Thin film separators with ion transport properties for energy applications

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Abstract. Recent years, along with the increasing need of energy, energy storage also becomes a challenging problem which we need to deal with. The batteries have a good developing prospect among energy storage systems in storing energy such as wind, solar and geothermal energy. One hurdle between the lab-scale experiment and industry-scale application of the advanced batteries is the urgent need for limiting charging capacity degradation and improving cycling stability, known as the shuttle effect in lithium-sulfur batteries or electroosmotic drag coefficient in fuel-cell batteries. The microporous separator between the cathode and anode could be molecular engineered to possess selective permeation properties, which can greatly improve the energy efficiency and extend application range of the battery. The present review offers the fundamental fabrication methods of separator film with different material. The review also contains the chemical or physical structure of different materials which are used in making separator film. A table offers the reader a summary of properties such as ionic conductivity, ionic exchange capacity and current density etc.

1. Introduction
Fossil fuels are the main resource of supporting human society. However, because of the contamination and greenhouse gas they emit, more and more energy is replaced by clean energy, and the battery plays an inevitable part in the usage and storage of it. The batteries have a good developing prospect among energy storage systems in storing energy such as wind, solar and geothermal energy. For the same time, the researches on improving the battery life and the ability of storing electricity also develop rapidly. Baring this issue in mind, integrating the microporous thin film as separator in the battery draws wide attention with one hurdle between the lab-scale experiment and industry-scale application of the advanced batteries is the urgent need for limiting charging capacity degradation and improving cycling stability, known as the shuttle effect in lithium-sulfur batteries or electroosmotic drag coefficient in fuel-cell batteries. In this review, I present the recent progresses of multiple kinds of separators for batteries. The structures and properties of separator with polymer, carbon and oxide were involved. The function of separators in different kinds of batteries were also involved.

2. Fabrication of the thin films

2.1 Polymer films
Dry process is a main kind of fabricating polymer films with its low consumption of solvents, feasible to scale-up and manufacture. It follows three steps: the first step is to processing polymer resin at the temperature higher than the melting point of polymer, and melt-extrudes into a uniaxially oriented tubular film or called precursor film. The second step is to anneal the film at a temperature relatively
lower than the melting point. The last step consists of a cold stretch, a hot stretch and a relaxation to make the film deform along the spinner direction.

Solvent casting method is also known as wet process through phase inversion of the dope solution and form polymer film, which enables processing of thermal instable or rigid polymers with ultrahigh melting points. Take the copolymers of poly (epichlorohydrin) and poly (ethylene oxide) for instance [1], the homogeneous solution containing Hydrin C-2000 and KOH could form through vigorous stirring for a long time. After casting this solution in petridishes, the flat-sheet film gradually formed by the two-stage solvent evaporation: at ambient pressure and room temperature, followed by vacuum heating at 40°C.

2.2 Inorganic composite films
Inorganic composite separator has a high hydrophilicity property and exhibits a predominant wettability, which attracts researchers’ huge attention. Two novel method have been developed to fabricate exceptional separators. One of them is phase inversion method. Taking the TiO$_2$/PVDF–HFP composite separator [2] for example, the liquid film was formed by spreading viscous slurries with 0–60 wt.% of TiO$_2$ on a clean glass plate and separate between a gap of 300 μm. Then the glass plate is dipped into a flowing water bath promptly to initiate phase separation between the solvent and the water bath. Post treatment includes peeling off the membrane after solidification and finally drying the solidified membranes under ambient condition for 24 h. The phase inversion membrane is obtained. Another method is thermal pressing method [3, 4]. Zhang et al directly mixed a small amount of ethanol, the weighed CaCO$_3$ powder and Teflon emulsion together and processing through a hot-roll. A flexible and self-standing membrane is acquired after evaporation of ethanol.

2.3 Carbon films
Slurry method is one of the conventional method to manufacture carbon films. For example, Zhang et al. [5] dispersed the slurry of polyvinylidene fluoride solution and N-methyl-2-pyrrolidinone solution with commercial conductive carbon powder by 1 h. After the slurry was coated on a routine separator, it was dried at 55°C in vacuo for 24 h followed by ball milling. There is also a patent published by A Satoh and N Mori making carbon separators.

3. Structure and properties of the thin films

3.1 Microporous membranes

3.1.1 Polymer film. a. Polyolefins (PE, PP, and PVDF) are the earliest materials used in fabricating separator membranes. The PP-PE-PP [6] trilayer structure have been widely used. The thickness of this layer in the range of 0.2 and 4.0 μm. In this structure, the PP layer has a good mechanical strength and the PE layer is able to melt and fill the pores at a temperature lower than thermal runway.

Polyvinylidene fluoride (PVDF) is also widely used because of the function of being able to swell in liquid electrolyte. Poly (vinylidene fluoride-co-hexafluoropropylene) copolymer [7] with a “sponge-like” structure was reported by Zhang et al. The pores distributed on both sides of the membrane asymmetrically. The size of the pores is no larger than 1.5 μm and pores on the top side are quite larger than the bottom ones. The morphology of another PVDF based polymer: PVDF-HFP [8] is dominated by a dense layer and has a limited porous structure, and the interconnected gel electrolytes in the film enabled the high conductivity proformance. Coating polydopamine (PD) layers onto routine porous separators could [9, 10] change the original hydrophobic surface into hydrophilic ones, which leads to an improvement in electrochemical performance.

b. Polyethylene oxide (PEO) could interact well with metal ions, which leads to formation of hydrated ion channels, but the easily of crystallization reduce the connectivity of ion channels and thus reduced the ionic conductivity. The PEO–KOH–H$_2$O system exhibits a spherulitic-type crystallization (typical Maltese cross) at 60°C, while another phase is reported without radial orientation at nearly
110°C [11]. Through copolymerizing with poly (epichlorohydrin) and poly (ethylene oxide) [called poly (ECH-co-EO)], the amorphous region increased, which makes a large increase of anionic transfer number [1].

\textit{c. Poly vinylalcohol (PVA)} was well known for its good properties such as chemical stability and hydrophilicity, ascribed to pending hydroxyl groups on the backbone, while the high crystallinity compromised its performance. Poly (epichlorohydrin) [12] or PEO [13] was blended with PVA to limit the crystallinity and enlarged amorphous region. Tetraethyl ammonium chloride (TEAC) [14] with anion ionomers was blended to enable the ion-exchange properties. Poly (acrylic acid) (PAA) cross-linked with PVA enhanced both thermal and mechanical properties [15]. The membranes were stable at a wide temperature range (25–90 oC).

Other membranes using PVA as the matrix are also reported. By using a sol-gel process, two kinds of membranes were made by directly blending TiO2 [16, 17] or ZrO2 [18] with PVA and KOH solution. Both polymer film exhibit a semi-crystalline structure, and ZrO2 filter reduce the degree of crystalline. The partial aggregation morphology was observed due to the dispersion of filters are not very well.

Through cross-linking the polyethyleneimine (PEI) and PVA matrix with dibromoethane as cross-linking agent, a good property membrane was obtain [19]. Another membrane was also acquired by rossing poly (1, 3-diethyl-1-vinylimidazolium bromide) (PDVIBr) with PVA matrix [20]. Both membranes mentioned above have an interpenetrating polymer network. There is no covalent bonds between the two polymers of these membranes and the systems are both heterogeneous.

Xiong et al [21, 22] grafted quaternary ammonium group on the backbone of PVA by using (2, 3-epoxypropyl) trimethylenammonium chloride and cross-linked by glutaraldehyde. Glutaraldehyde improves the stability in the water and quaternary ammonium group help to carry charges. However, along with the increasing degree of cross-linking, the ionic conductivity decreased.

\textit{d. Chitosan} has a high degree of hydrophilicity because of hydroxy amino group and amino group on its backbone. A porous layer made of KOH stuck in the middle of two same layers made of chitosan cross-linked with glutaraldehyde composed a three-layer system membrane. After hydration, this film exhibited a good performance [23]. N-[(2-Hydroxy-3- trimethylammonium) propyl] chitosan chloride cross-linked by glutaraldehyde was used to form the membrane. The chitosan matrix of this membrane is connected with quaternary ammonium groups. Using inorganic centers such as silane and siloxane with covalent bond to organic oligomers to fabricate membranes by sol-gel process opened a new degree of freedom to design the composite materials. PEO-[-Si (OCH3)3]2 membrane is prepared by using (N-triethoxysilylpropyl-N, N, N-trimethyl ammonium iodine) and trimethoxy silyl [24]. The cationic charges of this membrane are connected with the backbone of polymer. A PPO-based membrane blended with 3-aminopropyl-trimethoxysilane [called PPO–Si (OCH3)3(+) ] [25] through the same method had a good properties such as the anion exchange capacity. Recently, by increasing the silica content and the degree of cross-linking between the PPO and the silica. The ionic conductivity have a big improvement especially at 90°C.

\textit{e. Polystyrene A styrene-based membrane} was reported by Vinodh et al. They use paraformaldehyde and concentrated hydrochloric acid to chloromethylethylene based membranes polystyrene to quaternize the poly (divinylbenzene-co-styrene) [26]. The membrane exhibit a flexible, chemical and mechanically stable performance. Copolymerizing polyethylene and poly (divinylbenzene-co-styrene) could obtain a good performance membrane [27, 28]. The structure of this membrane is interpenetrating network as mentioned above.

\textit{f. Poly (epichlorohydrin). Agel} and co-workers synthesis the membrane by attaching 4, 4’-diazabicyclo-[2.2.2]-octane (DABCO) onto epichlorohydrin and then reticulated with trithiocyanuric acid [29, 30]. Poly (epichlorohydrin) cross-linked by allyl glycidyl ether and connected with DABCO and 1-azabicyclo-[2.2.2]-octane (quinuclidine) to obtain anionic properties is also used to fabricate alkaline fuel-cell battery membrane. This membrane reach a high conductivities without any KOH addition.
3.1.2 Inorganic composite films. a. Graphene: The graphene has a plenty of outstanding characteristics in surface adsorption, mechanical strength, ionic channel transport and electron conductivity. The separator based on graphene also develops rapidly and mesporous cellular graphene/separator is one of them [31]. 30 µm thick CGF layer with light graphene-like cellular structure tightly attached on the PP substrate. The separator with average mesopore size of 7.6 nm and mesopore volume of 3.1 cm³ g⁻¹.

b. Carbon nanotubes: A multi-walled CNT (MWCNT)-modified separator reported by Manthiram’s group [32] has a high property. The layer consisted of interwoven curved MWCNTs deposited into a dense filter. The layer has a high surface area of 410.4 m² g⁻¹ with a total pore volume of 2.76 cm³ g⁻¹ (0.18 cm³ g⁻¹ for micropore volume). For the sake of the special morphology and structure, the layer could obscure the diffusing polysulfides, improve the utilization of sulfur and also guarantee the reactivation of the trapped active material.

c. Oxide metal-ion nanomaterials: Some oxide metals with high thermal and mechanical stability could also be ideal material for separator since their layer have an efficient ion selective property. Al₂O₃ powder coated on conventional separator with PVDF binder was reported by Zhang et al [33]. The thickness of the whole separator is 24 µm and the Al₂O₃ porous layer could adheres to
the routine separator very well. Its unique porous structure (well-connected interstitial voids) between the Al2O3 nanoparticles will be occupied by liquid electrolytes and provide pathway for ion and prevent polysulfide species. A TiO2/PVDF-HFP [2] composite separator fabricated through phase membrane method also has an exceptional porous structure. The thickness of this membrane is 80-100 μm and the highly porous surface with a slightly distorted honeycomb cross-sectional view could promote the electrolyte filling process and improve the electrochemical properties.

![Fig.4 Configuration of Al2O3-coated separator, and the morphology of Al2O3-coated separator](image)

### Table: Ion transport properties

| Material                                      | Ionic conductivity (10⁻³ S cm⁻¹, 25 °C) | Ionic exchange capacity (10⁻³ mol g⁻¹) | anionic ionic transport number | Power density (W cm⁻²) |
|----------------------------------------------|----------------------------------------|---------------------------------------|--------------------------------|------------------------|
| Polysulfone cross-linked via tetraphenylol ethane glycidyl ether | (-) 10 (+) 75000 (80 °C)              | NM                                    | NM                             | NM                     |
| Poly(arylene ether sulfone) functionalized with benzyl trimethyl ammonium | (+) 6.3 (70 °C)                      | NM                                    | 4.1                            | NM                     |
| Polyether sulfone (Chloromethylated and quaternized) | NM                                     | 0.17– 0.6                             | NM                             | NM                     |
| Polysulfone (quaternary ammonia)             | (±)> 10                                | NM                                    | NM                             | 110×10⁻³ at 0.55 V     |
| Poly(arylene ether sulfone) (grafting guanidinium) | (±)45 74 (60 °C)                      | 0.945                                 | NM                             | NM                     |
| PEO–[Si(OCH3)3]2                            | (-) 3                                  | NM                                    | NM                             | NM                     |
| poly(ECH-co-EO), with KOH as a conducting salt | (-) 1                                  | NM                                    | NM                             | NM                     |
| PVA/KOH/H2O                                  | (±) –1                                 | NM                                    | NM                             | NM                     |
| PVA-blend-poly(epichlorohydrin) (PECH)        | (±)20                                  | NM                                    | NM                             | NM                     |
| PVA, triethoxysilylpropyl-N,N,N-             | NM                                    | 0.76- 1.01                            | 0.69-0.80                      | NM                     |
| Material Description                                                                 | Diameter (±) | Thickness (nm) | Conductivity (×10⁻³ A cm⁻²) | Temperature (°C) |
|--------------------------------------------------------------------------------------|-------------|----------------|-------------------------------|------------------|
| Trimethylammonium iodine                                                              |             |                |                               |                  |
| PVA/TiO₂                                                                              | (±)102-170  | NM             | NM                            |                  |
| PVA/ZrO₂                                                                              | (±)267      | NM             | NM                            |                  |
| PVA/poly(acrylonitrile-2-dimethylaminoethylmethacrylate)                             | (±)3.45     | 1×10⁻³         | NM                            |                  |
| PPO-Si(OCH₃)₃(+)                                                                      | (-)8        | 2.44-2.95      | NM                            |                  |
| PPO (bromination and amination)                                                       | NM          | 3.80           | NM                            |                  |
| Poly(epichlorohydrin-co-allyl glycidyl ether) (quaternized)                           | (-)13       | 0.65           | 100×10⁻³                      |                  |
| PEO, KOH and optionally, water                                                       | (+)1        | NM             | NM                            |                  |
| Chitosan/KOH and glutaraldehyde/KOH                                                   | (±)10-30    | NM             | 35×10⁻³ A cm⁻²                |                  |
| Polybenzimidazole (PBI) doped with KOH                                               | (±)0.05-100 | 620×10⁻³       | at 0.6 V in a H₂/O₂ fuel cell test |                  |
| Poly(acrylonitrile) (quaternization/4,4_-diazabicyclo-[2.2.2]-octane (DABCO))       | (±)2        | NM             | NM                            |                  |
| Poly(styrene-co-divinylbenzene) (chloromethylated and quaternized)                   | NM          | 0.78×10⁻³ eq g⁻¹| NM                            |                  |
| Polyethylene functionalized by tetraalkylammonium groups                              | (±)40       | NM             | NM                            |                  |
| Poly(methyl methacrylate-co-butylacrylate-co-vinyl benzyl) (quaternized)             | (±)8.2 (80 °C) | NM           | 35×10⁻³ at 60 °C              |                  |
| Trifluorostyrene onto PE                                                              | NM          | 0.29           | NM                            |                  |
| Polystyrene ethylene butylenes Polystyrene                                           | (±)1        | NM             | NM                            |                  |
| Polystyreneblock-poly(ethylene-ran-butylene)-block-polystyrene (chloromethylated)    | (±)9.37 at 80 °C | NM           | NM                            |                  |
| Material                                           | Conductivity | Temperature | Conductivity | Temperature |
|---------------------------------------------------|--------------|-------------|--------------|-------------|
| Poly(epichlorohydrin) quaternized by TEA and DABCO| (±)10-20 at 25 °C | NM          | NM           | hydrogen/oxygen fuel cell 43×10⁻³ for 140×10⁻3 A cm⁻² at 25 °C |
| PEG/diallyldimethylammonium chloride              | (±)1 × 10⁻³ at 25 °C | NM          | NM           | NM          |
| Poly(diallyl dimethyl ammonium chloride) associated with an ammonium salt | (±)1 | NM | NM | NM |

* a (-), anion conductivity; (+) cation conductivity.

4 Applications in the batteries

4.1 Lithium-ion battery
The separator plays a inevitable application in batteries. It is placed between the positive and negative electrode to avoid the contact of them and isolates electronic flow but allows the transportation of free ionic.

4.2 Lithium-sulphur battery
The diffusion of high-order polysulfides into the electrolyte of battery results in the decreasing of performance of Li-S battery. This separator could block polysulfides and limit the parasitic reactions. The capacity of reactive dead sulfur is able to improve the cyclic stability of Li-S cells. And preventing the dendrite growth in the lithium metal surface also prolongs the longevity of Li-S battery.

4.3 Alkaline Fuel-cell battery
This kind of film is quite unique among other separators in their batteries. The membrane uses the solid polymer electrolyte to replace liquid electrolyte and functions as the separator and conductive support between the anode and cathode. The reaction of solid electrolyte is same as for the liquid ones, but it can eliminate the negative influence of CO₂. For the sake of no liquid, the erosion is minimized. Further benefits contain leakproofness, volumetric stability, solvent-free conditions and easy handling.

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