

Ionic Properties of an Organic–Inorganic Sol–Gel Hybrid Based on Polydimethylsiloxane and Tetraethoxysilane Doped with Sodium Dodecyl Sulfate

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ABSTRACT: In this work, we performed impedance spectroscopy measurements of organically modified silicate membranes based on polydimethylsiloxane (PDMS) and tetraethoxysilane (TEOS) with the inclusion of sodium dodecyl sulfate (SDS) at five different concentrations. The results indicated that the conduction in a pure PDMS/TEOS hybrid membrane mainly resulted from a hopping mechanism. The conduction of membranes modified with

the addition of SDS increased for SDS concentrations up to 20% and decreased for higher concentrations. This effect was explained on the basis of the porosity of the membranes due to SDS. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 851–854, 2010

Key words: charge transport; composites; interpenetrating network (IPN)

INTRODUCTION

Since the seminal work of Schmidt,¹ the organic–inorganic hybrids known as organically modified silicates (ORMOSILs), compounds in which inorganic and organic phases form chemical bonds, have attracted much attention because of their vast applicability and simple synthesis. The commonest and simplest way of obtaining these materials is sol–gel synthesis; these materials can provide both molecular accessibility and rapid mass transport via diffusion because their structure consists of nanometer-sized particles surrounded by a continuous mesoporous volume.² Thus, ORMOSILs, based on the incorporation of oligomer and polymer species into an inorganic matrix consisting primarily of Si–O–Si networks, have been proposed to be used in many applications, especially optical applications, because of their transparency (e.g., hard coatings,^{3–7} wave guides and high near-IR transmission materials,⁸ and gradient refractive index materials⁴). Several other applications are related in the good reviews

presented by Mackenzie and Bescher⁹ and Schmidt and Wolter¹⁰ and references therein.

These hybrid organic–inorganic sol–gel-synthesized materials are also suitable as hosts for the incorporation of high amounts of several compounds with high conductivity, such as sodium dodecyl sulfate (SDS), phosphotungstic acid, and silicotungstic acid. This doping is interesting because these compounds are small and show high protonic conductivity (0.02–0.1 S/cm) at room temperature. This procedure has been employed in the search for good protonic conductors that can be employed in protonic electrolyte membrane fuel cells as well as other applications.^{11–13} The ion-exchange and ion-transport properties and, consequently, conductivity properties of these materials are of fundamental interest and can be applied in several important applications, such as sensors, batteries, supercapacitors, and fuel cells. Thus, in this work, we determined the ionic properties of sol–gel-synthesized ORMOSIL membranes derived from polydimethylsiloxane (PDMS) and tetraethoxysilane (TEOS) with immobilized SDS at five different mass concentrations with the aim of investigating the contribution to the conductivity from SDS in comparison with the pure membrane.

EXPERIMENTAL

PDMS, supplied by Dow Corning [Midland, MI (USA)] with a number-average molecular weight of 2200 g/mol, TEOS from Aldrich, and SDS from Qeel

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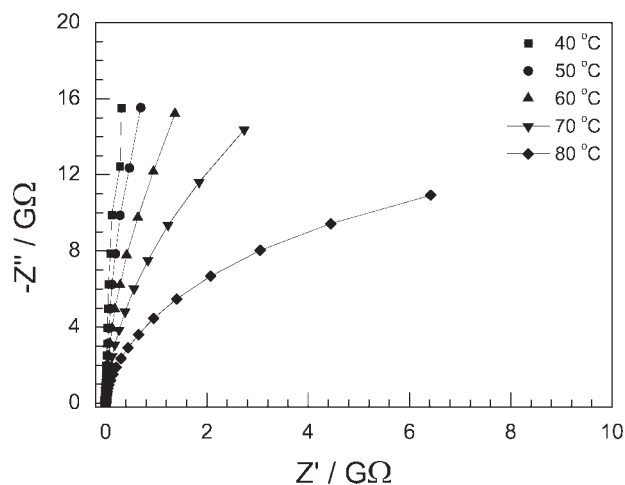


Figure 1 Complex impedance plot of the pure membrane impedance at several temperatures. Z' and Z'' are the real and imaginary parts of the complex impedance.

[St Louis, MO (USA)] were used as raw materials to obtain ORMOSIL membranes. Isopropyl alcohol from Vetec (São Paulo, Brazil) and dibutyl tin dilaurate from Aldrich were used as the solvent and catalyst, respectively. The pure PDMS/TEOS compound, without the inclusion of SDS, was synthesized via the hydrolysis and condensation of PDMS and TEOS with a mass ratio of 70 : 30. For the SDS-containing membranes, the SDS conductor was added to the matrix in different mass proportions with respect to TEOS (5, 10, 20, and 30%) near the gel point. After that, the modified membranes were allowed to dry at room temperature for 7 days in Teflon molds. Finally, the obtained membranes were dried *in vacuo* for 2 days.

The impedance spectroscopy measurements were performed with a Solartron model 1260 (Farnborough, Hampshire, UK) frequency response analyzer coupled to a Solartron model 1296A dielectric inter-

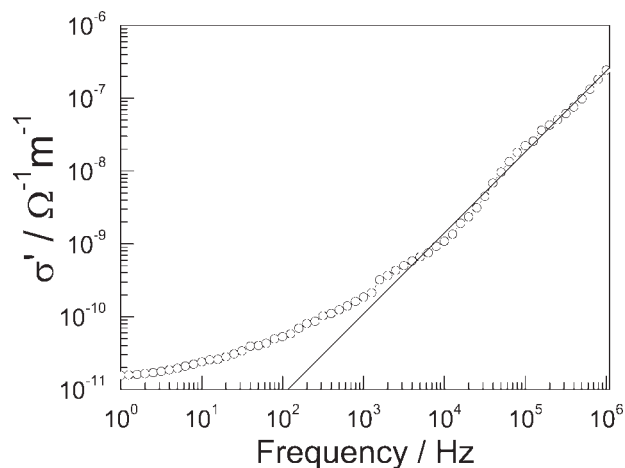


Figure 2 Conductivity of the pure PDMS/TEOS membrane at 80 °C. The line indicates the linear adjustment of the high-frequency region. σ as conductivity.

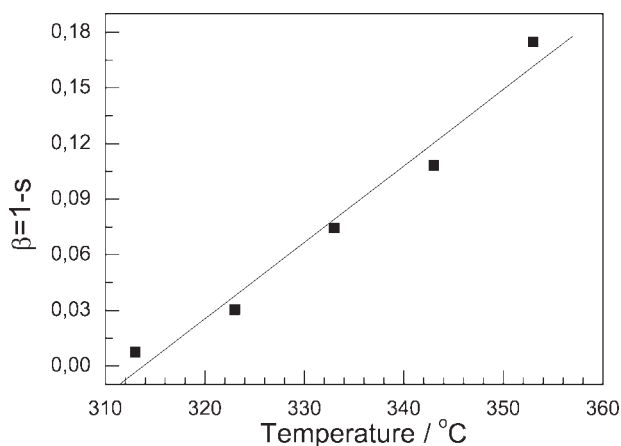


Figure 3 Temperature dependence of the Pike parameter ($\beta = 1 - s$) for the pure PDMS/TEOS membrane.

face. The measurements were carried out in the frequency range of 1 Hz to 1 MHz and in the temperature range of 40–80 °C. The electric contact was performed with brass electrodes molded at 110 °C to the membranes in a two-electrode configuration. The temperature was changed with a homemade furnace controlled with a Coel HW4900 PID controller (São Paulo, Brazil). As we were interested only in the intrinsic properties of the membranes, we increased the temperature above 100 °C and measured the impedance on cooling to room temperature.

The membrane microstructures were investigated via scanning electron microscopy (SEM) with a Shimadzu model SS-550 microscope (Kyoto, Japan) at acceleration voltages of 15 and 7 kV.

RESULTS AND DISCUSSION

Dielectric properties of the pure membrane

Figure 1 shows the complex impedance plot of the pure membrane impedance at several temperatures.

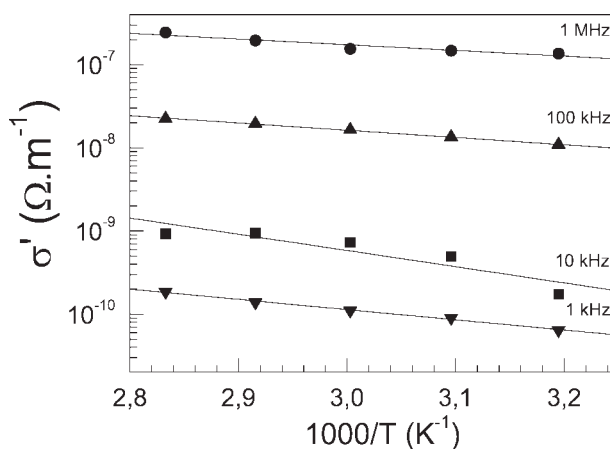


Figure 4 Temperature dependence of the conductivity of the pure PDMS/TEOS membrane at several frequencies.

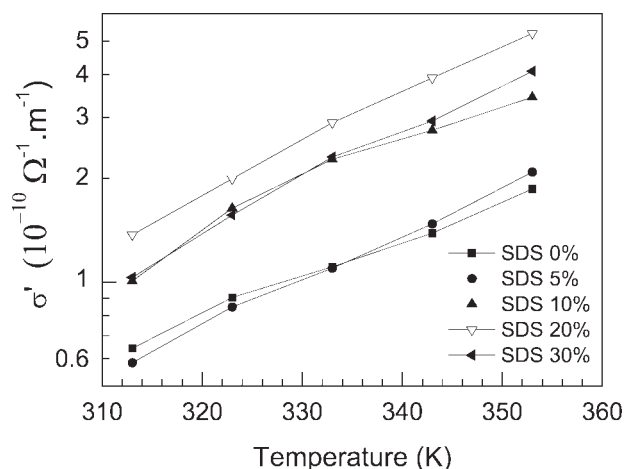


Figure 5 Temperature dependence of the conductivity of the doped investigated membranes at 1 kHz. The lines are guides for the eyes.

The impedance decreased when the temperature increased, as expected for a common dielectric.

The conductivity (σ) of this membrane was obtained with the Maxwell relation:

$$\sigma(\omega) = j\omega\epsilon_0\epsilon(\omega)$$

where j is the purely imaginary number, ω is the frequency oscillation of the applied field, ϵ_0 is the vacuum permittivity, and $\epsilon(\omega)$ is the dielectric constant of the membrane. ϵ was obtained from the impedance response with the following relation:

$$\epsilon(\omega) = [j\omega C_0 Z(\omega)]^{-1}$$

where $Z(\omega)$ is the complex impedance, C_0 is the capacitance of the open cell. Figure 2 shows the ac conductivity at 80°C.

In a general way, we can express the conductivity frequency dependence as follows:

$$\sigma = \sigma_0 + \sigma(\omega) \tag{1}$$

where σ_0 is a constant term.

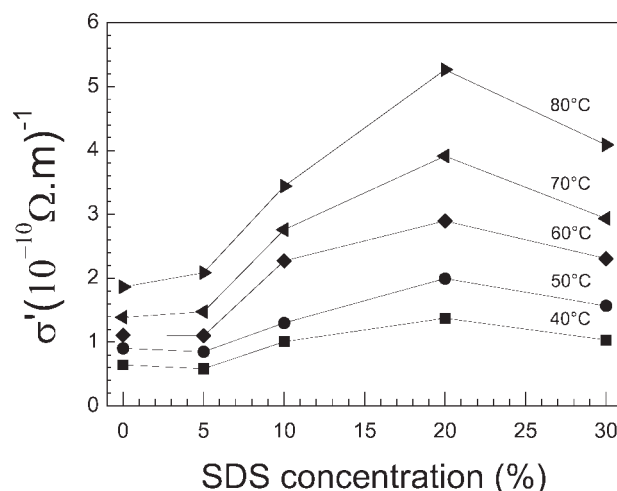


Figure 6 Dependence of the conductivity of the doped investigated PDMS/TEOS membranes with the SDS concentration at several temperatures.

For an amorphous material, the frequency-dependent part [$\sigma(\omega)$] in the last equation has the following form:¹⁴

$$\sigma(\omega) = A\omega)^{s(T)} \tag{2}$$

where A is a constant and $s(T)$ is a function to be found. Using the linear-adjustment, high-frequency regime (see Fig. 2), we can obtain the $s(T)$ temperature dependence. In Figure 3, we show the curve of the Pike parameter [$\beta = 1 - s(T)$] versus the temperature.¹⁵ Through this procedure, we can conclude that the conduction in the pure membrane followed the hopping model with a barrier energy (W_N) of 0.125 eV, which was obtained with the following expression:¹⁵

$$\beta = 1 - s = \frac{6k_B T}{W_N} \tag{3}$$

k_B is the Boltzmann constant

The dependence of the conductivity on the reciprocal temperature is shown in Figure 4 for several

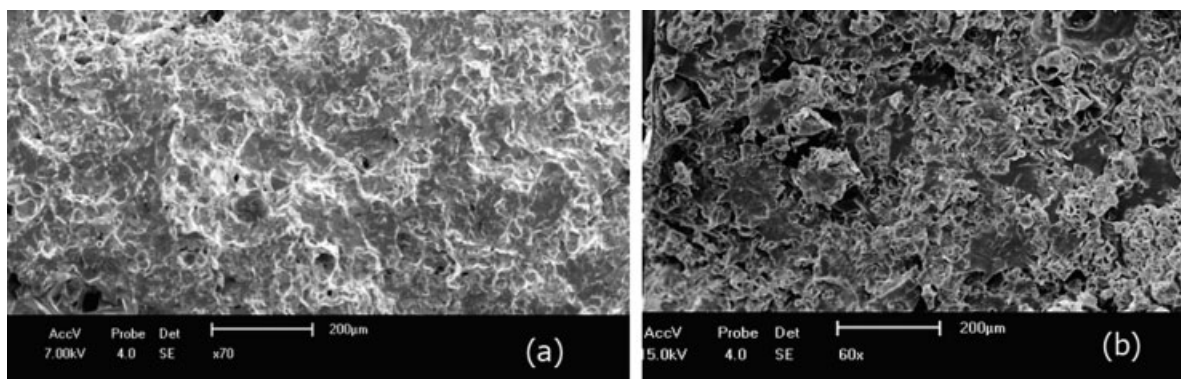


Figure 7 SEM micrographs obtained for the ORMOSIL membranes with (a) 20 and (b) 30% SDS.

frequencies. The conductivity increased exponentially with the temperature, as occurs for materials whose conductivity originates from the hopping model.

Doped membranes

The temperature dependence of the ac conductivity for the doped membranes is shown in Figure 5. The conductivity of the pure membrane is also shown for the sake of completeness and comparison. We observe that for all doped concentrations, the conductivity increased exponentially with the temperature, and the activation was practically independent of the SDS inclusion. We can emphasize two important observations. First, for low SDS concentrations (5%), the conductivity was practically the same as that for the pure membrane. Second, the increase in the SDS content did not imply an increase in the conductivity. We observe that the conductivity increased for SDS contents of 10 and 20% but decreased when the SDS content was 30%. This observation is an interesting effect in these modified ORMOSILs. Normally, the conductivity increases or saturates at high concentrations of ionic conductor dopants.^{11,12,16}

This behavior can be better observed for the conductivity dependence of the SDS contents in Figure 6, which was measured at 1 kHz and several temperatures. We see that, independently of the temperature, the ac conductivity was higher with an SDS content of 20%. This effect can be explained on the basis of the composite microstructure. High concentrations of SDS imply an increase in the modified membrane porosity. This assumption was confirmed by the SEM micrographs obtained for the samples with SDS contents of 20 and 30%, which are shown in Figure 7.

CONCLUSIONS

We performed an ionic characterization of ORMOSILs based on PDMS and TEOS membranes modi-

fied by the inclusion of SDS at five different concentrations and at several temperatures with impedance spectroscopy. The results showed that the conduction mechanism in the pure membrane was mainly due to hopping along the polymeric chains. For the doped membranes, the conductivity was increased by the inclusion of SDS until a concentration of 20%. After this concentration, the conductivity decreased, probably because of the porosity of the samples.

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