Chapter 3

Materials and Applications for Functional Polymer Membranes

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Abstract

This chapter covers an inclusive overview of the polymeric membranes with advanced functions in numerous applications such as water and gas separation, medical and emerging technologies include fuel cells, lithium-ions batteries, electroconductive, and optoelectronics. The membrane's performance and behavior in terms of selectivity, permeability, and separation process for these applications are determined by the materials used in the membrane's construction. Thus, in this chapter, the potential of different polymers for functional membranes are discussed including their applications based on their suitability in terms of types, fabrications, and mechanisms. For each application, the polymer membrane technology, the challenges, and the future direction are also discussed. The membrane technology is also always evolving, especially the development of functional polymer membranes for a variety of applications, so that quality of life is improved.

Keywords

Membrane, Water/Gas Separation, Medical, Fuel Cell, Lithium-ions Battery, Electric Conductive, Optoelectronic

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1. Introduction

Membranes are selective barriers that qualify components of varying sizes or physical/chemical qualities to be separated. The selectivity and permeability of the membranes utilized determine the efficiency of a membrane separation process [1]. Generally, membranes can be categorized based on different nature of materials (natural or synthetic), type of materials (polymer or inorganic) and structure (porous or non-porous) [2]. Natural membrane is a membrane in nature such as biological membrane, consists of phospholipid bilayer which involving biochemical reaction for the ions and chemicals transportation, whereas, synthetic membrane is basically artificially created membrane typically made up of cellulose, filter and synthetic polymer for laboratory or industry applications. On the other hand, the organic membrane is a membrane constructed from the organic polymer materials which include polyethylene (PE), polypropylene, polytetrafluorethylene (PTFE), and cellulose acetate. Meanwhile, inorganic membrane refers to membrane made by ceramics, metals, zeolites, or silica [3]. Apart from that, porous and non-porous membranes are dissimilar in terms of selectivity, permeability and separation process, where porous membrane is normally used for micro- and ultrafiltration via particle size differentiation, whereas, non-porous membrane is usually applied for nanofiltration and reverse osmosis using pressure or concentration gradient [2].

In this chapter, the focus is on the polymeric membranes in various applications. Polymeric membranes, also known as organic membranes, are a class of liquid separation technologies that are among the best in the industries in terms of performance and efficiency. Because of their great manufacturability, low cost, and abundance, polymeric materials have played a significant role in membrane development, and they will preserve to do so in the future, as demonstrated by the chemistry-processing-structure-performance paradigm [4]. Polymeric materials versatility to be tailor made with various functionalities have elevated their usage in the membranes field. Furthermore, polymer membranes are more appealing because of their simple production and processability. This is owing to the broad range of barrier structures and features that polymer materials can create [5].

In fact, polymer-based membranes are also utilized to control the selective transport of ions and/or water in applications such as water purification, batteries, and fuel cells. The precise nature of ion and water transport is frequently confusing, and it is dependent on the intricate interplay between polymer structure and dynamics that allow movement [6]. Therefore, the relevance of polymeric materials in membrane technology is highlighted in this special chapter focusing on water and gas separation, medical and emerging technologies (fuel cells, lithium-ions batteries, electroconductive, optoelectronic) applications. Whereas, the later part of this chapter is discussed on the challenges and future direction of polymer membrane technology highlighted on the aforementioned applications.

2. Functional polymer membrane for water and gas separation applications

Membranes are used in water purification and treatment, detoxification of polluted water and desalination of seawater and brines. Water treatment and detoxification involve the removal of contaminants such as natural organic matter (dissolved and non-dissolved), nutrient ions (phosphate and nitrate) and emerging pollutants including organics, chemical dyes and heavy metals [7]. Meanwhile, seawater desalination involves the removal of dissolved salts to produce saltwater appropriate for domestic, human consumption, or industrial/agricultural applications.

In water treatment sectors, membrane technology is dominating and is considered easier operation, more economical, versatile, low-energy intensive, and efficient compared to other techniques such as chemical precipitation, adsorption, electrolysis and conventional coagulation [7]. The use of a membrane in water treatment also allows large quantities of material to be separated at a molecular scale without phase changes producing high-quality water with low chemical sludge effluent.

Membranes are also used to clean exhaust gases and are commercially used in purification and gas separation mainly hydrogen recovery from gas streams, vapor/gas separation, air dehydration, and treatment of natural gas and biogas [8].

2.1 Types of water and gas membranes

In water treatment and gas separation processes, a porous membrane or dense membrane can be used. However, dense membranes are less frequently chosen due to the low flow of the permeate across the membrane [7]. The cross-section of these membranes can be isotropic (i.e: symmetric) or anisotropic (i.e: asymmetric). Isotropic membranes such as porous, nonporous dense and electrically charged membranes are chemically homogeneous in composition. The porous membranes can be found in different classes according to their pore sizes.

Meanwhile, two main types of anisotropic membranes are composite and phase-separation membranes. The phase separation membranes have a homogeneous chemical composition as in isotropic membranes however, the porosity and pore sizes are different across the membrane thickness. Composite membranes, for instance, coated films and thin-film are structurally and chemically homogeneous in which a thin surface layer is supported by a thicker porous structure. Both layers are typically made from different classes of polymeric materials [9]. Nowadays, most of the dense membranes are fabricated with a dense top layer on a porous structure [7].

For industrial gas and liquid separation, thin-film composite membranes are usually applied. This type of membrane commonly consists of high permeability protective or

sealing layers (to prevent damage during handling), selective polymer layer (to provide the desired separation properties), gutter layer made up of a high permeable polymer (to improve interlayer compatibility and support layers) and support layers that highly permeable (to provide mechanical strength to the membrane) [10].

2.2 Water and gas membrane materials

For water treatment, membranes can be produced from inorganics materials such as titanium dioxide, zeolites or ceramics that possess advantages compared to polymeric membranes type in terms of mechanical, chemical, and thermal stabilities, fouling-resistance, reusability and photocatalytic ability [9]. However, their large-scale applications are limited due to brittleness (fragile) and high operational cost.

Industrially established membranes for water filtration using microfiltration (MF), nanofiltration (NF), and ultrafiltration (UF) membranes are mainly made from organic polymers such as polysulfone (PSU), polyetherimide (PEI), polyacrylonitrile (PAN), polyethersulfone (PES), polyvinyl chloride (PVC), polycarbonates (PC), polyamides (PA), polypropylene (PP), polyvinylidene fluoride (PVDF), and cellulose acetate (CA) [9]. Table 1 lists the types of membranes used for different water treatment processes based on their pore sizes, membrane materials and applications. Preparation methods of these membranes may be different to produce different pore sizes to suit different applications. Membrane distillation is different from water filtration in which the driving force for separation is thermal and the requirement for more hydrophobic, more porous and higher chemical/thermal resistance membrane materials in the former [11].

Polymeric membranes are extensively used in water treatment and desalination because of the high modification flexibility, simple pore fabrication procedure, high efficiency in separating particles and dispersed oil, easy operation and fabrication and relatively lower cost compared with inorganic membranes [7]. However, the use of polymeric membranes in water filtration processes leads to problems with poor wettability, pH-dependency and fouling tendency mainly due to their inherent hydrophobicity. Table 1 shows the type of membranes in different water treatment processes.

To overcome the problems, surface modifications, functionalization or synthesis/fabrication of well-defined structures can be done. Other functionalized polymers (e.g: polyacrylic acid or polymethyl methacrylate) have been incorporated as a second component in the membranes material to enhance the membranes' hydrophilicity. Organic nanofillers also are added to the polymeric membranes to improve their performance. Clay is one of the preferred fillers due to its water purification capability and other advantages including economical, easy to synthesize with enhanced thermo-mechanical properties [7].

In addition, functionalization of the clay and/or polymer can be done to enhance performance as well as mechanical, thermal, and chemical stability to suit specific needs in target membrane applications. Functionalization of clay can be conducted using surfactant, coupling agent or salt (intercalation modification). Surface modification of clay using surfactants such as alkyl ammonium salts makes the clay surface more hydrophobic for better dispersion stabilization.

Table 1 Types of membranes used in different water treatment processes [9,10].

Process	Pore sizes (µm)	Driving force	Filtrate	Membrane materials	Applications
Microfiltration (MF),	0.1-5	Induced Pressure	Particles, asbestos, cellular materials (red blood cell and bacteria)	PP, PVDF, PVC, PTFE	Desalination
Ultrafiltration (UF),	0.01-0.1	Induced Pressure	Large particles, microorganisms, dissolved bio-macromolecules (pyrogen, protein and viruses)	PSU, PES, PVC, PTFE, CA	Wastewater treatment, protein separation, food processing, water remediation, recovery of surfactants in industrial cleaning
Nanofiltration (NF),	0.001-0.01	Induced Pressure	Organic molecules, viruses, a range of salts, divalent ions	PSU and PES (supporting substrates), CA	Soften hard water, remove organic matter, wastewater treatment and recovery
Reverse osmosis (RO)	0.0001-0.001	Induced Pressure	Aqueous organic solids (minerals, salt ions, and metals ions) and organic substances	PSU and PES (supporting substrates), CA PA	Brackish seawater and groundwater desalination, potable water production
Membrane distillation	0.1-0.6	Thermal	Salt	PP, PTFE, PVDF, zeolites, ceramics (support)	Desalination

Surface functionalization with the polymer can be carried out by either physical adsorption polymers or chemical grafting. Physical adsorption using anionic or non-ionic polymers causes adsorption of clay physically on the surface of the polymer leads to alteration of physical and chemical properties. Chemical grafting leads to covalent bonding of the polymer and the clays. Further explanation on each of the methods is reported by Buruga et al. (2019).

Multiple functionalities can help not only to sieve the contaminants from the aqueous solution but also able to absorb, degrade or deactivate the contaminants. In fact, functional polymer-clay membranes can be used for heavy metal removal, dye removal, microbial/fungal removal, desalination of seawater and as superabsorbent for pollutants removal [7]. These membranes are also attractive for their antifouling properties. However, the modifications lead to higher costs and difficulty in fabrication and scale-up.

In gas separation membrane, the main commercial application and the types of polymer used as selective layers are listed in Table 2.

Table 2 Main commercial membrane gas separation applications [10,12,13].

Application	Gas separation	Selective polymeric layer
Nitrogen production	N ₂ /O ₂	PSU, polyphenylene oxide (PPO) polyimides (PI), substituted polycarbonates
Hydrogen recovery	H ₂ /N ₂ , H ₂ /CO, H ₂ /CH ₄	PI, PSU, aramids
Vapor recovery	C ₂ H ₄ /N ₂ , C ₃ H ₆ /N ₂ , C ₂ H ₄ /Ar, gasoline/air, CH ₄ /N ₂	Silicone rubber
Natural gas treatment	H ₂ S/CH ₄ , CO ₂ /CH ₄ , He/CH ₄	PI, CA
Air dehydration	H ₂ O/air, H ₂ O/N ₂	PSU

Similar to membranes used in water treatment, membranes for gas separation are also made from two main categories, synthetic polymeric materials and inorganic materials such as ceramic, carbon and metal (especially palladium). The separation of gases will occur based on different transport mechanisms, which depends on the physical properties of the gases and intrinsic membrane material properties [8].

Even though many different polymeric membranes are available which are less brittle, ease on mechanical handling, and cheap in production as compared to ceramic membranes, the polymeric membranes may not be useful in harsh oxidizing agents and high temperatures

conditions [14]. For these conditions, the inorganic membrane may be more suitable. For example, the use of palladium for selective transport of hydrogen or perovskites for selective transport of oxygen [2]. Due to this reason, selective polymeric layers that are used for gas separation are commonly added with inorganic materials such as carbon, zeolite or metal-organic frameworks to harness processability and increase solubility selectivity [10].

2.3 Fabrication and functionalization of water and gas membranes

Membranes can be constructed to obtain the desired selectivity and permeability suit the requirements for the component to be separated. Generally, the performance is dependent on membrane's fundamental properties such as selectivity, flux rate, chemical, thermal or mechanical stability under operating conditions, adaptability to operating conditions and resistance toward fouling. In addition, the membranes should have suitable surface morphology in terms of surface roughness, pore size and structure as well as physicochemical properties [7].

For water treatment applications, isotropic membranes can be produced using various methods such as polymer-based track-etched (i.e: irradiated with heavy ions to create tracks through the film), phase inversion (homogeneous polymeric is transformed to solid-state by immersion precipitation as commonly done on PVDF since PVDF is soluble in common solvents) or stretched polymer film (polymers are heated beyond their melting point, followed by extruded into a thin film and then stretched which are commonly applied for PP and PTFE) [9].

The nanofiller can be incorporated into polymers by various methods including melt intercalation, phase inversion (producing well-mixed nanomaterial in a polymer matrix), interfacial polymerization (producing a thin layer with nanocomposites membrane substrates or a thin layer of nanocomposite on the membranes' surface), surface grafting or surface coating [9]. Surface modification of either polymer or nanofiller (e.g: clay) to improve the performance of the membranes can be carried using various fabrication methods. However, fabrication of these functional polymer-nanofiller composite membranes requires advanced technologies and organized design/architecture as well as a good membrane formation [7] for a successful intended application.

For gas separation, membranes are commonly produced by phase inversion since this method can produce thin membranes (approximately 100 nm or less) and defect-free membranes with sufficiently high surface areas for practical applications. Furthermore, asymmetric membranes with dense, thin film on a porous substrate can be produced using this method [12].

The membranes produced from various fabrication methods as mentioned earlier are commonly flat sheet or cylindrical configurations either hollow fibre membranes (diameter below 300 μm), capillary membranes (diameter of 300-1000 μm) or tubular membranes (diameter of few cm) [12]. These membranes are typically assembled into various geometries/modules to maximize the surface area that can be assimilated in a certain volume.

The flat sheet geometry is frequently mounted into spiral wound modules or less frequently into envelope-type modules while hollow-fibre configuration would be assembled into hollow fiber modules. For gas separation, the hollow fibre module is more commonly chosen than spiral wound modules due to higher specific surface area leading to higher productivity, easier fabrication method and lower production cost [12,15]. Spiral wound module is preferred for water purification and RO applications since it induces less pressure drop and reduces the feed pre-treatment needed to prevent fouling compared with hollow fiber modules [12]. The spiral wound module is also used in the separation of CO_2 industrial waste or flue gases with high permeances [2].

2.4 Mechanisms for water/gas separation

For MF, NF, UF and RO, transport through membranes is driven by pressure difference while in gas separation, the driving force is based on chemical potential (or concentration) difference [7]. Based on the phase separation's mechanism, membranes can be categorized into three: (i) the sieve mechanism (different size of solute particles), (ii) the solution-diffusion mechanism (different in solubility and diffusivity of the membrane materials) and, (iii) the electrochemical mechanism (different in charges of the solute components) [7].

In the separation of gas by a porous membrane, the kinetics effect is important and depends on average free path length value, which is the distance of a gas molecule can move between collisions with other gas molecules. If large pores are used (larger than average free path length), separation may not occur but only viscous hydrodynamic flow since the collision between molecules happens more often compared with particles and pore walls. Meanwhile, if the pores are below the average path length, the molecules collide more frequent with the pore wall compared to each other, allowing the movement of light gas molecules faster than heavier gas molecules. Permeability, which is determined by the mass of the gas molecules, defines selectivity [2].

2.5 Challenges and future direction of functional polymer membrane for water and gas separation applications

Gas and water separation can be utilized to increase the quality of life and environment. For example, carbon dioxide removal from coal-fired power plant flue gas is helpful to lessen its effect on climate change [2]. In addition, the development of bio-inspired and environmentally responsive membranes with other special features such as antifouling/self-cleaning, antibacterial/antifungal and ability to withstand extreme conditions are of interest.

However, continuous effort needs to be conducted in altering the structure and/or compositions of the membrane to enhance selectivity and permeability, membrane lifetime, chemical/thermal/mechanical stability and antifouling capability. Tremendous research has been conducted in developing membranes for especially functionalized polymer composites for water treatment. However, most of the research has been conducted at a laboratory scale, thus requires to be extended to large-scale production and industrial applications.

Optimization of separation can be done by combining membrane technology with other technologies, for instance adsorption and thermal separation. The use of membrane modelling and computer simulation, in addition to experimental approaches, will become crucial in membranes development, modules and overall processes [2].

In gas membrane applications especially, there is an inter-relationship between selectivity and permeability as well as between mechanical properties and gas transport [10]. Plasticization and physical aging are commonly encountered issues in mix-gas separation performance over time [12]. Through innovative materials selection, processing methods, fabrication and systematic studies, the performance of the membranes can be improved to enhance the overall quality of life and the environment.

3. Functional polymer membrane for medical applications

Chronic kidney disease has been known as a worldwide public health problem. Patients with chronic kidney disease survived by haemodialysis treatment apart from peritoneal dialysis and renal transplantation. The use of membrane as separation in blood purification in haemodialysis treatment has kicked start the recognition usage of functional polymer membrane in the medical field. Functional polymer membrane has found its usage in various medical applications such as for supporting scaffold in tissue engineering as guided bone regeneration (GBR), ophthalmology applications, plasma collection oxygenation blood during cardiac surgery and as therapeutic drug delivery system since then. The following section discussed on the medical application of various type of functional

polymer membrane, the fabrication techniques, the mechanism of dense and porous membrane and challenges and future direction of functional polymer membrane for medical applications.

3.1 Types of functional polymer membrane for medical applications

Kidneys are the organs in renal system that regulate the blood chemistry via removing harmful substances, preserving essential substances in the blood and also regulate blood's ionic concentration. However, patients diagnosed with chronic kidney disease (CKD) or end-stage renal disease (ESRD) will encounter accumulation of metabolic waste products in the body. This failure eventually resulted in deficient performance of other organs and complications related to renal failure [16]. With the increase in number of patients with CKD or ESRD, the need for haemodialysis membrane is expected to constantly increase. During haemodialysis, the membrane in the dialyzer acts as a medium for separation between the blood and fluid compartment. Basic requirement for the membrane is to be able to remove solutes as well as fluid accumulation in the body, while maintaining electrolyte balance of the patient, good biocompatibility with minimal effect on blood components and ample chemical and mechanical stability to allow sterilization by different approaches [17].

To achieve the basic requirements materials for membrane, the material should possess particular characteristics such as naturally hydrophilic, biocompatible, semipermeable, asymmetric, improved pore size as well as surface chemistry [18]. Although, the current treatment for CKD and ESRD is through haemodialysis treatment, but haemodialysis also has been incorporated with acute/chronic side effects that threatens the patients. This is because during haemodialysis, the interactions between blood and the membrane leads to various body system activation such as coagulation of blood components, leukocytes, cytokine production and existent of free oxygen radicals [16]. Therefore, materials biocompatibility is crucial when selecting materials for membrane.

Cellulose was the first generation for dialysis membrane. However, its major drawbacks were its poor biocompatibility which triggered by the free hydroxyl (OH) groups in the molecular units of the cellulosic polymer [19]. Thus, to overcome this issue, a number of modifications have been introduced to increase biocompatibility such as esterification on the OH groups with benzyl or diethylaminoethyl groups, or via replacing the OH groups with acetyl groups such as diacetate, triacetate, or cellulose acetate [17,19]. In a study by Sirolli et al. (2000), cellulosic membrane chain was grafted with polyethylene glycol (PEG) and the performance was compared to cellulose diacetate and polymethylmethacrylate. The findings from this study showed that PEGylated cellulose is a useful mean to increase the biocompatibility of the cellulosic polymer [19]. However, it was also concluded that

biocompatibility of the derivatized cellulosic membranes has wide range variability which may be due to the structural modification compared to the degree of OH replacement.

Moving forward to a more recent study, there are a few methods that has been proposed to improve the biocompatibility of polymeric membrane by using polymer blending, biopolymers, surface chemical modification or biomimetic membranes. Kaleekkal et al. (2015) prepared polysulfone (PSf)/ sulfonated polyethersulfone (SPES) blend to evaluate the performance and its biocompatibility. In this study polyethersulfone (PES) was sulfonated resulting in a hydrophilic SPES which are then blended with PSf. PSf/ SPES blend showed higher ultrafiltration rate (UFR), extended blood clotting time, eliminated platelet adhesion, decreased protein adsorption and reduced complement activity. These findings indicate an increased in biocompatibility when compared to pristine PES membrane [20]. Although PES membrane offers outstanding oxidative, thermal, chemical and mechanical stability, its hydrophobicity remains a challenge in haemodialysis treatments. Hydrophobic surface results in a severe fouling of the membrane materials. As discussed earlier, sulfonated PES gives a hydrophilicity to PES, another method to improve hydrophilicity is to develop mixed matrix membranes (MMM). PES filled with nanofiller of poly(citric acid)-grafted-multi wall carbon nano tube (MWCNT) was fabricated as mixed matrix membrane for haemodialysis. This study showed the improvement of surface hydrophilicity and porosity of PES/MWCNTs MMMs. PES/ MWCNTs MMMs also showed better protein resistance and antifouling properties when compared to PES membrane [21]. For surface chemical modification, polyvinylpyrrolidone (PVP) and polyetherimide (PEI) with heparin immobilization was synthesized to improve blood compatibility. Immobilization of heparin resulted in more hydrophilic membranes properties with significant platelet and protein resistant. These findings suggest an anti-thrombogenic characteristic was observed on the PEI/PVP immobilize heparin membrane [22].

Diseases such as periodontal disease, congenital defects, tumours extraction, pathological bone tissues defects or alveolar bone resorption which may lead to total or partially lost bone [23-24] requires guided bone regeneration (GBR) treatment to prevent soft tissue invasion and provide capacity for guiding new bone formation/growth into the bone defect. For this application, the membrane is required to provide physiological barrier towards fibroblast infiltration, restrain the proliferation of progenitor cell and act as scaffold for bone regeneration [25]. GBR membranes are divided into two groups: resorbable membranes and non-resorbable membranes. High density polytetrafluoroethylene (d-PTFE), expanded polytetrafluoroethylene (e-PTFE, Gore-Tex[®]), and titanium reinforced expanded polytetrafluoroethylene (Ti-e-PTFE) are among the widely used non-resorbable membranes [25-27]. It was reported that e-PTFE was among the first non-resorbable

membranes for dental use due to its stability, chemical and biologically inert, resistant to enzymatic and microbiological attack. Also, e-PTFE features with macro porosity encourages bone regeneration and improved wound stability [27]. However, it has been reported that the main drawbacks of PTFE were the need for secondary surgical [27-29].

Unlike non-resorbable membranes, resorbable membranes made of either natural or synthetic based polymers. Synthetic polymers used include poly(lactid acid) (PLA), poly(glycolic acid) (PGA), poly(ϵ -caprolactone) (PCL), poly(hydroxyl butyric acid) and poly(hydroxyl valeric acid) [30], while natural polymers are collagen (from human or animal tissues) [25], calcium alginate, chitosan [31-32] and nanocellulose [33-34]. Synthetic resorbable membranes has the advantages of processability, drug-encapsulating ability, tuned biodegradation, and low rigidity [30] while natural polymers are known for their non-antigenicity, biocompatibility, and tuneable resorption via cross-linking treatment [35]. However, resorbable membranes has the disadvantages of low mechanical strength and wide variable degree of resorption which significantly interrupt the amount of bone formation [29]. To overcome these shortcomings of resorbable membranes, bioactive composite, the combination of bioactive ceramic phase and biodegradable polymeric phase are proposed to give mechanical stability for maintenance and induce bone formation bioactivity [24]. Among the most sought bioactive ceramics that has been investigated was hydroxyapatite (HA) [36], bioactive glass [37-38], tricalcium phosphate [24], precious metals [33], clay silicates, zirconia and carbon nanotubes [39]. For instance, study by Fu et al. (2017) was concluded that the synthesized bilayer PLGA/nano-HA with different surfaces and structures showed excellent fibroblastic barrier and favourable osteogenesis effect. The porous layer was claimed to increase osteoblast homing, proliferation and differentiation [29]. In an *in vivo* study, a comparison between polycaprolactone/tricalcium phosphate (PCL/TCP) membrane and collagen membrane, it was reported that PCL/TCP membrane showed a statistically increased in percentage bone area fraction (BAF%) compared to collagen membrane after 2 months in rabbit model. Whereas, in the first month of evaluation, there was no statistical difference observed. The researcher postulated that the significant observation in second month time frame was due to the higher stiffness and slower degradation of PCL/TCP [24]. Dascalu et al. (2019) synthesis a cellulose acetate/ hydroxyapatite (CA/HA) membrane and concluded that CA/HA composite membrane showed that the hydrophilicity, water permeation, protein resorption is suitable for bone regeneration applications. While *in vitro* using osteoblast, cell showed good cell adhesion and viability [40].

In cardiovascular applications, polymer blend and composites has been utilised due to its similarity with the human myocardium. These polymer blend and composites showed improved hydrophilicity and better cell interaction. In this field, these polymers are used

as bioresorbable stent, as coatings in cardiac stent, cardiac patches to repair the myocardium, heart valves and etc. In cardiovascular applications, natural polymers, for instance alginate, silk, gelatine, collagen and chitosan has been utilised. While synthetic polymers that offers versatility in their physical and chemical properties such as polyesters (ex: PLA, PLLA, PDLA, PCL), polymethylmethacrylate (PMMA), polytetrafluoroethylene (PTFE) and polyethylene (PE) has been used in cardiovascular treatment [41]. For example, Castilho et al. (2017) investigated on fabricating ultrafine fibre scaffolds of hydroxyl-functionalized (poly(hydroxymethylglycolide-co- ϵ -caprolactone) (pHMGCL) to improve the biocompatibility and architecture to promote cell retention and help cardiac cell growth. It was reported that pHMGCL has improved hydrophilicity when compared to PCL with tuneable degradation rate [42]. PLLA and PLLA/PLGA blend has been explored as coatings in cardiac stents to offer biodegradable stents coatings [43].

In drug delivery system, functional polymer is of interest as a promising transdermal drug delivery (TDD). The advancement in transdermal drug delivery is due to the simpler and non-invasive administration. TD also increases drug bioavailability and reduces the degradation effects of metabolism encountered in the oral route, reduces toxic nature with oral delivery due to low bioavailability and liver damage. Examples natural polymers used as TDD are chitosan and cellulose [44]. While examples of synthetic polymers used in TDD are PCL, PMMA, polycarbonate (PC), PLGA, vinyl polymer and polyvinylidene fluoride (PVDF) [44-45]. In a study by Grilloa et al. (2019), a hybrid drug delivery system has been synthesized. In this finding, benzocaine-loaded poly- ϵ -caprolactone nano particles were incorporated in Poloxamer 407-based hydrogel and to investigate the drug permeation in transdermal diffusion membrane, Strat-M. Results show that the nano particles exhibited increased drug encapsulation efficiency, efficient physicochemical stability as well as rheological properties. These nano particles also showed permeation across Strat-M membrane. These findings suggest that the incorporation of hydrogels nano particles in transdermal synthetic membranes are capable to modulate local anesthetic permeation rate [46].

The polymers discussed are of great interest in biomedical applications due to its numerous advantages regardless natural or synthetic polymers. To improve the functionality of these polymer membranes, many researchers has loaded the membranes with antibiotics, non-antibiotic antibacterial agents, growth factors to enhance osteogenic progenitor cell differentiation such as bone morphogenetic proteins, salicylic acid base poly(anhydride-esters) or platelet-rich fibrin [47].

3.2 Fabrication techniques to fabricate functional polymer membrane for medical applications

In this subsection, the three most common and versatile fabrication techniques utilized to prepare functional polymer membrane for medical applications will be described. The fabrication techniques are electrospinning, solvent casting, and phase inversion.

3.2.1 Electrospinning

Electrospinning method has the advantage of feasibility to obtain micro- or nano-scale fibres with high surface area, controlled porosity and ease of functionalization for numerous applications, superior physicochemical as well as ease of processing. Briefly, this process involves the extrusion of a polymer through an opening prior to external driving force. To date, different modification has been done on the conventional electrospinning techniques to fabricate functional polymer membrane that suits specific medical applications. For example, Fu et al. (2017) combines the electrospinning and phase inversion techniques to fabricate porous and dense layer of poly(lactic-co-glycolic acid)/nano HA membrane with barrier function. This bilayer membrane showed significant tissue ingrowth and optimum therapeutic result for bone tissue regeneration [29]. This technique has also been utilized to incorporate growth factors in silk chitosan/fibroin/nano HA core-shell nanofibrous membranes. In this study, bone morphogenic protein-2 (BMP-2) was incorporated in the core of the membranes. The results obtained from histological and immunohistochemical staining confirmed the formation of bone and osteogenesis [48]. It has also been reported that polymeric material and living cell were directly electrospun to form membranes. This modified technique is called ‘cell electrospinning’ [49-52].

3.2.2 Solvent Casting

Solvent casting is a conventional fabrication method that has been used to fabricate membranes, composite films, or blend. In short, this technique involves polymers and/or fillers dissolved in a solvent where both materials are soluble. In fact, water is the commonly used solvent for hydrophilic polymers [53-55] while for hydrophobic polymers, organic solvents are used. Mota et al. (2012) fabricated novel guided tissue and bone generation of chitosan/ bioactive glass nanoparticle (CHT/BG-NPS) membrane using solvent casting. In this study acetic acid was used as the solvent for the preparation of CHT/BG-NPS membrane [56]. In solvent casting, the significant parameter that affect the membrane properties are the type of solvent used. In a comparison study of the different solvent used effect on tensile strength of poly(vinyl acetate) membrane by Hansen et al. (2013), it was concluded that when ethanol was used as the solvent showed lower elongation and higher strength rather than membrane cast from chloroform or toluene as

solvent that showed lower strength and higher elongation [57]. Solvent casting has the advantage of simplicity whereby it does not imply further thermal or mechanical stress to dry the membrane and it is a less time-consuming technique. A modified approach of solvent casting with freeze casting was proposed by Gorgieva et al. (2018) fabricate a bilayer membrane with micro structural diversity of chitosan/gelatine bilayer membranes with mineralized interface. The study concluded that the obtained membrane showed non- and highly micro-porous and pore interconnecting region [58]. Due to the ease of processing, many functionalized polymer membranes utilize this method for medical applications.

3.2.3 Phase Inversion

Phase inversion techniques was first introduced by Loeb and Sourirajan to fabricate asymmetric polymer membrane. Since then, this technique has caused vigorous growth in membrane technology. In phase inversion technique, a homogenous polymer solution becomes thermo-dynamically unstable and separates between polymer-rich and polymer-lean phases [59]. Recently, cellulose acetate (CA) hybrid membrane was synthesized with enhanced permeability and excellent anti-fouling property was fabricated by combination of phase inversion and chemical reaction. In this study, CA hybrid membrane was fabricated using Loeb-Sourirajan techniques followed by introducing various solvents and organic acids in chemical reaction method. The objective of the study was to improve the morphological structure and anti-fouling property of the membrane [60]. Phase inversion techniques were also reported to enable the production of membrane with surfaces of different structures, a dense and porous surface. A study by Liu et al. (2021) succeeded to fabricate membrane with dense and porous surface of PLA membranes via phase inversion stimulated by water droplets at various temperatures. Cytocompatibility on 3T3 cells showed that the pore size obtained at water droplet temperature of 25 °C are sufficient for cell proliferation and promotes 3D culture of 3T3 cells on the membrane [61].

3.3 Challenges and future direction of functional polymer membrane in medical applications

The major challenges for functional polymer membrane in medical applications is to achieve biocompatibility properties without sacrificing mechanical and structural requirements. For haemodialysis membrane for example, the major concern is the proinflammatory molecules activation once the blood is exposed to the membrane and that current available dialysis membrane are not applicable to eliminate some larger toxic molecules. Thus, to overcome the wide spread of disadvantages of polymer membranes in various medical applications and to cater specific needs of each application, improvements in term of materials selections and improved/modified techniques has been explored. In

terms of materials selections, new polymer blends and composites has been evaluated to optimize the significant properties of each material. Incorporation of various inorganic materials such as HA and carbonate apatite as fillers are also actively research to improve properties of the polymeric membranes. In terms of fabrication techniques, new hybrid techniques have been utilised to improve yield, architecture, porosity, hydrophilicity/hydrophobicity, flexibility and etc. The combination of techniques used enables the feasibility to control numerous properties and improved functionality of the polymer membrane.

4. Functional polymer membranes for emerging technologies

Functional polymer membrane for emerging technologies can be divided into four major applications, fuel cell membrane, membrane for lithium battery, electrically conductive membrane, and optoelectronic thin film. The following sub sections discussed the functional polymeric membranes for the emerging technologies.

4.1 Fuel cell membrane

Fuel cell is defined as an electrochemical cell that uses a pair of redox processes to transform the chemical energy of a fuel (typically hydrogen) and an oxidizing agent (commonly oxygen) into electricity. It is unique as it can use a wide range of fuels and feedstocks, as well as can power large systems (i.e: power plant) and small systems (i.e: computer). Fuel cell can be utilized in a variety of applications such as transportation, industrial/commercial/residential structures, and long-term grid energy storage in reversible systems [62].

In fact, fuel cell has several advantages compared to conventional combustion-based technologies. Fuel cell can run with excellent efficiencies (> 60%) and lower emissions than combustion engines, as well as can convert chemical energy in the fuel directly to electrical energy [63]. Furthermore, the operation of hydrogen fuel cell emits only water, addressing critical climate challenges as no carbon dioxide (CO₂) emissions which resulted significant decrease in air pollutants that produce smog which directly cause health problems. Other than that, fuel cell is also silent during its operation as it only has few moving parts compared to conventional combustion [64].

4.1.1 Fuel cell part

Polymer electrolyte membrane (PEM) fuel cell basically consists of membrane electrode assembly (MEA), which consists of the membrane itself, layers of catalyst, and gas diffusion layers (GDL). Whereas, the parts used to assemble an MEA into a fuel cell are

gaskets (seal the MEA to avoid gas leakage), and bipolar plates (assemble PEM into a stack and passages for the fuel and air) [65].

Firstly, the membrane is a specifically treated material which conducts only positively charged ions while blocking electrons. It is the critical component to fuel cell because it must allow the required ions only to travel between the cathode and anode. The chemical process would be disrupted if other chemicals passed through the electrolyte. Basically, the membrane used in transportation applications is exceedingly thin (under 20 microns) [66].

Secondly, catalyst layer is applied on both membrane's sides (one side on anode layer and the other on cathode). Nanometer-sized platinum particles are spread on a large surface area carbon substrate for the catalytic layers. This supported platinum catalyst is sandwiched between the membrane and the GDL, together with an ionomer (ion-conducting polymer). The platinum catalyst on anode allows hydrogen to be separated into electrons and protons. Whereas, the platinum catalyst on cathode reduces oxygen via interaction with protons produced by anode, resulting in the formation of water. On the other hand, the ionomer that is incorporated into catalyst layers permits protons to pass through [67].

Thirdly, the GDL is located outside the catalytic layers and aid in the transport of reactants as well as the elimination of water. In fact, each GDL is usually made up of a carbon sheet with polytetrafluoroethylene (PTFE) partly coated carbon fibers. Gases diffuse quickly via the GDL's pores. The hydrophobic PTFE keeps these pores open, preventing excessive water buildup. While, the microporous layer is a thin coating of large surface area carbon mixed with PTFE that is applied to inner surface of the GDL in many circumstances. This microporous layer can assist water retention (to preserve membrane conductivity) other than water release (to keep the pores open for oxygen and hydrogen diffuse into electrodes) [68].

In order to create useable output voltage, MEAs are commonly incorporated by connecting them on top of each other (series stacked). In order to keep nearby cells apart, each cell is placed between the two bipolar plates. These plates can be constructed of metal, carbon, or composite materials, give both electrical conduction and physical strength to the stack. A flow field or set of channels is machined into the plate to permit gases to flow, commonly found on the plate's surface. Other than that, a liquid coolant can be circulated through additional tubes inside each plate. In addition, each MEA is sandwiched between two bipolar plates, however to achieve a gas-tight seal, the gaskets have to be applied at the edges of the MEA. Typically, these gaskets are constructed of a rubbery polymer [69]. Figure 1 shows the schematic of general fuel cells mechanism.

Figure 1 The general mechanism of fuel cells [70]. Permission is granted by ACS Publications.

4.1.2 Fuel cell membrane

The membrane is a thin barrier which serves as a dam because of its selective permeability where the chemical composition determines its property. In fact, membrane in fuel cell technology can be categorized into several types based on its separation processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF is a large pores membrane which used to separate solid particles (around 0.2 to 10 μm) and suspensions with high outflow (approximately 0.1 to 5 bar). Typically, MF is used in biological and food industries to separate bacteria and suspended particles. While, UF is usually used in water-oil emulsion isolation, dye bath purification via electrophoresis and, water purification and disinfection. Normally, low molecular weight of solute can easily pass through UF as it is used to condense emulsion or macromolecules. Whereas, NF can be used to separate particles ranging 2 to 10 μm which usually applied in water treatment, and food and milk industries (isolation of minerals). On the other hand, RO has a retention rate higher than 95% because the diameter of the pores is very dense and less than nanometer in size. Due to that, the flow rate is low while the pressure used is high around 60 to 80 bar. RO is basically used in salt/sea water desalination, purification of used water, and ultra-puring water for pharmaceutical and electronic intended [71]. Figure 2 shows the classification of the membrane based on its different separation processes.

Figure. 2 Classification of membrane by different separation processes [72]. Permission is granted from Elsevier.

On the other hand, several polymers are used in manufacturing membrane for fuel cell technology include cellulose acetate, polysulfone, polyethersulfone, and polyacrylonitrile. Cellulose is a natural, linear and inflexible polymer which gives good mechanical resistance to the membrane. Cellulose acetate is produced via the acetylation process using acetic anhydride, in which increasing the degree of acetylation, basically, increasing its amount of retention while decreasing the permeability. Other than that, the production of cellulose acetate via acetylation is also promising in increasing the mechanical resistance and resistance to hydrolysis of the membrane. Normally, this membrane is asymmetrical and has a retention rate around 99.5%, and range of pressure between 103 to 140 bar. The advantages of cellulose acetate membrane include ease of preparation, relatively high permeability and excellent mechanical property, while the disadvantages are sensitive to pH changes and reduce the salt retention when increasing the temperature [73].

Other polymers used in fuel cell membrane are polysulfone and polyethersulfone. These polymers are basically used for MF or UF type of membrane because of their homogenous property, which gives chemical, thermal and mechanical resistance. The benefits of this membrane include resistance to heat (up to 125°C), chlorine, and acid or alkali washings, as well as ease of production in many different geometries [74]. Whereas, polyacrylonitrile has a high crystallinity, glass transition of 87°C, and melting point at 319°C, which basically suitable for many applications such as shipping, construction, gas filtration system, and UF membrane. In fact, the nitrile groups in acrylonitrile units are extremely

polar, as a result, they are strongly attracted and causing the polymer chains to approach one another which in turn, increases the resulting polymer strength. The advantages of polyacrylonitrile membrane are high thermal, chlorine and solvent resistance, high hydrophobicity, as well as ease of manufacture and modification [75].

4.1.3 Classifications

Currently, there are few types of functional polymer membrane fuel cells in market such as polymer electrolyte, alkaline, molten carbonate, direct methanol, phosphoric acid, and solid oxide.

Polymer electrolyte membrane (PEM) fuel cells are having excellent power density, lighter and smaller compared to other fuel cells. In PEM, solid polymer is used as an electrolyte, while carbon electrodes with a platinum catalyst are assembled in PEM fuel cells. PEM fuel cells are most commonly employed and well suited in transportation and some stationary applications [76]. However, the usage of a platinum catalyst to separate the electrons and protons of hydrogen increases the expense of the system. Furthermore, if the hydrogen is obtained from a hydrocarbon fuel, the catalyst is also particularly sensitive to carbon monoxide which lead to poisoning, necessitating the use of an extra reactor in order to remove the carbon monoxide [77].

The other type is direct methanol (DM) fuel cells. Methanol is commonly combined with water and delivered directly to the anode in DM fuel cells. In fact, DM fuel cells avoid a lot of fuel storage issues compared to other fuel cell systems because methanol has a higher energy density compared to hydrogen. The liquid property of methanol made it easy to transport and deliver to the consumers which utilizing recent infrastructure. DM fuel cells are frequently installed to power portable devices such as computers and cellular phones [78].

Other than that, alkaline fuel cells are one of the earliest technologies invented to produce electrical energy and water in spacecraft industry. The electrolyte in alkaline fuel cells is potassium hydroxide in solvent of water, and the anode and cathode are be made of various non-precious metals. In fact, these fuel cells are similar as PEM fuel cells, however, instead of an acid, they use an alkaline as a membrane. Furthermore, the great efficiency of alkaline fuel cells is attributed to the fast rate of electrochemical reactions in the cell where they can achieve more than 60% in space applications [79]. However, higher temperature operation, carbon dioxide (CO₂) poisoning, membrane durability and conductivity, power density, as well as anode electrocatalysis are challenges for alkaline fuel cells [80].

Another fuel cell type is phosphoric acid (PA) fuel cells, where the electrolyte is liquid phosphoric acid, which is located in Teflon-bonded carbide matrix. Whereas, the electrodes

are carbon electrodes with a platinum catalyst. Although PA fuel cells are primarily utilized for stationary power generation, they have also been applied to power big vehicles [81]. Given the same weight and volume, PA fuel cells are less potent as compared to other type of fuel cells, therefore, they are often bulky and heavy. Furthermore, PA fuel cells are also expensive which require costly platinum catalyst loadings compared to other types of fuel cells [82].

On the other hand, for electrical utility, industrial, and military uses, molten carbonate (MC) fuel cells are recently produced for coal power plant and natural gas. MC fuel cells operate at high temperature which use a molten carbonate salt combination which sustained in a porous and inert ceramic lithium aluminium oxide matrix (electrolyte). The use of non-precious metals as catalysts can be incorporated at cathode and anode since MC fuel cells work at high temperature about 650°C, which reduce the expenses [83]. However, the main drawback of MC fuel cells technology is its lack of endurance. The high temperature employed in these cells, along with corrosive electrolyte, hasten the component corrosion which leads to breakdown and resulting in reducing cell life. Therefore, scientists are actively searching for corrosion-resistant components as well as designs that can prolong cell life without sacrificing its performance [84].

Other than that, there are solid oxide (SO) fuel cells type, where the electrolyte is hard and non-porous ceramic composition. Basically, SO fuel cells operate at extreme temperature up to 1000°C. The usage of a high-temperature operation eliminates the requirement of a precious-metal catalyst, which lowering costs. It also allows SO fuel cells to reform fuels internally, permitting them to use a wider range of fuels while reducing the expense of adding a reformer into the system [85]. However, there are drawbacks to operate at high temperature where it causes a slow starter and necessitates thermal shielding to keep the heat in and protect the people, which is fine for utility applications but not for transportation. Furthermore, material durability is also a concern due to high working temperature. Therefore, difficulty of this technology is the fabrication of low-cost materials with excellent durability at cell operating temperature. Currently, scientists are actively looking into the possibility of building lower-temperature SO fuel cells that operate under 700°C, less expensive, and fewer durability issues [86].

Lastly, reversible fuel cells, like conventional fuel cells, generate electricity from oxygen and hydrogen while also releasing water and heat byproducts. Reversible fuel cell systems can divide water into oxygen and hydrogen fuel using electricity from solar, wind, or other sources which known as electrolysis. Apart from producing electricity when required, reversible fuel cells can also store extra energy in the form of hydrogen during periods of high-power generation from other technologies, for instance, vigorous winds result in

excess available wind power. This energy storage potential is crucial for renewable energy systems that are intermittent [87].

4.2 Membranes for lithium-ion battery

Lithium-ion (Li-ion) battery is a rechargeable battery type. Li-ion batteries are commonly utilized in portable electric and electronic vehicles, medical devices, and their use in military and aerospace applications is on the rise. Basically, Li-ions travel from negative to positive electrode via an electrolyte during discharge, and vice versa while charging. The positive electrode of Li-ion battery is constructed from an intercalated lithium compound which allows for a higher energy density and specific capacity, while the negative electrode is commonly made of graphite. Other advantages of Li-ion battery include prolong life cycle, high efficiency and comparatively low self-discharge rate [88]. Figure 3 shows the schematic of a Li-ion battery which consists of graphitic carbon negative electrode and Li-intercalated compound positive electrode.

Figure. 3 Schematic of Li-ion battery mechanism [89]. Permission is granted from ACS Publications.

However, there are problems encountered with Li-ion battery include operational temperature, materials availability and cost. Li-ion battery also arises a safety issue because it contains flammable electrolytes that, if damage or wrongly charged, can cause explosion and fire. Therefore, the separator membrane is an important part of Li-ion battery because it acts as physical barrier between negative and positive electrodes, preventing electrical short connections as well as serves as an electrolyte reservoir for ions transport. The

membrane, basically, is placed between the two electrodes and must have a strong ionic conductivity and excellent thermal and mechanical stability. Other than that, this membrane has to be porous in order to permit the electrolyte to flow through [90].

4.2.1 Lithium-ion battery membrane

There are several types of membrane separators used in Li-ion battery include composite, microporous, electrospun, nonwoven, polymer blends, and membranes with external surface modification. Whereas, types of membrane used in Li-ion battery based on different types of electrolytes are polymer gel, microporous filter, and polymer solid ion conductor.

Solid polymer such as polyethylene oxide (PEO) is dry, solid and contains no organic liquid. The transportation of Li-ions between the sites is basically aided by segmental movement of the PEO matrix for the mechanism of Li-ions transport. Based on this concept, the good conductivity of PEO can attribute to Li-ions transport at the amorphous region. Thus, there are two approaches to enhance Li-ions conductivity, PEO crystallization is reduced, and the interaction between Li-ions and PEO chains is weakened [91].

On the other hand, semi-crystalline polyolefin polymers such as polyethylene and polypropylene are used for microporous membrane. These polymers are having fuse function, where they can be flowable if the temperature achieves their melting point, which decreases the ionic conductivity and shut the electrochemical reactions of the battery to protect from thermal runaway. It is very crucial for cell over-charge and external short-circuit protection. Moreover, some functional groups can be attached via surface modification on both polymers to increase their compatibility of membrane-electrodes interfaces [92].

Other than that, liquid electrolyte is incorporated in the polymer matrix to generate the polymer gel. In fact, polymer gel has more shape flexibility compared to liquid and polymer chains usually hold liquid electrolyte in the polymer gel. The copolymer of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) introduces amorphous regions in the polymer gel that improve ionic conductivity, while the crystalline domains increase the mechanical strength. Other than that, poly(methyl methacrylate) (PMMA) polymer gel has good compatibility and normally used as a layer to reduce the evaporation and leakage of the liquid electrolyte. This strong affinity, as a result, increases electrolyte retention and ions transport which improves cell performance. On the other hand, poly(acrylonitrile) (PAN) polymer gel provides high conductivity and forms stable dimension, as well as increases cycling performance because of the low diffusion resistance [93].

4.2.2 Classification

In fact, various types of Li-ion battery in terms of shape, size and composition are utilized based on their specific applications.

Firstly, lithium cobalt oxide (LCO) battery which made of cobalt and lithium carbonate. LCO battery also known as Li-ion cobalt or lithium cobaltate usually utilized in laptops, electronic cameras and cell phones because of its high specific energy. LCO consists of cobalt oxide cathode and graphite carbon anode, where the lithium ions migrate from anode to cathode during discharge, while the flow is reversed during charging. However, LCO has a number of disadvantages, including a short battery life and low specific power. Furthermore, according to Battery University, LCO is not as safe as other types of Li-ion battery. Despite this, LCO is still a popular choice for portable electronic devices because of its high specific energy property [94].

Secondly, lithium manganese oxide (LMO) battery which is also known as lithium manganate or Li-ion manganese, as well as Li-manganese or manganese spinel. Historically, LMO technology battery was found in early 1980s with the first publication reported in the Materials Research Bulletin. In 1996, Moli Energy manufactured the first commercial Li-ion battery utilizing LMO as the cathode material. LMO battery, in fact, has a higher temperature stability and safer compared to other Li-ion battery types. Therefore, LMO is frequently found in medical equipment and devices, and can also be used in electric vehicles, power tools, and other applications [95].

Other than that, phosphate is basically used as a cathode in lithium iron phosphate (LPO) battery, which often known as Li-phosphate battery. LPO has low resistance qualities, which significantly improve its thermal stability and safety. Furthermore, durability and a long lifecycle are other advantages of LPO where fully charged LPO can be kept with no effect on the charge's overall lifespan. In addition, considering the lengthy battery life of LPO, it is frequently the most cost-effective option. As a result, LPO is commonly employed in electric vehicles and other applications requiring a long lifecycle and high levels of safety [96].

The other type of Li-ion battery is lithium nickel manganese cobalt oxide (LNMCO) which also known as NMC battery. Basically, LNMCO is constructed of a variety of materials that are common in Li-ion battery including a mix of nickel, manganese, and cobalt to build its cathode. LNMCO battery, like other Li-ion battery types, can have a high specific energy density or power other than very low self-heating rate which most commonly used in power tools and automobile powertrains. 60% nickel, 20% manganese, and 20% cobalt are commonly the combination ratio for the cathode. This means that the cost of the raw material is lower than other Li-ion battery solutions, as cobalt may be fairly costly. In the

future, the price of LNMCO battery may drop even more because some battery manufacturers plan to convert their battery chemistry to a larger percentage of nickel, in order to utilize less cobalt [94].

Lithium nickel cobalt aluminium oxide (LNCAO) is another type of Li-ion battery, which also called as NCA battery. Nowadays, this type of battery is becoming significantly increasing in grid storage and electric powertrains. To ensure driver safety, LNCAO battery must be accompanied by monitoring systems. Although LNCAO battery is not widely used in consumer electronics, it has a great potential in the automobile industry because it offers a high-energy choice with a long lifespan, however it is rather expensive and less safe than other Li-ion battery types. As a result, given the widespread use of LNCAO battery in electric vehicles, demand for this battery may increase as the number of electric vehicles grows [94].

Lastly, lithium titanate (LT) battery which familiar with Li-titanate is a type of battery that has a growing number of uses. According to Battery Space, the key benefit of LT battery is its very fast recharge time, which is due to sophisticated nanotechnology. LT battery is being employed by manufacturers of electric vehicles, and this type of battery has the potential to be used in electric buses for public transit. However, the disadvantage of LT battery is it has a lower intrinsic voltage or energy density than other Li-ion battery types, which might cause problems when it comes to efficiently powering automobiles. Despite this, LT battery still has a higher density compared to non-Li-ion battery, which is a benefit. Other than that, LT battery also could be used for military and aerospace applications, as well as storing wind and solar energy and constructing smart grids. Furthermore, according to Battery Space, LT battery could be employed in power system for system-critical backups [97].

In short, Li-ion battery exists in a variety number of shapes and sizes and can be used for various applications. As a result, some Li-ion battery in the market currently is more suited to specific applications than others. The most important point is to select the battery that is most appropriate for the task required. Thus, it is crucial to determine the best polymer used to construct a membrane to be incorporated in the Li-ion battery. It is also noteworthy that the Li-ion battery market is always evolving where companies and scientists all over the world are developing novel batteries to supply or replace Li-ion battery. It will be interesting to perceive which of this new battery rise to the top as time goes on.

4.3 Electrically conductive membranes

Advancements in the area of materials science and membrane preparation processes significantly leading to novel possibilities for mitigating the issues of conventional membrane filtration by the usage of electrically conductive membrane (ECM). Over

traditional technologies, there are numerous advantages of ECM such as high efficiency, easy to operate, low chemical consumption, and smaller footprint. Other than that, ECM also benefits in terms of the separation effect by the membrane and the electrical effect via conducting elements. Recently, various types of conducting elements had been used for ECM such as carbon nanotube, conducting polymers, and graphene. However, membrane technology still has some drawbacks, such as fouling, selectivity in pressure-driven membranes for uncharged contaminants as well as energy consumption [98].

Basically, ECM is studied in terms of synthesis/fabrication, mechanism of action, and application. Mode of ECM's operations are usually divided into three major types, thermal-driven, osmotically-driven, and pressure-driven. Currently, several types of ECM were synthesized with promising properties, cost-effective, and stability in conducting electricity. For instance, stacked graphene oxide, carbon nanotube, Cu-nanowires conductive, polyurethane, polypyrrole, poly(ether sulfone), poly(vinylidene fluoride) (PVDF), polyaniline-poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PANI-PAMPSA), porous conductive diamond, and membrane in dilute electrolyte solutions [98].

Currently, numerous polymers are used for ECM such as polyacetylene (PAC), polyaniline (PANI), polypyrrole (PPy), polyetheretherketone (PEEK), polythiophene (PTh), poly(p-phenylene) (PPP), polyazulene (PAZ), polyfuran (PFu), polyisoprene (PIP) and polybutadiene (PBD) in various applications include biosensors (food, medicine, environment), gas sensors, electrochemical sensors, corrosion inhibitors and functionalized biomaterials [99-101].

4.4 Thin film for optoelectronic

Optoelectronic is a wide application for electronic devices to detect and control light includes visible light and invisible radiation. Lighting, sensor, and energy harvesting devices made of thin-film optoelectronics are commonly used in medical devices, semiconductor lasers, consumer electronics and aerospace. Therefore, the study of important classes of materials such as colloidal quantum dots and perovskites is being done to improve device's knowledge and performance as industrial, military and consumer demands are constantly expanding [102].

Enhanced properties such as hardness, transmission, reflectivity and damage threshold of optoelectronic devices require thin film coating because of the sensitivity of these core devices. This thin film coating also can protect the optoelectronic devices from external factors such as heat, dust and abrasion. For instance, conjugated and crystalline semiconductor thin film of poly(o-phenylene diamine-co-m-phenylene diamine) copolymer [PoPmP]TF is used for polymer solar cell. Other than that, the properties of zinc oxide (ZnO) which are high chemical stability, high binding energy, wide band gap, and

transparency make its thin film and nanostructures promising to be applied for sensor, thin film transistor, and dye-sensitized solar cell industries. While, indium monoselenide (InSe) is considered as an emerging two-dimensional semiconductor with excellent optical and electrical properties that potential for high performance optoelectronics application [103].

In optoelectronic, the whole device can be twisted, bent, or stretched to achieve the requirements for numerous applications, in which not applicable via conventional devices that can twist or bend only. Moreover, rapid development in optoelectronic devices has been benefited in the advancements of science and engineering of photon detection and manipulation, image sensing, high efficiency and power density light emission, displays, communications and renewable energy harvesting. Particularly, promising material class for optoelectronics is colloidal nanomaterials because of their functionality, cost effectiveness, low dimensionality, and solution processability which reduces the time and cost required to fabricate thin film devices. As a result, it provides broad compatibility with existing materials interfaces and device structures [104].

4.4.1 Classifications

Currently, optoelectronics can be classified in several types include photodiode (PD), solar cell (SC), light emitting diode (LED), optical fiber (OF), and laser diode (LD). PD is a light sensor which basically made up of an active P-N junction that is biased in the opposite direction. It works in three different modes, forward bias (LED), reverse bias (photo detector) and photovoltaic (SC) by producing current or voltage when light falls on the junction. PD usually used in safety, medical and industrial equipment as well as cameras. While, SC is a device that transforms sunlight directly into electricity. When photons from the sun collide with SC, it produces a current and voltage, which generates electricity. Typically, SC is applied for rural electrifications, communications and nautical navigations [105].

On the other hand, LED is a semiconductor diode which usually used in household appliances, computer components, medical equipment and instrument panels. Electroluminescence (EL) is the effect of the photon produced via the recombination of electrons and holes in LED. The advantages of LED include uses less energy, emits less heat and long-lasting compared to incandescent lamp [106]. Whereas, the reasons of OF is preferable compared to electrical cable are mainly due to very low degradation, higher bandwidth, not vulnerable to EMI/EMC interference and can deliver different wavelengths of signals without interfering one another. OF is commonly used in sensors, biomedical, lasers and telecommunications to transmit information via modulated light [107]. While, LD resembles LED in appearance and operation, which basically converts electrical energy into light, that typically found in telecommunications, surgical and military applications.

The advantages of LD include more efficient and reliable compared to conventional LED, and reduces signal losses due to higher coherence light and single optical wavelength [108].

4.5 Challenges and future direction of functional polymer membranes for emerging technologies

Several challenges encountered for functional polymer membranes in emerging technologies. In fuel cell, the membrane must enable only the suitable ions to move between anode and cathode, thus, it is a vital component in fuel cell technology, because, if additional chemicals went through the electrolyte of the fuel cell, the chemical process would be disrupted. While membrane in Li-ion battery acts as a barrier between positive and negative electrodes, preventing electrical short connections as well as serves as an electrolyte reservoir for ions transport. Therefore, the membrane must have strong ionic conductivity with excellent thermal and mechanical stability. Whereas, in the electrically conductive membrane, challenges such as fouling, selectivity in pressure-driven membranes for uncharged contaminants, as well as energy consumption are quite significant. On the other hand, thin film coating can be used to protect the devices from external factors such as heat, dust and abrasion for optoelectronic membrane application. Tremendous studies have been performed in developing and innovating functional polymer membranes for emerging technologies to be extended to large-scale production and industrial applications to improve the environment and quality of life. Apart from that, it is also noteworthy that the market is always evolving over the world as researchers are developing novel membrane for the emerging technologies which will be fascinating to observe which of the new membrane technology escalate to the top as the time pass by. Functional polymeric membranes have shown very significant evolution in many applications including these new emerging technologies applications.

Conclusion

The effectiveness of the membrane selectivity, permeability and separation process is determined by the polymer properties. Regardless, the functional polymer selection is crucial in the development of membrane technology for the water/gas separation, medical, and emerging technologies (fuel cells, Li-ion batteries, electric conductive, optoelectronic) owing to its manufacturability, cost, mechanism, type, and resources. Other factors such as challenges and future direction also must be considered in determining the best polymers to be used for the development of the membrane. The objective of the specific tasks requires a critical consideration in determining the best membrane technology suits the applications where it is performed, therefore, the advancement of the membrane used can be benefited thoroughly. It is also remarkable that the membrane technology is always

evolving especially in the functional polymer membrane development in various applications, so that the quality of life is improved.

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