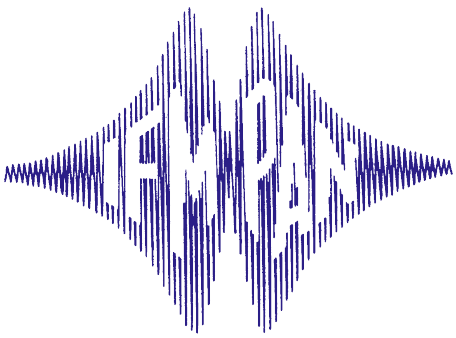
Własności optyczne, termiczne oraz transportowe przewodników protonowych soli kwasów dikarboksylowych o różnej wymiarowości sieci wiązań wodorowych

rozprawa doktorska

mgr inż. Małgorzata Widelicka

promotor: dr hab. Andrzej Łapiński, prof. IFM PAN

promotor pomocniczy: dr inż. Katarzyna Pogorzelec-Glaser



Instytut Fizyki Molekulanej PAN

Poznań, 2020

Abstract

The main aim of the research is to gather a knowledge about the physical properties of a new, organic, high-temperature proton conductors and to determine the role of dimensionality of the hydrogen bonding network in proton conductive materials. Six proton-type anhydrides with one-, two-, and three-dimensional hydrogen-bonding networks were selected for the study.

The conducted research concerns materials that can be used as membranes in fuel cells. Currently used fuel cells utilize electrolytes in their action, where the conduction mechanism is associated with the phenomenon of hydration. The presence of water and high humidity of the environment are a prerequisite for the existence of such conductivity, which limits their practical application at temperatures above 373 K. Alternatives to this type of solution are solid electrolytes that do not have these drawbacks. They have less volatility and much better thermal stability than liquid electrolytes. Such materials are, for example, dicarboxylic acid salts containing amphoteric heterocyclic molecules that are the subject of this research.

The Grotthuss mechanism is used to describe the conductivity of these electrolytes. The proton transport is accomplished by breaking the hydrogen bond, reorientation of the molecule and transfer of the proton through a newly created hydrogen bond to the neighboring molecule. Next, the proton can be transferred through a hydrogen bridge by hopping or tunneling processes through the energy barrier. Since this mechanism is closely related to the hydrogen-bonding network, having detailed information about the hydrogen-bonding system is essential in designing new compounds with desirable properties.

In order to obtain a full description of the hydrogen-bonding network and interactions in the crystal, an analysis was carried out using experimental and theoretical solid-state physics methods. The strength and the type of hydrogen bonds were analyzed using crystal structure analysis and Quantum Theory of Atoms in Molecules (QTAiM) calculations. The study of the infrared spectra of deuterium substituted materials was used to determine the shape of potential energy in hydrogen bonds. The proton dynamics in the hydrogen bridge, as well as in the crystal was studied using Potential Energy Scans (PES) calculations. It allows the calculation of the energy activation of: proton transfer through the hydrogen bond and rotation of proton with the cation. Thermal stability studies were performed using Differential Scanning Calo-

rimetry (DSC) and Thermogravimetric Analysis (TGA) methods. These studies allow determining the range of temperature in which proton conductors can work as membranes in fuel cells and define the temperatures of phase transitions. The nature of observed phase transitions was explained using Raman and infrared spectroscopies in the function of temperaure supported by normal modes Density Functional Theory (DFT) calculations. Study of those temperature-induced transitions was essential to identify the reason for abrupt changes in the physical properties. Conductivity studies in the function of temperature were studied using impedance spectroscopy. The reasons provoked the conductivity changes were related to the number and type of possible proton pathways and change of the dynamics of molecules within the crystal.

The most important conclusions of this work are:

- In the structures with similar hydrogen-bonding pattern, the undulation of the conductive layers results in higher thermal stability of the material than in the planar layered structures.

- In the conductivity process, the dynamics of the acids can also play an important role. In the previous studies, only the rotation of amphoteric heterocycles was considered to participate in the conduction process.

- Rising the temperature can affect the number of possible pathways of proton diffusion. In the investigated crystal with one-dimensional hydrogen-bonding network, in the high temperatures, this network becomes quasi-two-dimensional.

- With an increase in the volume of the crystal voids in the unit cell, the degradation temperature falls.

- With an increase in the number and strength of hydrogen bonds, the degradation temperature and energy activation of conduction are rising, while the conductivity value is decreasing.

The highest values of conductivity and the smallest values of activation energy were obtained for crystals with three-dimensional hydrogen-bonding networks. The highest degradation temperatures were obtained for materials with two-dimensional hydrogen-bonding networks.