



# Protonic conductivity and fuel cell tests of nanocomposite membranes based on bacterial cellulose



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## ARTICLE INFO

### Article history:

Received 1 November 2016  
Received in revised form 2 February 2017  
Accepted 26 February 2017  
Available online 6 March 2017

### Keywords:

Bacterial cellulose  
poly(4-styrene sulfonic acid)  
Nanocomposite membrane  
Protonic conductivity  
Fuel cell

## ABSTRACT

The effect of the preferential orientation of supporting bacterial cellulose (BC) nanofibrils on the conductivity of composite proton conducting electrolytes with poly(4-styrene sulfonic acid) (PSSA) is reported. Data obtained by impedance spectroscopy show that the in-plane conductivity at 40% relative humidity (RH) is more than half order of magnitude higher than that measured through-plane, indicating significant discontinuity of proton transport at the PSSA/BC interface. The difference becomes less than 20% in nearly saturated conditions (98% RH), demonstrating the key role of water in ensuring proton transport through those interfaces. The negative impact of the conductivity anisotropy in fuel cell performance is mitigated due to operation in wet conditions and fuel cell tests of PSSA/BC-based membrane electrode assemblies under humidified hydrogen/air gradients at room temperature yield 40 mW cm<sup>-2</sup> at 125 mA cm<sup>-2</sup>, which is amongst the highest values reported for a biopolymer-based electrolyte. It also results from the presented investigation that conventional electrode preparation used for thermoplastic polymer electrolytes must be modified in order to ensure proper adhesion to BC-based MEAs and thus to lower polarization losses.

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## 1. Introduction

The research associated with polymer electrolyte fuel cells is extensive, as emphasized by a large number of original scientific papers, reviews and books [1–23]. However, only a small number of studies have addressed the use of alternative bio-based materials to replace the state-of-the-art perfluorinated sulfonic acid membranes (PFSA) [6]. Bacterial cellulose (BC) is a highly pure and crystalline form of cellulose with a tridimensional nanofibrillar structure allying an intrinsic “green” character with excellent thermo-mechanical stability and low hydrogen

permeation [24]. Evans and co-workers were the first (in 2003) to recognise the potential of this biopolymer as an alternative to PFSA's such as Nafion<sup>®</sup> [12], and the interest has recently started to grow, either as a mechanical reinforcement for another phase of high protonic conductivity, e.g. polymers such as poly(4-styrene sulfonic acid) (PSSA), Nafion<sup>®</sup>, poly(methacryloyloxyethyl phosphate) (see [16,19,25,26] and references therein), simple mixtures with phosphotungstic, phosphoric or phytic acids [11,14], and also as a single phase membrane grafted with 2-Acrylamido-2-methyl-1-propanesulfonic acid functional groups [10]. Recently, Bayer et al. reported fuel cells based on membranes of cellulose nanofibers (CNF) and cellulose nanocrystals (CNC), which like BC are highly crystalline forms of cellulose but, instead of the bacterial origin, are obtained by purification of vegetable cellulose fibre pulps in order to remove lignin or pectin impurities (in the case of CNFs), as well as to dissolve the amorphous regions (in CNCs) [27]. The authors report a protonic conductivity of ~10 μS cm<sup>-1</sup> for CNF membranes at room temperature and 100% RH, which is remarkably similar to what we have measured for BC [16], thus

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confirming the strong resemblance between CNFs and BC. CNCs are more conductive ( $\sim 500 \mu\text{S cm}^{-1}$ ) due to the presence of sulfuric acid groups introduced during acid hydrolysis. In fact, the excellent mechanical properties of nano-crystalline cellulose are severely affected by the hydrolysis and the CNC membranes are brittle. In addition, they are easily dispersed in water [27], which may also preclude their long-term use in a fuel cell where water is the reaction product.

The overall performance of fuel cells based on those BC-based membranes is lacking behind other massively studied materials such as Nafion<sup>®</sup>. This is partly due to the significant electrode polarization, which is apparent in the I-V curves reported in the various aforementioned cases, or may also result from the anisotropic microstructure of these membranes. The latter effect has not been studied so far, and yet the strong alignment of the BC nanofibrillar layers with the plane of the membrane is likely to favour proton transport along that direction, whereas the layer-to-layer contact resistance should lead to a lower conductivity through the plane of the membrane. Moreover, in the case of BC composites, the distribution of the second conducting phase is likely to occupy the BC interlayer space, thus displaying regions of preferential orientation along the membrane plane with enhanced proton transport.

This paper resumes our previous work on PSSA/BC composite membranes [16] to assess the effect of the preferential orientation of the host BC nanofibrils and of the PSSA bulk domains along the membrane plane on both the protonic conductivity and in the performance of air/hydrogen fuel cells, thus also demonstrating their technological application.

## 2. Materials and Methods

### 2.1. Chemicals and materials

Sodium 4-styrene sulfonate (NaSS,  $\geq 90\%$ , Aldrich), potassium persulfate (KPS, 98%, Panreac), poly(ethylene glycol) diacrylate

(PEGDA,  $M_n$  258, Aldrich) were used as received without any further purification. Other chemicals and solvents were of laboratory grades. Bacterial cellulose (BC) (tridimensional network of nano and microfibrils with 10–200 nm width) in the form of wet membranes was produced in our laboratory using the *Gluconacetobacter sacchari* bacterial strain [28] and following established culture procedures [29].

### 2.2. Preparation and characterization of PSSA/BC membranes

Nanocomposite membranes of PSSA/BC were prepared according to the scheme in Fig. 1, following the procedure reported in our previous study.[16]

Briefly, wet BC membranes with 40% water content ( $\sim 400$  mg dry weight) were placed in Erlenmeyers stoppered with rubber septa and purged with nitrogen. Simultaneously, aqueous solutions of NaSS, KPS (1.2%, w/w relative to monomer) and PEGDA were prepared (Table 1) and transferred with a syringe to the Erlenmeyers containing the drained BC membranes. After the complete incorporation of the solutions, the reaction mixtures were placed in an oil bath at  $70^\circ\text{C}$  during 6 h. The nanocomposite membranes were then repeatedly washed with water and dried at  $40^\circ\text{C}$  in a ventilated oven for 12 h, before being converted into the acid form by ionic exchanging with an aqueous solution of 0.5 M HCl for 24 h at room temperature. The acidic membranes were again washed with distilled water following the above mentioned protocol, dried at  $40^\circ\text{C}$ , and kept in desiccators until their use. All experiments were performed in triplicate and analysed in the form of thin nanocomposite membranes.

The ion exchange capacity (IEC) of the membranes was determined by the usual back titration method after immersion of the membranes in an aqueous 0.1 M NaCl solution for 24 h. The water uptake of the membranes was also assessed by usual procedures and expressed as the fractional increase of weight from a dry condition and after immersion in distilled water for 24 h. Details can be found in [16]. Scanning electron microscopy (SEM)



Fig. 1. Scheme of fabrication of the nanocomposite membranes.

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