

Review of Advanced Materials for Proton Exchange Membrane Fuel Cells

Alexander Kraytsberg[†] and Yair Ein-Eli^{*,†,‡}

[†]Department of Materials Science and Engineering, and [‡]The Nancy and Stephan Grand Technion Energy Program (GTEP), Technion—Israel Institute of Technology, Haifa 3200003, Israel

ABSTRACT: The scientific community is focused on the development of inexpensive and high-performing membrane materials for proton exchange membrane (PEM) fuel cells (FCs). The major approach to reducing the cost of FCs, which is crucial for the widespread acceptance of FCs as energy sources for various practical applications, is reducing the cost of the membrane. Efforts are being made in the development of advanced polymeric materials, which will satisfy the technical and economic demands of the consumers. Because most alternative membranes are outperformed by Nafion membranes over an entire set of important properties, it may be worthwhile to compromise on certain parameters to develop alternative specialized membranes. This review presents the properties (mainly conductivity and chemical and mechanical stability) of modern solid polymer electrolytes (SPEs) for PEM FCs.

1. INTRODUCTION

Fuel cells (FCs) are electrochemical devices that produce electrical energy from the chemical energy of a fuel and oxygen. Although the most common fuel is hydrogen, other fuels, such as methanol, are also used. For the past 5 decades, FCs have been recognized as a preferred energy source for a wide variety of applications. Hydrogen contains more energy per unit weight than any other fuel, and therefore, a hydrogen-based power plant may be more efficient on a weight basis than a conventional power plant that uses other fuels; this aspect is particularly important for air, ground, and marine transportation. Moreover, the advantage of direct electricity generation from hydrogen via a FC is evident if electrical energy is used directly (e.g., in domestic power supplies, communication equipment, electronic devices, and portable electronics) rather than indirectly to generate mechanical movement. Since the 1960s, FCs have been used to power numerous mechanical and electronic systems, from spacecraft systems to electric vehicles, submarines, and portable electronics.

In a FC, hydrogen (or another fuel) is supplied to the anode side, whereas oxygen (pure oxygen or air) is supplied to the cathode side. At the anode, electrons are stripped from hydrogen atoms; the process is facilitated by a catalyst [e.g., platinum (Pt)-containing compounds]. The produced protons pass through a proton-conducting electrolyte, whereas the electrons are directed through an external path, powering an attached device and leading to the cathode, reducing oxygen. At the cathode, the protons are combined with oxygen, forming water. Overall, the FC combines hydrogen and oxygen to produce water and electricity.

The first FC was developed as early as 1839 by Sir William Robert Grove (1811–1896); at that time, his work was not considered for the development of a chemical power source but as a demonstration of a process, which was to invert electrolytic water decomposition. Sir Grove employed several electrolytic cells with separated anodic and cathodic compartments equipped with Pt electrodes and filled with a sulfuric-acid-

based electrolyte; the anodic compartments contained gaseous hydrogen, while the cathodic compartments contained gaseous oxygen. He discovered that a voltage was generated between the electrodes of the cell and that several of these cells connected in series comprised a battery that produced a voltage that was sufficiently high to decompose water.¹ The original drawing of Sir Grove's experiment is presented in Figure 1.

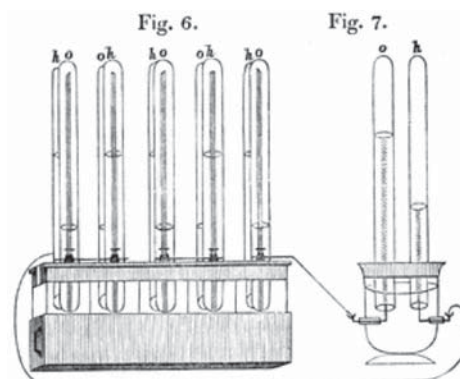


Figure 1. Grove's drawing of his wet cell or "gas battery" (acquired with permission from ref 1).

Further research explaining how these "gas cells" actually work was conducted for over a century by Christian Schönbein,² Friedrich Wilhelm Ostwald,³ Ludwig Mond,⁴ Charles R. Alder Wright,⁵ William W. Jacques,⁶ Emil Bau,⁷ and Francis Thomas Bacon.^{8,9} The construction of the first practical and operational FC is commonly attributed to Francis Thomas Bacon. Research continued during World War II but with few practical implementations. In the early 1950s, military

Received: September 4, 2014

Revised: October 21, 2014

Published: October 21, 2014

demands for a robust power supply for space and mobile applications began to promote the idea of producing electricity via an electrochemical process that used atmospheric or stored oxygen and employed a device without moving parts. Because these technological improvements were designed for space and military applications, the research costs were often of secondary importance. Because air is not available in space or underwater and it is impractical to store oxygen for internal combustion engines, chemical power sources (i.e., batteries) may serve as reliable power sources.

The conventional batteries of the 1950s were extremely heavy. This fact stimulated the National Aeronautics and Space Administration (NASA) to develop FCs as a provisional chemical power source. The full implementation of FCs in submarines required an additional 40 years, with the first non-nuclear, air-independent-propulsion submarines entering service in European fleets in the early 2000s.

FCs with solid polymer electrolyte (SPE) membranes separating the anodic (fuel) compartment from the cathodic (oxidant) compartment were first introduced in the Gemini space program in the early 1960s. Those cells were expensive and had short lifetimes because of the poor stability of the SPE membranes. The sulfonated polystyrene–divinylbenzene membranes suffered from rapid oxidative degradation. Additionally, this material was prohibitively expensive for practical commercial applications.

Commercial applications of FCs gradually became more attractive over the past 5 decades. This acceptance was primarily driven by the growing demand for environmentally friendly power plants, for vehicle and stationary energy applications (see Figure 2), zero-emission power sources for

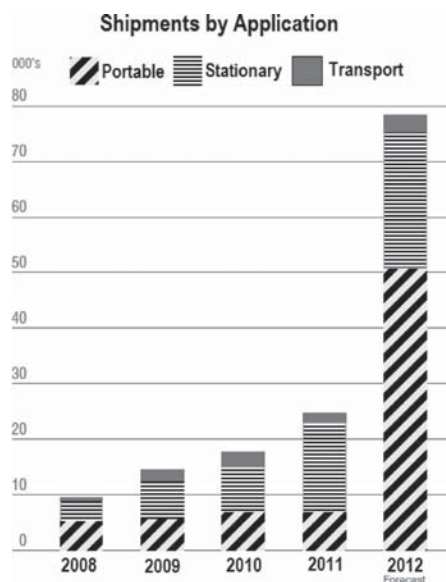


Figure 2. Annual FC system shipments worldwide (acquired and modified with permission from ref 10).

confined environments, and high energy density power sources for mobile devices. The major types of FCs are schematically presented in Figure 3. FCs are classified by the type of electrolytes that they use. Table 1 presents a comparison of different FC technologies.

Polymer electrolyte membrane (PEM) FCs are considered the optimum FC for applications such as backup power

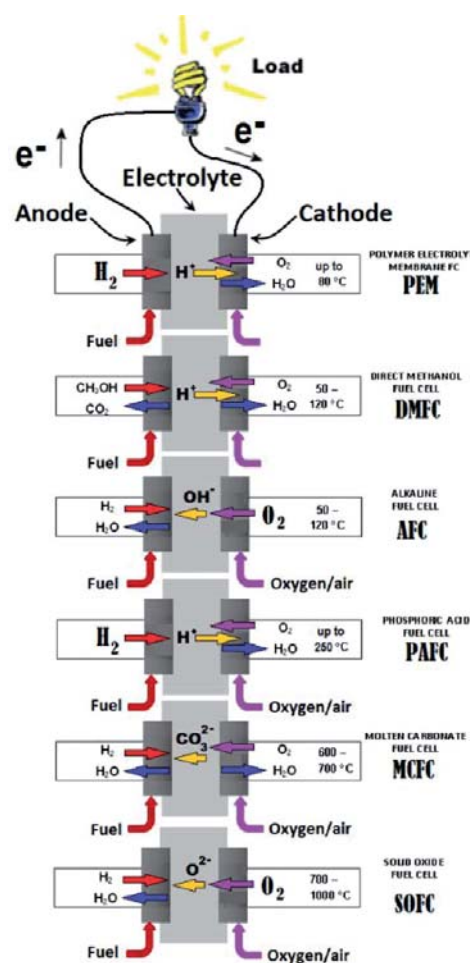


Figure 3. Summary of FC types.

sources, power sources for portable electronics, distributed power generation, and electric vehicles. An exemplified structure of a PEM FC is shown in Figure 4.

A practical FC-based power source is composed of a FC stack (as presented in Figure 5) and auxiliary devices (e.g., manifolds, humidifiers, air pumps, and thermal controls). The FC stack is, in turn, composed of a membrane electrode assembly (MEA) and bipolar plates, which serve as current collectors and supply reagents to the MEA electrodes. Bipolar plates also electrically connect multiple MEAs in series.

Many important PEM FC features depend upon the properties of the PEM. The important properties of the SPE for a PEM are (a) high proton conductivity, (b) low electronic conductivity, (c) low fuel and oxidant permeability, (d) adequate electrochemical and chemical stability in a real (i.e., a highly aggressive) FC environment, (e) high stability under FC operation conditions (i.e., the SPE should have good thermal and hydrolytic stability) (water and peroxides are the reaction products in a FC), (f) significant dimensional and morphological stability, (g) adequate water transport (diffusion and electro-osmotic) properties because the proton-transporting properties of most PEMs depend upon the membrane hydration, (h) good mechanical properties in all hydration states (this feature is essential for the reliable operation of the MEA and facilitates the FC manufacturing process), (i) a

Table 1. Comparison of FC Technologies¹¹

FC type	common electrolyte	operating temperature	typical stack size	efficiency	application	advantage	disadvantage
PEM	perfluorosulfonic acid	50–100 °C 122–212 °F typically 80 °C	<1–100 kW	60% 35% stationary	backup power portable power distributed generation transportation specialty vehicles military space distributed generation	solid electrolyte reduces corrosion and electrolyte management problems low temperature quick startup	expensive catalysts sensitive to fuel impurities low-temperature waste heat
alkaline (AFC)	aqueous solution of potassium hydroxide soaked in a matrix	90–100 °C	10–100 kW	60%	military	cathode reaction faster in alkaline electrolyte, leads to high performance	sensitive to CO ₂ in fuel and air
phosphoric acid (PAFC)	phosphoric acid soaked in a matrix	194–212 °F 150–200 °C	400–100 kW modules	40%	space distributed generation	low-cost components higher temperature enables CHP	electrolyte management Pt catalyst
molten carbonate (MCFC)	solution of Li, Na, and/or K carbonates, soaked in a matrix	302–392 °F 600–700 °C	0.3–3 MW	45–50%	electric utility	increased tolerance to fuel impurities high efficiency	long startup time low current and power high-temperature corrosion and breakdown of cell components
solid oxide (SOFC)	yttria-stabilized zirconia	1112–1292 °F 700–1000 °C 1202–1832 °F	300 kW module 1 kW–2 MW	60%	distributed generation auxiliary power electric utility distributed generation	fuel flexibility can use a variety of catalysts suitable for CHP high efficiency fuel flexibility can use a variety of catalysts	low power density high-temperature corrosion and breakdown of cell components high-temperature operation requires long startup time and limits

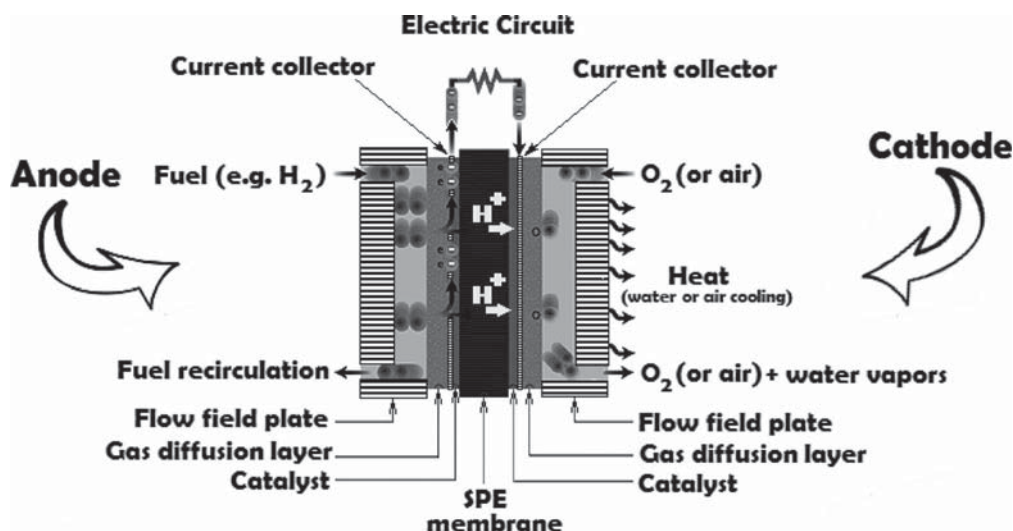


Figure 4. Schematic representation of a PEM FC design (acquired and modified with permission from ref 12).

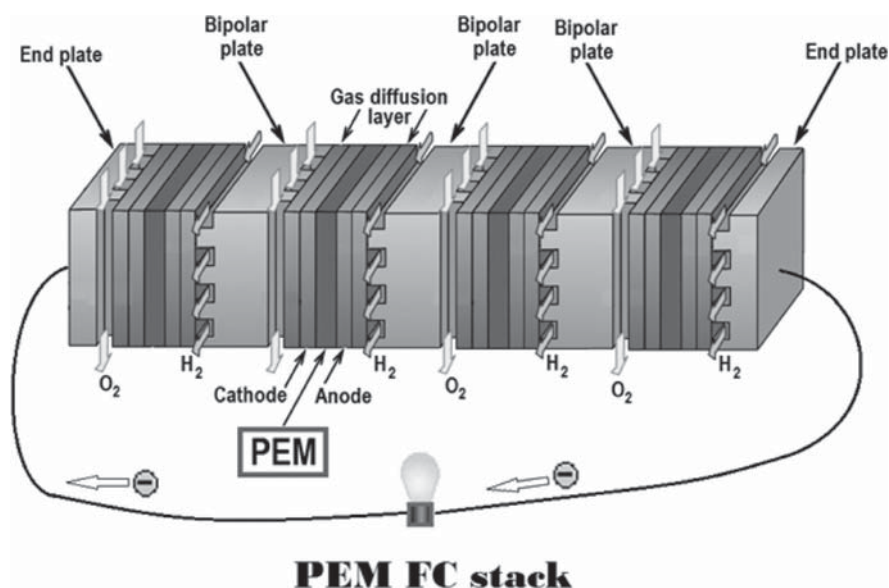


Figure 5. PEM FC stack (acquired and modified with permission from ref 13).

sufficiently long lifetime under FC operation conditions, and (j) a satisfactorily low cost.

Indeed, the PEM is the largest contributor to the overall FC cost (see Figure 6). The current shipment statistics indicate that less than 1000 pieces of 80 kW PEM FCs are shipped per year, which can also be inferred from the data presented in Figure 2 (PEM FCs account for approximately 90% of all FC shipments).¹⁰

For portable applications, a methanol FC [direct methanol FC (DMFC)] is currently being considered as a promising power source. A low rate of methanol crossover is a requirement for such FCs. Methanol diffusion from the anode to the cathode results in cathode depolarization and, thus, lowers the cell voltage efficiency and reduces the fuel efficiency of the system. Methanol is also poisonous for many cathode catalysts.

A few extensive reviews on SPE materials are available, and the reader is kindly directed to them.^{15–24} The present work

aims to discuss recent developments in the field of practical and viable SPE materials for H_2/O_2 PEM FCs and DMFCs.

2. POLY(PERFLUOROSULFONIC ACID) (NAFION)-TYPE MEMBRANES

2.1. Introduction. The use of organic cation exchange membrane polymers in FCs was originally developed in 1959 by GE researcher Willard T. Grubb.^{25,26} The intended function of the membrane was to provide a proton-conducting gas barrier. Strong acids were used to provide contact between the membrane and catalytic surfaces. Further development demonstrated that the cell could function well without the acid contact layer; at present, PEM FCs do not use any electrolytes other than the membrane itself. In the 1960s, the membrane was found to be a key factor in the FC because the PEM acts as an electrolyte and the structure of the PEM/(electrode catalyst) interface controls the reaction kinetics. From this understanding, a substantial part of the FC-related

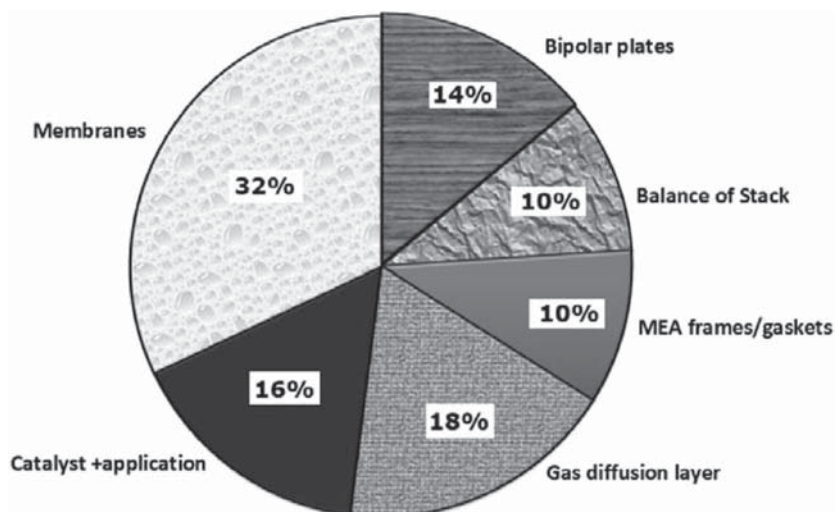


Figure 6. Breakdown of the 2013 projected FC stack cost at 1000/year production of 80 kW systems (data acquired with permission from ref 14).

research was focused on improving PEM properties, developing a stronger, more durable, and flexible SPE, and increasing SPE proton conductivity.

Currently, Nafion is the PEM that serves as a benchmark in the FC industry. This material was developed in the late 1960s by Dr. Walther Grot from DuPont (this material was originally suggested to be employed as a permselective separator in chloralkali electrolyzers).²⁷ Nafion was developed by modifying another DuPont product, Teflon,²⁸ which was the first synthetic polymer with ionic properties (ionomers) ever developed. Ionic properties are imparted to Nafion by adding a pendant sulfonic acid group into the polymer backbone. The exemplified structure of Nafion is shown in Figure 7, where the sulfonic

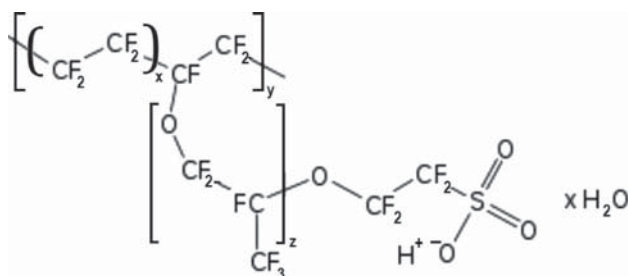


Figure 7. Nafion formula (acquired and modified with permission from ref 29).

acid group is shown in its anhydrous form, SO_3H . When exposed to water, the hydrolyzed form ($\text{SO}_3^-\text{H}_3\text{O}^+$) appears, allowing for proton transport across the material.

Commercial Nafion membranes with thicknesses of 2, 5, 7, and 10 mil (1 mil = 25.4 μm ; Nafion 112, 115, 117, and 1110, respectively) appear to be the most widely used grades of Nafion. This material provides high proton conductivity and moderate water swelling. The thinner membranes are generally applied to hydrogen/air applications to minimize ohmic losses, whereas the thicker membranes are employed for DMFCs for methanol crossover reduction.²²

Being similar to Teflon, Nafion exhibits excellent resistance to chemical attacks and an extremely low release rate of degradation products into the surrounding medium; it also has a relatively high operation temperature range and may be used

in many applications at temperatures up to 190 $^\circ\text{C}$. Nafion has a high proton conductivity and acts as a superacid catalyst because its sulfonic acid groups act as an extremely strong proton donor. The interaction of sulfonic acid groups with water results in rapid water absorption and water transport through the Nafion material.

2.2. Nafion Membrane Conductivity. Hydrophilic sulfonic groups, which are side-attached to the fluorinated hydrophobic backbone of Nafion, may be subjected to hydration; i.e., water molecules may accumulate around these groups. Water affects the Nafion proton conductivity by controlling the formation, dimensions, and connectivity of proton pathways in Nafion. As more water molecules become available, these water clusters grow in size and the Nafion material separates into hydrophobic regions and water-filled hydrophilic domains.^{30–35} Nafion with a low water content contains only small isolated water clusters and behaves as an insulator. Eventually, a percolation threshold of proton conductivity is passed. At this point, the water clusters are connected in a random network embedded in a continuous, sponge-like fluorocarbon phase. However, most of the water molecules are still located at the borders of the clusters, and thus, most of the water molecules inside the percolation channels accumulate in sulfonate group solvation shells. This leads to a high activation energy for proton transfer, which impedes a “hop-turn” (i.e., Grotthuss-type) proton conductivity and results in a primarily proton-diffusion-based conductivity. At the same time, the low proton mobility results in small proton conductivity. As the water content increases, the channels become broader and more free water molecules become available. However, the strong electrostatic interaction between the hydronium ions and multiple sulfonate groups still impedes Grotthuss-type proton conductivity and results in a predominantly diffusion-based proton conductivity. Under this hydration state, proton mobility is a key factor that determines the proton conductivity.

As the water content increases, the water clusters and channels increase in size and the amount of available free water inside the aqueous phase increases. This results in an increasing dominance of the Grotthuss-type conductivity, which increases proton transport capabilities. Once Nafion becomes fully saturated with water, its structure is patterned with highly

interconnected water channels and nearly spherical small hydrophilic domains containing water drops. These nearly spherical domains are surrounded by the hydrophobic polymer backbone chains, with the hydrophilic ionic groups located at the interface. A well-developed percolated network is formed, with the network comprising channels filled with free water. Thus, a saturated Nafion membrane resembles a phase-separated system containing hydrophobic main chain agglomerates and hydrophilic water/acid segments. The proton conductivity of the Nafion membrane approaches a value close to the conductivities of bulk aqueous electrolytes, and the conductivity is controlled by a Grotthuss-type mechanism. DuPont's Nafion is not entirely unique, and similar perfluorinated ionomers have been developed by other companies (e.g., Aciplex and Flemion of Asahi Chemical Company).^{36–38} Nafion-type perfluorinated ionomers with shorter pendant groups (such as AQUIVION of Solvay Solexis) are also currently marketed and appear to outperform Nafion, having a lower methanol crossover and superior water management.^{39,40}

2.3. Nafion Membrane Drawbacks. Although Nafion currently dominates the market, particularly in FC design and production,⁴¹ it has some serious drawbacks. (a) Because the proton conductivity is determined by the water-filled channels, Nafion is not adequate for temperatures materially lower than 0 °C or significantly over 100 °C.^{42,43} (b) Nafion is seemingly stable against peroxide-type ion and radical degradation (which are intermediate products of the reactions at the electrodes of the FC);⁴⁴ e.g., it is stable against 30% H₂O₂ even at 80 °C. However, alien cations (i.e., other than H⁺) are known to catalyze the polymer chain decomposition.^{45,46} Additionally, a few of the hydrogen-containing terminal groups of the polymer are susceptible to peroxide radical attacks.⁴⁷ (c) Contaminating ions, especially multi-charged ions,^{44,48} may also drastically decrease the membrane conductivity and decrease the water content of the Nafion membrane.^{44,49} Thus, alien ion impurities should be minimized during membrane production and operation. (d) Nafion has poor mechanical and chemical stabilities at elevated temperatures.^{50–53} Being a part of an assembled MEA, the membrane suffers from severe degradation in the course of multiple thermal and hydration/dehydration cycles.^{54–56} Because membrane mechanical degradation is typically the limiting parameter in determining FC lifetimes, substantial efforts were made to avoid or at least minimize this type of degradation. The membrane operational life also largely depends upon the MEA design and MEA assembly process.^{57–59} The appropriate routes for improving the mechanical stability of a Nafion membrane are through the precise controls of membrane swelling, temperature, and temperature gradient^{36,60–63} and the reinforcement of the membranes with an inert matrix,^{64–66} which may be composed of a polymer structure^{36,50,67–75} or an inorganic matrix. Composite membranes comprising Nafion and inorganic fillers have been used. This is the general method to improve the membrane chemical and temperature stabilities; the method is less commonly used to enhance the membrane mechanical stability.^{36,65,76–82} The introduction of a reinforcing matrix typically decreases the membrane-specific conductivity and water vapor permeability. These changes appear because a part of Nafion is substituted with the matrix material, which is impermeable to water and protons. The effects of the matrix extend beyond a simple substitution of a portion of an active material with inert media. An inert matrix-embedded Nafion

membrane may have lower proton conductivity and water vapor permeability than bulk Nafion because of a decrease in the membrane connectivity and because of the matrix-restricted macromolecular transport.⁷⁰ However, several additives may be used to enhance the proton conductivity of the reinforced Nafion membranes (e.g., phosphotungstic acid).⁸³ The employment of a reinforcing matrix may result in an increase in the overall membrane conductivity because the reinforced membrane may be substantially thinner than the Nafion membrane.⁶⁰ The presence of inorganic fillers with grafted functional groups is more efficient and enhances the overall composite membrane properties, such as water uptake, ion exchange capacity (IEC), and conductivity, while maintaining the mechanical properties of the composite membrane. The shape of the inorganic fillers also strongly affects the properties of the composite membranes.⁸⁴ Surface treatments may also result in the improvement of membrane mechanical properties.^{85,86} (e) Nafion has insufficient resistance to methanol crossover. This feature stems from the fact that, although the water-filled network provides a path for proton transfer, it also provides a route for methanol diffusion. This drawback of Nafion may be addressed by the addition of fine inorganic particles to the polymer matrix.⁸⁷ Another way to overcome the high methanol permeability of Nafion is to introduce other polymers with different properties inside the Nafion void space.⁸⁸ There are two approaches to such a modification: the first approach suggests the introduction of individual polymer molecules inside the voidspace (i.e., semi-interpenetrating polymer networks or a semi-IPN architecture),^{88–90} and the second approach suggests the introduction of an interconnected polymer net comprising cross-linked polymer molecules (i.e., interpenetrating polymer network or IPN).⁹¹ The high methanol permeability of Nafion is an issue, particularly if a PEM DMFC uses only this membrane. (f) The cost of a SPE is critical from a practical perspective. Nafion membranes are prohibitively expensive because of their complex manufacturing process.

3. NON-NAFION SPE

The development of Nafion in the early 1960s was followed by a significant decline in the development of non-Nafion SPE materials in subsequent decades. However, the aforementioned drawbacks (particularly the high price of Nafion) has become a driving force for the development of new polymer electrolytes, which are expected to be more affordable, more mechanically and chemically stable, and less permeable to methanol compared to Nafion. There has also been a growing demand for materials capable of operating at high (>100 °C) and medium (>80 °C) temperatures with high conductivity at low hydration levels. The operation of FCs at elevated temperatures offers several substantial advantages.^{20,40,92–95}

First, the commonly used Pt-based catalysts are poisoned by carbon monoxide (CO) at low operational temperatures; unfortunately, CO is often present in fuel-grade H₂. This requires an expensive H₂ fuel purification process for PEM FCs. At high temperatures (particularly at temperatures above approximately 160 °C), catalyst poisoning does not occur and the cell may tolerate up to 3% CO in the H₂ fuel without significant power losses.^{40,96} Second, faster electrode kinetics are expected at elevated temperatures, which increases the FC efficiency. Third, the absence of biphasic water (vapor and liquid) simplifies water management.

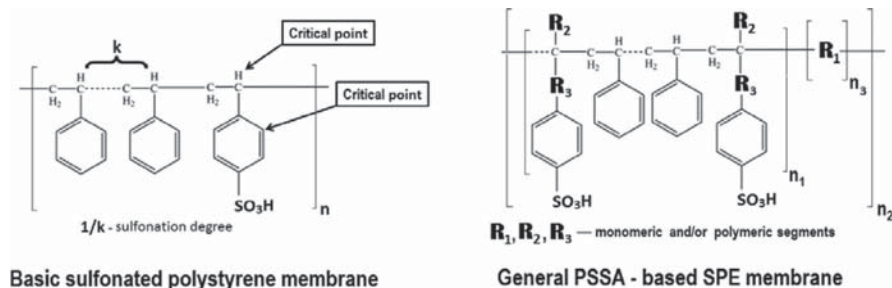


Figure 8. PSSA-based membranes for FCs.

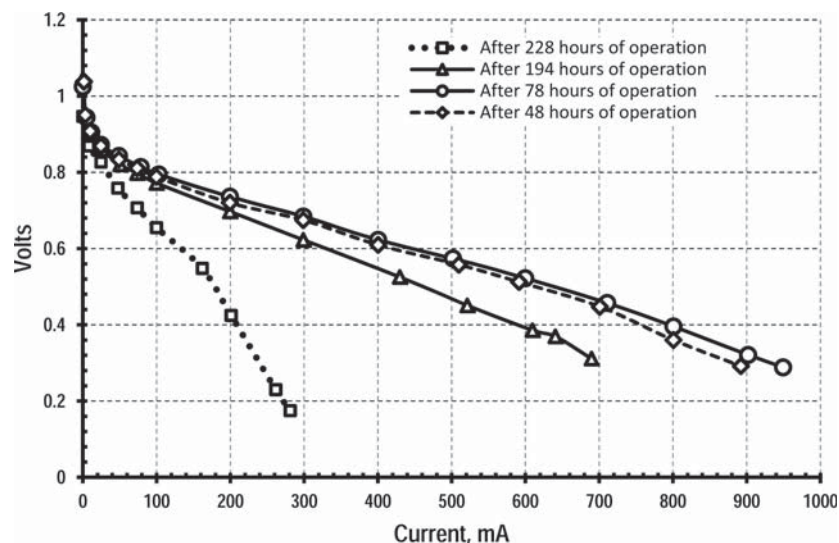


Figure 9. Performance degradation of a PEM FC with a PSSA membrane for different operation times, H_2/O_2 FC, 80 °C, 0.20 MPa, and 1000 mA/ cm^2 (data acquired with permission from ref 110).

Modern SPE-related research is focused on the following areas: (a) developing SPEs for H_2/O_2 FCs with high operation temperatures (such SPEs are expected to operate under low-humidity conditions), (b) developing SPEs for DMFCs with high protonic conductivity but low methanol permeability, and (c) developing low-cost substitutes for Nafion-type membranes.

Numerous partially fluorinated SPE and non-fluorinated (hydrocarbon) SPE materials have been investigated⁹⁷ (ref 98 provides an extensive review of methods using such SPEs). These SPE materials have similar proton conductivity mechanisms as Nafion. However, these materials may potentially offer advantages over Nafion depending upon the presence of water inside the polymer,^{99–101} the specifics of production costs, water management, methanol crossover, and thermal cycling stability.

3.1. Polystyrene-Based Membranes. Polystyrene-sulfonic acid (PSSA) membranes were the first commercial polymer membranes²⁵ (see Figure 8). The first polystyrene membranes were developed in 1955 by GE and were used in the first-ever operational PEM FC (the Grubb–Niedrach FC) in the Gemini program.^{102,103} However, the system exhibited a short lifetime (<200 h) because of membrane degradation, and the emergence of Nafion reduced interest in the development of polystyrene-based membrane materials.

The call for materials with medium and high operating temperatures and with high conductivity at low water contents has revived the interest in polystyrene-based membrane

materials.²² Given that the cost of SPE is a focus of the FC industry, the attractive feature of PSSA-based membranes is that polystyrene, its derivatives, and many styrene-containing copolymers are relatively inexpensive. Furthermore, the methanol permeability of PSSA-based membranes is lower than that of Nafion^{104,105} (i.e., the methanol selectivity β^{106} of the PSSA membrane is larger).

However, PSSA membranes are unstable¹⁰⁷ under practical FC operation conditions. SSA fragments are lost at high rates (i.e., up to approximately 0.1% per hour),^{108,109} which results in IEC and conductivity loss and membrane performance degradation (see Figure 9).

The PSSA polymer chain contained weak points at a ternary benzylic hydrogen and the aromatic ring protons (see Figure 8). The degradation of PSSA is due to peroxide attacks on the hydrogen atoms in these positions.^{104,111–114}

Relatively stable PSSA-based membranes were developed by eliminating the ternary hydrogens through various modifications of the styrene group.¹¹⁵ The ternary hydrogens were substituted for methyl groups¹¹² and fluorine [which gives phosphonated or sulfonated poly(α,β,β -trifluorostyrene) membranes];^{116–123} all substitutions resulted in a more stable membrane. However, the reported poly(α,β,β -trifluorostyrene) membrane lifetime was strongly dependent upon the operating conditions, e.g., 3000 h at 50 °C and a low current density and only 500 h “under practical FC conditions”.¹¹⁹ A maximum operation time of 15 000 h (BAM3G membrane, H_2/air , and 85

°C) was reported for the pre-commercial BAM3G series SPE membranes. These membranes contained (α,β,β -trifluorostyrene)-sulfonated pendant groups and perfluorinated backbones (see Figure 10).^{101,119,123} BAM membranes also demonstrated fair conductivity values of between 5×10^{-2} and 9×10^{-2} S/cm.¹⁰¹

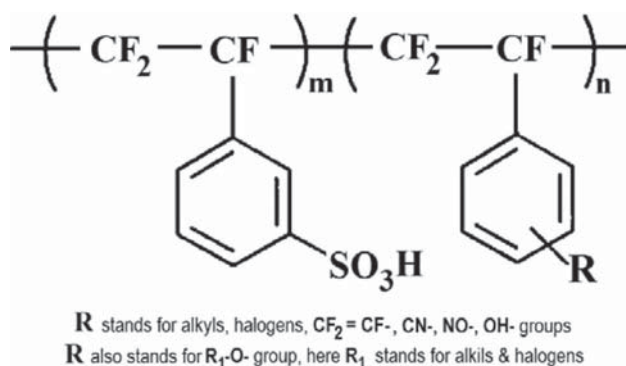


Figure 10. General structure of the sulfonated poly(α,β,β -trifluorostyrene) BAM3G membrane (acquired with permission from ref 119).

We were unable to find substantial information on the critical parameters of these membranes (e.g., available thickness and mechanical strength). These membranes may not be commercially available. Because this material is partially fluorinated, it is expected to have several of the same disadvantages as Nafion membranes, such as being non-environmentally friendly, which poses a problem with their safe production and disposal. The costs and unit pricing for these membranes were also not available. The PSSA-based membrane material has a substantially higher water content than Nafion membranes but a lower conductivity (see Figure 11).^{101,124} These conductivity values are still acceptable for FC applications.

This suggests that PSSA-based materials offer a slimmer and less interlinked water-filled network (the presence of such a hydrophilic network is now considered a requirement for SPE proton conductivity¹²⁵). The amount of sulfonic acid functional groups is also lower. These factors result in unfavorable

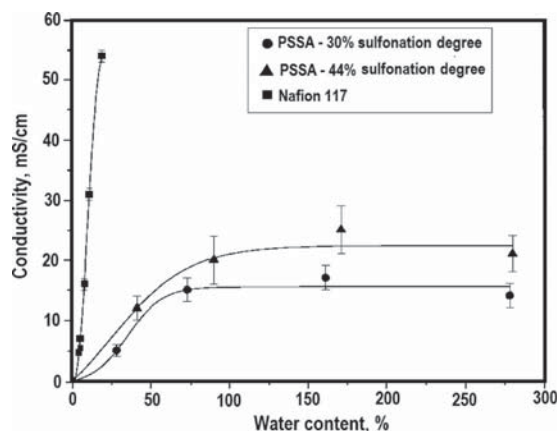


Figure 11. Proton conductivity versus water content for PSSA material with different degrees of sulfonation and for Nafion 117 (acquired and modified with permission from ref 124).

material swelling and a steep decline in conductivity with a decreasing membrane water content. However, the electro-osmotic water drag is expected to be advantageously reduced in comparison to Nafion.¹²⁶ The attempts to control these parameters of a PSSA-based SPE led to the use of various SSA copolymers^{127,128} [using polymers with various (R_1) groups of different lengths (n_3); see Figure 8] because the features of the SPE depend upon the properties of the polymer backbone.^{31,129}

SPEs containing various SSA copolymers, including sulfonated poly(styrene-*block*-isobutylene-*block*-styrene) triblock copolymers,^{130,131} sulfonated polystyrene-*block*-(ethylene-*ran*-butylene)-*block*-polystyrene,^{132,133} sulfonated styrene-ethylene copolymers,¹³⁴ sulfonated polystyrene(ethylene-butylene)-polystyrene triblock copolymers,^{135,136} and poly[norbornenylethylstyrene-*s*-styrene]-poly(*n*-propyl-*p*-styrene-sulfonate) (PNS-PSSP) block polymers,¹³⁷ were prepared and investigated. These SPEs often demonstrated higher proton conductivity (up to 10^{-1} S/cm) than Nafion. These materials also often demonstrated superior methanol selectivity compared to Nafion. However, the stability data for these membranes were typically not reported in the literature, and the applicability of PSSA-*co*-polymer polymers in FCs is likely limited because the sulfonated polystyrene unit has a rather low oxidative stability.

The next step was to graft oligomer SSA fragments onto the backbone of a highly stable polymer. Such grafted polymer membranes offered a substantially higher IECs with moderate swelling because these membranes possessed isotropically connected ionic domains with high proton concentrations. Block copolymer membranes swelled excessively even at low IEC, which resulted in lower proton concentrations and conductivity. This prevented copolymer-based SPEs from attaining a high IEC; furthermore, high hydration compromised membrane mechanical properties.¹³⁸

Next, polystyrene SSA-grafted membranes were investigated.^{139–141} These membranes were synthesized by the preliminary preparation of SSA-oligomer segments, followed by their copolymerization with styrene. The prepared membranes demonstrated high proton conductivity (up to 0.24 S/cm), and these results have stimulated further development in the field.

Stable polymers, such as tetrafluoroethylene (PTFE, Teflon), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA), polyvinylidene fluoride (PVDF), poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-*co*-HEP), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), polyvinyl fluoride (PVF), and polyethylene, present attractive skeleton structures for SSA-grafted membranes.^{120,142–145} Radiation-induced grafting is a common method for the preparation of such polymers with SSA and modified SSA segments.

PVDF-*g*-SSA membranes (see Figure 12) demonstrated good proton conductivity (up to 0.13 S/cm). Unfortunately, these membranes exhibited substantially higher water absorption (up to 59 water molecules per SO_3 unit) than Nafion, which is a disadvantage for SPE materials.^{146,147}

Teflon-*g*-SSA, (low-density polyethylene)-*g*-SSA, and [tetrafluoroethylene-*co*-perfluoropropylene (FEP, Teflon 100)]-*g*-SSA materials were prepared by radiation-induced grafting and also demonstrated initial conductivities in the range from 0.1×10^{-2} to 10×10^{-2} S/cm, but the conductivity diminished by several orders of magnitude after treating the membranes

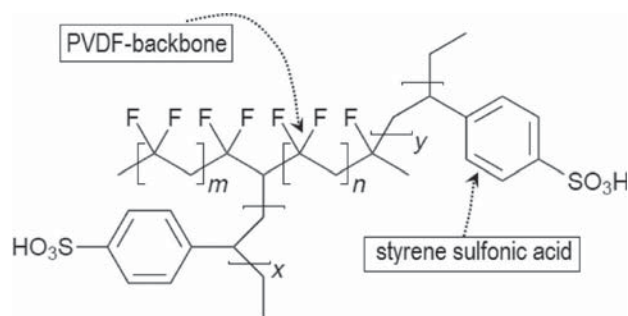


Figure 12. Suggested PVDF-g-PSSA structure (acquired and modified with permission from ref 148).

with 30% H_2O_2 .¹⁴⁹ FEP-g-SSA membranes promptly lose the SSAs at FC operation conditions (up to approximately 0.1% of the initial IEC value per hour).¹⁰⁹

The substrate structure has a substantial impact on the properties of the grafted membranes. SSA-PTFE membranes have higher conductivities than SSA-g-PVDF membranes, and the latter have higher conductivities than SSA-g-ETFE membranes. SSA-g-ETFE membranes are the most chemically stable, and SSA-g-PVDF membranes are the least stable (3% H_2O_2 at 60 °C).¹⁴⁴ The employment of a pre-irradiated and cross-linked PTFE substrate film is advantageous. Such SSA-g-(cross-linked PTFE) membranes offer a considerably higher grafting degree than SSA-g-(regular PTFE). Such membranes have higher IECs and exhibit less swelling than Nafion membranes.^{150,151}

Whereas membranes grafted with styrene sulfonic acid exhibit low stability, the membranes grafted with an α -substituted styrene sulfonic acid (e.g., α,β,β -trifluorostyrene and α -methylstyrene) exhibit improved stability: α -methylstyrene-g-ETFE did not show degradation after a 1053 h test in H_2/O_2 FC at 60 °C.¹⁵² However, the preparation of such membranes is problematic because of the low grafting rate.^{112,120,153} To address this problem, styrene sulfonic acid was grafted with other monomers (i.e., co-grafted membranes). Specifically, such monomers as methacrylonitrile (MAN), acrylonitrile (AN), methyl methacrylate (MMA), and methacrylic acid (MAA) were co-grafted to an ETFE substrate. This approach provided a route to synthesize modified SSA-g-ETFE membranes with conductivities of up to 0.16 S/cm at room temperature at adequate membrane IEC and hydration. However, the addition of these comonomers increased the water uptake of the membrane with the same IEC without improving the conductivity. Additionally, the presence of a comonomer resulted in a loss of conductivity at low hydration levels. All co-grafted membranes demonstrated a substantially lower conductivity than the Nafion and SSA-g-ETFE membranes at the same hydration levels.^{152,154}

It was suggested that this behavior is due to the inhomogeneous distribution of the SSA-pendant segments, thereby impairing proton conductivity at low hydration levels. A more uniform distribution may result in better connectivity between the hydrophilic clusters and thus in better conductivity at low hydration.¹⁵⁴ To date, DMFCs with PSSA membranes have maintained performance levels that are inferior to the performance of Nafion MEA-based FCs (18 versus 31 mW/

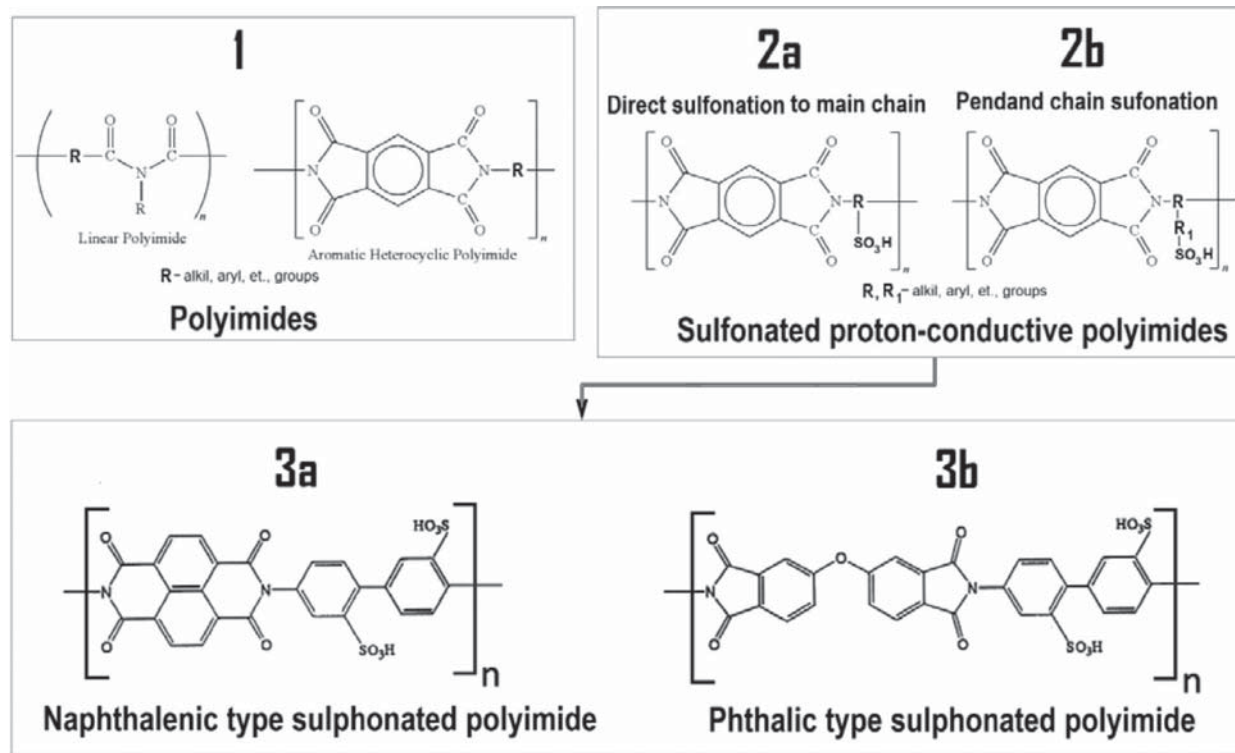


Figure 13. (1) Polyimides, sulfonated polyimides with (2a) sulfonated main chain and (2b) sulfonated pendant chain, (3a) phthalic type (with a five-membered heterocycle ring) sulfonated polyimide, and (3b) naphthalenic (with a six-membered heterocyclic ring) sulfonated polyimide (3a and 3b acquired and modified with permission from ref 159).

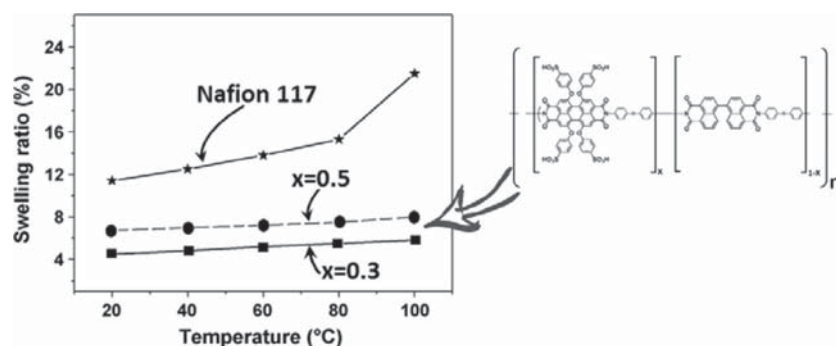


Figure 14. Temperature dependence of the swelling ratio of aromatic SPI membranes and Nafion 117 membrane (acquired and modified with permission from ref 161).

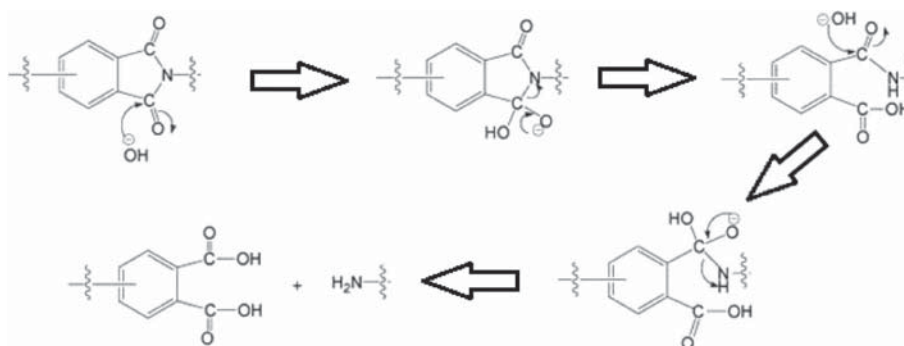


Figure 15. Mechanism of hydrolytic degradation in polyimides (acquired and modified with permission from ref 169).

cm²), despite the lower methanol permeability of PSSA membranes.¹⁵⁵

3.2. Sulfonated Polyimide (SPI)-Based Membranes.

Polyimides are a family of thermostable polymers, featuring a combination of high mechanical and thermal properties and a durability against aggressive chemicals and heat.^{22,23,156–158} These polymers are typically good insulators and may be modified with sulfonic groups. This modification imparts hydrophilicity and proton conductivity. The two routes for the sulfonation of polyimides are illustrated in Figure 13: sulfonation of the main polymer chain and sulfonation of the pendant polymer chains.¹⁵⁸

The use of SPI in FC membrane applications was first demonstrated by Zhang et al.¹⁶⁰ The major driving force of polyimide-based membrane development was the expectation that polyimide-based materials would be substantially less expensive than Nafion. It was soon discovered that, although SPI swelled in humid environments and required hydration to enable proton conductivity (which is similar to Nafion features), the water uptake, swelling ratio, and water osmotic drag coefficient did not substantially vary over a broad temperature range, in contrast to Nafion (see Figure 14). These features are favorable for medium-temperature FC operations (these features diminish as membrane degradation occurs during the on/off cycling and also reduce the dehydration of the anode side of the MEA).

Whereas the first generation of SPI materials demonstrated conductivities from 2×10^{-3} to 4×10^{-2} S/cm,^{162,163} which were substantially lower than the conductivity of Nafion, the next generation of SPI electrolytes exhibited adequate conductivities of up to 1.67 S/cm at 120 °C¹⁶⁴ and 1.201 S/cm at 80 °C for a SPI–graphene composite.¹⁶⁵ These materials

are currently believed to be promising candidates for PEM applications for temperatures between 40 and 100 °C; in addition, SPI membranes demonstrate methanol permeabilities several times lower than the methanol permeability of Nafion, particularly at elevated temperatures.^{166,167}

The major obstacle to the commercialization of SPI-based membranes is their instability in hydrated states. There are several facets to this problem: hydrolytic stability, oxidative stability, and swelling-stress stability. The overall stability of any PEM FC membrane is a combination of these membrane material parameters.

With regard to the hydrolytic stability of the material, imide-type links are highly susceptible to hydrolysis. This feature results in main polyimide chain scissions (see Figure 15),^{165–170} e.g., a substantial decrease in the average length of the SPI molecules (approximately 4-fold after nearly 200 h at 130 °C) was reported.¹⁷¹ This decreased length, in turn, resulted in the degradation of the mechanical properties of the SPI membrane, as evidenced by cracking and increased gas permeability, which ultimately led to the low FC operational lifetime.

The hydrolysis of imide is the result of the nucleophilic interaction of water with the carbon atom of the neighboring carbonyl group. Thus, molecules with higher electron densities at the carbonyl carbon are more stable against hydrolysis.^{172,173} These considerations serve as the theoretical basis for numerous works focused on improving the hydrolytic stability of SPI membranes. In course of these studies changed the formulation of the polyimide repeating unit was changed and the electron density at the carbonyl carbon was increased. (a) The electron density at the carbonyl carbon increased when switching from five-membered heterocycles (i.e., phthalic

polyimides) to six-membered heterocycles (i.e., naphthalenic polyimides). This results in naphthalenic polyimides with higher hydrolytic stability.^{159,167,174,175} (b) The electron density distribution may be changed by the introduction of bulky aliphatic fragments in both the main chain and pendant fragments.^{176,177} (c) The electron density on carbonyl may also be increased by introducing “bridging” electron-donating sulfur in the main polyimide chain. This sulfur substantially decreases the electrophilicity of the carbonyl carbon, and such modified polyimides demonstrate a higher resistance to hydrolysis.^{178–180} (d) Electron-donating phenoxy groups can also be introduced into the imide rings. These groups decrease the electrophilicity of the imide rings, thus enhancing their susceptibility to hydrolysis.¹⁸¹ Additionally, the benzophenone group at the meta position of the imide group positively influences on the hydrolytic stability of the SPI materials.¹⁸² (e) The electron density on the carbonyl carbons of the naphthalimide ring strongly depends upon the monomer structure. If the main chain of the polyimide comprises monomer units with a common aromatic moiety (type A in Figure 14), it actually contains four carbonyl groups in the same aromatic system. This structure offers a lower electron density for each amide group than in the case of the monomer units composed of two naphthyl rings separated by an aliphatic-type link (type B in Figure 16). As a result, the binaphthylimide

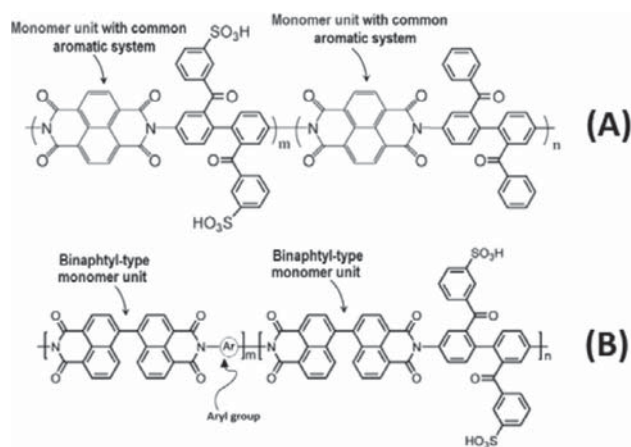


Figure 16. SPIs with (A) monomer unit with common aromatic (naphthyl) system and (B) binaphthyl-type monomer unit, i.e., two naphthyl rings separated with aliphatic-type link (acquired and modified with permission from refs 183 and 185).

configuration decreases the possibility of a nucleophilic attack at this position. This enhances the material hydrolytic stability, and SPIs of type B have an improved hydrolytic stability compared to SPIs of type A.^{183,184} (f) Because the sulfonic acid group is a strong electron-withdrawing group, the distancing from the imide is also expected to result in an increase in the hydrolytic stability of the polyimide main chain. Indeed, the membranes, which are made of SPIs with sulfonated pendant chains, were found to be more stable when compared to a similar main chain of sulfonated polyimides.^{177,186} (g) In contrast, the introduction of trifluoromethyl groups, which have a strong electron-withdrawing ability, compromised the stability of the imide group.¹⁸⁷ (h) The hydrolysis reaction of the imide rings was found to be equilibrated by a reverse condensation reaction.¹⁸⁸ This is the basis of the assumption that the main polyamide chain may be regenerated. The rigidity of the main

polymer chain helped the two ends of the scissored chain remain to be close to one another and, thus, assist in chain repolymerization.¹⁸⁹ This assumption was supported by the observations that, in the case of the cross-linked SPIs with different cross-linker alkyl chain lengths, the hydrolytic resistance of the membrane decreased with an increased alkyl chain length (i.e., with an increased polymer net flexibility).¹⁹⁰

With regard to swelling-stress stability, it is commonly accepted that water absorption causes polymer chain tension, which results in SPE degradation. The conductivity of a proton-conductive SPE was found to increase with an increasing material water content.¹⁹¹ The latter is particularly true with respect to the SPIs, which have a substantially lower conductivity than Nafion at low water contents. Nafion contains a substantial amount of small water clusters, even at an overall low water content. These clusters form channels for proton transport;³⁴ this is not the case for the SPIs.¹⁸⁶ Proton conductivity also increased with increasing IEC (i.e., the density of the sulfonic acid groups).¹⁹ The water absorption of SPE materials also increased with increasing IEC because the SO_3 groups are strongly hydrophilic.¹⁹² This general provision is also true for SPIs (e.g., the absorption of up to 12 water molecules per acid group has been reported).¹⁹³

Branched and/or cross-linked polymers counteract the hydration-related stresses better than their linear-chain counterparts; such types of SPIs have been reported.^{190,194–197} Branched and/or cross-linked polymers have typically demonstrated higher degradation stability than their linear equivalents. Another way to reduce the polymer chain tension upon hydration is the use of flexible polyimide chains.^{198–202} However, although the polymer chain flexibility accommodates the mechanical stresses of water absorption, the flexibility also interferes with the repolymerization of the polyimide backbone (see point h). No solution to this issue has been found to date.

Interestingly, it was recently found that compound membranes comprising a porous spongy-like polyimide film with pores filled with a series of SPIs demonstrated higher hydrolytic stability than membranes prepared from these SPIs without matrices.²⁰³

FCs (H_2/O_2 FC at 0.2 A/cm²) with various main-chain sulfonated polyimide membranes were tested between 60 and 90 °C.²⁰⁴ The MEA lifetime strongly depended upon the temperature and sulfonation. The MEA operational time was small at 90 °C. FCs (H_2/O_2 FC at 0.2 A/cm² and 80 °C) with SPI with sulfonated pendant segments demonstrated substantially higher stability over 5000 h of operation.^{205,206} These MEAs demonstrated a fair performance; however, they were outperformed by a Nafion-based MEA (see Figure 17).

FC testing (H_2/O_2 FC at 0.2 A/cm² and 70 °C) revealed that cross-linked sulfonated poly(imide-siloxane) MEAs perform substantially better than Nafion 212 MEAs at lower humidification levels¹⁹⁶ but have similar performance levels at higher humidification. Unfortunately, the authors did not report data on the operational lifetime of their MEAs. The SPI MEA performance and conductivity also strongly depended upon the FC operational mode such that the membrane conductivity and FC performance degraded rapidly for a higher testing current density.²⁰⁷

Although testing SPI MEA membranes using practical FC operation conditions is an appropriate approach, the results of this testing are influenced by the stability of the membrane and the stability of the membrane/catalyst interface.

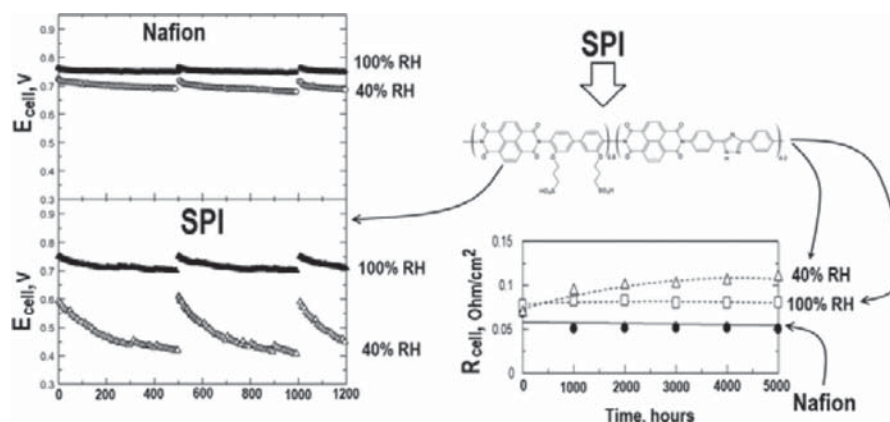


Figure 17. FC performance and membrane conductivity decay for MEA with an SPI membrane and MEA with a Nafion membrane: H_2/O_2 FC at 0.2 A/cm^2 , constant current mode, and 80°C (acquired and modified with permission from refs 205 and 206).

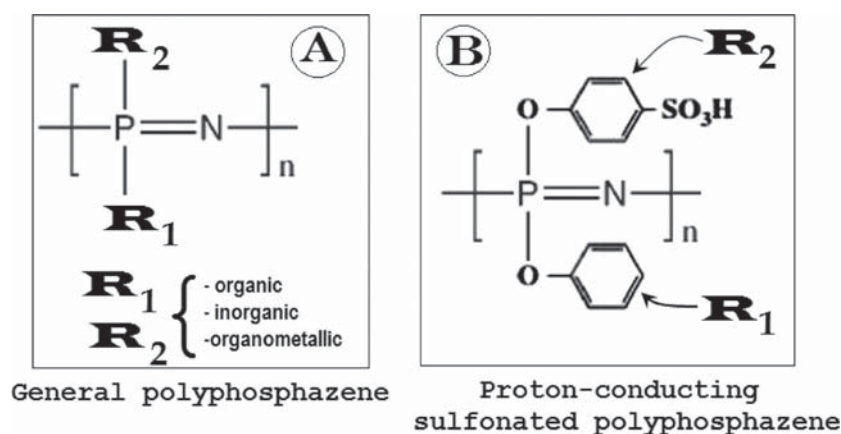


Figure 18. General formulas of polyphosphazenes.²⁰⁹

3.3. Polyphosphazene-Based Membranes. Polyphosphazenes have backbones composed of alternating phosphorus and nitrogen atoms and organic, inorganic, or organometallic side groups attached to the phosphorus atoms (Figure 18). A thorough review of polyphosphazene synthesis methods and properties may be found in refs 208–210.

Phosphazenes [PPZs, polymers with repeating subunits of $(-\text{N}=\text{P}-)$] offer many advantageous properties because of their modifications through diverse pending groups. The phosphorus–nitrogen bonds have a high torsional mobility (the polymers have a low glass-transition temperature).²¹¹ Most phosphazenes are non-flammable and resistant to aggressive conditions²¹² because the phosphorus and nitrogen atoms of each subunit are in their highest oxidation states. The most valuable feature is that the $(-\text{N}=\text{P}-)$ backbone is particularly stable against free-radical cleavage reactions, which renders phosphazenes advantageous for PEM FCs. These features, along with their relatively low cost, make phosphazenes an attractive platform for PEM FCs. The first attempt to synthesize a phosphazene-based ion-conducting material was made by Blonsky and Shriver.²¹³ The first preparations of sulfonated phosphazenes (S-PPZs), which would be capable of being used as a material for a proton-conducting FC membrane, were reported by Wysys et al. and Allcock et al.^{214,215}

The considerable hydrophilicity of the $(-\text{N}=\text{P}-)$ backbone suggests that conductivity takes place via a Grotthuss

mechanism.²¹⁶ This also indicates the possibility of using phosphazene in osmotic drug carriers with a low water content and a low methanol permeability. These features, along with the high-temperature backbone stability, make S-PPZ attractive for high-temperature FC and DMFC applications. S-PPZ-made FC membranes were first demonstrated in refs 217 and 218.

Linear and cross-linked S-PPZs {sulfonated [bis(3-methylphenoxy)]phosphazene; compound B in Figure 18} were employed. The materials exhibited a substantially low water (and methanol) diffusivity; i.e., the corresponding diffusion coefficients D_{aq} were nearly 2 orders of magnitude lower for the S-PPZ membrane than for the Nafion 117 membrane. Furthermore, the D_{aq} for linear S-PPZ was higher than the D_{aq} for cross-linked S-PPZ. Many water molecules are bonded to the polymer backbone of S-PPZ polymers (because of the lone electron pair on the nitrogen atom) and are relatively immobile. Proton conductivity is maintained through Grotthuss chains without requiring the displacement of water molecules. The only available water for diffusion is the small amount bound to the SO_3 groups in cross-linked S-PPZ membranes (even at high water activity). Additionally, cross-linked S-PPZs have lower swelling compared to linear S-PPZs, which results in increased pathway tortuosity.

The conductivities of S-PPZ materials are in the range from approximately 1×10^{-2} to $12 \times 10^{-2} \text{ S/cm}$ and increase with increasing IEC (i.e., the degree of sulfonation).^{208,214–217,219} The typical conductivity of Nafion is approximately 0.1 S/cm at

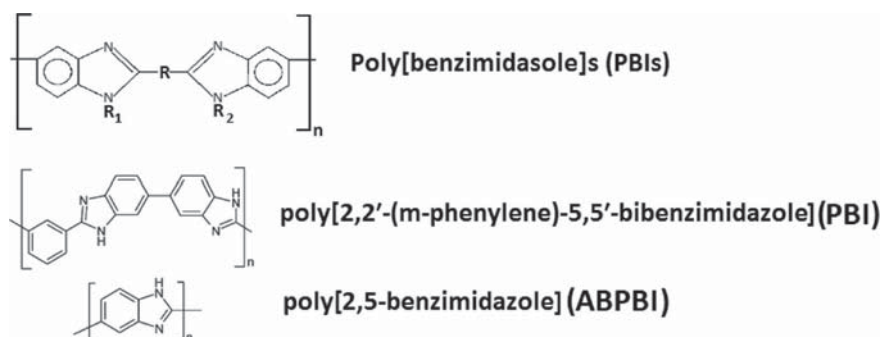


Figure 19. General structures of poly(benzimidazole) compounds, PBI compounds, and ABPBI compounds (acquired and modified with permission from ref 241).

room temperature.²²⁰ Low methanol permeability is the most distinguishable (and practically appreciated) PPZ membrane feature.²²¹ There was some variance in the reported data on methanol crossover through PPZ-based membranes, which might be due to the differences in experimental conditions and PEM preparation techniques (i.e., different membrane morphologies). The following are well-established facts on the methanol/(PPZ-based membrane) permeability: (a) The methanol permeability of S-PPZ membranes is substantially lower than methanol permeability of Nafion.^{208,219,222–224} For example, the reported permeability value of cross-linked sulfonated poly[bis(3-methylphenoxy)]phosphazene is 75 times lower than the permeability of the Nafion membrane.²²⁵ (b) The permeability of cross-linked S-PPZ is lower than the permeability of non-cross-linked S-PPZ;^{208,225} its conductivity may also be lower.²²⁶ (c) Phosphonic-group-functionalized PPZ (P-PPZ) has a lower methanol permeability than S-PPZ.^{208,222,223}

P-PPZ membranes have lower conductivity than S-PPZ.^{208,219,227} Sulfonic-group-functionalized materials typically require some hydration to demonstrate superior conductivity over phosphonic-functionalized materials.^{228,229} However, water is always available in practical FC operations because it is a reaction product. The reported selectivity, β ,¹⁰⁶ is often higher for P-PPZ. For example, the reported β for a S-PPZ membrane is greater than that of Nafion 117 only at temperatures below 85 °C, whereas the selectivity of a P-PPZ membrane is greater than that of Nafion 117 up to 125 °C.²²⁴

Adequate mechanical properties are also important for the implementation of ion-functionalized PPZ membranes for FC. It was found that a high IEC compromises the mechanical stability of the material but is necessary for good proton conductivity.²¹⁴ To maintain conductivity and address the mechanical stability, functionalized PPZ were cross-linked and blended with other polymers.^{208,230–232}

Blending may occur on the chemical level, and such mixing was demonstrated.^{232,233} The membranes were prepared by cross-linking S-PPZ with segments of polybenzimidazole. It was reported that a DMFC with such a membrane demonstrated maximum power close to that of a DMFC with a Nafion membrane at 60 °C. The MEA degradation test (100 h, DMFC at 0.10 A/cm, and 60 °C) revealed a cell voltage degradation of approximately 0.8 mV/h. Additionally, S-PPZ membranes prepared by the cross-linking of S-PPZ with polyacrylonitrile were reported.²³¹ The membrane, which was prepared via a physical mixture of S-PPZ and PVDF, was reported.²²⁶

Unfortunately, in all cases, detailed data on the improvements to the mechanical stability were not presented. Data on PPZ-based membranes testing under real FC operation conditions are scarce. H₂/O₂ FC with S-PPZ MEA exhibited a power density of 0.47 W cm⁻² at 80 °C and 0.36 W cm⁻² at room temperature (maximum power).²¹⁹ We are not aware of any reported data on the operational life of PPZ-based MEAs.

3.4. Polybenzimidazole (PBI)-Based Membranes. The concept of a PBI-based FC membrane originates from the design of a phosphoric acid FC (PAFC). PAFCs operate between 160 and 220 °C, and thus, they demonstrate high-temperature operation advantages. PAFCs contain a “liquid-in-sponge” proton-conducting membrane: a thin silicon carbide ceramic-type matrix impregnated with H₃PO₄.^{234,235}

Although PAFC is well on its way toward commercialization, there are still problems that stem from employing a liquid electrolyte: (a) electrolyte leakage and its loss via evaporation, which necessitate refills during operation, or providing an acid reservoir (acid reservoir plates with an acid recovery system are commonly employed),²³⁶ (b) the presence of a liquid electrolyte, suggesting the possibility of gas diffusion layer flooding, and (c) conventional PAFCs having low thermal cyclability and, thus, not being suitable for portable and transport applications.²³⁷

The above matter implied the development of an improved matrix for H₃PO₄; the natural choice is “molecular-scale” matrices to impregnate a polymer with H₃PO₄. Although the common macroporous matrices maintain the acid by capillary forces, the molecular-scale polymer matrix fixes the acid by chemical-type interactions. Such matrices may be formed by polymers with chains containing basic sites, such as ethers, alcohols, imines, amides, and imides. These groups react with acids, acting as proton acceptors and forming ion pairs.²³⁸ Such acid–base poly salt systems are a new class of proton-conducting PEMs.

Many polymers and acids have been tested [e.g., poly(vinylpyrrolidone), poly(4-vinylpyridine), poly(ethylene oxide), polyacrylamide, poly(2-vinylpyridine), linear/branched poly(ethylenimine), poly(aminosilicate) aminosils] and combined with phosphoric, sulfuric, and perchloric acids.^{239–244} Many low-acid-content poly salts demonstrated reduced (<10⁻³ S) conductivity. Membranes with a high acid content possessed poor mechanical properties, particularly at temperatures over 100 °C.²⁴⁵ The highest conductivity of acid–polymer combinations can be secured by the employment of amphoteric acids, e.g., phosphoric or phosphonic acids. The mechanically and thermally stable poly(benzimidazole)-based polymers²⁴⁶

are the most appropriate materials for high-temperature FC membranes.^{243,247}

FC-related application of (PBI/ H_3PO_4) poly salts was first demonstrated in ref 248. A detailed explanation of such a FC was first reported in ref 249. The development of PBI/(phosphoric acid) membranes has progressed to the stage at which such membranes are commercially available (e.g., CeltecL, CeltecP1000, and CeltecV from BASF).^{250,251} Poly-[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) and poly(2,5-benzimidazole) (ABPBI) are the most frequently employed membranes for FCs. Their structures are presented in Figure 19.²⁴¹ The mechanism of proton conductivity of the (PBI/ H_3PO_4) poly salt is illustrated in Figure 20.

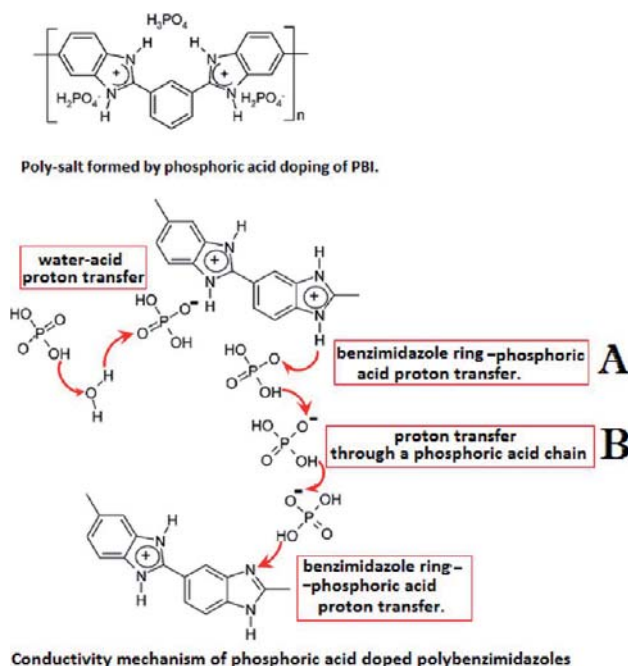


Figure 20. (PBI/ H_3PO_4) poly salt and its proton conductivity (acquired and modified with permission from ref 241).

There are two possibilities for proton transfer: the [(benzimidazol ring) \Rightarrow (phosphoric acid)] path (path A) and proton transfer through a chain of phosphoric acid molecules (path B). Nearly all acid molecules donate protons to unprotonated imino groups at all acid-doping levels with less than two acid molecules per repeating polymer unit (as observed for other acids).²⁴³ Thus, all acid molecules are strongly bound to the polymer.^{255,256} As this process takes place, proton exchange occurs via path A. However, this type of proton exchange suggests a considerably low conductivity (less than 10^{-5} S for two acid molecules per PBI unit at 160 °C).²⁴³

Proton transfer by path B is possible if the acid content is over two acid molecules per repeating polymer unit. Path B provides substantially higher membrane conductivities.^{252–254} This Grotthuss-type mechanism^{255,256} suggests that the membranes have proton transference numbers close to 1²³⁸ and a nearly 0 water drag coefficient.²⁵⁷

The conductivity of (PBI/ H_3PO_4) poly salts is typically lower than the conductivity of the corresponding pure acids or macroporous material impregnated with the acid (see Figure 21).²⁵⁸

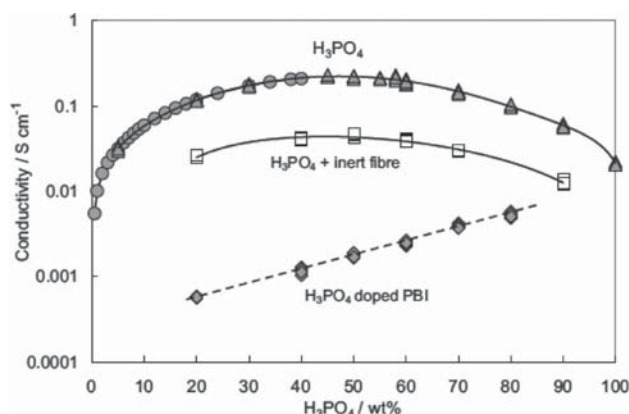


Figure 21. Conductivities of liquid H_3PO_4 , a glass fiber film impregnated with H_3PO_4 , and PBI/ H_3PO_4 membrane at different acid contents at room temperature (acquired with permission from ref 258).

A greater acid content results in a higher membrane conductivity. Indeed, a low acid content (up to 2.4 H_3PO_4 per PBI monomer unit) provides conductivities of less than approximately 10^{-4} S/cm at 160 °C, whereas a high acid content (11 acid molecules per repeating polymer unit) provides high conductivity values of up to 0.15 S at 160–180 °C.^{243,259,260} Overall, the conductivity of PBI exceed the conductivity target value of 0.1 S cm^{-1} for high-temperature membranes.²⁶¹

An increase in the H_3PO_4 content results in the mechanical deterioration of the membrane: tensile strength decreases, the membrane becomes inhomogeneous (i.e., the acid phase separates from the polymer matrix),²⁶² and the membrane gas permeability increases.^{263–265} An example of these related properties is presented in Figure 22. Phosphoric acid also tends to be easily detached and may corrode the electrodes and bipolar plates of the FC.²⁶⁶

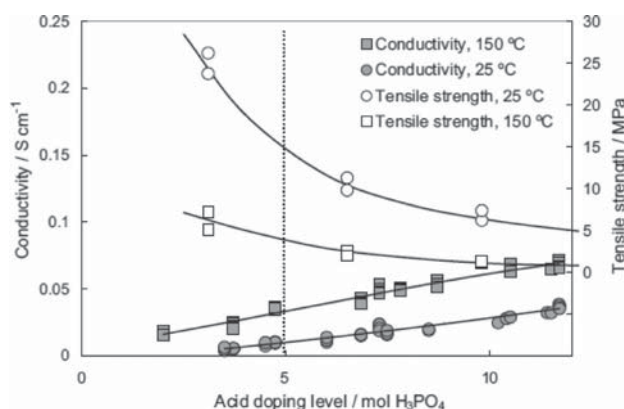


Figure 22. Tensile strength and conductivity of a H_2PO_4 /PBI membrane at different acid loadings (acquired with permission from ref 258).

Additionally, phosphate ions, which adsorb onto electrodes at high acid concentrations, inhibit catalyst activity.²⁶⁷

An optimal H_3PO_4 content must be maintained²⁶⁸ to achieve membrane strength and conductivity. This optimal acid content depends upon the particularities of the polymer matrix and membrane structure. The cross-linking of the linear PBI

polymer is a robust technique to enhance both mechanical and conductive properties.^{269–273} The modification of the main PBI chain [using poly(imide benzimidazole) random copolymers²⁷⁴ and partially fluorinated PBI membranes]²⁷⁵ offers an enhanced mechanical strength at high acid-doping levels. Additionally, attempts were made to introduce sulfonic groups into the main chains of PBI-based material to enhance the conductivity for low H_3PO_4 content. This would increase the mechanical properties of the membrane without compromising its conductivity. However, a substantial increase in the membrane mechanical properties was not observed.²⁷⁶ Another approach uses reinforced membranes. Reinforced PBI/ H_3PO_4 membranes demonstrated good conductivity (up to 0.14 S/cm at 160 °C) and improved mechanical properties.²⁷⁷ Nevertheless, the development of PBI membranes with high strength (and high conductivity) at high acid contents remains a challenge.

Another aspect of FC membrane stability is chemical stability. The membrane material is under OH^\bullet and OOH^\bullet radical attack during FC operation.⁴⁴ The PBI in H_3PO_4 -impregnated poly(benzimidazole) membranes is a peroxide-radical-vulnerable component. The Fenton reactive tests²⁷⁸ revealed that the chemical degradation of PBI generally occurs at higher rates than that of Nafion.^{270,279} PBI undergoes weight loss and depolymerization.²⁸⁰ The degradation of higher molecular weight and cross-linked PBI proceeds at a slower pace than that of the linear and lower molecular weight polymers.^{270–272,281,282} The presence of phosphoric acid significantly moderated the degradation of PBI polymers and increased membrane stability.²⁸¹

H_3PO_4 evaporates and slowly leaches out of PBI-type molecular matrices (see Figure 23).^{282–285} After an initial

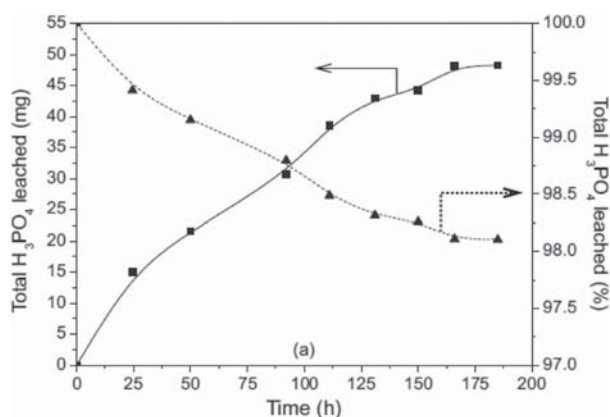


Figure 23. H_3PO_4 leached/evaporated from a FC stack during a durability test: PBI/ H_3PO_4 membrane, total membrane area of 150 cm^2 , 0.2 A/ cm^2 , and initial membrane doping level of 6.6 acid molecules per polymer repeating unit (acquired with permission from ref 285).

period, acid leaching stops and the membrane acid content stabilizes.²⁸⁵ The employment of grafted phosphoric groups is a promising approach to increasing acid retention.²⁸⁶

3.4.1. MEAs with PBI/ H_3PO_4 Membranes under FC Operational Conditions. Most results on the overall PBI membrane durability are reported on the basis of MEA testing under practical FC operations. Such tests are practical and reveal the stability of the entire MEA complex but are not scientifically informative. MEAs with PBI-based membranes demonstrate diverse stability depending upon the test mode.

Membrane degradation mainly involves H_3PO_4 leaching and chemical polymer degradation, which result in conductivity decay. The degradation of membrane mechanical properties is important for variable loads. For example, FCs with poly(2,5-benzimidazole)/ H_3PO_4 membranes (160 °C and H_2 /air operation) were tested in ref 284; the voltage loss amounted to $-20 \mu\text{V/h}$ for constant-current tests (an approximately 3% decrease in cell voltage during 1000 h of operation). The degradation rates for dynamic and start/stop tests were reported to be substantially larger (-180 and $-120 \mu\text{V/h}$, respectively).

BASF reported on the long-term stability of its Celtec-P1100W membranes of more than 20 000 h with a 6 $\mu\text{V/h}$ voltage drop (160 °C and H_2 /air operation) “at optimized conditions”.²⁸⁷ Similar stability data were reported for the BASF Celtec-P2100 membrane,²⁸⁸ with a voltage drop in the range of 6–9 $\mu\text{V/h}$ (6000 h test, 160 °C, H_2 /air, and 0.2 A/ cm^2). Operation at high temperatures resulted in a more rapid voltage drop (19 $\mu\text{V/h}$ at 180 °C). Other reported voltage drop data range between 6 and 45 $\mu\text{V/h}$ (from MEA tests conducted in the range of 80–180 °C and H_2/O_2 and H_2 /air operations).²⁸⁹ The lifetime requirements for commercially viable stationary FC are greater than approximately 40 000 h.⁹³

It is widely believed that PBI/ H_3PO_4 MEA may be used in DMFCs. This belief is based on the low methanol permeability of acid-free PBI films.²⁹⁰ The apparent phosphoric acid leaching in hot methanol solution from the membrane may be addressed by the addition of high-molecular-weight inorganic acids (e.g., phosphotungstic and silicotungstic acids).^{291–293}

There are still challenges to be met in employing PBI/ H_3PO_4 MEAs for DMFCs.

First, poor methanol oxidation kinetics on common catalysts in a phosphoric acid environment were reported.²⁹⁴

Second, the methanol permeability of PBI/ H_3PO_4 is substantially higher than the permeability of films without phosphoric acid (i.e., plain PBI) and increases with the acid content. Unfortunately, crossover values were reported for different λ values (i.e., the number of H_3PO_4 molecules per monomer unit). Specifically, λ was 5.6,²⁹⁴ 6.7,²⁹⁵ and 1.5–3.²⁹⁶ Methanol crossover strongly increases for high methanol concentrations.²⁹⁴

The performance of a methanol FC using a PBI/ H_3PO_4 acid membrane-based MEA is still low because of catalyst inhibition and methanol vapor crossover.^{294–296}

3.5. Sulfonated Aromatic Main-Chain Polymers I: Poly(arylene ether)-Based SPEs. Sulfonated aromatic main-chain polymers have attracted considerable interest because of their low cost, high mechanical strength, and excellent chemical and thermal stability (even considering that sulfonation compromises thermal stability to some extent).^{297,298} Among these compounds, sulfonated poly(arylene ether ketone)s (SPAEEKs) and sulfonated poly(ether ether ketone)s (SPEEKs), in particular, are the most studied.^{22,299–301} SPEEK-type membranes are the most thoroughly investigated membranes among other SPAEK membranes because their progenitor polymers (PEEK) are commercially available and feature important properties of many other aromatic polymers.²³ The exemplified formulas of such membranes are presented in Figure 24.

Although operational times of over 3000 h have been reported for SPAEK-based MEA,³⁰² the material durability of SPAEK is inferior to that of Nafion under practical FC operating conditions. Material degradation begins with the

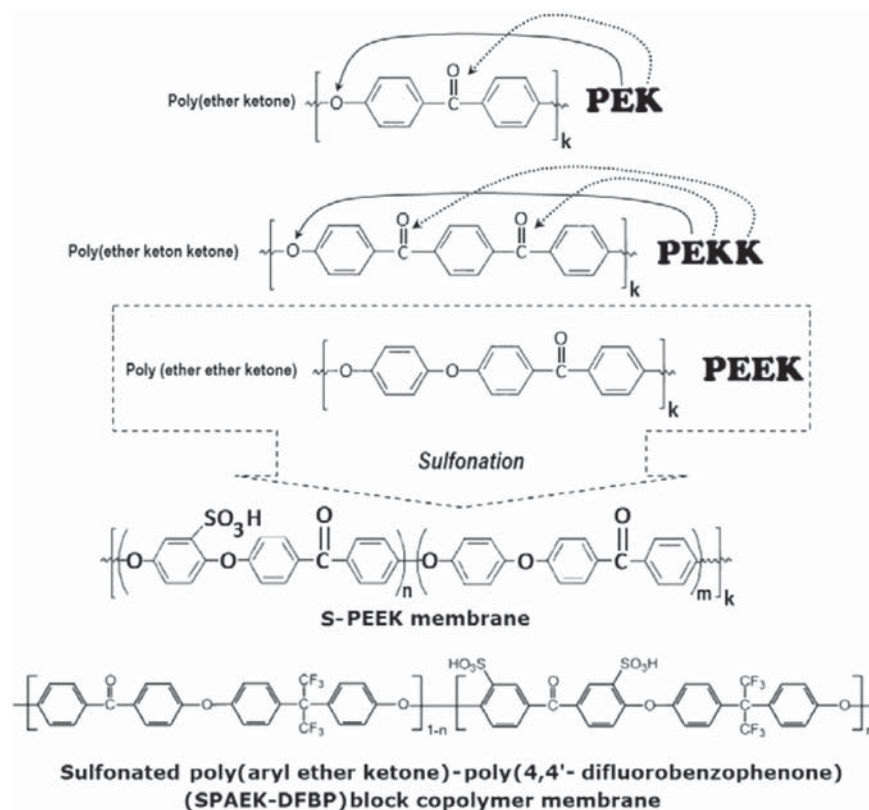


Figure 24. Exemplified formulas of sulfonated poly(ether ketone) and its copolymer membranes.

addition of hydroxyl radicals on the non-sulfonated phenyl ether aromatic rings. The resulting phenolic groups are prone to oxidation, which results in scissions in the main SPAEK chain.³⁰³ The vulnerable points of SPAEK materials are indicated by arrows in Figure 25.

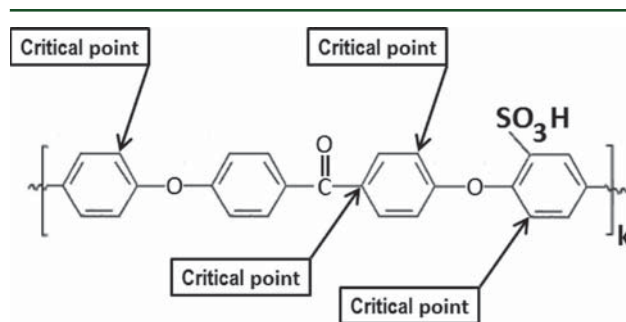


Figure 25. Possible sites for HO[•] radical attacks on SPAEK (acquired and modified with permission from ref 304).

Attempts to improve the stability of SPAEK have included optimization of the sulfonic group position (SPAEEK is more stable if SO₃ groups are attached to the pendant chain than to the main chain) and fluorination of the main-chain phenyl groups.³⁰⁴ The proton conductivity of SPAEK reached the FC range at high sulfonation levels. The hydrophilic channels are substantially narrower in SPAEEKs compared to Nafion channels because of the rigid aromatic backbone. Being strongly restricted to these narrow channels water has a rather low dielectric constant, which results in a reduced dissociation level of sulfonic groups. However, these narrow hydrophilic channels

are also branched and have numerous cul-de-sacs. This results in a larger average partition between sulfonic acid functional groups, which impedes proton transport. These percolation and proton localization issues cause a steep decline in proton conductivity, in addition to the decreased conductivity with reduced hydration in SPAEEK membranes.¹²⁶ For example, SPEEK membranes with sulfonation levels of over 74% exhibit conductivities of over 10⁻² S/cm at 60 °C.³⁰⁵ A high sulfonation degree compromises the chemical stability of SPEEK membranes as hydroxyl radicals initiate material deterioration and induce high swelling.^{302,306} For example, a SPEEK membrane with an IEC of 2.2 mmol/g is extensively deformed after prolonged immersion in hot water³⁰⁷ and may even turn into a gel-like material.³⁰⁸ High water absorption, in turn, results in degraded mechanical properties (the hydrophobic domains of the polymer backbone provide the hydrated membrane with mechanical strength; the sulfonic-acid-group-containing hydrophilic domains provide proton conductivity and also determine the water absorption)¹²⁶ and leads to elevated hydrogen and methanol crossover during FC operation. The increased fuel crossover counterbalances the gain in conductivity, and SPEAK membrane-based FCs exhibit optimum performance at a certain threshold sulfonation level, which depends upon the specific polymer backbone structure and membrane morphology; optimal DMFC performance was reported for a SPEEK membrane with 43% sulfonation²⁹⁹ and a SPEEK membrane with 71% sulfonation.³⁰⁹

Two characteristics of SPAEK are responsible for such behaviors. First, the sulfonic acid functional groups of SPAEEKs have relatively low pK_a values (Nafion has a substantially higher acidity than SPAEEKs). Second, there are fewer hydrophobic/hydrophilic areas in SPAEEKs compared to Nafion membranes,

which results in a slimmer and poorly connected water-filled network; the latter suggests larger separations between the sulfonic groups (i.e., less acidic than in Nafion case).^{126,310–313} Currently, SPAEK membranes with fair conductivity (up to 0.048 S/cm at room temperature) are being developed.^{299,306,314} SPEEK membranes with conductivities over 0.1 S/cm were also reported.³¹¹

Differently modified SPAEK membranes have been developed to improve their properties.²³ Cross-linking SPEEK improves the thermal stability, mechanical strength, and hydrolytic and oxidative stabilities of the membranes. The cross-linked membranes also demonstrate lower water uptake and methanol diffusion compared to their non-cross-linked counterparts. However, cross-linking compromises the elongation-at-break and proton conductivities of the membranes.^{315–321} Naturally, the degree of changes in the aforementioned properties, particularly the transport properties and water absorption, depends greatly upon the cross-linking density (see Figure 26).³²²

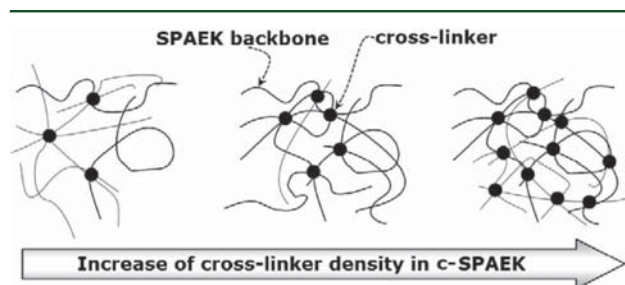


Figure 26. Effect of the cross-linking density on the structure of cross-linked SPAEK (c-SPAEC) (acquired and modified with permission from ref 322).

Recent advancements in the development of new cross-linkers and cross-linking techniques has resulted in the improvement of properties of cross-linked SPEEKs.³¹⁹ The results suggest that cross-linked SPAEK membranes may be

adequate for use in medium- and high-temperature FCs.^{323–325}

Figure 27 illustrates that it is possible to prepare a material that combines high conductivity with moderate water absorption.³²⁴ SO₂-cross-linked SPEEK has a high proton conductivity of approximately 0.1 S/cm and moderate water absorption.³¹⁷

A new SPEEK cross-linker was used.³²⁶ It provided membranes with a proton conductivity of 0.122 S cm⁻¹ (at 60 °C), low methanol permeability (equal to just 1/12 of that of Nafion membranes), exceptional stability, and low swelling. Branched SPAEKs have also been reported.³²⁷ Such materials may be classified as intermediates between the linear and cross-linked materials.

The hydrophilic backbone domains of the polymer control conductivity and water absorption, whereas the hydrophobic domains control the mechanical strength. SPAEK copolymers have a backbone composed of hydrophilic (sulfonated) and hydrophobic segments. This multi-block copolymer structure presents an advantageous structure having interconnected hydrophilic domains and hydrophobic moieties. The hydrophilic net supports proton conductivity even under low hydration, and the hydrophobic moiety maintains the mechanical properties. Furthermore, the ordered hydrophilic–hydrophobic block sequence provides higher proton conductivity than random copolymers.^{328–331} In this manner, membranes with excellent mechanical properties, fair proton conductivity, and good chemical stability at relatively lower IEC were prepared. The membranes demonstrated conductivities of 0.92×10^{-2} and 2.09×10^{-2} S/cm at IEC = 1.13 mequiv/g and temperatures of 30 and 80 °C, respectively.³³² Employed copolymers may also be SPAEKs but with various pendant chains.³³³

The hydrophilic sulfonic groups may also be located in the pendant groups of PAEK³³⁴ and PAEK copolymers.^{23,335–339} Such materials may present low swelling with fair FC-range conductivity (see Figure 28). PAEKs with pendant chains may also be cross-linked.³⁴⁰ Cross-linking and main-chain copolymerization may be combined. Such materials may provide a membrane with an exceptional water uptake of 37.5%, a good

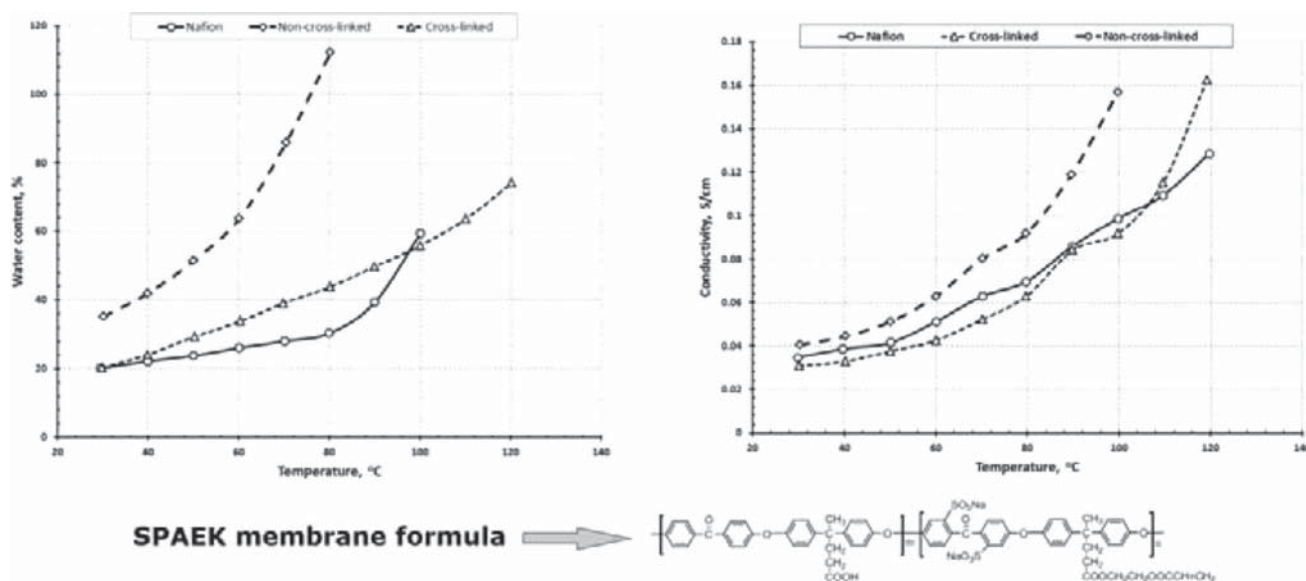


Figure 27. Water uptake and conductivity of Nafion, SPAEK, and c-SPAEC (80% sulfonation) membranes at different temperatures (data acquired with permission from ref 324).

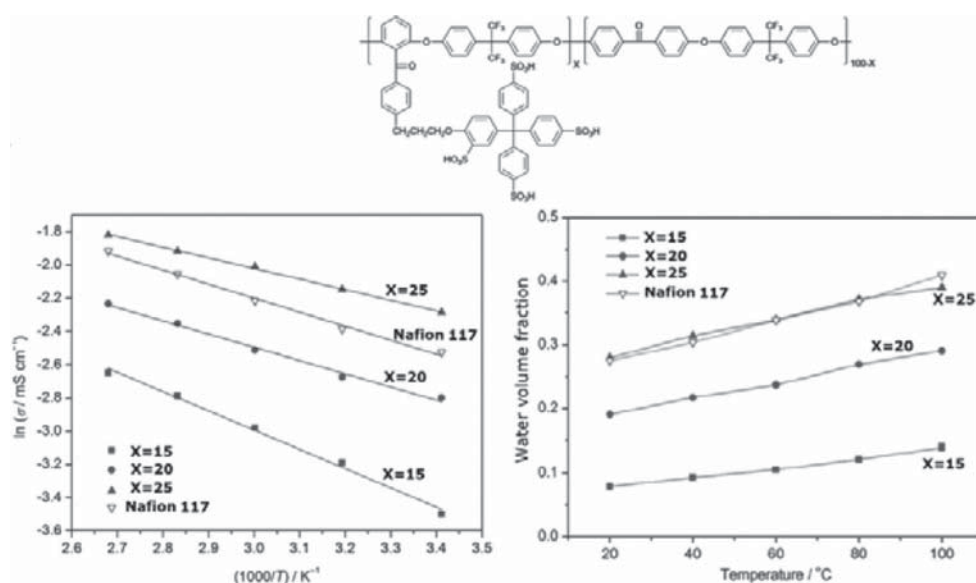


Figure 28. Arrhenius plot of proton conductivity (the membranes are immersed in water) and water volume fraction versus temperature for PAEK with flexible tetrasulfonated pendant chains.³³⁸

proton conductivity of 0.091 S/cm, and a methanol selectivity β , which is approximately 30 times larger than the β of Nafion.³²²

Other common ways to improve the properties of SPAEK membranes is to mix SPAEK material with other polymers or to incorporate inorganic fillers into the membrane. Recently, several good reviews on such composite SPAEK membranes were published.^{38,82,126,315} SPAEK has been combined with polybenzimidazole,^{341,342} poly(ether sulfone),^{343–345} sulfonated/silylated polyphenylsulfone,³⁴⁶ sulfonated cyclodextrin,³⁴⁷ poly(vinylidene fluoride)^{348–351} (a model DMFC with such a membrane demonstrated a low decay of maximum power density of approximately 5.7×10^{-9} W/cm² per hour for a cell operating up to 1300 h),³⁵² poly(vinylidene fluoride-co-hexafluoro propylene),³⁵¹ phosphonated polysulfone,³⁵³ 3-aminopropyltriethoxysilane,³⁵⁴ sulfonated phenolphthalein poly(ether sulfone),³⁵⁵ acrylic acid-co-4-vinylimidazole,³⁵⁶ phenoxy resin,³⁵⁷ polyimide,³⁵⁸ poly(ether imide),³⁵⁹ polypyrrole,³⁶⁰ Nafion (SPAEK and Nafion are incompatible; SPAEK demonstrates a “flaky” sediment inside the Nafion matrix),³⁶¹ covalent-type Nafion introduction into SPAEK followed by cross-linking,³⁶² polyacrylonitrile,³⁶³ epoxy resins,^{364,365} polystyrenesulfonic acid,³⁶⁶ sulfonated and/or silylated polyphenylsulfone,³⁶⁷ and poly(vinyl alcohol).³⁶⁸ Although the blended membranes are mainly linear, the blended membranes may be prepared by cross-linking the mixture of linear polymers (SPAEK and the additive), which results in interpenetrating polymer nets.^{369–371}

Composite, multi-layer SPAEK membranes have also been developed to account for the apparent asymmetry in FCs; i.e., fuel diffusion occurs on the cell anode side, whereas peroxide-related issues (the major source of the membrane degradation) occur at the cathode side. The idea of a multi-layer membrane is that the anode protective layer would be prepared from a material with a low fuel permeability and, thus, may be extremely thin and will not compromise the overall membrane conductivity and mechanical properties. The cathode layer would be prepared from a thin material that is stable against peroxide.³⁷²

It was reported that thin (10 μm or thinner) layers of a cross-linked chitosan increased the membrane methanol selectivity β by 5-fold while not significantly decreasing the membrane conductivity.³⁷³ A thin layer of poly(vinyl alcohol) was also tested as a barrier against methanol diffusion.³⁷⁴ The SPAEK may be used as a thin layer to block methanol diffusion in the Nafion/SPAEK/Nafion structure.³⁷⁵

Preparation of SPAEK/inorganic filler composites is a common technique to improve proton conductivity, water retention (particularly at high temperatures), and mechanical properties.⁶⁶

The combination of SPAEK with solid heteropolyacids is a promising way to improve the membrane proton conductivity and hydrolytic stability and to diminish methanol permeability.³⁷⁶ Such heteropolyacids and their salts, e.g., H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀, H₃PMo₁₂O₄₀,³⁷⁷ Na₂HPW₁₂O₄₀, CsH₂PW₁₂O₄₀, Cs₂HPW₁₂O₄₀, Cs_{2.5}H_{0.5}PW₁₂O₄₀, Cs_{2.5}H_{0.5}PW₁₂O₄₀/Pt, H₃PW₁₂O₄₀/SiO₂, H₃PW₁₂O₄₀/molecular sieve, γ-K₉SiW₁₀O₃₆,²⁹¹ H₃SiW₁₂O₄₀/SiO₂-Al₂O₃,³⁷⁸ and H₃SiW₁₂O₄₀/montmorillonite, were reported.³⁷⁹ Composite SPAEK-based membranes with incorporated small cross-linked polycarboxylic acid spheres (150 nm in diameter)³⁸⁰ and polymeric phosphonic acid sub-micrometer spheres³⁸¹ were also reported.

The combination of SPAEK with non-acid inorganic materials is another promising method to improve SPAEK-based membranes.^{66,382} SPAEK was combined with zirconium hydrogen phosphate, which diminished the methanol permeability and water uptake without compromising mechanical stability; however, proton conductivity decreased.^{66,383} SPAEK was also combined with zirconium phosphate sulfophenylene-phosphonates; these membranes demonstrated a high conductivity (up to 0.1 S/cm at 80 °C).^{66,384,385} The SPAEK composite membranes with surface-modified SiO₂,^{382,386–388} ZrO₂,^{389,390} TiO₂, and TiO₂ with a modified surface,^{389–393} and Zr/Ti/phosphate³⁹⁴ and SPAEK composite membranes with methanesulfonic-acid-modified zeolite 4A,³⁹⁵ Fe₃O₄,³⁹⁶ and boron orthophosphate (BPO₄)^{397,398} were also reported.

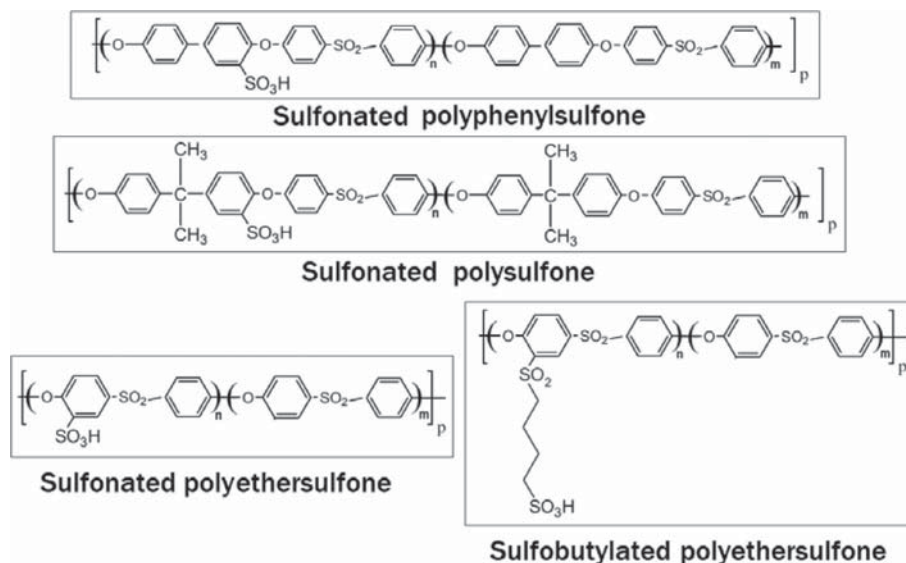


Figure 29. Exemplified formulas of sulfonated polysulfone and sulfonated polyphenylsulfone SPEs (acquired and modified with permission from ref 402).

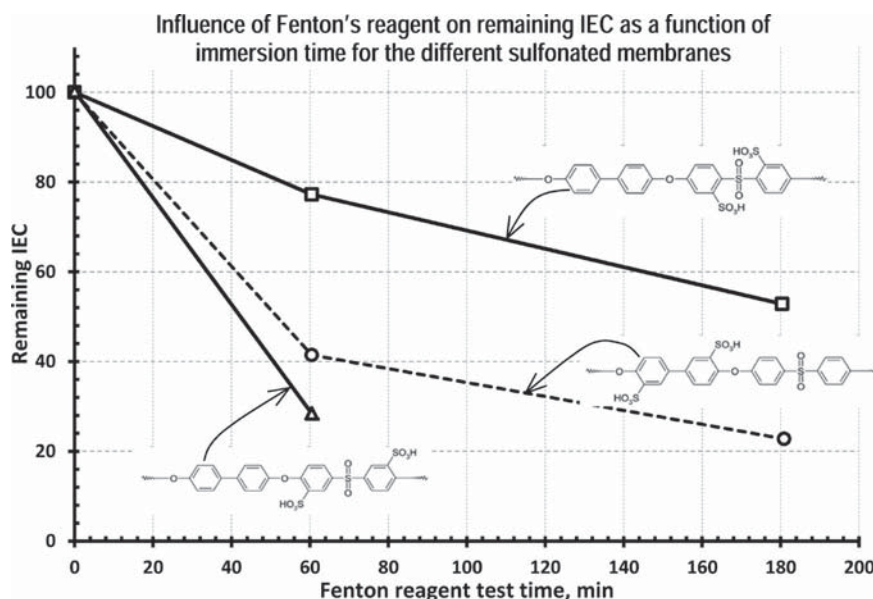


Figure 30. Influence of Fenton's reagent on remaining IEC as a function of the immersion time for the different sulfonated membranes (acquired and modified with permission from ref 407).

SPAEEK-based membranes exhibit inferior performance compared to current Nafion membranes in H_2 /air FCs because of their inadequate proton conductivity and lower membrane stability. Current efforts on these membranes are focused on improving the conductivity, maintaining a low water uptake, and improving the membrane lifetime. SPAEK membranes often exhibit significantly higher methanol selectivity compared to Nafion membranes.^{298,300–302,399}

3.6. Sulfonated Aromatic Main-Chain Polymers II: Polysulfone-, Polysulfone-Ether-, and Polyphenylsulfone-Based SPEs. Sulfonated poly(aryl sulfones) (SPAS), such as polysulfones (SPSUs), polysulfone ethers (SPSEs), and polyphenylsulfones (SPPSUs), are sulfonated aromatic main-chain polymers, similar to SPAEEKs. The first preparation of SPAS membranes was reported in ref 400, and the first

chemical power source (alkaline Zn/redox battery) was reported in ref 401. The precursor polymers are commercially available and inexpensive as well as thermally and chemically stable; thus, the sulfonated modifications of these materials are also expected to retain these features. These polymers are fully amorphous, and therefore, their mechanical properties depend upon chemical modification,^{402,403} as opposed to SPAEEKs. The exemplified formulas of PPSUs, SPPSUs, and SPSEs are presented in Figure 29.

Materials with such properties are considered potentially viable for SPE applications.^{404,405} As in the case of SPAEEK-based materials, SPAS-based materials demonstrated lower stability against superoxides than Nafion.⁴⁰⁶ The material degradation mechanism and critical points of the SPAS molecule are similar to those of SPAEEK (see Figure 25).³⁰⁴

Factors such as the specific parameters of the sulfonation process⁴²² and the particular positions of the sulfonic acid groups have a substantial influence on the conductivity, water absorption, and stability of SPAS materials (see Figure 30).⁴⁰⁷

Other ways to improve the material stability of SPAS include³⁰⁴ attaching SO_3 groups to the pendant chains (such SPAS are more stable than SPAS with sulfonated main chains),^{408–410} fluorination of the main-chain phenyl groups (partial fluorination increases the chemical stability of sulfonated arylenes),⁴¹¹ designing main-chain SPAS with only strong electron-withdrawing groups (e.g., SO_2 groups),^{412–415} and substitution of the main-chain ether group with a thioether group [poly(arylenethioethersulfone)-type SPE].^{416–420} SPAS membranes with a sulfonation degree of up to 4.1 mequiv/g⁴²¹ and with a conductivity up to 159.0 mS cm^{-1} at 80°C were reported.⁴²² However, the proton conductivity of SPAS can only reach the FC range with high sulfonation levels because of a similar phenomenon that was previously discussed for SPAEK, i.e., the combined action of the proton mobility restrictions (because of the narrow hydrophilic channels) and the low dielectric permeability of the confined water inside the hydrophilic channels.¹²⁶ Furthermore, a high sulfonation degree compromises physical properties of SPAS and increases methanol permeation in the same manner as that with SPAEKs.

Considerable research has focused on modifying SPAS membranes. Methods include the introduction of pendant functional groups,^{423–425} designing SPAS-co-polymers with preset hydrophobic/hydrophilic balances,⁴²⁶ grafting pendant chains with sulfonic and other functional groups to the main aromatic chain, blending SPAS with other polymers, and preparing SPAS/inorganic filler composites.^{82,427–431} In some cases, SPAS with sulfonic acid units on the side chains have exhibited a substantially higher dimensional stability than membranes based on directly sulfonated SPE with the same IEC.^{429,432} There are optimal lengths, types, and flexibilities of pendant sulfonated chains that provide the highest SPE conductivity.^{432,433}

Cross-linking is also extensively used to improve SPSU membrane properties, such as methanol permeability, hydrolytic stability, and mechanical strength (the cross-linked materials often have lower conductivity than the non-cross-linked materials).^{319,434–440}

Information on the testing and evaluation of FC with SPAS-based membranes is limited; usually the reported performance of DMFCs with SPAS-based membranes is lower than the performance of DMFCs with Nafion.⁴⁴¹

3.7. Natural Polymer-Based SPEs.⁴⁴² SPEs based on inexpensive and environmentally friendly natural materials are promising candidates to replace synthetic polymer-based SPEs (particularly Nafion) in FCs. There are only a few studies investigating natural SPEs based on such natural polymers as pectin,⁴⁴³ chitin phosphate,⁴⁴⁴ gelatin,^{445,446} agar and alginic acid,^{444,447} and uracil.^{444,448,449}

The research on cellulose and its derivative-based membranes is more extensive.^{450–454} Recently, the study on [2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)]-grafted bacterial cellulose membranes was presented.⁴⁵⁵ The conductivity of these membranes may be close to the conductivity of Nafion; FCs with these membranes have demonstrated a maximum power density of 95 mW/cm^2 (H_2/O_2 , at 50°C) and 16 mW/cm^2 (DMFC, at room temperature). The last value is only 35% of the performance of the same DMFC with a Nafion membrane.

Chitosan-based SPEs are the most extensively studied among all natural polymer-based SPEs.

3.7.1. Chitosan (CS). CS is an easily modified linear polysaccharide;^{456–458} its formula is presented in Figure 31. A

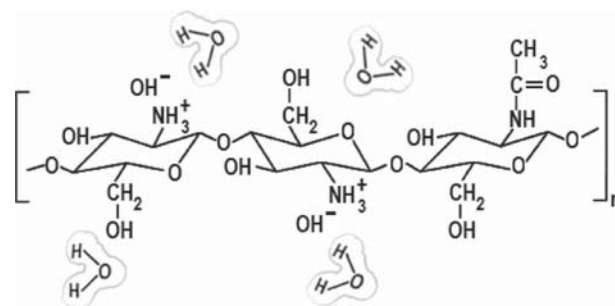


Figure 31. Partially acetylated/hydrated CS (acquired and modified with permission from ref 460).

hydrated CS is a cationic polyelectrolyte (i.e., a hydroxide conductor). Because the weak alkaline groups of its main chain are only partially protonated ($\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3^+ + \text{OH}^-$),⁴⁵⁹ the intrinsic conductivity of CS is extremely low. The conductivity occurs via OH^- transport across the amorphous areas of CS, despite of the highly crystalline nature of the most part of CS structure. The intrinsic conductivity of hydrated CS was reported to be approximately 10^{-4} S/cm , which is inadequate for FC applications.⁴⁶⁰

Proton conductivity is also possible if the proton donors are introduced into the CS matrix, which may be achieved by mixing different acids, heteropolyacids, and acid salts,^{461–468} by introducing inorganic fillers, such as acidic oxide particles^{469–472} and ammonium salts,^{473–476} and grafting acidic groups to the main CS chain.⁴⁷⁷ Proton conductivity occurs via both transport mechanisms and the Grotthuss-type mechanism.^{478,479} The additives typically increase the conductivity but compromise the mechanical properties. Such negative effects may be addressed by covalently or ionically cross-linking CS.⁴⁸⁰ Additionally, acidic group grafting and polybasic acid addition results in ionic cross-linking; the acidic groups may react with the amino groups in CS.^{466,464,478,481}

Transport-type conductivity, which is related to the diffusion of hydronium ions (e.g., H_3O^+ , H_5O_2^+ , and H_9O_4^+), depends strongly upon CS hydration.⁴⁷⁹ The amorphous domains have larger free volume cavities; thus, ion transport occurs through the amorphous polymer. Polymer amorphization favors an increased conductivity.^{482–484} CS amorphization may be achieved by the addition of salts and plasticizers,^{473–475,485–487} covalent cross-linking with glutaraldehyde,⁴⁸⁸ substitution of the CS backbone hydroxyl group with a large and bulky butyryl group,⁴⁸⁹ or grafting of the CS backbones with oligo-D,L-lactic acid.⁴⁹⁰

The conductivity mechanism of hydrated and partially hydrated CS–acid mixed membranes (which are acid–base complexes) depends upon the degree of hydration and combines transport and Grotthuss-type proton transfer. The conductivity of anhydrous CS–acid membranes has a Grotthuss-type character (see Figure 32). FCs with such membranes are able to operate at substantially elevated temperatures (up to 160°C) and at low hydration.^{448,491}

CS-based membranes have demonstrated considerably low conductivity^{457,479,480,492} but have markedly lower methanol

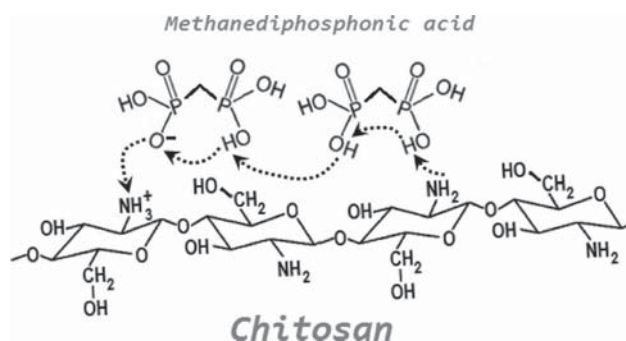


Figure 32. Anhydrous proton-conducting mechanism of CS/mix; arrows denote proton transfer (acquired and modified with permission from ref 491).

permeabilities than Nafion.^{457,466} The latter characteristic suggests the possibility of using relatively thin CS membranes for DMFC, which may counter the low conductivity of the CS membranes.

Information on FCs using CS-based membranes is scarce. The model H_2/O_2 FC with a composite CS membrane demonstrated a maximum power density of 16 mW/cm^2 at 75°C . It was suggested that the reported poor performance of this cell might be due to a problematic MEA fabrication.⁴⁹³ A DMFC using an acid-cross-linked CS membrane demonstrated maximum power densities of 27.4 and 42.4 mW/cm^2 at room temperature (for CS membranes with different degrees of deacetylation), whereas the same DMFC using a Nafion-117-based MEA demonstrated a maximum power density of 74.7 mW/cm^2 .^{494,495} The DMFC that used a membrane composed of CS mixed with phosphotungstic acid and montmorillonite demonstrated a maximal power density of 60.7 mW/cm^2 and an operation stability for more than 100 h at 70°C . The same model DMFC using a Nafion 117 membrane demonstrated a maximal power density of 47 mW/cm^2 .

4. OVERVIEW AND FUTURE PERSPECTIVE

The emerging FC market is a strong driving force, pushing the scientific community to develop inexpensive and high-performing membrane materials. The cost of a FC system should be reduced by 40%; currently, the cost is approximately $\$50/\text{kW}$, whereas the goal of the U.S. Department of Energy (DOE) is $\$30/\text{kW}$.⁴⁹⁶ However, the costs for the manufacturing plants account for more than 50% of the total system cost. This cost component has not been significantly reduced in the past few years.⁴⁹⁷ The membrane contributes the largest factor of the overall FC cost (see Figure 6). The cost reduction of the catalyst (the other essential FC cost component) is possible only through a reduction in Pt content. However, in the past few years, the amount of Pt in FCs has remained relatively constant.⁴⁹⁸ The one major approach to reducing the cost of FCs, which is crucial for the widespread acceptance of FCs as the primary energy source for various practical applications, is to reduce the membrane cost.

Considering that Nafion prices have not changed significantly from 2006 to 2011⁴⁹⁹ (even considering inflation),⁵⁰⁰ research and development will be focused on non-Nafion-type materials. DMFCs are the most promising FCs for transportation and portable electronic applications because of major concerns related to hydrogen storage (hydrogen has a high gravimetric specific energy but a low volumetric energy density). This has motivated the development of membranes

having a high methanol selectivity, β . Although Nafion membranes have a low β value, they may be improved by developing proper Nafion/inorganic and Nafion/polymer composite materials. In addition, many alternative ionomers have a substantially higher β than Nafion. Another issue concerns the limited ability of Nafion to operate at elevated temperatures. This drawback may be addressed by resorting to Nafion/inorganic and Nafion/polymer composite membranes. Furthermore, many alternative ionomers have a significantly higher temperature operation range than Nafion.

Most alternative membranes are ranked below Nafion membranes over an entire set of important properties. It may be worthwhile to compromise on conductivity and develop alternative membranes that are superior to Nafion in terms of temperature stability, operability over a wider range of conditions (e.g., lower humidity) with reduced overall swelling, lower fuel crossover, and particularly, lower cost. There are good reasons to believe that the scientific community is capable of overcoming the problems currently associated with PEM membranes. Commercially viable FC membranes are “just around the corner”.

AUTHOR INFORMATION

Corresponding Author

*E-mail: eineli@tx.technion.ac.il.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support for this work was provided by the Grand Technion Energy Program (GTEP) and the Leona and Harry B. Helmsley Charitable Trust.

REFERENCES

- (1) Grove, W. R. *Philos. Mag. J. Sci.* **1842**, 21, 417 <https://archive.org/details/londonedinburghp21lond>.
- (2) Schönbein, C. F. *Ann. Phys.* **1849**, 154, 289.
- (3) Ostwald, W. Z. *Elektrotech. Elektrochem.* **1894**, 1, 122.
- (4) Mond, L.; Langer, C. *Proc. R. Soc. London* **1889**, 46, 296.
- (5) Wright, C. R. A.; Thompson, C. *Proc. R. Soc. London* **1889**, 46, 372.
- (6) Jacques, W.W. U.S. Patent 555,511, 1896.
- (7) Baur, E.; Tobler, J. Z. *Elektrochem. Angew. Phys. Chem.* **1933**, 39, 169.
- (8) Bacon, F. T. *Electrochim. Acta* **1969**, 14, 569.
- (9) Thomas, B. F.; Wiliam, J. P. U.S. Patent 2,716,670, 1955.
- (10) Fuel Cell Today. *The Fuel Cell Industry Review*; Fuel Cell Today: London, U.K., 2012; www.fuelcelltoday.com, http://www.fuelcelltoday.com/media/1713685/fct_review_2012.pdf (accessed June 14, 2014).
- (11) http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/fc_comparison_chart.pdf.
- (12) http://www.ballard.com/be_informed/fuel_cell_technology/how_the_technology_works.
- (13) http://wikieducator.org/File:Fuel_Cell.png.
- (14) Spendelov, J.; Marcinkoski, J. DOE Fuel Cell Technologies Office Record 13012: Fuel Cell System Cost—2013; U.S. Department of Energy (DOE): Washington, D.C., 2013; http://www.hydrogen.energy.gov/pdfs/13012_fuel_cell_system_cost_2013.pdf (accessed June 14, 2014).
- (15) Smitha, B.; Sridhar, S.; Khan, A. A. *J. Membr. Sci.* **2005**, 259, 10.
- (16) Roziere, J.; Jones, D. J. *Annu. Rev. Mater. Res.* **2003**, 33, 503.
- (17) Iojoiu, C.; Chabert, F.; Mařechal, M.; Kissi, N. El.; Guindet, J.; Sanchez, J.-Y. *J. Power Sources* **2006**, 153, 198.
- (18) Deluca, N. W.; Elabd, Y. A. *J. Polym. Sci.* **2006**, 44, 2201.

- (19) Kerres, J. A. *J. Membr. Sci.* **2001**, 185, 3.
- (20) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, 15, 4896.
- (21) Sopian, K.; Daud, W. R. W. *Renewable Energy* **2006**, 31, 719.
- (22) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, 104, 4587.
- (23) Zhang, H.; Shen, P. K. *Chem. Rev.* **2012**, 112, 2780.
- (24) Kreuer, K.-D. *Chem. Mater.* **2014**, 26, 361.
- (25) Grubb, W. T., Jr. U.S. Patent 2,913,511, 1955.
- (26) Grubb, W. T. *J. Electrochem. Soc.* **1959**, 106, 275.
- (27) Grot, W.; Resnick, P. U.S. Patent 4,113,585, 1978.
- (28) (a) Grot, W. U.S. Patent 3,969,285, 1976. (b) Grot, W. U.S. Patent 4,026,783, 1977. (c) Grot, W. U.S. Patent 4,030,988, 1977.
- (29) <http://en.wikipedia.org/wiki/Nafion#mediaviewer/File:Nafion2.svg>.
- (30) Kreuer, K.-D. *Chem. Mater.* **1996**, 8, 610.
- (31) Gebel, G. *Polymer* **2000**, 41, 5829.
- (32) Haubold, H.-G.; Vad, Th.; Jungbluth, H.; Hiller, P. *Electrochim. Acta* **2001**, 46, 1559.
- (33) Eikerling, M.; Kornyshev, A. A.; Stimming, U. *J. Phys. Chem. B* **1997**, 101, 10807.
- (34) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci.* **1981**, 19, 1687.
- (35) Halim, J.; Büchi, F. N.; Haas, O.; Stamm, M.; Scherer, G. G. *Electrochim. Acta* **1994**, 39, 1303.
- (36) Souzy, R.; Ameduri, B.; Boutevin, B.; Gebel, G.; Capron, P. *Solid State Ionics* **2005**, 176, 2839.
- (37) Di Noto, V.; Zawodzinski, T. A.; Herring, A. M.; Giffin, G. A.; Negro, E.; Lavina, S. *Int. J. Hydrogen Energy* **2012**, 37, 6120.
- (38) Peighambari, S. J.; Rowshanzamir, S.; Amjadi, M. *Int. J. Hydrogen Energy* **2010**, 35, 9349.
- (39) Kreuer, K.-D.; Schuster, M.; Obliers, B.; Diat, O.; Traub, U.; Fuchs, A.; Klock, U.; Paddison, S. J.; Maier, J. *J. Power Sources* **2008**, 178, 499.
- (40) Li, J.; Pan, M.; Tang, H. *RSC Adv.* **2014**, 4, 3944.
- (41) Beuscher, U.; Cleghorn, S. J. C.; Johnson, W. B. *Int. J. Energy Res.* **2005**, 29, 1103.
- (42) Uosaki, K.; Okazaki, K.; Kita, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, 287, 163.
- (43) Cappadonia, M.; Erning, J. W.; Saberi Niaki, S. M.; Stimming, U. *Solid State Ionics* **1995**, 77, 65.
- (44) Borup, R.; Meyers, J.; Pivovar, B.; Kim, S.; Mukundan, R.; et al. *Chem. Rev.* **2007**, 107, 3904.
- (45) Zamel, N.; Li, X. *Prog. Energy Combust. Sci.* **2011**, 37, 292.
- (46) Kinumoto, T.; Inaba, M.; Nakayama, Y.; Ogata, K.; Umebayashi, R.; et al. *J. Power Sources* **2006**, 158, 1222.
- (47) Curtin, D. E.; Lousenberg, R. D.; Henry, T. J.; Tangeman, P. C.; Tisack, M. E. *J. Power Sources* **2004**, 131, 41.
- (48) St-Pierre, J.; Wilkinson, D. P.; Knights, S.; Bos, M. *J. New Mater. Electrochem. Syst.* **2000**, 3, 99.
- (49) Shi, M.; Anson, F. C. *J. Electroanal. Chem.* **1997**, 425, 117.
- (50) Wu, J.; Yuan, X. Z.; Martin, J. J.; Wang, H.; Zhang, J.; et al. *J. Power Sources* **2008**, 184, 104.
- (51) Tang, Y.; Karlsson, A. M.; Santare, M. H.; Gilbert, M.; Cleghorn, S.; et al. *Mater. Sci. Eng., A* **2006**, 425, 297.
- (52) Healy, J.; Hayden, C.; Xie, T.; Olson, K.; Waldo, R. *Fuel Cells* **2005**, 5, 302.
- (53) Rodgers, M. P.; Bonville, L. J.; Kunz, H. R.; Slattey, D. K.; Fenton, J. M. *Chem. Rev.* **2012**, 112, 6075.
- (54) Kusoglu, A.; Karlsson, A. M.; Santare, M. H.; Cleghorn, S.; Johnson, W. B. *J. Power Sources* **2006**, 161, 987.
- (55) Shi, S.; Chen, G.; Wang, Z.; Chen, X. *J. Power Sources* **2013**, 238, 318.
- (56) Tang, H.; Peikang, S.; Jiang, S. P.; Wang, F.; Pan, M. *J. Power Sources* **2007**, 170, 85.
- (57) Mindt, H.-W.; Megahed, M. *ECS Trans.* **2012**, 40, 25.
- (58) Ye, D. H.; Zhan, Z. G.; Lee, Y. J.; Tu, Z. K.; Zhang, Y.; Pan, M. *Fuel Cells* **2013**, 13, 1205.
- (59) Moukheiber, E.; Bas, C.; Flandin, L. *Int. J. Hydrogen Energy* **2014**, 39, 2717.
- (60) Kai, Y.; Kitayama, Y.; Omiya, M.; Uchiyama, T.; Kato, M. *J. Fuel Cell Sci. Technol.* **2013**, 10, 21007.
- (61) Ozmaiana, M.; Naghdabadi, R. *Phys. Chem. Chem. Phys.* **2014**, 16, 3173.
- (62) Silberstein, M. N.; Boyce, M. C. *J. Power Sources* **2010**, 195, 5692.
- (63) Goulet, M.-A.; Khorasany, R. M. H.; De Torres, C.; Lauritzen, M.; Kjeang, E.; et al. *J. Power Sources* **2013**, 234, 38.
- (64) Khattra, N. S.; Lu, Z.; Karlsson, A. M.; Santare, M. H.; Busby, F. C.; Schmiedel, T. *J. Power Sources* **2013**, 28, 256.
- (65) Ma, J.; Ni, H.-J.; Su, D.-Y.; Huang, M.-Y.; Wang, X.-X. *Int. J. Hydrogen Energy* **2012**, 37, 13185.
- (66) Tripathi, B. P.; Shahi, V. K. *Prog. Polym. Sci.* **2011**, 36, 945.
- (67) Bahar, B.; Cavalca, C.; Cleghorn, S.; Kolde, J.; Lane, D.; Murthy, M.; Rusch, G. *J. New Mater. Electrochem. Syst.* **1999**, 2, 179.
- (68) Tang, H.; Pan, M.; Wang, F.; Shen, P. K.; Jiang, S. P. *J. Phys. Chem. B* **2007**, 111, 8684.
- (69) Ballengee, J. B.; Pintauro, P. N. *J. Membr. Sci.* **2013**, 442, 187.
- (70) Rodgers, M. P.; Berring, J.; Holdcroft, S.; Shi, Z. *J. Membr. Sci.* **2008**, 321, 100.
- (71) Saleem, J.; Gao, P.; Barforda, J.; McKay, G. *J. Mater. Chem. A* **2013**, 1, 14335.
- (72) Saccà, A.; Pedicini, R.; Carbone, A.; Gatto, I.; Fracas, P.; Passalacqua, E. *Chem. Phys. Lett.* **2014**, 591, 149.
- (73) Yildirim, M. H.; Stamatialis, D.; Wessling, M. *J. Membr. Sci.* **2008**, 321, 364.
- (74) Yang, L.; Li, H.; Ai, F.; Chen, X.; Tang, J.; et al. *J. Power Sources* **2013**, 243, 392.
- (75) Wu, B.; et al. *Int. J. Hydrogen Energy* **2014**, 39, 14381.
- (76) Tripathi, B. P.; Shahi, V. K. *Prog. Polym. Sci.* **2011**, 36, 945.
- (77) Jung, G.-B.; Weng, F.-B.; Su, A.; Wang, J.-S.; Yu, T. L.; et al. *Int. J. Hydrogen Energy* **2008**, 3, 2413.
- (78) Nagarale, R. K.; Shin, W.; Singh, P. K. *Polym. Chem.* **2010**, 1, 388.
- (79) Di Noto, V.; Lavina, S.; Negro, E.; Vittadello, M.; Conti, F.; et al. *J. Power Sources* **2009**, 187, 57.
- (80) Matos, B. R.; Santiago, E. I.; Rey, J. F. Q.; Ferlauto, A. S.; Traversa, E.; et al. *J. Power Sources* **2011**, 196, 1061.
- (81) Ghassemzadeh, L.; Pace, G.; Di Noto, V.; Müller, K. *Phys. Chem. Chem. Phys.* **2011**, 13, 9327.
- (82) Laberty-Robert, C.; Valle, K.; Pereira, F.; Sanchez, C. *Chem. Soc. Rev.* **2011**, 40, 961.
- (83) Lin, J. C.; Kuntz, H. R.; Fenton, J. M.; Cutlip, M. B. In *Power Sources for the New Millennium: Proceedings of the International Symposium*; Jain, M., Ryan, M. A., Surampudi, S., Eds.; The Electrochemical Society, Inc.: Pennington, NJ, 2001; pp 48–63.
- (84) Klayson, C.; Moon, S.-H.; Ladewig, B. P.; Lu, G. Q. M.; Wang, L. *J. Colloid Interface Sci.* **2011**, 363, 431.
- (85) Nagata, S.; Konishi, Y.; Tsuchiya, B.; Toh, K.; Yamamoto, S.; et al. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, 257, 519.
- (86) Lue, S. J.; Hsiaw, S.-Y.; Wei, T.-C. *J. Membr. Sci.* **2007**, 305, 226.
- (87) Ma, J.; Ni, H.-J.; Su, D.-Y.; Huang, M.-Y.; Wang, X.-X. *Int. J. Hydrogen Energy* **2012**, 37, 13185.
- (88) Chikh, L.; Delhorbe, V.; Fichet, O. *J. Membr. Sci.* **2011**, 368, 1.
- (89) Kang, D. H.; Kim, D. *Korean J. Chem. Eng.* **2007**, 24, 1101.
- (90) Li, T.; Zhong, G.; Fu, R.; Yang, Y. *J. Membr. Sci.* **2010**, 354, 189.
- (91) Delhorbe, V.; Reijerkerk, S. R.; Cailleteau, C.; Bathfield, M.; Chikh, L.; et al. *J. Membr. Sci.* **2013**, 429, 168.
- (92) Wieser, C. *Fuel Cells* **2004**, 4, 245.
- (93) Chandan, A.; Hattenberger, M.; El-kharouf, A.; Du, S.; Dhir, A.; et al. *J. Power Sources* **2013**, 231, 264.
- (94) Shao, Y.; Yin, G.; Wang, Z.; Gao, Y. *J. Power Sources* **2007**, 167, 235.
- (95) Roziere, J.; Jones, D. *J. Annu. Rev. Mater. Res.* **2003**, 33, 503.
- (96) Pan, C.; He, R.; Li, Q.; Jensen, J. O.; Bjerrum, N. J.; et al. *J. Power Sources* **2005**, 145, 392.

- (97) Park, C. H.; Lee, C. H.; Guiver, M. D.; Lee, Y. M. *Prog. Polym. Sci.* **2011**, *36*, 1443.
- (98) Voel, C.; Haack, J. M. *Desalination* **2014**, *342*, 156.
- (99) Peckham, T. J.; Holdcroft, S. *Adv. Mater.* **2010**, *22*, 4667.
- (100) Basura, V. I.; Chuy, C.; Beattie, P. D.; Holdcroft, S. J. *Electroanal. Chem.* **2001**, *501*, 77.
- (101) Beattie, P. D.; Orfino, F. P.; Basura, V. I.; Zychowska, K.; Ding, J.; et al. *J. Electroanal. Chem.* **2001**, *503*, 45.
- (102) Grubb, W. T.; Niedrach, L. W. *J. Electrochem. Soc.* **1960**, *107*, 131.
- (103) Behling, N. *Fuel Cells—Current Technology Challenges and Future Research Needs*, 1st ed.; Elsevier: Amsterdam, Netherlands, 2013.
- (104) Carretta, N.; Tricoli, V.; Picchioni, F. *J. Membr. Sci.* **2000**, *166*, 189.
- (105) Ahmed, M.; Dincer, I. *Int. J. Energy Res.* **2011**, *35*, 1213.
- (106) β is the ratio of the membrane methanol permeability to the membrane conductivity and actually presents the balance of the ohmic losses and methanol diffusion losses. See (a) Pivovar, B. S.; Wang, Y.; Cussler, E. L. *J. Membr. Sci.* **1999**, *154*, 155. (b) Lufrano, F.; Baglio, V.; Staiti, P.; Antonucci, V.; Arico, A. S. *J. Power Sources* **2013**, *243*, 519.
- (107) Chen, S.-L.; Krishnan, L.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J. Membr. Sci.* **2004**, *243*, 327.
- (108) Mattsson, B.; Ericson, H.; Torell, L. M.; Sundholm, F. *Electrochim. Acta* **2000**, *45*, 1405.
- (109) Büchi, F. N.; Gupta, B.; Haas, O.; Scherer, G. G. *Electrochim. Acta* **1995**, *40*, 345.
- (110) Yu, J.; Yi, B.; Xing, D.; Liu, F.; Shao, Z.; et al. *Phys. Chem. Chem. Phys.* **2003**, *5*, 611.
- (111) Hubner, G.; Roduner, E. *J. Mater. Chem.* **1999**, *9*, 409.
- (112) Assink, R. A.; Arnold, C., Jr.; Hollandsworth, R. P. *J. Membr. Sci.* **1991**, *56*, 143.
- (113) Collier, A.; Wang, H.; Yuan, X. Z.; Zhang, J.; Wilkinson, D. P. *Int. J. Hydrogen Energy* **2006**, *31*, 1838.
- (114) Dockheer, S. M.; Gubler, L.; Bounds, P. L.; Domazou, A. S.; Scherer, G. G.; et al. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11609.
- (115) Fan, Q.; Hussain, H. U.S. Patent 7,323,265, 2002.
- (116) Hodgdon, R. B., Jr. *J. Membr. Sci.* **1968**, *6*, 171.
- (117) Steck, A. E.; Stone, C.; Wei, J. U.S. Patent 5,422,411, 1993.
- (118) Basura, V. I.; Chuy, C.; Beattie, P. D.; Holdcroft, S. J. *Electroanal. Chem.* **2001**, *501*, 77.
- (119) Savadogo, O. *J. New Mater. Electrochem. Syst.* **1998**, *1*, 47.
- (120) D'Agostino, V. F.; Lee, J. Y.; Cook, E. H., Jr. U.S. Patent 4,012,303, 1974.
- (121) Stone, C.; Daynard, T. S.; Hu, L.-Q.; Mah, C.; Steck, A. E. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 43.
- (122) Chuy, C.; Basura, V. I.; Simon, E.; Holdcroft, S.; Horsfall, J.; Lovell, K. V. *J. Electrochem. Soc.* **2000**, *147*, 4453.
- (123) Zaidi, S. M. J. Research trends in polymer electrolyte membranes for PEMFC. In *Polymer Membranes for Fuel Cells*; Zaidi, S. M. J., Matsuura, T., Eds.; Springer Science and Business Media, LLC: New York, 2009; Chapter 2.
- (124) Borriello, A.; Lavorgna, M.; Malagnino, N.; Mensitieri, G.; Napoletano, T.; Nicolais, L. *Macromol. Symp.* **2004**, *218*, 293.
- (125) Schmidt-Rohr, K.; Chen, Q. *Nat. Mater.* **2008**, *7*, 75.
- (126) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.
- (127) Ehrenberg, S. G.; Serpico, J.; Wnek, G. E.; Rider, J. N. U.S. Patent 5,468,574, 1994.
- (128) Sheikh-Ali, B. M.; Wnek, G. E. U.S. Patent 6,110,616, 1998.
- (129) Schauer, J.; Llanos, J.; Žitka, J.; Hnát, J.; Bouzek, K. *J. Appl. Polym. Sci.* **2012**, *124*, E66.
- (130) Elabd, Y. A.; Napadensky, E.; Walker, C. W.; Winey, K. I. *Macromolecules* **2006**, *39*, 399.
- (131) Elabd, Y. A.; Napadensky, E.; Sloan, J. M.; Crawford, D. M.; Walker, C. W. *J. Membr. Sci.* **2003**, *217*, 227.
- (132) Elamathi, S.; Nithyakalyani, G.; Sangeetha, D.; Ravichandran, S. *Ionics* **2008**, *14*, 377.
- (133) Kim, J.; Kim, B.; Jung, B. *J. Membr. Sci.* **2002**, *207*, 129.
- (134) Serpico, J. M.; Ehrenberg, S. G.; Fontanella, J. J.; Jiao, X.; Perahia, D.; et al. *Macromolecules* **2002**, *35*, 5916.
- (135) Sangeetha, D. *Eur. Polym. J.* **2005**, *41*, 2644.
- (136) Muller, F.; Ferreira, C. A.; Franco, L.; Puiggali, J.; Aleman, C.; Armelin, E. *J. Phys. Chem. B* **2012**, *116*, 11767.
- (137) Chen, L.; Hallinan, D. T., Jr.; Elabd, Y. A.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 6075.
- (138) Tsang, E. M. W.; Zhang, Z.; Shi, Z.; Soboleva, T.; Holdcroft, S. *J. Am. Chem. Soc.* **2007**, *129*, 15106.
- (139) Ding, J.; Chuy, C.; Holdcroft, S. *Adv. Funct. Mater.* **2002**, *12*, 389.
- (140) Ding, J.; Chuy, C.; Holdcroft, S. *Macromolecules* **2002**, *35*, 1348.
- (141) Ding, J.; Chuy, C.; Holdcroft, S. *Chem. Mater.* **2001**, *13*, 2231.
- (142) Enomoto, K.; Takahashi, S.; Rohani, R.; Maekawa, Y. *J. Membr. Sci.* **2012**, *415–416*, 36.
- (143) Gubler, L.; Gürsel, S. A.; Scherer, G. G. *Fuel Cells* **2005**, *5*, 317.
- (144) Chen, J.; Septiani, U.; Asano, M.; Maekawa, Y.; Kubota, H.; Yoshida, M. *J. Appl. Polym. Sci.* **2007**, *103*, 1966.
- (145) Gubler, L. *Adv. Energy Mater.* **2014**, *4*, 1300827.
- (146) Holmberg, S.; Lehtinen, T.; Näsmän, J.; Ostrovskii, D.; Paronen, M.; et al. *J. Mater. Chem.* **1996**, *6*, 1309.
- (147) Lehtinen, T.; Sundholm, G.; Holmberg, S.; Sundholm, F.; Bjornbom, P.; Bursell, M. *Electrochim. Acta* **1998**, *43*, 1881.
- (148) Hietala, S.; Koel, M.; Skou, E.; Elomaa, M.; Sundholm, F. *J. Mater. Chem.* **1998**, *8*, 1127.
- (149) Guzman-Garcia, A. G.; Pintaro, P. N. *J. Appl. Electrochem.* **1992**, *22*, 204.
- (150) Yamaki, T.; Asano, M.; Maekawa, Y.; Morita, Y.; Suwa, T.; et al. *Radiat. Phys. Chem.* **2003**, *67*, 403.
- (151) Yamaki, T.; Kobayashi, K.; Asano, M.; Kubota, H.; Yoshida, M. *Polymer* **2004**, *45*, 6569.
- (152) Gubler, L.; Slaski, M.; Wallasch, F.; Wokaun, A.; Scherer, G. G. *J. Membr. Sci.* **2009**, *339*, 68.
- (153) Momose, T.; Yoshioko, H.; Ishigaki, I.; Okamoto, J. *J. Appl. Polym. Sci.* **1989**, *38*, 2091.
- (154) Jetsrisuparb, K.; Balog, S.; Bas, C.; Perrin, L.; Wokaun, A.; Gubler, L. *Eur. Polym. J.* **2014**, *53*, 75.
- (155) Baglio, V.; Stassi, A.; Modica, E.; Antonucci, V.; Aricò, A. S.; Caracino, P.; Ballabio, O.; Colombo, M.; Kopnin, E. *Electrochim. Acta* **2010**, *55*, 6022.
- (156) Cao, Z.; Cao, X.; Sun, L.; He, Y. *Adv. Mater. Res.* **2011**, *239*, 3032.
- (157) *Polyimides: Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker, Inc.: New York, 1996.
- (158) Okamoto, K.-i. *J. Photopolym. Sci. Technol.* **2003**, *16*, 247.
- (159) Genies, C.; Mercier, R.; Sillion, B.; Petiaud, R.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 5097.
- (160) Faure, S.; Pineri, M.; Aldebert, P.; Mercier, R.; Sillion, B. U.S. Patent 6,245,881, 1996.
- (161) Zhang, F.; Li, N.; Zhang, S.; Li, S. *J. Power Sources* **2010**, *195*, 2159.
- (162) Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. *J. Membr. Sci.* **1999**, *160*, 127.
- (163) Woo, Y.; Oh, S. Y.; Kang, Y. S.; Jung, B. *J. Membr. Sci.* **2003**, *220*, 31.
- (164) Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem. Commun.* **2003**, 368.
- (165) He, Y.; Tong, C.; Geng, L.; Liu, L.; Lü, C. *J. Membr. Sci.* **2014**, *458*, 36.
- (166) Yin, Y.; Yamada, O.; Tanaka, K.; Okamoto, K.-i. *Polymer* **2006**, *38*, 197.
- (167) Peinemann, K.-V.; Nunes, S. P. *Membrane Technology: Membranes for Energy Conversion*; John Wiley and Sons: Weinheim, Germany, 2008; Vol. 2.
- (168) De Iasi, R.; Russell, J. *J. Appl. Polym. Sci.* **1971**, *15*, 2965.
- (169) Jang, W.; Lee, C.; Sundar, S.; Shul, Y. G.; Han, H. *Polym. Degrad. Stab.* **2005**, *90*, 431.

- (170) Aoki, M.; Asano, N.; Miyatake, K.; Uchida, H.; Watanabe, M. *J. Electrochem. Soc.* **2006**, *153*, A1154.
- (171) Chen, X.; Chen, K.; Chen, P.; Higa, M.; Okamoto, K.-I.; Hirano, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 905.
- (172) Yan, J.; Liu, C.; Wang, Z.; Xing, W.; Ding, M. *Polymer* **2007**, *48*, 6210.
- (173) Rehman, S.; Li, P.; Zhou, H. W.; Zhao, X. G.; Dang, G. D.; Chen, C. H. *Polym. Degrad. Stab.* **2012**, *97*, 1581.
- (174) Savadogo, O. *J. New Mater. Electrochem. Syst.* **1998**, *1*, 47.
- (175) Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 359.
- (176) Asano, N.; Miyatake, K.; Watanabe, M. *Chem. Mater.* **2004**, *16*, 2841.
- (177) Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J. Am. Chem. Soc.* **2006**, *128*, 1762.
- (178) Wei, H.; Chen, G.; Cao, L.; Zhang, Q.; Y. Q.; Fang, X. *J. Mater. Chem. A* **2013**, *1*, 10412.
- (179) Wei, H.; Fang, X. *Polymer* **2011**, *52*, 2735.
- (180) Zhang, F.; Li, N.; Cui, Z.; Zhang, S.; Li, S. *J. Membr. Sci.* **2008**, *314*, 24.
- (181) Zhang, F.; Li, N.; Zhang, S.; Li, S. *J. Power Sources* **2010**, *195*, 2159.
- (182) Zhang, F.; Li, N.; Zhang, S. *J. Appl. Polym. Sci.* **2010**, *118*, 3187.
- (183) Li, N.; Cui, Z.; Zhang, S.; Li, S.; Zhang, F. *J. Power Sources* **2007**, *172*, 511.
- (184) Yan, J.; Huang, X.; Moore, H. D.; Wang, C.-Y.; Hickner, M. A. *Int. J. Hydrogen Energy* **2012**, *37*, 6153.
- (185) Li, N.; Cui, Z.; Zhang, S.; Xing, W. *J. Membr. Sci.* **2007**, *295*, 148.
- (186) Yin, Y.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-i. *J. Mater. Chem.* **2004**, *14*, 1062.
- (187) Zhang, Q.; Li, Q. *Chin. J. Chem.* **2011**, *29*, 1460.
- (188) Perrot, C.; Gonon, L.; Marestin, C.; Gebel, G. *J. Membr. Sci.* **2011**, *379*, 207.
- (189) Marestin, C.; Gebel, G.; Diat, O.; Mercier, R. *Adv. Polym. Sci.* **2008**, *216*, 185.
- (190) Sundar, S.; Jang, W.; Lee, C.; Shul, Y.; Han, H. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2370.
- (191) Belkhir, Z.; Zeroual, M.; Ben Moussa, H.; Zitouni, B. *Rev. Energies Renouvelables* **2011**, *14*, 121.
- (192) Chang, Y.; Brunello, G. F.; Fuller, J.; Hawley, M.; Kim, Y. S.; et al. *Macromolecules* **2011**, *44*, 8458.
- (193) Deligöz, H.; Vantanser, S.; Koç, S. N.; Öksüzömer, F.; Özgümüş, S.; Gürkaynak, M. A. *J. Appl. Polym. Sci.* **2008**, *110*, 1216.
- (194) Yin, Y.; Hayashi, S.; Yamada, O.; Kita, H.; Okamoto, K.-i. *Macromol. Rapid Commun.* **2005**, *26*, 696.
- (195) Jin, R.; Li, Y.; Xing, W.; Qiu, X.; Ji, X.; Gao, L. *Polym. Adv. Technol.* **2012**, *23*, 31.
- (196) Lin, C.-C.; Chang, C.-B.; Wang, Y.-Z. *J. Power Sources* **2013**, *223*, 277.
- (197) Sung, K. A.; Kim, W.-K.; Oh, K.-H.; Choo, M.-J.; Park, J.-K. *J. Korean Electrochem. Soc.* **2009**, *12*, 245.
- (198) Einsla, B. R.; Kim, Y. S.; Hickner, M. A.; Hong, Y.-T.; Hill, M. L.; Pivovar, B. S.; McGrath, J. E. *J. Membr. Sci.* **2005**, *255*, 141–148.
- (199) Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-I. *Macromolecules* **2002**, *35*, 9022.
- (200) Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K.-I. *Macromolecules* **2002**, *35*, 6707.
- (201) Mistri, E. A.; Mohanty, A. K.; Banerjee, S. *J. Membr. Sci.* **2012**, *411–412*, 117.
- (202) Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K.-I.; Hirano, T. *J. Membr. Sci.* **2004**, *230*, 111.
- (203) Wang, T.; Sun, F.; Wang, H.; Yang, S.; Fan, L. *Polymer* **2012**, *53*, 3154.
- (204) Meyer, G.; Gebel, G.; Gonon, L.; Capron, P.; Marscaq, D.; Marestin, C.; Mercier, R. *J. Power Sources* **2006**, *157*, 293.
- (205) Kabasawa, A.; Saito, J.; Yano, H.; Miyatake, K.; Uchida, H.; Watanabe, M. *Electrochim. Acta* **2009**, *54*, 1076.
- (206) Kabasawa, A.; Saito, J.; Miyatake, K.; Uchida, H.; Watanabe, M. *Electrochim. Acta* **2009**, *54*, 2754.
- (207) Okanishi, T.; Tsuji, Y.; Sakiyama, Y.; Matsuno, S.; Bae, B.; Miyatake, K.; Uchida, M.; Watanabe, M. *Electrochim. Acta* **2011**, *58*, 589.
- (208) Allcock, H. R.; Wood, R. M. *J. Polym. Sci., Part B, Polym. Phys.* **2006**, *44*, 2358.
- (209) Allcock, H. R. *Soft Matter* **2012**, *8*, 7521.
- (210) Allcock, H. R. *Appl. Organomet. Chem.* **2013**, *27*, 620.
- (211) Tang, H.; Pintauro, P. N.; Guo, Q.; O'Connor, S. *J. Appl. Polym. Sci.* **1999**, *71*, 387.
- (212) Gleria, M.; De Jaeger, R. *Phosphazenes: A Worldwide Insight*; Nova Science Publishers: Hauppauge, NY, 2004.
- (213) Blonsky, P. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
- (214) Wycisk, R.; Pintauro, P. N. *J. Membr. Sci.* **1996**, *119*, 155.
- (215) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 1120.
- (216) Tang, H.; Pintauro, P. N. *J. Appl. Polym. Sci.* **2001**, *79*, 49.
- (217) Guo, Q.; Pintauro, P. N.; Tang, H.; O'Connor, S. *J. Membr. Sci.* **1999**, *154*, 175.
- (218) Pintauro, P. N.; Tang, H. U.S. Patent 6,365,294, 2002.
- (219) Lvov, S. N.; Zhou, X.; Chalkova, E.; Weston, J. A.; Ambler, C. M.; Maher, A. E.; Wood, R. M.; Allcock, H. R. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2003**, *48*, 480.
- (220) DuPont. *DuPont Nafion PFSA Membranes*; DuPont: Wilmington, DE, 2009; http://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc101.pdf (accessed July 17, 2014).
- (221) Ahmed, M.; Dincer, I. *Int. J. Energy Res.* **2011**, *35*, 1213.
- (222) Fedkin, M. V.; Zhou, X.; Hofmann, M. A.; Chalkova, E.; Weston, J. A.; Allcock, H. R.; Lvov, S. N. *Mater. Lett.* **2002**, *52*, 192.
- (223) Allcock, H. R.; Hofmann, M. A.; Ambler, C. M.; Lvov, S. N.; Zhou, X. Y.; Chalkova, E.; Weston, J. *J. Membr. Sci.* **2002**, *201*, 47.
- (224) Zhou, X.; Weston, J.; Chalkova, E.; Hofmann, M. A.; Ambler, C. M.; Allcock, H. R.; Lvov, S. N. *Electrochim. Acta* **2003**, *48*, 2173.
- (225) Carter, R.; Evilia, R. F.; Pintauro, P. N. *J. Phys. Chem. B* **2001**, *105*, 2351.
- (226) Hofmann, M. A.; Ambler, C. M.; Maher, A. E.; Chalkova, E.; Zhou, X. Y.; Lvov, S. N.; Allcock, H. R. *Macromolecules* **2002**, *35*, 6490.
- (227) Li, X.; Liao, S.; Piao, J.; Wang, X. *Eur. Polym. J.* **2009**, *45*, 2391.
- (228) Schuster, M.; Rager, T.; Noda, A.; Kreuer, K. D.; Maier, J. *Fuel Cells* **2005**, *5*, 355.
- (229) Herath, M. B.; Creager, S. E.; Kitaygorodskiy, A.; DesMarteau, D. D. *ChemPhysChem* **2010**, *11*, 2871.
- (230) Burjanadze, M.; Paulsdorf, J.; Kaskhedikar, N.; Karatas, Y.; Wiemhöfer, H.-D. *Solid State Ionics* **2006**, *177*, 2425.
- (231) Carter, R.; Wycisk, R.; Yoo, H.; Pintauro, P. N. *Electrochem. Solid-State Lett.* **2002**, *5*, A195.
- (232) Wycisk, R.; Lee, J. K.; Pintauro, P. N. *J. Electrochem. Soc.* **2005**, *152*, A892.
- (233) Pintauro, P. N.; Wycisk, R.; Yoo, H.; Lee, J. *Polyphosphazene-Based Proton-Exchange Membranes for Direct Liquid Methanol Fuel Cells*; U.S. Army Research Office: Research Triangle Park, NC, 2005; Grant DAAD19-03-1-0018, <http://www.dtic.mil/dtic/tr/fulltext/u2/a441576.pdf> (accessed July 17, 2014).
- (234) Sammes, N.; Bove, R.; Stahl, K. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 372.
- (235) Carrette, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* **2001**, *1*, 5.
- (236) Remick, R.; Wheeler, D. *Molten Carbonate and Phosphoric Acid Stationary Fuel Cells: Overview and Gap Analysis*; National Renewable Energy Laboratory (NREL): Golden, CO, Sept 2010; Technical Report NREL/TP-560-49072, <http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/49072.pdf> (assessed June 10, 2014).
- (237) Lan, R.; Xu, X.; Tao, S.; Irvine, J. T. S. *J. Power Sources* **2010**, *195*, 6983.
- (238) Li, Q.; Jensen, J. O.; Savinell, R. F.; Bjerrum, N. J. *Prog. Polym. Sci.* **2009**, *34*, 449.

- (239) Lasségues, J. C. In *Proton Conductors, Solids, Membranes and Gels Materials and Devices*; Colomban, P., Ed.; Cambridge University Press: Cambridge, U.K., 1992; pp 311–328.
- (240) Xing, B.; Savadogo, O. *J. New Mater. Electrochem. Syst.* **1999**, *2*, 95.
- (241) Asensio, J. A.; Sanchez, E. M.; Gomez-Romero, P. *Chem. Soc. Rev.* **2010**, *39*, 3210.
- (242) Glipa, X.; Bonnet, B.; Mula, B.; Jones, D. J.; Rozière, J. *J. Mater. Chem.* **1999**, *9*, 3045.
- (243) Kawahara, M.; Morita, J.; Rikukawa, M.; Sanui, K.; Ogata, N. *Electrochim. Acta* **2000**, *45*, 1395.
- (244) Narayanan, S. R.; Yen, S.-P.; Liu, L.; Greenbaum, S. G. *J. Phys. Chem. B* **2006**, *110*, 3942.
- (245) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Fuel Cells* **2004**, *4*, 147.
- (246) Polybenzimidazoles were first introduced by H. Vogel and C. S. Marvel; the polymers have demonstrated exceptional thermal and chemical stability. Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.
- (247) Savadogo, O.; Xing, B. *J. New Electrochem. Syst.* **2000**, *3*, 345.
- (248) Savinell, R. F.; Litt, M. H. U.S. Patent 5,525,436, 1994.
- (249) Wainright, J. S.; Wang, J.-T.; Weng, D.; Savinell, R. F.; Litt, M. *J. Electrochem. Soc.* **1995**, *142*, L121.
- (250) http://www.fuel-cell.basf.com/cm/internet/Fuel_Cell/ (accessed June 30, 2014).
- (251) Seel, D. C.; Benicewicz, B. C.; Xiao, L.; Schmidt, T. J. High-temperature polybenzimidazole-based membranes. In *Handbook of Fuel Cells—Fundamentals, Technology and Applications*; Vielstich, W., Yokokawa, H., Gasteiger, H. A., Ed.; John Wiley and Sons: Hoboken, NJ, 2009; Vol. 5: Advances in Electrocatalysis, Materials, Diagnostics and Durability, Chapter 19.
- (252) Parrondo, J.; Rao, C. V.; Ghattay, S. L.; Rambabu, B. *Int. J. Electrochem.* **2010**, *2011*, 261065.
- (253) Mamlouk, M.; Scott, K. *Int. J. Energy Res.* **2011**, *35*, 507.
- (254) Asensio, J. A.; Borrós, S.; Gómez-Romero, P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3703.
- (255) Bouchet, R.; Siebert, E. *Solid State Ionics* **1999**, *118*, 287.
- (256) Bouchet, R.; Miller, S.; Duclot, M.; Souquet, J. L. *Solid State Ionics* **2001**, *145*, 69.
- (257) Weng, D.; Wainright, J. S.; Landau, U.; Savinell, R. F. *J. Electrochem. Soc.* **1996**, *143*, 1260.
- (258) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Fuel Cells* **2004**, *4*, 147.
- (259) Qingfeng, L.; Hjuler, H. A.; Bjerrum, N. J. *J. Appl. Electrochem.* **2001**, *31*, 773.
- (260) Yang, J. S.; Cleemann, L. N.; Steenberg, T.; Terkelsen, C.; Li, Q. F.; et al. *Fuel Cells* **2014**, *14*, 7.
- (261) Scott, K.; Xu, C.; Wu, X. *WIREs Energy Environ.* **2014**, *3*, 24.
- (262) He, R.; Li, Q.; Bach, A.; Jensen, J. O.; Bjerrum, N. J. *J. Membr. Sci.* **2006**, *277*, 38.
- (263) Perry, K. A.; More, K. L.; Payzant, E. A.; Meisner, R. A.; Sumpter, B. G.; Benicewicz, B. C. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 26.
- (264) Qingfeng, L.; Hjuler, H. A.; Bjerrum, N. J. *J. Appl. Electrochem.* **2001**, *31*, 773.
- (265) Ergun, D.; Devrim, Y.; Bac, N.; Eroglu, I. *J. Appl. Polym. Sci.* **2012**, *124*, E267.
- (266) Matar, S.; Higier, A.; Liu, H. *J. Power Sources* **2010**, *195*, 181.
- (267) Mamlouk, M.; Scott, K. *Int. J. Hydrogen Energy* **2010**, *35*, 784.
- (268) Oono, Y.; Sounai, A.; Hori, M. *J. Power Sources* **2009**, *189*, 943.
- (269) Kim, S.-K.; Ko, T.; Choi, S.-W.; Park, J. O.; Kim, K.-H.; et al. *J. Mater. Chem.* **2012**, *22*, 7194.
- (270) Noyé, P.; Li, Q.; Pan, C.; Bjerrum, N. J. *Polym. Adv. Technol.* **2008**, *19*, 1270.
- (271) Wang, S.; Zhang, G.; Han, M.; Li, H.; Zhang, Y.; et al. *Int. J. Hydrogen Energy* **2011**, *36*, 8412.
- (272) Wang, S.; Zhao, C.; Ma, W.; Zhang, N.; Zhang, Y.; et al. *J. Mater. Chem. A* **2013**, *1*, 621.
- (273) Yang, J.; Aili, D.; Li, Q.; Cleemann, L. N.; Jensen, J. O.; Bjerrum, N. J.; He, R. *ChemSusChem* **2013**, *6*, 275.
- (274) Yuan, S.; Guo, X.; Aili, D.; Pan, C.; Li, Q.; Fang, J. *J. Membr. Sci.* **2014**, *454*, 351.
- (275) Li, Q. F.; Rudbeck, H. C.; Chromik, A.; Jensen, J. O.; Pan, C.; Steenberg, T.; Calverley, M.; Bjerrum, N. J.; Kerres, J. *J. Membr. Sci.* **2010**, *347*, 260.
- (276) Angioni, S.; Villa, D. C.; Barco, S. D.; Quartarone, E.; Righetti, P. P.; et al. *J. Mater. Chem. A* **2014**, *2*, 663.
- (277) Li, H.-Y.; Liu, Y.-L. *J. Mater. Chem. A* **2013**, *1*, 1171.
- (278) *Proton Exchange Membrane Fuel Cells: Materials Properties and Performance*; Wilkinson, D. P.; Zhang, J.; Hui, R.; Fergus, J.; Li, X., Eds.; CRC Press (Taylor & Francis Group): Boca Raton, FL, 2010.
- (279) Yang, J. S.; Cleemann, L. N.; Steenberg, T.; Terkelsen, C.; Li, Q. F.; et al. *Fuel Cells* **2014**, *14*, 7.
- (280) Chromik, A.; Kerres, J. A. *Solid State Ionics* **2013**, *252*, 140.
- (281) Liao, J.; Yang, J.; Li, Q.; Cleemann, L. N.; Jensen, J. O.; et al. *J. Power Sources* **2013**, *238*, 516.
- (282) Oono, Y.; Fukuda, T.; Sounai, A.; Hori, M. *J. Power Sources* **2010**, *195*, 1007.
- (283) De Castro, E. *PBI-Phosphoric Acid Based Membrane Electrode Assemblies: Status Update*, PAFC Workshop, Nov 16, 2009; http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/mcfc_paafc_workshop_de_castro.pdf (assessed June 23, 2014).
- (284) Wannek, C.; Kohnen, B.; Oetjen, H.-F.; Lippert, H.; Mergel, J. *Fuel Cells* **2008**, *8*, 87.
- (285) Pinar, F. J.; Cañizares, P.; Rodrigo, M. A.; Úbeda, D.; Lobato, J. *J. Power Sources* **2011**, *196*, 4306.
- (286) Subianto, S. *Polym. Int.* **2014**, *63*, 1134.
- (287) http://www.fuel-cell.basf.com/cm/internet/Fuel_Cell/en/function/conversions:/publish/content/Microsite/Fuel_Cell/2474_Flyer_Celtec_P_Mea_ak3_jk.pdf (accessed July 14, 2014).
- (288) Galbiati, S.; Baricci, A.; Casalegno, A.; Marchesi, R. *Int. J. Hydrogen Energy* **2013**, *38*, 6469.
- (289) Jensen, J. O.; Li, Q.; Pan, C.; Bjerrum, N. J.; Rudbeck, H. C.; Steenberg, T. *Ongoing Efforts Addressing Degradation of High Temperature PEMFC*; Forschungszentrum Jülich GmbH: Jülich, Germany, 2010; http://user.fz-juelich.de/record/135324/files/FC2_5_Jensen.pdf?version=2.
- (290) Pivovar, B. S.; Wang, Y. X.; Cussler, E. L. *J. Membr. Sci.* **1999**, *154*, 155.
- (291) Kourasi, M.; Wills, R. G. A.; Shah, A. A.; Walsh, F. C. *Electrochim. Acta* **2014**, *127*, 454.
- (292) He, R.; Li, Q.; Xiao, G.; Bjerrum, N. J. *J. Membr. Sci.* **2003**, *226*, 169.
- (293) Neburchilov, V.; Martin, J.; Wang, H.; Zhang, J. *J. Power Sources* **2007**, *169*, 221.
- (294) Mamlouk, M.; Scott, K.; Hidayati, N. *J. Fuel Cell Sci. Technol.* **2011**, *8*, 61009.
- (295) Lobato, J.; Cañizares, P.; Rodrigo, M. A.; Linares, J. J.; López-Vizcaino, R. *Energy Fuels* **2008**, *22*, 3335.
- (296) Diaz, L. A.; Abuin, G. C.; Corti, H. R. *J. Membr. Sci.* **2012**, *411–412*, 35.
- (297) Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. *Br. Polym. J.* **1985**, *17*, 4.
- (298) Liu, B.; Guiver, M. D. In *Solid State Proton Conductors: Properties and Applications in Fuel Cells*; Knauth, P., Di Vona, M. L., Eds.; John Wiley and Sons, Ltd.: Chichester, U.K., 2012.
- (299) Vetter, S.; Ruffmann, B.; Buder, I.; Nunes, S. P. *J. Membr. Sci.* **2005**, *260*, 181.
- (300) Liu, B.; Kim, D.-S.; Guiver, M. D.; Kim, Y. S.; Pivovar, B. S. In *Membranes for Energy Conversion*; Peinemann, K.-V., Nunes, S. P., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2008; Vol. 2.
- (301) Maharana, T.; Sutar, A. K.; Nath, N.; Routaray, A.; Negi, Y. S.; Mohanty, B. Polyetheretherketone (PEEK) membrane for fuel cell applications. In *Advanced Energy Materials*; Tiwari, A., Valyukh, S., Eds.; John Wiley and Sons, Inc.: Hoboken, NJ, 2014.
- (302) Iulianelli, A.; Basile, A. *Int. J. Hydrogen Energy* **2012**, *37*, 15241.
- (303) Perrot, C.; Gonon, L.; Bardet, M.; Marestin, C.; Pierre-Bayle, A.; Gebel, G. *Polymer* **2009**, *50*, 1671.

- (304) Hou, H.; Di Vona, M. L.; Knauth, P. *ChemSusChem* **2011**, *4*, 1526.
- (305) Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J. Membr. Sci.* **2000**, *173*, 17.
- (306) Chen, Y.; Meng, Y.; Wang, S.; Tian, S.; Chen, Y.; Hay, A. S. *J. Membr. Sci.* **2006**, *280*, 433.
- (307) Li, L.; Zhang, J.; Wang, Y. *J. Membr. Sci.* **2003**, *226*, 159.
- (308) Chen, J.; Maekawa, Y.; Asano, M.; Yoshida, M. *Polymer* **2007**, *48*, 6002.
- (309) Silva, V. S.; Ruffmann, B.; Vetter, S.; Boaventura, M.; Mendes, A. M.; Madeira, L. M.; Nunes, S. P. *Electrochim. Acta* **2006**, *51*, 3699.
- (310) Komarov, P. V.; Veselov, I. N.; Chu, P. P.; Khalatur, P. G. *Soft Matter* **2010**, *6*, 3939.
- (311) Swier, S.; Chun, Y. S.; Gasa, J.; Shaw, M. T.; Weiss, R. A. *Polym. Eng. Sci.* **2005**, 1081.
- (312) Jiang, R.; Kunz, H. R.; Fenton, J. M. *J. Power Sources* **2005**, *150*, 120.
- (313) Yang, B.; Manthiram, A. *J. Power Sources* **2006**, *153*, 29.
- (314) Li, X.; Liu, C.; Lu, H.; Zhao, C.; Wang, Z.; Xing, W.; Na, H. *J. Membr. Sci.* **2005**, *255*, 149.
- (315) Kerres, J. A. *Fuel Cells* **2005**, *5*, 230.
- (316) Zhong, S.; Cui, X.; Cai, H.; Fu, T.; Zhao, C.; Na, H. *J. Power Sources* **2007**, *164*, 65.
- (317) Di Vona, M. L.; Pasquini, L.; Narducci, R.; Pelzer, K.; Donnadio, A.; Casciola, M.; Knauth, P. *J. Power Sources* **2013**, *243*, 488.
- (318) Han, S.; Zhang, M.-S.; Shin, J.; Lee, Y.-S. *Radiat. Phys. Chem.* **2014**, *97*, 313.
- (319) Hou, H.; Di Vona, M. L.; Knauth, P. *J. Membr. Sci.* **2012**, *423–424*, 113.
- (320) Zhong, S.; Cui, X.; Cai, H.; Fu, T.; Shao, K.; Na, H. *J. Power Sources* **2007**, *168*, 154.
- (321) Zhang, W.; Gogel, V.; Friedrich, K. A.; Kerres, J. *J. Power Sources* **2006**, *155*, 3.
- (322) Jeong, M.-H.; Lee, K.-S.; Lee, J.-S. *Macromolecules* **2009**, *42*, 1652.
- (323) Wang, J.; Zhao, C.; Zhang, L.; Li, M.; Ni, J.; Wang, S.; et al. *Int. J. Hydrogen Energy* **2012**, *37*, 12586.
- (324) Zhou, S.; Kim, D. *Electrochim. Acta* **2012**, *63*, 238.
- (325) Kim, J.-E.; Kim, D. *J. Membr. Sci.* **2012**, *405–406*, 176.
- (326) Li, M.; Zhang, G.; Xu, S.; Zhao, C.; Han, M.; Zhang, L.; et al. *J. Power Sources* **2014**, *255*, 101.
- (327) Guo, W.; Li, X.; Wang, H.; Pang, J.; Wang, G.; et al. *J. Membr. Sci.* **2013**, *444*, 259.
- (328) Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Macromolecules* **2004**, *37*, 7960.
- (329) Lee, H.-S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E. *Polymer* **2008**, *49*, 715.
- (330) Roy, A.; Hickner, M. A.; Yu, X.; Li, Y.; Glass, T. E.; McGrath, J. E. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2226.
- (331) Li, X.-F.; Paoloni, F. P. V.; Weiber, E. A.; Jiang, Z.-H.; Jannasch, P. *Macromolecules* **2012**, *45*, 1447.
- (332) Wang, S. J.; Luo, J. J.; Xiao, M.; Han, D. M.; Shen, P. K.; Meng, Y. Z. *Int. J. Hydrogen Energy* **2012**, *37*, 4545.
- (333) Park, H. S.; Seo, D. W.; Choi, S. W.; Jeong, Y. G.; Lee, J. H.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1792.
- (334) Lin, C.-K.; Tsai, J.-C. *J. Mater. Chem.* **2012**, *22*, 9244.
- (335) Pang, J.; Zhang, H.; Li, X.; Jiang, Z. *Macromolecules* **2007**, *40*, 9435.
- (336) Jeong, M.-H.; Lee, K.-S.; Hong, Y.-T.; Lee, J.-S. *J. Membr. Sci.* **2008**, *314*, 212.
- (337) Pang, J.; Zhang, H.; Li, X.; Liu, B.; Jiang, Z. *J. Power Sources* **2008**, *184*, 1.
- (338) Pang, J.; Feng, S.; Yu, Y.; Zhang, H.; Jiang, Z. *Polym. Chem.* **2014**, *5*, 1477.
- (339) Na, T.; Shao, K.; Zhu, J.; Liu, Z.; Sun, H.; Lew, C. M.; et al. *Polymer* **2012**, *53*, 4413.
- (340) Dang, H.-S.; Kim, D. *J. Power Sources* **2013**, *222*, 103.
- (341) Kerres, J.; Tang, C.-M.; Graf, C. *Ind. Eng. Chem. Res.* **2004**, *43*, 4571.
- (342) Zhang, H.; Li, X.; Zhao, C.; Fu, T.; Shi, Y.; Na, H. *J. Membr. Sci.* **2008**, *308*, 66.
- (343) Wu, H.-L.; Ma, C.-C. M.; Liu, F.-Y.; Chen, C.-Y.; Lee, S.-J.; Chiang, C.-L. *Eur. Polym. J.* **2006**, *42*, 1688.
- (344) Lim, S. S.; Daud, W. R. W.; Jahim, J. M.; Ghasemi, M.; Chong, P. S.; Ismail, M. *Int. J. Hydrogen Energy* **2012**, *37*, 11409.
- (345) Daud, W. R. W.; Ghasemi, M.; Chong, P. S.; Jahim, J. M.; Swee, S. L.; Ismail, M. SPEEK/PES composite membranes as an alternative for proton exchange membrane in microbial fuel cell (MFC). *Proceedings of the 1st Conference on Clean Energy and Technology (CET)*; Kuala Lumpur, Malaysia, June 27–29, 2011; p 400.
- (346) De Bonis, C.; D'Epifanio, A.; Di Vona, M. L.; D'Ottavi, C.; Mecheri, B.; Traversa, E.; Trombetta, M.; Licocchia, S. *Fuel Cells* **2009**, *9*, 387.
- (347) Yang, T.; Liu, C. *Int. J. Hydrogen Energy* **2011**, *36*, 5666.
- (348) Swier, S.; Ramani, V.; Fenton, J. M.; Kunz, H. R.; Shaw, M. T.; Weiss, R. A. *J. Membr. Sci.* **2005**, *256*, 122.
- (349) Jung, H.-Y.; Park, J.-K. *Electrochim. Acta* **2007**, *52*, 7464.
- (350) Li, Z.; Xi, J.; Zhou, H.; Liu, L.; Wu, Z.; Qiu, X.; Chen, L. *J. Power Sources* **2013**, *237*, 132.
- (351) Inan, T. Y.; Dogan, H.; Unveren, E. E.; Eker, E. *Int. J. Hydrogen Energy* **2010**, *35*, 12038.
- (352) Jung, H.-Y.; Park, J.-K. *Int. J. Hydrogen Energy* **2009**, *34*, 3915.
- (353) Abu-Thabit, N. Y.; Shaikh, A. A.; Zaidi, S. M.; Javaid, M. K. *J. Mater. Res.* **2012**, *27*, 1958.
- (354) Xue, Y.; Fu, R.; Wu, C.; Lee, J. Y.; Xu, T. *J. Membr. Sci.* **2010**, *350*, 148.
- (355) Gao, Q.; Wang, Y.; Xu, L.; Wang, Z.; Wei, G. *Chin. J. Chem. Eng.* **2009**, *17*, 934.
- (356) Jithunsa, M.; Tashiro, K.; Nunes, S. P.; Chirachanchai, S. *Int. J. Hydrogen Energy* **2011**, *36*, 10384.
- (357) Cai, H.; Shao, K.; Zhong, S.; Zhao, C.; Zhang, G.; Li, X.; Na, H. *J. Membr. Sci.* **2007**, *297*, 162.
- (358) Maab, H.; Schieda, M.; Yave, W.; Shishatskiy, S.; Nunes, S. P. *Fuel Cells* **2009**, *9*, 401.
- (359) Liu, S.; Wang, L.; Ding, Y.; Liu, B.; Han, X.; Song, Y. *Electrochim. Acta* **2014**, *130*, 90.
- (360) Li, X.; Liu, C.; Xu, D.; Zhao, C.; Wang, Z.; Zhang, G.; Na, H.; Xing, W. *J. Power Sources* **2006**, *162*, 1.
- (361) Tsai, J.-C.; Cheng, H.-P.; Kuo, J.-F.; Huang, Y.-H.; Chen, C.-Y. *J. Power Sources* **2009**, *189*, 958.
- (362) Zhang, N.; Zhang, G.; Xu, D.; Zhao, C.; Ma, W.; Li, H.; Zhang, Y.; Xu, S.; Jiang, H.; Sun, H.; Na, H. *Int. J. Hydrogen Energy* **2011**, *36*, 11025.
- (363) Wang, J.; Yue, Z.; Economy, J. *J. Membr. Sci.* **2007**, *291*, 210.
- (364) Fu, T.; Zhao, C.; Zhong, S.; Zhang, G.; Shao, K.; Zhang, H.; Wang, J.; Na, H. *J. Power Sources* **2007**, *165*, 708.
- (365) Na, T.; Shao, K.; Zhu, J.; Sun, H.; Xu, D.; Zhang, Z.; Lew, C. M.; Zhang, G. *J. Power Sources* **2013**, *230*, 290.
- (366) Yang, T.; Meng, L.; Huang, N. *J. Power Sources* **2013**, *224*, 132.
- (367) Sgreccia, E.; Di Vona, M. L.; Knauth, P. *Int. J. Hydrogen Energy* **2011**, *36*, 8063.
- (368) Yang, T. *Int. J. Hydrogen Energy* **2008**, *33*, 6772.
- (369) Zhong, S.; Cui, X.; Cai, H.; Fu, T.; Shao, K.; Na, H. *J. Power Sources* **2007**, *168*, 154.
- (370) Deivanayagam, P.; Ramamoorthy, A. R. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2012**, *49*, 191.
- (371) Fu, T. Z.; Liu, J.; Cui, Z. M.; Ni, J.; Zhang, G.; Yu, H. B.; Zhao, C. J.; Shi, Y. H.; Na, H.; Xing, W. *Fuel Cells* **2009**, *9*, 570.
- (372) Wang, L.; Yi, B. L.; Zhang, H. M.; Liu, Y. H.; Xing, D. M.; Shao, Z.-G.; Cai, Y. H. *J. Power Sources* **2007**, *164*, 80.
- (373) Zhong, S.; Cui, X.; Fu, T.; Na, H. *J. Power Sources* **2008**, *180*, 23.
- (374) Yang, T.; Xu, Q.; Wang, Y.; Lu, B.; Zhang, P. *Int. J. Hydrogen Energy* **2008**, *33*, 6766.
- (375) Yang, B.; Manthiram, A. *Electrochem. Commun.* **2004**, *6*, 231.

- (376) Kourasi, M.; Wills, R. G. A.; Shah, A. A.; Walsh, F. C. *Electrochim. Acta* **2014**, 127, 454.
- (377) Fontananova, E.; Trotta, F.; Jansen, J. C.; Drioli, E. *J. Membr. Sci.* **2010**, 348, 326.
- (378) Ismail, A. F.; Othman, N. H.; Mustafa, A. J. *Membr. Sci.* **2009**, 329, 18.
- (379) Mohtar, S. S.; Ismail, A. F.; Matsuura, T. *J. Membr. Sci.* **2011**, 371, 10.
- (380) Wang, J.; Jiang, S.; Zhang, H.; Lv, W.; Yang, X.; Jiang, Z. *J. Membr. Sci.* **2010**, 364, 253.
- (381) Nie, L.; Wang, J.; Xu, T.; Dong, H.; Wu, H.; Jiang, Z. *J. Power Sources* **2012**, 213, 1.
- (382) Tchicaya-Bouckary, L.; Jones, D. J.; Rozière, J. *Fuel Cells* **2002**, 2, 40.
- (383) Silva, V. S.; Ruffmann, B.; Vetter, S.; Mendes, A.; Madeira, L. M.; Nunes, S. P. *Catal. Today* **2005**, 104, 205.
- (384) Alberti, G.; Casciola, M.; D'Alessandro, E.; Pica, M. *J. Mater. Chem.* **2004**, 14, 1910.
- (385) Regina, A.; Fontananova, E.; Drioli, E.; Casciola, M.; Sganappa, M.; Trotta, F. *J. Power Sources* **2006**, 160, 139.
- (386) Carbone, A.; Pedicini, R.; Saccà, A.; Gatto, I.; Passalacqua, E. *J. Power Sources* **2008**, 178, 661.
- (387) Roelofs, K. S.; Hirth, T.; Schiestel, T. *J. Membr. Sci.* **2010**, 346, 215.
- (388) Zhao, Y.; Jiang, Z.; Lin, D.; Dong, A.; Li, Z.; Wu, H. *J. Power Sources* **2013**, 224, 28.
- (389) Nunes, S. P.; Ruffmann, B.; Rikowski, E.; Vetter, S.; Richau, K. *J. Membr. Sci.* **2002**, 203, 215.
- (390) Kawaguti, C. A.; Dahmouche, K.; Gomes, A. D. S. *Polym. Int.* **2012**, 61, 82.
- (391) Dou, Z.; Zhong, S.; Zhao, C.; Li, X.; Fu, T.; Na, H. *J. Appl. Polym. Sci.* **2008**, 109, 1057.
- (392) Ayyarua, S.; Dharmalingam, S. *RSC Adv.* **2013**, 3, 25243.
- (393) Wu, H.; Shen, X.; Xu, T.; Hou, W.; Jiang, Z. *J. Power Sources* **2012**, 213, 83.
- (394) Rani, G. S.; Beera, M. K.; Pugazhenth, G. *J. Appl. Polym. Sci.* **2012**, 124, E45.
- (395) Meenakshi, S.; Bhat, S. D.; Sahu, A. K.; Sridhar, P.; Pitchumani, S. *Fuel Cells* **2013**, 13, 851.
- (396) Prabhu, N. V.; Sangeetha, D. *Chem. Eng.* **2014**, 243, 564.
- (397) Mikhailenko, S. D.; Zaidi, S. M. J.; Kaliaguine, S. *Catal. Today* **2001**, 67, 225.
- (398) Krishnan, P.; Park, J.-S.; Kim, C.-S. *J. Membr. Sci.* **2006**, 279, 220.
- (399) Lakshmanan, B.; Huang, W.; Olmeijer, D.; Weidner, J. W. *Electrochim. Solid-State Lett.* **2003**, 6, A282.
- (400) Zschocke, P.; Quellmalz, D. *J. Membr. Sci.* **1985**, 22, 325.
- (401) Arnold, C., Jr.; Assink, R. A. *J. Membr. Sci.* **1988**, 38, 71.
- (402) Ioioiu, C.; Maréchal, M.; Chabert, F.; Sanchez, J.-Y. *Fuel Cells* **2005**, 5, 344.
- (403) Dizman, C.; Tasdelen, M. A.; Yagci, Y. *Polym. Int.* **2013**, 62, 991.
- (404) Iwasaki, K.; Yamamoto, T.; Harada, H.; Terahara, A.; Satoh, K. U.S. Patent 5,985,477, 1996.
- (405) Schuster, M.; Kreuer, K.-D.; Andersen, H. T.; Maier, J. *Macromolecules* **2007**, 40, 598.
- (406) He, S.; Yu, J.; Li, C.; Fang, J.; Xu, J.; Guan, R. *Polym. Eng. Sci.* **2011**, 51, 264.
- (407) Takamuku, S.; Jannasch, P. *Polym. Chem.* **2012**, 3, 1202.
- (408) Miyatake, K.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, 39, 3211.
- (409) Miyatake, K.; Chikashige, Y.; Watanabe, M. *Macromolecules* **2003**, 36, 9691.
- (410) Chikashige, Y.; Chikyu, Y.; Miyatake, K.; Watanabe, M. *Macromolecules* **2005**, 38, 7121.
- (411) Katzfuß, A.; Krajnovic, K.; Chromik, A.; Kerres, J. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, 4, 1919.
- (412) Schuster, M.; de Araujo, C. C.; Atanasov, V.; Andersen, H. T.; Kreuer, K.-D.; Maier, J. *Macromolecules* **2009**, 42, 3129.
- (413) de Araujo, C. C.; Kreuer, K. D.; Schuster, M.; Portale, G.; Mendil-Jakani, H.; Gebel, G.; Maier, J. *Phys. Chem. Chem. Phys.* **2009**, 11, 3305.
- (414) Weiber, E. A.; Takamuku, S.; Jannasch, P. *Macromolecules* **2013**, 46, 3476.
- (415) Schuster, M.; Kreuer, K.-D.; Andersen, H. T.; Maier, J. U.S. Patent 8,349,993, 2005.
- (416) Yoonessi, M.; Dang, T. D.; Heinz, H.; Wheeler, R.; Bai, Z. *Polymer* **2010**, 51, 1585.
- (417) Yoonessi, M.; Baiand, Z.; Dang, T. D. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, 45, 2813.
- (418) Zhao, D.; Li, J.; Song, M.-K.; Yi, B.; Zhang, H.; Liu, M. *Adv. Energy Mater.* **2011**, 1, 203.
- (419) Wiles, K. B.; Wang, F.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, 43, 2964.
- (420) Ma, X.; Zhang, C.; Xiao, G.; Yan, D. *J. Power Sources* **2009**, 188, 57.
- (421) Jutemar, E. P.; Takamuku, S.; Jannasch, P. *Polym. Chem.* **2011**, 2, 181.
- (422) Unveren, E. E.; Erdogan, T.; Çelebi, S. S.; Inan, T. Y. *Int. J. Hydrogen Energy* **2010**, 35, 3736.
- (423) Di Vona, M. L.; Luchetti, L.; Spera, G. P.; Sgreccia, E.; Knauth, P. C. *R. Chim.* **2008**, 11, 1074.
- (424) Zhao, C.; Xue, J.; Ran, F.; Sun, S. *Prog. Mater. Sci.* **2013**, 58, 76.
- (425) Wang, C.; Shin, D. W.; Lee, S. Y.; Kang, N. R.; Lee, Y. M.; Guiver, M. D. *J. Membr. Sci.* **2012**, 405–406, 68.
- (426) Bae, B.; Miyatake, K.; Watanabe, M. *Macromolecules* **2009**, 42, 1873.
- (427) Kim, D. S.; Robertson, G. P.; Guiver, M. D. *Macromolecules* **2008**, 41, 2126.
- (428) Manea, C.; Mulder, M. *J. Membr. Sci.* **2002**, 206, 443.
- (429) Jannasch, P. *Fuel Cells* **2005**, 5, 248.
- (430) Lafitte, B.; Jannasch, P. *Adv. Funct. Mater.* **2007**, 17, 2823.
- (431) Bi, H.; Wang, J.; Chen, S.; Hu, Z.; Gao, Z.; Wang, L.; et al. *J. Membr. Sci.* **2010**, 350, 109.
- (432) Karlsson, L. E.; Jannasch, P. *J. Membr. Sci.* **2004**, 230, 61.
- (433) Nielsen, M. M.; Dimitrov, I.; Takamuku, S.; Jannasch, P.; Jankova, K.; Hvilsted, S. *Fuel Cells* **2013**, 13, 342.
- (434) Oh, Y.-S.; Lee, H.-J.; Yoo, M.; Kim, H.-J.; Han, J.; Kim, T.-H. *J. Membr. Sci.* **2008**, 323, 309.
- (435) Di Vona, M. L.; Sgreccia, E.; Tamilvanan, M.; Khadhraoui, M.; Chassigneux, V.; Knauth, P. *J. Membr. Sci.* **2010**, 354, 134.
- (436) Thankamony, R. L.; Won, M.; Kim, T.-H. *Int. J. Hydrogen Energy* **2013**, 38, 5084.
- (437) Oh, Y.-S.; Lee, M.-G.; Kim, T.-H. *J. Korean Chem. Soc.* **2009**, 53, 345.
- (438) Sgreccia, E.; Chailan, J.-F.; Khadhraoui, M.; Di Vona, M. L.; Knauth, P. *J. Power Sources* **2010**, 195, 7770.
- (439) Gil, S. C.; Kim, J. C.; Ahn, D.; Jang, J.-S.; Kim, H.; Jung, J. C.; et al. *J. Membr. Sci.* **2012**, 417–418, 2.
- (440) Zhang, C.; Guo, X.; Fang, J.; Xu, H.; Yuan, M.; Chen, B. *J. Power Sources* **2007**, 170, 42.
- (441) Kim, H.-J.; Krishnan, N. N.; Lee, S.-Y.; Hwang, S. Y.; Kim, D.; et al. *J. Power Sources* **2006**, 160, 353.
- (442) Varshney, P. K.; Gupta, S. *Ionics* **2011**, 17, 479.
- (443) Mishra, R. K.; Datt, M.; Banthia, A. K.; Majeed, A. B. A. *Int. J. Plast. Technol.* **2012**, 16, 80.
- (444) Honma, I.; Yamada, M. *Bull. Chem. Soc. Jpn.* **2007**, 80, 2110.
- (445) Mattos, R. I.; Pawlicka, A.; Lima, J. F.; Tambelli, C. E.; Magon, C. J.; Donoso, J. P. *Electrochim. Acta* **2010**, 55, 1396.
- (446) Pawlicka, A.; Mattos, R. I.; Lima, J. F.; Tambelli, C. E.; Magon, C. J.; Donoso, J. P. *Electrochim. Acta* **2011**, 57, 187.
- (447) Raphael, E.; Avellaneda, C. O.; Manzolli, B.; Pawlicka, A. *Electrochim. Acta* **2010**, 55, 1455.
- (448) Yamada, M.; Honma, I. *Biosens. Bioelectron.* **2006**, 21, 2064.
- (449) Yamada, M.; Honma, I. *ChemPhysChem* **2004**, 5, 724.
- (450) Seo, J. A.; Kim, J. C.; Koh, J. K.; Ahn, S. H.; Kim, J. H. *Ionics* **2009**, 15, 555.

- (451) Lopes, L. V. S.; Machado, G. O.; Pawlicka, A.; Donoso, J. P. *Electrochim. Acta* **2005**, *50*, 3978.
- (452) Harun, N. I.; Ali, R. M.; Ali, A. M. M.; Yahya, M. Z. A. *Ionics* **2012**, *18*, 599.
- (453) Gadim, T. D. O.; Figueiredo, A. G. P. R.; Rosero-Navarro, N. C.; Vilela, C.; Gamelas, J. A. F.; Barros-Timmons, A.; Neto, C. P.; Silvestre, A. J. D.; Freire, C. S. R.; Figueiredo, F. M. L. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7864.
- (454) Choi, Y.-J.; Ahn, Y.; Kang, M.-S.; Jun, H.-K.; Kim, I. S.; Moon, S.-H. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 79.
- (455) Lin, C. W.; Liang, S. S.; Chen, S. W.; Lai, J. T. *J. Power Sources* **2013**, *232*, 297.
- (456) Vaghari, H.; Jafarizadeh-Malmiri, H.; Berenjian, A.; Anarjan, N. *Sustainable Chem. Processes* **2013**, *1*, 16.
- (457) Ma, J.; Sahai, Y. *Carbohydr. Polym.* **2013**, *92*, 955.
- (458) Rinaudo, M. *Prog. Polym. Sci.* **2006**, *31*, 603.
- (459) Philipp, B.; Dautzenberg, H.; Linow, K.-J.; Kötzt, J.; Dawydoff, W. *Prog. Polym. Sci.* **1989**, *14*, 91.
- (460) Wan, Y.; Creber, K. A. M.; Peppley, B.; Bui, V. T. *Polymer* **2003**, *44*, 1057.
- (461) Xiao, Y.; Xiang, Y.; Xiu, R.; Lu, S. *Carbohydr. Polym.* **2013**, *98*, 233.
- (462) Cui, Z.; Liu, C.; Lu, T.; Xing, W. *J. Power Sources* **2007**, *167*, 94.
- (463) Kourasi, M.; Will, R. G. A.; Shah, A. A.; Walsh, F. C. *Electrochim. Acta* **2014**, *127*, 454.
- (464) Fadzaallah, I. A.; Majid, S. R.; Careem, M. A.; Arof, A. K. J. *Membr. Sci.* **2014**, *463*, 65.
- (465) Smitha, B.; Sridhar, S.; Khan, A. A. *Macromolecules* **2004**, *37*, 2233.
- (466) Gümüşoğlu, T.; Arı, G. A.; Deligöz, H. *J. Membr. Sci.* **2011**, *376*, 25.
- (467) Göktepe, F.; Çelik, S. Ü.; Bozkurt, A. *J. Non-Cryst. Solids* **2008**, *354*, 3637.
- (468) Smitha, B.; Sridhar, S.; Khan, A. A. *Eur. Polym. J.* **2005**, *41*, 1859.
- (469) Ramirez-Salgado, J. *Electrochim. Acta* **2007**, *52*, 3766.
- (470) Hassan, F.; Woo, H. J.; Aziz, N. A.; Kufian, M. Z.; Majid, S. R. *Ionics* **2013**, *19*, 483.
- (471) Aziz, N. A.; Majid, S. R.; Yahya, R.; Arof, A. K. *Polym. Adv. Technol.* **2011**, *22*, 1345.
- (472) Magalad, V. T.; Pattanashetti, S. S.; Gokavi, G. S.; Nadagouda, M. N.; Aminabhavi, T. M. *Chem. Eng.* **2012**, *189–190*, 1.
- (473) Du, J. F.; Bai, Y.; Pan, D. A.; Chu, W. Y.; Qiao, L. J. *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 549.
- (474) Ng, L. S.; Mohamad, A. A. *J. Power Sources* **2006**, *163*, 382.
- (475) Du, J. F.; Bai, Y.; Pan, D. A.; Chu, W. Y.; Qiao, L. J. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *48*, 880.
- (476) Khair, A. S. A.; Puteh, R.; Arof, A. K. *Phys. B* **2006**, *373*, 23.
- (477) Xiang, Y.; Yang, M.; Guo, Z.; Cui, Z. *J. Membr. Sci.* **2009**, *337*, 318.
- (478) Srinophakun, T.; Martkumchan, S. *Carbohydr. Polym.* **2012**, *88*, 194.
- (479) Bai, H.; Zhang, H.; He, Y.; Liu, J.; Zhang, B.; Wang, J. *J. Membr. Sci.* **2014**, *454*, 220.
- (480) Sahai, Y.; Ma, J. High performance polymer hydrogel based materials for fuel cells In *Polymers for Energy Storage and Conversion*; Mittal, V., Ed.; Scrivener Publishing LLC: Beverly, MA, 2013.
- (481) Berger, J.; Reist, M.; Mayer, J. M.; Felt, O.; Peppas, N. A.; Gurny, R. *Eur. J. Pharm. Biopharm.* **2004**, *57*, 19.
- (482) Mukoma, P.; Jooste, B. R.; Vosloo, H. C. M. *J. Power Sources* **2004**, *136*, 16.
- (483) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.
- (484) Missan, H. P. S.; Chu, P. P.; Sekhon, S. S. *J. Power Sources* **2006**, *158*, 1472.
- (485) Pawlicka, A.; Mattos, R. I.; Tambelli, C. E.; Silva, I. D. A.; Magon, C. J.; Donoso, J. P. *J. Membr. Sci.* **2013**, *429*, 190.
- (486) Shukur, M. F.; Yusof, Y. M.; Zawawi, S. M. M.; Illias, H. A.; Kadir, M. F. Z. *Phys. Scr., T* **2013**, *157*, 014050.
- (487) Yahya, M. Z. A.; Arof, A. K. *Eur. Polym. J.* **2003**, *39*, 897.
- (488) Chávez, E. L.; Oviedo-Roa, R.; Contreras-Pérez, G.; Martínez-Magadán, J. M.; Castillo-Alvarado, F. L. *Int. J. Hydrogen Energy* **2010**, *35*, 12141.
- (489) Wan, Y.; Creber, K. A. M.; Peppley, B.; Bui, V. T. *J. Appl. Polym. Sci.* **2004**, *94*, 2309.
- (490) Ciulik, C. B.; Bernardinelli, O. D.; Balogh, D. T.; de Azevedo, E. R.; Akcelrud, L. *Polymer* **2014**, *55*, 2645.
- (491) Yamada, M.; Honma, I. *Electrochim. Acta* **2005**, *50*, 2837.
- (492) Tohidian, M.; Ghaffarian, S. R.; Shakeri, S. E.; Dashtimoghadam, E.; Hasani-Sadrabadi, M. M. *J. Solid State Electrochem.* **2013**, *17*, 2123.
- (493) Ramirez-Salgado, J. *Electrochim. Acta* **2007**, *52*, 3766.
- (494) Osifo, P. O.; Masala, A. *J. Power Sources* **2010**, *195*, 4915.
- (495) Osifo, P. O.; Masala, A. *Fuel Cell Sci. Technol.* **2011**, *9*, 11003.
- (496) Satyapal, S. *Hydrogen and Fuel Cell Technologies Update*; U.S. Department of Energy (DOE): Washington, D.C., 2010; http://www.fch-ju.eu/sites/default/files/documents/ga2010/sunita_satyapal.pdf (accessed on June 18, 2014).
- (497) Breakthrough Technologies Institute, Inc. *2011 Fuel Cell Technologies Market Report*; U.S. Department of Energy (DOE): Washington, D.C., July 2012; http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/2011_market_report.pdf (accessed on June 18, 2014).
- (498) Adamson, K.-A.; Jerram, L.; Lawrence, M. *The Fuel Cell and Hydrogen Industries: 10 Trends to Watch in 2013 and Beyond*; Navigant Consulting, Inc.: Boulder, CO, 2013; <http://www.navigantresearch.com/wp-assets/uploads/2013/01/WP-FC10T-13-Navigant-Research.pdf> (assessed on June 18, 2014).
- (499) Yee, R. S. L.; Rozendal, R. A.; Zhang, K.; Ladewig, B. P. *Chem. Eng. Res. Des.* **2012**, *90*, 950.
- (500) Eliassen, A. *Historical Currency Conversions*; <http://futureboy.homeip.net/fsp/dollar.fsp>.