

Electrochemical properties of poly(decaviologen) in polymer media

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Poly(decaviologen) (DV^{2+} , $2 ClO_4^-$) has been prepared and used in the characterization of two redox couples: dication/cation radical ($(DV^{2+}, 2 ClO_4^-)/(DV^{+\bullet}, ClO_4^-)$) and cation radical/decaviologen ($(DV^{+\bullet}, ClO_4^-)/(DV^0)$) in a polyethylene oxide-LiClO₄ medium by linear potential sweep voltammetry. The $(DC^{2+}, 2 ClO_4^-)/(DV^{+\bullet}, ClO_4^-)$ couple has been used to determine the transport number of lithium in poly(ethylene oxide)-LiClO₄ or LiCF₃SO₃ complex media.

1. Introduction

A new class of electrolytes based on complexes of alkaline metal salts and polymers was developed in 1972 [1]. These materials were rapidly used in electrochemical battery applications with lithium anodes and lithium ion intercalation material cathodes, and theoretical electrochemical investigations have been conducted only later.

Results concerning ionic conduction properties have shown the complex behaviour of these new media, depending on the nature of the phases present [2, 3]. On the basis of conductivity and calorimetric measurements, Steele *et al.* [4] have concluded that reproducible and comparable results require a comprehensive experimental protocol.

Many different techniques [5–9] for determining the cation transport number have been tested on these materials (impedance spectroscopy, RMN, radiotracer, etc.). These tests have been reviewed and discussed in a previous paper [10].

We have conducted voltage measurements on lithium concentration cells of the form: Li/PEO_m-LiX/PEO_n-LiX/Li. The lithium salts used were LiI, LiClO₄ or LiCF₃SO₃. This is our preferred method since it gives both the transport number and the diffusion coefficient of the ion or its complexes [11] in the electrolyte without any disturbance imposed to the system, requiring only the concentration cell voltage to be measured.

It is however necessary to determine the activity of the ions in the electrolyte. These values are obtained by measuring the e.m.f. of, for example, the electrochemical chain Li/PEO_m-LiX/XM-M.

Results obtained for iodide ions ($X^- = I^-$, $M = Pb$) are consistent with currently accepted results. However, for ClO_4^- or $CF_3SO_3^-$ anions, no existing electrode could be used in PEO electrolytes as an electrode of the second kind due to the solubility of most perchlorate derivatives in PEO (Ag, Pb . . .). Consequently we have extended our measurements to perchlorate and trifluoromethane sulphonate (triflate)

ions by using insoluble redox polymers derived from poly(decaviologen) as the indicating electrode.

In the present paper, we present a comparison of the results obtained with perchlorate and trifluoromethane sulphonate ions.

2. Experimental details

2.1. Electrolyte

The polymer electrolyte was prepared either from polyethylene oxide (ALDRICH) with an average molar mass of 5×10^{-6} , lithium perchlorate (F. Smith) first dehydrated at 140°C for 24 h under vacuum, or lithium triflate, obtained by reacting lithium carbonate (MERCK) with HCF₃SO₃ (MERCK) and dried as for the lithium perchlorate.

A thin film was obtained by pouring a solution of PEO and lithium salt co-dissolved in acetonitrile in a glass ring placed on a PTFE disc. Solvent removal by evaporation was obtained by circulating argon in a closed-loop circuit *t* through an activated molecular sieve column (13X). The solid thin film electrolyte was further dehydrated under a reduced pressure in a BÜCHI TO 50 oven at 140°C for 24 h and then stored in a glove box (water content < 1ppm, free of oxygen and nitrogen). The lithium salt concentrations in these electrolytes are expressed by the ratios O/Li or in molality ($mol\ kg^{-1}$).

2.2. Synthesis of poly(decaviologen) (DV^{2+} , $2 Br^-$)_n

Dibromo poly(decaviologen) (DV^{2+} , $2 Br^-$)_n was prepared by the Menchustkin reaction [12] from 20×10^{-3} moles of dibromo α , ω decane and the same stoichiometric quantity of 4,4' bipyridine in 10 ml of a 1 : 1 dimethylformamide-methanol solution. The solution was continuously stirred during synthesis.

The initial reddish colour turned yellow after several hours. The stirring was maintained for one week. The product obtained was then precipitated

Table 1. Composition of $(DV^{2+}, 2 Br^-)_n$

Element: wt % Experimental; (Theoretical)			
C: 49.71 (52.63)	H: 6.55 (6.14)	N: 5.85 (6.14)	Br: 31.15 (35.5)

with an excess of acetone, centrifuged and washed with the same non-solvent several times and oven-dried. The composition of the product obtained is given in Table 1.

2.3. Ion exchange. Synthesis of poly(decaviologen) $(DV^{2+}, 2 ClO_4^-)_n$ and $(DV^{2+}, 2 CF_3SO_3^-)_n$

The poly(decaviologen) bromide $(DV^{2+}, 2 Br^-)_n$ was dissolved in 20 ml of water containing an excess of either $LiClO_4$ or $LiCF_3SO_3$. The solution was stirred, heated to 40°C, centrifuged, and then the water was removed. The process was repeated on the remaining solution after adding lithium salt and water. The exchanged poly(decaviologen) $(DV^{2+}, 2 ClO_4^-)_n$ or $(DV^{2+}, 2 CF_3SO_3^-)_n$ was then filtered and oven-dried, then ground and vacuum dried at 80°C in a BÜCHI unit.

The compositions of the poly(decaviologens) obtained after ion exchange are given in the following tables (Tables 2 and 3). The ion exchange efficiencies were estimated at 93% and 95%, respectively.

2.4. Thin film deposition

Three techniques for depositing the poly(decaviologen) on the stainless steel substrate were studied:

- Spraying, using a FISCHER air brush, of several millilitres of a polyviologen solution diluted in dimethylformamide (DMF) on a hot substrate followed by evaporation of the solvent.

- Painting, using a paint brush, of the substrate using the same solution as above followed by evaporation of the solvent by oven drying at 60°C.

- Spin-coating of the solution containing the polyviologen onto the stainless disk while the disk was rotated at an adjustable speed.

The most adhesive deposits were obtained by spraying and the most uniform by spin-coating on a rotating disk. For the subsequent tests, we chose to use the sprayed deposits. The thicknesses were approximately 10 µm as measured by SEM.

Table 2. Composition of $(DV^{2+}, 2 ClO_4^-)_n$

Element: wt % Experimental; (Theoretical)		
C: 48.83 (48.48)	H: 5.81 (5.65)	N: 5.37 (5.66)
O: 24.22 (25.86)	Cl: 13.55 (14.34)	Br: 2.71 (0)

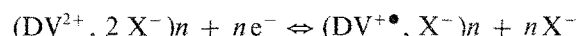
Table 3. Composition of $(DV^{2+}, 2 CF_3SO_3^-)_n$

Element: wt % Experimental; (Theoretical)		
C: 44.87 (44.44)	H: 5.07 (4.71)	N: 4.58 (4.71)
S: 9.90 (10.77)	F: 19.53 (19.19)	Br: 1.42 (0)

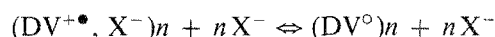
3. Results and discussion

3.1. Electrochemical studies

Three different oxidation states were expected with these materials, corresponding to the following redox equilibria:

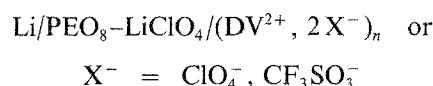


and



These electrochemical reactions are equivalent to anion intercalation (or de-intercalation) or 'n' doping of the poly(decaviologen).

3.1.1. Linear potential sweep voltammograms of $(DV^{2+}, 2 X^-)_n$: $X^- = ClO_4^-, CF_3SO_3^-$. Linear potential sweep voltammograms were made at 90°C on the chain:



The three-electrode cell described in a previous paper [10] was used. Li/Li^+ was chosen as the reference redox couple.

Two anodic peaks (2.24 and 2.66 V) and the corresponding cathodic peaks (2.34 and 2 V) were observed with $LiClO_4$ (Fig. 1). The same pattern is observed with $CF_3SO_3^-$ (Fig. 2).

The $E_{1/2}$ voltages of the couples $(DV^{2+}, 2 X^-)_n / (DV^{+\bullet}, X^-)_n$ and $(DV^{+\bullet}, X^-)_n / (DV^0)_n$ in the $PEO_8-LiClO_4$ and $PEO-LiCF_3SO_3$ complexes were, respectively, as given in Table 4. At this sweep rate (0.5 mV s^{-1}), the ratio of the anodic and cathodic charges for the first cycle is better than 80%. The following cycles give identical steady-state plots.

The variations of the peak anodic current (A) were

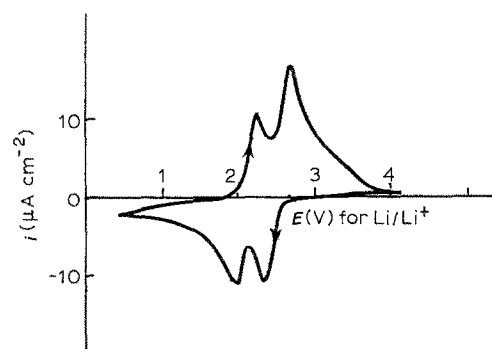


Fig. 1. Cyclic voltammogram of the cell $Li/PEO_8-LiClO_4/(DV^{2+}, 2 ClO_4^-)_n$. Operating temperature: 90°C; scan rate: 0.5 mV s^{-1} .

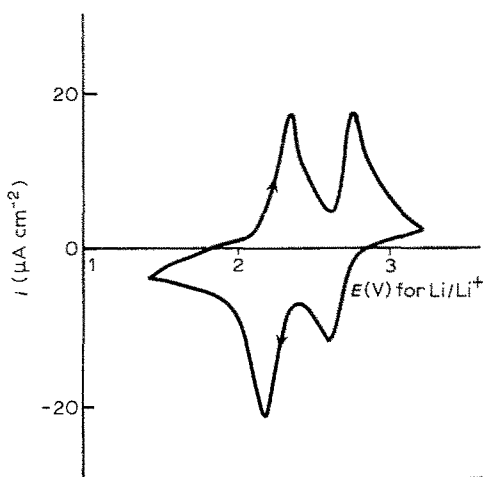


Fig. 2. Cyclic voltammogram of the cell Li/POE₃₀-LiCF₃SO₃/(DV²⁺, 2CF₃SO₃)_n. Operating temperature: 90°C; scan rate: 0.5 mV s⁻¹.

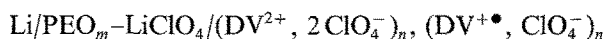
plotted as a function of the square root of the sweep rate ($v^{1/2}$) for the perchlorate ion (Fig. 3). The relationship between I_p and $v^{1/2}$ may be considered to be linear. Moreover, at slow sweep rates, the difference between the anodic and cathodic peaks shows little variation.

3.1.2. Preparation of the (DV²⁺, 2X⁻)_n/(DV^{+•}, X⁻)_n couples. The (DV²⁺, 2X⁻)_n/(DV^{+•}, X⁻)_n couple was obtained by *in situ* reduction of the following cell (Figs 4 and 5): Li/PEO_m-LiX/(DV²⁺, 2X⁻)_n with $m = 30, 60$ and X⁻ = ClO₄⁻ or CF₃SO₃⁻. We adopted the following experimental procedure:

- Constant temperature of 90°C.
- Slow galvanostatic discharge (C/100) up to total reduction of (DV²⁺, 2X⁻)_n. A rapid voltage variation at the transition between oxidation states (II/I) made it possible to accurately characterize the discharge duration.
- Rest period until reaching a steady-state voltage.
- Slow galvanostatic recharge (C/100) to half capacity. Isoactivity was then observed between (DV²⁺, 2X⁻)_n/(DV^{+•}, X⁻)_n.

The half-discharge voltages were measured by potential sweep voltammetry.

3.1.3. Measurement of the junctionless concentration cell e.m.f.. The following cell was prepared:



The redox couple (DV²⁺, 2ClO₄⁻)_n/(DV^{+•}, ClO₄⁻)_n must be reversible with respect to the ClO₄⁻ anion. We recorded the e.m.f. of these cells at equilibrium.

The influence of salt activity and temperature on the value of the e.m.f. was studied.

Table 4. $E_{1/2}$ voltages for CV scans of the polyviologen polymers operating temperature: 90°C scan rate: 0.5 mV s⁻¹

	LiClO ₄ (V)	LiCF ₃ SO ₃ (V)
$E_{1/2}(\text{V}^{2+}, 2\text{X}^-)/(\text{DV}^{+\bullet}, \text{X}^-)_n$	2.5	2.56
$E_{1/2}(\text{DV}^{+\bullet}, \text{X}^-)/(\text{DV}^0)_n$	2.1	2.20

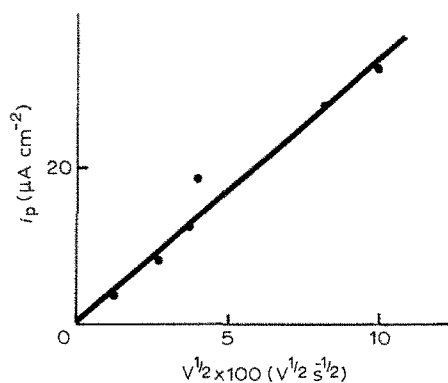


Fig. 3. Peak current density as a function of the square root of potential sweep rates. Operating temperature: 90°C; Cell Li/POE₈-LiClO₄/(DV²⁺, 2ClO₄⁻)_n.

(a) Influence of salt activity

The voltage values increased with decreasing salt activity (Table 5).

The e.m.f. values of junctionless concentration cells may be determined using the redox couple (DV²⁺, 2ClO₄⁻)_n/(DV^{+•}, ClO₄⁻)_n specific to the perchlorate ion.

Analogous tests could be conducted with the CF₃SO₃⁻ ion. However the measurement uncertainty would be higher since the molality interval is more restricted than with LiClO₄ for a single elastomeric phase [2, 3].

(b) Influence of temperature

The e.m.f. variations of the Li/PEO_m-LiX/(DV²⁺, 2X⁻)_n, (DV^{+•}, X⁻)_n cells were measured as a function of temperature (X⁻ = ClO₄⁻ or CF₃SO₃⁻).

With the perchlorate ion, two different regions may be distinguished (Fig. 6): (i) below 60°C, the e.m.f. decreases and then levels off; (ii) above 60°C, the e.m.f. decreases linearly. Two temperature domains may also be distinguished with CF₃SO₃⁻ (Fig. 7): (i) below 70°C, the e.m.f. is stable; (ii) above 70°C, the e.m.f. decreases as the temperature rises.

According to the phase diagrams [2, 3] (PEO-LiClO₄ or PEO-Li CF₃SO₃) the slope change with

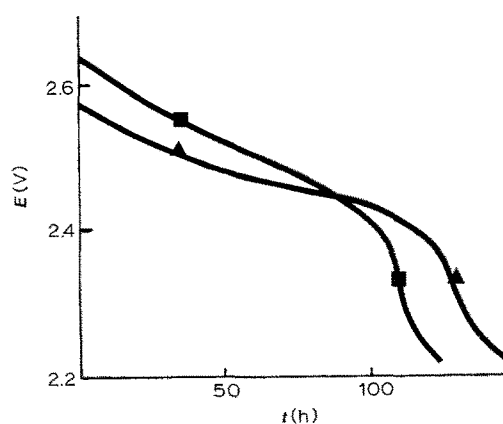


Fig. 4. Discharge curves of cells Li/PEO_m-LiClO₄/(DV²⁺, 2ClO₄⁻)_n. Operating temperature: 90°C; (▲) $m = 30$; (■) $m = 60$.

Table 5. Variation of the e.m.f. chain $\text{Li}/\text{PEO}_m\text{-LiClO}_4/(\text{DV}^{2+}, 2\text{ClO}_4^-)_n, (\text{DV}^{+\bullet}, \text{ClO}_4^-)_n$ as a function of salt activity.

e.m.f. (V)	2.533	2.594	2.624	2.631
m	8	30	60	120

temperature corresponds to the following equilibria for LiClO_4 at 60°C :



and



At temperatures less than 60°C or 70°C , the $\text{PEO}_8\text{-LiClO}_4$ and $\text{PEO}_{30}\text{-LiClO}_4$ complexes are in reality made up of the mixture $\text{PEO} + \text{PEO}_6\text{-LiClO}_4$ stoichiometric complex.

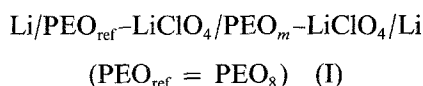
The activity is defined by the couple which is rich in $\text{PEO}_6\text{-LiClO}_4$. The same is true for the $\text{PEO}_m\text{-LiCF}_3\text{SO}_3$ complexes ($m = 30$ or 60), which are, in reality, made up of a mixture of PEO and $\text{PEO}_m\text{-LiCF}_3\text{SO}_3$ where m is likely in the neighbourhood of 6 [13].

At temperatures greater than 60°C or 70°C , the $\text{PEO}_m\text{-LiClO}_4$ or $\text{PEO}_m\text{-LiCF}_3\text{SO}_3$ complexes are amorphous and the e.m.f. varies according to the relationship:

$$E_m = E_{(\text{ref})} - \frac{2RT}{F} \ln a_{\pm}(m)$$

3.2. Measurement of the transport number in $\text{PEO}_m\text{-LiClO}_4$ media

3.2.1. Principle. We determined the transport number of lithium in PEO media from measurements of the e.m.f. of the concentration cell with a junction (I):



The average activity involved in the determination of the transport number is obtained using the e.m.f. of

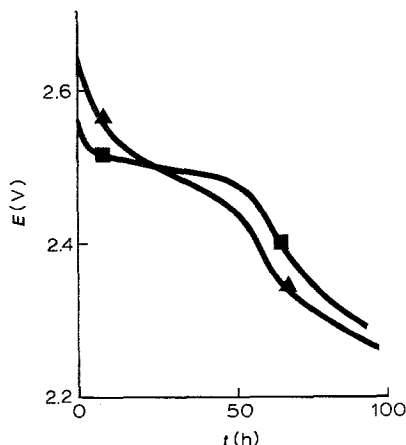


Fig. 5. Discharge curves of cells $\text{Li}/\text{PEO}_m\text{-LiCF}_3\text{SO}_3/(\text{DV}^{2+}, 2\text{CF}_3\text{SO}_3^-)_n$. Operating temperature: 90°C . (\blacktriangle) $m = 30$; (\blacksquare) $m = 60$.

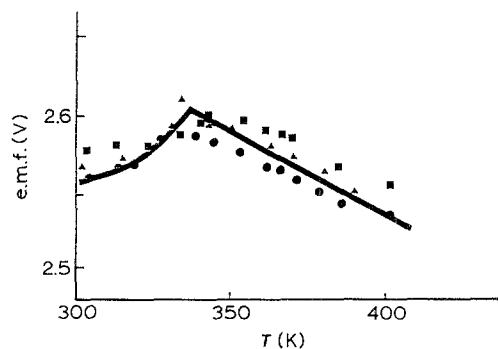
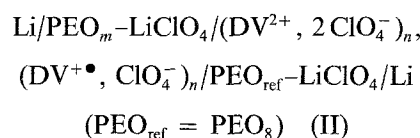
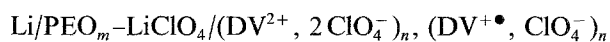


Fig. 6. Cell (1) e.m.f. variation with temperature. $\text{Li}/\text{PEO}_{30}\text{-LiClO}_4/(\text{DV}^{2+}, 2\text{ClO}_4^-)_n, (\text{DV}^{+\bullet}, \text{ClO}_4^-)_n$ (1) Values plotted for cooling temperatures. (\bullet), (\blacktriangle) and (\blacksquare) were 3 different cells.

the junctionless galvanic chain (II).



The e.m.f. of this cell is calculated from the e.m.f.'s of the cells:



The transport number expression is:

$$t_c^{X^-} = \frac{\partial E_j^{\text{ref}}(m)}{\partial E_{\text{sj}}^{\text{ref}}(m)}$$

where $t_c^{X^-}$ = transport number of X^- , E_j^{ref} = e.m.f. of the concentration cell with a junction, $E_{\text{sj}}^{\text{ref}}$ = e.m.f. of the junctionless concentration cell.

3.2.2. Results. The e.m.f. values of the concentration cells with junctions ($\text{PEO}_{\text{ref}} = \text{PEO}_8$) are plotted as a function of the junctionless concentration cells for the case of the ClO_4^- ion (Fig. 8). The measurements were made at 90°C .

The transport number is: $t_c^{\text{Li}^+} = 0.21 \pm 0.08$. This result is similar to those obtained using other methods [4, 5] and to the result we have already published for the PEO-LiI complex [10]. Moreover, the value is similar to those measured in aprotic organic electrolytes [14]. This lends support to the analogy of solvation mechanisms in these different media.

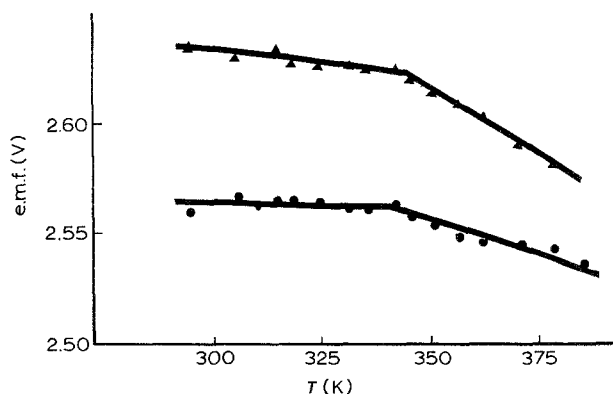


Fig. 7. Cell (2) e.m.f. variation with temperature. $\text{Li}/\text{PEO}_m\text{-LiCF}_3\text{SO}_3/(\text{DV}^{2+}, 2\text{CF}_3\text{SO}_3^-)_n, (\text{DV}^{+\bullet}, \text{CF}_3\text{SO}_3^-)_n$ (2). (\blacktriangle) $m = 30$; (\blacksquare) $m = 60$.

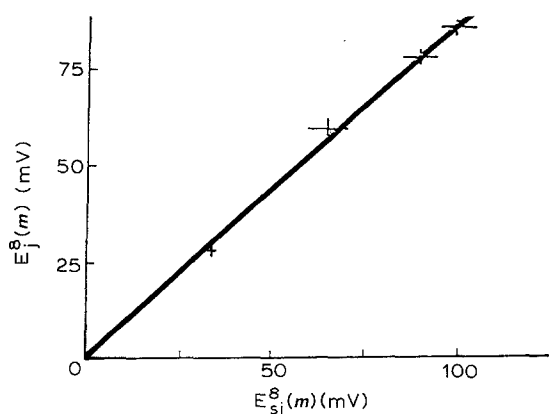


Fig. 8. Cell (3) e.m.f. variation versus cell (4) e.m.f. variation. Reference electrolyte O/Li ratio = 8, operating temperature 90°C. Cell (3): Li/PEO₈-LiClO₄/PEO_m-LiClO₄/Li; Cell (4): Li/PEO₈-LiClO₄/(DV²⁺, 2ClO₄⁻)_n, (DV^{+•}, ClO₄⁻)_n/PEO_m-LiClO₄/Li.

For liquid electrolytes, the transport numbers have been related to the respective sizes of the solvated positive and negative charges, but such an approach cannot be considered for polymer electrolytes. The mobility of the cations in solvating macromolecules is definitely related to the kinetics of ligand (ether oxygen) around the central ion and the ratio cation/anion mobility appears relatively insensitive to size, as shown already for the bulky tetraphenylborate anion [15]. On the other hand, the triflate anion give an apparent value:

$$t_c^{\text{Li}^+} = 0.75$$

Such a high value has to be compared with a mobility ratio $D_F/D_{\text{Li}} \approx 2$ as determined by fluorine-19 and lithium-7 NMR pulsed field gradient technique [16] for the same salt. These two conflicting results can only be reconciled if we consider the existence of triplet ions, like $[(\text{CF}_3\text{SO}_3)_2\text{Li}]^-$ with Li^+ as countercharge. The diffusion of neutral species (LiCF_3SO_3), not detected by our potentiometric technique, would result in apparently equal mobilities for the + and - species seen by the NMR PFG technique.

4. Conclusions

Poly(decaviologen) (DV²⁺, 2X⁻)_n (X⁻ = ClO₄⁻ or

CF₃SO₃⁻) has been synthesised by ion exchange on the bromide derivative.

The voltammograms of these products confirms three degrees of oxidation (II, I and O). The $E_{1/2}$ voltage values are comparable for both ions (perchlorates or trifluoromethane sulphonates).

The redox couple was prepared *in situ* by coulometry.

The e.m.f. variation of the Li/PEO_m-LiX/(DV²⁺, 2X⁻)_n, (DV^{+•}, X⁻)_n cells with temperature depends on the nature of the phases present in the electrolyte and is consistent with the PEO-LiX phase diagrams.

Other thermodynamic quantities could be determined by this type of study, in particular those of salts complexing by the PEO chain.

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