

Instytut Fizyki Molekularnej  
Polskiej Akademii Nauk

Rozprawa doktorska

Otrzymywanie i własności polimerowych  
przewodników protonowych  
zbudowanych z mikrokrystalicznej celulozy  
funkcjonalizowanej  
molekułami heterocyklicznymi

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Praca doktorska wykonana  
w Środowiskowym Laboratorium Badań Radiospektroskopowych  
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Poznań 2016

## Abstract

The aim of this dissertation is the synthesis and characterization of new biodegradable proton conductors based on microcrystalline cellulose (abbreviation: Cell) as the host polymer functionalized by heterocyclic molecules, such as: imidazole (Im), triazole (Tr), benzimidazole (benzi), pyrazole (Pir), and oxazole (Ox), used as dopants. Additionally, the composite consisting of the Cell and niacin (Nik) was synthesized. The combination of selected natural polymers and molecules containing nitrogen atoms is the strategy which allows to find new biodegradable and flexible proton conducting materials, which can be used in the temperature range above 100 °C, under anhydrous conditions. Potentially, polymer proton conductors can be applied in fuel cells, batteries, or sensors, as solid electrolytes.

The dissertation consists of three main parts: theoretical, methodological, and experimental; preceded by a foreword explaining the motivation, objectives, and the extent of the study. The theoretical part introduces issues related to proton conductors, describes the properties of cellulose and heterocyclic compounds, in particular imidazole, benzimidazole, and triazole. The experimental section describes the synthesis of novel composites and obtained results. The summary contains the most important research conclusions. The dissertation ends with a list of literature, scientific biography of the author, lists of publications and conference presentations, and supplements.

All of synthesized samples were examined by means of elemental analysis to establish the chemical composition of new composites. The new proton conductors were investigated for thermal stability and thermal decomposition by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The crystallinity indexes of the composites were checked by wide-angle X-ray diffraction technique. The surfaces of the materials were examined by scanning electron microscopy (SEM). The structure of hydrogen bonds network was studied by Fourier transform infrared spectroscopy (FTIR). In order to investigate the temperature behavior of the electrical property of the composites, the electrical impedance spectroscopy (EIS) measurements were performed. The percolation nature of the electrical conductivity has been studied in new materials consisting of microcrystalline cellulose as the polymer matrix functionalized with different concentration of imidazole as a dopant. Powdered samples of composites and pure cellulose were studied by means of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  solid-state MAS NMR and two dimensional heteronuclear correlation

experiments (HETCOR) in various temperatures. Additionally, dynamic nuclear polarization (DNP) NMR experiments were performed. These selected NMR techniques allowed to find the local structure, molecular dynamics of the imidazole molecules within the composites, and proposed the mechanism describing the proton transport.

The functionalization of the cellulose matrix by heterocyclic molecules improves the thermal stability of the composites due to forming a new hydrogen bonds network. The impedance spectroscopy spectra were obtained for the samples of pure microcrystalline cellulose and cellulose composites. These results have shown that the sample which contains the highest concentration of imidazole, 5Cell-Im, under anhydrous conditions at 160 °C, exhibits close to five orders of magnitude higher electric conductivity, up to approximately  $2.0 \times 10^{-4}$  S/m, than the pure cellulose. It proves that the presence of the imidazole molecules plays the major role in the proton transport in anhydrous conditions, at the high temperature regime. Moreover, obtained Nyquist plots of 5Cell-Im are asymmetric in the temperature range from 60 °C to 150 °C and can be fitted with two semicircles, reflecting two contribution to the conductivity: one due to the imidazole layers at the grain surface, and the second one due to contacts between the grains.

$^{15}\text{N}$  CP MAS NMR and 2D  $^1\text{H}$ - $^{15}\text{N}$  HETCOR experiments allowed to establish that the imidazole molecules can be attached to the cellulose matrix via hydrogen bonds  $\text{N}-\text{H}\cdots\text{O}$  i  $\text{O}-\text{H}\cdots\text{N}$ , created with OH cellulose group and water molecules.  $^{15}\text{N}$  CP MAS NMR experiments showed tautomerism of imidazole molecules, associated with reorientation of the imidazole ring, above the -10 °C, where we observe a broad distribution of slow and fast exchanging protons. The fast reorientation fraction of the imidazole molecules is increasing in the function of temperature. The analysis of the temperature-dependent fraction of both, fast and slow reorientation phases, allowed to obtain the distribution of activation energies of tautomerization assisted by a fast imidazole reorientation, exhibiting a maximum value of energy equals 42.0 kJ/mol and a width of 8.2 kJ/mol. Proton conductivity phenomenon is conditioned by the existence of a dynamic network of hydrogen bonds in the composite, which allows for dissociation of imidazole on cation and anion and, thus, for the proton exchange. This process is assisted by reorientation of imidazole molecules. The research using DNP technique proved that this method does not change the structure of measured compounds. As a result, it is possible to use DNP to study compounds containing heterocycles, which have a natural abundance of nitrogen isotope  $^{15}\text{N}$ .

During my study I was able to get valuable information about structure, molecular dynamics, and mechanism of proton conductivity in the new cellulose composites. The values obtained for the conductivity 5Cell-Im are remarkable and suggest that the conductivity of nanocellulose composites with imidazole will be even higher. Preliminary studies of such composites have confirmed this hypothesis.