



# Quantum-beam technology: A versatile tool for developing polymer electrolyte fuel-cell membranes

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## ABSTRACT

This paper describes the versatile application of quantum beam-based technology to the development of proton exchange membranes (PEMs) for fuel-cell applications. The  $\gamma$ -ray or electron-beam induced radiation grafting offers a way to prepare PEMs; typically, the radical-initiated polymerization of a styrene or styrene-derivative monomer on a base polymer is followed by a sulfonation step. Novel PEMs were previously obtained using radiation-crosslinked fluoropolymers as the base material. Interestingly, combining this radiation-crosslinking process with the well-known chemical crosslinker method enabled one to obtain the “multiply”-crosslinked PEMs, in which both the main and grafted chains have covalently bridged structures leading to a high durability. The bombardment of heavy ions accelerated to MeV or higher energies produces a continuous trail of excited and ionized molecules in polymers, which is known as a latent track. The approach using this ion-track technology is based on the chemical etching and/or modification of each track with diameters of tens to hundreds of nanometers. The resulting “nano-structure controlled” PEM was found to have perfect one-dimensional proton-conductive pathways parallel to its thickness direction, while, in contrast, other existing PEMs mostly exhibited proton transport in the three-dimensional random media. The hierarchical structures of the PEMs, ranging from nanometers to micrometers, were revealed by small-angle neutron scattering experiments using a cold or thermal neutron beam. The information in such a wide length scale led to a deep insight into the dynamic properties inside the PEM from a molecular to macroscopic level, which can provide feedback for the reconsideration and optimization of the preparation procedure. As demonstrated above in the author's studies, it is important to understand that every quantum beam is different, thereby making the right beam choice.

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## 1. Introduction

Recent technological advancements of controlling various beams have led to the highly sophisticated way to use their full capability in many research fields ranging from basic science to industrial applications. Such purpose-oriented, excellently controlled, high-quality beams are recently called “quantum beams”. These quantum beams include electromagnetic waves (laser, X-ray,  $\gamma$ -ray, etc.) and particle beams (electron, positron, proton, neutron, ion, etc.), both of which have a wave-particle duality within quantum mechanics. Research and development activities on quantum-beam technology, like the author's, have been making much progress as a core technology for scientific discovery and engineering innovation.

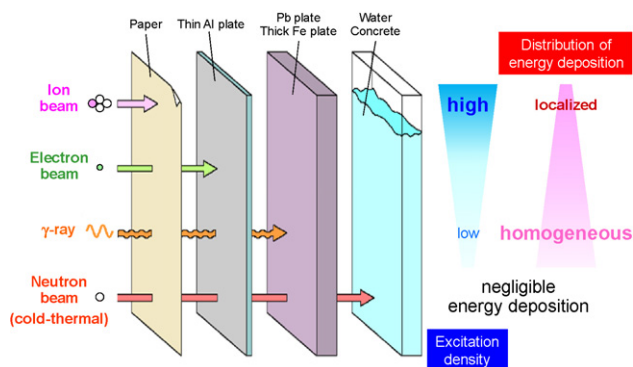
As a matter of fact, the Japan Atomic Energy Agency (JAEA) has a comprehensive platform to support the cross-functional use of

various quantum beams for promoting material science, bioscience and their industrial applications. The JAEA-owned large-scale facilities are all well-coordinated and well-distributed in Japan: (i) a JRR-3 reactor and J-PARC spallation neutron source in Tokai, (ii)  $\gamma$ -ray and electron-beam facilities and ion-beam accelerators in Takasaki, and (iii) a laser facility and SPring-8 synchrotron facility in the Kansai district. This is undoubtedly one of the distinct advantages of the JAEA research.

Like many others, researchers at JAEA have been intensively working on the application of quantum beam-based technology for the development of the proton exchange membrane (PEM) for fuel-cell applications since 2001. There can be no doubt that significant attention is being focused on the preparation of a variety of PEMs as alternatives to commercially available perfluorinated PEM materials such as Nafion. Specifically, there have been several reviews of hydrocarbon polymers [1], organic/inorganic hybrid PEMs [2], acid-base polymer complexes [3], etc. Fuel-cell applications require that the PEM should meet certain characteristics; for example, proton conductivity, mechanical strength, swelling properties, chemical stability and methanol permeability. When a higher proton con-

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**Fig. 1.** Comparison of characteristics between the four quantum beams described in this paper, i.e.,  $\gamma$ -rays, electron beams, ion beams, and neutron beams. The most notable difference is the radiation penetration distance.

ductivity is pursued for practical applications, at least one of the other PEM properties is usually reduced; these trade-offs must be assessed in the current stage of technology.

JAEA's knowledge based on many years of research and experience in the radiation chemistry of polymers has enabled the project to be very efficiently developed, and so its scope includes many radiation-induced reactions such as graft polymerization, self-polymerization, crosslinking, degradation, etc. The present paper demonstrates the versatile application of the author's quantum beam-based technology, especially using  $\gamma$ -rays, electron beams, ion beams, and neutron beams, for the PEM development. The author emphasizes here that this project is not all his group is involved in; the important missions are to establish the guiding principle for membrane design and to define new fields of industrial applications of quantum-beam technology.

## 2. What we must know about quantum-beam technology

From the standpoint of a quantum-beam or radiation-chemical technology, the author can say that the right beam choice is the most factor for a good job. That will also be true for the development of the PEM. Then, what's important for right beam choice? The answer is to understand that every quantum beam is different. This is the subject of this paper.

Fig. 1 is a picture showing clearly the characteristics of the four quantum beams used in this study; i.e.,  $\gamma$ -rays, electron beams, ion beams, and neutron beams. The first three beams are called ionizing radiation having enough energy per photon or particle to ionize atoms (i.e., remove electrons from atoms).  $\gamma$ -rays are electromagnetic waves from the decay of individual radioactive atoms such as  $^{60}\text{Co}$  and  $^{137}\text{Ce}$ , while the electron and ion beams consist of a stream of charged particles produced using radio frequency, microwave, static electric fields, or magnetic fields in accelerators. As a major characteristic phenomenon in the figure, one can notice

the different penetration lengths because of different interactions with matter. Ion beams are the least penetrating type of radiation and thus their interaction with a material is very large. This means that an ion beam induces an extremely high-density excitation compared to the other beams, and it occurs very locally. Interestingly, on the other hand,  $\gamma$ -rays and electron beams are extremely- and relatively-penetrating radiations, respectively. The excitation or ionization density is low enough to very homogeneously deposit the energy in materials.

As for neutrons produced by the fissioning or splitting the atoms, the beam in the cold or thermal range is suitable for the structural analysis of materials. This is because its corresponding energy ranges from  $5 \times 10^{-5}$  to 0.025 eV thus producing a very small and negligible energy deposition

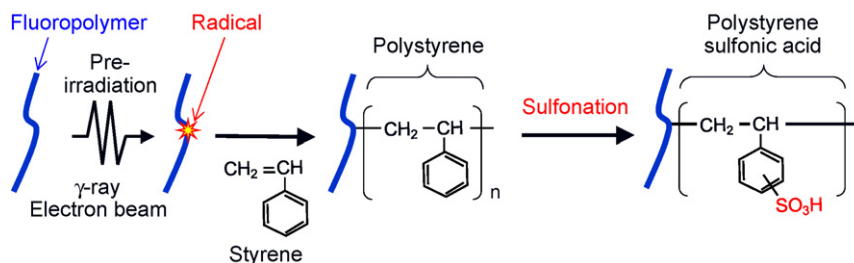
## 3. $\gamma$ -ray and electron beam-based technique

### 3.1. Radiation grafting

Radiation-induced graft polymerization, sometimes shortened to radiation grafting, is a well-established technique involving the polymerization of a monomer or a mixture of monomers onto a base polymer film (also referred to as a substrate, matrix, or host). Polymer chains of the grafted moiety are thereby grown on the base polymer backbone from active sites, which may be free radicals or ionic chemical groups. From a practical standpoint,  $\gamma$ -ray and electron beam irradiations have been mostly used in the study of radiation grafting. The latter is highly recommended when industrial use and pilot scale production are sought, because the accelerator has an on/off function facilitating radiation safety management and the higher dose-rate electrons shorten the processing time for a high throughput.

Radiation grafting offers a way to introduce a functional property, i.e., proton conductivity in this case, into a preformed commodity polymer film. The procedure for obtaining PEMs by radiation grafting is illustrated in Fig. 2. In the most widely used approach, the base film is pre-irradiated using  $\gamma$ -radiation or an electron beam. During the next stage, for the grafting reaction, the activated film is brought into contact with the monomer in a liquid or vapor form. The grafted side chains are subsequently sulfonated to form ionic  $\text{SO}_3\text{H}$  groups in the PEMs.

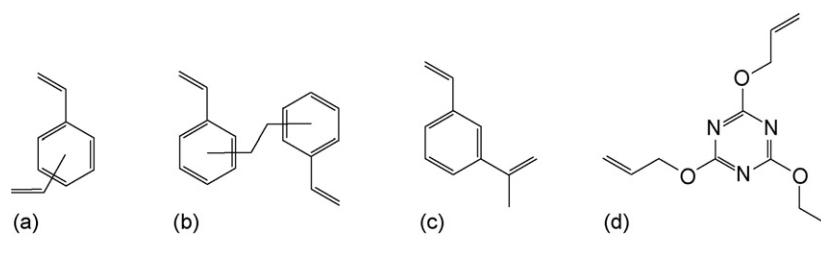
In principle, a wide selection of polymer films, fluorocarbon and hydrocarbon materials, would be possible for a base film in the radiation grafting process. However, fluoropolymers possess better chemical and thermal stabilities than hydrocarbon polymers and a high ability to generate stable radicals when exposed to ionizing radiation. These make the fluoropolymer film a favorable graft substrate, particularly in the preparation of PEMs, which would need a higher stability. Various kinds of commercially available fluoropolymer films, typically of thicknesses from 25 to 100  $\mu\text{m}$ , have been employed as a host matrix for maintaining a reasonable mechanical stability, including a defined swelling behavior in the



**Fig. 2.** PEM preparation by pre-irradiation-induced graft polymerization (radiation grafting) and sulfonation.

**Table 1**  
Some common base polymer films used for the preparation of the radiation-grafted PEMs.

Polymer	Abbreviation	Structure
<i>Perfluorinated polymers</i>		
Polytetrafluoroethylene	PTFE	$-(CF_2-CF_2)_n-$
Poly(tetrafluoroethylene-co-hexafluoroethylene)	FEP	$-\left[ (CF_2-CF_2)_x (CF_2-CF_2)_y \right]_n-$ CF <sub>3</sub>
Poly{tetrafluoroethylene-co-perfluoro(alkyl vinyl ether)}	PFA	$-\left[ (CF_2-CF_2)_x (CF_2-CF_2)_y \right]_n-$ OR <sub>f</sub>
<i>Partially fluorinated polymers</i>		
Poly(ethylene-co-tetrafluoroethylene)	ETFE	$-\left[ (CF_2-CF_2)_x (CH_2-CH_2)_y \right]_n-$
Poly(vinylidene fluoride)	PVDF	$-(CF_2-CH_2)_n-$

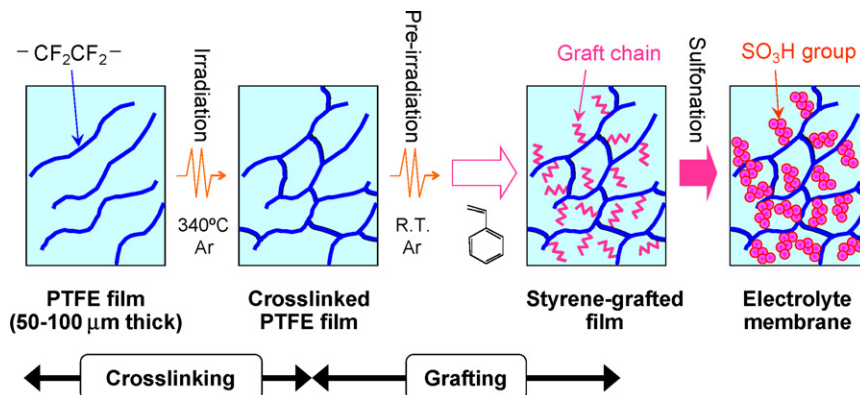


**Fig. 3.** Crosslinkers used as co-monomers in the radiation grafting process: (a) DVB, (b) BVPE, (c) *m*-diisopropenylbenzene (DIPB), and (d) TAC.

presence of water. Some of these polymers are listed in Table 1 together with their molecular structure.

Styrene has been used widely as a grafting monomer because it shows a favorable radical polymerization kinetics and the aromatic ring is readily sulfonated to introduce the ion exchange functionality. At the JAEA group, the grafted films were sulfonated with 0.2 mol dm<sup>-3</sup> chlorosulfonic acid in 1,2-dichloroethane at 50 °C for 6 h, followed by hydrolysis to obtain the SO<sub>3</sub>H functional group [4–17]. In most cases, the degree of sulfonation achieved was around 95%, in which complete sulfonation (100%) corresponds to one SO<sub>3</sub>H group per aromatic ring. Thus the number of ion exchange sites in the final PEM, characterized by the ion exchange capacity (IEC), will be a function of the degree of grafting.

Monomers with two or three vinyl groups are called crosslinkers, by which the grafted polymer chains are bridged and linked together (Fig. 3). Radiation-grafted sulfonated PEMs crosslinked chemically with divinylbenzene (DVB) have been extensively studied using various fluoropolymer substrates at the Paul Scherrer Institut (PSI) since the early 1990s [18–26]. The DVB-based crosslinks in the graft chain also had a significant influence on the water uptake, proton conductivity, and thermal or chemical stability of the PEMs [21–23]. It was also reported that crosslinking reduced the extent of the fuel/gas permeability [23]. Despite the importance of DVB regarding the improvement of the chemical stability, a major challenge in handling these crosslinked radiation-grafted PEMs was always their rather poor mechanical properties and relatively low proton conductivity, especially in the case of the



**Fig. 4.** Procedure for preparing radiation-grafted PEMs by two-step radiation technique, i.e., combining radiation crosslinking of PTFE with radiation grafting.

highly crosslinked PEMs. Recently, according to a careful design involving the balancing of the conductivity, mechanical properties, and actual fuel-cell performance or durability, the PSI researchers achieved a long-term operation up to 10,000 or 7,900 h at a cell temperature of 60 [25] or 80 °C [19], respectively.

### 3.2. Radiation crosslinking

A series of the author's studies originated from a strong motivation to use a radiation-crosslinked polytetrafluoroethylene (PTFE) film as a substrate for improving the PEM properties [4,5]. For the first time, the author's group combined the radiation grafting with another radiation technology, i.e., the crosslinking of the base polymer. Fig. 4 shows an example of his PEM preparation procedure. This two-step radiation process is a new concept of methodologies for radiation-grafted PEMs. In the following paragraphs, the radiation crosslinking of PTFE and preparation of the crosslinked PTFE-based PEMs are described.

In previous studies concerning the radiation chemistry of fluoropolymers [27,28], it was found that PTFE was crosslinked by  $\gamma$ -ray or electron beam irradiation in its molten state in an oxygen-free atmosphere. This was a surprising result because, until then, the effective degradation through main-chain scission was known to occur in PTFE irradiated at lower temperatures [29]. Crosslinked PTFE showed remarkable improvements in its radiation resistance and thermal and mechanical properties compared to the non-crosslinked one. Also, the crosslinking reduced the crystallinity by decreasing the crystalline size. The new substance possessing such unique properties has become the focus of the author's research from the standpoint of the development of high-performance PEMs.

Due to the high radiation resistance of the crosslinked PTFE, it is possible to irradiate it with higher irradiation doses than the non-crosslinked PTFE [30]. Over the investigated time range, the degree of grafting clearly increased with the pre-irradiation dose. It can be concluded that the degree of grafting was widely controlled by both the crosslinking density in the crosslinked PTFE film and the grafting conditions, such as the time and pre-irradiation dose.

It should also be noted that the crosslinking process of PTFE is necessary for improving the various properties of the resulting PEMs as well as for enhancing the graft yield of styrene. PEMs with an even distribution of sulfonic acid groups were successfully prepared by complete sulfonation of the graft polystyrene. The IEC of the PEMs, which was as high as or greater than  $3 \text{ meq g}^{-1}$ , was superior to Nafion. The PEMs with such a high ionic content, however, exhibited moderate osmotic swelling properties in water. For example, the area of Nafion in the water-swollen state increased by 42% over the dried state; in contrast, the PEMs based on the 320-kGy crosslinked PTFE, in spite of their high IEC reaching  $1.9 \text{ meq g}^{-1}$ , showed a lower area increase (36%) compared to Nafion. This dimensional stability is due to the use of the crosslinked PTFE films as radiation-graft substrates.

Crosslinked PTFE-based PEMs were investigated in terms of their proton conductivity [7,13] and methanol permeability [11,13]. The PEM with a higher IEC became more conductive; the PEM with an IEC of  $>3 \text{ meq g}^{-1}$  exhibited the maximum conductivity,  $0.27 \text{ S cm}^{-1}$  at a temperature of 80 °C and at a relative humidity (R.H.) of 95%, which is twice as high as that of Nafion. On the other hand, the present PEM is expected to exhibit a lower methanol permeability,  $P$ , because, in contrast to the linear-chain Nafion, it has a network structure due to the crosslinks in the PTFE substrate; in fact, it provided a defined swelling behavior in the water/methanol mixture at all concentrations. The  $P$  values appeared to increase with the IEC and, however, they all were lower than those of Nafion. The swelling and permeability decreased as the crosslinking den-

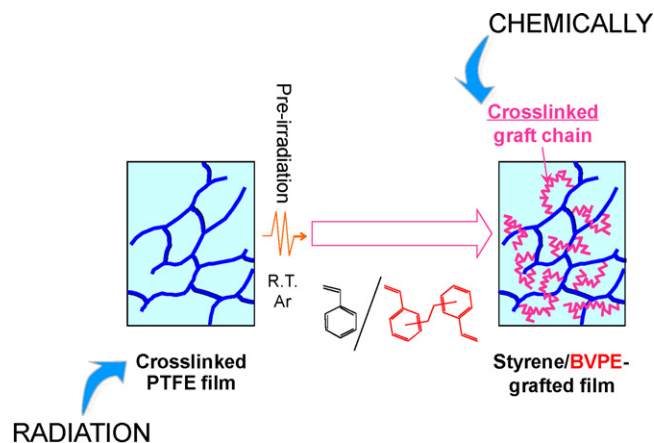


Fig. 5. Procedure for preparing “multiply” crosslinked PEMs by two-step radiation technique, i.e., combining radiation crosslinking of PTFE with radiation grafting of styrene/BVPE.

sity of the crosslinked PTFE increased, undoubtedly demonstrating the contribution of the crosslinking to the excellent barrier properties against methanol.

### 3.3. Recent progress

The author's JAEA group then tried to combine the crosslinked PTFE main chain with the grafts crosslinked via the crosslinker method mentioned in Section 3.1, expecting that the resulting “multiple” crosslinking structure will effectively improve the PEM performance and durability for fuel-cell applications. A similarly named concept, “double” crosslinking was previously introduced as a PEM preparation procedure, in which two types of crosslinkers, such as DVB and tricyanurate (TAC), were simultaneously grafted with styrene in the same grafting solution [22]. On the other hand, the strategy of “multiple” crosslinking is very different from this method. Fig. 5 shows a schematic structure of the copolymers comprising the “multiple”-crosslinked PEMs. The term “multiple” refers to a combination of a crosslinker-based graft network with a radiation-crosslinked fluoropolymer substrate; i.e., the crosslinking in both the main and side chains. Indeed, a recent paper dealt with the radiation grafting of styrene and a new crosslinker bis(vinyl phenyl)ethane (BVPE) using the base film of crosslinked PTFE [14]. The important result is that the BVPE-based crosslinks in the graft chain improved the chemical stability more than the conventional DVB-based ones, as well as decreased the water uptake and maintained a reasonable proton conductivity. It follows that the BVPE crosslinker was highly compatible with the radiation grafting into the crosslinked PTFE films for the development of high-performance PEMs. This is probably because, in contrast to DVB, BVPE should crosslink the graft chains rather uniformly and densely even when co-grafted into a diffusion-limited, crosslinked polymer [14].

Thus the author et al. investigated the  $\text{H}_2/\text{O}_2$  fuel-cell performance of this multiply crosslinked PEM, which comprises the crosslinked PTFE main chain and styrene/BVPE-based grafts [17]. The PEMs based on non-crosslinked or crosslinked PTFE, and grafted without any crosslinker were also obtained and compared for elucidating how the radiation or chemical crosslinking (in the main or graft chain, respectively) affected the characteristics of the membrane-electrode assembly (MEA). It is important that the cell performance of the multiply crosslinked PEM was found to be comparable to that of a Nafion112 membrane. This is probably because the BVPE crosslinks in the graft component improved not only the quality of the membrane-electrode interface, but also the PEM durability. Another advantage of the PEM was its low  $\text{H}_2$

permeation rate, which seemed to correlate with the observed high chemical stability. Consequently, a synergetic effect was seen as a joint result of the homogeneous crosslinking structures in the PTFE main chain and styrene/BVPE-based grafts. This satisfactory multiple crosslinking system could allow for decreasing the reactant permeability and for directly strengthening the chemical stability.

Until recently, a few research groups have attempted to apply the pre-irradiation method to new substrates of super engineering plastics, mostly based on aromatic polymers with high thermal and mechanical stabilities (for example, polyimide (PI) [31], polyether-sulfone (PES) [32], and poly(ether ether ketone) (PEEK) [33–35]). However, they were not sure that the grafting reactions had occurred; the active sites on the base polymer backbone, which would initiate the grafting, were not confirmed. The reason for this is that the aromatic polymers have mainly been investigated in terms of radiation resistivity from the standpoint of their practical applications in radioactive environments such as outer space and nuclear facilities. What is worse, a PEEK substrate incorporated poly(ethyl styrenesulfonate) (ETSS) graft chains even without any pre-irradiation; just immersing the base film in a hot monomer solution seemed to initiate some type of polymerization. None of the graft polymerizations could occur even if the graft methods were used in the preparation procedure.

Thus, a detailed  $\gamma$ -ray or electron beam radiolysis study on such new substrate materials should be done in order to understand the stability (lifetime and density) of free radicals and/or ionic chemical groups, post-irradiation products, and their properties. Electron spin resonance (ESR) will be used for detecting the transient species and for investigating their dynamic behavior in different atmospheres. The common methods of identifying molecular structures of organic compounds, Fourier transformed infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR), will also give one an insight into the radiolysis products on a molecular level. A measurement in contact with the monomers should work as an *in situ* analysis to understand the ongoing polymerization reactions.

## 4. Application of swift heavy ion beams

### 4.1. Ion-track technology and strategy for PEM preparations

In Section 3, attention was focused on the graft polymerization induced by a  $\gamma$ -ray or electron beam, which can randomly deposit energy in the polymer substrate. In most of these cases, it is crucial to consider that the proton-conductive graft polymers penetrate the entire substrate in order to prepare the fluoropolymer-based PEM for fuel cells. On the other hand, this section is concerned with the application of swift heavy ions, which enables one to obtain PEMs with the graft chains *partly* or *heterogeneously* introduced into the fluoropolymer film (Fig. 6).

The bombardment of heavy ions accelerated to energies from a few MeV amu<sup>-1</sup> to about 100 MeV amu<sup>-1</sup> (amu stands for atomic mass unit) produces a continuous trail of excited and ionized molecules in the polymers [36]. The high energy deposition unique to heavy-ion beam irradiation results in the formation of a highly localized damage area with a cylindrical shape, called a latent track. If proton-conductive SO<sub>3</sub>H groups are introduced only into these irradiated cylindrical regions, the surrounding substrate matrix without any modifications is expected to mechanically prevent any excess swelling, thereby reducing fuel permeation, and also to improve the thermal stability while the PEM maintains its proton conductivity.

The author et al. [37–39] tried to prepare PEMs characterized by their “controlled nano-scale structure” according to the two techniques shown in Fig. 7:

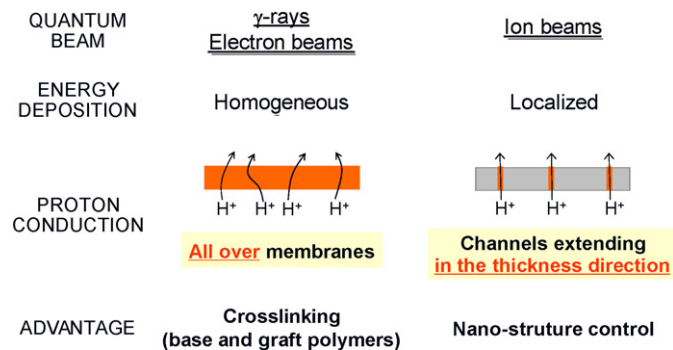


Fig. 6. Comparison between the two PEMs prepared by  $\gamma$ -ray or electron-beam based two-step process and ion-track technology.

Ion-track grafting in latent tracks [37]: this was extensively investigated as an alternative to reveal the latent tracks after the pioneering work of Monnin and Blanford [40]. Irradiation with high-energy heavy ions creates reactive species such as free radicals and their air-oxidized groups (peroxides and hydroperoxides) within the latent tracks. Thus, these are able to initiate the grafting of molecules or monomers to produce the graft polymer.

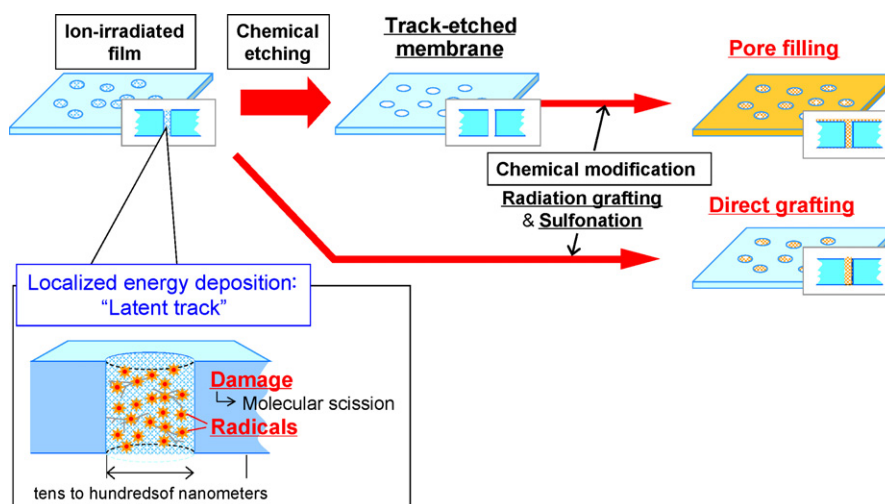
Radiation grafting into track-etched pores [38,39]: the other method is the preparation that involves chemical track etching for obtaining uniform nanometer to submicrometer pores and then chemical modification of the internal surfaces of the etched pores in order to fill them with proton-conductive parts (upper). In most cases, the surface modification could be completed by radiation grafting using various excitation sources:  $\gamma$ -ray, electron beam, X-ray, ultraviolet light and plasmas.

Both of these are the first successful applications of swift-heavy-ion-track technology for the development of PEMs for fuel-cell applications.

### 4.2. Ion track grafted membranes

Monnin and Blanford first performed ion-track grafting in latent tracks thirty-seven years ago for the detection of nuclear tracks [40]. Following their study, grafting onto PVDF films initiated by swift ion beams was accomplished by Betz's group at Saclay, France [40–42]. They optimized the conditions of the grafting in terms of the irradiation parameters, polymer substrate (type and thickness), type of ions (Xe, O, C, Ar, Kr, Sn, Pb), and polymerization parameters (temperature and monomers, e.g., methyl methacrylate, styrene, and acrylic acid). It was found that, because of the large mass of the particles used, the ion-track grafting was different from the  $\gamma$ -ray-induced one. Furthermore, the grafting yield and molar mass distribution were changed depending on the type of ions, i.e., the mass or energy. The chain length of the grafts and their polydispersities were also investigated. Basically, according to the ion-track grafting process as above, this methodology has been used for developing the fuel-cell PEMs (see the lower process in Fig. 7); the subsequent sulfonation, followed by hydrolysis, easily produces polystyrene sulfonic acid grafts [37].

The ion-track grafting of styrene was also carried out for the subsequent functionalization [42,43]. At equal doses, the degree of grafting increased with decreasing fluence of ions (the number of actually irradiated ions per 1 cm<sup>2</sup>); this was explained by a decrease in the intratrack recombination of active radicals with an increase in the distance between the tracks. An advantage of the heavy-ion based method is the possibility of attaining a high dose within a very short irradiation time. When the degree of grafting increased, the graft polymer progressively spread around the latent track, destroying the crystalline structure in the PVDF substrate and progressively covering its surface. However, the ion-track grafting



**Fig. 7.** Scheme for PEM preparation based on a heavy-ion irradiation method. Upper: the chemical track etching and subsequent grafting in etched pores pre-irradiated with other ionizing radiations. Lower: the ion-track grafting, i.e., the direct grafting into the localized tracks.

exhibited higher grafting yields and still had a more heterogeneous distribution of grafting at high graft yields than the  $\gamma$ -ray-induced one.

#### 4.3. PEMs prepared by filling track-etched pores

This sub-section deals with the preparation of PEMs characterized by their “controlled nano-scale structure” according to the process of the radiation grafting into track-etched pores (see the upper route in Fig. 7). To be specific, as reported by the Yamaki et al. [38,39], latent tracks in the PVDF film were preferentially dissolved in an alkaline etching solution to produce uniform pores with a diameter of less than a few hundred nanometers, which were then filled with proton-conductive  $\text{SO}_3\text{H}$  groups via the  $\gamma$ -ray-induced graft polymerization of styrene.

A similar concept of PEM development was previously proposed [44,45]. The pore-filling type PEM was prepared by anchoring the ion exchange polymer within the pores of a commercially available porous polymer matrix for DMFC applications [45]. However, the present approach of using the ion tracks is different in that the porous substrate had an excellent uniformity of pore diameters in contrast to the three-dimensional random porous media used in a previous study. Another difference was the membrane porosity, which is widely controlled by a change in the experimental conditions. This was maintained as low as possible (up to 30% at most) in expectation of an improvement in the mechanical properties, while the usual porous substrate exhibited a porosity of 50% or greater.

The characterization of the styrene-grafted, sulfonated PEMs was provided in terms of the proton conductivity, water uptake, and microscopic morphology. Table 2 lists the results for the PEMs prepared by filling the track-etched, 100-nm diameter pores [39]. The proton conductivities were compared between that perpendicular to and along the surface direction. The latter in-plane measurement was carried out using two electrodes in an alternate configuration on either side. The conductivity value in the thickness direction appeared to increase with the IEC. Surprisingly, however, no in-plane value was obtained at  $<1.6 \text{ meq g}^{-1}$ , probably because it was too low to be detected. This anisotropic conductive property undoubtedly indicates the formation of one-dimensional straight proton-conductive pathways parallel to the ion-beam incident axis. A transmission electron microscopy (TEM) image of a section of the PEM convinced one that it had a cylindrical conductive part with a diameter comparable to the size of the etched pore. This result demonstrates that grafting mainly occurred on the surface and

inner pore wall of the track-etched membrane without extensive styrene diffusion into the internal bulk layer.

A notable result was apparent from the comparison with the properties of not only a Nafion membrane, but also the PEMs obtained by the usual  $\gamma$ -ray-induced homogeneous grafting (see Fig. 6). The water uptake of the nano-structure controlled PEMs was found to be lower than the homogeneously grafted PEMs in spite of the same IEC; for example, it decreased from 36% to 23% (up to about two-thirds) at an IEC of  $1.6 \text{ meq g}^{-1}$ . An inert fluoropolymer host was found to restrict the swelling of the entire PEM.

## 5. Neutron beam application and future directions

### 5.1. Small-angle neutron scattering (SANS)

In fact, the research for the next-generation PEMs will be conducted with the objective of strengthening the fundamental study of the PEM characteristics and finding the optimum processing conditions for the most efficient cell operation possible. The latter includes the fabrication of an MEA, in which the PEMs were generally hotpressed together with electrodes having a catalyst loading. In the case of the radiation-grafted PEMs, their interface with the electrodes was found to have a poor quality compared to when Nafion or similar perfluorosulfonic acid PEMs are used. In other words, a higher interface resistance occurred in the MEA during the cell operation. Surface treatment made the PEM surface more hydrophilic, and control of the PEM properties, especially the mechanical properties, resulted in an extension of the reaction center, i.e., a microscopic three phase boundary between the catalyst, fuel gas, and electrolyte.

On the other hand, the basic research has also been critical for bridging the enormous gap between the present-day capability for PEM development and technology required for the market introduction of fuel-cell products, a gap faced in stationary and automotive applications; specifically, the cost of fuel cells must be lowered by a factor of ten or more, and the lifetimes should be thousands to tens thousands of hours at an operating temperature of  $100^\circ\text{C}$  or higher. Revolutionary conceptual breakthroughs only come from comprehensive basic investigations to figure out the structure and dynamic behavior in the PEM.

As to the above back-to-basics research on the radiation-grafted PEMs, for example, the author's group [46] at JAEA have been carrying out a SANS analysis of the crosslinked PTFE-based PEMs, which

**Table 2**  
Representative characterization results for the PEMs prepared by filling track-etched, 100-nm diameter pores.

Sample #	IEC (meq g <sup>-1</sup> )	Proton conductivity (S cm <sup>-1</sup> ) <sup>a</sup>		Water uptake <sup>b</sup> (%)
		(Thickness)	(In-plane)	
1	0.40	0.003	Not detectable	2.1
2	0.70	0.004	Not detectable	11
3	1.6	0.024	Not detectable	23
4	2.6	0.054	0.043	75
Nafion117	0.91	0.080	0.08	37

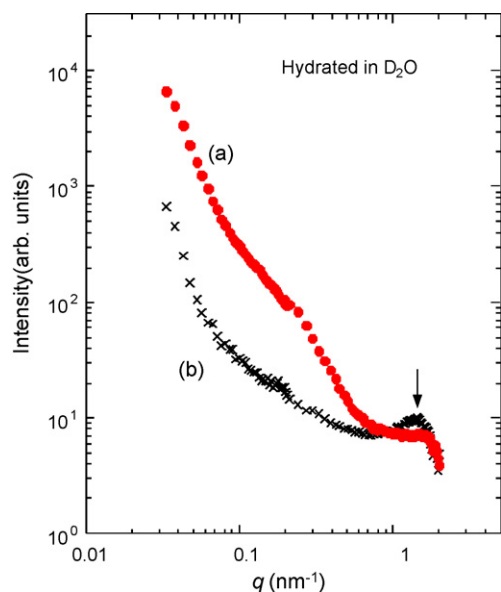
<sup>a</sup> Measured in the fully hydrated state at room temperature.

<sup>b</sup> Defined as:  $100(W_w - W_d)/W_d$ , where  $W_w$  and  $W_d$  are the membrane weights in the wet and dry states, respectively.

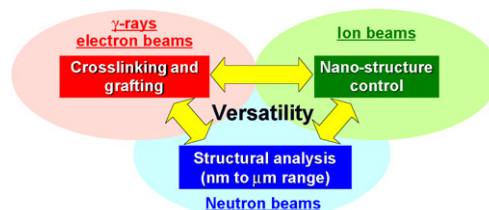
they originally developed as shown in Section 3.2. The vacuum-dried PEMs in the acid form were stored in deuterated water (D<sub>2</sub>O) before use. SANS experiments were carried out using the SANS-J instrument at the JRR-3M research reactor of JAEA. The scattering intensity was measured as a function of  $q$ , the magnitude of the scattering vector.  $q$  is related to the scattering angle,  $\theta$ , by the relationship  $q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  is the wavelength of the incident neutron beam (0.65 nm). The  $q$  range was varied from 0.03 to 2 nm<sup>-1</sup>.

Fig. 8 shows the SANS profile of the PEM based on the crosslinked PTFE (IEC = 2.0 meq g<sup>-1</sup>) together with that of Nafion for comparison. Nafion exhibited a characteristic scattering peak around  $q = 1.4 \text{ nm}^{-1}$ , corresponding to a Bragg distance of 4.2 nm. This so-called “ionomer peak” is due to a microphase separation between the hydrophilic ionic domains and hydrophobic polymer matrix. According to previous SANS experiments, water in Nafion was found to be localized and form pools embedded in the matrix. In contrast, an entirely different profile was obtained for the new PEM; an intense small-angle upturn in the intensity and no well-defined peak. This demonstrates that the crosslinked PTFE sulfonic acid PEMs will possess the structural properties which cannot be rationalized by the already presented models.

This analysis enabled them to compare their hierarchical structure, ranging from a molecular (nanometer) to higher-order architecture (micrometer) scale, with that of the Nafion membranes. The information in such a wide length scale led to a deep insight into the dynamic properties inside the PEM from the microscopic to macroscopic level, which can be of great value for the reconsideration and optimization of the preparation procedure.



**Fig. 8.** SANS profiles of the crosslinked PTFE-based electrolyte membrane and Nafion, both of which were swollen in deuterated water. The arrow indicates the “ionomer peak” on the Nafion pattern.



**Fig. 9.** Summary of the author's quantum-beam technology: a combination of three strategies has been emerging to produce a potential breakthrough in the existing research field.

## 5.2. Linkage with theoretical aspects

Quite interestingly, the same group [47] also started a theoretical simulation for understanding the structure of the PEMs and behavior of the species diffusing in them, i.e., protons, water, methanol, etc. The information mainly obtained from these fundamental studies will also provide feedback for the innovative design of radiation-grafted PEMs.

The researchers investigated the mesoscopic structure of crosslinked PTFE-based radiation-grafted PEMs using a dissipative particle dynamics (DPD) simulation. Based on the molecular structures, the fully hydrated PEM systems were constructed with the coarse-grained particles representing several atom groups. In the equilibrium state, water appeared to percolate into the poly(styrene sulfonic acid) (PSSA) graft chains to give a mixed phase, separated from the hydrophobic PTFE chains. This phase-separation picture is quite different from that of Nafion, in which only water gathered excluding any polymer parts and then formed its cluster. The radial distribution function between the water particles was then calculated in order to clarify the phase-separation structure quantitatively. As a result, there were found to be small-size water clusters with a diameter of only 1.8 nm in the water/graft polymer mixture regions.

## 6. Conclusions

The present paper summarizes up-to-date results of just the PEM synthesis using the author's quantum-beam technology. In particular, three brand-new strategies have been emerging to bring a potential breakthrough in the existing research field. The principles of these were emphasized as follows (Fig. 9):

- (i) As for application of  $\gamma$ -rays and electron beams, the radiation grafting was combined with another radiation technology, i.e., the crosslinking of the base polymer. As an example, the PEMs were prepared by the radiation crosslinking of fluoropolymers, including, but not limited to PTFE, and the subsequent styrene grafting followed by sulfonation. Of great interest was that this produced a crosslinked fluorocarbon main chain, which was absent in the Nafion-like membranes. The styrene/BVPE co-grafting appeared to be very compatible

with the crosslinked PTFE substrate; the combination of the crosslinked PTFE main chain and BVPE-based grafts, i.e., a perfect “multiple” crosslinking structure, is likely to effectively improve the PEM performances for fuel-cell applications, thus extending the performance beyond the limit of conventional PEMs.

- (ii) The swift heavy ions from the accelerators were used as a radiation source to modify only small regions of the substrate along the ion tracks. Researchers took the approach using this ion-track technology according to two techniques. One was the track etching and subsequent chemical modification inside the etched pores; and the other was ion-track grafting, i.e., direct grafting into the activated zone. For example, as the former case, PEMs were prepared by the  $\gamma$ -ray pre-irradiation grafting of styrene onto PVDF-based ion track membranes. One-dimensional straight proton-conductive pathways were formed in the direction perpendicular to the PEM surface. Its “controlled nano-scale structure” restricted the water uptake.
- (iii) The hierarchical structures of the PEMs, ranging from nanometers to micrometers, are revealed by SANS experiments using a cold or thermal neutron beam. The information in such a wide length scale led to a deep insight into the dynamic properties inside the PEM from the microscopic to macroscopic level, giving one feedback for the reconsideration and optimization of the preparation procedure.

It should be noted that these innovative-concept based approaches are applicable not only to high-performance fuel-cell PEMs, but, more broadly, to materials in other fields, such as separation processes and biological or biomedical uses. To this extreme end, the right beam choice has to be made on a basis of understanding that every quantum beam is different.

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