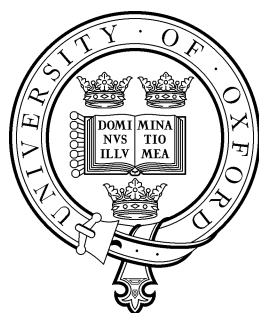


Characterisation of Transport and Thermodynamic Properties for Various Binary Electrolytes



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This thesis is dedicated to
my parents
my wife, Chencheng Ouyang
and my baby girl, Anna.

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Abstract

The electrolyte is an essential component in any electrochemical device. During the operation of a battery, an applied current introduces a concentration profile of salt within the electrolyte, whose shape is controlled by transport and thermodynamic properties of its constituent species. Concentration gradients are associated with overpotentials that can limit battery performance at high power. A better understanding of transport in battery electrolytes could help scientists optimize cell performance and design. To fully describe transport processes, techniques are needed to measure six key properties. We have accurately quantified some or all of the properties for binary electrolytes used in various energy storage systems, including redox flow, alkaline, lithium-ion, and magnesium-ion batteries.

Density and ionic conductivity for aqueous VOSO_4 solutions were quantified with respect to VOSO_4 concentration up to 0.53 M at five temperatures: 15, 20, 25, 30, and 35 °C. The partial molar volumes of VOSO_4 and water were calculated from the density/composition correlations. This was the first characterisation of both density and conductivity for aqueous VOSO_4 . The characterisation work was also used by a colleague to measure concentration dynamically during membrane cross-over experiments for all vanadium redox flow batteries.

We further measured the density, ionic conductivity, and dynamic viscosity of aqueous KOH over concentrations ranging from 0.05 M to 12.00 M at three temperatures: 15, 25, and 35 °C. The partial molar volume of KOH

risks with respect to concentration, while that of water stays relatively constant across the whole concentration range. The conductivity of aqueous KOH solutions reaches the maximum value around 6 M, which is the concentration used for commercial alkaline-battery electrolytes. We further attempted to quantify the diffusion coefficient using restricted-diffusion measurements. A MnO₂-deposited nickel electrode was prepared and used to perform potentiometric restricted-diffusion measurements. The diffusion coefficient of 1 M KOH solution was determined to be $3.12 \times 10^{-5} \text{ cm}^2/\text{s}$. Although the diffusion coefficient obtained agreed with literature, we have noticed that the MnO₂-plated electrode was consumed during the measurements, causing a variability in the open circuit potential before and after measurements. Thus, the accuracy of our characterisation method for aqueous KOH solution may be doubtful.

Leveraging the experience gained from aqueous solutions, we performed the first complete characterisation of transport and thermodynamic properties for LiPF₆ in PC, a non-aqueous electrolyte commonly used in commercial Li-ion batteries. Partial molar volumes of solute and solvent were calculated from a density-molarity correlation, which was established by densitometry. Ionic conductivity was quantified by AC conductometry within a customized, air-tight conductivity vial. A Hittorf cell was designed and fabricated to measure transference number. Thermodynamic factor was measured *via* a customized concentration cell. A potentiometric restricted-diffusion method was applied to determine Fickian diffusion coefficient, which was used in combination with other data to extract thermodynamic diffusivity. All six properties were characterised with respect to LiPF₆ concentration up to 2 M. Density and ionic conductivity were measured at three temperatures: 20, 25, 30 °C, while transference number, thermodynamic factor, and diffusion coefficient were determined at 25 °C only. Each property was fitted with a mathematical expression

to describe its concentration dependence. Once the values of the six properties were obtained, we used them in a numerical model that simulated the OCP relaxation of our polarization measurements. The model fit new experimental results very well, verifying the measured property correlations.

We further developed and characterised a new Mg^{2+} -conductive electrolyte for use in Mg batteries with Mg metal anodes, which could be a potentially promising beyond-Li-ion technology. We started by producing previously reported conditioning-free Magnesium/Aluminum Chloride Complex (MACC) electrolytes, and discovered two alternative promoters that can be used to synthesise them: CuCl_2 and ZnCl_2 to synthesise the 'MaCC' electrolytes. Then, a novel conditioning-free, promoter-free Mg^{2+} -conductive electrolyte was developed. It has been discovered that metal Mg can be spontaneously oxidised from non-aqueous ZnCl_2/THF , CuCl_2/THF , or SnCl_2/THF solutions, generating Mg^{2+} -conductive electrolytes. Electrolytes synthesised from ZnCl_2/THF solutions were completely studied. Various characterisation techniques, including electrochemical method, XRD, SEM-EDS, ICP-MS, ^1H -NMR, ^{35}Cl -NMR, and Raman spectroscopy were employed to explore the mechanism of electrolyte formation and the structure of the electrolytic solutions. The MZCC electrolyte (we synthesised from ZnCl_2/THF solutions) can support reversible Mg plating and stripping with a Coulombic efficiency of essentially 100%, a deposition overpotential less than 150 mV, and a stability window up to 3.2 V *vs.* Mg/Mg^{2+} . We propose that the electrolytes are Mg-chloride-complex based, with a positive Mg dimer, $[\text{Mg}_2\text{Cl}_3 \cdot 6(\text{THF})]^+$, as cation, and Cl^- as anion. Thus the MZCC electrolyte is a binary system. We further quantified density, ionic conductivity, and Fickian diffusion coefficient of 0.3 M MZCC in THF. The density is 991.4 g/L at 25 °C, ionic conductivity is 0.23 mS/cm at 25 °C, and diffusion coefficient is $8.93 \times 10^{-7} \text{ cm}^2/\text{s}$ at 25

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List of Symbols

a_i^θ	Property expression secondary reference
A	Surface area
c_i	Molarity of species i
c	Salt molarity
c_T	Total concentration
d	Diameter
D	Fickian diffusion coefficient of electrolyte
D_i	Diffusivity of species i
D_{eff}	Effective diffusion coefficient of electrolyte in porous medium
$\mathcal{D}$	Thermodynamic diffusion coefficient of electrolyte
$\mathcal{D}_{ij}$	Stefan–Maxwell coefficient between species i and j
e	Unit charge of electron
f_i	Molar activity coefficient of species i
f_{+-}	Mean molar activity coefficient
F	Faraday constant
G	Gibbs free energy
i	Current density
K_{ij}	Drag coefficient between species i and j
L	Distance of the cell
m_i	Molality of species i
m	Molality of electrolyte
M_i	Molar mass of species i
n_i	Numbers of moles of species i
N_i	Molar flux of species i
Q	Total numbers of charge
R	Gas constant
R_i	Reaction rate of species i
s_i	Stoichiometry of species i
t	Time
t_i	Transference number of species i with respect to mass average velocity
t_i^0	Transference number of species i with respect to solvent velocity
u_i	Mobility of species i
U	OCP difference

v	Mass average velocity
v^*	Molar average velocity
v_0	Solvent velocity
$v^\square$	Volume average velocity
$\bar{V}_e$	Partial molar volume of salt
$\bar{V}_0$	Partial molar volume of solvent
x	Molar fraction
y	Particle fraction
z_i	Numbers of charge carried by species i
β	Bruggeman coefficient
χ	Thermodynamic factor
ε	Porosity
η	Dynamic viscosity
γ_i	Molal activity coefficient of species i
γ_{+-}	Mean molal activity coefficient
κ	Ionic conductivity
κ_{eff}	Effective ionic conductivity in porous medium
λ	Activity of species i
Λ	Equivalent conductance
Λ_j	Fitting parameter for equivalent conductance
μ_i	Chemical potential of species i
v_+ / v_-	Numbers of cations and anions into which a molecule of electrolyte dissociates
v	Total numbers of cation and anions into which a molecule of electrolyte dissociates
ω	Mass fraction
Ω	Ohmic resistance
Φ	Electrical potential
ρ	Density
ρ_j	Fitting parameter for density
τ	Dimensionless time

Chapter 1

Introduction

Batteries, first invented in 1800 by Italian physicist Alessandro Volta, are devices consisting one or multiple electrochemical cells that are able to power electrical devices.¹ A battery that can only be used once, such as alkaline battery, zinc-carbon battery, or lithium battery, is defined as primary battery; batteries that can be discharged or charged multiple times secondary, or rechargeable batteries. Presently, batteries, either primary or secondary, are being used in many aspects in our life. It has been predicted that the global battery market will be US \$120 billion in 2019.² The market size is expected to keep growing alongside the increasing demand for portable electrical devices, electric vehicles, and electricity storage systems.

Most typical batteries include three key components: cathode, anode, and electrolyte (see Fig. 1.1); the electrodes are named based on their electrochemistry during the discharge process. Redox reactions occur on the cathode (where reduction occurs during discharge) and anode (oxidation) as electrons flow through the external circuit. Between cathode and anode, an electrolyte (which can be either solid or liquid) puts the two electrodes in chemical contact while providing electrical insulation. During charging and discharging, ions must move through the electrolyte to maintain the balance of charge between the cathode and anode as they react. The transport process within the electrolyte is, therefore, a key factor that determines the performance of a battery cell.

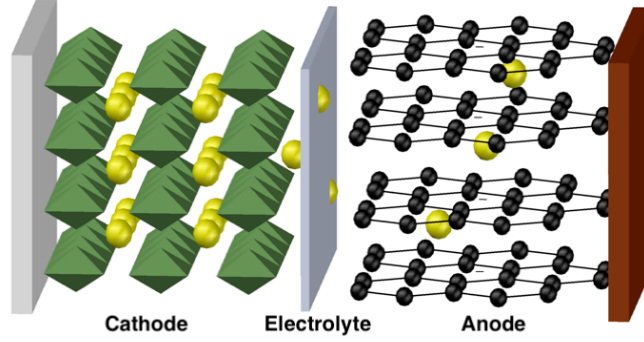


Fig. 1.1: Microscopic structure of a lithium ion battery with lithium iron phosphate cathode and graphite anode.

1.1 Mass transfer in electrolytes

Mass transfer within an electrolytic solution requires a description of the movement of ionic species, which accounts for material balances, charge balances, and fluid mechanics. According to the Nernst–Planck dilute-solution theory, the flux density of chemically distinct solute species i in an electrolytic solution is given by³

$$\vec{N}_i = -z_i u_i F c_i \vec{\nabla} \Phi - D_i \vec{\nabla} c_i + c_i \vec{v}, \quad (1.1)$$

where $\vec{N}_i$, expressed in $\text{mol}/(\text{cm}^2 \text{ s})$, represents the molar flux of i . Here F is the Faraday constant, Φ is the electric potential, and $\vec{v}$ is the bulk flow velocity of the solution; z_i is the number of charge equivalents carried by i ; u_i is its mobility, D_i is its diffusivity, and c_i , its molarity.

Based on Eq.1.1, three different forms of motion may contribute to the movement of a species. They are *migration* (first term on the right side of Eq.1.1), *diffusion* (second term), and *convection* (third term). Movement of a species is, first of all, driven by the overall motion of the medium containing it. When there is a concentration gradient of a species, diffusion will also contribute to its movement, causing deviation of the species

velocity from the bulk velocity. If there is electric field and the solute species in question is charged, it will experience an electrical force that further changes its flux relative to $\vec{v}$.

Motion of charged species causes an electric current within an electrolyte, expressed through Faraday's law as

$$\vec{i} = F \sum_i z_i \vec{N}_i. \quad (1.2)$$

The local material balance of a species is governed by

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla} \cdot \vec{N}_i + R_i. \quad (1.3)$$

Here accumulation $\frac{\partial c_i}{\partial t}$ comprises net flux input $-\vec{\nabla} \cdot \vec{N}_i$ and can also arise from production of the species due to the homogeneous chemical reactions in the bulk of the solutions, whose rate is R_i .

Finally, on scales much larger than the Debye length, local electroneutrality should apply to the electrolyte,

$$\sum_i z_i c_i = 0, \quad (1.4)$$

which should be observed in all solutions except in a thin double charge layer near the electrode.³ With Eq. 1.1-1.4, we will be able to describe the isothermal, isobaric transport process within dilute electrolytic solutions. Through Eq. 1.2 and Eq. 1.4, the species balances can be used to show that

$$\vec{\nabla} \cdot \vec{i} = F \sum_i z_i R_i = 0. \quad (1.5)$$

If we insert Eq.1.1 into Eq.1.2, current density turns to:

$$\vec{i} = -F^2 \vec{\nabla} \Phi \sum_i z_i^2 u_i c_i - F \sum_i D_i z_i \vec{\nabla} c_i + F \vec{v} \sum_i z_i c_i. \quad (1.6)$$

If we apply electroneutrality and assume no concentration variations in the solution, Eq.1.5

is reduced to a common Ohmic form:

$$\vec{i} = -\kappa \vec{\nabla} \Phi, \quad (1.7)$$

where κ is the ionic conductivity, written in terms of mobilities as

$$\kappa = F^2 \sum_i z_i^2 u_i c_i. \quad (1.8)$$

Under the assumption that concentration is uniform, the current carried by a certain species j can be expressed as

$$t_j \vec{i} = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \vec{i} \quad (1.9)$$

where

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i}, \quad (1.10)$$

is the fraction of conductivity due to motion of species j and is called the *transference number*. The migration flux density of species i can also be written as

$$N_i^{\text{migr}} = \frac{t_i}{z_i F} \vec{i}. \quad (1.11)$$

1.2 Binary electrolytes

A binary electrolyte is a solution comprising a single solvent and a single salt, which can only dissociate into one kind of cation (positively charged) and one kind of anion (negatively charged). If one salt formula unit dissociates into ν_+ cations and ν_- anions, then the molarity of the electrolyte is defined by

$$c = \frac{c_+}{v_+} = \frac{c_-}{v_-}. \quad (1.12)$$

The material balance equations for each of the ionic species are, thereby,

$$\frac{\partial c}{\partial t} + \vec{\nabla} \cdot (c\vec{v}) = z_+ u_+ F \vec{\nabla} \cdot (c\vec{\nabla}\Phi) + \vec{\nabla} \cdot (D_+ \vec{\nabla} c), \quad (1.13)$$

$$\frac{\partial c}{\partial t} + \vec{\nabla} \cdot (c\vec{v}) = z_- u_- F \vec{\nabla} \cdot (c\vec{\nabla}\Phi) + \vec{\nabla} \cdot (D_- \vec{\nabla} c). \quad (1.14)$$

Subtraction of Eq. 1.13 and Eq. 1.14 gives

$$(z_+ u_+ - z_- u_-) F \vec{\nabla} \cdot (c\vec{\nabla}\Phi) + \vec{\nabla} \cdot ((D_+ - D_-) \vec{\nabla} c) = 0. \quad (1.15)$$

From Eq. 1.6, we are able derive the current distribution in a binary electrolyte, as

$$-\frac{\vec{i}}{z_+ v_+ F} = F c (z_+ u_+ - z_- u_-) \vec{\nabla}\Phi + (D_+ - D_-) \vec{\nabla} c. \quad (1.16)$$

The cation transference number is

$$t_+ = \frac{z_+ u_+}{z_+ u_+ - z_- u_-}. \quad (1.17)$$

Incorporating this definition, transformation of Eq. 1.16 gives expression for potential:

$$z_+ u_+ F c \vec{\nabla}\Phi = -\frac{\vec{i} t_+}{z_+ v_+ F} - \frac{z_+ u_+ (D_+ - D_-)}{z_+ u_+ - z_- u_-} \vec{\nabla} c. \quad (1.18)$$

Replacing the potential term in Eq. 1.13 with Eq. 1.18 gives

$$\frac{\partial c}{\partial t} + \vec{v} \cdot \vec{\nabla} c = -\vec{\nabla} \cdot \left(\frac{\vec{i} t_+}{z_+ v_+ F} - D \vec{\nabla} c \right). \quad (1.19)$$

in which the salt diffusivity is defined as

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-}. \quad (1.20)$$

Note that D and t_+ are composition-dependent variables, because the underpinning ion mobilities and diffusivities are, as well. If the material properties are constant with respect to composition, Eq. 1.19 becomes

$$\frac{\partial c}{\partial t} + \vec{v} \cdot \vec{\nabla} c = D \vec{\nabla}^2 c \quad (1.21)$$

because $\vec{\nabla} \cdot \vec{i} = 0$. Thus salt in a binary electrolyte obeys a diffusion equation similar to a solute in a non-electrolytic solution, despite the charges on the anions and the presence of current. It is worth emphasizing that both Eq. 1.19 and Eq. 1.21 are derived from Eq. 1.3 based on an assumption that

$$\vec{\nabla} \cdot \vec{v} = 0. \quad (1.22)$$

This equation, which follows from mass continuity, is only valid when the density of the fluid is constant. For the case of a concentrated solution, Eq. 1.22 will not stand, which will be discussed in the following section.

1.3 Concentrated solution theory

The description of one-dimensional mass transfer within an electrolytic solution requires solute flux laws (Eq. 1.1), species material balance (Eq.1.3), a definition of current (Eq.1.2), a local charge balance (Eq.1.4), and a kinematic relation (Eq. 1.22). For concentrated solutions, Eq. 1.2, 1.3, and 1.4 will still be valid; Eq. 1.1, however, breaks down. To explain the reasons why Eq. 1.1 fails for concentrated solutions, one must understand the assumptions that lie behind it.

Eq. 1.1 states that flux density comprises migration, diffusion, and convection. Mi-

gration and diffusion fluxes, therefore, must be defined with respect to an average velocity, which is the solvent velocity in the dilute-solution approximation. Because solvent is in vast excess, fluid mechanics can be modelled by considering the solvent alone: the incompressibility assumption is valid (Eq. 1.22). The average solution velocity is not solely controlled by the solvent in concentrated solutions, so the average velocity has to be redefined.

Furthermore, Eq. 1.1 only considers that solute species interact with solvent, essentially neglecting interactions of a solute with other solute species. Models based on Eq. 1.1 therefore contain an incorrect number of transport properties.

Finally, the driving forces for diffusion and migration are not correct in Eq.1.1. The equation assumes that diffusion is driven by molar concentration gradients. Thermodynamically speaking, the real driving force for diffusion should be an activity gradient, which only identifies with molar concentration in ideal dilute solutions. Species flux with molarity-driven diffusion will deviate from the flux observed in experiments. The definition of potential in media of varying composition should also be treated carefully. Potential in Eq. 1.1 is an ideal electric potential that is the result of moving idealized electric charges from one place to another, ignoring the chemical environment that the electrons experience. The real driving force of the migration is electrochemical potential, which is all related to salt activity. The electric potential appearing in Eq. 1.1 is only an idealized concept, and is not clearly related to the potential measured by a reference electrode. To avoid the difficulties above, a more general description of transport processes is needed.

Before the detailed discussion of concentrated-solution theory, we should talk about electrochemical potential first. Thermodynamics defines the chemical potential as

$$\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{T, p, n_{B \neq A}}, \quad (1.23)$$

where G is the total Gibbs free energy of the system and n_A is the total number of moles of species A . It describes the response of total Gibbs energy to addition of a differential amount

of species A to a finite amount solution under isothermal, isobaric condition. In light of this definition, chemical potential can also be regarded to be the partial molar Gibbs free energy. One of the characteristics of chemical potential, developed in thermodynamics, is that the reversible work of transferring one species from one point to another is proportional to the difference in chemical potential between the two points.

Guggenheim⁴ further extends this concept to define electrochemical potential of ions, so that the work to reversibly transfer ions between the two phases, with constant temperature, pressure, and chemical composition, is also proportional to the difference of electrochemical potential between the two phases. Generally, electrochemical potential is a function of temperature, pressure, chemical composition, and electrical state of the phase.

In a binary electrolyte, the chemical potential of the neutral salt A is

$$\mu_A = \nu_+ \mu_+ + \nu_- \mu_-, \quad (1.24)$$

where μ_+ and μ_- are electrochemical potential for cation and anion. With Eq. 1.24, we are able to establish the connection between chemical potential of a neutral salt and the electrochemical potential of corresponding dissociated ions. Guggenheim's definition of electrochemical potential was

$$\mu_i = RT \ln \lambda_i + z_i F \Phi. \quad (1.25)$$

where λ_i is the absolute activity of charged ion, which is also a function of temperature, pressure, and chemical composition.

For solute species in the solution, activity can be further broken down as

$$\lambda_i = m_i \gamma_i \lambda_i^\theta, \quad (1.26)$$

or

$$\lambda_i = c_i f_i a_i^\theta, \quad (1.27)$$

where m_i and c_i measure concentration on the molal and molar scales, respectively, γ_i and f_i are activity coefficients in the corresponding scales, and λ_i^θ and a_i^θ are proportionality constants, independent of composition and electrical state, but characteristic of the solute species and the solvent and dependent on temperature and pressure. Because electroneutrality of the dissociation reaction makes Φ cancel, the chemical potential of the neutral salt can be expressed as (derived from a combination of Eqs. 1.24, 1.25, and 1.26)

$$\mu_A = \mu_A^\theta + vRT \ln(m\gamma_{+-}) + RT \ln(v_+^{v_+} v_-^{v_-}) \quad (1.28)$$

where μ_A^θ is the reference chemical potential in a secondary reference state, γ_{+-} is the mean molal activity coefficient, defined by

$$\gamma_{+-}^v = \gamma_+^{v_+} \gamma_-^{v_-}, \quad (1.29)$$

and the formula-unit stoichiometry is

$$v = v_+ + v_-. \quad (1.30)$$

On a molar basis, the expression of chemical potential is expressed as

$$\mu_A = \mu_A^\theta + vRT \ln(cf_{+-}) + RT \ln(v_+^{v_+} v_-^{v_-}). \quad (1.31)$$

With the understanding of chemical potential of a single salt, we will be able to further discuss the connection between chemical potential and electrical potential.

Imagine an arbitrary electrochemical cell with cathode and anode submerged in a single electrolyte with a concentration gradient (Fig. 1.2) The cathode and anode are identical,



Fig. 1.2: Conceptual diagram of a cell filled with solution with concentration profile between two identical electrodes.

placed in different positions of the electrolyte. A general electrode reaction occurs on the electrode surface:



where s_i is the stoichiometric coefficient of species i whose chemical formula is M_i and n_e is the number of electrons exchanged during the reaction. Thus, the electrochemical potential balance of the phase equilibrium for this reaction is

$$\sum_i s_i \mu_i = n_e \mu_{e^-}. \quad (1.33)$$

The variation of the voltage of a reference electrode that sustains this reaction relates to the change in the electrochemical potential of electrons within it through

$$s_+ \vec{\nabla} \mu_+ + s_- \vec{\nabla} \mu_- + s_0 \vec{\nabla} \mu_0 = n \vec{\nabla} \mu_{e^-} = -nF \vec{\nabla} \Phi, \quad (1.34)$$

As well as giving thermodynamic meaning to the electric potential, the electrochemical potential concept also helps to describe mass transfer in concentrated solutions. To overcome the difficulties mentioned in dilute solution theory. Eq. 1.1 can be replaced by the multicomponent diffusion equation

$$c_i \vec{\nabla} \mu_i = \sum_j K_{ij} (\vec{v}_j - \vec{v}_i) = RT \sum_j \frac{c_i c_j}{c_T D_{ij}} (\vec{v}_j - \vec{v}_i), \quad (1.35)$$

where K_{ij} are friction coefficients or interaction coefficients. Here $\vec{v}_i$ is the mass-average velocity of species i , related to its flux density through $\vec{N}_i$. In Eq. 1.35, it is typical to break

down the friction coefficient further, following the Stefan–Maxwell theory, as

$$K_{ij} = \frac{RT c_i c_j}{c_T D_{ij}}, \quad (1.36)$$

in which c_T is the total molar concentration, including all solutes (both charged and uncharged) and the solvent (or solvents).

For a binary electrolyte, the diffusion equations for cations and anions can be written following Newman as^{3,5}

$$c_+ \vec{\nabla} \mu_+ = K_{0+} (\vec{v}_0 - \vec{v}_+) + K_{+-} (\vec{v}_- - \vec{v}_+), \quad (1.37)$$

$$c_- \vec{\nabla} \mu_- = K_{0-} (\vec{v}_0 - \vec{v}_-) + K_{+-} (\vec{v}_+ - \vec{v}_-). \quad (1.38)$$

These invert to produce flux laws for cations and anions:

$$\vec{N}_+ = c_+ \vec{v}_+ = -\frac{\mathcal{D} c_T c_+}{v R T c_0} \vec{\nabla} \mu_A + \frac{\vec{i} t_+^0}{z_+ F} + c_+ \vec{v}_0, \quad (1.39)$$

$$\vec{N}_- = c_- \vec{v}_- = -\frac{\mathcal{D} c_T c_-}{v R T c_0} \vec{\nabla} \mu_A + \frac{\vec{i} t_-^0}{z_- F} + c_- \vec{v}_0. \quad (1.40)$$

in which $v = v_+ + v_-$ and $\mu_A = v_+ \mu_+ + v_- \mu_-$ as mentioned earlier. The total concentration c_T is⁶

$$c_T = c_+ + c_- + c_0 = \frac{1}{\bar{V}_0 + (\bar{V}_e - v \bar{V}_0) y}. \quad (1.41)$$

Here the $\bar{V}_0$ and $\bar{V}_e$ are partial molar volume for solvent and solute, and y is the particle fraction with a form of $y = \frac{c}{c_T}$. The diffusion coefficient of the electrolyte, based on thermodynamic driving force, is

$$\mathcal{D} = \frac{\mathcal{D}_{0+} \mathcal{D}_{0-} (z_+ - z_-)}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}}, \quad (1.42)$$

and the transference numbers with respect to solvent velocity are

$$t_+^0 = 1 - t_-^0 = \frac{z_+ \mathcal{D}_{0+}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}}. \quad (1.43)$$

Instead of a concentration gradient, the driving force for diffusion in Eqs. 1.39 and 1.40 is a gradient of chemical potential, a colligative property that can be measured in various ways, and which properly involves the activity. The diffusion coefficient based on a thermodynamic driving force is related to Fickian diffusion coefficient based on concentration gradient through a thermodynamic factor,

$$D = \mathcal{D}\chi = \mathcal{D} \frac{c_T}{c_0} \left(1 + \frac{d \ln \gamma_{+-}}{d \ln m} \right) = \mathcal{D} c_T \tilde{V}_0 \left(1 + \frac{d \ln f_{+-}}{d \ln c} \right). \quad (1.44)$$

Although some sources use forms including activity coefficients, it is simpler to express the thermodynamic factor by the single symbol χ .^{3,5-7} Combination of Eq. 1.44 and Eq. 1.31 gives an expression for the gradient of neutral-salt chemical potential in terms of its molarity gradient:

$$\frac{\mathcal{D}}{vRT} \frac{c_T}{c_0} c \vec{\nabla} \mu_A = D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \vec{\nabla} c. \quad (1.45)$$

Therefore the material balance for a concentrated solution can be written as

$$\frac{\partial c}{\partial t} + \vec{\nabla} \cdot (c \vec{v}_0) = \vec{\nabla} \cdot \left[D \left(1 - \frac{d \ln c_0}{d \ln c} \right) \vec{\nabla} c \right] - \frac{\vec{i} \cdot \vec{\nabla} t_+^0}{z_+ v_+ F}. \quad (1.46)$$

which does not involve the assumption of $\vec{\nabla} \cdot \vec{v}_0 = 0$.

Eq.1.46 is applied in most contemporary models of Li-ion batteries that include liquid-phase transport,⁸⁻¹² but this requires consideration of the convection term and the excluded-volume factor $\left(1 - \frac{d \ln c_0}{d \ln c} \right)_{T,P}$. The canonical references neglect convection and assume that the $(d \ln c_0 / d \ln c)|_{T,P}$ term is negligible.¹³⁻¹⁷ Unfortunately, these assumptions require that the salt occupies no volume, which is similar to a dilute-solution constraint. Concentration gradients (eg. those generated by large operation current) could

cause significant local variation in the excluded-volume factor, which causes an extra driving force for bulk diffusion. Liu and Monroe have discussed how the excluded-volume factor and Faradaic convection affect theoretical simulations.⁶ They showed that the impacts of both excluded-volume effects and Faradaic convection increase with electrolyte concentration, and may also be important at moderate concentrations in non-aqueous electrolytes, suggesting the assumptions that $(d \ln c_0 / d \ln c)|_{T,P} \approx 0$ and $\vec{v}_0 \approx 0$ may not be valid for all circumstances.

1.4 Concentrated-solution theory with different reference velocities

Following Newman,⁵ the solvent velocity was used to account for bulk fluid motion in flux law so far. The forms of the flux laws change somewhat with alternative choices of reference velocity. Instead of solvent velocity, mass-average velocity $\vec{v}$, molar-average velocity $\vec{v}^*$, and volume-average velocity $\vec{v}^\square$ can be used as reference velocities. For each reference velocity, any measure of concentration can be adopted to develop a mass balance equation. Conventionally, however, mole fraction x is used with molar-average velocity, mass-fraction ω with mass-average velocity, and molarity c or particle fraction y with volume-average velocity for simplicity. Although the choice of which reference velocity to use is arbitrary, one reference velocity may be more advantageous than another in particular situations. Cation flux laws with different reference velocities are listed below:^{3, 18}

$$\vec{N}_+ = -v_+ c_T D \vec{\nabla} x + \frac{\vec{i} t_+^*}{z_+ F} + c_+ \vec{v}^*, \quad (1.47)$$

$$\vec{N}_+ = -v_+ \frac{\rho D}{M_e} \vec{\nabla} \omega + \frac{\vec{i} t_+}{z_+ F} + c_+ \vec{v}, \quad (1.48)$$

$$\vec{N}_+ = -v_+ D \vec{\nabla} c + \frac{\vec{i} t_+^0}{z_+ F} + c_+ \vec{v}^\square. \quad (1.49)$$

From Eq.1.49, one could notice that the excluded-volume term vanishes when the volume-average velocity is applied. This simplifies the flux equation. Based on the work of Liu and Monroe, flux density equations with volume-average velocity can also be expressed with a measure of particle fraction y ,⁶

$$\vec{N}_+ = -v_+ \mathcal{D} \chi \bar{V}_0 c_T^2 \vec{\nabla} y + \frac{t_+^0 \vec{i}}{z_+ F} + v_+ c_T y \vec{v}^\square, \quad (1.50)$$

$$\vec{N}_- = -v_- \mathcal{D} \chi \bar{V}_0 c_T^2 \vec{\nabla} y + \frac{t_-^0 \vec{i}}{F z_-} + v_- c_T y \vec{v}^\square, \quad (1.51)$$

$$\vec{N}_0 = \mathcal{D} \chi \bar{V}_0 c_T^2 \vec{\nabla} y + c_T (1 - v y) \vec{v}^\square. \quad (1.52)$$

The volume-average velocity can be expressed in terms of species fluxes as⁵

$$\vec{v}^\square = \bar{V}_e \left[\frac{(1 - t_+^0)}{v_+} \vec{N}_+ + \frac{t_+^0}{v_-} \vec{N}_- \right] + \bar{V}_0 \vec{N}_0. \quad (1.53)$$

With Eqs. 1.50 -1.53, we can describe mass and volume continuity of a binary electrolytic system with

$$\frac{\partial (c_T y)}{\partial t} = -\vec{\nabla} \cdot \left(-\mathcal{D} \chi \bar{V}_0 c_T^2 \vec{\nabla} y + \frac{t_+^0 \vec{i}}{F z_+ v_+} + c_T y \vec{v}^\square \right), \quad (1.54)$$

$$\vec{\nabla} \cdot \vec{v}^\square = -\frac{\bar{V}_e \vec{i} \cdot \vec{\nabla} t_+^0}{F z_+ v_+} - \frac{\mathcal{D} \chi c_T}{1 - v y} \vec{\nabla} y \cdot \vec{\nabla} \bar{V}_e, \quad (1.55)$$

which hold alongside charge continuity:

$$\vec{\nabla} \cdot \vec{i} = 0. \quad (1.56)$$

Eqs. 1.54 - 1.56 do not completely close the system. To specify the mass, volume, and charge distributions, equation of state (Eq. 1.41) must also be included. Finally, to derive

potential distributions, one can use a MacInnes equation including the particle fraction y :

$$\bar{\nabla} \frac{\mu_+}{Fz_+} = -\frac{i}{\kappa} + \frac{vRT(1-t_+^0)}{Fz_+v_+} \chi \bar{\nabla} \ln y, \quad (1.57)$$

which connects the potential distribution to concentration distribution.

1.5 Transport and thermodynamic properties

According to the concentrated-solution theory proposed by Newman and Tobias, $n(n-1)/2$ transport properties are needed to fully describe the species-species interactions within an electrolytic solution comprising n species.⁵ In a binary electrolyte, Eqs. 1.41 and 1.54 - 1.57 can fully describe the mass transfer. Thus the following six transport and thermodynamic properties are needed to be carefully quantified to fully simulate the mass transfer in the binary electrolytes: they are thermodynamic diffusion coefficient $\mathcal{D}$, cation transference number relative to solvent t_+^0 , ionic conductivity κ , partial molar volumes of salt and solvent $\bar{V}_e/\bar{V}_0$, and thermodynamic factor χ . Each property bears specific physical meaning. Ionic conductivity of an electrolytic solution is a measure of its ability to conduct electricity. In the electrolytes, electricity is conducted by the movement of free ions. Ionic conductivity, therefore, is a comprehensive description of the mobilities of all ionic species. Thermodynamic diffusion coefficient is the proportionality constant between the molar flux due to molecular diffusion and the chemical potential gradient of the species. The transference number is a measure of relative ionic mobility. The transference number with respect to mass average velocity, which is also called the transport number, can be interpreted as the fraction of the total electrical current carried by a given ionic species. The transference number relative to the solvent velocity, on the other hand, describes how fast an ionic species travels under an electric field with respect to the velocity of solvent. Note that one can think of two transference numbers in a binary electrolyte: one for cations, another for anions. The sum of these two transference numbers equals unity. Thermodynamic factor is

a quantity that describes how salt activity in the electrolyte varies with salt concentration. Since the definition of activity coefficient depends on the concentration measure, the thermodynamic factor also has different definitions with different concentration measures (see Eq.1.45). Partial molar volume is a thermodynamic property that describes how electrolyte volume varies with the concentration of each individual species under isothermal, isobaric condition. Each property, in principle, is a function of salt composition, temperature and pressure. To reduce the complexity of the quantification, one can always measure the properties under an isothermal, isobaric condition to eliminate the temperature and pressure effect on properties.

Among the six properties, the measurements of the ionic conductivity and partial molar volumes are relatively straightforward. Ionic conductivity is normally measured *via* AC conductometry. An alternating current is applied between two electrodes immersed in a solution. The two-electrode arrangement is fabricated with fixed distance and surface area and the resulting voltage is recorded to calculate the conductivity. Ionic conductivity is always reported as equivalent conductance (molar conductivity), which is defined as the conductivity divided by the molar concentration of the electrolyte. Based on the Onsager–Fuoss theory,^{19,20} equivalent conductance can be described as a function of molarity under isothermal and isobaric condition:

$$\Lambda = \Lambda_0 + \Lambda_1 \sqrt{c} + \Lambda_2 c + \Lambda_3 c \ln c + \dots \quad (1.58)$$

where Λ is the equivalent conductance, and Λ_i are parameters that are temperature and pressure dependent.

Partial molar volume is related to solution density and composition by³

$$\bar{V}_e = \frac{M_e - \frac{d\rho}{dc}}{\rho - c \frac{d\rho}{dc}}, \quad (1.59)$$

$$\bar{V}_0 = \frac{M_0}{\rho - c \frac{d\rho}{dc}}. \quad (1.60)$$

where M_e and M_0 are the molar mass of solute and solvent, and ρ is the solution density. For aqueous solutions, dependence of solution density on molar concentration at certain temperature can be empirically expressed by²¹

$$\rho = \rho_0 + \rho_1 + \rho_2 c^{3/2}. \quad (1.61)$$

Here ρ_0 should be the density of pure solvent, and the other ρ_i are equation parameters, which are temperature and pressure dependent. For non-aqueous electrolytes, the same empirical form can describe the concentration dependence on electrolyte density. Partial molar volume, therefore, can be calculated from a correlation between solution density and molarity under isothermal and isobaric conditions. Even though both Eq.1.61 and ?? states that solution density varies nonlinearly with molarity, linear dependence between density and molarity dominates for most solutions when the concentration range is not too great. Therefore, partial molar volumes have been treated as constant for most electrolyte analyses.

Unlike the measurement of ionic conductivity and density, the measurements for ion transference number, diffusion coefficient, and thermodynamic factor are far less straightforward. Transference number for liquid electrolytes have traditionally been measured by the Hittorf method or the moving boundary method, electromotive force method, or Vincent-Bruce steady-state current method.^{22–24} Transference number can also be measured with a concentration cell if there is an independent measure of χ .^{3,25–28} Thermodynamic factors are independently accessible through freezing-point depression, vapor-pressure measurements, or the isopiestic method.^{25,26} Diffusion coefficient can be quantified *via* the Diaphragm Cell method^{29,30} and the Harned conductometry method or by optical methods.^{18,31} In 1995, Ma et al. innovatively proposed a suite of three potentiometric measurements that could be used to establish all three properties (χ , t_+^0 , and D) for solid

polymer electrolytes.³² These potentiometric measurements include the concentration-cell with transference, restricted diffusion method, and galvanostatic polarization method. Each method is interdependent and requires meticulous experimental design. These methods have been proved reliable for later characterizations of liquid electrolytes.^{33,34} In my work, the Hittorf method is adopted to quantify transference number, and various two-electrode potentiometric methods are used to quantify thermodynamic factor and thermodynamic diffusion coefficient. The detailed descriptions of these three methods will be introduced in Chapter 4.

Chapter 2

Density and Conductivity

Characterisation for Aqueous Vanadyl Sulfate (VOSO_4) Solutions

Aqueous VOSO_4 solutions, commonly utilized in redox flow batteries, were investigated first. Aqueous solutions are more easily characterised than non-aqueous solutions because of their stability in ambient conditions. Density and ionic conductivity of aqueous VOSO_4 solutions were characterised at five different temperatures. The results from the density and conductivity characterisation were applied by another student to study crossover dynamics.

2.1 VOSO_4 as the electrolyte component in redox flow batteries

VOSO_4 is one of the key electrolyte components in all-vanadium redox flow batteries. In redox flow battery systems, membrane transport properties are one of the key determinants of battery performance.^{35–39} Ideally, a perfect membrane should block ac-

tive species crossover, so that no inefficiency will be caused by self-discharge. At the same time, an ideal membrane should allow support ions to move freely between the two sides of the battery to maintain electroneutrality. In reality, active species do cross the membrane, which degrades cycle performance; it is therefore essential to quantify how significant the crossover phenomenon is for particular membrane materials. Membrane crossover experiments can be performed in an H-cell shown in Fig. 2.1, and composition gradient can be determined dynamically and non-invasively using conductometry.

In crossover relaxation experiments, 0.1 M aqueous vanadyl sulfate is put on one side of the membrane and pure water is put on the other side. The transient relaxation of the concentration difference is used to quantify VOSO_4 diffusivity. Non-invasive, transient concentration determination is difficult, however. In principle, solution composition can be measured non-invasively by tracking the solution conductivity in each chamber of the H-cell as a function of time.

Membrane-crossover experiments were complicated by three factors. First, no conductivity/composition correlation was available at the time of this experiment (2014) for aqueous VOSO_4 solutions.^{40,41} Second, the experiment is conducted in an ambient environment, without strict temperature control. Fluctuations in ambient temperature affect solution conductivity substantially more than diffusivity, so the temperature dependence of conductivity needs to be understood in detail. Third, solid VOSO_4 powders contain an un-



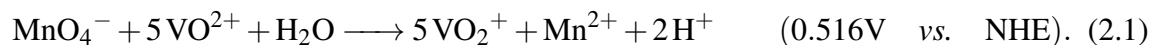
Fig. 2.1: Experiment to determine crossover rate of VOSO_4 through Celgard membrane.

known amount of water. Although not hygroscopic, VOSO₄ salt may have anywhere from three to five waters of hydration. Thus, VOSO₄ solutions require some sort of titration to determine their vanadium concentration accurately. To implement composition assay relevant to aqueous vanadium redox flow batteries, we characterised the properties of VOSO₄ solutions. We developed techniques for precise concentration assay to quantify the density and conductivity of aqueous VOSO₄ solutions up to 0.53 M. This system puts forward several barriers to achieving solutions with precise molar concentration. Strategies learned here, such as composition assay via densitometry, were carried forward to all other works on other electrolyte systems.

2.2 Experimental

2.2.1 Preparation of solutions and potentiometric titration

Aqueous VOSO₄ stock solution was prepared by dissolving a predetermined amount of VOSO₄ salt in water. Due to the unknown hydration of the VOSO₄ salts, the composition of VOSO₄ in aqueous stock solutions had to be determined. VOSO₄ composition cannot be measured by traditional titration with an indicator, because both oxidation and reduction of V⁴⁺ occurs with slow reaction kinetics, and the blue colour of VOSO₄ solutions interferes with the colour changes of indicators. To solve the two problems above, we used potentiometric titration to determine the mass fraction of our stock solutions. Fig. 2.2 shows a diagram of the potentiometric titration setup. For the potentiometric titration, 0.2 M potassium permanganate standard solutions were used as titer, Hg/HgSO₄ reference electrodes were used, and platinum wire was selected as an inert working electrode. When vanadyl ions are present, the overall reaction during the titration is⁴²



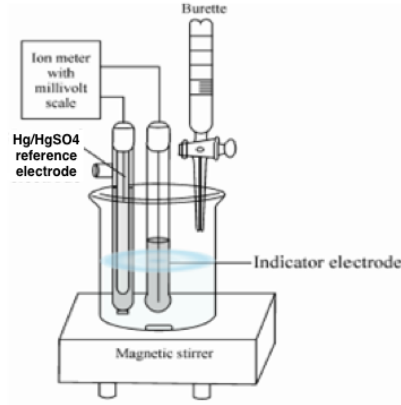


Fig. 2.2: A diagram of potentiometric titration for aqueous VOSO_4 solutions.

The measured potential of the cell changes steeply after all of the vanadyl ion is consumed. The mass fraction of vanadyl in the original solution can then be calculated through

$$\omega_{\text{VOSO}_4} = \frac{5 \times \omega_{\text{KMnO}_4} \times m_{\text{KMnO}_4} \times M_{\text{VOSO}_4}}{m_{\text{stock}} \times M_{\text{KMnO}_4}}, \quad (2.2)$$

where ω_{VOSO_4} is the mass fraction of VOSO_4 in the stock solution, ω_{KMnO_4} is the mass fraction of potassium permanganate standard solution titrated into the stock solution sample, m_{KMnO_4} is the total mass of potassium permanganate standard consumed, M_{VOSO_4} is the molar mass of VOSO_4 , M_{KMnO_4} is the molar mass of KMnO_4 , and m_{stock} is the mass of the VOSO_4 stock-solution sample. After concentration assay of stock solutions by potentiometric titration, a series of solutions with lower molarity was prepared by diluting the stock solutions to target mass fraction for density and conductivity measurements.

Mass fraction was used as the concentration measure for any concentration determination practice. Unlike molarity, which is the most common concentration measure, mass fraction is independent of temperature, because determination of solution volume is not involved in quantification of mass fraction. Because balances are very precise, mass fraction can be measured to many more significant digits than molar concentrations. Also, unlike

molality, which is commonly used for characterisation experiments, mass fraction remains bounded in the limit that there is no solvent present. This makes mass fraction a more sensible choice for the analysis of concentrated solutions, where it may not always be possible to designate a particular species as the solvent.

2.2.2 Density measurements

Densities were measured using a DMA 4100 density meter (Anton– Paar) with inner temperature controller (readability: 0.00005 g/cm^3 , accuracy: 0.0001 g/cm^3). The densitometer was periodically calibrated using ultrapure water and air. Samples were delivered to the dry vibrating tube from a 3 mL caustic-resistant polyethylene syringe. After filling, the tube was carefully checked for the presence of air bubbles and left to rest for 10 minutes, to allow the solution to reach thermal equilibrium. Periodic measurements were taken and repeated until stable readings were achieved. At least three measurements were performed for each solution and the average value was reported. After measurements, the tube was washed with ultra-pure water for three times, then washed with acetone and then dried with compressed air. The characteristic period of the air-filled tube was measured to check the integrity of the cleaning procedure.

2.2.3 Ionic conductivity measurements

Ionic conductivity of aqueous VO_2SO_4 solutions was measured with AC conductometry within a heating/cooling water circulator (Thermo Scientific) for temperature control. The AC conductivity meter was regularly calibrated with conductivity standards every month. Sample solutions were kept within a water bath at precisely controlled temperature for at least two hours to ensure thermal equilibrium. The conductivity probe was then submerged into the samples to measure the conductivity. Between each measurement, the conductivity probe was cleaned with ultrapure water and dried with paper tissue. Conductivities were measured at five temperatures ($15.00 \pm 0.02 \text{ }^\circ\text{C}$, $20 \pm 0.02 \text{ }^\circ\text{C}$, $25 \pm 0.02 \text{ }^\circ\text{C}$,

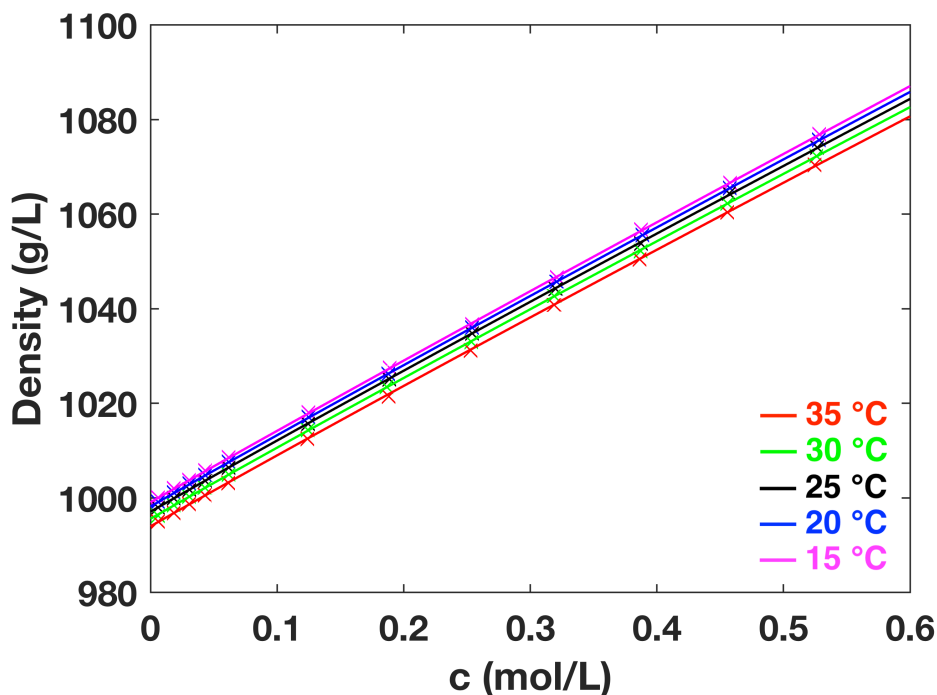


Fig. 2.3: Measured density of aqueous VOSO_4 solutions (x) and the least squares fittings with respect to VOSO_4 molarity from 0.006 M to 0.52 M at 15 (magenta), 20 (blue), 25 (black), 30 (green) and 35 °C (red).

30 ± 0.02 °C and 35 ± 0.02 °C). Each sample was measured at least three times and the average value was reported.

2.3 Density of aqueous VOSO_4 solutions

Densities were quantified for aqueous VOSO_4 solutions with molarities ranging from 0.006 M to 0.53 M. The results of density measurements are summarized in Table 2.1 and plotted in Fig. 2.3. We have fitted the density measurements with the functional form: Eq. 1.61, which is normally used to describe dependence of density on molarity for aqueous

solutions. The expression for each temperature is summarized below:

$$\rho (15^{\circ}C) = 999.1 + 153.9c - 9.35c^{1.5} \quad (2.3)$$

$$\rho (20^{\circ}C) = 998.2 + 153.9c - 10.05c^{1.5} \quad (2.4)$$

$$\rho (25^{\circ}C) = 997.0 + 153.9c - 10.76c^{1.5} \quad (2.5)$$

$$\rho (30^{\circ}C) = 995.6 + 153.9c - 11.41c^{1.5} \quad (2.6)$$

$$\rho (35^{\circ}C) = 994.0 + 153.9c - 12.13c^{1.5} \quad (2.7)$$

The term ρ_0 in each equation is forced to be the density of water at the corresponding temperature. The ρ_1 terms, on the other hand, are constant for all equations. With this constraint, the corresponding ρ_2 terms display a linear temperature dependence. The temperature-dependent equations allow for calculation of the density of any aqueous VOSO_4 solution with given concentration within the tested temperature range. One must notice that the format of Eq. 2.3-2.7 does not bear deep physical meaning, although it is roughly consistent with the concentration dependence one might expect from Debye–Hückel theory. Primarily, the functional form was adopted for its simple temperature dependence and its convenience of use. (Note: the error bar for density measurements is too small to be noticed. We therefore did not include them in all density plots in this and following chapters.)

With the density expressions, the partial molar volumes of aqueous VOSO_4 solutions were calculated; these are summarized in Table 2.2 and displayed graphically in Fig. 2.4. The solute partial molar volume increases with concentration, while the solvent partial molar volume stays relatively constant. Compared with the first two terms, the third term in Eqs. 2.3 - 2.7 are relatively small, especially in dilute range. Neglecting the third term will give us a linear concentration dependence of density, thus leading to constant partial molar volumes. This operation would be acceptable for engineering application when the

target concentration is low and the concentration dependence of partial molar volume is trivial. For concentrated solutions, however, the third term will become significant.

Table 2.1: Densities of aqueous VOSO_4 solutions at 15 °C, 20 °C, 25 °C, 30 °C and 35 °C

15 ° C			20 ° C			25 ° C		
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)
0.006	0.001	1000.1	0.006	0.001	999.2	0.006	0.001	998.0
0.018	0.003	1002.0	0.018	0.003	1001.1	0.018	0.003	999.9
0.031	0.005	1003.8	0.031	0.005	1003.0	0.031	0.005	1001.7
0.043	0.007	1005.8	0.043	0.007	1004.8	0.043	0.007	1003.6
0.062	0.010	1008.6	0.062	0.010	1007.6	0.062	0.010	1006.4
0.125	0.020	1018.1	0.125	0.020	1017.1	0.125	0.020	1015.7
0.189	0.030	1027.5	0.188	0.030	1026.2	0.189	0.030	1025.1
0.254	0.040	1036.7	0.254	0.040	1036.0	0.254	0.040	1034.8
0.321	0.050	1046.6	0.321	0.050	1045.7	0.320	0.050	1044.2
0.388	0.060	1056.7	0.389	0.060	1055.6	0.387	0.060	1053.8
0.458	0.070	1066.6	0.458	0.070	1065.5	0.457	0.070	1064.4
0.528	0.080	1076.9	0.528	0.080	1075.7	0.527	0.080	1074.1
30 ° C			35 ° C					
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)			
0.006	0.001	996.2	0.006	0.001	995.0			
0.018	0.003	998.5	0.018	0.003	996.8			
0.030	0.005	1000.3	0.031	0.005	998.7			
0.043	0.007	1002.2	0.043	0.007	1000.6			
0.062	0.010	1005.0	0.061	0.010	1003.2			
0.124	0.020	1014.4	0.124	0.020	1012.5			
0.187	0.030	1023.5	0.188	0.030	1021.5			
0.254	0.040	1033.0	0.253	0.040	1031.2			
0.319	0.050	1042.7	0.319	0.050	1040.8			
0.387	0.060	1052.2	0.386	0.060	1050.5			
0.456	0.070	1062.3	0.456	0.070	1060.4			
0.526	0.080	1072.3	0.525	0.080	1070.4			

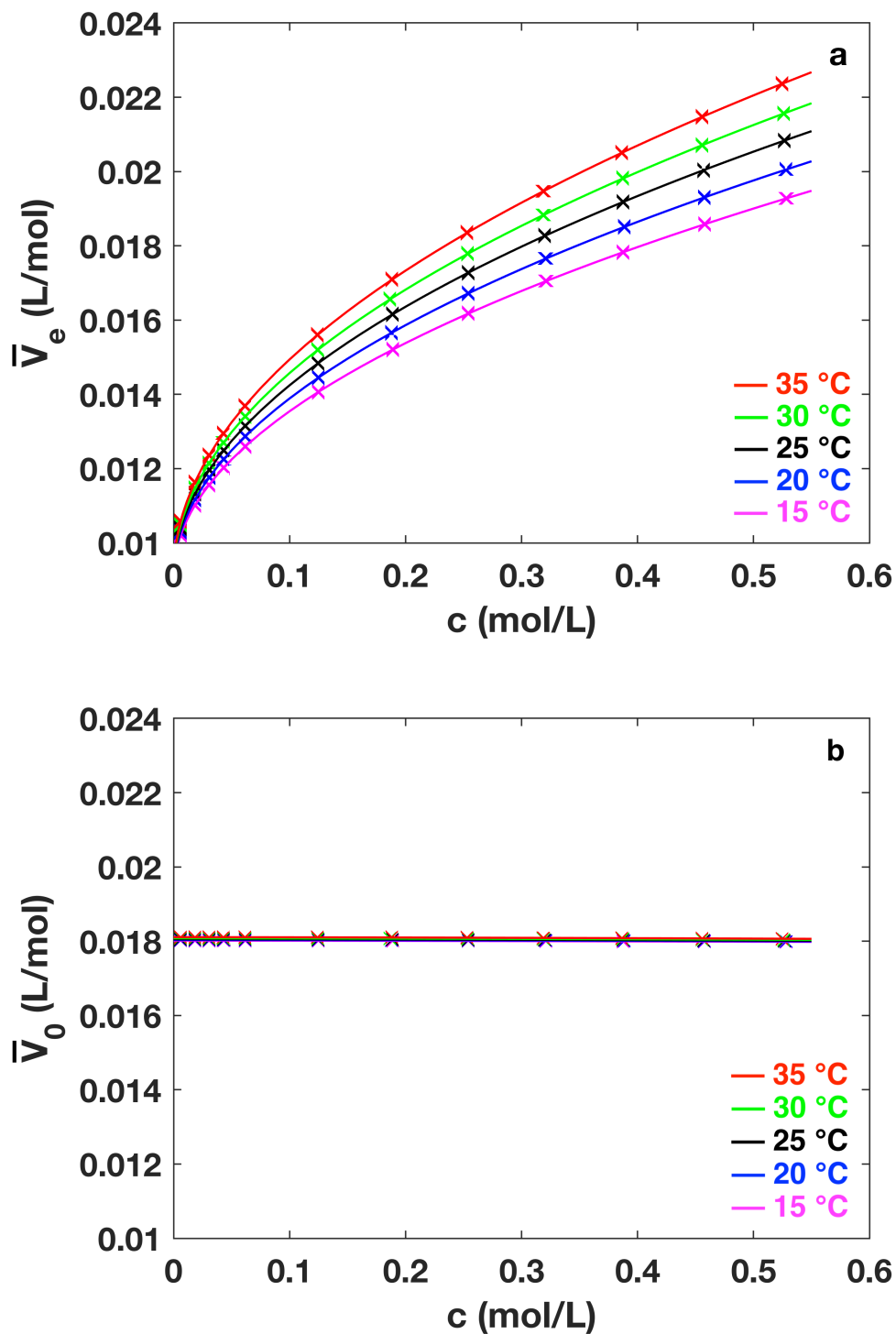


Fig. 2.4: (a) Partial molar volumes of salt for aqueous VOSO_4 solutions; (b) Partial molar volumes of solvent for aqueous VOSO_4 solutions.

Table 2.2: Partial molar volumes of aqueous VOSO₄ solutions at 15, 20, 25, 30 and 35 °C

15 ° C			20 ° C			25 ° C		
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)
0.006	10.2 ± 0.1	18.0	0.006	10.3 ± 0.1	18.0	0.006	10.4 ± 0.1	18.1
0.018	11.0 ± 0.1	18.0	0.018	11.2 ± 0.1	18.0	0.018	11.3 ± 0.1	18.1
0.031	11.6 ± 0.1	18.0	0.031	11.8 ± 0.1	18.0	0.031	12.0 ± 0.1	18.1
0.043	12.0 ± 0.1	18.0	0.043	12.3 ± 0.1	18.0	0.043	12.5 ± 0.1	18.1
0.062	12.6 ± 0.1	18.0	0.062	12.9 ± 0.1	18.0	0.062	13.1 ± 0.1	18.1
0.125	14.1 ± 0.1	18.0	0.125	14.4 ± 0.1	18.0	0.125	14.8 ± 0.1	18.0
0.189	15.2 ± 0.1	18.0	0.188	15.7 ± 0.1	18.0	0.189	16.2 ± 0.1	18.0
0.254	16.2 ± 0.1	18.0	0.254	16.7 ± 0.1	18.0	0.254	17.3 ± 0.1	18.0
0.321	17.1 ± 0.1	18.0	0.321	17.7 ± 0.1	18.0	0.32	18.3 ± 0.1	18.0
0.388	17.8 ± 0.1	18.0	0.389	18.5 ± 0.1	18.0	0.387	19.2 ± 0.1	18.0
0.458	18.6 ± 0.1	18.0	0.458	19.3 ± 0.1	18.0	0.457	20.0 ± 0.1	18.0
0.528	19.3 ± 0.1	18.0	0.528	20.1 ± 0.1	18.0	0.527	20.8 ± 0.1	18.0
30 ° C			35 ° C					
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$			
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)			
0.006	10.5 ± 0.1	18.1	0.006	10.6 ± 0.1	18.1			
0.018	11.5 ± 0.1	18.1	0.018	11.6 ± 0.1	18.1			
0.030	12.1 ± 0.1	18.1	0.031	12.4 ± 0.1	18.1			
0.043	12.7 ± 0.1	18.1	0.043	12.9 ± 0.1	18.1			
0.062	13.4 ± 0.1	18.1	0.061	13.7 ± 0.1	18.1			
0.124	15.2 ± 0.1	18.1	0.124	15.6 ± 0.1	18.1			
0.187	16.6 ± 0.1	18.1	0.188	17.1 ± 0.1	18.1			
0.254	17.8 ± 0.1	18.1	0.253	18.3 ± 0.1	18.1			
0.319	18.8 ± 0.1	18.1	0.319	19.5 ± 0.1	18.1			
0.387	19.8 ± 0.1	18.0	0.386	20.5 ± 0.1	18.1			
0.456	20.7 ± 0.1	18.0	0.456	21.5 ± 0.1	18.1			
0.526	21.6 ± 0.1	18.0	0.525	22.4 ± 0.1	18.1			

2.4 Ionic conductivities of aqueous VOSO₄ solutions

The results of ionic conductivity measurements for aqueous VOSO₄ solutions are shown in Table 2.3 and plotted in Fig. 2.5. The corresponding equivalent conductance is also depicted in Table 2.3 and plotted Fig. 2.6 . We have least squares fitted equivalent conductance with an empirical expression, which is derived from Onsager–Fuoss theory. The expressions at each temperature are stated below:

$$\Lambda(15^{\circ}\text{C}) = 1.490c^{0.5} - 0.7726c - 0.3396\ln c - 0.4948, \quad (2.8)$$

$$\Lambda(20^{\circ}\text{C}) = 1.861c^{0.5} - 0.9268c - 0.3853\ln c - 0.6911, \quad (2.9)$$

$$\Lambda(25^{\circ}\text{C}) = 2.232c^{0.5} - 1.106c - 0.4409\ln c - 0.8669, \quad (2.10)$$

$$\Lambda(30^{\circ}\text{C}) = 2.661c^{0.5} - 1.377c - 0.4948\ln c - 1.038, \quad (2.11)$$

$$\Lambda(35^{\circ}\text{C}) = 3.089c^{0.5} - 1.582c - 0.5568\ln c - 1.252. \quad (2.12)$$

The parameters in the equations show linear temperature dependences, which can be applied to calculate the equivalent conductance of any aqueous VOSO₄ solution with any given concentration within the temperature range we have tested. The composition correlation, along with the knowledge of linear temperature dependence would allow for tracking the concentration change within the cross-over experiment as mentioned previously.

Table 2.3: Ionic conductivity and equivalent conductance of aqueous VOSO₄ solutions at 15, 20, 25, 30, and 35 °C

15 ° C			20 ° C			25 ° C		
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)
0.006	0.0077	1.2577	0.006	0.0087	1.4178	0.006	0.0095	1.5523
0.018	0.0180	0.9769	0.018	0.0198	1.0761	0.018	0.0215	1.1731
0.031	0.0264	0.8636	0.031	0.0291	0.9455	0.031	0.0311	1.0132
0.043	0.0343	0.7936	0.043	0.0373	0.8649	0.043	0.0403	0.9349
0.062	0.0448	0.7257	0.062	0.0487	0.7875	0.062	0.0532	0.8615
0.125	0.0755	0.6040	0.125	0.0824	0.6601	0.125	0.0883	0.7089
0.189	0.1026	0.5430	0.188	0.1106	0.5886	0.189	0.1184	0.6276
0.254	0.1274	0.5011	0.254	0.1369	0.5386	0.254	0.1468	0.5780
0.321	0.1505	0.4686	0.321	0.1607	0.5009	0.320	0.1732	0.5411
0.388	0.1684	0.4345	0.389	0.1830	0.4707	0.387	0.1960	0.5059
0.458	0.1884	0.4114	0.458	0.2030	0.4435	0.457	0.2210	0.4834
0.528	0.2040	0.3861	0.528	0.2220	0.4204	0.527	0.2410	0.4576
30 ° C			35 ° C					
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)			
0.006	0.0103	1.6847	0.006	0.0111	1.8222			
0.018	0.0233	1.2681	0.018	0.0249	1.3583			
0.030	0.0336	1.1043	0.031	0.0361	1.1784			
0.043	0.0439	1.0205	0.043	0.0461	1.0742			
0.062	0.0569	0.9217	0.061	0.0597	0.9723			
0.124	0.0956	0.7685	0.124	0.1002	0.8076			
0.187	0.1278	0.6849	0.188	0.1357	0.7213			
0.254	0.1583	0.6242	0.253	0.1691	0.6686			
0.319	0.1861	0.5834	0.319	0.1966	0.6164			
0.387	0.2120	0.5472	0.386	0.2250	0.5824			
0.456	0.2370	0.5200	0.456	0.2500	0.5485			
0.526	0.2600	0.4943	0.525	0.2730	0.5203			

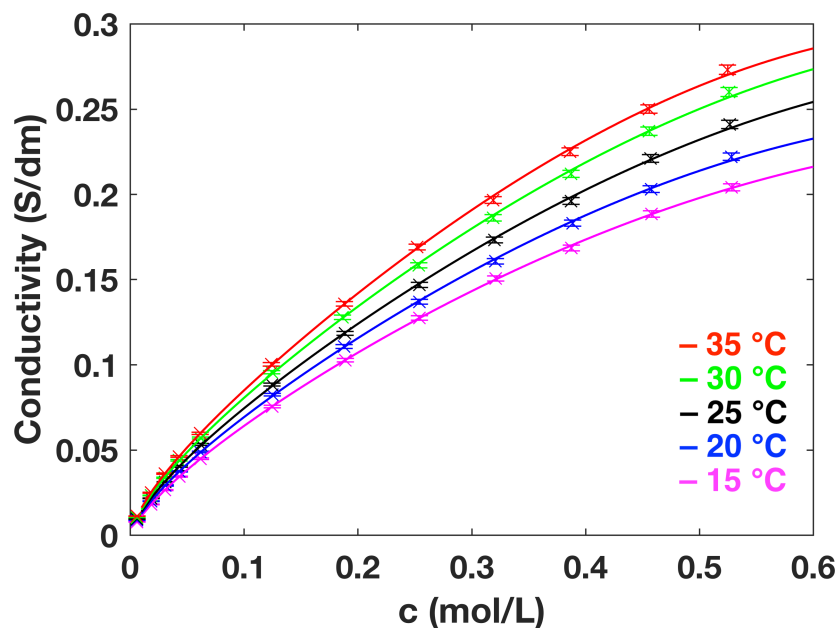


Fig. 2.5: Measured ionic conductivity of aqueous VOSO_4 solutions (x) and the least squares fittings (–) with respect to VOSO_4 molarity from 0.006 M to 0.52 M at 15 (magenta), 20 (blue), 25 (black), 30 (green), and 35 °C (red) (with 1% intrinsic error).

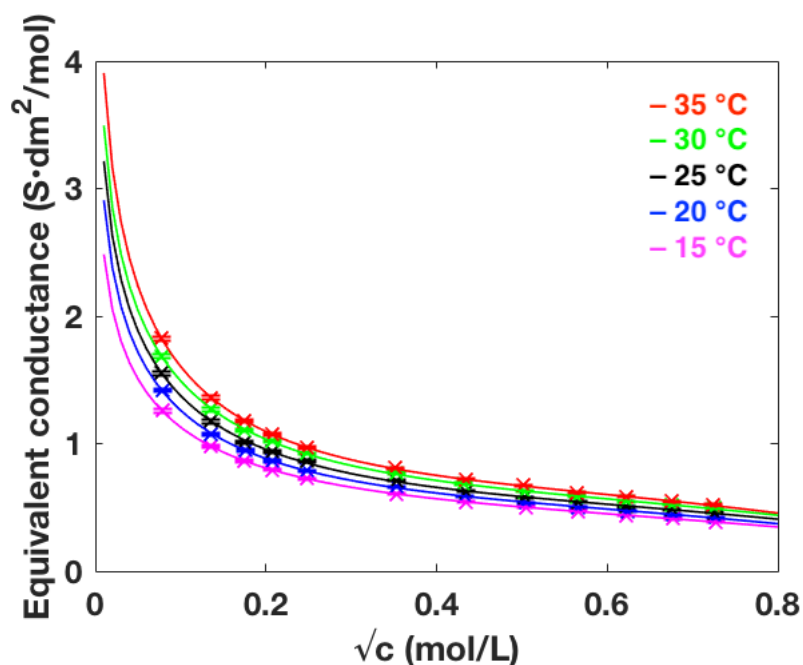


Fig. 2.6: Equivalent conductance of aqueous VOSO_4 solutions (x) and the least squares fittings (–) with respect to square root of VOSO_4 molarity from 0.006 M to 0.52 M at 15 (magenta), 20 (blue), 25 (black), 30 (green), and 35 °C (red) (with 1% intrinsic error).

Chapter 3

Transport and Thermodynamic Properties for Aqueous KOH (KOH) Solutions

Following the work of aqueous VOSO_4 solutions, we have further characterised the transport and thermodynamic properties of very concentrated aqueous KOH solutions, which pose challenges because of their caustic and hygroscopic character, as well as their instability in contact with CO_2 from air. This chapter addresses characterisation work that was undertaken for KOH under the auspices of a project funded by Duracell (at that time a subsidiary of Procter & Gamble). Density, ionic conductivity, and viscosity of aqueous KOH solutions were measured with respect to KOH concentrations up to 12 M at 15, 25 and 35 °C. Beyond the simple rheometry, diffusion coefficient was quantified *via* restricted-diffusion measurements.

3.1 Literatures for characterisation of properties for aqueous KOH solutions

Aqueous KOH solutions are commonly used electrolytes in many electrochemical systems, including alkaline batteries and alkaline fuel cells. Data for transport and thermodynamic properties of aqueous KOH solutions mainly focus on dilute solutions.^{43–46} Literature about the properties of highly concentrated aqueous KOH is surprisingly limited, despite its use in all typical alkaline batteries.^{21,47–52} Akerlof and Bender quantified the density of aqueous KOH solutions up to the saturation concentration at different temperatures.⁴⁷ Klochko *et al.* measured the conductivity and viscosity of concentrated KOH and NaOH solutions at different temperatures.⁴⁸ Sipos *et al.* characterised the density and viscosity for concentrated KOH at 25 °C.²¹ Lengyel *et al.* quantified the transference number of concentrated aqueous KOH solutions.⁴⁹ Balej determined the activity coefficients of KOH across wide concentration and temperatures ranges.⁵⁰ Bhatia *et al.* measured the diffusion coefficient of KOH in water up to 12 M.⁵¹ There has been no literature summarizing density, viscosity, and conductivity for concentrated aqueous KOH solutions at different temperatures and no complete characterisation of transport and thermodynamic properties.

The paucity of data for aqueous KOH owes to two experimental challenges. First, KOH is very hygroscopic. Solid KOH pellets absorb water from the atmosphere. Whenever one wants to make a KOH solution by dissolving solid KOH pellets, the composition is unknown and must be determined by other methods (normally titration). At the same time, highly concentrated KOH is very reactive with atmospheric CO₂, spontaneously forming carbonate species. This causes a severe aging problem. These two facts make the characterisation, especially the precise determination of the solution composition, both complicated and tedious. A densitometer with temperature control can easily and accurately measure density at a certain temperature. With a good density-composition correlation, the composition of an unknown aqueous KOH solution can be determined by quantifying density.

Therefore, the first step toward characterisation of highly concentrated aqueous KOH is to establish partial molar volumes through precise quantification of the variation of density with composition.

3.2 Experimental

3.2.1 Solutions preparation

To perform an accurate characterisation, the first challenge is to determine the composition of the solutions both accurately and precisely. As we have mentioned in Chapter 2, molarity is normally used as the concentration measure. However, temperature fluctuations easily influence the precision of molarity determination, due to the relatively strong temperature dependence of solution volume. Thus, we used mass fraction as the concentration measure, as for aqueous VOSO_4 in the prior chapter.

Solution series, usually consisting of 20 mL samples, were prepared from concentrated stock solutions. Stock solutions were prepared by dissolving KOH pellets (99.99%, semiconductor grade, Sigma Aldrich) in ultrapure water. High precision base-acid titrations, with sodium hydrogen carbonate (BioXtra, 99.95%, Sigma Aldrich) as titter and phenolphthalein solution (1% in ethanol, Fluka) as indicator, were used to determine KOH mass fractions in the stock solutions. The average systematic error of the titration is 0.5%. Pure nitrogen gas was then bubbled into solutions to displace dissolved O_2 and CO_2 , which makes strongly basic solutions chemically unstable. Since highly concentrated aqueous KOH solutions are also highly hygroscopic, all stock solutions were freshly made prior to use.

3.2.2 Density measurements

Densities were measured using DMA 4100 density meter (Anton- Paar) with inner temperature controller (readability: 0.00005 g/cm^3 , accuracy: 0.0001 g/cm^3). Calibration, sample preparation, and assessment of tube cleaning followed the procedures listed in Chapter 2. At least three measurements were performed on each solution and the average value was reported. After the measurements, the tube was washed with ultra-pure water for three times and acetone and then dried with compressed air.

3.2.3 Ionic conductivity measurements

Ionic conductivity of aqueous KOH solutions was measured with AC conductometry. Calibration of the meter and cleaning of the probe followed the procedures described in Chapter 2. Sample solutions were kept in airtight glass vials, which were stored in a water bath for at least two hours to allow for thermal equilibrium. The conductivity probe was then submerged into the samples to measure their conductivity. Conductivities were measured at three temperatures ($15.00 \pm 0.02 \text{ }^\circ\text{C}$, $25 \pm 0.02 \text{ }^\circ\text{C}$ and $35 \pm 0.02 \text{ }^\circ\text{C}$). Each sample was measured at least three times, and the average value was reported.

3.2.4 Viscosity measurements

A DV-II Prime Digital Viscometer (Brookfield Engineering, US) with ultra-low adapter was used to determine the solution viscosities. The ultra-low adapter is an accessory that limits the sample volume to 16 ml and can deal with solutions whose viscosities are less than that of water. The viscometer was periodically checked and calibrated with viscosity standard solutions. During the measurements, the ultra-low adapter was attached to the viscometer and to the heating and cooling circulator simultaneously, controlling the temperature during measurement. Sample solutions were first stored in a water bath to reach thermal equilibrium and then injected into the adapter chamber for measurements. Each

measurement was allowed to proceed for ten minutes so that the target temperature could be achieved. After measurement of a given sample, the adapter was washed with distilled water and acetone and then dried with flowing air. Viscosities of all aqueous KOH samples were measured at three different temperatures (15.00 ± 0.02 °C, 25 ± 0.02 °C and 35 ± 0.02 °C).

3.2.5 Preparation of MnO₂-plated Ni foil

To perform polarization-cell measurements such as restricted-diffusion measurements or galvanostatic polarization measurements, an applied current is used to introduce a non-uniform concentration profile within the electrolytes. In principle, potassium foils can be used as electrodes to induce concentration gradients, but such electrodes are not stable in contact with water. Instead, a sacrificial electrode that reacts with OH⁻ is favorable. To perform polarization cell measurements with the OH⁻ reaction, a zinc foil was used as anode and a MnO₂-plated nickel foil as cathode, which had the added benefit of simulating the configuration within typical alkaline batteries.

MnO₂-plated nickel foil was prepared *via* a potentiometric method.^{53–55} A cleaned nickel foil was submerged into a mixture of 0.1 M Na₂SO₄ and 0.1 M Mn(CH₃COO)₂ solutions as the working electrode. A saturated calomel electrode was used as reference electrode, and a platinum foil as counter electrode. A constant potential was then applied between the working and reference electrodes for 600 seconds. The applied potential electrodeposits MnO₂ on the surface of the nickel foil, which appears as a golden layer. The MnO₂-plated nickel foil was then cleaned with ultrapure water and dried at 75 °C under air environment. Fig. 3.1 shows a picture of the resultant MnO₂-plated nickel foil resulting from the electrodeposition method.

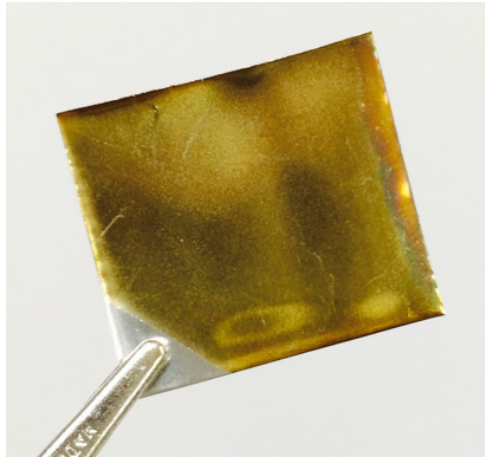


Fig. 3.1: A picture of MnO₂-plated Ni foil.

3.2.6 Restricted-diffusion measurements

Restricted-diffusion measurements were performed at room temperature, using a parallel-plate test cell produced by MTI (USA), with a customized PEEK spacer. The inner diameter of the spacer was 5.0 mm and the length was 2.0 cm. A zinc disk foil was used as the anode, and a MnO₂-plated nickel disk foil as the cathode. A potentiostat/galvanostat performed chronopotentiometry on the cell to induce the desired concentration profile, and then tracked the open circuit potential (OCP) relaxation. A picture of the cell and a diagram of the spacer are shown in Fig. 3.2.

3.3 Density of Aqueous KOH Solutions

Density was quantified with unit of g/L. Mass fraction was used as the concentration measure initially. Once the density measurements were finalized, the molarity with unit of mol/L was then calculated by

$$c(\text{mol/L}) = \frac{\omega \rho}{M_{\text{KOH}}} \quad (3.1)$$

where ω represents the mass fraction and M_{KOH} is the molar mass of KOH. The results of density measurements are summarized in Table 3.1 and plotted in Fig. 3.3. The density of aqueous KOH solutions was accurately described as a function of molarity at each

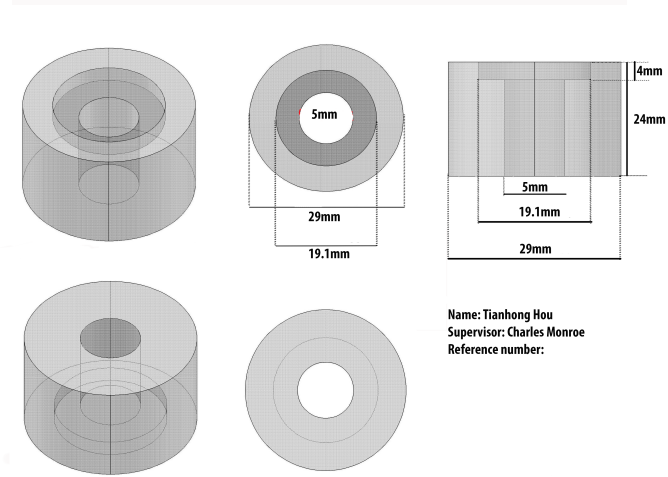
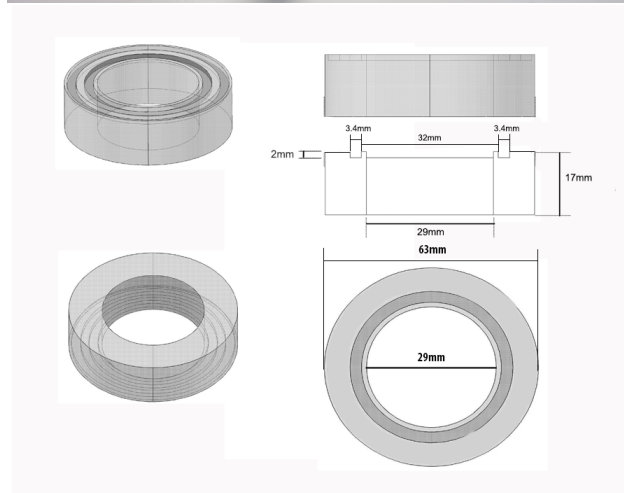


Fig. 3.2: A picture of the customized restricted-diffusion cell and the diagrams of the inner spacers.

temperature through

$$\rho (15^{\circ}C) = 999.1 + 52.57c - 4.002c^{1.5}, \quad (3.2)$$

$$\rho (25^{\circ}C) = 997.0 + 52.02c - 3.874c^{1.5}, \quad (3.3)$$

$$\rho (35^{\circ}C) = 994.0 + 51.23c - 3.688c^{1.5} \quad (3.4)$$

The intercept of each equation was forced to be the density of pure water and each parameter in Eqs. 3.2, 3.3, and 3.4 shows a significant temperature dependence. According to literature, the density of water is not a linear function of temperature, and a second-order-polynomial function could be used to describe the temperature dependence of water density. Since we have only quantified density at three temperatures, we can hardly propose a function that accurately describes the temperature dependence of the density of aqueous KOH solutions. To further explore the temperature effect, at least two more temperatures should be quantified.

Once the density correlations were determined, partial molar volumes of the electrolytes were then calculated by applying Eqs. 1.59 and 1.60. As the Fig. 3.4 shows, the partial molar volume of KOH salt increases with concentration, while that of solvent descends. The measured data is summarized in Table 3.2.

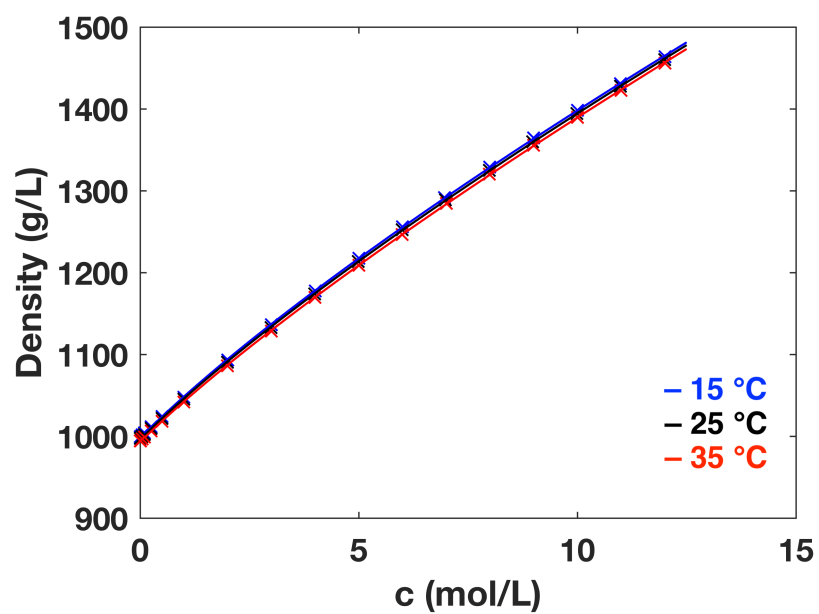


Fig. 3.3: Measured density of aqueous KOH solutions and the least squares fittings with respect to KOH molarity up to 12 M at 15 (blue), 25 (black), and 35 (red) °C.

Table 3.1: Densities of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c (mol/L)	ω	$\rho \pm 0.1$ (g/L)	c (mol/L)	ω	$\rho \pm 0.1$ (g/L)	c (mol/L)	ω	$\rho \pm 0.1$ (g/L)
0.0050	0.028	999.5	0.0050	0.028	997.3	0.0050	0.028	994.3
0.0100	0.056	999.7	0.0100	0.056	997.7	0.0100	0.056	994.5
0.0499	0.280	1001.8	0.0500	0.281	999.7	0.0499	0.281	996.6
0.0999	0.558	1004.2	0.1000	0.559	1002.3	0.0999	0.561	999.0
0.2500	1.386	1011.7	0.2499	1.387	1009.7	0.2500	1.394	1006.4
0.5001	2.740	1024.0	0.4999	2.744	1021.8	0.5001	2.755	1018.4
1.0005	5.358	1047.7	0.9987	5.361	1045.4	1.0001	5.387	1041.6
2.0019	10.276	1093.0	1.9987	10.288	1090.2	1.9996	10.330	1086.1
3.0036	14.833	1136.1	2.9945	14.832	1132.6	2.9987	14.908	1128.5
4.0040	19.079	1177.5	3.9952	19.095	1173.8	4.0000	19.190	1169.5
5.0043	23.065	1217.3	4.9921	23.081	1213.7	5.0026	23.215	1209.0
6.0015	26.816	1255.9	5.9953	26.866	1252.2	5.9921	26.963	1246.6
6.9626	30.247	1291.7	6.9855	30.408	1288.7	7.0024	30.588	1284.7
7.9924	33.748	1328.8	7.9877	33.820	1325.0	7.9902	33.961	1320.2
9.0017	37.024	1364.4	8.9778	37.040	1359.7	9.0004	37.254	1355.3
10.0027	40.138	1398.4	9.9887	40.191	1394.4	10.0038	40.387	1389.8
10.9881	43.086	1430.9	10.9853	43.175	1427.6	10.9988	43.370	1422.7
12.0016	46.011	1463.7	11.9947	46.088	1460.1	12.0044	46.274	1455.8

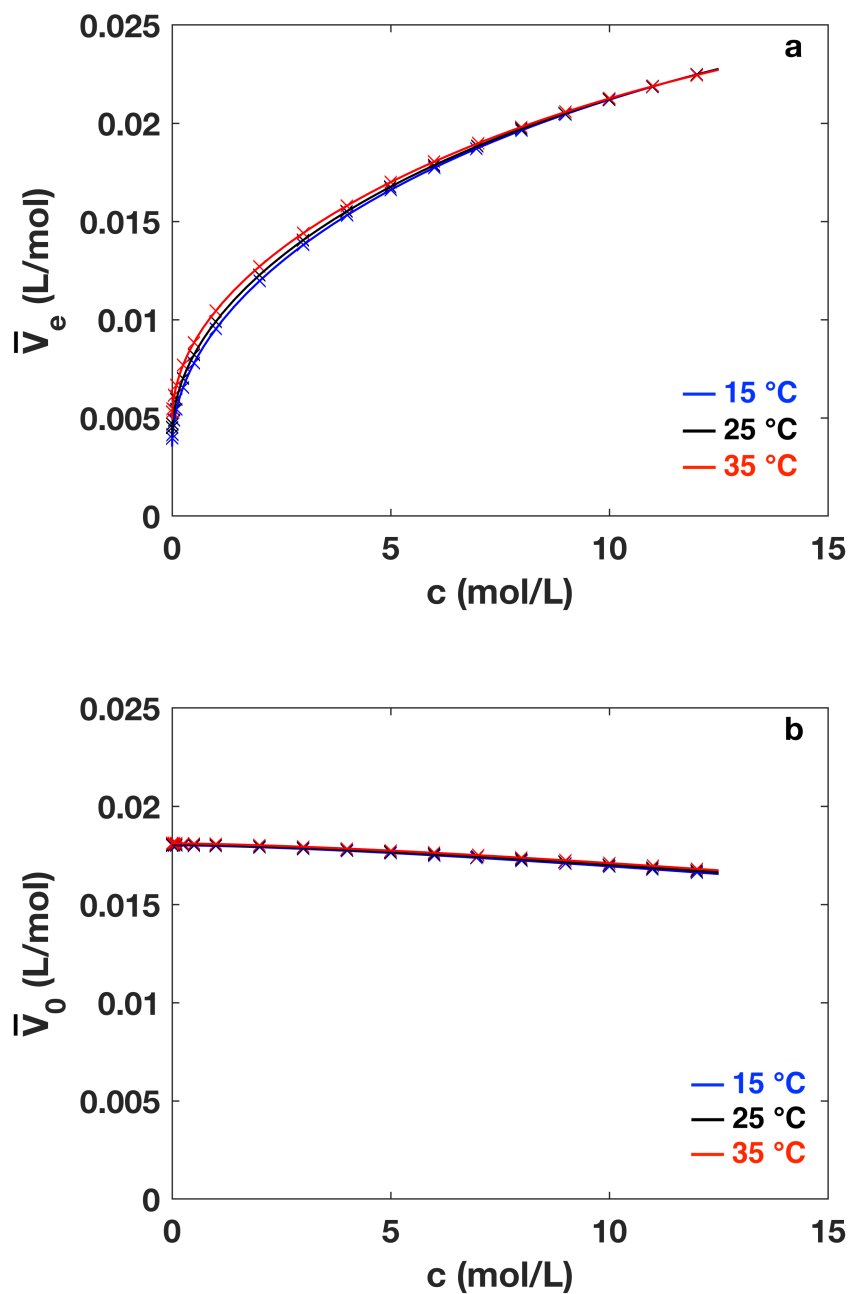


Fig. 3.4: (a) Partial molar volumes of salt for aqueous KOH solutions; (b) Partial molar volumes of solvent for aqueous KOH solutions at 15 (blue), 25 (black), and 35 (red) °C.

Table 3.2: Partial molar volumes of KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)
0.005	4.0 ± 0.01	18.0	0.005	4.6 ± 0.01	18.1	0.005	5.3 ± 0.01	18.1
0.010	4.2 ± 0.01	18.0	0.010	4.7 ± 0.01	18.1	0.010	5.5 ± 0.01	18.1
0.050	4.9 ± 0.01	18.0	0.050	5.5 ± 0.01	18.1	0.050	6.2 ± 0.01	18.1
0.100	5.5 ± 0.01	18.0	0.100	7.1 ± 0.01	18.0	0.100	6.7 ± 0.01	18.1
0.250	6.6 ± 0.01	18.0	0.250	8.3 ± 0.01	18.0	0.250	7.7 ± 0.01	18.1
0.500	7.8 ± 0.01	18.0	0.500	4.7 ± 0.01	18.1	0.500	8.8 ± 0.01	18.1
1.001	9.5 ± 0.01	18.0	0.999	9.9 ± 0.01	18.0	1.000	10.5 ± 0.01	18.1
2.002	12.0 ± 0.01	17.9	1.999	12.3 ± 0.01	18.0	2.000	12.7 ± 0.01	18.0
3.004	13.8 ± 0.01	17.8	2.995	14.1 ± 0.01	17.9	2.999	14.4 ± 0.01	17.9
4.004	15.3 ± 0.01	17.7	3.995	15.5 ± 0.01	17.8	4.000	15.8 ± 0.01	17.8
5.004	16.6 ± 0.01	17.6	4.992	16.8 ± 0.01	17.7	5.003	17.0 ± 0.01	17.7
6.002	17.7 ± 0.01	17.5	5.995	17.9 ± 0.01	17.6	5.992	18.1 ± 0.01	17.6
6.963	18.7 ± 0.01	17.4	6.986	18.8 ± 0.01	17.4	7.002	19.0 ± 0.01	17.5
7.992	19.6 ± 0.01	17.2	7.988	19.7 ± 0.01	17.3	7.990	19.8 ± 0.01	17.4
9.002	20.5 ± 0.01	17.1	8.978	20.5 ± 0.01	17.2	9.000	20.6 ± 0.01	17.2
10.003	21.2 ± 0.01	16.9	9.989	21.2 ± 0.01	17.0	10.004	21.3 ± 0.01	17.1
10.988	21.9 ± 0.01	16.8	10.985	21.9 ± 0.01	16.9	10.999	21.9 ± 0.01	17.0
12.002	22.5 ± 0.01	16.6	11.995	22.5 ± 0.01	16.7	12.004	22.5 ± 0.01	16.8

3.4 Ionic Conductivity of Aqueous KOH Solutions

Ionic conductivity was quantified with units of S/dm. The results of conductivity measurements are shown in Fig. 3.5(a) and summarized in Table 3.3. Conductivity reaches a maximum value at 6 M, which is consistent with literature.^{48,52} Equivalent conductance was then calculated by dividing ionic conductivity by molarity. Conventionally, equivalent conductance is plotted with respect to the square root of molarity, which representation is shown in Fig. 3.5(b). The results of equivalent conductance are also summarized in Table 3.3. Mathematical expressions with a form similar to the Onsager–Fuoss prediction fit the equivalent conductance well:

$$\Lambda(15^\circ\text{C}) = -0.2585c^{0.5} - 0.1328c + 0.004373c^2 + 2.148, \quad (3.5)$$

$$\Lambda(25^{\circ}\text{C}) = -0.3438c^{0.5} - 0.1485c + 0.005133c^2 + 2.620, \quad (3.6)$$

$$\Lambda(35^{\circ}\text{C}) = -0.4293c^{0.5} - 0.1631c + 0.006014c^2 + 3.080. \quad (3.7)$$

The fittings in Fig. 3.5(a) come from the multiplication of Eq. 3.5, 3.6, and 3.7 by molarity, which describes the trend of conductivity variation very well.

Table 3.3: Ionic conductivities, κ , and equivalent conductance, Λ , of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)
0.0050	0.0106	2.120	0.005	0.0130	2.590	0.005	0.0152	3.038
0.010	0.0211	2.111	0.010	0.0258	2.579	0.010	0.0303	3.031
0.050	0.1039	2.082	0.050	0.1268	2.535	0.050	0.1482	2.968
0.100	0.2043	2.045	0.100	0.25	2.501	0.100	0.291	2.912
0.250	0.496	1.984	0.250	0.606	2.425	0.250	0.707	2.828
0.500	0.936	1.872	0.500	1.155	2.311	0.500	1.349	2.697
1.001	1.745	1.744	0.999	2.12	2.123	1.000	2.47	2.470
2.002	3.08	1.539	1.999	3.69	1.846	2.000	4.34	2.171
3.004	4.05	1.348	2.995	4.87	1.626	2.999	5.71	1.904
4.004	4.72	1.179	3.995	5.70	1.427	4.000	6.73	1.683
5.004	5.09	1.017	4.992	6.19	1.240	5.003	7.41	1.481
6.002	5.23	0.871	5.995	6.46	1.078	5.992	7.71	1.287
6.963	5.21	0.748	6.986	6.44	0.922	7.002	7.76	1.108
7.992	5.03	0.629	7.988	6.30	0.789	7.990	7.64	0.956
9.002	4.84	0.538	8.978	6.00	0.668	9.000	7.33	0.814
10.003	4.34	0.434	9.989	5.60	0.561	10.004	6.92	0.692
10.988	3.94	0.359	10.985	5.15	0.469	10.999	6.43	0.585
12.002	3.52	0.293	11.995	4.64	0.387	12.004	5.91	0.492

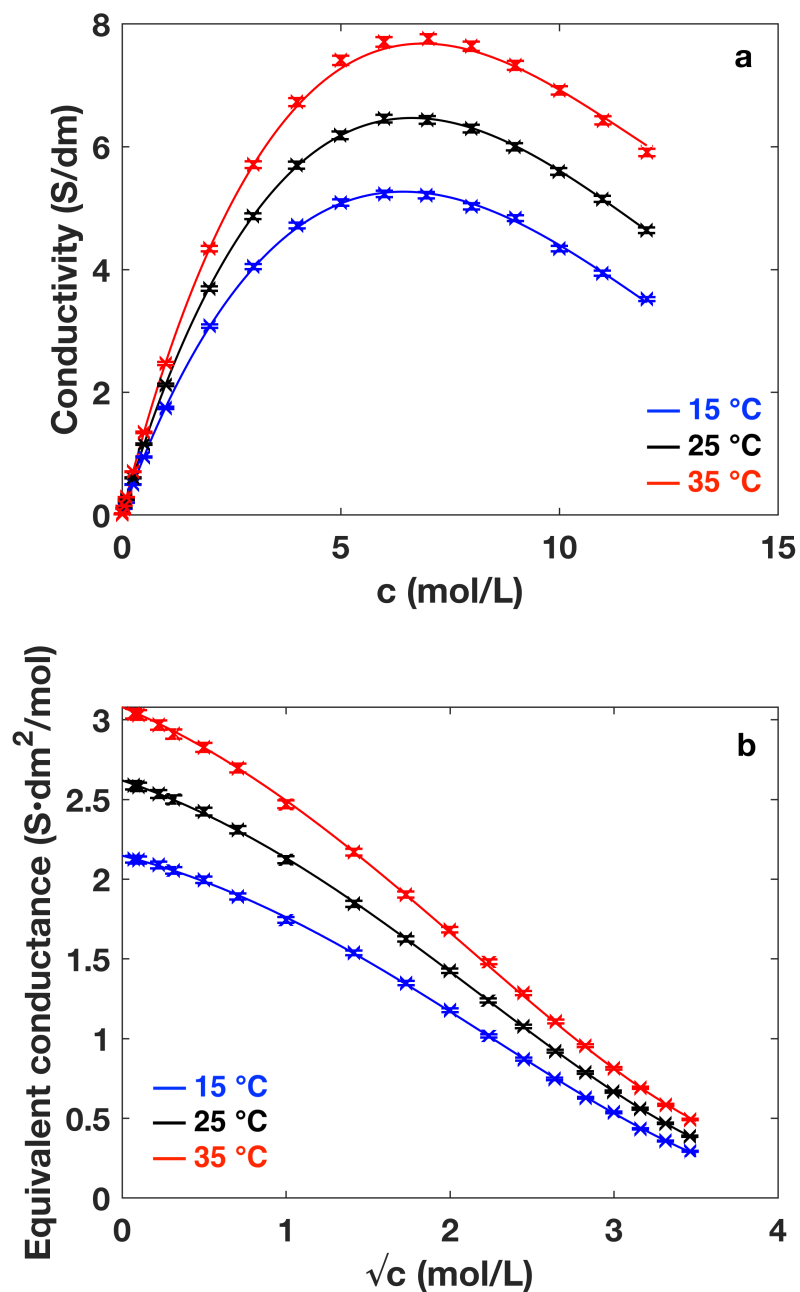


Fig. 3.5: (a) Ionic conductivity of aqueous KOH solutions with respect to KOH molarity from 0.05 M to 12 M at 15 (blue), 25 (black), and 35 (red) °C; (b) equivalent conductance of aqueous KOH solutions with respect to the square root of KOH molarity at 15 (blue), 25 (black), and 35 (red) °C (with 1% intrinsic error).

3.5 Dynamic viscosities of aqueous KOH solutions

Viscosities of aqueous KOH solutions at different temperatures are presented in Table 3.4 and plotted against molarity in Fig. 3.6. According to the work from Sipos *et al.*,⁵⁶ an empirical fifth-order polynomial function can describe the viscosity variation in aqueous solutions. Therefore, the results have been fit with fifth-order polynomial functions:

$$\eta = 7.89 \times 10^{-5}c^5 - 1.87 \times 10^{-3}c^3 + 1.79 \times 10^{-2}c^2 + 0.183c + 1.29, \quad (3.8)$$

$$\eta = 9.27 \times 10^{-5}c^5 - 2.32 \times 10^{-3}c^4 + 2.48 \times 10^{-2}c^3 - 9.52 \times 10^{-2}c^2 + 0.191c + 1.01, \quad (3.9)$$

$$\eta = 2.73 \times 10^{-5}c^5 - 6.80 \times 10^{-3}c^4 + 6.78 \times 10^{-5}c^3 - 1.69 \times 10^{-2}c^2 + 0.100c + 0.84. \quad (3.10)$$

One should note that these functions are empirical, and do not bear any specific physical meaning; their parameters do not provide much insight into the temperature dependence of viscosity.

3.6 Fickian diffusion coefficient of 1 M aqueous KOH solution

Restricted-diffusion cell measurements have been applied to attempt to quantify the diffusion coefficient of 1 M KOH in water. The result of one of our measurements is shown in Fig. 3.7. The Fickian diffusion coefficient we have obtained is $3.12 \times 10^{-5} \text{ cm}^2/\text{s}$, which shares the same order of magnitude of literature data.⁵¹ However, we have also spotted some problems with the restricted-diffusion measurements. The $-\ln \text{OCP}$ vs. time plot displays significant noise, which makes the analysis of the data extremely difficult. Moreover, the application of asymmetric structure (the cathode and anode are made of different materials) makes the initial OCP not zero. This OCP will vary with the concentration of KOH, which brought inconsistency to different measurements. We have noticed that the initial OCP of the cell is different from the equilibrium OCP after relaxation, and the trend of how OCP change behaves differently between short time range (OCP increases) and

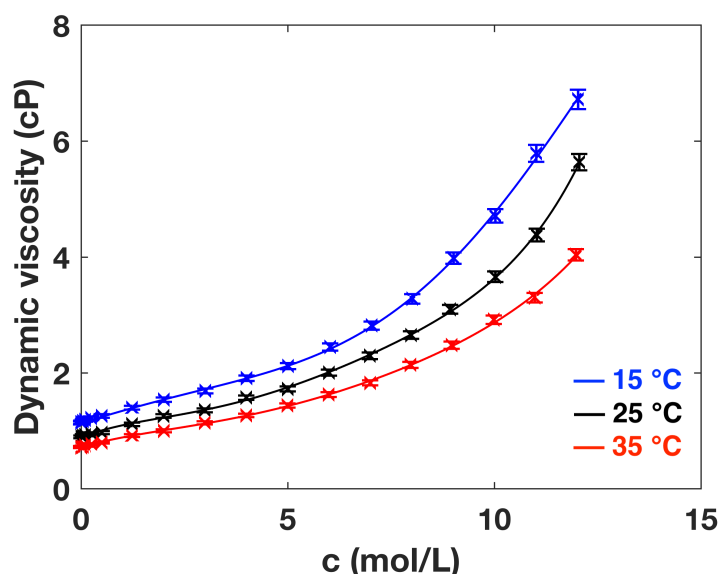


Fig. 3.6: Measured dynamic viscosity of aqueous KOH solution with respect to KOH molarity from 0.05 M to 12 M at 15 (blue), 25 (black), and 35 (red) °C (with 2% intrinsic error).

Table 3.4: Dynamic viscosity of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C		25 ° C		35 ° C	
c (mol/L)	$\eta \pm 2\%$ (cP)	c (mol/L)	$\eta \pm 2\%$ (cP)	c (mol/L)	$\eta \pm 2\%$
0.005	1.26	0.005	1.00	0.005	0.83
0.010	1.28	0.010	1.01	0.010	0.84
0.050	1.30	0.050	1.02	0.050	0.85
0.100	1.32	0.100	1.04	0.100	0.86
0.250	1.36	0.250	1.06	0.250	0.88
0.500	1.38	0.500	1.08	0.500	0.90
1.001	1.40	0.999	1.12	1.000	0.92
2.002	1.54	1.999	1.26	2.000	1.00
3.004	1.69	2.995	1.36	2.999	1.14
4.004	1.91	3.995	1.58	4.000	1.27
5.004	2.12	4.992	1.73	5.003	1.44
6.002	2.45	5.995	2.01	5.992	1.63
6.963	2.82	6.986	2.30	7.002	1.83
7.992	3.28	7.988	2.66	7.990	2.14
9.002	3.98	8.978	3.14	9.000	2.48
10.003	4.71	9.989	3.66	10.004	2.92
10.988	5.79	10.985	4.38	10.999	3.30
12.002	7.41	11.995	5.64	12.004	4.04

long time range (OCP decreases). This may be caused from the depletion of MnO_2 on the MnO_2 -plated Ni electrode, which exposes Ni directly to KOH solutions. To overcome this problem, we may need to establish the concentration profile by directly letting solution with different concentration contact with each other (see Harned's setup in Chapter 4), rather than through the electrochemical method.

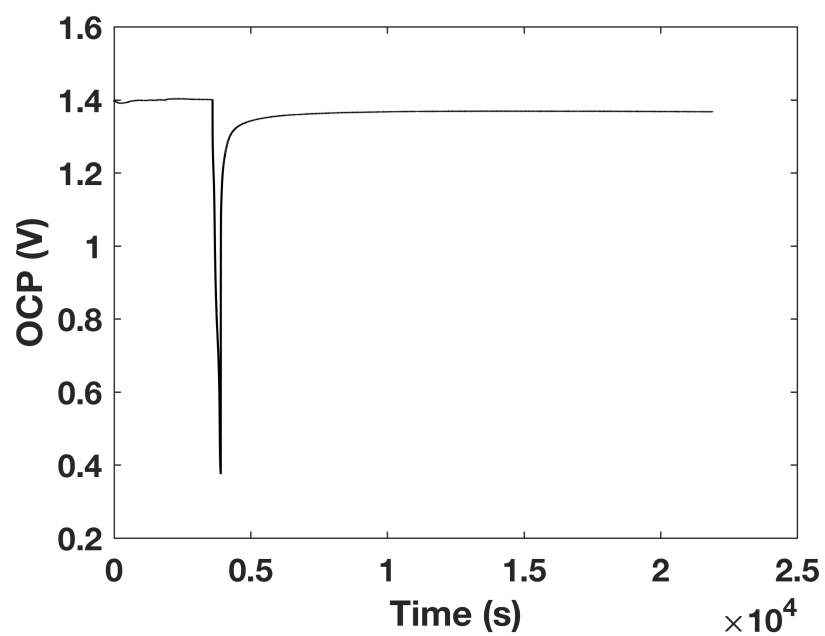


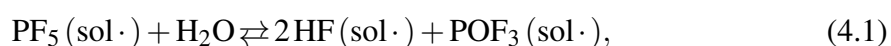
Fig. 3.7: Cell voltage response in a restricted-diffusion measurements for 1 M aqueous KOH solutions. Pulse time: 300s, pulse current: 0.51 mA/cm²

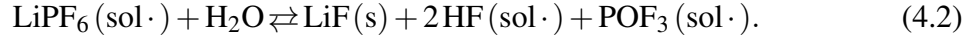
Chapter 4

Transport and Thermodynamic Properties for LiPF₆ in PC

The previous chapters addressed challenges that occur when characterising the properties of aqueous solutions whose composition is difficult to assess precisely, and which may be chemically unstable (VOSO₄ and KOH). Tackling these problems helped us to develop proficiency in handling air and moisture sensitive solutions. The previous characterizations did not involve detailed measurements of transport properties. We therefore set out to explore the complete set of thermodynamic and transport properties for a non-aqueous electrolyte. The non-aqueous electrolytic solution we chose is lithium hexafluorophosphate (LiPF₆) in propylene carbonate (PC), an exemplary solution of the type used in Li-ion batteries.^{57–59}

Unlike aqueous solutions, non-aqueous solutions, especially non-aqueous electrolytic solutions, are normally sensitive to heat, moisture, and impurity. In the case of LiPF₆-based electrolytes, it has been proposed that the presence of even trace (>50 ppm) amounts of water will jeopardize electrolyte performance.⁵⁷ Hydrolysis of LiPF₆, following the scheme





produces soluble and corrosive by-products, which can damage other parts of the battery and lead to a decreased cycle life. For LiPF_6 salt itself, an equilibrium exists, even at room temperature:



This decomposition is favoured by elevated temperature, and the existence of PF_5 tends to initiate a series of side reactions with organic solvents. As an indication of the difficulties of working with these materials, note that it has been suggested that LiPF_6 , either as a salt or in a solution, should not be stored in glass containers, because LiPF_6 etches glass.⁶⁰ All these factors have made the characterisation of non-aqueous LiPF_6 -based electrolytes an interesting challenge. To that end, this chapter presents a complete characterisation of transport and thermodynamic properties for LiPF_6 in PC. We quantify the composition dependences of three transport properties: ionic conductivity, thermodynamic diffusion coefficient and transference number; and three thermodynamic properties: partial molar volume of solute, partial molar volume of solvent, and thermodynamic factor.

4.1 LiPF_6 in PC solutions as electrolytes for Li-ion chemistry

An electrolyte for Li-ion system should meet the following criteria: (1) It should be an electronic insulator with good ionic conductivity, so that the Li^+ can be transferred easily between anode and cathode; (2) The electrochemical stability window should be wide enough to avoid electrolyte degradation within the working potential ranges of both cathode and anode; (3) It should be thermally stable, meaning its melting point is low and boiling point is high, which allows a wide operation temperature range of the battery; (4) It should be chemically stable against other parts of the battery such as current collector,

cell separator, and cell packing materials; (5) It should have low toxicity, pose minimal environmental hazard, and ideally be inexpensive.⁵⁷

Most of the electrolytes used in modern commercial Li-ion batteries use LiPF_6 salt as solute and various organic carbonates, such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC), as solvent.⁶¹ LiPF_6 was first proposed for use in Li-based batteries during the 1960s.⁵⁹ If we compare any single property for different Li salts, LiPF_6 is not necessarily the best. LiPF_6 , however, possesses the most well-balanced performance among all Li salts, making it the most commonly used Li salt for modern commercial Li-based batteries.⁵⁷ PC was first recognised as a useful solvent for Li-based batteries in 1958, when a solution of LiClO_4 in PC was found to enable reversible electrochemical plating and stripping of Li.⁶⁰ Compared with other carbonate solvents, PC exhibits high Li salt solubility, a wide stability window, and a wide temperature operation range. Its excellent performance makes PC one of the essential components in most modern Li^+ -conductive electrolytes.⁶¹

4.2 Prior works on characterisation of transport and thermodynamic properties of Li^+ -conductive electrolytes

Many groups have performed transport-property characterisation for different non-aqueous Li^+ -conductive electrolytes. Most work focuses on the measurements of the ionic conductivity.^{62–66} Literature discussing transference-number and diffusivity measurement is rare but available.^{67–72} One of the first detailed studies of thermodynamic factor (activity-coefficient) measurement for liquid Li-based electrolytes was performed by Georén and Lindbergh.⁷³ Then more literature about the activity coefficient of non-aqueous Li-based electrolytes started to show up. In 2005, Valøen *et al.* performed a complete characterisation of transport and thermodynamic properties for solutions of LiPF_6 in PC/EC/DMC, making them the first group to obtain all essential properties that required to fully describ-

ing the transport process within a liquid Li^+ -conductive electrolyte.⁷⁴ This work has drawn such a great attention that more similar works have been done up to now.^{34,75–77}

Isolated measurements of a few individual properties of LiPF_6 in PC have been reported,^{66,78,79} but to date no effort has been found to undertake the complete measurement program necessary to establish all the properties unambiguously. Moreover, partial molar volumes of solute and solvent, which have been demonstrated to be crucial for accurate simulation of non-aqueous electrolytic transport at high currents, have only been considered by a few groups.^{34,75,80} Therefore we set out to perform complete measurements of transport and thermodynamic properties for solutions of LiPF_6 in PC, with the specific aim of quantifying precisely the composition dependence of ionic conductivity, density (partial molar volumes), transference number, thermodynamic factor, and thermodynamic diffusivity.

4.3 Methodology to quantify transference number, thermodynamic factor, and diffusion coefficient

4.3.1 Concentration-cell measurements

The thermodynamic factor, which describes how activity or activity coefficient varies with composition, can be quantified by freezing-point depression, vapor-pressure measurements, or concentration-cell measurements.^{3,25–27} The concentration-cell method was first carried out by MacInnes and Parker to measure the activity coefficient of potassium chloride in water.⁸¹ Fig. 4.1 shows the schematic design of our customized concentration cell. Two glass chambers are separated by a porous frit, which allows chemical contact between the chambers, but has porosity sufficiently low that inter-diffusion rates between chambers are negligible. Electrolytic solutions with the same salt and solvent species but different salt content fill the two chambers. Solutions with different salt content have different free

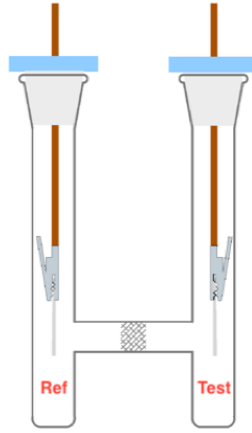


Fig. 4.1: A diagram of self-designed concentration cell apparatus.

energy, which can be quantified by placing electrochemically reversible electrodes into the chambers and measuring the OCP difference between them. Under isothermal, isobaric conditions, a thermodynamic analysis suggests that OCP depends on the salt activity and the transference number.^{3,25}

To better understand the fundamental principles underpinning concentration-cell measurements, one needs to go back to the discussion of chemical potential of the neutral salt. As Eq.1.34 suggests, the OCP of a concentration cell is related to the chemical potentials of salt and solvent. Taking into account the isothermal, isobaric Gibbs–Duhem equation for a binary electrolyte,

$$y_0 \nabla \mu_0 + y_A \nabla \mu_A = 0, \quad (4.4)$$

Eq.1.34 becomes

$$\left(-\frac{s_+}{n v_+} - \frac{t_+^0}{z_+ v_+} - \frac{s_0 y}{n(1 - v y_A)} \right) d\mu_A = F d\Phi \quad (4.5)$$

Let ΔU be the potential increase between two electrodes (α and α'), then $F\Delta U = F \int_{\alpha}^{\alpha'} d\Phi$.

One can thus convert Eq. 4.5 to another form,

$$\frac{d\Delta U}{d\ln y} = \frac{vRT\chi}{F} \left(-\frac{s_+}{nv_+} - \frac{t_+^0}{z_+v_+} - \frac{s_0y}{n(1-vy_A)} \right), \quad (4.6)$$

which expresses the OCP change measured by a reversible reference electrode to the thermodynamic factor and transference number.

If one assumes χ , t_+^0 , and partial molar volumes to be constant with composition, which is valid when the composition difference is small, Eq. 4.6 can be integrated directly, yielding⁷

$$\Delta U = \frac{RT\chi}{nF} \left[\frac{v}{v_+} \left(-\frac{s_+}{n} - \frac{t_+^0}{z_+} \right) \ln \frac{y_{\text{test}}}{y_{\text{ref}}} + \frac{s_0}{n} \ln \frac{1-vy_{\text{test}}}{1-vy_{\text{ref}}} \right]. \quad (4.7)$$

One could further simplify Eq. 4.7 by linearising the OCP difference about the reference composition:

$$\Delta U \approx \left. \frac{dU}{d\ln y} \right|_{y_{\text{ref}}} \frac{\Delta y}{y_{\text{ref}}}. \quad (4.8)$$

a proportionality of this type is often assumed in theoretical analysis, because it makes OCP a direct proxy for the composition difference between electrodes.^{6,32,74,78} But one must aware that both Eq. 4.7 and Eq. 4.8 are valid only when Δy is small. Experiments have found that transference number and thermodynamic factor are both relatively strong functions of salt concentration.^{34,75} Therefore, the approximations in Eq. 4.7 and Eq. 4.8 are suspect.

If one keeps the salt composition of the electrolyte constant on one side of the concentration cell, and varies the salt concentration on the other side, the OCP difference between the two sides is then a function of the salt concentration. There is not a universally agreed-upon form for this functionality, but normally a high-order polynomial function can fit the trend of OCP difference fairly well. The derivative of the polynomial function with respect to the natural logarithm of salt concentration will give an empirical expression of the product of transference number and thermodynamic factor. It is worth emphasizing also that concentration-cell measurements do not directly give the value of thermodynamic fac-

tor. One can only isolate the thermodynamic factor from concentration-cell measurements when accurate transference-number data is available from another source.

4.3.2 Restricted-diffusion measurements

Restricted-diffusion measurements can be used to quantify the Fickian diffusion coefficient. The method was first proposed by Harned and French.³¹ Fig. 4.2 shows a conceptual diagram of Harned's conductance cell. The essential feature of Harned's method is that it involves a cell with finite length such that diffusion only occurs within a restricted range and that the decay of an initial concentration gradient with time is tracked by measuring the conductivity difference between two predetermined points in the cell. The experiments are performed in a rectangular cell in which the height L is very precisely measured. The diffusion channel is closed permanently at the top, and the bottom fits against a sliding plate containing two small reservoirs B and C, which have the same cross-section as the channel A, so that by suitably sliding the plate either of them may be made to form a downward continuation of the channel.

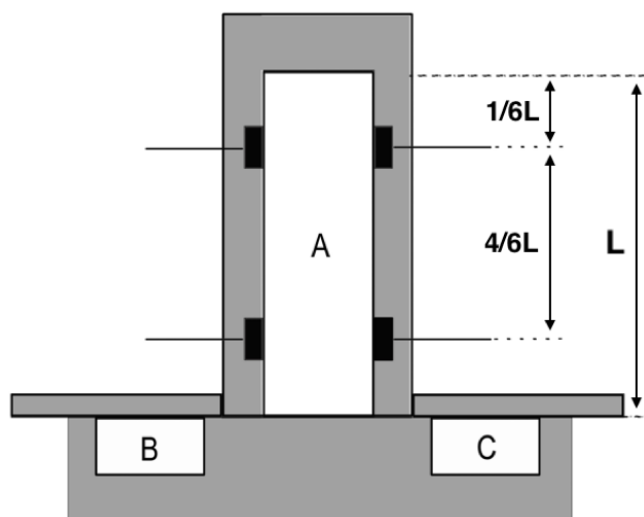


Fig. 4.2: A diagram of Harned's conductance diffusion cell.

In an inverted position, the channel A is filled with water and the plate is placed in position with the reservoir B in line with A. Then the whole cell is turned upside down. On sliding placed in position shown, the excess water is carried off in B, leaving A completely filled. Reservoir C is filled with a salt solution of suitable concentration. The whole system is then put into a thermostatically controlled chamber to ensure constant temperature. Finally, the diffusion channel A is put in line with reservoir C so that salt in C starts to diffuse into the water. When a suitable amount of salt has entered, the plate is moved back to the original position and conductivity recording begins. Ionic conductivity is measured at two positions in the cell by means of pairs of very small electrodes set in opposite walls at heights $L/6$ and $5L/6$ above the sliding plate. With suitable mathematical analysis, one can find the transient concentration distribution can be expressed by

$$c = c_0 + \sum_{n=1}^{\infty} B_n \exp(-n^2 \pi^2 Dt / L^2) \cos \frac{n\pi y}{L}, \quad (4.9)$$

where c_0 and B_n are constants. Hence the concentration difference between two positions $y = L/6$ and $y = 5L/6$ are

$$c_{L/6} - c_{5L/6} = \sum_{n=1}^{\infty} B_n \exp\left(-n^2 \pi^2 \frac{Dt}{L^2}\right) \left[\cos \frac{n\pi}{6} - \cos \frac{5n\pi}{6} \right]. \quad (4.10)$$

For even value of n , $\cos \frac{5n\pi}{6} = \cos \frac{n\pi}{6}$ and for odd n , and $\cos \frac{5n\pi}{6} = -\cos \frac{n\pi}{6}$ so that all terms for even n vanish since the factor in square bracket is zero; and for odd n the square bracket becomes $2 \cos \frac{n\pi}{6}$ which equals $\sqrt{3}$ for $n = 1$, 0 for $n = 3$, $-\sqrt{3}$ for $n = 5$ and 6, etc. Eq. 4.10 therefore becomes

$$c_{L/6} - c_{5L/6} = B_1' \exp(-\pi^2 \frac{Dt}{L^2}) + B_5' \exp(-25\pi^2 \frac{Dt}{L^2}) + \dots, \quad (4.11)$$

where $B_1' = \sqrt{3}B_1$, etc. Since the first term of this expression exceeds the second term by the factor of $\exp(-24\pi^2 \frac{Dt}{L^2})$, the second term is negligible compared with the first term

even for small diffusion times $\frac{D\pi^2 t}{L^2}$. Thus, Eq. 4.11 can be approximated as

$$c_{L/6} - c_{5L/6} = B_1' \exp(-\pi^2 \frac{Dt}{L^2}). \quad (4.12)$$

If one differentiates the natural logarithm of the left part with respect to time t , we find

$$\frac{d \ln(c_{L/6} - c_{5L/6})}{dt} = -\frac{\pi^2 D}{L^2}. \quad (4.13)$$

In other words, a plot of $\ln(c_{L/6} - c_{5L/6})$ vs. time can be fitted with a straight line, whose slope yields the Fickian diffusion coefficient.

This method is extremely important because it provides a means by which diffusivity accurate to 0.1% can be obtained for electrolytic solutions more dilute than about 0.05 M. However, it requires great care and elaborate control schemes to prevent interference from vibration and thermal convection, owing to the long duration of runs. Furthermore, the conductance method is only valid for very dilute solutions, because the fitting method requires a linear dependence of conductance on molarity.

To extend the restricted-diffusion method to more concentrated solutions, Newman and Chapman proposed a route to examine concentration differences directly.¹⁸ They used Rayleigh interferometry to monitor the concentration relaxation in a glass diffusion cell. In this configuration, they found that measurements did not need to be measured 1/6 of the way from either end of the cell; the precision of Δc was high, permitting experiments to be run for long enough (sometimes days or weeks) that a state could be reached wherein the first term of the series in Eq. 4.9 dominated. However, the optical method added a great deal of complexity to the experimental design.

In 1995, Ma *et al.* adapted the restricted-diffusion method by using chronopotentiometry to track concentration.³² A constant current was applied to generate a non-uniform concentration distribution in a symmetric electrochemical cell with a finite length. It was required that the magnitude of the pulse current be sufficiently small that the concentration

difference between the two electrode surfaces could be modeled by Eq. 4.8. The pulse current was applied for a sufficiently long duration that the concentration profile extended all the way across the cell. The OCP relaxation was then recorded as a function of time after the applied current is shut off. At long times after the pulse terminates, the concentration difference across the cell relaxes exponentially, as can be seen from Eq. 4.9. If one further assumes the transference number and thermodynamic factor are constant throughout the whole cell, the OCP should relax exponentially at long times. Therefore, when one plots $-\ln(\text{OCP})$ vs. time, the slope m at long times should reach a constant value of

$$m = \frac{\pi^2 D}{L^2} \quad (4.14)$$

It has been observed that the potentiometric restricted-diffusion techniques tend to yield higher diffusivity. This is expected because of the inaccuracy that the linear approximation (Eq. 4.8) can induce in data processing.⁷ As the concentration polarization decreases during the relaxation period, the difference between the real concentration difference and the concentration difference obtained from the OCP difference gets smaller, and the linearisation in Eq. 4.8 eventually becomes valid. Thus, one should always be careful to ensure that one processes data after sufficiently long relaxation times.

In addition to the OCP tracking technique proposed by Ma, restricted-diffusion measurements can be performed in a number of ways. NMR-based techniques have been used by several groups to track the concentration relaxation in restricted diffusion region.^{80,82} Farkhondeh *et al.* have proposed a four-electrode electrochemical method to quantify transport properties for concentrated binary electrolytes.⁷⁷ Although each method involves a different technique to monitor concentration relaxation, the underlying theory is generally identical.

4.3.3 Hittorf method

The Hittorf method of transference number measurement, named after Johann Wilhelm Hittorf, was first proposed in 1853.²⁵ The general principle is described below. As Fig. 4.3 suggests, in an apparatus filled with electrolytic solution, the solution is arbitrarily divided into three portions, called respectively the anodic, neutral, and cathodic parts. The cathode and anode react to produce or consume a particular species within the electrolyte. When a current is passed between the cathode and anode, the same species are consumed on one side and produced on the other. Assuming that the cation in the solution reacts, the applied current will induce a concentration profile with higher concentration near the anode and lower concentration near the cathode; if time is kept sufficiently low, the concentration in the neutral chamber will remain unchanged. Let us assume the cation is M^+ , and the corresponding anion is X^- . When a unit of charge is passed through the apparatus, an equivalent of M^+ is produced at the anode; t_+ equivalents of M^+ migrate from anode to cathode, and t_+ equivalents of X^- migrate from cathode to anode. Consequently, the

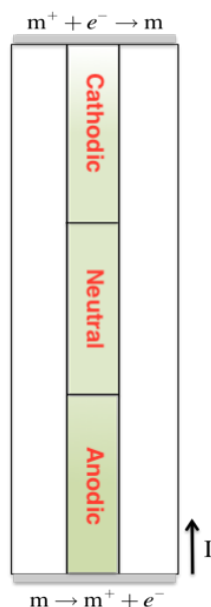


Fig. 4.3: A diagram of electrolyte condition during Hittorf-cell measurements.

number of equivalents of M^+ in the anode chamber is t_- equivalents more than that in the neutral chamber; the transport number is

$$t_- = (1 - t_+) = \frac{n_{\text{anode}} - n_0}{n_{\text{net}}}, \quad (4.15)$$

where n_0 is the initial number of equivalents of cation in anodic portion, n_{anode} is the final number of equivalents of cation in anodic portion, and n_{net} is the number of equivalents of cation produced by the current.

Observe that the calculation described above yields the transference number relative to the mass-average velocity (sometimes called the transport number). To convert the reference velocity to that of the solvent, one can use⁷⁵

$$(1 - t_+) = (1 - t_+^0)(1 - c\bar{V}_e). \quad (4.16)$$

Based on the discussion from chapter one, it should also be clear that the derivation above (Eq. 4.15) does not apply to concentrated solutions because it neglects bulk convection that could be induced by the applied current. To obtain a formula for transference number measurement by the Hittorf method valid for concentrated solutions whose density variation with composition is strong, one should adopt Eq. 1.54. Under electroneutrality, the cation balance is

$$\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{N}_+ \quad (4.17)$$

If one integrates both sides across the volume of the anode or cathode chamber, and applies the divergence theorem, then

$$\frac{dn}{dt} = - \iiint \vec{\nabla} \cdot \vec{N}_+ dV \quad (4.18)$$

where n represents the total number of moles of salt in the chamber. By experimental design, the current pulse is short enough that the concentration boundary layer remains

entirely within the electrode chamber. Thus, at the far boundary there is no concentration gradient. Because the total flux at the electrode is directly proportional to the applied flux through Faradays law, it follows through flux law Eq. 1.54 that

$$\frac{dn}{dt} = \frac{iA}{z_+ v_+ F} - A \left(\frac{it_+^0}{z_+ v_+ F} + c_\infty v^\square \right) \quad (4.19)$$

If the electrode only reacts with cations, the volume-average velocity can be expressed as⁶

$$\bar{v}^\square = \frac{\Delta \bar{V}_{\text{rxn}}^{\text{sol}}}{z_e n_e F} \bar{i} = \frac{\bar{V}_e (1 - t_+^0)}{z_e n_e F} \bar{i}. \quad (4.20)$$

Eq. 4.19 ultimately simplifies to

$$\frac{dn}{dt} = \frac{iA}{F} (1 - t_+^0) (1 - c_\infty \bar{V}_e). \quad (4.21)$$

Assuming the right side of the Eq. 4.21 remains constant during the measurement, the transference number of the of the measured electrolyte can be expressed as

$$t_+^0 = 1 - \frac{\Delta n F}{Q(1 - c_\infty \bar{V}_e)}, \quad (4.22)$$

where Δn is the change of numbers of moles of salt in the anode or cathode chamber and Q is the total amount of charge passed through the whole system (positive if the anode is used, negative if the cathode is used).

One must realize that the transference number measured by this method is actually an integral (average) property, because it cannot be measured without inducing a concentration change at the electrode surface; the properties in Eq. 4.21 are technically measured at this surface concentration. Eq. 4.22 should therefore be restricted to situations where the surface concentration after the applied current is not too different from the bulk. The Hittorf experiment should also be designed so that composition changes do not reach the neutral chamber. In other words, the length of the cathodic or anodic part should be much larger

than the size of the diffusion boundary layer.

4.3.4 Galvanostatic polarization measurements

Galvanostatic polarization is a potentiometric method initially proposed by Ma *et al.* to quantify the transference number of Na^+ in polymer electrolytes.³² Its application was later extended to transference number measurements for liquid lithium-based electrolytes.^{34,74,75} Similar to potentiometric restricted-diffusion measurements, galvanostatic polarization measurements begin with a constant-current pulse, which generates a concentration gradient across a slab of electrolytic solution. Instead of a long pulse period, the pulse is applied for a short time, inducing concentration boundary layers, which can be modelled in a semi-infinite geometry. The difference between concentration profiles in galvanostatic polarization and restricted diffusion regimes is shown in Fig. 4.4.

In the procedure of Ma *et al.*, the OCP relaxation is tracked as a function of a trans-

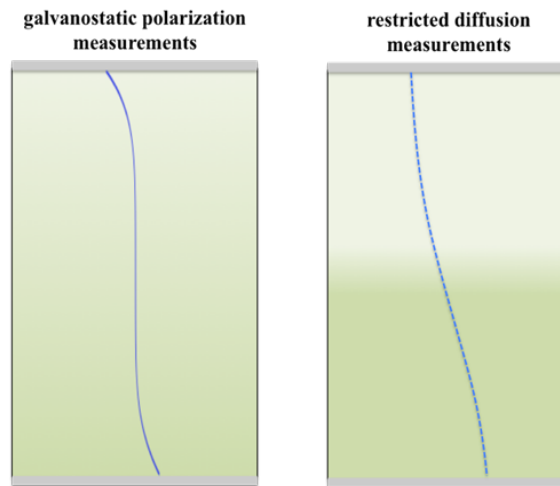


Fig. 4.4: Concentration distributions in galvanostatic polarization measurements and restricted diffusion measurements.

formed time, τ , which has the form^{32,33}

$$\tau = \frac{\sqrt{t_{\text{pulse}}}}{\sqrt{t} + \sqrt{t - t_{\text{pulse}}}}. \quad (4.23)$$

Here t is the experimental time and t_{pulse} is the pulse duration. τ is conveniently restricted between 0 and 1, where 0 corresponds to time infinity and 1 to the initial instant of relaxation right after the pulse current is off. If the concentration difference is small enough, OCP should vary linearly with τ . ΔU vs. τ data can be extrapolated to $\Delta U|_{\tau=1}$, which is the diffusion potential right after the pulse. $\Delta U|_{\tau=1}$ will vary with different pulse current magnitude and pulse duration. Ideally, a plot of $\Delta U|_{\tau=1}$ vs. $I_{\text{pulse}}\sqrt{t_{\text{pulse}}}$ should be linear. The slope m is:

$$m = \frac{4(1 - t_+^0)}{z_+ v_+ F c_\infty \sqrt{\pi D}} \left(\frac{dU}{d \ln c} \right) \bigg|_{c_\infty}. \quad (4.24)$$

As Eq. 4.24 shows, galvanostatic polarization does not produce any of the fundamental transport or thermodynamic properties in isolation. If galvanostatic polarization is used to quantify (say) transference number, then one must have diffusivity and thermodynamic-factor data from other sources. Reliance on such external measurements introduces systematic error into properties obtained from galvanostatic polarization, which is usually not analysed.⁷⁴ One should also be aware that Eq. 4.24 is only valid when D , t_+^0 , and χ are constant with composition; and when the OCP satisfies Eq. 4.8. Many groups have observed curvature in OCP relaxation when τ approaches to 1. The common solution is to linearly extrapolate from a region where the OCP relaxation is relatively linear back to $\tau = 1$.^{33,74} It has been discussed that curvature in the relaxation primarily owes to the failure of approximation (Eq. 4.8), and also to excluded-volume effects. Liu and Monroe showed that extrapolation can result in artificially large m values, producing low or even negative transference numbers. The pulse current must be low to assure the concentration profile is small so that Eq. 4.8 is valid.

4.4 Experimental

4.4.1 Electrolytes preparation

LiPF₆/PC solutions were prepared in an argon-filled glovebox with extremely low H₂O (0.1ppm) and O₂ (0.1ppm) content. A thermostat controlled the glovebox temperature at 25±0.5 °C in the glovebox. Electrolytic solutions with LiPF₆ molarity from 0.05 to 2.00 M were made by dissolving predetermined amount of LiPF₆ salts (99.99%, anhydrous, Sigma Aldrich) in PC (99.9%, anhydrous, Sigma Aldrich). Mass fraction was used as the concentration measure when the solutions were initially produced. Molarity of each LiPF₆ solution was later calculated after its density measurement. LiPF₆ salts were used as received without any further process. PC solvent was pre-dried by immersing molecular sieves (3 Å, Sigma Aldrich) for at least a week before use. The water content within the PC, measured by Karl Fischer titration (C30 titrator, Mettler Toledo), was less than 10 ppm. All solutions were stored in aluminum bottles, which were vacuum-dried at 100 °C prior to use. All plastic consumables were vacuum dried at 80 °C overnight prior to use.

It has been discussed above that LiPF₆ is extremely sensitive to impurity contamination. To ensure accuracy, all apparatus and containers were cleaned and rinsed with ultrapure water, which was necessary to avoid introducing organic impurities to the materials. Even at high temperatures, air drying left significant water attached to apparatus and containers. Thus it was critical to vacuum dry all containers and consumables used for characterisation, at temperatures as close to the boiling point of water as possible.

Fig. 4.5 shows 1 M LiPF₆/PC solutions contained in two aluminum bottles: one was vacuum-dried under 100 °C for 24 hours, another was air-dried under 100 °C for 24 hours. After a week, there was noticeable change in the exterior appearance. The solution in the vacuum-dried container remained colourless, while the solution in an air-dried container turned brown. The brown colour has been proposed to arise from the hydrolysis of LiPF₆.⁵⁷ Water contents of both sets of solutions were determined with Karl Fischer titration. The



Fig. 4.5: 1 M LiPF_6 solutions: (left) solution that had been stored in a vacuum-dried aluminum bottle; (right) solution stored in an air-dried aluminum bottle.

water content was 23 ppm in the solutions with vacuum-dried containers, and 78 ppm in solutions with air-dried containers.

4.4.2 Density measurements

Densities of LiPF_6/PC solutions at three temperatures (20, 25, and 30 °C) were measured with a high-precision oscillation density meter with integrated temperature control system (DMA4100, Anton Paar) in an argon-filled glovebox. Measured density is accurate up to the fourth digit after the decimal. The density meter was cleaned with isopropanol ($\geq 99.9\%$, HPLC grade, Fisher Chemical) for at least three times and followed by drying in ambient argon between each measurement. For each solution sample, density was measured at least three times and reported as the average value.

4.4.3 Ionic conductivity measurements

Ionic conductivities of solutions were measured by AC conductivity meter within a heating and cooling water bath. The conductivity meter was calibrated with commercial conductivity standard solutions at 25 °C. Temperature calibration was performed with ultra-pure water for three temperatures: 20, 25 and 30 °C. Prior to measurement, the sample was injected into a customized airtight conductivity-measurement cell (Fig. 4.6) within

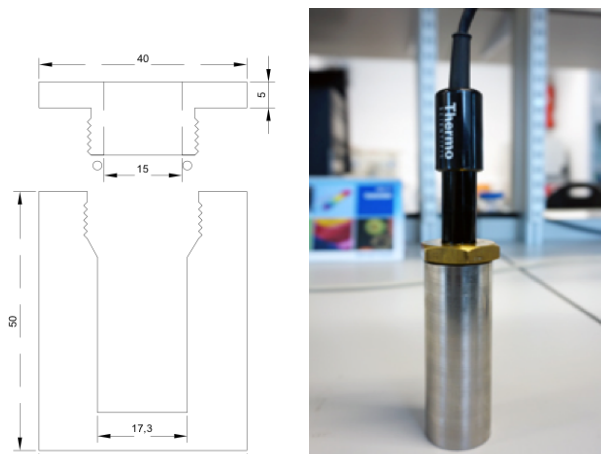


Fig. 4.6: A diagram and a picture of the customized conductivity cell. The cell body is made of stainless steel; the cap is made of brass. The o-ring between the cap and the cell keeps the vial airtight.

an argon-filled glovebox. The cell was later brought outside of the glovebox and kept in a heating/cooling water bath to reach temperature equilibrium. Ionic conductivity was measured three times for each solution and reported as the average value.

4.4.4 Hittorf-cell measurements

Hittorf-cell measurements were conducted with a custom-fabricated Hittorf cell made of PEEK plastic with a total length of 20 cm (see Fig. 4.7). The cell was designed to be long enough so that the concentration in the neutral section would not change after polarization. Two stoppers evenly divide the cell into three parts. The volumes of the cathode chamber ($4.05 \pm 0.05\text{mL}$) and anode chamber ($4.00 \pm 0.05\text{ mL}$) were quantified by volumetric pipette. Density of the test solution was measured prior to the Hittorf-cell measurement to provide a reference. Electrolytes were loaded into the cell with care to fill the chambers completely and avoid introducing bubbles. Two pieces of lithium foil were attached at either end before screwing the endcaps on to close the cell.

A constant current was applied to induce a concentration difference. As soon as the

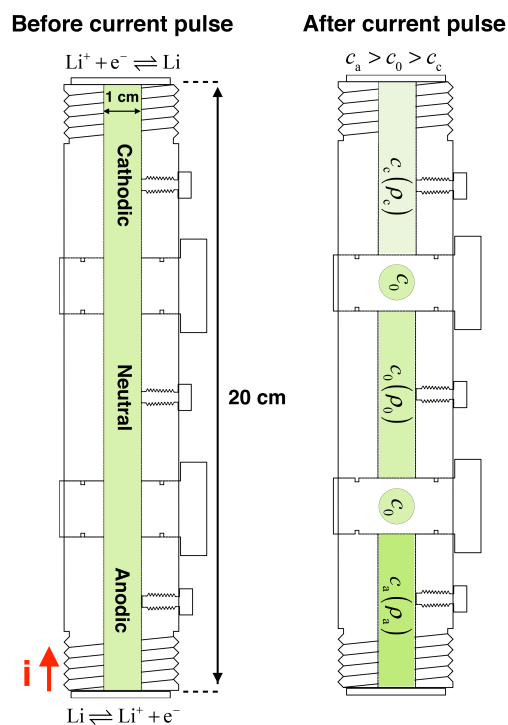


Fig. 4.7: A diagram of the custom Hittorf cell.

applied current was shutt off, the two stopcocks were closed. The solution in each chamber was stirred for 2 hours to guarantee concentration uniformity, after which the density was measured. The LiPF_6 composition was calculated from measured density using a density/composition correlation obtained from the independent measurements described in section 4.4.2. Measurements were performed at six different LiPF_6 concentrations (0.15, 0.20, 0.60, 0.98, 1.41, and 1.97 M). For each concentration, three measurements were applied, and the average transference number was reported. For the three measurements, two shared the same experimental conditions (0.1 mA, 20 hours), while the third measurement used a higher current (0.2 mA, 20 hours).



Fig. 4.8: A picture of our custom concentration cell.

4.4.5 Concentration-cell measurements

Concentration-cell measurements were conducted in a customized glass cell, which is shown in the Fig. 4.8. The volumes of both glass chambers are 15 mL. The amount of electrolyte, on both test side and reference side, was controlled to be 5 mL to ensure the absence of hydraulic pressure, which could drive Darcy flow through the frit. Commercial 1.0 M LiPF_6/PC solution (99.99%, battery grade, Sigma Aldrich) was used as the reference solution; the composition of the reference solution was determined more precisely to be 0.998 M using the density/composition correlation generated from our independent density measurements. Lithium strips were submerged in the solutions and used as electrodes to measure equilibrium OCP between the two sides. OCP was measured with a potentiostat using an integrated OCP determination procedure. The OCP was recorded for at least 2 hours, allowing equilibrium to be reached.

4.4.6 Restricted-diffusion measurements

Measurements of the diffusivity of LiPF_6 in PC were performed in a customized restricted-diffusion cell within the argon-filled glovebox at 25 ± 0.5 °C. The design of the

restricted-diffusion cell is schematized Fig. 4.9: a customized PEEK spacer (ID: 5mm, OD: 12.7mm, L: 5mm) was fabricated and placed in a commercial Swagelok cell. The inner space of the spacer was completely filled with glass fibre (FisherBrand, porosity: 0.85) soaked with electrolyte. Two trimmed pieces of lithium ribbon (99.9%, 0.75 mm thick $\times$ 19 mm wide, Alfa Aesar) were attached at the two ends of the spacer to serve as reference electrodes reversible to lithium cations.

We have observed that restricted-diffusion measurements can yield inconsistent results due to natural convection and forced convection introduced by external vibrations. To eliminate these effects, porous separators are often introduced to house the electrolytic solution. When porous media such as glass fiber filters are introduced, the salt material balance should be converted to

$$\varepsilon \frac{\partial (c_T y)}{\partial t} = -\vec{\nabla} \cdot \left(-D_{\text{eff}} \vec{\nabla} c_T^2 y + \frac{t_+^0 i}{F z_+ v_+} + c_T y \vec{v} \right), \quad (4.25)$$

where ε is the porosity of the glass fibre filter and D_{eff} represents an effective diffusivity within the porous medium. Correspondingly, the slope m should be corrected to the form

$$m = \frac{D_{\text{eff}} \pi^2}{L^2 \varepsilon}. \quad (4.26)$$

According to the Bruggeman correlation of diffusion coefficients in porous media, D_{eff} should relate to the Fickian diffusivity in bulk liquid *via*⁷³

$$D_{\text{eff}} = D \beta. \quad (4.27)$$

Here β is the ratio between effective diffusion coefficient and real Fickian diffusion coefficient. Thus it is essential to quantify the ratio constant of the porous medium to calculate Fickian diffusivity.

When incorporated into concentrated-solution transport theory, Bruggeman correc-

tions to Stefan–Maxwell diffusivities are consistent with Eq. 4.27; they also suggest that a similar form can be used to describe effective ionic conductivity κ_{eff} :

$$\kappa_{\text{eff}} = \kappa\beta. \quad (4.28)$$

κ_{eff} , can be calculated from the bulk resistance, Ω_{bulk} , which is readily measured by electrochemical impedance spectroscopy (EIS) in the high-frequency limit. Since ionic conductivity of the bulk liquid electrolyte can be measured readily by the techniques described in previous chapters, one can use the effective conductivity established by EIS of the restricted-diffusion cell and the bulk-liquid conductivity from AC conductometry together to establish the value of the ratio β , allowing D to be computed from measurements *via* Eq. 4.27.

EIS was applied to determine the bulk resistance of the cell before the restricted-diffusion measurements were performed. The measured bulk resistance was then used to calculate the effective ionic conductivity, κ_{eff} , which was used to establish porosity *via* Eq. 4.28. To conduct the restricted-diffusion measurement, a constant current was passed for 20 h to generate a concentration profile between the two electrodes. This pulse period was determined according to the boundary-layer-thickness calculation procedure proposed by Liu and Monroe.⁷ The OCP was then tracked with respect to time after the current shut off. According to the analysis laid out above, this OCP was expected to relax exponentially; the slope of $-\ln(\text{OCP})$ vs. time was used to calculate the effective Fickian diffusivity *via* Eqs. 4.26 and 4.27, using the porosity from manufacture data.

4.4.7 Galvanostatic polarization measurements

Galvanostatic polarization was performed using a commercial airtight test cell with a customized PEEK spacer. The cell was assembled and stored in the glovebox with temperature controlled at 25 ± 0.5 °C. Similar to the restricted-diffusion cell, electrolytes filled the PEEK spacer, and the cell was sealed by lithium foils at either end. The critical theoretical

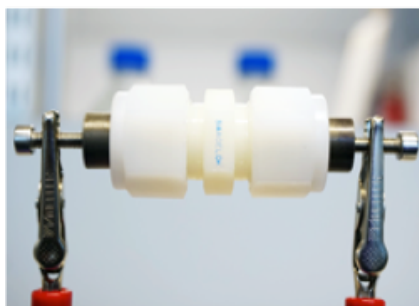
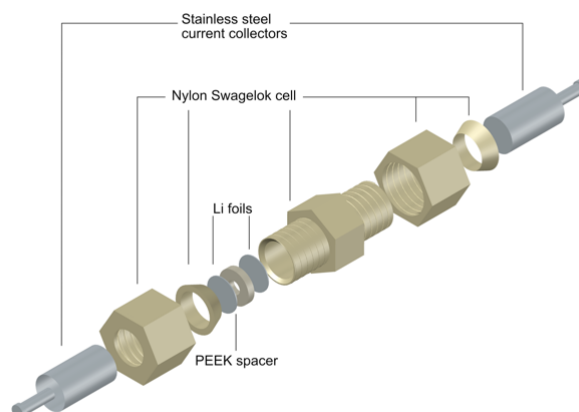


Fig. 4.9: A diagram and a picture of the customized cell used in the restricted-diffusion measurements.

assumption in galvanostatic polarization measurement is that the concentration profile established by constant current should abide with a semi-infinite boundary condition, with no concentration variation in the neutral chamber. Therefore, instead of a long pulse, a short pulse time (<100 s) was applied.

4.5 Results and discussions

4.5.1 Density of LiPF_6/PC solutions

Density was measured with unit of g/L. Mass fraction was used as the measure of concentration to maximize the accuracy during composition determination. Mass fraction

is independent of temperature, which eliminates the error arising from temperature fluctuation. Meanwhile, mass measurements with a high-precision analytical balance are much more precise than volume measurements gathered with traditional apparatus such as a volumetric flask or graduated cylinder. Once density measurements were complete, molarity with unit of mol/L was calculated by

$$c (\text{mol/L}) = \frac{w\rho}{M_{\text{LiPF}_6}}, \quad (4.29)$$

where w represent mass fraction and is the molar mass of LiPF_6 . According to the Onsager–Fuoss theory, the correlation between density and molarity under isothermal, isobaric conditions can be expressed by Eq. 1.61, as reemphasized here,

$$\rho = \rho_0 + \rho_1 c + \rho_2 c^{3/2}. \quad (4.30)$$

The results of density measurements are summarized in Table 4.1 and plotted in Fig. 4.10. Density data was fitted with respect to molarity by Eq. 4.30, *via* the method of least squares, yielding the density-molarity correlations

$$\rho = 1205.0 + 84.67c - 2.753c^{3/2} \quad \text{at } 20^\circ\text{C}, \quad (4.31)$$

$$\rho = 1199.7 + 85.06c - 2.814c^{3/2} \quad \text{at } 25^\circ\text{C}, \quad (4.32)$$

$$\rho = 1194.4 + 85.46c - 2.877c^{3/2} \quad \text{at } 30^\circ\text{C}. \quad (4.33)$$

During the least squares fitting, the intercept was forced to the density of pure PC at each temperature, in line with the requirement that the density of a solution should achieve the pure solvent density in the limit that concentration goes to zero. (Many experimental measurements of partial molar volumes have not taken this constraint into account.^{75, 83})

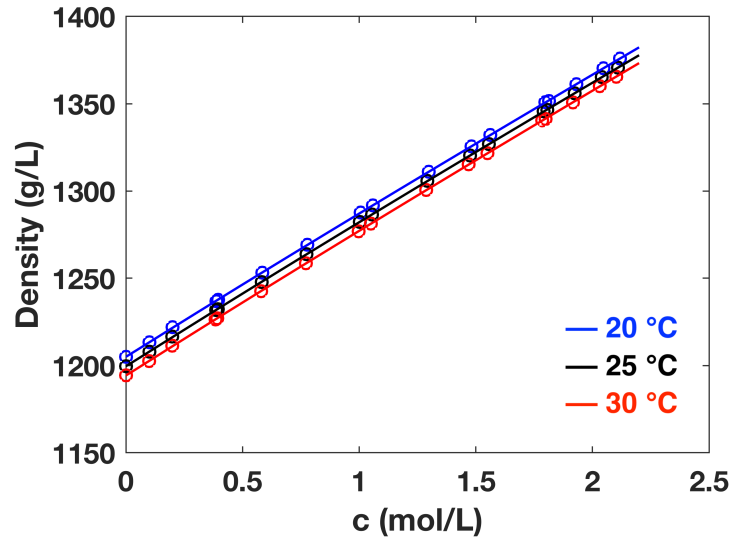


Fig. 4.10: Measured density of LiPF_6 in PC and fitted Eq.4.30 at 20 (blue), 25 (black), and 30 (red) °C.

Table 4.1: Summary of density measurements results for LiPF_6/PC solutions at 20 °C, 25 °C, and 30 °C

20 ° C			25 ° C			30 ° C		
c (mol/L)	ω	$\rho \pm 0.1$ (g/L)	c (mol/L)	ω	$\rho \pm 0.1$ (g/L)	c (mol/L)	ω	$\rho \pm 0.1$ (g/L)
0.0000	0.0000	1205.0	0.0000	0.0000	1199.7	0.0000	0.0000	1194.4
0.1009	0.0126	1213.3	0.1005	0.0126	1207.9	0.1000	0.0126	1202.6
0.1999	0.0249	1222.0	0.1990	0.0249	1216.6	0.1982	0.0249	1211.3
0.3882	0.0477	1236.9	0.3865	0.0477	1231.7	0.3849	0.0477	1226.4
0.3952	0.0485	1237.7	0.3935	0.0485	1232.3	0.3918	0.0485	1227.0
0.5849	0.0709	1253.2	0.5824	0.0709	1247.8	0.5799	0.0709	1242.5
0.7777	0.0931	1269.2	0.7743	0.0931	1263.8	0.7711	0.0931	1258.5
1.0064	0.1186	1287.6	1.0021	0.1186	1282.2	0.9972	0.1186	1276.9
1.0589	0.1245	1291.8	1.0546	0.1245	1286.6	1.0503	0.1245	1281.3
1.2978	0.1504	1311.0	1.2926	0.1504	1305.8	1.2875	0.1504	1300.6
1.4813	0.1698	1325.6	1.4755	0.1698	1320.4	1.4697	0.1698	1315.2
1.5624	0.1782	1332.1	1.5563	0.1782	1326.9	1.5502	0.1782	1321.7
1.7981	0.2022	1350.9	1.7912	0.2022	1345.7	1.7842	0.2022	1340.5
1.8135	0.2038	1351.6	1.8066	0.2038	1346.5	1.7995	0.2038	1341.2
1.9314	0.2155	1361.2	1.9240	0.2155	1356.0	1.9167	0.2155	1350.8
2.0472	0.2269	1370.3	2.0396	0.2269	1365.2	2.0318	0.2269	1360.0
2.1180	0.2338	1375.9	2.1099	0.2338	1370.7	2.1019	0.2338	1365.5

Table 4.2: Summary of partial molar volume values for LiPF₆/PC solutions

20 ° C			25 ° C			30 ° C		
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)
0.0000	N/A	84.7	0.0000	NA	85.1	0.0000	N/A	85.5
0.1009	56.9 ± 0.7	84.7	0.1004	56.8 ± 0.6	85.1	0.1000	56.8 ± 0.5	85.5
0.1999	57.3 ± 0.8	84.7	0.1990	57.3 ± 0.6	85.1	0.1982	57.2 ± 0.6	85.4
0.3881	57.9 ± 0.8	84.7	0.3865	57.9 ± 0.7	85.1	0.3848	57.9 ± 0.6	85.5
0.3952	57.9 ± 0.9	84.7	0.3935	57.9 ± 0.7	85.1	0.3918	57.9 ± 0.7	85.5
0.5849	58.4 ± 0.9	84.7	0.5824	58.4 ± 0.7	85.1	0.5799	58.4 ± 0.7	85.4
0.7776	58.8 ± 1.0	84.6	0.7743	58.8 ± 0.8	85.0	0.7711	58.7 ± 0.7	85.4
1.0055	59.2 ± 1.0	84.6	1.0013	59.2 ± 0.9	85.0	0.9972	59.2 ± 0.8	85.4
1.0588	59.2 ± 1.0	84.6	1.0545	59.3 ± 0.9	85.0	1.0501	59.3 ± 0.9	85.4
1.2977	59.6 ± 1.1	84.6	1.2924	59.6 ± 0.9	84.9	1.2872	59.6 ± 0.9	85.3
1.4812	59.8 ± 1.1	84.5	1.4753	59.9 ± 1.0	84.9	1.4694	59.9 ± 0.9	85.3
1.5623	59.9 ± 1.1	84.5	1.5561	60.0 ± 1.0	84.9	1.5499	60.0 ± 1.0	85.3
1.798	60.2 ± 1.1	84.5	1.7909	60.2 ± 1.0	84.8	1.7838	60.3 ± 1.0	85.2
1.8133	60.3 ± 1.1	84.5	1.8062	60.3 ± 1.0	84.9	1.7991	60.3 ± 1.0	85.2
1.9313	60.4 ± 1.1	84.5	1.9238	60.4 ± 1.0	84.8	1.9162	60.4 ± 1.0	85.2
2.0470	60.5 ± 1.1	84.4	2.0391	60.5 ± 1.1	84.8	2.0312	60.6 ± 1.0	85.2
2.1178	60.6 ± 1.1	84.4	2.1096	60.6 ± 1.1	84.8	2.1015	60.6 ± 1.1	85.2

For the expressions above, each parameter shows significant temperature variation, but the variation is linear in all cases. The linear temperature variation was used to establish density/composition correlations in situations where temperature was not as precisely controlled as the densitometry measurements.

The density/molarity correlation was further used to calculate partial molar volumes of solute and solvent using Eq. 1.59 and Eq. 1.60. The partial molar volumes are summarized in Table 4.2 and plotted in Fig. 4.11.

The partial molar volume of LiPF₆ increases by about 4 mL/mol (7.1%) from 0.1 M to 2.11 M, while partial molar volume of PC decreases by less than 0.4 mL/mol (0.35%), showing that the solvent molar volume remains relatively constant. The increase of LiPF₆ partial molar volume with concentration suggests that units of solvated LiPF₆ occupy an apparently higher volume fraction in concentrated solutions than they do in dilute solutions, perhaps due to greater interactions between the ions and the PC molecules that solvate

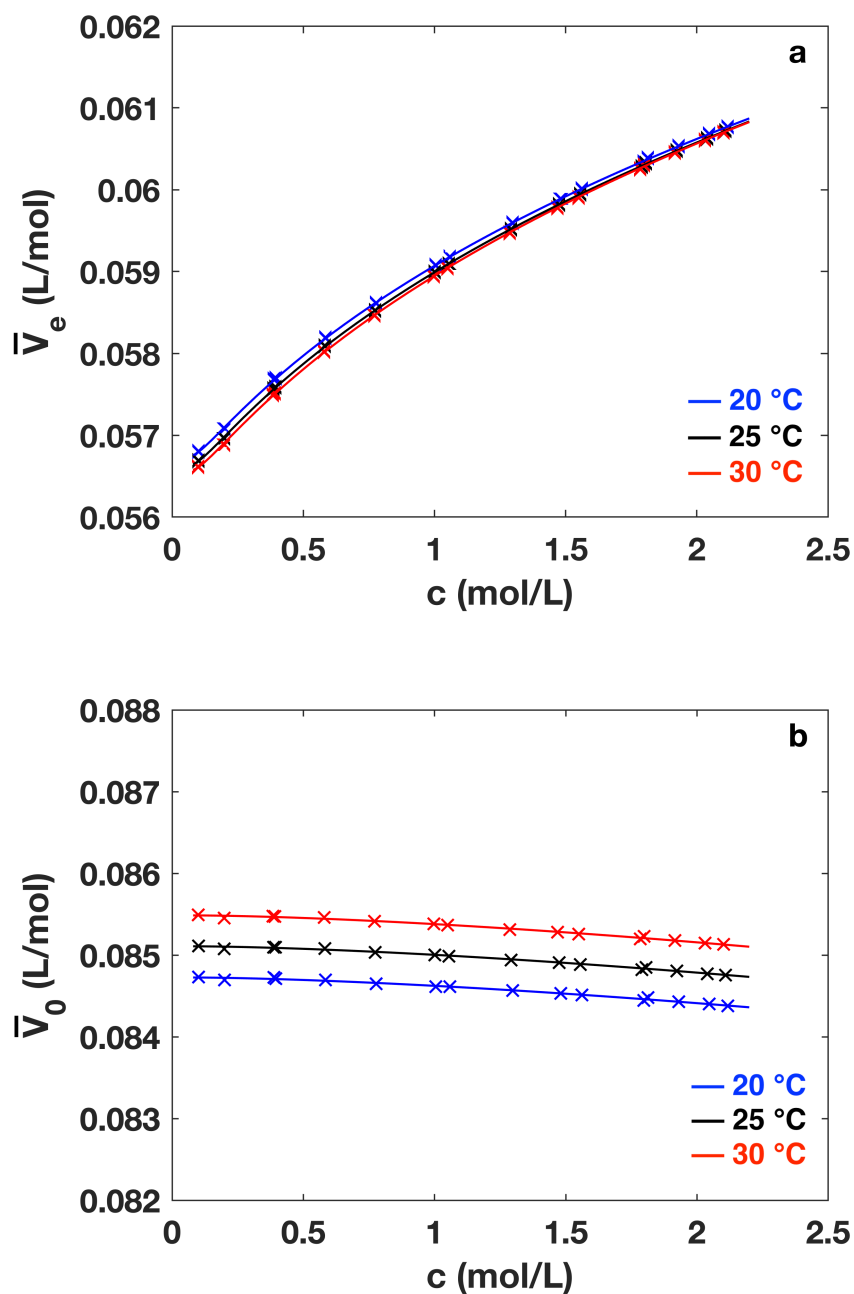


Fig. 4.11: (a) Partial molar volumes of salt for LiPF_6 in PC solutions; (b) partial molar volumes of solvent for LiPF_6 in PC solutions at 20 (blue), 25 (black), and 30 (red) °C.

them.

After preparing solutions with given mass fractions and using the density/composition correlation to back-calculate their composition from the density, it was found that the difference between calculated and experimental composition was negligible (average 0.2% deviation). Therefore, the density was used as the primary variable to establish composition, significantly simplifying the process of molarity determination.

One must note that partial molar volumes are often assumed to be constant,^{34,75,83} an approximation that is fairly well justified by our measurements if the concentration range is sufficiently low. In comparison to a composition-dependent partial molar volume, assuming a constant value gives a maximum of 3.8% error in the density/concentration correlation (using the partial molar volume calculated from a linear density/composition correlation), which may be tolerable for engineering applications.

4.5.2 Results of ionic conductivity measurements

The results of conductivity measurements are summarized in Table 4.3 and depicted in Fig. 4.12. As can be seen in the figure, the maximum conductivity is observed for 0.8 M LiPF₆. The conductivity increases with the salt concentration at low concentration. However, conductivity passes through a maximum as salt concentration increases, because viscosity rises and ions begin to associate, as described in the literature.^{34,74,75} Equivalent conductance is calculated and plotted against the square root of particle fraction in Fig. 4.13. Equivalent conductance can be fitted with a mathematical form derived from Eq. 1.58:

$$\Lambda = \Lambda_0 + \Lambda_1 y^{1/2} + \Lambda_2 y^2. \quad (4.34)$$

The mathematical expressions for equivalent conductance are listed below:

$$\Lambda = 0.2419 - 0.7222y^{1/2} + 1.889y^2 \quad \text{at } 20^\circ\text{C}. \quad (4.35)$$

$$\Lambda = 0.2670 - 0.7842y^{1/2} + 1.927y^2 \quad \text{at } 25^\circ\text{C}. \quad (4.36)$$

$$\Lambda = 0.2920 - 0.8448y^{1/2} + 1.950y^2 \quad \text{at } 30^\circ\text{C}. \quad (4.37)$$

Once again, the parameters in Eq. 4.35 - 4.35 have a relatively linear temperature dependence. The linear dependence was used to determine conductivity in situations when temperature was less accurately controlled.

As revealed in the figure, equivalent conductance changes linearly with square root of molarity as the concentration approaches infinite dilution, consistent with the predictions of dilute-solution theories. Note that the lowest concentration we investigated was 0.1 M, at which the third term on right side of Eq. 4.34 still contribute significantly to the predicted equivalent conductance. Thus the observed data in Fig. 4.13 indicates non-ideality of the solution throughout the range tested.

It has to be noticed that the concentration measure in Eq. 4.34 is particle fraction y . To convert molarity, one of the most commonly used concentration measures, into particle

Table 4.3: Summary of conductivity measurements for LiPF₆/PC solutions

20 ° C			25 ° C			30 ° C		
c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$	c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$	c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$
(mol/L)	(S/dm)	(Sdm ² /mol)	(mol/L)	(S/dm)	(Sdm ² /mol)	(mol/L)	(S/dm)	(Sdm ² /mol)
0.0942	0.0168	0.1785	0.0938	0.0186	0.1983	0.0934	0.0204	0.2184
0.2050	0.0302	0.1471	0.2041	0.0335	0.1640	0.2044	0.0368	0.1799
0.3967	0.0453	0.1141	0.3950	0.0506	0.1281	0.3933	0.0559	0.1421
0.6034	0.0535	0.0887	0.6021	0.0604	0.1002	0.5995	0.0672	0.1121
0.7930	0.0559	0.0705	0.7922	0.0635	0.0802	0.7889	0.0712	0.0902
0.9874	0.0538	0.0545	0.9846	0.0619	0.0629	0.9817	0.0701	0.0714
1.2351	0.0474	0.0383	1.2314	0.0555	0.0450	1.2276	0.0636	0.0518
1.4191	0.0414	0.0291	1.4147	0.0489	0.0346	1.4102	0.0565	0.0401
1.5648	0.0355	0.0227	1.5599	0.0427	0.0273	1.5549	0.0498	0.0320
1.8220	0.0259	0.0142	1.8162	0.0322	0.0177	1.8103	0.0384	0.0212
2.0349	0.0179	0.0088	2.0296	0.0231	0.0114	2.0229	0.0283	0.0140

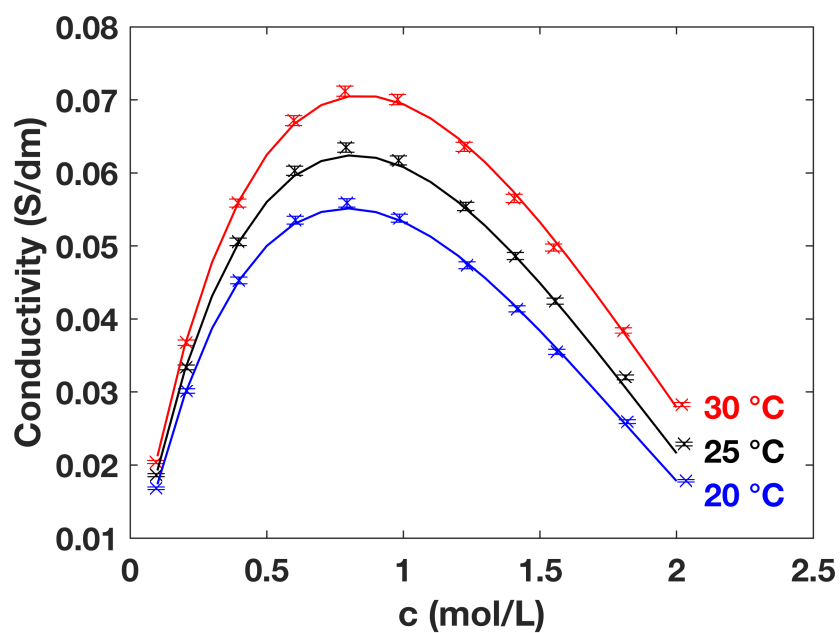


Fig. 4.12: The conductivity of LiPF_6 in PC with 1% intrinsic error (+) and polynomial fittings (–) at 20, 25, and 30 °C.

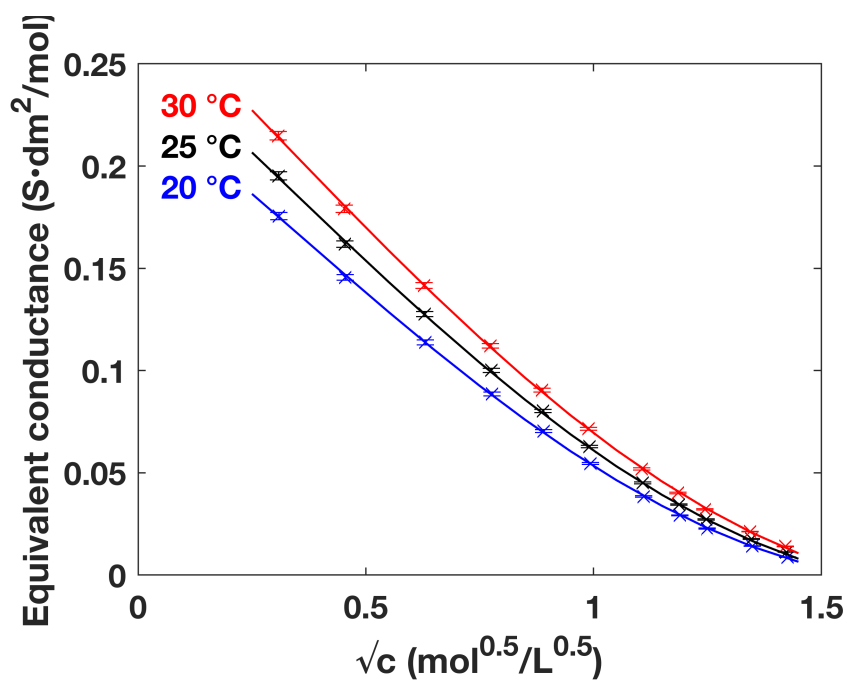


Fig. 4.13: The equivalent conductance of LiPF_6 in PC (x) and fitted Eq. 4.35, 4.36, and 4.37 with 1% intrinsic error (–).

fraction, Eq. 4.38 applies:

$$y = \frac{c}{vc + c_0} = \frac{c}{vc + \left(1 - \frac{cM_{\text{LiPF}_6}}{\rho}\right) \frac{\rho}{M_{\text{PC}}}} = \frac{c}{vc + \frac{\rho}{M_{\text{PC}}} - \frac{cM_{\text{LiPF}_6}}{M_{\text{PC}}}}. \quad (4.38)$$

ρ can be obtained from Eq. 4.30. Since y is a dimensionless concentration measure, which is independent of temperature and pressure, molarities at different temperatures share the same y value.

4.5.3 Results of the Hittorf-cell measurements

The Hittorf method was used to measure the transference number of Li^+ . Fig. 4.14 shows the results of Li^+ transference number with respect to solvent and transference number with respect to mass average velocity (transport number) yielded by the experiments. The error bar (2.5 %) was calculated from the uncertainty of the volume determination of the chambers in Hittorf cell.

The data are presented both as measured points and with a best-fit concentration-dependent function. Measurement error was introduced due to the error in volume determination for the various chambers in the cell. Note that the Li^+ transference number with respect to solvent is generally lower than the transport number, although both decrease with salt content; the difference between the two numbers increases with LiPF_6 concentration. These trends agree with observations from literature.⁷⁵ Second-order polynomial functions were used fit the measurements *via* the method of least squares:

$$t_{\text{Li}^+} = 0.298 - 0.423y + 0.808y^2, \quad (4.39)$$

$$t_{\text{Li}^+}^0 = 0.298 - 0.847y - 1.395y^2. \quad (4.40)$$

Observe that in the limit of infinite dilution, both transference numbers reach the same value, as one would expect, justifying the goodness of fit.

Table 4.4: A comparison of transference number for different Li^+ -conductive electrolytes from literatures and this work

System	Molarity	Transference number	Ref.
LiPF_6 in GBL	0.75 mol/L	0.35 (mass)	69
LiPF_6 in PC/EC/DMC	1.0 mol/L	0.38 (mass)	74
LiPF_6 in EC/EMC	1.0 mol/L	0.25 (solvent)	34
LiPF_6 in EC/DEC	1.0 mol/kg	0.24 (mass)	71
LiPF_6 in EC/DEC	1.0 mol/L	0.16 (solvent)	75
LiPF_6 in EC/DEC	1.0 mol/L	0.22 (solvent)	77
LiPF_6 in PC	1.0 mol/L	0.41 (mass)	72
LiPF_6 in PC	1.0 mol/L	0.15 (mass)	84
LiPF_6 in PC	1.0 mol/L	0.23 (solvent)	this work

Zhao *et al.* measured the transport number of LiPF_6 in PC with both pfg-NMR method and Bruce–Vincent method.⁷² The maximum LiPF_6 concentration they used was 1.5 M. They found that transference number decreased from 0.557 at 0.25 M to 0.370 at 1.5 M. Riley *et al.* also measured Li^+ transport number for LiPF_6 in PC using the Bruce–Vincent method.⁸⁴ Their transference number varied from 0.3 at 0.1 M to 0.1 at 1 M. Zhao’s work shows much higher values of transference numbers than we observed. We notice that their applied voltage for EIS was 50 mV, much higher than the voltage (≤ 10 mV) that Bruce and Vincent suggested.⁸⁵ It has been also suggested that transference number tended to be overestimated with pfg-NMR method.⁷¹ These facts may explain the high Li^+ transference number produced by Zhao and colleagues. Our results agree with Rileys at low concentration and disagree at high concentrations, consistent with the fact that the Bruce–Vincent method is based on dilute-solution theory.^{85, 86}

Other groups have measured the Li^+ transference number for LiPF_6 in other solvents. Their results are summarized in Table 4.4. Li^+ transference numbers from different systems and from different research groups vary dramatically. Compared to other systems, LiPF_6/PC solutions appear to have relatively lower transference number.

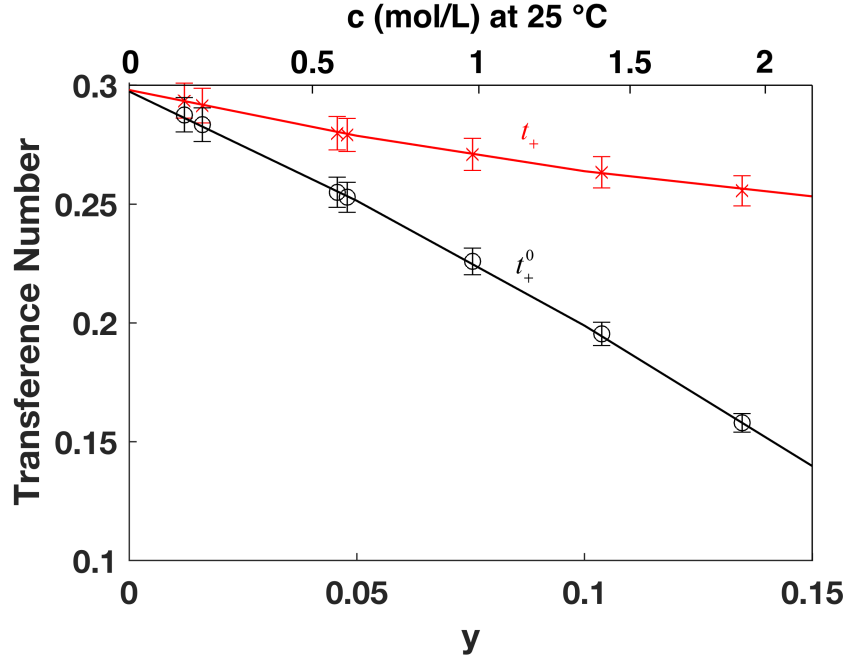


Fig. 4.14: Transport number of LiPF_6 in PC (x) and transference number with respect to solvent of LiPF_6 in PC (o).

4.5.4 Results of concentration-cell measurements

Concentration-cell measurements were conducted to quantify the product $(1 - t_+^0) \chi$. The reference solution was 1.0 M LiPF_6/PC solution. The concentration on the test side varied from 0.05 M to 2.0 M. Density of each solution was measured and Eq. 4.32 was used to back-calculate the particle fraction y . The results of the concentration-cell measurements were plotted in Fig. 4.15. Data points were fitted with an empirical form suggested by Nyman's work:³⁴

$$\begin{aligned} \Delta U &= \int \frac{vRT}{F} \chi (1 - t_+^0) d \ln y \\ &= 0.0582 + 0.171y + 3.736y^2 + 0.0363 \ln y. \end{aligned} \quad (4.41)$$

Differentiating Eq. 4.41 with respect to $\ln y$ and combining with Eq. 4.6, one obtains an empirical expression for the composition dependence of the product of anion transference

number and thermodynamic factor (Fig. 4.16):

$$(1 - t_{\text{Li}^+}^0) \chi = 0.704 + 3.1439y + 145.006y^2. \quad (4.42)$$

The error of the product was estimated from the uncertainties of the each parameter in Eq. 4.41 with 95 % confidence interval (refer Appendix A for detailed uncertainty analysis). Eq. 4.42 suggests that when the salt concentration approaches infinite dilution, $(1 - t_{\text{Li}^+}^0) \chi$ is approximately 0.7045. According to Debye–Hückel theory, thermodynamic factor should approach 1 as the solution approaches infinite dilution.³ In other words, the anion transference number $t_{\text{PF}_6^-}^0 = 1 - t_{\text{Li}^+}^0$ should be around 0.7045 at infinite dilution. This prediction agrees with our results from Hittorf measurements (Eq. 4.40), showing consistency between the Hittorf measurements and concentration-cell measurements.

Along with the results of our transference number measurement, we have calculated the thermodynamic factor based on concentration-cell measurements. Fig. 4.17 plots the

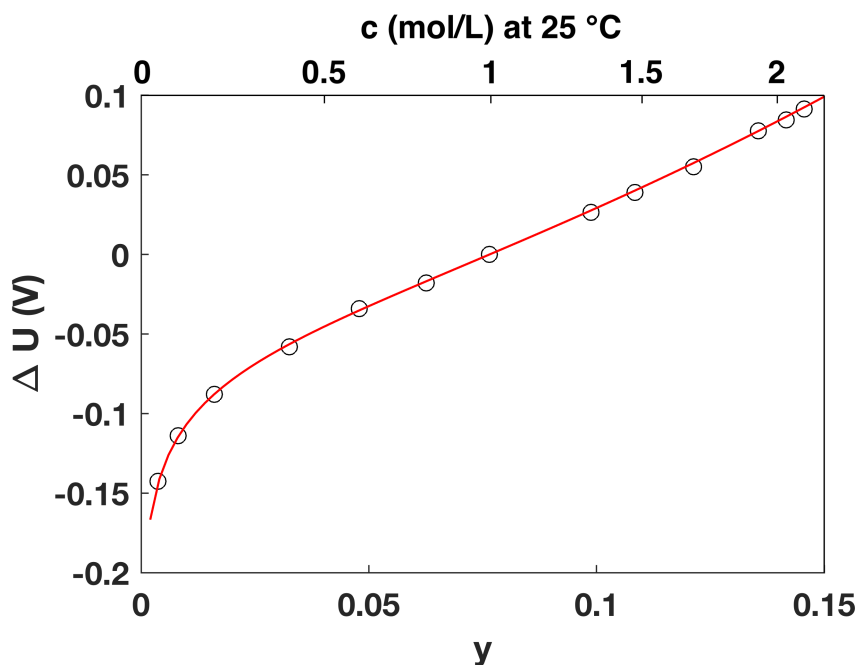


Fig. 4.15: Concentration-cell data at 25 °C with 1 M LiPF₆ in PC as the reference solution.

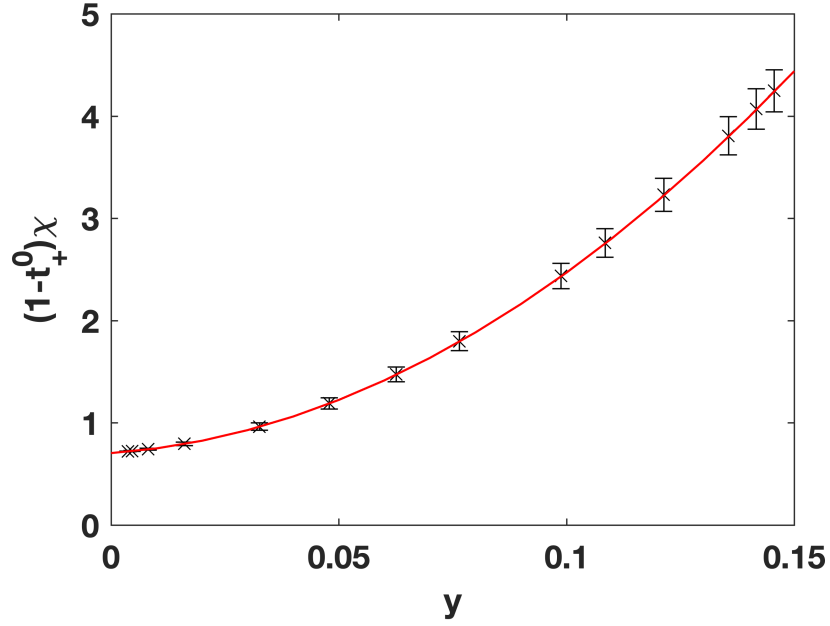


Fig. 4.16: Transference number times thermodynamic factor for LiPF_6 in PC at 25 °C.

thermodynamic factor of LiPF_6 in PC with respect to the particle fraction y . The error bars of the plot are evaluated from the combination of the uncertainties of both measurements of $(1 - t_{\text{Li}^+}^0)$ and $t_{\text{Li}^+}^0\chi$. The thermodynamic factors are fitted with a mathematical form based on Guggenheim’s extension of the Debye–Hückel activity equation,⁷⁸

$$\chi = 1 + \frac{0.863\sqrt{y}}{1 - 1.612\sqrt{y}} - 13.96y + 92.65y^{3/2}. \quad (4.43)$$

The variation of thermodynamic factor with composition is similar to that found in previous studies.⁷⁸ Starting from 1 at infinite dilution, the thermodynamic factor of LiPF_6 in PC steadily increases. Compared with the thermodynamic factors measured by Stewart and Newman,⁷⁸ the present results are consistently lower. Their work assumed a constant transference number of 0.38, much higher than the transference number obtained presently. Incorporation of this value would naturally lead to an overestimate of the thermodynamic

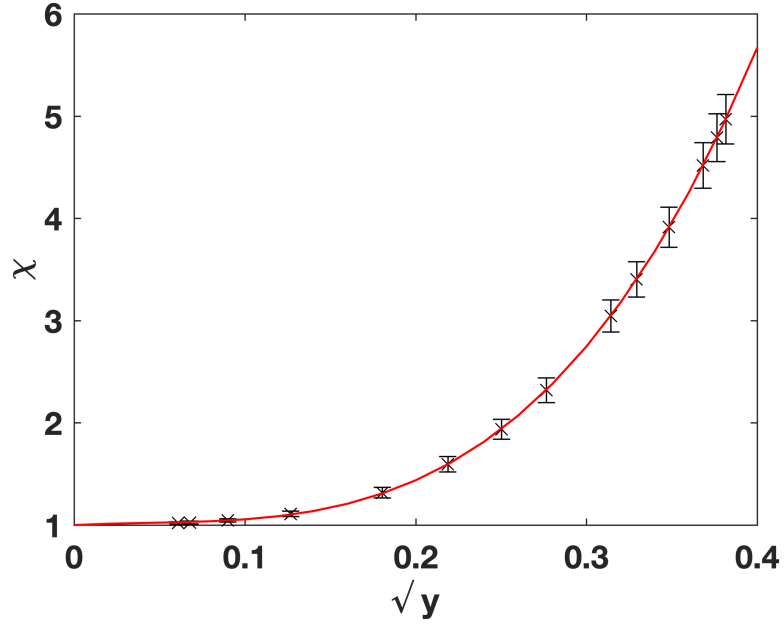


Fig. 4.17: Thermodynamic factors for LiPF_6 in PC derived from the results of concentration-cell measurements and of transference number measurements.

factor. Finally, note that composition in Eqs. 4.42 and 4.43 is measured on a particle fraction basis, and this choice affects the definition of the thermodynamic factor. To use other concentration measures, such as molarity or molality, the corresponding conversions of the thermodynamic factor are required:

$$\chi = 1 + \frac{d \ln \lambda_{+-}}{d \ln y} = c_T \bar{V}_{\text{PC}} \left(1 + \frac{d \ln f_{+-}}{d \ln c} \right) = \frac{c_T}{c_{\text{PC}}} \left(1 + \frac{d \ln \gamma_{+-}}{d \ln m} \right). \quad (4.44)$$

4.5.5 Results of diffusion coefficient measurements

The restricted-diffusion method was used to measure Fickian diffusivity. Initially, the restricted-diffusion measurements were conducted in a cylindrical cell filled with bulk electrolyte between two lithium disk electrodes. These measurements produced inconsistent results, however. The lithium disk electrodes deform as one presses them into the two ends of the spacer, resulting in a variable distance between two electrodes for each mea-

surement. Thus, a different OCP relaxation is generated when the same current signal is used. Furthermore, restricted-diffusion measurements with bulk liquid required meticulous experimental controls to eliminate the inconsistency caused by vibration and by bubbles at solid/liquid interphase. The problems mentioned above cannot be sufficiently mitigated in practice.

We have obtained consistent results by soaking electrolyte into porous glass fiber filters. Glass fibre filters not only prevent leakage and convection, but also fix the distance between two electrodes. With glass fiber filters, effective diffusivity, instead of bulk diffusivity, is measured.

Compared with the restricted-diffusion measurements applied in the literature, the data is much more reproducible, although Eq. 4.26 has to be used to correct for the effects of the porous separator. EIS measurements were applied prior to every restricted-diffusion measurement to evaluate the effective conductivity of the electrolytes in porous medium.

Fig. 4.18 shows a typical result of the restricted-diffusion measurement. The linear region is fit linearly to obtain the slope. The Fickian diffusivity is then calculated with Eq. 4.15, combining the values of ionic conductivity and bulk resistance from previous measurements.

Measured Fickian diffusivities of LiPF_6 in PC solutions at 25 °C are plotted in Fig. 4.19. Diffusivity at each concentration was measured three times to yield an average value. As the plot suggests, Fickian diffusivity of LiPF_6 decreases from $2.48 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.2 M to $4.67 \times 10^{-7} \text{ cm}^2/\text{s}$ at 2 M. A 2nd-order polynomial can fits the data well. The fitting is expressed as

$$D(\text{cm}^2/\text{s}) = (2.61 - 5.33y - 68.13y^2) \times 10^{-6}. \quad (4.45)$$

Thermodynamic diffusion coefficients were calculated by dividing Fickian diffusivity by the thermodynamic factor:

$$D = \mathcal{D}\chi \quad (4.46)$$

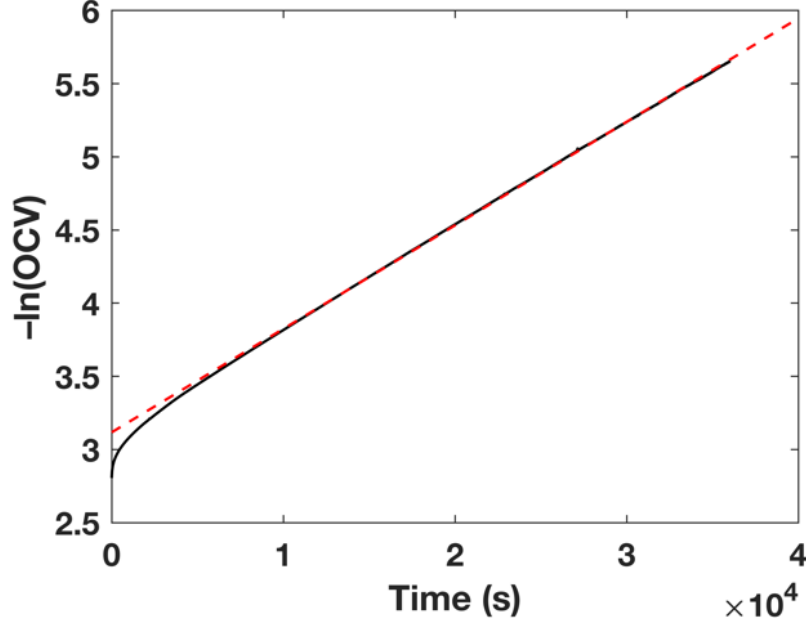


Fig. 4.18: A typical restricted-diffusion measurement. Data at longer times is fitted linearly (red dashed line). The slope of this line is used to calculate effective Fickian diffusivity.

A 2nd-order polynomial function was also used to describe the concentration dependence of the thermodynamic diffusion coefficients, which decrease with LiPF_6 concentration as well and are generally smaller than Fickian diffusion coefficient:

$$\mathcal{D} (\text{cm}^2/\text{s}) = (2.80 - 34.94y + 113.55y^2) \times 10^{-6}. \quad (4.47)$$

In an infinitely dilute solution, both diffusivities share the same value. Nishida *et al.* quantified the Fickian diffusion coefficient of LiPF_6 in PC and found the diffusion coefficient was about $4.0 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C .³⁰ Our result has the same order of magnitude. However, they observed that diffusion coefficient is relatively constant with respect to LiPF_6 concentration while our results show a decreasing trend, which has been observed in previous studies for LiPF_6 in other solvents.^{32,34,75}

4.5.6 Stefan–Maxwell coefficients of LiPF₆ in PC

Stefan–Maxwell coefficients described the microscopic species-species interaction within the electrolytes. *Via* concentrated-solution theory, macroscopic transport properties and thermodynamic data can be used to determine the Stefan–Maxwell coefficients. In a binary system, the relations are

$$\mathcal{D}_{0-} = \frac{z_+}{z_+ - z_-} \frac{\mathcal{D}}{t_{\text{Li}^+}^0}, \quad (4.48)$$

$$\mathcal{D}_{0+} = \frac{-z_-}{z_+ - z_-} \frac{\mathcal{D}}{t_{\text{PF}_6^-}^0}, \quad (4.49)$$

$$\frac{1}{\mathcal{D}_{+-}} = -\frac{z_+ z_- c_T F^2}{RT \kappa} - \frac{z_+ - z_-}{z_+ \nu_+} \frac{c_0 t_{\text{Li}^+}^0 t_{\text{PF}_6^-}^0}{c \mathcal{D}}. \quad (4.50)$$

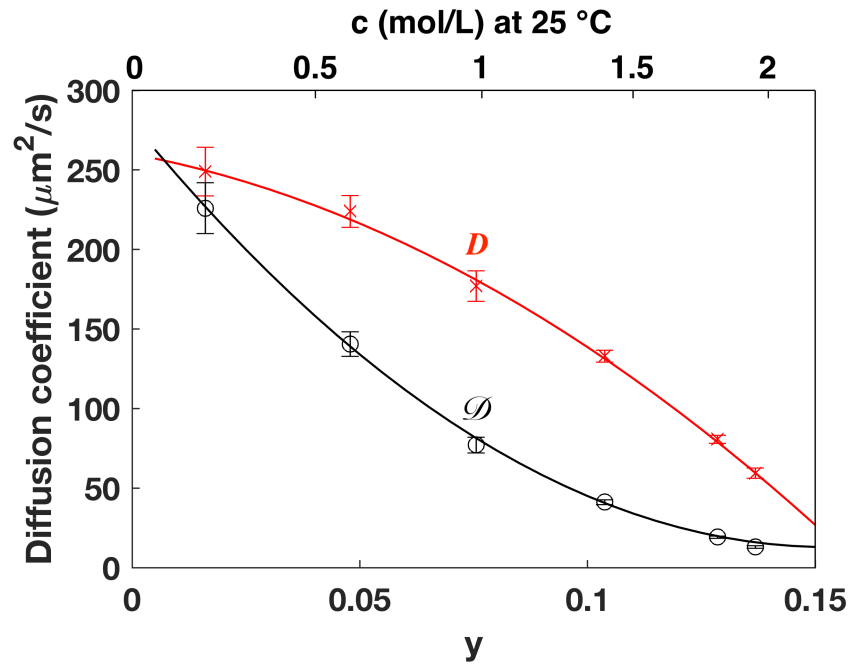


Fig. 4.19: Results of Fickian diffusivity (o) and thermodynamic diffusion coefficient (x) of LiPF₆ in PC.

Fig. 4.20 shows the Stefan–Maxwell coefficients for LiPF_6 in PC, which were calculated from Eq. 4.48, 4.49, and 4.50, using the measured transport properties above. The uncertainties of the $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ are determined from the combination of the uncertainties of each individual properties (refer Appendix A for detailed uncertainty analysis). Both $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ decrease with LiPF_6 concentration, while the difference between $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ increases. The former suggests that ion-solvent drag interactions become stronger as the salt concentration increases, whereas the latter indicates that PF_6^- carries more of the current. Since Li^+ ions are always coordinated with solvent molecules, the Li^+ clusters exhibit stronger interactions with the solvent, thus giving a lower $\mathcal{D}_{0+}$. $\mathcal{D}_{+-}$, on the other hand, has a maximum value around 0.8 M, which agrees with the trend of ionic conductivity variation. This trend has been seen and discussed in other literature.^{34,75}

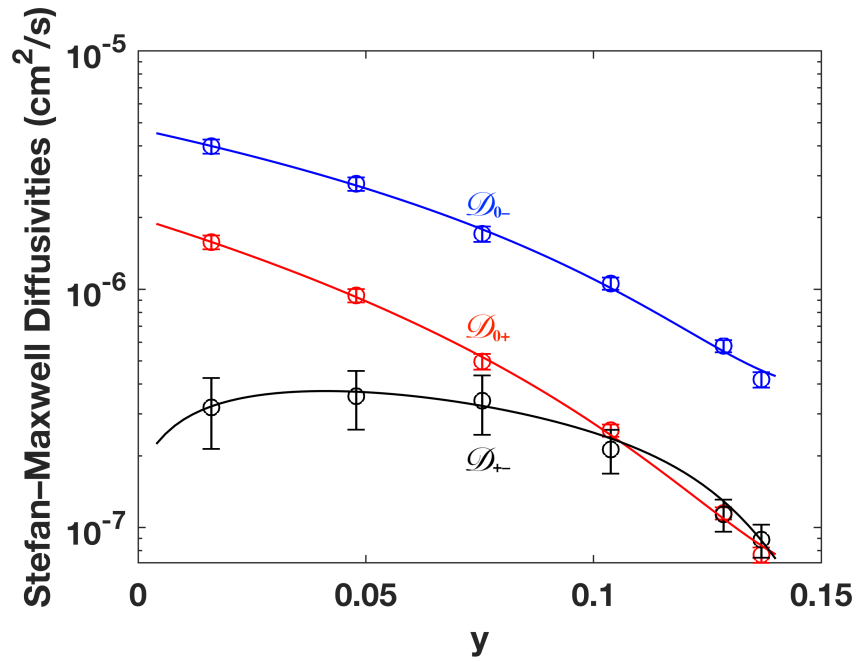


Fig. 4.20: Stefan-Maxwell coefficients of LiPF_6 in PC calculated from Eq.4.48, 4.49, and 4.50.

4.5.7 Simulation validation

To validate the property measurements, we applied the measured values in a mathematical model. We simulated OCP relaxation for several restricted-diffusion measurements with different LiPF_6 concentrations and different current densities, using the property correlations reported above. The results are shown in Fig. 4.21. The major difference between simulation and experiments is most likely to occur at short times after polarization. This could owe to double-layer relaxation, which is not included in the transport model and is typically neglected. At long times, the simulation fits the experimental response well, validating the properties we quantified. Instead of setting all properties constant in the model, they are composition dependent with the composition correlations discussed earlier.

4.5.8 Discussion about galvanostatic polarization measurements

Prior to Hittorf cell measurements, attempts were made to perform galvanostatic polarization measurements to quantify the transference number of LiPF_6 in PC. The experiments were conducted with bulk electrolytes, without porous separator. As discussed earlier, galvanostatic polarization measurements cannot give the value of the transference number value directly. The accuracy of transference numbers extracted from galvanostatic polarization relies heavily on the accuracy of both diffusion coefficient measurements and concentration-cell measurements. We have performed multiple galvanostatic polarization measurements for 1 M LiPF_6 /PC solution. The results are summarized in Fig. 4.22.

As the figure suggests, galvanostatic polarizations are not reproducible. This inconsistency could owe to two factors. First, in the absence of a porous separator, lithium electrodes tend to deform when the cell is assembled. This changes the reaction area, causing variability in the current density from measurement to measurement. Second, convection in the liquid can occur, convoluting the diffusion process during concentration relaxation. These two problems also occur in restricted-diffusion measurements without porous separators. Furthermore, the error introduced by Eq. 4.8 can cause concentration differences

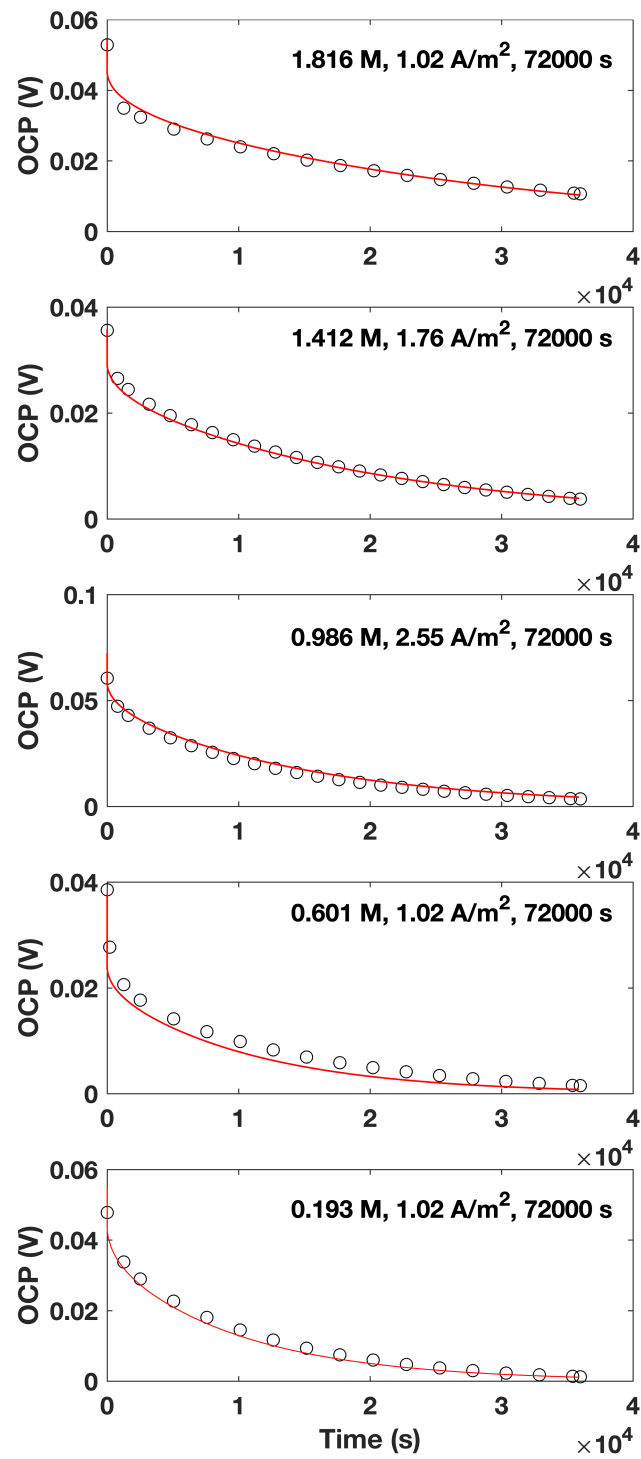


Fig. 4.21: Comparison between experimental results (o) and simulation results (red solid line) of restricted diffusion measurements. Measured transport and thermodynamic properties were used in the numerical simulations.

to be estimated incorrectly, causing smaller (or even negative) transference numbers to be observed. Thus, galvanostatic polarization may not be sufficiently accurate to quantify the transference numbers, a problem which has also been discussed in work from Newman's group.³³

In a series of characterisation works from Lindbergh's group, glass fibre filters were used as the host for electrolytes in galvanostatic polarization. This work combined galvanostatic polarization, concentration-cell measurements, and numerical models to determine the diffusion coefficient, transference number and thermodynamic factors simultaneously.^{34,73,75} We have also performed galvanostatic polarization measurement with a glass fibre separator, for which results are shown in Fig. 4.23. The reproducibility of the measurements was dramatically improved. The use of a porous medium, however, does not eliminate the errors introduced from Eq. 4.8 and from the deconvolution of multiple measurements required to isolate transference. As a result, the author does not think that the galvanostatic polarization technique is sufficiently reliable. Instead, galvanostatic po-

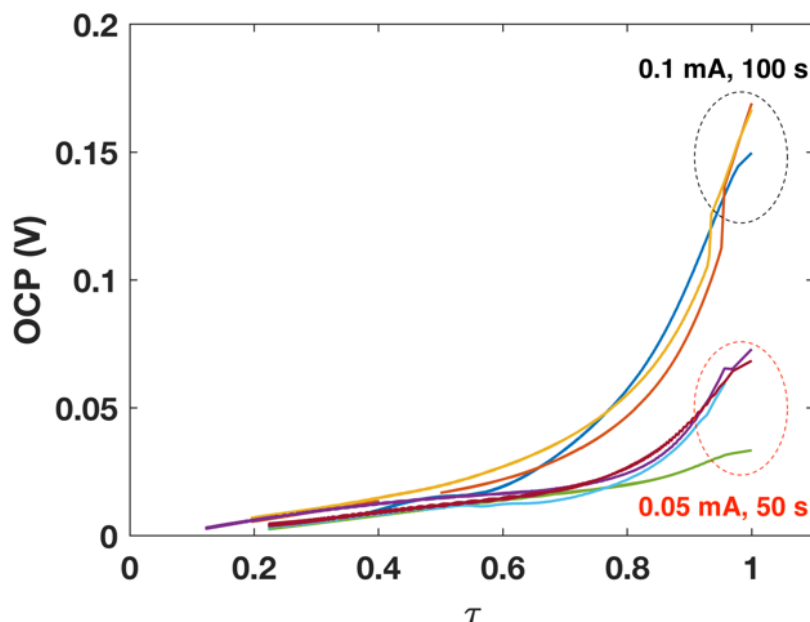


Fig. 4.22: A demonstration of the poor reproducibility in the galvanostatic polarization measurements with bulk LiPF_6/PC solutions.

larization measurements were used as another method to check the accuracy of our other measurements. Galvanostatic polarization measurements have been simulated using the properties quantified from experiments. As Fig. 4.23 shows, the simulation fits the experimental data at longer times ($\tau < 0.7$), again supporting the accuracy of the properties we have obtained.

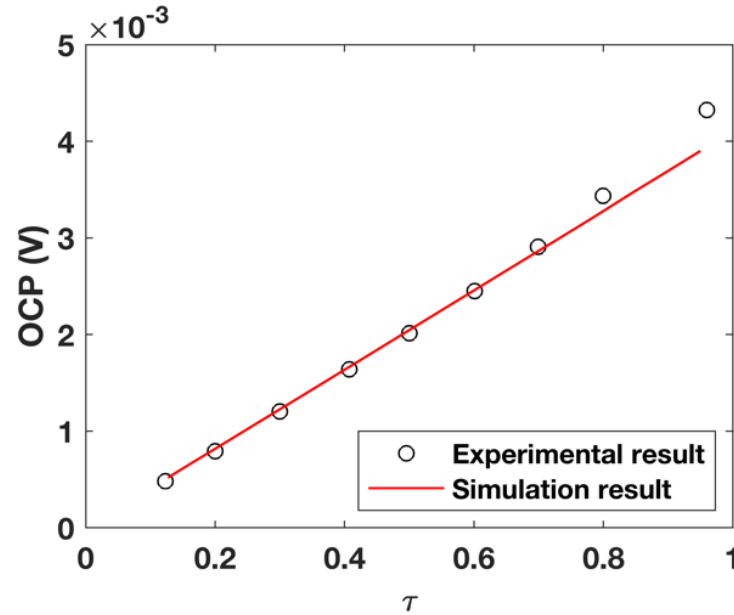


Fig. 4.23: A comparison between experimental result of galvanostatic polarization measurement with glass fiber filter and result of numerical simulation. Pulse current density: 2.55 A/m^2 , pulse time: 75 s.

Chapter 5

Conditioning-free Electrolytes Based on Magnesium-chloride-complex: Synthesis and Characterisation

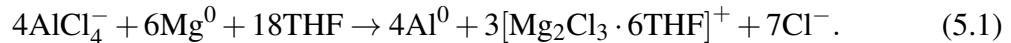
Magnesium (Mg) is one of several candidates that could potentially replace lithium (Li) in future batteries. Compared to Li, Mg is more abundant and more accessible. Mg also provides higher theoretical energy density (3833 mAh/cm^3) than Li (2046 mAh/cm^3) due to its multivalent character. Also dendrite formation, a key problem that leads to failure in Li-ion batteries, has been shown less likely on Mg.⁸⁷ This chapter explores synthetic routes to produce non-aqueous electrolytes that can reversibly plate and strip Mg metal, as well as characterising their properties.

5.1 Introduction of conditioning-free “MaCC” electrolytes

Although it is a promising beyond-Li-ion technology, Mg batteries remain commercially unavailable. Several materials challenges have prevented the development of practical Mg batteries, but the lack of suitable Mg^{2+} -conductive electrolytes is among the most

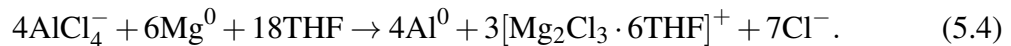
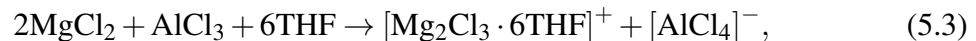
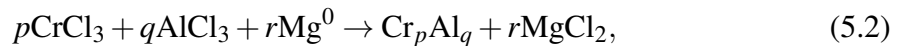
significant barriers.^{88–90} Electrolytes based on aprotic solvents that contain conventional inorganic salts, such as $\text{Mg}(\text{ClO}_4)_2$ or $\text{Mg}(\text{BF}_4)_2$ have been found to be incompatible with Mg anodes. Reduction of these electrolytes forms ion-blocking surface layers on Mg, inhibiting further Mg deposition.^{91–94} As far back as 1927, however, efficient Mg deposition was observed in ethereal solutions of Grignard reagents.⁹⁵ In 1990, Gregory *et al.* had showed that Grignard-based electrolytes were able to avoid the formation of passivation layers, allowing reversible Mg deposition.⁹⁶ In the early 2000s, Aurbach *et al.* reported electrolytes based on magnesium organohaloaluminate salts and designed the first prototype Mg-ion battery with a metallic Mg anode.^{97,98} Mg organohaloaluminates are generated from the reaction between an organomagnesium compound (a Lewis base) and a Lewis acid like AlCl_3 , and support fully reversible Mg stripping and plating. The anodic voltage stability and Coulombic efficiency of Mg stripping and plating depend strongly on the ratio of Lewis acid and Lewis base. This pioneering work inspired multiple groups to study Grignard-based electrolytes.^{99–102} Many groups are also focusing on developing Mg^{2+} -conductive electrolytes based on inorganic Mg salts.^{103–114} In 2014, Aurbach *et al.* and Liu *et al.* reported a Mg electrolyte synthesised by reacting MgCl_2 with AlCl_3 in tetrahydrofuran (THF).^{113,114} This magnesium aluminum chloride complex (MACC) electrolyte shows high coulombic efficiency, low Mg-deposition overpotential, and provides a wide electrochemical stability window, up to 3.1 V vs. Mg/Mg^{2+} . Reversible Mg stripping and plating, however, can only be achieved after MACC is subjected to a unique electrochemical conditioning process, in which the bulk electrolyte is repeatedly cycled across a wide voltage window using a voltage profile similar to a plating/stripping voltammetry experiment. The mechanism underlying MACC conditioning has been discussed in several recent papers.^{115,116} It has been proposed that conditioning involves the irreversible reduction of Al^{3+} from the electrolytic solution and Mg oxidation from the Mg counter electrode,

releasing Mg-dimer complex, $[\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+$, and free Cl^- into the solution:



Free Cl^- , produced from the reaction, is able to facilitate the reversible Mg deposition as well.^{115–117}

In 2016, Ha *et al.* reported a conditioning-free magnesium-chloride-complex electrolyte.¹¹⁸ CrCl_3 was used as a promoter to enhance the dissolution of Mg metal in AlCl_3/THF solutions. The authors hypothesised that a high concentration of Mg dimer was produced by catalytic dissolution of Mg and additional reaction between AlCl_4^- and Mg metal:



It was claimed that the new “MaCC” (with the small ‘a’ representing the much lower Al content) shows performance similar to traditional conditioned MACC, but without the need for electrochemical conditioning. The reaction mechanism within the Mg- CrCl_3 - AlCl_3 -THF electrolyte has not been completely understood, however. It was found that Mg dissolution only occurs when CrCl_3 is present; metallic Mg cannot reduce Al^{3+} from an AlCl_3 -THF solution.

5.2 Experimental for synthesis of MaCC electrolytes with different promoters

5.2.1 Solution preparation

MaCC electrolytes were prepared followed the procedure described in literature.¹¹⁸ Instead of CrCl_3 , we used 0.1000 g CuCl_2 ($\geq 99.995\%$ trace metal basis, anhydrous, Sigma Aldrich) or 0.1363 g ZnCl_2 ($\geq 99.99\%$, anhydrous, Sigma Aldrich) as the promoter. In an argon-filled glovebox (Argon: 99.999%, O_2 level ≤ 0.1 ppm, H_2O level ≤ 0.1 ppm), a predetermined amount of AlCl_3 ($\geq 99.99\%$ trace metal basis, anhydrous, Sigma Aldrich) and CuCl_2 or ZnCl_2 were added to 10 mL tetrahydrofuran ($\geq 99.99\%$, anhydrous, Sigma Aldrich) in a glass vial and stirred continuously at room temperature until all salts were completely dissolved. 0.2000 g of magnesium metal powder ($\geq 99\%$, Sigma Aldrich) was then added into the solutions and stirred for 24 h at room temperature. During the stirring, a black precipitate appeared. The solutions were then filtered with a syringe filter (Nylon membrane, $0.45\ \mu\text{m}$ pore size, FisherBrand) and the filtrate was collected to serve as the electrolytic solutions. AlCl_3 , ZnCl_2 , and CuCl_2 salts were used as received, while THF solvent was further dried with $3\ \text{\AA}$ (Sigma Aldrich) molecular sieves for more than a week prior to use. Karl Fischer titration was used to quantify the water content of the THF precursor, which was less than 10 ppm. All glassware and plastic consumables were carefully cleaned with ultrapure water and vacuum dried at $100\ ^\circ\text{C}$ for overnight prior to use.

5.2.2 Electrochemical measurements

All electrochemical measurements were performed in a three-electrode glass electrochemical cell. Mg ribbons ($\geq 99.5\%$, $3\ \text{mm} \times 0.2\ \text{mm}$, Sigma Aldrich) were used as counter and reference electrodes. A Pt-disk microelectrode ($100\ \mu\text{m}$ diameter) was used as

the working electrode. Electrochemical tests were performed with an Autolab PGSTAT204 potentiostat. Plating/stripping voltammetry was performed with a scan voltage between 1.0 V and 2.0 V and scan rate of 10 mV/s. Coulombic efficiency was calculated as the ratio of oxidation charge and reduction charge,

$$CE\% = \frac{Q_{\text{oxidation}}}{Q_{\text{reduction}}} \times 100. \quad (5.5)$$

Linear sweep voltammetry was used to examine the electrochemical anodic stability window of the solutions. It was performed from 0.0 V to 3.5 V with a scan rate of 100 mV/s.

5.2.3 X-ray diffraction (XRD) analysis

XRD analysis was performed for MaCC electrolytes synthesis with CuCl_2 as the promoter in a Rigaku Smartlab high-resolution (9 kW) X-ray diffractometer. Scan angle was from 10 - 80° . The black precipitates were chemically deposited on two Mg substrates in an argon-filled glovebox. The deposition process was divided into two stages. First stage obtained the black precipitates from the first one hour, then the second stage received the deposition after. Mg substrates were brought out of glovebox to perform XRD analysis directly.

5.3 Characterisation of MaCC electrolytes with different promoters

5.3.1 MaCC electrolytes with CuCl_2 promoter

Ha *et al.* have innovatively increased the Mg ion content in MaCC by direct chemical reaction, rather than a time-consuming electrochemical conditioning process. They proposed that CrCl_3 has a ‘catalytic’ effect on Mg dissolution in non-aqueous AlCl_3 solutions,

and also observed that Mg was almost insoluble without CrCl_3 being present. It is worth investigating whether CrCl_3 , the precipitated Cr, or some other reaction by-product facilitated Mg dissolution. When we replaced CrCl_3 with metallic Cr and made the electrolytic solution, there was no black precipitate produced. As the plating/stripping voltammogram in Fig. 5.1 suggests, the solution barely supports any Mg deposition/dissolution, suggesting that less Mg dissolution occurred when Cr was used instead of CrCl_3 . We can, therefore, conclude that Cr metal itself does not facilitate Mg dissolution. Ha's work called CrCl_3 a catalyst, but it is worth noting that CrCl_3 was observed to reduce irreversibly into a metallic Cr/Al alloy. Since it is consumed during the synthesis, CrCl_3 cannot correctly be qualified as a catalyst; it is not a simple reagent either, however, because much more Mg is dissolved during the MaCC synthesis than CrCl_3 is consumed. It is possible that a Cr/Al alloy formed by reaction with CrCl_3 might perform as a catalyst in the technical sense, but it was not possible to produce this substance in isolation to test its catalytic effect.

To further explore the nature of what we choose to call the promoter effect of CrCl_3

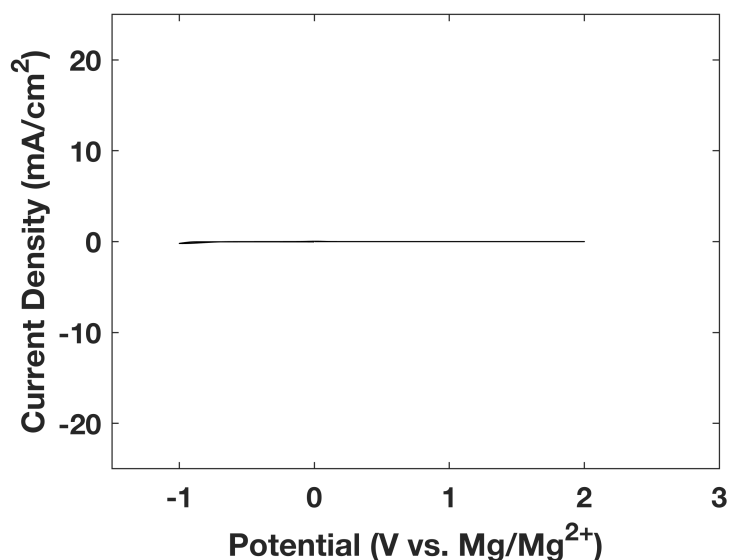


Fig. 5.1: Plating/stripping voltammogram of MaCC electrolyte synthesised with Cr metal as promoter. Pt was used as working electrode, Mg as counter and reference electrodes. Scan rate was 10mV/s.

(rather than a catalytic effect), salts of other metals were investigated to see if they could function as promoters. Literature has shown that copper chromite ($\text{Cu}_2\text{Cr}_2\text{O}_5$) can be used as a catalyst in various chemical systems.¹¹⁹ Therefore, we hypothesised that CuCl_2 might facilitate Mg dissolution.

The desired black precipitate was produced upon replacement of CrCl_3 by CuCl_2 in the MaCC synthesis protocol. Plating/stripping voltammetry was performed to evaluate the reversibility of Mg deposition/dissolution. Fig. 5.2 shows that CuCl_2 does enhance Mg dissolution, and electrolytic solution enabled reversible Mg deposition/dissolution as well. However, the Coulombic efficiency could only reach up to 92%.

X-ray diffraction was employed to examine the composition of the black precipitate. The XRD pattern (Fig. 5.3a) shows signals of metallic Mg, metallic Cu, and an Al/Cu alloy at the first stage of the reaction. Only metallic Mg and metallic Al can be detected from the black precipitate produced from the second stage, suggesting that either the signal of Cu is

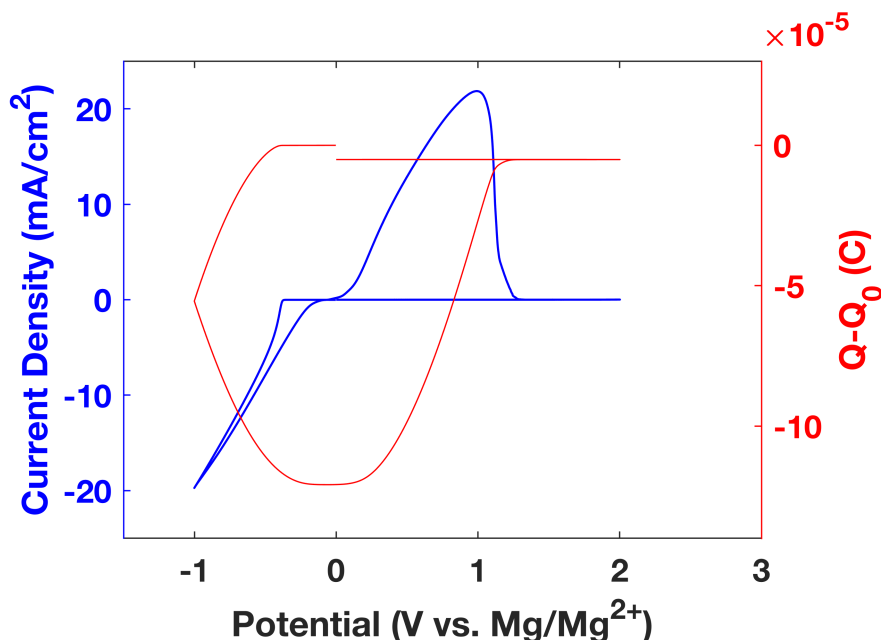


Fig. 5.2: Plating/stripping voltammogram of a MaCC electrolyte synthesised with CuCl_2 as promoter. Pt was used as working electrode, with Mg as counter and reference electrodes. The scan rate was 10 mV/s.

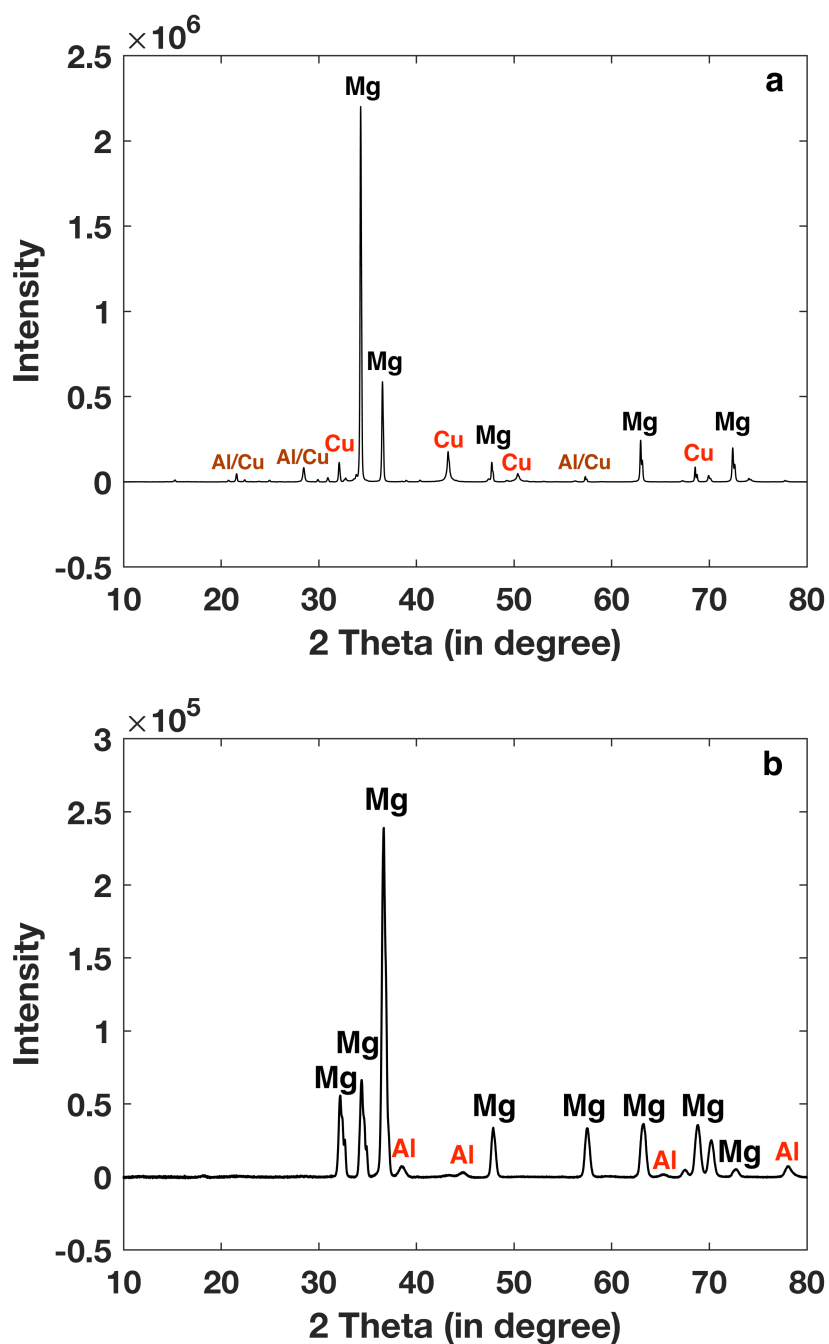
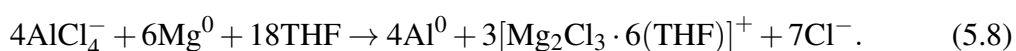
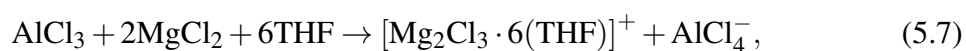


Fig. 5.3: X-ray diffraction diagram of (a) black precipitate formed from the first stage of reaction. (b) black precipitate formed from the second stage of reaction.

too weak to be detected or all Cu^{2+} ions were consumed during the first stage (Fig. 5.3b).

Based on the XRD results it can be concluded that the reduction of Cu^{2+} is sponta-

neous and runs to completion as the electrolyte is formed. Thus it appears that the system follows the same reaction process that occurs in MaCC formed with CrCl_3 as promoter. According to the reaction mechanism (Eqs. 5.2 - 5.4) proposed by Ha *et al.*, these following reactions may explain the synthesis:



5.3.2 MaCC electrolytes with ZnCl_2 promoter

Beside CuCl_2 , it was also found that ZnCl_2 worked as a promoter to synthesise MaCC. Compared with CuCl_2 , ZnCl_2 has better solubility. It was straightforward to dissolve 0.4 M ZnCl_2 in THF. During the electrolyte synthesis, black precipitates were again produced upon the addition of metallic Mg. Fig. 5.4 shows the plating/stripping voltammogram of a “MaCC electrolyte synthesised from 0.2 M AlCl_3 plus 0.1 M ZnCl_2 in THF. The electrolyte shows exceptional performance, with a deposition overpotential around 250 mV, a Coulombic efficiency around 97%, and a stability window up to 3.1 V. Compared with the MaCC synthesis promoted by CuCl_2 as the promoter, this electrolyte shows a much higher reduction and oxidation current density, which likely signifies a much higher Mg carrier content or higher mobility of the carriers. Additionally, the Coulombic efficiency of this electrolyte is also higher. This may suggest that the reduction of Al^{3+} is more complete when ZnCl_2 is used as promoter. Qualitatively speaking, the MaCC electrolytes with ZnCl_2 promoter have properties very similar to the MaCC put forward by Ha *et al.* Although both ZnCl_2 and CuCl_2 can function as promoters, electrolyte synthesised with ZnCl_2 achieves better performance. The specific reason why ZnCl_2 performs better than CuCl_2 as a promoter is still unclear. Elucidating this question requires comprehensive re-

search into every aspect of the synthesis, including the electrolyte components, the nature of black precipitates, and chemical or electrochemical mechanism.

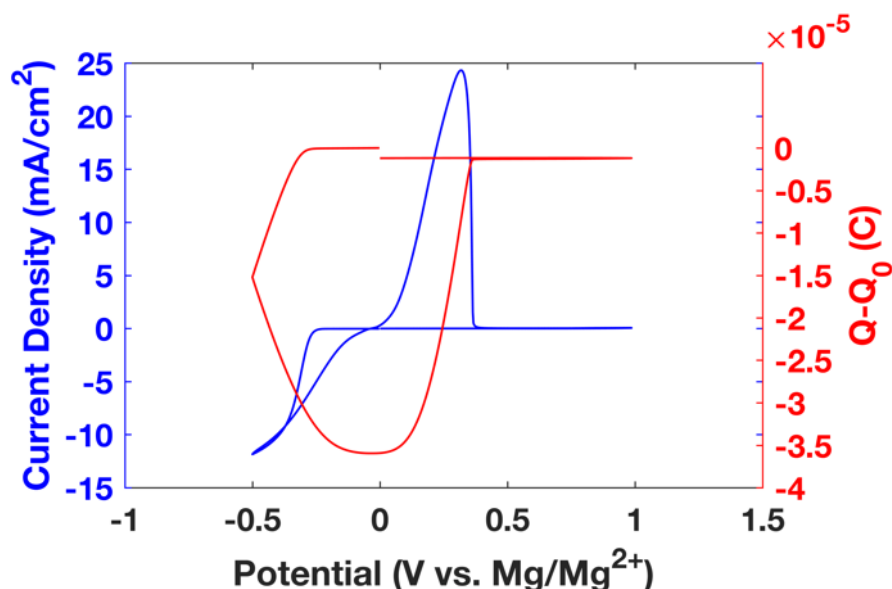
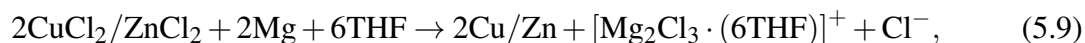


Fig. 5.4: Plating/stripping voltammogram of a MaCC electrolytes synthesised from 0.2 M AlCl_3 and 0.1 M ZnCl_2 with scan rate of 10 mV/s.

5.3.3 Discussion of synthesis mechanism of MaCC electrolytes

Studies of the precipitates produced during the electrolyte synthesis showed that the promoters (CrCl_3 , ZnCl_2 or CuCl_2) were completely reduced by Mg. Apparently, promoters cannot be characterised as catalysts, but the fact remains that their inclusion in the synthesis appears to facilitate subsequent reduction of Al^{3+} . We hypothesise that promoter reduction introduces a component that does act as a catalyst for aluminum reduction. We propose an alternative reaction mechanism to describe the MaCC synthesis process:





What we propose is slightly different from Ha's mechanism. In this mechanism, reduction of Cu^{2+} or Zn^{2+} directly releases positive chloromagnesium ions and free Cl^- anions into the solution. No MgCl_2 is formed. Cl^- combines with AlCl_3 , forming tetrachloroaluminate, AlCl_4^- . AlCl_4^- reacts with metallic Mg, producing $[\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+$ and liberating chloride ions. In this scheme, reaction 5.10 can run to completion, but Mg dissolution continues to be driven because the chloride produced by reaction 5.11 drives reaction 5.10 to the right, a feedback mechanism in which Cl^- acts as a catalyst for chloromagnesium cation formation.

5.4 Conditioning- and promoter-free Mg-chloride-complexed based electrolytes

We have found that both CuCl_2 and ZnCl_2 can be used as the alternative promoters to synthesise MaCC electrolytes. The exact mechanism by which promoters function is still unclear. But the work on exploring alternative promoters provided some insight, and suggested a method by which one could directly synthesise salts of the chloromagnesium cation. Inspection of the redox series shows that Al^{3+} (-1.66 V vs. NHE) has a higher standard reduction potential than Mg^{2+} (-2.37 V vs. NHE).⁴² In an aqueous system, one would expect that metallic Mg would spontaneously displace Al^{3+} from AlCl_3 solutions. It seems that negligible amounts of Mg react in non-aqueous solutions of AlCl_3 , however. One potential explanation is that the activation energy required to trigger the displacement of Al^{3+} with Mg is higher than the driving force provided by the difference between the standard reduction potentials of the metal cations. It is possible that electrochemical conditioning provides energy to overcome the activation barrier, whereas the addition of chemical pro-

motors lowers it. An argument based on reduction potentials is consistent with the redox series, which suggests that Cu^{2+} , Zn^{2+} , and Cr^{3+} should all be spontaneously reduced by Mg in non-aqueous solutions. Cu^{2+} (+0.337 V vs. NHE), Zn^{2+} (−0.763 V vs. NHE), and Cr^{3+} (−0.744 V vs. NHE) have much higher standard reduction potentials than Mg^{2+} does, which may explain why Cu^{2+} , Zn^{2+} , and Cr^{3+} spontaneously reduce during the formation of MaCC. Therefore, we hypothesised that metallic Mg might be able to directly reduce metallic ions from non-aqueous solutions of metal chloride salts if their standard reduction potential was sufficiently high, yielding chloromagnesium-cation salts directly.

5.5 Experimental for synthesis of conditioning-free/promoter-free Mg-chloride-complex-based electrolytes

5.5.1 Synthesis procedure and materials

ZnCl_2 (99.99%, anhydrous), SnCl_2 (99.99%, anhydrous), AlCl_3 (99.99%, anhydrous), MgCl_2 (99.99%, anhydrous), Mg ribbon (99%), DME (99.9%, anhydrous), DMSO (99.9%, anhydrous), 2-methyl-THF (99.95%, anhydrous), triglyme (99.5%, anhydrous), and THF solvent (99.95%, anhydrous) were purchased from Sigma Aldrich. Mg foils (99.95%) were purchased from GalliumSource.

ZnCl_2 , CuCl_2 , SnCl_2 , AlCl_3 , and MgCl_2 salts were vacuum-dried at 150 °C for 24 hours before being transferred into an argon-filled glovebox. Solvents were further dried with activated 3 Å molecular sieves (Sigma Aldrich) under argon for at least a week prior to use. The water content of the solvents was found to be less than 10 ppm by Karl Fischer titration (C30 compact Karl Fischer Coulometer, Mettler Toledo). ZnCl_2 /THF solutions were made by directly adding a predetermined mass of ZnCl_2 salt into the THF solvent. ZnCl_2 /THF solutions were continuously stirred for 2 hours at room temperature until the ZnCl_2 was completely dissolved. An excess amount of Mg powder was then added into

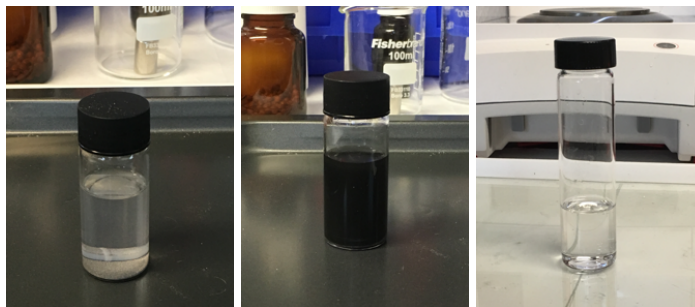


Fig. 5.5: Phase change of the MZCC electrolyte during electrolyte synthesis. Left: ZnCl_2/THF solution right after adding Mg powder; middle: $\text{ZnCl}_2/\text{THF}/\text{Mg}$ solutions after 24 h of stirring; right: resultant electrolyte after double filtration.

the ZnCl_2 solutions, and they were further stirred for 24 h at room temperature. During the stirring, black precipitates were produced (see Fig. 5.5). The solutions were then filtered by a syringe filter (Nylon membrane, $0.45\ \mu\text{m}$ pore size, 25 mm diameter, Fisherbrand). The resulting filtrates were mixed with the residual black precipitates and Mg powder previously left in the glass vials and stirred for another 2 hours at room temperature. Solutions were finally filtered and stored in airtight glass vials for electrochemical tests and characterisation. Similar electrolytes were synthesised from SnCl_2/THF and CuCl_2/THF solutions by following a similar procedure to the above.

All glassware and plastic consumables were vacuum-dried at $100\ ^\circ\text{C}$ for over 8 h before being brought into an argon-filled glovebox, to minimize the effects of residual moisture.

5.5.2 X-ray diffraction (XRD) analysis

XRD patterns were obtained using a 9 kW Rigaku X-ray diffractometer with $\text{Cu K}\alpha$ radiation at $\lambda = 1.5406\ \text{\AA}$. Samples were assembled in an argon-filled glovebox and sealed in an airtight XRD sample holder that prevents oxygen and moisture exposure. Black precipitates were deposited on Mg foil by immersing the foil in ZnCl_2/THF solutions. The foil was later washed with THF solvent and vacuum-dried at room temperature overnight.

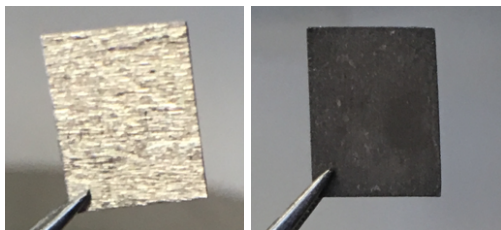


Fig. 5.6: An image of polished Mg foil prior to immersion in the THF solution (left) and foil coated in black precipitate after immersion (right).

prior to XRD measurements (see Fig. 5.6). Mg foils were mechanically polished with a razor blade in the glovebox prior to use.

5.5.3 Raman spectroscopy analysis

Raman spectra were gathered using a Renishaw Raman system with a laser wavelength of 633 nm or 785 nm. Samples were loaded into airtight glass vials in an argon-filled glovebox, after which the vials were brought into the ambient environment for testing.

5.5.4 Inductively coupled plasma mass spectroscopy (ICP-MS)

ICP-MS measurements were conducted by a Perkin Elmer 6100-DRC ICP-MS. The samples were contained in airtight glass vials with sample size of 5 mL. A sample of pure THF solvent was used as the blank reference.

5.5.5 Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis

SEM measurements were carried out with a Hitachi TM3000 benchtop SEM with Bruker EDS. Samples were placed on a stainless sample holder with carbon tape. All samples were prepared in an argon-filled glovebox and stored in airtight glass vials. Samples were only exposed to air right before SEM test to limit the oxidation reaction.

5.5.6 Nuclear magnetic resonance (NMR) analysis

^1H NMR was performed on a Bruker BioSpin AVIIIHD 400 MHz spectrometer in 5 mm screw cap NMR tubes. Electrolytes were evaporated at 40 °C. Dried salts were re-dissolved in CDCl_3 solvent for ^1H NMR tests. ^{35}Cl NMR was performed on a Bruker BioSpin AVIIIHD 500 MHz spectrometer in 5 mm screw cap NMR tubes. Samples were prepared in an argon-filled glovebox and measured without further processing. Aqueous NaCl solutions were used as the references.

5.5.7 Electrochemical tests

All electrochemical experiments were carried out in an argon-filled glovebox with both O_2 and H_2O contents less than 0.1 ppm. Cyclic voltammetry (CV) experiments and linear sweep voltammetry (LSV) experiments were performed with an Autolab PG-STAT302N potentiostat/galvanostat. CV measurements were performed within the scan range between -1.0 V and $+2.0$ V with a scan rate of 10 mV/s. LSV measurements were scanned between 0.0 V and 3.8 V with a scan rate of 10 mV/s. A customized Pt-disk electrode with 100 μm diameter was used as the working-electrode for all electrochemical tests. Prior to each measurement, the Pt electrode was polished with Al_2O_3 sanding paper, then electrochemically cleaned in 0.5 M H_2SO_4 solution, and vacuum dried at 80 °C overnight. Freshly-polished Mg ribbons were used as counter and reference electrodes.

Mg deposition was conducted on a piece of Pt wire (99.95%, 0.5 mm diameters, Alfa Aesar) galvanostatically at 5 mA/cm^2 . The wire was later washed with THF solvent and vacuum-dried at room temperature overnight to prepare it for XRD and SEM-EDS measurements.

The electrolyte conductivity was measured with a Thermo Scientific Orion Star A212 Benchtop meter in a glovebox. The conductivity probe was cleaned with ultrapure water and vacuum-dried at 80 °C overnight prior to use.

5.6 Electrochemical characterisation of the Mg/ZnCl₂/THF electrolytes

We have hypothesised that metal chloride salts whose metallic species have similar or higher reduction potential than Cr/Cr³⁺ might oxidize Mg in non-aqueous solutions, and the resultant solutions could support Mg²⁺ conduction. To test this hypothesis, we employed three salts whose cations have high reduction potentials relative to Mg²⁺: ZnCl₂, CuCl₂ and SnCl₂. ZnCl₂ was studied first because of its low cost, low toxicity, high solubility in THF, and the high reduction potential of Zn/Zn²⁺ (−0.763 V vs. SHE), which is comparable to that of Cr/Cr³⁺.

Black precipitates were produced as soon as Mg metal was introduced into the ZnCl₂/THF solutions, a phenomenon also observed in Ha's MaCC synthesis. The resulting electrolytes, which we describe using the abbreviation "MZCC" to represent their synthesis from ZnCl₂/THF solutions, were electrochemically characterised without any further purification. The plating/stripping voltammogram of 0.3 M MZCC (i.e., an electrolyte synthesised by addition of Mg powder to a 0.3 M ZnCl₂/THF solution), presented in Fig. 5.7a, shows that the electrolyte is able to support reversible plating and stripping reaction with a Coulombic efficiency up to 100% and a deposition overpotential less than 150 mV on the first cycle. The stability window of the electrolyte, based on the LSV measurements (Fig. 5.7b), ranges up to 3.2 V vs. Mg/Mg²⁺. The electrolytes stability with respect to electrochemical cycling and calendar age was also investigated.

For fresh electrolyte, electrochemical cycling did not affect the performance within the 50 plating/stripping cycles tested (see Fig. 5.8). Coulombic efficiencies stayed between 99% and 100% across all cycles. Deposition overpotentials remained below 150 mV. The total amount of charge passed increased with cycle number, consistent with observations in literature.¹¹⁷ Samples that are left to rest, however, undergo substantial changes in performance. After being rested for a week, the MZCC exhibits higher deposition overpotential,

a diminished stripping peak, and a lower Coulombic efficiency (see Fig. 5.9). A similar aging problem was discussed in Gewirth's work on MACC conditioning: after one week,

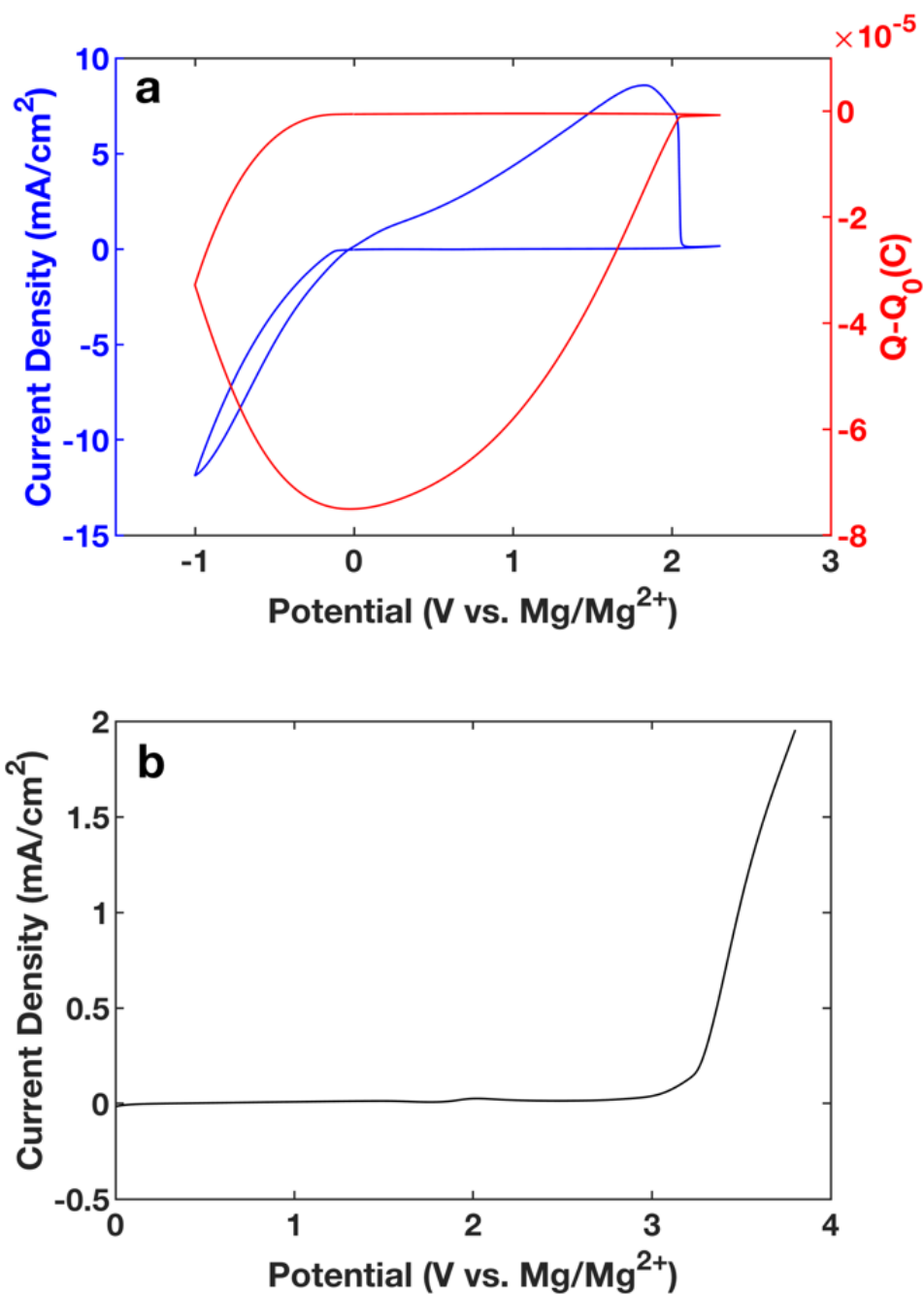


Fig. 5.7: (a) Plating/stripping voltammogram of a 0.3 M MZCC electrolyte with scan rate of 10 mV/s. (b) Linear sweep voltammogram of a 0.3 M MZCC electrolyte with scan rate of 10 mV/s.

the Coulombic efficiency of a conditioned MACC electrolyte diminishes by 35%, and overpotential increases from 250 mV to 600 mV.¹¹⁷ In comparison to MACC, the performance decay of MZCC is less. The performance of aged MACC electrolytes can be recovered by electrochemical conditioning, a strategy which was not tested for MZCC.

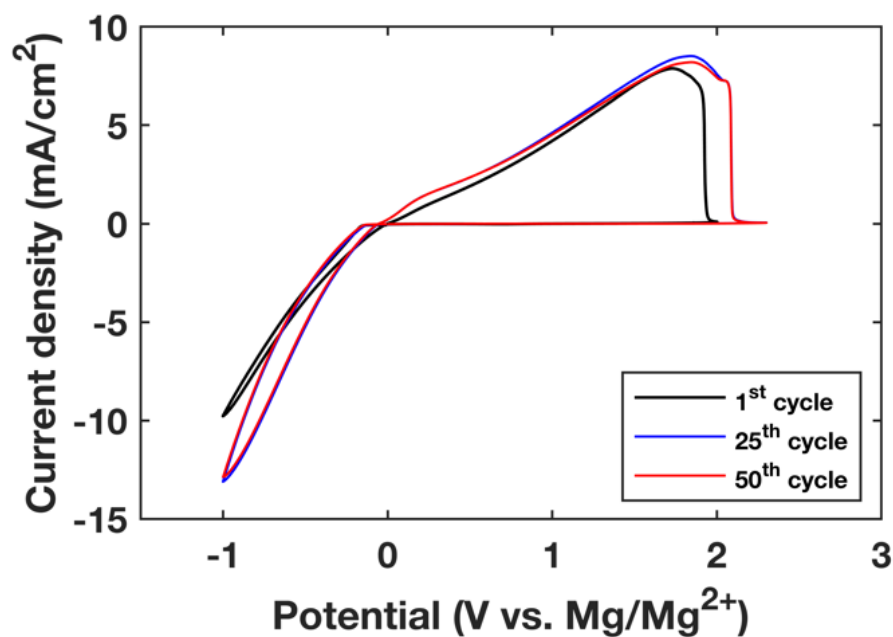


Fig. 5.8: Plating/stripping voltammogram of a 0.3 M MZCC electrolytes at three different cycles. Black line: 1st cycle; blue line: 25th cycle; red line: 50th cycle.

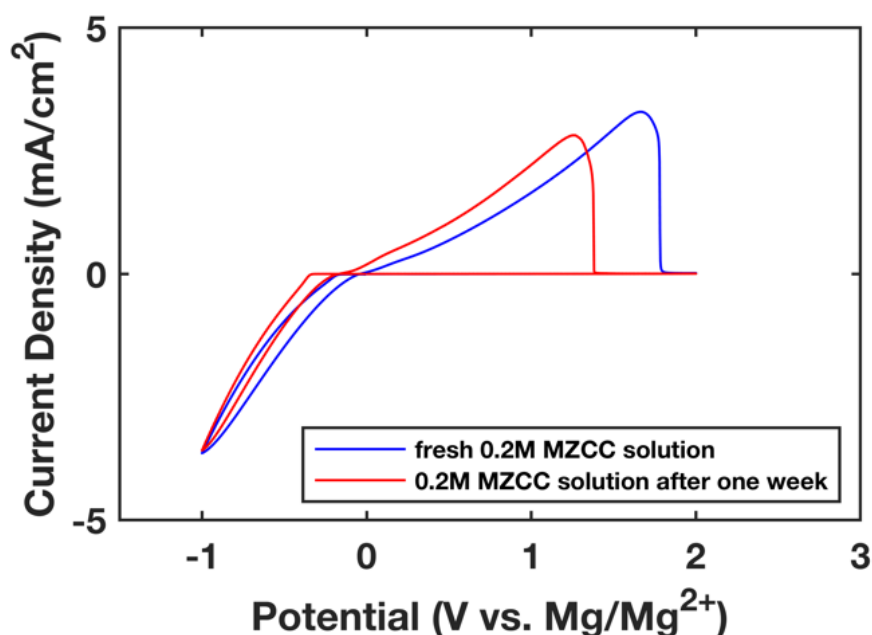


Fig. 5.9: Comparison between plating/stripping voltammograms of a fresh 0.2 M MZCC electrolyte (blue line) and of the MZCC electrolyte after one week of resting (red line).

5.7 Exploration of the synthesis mechanism of MZCC electrolytes

We applied multiple characterisation techniques to elucidate the structure and plating/stripping behavior of MZCC. Electrochemical products were galvanostatically deposited on a Pt wire and characterised by SEM-EDS and XRD. Needle-shaped deposits, as shown in Fig. 5.10a-c, were uniformly distributed on the surface of the Pt wire. EDS analysis (Fig. 5.10d) suggests that the deposits mainly comprise elemental Mg. The signatures of other elements, including Cl and O, were negligible. XRD detected peak signals of metallic Mg and metallic Pt (Fig. 5.11) from the deposition of Pt wire, further confirming that the needle-like deposits comprised metallic Mg. Neither SEM-EDS nor XRD indicated any

reduction of Zn^{2+} ions out of the MZCC.

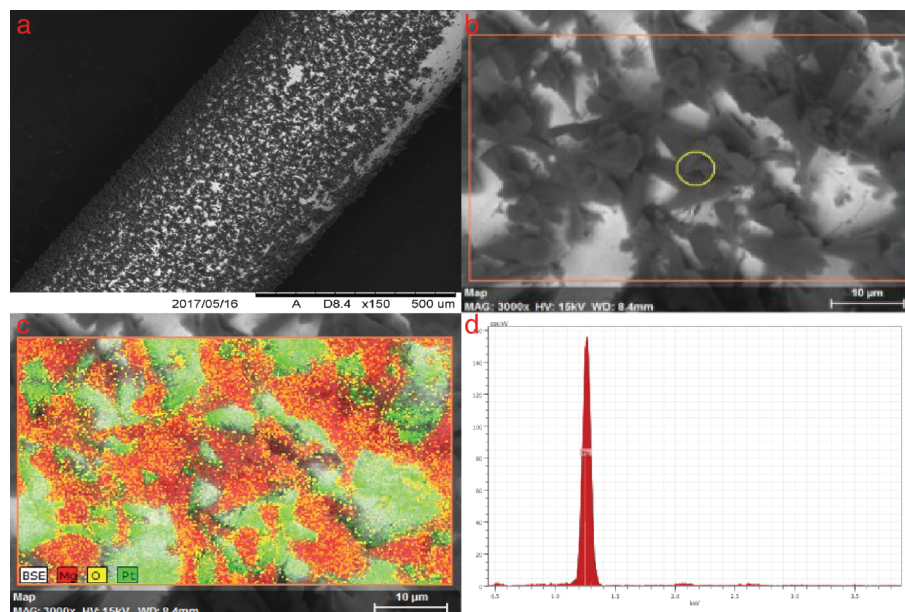


Fig. 5.10: (a) SEM image of products electrochemically deposited from MZCC onto a Pt wire. (b) SEM image of the deposit at higher magnification. (c) EDS analysis of electrochemical deposition on a Pt wire. (d) Elemental composition assay of the electrochemical deposit.

The composition of the black precipitate produced during electrolyte synthesis was also studied in detail. The precipitate deposited onto Mg foil was studied *via* XRD and SEM-EDS. The XRD pattern (Fig. 5.12) confirms the presence of metallic Mg and metallic Zn. SEM-EDS results (Fig. 5.13) suggest that the Mg signals most likely come from the Mg substrate and Zn signals from the black precipitate. Taking the XRD and SEM-EDS together, it is reasonable to say that the black precipitate comprises metallic zinc. This is consistent with the hypothesis that during the electrolyte synthesis, Mg metal reduces Zn^{2+} into zinc metal, performing a cation exchange. It is also worth noting that the precipitate shares a similar qualitative appearance to Rieke zinc, a catalyst used in organometallic chemistry.^{120,121} Rieke zinc is normally synthesised from displacement reactions of alkali metals, such as Li, K, and Na, in ZnCl_2/THF . Given that the alkaline earth metals share

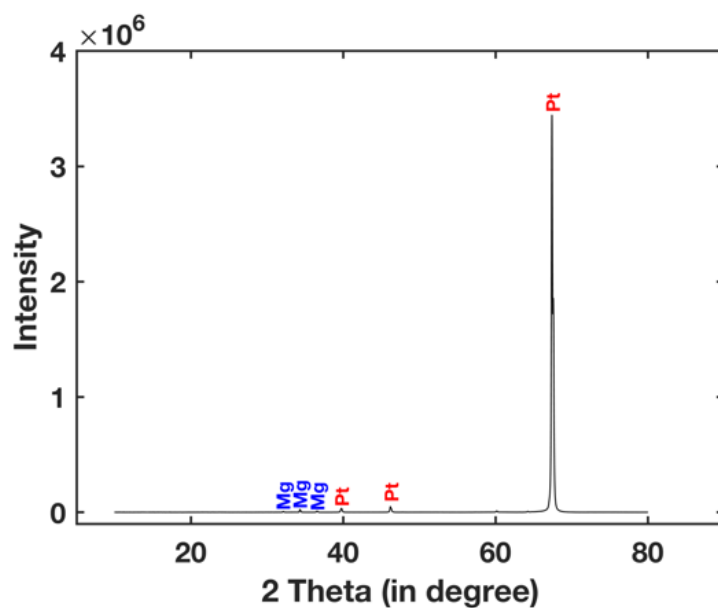


Fig. 5.11: X-ray diffraction pattern of the electrochemical deposit formed galvanostatically from 0.3 M MZCC electrolyte onto Pt foil.

many properties with alkali metals, it is possible that Rieke zinc is produced as a byproduct of MZCC synthesis, which could be interesting to explore in the future.

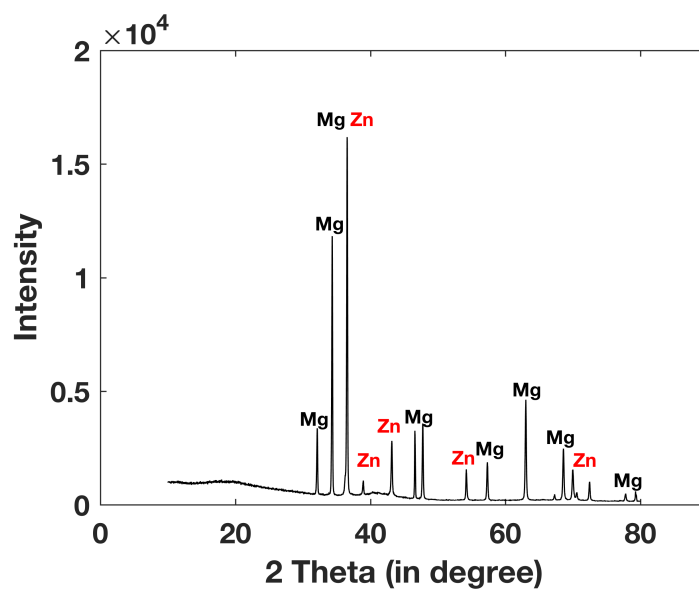


Fig. 5.12: X-ray diffraction pattern of the black precipitate deposited from a 0.3 M MgCl_2 /THF solution on a Mg foil.

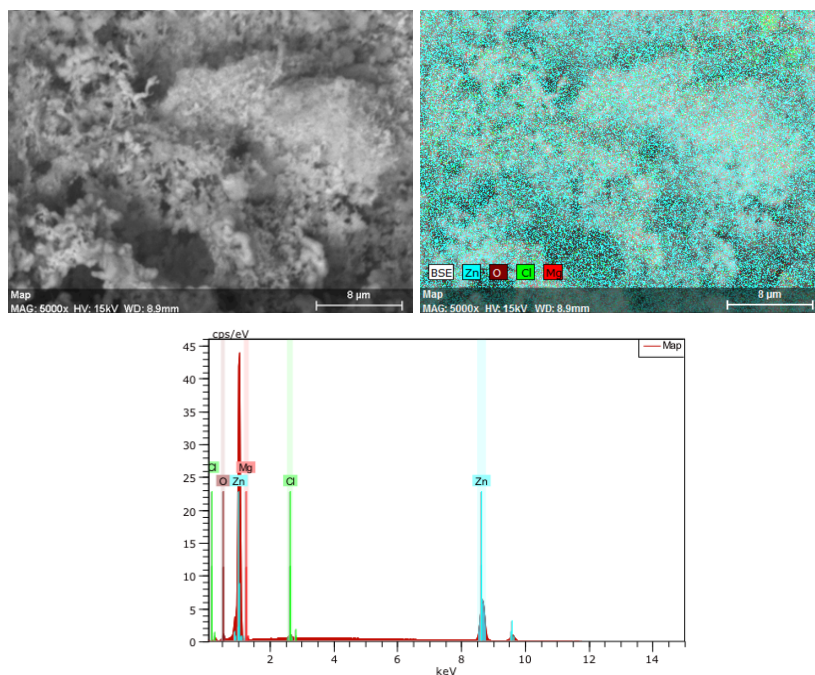


Fig. 5.13: SEM and EDS images of the black precipitates from a 0.3 M MgCl_2/THF solution.

To investigate the composition changes during the electrolyte synthesis, ICP-MS was employed to examine the Mg and Zn content of both initial ZnCl_2/THF solution and the MZCC electrolyte. As the results in Table 5.1 show, the electrolytic solution is rich in Mg and only contains a trace amount of Zn. The molar concentration of Mg in the electrolyte is consistent with that of Zn in the initial ZnCl_2 solution, suggesting the displacement reaction of Zn^{2+} is favored and that Mg displaces most of the Zn^{2+} ions during the synthesis.

Fig. 5.14 shows the Raman spectra obtained from THF, MgCl_2/THF solution, and MZCC electrolyte. Table 5.2 lists the band assignments. The 212 cm^{-1} peak characterises the Mg-Cl stretching, which has been noticed in different Mg-chloride-complex-based electrolytes.¹¹⁸ Compared to MgCl_2/THF solution, MZCC electrolyte exhibits much

Table 5.1: Mg and Zn contents in 5 mL electrolytic solutions

Solution (5 mL THF)	Mg (μg)	Zn (μg)
ZnCl_2/THF	N/A	8.11×10^4
MZCC electrolyte	2.88×10^4	229

higher Mg-Cl intensity, indicating a higher content of Mg-Cl-containing species in MZCC electrolytes. In the high wavelength range, all three systems share the same mode at 914 cm^{-1} . The red-shift of peak e reported in literature was not observed in our samples.

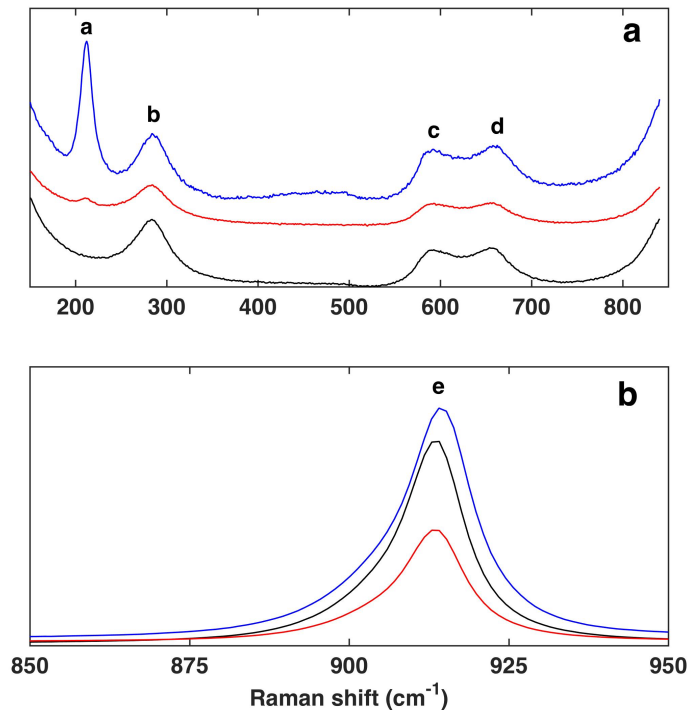


Fig. 5.14: Raman spectra of THF (black), MgCl_2/THF solution (red), and 0.3 M MZCC electrolyte (blue). (a) Peak at 212 cm^{-1} is observed in both MgCl_2/THF solution and MZCC electrolyte, which corresponds to Mg-Cl stretching. (b) Peak for symmetric ether O stretching is detected around 914 cm^{-1} for all three systems.

Table 5.2: Raman Shifts for Peaks in the THF, MgCl_2/THF solution, and MZCC electrolyte

Raman shifts					
Peak ID	THF	Mg-Cl ₂	MZCC	species	ref.
a	N/A	212	212	Mg-Cl	118, 122, 123
b	284	284	284	THF	122, 123
c	593	593	592	THF	122, 123
d	654	655	654	THF	122, 123
e	914	913	914	THF	122, 123

NMR was carried out to further elucidate the electrolytes structure. The ^1H NMR spectrum (Fig. 5.15a) of the dried salt re-dissolved in CDCl_3 shows three peaks. The residual CHCl_3 solvent peak is at 7.19 ppm and the other two peaks (1.79 ppm, 3.74 ppm) could arise from the coordinated THF molecules in the $[\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+$. The ^{35}Cl NMR spectrum (Fig. 5.15b) of the electrolytic solution only shows a broad peak around -26.7 ppm.² The peak location is similar to the Cl environment in the MgCl_2/THF solutions reported by other groups.¹¹⁵ Note that the ^{35}Cl NMR spectrum does not provide direct evidence for the presence of free Cl^- . The single peak in the ^{35}Cl NMR spectrum, however, does not necessarily imply a single environment: broadening of the Cl peak could owe to an asymmetric Cl environment in the solution. It has been discussed that the fast exchange between Cl^- and Mg complexes could result in the lack of a Cl^- signal.¹¹⁵

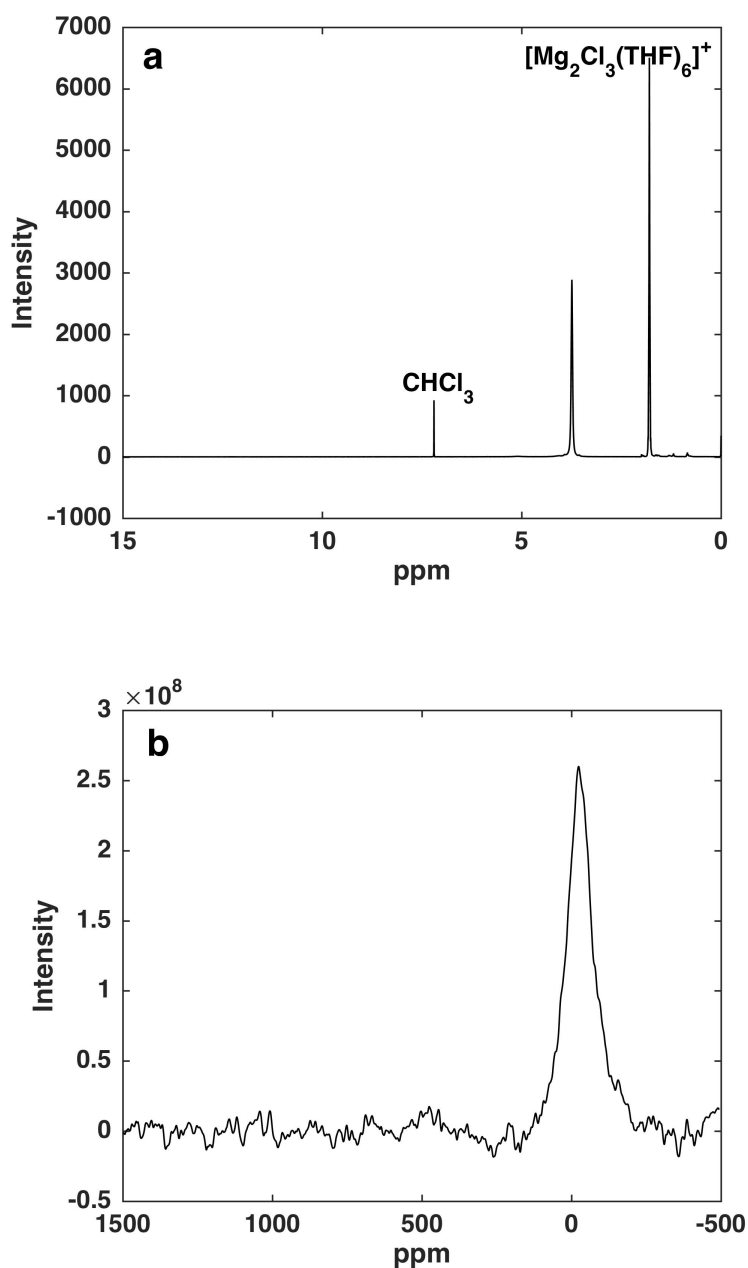


Fig. 5.15: (a) ^1H NMR spectrum of the residue obtained after drying MZCC re-dissolved in CDCl_3 . Three peaks indicate residual CHCl_3 solvent ($\gamma = 7.20$ ppm) and $[\text{Mg}_2\text{Cl}_3 \cdot 6(\text{THF})]^+$ cation ($\gamma = 1.76, 3.74$ ppm). (b) ^{35}Cl NMR spectrum of a MZCC electrolyte. The single peak ($\gamma = 26.7$ ppm) suggests a single Cl environment, but its breadth may conceal some features.

It is important to note that the second filtration step described in the procedure outlined above plays a critical role in electrolyte synthesis. Electrolytes synthesised with single filtration exhibited very inconsistent electrochemical performance. Coulombic efficiency varied from 50% to 90%, and the $\geq 99\%$ efficiency characteristic of twice-filtered samples was never achieved. As shown in Fig. 5.16, the second filtration and extra stirring boost electrolyte performance significantly. This observation can be rationalized by incomplete displacement of Zn^{2+} before the second filtration. Mg oxidation reaction reaches an equilibrium state after a certain amount of time, leaving a high Zn^{2+} content in the solution. The first filtration removes precipitate, which could drive further Mg oxidation in accord with Le Châtelier's principle. It was observed, however, that further Mg oxidation/ Zn^{2+} reduction could not be triggered by the simple addition of more Mg powder. The presence of some black zinc metal seems essential to facilitate ongoing Mg oxidation. The exact reason for this behavior is not completely understood.

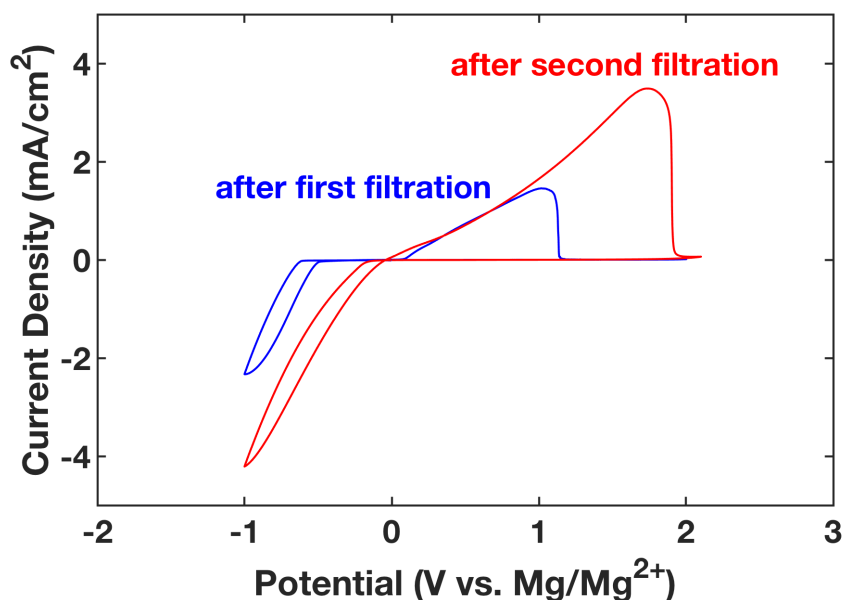
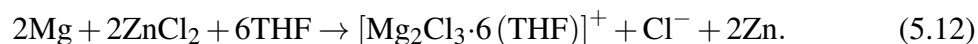


Fig. 5.16: Comparison of plating/stripping voltammograms of MZCC electrolyte after first filtration (blue) and second filtration (red).

Based on the experimental results and a review of prior literature, we are in a position to propose a mechanism to explain the electrolyte synthesis. It is likely that the oxidation of Mg metal reduces Zn^{2+} ions into Rieke zinc and produces Mg^{2+} -conductive ions that subsequently enable reversible Mg plating and stripping. It has been discussed that Mg dimers, $[\text{Mg}_2\text{Cl}_3 \cdot 6(\text{THF})]^+$, behave as the Mg^{2+} carriers in Mg-chloride-complex-based electrolytes.^{113, 114, 117} The following equation may describe the reaction occurring during electrolyte synthesis:



Mg oxidation provides the Mg-dimer cations. The free Cl^- should exist as an anion to maintain the charge balance.

5.8 Electrolytes synthesised from other salts and solvents

Besides ZnCl_2 , the alternative salts SnCl_2 and CuCl_2 were also used to synthesise Mg^{2+} -conductive electrolytes. Similar to ZnCl_2 , SnCl_2 also has high solubility in THF as well.

After adding Mg powder into the SnCl_2/THF solution, a black precipitate, which was confirmed to be Sn metal by XRD analysis (Fig. 5.17), immediately appeared and covered the surface of the Mg powder. The results from electrochemical testing of the resultant solution are shown Fig. 5.18. Similar to MZCC electrolyte, the electrolyte generated from SnCl_2/THF solution can also support reversible Mg plating and stripping with a Coulombic efficiency up to 93% and a deposition overpotential less than 250 mV. The reduction of Sn^{2+} was apparently more vigorous than that of Zn^{2+} . Metallic Sn powder appeared instantaneously and sintered into a large Sn cluster. this phenomenon could be explained by the relatively high redox potential of Sn/Sn^{2+} (0.140 V vs. SHE).

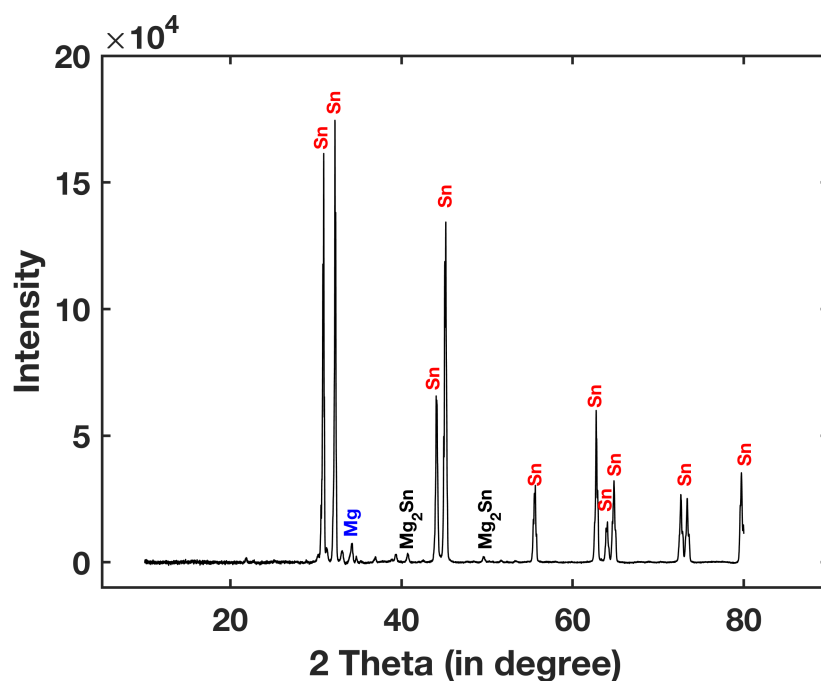


Fig. 5.17: X-ray diffraction pattern of the black precipitates from a 0.2 M SnCl_2/THF solution.

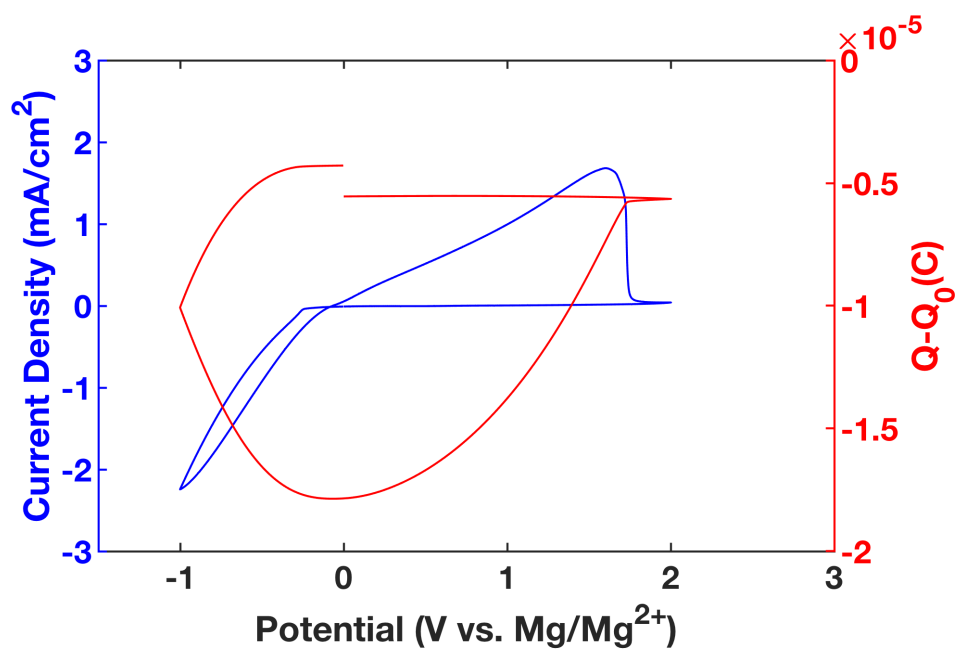


Fig. 5.18: Plating/stripping voltammogram of electrolyte synthesised from 0.2 M SnCl_2/THF solutions.

Cu/Cu^{2+} has positive standard reduction potential (Cu/Cu^{2+} : +0.337 V vs. SHE), which should make it an excellent candidate for the proposed synthesis method. However, unlike ZnCl_2 or SnCl_2 , CuCl_2 does not have high solubility in THF. When making a CuCl_2/THF solution, CuCl_2 salts suspend in the solution, and cannot completely dissolve. What is interesting is that Mg metal is still able to displace Cu^{2+} from both the dissolved and undissolved CuCl_2 salts, generating black Cu/Mg alloy (Fig. 5.19). The resultant solution, as shown in Fig. 5.20, provides Coulombic efficiency up to 98% and a deposition overpotential less than 150 mV for plating/stripping.

The success of syntheses with all three salts suggests the validity of our hypothesis that most metal chloride salts with similar or higher standard reduction potentials than Cr/Cr^{3+} should be able to reduce Mg metal in non-aqueous solutions to produce Mg^{2+} -conductive electrolytes. The reason as to why Coulombic efficiency is less than 100% for electrolytes synthesised from SnCl_2 and CuCl_2 is not completely understood, but it seems

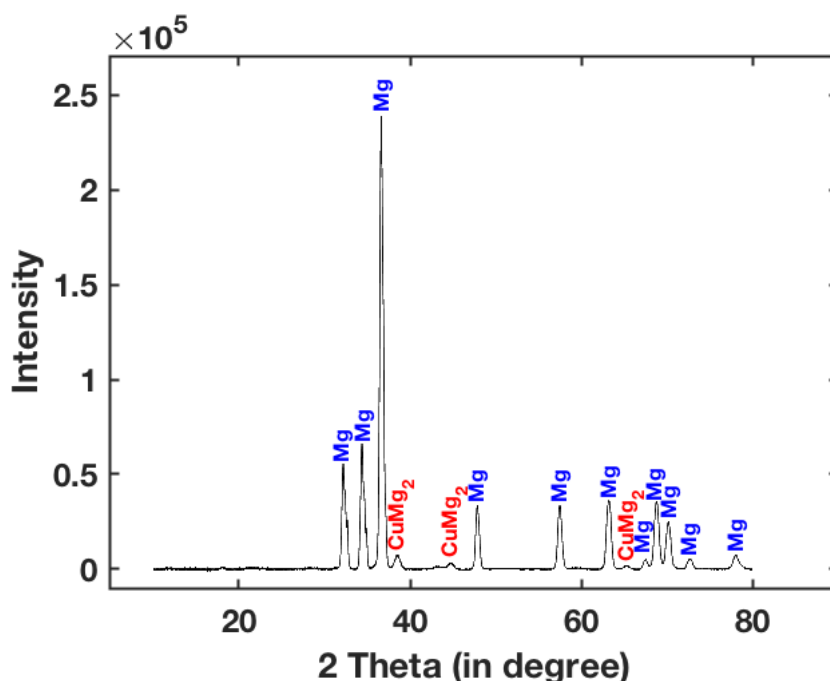


Fig. 5.19: X-ray diffraction pattern of the black precipitates from a 0.2 M CuCl_2/THF solution.

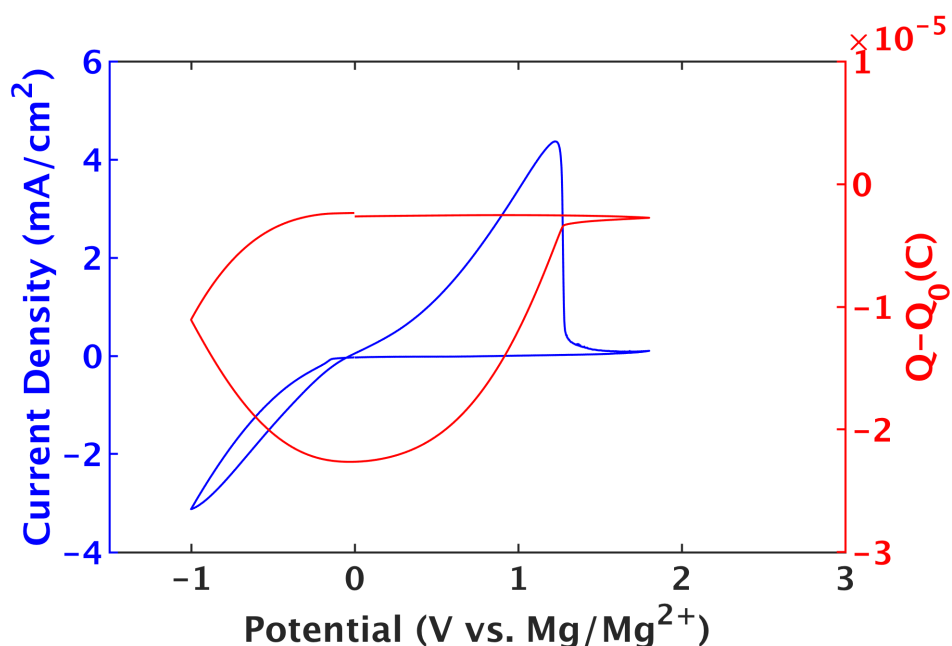


Fig. 5.20: Plating/stripping voltammogram of electrolyte synthesised from 0.2 M CuCl₂/THF solutions.

likely that the incomplete displacement reaction of Sn²⁺ or Cu²⁺ may explain this behavior.

Other solvents, including DME, DMSO, 2-methyl-THF, and triglyme, have also been examined with ZnCl₂ salt. So far, only THF serves as the solvent for MZCC system. For DME, 2-methyl-THF, and triglyme, displacement reaction occurred along with the production of unknown white powder. The white powders could not dissolve in these solvents at room temperature. Solutions after filtration did not bear any electrochemical activity within the scan range. The white powders may be the active Mg²⁺-contained salt in the MZCC electrolytes. The salt is apparently insoluble in these solvents. For DMSO, the displacement reaction cannot be triggered.

5.9 Characterisation of transport and thermodynamic properties for 0.3 M MZCC electrolytes

As we proposed, the effective cation is the positive Mg dimer, $[\text{Mg}_2\text{Cl}_3 \cdot (6\text{THF})]^+$, and the effective anion is Cl^- in MZCC electrolytes. The MZCC electrolytes can also be treated as binary electrolytes. We applied property characterisation techniques described in prior chapters to quantify the density, ionic conductivity, and diffusion coefficient for a 0.3 M MZCC electrolyte. The density is 902.1 g/L at 25 °C; ionic conductivity is 0.23 mS/cm at 25 °C; and diffusion coefficient is $8.93 \times 10^{-7} \text{ cm}^2/\text{s}$ at 25 °C. Both ionic conductivity and diffusion coefficient are not comparable with commercial Li-ion batteries. The concentration of a MZCC electrolyte mainly depends on the extent of Zn^{2+} reduction. In our 0.3 M MZCC electrolytes, the content of Zn element is negligible. However, we have noticed the completion of Zn^{2+} reduction becomes more and more difficult as the ZnCl_2 concentration increases. To improve the electrolyte performance, the priority may be to increase the concentration of mobile Mg^{2+} -conductive species.

Chapter 6

Summary and Future Work

To fully describe transport processes within binary electrolytic solutions, accurate measurements of six electrolyte properties are required. The six properties include three transport properties: ionic conductivity, transference number, and thermodynamic diffusion coefficient; and three thermodynamic properties: thermodynamic factor, partial molar volume of salt, and partial molar volume of solvent. We have quantified many of these properties for various binary electrolytes used for batteries, including aqueous VOSO_4 solutions, aqueous KOH solutions, non-aqueous LiPF_6/PC solutions, and non-aqueous MZCC electrolytes.

For aqueous VOSO_4 solutions, density and ionic conductivity were measured with respect to VOSO_4 concentration up to 0.5 M at five temperature: 15, 20, 25, 30, and 35 °C. To determine the VOSO_4 mass fraction of the stock solutions, we have designed a customized potentiometric titration technique with aqueous KMnO_4 solutions as the titer. The results of density and conductivity measurements were fitted with a function of molarity, whose parameters shows temperature dependence. Partial molar volume of salt and that of solvent were calculated from density/composition correlation. And equivalent conductance was calculated from ionic conductivity and fitted with a mathematical expression derived from Onsager–Fuoss theory. It was the first work to characterise the density and ionic

conductivity for aqueous VOSO_4 solutions.

The characterisation of aqueous KOH solution includes density and ionic conductivity measurements with respect to KOH concentration up to 12 M at three temperatures: 15, 25, and 35 °C. Partial molar volumes of salt and solvent were calculated from density/composition correlation, which can be expressed by Onsager–Fuoss theory. Equivalent conductance, derived from ionic conductivity, was fitted with a molarity dependent function. We have also attempted to quantify the thermodynamic factors with concentration-cell measurements with 1 M reference concentration, assuming a constant transference number from literatures, and the apparent (Fickian) diffusion coefficient for 1M KOH solution with restricted-diffusion measurements. To perform the restricted-diffusion measurements, a MnO_2 -plated nickel foil has been synthesised, using a potentiometric method. Diffusion coefficient of 1 M KOH solution was determined as $3.12 \times 10^{-5} \text{ cm}^2/\text{s}$, which agreed with the literature value. The works for aqueous KOH solutions have helped us accumulate enough experience about handling air-sensitive electrolytes, which benefits our work for the property characterisation for non-aqueous electrolytes.

Later, we have performed a complete characterisation of transport and thermodynamic properties for LiPF_6 in PC. All six properties were quantified with respect to LiPF_6 concentration up to 2 M. Density and ionic conductivity were measured at three temperatures: 20, 25, and 30 °C, while transference number, diffusion coefficient, and thermodynamic factor were quantified at 25 °C only. Density/composition correlations, which are described by functions with Onsager–Fuoss form, are used to calculate partial molar volume of salt and solvent. The correlations are also applied to determine the molarity of any given LiPF_6/PC solution by measuring its density. Equivalent conductance was calculated from ionic conductivity and fitted with temperature dependent Onsager–Fuoss expression. Transference number was measured with a customized Hittorf-cell. Then concentration-cell measurements were performed to quantify thermodynamic factor. Transference number, which is fitted with second-order polynomial functions, decreases from 0.287 at 0.15

M to 0.153 at 2 M. Thermodynamic factor increases with LiPF_6 concentration and is fitted with a form derived from Debye–Hückel theory. The results of transference number and thermodynamic factor show consistency between each other. Diffusion coefficient was determined by restricted-diffusion measurements with a customized cell. A glass fiber filter was used to hold the electrolytes to limit the effect of convection and external vibration during the measurements. The Bruggeman approximation was found to be able to describe the ratio between effective diffusion coefficient in the glass fiber and the liquid diffusion coefficient. Once the Fickian diffusion coefficient was determined, the thermodynamic diffusion coefficient was calculated by applying the value of thermodynamic factor measured from concentration-cell measurements. The Fickian diffusion coefficient decreases from $2.48 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.2 M to $4.67 \times 10^{-7} \text{ cm}^2/\text{s}$ at 2.0 M. The Stefan–Maxwell diffusivities that describe cation-solvent, anion-solvent, and cation-anion interaction were then calculated, using the three transport properties we have quantified. Both $\mathcal{D}_{0+}$ and $\mathcal{D}_{0-}$ decrease with salt concentration, while $\mathcal{D}_{+-}$ reaches the maximum value around 0.8 M. The trend of how $\mathcal{D}_{+-}$ varies with LiPF_6 concentration agrees with the trend of ionic conductivity. We have also developed a numerical model to simulate the OCP relaxation in several restricted-diffusion measurements, using the results of our characterisation. The simulation results highly agree with our experimental results, suggesting a satisfying accuracy of our experiments. Our characterisation is the first work to completely characterise the transport and thermodynamic properties for LiPF_6 in PC. Meticulous experimental designs and the numerical validation ensure the accuracy of our characterisation.

Our research on conditioning-free Mg^{2+} -conductive electrolytes went far beyond property characterisation. Our work included electrolyte synthesis, optimization, and characterisation, as well as performance evaluation. We discovered that both CuCl_2 and ZnCl_2 were able to perform as promoters to synthesise conditioning-free MaCC electrolytes. Inspired by this work, we further proposed a novel route to a conditioning-free/promoter-free Mg^{2+} -conductive electrolyte based on a single displacement reaction between ZnCl_2 and

Mg in THF. The resultant MZCC electrolyte was carefully studied to explore its nature and mechanism of electrolyte synthesis. We have proposed that the Mg^{2+} -carriers are Mg dimers, $[\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+$. Cl^- behaves as an anion to maintain overall electroneutrality. The Mg dimers are formed as a consequence of the reduction of Zn^{2+} by metallic Mg. We also found that both SnCl_2 and CuCl_2 could perform as precursors to produce Mg-chloride-complex-based electrolytes. Note that THF solvent was the only functional solvent so far; the conductivity and diffusivity of 0.3 M MZCC were found to be relatively low.

6.1 Future works

The detailed characterisation of bulk electrolyte properties can help to better understand transport processes within batteries. Exploring transport phenomena suggests routes to optimize battery operation and assess electrolytes for use in more advanced batteries. We quantified the transport and thermodynamic properties for various binary electrolytes. Our progress to date poses a number of questions that might be addressed in the future.

6.1.1 Transport and thermodynamic properties of MZCC electrolytes with respect to Mg content

We were only able to quantify the density, ionic conductivity, and diffusion coefficient for 0.3 M MZCC electrolytes. It would be interesting to perform a complete characterisation of transport and thermodynamic properties for MZCC. To achieve the full characterisation, the first task would be the determination of the active-species concentration. Due to the single displacement reaction that occurs between ZnCl_2 and Mg, the content of Mg^{2+} -conductive species would depend on the initial concentration of ZnCl_2 and the extent of displacement reaction. As we have observed, increasing the initial ZnCl_2 concentration cannot improve either the content of Mg^{2+} -conductive species or MZCC performance. Therefore, it is necessary to find the maximum obtainable content of Mg^{2+} -conductive species content

we can obtain. The transference number can still be quantified through Hittorf cell measurements combined with densitometry. Thermodynamic factor can only be quantified with concentration-cell measurements once the maximum content of Mg^{2+} -conductive species is determined. Alternatively it might be possible to apply a traditional method, such as boiling-point depression or vapor-pressure regression, to measure the thermodynamic factor.

6.1.2 Transport and thermodynamic properties for super-concentrated solution

In recent years, the idea of super-concentrated electrolytes for Li-ion batteries (also known as solvent-in-salt electrolytes) has attracted a lot of attention.^{124–136} Conventionally, electrolytes with 1 M Li salts (i.e., electrolytes with compositions near the conductivity maximum) are utilized in commercial Li-ion batteries. As the concentration of Li salts increases, ionic conductivity falls and viscosity increases, which one would expect to be a drawback. When the concentration reaches a very high level, however, superconcentrated solutions have shown great electrochemical performance, possibly due to higher cation transference. Compared to conventional electrolytes, superconcentrated electrolytes have the following advantages:

1. The stability window of the electrolytes is significantly improved. Both reductive stability and oxidative stability are enhanced, which could enable low-potential negative electrodes and suppress oxidative corrosion of Al current collectors without the aid of F^- .^{137, 138}

2. Solvent volatility is remarkably lowered, and thermal stability is dramatically enhanced in superconcentrated solutions.

3. Carrier density is very high.

4. Very fast electrode kinetics is sometimes achieved, which can far exceed those in state-of-the-art commercial LiPF_6/EC -based electrolyte.^{134, 135}

Although research into superconcentrated electrolytes is popular, detailed studies of their transport and thermodynamic properties are limited. Lindberghs group has performed a full characterisation of mass-transport phenomena in superconcentrated LiTFSI/ACN electrolyte, which may be the only work to quantify transport properties for superconcentrated solutions.¹³⁹

We performed a complete characterisation of transport and thermodynamic properties for LiPF₆/PC solutions with LiPF₆ concentration up to 2 M. PC is a solvent with high dielectric constant; the LiPF₆ solubility limit is around 4 M. It will be interesting to extend the property study into a more concentrated range to explore how the properties change. To perform this characterisation, one has to pay great attention to the dissociation of Li salt in highly concentrated solutions. Ideally, the Li salt is assumed to be fully dissociated. But the dissociation extent will decrease as the concentration of Li salt increases. When there is undissociated salt, an extra species is introduced into the system, making a binary electrolyte into a multicomponent system with four species. According to the concentrated solution theory, for an electrolytic solution with four species, six transport properties are required to fully describe the transport phenomenon in the electrolyte. So, more concerns are needed to quantify these transport properties.

6.1.3 Transport and thermodynamic properties for LiPF₆ in fluoroethylene carbonate

Fluoroethylene carbonate (FEC) solvent is normally used as the additive in the electrolytes for commercial Li-ion batteries. The addition of FEC can significantly increase the cycle life of the battery, especially for batteries with high-capacity or high-power density. It has been discussed that FEC can also widen the stability window of electrolytes and stabilize SEI layer on the anode surface.^{140,141} Recent studies have shown that the addition of FEC can also improve the stability of the SEI layer on Si anode or on Li metal anode, which may arise from the formation of nanostructured LiF layer on the surface.^{142–146} This

finding has triggered the interest to use pure FEC as the solvent for the electrolytes for Li-ion batteries. Therefore, it will be worth exploring the transport and thermodynamic properties of LiPF_6 in FEC.

Appendix A

Summary of Properties Measurements

A.1 Methods for uncertainty analysis

In the project of property characterisation, some quantities are determined by combining two or more separate measurements. The uncertainty for each measurement, therefore, must be combined to arrive at an uncertainty for the derived quantity. The propagation of uncertainty can be treated with a linearised approximation. Given a dependent quantity F is a function of several independent measurements a_i . The uncertainty of dependent quantity F is evaluated by

$$\Delta F(a_1, a_2, \dots, a_i) \approx \sqrt{\frac{\partial F}{\partial a_1} \Delta a_1^2 + \frac{\partial F}{\partial a_2} \Delta a_2^2 + \frac{\partial F}{\partial a_3} \Delta a_3^2 + \dots \frac{\partial F}{\partial a_i} \Delta a_i^2} \quad (\text{A.1})$$

In this thesis, the uncertainty source of each individual independent quantity may come from the intrinsic error of the equipment (eg. density metre, conductivity metre, viscometre), the standard deviation of the results from multiple measurements (eg. restricted diffusion measurements), or the 95% confidence bounds of the parameters in the least-square fittings (eg. density correlation for the calculation of partial molar volume, and OCV-composition correlation for the calculation of $(1 - t_+^0)\chi$). For some cases, different sources of error would be compared, and the largest uncertainty would apply in the data

analysis.

A summary of the raw data from properties characterisation is presented in the following sections, including the uncertainties for each measured quantity. For some quantities, such as partial molar volume or concentration measure, the uncertainty is smaller than the unity on last digit of the measured value. Such uncertainty will neither be listed in the tables, not be presented in the plots.

A.2 Properties of aqueous VOSO_4 solutions

Density:

$$\rho (15^\circ\text{C}) = 999.1 + 153.9c - 9.35c^{1.5} \quad (\text{A.2})$$

$$\rho (20^\circ\text{C}) = 998.2 + 153.9c - 10.05c^{1.5} \quad (\text{A.3})$$

$$\rho (25^\circ\text{C}) = 997.0 + 153.9c - 10.76c^{1.5} \quad (\text{A.4})$$

$$\rho (30^\circ\text{C}) = 995.6 + 153.9c - 11.41c^{1.5} \quad (\text{A.5})$$

$$\rho (35^\circ\text{C}) = 994.0 + 153.9c - 12.13c^{1.5} \quad (\text{A.6})$$

Table A.1: Densities of aqueous VOSO₄ solutions at 15 °C, 20 °C, 25 °C, 30 °C and 35 °C

15 ° C			20 ° C			25 ° C		
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)
0.006	0.001	1000.1	0.006	0.001	999.2	0.006	0.001	998.0
0.018	0.003	1002.0	0.018	0.003	1001.1	0.018	0.003	999.9
0.031	0.005	1003.8	0.031	0.005	1003.0	0.031	0.005	1001.7
0.043	0.007	1005.8	0.043	0.007	1004.8	0.043	0.007	1003.6
0.062	0.010	1008.6	0.062	0.010	1007.6	0.062	0.010	1006.4
0.125	0.020	1018.1	0.125	0.020	1017.1	0.125	0.020	1015.7
0.189	0.030	1027.5	0.188	0.030	1026.2	0.189	0.030	1025.1
0.254	0.040	1036.7	0.254	0.040	1036.0	0.254	0.040	1034.8
0.321	0.050	1046.6	0.321	0.050	1045.7	0.320	0.050	1044.2
0.388	0.060	1056.7	0.389	0.060	1055.6	0.387	0.060	1053.8
0.458	0.070	1066.6	0.458	0.070	1065.5	0.457	0.070	1064.4
0.528	0.080	1076.9	0.528	0.080	1075.7	0.527	0.080	1074.1
30 ° C			35 ° C					
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)			
0.006	0.001	996.2	0.006	0.001	995.0			
0.018	0.003	998.5	0.018	0.003	996.8			
0.030	0.005	1000.3	0.031	0.005	998.7			
0.043	0.007	1002.2	0.043	0.007	1000.6			
0.062	0.010	1005.0	0.061	0.010	1003.2			
0.124	0.020	1014.4	0.124	0.020	1012.5			
0.187	0.030	1023.5	0.188	0.030	1021.5			
0.254	0.040	1033.0	0.253	0.040	1031.2			
0.319	0.050	1042.7	0.319	0.050	1040.8			
0.387	0.060	1052.2	0.386	0.060	1050.5			
0.456	0.070	1062.3	0.456	0.070	1060.4			
0.526	0.080	1072.3	0.525	0.080	1070.4			

Table A.2: Partial molar volumes of aqueous VOSO₄ solutions at 15, 20, 25, 30 and 35 °C

15 ° C			20 ° C			25 ° C		
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)
0.006	10.2 ± 0.1	18.0	0.006	10.3 ± 0.1	18.0	0.006	10.4 ± 0.1	18.1
0.018	11.0 ± 0.1	18.0	0.018	11.2 ± 0.1	18.0	0.018	11.3 ± 0.1	18.1
0.031	11.6 ± 0.1	18.0	0.031	11.8 ± 0.1	18.0	0.031	12.0 ± 0.1	18.1
0.043	12.0 ± 0.1	18.0	0.043	12.3 ± 0.1	18.0	0.043	12.5 ± 0.1	18.1
0.062	12.6 ± 0.1	18.0	0.062	12.9 ± 0.1	18.0	0.062	13.1 ± 0.1	18.1
0.125	14.1 ± 0.1	18.0	0.125	14.4 ± 0.1	18.0	0.125	14.8 ± 0.1	18.0
0.189	15.2 ± 0.1	18.0	0.188	15.7 ± 0.1	18.0	0.189	16.2 ± 0.1	18.0
0.254	16.2 ± 0.1	18.0	0.254	16.7 ± 0.1	18.0	0.254	17.3 ± 0.1	18.0
0.321	17.1 ± 0.1	18.0	0.321	17.7 ± 0.1	18.0	0.32	18.3 ± 0.1	18.0
0.388	17.8 ± 0.1	18.0	0.389	18.5 ± 0.1	18.0	0.387	19.2 ± 0.1	18.0
0.458	18.6 ± 0.1	18.0	0.458	19.3 ± 0.1	18.0	0.457	20.0 ± 0.1	18.0
0.528	19.3 ± 0.1	18.0	0.528	20.1 ± 0.1	18.0	0.527	20.8 ± 0.1	18.0
30 ° C			35 ° C					
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$			
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)			
0.006	10.5 ± 0.1	18.1	0.006	10.6 ± 0.1	18.1			
0.018	11.5 ± 0.1	18.1	0.018	11.6 ± 0.1	18.1			
0.030	12.1 ± 0.1	18.1	0.031	12.4 ± 0.1	18.1			
0.043	12.7 ± 0.1	18.1	0.043	12.9 ± 0.1	18.1			
0.062	13.4 ± 0.1	18.1	0.061	13.7 ± 0.1	18.1			
0.124	15.2 ± 0.1	18.1	0.124	15.6 ± 0.1	18.1			
0.187	16.6 ± 0.1	18.1	0.188	17.1 ± 0.1	18.1			
0.254	17.8 ± 0.1	18.1	0.253	18.3 ± 0.1	18.1			
0.319	18.8 ± 0.1	18.1	0.319	19.5 ± 0.1	18.1			
0.387	19.8 ± 0.1	18.0	0.386	20.5 ± 0.1	18.1			
0.456	20.7 ± 0.1	18.0	0.456	21.5 ± 0.1	18.1			
0.526	21.6 ± 0.1	18.0	0.525	22.4 ± 0.1	18.1			

Ionic conductivity and equivalent conductance:

$$\Lambda(15^{\circ}\text{C}) = 1.490c^{0.5} - 0.7726c - 0.3396\ln c - 0.4948, \quad (\text{A.7})$$

$$\Lambda(20^{\circ}\text{C}) = 1.861c^{0.5} - 0.9268c - 0.3853\ln c - 0.6911, \quad (\text{A.8})$$

$$\Lambda(25^{\circ}\text{C}) = 2.232c^{0.5} - 1.106c - 0.4409\ln c - 0.8669, \quad (\text{A.9})$$

$$\Lambda(30^{\circ}\text{C}) = 2.661c^{0.5} - 1.377c - 0.4948\ln c - 1.038, \quad (\text{A.10})$$

$$\Lambda(35^{\circ}\text{C}) = 3.089c^{0.5} - 1.582c - 0.5568\ln c - 1.252. \quad (\text{A.11})$$

Table A.3: Ionic conductivity and equivalent conductance of aqueous VOSO₄ solutions at 15, 20, 25, 30, and 35 °C

15 ° C			20 ° C			25 ° C		
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)
0.006	0.0077	1.2577	0.006	0.0087	1.4178	0.006	0.0095	1.5523
0.018	0.0180	0.9769	0.018	0.0198	1.0761	0.018	0.0215	1.1731
0.031	0.0264	0.8636	0.031	0.0291	0.9455	0.031	0.0311	1.0132
0.043	0.0343	0.7936	0.043	0.0373	0.8649	0.043	0.0403	0.9349
0.062	0.0448	0.7257	0.062	0.0487	0.7875	0.062	0.0532	0.8615
0.125	0.0755	0.6040	0.125	0.0824	0.6601	0.125	0.0883	0.7089
0.189	0.1026	0.5430	0.188	0.1106	0.5886	0.189	0.1184	0.6276
0.254	0.1274	0.5011	0.254	0.1369	0.5386	0.254	0.1468	0.5780
0.321	0.1505	0.4686	0.321	0.1607	0.5009	0.320	0.1732	0.5411
0.388	0.1684	0.4345	0.389	0.1830	0.4707	0.387	0.1960	0.5059
0.458	0.1884	0.4114	0.458	0.2030	0.4435	0.457	0.2210	0.4834
0.528	0.2040	0.3861	0.528	0.2220	0.4204	0.527	0.2410	0.4576
30 ° C			35 ° C					
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)			
0.006	0.0103	1.6847	0.006	0.0111	1.8222			
0.018	0.0233	1.2681	0.018	0.0249	1.3583			
0.030	0.0336	1.1043	0.031	0.0361	1.1784			
0.043	0.0439	1.0205	0.043	0.0461	1.0742			
0.062	0.0569	0.9217	0.061	0.0597	0.9723			
0.124	0.0956	0.7685	0.124	0.1002	0.8076			
0.187	0.1278	0.6849	0.188	0.1357	0.7213			
0.254	0.1583	0.6242	0.253	0.1691	0.6686			
0.319	0.1861	0.5834	0.319	0.1966	0.6164			
0.387	0.2120	0.5472	0.386	0.2250	0.5824			
0.456	0.2370	0.5200	0.456	0.2500	0.5485			
0.526	0.2600	0.4943	0.525	0.2730	0.5203			

A.3 Properties of aqueous KOH solutions

Density and partial molar volumes:

$$\rho(15^{\circ}\text{C}) = 999.1 + 52.6c - 4.00c^{1.5}, \quad (\text{A.12})$$

$$\rho(25^{\circ}\text{C}) = 997.0 + 52.0c - 3.87c^{1.5}, \quad (\text{A.13})$$

$$\rho(35^{\circ}\text{C}) = 994.0 + 51.2c - 3.69c^{1.5} \quad (\text{A.14})$$

Table A.4: Densities of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)
0.0050	0.028	999.5	0.0050	0.028	997.3	0.0050	0.028	994.3
0.0100	0.056	999.7	0.0100	0.056	997.7	0.0100	0.056	994.5
0.0499	0.280	1001.8	0.0500	0.281	999.7	0.0499	0.281	996.6
0.0999	0.558	1004.2	0.1000	0.559	1002.3	0.0999	0.561	999.0
0.2500	1.386	1011.7	0.2499	1.387	1009.7	0.2500	1.394	1006.4
0.5001	2.740	1024.0	0.4999	2.744	1021.8	0.5001	2.755	1018.4
1.0005	5.358	1047.7	0.9987	5.361	1045.4	1.0001	5.387	1041.6
2.0019	10.276	1093.0	1.9987	10.288	1090.2	1.9996	10.330	1086.1
3.0036	14.833	1136.1	2.9945	14.832	1132.6	2.9987	14.908	1128.5
4.0040	19.079	1177.5	3.9952	19.095	1173.8	4.0000	19.190	1169.5
5.0043	23.065	1217.3	4.9921	23.081	1213.7	5.0026	23.215	1209.0
6.0015	26.816	1255.9	5.9953	26.866	1252.2	5.9921	26.963	1246.6
6.9626	30.247	1291.7	6.9855	30.408	1288.7	7.0024	30.588	1284.7
7.9924	33.748	1328.8	7.9877	33.820	1325.0	7.9902	33.961	1320.2
9.0017	37.024	1364.4	8.9778	37.040	1359.7	9.0004	37.254	1355.3
10.0027	40.138	1398.4	9.9887	40.191	1394.4	10.0038	40.387	1389.8
10.9881	43.086	1430.9	10.9853	43.175	1427.6	10.9988	43.370	1422.7
12.0016	46.011	1463.7	11.9947	46.088	1460.1	12.0044	46.274	1455.8

Table A.5: Partial molar volumes of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$	c	$\bar{V}_e$	$\bar{V}_0$
(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)	(mol/L)	(cm ³ /mol)	(cm ³ /mol)
0.005	4.0 ± 0.01	18.0	0.005	4.6 ± 0.01	18.1	0.005	5.3 ± 0.01	18.1
0.010	4.2 ± 0.01	18.0	0.010	4.7 ± 0.01	18.1	0.010	5.5 ± 0.01	18.1
0.050	4.9 ± 0.01	18.0	0.050	5.5 ± 0.01	18.1	0.050	6.2 ± 0.01	18.1
0.100	5.5 ± 0.01	18.0	0.100	7.1 ± 0.01	18.0	0.100	6.7 ± 0.01	18.1
0.250	6.6 ± 0.01	18.0	0.250	8.3 ± 0.01	18.0	0.250	7.7 ± 0.01	18.1
0.500	7.8 ± 0.01	18.0	0.500	4.7 ± 0.01	18.1	0.500	8.8 ± 0.01	18.1
1.001	9.5 ± 0.01	18.0	0.999	9.9 ± 0.01	18.0	1.000	10.5 ± 0.01	18.1
2.002	12.0 ± 0.01	17.9	1.999	12.3 ± 0.01	18.0	2.000	12.7 ± 0.01	18.0
3.004	13.8 ± 0.01	17.8	2.995	14.1 ± 0.01	17.9	2.999	14.4 ± 0.01	17.9
4.004	15.3 ± 0.01	17.7	3.995	15.5 ± 0.01	17.8	4.000	15.8 ± 0.01	17.8
5.004	16.6 ± 0.01	17.6	4.992	16.8 ± 0.01	17.7	5.003	17.0 ± 0.01	17.7
6.002	17.7 ± 0.01	17.5	5.995	17.9 ± 0.01	17.6	5.992	18.1 ± 0.01	17.6
6.963	18.7 ± 0.01	17.4	6.986	18.8 ± 0.01	17.4	7.002	19.0 ± 0.01	17.5
7.992	19.6 ± 0.01	17.2	7.988	19.7 ± 0.01	17.3	7.990	19.8 ± 0.01	17.4
9.002	20.5 ± 0.01	17.1	8.978	20.5 ± 0.01	17.2	9.000	20.6 ± 0.01	17.2
10.003	21.2 ± 0.01	16.9	9.989	21.2 ± 0.01	17.0	10.004	21.3 ± 0.01	17.1
10.988	21.9 ± 0.01	16.8	10.985	21.9 ± 0.01	16.9	10.999	21.9 ± 0.01	17.0
12.002	22.5 ± 0.01	16.6	11.995	22.5 ± 0.01	16.7	12.004	22.5 ± 0.01	16.8

Ionic conductivity and equivalent conductance

$$\Lambda(15^\circ\text{C}) = -0.2585c^{0.5} - 0.1328c + 0.004373c^2 + 2.148, \quad (\text{A.15})$$

$$\Lambda(25^\circ\text{C}) = -0.3438c^{0.5} - 0.1485c + 0.005133c^2 + 2.620, \quad (\text{A.16})$$

$$\Lambda(35^\circ\text{C}) = -0.4293c^{0.5} - 0.1631c + 0.006014c^2 + 3.080. \quad (\text{A.17})$$

Table A.6: Ionic conductivities, κ , and equivalent conductance, Λ , of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C			25 ° C			35 ° C		
c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)	c (mol/L)	$\kappa \pm 1\%$ (S/dm)	$\Lambda \pm 1\%$ (Sdm ² /mol)
0.0050	0.0106	2.1201	0.0050	0.01295	2.5900	0.0050	0.01519	3.0382
0.0100	0.0211	2.1108	0.0100	0.0258	2.5794	0.0100	0.0303	3.0308
0.0499	0.1039	2.0816	0.0500	0.1268	2.5348	0.0499	0.1482	2.9676
0.0999	0.2043	2.0452	0.1000	0.25	2.5008	0.0999	0.291	2.9117
0.2500	0.496	1.9841	0.2499	0.606	2.4246	0.2500	0.707	2.8280
0.5001	0.936	1.8715	0.4999	1.155	2.3107	0.5001	1.349	2.6973
1.0005	1.745	1.7441	0.9987	2.12	2.1228	1.0001	2.47	2.4699
2.0019	3.08	1.5386	1.9987	3.69	1.8462	1.9996	4.34	2.1705
3.0036	4.05	1.3484	2.9945	4.87	1.6263	2.9987	5.71	1.9042
4.0040	4.72	1.1788	3.9952	5.7	1.4267	4.0000	6.73	1.6825
5.0043	5.09	1.0171	4.9921	6.19	1.2400	5.0026	7.41	1.4812
6.0015	5.23	0.8714	5.9953	6.46	1.0775	5.9921	7.71	1.2867
6.9626	5.21	0.7483	6.9855	6.44	0.9219	7.0024	7.76	1.1082
7.9924	5.03	0.6294	7.9877	6.3	0.7887	7.9902	7.64	0.9562
9.0017	4.84	0.5377	8.9778	6	0.6683	9.0004	7.33	0.8144
10.0027	4.34	0.4339	9.9887	5.6	0.5606	10.0038	6.92	0.6917
10.9881	3.94	0.3586	10.9853	5.15	0.4688	10.9988	6.43	0.5846
12.0016	3.52	0.2933	11.9947	4.64	0.3868	12.0044	5.91	0.4923

Dynamic viscosity:

$$\eta = 7.89 \times 10^{-5}c^5 - 1.87 \times 10^{-3}c^3 + 1.79 \times 10^{-2}c^2 + 0.183c + 1.29, \quad (\text{A.18})$$

$$\eta = 9.27 \times 10^{-5}c^5 - 2.32 \times 10^{-3}c^4 + 2.48 \times 10^{-2}c^3 - 9.52 \times 10^{-2}c^2 + 0.191c + 1.01, \quad (\text{A.19})$$

$$\eta = 2.73 \times 10^{-5}c^5 - 6.80 \times 10^{-3}c^4 + 6.78 \times 10^{-5}c^3 - 1.69 \times 10^{-2}c^2 + 0.100c + 0.84. \quad (\text{A.20})$$

Table A.7: Ionic conductivities, κ , and equivalent conductance, Λ , of aqueous KOH solutions at 15 °C, 25 °C and 35 °C

15 ° C		25 ° C		35 ° C	
c (mol/L)	$\eta \pm 2\%$ (cP)	c (mol/L)	$\eta \pm 2\%$ (cP)	c (mol/L)	$\eta \pm 2\%$ (cP)
0.005	1.26	0.005	1.00	0.005	0.83
0.010	1.28	0.010	1.01	0.010	0.84
0.050	1.30	0.050	1.02	0.050	0.85
0.100	1.32	0.100	1.04	0.100	0.86
0.250	1.36	0.250	1.06	0.250	0.88
0.500	1.38	0.500	1.08	0.500	0.90
1.001	1.40	0.999	1.12	1.000	0.92
2.002	1.54	1.999	1.26	2.000	1.00
3.004	1.69	2.995	1.36	2.999	1.14
4.004	1.91	3.995	1.58	4.000	1.27
5.004	2.12	4.992	1.73	5.003	1.44
6.002	2.45	5.995	2.01	5.992	1.63
6.963	2.82	6.986	2.30	7.002	1.83
7.992	3.28	7.988	2.66	7.990	2.14
9.002	3.98	8.978	3.14	9.000	2.48
10.003	4.71	9.989	3.66	10.004	2.92
10.988	5.79	10.985	4.38	10.999	3.30
12.002	7.41	11.995	5.64	12.004	4.04

Diffusion coefficient of 1 M aqueous KOH solution:

$$D = 3.12 \times 10^{-5} \text{ cm}^2/\text{s}$$

A.4 Properties of non-aqueous LiPF₆ in PC solutions

Density and partial molar volumes:

$$\rho = 1205.0 + 84.67c - 2.753c^{3/2} \quad \text{at } 20^\circ\text{C}, \quad (\text{A.21})$$

$$\rho = 1199.7 + 85.06c - 2.814c^{3/2} \quad \text{at } 25^\circ\text{C}, \quad (\text{A.22})$$

$$\rho = 1194.4 + 85.46c - 2.877c^{3/2} \quad \text{at } 30^\circ\text{C}. \quad (\text{A.23})$$

Table A.8: Summary of density measurements results for LiPF₆/PC solutions at 20 °C, 25 °C, and 30 °C

20 ° C			25 ° C			30 ° C		
c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)	c (mol/L)	w	$\rho \pm 0.1$ (g/L)
0.0000	0.0000	1205.0	0.0000	0.0000	1199.6	0.0000	0.0000	1194.3
0.1009	0.0126	1213.3	0.1005	0.0126	1207.9	0.1000	0.0126	1202.6
0.1999	0.0249	1222.0	0.1990	0.0249	1216.6	0.1982	0.0249	1211.3
0.3882	0.0477	1236.9	0.3865	0.0477	1231.7	0.3849	0.0477	1226.4
0.3952	0.0485	1237.7	0.3935	0.0485	1232.3	0.3918	0.0485	1227.0
0.5849	0.0709	1253.2	0.5824	0.0709	1247.8	0.5799	0.0709	1242.5
0.7777	0.0931	1269.2	0.7743	0.0931	1263.8	0.7711	0.0931	1258.5
1.0064	0.1186	1287.6	1.0021	0.1186	1282.2	0.9972	0.1186	1276.9
1.0589	0.1245	1291.8	1.0546	0.1245	1286.6	1.0503	0.1245	1281.3
1.2978	0.1504	1311.0	1.2926	0.1504	1305.8	1.2875	0.1504	1300.6
1.4813	0.1698	1325.6	1.4755	0.1698	1320.4	1.4697	0.1698	1315.2
1.5624	0.1782	1332.1	1.5563	0.1782	1326.9	1.5502	0.1782	1321.7
1.7981	0.2022	1350.9	1.7912	0.2022	1345.7	1.7842	0.2022	1340.5
1.8135	0.2038	1351.6	1.8066	0.2038	1346.5	1.7995	0.2038	1341.2
1.9314	0.2155	1361.2	1.9240	0.2155	1356.0	1.9167	0.2155	1350.8
2.0472	0.2269	1370.3	2.0396	0.2269	1365.2	2.0318	0.2269	1360.0
2.1180	0.2338	1375.9	2.1099	0.2338	1370.7	2.1019	0.2338	1365.5

Table A.9: Summary of partial molar volume values for LiPF₆/PC solutions

20 ° C			25 ° C			30 ° C		
c (mol/L)	$\bar{V}_e$ (cm ³ /mol)	$\bar{V}_0$ (cm ³ /mol)	c (mol/L)	$\bar{V}_e$ (cm ³ /mol)	$\bar{V}_0$ (cm ³ /mol)	c (mol/L)	$\bar{V}_e$ (cm ³ /mol)	$\bar{V}_0$ (cm ³ /mol)
0.0000	N/A	84.7	0.0000	NA	85.1	0.0000	N/A	85.5
0.1009	56.9 ± 0.7	84.7	0.1004	56.8 ± 0.6	85.1	0.1000	56.8 ± 0.5	85.5
0.1999	57.3 ± 0.8	84.7	0.1990	57.3 ± 0.6	85.1	0.1982	57.2 ± 0.6	85.4
0.3881	57.9 ± 0.8	84.7	0.3865	57.9 ± 0.7	85.1	0.3848	57.9 ± 0.6	85.5
0.3952	57.9 ± 0.9	84.7	0.3935	57.9 ± 0.7	85.1	0.3918	57.9 ± 0.7	85.5
0.5849	58.4 ± 0.9	84.7	0.5824	58.4 ± 0.7	85.1	0.5799	58.4 ± 0.7	85.4
0.7776	58.8 ± 1.0	84.6	0.7743	58.8 ± 0.8	85.0	0.7711	58.7 ± 0.7	85.4
1.0055	59.2 ± 1.0	84.6	1.0013	59.2 ± 0.9	85.0	0.9972	59.2 ± 0.8	85.4
1.0588	59.2 ± 1.0	84.6	1.0545	59.3 ± 0.9	85.0	1.0501	59.3 ± 0.9	85.4
1.2977	59.6 ± 1.1	84.6	1.2924	59.6 ± 0.9	84.9	1.2872	59.6 ± 0.9	85.3
1.4812	59.8 ± 1.1	84.5	1.4753	59.9 ± 1.0	84.9	1.4694	59.9 ± 0.9	85.3
1.5623	59.9 ± 1.1	84.5	1.5561	60.0 ± 1.0	84.9	1.5499	60.0 ± 1.0	85.3
1.798	60.2 ± 1.1	84.5	1.7909	60.2 ± 1.0	84.8	1.7838	60.3 ± 1.0	85.2
1.8133	60.3 ± 1.1	84.5	1.8062	60.3 ± 1.0	84.9	1.7991	60.3 ± 1.0	85.2
1.9313	60.4 ± 1.1	84.5	1.9238	60.4 ± 1.0	84.8	1.9162	60.4 ± 1.0	85.2
2.0470	60.5 ± 1.1	84.4	2.0391	60.5 ± 1.1	84.8	2.0312	60.6 ± 1.0	85.2
2.1178	60.6 ± 1.1	84.4	2.1096	60.6 ± 1.1	84.8	2.1015	60.6 ± 1.1	85.2

Ionic conductivity and equivalent conductance:

$$\Lambda = 0.2419 - 0.7222y^{1/2} + 1.889y^2 \quad \text{at } 20^\circ\text{C.} \quad (\text{A.24})$$

$$\Lambda = 0.2670 - 0.7842y^{1/2} + 1.927y^2 \quad \text{at } 25^\circ\text{C.} \quad (\text{A.25})$$

$$\Lambda = 0.2920 - 0.8448y^{1/2} + 1.950y^2 \quad \text{at } 30^\circ\text{C.} \quad (\text{A.26})$$

Table A.10: Summary of conductivity measurements for LiPF₆/PC solutions

20 ° C			25 ° C			30 ° C		
c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$	c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$	c	$\kappa \pm 1\%$	$\Lambda \pm 1\%$
(mol/L)	(S/dm)	(Sdm ² /mol)	(mol/L)	(S/dm)	(Sdm ² /mol)	(mol/L)	(S/dm)	(Sdm ² /mol)
0.0942	0.0168	0.1785	0.0938	0.0186	0.1983	0.0934	0.0204	0.2184
0.2050	0.0302	0.1471	0.2041	0.0335	0.1640	0.2044	0.0368	0.1799
0.3967	0.0453	0.1141	0.3950	0.0506	0.1281	0.3933	0.0559	0.1421
0.6034	0.0535	0.0887	0.6021	0.0604	0.1002	0.5995	0.0672	0.1121
0.7930	0.0559	0.0705	0.7922	0.0635	0.0802	0.7889	0.0712	0.0902
0.9874	0.0538	0.0545	0.9846	0.0619	0.0629	0.9817	0.0701	0.0714
1.2351	0.0474	0.0383	1.2314	0.0555	0.0450	1.2276	0.0636	0.0518
1.4191	0.0414	0.0291	1.4147	0.0489	0.0346	1.4102	0.0565	0.0401
1.5648	0.0355	0.0227	1.5599	0.0427	0.0273	1.5549	0.0498	0.0320
1.8220	0.0259	0.0142	1.8162	0.0322	0.0177	1.8103	0.0384	0.0212
2.0349	0.0179	0.0088	2.0296	0.0231	0.0114	2.0229	0.0283	0.0140

Transference number:

$$t_{\text{Li}^+} = 0.298 - 0.423y + 0.808y^2, \quad (\text{A.27})$$

$$t_{\text{Li}^+}^0 = 0.298 - 0.847y - 1.395y^2. \quad (\text{A.28})$$

Table A.11: Summary of transference number for LiPF₆/PC solutions.

c (mol/L)	y	t_+	t_+^0
0.145	0.0122	0.293 $\pm$ 0.007	0.288 $\pm$ 0.007
0.193	0.0161	0.291 $\pm$ 0.007	0.283 $\pm$ 0.007
0.601	0.0479	0.279 $\pm$ 0.007	0.253 $\pm$ 0.006
0.985	0.0755	0.271 $\pm$ 0.007	0.226 $\pm$ 0.006
1.412	0.1038	0.263 $\pm$ 0.007	0.195 $\pm$ 0.005
1.959	0.1369	0.255 $\pm$ 0.006	0.155 $\pm$ 0.004

Concentration-cell data and thermodynamic factor:

$$\Delta U = \int \frac{vRT}{F} \chi (1 - t_{+}^0) d \ln y \quad (\text{A.29})$$

$$= 0.0582 + 0.162y + 3.736y^2 + 0.0363 \ln y.$$

$$(1 - t_{\text{Li}+}^0) \chi = 0.704 + 3.1439y + 145.006y^2. \quad (\text{A.30})$$

$$\chi = 1 + \frac{0.863\sqrt{y}}{1 - 1.612\sqrt{y}} - 13.96y + 92.65y^{3/2}. \quad (\text{A.31})$$

Table A.12: Results from concentration-cell measurements with 1 M reference concentration

c (mol/L)	y	ΔU (V)	$(1 - t_{+}^0)\chi$ (95% confident interval)	χ
0.0438	0.0037	-0.143	0.720 ± 0.004	1.020 ± 0.012
0.3999	0.0326	-0.058	0.963 ± 0.037	1.316 ± 0.052
0.6009	0.0479	-0.034	1.191 ± 0.055	1.595 ± 0.075
0.8020	0.0626	-0.018	1.474 ± 0.073	1.936 ± 0.098
0.9994	0.0765	0.000	1.798 ± 0.092	2.318 ± 0.120
1.3336	0.0988	0.027	2.436 ± 0.124	3.046 ± 0.157
1.4860	0.1085	0.039	2.759 ± 0.140	3.404 ± 0.173
1.6954	0.1214	0.055	3.231 ± 0.161	3.913 ± 0.196
1.9361	0.1356	0.078	3.806 ± 0.187	4.518 ± 0.223
2.0422	0.1416	0.085	4.071 ± 0.198	4.790 ± 0.234
2.1119	0.1456	0.092	4.247 ± 0.206	4.969 ± 0.242
0.1933	0.0161	-0.088	0.795 ± 0.018	1.109 ± 0.027
0.0962	0.0081	-0.114	0.742 ± 0.009	1.045 ± 0.017
0.0545	0.0046	-0.138	0.724 ± 0.005	1.025 ± 0.013

Diffusion coefficient:

$$D (\text{cm}^2/\text{s}) = (2.61 - 5.33y - 68.13y^2) \times 10^{-6}. \quad (\text{A.32})$$

$$\mathcal{D} (\text{cm}^2/\text{s}) = (2.80 - 34.94y + 113.55y^2) \times 10^{-6}. \quad (\text{A.33})$$

Table A.13: Stefan–Maxwell diffusivities of LiPF₆ in PC, calculated by applying the properties measured in previous experiments

c (mol/L)	y	$D \times 10^6$ (cm ² /s)	$\mathcal{D} \times 10^6$ (cm ² /s)	$\mathcal{D}_{0-} \times 10^6$ (cm ² /s)	$\mathcal{D}_{0+} \times 10^6$ (cm ² /s)	$\mathcal{D}_{+-} \times 10^7$ (cm ² /s)
0.1933	0.0161	2.49 ± 0.15	2.26 ± 0.29	3.98 ± 0.53	1.58 ± 0.21	3.19 ± 0.93
0.6009	0.0479	2.24 ± 0.10	1.41 ± 0.23	2.77 ± 0.46	0.94 ± 0.16	3.56 ± 0.88
0.9858	0.0755	1.77 ± 0.10	0.77 ± 0.14	1.71 ± 0.30	0.50 ± 0.09	3.40 ± 0.75
1.4122	0.1038	1.33 ± 0.04	0.41 ± 0.07	1.06 ± 0.18	0.26 ± 0.04	2.12 ± 0.44
1.8162	0.1286	0.81 ± 0.02	0.19 ± 0.03	0.58 ± 0.09	0.11 ± 0.02	1.14 ± 0.17
1.9590	0.1369	0.59 ± 0.03	0.13 ± 0.02	0.42 ± 0.07	0.08 ± 0.01	0.89 ± 0.14

Appendix B

Discussion about the Roles of MgCl_2 and AlCl_3 in Mg-Cl-Complex-Electrolytes

From common knowledge, MgCl_2 should be produced when Mg metal reduces Zn^{2+} , Sn^{2+} , or Cu^{2+} in their chloride solutions. But MgCl_2 salts have low solubility in THF (less than 0.1 M) and are relatively chemically inert. Based on the study of MACC electrolytes, the presence of AlCl_3 , which enables an acid-base reaction between MgCl_2 and AlCl_3 , increases the solubility of MgCl_2 in THF. In our case, the interesting part is that high MgCl_2 content is achieved without the help of AlCl_3 . The observation is quite counterintuitive and definitely worth more exploration.

We have further performed several experiments, attempting to unveil the roles of MgCl_2 and AlCl_3 in Mg-chloride-complex-based electrolytes. Some results are very interesting. For a ready-to-use MZCC electrolyte, MgCl_2 salts could further dissolve in the solutions. But the addition of MgCl_2 undermined electrolyte performance. After adding 0.1 M MgCl_2 into MZCC electrolyte, the Coulombic efficiency dropped from 100% to 60% (see Fig.B.1). The performance decay could be attributed to the extra water content introduced from the MgCl_2 salts, as the water content of the solution increased from 11 ppm to 33 ppm after MgCl_2 addition. It has been discussed that moisture level plays a significant

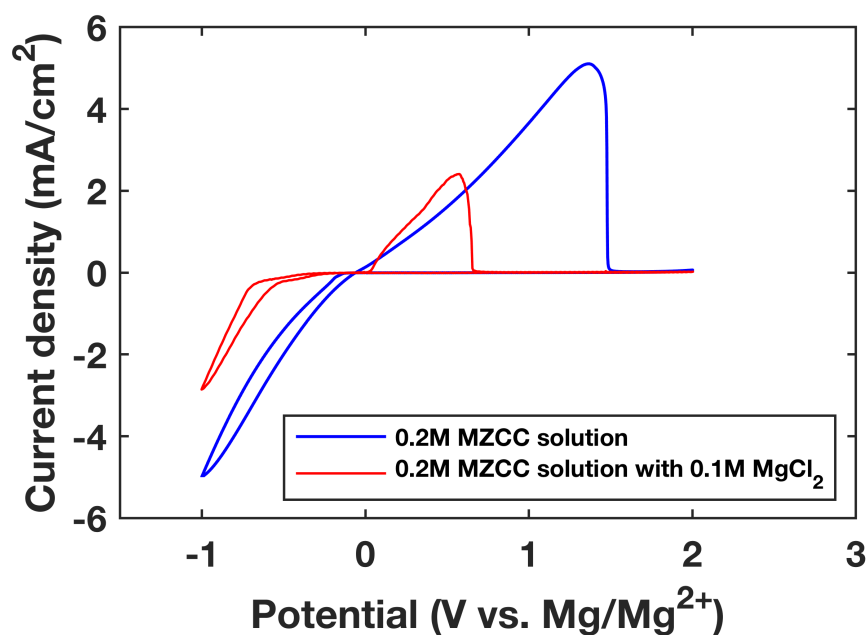


Fig. B.1: Comparison between cyclic voltammograms of a 0.2 M MZCC electrolyte and of the MZCC electrolyte after adding 0.1 M MgCl₂ salts.

role in non-aqueous Mg²⁺-conductive electrolytes as high water impurities may jeopardise the electrochemical performance of Mg-chloride-complex electrolytes.

However, if we dissolved both ZnCl₂ and MgCl₂ salts in THF and followed the same procedure to make electrolytes, the resultant solutions work surprisingly well. The addition of MgCl₂ prior to Mg powder did not result in high water content (13 ppm), and therefore did not cause performance decay. Compared to the electrolytic solution synthesised from ZnCl₂/THF solution, the one from ZnCl₂/MgCl₂/THF solution exhibits higher Mg plating and stripping current density, which may be resulting from higher Mg²⁺-conductive species (Fig. B.2). It is worth noting that solubility of MgCl₂ has been dramatically improved in both ZnCl₂/THF solution and MZCC electrolytic solution. The extra reason for the improved solubility is not completely understood. Our hypothesis is that the free Cl⁻ ions may trigger the dissociation of MgCl₂, which improves MgCl₂ solubility and introduces Mg²⁺ species. Further research is required to fully unveil the reason of the phenomenon.

We further explored the role of AlCl₃ in Mg²⁺-conductive electrolytes. It has been

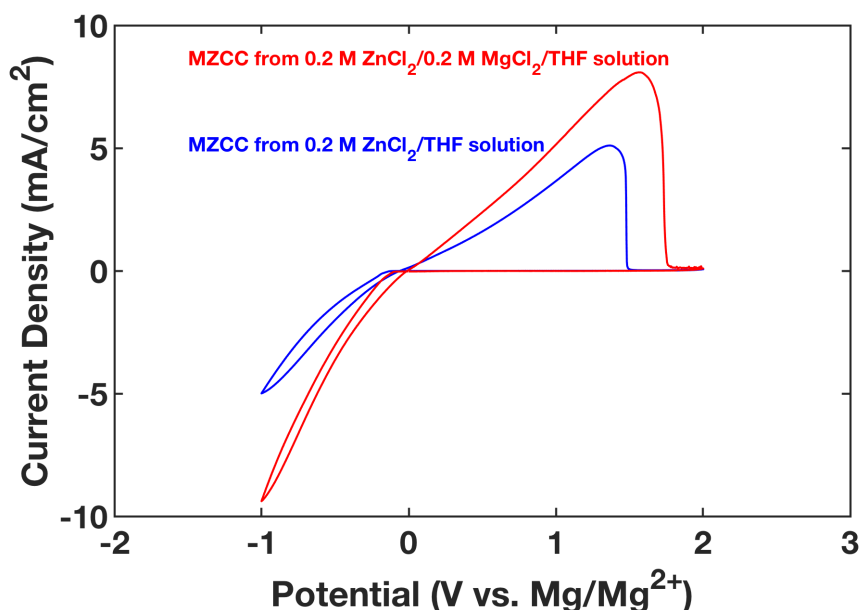


Fig. B.2: Comparison of cyclic voltammograms of electrolytes synthesised from $\text{ZnCl}_2/\text{MgCl}_2/\text{THF}$ solution and from ZnCl_2/THF solution.

discussed that AlCl_3 is necessary to increase the solubility of MgCl_2 in MACC electrolytes, but addition of AlCl_3 salts to conditioned MACC electrolyte causes performance decay. According to our experiments, as shown in Fig. B.3, addition of AlCl_3 salts worsened the performance of MZCC electrolyte, but increased the Mg plating and stripping current density. The performance, however, can be restored or even promoted by additional reaction with Mg powder. Metallic Al was produced from Mg oxidation. Interestingly, the resultant solution not only supported highly reversible Mg plating and stripping, but also maintained higher Mg plating and stripping current density. The magnitude of current density matches the previous results for MACC electrolyte with high contents of MgCl_2 and AlCl_3 . The enhanced electrochemical performance may be due to two reasons: firstly, the reduction of Al^{3+} produces more Mg^{2+} -conductive species, which facilitate Mg^{2+} transfer; secondly, addition of AlCl_3 introduces AlCl_4^- , an anion species that maybe more conductive than Cl^- in THF. To completely explain this observation, a more comprehensive elemental analysis will be needed in the future.

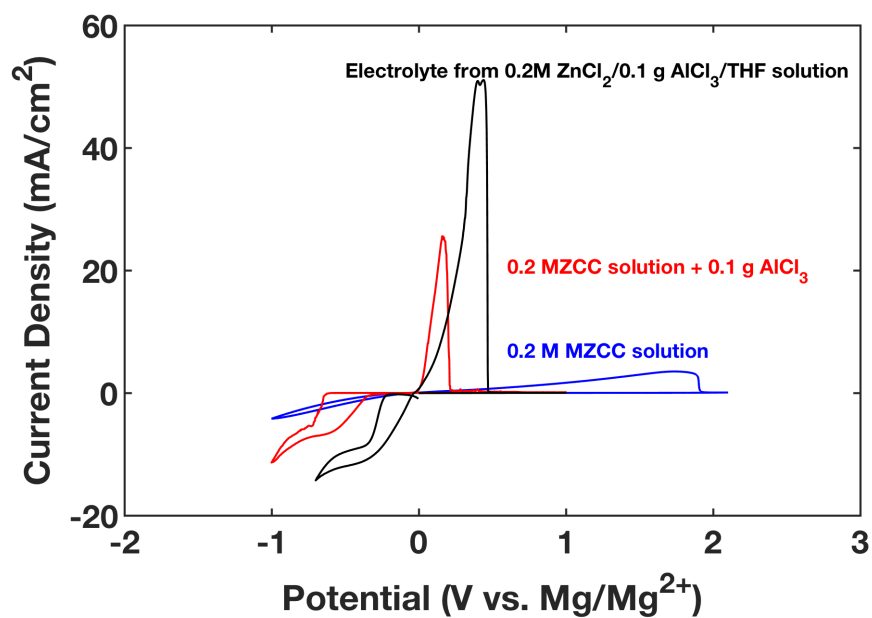


Fig. B.3: Comparison of cyclic voltammograms of electrolytes synthesised from 0.2 M ZnCl₂/THF solution (blue), 0.2 M MZCC electrolyte after adding 0.1 g AlCl₃ (red), and electrolyte synthesised from 0.2 M ZnCl₂/0.1g AlCl₃/THF solution (black).

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