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Date: October 17, 1995

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Subject: Annual report regarding the project "Ambient and Subambient Temperature Polymeric Electrolytes. Synthesis and Physical - Chemical Characterization of Polymer Conductors with Immobilized Ions." (Contract SPC-94-4074)

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INTRODUCTION

The results obtained in several laboratories have clearly demonstrated that the lithium electrode undergoes serious passivation when in contact with highly conducting gel electrolytes [1, 2]. This results mainly from the high reactivity of lithium toward the organic solvents present in gels. In order to decrease the interfacial resistance, electrolytes are sought for, which would be less aggressive towards lithium, or systems are used, in which the lithium metal electrode is replaced by lithium intercalated materials. A majority of works in this field are carried out by the trial-and-error method since phenomena at electrode interfaces are still not well investigated.

Within this work we are studying the possibility of elaborating highly conducting systems not containing organic solvents, as well as the passivation reactions of the lithium electrode and intercalating electrodes in gel systems.

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13. ABSTRACT (Maximum 200 words)

The results obtained in several laboratories have clearly demonstrated that the lithium electrode undergoes serious passivation when in contact with highly conducting gel electrolytes [1, 2]. This results mainly from the high reactivity of lithium toward the organic solvents present in gels. In order to decrease the interfacial resistance, electrolytes are sought for, which would be less aggressive towards lithium, or systems are used, in which lithium metal electrode is replaced by lithium intercalated materials. A majority of works in this field are carried out by the trial-and-error method since phenomena at electrode interfaces are still not well investigated.

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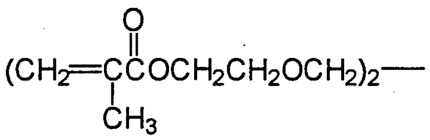
Solid electrolytes were based on:

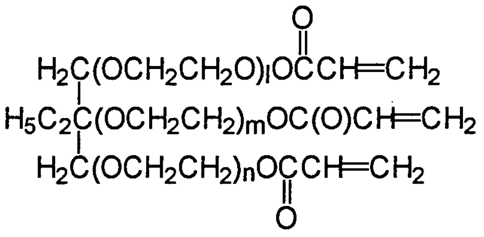
1. blends of the ethylene oxide - propylene oxide copolymer with poly(*N,N*-dimethylacrylamide) (PNNDMAA)
2. blends of poly(ethylene oxide) (PEO) with organic-inorganic polymers

The gel electrolytes were obtained using three types of network precursors.

1. Homopolymers and copolymers of triethylene glycol dimethacrylate (TEGDM) and trimethylopropane ethoxylate triacrylate (TMPETA)



$$(CH_2{=}\underset{\underset{CH_3}{|}}{C}\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2)_2{-}$$



$$\begin{array}{l} H_2\underset{|}{C}(OCH_2CH_2O)_lO\overset{\overset{O}{\|}}{C}CH{=}CH_2 \\ H_5C_2\underset{|}{C}(OCH_2CH_2)_mOC(O)CH{=}CH_2 \\ H_2C(OCH_2CH_2)_nO\underset{\underset{O}{\|}}{C}CH{=}CH_2 \end{array}$$

TEGDM (Mw 286)

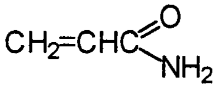
Aldrich (26,154-8)

TMPETA (l + m + n ~ 14; Mw 913)

Aldrich (41,219-8)

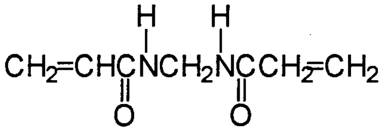
Optimization studies showed that as far as mechanical properties are concerned, it is most favorable to use copolymers in which the mole ratio of components is 1.5 - 3.0.

2. Acrylamide (AA) and *N,N'*-methylenebisacrylamide (bisAA) copolymers



AA (Mw 71)

Aldrich (14,875-1)



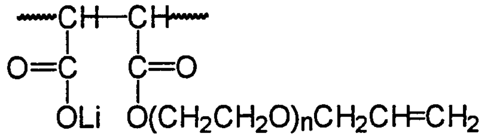
$$CH_2{=}CH\underset{\underset{O}{\|}}{C}\overset{\overset{H}{|}}{N}CH_2\overset{\overset{H}{|}}{N}\underset{\underset{O}{\|}}{C}CH_2{=}CH_2$$

bisAA (Mw 154)

Aldrich (14,832-6)

AA/bisAA weight ratio ≈ 24.

3. Crosslinked lithium salt of maleic anhydride half ester copolymers of the structure **A**



$$\sim CH(COOLi)-CH(COO(CH_2CH_2O)_nCH_2CH{=}CH_2)\sim$$

n (average) = 4

A

EXPERIMENTAL PART

Materials

The polymers, monomers, plasticizers and salts used are characterized in the next section. Solid polymers (reagent grade) were used without further purification after drying under vacuum at 50 - 70 °C [poly(ethylene glycol)s were stored over 4A molecular sieves]. Acrylamide (AA) and N,N'-methylenebisacrylamide (bisAA) were purified by crystallization from a chloroform / acetonitrile mixture. Acetonitrile, propylene carbonate (PC), methyl methacrylate (MMA) and acrylonitrile (AN) were distilled twice and stored over 4A molecular sieves. Lithium salts were dried under vacuum at 120 - 165 °C prior to use.

Synthesis of diethyl polyoxyethylenealuminum

An equimolar amount of a 20 wt. % toluene solution of $(C_2H_5)_3Al$ was added dropwise at room temperature to a 10 wt. % toluene solution of poly(ethylene glycol) methyl ether. The reaction course was controlled by measuring the amount of ethane evolved. After mixing the reactants, the mixture was kept for one hour in boiling toluene, and the solvent was removed under vacuum. The thick oil obtained was analyzed for aluminum content (Al found: 6.20 %; Al calculated: 6.23 %), and the molecular weight was determined cryometrically in benzene (M_n = 650, which corresponds to an average association degree ~ 1.5).

Preparation of electrolytes

Blend based electrolytes

All the electrolytes were prepared by casting from acetonitrile.

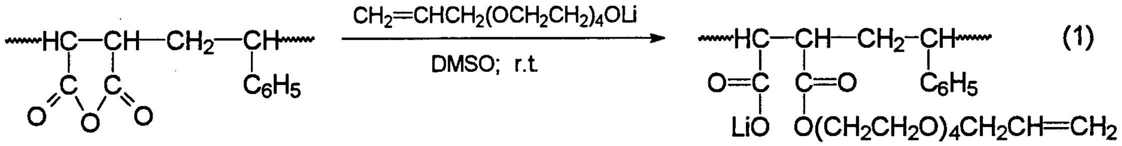
To a 8 wt. % acetonitrile solution of PEO, 10 wt. % solution of the salt and 20 wt. % solution of other polymers were added. The whole was stirred by means of a magnetic stirrer at room temperature for 3 h. 15 cm^3 samples were poured in the atmosphere of dry air onto glass plates or silicon coated paper covering an area of about 50 cm^2. The samples were left for the solvent to evaporate off. Acetonitrile residue was removed in a vacuum chamber at 50 °C for 2h. The films obtained were 0.2 - 0.3 mm thick and could be easily removed from the surface. In systems with PAA and polyacrylonitrile (PAN) the powdered polymer was added to the solution of PEO and the salts. The suspension was then stirred for 6 h at room temperature by means of a mechanical stirrer at 1500 r.p.m.

A similar technique was used when preparing composite electrodes.

Interpenetrating network systems

Systems based on maleic anhydride and styrene copolymers

An alternating maleic anhydride and styrene copolymer of $M_n \approx 3.2\times10^5$ was used as the initial polymeric product for the synthesis of electrolytes. The copolymer was obtained by free radical copolymerization carried out at 60 °C in toluene. A solution of the copolymer (0.5 g) in 15 cm^3 of DMSO was added dropwise to an equimolar amount of poly(ethylene glycol) alcoholate obtained from corresponding glycols and *n*-butyllithium (~ 25 mmol in 15 cm^3 of DMSO).



(1)

The reaction course was controlled by measuring the intensity of bands of the C=O bonds stretching vibrations at 1770 cm^{-1} (in anhydride groups) and at 1720 cm^{-1} (in ester groups). The electrolyte solution in DMSO was poured onto acidified water. The polymer precipitated was filtered off and purified by dissolution in methanol and precipitation in water. Finally, the acidic form of the electrolyte (0.2 g) was dissolved in 3 cm^3 of absolute methanol and converted into a salt by dropping in solutions of lithium, sodium and potassium methanolates. An appropriate amount of plasticizers and free radical initiator or photoinitiator were added to the solution. A thin layer was poured out and methanol was removed . Gels were obtained by thermal crosslinking at 70 °C for ~ 1 hour or by UV irradiation for ~ 10 minutes.

Systems based on acrylic polymers

To a reaction vessel equipped with a efficient mechanical stirrer were added: the solutions of polymers in acetonitrile (PEO *Mw* 5×10^6, PMMA *Mw* 1.3×10^5, PNNDMAA *Mw* 0.8×10^5, PEGDME *Mw* 500), solution of a lithium salt [$LiClO_4$, CF_3SO_3Li, $LiN(CF_3SO_2)_2$] curing acrylic monomers (like TMPETA *Mw* 912, TEGDM *Mw* 286, bisAA] and free radical initiator (AIBN, benzoyl peroxide) or photoinitiator (Irgacure 184) (1 wt. % with respect to the crosslinking monomers). The reactor content was stirred for 3 h (stirring rate 1000 r.p.m.) at room temperature. Films were then cast onto Teflon or glass plates. The solvent was removed at room temperature under reduced pressure (20 Torr). The films were then thermally cured at 70 °C for 30 minutes or photochemically by UV irradiation for 1 minute by means of a 100 W high pressure mercury lamp. All operations were carried out in the atmosphere of dry nitrogen. Films of 200 - 500 μm thickness were obtained.

Conductivity measurements

AC impedance analysis was used to determine the bulk conductivity of electrolytes using a Solartron 1255 frequency analyzer (10^{-2} - 10^6 Hz frequency range). Fig. 1 presents a schematic diagram of the conductivity cell of controlled geometry constructed for these measurements. Test studies show that due to using a PID type control system, the temperature can be controlled with a 0.01 deg accuracy in the -50 - +120 temperature range. At changes of 10 °C the temperature stabilizes within several minutes. The range of measurable resistance lies within the 50 Ω - 500 kΩ limit. The distance between the electrodes during conductivity measurements was controlled by spacers. The experimental data were analyzed using the NLLSQ program. We estimate that the experimental error should not exceed 10 % of the reported conductivity data.

Tests for dimensional and thermal studies

Strips (~ 5 mm wide and ~ 10 mm long) were cut out from the electrolyte or electrode samples and vertically placed in glass ampoules filled with nitrogen or dry air. They were kept at 100 - 120 °C for at least 100 hours. Samples, which flew under their own weight or underwent degradation to low molecular weight products were assumed as unstable.

Stable samples were subjected to impedance studies during ~ 200 h at 70 °C using the same instrumentation as for conducting measurements, but without spacers.

The stability of electrode - electrolyte systems was tested using cells designed in the Wright Lab POOS-2 (Wright-Patterson AFB) according to the general procedure described in ref. [3].

DSC, FT-IR and SEM studies were carried out on a DuPont TA 2910 scanning calorimeter, Nicolet FT-IR system 4.4 instrument and Hitachi S-570 scanning microscope, respectively .

RESULTS AND DISCUSSION

Composite polymer electrolytes

Polyether, poly(N,N-dimethylacrylamide) blends

In our previous works we showed that solid electrolytes, in which ethylene oxide and propylene oxide copolymers constitute the polymer matrix, exhibit conductivities of two to three orders of magnitude higher than analogous systems with poly(ethylene oxide) (PEO), which is commonly accepted as a reference solid solvent [4, 5]. We observed also that the conductivity of classic electrolytes based on PEO considerably increases after the addition of 10 - 20 wt. % of polar acrylic polymers, such as e.g. polyacrylamide or poly(methyl methacrylate) of an isotactic structure [6-8]. At present we decided to check whether a further increase in the conductivity of solid systems is possible by the formation of compositions comprising ethylene oxide and propylene oxide copolymers as well as polar acrylic polymers.

A copolymer containing 84 mol % of ethylene oxide monomeric units and 16 mol % of propylene oxide monomeric units of an number-average molecular weight M_n = 4700 and weight-average molecular weight = 45000 (determined by GPC using a styrene standard in tetrahydrofuran at 25 °C) was chosen for studies. Polyacrylamide (PAA) and poly(N,N-dimethylacrylamide) (PNNDMAA) of M_n 1.6×10^5 and 1.3×10^5 were used as the acrylic polymers. $LiClO_4$ was used as the salt (10 mol % with respect to oxygen in the ether chain).

In Fig. 2 are presented conductivity isotherms of composites with PNNDMAA at -20, 0, 25 and 100 °C versus PNNDMAA concentration. It can be noticed that the addition of 20 - 25 wt. % of PNNDMAA causes a clear increase in the conductivity of the electrolyte (by over one order of magnitude) at subambient temperatures. At a higher PNNDMAA content the conductivity of the system decreases. At room temperature the favorable effect of a polar additive is already scarce and at 100 °C the addition of PNNDMAA causes a decrease in conductivity. At a PNNDMAA content of up to ~15 wt. % the decrease in conductivity is small. Samples comprising an acrylic monomer exhibit much better mechanical properties than $LiClO_4$ complexes with the copolymer, and maintain dimensional stability during prolonged heating (~200 h) at 100 °C.

Similar relationships were observed for composites containing PAA (Fig. 3). The conductivity values obtained in this system are somewhat higher than those in systems with PNNDMAA. However, since PAA is not well soluble in organic solvents (contrary to PNNDMAA), it is difficult to obtain homogeneous films with the addition of PAA. Moreover, we found that at elevated temperatures (above 80 °C) rapid degradation to polyethers proceeds in systems with PAA. Therefore, the use of systems with PNNDMAA seems to be more favorable.

In Fig. 4 we presented, for comparison, conductivity isotherms obtained for blends containing PEO and PNNDMAA. In these systems, at ambient and subambient temperatures, the addition of a small amount of PNNDMAA causes a remarkable increase in conductivity . The highest conductivity values are obtained at the PNNDMAA content of ca. 15 wt. %, and they are only slightly smaller than those obtained in systems with the copolymer. At 100 °C the conductivity of both types of electrolytes is practically the same.

DSC curves obtained for the copolymer-$LiClO_4$-PNNDMAA systems containing up to 25 wt. % of PNNDMAA shows that these electrolytes are completely amorphous. They contain two amorphous phases clearly differing in the T_g values (Table 1). The lower one appears in the -60 - -65 °C range, which is very close to the glass transition temperature of the undoped copolymer. The higher one appears in the -30 - -45 °C, which is close to T_g registered for the copolymer - $LiClO_4$ electrolyte. For samples containing more than 25 wt. % of PNNDMAA, only one T_g value is observed, which decreases with an increase in the PNNDMAA concentration and for samples containing 40 or more wt. % of PNNDMAA, traces of crystallinity are observed.

Since the electrolytes studied are amorphous, they display a VTF type temperature dependence of conductivity (Fig. 5 - 7). However, for all of the samples studied, a deviation from the VTF curve at a temperature in the 1.2 - 1.4 T_g region is observed. Below this temperature ionic motion results mainly from the activated hopping. It is largely decoupled from segmental motion and can be described by an Arrhenius type relationship. An increase in conductivity measured at low temperature for composite systems suggests the creation of new sites available for hopping. The FT-IR studies of these systems indicate the formation of mixed complexes, in which the lithium cation is linked with the amide group of PNNDMAA and etheral group. This causes an increase in the number of available (uncomplexed) polyether oxygens. At high PNNDMAA concentration the lithium ions may form complexes only with amide groups. Due to this the T_g value undergoes a decrease and there also appears the possibility of crystallization of small segments of the polyether.

A similar phenomenon occurs in systems with PEO (Fig. 8), where the addition of up to 20 wt. % of PNNDMAA causes a considerable decrease in the degree of crystallinity (and hence of conductivity). A further increase in the PNNDMAA concentration in the system leads to an increase in the degree of crystallinity of PEO. This is clearly connected with interactions with Li^+ ions, since similar effects do not occur in undoped composites (Fig. 8).

The concentration of free ions in the systems studied was determined on the basis of the analysis of the peak characteristic for $\nu(ClO_4)$ vibrations. A Galactic Grams 386 software package was used to separate this signal into two contributions with maxima in the 620 - 624 cm^{-1} ranges. An example of this separation is shown in Fig. 9. The $\nu(ClO_4)$ band centered at 620 - 624 cm^{-1} can be attributed to spectroscopically "free" ClO_4^-, whereas the band centered between 630 - 635 cm^{-1} is associated with the presence of contact ion pairs. [9].

The fraction of "free" anions has been calculated as the ratio of the area under the peak attributed to these species to the total area for the $\nu(ClO_4)$ vibrations. The results are shown in Fig. 10. For the copolymer/PNNDMAA/$LiClO_4$ the fraction of free ions is close to 100 % for samples containing more than 5 wt. % of PNNDMAA. In the systems with PEO it reaches maxima for the concentration of PNNDMAA ~25 wt. % (which corresponds to the highest conductivity of the system) and for the concentration of PNNDMAA, when Li cations are complexed only by amide groups.

We have also observed that the fraction of ion pairs increases with a rise of temperature.

The results obtained were also interpreted in terms of the Effective Medium Theory (EMT) according to the method described by us previously [10].

As can be seen from Fig. 11 there is a reasonable fit of the model up to 25 % of PNNDMAA.. The differences observed between experimental data and the model for higher concentration of PNNDMAA we attributed to the strong interactions between Li cations and amide groups leading to the immobilization of the charge carriers.

PEO blends with organic - inorganic polymers

Mixed organic - inorganic hybrid materials have been developed over the last decade and have been known as organically modified ceramics (ORMOCER). These materials contain organic components attached to the inorganic network and are usually obtained in the so called sol - gel processes. The typical processing steps involve the hydrolysis of alkoxides or halides and polycondensation reactions with the evolution of water or other small molecules like HCl, amines and carboxylic acids.

The formation of compounds with active hydrogen bonds rather excludes the possibility of using this type of systems in lithium batteries and until now they are mainly used as proton conductors.

Within this work we carried out initial studies on the possibility of obtaining similar materials in processes, in which compounds not aggressive towards the electrolytes and electrodes evolve as a result of condensation.

As starting materials we used triethylaluminum (Fluka) and poly(ethylene glycol) methyl ether *Mw* 350 (Aldrich, 20,247-9

$$(C_2H_5)_3Al + \underset{n = 2,3}{CH_3(OCH_2CH_2)_nOH} \longrightarrow \underset{\mathbf{B}}{1/n\,[CH_3(OCH_2CH_2)OAl(C_2H_5)_2]_n} + C_2H_6 \qquad (2)$$

The product of this reaction occurs in the form of dimers and contrary to $(C_2H_5)_3Al$ it can be dealt with in the atmosphere of dried air.

In further stages, as a result of reaction with substances containing active hydrogen atoms, this compound forms an organic - inorganic network with ethane evolution.

In initial studies we used this compound as an agent modifying PEO and the condensation was limited only to the reaction with the impurities present in the electrolyte (moisture, catalyst residue, eventually contamination with acid in the salt). After mixing the reactants in acetonitrile and film casting, homogeneous membranes are formed of very good mechanical properties, which did not undergo degradation during storing at 100 °C for several weeks.

In Fig. 12 are presented exemplary conductivity values of thus obtained materials. Similarly as in systems studied earlier, the highest conductivity values were obtained when using $LiN(CF_3SO_3)_2$ ($\sim 4\times10^{-5}$ S/cm at 20 °C and $\sim 3\times10^{-3}$ S/cm at 90 °C). Conductivity values above 10^{-5} S/cm can be obtained also by using $LiClO_4$ at the added compound content ~ 33 wt. %. In the case of $LiCF_3SO_3$ at an analogous blend composition, the conductivities are lower by about 50 %. This results from the relatively high contents of the crystalline phase. In the DSC spectrum (Fig. 13) are observed: a peak corresponding to the PEO crystalline phase melting at 49 °C (degree of crystallinity is ~ 18 %) and a strong endothermic peak (Q = 57.5 J/g) at ~ 100 °C, probably corresponding to the melting of the $P(EO)_3 \times LiCF_3SO_3$ complex.

Due to the presence of polyglycol side chain, these systems are characterized by a very low T_g value (~ -65 °C), which assures high mobility of the amorphous phase.

In our opinion this is an ideal structure for the matrix, in which the inorganic segments (capable of complexing ethereal chains) assure high dimensional stability at elevated temperatures and the organic segments act as internal plasticizers assuring high conductivity of the system. Moreover, this type of additives should act as traps for impurities.

Further studies showed that in the presence of PEO and a salt in an acetonitrile solution the organometallic compound studied may undergo further condensation with bifunctional monomers (e.g. H_2O, diphenols) forming organic - inorganic polymers. Such transformation does not cause a decrease in the conducting properties and may be used for the formation of interpenetrating PEO and organic - inorganic polymers networks.

Taking into account the very low cost of the starting materials and simplicity of preparing the electrolyte, this method seems to be very attractive. However, further electrochemical studies with transporting electrodes should prove its applicability. This method can also be a valuable supplement of classic sol - gel processes, since it enables the introduction of organic species after the hydrolysis step. It can also be carried out involving other organic derivatives of metals. However, from the economic point of view, aluminum alkyls industrially produced seem to be most appropriate.

Gel electrolytes

Polymeric networks plasticized by poly(ethylene glycol)s

It is known that the addition of low molecular weight plasticizers, like cyclic esters (especially carbonates) and ethers causes an increase in the room temperature conductivity of PEO based electrolytes to 10^{-4} - 10^{-3} S/cm, but apparently with significant reduction in their dimensional stability [11]. High conductivity and satisfactory dimensional stability are exhibited by gel electrolytes comprising spatial macromolecule networks, salts and organic solvents. The spatial structure may result from the specific interactions between linear polymers (e.g. by the formation of micro crystallites like in PAN based electrolytes) or from chemical or higher energy crosslinking reactions.

In the case of electrolytes which are supposed to work for a long time at temperatures up to 120 °C, practically only poly(ethylene glycol)s or poly(propylene glycol)s can be considered as non-volatile plasticizers. In the patent of Bauer *et al.* [12] and in the papers of Tsuchiya [13] and Sander *et al.* [14] methods of the synthesis of some polymeric networks plasticized by this type of polyether have been described. PAN and crosslinked epoxy PMMA or oligo(ethylene glycol) methacrylates have been used as polymeric matrixes. Ambient temperature conductivities of the order of 10^{-5} - 10^{-4} S/cm were reported for these systems.

Poly(ethylene glycol) dimethyl ether (PEGDME, average molecular weight M_w = 420 and 500, Fluka) was used as the plasticizer in our studies. Crosslinked polymeric networks were obtained using three basic systems described in the introduction.

The crosslinking was performed either thermally at 70 - 80 °C using 0.1 wt. % of AIBN as initiator or photochemically by irradiating the system for 1 - 5 minutes with a 100 W high pressure mercury lamp. $LiCF_3SO_3$ (Aldrich, 28,266-9), $LiClO_4$ (Fluka, 62579) and $LiN(SO_2CF_3)_2$ (3M) were used as salts.

In some experiments PEO (Aldrich, 18,947-2 Mw = 5,000,000), PMMA Mw 150,000 g/mol (obtained by free radical polymerization in bulk) and PC (Aldrich, 31,032-8) were introduced to the reaction system.

In Tables 2 and 3 are presented the compositions of the gels studied and conductivities at 20 and 90 °C determined by means of impedance spectroscopy. Figs 14 and 15 present the temperature relationship of conductivity for the samples studied.

The highest conductivity values were obtained for electrolytes containing a matrix of the structure **A** (page3). This probably results from the occurrence of oxyethylene units not only in PEGDME but also in the solid frame. Systems containing ~ 50 wt. % of PEGDME and 5 - 15 wt. % of $LiClO_4$ exhibit conductivities above 10^{-4} S/cm at 20 °C and ~ 10^{-3} S/cm at 90 °C. These systems exhibit some conductivity in the absence of $LiClO_4$ (~ 10^{-7} at 20 °C and ~ 10^{-5} at 90 °C). Selective cationic transport probably takes place here, since carboxylic anions are immobilized in the network. The conductivity of these systems can be increased by about two orders of magnitude after the introduction of BF_3 to the system, which complexes carboxylic ions and thus causes an increase in the dissociation constant of the carboxylic salts (Fig. 16).

However, it appeared that systems containing more than 40 wt. % of PEGDME are not thermally stable and at room temperature after about 24 hours the separation of some amount of PEGDME can be observed. Therefore, transient crosslinking of PEGDME *via* the formation of complexes with Li^+ ions does not assure the formation of a stable system of interpenetrating polymer networks. Microscopic observations indicate that at 90 °C phase separation occurs within a few hours. We found that stable systems can contain maximally up to 35 % of PEGDME. However, a considerably lower conductivity value is then obtained (~ 10^{-5} S/cm at 20 °C and 6×10^{-4} S/cm at 90 °C).

Phase separation can be inhibited by the introduction of BF_3, but the mechanical properties of thus obtained electrolytes are unsatisfactory.

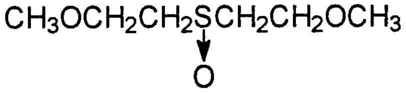
The phenomenon of partial separation of the crosslinked matrix and PEGDME occurs also in matrices 1 and 2 (page 2) of high PEGDME content (60 - 75 wt. %), which exhibit conductivity in the 10^{-5} - 5×10^{-5} S/cm range at 20 °C. The separation can be inhibited by additionally introducing to the electrolytes certain linear polymers: PEO, PMMA or PNNDMAA. However, after storing the samples for several weeks, their surfaces become moistured due to the isolation of the glycol.

In connection with this it seems that by changing the type of polymeric matrix one can only decrease the rate of diffusion of PEGDME from the polymeric matrix, but the mutual solubility of the matrix and plasticizer cannot be changed. Systems of high PEGDME content and high conductivity are thermodynamically unstable and phase separation occurs within time. A similar phenomenon was observed also for other types of matrixes [12].

Systems comprising polar organic solvents

The conducting properties of polymeric networks based on a crosslinked lithium salt of the structure A plasticized with various polar solvents were described in our previous report presented in October 1994.

We now synthesized one more type of solvent, which in our opinion should be sufficiently polar to maintain good conducting properties, and simultaneously exhibit small aggression towards the lithium electrode. Its structure is as follows:

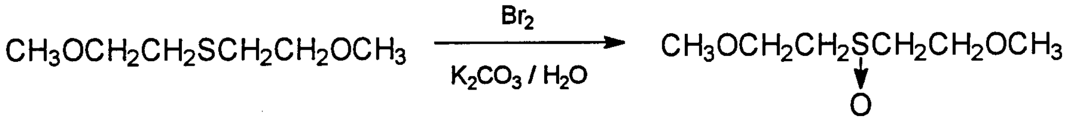


$$CH_3OCH_2CH_2\underset{\substack{\downarrow\\ O}}{S}CH_2CH_2OCH_3$$

DMOSO

It was obtained from the following reactions:

$$CH_3OCH_2CH_2Cl\ +\ Na_2S \longrightarrow CH_3OCH_2CH_2SCH_2CH_2OCH_3$$



$$CH_3OCH_2CH_2SCH_2CH_2OCH_3 \xrightarrow[K_2CO_3\,/\,H_2O]{Br_2} CH_3OCH_2CH_2\underset{\substack{\downarrow\\ O}}{S}CH_2CH_2OCH_3$$

The conductivity values of gels containing this solvent are presented in Fig. 17. At an ~ 45 % content of this solvent monoconducting gels are obtained of good mechanical properties and conductivities above 10^{-5} S/cm at 20 °C. A further increase in conductivity can be obtained by the additional introduction of propylene carbonate.

Stability of Li - electrode - electrolyte interface

A list of the systems studied and their ambient temperature conductivities measured in systems with blocking steel electrodes are presented in Table 4. In systems with blocking electrodes all the samples studied were stable at room temperature and no increase in their resistance during over 200 h was observed.

In Li|electrolyte|Li systems the impedance spectra are a combination of several semicircles, more or less "disfigured" (i.e. depressed and non-symmetrical), indicating two or more (RC) parallel elements in the equivalent electrical circuit. The proportion between semicircles changes, indicating that a process is taking place during the experimental cycle. This process (or processes) may be followed by analyzing the values of R and C (or Q constant phase element characterized by Q and n values), derived from numerical analysis of the z' - z" curves.

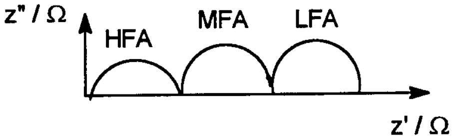
In all the systems studied, in the initial stage (1 h after preparation of the cell) spectra are obtained containing two semicircles. The first one, at frequencies higher than approximately 1 kHz, can be attributed to the bulk properties of the polymer electrolyte [15].

The second relaxation phenomenon observed at lower frequencies is generally attributed to the charge transfer reaction at the lithium / electrolyte interface.

After prolonged storage under open circuit conditions three types of impedance spectra were obtained:

1. Spectra with semi-circles denoted as HFA (high frequency arc), MFA (medium frequency arc) and LFA (low frequency arc) (e.g. fig. 18, 19)

   In Table 5 are presented the values obtained on the basis of equivalent circuit (EQC) analysis of sample 2, for an idealized system composed of three semicircles (HFA, MFA and LFA).



The R_i values are expressed in Ω, those of Q and C in S^{-1} and F, respectively, and n is an exponent. One can observe that the HFA values are practically constant and we attributed them to the resistance and capacitance of the electrolyte. The values for MFA change within time: the R value increases (from 4×10^3 to 1.1×10^4) and stabilizes after ca. 100 h for the next 100 h; the Q value increases. The plausible physical interpretation is that MFA corresponds to the electrode/ electrolyte interface. Its resistance increases up to a certain value (here ca. 1.1×10^4 Ω) and remains fairly constant during the next 100 h. The Q and R values for LFA do not increase within time. In the case of the Q value: if capacitance is approximated with it, values of about 10^{-6} F cm^{-2} are obtained, characteristic for the capacitance of an electrical double layer at solid electrodes. A tentative interpretation is that LFA is an electrical response of a charge transfer reaction $Li \longleftrightarrow Li^+$ at the electrode.

2. Spectra with two semicircles denoted as HFA and LFA. The semi-circle LFA corresponds to the impedance response of the charge transfer reaction ($Li \longleftrightarrow Li^+$), overlaid with the growing interface layer. The increase in the R_{LFA} value results from the formation of a resistance layer on the metallic surface and hence and an increase in the charge transfer resistance occurs. Although the LFA shape changes towards a more irregular semi-circle, indicating the possibility of an overlapping response from two sources (electrochemical reaction and resistance layer), these two responses cannot be separated by means of numerical analysis, probably due to the close values of time constants RC of these two electrical elements. The LFA increases all the time. The R values for LFA of sample 6 are presented in Table 6.
3. Spectra with two semicircles (HFA and LFA), the resistance of which changes within time. The capasitance characteristics for LFA are close to 10^{-} F/cm^2, which permits to suggest that similarly as in the initial stage it can be attributed to the charge transfer reaction. The capacitance characteristics for HPA are in the 10^{-9} - 10^{-10} F/cm^2 range. This suggests that in these systems the passivation layer does not give measurable capacitance effects and its resistance adds to the electrolyte resistance. It can be assumed wit some approximation that the resistance of the passivation layer formed R_i is equal to the difference between the R_{HFA} value determined and the R_{oHFA} value measured after installing the cell (which is a sum

of the electrolyte resistance and initial interfacial resistance resulting from the thin passive film formed on the Li surface during cell preparation.

$$R_i \approx R_{HFA} - R_{oHFA}$$

Examples of such spectra are shown in Figs 20 - 23 and the R_i evolution in time is shown in Fig. 24.

Systems composed of EO-PO copolymer, PNNDMAA and $LiClO_4$ (sample 1) are characterized by the highest stability. The total increase in resistance of the Li|electrolyte|Li cell ends after about 40 h and is ca. 20 % (Fig. 25). The values of the electrolyte resistance in the samples studied were constant (~ 20 kΩ), R_i values in the 20 - 40 kΩ range and charge transfer resistance from 40 to 75 kΩ.

Spectra of the first type were observed also for a gel system containing PEG and PC (sample 2). The stabilization of the total resistance of the cell occurs after about 60 h (Table 7, Fig. 26). It is about three times larger than the initial resistance of the cell.

Therefore it can be assumed that in these systems passive layers are mainly formed as result of the reaction of lithium with impurities, or thin layer of the electrolyte, upon which further increase of the passive layer is inhibited due to slow diffusion processes.

The introduction of additionally a lithium salt with mobile ClO_4^- anions to sample 2 (sample 3) leads to a significant increase in conductivity and at the same time to a considerable decrease in the interface stability. As can be seen from Tables 8 and plot, after about 190 h no resistance stability of the cell is reached, and the R_i value rises ca. 14 times and the R_{oi} value increases over 100 times. The reason for this is probably the anion diffusion through the passive layer and its participation in the electrode corrosion.

The rate of this process can be decreased by decreasing the polarity of the system. For example, by eliminating PC from the gel it is possible to obtain systems, the resistance of which is decreased only slightly after 150 h (Sample 4, Table 9). The porous passive layers are probably saturated with the low molecular weight organic compounds used, which is decisive of the ion migration rate.

Initial observations indicate that the stability of these systems additionally increases when traps of impurities are introduced to the polyglycol structure in the form of an organic - inorganic polymer based on organoaluminum compounds (sample 5, Table 10, Fig. 27). However, it seems that the molecular weight of the polymer added should be considerably increased in order to still further limit the diffusion processes.

The monoconducting gels obtained by us of conductivities above 10^{-5} S/cm usually contained DMSO as one of the solvents. Unfortunately, the presence of this solvent inhibits the obtaining of stable passive layers and a systematic increase in the cell resistance during storing at room temperature is observed (sample 6, Table 6 Fig. 28). This solvent probably easily undergoes diffusion through the passive layers and participates in the corrosion of lithium.

An analog of DMSO obtained by us: di-(2-methoxyethyl) sulfoxide (DMOSO) seems to be a much better solvent from the interface stability point of view. For example, the data obtained for sample 7 (Table 11, Fig. 24) indicate that after about 140 h stabilization of resistance occurs and it is about five times larger than in the initial period.

The passivation processes undergo considerable acceleration when additionally PC is present in the system (sample 8, Table 12, Fig. 24), which probably reacts with lithium much faster than with DMOSO.

A number of experiments were carried out of initial passivation of a lithium film by means of SO_2, SO_2Cl_2 and also organoaluminum compounds. The films were then used as electrodes in systems with gels containing PC and DMSO. A considerably quicker increase of the cell resistance with respect to the unmodified samples was observed in all the systems. Thus, it seems that in a strongly polar medium dissolution of the initial passive layer occurs with the formation of a solution causing quicker corrosion of the lithium electrode. A small increase in stability was observed only in the case when using PEG as the electrolyte after passivation with SO_2, but this observation still requires statistical confirmation with a larger number of samples.

Taking into account that at present the main stress is put rather on "lithium free" ("rocking chair") batteries, we also carried out studies on the stability of composite electrodes based on LONZA KS-6 and $LiNiO_2$ in gel systems and systems comprising PEO / organic-inorganic polymer blends and PEG. In Figs 29 and 30 impedance spectra are presented obtained at 70 °C for these systems. As can be seen, they are analogous to those with blocking electrodes and the formation of passive layers during storing at elevated temperatures is not observed.

CONCLUSIONS

1. The results obtained in this project suggest that from the point of view of stability of the lithium electrode - electrolyte interface and total cell resistance, systems containing solid electrolytes seem to be most suitable. At present it is possible to obtain electrolytes exhibiting conductivities of $5 - 5.5\times10^{-5}$ S/cm at 25 °C, which in a cell with lithium electrodes under open circuit conditions form stable passivation layers and the increase in the cell resistance resulting from this does not exceed 50 %. With respect this, PEO blends and inorganic - organic polymers obtained from poly(ethylene glycols) and organoaluminum compounds seem to be especially interesting. They can be obtained by simple mixing of commercially available and cheap components in solution. These electrolytes are dimensionally stable up to 120 °C and do not undergo thermal degradation during prolonged storage at this temperature. They do not react with composite electrodes based on LONZA KS-6 and $LiNiO_2$ even at elevated temperature. Thus, one can expect that in uncharged cells of a "rocking chair" type containing these materials, the passivation phenomena can be neglected.
2. The conductivity of solid electrolytes is still too low to consider them as practical materials for lithium batteries working at ambient temperature. In order to improve the conductivity it seems to be necessary to additionally introduce a strongly polar low molecular weight compound. In our opinion di(2-methoxyethyl) sulfoxide is a very suitable candidate for this purpose. This compound reacts very slowly with lithium at room temperature producing a stable passivation layer of small resistance and presently we are carrying out studies on its applicability for different types of lithium cells.
3. The results obtained indicate that passivation processes of the lithium electrode proceed slower in systems with immobilized anions. From our initial observations it appears that such systems can be also obtained in the form of organic - inorganic polymers. It seems that thin monoconducting flexible blends from these materials, saturated with a solvent which is less reactive toward lithium

than commercially used organic carbonates, are the most promising candidates for practical application in lithium batteries.

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Table 1

DSC Data for the Copolymer-PNNDMAA-LiClO$_4$ Composite Polymeric Electrolytes

wt. %[a]	Run 1					Run 2				
	T_{g1}	T_{g2}	T_m	Q_m	X_c[b]	T_{g1}	T_{g2}	T_m	Q_m	X_c[b]
	°C	°C	°C	J g^{-1}	%	°C	°C	°C	J g^{-1}	%
0[c]	-58		10	37	18	-57		4	38	18
0	-36					-36				
5	-29	-62				-30	-52			
10	-34	-64				-31	-65			
15	-35	-61				-35	-58			
20	-44	-62				-49	-62			
25	-39	-65				-40	-55			
30	-43					-41				
40	-48		6	0.3	0.2	-49		6	0.6	0.5
50[d]	-55		-10.9	8.5	7.9	-56		-11.9	13.1	12.2

[a] Concentration of PNNDMAA in wt. %; [b] X_c has been calculated with respect to the copolymer concentration in the composite electrolyte; [c] Undoped copolymer sample; [d] Two numbers in the T_m column indicate onsets of two melting peaks. Q_m is calculated as a sum of melting heats of both transitions.

Table 2

Conductivity of plasticized networks based on acrylic monomers

Network composition										σ	
PEO	PMMA	PEGDME *Mw* 500	TEGDM	TMPETA	NNDMAA	AA	bisAA	Salt	O/Li mole ratio	S/cm	
wt. %										20 °C	90 °C
5		75	5	15				CF_3SO_3Li	25	6.2×10^{-4}	7.3×10^{-4}
15		65	5	15				CF_3SO_3Li	15	1.5×10^{-5}	5.1×10^{-4}
10		60	20	10				CF_3SO_3Li	10	3.9×10^{-5}	8.9×10^{-4}
	15	65	5	15				CF_3SO_3Li	25	3.2×10^{-5}	4.2×10^{-4}
	15	60		10	15			CF_3SO_3Li	25	1.8×10^{-5}	1.3×10^{-4}
	15	60		17.5			7.5	CF_3SO_3Li	25	1.6×10^{-5}	7.7×10^{-5}
	20	65	5	10				CF_3SO_3Li	25	3.0×10^{-5}	2.1×10^{-4}
	20	75		5				CF_3SO_3Li	25	4.4×10^{-5}	6.0×10^{-4}
		75				20	5	$LiClO_4$	15	5.6×10^{-5}	2.0×10^{-3}

Table 3. Conductivity of plasticized networks based on styrene - maleic anhydride copolymer

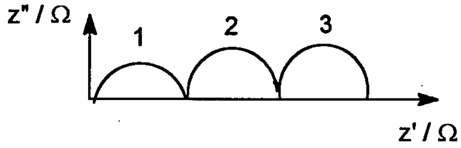
System with (wt. %)	σ, Scm^{-1}	
	20 °C	90 °C
$LiClO_4$ (0) - PEGDME (45)	3.1×10^{-7}	7.2×10^{-6}
$LiClO_4$ (5) - PEGDME (57)	2.4×10^{-4}	1.4×10^{-3}
$LiClO_4$ (10) - PEGDME (54)	2.1×10^{-4}	4.5×10^{-4}
$LiClO_4$ (15) - PEGDME (51)	3.3×10^{-4}	3.3×10^{-3}
$LiClO_4$ (7) - PEGDME (35)	2.1×10^{-5}	6.1×10^{-4}
$LiClO_4$ (0) - PC (30) - PEGDME (30)	6.7×10^{-6}	1.7×10^{-5}
$LiClO_4$ (5) - PC (34) - PEGDME (34)	2.6×10^{-4}	3.0×10^{-3}
$LiClO_4$ (10) - PC (32) - PEGDME (32)	4.8×10^{-4}	3.3×10^{-3}
$LiClO_4$ (15) - PC (30) - PEGDME (30)	5.7×10^{-4}	4.0×10^{-3}
$LiClO_4$ (5) - PEGDME (65) - $BF_3\times Et_2O$ (1:1 by mole)[a]	1.0×10^{-5}	1.8×10^{-3}
PEGDME (68) - $BF_3\times Et_2O$ (1:1 by mole)[a]	5.4×10^{-5}	7.9×10^{-4}

[a] with respect to copolymer

Table 4. List of systems studied based on the matrix A

Sample number	Sample composition	σ_{20} / S cm^{-1}
2	25 % PC, 25 % PEG	5×10^{-6}
3	25 % PC, 25 % PEG, 5 % $LiClO_4$	2×10^{-4}
4	35 % PEG, 7 % $LiClO_4$	2×10^{-5}
6	35 % PC, 25 % DMSO	9×10^{-5}
7	45 % DMOSO	1.5×10^{-5}
8	30 % PC, 30 % DMOSO	4×10^{-5}

Table 5. EQC parameters for sample **2**



Time	Parameters					
h	R_1	C_1	R_2	Q_2 / n	R_3	Q_3 / n
1.5	4.58×10^{3}	6.2×10^{-10}	1.78×10^{3}	6.9×10^{-5} 0.39		
5	3.40×10^{3}	9.7×10^{-10}	4.27×10^{3}	4.1×10^{-9} 0.93	9.35×10^{3}	2.3×10^{-6} 0.67
10	5.46×10^{3}	7.8×10^{-10}	3.84×10^{3}	2.4×10^{-8} 0.85	1.77×10^{4}	1.6×10^{-6} 0.70
25.5	6.89×10^{3}	7.5×10^{-10}	6.23×10^{3}	6.3×10^{-8} 0.80	3.21×10^{4}	1.7×10^{-6} 0.66
49.5	6.16×10^{3}	7.4×10^{-10}	7.32×10^{3}	6.4×10^{-8} 0.81	3.05×10^{4}	1.9×10^{-6} 0.61
56.5	5.50×10^{3}	7.5×10^{-10}	6.92×10^{3}	6.5×10^{-8} 0.81	2.63×10^{4}	2.02×10^{-6} 0.60
73.5	5.98×10^{3}	7.6×10^{-10}	8.98×10^{3}	5.9×10^{-8} 0.81	3.02×10^{4}	1.6×10^{-6} 0.61
97.5	5.42×10^{3}	7.8×10^{-10}	1.08×10^{4}	4.7×10^{-8} 0.81	2.17×10^{4}	1.4×10^{-6} 0.63
121.5	5.46×10^{3}	7.9×10^{-10}	1.09×10^{4}	4.3×10^{-8} 0.81	2.03×10^{4}	1.5×10^{-6} 0.63
169.5	5.67×10^{3}	7.7×10^{-10}	1.11×10^{4}	3.6×10^{-8} 0.83	1.89×10^{4}	1.4×10^{-6} 0.64
193.5	5.37×10^{3}	7.9×10^{-10}	1.09×10^{4}	3.6×10^{-8} 0.82	1.69×10^{4}	1.5×10^{-6} 0.64

Table 6. Z' values (Z_{REAL} / Ω) for Three Parallel Samples of 6 in Li | Sample 6 | Li Cells

Time / h	I	II	III
0	0.9×10^4	0.5×10^4	0.8×10^4
1.5	0.9×10^4	0.5×10^4	0.9×10^4
3	1.0×10^4	0.6×10^4	0.95×10^4
5	1.2×10^4	0.7×10^4	1.1×10^4
6.5	1.5×10^4	0.9×10^4	1.3×10^4
10	2.5×10^4	1.7×10^4	2.2×10^4
25	$4\ \times10^4$	3.5×10^4	4.5×10^4
27	$5\ \times10^4$	3.5×10^4	$5\ \times10^4$
29	$5\ \times10^4$	3.7×10^4	$5\ \times10^4$
48.5	5.5×10^4	3.8×10^4	$6\ \times10^4$
54.5	5.5×10^4	3.8×10^4	$6\ \times10^4$
120	1.2×10^5	$8\ \times10^4$	1.25×10^5
144	1.3×10^5	$1\ \times10^5$	1.6×10^5
168	1.8×10^5	1.3×10^4	2.5×10^5

Table 7. Dependence of $R_{2(HFA)}$ and $R_{3(LFA)}$ on time for sample 2

Time / h	R_2 / Ω	R_3 / Ω
1.5	1.78×10^3	9.35×10^3
5	4.27×10^3	1.77×10^4
10	3.84×10^3	3.21×10^4
26	6.23×10^3	3.05×10^4
50	7.32×10^3	2.63×10^4
57	6.92×10^3	3.02×10^4
74	8.98×10^3	2.17×10^4
98	1.08×10^4	2.03×10^4
122	1.09×10^4	2.01×10^4
170	1.11×10^4	1.89×10^4
194	1.09×10^4	1.69×10^4

Table 8. Dependence of $R_{i(HFA + MFA)}$ and $R_{3(LFA)}$ on time for sample 3

Time / h	R_i / Ω	R_3 / Ω
1	1.2×10^2	1.3×10^3
24	1.9×10^2	1.1×10^4
48	3.2×10^2	2.1×10^4
72	4.2×10^2	2.7×10^4
144	6.9×10^2	6.5×10^4
168	8.9×10^2	8.5×10^4
192	1.8×10^3	1.7×10^5

Table 9. Dependence of $R_{i(HFA + MFA)}$ and $R_{3(LFA)}$ on time for sample 4

Time / h	R_i / Ω	R_3 / Ω
1	2.0×10^3	1.3×10^3
24	5.2×10^3	2.3×10^3
48	8.1×10^3	2.8×10^3
72	1.2×10^4	3.2×10^3
144	2.8×10^4	5.8×10^3
168	3.2×10^4	5.2×10^3
216	3.1×10^4	4.3×10^3
240	3.5×10^4	7.6×10^3

Table 10. Dependence of $R_{i(HFA + MFA)}$ and $R_{3(LFA)}$ on time for sample 5

Time / h	R_i / Ω	R_3 / Ω
1	6.5×10^3	3.2×10^3
24	1.2×10^4	3.5×10^3
48	2.4×10^4	5.8×10^3
72	2.3×10^4	5.0×10^3
168	4.7×10^4	8.4×10^3
192	5.1×10^4	9.5×10^3
216	6.1×10^4	1.3×10^4

Table 11. Dependence of $R_{i(HFA + MFA)}$ and $R_{3(LFA)}$ on time for sample 7

Time / h	R_i / Ω	R_3 / Ω
1	6.2×10^3	4.9×10^3
24	7.1×10^3	2.2×10^4
144	8.9×10^3	3.8×10^4
168	1.0×10^4	4.3×10^4
192	8.5×10^3	3.3×10^4
216	9.5×10^3	3.7×10^4
288	1.0×10^4	3.8×10^4

Table 12. Dependence of $R_{i(HFA + MFA)}$ and $R_{3(LFA)}$ on time for sample 8

Time / h	R_2 / Ω	R_3 / Ω
1	3.9×10^2	7.6×10^3
24	5.6×10^2	4.4×10^3
48	7.8×10^2	9.3×10^3
72	9.2×10^2	1.6×10^4
168	1.9×10^3	6.9×10^4
192	2.2×10^3	7.6×10^4
216	2.3×10^3	7.6×10^4
240	$2,6\times10^4$	7.9×10^4
288	3.5×10^4	8.1×10^4

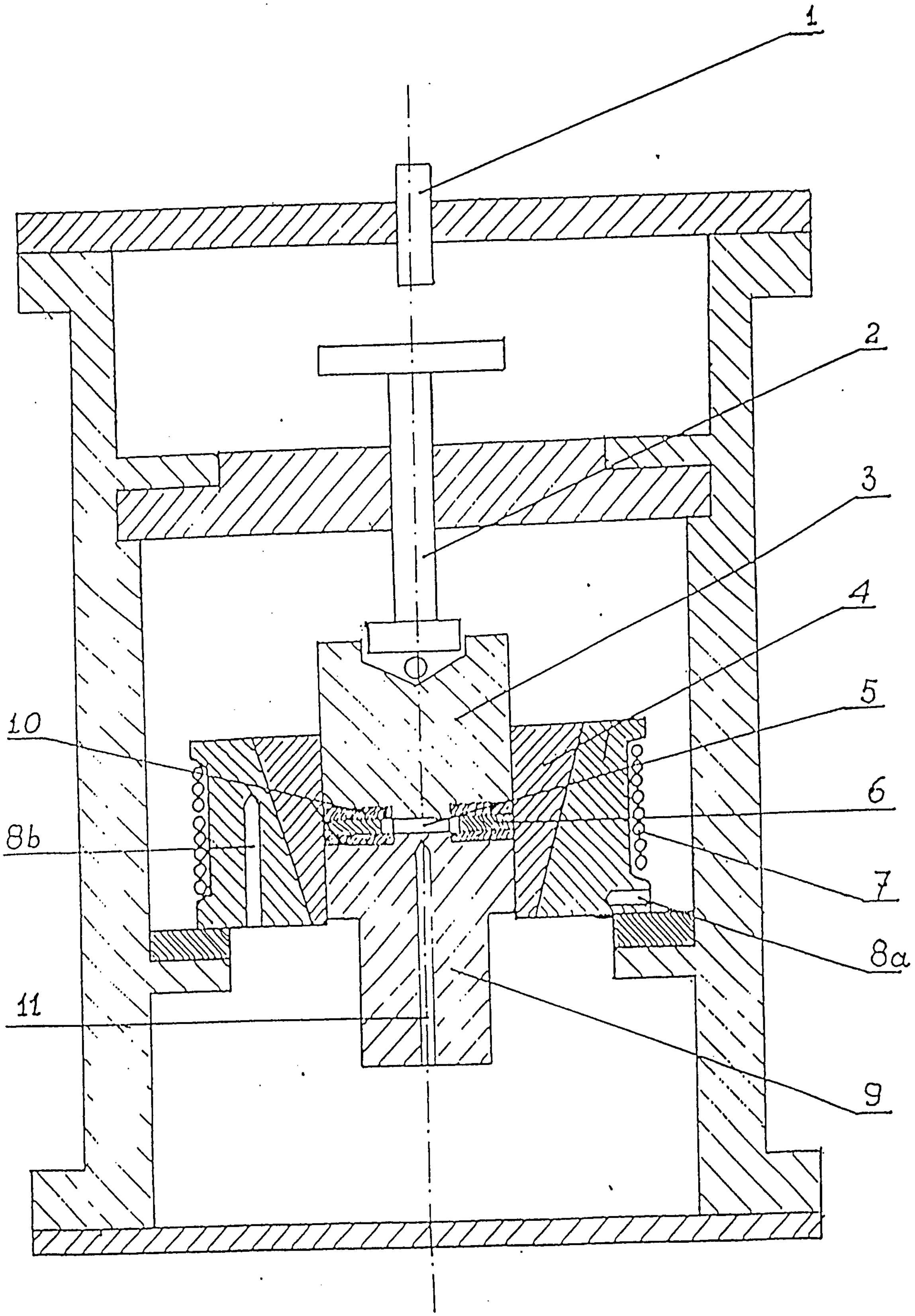
Figure 1

Simplified schema of the cell (vessel) for impedance measurements

1. To vacuum pump / inert gas line. The cell is gas-tight and on demand the inner space (in contact with the sample) can be either evacuated or filled with an inert gas.
2. Load screw.
3. Upper electrode block. Upper and lower electrodes with 0.5 cm^2 discs exposed for measurement, isolated from spacers and chassis.
4. Copper heating block.
5. Sample - polymer foil or complete cell.
6. Spacer. Movable rings controlling the thickness of the sample in the 100 µm - several mm range.
7. Heater.
8. a) and b): Pt 100 resistance thermometers - coupled with a PID type temperature controller.
9. Lower electrode block.
10. Isolating rings.
11. Pt 100 resistance thermometer - direct measurement under the sample.

Figure 1

Simplified schema of the cell for impedance measurements



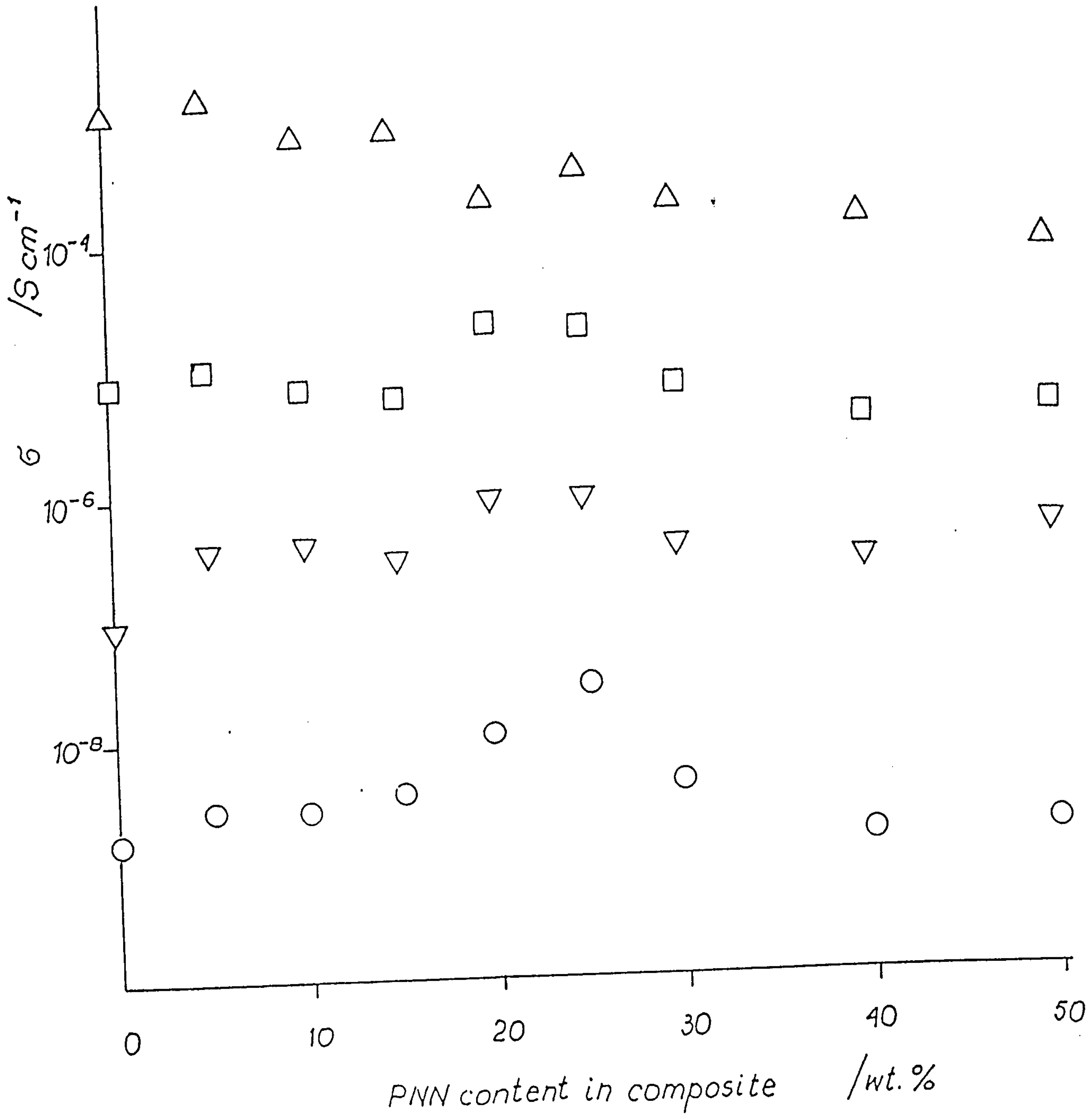


Fig. 2.

Isotherms of ionic conductivity of EOPO copolymer - PNN - $LiClO_4$ versus PNN concentration. Ether oxygen to Li mole ratio = 10.

(O) - 25 °C; (∇) - 0 °C; (□) - 25 °C; (Δ) - 100 °C.

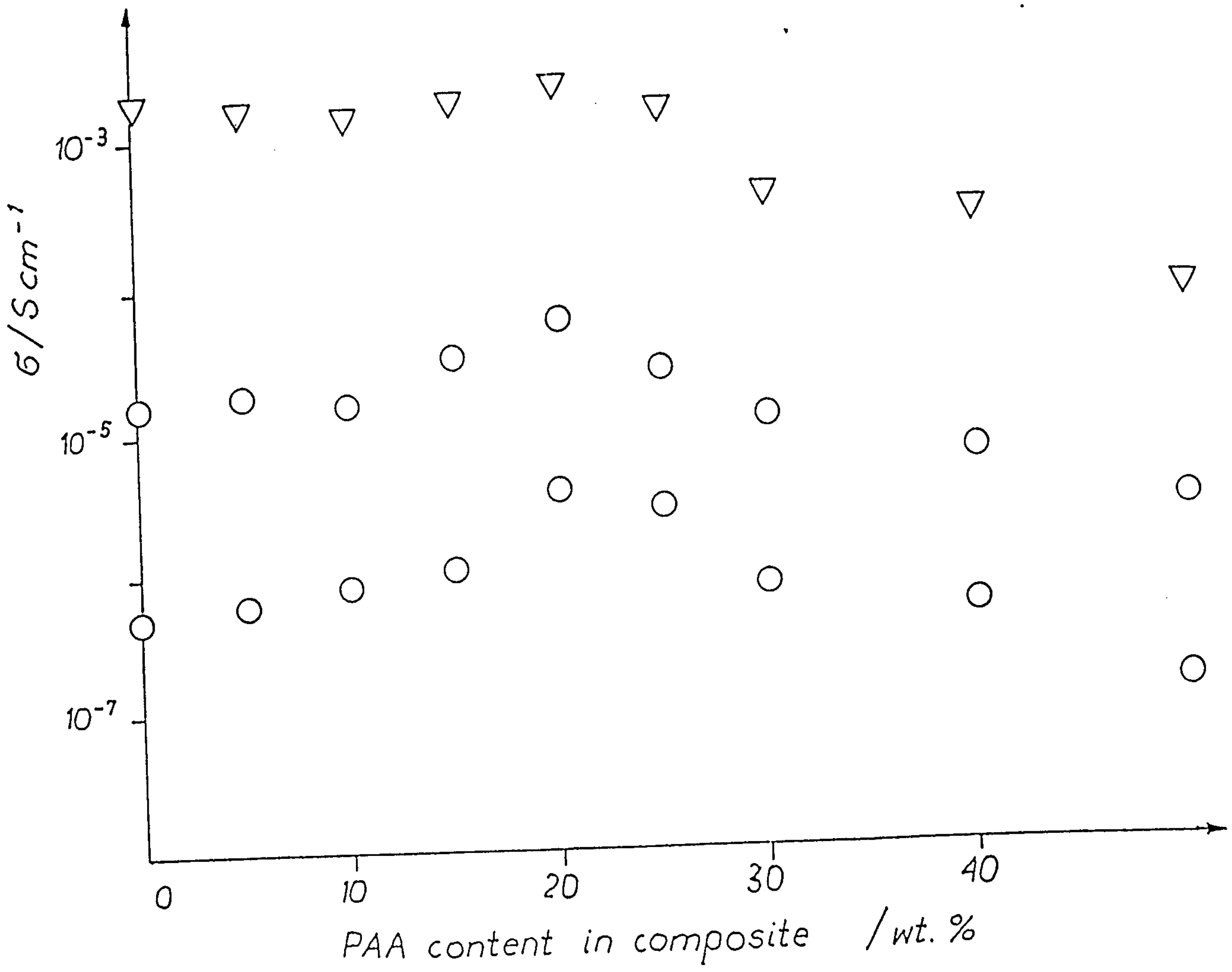


Fig. 3.

Isotherms of ionic conductivity of EOPO copolymer - PNN - $LiClO_4$ versus PAA concentration. Ether oxygen to Li mole ratio = 10.

(O) - 0 °C; (●) - 25 °C; (∇) - 100 °C.

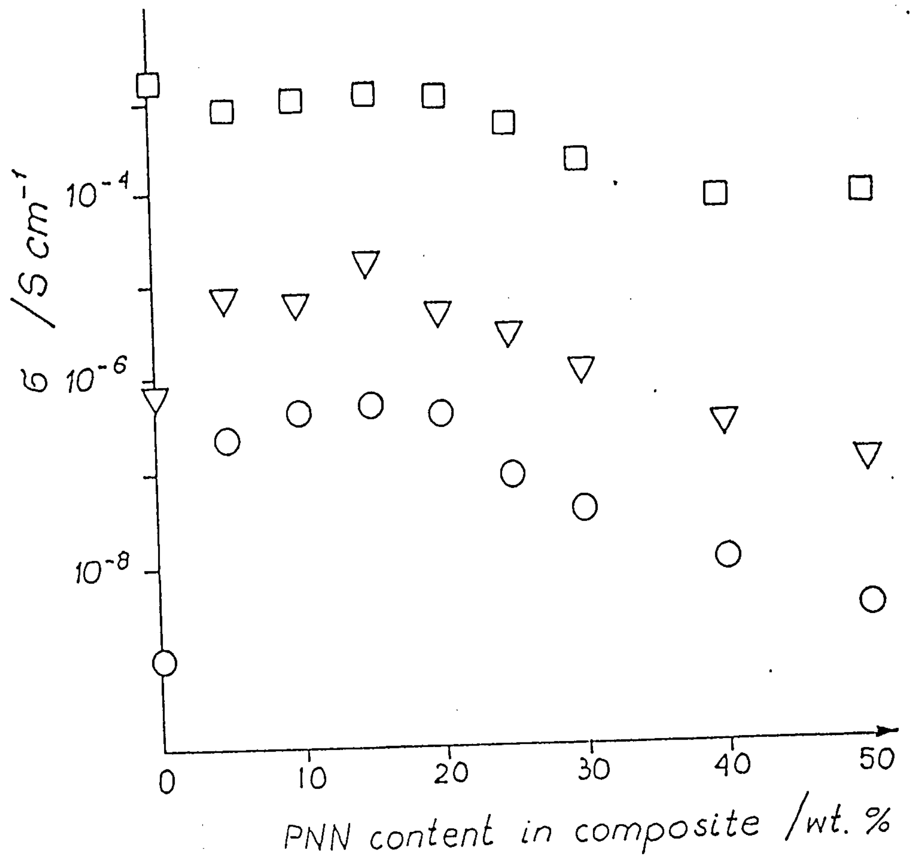


Fig. 4.

Isotherms of ionic conductivity of PEO - PNN - $LiClO_4$ versus PAA concentration. Ether oxygen to Li mole ratio = 10.

(O) - 0 °C; (∇) - 25 °C; (□) - 100 °C.

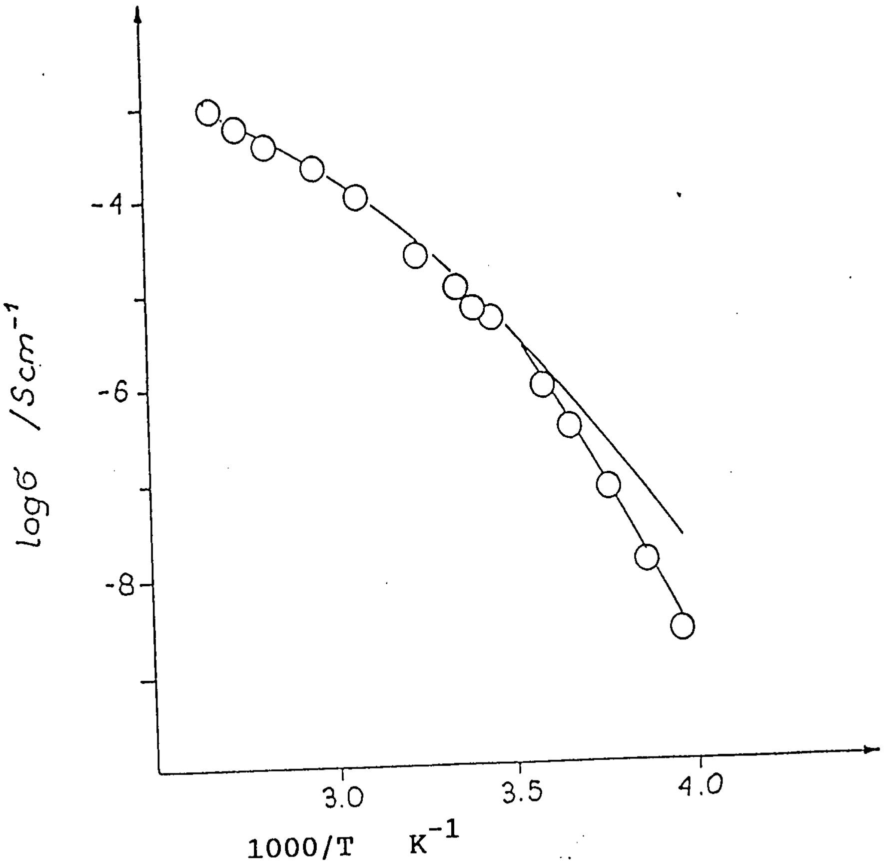


Fig. 5.

Changes in ionic conductivity versus reciprocal temperature for EOPO copolymer - PNN - LiClO$_4$ electrolyte. Ether oxygen to Li mole ratio = 10. PNN - 5 wt. %.

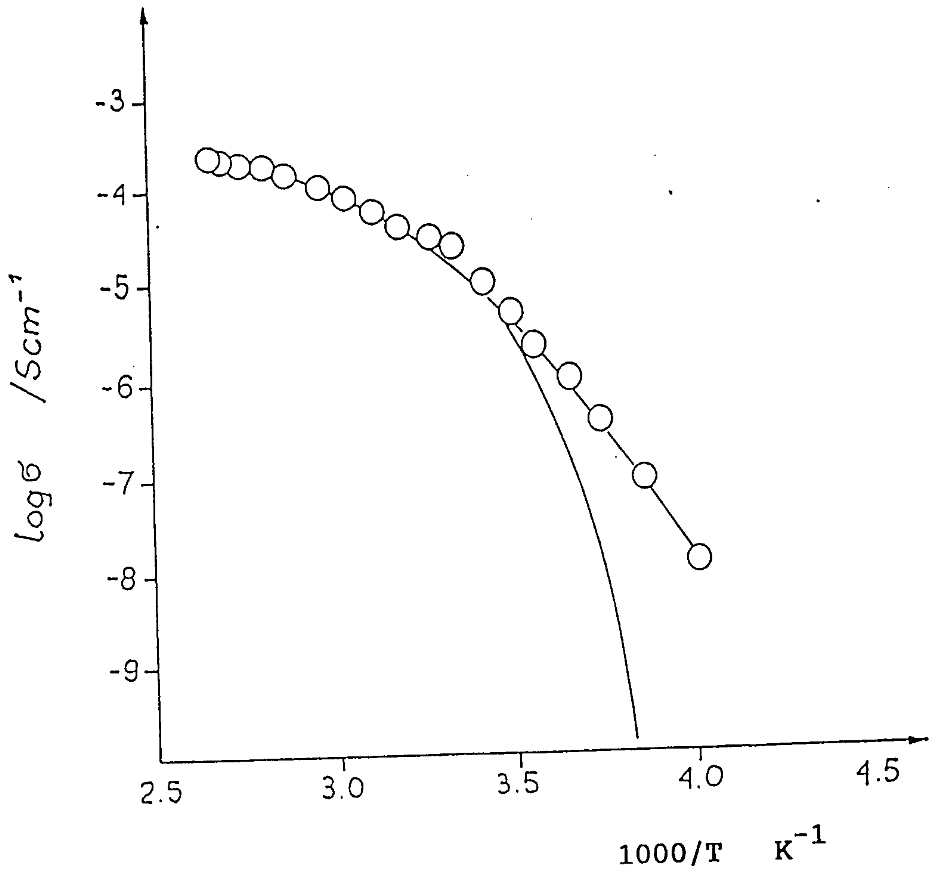


Fig. 6.

Changes in ionic conductivity versus reciprocal temperature for EO/PO copolymer - PNN - $LiClO_4$ electrolyte. Ether oxygen to Li mole ratio = 10. PNN - 20 wt. %.

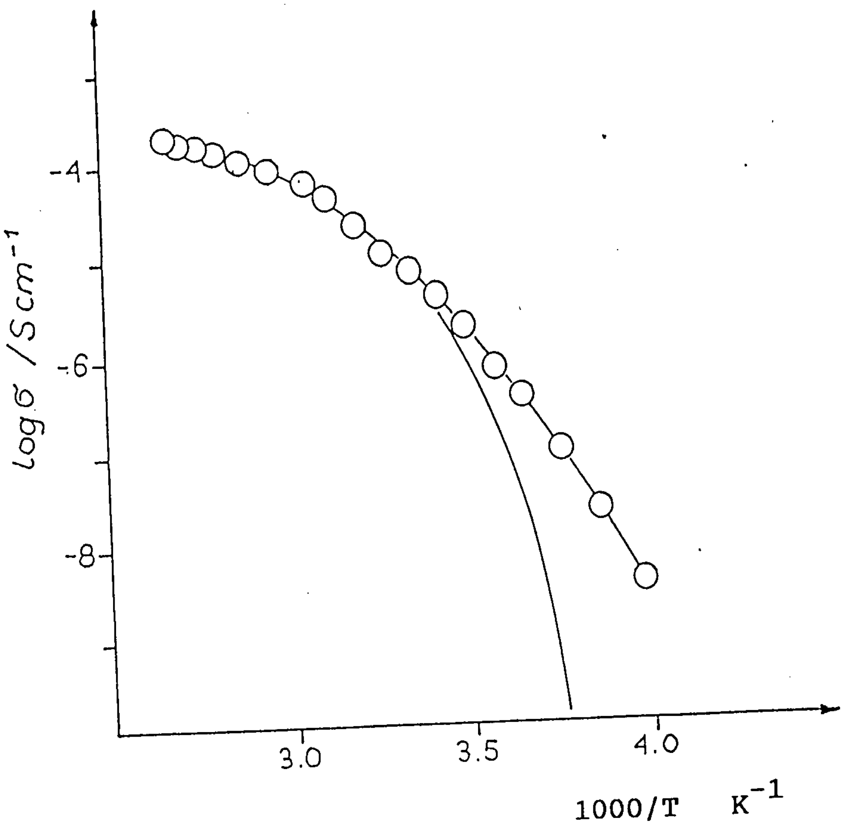


Fig. 7.

Changes in ionic conductivity versus reciprocal temperature for EO/PO copolymer - PNN - LiClO$_4$ electrolyte. Ether oxygen to Li mole ratio = 10. PNN - 30 wt. %.

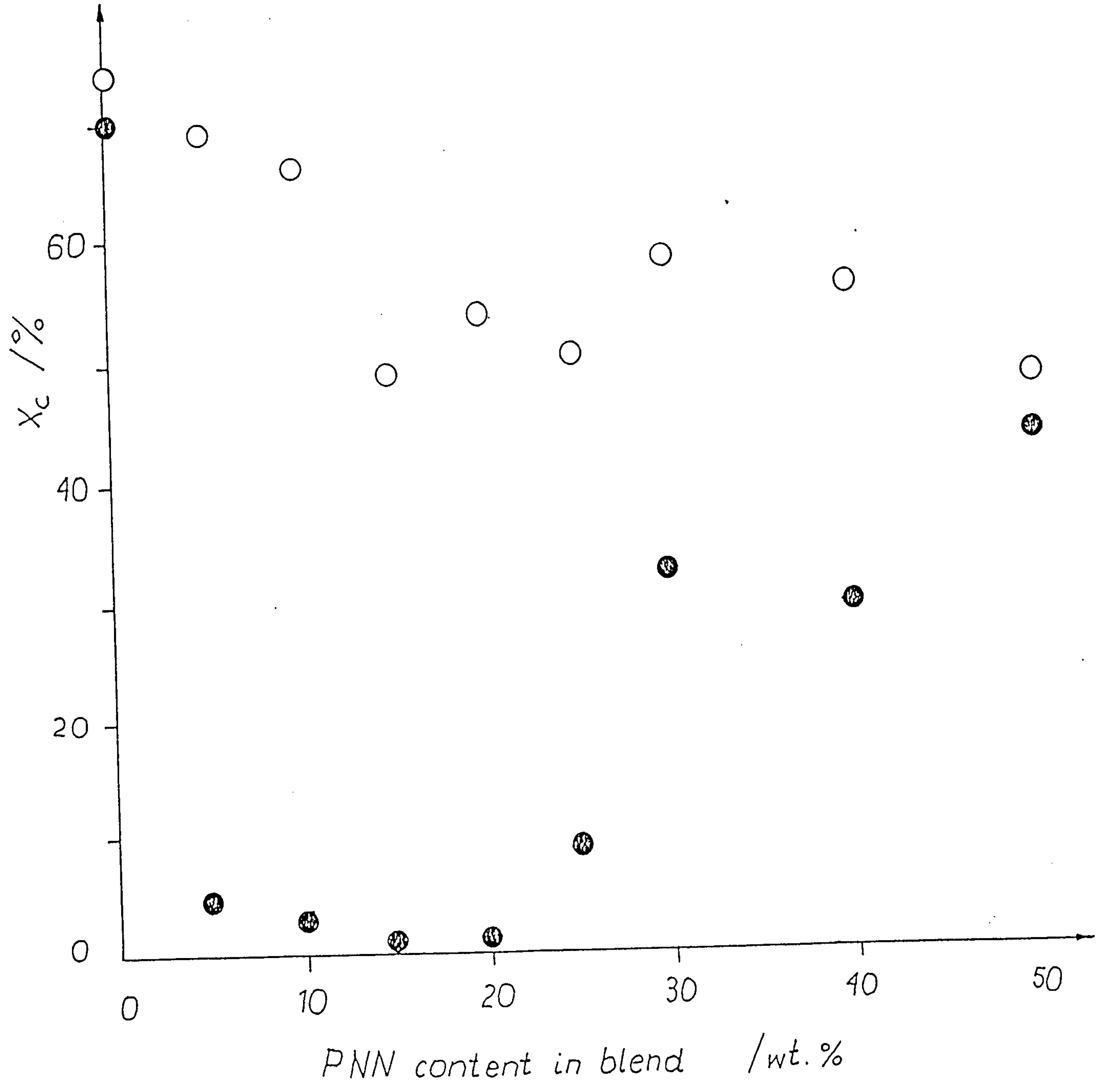


Fig. 8.
Degree of crystallinity versus PNN concentration for PEO - PNN blends

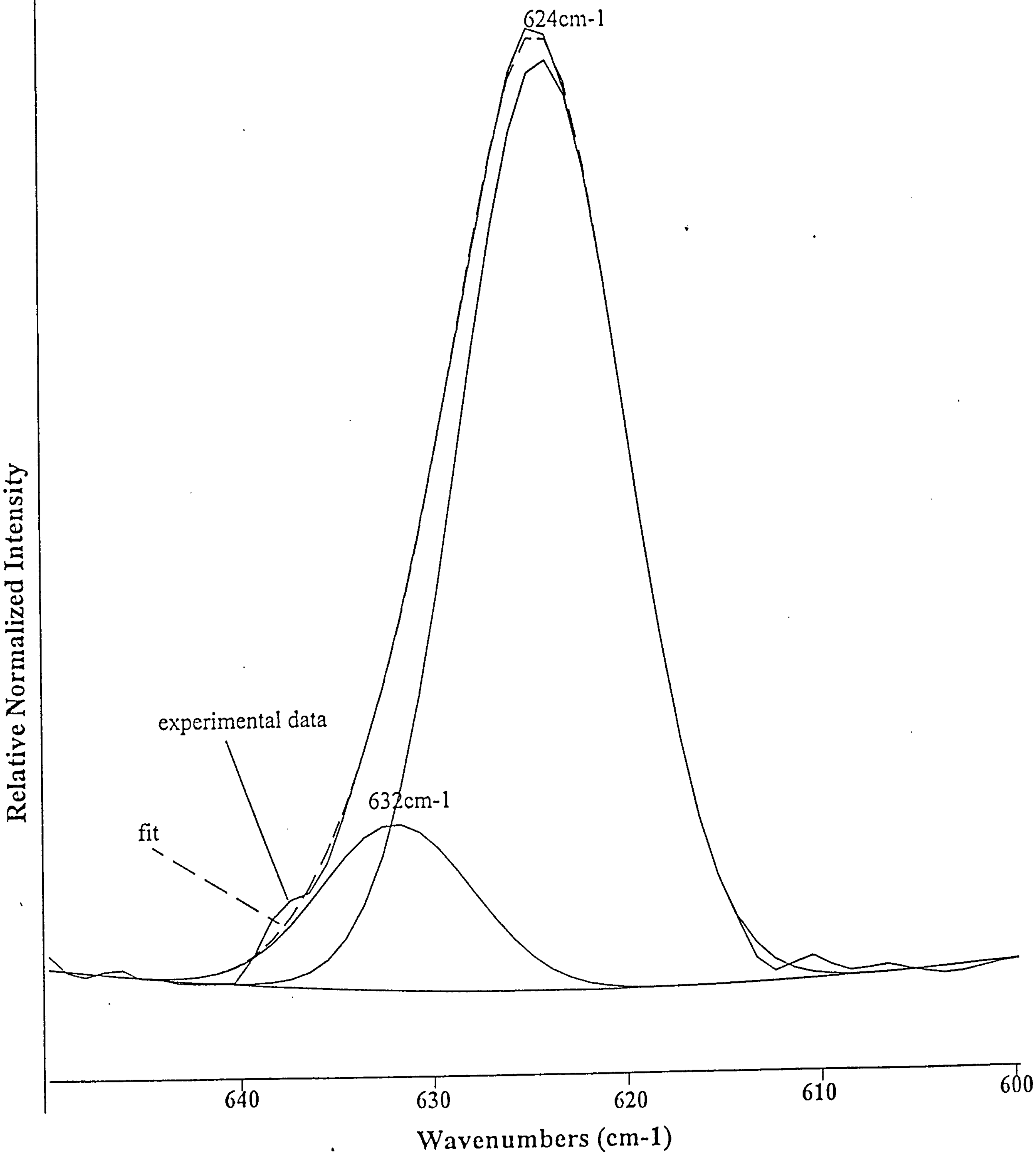


Fig. 9. Peak fitting for the ν(CLO_4^-) FT-IR region for the PEO - PNNDMAA (10 wt. %) - $LiClO_4$ sample at 25 °C.

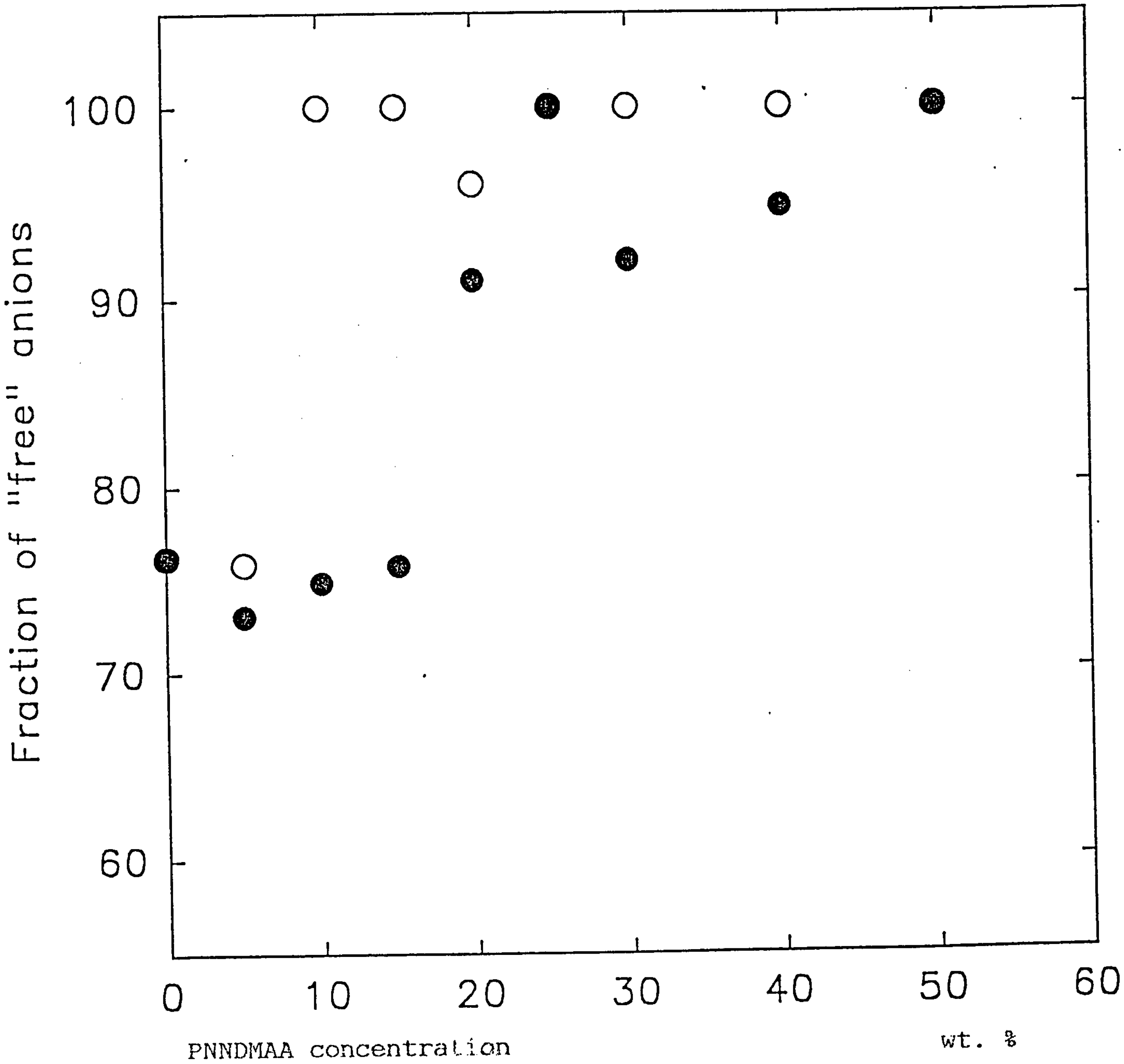


Fig. 10. Changes in the fraction of "free" ClO_4^- anions as a function of PNNDMAA concentration (wt. %) for: (○) copolymer-PNNDMAA-$LiClO_4$ composite electrolytes (●) PEO-PNNDMAA-$LiClO_4$ composite electrolytes. Data were obtained on the basis of FT-IR spectra recorded at 25 °C.

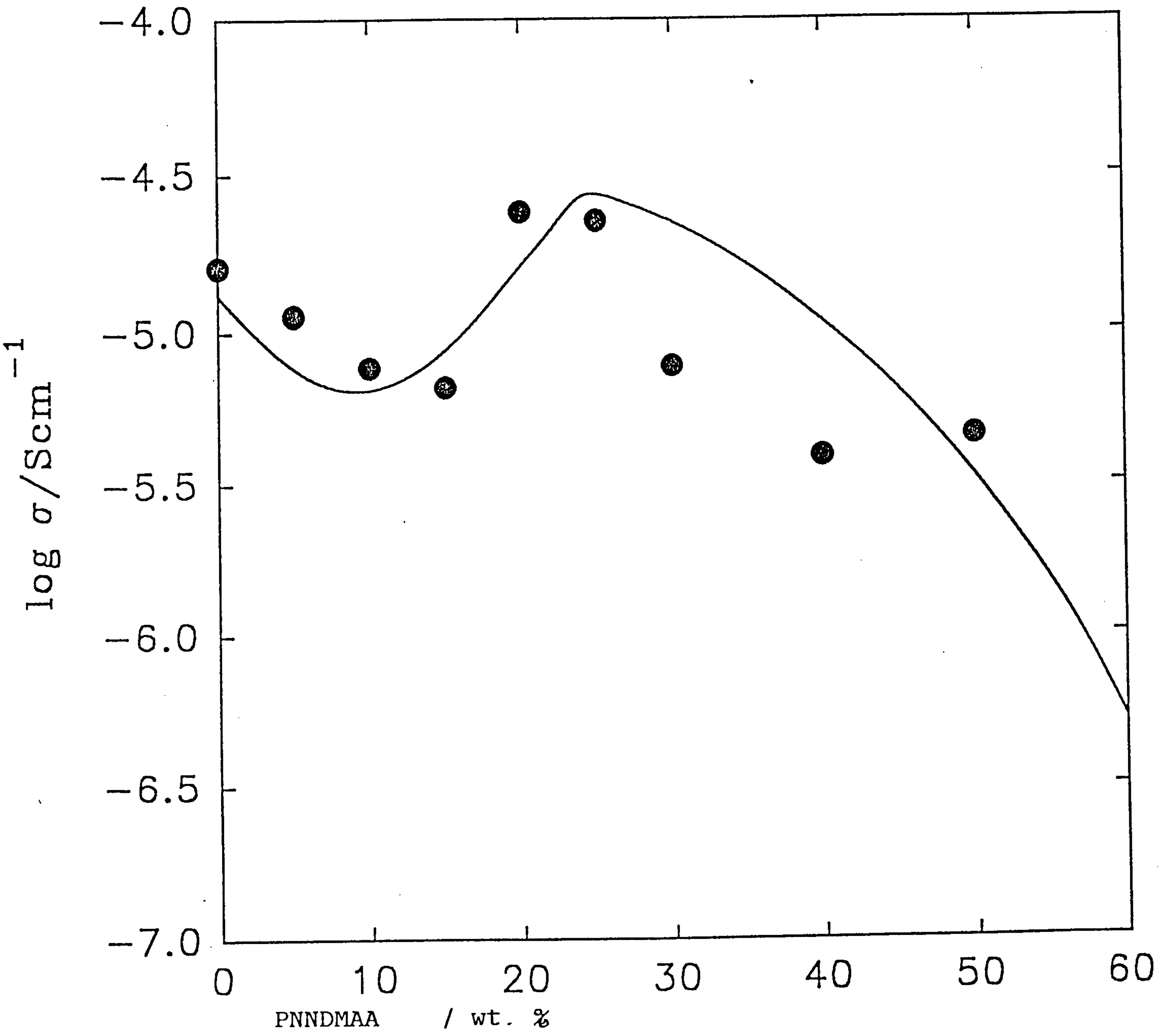


Fig. 11. Comparison of the experimentally measured isothermal conductivities (T = 25 °C) with theoretically calculated conductivities on the basis of the EMT model. Data presented for copolymer-PNNDMAA-$LiClO_4$; (●) - experimental data, solid line - theoretical.

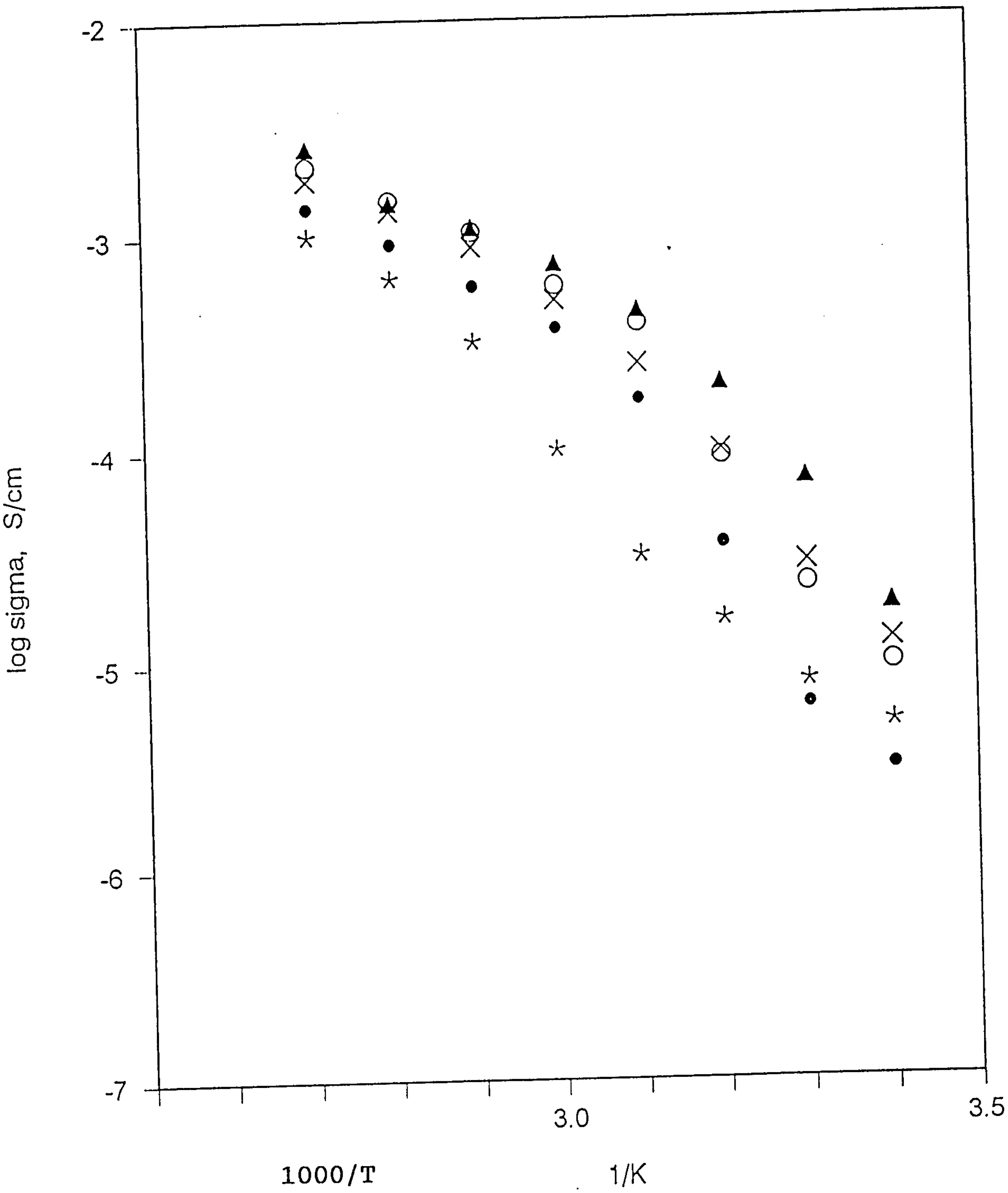


Fig. 12.

Ionic conductivity as a function of inverse temperature for PEO - organic / inorganic polymer systems:: (●) - $P(EO)_{10}LiClO_4$ - OMC (19 wt. %); (o) - $P(EO)_{10}LiClO_4$ - OMC (33 wt. %); (×) - $P(EO)_{10}LiClO_4$ - (OMC + H_2O 1:1 by mole) (33 wt. %); (▲) - $P(EO)_{10}LiN(CF_3SO_2)_2$ - MC (33 wt. %). (*) - $P(EO)_{10}CF_3SO_3Li$ - OMC 33 wt. %).

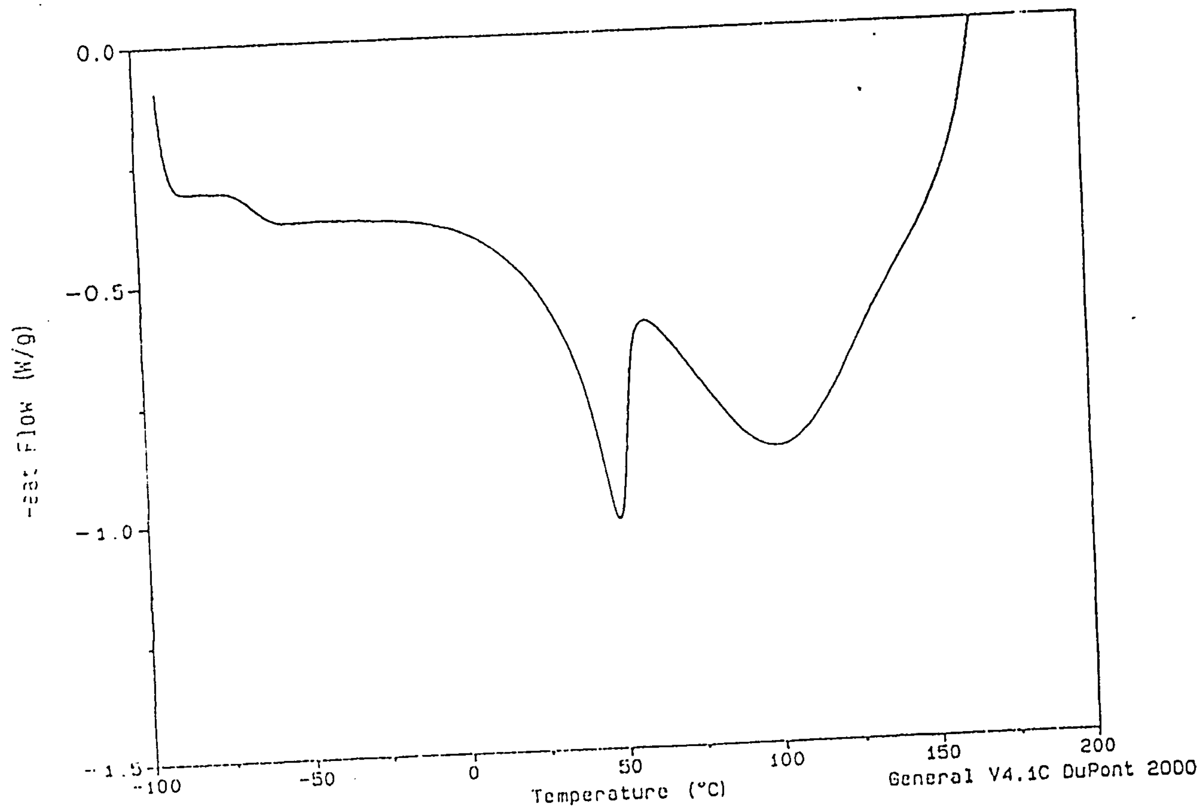


Fig. 13.

DSC curve obtained for the PEO - LiCF$_3$SO$_3$ - organometallic compound electrolyte

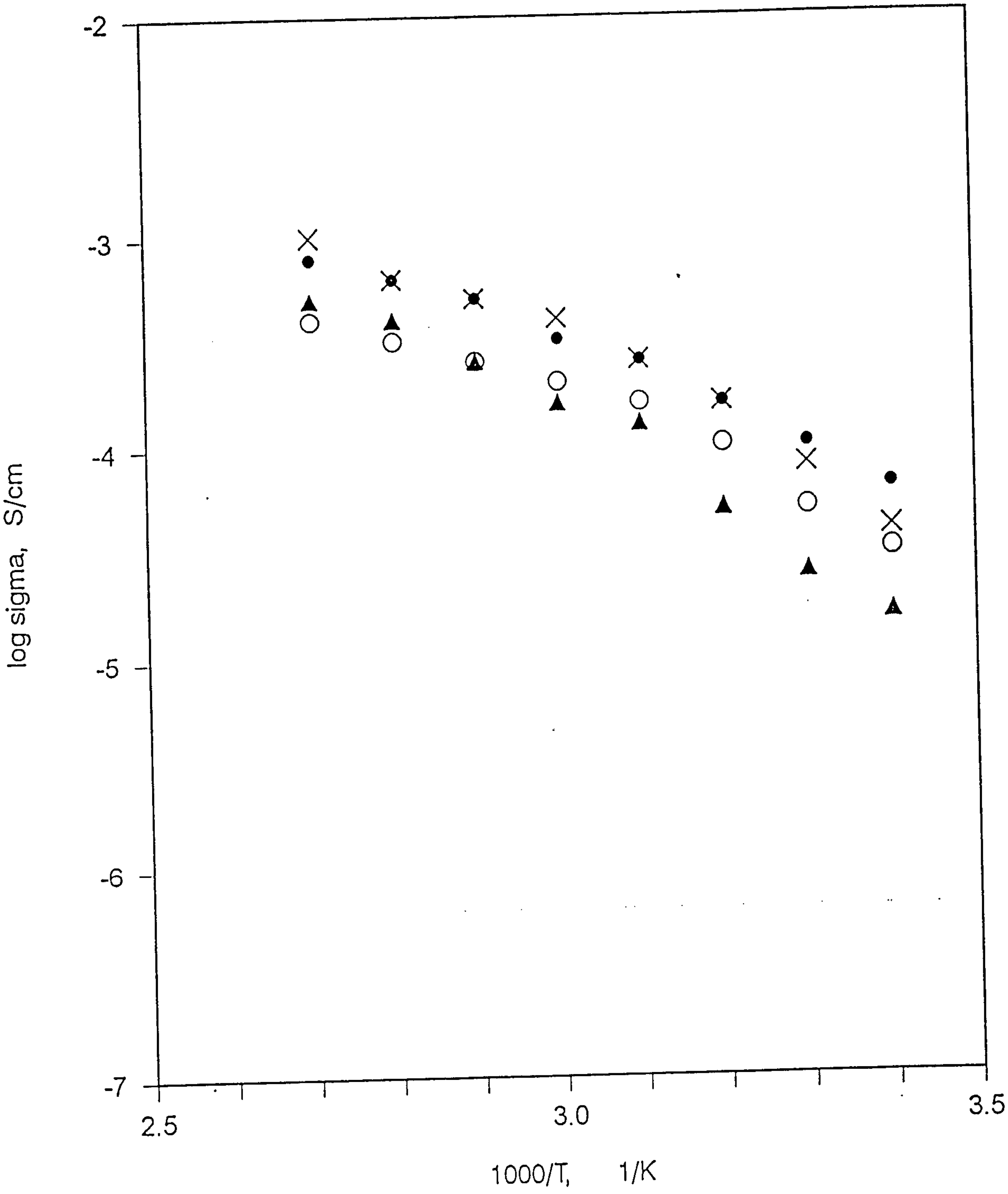


Fig. 14.

Ionic conductivity as a function of inverse temperature for plasticized networks based on triethylene glycol dimethacrylate (TMGDM) and trimethylolpropane ethoxylate triacrylate (TMGETA): (•) - PEO (5 wt. %) - PEGDME [*Mw* = 500] (75 wt. %) - CF_3SO_3Li (EO/Li = 25) - P(TEGDM 5 wt. % - *co* - TMPETA 15 wt. %); (▲) - PEO (15 wt. %) - PEGDME [*Mw* = 500] (65 wt. %) - CF_3SO_3Li (EO/Li = 15) - P(TEGDM 5 wt. % - *co* - TMPETA 15 wt. %); (×) - PEO (10 wt. %) - PEGDME [*Mw* = 500] (60 wt. %) - CF_3SO_3Li (EO/Li = 10) - PNNDMAA (10 wt. %) - PTMPETA (20 wt. %); (o) - PMMA (15 wt. %) - PEGDME [*Mw* = 500] (65 wt. %) - CF_3SO_3Li (EO/Li = 25) - PTEGDM (20 wt. %).

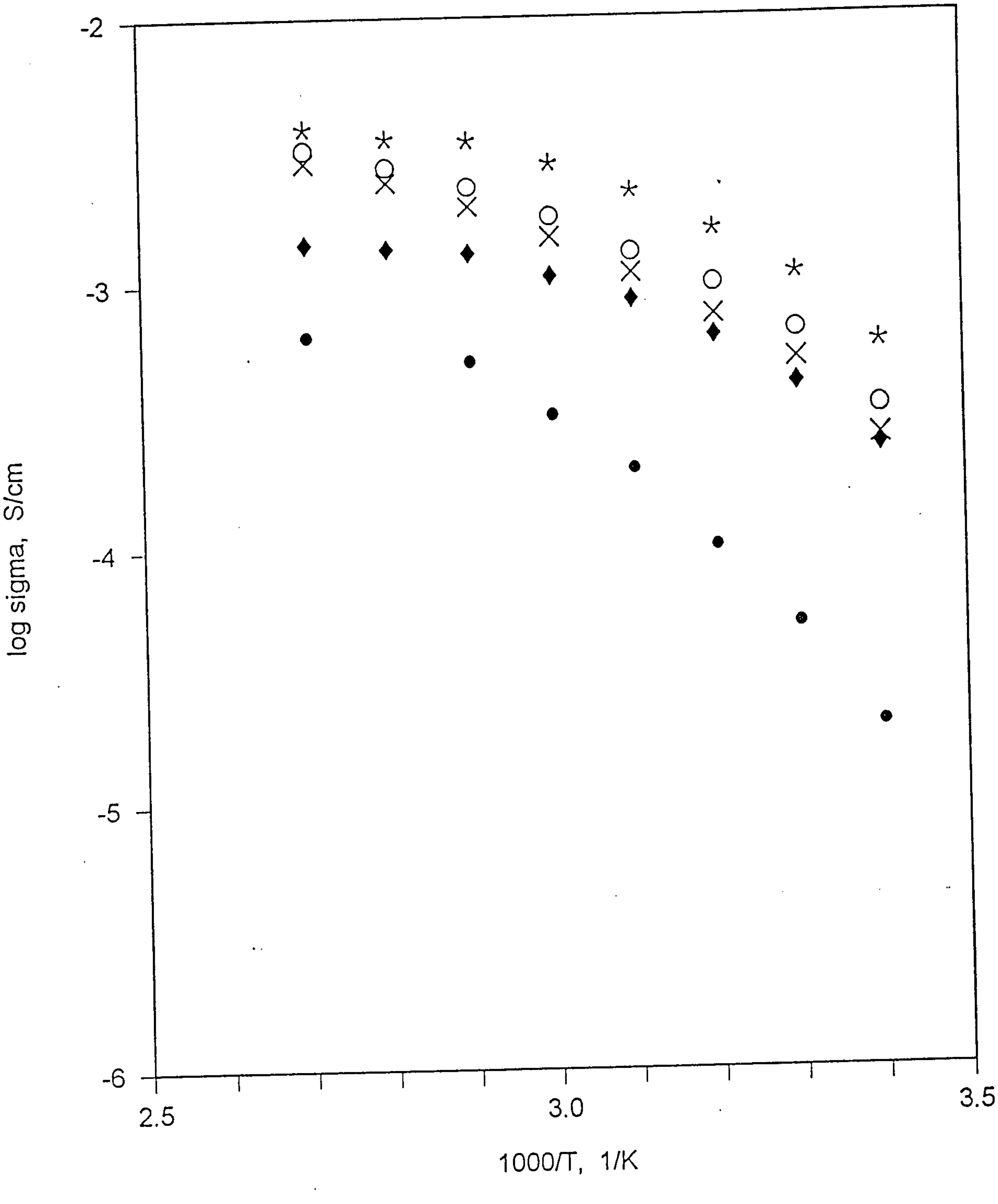


Fig. 15.

Ionic conductivity as a function of inverse temperature for plasticized networks based on the maleic anhydride and styrene copolymer: (◆) - PEGDME [*Mw* 420] (57 wt. %) - $LiClO_4$ (5 wt. %); (o) - PEGDME [*Mw* 420] (51 wt. %) - $LiClO_4$ (15 wt. %); (x) - PEGDME [*Mw* 420] (34 wt. %) - PC (34 wt. %) - $LiClO_4$ (5 wt. %); (✻) - PEGDME [*Mw* 420] (30 wt. %) - PC (30 wt. %) - $LiClO_4$ (15 wt. %); (•) - PEGDME [*Mw* 420] (35 wt. %) - $LiClO_4$ (7 wt. %).

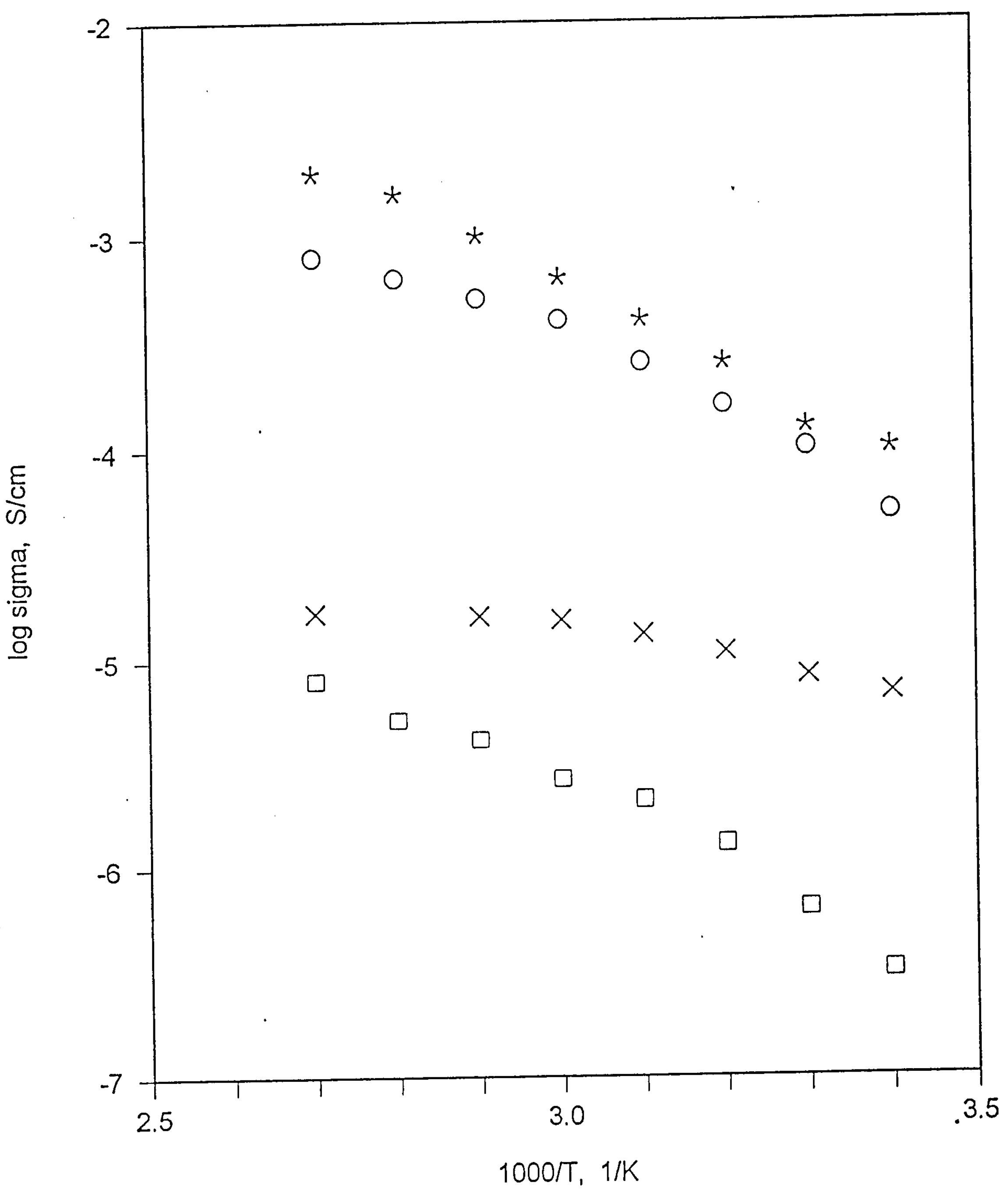


Fig. 16.

Ionic conductivity as a function of inverse temperature for plasticized networks based on the maleic anhydride and styrene copolymer: (✱) - PEGDME [*Mw* 420] (65 wt. %) - $LiClO_4$ (5 wt. %) - $BF_3 \times Et_2O$ (1:1); (o) - PEGDME [*Mw* 420] (68 wt. %) - $BF_3 \times Et_2O$ (1:1); (×) - PEGDME [*Mw* 420] (30 wt. %) - PC (30 wt. %); (□) - PEGDME [*Mw* 420] (45 wt. %).

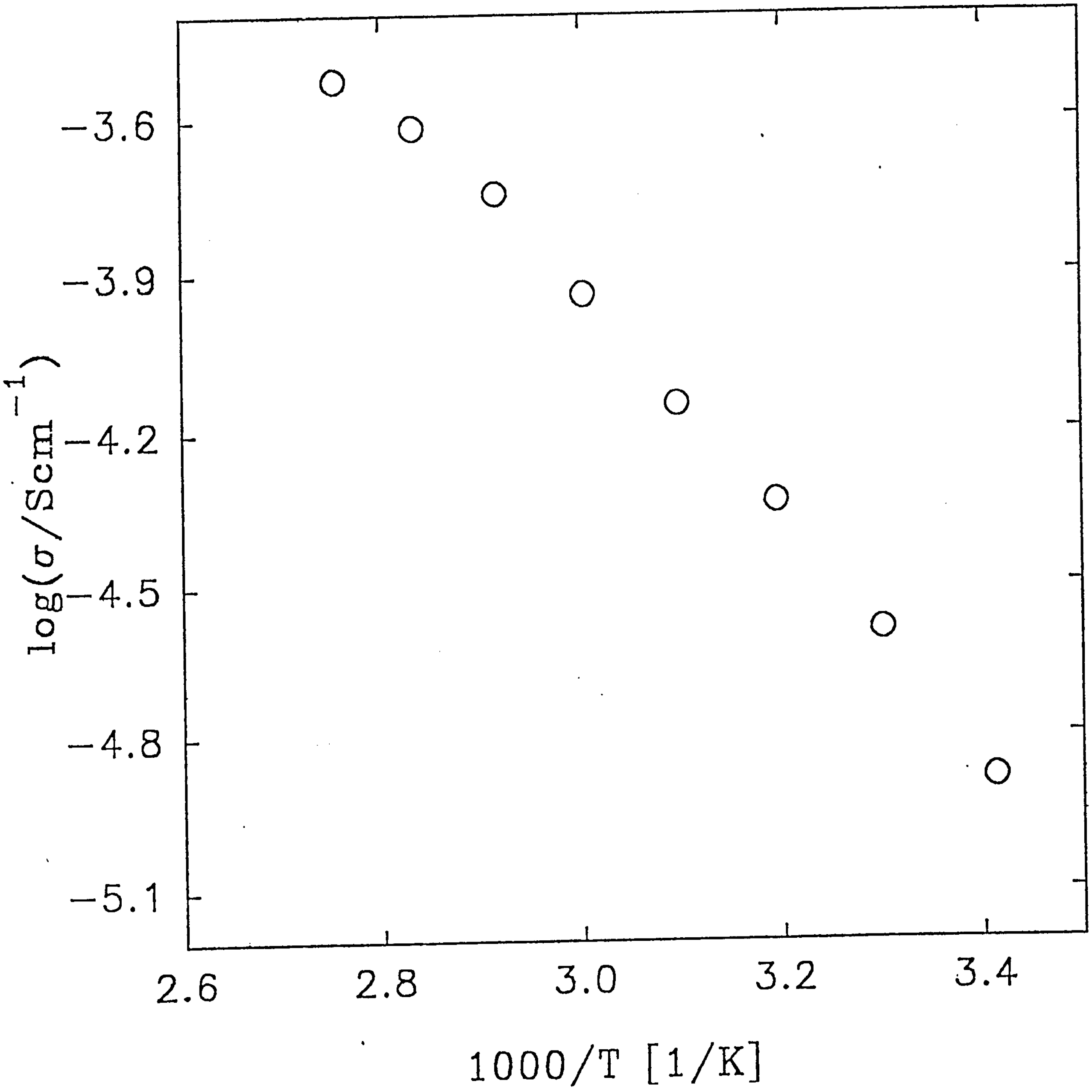


Fig. 17. Ionic conductivity as a function of inverse temperature for networks plasticized with DMSO and based on the maleic anhydride and styrene copolymer.

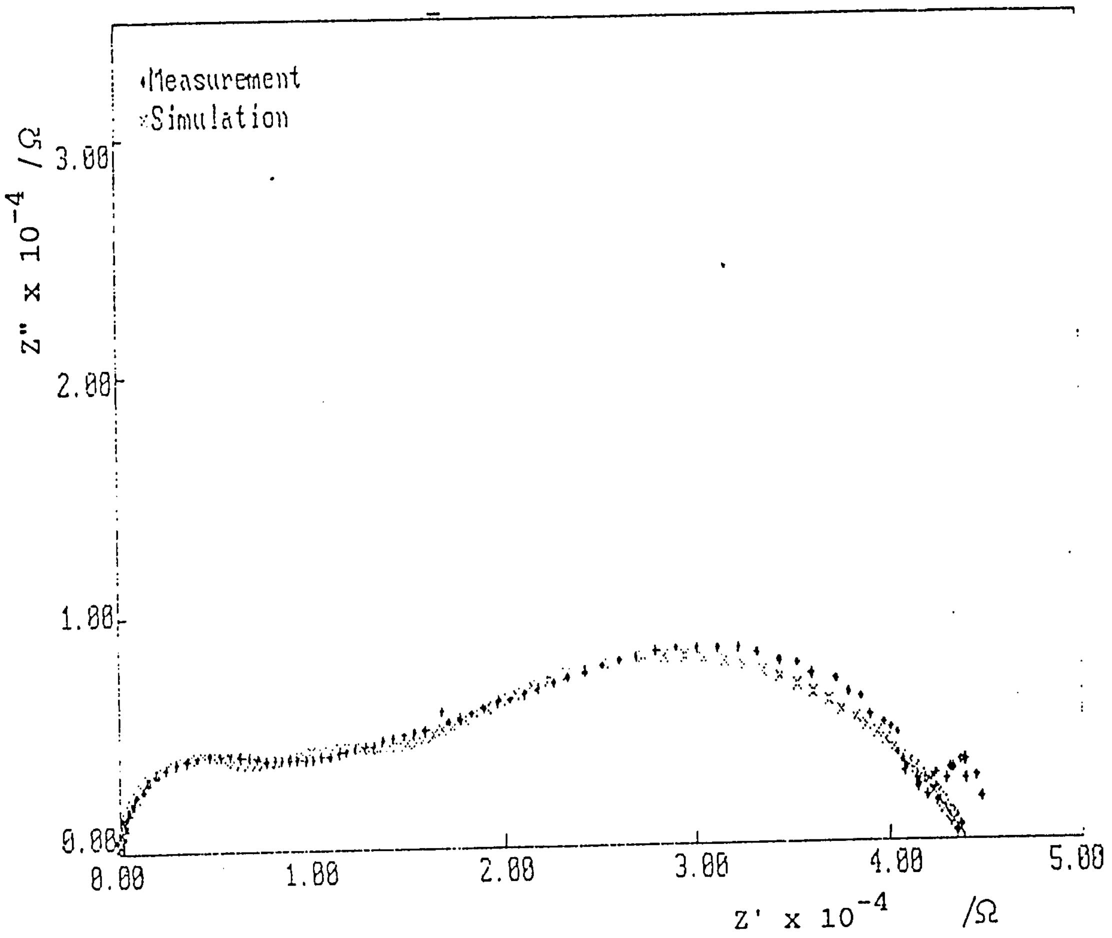


Fig. 18. Impedance graph for sample 2 after 1 h.

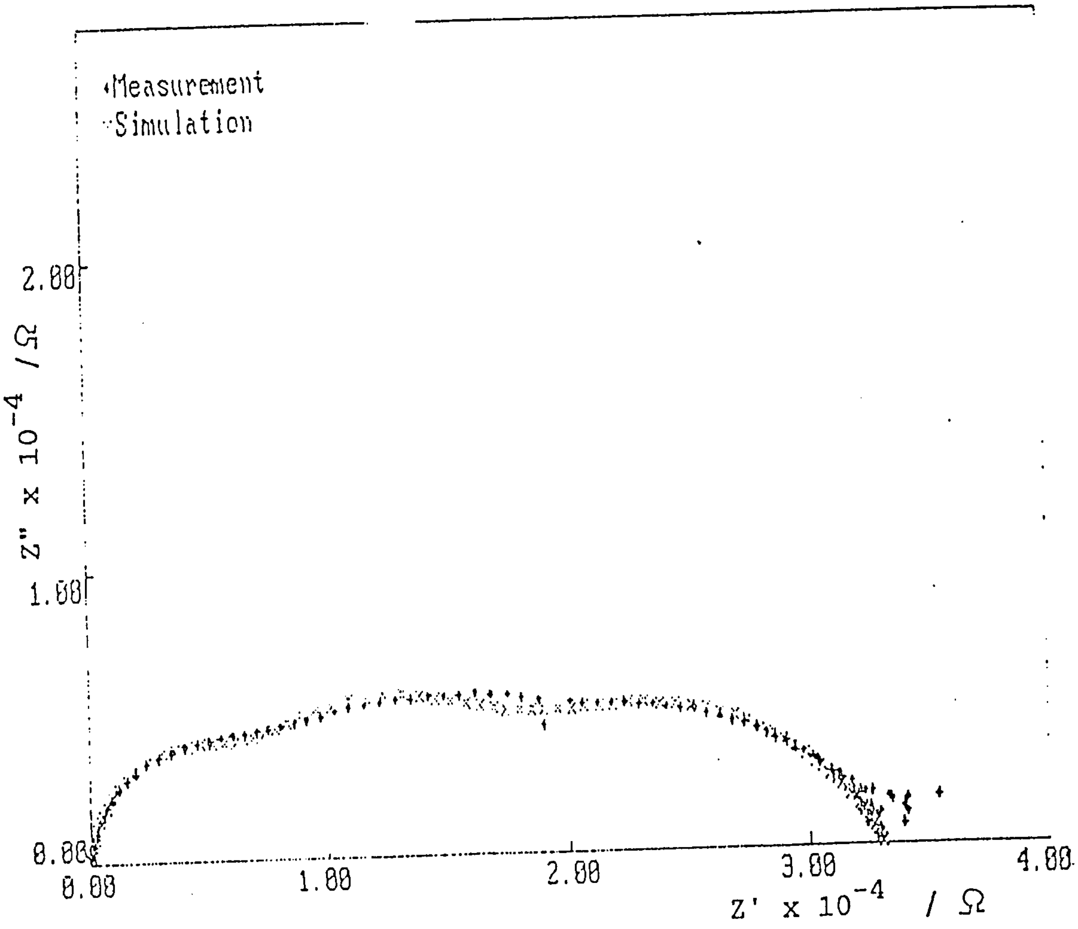


Fig. 19. Impedance graph forsample 2 after 200h.

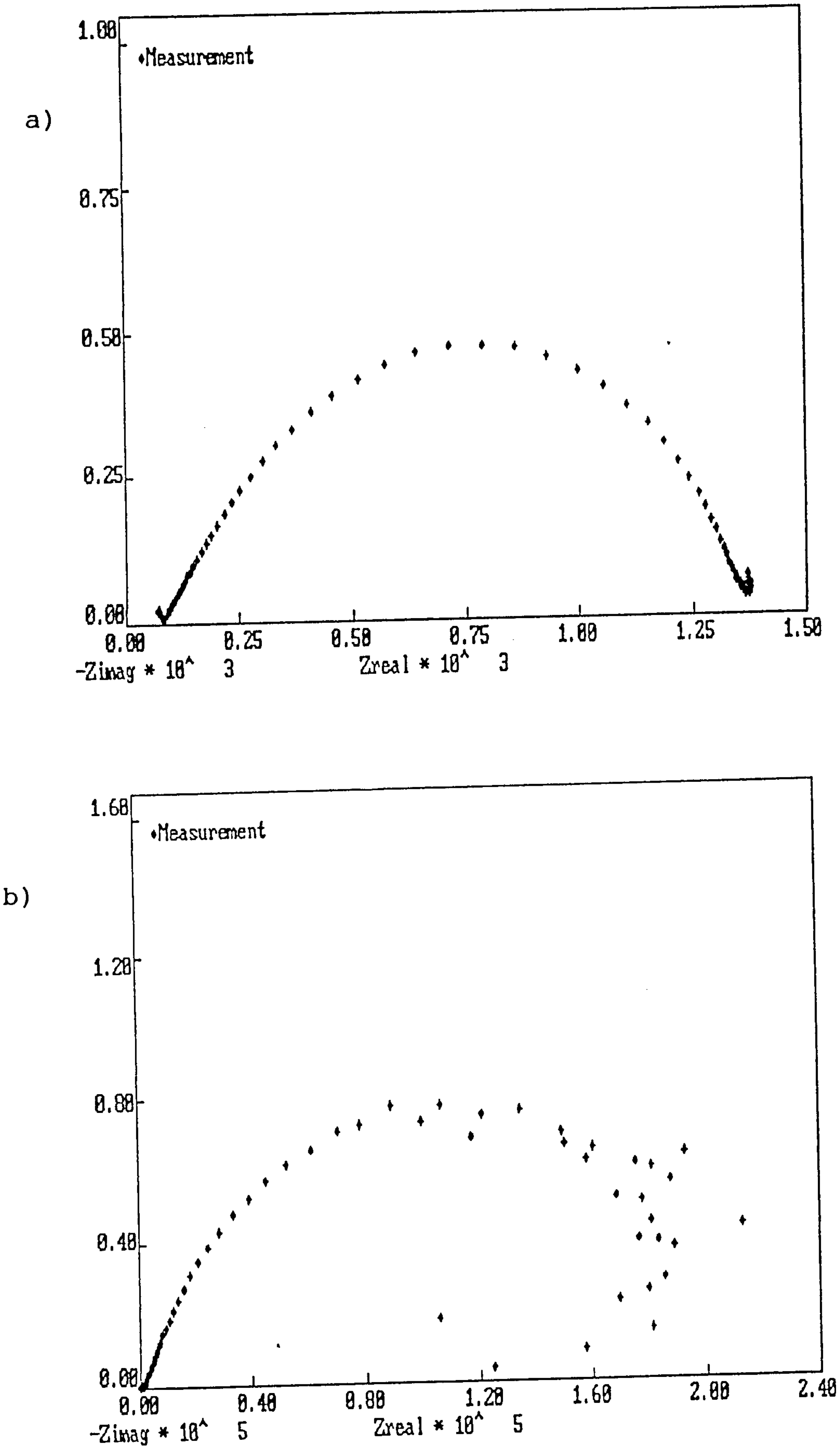


Fig. 20. Impedance graphs for sample 3 after:a) 1 h, b) 216 h.

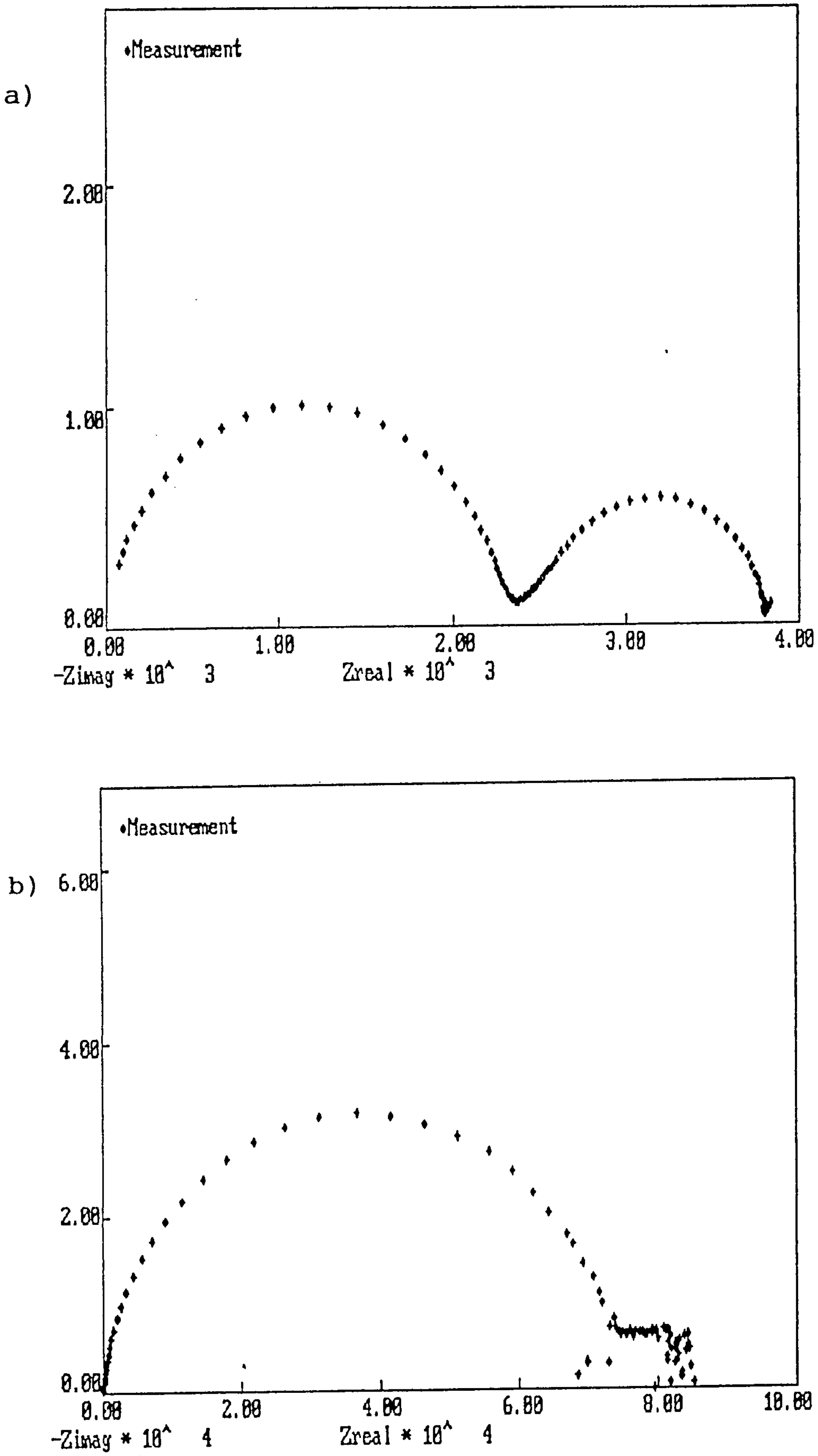


Fig. 21. Impedance graphs for sample 4 after : a) 1h, b) 240h.

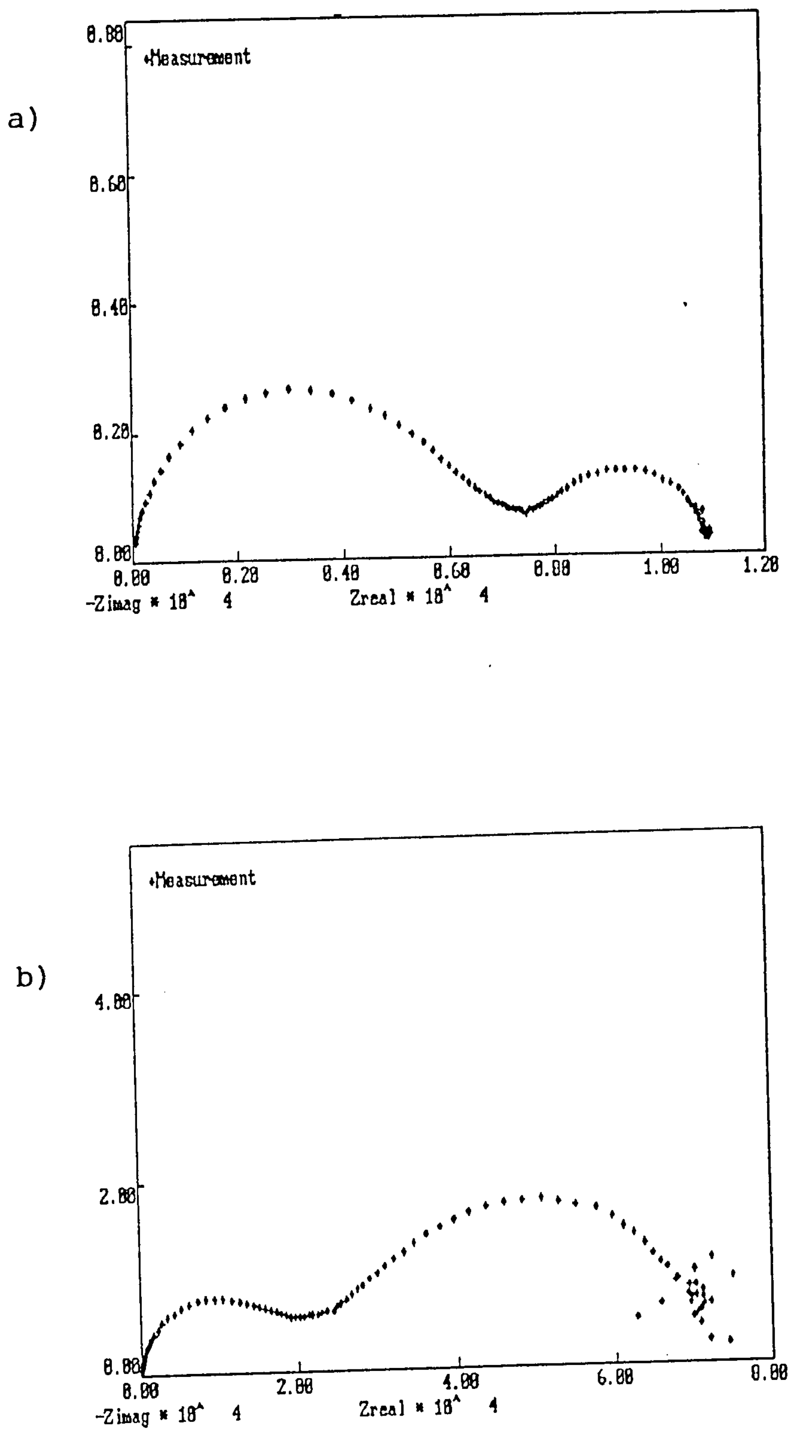


Fig. 22. Impedance graphs for sample 7 after a) 7h, b) 288h

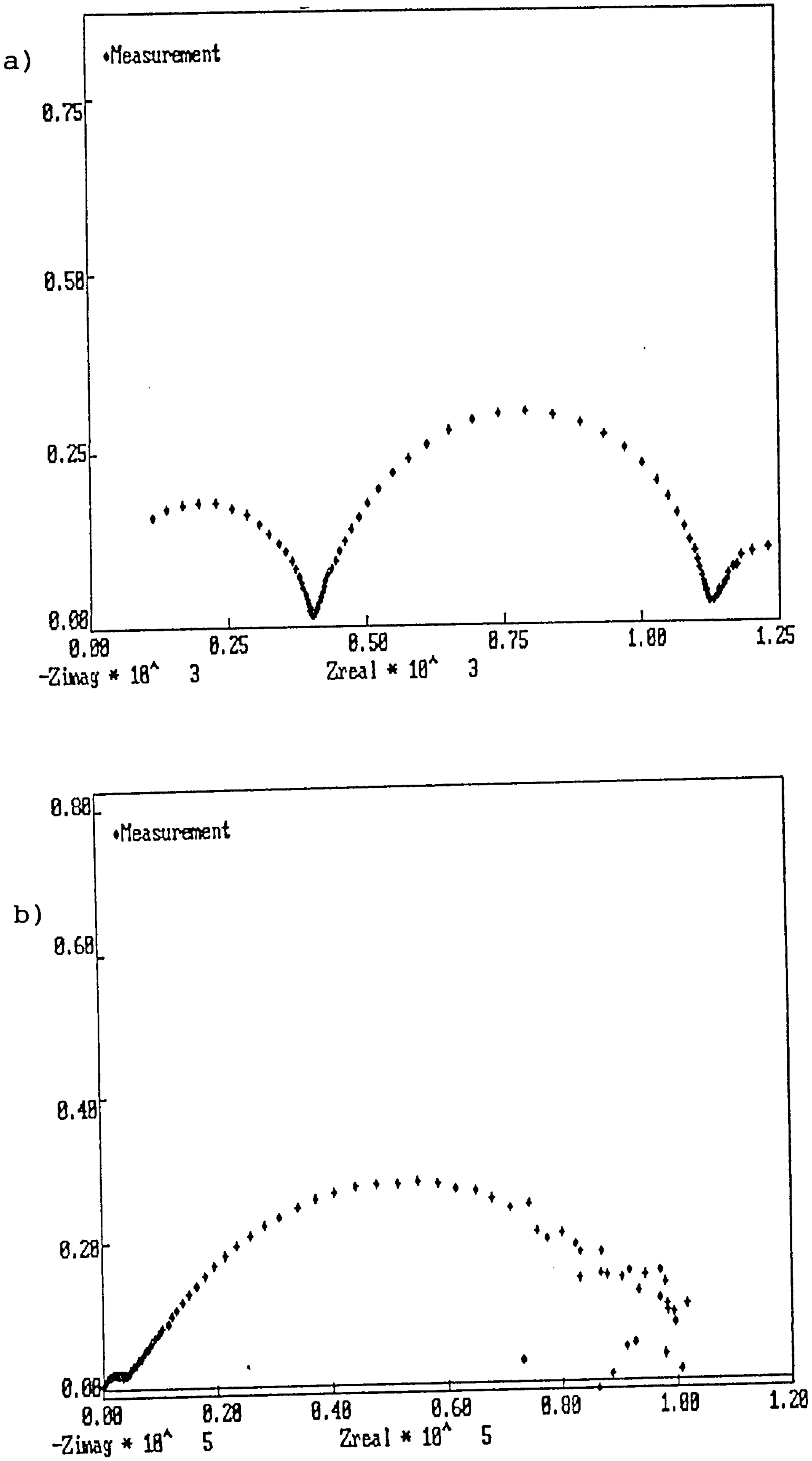


Fig. 23. Impedance graphs for sample 8 after a) 1h, b) 280h.

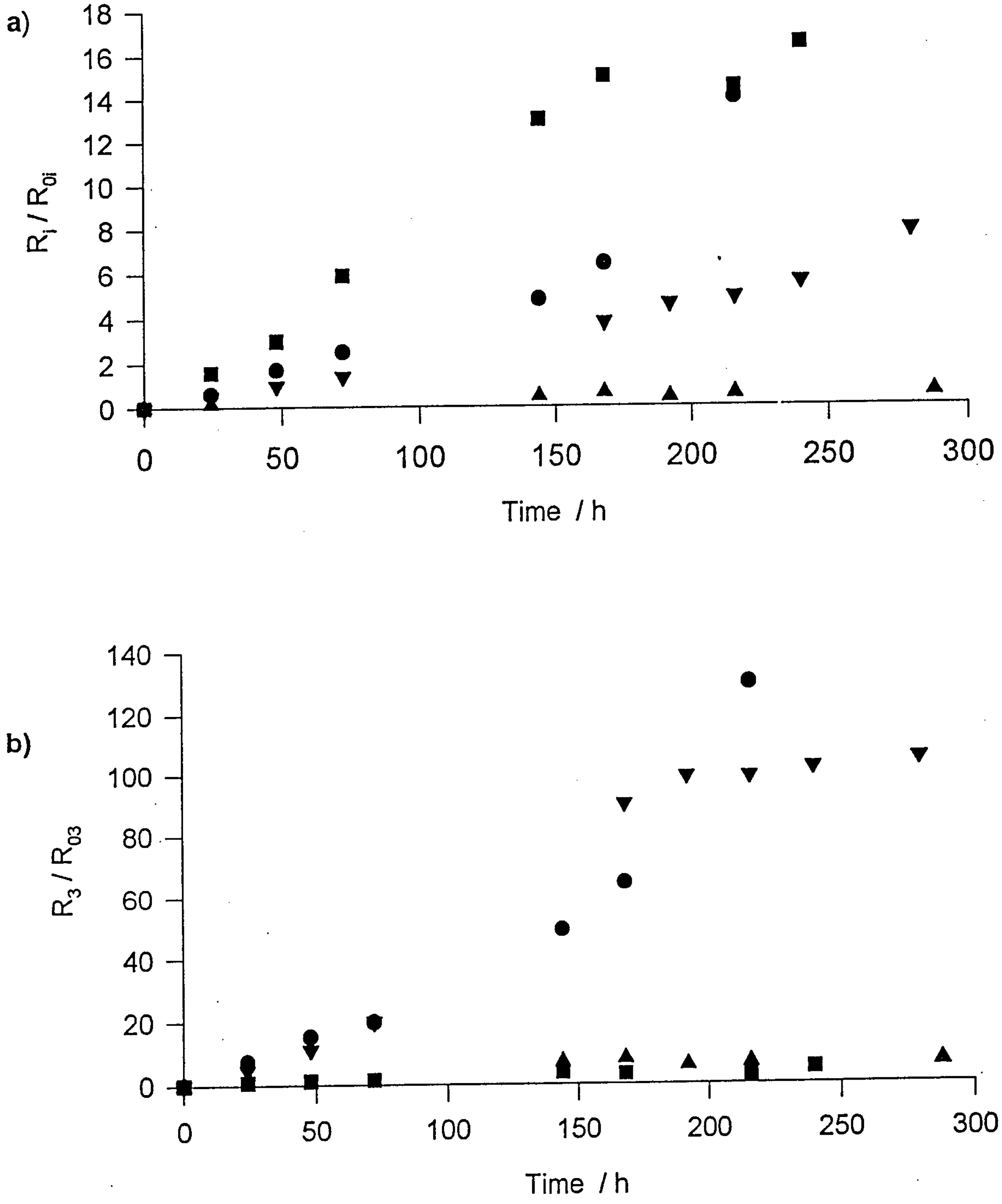


Fig. 24. Dependence of R_i / R_{0i} (**a**) and R_3 / R_{03} (**b**) on time.

(●) - sample 3; (■) - sample 4; (▲) - sample 7; (▼) - sample 8

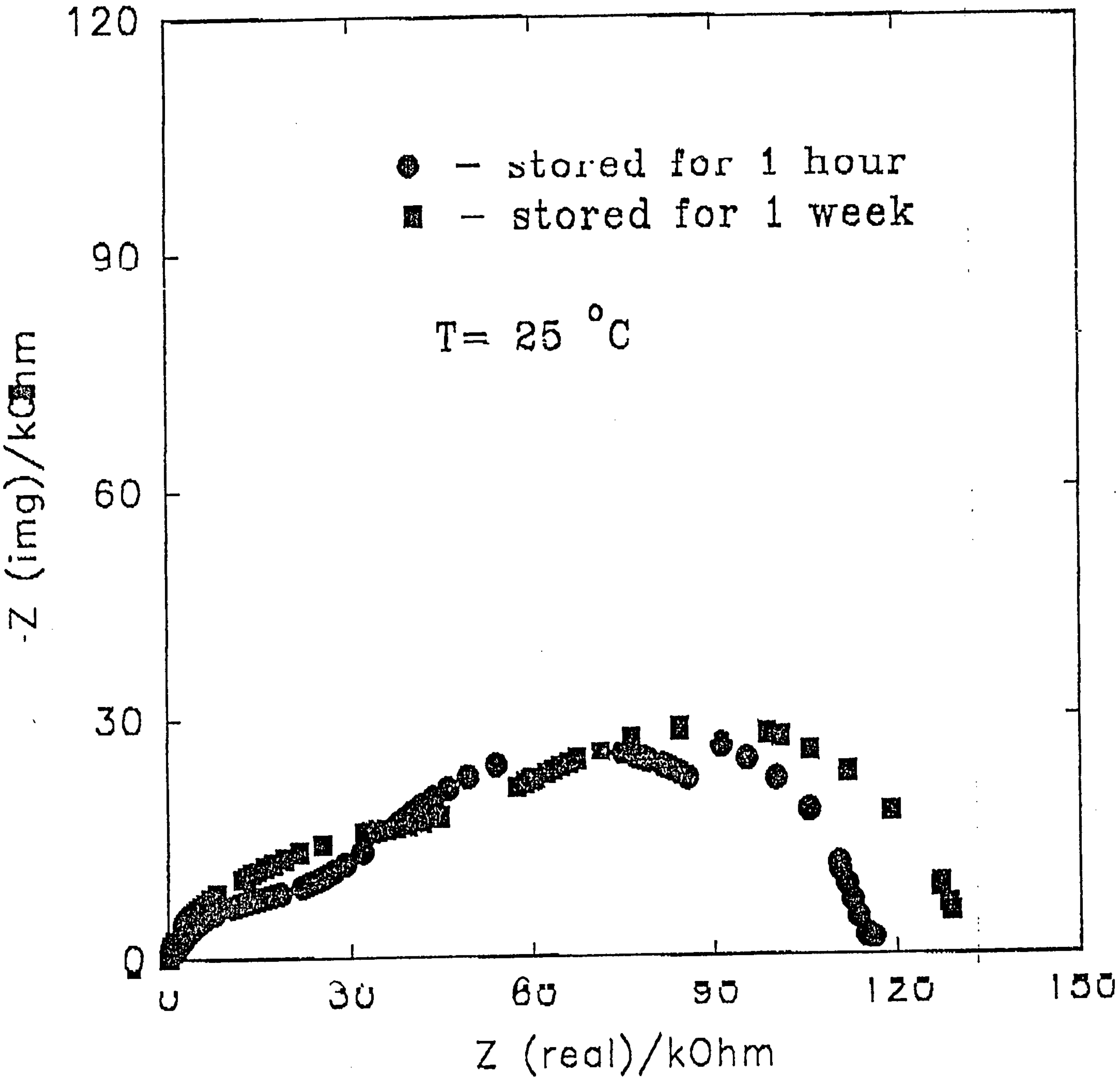


Fig. 25. Impedance spectra obtained for a Li-electrolyte-Li cell. Electrolyte: PEO-PNNDMAA(15 wt. %)-$LiClO_4$

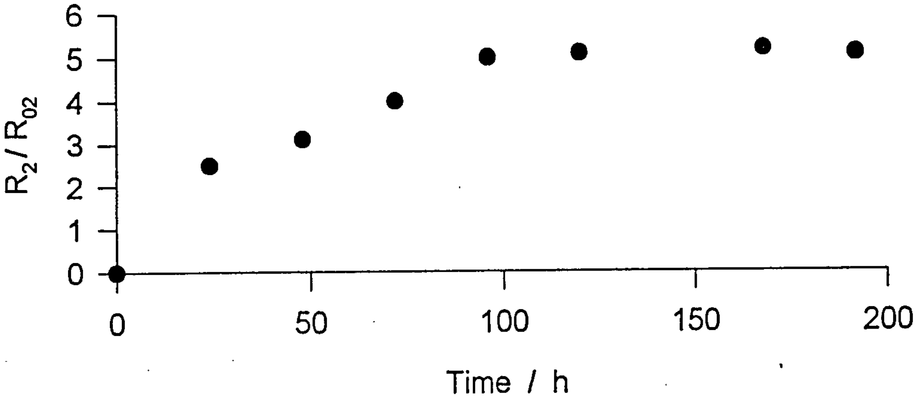


Fig. 26. Dependence of $R_{2(LFA)} / R_{o2(LFA)}$ on time for sample 2

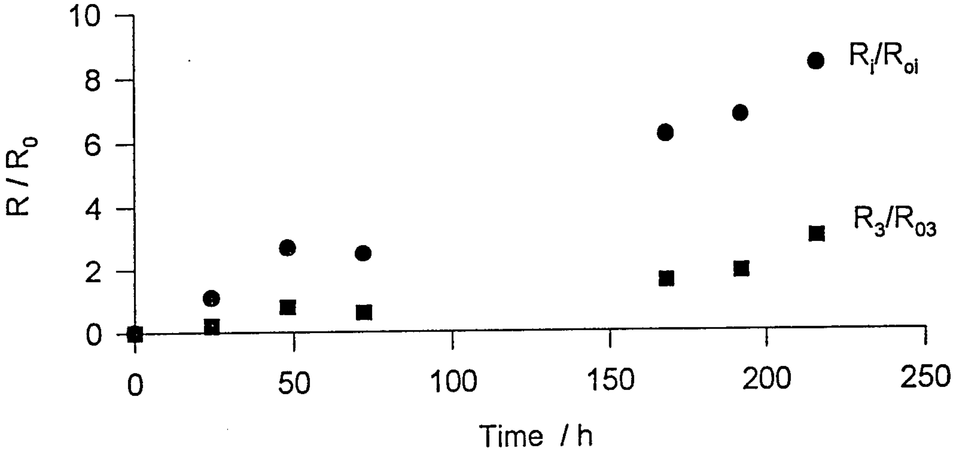


Fig. 27. Dependence of R_i / R_{0i} and R_3 / R_{03} on time for sample 5

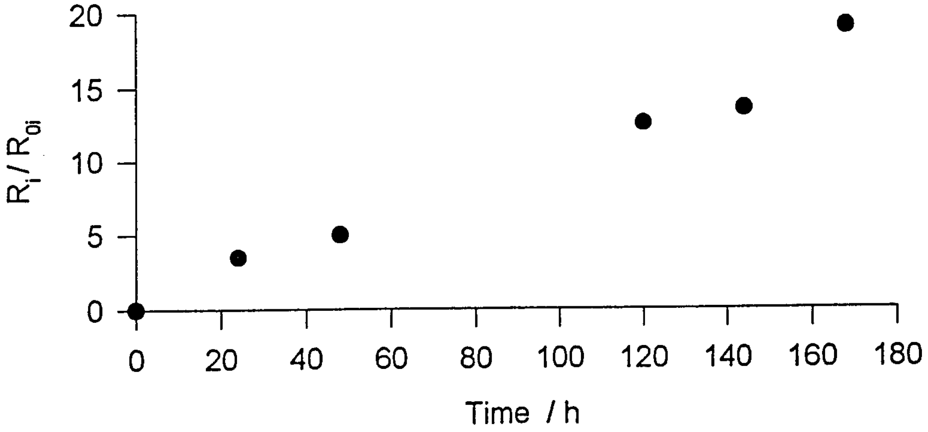


Fig. 28. Dependence of $R_{2(LFA)} / R_{02(LFA)}$ on time for sample 6

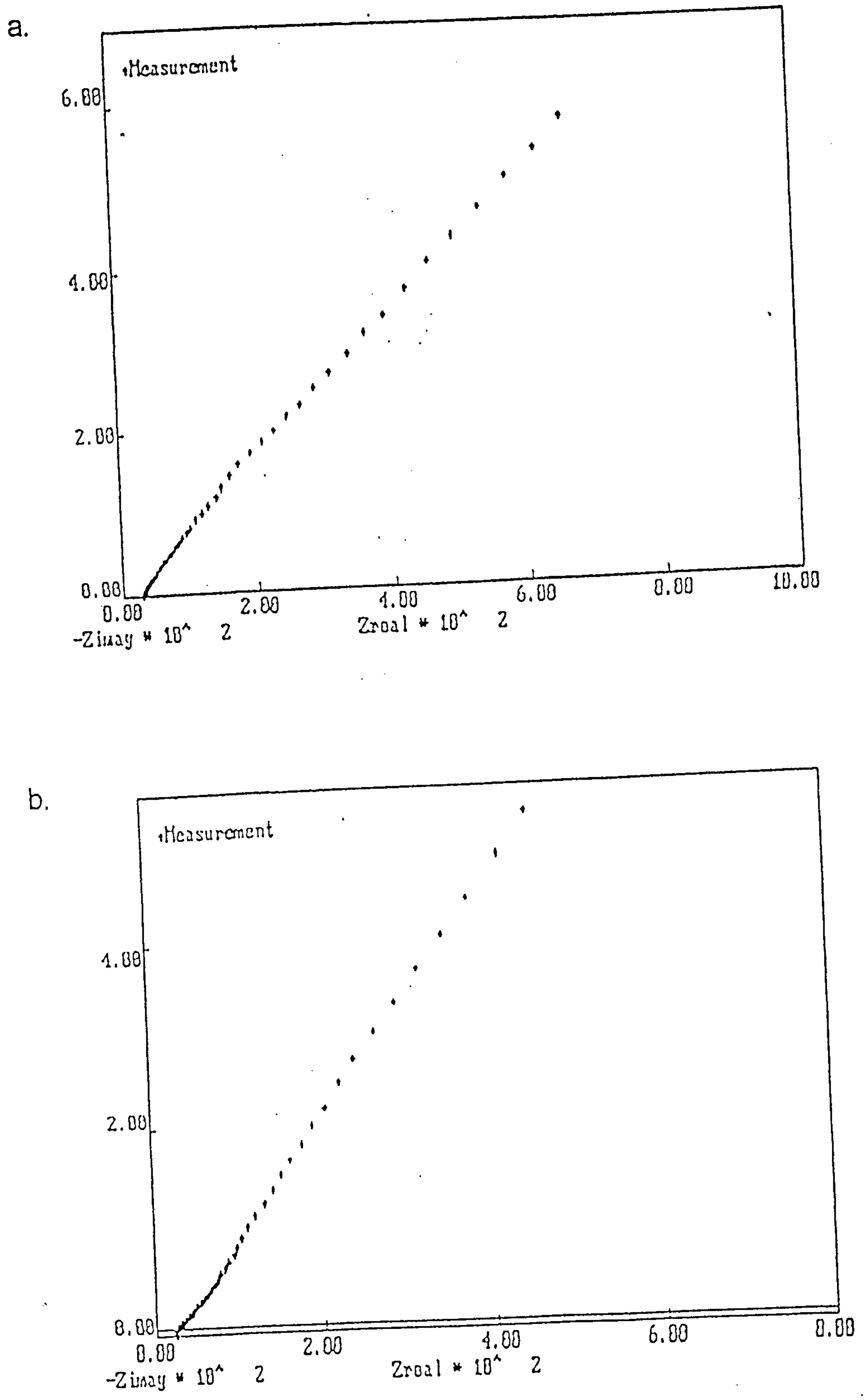


Fig. 29.

Impedance spectra for cells with graphite composite electrodes and electrolytes based on PEO - $LiCF_3SO_3$ - organometallic compound polymer. (measured at 70 °C after: a. - 5 h; b. - 100 h)

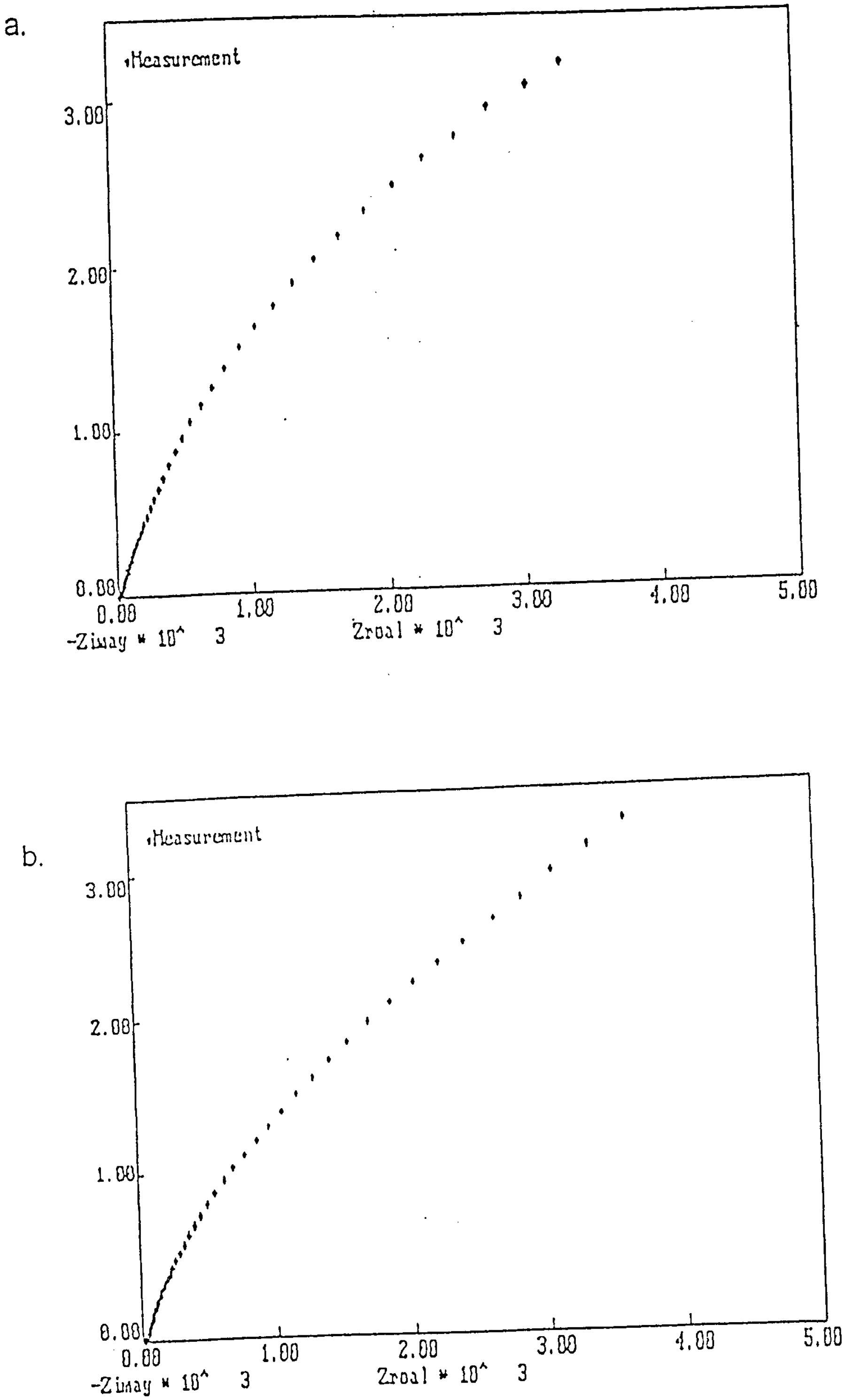


Fig. 30.

Impedance spectra for cells with $LiNiO_2$ composite electrodes and electrolytes based on PEO - $LiCF_3SO_3$ - organometallic compound polymer. (measured at 70 °C after: a. 5 h; b. - 100 h)