JOURNAL OF MATERIALS SCIENCE **32** (1997) 4415–4420

Sol–gel hybrid materials based on hydroxylated poly[bis(methoxy–ethoxy–ethoxy)phosphazene] and silica: a ceramic ionic conductor

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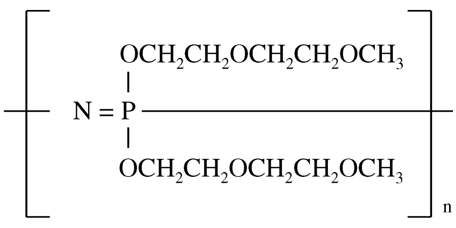
The sol–gel synthesis of hybrid materials based on poly[bis(methoxy–ethyoxy–ethoxy) phosphazene] (MEEP) and silica and their characterization are described.

MEEP is a polymer with a low glass transition temperature of −71 °C, that bears ethyleneoxide oligomers as phosphorus side groups, able to impart to the macromolecule metal co-ordination ability. This property makes MEEP an ionic conductor, but unfortunately its flow behaviour at room temperature limits its industrial development. The linkage of MEEP to a rigid inorganic network, which would overcome this problem, was pursued using the sol–gel method. The functionalization of MEEP by the introduction of free hydroxyl groups allows the formation of chemical bonds with hydrolysed tetraethoxysilane. Phosphazene-based hybrid materials with no phase separation could be obtained by this procedure. The ionic conductivity of these materials doped with lithium triflate has been investigated using a.c. impedance techniques. A conductivity value of about $3 \times 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ was measured which is comparable to typical values of poly(ethylene oxide) solid electrolytes. A thermal treatment of the Li-doped samples decreases the conductivity but it still remains above $5 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

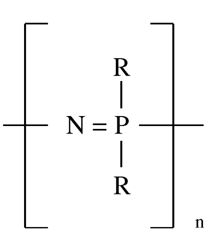
1. Introduction

Poly[bis(methoxy–ethoxy–ethoxy)phosphazene], MEEP [1],



$$\left[\mathrm{N} = \underset{\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}}{\overset{\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}}{\mathrm{P}}} \right]_n$$

is an important member of the new class of macromolecules named poly(organophosphazenes), POPs [2]



$$\left[\mathrm{N} = \underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{P}}} \right]_n$$

initially investigated by Allcock and co-workers [3–5] and recently industrialized in the USA [6, 7], Europe [8, 9] and Japan [10].

The importance of this polymer is related to its potential application in several different research and

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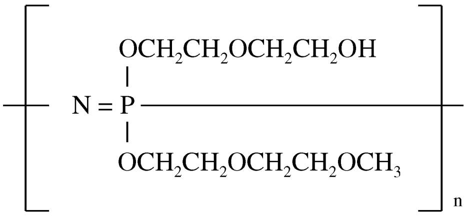
industrial fields, such as ionic conductivity [11–27], biomaterial technologies [28], phase-transfer catalysis [29] and ceramics [27, 30–32].

MEEP is, in fact, an amorphous material [33], with a very low glass transition temperature T_g [11], that bears ethylenoxide oligomers as phosphorus side groups. These groups are able to impart good water solubility to the macromolecule [1, 34], which allows the preparation of water-swellable hydrogels or membranes [36], and their exploitation as phase transfer catalysis [29]. In addition its metal co-ordination ability [35] makes MEEP an excellent candidate for use as a solid electrolyte in light batteries [11].

The major drawback associated with MEEP, is its flow behaviour at room temperature which may cause problems for the industrial application of this material [33]. However this problem can be overcome by chemical [15], γ-ray [17–19, 36] or UV-induced [37] controlled reticulation reactions, or by composite formation with polymers [23, 25]. Recently, sol–gel routes to the formation of organic-inorganic hybrid materials have been pursued [27, 30–32]. These processes substantially preserve the original ionic conductivity values of MEEP while preventing the problem of flow extrusion from electrolytic cells [34].

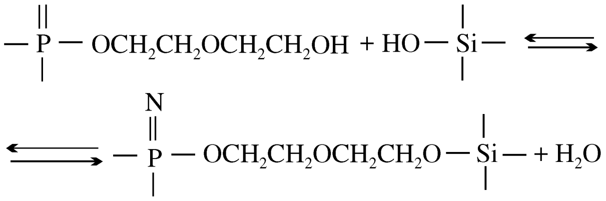
In our previous work in the field of phosphazene-based hybrid materials [38–40], we have shown that it is possible to obtain homogeneous materials by using suitable functionalized polymers. MEEP functionalized by the introduction of free hydroxyls has been recently obtained [41, 42] and is shown as Scheme (1).



$$\left[-N=\overset{OCH_2CH_2OCH_2CH_2OH}{\underset{OCH_2CH_2OCH_2CH_2OCH_3}{P}}- \right]_n$$

MEEP–OH (1)

These functions may be reasonably expected to induce the formation of chemical bonds in the reaction with hydrolysed tetraethoxysilane (TEOS) in Scheme 2, to form new homogeneous phosphazene-based ceramic materials with no phase separation.



$$-\overset{N}{\overset{\|}{P}}-OCH_2CH_2OCH_2CH_2OH + HO-Si- \rightleftharpoons -\overset{N}{\overset{\|}{P}}-OCH_2CH_2OCH_2CH_2O-Si- + H_2O$$

(2)

In this paper we present results on the reaction between hydroxylated MEEP (MEEP–OH) and hydrolysed TEOS, the characterization of the new materials using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM) and also the measurement of their ionic conductivity values by impedance techniques.

2. Experimental procedure

The hydrolysed poly[bis(methoxy–ethoxy–ethoxy)-phosphazene] (MEEP–OH) used in this work was obtained by the reaction of poly[bis(methoxy–ethoxy–ethoxy)phosphazene] (MEEP) with trimethylsilyl iodide, as previously reported [41, 42]. The $^-$OH content of the repetitive units, shown as (1), can be controlled by the reaction conditions; in our case the ratio $OH:OCH_3$ was 40:60.

The phosphazene composite was prepared by dissolving MEEP–OH in an ethanol solution of tetraethoxysilane (TEOS), successively adding the water necessary for the hydrolysis and the HCl in a molar ratio $TEOS:H_2O:HCl = 1:4:0.01$, and allowing the reaction to proceed at 40 °C for 4 h. The molar ratio $MEEP–OH/SiO_2$ was varied between 0.125 and 0.8. The former was used for studying the synthesis of the hybrid, the latter for preparing samples for impedance measurements. Lithium triflate was added to some samples at the beginning of the hydrolysis to produce a 1 M concentration in the hybrid.

Differential scanning calorimetry measurements were performed using a Mettler DSC 30, in which the powders were heated under a N_2 atmosphere at a rate of 10 °C min^{-1}, between −150°–300 °C. Two successive runs were made for each sample because of the presence of large endothermic effects in the first scan (due to solvent or H_2O evaporation, this is especially noticeable in the silica compounds) that hide heat capacity changes. During the first scan the melting temperature of the MEEP–OH polymer, that is partially crystalline, was observed. This was no longer observable during the second scan, due to the quick cooling of the compound after the first measurement.

The FTIR spectroscopy measurements were performed using a Perkin Elmer FTIR spectrophotometer model 2000.

Hybrid samples were submitted to acetone extraction by treating 100 mg of powder with 5 ml of acetone, which is a good solvent for the polyphosphazene, at room temperature for 1 h under stirring. After evaporation of the resulting solution on silicon substrates, FTIR spectroscopy measurements were performed.

SEM and EDX (energy dispersive spectroscopy) analyses were carried out on bulky specimens using a Cambridge Stereo Scan 250.

The a.c. impedance measurements, performed to measure the ionic conductivity of the hybrid, were carried out with a Solartron 1250 frequency response analyser and a Solartron 1286 electrochemical interface. Both of them were computer driven, through commercial software (Fracom by P. Bernard and H. Takenouti, UPR 15 CNRS, Paris, France). The samples, $MEEP–SiO_2$ discs of various thicknesses (in the range 105–735 μm), were contacted on both faces with blocking electrodes, generally Pt of area 0.29 cm^2 or C (0.25 cm^2) when specified. All measurements were performed under potentiostatic control, with a zero d.c. bias and an a.c. voltage of 25 mV (r.m.s.). The frequency range 1 Hz to 63 kHz was covered with 10 points per decade (the upper frequency limit is imposed by the available instrumentation). Measurements were carried out at room temperature and in contact with atmosphere, and thus no attempt was made to prevent water absorption by the sample. Additional impedance measurements were carried out after heating the samples at 120 °C (for 1 h) and re-equilibrating them with the environment for 1 h.

3. Results and discussion

In Fig. 1 the FTIR spectra of (a) the original MEEP–OH, (b) the acetone extract from the composite powder, and (c) the acetone extract from powders previously treated in water at 60 °C for 30 min under stirring and then in acetone, are reported. Each spectrum was obtained by evaporating on to the same area the acetone solution; for spectrum (a) the solution was obtained by dissolving an amount of MEEP–OH equal to that contained in the hybrid powder submitted to acetone extraction.

Fig. 1 shows that the amount of polymer extracted from the hybrid material by the acetone is quite negligible. In the case of water treated powders one could expect that the C–O–Si bond previously formed could be hydrolysed leading to a polymer soluble in acetone, Scheme 2. However, even after this treatment the amount of MEEP–OH extracted from the powder is not such larger as can be seen by comparing curves (a) and (b). In contrast to the behaviour with poly[bis(4-hydroxyphenoxy)phosphazene], where the hybrid material was significantly decomposed by hydrolytic thermal reactions [40], the MEEP–OH/SiO_2 hybrid is relatively unaffected by water.

Fig. 2 shows the differential scanning calorimetry measurements carried out on the pure MEEP–OH (curve (a)), and the MEEP–OH/SiO_2 composite. The T_g of MEEP–OH, that can be observed at -71 °C in curve (a), is completely absent in curve (b). The disappearance of the glass transition in the MEEP–OH polymer when it is embodied in the ceramic matrix is a further indication that a bond has formed between the components of the hybrid material.

Fig. 3 shows a photograph of a disc of the hybrid material with a MEEP–OH/SiO_2 of 0.8 and a thickness of 120 μm. The transparency indicates that no macroscopic phase separation occurs. In fact no phase separation on a microscopic scale could be detected in the SEM analyses of hybrid bulk samples and films of this material with MEEP–OH/SiO_2 values of 0.125 and 0.8. These observations confirm the homogeneity of the MEEP–OH/SiO_2 composites.

It may be worth noting that previous attempts [31] to obtain composites between MEEP and inorganic oxides led to the formation of inhomogeneous materials containing small SiO_2 particles and polymer aggregates. This was possibly due to the absence of free hydroxyl functions suitable for reactions with the hydrolysed silica precursor in the exploited polymer.

As a result of composite formation the poor mechanical stability of MEEP, which represents the most serious obstacle to its practical exploitation as an ionic conductor in electrochemical devices, is considerably improved. For instance, this material could be drawn into fibres as is shown in the SEM micrograph presented as Fig. 4. The fibres and other bulk samples produced in this study remain unaltered in shape after one year and exhibit a fragile fracture when broken (Fig. 3).

Fig. 5a shows the Nyquist plot of the impedance of a MEEP–OH/SiO_2 sample containing no $LiCF_3SO_3$ treated at 120 °C. Under the utilized experimental

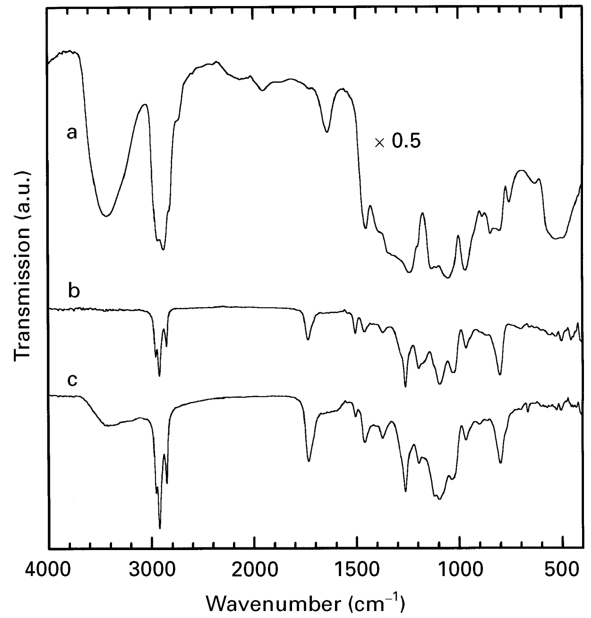


Figure 1(a) FTIR spectra of MEEP–OH, (b) acetone extract of composite powder (MEEP–OH:SiO_2 = 1:8) and (c) after hydrolytic treatment.

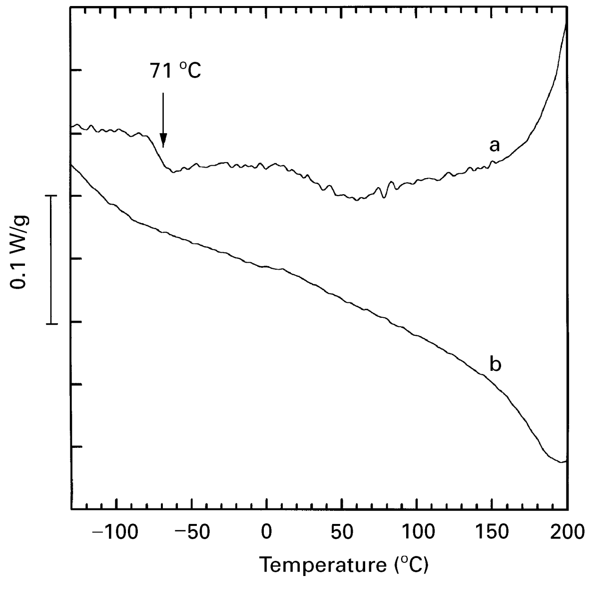


Figure 2 DSC analyses of (a) MEEP–OH and (b) the MEEP–OH/SiO_2 hybrid with MEEP–OH:SiO_2 = 1:8.

Figure 3 Photograph of a disc of a hybrid with a MEEP–OH:SiO$_2$ = 0.8 and a thickness of 120 μm.

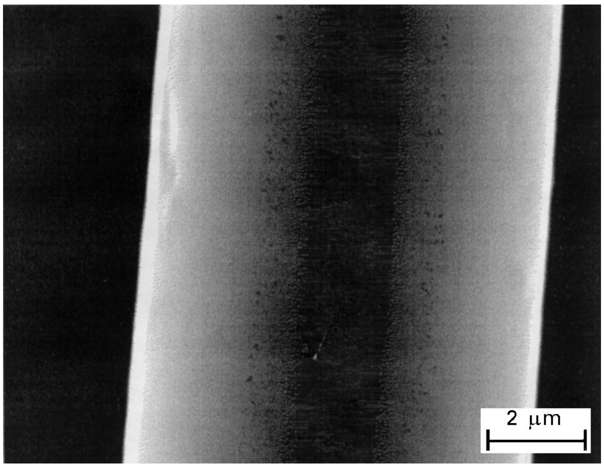


Figure 4 SEM micrograph of a fibre drawn from sol with MEEP–OH:SiO$_2$ = 1:8.

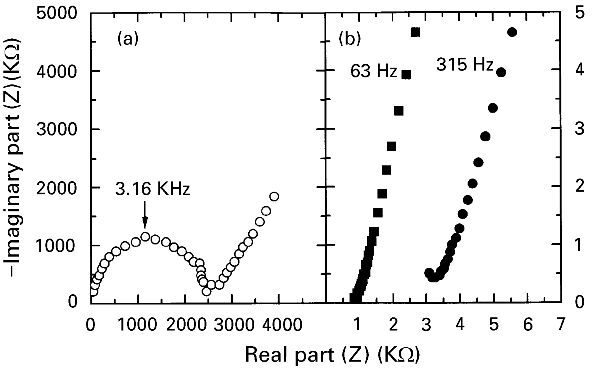


Figure 5 Impedance plots of MEEP–OH/SiO$_2$ hybrids (a) treated at 120 °C without any added lithium triflate and (b) treated at 60 °C (●) and 120 °C (■) with added lithium triflate. Sample thickness: (a) 142 and (b) 105 μm.

conditions, both of the Pt/sample interfaces are ion-blocking, and thus an impedance plot consisting of a high frequency semicircle and a low frequency straight line is expected. The plot of the experimental data actually shows these features, although the low frequency straight line is not vertical but inclined to form an angle of about 50° with the real axis. Such a deviation from ideality is common in real systems.

The high frequency semicircle is due to the parallel combination of the sample bulk resistance (R_b) and its geometric capacitance (C_g). For the sample of Fig. 5a (142 μm thick), R_b is 2.5 MΩ, corresponding to a conductivity of $1.9 \times 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The value of C_g can be either calculated from the simple formula $C_g = (\omega^* R_b)^{-1}$, where $\omega^* = 2\pi f^*$ where f^* is the frequency at which in the spectrum the imaginary part has a maximum, or, more accurately, from frequency analysis of the data. One obtains $C_g = 2.3 \times 10^{-11}$ F. From the relation:

$$C_g = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (1)$$

where $\varepsilon_0 = 8.8 \times 10^{-12}$ (in MKSA units), the corresponding relative dielectric constant ε_r has a value of 13.

Fig. 5b shows the impedance plots obtained on a 105 μm thick MEEP–OH/SiO$_2$ sample containing 1 M LiCF$_3$SO$_3$, after treatment at either 60 or 120 °C. In both these cases no high frequency loop is visible instead the high frequency data accumulate around a point close to the real axis. Thus, R_b may be determined to be 0.9 and 3.3 kΩ respectively, corresponding to a conductivity of 4×10^{-5} and $1.1 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Table 1 summarizes the conductivity data obtained on various samples as a function of Li content, thickness and thermal treatment (it should be noted that the nature of the electrode has little relevance). For Li-free samples treated at 60 °C, the conductivity value is close to $3 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The high conductivity value of this Li-free sample is probably the result of H$^+$ transport. As already shown in Fig. 5(a and b), differences between Li-free and Li-containing samples become much sharper for samples submitted to a thermal treatment at 120 °C. This treatment probably removes water from the samples and induce a more complete reaction between the inorganic and organic components of the hybrid material, with the formation of a large number of Si–O–C bonds. With

TABLE I Conductivity data for MEEP-SiO$_2$ samples with and without Li triflate

Li content (M)	Thickness (μm)	σ (Ω^{-1}cm^{-1}) 60 °C	σ (Ω^{-1}cm^{-1}) 120 °C
0	110	2.7×10^{-6}	–
0	138	3.3×10^{-6}	–
0	142	4.0×10^{-6}	1.9×10^{-8}
0	400	5.4×10^{-6}	4.6×10^{-8}
1	105	4.0×10^{-5}	1.1×10^{-5}
1	125	2.5×10^{-5}	–
1	136	3.3×10^{-5}	–
1	400	1.7×10^{-5}	5.6×10^{-6}
1	400	2.1×10^{-5}	–
1	735	6.9×10^{-5}	5.0×10^{-6}
1	120	3.4×10^{-5}	–

this treatment the conductivity of Li-free samples drops by about two orders of magnitude, whilst that of the Li-containing samples only decreases by a factor 4.

A diffusion coefficient D of the mobile charge carriers may be also computed from the conductivity data, according to the formula:

$$D = \frac{RT}{F^2} \sigma \frac{1}{c} \tag{2}$$

where R is the universal gas constant, T the absolute temperature, F the Faraday constant and c the concentration of the charge carriers. For Li-containing samples one obtains $cD = 7.5 \times 10^{-12}$ mol cm^{-1} s^{-1}. Since $c = 5 \times 10^{-4}$ mol cm^{-3}, assuming that only Li ions are mobile, their D has a value of 1.2×10^{-8} cm^2 s^{-1}. An analogous calculation cannot be made for Li-free samples for which neither the nature nor the concentration of the charge carriers is known.

4. Conclusions

It has been shown that homogeneous, transparent and mechanically stable hybrid materials may be obtained by the reaction of MEEP–OH with TEOS. FTIR spectroscopy and DSC investigations provided indications that bonds were formed between the organic and inorganic moieties under the adopted reaction conditions.

The ionic conductivity of the MEEP–OH/SiO_2 hybrids, determined by impedance measurements, is unexpectedly high ($3 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}), presumably due to proton transport. Indeed, thermal treatment to 120 °C (likely to induce water expulsion) decreases it by two orders of magnitude. Doping with 1 M lithium triflate enhances the conductivity to 3×10^{-5} Ω^{-1} cm^{-1}, a value comparable to that typical of poly(ethylene-oxide) solid electrolytes. Thermal treatment of the Li-doped samples has a less marked effect on the conductivity which remains above $5 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}.

The conductivity measured on Li-doped samples heated at 60 °C ($3 \times 10^{-5}\ \Omega^{-1}$ cm^{-1}) cannot be obtained as the sum of two contributions, one solely due to Li ($5 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}, obtained after heating at 120 °C) and the other solely due to protons ($3 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}). Therefore one is led to conclude that either Li^+ transport is enhanced by some water content in the hybrid, or that treatment at 120 °C strongly increases the cross-linking of the chains, thus reducing ion mobility.

Whether covalent Si–O–C or hydrogen bonds between uncondensed groups are formed, cannot be conclusively established from our experiments. However, the goals of an homogeneous, hydrolytical and mechanically stable entity were achieved. This result was made possible by the presence of $^-$OH groups in the polymer molecule.

The presence of residual $^-$OH groups and absorbed water prevents the use of these electrolytes in combination with Li electrodes. However their conductivity and optical transparency makes them interesting candidates for use in electrochromic devices.

Acknowledgements

L. Fambri and C. Gavazza are greatly acknowledged for the DSC measurements. M. Guglielmi is indebted to C.N.R. "Progetto Finalizzato Materiali Speciali per Technologie Avanzate" and MURST for financial support. M. Gleria is indebted to the Progetto Finalizzato Chimica Fine e Secondaria II del C.N.R. for partial financial support.

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Received 6 February 1996
and accepted 28 January 1997