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A humidity-sensitive nanocomposite solid ion conductor: sulfonated poly-ether-ether-ketone in nanotubular TiO₂ or ZrO₂ matrix

O. Ruzimuradov^{1,2} · M. Braglia^{1,3,4} · F. Vacandio^{1,3,4} · P. Knauth^{1,3,4}

Abstract

A nanocomposite solid ion conductor was prepared by infiltrating zirconia or titania nanotube arrays, made by electrochemical anodization of Zr or Ti metal, with proton-conducting sulfonated poly(ether-ether-ketone) (SPEEK) ionomer. The resulting material was characterized using scanning electron microscopy, X-ray diffraction, and infrared spectroscopy showing the successful filling of the nanotubular matrix with the ionomer. Impedance spectroscopy revealed a conductivity increase by several orders of magnitude after infiltration; furthermore, the impedance of the TiO₂nt-SPEEK nanocomposite is very sensitive to the relative humidity. Possible applications of these ionic conducting nanocomposites include solid-state humidity sensors or heterogeneous catalytic materials.

Keywords Nanocomposite materials · Polymer electrolytes · Proton conductivity · Humidity sensing

Introduction

The ionic conductivity of low-dimensional solid ion conductors [1-3] in special structure types, especially those

Highlights ZrO_2 and TiO_2 nanotube arrays were infiltrated with a proton-conducting ionomer.

Phase composition and electrical properties of the nanocomposite solids were analyzed.

After ionomer infiltration, the impedance is very sensitive to the relative humidity.

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containing one-dimensional conduction channels (e.g., Hollandites [2]) or two-dimensional lattice planes (e.g., β -alumina [4]), is often highly anisotropic. Composite materials can also be prepared [5]; in this case, the composite structure must have a highly ordered arrangement of the ion conducting phase to present anisotropic conduction properties, for example in mesoscopic ionic conducting heterostructures [6].

Nanocomposite ionic conductors with highly oriented conduction paths can in principle be constructed using nanotubular templates, which are filled with an ionic conducting phase [7]. Besides the fundamental aspect of the investigation of highly anisotropic ion conduction properties, the potential applications of low-dimensional solid ion conductors are widespread, including solid-state sensors [8] or heterogeneous catalysis [9].

In this work, we use self-organized ZrO_2 or TiO_2 nanotubes as template for the deposition of a proton-conducting sulfonated aromatic polymer [10–13]. Pristine ZrO_2 or TiO_2 nanotubes can be prepared by electrochemical anodization of zirconium or titanium metal films in a fluoride-ion containing electrolyte [14, 15]. The electrochemical growth of selfordered zirconia nanotubes in organic and aqueous electrolyte systems containing fluoride ions with the limiting voltages were reported in references [16–18]. Guo et al. [19] investigated the formation and growth of a self-organized zirconia porous layer by anodization of Zr in chloride containing electrolytes. The morphology of the porous layers was affected by



Fig. 1 Schematic of contact arrangement

the electrochemical conditions, including the Cl⁻ concentration. Zirconia nanotubes with smooth and straight walls, diameters ranging from 250 to 300 nm and a length of 33 μ m can be produced by anodization under proper conditions.

Sakai et al. [20] reported the proton conduction properties of sulfuric acid modified nano-titania. The proton conductivity was almost the same as that of hydrous sulfated nanotitania, when the amount of adsorbed sulfate groups was almost the same. Highly ordered and ultrafine TiO_2 nanotubes were also fabricated by a modified rapid anodization method [21]. Polypyrrole–titania nanotube hybrids were prepared by electrodeposition of polypyrrole into well-aligned titania nanotubes and also through an electrochemical reduction and deposition method [22].

Nanotubular ZrO_2 is highly resistive at room temperature [23], whereas TiO_2 nanotubes show n-type semiconducting behavior [24]. The electrochemical reduction of zirconia nanotubes is much more difficult than that of TiO_2 nanotubes, because Zr^{4+} ions are less easily reduced than Ti^{4+} ions [24]. In that sense, zirconia nanotubes represent a model insulating matrix and titania nanotubes a model semiconducting matrix to infiltrate with a room temperature ion conductor.

A model solid ion conductor was used for infiltration: sulfonated poly-ether-ether-ketone (SPEEK) is a familiar proton-conducting ionomer at room temperature and most properties, including the proton conductivity, are very well known [25–27]. The presence of water molecules in the channels of the nanophase-separated polymer structure provides a water-mediated pathway for ion transport [26].

The first decisive step for the realization of such highly anisotropic nanocomposites is to prepare a highly wetting ionomer solution, which allows completely filling the nanotubular templates. The crucial aspect is to find an appropriate solvent for the ionomer with excellent wetting capability of ZrO_2 or TiO_2 surfaces [28].

The resulting nanocomposite structure presents a high aspect ratio of the ionic conductor and highly oriented conduction paths.

We study the water vapor pressure dependence of the ionic conductivity of these nanocomposites with semiconducting titania matrix in order to realize humidity-sensitive detectors. The proton mobility opens also the possibility to realize model heterogeneous catalysts for proton-catalyzed reactions.

Material and methods

About 2-µm-thick Zr of Ti metal films were deposited by cathodic sputtering on Si substrates as previously reported [14]. The Zr films were anodically oxidized at room temperature in a 0.35 M NH₄F solution in glycerol containing 5 vol% water at a voltage of 40 V during 10 min using a conventional two-electrode configuration. Ti films were anodized in a glycerol solution containing 1.3 wt% NH₄F and 2 wt% water at 60 V for 3 h. The glycerol solution was slightly stirred (100 rpm) to promote the detachment of oxygen bubbles from the surface of the electrodes, resulting in a better morphology and overall quality of the nanotubes. A platinum grid was used as counter electrode [14]. The zirconium or titanium metal remaining after the anodization at the base of the ZrO₂ or TiO₂ nanotubes is used as back electrode for the impedance measurements. After the anodization, the nanotubes were abundantly rinsed with deionized water and dried at 80 °C under vacuum for 2 h.

Sulfonated poly-ether-ether-ketone (SPEEK) with a degree of sulfonation of 0.9 (corresponding to an ion exchange capacity IEC = 2.5 meq/g) was prepared by reaction of PEEK with concentrated sulfuric acid at 50 °C, as reported previously [29, 30]. The infiltration was done by dissolving 7.1 mg of SPEEK into 10 mL of dimethylformamide (DMF). A drop of



Fig. 2 SEM images of a unfilled and b SPEEK-filled ZrO₂ nanotubes

Fig. 3 FTIR spectra of pristine (black) and ionomer-filled (red) ZrO_2 nanotubes. The chemical formula of the repeat unit of SPEEK is inlaid



this solution was deposited on a $\sim 0.5 \text{ cm}^2$ sample of zirconia or titania nanotubes. The quantity of SPEEK included in 1 drop ($\sim 0.1 \text{ mL}$) solution was calculated to be sufficient to fill the nanotubes completely.

Samples were analyzed by X-ray diffraction (XRD) with CuK α radiation using a Siemens D5000 diffractometer. The surface morphology and composition of the nanocomposite were investigated by scanning electron microscopy (SEM, Hitachi, S-570). Fourier-transform infra-red (FTIR) spectra were recorded in transmission mode from 4000 to 400 cm⁻¹ wave number using a Bruker Equinox 55 spectrometer.

Impedance diagrams were recorded with signal amplitude of 20 mV in a frequency range from 100 kHz to 1 Hz using Parstat 2273 or 4000 impedance analyzers. The back contact was taken on the remaining Ti metal film; the front contact was a stainless steel disk of 6-mm diameter (Fig. 1). Several experiments were made in order to verify the reproducibility and accuracy of the data, changing the area and position of the contact.

Impedance measurements with TiO_2nt -SPEEK nanocomposites were also performed under different relative humidity (RH). For dry conditions, the sample was dried in an oven at 100 °C overnight and the Swagelok cell assembled in a dry box. For simulation of saturated water vapor, a drop of water was added before closing the Swagelok cell. For atmospheric humidity conditions, the sample was assembled in ambient air; RH was measured using a humidity sensor.

Results and discussion

A first essential step of the nanocomposite preparation was to find a solvent with excellent wetting properties for the nanotubular matrix. Dimethylformamide was reported to wet different ceramic-carbon nanotube composites, including ZrO₂ [23, 24], and it is capable to dissolve a sufficient amount of SPEEK with sulfonation degree of 90%. As known, sulfonation increases the hydrophilicity of the polymer and promotes the transport of cations [23]. The hydrophilicity and solubility of the polymer increase with the sulfonation degree [10, 25, 31]. At sulfonation degrees lower than 60%, SPEEK is only soluble in strong acids such as sulfuric acid. Above sulfonation degrees of 80%, the SPEEK polymer becomes soluble in methanol, DMF and hot water.

A water uptake between 20 and 40% is most suitable for high levels of ion conductivity while keeping a mechanically stable polymer. The proton conductivity of hydrated SPEEK membranes measured by impedance spectroscopy ranged from 10^{-3} to 10^{-1} S/cm as the IEC increased from 1.0 to

Table 1FTIR band assignments of SPEEK-filled ZrO_2 nanotubes (v_{as} :Asymmetric stretching, v_s : symmetric stretching, ds: bending, φ : ringdeformation, OP: out of plane, IP: in plane). Index "a": ring a; index"b": ring b, see repeat unit in Fig. 2

Band assignment			
Wave number/cm ⁻¹	SPEEK [34]	ZrO_2 nanotubes [9, 32]	
870	ν_{as} COC, ϕa OP, ϕb IP		
1000		Zr-OH surface	
1023	$\phi a \text{ IP}, \nu_s \text{ SO}_3$		
1054		Zr-OH surface	
1080	ϕa IP, ν_{as} CHa, ν_{s} SO_3		
1130		Zr-OH surface	
1205		Zr-OH surface	
1230	ϕb IP, ν_{as} CHb, ν_{as} SO_3		
1255	ν_{as} CHa, ϕa IP, ν_{as} SO_3		
1400		Zr-OH surface	
1476	ν_{as} COC, ϕa IP, ϕb IP		
1610	ν_{s} C=O, ϕb IP		





2.7 meq/g [27]. Therefore, SPEEK with a degree of sulfonation of 90% was chosen in this work.

The solution concentration was adapted in order to have in one drop of solution a quantity of SPEEK sufficient to fill the nanotubular volume completely without forming an ionomer layer on top. The nanotubular volume to be filled with SPEEK can be calculated from the previously reported dimensions of the ZrO₂ and TiO₂ nanotubes, which were confirmed in this work (see Fig. 2a). The average ZrO₂ nanotube length is about 1 μ m; the nanotube diameter, observable in the inlaid image, is around 40 nm. The wall thickness of about 5 nm was reported previously [14]. For TiO₂, the average length and diameter are 1.5 μ m and 100 nm, respectively, and the wall thickness about 10 nm.

Ionomer-filled ZrO_2 nanotube arrays can be observed in Fig. 2b. One can distinguish the regular microstructure of

the oxide nanotubes. Indeed no ionomer layer is formed on top and most nanotubes appear filled, as can be concluded from the different contrast.

The XRD pattern of ionomer-filled nanotubes confirms the partly crystalline structure of the ZrO₂ nanotubes, containing both monoclinic and tetragonal phases, as reported earlier [23, 32]; in polymer-filled nanotubes, a broad reflection observed around a Bragg angle $2\theta = 20^{\circ}$ is due to fully amorphous SPEEK, as previously discussed [33].

Figure 3 shows the FTIR spectra of pristine and ionomerfilled ZrO_2 nanotubes. The main bands are reported in Table 1. The broad absorption band between 550 and 800 cm⁻¹ corresponds to the vibration of Zr–O bonds in zirconia [32]. The peaks between 900 and 1500 cm⁻¹ are attributed to hydroxyl surface groups. The peak at 1630 cm⁻¹ was previously assigned to NH₄⁺ ions, given that zirconia nanotube arrays





Table 2Electrical properties of TiO_2nt -SPEEK nanocomposites atdifferent relative humidities

RH/ %	R1/Ω	Y°1/F s ⁻ⁿ	nl
0	16,150	6×10^{-11}	0.98
30	760	$1.2 imes 10^{-10}$	0.95
100	40	-	-

were prepared in an electrolyte containing NH_4F [9]. The peaks related to the ionomer (Table 1) are consistent with previous reports [30].

The frequency dependence of the impedance modulus (Bode plot) of pristine and ionomer-filled ZrO_2 nanotubes is reported in Fig. 4. Within the investigated frequency range, the impedance modulus |Z| of the pristine ZrO_2nt is inversely proportional to the frequency (slope = -1 in the double logarithmic plot of Fig. 4), which is consistent with a capacitive response, according to the equation (where f is the frequency and C the capacitance):

$$Z = 1/(2\pi fC) \tag{1}$$

One can clearly observe the significant decrease of impedance after infiltration of SPEEK, given that the conductivity of SPEEK [27, 35–37] is much higher than that of the nanotubular ZrO_2 matrix [23].

We have also analyzed the impedance response of TiO₂nt-SPEEK nanocomposites under different relative humidity. This experiment is a proof-of-concept for the realization of humidity-sensitive detectors. Figure 5 shows a comparison of the impedance in dry conditions, under ambient humidity (RH = (30 ± 10) %) and in presence of a drop of water, representing saturated vapor pressure. One can observe that the impedance in Nyquist plots is very sensitive to these changes in humidity. The equivalent circuit (a series arrangement of two parallel resistance-constant phase elements Q) used for non-linear least-square fitting is shown in the Fig. 5. The impedance of a constant phase element can be written:

 $Z(Q) = Y^{\circ} (i\omega)^{-n}$ (2).where *i* is the imaginary unit, ω the angular frequency, Y° the CPE value and *n* the CPE exponent, indicating the physical nature of the element: a value near 1 designates an imperfect capacitance. Non-linear least-square fitting of the spectra gave the resistance and CPE values of TiO₂nt-SPEEK nanocomposites reported in Table 2 for different RH.

Whereas the CPE values and exponents are typical of thin materials, the resistance decreases very strongly with the relative humidity, indicating potentialities for the conception of a high performance humidity detector. Further work to characterize the d.c. properties and interfacial effects on the conductance are currently in progress.

Conclusion

The preparation and properties of a nanocomposite solid ion conductor, made by infiltration of SPEEK into ZrO_2 or TiO_2 nanotubes, are reported. The microstructure and phase composition are confirmed by SEM, XRD, and FTIR spectroscopy. The strong decrease of sample resistance by infiltration of ionic conducting polymer is revealed by impedance spectroscopy. The proof-of-concept of a humidity-sensitive detector is demonstrated with TiO₂nt-SPEEK nanocomposites. Other applications of these promising nanocomposite solid ion conductors, especially in the domain of chemical sensors and heterogeneous catalysis, will be investigated in the future.

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