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An unusual conductivity enhancement occurs in PEO-based $ZnBr_2$/LiBr electrolytes of composition, $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ with x = 0..00, 0.05, 0.50, 0.75, 1.00 in mol%. The conductivity of the mixed-salt electrolytes is higher than that of either pure salt electrolyte. The highest conductivity, observed for x = 0.5, is two orders of magnitude higher than that of pure $LiBr(PEO)_{16}$ and one order higher than $ZnBr_2(PEO)_{16}$. In contrast, the conductivity of mixed $Mg(ClO_4)_2/LiClO_4$ electrolytes, $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO]_{16}$ where x = 0.00, 0.20, 0.50, 0.80, 1.00 in mol%, increases monotonically with the mole fraction of the higher conductivity component, $LiClO_4(PEO)_{16}$. The conductivity and DSC results suggest that the conductivity enhancement in the $ZnBr_2$/LiBr electrolytes results from a change in charge carrier type and concentration, whereas the conductivity change in the $Mg(ClO_4)_2/LiClO_4$ electrolytes arises from a change in the microscopic viscosity of the electrolytes.

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Poly(ethylene oxide) Electrolytes Containing Mixed Salts

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Synopsis

An unusual conductivity enhancement occurs in PEO-based $ZnBr_2$/LiBr electrolytes of composition, $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ with $x = 0.00, 0.05, 0.50, 0.75, 1.00$ in mol%. The conductivity of the mixed-salt electrolytes is higher than that of either pure salt electrolyte. The highest conductivity, observed for $x = 0.5$, is two orders magnitude higher than that of pure $LiBr(PEO)_{16}$ and one order higher than $ZnBr_2(PEO)_{16}$. In contrast, the conductivity of mixed $Mg(ClO_4)_2/LiClO_4$ electrolytes, $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$ where $x = 0.00, 0.20, 0.50, 0.80, 1.00$ in mol%, increases monotonically with the mole fraction of the higher conductivity component, $LiClO_4(PEO)_{16}$. The conductivity and DSC results suggest that the conductivity enhancement in the $ZnBr_2$/LiBr electrolytes results from a change in charge carrier type and concentration, whereas the conductivity change in the $Mg(ClO_4)_2/LiClO_4$ electrolytes arises from a change in the microscopic viscosity of the electrolytes.

Keywords: polymer electrolytes, mixed-salt effect, ionic conductivity

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INTRODUCTION

Poly(ethylene oxide) (PEO) dissolves a wide range of ionic salts to form solid polymer electrolytes many of which have relatively high ionic conductivities. These materials are neither true liquids nor true solids, but a new electrochemical medium of both fundamental and technological interest. Considerable effort has been devoted to understanding the properties of PEO-based Li(I) conductors because of their potential application in high energy density batteries. More recent efforts have focused on exploring the properties of PEO solutions of more exotic metal salts, in particular those of divalent cations.

This study grew out of an exploration of the electrochemistry of PEO-based electrolytes containing Zn(II). A rather interesting and unexpected phenomenon was observed in experiments initially designed to measure the diffusion coefficient of Zn(II) in PEO-based polymer electrolytes using electrochemical techniques. A $[0.05ZnBr_2+0.95LiBr](PEO)_{16}$ electrolyte was prepared in the hope that the LiBr would act as a supporting electrolyte to minimize Zn(II) migration. However, the electrochemical processes observed were still found to be controlled by migration, rather than by diffusion, despite the large quantity of "supporting" electrolyte (95 mol% LiBr)[1]. In addition, the conductivity of this mixed-salt composition was found to be higher than that of either single salt electrolyte, $ZnBr_2(PEO)_{16}$ or $LiBr(PEO)_{16}$, at temperatures above the melting point of the pure PEO crystalline phase. Clearly, the LiBr does not behave as a supporting electrolyte; rather, it appears to result in a fundamental change in the chemistry of the electrolyte system. Interestingly, this mixed-salt behavior in polymer electrolytes is the inverse of that observed in ionically conducting glasses [2] or the β"-alumina families [3], which often reveal a dramatic decrease in conductivity upon the mixing of cations, a phenomenon known as the mixed-alkali effect.

Conductivity enhancement in PEO-based electrolytes containing mixed salts has been observed for electrolytes with mixed cations (either both divalent cations or divalent and monovalent cations), mixed monovalent anions, and both mixed cations and anions, as summarized in Table 1.

Table 1. Mixed-salt effect in PEO-based polymer electrolytes. [The symbols, "+" and "-" indicate that the conductivity of the mixed-ion system is higher or lower than that of the respective single salt system. For example, in the first composition, +/+ denotes that the mixed electrolyte has a higher conductivity than that of either pure composition.]

System	Mixed-ion Effect T = 70 to 160°C	Ref.
Mixed Cations Only		
$[0.5Ca(CF_3SO_3)_2+0.5Mg(CF_3SO_3)_2](PEO)_{15}$	+ / +	[4]
$[xZnBr_2+(1-x)LiBr](PEO)_{16}$ x = 0.0, 0.05, 0.25, 0.50, 0.75, 0.95 and 1.0 in mol%	+ / +	This work
$[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{20}$ x = 0.0, 0.2, 0.50, 0.80 and 1.0	+ / -	This work
$[0.05MBr_2+0.95LiBr](PEO)_{16}$ M = Mg, Cd and Zn	+ / + for Zn + / ? for Cd - / - for Mg	This work
Mixed Anions Only		
$[0.5CaBr_2+0.5CaI_2](PEO)_{15}$	+ / +	[4]
$[0.5LiI+0.5LiClO_4](PEO)_?$	+ / +	[7]
Mixed Cations and Anions		
$[0.5Ca(CF_3SO_3)_2+0.5NaI](PEO)_{15}$	+ / +	[4]
$[0.5LiCF_3SO_3+0.5NaI](PEO)_n$	+ / + for n = 4 + / + for n = 8	[5,6]

The mixed-salt effect in PEO-based electrolytes was first reported by Moryoussef et al.[4]. They observed conductivity enhancement due to mixing of either cations or anions for the following three electrolyte compositions:

$[0.5CaI_2+0.5CaBr_2](PEO)_{15}$

$[0.5Ca(CF_3SO_3)_2+0.5Mg(CF_3SO_3)_2](PEO)_{15}$

$[0.5Ca(CF_3SO_3)_2+0.5NaCF_3SO_3](PEO)_{15}$

Moryoussef et al. suggested that the conductivity enhancement is due to a plasticizing effect which favors the formation of an amorphous phase at the expense of the crystalline phase, although they provided no experimental verification of this idea. The effect was considered to arise from the topological disorder introduced into the system by the mixing of salts.

More recently, MacCallum et al.[5,6] have studied the mixed-salt effect in the highly-concentrated PEO-based $LiCF_3SO_3/NaI$ electrolytes:

$[0.5LiCF_3SO_3+0.5NaI](PEO)_4$

$[0.5LiCF_3SO_3+0.5NaI](PEO)_8$

Pulsed n.m.r was used to measure the volume of the amorphous phase in these electrolytes. The results indicate that the mixed-salt compositions contained more charge carriers in a more extensive amorphous polymer phase than in the corresponding pure systems. These results provide some support for the conductivity enhancement mechanism suggested by Moryoussef.

Knowledge of the mixed-salt effect in polymer electrolytes is still quite limited. As shown in Table 1, most studies have been confined to compositions in which the ratio of salt (I)/salt (II) is 50/50 mol%. There have been no reports of the variation of conductivity with mixed salt ratio. In order to gain more insight into this curious phenomenon, three systems were studied in the work described in this paper:

$[xZnBr_2+(1-x)LiBr](PEO)_{16}$, x = 0.00, 0.05, 0.50, 0.75, 0.95 and 1.00 in mol%

$[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$, x=0.0, 0.2, 0.5, 0.8 and 1.0 in mol%

$[0.05MBr_2+0.95LiBr](PEO)_{16}$, M = Zn, Mg and Cd

EXPERIMENTAL PROCEDURES

All samples were prepared by a solution-casting technique from the starting materials listed in Table 2. Stoichiometric amounts of salts and PEO were dissolved in ethanol/acetonitrile mixtures and then stirred at room temperature for about 24 hours to produce homogeneous solutions. These solutions were then cast in glass rings on silicone release paper and allowed to stand at room temperature for about 24 hours to evaporate the solvent. The rings, with polymer film attached, were then transferred to a vacuum line and vacuum dried, first at room temperature for about 24 hours and then at about 110°C for another 24 hours. Samples were then stored in a purified, argon-filled drybox until further study.

Table 2. Starting materials for preparing PEO-based polymer electrolytes

Starting Materials	Source	Pre-treatment
LiBr	Aldrich, 99.995%	Used as received
$LiClO_4$	Aldrich, anhydrous	Vacuum dried at 120°C
$CdBr_2$	Alfa, 98%	Used as received
$Mg(ClO_4)_2$	Aldrich, ACS reagent	Vacuum dried at 120°C
$MgBr_2$	Aldrich, 98%	Vacuum dried at 120°C
$ZnBr_2$	Aldrich, 99.999%	Used as received
Poly(ethylene oxide) PEO $MW = 5x10^6$	Aldrich	Vacuum dried at 50°C
Ethanol C_2H_5OH	Aldrich, anhydrous	Used as received
Acetonitrile CH_3CN	Aldrich, anhydrous	Used as received

The total ionic conductivities of the electrolytes were determined using ac impedance analysis with blocking platinum electrodes. The measurements were carried out over the temperature range of 30 to 160°C and the frequency range of 10^2 to 10^5 Hz using a Solartron 1174 frequency response analyzer under computer control. Samples were allowed to equilibrate at each temperature for 10 minutes before data collection.

Differential scanning calorimetry (DSC) was carried out in a DuPont 910 DSC cell over the temperature range of -110 to 200°C. Samples, approximately 10 mg in weight, were hermetically sealed in aluminum pans in an argon-filled drybox. They were then heated at 10°C/min (first heating), held isothermally at 200°C for 20 minutes, then quenched with liquid nitrogen and rerun from -110 to 200°C (second heating). The glass transition temperature, T_g, for all compositions studied, was taken as the onset point of the transition, i.e. the point at which the extrapolated baseline intersects the extrapolated slope in the transition state.

RESULTS AND DISCUSSION

PEO-based Zn(II)/Li(I) mixed system

The conductivities of PEO-based Zn(II)/Li(I) mixed-salt electrolytes, $[xZnBr_2+(1-x)LiBr](PEO)_{16}$, where x = 0.00, 0.05, 0.25, 0.50, 0.75, 0.95 and 1.00 mol%, were measured as a function of temperature and composition. As clearly shown in Figure 1(b), mixing any proportion of $ZnBr_2$ and LiBr results in an increase in the total conductivity of the electrolyte at temperatures above 70°C. The highest conductivity appears to be at the composition of $ZnBr_2$/LiBr = 50/50, at which the conductivity of the mixed-salt electrolyte is about two orders of magnitude higher than that of the pure LiBr electrolyte and about one order of magnitude higher than that of the pure $ZnBr_2$ electrolyte.

At temperatures below 70°C, all compositions studied contain a large fraction of pure PEO crystalline phase as observed in the DSC studies (see Figure 3). The absence of a trend in the composition dependence of conductivity is not surprising because of the difficulties in accurately measuring conductivity caused by the high crystallinity. As a result, all of the following discussion will be focused on conductivity data taken at or above 70°C.

As shown in Figure 1(a), the temperature dependence of conductivity for all the compositions studied closely follows an Arrhenius-like relationship (Eqns. 1 and 2) within the temperature range 70 to 160°C:

$$\sigma = A \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

or

$$\log \sigma = \log A + \left(- \frac{E_a}{2.303\,RT} \right) \qquad (2)$$

where A is a constant which is independent of temperature within the temperature range studied, E_a is the apparent thermal activation energy, and R is the gas constant, 8.314 $JK^{-1}mol^{-1}$. E_a for every composition can be estimated from the slope of the Arrhenius plot between 70 and 160°C.

It can be easily seen that log (σ) comprises two terms: (i) the log A term, in which A is proportional to the number of charge carriers (an increase in log A increases the total conductivity); and (ii) an activation energy term $(-(E_a/2.303RT))$, henceforth called the "E_a term" (an increase in the E_a term decreases conductivity). In Figure 2, log A and the E_a term are plotted against the concentration of $ZnBr_2$, together with log (σ) at 100°C. It can be seen that log A exhibits a maximum at x = 0.5 and the E_a term exhibits a minimum at the same concentration. However, the effect of the maximum in log A overrides the effect of the minimum in E_a term, so that log σ over this composition range reaches a maximum. This result implies that ionic conduction in the mixed Zn(II)/Li(I) electrolyte system is not an activation energy dominated process.

DSC studies were carried out on both pure and mixed Zn(II)/Li(I) compositions to gain insight into the phases present in the mixed electrolytes. Samples were first cooled from room temperature to -110°C using liquid N_2 and then heated to 220°C at 10°C/min. DSC results for this first heating cycle are shown in Figure 3. A multi-phase morphology was observed for all the compositions; the mixing of Zn(II) and Li(I) did not significantly alter the macroscopic phase morphology of the electrolytes.

To determine the glass transition temperatures of the fully amorphous compositions, electrolyte melts were thermally quenched to suppress the recrystallization of pure PEO and the complex phases. All samples were first held isothermally for 20 minutes at 220°C after the first heating cycle, quenched to -110°C using liquid N_2, and then re-heated to 220°C at 10°C/min. DSC results for this second heating cycle are shown in Figure 4. Two points are clear: (i) fast cooling suppressed the recrystallization of the high melting complex phase for all compositions studied; and (ii) compositions with high $ZnBr_2$ mole fractions, $x \geq 0.5$ in mol%, appear to be fully amorphous, while in compositions having high LiBr mole fractions, recrystallization of pure PEO occurs during cooling.

Summarized in Table 3 are glass transition temperatures for fully amorphous Zn(II)/Li(I) electrolyte compositions. The value of T_g reflects the mobility of the polymer segments in the amorphous phase. The lower the value of T_g, the higher the mobility of the polymer segments and the lower the local or microscopic viscosity of the electrolyte. Therefore, a significant reduction in T_g is expected if the unusual conductivity enhancement in mixed-salt electrolytes is mainly a result of increasing mobility. However, the observed glass transition temperatures are almost constant for most compositions, which implies that the dominant factor in conductivity enhancement is not mobility. The results suggest that the type and number of charge carriers may be the factors that control conductivity.

Table 3. T_g of fully amorphous electrolytes $[xZnBr_2+(1-x)LiBr](PEO)_{16}$

x in mol%	Tg (°C)
x = 0.50	-39
x = 0.75	-41
x = 0.95	-38
x = 1.00	-35

PEO-based mixed Mg(II)/Li(I) electrolytes

Parallel studies were carried out with mixed Mg(II)/Li(I) electrolytes of the type, $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$, where x = 0.0, 0.22, 0.5, 0.8 and 1.0 mol%. In contrast with the results obtained for Zn(II)/Li(I) electrolytes, conductivity in the Mg(II)/Li(I) system decreases linearly with increasing mole fraction of $Mg(ClO_4)_2$. Figure 5 shows that the total conductivity of the mixed system falls between that of the two pure salt compositions and increases linearly with the fraction of the higher conductivity component, in this case $LiClO_4(PEO)_{16}$.

When log A, the E_a term, and log (σ) are plotted against x, the mol% of $Mg(ClO_4)_2$, log A increases monotonically with x, whereas the E_a term and log (σ) decrease linearly with x, as shown in Figure 6. Therefore, in this mixed-salt system, the activation energy appears to be the dominant factor in the conduction process.

DSC studies have also been carried out for the mixed Mg(II)/Li(I) electrolytes. The results of the first heating cycle are shown in Figure 7. Only the pure Li(I) composition contains both a pure PEO and a high melting complex crystalline phase; other compositions contain only a pure PEO crystalline phase. Fast cooling effectively suppresses the recrystallization of either a high melting complex phase or the pure PEO crystalline phase in all compositions, as shown in Figure 8. The endothermic peak observed is simply due to the melting of the cold crystalline phase formed at lower temperature.

Summarized in Table 4 are the glass transition temperatures for fully amorphous compositions. The values of T_g are found to decrease with increased mole fraction of $LiClO_4$ in the mixed electrolyte system. This observation suggests that the mobility may be a dominant factor which controls the total conductivity of these electrolytes.

Table 4. T_g of fully amorphous electrolytes $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$

x in mol%	Tg (°C)
x = 0.0	-43
x = 0.2	-32
x = 0.5	-33
x = 0.8	-23
x = 1.0	-11

To summarize the above discussion, the conductivity enhancement observed in mixed Zn(II)/Li(I) electrolytes is most likely the result of a change in both the type and number of charge carriers rather than the mobility of existing charge carriers. However, in mixed Mg(II)/Li(I) systems, the mobility of the charge carriers seems to be the dominant factor controlling total conductivity. It is also worthwhile to point out that, although the properties of the mixed-salt systems studied are apparently the result of the mixed cations, the different anions may also have an effect. The Br(-I) and ClO_4(-I) anions in these materials are very different in terms of size, polarizability, and other characteristics. More systematic work needs to be done before any general conclusions on the relative importance of mixed cations vs. mixed anions can be drawn.

Effect of cation type on mixed M(II)/Li(I) electrolytes

As already mentioned, it has been suggested that the conductivity enhancement in mixed ion electrolytes results from topological disorder [4-6], that is, the effect involves changes in entropy rather than enthalpy. If true, then the substitution of even a small percentage, e.g. 5 mol%, of a foreign species into a PEO-based LiBr electrolyte should increase the total conductivity, regardless of the nature of the second cation.

To test this point, electrolytes of composition, $[0.05MBr_2+0.95LiBr](PEO)_{16}$, where M = Zn, Cd and Mg, were studied. As pointed out earlier, the introduction of 5 mol% $ZnBr_2$ to pure $LiBr(PEO)_{16}$ increases the electrolyte conductivity by more than one order of magnitude. The substitution of 5 mol% Cd(II) also increases the total conductivity of the electrolyte (Figure 9), although the magnitude of the increase is less than in the Zn(II)/Li(I) electrolyte. However, the conductivity of a mixed Mg(II)/Li(I) electrolyte is slightly lower than that of a pure Li(I) electrolyte. $MgBr_2$ and $CdBr_2$ were chosen because previous studies by Yang et al. [8] and Huq et al. [9] have shown that Mg(II) is immobile while Cd(II) is highly mobile in PEO-based pure Mg(II) or Cd(II) electrolytes. DSC studies reveal no significant differences in phase morphology or crystallinity among the three compositions.

These results suggest that the mixed-salt effect in PEO-based electrolytes is not simply the result of topological disorder, since the ion type has an obvious influence on the total conductivity of the electrolytes.

CONCLUSIONS

A significant conductivity enhancement results when $ZnBr_2$ and LiBr are mixed in PEO over the composition range of $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ with x = 0.05, 0.50, 0.75, 0.95 in mol% and the temperature range 70 to 160°C. The highest conductivity occurs at a $ZnBr_2$/LiBr mole ratio of 50/50, at which the conductivity of the mixed electrolyte is about two orders of magnitude higher than $LiBr(PEO)_{16}$ and about one order higher than $ZnBr_2(PEO)_{16}$. Mixing of $ZnBr_2$ and LiBr does not significantly alter the macroscopic phase morphology of the electrolytes at room temperature. The glass transition temperatures of the amorphous forms of all the compositions are nearly identical for values of $x > 0.05$, indicating that mixing the salts does not result in any significant increase in the segmental mobility of the PEO chains in the amorphous conducting phase. The implication is that the conductivity enhancement in the mixed electrolytes is directly related to the number and/or type of charge carriers, rather than from an increased mobility resulting from a decreased microscopic viscosity of the polymer solvent.

In contrast, mixtures of $Mg(ClO_4)_2$ and $LiClO_4$ in PEO show no unusual conductivity behavior. Compositions studied were $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$ with x = 0.00, 0.20, 0.50, 0.80, and 1.00. From 70 to 160 °C, the conductivity of these mixed-salt electrolytes increases monotonically with the mole fraction of the higher conductivity component, in this case, $LiClO_4(PEO)_{16}$. DSC studies show that in the fully amorphous $Mg(ClO_4)_2/LiClO_4$ electrolyte the glass transition temperature decreases with increasing mole fraction of $LiClO_4$. The results indicate that, in the Mg(II)/Li(I) electrolytes, it is the mobility of the charge carriers that principally determines the ionic conductivity.

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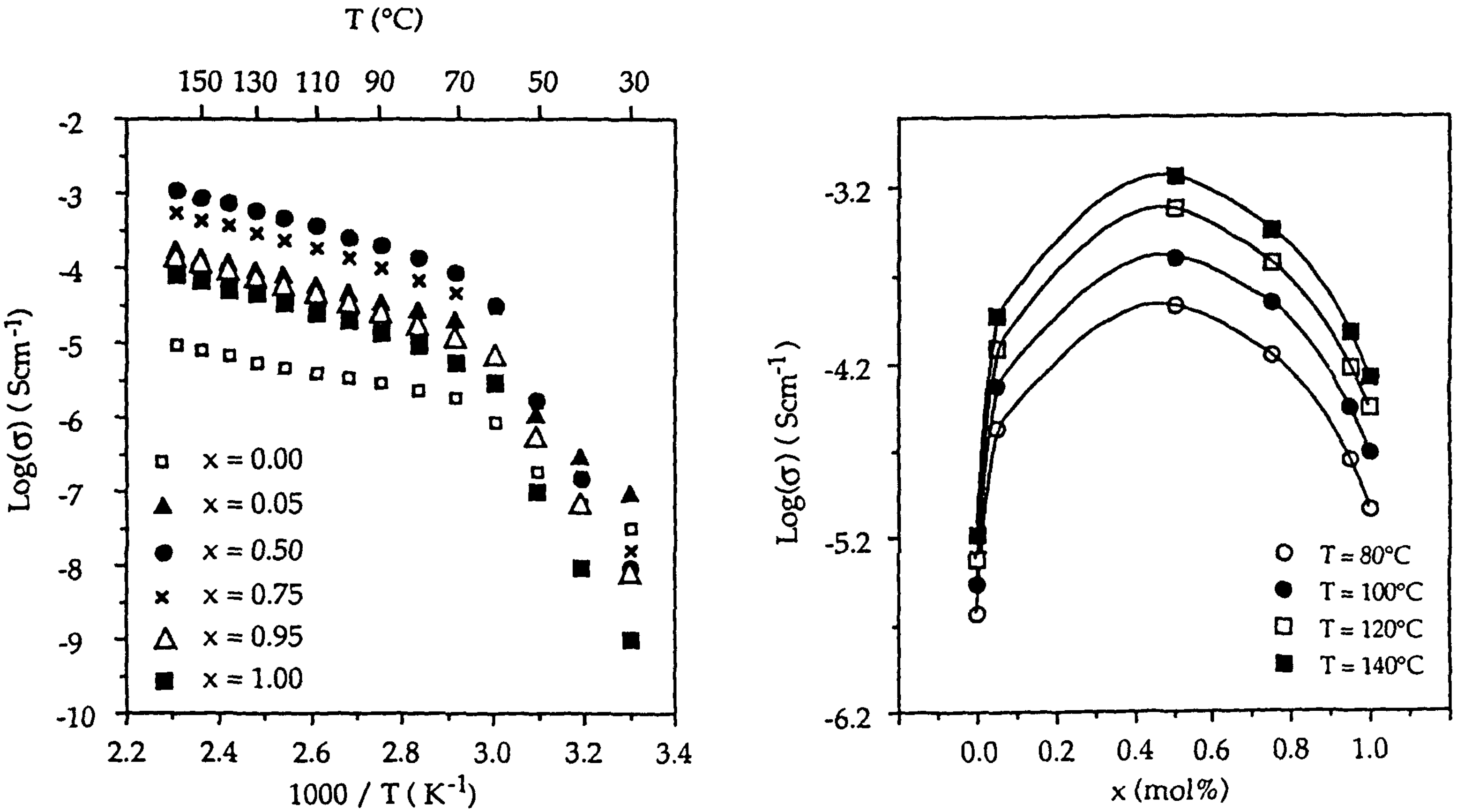


(a)

(b)

Figure 1 Conductivity of mixed $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ electrolytes
(a) temperature-dependence and (b) composition-dependence

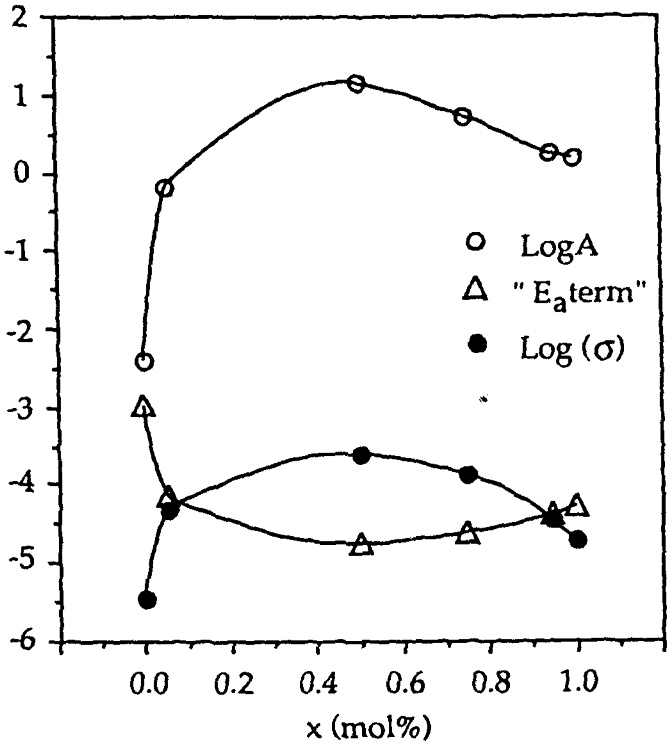


Figure 2 Compositional dependence of logA, the "E_a term", and log σ at 100°C for $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ electrolytes

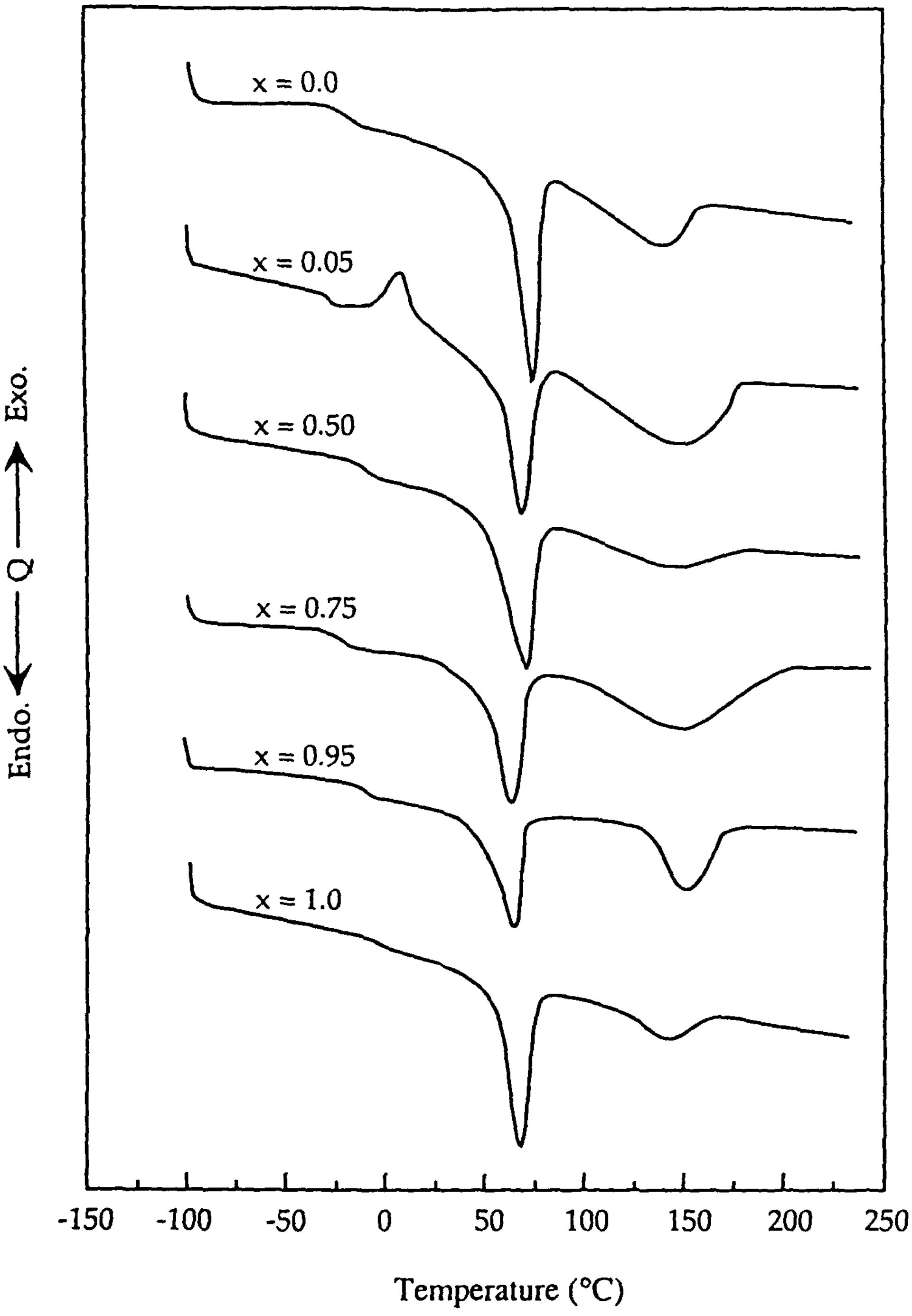


Figure 3 DSC curves for [$xZnBr_2+(1-x)LiBr](PEO)_{16}$ electrolytes at the first heating cycle

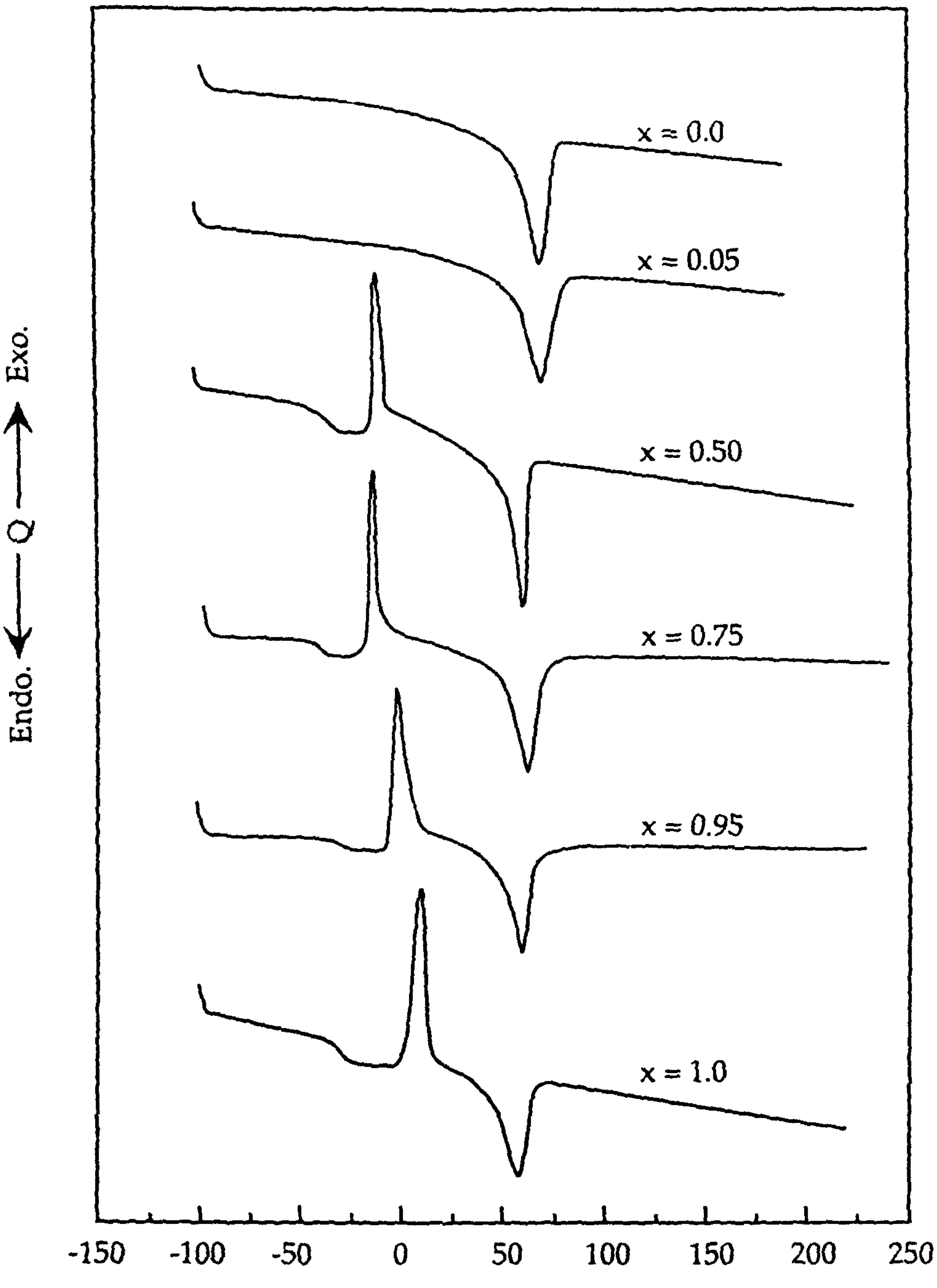
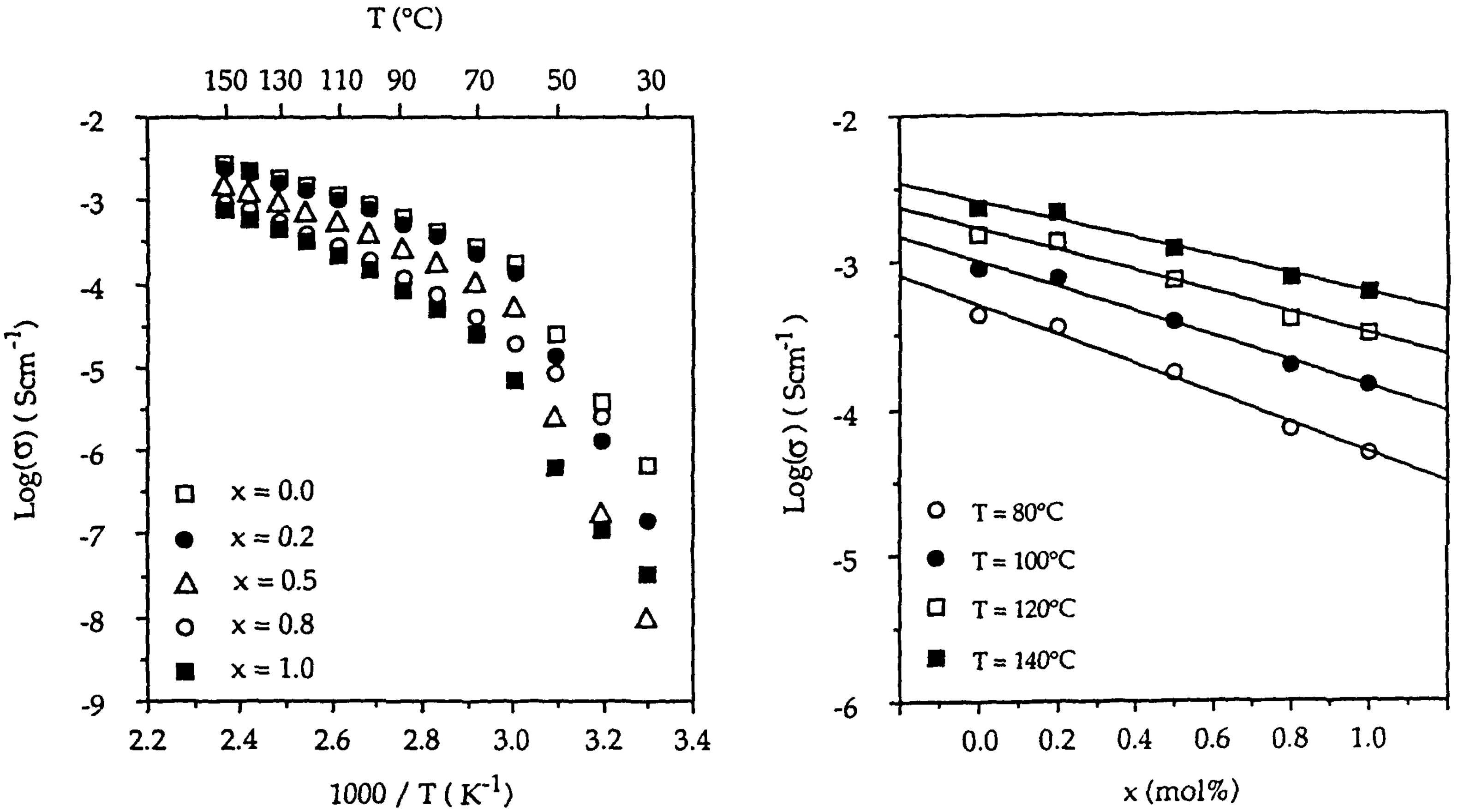


Figure 4 DSC curves for $[xZnBr_2+(1-x)LiBr](PEO)_{16}$ electrolytes at the second heating cycle



(a)

(b)

Figure 5 Conductivity of mixed [$xMg(ClO_4)_2$+(1-x)$LiClO_4$]$(PEO)_{16}$ electrolytes
(a) temperature-dependence and (b) composition-dependence

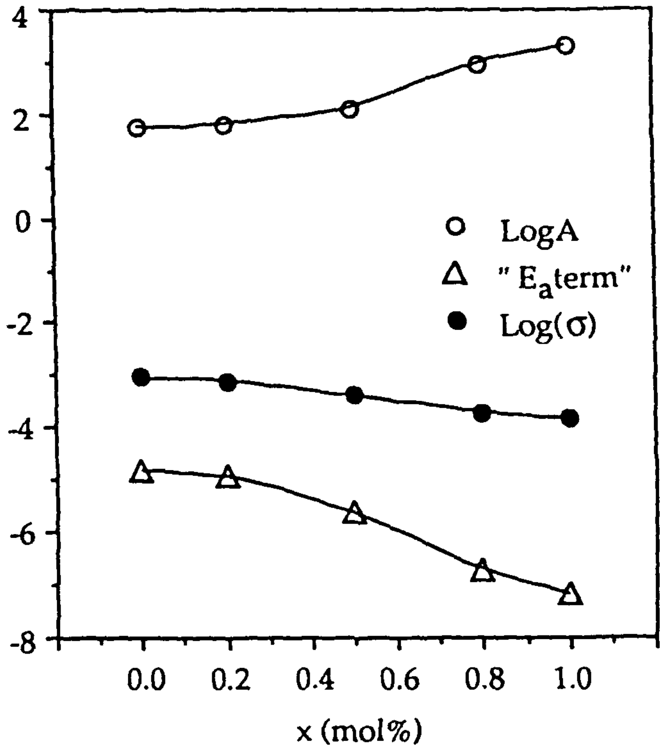


Figure 6 Compositional dependence of logA, the "E_a term", and log σ at 100°C for $[x\text{Mg(ClO}_4)_2 + (1-x)\text{LiClO}_4](\text{PEO})_{16}$ electrolytes

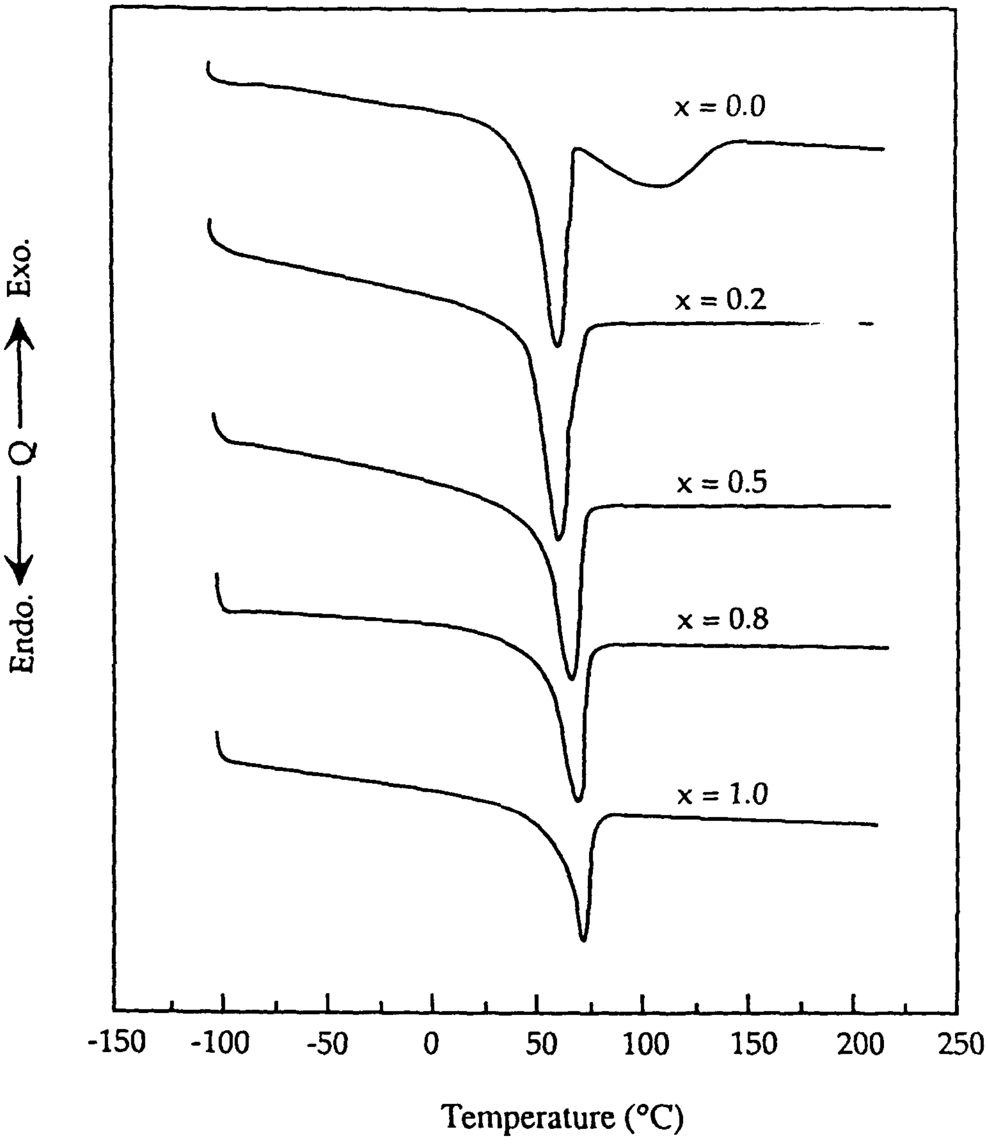


Figure 7 DSC curves for [$xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$ electrolytes at the first heating cycle

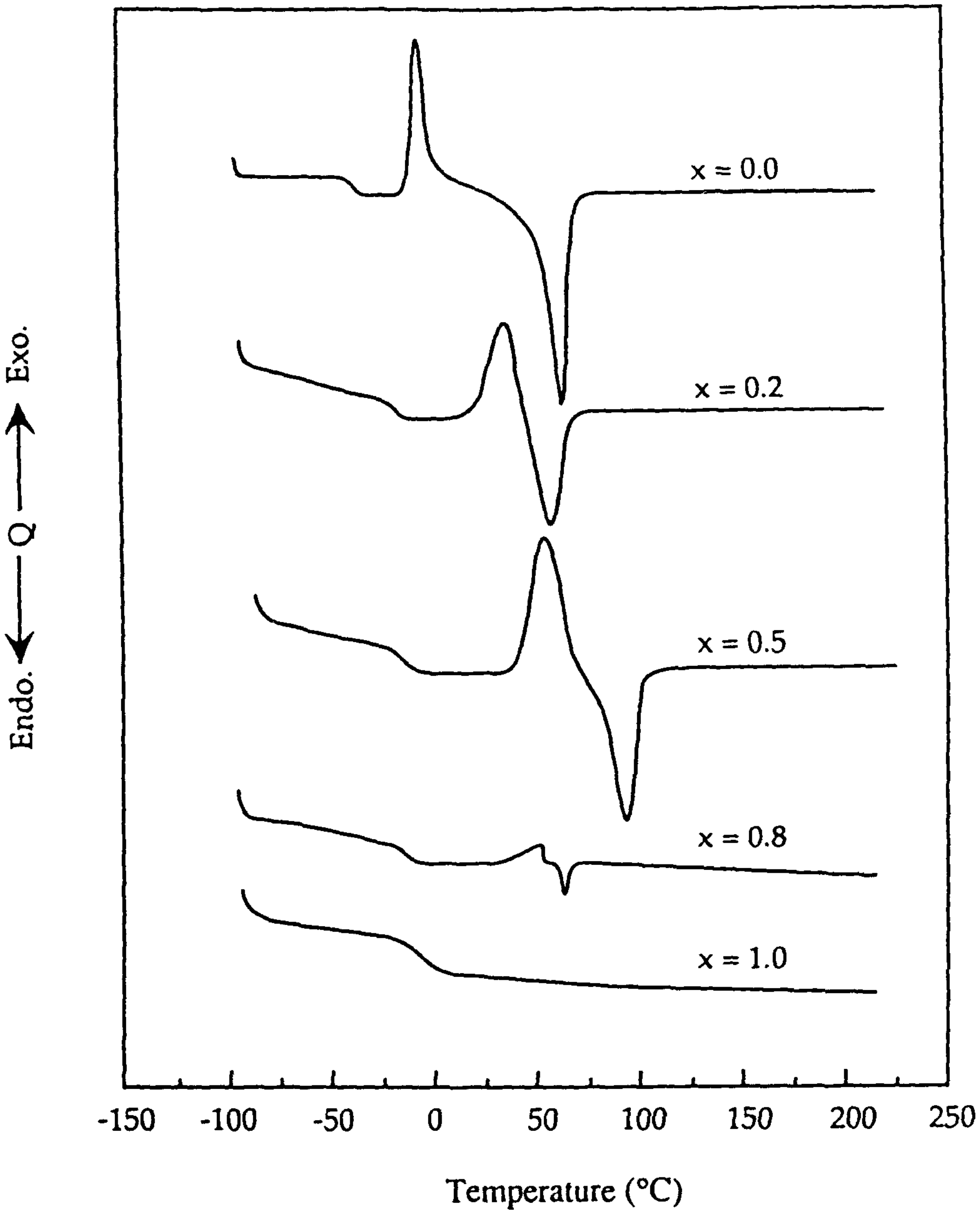


Figure 8 DSC curves for $[xMg(ClO_4)_2+(1-x)LiClO_4](PEO)_{16}$ electrolytes at the second heating cycle

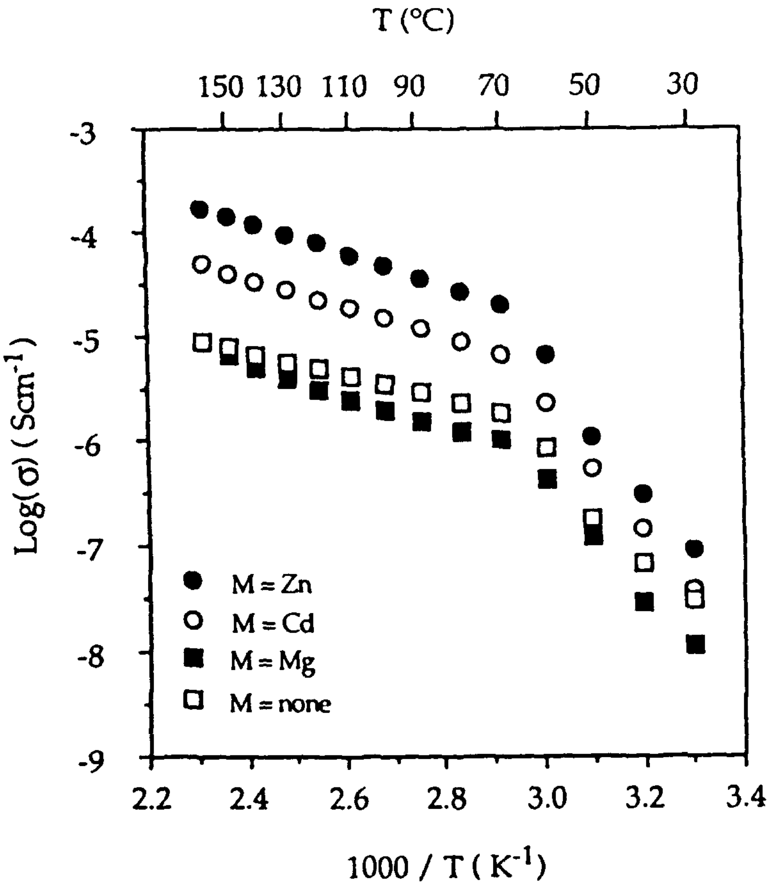


Figure 9 Conductivity of $[0.05MBr_2+0.95LiBr](PEO)_{16}$ for M = Zn, Cd & Mg