Review Article

Membranes and separators for redox flow batteries
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Abstract
Ion-exchange membranes are performance- and cost-relevant components of redox flow batteries. Currently used materials are largely ‘borrowed’ from other applications that have different functional requirements. The trend toward higher current densities and the complex transport phenomena of the different species in flow batteries need to be taken into consideration for the design of next-generation membrane/separator materials. In this article, the key requirements and current development trends for membranes and separators for the vanadium redox flow battery are highlighted and discussed.

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Introduction
A redox flow battery (RFB) is an electrochemical energy storage device that comprises an electrochemical conversion unit, consisting of a cell stack or an array thereof, and external tanks to store electrolytes containing redox-active species [1]. Owing to this design principle, the power and energy rating of the battery can be independently scaled (Figure 1a). Flow batteries with different chemistries have been commercialized, such as the Fe−Cr, Zn−Br2, and H2−Br2 type [2]. The all-vanadium RFB (VRFB) is technically the most advanced system. It uses vanadium ions in the oxidation states II/III and IV/V in the negative and positive electrolyte, respectively. The ions are most commonly dissolved as (bi)sulfate at a concentration of 1−2 M in a sulfuric acid solution of 2−4 M. Owing to the majority of technical and commercial developments being related to the VRFB, this review will be primarily focused on this RFB technology.

The electrochemical conversion unit of a VRFB, the cell stack, comprises porous carbon fiber−based electrodes on both sides and a membrane sandwiched between the two electrodes to separate the negative and the positive electrode and electrolyte compartments from each other. The primary function of the membrane in a VRFB is to conduct ions of the supporting electrolyte between the negative and positive compartment and prevent the passage of the redox-active vanadium ions. In addition, it should avoid excessive solvent (water) transfer (Figure 1b). Currently used state-of-the-art ion-exchange membranes (IEMs) based on polymer electrolytes account for up to 30−40% of the cost of the stack hardware [3,4]. Most commercially available IEMs have not been specifically developed for this application and have specific functional shortcomings (cf. section ‘Ion-exchange membranes’ below). The VRFB development over the past decade has brought about a significant increase in power density, mostly due to cell and component engineering [5,6]. Therefore, the research and development of next-generation membranes or separators currently underway is aimed at (i) lowering the ionic resistance to enable operation at higher current densities, (ii) improving the barrier properties, (iii) balancing net electrolyte transport to minimize capacity imbalance, and (iv) ensuring the chemical stability of the material for lifetimes in the range of 10 years or more, while being cost competitive to existing membranes.

Ion-exchange membranes
Most RFBs use a dense IEM as polymer electrolyte [7]. The type of fixed charge provides some selectivity for the uptake and transport of the corresponding counterions. However, at the concentration ranges of the electrolytes used (1−2 M vanadium, 2−5 M acid) the exclusion of coions from the membrane (‘Donnan exclusion’) breaks down [8]. Both cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs) are used in VRFBs. CEMs offer low ionic resistance because they take advantage of the high mobility of the acid protons, yet they also suffer from high crossover of vanadium ions. Perfluoroalkylsulfonic acid (PFSA) CEMs, such as Nafton®, are often used...
Transport properties

Transport phenomena in IEMs in contact with a VRFB electrolyte are very complex. Transport is caused by various driving forces, that is, concentration, pressure, and potential gradients, and transport coefficients are strongly concentration dependent as well as coupled. For instance, the movement of water is coupled to the movement of ions (electro-osmotic drag) [10]. Darling et al. [11] boiled down transport property requirements for flow batteries to three main parameters: (i) area-specific ohmic resistance, which affects the voltage efficiency; (ii) crossover of vanadium ions, which impairs coulombic efficiency; and (iii) the asymmetry of crossover phenomena, which cause capacity imbalance and fading. Furthermore, water flux through the membrane also takes place through osmosis owing to the difference in proton concentration between the negative and positive electrolyte [12,13], which also changes with the state of charge.

It is important to note the effect and difference of diffusive and migrative vanadium ion-transport mechanisms. Migrative transport is driven by the potential gradient in the membrane (i.e., electric field) and is thus proportional to the current density (Figure 2a). At high current density, migration dominates, and this leads to an increasing flux toward the positive electrolyte owing to the higher average charge of vanadium ions on the negative side (V$^{2+}$ and V$^{3+}$) compared with the positive side (VO$^{2+}$ and VO$_2^-$) [14]. At low current density, diffusion dominates. Higher diffusivity of V$^{2+}$ and V$^{3+}$ than that of VO$^{2+}$ and VO$_2^-$ in a CEM yields a net vanadium transport toward the positive electrolyte. In an AEM, Donnan exclusion of V$^{2+}$ and V$^{3+}$ is stronger than that of VO$^{2+}$ and VO$_2^-$; hence, net vanadium flux is directed toward the negative electrolyte [15]. With an amphoteric IEM, containing both fixed anionic and cationic groups, the fluxes in the two directions can be balanced and the capacity fading can be minimized [15]. This can be seen in bilayer membranes consisting of Nafion® topcoated with a layer of an AEM (protonated polybenzimidazole [PBI]) (Figure 2b). For a stable capacity over extended charge–discharge cycles, it is therefore possible to avoid excessive and asymmetric crossover in a given current density range by proper membrane engineering.

For the understanding of transport properties, the fundamentals of the different mechanisms and coupled phenomena in IEMs need to be studied and correlated to device-level properties, such as crossover and capacity imbalance effects. Model development can be of great value as a complementary method to promote insight.

Membranes beyond the state of the art

There is a sizeable body of literature on alternative membranes for VRFBs, meaning mostly ‘non-PFSA’-type membranes. The work is often aimed at improving specific properties, such as the ‘selectivity’ of transport, meaning reducing vanadium ion crossover, while maintaining conductivity or ‘not affecting it too much,’ often although the conductivity of alternative membranes is inferior to that of PFSA membranes. This results in improved energy efficiency at low current density, where it is governed by the vanadium barrier properties of the membrane. At high current density, however, for instance, >150 mV/cm$^2$, a lower efficiency is observed because of the higher ohmic resistance than that of Nafion®. Generally, polyarylene-type membranes, anion- or cation-exchange type [18], display interesting properties, which is probably related to their typically smaller ionic cluster size [19], which provides some selectivity for proton transport. Yet chemical stability is generally a challenge for such materials (cf. below).

A number of groups have put forward the concept of amphoteric IEMs made, for example, by blending an acidic polymer with one that contains basic groups [20] or by copolymerizing monomers that can be post-functionalized to yield cation- and anion-exchange groups [21]. An interesting approach is the use of bipolar membranes with a layer of a cation- and an anion-
exchange polymer, which can provide more symmetric vanadium ion-transport properties (cf. Figure 2b) and thus reduced capacity fading. The potential delamination of the two layers has been addressed by designing an ‘interlocking’ interface (i.e. interphase) between the two layers [22,23], or using a reinforcement interlayer [24]. It should be considered, however, that bipolar membranes should be used in electrolytes with concentration beyond the Donnan exclusion limit to avoid osmosis-driven accumulation of water at the interface, which could lead to delamination or ‘ballooning’ of the membrane.

**Separators**

Redox flow batteries already comprise an ionically conducting solution in the form of the positive and negative electrolyte. Hence, as in conventional batteries, a porous material imbibed with electrolyte may be considered as a separator, which would dramatically reduce cost. Unfortunately, the electrolytes also contain redox-active species, and the lack of a physical barrier causes deleterious electrolyte transfer [11]. The use of porous separators for flow batteries has already been put forward by the National Aeronautics and Space Administration (NASA) in the 1970s: “A further method to produce highly selective low resistance membranes is to use a porous plastic film as the substrate for a thin layer of ion exchange resin. … This type of membrane, referred to as a composite or skin membrane, could be mass-produced using various spray, evaporate and bake steps on a continuous sheet of film substrate” [25]. In recent years, the approach has been revisited using nonionic polymers, such as poly(ether sulfone) [26–31]. These can be easily processed by solvent casting; therefore, they offer a low cost potential of <50 $/m² [27]. Thicknesses were in the range of 100 µm, but could be made thinner for reduced resistance. The porous membranes were prepared through the phase inversion method. This method typically yields a porous membrane bulk and a thin ‘skin’ layer. This relatively dense polymer layer with thickness in the micrometer range provides selectivity without excessively affecting the ohmic resistance of the cell because the macro-porous sublayer is imbibed with the liquid electrolyte. High charge—discharge cycling efficiencies of 90% and 80% were reported by Yuan et al. [27] at a current density of 80 and 120 mA/cm², respectively, and a stable cycling performance for 13,500 cycles. Most importantly, the coulombic efficiency, which is normally problematic for porous separators, was >96%, better than that of Nafion 115. An alternative approach to prepare an asymmetric membrane is to use a porous polymer substrate and coat it with a thin polymer in the micrometer thickness range that is dense or has much smaller pores (Figure 3). These developments show that with a carefully engineered porous polymer structure, a material can be successfully tuned to the requirement of the VRFB.

**PBI-based membranes**

Recently, there has been a growing interest in PBI for separators/membranes for VRFBs, see for example the recent review article [1]. PBI is an interesting polymer for electrochemical applications that require high chemical and oxidative stability. It is also used in phosphoric acid—doped high-temperature polymer
electrolyte fuel cells. It is more of a material class than a single polymer type. PBI takes up acid and is protonated, developing anion-exchange properties. As a dense film, it has to be thin (<~20 μm) [23] owing to the rather low conductivity of the acid-doped material (1–5 mS/cm). It can also be modified to introduce anionic or cationic fixed charges [33,34]. As highlighted in the previous section, it can be processed into an asymmetric porous membrane. It has also been used in bilayer configurations with other polymers, for example, to tune vanadium transport properties [17], or as thin 'skin' on a porous PVDF substrate [31]. The key challenge of PBI for nonporous films is to increase its conductivity by chemical modification while maintaining reasonable vanadium barrier properties without impairing its chemical stability and without excessively increasing the cost of manufacture and processing.

Assessing chemical stability

The characterization of chemical stability of candidate membrane materials for application in the VRFB is of importance, considering that the target lifetime in the stack is 10–20 years. Therefore, extended lifetime tests in the cell are impractical. In particular, stability is critical for nonperfluorinated materials and needs to be studied, understood, and improved. In a widely used test, membranes are immersed in a solution of V(V)O$_2^+$ to assess their oxidative stability, see, for instance, the study by Shin et al. [35]. A comparison of stability — or the lack thereof — for the screening or down selection of membranes can thus be performed using an ex situ test, yet estimating the lifetime of the cell based on such tests is not straightforward. There is currently a lack of mechanistically sound and statistically robust accelerated stress test (AST) methods for VRFB membranes. An AST must be designed to trigger and accelerate a specific degradation mode, such as oxidative aging. For this, relevant stressors need to be identified. A possible approach is to use elevated temperatures. However, with a solution of V(V)O$_2^+$, this will result in precipitation of V$_2$O$_5$. A promising method may be the use of a stronger oxidant, such as Ce(IV), to accelerate degradation, yet the transfer function to the real cell behavior has to be established [36]. For estimation of lifetimes from ASTs, one has to be aware of potential competing degradation modes, such as mechanical disintegration of the membrane, which may become dominant at some point over the lifetime of a cell. The flow battery community has a strong need for such AST methods, which would help to increase sample throughput and reduce innovation times for new membranes.

Concluding remarks

Currently, many of the membranes used in vanadium and other redox flow batteries have not been designed for this type of device but have been ‘borrowed’ from other applications, such as fuel cells. Their properties therefore do not match well with the requirements of their use environment. The need for cost reduction and
Improvement of functional properties has sparked research and development of new materials with diverse architectures (cf. Figure 4) and composition, such as amphoteric membranes, bilayer membranes, or membranes based on a porous separator or support. In view of the trend toward higher current densities, low ohmic resistance is a key requirement, and a number of approaches have been presented where a thin polymer film of micrometer thickness is supported on a porous substrate.

Ultimately, for a commercial breakthrough, new membranes/separators must in addition be chemically stable, the fabrication process must be easy to be scaled up, and the quality assurance must be robust to enable high production volumes and low cost.

Conflict of interest statement
Nothing declared.

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References
Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

This review article stresses the importance of component, cell and stack engineering for flow battery development and highlights techno-economical considerations for cost reduction.
The article provides an excellent insight into species transport phenomena relevant for flow battery separators and membranes, in general terms but also specifically with respect to the vanadium redox flow battery. This study is the perfect starting point for researchers and engineers that aim to understand device-relevant ion and solvent transport characteristics.
With the help of a clever experimental setup, transport coefficients for the different vanadium-ions and coupling parameters are determined. Especially, the influence of the electric field induced transport is studied.
The interesting characteristics of amphoteric ion exchange membranes with respect to imbalance phenomena are shown. Effective vanadium-transport properties of different membranes over one charge-discharge cycle are shown.
Anion and cation exchange membranes based on a heteroatom-free hydrocarbon polymer are compared and their prospects in replacing Nafion type membranes are highlighted. These materials show interesting resistance-crossover trade-off characteristics.
The challenge of ensuring adhesion between the two different layers in a bilayer membrane is addressed in an interesting manner here, using a mechanical interlocking architecture as interface.


The porous, asymmetric, uncharged PBI membranes prepared by the phase inversion method show excellent cell performance and capacity retention data. The article demonstrates what a possible future flow battery membrane / separator could look like.


Similar to reference 27, this article features an asymmetric porous separator. In this case, a thin polymer 'skin' with high free volume is coated onto a porous polymer substrate. Also here there are no ion-exchange sites in the polymer, the electrolyte functionality and vanadium barrier properties are achieved by proper polymer choice and component architecture.


