



Synthesis of transport layers with controlled anisotropy and application thereof to study proton exchange membrane fuel cell performance



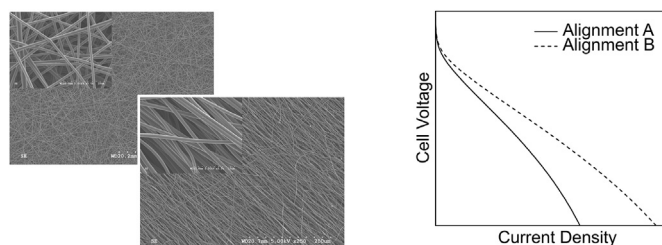
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HIGHLIGHTS

- Novel PEM fuel cell transport layers with controlled anisotropy are presented.
- Electrospinning enables transport layers with progressive fibre alignment.
- Preferential fibre alignment creates anisotropic transport properties.
- Anisotropy is confirmed qualitatively (SEM) and quantitatively (resistivity).
- Electrospun layers are applied to probe effect of anisotropy upon cell performance.

GRAPHICAL ABSTRACT



Anisotropic Transport Layer Synthesis → Fuel Cell Performance Diagnostic

ARTICLE INFO

Article history:

Received 12 November 2015

Received in revised form

5 February 2016

Accepted 8 February 2016

Available online 19 February 2016

Keywords:

Fuel cell
Anisotropy
Transport layer
Electrospinning
Fibre
Resistivity

ABSTRACT

We report on a novel method for the synthesis of fibre-based proton exchange membrane (PEM) fuel cell porous transport layers (PTLs) with controllable fibre alignment. We also report the first application of such layers as diagnostics tools to probe the effect of within-plane PTL anisotropy upon PEM fuel cell performance. These structures are realized via adaptation of electrospinning technology. Electrospun layers with progressive anisotropy magnitude are produced and evaluated. This novel approach is distinguished from the state-of-the-art because an equivalent study using commercially available materials is impossible due to lack of structurally similar substrates with different anisotropies. The anisotropy is visualized via scanning electron microscopy, and quantified using electrical resistivity. The capacity is demonstrated to achieve fibre alignment, and the associated impact on transport properties. A framework is presented for assessing the in-situ performance, whereby transport layer orientation versus bipolar plate flow-field geometry is manipulated. While an effect upon the commercial baseline cannot be discerned, electrospun transport layers with greater anisotropy magnitude suggest greater sensitivity to orientation; where greater performance is obtained with fibres cross-aligned to flow-field channels. Our approach of electrospun transport enables deterministic structures by which fuel cell performance can be explained and optimized.

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1. Introduction

Proton exchange membrane (PEM) fuel cell systems command attention in the nascent hydrogen energy paradigm. The

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membrane electrode assembly (MEA) is the critical component which facilitates the chemical to electrical energy transformation. MEAs themselves comprise multiple (sub-) functional layers; of which the porous transport layer (PTL) is one. The PTLs are interposed between catalyst layer and bipolar plates, and between them mediate energy and mass-transport. As the PEM fuel cell industry moves towards production emphasis, there is a growing demand for refined characterization and optimization capabilities at material, cell, and system levels.

Contemporary PTL research comprises: the characterization of ex-situ structural and transport properties, and the in-situ description of water-transport phenomena. Generally, these efforts draw from a limited pool of commercial PTL products; often derived from carbon fibre papers. Compared to catalyst layer or membrane synthesis research, few transport layer studies have investigated unconventional structures or synthesis paths.

Functional (planar) layers within the fuel cell can demonstrate anisotropic material behaviour; overt may be property differences between through-plane and in-plane directions, more subtle is the possibility of different principal components within in-plane. The latter case is demonstrable in fibre-based porous transport media [1–3]. Furthermore, PEM fuel cells exhibit operational inhomogeneities; these may occur at flow-field land-to-groove scale, or at the active area scale [4–6]. The literature, experimental and modelling, which acknowledges fuel cell material anisotropy is sparse.

We report on an experimental investigation of transport layer anisotropy implications upon PEM fuel cell performance. We escape the restrictions imposed by limited transport layer permutations by leveraging electrospinning synthesis. Our previous efforts demonstrated proof-of-concept of this approach for synthesizing transport layers [7]. In this study, the technology is employed to create structures with controlled in-plane anisotropic structures. Our two-fold aim is to further the viability of electrospinning: as a means of creating rationally designed transport media; and also as a diagnostics tool to elucidate the PEM fuel cell structure-property-performance relationship.

2. Background

Three directions may be used to resolve the properties of fibre-based transport layers: within-plane are fibre aligned (FAD) and cross (FXD) directions; and through-plane direction. The transport layers interface with adjacent functional layers within the fuel cell: catalyst layer or microporous layer (MPL), and bipolar plate flow-field channels. Owing to different transport characteristics along different directions, by rotating a transport layer a performance effect may be anticipated. Assuming isotropy of the catalyst layer (or MPL), transport layer orientation within the cell can be described by the alignment of FAD versus flow-field channel

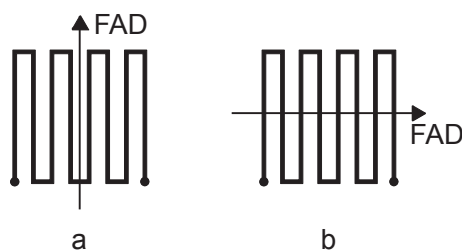


Fig. 1. Illustration of transport layer anisotropy orientation versus flow-field channel geometry. With transport layer FAD either aligned (a) or rotated 90° for cross-aligned (b).

geometry. Fig. 1 illustrates this study's definitions of aligned and cross-aligned orientations.

The effects of transport layer in-plane anisotropy may manifest within its bulk and/or at the interfaces with adjacent layers. Furthermore, transport layer anisotropy may interact with the operational inhomogeneities at the land-channel and/or active area length scales. While the former is relatively more studied (e.g. in unit cell modelling), implications of the latter may develop as commercial systems move towards higher aspect ratio designs. There is presently no consensus on which mechanisms determine the contribution to cell performance, nor if said contribution is significant in magnitude. Fig. 2 illustrates possible mechanisms.

Han et al. investigated the relation between anisotropic PTL bending stiffness and PEM fuel cell performance [8]. Ex-situ, they measured a greater bending stiffness in the machine direction versus the cross machine direction. In-situ, they tested both aligned and cross-aligned transport layer orientations; a consistently lower high-frequency resistance for the cross-aligned configuration produced better performance. Han et al. attributed this to delamination between the PTL and catalyst layer caused by PTL bending from non-continuous bipolar plate contact, whereby the PTL orientation which better resisted the bending yielded less delamination (and flow-field channel intrusion). Soe Naing et al. investigated the role of PTL orientation from a water management perspective [9], using a visually accessible cell to monitor in-situ liquid water motion at the cathode. They observed smoother water removal for the cross-aligned PTL configuration. Additionally, a second cell platform was used to freeze water in-situ. Imagery suggested greater water saturation of PTLs below lands for aligned configurations, and a more even land-to-channel distribution for the cross-aligned configuration. Soe Naing et al. attributed their orientation dependent cell performance to this difference in liquid water saturation. Additional performance influences may derive from preferential in-plane transport for: reactants [2], charge [1,3], and heat [10].

The aforementioned studies are encumbered by limited selection of commercial PTL products. Soe Naing et al. reported results for one substrate, while Han et al. reported for a pair each of papers and felts. To probe the influence of transport layer orientation, it may be desirable to evaluate substrates with differing magnitudes of in-plane fibre alignment. Selecting commercial paper and felt substrates might offer two points on this spectrum, but there is no progression in between. Moreover, the morphology between these substrates is so strikingly different, that it may not be prudent to amalgamate results.

Electrospinning offers a synthesis path for producing fibre-based layers not unlike commercial PEM fuel cell PTLs [7]. Electrospinning is a procedure whereby a polymer solution (or melt) is drawn by an electric field from a capillary tip onto a target. The technology is attractive because manipulations of solution, spinning, or hardware configurations can effect different product layer morphology [11]. Methods of creating aligned fibre mats are reported in the literature; these are broadly classified into methods acting mechanically (e.g. rotating drum target) or via electric field perturbation (e.g. parallel strip target). Teo and Ramakrishna offer an illustrated review in Ref. [12]. In the present study we use the high-speed drum target technique. This permits us to generate layers of consistent general appearance with progressively greater alignment as drum rotation speed is increased—and escapes the major limitation of using commercial substrates. Alignment within our layers is quantified by an electronic resistivity approach. Current may transport preferentially along fibre versus across adjacent fibres, so a higher FXD value is predicted versus the FAD result. This approach is supported by analogous work by Kok and Gostick, who studied the in-plane permeabilities of electrospun membranes [13].

Our study is distinguished by application of our novel PEM fuel

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