pores of the Celgard 2400 support and polymerizes inside the pores (defined this membrane as polyDDA/urushi). With the polyDDA/urushi pore-filled Celgard 2400 membrane, the CE and EE of the Fe (BiPy)₃(BF₄)₂/Ni(BiPy)₃(BF₄)₂ NARFB in TEABF₄/propylene carbonate reached 90.7% and 76.2%, respectively, at *j* = 0.5 mA cm⁻², which are higher than that of FAP-450 membranes, as shown in Fig. 5d. They also



Fig. 6. (a) Ion-selectivity principle of the Y-PVDF composite membrane. (b) Structure, and characteristic of the Y-PVDF and Y-PVDF composite membrane. (c) Long-term stability of the battery by repeated charge/discharge cycling over 200 cycles at j = 1 mA cm⁻². Reproduced with permission [128].



Fig. 7. (a) Process of fabricating the QPPO membrane: the general fabrication method of the QPPO membrane and electrically treated QPPO membrane. (b) Efficiencies of a single cell with $0.05 \text{ M V}(\text{acac})_3/1 \text{ M TEABF}_4$ by applying the electrically treated QPPO membrane. (c) Synthesis scheme for the CuBTC/Celgard composite membrane by in situ seeding and crystallization of MOFs; (d) Discharge capacity with corresponding CE over cycling. Reproduced with permission [61,132].

confirmed the positive contributions of both the Celgard 2400 and the urushi network to the mechanical strength as demonstrated in Fig. 5e. The results indicate that the presence of the chemically stable urushi in the composite membrane reduced the crossover contamination, while maintaining chemical and mechanical stability.

Moon and his coworkers described two treatments i.e. pore filling a polymer with guaternization [129,130] and polymerization with electrical treatment [131,132]. The composite membranes using porous polyethylene (PE) substrates, cross-linked with vinylbenzyl chloride, divinylbenzene, and benzoyl peroxide, subsequently with different functional groups quaternization [129]. The cross-linked composite membrane with triethylamine quaternization (defined this membrane as PE-TEA) showed better oxidative stability than other composite membranes. The V(acac)₃ NARFB show that the PE-TEA membrane performed well with the VE 95.7% and EE 58.2% for 10 cycles except the first cycle at low current density of 0.01 mA cm^{-2} . They synthesized another pore-filled composite membrane cross-linked by styrene, vinylbenzyl chloride, divinylbenzene, and benzoyl peroxide, and under trimethylamine quaternization [130]. The NARFB based on Fe (BiPy)₃(BF₄)₂/Ni(BiPy)₃(BF₄)₂ in TEABF₄/propylene carbonate constructed with their membrane exhibited a CE 83.3% and EE 77.2% at a current of 20 mA. However, the authors only gave data of 5 cycles for the flow battery performance. Moreover, the electrically aligned composite membrane was obtained with an electrical treatment applying a direct electric field after filling the pores with quaternary-aminated polymerized 2,6-dimethyl-1,4-phenylene oxide (QPPO), as shown in Fig. 7a [132]. The channels made of QPPO for ion transfer in the substrate are aligned according to the direction of the electric field. Owing to the oriented ion channels of the QPPO polymer, the anion can be directly transferred. Accordingly, their electrically treated composite membrane showed high ionic conductivity and mechanical stability, with enhanced stabilities in organic solvents. The assembled V(acac)3 NARFB in TEABF₄/acetonitrile achieved CE 97.1% and EE 69.3% at j = 80 mA cm^{-2} for 100 cycles, see Fig. 7b.

Peng et al. [61] reported a copper benzene-1,3,5-tricarboxylate (CuBTC) MOF filled in the pore of a Celgard membrane (no specific number) with gradient distribution of MOF synthesized in situ. The three-dimensional channel structure of CuBTC with ordered micropores at a size window of ~ 0.9 nm, might act as an efficient barrier for blocking redox active species, ferrocene, and meanwhile allow the transfer of the supporting electrolyte ions, Li⁺. However, the crowded filling of MOF particles inside the porous substrate can also inevitably affect the membrane resistance. Therefore, to obtain a well-controlled growing a thin and dense layer of MOF inside the membrane, the authors proposed a gravity-assisted solvent evaporation method, as illustrated in Fig. 7c. Their Li/ferrocene hybrid NARFB with LiClO4 as supporting electrolyte in DOL/DME (volumetric ratio of 1:1) solvent delivered a high CE ~99% at $j = 4 \text{ mA cm}^{-2}$, while their EE was 78.6%, seen as in Fig. 7d. The capacity decay rate of their cell with the composite membrane was 0.09% per cycle, which was much slower than that, 0.24% per cycle, of the cell with the pristine Celgard membrane.

5. Summary

The demand for large scale energy storage devices has promoted a continuous development of NARFBs. Although many researches on NARFBs in recent years have been reported, the development of membrane in the device is still facing a lot of challenges. Inappropriate membrane is one of the mainly reasons causing the performance of the real NARFBs far behind the commercial need. As mentioned, an ideal membrane in NARFBs should have high ionic conductivity and selectivity, low swellability, low-cost, and high mechanical and chemical stability in organic solvent. Thus, we must compromise and optimize among the six properties of these membranes.

- (1) For ionic selectivity, dense ceramic membrane possesses high ionic selectivity which allows only the transfer of supporting electrolyte ions, Li⁺ or Na⁺, through the vacancy and block other ions. CEMs, and AEMs also exhibit high ionic selectivity due to the negatively or positively ionic functional groups in the transfer path selectively allowing the passage of only one kind of ions while rejecting the opposite ones. In contrast, the porous membranes normally have extremely low ionic selectivity due to their pore size is still too large to block the redox active species with the present materials. Modified composite membranes, viz. loading the porous substrate with the ion selective components, show enhanced ionic selectivity due to its ionic selective and pore size limitation components.
- (2) For chemical stability, the LAGP dense ceramic membrane is unstable with the existence of lithium metal, while the other dense ceramic membranes, such as LATP and Na- β -Al₂O₃, show good chemical stability during the cycling. Porous membrane also exhibits high chemical stability during the battery operation. Nevertheless, the morphology of the structure of CEMs and AEMs may change after cycling, even some IEMs decompose in the organic solvent, which cause chemical instability. Obviously, modified and intrinsic composite membranes have a potential to achieve high chemical stability, because both can select chemically stable materials to form the membrane.
- (3) For swellability, IEMs, i.e. both CEM and AEM, exhibit high swelling ratio in organic solvent, which may lead to structure instability of the membrane. Dense ceramic and porous membrane do not swell when soak in organic solvent, while modified composite membrane also show low swellability because of its porous substrate. However, intrinsic composite membrane swells notably due to the polymer component, but much lower than those of IEMs.
- (4) The ionic conductivity of dense ceramic membrane is quite low which leads to the fact that the cell only can be tested at extremely low current density, less than 1 mA cm⁻². Porous membrane owns large pore size which contributes to ion transfer and thus exhibits high ionic conductivity. However, for membranes, high ionic selectivity often leads to low ionic conductivity. IEMs, modified composite membrane, and intrinsic composite membrane exhibit high ionic selectivity but low ionic conductivity. The trade-off should always be balanced and optimized.
- (5) For mechanical stability, the fragile nature of dense ceramic membrane leads to its poor mechanical strength. The high swelling ratio of IEMs will also influence the mechanical stability in organic solvents. Porous polymer membrane exhibits good mechanical strength, and modified composite membrane shows high mechanical stability due to the excellent mechanical strength of the porous polymeric substrate. The mechanical stability of intrinsic composite membrane needs to be further enhanced.
- (6) Low cost is highly desirable for large-scale energy storage. Compared to the porous membranes, dense ceramic membranes and IEMs are more expensive. Nonetheless, modified and intrinsic composite membrane have been only synthesized in lab and their large-scale production needs to be enabled.

From the above description of the recent progress of membranes in NARFBs, a summary of the membrane performances, advantageous aspects, and shortcomings, can be illustrated as the radar plots in Fig. 8. Fig. 8a show that dense ceramic membranes possess high ionic selectivity and low swellability, but they are still not practical due to their poor mechanical stability, low ionic conductivity, and high cost. As shown in Fig. 8b and c, CEMs and AEMs, which show high ionic selectivity and not low mechanical stability, encounter the major challenges



Fig. 8. Radar plots of the performance properties of different membranes.

of high swellability and poor chemical stability in organic solvents. Porous membranes have high ionic conductivity, low swellability, lowcost, high chemical and mechanical stability, however, extremely low ionic selectivity will cause serious crossover and self-discharge, which limit their application, see Fig. 8d. As shown in Fig. 8e, modified composite membranes achieve high ionic selectivity, low swelling ability, high ionic conductivity, meanwhile, exhibit chemical and mechanical stability simultaneously because of excellent chemical stability and mechanical strength of the porous substrate. Intrinsic composite membranes also have a potential of achieving high ionic selectivity and conductivity, low swelling ability, chemical and mechanical stability simultaneously because of the possibilities in monitoring their component materials, as shown in Fig. 8f. However, the present state-of-the-art ionic conductivity of them still needs to be enhanced which decides the power density of the battery. Power density describes the rate performance of the battery, i.e., how fast the energy can be stored or released, which is crucible for the large-scale energy storage. For membranes, high ionic selectivity often ensures high CE, but leads to low current density. The trade-offs should be balanced and optimized. Among these reported state-of-the-art membranes, porous membranes can cycle under high current density, but the ion selectivity is an issue which lowers the CE & EE. Most modified and intrinsic composite membranes can obtain high CE, but quite low current density. The composite membranes which own oriented ion channels have potential to achieve high CE and current density. Thus, developing suitable membranes to obtain high power density with high CE is highly desirable for largescale energy storage.

6. Perspective

The membranes in NARFBs have already become a noticed research topic, and in recent years we observed a fast progress and great effort input. However, the present state-of-the-art membranes are still far from the requirement of the large scale commercial application of NARFBs. The key issue is to develop the membrane simultaneously possessing high ionic selectivity and conductivity, meanwhile, having high chemical, electrochemical and mechanical stability during the NARFB operation. Three concerted strategies are proposed here.

- (1) Surface and pore modification of the porous substrate to enhance the ionic selectivity of porous membrane. Thus, the approach of pore modification with incorporation of ionic selectivity and pore size limitation elements will be manipulated towards better performance of the membrane. Microporous materials and ion exchange polymers will be optimized and incorporated to improve the ionic selectivity and to enhance the transfer rate of the composite membrane based on the monitoring of ion exchange and size selection effects.
- (2) Making intrinsic composite membrane with organic and inorganic bulk domains and continues phases. The selecting of the component materials is flexible, which can use chemically stable materials to achieve high chemical stability and add polymer to enhance the mechanical stability. Though the performance of the reported work on intrinsic composite membrane still needs a great improvement, there exists a great room for monitoring the component materials to achieve high ionic selectivity and conductivity.
- (3) Preparation of free-standing membrane with nanofilms or nanosheets. 2D nanosheets can readily stack to form flexible, freestanding films with lamellar microstructure, such as MOF nanosheets, covalent organic framework nanosheets, graphene oxide, vermiculite nanosheets, molybdenum disulfide nanosheets, boron nitride nanoflakes. The membrane allows the transfer of supporting electrolyte ions through the interlayer spaces formed by the nanosheets assembling, especially for MOF and covalent organic framework which also have the intracrystalline pores to transfer supporting electrolyte ions.

Credit authorship contribution statement

Jiashu Yuan: Writing - Original Draft, and revisions. Zheng-Ze Pan: Writing - Review & Editing. Yun Jin: Writing - Review & Editing. Qianyuan Qiu: Discussion. Cuijuan Zhang: Discussion. Yicheng Zhao: Discussion. Yongdan Li: Methodology, Review & Editing, Supervision.

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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References

- H.E. Murdock, T.A.D. Gibb, F. Appavou, A. Brown, B. Epp, B. Kondev, A. McCrone, E. Musolino, L. Ranalder, J.L. Sawin, Renewables, Global status report, in: Renewable Energy Policy Network for the 21st Century, 2019, 2019.
- [2] International energy outlook, in: Energy Information Administration, U.S. Department of Energy, Washington, DC, 2019.
- G.L. Soloveichik, Flow batteries: current status and trends, Chem. Rev. 115 (2015) 11533–11558, https://doi.org/10.1021/cr500720t.
- [4] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices, Science 334 (2011) 928–935, https://doi.org/10.1126/ science.1212741.
- [5] A.M. Posner, Redox fuel cell, Fuel 34 (1955) 330-338.
- [6] L.H. Thaller, Electrically rechargeable redox flow cells, in: 9th Intersociety Energy Conversion Engineering Conference, 1974, pp. 924–928.
- [7] M. Park, J. Ryu, W. Wang, J. Cho, Material design and engineering of nextgeneration flow-battery technologies, Nat. Rev. Mater. 2 (2017) 16080, https:// doi.org/10.1038/natrevmats.2016.80.
- [8] E. Sum, M. Skyllas-Kazacos, A study of the V(II)/V(III) redox couple for redox flow cell applications, J. Power Sources 15 (1985) 179–190.
- [9] E. Sum, M. Rychcik, M. Skyllas-kazacos, Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery, J. Power Sources 16 (1985) 85–95.
- [10] M. Skyllas-Kazacos, M. Rychick, R. Robins, All-vanadium Redox Battery, 1988. U. S.
- [11] C.G. Armstrong, K.E. Toghill, Stability of molecular radicals in organic nonaqueous redox flow batteries: a mini review, Electrochem. Commun. 91 (2018) 19–24, https://doi.org/10.1016/j.elecom.2018.04.017.
- [12] Y. Matsuda, K. Tanaka, M. Okada, Y. Takasu, M. Morita, A rechargeable redox battery utilizing ruthenium complexes with non-aqueous organic electrolyte, J. Appl. Electrochem. 18 (1988) 909–914.
- [13] Q. Liu, A.E.S. Sleightholme, A.A. Shinkle, Y. Li, L.T. Thompson, Non-aqueous vanadium acetylacetonate electrolyte for redox flow batteries, Electrochem. Commun. 11 (2009) 2312–2315, https://doi.org/10.1016/j.elecom.2009.10.006.
- [14] Z. Li, S. Li, S. Liu, K. Huang, D. Fang, F. Wang, S. Peng, Electrochemical properties of an all-organic redox flow battery using 2,2,6,6-tetramethyl-1-piperidinyloxy and N-methylphthalimide, Electrochem. Solid State Lett. 14 (2011) A171, https://doi.org/10.1149/2.012112esl.
- [15] J.D. Milshtein, A.P. Kaur, M.D. Casselman, J.A. Kowalski, S. Modekrutti, P. L. Zhang, N. Harsha Attanayake, C.F. Elliott, S.R. Parkin, C. Risko, F.R. Brushett, S.A. Odom, High current density, long duration cycling of soluble organic active species for non-aqueous redox flow batteries, Energy Environ. Sci. 9 (2016) 3531–3543, https://doi.org/10.1039/c6ee02027e.
- [16] C.S. Sevov, R.E. Brooner, E. Chenard, R.S. Assary, J.S. Moore, J. Rodriguez-Lopez, M.S. Sanford, Evolutionary design of low molecular weight organic anolyte materials for applications in nonaqueous redox flow batteries, J. Am. Chem. Soc. 137 (2015) 14465–14472, https://doi.org/10.1021/jacs.5b09572.
- [17] K.H. Hendriks, C.S. Sevov, M.E. Cook, M.S. Sanford, Multielectron cycling of a low-potential anolyte in alkali metal electrolytes for nonaqueous redox flow batteries, ACS Energy Lett. 2 (2017) 2430–2435, https://doi.org/10.1021/ acsenergylett.7b00559.
- [18] J.A. Kowalski, M.D. Casselman, A.P. Kaur, J.D. Milshtein, C.F. Elliott, S. Modekrutti, N.H. Attanayake, N. Zhang, S.R. Parkin, C. Risko, F.R. Brushett, S. A. Odom, A stable two-electron-donating phenothiazine for application in

nonaqueous redox flow batteries, J. Mater. Chem. 5 (2017) 24371–24379, https://doi.org/10.1039/c7ta05883g.

- [19] X. Wei, W. Xu, J. Huang, L. Zhang, E. Walter, C. Lawrence, M. Vijayakumar, W. A. Henderson, T. Liu, L. Cosimbescu, B. Li, V. Sprenkle, W. Wang, Radical compatibility with nonaqueous electrolytes and its impact on an all-organic redox flow battery, Angew. Chem. Int. Ed. 54 (2015) 8684–8687, https://doi.org/10.1002/anie.201501443.
- [20] R.M. Darling, K.G. Gallagher, J.A. Kowalski, S. Ha, F.R. Brushett, Pathways to low-cost electrochemical energy storage: a comparison of aqueous and nonaqueous flow batteries, Energy Environ. Sci. 7 (2014) 3459–3477, https:// doi.org/10.1039/c4ee02158d.
- [21] P. Leung, A.A. Shah, L. Sanz, C. Flox, J.R. Morante, Q. Xu, M.R. Mohamed, C. Ponce de León, F.C. Walsh, Recent developments in organic redox flow batteries: a critical review, J. Power Sources 360 (2017) 243–283, https://doi. org/10.1016/j.jpowsour.2017.05.057.
- [22] M. Ue, I. Kazuhiko, M. Shoichiro, Electrochemical properties of organic liquid electrolytes based on quaternary onium salts for electrical double-layer capacitors, J. Electrochem. Soc. 141 (1994) 2989–2996.
- [23] M.H. Chakrabarti, N.P. Brandon, S.A. Hajimolana, F. Tariq, V. Yufit, M. A. Hashim, M.A. Hussain, C.T.J. Low, P.V. Aravind, Application of carbon materials in redox flow batteries, J. Power Sources 253 (2014) 150–166, https:// doi.org/10.1016/j.jpowsour.2013.12.038.
- [24] H. Chen, G. Cong, Y.-C. Lu, Recent progress in organic redox flow batteries: active materials, electrolytes and membranes, J. Energy Chem. 27 (2018) 1304–1325, https://doi.org/10.1016/j.jechem.2018.02.009.
- [25] K. Gong, Q. Fang, S. Gu, S.F.Y. Li, Y. Yan, Nonaqueous redox-flow batteries: organic solvents, supporting electrolytes, and redox pairs, Energy Environ. Sci. 8 (2015) 3515–3530, https://doi.org/10.1039/c5ee02341f.
- [26] Y. Ding, C. Zhang, L. Zhang, Y. Zhou, G. Yu, Molecular engineering of organic electroactive materials for redox flow batteries, Chem. Soc. Rev. 47 (2018) 69–103, https://doi.org/10.1039/c7cs00569e.
- [27] Q. Zhao, Z. Zhu, J. Chen, Molecular engineering with organic carbonyl electrode materials for advanced stationary and redox flow rechargeable batteries, Adv. Mater. 29 (2017), https://doi.org/10.1002/adma.201607007.
- [28] X. Wei, W. Pan, W. Duan, A. Hollas, Z. Yang, B. Li, Z. Nie, J. Liu, D. Reed, W. Wang, V. Sprenkle, Materials and systems for organic redox flow batteries: status and challenges, ACS Energy Lett. 2 (2017) 2187–2204, https://doi.org/ 10.1021/acsenergylett.7b00650.
- [29] X. Wei, L. Cosimbescu, W. Xu, J.Z. Hu, M. Vijayakumar, J. Feng, M.Y. Hu, X. Deng, J. Xiao, J. Liu, V. Sprenkle, W. Wang, Towards high-performance nonaqueous redox flow electrolyte via ionic modification of active species, Adv. Energy Mater. 5 (2015) 1400678, https://doi.org/10.1002/aenm.201400678.
- [30] C. Jia, F. Pan, Y.G. Zhu, Q. Huang, L. Lu, Q. Wang, High-energy density nonaqueous all redox flow lithium battery enabled with a polymeric membrane, Sci. Adv. 1 (2015) 1500886, https://doi.org/10.1126/sciadv.1500886.
- [31] L. Su, D. Zhang, S. Peng, X. Wu, Y. Luo, G. He, Orientated graphene oxide/Nafion ultra-thin layer coated composite membranes for vanadium redox flow battery, Int. J. Hydrogen Energy 42 (2017) 21806–21816, https://doi.org/10.1016/j. ijhydene.2017.07.049.
- [32] L. Ling, M. Xiao, D. Han, S. Ren, S. Wang, Y. Meng, Porous composite membrane of PVDF/Sulfonic silica with high ion selectivity for vanadium redox flow battery, J. Membr. Sci. 585 (2019) 230–237, https://doi.org/10.1016/j. memsci.2018.11.082.
- [33] H. Zhang, H. Zhang, X. Li, Z. Mai, J. Zhang, Nanofiltration (NF) membranes: the next generation separators for all vanadium redox flow batteries (VRBs), Energy Environ. Sci. 4 (2011) 1676–1679, https://doi.org/10.1039/c1ee01117k.
- [34] L. Qiao, H. Zhang, W. Lu, Q. Dai, X. Li, Advanced porous membranes with tunable morphology regulated by ionic strength of nonsolvent for flow battery, ACS Appl. Mater. Interfaces 11 (2019) 24107–24113, https://doi.org/10.1021/ acsami.9b06142.
- [35] S.-H. Shin, S.-H. Yun, S.-H. Moon, A review of current developments in nonaqueous redox flow batteries: characterization of their membranes for design perspective, RSC Adv. 3 (2013) 9095–9116, https://doi.org/10.1039/ c3ra00115f.
- [36] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, A review of recent developments in membrane separators for rechargeable lithium-ion batteries, Energy Environ. Sci. 7 (2014) 3857–3886, https://doi.org/10.1039/c4ee01432d.
- [37] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, A lithium superionic conductor, Nat. Mater. 10 (2011) 682–686, https://doi.org/10.1038/nmat3066.
- [38] Q. Dai, Z. Liu, L. Huang, C. Wang, Y. Zhao, Q. Fu, A. Zheng, H. Zhang, X. Li, Thinfilm composite membrane breaking the trade-off between conductivity and selectivity for a flow battery, Nat. Commun. 11 (2020) 13, https://doi.org/ 10.1038/s41467-019-13704-2.
- [39] T. Xu, Ion exchange membranes: state of their development and perspective, J. Membr. Sci. 263 (2005) 1–29, https://doi.org/10.1016/j.memsci.2005.05.002.
- [40] H. Prifti, A. Parasuraman, S. Winardi, T.M. Lim, M. Skyllas-Kazacos, Membranes for redox flow battery applications, Membranes 2 (2012) 275–306, https://doi. org/10.3390/membranes2020275.
- [41] T.J. Peckham, S. Holdcroft, Structure-morphology-property relationships of nonperfluorinated proton-conducting membranes, Adv. Mater. 22 (2010) 4667–4690, https://doi.org/10.1002/adma.201001164.
- [42] G. He, J. Zhao, S. Hu, L. Li, Z. Li, Y. Li, Z. Li, H. Wu, X. Yang, Z. Jiang, Functionalized carbon nanotube via distillation precipitation polymerization and its application in nafion-based composite membranes, ACS Appl. Mater. Interfaces 6 (2014) 15291–15301, https://doi.org/10.1021/am503760u.

- [43] M. Monchak, T. Hupfer, A. Senyshyn, H. Boysen, D. Chernyshov, T. Hansen, K. G. Schell, E.C. Bucharsky, M.J. Hoffmann, H. Ehrenberg, Lithium diffusion pathway in Li1.3Al0.3Ti1.7(PO4)3 (LATP) superionic conductor, Inorg. Chem. 55 (2016) 2941–2945, https://doi.org/10.1021/acs.inorgchem.5b02821.
- [44] Y. Zhao, Y. Ding, J. Song, G. Li, G. Dong, J.B. Goodenough, G. Yu, Sustainable electrical energy storage through the ferrocene/ferrocenium redox reaction in aprotic electrolyte, Angew. Chem. Int. Ed. 53 (2014) 11036–11040, https://doi. org/10.1002/anie.201406135.
- [45] X.L. Zhou, T.S. Zhao, L. An, Y.K. Zeng, L. Wei, Modeling of ion transport through a porous separator in vanadium redox flow batteries, J. Power Sources 327 (2016) 67–76, https://doi.org/10.1016/j.jpowsour.2016.07.046.
- [46] K. Oh, S. Won, H. Ju, A comparative study of species migration and diffusion mechanisms in all-vanadium redox flow batteries, Electrochim. Acta 181 (2015) 238–247, https://doi.org/10.1016/j.electacta.2015.03.012.
- [47] H. Zhu, R.J. Kee, Membrane polarization in mixed-conducting ceramic fuel cells and electrolyzers, Int. J. Hydrogen Energy 41 (2016) 2931–2943, https://doi. org/10.1016/j.ijhydene.2015.10.100.
- [48] K. Li, Ceramic Membranes for Separation and Reaction, John Wiley & Sons, 2007.
 [49] E. Vøllestad, H. Zhu, R.J. Kee, Interpretation of defect and gas-phase fluxes through mixed-conducting ceramics using Nernst–Planck–Poisson and integral
- formulations, J. Electrochem. Soc. 161 (2013) F114–F124, https://doi.org/ 10.1149/2.067401jes.
- [50] K. Kontturi, L. Murtomäki, J. Manzanares, Ionic Transport Processes: in Electrochemistry and Membrane Science, Oxford University Press, 2008.
- [51] K. Izutsu, Properties of solvents and solvent classification, in: K. Izutsu (Ed.), Electrochemistry in Nonaqueous Solutions, Wiley VCH Verlag GmbH, 2002, pp. 1–24, https://doi.org/10.1002/3527600655.ch1.
- [52] C. Wohlfarth, Viscosity of Pure Organic Liguids and Binary Liquid Mixtures, Springer-Verlag Berlin Heidelberg, 2009.
- [53] M.A. Rivas, S.M. Pereira, T.P. Iglesias, Relative permittivity of the mixtures (dimethyl or diethyl carbonate)+n-nonane from T=288.15K to T=308.15K, J. Chem.Thermodyn. 34 (2002) 1897–1907, https://doi.org/10.1016/s0021-9614(02)00260-4.
- [54] N. Nanbu, Y. Suzuki, K. Ohtsuki, T. Meguro, M. Takehara, M. Ue, Y. Sasaki, Physical and electrochemical properties of monofluorinated ethyl acetates for lithium rechargeable batteries, Electrochemistry 78 (2010) 446–449.
- [55] A.K. Kushwaha, M.R. Sahoo, S.K. Nayak, Understanding the role of fluorination on the interaction of electrolytic carbonates with Li⁺ through an electronic structure approach, Chemistry 4 (2019) 1251–1258, https://doi.org/10.1002/ slct.201803372.
- [56] J. Ugelstad, A. Berge, H. Listou, The effect of the solvent on the reactivity of sodium and potassium phenoxides in nucleophilic substitution reactions, Acta Chem. Scand. 19 (1965) 208–216.
- [57] J. He, M. Liu, K. Huang, T.W. Walker, C.T. Maravelias, J.A. Dumesic, G.W. Huber, Production of levoglucosenone and 5-hydroxymethylfurfural from cellulose in polar aprotic solvent–water mixtures, Green Chem. 19 (2017) 3642–3653, https://doi.org/10.1039/c7gc01688c.
- [58] E. Cho, J. Won, Novel composite membrane coated with a poly (diallyldimethylammonium chloride)/urushi semi-interpenetrating polymer network for non-aqueous redox flow battery application, J. Power Sources 335 (2016) 12–19, https://doi.org/10.1016/j.jpowsour.2016.10.020.
- [59] S. Maurya, S.-H. Shin, K.-W. Sung, S.-H. Moon, Anion exchange membrane prepared from simultaneous polymerization and quaternization of 4-vinyl pyridine for non-aqueous vanadium redox flow battery applications, J. Power Sources 255 (2014) 325–334, https://doi.org/10.1016/j.jpowsour.2014.01.047.
- [60] S.-H. Shin, Y. Kim, S.-H. Yun, S. Maurya, S.-H. Moon, Influence of membrane structure on the operating current densities of non-aqueous redox flow batteries: organic–inorganic composite membranes based on a semi-interpenetrating polymer network, J. Power Sources 296 (2015) 245–254, https://doi.org/ 10.1016/j.jpowsour.2015.07.045.
- [61] S. Peng, L. Zhang, C. Zhang, Y. Ding, X. Guo, G. He, G. Yu, Gradient-distributed metal-organic framework-based porous membranes for nonaqueous redox flow batteries, Adv. Energy Mater. 8 (2018) 1802533, https://doi.org/10.1002/ aenm.201802533.
- [62] Y. Li, J. Sniekers, J.C. Malaquias, C. Van Goethem, K. Binnemans, J. Fransaer, I.F. J. Vankelecom, Crosslinked anion exchange membranes prepared from poly (phenylene oxide) (PPO) for non-aqueous redox flow batteries, J. Power Sources 378 (2018) 338–344, https://doi.org/10.1016/j.jpowsour.2017.12.049.
- [63] H.S. Bang, D. Kim, S.S. Hwang, J. Won, Surface-modified porous membranes with electrospun Nafion/PVA fibres for non-aqueous redox flow battery, J. Membr. Sci. 514 (2016) 186–194, https://doi.org/10.1016/j.memsci.2016.04.068.
- [64] Z. Mai, H. Zhang, X. Li, C. Bi, H. Dai, Sulfonated poly(tetramethydiphenyl ether ether ketone) membranes for vanadium redox flow battery application, J. Power Sources 196 (2011) 482–487, https://doi.org/10.1016/j.jpowsour.2010.07.028.
- [65] K. Lin, Q. Chen, M.R. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A.W. Valle, D. Hardee, R.G. Gordon, M.J. Aziz, M.P. Marshak, Alkaline quinone flow battery, Science 349 (2015) 1529–1532, https://doi.org/10.1126/science.aab3033.
- [66] V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, M. Kintner-Meyer, V. Sprenkle, Cost and performance model for redox flow batteries, J. Power Sources 247 (2014) 1040–1051, https://doi.org/10.1016/j.jpowsour.2012.12.023.
- [67] M.O. Bamgbopa, S. Almheiri, Influence of solvents on species crossover and capacity decay in non-aqueous vanadium redox flow batteries: characterization of acetonitrile and 1, 3 dioxolane solvent mixture, J. Power Sources 342 (2017) 371–381, https://doi.org/10.1016/j.jpowsour.2016.12.050.

- [68] A.M. Kosswattaarachchi, T.R. Cook, Mixed-component catholyte and anolyte solutions for high-energy density non-aqueous redox flow batteries, J. Electrochem. Soc. 165 (2018) A194–A200, https://doi.org/10.1149/ 2.0751802jes.
- [69] D. Singh, D. Pratap, Y. Baranwal, B. Kumar, R.K. Chaudhary, Microbial fuel cells: a green technology for power generation, Ann. Biol. Res. 1 (2010) 128–138.
- [70] X.O. Xing, Y.J. Huo, X. Wang, Y.C. Zhao, Y.D. Li, A benzophenone-based anolyte for high energy density all-organic redox flow battery, Int. J. Hydrogen Energy 42 (2017) 17488–17494, https://doi.org/10.1016/j.ijhydene.2017.03.034.
- [71] Y.J. Huo, X.Q. Xing, C.J. Zhang, X. Wang, Y.D. Li, An all organic redox flow battery with high cell voltage, RSC Adv. 9 (2019) 13128–13132, https://doi.org/ 10.1039/c9ra01514k.
- [72] I.L. Escalante-Garcia, J.S. Wainright, L.T. Thompson, R.F. Savinell, Performance of a non-aqueous vanadium acetylacetonate prototype redox flow battery: examination of separators and capacity decay, J. Electrochem. Soc. 162 (2015) A363–A372, https://doi.org/10.1149/2.0471503jes.
- [73] J.M. Stauber, S. Zhang, N. Gyozdik, Y. Jiang, L. Avena, K.J. Stevenson, C. C. Cummins, Cobalt and vanadium trimetaphosphate polyanions: synthesis, characterization, and electrochemical evaluation for non-aqueous redox-flow battery applications, J. Am. Chem. Soc. 140 (2018) 538–541, https://doi.org/10.1021/jacs.7b08751.
- [74] N.S. Hudak, L.J. Small, H.D. Pratt, T.M. Anderson, Through-plane conductivities of membranes for nonaqueous redox flow batteries, J. Electrochem. Soc. 162 (2015) A2188–A2194, https://doi.org/10.1149/2.0901510jes.
- [75] S.-K. Park, J. Shim, J. Yang, K.-H. Shin, C.-S. Jin, B.S. Lee, Y.-S. Lee, J.-D. Jeon, Electrochemical properties of a non-aqueous redox battery with all-organic redox couples, Electrochem. Commun. 59 (2015) 68–71, https://doi.org/10.1016/j. elecom.2015.07.013.
- [76] C.G. Armstrong, K.E. Toghill, Cobalt(II) complexes with azole-pyridine type ligands for non-aqueous redox-flow batteries: tunable electrochemistry via structural modification, J. Power Sources 349 (2017) 121–129, https://doi.org/ 10.1016/j.jpowsour.2017.03.034.
- [77] Y.C. Yan, S.G. Robinson, M.S. Sigman, M.S. Sanford, Mechanism-based design of a high-potential catholyte enables a 3.2 V all-organic nonaqueous redox flow battery, J. Am. Chem. Soc. 141 (2019) 15301–15306, https://doi.org/10.1021/ jacs.9b07345.
- [78] D. Kim, J. Song, J. Won, Structural effects of anion exchange composite membranes in non-aqueous redox flow batteries, J. Membr. Sci. 564 (2018) 523–531, https://doi.org/10.1016/j.memsci.2018.07.061.
- [79] Y. Zhen, C. Zhang, J. Yuan, Y. Zhao, Y. Li, A high-performance all-iron nonaqueous redox flow battery, J. Power Sources 445 (2020) 227331, https://doi. org/10.1016/j.jpowsour.2019.227331.
- [80] F.R. Brushett, J.T. Vaughey, A.N. Jansen, An all-organic non-aqueous lithium-ion redox flow battery, Adv. Energy Mater. 2 (2012) 1390–1396, https://doi.org/ 10.1002/aenm.201200322.
- [81] T. Herr, P. Fischer, J. Tübke, K. Pinkwart, P. Elsner, Increasing the energy density of the non-aqueous vanadium redox flow battery with the acetonitrile-1,3dioxolane-dimethyl sulfoxide solvent mixture, J. Power Sources 265 (2014) 317–324, https://doi.org/10.1016/j.jpowsour.2014.04.141.
- [82] T. Herr, J. Noack, P. Fischer, J. Tübke, 1,3-Dioxolane, tetrahydrofuran, acetylacetone and dimethyl sulfoxide as solvents for non-aqueous vanadium acetylacetonate redox-flow-batteries, Electrochim. Acta 113 (2013) 127–133, https://doi.org/10.1016/j.electacta.2013.09.055.
- [83] Q. Liu, A.A. Shinkle, Y. Li, C.W. Monroe, L.T. Thompson, A.E.S. Sleightholme, Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries, Electrochem. Commun. 12 (2010) 1634–1637, https://doi.org/10.1016/j. elecom.2010.09.013.
- [84] A.A. Shinkle, A.E.S. Sleightholme, L.D. Griffith, L.T. Thompson, C.W. Monroe, Degradation mechanisms in the non-aqueous vanadium acetylacetonate redox flow battery, J. Power Sources 206 (2012) 490–496, https://doi.org/10.1016/j jpowsour.2010.12.096.
- [85] P.S. Son, M.-S. Oh, J.-H. Ye, S.-H. Choi, Counter anion effects in anion exchange membrane-fabricated non-aqueous vanadium redox flow battery, J. Anal. Sci. Technol. 28 (2015) 341–346, https://doi.org/10.5806/ast.2015.28.5.341.
- [86] A.P. Kaur, N.E. Holubowitch, S. Ergun, C.F. Elliott, S.A. Odom, A highly soluble organic catholyte for non-aqueous redox flow batteries, Energy Technol. 3 (2015) 476–480, https://doi.org/10.1002/ente.201500020.
- [87] J. Lee, M.-S. Park, K.J. Kim, Highly enhanced electrochemical activity of Ni foam electrodes decorated with nitrogen-doped carbon nanotubes for non-aqueous redox flow batteries, J. Power Sources 341 (2017) 212–218, https://doi.org/ 10.1016/j.jpowsour.2016.12.005.
- [88] I. Mustafa, M.O. Bamgbopa, E. Alraeesi, Y. Shao-Horn, H. Sun, S. Almheiri, Insights on the electrochemical activity of porous carbonaceous electrodes in nonaqueous vanadium redox flow batteries, J. Electrochem. Soc. 164 (2017) A3673–A3683, https://doi.org/10.1149/2.0621714jes.
- [89] P.M. McCormack, H. Luo, G.M. Geise, G.M. Koenig, Conductivity, permeability, and stability properties of chemically tailored poly(phenylene oxide) membranes for Li+ conductive non-aqueous redox flow battery separators, J. Power Sources 460 (2020), https://doi.org/10.1016/j.jpowsour.2020.228107.
- [90] L. Su, R.M. Darling, K.G. Gallagher, W. Xie, J.L. Thelen, A.F. Badel, J.L. Barton, K. J. Cheng, N.P. Balsara, J.S. Moore, F.R. Brushett, An investigation of the ionic conductivity and species crossover of lithiated Nafion 117 in nonaqueous electrolytes, J. Electrochem. Soc. 163 (2015) A5253–A5262, https://doi.org/10.1149/2.03211601jes.

- [91] S. Hwang, H.-S. Kim, J.H. Ryu, S.M. Oh, Ni(II)-chelated thio-crown complex as a single redox couple for non-aqueous flow batteries, Electrochem. Commun. 85 (2017) 36–39, https://doi.org/10.1016/j.elecom.2017.10.015.
- [92] S. Hwang, H.-s. Kim, J.H. Ryu, S.M. Oh, N-ferrocenylphthalimide, A single redox couple formed by attaching a ferrocene moiety to phthalimide for non-aqueous flow batteries, J. Power Sources 395 (2018) 60–65, https://doi.org/10.1016/j. jpowsour.2018.05.053.
- [93] L. Bahadori, M.A. Hashim, N.S.A. Manan, F.S. Mjalli, I.M. AlNashef, N. P. Brandon, M.H. Chakrabarti, Investigation of ammonium- and phosphoniumbased deep eutectic solvents as electrolytes for a non-aqueous all-vanadium redox cell, J. Electrochem. Soc. 163 (2016) A632–A638, https://doi.org/10.1149/ 2.0261605jes.
- [94] X.Q. Xing, Y.C. Zhao, Y.D. Li, A non-aqueous redox flow battery based on tris (1,10-phenanthroline) complexes of iron(II) and cobalt(II), J. Power Sources 293 (2015) 778–783, https://doi.org/10.1016/j.jpowsour.2015.06.016.
- [95] S.-J. Gong, D. Kim, E. Cho, S.S. Hwang, J. Won, A chitosan/urushi anion exchange membrane for a nonaqueous redox flow battery, Chemistryselect 2 (2017) 1843–1849, https://doi.org/10.1002/slct.201601772.
- [96] Y. Liu, C. Li, B. Li, H. Song, Z. Cheng, M. Chen, P. He, H. Zhou, Germanium thin film protected lithium aluminum germanium phosphate for solid-state li batteries, Adv. Energy Mater. 8 (2018), https://doi.org/10.1002/ aenm.201702374.
- [97] G. Muthuraman, L. Boyeol, M. Il-Shik, Na-beta-alumina as a separator in the development of all-vanadium non-aqueous tubular redox flow batteries: an electrochemical and charging-discharging examination using a prototype tubular redox flow cell, J. Electrochem. Soc. 165 (2018) A1920–A1924, https://doi.org/ 10.1149/2.1461809jes.
- [98] B. Zhang, R. Tan, L. Yang, J. Zheng, K. Zhang, S. Mo, Z. Lin, F. Pan, Mechanisms and properties of ion-transport in inorganic solid electrolytes, Energy Storage Mater 10 (2018) 139–159, https://doi.org/10.1016/j.ensm.2017.08.015.
- [99] G. Cong, Y. Zhou, Z. Li, Y.-C. Lu, A highly concentrated catholyte enabled by a low-melting-point ferrocene derivative, ACS Energy Lett. 2 (2017) 869–875, https://doi.org/10.1021/acsenergylett.7b00115.
- [100] Y. Ding, Y. Zhao, Y. Li, J.B. Goodenough, G. Yu, A high-performance allmetallocene-based, non-aqueous redox flow battery, Energy Environ. Sci. 10 (2017) 491–497, https://doi.org/10.1039/c6ee02057g.
- [101] C. Zhang, Z. Niu, Y. Ding, L. Zhang, Y. Zhou, X. Guo, X. Zhang, Y. Zhao, G. Yu, Highly concentrated phthalimide-based anolytes for organic redox flow batteries with enhanced reversibility, Inside Chem. 4 (2018) 2814–2825, https://doi.org/ 10.1016/j.chempr.2018.08.024.
- [102] H. Kitaura, H. Zhou, Electrochemical performance and reaction mechanism of allsolid-state lithium-air batteries composed of lithium, Li1+xAlyGe2-y(PO4)3 solid electrolyte and carbon nanotube air electrode, Energy Environ. Sci. 5 (2012), https://doi.org/10.1039/c2ee22381c.
- [103] K. Takechi, Y. Kato, Y. Hase, A highly concentrated catholyte based on a solvate ionic liquid for rechargeable flow batteries, Adv. Mater. 27 (2015) 2501–2506, https://doi.org/10.1002/adma.201405840.
- [104] G.-M. Weng, Z. Li, G. Cong, Y. Zhou, Y.-C. Lu, Unlocking the capacity of iodide for high-energy-density zinc/polyiodide and lithium/polyiodide redox flow batteries, Energy Environ. Sci. 10 (2017) 735–741, https://doi.org/10.1039/c6ee03554j.
- [105] X. Wei, W. Duan, J. Huang, L. Zhang, B. Li, D. Reed, W. Xu, V. Syrenkle, W. Wang, A high-current, stable nonaqueous organic redox flow battery, ACS Energy Lett. 1 (2016) 705–711, https://doi.org/10.1021/acsenergylett.6b00255.
 [106] W. Duan, J. Huang, J.A. Kowalski, I.A. Shkrob, M. Vijayakumar, E. Walter, B. Pan,
- [106] W. Duan, J. Huang, J.A. Kowalski, I.A. Shkrob, M. Vijayakumar, E. Walter, B. Pan, Z. Yang, J.D. Milshtein, B. Li, C. Liao, Z. Zhang, W. Wang, J. Liu, J.S. Moore, F. R. Brushett, L. Zhang, X. Wei, "Wine-dark sea" in an organic flow battery: storing negative charge in 2,1,3-benzothiadiazole radicals leads to improved cyclability, ACS Energy Lett. 2 (2017) 1156–1161, https://doi.org/10.1021/ acsenergylett.7b00261.
- [107] Y. Zhao, Z. Yuan, W. Lu, X. Li, H. Zhang, The porous membrane with tunable performance for vanadium flow battery: the effect of charge, J. Power Sources 342 (2017) 327–334, https://doi.org/10.1016/j.jpowsour.2016.12.058.
- [108] J. Yuan, C. Zhang, Y. Zhen, Y. Zhao, Y. Li, Enhancing the performance of an allorganic non-aqueous redox flow battery, J. Power Sources 443 (2019) 227283, https://doi.org/10.1016/j.jpowsour.2019.227283.
- [109] W. Duan, R.S. Vemuri, J.D. Milshtein, S. Laramie, R.D. Dmello, J. Huang, L. Zhang, D. Hu, M. Vijayakumar, W. Wang, J. Liu, R.M. Darling, L. Thompson, K. Smith, J.S. Moore, F.R. Brushett, X. Wei, A symmetric organic-based nonaqueous redox flow battery and its state of charge diagnostics by FTIR, J. Mater. Chem. 4 (2016) 5448–5456, https://doi.org/10.1039/c6ta01177b.
- [110] C. Zhang, Y. Qian, Y. Ding, L. Zhang, X. Guo, Y. Zhao, G. Yu, Biredox eutectic electrolytes derived from organic redox-active molecules for high-energy storage systems, Angew. Chem. Int. Ed. 131 (2019) 7119–7124, https://doi.org/10.1002/ anie.201902433.
- [111] S.M. Laramie, J.D. Milshtein, T.M. Breault, F.R. Brushett, L.T. Thompson, Performance and cost characteristics of multi-electron transfer, common ion exchange non-aqueous redox flow batteries, J. Power Sources 327 (2016) 681–692, https://doi.org/10.1016/j.jpowsour.2016.07.015.

- [112] J.D. Milshtein, J.L. Barton, R.M. Darling, F.R. Brushett, 4-acetamido-2,2,6,6tetramethylpiperidine-1-oxyl as a model organic redox active compound for nonaqueous flow batteries, J. Power Sources 327 (2016) 151–159, https://doi. org/10.1016/j.jpowsour.2016.06.125.
- [113] X. Xing, Q. Liu, W. Xu, W. Liang, J. Liu, B. Wang, J.P. Lemmon, All-liquid electroactive materials for high energy density organic flow battery, ACS Appl. Energy Mater. 2 (2019) 2364–2369, https://doi.org/10.1021/acsaem.8b01874.
- [114] X. Xing, Q. Liu, B. Wang, J.P. Lemmon, W.Q. Xu, A low potential solvent-miscible 3-methylbenzophenone anolyte material for high voltage and energy density allorganic flow battery, J. Power Sources 445 (2020), https://doi.org/10.1016/j. jpowsour.2019.227330.
- [115] J. Huang, Z. Yang, M. Vijayakumar, W. Duan, A. Hollas, B. Pan, W. Wang, X. Wei, L. Zhang, A two-electron storage nonaqueous organic redox flow battery, Adv. Sustain. Syst. 2 (2018) 1700131, https://doi.org/10.1002/adsu.201700131.
- [116] J. Yuan, C. Zhang, T. Liu, Y. Zhen, Z.-Z. Pan, Y. Li, Two-dimensional metalorganic framework nanosheets-modified porous separator for non-aqueous redox flow batteries, J. Membr. Sci. 612 (2020) 118463, https://doi.org/10.1016/j. memsci.2020.118463.
- [117] C. Xie, W. Xu, H. Zhang, X. Hu, X. Li, A multi-electron transfer ferrocene derivative positive redox moiety with improved solubility and potential, Chem. Commun. 54 (2018) 8419–8422, https://doi.org/10.1039/c8cc04099k.
- [118] T.P. Vaid, M.S. Sanford, An organic super-electron-donor as a high energy density negative electrolyte for nonaqueous flow batteries, Chem. Commun. 55 (2019) 11037–11040, https://doi.org/10.1039/c9cc06080d.
- [119] G. Kwon, K. Lee, M.H. Lee, B. Lee, S. Lee, S.-K. Jung, K. Ku, J. Kim, S.Y. Park, J. E. Kwon, K. Kang, Bio-inspired molecular redesign of a multi-redox catholyte for high-energy non-aqueous organic redox flow batteries, Inside Chem. 5 (2019) 2642–2656, https://doi.org/10.1016/j.chempr.2019.07.006.
- [120] G. Kwon, S. Lee, J. Hwang, H.-S. Shim, B. Lee, M.H. Lee, Y. Ko, S.-K. Jung, K. Ku, J. Hong, K. Kang, Multi-redox molecule for high-energy redox flow batteries, Joule 2 (2018) 1771–1782, https://doi.org/10.1016/j.joule.2018.05.014.
- [121] J.D. Saraidaridis, B.M. Bartlett, C.W. Monroe, Spectroelectrochemistry of vanadium acetylacetonate and chromium acetylacetonate for symmetric nonaqueous flow batteries, J. Electrochem. Soc. 163 (2016) A1239–A1246, https://doi.org/10.1149/2.0441607jes.
- [122] H.-G. Kwon, I. Bae, S.-H. Choi, Crosslinked poly(arylene ether ketone) membrane with high anion conductivity and selectivity for non-aqueous redox flow batteries, J. Membr. Sci. 620 (2021) 118928, https://doi.org/10.1016/j. memsci.2020.118928.
- [123] S.E. Doris, A.L. Ward, A. Baskin, P.D. Frischmann, N. Gavvalapalli, E. Chenard, C. S. Sevov, D. Prendergast, J.S. Moore, B.A. Helms, Macromolecular design strategies for preventing active-material crossover in non-aqueous all-organic redox-flow batteries, Angew. Chem. Int. Ed. 56 (2017) 1595–1599, https://doi.org/10.1002/anie.201610582.
- [124] K.H. Hendriks, S.G. Robinson, M.N. Braten, C.S. Sevov, B.A. Helms, M.S. Sigman, S.D. Minteer, M.S. Sanford, High-performance oligomeric catholytes for effective macromolecular separation in nonaqueous redox flow batteries, ACS Cent. Sci. 4 (2018) 189–196, https://doi.org/10.1021/acscentsci.7b00544.
- [125] J. Jung, J. Won, S.S. Hwang, Highly selective composite membranes using ladderlike structured polysilsesquioxane for a non-aqueous redox flow battery, J. Membr. Sci. 595 (2020) 117520, https://doi.org/10.1016/j. memsci.2019.117520.
- [126] X. Xi, X. Li, C. Wang, Q. Lai, Y. Cheng, P. Xu, H. Zhang, Non-aqueous lithium bromine battery of high energy density with carbon coated membrane, J. Energy Chem. 26 (2017) 639–646, https://doi.org/10.1016/j.jechem.2017.04.013.
 [127] M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu,
- [127] M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu, H. Xu, Y. Zhao, H. Zhang, Ultrathin 2D metal-organic framework nanosheets, Adv. Mater. 27 (2015) 7372–7378, https://doi.org/10.1002/adma.201503648.
- [128] T. Ma, Z. Pan, L. Miao, C. Chen, M. Han, Z. Shang, J. Chen, Porphyrin-based symmetric redox-flow batteries towards cold-climate energy storage, Angew. Chem. Int. Ed. 57 (2018) 3158–3162, https://doi.org/10.1002/anie.201713423.
- [129] S. Maurya, S.-H. Shin, M.-K. Kim, S.-H. Yun, S.-H. Moon, Stability of composite anion exchange membranes with various functional groups and their performance for energy conversion, J. Membr. Sci. 443 (2013) 28–35, https://doi.org/ 10.1016/j.memsci.2013.04.035.
- [130] D.-H. Kim, S.-J. Seo, M.-J. Lee, J.-S. Park, S.-H. Moon, Y.S. Kang, Y.-W. Choi, M.-S. Kang, Pore-filled anion-exchange membranes for non-aqueous redox flow batteries with dual-metal-complex redox shuttles, J. Membr. Sci. 454 (2014) 44–50, https://doi.org/10.1016/j.memsci.2013.11.051.
- [131] J.-H. Kim, S. Ryu, J.-Y. Lee, S.-H. Moon, Preparation of high-conductivity QPPO (quaternary-aminated poly (2,6-dimethyl-1,4-phenyleneoxide)) membranes by electrical treatment, J. Membr. Sci. 553 (2018) 82–89, https://doi.org/10.1016/j. memsci.2017.12.009.
- [132] J.-H. Kim, S. Ryu, S. Maurya, J.-Y. Lee, K.-W. Sung, J.-S. Lee, S.-H. Moon, Fabrication of a composite anion exchange membrane with aligned ion channels for a high-performance non-aqueous vanadium redox flow battery, RSC Adv. 10 (2020) 5010–5025, https://doi.org/10.1039/c9ra08616a.