



# Electrosynthesized polypyrrole/zeolite composites as solid contact in potassium ion-selective electrode



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## ABSTRACT

Polypyrrole/zeolite composites were studied as solid contact material in potassium ion-selective electrodes ( $K^+$ -ISEs). Proton-exchanged Zeolite Socony Mobil-5 (H-ZSM-5) with  $SiO_2/Al_2O_3$  ratios of 23, 80 and 280 were electrochemically synthesized with polypyrrole (PPy). The anionic groups on the zeolite framework functioned as the counter ions for PPy during the reaction. H-ZSM-5 particles were observed on the surface as well as inside the composite films. PPy/H-ZSM-5 composites gave a similar cyclic voltammogram as PPy doped with chloride,  $PPy(Cl^-)$ . The hydrophobicity of the composites decreased in the order  $PPy/H-ZSM-5-23 > PPy/H-ZSM-5-80 > PPy/H-ZSM-5-280$ . The redox capacitance of the composite was better utilized than that of  $PPy(Cl^-)$  after they were coated with a plasticized PVC membrane. PPy/H-ZSM-5 composite-based  $K^+$ -ISEs exhibited similar potential stability as the  $PPy(Cl^-)$ -based  $K^+$ -ISE. However, when compared with the  $PPy(Cl^-)$ -based  $K^+$ -ISE, the detection limit of PPy/H-ZSM-5 composite-based  $K^+$ -ISEs was enhanced after a long-term conditioning.

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## 1. Introduction

Both liquid contact and solid contact (SC) based ion-selective electrodes (ISEs) have widely been used in medical, environmental and industrial analysis as well as in physiology and process control [1–4]. SC is more attractive than the traditional liquid contact due to its compatibility with mass production of miniaturized ISEs [5,6]. There are also other benefits offered by the SC, such as low cost and less need for maintenance of SC ISEs compared to liquid-contact ISEs [7–10].

In order to obtain a stable and reliable response of solid-contact ISEs, the SC has to fulfill three main criteria, i.e. reversible transition from ionic conduction (in the ion-selective membrane) to electronic conduction and vice versa, ideally no polarizable interfaces with high exchange current densities, and absence of side reactions within the SC [11]. For example, thin conducting polymers films [12,13], high surface area nanostructured materials [14] and redox-active monolayers [15] have been introduced as the SC based on the above requirements, resulting in improved performance of SC ISEs in the last decades. Recently, incorporation of conducting polymer with an inorganic host was proposed to develop novel hybrid materials that have both the unique

properties of semiconducting organic polymers and the mechanical strength and chemical properties of inorganic materials [16]. Also carbon-based materials such as carbon nanotubes, graphene and fullerenes were synthesized with conducting polymers to generate new types of SCs. Such composite-based solid contact in ISEs exhibit excellent properties including a high redox capacitance, resulting in solid-contact ISEs with Nernstian slope of the calibration line, large dynamic response range and short response time [17–20].

In the present work, microporous zeolite, an aluminosilicate inorganic material that has widely been used as catalysts in petrochemicals, oil refining processes and fine chemical synthesis, was combined with a conducting polymer. The obtained composite was characterized and tested as an ion-to-electron transducer in a potassium-selective ISE. The advantage of using microporous zeolite as the matrix for synthesis of conducting polymer/zeolite composite is the high thermal stability, shape selectivity, and stability towards leaching in the reaction media for application as ion-selective electrode [21,22]. In addition, the anionic groups on the zeolite framework can function as the counter ions for the conducting polymer. Furthermore, by variation of the  $SiO_2/Al_2O_3$  ratios of the particular zeolites, the type and the concentration of the anionic groups can be altered. Hence, the surface and textural properties as well as the electrochemical behavior of the composite material are modified. In other words, the change in

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the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio not only influences the acidic, hydrophilic and hydrophobic properties, but also the hydrothermal stability of the zeolite and even the conducting polymer/zeolite composite [23–25].

Polypyrrole (PPy) was the selected conducting polymer in this study because it can be synthesized by chemical and electrochemical methods in both organic and aqueous solutions and it shows good environmental and thermal stability. The size of the pyrrole monomer is small enough to enter the channels of the studied zeolites [26]. Proton-exchanged Zeolite Socony Mobil-5 (H-ZSM-5) zeolite was used as the host for PPy. The three-dimensional network of this zeolite consists of straight and sinusoidal 10-ring channels with pore diameters of 5.1 × 5.5 and 5.3 × 5.6 Å, respectively [27,28]. Considering that the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio in the zeolite may influence the property of the PPy/H-ZSM-5 composite, three H-ZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 23, 80 and 280 were selected for this research.

## 2. Experimental

### 2.1. Chemicals

ZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 23, 80 and 280 were obtained in the NH<sub>4</sub>-form from Zeolyst International. All the zeolites were calcined in a muffle oven at 450 °C for 4 hours to convert them to the protonated form, i.e. H-ZSM-5-23, H-ZSM-5-80 and H-ZSM-5-280. The zeolite particles were then filtered through a mesh sieve with the pore size of 63 μm. Pyrrole was obtained from Sigma-Aldrich and distilled prior to use. All the other chemicals were of analytical-reagent grade. Distilled and deionized water with the resistivity of 18 MΩ cm was used to prepare all solutions.

Tetrahydrofuran (THF) and the membrane components including valinomycin (potassium ionophore I), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (KTFPB), poly(vinyl chloride) (PVC) and bis(2-ethylhexyl)sebacate (DOS) were obtained from Fluka AG.

### 2.2. Synthesis of the PPy/H-ZSM-5 composites

The suspension containing the zeolite particles (0.02 g/mL, zeolite/distilled water) and pyrrole monomer (0.2 mmol/mL) was deaerated by bubbling with nitrogen for 15 minutes prior to the electrochemical synthesis of the PPy/H-ZSM-5 composite. Thus, the ratio of pyrrole/zeolite in the suspension was 10 mmol/g. It should be noticed that the zeolite particles were first dispersed in distilled water and stirred for 24 hours at room temperature (22 ± 1 °C) in order to achieve a stable suspension. The suspension, containing the zeolites and the pyrrole monomer, was then ultrasonicated for 10 minutes to let the pyrrole to diffuse evenly both in the inner and the outer framework of the zeolites. The suspension was kept under stirring during the entire electrochemical polymerization which took approximately two to three hours depending on the zeolite.

The synthesis reaction was performed in a conventional three-electrode cell connected to an Autolab PGSTAT20 (Metrohm), and the procedure has been described in detail earlier [29]. The working electrode was a platinum (Pt) disk with the surface area of 0.07 cm<sup>2</sup> encapsulated in a polyether ether ketone (PEEK) body. A platinum wire was used as the counter electrode and a Ag/AgCl/sat. KCl electrode was used as the reference electrode. The PPy/zeolite composite was deposited on the Pt electrode by applying a constant potential of 0.7 V and the total amount of charge passed during the polymerization was 30 mC (approx. 430 mC/cm<sup>2</sup>). The anionic groups on the zeolite framework functioned as counter

ions for PPy, resulting in a (PPy)<sup>n+</sup>/(zeolite)<sup>n-</sup> composite material. The exact degree of doping is unknown. A parallel experiment was carried out by synthesizing PPy(Cl<sup>-</sup>) on Pt electrode in 0.02 mM pyrrole + 0.1 M NaCl solution with the same method.

### 2.3. Characterization

The chemical composition (aluminum and silicon) and the anionic groups in H-ZSM-5-23, H-ZSM-5-80, and H-ZSM-5-280 were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 5300DV, Perkin Elmer) and by potentiometric acid-base titration, respectively. Cyclic voltammetric measurements were carried out in aqueous solutions of both 1 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] and 1 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> having 0.1 M KNO<sub>3</sub> as the background electrolyte. The Autolab General Purpose Electrochemical System connected to a conventional three-electrode cell was used in recording the cyclic voltammograms. The morphology and the film thickness were characterized by scanning electron microscopy (SEM) (Leo Gemini 1530) having a ThermoNORAN X-ray detector. Electrochemical impedance spectroscopy measurements (EIS) of PPy(Cl<sup>-</sup>) and PPy/H-ZSM-5 composites were done in 0.1 M KCl solution by using the Autolab Frequency Response Analyzer System. Contact angle measurements were performed on the surface of the composite film by using the CAM200 (KSV NIMA) instrument.

### 2.4. Potentiometric measurements

The potassium ion-selective electrodes with PPy/H-ZSM-5 and PPy(Cl<sup>-</sup>) as the solid contacts (K<sup>+</sup>-SC-ISE) were prepared by applying 40 μL of the potassium ion-selective-membrane (ISM) cocktail on top of the solid contact. The composition of the ion-selective membrane (after evaporation of THF) was (in wt.%) 1% valinomycin, 0.4% KTFPB, 32.9% PVC and 65.7% DOS.

The potentiometric response of the PPy(Cl<sup>-</sup>)- and PPy/H-ZSM-5-based ISEs were studied at room temperature (22 ± 1 °C) by using a Lawson Labs, Inc. potentiometer, with an input impedance of 10<sup>15</sup> Ω. A double junction Ag/AgCl/3 M KCl with a salt bridge containing 1 M lithium acetate was selected as the reference electrode in this work. Three identical PPy/H-ZSM-5-based ISEs were always used in the potentiometric measurements and their response characteristics were compared with three PPy(Cl<sup>-</sup>)-based ISEs.

The potentiometric aqueous layer measurement was carried out by recording the changes in the potential of the ISEs in 0.1 M KCl for 1 hour, then in 0.1 M NaCl for 4 hours and finally in 0.1 M KCl for 4 hours.

Before the potentiometric sensitivity test, the ISEs were equilibrated in 10<sup>-3</sup> M KCl solution for ca 2 days. The calibrations were done in KCl solution with the concentration from 10<sup>-2</sup> to 10<sup>-7</sup> M then back to 10<sup>-2</sup> M, and the potentials were recorded for 5 minutes at each concentration step. These ISEs were then placed again in the 10<sup>-3</sup> M KCl solution with stirring for a 6-day potential stability test. After this long-term measurement, the potentiometric sensitivity test was repeated with the same parameters. The Debye-Hückel equation [30] was used to convert the concentrations to activities, and the potential (EMF) values were corrected for the liquid-junction potentials by using the Henderson equation [31]. The standard potential (*E*<sup>0</sup>) reported is corresponding to extrapolation of the linear potential response to *a*<sub>K<sup>+</sup></sub> = 1.

Additional electrochemical impedance spectroscopy measurements were done when the PPy(Cl<sup>-</sup>) and PPy/H-ZSM-5 based K<sup>+</sup>-ISEs were freshly prepared as well as after the 6-day potentiometric stability test.

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