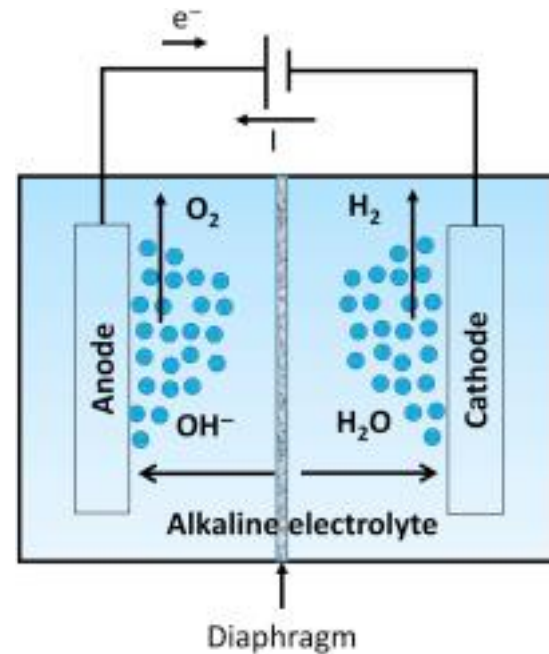# Heat transfer issues in large-scale electrolysis

Lorenzo Botto

Process and Energy Department, Delft University of Technology

TUDelft

Motivation

EU target of 80%–95% greenhouse gas reductions by 2050 compared with the 1990 levels

Aim: current densities >200 mA cm^{-2}

Current operational range: ~35 mA cm^{-2}

CO2

↓

Electrolysis
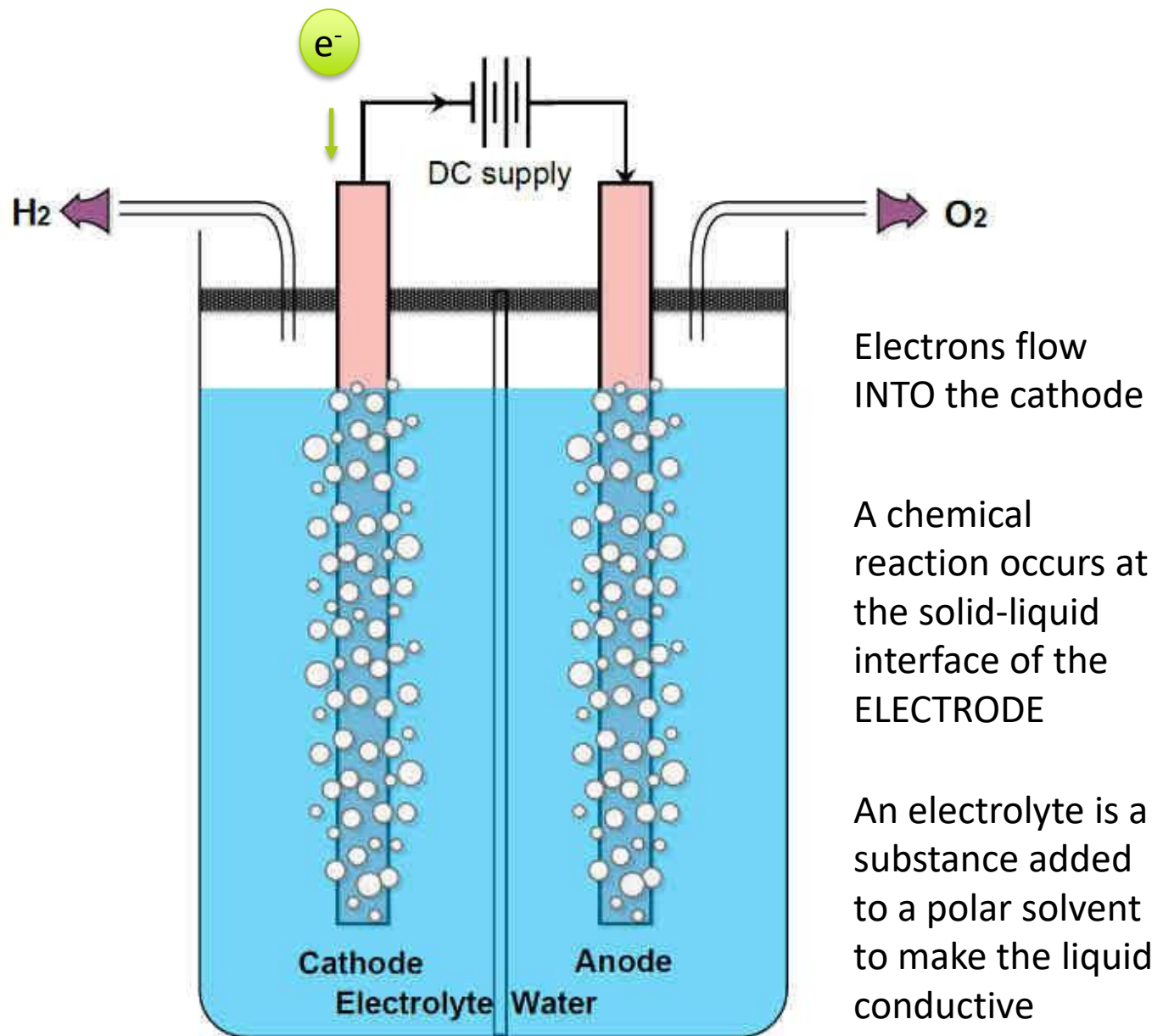
↓

Fuels

Chemical precursors (e.g. methane, etylene)

Electrons flow INTO the cathode

A chemical reaction occurs at the solid-liquid interface of the ELECTRODE

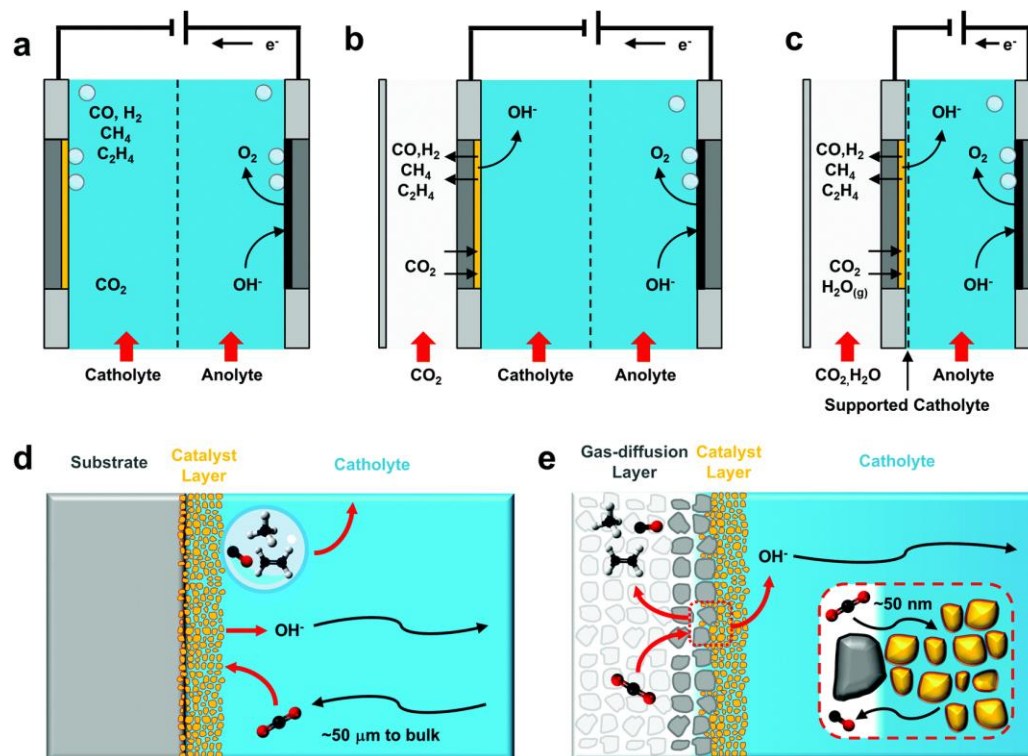An electrolyte is a substance added to a polar solvent to make the liquid conductive

Modelling literature focussed on ALKALINE WATER ELECTROLYSIS. CO2?

Thomas Burdyny

CO2 electrolysis

Reaction "at the wall"

Reaction at a gas-fluid intercace inside a porous medium

Configurations can be very different (reduction of CO2 saturated catholyte vs gas-diffusion layer; flowing or non-flowing catholyte)

Bubbles can form (reaction products, e.g. methane CH4; oxygen at the anode)

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Loss: drop in voltage due to an inefficiency in the process

WB3595 Final Report Group 1

Scaling Up Electrolysis:
## Multiphase and Heat Transfer Problems

Frederieke Backelandt 4978501
Pepijn van den Bent 4660390
Rohit Bissumbhar 4565606
Wout Dekkers 4928377
Dirk Jacobs 4872509

- The **Ohmic overpotential** is an overpotential due to the transport of the ions between the electrodes. The resistance that these ions will endure comes out in the form of heat and can be derived from Ohm's law (Wang and Sun, 2015).

- The **electric overpotential** is caused by the resistance the electrons encounter flowing through the electrodes. Since the electrodes' material is highly conductive, this overpotential has a small contribution to the heat generation (Cretti, 2020).

- The **activation overpotential** is caused by the activation energy for the cell reaction at the electrode-electrolyte interface. The activation energy barrier is caused by multiple phenomena, such as the activation energy of the chemical reactions, the absorption and desorption mechanisms of the molecule on the electrode surface, and the molecules' rearrangement after the reaction etc (Menictas et al., 2014).

- The **concentration overpotential** is caused by the limited rate of mass transport, the product accumulates on the surface of the electrodes and creates a lack of the reactant in order for the process to continue. This phenomenon can occur when the mass transfer is relatively slow compared to the conversion (Cretti, 2020)

- the **decomposition overpotential** correlates with a increasing potential. When this occurs the anodic dissolution starts and the so-called **decomposition overpotential** is obtained (Wang and Sun, 2015).
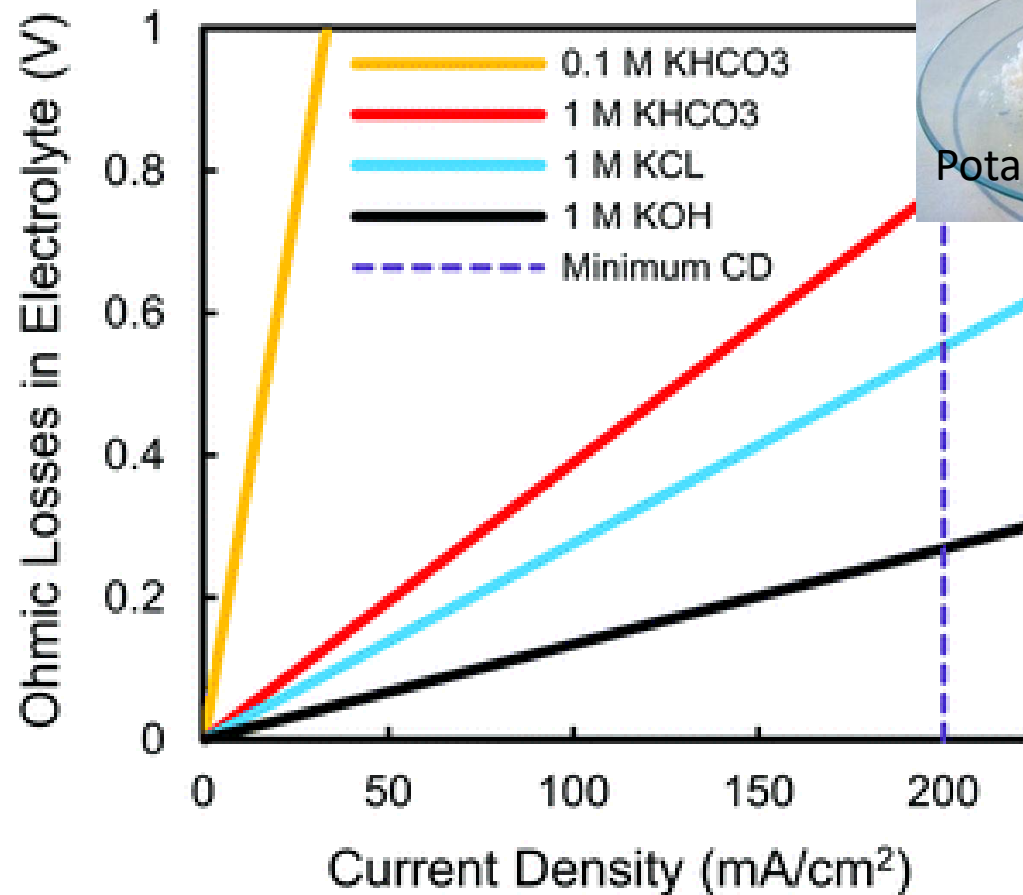
Expected ohmic losses as a function of current density for commonly-used electrolytes in an electrochemical cell with a combined 3 mm catholyte and anolyte thickness at 25 °C.

For 0.1 M $KHCO_3$ (a common concentration) loss is 6V!
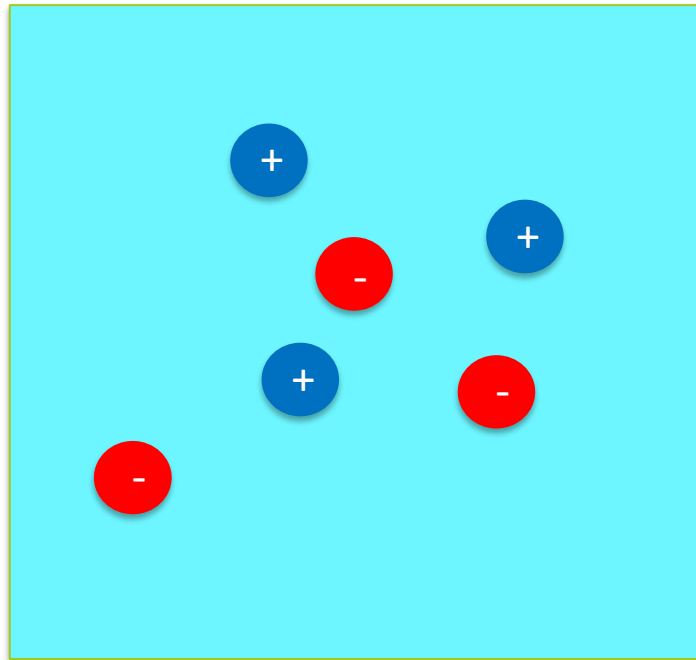
Scale up
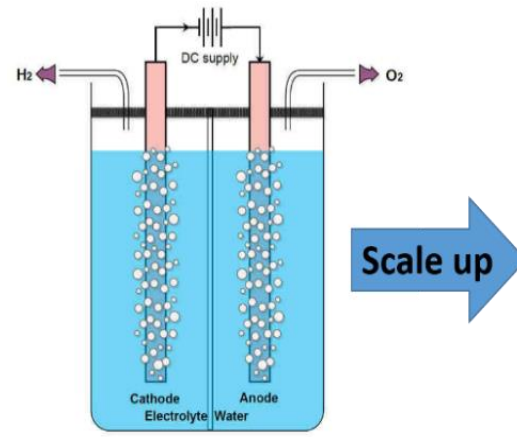
Project E-Heat:
understanding/quantifying heat production in CO2 electrolytes

- A BIG fraction (30%) of the input electrical power is LOST in heat
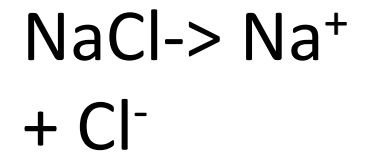- If we understand the physics, we can mitigate ohmic loss or REUSE THE WASTE HEAT

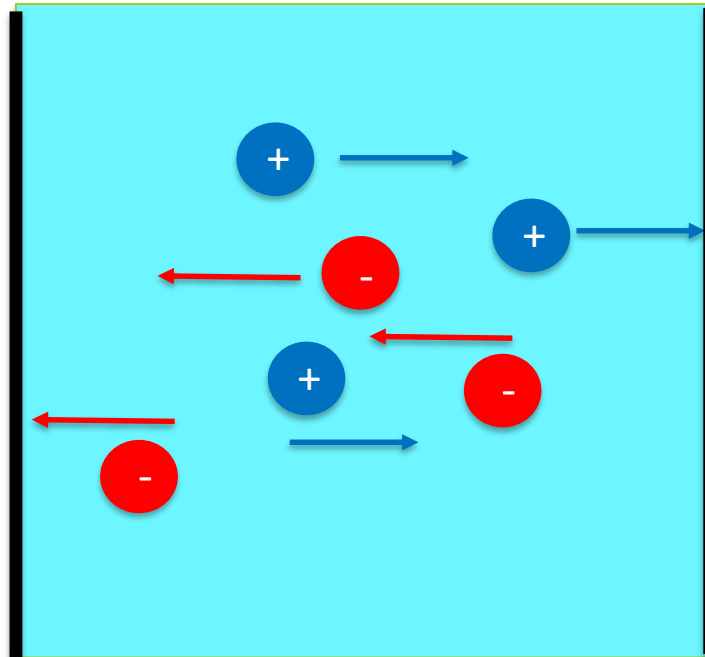# Microphysics of heat loss due to ion migration

No electric field

Electric field applied

+   −

Dissociated ions, e.g.:

NaCl-> Na$^+$ + Cl$^-$

Single-ion hydrodynamics

Force balance: $\quad \boldsymbol{F}_{ext} + \boldsymbol{F}_{hd} = 0$
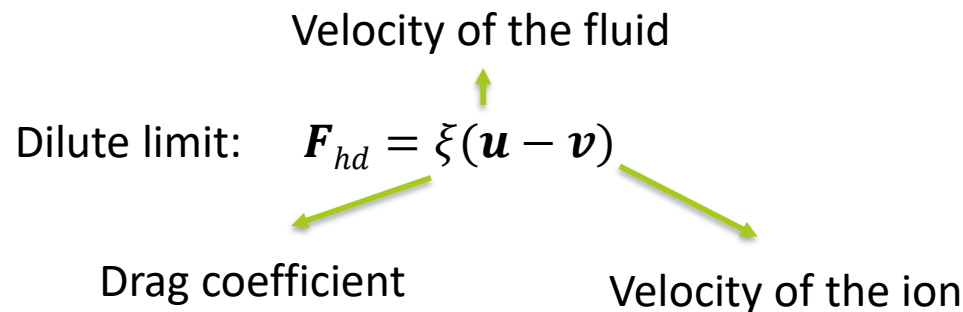
Closure for the drag:

Velocity of the fluid

Dilute limit: $\quad \boldsymbol{F}_{hd} = \xi(\boldsymbol{u} - \boldsymbol{v})$

Drag coefficient $\qquad$ Velocity of the ion
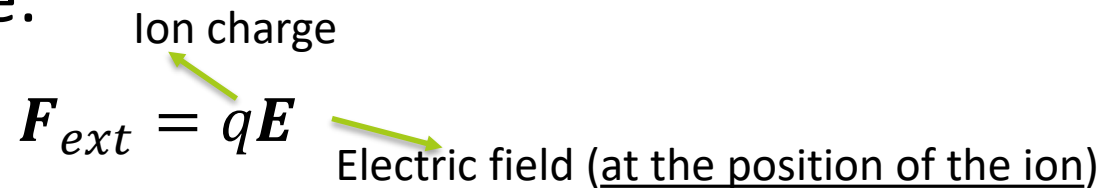
External force:

Ion charge

$$\boldsymbol{F}_{ext} = q\boldsymbol{E}$$

Electric field (at the position of the ion)

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Link with notion of ion mobility

If fluid velocity is zero, and E is uniform:

$$v = qE/\xi \qquad \text{(unidirectional motion)}$$

Definition: **electrical mobility**

$$\mu_e = v/E$$

Drag coefficient is related to mobility: $\mu_e = q/\xi$

The mobility of the sodium ion (Na^+) in water at 25 °C is $5.19{\times}10^{-8}$ $m^2/(V{\cdot}s)$. A sodium ion in an electric field of 1 V/m has an average drift velocity of $5.19{\times}10^{-8}$ m/s.

Can be measured by measuring ionic conductivity
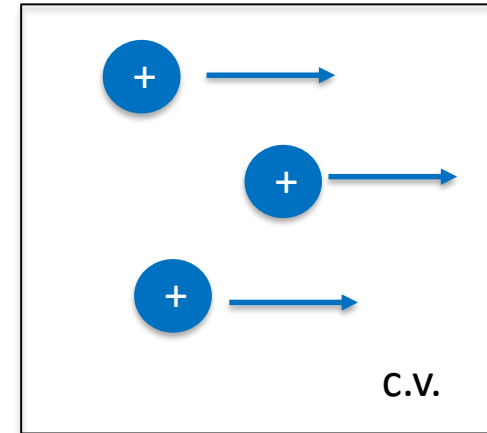
Effect of ion migration on the fluid

Hydrodynamic force per unit volume on the fluid by multiple ions

n^k: number density of ion species k

$$\frac{1}{V} \sum \boldsymbol{F}_{hd}^k = n^k q^k \boldsymbol{E}$$

$$(\partial_t \boldsymbol{u} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}) = (\nabla \cdot \boldsymbol{\sigma} + \rho^{(f)} \boldsymbol{E})$$

c.v.

See e.g. Russel, William Bailey, et al. *Colloidal dispersions*. Cambridge university press, 1991 (pag 216).

Can we calculate heat loss from this expression?

Viscous dissipation by moving ions

$$\boldsymbol{u} \cdot (\textit{momentum equation }) = 0$$

$$\boldsymbol{u} \cdot (\partial_t \boldsymbol{u} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}) = \boldsymbol{u} \cdot (\nabla \cdot \boldsymbol{\sigma} + \rho^{(f)} \boldsymbol{E})$$

$$\partial_t \left(\frac{1}{2} \rho u^2 \right) + \boldsymbol{u} \cdot \nabla \left(\frac{1}{2} \rho u^2 \right) = \nabla \cdot (\boldsymbol{u} \cdot \boldsymbol{\sigma}) - \nabla \boldsymbol{u} : \boldsymbol{\sigma} + \rho^{(f)} \boldsymbol{E} \cdot \boldsymbol{u}$$

<0: viscous dissipation (loss of mechanical energy of the fluid)

$$\rho^{(f)} \boldsymbol{E} \cdot \boldsymbol{u} = ?$$

Electric body force in general is NOT in the same direction of the fluid velocity

Electrokinetic dissipation term

$$\rho^{(f)} \boldsymbol{E} \cdot \boldsymbol{u} = ?$$

A component of this work must be dissipated. Let's calculate it..

$$\boldsymbol{u} = \boldsymbol{v^k} + (\boldsymbol{u} - \boldsymbol{v^k})$$

$$-q^k \boldsymbol{E}/\xi^k$$

$$\rho^{(f)} \boldsymbol{E} \cdot \boldsymbol{u} = \sum_{\boldsymbol{k}} n^{\boldsymbol{k}} q^{\boldsymbol{k}} \boldsymbol{E} \cdot (\boldsymbol{v^k} - q^k \boldsymbol{E}/\xi^k)$$

$$= \sum_{\boldsymbol{k}} n^{\boldsymbol{k}} q^{\boldsymbol{k}} \boldsymbol{E} \cdot v^k - \sum_k q^{k^{\boldsymbol{2}}} n^k \ |\boldsymbol{E}|^{\boldsymbol{2}}/\xi^k$$

Electrokinetic dissipation term

$$\Phi_E = \sum_k q^{k^2} n^k \quad |\boldsymbol{E}|^2 / \xi^k$$

Dissipation due to friction of ions with the fluid during migration

Similar term used in the literature:

$$\rho C_p \left(\frac{\partial T}{\partial t} + (\vec{u}\nabla)T \right) = \nabla(k\nabla T) + \Phi + \frac{(\vec{u}\rho_e - \lambda\nabla\phi)^2}{\lambda}$$

Cetin, Barbaros, and Dongqing Li. "Effect of Joule heating on electrokinetic transport." *Electrophoresis* 29.5 (2008): 994-1005

(derived using the "ohm's law" $\frac{I^2}{\lambda}$, where I is the current and λ is the ion conductivity,

Tang, G. Y., et al. "Modeling of electroosmotic flow and capillary electrophoresis with the joule heating effect: The Nernst− Planck equation versus the Boltzmann distribution." *Langmuir* 19.26, 2003)

Proportional to ion concentration

Proportional to square of LOCAL electric field

15

Transport equations for electrolysis

Cetin, Barbaros, and Dongqing Li. "Effect of Joule heating on electrokinetic transport." *Electrophoresis* 29.5 (2008): 994-1005

$$\nabla(\lambda(T)\nabla\phi) = 0 \tag{13}$$

$$\nabla\vec{u} = 0 \tag{14}$$

This should be a divergence

$$\nabla(\mu(T)\nabla\vec{u}) = \nabla P \tag{15}$$

conductivity

$$\rho C_{\mathrm{p}}\left(\frac{\partial T}{\partial t} + (\vec{u}\nabla)T\right) = \nabla(k(T)\nabla T) + \lambda(T)(\nabla\phi)^2 \tag{16}$$

$$\frac{\partial C}{\partial t} + \nabla((\vec{u} + \vec{u}_{\mathrm{ep}})C - D(T)\nabla C) = 0$$

Nernst-Plank equation

$$\vec{u}_{\mathrm{ep}} = \mu_{\mathrm{ep}}\nabla\phi \tag{18}$$

The electrophoretic velocity is RELATIVE TO THE FLUID; the electrophoretic mobility of the ions is equal to $1/\xi$

+ B. C. for C, T, phi and u

Analogy mass/heat transport

$$\nabla(\lambda(T)\nabla\phi) = 0 \tag{13}$$

$$\nabla\vec{u} = 0 \tag{14}$$

$$\nabla(\mu(T)\nabla\vec{u}) = \nabla P \tag{15}$$

$$\rho C_p \left(\frac{\partial T}{\partial t} + (\vec{u}\nabla)T \right) = \nabla(k(T)\nabla T) + \lambda(T)(\nabla\phi)^2 \tag{16}$$
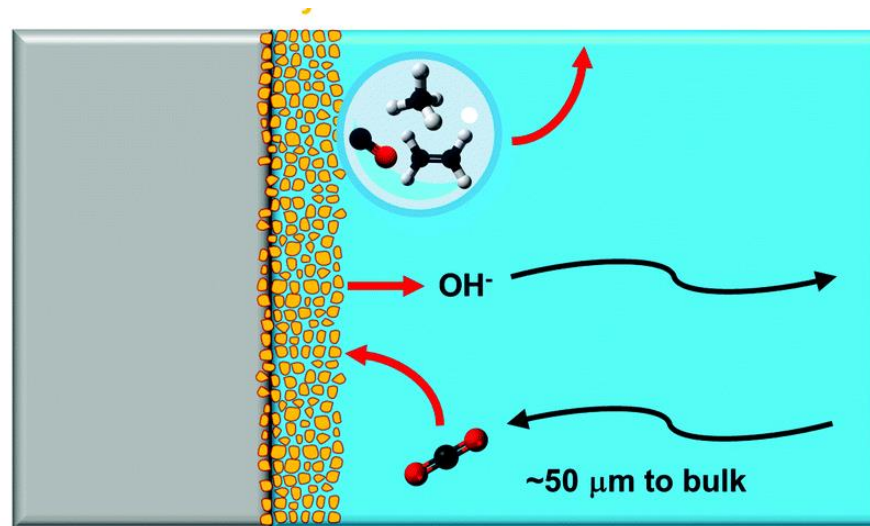
$$\frac{\partial C}{\partial t} + \nabla\left((\vec{u} + \vec{u}_{ep})C - D(T)\nabla C\right) = 0 \tag{17}$$

$$\vec{u}_{ep} = \mu_{ep}\nabla\phi \tag{18}$$

Research questions

Single-phase flow

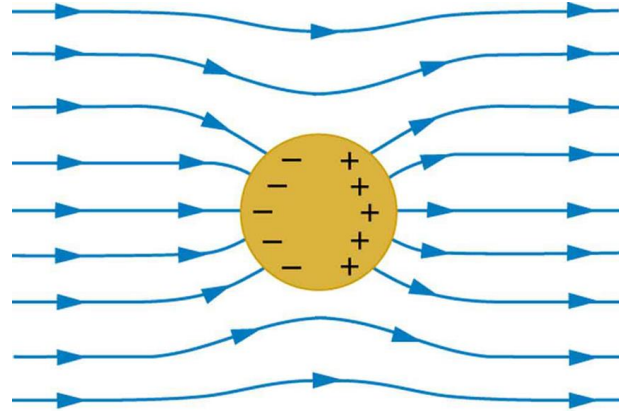Distribution of heat generation in a channel with reacting walls

There will be an excess/defect of reactants or products near the wall

-> Concentration overpotential
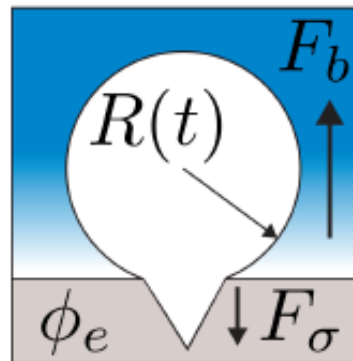
Multi-phase flow

Effect on E

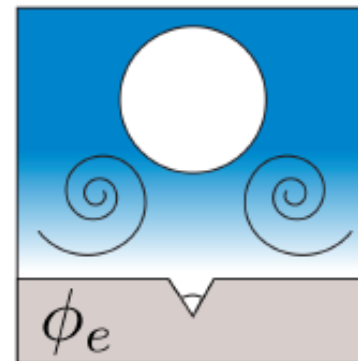Distortion of a uniform electric field by a conducting sphere

Bubbles can become local heat generators

Effect on n^k

B) Growth

F_b

$R(t)$

ϕ_e $\downarrow F_\sigma$

C) Detachment

ϕ_e

van der Linde, Peter, et al. "Gas bubble evolution on microstructured silicon substrates." *Energy & environmental science* 11.12 (2018): 3452-3462.

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https://youtu.be/T-OwWOYHhMI?t=184

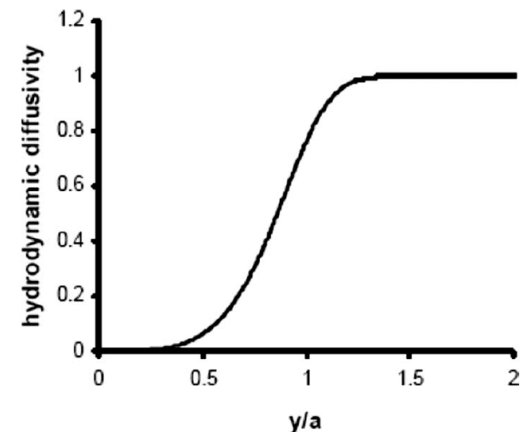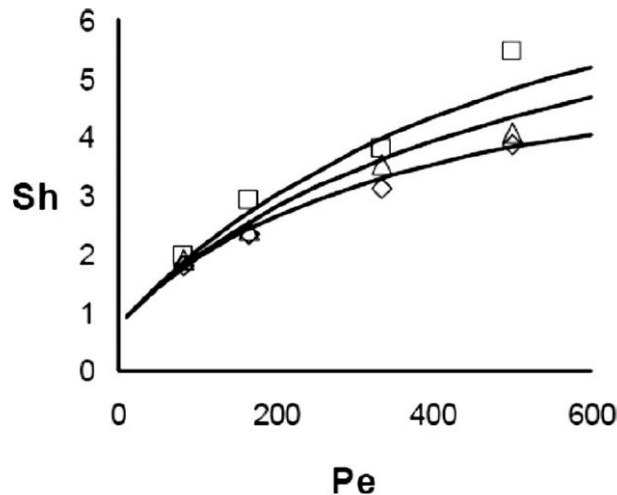High concentration of bubbles near the wall, low concentration far

Bubbles translate because of buoyancy, mixing the fluid

Bubbles are EXTREMELY polydispersed (as in BOILING)

Multi-phase flow

How does a mono or polydispersed
suspension of spheres enhance mixing of
a passive scalar (heat, concentration)?

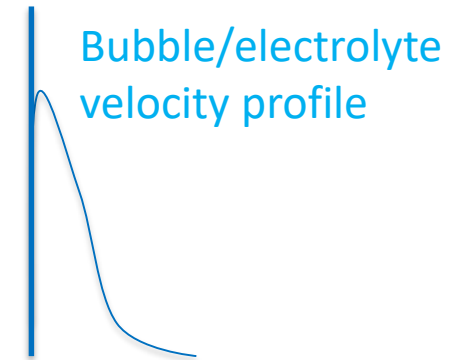Neutrally-buoyant spheres in simple shear flow

Wang, Luying, et al. "Hydrodynamic diffusion and mass transfer
across a sheared suspension of neutrally buoyant
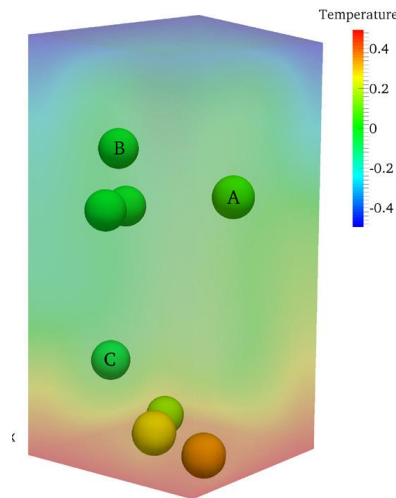spheres." *Physics of Fluids* 21.3 (2009): 033303.

Polydispersity has not been considered

Bubble rich region

Clear fluid

Bubble/electrolyte velocity profile

Nucleation region
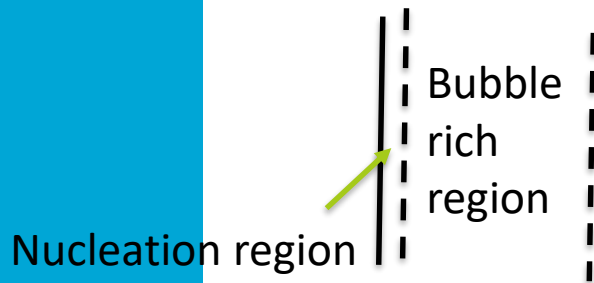
Combined effect of shear/pseudo-turbulence?

Temperature
0.4
0.2
0
-0.2
-0.4

B
A
C

Sun, Bo, et al. "Pseudo-turbulent heat flux and average gas-phase conduction during gas-solid heat transfer: flow past random fixed particle assemblies." *Journal of Fluid Mechanics*798 (2016): 299.

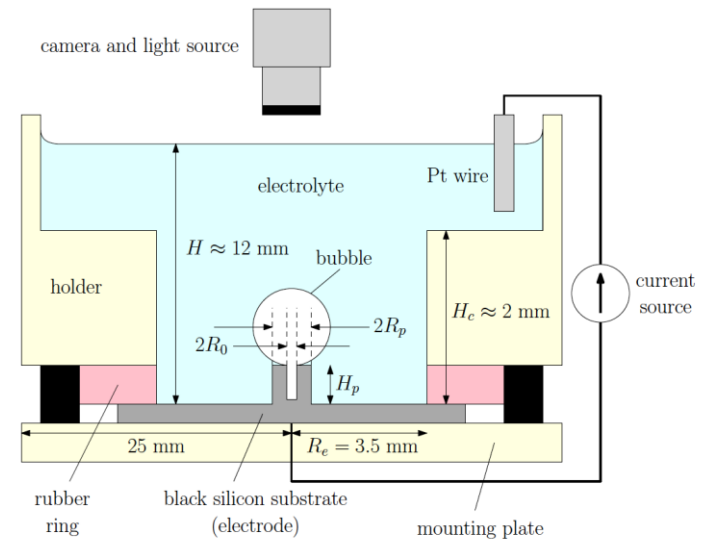Project of Shyam with Physalis code

TU Delft

Summary

- Expression for heat loss by moving ions (electrokinetic viscous loss) derived from simple hydrodynamic considerations

- Need to understand how dispersed phase (bubble) affect ion transport and heat transport (<u>current work of Shyam</u>)

- Need to better understand the link between heat generation by electrokinetic viscous loss and ohmic overpotential

$$\overline{\Delta\Phi}_{ohm} = \frac{iL(1 - K_m)}{\kappa K_m} + \frac{iL}{\kappa}$$

Leistra, James A., and Paul J. Sides. "Voltage components at gas evolving electrodes." *Journal of The Electrochemical Society* 134.10 (1987): 2442.

At TU Delft

Physics of Electrolytic Gas Evolution

C. A. C. Sequeira · D. M. F. Santos · B. Šljukić · L. Amaral

At TU Twente:

van der Linde, Peter. "On electrolytic bubbles." (2019).

$$\rho C_{\mathrm{p}}\left(\frac{\partial T}{\partial t} + (\vec{u}\nabla)T\right) = \nabla(k\nabla T) + \Phi + \frac{(\vec{u}\rho_{e} - \lambda\nabla\phi)^2}{\lambda}$$

See also: Tang, G. Y., et al. "Modeling of electroosmotic flow and capillary electrophoresis with the joule heating effect: The Nernst− Planck equation versus the Boltzmann distribution." *Langmuir* 19.26 (2003): 10975-10984.

Important:

Ohmic dissipation proportional to square of LOCAL electric field

Need to know distribution of electric field

Ohmic dissipation proportional to electrolyte concentration

Need to know how electrolyte concentration depends on diffusion, convection and presence of a dispersed phase

Heat is also transported
Local temperature depends on diffusion, convection and presence of a d