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# A vibrational spectroscopic and modeling study of poly(2,5-benzimidazole) (ABPBI) – Phosphoric acid interactions in high temperature PEFC membranes

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ABSTRACT

This paper reports a FT-ATR-IR spectroscopic study on proton conducting poly(2,5-benzimidazole) (ABPBI) membranes doped with orthophosphoric acid. The analysis of the vibrational profiles is a good diagnostic tool to help understand the interactions occurring between the phosphoric acid and the polymer membranes. The experimental data show evidence that an acid-base proton exchange reaction has occurred between the imidazole moieties in the polymer chain and phosphoric acid to produce dihydrogen phosphate ions and protonated imidazolium cations in $ABPBI^{n+}$. Vibrational modes associated with the dihydrogen phosphate ions are evident in the FT-IR spectra at lower doping levels and then become partially masked by the large amount of free phosphoric acid at high acid concentrations. Several bands in the FT-IR and FT-Raman spectra attributed to mixed modes containing varying contributions from NH bending motions exhibit high frequency shifts upon protonation the imidazole moieties. The correlatively assigned experimental vibrational bands were compared with calculated normal modes for small molecule models. The optimized geometry of the benzimidazolium dimer suggests that protonation of ABPBI results in a perturbation of the extended conjugated $\pi$ system and allows rotation of the benzimidazole monomer units along the polymer chain. The results described here provide insight into the roles of phosphoric acid and ABPBI in the conduction mechanism of polybenzimidazole systems.



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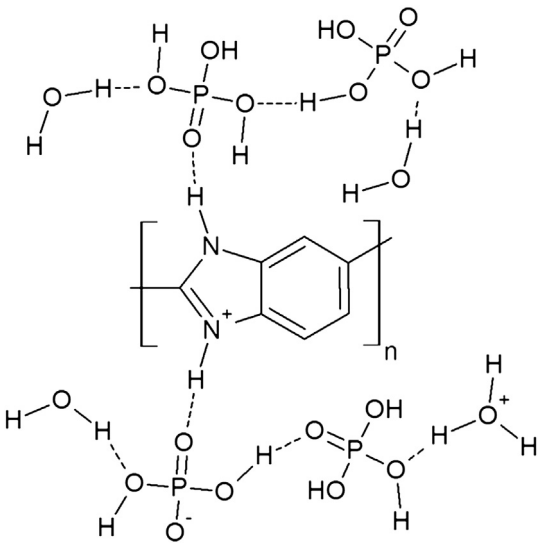
## 1. Introduction

Phosphoric acid-doped polybenzimidazole (PBI) membranes have been extensively studied in the last decade as electrolytes for the use in High Temperature Polymer Electrolyte Fuel Cells (HT-PEFCs). They possess high thermal, chemical and mechanical stability [1] in addition to suitably high conductivity even at low humidity [2–7]. High working temperatures would benefit PEFC performances because of a higher tolerance to carbon monoxide, which even at very low levels poisons a conventional PEFC at room temperature [8]. Moreover, a HT-PEFC is more resistant to hydrogen sulfide, shows faster electrode kinetics and low gas crossover [9], and exhibits a residual heat useful for energy cogeneration [10,11]. Among the many possible PBI derivatives [12,13], a very promising material is poly(2,5-benzimidazole) (ABPBI) [14–16]. It has been found that ABPBI absorbs phosphoric acid more efficiently than PBI when treated with equally concentrated acid solutions [14,17–19]. Additionally, ABPBI membranes have the same performances as PBI under the same conditions and can be produced easily and more safely from a single cheap monomer precursor [20].

FT-IR spectroscopy is a powerful tool to study the effects of acid doping on PBI-type polymers because infrared spectroscopy is highly sensitive to changes in molecular structure which occur as a result of the acid-base proton exchange reaction between PBI and $H_3PO_4$ and the dipole–dipole interactions between membrane components. In addition, FT-ATR-IR (attenuated total reflectance, ATR) offers many other beneficial aspects: the method is rapid, non-destructive, requires little sample preparation and is not affected by the membrane thickness. Furthermore, the infrared properties are complementary to the information on the molecular structure of materials, which can be determined using standard FT–Raman measurements [21].

In the present study, FT-ATR spectroscopy is used to investigate ABPBI membranes doped with varying amounts of phosphoric acid. By examining samples with different levels of doping, a correlation between the vibrational modes active in the infrared and the structural modification of the system is obtained. To complete this study the infrared profiles are compared with the complementary FT-Raman spectra of $H_3PO_4$-doped ABPBI previously reported by Conti et al. [22,23]. A unified assignment of the vibrational modes detected in the FT-ATR-IR and FT-Raman spectra is proposed. Particular attention is devoted to the critical analysis of the vibrational modes correlated to the peak shifts occurring upon acid doping. The correlative assignments are based on these peaks shifts, results reported elsewhere for benzimidazole [24], poly-2,2′-(2,6-pyridine)-5,5′-bibenzimidazole [7], and phosphoric acid [25,26]. These assignments are then completed and confirmed with the DFT calculated modes for benzimidazole, benzimidazolium and dimers of both benzimidazole and benzimidazolium determined with DMol3 [27,28]. The results presented here provide a better assignment of the vibrational spectra of ABPBI and a clearer understanding of the interactions between phosphoric acid and ABPBI membranes in HT-PEFCs.



**Scheme 1 – The chemical structure of the repeat unit of poly(2,5-benzimidazole) (ABPBI) is shown and illustrates possible interactions between ABPBI, water and phosphoric acid.**

## 2. Experimental section

### 2.1. Materials and sample preparation

Cross-linked poly(2,5-benzimidazole) (ABPBI) membranes were obtained from FuMA-Tech GmbH, St. Ingbert, Germany, and additionally purified by heating at 150 °C for 30 min. In Scheme 1 the chemical structure of the repeating unit of the polymer is depicted.

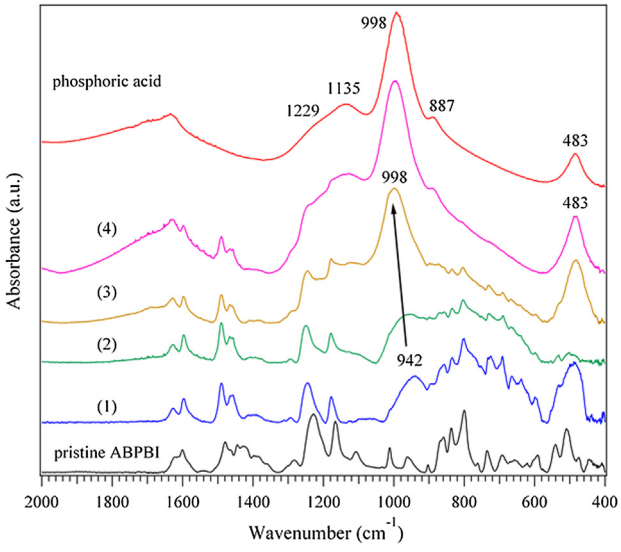



**Fig. 1 – FT-ATR spectra of pristine ABPBI, acid-doped ABPBI and phosphoric acid. The spectra numbered (1)–(4) correspond to the ABPBI membranes treated with phosphoric acid, where increasing number indicates increasing degrees of doping.**

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