

1 **Comparing measurements of limiting**
2 **current of electrolytes with**
3 **theoretical predictions up to the**
4 **solubility limit**

5

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1

Abstract

2Imposing a steady ionic current through an electrolyte results in the
3formation of salt concentration gradients that compromise battery
4performance. The limiting current is usually defined as the current at which
5the salt concentration at the cathode approaches zero. Higher currents
6cannot be imposed on the cell as larger concentration gradients are
7unsustainable. We study the limiting current in electrolytes comprising a
8perfluorinated oligomer, C8-DMC, and lithium bis(fluorosulfonyl)imide salt in
9symmetric lithium cells. The time-dependence of the potential, which
10increases as salt concentration gradients develop, was also measured. Both
11steady-state and transient behaviors are modeled using Newman's
12concentrated solution theory; transport and thermodynamic parameters
13needed to perform the calculations were measured independently and
14reported in a previous publication [Shah et al., *Phys. Chem. Chem. Phys.*,
152019, **21**, 7857-66]. The limiting current is a non-monotonic function of salt
16concentration in both theory and experiment. The model shows that at low
17salt concentrations (below 0.88 mol/kg solvent), the concentration at the
18cathode approaches zero at limiting current. In contrast, at high salt
19concentrations (above 0.88 mol/kg solvent), the concentration at the anode
20approaches the solubility limit (2.03 mol/kg solvent). The experimentally
21determined salt concentration at which the limiting current is maximized is in
22excellent agreement with theoretical predictions made without resorting to
23any adjustable parameters.

1

Keywords

2Fluorinated electrolyte, limiting current, lithium batteries, modeling, PFPE,

3PFPE, solubility limit

11. Introduction

1A barrier to the development of next-generation rechargeable lithium-based
2batteries is the electrolyte. Conventional electrolytes, comprising a lithium
3salt, LiPF_6 , dissolved in a mixture of cyclic carbonates, exhibit limited
4electrochemical stability windows ($< 4.5 \text{ V vs Li}^+/\text{Li}$), and are susceptible to
5thermal runaway.^{1,2} One approach has been to replace conventional,
6carbonate electrolytes with fluorinated, electrolytes that have reduced
7flammability.³⁻⁷ Fluorinated electrolytes also exhibit high oxidation potentials
8($> 5 \text{ V vs. Li}^+/\text{Li}$), and thus have the potential to enable high voltage
9cathodes.^{8,9}

11

12The operation of a battery results in the development of salt concentration
13gradients within the electrolyte. These gradients arise due to existence of
14two mobile charge carriers: the anion and cation, and the magnitudes of the
15gradients increase with increasing current density. The limiting current is
16defined as the largest current that can be imposed on the electrolyte.
17Conventional wisdom suggests that at the limiting current, the salt
18concentration gradient is so large that the salt concentration at the cathode
19approaches zero.¹⁰ A few studies report experimentally determined limiting
20current, but the factors that govern this parameter have not been fully
21elucidated.^{11,12}

22

1 Complete electrochemical characterization for a binary electrolyte requires
2 the measurement of the thermodynamic factor, T_f , and three transport
3 properties: conductivity, κ , the salt diffusion coefficient, D , the cation
4 transference number with respect to the solvent t_{+}^{0} .¹⁰ All of the parameters
5 must be measured as a function of salt concentration to obtain a complete
6 picture.¹³⁻¹⁷ In a recent study, Pesko et al. used measured values of T_f , κ , D ,
7 and t_{+}^{0} in mixture of poly(ethylene oxide) (PEO) and lithium
8 bis(trifluoromethanesulfonyl)imide salt (LiTFSI) to predict limiting current
9 based on the conventional definition of limiting current.¹⁸

10

11 Recently, we reported T_f , κ , D , and t_{+}^{0} for a perfluoropolyether, C8-DMC,
12 mixed with lithium bis(fluorosulfonyl)imide salt (LiFSI).¹⁹ We use Newman's
13 concentrated solution theory to predict concentration and potential profiles
14 as a function of salt concentration and current density in lithium symmetric
15 cells at steady-state. We also use the theory to calculate transient
16 concentration and potential profiles in the electrolyte. We note conditions
17 (salt concentration and current density) under which the salt concentration
18 at the cathode approaches zero. We also note the conditions under which
19 salt concentration at the anode approaches the solubility limit. These
20 predictions are compared with experimental data without the use of any
21 adjustable parameters.

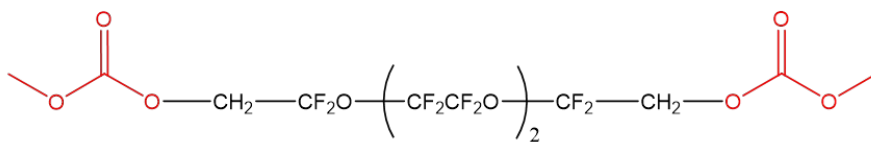
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12. Experimental Details

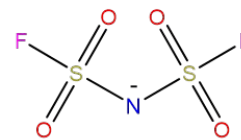
2Electrolyte Preparation

3The perfluoroether, C8-DMC (CAS-No. 1976035-41-2), was synthesized from
4a diol terminated precursor following procedures described in previous
5work.^{3,5,19,20} The chemical formula of C8-DMC is given in Figure 1a. All sample
6preparation was done within an argon filled Vac glovebox with H₂O and O₂
7concentrations kept below 1 ppm. Lithium bis(fluorosulfonyl)imide (LiFSI)
8(cat. no. 097602) was purchased from Oakwood Products, Inc. Figure 1b
9contains the chemical formula of the FSI anion. The salt was $\geq 99\%$ pure, as
10confirmed by a Certificate of Analysis form. The salt was dried at 100 °C
11under dynamic vacuum for three days inside a glovebox antechamber. Prior
12to transfer into the glovebox, C8-DMC was dried under active vacuum inside
13the glovebox antechamber at 50 °C for 72 hours. In order to form
14electrolytes, a predetermined amount of Li salt was added to a known mass
15of C8-DMC. Once the salt was added, the electrolytes were placed on a
16magnetic stirrer and were allowed to mix for 12 hours or more using a
17magnetic stir bar. The salt concentration of prepared electrolytes is
18described as m_{av} , the molality of the electrolyte in units of mol LiFSI/kg C8-
19DMC. Electrolytes were prepared within a concentration window of 0.28
20 $\leq m_{av} \leq 1.78$ mol/kg.

(a)



(b)



1
2 **Figure 1:** (a) C8-DMC and (b) FSI anion.

3

4 *Lithium symmetric cells and limiting current measurements*

5 Lithium symmetric cells were assembled by sandwiching an electrolyte-
6 soaked separator, Celgard 2500 (Celgard Company), with lithium discs, cut
7 from lithium chips (MTI Corp.). Celgard 2500 was cut to 19 mm in diameter
8 and had an average thickness, L , of $25.4 \pm 0.6 \mu\text{m}$. The diameter of the 150
9 μm thick Li disc was 12.7 mm. Three replicate cells were produced for each
10 electrolyte and the reported data is the average of those three cells, with
11 error bars representing the standard deviation between the replicate cells.
12 Data were collected on a Bio-Logic VMP3 potentiostat. Each sample cell was
13 subjected to a conditioning treatment, which consisted of charge and
14 discharge cycles at 0.02 mA/cm^2 in order to help stabilize the interfacial
15 layer. The sequence performed was a 4 hour charge, 30 minutes rest, a 4
16 hour discharge, 30 minutes rest, and repeated for a total of 6 times. To track
17 the cell impedance with time, ac impedance spectroscopy was performed
18 before the beginning of conditioning, after each rest step, and at the end of
19 conditioning. Complex impedance plots were obtained within a frequency
20 range of 1 MHz to 100 mHz. Each sample was then polarized at all of the
21 following current densities for 30 minutes: $i_{ss} = 0.20, 0.40, 0.50, 0.60, 0.70,$

10.75, 0.80, and 1.00 mA/cm² with potential and current data recorded every
 2five seconds. Ac impedance spectroscopy followed each polarization and the
 3data were analyzed in the form of a Nyquist plot. The data were fit to an
 4equivalent electrical circuit and the interfacial impedance, R_i , was extracted,
 5as described in a previous publication.⁵ The interfacial impedance was used
 6to correct for the potential drop, Φ , across an electrolyte, as described in Eq.
 71 below

$$\Phi(t) = \Phi_{measured}(t) - R_i i_{ss} A \quad (1)$$

8

9where $\Phi_{measured}$ is the potential across the lithium symmetric cell as measured
 10by the potentiostat under a given steady-state current density, i_{ss} , and A is
 11the active area of the electrode. All electrochemical characterization was
 12done at 30 C.

13

143. Theory

15Steady-state model

16The relationship between i_{ss} and the electrochemical properties of an
 17electrolyte, based on Newman's concentrated solution theory,¹⁰ was derived
 18in ref. 18. This relationship changes slightly when the electrolyte is contained
 19in a porous separator (we call this the electrolyte/separator composite), and
 20is given by Eq. 2

$$\int_{m(x=0)}^{m(x)} \frac{c(m) D_s(m)}{m t_{-i^0(m)}} dm = \frac{i_{ss} L}{F z_{-i^0(x/L)}} i \quad (2)$$

1

2 where c is the concentration of the salt in the electrolytic phase in mol/cm³,

3 D_s is the salt diffusion coefficient measured by restricted diffusion on the

4 electrolyte/separator composite, m is the molality, t_{-i} is the anion

5 transference number relative to the velocity of the solvent ($t_{-i}^0 = 1 - t_{+i}^0$), z_{-i} is

6 the charge number on the anion, v_{-i} is the number of anions the salt

7 disassociates into, L is the thickness of the electrolyte/separator composite,

8 x/L is the normalized thickness, and F is Faraday's constant (the transference

9 number is unaffected by the presence of the separator). All of the ion

10 transport properties depend on salt concentration, as indicated in Eq. 2.

11 During an experiment, the average salt concentration of the electrolyte, m_{av} ,

12 is controlled. The molality profile predicted by Eq. 2 must be averaged from

13 $x = 0$ to $x = L$ to ensure that the model predicted average concentration is

14 equal to m_{av} .

15

16 The relationship between the electric potential within an

17 electrolyte/separator composite to the measurable transport properties is

18 given by

$$\Phi_{SS}(x) = -F z_{-i} v_{-i} \int_{m(x=L)}^{m(x=0)} \frac{c(m) D_s(m)}{m t_{+,id}(m) \kappa_s(m) t_{-,i}(m)} dm \quad (3)$$

19

20 where $t_{+,id}$ is the ideal transference number (unaffected by the presence of

21 the separator) and κ_s is the conductivity of the electrolyte/separator

1 composite. The ideal transference number, $t_{+,id}$, is determined by the steady-
2 state current method.^{21,22} The relationship between the ideal transference
3 number and κ , $t_{-,i}$, $1 + \frac{d \ln \gamma_{\pm}}{d \ln m}$ (the thermodynamic factor), and D is given in
4 ref. 23 and a relationship was first noted in ref. 24. In this paper, Eqs 2 and 3
5 were solved numerically using MATLAB and published data¹⁹ for the relevant
6 parameters.

7

8 *Transient model*

9 As is the case for the steady-state model, the transient model is also based
10 on Newman's concentrated solution theory.¹⁰ We solve the governing
11 differential equation along the thickness direction (denoted as the x-direction
12 in the present analysis) of the polymer electrolyte. Since lithium metal exists
13 on both ends of the electrolyte domain, these lithium/polymer interfaces
14 have been considered as the two boundaries of the one-dimensional
15 computational domain. Table 1 summarizes the governing equations and
16 boundary conditions used in this study. The mass balance relation for
17 electrolyte salt is expressed in Eq. 4, which was derived based on
18 concentrated solution theory, is used to obtain transient concentration
19 profiles ($c(x, t)$) across the polymer electrolyte. Note that the effect of
20 transference number gradient is also taken into account, as shown in the
21 second term on the right of Eq. 4. The modified Ohm's law expressed in Eq.
22 7, which includes the polarization in the electrolyte due to concentration

1gradients, is used to obtain transient ionic potential profiles, $\Phi_1(x, t)$, across
 2the polymer. The potential drop across the polymer electrolyte is denoted as
 3 $\Phi_{1,(x=0)} - \Phi_{1,(x=L)}$. The model parameters used in this study are listed in Table 2.

4

5Table 1: Summary of governing equations for C8-DMC/LiFSI with a Celgard
 62500 separator in a Li symmetric cell

	Governing equation	Boundary conditions
Mass balance (polymer electrolyte)	$\frac{\partial c}{\partial t} = \nabla \cdot \left[D_s \left(1 - \frac{d \ln c}{d \ln c_0} \right) \nabla c \right] - i_{ss} \cdot \nabla$ (4)	$-D_s \frac{\partial c}{\partial x} \Big _{x=0} = 1 - \frac{t_{+}^{Li^0}}{F} i_{ss} \dot{i}$ (5)
		$-D_s \frac{\partial c}{\partial x} \Big _{x=L} = -1 - \frac{t_{+}^{Li^0}}{F} i_{ss} \dot{i}$ (6)
Modified Ohm's law (Ionic phase)	$i_{ss} = -K_s \nabla \Phi_2 + \frac{2K_s RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c} \right) \dot{i}$ (7)	$\Phi_{2,L} = 0$ (8)

7

8Table 2: Parameters used for Li symmetric transient modeling of
 9C8-DMC/LiFSI with a Celgard 2500 separator

Symbol	Parameter	Initial Value	Reference
L	Thickness of separator	2.54e-3 [cm]	Measured
K	Ionic conductivity of C8-DMC	Function of concentration	Measured
D	Diffusion coefficient of LiFSI in C8-DMC	Function of concentration	Measured
$t_{+}^{Li^0}$	Cation transference number	Function of concentration	Measured
F	Faraday constant	96450 [C/mol]	-
R	Universal gas constant	8.314 [J/mol/K]	-
T	Temperature	30 [°C]	-

10

114. Results and Discussion

12Our objective is to compare potential versus time curves determined
 13experimentally in Li symmetric cells as a function of average salt
 14concentration and current density up to the salt solubility limit and the
 15limiting current with theoretical predictions. Table 3 shows the
 16aforementioned transport and thermodynamic properties of

1electrolyte/separator composites for a range of salt concentrations taken
 2from ref. 19. It is convenient to work with units of molality for steady-state
 3calculations while transient calculations are best done using molar
 4concentrations. In Table 3, we list both m and c , based on measurements
 5reported in ref. 19. Note that t_{+c^0i} is negative over the entire concentration
 6range, indicating the formation of charged clusters. The interactions that
 7lead to the formation of these clusters has not yet been elucidated.

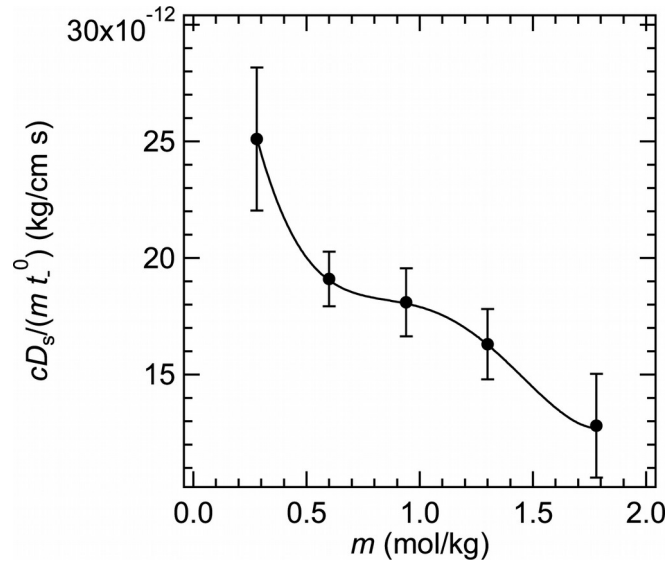
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10**Table 3:** Transport properties of C8-DMC/LiFSI with a Celgard 2500
 11separator at 30 °C¹⁹

m (mol/kg)	c (mol/cm ³)	K_s (S/cm)	D_s (cm ² /s)	$t_{+,id}$	t_{+c^0i}	$1 + \frac{d \ln \gamma_{\pm}}{d \ln m}$
0.28	3.87×10^{-4}	$[2.91 \pm 0.19] \times 10^{-6}$	$[3.66 \pm 0.39] \times 10^{-8}$	0.89 ± 0.01	-1.002 ± 0.06	0.15 ± 0.02
0.60	8.89×10^{-4}	$[9.82 \pm 0.90] \times 10^{-6}$	$[2.24 \pm 0.12] \times 10^{-8}$	0.77 ± 0.01	-0.751 ± 0.04	0.19 ± 0.02
0.94	1.36×10^{-3}	$[1.17 \pm 0.07] \times 10^{-5}$	$[1.72 \pm 0.13] \times 10^{-8}$	0.71 ± 0.07	-0.378 ± 0.04	0.42 ± 0.06
1.30	1.70×10^{-3}	$[1.14 \pm 0.09] \times 10^{-5}$	$[1.34 \pm 0.11] \times 10^{-8}$	0.67 ± 0.02	-0.070 ± 0.00	0.85 ± 0.11
1.78	2.36×10^{-3}	$[7.92 \pm 0.75] \times 10^{-6}$	$[1.20 \pm 0.21] \times 10^{-8}$	0.67 ± 0.02	-0.232 ± 0.01	1.12 ± 0.23

12



1

2 **Figure 2:** Fit of the integrand term of Eq. 2, $\frac{cD_s}{mt_{-i}^0}$, with LiFSI salt molality.

3 The solid curve shows the least-squares polynomial fit given by Eq. 9.

4

5 To calculate the concentration profile within an electrolyte given a steady-

6 state current density, i_{ss} , and thickness, L , the transport parameters given in

7 Table 3 were fit as a continuous function to salt concentration. In Figure 2,

8 we show the 4th order polynomial fit to the product appearing on the right

9 side of Eq. 2,

$$\frac{c(m)D_s(m)}{mt_{-i}^0(m)} = k_0 + k_1 m + k_2 m^2 + k_3 m^3 + k_4 m^4 \quad (9)$$

10

11 with fitting parameters

$$\begin{aligned} k_0 &= 2.03 \times 10^{-10} & k_1 &= -4.52 \times 10^{-10} & k_2 &= 6.46 \times 10^{-10} \\ k_3 &= -3.99 \times 10^{-9} & k_4 &= 8.861 \times 10^{-11} & & \end{aligned}$$

13 where t_{-i}^0 is equal to $1 - t_{+i}^0$, D_s is in cm²/s, c is in mol/cm³, and m is in

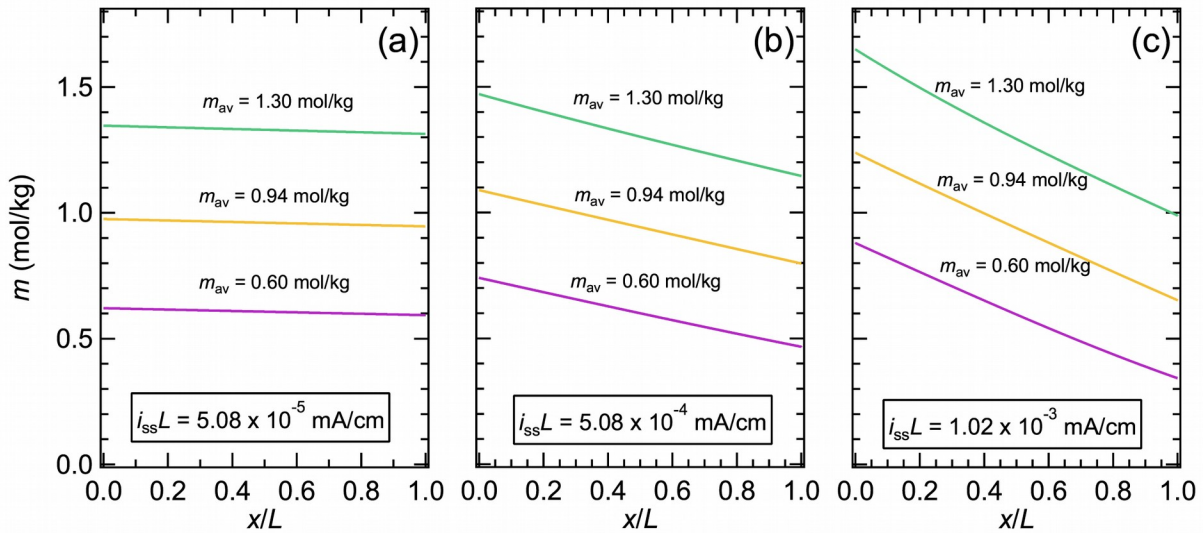
14 mol/kg. The parameters apply to the range $0.28 \leq m \leq 1.78$ mol/kg and for T

15 = 30 °C.

1

2The concentration profile within a lithium symmetric cell under a steady-
3state operation is governed by the thickness of the electrolyte, L , the salt
4concentration, m_{av} , and the steady-state current density, i_{ss} .

5



6

7**Figure 3:** Concentration profiles of LiFSI in C8-DMC predicted by Eq. 2 at
8steady-state for three different normalized current densities: (a) $i_{ss}L = 5.08 \times$
9 10^{-5} , (b) $i_{ss}L = 5.08 \times 10^{-4}$, and (c) $i_{ss}L = 1.02 \times 10^{-3}$ mA/cm.

10

11Fig. 3 shows the concentration profiles across a mixture of C8-DMC/LiFSI for
12three initial concentrations of $m_{av} = 0.60, 0.94,$ and 1.30 mol/kg and for
13three values of normalized current density, $i_{ss}L$. We have chosen the product
14 $i_{ss}L$ for this plot because i_{ss} is inversely proportional to L ; Fig. 3 may thus be
15used to determine i_{ss} values for L values different from that used in this
16particular study. The concentration profiles were obtained by numerically
17solving Eq. 2 using the fitted Eq. 4. The figures correspond to $i_{ss}L = 5.08 \times 10^{-}$
18 $5, 5.08 \times 10^{-4},$ and 1.02×10^{-3} mA/cm (relating to $i_{ss} = 0.02, 0.20,$ and 0.40

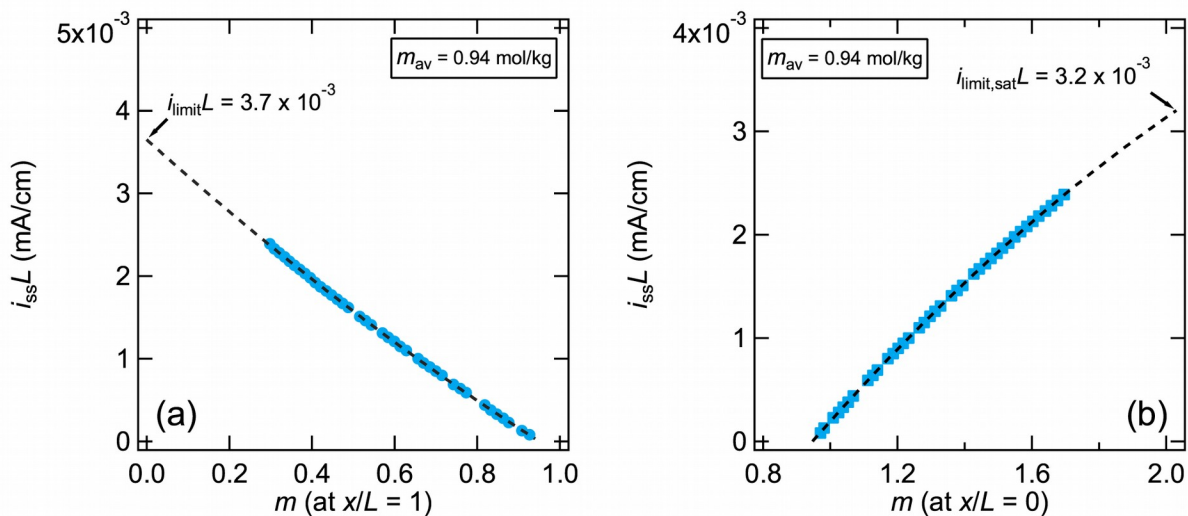
1mA/cm² for $L = 0.00254$ cm). It is evident from Fig. 3a that under small
2applied normalized current densities ($i_{ss}L = 5.08 \times 10^{-5}$ mA/cm), the
3concentration profiles are approximately linear and the gradients are small.
4However, with increasing normalized current densities, the concentration
5gradients become **steeper**, as shown in Figs. 3b and c. Note that the overall
6flux of lithium cations, at steady-state, is toward the negative electrode in
7spite of the fact that the transference number is negative at all salt
8concentrations. The sign of the transference number only gives the direction
9of the flux of lithium cations in a solution of uniform composition in response
10to an applied electrochemical potential. Thus, at the instant that a dc
11potential is applied to the cell, the net lithium cation flux is toward the
12positive electrode. At steady-state after the salt concentration gradients are
13fully developed, the net lithium cation flux is toward the negative electrode.²⁵

14

15One can estimate the normalized limiting current, $i_{limit}L$, within an electrolyte
16using model predicted concentration profiles. In order to do so, an electrolyte
17of known m_{av} must be modeled under a number of $i_{ss}L$ values and the salt
18concentration at the cathode ($x/L = 1$) is extracted at each normalized
19current density. An example of such an analysis is shown in Fig. 4a. In Fig.
204a, $i_{ss}L$ is plotted against the model predicted salt concentration, m , at $x/L =$
211 in blue circles for an electrolyte with an average salt concentration of m_{av}
22= 0.94 mol/kg. As the model is limited between $0.28 \leq m \leq 1.78$ mol/kg, the
23conventional limiting current must be predicted by extrapolating m (at $x/L =$

11) to zero. The dashed, black curve is a 2nd order polynomial fit to the model
 2predicted values in Fig. 4a, and predicts $i_{limit}L = 3.7 \times 10^{-3}$ mA/cm. It should
 3be noted that the solubility limit of LiFSI in C8-DMC is 2.03 mol/kg.⁵ It is
 4obvious that the concentration at any x/L in the cell must not exceed this
 5value for stable operation. The highest salt concentration occurs at the
 6anode ($x/L = 0$). In Fig. 4b, we thus plot $i_{ss}L$ versus $m(x/L = 0)$ for the same
 7average salt concentration used in Fig. 4a ($m_{av} = 0.94$ mol/kg). A 2nd order
 8polynomial is fit through the data and extrapolated to $m = 2.03$ mol/kg is
 9shown as a dashed curve. We define the normalized limiting current at which
 10this occurs as $i_{limit,sat}L$ which is 3.2×10^{-3} mA/cm for $m_{av} = 0.94$ mol/kg.

11



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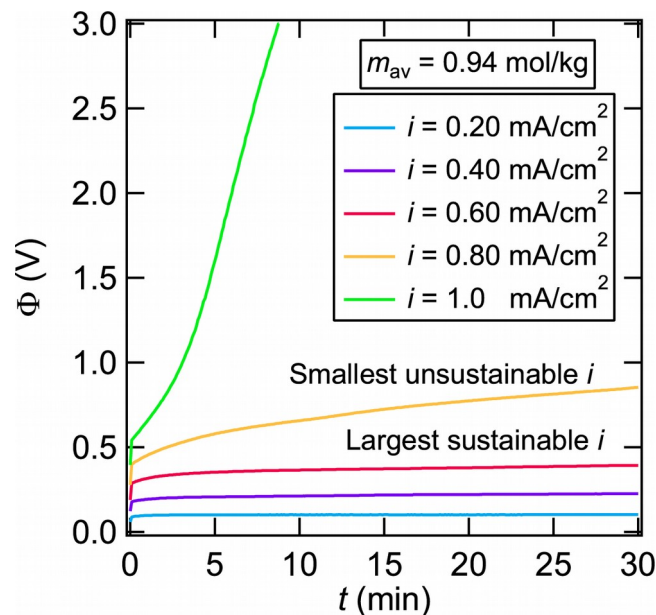
13**Figure 4:** Concentration predictions at the anode ($x/L = 1$) and cathode (x/L
 14= 0) for varying $i_{ss}L$ values for an electrolyte with an average concentration
 15of $m_{av} = 0.94$ mol/kg. (a) Model predictions of the concentration at the
 16anode, $x/L = 1$. The black dashed curve shows the least-squares polynomial
 17fit, which was extrapolated to $m = 0$ mol/kg to determine the normalized
 18limiting current density (marked as $i_{limit}L$). (b) Model predictions of the
 19concentration at the cathode, $x/L = 0$. The black dashed curve is a least-
 20squares polynomial fit, which was extrapolated to the salt solubility limit of

1 $m = 2.03$ mol/kg. This determined the normalized limiting current density
2 caused by salt saturation at the cathode (marked as $i_{limit, sat} L$).

3

4 There is an important question: for a given m_{av} , which mode of the limiting
5 current will be observed? We posit that the mode will correspond to the one
6 that is obtained at the lower normalized limiting current. For $m_{av} = 0.94$ mol/
7 kg, we conclude that the normalized limiting current will occur due to salt
8 precipitation. Similar analysis was repeated at all values of m_{av} .

9



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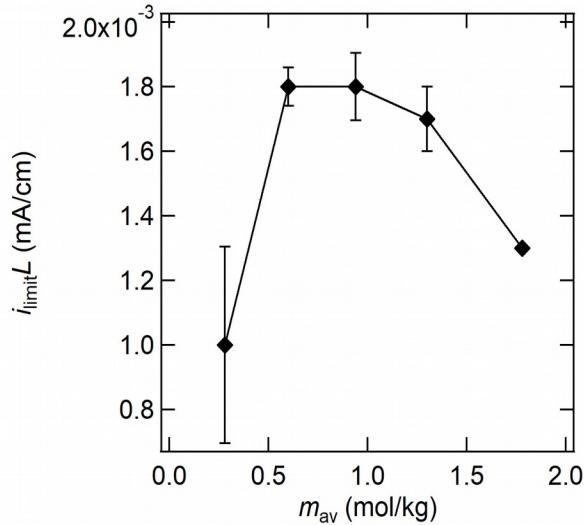
11 **Figure 5:** Time dependent potential behavior of C8-DMC/LiFSI with an
12 average salt concentration of $m_{av} = 0.94$ mol/kg in response to applied
13 current densities from $i = 0.20$ to 1.0 mA/cm² (no interfacial impedance
14 correction). The largest sustainable current density, i , as determined by
15 plateau in measured potential, was 0.60 mA/cm², shown as a solid red curve.
16 The smallest unsustainable i , as determined by the lack of a plateau in the
17 potential within the measurement window, was 0.80 mA/cm² and is shown as
18 a solid yellow curve.

19

20 Turning to experiments, we now discuss potential versus time curves for an
21 electrolyte/separator composite in a lithium symmetric cell ($L = 0.00254$ cm)

1at a fixed applied current. In Fig. 5, we show the potential profile versus time
2for current densities ranging from $i_{ss} = 0.20 \text{ mA/cm}^2$ to 1.00 mA/cm^2 in 0.2
3 mA/cm^2 increments for an initial concentration of $m_{av} = 0.94 \text{ mol/kg}$. At low
4current densities (below 0.60 mA/cm^2), the potential increases
5instantaneously at $t = 0^+$ due to the resistance of the cell when
6concentration is uniform, increases with time as concentration gradients
7develop, and reaches a plateau when the concentration profile in the cell
8approaches steady-state. At a slightly higher current density of 0.80 mA/cm^2 ,
9the potential increases monotonically with time and does not reach a
10plateau. We refer to 0.60 mA/cm^2 as the largest sustainable current density
11and 0.80 mA/cm^2 as the smallest unsustainable current density. Increasing
12the current density beyond 0.80 mA/cm^2 leads to potential increases
13exponentially with time with no hint of a plateau. Data similar to that shown
14in Fig. 5 was obtained for all of the electrolytes. The normalized limiting
15current density, $i_{limit}L$, was determined for each electrolyte by averaging the
16largest sustainable current and smallest unsustainable current. In Fig. 6, we
17plot the experimental limiting current, $i_{limit}L$, as a function of m_{av} . The
18normalized limiting current for $m_{av} = 0.28 \text{ mol/kg}$ is $1 \times 10^{-3} \text{ mA/cm}$. It
19increases with increasing salt concentration, reaching a broad maximum of
20 $i_{limit}L = 1.8 \times 10^{-3} \text{ mA/cm}$ between $m_{av} = 0.60$ and 0.94 mol/kg . Further
21increase in m_{av} results in a decrease in $i_{limit}L$ until $m_{av} = 1.78 \text{ mol/kg}$, a value
22that is close to the salt solubility limit.

23



1
2 **Figure 6:** Experimental limiting current as a function of salt concentration.
3 The limiting current was taken as the average between the largest
4 sustainable current and smallest unsustainable current. The solid line is
5 drawn to guide the eye.
6

7 In Fig. 7a, $i_{limit}L$ is plotted against m_{av} ; the black diamonds show experimental
8 measurements that were shown in Fig. 6, red squares represent the
9 predicted $i_{limit}L$ when concentration reaches zero at the cathode ($x/L = 1$),
10 and blue circles are the predicted $i_{limit}L$ values when the solubility limit of $m =$
11 2.03 is reached at the anode ($x/L = 0$). The cathode-dominated $i_{limit}L$ (the
12 traditional limiting current) increases with increasing concentration. In
13 contrast, the anode-dominated $i_{limit,sat}L$ decreases with increasing
14 concentration. The two normalized limiting currents are equal to each other
15 at $m_{av} = 0.88$ mol/kg. Following our assumption that the failure mode
16 obtained experimentally corresponds to the one that requires the lower
17 current density, we conclude that salt depletion at the cathode causes the
18 limiting current at $m_{av} < 0.88$ mol/kg, while salt precipitation at the anode
19 causes the limiting current at $m_{av} > 0.88$ mol/kg. The two solid curves

1 through the theoretical predictions in Fig. 7a show these two branches. The
2 theoretical predictions provide a qualitative explanation for the observed
3 non-monotonic dependence of the measured limiting current on salt
4 concentration. There are two important quantitative differences between
5 theory and experiment in Fig. 7a: (1) The theoretical limiting currents are
6 about a factor of 2 higher than those measured experimentally and (2) The
7 peak in the limiting current versus salt concentration predicted by theory is
8 sharper than that observed experimentally. We do not have definitive
9 explanations for these deviations, except to note that the interface between
10 the electrode and electrolyte is complex, and that failure in the experimental
11 cells may begin before the salt concentration at the cathode reaches zero or
12 the salt concentration at the anode reaches the solubility limit.

13

14 Approximate expressions are often used to determine the normalized
15 limiting current due to salt depletion at the cathode.²⁶⁻²⁸ One such
16 expression can be derived by combining equations 11.22, 11.41, 11.43, and
17 11.57 in ref. 10:

$$i_{limit}L = \frac{2c_{av}D_sF}{1-t_{+,id}} \quad (10)$$

18

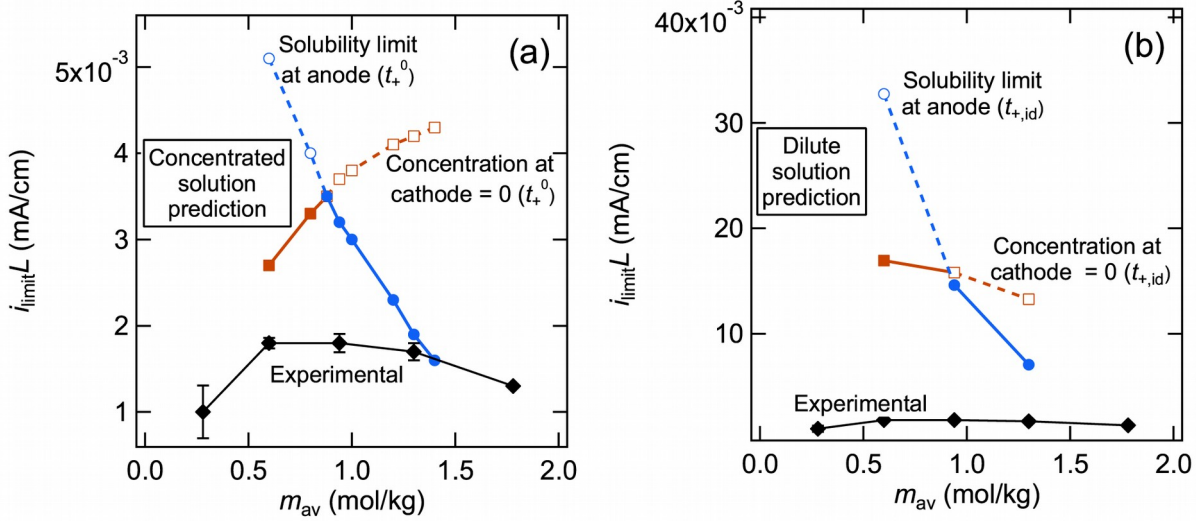
19 where c_{av} is the average electrolyte concentration in mol/cm³, D_s is the
20 restricted diffusion coefficient in the electrolyte/separator composite, and we
21 have taken the liberty of using the $t_{+,id}$. Similarly, the normalized limiting

1current that causes the concentration at the anode to approach the solubility
2limit is:

$$i_{limit,sat}L = 2 \frac{(c_{sat} - c_{av})D_s F}{1 - t_{+,id}} i \quad (11)$$

3

4where c_{sat} is salt solubility limit. For mixtures of C8-DMC and LiFSI, $c_{sat} = 2.61$
5 $\times 10^{-3}$ mol/cm³. Equations 10 and 11 were derived using dilute solution
6theory, thus the ideal transference number, $t_{+,id}$, is used in both equations. In
7Fig. 7b, we plot $i_{limit}L$ vs. m_{av} ; red squares denote the predicted $i_{limit}L$ using Eq.
810, and blue circles represent the predicted $i_{limit,sat}L$ using Eq. 11. Both
9predictions for the normalized limiting current decrease with increasing salt
10concentration. The cross-over from the salt-depletion limit to the salt
11precipitation limit occurs at a reasonable value of m_{av} , but the predicted
12trend is monotonic with salt concentration and inconsistent with the
13experimental data. In addition, the theoretical predictions for normalized
14limiting current based on dilute solution theory are an order of magnitude
15higher than those measured experimentally (black squares in Fig. 7b). It is
16obvious from Fig. 7 that concentrated solution theory is essential for
17establishing the underpinnings of the normalized limiting current in our
18system.



1
2 **Figure 7:** Normalized limiting current predictions as a function of m_{av} and
3 compared to experimental values (shown in black). (a) Concentrated solution
4 theory predictions of the normalized limiting current. The red dashed and
5 solid curves are the $i_{limit}L$ predicted when extrapolating m_{av} to 0 mol/kg at the
6 cathode ($x/L = 1$). The blue dashed and solid curves are the $i_{limit,sat}L$
7 predicted by extrapolating m_{av} to 2.03 mol/kg at the anode ($x/L = 0$). (b)
8 Normalized limiting current predictions using dilute solution theory. The red
9 dashed and solid curves are the $i_{limit}L$ predicted by Eq. 10 (concentration
10 equal to 0 mol/cm³ at the cathode). The blue dashed and solid curves are the
11 $i_{limit,sat}L$ predicted by Eq. 11 (salt saturation at the anode, $c_{sat} = 2.61 \times 10^{-3}$
12 mol/cm³). Normalized limiting current predictions using dilute solution theory
13 are an order of magnitude higher than the experimental values.
14

15 We now return to the potential that can be predicted using Eq. 3. In Fig. 8,
16 we plot the integrand in Eq. 3 along with a fit to the following empirically
17 determined function:

$$\frac{c(m)D_s(m)}{mt_{+,id}(m)\kappa_s(m)t_{-,c^0(m)} = b_0 \exp(-\tau_3 m) + b_1 \exp(-\tau_4 m)} \quad (12)$$

18

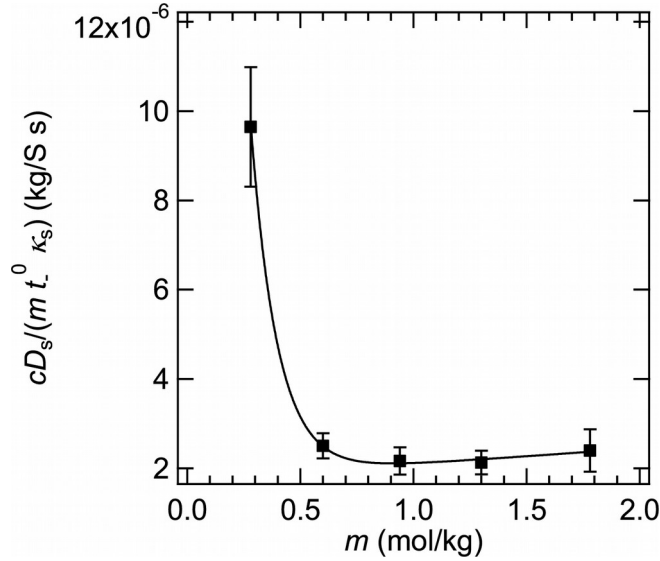
19 with fitting parameters

$$20 \quad b_0 = 1.802 \times 10^{-6} \quad b_1 = 8.566 \times 10^{-5}$$

$$\tau_3 = 0.1541 \quad \tau_4 = 8.525$$

1 where κ_s is the conductivity of the separator/electrolyte composite in S/cm.

2



3

4 **Figure 8:** Fit of the integrand term of Eq. 3, $\frac{cD_s}{m t_{+,id} \kappa_s t_{-,c} i}$, with LiFSI salt
5 5 molality. The solid curve shows the least-squares fit to the double
6 exponential given by Eq. 7.

7

8 The fit from Fig. 8 allows for potential predictions across the C8-DMC/LiFSI

9 electrolyte. In Fig. 9, we show the predicted potential profile, $\Phi(x/L)$, across

10 the electrolyte from $x/L = 0$ to 1 for selected values of m_{av} and $i_{ss}L$. We define

11 $\Phi = 0$ at $x/L = 1$. The purple, yellow, and green solid curves are potential

12 profiles for $m_{av} = 0.60, 0.94,$ and 1.30 mol/kg, respectively. From left to right,

13 each figure provides profiles for $i_{ss}L = 5.08 \times 10^{-5}, 5.08 \times 10^{-4},$ and 1.02×10^{-3}

14 mA/cm, respectively. Note that these values of $i_{ss}L$ correspond to the applied

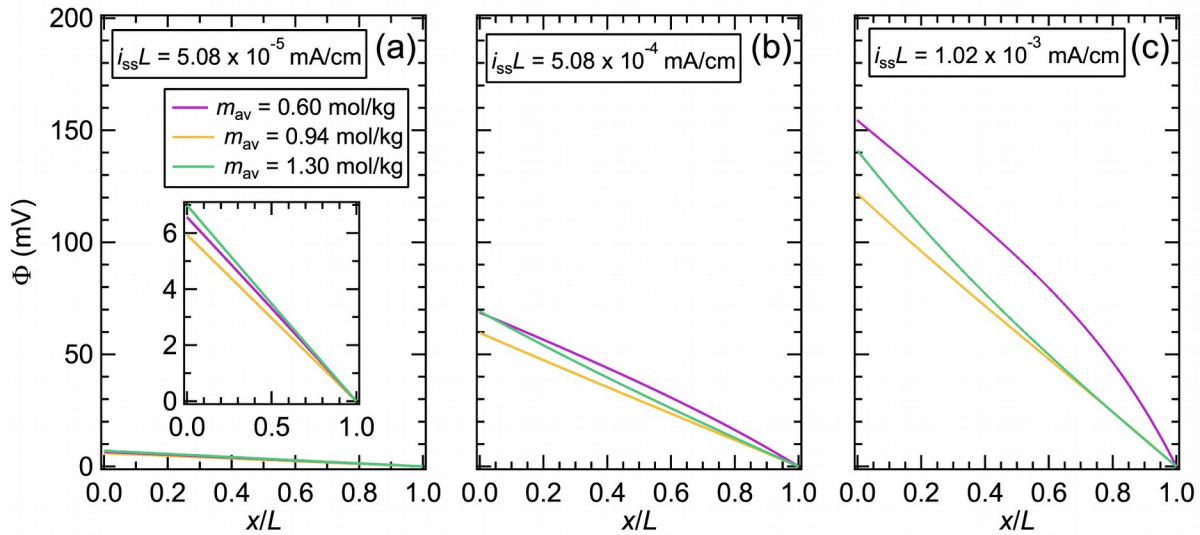
15 i_{ss} in our cell equal to $0.02, 0.20,$ and 0.40 mA/cm² ($L = 0.00254$ cm). At $i_{ss}L =$

16 5.08×10^{-5} mA/cm, the potential profile across the electrolyte is linear and

17 the gradient is small, as shown in Fig. 9a, but the potential behavior

1 becomes less linear with increasing $i_{ss}L$. Interestingly, the intermediate
 2 concentration of $m_{av} = 0.94$ mol/kg shows a lower $\Phi(x)$ across the electrolyte
 3 at all values of $i_{ss}L$, compared to $m_{av} = 0.60$ or 1.30 mol/kg. The potential
 4 drop for $m_{av} = 0.60$ shows more complex behavior: it has a lower potential
 5 drop across the electrolyte when compared to $m_{av} = 1.30$ at both $i_{ss}L = 5.08$
 6 $\times 10^{-5}$ and 5.08×10^{-4} mA/cm, but has the largest potential drop across the
 7 electrolyte at $i_{ss}L = 1.02 \times 10^{-3}$ mA/cm. Next, we compare the model
 8 predicted potential drop across the electrolyte to experimental
 9 measurements of potential, Φ_{exp} , for a range of m_{av} . The experimentally
 10 accessible potential is at $x/L = 0$. We thus define Φ_0 as to be the theoretically
 11 predicted potential at $x/L = 0$ for a given m_{av} and i_{ss} .

12



13

14 **Figure 9:** Potential profiles in C8-DMC/LiFSI electrolytes predicted by
 15 concentrated solution theory at steady-state. These are calculated using Eq.
 16 3 based on the fit shown in Fig. 8. Potential profile for (a) $i_{ss}L = 5.08 \times 10^{-5}$
 17 mA/cm, (b) $i_{ss}L = 5.08 \times 10^{-4}$ mA/cm, and (c) $i_{ss}L = 1.02 \times 10^{-3}$ mA/cm.

18 Interestingly, the potential drop across C8-DMC/LiFSI with $m_{av} = 0.60$ at $i_{ss}L$

1 = 5.08×10^{-5} mA/cm is less than that of $m_{av} = 1.30$, but has a higher
2 potential drop at $i_{ss}L = 1.02 \times 10^{-3}$ mA/cm.

3

4 The experimentally applied potential drop, Φ_{exp}/L , for the electrolyte with m_{av}

5 = 0.94 mol/kg is plotted as a function of i_{ss} in Fig. 10a. The experimental

6 potential drop is corrected for the lithium/electrolyte interfacial impedance

7 using Eq. 1. Also shown in Fig. 10a is the predicted potential drop, Φ_0/L ,

8 calculated from Fig. 9 for $m_{av} = 0.94$ mol/kg. Both theory and experiment

9 indicate that Φ/L increases with increasing i_{ss} . At $i_{ss} = 0.20$ mA/cm², the

10 theoretically predicted potential drop, Φ_0/L , is within experimental error. The

11 deviation between experiments and theory increases with increasing current

12 density. Further work is needed to resolve this discrepancy. In Fig. 10b, we

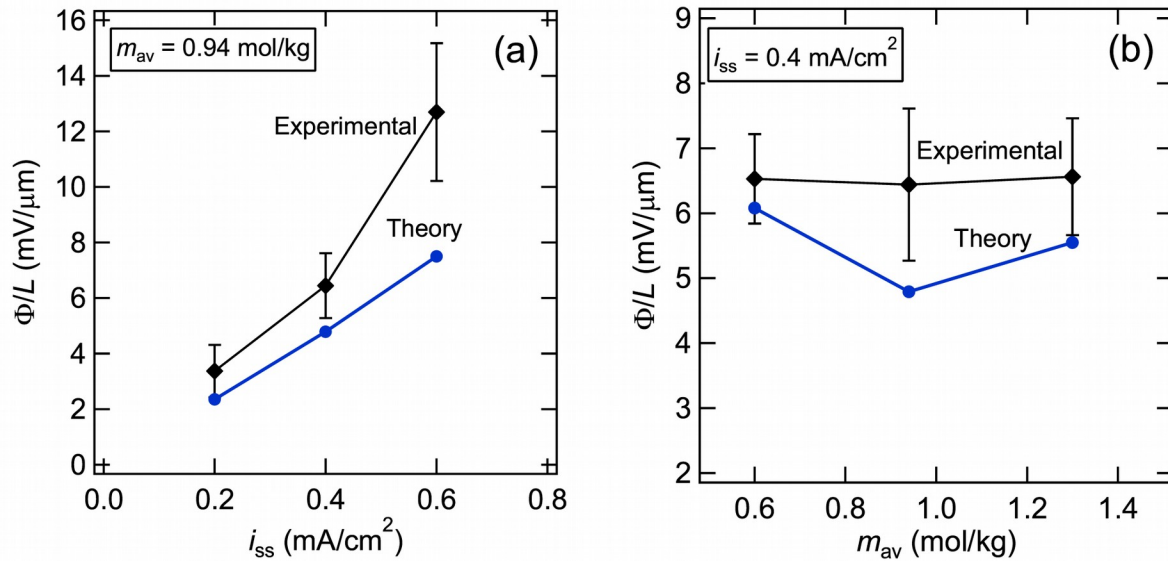
13 plot Φ_{exp}/L versus m_{av} for $i_{ss} = 0.4$ mA/cm². Φ_{exp}/L is a weak function of m_{av} .

14 Theoretical predictions, also shown in Fig. 10b, support this observation.

15 While the theoretical predictions generally lie below the experimental data,

16 they are within experimental error at $m_{av} = 0.60$ and 1.30 mol/kg.

17

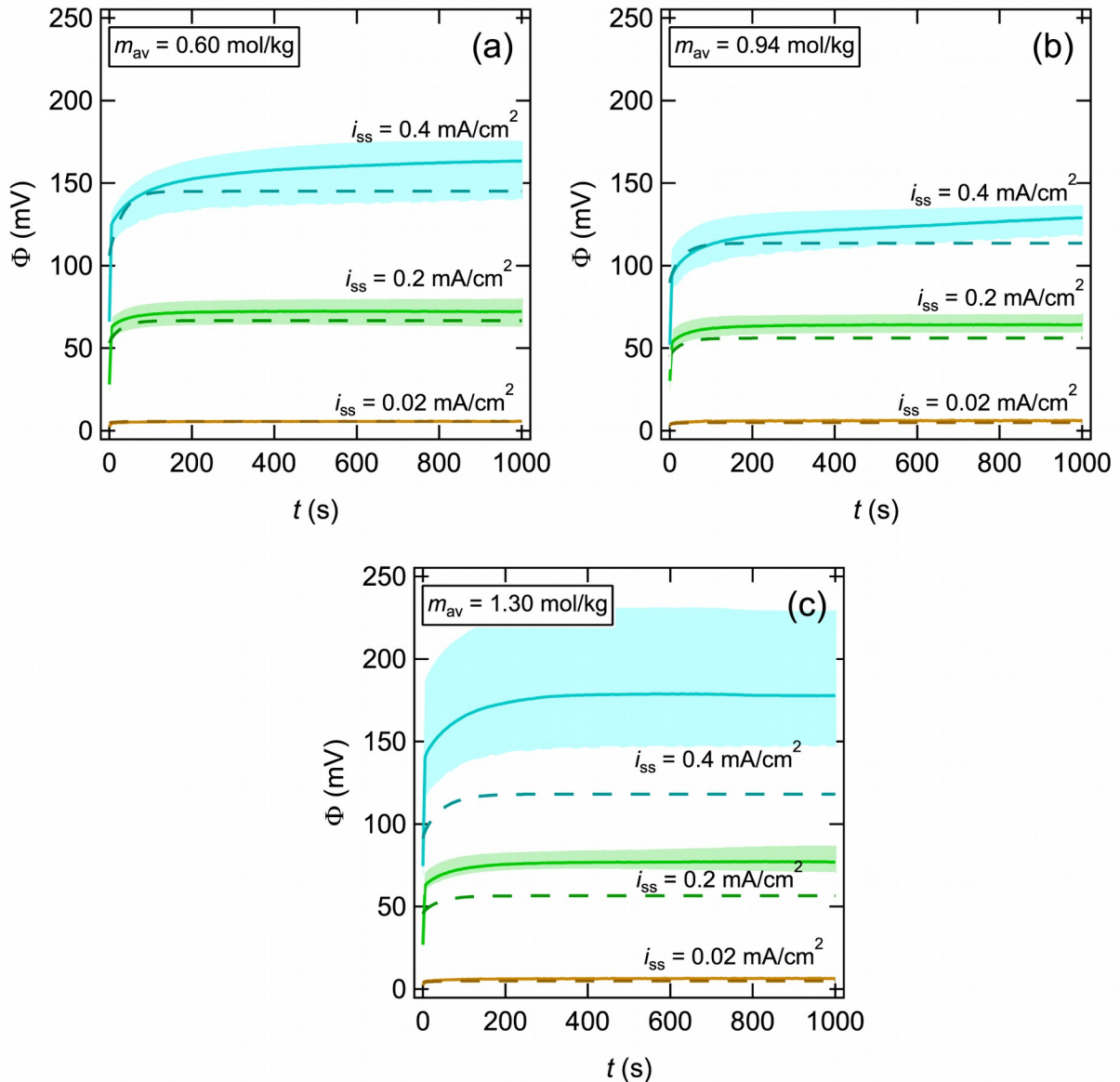


1
2 **Figure 10:** Experimental (black) and model predicted (blue) potential as a
3 function of (a) i_{ss} for a concentration of $m_{av} = 0.94$ mol/kg and (b) m_{av} for $i_{ss} =$
4 40.40 mA/cm².
5

6 Figure 11 shows the comparison between the experimentally measured and
7 predicted time evolution of cell potential based on the transient model (Table
8 81) using the same thermodynamic and transport parameters used in the
9 analysis of steady-state data presented in Figs. 2-10. The transient model, as
10 described in Table 1, is used for the numerical predictions of cell potential for
11 different average salt concentrations of $m_{av} = 0.60$ mol/kg ($c_{av} = 8.89 \times 10^{-4}$
12 mol/cm³), $m_{av} = 0.94$ mol/kg ($c_{av} = 1.36 \times 10^{-3}$ mol/cm³), and $m_{av} = 1.30$
13 mol/kg ($c_{av} = 1.70 \times 10^{-3}$ mol/m³). The experimental results, denoted by the
14 solid curves, are obtained from averaged potentials measured from three
15 separate cells; whereas, the highlighted regions show the range of measured
16 potentials across the cells. The dashed curves indicate the transient model
17 results. As shown in Figure 11a and b, the transient model predictions are in
18 quantitative agreement with experiments at all applied current densities for

1 $m_{av} = 0.60$ and 0.94 mol/kg. The theoretical and experimental potential
2 jumps at $t = 0^+$ are in agreement, as is the approach to steady-state wherein
3 the cell potential increases with time as concentration gradients develop.
4 The agreement between theory and experiment is only qualitative at $m_{av} =$
5 1.30 mol/kg (Figure 11c). While the time-scale over which concentration
6 gradients develop are similar in both theory and experiment, both the
7 instantaneous potential at $t = 0^+$ and the steady-state potential measured
8 experimentally are higher than theoretical predictions. While it is not clear
9 why this discrepancy is seen at $m_{av} = 1.30$, the agreement between the
10 model and the data seen in Figure 11 is noteworthy, as there are no
11 adjustable parameters in the model.

12



1
2 **Figure 11:** Time dependent experimental potentials (solid curves) are
3 compared to our transient model (dashed curves) for lithium symmetric
4 cells. The experimental data was averaged from three replicate cells (solid
5 curves) and the error is given by the standard deviation (light shaded areas).
6 Transient potential behavior for $i_{ss} = 0.02, 0.20,$ and 0.40 mA/cm^2 for (a) m_{av}
7 $= 0.60 \text{ mol/kg}$, (b) $m_{av} = 0.94 \text{ mol/kg}$, and (c) $m_{av} = 1.30 \text{ mol/kg}$.

8

9

10

11

1

25. Conclusion

3The performance of an electrolyte in a battery is limited, in part, by the
4maximum current that can be drawn through it. Traditionally, this maximum
5is calculated by predicting salt concentration profiles as a function of current
6density and noting the current density at which the salt concentration at the
7cathode is zero. Another limitation arises when the salt concentration at the
8anode exceeds the solubility limit. Our analysis considers both possibilities.
9We have used Newman's concentrated solution theory to predict steady-
10state salt concentration profiles as a function of current density for mixtures
11of C8-DMC and LiFSI. These predictions were enabled by the complete
12electrochemical characterization of these mixtures (i.e., measurement of κ ,
13 D , $t_{+,-}^0$, and T_f as functions of salt concentration) that was reported in ref. 19.
14An interesting feature of these electrolytes is that $t_{+,-}^0$ is negative across all
15salt concentrations. The dc potential across Li symmetric cells containing C8-
16DMC/LiFSI was measured experimentally as a function of applied current
17density and salt concentrations. At high enough current densities, clear
18signatures of the limiting current were observed. The experimentally
19determined limiting current was a non-monotonic function of salt
20concentration. It increases with increasing salt concentration up to $m_{av} =$
210.94 mol/kg and decreases with increasing salt concentration at higher
22values of m_{av} . The solubility limit of LiFSI in C8-DMC is 2.03 mol/kg. Our
23theoretical analysis indicates that the limiting current, up to $m_{av} = 0.88$

1mol/kg, occurs due to depletion of salt at the cathode, while the limiting
2current at higher values of m_{av} occurs due to the salt saturation at the anode.
3The experimentally determined time dependence of the potential across the
4lithium symmetric cells was also compared to predictions based on
5Newman's concentrated solution theory. Our approach enables comparing
6theory with experiment with no adjustable parameters.

7

1

Conflicts of interest

2There are no conflicts to declare.

1

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9

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1

Nomenclature

2

A	Active surface area of electrode (cm ²)
c	Concentration (mol/cm ³)
D	Salt diffusion coefficient of electrolytic phase (cm ² /s)
D_s	Salt diffusion coefficient of electrolyte in separator (cm ² /s)
F	Faraday's constant (96,485 C/mol)
i_{ss}	Steady-state current density (mA/cm ²)
i_{limit}	Limiting current density (mA/cm ²)
$i_{limit,sat}$	Limiting current density due to salt precipitation (mA/cm ²)
L	Thickness of electrolyte/separator (cm)
m	Molality (mol/kg)
R	Ideal gas constant (J/mol K)
R_i	Resistance of electrolyte/electrode interface when i_{ss} is reached (Ω)
T	Temperature (K)
T_f	Thermodynamic factor
t	Time (s)
t_{+i^0i}	Cation transference number relative to the solvent velocity. Obtained using the Balsara and Newman method
t_{-i^0i}	Anion transference number relative to the solvent velocity; $t_{-i^0} = 1 - t_{+i^0i}$
$t_{+,id}$	Ideal transference number using steady-state current method
x	Position (cm)
z_{-ii}	Anion charge
$1 + \frac{d \ln \gamma_{\pm}}{d \ln m}$	Thermodynamic factor

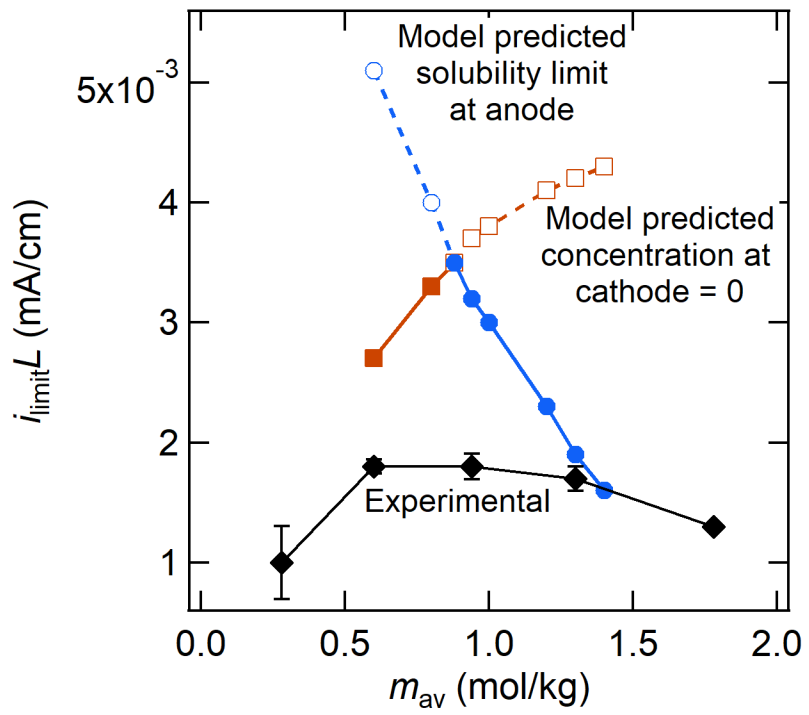
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4Greek

γ_{\pm}	Mean molal activity coefficient of the salt
κ	Conductivity of the electrolytic phase; (S/cm)
κ_s	Conductivity of the electrolyte and separator combined; (S/cm)
ν_i	Number of cations/anions per molecule of salt ($i = +$ or $-i$)
Φ	Electrolyte potential (mV)
Φ_{exp}	Experimental electrolyte potential (mV)
$\Phi_{measured}$	Measured cell potential (mV)
Φ_0	Steady-state model predicted electrolyte potential taken at $x = 0$ (mV)

Φ_1 Potential of the electrolyte at the electrode boundary
for the transient model (mV)

1Table of Contents Graphic



2