



# Proton-conducting Microcrystalline Cellulose Doped with Imidazole. Thermal and Electrical Properties



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## ARTICLE INFO

### Article history:

Received 10 October 2014

Received in revised form 5 November 2014

Accepted 7 November 2014

Available online 31 December 2014

### Keywords:

microcrystalline cellulose

imidazole

proton conductivity

thermal properties

biopolymer membrane

## ABSTRACT

A new biodegradable polymeric material (Cell-Im) consisting of microcrystalline cellulose (Cell) and imidazole (Im) dopant was successfully synthesized. The thermal properties and proton conductivity of Cell-Im were determined and compared with that of pure microcrystalline cellulose. It was found that the Cell-Im exhibits close to four orders of magnitude higher conductivity than a pure cellulose sample, up to approximately  $2 \times 10^{-4}$  S/m at 160 °C under anhydrous conditions. Thermal stability of Cell-Im was confirmed above water boiling point in a temperature range from 110 to about 150 °C. The Cell-Im is inexpensive to obtain, non-hazardous and environmentally friendly and can have potential for possible application as a solid electrolyte in electrochemical devices.

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## 1. Introduction

The fast development of our civilization leads to continuous increase of energy consumption and requires continuous improvement in electrochemical devices. Among them fuel cells are of special interest because they permit a clean and promising technology for direct conversion from the chemical to electrical energy. The electrolyte membrane is the most important unit of a fuel cell. Among the various types of solid conducting membranes, polymer electrolyte membranes (PEMs) are promising due to their good mechanical properties, chemical stability, easy fabrication, and a relatively high conductivity at room temperature [1–11]. The sulfonic acid polymers, including the well known Nafion, are commonly used as separator materials in PEM for fuel cells applications [8,9]. However, they provide high proton conductivity only in high moisture conditions. The water is essential for the formation and mobility of proton charge carriers [8,10]. The limitation of such membranes for the use in fuel cells is related to operating temperature under water's boiling point and relatively high material cost. Therefore, a big attempt in polymer electrolyte fuel cell research is to find proton conducting materials operating

above 100 °C under low humidification and preferentially under anhydrous conditions. Additionally, they should be inexpensive and environmentally friendly. Biopolymers such as chitin, chitosan, alginic acids, bacterial cellulose or derivatives of cellulose doped with nitrogen-containing heterocycles, such as imidazole, benzimidazole and pyrazole seem to be very promising candidates to fulfill these requirements and are being extensively studied [12–23]. The heterocycles are attractive due to their amphoteric nature and high thermal stability. Their protonated and unprotonated nitrogen function may act both as donors or acceptors in proton transfer reactions while the ring itself is rather non-polar. The melting points of heterocycles are higher than that of water, which makes them interesting candidates for supporting proton conductivity at intermediate temperature. Their high basicities provide another interesting feature with respect to the chemical compatibility with other compounds. The nitrogen-containing heterocycles molecules also formed hydrogen bonded networks similar to that found in water, and their transport properties are similar to that of water with proton transfer occurring via structure diffusion (Grotthuss mechanism) [24,25].

In the present work we focused on synthesizing proton-conducting polymeric material from microcrystalline cellulose (Cell) as the host polymer, and imidazole (Im) dopant, one of the basic heterocycle molecules. To the best of our knowledge this is the first successful fabrication of this type of the material (Cell-Im) based on pure microcrystalline cellulose doped with imidazole.

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Moreover, Cell-Im is also a new material in which a significant improvement of conductivity under anhydrous environment has been achieved.

The prepared Cell-Im powder has been characterized by elementary analysis, differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). To investigate the temperature behavior of the electrical property of the samples, the electrical impedance spectroscopy (EIS) measurements were performed.

## 2. Material and experimental methods

### 2.1. Synthesis

The commercially available polycrystalline imidazole 1.904 g (28 mmol) was dissolved in 50 mL of  $\text{CHCl}_3$ . Then, 1.000 g (5.6 mmol) of a commercially available microcrystalline (20  $\mu\text{m}$ ) cellulose was added to this solution upon vigorous stirring. The stirring was continued at room temperature for 1 hour. Afterwards, the suspension was ultrasonicated for 1 hour at 30 °C. Next, suspension of cellulose was filtered off under reduced pressure. The residue at the glass frit was well rinsed by a large amount of chloroform and dried at 40 °C for 2 hours. Finally, about 1 g of white powder of cellulose doped with imidazole was obtained.

Cellulose is not soluble in chloroform and only forms a suspension. The interaction with the molecules of the imidazole can only be done at the surface of the monocrystals. This fact limited imidazole-cellulose ratio in the resulting product.

### 2.2. Elementary analysis

The elementary analysis was carried out on Vario EL III (Elementar Analysensystem GmbH Germany) equipped with a standard CHN detector. The mass of samples was 20 mg. Every analysis was repeated three times with differences less than 0.2%.

### 2.3. Thermogravimetry analysis (TGA)

Thermogravimetric measurements for pure cellulose and cellulose doped with imidazole sample were performed on a Q50 (TA Instruments) instrument. The chemical changes in samples as a function of temperature and time were recorded upon heating samples at a rate of 2.5 °C/min in the temperature range from room temperature to 400 °C.

### 2.4. Differential scanning calorimetry (DSC)

DSC experiments of pure cellulose and cellulose doped with imidazole were performed using NETZSCH DSC 200F3 calorimeter under helium atmosphere, in the temperature range from 5 to 250 °C. The powder samples of about 5 mg in mass were placed in closed pans with a small hole punctured at the top. DSC scans were run on heating and cooling cycles with a scanning rate of 10 °C/min.

### 2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy measurements were carried out using a Bruker Equinox 55 FT-IR spectrometer within the spectral range from 400 to 4000  $\text{cm}^{-1}$  with a spectral resolution of 2  $\text{cm}^{-1}$ . The spectra were collected at the temperature range from 25 to 150 °C. The measured samples were dispersed in KBr pellets.

### 2.6. Electrical impedance spectroscopy (EIS)

The electric conductivity of powdered samples Cell and Cell-Im were characterized by EIS method using a computer controlled

AlphaA High Performance Frequency Analyzer from Novocontrol GmbH in a frequency range between 0.1 Hz to 10 MHz and with the voltage oscillations of  $\pm 1$  V. The samples were prepared from powdered materials and compressed at room temperature under a pressure of 10 MPa to form a pellet of 1.15 mm in thickness and 5.15 mm in diameter, which was covered with Hans Wolbring GmbH silver paste electrodes. The sample of Cell-Im was measured during a first heating cycle in the temperature range from -30 to 110 °C then cooled to 0 °C. The second heating cycle was performed in the range from 0 to 220 °C. Additionally, the conductivity measurements of Cell-Im were carried out as a function of time at selected temperatures from the range of 90–160 °C. The measurement of Cell sample was performed from room temperature to 110 °C. The temperature was controlled using a Quatro Cryosystem with accuracy better than  $\pm 0.01$  °C.

## 3. Results and discussion

### 3.1. Structure of Cell and Cell-Im samples

The microcrystalline cellulose (Cell), with a number-average molecular weight of 74,500 and an average grain size of 20  $\mu\text{m}$ , was purchased from Sigma-Aldrich Company. The crystallinity index of the pure cellulose measured previously is about 66% [26]. The X-ray diffraction spectra of Cell-Im (not shown) mostly coincide with that of an untreated sample of Cell. Thus, we can assume that the crystallinity of Cell-Im is not much different from a pure Cell. The initial water content of Cell-Im was determined directly from TG experiment to be about 3%. The attempt to dope anhydrous cellulose with imidazole failed. Therefore, one can suppose that the imidazole molecules form the hydrogen bonding network with cellulose chains through the water molecules. The FTIR data will prove this assumption. The chemical composition of doped cellulose was measured by elemental analysis. The average data obtained are 43.93, 7.93, and 2.95% of carbon, hydrogen, and nitrogen atoms, respectively. Imidazole content of the sample was calculated through nitrogen and carbon data. On average one imidazole molecule is attached to 5 glucose rings.

### 3.2. Thermal properties

Thermal analysis is carried out to examine thermal properties and transition behavior of studied sample. Fig. 1 depicts a thermogravimetric curve of Cell-Im. For comparison data for pure cellulose are also presented, which are consistent with those previously published [26]. The initial weight loss of about 4% observed during the increase of temperature from room temperature to 115 °C in Cell-Im sample is due to the evaporation of absorbed humidity and weakly bonded water. Above 115 °C thermal degradation of the sample follows two broad stages. The first one involves the weight loss due to the evaporation of strongly bonded water and to the thermal decomposition of the Cell-Im sample caused by the disruption of the hydrogen bonding network formed between the imidazole and cellulose chains. As a result a slow loss of Im molecules from the material occurs. The second stage is related to the decomposition of the remaining Cell-Im matrix. The extrapolated temperature of the beginning of this stage (defined as shown in Fig. 1) is equal to 313 °C for Cell-Im sample whereas for pure Cell this temperature is lowered by about 15 °C and equals to 298 °C. The increase of the thermal stability of Cell-Im matrix, with comparison to pure cellulose, can be attributed to hydrogen bonding network formation between the imidazole molecules and cellulose.

Fig. 2 shows DSC thermograms of Cell and Cell-Im samples. The data were obtained during two heating cycles performed for each sample. During the first run the pure Cell sample was heated from

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