

Protonenleitende *Composite*-Membranen für
Brennstoffzellen-Anwendungen

Dissertationsschrift
zur
Erlangung des akademischen Grades
Doktor-Ingenieur (Dr.-Ing.)
der
Fakultät für Angewandte Naturwissenschaften
der
Universität Bayreuth

verfasst am Lehrstuhl für Werkstoffverarbeitung
unter Betreuung von
Frau Prof. Monika Willert-Porada

vorgelegt im Dezember 2005
von
Felix Bauer
aus München

Hauptberichter: Prof. Dr. rer. nat. Monika Willert-Porada
Mitberichter: Prof. Dr.-Ing. Ralf Moos

Tag der mündlichen Prüfung: 30.5.2006

Berichte aus der Materialwissenschaft

Felix Bauer

**Protonenleitende *Composite*-Membranen für
Brennstoffzellen-Anwendungen**

Shaker Verlag
Aachen 2006

Bibliografische Information der Deutschen Nationalbibliothek

Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.d-nb.de> abrufbar.

Zugl.: Bayreuth, Univ., Diss., 2006

Copyright Shaker Verlag 2006

Alle Rechte, auch das des auszugsweisen Nachdruckes, der auszugsweisen oder vollständigen Wiedergabe, der Speicherung in Datenverarbeitungsanlagen und der Übersetzung, vorbehalten.

Printed in Germany.

ISBN-10: 3-8322-5505-2

ISBN-13: 978-3-8322-5505-3

ISSN 1618-5722

Shaker Verlag GmbH • Postfach 101818 • 52018 Aachen

Telefon: 02407 / 95 96 - 0 • Telefax: 02407 / 95 96 - 9

Internet: www.shaker.de • E-Mail: info@shaker.de

Danksagung

Die vorliegende Arbeit entstand am Lehrstuhl für Werkstoffverarbeitung an der Fakultät für angewandte Naturwissenschaften der Universität Bayreuth im Zeitraum zwischen April 2000 und Mai 2005 unter Leitung von

Frau Prof. Dr. Willert-Porada,

der ich an dieser Stelle für die engagierte Betreuung, die exzellenten Forschungsmöglichkeiten und die gestalterische Freiheit während meiner Arbeit danke.

Meinen Arbeitskollegen Christian Gerk, Jens Große-Berg, Achim Müller, Panneerselvam Marudhachalam, Zeljko Pajkic, Ho-Seon Park, Stefan Schoemaker, Tim Schubert, Roland Tap, Marc Wildersohn und Hannes Wolf danke ich für die gute Zusammenarbeit und die stets als angenehm empfundene Atmosphäre am Lehrstuhl.

Den Angestellten des Lehrstuhls Klaus Decker, Ingrid Otto und Peter Kostolansky danke ich für deren tatkräftige Unterstützung, ohne welche die Arbeit nicht möglich gewesen wäre.

Den Mitarbeitern der mechanischen und elektronischen Werkstätten, der zentralen Technik und der Glasbläserei gilt mein Dank für die Realisierung experimenteller Aufbauten und die technische Unterstützung.

Weiterhin gilt mein Dank:

- den studentischen Hilfskräften Roman Bispin, Stefan Denner, Anette Runtemund und Anna Wojtkowiak für die Präparation und Charakterisierung von Proben und die Erstellung von Konstruktionszeichnungen.
- Dieter Will am Lehrstuhl Anorganische Chemie I für die Aufnahme von IR-Spektren.
- Dr. Bastian Ruffmann, Abt. Polymertechnologie am Institut für Chemie, GKSS-Forschungszentrum Geesthacht für die Hilfestellung bei der Weiterentwicklung der Leitfähigkeitsmesszelle und Referenzmessungen.
- Dr. Schindler, Netzsch Gerätebau in Selb für die thermische Analyse.
- der Deutschen Forschungsgemeinschaft für die finanzielle Förderung im Zeitraum von 2000 bis 2004.

Silke Herrmann danke ich für das Korrekturlesen der Arbeit.

Meinen Eltern danke ich für alles, was sie für mich getan haben.

Sprach-Kürze gibt Denk-Weite

Jean Paul

Abstract

Composite-Effects in Proton Conducting Membranes for Fuel Cell Applications

Inorganically modified composite ionomer membranes comprise an inorganic compound which is distributed in a polymeric matrix. Composite-effects, i. e. effects which originate from the specific interactions between inorganic and polymeric phase in the composite, were investigated aiming at an improved understanding of fundamental interactions on a molecular scale. In addition, it was intended to gain practical experience about the application of such materials in fuel cells.

Composite membranes were prepared from commercially available sulfonic acid PFSA membranes (Nafion[®] 117) by ion-exchange with a zirconium precursor followed by precipitation of $\text{Zr}(\text{HPO}_4)_2$ with phosphoric acid. Characterization of the composites was mainly based on X-ray diffraction (XRD), impedance spectroscopy (IS) and dynamic mechanical analysis (DMA). XRD was used to determine the crystalline phase, size and shape of the crystallites. The proton conductivity was measured by IS. The stiffness and the glass transition of the composite was investigated by means of DMA. The last mentioned method was used within this work first-time to characterize mechanical properties of an ionomer under application-relevant temperatures as a function of water activity. The sorption isotherm of the membrane was recorded in order to correlate conductivity and mechanical properties in a direct manner with their water content.

The inorganic compound was identified as the α -phase of zirconium layer phosphate by means of XRD. The analysis of the position, intensity and broadness of the reflections led to the conclusion that the inorganic particles are monolayered, have a size of up to 20 nm and are distributed uniformly in the membrane on a nanometer scale. The preferred orientation direction of the crystallite is (010) and they are of tape-like shape. The shape of the particles may be explained by the template effect of the membrane since it is compatible with the

interconnected-cluster-morphology of the bare membrane. The spatial constraints hinder the formation of multilayers. Therefore, the highest possible interface area and the strongest interactions between both phases are expected from such composites.

In the water saturated state no improvement of the proton conductivity was found in the composites as compared to the unmodified membrane. Up to a molar phosphate-to-sulfonate-group ratio of one the observed change in conductivity is small. At higher ratios the conductivity drops significantly as compared to the unmodified membrane. This effect is explained by the ionic interaction between the groups. At ratios below one proton conductivity proceeds along highly conductive sulfonic acid $\text{-SO}_3\text{H}$ and phosphateacidium ion $\text{-PO}_4\text{H}_2^+$ groups, at ratios above one less conductive phosphate $\text{-PO}_4\text{H}$ groups are inserted into the conduction pathways. At a ratio of one the inorganic weight fraction in the dry Nafion[®] 117 membrane corresponds to 11.4 %. Using composites with a ratio smaller than one at water contents below the saturation level an increase in conductivity is achieved. The effect is the more pronounced the closer the ratio approached one.

Increasing temperature increases the conductivity of the composites stronger than the conductivity of the unmodified membrane.

As a conclusion it is stated that as far as conductivity is concerned the advantages of composites are most significant at high temperature, low water activity and inorganic content slightly below a molar fraction of one.

The dynamic mechanical analysis revealed a new effect of the unmodified ionomer: Hitherto water was considered to decrease the stiffness of the ionomer monotonously with increasing vapor pressure due to its plasticizing effect. It could be shown in this work that from a certain temperature T_{crit} the stiffness as a function of water vapor pressure exhibits a maximum which shifts with increasing temperature to higher vapor pressure. Therefore, above T_{crit} water acts as a stiffener at low vapor pressure and as a plasticizer at high vapor pressure. The effect appears in the high temperature region where future application of improved fuel cell membranes is strived for.

The inorganic intercalation effects a significant increase of the membrane stiffness and a shift of the α -transition temperature by more than 100 K. The α -transition is initiated by the increasing mobility of side chain groups which build the hydrophilic regions of the ionomer. The intensity of this effect again correlates with the molar ratio of phosphate to sulfonate

groups. Up to a ratio of one a significant increase of the stiffness is observed whereas higher ratios showed nearly no additional effect as compared to the one-to-one ratio.

The stiffening effect was also investigated as a function of water vapor pressure. The interpretation by ionic acid-base interactions between sulfonate and phosphate groups was supported by the results of this investigation: Starting at the dry composite material an exponential decrease of the stiffness was observed which is explained by the formation of the first hydrate shell around the ion pairs. Upon further increase of the vapor pressure the stiffness decreases only linearly. In the water saturated composite membrane the stiffening effect is lowest as compared to the unmodified material.

The cross-linking effect is expected to be the stronger the lower the dielectric strength of the solvent. Methanol exhibited a stronger stiffening effect in the composites than water.

As a conclusion it is stated that as far as mechanical properties are concerned the advantages of composites are most significant at a temperature above the α -transition, low water vapor pressure and inorganic content above a molar fraction of about 0.7.

Comparing the composites prepared by the recast-method, where inorganic particle size is in the μm -region, with the composites prepared by the ion-exchange-precipitation-method it turns out that composite-effects are the stronger the higher the interface area between inorganic and polymeric phase.

The degree of ionic cross-linking plays an important role for the strength of the observed effects. Molar ratios of phosphate to sulfonate groups between 0.7 and 1 are most preferable in order to yield good conductivity performance and mechanical properties at the same time. This range corresponds to inorganic weight fractions between 8.3 % and 11.4 % in the dry Nafion[®] 117 membrane.

Investigations on another PFSA ionomer prepared from a different perfluorovinylether monomer suggest that the results gained for Nafion[®] apply to all phase segregated ionomers.

In a second section application oriented information about the composite membranes was ascertained.

The comparison of stability properties between different titanium-, zirconium- and titanium-zirconium -layerphosphates led to the result that zirconium phosphate is the most preferable additive since its stability against hydrolysis is highest. Titanium was found to increase the

susceptibility towards hydrolysis in the layer phosphates. Binary titanium zirconium phosphates were only stable in concentrated phosphoric acid.

The choice of zirconium precursor drastically influences the morphology of the inorganic compound in the resulting composite. The hydrophilic zirconium oxychloride precursor led to crystallite sizes up to a maximum of 7 nm, whereas the hydrophobic zirconium butylate precursor led to crystallite sizes of 21 nm.

The fuel cell testing was carried out under optimal conditions of humidification of the reactant gases. Due to their lower conductivity the composite membranes exhibited lower power density than the Nafion[®] 117 membrane over the whole range of current density when operated in a hydrogen/oxygen cell. In the direct methanol fuel cell higher rest potentials were found for the composites. Also, in the low current density range up to 100 mA cm⁻² the power density was increased as compared to Nafion[®]. In the range of higher current densities the power density was decreased. Nevertheless, the significant reduction of methanol permeability in the composites led to an increased efficiency of the direct methanol conversion.

Cross-sections of the membrane-electrode-assemblies were investigated after the fuel cell testing. The analysis showed improved mechanical stability of the composites and morphological as well as chemical stability of the zirconium phosphate phase in the composite.

Inhaltsverzeichnis

1	Einleitung.....	1
2	Problemstellung und Zielsetzung	3
3	Grundlagen	9
3.1	Ionogene Materialien.....	9
3.1.1	Perfluorierte Ionomere	10
3.1.2	Ionenleitende anorganische Schichtverbindungen	16
3.2	Protonenleitung in ionogenen Materialien	21
3.2.1	Mechanismen	22
3.2.2	Klassifizierung	23
3.2.3	Materialien	26
3.2.4	Methoden der Leitfähigkeitsmessung	29
3.3	Dynamisch mechanisches Verhalten der Ionomere	39
3.4	PEM-Brennstoffzellen.....	42
3.5	Anorganische Modifizierung von Ionomeren	45
4	Konzept.....	47
4.1	Materialkonzept.....	47
4.2	Synthesestrategie.....	49
4.3	Anwendungsbezogenes Verarbeitungskonzept.....	52
4.4	Charakterisierungskonzept	55
5	Experimenteller Teil.....	57
5.1	Synthese und Herstellung von <i>Composite</i> -Membranen	57
5.2	Charakterisierung der synthetisierten Schichtverbindungen.....	60
5.2.1	Strukturmorphologische Charakterisierung	60
5.2.2	Protonenleitfähigkeit	63
5.2.3	Ionenaustauschkapazität.....	64
5.3	Charakterisierung der <i>Composite</i> -Membranen	66
5.3.1	Strukturmorphologische Charakterisierung	66
5.3.2	Protonenleitfähigkeit	69
5.3.3	Dynamisch mechanische Analyse.....	71
5.3.4	Sorption, Permeation und Ionenaustauschkapazität	72
5.4	Zellmessungen.....	78
5.4.1	Membran-Elektroden-Verbund	78
5.4.2	Leistungskennlinien	79
5.4.3	Methanoldurchtritt.....	80

5.4.4	Langzeitstabilität	80
6	Ergebnisse.....	81
6.1	Synthetisierte Verbindungen	81
6.1.1	Binäre Alkoholate	81
6.1.2	Schichtphosphate.....	83
6.2	<i>Composite</i> -Membranen	96
6.2.1	Struktur und Morphologie.....	96
6.2.2	Protonenleitfähigkeit	102
6.2.3	Dynamisch mechanische Analyse.....	110
6.2.4	Sorption, Permeation und Ionenaustauschkapazität.....	115
6.3	Zellmessungen.....	127
6.3.1	H ₂ -PEMFC	127
6.3.2	DMFC.....	128
6.3.3	Langzeitstabilität	131
7	Diskussion	135
7.1	Synthetisierte Verbindungen	135
7.1.1	Binäre Alkoholate	135
7.1.2	Schichtphosphate.....	136
7.2	<i>Composite</i> -Membranen	144
7.2.1	Herstellungsverfahren	144
7.2.2	Eigenschaften der Ionenaustausch-Fällungs- <i>Composites</i>	145
7.2.3	Eigenschaften weiterer <i>Composites</i>	161
7.3	Zellmessungen.....	162
7.3.1	Wasserstoff-Brennstoffzelle.....	162
7.3.2	Methanol-Brennstoffzelle.....	162
7.3.3	Zellruhepotential	162
7.3.4	Langzeitstabilität der Einlagerung	163
7.3.5	Vergleichende Bewertung	164
8	Zusammenfassung und Ausblick.....	165
9	Anhang.....	169
10	Literatur	211