

Zirconia Aerogel - Polyxometalate Composites Synthesis with Applications in Solid Oxide/Acid Fuel Cells

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ABSTRACT

Zirconia is an important material that has attracted interest in catalysis, oxygen sensors, solid oxide fuel cells and electrochemical pumps. Zirconia aerogel combines the aerogel characteristics (high porosity, low-density and large surface) with acid and basic properties, as well as oxidizing and reducing properties [1]. Due to its high protonic conductivity at room temperature and high solubility, polyoxometalates (e.g. phosphotungstic acid) was successfully employed as electrolyte in H₂/O₂ fuel cells [2]. Ionic-conducting zirconia aerogels doped with heteropolyacids (phosphotungstic and phosphomolibdic acids) were synthesized by sol-gel method followed by low temperature supercritical drying. These materials were characterized using TG/DTA, BET techniques and Raman spectroscopy. Conductivity of the zirconia aerogels – heteropolyacid composites was evaluated by impedance method. Activation energy of the zirconia aerogel-polyoxometalate is less 25-35 Kcal/mol [3] that proves high proton conduction. The results show zirconia aerogel - H₄SiW₁₂O₄₀ composites can be an alternative for medium temperature SOFC due to their high ionic conductivity.

Keywords: zirconia, heteropolyacid, composite, fuel cell

1 INTRODUCTION

Solid fuel cells are promising energy production devices. For long-term stability and cost, great efforts are made to drop their operating temperatures by at least several hundred degrees. This requires increased solid electrolyte conductance and enhanced reaction kinetics at the electrode level i.e. at the electrode material/solid electrolyte interfaces. Among the ionic conductors explored zirconia is the prime candidate to serve as a solid electrolyte [3, 4]. Zirconia aerogel corroborates the aerogel characteristics with zirconia properties. Aerogels have a very porous internal structure and a huge internal surface

area (400 - 600 m²/g). They can be made hydrophilic or hydrophobic, depending on which gel drying process is used. Alcohol drying (now uncommon because of the high temperature and pressure required) results in pore surfaces covered with alkoxy-groups. These hydrophobic aerogels, if sealed, are completely impervious to water, and will float indefinitely. Carbon dioxide drying results in pore surfaces covered with hydroxyl (OH) groups. When one of these hydrophilic aerogels is placed in a humid environment, it adsorbs water into its pores, up to 20% of its mass.

In the last decade heteropolyacid based proton conducting electrolytes have aroused a considerable interest for their protonic activity and oxygen affinity properties [2]. Among the various heteropolyacids, silicotungstic and phosphomolibdic acids, in their 29-water molecules hydrate form (H₄SiW₁₂O₄₀ · 29 H₂O and H₃Mo₁₂O₄₀ · 29 H₂O) are characterized by high protonic conductivity, i.e. 0.17 and 0.18 Ohm⁻¹ cm⁻¹, respectively [5]. Such high ionic conductivity properties together with the lower cost with respect to polymer membranes make heteropolyacids very attractive for fuel cells.

In order to obtain new solid electrolyte materials, zirconia aerogel - H₄SiW₁₂O₄₀ and zirconia aerogel - H₃Mo₁₂O₄₀ composites were prepared and characterized by TG/DTA, BET techniques, Raman spectroscopy and impedance method.

2 EXPERIMENTAL

Zirconia aerogels were prepared by sol-gel method in acid catalysis followed by supercritical drying at low temperature using CO₂. The following precursors were used: zirconium(IV) propoxide (70% wt Merck) – **ZrPr**, propanol (Merck) – **PrOH**, deionized water and nitric acid (70% wt Merck). The molar ratios of the reactants are presented in table 1. Zirconia aerogel – heteropolyacid composites were obtained by the aerogel impregnation with 0,01 M ethanolic solutions of H₄SiW₁₂O₄₀ (Fluka) and H₃PMo₁₂O₄₀ (Fluka), respectively.

Heteropolyacid	Molar ratios				Concentration [%]				S_{BET} [m^2/g]
	ZrPr	PrOH	H ₂ O	HNO ₃	Zr	W	Mo	P	
H ₄ SiW ₁₂ O ₄₀	1	10.10	5.66	0.99	46	0.75	-	-	12
H ₃ PMo ₁₂ O ₄₀	1	10.10	5.66	0.98	35.0	-	5.0	0.18	40.8

Table 1. Sol-gel synthesis conditions, specific surface area and elemental analysis for zirconia-heteropolyacid composites

The BET surface areas (S_{BET}) were derived from krypton physisorption measurements at 77 K using a home-made installation. Prior to measurements, the samples were degassed to 0.001 Pa at 393 K. S_{BET} was calculated in the relative pressure range 0.05-0.3, assuming a cross-sectional area of 0.195 nm² for the krypton molecule.

Thermogravimetric analyses were made using a Mettler Toledo thermal analysis system with TGA/SDTA851 thermogravimetric cell (heating rate 5° C/min; nitrogen flow) and a DSC822 thermal analysis cell.

Elemental analyses were performed with an inductively coupled plasma-mass spectroscopy (ICP-MS).

A radiation of 1064 nm from a Nd-YAG laser was employed for the recording of the Raman spectra of the untreated and heat-treated TiO₂ aerogels. The FT-Raman spectra were recorded using a Bruker Equinox 55 spectrometer with an integrated FRA 106 Raman module, a power of 100 mW incident on sample and a resolution of 1 cm⁻¹.

Impedance spectrums were recorded using a Parstat 2273 (PAR, USA) computer controlled potentiostat. Powder samples of dried composites were introduced in a conductivity cell, with the constant $k = 2.85 \text{ cm}^{-1}$, made from two platinum electrodes. Measurements were performed for imposed temperatures from room temperature up to 200°C, in a temperature controlled drying oven VacuCell (BMT, Czech Republic).

3 RESULTS AND DISCUSSION

Elemental analysis and specific surface area of the zirconia-heteropolyacid composites are presented in table 1.

Raman investigation of synthesized aerogels, presented in figure 1, exhibits a series of mostly weak-defined vibration bands specific for amorphous materials. The bands between 340 cm⁻¹ and 385 cm⁻¹ correspond to Zr-O vibrations, whereas those between 385 and 780 cm⁻¹ are associated to O-O vibrations. In the presence of polyoxometalate, several bands appear in 950-1015 cm⁻¹ range which are attributed to Mo=O vibrations [6, 7].

Thermal stability of obtained composites was investigated by thermogravimetry. Mass loss of the composite samples presents same behavior regardless the nature of polyoxometalate and synthesis method. Figure 2

presents the thermogravimetric plots of the composite with H₃[PMo₁₂O₄₀] obtained by zirconia aerogel impregnation. Several mass loss processes can be observed. Around 90 and 120°C, at first excess than crystallization water is lost, with ~17% mass decrease.

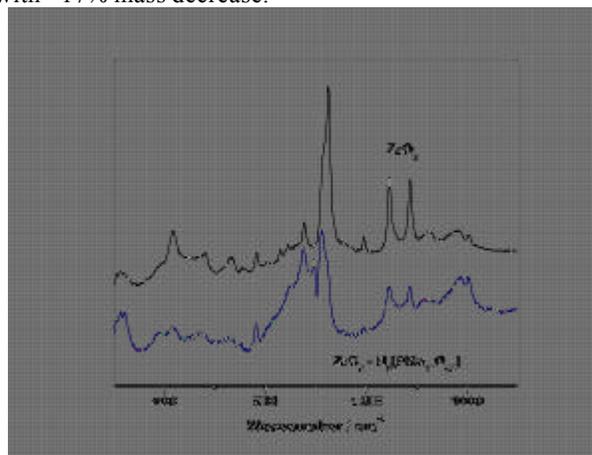


Figure 1. Raman spectra of zirconia aerogel and zirconia-polyoxometalate composite.

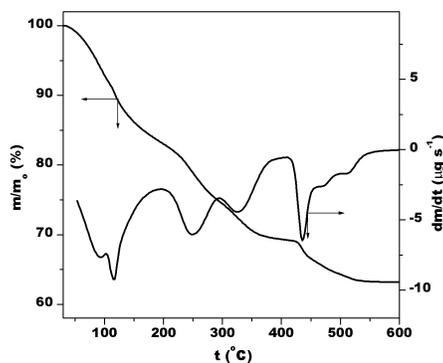


Figure 2. Thermogravimetric plots for the zirconia aerogel – polyoxometalate composite using H₃[PMo₁₂O₄₀] as heteropolyacid.

Further processes, of constitution water loss and polyoxometalate decomposition, occur at ~250, 340 and 450°C. These findings prove chemical stability of the composite up to 220°C, allowing it's utilization as proton conduction electrolyte in a proper humid environment.

Conduction of zirconia aerogel-polyoxometalate composites was determined by means of electrochemical impedance spectroscopy. A typical impedance spectroscopy spectrum is presented in figure 3 as a Bode plot for zirconia aerogel at 25°C. In the investigated frequency range several phenomena can be evidenced. Being of resistive nature, charge conduction is independent of frequency and can be approximated as the impedance modulus at inflection point of the Bode plot. For frequencies higher than 0.1MHz, impedance modulus decreases as the dielectric relaxation phenomenon controls the system's response, whereas for frequencies less than 1Hz, effects of solid state diffusion are present. More important, the absence of a lower frequency loop suggests good material homogeneity as the grain boundary resistivity effects are absent.

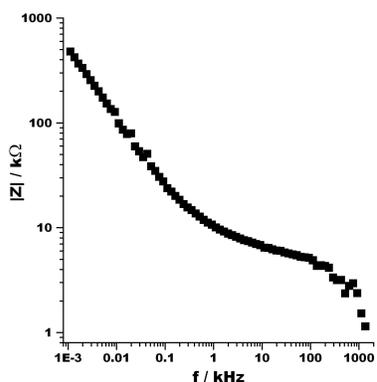


Figure 3. Bode plot of impedance spectrum measured for zirconia aerogel at 25 °C.

Calculation of conductivity is based on a nonlinear fit of impedance spectrums that uses the Levenberg-Marquardt algorithm to correlate modulus of impedance with the frequency, f , namely:

$$|Z(f)| = \left\{ \left[\frac{R}{1 + (2pfRC)^2} + \frac{W}{(2pf)^{1/2}} \right]^2 + \left[\frac{2pfR^2C}{1 + (2pfRC)^2} + \frac{W}{(2pf)^{1/2}} \right]^2 \right\}^{1/2} \quad (1)$$

The results of the fitting procedure are the parameters of the model, namely the bulk resistance, R , double layer capacitance, C , and Warburg coefficient, W , only the first being of interest for present study. Calculation of charge conductivity, σ , is possible taking into account the constant of the conductivity cell, being given by:

$$\sigma = k/R \quad (2)$$

In order to obtain information about involved transport mechanism, Arrhenius plots of de conductivity were

presented in figure 4 for the composites between zirconia aerogel and the polyoxometalate. Insensitive to the nature of polyoxometalate employed, charge conduction obeys Arrhenius law only up to app. 60-70°C, conductivity peaking at 80-90°C. This decrease of conductivity as predicted by Arrhenius law is closely correlated to the water loss evidenced by thermogravimetry.

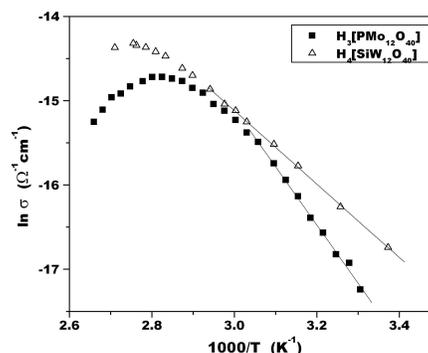


Figure 4. Arrhenius plots of conductivity for the zirconia aerogel – polyoxometalate composites employing the heteropolyacid indicated in legend.

Activation energy, E_a , and room temperature conductivity $\sigma(25^\circ\text{C})$ were calculated by fitting the linear regions of experimental Arrhenius plots, being presented in table 2 together with extrapolated conductivity at 200 °C. The room temperature conductivity of the powder samples of zirconia aerogel-polyoxometalate composites is significantly smaller than those of the crystalline polyoxometalates ($\sim 0.1 \text{ O}^{-1}\text{cm}^{-1}$). However, the powder nature of the samples seems to be the main cause of obtaining of such small values, as long as the measured conduction of microcrystalline polyoxometalate samples was found to be in range of $10^{-5} \text{ O}^{-1}\text{cm}^{-1}$.

Determined value for activation energy is an indication of occurring charge transport mechanism. It is reported that pure heteropolyacids, like those studied, are characterized by small activation energy ($\sim 10 \text{ kJ mol}^{-1}$). For instance, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ($n \sim 29$) has a cubic crystal structure, in which two diamond-type sublattices, polyanion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and cationic cluster $[\text{H}_3 \cdot 29\text{H}_2\text{O}]^{3+}$ are interpenetrated [8]. The other employed heteropolyacid, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ($n \sim 22$) of which two are constitution water, has a similar structure. The proton conduction takes place from a H_3O^+ molecule to an adjacent H_2O molecule from cationic cluster by the tunneling effect in the hydrogen bonding, followed by the rotation of molecules to allow the next transfer throughout the formed hydrogen bonding network. Charge conduction with this Grotthus-type proton conduction mechanism depends slightly on temperature, thus takes place with lower activation energy. Reported values for other types of ionic conduction in zirconia-based materials, namely oxide ion conduction, are greater than 60

kJ mol^{-1} , making possible such a mechanism only in high temperature devices [9].

Better conductivity is assured by the use of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ which has more charge carrier and posses a lower activation energy. Consequently, as the employed temperature rises, the conductivity difference between the two utilized polyoxometalates decreases.

For investigated zirconia aerogel-polyoxometalate composites, determined values of activation energy suggest a Grotthus-type mechanism of proton conduction. Because deviations from Arrhenius law occur not earlier than the evidenced mass loss by thermogravimetry, it is expected that excess water of composite sample has an important role in proton conduction. Under utilized dry atmosphere, conduction is drastically reduced by increasing the temperature because evaporation of water, on initial stages, and destroying the cationic clusters, afterwards. In practical fuel cells, with controlled humid atmosphere, proton conduction obeys Arrhenius law due to a better water management [10].

Polyoxo-metalate	E_a (kJ mol^{-1})	σ ($\text{O}^{-1}\text{cm}^{-1}$)	
		25°C	200°C
$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$	13.8	$2.86 \cdot 10^{-9}$	$1.28 \cdot 10^{-5}$
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$	10.7	$2.3 \cdot 10^{-7}$	$1.75 \cdot 10^{-4}$

Table 2. Activation energy and conductivities determined by Arrhenius plot fitting (at 25°C) and by extrapolation (at 300°C).

CONCLUSIONS

Zirconia aerogel-polyoxometalate composites were obtained by the aerogel impregnation with 0,01 M ethanolic solutions of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Sol-gel method in acid catalysis followed by supercritical drying was used to prepare the aerogel.

Synthesized zirconia aerogel-polyoxometalate composites were found to be stable at least up to 220 °C restricting their utilization to low temperature SOFC and to acid fuel cells. They prove good proton conduction if utilized in proper humid environment with good water management.

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