Comparative determination of effective transport numbers in solid lithium electrolytes

H. P. Fritz

Institute for Inorganic Chemistry, Technical University of Munich, Lichtenbergstraße 4, D-8046 Garching (Germany)

A. Kuhn

CNRS Centre de Recherche Paul Pascal, avenue Schweitzer, F-33600 Pessac (France)

Abstract

A comparison of the effective transport numbers t_+ of the lithium cation in immobilized liquid electrolytes, obtained by mixing molar solutions of $LiClO_4$ in propylene carbonate with varying amounts and types of highly-dispersed pyrogenic silica is presented. The results vary from 0.1 to 0.4 as determined by (i) a.c. complex impedance spectroscopy; (ii) isothermal transient ionic current method; (iii) steady-state current method, and (iv) Tubandt method. Main object of this study was to evaluate the value of the four methods as simple, practically useful means to check effective cationic transport numbers of ionic conductors without extensive ion aggregation.

Zusammenfassung

Ein Vergleich der effektiven Überführungszahl t_+ des Lithium-Kations in immobilisierten Flüssigelektrolyten, die durch Mischen molarer Lösungen von $LiClO_4$ in Propylencarbonat mit wechselnden Mengen und Arten hoch-disperser, pyrogener Kieselsäure erhalten werden, wird vorgestellt. Die Resultate variieren von 0,1 bis 0,4, wie Messungen (i) mittels Impedanz-Spektroskopie; (ii) nach der 'isothermal transient ionic current'-Methode; (iii) nach der 'steady-state current'-Methode und (iv) nach Tubandt ergaben. Hauptzweck dieser Studie war die Überprüfung der vier Methoden auf ihre Eignung als einfacher, in der Praxis nutzbarer Weg zur Festlegung effektiver Überführungszahlen von Ionenleitern ohne erhebliche Ionenaggregation.

Introduction

In the course of the last decade a whole series of lithium batteries have appeared on the market. Current interest concentrates on constructing all-solid-state batteries and this has stimulated research in solid electrolytes. Various polymer and ceramic electrolytes have, therefore, been examined, mostly without great success because of their low ionic conductivity at ambient temperature, the poor interfacial contact between electrode and electrolyte, or their unsatisfactory stability. For a highly efficient electrolyte, it is desirable to have a transport number near unity for the relevant ion, i.e., it should carry a fraction of current as big as possible. A variety of methods has been used over recent years to examine this property. However, the reported transport numbers

differ considerably for one and the same electrolyte [1, 2]. These discrepancies might be due to the principally questionable validity and experimental limitations of the various methods. It seemed worthwhile to compare results and thus the validity of the most often used electrochemical methods. Therefore, we decided to examine the immobilized liquid electrolytes described by us recently [3] by using (i) a.c. complex impedance analysis; (ii) isothermal transient ionic current (ITIC) method; (iii) steady-state current (SSC) method, and (iv) the classical Tubandt method.

Experimental

Samples of the immobilized liquid electrolytes were prepared as follows: Propylene carbonate (PC) (Aldrich 99 + %) was distilled once and stored over molecular sieves (3 Å). The water content was established by coulommetric Karl Fischer titration to be less than 20 ppm. $LiClO_4$ and $LiCF_3SO_3$ (Aldrich) were dried 10 h under high vacuum at 50 °C prior to use. Three types of pyrogenic, highly-dispersed silica (Aerosil, Degussa: A 90, A 200, and A 380) with specific surface areas: 90, 200 and 380 m^2 g^{-1} and an approximate density of surface silanol groups of 0.2, 0.35 and 0.5 nm^2/ SiOH, respectively, were used. The silica was also dried 10 h under high vacuum but at a temperature of 100 °C prior to use. A 1 M solution of $LiClO_4$ or $LiCF_3SO_3$ in PC was added dropwise under argon atmosphere to the silica samples and intensely mixed; gas bubbles were removed by applying vacuum. A transition from powder to gel was observed on addition of 5 ml electrolyte per g A 380, of 4 ml per g A 200, and 2.5 ml per g A 90, corresponding to ∼ 50 PC molecules per surface OH group. In the ^7Li-NMR spectrum, the line width decreases by the factor 10 in this concentration range. Since, due to the thixotropic behaviour definite viscosities of the products were difficult to establish and measure, this well-defined transition was accepted as the standard state of gel formation. All gels were stored under argon for the same period of time, prior to the comparative measurements, because of an ageing effect observed previously [3].

For the impedance measurements, as well as for the steady-state current method, an electrochemical cell with a diameter of 13 mm containing lithium electrodes at the bottom and the top was filled with a 0.3 mm thick layer of the electrolyte under argon atmosphere. The spectra were recorded with a Zahner IM5d equipment, typically in the frequency range form 10^5 to 10^{-4} Hz. ITIC measurements were carried out in a cell with platinum electrodes of a diameter of 10 mm and an electrolyte layer of 1 mm in between. The potential was kept at constant values with a commercial potentiostat (MP75, Fa. Gerhard Bank Elektronik).

For the Tubandt method a Knick precision power supply was used to apply a constant current of 5 μA to a cell containing 2.2 mm of electrolyte between two platinum electrodes with a diameter of 15 mm.

Results and discussion

Ion association
It is known that in ionic conductors on the basis of $LiClO_4$ dissolved in e.g. polyethylene oxide (PEO) or in aprotic solvents with low dielectric constants, such as tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), ($\epsilon < 10$), ion pairing/aggregation is to be preferentially expected [4], which can make the determination or interpretation

of transition numbers impossible [5]. However, in solutions of alkali salts in PC ($\varepsilon = 64.4$) ion pair formation is not significant [6]. Very recently, no evidence for ion association was detected even in a poly(propylene oxide)–LiClO$_4$ solid electrolyte [7]. It is understandable, that Li$^+$ ions will be strongly solvated in PC [8, 9], while the ClO$_4^-$ ion is known to coordinate and solvate only poorly.

We checked the LiClO$_4$/PC system by Raman spectroscopy, since interactions of the ions with solvent support or each other should be manifested by additional or shifted lines [11, 12].

For LiClO$_4$ we find ν_1 (of the tetrahedral anion) with high intensity in the crystalline state at 959.6 cm^{-1}, in H$_2$O solution at 935.2 cm^{-1}, in 1 M solution in PC at 933.8 cm^{-1}, and in 1 M solution in PC + A380 at 932.0 cm^{-1} without any accompanying lines. The three degenerate modes ν_2, ν_3, and ν_4, should be sensitive to symmetry changes as a consequence of ion aggregation. They appear at 448, 1082, and 638 cm^{-1}, respectively, in the immobilized electrolyte again without any 'splitting', as it is found for ν_3 in the crystalline state (1061 and 1147 cm^{-1}) [10]. For polymeric conductors this aspect is discussed in refs. 7, 11, and 12.

On the other hand, interaction of PC via its C=O group with lithium ions and additionally with (Si–OH) surface groups of silica [13] is manifested by the appearance of shoulders of the 1786 cm^{-1} line at 1802 and 1822 cm^{-1}. The first coordination sphere of Li$^+$ in PC can be assumed to contain 4 PC molecules out of the c. 11 mol PC/mol LiClO$_4$ in our 1 M solutions. It is certainly this complex formation and separation of the ions by solvation, which effectively hinders ion pairing in our system.

Impedance spectroscopy

The impedance of an electric system is given by the equation:

$$Z(\omega) = E_o/I_o \, \exp(-i\Delta\Phi) \tag{1}$$

where E_o and I_o are the amplitudes of the applied potential and the obtained current response, respectively. The phase difference $\Delta\Phi$ depends on the nature of the system which can be described by coupling the charge-transfer resistance R_t, the double layer capacity C_{dl}, the bulk resistance of the electrolyte R_b and the geometrical capacity C_g of the sample. Each frequency is related to a vector in the complex impedance plane, which results in a whole spectrum, the Nyquist diagram. According to MacDonald [14, 15] and Soerensen and Jacobsen [16], at very low frequencies the amount of charge transferred during a half-cycle produces concentration gradients. This gives rise to an additional arc in the spectrum which reflects the diffusion impedance Z_d. With blocking electrodes for one ion and nonblocking electrodes for the other one, it has been shown [16] that in the limit of very thin electrolyte films and reversible electrode reaction and assuming sufficiently strong dissociation – as we consider it justified in our case –

$$Z_d = R_b \mu_2/\mu_1 \ (\text{or in our case } Z_d = R_b \mu_-/\mu_+) \tag{2}$$

where μ_1 is the mobility of the ion participating in the electrode reaction and μ_2 the mobility of the counter ion. As the transport number in a monovalent electrolyte is given by:

$$t_+ = \mu_+/(\mu_+ + \mu_-) \tag{3}$$

t_+ can be expressed by:

$$t_+ = (Z_d/R_b + 1)^{-1} \tag{4}$$

The main problem in real measurements is that the arc corresponding to Z_d is difficult to observe, because the characteristic diffusion time should be at least of the same order as the time constant of the Faradaic process [17]. This may be achieved by heating the sample but degradation of the lithium electrodes is a limiting factor. Accelerated formation of a solid electrolyte interface (SEI) is the consequence [18–20]. It governs the characteristics of the sample at the end of the long-lasting measurements and makes the results nonreproducible. Therefore, all measurements were carried out at ambient temperature and the partly formed arc was completed approximately by extrapolation. A typical spectrum in the range from 10^5 to 10^{-4} Hz is shown in Fig. 1.

In the case of gels prepared with 1 M LiClO$_4$/PC we found $t_{Li^+} = 0.12 \pm 0.1$, 0.13 ± 0.1, and 0.17 ± 0.1 for A 90, A 200, and A 380, respectively. Since a value of 0.19 is reported for pure 1 M LiClO$_4$/PC [9, 21], there is no strong specific interaction of the oxide surface with the ions. The reliability of these results, however, remains doubtful, since even at ambient temperature the formation of a SEI is not negligible, see Fig. 2, as has been shown by other authors [22].

Using 1 M LiCF$_3$SO$_3$/PC a significant increase of the lithium ion transport number to 0.44 was observed. This is probably due to the enhanced ability of the CF$_3$SO$_3{}^-$ anion to interact via hydrogen bonds [23] with silanol groups of the silica surface [24]. It should be mentioned that with this electrolyte lower specific conductivities are registered than with LiClO$_4$/PC.

Steady-state current method

Another possibility to measure the cationic transport number is the SSC method, originally developed by Bruce and Vincent [5] for solid electrolytes having no supporting electrolytes, no convection and no ion-associated species. Since our immobilized
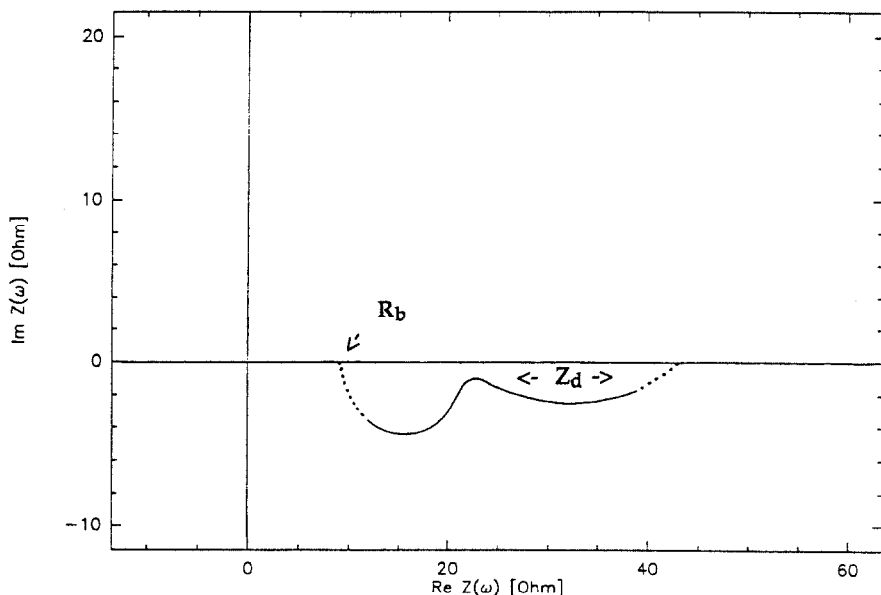

Fig. 1. Typical impedance spectrum of a gel electrolyte in the range from 10^5 to 10^{-4} Hz at room temperature.
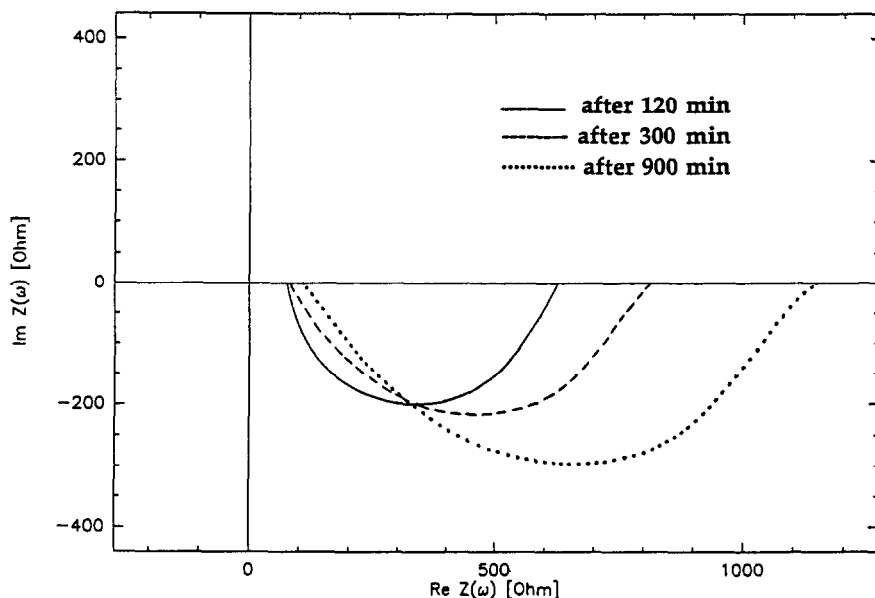
Fig. 2. Evidence for formation of the solid electrolyte interface at room temperature as a function of time.

LiClO$_4$/PC electrolyte must be considered as liquid electrolyte in the pores of a ceramic material and without significant ion pairing, we were interested to study the practical value of the method for a simple determination of an effective transport number, aware of the limitations listed by the authors.

An electrochemical cell with nonblocking electrodes for the cation is polarized by the application of a small potential. The initial current I_i is found to decrease to a steady-state value I_s. The main part of this drop is considered to result from the establishment of a concentration gradient in the electrolyte, but an additional decrease due to the formation of a passivating layer (SEI) cannot be neglected. Using impedance spectroscopy to determine the resistance of the passivating layer in the initial (R_i) and the steady state (R_s) the transport number is obtained by:

$$t_+ = (I_s(\Delta V - I_i R_i))/(I_i/(\Delta V - I_s R_s)) \tag{5}$$

where ΔV is the applied polarization potential.

It was observed that the smaller the specific surface of the silica the sooner the current reaches a steady state (Fig. 3). Obviously the addition of the silica slows down the diffusion and migration of both the cation and the anion because of interaction with the solvent. However, the calculated transport number does not vary with the specific surface of the silica. It is 0.3 $\pm$0.05 for all three silica types with LiClO$_4$/PC and 0.6$\pm$0.1 with LiCF$_3$SO/PC. Compared with the results of the impedance analysis an increase by a factor 2 occurs. This can be explained by the fact that after reaching the steady state of migration and back diffusion a further small decrease in current proceeds. This decrease is caused by the slow growth of a SEI which already exists during the former polarization. The estimated values of t_+, therefore, should be considered as upper limits of the effective transport numbers.
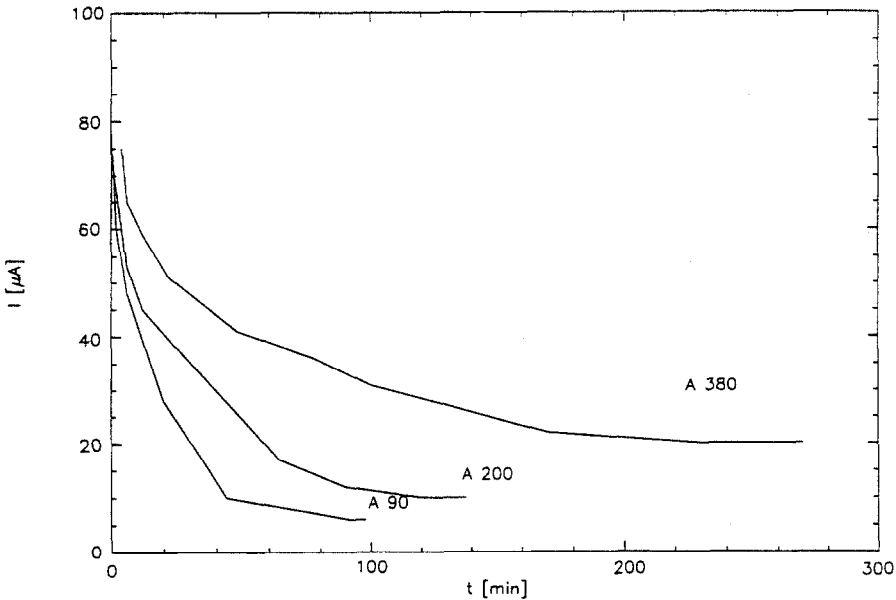
Fig. 3. Polarization characteristics of gel electrolytes at a potential of 10 mV.

Isothermal transient ionic current method

For considerably different mobilities of cation and anion in a solid electrolyte Watanabe *et al.* [25] suggested the determination of the mobilities of both species by means of the ITIC method. This 'time-of-flight' technique yields significant results by the formation of space charges by the ions in the sample accommodated in the vicinity (double layer) of ion-blocking (platinum) electrodes on applying a d.c. potential across the electrolyte for a certain time. Subsequently the polarity is reversed and the time dependence of the current is monitored. It shows a peak at the time τ required by each kind of ion to move from one electrode to the other. The ion mobility can then be calculated from:

$$\mu = d^2/V\tau \tag{6}$$

where d is the sample thickness and V is taken to be sufficiently approximated by the applied voltage. Assuming application of a bias voltage for 1 h will sufficiently shift the main part of the mobile ions to form space charges, we considered the ITIC method as worth studying. At least relative values of ion mobilities can be expected for similar electrolytes, when time and bias voltage are kept constant.

For potentials lower than 3 V we observed a quite normal exponential decay of the current with time. Typically after about 1 h the polarity was reversed and the potential stepped up to 4 to 5 V. An exponential decay with two shoulders was registered for LiClO$_4$ electrolytes, see Fig. 4.

The mobilities, calculated for the Li$^+$ and ClO$_4^-$ ions are 2.0×10^{-6} and 6.0×10^{-6} cm^2 V^{-1} s^{-1}, respectively, and independent of the choice of Aerosil type within the margin of error. This corresponds to a transport number of 0.25 for the cation.

Using LiCF$_3$SO$_3$/PC only one broad shoulder could be observed, confirming about equal mobilities for anion and cation of about 1.9×10^{-6} cm^2 V^{-1} s^{-1}, i.e., $t_+ = 0.5$.
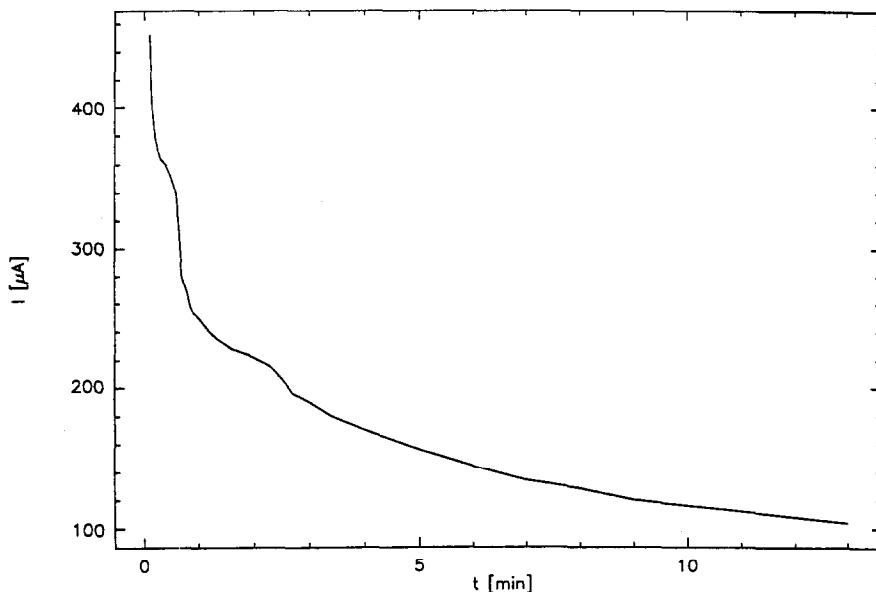
Fig. 4. Typical current decay after reversal and stepping up of the potential.

The results of the ITIC method — despite severe objections of a referee — correspond satisfactorily with those of impedance measurements.

Tubandt method

One of the classical methods to determine effective transport numbers is the Tubandt method [26]. In an adapted version, after the passage of a current of a few mA for several hours through an electrolyte sample contacted by platinum electrodes, the volume of the electrolyte is divided into a cathodic and an anodic half. The lithium contents are estimated by atom absorption spectroscopy and compared to the charge passed.

Applying Faraday's law the transport number is calculated by:

$$t_+ = (C_{Lic} - C_{Lin})/It \tag{7}$$

where C_{Lic} is the lithium content of the cathodic half of the electrolyte and C_{Lin} is the lithium content of the unpolarized electrolyte. In this way we obtained an approximate cationic transport number of 0.15 for the LiClO$_4$/PC electrolyte. This value is considerably lower than those obtained by the ITIC or SSC methods and may be due to an underpotential deposition of lithium at the cathode.

Conclusions

In this study we evaluated the effective cationic transport numbers of gel electrolytes by four methods and obtained for one definite electrolyte values of 0.17, 0.25, 0.3, and 0.15, i.e. an arithmetic average of 0.22. The uncertainty of each technique under certain circumstances, which had been already pointed out previously, [27], was confirmed.

In the case of our immobilized liquid electrolytes the proportion of the ion mobilities is not markedly influenced by the addition of silica, because lithium transport numbers of 0.19 for pure LiClO$_4$/PC solutions, and of about 0.25 for PEO/LiClO$_4$ (O/Li = 8) at 110 to 130 °C (19.2) are reported. LiClO$_4$/PC and LiCF$_3$SO$_3$/PC show different transport numbers. This is due to the interaction of the CF$_3$SO$_3^-$ anions with other ions and via hydrogen bonds with surface silanol groups of silica, as well as due to their size and shape [6]. Despite their high ionic conductivities the examined gels are still not the ideal candidates for application in all-solid-state batteries with Li$^+$ being incorporated in the cathodes. On the other hand, these results explain the excellent functioning of LiClO$_4$/PC/SiO$_2$ electrolytes in lithium/polypyrrole batteries, where ClO$_4^-$ is incorporated into the polymer during discharge.

List of symbols

E	potential, V
I	current, A
κ	conductivity, S cm^{-1}
$\mu_{+/-}$	mobility of cation/anion, cm^2 V^{-1} s^{-1}
$t_{+/-}$	transference number of cation/anion
t, τ	time, s
ΔV	applied polarization potential, V
$Re\ Z(\omega)$	real part of impedance, Ω
$Im\ Z(\omega)$	imaginary part of impedance, Ω

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