

博士論文（要約）

Application of Ion Track Technology to the Preparation of Anion Exchange Membranes for Fuel Cells

(燃料電池用アニオン交換膜の作製に向けたイオン飛跡技術の応用)

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論文の内容の要約

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Fuel cell is an electrochemical device that converts chemical energy into electricity. An important part of this device is the fuel cell membrane, which acts as the electrolytes that conduct ion. In this research, the author developed an anion exchange membrane type that has an advantage of allowing the use of non-noble metals as its electrode catalyst. Two of the most important properties in the AEMs are the OH⁻ conductivity and water uptake. The balance between these two properties is very important, as the ions need sufficient water content to mobilize but, on the other hand, the water content needs to be limited for maintaining the membrane physical properties. Until now, this requirement has not been satisfied by any membrane preparation methods.

The author applied the ion-track grafting technique to develop the AEMs adding a functional monomer such as a vinylbenzyl chloride (VBC) directly into the ion-irradiated base polymer *e.g.*, fluoropolymer film such as poly(ethylene-*co*-tetrafluoroethylene) (ETFE). In the ion-track grafting, the process specifically took place inside the latent track and thus it will create a heterogeneous grafted structure in the resulting membrane, which consist of the grafted and ungrafted area. The grafted area will increase the OH⁻ conductivity while the ungrafted area will limit the water uptake of the membrane.

In order to achieve the good properties of AEMs in the ion-track grafting method, a control of the heterogeneous grafted area is needed *i.e.*, the ratio of grafted and ungrafted area. This ratio can only be controlled through the ion-track structure *e.g.*, tracks size. Different ion-irradiation representing different linear energy transfer (LET) were applied to investigate the ion-track structure control.

The author investigated the ion-track structure from both theoretical and experimental point of view.

A 25- μm thick PVDF films were irradiated in a vacuum chamber with 450-MeV ^{129}Xe ions and 2.2-GeV ^{197}Au at fixed fluence of 3×10^7 ions cm^{-2} . Chemical etching was then performed in a 9 mol dm^{-3} KOH aqueous solution at 80°C while measuring the conductance through the film, which then converted into the effective pore diameter, d_{eff} .

The Katz-Waligórski radial dose distribution model was used for describing the LET effect on the ion-track structure. Higher LET ions showed higher energy deposition and larger radius track. In the experimental investigation, the conductometric track etching technique was applied to monitor the pore evolution during the etching. In this track structure studies, the author used poly(vinylidene fluoride) (PVDF) film for the track etching instead of the ETFE film due the difficulties in performing the etching on ETFE, however, the PVDF have similar chemical structure with ETFE. Interesting point in this result is that the ^{197}Au -irradiation increased the final stage of d_{eff} by 1.7 times over ^{129}Xe -, producing larger track-etched pores. This showed that the track structure can be controlled by employing ion irradiation with LET.

In the grafting reaction, it is well known that the amount of grafted polymer is influenced by its irradiation parameter, in the case of ion-track grafting; it will be the ion fluence. Thus, the author finds the necessity to find the method for evaluating the absolute fluence and its areal distribution in order to obtain clear fluence dependence in the ion-track grafting.

The author combined two familiar analysis factors, *i.e.*, the optical density of Gafchromic radiochromic film and pore density of irradiated polymer. The Gafchromic radiochromic film (GAF film), typically of HD-V2 type, was irradiated with 560 MeV ^{129}Xe at fluences of 10^8 to 10^9 ions/ cm^2 , and then analyzed in terms of a change in the optical density and its digitized data. After the track etching of the irradiated nuclear track detector, HARZLAS TNF-1, the resulting pore density was investigated by electron microscopic observations. Finally, a calibration curve could be used for conversion of the GAF film's absorbance to the absolute fluence, thereby enabling us to estimate the fluence distribution very easily. In principle, our new method can be applied for all of track-etchable polymer materials.

A key for success in preparing the AEMs is to obtain high graft levels (for higher conductivity) in as small a number of tracks as possible (for improving the other membrane properties). The strategy is to enhance the reactivity of the grafting by controlling the grafting conditions. In this section, the author utilized the poor solvent system as the grafting medium *i.e.*, the mixtures of H₂O-*i*PrOH at various compositions. The investigation deals with the analysis of the kinetic parameters of grafting because it is important to understand how the media would affect the apparent reaction rate for obtaining a method to prepare rapid and reproducible membrane.

A 25 μm-thick ETFE film was irradiated in a vacuum chamber with 560-MeV ¹²⁹Xe ions at fluence of 3×10⁹ ions cm⁻². After the irradiation, the films were exposed to air and then stored in -80°C until just before used. The grafting polymerization was initiated by immersing the irradiated ETFE films at a constant concentration of 20vol% VBC monomer in the H₂O-*i*PrOH mixture. The volume fraction of H₂O in the grafting medium was varied from 0 to 1. The monomer mixture was kept under continuous stirring at 60°C after bubbling with Ar for 15 min. The grafted films were then washed with toluene at 60°C and dried at 40°C in a vacuum; this was done until a constant weight was achieved. The DG was calculated by

$$DG = \frac{(W_g - W_0)}{W_0} \times 100 (\%) \quad (1)$$

where W₀ and W_g are the weights of the film before and after the grafting, respectively.

The optimum H₂O-*i*PrOH composition was identified by the kinetic parameters including the time required for the monomer to penetrate from the surface into the center of the substrate (t₀), the initial polymerization rate (r_{p0}), the radical recombination rate (γ) and the grafting efficiency (r_{p0}/γ). These parameters changed depending on the VBC-grafting/chain-transfer reaction competition for the radicals on ETFE and the Trommsdorff effect; the swelling of the grafting substrate gave an additional effect.

As discussed above, the author needs to control the track structure for obtaining the desired membrane properties, which can be achieved by using ion

irradiation with different mass and energy. Therefore, in this section, the author investigated the effect of different track structure on the ion track grafting *i.e.*, 560-MeV ^{129}Xe and 330-MeV ^{40}Ar . In particular, free radicals play an important role as initiator in the grafting reaction, and so their behavior was analyzed by ESR measurements.

From the ESR analysis, a higher LET ion was found to have lower radical concentration due to high probability of radical recombination and the type of radical that probably existed in both irradiated films was an allyl peroxy radical because of its most stable chemical structure. Radical concentration as a function of dose showed a linear relationship, while the DG analysis as a function of dose showed saturated trend at higher dose for both Xe- and Ar-irradiated films.

Subsequently, no effect of fluence was found in the local radical density at room temperature, meanwhile the local grafting density showed significant decreased at increasing fluence. The decreased of local grafting density was assumed due to the temperature increased in the grafting reaction that led to a decreased of the radical density. Further analysis on the local DG density, the decreasing of the local DG was found to be started from a certain value of fluence that signified the probability of overlapping fluence.

The grafted membranes were changed into anion exchange form by quaternized the grafted chain with amine group and subsequently immersed in alkaline solution to obtain the $-\text{OH}$ AEMs type. This form of membrane is very sensitive as it can interact with CO_2 from the air and cause a decreased in the membrane performance. Thus, during the measurements, the membranes should have as minimum as possible contact with air.

It was found that by diversifying the DG, we can control the IEC and that higher IEC will lead to high OH^- conductivity as well as high water uptake. However, higher IEC was not a key factor to give better fuel cell performance of AEMs. The most important is to keep the balance between the OH^- conductivity and water uptake and this can be achieved by the control of track structure.