



Transport property measurement of binary electrolytes using a four-electrode electrochemical cell



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ABSTRACT

An electrochemical method that is more accurate and less complicated than state-of-the-art techniques is presented to estimate transport properties of concentrated binary electrolytes. The method involves the application of a single galvanostatic polarization pulse to working and counter electrodes in a four-electrode symmetric cell and measurement of both the closed-circuit and open-circuit potential responses across two electrode sensors. A mathematical model is then fitted to the experimental data to obtain the transport properties. This method provides a fast and reliable means to determine transport properties for a wide variety of electrolytes such as in high-power battery applications.

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1. Introduction

Further improvement of the power capability of advanced batteries requires optimization of their mass transport properties among other things. Despite their rigor, state-of-the-art methods that estimate electrolyte transport properties are arduous, time-consuming and prone to error [1,2]. In most cases, battery electrolytes are concentrated solutions containing at least one salt dissolved in one or more solvents [3]. Three independent properties (ionic conductivity, salt diffusion coefficient and cation transference number) must be determined as functions of concentration and temperature to fully characterize a concentrated binary electrolyte [4]. Because the solution is non-ideal, thermodynamic measurements usually conducted in concentration cells are required to accurately determine transport properties [4].

Ionic conductivity is the most frequently measured of these parameters, usually by a standard AC impedance method. On the other hand, measurement of the salt diffusion coefficient and cation transference number is very difficult and so has been limited to the most commonly used electrolytes [1,5–17].

Restricted diffusion theory for concentrated solutions [18] is a powerful basis for estimating the salt diffusion coefficient at a given concentration. Restricted diffusion experiments track the exponential decay of an established concentration gradient in a cell either electrochemically from the electric potential difference between two reversible electrodes [19] or non-electrochemically from changes of properties such as the

local refractive index of the solution [18]. Experiments based on semi-infinite diffusion are commonly employed in place of the Hittorf [20], moving boundary [21] or electromotive force [22] methods to indirectly estimate the transference number [1,2]. A symmetric two-electrode cell is first polarized by applying a constant current for a short time so that the concentration boundary layer at the surface of the electrodes does not reach the center of the cell and semi-infinite conditions are established. The current is then interrupted and the open-circuit cell voltage immediately recorded. This process is repeated for different applied currents and the resulting open-circuit voltages are plotted versus current \times (interruption time)^{1/2}. The transference number is directly proportional to the slope of this curve and to the polarization from the concentration cell experiments. The thermodynamic factor can be determined once the transference number is known [1,2]. Thus, three separate sets of measurements obtained from the semi-infinite diffusion, restricted diffusion and concentration-cell experiments must be combined in order to obtain the salt diffusivity, transference number and thermodynamic factor at a given concentration.

In this communication, we present a novel electrochemical method based on the use of a single galvanostatic pulse and concentration-cell experiments to simultaneously determine the three transport properties and thermodynamic factor of a binary electrolyte. It requires the use of only one cell and fully uses both the measured closed-circuit and open-circuit potential responses to the galvanostatic pulse.

2. Experimental

The experimental setup consists of a custom-built four-electrode cylindrical electrochemical cell (Fig. 1). Counter (CE) and working

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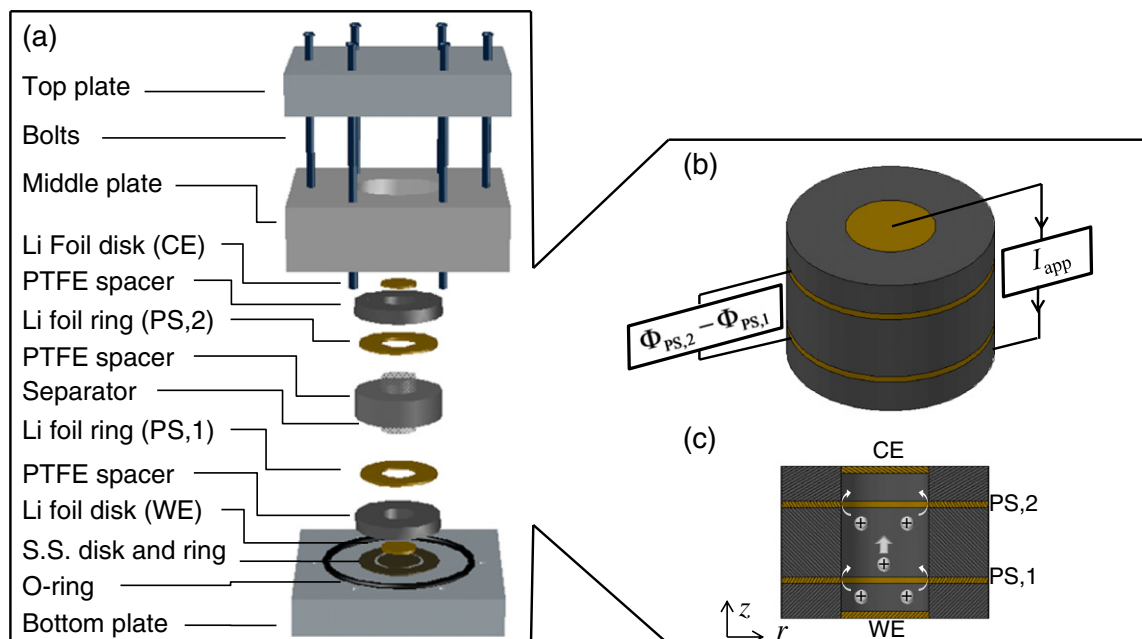


Fig. 1. (a) Expanded view of the four-electrode cell, (b) actual working parts of the cell: working and counter electrodes (yellow disks), potential sensors (yellow rings) and spacers (dark gray rings) and (c) cross-section of the cell working parts shown in (b).

(WE) electrodes are fitted at the two ends of the cell on top of stainless steel current collectors. Two potential sensors (PS) of annular geometry are sandwiched between insulating ring-shaped spacers of the same inner diameter and placed midway between the CE and WE. The spacing between the two sensors and between the sensors and CE/WE are chosen to be symmetric. The potential sensors are wired to stainless steel rings surrounding the current collectors through the PS-CE and PS-WE spacers. The spacers as well as the top, intermediate and bottom plates of the cell are made of PTFE. The cell is made air-tight by embedding two EPDM rubber O-rings in the top and bottom plates and held together using six bolts and nuts through the cell body.

The CE and WE are 12.98 mm diameter disks punched from a 200- μm -thick Li metal foil. The sensors are rings prepared from the same Li foil with a 12.98 mm inner diameter identical to that of the cell. The thickness of the Li rings after the cell is disassembled is measured to be 191 μm . A 1 mol L⁻¹ LiPF₆ solution dissolved in 1:1 vol. (~4:3 wt.) ethylene carbonate (EC) and diethyl carbonate (DEC) (Sigma Aldrich, battery grade) is chosen as a model electrolyte. A 7-layer stack of grade D Whatman borosilicate glass microfiber filter (GF) disks is soaked with the electrolyte and placed between the CE and WE. The GF has a density of 2.500 g cm⁻³ measured using an AccuPyc 1330 He pycnometer (Micromeritics Instrument Corp., USA). Given the cell volume, the number of GF layers and the measured density, the porosity of the 7-layer stack is calculated to be ~0.923. The GF is used to minimize convection and avoid seepage of the electrolyte from the cell working volume [12]. Current flows through the WE and CE while potential differences are measured across the PSs.

The cell is operated galvanostatically at 25 °C (Cincinnati Sub-Zero MCB-1.2 temperature chamber, USA) using a multi-channel potentiostat/galvanostat (VSP, Bio-Logic, France). The cell is oriented vertically in order to minimize buoyancy effects (i.e., anodic reaction occurs on the WE at the cell bottom). The following current waveform is applied to the WE: 0.2 mA anodic current (~0.151 mA cm⁻²) for 8 h, open-circuit for 16 h, 0.2 mA cathodic current for 8 h and open-circuit for 16 h. The cell is conditioned by applying two cycles of this waveform prior to the measurement.

3. Theory

The model is based on the concentrated solution theory [4] and simplified using the following assumptions:

- i) The 1:1 EC and DEC mixture behaves as a single solvent.
- ii) The solution obeys local electroneutrality.
- iii) The Li metal electrodes react reversibly with Li⁺ but not with PF₆⁻.
- iv) The process is isothermal and isobaric.
- v) Boundary displacement due to WE/CE reactions is negligible.
- vi) Electro-osmotic effects across the porous silicate separator are negligible.
- vii) Solvent velocity is taken as the frame of reference for transport.
- viii) Convection is negligible and solvent velocity is set to zero.
- ix) Li moss formation and parasitic reactions at the surface of the WE/CE are insignificant.
- x) Transport and thermodynamic properties remain unchanged by the experimental conditions.
- xi) Double layer charging is negligible.
- xii) No homogeneous chemical reactions occur.

The Stefan–Maxwell equations describe the flux densities in concentrated solutions. Insertion of the flux-explicit Stefan–Maxwell expressions for the three species in the conservation of mass equation (no homogeneous reaction) followed by some algebraic manipulation yields [4]:

$$\varepsilon \frac{\partial c}{\partial t} = \nabla \cdot \left(\varepsilon^{\nu} \mathcal{D} \frac{c_{\Gamma}}{c_0} \alpha \nabla c \right) \quad (1)$$

where ε is porosity (0.923), t is time, c and c_0 are the concentrations (mol m⁻³) of solute and solvent, respectively, and $c_{\Gamma} = 2c + c_0$. c_0 is related to c according to:

$$c_0 = \frac{1 - c \bar{V}_e}{\bar{V}_0} \quad (2)$$

where \bar{V}_e and \bar{V}_0 are partial molar volumes of the solute and solvent,

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