



Effect of surface coating of microcrystalline cellulose by imidazole molecules on proton conductivity

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ABSTRACT

The proton conductivity properties of a newly synthesized proton-conducting composite (Cell-Im) composed of the microcrystalline cellulose grains (Cell) coated with different amount of imidazole molecules (Im) have been investigated. For the composite with the highest concentration of Im (on average 1 Im molecules is bonded to approximately 5.44 glucose rings; 5Cell-Im), the increase in the maximum conductivity by nearly 3 orders of magnitude with respect to that of neat cellulose, and the extension of the temperature range application up to 160 °C was evidenced in anhydrous conditions. Under these conditions two contributions to the overall conductivity of 5Cell-Im were recognized in the temperature range of 60–150 °C. They are related to the imidazole layers at grain surfaces and intergrain contacts, respectively. The interior of the cellulose grains is treated as a nearly “perfect” dielectric with a negligible contribution to conductivity. The lowering of the Im concentration at the cellulose grain surface leads to decreasing of the surface conductivity. A characteristic phase transition from proton conductivity state to non-conductivity one with typical percolation threshold is well documented.

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1. Introduction

The need to design “water-free” electrolytes for application in various electrochemical devices (e.g., fuel cells, batteries, sensors, etc.) forces the search for new materials which exhibit the desired electrical properties in anhydrous conditions. Among different advanced materials some hydrophilic biopolymers as chitin, chitosan, or cellulose (and its derivatives) functionalized to replace water by nitrogen-containing heterocycles such as imidazole, benzimidazole, or triazole are especially promising [1–7]. The heterocycles are attractive due to their amphoteric nature (the structure contains both a proton donor (NH) and a proton acceptor (N:) side), and high thermal stability [6,7]. Their melting points are higher than water, which makes them interesting candidates for supporting proton conductivity at intermediate temperature. Moreover, the nitrogen-containing heterocycles molecules form hydrogen bonded networks similar to that found in water, and possess transport properties comparable to that of water with proton transfer occurring via *Grotthuss mechanism*, also called “structural diffusion” [8,9]. Proton transfer requires structural diffusion because heterocyclic molecules, e.g. imidazole, are bonded to the polymer backbone. Proton hopping between adjusted imidazole molecules involves some configuration

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changes, for instance, imidazole reorientations and polymer backbone segmental motions. Generally, to support proton conduction in the polymer system the heterocyclic groups need to maintain high local mobility of protonic charge carriers and their concentrations should be large enough.

Among biopolymers cellulose seems to be the most attractive because it is cheap, occurs in different forms and can be extensively derivatized and therefore can form a strong, stable and homomolecular matrix for the fabrication of new functional materials among them those with high electrical conductivity. As shown previously, we successfully synthesized cellulose-based composite prepared by combining microcrystalline cellulose (Cell) and imidazole (Im) molecules [10]. The Im molecules were introduced into the cellulose matrix through coating. Therefore, the Im molecules were bounded to cellulose chains appearing only on the cellulose grains' surfaces and not to those within grains. The composite shows the highest anhydrous proton conductivity of 2×10^{-4} S/m at 160 °C.

Inspired by this result we continued our studies by synthesizing the Cell-Im composite with different concentration of imidazole. In this paper we focused on the conductivity properties of Cell-Im samples in particular on the origin and percolation nature of the conductivity. From economic reasons, the amount of conductive phase necessary to produce materials with high conductivity should be as small as possible. Therefore, the possibility to estimate the conductivity dependence on the concentration of the conductive additive is of great value. Percolation theory has been successfully applied to a variety of physical phenomena including conductivity in polymer composites [11–14] where the conductivity usually does not increase continuously with increasing additive content but experiences a significant, abrupt increase at critical concentration [15].

The prepared Cell-Im composites have been characterized by elementary analysis and differential scanning calorimetry (DSC). To investigate the temperature behavior of the ionic property of the samples, the electrical impedance spectroscopy (EIS) measurements were performed. The careful analysis of the impedance data allows to postulate two fractions of the proton-conducting phase: the main one associated with the cellulose grain surfaces and that between the grains which can lead to the additional conductivity. The percolation model has been applied to explain the conductivity dependence on the Im concentration.

2. Material, methods and theory

2.1. Synthesis

Cellulose (Cell) and imidazole (Im) obtained from Sigma–Aldrich Company were used for preparation of the biopolymer composite. The number-averaged molecular mass, M_n , of microcrystalline cellulose is equal to 74,000 and the average particle size corresponds to 20 μm . The degree of polymerization and the crystallinity index amounted to about 230 and 66%, respectively. The chloroform (CHCl_3) was chosen as a solvent. The cellulose composite with different amount of imidazole were prepared according to the procedure reported previously [10]. Cellulose, contrary to the imidazole, is not soluble in chloroform and forms a suspension. Therefore, the imidazole molecules were bonded only to the polymer chains on the cellulose grains' surfaces. This fact limited imidazole–cellulose ratio in the resulting product. Finally, three samples, each of about 1 g of white powder of cellulose doped with different concentration of imidazole were obtained (see Table 1).

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. For each of the prepared sample the analysis was repeated three times with differences less than 0.2%.

2.3. Differential scanning calorimetry (DSC)

The DSC measurements were performed using NETZSCH DSC 200F3 calorimeter. Approximately 5 mg of sample was used in each test, and all tests were conducted in closed pans with a small hole punctured at the top under helium atmosphere. DSC scans were conducted on heating and cooling cycles with a scanning rate of 10 °C/min. Each sample was first heated from 5 to 130 °C (the first heating scan), and then held at 130 °C for 30 min before being cooled to 5 °C. The samples were then held at 5 °C for 10 min before being heated to 250 °C (the second heating scan).

Table 1

The chemical composition of synthesized Cell-Im samples determined by elementary analysis.

Sample	Carbon content (%)	Hydrogen content (%)	Nitrogen content (%)	Number of glucose rings per one Im molecule
5Cell-Im	43.93	7.93	2.95	5.44
14Cell-Im	43.37	7.73	1.15	14.63
38Cell-Im	43.05	8.02	0.45	38.36

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