

## CATIONIC TRANSPORT NUMBERS IN POLYETHER-BASED NETWORKS CONTAINING LITHIUM SALTS

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### Summary

Measurements of the  $\text{Li}^+$  transport number by the Tubandt method on solid electrolytes based on polyethers crosslinked with triisocyanates containing various lithium salts gave values consistently indicating the predominance of anionic conduction. Transport numbers ( $t^+$ ) were found to be temperature independent between 70 and 120 °C, but to decrease as the salt concentration increased. The other parameters studied were the nature of the anion and the structure and length of the polyether segments.

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### Introduction

Organic polymer/alkali metal salt combinations as potential solid electrolytes for high-energy density batteries are being studied in several laboratories using different approaches. We have concentrated on using polyether-based networks possessing both a strong solvating action on the salt's cation and a good mechanical and dimensional stability. The relevant literature on these investigations is given in two of our most recent publications [1, 2].

Only in the last few years has the problem of transport numbers been tackled. The techniques used include e.m.f. measurements on concentration batteries [3],  $^7\text{Li}$  NMR studies [4, 5], complex impedance diagrams [6 - 8], and diffusion coefficient determinations with radioactive tracers [9]. The values of the cationic transport number ( $t^+$ ) reported for the first two methods were close to unity, while with the latter two techniques  $t^+$  was close to 0.5. All these results refer to *linear*, high molecular-weight poly(ethylene oxide)s charged with different alkali metal salts. The important discrepancies encountered in the literature concerning the value of  $t^+$  and the well-known problems associated with the pronounced tendency displayed by poly(ethylene oxide) (PEO) towards crystallisation [1] prompted us to investigate the issue of transport numbers with a more rigorous technique on the amorphous polyether networks previously developed [1, 2]. The Tubandt method [10] was selected for such studies, and the first set of results [11] showed unequivocally that the conduction arising from a

variety of salts dissolved in our crosslinked materials was essentially anionic, *i.e.*,  $t^+$  was small except with very large anions. We now report further results dealing more specifically with lithium salts and with the effect of various parameters upon  $t^+$ .

## Experimental

The synthesis of polyether networks crosslinked with polyisocyanates in the presence of alkali metal salt has been described in detail in a previous paper [12]. Three commercial polyethers were used, *viz.*, a poly(ethylene oxide)  $\bar{M}_n = 1000$  (POE 1000), a poly(propylene oxide)  $\bar{M}_n = 1025$  (POP 1025), and a triblock copolymer POE(2000)-*b*-POP(1000)-*b*-POE(2000), each oligomer possessing two terminal hydroxyl groups. A fourth polymer was also tested as precursor for crosslinking with isocyanates, *viz.*, a poly(dimethylsiloxane)-*g*-POE,  $\bar{M}_n = 21\,300$  containing 75% of POE and an average OH functionality of 16. Network formation with the linear polyethers was induced by 4,4',4''-methylidyne-tris(phenyl isocyanate), while 1,6-hexamethylene-diisocyanate was used to crosslink the graft silicone-POE copolymer [12]. The two salts selected for this study were  $\text{LiClO}_4$  and  $\text{LiCF}_3\text{SO}_3$ .

Transport numbers were determined following the Tubandt technique [10] which consists in measuring the weight changes induced by the passage of a known amount of current through an electrochemical assembly comprising the electrolyte and the two electrodes. Five disks of the present electrolyte (network plus salt) were carefully assembled between two silver electrodes after determining their individual weights. The system was introduced into the measurement cell which was then evacuated and brought to constant temperature. A precisely known amount of current was passed through the electrolyte, typically about  $10^{-4}$  A during about 20 h, and thereafter the system was dismantled and each disk reweighed. The calculations leading to the  $t^+$  values are based on elementary electrochemical considerations, as developed in a previous publication [11].

## Results and discussion

The first basic check we carried out was to verify that the values of transport numbers did not depend on either the voltage or the total amount of current used. Having established that this was indeed the case, and that reproducibility was satisfactory for any two sets of experiments conducted under identical conditions, we proceeded to study the effect of some physical and chemical parameters.

(a) *The temperature.* No significant change in  $t^+$  was observed in any given system when the temperature was varied between 70 and 120 °C.

(b) *The polymer.* As shown in Table 1 and in the previous investigation [11], anionic conduction prevails ( $t^- > 0.60$ ) with all networks studied.

TABLE 1

Transport numbers ( $t^+$ ) due to  $\text{Li}^+$  conduction across polyether membranes crosslinked with isocyanates (see text)

Polyethers*	Lithium salt	$\frac{\text{O}^{**}}{\text{Li}}$	$t^+$
POE 1000	$\text{LiClO}_4$	59	0.37
POE 1000	$\text{LiClO}_4$	36	0.30
POE 1000	$\text{LiClO}_4$	24	0.19
POE 1000	$\text{LiClO}_4$	20	0.23
POE 1000	$\text{LiClO}_4$	12	0.23
POE 1000	$\text{LiClO}_4$	8	0.23
POE 1000	$\text{LiCF}_3\text{SO}_3$	24	0.21
TC	$\text{LiClO}_4$	227	0.30
TC	$\text{LiClO}_4$	26	0.36
TC	$\text{LiClO}_4$	14	0.16
TC	$\text{LiClO}_4$	10	< 0.02
POP 1025	$\text{LiClO}_4$	34	0.25
GPDMS	$\text{LiClO}_4$	11	0.20

\*POE: Poly(ethylene oxide),  $\bar{M}_n = 1000$ ; POP: poly(propylene oxide),  $\bar{M}_n = 1025$ ; TC: triblock copolymer POE(2000)-*b*-POP(1000)-*b*-POE(2000); GPDMS: poly(dimethyl siloxane)-*g*-POE(1000).

\*\* $\frac{\text{O}}{\text{Li}}$  : ratio of ether oxygen atoms to lithium cations.

The mechanism of ionic transport seems to be essentially independent of the chemical nature of the segments formed between crosslink points and of their length. In order to rule out the possible contribution of the urethane linkages, we also studied the  $\text{Ag}^+$  transport number in linear, pure polyethers containing  $\text{AgClO}_4$ . Because of adhesion problems, both among the disks and between the disk and the electrode, a modified Tubandt technique was applied [11]. With POEs ranging in molecular weight from 1000 to  $9 \times 10^5$ , the trend shown by all networks was clearly confirmed, since the cationic transport numbers never exceeded 0.2 with these linear polyethers.

Networks containing lithium perchlorate were analysed, after electrolysis, by X-ray fluorescence. Scanning through the whole membrane proved that  $\text{ClO}_4^-$  had, indeed, migrated towards the anode.

(c) *The anion.* All other parameters being kept constant, transport numbers were determined with  $\text{LiClO}_4$  and  $\text{LiCF}_3\text{SO}_3$ . As shown in Table 1, no significant difference in quantitative behaviour could be detected.

(d) *Salt concentration.* The results in Table 1 clearly show that transport numbers in the various networks studied depend on the salt concentration used.

In the case of POE 1000-based networks,  $t^+$  decreases monotonically with increasing salt concentration up to a "critical" value corresponding to one lithium ion *per* polyether segment ( $\text{O}/\text{Li} = 22$ ). Above that concentra-

tion,  $t^+$  tends to level off to a constant value of about 0.23. At low salt concentrations, the lithium cations are solvated by the ether oxygen atoms, one such ion being placed on a given polyether segment. The number of "free" segments decreases with increasing salt concentration: this induces a decrease in the mobility of lithium cations and a corresponding increase in the mobility of the anion, due to the growing number of positive sites along the network facilitating its migration towards the anode. The presence of a second lithium cation on some polyether segments above the "critical" concentration discussed above must introduce electrostatic repulsion phenomena of growing importance. The formation of multiplets could rationalise the observed constancy of  $t^+$  above the "critical" concentration.

In the case of networks prepared from the triblock copolymer, the cationic transport number was found to decrease with increasing salt concentration, as in the previous system, but no "critical" concentration could be detected and  $t^+$  approached values close to zero at the highest salt concentrations used. It can be argued that, in this context, the formation of multiplets is unlikely because of the enhanced structural disorder of the chain segments between urethane linkages. The progressive decrease of the cationic transport number with increasing salt concentration is probably due, again, to electrostatic interactions among lithium ions which reduce their mobility, thus inducing a corresponding increase in  $t^-$ .

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