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Radiation Grafted Membranes for Fuel Cells: Strategies to Compete with PFSA Membranes

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Proton exchange membranes based on chemistries other than perfluoroalkylsulfonic acid (PFSA) are developed with the prospect of low cost, while aiming at maintaining or improving the functionalities of PFSA ionomer membranes, such as the dimensional stability or the creep resistance at temperatures above 90°C.

Radiation grafted membranes offer several combined key benefits of PFSAs and hydrocarbon (HC) membranes. The synthesis involves the electron beam irradiation of a preformed polymer film, such as ETFE, followed by grafting of styrene or styrene derivatives, in many cases in combination with additional co-monomers, and subsequent sulfonation to obtain a proton conducting membrane (Fig. 1). The use of low-cost materials and processing steps offers the potential of producing low-cost membranes if fabricated on a reel-to-reel facility [1]. The flexible alkyl chains favor phase separation of the graft component from the hydrophobic, partially fluorinated backbone [2]. In addition, the membrane architecture can be designed in a wide parameter space based on the choice of suitable co-monomers, e.g., crosslinkers or compounds that improve gas barrier properties, and the adjustment of key properties, such as degree of grafting, ion exchange capacity, and extent of crosslinking [3].

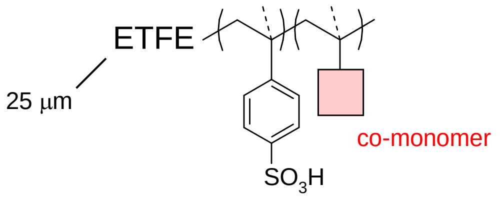

Fig. 1: Schematic structure of radiation grafted membrane based on sulfonated styrene or its derivatives.

The conductivity of radiation grafted membranes can easily reach or exceed that of PFSA membranes. Pure styrene grafted and sulfonated membranes, however, suffer from poor chemical stability in the fuel cell environment and fail typically within 50 to 100 h at 80°C. The durability and lifetime of grafted membranes can be substantially improved based on the following approaches:

i) Crosslinking leads to an improved dimensional stability, lower reactant crossover and superior resistance to chemical degradation.

ii) The replacement of styrene by α-methylstyrene (AMS) reduces the vulnerability of the grafted chain to radical attack, owing to the protected α-position. Due to the poor radical polymerization kinetics of AMS, a suitable co-monomer has to be used as polymerization promoter.

iii) The use of non-crosslinking co-monomers with specific functionality has been shown to be of advantage. Acrylonitrile and methacrylonitrile improve the gas barrier properties of the membranes and thereby improve the chemical stability.

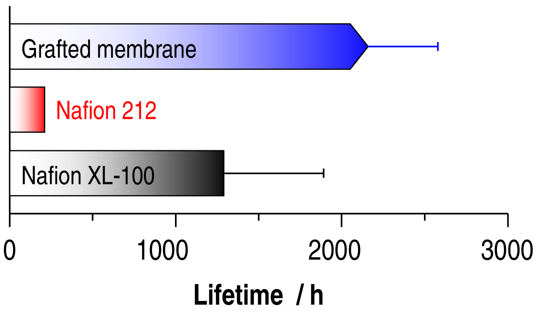

Fig. 2: MEA lifetime under dynamic operating conditions (80°C, 2.5 bar$_a$, 50 % r.h.). 2/3 of the grafted membranes were still intact at the end of test after 2’400 h.

Based on the insights gained, an optimized membrane was designed and tested, using commercial gas diffusion electrodes, under simulated automotive operating conditions with dynamic load protocol and compared against MEAs based on commercially available PFSA membranes (Fig. 2). The grafted membranes outlasted Nafion 212 by a large margin and also compared favorably against Nafion XL-100, a mechanically and chemically stabilized PFSA membrane.

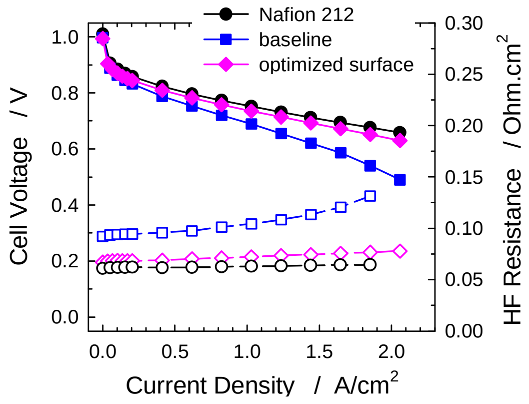

Fig. 3: Single H_2/O_2 cell performance at 80°C and 2.5 bar$_a$ pressure (gases fully humidified).

Optimization of membrane performance involves, on the one hand, the adjustment of the bulk composition and morphology of the material to maximize conductivity while maintaining chemical and mechanical stability. On the other hand, the process of radiation induced grafting can lead to limited functional (i.e., ion exchange) groups in surface-near regions. Therefore, the synthesis steps need to be adapted to prevent surface deactivation in order to result in improved performance (Fig. 3).

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