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TGA-GC/MS - an adjuvant tool for analysis of polymer membranes designed for fuel cell use

W. Germer*[1], J. Leppin[1], C. Nunes Kirchner[1], D. Henkensmeier[2], A. Dyck[1]
[1]Forschungszentrum für Energietechnologie, Germany, [2]KIST, Republic of Korea

Introduction

Beside the electrochemical and mechanical properties, the thermal behaviour of polymeric membranes is of a great importance in fuel cell applications. Valuable information about the membrane thermal stability can be obtained by means of thermo gravimetric analysis (TGA). At higher temperatures, usually above ca. 150 °C, information about the polymer backbone and side chain structure can be obtained. By this means important data acquired by the TGA supports the synthesis of polymeric membranes. For deeper analysis of the pyrolysis products, a gas chromatograph (GC) and a mass spectrometer (MS) can be hyphenated with the TGA, forming a powerful analytic tool (TGA-GC/MS) – shown in Fig. 1 – for elucidation of pyrolysis degradation products.
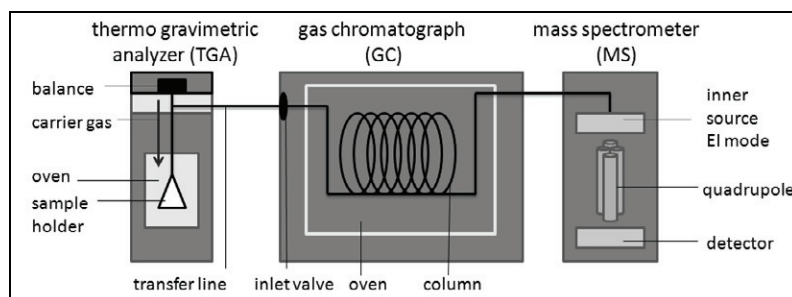

Fig. 1. Schematic assembly of the TGA-GC/MS system.

During pyrolysis the occurring weight reduction is plotted versus temperature and the evaporated compounds are transferred by a carrier gas (helium) via a heated transfer line from the TGA to the GC/MS system. To prevent contamination of the GC/MS the constant gas flow between TGA and GC/MS is inhibited by an inlet valve in the GC. This valve is only opened at degradation steps that are to be examined more closely.

Mixtures of substances retained from one decomposition step are separated on the GC column. By programming a discrete temperature ramp for the GC oven this separation can be optimized, so that the components can be identified in the MS individually.

In this presentation the analysis of O-PBI-based polymer membranes (Fig. 2) [1] for use in alkaline anion exchange membrane fuel cells (AAEMFC) exemplifies the utilisation of the TGA-GC/MS system to gain detailed information on thermal stability and material composition.
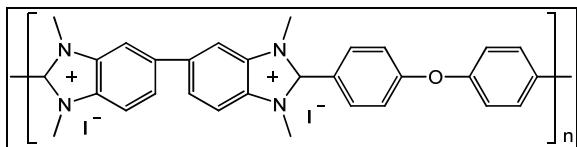
Fig. 2. Methylated O-PBI-based polymer.

AAEMFCs require polymer membranes with positively charged functional groups immobilized at the polymer backbone and free moving counterions, e.g. hydroxide. AAEMFCs fuelled with carbon dioxide instead of oxygen are not only attractive because of high theoretical energy conversion efficiency, but also for application in carbon capture and storage (CCS) [2]. The supplied CO_2 is converted to carbonate or hydrogen carbonate ions that pass through the anion exchange membrane (AEM) to react with hydrogen fed at the anode side [3].

Methods

To gain suitable membranes for use in an AAEMFC fuelled with CO_2 an O-PBI polymer was methylated to obtain positively charged imidazolium ions [1]. Additionally 10% of α,α'-dibromo-*p*-xylene were added as cross-linker. The outcome of this synthesis is the weakly cross-linked membrane PBI-*p*X-I$^-$ with positively charged imidazolium systems located in the backbone and exchangeable iodide ions. Subsequently the iodide is exchanged with carbonate ions by immersion in 1 M sodium carbonate solution at 25 °C for 24 h resulting in membrane PBI-*p*X-CO_3^{2-}. Before TGA-GC/MS measurements were performed both membranes are dried in a vacuum oven at 55 °C for 24 h.

The TGA-GC/MS system consists of a Perkin Elmer TGA Pyris 1, Perkin Elmer GC Clarus 600 with a polydimethylsiloxane column, inner diameter 0.25 mm, and Perkin Elmer MS Clarus 600 T with a quadrupole mass analyzer. Mass spectra were generated by electron impact (EI) and 70 eV. For data recording at the TGA Pyris software was used and Turbo Mass program for the GC/MS.

In the TGA the sample is heated from 30 °C to 900 °C with 20 °C/min under helium atmosphere. By means of the minima of the first derivative of the weight/temperature curve the opening times for the inlet valve of the GC/MS are determined. In an adjacent measurement decomposition products are passed into the GC/MS. The GC oven was set to 30 °C and baked-out at 280 °C after each measurement.

Results

Fig. 3a shows the thermogram of membrane PBI-*p*X-I$^-$. In this investigation the inlet valve of the GC/MS was opened two times (ca. 2 min and ca. 14 min) for 0.5 sec. Fig. 3b shows the respective chromatograms at the particular times that were analyzed with the quadrupole mass spectrometer as detector, results are presented in Fig. 4. The first weight loss at about 2 min (50-100 °C) is assigned to the evaporation of residual water remaining in the sample. The chromatogram of the second degradation step at ca. 15 min (250-400 °C) consists of several peaks, which could be identified as dimethyl sulfoxide (14.9 min) and methyl bromide (15.2 min) – both residues from the preparation process [4] – and methyl iodide (15.7 min) from decomposition of the modified O-PBI polymer.
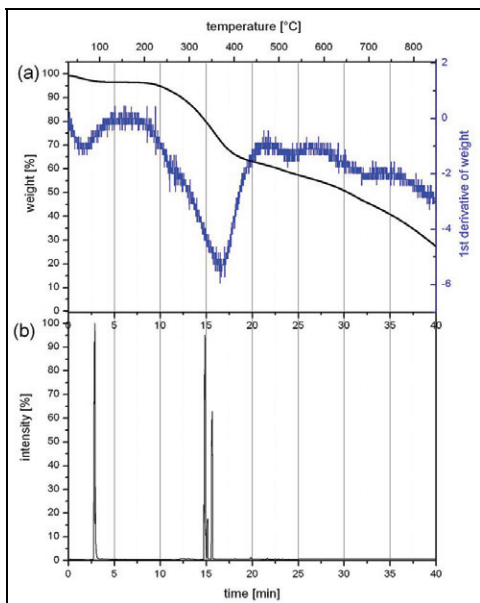
Fig. 3. Results of the measurement of PBI-*p*X-I⁻. (a) thermogram and the first derivate of weight from 30 °C till 850 °C at a heating rate of 20 °C/min. (b) chromatogram of pyrolysis products evaporated during the degradation steps.
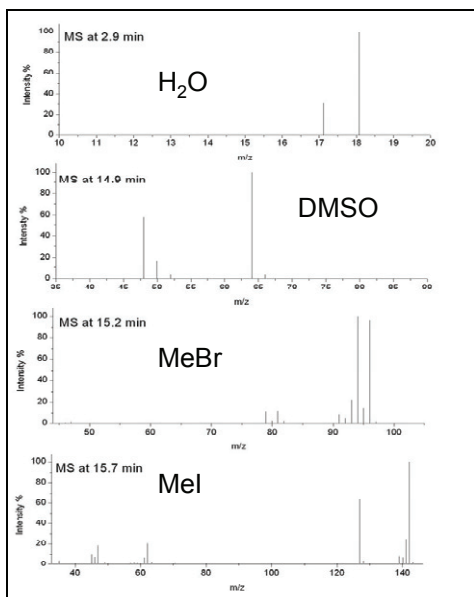

Fig. 4. Mass spectra of PBI-*p*X-I⁻ at different points of time of the chromatogram.

The result of the TGA analysis of PBI-*p*X-CO_3^{2-} is shown in Fig. 5a. In comparison with the thermal analysis of the PBI-*p*X-I⁻ an additional degradation step at 200 °C was observed. So the GC inlet valve was opened three times, the respective chromatograms are displayed in Fig. 5b.

The additional peak at 7 min (180-220 °C) can be assigned to the disposal of carbon dioxide from the carbonate anion. The correspondent mass spectrum is given in Fig. 6. As for PBI-*p*X-I⁻, water, dimethyl sulfoxide and methyl bromide can be detected as well for PBI-*p*X-CO_3^{2-} at the corresponding decomposition steps. The fact that methyl iodide can still be discovered in the degradation step between 300-400 °C reveals that the ion exchange was not complete. To obtain reliable electrochemical data e. g., conductivity, of PBI-*p*X-CO_3^{2-} in further investigations, modification of the ion exchange procedure is recommended.
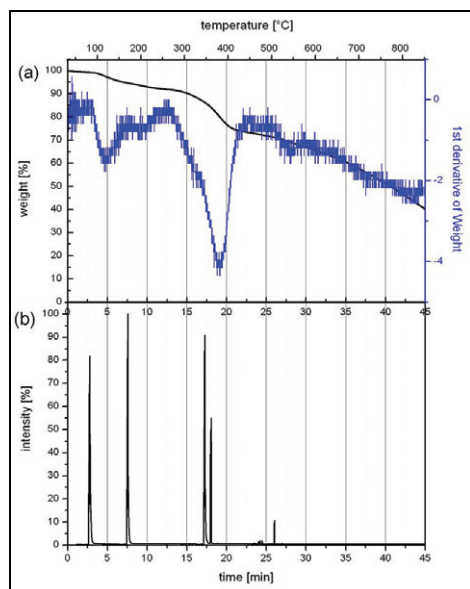

Fig. 5. Results of the measurement of PBI-*p*X-CO_3^{2-}. (a) thermogram and the first derivate of weight from 30 °C till 850 °C at a heating rate of 20 °C/min. (b) chromatogram of pyrolysis products evaporated during the degradation steps.
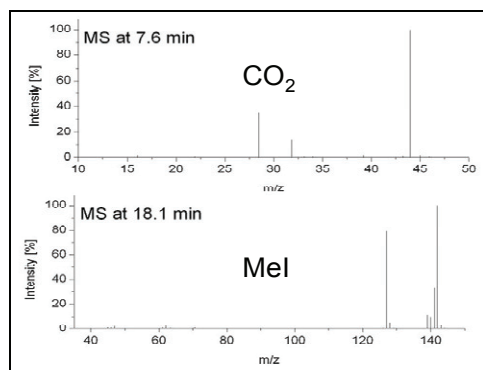

Fig. 6. Mass spectra of PBI-*p*X-CO_3^{2-} at different points of time of the chromatogram.

Discussion

The hyphenation of TGA and GC/MS gives an adjuvant tool for the evaluation of the thermal stability of materials like polymer membranes for fuel cell use. Concurrently the degradation products of each decomposition step can be analyzed separately to get useful information for further improvement of the material stability. Furthermore the progress of preparation processes can be monitored, as it was exemplified in this work on the ion exchange in a polybenzimidazolium membrane. The applied procedure of submersion in an aqueous saline solution for 24 h is a widespread method for ion exchange in polymer membranes [5-7]. The present TGA-GC/MS analysis shows that in some cases this method has to be regarded with caution as the ion exchange might not be complete.

Literature

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