Method of the Four-Electrode Electrochemical Cell for the Characterization of Concentrated Binary Electrolytes: Theory and Application

Supporting Information: Dependence of Potential Sensor Equilibrium Locus on Electrode Kinetic Properties

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Assume that a known constant electric field is applied to the electrolyte along the z-direction and the resulting potential profile is not disturbed by the potential sensor, i.e., electric potential varies linearly along the potential sensor. Then, using Eqs. (34) and (35), one can obtain an analytical expression for the equilibrium locus $z_{\text{eq},l}$ that separates the cathodic and anodic poles of the potential sensor.[1] Let $U_{\text{PS}} = 0$ and the overpotential at the surface $\eta_{\text{PS},l}(z) = \Phi_{\text{PS},l}(z) - \Phi(z)$ be linear with respect to z:

$$\eta_{\text{PS},l}(z) = \eta_{\text{PS},l}(z_{\text{eq},l}) + \frac{d\eta_{\text{PS},l}}{dz}(z - z_{\text{eq},l}) \tag{S.1}$$

where $\eta_{\text{PS},l}(z_{\text{eq},l}) = 0$. Moreover, assuming a uni-potential metallic electrode (i.e., $d\Phi_{\text{PS},l}/dz = 0$), the overpotential becomes:

$$\eta_{\mathrm{PS},l}(z) = -\frac{d\Phi}{dz}\Big|_{z_{\mathrm{eq},l}}(z - z_{\mathrm{eq},l}) = E(z - z_{\mathrm{eq},l}) \tag{S.2}$$

where $E = -d\Phi/dz$ is the electric field uniform across the electrode width. On the other hand,

$$\int_a^b I_{\mathrm{PS},l}dz = \int_a^{z_{\mathrm{eq},l}} I_{\mathrm{PS},l}dz + \int_{z_{\mathrm{eq},l}}^b I_{\mathrm{PS},l}dz = 0 \tag{S.3}$$

where $a = \sigma$ and $b = \sigma + \delta$ for $l = 1$ and $a = L - (\sigma + \delta)$ and $b = L - \sigma$ for $l = 2$. By making use of Eqs. (S.2) and (34) and carrying out some manipulation, the integrals of Eq. (S.3) can be evaluated to yield an expression for $z_{\mathrm{eq},l}$. In the case of $z_{\mathrm{eq},1}$ it simplifies to:

$$z_{\mathrm{eq},1} = \sigma + \frac{1}{2}\delta - \frac{RT}{nFE}\ln\left(\frac{\beta_{\mathrm{PS}}}{1 - \beta_{\mathrm{PS}}}\frac{\sinh\left(-\frac{(1 - \beta_{\mathrm{PS}})nF}{2RT}\delta E\right)}{\sinh\left(-\frac{\beta_{\mathrm{PS}}nF}{2RT}\delta E\right)}\right) \tag{S.4}$$

Under the condition of no local perturbation, the equilibrium locus is independent of the reaction rate constant k_{PS}^0. Moreover, one expects $z_{\mathrm{eq},l}$ to fall exactly at the middle of the electrode for a perfectly symmetric anodic/cathodic reaction, i.e., for $\beta_{\mathrm{PS}} = 1/2$, regardless of the electric field intensity. Under the operating conditions of relevance to transport property measurement experiments, the amplitude of the electric field is small enough to allow linear approximation of the hyperbolic sine term on the right side of Eq. (S.4), i.e.:

$$\sinh\left(-\frac{(1 - \beta_{\mathrm{PS}})nF}{2RT}\delta E\right) = -\frac{(1 - \beta_{\mathrm{PS}})nF}{2RT}\delta E$$

$$\text{and} \tag{S.5}$$

$$\sinh\left(-\frac{\beta_{\mathrm{PS}}nF}{2RT}\delta E\right) = -\frac{\beta_{\mathrm{PS}}nF}{2RT}\delta E$$

Substitution of Eq. (S.5) into Eq. (S.4) causes the third term on the right side to vanish and shows that the equilibrium locus is unaffected by changing β_{PS}. In line with the above linear approximation, a plot of the percent difference in $z_{\mathrm{eq},1}$ according to Eq. (S.4) in Figure S.1 demonstrates a maximum of ~0.6% variation in $z_{\mathrm{eq},1}$ as a function of β_{PS} when exposed to an electric field as high as $E = 24.65$ V m^{-1}. Such an electric field is equivalent to four times the potential gradient along the centerline of the cell containing 1 M LiPF$_6$ in EC/DEC and operating

at $I_{\text{app}} = 0.2\,\text{mA}$ at $t = 8\,\text{h}$ (i.e., maximum potential gradient during the galvanostatic polarization experiment).
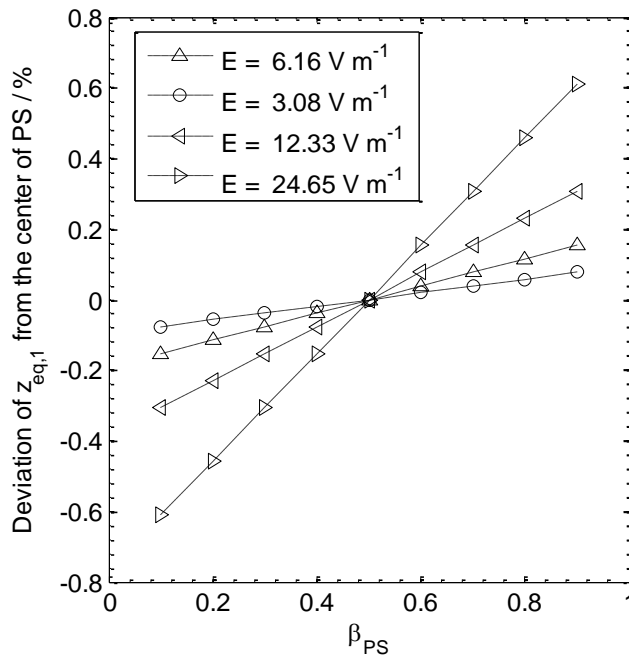

Figure S.1. Variation of the equilibrium locus of PS,1 as a function of charge-transfer coefficient exposed to electric fields with different amplitudes assuming no local perturbation (i.e., Eq. (S.4)).

List of Symbols

    A   symbol for single salt

    c concentration of the electrolyte in the solution, mol m^{-3}

    c_i concentration of species i in the solution, mol m^{-3}

    c_{T} total concentration of solution, mol m^{-3}

    c_q concentration of reacting species in $q = \text{PS, WE, CE}$, mol m^{-3}

    $\mathcal{D}$ diffusion coefficient of electrolyte based on a thermodynamic driving force, $\text{m}^2\,\text{s}^{-1}$

$\mathcal{D}_{ij}$ Stefan-Maxwell diffusion coefficients, $m^2\,s^{-1}$

D chemical diffusion coefficient on a molar basis, $m^2\,s^{-1}$

E electric field applied to electrolyte, $V\,m^{-1}$

e^- symbol for electron

F Faraday's constant, $C\,mol^{-1}$

f_i molar activity coefficient of species i in solution

$f_{\pm}$ mean molar activity coefficient of electrolyte

$\mathbf{i}$ ionic current density, $A\,m^{-2}$

I_{app} applied current, A

I_q current density normal to the surface of electrode $q = PS, l, WE, CE$, $A\,m^{-2}$

k_q^0 charge-transfer reaction rate constant $q = PS, WE, CE$, $mol^{\beta_q}\,m^{1-3\beta_q}\,s^{-1}$

L cell length, m

$M_i^{z_i}$ symbol for species i in solution

M_i molar weight of species i, $g\,mol^{-1}$

M_e molar weight of electrolyte, $g\,mol^{-1}$

M_0 molar weight of solvent, $g\,mol^{-1}$

N total number of species in solution

$\mathbf{N}_i$ molar flux density of species i

n number of electrons involved in electrode reaction

p pressure, Pa

R universal gas constant, $J\,mol^{-1}\,K^{-1}$

R_c cell radius, m

$\mathcal{r}$	borosilicate glass fiber radius, m
r	radial distance from the centerline of the cell, m
$\hat{\mathbf{r}}$	radial component unit vector
s_i	stoichiometric coefficient of species i in electrode reaction
T	temperature, K
t	time, s
t_i^0	transference number of species i with respect to the solvent velocity
U_q	equilibrium potential of electrode $q = \text{PS, WE, CE}$ vs. reference electrode used to define solution electric potential, V
$\bar{V}_i$	partial molar volume of species i in solution, $\text{m}^3 \text{ mol}^{-1}$
$\bar{V}_e$	partial molar volume of electrolyte in solution, $\text{m}^3 \text{ mol}^{-1}$
$\mathbf{v}_i$	velocity of species i in solution, m s^{-1}
$\mathbf{v}$	mass-average velocity of solution, m s^{-1}
y_i	mole fraction of species i in solution
z	axial distance along centerline, m
$\hat{\mathbf{z}}$	axial component unit vector
z_i	charge number of species i in solution
$z_{\text{eq},l}$	equilibrium locus between cathodic and anodic poles of the potential sensor l, m

Greek

β_q	Charge-transfer coefficient $q = \text{PS, WE, CE}$
Γ	concentration polarization, V
δ	potential sensor width, m
$\eta_{\text{PS},l}$	overpotential at interface between solution and potential sensor l, V

κ	ionic conductivity, S m^{-1}
K	permeability of separator, m^2
μ	dynamic viscosity of solution, Pa.s
μ_i	chemical potential of species i in solution, J mol^{-1}
μ_e	chemical potential of electrolyte, J mol^{-1}
μ_e^θ	chemical potential of electrolyte at the secondary reference state θ, J mol^{-1}
ν	total number of moles of ions into which one mole of salt dissociates
ν_i	number of moles of ion i produced by salt dissolution
ρ	solution density, kg m^{-3}
σ	spacing between working/counter electrode and potential sensor, m
Φ	electric potential of solution, V
Φ_{WE}	electric potential of WE, V
Φ_{CE}	electric potential of CE, V
$\Phi_{PS,l}$	electric potential of potential sensor l, V

References

1   Arora, A.; Eijkel, J. C. T.; Morf, W. E.; Manz, A. *Anal. Chem.* **2001**, *73*, 3282–3288.