Aalto-yliopisto
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Bachelor's Programme in Chemical Engineering

Factors affecting mass transfer in non-aqueous redox flow batteries

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**Bachelor's thesis
2025**

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Aalto University

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Title of thesis	Factors affecting mass transfer in non-aqueous redox flow batteries
Programme	Bachelor's Programme in Chemical Engineering
Major	Chemical and Metallurgical Engineering
Thesis supervisor	Jari Aromaa, DSc
Thesis advisor(s)	Mitra Ila, PhD
Date 14.12.2025	**Number of pages** 37 **Language** English

Abstract

Redox flow batteries (RFB) are among the most promising alternatives for sustainable large-scale energy storage. Their widespread adoption has been limited, for example, by their lower energy densities. Non-aqueous electrolytes would allow the battery to operate at wider voltage ranges compared to aqueous systems, thus improving battery performance. However, the characteristics affecting mass transfer in non-aqueous electrolyte solutions differ from those in aqueous solutions.

This thesis examines mass transfer in non-aqueous redox flow batteries. The study was conducted as a literature review, specifically focusing on mass transfer to electrode surfaces. This thesis presents the operating principle of redox flow batteries, the role of mass transfer in their operation, as well as the factors impacting mass transfer. Mass transfer is affected by the properties of the electrolyte solution, the electrode structure, flow rate and the flow field design.

In non-aqueous systems, mass transfer is hindered by limited solubilities of active species and lower conductivities of organic solvents. The viscosities of the solvents vary. From the perspective of mass transfer, viscosity is an important parameter, as it affects both diffusive and convective transport mechanisms. In addition, viscosity influences the ionic conductivity of the electrolyte. The efficiency of mass transfer can also be enhanced by modifying the structure of the electrode and the flow conditions, for which the design principles remain largely similar to those in aqueous systems.

Keywords redox flow battery, mass transfer, non-aqueous electrolytes, viscosity

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Tekijä Salla Palander

Työn nimi Aineensiirtoon vaikuttavat tekijät vedettömissä virtausakuissa

Koulutusohjelma Kemian tekniikan kandidaattiohjelma

Pääaine Kemian tekniikka ja prosessit

Vastuuopettaja/valvoja Jari Aromaa, DSc

Työn ohjaaja(t) Mitra Ila, PhD

Päivämäärä 14.12.2025 **Sivumäärä** 37 **Kieli** englanti

Tiivistelmä

Virtausakut ovat lupaava vaihtoehto pitkäaikaiseen energian varastointiin. Toistaiseksi akkujen laajamittaista käyttöönottoa on rajoittanut muun muassa niiden alhaisempi energiatiheys. Yksi vaihtoehto virtausakkujen toiminnan parantamiseen on elektrolyyttiliuoksissa käytettävän veden korvaaminen orgaanisilla liuottimilla, mikä mahdollistaa akun operoinnin korkeammilla jännitteillä. Vedettömien elektrolyyttiliuosten aineensiirtoon vaikuttavat ominaisuudet kuitenkin poikkeavat vesipohjaisista liuoksista.

Tämä kandidaatintyö tarkastelee aineensiirtoa vedettömissä virtausakuissa. Työ toteutettiin kirjallisuuskatsauksena ja se rajattiin koskemaan erityisesti aineensiirtoa elektrodin pinnoille. Työssä esitellään virtausakkujen toimintaperiaate, aineensiirron mekanismit ja niiden merkitys akuissa sekä aineensiirtoon vaikuttavat tekijät. Aineensiirtoon vaikuttavat elektrolyyttiliuoksen ominaisuudet, elektrodin rakenne, virtausnopeus sekä tapa, jolla elektrolyyttiliuos ohjataan elektrodin pinnalle.

Vedettömien virtausakkujen aineensiirtoa vaikeuttavat erityisesti redox-aktiivisten aineiden alhainen liukoisuus, alhainen johtavuus sekä joidenkin orgaanisten liuottimien korkeat viskositeetit. Elektrolyyttiliuoksen viskositeetti on olennainen parametri virtausakuissa, sillä se vaikuttaa aineensiirtoon sekä diffuusiokertoimen että virtausnopeuden kautta. Viskositeetti vaikuttaa lisäksi elektrolyytin ionijohtavuuteen. Aineensiirtoa on mahdollista tehostaa myös elektrodien rakennetta ja virtausolosuhteita muuttamalla, jolloin periaatteet ovat pääosin samat kuin veteen perustuvissa virtausakuissa.

Avainsanat virtausakku, aineensiirto, elektrolyyttiliuos, viskositeetti

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Symbols and abbreviations

Symbols

A_v	specific surface area, m^{-1}
c_i	concentration of species i, mol m^{-3}
D_i	diffusion coefficient of species i, m^{2} s^{-1}
F	Faraday constant, 96 485 C mol^{-1}
i	current density, A m^{-2}
j	interfacial reaction current density, A m^{-3}
j_0	exchange current density, A m^{-2}
k	permeability, m^{2}
k_B	Boltzmann constant X
k_m	mass transfer coefficient, m s^{-1}
k_0	kinetic reaction rate constant,
N_i	flux of species i, mol m^{-2} s^{-1}
p	pressure, Pa
R	gas constant
R_i	reaction rate for species i, mol m^{-3} s^{-1}
r_{eff}	effective radius, m
T	temperature, K
U_{cell}	open-circuit potential, V
u_i	ionic mobility of species i, m^{2} mol J^{-1} s^{-1}
V_{cell}	cell potential, V
v	bulk electrolyte velocity, m s^{-1}
z_i	charge number of species i
$\mathrm{\alpha}$	charge transfer coefficient
ε	porosity
η	overpotential, V
κ	specific conductivity, S m^{-1}
$\mathrm{\mu}$	viscosity, Pa s
τ	tortuosity
Φ	electric potential, V

Operators

∇	gradient or divergence
Σ_i	sum over index i

1 Introduction

The global demand for energy storage is rising rapidly both in portable applications and large-scale stationary solutions. The growing share of solar and wind power effectively reduces greenhouse gas emissions in energy production. However, it presents a new challenge for the energy system: the production of renewable energy varies with the weather, but the demand for electricity needs to be matched with the supply at all times.

While the performance of lithium-ion batteries has improved significantly over the past years, the development is mostly focused on batteries in electric vehicles and personal electronics. The requirements differ for stationary energy storage systems compared to portable applications (Liu et al. 2011). For example, minimizing the size and the weight of the components is not as essential in stationary storage systems compared to portable ones. Moreover, the wider adoption of grid-scale lithium-ion batteries is still facing limitations related to lifetime, safety and resource scarcity (Hasan et al. 2025).

One alternative solution to these challenges is a redox flow battery. Redox flow batteries (RFB) differ from conventional batteries by facilitating the reversible redox reactions entirely within the electrolyte, thus allowing energy storage in a liquid phase. This contrasts with conventional batteries, in which the energy is predominantly deposited in solid-phase electrodes.

The configuration of a redox flow battery has some important advantages compared to the conventional alternatives. The system allows power and energy capacity to be independent from each other, which enables more flexibility in large-scale installations (e.g. Liu et al. 2011). Redox flow batteries also avoid some common issues faced by current lithium-ion batteries, offering improved durability and safety (Tolmachev 2023, Wang et al. 2013). Using abundant materials, such as organic molecules, as redox active species could also alleviate the supply constraints of current battery technologies (Luo et al. 2019).

Generally, there are two pathways for improving battery performance. The first method centres around altering the battery chemistry and finding novel active materials. The second method focuses on optimizing the operational efficiency. Non-aqueous electrolytes in redox flow batteries allow the use of wider voltage ranges, thus enabling higher power output (e.g. Huang et al. 2015). However, the transition to non-aqueous systems can have adverse impacts on the battery performance by increasing mass transfer resistances in the system (Milshtein et al. 2017a).

The main goal of the thesis is to describe factors affecting mass transfer in non-aqueous redox flow batteries. In batteries, mass transfer refers to the movement of redox active species and charge-balancing ions within each electrolyte. Limitations in mass transfer restrict the current density and overall performance as well as the available capacity of the battery (Milshtein et al. 2017b).

To some extent, mass transfer phenomena are unique to each flow battery chemistry. Current research has not yet identified a non-aqueous chemistry that would clearly outperform others (e.g. Zheng et al. 2022). Therefore, this thesis investigates general factors influencing mass transfer primarily from a chemistry-agnostic perspective. The focus of the study is on mass transfer on a single electrode, which limits the discussion on separators and membranes.

This thesis is structured into five chapters. Chapter 2 presents the main operating principle of a redox flow battery which is contrasted with the structure of a conventional battery. Chapter 3 describes the fundamental equations and phenomena of mass transfer in the context of electrochemical systems. Chapter 4 analyses the mass transfer phenomena and the factors affecting it in non-aqueous redox flow batteries. Finally, Chapter 5 summarizes the main findings of the study.

2 Redox flow batteries

The main idea of batteries is to store electrical energy in chemical compounds. The energy is stored and released in redox reactions that are, at least in theory, reversible.

Redox or oxidation-reduction reactions are reactions where electrons are transferred between two species. Redox reactions occur always in couples: one of the species gives the electrons while the other species accepts them. Redox reactions cause a change in each of their oxidation states. The half-reaction for oxidation is written $A \rightarrow A^{n+} + ne^-$. For reduction, the half-reaction is $B^{n+} + ne^- \rightarrow B$.

In batteries, or in electrochemical systems in general, the half-reactions happen on separate electrodes through a conductor. If the electrodes are not connected by a conductor and current is not flowing, both half-reactions are at equilibrium and the reactions are reversible with no net current. The energy of the electrons is different on each side, and each side has its own equilibrium potential defined by thermodynamics.

In ideal conditions, the equilibrium potential equals the so-called open-circuit potential. In practise, however, the components in the system have resistance and the kinetics and mass transfer limitations restrict the redox reactions. The potential, which acknowledges the different kinds of losses and applies when the electrodes are connected, is called cell potential.

When the circuit is closed and the electrons can move between the electrodes, the system seeks to balance the potential difference. The electrode with a lower relative potential loses its electrons to the circuit, causing the redox-active species in the electrolyte to oxidize. Conversely, the electrode that has a higher relative potential draws electrons from the external circuit and causes a reduction of the species.

In a discharging battery, the electrode where oxidation occurs is called the anode and the electrode where reduction occurs is called the cathode. In a charging battery, the reactions happen to the opposite direction, and the roles of the anode and cathode are reversed. The anodic current refers to the flow of electrons from a species to the electrode, and the cathodic current to the flow of electrons from the electrode to a species. The convention in electrochemical engineering is to mark the anodic current as positive.

2.1 Main components

The main components of a redox flow battery are analogous to lithium-ion batteries. Similarly to conventional batteries, a flow battery cell is composed of electrolyte solution in which the ions can move, two electrodes, and a separator between them.

The functioning of the components distinguishes from the conventional design and there are two electrolyte solutions with differing compositions. As mentioned earlier, in flow batteries the redox active species are dissolved in the liquid-phase electrolytes throughout charge-discharge cycles. This means that unlike in traditional batteries, in which the redox active species form solid-phase compounds with the electrode materials, the electrodes in flow batteries do not undergo any reactions but act only as a donor or receiver of electrons.

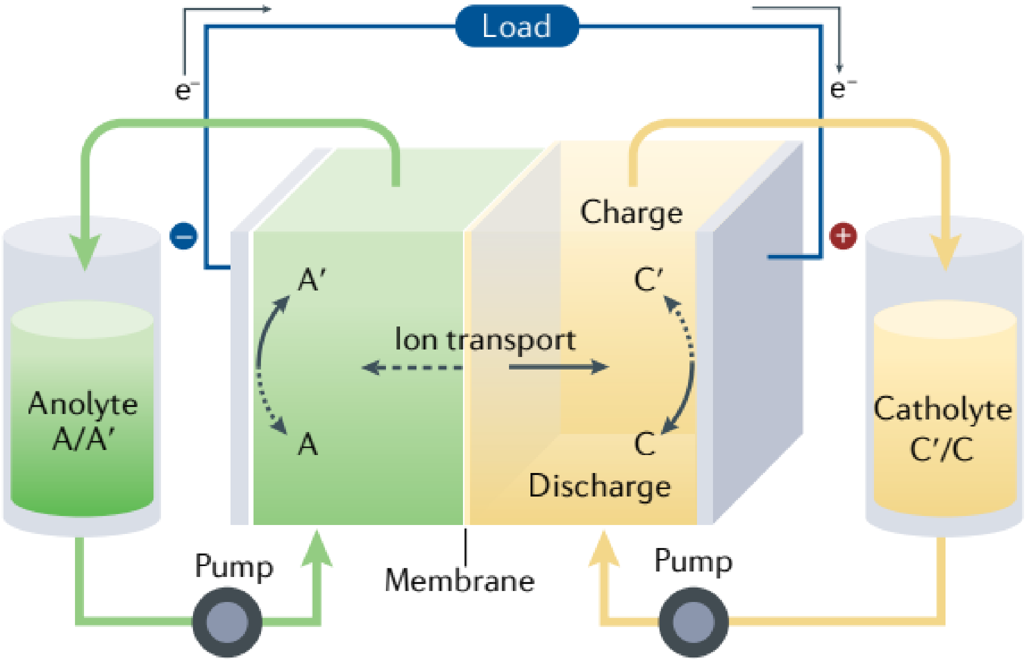

Figure 1 Schematic drawing of a redox flow battery. From Zhang et al. 2022.

In redox flow batteries, the liquid electrolytes with opposite redox potentials are frequently called catholytes and anolytes. The electrolyte solutions include a solvent and the dissolved active species in addition to possible supporting electrolytes. A common way to categorize redox flow batteries is the division to aqueous and non-aqueous designs based on the electrolyte solvent.

According to Hou et al. (2024), some of the most common active species in aqueous solutions include vanadium-, zinc- and iron-based redox couples. Non-aqueous redox flow batteries use electrolytes usually based on organic solvents. The earlier suggested redox couples were metal-ligand complexes but recently the research has turned to organic molecules, whose use is also investigated in aqueous systems (Huang et al. 2015). Naturally, the chemistries of the catholyte and anolyte must differ from each other to create a potential difference in the system.

The electrodes are connected by a metal conductor through which electricity is either drawn from the system or supplied to it. For the redox reactions to happen, the electrolyte must be in contact with the electrode. As noted by Weber et al. (2011), the electrodes in redox flow batteries are usually porous, three-dimensional carbon materials that allow electrolyte flow through their structure.

The system described above enables the use of external containers for electrolyte storage. Pumps circulate the electrolyte solution through the battery cells during charge and discharge cycles. During operation, the electrolyte flow should be evenly distributed to the porous electrode to enhance mass transfer. A flow field controls the distribution of the electrolyte. Flow fields are typically moulded on bipolar plates that connect the individual cells into a cell stack (Lu et al. 2024).

To complete the circuit in the cell, ions need to be able to pass through the electrolyte from one side to another. However, the anolyte and catholyte have different chemistries and should not be mixed to maintain a high performance and the reversibility of the reactions. Therefore, a separator is needed to prevent the crossover of the active species.

The separators can be classified into neutral and ion conducting membranes (e.g. Yuan et al. 2021). The neutral separators are porous, and the selectivity is based on the smaller size of supporting ions. The ion conducting membranes are dense but allow certain ions to pass through. Redox flow batteries typically have either cation or anion exchange membranes because they perform better at preventing undesirable crossover (Weber et al. 2011).

2.2 Prospects and challenges

The key benefits of redox flow batteries are the decoupling of capacity and power, as well as increased durability and safety (Wang et al. 2013). In lithium-ion batteries the storage capacity depends on the thickness and mass loading of the electrodes since they are active participants in the redox reactions. Increasing the amount of active material has an adverse impact on the mass transfer and increases resistance while also leading to side reactions that impede the power output (e.g. Gallagher et al. 2016, Weber et al. 2011).

In redox flow batteries, the capacity to store energy is defined by the energy density and the volume of the electrolytes, while the power output depends on the size of the cell stack. The configuration allows increasing the capacity without compromising the rate of charge and discharge, as the electrolytes can be stored externally. Therefore, redox flow batteries are well-suited for stationary applications that require long durations of power output (Tolmachev 2023).

As Wang et al. (2013) report, electrodes in redox flow batteries are expected to last longer since they do not undergo physical or chemical changes. The possibility to store the liquid electrolytes in separate containers prevents uncontrolled reactions. In lithium-ion batteries, common issues affecting the durability include side reactions with the solid-phase electrode that alter the morphology and increase resistance. The avoidance of these side reactions impacts also the safety of the batteries, and redox flow batteries are often given credit as a safer alternative to lithium-ion batteries. According to Wang et al, the improved heat-management provides another safety benefit as the flowing electrolyte carries thermal energy away.

Despite the many advantages of redox flow batteries, several challenges persist. The most advanced type is aqueous vanadium redox flow battery with existing industrial applications (e.g. Hou et al. 2024, Shoaib et al. 2024, Tolmachev 2023, Sánchez-Díez et al. 2021). Its main benefit stems from the utilization of vanadium both as anolyte and catholyte which mitigates the impact of crossover and improves durability. However, the widespread adoption of the vanadium redox flow batteries is limited by the cost and availability of the active material as well as lower energy densities.

One limiting factor for aqueous flow batteries is the solvent itself. Water has a relatively narrow electrochemical stability window that restricts cell voltages as its electrolysis begins at approximately 1.23 V (e.g. Huang et al. 2015). The cell voltage is crucial parameter for a battery since it affects energy density but also power output and energy efficiency.

Non-aqueous redox flow batteries use electrolytes typically based on organic solvents which allow the use of higher voltages (e.g. Tang et al. 2022). Non-aqueous redox flow batteries are much less researched and developed compared to the aqueous alternatives. They still face multiple challenges related to reversibility of the redox reactions, stability of the active species and finding suitable membranes (Huang et al. 2015, Tang et al. 2022).

In addition, the properties of non-aqueous electrolytes differ from aqueous counterparts. For example, they have much more varied viscosities and lower conductivities than water (Milhstein et al. 2017a). These characteristics also influence mass transfer in the system, which is critical for battery performance, as explained in the next chapter.

3 Mass transfer in batteries

Mass transfer refers to the net movement of a species in a multicomponent system. In batteries, mass transfer refers to the movement of mobile ionic species through the electrolyte solution to and from the electrode surface, where the current-generating reactions occur. Mass transfer can also be used to explain the movement of the charged species through the membrane.

The mass transfer of ions is directly linked to the current density. If mass transfer is inefficient at any step, the concentration of the redox active species depletes at the electrode surface which leads to concentration gradients. This restricts further reactions, sets a limit for the current density and reduces cell voltage. Consequently, mass transfer limitations lower the power output and the accessible capacity of the battery (Milshtein et al. 2017b).

The discussion of mass transfer mechanisms begins by introducing Nernst-Planck equation that is used to depict mass transfer in the bulk electrolyte which is assumed to be dilute. Each term of the equation, corresponding migration, diffusion and convection, are analysed separately and expanded to acknowledge porous media. Mass transfer is also linked to mass balances and to the performance of a battery, including overpotentials and current density.

This chapter is based on the textbook Electrochemical Engineering (2018) which is edited by Thomas Fuller and John Harb. This section relies especially on the book's chapters on electrochemical kinetics (by Alexander Naumovich Frumkin), and transport (by Carl Wagner).

3.1 Mass transfer within the electrolyte

The fundamental equation of mass transfer in a fluid medium is the Nernst-Planck equation which is used to determine the flux of a certain species in a solution. The flux of the species is given as a combination of three terms, each of which describes a different method of mass transport.

$$\boldsymbol{N_i} = -z_i u_i F c_i \boldsymbol{\nabla \Phi} - D_i \boldsymbol{\nabla c_i} + c_i \boldsymbol{v} \tag{1}$$

The molar flux of the species is expressed in units of $[\mathrm{mol\ m^{-2} s^{-1}}]$. The first term on the right side of the equation characterizes the movement of ions as a response to an electric field, the second term describes diffusion and the third refers to the convective transportation.

In Nernst-Planck equation the solution is presumed to be dilute, meaning that most of the interactions in the solution are between the ions and the solvent molecules. Interactions between solute particles are ignored, although this is a simplification. In addition, fluid flow through a porous material, such as the electrodes, is considered to be laminar.

As explained in the previous chapter, the redox reactions in batteries occur on the surface of the electrodes. The consumption or the generation rate of a certain ion on the electrode surface is denoted with R_i. Under a steady-state condition, the divergence of the active species flux equals the local reaction rate. The following equation for mass conservation holds for the species.

$$\nabla \boldsymbol{N}_i = R_i \tag{2}$$

3.1.1 Migration

The mass transfer of charged species because of an electric field is called ion migration. In batteries, ion migration accounts for the current continuity between the electrodes and ensures local charge balance in the electrolyte. The driving force of the ion migration is the electric field created by the difference in potential, expressed as $\nabla\Phi$ in the equation 3.

$$\boldsymbol{J}_i^{migration} = -z_i u_i F c_i \boldsymbol{\nabla\Phi} \tag{3}$$

The force resulting from the electric field is given by $-z_i F\boldsymbol{\nabla\Phi}$, in which z_i is the charge of the species and F is Faraday constant. Faraday constant is the total charge carried by one mole of electrons and equals 96 485 C mol^{-1}. Ion migration also depends on the concentration of the species c_i and on the mobility of the ion u_i. In dilute solutions, the mobility of an ion connects to the diffusion coefficient by the equation $D_i = RTu_i$. The diffusion coefficient is discussed further in the context of diffusion.

The equation can be simplified by introducing the concept of electrical conductivity κ. The movement of all charged species results to current which is depicted in the equation $\boldsymbol{i} = F\sum z_i \boldsymbol{N}_i$. If the migration term is inserted on the place of the flux, a following relation is obtained.

$$\boldsymbol{i} = -F^2\nabla\Phi\sum_i z_i^2 u_i c_i \tag{4}$$

The equation 4 is an extended form of Ohm's law which relates current to potential difference with a proportionality factor defined as specific conductivity. The general form in equation 5 considers the effect of all charged species instead of focusing on one.

$$\boldsymbol{i} = -\kappa \boldsymbol{\nabla\Phi} \tag{5}$$

Specific conductivity has the units of [S m^{-1}] and it refers to the ability of the material to conduct current. However, this version of Ohm's law applies only when the other mass transfer pathways do not contribute to the current, and especially the total diffusive flux is zero. It also assumes the solution to be dilute. If this is the case, conductivity is inversely proportional to specific resistance of the electrolyte. The overall resistance regards also the geometry of the system, namely the cross-sectional area of the system and the distance between the electrodes. More commonly, Ohm's law is written as $V = IR$, in which V means voltage, I is current and R is resistance or the reciprocal of conductivity.

If the electrolyte conducts current inefficiently, more energy is required to drive the same current than in a system with higher conductivity. The resistance results to differences between the over-circuit potential and cell potential which are called ohmic losses. Ohmic losses can be minimized by increasing the concentration of the active species or the concentration of other electrolytes.

A central method for reducing ohmic losses is the use of a supporting electrolyte. A supporting electrolyte is highly conductive but most often does not participate in the redox reactions itself. The added ions enhance the ionic conductivity of the solution which means that more of the applied voltage can drive the reactions of the active species on the electrode surface.

In porous media, both the porosity ε and the tortuosity τ affect conduction. The effective conductivity in the electrode can be written as follows.

$$\kappa_{eff} = \kappa_{bulk} \frac{\varepsilon}{\tau} \tag{6}$$

The coefficient including the porosity and the tortuosity factors can be used for diffusion as well (Newman 2018).

3.1.2 Diffusion

The outcome of diffusive movement in solutions is described by Fick's law. According to it, the driving force of diffusion is concentration gradients, and the direction of movement is from the high concentrations into low concentrations.

$$\boldsymbol{J}_{\boldsymbol{i}}^{\boldsymbol{diffusion}} = -\, D_i \boldsymbol{\nabla} \boldsymbol{c}_{\boldsymbol{i}} \tag{7}$$

In the equation, D_i is the diffusivity or the diffusion coefficient of the species. The diffusion coefficient is specific for the solvated species and solvent. There are many different models for diffusion coefficients. As Cussler (2008) denotes, one of the most widely used models for diffusion in liquids is the Stokes-Einstein relation. It expresses the diffusion coefficient using the Boltzmann constant k_B, temperature T, viscosity of the solvent μ and the effective hydrodynamic radius of the diffusing (spherical) particle r_{eff}.

$$D = \frac{k_B T}{6\pi \mu r_{eff}} \tag{8}$$

The Stokes-Einstein relation shows that the diffusive flux of a species grows with temperature and decreases when the size of the diffusing particles or the viscosity of the solvent is increased. The relation has multiple presumptions. As throughout this chapter, the solution is assumed to be dilute. More importantly, the relation assumes that the size of the diffusing particle is significantly larger compared to the solvent molecules.

Furthermore, in porous media, such as the electrodes or membranes, the diffusion coefficient is usually replaced with the effective diffusion coefficient. The effective diffusion coefficient acknowledges also the porosity and the tortuosity of the medium in a similar manner as presented for the conductivity.

3.1.3 Convection

A central difference between conventional battery designs and flow batteries is the forced convection of the electrolyte from the storage tanks through the electrodes. In other words, flow batteries use pumps which are used to control the flow rate in the system and can compensate other inefficiencies in mass transfer (Forner-Cuenca et al. 2019).

In the Nernst-Planck equation convection is given as a product of the concentration of given species and the average velocity of the fluid. In dilute solutions, the average velocity of the fluid is approximately equal the average velocity of the solvent.

$$\boldsymbol{J}_i^{convection} = c_i \boldsymbol{v} \qquad (9)$$

One method of considering fluid flow in porous media is to replace the average velocity with Darcy's velocity (e.g. Zu & Zhao 2013, Forner-Cuenca et al. 2019). Darcy's velocity considers the permeability of the medium k, viscosity of the solution μ, and the pressure gradient ∇p that drives the motion. The equation below is valid for a slow laminar flow.

$$\boldsymbol{u} = -\frac{k}{\mu}\boldsymbol{\nabla p} \qquad (10)$$

The permeability of a medium depends on the size and shape of the pores. For example, larger pores will lead to a higher permeability and thus to an increased velocity of a fluid. However, larger pores also reduce the available area for desired surface reactions to occur. In redox flow batteries, permeability and the pressure gradient tie into the concepts of flow field and flow rate.

In general, gas evolution and thermal gradients can also generate convection of the fluid, but these are not relevant in most redox flow batteries. Typically, none of the species form gases, and the forced convection carries the heat away effectively from the reaction site.

3.2 Mass transfer, overpotential and current density

In electrochemical systems, the rate of the redox reactions can be controlled by changing the potential. The open-circuit potential U_{cell} and the actual cell potential V_{cell} differ from each other. In practice, the battery needs additional drive to overcome hindrances in the system and reach a certain current. This is called overpotential.

The overpotential comprises of kinetic and mass transfer losses both for the anodic and cathodic sides as well as ohmic losses. During discharge the overpotential lowers the overall cell voltage and during charge is increases the required voltage. Therefore, the signs of overpotential are different for discharge (11) and charge (12).

$$V_{cell} = U_{cell} - |\eta_{anode}| - |\eta_{cathode}| - |\eta_{ohmic}| \qquad (11)$$

$$V_{cell} = U_{cell} + |\eta_{anode}| + |\eta_{cathode}| + |\eta_{ohmic}| \qquad (12)$$

Kinetic losses refer to the activation energies of the electron transfer reactions at the surface. The kinetic contribution to overpotential is commonly governed by the Butler-Volmer equation which is discussed further in the context of current density. In turn, ohmic losses result from the resistance of the cell components. Ohmic losses can also be expressed as iR_{cell} since the overpotential increases linearly with the current.

Ideally, mass transfer would occur at the same rate as the electrochemical reactions proceed. However, this is rarely the case. On the electrode surface, the concentration of the unreacted active species decreases as the reactions occur. If mass transfer cannot keep up with the rate of reaction at the surface of the electrode, the products are unable to move away from the surface and cannot be replaced with new reactants. This means that the mass transfer limitations hinder the surface reactions and concentration gradients form. The resulted potential difference is referred as mass transfer overpotential or concentration overpotential.

Consequently, the consumption or the generation of a species on the surface is dependant of mass transfer. Therefore, it can be written using a mass transfer coefficient k_m, the specific surface area of the porous electrode, and the difference between concentrations in bulk electrolyte and on the surface of the electrode.

$$R_i = k_m A_v (c_{i,b} - c_{i,s}) \tag{13}$$

The mass transfer coefficient incorporates various factors influencing mass transfer into a single parameter. Its value is often expressed as a function of the diffusion coefficient and dimensionless numbers that characterize convective fluid flow (e.g. Xu and Zhao 2013). The specific surface area of the porous electrode equals the ratio of the total surface area and the volume of the electrode (Newman 2018).

At a steady state, the reaction rate equals the divergence of the flux of the redox active species N_i, as shown by the previously presented mass conservation equation. Furthermore, the current in the electrolyte solution resulted from the flux of the charged species as stated by Faraday's law in equation 14.

$$\boldsymbol{i} = F \sum_i z_i \boldsymbol{N_i} \tag{14}$$

At the electrode surface, the flux of the active species must equal the flux of electrons. The currents induced by the fluxes are also the same. The following presentation of the boundary conditions (equations 15 and 16) is adopted from Delgado et al. (2020).

$$\nabla \boldsymbol{i} = j \tag{15}$$

The redox reactions at the surface result in changes in concentration. Combining previous equations, the transfer current density can be connected to the change in concentration of the active species. Below the relation is written for an anodic reaction where n represents the number of electrons transferred per molecule.

$$\frac{j}{nF} = k_m(c_{i,b} - c_{i,s}) \tag{16}$$

Mass transfer limitations can become the primary factor restricting the current density if the reactions occur readily at the surface. In this case, the concentration at the surface approaches zero and the system is said to be operating at a limiting current.

$$j_{lim} = nFk_m c_{i,b} \tag{17}$$

The general form of the Butler-Volmer equation is used if the reaction is limited by the reaction kinetics. Butler-Volmer equation is written for a unimolecular reaction $O + e^- \rightleftarrows R$ on a single electrode.

$$j = j_0 A_v \left[\exp\left(\frac{\alpha_a F \eta_a}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_a}{RT}\right)\right] \tag{18}$$

In the equation, j is the reaction current density at the electrode interface in units of [A m^{-3}]. It is given as a product of the exchange current density j_0 and the difference between the anodic and cathodic reaction rates. The exchange current density measures the rate of the redox reactions at equilibrium potential, and it is dependent on temperature and concentration.

Inside the brackets of equation 18, the first term describes the anodic reaction with a charge transfer coefficient α_a, Faraday constant F, the activation overpotential η_a, the gas constant R, and temperature T. The term for the cathodic reaction is similar, except it has its own charge transfer coefficient α_c and the sign is negative for the opposite direction of the current. The charge transfer coefficient describes how the activation energy changes with applied overpotential for each half-reaction.

An extension of the general equation acknowledges also mass transfer limitations. In the equation 19, concentration ratios appear for both anodic and cathodic reactions, scaling the reaction rates based on the availability of reactants and products at the surface relative to their equilibrium values.

$$j = j_0 A_v \left(\left(\frac{c_{red}^{s,i}}{c_{red}^{i}} \right) \exp\left(\frac{\alpha^{ox} F \eta^{i}}{RT} \right) - \left(\frac{c_{ox}^{s,i}}{c_{ox}^{i}} \right) \exp\left(- \frac{\alpha^{red} F \eta^{i}}{RT} \right) \right) \tag{19}$$

The overpotential in equation 19 includes both kinetic and mass transfer losses. The contribution of mass transfer losses can be evaluated by operating the battery at a limiting current at a known bulk concentration. For example, Xu and Zhao (2013) and Milshtein et al. (2017b) use this method to calculate mass transfer coefficients in redox flow batteries. However, as Xu and Zhao (2013) infer, this method requires certainty that mass transfer is indeed the limiting factor.

Overall, mass transfer significantly influences the battery performance. Mass transfer in bulk electrolyte can be depicted with the Nernst-Planck equation, which gives the flux for a certain species. For the active species participating in redox reactions, the divergence of the flux equals the reaction rate on the electrode surface at steady state. The redox reactions generate current, which is therefore linked to the mass balance on the surface.

The mass transfer coefficient impacts on the surface concentration of the active species by incorporating contributions from all three transport mechanisms into one value. If the mass transfer coefficient is low and the reactants deplete at the surface, the surface concentration drops. Then, a larger overpotential is required to maintain a given current density. High overpotentials indicate inferior performance of the battery as the energy efficiency decreases. In addition, high overpotentials restrict the available state-of-charge, thereby limiting the storage capacity (Milshtein et al. 2017b).

4 Mass transfer in non-aqueous redox flow batteries

In redox flow batteries, the electrodes act only as an electrochemically active surface. This contrasts with conventional lithium-ion batteries where the electrode materials themselves participate in the reactions, but also in flow batteries the reactants and products need to be in contact (or at least in close proximity) with the electrode for the redox reactions to occur.

Many researchers have identified mass transfer as a central issue in redox flow batteries (e.g. Forner-Cuenca et al. 2019, Milshtein et al. 2017b, Weber et al. 2011). According to Weber et al., overpotentials resulting from kinetics are typically not as challenging as the mass transfer of redox active species. Similarly, Forner-Cuenca et al. observed that the discovery of multiple novel redox couples with fast kinetics has made mass transfer a subject of increasing interest.

The mass transfer phenomena in redox flow batteries can be divided into micro- and macrolevel transfer (Zhao et al. 2017). On the microscale, the reactants and products are transferred from the pores to the surface and vice versa. On the macroscale, the electrolyte solution (containing the reactants and products) flows to the electrode pores and away from them. On the microscale, diffusion dominates as a transport mechanism (Weber et al. 2011), whereas on the macroscale, convection is much more significant. Moreover, ion migration explains how ions move between the electrodes to create a continuous current.

The discussed factors affecting mass transfer include the properties of the electrolyte, characteristics of the electrode, flow field and flow rate. The chemistry and the properties of the electrolyte define the operational limits for any redox flow battery, as the electrolyte contains the redox-active species responsible for current-generation. However, for a given electrolyte composition, the electrode structure and the flow field define the efficiency of mass transfer in the system (Zhao et al. 2017).

Separators and membranes also play an important role as they prevent the crossover of anolyte and catholyte, thus preserving the reversibility of the redox reactions. Nonetheless, the focus of this thesis is on the mass transfer phenomena within the electrode.

4.1 Electrolyte properties

The composition of the electrolyte plays a fundamental role in mass transfer, since all active species are dissolved in the electrolyte throughout the charge-discharge cycles. An ideal electrolyte solution would have high concentration of redox active species, high conductivity, low viscosity and high diffusion coefficient (Liu et al. 2025). However, the desired properties are often trade-offs with each other. These factors are discussed below.

In non-aqueous redox flow batteries, solvents are typically organic. The most used solvent is acetonitrile because of its low viscosity and high conductivity (Huang et al. 2015, Zhang et al. 2018). Also, propylene carbonate, DMSO, DME and others can be used as solvents in non-aqueous configurations (Luo et al. 2019).

4.1.1 Concentration

An adequate solubility of the reactants is a prerequisite for a viable battery. The concentration contributes to the energy density, but it also appears in each term of Nernst-Planck equation and is directly linked to the current density or the power output of the battery.

The reports on solubility in non-aqueous redox flow batteries vary which reflects the variety in redox couples in non-aqueous solvents. Huang et al. (2015) state that the solubility of commonly explored redox active species (e.g., metal-ligand redox compounds) in acetonitrile is low compared to aqueous batteries. Luo et al. (2019) have made a similar observation in their review study that focused on all-organic chemistries. Generally, the solubilities of active species in non-aqueous solutions are limited (Zhang et al. 2022).

On the other hand, non-aqueous solutions are often given credit for the theoretical possibilities of being compatible with a multitude of possible redox-active materials (Gong et al. 2015). The active species can also be tailored to increase solubility. The modification of the active species usually involves an addition of a functional group that strengthens the solute-solvent interactions (Luo et al. 2019).

The addition of a supporting electrolyte can also affect the solubility of the active materials. Increasing the concentration of a supporting electrolyte, the solubility of the active species is decreased due to competing solubility (Gong et al. 2015). The effect of competing solubility differs for different chemistries.

The concentration of active species also contributes to the physicochemical properties of the electrolyte solution, such as conductivity and viscosity (Zhang et al. 2018, Liu et al. 2025). High concentration can also promote forming of complexes as an unwanted side reaction (Zhang et al. 2018). Therefore, the composition of the electrolyte solution needs to be optimized considering the overall performance of the battery.

4.1.2 Conductivity

The electrolytic solution should be highly conductive to enable ion migration from electrode to another. The choice of solvent is, of course, essential. As mentioned before, acetonitrile is the most widely applied solvent in non-aqueous flow batteries. One reason for this is its relatively high dielectric constant which reflects the ability of the solvent to separate and stabilize ions. This allows more ions to dissolve and convey the current. The dielectric constants of non-aqueous solvents are lower than the dielectric constant of water (Gong et al. 2015).

As discussed in the context of migration in Nernst-Planck equation, the enhanced conductivity allows more of the applied voltage to drive the reactions of the active species by decreasing Ohmic losses. The main method for increasing the conductivity in a given solute is to add a supporting electrolyte. The solubilities of supporting salts are also more limited in organic solvents compared to water (Gong et al. 2015).

The supporting electrolytes are salts that dissolve into cations and anions. According to Gong et al. (2015), the most used supporting anions are tetrafluoroborate, perchlorate and hexafluorophosphate, and the most applied supporting cations are tetraalkylammoniums. The common feature is the small radius of the ions which improves conductivity. The radius is in the denominator of the Stokes-Einstein relation for diffusion coefficient which is also included in the ion migration term as seen in the previous chapter.

As demonstrated by Zhang et al. (2018), increasing the concentrations in non-aqueous solutions first increases the conductivity, until it drops significantly. The drop of conductivity is caused by higher viscosities and increased ion-ion interactions that prevent ion mobility. Therefore, battery performance deteriorates at high concentrations as ohmic overpotential grows.

4.1.3 Viscosity

The viscosity of the electrolyte solution impacts the diffusion coefficient in both migration and diffusion terms of Nernst-Planck equation and the velocity term in convection. As a result, elevated viscosity hinders mass transfer in the electrode, and ion mobility in general, but also requires more pumping power to achieve a certain flow rate.

Primarily, the choice of solvent determines the viscosity, but added salts have an impact as well. From non-aqueous solvents, acetonitrile and dichloromethane (DCM) have especially low viscosities (Gong et al. 2014). For example, acetonitrile has a viscosity of 0.34 mPa s, whereas water has a viscosity of 0.89 mPa s. Nevertheless, high viscosities of non-aqueous electrolytes are considered as a general hindrance for achieving high current densities and power outputs (Luo et al. 2019). This is due to the needs to adjust conductivity by adding a supporting electrolyte, and sometimes also because of the use of larger molecules as redox active species (Barton et al. 2018). In addition, the viscosities of different non-aqueous solvents vary significantly. For example, propylene carbonate has a significantly higher viscosity of 2.53 mPa s (Gong et al. 2015).

Barton et al. (2018) have studied the effect of viscosity on mass transfer by adding different amounts of glucose to aqueous electrolytes. They concluded the impact of viscosity to follow the Stokes-Einstein equation for the diffusion coefficients of active species. The effects of increased viscosity varied for different flow rates and flow fields, but viscosity had a significant impact on the limiting current at all examined flow rates. The internal resistances were controlled which means that increased viscosity affected the mass transfer coefficient. The effect was especially significant on low flow rates when diffusion is the most dominant mode of mass transfer. Also Milshtein et al. (2017a) observed the impact of viscosity on mass transfer in an earlier study when comparing electrolytes based on acetonitrile and propylene carbonate. Acetonitrile-based electrolyte allowed higher current densities than the more viscous solvent.

The addition of active species and supporting electrolytes can have a significant effect on viscosity especially at higher concentrations (Zhang et al. 2018, Liu et al. 2025). As explained above, in the study concerning solution properties of acetonitrile, Zhang et al. found that the viscosities increase drastically when a flow cell is operated at high concentrations. Since the viscosity affects both conduction and the mass transfer coefficients, the optimal concentration of the electrolyte solution might be less than the maximum solubility limit. Therefore, increased viscosity limits concentrations of non-aqueous solutions which consequently limits the achievable energy density of the electrolyte. A similar conclusion is reached by Milshtein et al. (2017a).

Higher viscosities and lower conductivities in non-aqueous systems set further conditions for the other battery components (Barton et al. 2018). Since electrolytes with higher viscosities generally require more pumping power, the hydraulic resistances should otherwise be minimized. Also, low-conductive electrolyte solutions are more susceptible to high resistances elsewhere (Milshtein et al. 2017a). The potentially inferior characteristics of non-aqueous electrolytes thus highlight the optimization of electrode structure and convective electrolyte flow.

4.2 Electrode characteristics

Since the redox reactions occur at the electrode surface, the amount of available surface area is directly connected to the current in batteries. Therefore, increasing the surface area increases the power output. This motivates the use of porous electrodes that allow electrolyte flow through their structure.

However, the amount of surface area becomes irrelevant if mass transfer limitations prevent its utilization and the current densities are low. In addition to fostering a large surface area, the electrode should also have high permeability and conductivity to respectively allow effortless conductive and current flow.

Electrodes are typically made of fibrous carbon materials in both aqueous and non-aqueous redox flow batteries since they have high permeability accompanied with good conductivity (e.g. Zhou et al. 2017). The choice of material impacts also to the spreading of the liquid electrolyte, which is called wettability. According to Forner-Cuenca et al. (2019), in aqueous redox flow batteries, the wettability of the electrode material is recognized as a challenge, and the surfaces are pretreated to improve it. Conversely, the wettability of non-aqueous electrolytes is enhanced because of their lower surface tensions. A better wettability reflects to better utilization of the surface area and thus to higher current densities.

The electrode microstructure should allow uniform flow distribution and avoid the formation of stagnant regions (Weber et al. 2011). The main characteristics for the electrode microstructure include porosity ε and characteristic pore size r_p, in addition to tortuosity τ (Newman 2018). These qualities impact permeability and resistance in the electrode, which also have an effect to mass transfer in the system (Forner-Cuenca et al. 2019).

Electrode thickness is also an important factor for conductivity as it defines the distance that the ions need to migrate. Reducing thickness limits ohmic losses but also decreases the surface area which reflects in the achievable current (Zhou et al. 2017). In addition, the electrode thickness has implications for flow field design, which is discussed in Chapter 4.3.

4.2.1 Porosity and pore size

The porosity refers to the ratio of the empty space and total volume of the electrode. Higher porosity leads to higher permeability, allowing the electrolyte to flow more easily though the electrode and resulting in more efficient mass transfer. Higher permeability is also reflected in a reduced need for pumping. According to Zhao et al. (2017), the typical porosity ranges from 60 to 80 % for a redox flow battery electrode.

Porosity is also related to the ionic conductivity of the electrolyte. The relationship was seen earlier in the context of effective conductivity as defined by Newman (2018). The effective conductivity is directly proportional to the porosity and inversely proportional to tortuosity. The tortuosity refers to the length of the path that a diffusing particle must pass, considering the necessary twists and turns.

As Weber et al. (2011) observe, porosity cannot be increased indefinitely. Increase in porosity results in a decreased surface area at the cost of permeability and conductivity. Yet, researchers have also suggested that amount of surface area does not limit performance when comparing different porous carbon materials (Forner-Cuenca et al. 2019, Simon et al. 2022). The researchers suggest that this is because mass transfer and ohmic losses are much more significant in redox flow batteries than the contribution from charge transfer losses.

4.2.2 Pore size distribution

The characteristic pore size is closely related to the porosity of the material, and similar principles apply. Forner-Cuenca et al. (2019) summarize the effects of the pore size as follows. Large pore size allows for high permeability and rapid electrolyte replenishment, but the total active surface area is smaller. On the contrary, small pore size imply an increased active surface area with more efficient diffusion rates, but a greater pressure drop that affects overall efficiency.

In practice, the porous electrodes are heterogeneous, and the pore size varies. Thus, pore distribution is also an important measure of the electrode microstructure. Forner-Cuenca et al. (2019) have researched the optimum pore size and distribution in redox flow batteries. They examined the performance of three different electrode materials, carbon papers, felt and papers, with an electrolyte based on acetonitrile. The redox active species were organic molecules with fast kinetics to control kinetic losses.

Their main finding was that the highest performing electrode material was carbon felt with a mixture of smaller (10-15 µm) and larger pores (85 µm). Other materials had a more uniform pore size distribution of either small or large pores that lead to either a greater pressure drop or decreased electrochemical performance. According to the researchers, the bimodal pore size distribution of cloth managed to combine the advantages of both structures, thus allowing robust diffusion rates with a limited pressure drop.

The result was replicated by Simon et al. (2022) who experimented on electrolyte solutions based on acetonitrile and propylene carbonate. According to their study, carbon cloth outperformed carbon paper because of higher permeability and inter-pore connectivity. The permeability and conductivity allow the electrolyte distribution to be more uniform as convective flow is eased. Interestingly, they did not observe a coherent impact from variations of the active surface area, tortuosity or porosity. This was attributed to the interconnectedness of the pores and to the importance of convective transfer in flow-through electrodes. Regardless, acetonitrile exhibited lower mass transfer losses with all electrode types, as seen in the figure 2.

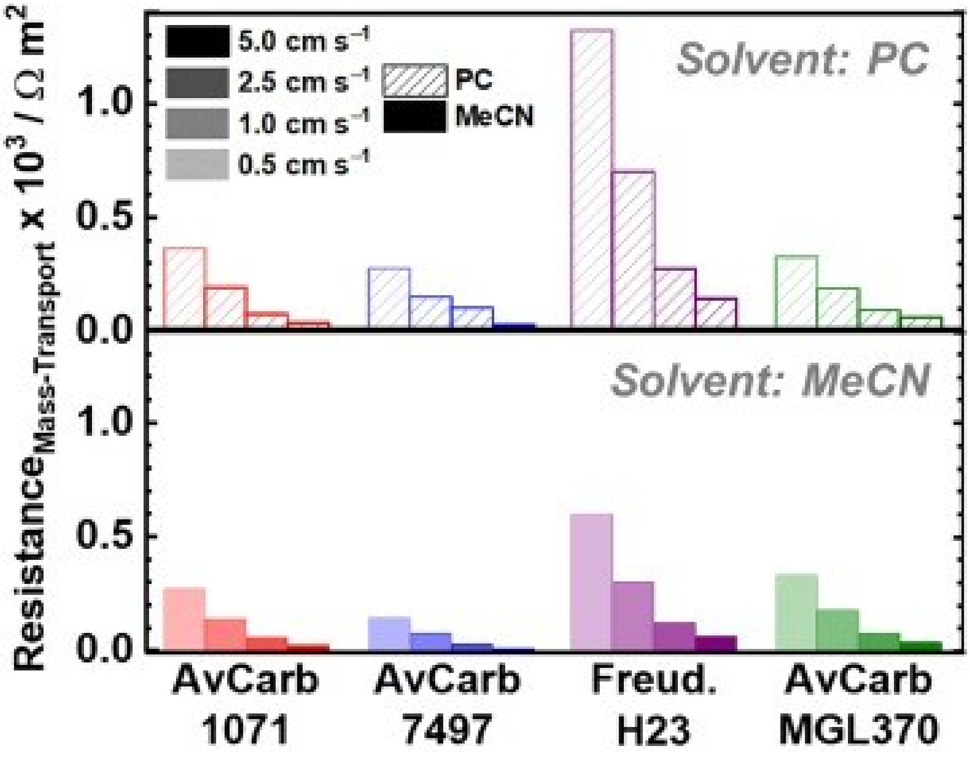

Figure 2 Mass transfer resistances of electrolytes based on acetonitrile (MeCN) and propylene carbonate (PC) in four different electrode materials at four different flow rates. AvCarb 1071 and 7497 are carbon cloths and Freud. H23 and AvCarb MGL370 are carbon papers. From Simon et al. 2022.

Forner-Cuenca et al. and Simon et al. researched flow-through configurations. An analogous result for flow-by configurations was achieved earlier by Zhou et al. in 2016. They developed a dual-scale porous electrode from carbon paper whose surface was etched to create smaller pores. As a result, the total surface area increased 16-fold while permeability remained unchanged. The dual-scale electrode also had a significant impact on the performance of an aqueous vanadium redox flow battery. The battery was able to maintain high energy efficiency even at high current densities. Correspondingly to Forner-Cuenca et al., the researchers observed smaller pores facilitated high diffusion rates while the larger pores allowed the bulk electrolyte to flow.

To summarize, the principles of electrode design are the same for both aqueous and non-aqueous electrolytes. The wettability of the electrode might be superior for non-aqueous electrolytes but higher viscosities of certain solvents impact mass transfer adversely. To some extent, this can be compensated by a suitable electrode structure.

4.3 Flow rate and flow field

In redox flow batteries, pumps circulate the electrolyte solution from external containers through the electrode. Flow rate describes how fast the electrolyte is pumped through the system. Increasing the flow rate improves mass transfer and influences the effective diffusion rate (e.g. Barton et al. 2018, Xu and Zhao 2013). However, an increased flow rate also requires increased pumping which also reflects in higher associated costs.

A flow field guides the convective flow of the bulk electrolyte, ensuring even distribution across the porous electrode. Uniform distribution of the electrolyte is necessary for efficient and controlled mass transfer. A well-designed flow field is also used to decrease pressure drop, thus minimizing pumping costs (Lu et al. 2024).

4.3.1 Flow rate

The flow rate determines the initial velocity of the bulk electrolyte entering the porous electrode. Increasing the flow rate generally enhances mass transfer by replenishing the reactants at the electrode surfaces more efficiently. In addition, a higher flow rate also prevents the formation of stagnant areas in the electrode (Simon et al. 2022). Therefore, concentration overpotential decreases, thus allowing the cell to operate more efficiently, and the limiting current is increased (Milshtein et al. 2017b).

There are limits to the benefits for two reasons. First, higher flow rate requires more pump work which affects the energy efficiency of the battery. The pumping costs also depend on the viscosity of the solution. Moreover, the viscosity impacts how changes in pumping power reflect to the electrolyte velocities (Simon et al. 2022). Naturally, the velocities of less viscous solutions increase more readily than those of viscous solutions.

Second, increasing the flow rate has a smaller impact as the velocity increases and mass transfer becomes more efficient. Both Forner-Cuenca et al. (2019) and Milshtein et al. (2017a) report "diminishing returns" when measuring battery performance on varied flow rates. They hypothesize that this is due to mass transfer reaching its maximum. At this point, ohmic resistance and reaction kinetics become limiting factors instead of mass transfer.

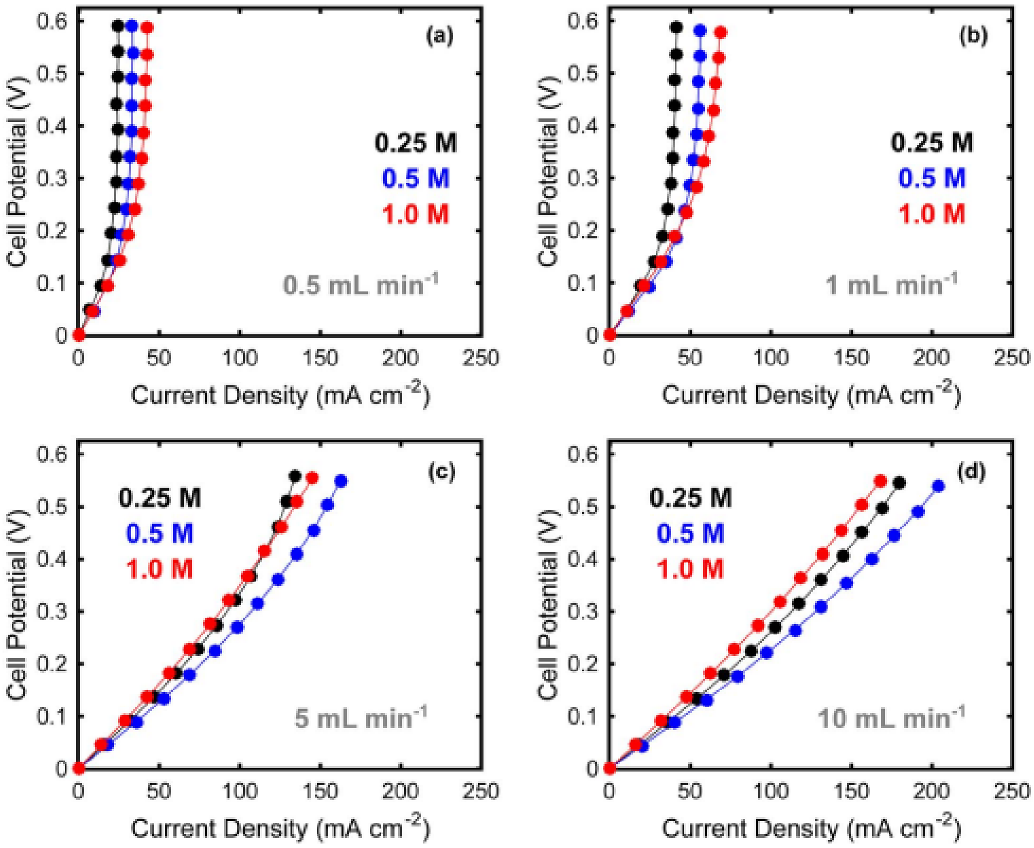

Figure 3 The cell polarization graphs for increasing flow rates. The flow rates for (a), (b), (c) and (d) are 0.5, 1.0, 5.0 and 10.0 mL min^{-1} respectively. From Milshtein et al. 2017a.

The impact of the electrolyte velocity varies also for different electrode structures. Forner-Cuenca et al. (2019) report that increased velocity minimizes mass transfer losses especially when examining electrodes with hierarchical structure and smaller pore size. Also Simon et al. (2022) note that mass transfer coefficients in carbon cloths are more sensitive to velocity changes than carbon papers.

In addition, state-of-charge should be considered when determining the optimal flow rate. State-of-charge defines the active species concentration of the electrolyte entering the electrode. Therefore, Ma et al. (2012) suggest increasing the flow rate at the end of charge and discharge processes when the concentration of the active species decreases. This method allows the optimization of pump work based on mass transfer limitations and enables higher capacity. They also note that the flow rate should be optimized separately for the charge and discharge cycles as they exhibit varying overpotentials (see also Delgado et al. 2020).

4.3.2 Flow field

Flow fields are typically moulded on bipolar plates that connect the individual cells into a cell stack. As explained in the previous section, a flow field determines the direction of the convective flow of the bulk electrolyte to and from the porous electrode. It also affects the pressure drop across the cell stack (Lu et al. 2024).

Flow fields are divided into flow-through and flow-by configurations (Newman 2018). In a flow-through design, the electrolyte is forced to flow through the electrode matrix which enhances mass transport. As reported by Zhou et al. (2017), however, a flow-through design necessitates thicker electrodes to reduce the pressure drop especially in commercial-scale solutions. Increasing the electrode thickness increases ohmic losses which deteriorates battery performance. Following Zhou et al., this has led researchers to investigate flow-by configurations. The flow-by design allows the use of thinner electrodes, thus avoiding the large ohmic losses.

There are multiple configurations of flow-by designs. Lu et al. (2024) discuss the impact of these various alternatives on mass transfer in redox flow batteries. The review article categorizes flow fields into four traditional designs and presents novel structures for enhanced performance. The traditional flow fields include no-flow, parallel, serpentine and interdigitated configurations. The research has focused more on the latter two designs because of their superior performance in flow batteries.

A serpentine flow field has a channel or channels that meander across the entire electrode. An interdigitated flow field resembles a flow-through configuration, as the field forces the electrolyte flow through the porous electrode but via interlaced channels. According to Lu et al., the latter design allows more uniform distribution of velocity and mass transfer and results in the smallest pressure drop across the stack. The researchers note that in large-scale stacks with serpentine flow field, the pressure drop increases considerably (see also Milshtein et al. 2017b), but the performance can be improved by adding multiple parallel serpentine channels.

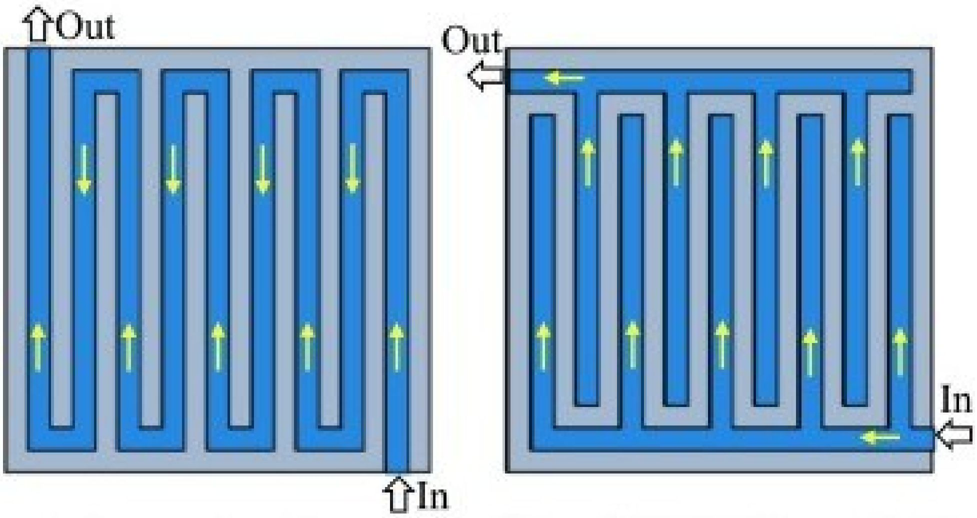

Figure 4 The structures of a single serpentine flow field and an interdigitated flow field. From Lu et al. 2024.

The choice of a flow field should be optimized considering the whole system. According to Lu et al., for example increasing the flow rate and the electrode permeability have varying effects on the performance of different flow fields. Barton et al. (2018) reported that also electrolyte viscosity affects the behaviour of different flow fields. At low flow rates, the performance of an interdigitated flow field was more sensitive to an increased viscosity compared to flow-through configuration. This effect was mitigated at higher flow rates, but it demonstrates the complexity of battery design.

5 Summary

Mass transfer has been identified as a challenge for redox flow batteries (e.g. Tang et al. 2022, Forner-Cuenca et al. 2019, Milshtein et al. 2017b, Weber et al. 2011). Mass transfer is critical for the battery performance, as it can limit the achievable current density and storage capacity (Milshtein et al. 2017b). Mass transfer in redox flow batteries differ from the conventional batteries as the electrolyte is circulated through the electrodes with forced convection.

The composition of the electrolyte is fundamental for mass transfer. Ideally, the electrolyte solution would have high concentration of active species, high conductivity, low viscosity and high diffusion coefficient (Liu et al. 2025). Although non-aqueous solvents enable the use of various redox active couples, until now the solubilities have generally been low (Zhang et al 2022). This is among the primary issues for redox flow batteries as the concentration of active species determines the energy density of the battery. Nevertheless, as mentioned above, an adequate solubility of the active species is not the only criterion for the electrolyte chemistry.

One of the key factors impacting mass transfer is viscosity. First, viscosity affects the effective diffusion coefficient, as high viscosities hinder diffusion in the electrode pores. This impacts also ion migration, or the ionic conductivity of the electrolyte. Second, high viscosities decrease the velocity of the bulk electrolyte which slows down the replenishment of reactants on the electrode surface. Therefore, the effect of viscosity is greater compared to conventional ones where conduction is not a dominant transport mechanism (Milshtein et al. 2017b).

The viscosities of different non-aqueous solvents vary but the conductivities are generally lower compares to water (Gong et al. 2025). The concentration of active species and supporting salts also impact these parameters. The electrolyte composition should be optimized considering mass transfer, which might require limiting the concentration for lower viscosity and more efficient mass transfer (Zhang et al. 2018, Milshtein et al. 2017a).

For a given electrolyte composition, the efficiency of mass transfer is determined by the electrode structure, flow rate and flow field. The better wettability of non-aqueous electrolytes is an advantage compared to aqueous systems, as it removes the need to pre-treat the electrode surfaces (Forner-Cuenca et al. 2019). Otherwise, the design principles are essentially the same for aqueous and non-aqueous electrolytes. The research suggests that highly permeable electrode materials with a bimodal pore size distribution result in more efficient mass transfer (Forner-Cuenca et al. 2019, Simon et al. 2022).

Increasing the flow rate accelerates mass transfer on the electrode surface and prevents the formation of stagnant areas in the electrode (Simon et al. 2022). However, maintaining a higher flow rate requires more pump work, which decreases the overall energy efficiency and increases costs. This is especially notable with more viscous electrolyte solutions (Simon et al. 2022).

Finally, mass transfer is also impacted by the flow field which distributes the electrolyte solution to the electrode. Traditionally, redox flow batteries have utilized flow-through configurations because of mass transfer efficiency (Weber et al. 2011). In commercial applications flow-by structures might be preferred because they exhibit lower ohmic losses (Zhou et al. 2017). Novel flow field types can facilitate more uniform electrolyte distribution with a reduced pressure drop, which in turn improve mass transfer rates (Lu et al. 2024).

To date, non-aqueous redox flow batteries are much less researched and the methods to measure performance are less coherent than in aqueous systems (Zhang et al. 2022). For example, multiple studies have provided quantitative estimates for mass transfer correlations and effective diffusion coefficients in aqueous systems (e.g. Xu and Zhao 2013). For non-aqueous systems, such studies have been considerably more limited. This is likely due to the ongoing search for optimal combination of high-performing redox active couple and a suitable solvent.

The scope of this study was restricted to the general factors affecting mass transfer to and from the electrode surface. Consequently, the investigation of membranes and separators was excluded, although finding suitable membranes has proved to be one of the crucial bottlenecks for the development of non-aqueous redox flow batteries (Zhang et al. 2022, Yuan et al. 2021). Non-aqueous systems are still in an early phase of development, but the research is showing continued progress in discovering new redox chemistries and improving overall system design.

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