Solid State Ionics 424 (2025) 116852

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

New proton exchange membranes based on ionic liquid doped chitosan

Naima Naffati [a], Fátima C. Teixeira [a], António P.S. Teixeira [b], C.M. Rangel [a,*]

[a] Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

[b] Departamento de Ciências Médicas e da Saúde, ESDH & LAQV- REQUIMTE, IIFA, Universidade de Évora, R. Romão Ramalho, 59, 7000-671 Évora, Portugal

ARTICLE INFO

Keywords:
Proton exchange membranes
Chitosan membranes
Ionic liquids
Fuel cells
Electrolyser

ABSTRACT

The development of new proton exchange membranes (PEM) for electrochemical devices have attracted researcher's attention in the pursuit for more sustainable and cost-effective technologies for clean energy production and conversion. In this work, new doped chitosan (CS) membranes were prepared by the casting method. Chitosan is an abundant, biodegradable and non-toxic material, and as a membrane, a sustainable and cheaper alternative to those perfluorinated and commonly used, such as Nafion. Three different ionic liquids were employed as dopants, ([EMIM][OTf], [EMIM][FSI] and [MIMH][HSO_4]), in various concentrations and up to 50 wt% load. The new membranes were characterized by ATR-FTIR, thermogravimetry, using TGA and DSC techniques to assess their thermal properties, and by SEM, to analyse their surface morphology. Proton conduction properties of the new membranes were assessed by Electrochemical Impedance Spectroscopy (EIS). The new doped membranes showed an increase in the proton conduction compared with pristine chitosan membranes. The incorporation of ionic liquids into chitosan membranes improved their proton conductivity and thermal properties, with [EMIM][OTf] and [MIMH][HSO_4] showing the most promising results. A 2-fold increment in the proton conduction was generally observed with the increase of the temperature from 30 to 60 °C. The best proton conductivity was found at 60 °C for the membrane doped with [EMIM][OTf], with a value of 47 $mS.cm^{-1}$.

1. Introduction

The pursuit for new advances in clean, renewable and environmentally friendly energy technologies is a major demanding scientific endeavour. To fulfil this societal ambition, significant efforts are being made in the development of associated technologies promoting the interest on new and better components and cost-effective solutions [1–4]. Electrochemical devices, such as fuel cells and electrolysers, including CO_2 electrolysers, assume an important role in clean energy technologies contributing to the mitigation of climate changes [5], through decarbonization of various sectors of the economy and using capture carbon as a feedstock for the production of added value products [6,7]. These devices rely on critical key components such as their membranes, which durability prerequisites limit their operational conditions and lifetime. These membranes can simultaneously support diverse crucial functions, such as acting as the transport media for proton conduction on the system or as an effective separation component between the different media of the electrochemical devices where the energy conversion is occurring [8–11].

The development of more sustainable and cost-effective membranes for electrochemical devices for clean energy production, such as fuel cells and electrolysers and those for CO_2 reduction and conversion, are still requesting a special attention from researchers in the field. Despite all efforts that are being made, materials for key components of electrochemical devices still need to be implemented with optimized properties [12–14]. A strategy that has been implemented is the development of alternative materials based on renewable and cost-effective starting materials, that may present mechanical, chemical and thermal properties suitable for their application as membranes with the desired ionic conduction [15–19]. Among the renewable starting materials, plant materials such as lignin [20,21] or cellulose [22,23], with organic or inorganic dopants, in polymeric or metal-organic frameworks [24] are being evaluated for applications as PEM [17].

A promising research strategy for a base material for proton exchange membranes (PEMs) involves the use of chitosan (CS), a natural polymer obtained from partial deacetylation of chitin. Chitosan has risen tremendous research interest and impact, due to its wide availability, biodegradability, non-toxicity, in fields that include food,

* Corresponding author.
E-mail address: carmen.rangel@lneg.pt (C.M. Rangel).

https://doi.org/10.1016/j.ssi.2025.116852
Received 31 January 2025; Received in revised form 15 March 2025; Accepted 26 March 2025
Available online 9 April 2025