

Short communication

Direct determination of transference numbers of LiClO_4 solutions in propylene carbonate and acetonitrile

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The authors wish to dedicate this work to the memory of Prof. Alessandro D'Aprano.

Abstract

Transference number measurements were determined by a direct method for LiClO_4 solutions in propylene carbonate and acetonitrile at 25 °C. A comparison is reported between theoretical calculations of transference numbers using a model based on the Lee–Wheaton theory with values of conductometric parameters, and thermodynamic ion pairing constants determined from previously reported conductivity data. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Transference numbers in liquid electrolyte solutions are generally obtained from classical techniques involving extensive experimental determinations of conductivities for numerous salts (e.g. alkali metal perchlorates) in a given solvent and combined with data from e.m.f., moving boundary and Hittorf methods, and non-thermodynamic methods involving the assumption of equal mobilities for the cation and anion of a reference electrolyte [1,2]. Given the importance of transference numbers in rechargeable lithium batteries, the need for rapid determination of accurate values by a simple method is important. Bruce et al. [3–5] have used a *direct-current polarization method* based on the technique of Sorensen and Jacobsen [6] to determine transference numbers in polymer

electrolytes, and the method has been proven valuable. However, unlike liquid electrolyte solutions, ionically conducting polymer electrolytes are, for all practical purposes, free of convection effects which leads to the success of the *direct* method by Bruce et al. The object of the present study was to determine whether the methods of Bruce et al. could be used for liquid electrolyte solutions. In the present work the transference numbers for LiClO_4 in two liquids (propylene carbonate and acetonitrile) determined in [7–9] from precision conductivity data are confirmed by the method of *direct* transference number measurements. Another simplicity of the direct method of Bruce et al. is that it avoids the need to determine ion association formation constants which, for liquid electrolyte solutions, must be determined using classical methods involving Fuoss or Lee–Wheaton analyses. We believe that the present work reports the first study in which the *direct* method has been used to determine transference numbers in non-blocking conductivity cells with metallic Li which exhibits dynamic passivation in liquid electrolyte solutions.

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Table 1
Physical Properties of PC and AN at 25 °C

Solvent	ρ (g cm ⁻³)	η (mPa s)	ε	$10^6 \chi_0$ (S cm ⁻¹)
PC	1.2001	2.511	64.97	0.32
AN	1.13020	0.3448	36.02	0.05

2. Experimental

2.1. Chemicals

Acetonitrile for UV spectroscopy was further purified by refluxing over phosphorus pentoxide followed by distillation. Propylene Carbonate B. & J. Brand High Purity Solvent from FLUKA was used as received without further purification. The physical properties of the two solvents at 25 °C, determined as described elsewhere [7–9] and reported in Table 1, are in good agreement with literature values.

Lithium perchlorate, reagent grade product, was recrystallized three times from conductivity water and dried by heating under vacuum at 150 °C.

2.2. Preparation of the samples

The following two solutions were prepared by weight and corrected to vacuum conditions:

- sample 1: LiClO₄/PC— $c_{\text{LiClO}_4} = 0.01180 \text{ mol dm}^{-3}$;
- sample 2: LiClO₄/AN— $c_{\text{LiClO}_4} = 0.05457 \text{ mol dm}^{-3}$.

2.3. Instruments

Chronoamperometric data were recorded by using a P.A.R. 273 potentiostat, able to acquire up to 1000 points per second. Impedance spectra were obtained from a Solartron 1260 Frequency Response Analyzer. Due to the high reactivity of metallic lithium, the preparation of the cells and the measurements were performed in a MBRAUN LabMaster 130 dry-box, under an argon atmosphere continuously circulating over molecular sieves and Cu powder in order to maintain levels of H₂O and O₂ under 1 ppm.

3. Description of the method

A two-electrode non-blocking cell was used: two stainless steel current collectors are in close contact with two lithium metal discs sandwiched between a felt separator filled with the solution to be analyzed. If a constant dc bias (which must be $\leq 0.03 \text{ V}$ in order to obtain a linear response from the system) is applied to the electrodes of the cell, a current is measured which falls from an initial value i_0 to a steady-state value i_s that is reached after 2–6 h. The electrochemical processes that occur at the electrode surfaces are represented below:

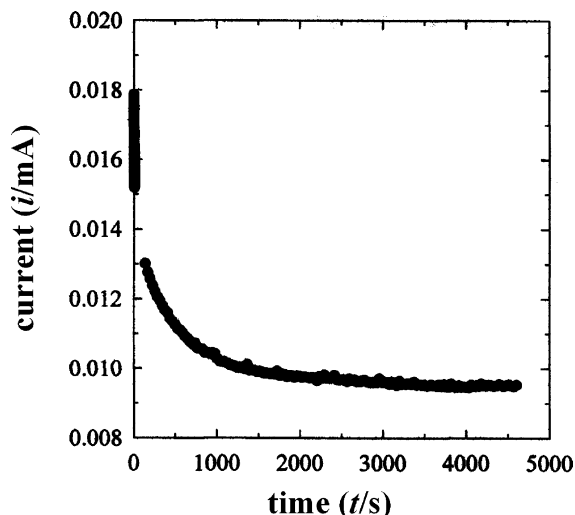
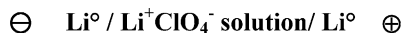


Fig. 1. Chronoamperometry of the cell with sample 2 as electrolytic medium.

With the passage of time, anions accumulate at the anode and are depleted at the cathode and a salt concentration gradient is formed. At the steady-state, the net anion flux falls to zero and only cations carry the current: therefore the cation transference number can be evaluated from the ratio i_s/i_0 .

Fig. 1 shows the chronoamperometric curve obtained from sample 2: the value of i_s (the steady-state current) is obtained from the end of the curve. In order to determine the initial value i_0 , about 1000 points of the chronoamperometric curve recorded over the first second (Fig. 2) were analyzed assuming an exponential decay for the extrapolation to zero time. For this extrapolation, we applied the least squares method to the experimental points using the following empirical equation:

$$i(t) = i' + (i_0 - i') \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where i' , τ and i_0 are variable parameters. In real cells, particularly in cells with active electrodes, the processes that occur at the surface are basically the charge transfer and the conduc-

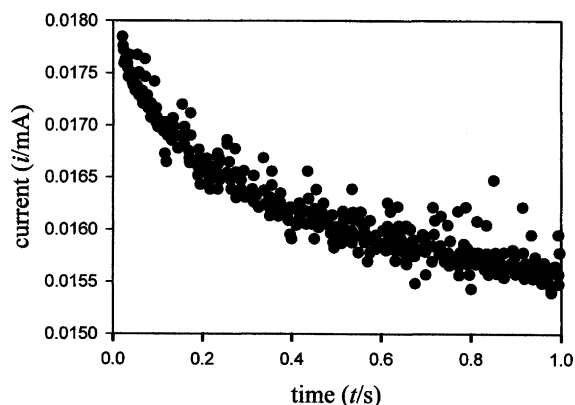


Fig. 2. First second of chronoamperometry of the cell with sample 2 as electrolytic medium.

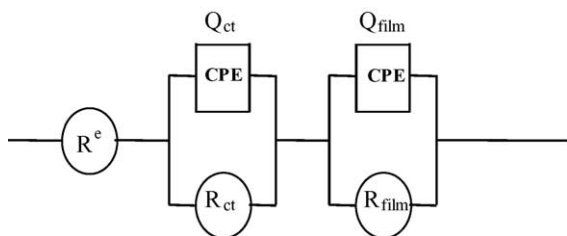
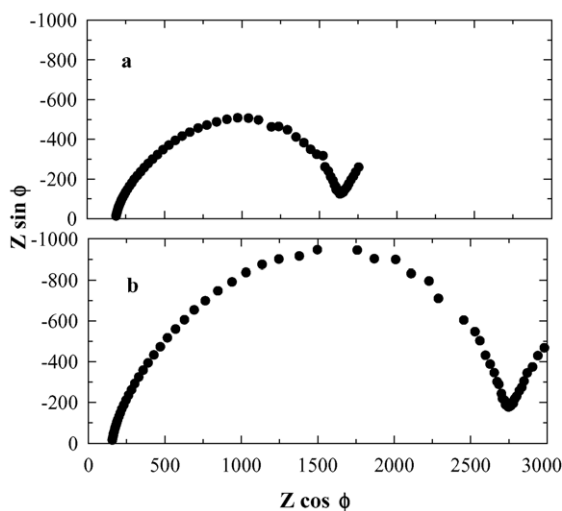


Fig. 3. Equivalent circuit for deconvolution of the EIS spectra.

Fig. 4. Impedance spectra of the cell (from 1 Hz to 100 kHz) with sample 2 as electrolytic medium at $t=0$ (a) and $t=t_s$ (b).

tion through the dynamic passivating layer on the electrode, i.e. the intrinsic electrical resistance of the passive film. Since the thickness of the passivating film on the electrode will vary over the time required to reach a steady-state current, the values of the intrinsic resistance must be measured shortly before the application of the dc bias potential and immediately after the attainment of steady state in order to determine the correct cationic transference numbers t_+ , by using the equation:

$$t_+ = \frac{i_s(\Delta V - i_0 R'_0)}{i_0(\Delta V - i_s R'_s)} \quad (2)$$

In Eq. (2), the subscripts 0 and s indicate initial values and steady-state values respectively, R' the sum of the charge transfer resistance R_{ct} and the passivating film resistance R_{film} , ΔV the applied voltage, and i the current. The measurement of R'_s and R'_0 can be easily achieved by recording two impedance spectra on the cell in the frequency range be-

Table 2
Lithium transference numbers determined by the steady-state method

Sample	t_+
LiClO ₄ /PC: $c_{\text{LiClO}_4} = 0.01180 \text{ mol dm}^{-3}$	0.29
LiClO ₄ /AN: $c_{\text{LiClO}_4} = 0.05457 \text{ mol dm}^{-3}$	0.39

Table 3

Conductometric parameters (limiting molar conductivity Λ^0 , gurney radius R) and thermodynamic constants (ion pair association constants K_a) of LiClO₄ systems in PC and AN at 25 °C from references [7–9]

Solvent	$\Lambda^0_{\text{LiClO}_4}$ (S cm ² mol ⁻¹)	$K_{a\text{LiClO}_4}$ (dm ³ mol ⁻¹)	R (10 ⁻⁸ cm)
PC	26.72 ± 0.03	4.4 ± 0.3	18 ± 2
AN	73.27 ± 0.03	18.4 ± 0.1	7 ± 2

tween 0.1 Hz and 100 kHz before the application of the bias potential, and after the steady-state has been reached and the dc bias potential has been removed.

The deconvolution of the spectra was made using the equivalent circuit shown in Fig. 3 where the processes of charge transfer and of conduction through the passivating layer are treated as two sub-circuits of a resistance and a constant phase element (CPE) in parallel (the CPE is more suitable than a pure capacitive element because of the fractal nature of the electrode–solution interface). Fig. 4 shows the impedance spectra of the cell in the complex plane, recorded at $t=0$ and $t=t_s$ with sample 2 as electrolytic medium. The diameter of the semicircle is approximately equal to the sum of R_{ct} and R_{film} , the exact value of which is obtained from the deconvolution of the spectrum. Growth of the passivating film on the lithium surface can be deduced from the measured increase of resistance.

4. Results and discussion

Table 2 lists the values of the cationic transference number determined by the method described above. Theoretical values of transference number calculated using transport parameters and thermodynamic constants determined from conductivity data in references [7–9] are summarized in Table 3. Limiting molar conductivities of single ionic species were determined using literature values for ClO₄⁻ anion in PC and AN [10,11]:

$$\lambda^0_{\text{ClO}_4^-}(\text{PC}) = 18.51 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^0_{\text{ClO}_4^-}(\text{AN}) = 103.62 \text{ S cm}^2 \text{ mol}^{-1}$$

Table 4

Lithium transference numbers calculated from the Lee–Wheaton equation [12–14] compared to those experimentally determined by the dc–ac polarization method

LiClO ₄ /PC $c_{\text{LiClO}_4} = 0.01180 \text{ mol dm}^{-3}$		LiClO ₄ /AN $c_{\text{LiClO}_4} = 0.05457 \text{ mol dm}^{-3}$	
Experimental (present work)	Theoretical (Lee–Wheaton)	Experimental (present work)	Theoretical (Lee–Wheaton)
0.29	0.296	0.39	0.3389

An inspection of Table 4 reveals that theoretical values of the transference numbers are in very good agreement with those experimentally determined by the direct method. It is noted that the theoretical transference numbers are based on infinitely dilute solutions, and the agreement of values obtained by the direct or steady-state method is attributable to the dilute solutions used in the present work.

Acknowledgments

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