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Review

The control and optimization of macro/micro-structure of ion conductive membranes for energy conversion and storage☆

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ABSTRACT

Ion conductive membranes (ICMs) are frequently used as separators for energy conversion and storage technologies of fuel cells, flow battery, and hydrogen pump, because of their good ion-selective conduction and low electronic conductivity. Firstly, this feature article reviews the recent studies on the development of new non-fluorinated ICMs with low cost and their macro/micro-structure control. In general, these new non-fluorinated ICMs have lower conductivity than commercial per-fluorinated ones, due to their poor ion transport channels. Increasing ion exchange capacity (IEC) would create more continuous hydrophilic channels, thus enhancing the conductivity. However, high IEC also expands the overall hydrophilic domains, weakens the interaction between polymer chains, enhances the mobility of polymer chains, and eventually induces larger swelling. The micro-scale expansion and macro-scale swelling of the ICMs with high IEC could be controlled by limiting the mobility of polymer chains. Based on this strategy, some efficient techniques have been developed, including covalent crosslinking, semi-interpenatrating polymer network, and blending. Secondly, this review introduces the optimization of macro/microstructure of both per-fluorinated and non-fluorinated ICMs to improve the performance. Macro-scale multilayer composite is an efficient way to enhance the mechanical strength and the dimensional stability of the ICMs, and could also decrease the content of perfluorosulfonic acid resin in the membrane, thereby reducing the cost of the per-fluorinated ICMs. Long side chain, multiple functionalization, small molecule inducing micro-phase separation, electrospun nanofiber, and organic–inorganic hybrid could construct more efficient ion transport channels, improving the ion conductivity of ICMs.

1. Applications of Ion Conductive Membranes in Energy Conversion and Storage Devices

Ion conductive membranes (ICMs), including proton exchange membrane (PEM) and anion exchange membrane (AEM), are good ion-selective conductors with low electronic conductivity [1]. Therefore, ICMs are frequently used as separators for energy conversion and storage technologies of proton exchange membrane fuel cells, alkaline anion exchange membrane fuel cells, flow battery, and hydrogen pump.

PEM, as an excellent proton-selective conductor and fuel/oxidant separator, is a good choice as a separator for fuel cells. PEM fuel cells (PEMFCs) show high energy conversion efficiency and high power density due to those advantages of PEM [2,3]. The schematic principle of PEMFCs is shown in Fig. 1(a). Fuel cells with proton exchange membranes as the separators run in the acidic media. The electrode electrochemical kinetics are slow so that precious metal Pt is required as the catalyst. Moreover, the stability of nanosized Pt catalyst in the acidic operation media also needs to be improved [4]. This triggered some researcher to look for alternative non-precious metal catalysts [5–7]. On the other hand, by switching the operation media from acidity to basicity, alkaline AEM (AAEM) can be used as the separator in fuel cells [8]. In the basic media, electrode kinetics are enhanced [9–12], and non-Pt metals (*e.g.*, silver, nickel, and Pd) are allowed to be used as catalyst [13–17], which are more stable [18–20]. In addition, the direction of hydroxide conduction opposes that of alcohol fuel crossover, consequently alleviating or even eliminating alcohol fuel crossover, particularly at the high current density [21]. The schematic principle of AAEM fuel cells is illustrated in Fig. 1(b).

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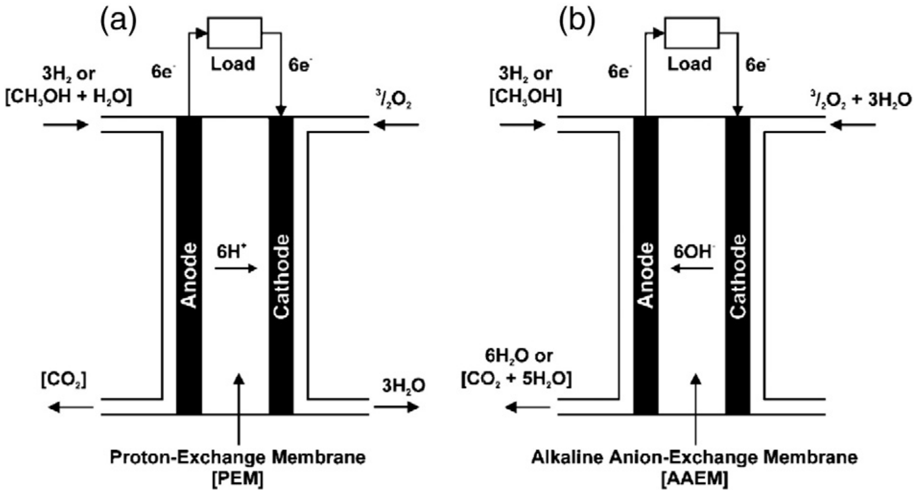

Fig. 1. The schematic principle of PEMFC and AAEMFCs [3].

PEM is also central to electrochemical hydrogen pump, which produces pure hydrogen (99.7% and more) in an environmentally friendly way [22], thus receiving more attentions. With an external potential applied, hydrogen in the mixture is oxidized to protons at the anode, which are transported across the proton exchange membrane and reduced to hydrogen again at the cathode. Other advantages for hydrogen pump separation are related to the ability of compressing hydrogen up to 50 bar at the cathode and the capture of concentrated CO_2 effluent at the anode without further regeneration. The significant challenges for hydrogen pump separation are CO poisoning and the total cost consisting of the cost of the catalyst (Pt) and PEM (Nafion) [22,23]. In addition, ICMs are also the key components of flow batteries which is an electricity energy storage device. Vanadium redox flow battery (VRB) is one of the most promising flow batteries. ICMs play the roles of isolating electrolytes (vanadium ions) while still transferring ions (protons or SO_4^{2-}) to complete the circuit [24]. The schematic principle of VRB is shown in Fig. 2.

In general, ICMs are required to possess some critical properties, including good thermal stability, high ion conduction, and low fuel/vanadium permeability, excellent chemical stability, and outstanding mechanical properties [3,25]. Highly selective ion conduction essentially determines the energy efficiency and power density. Mechanical properties of fuel cell membranes are important, especially for the fuel cell durability, since variations in temperature and humidity can cause cyclic stresses and strains (mechanical loading) in the membrane during the fuel cell operation. In addition, it is desirable for ICM materials to be soluble in low-boiling-point water-soluble solvents, in order to build an efficient triple phase boundary by adding them into the catalyst layers, thus drastically reducing the internal resistance for use in fuel cells [18,26].

2. Molecular Design and Synthesis of ICM Materials

2.1. Proton exchange membranes

Dupont's Nafion is the most frequently used PEM material, because of its excellent proton conductivity, oxidative resistance, chemical stability and commercial availability [27]. However, it suffers from high cost and great loss of conductivity at high temperature (>80 °C) due to dehydration. These limitations have stimulated many efforts in the modification of per-fluorinated membranes and the development of alternative membrane materials.

To improve the performance of PEMFC at elevated operation temperature, short-side-chain perfluorosulfonic acid ionomer (SSC-PFSA) has been considered as good alternative materials [28], owing to their higher crystallinity and glass transition temperature (T_g) than long-side-chain (LSC) PFSA ionomer. More importantly, SSC-PFSA possesses better water retention at elevated temperature (>100 °C), which is essential to maintain higher conductivity [29]. As a result, the PEMFCs with both SSC-PFSA membrane and ionomer exhibit higher performances than those with long-side-chain (LSC) PFSA at high temperatures (> 100 °C). At a potential of 0.6 V, the current density of the Aquivion™ E87-05S SSC-PFSA cell ($0.524\ A\cdot cm^{-2}$) is 2.43 times higher

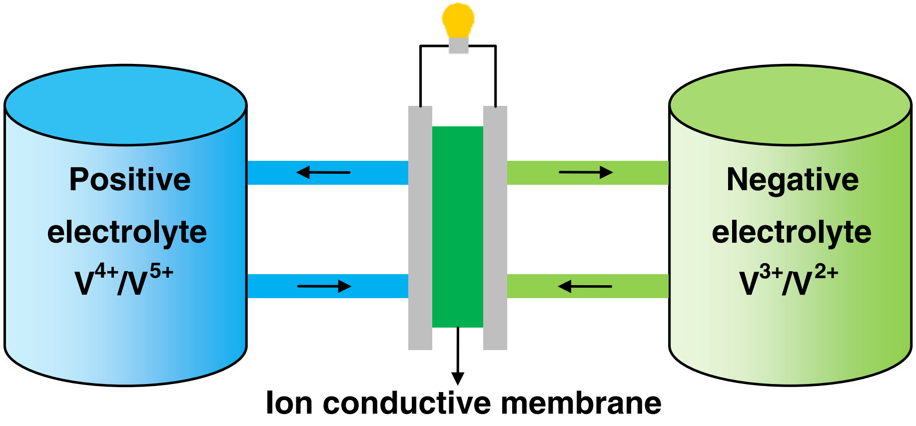

Fig. 2. The schematic principle of VRB.