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

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 ZrO₂ or TiO₂ nanotubes as template for the deposition of a proton-conducting sulfonated aromatic polymer [10–13]. Pristine ZrO₂ or TiO₂ 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 self-ordered 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

Highlights ZrO₂ and TiO₂ 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.

✉ O. Ruzimuradov
o.ruzimuradov@polito.uz; ruzimuradov@rambler.ru

✉ P. Knauth
philippe.knauth@univ-amu.fr

¹ CNRS, Madirel (UMR 7246), Electrochemistry of Materials Group, Aix Marseille University, Campus St Jérôme, 13397 Marseille, France

² Department of Natural and Mathematic Sciences, Turin Polytechnic University in Tashkent, Malaya Kolsevaya 17, Tashkent, Uzbekistan 100095

³ International Associated Laboratory (L.I.A.) Ionomer Materials for Energy (Aix Marseille University, CNRS, Univ. Rome Tor Vergata), Marseille, France

⁴ International Associated Laboratory (L.I.A.) Ionomer Materials for Energy (Aix Marseille University, CNRS, Univ. Rome Tor Vergata), Rome, Italy

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 μm 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 nano-titania, 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 or 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 NH_4F 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% NH_4F 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 ZrO_2 or TiO_2 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 $^\circ\text{C}$ 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 $\text{IEC} = 2.5 \text{ meq/g}$) was prepared by reaction of PEEK with concentrated sulfuric acid at 50 $^\circ\text{C}$, 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 ZrO_2 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 $\text{CuK}\alpha$ 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 $\text{TiO}_2\text{nt-SPEEK}$ 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

ZrO_2 [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 1 FTIR band assignments of SPEEK-filled ZrO_2 nanotubes (ν_{as} : Asymmetric stretching, ν_{s} : symmetric stretching, ds: bending, ϕ : ring deformation, 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	$\nu_{\text{as}} \text{COC}$, ϕa OP, ϕb IP	
1000		Zr-OH surface
1023	ϕa IP, $\nu_{\text{s}} \text{SO}_3$	
1054		Zr-OH surface
1080	ϕa IP, $\nu_{\text{as}} \text{CHa}$, $\nu_{\text{s}} \text{SO}_3$	
1130		Zr-OH surface
1205		Zr-OH surface
1230	ϕb IP, $\nu_{\text{as}} \text{CHb}$, $\nu_{\text{as}} \text{SO}_3$	
1255	$\nu_{\text{as}} \text{CHa}$, ϕa IP, $\nu_{\text{as}} \text{SO}_3$	
1400		Zr-OH surface
1476	$\nu_{\text{as}} \text{COC}$, ϕa IP, ϕb IP	
1610	$\nu_{\text{s}} \text{C=O}$, ϕb IP	

Fig. 4 Impedance spectra (Bode modulus plots) for pristine and ionomer-filled ZrO_2 nanotubes at ambient humidity ($\text{RH} = (30 \pm 10) \%$)

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 ZrO_2 and TiO_2 nanotubes, which were confirmed in this work (see Fig. 2a). The average ZrO_2 nanotube length is about 1 μm ; the nanotube diameter, observable in the inlaid image, is around 40 nm. The wall thickness of about 5 nm was reported previously [14]. For TiO_2 , the average length and diameter are 1.5 μm 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 ZrO_2 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 ionomer-filled 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 NH_4^+ ions, given that zirconia nanotube arrays

Fig. 5 Humidity dependence of the impedance of $\text{TiO}_2\text{nt-SPEEK}$ nanocomposites at 25°C . The lines represent non-linear least-square fits using the equivalent circuit shown in the figure. The inset shows a zoom on the impedance plot at 100% RH

Table 2 Electrical properties of TiO₂nt-SPEEK nanocomposites at different relative humidities

RH/ %	R1/Ω	Y°1/F s ⁻ⁿ	n1
0	16,150	6×10^{-11}	0.98
30	760	1.2×10^{-10}	0.95
100	40	—	—

were prepared in an electrolyte containing NH₄F [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 ZrO₂ nanotubes is reported in Fig. 4. Within the investigated frequency range, the impedance modulus $|Z|$ of the pristine ZrO₂nt 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):

$$Z = 1/(2\pi fC) \quad (1)$$

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 ZrO₂ 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 ZrO₂ or TiO₂ 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.

Acknowledgments O.R. acknowledges the European Union Erasmus Mundus Master Program MESC (Materials for Energy Storage and Conversion) for a Visiting Scholarship under which the present study was carried out.

The authors want to express their gratitude to Amélie Démoulin for help with the SEM observations.

References

- Gellings PJ, Bouwmeester HJM (1997) Handbook of solid state electrochemistry. CRC Press, Boca Raton
- Kudo T, Fueki K (1990) Solid state ionics. Kodansha-VCH, Tokyo
- Rickert H (1982) Electrochemistry of solids. Springer, Berlin
- Yao YFY, Kummer JT (1967) Ion exchange properties of and rates of ionic diffusion in beta-alumina. J Inorg Nucl Chem 29(9):2453–2466
- Croce F, Appetecchi GB, Persi L, Scrosati B (1998) Nanocomposite polymer electrolytes for lithium batteries. Nature 394(6692):456–458
- Sata N, Eberman K, Eberl K, Maier J (2000) Mesoscopic fast ion conduction in nanometre-scale planar heterostructures. Nature 408(6815):946–949
- Steinhart M, Wendorff JH, Greiner A, Wehrspohn RB, Nielsch K, Schilling J, Choi J, Gosele U (2002) Polymer nanotubes by wetting of ordered porous templates. Science 296(5575):1997–1997. <https://doi.org/10.1126/science.1071210>
- Adhikari B, Majumdar S (2004) Polymers in sensor applications. Prog Polym Sci 29(7):699–766. <https://doi.org/10.1016/j.progpolymsci.2004.03.002>
- Wang XX, Zhao JL, Hou XR, He Q, Tang CC (2012) Catalytic activity of ZrO₂ nanotube arrays prepared by anodization method. J Nanomater 5:1–5. <https://doi.org/10.1155/2012/409571>
- Roziere J, Jones DJ (2003) Non-fluorinated polymer materials for proton exchange membrane fuel cells. Annu Rev Mater Res 33(1): 503–555. <https://doi.org/10.1146/annurev.matsci.33.022702.154657>
- Kreuer KD (1997) On the development of proton conducting materials for technological applications. Solid State Ionics 97(1–4):1–15. [https://doi.org/10.1016/S0167-2738\(97\)00082-9](https://doi.org/10.1016/S0167-2738(97)00082-9)
- Di Vona ML, Knauth P (2013) Sulfonated aromatic polymers as proton-conducting solid electrolytes for fuel cells: a short review.

- Zeitschrift Fur Physikalische Chemie-Int J Res Phys Chem Chem Phys 227(5):595–614. <https://doi.org/10.1524/zpch.2013.0337>
13. Knauth P, Di Vona ML (2012) Solid proton conductors: properties and applications in fuel cells. Wiley, Chichester
 14. Vacandio F, Eyraud M, Chassigneux C, Knauth P, Djenizian T (2010) Electrochemical synthesis and characterization of zirconia nanotubes grown from Zr thin films. *J Electrochem Soc* 157(12):K279–K283. <https://doi.org/10.1149/1.3496013>
 15. Premchand YD, Djenizian T, Vacandio F, Knauth P (2006) Fabrication of self-organized TiO₂ nanotubes from columnar titanium thin films sputtered on semiconductor surfaces. *Electrochem Commun* 8(12):1840–1844. <https://doi.org/10.1016/j.elecom.2006.08.028>
 16. Fang D, Yu JG, Luo ZP, Liu SQ, Huang KL, Xu WL (2012) Fabrication parameter-dependent morphologies of self-organized ZrO₂ nanotubes during anodization. *J Solid State Electrochem* 16(3):1219–1228. <https://doi.org/10.1007/s10008-011-1516-3>
 17. Stepien M, Handzlik P, Fitzner K (2014) Synthesis of ZrO₂ nanotubes in inorganic and organic electrolytes by anodic oxidation of zirconium. *J Solid State Electrochem* 18(11):3081–3090. <https://doi.org/10.1007/s10008-014-2422-2>
 18. Sowa M, Lastowska D, Kukharensko AI, Korotin DM, Kurmaev EZ, Cholakh SO, Simka W (2017) Characterisation of anodic oxide films on zirconium formed in sulphuric acid: XPS and corrosion resistance investigations. *J Solid State Electrochem* 21(1):203–210. <https://doi.org/10.1007/s10008-016-3369-2>
 19. Guo LM, Zhao JL, Wang XX, Xu RQ, Li YX (2009) Synthesis and growth mechanism of zirconia nanotubes by anodization in electrolyte containing Cl⁻. *J Solid State Electrochem* 13(9):1321–1326. <https://doi.org/10.1007/s10008-008-0669-1>
 20. Sakai T, Kim SJ, Kajitani S, Hamagami J, Oda H, Matsuka M, Ishihara T, Matsumoto H (2012) Proton conduction properties of nano-titania modified by sulfuric acid impregnation. *J Solid State Electrochem* 16(6):2055–2059. <https://doi.org/10.1007/s10008-011-1616-0>
 21. Zhong P, Liao YL, Que WX, Jia QY, Lei TM (2014) Enhanced electron collection in photoanode based on ultrafine TiO₂ nanotubes by a rapid anodization process. *J Solid State Electrochem* 18(8):2087–2098. <https://doi.org/10.1007/s10008-014-2463-6>
 22. Li Q, Xia ZB, Wang SM, Zhang YJ, Zhang YH (2017) The preparation and characterization of electrochemical reduced TiO₂ nanotubes/polypyrrole as supercapacitor electrode material. *J Solid State Electrochem* 21(8):2177–2184. <https://doi.org/10.1007/s10008-017-3555-x>
 23. Vacandio F, Eyraud M, Knauth P, Djenizian T (2011) Tunable electrical properties of self-organized zirconia nanotubes. *Electrochem Commun* 13(10):1060–1062. <https://doi.org/10.1016/j.elecom.2011.06.032>
 24. Hanzu I, Djenizian T, Knauth P (2011) Electrical and point defect properties of TiO₂ nanotubes fabricated by electrochemical anodization. *J Phys Chem C* 115(13):5989–5996. <https://doi.org/10.1021/jp1111982>
 25. Xing PX, Robertson GP, Guiver MD, Mikhailenko SD, Wang KP, Kaliaguine S (2004) Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. *J Membr Sci* 229(1–2):95–106. <https://doi.org/10.1016/j.memsci.2003.09.019>
 26. Di Vona ML, Sgreccia E, Licoccia S, Alberti G, Tortet L, Knauth P (2009) Analysis of temperature-promoted and solvent-assisted cross-linking in sulfonated poly(ether ether ketone) (SPEEK) proton-conducting membranes. *J Phys Chem B* 113(21):7505–7512. <https://doi.org/10.1021/jp9006679>
 27. Di Vona ML, Pasquini L, Narducci R, Pelzer K, Donnadio A, Casciola M, Knauth P (2013) Cross-linked sulfonated aromatic ionomers via SO₂ bridges: conductivity properties. *J Power Sources* 243:488–493. <https://doi.org/10.1016/j.jpowsour.2013.05.127>
 28. Steinhart M, Wehrspohn RB, Gosele U, Wendorff JH (2004) Nanotubes by template wetting: a modular assembly system. *Angew Chem Int Ed* 43(11):1334–1344. <https://doi.org/10.1002/anie.200300614>
 29. Di Vona ML, Alberti G, Sgreccia E, Casciola M, Knauth P (2012) High performance sulfonated aromatic ionomers by solvothermal macromolecular synthesis. *Int J Hydrog Energy* 37(10):8672–8680
 30. Di Vona ML, Luchetti L, Spera GP, Sgreccia E, Knauth P (2008) Synthetic strategies for the preparation of proton-conducting hybrid polymers based on PEEK and PPSU for PEM fuel cells. *C R Chim* 11(9):1074–1081. <https://doi.org/10.1016/j.crci.2008.06.001>
 31. Kaliaguine S, Mikhailenko SD, Wang KP, Xing P, Robertson G, Guiver M (2003) Properties of SPEEK based PEMs for fuel cell application. *Catal Today* 82(1–4):213–222. [https://doi.org/10.1016/S0920-5861\(03\)00235-9](https://doi.org/10.1016/S0920-5861(03)00235-9)
 32. Zhao JL, Wang XX, Xu RQ, Meng FB, Guo LM, Li YX (2008) Fabrication of high aspect ratio zirconia nanotube arrays by anodization of zirconium foils. *Mater Lett* 62(29):4428–4430. <https://doi.org/10.1016/j.matlet.2008.07.054>
 33. Marani D, Di Vona ML, Traversa E, Licoccia S, Beurroies I, Llewellyn PL, Knauth P (2006) Thermal stability and thermodynamic properties of hybrid proton-conducting polyaryl etherketones. *J Phys Chem B* 110(32):15817–15823. <https://doi.org/10.1021/jp062085h>
 34. Doan J, Kingston E, Kendrick I, Anderson K, Dimakis N, Knauth P, Di Vona ML, Smotkin ES (2014) Theoretical and experimental infrared spectra of hydrated and dehydrated sulfonated poly(ether ether ketone). *Polymer* 55(18):4671–4676. <https://doi.org/10.1016/j.polymer.2014.07.011>
 35. Bauer B, Jones DJ, Roziere J, Tchicaya L, Alberti G, Casciola M, Massinelli L, Peraio A, Besse S, Ramunni E (2000) Electrochemical characterisation of sulfonated polyetherketone membranes. *J New Mater Electrochem Syst* 3(2):93–98
 36. Alberti G, Casciola M, Massinelli L, Bauer B (2001) Polymeric proton conducting membranes for medium temperature fuel cells (110–160 degrees C). *J Membr Sci* 185(1):73–81
 37. Knauth P, Di Vona ML (2012) Sulfonated aromatic ionomers: analysis of proton conductivity and proton mobility. *Solid State Ionics* 225:255–259. <https://doi.org/10.1016/j.ssi.2012.01.043>