



Salt concentration polarization of liquid electrolytes and determination of transport properties of cations, anions, ion pairs and ion triples



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ABSTRACT

Specifically blocking of cations or anions in an electrochemical polarization experiment is a standard procedure to determine transport numbers. This is non-trivial in the case that internal interaction (ion pairs, ion triples etc.) have to be taken account of. Besides the trivial concentration redistribution owing to mass action laws, it is the dynamics that is affected in a more complex way. The steady state behavior of such a polarization is calculated using the concept of Conservative Ensembles. By the same procedure also the relaxation time of the galvanostatic transient is addressed. Finally it is shown how the individual transport parameters of cations, anions, ion pairs and ion triples can be obtained by a combination of polarization, impedance spectroscopy and cationic as well as anionic tracer (or PFG-NMR) experiments.

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1. Introduction

Salt containing liquids form a very important class of electrolytes and have become very popular in the context of Li-based batteries. In particular in quite unpolar organic solvents the salts are far from being completely dissociated. Though details of the interactions can be very complex the distinction in terms of dissociated ions, ion pairs and higher order ion tuples, in particular ion triples proved to be a reasonable approximation in many cases [1–3].

Polarizing a liquid electrolyte by using one or two electrodes that are specifically blocking one sort of carrier, has become a standard method of determining individual conductivities and hence also the respective transport numbers. This method has been introduced into the field of polymer and liquid electrolytes by Bruce and Vincent [4].

Such a concentration polarization also occurs automatically in a Li-based battery cell, where the electrodes – in particular in the presence of a single-ion conductive passivation layer – block anionic transfer. At high current the resulting salt concentration gradient can even lead to salt precipitation.

If only primitive cations or anions are mobile, the situation is straight-forward. In the case that the electrolyte has a Li⁺-transport number less than unity, a stoichiometric gradient builds up owing

to X⁻-blocking until it nullifies the anionic current and the total current is carried by Li⁺ [4]. If in addition to Li⁺ and X⁻ also neutral ion pairs (±) (and higher associates) have to be taken account of, the situation is more delicate [5–9]. This has been addressed by various authors, in particular by Bruce and Vincent [4–6,8–11].

Let us first concentrate on the neutral ion pair. The rather trivial part that the free Li⁺ and X⁻ concentrations are lower, is regulated by the mass action law of the association reaction



Much more subtle is the enabling of an indirect conduction path that does not lead to polarization as well. In the steady state the lithium is not only transported by Li⁺ but also indirectly via counter motion of LiX and X⁻: At the cathode the lithium ion belonging to LiX is discharged, while at the anode Li is oxidized to Li⁺ which reacts with X⁻ to LiX. Hence the X⁻ current does not disappear in the steady state rather it is compensated by internal reaction rates [6,7]. There is no X⁻ transfer and no X⁻ discharge, and diffusivities of LiX and X⁻ provide transport continuity. Such problems where transport is coupled to quick internal reactions can be handled on a general level by the concept of Conservative Ensembles originally developed by the author [7,12]. The mathematical reason for the complication is that owing to the internal reactions source/sink

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terms have to be considered. Based on this concept, it can be shown [6,8] that in the polarized state σ_{pol} is not just σ_{Li^+} but rather

$$\sigma_{\text{pol}} = \sigma_{\text{Li}^+} + \frac{s\sigma_{\text{X}^-}}{s + \sigma_{\text{X}^-}} \quad (2)$$

where the second term describes the indirect transport for which non-zero transport coefficients for both the ion pair ($s \equiv \frac{F^2 c_{\pm} D_{\pm}}{RT}$) and the anion (σ_{X^-}) are necessary.

It is worthy of note that the same result was derived by Bruce and Vincent (cf. p. 51 in Ref. [5]). In Ref. [6] – considering the detailed continuity equations in bulk and at the boundary explicitly and hence dealing with conservative ensembles – it has been put into a more rigorous and generalizable context.

There it is also shown that the result is directly obtainable from the isomorphic problem of ion/electron interaction treated in Ref. [7].

It is interesting to consider the special case that $s \gg \sigma_{\text{X}^-}$, for which one gets

$$\sigma_{\text{pol}} = \sigma_{\text{Li}^+} + \sigma_{\text{X}^-} = \sigma. \quad (3)$$

Obviously in such a case no polarization occurs even if σ_{Li^+} is much smaller than σ_{X^-} , a point then had been highlighted in Refs. [5,10]. (Here and in the following we assume other polarizations to be absent or to be corrected for, e.g. SEI contributions that can be separated from AC-experiments.) Eq. (2) can also be represented by an equivalent circuit (eqc) consisting of a parallel switching (Par) of the direct (resistor $\propto \sigma_{\text{Li}^+}^{-1}$) and indirect channel (resistor $\propto \left(\frac{s\sigma_{\text{X}^-}}{s + \sigma_{\text{X}^-}}\right)^{-1} = \frac{1}{s} + \frac{1}{\sigma_{\text{X}^-}}$) the latter being characterized by a series switching (Ser) of two resistors (one determined by $1/s$, the other by $\frac{1}{\sigma_{\text{X}^-}}$ (eqc = Par (σ_{Li^+} , Ser(s, σ_{X^-}))). Parallel and serial switching must be understood in a logical sense: indirect and direct channel are two options (OR) while for the indirect channel ion-pair AND X^- transport are necessary. It must be added that as far as applications are concerned it is not $t_{\text{Li}^+} \equiv \sigma_{\text{Li}^+}/\sigma$ that matters but rather $t_{\text{Li}^+, \text{eff}} \equiv \sigma_{\text{pol}}/\sigma$ as undesired polarization is avoided in both the direct and the indirect Li^+ -transport mode. A key feature regarding the relevance of ion pairs lies in the steady state condition which also is influenced by the interactions (see next paragraph).

Unlike previous work we analytically analyze – for dilute conditions – the more complex case that also ion triples are important. Then two other reactions must be added,



and



The qualitative issue here is that complexity is increased not so much due to the fact that further particles occur the dissociation of which has to be taken in account, but rather that these particles are both interactive and (in contrast to the binary ion pair) charged. In other words: in addition to acting as sources/sinks, i.e. supplying (or annihilating) Li^+ and X^- through dissociation (association) whenever required, they also act as charge carriers for Li and X and are hence also influenced by electrical potential gradients. The situation is similar to a polarization of a mixed ionic/electronic conductor using electron-blocking electrodes if ionic defects in various valence states are used [7,12,13]. (There also effectively neutral and charged associates are of significance.) Yet because of the varying Li-content in the various species the detailed relations will not be completely isomorphic and the entire analysis has to be set out.

In this contribution, we will, for the above mentioned polarization situation, inspect currents and voltages in the steady state. We will also investigate the transient of a (galvanostatic) polarization governed by an effective interdiffusion coefficient the analytical

form of which will be derived [7,12,13]. Note again that a basic – but usually well-fulfilled – assumption is that the internal reactions are quick and the entities locally in chemical equilibrium. It is evident that one has to avoid large overvoltages (i.e. one has to refer to very small polarization currents) as to be able to stay within the regime of linear irreversible thermodynamics. In the linear regime we can consider transport coefficients as unperturbed quantities even though concentration dependent (cf. linear term in Taylor-expansion). For higher order correction cf. Ref. [14]. Furthermore we neglect any non-idealities other than internal reactions.

In various papers the significance of combining various transport experiments as to discriminate between the different contributions has been highlighted [1,5,9,15–18]. Here we will show how by using a combination of DC-polarization, AC-impedance and Tracer diffusion experiments (Isotope or Pulsed Field Gradient NMR) for both Li^+ and X^- the individual diffusivities can be obtained in such a complex case.

Let us start with discussing the boundary conditions.

2. Boundary conditions

Here we use Li-electrodes or non-polarizable Li redox electrodes and assume that no other redox processes than $\text{Li} \rightleftharpoons \text{Li}^+ + \text{e}^-$ occur at the contacts. A very well suited X^- blocking electrode is formed by the combination of a solely Li^+ conducting solid electrolyte and a Li-electrode. Such a combination is automatically formed on contacting Li with various liquid electrolytes, and is similar to an electron blocking electrode used in solid state ionics used to discriminate between ion and electron conductivities [19–21]. In the same manner the Li^+ -conducting passivation layer also interrupts any redox shuttle contribution (effective electronic conductivity). Corresponding interfacial polarization effects can usually be easily separated and corrected for (cf. section 8).

Fig. 1 gives various possibilities of how a steady state flux can be maintained in the presence of mobile ion pairs and triples. The treatment here takes account of the simultaneous presence of all these species.

A relevant treatment of boundary conditions in the case of reversible and blocking electrodes in the presence of local source and sink terms is given in Ref. [7]. From these considerations it is obvious that at such a blocking boundary it is the current of the conservative X^- ensemble $i_{\text{X}^-}^*$ and not simply the X^- -current i_{X^-} that vanishes on the electrolyte site of the blocking contact, while $i_{\text{Li}^+}^*$, the current of the conservative Li-ensemble, carries the total outer current. (Here and in the following all quantities marked by a star refer to such conservative ensembles. The extension by also considering internal, indirect electronic pathways is straight-forward.) This holds true because at the boundary – ignoring local accumulation in the boundary – according to Gauss-law the jump of the individual flux densities is not zero but given by the local source/sink term. In other words: In the experiment under consideration the X^- flux is zero only on the solid side of the electrolyte contact. Within the electrolyte a steady state X^- flux can be maintained at the expense of stationary reaction effects. Inside the electrolyte only the flux of the conservative ensemble is zero, that is for that combination of fluxes for which the source/sink term disappears [7]. So the flux of the X-ensembles consists of contributions from all the X-containing species. Since any of the individual fluxes is zero in the solid phase, the flux of the conservative X-ensemble on the liquid side is balanced by the corresponding combination of the source/sink terms which is identical to zero. This more general steady state conditional enables the occurrence of cases shown in Fig. 1.

These flux densities $j_{\text{Li}^+}^*$ and $j_{\text{X}^-}^*$ (current densities $i_{\text{Li}^+}^*$ and $i_{\text{X}^-}^*$) can also be understood as flux-densities (current densities) referring to

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