

Phase diagram of polymer electrolyte: (x)(PEO) – (1-x)CF₃COOLi

Diagrama de fases del polímero electrolito: (x) (PEO) – (1 - x)CF₃COOLi

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Abstract

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) and lithium trifluoroacetate (CF₃COOLi) were prepared by a solvent casting method by different concentrations of salt. The membranes resulting of slow evaporation were analyzed by differential scanning calorimetry (DSC) and its phase diagram was drawing for a second thermal scan. The DSC curves on the first thermal cycle show three anomalies at 303, 338 and 393 K, that are slightly shifted with the salt content. For high concentrations, the intensity of the endothermic peak associated with the melting point of PEO (338 K) decreases, that one for the third transition increases with the salt content, the second peak (melting point of PEO) disappear when the concentration reaches the value of X = 0,405 (given in fraction of mass: salt/(salt + polymer)). These results and the change of conductivity demonstrate the formation of a new complex between the PEO and the CF₃COOLi.

----- *Keywords:* poly(ethylene oxide); ionic conductivity, polymer electrolytes

Resumen

A partir de poli(óxido de etileno) y trifluoro acetato litio (CF₃COOLi), se prepararon electrolitos sólidos poliméricos por el método de solución, para diferentes concentraciones de sal. Las membranas resultantes de la evaporación lenta, se analizaron por calorimetría diferencial de barrido (DSC) y se realizó un diagrama de fases a partir de los segundos calentamientos. Las curvas de DSC para un primer barrido muestran tres anomalías a 303, 308 y 393 K, las

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que cambian lentamente con el contenido de sal. Para altas concentraciones, la intensidad del pico endotérmico asociado con el punto de fusión del PEO (338K) decrece, mientras que para la tercera anomalía (asociada a la fusión del complejo PEO:sal) la intensidad aumenta. La segunda anomalía desaparece por completo, cuando la concentración de sal alcanza un valor de $X = 0,405$ (dada en fracción de masa: $\text{sal}/(\text{sal} + \text{PEO})$). Estos resultados junto a la alta conductividad del sistema, muestran la formación de un nuevo complejo entre el PEO y la sal.

----- *Palabras clave:* Poli (óxido de etileno), conductividad iónica, polímeros electrolitos

Introduction

Polymer electrolytes have been the focus of intense research efforts due their potential application in rechargeable batteries and electrochemical sensors [1, 2]. Systems of poly (ethylene oxide) PEO with different lithium, sodium and potassium salts have received considerable attention, since they exhibit solid phases with high ionic conductivity at room temperature.

The high conductivity is assigned to the amorphous phase of the polymeric matrix, assisted by the segmental motion of the polymeric backbone [3, 4]. With this in mind, other authors have used the route of increasing the flexibility of the polymer chains, by preparing crosslinked polymer networks in block and comb-like structures [5, 6].

It is well known that PEO forms complex with inorganic salts, where cations are coordinated by several oxygen atoms from helical polymer chain winding around cation [7,8]. Crystalline complexes formed have typically melting temperature higher than PEO (e.g. 452 K for $\text{PEO}_3:\text{LiCF}_3\text{SO}_3$ and 353 K for $\text{PEO}_3:\text{LiN}(\text{CF}_3\text{SO}_2)_2$) [9]. In general, amorphous polymer salt complexes exhibit higher conductivity compared with their crystalline counterparts. Flexibility on the chains, which is higher in amorphous phase, is crucial in improving the ionic transport. The spectroscopic studies indicate that local coordination structure

is essentially the same in amorphous and crystalline complexes [7, 10].

In previous works, we investigated the thermal and the electrical behavior of complex PEO and the organic sodium trifluoroacetate salt (CF_3COONa) [11]. The samples showed good thermal stability and high ionic conductivity in solid state. In the present work we study the phase behavior of a new electrolyte, $\text{PEO}:\text{CF}_3\text{COOLi}$, which has good mechanical, thermal and electrical properties that can be used in batteries and electrochemical devices.

Experimental

The lithium trifluoroacetate salt and poly (ethylene oxide) (Aldrich) were purchased and dissolved independently in acetonitrile at a temperature of 348 K. The resulting solution were mixed in a stirrer for several hours and then poured into Teflon vessels where the solvent was evaporated under a dry atmosphere (desiccator with silica gel). After two weeks we got transparent, uniform and smooth polymeric membranes with thickness of 0.1mm.

The thermal characterization was carried out using a modulated differential calorimetry at a temperature rate of 10 K min^{-1} . The measurement were done in the 281-423 K temperature range for a first run with an isothermal at 423 K and then heated from 281 K to 494 K for a second scan. The thermal treatment is used to enhance the contact between the sample and the pans, as well for dehydration of it.

Results and discussion

Figure 1 shows the first heating DSC curves for freshly prepared samples of PEO:CF₃COOLi with various concentrations which were first quenched to 270 K and then heated. Notice the low temperature exothermic peak for some concentrations of salt ($x = 0.405, 0.254, 0.150, 0.037$) which is due to the cold crystallization of the corresponding polymer blend which is frequently shown when a polymer is quenched below room temperature [12].

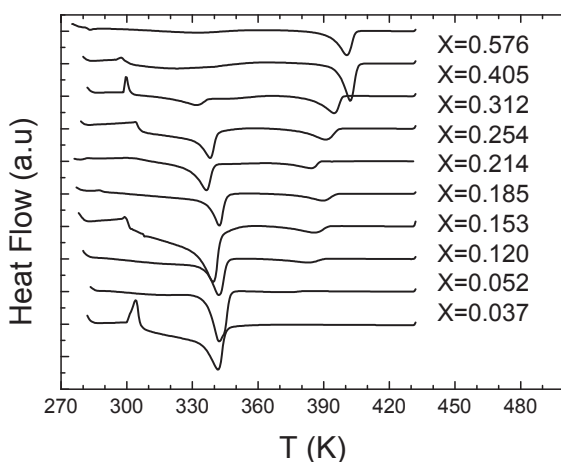


Figure 1 First DSC heating curves for different salt concentration of freshly prepared PEO:CF₃COOLi

The table 1 shows the enthalpies (E) of the three anomalies, first anomaly (Fi. An.), second anomaly (Sec. An.) and third anomaly (Th. An.). Notice that when the enthalpies of the second anomaly decrease, the third anomaly increase.

Figure 2 shows the second heating DSC curves, whose thermal events remained unaltered on subsequent runs. Its measurement was taken after keeping the sample at 423 K during 20 minutes and then slowly cooled to 281 K. Notice that the first exothermic pick, does not appear after the thermal treatment. The endothermic peak observed for samples with very low salt concentration ($x < 0.1$) about 335 K corresponds to the melting point of PEO. Notice that for

$x = 0.405$, the endothermic peak for the melting point of PEO has vanished completely indicating that this phase is no longer present in the polymer.

Table 1 Enthalpies for the blends in the 270-433 K temperature range for the three thermal events observed in the first heating cycle for freshly samples

C (x)	Fi. An.	Sec. An.	Th. An.
	E(J/g)	E(J/g)	E(J/g)
0.037	34.35	--	--
0.052	--	139.5	--
0.120	--	88.84	13.53
0.153	2.089	238.80	30.98
0.185	1.115	68.60	30.33
0.214	8.768	69.19	33.15
0.254	0.206	63.56	39.06
0.312	10.24	17.55	60.37
0.405	2.215	--	92.08
0.576	--	--	71.23

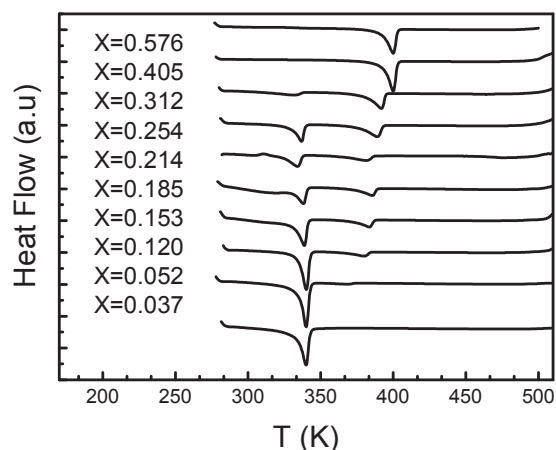


Figure 2 Second heating curves for different salt concentration of the PEO:CF₃COOLi blends after thermal treatment of the samples at 433 K for 20 minutes

On the other hand, in Figure 2 a first endothermic peak is observed at $T \approx 393$ K for higher concentrations than $x > 0.052$ whose enthalpies are showed in the table 2.

Table 2 DSC parameters for the blends in the 270-433 K temperature range for the two thermal events observed during the second heating cycle of PEO:CF₃COOLi

Con.	Sec. An.	Th. An.
	E (J/g)	E (J/g)
0.037	101.7	--
0.052	111.5	3.138
0.12	87.12	15.99
0.153	108.4	25.16
0.185	53.41	27.64
0.214	45.91	33.63
0.254	46.14	45.66
0.312	13.57	56.65
0.405	--	80.88
0.576	--	71.00

A temperature composition diagram for the PEO:CF₃COOLi system is presented in figure 3 as a result of the second DSC scans.

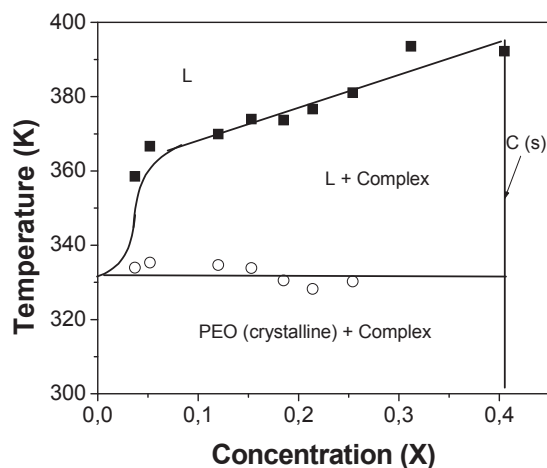


Figure 3 Temperature-Composition diagram of the PEO:CF₃COOLi system from DSC measurements

The phase diagram obtained by DSC thermograms shows three regions with combination of different phases: when the temperature is below 330 K,

PEO and complex PEO:CF₃COOLi crystalline are found, when the temperature is above 330 K, liquid (likely PEO) and complex coexist. In the region of low concentrations is possible to find only liquid, however at highest temperature, the liquid phase is the only one present. The DSC results show evidence for a crystalline complex in the PEO:CF₃COOLi system for concentration of x = 0,405, whose melting point is about 392 K. The DSC results then show evidence for a crystalline complex in the PEO-CF₃COOLi system, corresponding a mass fraction concentration of x = 0,405, whose melting point is at about 392 K with an enthalpy of about 81 J/g.

Figure 4 shows the Arrhenius plots, log σ vs. 1000/T for dried samples with different salt concentrations; strong variation of conductivity is observed in a temperature range of 298–433 K. The highest conductivity was obtained for the highest salt concentration as a result of the increase of the density of charge carriers. Some values of conductivity for different concentrations of salt are show in the table 3.

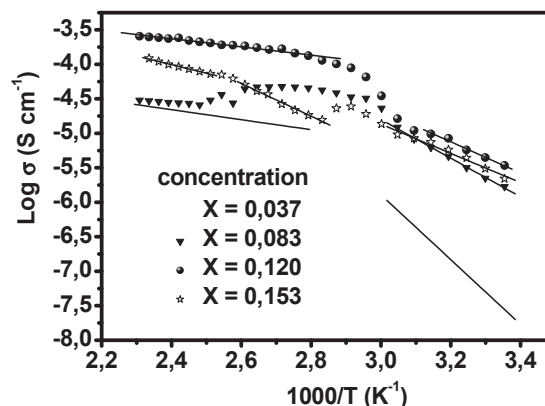


Figure 4 Plots of Log σ vs. 1000/T for high concentration of salt for the PEO:CF₃COOLi system

The activation energy values obtained by a fit to Arrhenius relation ($\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$), are show in the table 4. We can see two different regions: 298 K < T < 333 K (low temperatures region) and 353 K < T < 433 K (high temperatures

region) with Arrhenius behavior; between these regions there is a transition region, which is in

agree with melting point of crystalline PEO observed with DSC.

Table 3 Conductivity values σ (S cm⁻¹) for different temperatures and concentrations of polymer electrolyte PEO/CF₃COOLi

Conc. x	T = 298 K	T = 333 K	T = 355 K	T = 433 K
0.037	3.0x10-8	1.8x10-6	8.8x10-6	2.0x10-5
0.083	1.7x10-6	2.3x10-5	4.2x10-5	3.1x10-5
0.120	3.4x10-6	3.5x10-5	1.1x10-4	2.6x10-4
0.153	2.2x10-6	1.4x10-5	1.3x10-5	1.2x10-4
0.214	5.4x10-6	5.7x10-5	1.0x10-4	1.5x10-3
0.312	1.4x10-6	6.7x10-5	1.0x10-4	8.7x10-4
0.576	3.9x10-6	3.5x10-4	6.8x10-4	4.8x10-3

Table 4 Activation energy values for different concentrations of polymer electrolyte PEO/CF₃COOLi

Conc. x	298 < T < 333 K E _a (eV)	353 < T < 433 K E _a (eV)
0.037	0.175	0.027
0.083	0.104	-
0.120	0.085	0.022
0.153	0.079	0.089
0.214	0.100	0.082
0.312	0.165	0.047
0.576	0.223	0.063

Conclusions

We have obtained new polymer electrolytes membranes based on the PEO:CF₃COOLi system with good mechanical, thermal and electrical properties for potential application in all solid rechargeable alkaline batteries.

A phase diagram obtained by DSC thermograms, it shows three regions with combination of amorphous and crystalline phases.

The change of phases shown with DSC data as a function of the salt content and the high conductivity in the blends support the formation of the crystalline complex in this polymeric system, with best values of conductivity at high concentrations of salt.

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