Fabrication of PEFC Membrane Based on Fluorinated Polymer-alloy Thin Film by EB-Grafting

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Polymer electrolyte fuel cells (PEFC) using proton exchange membranes (PEM) have attracted much attention for the electrical vehicle and other mobile applications. The conventional type PEM like perfluoro-sulfonic acid membranes (PFSA) such as Nafion® (DuPont de Nemours LTD.) has some problems such as insufficient gas barrier properties, mechanical properties, low thermal resistance, and so on.

In this study, we have fabricated very thin fluorinated-polymer films with 3D-structure (PTFE/PFA polymer-alloy and PTFE/FEP polymer-alloy) by new compact coating equipment and electron beam (EB) irradiation system. Thus, we have fabricated PEM by EB-grafting of styrene onto crosslinked fluorinated-polymers by liquid phase reaction method and subsequent sulfonation. The characteristic properties of obtained materials have been discussed.

The grafting yields of all PTFE/PFA and PTFE/FEP polymer-alloys with various network densities increased with progress of reaction periods, and then saturated about 5~8hrs. The higher amount of PFA or FEP contents showed the higher grafting yields. And also the higher network densities showed higher grafting yields.

The glass transition temperature (T_g) of the styrene-grafted materials was measured by differential scanning calorimeter (DSC). Tg showed about 105±5°C.

The grafted materials were sulfonated by chlorosulfonic acid. Figure 1 shows the thermogravimetric curves of sulfonated PTFE/PFA polymer-alloys with various network densities: 150kGy, 450kGy and 600kGy. Water uptake was determined as the weight change from room temperature to 150°C. The water uptake decreased with increment of network density. It is indicating that the network structure would prevent from swelling. The weight loss about 300°C suggests removal of sulfonic acid groups, about 400°C indicates decomposition of grafted styrene, from 520°C~ indicates decomposition of the main chain of polymer.

The IEC values of sulfonated materials based on PTFE/PFA and PTFE/FEP polymer-alloys have been achieved ~3.0meq/g, which are about three times higher than those of commercial PFSA.

By SAXRD, it is found that the higher network densities would give the smaller cluster sizes in sulfonated materials. Thus, the higher amounts of PFA and FEP will give the smaller cluster formation of sulfonated materials.

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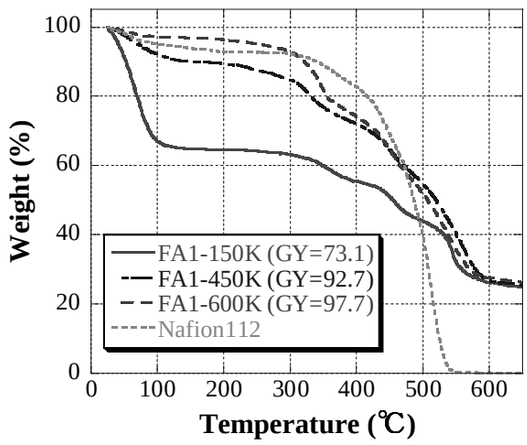

Fig.1 The results of thermogravimetric analysis of sulfonated membranes with various crosslinking density. Heating rate : 10℃/min