Effect of Supercritical CO_2 on Ionic Conductivity of Hybrid Inorganic-Organic Networks by Broad Band Dielectric Spectroscopy

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ABSTRACT

The aim of this work is the study of behaviour of polymer electrolytes treated with CO_2 under pressure. The changes in conductivity and conformation of the polymer were investigated by Broad Band Dielectric Spectroscopic. Eleven inorganic-organic hybrid materials with generic formula $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_z\}_n$ were treated by applying CO_2 at 293 K, 5 MPa. The CO_2 treatment depressed the conductivity of about one order of magnitude and changed the polymeric chain motion.

INTRODUCTION

Classical polymer electrolytes (PE) are based on polyethylene oxide matrices doped with low dissociation energy lithium salts [1]. Recently, to increase the ionic conductivity of these latter materials, many authors devoted great attention to the preparation and characterization of hybrid inorganic-organic systems. It was demonstrated that in many of these materials, an increase in lithium ionic conductivity up to two orders of magnitude with respect to classical PE was registered.

Polymer processing by supercritical fluids (SCF) or compressed-gas based techniques have received much attention for the possibility of modifying the chemical-physical properties of polymers by new solvent-free process. Kwak *et al.* [2] have reported that the conductivity of amorphous PE of the type ($PMEO_x$-$LiCF_3SO_3$) is improved by treatment with supercritical CO_2. It was claimed that this treatment increases the ion conductivity of investigated PE of about one order of magnitude.

The aim of this study is to investigate the effect of CO_2 under pressure on structure, molecular dynamics and conductivity of hybrid inorganic-organic polymer electrolytes. Different materials, with general formula $[Al[(CH_2CH_2O)_{8.671}]_{\rho}/(LiClO_4)_z]_n$, were processed with subcritical CO_2 for 90 minutes. The samples thus obtained were studied by Broad Band Dielectric Spectroscopy in the ranges 40Hz-10Mz between –80 - +120 °C.

I. MATERIALS AND METHODS

Inorganic-organic hybrid materials with generic formula $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_z\}_n$, where $1.85 \le \rho \le 2.24$ and $0 \le z \le 1.06$, were prepared by polycondensation reaction between a $PEG400/(LiClO_4)_x$ solution with $0 \le x \le 0.49$ and aluminium isopropoxide, as described elsewhere [3]. The chemical composition of the eleven samples are reported on Table 1.

The apparatus for the treatment of sample with CO_2 is represented in Fig. 1. It is composed by a pressure chamber (R2) and a chamber (R1) with zeolite to dry the gas. The pressure chamber is located in a dry box and is heated by an electrical resistance (R). The temperature is measured by a Pt100Ω and the pressure by a gauge. All valve are on-off type.

Table 1: Compositional data for $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{z}\}_{n}$ complexes

Sample	C_{Li} (mol/kg)	$C_{Li}^{1/2}$ $(mol/kg)^{1/2}$	ρ (n_{PEG400}/n_{Al})	z (n_{LiClO_4}/n_{Al})
1	1.01691	1.00842	2.24130	1.05994
2	0.49114	0.70081	2.06241	0.44815
3	0.23592	0.50391	2.07510	0.22276
4	0.13411	0.36621	1.86523	0.10467
5	0.06879	0.26228	1.95005	0.05559
6	0.04014	0.20034	1.91465	0.03165
7	0.01778	0.13332	1.88845	0.01383
8	0.00866	0.09305	1.96119	0.00702
9	0.00433	0.06578	1.85089	0.00330
10	0.00227	0.04760	1.85480	0.00174
11	0.00000	0.00000	1.93830	0.00000

First, the material was put into the pressure chamber, and the vacuum was done. Then CO_2 was loaded into the chamber until the pressure reached the desired value. After 90 min, the chamber was rapidly depressurized and exposed to low vacuum for 5 min. Then it was opened and the sample was prepared as a bottom battery for the AC impedance measurement.

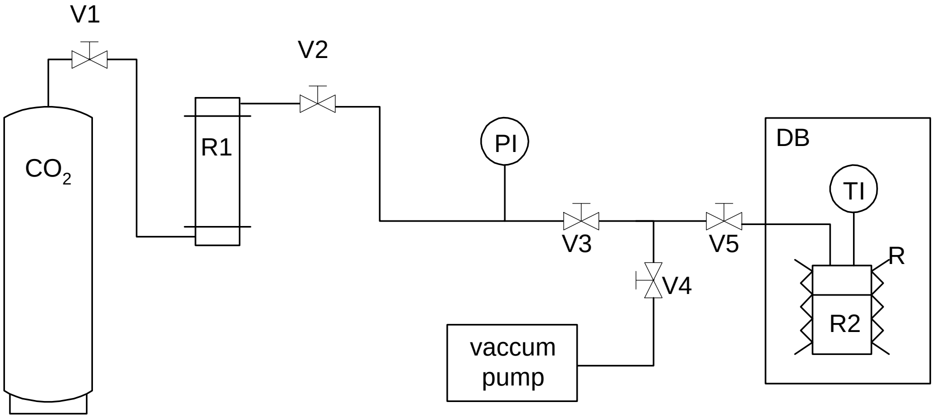


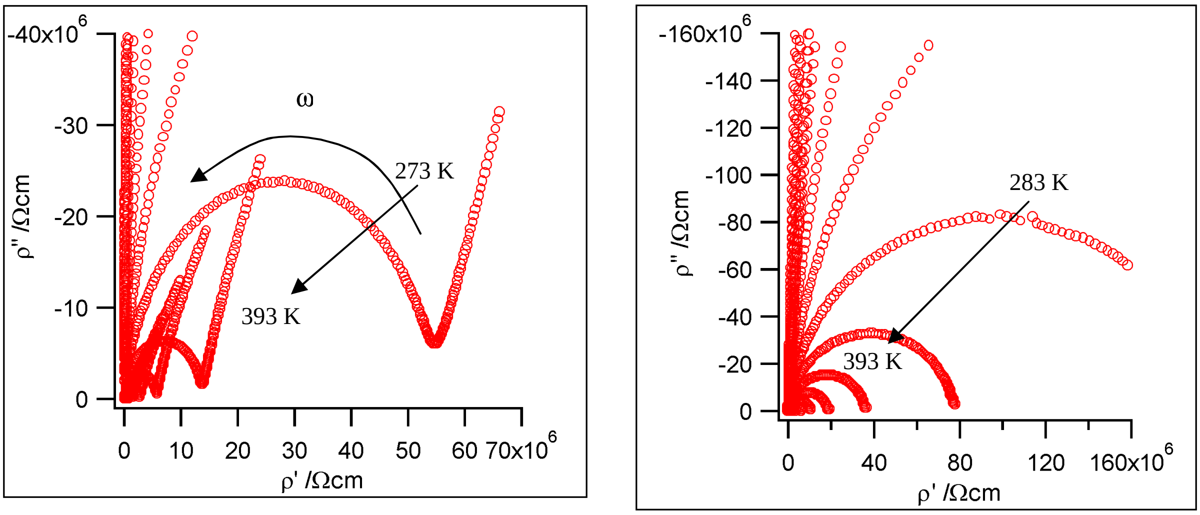
Figure 1: Experimental plant for the treatment of materials by CO_2 under pressuere: DB: dry boxd, R1: zeolit chamber, R2: pressure chamber, R: electrical resistance, TI: temperature indicator, PI: pressure indicator, V1, V2, V3, V4 and V5: on-off valves

The battery is composed by a teflon ring, two steel discs (thickness 0.5mm), two platinum discs (thickness 0.2mm), a spring and three glass fibres (thickness 0.2mm) as spacers.

The polymer is located between the two platinum discs (electrodes) and the glass fibre are used to have an exact and constant thickness of the sample. Studied by Broad Band Dielectric Spectroscopy were carried out in the range from –80°C to 120°C and from 40 Hz to 1 MHz. The instrument used was Agilent 4294A (precision Impedance Analyzer) with Oxford cryostat.

II. RESULTS

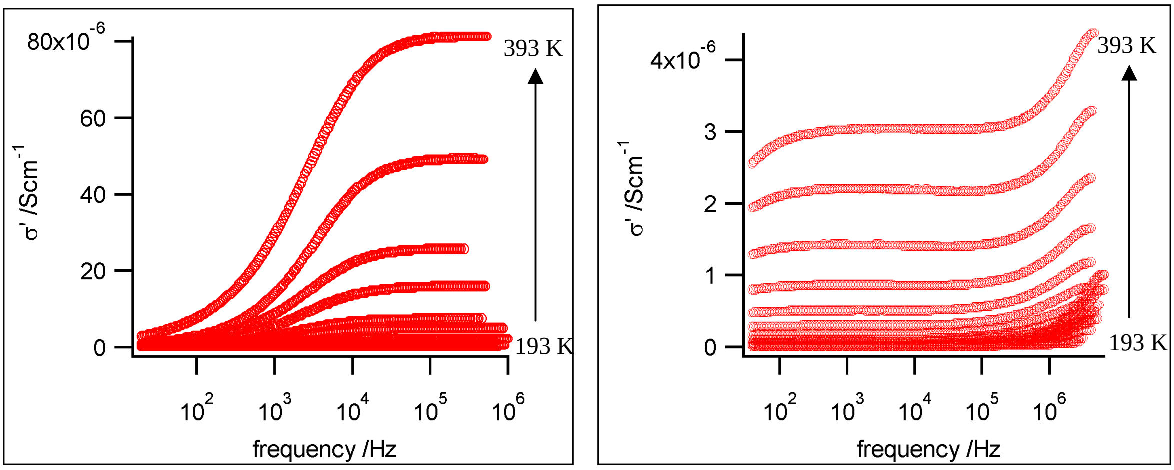
All the materials were processed at 293K and 5 MPa of CO_2. After the treatment, the physical aspect of samples were changed: they were more friable, while the initial samples were rubbery.



a) b)

Figure 2: Nyquist plots for: a) $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{0.22}\}_{n}$, and b) $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{0.002}\}_{n}$. The measurements were carried out from 40 Hz to 1 MHz

The electric characteristics of the sample can be represented by Nyquist plots (Fig. 2). In these graphics, the imaginary resistivity is plotted versus real resistivity, measured in the 40 Hz to 1 MHz frequency range. They show semicircular arcs at high frequencies and spikes at low frequencies. Figure 2 reports the Nyquist plot for sample 3 (z=0.22276) and 10 (z=0.00174). It is possible to see the strong influence of temperature and polymer composition on the electric behaviour of the sample. The resistivity decreases with an increase of temperature and an increase of lithium concentration.

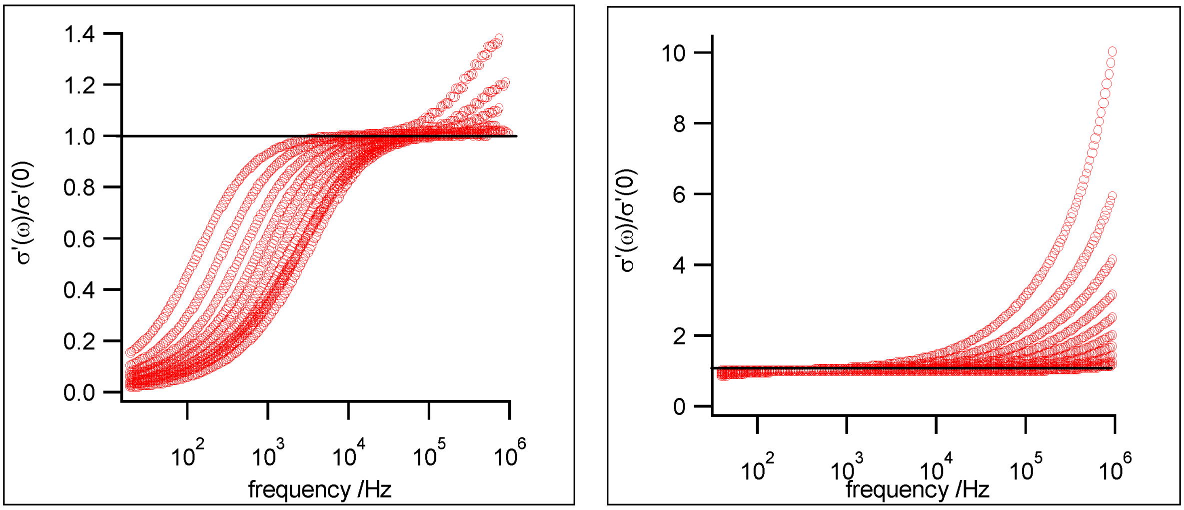


a) b)

Figure 3: $\sigma'(\omega)$ plots vs frequency for: a) $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{0.22}\}_{n}$, and b) $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{0.002}\}_{n}$. The measurements were carried out from 40 Hz to 1 MHz and from 193 K to 393K.

Figure 3 shows the profiles of real conductivity (σ’(ω)) and Figure 4 of σ’(ω)/σ’(0). In accordance with literature [4, 5, 6], σ’(ω)/σ’(0) was obtained by evaluating σ’(0) at the central plateau of the σ’(ω) spectra. These profiles display three regions:

1. a low-frequencies spike;
2. a medium-frequencies plateau;
3. a high-frequencies spike.



a) b)

Figure 4: (σ’(ω)/σ’(0) plots for: a) $\{Al[O(CH2CH2O)_{8.7}]_\rho/(LiClO4)_{0.22}\}_n$, and b) $\{Al[O(CH2CH2O)_{8.7}]_\rho/(LiClO4)_{0.002}\}_n$. The measurements were carried out from 40 Hz to 1 MHz and from 293 K to 393K.

The conductivity (σ’(0)) of the treated materials versus the reciprocal absolute temperature (Fig. 5) shows the dependence described by the empirical Vogel-Tamman-Fulcher (VTF) equation:

$$s\,(T) = A_s T^{-1/2} e^{-E_a / k_b (T - T_0)} \tag{1}$$

where A_s is proportional to the number of the carrier ions, k_b is the Boltzmann constant, E_a is a parameter related to the apparent activation energy for conduction, and T_o is the thermodynamic ideal glass transition temperature. For certain lithium compositions, the dependence described by the Arrhenius equation was found at high temperature.

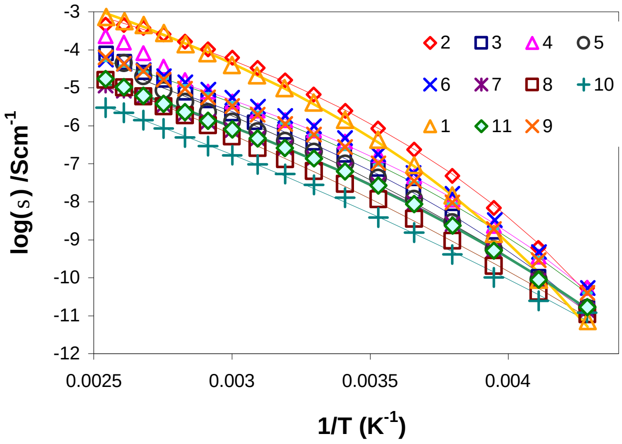


Figure 5: Dependences of log(σ’(0)) on the reciprocal of absolute temperature. The lines shows VTF fitted curves.

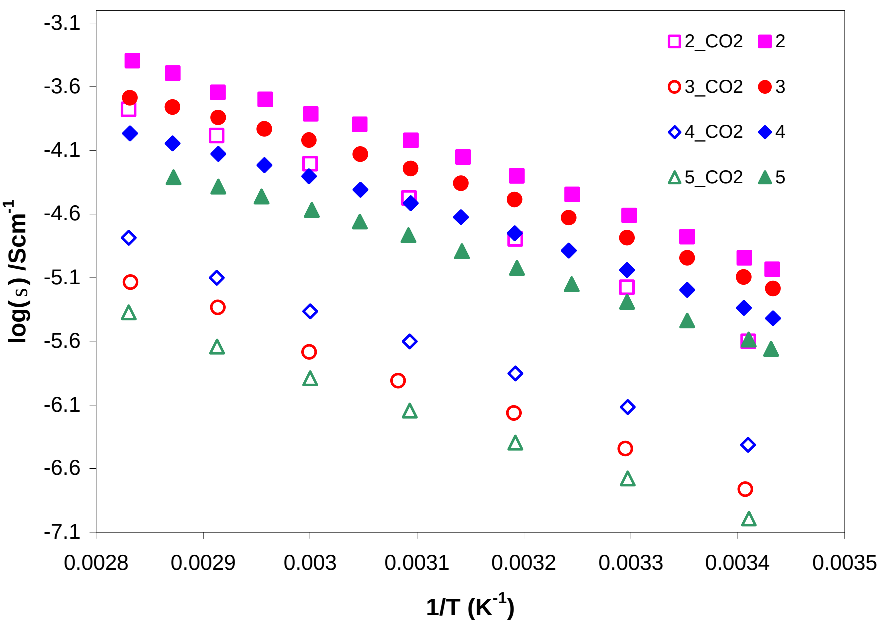


Figure 6: Dependences of log(σ'(0)) on the reciprocal of absolute temperature. The empty symbols were for the sample treated at 293 K, 5 MPa, while the filled symbol for untreated materials.

This fact can be ascribe to a change in material conformation and a reduction of the ion trapping phenomena. Figure 7 shows the change in the α-relaxation of the treated $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_{0.49}\}_{n}$ with the respect to untreated sample.

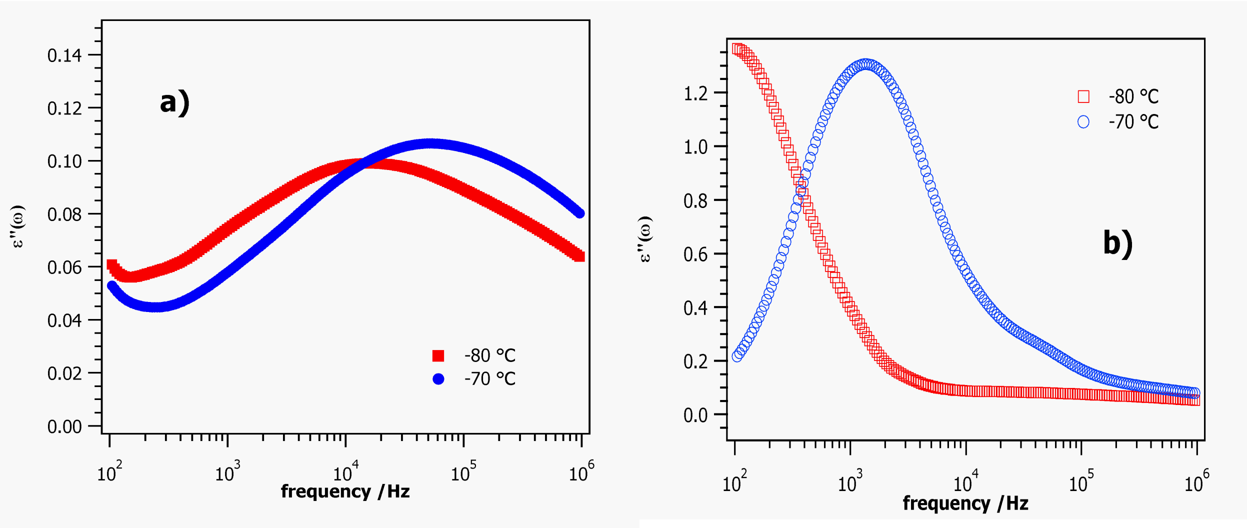


Figure 7: Effect of the CO_2 treatment on ε'' versus frequency of the complex $[Al[(CH_2CH_2O)_{8.671}]_{2.24}/(LiClO_4)_{1.06}]_n$: a) sample treated at 293K and 5 MPa of CO_2 and b) material untreated.

The peaks of treated materials were broader and about one order lower; besides, the frequency of the peak maximum of the treated sample was higher than untreated materials. These facts indicated an easier chain motion, but a decrease of the number of chain in movement, which bring to a reduction of material conductivity.

CONCLUSIONS

It is possible to change the conductivity of hybrid inorganic-organic by treatment with CO_2 under pressure. For the $\{Al[O(CH2CH2O)_{8.7}]_{\rho}/(LiClO4)_z\}_n$, the treatment with CO_2 reduced the conductivity, while for the sample without $LiClO_4$, the conductivity increase. These changes were due to a change in the physical conformation of the materials, which were studied by Broad Band Dielectric Spectroscopy.

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