Sulfonated poly(benzoyl paraphenylene) as a membrane for PEMFC: Ex situ and in situ experiments of thermal and chemical stability

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ABSTRACT

The stability of proton conducting polymers under aggressive conditions in a fuel cell (FC) is one of the major challenges in the development of FCs based on proton exchange membranes (PEMs). This study is focused on the determination of the stability of sulfonated poly(benzoyl paraphenylene) (SParmax) membranes exposed to elevated temperature (100−350 °C) and highly reactive radicals. To determine the durability of SParmax, attenuated total reflectance infrared spectroscopy (ATR-FTIR), electron spin resonance (ESR), and thermogravimetric analysis coupled with quadrupole mass spectrometry (TGA/QMS) methods were applied. In situ experiments using a FC inserted into the resonator of the ESR spectrometer combined with spin trapping offered the possibility to detect separately processes at the anode and cathode sides and to monitor the formation of radicals responsible for membrane degradation. The radical species ($H^•$, $D^•$, $HO^•$, $DO^•$) were detected immediately after the flow of feeding gases started. However, membrane-derived degradation products, such as carbon-centered radicals (CCRs) or formation of carbonyl bonds, were detected only in ex situ experiments when the samples were degraded at 250 °C during 1 h.

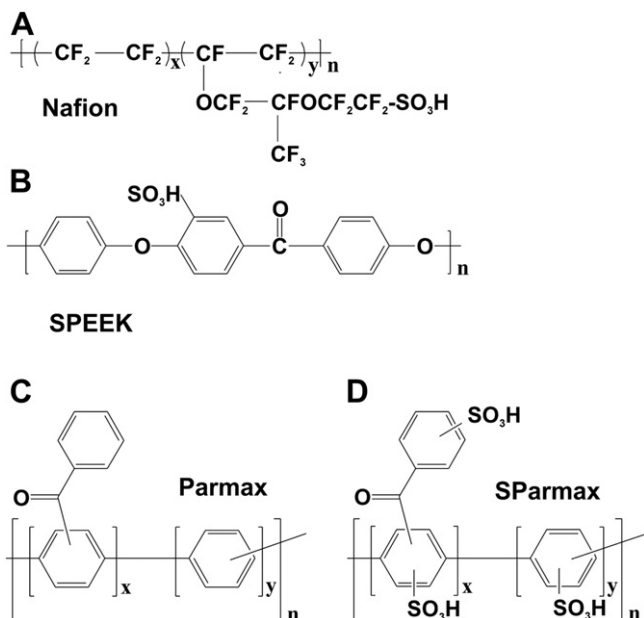© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Fuel cells (FCs), which are electrochemical devices that efficiently convert the chemical energy from the reaction of oxygen and hydrogen to electrical energy, have the potential to become alternative sources of clean energy for automotive, portable and stationary applications. Although FCs were invented in the first half of the nineteenth century, the real application happened only in the 1960s, when the fuel cells were used for energy and water in the U.S. Gemini program. The main advantages of FCs are their environmental friendliness and their efficiency, which is twice that of the internal combustion engines [1]. Proton exchange membrane fuel cells (PEMFC), with hydrogen or methanol as fuels, are the most studied of the wide range of FC types. In these FCs the ionomer membrane performs an essential role by separating the anode and cathode sections, and allowing proton conductivity.

The first proton exchange membrane used in the Gemini program was a crosslinked polystyrene sulfonic acid (PSSA), but most commercially used PEMs are based on perfluorinated hydrocarbons, and the best known is Nafion® (Fig. 1A) developed 50 years ago by Walther Grot of DuPont [2]. Perfluorosulfonic acid (PFSA) membranes offer good thermal and chemical stability as well as high proton conductivity (up to 0.30 S cm⁻¹) when the relative humidity is suitable [3]. However, these PFSA membranes have some limitations, among them their high cost and safety concerns related with use of tetrafluoroethylene, the molecule for the synthesis of all aliphatic perfluorinated hydrocarbons. In addition, the properties of PFSA membranes are not satisfactory for use above 100 °C or when methanol is used as fuel in direct methanol FC, due to high methanol permeability. Therefore use of alternative, hydrocarbon-based polymers is desirable. Durable aromatic polymers such as example poly(arylene ethers), polyimides, polyetherimides, poly-benzoimidazole, and poly(benzobisthiazole) functionalized with sulfonic acid groups are promising alternatives for perfluorinated PEMs and have been widely explored in recent years [4–7]. Among them the most suitable for PEM applications are sulfonated poly(-phenylene sulfones), poly(sulfones) poly(ether ketones); sulfonated poly(ether ether ketone) (SPEEK), commonly used as a benchmark

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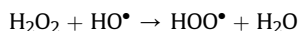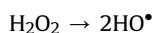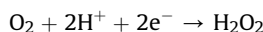 [1] On leave from the Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

Fig. 1. The structure of (A) Nafion®, (B) SPEEK, (C) Parmax™ 1200 and (D) sulfonated Parmax™ 1200. Parmax 1200 contains approximately 15% meta linkages that do not contain any side chains; $x = 15\%$, $y = 85\%$.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$H_2O_2 \rightarrow 2HO^\bullet$$

$$H_2O_2 + HO^\bullet \rightarrow HOO^\bullet + H_2O$$

Both $HO^\bullet$ and $HOO^\bullet$ are reactive oxygen species and it is commonly accepted that these radicals initiate PEMs degradation [28–30].

In the present study, a commercially available polymer has been investigated in order to determine its resistance to high temperature and to reactive species such as hydroxyl and peroxy radicals. The combination of different characterization methods gave wider perspective on SParmax stability and degradation pathways. The thermal resistance of SParmax was determined in ex situ experiments by thermogravimetric analysis and accelerated degradation at temperature range of 100–600 °C. The appearance of new bands in the ATR-FTIR spectra was used to follow degradation processes. The presence of radicals formed at the cathode and anode was determined by direct ESR and by spin trapping ESR spectroscopy [31]. The spin trapping method is based on scavenging of short-lived radicals by spin traps and formation of more stable adducts, typically nitroxide radicals [32]. In most cases the ESR spectra of spin adducts exhibit hyperfine splittings (hfs) from ^{14}N and H_β nuclei, a_N and a_H, respectively, and from these parameters it is often possible to identify the trapped radicals [33,34]. Identification of radicals formed during membrane degradation can provide useful information on the degradation mechanism. The detection and identification of reactive intermediates generated during FC operation can encourage the synthesis of polymers resistant in the oxidizing environment of FCs.

2. Experimental section

2.1. Materials

5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was obtained from Alexis Biochemicals and was used without further purification. Aqueous solutions of H_2O_2 (3%) were from Fisher Scientific. The other solvents used in this study were obtained from Sigma–Aldrich. Deionized "ultra pure" water with low conductivity and less than 10 ppb total organic carbon was provided by the Millipore Direct-Q UV system and used for preparation of the aqueous dispersions. Parmax 1200 manufactured by Mississippi Polymer Technologies Inc. (MPT) and Sulfonated Parmax (SParmax) was prepared by General Motors Electrochemical Energy Research Lab. Hydrogen (99.9%), oxygen (99.6%) and nitrogen (99.9%) gases were obtained from Purity Plus Specialty Gases. Deuterium (99.8%) was purchased from Sigma Aldrich.

Sulfonic acid functionalization was performed by sulfonation of Parmax 1200 in 30% oleum solution for 43 h. The density of the sulfonated polymer was 1.57 g/cm³. SParmax membranes with equivalent weight (EW) of 575 were obtained by casting, as follows: SParmax was dissolved in a 1:1:1 mixture of THF, methanol and N,N-dimethylacetamide. Water swelling of the SParmax membrane was 90 wt % at room temperature. The proton conductivity was measured by impedance spectroscopy. A sinusoidal voltage of 10 mV was applied to the sample in the frequency range of 10^7–10 Hz, and the resulting current was recorded. Measurements were performed on AUTOLAB PGSTAT302N spectrometer. In order to perform measurements on water-saturated membranes, the polymer sample was swollen in water for at least 24 h. Measurements of the membrane conductivity were carried in hermetically sealed battery casing (CR 1620). Springs were used to apply a constant pressure between casing and electrodes, thus facilitating good

hydrocarbon polymer (Fig. 1B) [8–11]. The membranes showed performance comparable to Nafion® combined with lower hydrogen and oxygen permeability [12–15]. The synthesis of functionalized polybenzoimidazole, the properties of native and doped polymers, and the membrane casting procedures and their performance in FC application have been studied [16–19]. Polybenzoimidazole membranes show the potential to be used at high temperature PEMFC (150–200 °C), particularly when doped with strong inorganic acids [20]. Properties of the aromatic based PEMs improved significantly when the ionic groups are located on short side chains. This enhances proton conductivity and stabilizes the membrane toward excessive swelling [21–23].

We have focused our attention on sulfonic acid functionalized poly(benzoyl paraphenylene) as a possible material for operating FCs. Poly(benzoyl paraphenylene), under the trademark Parmax 1200 (Fig. 1C) is a robust, commercially available, high performance amorphous thermoplastic polymer, which offers excellent chemical and physical properties, including great thermal-oxidative stability [24,25]. The paraphenylene chain provides a stiff and resistant backbone, whereas the pendant benzoyl group enables the solubility of the material, and also provides sites for chemical modifications. The reaction of Parmax 1200 with sulfuric acid leads to sulfonation of the phenyl units (Fig. 1D) and gives to this polymer the proton conductivity required for FC applications. Although the polymer properties are promising, the stability of sulfonated Parmax 1200 (SParmax) needs to be determined, since nonfluorinated polymers usually are susceptible to chemical degradation [26].

The chemical and thermal durability are very important since harsh conditions in operating FCs, such as elevated temperature and the presence of highly reactive radicals, lead to PEM degradation. In addition to desired reactions, the formation of a small amount of hydrogen peroxide during the two-electron oxygen reduction at the cathode side of the fuel cell takes place [27].

Although H_2O_2 is not considered a main damaging agent, the H_2O_2 molecules can dissociate into two hydroxyl radical, then hydrogen peroxide may react with $HO^\bullet$ forming hydroperoxyl radicals $HOO^\bullet$. The main expected reactions are: