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Short communication

Chitosan–phosphotungstic acid complex as membranes for low temperature H_2–O_2 fuel cell

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HIGHLIGHTS

- Freestanding chitosan/$H_3PW_{12}O_{40}$ membranes were made by in situ ionotropic gelation.
- Open circuit potential was up to 0.95 V using such membranes in H_2–O_2 PEMFC at 25 °C.
- A maximum power density of 350 mW cm^{-2} was obtained at 25 °C.
- The conductivity of the membrane was up to 18 mS cm^{-1}.

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ABSTRACT

Free-standing Chitosan/phosphotungstic acid polyelectrolyte membranes were prepared by an easy and fast in-situ ionotropic gelation process performed at room temperature. Scanning electron microscopy was employed to study their morphological features and their thickness as a function of the chitosan concentration. The membrane was tested as proton conductor in low temperature H_2–O_2 fuel cell allowing to get peak power densities up to 350 mW cm^{-2}. Electrochemical impedance measurements allowed to estimate a polyelectrolyte conductivity of 18 mS cm^{-1}.

1. Introduction

Chitosan (CS) is the N-deacetylated derivative of chitin, which is a cationic linear polysaccharide usually obtained by alkaline deacetylation of crustacean chitin and represents the second most abundant natural polymer. Due to its excellent properties, such as biocompatibility, biodegradability, non-toxicity, low-cost chitosan has found many applications in industrial areas. As cationic polyelectrolyte, CS can react with various natural and synthetic anionic species or anionic polyelectrolytes to form polyelectrolyte complexes (PECs). These complexes are generally water insoluble and make hydrogel. The gelation process is mainly related to the formation of ionic interactions between the cationic chitosan and negatively charged polyanion counterparts [1–3].

Heteropolyacids (HPAs) are strong Bronsted acid as well as solid electrolytes [4] and are considered promising materials in the fabrication of organic–inorganic nanocomposite membranes for fuel cell thanks to their high proton conductivity [5–8]. The major problems in using HPAs in fuel cell are their solubility in water and low mechanical strength, which might result in decline in cell performance with time [9–13]. To overcome this problem, it has been proposed to prepare CS and HPAs polyelectrolyte films to be employed as proton exchange membrane in low temperature fuel cell, since such PECs are reported to be insoluble [4]. A survey of the already published works showed that CS based PECs produced have been tested in direct methanol [5–8,14,15], in borohydride [16] and hydrogen [17] fed fuel cells. In the last case very poor performances were obtained due to a very low proton conductivity of the membrane.

In this paper we propose a novel procedure to fabricate homogeneous CS-HPA polyelectrolyte films using phosphotungstate acid

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(PTA) as cross-linking agent. In order to prepare flat and homogeneous membrane of controlled thickness, a porous mean, i.e. anodic alumina membrane (AAM), was firstly impregnated by PTA and then immersed in a CS containing aqueous solution to release the acid and induce the in situ gelation of chitosan [18,19]. The reaction between CS chains and PTA retained by the pores allows fabrication PEC thin films on AAM surface, that can be easily peeled off from the support, cut to any size and shape. The obtained membranes were tested in a H_2/O_2 fuel cell working at low temperature (25 °C), low humidity ($T_{gas} = 25$ °C) and Pt loading of 1 mg cm^{-2}. Impedance Spectroscopy was used to get information of the conductivity of the membrane as well as to model the overall electrical behaviour of the cell.

2. Experimental

Chitosan/PTA films were grown through ionotropic gelation by using commercial AAM (Anodisc-47 Whatman, pore diameters 200 nm, porosity 43% and thickness 50 μm) as support. Chitosan powder, acetic acid and $H_3PW_{12}O_{40} \times H_2O$ were supplied by Sigma–Aldrich.

CS powder (1, 2 and 3% w/v), acetic acid (2% w/v) and distilled water were mixed to achieve CS protonation and thus, solubilization. Solutions were stirred for 24 h before use and then put in contact for 30 s with PTA impregnated AAM, as depicted in Fig. 1a, in order to induce cross-linking reaction and, thus, chitosan membrane formation (see Fig. 1b and c).

Scanning Electron Microscopy analysis was performed by using a Philips XL30 ESEM coupled with EDX equipment.

The composite membranes prepared were sandwiched between two carbon paper electrodes (Toray 40% wet Proofed-E-Tek), covered with a mixture Pt black/C black (30% Pt on Vulcan XC-72, E-Tek) stirred in n-butyl acetate for at least 3 h. The catalyst loading was 1 mg cm^{-2} of platinum. The active area (2 cm^2) was delimited by insulating silicon rubber. The Membrane Electrode Assembly (MEA) was then assembled in a single fuel cell apparatus (Fuel Cell Technologies, Inc.) and fed with dry oxygen (99.5% purity, 1 bar), and hydrogen (99.5% purity, 1 bar) humidified at room temperature. Polarization curves were obtained by using a h-tec Fuel Cell Monitor (item 1950). The current density reported in the following are referred to the apparent area (2 cm^2).

Electrochemical Impedance Spectroscopy measurements were carried out through a Parstat 2263 potentiostat equipped with an Impedance Analyzer directly connected to the fuel cell. The impedance spectra were recorded in the range 10 kHz–0.1 Hz at 25 °C and open circuit potential with an ac amplitude of 10 mV. Before each measurement, the fuel cell was stabilized for at least 15 min. The Data analysis and equivalent circuit fitting were carried out through a Power Suite and a ZSimpleWin softwares.

3. Results and discussion

Chitosan solutions were prepared by dissolving CS powder in 2% w/v acetic aqueous electrolyte. CS, insoluble at neutral pH, becomes soluble at slightly acidic pH due to protonation of the NH_2 groups, according to the following reaction:

$$CS - NH_2 + CH_3COOH \rightarrow CS - NH_3^+ + CH_3COO^- \tag{1}$$

where CS-NH_2 is the chitosan under insoluble form, and CS-NH_3^+ is the protonated chitosan, soluble in water. Thus, in presence of acetic acid, the polymer behaves like a cationic polyelectrolyte, as illustrated in Fig. 1b, and can be ionically cross-linked by anionic species. Since highly concentrated PTA aqueous solution (0.38 M in this work) contains $(PW_{12}O_{40})^{3-}$ anions (lacunary or defective Keggin ions are not present, see Ref. [20]), once these two solutions are put in contact crosslinking reactions are expected to take place allowing the occurrence of in situ gelation processes. As can be appreciated in Fig. 1a if the crosslinking is pushed to take place on AAM thanks to electrolyte retained by the pores, it is possible to prepare flat and freestanding thin CS-PTA membranes (see Fig. 1c). The polyelectrolyte complexes gel is formed by cross-link of CS chains through the interaction of cationic amino groups of CS and Keggin anions (polyphosphotungstate) according to:

$$(PW_{12}O_{40})^{3-} + 3\left(CS - NH_3^+\right) \rightarrow (PW_{12}O_{40})^{3-}\left[CS - NH_3^+\right]_3 \tag{2}$$

In order to favour the interactions between PTA^{3-} and NH_3^+ groups, once formed films were kept immersed in 0.38 M PTA solution for 24 h (functionalization). The morphologies of polyelectrolyte CS/PTA membranes were investigated by scanning

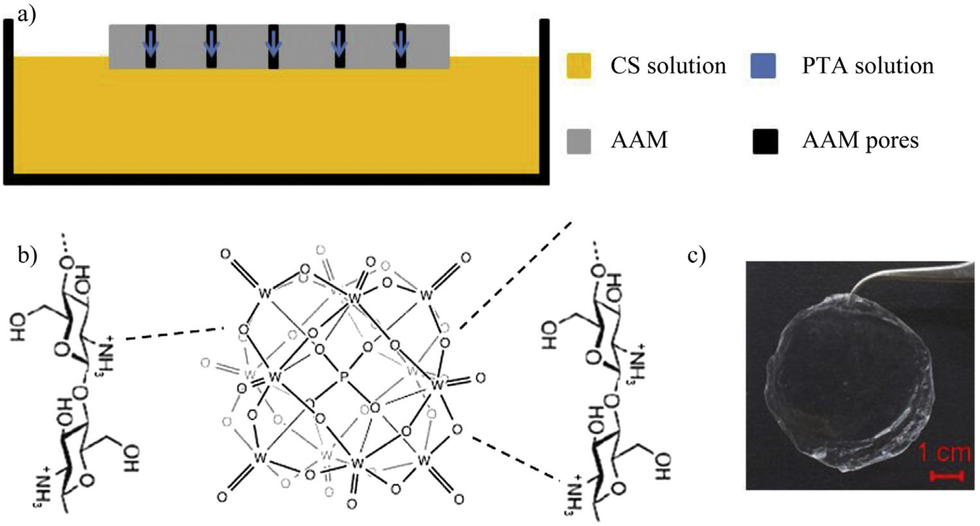

Fig. 1. a) Scheme of the contact between CS solution and PTA through the AAM pores, b) cross-linking of the CS thanks to the anionic specie PTA^{3-}, c) picture of the membrane soon after fabrication.