Development of Nanocellulose Proton-Conducting Membranes for Applications in Hydrogen Fuel Cells

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https://hdl.handle.net/2324/5068280

出版情報：Kyushu University, 2022, 博士（工学），課程博士
バージョン：

（様式３） Form 3

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論文名：Development of Nanocellulose Proton-Conducting Membranes for Applications in Hydrogen Fuel Cells
論文名：（水素燃料電池に目指したナノセルロース製プロトン伝導性膜の開発）

区分　：甲
Category: KO

論文内容の要旨
Thesis Summary

Proton transport is one of the most fundamental phenomena in nature, constantly happening in the environment of living cells. Recently, it has played a crucial and more technical role in proton exchange membrane (PEM) fuel cells and water electrolyzers. These two technologies are considered crucial for the ongoing energy transition, necessary to tackle the approaching catastrophe of climate change and strengthen the energy security of future generations. Specifically, electrochemical energy conversion in fuel cells will be a key technology for the development of the hydrogen economy. For this purpose, novel, lower cost PEM materials are needed.

In Chapter 1 an introduction to climate change, the inevitable energy transitions and perspectives on the hydrogen society will be given. The history of fuel cells and their role in the future energy landscape will be shortly discussed. Currently, Nafion® (DuPont) is the benchmark polymer used in PEMs. This is a sulfonated fluoropolymer (poly perfluorinated sulfonic acid) with high proton conductivity in hydrated conditions (~100 mS/cm), which has dominated the market since its discovery in the late 1960s. However, Nafion® is extremely expensive due to the complex manufacturing processes and has other drawbacks such as being difficult to recycle. Therefore, more sustainable and lower-cost alternatives to Nafion® could be highly beneficial. This chapter will introduce the recent new nature-derived biomaterial – nanostructured forms of cellulose and will explain why this is considered promising for the development of PEMs as well as other components of the fuel cell.

The experimental methods used in this work and relevant to the novel PEM research will be described in Chapter 2.

Cellulose is a polymer derived from biomass and is useful in a wide range of applications across society, most notably in paper and cardboard. Among the different morphological types, nanocellulose is a relatively newly discovered variant of cellulose with much smaller fibril size, leading to unique properties such as high mechanical strength. Recently, various different types of nanocellulose have emerged as potential candidates for several important applications within fuel cells.

Chapter 3 will summarize scientific developments in the area of cellulosic materials with specific emphasis on proton conductivity, which is the most important parameter for application in PEMs. The work will cover conventional cellulose and nanostructured cellulose materials, polymer composites or blends, and chemically modified cellulose. These developments will be critically reviewed, enabling identification of interesting trends in the literature data, and allowing perspectives on future research directions in this field.

Chapter 4 will focus on the investigation and development of nanocellulose for proton exchange membranes (PEMs). Two variants of nanocellulose were studied, namely: cellulose nanofibers (CNF), and cellulose nanocrystals (CNCs). As the Chapter explains, due to its better tolerance to

acidic environment, CNC is eventually chosen for further detailed study. Normally, CNC is a nanomaterial that is highly dispersible in water, preventing its use as an ionomer in many electrochemical applications that operate in aqueous environment or require high relative humidity. To solve the problem of water instability, sulfonic acid crosslinking was utilized. Specifically, an organic acid (sulfosuccinic acid) was chosen as a crosslinker, and this enabled simultaneous improvement of the mechanical robustness, water-stability, and proton conductivity (by introducing $-SO_3^-H^+$ functional groups in the composite structure). In particular, the conductivity was systematically investigated over a wide temperature and humidity range with the aid of impedance spectroscopy, and the conduction mechanism is elucidated via activation energy determination. Optimization of the proportion of crosslinker used and the crosslinking reaction time resulted in enhanced proton conductivity up to 15 mS/cm (in the fully hydrated state, at 120 °C). This is the highest currently reported conductivity achieved for this class of materials to the best of my knowledge.

Considering the many advantages of nanocellulose, I believe that these materials can act as a sustainable and low-cost alternative to conventional, expensive, non-sustainable and environmentally toxic perfluorosulfonic acid ionomers for applications in fuel cells and electrolyzers.

In Chapter 5, the main empirical results are shortly summarized, the conclusions of this work are outlined, and the prospects for application of nanocellulose for the PEM development are discussed. Finally, the planned future directions of this work are considered.