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Hans Aage Hjuler · Jens Oluf Jensen
Editors

High Temperature Polymer Electrolyte Membrane Fuel Cells

Approaches, Status, and Perspectives

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Editors
Qingfeng Li
Department of Energy Conversion and Storage
Technical University of Denmark
Lyngby, Denmark

David Aili
Department of Energy Conversion and Storage
Technical University of Denmark
Lyngby, Denmark

Hans Aage Hjuler
Danish Power Systems
Kvistgård, Denmark

Jens Oluf Jensen
Department of Energy Conversion and Storage
Technical University of Denmark
Lyngby, Denmark

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Preface

Since the concept of high temperature polymer electrolyte membrane fuel cells (HT-PEMFC) was proposed in early 1990s, it has attracted a large interest in the fuel cell community and over time spread around the world. Hundreds of patents have been filed and thousands of research papers have been published on the subject. Both research and development activities are flourishing at research institutions as well as in industrial companies. Many new scientists and engineers have been educated in the field and more are coming. Multiple products including polymer membranes, electrodes, cells, stacks, and systems are today available on the market, though a real commercial breakthrough is yet to be seen.

Thus, we decided that it was time to review and update the knowledge about the materials and technology in a book dedicated to the HT-PEMFC. Our aim is that it will be used as a reference for the fuel cell communities in universities and companies as well as for students around the world.

Going forward, the main challenges for HT-PEMFC—as for other fuel cell technologies—are the cost, performance, and the durability issues. The use of platinum and other noble metals as well as other expensive materials is a significant barrier for the technology to enter the market on a large scale. Also the durability or the lifetime of materials, components, and systems must be enhanced. Further, there might be even more barriers for an emerging technology that need to be overcome which can be customer adaptation, concerns about pressurized hydrogen, toxic fuels, and other hazards. We hope that this book can be helpful to overcome at least some of these challenges.

We are very pleased to have received so many well-written chapters from researchers and workers of expertise in the field. We would like to thank all the authors for the many hours they have spent. We are also grateful for the good discussions we have had with the authors. The authors of the individual chapters were granted a high degree of freedom to follow their own preferences with regard to use of abbreviations and to their choice of English orthography, though attempts are made to keep technical terms consistent. We would also like to mention that the group of contributors was not put together with the aim to include all key research groups or companies involved in the PBI-based HT-PEMFC development, but merely to cover, as we see it, the most important scientific aspects of the technology without too much redundancy. This means that several leading groups are not directly

represented as authors but well referred to in the chapters. We hope for their understanding.

A special thanks goes to Kenneth Howell, Abira Sengupta, and other staff from Springer Publishing in New York. They have been extremely helpful for all practical aspects of getting this book published.

Finally, on behalf of all the authors, we would like to thank all funding agencies, universities, and companies that have made it possible to do all the work in the laboratories around the world.

Lyngby, Denmark — Qingfeng Li
Lyngby, Denmark — David Aili
Lyngby, Denmark — Jens Oluf Jensen
Kvistgård, Denmark — Hans Aage Hjuler

Contributors

David Aili Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark

Søren Juhl Andreasen Department of Energy Technology, Aalborg University, Aalborg East, Denmark

Aikaterini K. Andreopoulou Department of Chemistry, University of Patras, Rio-Patras, Greece

Foundation for Research and Technology Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece

Simone Angioni Department of Chemistry and INSTM, University of Pavia, Pavia, Italy

Vincenzo Antonucci CNR-ITAE, Messina, Italy

Antonino S. Aricó CNR-ITAE, Messina, Italy

Vincenzo Baglio CNR-ITAE, Messina, Italy

Liliane C. Battirola Instituto de Química, Universidade de Campinas, Campinas, SP, Brazil

Peter Beckhaus ZBT GmbH – Zentrum für BrennstoffzellenTechnik, Duisburg, Germany

Brian C. Benicewicz Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA

Lars Nilausen Cleemann Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark

Fosca Conti Department of Chemical Sciences, University of Padova, Padova, Italy

Maria Daletou Foundation for Research and Technology Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece

Glenn Eisman H2Pump LLC, Latham, NY, USA

Tom Engl Electrochemistry Laboratory, Paul Scherrer Institut, Villigen PSI, Switzerland

Kayley Fishel Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA

Ed Fontes COMSOL AB, Stockholm, Sweden

K. Andreas Friedrich Institute of Engineering Thermodynamics, German Aerospace Center, Stuttgart, Germany

Irene Gatto CNR-ITAE, Messina, Italy

Lorenz Gubler Electrochemistry Laboratory, Paul Scherrer Institut, Villigen PSI, Switzerland

Ronghuan He Department of Chemistry, College of Sciences, Northeastern University, Shenyang, China

Dirk Henkensmeier Fuel Cell Research Center, Korea Institute of Science and Technology, Seongbukgu, Seoul, South Korea

Thorsten Hickmann Eisenhuth GmbH & Co. KG, Osterode am Harz, Germany

Hans Aage Hjuler Danish Power Systems, Kvistgård, Denmark

Suk-Gi Hong Samsung Advanced Institute of Technology, Samsung Electronics, Co. Ltd, Seoul, South Korea

Mark Tonny Dalsgaard Jakobsen Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark

Holger Janßen Forschungszentrum Jülich GmbH, Jülich, Germany

Jens Oluf Jensen Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark

Kristian Kjær Justesen Department of Energy Technology, Aalborg University, Aalborg East, Denmark

Joannis K. Kallitsis Department of Chemistry, University of Patras, Rio-Patras, Greece

Foundation for Research and Technology Hellas/Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece

Josef Kallo Institute of Engineering Thermodynamics, German Aerospace Center, Stuttgart, Germany

Jochen Kerres Institute of Chemical Process Engineering, University of Stuttgart, Stuttgart, Germany

Carsten Korte Institute for Energy and Climate Research, Electrochemical Process Engineering (IEK-3), Jülich, Germany

Isabel Kundler Eisenhuth GmbH & Co. KG, Osterode am Harz, Germany

Søren Knudsen Kær Department of Energy Technology, Aalborg University, Aalborg East, Denmark

Sebastian Lang Technische Universität Darmstadt, Fachgebiet Thermische Verfahrenstechnik, Darmstadt, Germany

Werner Lehnert Institute of Energy and Climate Research, Electrochemical Process Engineering (IEK-3), Forschungszentrum Jülich GmbH, Jülich, Germany

Qingfeng Li Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark

José J. Linares Instituto de Química, Universidade de Brasília, Brasília, DF, Brazil

Justo Lobato Chemical Engineering Department, Universidad de Castilla-La Mancha, Ciudad Real, Spain

Francesco Lufrano CNR-ITAE, Messina, Italy

Luca Merlo Solvay Specialty Polymers, Bollate (MI), Italy

Piercarlo Mustarelli Department of Chemistry and INSTM, University of Pavia, Pavia, Italy

Stylianos Neophytides Foundation for Research and Technology Hellas/ Institute of Chemical Engineering Sciences (FORTH/ICE-HT), Patras, Greece

Jung Ock Park Samsung Advanced Institute of Technology, Samsung Electronics, Co. Ltd, Seoul, South Korea

Markus Perchthaler Elcomax GmbH, Munich, Germany

Nadine Pilinski NEXT ENERGY, EWE Research Centre for Energy Technology, Oldenburg, Germany

F. Javier Pinar NEXT ENERGY, EWE Research Centre for Energy Technology, Oldenburg, Germany

Guoqing Qian Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, USA

Eliana Quartarone Department of Chemistry and INSTM, University of Pavia, Pavia, Italy

Maren Rastedt NEXT ENERGY, EWE Research Centre for Energy Technology, Oldenburg, Germany

Simon Lennart Sahlin Department of Energy Technology, Aalborg University, Aalborg East, Denmark

Robert F. Savinell Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH, USA

Johannes Schirmer Institute of Engineering Thermodynamics, German Aerospace Center, Stuttgart, Germany

Thomas J. Schmidt Electrochemistry Laboratory, Paul Scherrer Institut, Villigen PSI, Switzerland

Laboratory of Physical Chemistry, ETH Zürich, Zürich, Switzerland

Christian Siegel Siegel Schleimer Ingénieurs-conseils SARL, Belvaux, Luxembourg

Alessandro Stassi CNR-ITAE, Messina, Italy

Jen Supra Forschungszentrum Jülich GmbH, Jülich, Germany

Davide Carlo Villa Department of Chemistry and INSTM, University of Pavia, Pavia, Italy

Jürgen Wackerl Institute for Energy and Climate Research, Electrochemical Process Engineering (IEK-3), Jülich, Germany

Peter Wagner NEXT ENERGY, EWE Research Centre for Energy Technology, Oldenburg, Germany

Wendelin Waiblinger Institute of Engineering Thermodynamics, German Aerospace Center, Stuttgart, Germany

Jesse S. Wainright Case Western Reserve University, Cleveland, OH, USA

Marina Welsch Elcomax GmbH, Munich, Germany

Jingshuai Yang Department of Chemistry, College of Sciences, Northeastern University, Shenyang, China

T. Leon Yu Department of Chemical Engineering and Materials Science, Fuel Cell Center, Yuan Ze University, Chung-Li, Taoyuan, Taiwan

About the Editors

David Aili obtained his M.Sc. degree in Organic Chemistry in 2007 from the Institute of Technology at Linköping University after a diploma project at the Arrhenius Laboratory, Stockholm University. He subsequently moved to Technical University of Denmark to pursue a Ph.D. in the field of proton conducting membranes for electrochemical energy conversion technologies under the supervision of Professor Niels J. Bjerrum at the Department of Chemistry. After obtaining his Ph.D. degree in 2011 and after a shorter period as a development engineer in the phenolic resin business, he joined the newly formed Department of Energy Conversion and Storage at Technical University of Denmark in 2012 as a Postdoctoral Research Fellow. His current research covers fundamental and application-oriented aspects of ion conducting materials with special emphasis on polymer-based membranes.

Hans Aage Hjuler was educated as M.Sc. (Chemistry) at Technical University of Denmark in 1980. In 1983, he obtained his Ph.D. degree in Advanced Rechargeable Batteries at Technical University of Denmark. As postdoc, he formed a significant research group in batteries (from 1983) and fuel cells R&D (from 1988). He has worked with PAFC, MCFC, SOFC, and PEM-based fuel cell systems and materials. He worked as laboratory manager with superconducting materials (high Tc) at NKT Research Center from 1991 to 1994. He was director in Novo Nordisk from 1998 to 2009. He was one of the founders of Danish Power Systems in 1994 and chairman from

1994 to 2010. He was appointed Managing Director, CEO in 2010. H.A.H. is vice-chair of the Board of Directors of the Danish Partnership for Hydrogen and Fuel Cells, member of Annex 22, International Energy Agency (IEA) Implementing Agreement on Advanced Fuel Cells. He is member of the Scientific Committee of Fuel Cell and Hydrogen Joint Undertaking (FCH-JU), European Commission, Brussels, Belgium.

Jens Oluf Jensen is a full Professor at Technical University of Denmark, where he is heading the section named Proton Conductors (ca. 25 people) at Department of Energy Conversion and Storage. He is the coordinator of the technology tracks for PEM fuel cells and for low temperature electrolyzers at the department. In 1997, he received his Ph.D. for a study on metal hydrides for batteries. Today, his research fields include high temperature PEM fuel cells and alkaline electrolyzers. The approach is experimental and focused on materials like electrolytes, catalysts, and electrode structures. He has initiated and coordinated numerous national and international research projects, mostly in collaboration with industry, and arranged a number of symposia/workshops. Lately, he chaired the third International Carisma Conference in Copenhagen 2012 and the Danish Korean PEM Fuel cell workshop in Seoul 2013. He is a board member of the Partnership for

Hydrogen and Fuel cells in Denmark. At DTU, he has taught at numerous courses and is at present involved in teaching hydrogen energy and fuel cells as well as thermodynamics.

Qingfeng Li is a full professor at Department of Energy Conversion and Storage, Technical University of Denmark. His research areas include proton conducting electrolytes, electrocatalysts, and the related technologies particularly fuel cells and electrolyzers. He received his Ph.D. in electrochemistry from Northeastern University, China, in 1990 and was awarded Doctor Degree of Technices at DTU in 2006. As a postdoc, he started in the middle of 1990s the research on high temperature polymer electrolyte membrane fuel cells at DTU. He has participated/coordinated more than 20 EU and Nordic research projects within the fuel cell area and is currently the leader of 4M Centre devoted to fundamental research on mechanisms, materials, manufacturing, and management of high temperature polymer electrolyte membrane fuel cells, funded by Innovation Fund Denmark. He is an active member of, among other, the Electrochemical Society and the International Society of Electrochemistry (and currently the region representative of Denmark 2012-now). Prof. Li has been involved in teaching at all DTU levels including a lecturing and an experimental course on Hydrogen Energy and Fuel cells.

Overture: The Early History of PBI/Phosphoric Acid Membranes

Robert F. Savinell and Jesse S. Wainright

The two of us, Robert F. Savinell (R.F.S.) and Jesse S. Wainright (J.S.W.), have collaborated on the development of PBI/PA membranes for fuel cells at CWRU from the very early days, and are pleased to tell this story about the early history of the PBI/PA high temperature membrane for fuel cells.

It was in the late 1980s time period when R.F.S. was the Associate Director of the Case Center for Electrochemical Sciences (now the Yeager Center for Electrochemical Sciences at Case Western Reserve University) working with Professor Ernest B Yeager (see Fig. 1).

Robert F. Savinell (✉) • Jesse S. Wainright
Department of Chemical Engineering, A.W. Smith Building, Case Western reserve University, Cleveland, Ohio 44106, USA
e-mail: Robert.savinell@case.edu

Fig. 1. Robert F. Savinell on far left and Professor Yeager on right of plaque at the celebration of the renaming of the Case Center of Electrochemical Sciences to the Yeager Center for Electrochemical Sciences with CWRU administrators and Dorothy Hummel Hovorka, wife of Frank Hovorka, Professor Yeager's Ph.D. advisor

At that time, Professor Yeager's group was interested in enhancing the electrokinetics of oxygen reduction reaction in a phosphoric acid electrolyte. One approach he took was to add perfluorinated surfactants to a phosphoric acid electrolyte so as to enrich the oxygen activity near the electrocatalyst surface. Indeed, this worked to some extent and enhanced oxygen reduction polarization curves were demonstrated. It was this work that stimulated our thinking about fuel cells and the idea of using a high temperature membrane.

In early 1991, Professor Yeager and R.F.S. met with colleagues on a weekly basis to discuss research strategies to address the development of a high performance direct methanol fuel cell. These meetings explored many different aspects of improving methanol fuel cell performance from electrocatalysts and membrane materials to cell designs. A number of times we would go down a strategic path in great detail, but only to throw out the approach after weeks of deep discussion. After about 6 months of weekly discussions and as we rapidly drew near a proposal submission deadline, we concluded that if a proton conducting polymer membrane can be developed that operates at ~200 °C, then there would be "opportunities to overcome the catalyst's activity and stability problems." The thought was that the right membrane could lead to high performance direct methanol fuel cells.

Fig. 2. Professor Morton Litt examining an early sample of a cast PBI membrane (from *Case Alumnus*, Spring 1997)

We then set out to propose a research program with its principle objective being the development of a high proton conducting solid polymer electrolyte membrane which is chemically stable under the oxidizing and reducing conditions existing in a direct methanol fuel cell and operates at temperatures of 200 °C. Two approaches that were proposed involved new polymers with superacid functional groups such as the perfluorinated sulfonimides and the perfluorinated phosphonic acid materials, with the thought that they would retain water even at higher temperatures. Looking for alternative approaches, Professor Morton Litt of CWRU (see Fig. 2) brought to our attention the 1977 work of Hoel and Grunwald [J. Phys. Chem., 81 2135 (1977)] which reported evidence of proton conductivity in films of polybenzimidazole, although the conductivities were quite low (10^{-4} S cm^{-1}). Professor Litt suggested we explore poly(benzimidazoles) and poly(quinolones) by doping films with acid and even trying to functionalize the films with acid groups.

These polymers were known to be stable at elevated temperatures. As the PI for the research program, R.F.S. decided to include this idea to broaden our membrane approaches. The proposal was submitted to the US Defense Advanced Research Projects Agency (DARPA) on July 11, 1991, and included the three polymer approaches mentioned above, as well as new electrocatalysts for operating in these polymeric environments, and a variety of fundamental measurements. We also proposed integrating these new materials in a laboratory scale "microfuel cell" to demonstrate actual operating performance. The program was selected for funding and a contract awarded in 1992. This is when J.S.W., just completing his Ph.D. studies, joined R.F.S. and the team to pursue this research program (see Fig. 3).

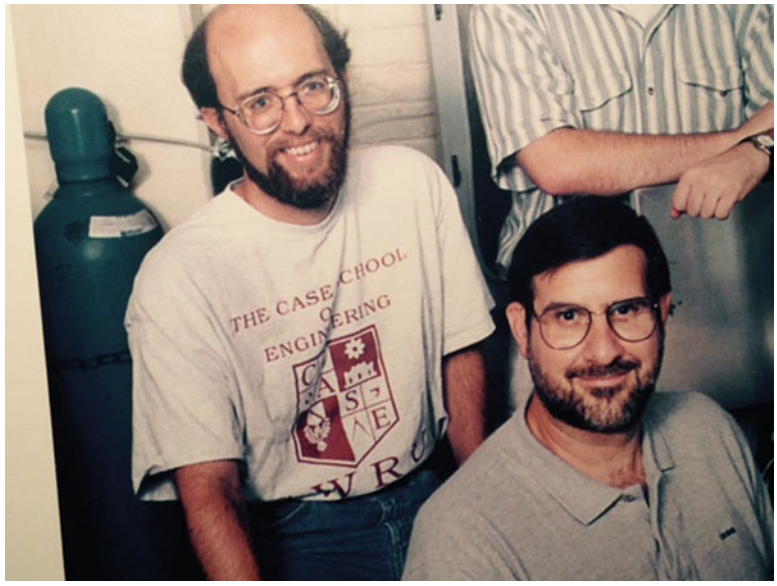

Fig. 3. Jesse S. Wainright and Robert F. Savinell in the early days of PBI/PA research (from *Case Alumnus*, Spring 1997)

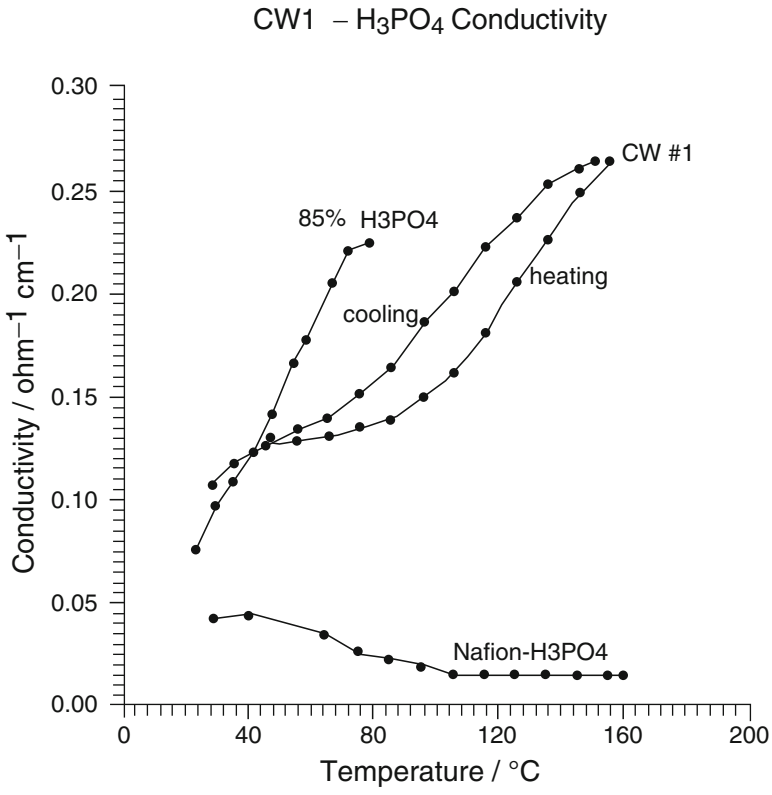

Fig. 4. Four-point conductivity measurements for Nafion 117 and polybenzimidazole films infused with phosphoric acid. Conductivity cell measurements of phosphoric acid shown for comparison. Figure 3 of the first quarter (ending September 1992) project report of the CWRU DARPA methanol fuel cell project

The CWRU DARPA program pursued all three polymer approaches simultaneously. Eventually, we learned that the superacid perfluorinated polymer strategy produced some very intriguing membrane films, but none performed any better at elevated temperatures than the state-of-the-art Nafion product of DuPont. Here, we will summarize of our early quarterly progress reports of the CWRU DARPA program that give some insight on our early thinking and contain much unpublished data and results. During the first quarter of the project, sulfuric acid and phosphoric acid sorption in PBI films studies were initiated. It was demonstrated that with a H_2SO_4/PBI molar ratio of 0.2, the PBI unit interacted so strongly with the acid that the acid could not be extracted from the polymer with water. The first conductivity measurements were made on acid-doped PBI, and the first quarterly project report for the period ending September 1992 stated: "The third set of results is for the CWRU undoped polybenzimidazole sample which has been given the designation CW1. As received, this material exhibited a very low conductivity, ca. 10^{-4} S cm^{-1}. Doped films are expected to have much higher proton conductivity. We pretreated the undoped film in H_3PO_4 for 1 h at 150 °C and the conductivity was found to be very high, as shown in Figure 3 (Fig. 4 of this article). This data was obtained in dry air. The conductivity of the CW1 sample is much greater than that of the hydrated Nafion sample and approaches the conductivity of the liquid phosphoric acid. It would appear that the CW1 sample is acting as an acid support."

During the second quarter, ending December 1992, it was shown that phosphoric acid-doped PBI was more thermally stable than undoped PBI films. Studies also measured sulfuric acid and phosphoric acid permeation through PBI films in order to predict doping times. More controlled experiments of conductivity as a function of acid doping took place during this quarter, with phosphoric acid doping levels of 25, 33, and 42 mol%, all showing relatively low conductivities.

In the third quarter of this program, ending March 1993, we demonstrated that as phosphoric acid doping levels increased from 40 to 170–190 mol% (mole acid to PBI repeat unit X100), the conductivity also improved substantially. J.S.W. was the persistent researcher in the lab who recognized the increasing conductivity trend with acid doping level and continued the studies to explore the effects on conductivity at even higher acid doping levels. We also showed that doping with excess sulfuric acid increased conductivity, and 250 mol% sulfuric acid-doped PBI at 160 °C had about a quarter of the conductivity of Nafion at 80 °C fully hydrated. But, high doping levels with sulfuric acid at temperatures of 350 °C for a few minutes sulfonated PBI, which decreased conductivity. During that quarter, we also

began to appreciate the importance of phosphoric acid dehydration and polymerization in low humidity conditions so we initiated experiments controlling the relative humidity during conductivity measurements. It was shortly after this quarter we discontinued using sulfuric acid, and focused attention on phosphoric acid doping of PBI. During the third quarter, we also started measuring oxygen and methanol permeation rates through a PBI/acid-doped film and compared the measured permeability with those of Nafion and acid-doped/Nafion films.

During the fourth quarter, ending June 1993, we started exploring various PBI-type structures. Also during the first year of the program, we studied the Nafion/PA system as well and used its conductivity, stability, and permeability characteristics as a basis for comparison with PBI/PA or PBI/SA results.

The research performed during the fifth quarter of the program, ending September 1993, was especially significant. We became fully aware of the importance of high molecular weight PBI polymers for film strength. We demonstrated high conductivity with PA doping levels of 350 mol%, approaching 0.02 S cm^{-1} at 190 °C. Doping levels would later be increased to over 500 mol% in our labs, and even higher by other researchers. We demonstrated methanol vapor cross over permeation rates an order of magnitude below that of the hydrated Nafion in direct liquid methanol fuel cells. The polarization curve and the operating stability under constant voltage and constant current load were demonstrated in a PBI/PA fuel cell. Some of these original data graphs are shown in Figure 5 (Figs. 6.5.1b, 6.5.1c, 6.5.1d of the September 1993 Progress Report). The efforts of two of our Ph.D. students, Jiang-Tao Wang and Dacong Weng, were particularly instrumental in obtaining these key early results. We learned that a Nafion/PA membrane in a fuel cell, although having high ac conductivity, could not sustain high dc current densities. This result bothered us and suggested that there were fundamental differences in the transport mechanism as compared to a PBI/PA membrane. It was shortly into the second year of the program that we stopped much of our work on the Nafion/PA system, with the exception of using it for evaluating elecrocatalyst performance under elevated temperature conditions. Recently, we collaborated with the DTU group to investigate the Nafion/PA system and repeated some of the observations we made earlier at CWRU. Although not fully understood, there are clearly some significant differences in proton conduction between the Nafion/PA and PBI/PA systems. As a colleague recently commented to one of us, "you may have just been lucky to stumble upon the PBI/PA system."

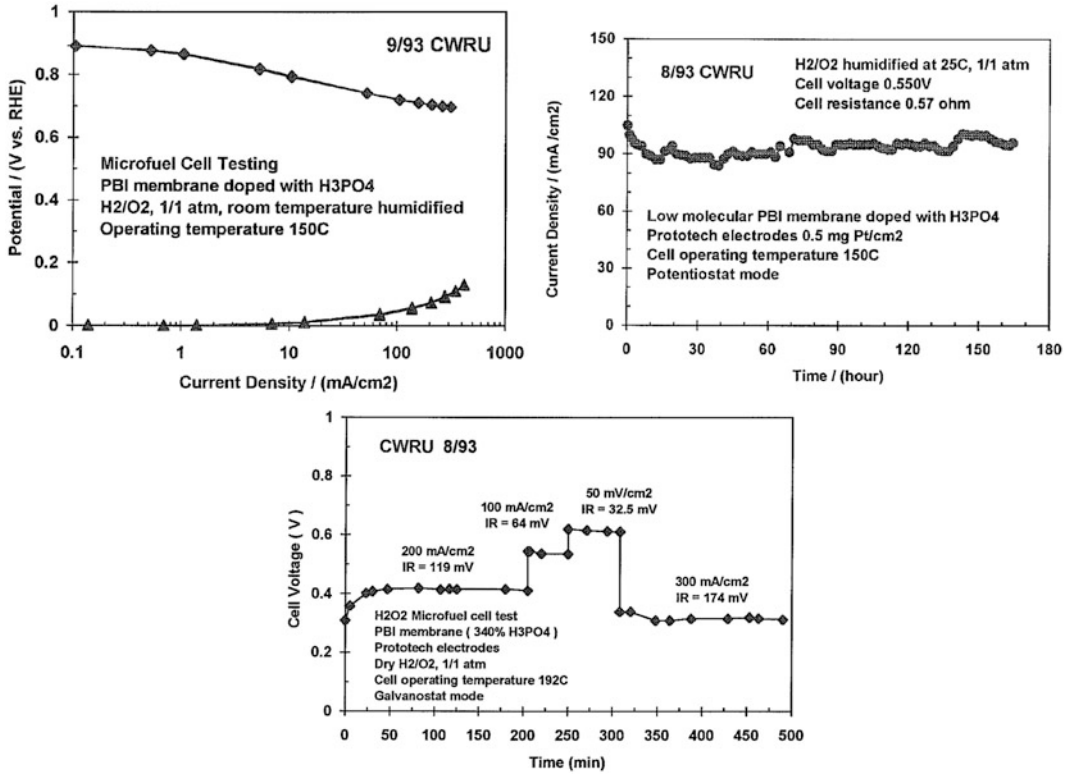

Fig. 5. These figures are taken from the fifth quarter progress report of the CWRU DARPA Direct Methanol Fuel Cell Program, dated September 1993. They show the first results of fuel cell testing with PBI/PA in a fuel cell

The DARPA program continued for another 3 years. During this period, Professor Litt and his students developed a way to cast doped films in one step that increased both the doping levels possible and the consistency of the acid content. We explored operating a PBI/PA membrane fuel cell with various fuels, fuel purities, and measured temperature effects. We began to appreciate the relevancy of the technology for fuel cells operating on reformed fuels. Our studies with PBI/PA evolved to become more thorough and under better controlled conditions, and our understanding of the conductivity mechanism became deeper by studying water drag and performing NMR studies. In addition to the electrolyte work, we developed new oxygen reduction reaction electrocatalysts, including methanol-tolerant high performance non-precious metal C–N ligands.

The CWRU patents were licensed to several companies, and our publications (>15 papers from 1995 to 1998) on PBI/PA fuel cell membranes garnered more attention in the USA and worldwide. These licensee companies as well as other corporate and university researchers from around the world further explored the PBI/PA approach to improve mechanical and proton conducting properties and to evaluate the membranes in operating fuel cells and electrolyzers at elevated temperatures.

So what will be the long-lasting significance of the PBI/PA system, if any? Well, the system does not represent the best environment for electrochemical reactions such as oxygen reduction, and it certainly cannot be used at lower temperatures with liquid water present. But we are sure PBI/PA and similar polymers and approaches will continue to find applications in electrochemistry. Phosphoric acid is a highly conductive electrolyte rich in fascination because of its fundamental mechanisms for proton transport. But other doping acids might also be explored as well. In our view, the most significant feature of the PBI/PA membrane discovery is that it opened the door to our thinking about high temperature proton conducting membranes in general, and stimulated global research to find a better approach. As a result, many researchers have been cross-trained in electrochemistry and polymer/materials science through their work on this technology. These cross-trained scientists and engineers are those who will likely find better solutions in the future for efficient and cost-effective energy conversion technologies. On a personal level, our work on this system has led to close collaboration and friendship with colleagues and students at CWRU, and especially between the two coauthors of this article. It also led to many fruitful and rewarding collaborations and friends from around the world. This is what we value the most.

Robert F. Savinell
Distinguished University Professor and George S. Dively Professor of Engineering
Case Western Reserve University

Jesse S. Wainright
Research Professor
Case Western Reserve University

Introduction

1

Jens Oluf Jensen, Hans Aage Hjuler, David Aili, and Qingfeng Li

High temperature polymer electrolyte membrane fuel cells (HT-PEMFC) have been an active field of research and development over more than two decades. The term *high temperature* used in this book refers to a temperature range from 100 to 200 °C, relative to the well-developed PEMFC technology typically operating at 80 °C. It should be stressed that fuel cells working at temperatures up to 200 °C still belong to the overall class of *low temperature fuel cells*, in contrast to *high temperature fuel cells* which are molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) all working at above 600 °C.

The temperature range from 100 to 200 °C does not sound very high in any engineering sense; however, a significant effort is indeed behind the development of high temperature polymer electrolyte membranes and their cells, from both materials science and technological points of view. Obviously, elevated temperatures tend to challenge thermal, chemical, and mechanical stability of polymer materials, but besides that, obtaining sufficient proton conductivity in a stable and practical way, most preferably under ambient pressure, is far from trivial. One might think that a proton, a positive hydrogen ion, being orders of magnitude smaller than any other ion will have the ability to travel easily through many materials simply due to its tiny size. The contrary is true. The extremely small size makes the charge density very high, and the protons are always associated to other species. In a liquid electrolyte, this is not a problem since other mobile molecules carry the proton as a charged species and establish a net movement of the protons. The first fuel cells were developed around liquid electrolytes, but from a construction and handling point of view and in order to make the electrolyte as thin as possible to minimize internal resistance, solid electrolytes are very attractive and the electrolyte of interest here is the proton-conducting polymer. The cells are referred to as polymer fuel cells, polymer electrolyte fuel cells (PEFC), or polymer electrolyte membrane fuel cells/proton exchange membrane fuel cells (PEMFC).

In traditional PEMFC (based on polyperfluorosulfonic acid, PFSA), water is used as such a proton shuttle and the polymer membrane must be highly humidified in order to maintain proton conductivity. An increase in operating temperature from 80 to 150 °C leads to an increase of the water vapor pressure from 0.47 to 4.8 bar (ten times) and the membrane will dry out and lose conductivity unless the fuel cell is

J.O. Jensen (✉) • D. Aili • Q. Li
Department of Energy Conversion and Storage, Kemitorvet 207, 2800 Lyngby, Denmark
e-mail: jojen@dtu.dk; larda@dtu.dk; qfli@dtu.dk

H.A. Hjuler
Danish Power Systems ApS, Egeskovvej 6C, 3490 Kvistgård, Denmark
e-mail: hah@daposy.dk

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operated under a correspondingly increased pressure, which is impractical in most cases. At 200 °C, the water vapor pressure is as high as 15 bar. Additionally, softening of PFSA membranes is mechanically limiting the operation at elevated temperatures.

The question is then: why increase the working temperature of a PEMFC? This fuel cell has been very successful and one of the key advantages is the low working temperature. Startup is easy, the gases need not to be preheated, the selection of construction materials is wide (including elastomers for sealing), and degradation processes are generally slower at lower temperatures. All this is true, but there are yet a number of advantages of a higher temperature.

Key drivers for the development have been (1) increased tolerance to fuel impurities (in particular, carbon monoxide) of the platinum catalyst, (2) easier water management or even no water management at all (when conduction is not depending on water), (3) easier thermal management (cooling) due to higher temperature difference to the surroundings, and (4) a higher quality of the waste heat.

The fact that the tolerance to carbon monoxide increases with increasing temperature is well known from phosphoric acid fuel cells (PAFC), which also apply platinum as electrocatalysts. The carbon monoxide tolerance is critical if the fuel is hydrogen obtained via reforming (chemical conversion) of carbon containing fuels. In this process, the carbonaceous fuel is converted into hydrogen and carbon dioxide, but traces of carbon monoxide are always present as a by- product. Carbon monoxide adsorbs strongly to platinum surfaces and blocks the access of hydrogen. At 80 °C, a carbon monoxide content as low as 20 ppm (0.002 %) in the fuel stream results in a significant loss in cell performance, but at 160 °C, even 0.5–1 % carbon monoxide has only a minor effect. Therefore, very pure hydrogen or a complicated cleaning system is mandatory for the low temperature PEMFC, but not for high temperature PEMFC. Cells can thus be easily operated on abundant fuels like methanol, natural gas (methane), or liquefied petroleum gas (LPG) through reforming when a hydrogen infrastructure is missing.

In a conventional low temperature PEMFC, a careful management of the water balance (water management) to maintain a high degree of hydration of the membrane is a delicate matter. It is crucial for maintaining high conductivity and is done by humidification of the gas flows into the fuel cell. Water is also produced in the cell and if the net content gets above saturation water condenses and blocks gas channels and porosities leading to a severe performance drop. The water management is further complicated by a high electroosmotic drag of water, i.e., water transport along with the protons, in PFSA membranes. At temperatures above the boiling point of water at the actual operating pressure, condensation cannot take place. This is indeed the case in a high temperature PEMFC. Moreover, if conduction is based on another proton carrier than water, then water management should be much less intensive or even needless.

Easier cooling of PEMFC is a wish of the automotive industry because even though fuel cells produce less heat than small internal combustion engines (ICE), heat removal is more challenging with a low temperature fuel cell. While the ICE rejects most of its heat through the exhaust and a smaller part through the cooler, the fuel cell does so mostly via the coolant loop and a radiator. Besides, the temperature difference between the coolant and the surrounding is smaller in case of an 80 °C fuel cell than of the ICE. The transfer of more heat by means of a smaller temperature difference calls for a much larger radiator, which is not convenient for the auto developers. A fuel cell working temperature of 120–130 °C should be enough to compensate for this effect. Similarly, if a high temperature PEMFC is air cooled, the air flow needed is much smaller because it carries more heat per volume and a smaller and less energy-intensive blower can be applied. Finally, as about half of the energy of the fuel is converted into heat in a fuel cell, it would be most desirable if this heat could be better utilized. The number of uses for this heat rises with temperature.

The doing away with CO purification, water management, and extensive coolers allows for a simpler and possibly less costly system architecture. The saying of the fuel cell company, Serenergy, encompasses this fact: "The power of simplicity."

There are two ways to a higher operating temperature of PEMFCs. One is to pursue more efficient humidification at high temperatures either by increasing pressure or by enhancing water retention or self-humidification by produced water. The other way is to use less volatile proton carriers in the membrane. Different approaches to better water retention at high temperature have been explored. Alternative PFSA membranes with shorter side chains and higher crystallinity and particularly their composites with inorganic fillers have shown some feasibility, often in association with a slightly higher pressure, as described in Chap. 2. In the search for alternative proton carriers, inorganic proton-conducting materials in the forms of oxyacid salts (e.g., phosphates and pyrophosphates) and solid acids (e.g., $CsHSO_4$ and CsH_2PO_4) have been extensively explored. Fuel cell electrolytes made of such solid inorganic proton conductors as the main constituent are however rather ceramic than polymer electrolytes and not included in this book. Interesting is also the significant amount of work on organic–inorganic composites, of which only selected work in connection to polybenzimidazole (PBI) is presented. The most successful nonvolatile proton carrier to replace water in the membrane is phosphoric acid (H_3PO_4).

Phosphoric acid is unique with respect to its high thermal stability and proton conductivity at high concentrations. Based on concentrated phosphoric acid (85–100 wt%) as electrolyte, the phosphoric acid fuel cell technology operates at temperatures up to 210 °C. The use of concentrated acid substantially minimizes the water vapor pressure. Significant dehydration of phosphoric acid takes place at above 200 °C under limited atmospheric humidity, resulting in the formation of condensed strong acids, which are relatively stable and possess reasonable conductivity. Consequently, the electrolyte is able to operate at very low water activity without significant loss of the proton conductivity. The combination of very low volatility and nearly anhydrous conductivity in a wide temperature range allows for an easy control of airflow, humidity, and stack temperature, compared with the PFSA-based PEM fuel cells. The stack temperature can be in a wide range, say, from 150 to 210 °C. This wide temperature range of operation, in turn, allows for a combination of the dynamic load and easy cooling by either process air, a liquid, or by evaporation. The conventional phosphoric acid fuel cells use a brittle ceramic matrix layer of silicon carbide in which the electrolyte is confined. It must be free from pinholes, cracks, and un-wetted areas in order to prevent the gas crossover. For the same reason, it should have a high bubble breakthrough resistance and it should have significant mechanical strength. Consequently, such electrolyte layers typically have a thickness of 100–200 μm. A strong, flexible, and elastic polymer matrix is highly desirable for phosphoric acid-based fuel cells.

Having found the proton carrier, the next step is to find a suitable host polymer that possesses the appropriate thermal stability and compatibility with phosphoric acid in the desired temperature range. Using a basic polymer is a general practice via acid–base interactions with the acid. For this, the most successful polymers are PBIs, a large family of heterocyclic polymers with excellent thermal, chemical, and mechanical stabilities. PBI variants, their blends as well as analogues such as pyridine containing aromatic polymers are chosen as the focal point of this book.

It has often been debated whether the fuel cell built around a phosphoric acid containing polymer is a PEM fuel cell or a phosphoric acid fuel cell in a polymeric disguise. The most correct understanding is probably that it is a hybrid between the two.

From a materials science point of view, the acid–base chemistry plays a key role in the acid doping and resulted in essentially one-phase solid membranes with good homogeneity. The membranes may contain up to about 90 wt%