

## Ex situ hydrolytic degradation of sulfonated polyimide membranes for fuel cells

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### Abstract

Ex situ hydrolytic stability of sulfonated polyimide (s-PI) membranes for fuel cells was studied depending on structural and external parameters including the ion exchange capacity, the block character, the temperature and the hydrogen peroxide concentration. Infrared spectroscopy was used to identify and quantify the chemical modifications such as the loss of imide functions and of ionic monomers. The decrease in ion exchange capacity due to the elution of sulfonated oligomers was confirmed by sulfur content analysis. A complete hydrolysis of some of the imide functions is observed leading to polymer chain scissions and to the loss of the mechanical properties. It is shown to be a thermo activated process and the activation energy (60 kJ/mol) is found in good agreement with the value determined from fuel cell lifetimes. The degradation in fuel cell conditions is similar but faster than in pure water. The same kinetic can be reproduced ex situ by addition 0.05% of hydrogen peroxide.  
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### 1. Introduction

Proton exchange membrane fuel cells (PEMFC) are considered as the most promising power source for automotive and portable applications [1]. The PEMFC core component is the membrane-electrode assembly (MEA) usually based on perfluorosulfonated ionomer membranes (Nafion<sup>®</sup> type). However, the development of PEMFC prototypes has pointed out some major drawbacks of the perfluorosulfonated materials such as the MEA degradation under cycling conditions, the loss of performance at elevated temperatures and excessive production costs. Alternative low cost membranes with improved properties are thus needed to be developed and many different structures were investigated during the last ten years [2–4]. These structures are mainly sulfonated aromatic thermostable polymers such as polyetherketones, polysulfones, polyparaphenylenes or polybenzimidazoles. Among these new

polymers, sulfonated polyimides (sPI) based on naphthalenic moieties are considered as promising materials owing to their interesting swelling, mechanical and conducting properties [5–10].

Sulfonated polyaromatic membranes exhibit a low stability in fuel cell conditions, which does not exceed 1000 h of operation even under stationary conditions [11]. Up to now, no PEMFC stack with such membranes has been disclosed mainly because of their lack of long-term stability. Surprisingly, the stability is not one of the studied properties for new polymers. Therefore, only few data have been published and adapted quantitative protocols have not been yet developed to evaluate the stability neither in situ in fuel cells nor ex situ. In the literature, most of the works on membrane stability deals with either sulfonated polystyrenes or sulfonated polyimides [12–16]. While polymer chain scissions due to radical attacks have been evidenced for sulfonated polystyrene membranes, the sPI degradation is attributed to a high sensitivity to hydrolysis. Their lifetime under operating conditions was shown to vary from only few tenths of hours to 1000 h depending on the membrane ion exchange capacity (IEC) and the operating temperature [16]. Sulfonated polyimides are synthesized by polycondensation using a commercial naphthalenic dianhydride

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monomer and different sulfonated and non-sulfonated diamines, which proportions are adjusted to control the IEC value. The main development in the field of sulfonated polyimide membranes is currently the use of chemically modified diamines to enhance the stability against hydrolytic and oxidative attacks [17,18]. The membrane stability is usually estimated through the loss of the mechanical properties when immersed at elevated temperature (80 °C) in either pure water or more or less concentrated hydrogen peroxide solutions (Fenton reactants). However, the evaluation of the loss of mechanical properties is restricted to the determination of the immersion time until membrane dissolution or breaking when lightly bent [19,20]. This measurement is somewhat approximate since there is no information about the degradation kinetics and it strongly depends on the operator. Moreover, the membrane rupture occurs at a critical polymer chain length, which depends on both the initial molecular weight and the polymer chain scission kinetic. Since, molecular weights are not measured independently, an anticipated breaking of the membrane could be attributed a lack of stability while it can be due to a problem encountered during the synthesis, which has limited the polymer chain length.

The main objective of the present work is to characterize the hydrolysis phenomenon by ex situ degradation studies depending on the relevant parameters such as IEC, temperature and block character. The second objective is the development and the validation of new protocols to evaluate quickly the membrane stability instead of performing long and expensive fuel cell tests. These protocols involve infrared spectroscopy (IR), sulfur content determination through the use of energy dispersive X-ray analysis by scanning electron microscopy (SEM EDX) and mechanical properties determination. Finally, the kinetics of ex situ degradation in hydrogen peroxide solutions are compared to the degradation in fuel cell conditions and the appropriate concentration is determined.

## 2. Experimental

### 2.1. Materials

Different series of sPI have been synthesized in *m*-cresol by the LMOPS (CNRS, Vernaison, France) based on naphthalenic

dianhydride, di amino biphenyl disulfonic acid (BDSA) and a 1:1 mixture of 4-4' and 3-4' oxydianiline (ODA) monomers according to the previously described procedure [21]. The one pot two step polycondensation leads to block copolymers characterized by *X* and *Y* the average sequence lengths of the sulfonated and non-sulfonated blocks (Fig. 1). The ion content (IEC) was adjusted by the ratio *X/Y* during the synthesis. In this work, the ionic block length sequence was varied from *X*=3 to 9. Random copolymers (*X*=1) were not studied since the synthesis cannot be performed using the same procedure. For each ionic block length, three polymers were prepared with different IEC values (0.9, 1.3 and 2 mequiv./g corresponding to *X/Y*=20/80, 30/70 and 50/50, respectively, as molar ratio between sulfonated and non-sulfonated diamines). In the following, the notation for sPI polymers will be as IEC/*X*–*Y* sPI.

sPI solutions were filtered (5 μm) at elevated temperature to remove the largest aggregates and so forth to avoid macroscopic defects. This filtration does not modify the ionomer composition since the ion exchange capacity of the final material was found to correspond to the theoretical value. Membranes were then prepared by solution casting on a hot glass plate by the CEA-Le Ripault (France). A thermal treatment at 150 °C was applied to eliminate the solvent and to insure a complete imidization reaction. After solvent evaporation, sPI membranes were washed 4 h in 1:1 water methanol solution to remove the residual *m*-cresol. They were then acidified in a 0.5 M sulphuric acid solution in order to eliminate the triethylammonium ion used to solubilize the sulfonated monomer during the polymer synthesis.

### 2.2. Membrane characterization

Stress–strain curves were obtained using an Instron 4301 with 3 mm/min as test rate. The membranes were cut using a punch with 4.25 and 0.95 mm as nominal gauge length and width, respectively. These small sample dimensions can be used since the membranes are very thin (40 μm) and it limits the area of samples necessary for the experiments. The membrane mechanical properties are very sensitive to the water content in terms of both Young modulus and elongation at break. The membranes were kept immersed in water during the measurements to insure reproducible experimental

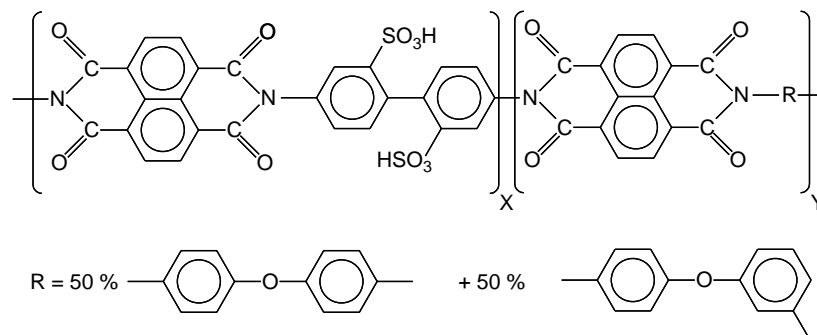


Fig. 1. General chemical formula of sulfonated polyimides.

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