Bio-analogue Amino Acid-Based Proton-Conduction Wires for Fuel Cell Membranes

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In contrast to still inefficient and expensive technical proton-conducting membranes, which rely on sulfonic acid activity, biology has solved its energy-related proton-conduction problems by evolving protein-bordered channels exposing amino acids for proton conduction (bacteriorhodopsin, CF0-channel of ATP-synthase, cytochrome oxidase complex). In this contribution, amino acids (L-lysine, aspartic acid, methionin) were attached to silica nanoparticles, which were incorporated into narrow (100−400 nm) channels produced in proton-inactive membranes (polyethlyene terephthalate, polycarbonate) forming nanowire structures for protons. The amino acid-modified porous membranes were shown to function in a real fuel cell setup with energy conversion efficiencies, corrected for the pore densities, approaching those of state-of-the-art fuel cell membranes. The dependence of proton-conduction properties of these channels on different parameters was studied. Further development of proton-conduction channels lined or filled with amino acid-grafted nanoparticles will not only give access to the wealth of amino acid chemistry for further optimization, but proton-conduction channels may also work as basic elements in hierarchic structures linking proton currents with chemical catalysis or mechanical work.

Introduction

Proton currents are an integral part of biology's most important energy conversion structures. They mediate the interconversion of electrochemical and chemical energy (ATP synthesis), the conversion of light into chemical energy (*Halobacterium halobium*), the generation of mechanical energy (bacterial flagellum), and the function of proton-requiring catalytical processes (oxygen reduction). Since all these mechanisms operate very efficiently, it may be concluded that evolution has managed to optimize proton transfer, which, in biology, occurs along amino acid-lined channels such as Asp-85, Arg-82, Glu-194, and Glu-204 in Halobacterium.[1−3] Indeed, with 10^5 protons conducted per second through one channel at a 100 mV potential drop in ATP synthase systems,[4,5] amino acid-lined or amino acid-filled channel membranes could meet technical requirements with respect to current density.

Presently used proton-conducting membranes for fuel cells, NAFION (tetrafluorethane with sulfonic acid groups), PEEK (polyether-etherketon with sulfonic acid groups), PES (polyether-sulfon) do not behave ideally (e.g., with respect to water management) and are, in addition, very expensive and delay the commercial introduction of polymer electrolyte membrane (PEM) fuel cells.[6]

It appeared, therefore, to be reasonable to develop standard polymer membranes such as polyethylene terephthalate (PET) or polycarbonate (PC) with pores and channels lined with amino acids as in biological energy systems. It is well-known that amino acids in their uncharged form or as hybrid ions (dipolar ions) can exchange and conduct protons within the amino acid molecule and if properly arranged may mediate a hopping transport of protons along chains. There are many proposals for proton conduction along amino acid aggregates and interfaces in biology.[7] Active synergetic interaction of occupied and vacant protonation sites along energized amino acid chains has been discussed for proton conduction in Bacteriorhodopsin channels.[8]

The concept in this publication was to use technically available porous membranes (PET, PC) with pores between 100 and 400 nm as well as ion beam perforated membranes with adjustable pore size and densities. A working PEM fuel cell arrangement was selected for measuring the efficiency of proton conduction in the amino acid-modified membranes. They were placed in series with an ordinary NAFION membrane in order to avoid hydrogen passage in case of malfunction, and zero power output was observed when the porous test membrane was not treated with amino acids. This geometry also assured that the activity of the oxygen reduction catalyst (Pt), attached to the additional NAFION membrane, could be kept identical during the comparison with technical membranes, which would not have been warranted if the Pt catalyst would have been attached to the amino acid-modified test membrane itself.

The approach presented here, to provide channels in an artificial proton-conduction membrane, the proton-conduction properties of which are controlled by amino acid assemblies, is new for scientific research. Also, in the vast patent literature on technical membranes, only one idea superficially related with our idea has been patented. That idea is to mix a technical material with channel-forming membrane proteins extracted from thermophyllic microorganisms or to add such microorganisms themselves. The channels provided by these microorganisms or by their specific proteins should support proton conduction.[9] The difference from our approach is that the proteins immobilized in the membrane may be subject to rapid degradation and may have statistically oriented channels and thus low effectively oriented channel densities. In addition, these patent applications seem to refer to a barely tested or untested idea, because experimental data are lacking.

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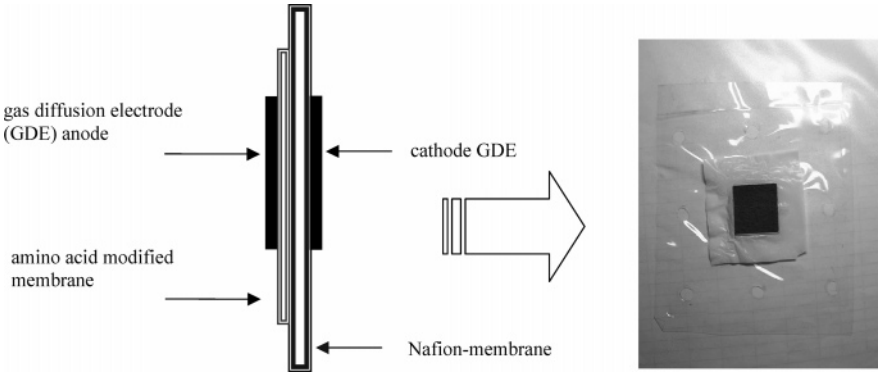

Figure 1. Scheme and photo showing how the amino acid-treated pore membranes were used in series with a NAFION membrane (to avoid hydrogen passage and to maintain identical catalytic properties) between gas diffusion electrodes.

The strategy to be followed in this work is a bionic one. An idea implemented in biological systems (proton conduction in amino acid-lined channels, which also involves bound water molecules) should be transferred to a much simplified (bionic) model based on realistically stable materials. What is essentially known from biological studies is that proton conduction occurs via amino acid arrays also involving bound water molecules. According to our present knowledge, no additional species seem to be involved. While the supporting biological protein structure is complicated, and since proteins themselves are not attractive for technical applications due to instability and costs, stable and cheap substrates are required to replace the supporting protein structure in the bionic model. SiO_2 and TiO_2 nanoparticles were selected for this purpose as support. Amino acids themselves support temperatures of between 200 and 300 °C, which is favorable for fuel cell applications. The amino acid arrangements obtained on artificial oxide surfaces may still significantly differ from the biological prototypes. But there will be a stepwise learning process which simply requires a first trial, such as that presented in this work.

Methods

Different methods (e.g., impedance spectroscopy, NMR studies) were considered for the determination of proton conduction in amino acid-modified nanowires. Since only specific and partial information was to be expected from such measurements, it was decided to use a working polymer electrolyte membrane (PEM) fuel cell arrangement for the determination of proton conduction. In this case, the functioning of the hydrogen oxygen fuel cell is definitive proof that protons are passing through the membrane. Comparatively little information about the mechanism can, however, be expected that way, but it can be determined whether it works and how well it works. This was considered an important first step.

Fuel Cell and Membrane Electrode Unit. The experiments were performed in a 10 × 10 cm fuel cell with an active electrode area of 5 cm^2. The single cell consisted of a membrane electrode unit between two graphite plates with a serpentine flow field for the fuel gases (H_2, O_2) and the electrical contacts. The setup included all infrastructure for supplying gases, for humidifying gases, for depositing water, and for controlling gas fluxes, pressure and temperature. The measurements were performed under galvanostatic load, and the cell potentials were recorded periodically. This is plotted in some of the given diagrams. If required, the power output can be calculated from the current by multiplying with the measured potential. For the presented work, 20 pore membranes with amino acid modification were produced and tested. Only 2 of these were prepared with glutamic acid and aspartic acid, 3 were prepared with methionine, and 13 were prepared with the best-functioning L-lysine. All amino acids were handled in aqueous solutions. The reproducibility was consistent for the conditions given.

Preparation of the Membrane Electrode Unit. Carbon paper (Toray Corp., 283 nm thickness) was cleaned with acetone and treated with a Teflon solution (Teflon 120 of ElectroChem) for hydrophobization. Then it was heated at 250 °C for 1 h in an oven. A commercial membrane (NAFION 1135, thickness 88.9 μm) was cleaned with a 3% H_2O_2 solution, then boiled in 2 M H_2SO_4 for 1 h, and finally, for removing residues of acid, boiled in distilled water. A catalyst suspension consisting of 20% platinum (cathode) and 20% Ru/Pt (anode) on Vulcan XC-72 (Denora Corporation), water, 5% NAFION solution (Aldrich), and 10% PTFE solution (ICI-Advanced Materials GP2, final content of PTFE on the GDE was 30%) was deposited. The carbon paper had been sprayed with the catalyst suspension and then joined with the amino acid-filled pore membrane (described below) and the NAFION membrane by applying at 130 °C for 5 min a 2 kN pressure and for 3 min a 5 kN pressure.[10] The membrane electrode unit was subsequently exposed to a humid atmosphere for 24 h for recovery of the required humidity.

Preparation of the Test Membranes. The test membranes with the pores or channels were always used in series with a NAFION membrane to allow a reference measurement (without amino acid filling) while avoiding possible oxygen/hydrogen intermixing (Figure 1) in case of malfunction. Commercial membranes of PET and PC (obtained from Sartorius AG, PET type 230 and PC type 154) were cut into 5 × 5 cm large squares and dipped into silica (Levasil (distributed by H.C. Starck) as 30% suspension in water) or TiO_2 (P25 from Degussa) suspensions.

The pore size of the PET membrane was 200 nm. The pore size of the PC membrane was approximately 400 nm with 120 × 10^6 pores per cm^2, which corresponds to a pore density of 60%. The pores were filled with silica (pH = 3.8) with a surface area of 200 m^2/g and an average particle diameter of 15 nm. A transmission electron microscopy (TEM) micrograph showing the distribution of the size and shape of these nanoparticles is presented below. In part, the pores were subsequently also treated with TiO_2 nanoparticles (Degussa, P 25, 15 nm average size) as shown in a side path in Figure 2, which explains the general procedure for preparing the membranes.

The membrane stayed in this solution for 24 h for filling the pores via diffusion. After wiping the remaining liquid away, it was then placed into a drybox. Then amino acid solution was added above the membrane and sucked through the pores by

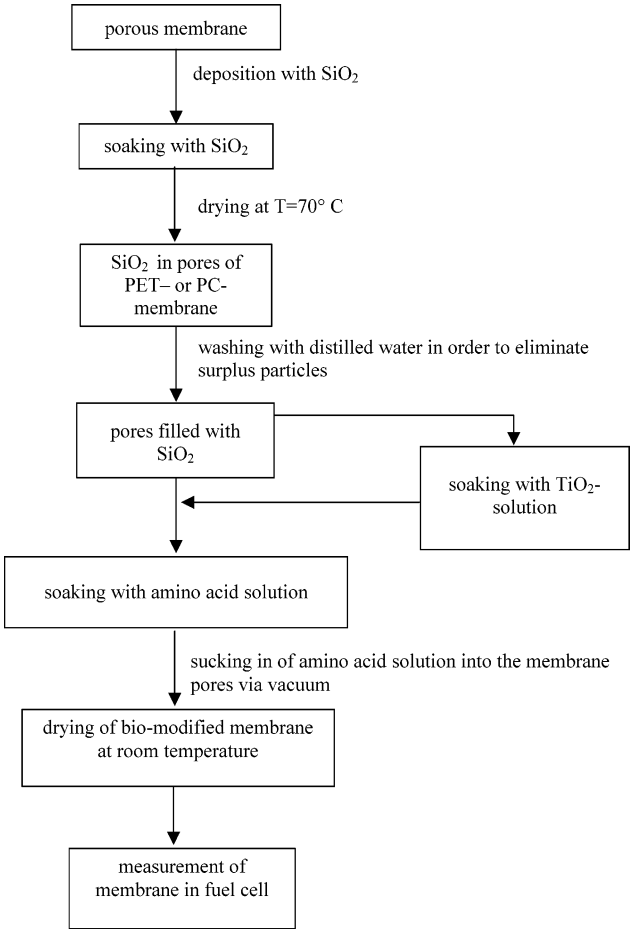

Figure 2. Scheme showing the different preparation steps for amino acid modification of membrane pores.

applying a vacuum below the membrane. A glass setup was used with analytical-grade amino acids (L-lysine, aspartic acid, methionine, glutamine acid (from Merck)). Figure 3 depicts the structures of amino acids used in combination with PET and PC membranes. The chemical composition of the membranes is also given. In the amino acids, a carboxyl group represents a proton donor, while the amino group presents a proton acceptor. As a consequence, protons can be conducted within the amino acid molecule, generating a hybrid ion (Figure 3a). The particular molecular structure of the amino acid molecule (Figure 3b) is expected to have an influence on intramolecular proton conduction. The intermolecular mechanism of proton transfer will depend on the molecular organization of the amino acids on the oxide nanoparticles and may also be influenced by the interaction of oxide particles and amino acids with the polymer membrane chemistry (Figure 3c).

Electron Microscopy. *TEM Sample Preparation*: The membrane was embedded into a resin and sliced with a microtome before TEM analysis was performed using a Phillips CM12 microscope operating at 120 kV.

Scanning Electron Micrograph (SEM): The membranes were cut into small pieces of 0.5 × 0.5 cm. A conducting carbon film was applied. The microscope used was a Leo440. The applied voltage was 10.000 kV, and the current passed was 100 pA.

Experimental Procedure. For the presented work, 20 pore membranes with amino acid modification were produced and tested. Only 2 of these were prepared with glutamic acid and aspartic acid, 3 were prepared with methionine, and 13 were prepared with the best-functioning L-lysine. The reproducibility

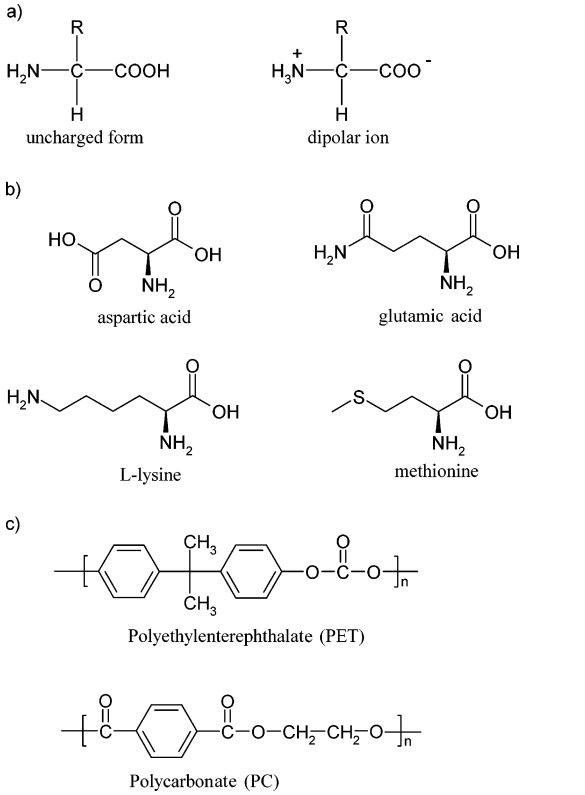

Figure 3. Molecular structure of compound used: (a) typical structure of amino acids and their dipolar behavior, (b) structure of amino acids used, and (c) chemical structure of the used membranes.

was found to be consistent for the conditions given. Two kinds of experimental plots are provided. Current density was given as potential plots as used in electrochemistry, and power output was given as current plots as used in fuel cell technology. This is expected to provide useful information for both areas.

Results

SiO_2 nanoparticles are well-known due to their applications in chromatography with cationic and anionic surface properties. Amino acids are known to interact with the particles via their amino groups but also via their carboxyl groups depending on the adjusted surface charge of the silica. As Figure 3a shows, amino acids can, via their caboxyl and amino groups, assume negative and positive charges, respectively. Via these charge they can chemically interact with the surface molecules of the polar-bonded oxides.

Silica is also commonly used to surface modify polymer interfaces. As described in the Methods, the silica particles were introduced into the channels and amino acids adsorbed to their interfaces. The sequence of experimental steps applied during this procedure is explained in Figure 2. The amino acids L-lysine, aspartic acid, glutamic acid, and methionine were closely investigated as proton carriers adsorbed to SiO*x* particles. Glutamic acid did not produce any energy turnover in the fuel cell. For some reason it did not generate proton conduction within the oxide particle-filled pore membranes.

Figure 4 shows SEM pictures of the pore structure of membranes before amino acid-modified silica particles were applied.

Figure 4a shows the pore distribution in a PET (polyethylene terephthalate, pore size 400 nm) membrane, and Figure 4b shows pore distribution in an artificially perforated (ion beams) PC (polycarbonate) membrane (manufactured at HMI). The pores

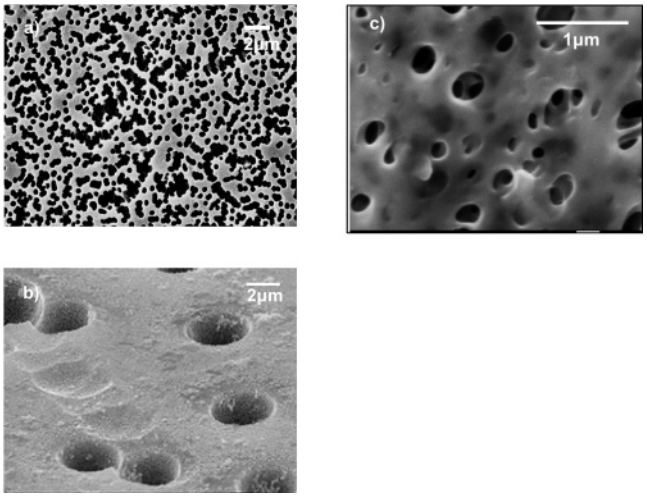

Figure 4. SEM pictures showing (a) the pore distribution in a PET membrane (pore diameter: 400 nm) and in (b) artificially produced (ion beams) pores in a PC membrane. (c) For comparison, the pores of a PES membrane are shown, in which the pores are branching out (not used for amino acid modification, but as a reference (Figure 11), since this material is itself proton-conducting on the basis of sulfonic acid groups).

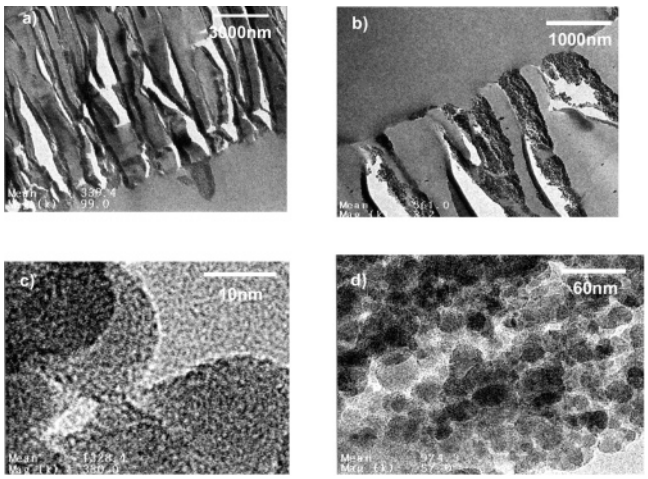

Figure 5. TEM cross sections of PET membrane with L-lysine-covered silica particles within the pores. (a and b) Pores and content of surface-grafted nanoparticles seen in different magnifications. High-resolution images (c) apparently allow the distinction of individual amino acid molecules (1 nm in size) on the surface of SiO_x nanoparticles (seen in lower resolution in d).

of both membranes show a channel-like structure, in comparison with the PES membrane (used as a reference, Figure 4c), where the pores branch out from bigger to smaller pores.

Cross-sectional TEM pictures performed with the prepared membranes (Figure 5a,b) verify the presence of amino acid-covered silica nanoparticles in pores of cross sections down to 30 nm. Figure 5a shows in a smaller magnification the parallel channels crossing the membrane (the thin microtome-sliced membrane layer is partially fractured along the channels, and the white background is exposed). In a higher magnification, Figure 5b shows four of these channels (with equally partially fractured membrane layer (white areas), which however clearly allows the identification of amino acid-covered silica nanoparticles within the channels. It is seen that the inner channel surface is not covered by a single nanosilica layer on the channel surface. Evidently the pores are largely filled with the nanoparticles of silica, to which the amino acids were attached.

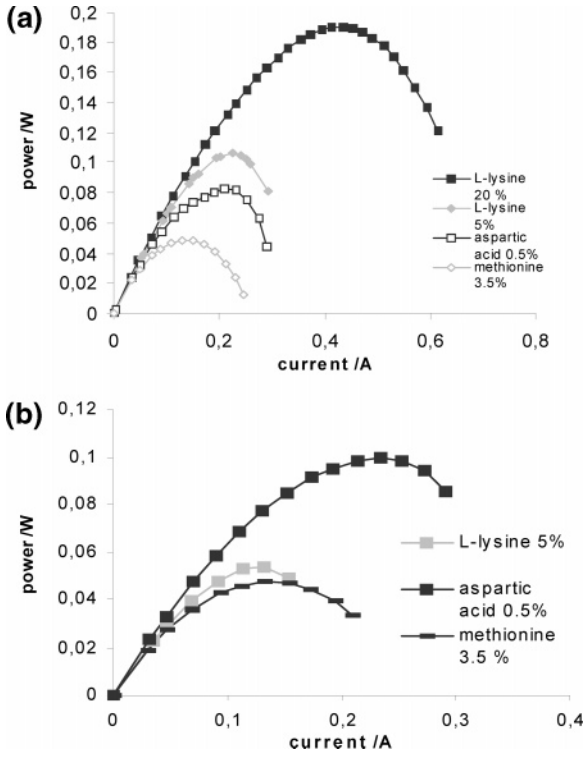

Figure 6. (a) Fuel cell power output−current characteristics obtained for different amino acid treatments, two concentrations of L-lysine, and aspartic acid as well as methionine, of a PET membrane treated with silica particles. (b) Fuel cell power output−current characteristics obtained for different amino acid treatments of a PC membrane with a mixture of silica and TiO_2 particles.

Figure 5c shows a higher and Figure 5d shows a lower amplified picture of the nanomaterial of amino acid-covered silica particles. Individual silica particles (15−20 nm) can be seen well in Figure 5d, and when a TEM picture of individual silica particle is made, the attached amino acids (1 nm) can be distinguished. Evidence for this conclusion is that occasionally they appear to arrange themselves in ordered chains. From Figure 5c,d, the size and shape of SiO_x nanoparticles can also be deduced. The average size, as given by the producing company, is 15 nm. As seen from Figure 5d, this is approximately correct, but smaller and larger particles, which have nonuniform, spherical shapes, can clearly be recognized. Also, the TiO_2 nanoparticles had a similar size of approximately 15 nm, but in TEM pictures (not shown here) looked more like irregularly grown tiny crystals.

Figure 6a shows the obtained fuel cell power output as a function of the fuel cell current for different concentrations of L-lysine, aspartic acid, and methionine, attached to silica particles introduced into PET membrane pores.

Figure 6b shows a similar plot for these amino acids, but for a PC membrane and with a mixture of silica and TiO_2 particles. Methionine worked sufficiently well neither with the PET nor with the PC membrane (glutamic acid, for some reason, did not work at all). L-Lysine and aspartic acid behaved both reasonably well, but L-lysine was better with a PET membrane and aspartic acid was better with a PC membrane. Altogether, the function of L-lysine was more efficient than that of aspartic acid.

It is seen from Figure 6a that increasing the concentration of L-lysine, which turned out to be the best amino acid for this application, significantly increased the power output. This indicates that the network of proton-conducting pathways via amino acids can be influenced by adjusting the concentration.

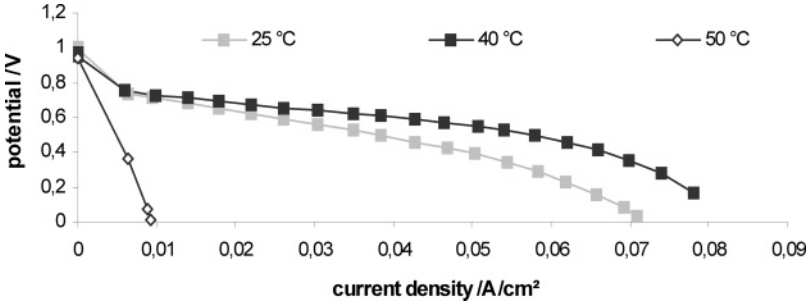

Figure 7. Fuel cell current−voltage characteristics for an aspartic acid-treated membrane (0.5%) at different temperatures.

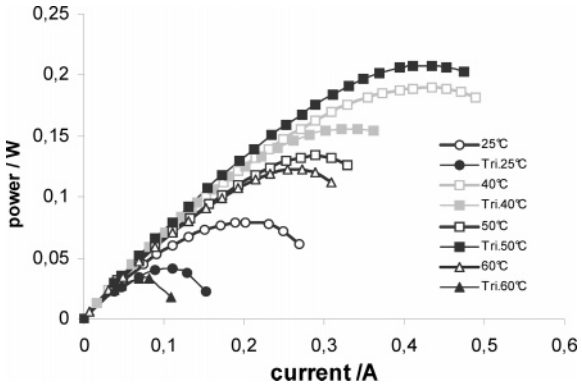

Figure 8. Power output current characteristics with L-lysine (20%)-modified PET membrane with and without Triton X 100 (1%) at different temperatures.

Figure 7 shows the current−voltage behavior of the fuel cell when aspartic acid was used at 1 bar of pressure at different temperatures (the power output can be calculated by multiplying the current with the corresponding voltage). It can be seen that the temperature of 40 °C was more favorable than temperatures of 25 or 50 °C.

In Figure 8, the fuel cell power−current characteristic is shown for L-lysine (20%, with and without 1% Triton X100) at different temperatures. Triton X is a nonionic tenside from the class of ethylphenolectoxylates. It is widely used in biochemistry because it dissolves proteins without denaturing them. Due to this known property, Triton X is expected to have an influence on the distribution of amino acids on oxide particles without chemically reacting with them. It is observed that Triton X-100, which is also known to disperse silica particles, leads to a decrease of the power output at lower temperatures but to an increase at higher temperatures.

L-Lysine in PET and aspartic acid in PC has shown the best performance of the amino acid-modified membranes. Pressure and temperature dependences, as well as the effect of Triton X, are provided as Supporting Information.

Figure 9 compares the fuel cell power output characteristics obtained with two technical proton-conducting membranes (NAFION, PES) and with amino acid (L-lysine)-modified pore membranes (PET, PC). It is seen that the new membranes with amino acid-lined channels work, though less efficiently than technical sulfonic acid-based membranes. Considering that only 40% of the PET membrane and 60% of the PC membrane are covered by pore areas, the power output can be recalibrated for the actually reactive surface area.

A corresponding plot of power output against fuel cell current is shown in Figure 10. A 100% pore area is, of course, only a calibration reference and technically not realistic. However, the correction, from 40 and 60% pore filling to 100% only involves factors of 2.5 and 1.6, respectively. Considering the early state of development of amino acid-based proton-conduction models, improvements of this order of magnitude due to directed research appear to be quite realistic.

This corrected power output obtained with the amino acid-modified membranes (L-lysine with PET and aspartic acid with PC) is of a similar order of magnitude as that for NAFION and shows this output already at a lower current. The power output of the fuel cell with the NAFION membrane was 0.44 W, while the power output with the L-lysine (20%)-modified PET membrane was 0.38 W. Considering that in the latter cases a NAFION membrane was still operating in series, thus contributing to the internal resistance and that part of the pores may have additionally been blocked for the passage of protons, the results are encouraging.

Discussion

An effort was made to demonstrate the feasibility of proton-conducting fuel cell membranes based on amino acids, attached to oxide nanoparticles and arranged within the pores of inert membranes. A fuel cell arrangement was selected, in which the catalytic parameters and the technical infrastructure of the fuel cell remained entirely unchanged. Only proton conduction via amino acid-bound water networks determined and limited the electrochemical and power output characteristic. This is clearly supported by the fact that no energy turnover is seen in the absence of amino acids and that a variable-energy output dependent on the nature of the amino acids and of the chemical additions is seen. Figure 11a shows an idealized scheme explaining the possible molecular arrangement of an amino acid-bound water structure supporting interfacial proton transfer on oxide nanoparticles. Figure 11b shows how protons can find their way through a three-dimensional network of amino acid-bound water structures across the fuel cell membrane. This scheme considers the observation, from TEM images (Figure 5), that the pores are reasonably filled with amino acid surface-conditioned silica particles. The filled pore itself, with the complex network of amino acids, can be considered as a nanowire for protons.

Experiments were performed with the amino acids L-lysine, aspartic acid, glutamine acid, and methionine. L-Lysine showed the best results while glutamine was not found to be reasonably active. Aspartic acid behaved better than L-lysine only in PC membranes and was generally superior to methionine. The reason for these differences in behavior are presently not understood but should be related to the structure of the amino acids, the amino acid−water surface layers formed on the silica and TiO_2 particles, and the proton conduction in these. The advantage of L-lysine in our experiments suggests that both the two positively charged amino groups (compare Figure 2) and the carboxyl groups are involved in interfacial bonding as well as in proton conduction, as indicated in Figure 11a. The proton may proceed via hopping processes between carboxyl groups

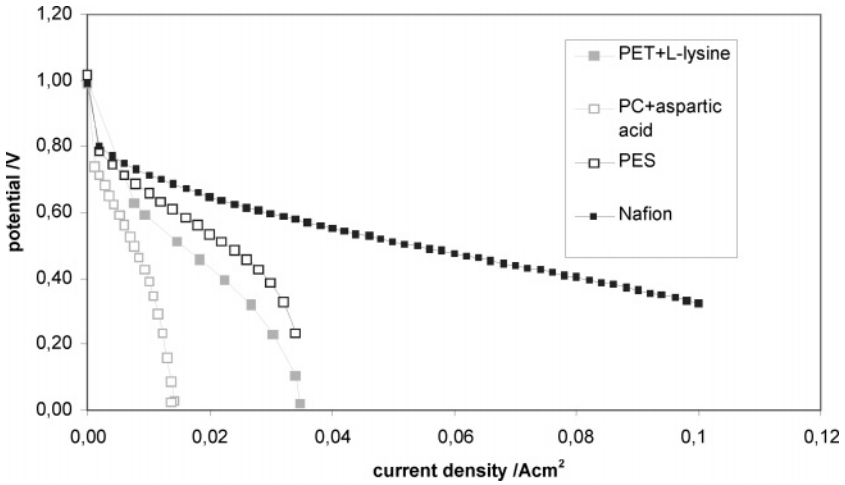

Figure 9. Current−voltage characteristics of NAFION and PES membrane operated fuel cells as compared with fuel cells operated with L-lysine (20%)-modified PET and aspartic acid (0.5%)-modified PC membranes.

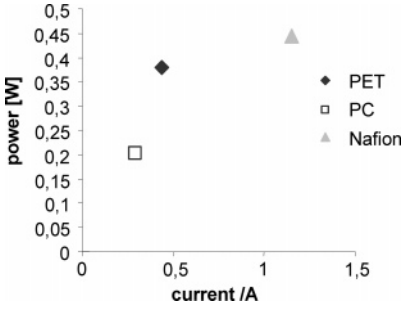

Figure 10. Power output at the respective fuel cell current for NAFION as compared with the pore-area-corrected performance of L-lysine (29%)-modified PET and aspartic acid (0.5%)-modified PC.

and amino groups much in the same way as within an amino acid during formation of a dipolar ion (Figure 3a). Alternatively, it may be considered that the chemical bonds between the amino acid molecules and the surface of silica (or TiO_2) nanoparticles may largely vary in strength. A proton may compete with some of these bonds for the carboxyl and amino groups, paving its way along the surface of the nano-oxide particle. It is obvious that the nature of the nanoparticles and their surface, as well as the chemistry of the amino acid adsorbed or of combinations of them, will have an influence on the nature and rate of proton transfer. In all amino acid-mediated proton-transfer mechanisms, bound water is also expected to play an active role as already discussed in the literature for biological proton-conduction pathways.[11] From the structure of glutamic acid (Figure 3b), which did not work at all in our proton-conduction experiments, it is not clear why there should be complications. In comparison with the well-functioning L-lysine (basic, pH = 9.59 character), it has an acidic (pH = 3.24) character and is 100 times less soluble in water (82.55 g/100 mL for L-lysine as compared with 0.86 g/100 mL for glutamic acid). It may be that bound water is critically involved in proton conduction also in this case. The concentration of the amino acid solution used to attach the amino acid had a clear influence on proton conduction and fuel cell performance. Also, this variable factor, which concerns the occupation of adsorption sites, will affect the proton-transfer properties of amino acid films. Aspartic acid might prefer to interact with its two carboxyl groups, which are known to interact well with nanoparticle TiO_2, which has been added in the experiment of Figure 6b. To find out more about structure−function relations in proton conduction, fundamental studies have been initiated.

The focus of research was on the nano-oxide pore structure (Figure 11b), in which both adsorbed amino acids and bound water are present. A first step was to identify the nature and dynamics of chemical bonds involving protons. Attenuated total reflection infrared studies of water within oxide (TiO_2) nanostructures (pore diameter 23 nm) which we performed[12] revealed that the hydrogen-bonded water structure, as measured within the stretch band between 2800 and 4000 cm^{-1}, was strongly dependent on the chemical water potential. With increasing extraction of water from the nanopores within the oxide particles and with increasing activity of capillary forces, the contribution of strongly bonded "network water", corresponding to low wave number OH stretch vibrations and a higher water coordination number, significantly increased. Evidence was given that the process is dynamically self-organized, driven by the energy turned over during the evaporation of water molecules.[12] Amino acids within a "tensile" water structure are expected to add even more complications which should be studied step-by-step. The main conclusion, for the moment, is that we have to learn more about the structural chemistry of hydrogen-bonded liquids in nanopores before being able to discuss details of proton-conduction dynamics.

For the present, only macroscopic information is available from the potential-dependent fuel cell currents, which are kinetically limited by the amino acid-modified membranes. They nevertheless indicate the essential parameters involved: Changing from a 5 to a 20% amino acid (L-lysine) solution increased the power output of the fuel cell by 77% (Figure 6a). This may indicate the relevance of a fully grown amino acid adsorption layer on the nano-oxide particles. Addition of the detergent Triton X (1%), which is expected to act against agglomeration, had an influence. It decreased the power output efficiency at lower temperatures (25 °C) but increased it at 50 °C. This indicates that a favorable distribution of amino acid molecules and of nanoparticles is essential.

The amino acid-modified membrane had a power output maximum between 40 and 50 °C. Mixing of silica particles with TiO_2 particles decreased the power output efficiencies. The internal electrical resistance for proton transport increased. Apparently, a different interaction with the amino acid disrupted to some extent the proton-conduction network by introducing less efficient pathways. However, a mixed SiO_2/TiO_2 nanoparticle substrate was favorable for the activity of aspartic acid in PC membranes, indicating that aspartic acid may favorably

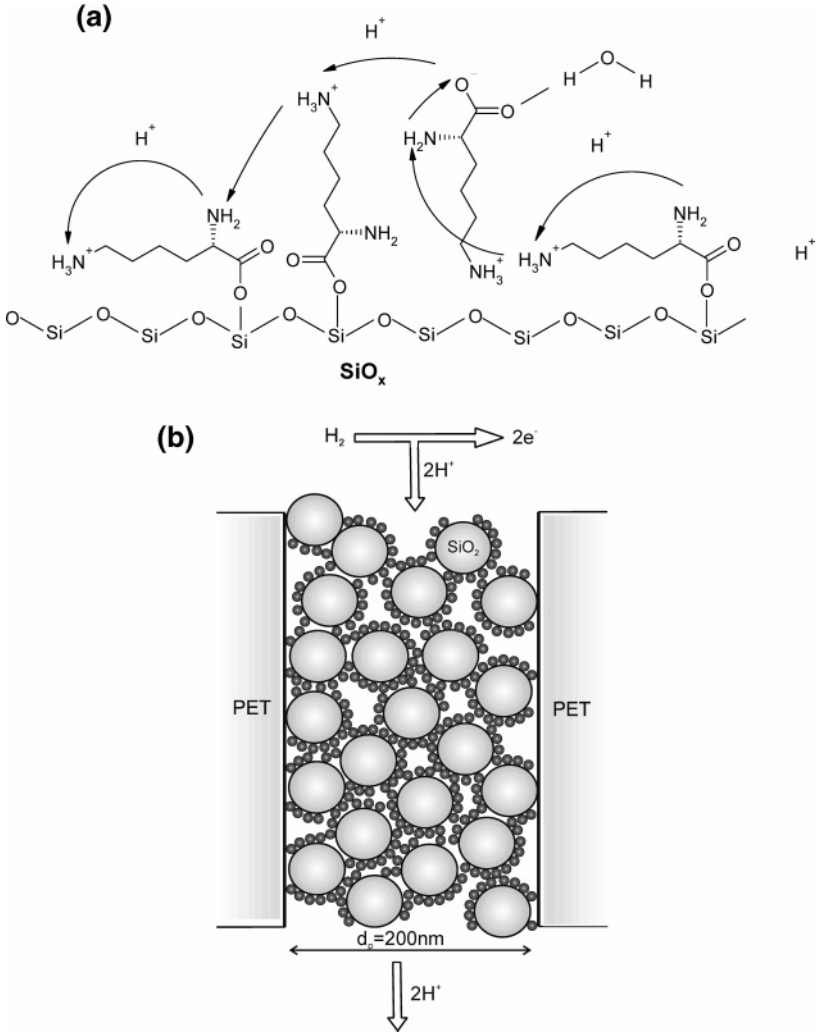

Figure 11. (a) Scheme of amino acid molecules attached to a silica nanoparticle surface explaining the propagation of protons via the adsorbed amino acid network. (b) Scheme of a pore filled with amino acid-conditioned silica particles. The arrows indicate how protons pass into and through the membrane channel filled with nano-oxide particles (larger spheres) via the surface-attached amino acid network (smaller spheres).

interact with TiO_2, via its two carboxyl groups, thus supporting proton transfer.

The power output of a fuel cell could thus be modified by controlling the chemistry within the pores of otherwise proton-isolating membranes. It changed with the introduction of the amino acids, with their concentration and chemical nature, but also with the pH of the environment during preparation and with the nature of the nanoparticles to which amino acids adsorb. Amino acids are thus mediating the transfer of protons, in analogy to proton-conduction channels as known from Bacteriorhodopsin, the ATP synthase system, or from the Cytochrome−oxidase complex.[11] As visualized in Figure 11b, the morphology attained in our experiments suggests that protons find their way along the three-dimensional network of amino acids attached to the oxide nanoparticles within the membrane pores. This is not yet proof that the proton-conduction mechanism is comparable to the optimized process in biology. But it demonstrates that proton conduction along amino acid-bound water arrays is technically feasible and that experimental efforts along this line may lead to a productive learning curve. Different substrates for amino acid chemisorption and also different amino acid combinations on selected substrates have to be explored. Bound water, which will always be present under realistic conditions within the pores of the oxide nanostructure, is an additional important factor. Eventually, even the understanding of the biological mechanism may take advantage from such simplified, but nevertheless complicated experimental approaches. In the present experiments, a NAFION membrane was applied in series with the studied amino acid-modified pore membranes. This was done as a safety precaution for the measurement of pore membranes without amino acid modification or with little pore filling, but also as a strategy aimed at keeping the catalytic parameters of the fuel cell arrangement constant (the Pt catalyst was attached to the NAFION layer). Without the NAFION membrane, hydrogen could have passed through empty pores of the test membrane. The hydrogen retention by amino acid-modified pore membranes has still to be investigated and optimized for fuel cell applications. Hydrogen is known to penetrate many materials and is held back by many others. Most of these materials are not single crystalline, but nanocrystalline. The pores filled with SiO_x or TiO_2 particles will, in fact, have properties close to those of nanomaterials. Hydrogen will have to diffuse along grain boundaries (surfaces of nanoparticles), the chemical properties of which are variable. Major work will be required before reliable conclusions can be drawn.

Due to the high potential for diversity of amino acid-based structural chemistry, and due to a range of possibilities in making membranes porous on a nano or molecular level, it is expected that amino acid-modified membranes could be developed for technical use in fuel cells. If "dry" proton conduction can in addition be achieved as in biological proton-conducting chan-

nels, a significant advantage as compared with the sulfonic acid-based technical membranes may be expected. The known temperature stability of amino acids at up to 200 °C and the fact that the amino acid-containing proteins of thermophyllic archaea survive temperatures up to 100 °C support the hope that sufficiently stable amino acid-based proton-conduction materials can be identified. A major effort toward the development of these amino acid-based proton-conducting membranes should thus be promising.

In addition, amino acid-lined or filled proton-conducting channels could in the future be directly linked with catalysts at their terminals on the membrane surface to obtain hierarchical structures for energy conversion. The proton-conducting channels could be linked with macromolecular complexes, attached to these terminals, which can turn over proton currents during catalytic reactions. Such a hierarchical structure could warrant high local proton concentrations, which would significantly shift chemical equilibria. In addition, an attempt could be made to convert the energy contained in proton currents into micromechanical energy via rotating macromolecules, such as those in the flagellar motors of bacteria. The presented approach of constructing amino acid-based proton-conducting channels may be a stepping-stone toward a bio-analogue adaptation of very successful proton-based biological energy conversion strategies. But more fundamental knowledge with respect to the performance of hydrogen-bonded molecules within oxide nanopores will have to be acquired.

Supporting Information Available: Pressure and temperature dependences, as well as the effect of Triton X, in PDF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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