# Determination of membrane degradation products in the product water of polymer electrolyte membrane fuel cells using liquid chromatography mass spectrometry

## Dissertation

zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften
– Dr. rer. nat. –

vorgelegt von

**Marco Zedda**

geboren in Duisburg

Fakultät für Chemie
der
Universität Duisburg-Essen

**2011**

Die vorliegende Arbeit wurde im Zeitraum von Februar 2007 bis Februar 2011 im Arbeitskreis von Prof. Dr. Torsten C. Schmidt im Fachbereich Chemie/Instrumentelle Analytische Chemie der Universität Duisburg-Essen durchgeführt.

Tag der Disputation: 12. Mai 2011

| | |
|---|---|
| Gutachter: | Prof. Dr. Torsten C. Schmidt |
| | PD Dr. Kai Bester |
| Vorsitzender: | Prof. Dr. Stephan Schulz |

*"No phenomenon is a real phenomenon until it is an observed phenomenon."*

*- John A. Wheeler -*

# Acknowledgements

My special thanks are devoted to Prof. Dr. Torsten C. Schmidt and Dr. Jochen Türk for their invaluable guidance, encouragement, suggestions and helpful discussions throughout this thesis.

Furthermore, I would like to thank Dr. Stefan Peil, Dr. Thorsten Teutenberg and Christoph Portner for their suggestions and helpful discussions.

Furthermore I would like to thank:

- The staff from the Department of Analytical Chemistry at University of Duisburg-Essen and the Departments Research Analysis, Environmental Hygiene & Toxins and Energy Supply & Hydrogen Technology at the Institute of Energy and Environmental Technology (IUTA) for suggestions, support and inspiring discussions.

- Dr. Jochen Kerres and Andreas Chromik from the Institute of Chemical Process Engineering at the University of Stuttgart for helpful discussions and excellent collaboration in this project.

- The German Federal Ministry of Economics and Technology within the agenda for the promotion of industrial cooperative research and development (IGF) organised by the AiF, Arbeitsgemeinschaft industrieller Forschungsvereinigungen (Cologne) for the financial support.

- Last, but not least, my wife and my family, for her and their constant support and encouragement throughout the entire course of the study.

# Abstract

The predominant long term failure of polymer electrolyte membranes (PEM) is caused by hydroxyl radicals generated during fuel cell operation. These radicals attack the polymer, leading to chain scission, unzipping and consequently to membrane decomposition products. The present work has investigated decomposition products of novel sulfonated aromatic hydrocarbon membranes on the basis of a product water analysis. Degradation products from the investigated membrane type and the possibility to detect these compounds in the product water for diagnostic purposes have not been discovered yet.

This thesis demonstrates the potential of solid phase extraction and liquid chromatography tandem mass spectrometry (SPE-LC-MS/MS) for the extraction, separation, characterization, identification and quantification of membrane degradation products in the product water of fuel cells. For this purpose, several polar aromatic hydrocarbons with different functional groups were selected as model compounds for the development of reliable extraction, separation and detection methods.

The results of this thesis have shown that mixed mode sorbent materials with both weak anion exchange and reversed phase retention properties are well suited for reproducible extraction of both molecules and ions from the product water. The chromatographic separation of various polar aromatic hydrocarbons was achieved by means of phase optimized liquid chromatography using a solvent gradient and on a C18 stationary phase. Sensitive and selective detection of model compounds could be successfully demonstrated by the analysis of the product water using tandem mass spectrometry. The application of a hybrid mass spectrometer (Q Trap) for the characterization of unknown polar aromatic hydrocarbons has led to the identification and confirmation of 4-hydroxybenzoic acid in the product water. In addition, 4-HBA could be verified as a degradation product resulting from PEM decomposition by hydroxyl radicals using an accelerated laboratory stress test procedure. Liquid chromatographic separation of the three possible isomers on a C18 stationary phase was used for identification of 4-HBA in all samples. Finally, this degradation product could be assigned to a monomer of the tested membrane. In conjunction with gel permeation chromatography (GPC) analysis a degradation mechanism for 4-HBA could be proposed.

# Kurzfassung

Eine der Hauptursachen für den Abbau von Polymer-Elektrolyt-Membranen (PEM) während des Betriebes in Brennstoffzellen ist die Bildung von Hydroxyl-Radikalen. Die Radikale greifen das Polymer an, was zu Kettenspaltung und folglich zur Zersetzung der Membran führt. Die vorliegende Arbeit untersucht Zersetzungsprodukte von sulfonierten aromatischen Kohlenwasserstoff-Membranen auf Basis einer Produktwasseranalytik. Abbauprodukte des untersuchten Membran-Typs sowie deren Nutzung für diagnostische Zwecke über eine Produktwasseranalytik wurden bisher noch nicht untersucht.

Diese Arbeit zeigt das Potential der Festphasenextraktion und der Flüssigkeitschromatographie Tandem-Massenspektrometrie (SPE-LC-MS/MS) zur Anreicherung, Trennung, Charakterisierung, Identifizierung und Quantifizierung von Membranabbauprodukten im Produktwasser von Brennstoffzellen. Zu diesem Zweck wurden mehrere polare aromatische Kohlenwasserstoffe mit verschiedenen funktionellen Gruppen als Modellverbindungen für die Entwicklung zuverlässiger Anreicherungs-, Trennungs- und Nachweismethoden verwendet.

Die Untersuchungen dieser Arbeit haben gezeigt, dass Mixed-Mode-Materialien mit schwachen Anionenaustauscher- und Umkehrphaseneigenschaften zur reproduzierbaren Aufkonzentrierung von Molekülen und Ionen aus dem Produktwasser geeignet sind. Die chromatografische Trennung für verschiedene polare aromatische Kohlenwasserstoffe konnte mittels Phasen optimierter Flüssigkeitschromatographie unter erstmaliger Anwendung eines Lösungsmittelgradienten als auch auf einer C18-Phase erreicht werden. Die empfindliche und selektive Detektion von Degradationsprodukten im Produktwasser mittels Tandem-Massenspektrometrie konnte erfolgreich anhand von Modellsubstanzen demonstriert werden. Mit der Hybrid-Massenspektrometrie (Q Trap) konnte die Hydroxybenzoesäure (HBA) im Produktwasser identifiziert und bestätigt werden. Weiterführende Untersuchungen haben gezeigt, dass HBA durch den Abbau der Polymer-Elektrolyt-Membran in einem oxidativem Stresstest mit Hydroxylradikalen gebildet wird. Durch eine flüssigchromatografische Trennung von drei möglichen Strukturisomeren der HBA auf einer C18-Phase konnte die 4-HBA in allen Proben identiziert werden. Die 4-HBA konnte weiterhin einem Monomer der getesteten Membran zugeordnet werden. In Verbindung mit der Gelpermeationschromatografie (GPC) Analyse konnte ein Degradationsmechanismus für die Bildung von 4-HBA vorgeschlagen werden.

# Contents

**Chapter 1**

**Chapter 2**

**Chapter 3**

Chapter 4

Chapter 5

Chapter 6

# Index of figures

# Index of tables

# Chapter 1

# General Introduction

## 1.1 Subject of this study

The polymer electrolyte membrane fuel cell (PEMFC) is a potential technology for versatile applications ranging from portable power generation, transportation vehicles to stationary devices [1, 2]. The core of a PEMFC is a thin ionomer embedded between two electrodes, the anode and cathode. The proton conductive polymer serves as electolyte and provides the transport of hydrogen ions from the anode to the cathode side of the fuel cell, while being impermeable for reactant gases, such as molecular oxygen and hydrogen. Figure 1-1 shows a schematic illustration of the principle of a PEMFC.

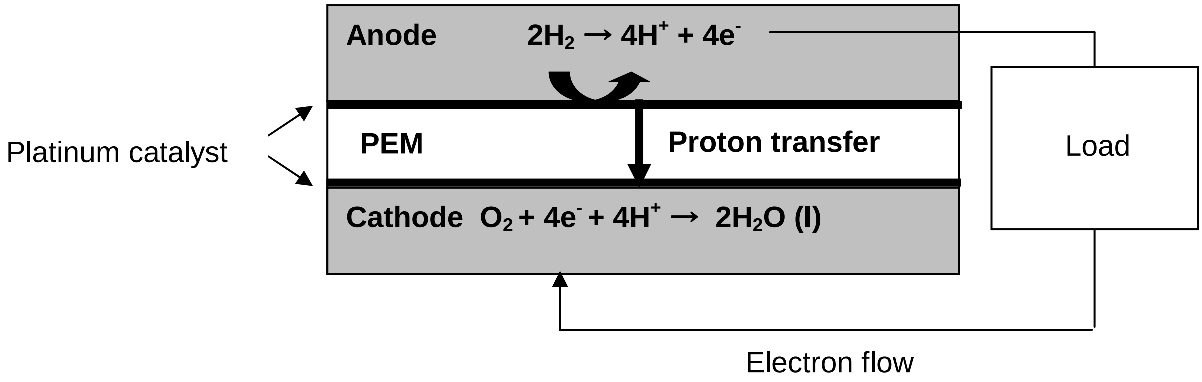


**Figure 1-1** Schematic illustration of the principle of a PEM fuel cell.

Molecular hydrogen supplied at the anode is split into protons and electrons by a platinum catalyst layer, which covers both sides of the membrane. The protons pass across the ionomer to the cathode while the electrons are conducted over an external circuit in order to produce electricity. Molecular oxygen (in the form of air) is supplied to the cathode and combines with the protons to produce the “waste product” liquid water. The most widely used ionomers for PEMFC applications are perfluorosulfonic acid (PFSA) membranes [3, 4]. These membranes have excellent physical characteristics such as high proton conductivity, good thermal stability, suitable mechanical strength and high durability against chemical stress [5]. However, high production costs and possible negative effects on the environment of PFSA membranes have led to the development of less expensive alternative membranes [6, 7]. Sulfonated nonfluorinated polyaromatic membranes represent one large group of promising and economically favorable alternative materials and are comparable to PFSA membranes in terms of their proton conductivity [5]. One of the major concerns for polyaromatic hydrocarbon membranes is their chemical stability. Typical bond strength in a perfluorinated polymer is C–H < C–C < C–F [8]. C–F bond strengths are generally in the range of 460 kJ/mol, while C–H bond strengths are approximately 410 kJ/mol [9, 10]. Generally, fluorinated polymers are considered to have better chemical stability. The stability of PEMs during fuel cell operation determines the membrane lifetime and influences the overall performance and lifetime of PEMFC. Current guidelines for fuel cell applications from the US Department of Energy from 2007 require a lifetime of 5,000 h for automobiles and 40,000 h for stationary applications. Durability concern of PEMFC systems is one of the major issues that impede the commercialization of fuel cell technology [11]. Besides mechanical and thermal issues, the chemical degradation has been identified as the major mechanism for PFSA membranes during fuel cell operation [12, 13]. It is widely accepted that hydrogen peroxide ($H_2O_2$) and related decomposition products such as the radical species hydroperoxyl ($HO_2^\bullet$) and hydroxyl ($HO^\bullet$) are generated during fuel cell operation. Several recent studies support this observation since hydrogen peroxide has been detected in the exhaust gas, product water and directly in the membrane [14-16]. Hydroxyl and hydroperoxyl radicals will attack the polymer, leading to chain scission, unzipping, and loss of functional groups [17]. Two main processes have been described for the formation of hydrogen peroxide and its related radicals in the literature. General Electric proposed a mechanism that occurs at the anode side (hydrogen side) of the fuel cell [11]. This mechanism assumes that molecular oxygen permeates through the membrane and reacts with atomic hydrogen chemisorbed on the surface of the platinum catalyst. This reaction initiates the formation of hydrogen peroxide, which in conjunction with traces of bivalent transition metal cations ($Fe^{2+}$, $Cu^{2+}$) found in the membrane electrode assembly (MEA) form hydroxyl and hydroperoxyl radicals. General Electrics postulated the possible reactions that are involved in this mechanism as follows:

$H_2 \rightarrow 2\ H^\bullet$ (via Pt catalyst) (1)

$H^\bullet + O_2 \rightarrow HO_2^\bullet$ (diffused through the PEM to anode) (2)

$HO_2^\bullet + H^\bullet \rightarrow H_2O_2$ (diffuses into PEM) (3)

$H_2O_2 + Me^{2+} \rightarrow {}^\bullet OH + OH^- + Me^{3+}$ (4)

$H_2O_2 + Me^{3+} \rightarrow HO_2^\bullet + H^+ + Me^{2+}$ (5)

Another mechanism suggested is independent of the gas permeation phenomenon. This mechanism occurs at the cathode side of the fuel cell (oxygen side), where hydrogen peroxide is formed by two-electron reduction of molecular oxygen (reaction 6) [18, 19]. Hydrogen peroxide can further react with metal ions to produce destructive hydroxyl and peroxyl radicals (reaction 4 and 5).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (6)$$

Reactions 4 and 5 have led to the use of Fenton test, an accelerated laboratory stress test, in order to investigate the chemical stability and degradation of PEMs [4, 12, 20]. Hydroperoxyl and hydroxyl radicals can be formed by iron catalyzed decomposition of hydrogen peroxide (reactions 7 and 8).

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \qquad (7)$$

$$H_2O_2 + Fe^{3+} \rightarrow HO_2^{\bullet} + H^+ + Fe^{2+} \qquad (8)$$

In these stress tests, the membranes are immersed into Fenton reagent containing 3% $H_2O_2$ aqueous solution mixed with up to 4 mg/L $Fe^{2+}$ at 68 °C (molar ratio 10000: 1) [21]. Degradation products of PFSA and polystyrene sulfonic acid extracted from used fuel cell degraded membrane have been found to be similar to the compounds found in Fenton test solutions [4, 13, 22]. Fenton test is easy to perform and has been considered as a benchmark for PEM evaluation but it has limitations. The degradation of PEMs in such an accelerated oxidative stress test does not consider electrode processes and variations in fuel cell operating conditions such as operating potential, relative humidity, lack of fuel and oxidant, etc. However, an accelerated oxidative stress test (ex-situ test) can still be useful to allocate degradation product findings from fuel cell experiments (in-situ test) to a degradation mechanism. This work will investigate the degradation of sulfonated poly(arylene ether sulfone) membranes (SPES) blended with polybenzimidazole [6, 23]. The structure is presented in Figure 1-2. It is functionalized with sulfonic acid groups, which provides the proton conductive property to the membrane. Until now, only limited information concerning durability of the sulfonated polyaromatic membranes in fuel cell operations is available. Points of attack in the structure of SPES membranes exposed to an oxidative environment have been previously identified [3, 21].

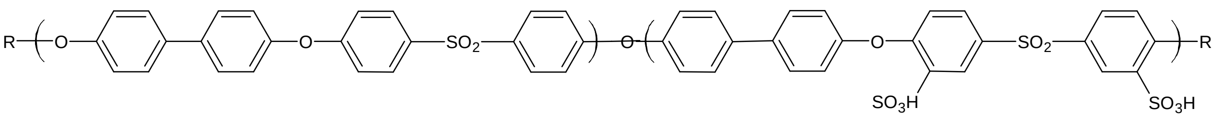
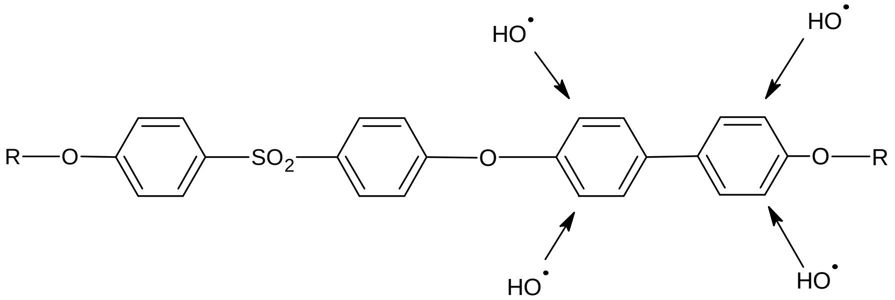


**Figure 1-2** Structure of the investigated sulfonated polyarylether membrane.

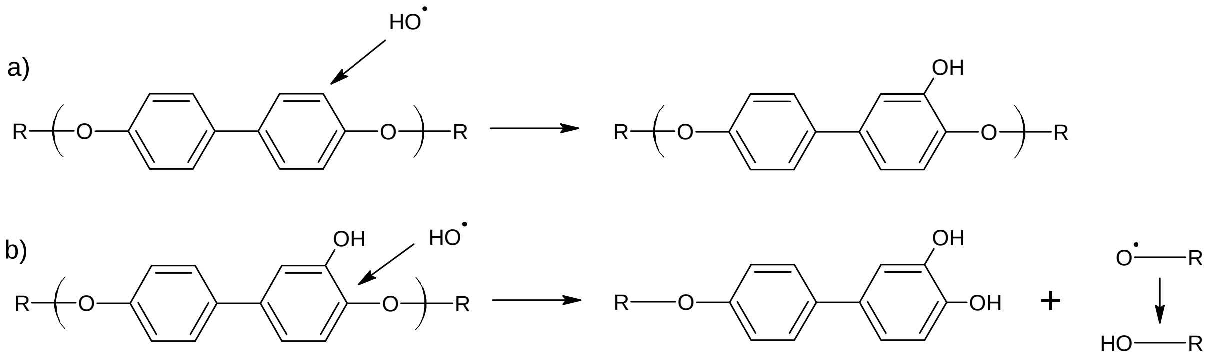
Lawrence et al. found that SPES degrades significantly when exposed to an accelerated hydroxyl radical test [3]. The degradation has been demonstrated to decrease molecular weights. The authors concluded that hydroperoxyl and hydroxyl radicals rupture the main chain of the polymer by addition to the benzene ring resulting in a ring opening reaction. A study from Zhang et al. supports the rupture of the main chain [21]. The authors proposed that the strong electron-withdrawing nature of the sulfone and pendent sulfonate groups decreases the electron densities of nearby aromatic rings, hence stabilizing them from the electrophilic attack by radicals. Therefore, the most sensitive sites for hydroxyl radical attack are the positions of the aromatic ring next to the ether bridge (Figure 1-3).



R = other parts of the polymer chain

**Figure 1-3** Most sensitive sites for hydroxyl radical attack on SPES.

An addition of an hydroxyl group to the sensitive sites at the ortho-position next to the ether bridge (Figure 1-4, a) may facilitate the ipso-attack (Figure 1-4, b) of an additional hydroxyl radical to the ether bridge resulting in the ultimate scission of the ether linkage. The authors suggested the analysis of the water released during fuel cell operation in order to identify decomposition products to aid the clarification of the degradation mechanism. However, screening and identification of resulting degradation products from the described mechanisms has not been reported yet.



R = other parts of the polymer chain

**Figure 1-4** Proposed degradation route of SPES by hydroxyl radicals.

## 1.2 Analytical methods for investigation of chemical degradation

The degradation of PEM is usually investigated by destructive methods in which fuel cell stacks are taken apart (pre-and post analysis) and analyzed by various techniques, such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, electron spin resonance spectroscopy (ESR), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), nuclear magnetic resonance spectroscopy (NMR) and mass spectrometry [24]. These techniques have been widely applied to characterize functional groups in polymers and organic compounds, detection of radicals, characterization of the chemical composition of the first several atomic layers on a surface, elemental composition analysis and structure characterization. However, there is a lack of reliable complementary analytical methods for in-situ membrane degradation product investigations during fuel cell operation. Such an analytical tool could be useful to monitor relationships between fuel cell operating parameters and quantity and/or identity of degradation products, which could give a better insight into membrane degradation processes. Membrane degradation products resulting from chemical degradation are oxidation products. Such oxidation products are more polar than the precursor compounds and therefore more water soluble and quite mobile [25]. These polar and mobile compounds should be detectable in the water produced during fuel cell operation. An early study published in 1995 by Büchi et al. have detected small quantities of small water soluble organic units resulting from chemical degradation of polymeric styrene sulfonic acid membranes in the product water using reversed phase high performance liquid chromatography with diode array UV detection (RP-LC-DAD) [22]. A more recent investigation has been presented by Carlsson et al. at the 216th electrochemical society meeting in 2009, with the focus on PFSA membrane degradation [26]. This research group has analyzed decomposition products of PFSA membranes in the product water using liquid chromatography tandem mass spectrometry (LC-MS) and found small organic carboxylates and sulfonates originating from chemical degradation of the membrane. However, screening and identification of degradation products from SPES has not been reported yet and will be determined in this thesis.

## 1.3 Extraction of possible membrane degradation products

Pre-concentration prior analysis of possible membrane degradation products was required in previous product water investigations (see previous section) [22]. These investigations imply the need of an extraction procedure, in order to enable the detection of traces of membrane degradation products for qualitative and quantitative regular monitoring. The most applied sample enrichment technique for liquid samples is solid phase extraction (SPE), which has replaced laborious and time consuming liquid liquid extraction (LLE) [27, 28]. Solid phase extraction with a weak anion exchange sorbent material has been used for the extraction of carboxylates and sulfonates originating from chemical degradation of PFSA membranes in the water produced from a fuel cell [26]. SPE requires less amounts of solvent for the extraction compared to LLE. Furthermore, the extraction procedure can be fully automated by modern auto samplers to enhance the throughput of analysis. Promising sorbent materials are mixed sorbents that consist of a polymeric skeleton and ion exchange groups, which provide reversed phase and ionic exchange interaction mechanisms. This type of sorbent material has been successfully applied for the extraction of both molecules and ions from complex matrices, such as food, biological fluids, animal tissue, waste water and wood extracts [29]. The advantage is that beside the extraction of molecules, the retention and release of ions can be controlled by switching pH during the SPE steps. Thus, mixed mode sorbent materials could be well suited for the extraction of a variety of possible SPES degradation products from the product water, which will be investigated in this thesis.

## 1.4 Chromatographic separation and mass spectrometric detection

Reversed phase high performance liquid chromatography (RP-HPLC) is a widely applied robust separation technique and compatible with various spectrometric, spectroscopic and electrochemical detectors. This separation technique enables separation of polar to non-polar aromatic compounds [30-33]. The major drawback of spectroscopic detection are possible interferences, which are disadvantageous for proper identification and quantification of the compounds of interest [34]. The hyphenation of RP-HPLC with a triple quadrupole tandem mass spectrometer (MS/MS) has been established as a powerful technique for the separation, ionization and detection of analytes in complex mixtures [30]. Figure 1-5 shows a schematic drawing of an HPLC-MS/MS system.

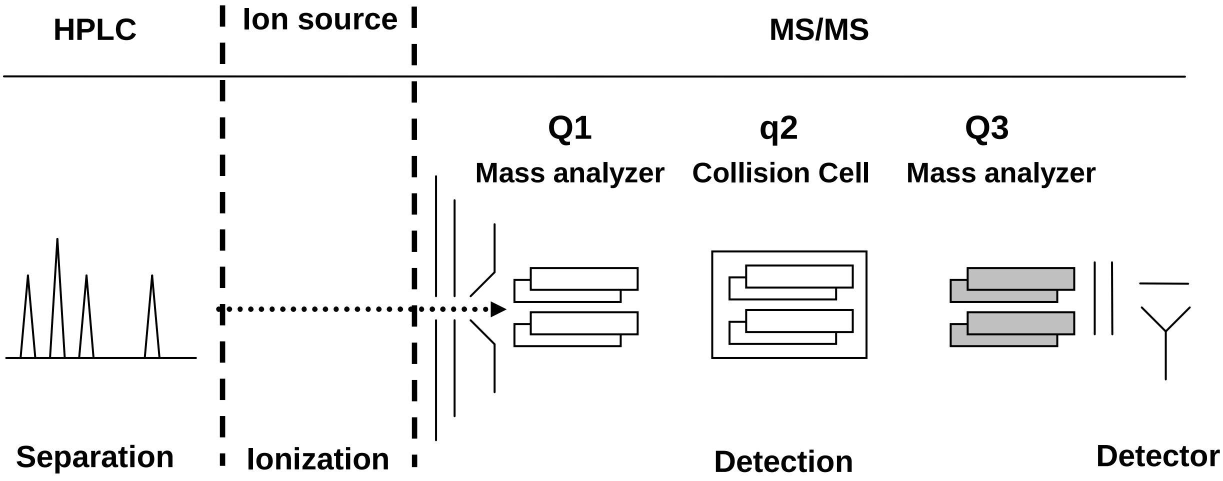
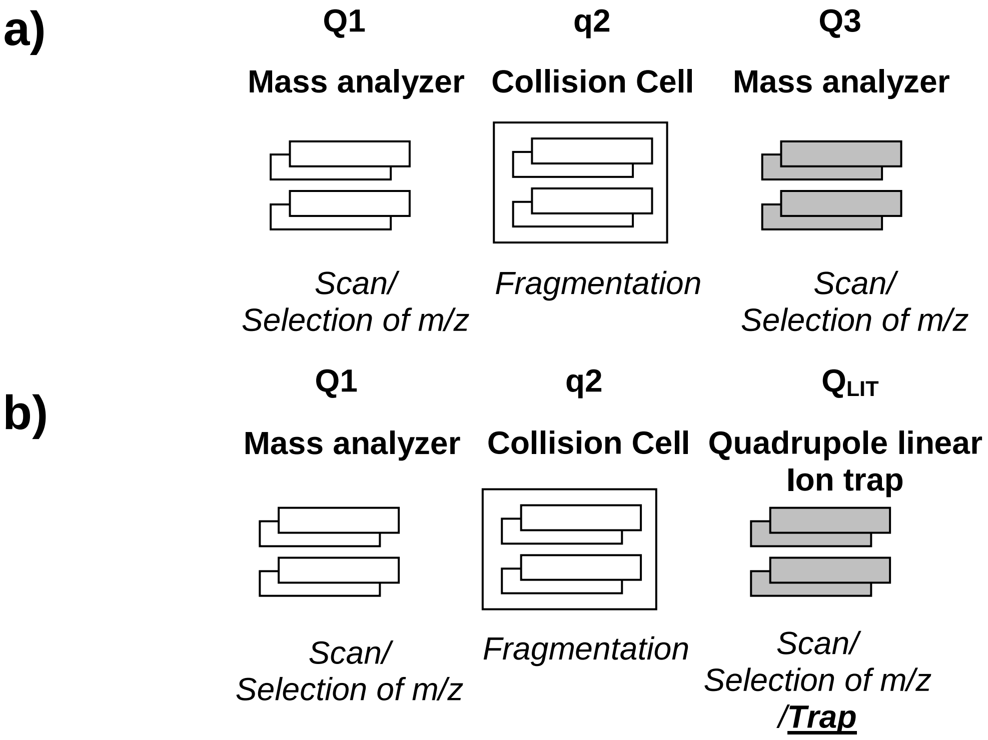


**Figure 1-5** Schematic drawing of a liquid-chromatography mass spectrometer.

Most LC-MS/MS systems are using two interface techniques, the electrospray ionization (ESI) and the atmospheric pressure chemical ionization (APCI) interface. Both interfaces are applicable to liquid phase samples, which is essential for hyphenating HPLC with MS. ESI is applicable for the ionization of moderately non-polar, polar and ionic compounds and therefore suitable for ionization of membrane oxidation products [35]. The ESI ion source as a soft ionization technique provides data in support of the molecular weight for unknown compounds. Triple quadrupole mass spectrometer (QqQ) consists of three quadrupoles, which enables selection, fragmentation and mass analysis of mass to charge ratios (*m/z*) in three discrete regions, which is also referred to as tandem in-space MS/MS. The instrument configuration presented in Figure 1-6 (a), allows the selection of a precursor ion in the first mass analyzer for fragmentation in the quadrupole collision cell to produce characteristic product ions via collision induced dissociation (CID) using nitrogen or argon as inert collision gas.



| a) Mode of operation | Q1 | q2 | Q3 |
|---|---|---|---|
| Multiple reaction monitoring (MRM) | Selection of *m/z* | Fragment | Selection of *m/z* |

| b) Mode of operation | Q1 | q2 | Q3 Operated as an LIT |
|---|---|---|---|
| Enhanced Q3 Single MS (EMS) | Ion transition | Ion transition | Trap/scan |
| Enhanced Product Ion (EPI) | Selection of *m/z* | Fragmentation | Trap/scan |

**Figure 1-6** Schematic diagrams of a triple-quadrupole tandem mass spectrometer (a) and triple quadrupole linear ion trap tandem mass spectrometer (b).

The third mass analyzer is used for selection and monitoring of one or more product ions for qualification and confirmation in conjunction with the precursor ion. This mode of operation is referred as “multiple reaction monitoring” (MRM). LC-MS/MS with the ability to perform MRM is highly suited for the purpose of quantitative analysis due to its large linear dynamic range. The MRM-measurement mode is nowadays “state of the art” for the analysis of polar compounds and pharmaceutical residues in environmental samples due its selectivity and sensitivity [30, 36]. The use of LC-MS/MS has increasingly attained importance for the qualitative screening of unknowns in complex aqueous samples [30]. Linear ion trap triple quadrupole tandem mass spectrometer ($QqQ_{LIT}$) represent an advancement of conventional triple quadrupole mass spectrometers. Because of the hybridization of triple quadrupole MS with the linear ion trap (LIT) technology, the sensitivity of the instrument is enhanced by accumulating ions in the trap region (Figure 1-6, b) [37].

Usually two injections with data processing in between are necessary in order to obtain information on molecular weight and structure of a compound. In a first MS experiment, ions of interest (*m/z*-ratios) are obtained by a survey scan using a full scan in a previously defined mass range. All ions produced in the ion source are detected continuously in a selected mass range (EMS scan). In order to obtain structure information of a compound of interest, a product ion scan is performed in a second MS experiment (EPI scan). The principle of both scan types is demonstrated in Figure 1-6 b. The drawback of this MS/MS approach is that precursor ions must be selected before fragmentation. These experiments must be repeated for each relevant precursor ion found in the survey scan. Therefore, the analysis of one water sample may consume a lot of time and high sample volumes for multiple injections.

To overcome this problem, software algorithms implemented into MS software are used to combine different mass scan functions. This enhances mass spectral information and the efficiency for the screening of unknown compounds. This mode of operation is also referred as “information dependent acquisition (IDA)”. The IDA mode uses data from a survey scan to determine the ions of interest. Based upon pre-defined selection criteria, the data dependent experiment is processed “on-the-fly” [37]. Figure 1-7 illustrates the principle of an IDA experiment using an EMS scan as the survey measurement and an EPI scan as the information dependent experiment. In the EMS scan, an *m/z* ratio is selected “on-the-fly” for further fragmentation in order to gain structure information. This IDA configuration has successfully been applied for the screening of unknown compounds and characterization of drugs, metabolites and toxic compounds using a $QqQ_{LIT}$ [38-41].

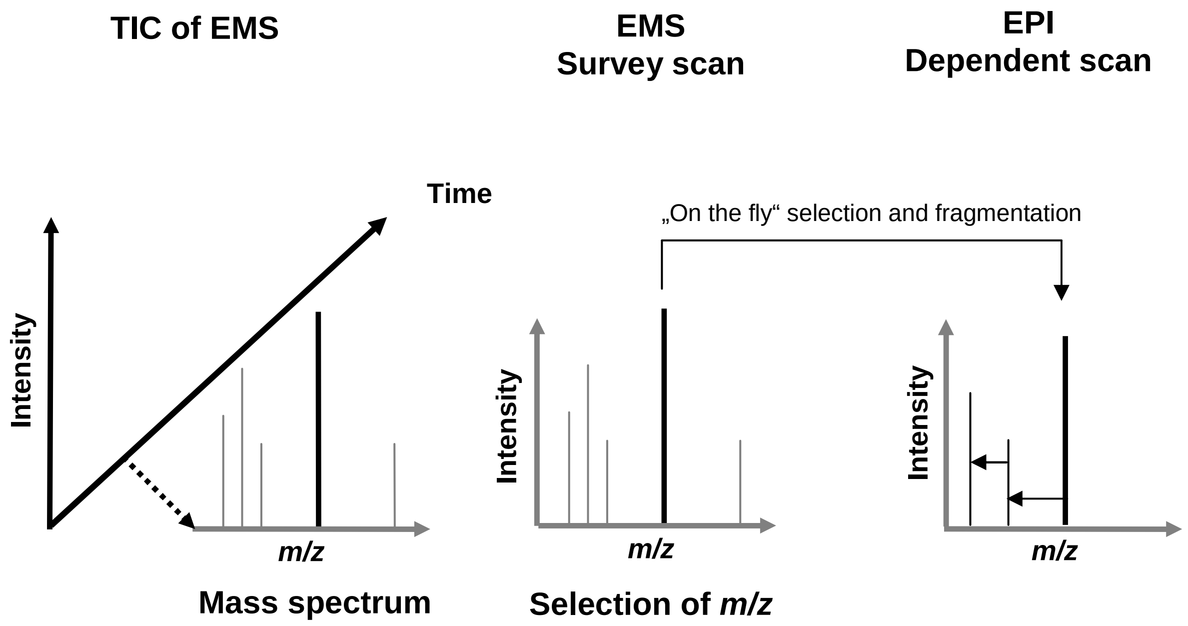


**Figure 1-7** Principle of an IDA experiment using an EMS scan as the survey measurement and an EPI scan as the information dependent measurement.

A further feature of $QqQ_{LIT}$ configuration is the possibility to change the collision energy CE (specification for the energy received by the precursor ions as they are accelerated into the collision cell) during the fill time of the trapped product ions. This enables the acquisition of low and high mass product ion spectra in one experiment. Product ion spectra produced at low, high and medium CE can be reconstructed to give a more informative MS/MS spectrum compared to a spectrum recorded at a single CE. Hence, this mode of operation could be a potential approach for a screening of unknown membrane degradation products in the product water of PEMFC, which will be investigated in this thesis.

## 1.5 References

[1] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), Chemical Reviews, 104 (2004) 4587-4611.

[2] B. Smitha, S. Sridhar, A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications - a review, J. Membrane Sci., 259 (2005) 10-26.

[3] J. Lawrence, T. Yamaguchi, The degradation mechanism of sulfonated poly(arylene ether sulfone)s in an oxidative environment, J. Membr. Sci., 325 (2008) 633-640.

[4] A. Collier, H.J. Wang, X.Z. Yuan, J.J. Zhang, D.P. Wilkinson, Degradation of polymer electrolyte membranes, Int. J. Hydrogen Energy, 31 (2006) 1838-1854.

[5] C. Perrot, L. Gonon, M. Bardet, C. Marestin, A. Pierre-Bayle, G. Gebel, Degradation of a sulfonated aryl ether ketone model compound in oxidative media (sPAEK), Polymer, 50 (2009) 1671-1681.

[6] J.K. Lee, J. Kerres, Synthesis and characterization of sulfonated poly(arylene thioether)s and their blends with polybenzimidazole for proton exchange membranes, J. Membrane Sci., 294 (2007) 75-83.

[7] J.R. Yu, B.L. Yi, D.M. Xing, F.Q. Liu, Z.G. Shao, Y.Z. Fu, Degradation mechanism of polystyrene sulfonic acid membrane and application of its composite membranes in fuel cells, Phys. Chem. Chem. Phys., 5 (2003) 611-615.

[8] S. Mitov, G. Hubner, H.P. Brack, G.G. Scherer, E. Roduner, In situ electron spin resonance study of styrene grafting of electron irradiated fluoropolymer films for fuel cell membranes, J. Polym. Sci., Part B: Polym. Phys., 44 (2006) 3323-3336.

[9] M. Pianca, E. Barchiesi, G. Esposto, S. Radice, End groups in fluoropolymers, J. Fluorine Chem., 95 (1999) 71-84.

[10] D.A. Schiraldi, Perfluorinated polymer electrolyte membrane durability, Polym. Rev., 46 (2006) 315-327.

[11] A.B. LaConti, M. Hamdan, R.C. McDonald, Mechanisms of membrane degradation, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.) Handbook of Fuel Cells - Fundamentals, Technology and Applications, 2003, pp. 647-677.

[12] F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Durability and degradation issues of PEM fuel cell components, Fuel Cells, 8 (2008) 3-22.

[13] J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo, A. Brundage, H. Gasteiger, J. Abbott, Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells, Fuel Cells, 5 (2005) 302-308.

[14] K. Teranishi, S. Tsushima, S. Hirai, Analysis of water transport in PEFCs by magnetic resonance imaging measurement, J. Electrochem. Soc., 153 (2006) A664-A668.

[15] W. Liu, D. Zuckerbrod, In situ detection of hydrogen peroxide in PEM fuel cells, J. Electrochem. Soc., 152 (2005) A1165-A1170.

[16] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Gas crossover and membrane degradation in polymer electrolyte fuel cells, Electrochim. Acta, 51 (2006) 5746-5753.

[17] V.O. Mittal, H.R. Kunz, J.M. Fenton, Membrane degradation mechanisms in PEMFCs, J. Electrochem. Soc., 154 (2007) B652-B656.

[18] Q.H. Guo, P.N. Pintauro, H. Tang, S. O'Connor, Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes, J Membrane Sci, 154 (1999) 175-181.

[19] C. Perrot, L. Gonon, C. Marestin, A. Morin, G. Gebel, Aging mechanism of Sulfonated poly(aryl ether ketone) (sPAEK) in an hydroperoxide solution and in fuel cell, J. Power Sources, 195 (2010) 493-502.

[20] S.S. Zhang, X.Z. Yuan, H.J. Wang, W. Merida, H. Zhu, J. Shen, S.H. Wu, J.J. Zhang, A review of accelerated stress tests of MEA durability in PEM fuel cells, Int. J. Hydrogen Energy, 34 (2009) 388-404.

[21] L. Zhang, S. Mukerjee, Investigation of Durability Issues of Selected Nonfluorinated roton Exchange Membranes for Fuel Cell Application, J. Electrochem. Soc., 153 (2006) A1062-A1072.

[22] F.N. Buchi, B. Gupta, O. Haas, G.G. Scherer, Study of Radiation-Grafted Fep-G-Polystyrene Membranes as Polymer Electrolytes in Fuel-Cells, Electrochim. Acta, 40 (1995) 345-353.

[23] J. Kerres, D. Xing, F. Schönberger, Comparative Investigation of Novel PBI Blend Ionomer Membranes from Nonfluorinated and Partially Fluorinated Poly Arylene Ethers, J. Polymer Sci., 44 (2006) 2311-2326.

[24] H. Liu, F. D. Coms, J. Zhang, H. Gasteiger, A.B. LaConti, Polymer Electrolyte Fuel Cell Durability, Springer, 2009.

[25] S.G. Schrank, U. Bieling, H.J. Jose, R.F.P.M. Moreira, H.F. Schroder, Generation of endocrine disruptor compounds during ozone treatment of tannery wastewater confirmed by biological effect analysis and substance specific analysis, Water Sci. Technol., 59 (2009) 31-38.

[26] A.H. Carlsson, L. Joerissen, Accelerated Degradation of Perfluorinated Sulfonic Acid Membranes, ECS Trans., 25 (2009) 725-732.

[27] M.C. Hennion, Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography, J Chromatogr A, 856 (1999) 3-54.

[28] V. Pichon, M. Bouzige, M.C. Hennion, New trends in environmental trace-analysis of organic pollutants: class-selective immunoextraction and clean-up in one step using immunosorbents, Anal Chim Acta, 376 (1998) 21-35.

[29] N. Fontanals, R.M. Marce, F. Borrull, New materials in sorptive extraction techniques for polar compounds, J. Chromatogr. A, 1152 (2007) 14-31.

[30] T. Reemtsma, Liquid chromatography-mass spectrometry and strategies for trace-level analysis of polar organic pollutants, J. Chromatogr. A, 1000 (2003) 477-501.

[31] M. Antolovich, D.R. Bedgood, A.G. Bishop, D. Jardine, P.D. Prenzler, K. Robards, LC-MS investigation of oxidation products of phenolic antioxidants, J. Agric. Food. Chem., 52 (2004) 962-971.

[32] W. Naidong, W. Shou, Y.L. Chen, X.Y. Jiang, Novel liquid chromatographic-tandem mass spectrometric methods using silica columns and aqueous-organic mobile phases for quantitative analysis of polar ionic analytes in biological fluids, J. Chromatogr. B, 754 (2001) 387-399.

[33] M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt, A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, J. Chromatogr., A, 1216 (2009) 8910-8917.

[34] P. Marquet, G. Lachatre, Liquid chromatography-mass spectrometry: potential in forensic and clinical toxicology, J. Chromatogr. B, 733 (1999) 93-118.

[35] E.M. Thurman, I. Ferrer, D. Barcelo, Choosing between atmospheric pressure chemical ionization and electrospray ionization interfaces for the HPLC/MS analysis of pesticides, Anal. Chem., 73 (2001) 5441-5449.

[36] M. Petrovic, M.D. Hernando, M.S. Diaz-Cruz, D. Barcelo, Liquid chromatography-tandem mass spectrometry for the analysis of pharmaceutical residues in environmental samples: a review, J. Chromatogr. A, 1067 (2005) 1-14.

[37] G. Hopfgartner, V. Emmanuel, V. Tschäppät, C. Grivet, E. Bourgogne, L.A. Leuthold, Triple quadrupole linear ion trap mass spectrometer for the analysis of small molecules and macromolecules, J. Mass Spectrom., 39 (2004) 845–855.

[38] P. Marquet, F. Saint-Marcoux, T.N. Gamble, J.C.Y. Leblanc, Comparison of a preliminary procedure for the general unknown screening of drugs and toxic compounds using a quadrupole-linear ion-trap mass spectrometer with a liquid chromatography-mass spectrometry reference technique, J Chromatogr B, 789 (2003) 9-18.

[39] J.G. Huang, S.P.R. Bathena, Y. Alnouti, Metabolite Profiling of Praziquantel and its Analogs During the Analysis of in vitro Metabolic Stability Using Information-Dependent Acquisition on a Hybrid Triple Quadrupole Linear Ion Trap Mass Spectrometer, Drug Metab. Pharmacokinet., 25 (2010) 487-499.

[40] M. Yao, L. Ma, W.G. Humphreys, M.S. Zhu, Rapid screening and characterization of drug metabolites using a multiple ion monitoring-dependent MS/MS acquisition method on a hybrid triple quadrupole-linear ion trap mass spectrometer, J. Mass Spectrom., 43 (2008) 1364-1375.

# Chapter 2

# Scope of this thesis

The analysis of possible degradation products of sulfonated poly(arylene ether sulfone) (SPES) membranes during fuel cell operation resulting from chemical degradation could lead to a better understanding of degradation processes. The product water seems well suited for this diagnostic purpose, since membrane decomposition products could be detected in previous studies (see introduction). Membrane degradation could be monitored by a non-destructive method and eventually before a decrease of cell performance is observed. Moreover, weak structural points of the membrane with regard to degradation could be determined, which might lead to the improvement of the membrane polymer. Before these investigations can be done, suitable and reliable trace analytical methods need to be developed. Degradation products from the investigated membrane type and the possibility to detect these compounds in the product water for diagnostic purposes have not been discovered yet. Therefore, the scientific purpose of this thesis was to answer the following questions:

Is it possible to

- measure membrane degradation products at trace levels?
- characterize and identify membrane degradation products?
- propose a degradation mechanism?

The scope of this thesis was to develop analytical methods for the determination of polar membrane degradation products in the product water during fuel cell operation to answer the scientific questions posed above. The possibilities for the analysis of trace organics in aqueous solutions with solid phase extraction (SPE) and liquid chromatography mass spectrometry (LC-MS) have been pointed out in the introduction. In this study, new SPE-LC-MS/MS approaches for the extraction, separation, characterization and quantification of possible polar SPES membrane degradation products in the product water of fuel cells have been investigated as described in detail in the following chapters:

The chemical degradation of aromatic hydrocarbon membranes can yield to polar and structurally similar compounds that could be detected during fuel cell operation. A sufficient chromatographic separation is essential for the characterization of unknown compounds with a mass spectrometer. Phase optimized liquid chromatography has been shown to enable the optimization of chromatographic selectivity through the stationary phase by connecting columns with different stationary phases and column length in series without changing the mobile phase type and conditions. **Chapter 3** shows investigations on this chromatographic approach regarding the systematic method development for the separation of polar and structural similar model compounds on five different stationary phases and the improvement of the chromatographic selectivity by connecting different stationary phases. Furthermore, its applicability for the use as a separation method for an LC-MS product water screening regarding unknown compounds has been shown.

Screening and identification of resulting degradation products from chemical degradation of SPES in the product water has not been reported yet. **Chapter 4** investigates SPES membrane chemical degradation during fuel cell operation. Based on a consideration of the molecular structure of the polymer, potential membrane degradation products of SPES membranes can be classified into the classes of aromatic sulfonic acids, phenolic acids and phenols. Therefore, five model compounds comprising these compound classes were selected. Application of a mixed mode sorbent material for the extraction and electrospray ionization tandem mass spectrometry for reliable detection and quantification of these potential membrane oxidation products is also shown in Chapter 4. For the validation that the theoretically selected model degradation products are generated through a chemical degradation process during fuel cell operation, their presence was investigated in product water from PEMFC use and in an accelerated laboratory stress test.

**Chapter 5** explores the origin and degradation mechanism of a major membrane degradation product found in the product water and Fenton test using a hybrid mass spectrometer. In order to allocate this degradation product to the membrane structure, the membrane and its building blocks were systematically investigated. The conclusions and future perspectives are given in **Chapter 6**.

# Chapter 3

## A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography.

---

* Redrafted from M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt: A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, Journal of Chromatography A (2009), 1216, 8910–8917. Copyright 2009 Elsevier.

## 3.1 Abstract

Within the scope of research for target and non-target LC-MS/MS analysis of membrane degradation products of polymer electrolyte membrane fuel cells, a systematic method development for the separation of structurally similar compounds was performed by phase optimized liquid chromatography. Five different stationary phases with different selectivities were used. Isocratic separation for 4-hydroxybenzoic acid, isophthalic acid, terephthalic acid, 4-hydroxybenzaldehyde and 4-formylbenzoic acid was achieved on a C18 and a Phenyl phase. Using the PRISMA model the separation efficiency was optimized. This was achieved on a serial connected mixed stationary phase composed of 30 mm C18, 150 mm Phenyl and 60 mm C30. For the LC-MS screening of unknown degradation products from polymer electrolyte membranes in the product water of a fuel cell, a solvent gradient is mandatory for less polar or later eluting compounds. By means of 4-mercaptobenzoic acid it could be shown that a solvent gradient can be applied in order to elute later eluting compounds in a short time. The adaptability of this method for the qualitative analysis by target and non-target LC-MS/MS screening has been shown by means of 4-hydroxybenzoic acid. The combination of solvent gradient and isocratic conditions makes this approach attractive for the purpose of a screening method for known and unknown analytes in a water sample.

## 3.2 Introduction

An integral part of polymer electrolyte membrane (PEM) fuel cells are proton conductive membranes. These membranes are subject of aging resulting in subsequent loss of performance of the fuel cell [1, 2]. Thus, the characterization of the chemical membrane degradation caused by hydroxyl or peroxyl radicals formed by (electro-) chemical side reactions is an important task for further membrane refinements. This process was studied for novel polyetherketone- and polyarylether-type membranes. Six potential degradation products (4-hydroxybenzoic acid, isophthalic acid, terephthalic acid, 4-hydroxybenzaldehyde, 4-formylbenzoic acid and 4-mercaptobenzoic acid) were selected considering the molecular structure of polyetherketone- and polyarylether-type membranes and were used for the development of an LC-UV-MS/MS method for the screening of degradation products in product water of a fuel cell.

In order to differentiate the selected target compounds from non target compounds a good chromatographic separation method for the structural similar compounds with high separation efficiency is needed. There are several ways to optimize the separation efficiency (selectivity and efficiency) in order to improve the resolution of a chromatographic separation. The separation can be improved by changing the selectivity of the chromatographic system. A change of the column type can be the most effective way to achieve an improvement of selectivity, but also the most expensive one since different types of columns are not always available in the laboratory. There are several approaches described in the literature related to phase optimization to give a high level of selectivity such as modification of the chemical composition of the stationary phase or mixed bed stationary phases [3-6]. Another way to optimize selectivity through the stationary phase is by connecting columns in series [7-12]**,** an approach that recently has been named phase optimized liquid chromatography. This technique allows the optimization of selectivity by using a segmented column with variable stationary phases and column length. The segments are connected without dead volume in series to give an optimal selectivity for a given separation problem without changing the mobile phase. This tool is based on the PRISMA model, which was originally derived from mobile phase optimization and was then adopted for stationary phase optimization [13]. This approach has been successfully applied for the isocratic separation of various analytes such as steroids, explosives and some pesticides [14-16]. Once the maximum level of selectivity is achieved further refinements of the efficiency (theoretical plates) might be necessary if higher resolution is required. The efficiency can usually be improved by changing the column conditions. In the context of the development of an LC-UV-MS/MS screening method for the analysis of the product water of a fuel cell, this paper shows the high potential of phased optimized liquid chromatography for the systematic method development and improvement of the separation efficiency for several model degradation products using a serially connected mixed stationary phase. In addition, this work has demonstrated the importance of isocratic and gradient conditions for the screening of known and unknown membrane degradation products.

## 3.3 Experimental

### Chemicals

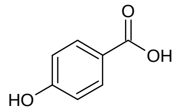
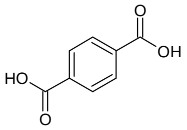
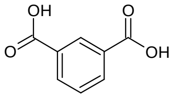
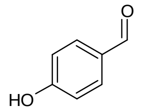
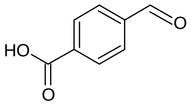
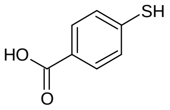
All chemicals were analytical grade and purchased from Sigma Aldrich (Steinheim, Germany). The solvents and eluents for the chromatographic separation (water, acetonitrile and methanol) and the additive formic acid were mass spectrometric grade quality and purchased from Biosolve (Valkenswaard, Netherlands).

Selected properties of 4-formylbenzoic acid, 4-hydroxybenzaldehyde 4-hydroxybenzoic acid 4-mercaptobenzoic acid, isophthalic acid and terephthalic acid are listed in Table 3-1.

### HPLC-System

The analytes were separated with a Shimadzu Prominence HPLC system consisting of a CBM-20A controller, a DGU-20A$_3$ degasser, two LC-20AD pumps, a SIL-20AC auto sampler, CTO20AC column oven and a SPD-20AV UV detector (Shimadzu, Duisburg, Germany).

**Table 3-1** Selected properties of the model degradation products used in this study (pka values were obtained from the SRC PhysProp Database).

| | Compound | Structure | $pK_a$ | Molecular weight [g/mol] |
|---|---|---|---|---|
| (a) | 4-hydroxybenzoic acid |  | 4.54 | 138.12 |
| (b) | Terephthalic acid |  | 3.51 | 166.13 |
| (b) | Isophthalic acid |  | 3.7 | 166.13 |
| (c) | 4-hydroxybenzaldehyde |  | 7.61 | 122.12 |
| (d) | 4-formylbenzoic acid |  | 3.77 | 150.13 |
| (e) | 4-mercaptobenzoic acid |  | 4.04 | 154.19 |

### Phase and gradient optimization

For this study a POPLink Column System (Bischoff Chromatography, Leonberg, Germany) consisting of segments of C18, EPS (C18 with enhanced polarity), C30, Phenyl and Cyanopropyl was used. To study the separation efficiency on five different columns with different selectivity and for further resolution optimization five isocratic basic measurements were accomplished.

The column length for the isocratic basic measurements was 100 mm for ProntoSil 100-5-C18 EPS 2, ProntoSil 100-5-C18 SH 2, ProntoSil 200-5-C30, and 200 mm for ProntoSil 100-5-Phenyl 2, and ProntoSil 100-5-CN 2. The column temperature was set to 30℃. The inner diameter of the columns was 3 mm and the particle size was

5 µm. The flow rate was adjusted to 0.5 mL/min. For all measurements, water with 0.1 % formic acid (A) and acetonitrile with 0.1 % formic acid (B) were used as eluents. A sample volume of 10 µL of a 100 ng/mL of a five component sample mixture of 4-formylbenzoic acid, 4-hydroxybenzaldehyde 4-hydroxybenzoic acid, isophthalic acid and terephthalic acid was injected. The isocratic elution of model compounds was done with 80 % water (A) / 20 % acetonitrile (B) (v/v).

The retention times as well as the theoretical plate numbers of each analyte were calculated from the derived chromatograms and entered to the POPLC Optimizer Software (Bischoff Chromatography, Leonberg, Germany) in order to estimate an optimal column composition of serial connected columns. The optimized column was assembled and installed into the HPLC-system to confirm the predicted chromatogram with a real isocratic measurement. The application of a gradient to the isocratic concept of phase optimized liquid chromatography was shown by means of a later eluting polar compound using 4-mercaptobenzoic acid. Therefore the final gradient optimization was accomplished by using a six component sample mixture containing 4-formylbenzoic acid, 4-hydroxybenzaldehyde 4-hydroxybenzoic acid, isophthalic acid, terephthalic acid and 4-mercaptobenzoic acid. For the real sample measurement a solid phase extract of 500 mL product water of a fuel cell equipped with a polyarylether-type membrane on an Oasis MAX cartridge (Waters GmbH, Eschborn Germany) was generated. The solid phase extraction has been validated at two concentration levels (data not shown). The compounds were eluted with 50 % acetonitrile and 50 % water. The solvent was then evaporated under a nitrogen stream and the residue was dissolved in 1 mL of water.

### Mass spectrometric detection

For sensitive detection of the analytes, the HPLC-system was coupled to a linear ion trap quadrupole mass spectrometer (API 3200 Q Trap, Applied Biosystems, Darmstadt, Germany). The recorded data were analysed with Analyst™ Software 1.5.The ionization of separated analytes eluted from the LC was made in the negative mode of turbo-electrospray ionization at atmospheric pressure. The ion source temperature was 550 °C and ion spray voltage -4200 V. Nitrogen was used as curtain (45 psi), nebulizer (45 psi) and collision gas (medium). For detection of the precursor ions in the first mass analyzer and the corresponding fragment ions in the second analyzer, multiple reaction monitoring (MRM) mode was used. A dwell time of

200 ms was set for the monitoring of each ion pair. The MRM transition scanning parameters that were individually optimized for each analyte in continuous-flow mode are shown in Table 3-2.

**Table 3-2** MRM parameter settings for each analyte.

| **Compound** | **MRM transition (Da) (Q1 / Q3)** [a] | **DP**[b] | **EP**[c] | **CEP**[d] | **CE**[e] | **CXP**[f] |
|---|---|---|---|---|---|---|
| 4-formylbenzoic acid | 148 >104 | -20 | -7 | -8 | 16 | -2 |
| 4-hydroxybenzaldehyde | 121 > 91 | -40 | -7.5 | -14 | 32 | -2 |
| 4-hydroxybenzoic acid | 137 > 93 | -25 | -7 | -10 | 18 | 0 |
| 4-mercaptobenzoic acid | 152 > 108 | -35 | -1 | -10 | 16 | -2 |
| Isophthalic acid | 164 > 120 | -30 | -3 | -12 | 14 | -4 |
| Terephthalic acid | 164 > 120 | -15 | -10.5 | -10 | 16 | -2 |

[a] Q1: precursor ion; Q3: fragment ion

[b] DP [V]: declustering potential (influences fragmentation)

[c] EP [V]: entrance potential (guides and focuses ions through Q0 region)

[d] CEP [V]: collision cell entrance potential (focuses ions into collision cell)

[e] CE [eV]: collision energy (energy received by precursor ions as they are accelerated into collision cell)

[f] CXP [V]: collision cell exit potential (transmits ions into Q3)

To characterize the unknown degradation products by their fragmentation pattern an enhanced MS (EMS) survey scan from 50 to 500 m/z was performed to find the precursor ion for fragmentation. The information dependent acquisition mode (IDA) was used for automatic generation of product ion spectra (EPI) for the most intensive molecule ion.

## 3.4 Results and discussion

**Separation experiments on five different stationary phases**

In the context of the method development for the screening of known and unknown degradation products in the product water of PEM-fuel cells equipped with polyarylether-type polymers, a column repertoire consisting of segments of C18, EPS (C18 with enhanced polarity), C30, Phenyl and Cyanopropyl was used as a screening kit for a given mixture of model degradation products for PEM-degradation during fuel cell operation. The screening experiment was conducted to evaluate a suitable stationary phase for the separation of a given sample mixture. The separation efficiency of the model substances on five different stationary phases was investigated by performing isocratic basic measurements on each column, which are also required for advanced selectivity optimization using an optimization software. Figure 3-1 shows the possibilities for a systematic method development using a segmented column system consisting of different stationary phases with different selectivities.

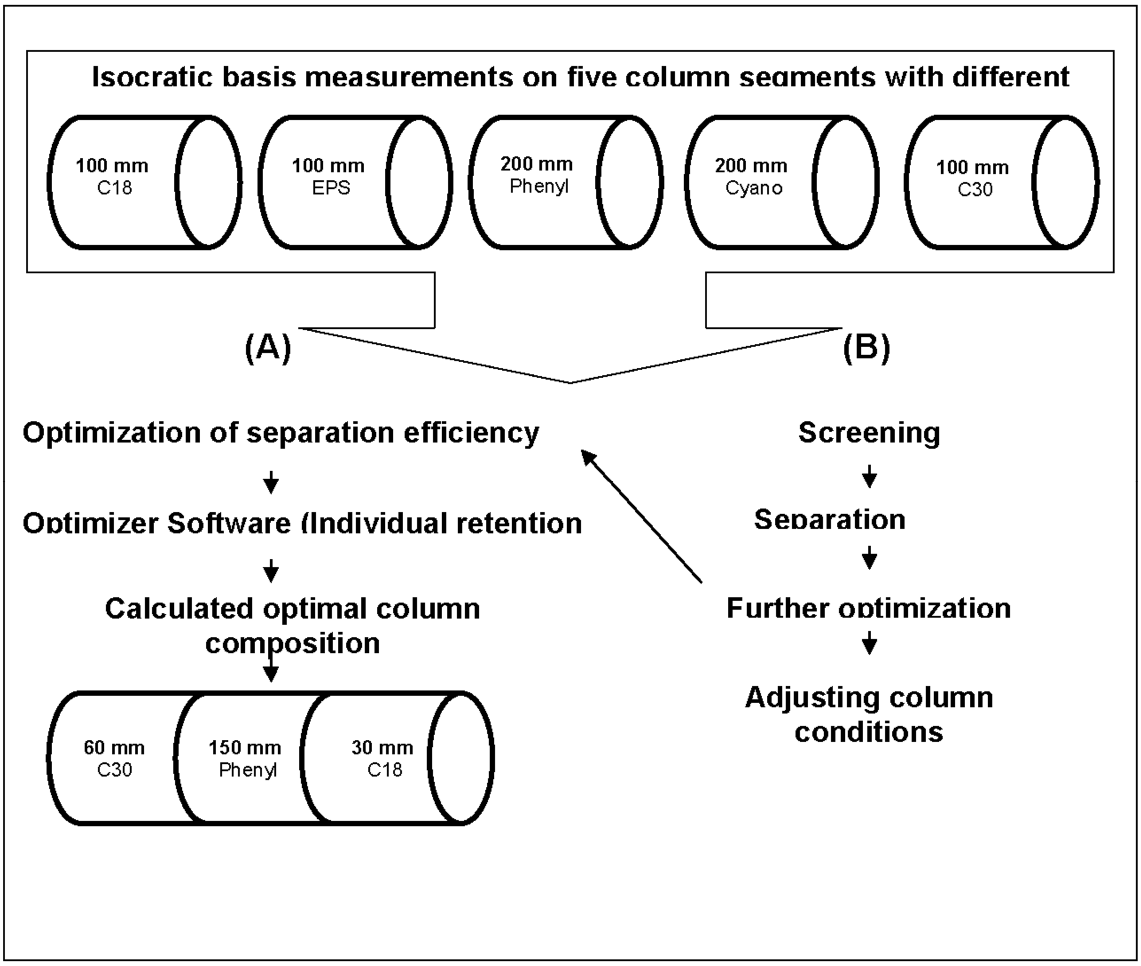


**Figure 3-1** Schematic view of the strategy using the POPLink Column System.

The derived chromatograms obtained from the isocratic separation of 4-hydroxybenzoic acid, terephthalic acid, isophthalic acid, 4-hydroxybenzaldehyde and 4-formylbenzoic acid on C18, EPS, C30, Phenyl and Cyanopropyl phase are presented in Figure 3-2. The selectivity factors of each compound for each isocratic separation were evaluated and are given in Figure 3-2. Overall, the ProntoSil 100-5-C18 SH 2 and the ProntoSil 100-5-Phenyl phases (Figure 3-2 a and d) showed the best separation characteristics in comparison to the other phases. All compounds could be separated, whereas a partial or complete co-elution was observed on C30, CN and EPS phases (Figure 3-2 b, c and e).

EPS (Figure 3-2 e) showed high retention due to its polar embedded groups. The elution order of the polar analytes on the EPS phase was different compared with C18, C30, CN and Phenyl phases. In addition, it showed low resolution. The CN phase (Figure 3-2 c) displayed the worst separation. This result suggests very low selectivity for acidic compounds, since cyano phases are commonly used for the separation of basic compounds [17]. A good separation of the constitutional isomers isophthalic and terephthalic acid was achieved on C18 and Phenyl phase, whereas only partial separation was observed on C30 and no separation on EPS and CN phase. According to the calculated values of the average plate number (Table 3-4), the C18 phase is a promising stationary phases for the development for the separation of the tested polar aromatic compounds.

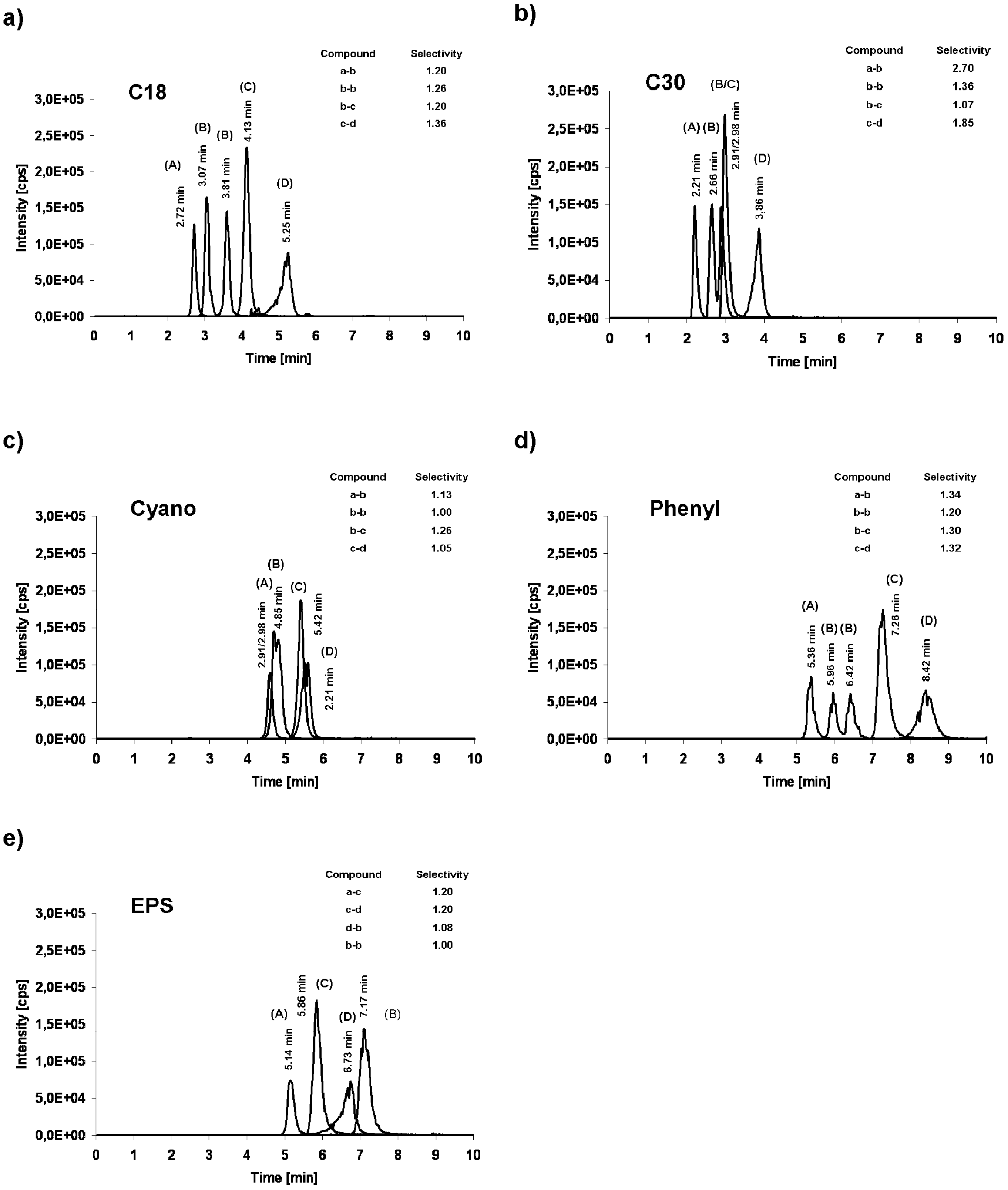


**Figure 3-2** Isocratic separation (basic measurements) of (A) 4-hydroxybenzoic acid, (B) either terephthalic or isophthalic acid, (C) 4-hydroxybenzaldehyde and (D) 4-formylbenzoic acid on (a) C18, (b) C30, (c) CN, (d) Phenyl and (e) EPS.

### Resolution optimization of five aromatic compounds using a serially connected mixed stationary phase

For the purpose of screening for known and unknown degradation products in the product water, it is advisable to create some extra space in the chromatogram because most probably other degradation products will appear with similar structures to those included for method development. Hence, a resolution greater than 2 was aimed for. On the basis of the experimental data obtained by the basic measurements an optimal serial connected mixed stationary phase was calculated using the optimization software. The software simulates all possible chromatograms according to the PRISMA model theory that has been described in detail elsewhere [13]**.** In this case the calculation is based on a multi-dimensional model for five different stationary phases. In contrast to mixed stationary phases, such as systematic modification of the chemical composition of the stationary phase or the so called “mixed bed” stationary phases [4, 5], the approach of connecting columns in series is very flexible. The columns can be composed and recombined for a given separation problem, whereas other approaches are tailor-made for a specific separation problem. Furthermore, it requires professional skills and time from the HPLC user to synthesize and pack columns, which are not available in many routine laboratories. In contrast, the optimizer software simulation allows the fast prediction of an optimal column composition. The optimal column composition calculated by the optimizer software consists of 30 mm C18, 150 mm Phenyl and 60 mm C30. The overall selectivity of the column is not influenced by the physical sequence of the column segments [13].

Table 3-3 shows the retention time and relative deviation of the predicted and measured data. The elution order and retention time of the constitutional isomers isophthalic and terephthtalic acid were confirmed by single measurements. The results show high accuracy of the prediction and measured chromatogram. The relative deviation of predicted and measured retention times were between 0.3 and 6.1 %. The experimentally obtained chromatogram is shown in Figure 3-3.

In order to show the improvement of separation of the serially connected mixed stationary phase compared with the homogenous stationary phase separations, the resolution and retention times of neighbouring peak pairs and the average plate numbers are listed in Table 3-4. The resolution obtained on a homogenous C18 phase was already acceptable (1.5) and resulted in baseline separation of all compounds. All other homogenous stationary phases showed no or only partial baseline separation with a resolution of less than 1 and are therefore not sufficiently selective. The resolution of the mixed stationary phase consisting of 30 mm C18, 150 mm Phenyl and 60 mm C30 was significantly enhanced. For all peak pairs the resolution was optimized to a value of above 2.

**Table 3-3** Predicted and measured retention times of the model degradation products on mixed serial connected stationary phase.

| Compound | Retention time predicted [min] | Retention time measured [min] | Deviation [%] predicted / measured |
|---|---|---|---|
| 4-hydroxybenzoic acid | 6.15 | 6.13 | -0.3 |
| Terephthalic acid | 7.35 | 6.93 | -6.1 |
| Isophthalic acid | 8.05 | 7.66 | -5.1 |
| 4-hydroxybenzaldehyde | 8.92 | 8.51 | -4.8 |
| 4-formylbenzoic acid | 10.74 | 10.22 | -5.1 |

Overall, the average number of theoretical plates of the serially connected stationary phase was higher compared to the homogenous stationary phases. The C18 already shows good separation characteristics and the highest value of theoretical plates compared with the other homogenous phases. The length of the column with mixed stationary phase differs from the ones with homogenous stationary phase. An extension of the column with C18 phase to 240 mm results in longer retention times for the analytes under isocratic conditions. Hence, further optimization of homogenous stationary phase C18 according the N value by changing the column conditions (e.g. flow rate, column length and particle size) is possible but not necessary if optimal resolution could be achieved by using a mixed stationary phase. Figure 3-3 a shows the isocratic separation of 4-hydroxybenzoic acid, terephthalic acid, isophthalic acid, 4-hydroxybenzaldehyde and 4-formylbenzoic acid using the mixed stationary phase consisting of 30 mm C18, 150 mm Phenyl and 60 mm C30.

### Gradient optimization for later eluting compounds

In order to create a screening method for known (targets) and unknowns (non-targets) in product water samples a gradient is mandatory. Many applications using phased optimized liquid chromatography are based on isocratic separation and selectivity optimization of a given separation problem [14-16, 18]. It is most likely that degradation products in the product water of PEM fuel cells have different polarity and retention behaviour. Less polar or later eluting polar aromatics are not eluted from the column in a reasonable analysis time if isocratic conditions are maintained although isocratic separation has its benefit due to a constant background if LC-MS/MS is used for quantification. However, in terms of a screening method a gradient is necessary in order to elute unknown later eluting compounds. Hence, the approach of gradient elution was tested by using 4-mercaptobenzoic acid as a model compound for a later eluting polar degradation product.

Figure 3-3 b shows the application of a solvent gradient after an isocratic hold-up of the five primary target compounds. The solvent gradient is indicated as a percentage of B in the chromatogram. It is corrected for the dwell time (solvent delay volume) of the chromatographic system and shows the exact real solvent gradient on the column.  The solvent gradient after an isocratic hold-up indicated in the chromatogram of Figure 3-3 b shows clearly the importance of a solvent gradient when less polar or later eluting polar compounds are present in the water sample. Since the isocratic separation in combination with gradient elution showed good separation characteristics for the polar and less polar analytes, it was decided to optimize the chromatogram with regard to the peak shape of 4-formylbenzoic and the retention time of mercaptobenzoic acid.

**Table 3-4** Resolution values and average plate number for the peak pairs obtained for unmixed and mixed stationary phase.

| Column | C18 | | EPS | | C30 | | Phenyl | | CN | | Mixed stationary phase (C18, Phenyl, C30) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Peak pair** | **Compound** | **Resolution** | **Compound** | **Resolution** | **Compound** | **Resolution** | **Compound** | **Resolution** | **Compound** | **Resolution** | **Compound** | **Resolution** |
| 1-2 | a-b | 1.54 | a-c | 0.59 | a-b | 0.97 | a-b | 0.64 | a-b | 0.25 | a-b | 2.80 |
| 2-3 | b-b | 2.19 | c-d | 0.49 | b-b | 0.61 | b-b | 0.66 | b-b | 0.00 | b-b | 2.35 |
| 3-4 | b-c | 1.90 | d-b | 0.29 | b-c | 0.09 | b-c | 0.82 | b-c | 0.48 | b-c | 2.35 |
| 4-5 | c-d | 2.31 | b-b | 0.00 | c-d | 0.77 | c-d | 0.70 | c-d | 0.12 | c-d | 2.35 |
| Average plate number | 2632 | | 327 | | 428 | | 718 | | 328 | | 6937 | |

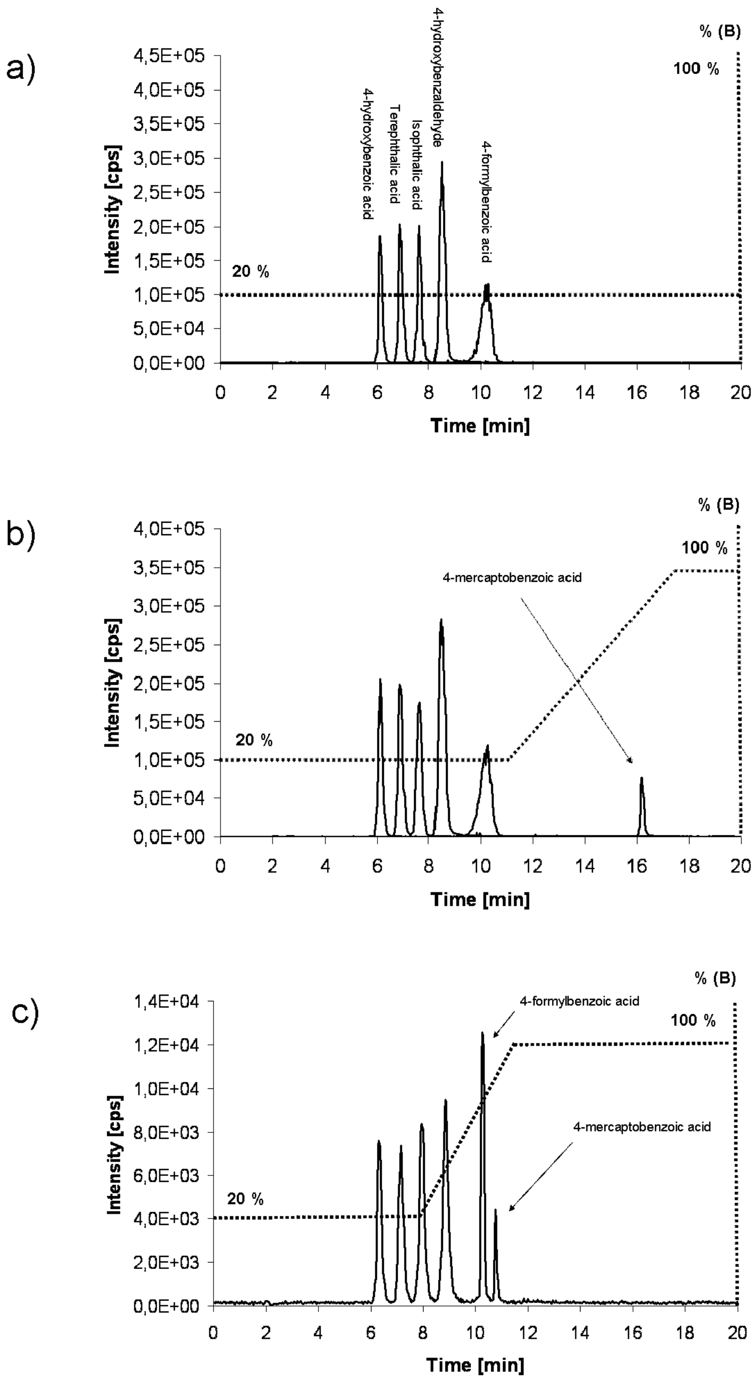


**Figure 3-3** (a) Isocratic separation (80 % water (A) / 20 % acetonitrile (B) (v/v)) of the sample mixture using a mixed stationary phase consisting of 30 mm C18, 150 mm Phenyl and 60 mm C30 (extracted ion chromatogram). (b) Chromatogram showing the inclusion of 4-mercaptobenzoic acid using a gradient on a mixed stationary phase consisting of 30 mm C18, 150 mm Phenyl and 60 mm C30 (extracted ion chromatogram). (c) Final optimized chromatogram according to peak shape and retention time of 4-formylbenzoic acid and 4-mercaptobenzoic acid respectively .

Figure 3-3 c shows the final optimized chromatogram for screening of the product water of a fuel cell equipped with a polyarylether-type polymer. The isocratic separation followed by gradient elution starting at 8 min could improve the peak shape of and therefore the sensitivity for 4-formylbenzoic acid. The peak width could be decreased from 0.84 min to less then 0.5 min. The retention time of 4-mercaptobenzoic acid was simultaneously reduced from 16.3 min to 10.9 min. It can be remarked that a software supported optimization of a gradient elution could be helpful for automated phase optimized liquid chromatography, especially when a gradient is mandatory for separation problems.

### Adaptability to a real product water sample

The adaptability of this screening method to an extracted product water sample is demonstrated in Figure 3-4. Hydroxybenzoic acid and hydroxybenzaldehyde have been unequivocally identified by using target-MRM-method. The UV-chromatogram at 254 nm indicates further unknown degradation products over the whole retention range. There are several unresolved peaks which are possible membrane degradation products eluting from the column using the solvent gradient. The investigation of these unknown membrane degradation products using an EMS scan in conjunction with EPI scans could not be accomplished due to sensitivity problems. Hence, the principle of the non-target approach is shown by means of hydroxybenzoic acid in the negative ionization mode. The $[M-H]^-$ molecule ion m/z = 137 of hydroxybenzoic acid was extracted from the total ion chromatogram (TIC). The extracted ion chromatogram of m/z = 137 is presented in Figure 3-5 a. The enhanced mass spectrum at 6.18 minutes, shows two significant molecule ions of m/z = 137and m/z = 93. The two most intensive molecules ion at 6.18 min (Figure 3-5 b) were automatically selected for fragmentation using information dependent acquisition. Figure 3-5 c shows the fragmentation pattern (EPI-spectrum) of m/z = 137 and m/z = 93.

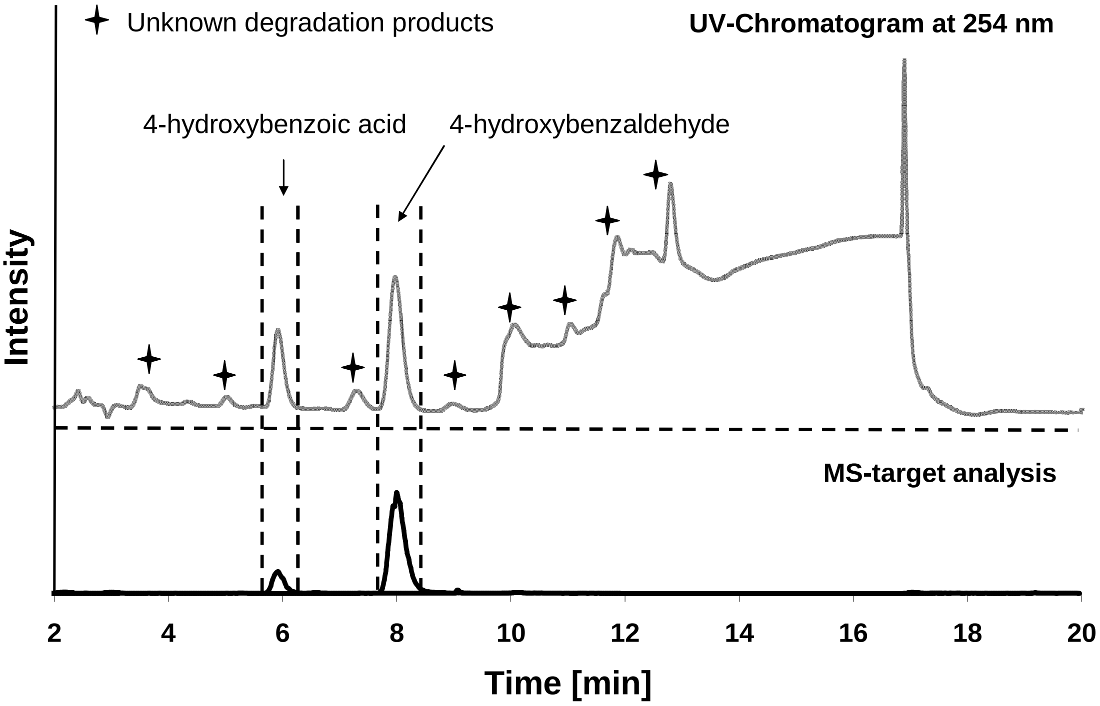


**Figure 3-4** LC-UV-MS/MS measurement of an solid-phase extract of the product water of a fuel cell (Enrichment factor 1:500) equipped with polyarylether-type membrane using the final optimized method. This figure shows the adaptability of a gradient after an isocratic hold-up for the screening of known and unknown membrane degradation products [19].

In this study model compounds are used for identification of membrane degradation products considering the molecular structure of the PEM.

Nevertheless, the generated fragmentation pattern using the unit resolution mass spectrometer is useful for the screening of unknown membrane degradation products. The precursor and fragment ions obtained through the product ion spectra can be used for MRM transitions for the selective screening of unknowns. Thus, the concept of phase optimized liquid chromatography is suitable for the investigation of known and unknown oxidation products in a water sample, particularly when using the separation technique with instruments for structure characterization and elucidation.

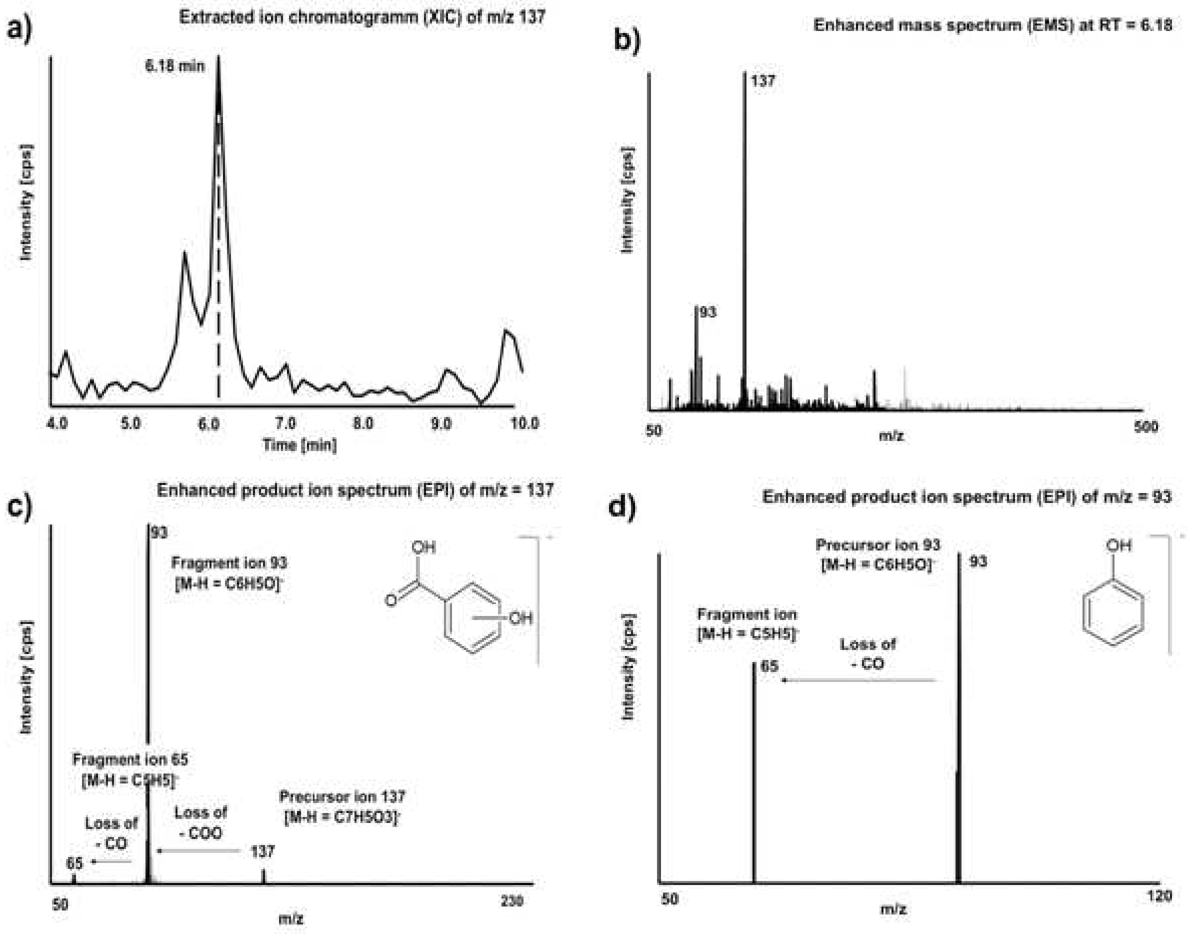


**Figure 3-5** a) Evaluation of the retention time of hydroxybenzoic acid (m/z =137) in the chromatogram using the extracted ion chromatogram (XIC) b) m/z of molecules found at RT: 6.18 shown by an enhanced mass spectrum (EMS), c) produced fragmentation pattern of m/z =137 and m/z = 93 using enhanced product ion scan (EPI) [19].

## 3.4 Acknowledgement

The authors would like to thank for financial support from the German Federal Ministry of Economics and Technology within the agenda for the promotion of industrial cooperative research and development (IGF) based on a decision of the German Bundestag. The access was opened by the Verein zur Förderung der Energie- und Umwelttechnik e.V, VEU Duisburg and organised by the AiF, Arbeitsgemeinschaft industrieller Forschungs-vereinigungen, Köln, (IGF-Project No. 14941 N). Furthermore, we would like to thank Bischoff Analysentechnik und -geräte GmbH for providing the POPLink column system, Jochen Kerres and Andreas Chromik for synthesizing the PEM´s, Kirsten Helle for providing the product water and Jacqueline Augusiak for the assistance in the laboratory work.

## 3.5 References

[1] J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo, A. Brundage, H. Gasteiger, J. Abbott, Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells, Fuel Cells, 5 (2005) 302-308.

[2] A.B. LaConti, M. Hamdan, R.C. McDonald, Mechanisms of membrane degradation, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.) Handbook of Fuel Cells - Fundamentals, Technology and Applications, 2003, pp. 647-677.

[3] B. Buszewski, M. Jezierska-Switala, S. Kowalska, Stationary phase with specific surface properties for the separation of estradiol diastereoisomers, J. Chromatogr. B., 792 (2003) 279-286.

[4] G.J. Eppert, P. Heitmann, Selectivity optimization of stationary phases, Lc Gc Europe, 16 (2003) 698.

[5] J.L. Glajch, J.C. Gluckman, J.G. Charikofsky, J.M. Minor, J.J. Kirkland, Simultaneous Selectivity Optimization of Mobile and Stationary Phases in Reversed-Phase Liquid-Chromatography for Isocratic Separations of Phenylthiohydantoin Amino-Acid Derivatives, J. Chromatogr., 318 (1985) 23-39.

[6] X.D. Yu, L. Lin, C.Y. Wu, Synergistic effect of mixed stationary phase in gas chromatography, Chromatographia, 49 (1999) 567-571.

[7] P.H. Lukulay, V.L. McGuffin, Solvent modulation in liquid chromatography: extension to serially coupled columns, J. Chromatogr A, 691 (1995) 171-185

[8] H.J. Maier, O.C. Karpathy, Prediction of Separation and Specifications of Chromatographic Columns, J. Chromatogr, 8 (1962) 308-&.

[9] J. Dungelova, J. Lehotay, J. Krupcik, J. Cizmarik, T. Welsch, D.W. Armstrong, Selectivity tuning of serially coupled (S,S) Whelk-O 1 and (R,R) Whelk-O 1 columns in HPLC, J. Chrom. Sci., 42 (2004) 135-139.

[10] E. Benicka, J. Krupcik, J. Lehotay, P. Sandra, D.W. Armstrong, Selectivity tuning in an HPLC multicomponent separation, J. Liq. Chromatogr. Related, 28 (2005) 1453-1471.

[11] M. De Beer, F. Lynen, M. Hanna-Brown, P. Sandra, Multiple Step Gradient Analysis in Stationary Phase Optimised Selectivity LC for the Analysis of Complex Mixtures, Chromatographia, 69 (2009) 609-614.

[12] F. Garay, Application of a flow-tunable, serially coupled gas chromatographic capillary column system for the analysis of complex mixtures, Chromatographia, 51 (2000) S108-S120.

[13] S. Nyiredy, Z. Szucs, L. Szepesy, Stationary phase optimized selectivity liquid chromatography: Basic possibilities of serially connected columns using the "PRISMA' principle, J. Chromatography A, 1157 (2007) 122-130.

[14] M. Kuehnle, J. Rehbein, K. Holtin, B. Dietrich, M. Gradl, H. Yeman, K. Albert, Phase optimized liquid chromatography as an instrument for steroid analysis, J. .Sep. Sci., 31 (2008) 1655-1661.

[15] F.M. Matysik, U. Schumann, W. Engewald, Isocratic liquid chromatography with segmented columns and simultaneous UV and dual electrochemical detection: Application to the selectivity enhancement for the determination of explosives, Electroanalysis, 20 (2008) 98-101.

[16] S. Nyiredy, Z. Szucs, L. Szepesy, Stationary-phase optimized selectivity LC (SOS-LC): Separation examples and practical aspects, Chromatographia, 63 (2006) S3-S9.

[17] M.R. Detaevernier, G. Hoogewijs, D.L. Massart, Development of a standardized analysis strategy for basic drugs, using ion-pair extraction and high-performance liquid chromatography - II. Selection of preferred HPLC-systems, J. Pharm. Biomed. Anal. , 1 (1983) 331-337.

[18] S. Lamotte, R. Brindle, K.D. Bischoff, Methodenentwicklung zur isokratischen Trennung von Triazinen mittels Phasenoptimierter Flüssigkeitschromatographie (Phase Optimized Liquid Chromatography, POPLC), LC GC, (2007) 46-47.

[19] M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt, A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, J. Chromatogr. A, 1216 (2009) 8910-8917.

# Chapter 4.

# Determination of polymer electrolyte membrane (PEM) degradation products in fuel cell water using electrospray ionization tandem mass spectrometry.

---

* Redrafted from M. Zedda, J. Tuerk, S. Peil, T.C. Schmidt: Determination of polymer electrolyte membrane (PEM) degradation products in fuel cell water using electrospray ionization tandem mass spectrometry, Rapid communications in mass spectrometry (2010), 24, 3531-3538, Copyright 2010 John Wiley & Sons.

## 4.1 Abstract

Within the scope of research of membrane degradation phenomena during fuel cell operationa reliable analytical procedure for extraction, detection and quantification of possible membrane oxidation products has been developed. These oxidation products originate from the attack of hydroxyl or peroxyl radicals on the membrane polymer. Such radicals are formed in-situ (during fuel cell operation) or ex-situ (Fenton test as oxidative stress simulation). The analysis of membrane oxidation products was done with electrospray ionization tandem mass spectrometry. Five potential membrane oxidation products (4-hydroxybenzoic acid (4-HBA), 4-hydroxybenzaldehyde (4-HBAD), 4,4-biphenol (4,4-BP), 4-hydroxybenzensulfonate (4-HBS), and 4,4-sulphonylbiphenol (4,4-SBP) were selected based on the molecular structure of the used sulfonated polyarylether membrane. In conjunction with the development of a multi reaction monitoring method (MRM), the ionization and fragmentation of the selected compounds were investigated. For 4,4-BP a molecular ion ($M^{+\bullet}$) was observed in the positive ionization mode and used for MRM method development. Reproducible extraction of the model compounds was achieved using a mixed mode sorbent material with both weak anion exchange and reverse phase retention properties. By using the developed analytical procedure, the identity of two conformable membrane degradation products (4-HBA and 4-HBAD) were determined in-situ and ex-situ. Besides the investigation of membrane degradation phenomena, the combination of extraction on a mixed mode sorbent material and tandem mass spectrometric detection is attractive for the analysis of aromatic sulfonic acids, phenolic acids and phenols.

## 4.2 Introduction

An integral part of polymer electrolyte membrane fuel cells are proton conductive membranes. These membranes are subject of aging resulting in subsequent loss of performance of the fuel cell [1, 2]. Possible reasons for membrane aging can be of mechanical, thermal and chemical nature and are discussed in recent reviews [3-6]. Chemical degradation has been determined to play a major role of membrane failure, leading to significant loss of membrane integrity [7]. Responsible for the chemical degradation mode are hydroxyl and peroxyl radicals. These radicals result from catalytic decomposition of hydrogen peroxide intermediates formed by incomplete reduction of molecular oxygen at the cathode side of the fuel cell [7, 8]. Hydroxyl and peroxyl radicals attack the polymer and consequently decrease the performance of the membrane during fuel cell operation. Thus, the analysis of the membrane degradation products during fuel cell operation is an important task for detection of the chemical degradation mode. Membrane degradation is usually investigated by destructive methods in which fuel cell stacks are taken apart (pre-and post analysis) and analyzed by various spectroscopic and spectrometric analytical methods including LC-MS [1, 4, 6, 9, 10]. However, the literature lacks of reliable analytical methods for real time in-situ membrane degradation product investigations during fuel cell operation. Such an analytical tool could be useful to study relationships between fuel cell operating parameters and identity and/or quantity of degradation products to give a better insight into membrane degradation processes. LC-MS/MS is an tool for trace analysis of polar compounds in aqueous samples. This technique is widely used for the research on the occurrence and fate of polar contaminants and polar transformation products in the environment [11]. In this study, five potential membrane degradation products (4-hydroxybenzoic acid (4-HBA), 4-hydroxybenzaldehyde (4-HBAD), 4,4-biphenol (4,4-BP), 4-hydroxybenzensulfonate (4-HBS), and 4,4-sulphonylbiphenol (4,4-SBP)) were selected for method development, based on the molecular structure of sulfonated polyarylether membranes (Figure 4-1). These potential degradation products can be classified into the classes of aromatic sulfonic acids, phenolic acids and phenols. The present status according to the selection of analyte separation (reversed phase chromatography, ion pair chromatography or capillary electrophoresis) and ionization conditions (electrospray ionization or atmospheric pressure chemical ionization) for trace level analysis of these compound classes by LC-MS has been reviewed by Reemstma [12]. However, detailed information on ionization and fragmentation of the selected model compounds is rare.

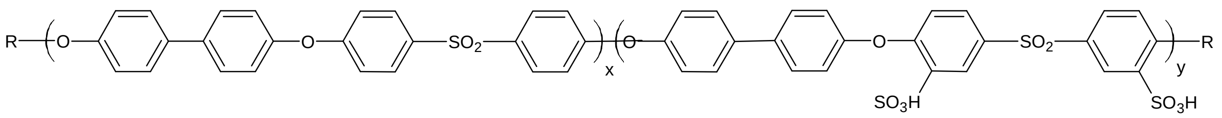


**Figure 4-1** Structure of the investigated sulfonated polyarylether membrane.

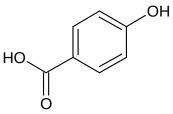
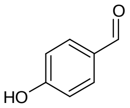
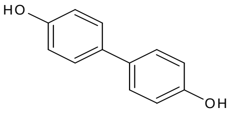
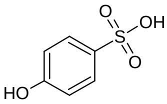
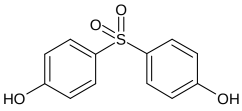
A further point is the extraction of both molecules and ions in a single solid phase extraction (SPE) procedure. The extraction is usually difficult and requires the extensive use of different types of sorbent materials. An alternative are mixed sorbent materials that consist of a polymeric skeleton and ion exchange groups which provide reversed phase and ionic exchange interaction mechanisms. This type of sorbent material has been successfully applied for the extraction of both molecules and ions from complex matrices, such as food, biological fluids, animal tissue, waste water and wood extracts [13]. The advantage is that analyte retention and release can be controlled by switching pH during the SPE steps for the efficient retention and release of molecules and ions from a water sample. In the whole context on the development of a non-destructive method for membrane degradation in the product water of fuel cells, the present work investigates the applicability of a mixed mode sorbent material for the extraction and electrospray ionization tandem mass spectrometry for reliable detection and quantification of possible membrane oxidation products.

## 4.3 Experimental and method development

*Chemicals*

All chemicals were analytical grade and purchased from Sigma Aldrich (Steinheim, Germany). The solvents for the chromatographic separation and extraction (water, acetonitrile and methanol) and the additive formic acid were LC-MS quality grade and purchased from Biosolve (Valkenswaard, Netherlands). Selected properties of five potential degradation products 4-hydroxybenzoic acid (4-HBA), 4-hydroxybenzaldehyde (4-HBAD), 4,4-biphenol (4,4-BP), 4-hydroxybenzensulfonate (4-HBS), and 4,4-sulphonylbiphenol (4,4-SBP) are listed in Table 4-1.

**Table 4-1** Selected properties of the model degradation products used in this study. The pka values were obtained from the SRC PhysProp Database and *SciFinder Scholar (calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02).

| Model compound | Structure | pK$_a$ | Molecular weight [g/mol] |
|---|---|---|---|
| 4-hydroxybenzoic acid<br>(4-HBA) |  | 4.5 | 138.1 |
| 4-hydroxybenzaldehyde<br>(4-HBAD) |  | 7.6 | 122.1 |
| 4,4-biphenol<br>(4,4-BP) |  | 9.7 | 186.2 |
| 4-hydroxybenzensulfonate<br>(4-HBS) |  | -0.2 | 174.2 |
| 4,4-sulphonylbiphenol<br>(4-SBP) |  | 7.6 | 150.1 |

### Preparation of stock and standard solutions

Individual stock solutions containing a concentration of 1 mg/mL of each model compound were prepared by individually dissolving 10 mg of 4-HBA, 4-HBAD, 4,4-BP, 4-HBS, and 4,4-SBP in 10 mL methanol. The standard solutions and quality control samples containing a mixture of the model compounds were prepared by mixing a certain volume from each stock solution. Further dilution to the desired concentrations was carried out with LC-MS water. All solutions were prepared in glass vials.

### *Solid phase extraction (SPE)*

### Cartridges

For low concentrated degradation products, a procedure for the extraction of degradation products with different chemical and physical properties was developed. For this study an Oasis WAX (Waters GmbH, Eschborn Germany) mixed mode sorbent material was chosen for selective sample preparation and cleanup. For 500 mL collected fuel cell water a cartridge with a volume of 6 mL, quantity of 150 mg packing material and a particle size of 30 µm was used. The SPE-cartridges were pre-conditioned with 10 mL methanol and equilibrated with 10 mL water followed by the extraction of 500 mL acidified fuel cell water (pH 2 with formic acid). The cartridges were subsequently washed with 5 mL 2 % formic acid in water. The following elution step (Elution 1) was done with 5 mL methanol to release neutral, basic and weak acidic compounds. The second elution (Elution 2) was done by adding 5 mL of a mixture containing 47.5 % methanol, 47.5 % acetonitrile and 5 % ammonium hydroxide (v/v/v) to neutralize the anion-exchange sites on the sorbent material for the release of strongly acidic compounds. Eluates of elution step 1 and 2 were evaporated separately to dryness under nitrogen stream. Each residue was reconstituted in 1 mL water and analyzed by LC-MS/MS. The washing step and both elution steps were analyzed regarding breakthrough of the model compounds. Blank samples (pure water) using the same extraction volume as the real samples were also processed in order to detect contamination originating from the sorbent material or other sources.

### 96-well-plate

For high throughput analysis of daily water samples, a 96-well-extraction plate was used for the simultaneous processing of multiple samples. Daily water samples of 10 mL produced during fuel cell operation were collected from the cathode side of the fuel cell. The 2 mL wells packed with 10 mg sorbent material were pre-conditioned with 2 mL methanol and equilibrated with 2 mL water followed by the extraction of 10 mL acidified fuel cell water (pH 2 with formic acid). The cartridges were subsequently washed with 1 mL 2 % formic acid in water. The analytes were finally eluted with 1 mL methanol (Elution 1) and 1 mL of a mixture containing 47.5% methanol, 47.5 % acetonitrile and 5 % ammonium hydroxide (v/v/v) (Elution 2). Elution 1 and Elution 2 were evaporated separately to dryness under nitrogen stream and were reconstructed in 0.1 mL water. Both solutions were analyzed by LC-MS/MS. The recovery rate and its precision were estimated by performing the experiments in triplicates.

### Liquid chromatography

A Shimadzu Prominence HPLC system consisting of a CBM-20A controller, a DGU-20A$_3$ degasser, two LC-20AD pumps, an SIL-20AC auto sampler, a CTO20AC column oven and an SPD-20AV UV detector (Shimadzu, Duisburg, Germany) were used. Baseline separation of the model compounds was achieved on an Atlantis T3 column (Waters GmbH, Eschborn, Germany). Stationary phase column length was 100 mm with an inner diameter of 2.1 mm and a particle size of 3 µm. The column oven temperature was set to 40 °C. Flow rate was adjusted to 0.3 mL/min for optimal spray conditions in the ion source. For all measurements, water with 0.1 % formic acid (A) and methanol with 0.1 % formic acid (B) were used as eluents. The gradient started from 5 % to 100 % (B) in 15 min.

### Mass spectrometry

For the detection of the model compounds, the HPLC-system was coupled to a linear ion trap quadrupole mass spectrometer (3200 Q Trap, AB SCIEX, Darmstadt, Germany). Ionization of separated analytes was made in the negative and positive mode with turbo-electrospray ionization at atmospheric pressure. Analysis of recorded data was accomplished with Analyst™ Software 1.5 (AB SCIEX, Darmstadt, Germany). The ionization of each compound was studied by enhanced full scan mass spectra regarding the formation of protonated molecules ($[M+H]^+$), deprotonated molecules ($[M-H]^-$), cationized molecules (e. g. $[M+Na]^+$) in positive and negative electrospray ionization mode. Fragmentation of the precurser ions produced in the ion source was investigated in the MS/MS mode by generating enhanced product ion spectra. The collision energy (manufacturer specification for the energy received by the precursor ions as they are accelerated into collision cell) was set to 30 eV for the positive and – 30 eV for the negative electrospray mode. Ionization and fragmentation were performed in continuous flow mode as well as the optimization of MRM transition scanning paramters. The precurser ions generated in the positive and negative ionization mode and their corresponding product ions are summarized in Table 4-2.

**Table 4-2** Observed ions and their corresponding product ions of the model compounds in the positive and negative electrospray ionization mode.

| Compound | Nominal Mass Da | Observed ion | Precursor ion [m/z] | Product ion [m/z] | CE [V] |
|---|---|---|---|---|---|
| 4-HBA | 138 | $[M-H]^-$ | 137 | 93, 65 | -30 |
| 4-HBAD | 122 | $[M-H]^-$ | 121 | 93 | -30 |
| 4,4-BP | 186 | $[M-H]^-$ | 185 | 156 | -30 |
| 4-HBS | 174 | $[M-H]^-$ | 173 | 108, 93, 92, 80 | -30 |
| 4,4-SBP | 250 | $[M-H]^-$ | 249 | 185, 156, 108, 92 | -30 |
| 4-HBA | 138 | $[M+H]^+$ | 139 | 121, 111, 95, 93, 77, 65 | 30 |
| 4-HBAD | 122 | $[M+H]^+$ | 123 | 105, 95, 77 | 30 |
| 4,4-BP | 186 | $M^{+\bullet}$ | 186 | 157,128, 115 | 30 |
| 4-HBS | 174 | $[M+H]^+$ | 175 | n. d. | 30 |
| 4,4-SBP | 250 | $[M+H]^+$ | 251 | 157,121, 109, 93, 65 | 30 |

The optimal ion source temperature was 550 °C and ion spray voltage -4200 V for negative and 5500 V positive ionization. Nitrogen was used as curtain (15 psi) and nebulizer (40 psi) and collsion gas (high: manufacturer specification). For detection of the precursor ions in the first mass analyzer and the corresponding product ions in the second analyzer, multiple reaction monitoring (MRM) mode was used. A dwell time of 60 ms was set to monitor each mass transition with a cycle time of 2.4 seconds. The result of MRM transition scanning parameters are listed in Table

4-3. The chromatographic separation of the model compounds using the MRM transition paramters is presented in Figure 4-2. The optimal ESI signals for positive and negative ionization were selected according to their intensity for MRM transitions of each tested compound.

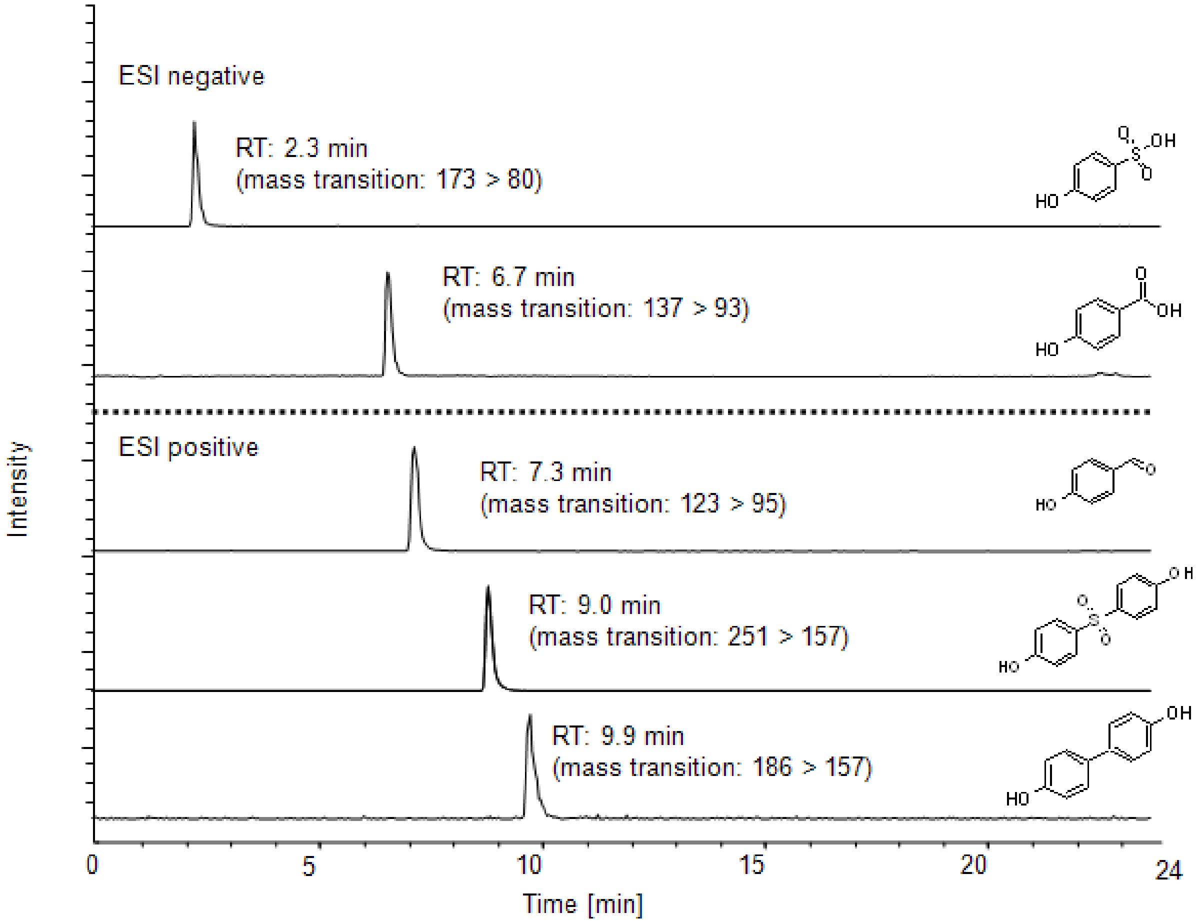


**Figure 4-2** Chromatographic separation presented by means of the individual mass transition of 4,4-sulphonylbiphenol, 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, 4-hydroxybenzensulfonate and 4,4-biphenol on an Atlantis T3 stationary phase (Waters GmbH, Eschborn, Germany) using gradient elution.

### *Quantification*

Model degradation standards consisted of a mixed standard solution in water (LC-MS Quality grade), which contained 4-HBA, 4-HBAD, 4,4-BP, 4-HBS, and 4,4-SBP. The instrument detection limit (IDL) for each analyte was determined as the lowest injected standard that gave a signal-to-noise ratio of at least 3 and a recovery rate of 70–130 %. Calibration standards from 0.1 to 100 mg/mL of the analyte mixture were injected before and after sample groups, and were analyzed using linear regression with inverse weighting (1/x). Satisfactory coefficients of determination ($r^2$) were obtained for all tested compounds (0.98–0.99). Blanks processed through the entire method were also analyzed with each sample set. Identification and quantification of the model compounds were made for samples with a signal to noise ratio of at least 3 and a minimum of two transitions observed at the expected retention time. The method precision was determined by the measurement of three spiked water samples processed through the entire analytical method (SPE, elution, concentration) at a low and medium calibration level (20 ng/mL and 60 ng/mL).

**Table 4-3** Optimized operating parameter settings for multi reaction monitoring (MRM) in the positive and negative electrospray mode and the limits of detection for the investigated model compounds.

| Analyte | Ionization-mode | | [a]Q1 [m/z] | [b]Q3 [m/z] | [c]CEP [V] | [d]CE [eV] | [e]CXP [V] | [f]IDL [ng/mL] |
|---|---|---|---|---|---|---|---|---|
| 4,4-SBP | positive | Quantification | 251 | 157 | 12 | 21 | 2 | 2 |
| | | Verification | 251 | 65 | 12 | 49 | 2 | |
| 4,4-BP | positive | Quantification | 186 | 157 | 10 | 37 | 2 | 20 |
| | | Verification | 186 | 128 | 10 | 51 | 2 | |
| 4-HBAD | positive | Quantification | 123 | 95 | 10 | 19 | 2 | 2 |
| | | Verification | 123 | 77 | 10 | 27 | 2 | |
| 4-HBA | negative | Quantification | 137 | 93 | -14 | -18 | -2 | 5 |
| | | Verification | 137 | 65 | -50 | -26 | -2 | |
| 4-HBS | negative | Quantification | 173 | 80 | -16 | -42 | -2 | 5 |
| | | Verification | 173 | 108 | -16 | -34 | -2 | |

[a] Q1: Precursor ion; [b] Q3: Product ion

[c] CEP [V]: Collision cell entrance potential (focuses ions into collision cell)

[d] CE [eV]: Manufacturer specification for the energy received by precursor ions as they are accelerated into collision cell.

[e] CXP [V]: Collision cell exit potential (transmits ions into Q3)

[f] IDL: Instrument detection limit

The method precision was less then 20 % for each analyte. The stability of the standard solutions was tested for a time period of 4 weeks by maintaining the prepared quality control samples at -18 and + 4 ℃. It was observed that the standard solutions were stable during the test period for both tested temperatures.

### Membrane stress tests

#### Ex-Situ

In order to verify that the selected model degradation products are formed by chemical degradation via hydroxyl and peroxyl radical attack on the polymer, a common laboratory stress test was applied [6]. The membrane degradation was simulated under extreme conditions (3 % $H_2O_2$ and 0.1 mg/L $Fe^{2+}$ at pH 2.8) to obtain membrane degradation products in a reasonable time. For this purpose, 100 mL glass vials were filled with 80 mL water and the pH was adjusted to 2.8 using 5 % $H_2SO_4$ for optimal Fenton reaction conditions. 10 mL of 1 mmol/L $Fe^{2+}$ solution ($FeSO_4$) was prepared and added to the pH 2.8 water solution. For the experimental batch, 100 mg of sulfonated polyarylether membrane was immersed in the solution. In order to start the Fenton reaction, 10 mL of 30 % $H_2O_2$ solution was added drop wise and stirred continuously. The solutions were kept at 68 °C in a water bath for 24 hours. The reaction was stopped by adjusting the pH to 7 using $NH_4OH$ for iron precipitation. The solution was stabilized with 5 % methanol. Membrane degradation products were extracted and analyzed by LC-MS/MS as described in the experimental section.

#### In-Situ

In situ tests are performed by operating a fuel cell stack (5 cells, active area of a single cell 100 $cm^2$) assembled with the corresponding membranes. An electronic load is used to regulate the power output of the fuel cell stack. The membranes have been tested by applying predefined operating procedures. On one hand, the stacks have been operated at 30 %, 50 % and 70 % of their maximum output for several hours. On the other hand, extreme operating conditions at highest electric power are applied to stress the membranes. Membranes were humidified by saturating the cathodic air at the stack-inlet with highly purified water. Product water and humidification water is carried out of the stack and collected for membrane degradation product analysis.

## 4.4 Result and discussions

### Solid phase extraction

Solid phase extraction was used for the enrichment of low concentrated chemical degradation products generated during fuel cell operation. Table 4-4 shows the recovery rate and the precision expressed as the relative standard deviation (RSD [%]) at two different concentrations using the extraction procedure described in the experimental section.

**Table 4-4** Summary of recovery rate and precision.

| Target concentration [ng/mL] | Validation parameters | 4-HBA | 4,4-BP | 4,4-SBP | 4-HBAD | 4-HBS |
|---|---|---|---|---|---|---|
| 20 | Mean [ng/mL] (n=3) | 19.8 | 8.6 | 14.7 | 16.9 | 18.7 |
| | Recovery rate | 98.9 | 43.2 | 73.6 | 84.5 | 93.3 |
| | RSD[%] | 7.8 | 10.6 | 5.5 | 6.5 | 10.1 |
| 60 | Mean [ng/mL] (n=3) | 60.9 | 24.8 | 45.2 | 44.3 | 54.8 |
| | Recovery rate | 101.5 | 41.3 | 75.4 | 73.8 | 91.4 |
| | RSD[%] | 7.8 | 5.9 | 2.2 | 12.9 | 9.9 |

Except 4,4-BP, all tested compounds were sufficiently extracted on the mixed mode weak anion-exchange material. Although, a low recovery rate of approximately 40 % was achieved for 4,4-BP, it was reproducible as well as for the other compounds. The precision for both tested concentration levels (20 and 60 ng/mL) is within an acceptable range of 2 to 13 %. The release of the species (4-HBA, 4-HBAD, 4,4-SBP and 4,4-BP) with high $pk_a$ values ($pk_a$ 4.5-9.7) was observed in first elution step. Only, 4-HBS ($pk_a$ -0.2) was not detected in the first elution step. Sulfonic acids are in general difficult to extract on common sorbent materials due to their polarity and hydrophilic properties. The release of this compound with relatively high rates of recovery in the second elution step was accomplished by neutralization the anion-exchange sites on the sorbent material using 5 % ammonium hydroxide. This shows that sulfonic acids are well retained by electrostatic interactions between the ionized sulfonic acid and the ionized amino-group, which has been also observed by Chen et al. [14]. Overall the extraction procedure showed high potential for the extraction of possible membrane degradation products from fuel cell water samples.

**Mass spectrometry**

Prior to MRM-method development all compounds were tested regarding electrospray ionization and sufficient fragmentation in the collision cell by enhanced MS scans (EMS) and enhanced product ion scans (EPI) in the positive and negative ionization mode. The precursor ions and their product ions are summarized in Table 4-2. All tested compounds showed the formation of protonated ($[M+H]^+$) and deprotonated ($[M-H]^-$) ions in the positive and negative electrospray mode, repectively. 4,4-BP showed an base peak signal in the EMS spectrum of *m/z* 186 which is equal to its nominal mass. The protonated molecule $[M+H]^+$ at *m/z* 187 was also observed but its intensity was approximately a third less than *m/z* 186. This observation could refer to the formation of a molecular ion ($M^{+\bullet}$) in the electrospray ion source. Such a formation is especially observed for organic substances with low oxidation potentials such as polycyclic aromatic hydrocarbons that are produced by removal of one or more electrons in the electrospray source [15]. Fragmentation of the selected compound class was studied by MS/MS experiments with nitrogen as collision gas. A fragmentation of the precursor ions into at least two product ions was desired in order to set up a multi reaction monitoring with two mass transitions for quantification and verification for the targeted analytes. All compounds showed sufficient fragmentation and at least two product ions were observed for each compound in the positive and negative ionization modes. Only 4-HBAD and 4,4-BP showed insufficient fragmentation in the negative ionization mode. However, Figure 4-3 (a, b, c, d and e) shows the enhanced product ion spectra of the investigated compounds. These mass spectra are shown and discussed because they were selected for MRM. The fragmentation of the 4-HBA precursor ion (*m/z* 137) in the negative ionization mode is presented in Figure 4-3 (a). The intensive product ion *m/z* 93 corresponds to the loss of $CO_2$ (-44 Da) originating from the carboxylic acid group. Gruz et al. have used this mass transition of 137 > 93 for the determination of

4-HBA in the analysis of phenolic acids in beverages [16]. The product ion *m/z* 65 could refer to $C_5H_5^+$, which could be a product of a carbonyl formed by α-cleavage of the phenol residue indicated by the loss of CO (-28 Da). Both product ions (*m/z* 93 and 65) were used for MRM detection of 4-HBA in the negative ionization mode. Figure 4-3 b shows the fragmentation of the 4-HBS precursor ion (*m/z* 173) in the negative ionization mode. The product ion spectrum shows product ions of *m/z* 108 and 109 which suggest the loss of $SO_2$ and $SO_2H$. A similar product ion was suggested for the fragmentation of sulfonated ortho-hydroxy azo dyes, where a further fragmentation of the hydroxybenzene sulfonic acid radical anion (*m/z* 172) gave a fragment of *m/z* 108 [12]**.** Furthermore, a phenol residue with *m/z* 93 is also observed in the product ion spectrum. The presence of *m/z* 80 corresponds to the common $SO_3{\bullet}^-$ ion, which is characteristic for the fragmentation of aromatic sulfonic acids [17]. This compound-specific fragment has been used as a marker to determine the presence of aromatic sulfonic acids in environmental samples using parent ion scans. Some researchers found that aromatic sulfonates frequently undergo loss of $SO_2$. This explains the presence of *m/z* 109 in the mass spectrum. The product ion *m/z* 93 corresponds to the loss of the sulfonate group. For MRM screening of 4-HBS the product ions 109 and 80 were used. The fragmentation of the 4-HBAD precursor ion (*m/z* = 123) in the positive ionization mode showed two dominating product ions at *m/z* 77 and 95 (Figure 4-3 (c)). This fragmentation pattern is in line with the loss of the carbonyl group and of both functional groups (carbonyl- and hydroxylgroup). Both product ions were used for MRM detection of 4-HBAD. Figure 4-3 d shows the fragmentation of the 4,4-BP precursor ion in the positive ionization mode. Three low abundant product ions (*m/z* 115, 128, 157) were obtained for this molecule ion at CE of 30 eV. It is interesting to note that the fragmentation of the observed molecular ion (*m/z* 186) for 4,4-BP by MS/MS is comparable to the fragmentation observed in electron impact (EI)-mass spectra registered in the NIST database. The product ion *m/z* 157 (M-29 Da) most probably corresponds to the loss of a formyl radical ($CHO^{\bullet}$), which is also observed from phenol fragmentation indicated by the loss of an odd mass difference to molecule ion. A further product ion observed is *m/z* 128. The elimination of 58 Da has been interpreted as the loss of 2 $CHO^{\bullet}$ [18]. Another possibility could be an elimination of $C_3H_6O$ (M-58 Da) resulting from ring opening and complex rearrangements. However, the product ions *m/z* 128 and 157 were used for the MRM-detection of 4,4-BP. The fragmentation of the 4,4-

SBP precursor ion (*m/z* = 251) in the positive ionization mode is presented in Figure 4-3 (e). The most abundant product ions observed for this molecule are m/z 157, 121, 109, 111, 93 and 65. The presence of the intensive product ions *m/z* 93 and 157 indicates bond fission between the sulfonyl-group and the phenol residue. The same fragmentation has been proposed by Shintani et al. where 4,4-SBP was studied in conjunction with the determination of inhibiting compounds for sterilization of medical devices using LC-MS/MS [19]. The product ion *m/z* 65 corresponds to the protonated sulfonyl-group resulting from the loss of both phenol residues. The product ions *m/z* 109 and 111 are most probably elimination products of *m/z* 157 $[C_6H_5O_3S]^+$, which could be assigned to common sulphur containing fragments $[H_3C\text{-}SH]^+$ and $[CH_2S]^+$. The product ions *m/z* 157 and 65 were used for MRM detection of 4,4-SBP. Overall, the product ion mass spectra show sufficient fragmentation ions for the tested compounds, which enable qualitative and quantitative screening using tandem mass spectrometry. The final and optimized MRM detection scanning and source parameter as well as the instrument detection limits (IDL), working range and linearity for all compounds are presented in the experimental section.

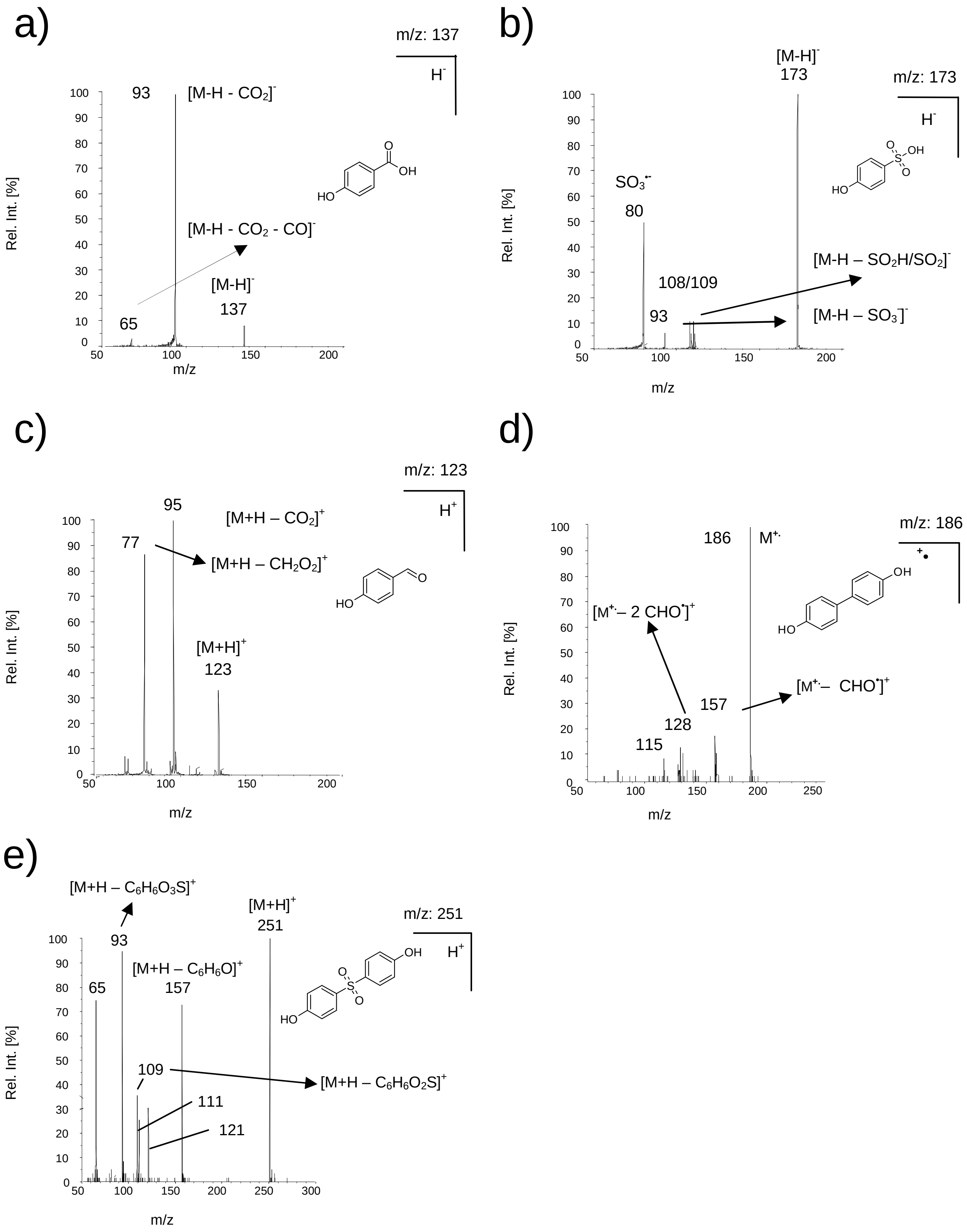


**Figure 4-3** Enhanced product ion spectra of (a) 4-HBA and (b) 4-HBS in the negative ionization mode, and (c) 4-HBAD, (d) 4,4-BP and (e) 4,4-SBP in positive ionization mode.

### Qualitative application of the developed analytical procedure

Prior to quantitative screening measurements of degradation products in daily fuel cell water samples, the presence of the selected possible low concentrated degradation products originating from the assembled sulfonated polyarylether membrane was studied by a qualitative MRM-screening of 500 mL collected and extracted fuel cell water. The findings were then compared with degradation products produced in an artificial laboratory stress test (Fenton test). This test should give similar degradation products to those theoretically selected and formed by the proposed chemical degradation mechanism. Figure 4-4 shows the result of the qualitative investigation of membrane degradation products in both stress test procedures.

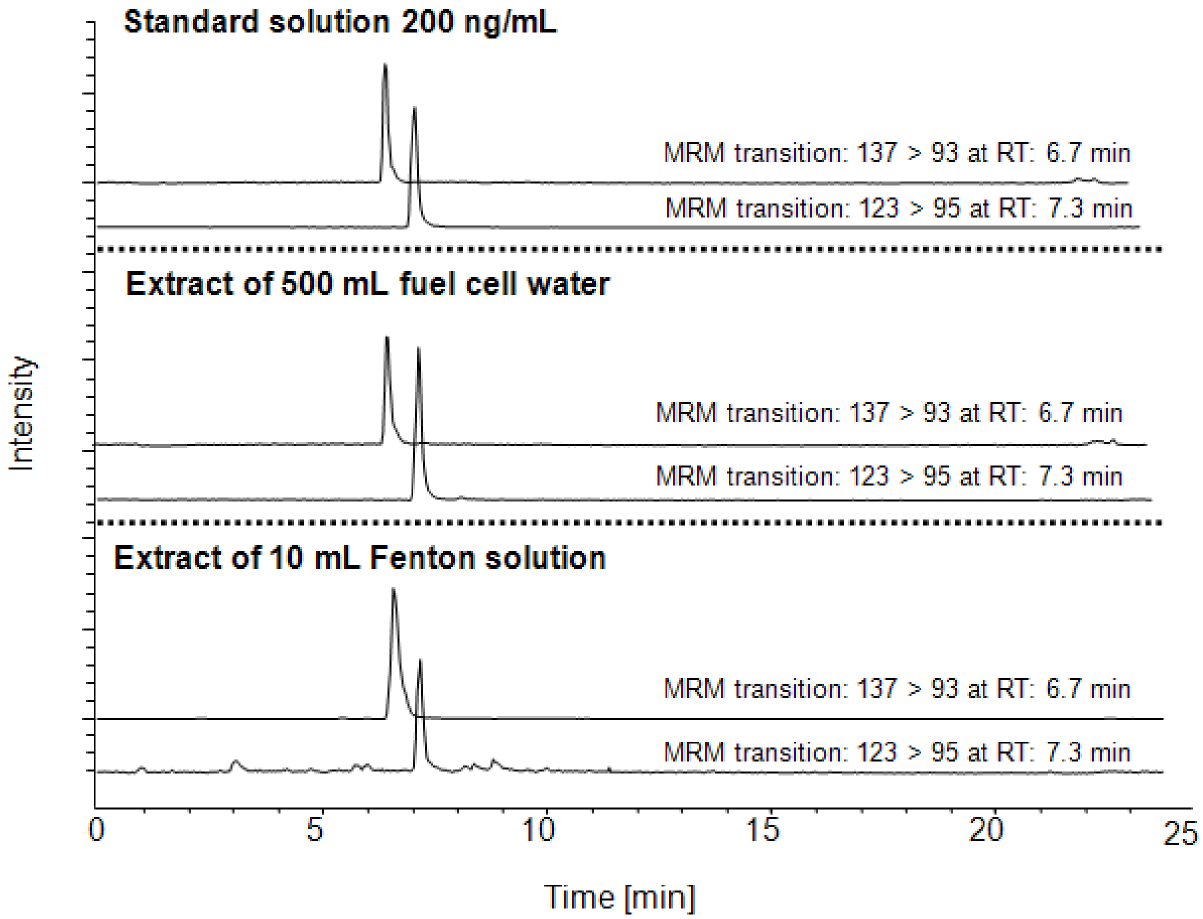


**Figure 4-4** Result of qualitative investigation of membrane degradation products using the developed SPE-LC-MS/MS method. 4-hydroxybenzoic acid (MRM transition: 137 > 93 at RT: 6.7 min) and 4-hydroxybenzaldehyde (MRM transition: 123 > 95 at RT: 7.3 min) were detected in the real fuel cell water sample and in the artificial stress test.

4-HBA (MRM transition: 137 > 93 at RT: 6.7 min) and 4-HBAD (MRM transition: 123 > 95 at RT: 7.3 min) were detected in the water as well as in the artificial laboratory stress test. The same degradation products were found in a previous study using phased optimized liquid chromatography and UV-MS/MS detection [20]. Compared to the present work, a different solid phase extraction material was used for the extraction of membrane degradation products from the product water. By using the artificial stress test, the presence of the indentified degradation products found in the fuel cell water could be assigned to membrane degradation by hydroxyl and hydroperoxyl radicals formed during fuel cell operation. 4-HBS, 4,4-SBP and 4,4-BP were not detected in the fuel cell water, whereas all of these were detected in the artificial stress test (data not shown). Based on the results, 4-HBA and 4-HBAD are potential marker substances for chemical degradation, which could be used for the detection of early stage membrane degradation during fuel cell operation in order to determine the oxidative stability of the membrane.

### Quantitative screening of membrane degradation products

For the sensitive MRM-screening of daily fuel cell water samples an analytical method for high sample throughput is needed. Such a method could be used for the determination of the actual state of the membrane during fuel cell operation and to study correlations between fuel cell operation parameters and identity and quantity of degradation products. Therefore, the extraction procedure was modified using 96-well extraction plates with the same sorbent material applied for qualitative screening, which enables the possibility for rapid parallel automated solid-phase extraction. The potential marker substances 4-HBA and 4-HBAD found by qualitative analyses in the ex-situ and in-situ test were used for method transfer. For this purpose, the recovery rate and the precision were compared between both extraction techniques for two concentration levels (20 and 60 ng/mL). The extraction efficiencies for 4-HBA achieved on the cartridge were 99 % ± 8 % at a concentration level of 20 ng/mL and 102 % ± 8 % and at a concentration of 60 ng/mL. The extraction efficiencies for 4-HBA achieved on the 96-well plate at 20 ng/mL and 60 ng/mL were 93 % ± 23 % and 95 % ± 4 %, respectively. Both extraction techniques provide comparable results for the recovery rate, which shows the good transferability of the method. Comparable results were found for 4-HBAD with extraction efficiencies of 85 % ± 7 % and 90 % ± 28 % at a concentration of 20 ng/mL and 74 % ± 13 and 62 % ± 19 % at a concentration level of 60 ng/mL for the cartridge and 96-well plate, respectively. The precision for the extraction efficiencies on the cartridges are below 10 %, the precision for the 96-well plate was found to be around 20 %. In order to improve the precision, automated SPE-systems could help to reduce manual errors, which are possible when handling small sample volumes. Despite the still rather high standard deviation, the developed analytical procedure has been applied to product water samples collected at the stack outlet from the cathode side of the fuel cell. A sample volume of 10 mL of fuel cell water was extracted on the 96-well plate. A concentration of 17 to 27 ng/mL and 27 to 43 ng/mL was detected during two weeks of fuel cell operation for 4-HBA and 4-HBAD, respectively. The concentrations found in the fuel cell water samples are well above the instrument detection limits for 4-HBA (5 ng/mL) and 4-HBAD (2 ng/mL). The presented analytical approach is attractive for the purpose of a regular monitoring of membrane degradation products in fuel cell water samples in order to study correlations between fuel cell operation parameters and quantity membrane degradation products in the future.

## 4.5 Conclusions

This work has shown that electrospray ionization tandem mass spectrometry is a reliable tool for the investigation of membrane degradation products in fuel cell water. The recorded mass spectra of each selected model compound as well as the developed extraction procedure enables further non-target investigations using the triple quadrupole linear ion trap mass spectrometer. Furthermore, the quantity of selected marker substances in daily fuel cell water samples can be analyzed by a high sample throughput extractions procedure (96 well-plate). The extraction procedure enables to study correlations between fuel cell operation parameters and membrane degradation products in the future for a better understanding of the membrane degradation phenomena.

## 5.6 Acknowledgement

The authors would like to thank for financial support from the German Federal Ministry of Economics and Technology within the agenda for the promotion of industrial cooperative research and development (IGF) based on a decision of the German Bundestag. The access was opened by the Verein zur Förderung der Energie- und Umwelttechnik e.V, VEU Duisburg and organised by the AiF, Arbeitsgemeinschaft industrieller Forschungs-vereinigungen, Cologne, (IGF-Project No. 14941 N). Furthermore, we would like to thank Jochen Kerres and Andreas Chromik for synthesizing the PEM, Kirsten Helle for providing the product water, Claudia vom Eyser and Karolin Wendrich for the assistance in the laboratory work, and for the comments and feedbacks from two anonymous reviewers, which have improved the quality of the manuscript.

## 4.6 Literature

[1] J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo, A. Brundage, H. Gasteiger, J. Abbott, Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells, Fuel Cells, 5 (2005) 302-308.

[2] A.B. LaConti, M. Hamdan, R.C. McDonald, Mechanisms of membrane degradation, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.) Handbook of Fuel Cells - Fundamentals, Technology and Applications, 2003, pp. 647-677.

[3] A. Collier, H.J. Wang, X.Z. Yuan, J.J. Zhang, D.P. Wilkinson, Degradation of polymer electrolyte membranes, Int. J. Hydrogen Energy, 31 (2006) 1838-1854.

[4] F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Durability and degradation issues of PEM fuel cell components, Fuel Cells, 8 (2008) 3-22.

[5] J.F. Wu, X.Z. Yuan, J.J. Martin, H.J. Wang, J.J. Zhang, J. Shen, S.H. Wu, W. Merida, A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies, J. Power Sources, 184 (2008) 104-119.

[6] S.S. Zhang, X.Z. Yuan, H.J. Wang, W. Merida, H. Zhu, J. Shen, S.H. Wu, J.J. Zhang, A review of accelerated stress tests of MEA durability in PEM fuel cells, Int. J. Hydrogen Energy, 34 (2009) 388-404.

[7] C. Perrot, L. Gonon, C. Marestin, A. Morin, G. Gebel, Aging mechanism of Sulfonated poly(aryl ether ketone) (sPAEK) in an hydroperoxide solution and in fuel cell, J. Power Sources, 195 (2010) 493-502.

[8] Q.H. Guo, P.N. Pintauro, H. Tang, S. O'Connor, Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes, J. Membr. Sci., 154 (1999) 175-181.

[9] F.N. Büchi, M. Inaba, T.J. Schmidt, Polymer Electrolyte Fuel Cell Durability, Springer, 2009.

[10] J. Lawrence, T. Yamaguchi, The degradation mechanism of sulfonated poly(arylene ether sulfone)s in an oxidative environment, J. Membr. Sci., 325 (2008) 633-640.

[11] C. Zwiener, F.H. Frimmel, LC-MS analysis in the aquatic environment and in water treatment--a critical review. Part I: Instrumentation and general aspects of analysis and detection, Anal Bioanal Chem, 378 (2004) 851-861.

[12] T. Reemtsma, Liquid chromatography-mass spectrometry and strategies for trace-level analysis of polar organic pollutants, J. Chromatogr. A, 1000 (2003) 477-501.

[13] N. Fontanals, R.M. Marce, F. Borrull, New materials in sorptive extraction techniques for polar compounds, J. Chromatogr. A, 1152 (2007) 14-31.

[14] H.C. Chen, S.P. Wang, W.H. Ding, Determination of fluorescent whitening agents in environmental waters by solid-phase extraction and ion pair liquid chromatography-tandem mass spectrometry, J. Chromatogr., A, 1102 (2006) 135-142.

[15] R. Vessecchi, A.E.M. Crotti, T. Guaratini, P. Colepicolo, S.E. Galembeck, N.P. Lopes, Radical ion generation processes of organic compounds in electrospray ionization mass spectrometry, Mini-Rev. Org. Chem. , 4 (2007) 75-87.

[16] J. Gruz, O. Novak, M. Strnad, Rapid analysis of phenolic acids in beverages by UPLC-MS/MS, Food Chem., 111 (2008) 789-794.

[17] M.J.F. Suter, S. Riediker, W. Giger, Selective determination of aromatic sulfonates in landfill leachates and groundwater using microbore liquid chromatography coupled with mass spectrometry, Anal. Chem., 71 (1999) 897-904.

[18] M. Gesell, E. Hammer, M. Specht, W. Francke, F. Schauer, Biotransformation of biphenyl by Paecilomyces lilacinus and characterization of ring cleavage products, Appl. Environ. Microbiol., 67 (2001) 1551-1557.

[19] H. Shintani, E. Suzuki, M. Sakurai, Determination of compounds inhibiting bacterial growth in sterilized medical devices, Chromatographia, 58 (2003) 193-199.

[20] M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt, A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, J. Chromatogr., A, 1216 (2009) 8910-8917.

# Chapter 5.

## Stability investigations of a polybenzimidazole-blended sulphonated polyarylether membrane during fuel cell operation by product water analysis.

---

* Redrafted from M. Zedda, J. Tuerk, S. Peil, T.C. Schmidt, J. Kerres, A. Chromik: A stability investigation of polybenzimidazole blended sulphonated polyarylether membrane during fuel cell operation on basis of a product water analysis, submitted to Journal of Membrane Science, 2011.

## 5.1 Abstract

The predominant long term failure of polymer electrolyte membranes (PEM) is caused by chemical degradation. Hydroperoxyl and hydroxyl radicals which are generated during operation attack the membrane, cause irreversible damage to it, and consequently decrease the performance of the fuel cell. The present work has investigated the stability of a polybenzimidazole blended sulphonated polyarylether membrane during fuel cell operation on basis of product water analysis. The study has been performed by a comparative analysis of the product water (in-situ) and an accelerated stress test with Fenton test (ex-situ). The analysis was performed using information dependent acquisition (IDA) experiments with a linear ion trap of a hybrid mass spectrometer. Structure identification was done using combination of enhanced mass scan (EMS) as a survey measurement and enhanced product ion scan (EPI) as the information dependent experiment. Hydroxybenzoic acid (HBA) was found in the Fenton test as well as in the product water. Chromatographic separation of the three possible isomers was used for identification of 4-HBA in all samples. This degradation product could be assigned to a monomer of the polybenzimidazole blended sulphonated polyarylether membrane. Gel permeation chromatography (GPC) analysis of virgin and stressed membranes suggests chain end scission of the membrane.

## 5.2 Introduction

Durability concern of polymer electrolyte membrane fuel cell (PEMFC) systems is one of the major issues that impede the commercialization of fuel cell technology [1]. Among mechanical and thermal stability issues, the chemical degradation has been identified as the major mechanism for perfluorosulfonic acid (PFSA) membranes during fuel cell operation [2, 3]. It has been widely accepted that hydrogen peroxide ($H_2O_2$) and related radical species such as hydroperoxyl ($HO_2^\bullet$) and hydroxyl ($HO^\bullet$) are generated during fuel cell operation [4, 5]. Several recent studies support this phenomenon, which have detected hydrogen peroxide in the exhaust gas, product water and directly in the membrane [6-8]. Hydroxyl and hydroperoxyl radicals will attack the polymer, leading to chain scission, unzipping, and loss of functional groups [9]. Therefore, the formation of hydroxyl and peroxyl radicals by catalytic decomposition of hydrogen peroxide with traces of bivalent transition metal cations ($Fe^{2+}$, $Cu^{2+}$) has been established as an accelerated laboratory stress test, in order to investigate the chemical stability and degradation of PEM [2, 10, 11]. The membranes are usually immersed into Fenton reagent containing 3% $H_2O_2$ aqueous solution mixed with up to 4 mg/L $Fe^{2+}$ at 68 ℃ [12]. Organic compounds resulting from degradation of PFSA and polystyrene sulfonic acids membranes that were extracted from degraded membranes in fuel cells have been found to be similar to the compounds detected in Fenton test [3, 10, 13]. Although the Fenton test has been considered as a benchmark for PEM evaluation, it has limitations. The deterioration of the membrane in such an accelerated oxidative stress test involves no electrode process and variations in fuel cell operating conditions such as operating potential, relative humidity, lack of fuel and oxidant, etc.. However, an accelerated oxidative stress test (ex-situ test) can still be useful to allocate degradation product findings from fuel cell experiments (in-situ test) to a degradation mechanism. This work will investigate the oxidative stability of sulfonated poly(arylene ether sulfone) (SPES) membranes blended with polybenzimidazole (PBI) (

Figure 5-1) [14, 15]. These membranes are functionalized with sulfonic acid groups, which provide the proton conductivity property to the membrane. With a high content of sulfonic acid groups of the sulfonated polymer we are able to use the method of ionical-cross linking to increase the chemical stability of these membranes compared to that of the pure acidic polymer. Until now, only limited information concerning durability of the sulfonated polyaromatic membranes during fuel cell operation is available. In two recently published articles possible sites for radical attack on SPES during fuel cell operation and artifical stress test have been identified [12, 16]. However, Zhang et al. suggested the analysis of the water released during fuel cell operation in order to identify decomposition products to aid the clarification of the degradation mechanism. Membrane degradation products resulting from chemical degradation are oxidation products similar to those resulting from advanced oxidation processes. Such oxidation products are expected to be more polar than the precursor compounds and therefore more water soluble and quite mobile [17]. These polar and mobile compounds should be detectable in the water produced during fuel cell operation. A sophisticated product analysis should be able to indicate chemical degradation during fuel cell operation and might aid to identify weak sites of the membrane. In an earlier study, the detection of small quantities of small water soluble organic units resulting from chemical degradation of polymeric styrene sulfonic acid membranes in the product water using reversed phase high performance liquid chromatography with diode array UV detection (RP-LC-DAD) [13]. A more recent investigation has been presented by Carlsson et al. with the focus on PFSA membrane degradation [18]. This research group has analyzed decomposition products of PFSA membranes in the product water using liquid chromatography tandem mass spectrometry (LC-MS) and found small organic carboxylates and sulfonates originating from chemical degradation of the membrane. Complementary to previous studies, this study investigates the chemical degradation phenomena of PBI blended SPES membranes on the basis of product water analysis using liquid chromatography linear ion trap tandem mass spectrometry. A procedure for the extraction, sensitive and selective detection of possible decomposition products has been developed earlier [19]. Intelligent software algorithms implemented into MS software allow automatic switching between acquisition modes based upon user-defined selection criteria in a single chromatographic run, which is also referred to as “information dependent acquisition (IDA)”. In this context we have used an enhanced mass scan (EMS) as a survey scan and an information dependent enhanced product ions scan (EPI) to aid structure identification of possible membrane degradation products.

## 5.3 Materials and methods

### Chemicals

All chemicals were analytical grade and purchased from Sigma Aldrich (Steinheim, Germany). The solvents for the chromatographic separation and extraction (water, acetonitrile and methanol) and the additive formic acid were LC-MS quality grade and purchased from Biosolve (Valkenswaard, Netherlands).

### Polymer Preparation

The polymer was synthesized by a procedure described earlier by Kerres et al. [20]. 40 mmol 4,4-biphenol (4,4-BP) was added to a 3-neck flask equipped with a mechanical stirrer, Ar-gas inlet, and reflux condenser. 200 ml of N-methyl-2-pyrrolidon (NMP) were added and the mixture was stirred until the monomer was dissolved. 240 mmol $K_2CO_3$ was added and the mixture was stirred under argon atmosphere at 100 ℃ for 6 hours. 20 mmol bis(4-fluorophenyl)sulfone (BFPS) and 20 mmol 3,3-disulfonated-4,4-difluorodiphenylsulfone (SDFDPS) were dissolved in 200 ml NMP. This solution was added into the reaction mixture and heated to 130 ℃ for 24 h. After the solution was cooled down to room temperature, the polymer was precipitated in 1 L of isopropanol. The polymer was filtered and washed for many times in water and then dialysed for 48 h, changing the water 3 times a day.

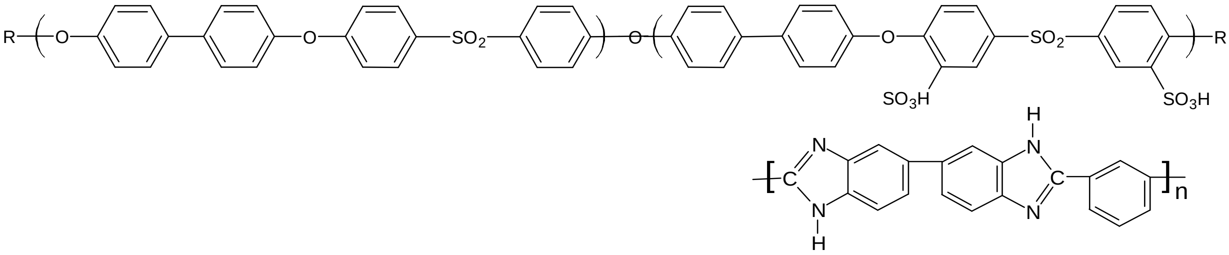


**Figure 5-1** Structures of the SPES as acidic polymer in excess and the PBI polymer (below) as basic blend component.

The ion-exchange capacity (IEC) describes the amount of ion-exchange groups per weight unit of dry ion-exchange resin in [meq/g] or [mmol/g] and is determined via titration. We can distinguish between the $IEC_{direct}$ and $IEC_{total}$. The first value gives information on the quantity of $SO_3H$ groups in ionical-crosslinked membranes whose protons contribute to proton conductivity, whereas the $IEC_{total}$ records all $SO_3H$ groups, therefore including those which are involved in the ionical cross-links and hence do not contribute to proton conductivity [21]. In Table 5-1 the specific data of the pure polymer and the blend membranes are listed. From these membranes a five cell stack was assembled at the Centre for Solar Energy and Hydrogen Research Baden-Wuerttemberg (ZSW, Ulm, Germany). It also can be seen that the PBI blended SPES membranes show lower water uptake and therefore a lower swelling degree, compared to SPES, which is also comparable to Nafion®. Another aspect is that the specific resistance of the blend membranes increases compared with the pure polymer. The resistance of the blend membranes was in the same range as for the pure polymer but not constant for all blend membranes (see Table 5-1). A small increase in the specific resistance can be explained by a reduction of number of free $SO_3H$ groups taking part in proton conduction by ionical cross-linking. The range of obtained values for the specific resistance can be explained by the sensitivity of membrane properties to small fluctuations in membrane preparation conditions (local temperature and pressure fluctuations, different solvent evaporation rates etc.)

**Table 5-1** Composition of the acid base blend membranes, their ion exchange capacity and specific resistance values.

| **Composition** | | **Water uptake** | **Water uptake** | **$IEC_{direct}$** | **$IEC_{total}$** | **Specific resistance** |
|---|---|---|---|---|---|---|
| **Acidic Polymer** | **PBI content** | | | | | |
| **[wt%]** | **[wt%]** | **[wt%] at 25 °C** | **[wt%] at 90 °C** | **[meq $g^{-1}$]** | **[meq $g^{-1}$]** | **[Ohm cm]** |
| 100 | 0 | 25 | 55 | 1.6 | 1.8 | 6 |
| 94 | 6 | 22 | 48 | 1.2 | 1.7 | 6-15 |

**Membrane and MEA preparation**

The membranes were prepared by casting the 10wt% solution in N,N-dimethylacetamide (DMAc) or NMP onto glass plates, followed by drying at 130 °C under vacuum at least for 3 h. Subsequently, pieces of 15 x 15 $cm^2$ in size were cut. All membranes were soaked in 10 wt% HCl at 90 °C for 48 h and subsequently washed with deionized water to pH 7. The amount of acidic polymer and basic PBI was calculated to obtain a theoretical IEC of 1.35 meq $SO_3H$/g membrane. The catalyst layer was sprayed on the membranes applying a wet spraying method at the ZSW with a loading of 0.5 mg/cm$^2$ Pt [22].

## Membrane stability investigation

### Molecular weight determination of polymers

The molecular weight distributions of the polymers and ionomers were determined by gel permeation chromatography (GPC) using an Agilent Technology GPC system (Series 1200) coupled with a viscosity detector (PSS ETA-2010), a refractive index detector (Shodex RI71) and a static light-scattering detector (PSS SLD 7000). A set of three PSS GRAM columns (30, 3000, 3000 Å) was used and calibrated with a series of polystyrene standards in N,N-dimethylacetamide containing 5 g/L LiBr.

### TGA-FTIR coupling experiments

The thermal stability of the membranes was determined via thermogravimetry analysis (TGA, Netzsch, model STA 449C) under a 65 - 70 % $O_2$ atmosphere (rest $N_2$). Heating rate was 20 K/min. The hot gases have been investigated via TGA-FTIR coupling, using a heated transfer line in order to identify the gaseous thermal degradation products. The occupied FTIR spectrometer was a Nicolet Nexus. For correlation of TGA with FTIR running time and temperature, a $CO_2$ gas injection was used for marking of the TGA traces and of the FTIR spectra.

## Product water analysis

### Solid phase extraction

For low concentrated degradation products, a procedure for the extraction of degradation products with different chemical and physical properties was developed and published earlier [19]. Briefly, for this study an Oasis WAX (Waters GmbH, Eschborn Germany) mixed mode sorbent material was chosen for selective sample preparation and clean-up. For 500 mL collected fuel cell water a cartridge with a volume of 6 mL, quantity of 150 mg packing material and a particle size of 30 µm was used. The SPE-cartridges were pre-conditioned with 10 mL methanol and equilibrated with 10 mL water followed by the extraction of 500 mL acidified fuel cell water (pH 2 with formic acid). The cartridges were subsequently washed with 5 mL 2 % formic acid in water. The following elution step (Elution 1) was done with 5 mL methanol to release neutral, basic and weak acidic compounds. The second elution (Elution 2) was done by adding 5 mL of a mixture containing 47.5 % methanol, 47.5 % acetonitrile and 5 % ammonium hydroxide (v/v/v) to neutralize the anion-exchange sites on the sorbent material for the release of strongly acidic compounds. Eluates of elution step 1 and 2 were evaporated separately to dryness under nitrogen stream. Each residue was reconstituted in 1 mL water and analyzed by LC-MS/MS. The washing step and both elution steps were analyzed regarding breakthrough of the model compounds. Blank samples (pure water) using the same extraction volume as the real samples were also processed in order to detect contamination originating from the sorbent material or other sources.

### Liquid chromatography triple quadrupole linear ion trap tandem mass spectrometry

A Shimadzu Prominence HPLC system consisting of a CBM-20A controller, a DGU-$20A_3$ degasser, two LC-20AD pumps, an SIL-20AC auto sampler, a CTO20AC column oven and an SPD-20AV UV detector (Shimadzu, Duisburg, Germany) were used. Separation of unknowns and identified compounds as well as structure isomers was done on an Atlantis T3 column (Waters GmbH, Eschborn, Germany). Stationary phase column length was 100 mm with an inner diameter of 2.1 mm and a particle size of 3 µm. The column oven temperature was set to 40 ℃. Flow rate was adjusted to 0.3 mL/min for optimal spray conditions in the ion source. For all measurements, water with 0.1 % formic acid (A) and methanol with 0.1 % formic acid (B) were used as mobile phases. The gradient started from 5 % to 100 % (B) in 15 min. The detection of possible membrane degradation products eluted from the HPLC-system was performed using a triple quadrupole linear ion trap tandem mass spectrometer (3200 Q Trap, AB SCIEX, Darmstadt, Germany). Ionization of analytes was done in the negative and positive mode with turbo-electrospray ionization at atmospheric pressure. The optimal ion source temperature was set to 550 ℃ and ion spray voltage -5000 V for negative and 5500 V for positive ionization. Nitrogen was used as curtain gas (15 psi pressure), nebulizer gas (40 psi pressure) and collision gas (adjustment “high”). For the acquisition of molecular mass and structure information a general unknown screening method has been developed using information dependent acquisition (IDA). This mode of operation was performed using a combination of EMS as a survey scan and EPI scan as the information dependent scan. Collision energy spread was used for the acquisition of more informative product ion mass spectra at collision energies 35 ± 15 eV. The mass range was set to m/z 50 to 1000 for both scan types. The scan rate was 4000 Da/s and the cycle time was 1.8 s. Analysis of recorded data was accomplished with Analyst™ Software 1.5 (AB SCIEX, Darmstadt, Germany). Multiple reaction monitoring (MRM) in negative ionization mode was used for the detection of the identified compound hydroxybenzoic acid. The instrumental settings for MRM have been published earlier [19]. Briefly, m/z 137 and m/z 93 was set as $Q_1$ mass and $Q_3$ mass, respectively. The ion source temperature was 550 °C and ion spray voltage -4200 V for negative ionization. Nitrogen was used as curtain gas (15 psi), nebulizer gas (40 psi) and collision gas (adjustment “high”). A dwell time of 60 ms was set to monitor the mass transition of 4-HBA with a cycle time of 2.4 seconds.

## Membrane stress tests

### Ex-Situ

In order to verify membrane degradation products in the product water formed by chemical degradation via hydroxyl and peroxyl radical attack on the polymer, a common laboratory stress test was applied [11]. The membrane and model compound degradation was simulated using Fenton reagent. For this purpose, 100-mL glass vials were filled with 80 mL water and the pH was adjusted to 2.8 using 5 wt% H2SO4 for optimal Fenton test conditions. 10 mL of 1 mmol/L Fe2+ solution (added as FeSO4) was prepared and added to the pH 2.8 water solution. For the experimental batch, 100 mg of PBI blended SPES membrane was immersed in the solution. In order to start the Fenton reaction, 10 mL of 30 wt% H2O2 solution was added dropwise and stirred continuously. The solutions were kept at 68 °C in a water bath for 24 hours. The reaction was stopped by adjusting the pH to 7 using $NH_4OH$ for iron precipitation. Furthermore, blank samples were prepared using the solution composition described above, without adding hydrogen peroxide. This test was performed to verify that the possible detected degradation products are not resulting from any pollution, leaching or hydrolysis. The solutions were stabilized with 5 % vol. methanol.

**In-Situ**

In-situ tests have been performed by operating a fuel cell stack (5 cells, active area of a single cell 100 $cm^2$) assembled with the corresponding membranes. An electronic load is used to regulate the power output of the fuel cell stack. The membranes have been tested by applying predefined operating procedures. On one hand, the stacks have been operated at 30 %, 50 % and 70 % of their maximum output for several hours. On the other hand, extreme operating conditions at highest electric power are applied to stress the membranes. Membranes were humidified by saturating the cathodic air at the stack-inlet with highly purified water. Product water and humidification water was collected at the stack outlet for membrane degradation product analysis.

## 5.4 Results and Discussion

**Degradation analysis via GPC and Thermogravimetry**

Gel permeation chromatography is an appropriate method to investigate degradation of polymers by measuring the decrease of the molecular weight distribution (MWD) as already shown for high temperature fuel cell membranes [23]. In this work the molecular weight distribution of the blend membrane before and after fuel cell operation in the stack was measured (Figure 5-2, a). In addition to the fuel cell experiments the molecular weight distribution of a membrane before and after Fenton test was measured (Figure 5-2, b). After 100 hours of running in the fuel cell a decrease of the molecular weight was observed. Compared to theoretic investigations of molecular weight decreasing processes, the main degradation mechanism in the Fenton test and in fuel cell operation for this type of polymer and his blends an unzip scission [16].

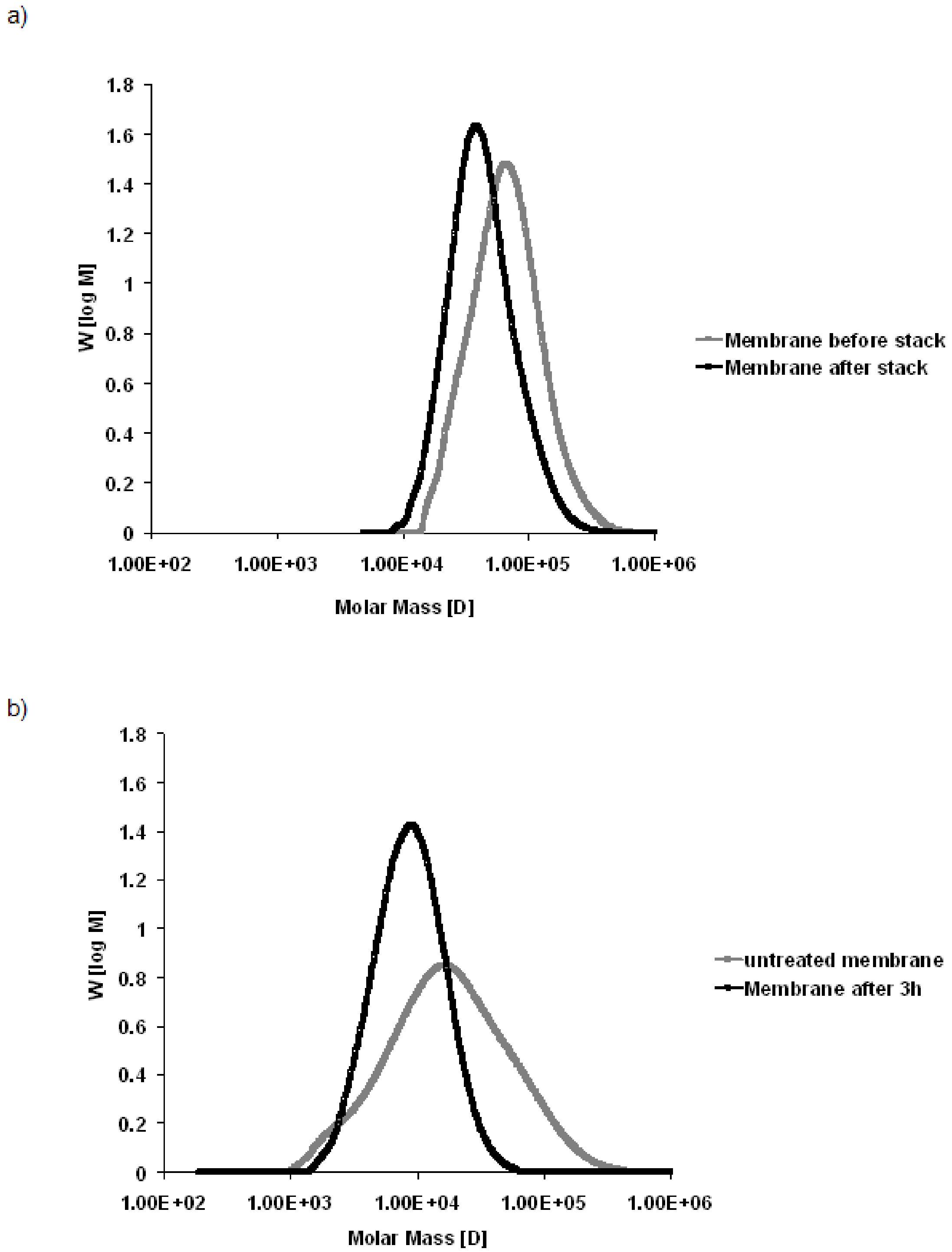


**Figure 5-2** Molecular weight distribution of the blend membrane before and after fuel cell operation (figure a) and application of Fenton test (figure b).

In the MWD curves of the blend membranes suffering from Fenton test a nearly similar curve shape is observable; the MWD curve shape is comparable to those of the membranes which were used in the fuel cell. The observation that the MWD curve shape of the membranes does not change during the degradation test from monomodal to bimodal is a strong indication for macromolecule radical degradation starting from the chain ends as pointed out in [26]. Furthermore, the MWD curves suggest that the smaller molecules have obviously been eluted from the membrane matrix by the product water formed during fuel cell operation since in the GPC-MWD curves no molecular masses lower than 1000 Da were observed during fuel cell operation. These low-molecular fragments generated by deterioration of the macromolecules should be detected during fuel cell operation by liquid chromatography linear ion trap tandem mass spectrometry.

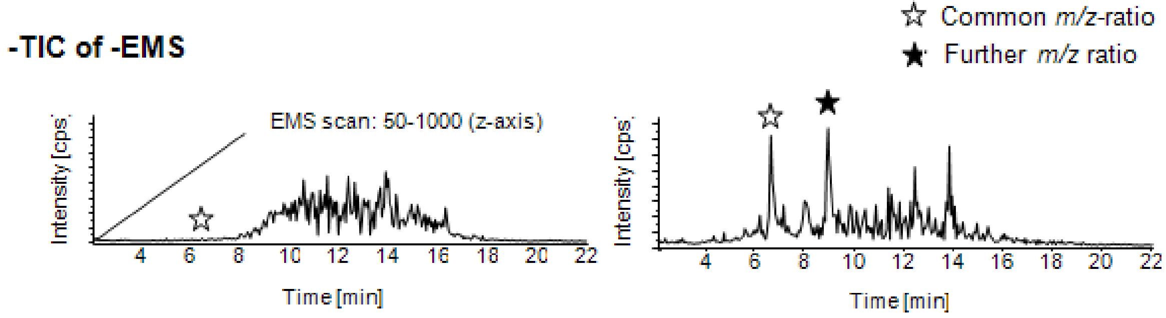
**Product water analysis**

Figure 5-3 shows the product water (in-situ) and Fenton test solution (ex-situ) investigation regarding membrane degradation products using the IDA mode. In contrast to an earlier study, where the product water and Fenton test solution was analyzed by UV detection and MRM of model compounds we expected to discover further unknown degradation products in the product water and Fenton test solution [19, 24]. Figure 3 (a) shows the total ion chromatograms (TIC) of the product water and Fenton solution. The comparison of both total ion chromatograms shows that the intensity of the total ion current is much lower for the product water which indicates that possible degradation products are most probably low concentrated compared to degradation products present in the Fenton test solution. Nevertheless, m/z 137 was found to be present in both samples indicated by the EMS spectra at 6.7 min in Figure 5-3 (b). In order to verify the presence and to distinguish the compound from the background noise, the signal to noise ratio should be at least 3 to 1, which was the case here. The peak area is one one order of magnitude higher in the Fenton test solution, which indicates that the compound is produced in high amounts in the accelerated stress test. Structure information were collected “on the fly” by performing EPI scans resulting in structure specific product ions. Figure 5-3 (c) shows the product ions m/z 93 and 65 of the precursor ion m/z 137. The product ions are similar in both mass spectra, which strongly suggest presence of an identical compound in the product water and Fenton test solution. These product ion spectra correspond to hydroxybenzoic acid, which has been investigated in an earlier study using model degradation products [19]. A further significant peak found in the test solution as indicated in Figure 5-3 (a) could also be identified as sulfonyl bisphenol using a reference compound. However, this degradation product has not been found in the water released by the fuel cell. It is plausible that hydroxybenzoic acid is detectable in the product water since it is a small mobile and well water soluble compound.

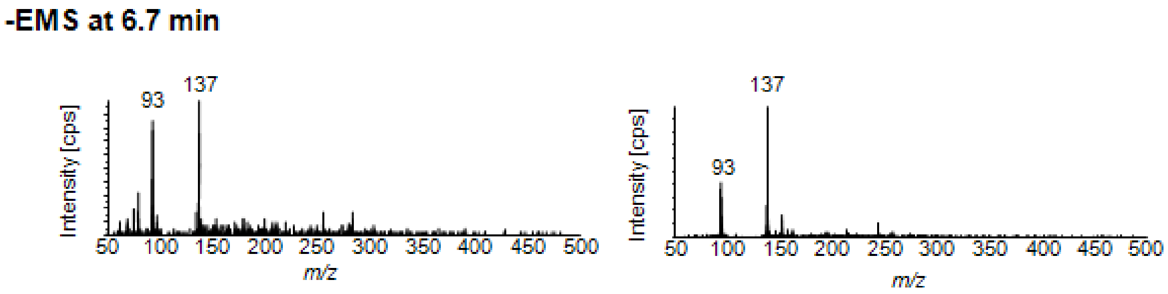
**Product water** **Fenton test**

**In-situ** **Ex-situ**

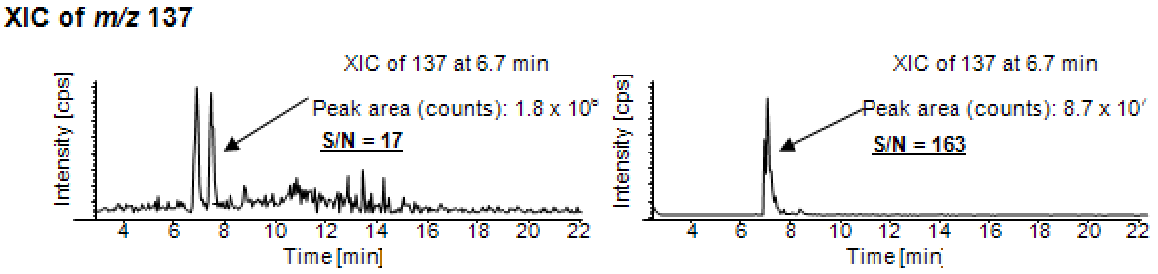
a) Evaluation of analogue *m/z*-ratios



b) Estimated analogue *m/z*-ratio



c) Peak verification of estimated analogue *m/z*-ratio



d) Inquiry of structure information using enhanced product ion scan

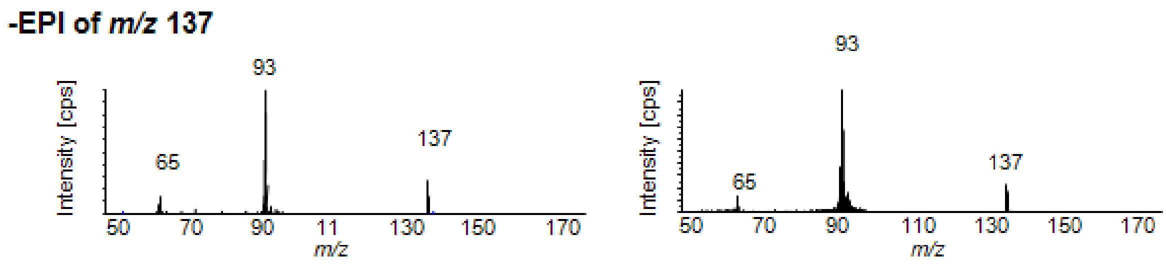


**Figure 5-3** Investigation of common structures in the product water and Fenton solution. a) Evaluation of analogue m/z-ratios in in-situ and ex-situ sample b) Estimated analogue m/z-ratio in in-situ and ex-situ sample c) Peak verification of estimated analogue m/z-ratio d) Inquiry of structure information using enhanced product ion scan.

In order to prove the reproducibility of hydroxybenzoic acid being produced by Fenton degradation, the degradation of the SPES has been simulated for 24 h in triplicates (Figure 5-4). The result indicates that hydroxybenzoic acid is produced reproducibly with a standard deviation of 12 % for the samples taken at 30, 60, 120 minutes and after 24 hours. This experiment could give an overview of equal compounds in the product water and Fenton solution, which identifies molecules resulting from chemical degradation during fuel cell operation. However, the degradation of SPES in Fenton solution is very complex.

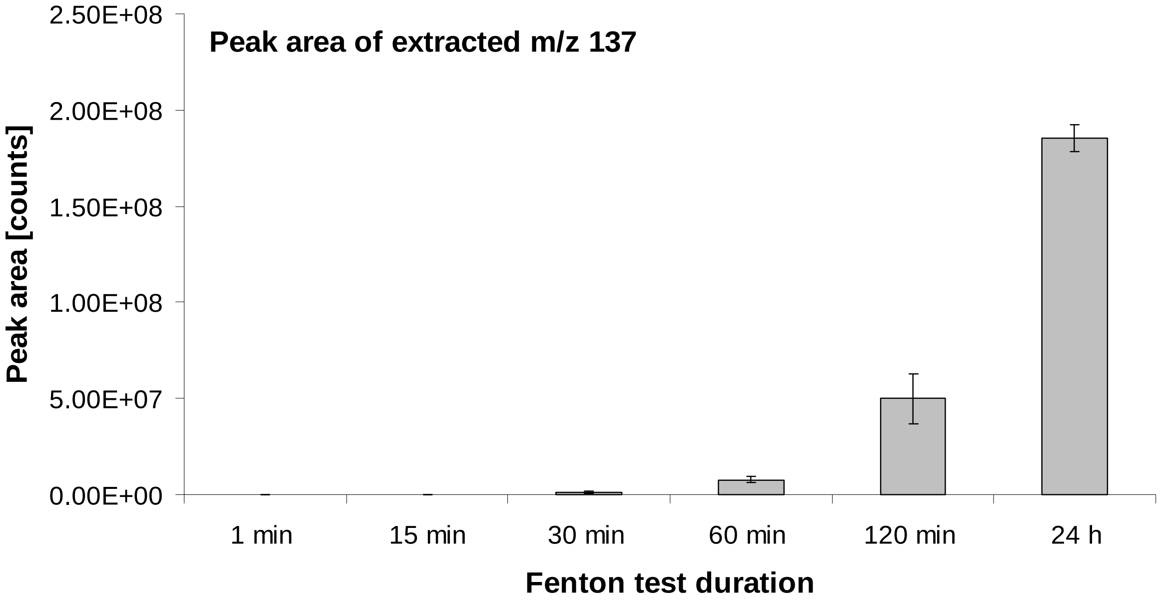


**Figure 5-4** Reproducibility of hydroxybenzoic acid (*m/z* 137) generated by the Fenton degradation of SPES.

Due to the complexity of the degradation of hydrocarbon membranes in Fenton test solutions, weak structural points of the membrane can not be proposed, unless the degradation product can be assigned to a building block of the polymer. Therefore, building blocks of the polymer were investigated by Fenton solution in order to allocate hydroxybenzoic acid to a membrane unit. For this purpose, 4,4-biphenol, 4,4-sulphonylbiphenol, disulfonated 4,4-difluorophenylsulfone and poly-benzimidazole has been investigated by Fenton reagent regarding the formation of hydroxybenzoic acid. Figure 5-5 shows schematically the result of this degradation study.

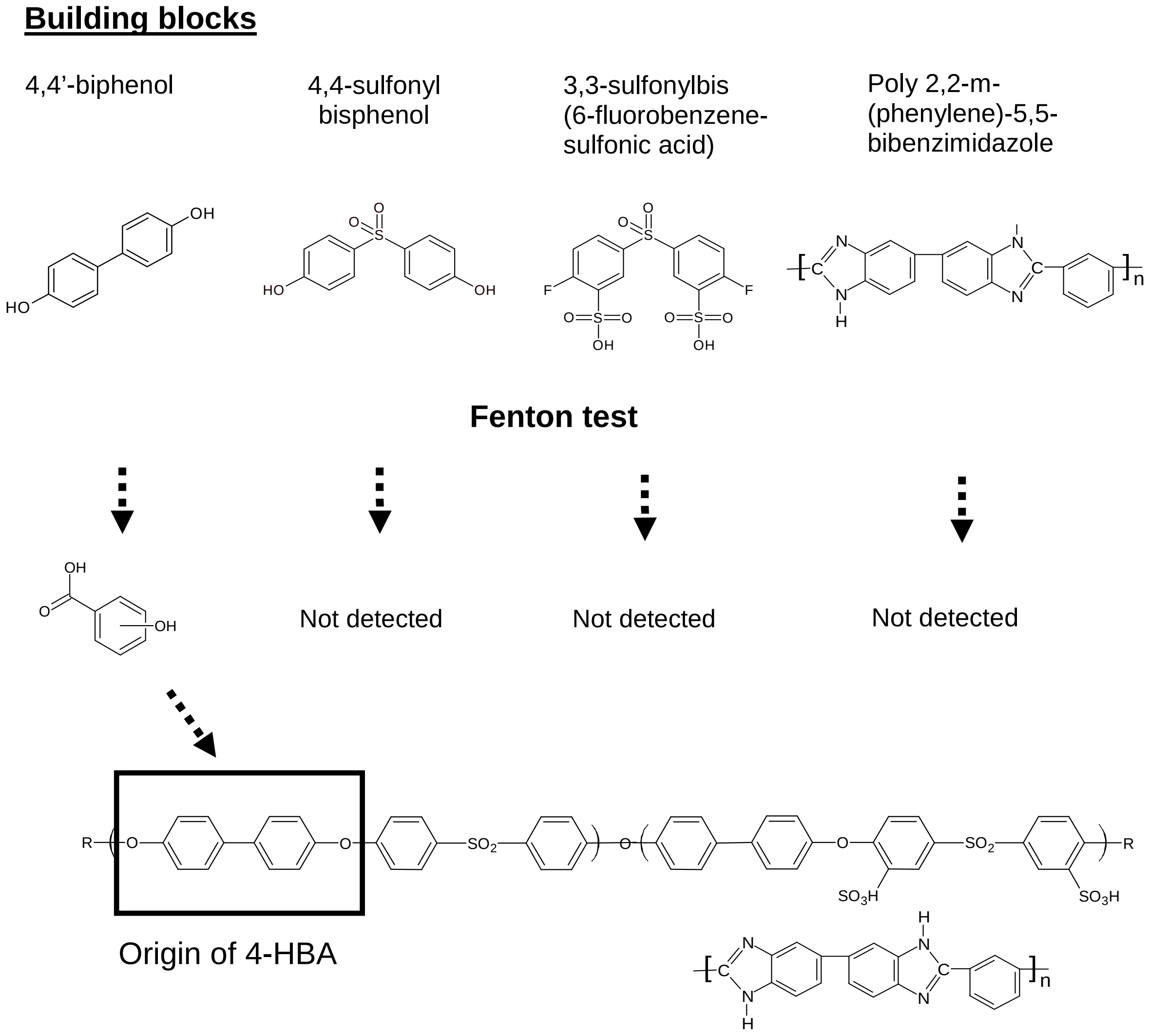


**Figure 5-5** Assignment of hydroxybenzoic acid to the membrane structure by a monomer degradation investigation using Fenton test. Hydroxybenzoic acid was detected by the degradation of 4,4’-biphenol.

Hydroxybenzoic acid has only been detected in the degradation of 4,4-biphenol. Hence, this degradation product could be assigned to a membrane unit. The degradation kinetic of 4,4-biphenol showed rapid degradation within one minute in a Fenton test solution, whereas 4,4-sulphonyl bisphenol only slightly degraded after a degradation time of 15 min. This result suggests that the electron withdrawing sulfone group stabilizes the aromatic rings nearby from the electrophilic attack by radicals. This experiment confirms observations made by Zhang et al. under fuel cell-like conditions .The structure isomer of HBA found in the product water and Fenton test samples was clarified by evaluating the chromatographic retention times of 4-, 3-, and 2-HBA. The result is presented in Figure 5-6.

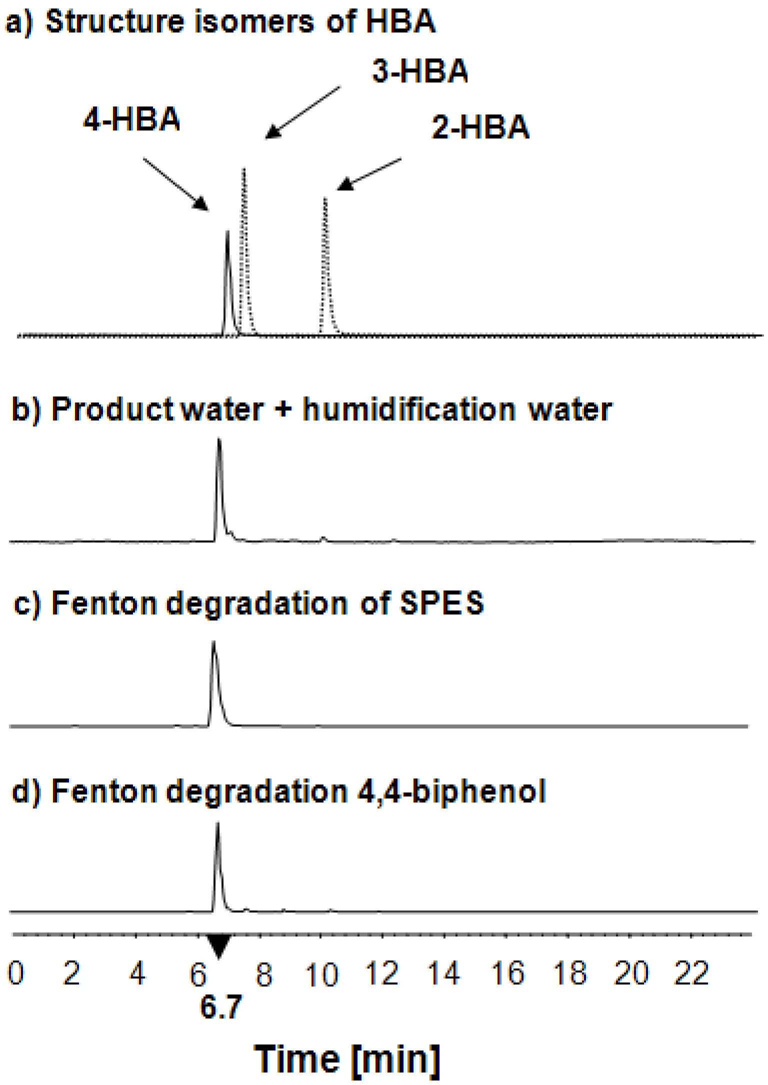


**Figure 5-6** (a) Chromatographic separation of three possible isomers (2-, 3-, 4-HBA) was used for identification of 4-HBA in the (b) produced water of the fuel cell and in the Fenton test solution of SPES (c) and 4,4-BP (d).

The result shows clearly that 4-hydoxybenzoic acid is formed by the degradation of SPES and 4,4-BP (Figure 5-6, c and d) indicated by the retention time of 4-HBA at 6.7 min. The fact that this isomer has also been detected in the product water (Figure 5-6, b) supports that this molecule results from chemical degradation of the membrane during fuel cell operation. Indeed, the formation of 4-HBA from 4-BP degradation by Fenton reaction has been reported earlier by Li et al. [25]. They have identified 4-hydroxybenzoic acid as a major degradation product of 4-hydroxybiphenyl by GC-MS analysis. According to the reported degradation routes for SPES in the Literature and the results discussed above, it is possible that the membrane polymer is being attacked at the 4-hydroxybiphenol chain end by ether and ring cleavage to form 4-HBA (Figure 5-7).

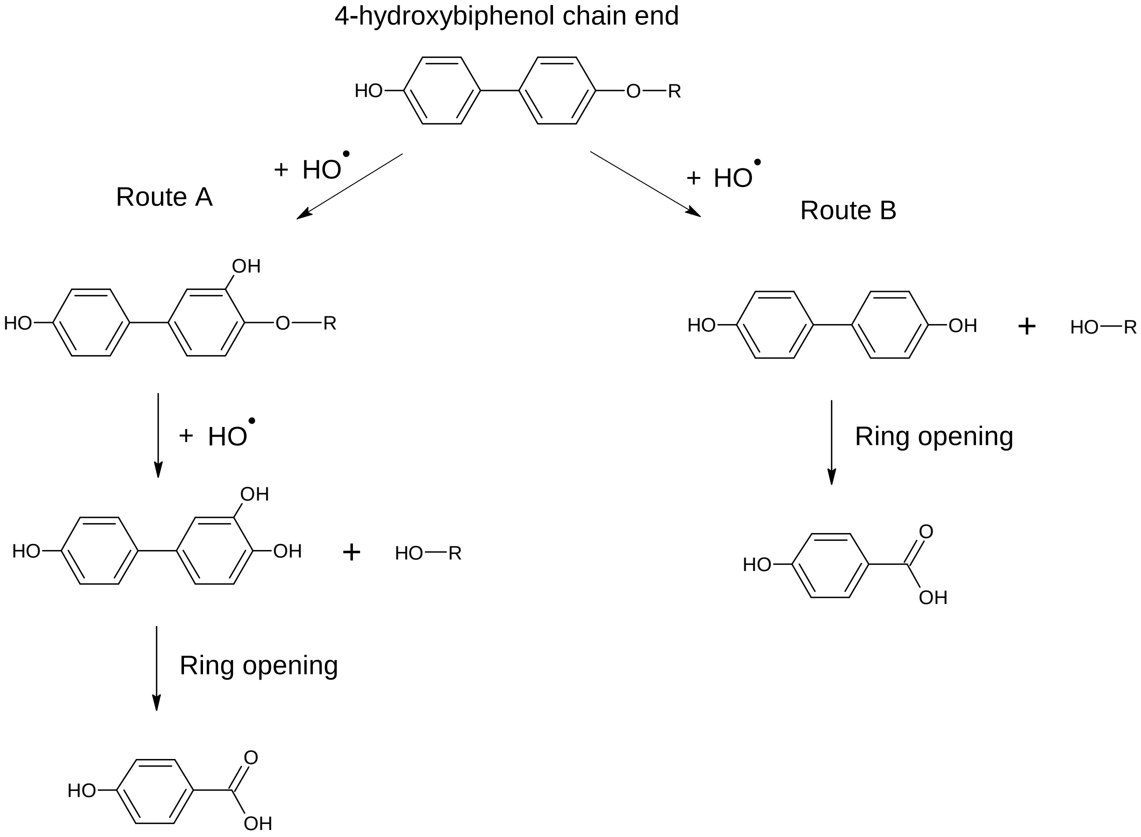


**Figure 5-7** Possible degradation route of 4-hydroxybiphenol chain end to 4-HBA by two possible radical induced ether cleavages (Route A and B) followed by ring opening.

A possible explanation could be that ether cleavage for this type of membrane occur most likely between two aromatic rings by ipso attack of hydroxyl radicals to the ether-linkage, either with (Route A) or without (Route B) ortho-activation by a hydroxyl radical followed by ring cleavage. Lawrence et al. have detected ring cleavage of SPES polymer in an accelerated hydrogen peroxide stress test. This could be due to organic radicals produced by hydroxyl radicals in Fenton solution or during fuel cell operation that may react with molecular oxygen ($O_2$) to give hydroperoxyl radicals ($HO^{\cdot}_2$), peroxyl radicals $R–O_2^{\cdot}$, or oxyl radicals $R–O^{\cdot}$ [26]. However, these reactions could lead to higher hydroxylated products and finally to bond breaking reactions of the aromatic ring [27] which may result in a carboxylic acid group.

## 5.5 Conclusions

Chemical degradation during fuel cell operation could successfully be detected by a comparative analysis of the product water and Fenton test solution using the linear ion trap functionalities of a tandem mass spectrometer and gel permeation chromatography analysis. The result of this study could be used for the monitoring of emerging degradation products depending on various fuel cell operating conditions for a better understanding of membrane degradation phenomena. Higher stability of SPES could be achieved by increasing the molecular weight of the acidic polymer to increase the lifetime in the fuel cells. This can be accomplished by further work with chain extenders which also lead to an end capping of the polymer chain. Also an optimized blend mixture and operating conditions can help to increase he lifetime of this membranes. Another way to get higher stabilities is to replace the 4,4-biphenol component by a partially fluorinated monomer like Biphenol AF where the possibility of a radical attack is lower.

## 5.6 Acknowledgement

The authors would like to thank for financial support from the German Federal Ministry of Economics and Technology within the agenda for the promotion of industrial cooperative research and development (IGF) based on a decision of the German Bundestag. The access was opened by the member organisation environmental technology and organised by the AiF, Arbeitsgemeinschaft industrieller Forschungsvereinigungen, Cologne, (IGF-Project No. 14941 N). Claudia vom Eyser and Karolin Wendrich are especially acknowledged for their assistance in the laboratory work.

## 5.7 References

[1] A.B. LaConti, M. Hamdan, R.C. McDonald, Mechanisms of membrane degradation, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.) Handbook of Fuel Cells - Fundamentals, Technology and Applications, 2003, pp. 647-677.

[2] F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Durability and degradation issues of PEM fuel cell components, Fuel Cells, 8 (2008) 3-22.

[3] J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo, A. Brundage, H. Gasteiger, J. Abbott, Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells, Fuel Cells, 5 (2005) 302-308.

[4] Q.H. Guo, P.N. Pintauro, H. Tang, S. O'Connor, Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes, J Membrane Sci, 154 (1999) 175-181.

[5] C. Perrot, L. Gonon, C. Marestin, A. Morin, G. Gebel, Aging mechanism of Sulfonated poly(aryl ether ketone) (sPAEK) in an hydroperoxide solution and in fuel cell, J. Power Sources, 195 (2010) 493-502.

[6] K. Teranishi, S. Tsushima, S. Hirai, Analysis of water transport in PEFCs by magnetic resonance imaging measurement, J. Electrochem. Soc., 153 (2006) A664-A668.

[7] W. Liu, D. Zuckerbrod, In situ detection of hydrogen peroxide in PEM fuel cells, J. Electrochem. Soc., 152 (2005) A1165-A1170.

[8] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Gas crossover and membrane degradation in polymer electrolyte fuel cells, Electrochim. Acta, 51 (2006) 5746-5753.

[9] V.O. Mittal, H.R. Kunz, J.M. Fenton, Membrane degradation mechanisms in PEMFCs, J. Electrochem. Soc., 154 (2007) B652-B656.

[10] A. Collier, H.J. Wang, X.Z. Yuan, J.J. Zhang, D.P. Wilkinson, Degradation of polymer electrolyte membranes, Int. J. Hydrogen Energy, 31 (2006) 1838-1854.

[11] S.S. Zhang, X.Z. Yuan, H.J. Wang, W. Merida, H. Zhu, J. Shen, S.H. Wu, J.J. Zhang, A review of accelerated stress tests of MEA durability in PEM fuel cells, Int. J. Hydrogen Energy, 34 (2009) 388-404.

[12] L. Zhang, S. Mukerjee, Investigation of Durability Issues of Selected Nonfluorinated roton Exchange Membranes for Fuel Cell Application, J. Electrochem. Soc., 153 (2006) A1062-A1072.

[13] F.N. Buchi, B. Gupta, O. Haas, G.G. Scherer, Study of Radiation-Grafted Fep-G-Polystyrene Membranes as Polymer Electrolytes in Fuel-Cells, Electrochim. Acta, 40 (1995) 345-353.

[14] J. Kerres, D. Xing, F. Schönberger, Comparative Investigation of Novel PBI Blend Ionomer Membranes from Nonfluorinated and Partially Fluorinated Poly Arylene Ethers, J. Polymer Sci., 44 (2006) 2311-2326.

[15] J.K. Lee, J. Kerres, Synthesis and characterization of sulfonated poly(arylene thioether)s and their blends with polybenzimidazole for proton exchange membranes, J. Membrane Sci., 294 (2007) 75-83.

[16] J. Lawrence, T. Yamaguchi, The degradation mechanism of sulfonated poly(arylene ether sulfone)s in an oxidative environment, J. Membr. Sci., 325 (2008) 633-640.

[17] S.G. Schrank, U. Bieling, H.J. Jose, R.F.P.M. Moreira, H.F. Schroder, Generation of endocrine disruptor compounds during ozone treatment of tannery wastewater confirmed by biological effect analysis and substance specific analysis, Water Sci. Technol., 59 (2009) 31-38.

[18] A.H. Carlsson, L. Joerissen, Accelerated Degradation of Perfluorinated Sulfonic Acid Membranes, ECS Trans., 25 (2009) 725-732.

[19] M. Zedda, J. Tuerk, S. Peil, T.C. Schmidt, Determination of polymer electrolyte membrane (PEM) degradation products in fuel cell water using electrospray ionization tandem mass spectrometry, Rapid Commun Mass Spectrom, 24 (2010) 3531–3538.

[20] D. Xing, J. Kerres, Improved performance of sulfonated polyarylene ethers for proton exchange membrane fuel cells, Polymers for Advanced Technologies, 17 (2006) 1-7.

[21] F. Schönberger, A. Chromik, J. Kerres, Synthesis and characterization of novel (sulfonated) poly(arylene ether)s with pendent trifluoromethyl groups Polymer, 50 (2009) 2010-2024.

[22] V. Gogel, L. Jörissen, A. Chromik, F. Schönberger, J. Lee, M. Schäfer, K. Krajinovic, J. Kerres, Ionomer Membrane and MEA Development for DMFC Sep. Sci. Technol., 43 (2008) 3955 — 3980.

[23] Q.F. Li, H.C. Rudbeck, A. Chromik, J.O. Jensen, C. Pan, T. Steenberg, M. Calverley, N.J. Bjerrum, J. Kerres, Properties, degradation and high temperature fuel

cell test of different types of PBI and PBI blend membranes, J Membrane Sci, 347 (2010) 260-270.

[24] M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt, A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, J. Chromatogr., A, 1216 (2009) 8910-8917.

[25] Y.C. Li, L.G. Bachas, D. Bhattacharyya, Selected chloro-organic detoxifications by polychelate (Poly(acrylic acid)) and citrate-based Fenton reaction at neutral pH environment, Ind. Eng. Chem. Res., 46 (2007) 7984-7992.

[26] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, Environ Sci Technol, 36 (2006) 1-84.

[27] G. Huebner, E. Roduner, EPR investigation of HO• radical initiated degradation reactions of sulfonated aromatics as model compounds for fuel cell proton conducting membranes, J. Mater. Chem., 9 (1999) 409–418.

# Chapter 6.

# General Conclusions and Future work

This thesis could demonstrate the potential of solid phase extraction and liquid chromatography tandem mass spectrometry for the extraction, separation, screening and identification of SPES membrane degradation products in the product water of fuel cells. Membrane decomposition products are present in the product water at trace levels and can be detected after enrichment and sensitive and selective tandem mass spectrometry. The developed analytical methods enable to study correlations between fuel cell operation parameters and membrane degradation products in the future for diagnostic purposes and a better understanding of the membrane degradation phenomena. The Fenton test provides stable and reproducible results for membrane degradation products. The analysis of a dominant degradation product in the Fenton test solution and its detection in the product water has lead to further investigations on its allocation to the membrane structure and finally to a proposed degradation mechanism. However, some degradation products present in the Fenton test solution could not be detected in the product water and vice versa. The degradation of PEM in such an accelerated oxidative stress test does not consider electrode processes and variations in fuel cell operating conditions such as operating potential, relative humidity, and lack of fuel and oxidant, which could explain these observations. However, there is still a lack of knowledge regarding suitable and uniform standard procedures for an accelerated test procedure for chemical degradation, especially for aromatic hydrocarbon membranes and its transferability to findings in the product water. This could be an interesting task for future investigations. Despite the possibility to monitor membrane degradation during fuel cell operation depending on various fuel cell operating conditions, the results of this study could be used to improve the oxidative stability of SPES, for example, by increasing the molecular weight of the acidic polymer or by replacement of weak by more stable monomers where the possibility of a radical attack is lower. Furthermore, the developed analytical procedures enable the analysis of polar aromatic hydrocarbons in water samples, which could be interesting for other research areas.

# Appendix

# List of abbreviations

| | |
|---|---|
| AOP | Advanced Oxidation Process |
| APCI | Atmospheric pressure chemical ionization |
| BP | 4,4-biphenol |
| CAD | Collision gas |
| CE | Collosion energy |
| CEP | Collision cell entrance potential |
| CES | Collosion energy spread |
| CID | Collision induced dissociation |
| CUR | Curtain gas |
| CXP | Collision cell exit potential |
| DAD | Dioden array detector |
| DP | Declustering potential |
| EDX | Energy dispersive X-ray spectroscopy |
| EMS | Enhanced mass scan |
| EP | Entrance potential |
| EPI | Enhanced product ion |
| ESI | Electrospray ionization |
| ESR | Electron spin resonance spectroscopy |
| FTIR | Fourier transform infrared spectroscopy |
| GS1 | Nebulizer gas |
| GS2 | Turbo gas |
| GPC | Gel permeation chromatography |
| HBA | Hydroxybenzoic acid |
| HBAD | Hydroxybenzaldehyde |
| HBS | 4-hydroxybenzene sulfonate |
| HPLC | High performance liquid chromatography |
| ICVT | Institute of chemical engineering |
| IDA | Information dependent acquisition |
| IDL | Instrument detection limit |
| IS | IonSpray voltage |
| LIT | Linear ion trap |
| LLE | Liquid liquid extraction |

| | |
|---|---|
| MEA | Membrane electrode assembly |
| MRM | Multiple reaction monitoring |
| MS | Mass spectrometry |
| MS/MS | Tandem mass spectrometry |
| *m/z* | Mass to charge ratio |
| NMR | Nuclear magnetic resonance spectroscopy |
| PBI | Poly 2,2´-m-(phenylene)-5,5´-bibenzimidazol |
| PEM | Proton exchange membrane |
| PEMFC | Proton exchange membrane fuel cell |
| PEK | Poly(etherketone) |
| PFSA | Perfluorosulfonic acid |
| pKa | Acid dissociation constant |
| POPLC | Phase optimized liquid chromatography |
| Q | Quadrupole |
| QqQ | Triple quadrupole |
| $QqQ_{LIT}$ | Triple quadrupole linear ion trap |
| RP | Reversed phase |
| RSD | Relative standard deviation |
| SBP | 4,4-sulfonylbisphenol |
| SPE | Solid phase extraction |
| SPES | Sulfonated poly(arylene ether sulfone) |
| TIC | Total ion chromatogram |
| TOF | Time of flight |
| UV | Ultraviolet |
| XIC | Extracted ion chromatogram |
| XPS | X-ray photoelectron spectroscopy |

# List of publications

## Publications in peer-reviewed journals

E. Steinle-Darling, M. Zedda, M. H. Plumlee, H. F. Ridgway, M. Reinhard: Evaluating the impacts of membrane type, coating, fouling, chemical properties and water chemistry on reverse osmosis rejection of seven nitroso- alkylamines, including NDMA, *Water research (2007)*, 41, 3959 – 3967.

M. M. Sein, M. Zedda, J. Türk, T. C. Schmidt, A. Golloch, C. von Sonntag: Oxidation of Diclofenac with Ozone in Aqueous Solution, *Environmental Science and Technology (2008)*, 42, 6656 – 6662.

M. Zedda, J. Tuerk, T. Teutenberg, S. Peil, T.C. Schmidt: A strategy for the systematic development of a liquid chromatographic mass spectrometric screening method for polymer electrolyte membrane degradation products using isocratic and gradient phase optimized liquid chromatography, *Journal of Chromatography A (2009),* 1216, 8910–8917.

M. Zedda, J. Tuerk, S. Peil, T. C. Schmidt: Determination of polymer electrolyte membrane (PEM) degradation products in fuel cell water using electrospray ionization tandem mass spectrometry, *Rapid communications in mass spectrometry (2010* ),24, 531–3538.

M. Zedda, J. Tuerk, K. Helle, S. Peil, T.C. Schmidt, J. Kerres, A. Chromik: Stability investigations of a polybenzimidazole-blended sulphonated polyarylether membrane during fuel cell operation by product water analysis, submitted to Journal of Membrane Science 2011.

## Oral presentations

M. Zedda, T. C. Schmidt, J. Türk, T. Teutenberg, S. Peil: Development of analytical methods for characterization of degradation products from novel membranes for PEM-fuel cell applications in the product water, 18. Doktorandenseminar in Hohenroda (Hohenroda, Germany, January 4-6, 2008.

M. Zedda: Development of analytical methods for characterization of degradation products from novel membranes for PEM-fuel cell applications in the product water, 11. JCF-Frühjahrssymposium (Essen, Deutschland), March 11-14, 2009.

M. Zedda, C. vom Eyser, J. Tuerk, K. Helle, S. Peil, A. Chromik, J. Kerres, T. C. Schmidt: Development of analytical methods for characterization of degradation products from novel membranes for PEM-fuel cell applications in the product water. Achema 2009 (Frankfurt am Main, Germany), May 11-15, 2009.

M. Zedda: Oxidation products from novel polymer electrolyte membranes (PEM) in the product water of fuel cells, GDCH Neujahrskolloquium (Essen, Germany), January 6, 2010.

M. Zedda: Development of a trace analytical procedure for the investigation of PEM-degradation products during fuel cell operation, IUTA Seminar "Spezielle Fragestellungen der Verfahrens-, Energie- und Umwelttechnik" (Duisburg, Deutschland), March 11, 2010.

M. Zedda, J. Türk, S. Peil, T. C. Schmidt: Liquid chromatography linear ion trap tandem mass spectrometry for membrane stability investigations in fuel cells, 44. Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), Dortmund (Germany), February 28, 2011.

**Poster presentations**

M. Zedda, T. Teutenberg, J. Tuerk, S. Peil, T.K. Kiffmeyer, T.C. Schmidt: Separation of model polymer electrolyte membrane (PEM) degradation products using isocratic and gradient Phase Optimized Liquid Chromatography. ISC 2008 - 27th International Symposium on Chromatography (Münster, Germany), September 21 -25, 2008.

M. Zedda, C. vom Eyser, J. Tuerk, K. Helle, S. Peil, A. Chromik, J. Kerres, T. C. Schmidt: Investigation of oxidation products from novel polymer electrolyte membranes (PEM) in the product water of fuel cells using LC-MS/MS. International Symposium on Diagnostic Tools for Fuel Cell Technolgies (Trondheim, Norway), June 23-24, 2009.

M. Zedda, C. vom Eyser, J. Tuerk, K. Helle, S. Peil, A. Chromik, J. Kerres, T. C. Schmidt: Development of a screening method for identification and characterization of membrane degradation products of PEM-fuel cells using information dependent acquisition (IDA). IMSC 2009 - 18th International Mass Spectrometry Conference (Bremen, Germany), August 30th to September 4th, 2009.

Zedda, M., Tuerk, J., Boergers, A., Portner, C., Schmidt, T.C.: New strategies for non-target analysis of oxidation by-products using LC-hybrid-linear ion trap and Q-TOF mass spectrometry. IMSC 2009 - 18th International Mass Spectrometry Conference (Bremen, Germany), August 30th to September 4th, 2009.

**Der Lebenslauf ist in der Online-Version aus Gründen des Datenschutzes nicht enthalten.**

# Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel

„ Determination of membrane degradation products in the product water
of polymer electrolyte membrane fuel cells using
liquid chromatography mass spectrometry ”

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Duisburg, 02 März 2011

UNTERSCHRIFT