

On the characterization of battery electrolytes with polarization cells



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ABSTRACT

The theoretical foundation of potentiometric diffusivity and transference-number measurements is revisited, through an analysis of the diffusion-potential relaxation a concentrated binary electrolyte exhibits after being subjected to a current pulse in a planar electrolytic cell. Earlier theory is extended to include solute-volume effects, as well as being modified to incorporate a particle-fraction basis for composition and to account for the nonlinear relationship between composition differences and cell voltage. The new theory provides significant corrections when concentration polarization is very large or when electrolytes are moderately concentrated, rationalizing the unexpected voltage responses seen during some previous transport measurements. Guidelines are developed to aid the design of galvanostatic-polarization experiments involving non-aqueous electrolytes similar to those used in lithium batteries. Complete property sets are provided for 0.85 M LiPF₆ in propylene carbonate and for 2.24 M LiPF₆ in a mixed-carbonate solvent.

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1. Introduction

The proper description of mass transfer requires that a transport property be associated with every pair of chemically distinct species a phase contains [1]. Since a binary electrolytic solution comprises cations, anions, and a solvent, three properties are needed. The ionic conductivity κ , the cation transference number relative to the solvent velocity t_+^0 , and the thermodynamic diffusivity \mathcal{D} are a sufficient set of transport parameters [2].

Several thermodynamic properties are also required to complete the macroscopic description of an isothermal, isobaric, multicomponent phase. A set of thermodynamic factors must be quantified to establish how changes in a solution's composition relate to changes in its free energy; an additional equation of state may also be adopted to account for how a solution's density depends on its composition. For an electroneutral binary electrolytic solution, there is a single thermodynamic factor, χ , and the state equation involves the partial molar volumes of the solvent and dissolved electrolyte, \bar{V}_0 and \bar{V}_e , respectively. Thermodynamic factors are particularly important because solution nonideality can be significant [3]. Also, the time scale over which concentration differences relax is determined by the Fickian diffusivity $D = \mathcal{D}\chi$, rather than \mathcal{D} alone [4].

Ionic conductivity is directly measurable, and is typically quantified using DC conductometry [5,6] or AC impedance spectroscopy [7,8]. Partial molar volumes are not directly measurable, but their composition dependences can be quantified independently of the other properties *via* densitometry [9,10]. The other three solution properties are not directly measurable, and cannot be measured in isolation; values of \mathcal{D} , t_+^0 , and χ are usually obtained by simultaneously analyzing results from several experiments.

Ma *et al.* proposed a suite of three potentiometric experiments to measure \mathcal{D} , t_+^0 , and χ [11], which all involve cells with two electrochemically reversible electrodes that produce or consume species from the solution phase. One measurement is performed with a 'concentration cell', in which similar binary electrolytes with different salt concentrations are put in chemical contact through a porous membrane that prevents significant mixing during the experimental period; the open-circuit potential (OCP) across a quasiequilibrated concentration cell relates to χ and t_+^0 [2,3,12]. The other two measurements are performed using a 'polarization cell': a planar electrolytic cell with parallel electrodes that allow a current to be driven through the electrolyte between them. In a 'restricted diffusion' measurement, an applied current is used to induce a non-uniform concentration distribution in the interelectrode gap; the relaxation at long times is exponential, with a time constant dependent on \mathcal{D} and χ [4,13] that can be tracked by recording the transient OCP [4,14]. In a 'galvanostatic polarization' measurement, a short current pulse is applied to produce diffusion boundary layers near the electrode surfaces; the OCP relaxation at times before the boundary layers come into contact depends on \mathcal{D} , t_+^0 , and χ

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[11,15]. The two polarization-cell measurements can in principle be implemented during a single experiment, since the current pulse that initiates the galvanostatic polarization can be used to establish the non-uniform initial concentration for restricted diffusion. In practice, separate experiments may be needed to achieve good signal-to-noise ratios for voltages in the short-time and long-time relaxation regimes.

Theoretical expressions derived by Ma *et al.* [11] relate the voltage transients during restricted-diffusion and galvanostatic-polarization experiments to \mathcal{D} , t_+^0 , and χ . A number of restrictions apply to their analysis. The theory requires that concentration differences are relatively small, despite the fact that large differences may be needed to get an adequate chronopotentiometry signal. Electrolyte convection associated with current pulses is also neglected – but this phenomenon can sometimes be significant for moderately concentrated non-aqueous electrolytes [16].

Although Ma *et al.* reported sensible property values [11], some implementations of their protocol by others have led to surprising results for lithium-battery electrolytes. These include unexpectedly high diffusivities [12] and low – or even negative – transference numbers [17]. In light of these observations, the present discussion has three main aims. First, the theory underpinning potentiometric measurement of \mathcal{D} , t_+^0 , and χ is extended, to relax the assumptions of low concentration polarization and negligible solute-volume effects. Second, the constraints on pulse currents are analyzed to guide experimentalists in the design of galvanostatic-polarization measurements. Third, the extended theory is used to rationalize some counterintuitive observations made by prior researchers. In the course of the discussion, complete property sets are developed for two typical lithium-battery electrolytes.

2. Thermodynamic fundamentals

2.1. Electrolyte composition bases

Solute molalities m_k are the most typical composition basis used to express the composition dependences of solution properties, primarily because they are very precisely quantifiable. To prepare a solution of a given molality does not require a volume measurement, and, since it is referred to solvent mass, molality is independent of temperature T and pressure p . Although a solvent's molality is conveniently constant (equaling the inverse of its molar mass M_0), the molalities of solutes become very large when little solvent is present, and diverge in the limit where there is no solvent. Thus molality is a difficult basis to use for very concentrated solutions. The need to specially identify a particular species as a 'solvent' also forces some degree of arbitrariness when describing the mixed-solvent solutions commonly used for lithium batteries.

Molar species concentrations c_k are finite throughout the entire domain of miscibility and treat all species on equal footing, avoiding the problems associated with molality in very concentrated or multi-solvent systems. The molar basis places strict limits on experimental precision, however, because solution preparation involves a volume measurement. Since solution densities depend on T and p , as well as local composition, the use of a molar basis can easily lead to systematic measurement errors. The T and p dependences of molarity also make it vague as a basis for properties in coupled transport scenarios where heat or momentum transfer accompanies mass transfer.

Species particle fractions y_k have the advantages of molality, because they are independent of T and p , and also of molarity, because they apply equitably to every species in a phase and are always finite. They are convenient from a theoretical standpoint because they are dimensionless and bounded between 0 and 1. As a basis for activity they are further useful, because chemical-potential constitutive laws based on particle fractions satisfy the



Fig. 1. Schematic drawing of a general electrolytic cell containing a binary electrolytic solution.

Gibbs-Duhem equation naturally in the ideal-solution limit, where every species' activity coefficient approaches 1.

When bulk electrolytic solutions are observed on the length scales relevant to macroscopic transport phenomena, their ion contents satisfy a local electroneutrality relationship. Thus one usually does not need to distinguish the cation particle fraction y_+ and the anion particle fraction y_- in a binary electrolytic solution. Letting ν_+ and ν_- represent the ion stoichiometries in a formula unit of salt, one can instead use a single composition variable

$$y = \frac{y_+}{\nu_+} = \frac{y_-}{\nu_-}. \quad (1)$$

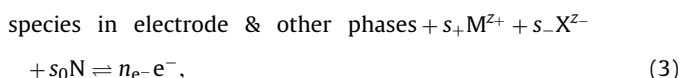
This quantity represents the number of salt formula units, scaled by the total number of ion and solvent particles (*i.e.*, the sum of the amounts of all three species) in the solution. The particle-fraction basis relates to salt molality m and salt molarity c through

$$y(m) = \frac{mM_0}{1 + \nu m M_0} \text{ and } y(c) = \frac{c\bar{V}_0}{1 + c(\nu\bar{V}_0 - \bar{V}_e)}, \quad (2)$$

where $\nu = \nu_+ + \nu_-$ is the total number of ions in a formula unit.

2.2. The open-circuit potential

Consider a general electrolytic cell containing a binary electrolytic solution, diagrammed using the standard schematic representation [2,18] in Fig. 1. Half-reactions at each of the electrodes can be expressed in the form



in which M, X, and N are the chemical symbols of cations, anions, and solvent, respectively, and z_+ and z_- are the ionic equivalent charges. The cell is taken to be 'symmetric', in the sense that the stoichiometric coefficients s_k for all liquid-phase species¹ are the same in both electrode reactions (the electron exchanges at α and α'), and the number of electrons transferred, n_e , equates. One also needs to stipulate that the species in the electrodes and other phases are uncharged, in which case conservation of charge requires that $\sum_k s_k z_k = n_e - z_e$, where $z_e = -1$ is the equivalent charge of electrons. Despite these restrictions, the fabrication of a symmetric electrolytic cell does not require that both half-reactions are the same: the components in other phases (if present) and their involvement in the electrode reactions can generally be dissimilar.²

¹ The coefficient s_k is positive for a product and negative for a reactant when half-reaction 3 is written as a reduction.

² For example, an alkaline battery is a symmetric cell: although one electrode is zinc and one is manganese oxide, both half-reactions involve the same number of electrons, and both electrodes react with solvent (water) and anions (hydroxide) in similar proportions.

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