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Plasma-polymerized phosphonic acid-based membranes for fuel cell

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ABSTRACT

In the highly competitive market of fuel cells, proton exchange membrane fuel cells operating in the range of 80–150 °C seem quite promising. One of the main hurdles for the emergence of such a technology is the development of phosphonic acid-based membranes characterized by high conductivity and stability beyond 80 °C. In this work, plasma polymers containing phosphonic acid groups have been successfully prepared using dimethyl allylphosphonate as a single precursor. Structural and transport properties of plasma polymers are logically correlated with the plasma discharge power. Under optimized plasma conditions, plasma films are thermally stable up to 150 °C and present the highest growth rate, concentration of ion exchange groups and proton conductivity, which make them competitive as membranes for fuel cells.

1. Introduction

Fuel cells are energy converters considered as an attractive solution to the rising price of fossil fuels, the increase of greenhouse gas emissions and the growing dominance of electricity [1,2]. Proton exchange membrane fuel cells (PEMFCs) are one of the most attractive fuel cells; it is a blooming technology that has recently attracted great interest for future energy supply in several areas like stationary, transportation, portable and micro fuel cell applications, due to its rapid start-up time, high power density, energy efficiency and low sensitivity to orientation [3,4].

PEMFCs commonly use perfluorosulfonic membrane commercialized by Du Pont de Nemours society (Nafion®) as electrolyte membrane. Several specific advantages of Nafion® have been demonstrated such as excellent chemical, mechanical, and thermal stabilities as well as high proton conductivity (90–120 mS cm^{-1} in the range of 25–80 °C) [5–7]. However, the dependence of Nafion® proton transport mechanism on water causes its poor conductivity at temperature above 80 °C and then motivates the search for a membrane which combines high proton conductivity and chemical stability at high temperature (>80 °C) or under low relative humidity [8–10]. Membranes based on phosphonic acid groups are good candidates for fuel cell operating at intermediate temperatures (80–150 °C) [11]. Indeed, $–PO_3H_2$ groups are amphoteric and possess a relatively high dielectric constant. The combination of these properties leads to a high degree of autodissociation which favors the formation of a hydrogen-bonding network making the proton conductivity independent of temperature and relative humidity, which eventually allows the proton transport through an anhydrous conduction mechanism, also known as the Grotthuss mechanism [12]. So the main interest of phosphonic acid-based electrolyte membranes is their high proton conductivity in dry conditions, that is to say at intermediate temperatures (80–150 °C) and low relative humidity, which are suitable conditions for the intended application. Schuster et al. have compared different protogenic groups including sulfonic acid, phosphonic acid and imidazole; they have concluded that the phosphonic acid group is the most suitable proton conductor at temperatures between 120 °C and 160 °C [13].

Most researchers have synthesized phosphonic acid functionalized membranes (polymeric, inorganic or composite ones) by conventional methods such as traditional polymerization and sol–gel technique, implemented separately or coupled [14–16]. According to the literature, phosphonic acid functionalized polymers exhibit promising performance in terms of physicochemical and transport properties. Indeed, at high temperature (up to 90 °C) and low relative humidity (30% RH), values of proton conductivity and ionic exchange capacity in the range of 0.0026–30 mS cm^{-1} and 1.38–4.64 meq g^{-1}, respectively, have been found [17–20]. In addition to these traditional approaches, the plasma-enhanced chemical vapor deposition (PE-CVD), also called plasma polymerization in the case of an organic compound as a precursor, has been very recently envisaged; it is a promising

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technique using a glow discharge to polymerize any kind of precursor [21]. Plasma polymerization allows the deposition of dense, uniform and defect-free thin films on the surface of a mechanical substrate. The highly cross-linked structure of plasma polymers gives them very good chemical and thermal stabilities and a very low permeability to organic liquids [22]. Plasma polymers mentioned in the literature as potential electrolyte membranes for PEMFCs generally contain sulfonic acid groups as proton exchange functions [23–26]. Up to now, only one paper has mentioned the preparation of phosphorus doped plasma membranes obtained from a mixture of SiH_4, PH_3 and N_2O [27]. Moreover, all plasma polymers mentioned in the literature as potential electrolyte membranes for PEMFCs have been prepared from at least two precursors, one being a hydrocarbon-based monomer (fluorocarbons, vinylbenzene, styrene, etc.) constituting the main chains of the polymer matrix, the other one being a functional precursor (very often trifluoromethane sulfonic acid) providing the proton conductive groups [22–27]. No author mentions the manufacture of fuel cell plasma membrane using one single precursor.

Here we report the preparation of plasma polymerized films based on phosphonic acid groups using dimethyl allylphosphonate as a single precursor. Six different membranes have been deposited changing the plasma discharge power in the plasma polymerization process. The prepared membranes have been characterized in terms of morphology and thickness by scanning electron microscopy (SEM), density by X-ray reflectometry (XRR), chemical composition by Fourier transform infra-red spectrometry (FTIR), energy dispersive X-ray microscopy (EDX) and X-ray photoelectron spectroscopy (XPS), thermal stability by thermogravimetric analysis (TGA), ion exchange capacity (IEC), and proton conductivity properties by electrochemical impedance spectroscopy (EIS). In addition, measurements of diffusion permeability to methanol, ethanol and glycerol (as potential fuels for fuel cell) have been performed using a Hittorf diffusion cell coupled with infrared spectroscopy. The aim of our work is to demonstrate the feasibility to prepare phosphonic acid-based membranes by plasma polymerization using dimethyl allylphosphonate as a single precursor and to investigate the influence of the plasma discharge power on the plasma polymer properties in order to establish correlations between the plasma conditions, the microstructural characteristics of the synthesized thin films (morphology, density, chemical structure) and their transport properties (proton conductivity and fuel permeability).

2. Experimental section

2.1. Membranes preparation

Using dimethyl allylphosphonate ([757-54-0], SP-61-001, supplied by SPECIFIC POLYMERS, Montpellier, France) as a single precursor, a series of plasma polymerized films was prepared in a 30 L commercial capacitively coupled plasma reactor built by MECA2000, pumped through a turbomolecular pump (Adixen Pascal 2015 SD coupled with a Boc Edwards EXC 120 module) for pre-treatment high vacuum and a primary pump (Adixen Pascal 2015 SD) for the plasma deposition [28]. A liquid nitrogen trap was positioned between the plasma chamber and the primary pump in order to trap the unreacted precursor and fragment vapors. The pressure inside the chamber was sensed and monitored, respectively, by a Leybold Vakuum Ceravak gauge and Edwards Speedivalve valve. A 13.56 MHz radiofrequency (RF) source (Dressler CESAR 136) was used to supply power to the parallel and vertical plate electrodes (gap between both electrodes: 2 cm). The RF and grounded electrodes were disk electrodes (10 cm diameter) being, respectively, immovable and rotative (speed: 6.98 rad s^{-1}). Argon (Air liquid, purity $>99.999\%$), used as treatment or carrier gas, was fed into the system via a UNIT Instruments Inc. (UFC1000) gas flow meter. The precursor was contained in a flask maintained at a temperature of 70 °C. The stainless steel pipe between the precursor flask and the reactor was maintained at a temperature of 80 °C, to avoid precursor condensation in the pipe.

The different substrates used to support plasma-polymerized films were: silicon wafer (Boron doped, type p, Si (1 0 0), resistivity: 1–50 Ω), Nafion®211 and polytetrafluoroethylene (PTFE) for SEM observations, glass wafer for density measurement by XRR, silicon wafer for investigation of chemistry composition (by FTIR, EDX and XPS), Nafion®211 for conductivity measurements and PTFE for IEC and fuel diffusion measurements. A 15 min long plasma pre-treatment of supports was implemented before plasma polymerization using argon as gaseous phase (argon flow rate: 24 sccm, discharge power: 100 W), in order to improve plasma film adherence. Fixed plasma parameters during plasma polymerization were: argon flow rate equal to 3 sccm (argon is here a carrier gas; precursor flow rate is not known), total pressure equal to 2×10^{-1} mbar, deposition duration equal to 1 h. The only variable plasma parameter during plasma polymerization was the continuous plasma discharge power (W) in the range of 20 W–100 W. After plasma deposition, films were post-treated for 15 min using argon as gaseous phase (argon flow rate: 24 sccm, discharge power: 100 W), in order to stabilize the film surface.

2.2. Membrane characterizations

2.2.1. SEM for films morphology and thickness

The cross section and surface of plasma polymers were observed using two different scanning electron microscopes, Hitachi S-4800 and Hitachi S-4500, to estimate the thickness d (error $\approx$ 10%) and examine the morphology, respectively. Before analysis, plasma films deposited onto Nafion®211 and PTFE were immersed in liquid nitrogen and broken in order to have a neat cut of the samples' cross-section, and all the samples (whatever the support may be) were stuck with double faced tape on microscope support and Pt-metalized by sputtering under vacuum.

2.2.2. X-ray reflectometry (XRR) for film's density

XRR technique (implemented on a Siemens/Bruker D5000 laboratory diffractometer) was used to investigate the film's density (error ≈ 0.05 g cm^{-3}). The analysis procedure is detailed in a previous paper by our group [28].

2.2.3. FTIR, EDX and XPS for film's chemical composition

The chemical composition of the plasma polymers deposited on silicon wafer was determined qualitatively by FTIR spectroscopy on a Nicolet 710 FT-IR spectrometer (wavenumbers range: 4000–400 cm^{-1}; scans number per sample: 64; resolution: 4 cm^{-1}) and quantitatively by XPS on an ESCALAB 250 from Thermo Electron (monochromatic source of Aluminum 1486.6 eV; diameter of the analyzed surface: 400 μm) and by EDX with a scanning electron microscope (S-4500 Hitachi). The XPS analysis procedure is detailed in a previous paper by our group [22]. EDX and XPS are complementary techniques on two accounts. Firstly, the EDX analysis (covering a material volume of 1 μm^3) enables us to investigate the bulk of films, whereas the XPS analysis (limited to an analysis depth of 10 nm) gives information on the surface composition. Secondly, the EDX analysis only gives the chemical composition in elemental atomic percentages (error $\approx$ 2 at%), whereas XPS also gives quantitative information on atomic chemical environments (error $\approx$ 10 at%).