THE SYNTHESIS AND CHARACTERIZATION OF A NEW COMPOSITE MATERIAL: POLYSULFONE-Fe_3O_4/TiO_2

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This paper presents the synthesis of a new composite material with potential applications in fuel cells manufacturing and/or in the photocatalytic degradation of the organic compounds from wastewater. This new composite material combines three basic materials with specific properties, and hence the resulting synergic effect, namely that of a conductive polysulfone-base polymer with high mechanical and thermic resistance (up to 140ºC), magnetic properties, high chemical and mechanical resistance. Moreover, being functionalized with titanium dioxide and containing iron ions its ionic conductivity and chemical stability are enhanced and also a high photocatalytic activity. The composite material was analysed by SEM, FT-IR and EIS.

Keywords: polysulfone, magnetic particles, titanium dioxide, magnetite

1. Introduction

Two major concerns regarding the sustainability of our future development have been observed nowadays: finding viable alternative for sustainable energy sources and minimising the water pollution (e.g. reducing the content of organic compounds and that of heavy metals ions). The polymer electrolyte membrane fuel cells (PEFC) based on novel types of proton exchange membranes may represent a suitable option for the first part. The research in this field is mainly focused on creating various types of polymer electrolyte membranes (PEM) with high ionic conductivity and high temperature resistance [1, 2]. For the second part one may consider a series of advanced oxidation processes (AOP) with potential applications in wastewater treatment. One of the most important catalysts used in AOP is titanium dioxide, which determines a high photocatalytic activity providing also the advantages of a chemical inertness

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product, a strong oxidizing power, low investment cost, and long-term stability versus photolytic and chemical degradation processes [3, 4].

Nafion is presently the most used membrane in fuel cells because of its high ionic conductivity (0.1 S/cm) and long lasting lifetime. However, this membrane has the disadvantage that it can be used in unpressurised cell up to the limit of 90 ºC. There is a continuously going research for the development of novel types of similar membranes with enhanced properties by blending the basic material with other conductive polymers or by making hybrid (composite) membranes with titanium dioxide and other metal oxides [5-8]. Recent studies have also shown promising results from the combination of one or more conductive polymers (sulfonated polyetheretherketone, sulfonated polysulfone with various metal oxides (titanium dioxide, yttrium oxide, zirconium oxide) [9-11].

As it was mentioned before, titanium dioxide is a very versatile inorganic material which can be used as a pigment, in pharmaceutical products, as a photocatalyst and in composite membranes for fuel cells. A number of theoretical and applied studies have shown that by combining titanium dioxide with iron ions (Fe^{2+}, Fe^{3+}) or with zero valence iron (Fe^0) the photocatalytic activity increases correspondingly [12-15].

The purpose of this study was to obtain a novel composite material with potential application in both fuel cells and in the degradation of organic compounds subjected to UV light (photocatalysis) by combining a polysulfone-based conductive polymer with titanium dioxide (to enhance the proton conductivity and to take advantage of its high photocatalytic activity) and magnetite particles (Fe_3O_4, for its magnetic properties, high mechanical stability, and the iron ions content for the enhancement of titanium dioxide photocatalitycal activity). In order to assess ionic conductivity, of paramount importance for the fuel cell potential applications, this composite material was subjected to Electrochemical Impedance Spectroscopy (EIS) measurements.

2. Experimental

The synthesis of this composite material consists in the following steps:

1) the synthesis of the Fe_3O_4 magnetic particles;
2) the functionalization of this particles with titanium dioxide;
3) the synthesis of the polysulfone-titanium dioxide covered magnetite particles.

The magnetite particles were obtained using the Massart method, described in details in [16], starting from iron (II) and iron (III) salts in an alkaline solution environment. The next step was to ensure its functionalisation with titanium dioxide. The method used is fully presented elsewhere [17] and this synthesis consists of *in situ* generation of titanium dioxide from titanium tetrabutoxide ($Ti(OBu)_4$) in the presence of dimedone (5,5-Dimethyl-1,3-cyclohexanedione, a chelating agent for titanium tetrabutoxide). The reaction scheme for these two steps is depicted below:

$$Fe^{2+} + Fe^{3+} \xrightarrow{HO^-} Fe_3O_4$$

$$Ti(OBu)_4 + Fe_3O_4 \xrightarrow[HO^-]{\text{Dimedone}} Fe_3O_4{-}TiO_2$$

Fig. 1. Reaction scheme for the synthesis of the Fe_3O_4/TiO_2 particles.

The third step consisted in the synthesis of the polysulfone composite material. The experimental procedure is as follows: 100 mL 12% polysulfone solution in N-methyl pyrrolidone and 5 g Fe_3O_4/TiO_2 magnetic particles were milled together with 40 grams of glass spheres (for a good dispersion of the particles) in a Retsch PM100 mill at 250 rpm for 8 hours. The homogenous mixture was then separated from the glass spheres and poured in a few Petri dishes. After 24 hours there was a separation of two phases, a solvent one and respectively, the polysulfone composite. The excess solvent was removed and the uniform layer from the bottom of the Petri dish was dried for 24 hour at 80 ºC.

The final dark-brownish product has a shiny surface and the appearance of a normal membrane (in the form of the Petri dish), is rigid and is attracted by a magnet, confirming its magnetic properties.

This new material was characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Electrochemical Impedance Spectroscopy (EIS).

3. Results and discussions

SEM analysis

The Scanning Electron Microscopy, performed with a Vega Tescan instrument shows, at a magnification of 51x (Fig. 2), indicates that the surface of the composite material is relatively uniform. By increasing the magnification to 10000x and by using a FEI Nova NanoSem 630 instrument, it could be observed that the titanium dioxide covered magnetite particles have a uniform distribution in the polysulfonic mass.

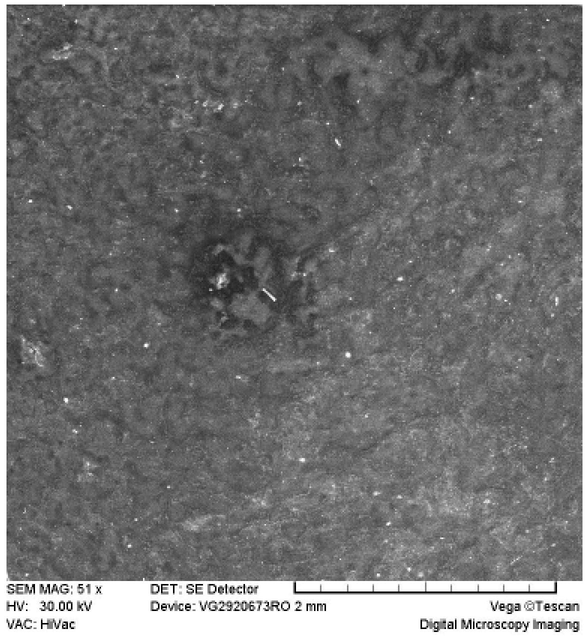

Fig. 2. SEM image of the composite material at 51x.

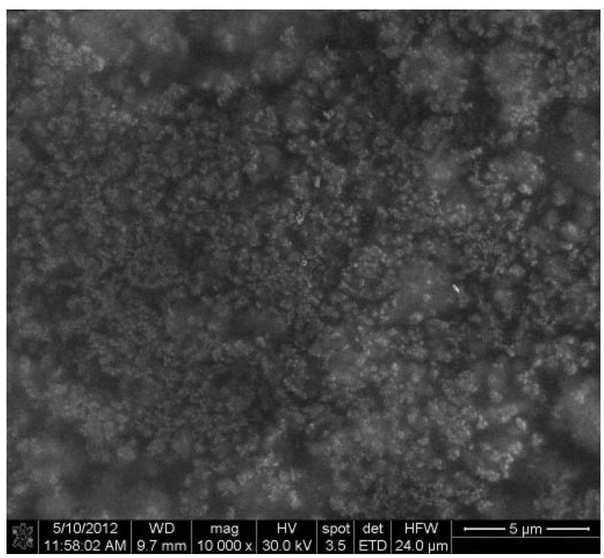

Fig. 3. SEM image of the composite material at 10000x.

FT-IR analysis

The FT-IR analysis was conducted using a Bruker Tensor 27 instrument provided with a diamond ATR annex. By comparing the 2 spectra one may observe that there are clear differences between the two of them. Practically, the peaks of polysulfone are masking the ones from the magnetic particles. This happens of course due to the fact that the polysulfonic group has many different bonds (S-O, C-S, C=C, C-C, etc.) which have higher intensity peaks than that of the bonds from the magnetite-titanium dioxide complex.

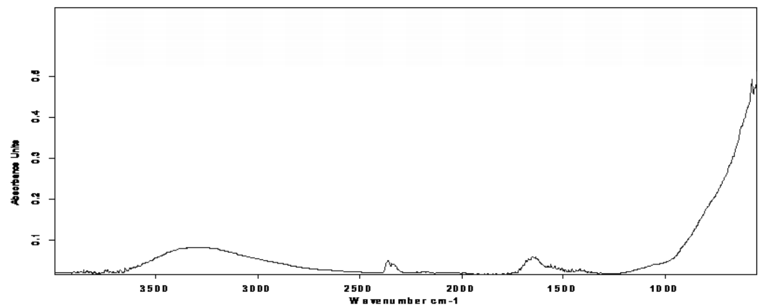

Fig. 4. FT-IR spectrum of Fe_3O_4/TiO_2 particles.

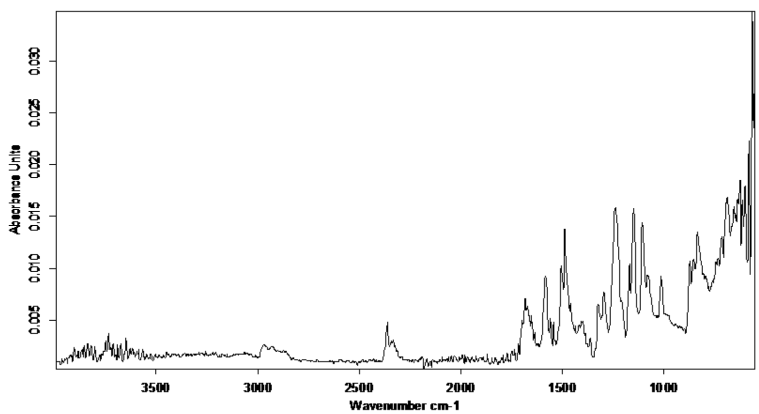

Fig. 5. FT-IR spectrum polysulfone- Fe_3O_4/TiO_2 material.

Ionic conductivity

In order to evaluate this ionic conductivity, one has used the Electrochemical Impedance Spectroscopy (EIS) method used in conjunction with a novel type of electrochemical cell, specifically designed for such evaluation purposes and presented extensively in [18]. A VoltaLab 40 Dynamic Electrochemical System was used as it allows a data post-measurements processing procedure using the integrated software provided by the manufacturer, and hence, the possibility to compare the standardised results with those published in literature. By processing the data obtained from the membrane evaluations, one obtains the actual value of the membrane impedance/resistance. By knowing the membrane thickness it was very easy now to calculate the value of the ionic conductivity:

$$\sigma = \frac{d}{R1} \qquad (1)$$

where:
σ - is the ionic conductivity in S/cm;
d - is the membrane thickness in cm;
R1 - is the ohmic resistance taken as the first intersection of the circular regression curve with the real impedance axis in $ohm \cdot cm^2$

In Fig. 6, one may see an electrochemical impedance spectrogram. The value of R1, obtained following the circular regression of the experimental points is 3918 $ohm \cdot cm^2$. The membrane thickness for this material was measured during the electrochemical impedance spectroscopy evaluation and was found 0.0112 cm. By applying the relation (1) one obtains a ionic conductivity of $2.85 \cdot 10^{-6}$ S/cm. By comparing this value to the one of Nafion membranes, 0.1 S/cm, it could be clearly noticed that this material cannot be used in a fuel cell due to its low ionic conductivity. Nonetheless, having a low ionic conductivity is compensated by its increased electronic conductivity, so that one potential application for this composite material could be in the field of electronics.

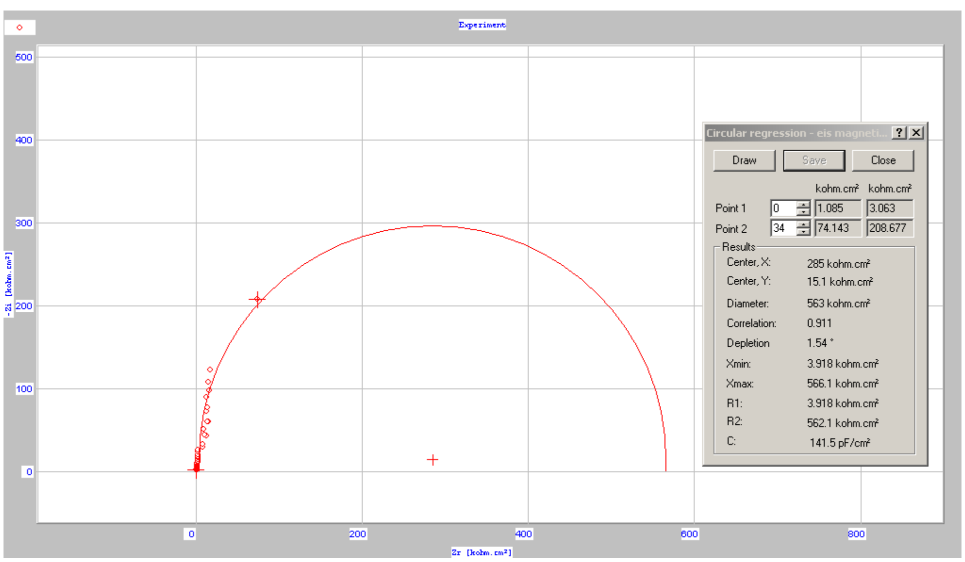

Fig. 6. Nyquist diagram of polysulfone-Fe_3O_4/TiO_2 membrane.

6. Conclusions

This newly synthesised polysulfone-magnetite/titanium dioxide composite material was obtained through a simple and accessible technique. The obtained Psf-Fe_3O_4/TiO_2 composite combines three materials with different properties. By analyzing the ionic conductivity of this material, it was concluded that it cannot be used in fuel cells applications, but it can still have some potential applications in photocatalitycal oxidation of organic compounds, because it contains in its structure iron ions which can enhance the photocatalytic activity, and also may be used where a fairly good electronic conduction is needed. Its magnetic activity allows it to be easily mounted on a magnetic support, and used where the magnetic properties come first before the electrical conductivity.

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