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Radiation Grafted Ion Conducting Membranes for Electrochemical Energy Systems: Status of Developmental and Upscaled Membranes

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ABSTRACT

Ion conducting membranes (ICMs) play a crucial role in the development of electrochemical energy systems supporting the conversion, storage, and management of renewable energy in various fields. Thus, this class of materials has received continuous intensive research efforts to obtain membranes/separators with superior properties, including high conductivity, durability, and cost-attractiveness. Radiation induced graft copolymerization (RIGC) techniques have been found to be most effective in developing a variety of ICMs due to their efficient endowment of desired types and levels of ionic functionality to preformed films to form hybrid materials with integrated physico-chemical properties. Various articles have reviewed the fundamental research aspects of radiation grafted ICMs' and battery separators' developments in many laboratories with little attention given to research activities at the developmental scale paving the way to commercialization of such materials. This article reviews the status of the development of emerging radiation grafted ICMs and separators for various types of fuel cells, batteries, and water electrolysers with a special focus on those undergoing developmental research activities and others successfully commercialized.

Keywords: Emerging ion conducting membranes, radiation induced graft copolymerization, commercial radiation separators, water electrolysers, polymer electrolyte membrane fuel cell

1.0 INTRODUCTION

There is a growing demand for reducing the reliance on fossil fuel due to limited reserves and potential supply disribution in addition to pollution by CO_2 emissions causing global warming. Thus, a renewable energy supply is urgently needed to drive the sustainable development. Electrochemical technologies play an important role in promoting renewable energy through electrochemical energy devices involving not only conversions such as fuel cells and water electrolysers, but also storage, including batteries [1, 2].

Polymer electrolyte (ion conducting) membranes play a crucial role in electrochemical cells, where the main interest is on redox reactions rather than the separation process. However, the membrane provides a medium for the ion transport between the electrodes. Commercial ion conducting membranes (ICMs) are challenged by high cost and dissatisfying durability, which has triggered various research efforts to develop alternative membranes with directed properties of high conductivity, low cost and chemical stability using various polymerization techniques [3].

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Of all, radiation-induced graft copolymerization (RIGC) technique is a distinctive means for development of functional ionic membranes by modification of polymer films that have found applications in various electrochemical energy devices [4]. The versatility of this method arises from its capability to modify a variety of preformed polymer substrates permanently by imparting covalently bonded functional groups. Such functionality originates from a variety of vinyl functional or non-functional monomers copolymerized during the grafting reaction or in a post-grafting chemical treatment without compromising the inherent properties of the parent polymers. Interestingly, the use of RIGC allows controlling the shape of the grafted products by selecting the desired starting substrates (e.g., film, fibre, or nonwoven fabric). Such a merit is of high significance when ionic membrane production is sought because the membrane shaping problem can be overcome by conducting grafting on a substrate having a film form [5, 6]. Moreover, RIGC has several additional merits compared to other chemical polymer modification methods, including catalytic polymerization, photoinduced grafting, and plasma polymerization [7]. They include not only the absence of chemical initiators, ease of handling, swift combination of incompatible monomers and polymers, and speedy treatment but also the ability to perform grafting onto substrates from the surface to the bulk and tune the density and distribution of the grafted polymer chains as well as the availability of industrial-scale high-energy radiation sources (e.g., Co-60 sources and electron beam, EB, accelerators) for upscaling. A comparison between the merits and demerits of RIGC with different initiators has been reported elsewhere [8].

The RIGC method has been widely used for preparing a variety of advanced neutral or ionic copolymers for resource recovery, pollution prevention, water purification, energy production, environmental monitoring, and quality control [9]. These radiation grafted materials comprise polymer electrolyte membranes, battery separators and ion exchange membranes in addition to selective adsorbents, water absorbing polymers, antifog films, antimicrobial, wrinkle-resistant or flame-retardant fabrics, scaffolds for tissue engineering and controlled-release drug carriers. The preparation of ICMs by RIGC has received intensive global research activities to meet the growing demands for applying electrochemical energy devices in promoting renewable energy utilization. This led to the emergence of various membranes with great potential for commercialization, and the field is broadly open for the development of timely needed materials supporting energy conversion and storage.

There have been several reviews addressing the development of radiation grafted ICMs for specific electrochemical applications such as proton exchange membrane fuel cells [10, 11], anion exchange membrane fuel cells [12], direct methanol fuel cells, vanadium redox flow batteries (VRFB) or a combination of fuel cells and energy conversion and storage devices at large [13, 14]. Nevertheless, most of the past articles focused only on reviewing fundamental research aspects of membranes investigated in laboratories by various groups, leaving a gap in the coverage of emerging and upscaled membranes obtained by RIGC in important electrochemical energy conversion and storage systems. The objective of this article is to review the progress taking place in the development of emerging and upscaled ICMs prepared by RIGC for various polymer electrolyte membrane-based fuel cell, water electrolysers and batteries applications.

2.0 OVERVIEW OF FUNDAMENTALS OF RIGC

The basic principles of RIGC relies on the exposure of the polymer substrate to ionizing radiation (γ-radiation and EB), which generates radicals capable of initiating copolymerization in the presence of vinyl monomers that propagate, forming covalently bonded side chain grafts upon termination. The distribution and length of grafted side chains depend on reaction parameters such as absorbed dose, monomer concentration, solvent type, reaction time and temperature. Thus, the reaction parameters must be optimized to achieve desired degree of grafting (DOG). Functionalization of the graft copolymer can be carried out in a single-step reaction by grafting an ionic monomer or by chemical treatment in a post-grafting reaction (2-step reaction) [6, 10].

2.1 Methods of Radiation Induced Graft Copolymerization

RIGC can be performed by simultaneous irradiation grafting or pre-irradiation grafting methods. The former involves irradiation of the polymer substrate with the monomer units together, whereas in the latter, the monomer reacts with the substrate after being irradiated in a prior separate step. Irradiation can be performed under various atmospheres, such as vacuum, inert gas, or air. The active species generated during simultaneous grafting are free radicals that initiate graft copolymerization immediately. This method is challenged by homopolymerization side reactions, which can be controlled by the addition of a small amount of an inhibitor (e.g., Fe^{3+}, Cu^{2+}) and using lower doses and dose rates. On the other hand, grafting with pre-irradiation can be performed under vacuum or in an inert atmosphere, leading to the formation of trapped radicals that are preserved by sub-ambient storage. If irradiation is carried out in air, hydroperoxy radicals are formed on the hydrocarbon substrates. Both trapped and hydropyroxy radicals can be activated by thermal treatment to start the grafting reaction in the presence of the vinyl monomer. The DOG (or grafting yield) is represented by the weight increase after grafting as in this equation: DOG (%) = $(W_g-W_0)/W_0) \times 100$, where W_0 and W_g denote the weights of the polymer film before and after grafting, respectively. The details of RIGC methods have been published elsewhere [14]. The effect of the type of RIGC method on the physicochemical properties of radiation grafted membranes was recently investigated in correlation with the properties of the obtained membrane [15].

2.2 Grafting Apparatus for Upscaling Membrane Production

Two types of ionizing radiation sources, including radioactive isotopes (e.g., Co-60) and EB accelerators, are available. Each source has its own merits and drawbacks, as reported elsewhere [16]. Noticeably, γ-rays provide deep penetration capability and can easily induce grafting into the bulk of polymer substrates, unlike EB, which depends on the acceleration energy and density of the polymeric substrate in achieving surface-to-bulk grafting. However, EB is most effective for applying a pre-irradiation method in which the irradiation step can be performed independently from the grafting reaction, which can be conducted in a different location, allowing distance processing of the samples. Grafting reactions are carried out in vessels allowing a control over the atmosphere to be inert by bubbling the monomer solution with a purified nitrogen or imposing vacuum through freeze-thaw cycles. Figure 1 shows a schematic diagram of the laboratory-scale grafting apparatus for the preparation of membranes by RIGC.

For preparation of membranes, EB is found to be more effective and can easily fit industrial usage and pilot-scale production because of its high irradiation dose rate, short processing time, ease of generation of free radicals in many polymers, moderate initiation reaction conditions and suitability for constructing continuous or semi-continuous lines.

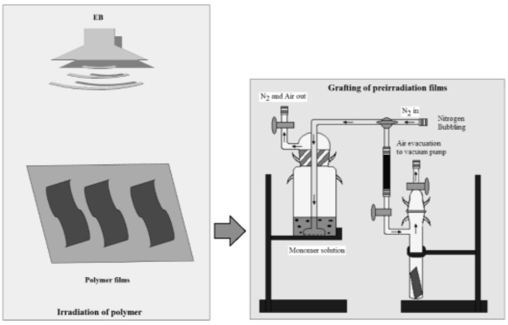

Figure 1 Schematic diagram of the laboratory-scale grafting apparatus for the preparation of grafted membranes by pre-irradiation grafting under an inert atmosphere

Moreover, the availability of a new flexible commercial EB accelerator of various accelerating energies, low (50-300 keV), medium (0.3-5 MeV) and high (5 to 10 MeV), brought synergy to EB processing in the polymer industry. The low-energy self-shielded EBs have been found to be very suitable for producing grafted fabrics and membranes in a continuous line that can be made suitable for simultaneous irradiation grafting and pre-irradiation grafting methods, as schematized in Figure 2.

3.0 OVERVIEW OF DEVELOPED AND EMERGING RADIATION GRAFTED ICMs

Radiation grafted ICMs provide attractive alternatives to counterparts prepared by conventional polymerization techniques for a variety of energy devices operating based on electrochemical mechanisms. This includes application in energy storage devices such as dry and redox flow batteries and energy conversion as in fuel cells and water electrolysers [14]. A schematic diagram showing the applications of radiation grafted IEMs for electrochemical energy conversion and storage devices is shown in Figure 3. In such applications, ICMs should ideally have high ionic conductivity, low electrical resistance, high selectivity for desired ions, low permeation for undesired species, low electroosmotic properties, low mechanical integrity swelling, high chemical stability and compatibility with electrode materials and low cost.

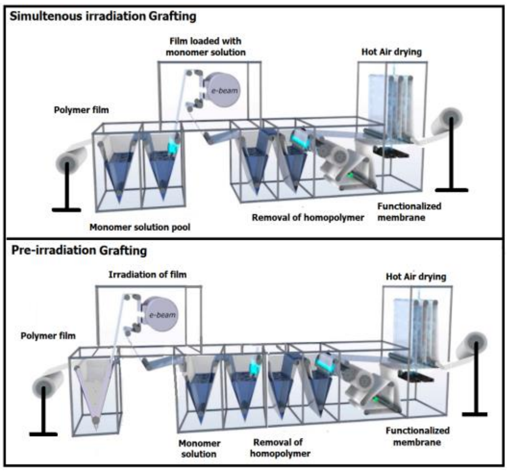

Figure 2 Schematic diagrams of the continuous system to produce grafted membranes with electron beams using simultaneous and pre-irradiation methods. Modified from [17]

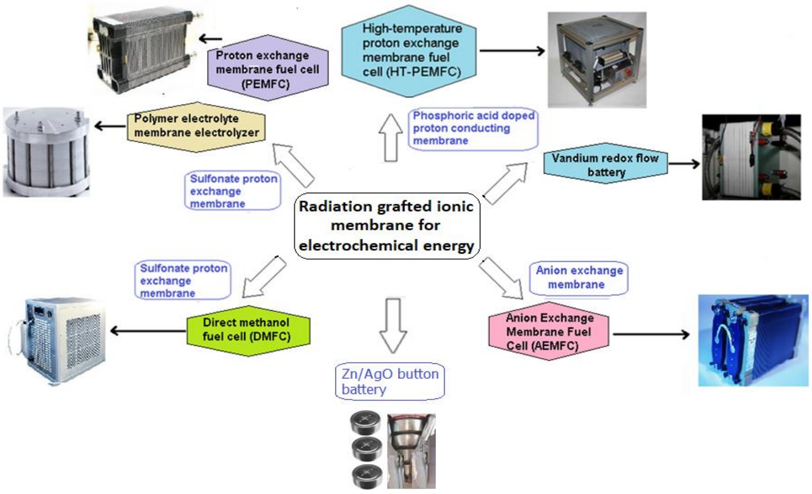

Figure 3 Schematic diagram of applications of radiation grafted ICMs for electrochemical energy conversion and storage devices

4.0 ICMs FOR FUEL CELLS

Fuel cells are a promising green systems for clean and efficient power generation in the twenty-first century and are suitable for mobile, stationary, and portable applications [18]. Polymer electrolyte membrane fuel cell is an electrochemical device converting the free energy of a gaseous fuel in presence of an oxidant into an electrical power using a catalyst without combustion. When PEMFC is operated using H_2 as a fuel and O_2 as an oxidant it is called H_2/O_2 fuel cell or best known as proton exchange membrane fuel cell (PEMFC). When a liquid fuel such as methanol is used as a fuel and O_2 as an oxidant, it is called a direct methanol fuel cell (DMFC), which simplifies the fuel cell design and allows its use in portable applications. Figure 4 shows a schematic diagram for PEMFCs and an anion exchange membrane fuel cells (AEMFCs) and their principles of operation. Air can replace O_2 in real applications, but the fuel/oxidant ratio must be adjusted to encounter the possible performance reduction.

The proton exchange membrane (PEM) is a key component in fuel cell systems. If the PEM is replaced by an anion exchange membrane (AEM), the fuel cell is denoted as AEMFC. The PEM conducts protons from the anode to the cathode and prevents the bulk mixing of oxygen and hydrogen whereas the AEM conducts OH- from the cathode to the anode in AEMFC in addition to its barrier properties. The replacement of PEM with AEM rendered AEMFC the potential to use nonprecious metal catalysts, which can reduce the cost and facilitate commercialisation.

Presently, PEMFC technology is based on the expensive perflouronated sulfonic acid PEMs such as Nafion® and its analogous membranes, which work efficiently only under full hydration conditions at temperatures up to 80 °C. Alternative PEMs with favourable properties balancing high proton conductivity, low permeability to fuel, low electronic conductivity, low electroosmotic drag coefficient, high chemical and thermal stability, good mechanical strength and low cost are highly sought.

Thus, considerable research efforts have been exerted to develop PEMs with desired properties using various approaches [19]. An evaluation for the developments of alternative PEMs of various structures has been recently published [20, 21]. RIGC is among the methods that have been used to prepare alternative PEMs and found to be convenient and appealing in modifying commercial, hydrocarbon, fluorinated and partially fluorinated polymer films by incorporating sulfonic acid moieties on covalently bonded side chain grafts originating from grafted vinyl monomers such as styrene or its derivatives [10, 11].

4.1 Commercial Radiation Grafted Membranes for Fuel Cells

The use of RIGC for preparation of ICMs containing sulfonic acid moieties was reported years ago, with the early work is dated back to the report by Behr *et al.* [23] in 1956 based on polyethylene film. The research was extended to use various vinyl monomers and substrates made from fluorinated films such as polytetrafluoroethylene (PTFE) in the subsequent 10 years [24-26]. It was until 1966, when the first commercially driven work that was initially targeting the development of dialysis membranes and battery separators was reported in a few patents [27, 28]. Later, in 1978, the applications of radiation grafted ionic membranes were extended to chlor-alkali process and fuel cells after fluorinated monomers such as trifluorostyrene were grafted onto fluorinated polymer films by D'Agostino *et al.* [29, 30].

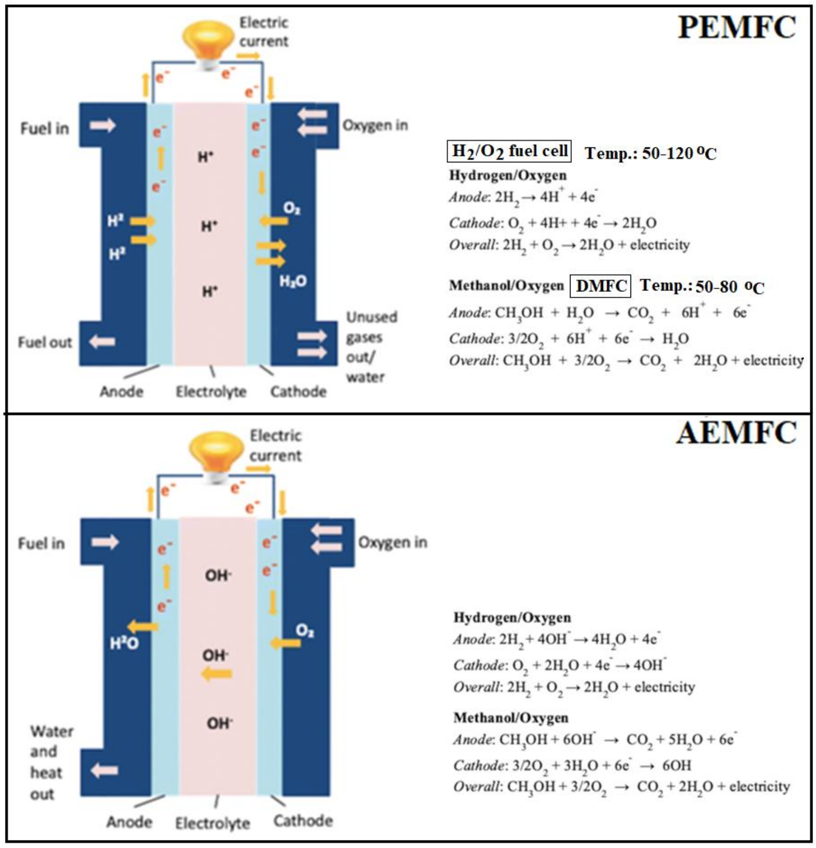

Figure 4 Schematic diagram for PEMFCs and AEMFCs and their principles of operation [22]

Several commercial radiation grafted PEMs, such as CEC from Chlorine Engineers Corp., Japan, which is made from sulfonated poly(trifluorostyrene)/poly(ethylene-co-tetrafluoroethyelne) (ETFE) and Permion® from RAI Research Corporation (USA), appeared in the early 1980s in different versions (e.g., Permion 5010: sulfonated polystyrene/PE and Permion 4010: sulfonated polystyrene/PTFE). The former membranes were prepared by RIGC of trifluorostyrene onto ETFE films followed by sulfonation, whereas the latter was obtained by RIGC of styrene onto PE or PTFE films followed by sulfonation. These membranes showed good performance in water electrolysers together with CEC radiation grafted membranes [31].

IonClad® sulfonated radiation grafted membranes, an improved version of Permion membranes, from Pall Gellman were also tested in PEMFC and showed superior response in terms of cell voltage compared to Nafion® 117 membranes but their stability was inferior, and their estimated lifetime was 500 h [32]. However, the IonClad® R-1010 (36 µm thick) and IonClad® R-4010 (63 µm thick) membranes showed rather better performance in DMFCs. Particularly, they exhibited 2.5–3.0 times lower methanol crossover than Nafion® 117 (180 µm thick) [33].

Table 1 List of commercial radiation grafted ICMs containing sulfonic acid group [14]

Company	Commercial name	Product	Origin
- United technology	-	- Fibrous ion-exchange sheets	Japan
Ebara Research Co., Ltd.	-	- Sulfonated nonwoven fabric - Ion-exchange fabrics and ion conductive spacer	Japan
Pall Gellman Sci. Inc.	IonClad®	- Sulfonated polystyrene/PTFE - Cation-exchange membranes	USA
RAI Research Corp.	R4010, R1010, and R4035	- Sulfonated polystyrene/PTFE - Cation-exchange membranes	USA
Solvay	R5010 CRA Morgan CDS Morgan ADP 100-2	Styrene/PE - Cation-exchange membrane - Cation-exchange membrane -Anion-exchange membrane	Belgium
Ashahi Glass Inc.	- Flemion	- Cation-exchange membrane	Japan
Shanghai Shilong Hi-Techn. Corp. Ltd.	-	-Sulfonic acid nonwoven fabric	China
Chlorine Engineers Corp., Japan	RAYMION/CEC	-Sulfonated polytrifluorostyrene/ETFE	Japan

Moreover, the selectivity parameter of Pall R4010 membranes at a temperature of 80 °C (ratio of proton conductivity to methanol crossover) was 130 compared to 37 for Nafion® 117, suggesting their higher potential for application in DMFCs [34]. Similar sulfonated membranes obtained by RIGC, denoted as CDS from DeMorgan, exhibited an inferior lifetime compared to Nafion® when tested in PEMFCs [35]. Today, more radiation grafted ICMs from different producers, such as those shown in Table 1 can be found and more details on them are discussed elsewhere [14].

4.2 Developmental Membranes for PEMFC

In attempts to improve the performance of radiation grafted PEMs against the benchmark PEMFC membrane (Nafion), an immense research effort has been undertaken in various research institutes worldwide to design new membranes using various strategies involving novel combinations of monomers/films, monomers/crosslinkers/films and monomers/comonomers/films.

Monomers such as styrene and its derivatives, including trifluorostyrene and pentafluorostyrene, have been used to host sulfonic acid groups. Fluorinated films such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), partially fluorinated films like ETFE and films of engineering plastics such as polyether ether ketone (PEEK) were among the most suitable substrates. Comonomers such as α-methylstyrene, acrylonitrile and methylacrylonitirile were also introduced to styrene during the grafting reaction to enhance stability by reducing chemical attack on the α-carbon of styrene. In another strategy, crosslinkers such as divinylbenzene (DVB), triallyl cyanurate (TAC), and diisopropenylbenzene (DIPB) with controlled amounts were also introduced to styrene during grafting to have crosslinked structures to control membrane swelling (dimensional stability) and enhance its mechanical integrity. Such efforts have conceived many developmental membranes that have reached a pilot-scale production. A comprehensive review of the research efforts that have been exerted in various institutes to design new radiation grafted PEMs capable of circumventing the shortcomings of old-generation of radiation grafted PEMs using diverse strategies has been published [10].

The research work conducted at the Paul Scherer Institute (Switzerland) on the first generation of developmental radiation grafted fuel cell membranes in 1991-2011 conceived several radiation grafted membranes with crosslinked structures that reached a few thousands of hours when tested in a single PEMFC under dynamic conditions, putting them ahead of other similar membranes researched elsewhere [11]. Among the most successful membranes is the DVB crosslinked PEM based on 25 µm FEP grafted polystyrene containing sulfonic acid (DOG of 18%, IEC of 2.0 mmolg^{-1}) prepared with an optimized combination of styrene/DVB ratio of 9:1. These membranes showed acceptable chemical stability, reduced water uptake, and improved mechanical properties. Particularly, the lower swelling inherited these membranes higher dimensional stability leading to minimum internal stress accumulation that reduced the membrane damage associated with dry–wet cycles during fuel cell operation. These membranes recorded stability (durability) in membrane/electrode assembly (MEA) of a single cell of a few thousands of hours at a temperature of 80 °C and under steady state conditions with a current density of 500 mAcm^{-2}, as shown in Figure 5 [36-38].

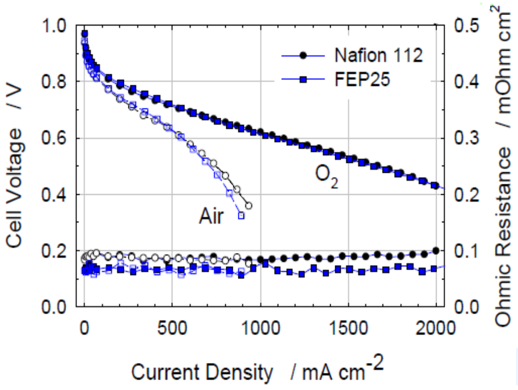

Figure 5 Polarization curves and stability results for DVB crosslinked PEM based on FEP grafted polystyrene. (Pt loading: 0.6 mg/cm, cell temperature: 80 °C, reactants: H_2/O_2 at a stoichiometry of 1.5/1.5, gas pressure 1 bar, H_2 humidified at 80 °C. When O_2 was replaced with air, the H_2/air ratio was set at a stoichiometry of 2.0/9.5 and gas pressure of 1 bar [36]

The membranes also exhibited over 2000 h stability under dynamic operating conditions with varying loads. The various aspects of PSI crosslinked FEP-based membranes, including their characterization methods and durability data, were early reviewed by Gubler *et al*. [37].

A second generation of radiation-grafted PEMs developed using an advanced combination of monomers and crosslinkers based on ETFE films also led to a recognisable improvement in chemical stability. Particularly, researchers at PSI developed membranes based on a 25 µm ETFE film grafted with a combination of styrene or α-methylstyrene, methacrylonitrile and *m*-diisopropenyl benzene (DIPB) crosslinker (preparation route is shown in Figure 6) and showed high chemical stability in terms of ion exchange capacity (IEC) loss of approximately 2400 h [39].

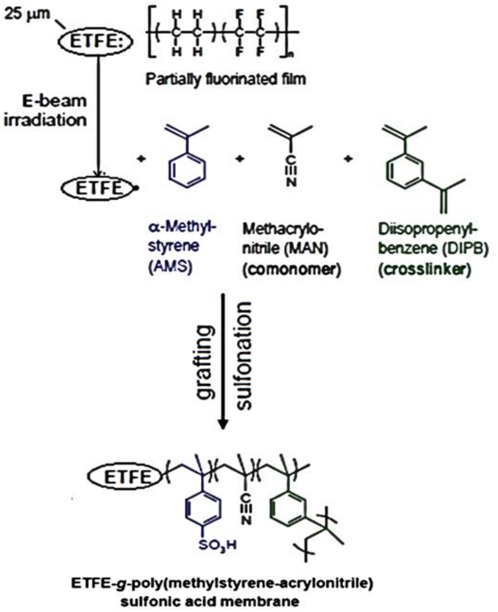

Figure 6 Schematic representation of the new generation of radiation-grafted membranes based on ETFE films obtained by comonomer grafting and crosslinking followed by sulfonation [39]

This membrane also outlasted Nafion 212 and Nafion XL-100 membranes in the fuel cell under dynamic operating conditions, as shown in Figure 7.

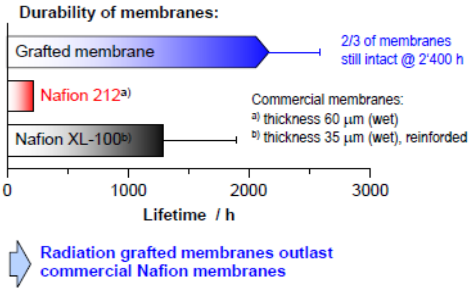

Figure 7 Results of the accelerated stability test for sulfonated polystyrene/polyacrylonitrile/DIPB grafted ETFE membranes [39]

4.3 Developmental Membranes for DMFC

The DMFC performance and long-term stability test were reported for a membrane electrode assembly (MEA) made with a membrane prepared by RIGC of styrene onto 50 µm poly (tetrafluoroethylene-*co*-perfluorovinyl ether) (PFA) using a simultaneous method followed by sulfonation [40]. The membrane exhibited a better DMFC performance than Nafion 115 membrane with a high-power density of 123 mWcm^{-2} at 0.4 V and 60 °C while maintaining higher selectivity and lower methanol crossover. The membrane noticeably showed (as depicted in Figure 8) a durability of 2066 h under a constant current density of 150 mAcm^{-2} and at a cell temperature of 60 °C [40]. It is noteworthy mentioning that the main challenges for commercialisation of radiation grafted PEMs relies on the ability to establish well-balanced properties that can provide high performance and durability under dynamic PEMFC operating conditions. In fact, the difficulty always lies in the conflicting requirements of the membrane properties. Moreover, the lack of understanding of the complex interplay of factors affecting membrane properties and performance also delayed the deployment of these membranes for commercial purposes [11].

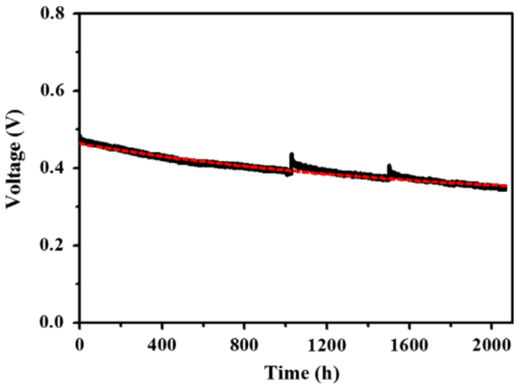

Figure 8 Long-term performance test of prepared MEA with the PFA-PSSA50 membrane (dashed lines represent the exponential fit). Operation conditions: 60 ^{o}C and 150 mAcm^{-2} [40]

The interest in the use of RIGC to develop AEMs evolved when a patent for the preparation of grafted membranes using γ,β,β-trifluorovinyl aromatic monomers on a polymeric film was applied [42]. The developed ion exchange membranes were used in few electrochemical applications including fuel cells. A decade later, Scott and co-workers reported the preparation of AEM by RIGC of vinylbenzyl chloride (VBC) onto low-density polyethylene (LDPE) followed by amination. The AEM membrane with a 110 µm thickness and an IEC of 1.77 mmolg^{-1} demonstrated an extraordinary performance in a H_2/O_2 fuel cell with a peak power density of 823 m cm^{-2} (Pt/C catalysts) at 60 °C and 718 mWcm^{-2} at 50 °C with no gas pressurisation, as shown in Figure 9.

Similar membranes based on cast LDPE radiation grafted with VBC and functionalised with trimethylamine (TMA) were also investigated. A membrane with a DOG of 74.6% and an IEC of 3.2 mmolg^{-1} showed an extremely stable ionic conductivity of 0.11 S cm^{-1} in the durability test over a period of 7 months under nitrogen at 80 °C. This boosted the peak power density to 608 mW cm^{-2} at 50 °C, with a low fuel crossover [44].

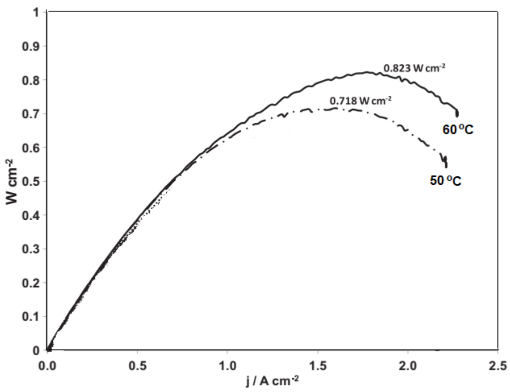

Figure 9 H_2/O_2 fuel cell performances in terms of power density at 50 °C and 60 °C for benzyltrimethylammonium head-group MEAs (Pt/C electrodes) with no back-pressurisation [43]

The performance of similar membranes based on LDPE film grafted with VBC was boosted after applying controlled procedures during RIGC that was carried using EB and pre-irradiation methods. The rise in the performance can be clearly seen from the polarisation curves of AEMFCs operated at 80 °C with a 100 µm thick membrane containing a benzyltrimethylammonium head group showing a power density of 1.21 Wcm^{-2} that was increased to 1.43 W cm^{-2} when the thickness was reduced to 70 µm as illustrated in Figure 10.

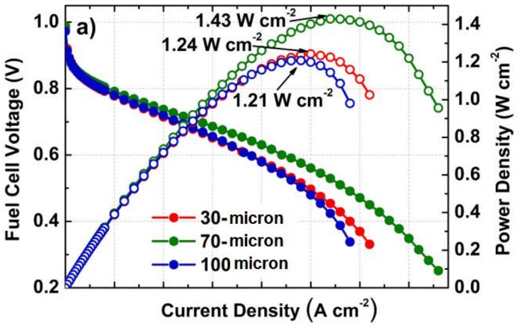

Figure 10 AEMFC performances at 80 °C for LDPE-based AEMs grafted by the pre-irradiation method and H_2 anode gas flow of 0.8 L min^{-1}, O_2 cathode gas flow is 0.5 L min^{-1}, both supplied without pressure with optimal dewpoint temperatures ranging from 77 to 80 °C [15]

Varcoe and co-workers developed a series of AEMs containing benzyl quaternary ammonium by RIGC of VBC onto poly(vinylidene fluoride) (PVDF) [45] and ETFE [46] films followed by quaternization reactions. These earlier versions did not have sufficient alkaline stability despite their reasonable ionic conductivity. The same research group further enhanced the alkaline stability by introducing saturated heterocyclic benzyl quaternary ammonium groups to the membrane. This was carried out by RIGC of VBC on ETFE films followed by quaternization with 1-methylpyrrolidine [47]. The obtained membrane (100 µm thick, 1.66 mmolg^{-1} IEC) demonstrated a stability in the OH conductivity at 60 °C and 95% RH for more than 334 h. This was coupled with the highest performance in the form of power density of 630 mW cm^{-2} when tested in a H_2/O_2 AEMFC at 60 °C after combining with a PtRu/C loaded anode and Pt/C cathode with a polysulfone ionomer binder and fully humidified feed without back-pressurisation. The power density increased to 800 mWcm^{-2} when a thinner membrane (52 µm) is used and subjected to back-pressurisation under the same conditions as depicted in Figure 11. Overall, the membrane with the benzyl-*N*-methylpyrrolidinium head group is superior to the membrane with a benzyltrimethylammonium head group.

Maekawa and co-workers developed a series of imidazolium-based AEMs by RIGC of monomers such as N-vinyl imidazolium (NVIm), 2-methyl-NV imidazolium (2MVIm), 1,2,3-trimethyl-4-vinyl imidazolium (4VIm), and 2- styryl-N,N-dipropyl imidazolium (StIm) onto ETFE film [48-52]. Of all, the membrane with a styrylimidazolium-type anion conducting head group and IEC of 1.72 mmolg^{-1} exhibited the highest power density reported to date for imidazolium-type membranes (710 mWcm^{-2}) and an open circuit voltage (OCV) (1.03 V) as shown in Figure 12 [52, 53].

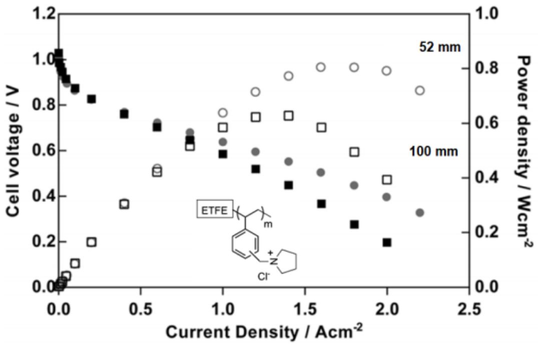

Figure 11 H_2/O_2 fuel cell performances at 60 °C for PVBC-methylpyrrolidine AEM (bottom) with catalyst-coated membrane-based MEAs (PtRu/C anodes and Pt/C cathodes, both with polysulfone-based ionomer) and either no back-pressurisation (squares) or 0.1 MPa back-pressurisation (dots) [47]

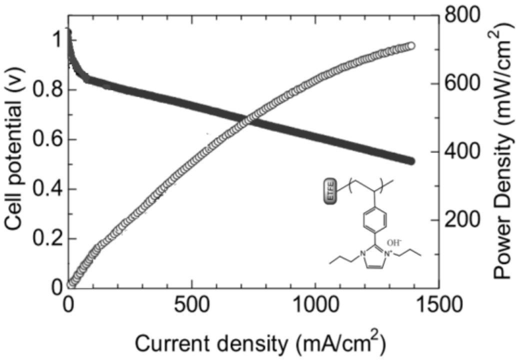

Figure 12 AEMFC voltage and maximum power densities in correlation with current density for styrylimidazolium-type anion exchange membranes with an IEC of 1.72 mmolg^{-1} [53]

The durability of the developed styrylimidazolium-type anion exchange membrane in a single cell under a constant current density of 50 mAcm^{-2} and gas flow rate of 100 ml/min for both H_2 and O_2 showed a lifetime of more than 670 h. The membrane maintained 78.6% of the initial voltage (0.72 V) as illustrated in Figure 13.

5.0 ICMs FOR WATER ELECTROLYSER

A water electrolyser is an electrochemical system comprising an electrolytic cell containing anode, cathode and alkaline water solutions that is used to split water into hydrogen and oxygen by applying DC current.

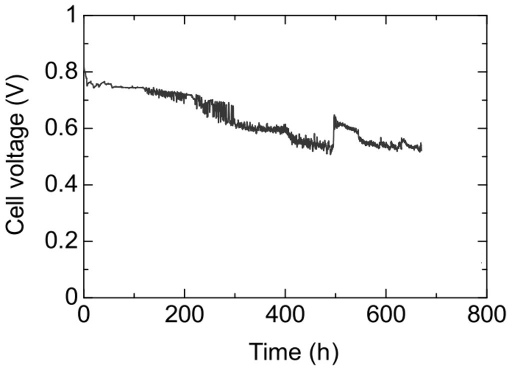

Figure 13 AEMFC Voltage in correlation of operating time of styrylimidazolium type (98% DOG, 1.72 IEC) at a constant current density (50 mAcm^{-2}) for 670 h in a single H_2/O_2 fuel cell at 60 °C [53]

Thus, it has the potential for green production of hydrogen, especially when the needed electricity is obtained from renewable sources (e.g., solar or wind). The use of a solid polymer electrolyte in the form of a proton exchange membrane (PEM) in a water electrolyser endowed in these electrolytic cells several advantages compared to the conventional alkaline counterparts. This includes not only simplification of the cell design, elimination of the alkaline solution, impartment of higher current densities and higher purity hydrogen but also generation of hydrogen at significantly higher pressures, increment of energy efficiency and improvement of production capacity at lower temperatures [1].

Generally, the main membrane used in PEM electrolysers is based on perfluorosulfonic acid such as Nafion® membranes (e.g., N117 and N115). Similar, to PEMFCs, the membrane has two main roles in the water electrolyser: transporting hydrogen ions formed at the anode to the cathode and preventing the bulk mixing of hydrogen and oxygen ions. Therefore, PEMs must have a proper thickness that is necessary for maintaining barrier properties. For PEM electrolyser operation at high pressure, PEM in a reinforced form is necessary to provide a suitable combination of high conductivity and high mechanical stability [54].

Historically, the first electrolysers using PEMs were developed by General Electric Co. in 1966 for space applications [309]. Years later, extensive research and development on PEM electrolysers to produce hydrogen was also conducted in the Japanese World Energy Network (WE-NET) program [55]. In this context, commercial PEMs known as CECs from Chlorine Engineers Corp. (Japan), which were made by RIGC of α,β,β-trifluorostyrene onto an ETFE film, followed by sulfonation were tested in water electrolysis by Scherer *et al* [56]. These authors reported a performance stability up to 10,000 h operation for such fluorinated membranes. This long performance demonstrated the potential of radiation grafted PEMs to replace commercially dominating perfluorinated membranes and provide a considerable reduction in the operating cost of water electrolysers [31]. Preparation of similar PEMs was previously reported by RIGC of styrene onto PE or PTFE films followed by sulfonation [57].

Gubler and co-workers (Paul Scherrer Institute) developed a series of membranes (having the molecular structures shown in Figure 14) for PEM for electrolyser application by RIGC of comonomers' combination of styrene (St), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) onto

ETFE films followed by sulfonation [58]. Unlike previous studies, the St/AN/DiPB grafted membranes underwent rigorous mechanical stability tests under wet conditions resembling the PEM electrolyser environment. The radiation grafted membranes displayed superior mechanical properties compared to Nafion (N115 and N117) membranes. The elongation at break of St/AN/DiPB membranes showed values that were approximately the same as those of the membrane under dry conditions. Considering the performance in the PEM electrolyser, the performance of the radiation grafted membrane was overall better than that of the commercial membrane at low current densities, unlike at higher current densities, at which the performance of the commercial membrane dropped, as illustrated in the polarization curves shown in Figure 15. This was coupled with a lower H_2 crossover in the grafted membranes.

The membranes obtained by RIGC of α-methylstyrene, acrylonitrile, and 1,3-diisopropenylbenzene (AMS/AN/DiPB) onto ETFE (50 µm) conceived a combination of interesting properties, including low hydrogen crossover, low area resistance, and encouraging stability in hot water, making them promising alternative membranes for water electrolyser applications [59].

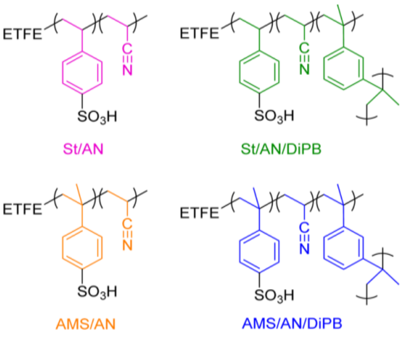

Figure 14 Ion conducting membranes prepared by RIGC of various comonomers

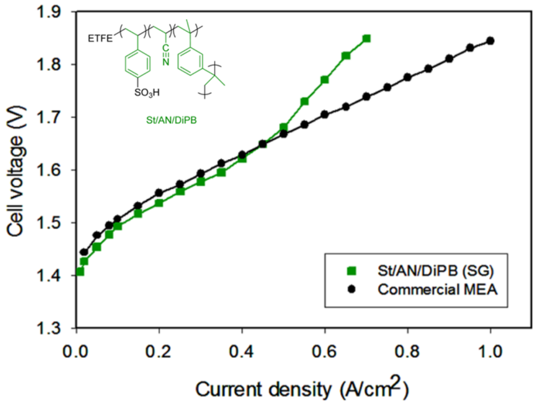

Figure 15 Polarization curve of MEA based on St/AN/DiPB (SG) radiation grafted membrane with a graft level of 39% and commercial MEA [58]

6.0 ICMs AND SEPARATORS FOR BATTERIES

6.1 Zn/AgO battery

Battery separators, which are key components located between electrodes to prevent direct contact of these opposite polarity electrodes while permitting the free flow of electrolyte, are among the most successful applications of RIGC for material development. The separator requires a large electrolyte retention volume while inhibiting active materials from passing through it, causing unwanted bridging of electrodes of opposite polarity [60]. Battery separators are commonly prepared by surface modification performed onto porous polyolefin films using various methods, including dip coating [61], photoinduced grafting with UV [62] , plasma processing [63] and RIGC [64]. Among all methods, RIGC is the most promising; thus, immense efforts have been made to produce polyolefin separators with high performance that have been recently reviewed [14]. These efforts were successful in upscaling a large variety of battery separators based on the surface modification of polyolefins by RIGC of monomers such as acrylic acid

(AA), methyl methacrylic acid (MMA) and derivatives. The use of EB, which enhances the rapid formation of active sites for initiating the reaction through the polymer film and promotes homogeneity as well as uniformity of polymer grafts across the films, enabled the development of continuous grafting process leading to commercialization of battery separators [63].

Historically, radiation-grafted PE film-based separators were introduced in the 1960s and later became an industrial standard for Zn/AgO cells. For example, separators prepared by RIGC of MMA onto a PE films such as Permion from RAI Research Corporation, Inc. (USA) were mass produced [65]. The introduction of PMMA grafts made the film hydrophilic and permeable to the liquid electrolyte. Permion 2192 (a low-resistance separator) was found to be suitable for high-rate KOH cells, while Permion 2193 (a higher-resistance separator) was suitable for low-rate NaOH cells. The use of these versions of Permion separators extended the service life of Zn/AgO button cells from 2 to 4−5 years [66]. An improved ion-exchange membrane (Silvergard) with a better selectivity toward silver-ion diffusivity than other ion-exchange membranes was later introduced by RAI Research Corporation (USA) [67]. PAA-grafted PE thin films (10-25 µm) have also made its commercial use as battery separator for Zn/AgO button batteries in Japan in the mid-1980s [68, 69]. The use of such a thin separator revolutionised the production and application of Zn/AgO button batteries with long lifetime and prompted their use in watches, medical equipment and measuring instruments. This was motivated by the long-term reliability, small and thin shape, high-energy density (2 times of alkaline button battery) and flat discharge characteristics of this battery. Today, the production of Zn/AgO button batteries based on PAA separators in Japan reaches 1 billion cells per day. The market size is 10 million dollars in Japan [70]. Similar radiation-grafted battery separators are also produced by companies such as Shanghai Shilong Hi-Tech. Corp. Ltd. (China) through simultaneous radiation grafting of AA into PE film.

6.2 Vanadium Redox Flow battery

VRFBs have attracted an increasing attention as energy storage systems due to their long cycle life, deep discharge ability, high energy efficiency and low cost in addition scalability to gigawatts (GWs) [71]. The ion exchange membrane (IEM) is one of the key components of VRFB to prevent the crossover of vanadium ions and allow the transport of ions to complete the conducting circuit. The ideal IEM should possess low permeation rates of vanadium ions to minimize self-discharging, high conductivity, good chemical stability, and cost effectiveness [72]. The currently available commercial membranes cannot satisfy all the above requirements [73].

Intensive research efforts have been carried out to develop alternative membranes using a variety of polymers and polymerization techniques. Such an effort yielded commercial products such as oxidation-stabilized AEM known as Selemion™ APS4 membrane, which is distributed by AGC [74]. The progress that took place in the development of membranes for VRFB in the past 25 years was recently reviewed [75]. Several developmental membranes, such as those prepared by Zhai and co-workers, were also prepared using RIGC with various monomers, such as dimethylaminoethyl methacrylate (DMAEMA) [76] or combinations of monomers/comonomers such as styrene and maleic anhydride [77], styrene and dimethylaminoethyl methacrylate (DMAEMA) groups [78] and sodium styrene sulfonate (SSS) and DMAEMA [79] onto partially fluorinated substrates (PVDF and ETFE). The adoption of two consecutive steps RIGC approach, in which styrene was grafted on ETFE films, followed by sulfonation and subsequent grafting of DMAEMA enabled preparation of an amphoteric IEM with both anionic and cationic groups [78]. The use of double grafting imparted remarkable stability and VRFB performance that maintained OCV higher than 1.3 V for 300 h (as depicted in Figure 16) [78], compared to 50 h in the earlier membranes obtained by grafting DMAEMA alone or its mixture with α-methyl styrene (AMS) on PVDF films, which demonstrated an OCV higher than 1.4 V for 50 and 60 h, respectively [77, 80]. Moreover, this membrane showed superior energy efficiency and columbic efficiency compared to the Nafion 117 membrane. The replacement of the PVDF film with ethylene-vinyl alcohol copolymer and the two-step RIGC by a single step RIGC led to a membrane with inferior properties, including an OCV of 1.45 V for 12 h [81].

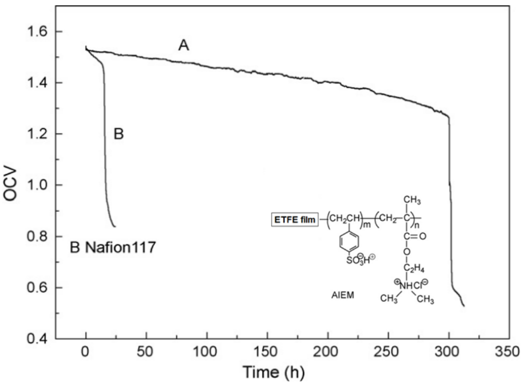

Figure 16 OCV test of VRFB with radiation grafted amphoteric ion exchange membrane and Nafion 117 [78]

A new amphoteric membrane containing sulfonic acid as proton exchange sites and amidoxime moieties as a vanadium barrier group was developed by Gubler and co-workers [82]. The membrane was prepared by RIGC of a mixture of styrene and acrylonitrile followed by a two-step functionalization involving amidoximation of the nitrile group and sulfonation of styrene. The membrane with a DOG of 36% showed an excellent vanadium barrier property, with the vanadium-ion crossover reduced 4-fold in the presence of amidoxime groups without compromising the conductivity of the membrane. The membranes with DOG of 36 and 32% maintained higher and more durable OCVs in the VRFB test than Nafion 117, as depicted in Figure 17. The performance of the membrane in VRFBs showed an increased energy efficiency and a little capacity loss over 122 charge/discharge cycles compared to the Nafion 117 membrane. The latter showed a discharge capacity loss of approximately 35% after 35 cycles coupled with a significant electrolyte imbalance.

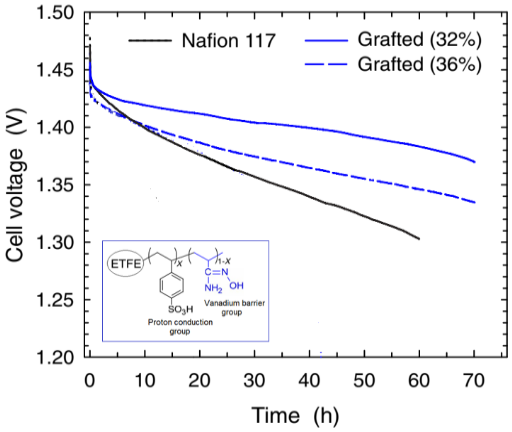

Figure 17 Open circuit voltage (OCV) hold test of VRFB with radiation grafted amphoteric membrane compared to Nafion 117 workers [82]

Another novel amphoteric membrane for application in VRFB was prepared by RIGC of 4-vinylpyridine (4-VP) monomer onto ETFE films followed by subsequent 2-step functionalization, including alkylation by 1,10-dibromodecane in *N*-methyl-2-pyrrolidone and subsequent nucleophilic substitution of alkyl bromide by 3-aminobenzenesulfonic acid. A molecular structure representation of the grafted membrane is shown in Figure 18. The introduction of alkylated 4-vinylpyridinium units improved the vanadium barrier properties, whereas the presence of protogenic sulfonic acid groups maintained the conductivity and reduced the area resistance, and such improvements were at par with Nafion®117. However, the long-term performance of the new membrane demonstrated a combination of higher energy efficiency, low-capacity loss, and less observed electrolyte volume change in the half-cells during the prolonged charge/discharge cycling compared to the Nafion®117 membrane.

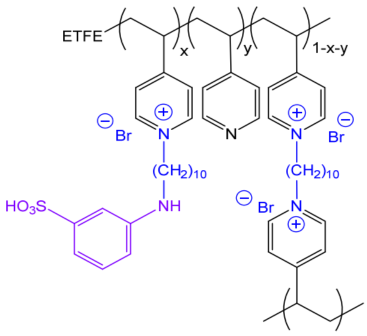

Figure 18 Molecular representation of an amphoteric radiation grafted membrane for VRFB [83]

6.3 Lithium Secondary Batteries

Secondary Li-ion batteries are pioneering batteries that have been widely used in portable electronics, electric vehicles, and electric storage reservoirs because of their high specific energy, superior coulombic efficiency, and outstanding cycle life. A Li-ion battery consists of an anode, cathode, electrolyte, and separator, which prevents an electrical short circuit while permitting the free flow of Li and this has a direct influence on the safety and power performance of the battery. Thus, immense efforts have been made to develop separators for this battery with superior mechanical strength, electrochemical stability, regular pore structure, good thermal shutdown properties and cost-effectiveness. Porous/nonporous sheets such as PE and PP impregnated with Li electrolyte have been widely investigated as separators using various surface modification methods [84].

RIGC was used to prepare a Li-ion battery separator by grafting glycidyl methacrylate (GMA) into an EB-irradiated porous PE film by Ko *et al* [85]. The obtained PGMA-grafted separator displayed a superior life cycle compared to the pristine PE separator, as depicted in Figure 19.

In another study, MMA was grafted on EB irradiated PE film yielding modified separators with different DOGs [86]. The grafted separator demonstrated an enhanced liquid electrolyte uptake, which was varied depending on DOG. The performance in the cell displayed a superior cycle life compared to the original PE separator and such a performance was a function of DOG.

A similar separator composed of PE film grafted with MMA was developed by Nho and co-workers at the Korean Atomic Energy Research Institute using RIGC with the peroxidation method [87].

The obtained separator reached an ionic conductivity of 2.0 mScm-1 at 127 wt% DOG. The battery test of the separator demonstrated a better electrochemical stability than the pristine PE separator.

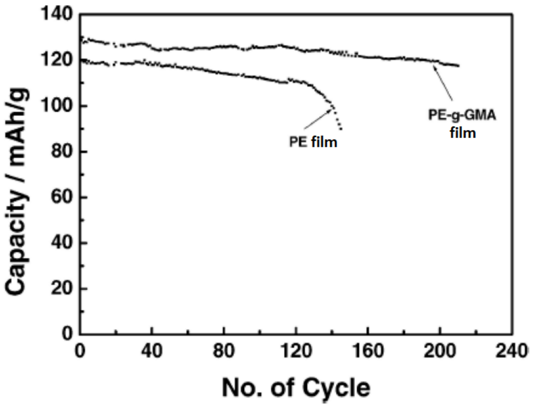

Figure 19 Cycling performance of Li-ion batteries using PE-*g*-PGMA and PE separator membranes [85]

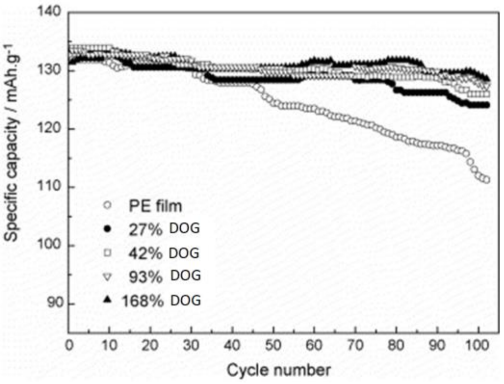

Figure 20 Cycle performance of the coin cell with PE and GMs at the *C*/5 rate [86]

Another separator containing polyacrylamide was also prepared by RIGC. The separator with 22.6% DOG demonstrated an improvement in the compatibility and uptake of the liquid electrolyte coupled with a rise in the ionic conductivity to values as high as 9 x10^{-3} S/cm at room temperature together with an improvement in the Li-ion cell cycle performance [88]. Moreover, the cell with the grafted separator showed more stable cycling performance compared to that with the pristine PE separator.

6.4 Ni-Cd Battery

Commercial radiation-grafted membranes such as Permion produced by RAI Research Corporation were used in the early 1970s as separators in alkaline batteries. These membranes showed an excellent oxidation resistance and a superior chemical resistance to alkali media. However, they are totally impermeable to electrolyte flow, and thus, their resistance is so high that it discouraged their use as a separator in this form. The properties of such membranes were improved by RIGC with monomers that can immobilise ionic groups to side chains imparting desirable hydrophilic properties to the films without materially impairing their excellent chemical resistance [67]. Later, radiation grafted films and nonwoven polyolefin separators were produced in the early 1990s and used to enhance the performance of various batteries, including Ni-Cd cells [89]. For example, in US Patent US 4287272 A, a battery separator with a patterned structure in which non-grafted areas are continuous and surrounded by discrete grafted areas was prepared by RIGC of AA in the presence of Mohr's salt onto a 25 μm thick high-density PE film. The obtained separator contains ion permeable areas surrounded by ion impermeable zones, had an average DOG of 105% and showed an electrical resistance of 70 mΩ·cm^2 coupled with a high dimensional stability. The membrane boosted the performance of the Ni-Cd battery and eliminated self-discharging in the small cells [90].

Goel *et al* (from Bhabha Atomic Research Center) [13] developed a Ni/Cd battery separator by RIGC of AA onto porous PP films with 20% DOG that was found to be suitable to impart desired properties at par with commercially available battery separators. Commercial radiated grafted separators, such as YUASA membrane produced by Yuasa Membrane Systems Co., Ltd. is exclusively used as a separator for Ni/Cd batteries [91]. The use of such a radiation-grafted separator demonstrated an excellent performance of high rate discharge and long service life (12-20 years). Particularly, a grafted PE separator was applied as in a Ni-Cd battery and displayed superior characteristics at high and low temperatures. These characteristics made Ni-Cd batteries advantageous for the use in emergency power supply applications [9, 14].

7.0 CONCLUSIONS AND FUTURE PERSPECTIVES

The status of the developmental and commercialized radiation grafted ICMs for electrochemical energy systems was reviewed. It was found that RIGC can be used to conveniently prepare a variety of ICMs, which were successfully applied in PEMFCs, DMFCs and AEMFCs. This method was also used to effectively prepare separators for various batteries including VRFBs, Li-ion batteries, Ni-Cd batteries, and Zn/AgO batteries with the separators for the last two types of batteries were successfully commercialized. Other radiation-grafted membranes for PEMFCs, DMFCs, Li-ion batteries and VRFBs have received an increasing attention and achieved major progress towards commercialization compared to their counterparts related to AEMFCs and water electrolysers, which are emerging. It was confirmed that membranes and separators fabricated by RIGC offer cost-competitiveness and greener alternative materials to conventional fluorinated counterparts since inexpensive commercial films were used as starting substrates and reaction parameters could be tightly controlled leading to reduction in the monomer consumption while allowing formation of a combination of balanced ion transport with good barrier, and stability properties. The chemical stability and durability of the membranes under dynamic conditions remain the crucial issue that determines the suitability of the adopted method for deploying the established membranes for commercialization. More work is needed to take many emerging ICMs from the laboratories to the industrial scale to further realize the advantages of RIGC for membrane development.

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