Expertise of perfluorosulfonic acid membranes by thermogravimetric analysis coupled to mass spectroscopy (TG-MS)

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Perfluorosulphonic acid (PFSA) ionomer membranes are used for fuel cell and electrolyser applications or sensors for chemical. Their properties depends on the side chain structure (Figure 1). This side chain bearing sulfonic acid moieties undergoes chemical degradation after operation such as crosslinking. One way to identify these chemical changes is to investigate PFSA with different Ion Exchange Capacity (IEC) using thermogravimetric analyser coupled to mass spectrometers (TG/MS).

First, in order to identify the key fragments and their corresponding mass numbers, MS analysis was performed using the m/z scan mode on the PFSA membrane. The scan reveals 25 main fragments, plus the isotopes. According to the signal shape and the temperature of evolved gases, m/z signals were then grouped to determine nature of the products formed during degradation. The thermal decomposition of the membrane exhibits three steps. Two of them originate from side chain degradation [1]. Indeed, the m/z 64 signal related to of SO_2 degradation products as a function of temperature shows two steps of the formation of the SO_2^+ fragment. The fraction of SO_2 formed in the first remains constant to 62 ± 1 % regardless of the IEC or the length of the side chain [2]. Thanks to the TGA signal, the first step degradation in the 210°C to 375°C temperature range was assigned to triflic acid formation.

Then, TGA-MS studies were done for PFSA membrane aged in low relative humidity conditions and foreign cation exchange PFSA membrane [3, 4]. These specific ageing results in covalent or ionic crosslinking, respectively occurring in FC operations. The m/z 64 signal (figure 2) analyses clearly allow the identification type and the quantification of the crosslinking of the sulfonic moieties.

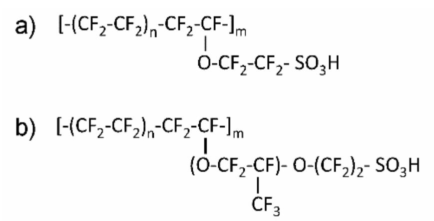

Figure 1 : *Chemical structures of PFSA membrane - a) Short Side Chain (SSC) type membrane, b) Long Side Chain (LSC) type membrane*

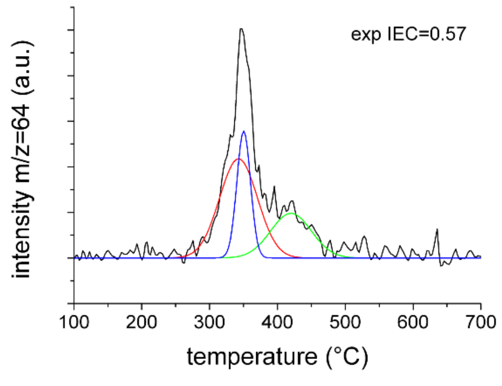

Figure 2 : m/z 64 signal versus temperature for membrane with 50% of covalent crosslinking

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4. Bas, C., N.D. Albérola, and L. Flandin, *Effects of contaminant on thermal properties in perfluorinated sulfonic acid membranes.* J. Memb. Sci., 2010. **363**: p. 67-71.