The thin membrane of sulfonated Crosslinked Polytetrafluoroethylene for Poly-Electrolyte Fuel Cell

- S. Ichizuri, S. Asano, F. Muto, J. Li (University of waseda), S. Ikeda, M. Iida (RAYTECH Corporation), T. Miura (University of waseda), C. Matsuura, Y. Katsumura (University of Tokyo), A. Oshima, and M. Washio (University of waseda)

The ready-made perfluoro-sulfonic acid membranes (PFSA) such as Nafion® (DuPont de Nemours LTD.) have been the popular proton exchange membrane (PEM) used in polymer electrolyte fuel cell (PFEC). However there are still several problems such as insufficient gas barrier properties, mechanical properties, low thermal resistance, and their high costs.
In this study, we have tried to fabricate PEM by radiation-induced grafting of styrene onto very thin crosslinked polytetrafluoroethylene (RX) with various crosslinking densities and subsequent sulfonation. The relationship between thermal durability of sulfonated RX (s-RX) and crosslinking dose has been examined. The characteristic properties of obtained materials have been discussed.

Ion exchange capacity (IEC) of obtained materials was determined by acid-base titration. Figure 1 shows the relationship IEC and the grafting yields (GY) of the s-RXs. Expected value means that one sulfonic acid group reacts to one styrene molecule. Experimental values were almost same with expected value. This means that the sulfonic acid groups react with styrene monomer by approximately one to one. Thus, IEC value is strongly dependent on grafting yields. IEC value of s-RX (GY: 72%) can be achieved about 2.8meq/g.

The thermal durability of obtained materials has been measured by TGA. Fig 2 shows TGA curves of s-RXs with various crosslinking densities. Water uptake was determined as the weight change from room temperature to 150°C. The water uptake decreased with increment of crosslinking densities. It is indicating that the network structure would prevent from swelling. The weight loss about 300°C suggests decomposition of sulfonic acid groups, about 400°C indicates decomposition of grafted styrene, from 520°C~ indicates decomposition of the main chain of polymer. By DSC, cluster size of s-RX has been measured. It was found that the higher crosslinking densities would give the smaller cluster sizes in s-RX. Thus, the higher crosslinking density would be forming the smaller cluster. Cluster size of s-RX-600K (IEC: 2.9meq/g, GY: 75%) and s-RX-150K (IEC: 2.8meq/g, GY: 64%) have cluster sizes of 7nm and 9.8nm, respectively. Ion conductivity of s-RX-450K had showed about 0.1S/cm at 80°C.

Acknowledgements
This research and development were supported by projects of “Research and Development of Polymer Electrolyte Fuel Cell” in NEDO.

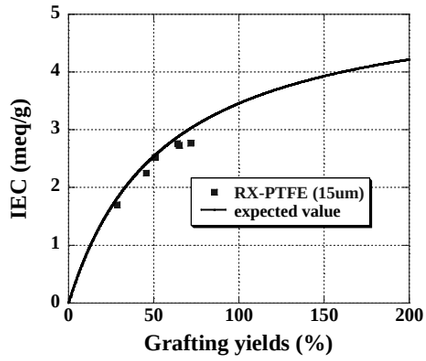

Figure 1: The relationship between IEC and the grafting yields of s-RXs.

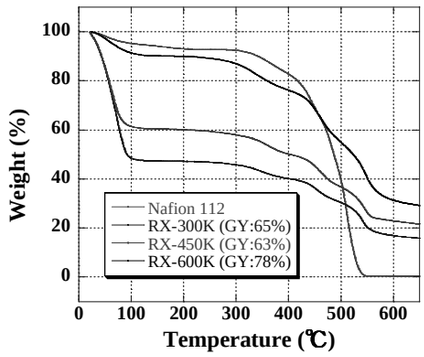

Fig 2 shows TGA curve s of s-RXs with various crosslinking densities