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PLASMA POLYMERIZED ELECTROLYTE MEMBRANES AND ELECTRODES FOR MINIATURIZED FUEL CELLS

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Miniaturized fuel cells for portable systems like cellular phones, laptops, or other conventionally battery-driven devices, as well as long-term stationary monitoring electronics, have a potential market, especially for direct methanol fuel cells. However, design and fabrication technologies have to be adopted that allow the desired miniaturization of such a fuel cell. Thin film technologies like plasma polymerization and sputtering are suitable techniques for realizing membrane electrode assemblies only several microns in thickness that can be deposited on thin substrates (e.g., silicon wafers, porous foils, or others). Furthermore, plasma polymerized films exhibit a high degree of cross-linkage and are pinhole free even for films of only a few hundred nanometer in thickness, in contrast to conventionally polymerized films. In case of an electrolyte membrane these benefits yield a reduction of membrane resistance and a decreased methanol crossover.

We have developed plasma polymerized electrolyte membranes using tetrafluoroethylene to generate the polymeric backbone of an ion-conductive membrane and vinylphosphonic acid to incorporate acid groups, which are responsible for the proton conductivity. Depending on the process parameters these films exhibit an ion conductivity in the range of 100 mS/cm to 200 mS/cm (at 80°C), determined by ac-impedance measurements. These films were

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optimized with respect to their use in direct methanol fuel cells to achieve a high ion conductivity and high thermal resistance.

Porous graphite electrodes were fabricated using an acetylene plasma polymerization process. These films are combined with the plasma polymerized electrolyte membrane to form a thin film membrane electrode assembly.

***Keywords*:** Miniaturized fuel cell; Plasmapolymerization; Ionconductive membrane

INTRODUCTION

The basic part of a polymer electrolyte fuel cell, the membrane electrode assembly (MEA), consists of two porous electrodes separated by an ion-conductive membrane. Commonly used membranes like Nafion membranes exhibit a Teflon-like polymeric backbone with incorporated sulfonic acid groups, which are responsible for the proton conductivity of the membrane. The typical thickness of these membranes ranges from 50 μm to 200 μm. A general problem of electrolyte membranes in direct methanol fuel cells is their high methanol permeability (Watanabe et al., 1998; Scott et al., 1999). In contrast to chemically polymerized polymers, plasma polymerized films exhibit a high degree of cross-linkage and are pinhole free even for thin films with a thickness of a few hundred nanometers. Hence, a reduction of the methanol permeability and a decrease in the resistance of a fuel cell electrolyte membrane is achieved by using plasma polymerized electrolytes.

Plasma polymerization of electrolyte membranes has already been accomplished by several research groups. Their membranes are polymerized either by copolymerization of trifluoromethansulfonic acid and different fluorocarbons (Yasuda et al., 1994; Brumlik et al., 1994) or by plasma polymerization of perfluoroallylphosphonic acid (Danilich et al., 1997; Tucker et al., 1997). The latter is not commercially available and has to be stored under rather sophisticated conditions, which restricts its use. Using trifluoromethansulfonic acid for the plasma polymerization of ion-conductive membranes involves the difficulty of preserving the sulfonic acid group while cracking the C-S bond for an incorporation of this functional group in the Teflon-like polymeric backbone. To prevent a distortion of the sulfonic acid group the glow discharge has to be adjusted to low power density. This implies a low mean energy in the energy distribution of the accelerated electrons in the plasma whose inelastic collisions are responsible for the fragmentation of chemicals in the gas atmosphere. Since the C-S bond energy and those of the sulfonic acid group of trifluoromethansulfonic acid are comparable, a low power density leads to inclusions of trifluormethansulfonic acid in the polymer without chemical bonds to the polymeric backbone. Under operation these inclusions are washed out, resulting in a drastic reduction of the performance of the membranes.

To overcome these problems we have chosen tetrafluoroethylene (TFE) and vinylphosphonic acid (VPA) as monomeres. Both exhibit π-bonds, which permits a plasma polymerization without a fragmentization of the phosphonic acid groups and ensures a chemical binding of these groups into the polymeric backbone of the membrane.

The thin film MEA is completed by two porous graphite electrodes. These are deposited by a different plasma polymerization process using oxygen and acetylene for the glow discharge atmosphere.

CONCEPT OF A MINIATURIZED FUEL CELL

Using a silicon wafer as a substrate for the thin film membrane electrode assembly, a gas feed for the bottom electrode is necessary (Figure 1). Therefore, a thin porous silicon layer on top of the silicon substrate is etched and the substrate material underneath this porous regions is removed by KOH etching. On top of this porous membrane the thin film MEA is deposited by subsequently building up a porous graphite electrode with incorporated Pt-catalyst, the electrolyte membrane, and the porous graphite counterelectrode with incorporated Pt/Ru-catalyst.

Structured Pyrex glass substrates anodically bonded on the silicon wafer serve as a gas-tight encapsulation. To prevent adhesion of water during fuel cell operation the Pyrex glass can be coated with a Teflon-like polymer. The central gas inlet and outlet is realized by capillaries inserted at the edges of the Pyrex lids. Several fuel cells can be fabricated on one substrate and connected parallel or in series to achieve a desired current and voltage. To avoid an electrical short circuit along the silicon p^+ regions, it is necessary to neighboring fuel cell compartments.

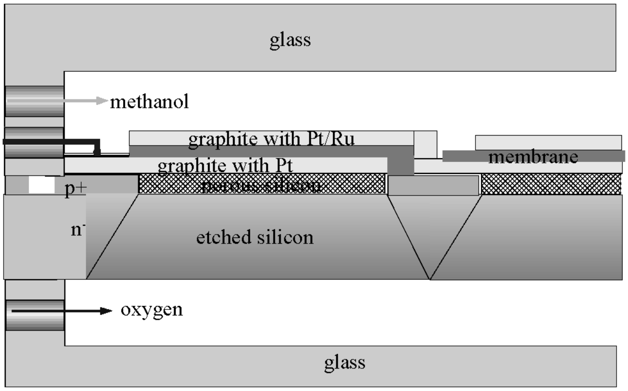

Figure 1. Scheme of a miniaturized fuel cell.

PLASMA POLYMERIZED ELECTROLYTE

For the deposition of the ion-conductive membranes a parallel-plate reactor powered by a 13.56 MHz rf power source is used. To vaporize the liquid vinylphosphonic acid (VPA; $C_2H_5O_3P$), it is stored in a container that is heatable up to 200°C by an oil-bath heater. Tetrafluoroethylene (TFE; C_2F_4) flows through this container, acting as a carrier gas. The gas inlet into the reactor chamber is heated up to a slightly higher temperature than the VPA container, as are the heatable electrodes of the reactor.

The plasma polymerized electrolyte membranes are characterized by means of ac impedance measurements and by infrared (IR) spectroscopy to determine their structure. The ac impedance is measured with an HP 4192A LF impedance analyzer in the frequency range between 150 Hz and 13 MHz. The test assembly consists of two membranes deposited on a glass slide embedding two parallel sputter deposited gold electrodes (2.5 mm × 20 mm × 100 nm, distance 4.4 mm). A tube is glued on top of the assembly and filled with deionized water so that the area of the electrodes is flooded. The electrodes are contacted in a four-point measuring technique. IR spectroscopy characterization is carried out in an attenuated total reflection technique with a 45° KRS-5 crystal and a Perkin Elmer 1800 Fourier transform infrared spectrometer.

To achieve stable membranes with high ion conductivity, the phosphonic acid group has to be preserved in the plasma. Therefore, the power density in the plasma is adjusted so that the polymerization occurs via the π-bonds of the monomers without cracking the bonds in the phosphonic acid group. This guarantees a chemical binding of the phosphonic acid group to the fluorocarbon polymeric backbone of the membrane. By increasing the applied power from 10 W to 30 W the deposition rate increases up to 300 nm/h at 20 W followed by a decrease (Figure 2, left). This indicates an intensified conversion of the monomers in the plasma contributing to the film growth with increasing power, while at powers above 20 W the phosphonic acid groups partially fragmentize in the plasma, yielding denser but thinner films.

This result is confirmed by the ion conductivity of these films (Figure 2, right) determined by ac impedance measurements. At higher power density the ion conductivity decreases due to the formation of polymers with a higher degree of cross-linkage, which hinders the water entering the membrane, especially at lower temperatures, perceptible at the increasing gradient to higher temperatures. Furthermore, the fragmentation of the VPA becomes significant with increasing power, contributing to an additional loss in ion conductivity.

For the application in direct methanol fuel cells operating at about 100°C the plasma polymerized electrolytes should exhibit a temperature

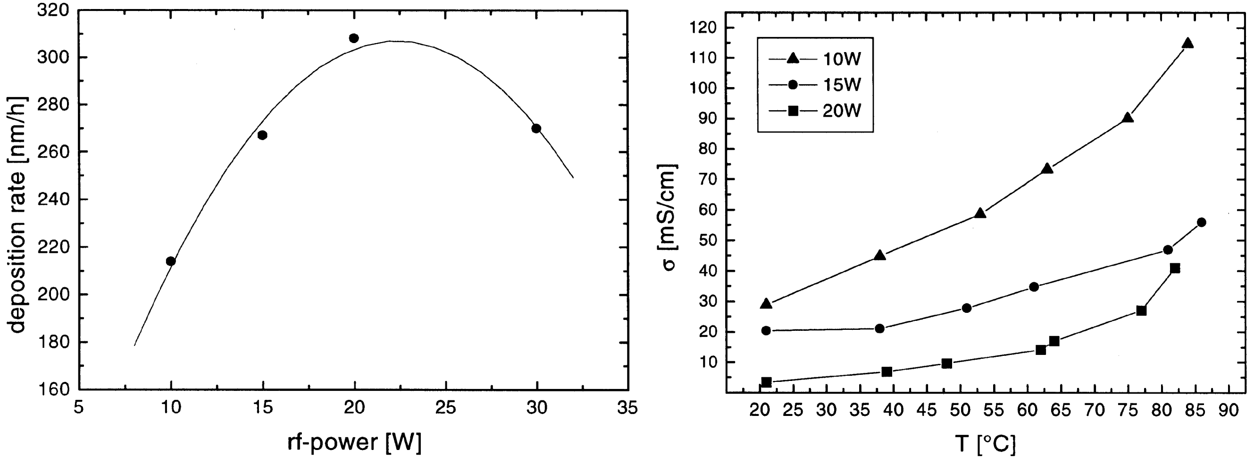

Figure 2. Left: Deposition rate versus power, and right: ion conductivity versus temperature of plasma polymerized electrolytes (5 sccm TFE carrier gas, 3 Pa, 140°C VPA reservoir temperature).

stability up to 200°C. To characterize the membranes' thermal stability they were exposed to 200°C at ambient air and pressure for 45 h, and their structural changes were determined by IR spectroscopy. The spectra shown in Figures 3 and 4, from before and after the temperature treatment, respectively, reveal no significant structural differences for the

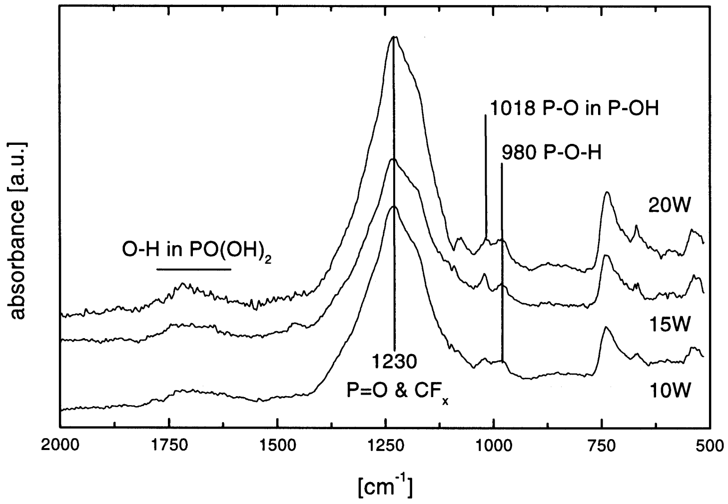

Figure 3. IR spectra of electrolytes deposited at different powers, (5 sccm TFE carrier gas, 3 Pa, 140°C VPA reservoir temperature).

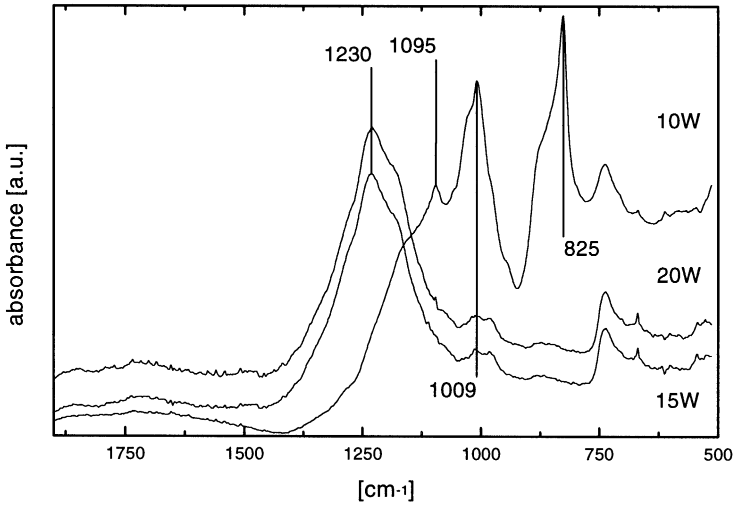

Figure 4. IR spectra of electrolytes deposited at different powers after 45 h at 200°C (5 sccm TFE carrier gas, 3 Pa, 140°C VPA reservoir temperature).

polymer membranes deposited at 15 W and 20 W. However, the 10 W membrane exhibited strong absorption bands at 1095 cm^{-1}(P-O-C and CF in CF_2), 1009 cm^{-1} (P-O in P-OH), and 825 cm^{-1} (P-O-C). This indicates inclusions of unbound VPA in the polymer, which polymerize because of the temperature treatment. Therefore, distinct vibration modes become visible, whereas in the liquid phase the VPA peaks appear less pronounced in one broad absorbance band. Consequently, the power has to be set to values in the range from 15 W to 25 W to ensure the deposition of temperature-stable membranes with a high ion conductivity.

Compared to conventional ion-conductive membranes (e.g., Nafion: $\sigma(80°C) = 140$ mS/cm, 130 μm thickness) the ion conductivity of 50 mS/cm at 80°C of the 15 W plasma polymerized membrane seems to be relatively low. Nevertheless, the necessary membrane thickness of the TFE/VPA-electrolytes of approximately 1 μm results in a drastic decrease of the membrane resistance. Furthermore, the phosphonic acid content and therefore the ion conductivity of the membranes can be increased by adjusting higher VPA reservoir temperatures. Membranes deposited at 170°C and 10 W exhibit an ion conductivity of $\sigma(80°C) = 200$ mS/cm, corresponding to an increase by a factor of 2 compared to membranes deposited at 140°C VPA reservoir temperature. However, the temperature has to be adjusted carefully because of significant spontaneous polymerization of the VPA at elevated temperatures.

PLASMA POLYMERIZED ELECTRODES

For the preparation of thin-film porous graphite electrodes we analyzed different deposition conditions of an acetylene plasma polymerization process in a rf parallel plate reactor. To determine the film structure, IR spectroscopy measurements were carried out. The resistance was measured in a standard four-point measuring technique, and the refractive index was determined by means of ellipsometry. The topography of the films was examined by scanning electron microscopy (SEM).

To achieve a porous structure a high deposition rate should be attained. Therefore a high pressure and maximum available power (300 W) were adjusted to initiate gas phase reactions and a clustered film growth. Pure acetylene atmosphere depositions with the substrate positioned at the cathode led to films with a smooth surface. The IR spectra of these films reveal a high hydrogen content (Figure 5(a)). Films grown at the anode exhibit rough surfaces when deposited with a process pressure of 20 Pa or higher (Figure 6), indicating the desired clustered film growth. However, the films exhibit a high hydrogen content with an increased fraction of sp^3 coordinated carbon-hydrogen bonds compared to the cathodic films (Figure 5(b)). For both types of films insulating

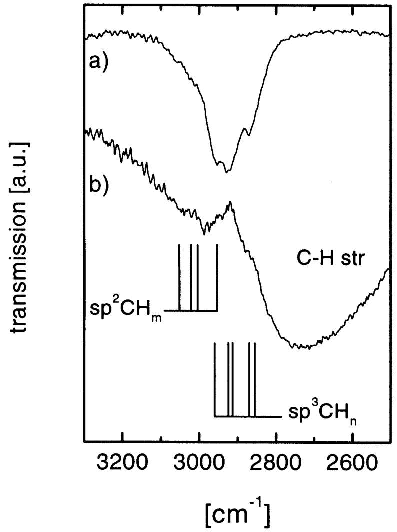

Figure 5. IR spectra of hydrocarbon polymers (300 W, 40 PA, acetylene atmosphere).

behavior was observed. This means that polymeric hydrocarbon films are deposited.

In order to minimize the hydrogen content in the films, oxygen was added to the process atmosphere and the power density was increased by lowering the pressure so that the fragmentation of the monomer is intensified. By increasing the oxygen content in the process atmosphere the amount of hydrogen in the films diminishes, which is more pronounced for the cathodic films as determined by IR measurements.

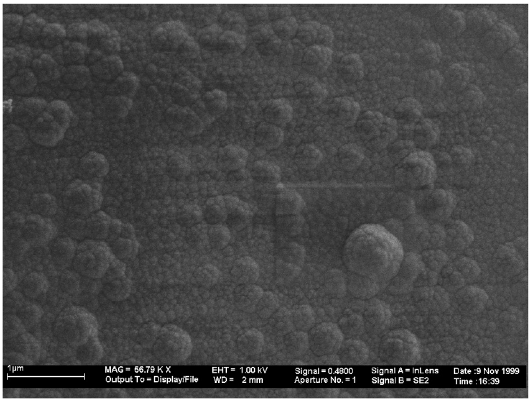

Figure 6. SEM picture of a hydrocarbon polymer (300 W, 20 Pa, acetylene atmosphere).

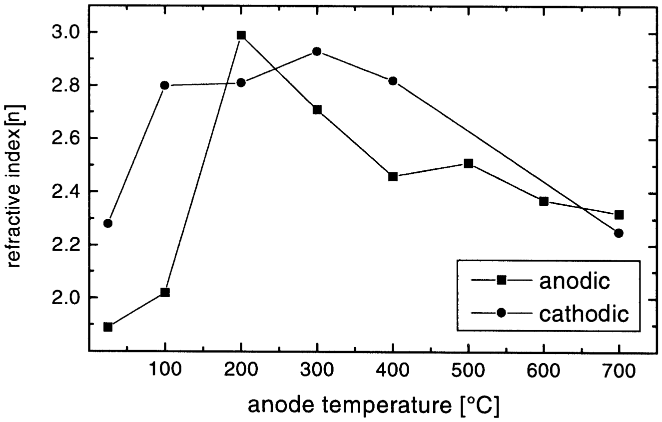

Figure 7. Refractive index of amorphous carbon films deposited at different process temperatures.

With an acetylene/oxygen flow ratio below 2.5, smooth, infrared transparent films are deposited typical of diamond-like carbon films.

Next, the anode temperature was varied from room temperature up to 700°C. The refractive index of films deposited on the anode increases from approximately 2.0 to 3.0 at an anode temperature between 100°C and 200°C and decreases again to 2.3 for higher temperatures, corresponding to an initial change in structure from hydrocarbon polymers to diamond-like films followed by a transition to graphitic layers. The same characteristic occurs for the cathodic deposition but is less pronounced. Due to the higher voltage drop between the plasma and the cathode films with less hydrogen content are achieved at lower anode temperatures. Since only the anode is heated, diamond-like films are deposited on the cathode in a wider temperature range (100–400°C). The resistance of the films deposited at an anode temperature of 500°C is in the order of $10^{-2}\,\Omega\text{m}$ and declines to $440\,\mu\Omega\text{m}$ for the anodic and $11\,\mu\Omega\text{m}$ for the cathodic film at 700°C.

SEM investigations confirm the dependence of the refractive index on the anode temperature. For deposition temperatures up to 300°C smooth surfaces are observed typical for hydrocarbon polymers and diamond-like films. For higher anode temperatures the surface exhibits a rough topography corresponding to an increase of sp^2 hybridized (graphitic) carbon. Porous structures were observed for cathodic films deposited at 700°C anode temperature, as shown in Figure 8.

With an anode temperature of 700°C the deposition of a porous graphite layer is practicable for the electrode on the silicon substrate only because of significant decomposition of the electrolyte at these

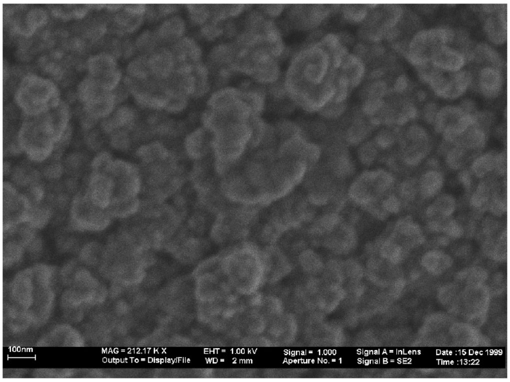

Figure 8. SEM picture of a porous graphite film (300 W, 6 Pa, T = 700°C, 1:1 C_2H_2/O_2 flow ratio).

temperatures. Therefore, the deposition process for the graphite layer on the electrolyte has to be modified to achive lower deposition temperatures. This can be done by applying a dc bias voltage to the anode, which intensifies the ion bombardment on the growing film, resulting in a lower deposition temperature for graphitic layers. Another possibility is the replacement of the graphite electrode on top of the electrolyte by a thin Pt/Ru film, which is permeable to the gaseous reactants and exhibits a suitable electron conductivity. This implies an island growth of the catalyst film with islands in partial contact to each other, which can be attained by a suitable sputtering process.

During the deposition of the graphite electrodes the required catalyst can be incorporated simultaneousely. The applied rf power of 300 W yields to a dc bias voltage exceeding 1000 V at the cathode. Therefore, a high ion bombardment occurs, resulting in sputtered particles from the cathode. To incorporate the required catalysts in the graphite layer, the cathode has to be made of the catalyst material.

CONCLUSION

A plasma polymerized electrolyte for use in miniaturized fuel cells has been developed. The ion conductivity of these membranes can be adjusted between 50 mS/cm and 200 mS/cm (at 80°C) depending on the deposition conditions. Temperature treatments confirm a stable configuration of the membranes up to 200°C. With a typical thickness on the order of 1 μm a drastic reduction in the membrane resistance is achieved compared to conventional membranes in direct methanol fuel cells.

Porous graphite electrodes are deposited with an acetylene plasma polymerization process. The resistance of these electrodes reaches 11 μΩm.

With this deposition technique an incorporation of a desired catalyst during the film growth of the electrodes is possible.

The porous electrode and the plasma polymerized electrolyte can be deposited on different substrates (e.g., silicon wafers, porous foils) to realize a miniaturized fuel cell. In case of a silicon wafer that contains porous silicon areas for the gas feed, the encapsulation is made of Pyrex glass lids.

Our future work will focus on a modified deposition process for a porous graphite layer with a deposition temperature compatible with polymer electrolyte. The Pt and Pt/Ru catalyst layers will be incorporated in the graphite film by taking advantage of the sputtering effects at the cathode during the deposition of the graphite layer or by a subsequent sputtering deposition process. Alternatively a sputtered porous metallic top-electrode could be used instead of the graphite film. With one of those films, complete thin-film membrane electrode assemblies will be deposited to build up miniaturized fuel cells. Furthermore, a characterization of the methanol permeability of the plasma polymerized electrolytes, which is preferably done under fuel cell operation conditions, and a characterization of the optimization of their deposition process with respect to low permeation values will be carried out.

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