RECENT DEVELOPMENTS IN HETEROGENEOUS ION-EXCHANGE MEMBRANE: PREPARATION, MODIFICATION, CHARACTERIZATION AND PERFORMANCE EVALUATION

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Abstract

Ion-exchange membranes (IEMs) have been used in different processes and applications and have shown the advantages over other comparative processes. The extensive applications of IEMs in many areas have necessitated the improvement in their properties to achieve better performance and lower cost. As the first commercialized IEMs, heterogeneous membranes face the challenge to improve their lower selectivity and conductivity which associated to the higher heterogeneity. Recently, development of the heterogeneous IEMs is steadily growing which is driven by the need to obtain IEMs with better electro-chemical properties, lower production cost, and easier preparation procedure. Additive blending, membrane surface modifications, and post-treatment are typical methods used to improve heterogeneous IEMs characteristics. The methods give the improvement in electro-chemical characteristics of heterogeneous membranes and provide the possibility to produce heterogeneous IEMs with comparable performance to homogeneous ones. In this paper, preparation, characterization, and performance of heterogenous IEMs are reviewed. In addition, recent progress on IEMs modifications is pointed out.

Keywords: Additive, Surface modification, Chemical Treatment, Electro-chemical properties.

1. Introduction

Ion-exchange membranes (IEMs) have been widely used in a number of different processes and applications. Electrodialysis (ED) is the first process that uses IEMs in large industrial scale for brackish water desalination. Nowadays, the basic concept of ED process has been modified into various ED-related processes that

also shown great potential to be applied in various applications such as desalination and seawater pre-concentration; production of chlorine-alkaline; production, demineralization, and concentration of organic acids and organic salts; production of ultrapure water; wastewater treatment; and energy conversion [1-6]. Integration of ED-based processes has also been considered as a versatile solution to separation in industries such as in chemical, biochemical, food, and pharmaceutical due to their cost and as promising techniques for clean production and separation that need some more development particularly in IEMs and equipment [7].

These extensive applications of IEMs in many areas have necessitated the improvement in their properties to achieve better performance of the processes since the IEMs are the key of separation. Generally, most commercial IEMs can be classified into two major categories, namely homogeneous and heterogeneous membranes with their typical properties and advantages. Homogeneous IEMs exhibits better electro-chemical properties than the heterogeneous membranes [8]. On the other hand, heterogeneous IEMs have better mechanical strength, easier preparation procedure, and lower production cost [9]. Even though heterogeneous membranes were the first commercial` IEMs, the interest of this type of membranes were subsided which attributed to the lower electro-chemical characteristics particularly on conductivity and selectivity [10]. Recently, development of the heterogeneous IEMs has gained much attention which has been driven by the need to obtain IEMs with better electro-chemical properties, lower production cost and easier preparation procedure. This development includes the selection of appropriate materials, incorporation of additive which has specific properties, membrane surface modification, post-treatment, and advances in characterizations. These attempts have shown improvement in electro-chemical characteristics of heterogeneous membranes and have provided the possibility to produce the membranes with comparable performance to homogeneous ones.

Comprehensive reviews on IEMs can be found in literature including their preparation procedures, applications, and ionic transfer even containing a special section of reviews on heterogeneous IEMs [11-14]. While an early review on heterogeneous IEMs has been found [10], this review is an attempt to summarize the recent development in heterogeneous IEMs which involves the preparations, modifications, characterizations and performance evaluation.

2. Preparation of Heterogeneous IEMs

Homogeneous and heterogeneous IEMS are distinguished based on the structure of the membrane, particularly on the phases incorporated in the membrane matrix [10]. The homogeneous membrane has a single polymer which acts as membrane structural material and the holder of the functional groups. Meanwhile, the heterogeneous has two different polymers which have different functions. The function of the first polymer is to hold the second polymer together and form the membrane sheet. Thus, this polymer should have high mechanical strength and generally, it is an inert material. Meanwhile, the second one should be very good in conductivity and ion-exchange capacity that usually provided by ion-exchange powder. Homogeneous IEMs are prepared by introducing functional groups into polymer structure that used for membrane preparation. The functional groups can be introduced directly into the monomer or subsequently after the membrane

sheet formed. Hence, the homogeneous IEMs have relatively even distribution of the functional sites. As a result, their electro-chemical properties are significantly higher than that of heterogeneous membranes. Meanwhile, the heterogeneous IEMs are prepared by incorporating of ion-exchange powder into an inert polymer material. The procedures could be calendaring ion-exchange powder into a polymer film, dry moulding of ion-exchange particle and polymer, or dispersing finely ground ion-exchange particles into polymer solution [13]. For the last method, membrane solution could be further cast into a sheet. Subsequently, to separate the solvent from the casted solution, the membrane can be either dried at room temperature, immersed in a coagulation bath, or treated through combined method (dry-wet phase inversion). Since the binder polymer is inert and the functional sites are in a granular form of ion-exchange particles, the functional sites are therefore distributed unevenly yet clustered. Thus, this procedure leads to heterogeneity of the membrane structure.

Several parameters of membrane preparation which strongly affect the characteristic of heterogeneous IEMs are summarized in Table 1. As the holder of the charged groups, ion-exchange particles determine to very large extent of membrane properties including its electro-chemical and mechanical characteristics. A membrane with relatively smaller particles exhibits lower resistance, higher ion-exchange capacity and more flexible [15, 16]. The improvement of membrane electro-chemical properties at smaller particle size is attributed to the wider area of the ion-exchange particles that enhances the accessibility of the functional sites and their distribution. Furthermore, as the size of the resin is smaller, the particles are well bonded in membrane matrix resulting in higher flexibility. The same effects are provided by increasing ion-exchange particles loading [15]. However, further loading of the particles gives negatives effect to mechanical strength and oxidative stability [17]. This opposite effect of particles size and loading to electro-chemical and mechanical properties is, therefore, should be optimised. Generally, ion-exchange particles with -300+400 mesh size (with average particle size of 39 µm) and 50-60%-wt loading are used. Vyas et al. [18] reported that heterogeneous membranes prepared by using suitable size and loading of ion-exchange particles exhibited almost similar or even better properties than interpolymer IEMs thus they may replace the interpolymer membranes in some applications.

Various polymers used for the preparation of heterogeneous IEMs are listed in Table 2. The matrix polymer should provide enough mechanical and dimensional stability to the entire structure of the membrane and it should give appropriate space for ion-exchange particle during swelling. The increase of polymer rigidity leads to conductivity declining as well as ion-exchange capacity deterioration [19, 20]. This is due to the inadequate degree of swelling which results in a narrower path for ion transport [19]. Polymer blending is usually used to improve membrane properties. Polymer blending allows obtaining a membrane with better properties than pure materials since it combines the advantages of each polymer.

In solution casting method, casted membrane can be dried to separate the solvent. The rate of solvent separation from membrane solution influences membrane characteristic. The solvent with lower volatility leads to particle aggregation and discontinuous binder polymer [21]. The aggregation of resin particles during solvent evaporation reduces particle accessibility and isolation that yields in lower

conductivity, permselectivity and ion-exchange capacity. During loss of solvent which occurs through solvent evaporation or solution immersion, solvent leaves macrovoid between particles and matrix polymer. As the result, a high solvent to polymer ratio produces a membrane with high void fractions which improves membrane conductivity and ion-exchange particles accessibility. On the other hand, a lower solvent to polymer ratio produces a membrane with less porosity thus showed better permselectivity which attributed to more effective Donnan exclusion. Klaysom et al. [22] reported that combination of dry phase inversion and wet phase inversion can be utilised for designing membrane with desired porosity and structure.

IEMs are also developed to obtain specific property such as high acid retention, permselectivity of specific ions and anti-fouling IEMs. For example, to reduce HCl permeability, anion-exchange membranes (AEMs) can be improved to have high acid retention by modifying the base membrane using a cross-linked layer of epoxide compounds and amines, thin anionic charged layers, poly(pyrrole) layers, etc. [23]. The IEMs with high permselectivty for monovalent ions can be obtained by changing cross-linkage of the membrane, using charge effect by electrostatic repulsion, and utilizing a specific interaction between the specific ion-exchange groups [24]. Additive (nanoparticle) blending may induce sieving mechanism since it could result in narrowing channel which leads to higher permselectivity of monovalent ions [25]. Meanwhile, in order to solve the problem of fouling during the separation of water containing organic foulant, the surface of AEMs can be modified to obtain anti-fouling properties [26, 27].

2.1. Additive blending

Modifications of heterogeneous IEMs can be classified as additive blending, surface modification and post-treatment. The Introduction of additive into membrane solution is a simple method for improving membrane characteristics. Activated carbon, carbon nanotube, zeolite, and metal oxide are the typical example of inorganic materials used for improving membrane electro-chemical properties (Fig. 1). Properties of the additive such as electrical conductivity, hydrophilicity, and adsorption capacity can be utilised to produce the membrane with better electro-chemical characteristics. Functional groups or charged groups provided by the additives may improve ion-exchange capacity and conductivity.

Surfactant could induce a uniform distribution of ion-exchange particles during membrane formation due to decreasing surface tension between the matrix polymer and ion-exchange particles [37]. Unfortunately, when the additive loading exceeds a certain concentration, an opposite trend was observed in both conductivity and permselectivity which attributed to void fraction occupied by the additives thus results in inacessability of functional groups. Consequently, both conductivity and permselectivity are decreased. Moreover, a nanoparticle additive may contribute to membrane solution viscosity [38, 39]. Since higher nanoparticle loading results in higher solution viscosity, it produces the membrane with less porosity.

Table 1. The effects of parameters on membrane properties.

Factors	Effects	Ref.
Size of ion-exchange resin	Smaller ion-exchange resin results in more flexible membrane, more homogeneous, and better electro-chemical properties.	[15]
Resin loading	• Conductivity and selectivity are improved with increasing resin loading.	[16]
	• Membrane with higher resin loading exhibits lower oxidative and mechanical stability.	[28]
Resin distribution	Membran with highly ordered resin shows better electro-chemical characteristics than those have random distribution.	[29]
Polymer	• Polymer with high rigidity results in lower permeability, ion-exchange capacity and conductivity.	[19]
	• Polymer which has lower elasticity inhibits the ideal degree of swelling required by ion-exchange resin.	
	• Characteristics of polymer influence membrane morphology significantly.	[30]
	• Polymer with high hydrophilicity increases water uptake and improves membrane conductivity.	[31]
Solvent	• Less volatile solvent leads to resin aggregation during solvent evaporation and discontinuity of matrix polymer.	[21]
	• The increasing solvent to polymer ratio results in more void fraction.	[9]
Method	• Solvent evaporation method produces membrane which has higher selectivity.	[32]
	• Gelation or solution immersion method could produce membrane that shows higher conductivity.	
	• Longer evaporation time at dry-wet phase inversion reduces membrane porosity.	[33]

Table 1. Various types of binder polymers, solvents and methods for preparation of heterogeneous IEMs.

Polymer	Solvent	Composition	Method	Ref.
Polyvinyl chloride (PVC)	THF	Total solid:THF = 1:10 (w/v)	Phase inversion (dry-wet); Spray coating; t_{ev}: 30 menit; T: ~35°C;	[15]
S-PVC/cellulose acetate (CA)	THF	THF:polymer= 20:1 (v/w)	Dry (1 h)-wet phase inversion	[31]
S-PVC/polycarbonate (PC)	THF	THF:polymer= 20:1 (v/w)	Phase inversion (dry-wet)	[30]
S-PVC/ styrene-butadiene-rubber (SBR)	THF	S-PVC:SBR= 95:5 (w/w); THF:polymer= 20:1 (v/w)	Phase inversion (dry-wet)	[34]
Polycarbonate (PC)	THF	THF:total solid= 8:1 (w/w)	Phase inversion (dry-wet)	[17]
Linear polyethylene (LPE)	-	-	Compression moulding; T: 150°C	[19]
Polystyrene (PS)	-	-	Compression moulding; T: 190°C	
Chlorinated polypropylene (C-PP)	Toluene	-	Dry (5-60 min, 24 h) - wet phase inversion	[33]
Polyvinyl butyral (PVB) and Polyethylene glycol (PEG) as modifier	Toluene & EtOH	-	Dry phase inversion	[35]
Polyaniline (PANI) / poly(vinylidene fluoride) (PVDF)	NMP	PVDF in NMP= 17 % (w/w)	Dry phase inversion; Wet phase inversion (immersed in ethanol/water= 2:1)	[36]

Note: DMF= N,N-dimethylformamide; EtOH= ethanol; NMP= 1-methyl-2-pyrrolidone; S-PVC= syndiotactic polyvinyl chloride; THF= Tetrahydrofuran; dry phase inversion= solvent evaporation; wet phase inversion= solution immersion or gelation method; t_{ev}= eaporation time.
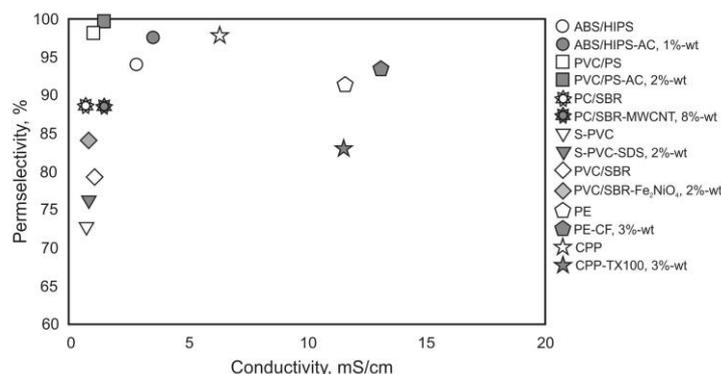
Fig. 1. Conductivity and permselectivity of heterogeneous membranes with and without additives. Data collected from [9, 17, 25, 37, 41-45].

For example, Hosseini et al. [40] synthesised cation-exchange membranes (CEMs) from PVC-THF solution by solution casting technique wherein iron oxide nanoparticles were employed as additive. Membrane properties including ion-exchange capacity, conductivity and permeability were increased by increasing additive content up to 2 wt%. The improvement of those membrane characteristics was reported as the results of increasing heterogeneity induced by the additive that increases the number of macrovoids and cavities throughout the membrane. However, those properties were decreased again by increasing additive loading which associated with pore or void filling by particles.

2.2. Surface modification

It is well known that membrane surface and morphology play an important role in the performance of membrane separation processes. Surface modification has been widely applied to achieve a better characteristic of membranes which contribute to the enhancement of their performance. Various methods of surface modification have been developed for membrane preparation. Among them, plasma treatment, in situ polymerization, solution casting, dip-coating, surface profiling, and electro-deposition have been reported in preparation and modification of heterogeneous IEMs. Some of them are summarized in Table 3. Results of some studies showed that surface modifications are able to improve membrane electro-chemical characteristics.

In a plasma treatment, the membrane is placed in a vacuum reactor (e.g. 10^{-7} mbar base pressure) [34]. The modifier such as a silver plate is placed in the reactor at a certain distance to membrane sample. Argon gas is used as plasma former in a magnetron sputtering system (at 25°C and 90 W power). The deposition rate of modifier can be adjusted so desired coating thickness is obtained. Hosseini et al. [46] modified PVC based heterogeneous CEMs wherein Ag nanoparticles were used as a surface modifier by plasma treatment. Subsequently, the modified membranes were treated in an oven at different temperatures (25 - 100°C) within 30 minutes. The thermal treatment increased the compatibility of particles with the polymer binder and improves the particle-polymer incorporation. For in situ

polymerization, a solution containing monomer, initiator, and cross-linker is poured on membrane surface then heated in oven for several hours (e.g., 90°C, 4 h) [47]. The membrane is then washed to remove the excess monomer and other reactants. Both plasma treatment and in situ polymerization could produce a fine deposition of the additional layer. However, plasma treatment requires high energy consumption due to thermal and power used and complex equipment. While for in situ polymerization, compatibility of the base membrane and the additional layer should be considered.

Membrane surface can be modified by depositing a layer on the base membrane through solution casting method or dip-coating method. The solution casting is a relatively simple technique wherein layer thickness, properties and structure could be easily controlled. However, it should be noted that the most important thing is compatibility between the modified layer and membrane surface. Moreover, since the deposited layer contains a solvent, it may affect the structure of the base membrane. Meanwhile, in the dip-coating method membrane is immersed in a modifier solution for a period of time. In this method, the layer thickness could be controlled by adjusting the number of immersions. Since the modification is only conducted by immersion, the reactivity of modifier and the base membrane is important to obtain the compatibility and stability of the modified layer. The deposition of additional layer may also be conducted through electro-deposition method when the layer of the modifier is ionic compounds (charged layer) [48]. Compared to the previous methods, electro-deposition is a relatively simple technique. The formation of modified layer could be controlled by adjusting operating parameters such as the concentration of modifier, time and current density. However, the stability of deposited layer at long term operation is not reported. Therefore, further investigation of modified layer stability under electrical field is needed.

Surface modification is also applied in commercial heterogeneous IEMs with the aim to create geometrical profiles on membrane surface [49]. Profiled membranes were fabricated by means of hot pressing under various temperature, pressure, and time. It was found that the major obstacle during membrane profiling was encapsulation of ion-exchange particles by inert binder polymer that resulted in an increase of membrane resistance and a decrease of the surface active area. In addition, surface profiling needs high pressure and temperature. Meanwhile, profiling method increased microscopic porosity and penetrability of the membranes.

Nafion is well known homogeneous type CEMs with excellent electro-chemical characteristics. Benefiting from its excellent properties, some researchers used Nafion type film to modify heterogeneous CEMs in order to achieve better characteristics. Surface modification of heterogeneous CEMs with 7 μm thickness of modifying agent leads to the almost complete elimination of water dissociation reaction [50]. Furthermore, the modification produces heterogeneous CEMs with properties that almost equal to the homogeneous membrane [50]. Modification of heterogeneous surface with homogeneous Nafion type film results in increasing overlimiting transfer and the effect is further improved when carbon nano-tube is incorporated in the Nafion film [51]. In addition, casting of thin film Nafion on membrane surface yields in a homogenization of the surface layer thus suppress water dissociation rate which

favours the development of electro-convection [52]. Despite the advantages, Nafion is still considered as an expensive material.

2.3. Post-treatment

At the end of preparation step, the prepared membrane may be further treated to achieve desired characteristics. The heterogeneous membranes could be activated through several routes as proposed by Brožová et al. [53]. The activation procedure consisted of alternating immersion of the synthesised membrane into the aqueous solution of acid (HCl) and basic (NaOH). The activation procedure converted CEMs from Na+ to H+ form in multiple times. Meanwhile, it converted AEMs from Cl- to OH-form. Results indicated that efficient activation procedure could improve membrane conductivity. The activation procedure depends on the total time of the treatment and number of the exchange of ions.

The effect of heat treatment on the properties of heterogeneous CEMs was reported by Hu et al., [54]. The heat treatment can be used to adjust membrane characteristics namely transport number, selectivity and water uptake. The heat treatment (0-10 h, 100-200°C) can produce membrane which has less void fraction due to polymer shrinkage. The treatment may also provide a different effect to membrane characteristic. The membrane hydrophilicity could be increased under prolonged heat treatment that led to conductivity enhancement [55]. The increase of hydrophilicity is related to substantial enlargement of cavities and cracks resulting from the partial destruction of the inert polymer. The effect was enhanced when heat treatment was combined with chemical treatment (in sulfuric acid). In addition, the heat treatment may also increase membrane porosity and inhomogeneity as well as the fraction of ion-exchange surface component [56].

3. Characterization of IEMs

IEMs are expected to have good electro-chemical and physico-chemical properties, mechanical stability and chemical stability. Conductivity and selectivity or permselectivity are two most important electro-chemical characteristics for IEMs-based processes. Ideally, IEMs excluded co-ions completely and transmits counter-ions only which results in excellent permselectivity. Selectivity or permselectivity determines the degree of separation that could be achieved by membrane separation. Meanwhile, energy consumption required for ionic transport and the rate of ionic transport depend on the membrane conductivity. Xu et al. [57] explained that the properties of IEMs are well related each others. Membrane properties including water transport number, salt permeation, co-ion diffusion, mechanical strength, selectivity of ions with the same charge, counter-ion transport number, conductivity and degree of swelling are qualitatively depend on water content and ion-exchange capacity (IEC). For example, conductivity and degree of swelling are increased with increasing water content and IEC. Meanwhile, the selectivity of same charged ion and counter-ion transport number are decreased with increasing water content and they are increased with increasing IEC.

IEMs need to be characterized to ascertain the applicability of the membrane and to determine the performance of the membrane in a process. Generally, IEMs are characterized to obtain several parameters including areal resistance or conductivity, thickness, transport number, water uptake, and the IEC. Recently, characterization of membrane structure is gaining interest in membrane fabrication since structure of the membrane determines to very large extent of membrane properties. There are three models that allow relating transport and structural properties of IEMs namely microheterogeneous, three-wire and extended three-wire models [58-60]. By using the models, inhomogeneity of the membrane and fraction of intergels and interstitial solution can be characterized.

4. Performance of Heterogeneous IEMs

Investigation on the heterogeneity of heterogeneous and homogeneous CEMs and its effect have been reported by Choi et al. [61]. The fraction of conducting region was determined by utilizing modified Sand equation. Meanwhile, the fraction of gel and intergel phase were determined from the microheterogeneous model. Obviously, homogeneous membranes exhibited larger conducting region than the heterogeneous membrane since the heterogeneous membrane contained a larger fraction of the inert polymer. Otherwise, the fraction of the intergel phase of a heterogeneous membrane was larger than that of the homogeneous membrane due to the larger void fraction.

Even though the heterogeneous membrane possesses higher intergel fraction, the presence of non-conducting phase reduces the overall membrane conductivity. Furthermore, it was observed that membrane heterogeneity influenced limiting current density (i_{lim}). Since heterogeneous membrane has a lower conducting region, it showed the lower i_{lim} than the homogeneous one. On the other hand, heterogeneous membrane showed the higher local i_{lim}. The higher local i_{lim} was associated to the enhancement of current transfer on conducting region. The phenomenon was also confirmed by Volodina et al. [62] in a study. Results of the study showed that the presence of non-conducting phase increased the local current density in conducting region. As the consequence, boundary condition near this area in a heterogeneous membrane is lower than that encountered in a homogeneous membrane at the same applied voltage. The decrease in boundary concentration near a conducting area was suggested as the result of tangential electrolyte diffusion along the neighbouring non-conducting regions and by coupled convection.

Water dissociation reaction is a well-known phenomenon that occurs during electro-membrane processes. Water dissociation contributes to current efficiency declining due to the usage some portions of electrical current used to transport ions. The rate of water dissociation depends on electrical current (or applied voltage) and membrane characteristics. Since heterogeneous membranes exhibit relatively higher electrical resistance than the homogeneous membrane, water dissociation is more intensive in the heterogeneous membrane. The dissociation would be further intensified when it is used in a dilute solution. It was observed that when water dissociation effect was eliminated such as through surface modification, mass transfer rate in the heterogeneous membrane could be higher than the homogeneous one [63]. It is also possibly implied that well-designed surface inhomogeneity could enhance ionic transfer through the membrane.

Table 3. Methods for surface modification of heterogenous IEMs.

No.	Modification	Method	Results	Ref.
1.	Surface coating with silver nanoparticle	Polymer: S-PVC dan SBR Method: argon plasma treatment, 2.5 nm/s Layer thickness: 20 – 120 nm	σ: unmo $\approx$ 7; mo $\approx$ 18; Ps: unmo $\approx$ 0.87; mo $\approx$ 0.993;	[34]
2.	Coating of membrane surface with polymeric layer of SBR containing activated carbon (AC).	Commercial membrane: RALEX CMH-PES Polymer: blending of SBR solution AC; Method: solution casting Additive:SBR= 5:100 w/w Thickness: 20-10 µm	R: unmo $\approx$ 11; mo $\approx$ 10; Ps: Unmo $\approx$ 0.95; mo $\approx$ 0.98;	[64]
3.	Immobilization of multilayer polyethyleneimine (PEI)	Commercial membrane Method: dip-coating Solution-1: poly(sodium4-styrene sulfonate), 2 g/L in 1 mol/l NaCl solution Solution-2: PEI, 2 g/L in 1 mol/l NaCl solution, 30 minutes Solution-3: glutaraldehyde GA (1%), 30 minutes.	PEI multilayer improves the selectivity due to additional charged groups provided by amine groups. The PEI multilayer also improves membrane homogeneity and hydrophylicity	[65]
4.	Polymerization of Poly(acrylic acid)-co-poly(methyl methacrylate), PAA-co-PMMA)	Polymer: S-PVC (membrane) Method: insitu polymerization Monomer: AA and MMA Surfactant: sodiumdodecyl benzene sulfonate (SDBS) Initiator: Benzyl peroxide (BP) Cross-linker: Ethylene glycol (EG) Pore former: water Solution: AA:MMA (6:10) (v/w); EG:monomer (1:16) (w/w); BPO:monomer (1:80) (w/w); H$_2$O:monomer (3:16) (w/w)	For modified membrane with SDBS:monomer= 1:4; R: unmo $\approx$ 20; mo $\approx$ 13; Ps: unmo $\approx$ 0,85; mo $\approx$ 0.94;	[66]

R = areal resistance, Ω.cm^2; unmo= unmodified membrane; mo= modified membrane; P_S= permselectivity; σ= conductivity, mS/cm;

Table 4. Performance of ED and EDI with heterogeneous IEMs.

Process	Membrane	Influent	Performance
Electrodialysis [67]	PVC-based cation-/anion-exchange membran	NaCl solution= 750 mg/L	Salt removal= 86%; E = 1.16 kWh/m³; CE= 58%; Q= 1.2 L/h;
Electrodialysis [68]	Ralex® AMH-PES/CMH-PES	Spent glycol solutions from heat-exchange fluids used in ventilation and air conditioning systems (HVAC) = 5.4 mS/cm	Conductivity reduction= 98%, Monovalent ion removal= 75–99 %;
Electrodeionization [69]	CMI-7000/AMI-7001	Dilute solution of nickel (1 mol/m³ NiSO₄).	CE= 14%; E= 208 Wh for 0.35 mol Ni(II).
Eelctrodeionization [70]	Polyethylene heterogeneous CEM/AEM	Electroplating rinse water containing copper (Cu^{2+}= 50 mg/L)	Copper removal > 99.5%; Enrichment factor= up to 14; Cu on purified water < 0.23 mg/L.
Electrodeionization with periodic polarity reversal [71]	Ionac MC3470/AMX (homogeneous AEMs)	Hard water, hardnesss = 250-1250 mg/L as $CaCO_3$.	Removal rate is lower than EDIR employing homogeneous CEMs while the stack resistance is higher.
Electrodeionization [72]	Ionac MC3470/MA3475	Citric acid acid solution with 2,000 mg/L concentration; pilot scale; I= 50 A/m²; Flow: 10 ton/h	Concentrating factor= 30;
Electrodeionization [73]	Ionac MC3470/MA3475	Synthetic sugar solution containing salt (about 50 mg/L)	Salt removal= 79% EDI is able to remove colour
Electrodeionization [74]	Ionac MC3470/MA3475	Synthetic sugary wastewater containing salt.	No sugar loss during desalting process. Membrane scaling problem.

Note: *CE*= Current efficiency; *E*= Energy consumption;

Benefiting from the chemical resistance characteristics, heterogeneous IEMs would show the applicability of the process in a harsh condition such as for wastewater treatment [37]. In addition, due to lower production cost, employing heterogeneous IEMs can reduce the investment cost for various applications. However, this applicability is limited by lower selectivity, higher resistance, and lower current efficiencies which consequently results in higher total energy consumption and the degree of separation. Hence, appropriate modifications are required to solve these problems. By using an appropriate modification, even the specific characteristic such as anti-fouling and anti-bacterial characteristic and enhanced ionic transfer can be obtained. Nevertheless, ED and EDI processes use heterogeneous IEMs for various applications (Table 4). If the selectivity is sufficient, mechanical stability seems more important for the processes than the others electro-chemical properties [75].

5. Conclusions

Recently, many attempts have been proposed to produce heterogeneous IEMs with better electro-chemical properties. Additive blending, membrane surface modifications, and post-treatment are typical methods used to improve heterogeneous IEMs characteristics. These attempts are able to improve electro-chemical characteristics of the membranes and provide the possibility to produce heterogeneous IEMs with comparable performance to homogeneous ones. Meanwhile, the advanced characterizations have been developed to gain a better understanding of the effect of membrane structure such as its heterogeneity on membrane properties. Information obtained from the characterization could be used to achieve advanced preparation of IEMs. By advanced preparation and appropriate modifications of heterogeneous IEMs, it would provide the possibility of producing inexpensive membrane for various applications.

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