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IONIC CONDUCTIVITY AND LITHIUM TRANSFERENCE NUMBER OF POLY (ETHYLENE OXIDE):LiTFSI SYSTEM

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ABSTRACT

Polymer electrolytes comprising $LiN(CF_3SO_2)_2$ salt (LiTFSI) and high molecular weight poly(ethylene oxide) PEO are prepared by casting from solution. A wide range of salt concentration is studied, from molar ratio EO:Li of 50:1 to 1.5:1. Samples of electrolytes are measured in symmetrical Li|electrolyte|Li cell. The values of lithium transference number t^+ of electrolytes are determined using a novel procedure, which involves impedance spectroscopy as well as two potentiostatic polarization segments with opposite sign of d.c. bias. The principles of this procedure are based on Bruce-Vincent method, which has been extended in order to compensate the possible differences in properties of the two Li|electrolyte interfaces, and ensure proper conditioning of the cell between different stages of the measurement process. The results are analyzed using Bruce-Vincent and Watanabe approaches, which give similar values of lithium transference number. The reported values of t^+ initially decrease with rising concentration of salt, but after passing a minimum at molar ratio EO:Li of around 6:1, a considerable increase is recorded, eventually leading to lithium transference number higher than 0.5 for "polymer in salt" systems. Such behavior of the studied system is discussed either in terms of formation of PEO:salt complexes, or formation of ionic aggregates.

1. Introduction

The choice of materials for solid electrolytes applied in rechargeable lithium-ion cells is usually based on the value of their ionic conductivity, electrochemical stability versus electrode materials and convenient mechanical properties. An equally important and often underestimated factor is the ratio of charge transported by lithium ions to the overall charge transport– quantitatively described by the cation transference number t^+. Unfortunately, for most electrolytes based on polymers with dissolved lithium salts, the values of cation transference number are found to be low, often below 0.5. Apart from decrease of efficiency of charge transport process in the cell, low cation transference number can possibly lead to unwanted phenomena, like precipitation of salt at the anode and depletion of electrolyte at cathode [1]. As an example of great practical importance of lithium transference numbers, the goals set by United States Advanced Battery Consortium (USABC) can be quoted: for electrolytes with two or more mobile ion species, the conductivity required for application in a battery is 1×10^{-3} S/cm at room temperature, whereas for single ion conducting electrolyte the threshold is much lower and equals 1×10^{-4} S/cm [2].

Correct determination of lithium transference number t^+ for polymer electrolytes often represents a challenging task. Most of experimental methods proposed so far involve assumptions, which can be fulfilled only in part for polymer electrolytes or involve calculation of quantities which are difficult to measure for solids. Hittorf method [3] and Tubandt method [4], based on measurement of changes of mass or concentration of ionic species in the vicinity of reversible electrodes when passing known amount of charge, are relatively simple and produce accurate results for liquid electrolytes. For polymer electrolytes in the form of thin films, measurement of changes in the concentration of ionic species is very difficult to carry out as the concentration gradients may quickly expand into the entire electrolyte volume after applying an external voltage, or simply because of the limited precision with which the concentration changes at the electrodes can be determined. For liquid electrolytes the ions move together with their solvation shell, and therefore the values obtained by the Hittorf method were also described as the "apparent" transference numbers.

Concentration cell method [5] involves the analysis of a junction potential between two electrolytes composed of the

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same solvents and salts but with different salt concentration. For this method, however, it is necessary to establish the dependence of both the transference number and the activity coefficient on the salt concentration. Another method – pulsed field gradient nuclear magnetic resonance imaging (pfg-NMR) [6] involves predicting contributions of ionic species to the overall conductivity in respect to the Nernst - Einstein relation between carriers mobility and diffusion coefficients. Condition of total ion dissociation, which is one of the assumptions of this method, may not be fulfilled in many types of solid electrolytes, especially in polymer electrolytes with high salt concentration.

Alternating current method, proposed by Sørensen and Jacobsen [7], is based on comparison of sample impedance values measured at high and very low frequencies. Due to low values of ion diffusion coefficient, measurements of transference number in polymer electrolytes by this technique might require very long time, which makes it vulnerable to possible time instability of the measured system. Method described by Bruce and Vincent [8] combines measurements of impedance spectra and data obtained by potentiostatic polarization of sample. The measurements are performed in a symmetrical cell with electrodes reversible for the lithium cation – in practice, lithium metal plates are usually applied. This method allows for relatively quick determination of t^+ but, in the original approach, seems to be vulnerable to numerous error sources, originating not only from measuring equipment but also from preparation and conditioning of the measurement cell. Another method, which involves galvanostatic measurements has been developed by Newman et al. [9]. This approach, intended for electrolytes with non-uniform distribution of ion concentration in the sample, has been described as relatively simple and independent from “unwarranted” assumptions. However, also in this case calculation of t^+ involves a number of experimental quantities, each adding a significant uncertainty to the final value.

As the methods described above are based on measurement of different physical quantities, and represent theoretical assumptions which can be fulfilled only partly in case of polymer electrolytes, the values of transference number may also show substantial differences. Bruce and Vincent [10] have proposed to divide the methods into three classes, with class I and II methods probing only the transport of charged species, and class III methods probing diffusion coefficient of all species (charged and neutral) which contain given constituent of the electrolyte. Following this classification, a differentiation between transference number (related to fraction of charge carried by cations or anions) and transport number can be made. Recalculation of both quantities requires a well-defined model of ionic transport in the system. Such models including the influence of dissociation and formation of ionic pairs on the ionic transport were presented for PEO-based electrolytes [11,12].

For PEO:LiTFSI system, studied in our work, the values of t^+ reported so far also exhibit a strong variation, depending on method of their estimation. The dependence of t^+ upon concentration of salt was studied by Gorecky et al. [13,14] and Edman et al. [15]. In the work of Gorecky et al. [13], based on results of pfg-NMR, values of the lithium transport number obtained for electrolytes with molar ratio between 20:1 and 6:1 EO:Li were generally lower than 0.3 and exhibited a minimum of about 0.16 for electrolyte with EO:Li of 8:1. However, later publication from the same group [14] shows that when the measurements were performed under external electric field, much higher value of cationic contribution to conductivity was obtained ($t^+ = 0.57$ for EO:Li of 8:1). On the other side Edman et al. [15] presented results of electrochemical measurements based on the Newman approach and concentrated solution theory. The obtained values of transference number exhibited a steadily increasing trend with increasing amount of salt, starting from $t^+ = 0.2$ for EO:Li of 30:1, and eventually reaching 0.6 at EO:Li of 5:1. Numerous publications report transference and transport number for just one electrolyte composition. The calculated values of t^+ for electrolytes with EO:Li up to 5:1 fall usually between 0.05 and 0.3 [16–21]. As reported recently, values of t^+ calculated according to diffusion coefficients depend also on the length of PEO chains used as electrolyte matrix, and systematically decrease with increasing molecular weight of PEO [22]. Low values of t^+ have been obtained also for LiTFSI dissolved in polymer matrix based on PEO-MEEGE copolymers with comb-like structure (0.07 for EO:Li = 25:1) [23] and with network structure (0.05–0.08 for molar ratio 17:1 EO:Li) [24].

Also the results of the reports on temperature dependence of lithium transference numbers are not unambiguous. The transport numbers obtained from pfg-NMR measurements between 60 °C and 100 °C have been described as temperature independent in the studied temperature range [13]. On the other hand, values calculated from electrochemical measurements in the range between 50 °C and 90 °C were reported to show a significant increase with temperature, from 0.11 to 0.18 [16]. Most reports give value only at a single temperature, usually above the melting point of the electrolyte. Therefore, the transport properties of electrolytes with lower melting point are usually reported at lower temperature [17,19], than corresponding properties of electrolytes with higher melting point [13,15]. Values of t^+ obtained for PEO:LITFSI system by different research groups are summarized in Fig. 1. For clarity of presentation, a differentiation between transport numbers and transference numbers has been made, although it should be noted that for some custom-developed methods such division had an arbitrary character.

As PEO:LiTFSI was initially considered to be one of most promising systems in terms of ionic conductivity and electrochemical stability, the low values of lithium transference numbers described above might seem discouraging. Various efforts have been made to improve the share of lithium cations in the overall charge transport. In one of the approaches to this problem, the poly (ethylene oxide) is replaced with other polymer hosts, which create much weaker coordination bonds with lithium. For polycarbonates with LiTFSI salt, values of t^+ as high as 0.8 were obtained for molecular ratio of monomer to salt of 8:1 [25]. Promising results in terms of both ionic conductivity and cation transference number were obtained also for poly(ε-caprolactone) (PCL) with carbonate units incorporated in the polymer backbone [21]. The architecture of PEO matrix can be also modified in order to improve lithium transference numbers. Recent reports show

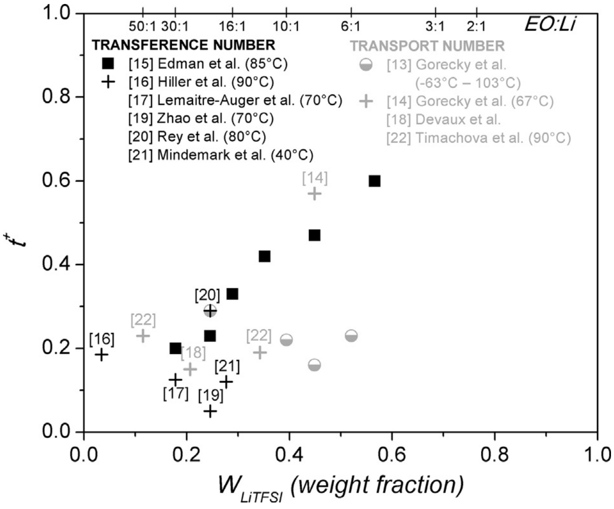

Fig. 1. Values of the cation transference number and lithium transport number obtained for PEO:LITFSI system by different research groups.