Harnessing Natural Convection in Membraneless Soluble Lead Acid Redox Flow Batteries

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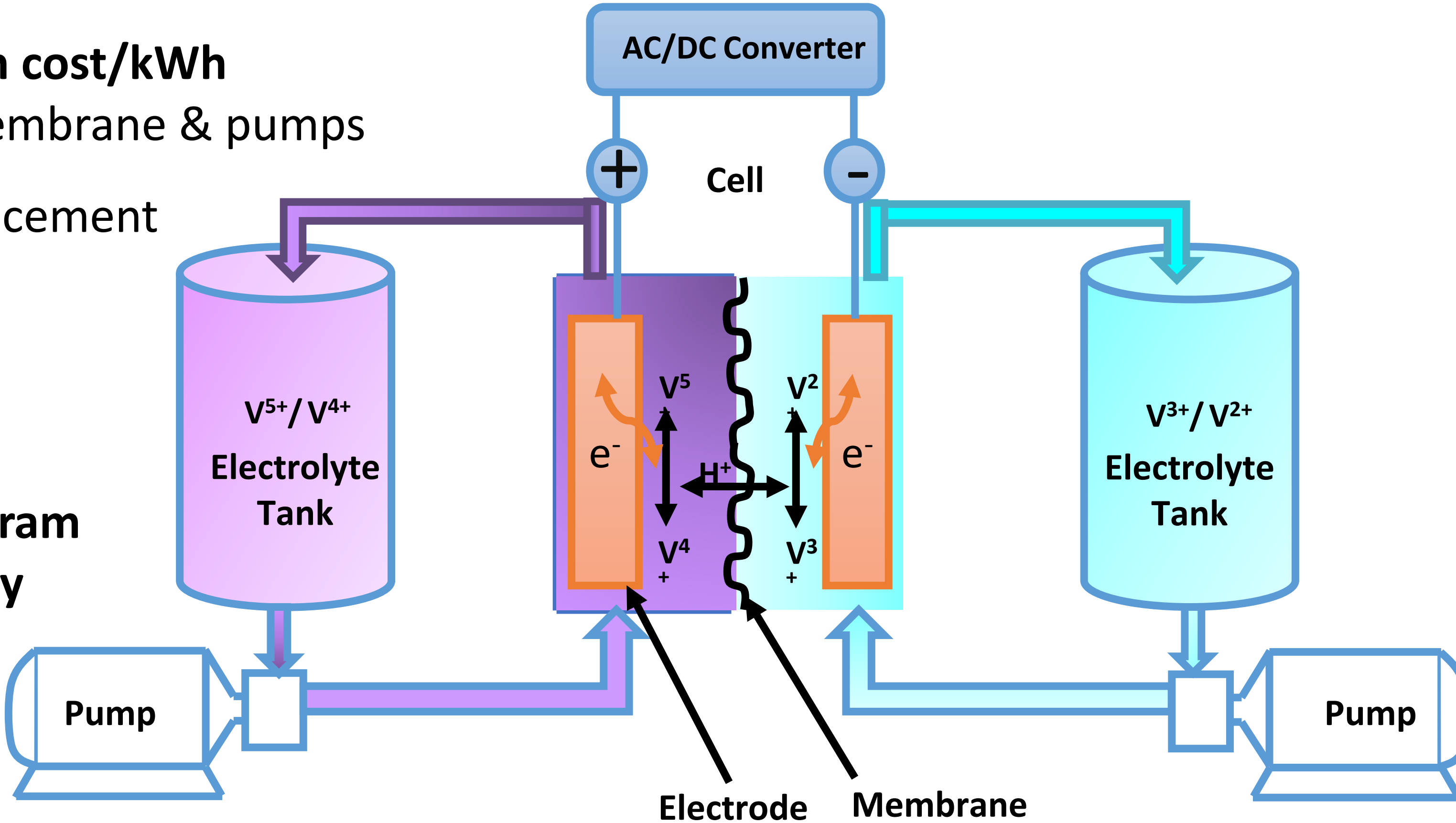
Vanadium Redox Flow Battery (VRFB)

Challenge: High cost/kWh

- Vanadium, membrane & pumps

- Periodic Replacement of membrane

Schematic diagram of VRFB battery



Positive Electrode:

$$VO^{2+} + H_2O \underset{discharge}{\overset{charge}{\rightleftarrows}} VO_2^{\ +} + 2H^+ + e^-$$

Negative Electrode:

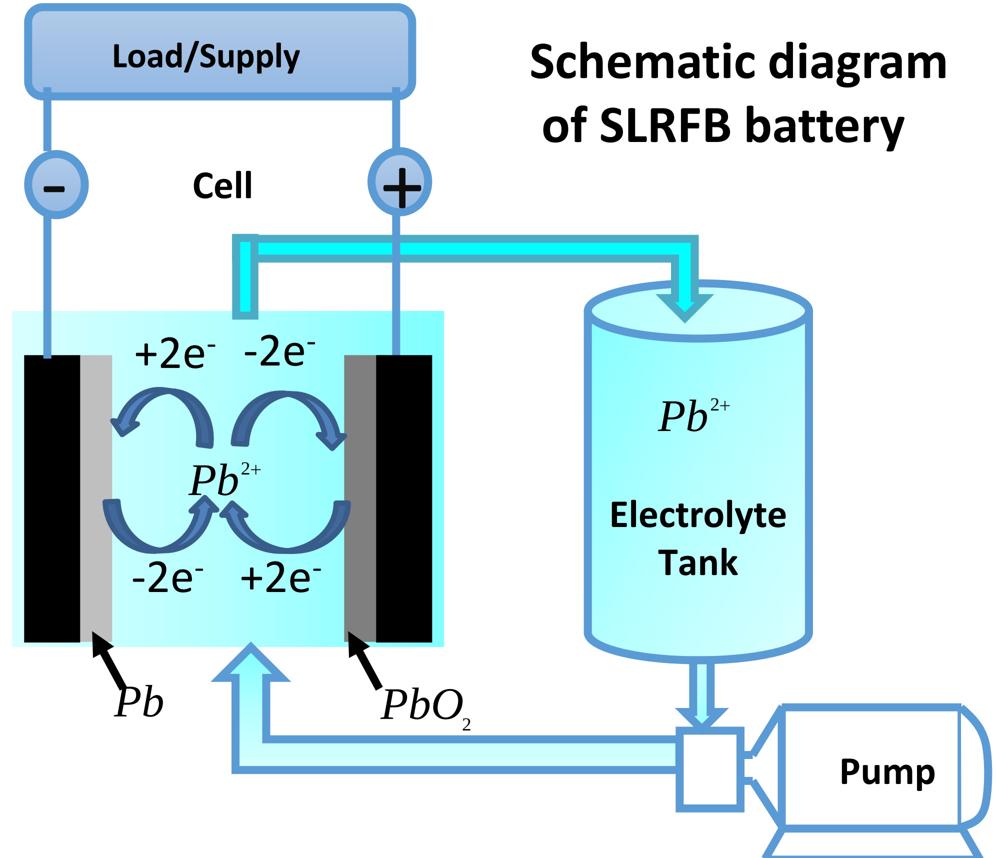
$$V^{3+} + e^- \underset{discharge}{\overset{charge}{\rightleftarrows}} V^{2+}$$

Need to reduce the cost!

http://energystorage.org/energy-storage/technologies/vanadium-redox-vrb-flow-batteries

Soluble Lead Redox Flow Battery (SLRFB)

Challenge: **Low cycle life (~100-2000)**



Schematic diagram of SLRFB battery

Anodic Reaction

$$Pb^{2+} + 2e^- \underset{discharge}{\overset{charge}{\rightleftarrows}} Pb$$

$$(E^0 = -0.13V/SHE)$$

Cathodic Reaction

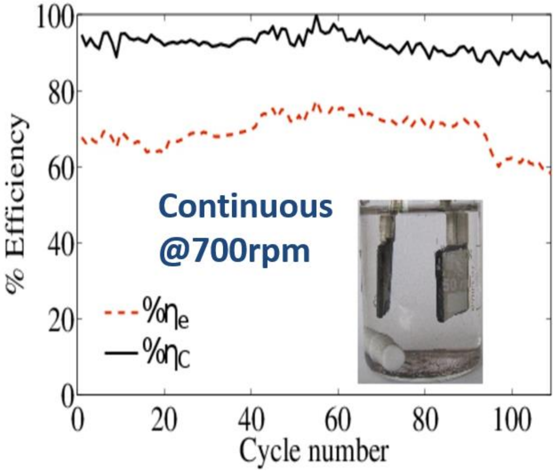
$$Pb^{2+} + 2H_2O \underset{discharge}{\overset{charge}{\rightleftarrows}} PbO_2 + 4H^+ + 2e^- \quad (E^0 = 1.56V/SHE)$$

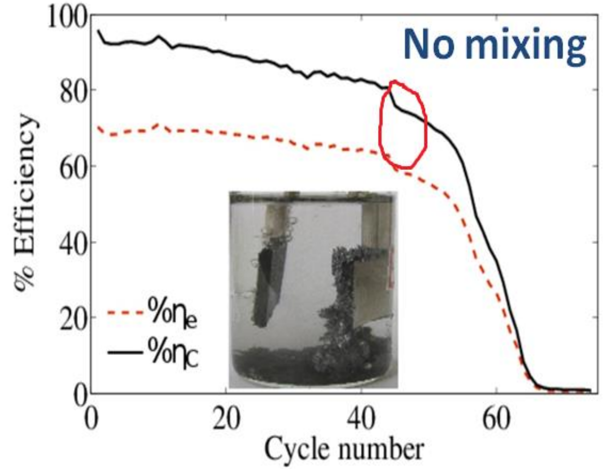
Side Reaction on Anode:

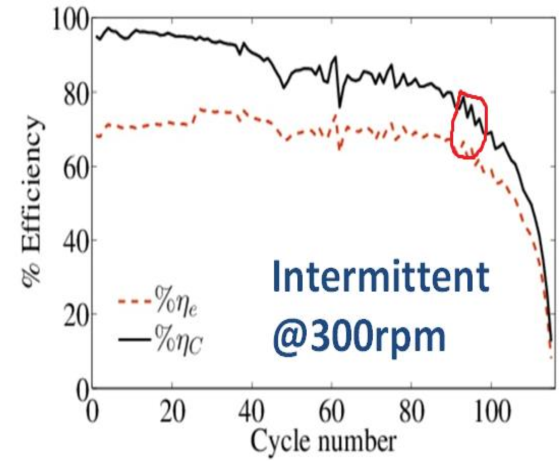
$$PbO + H_2O \underset{discharge}{\overset{charge}{\rightleftarrows}} PbO_2 + 2H^+ + 2e^-$$

It’s simple and economical!

Design Experiments to Probe the Role of Natural Convection

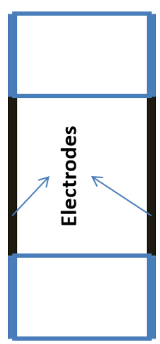


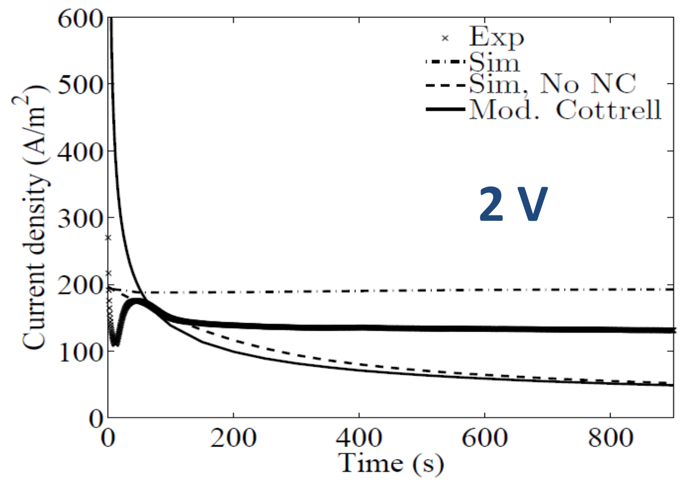




Diffusion limited Current
(Cottrell equation)

$$\frac{i}{A} = nFc\sqrt{\frac{D}{\pi t}}$$





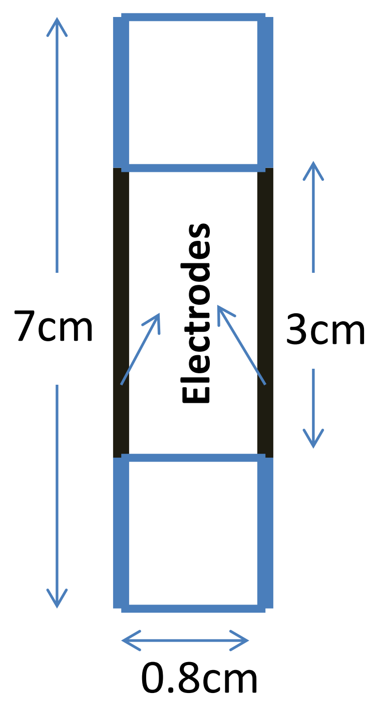
Without any mixing cell are able to run 40 cycles, why? Or why it is able to charge at constant current?

Nandanwar M. N., PhD thesis, 2016, IISc Bangalore

Objectives of Work

➢ **Detailed investigation of natural convection in standard and alternative cell designs of SLRFB**

➢ **Quantitative experimental validation of predicted flow field**



Schematic diagram of standard cell (On wall electrodes cell design)

Model Equations

Mass Balance Eqn: $\frac{\partial c_i}{\partial t} = -\nabla . N_i$ **Species:** $Pb^{2+}, CH_3SO_3^-, H^+$ **(1)**

Nernst-Planck Eqn: $N_i = -D_i \nabla c_i - F z_i c_i u_{m_i} \nabla \phi + c_i u$ **(2)**

Charge Neutrality: $\sum_i z_i c_i = 0$ **(3)**

Navier-Stokes Eqn: $\rho \frac{\partial u}{\partial t} + \rho (u \cdot \nabla) u = -\nabla p + \mu \nabla^2 u + \boldsymbol{F}$ **(4)**

$$\nabla . u = 0$$

Buoyancy Force: $\boldsymbol{F} = \rho g \sum_i \beta_i (c_i^0 - c_i)$ **(5)**

Volume Expansion Co-eff: $\beta_i = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c_i} \right)_{T,P,c_{j \neq i}}$ **(6)**

[Newman & Alyea. Electrochemical system(2004) Bockris & Reddy. Modern Electrochemistry(2006)

Initial & Boundary Conditions

Butler-Volmer Eqn:

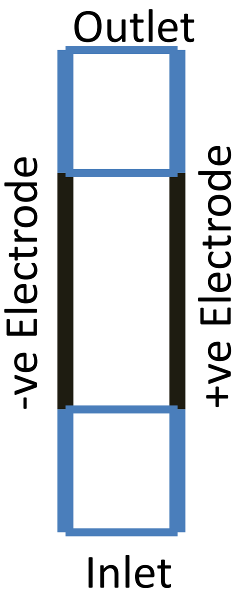
$$\boldsymbol{j} = zFk\frac{\boldsymbol{c}}{c_{ref}}[\exp(\frac{z\alpha F\boldsymbol{\eta}}{RT}) - \exp(-\frac{z\alpha F\boldsymbol{\eta}}{RT})]$$

Overpotential:

$$\boldsymbol{\eta} = V - (\phi + \boldsymbol{E}) \qquad \boldsymbol{E} = E^0 + \frac{RT}{zF}\ln\left(\frac{c_R}{c_O}\right)$$

Cell Potential:

$$V_{cell} = V_+ - V_-$$



Negative Electrode:

$$2F(N_{Pb^{2+}}.n) = j_{Pb}$$

$$j_{ca} = j_{Pb}$$

Positive Electrode:

$$2F(N_{Pb^{2+}}.n) = j_{PbO_2}$$

$$2F(N_{PbO_2}.n) = j_{PbO}$$

$$j_{an} = j_{PbO_2} + j_{PbO}$$

Inlet / Outlet:

$$D_i \nabla c_i . n = 0$$

$$j.n = 0$$

$$p_{out} = 3\times10^5\,Pa$$

Initial Condition:

$$c_i = c_i^0$$

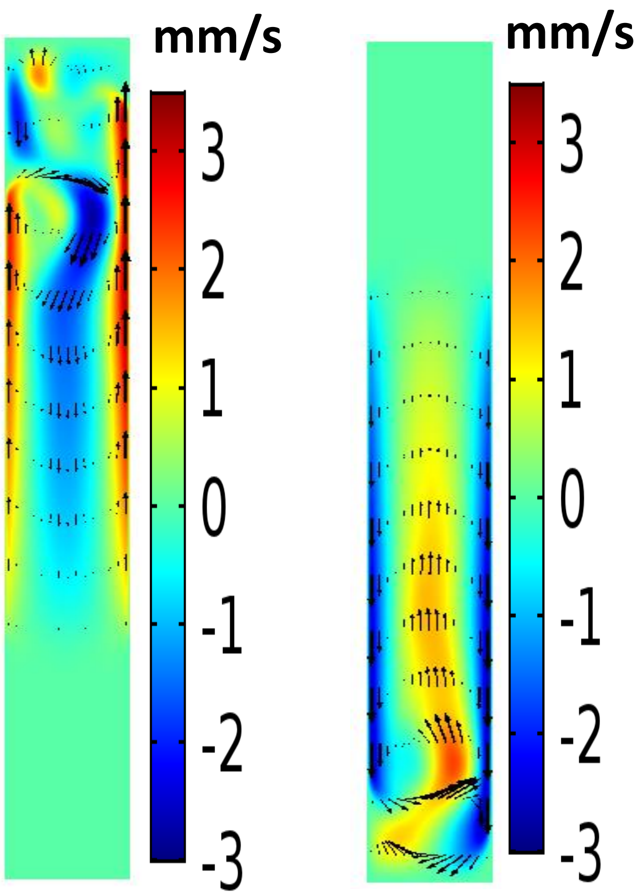
$$c^s_{PbO_2} = c^s_{PbO} = c^s_{Pb} = 0$$

$$p = 1\times10^5\,Pa$$

Walls: No-slip BC

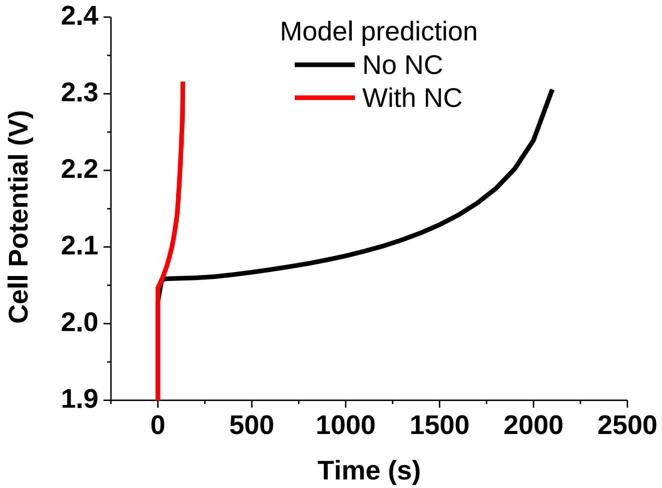
Modeling of Standard Cell (on wall electrodes design)

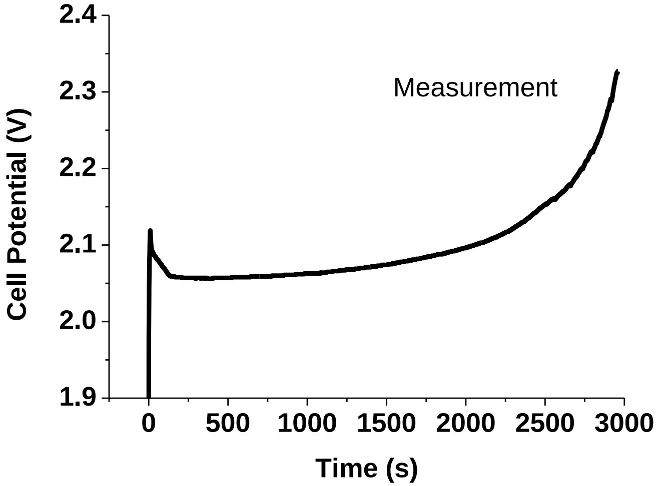
Velocity field



Charge Discharge

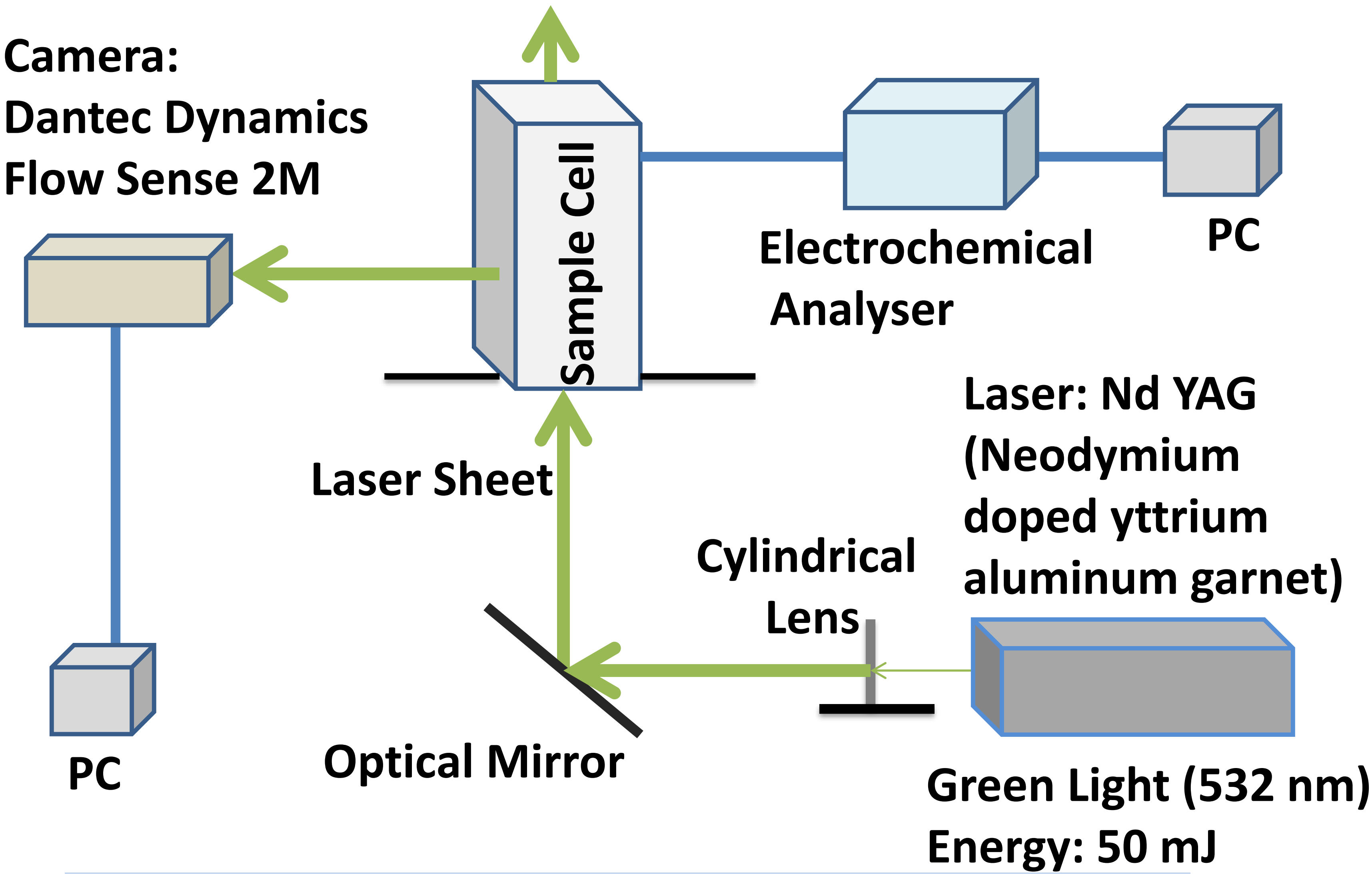
Cell performance





There is a strong electrolyte circulation due to natural convection!

Experimental Validation of Flow Field Using PIV Technique



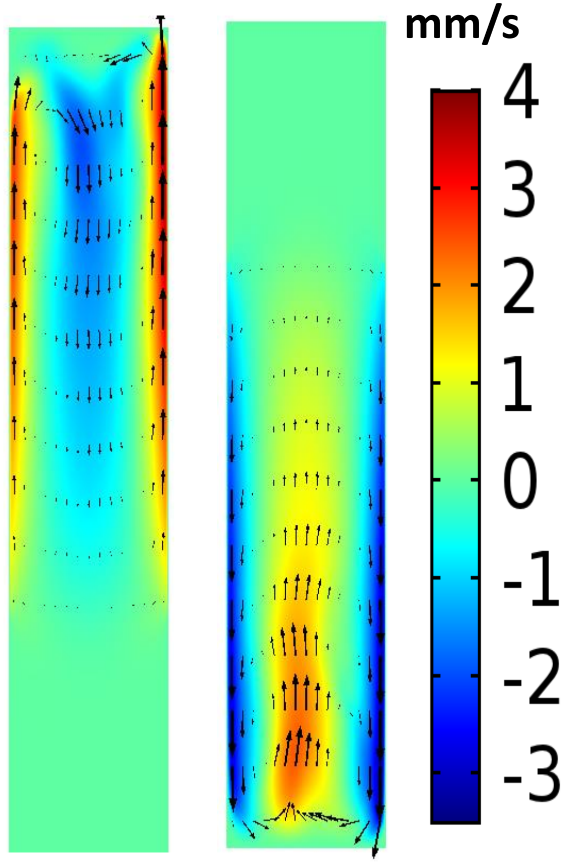
Experimental Set-up for Particle Image Velocimetry

Qualitative Validation of Flow Field in Standard Cell

std-15mm

PIV Experiment

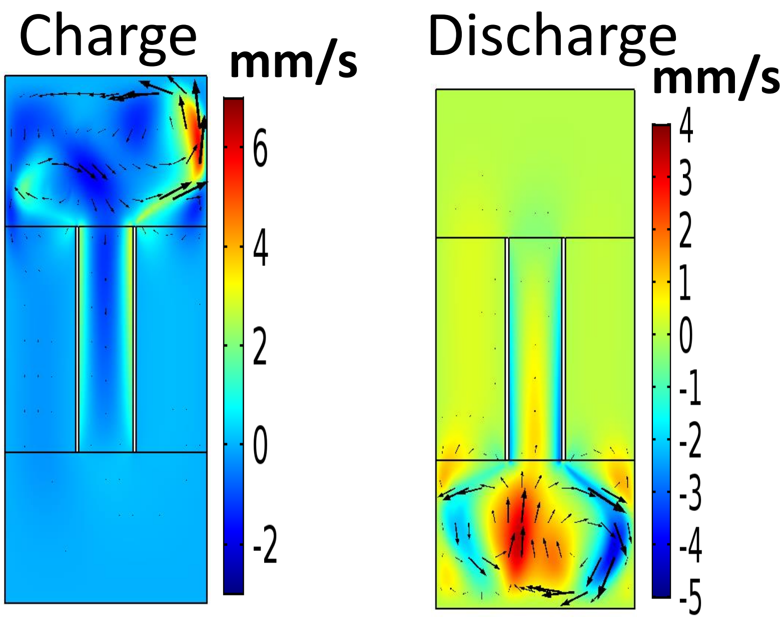
Flow prediction: @20s

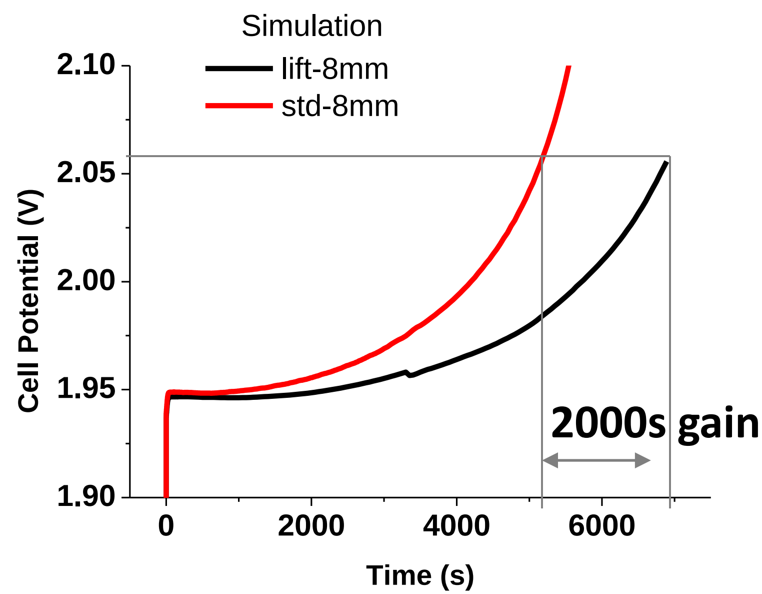


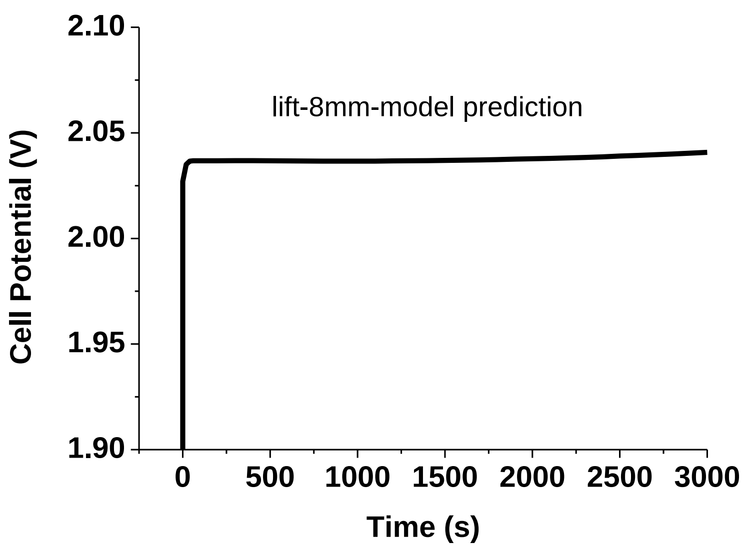
Charge **Discharge**

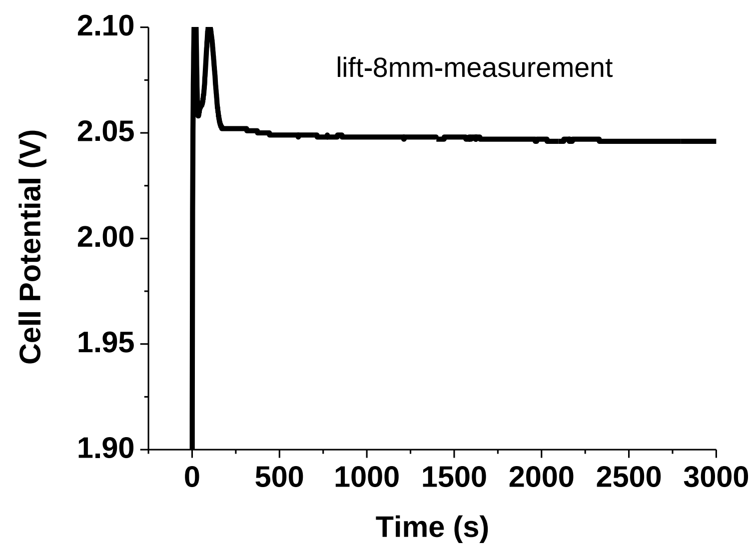
Simulations are able to predict the actual flow pattern!

Modeling of Lift Cell (off wall electrodes design)





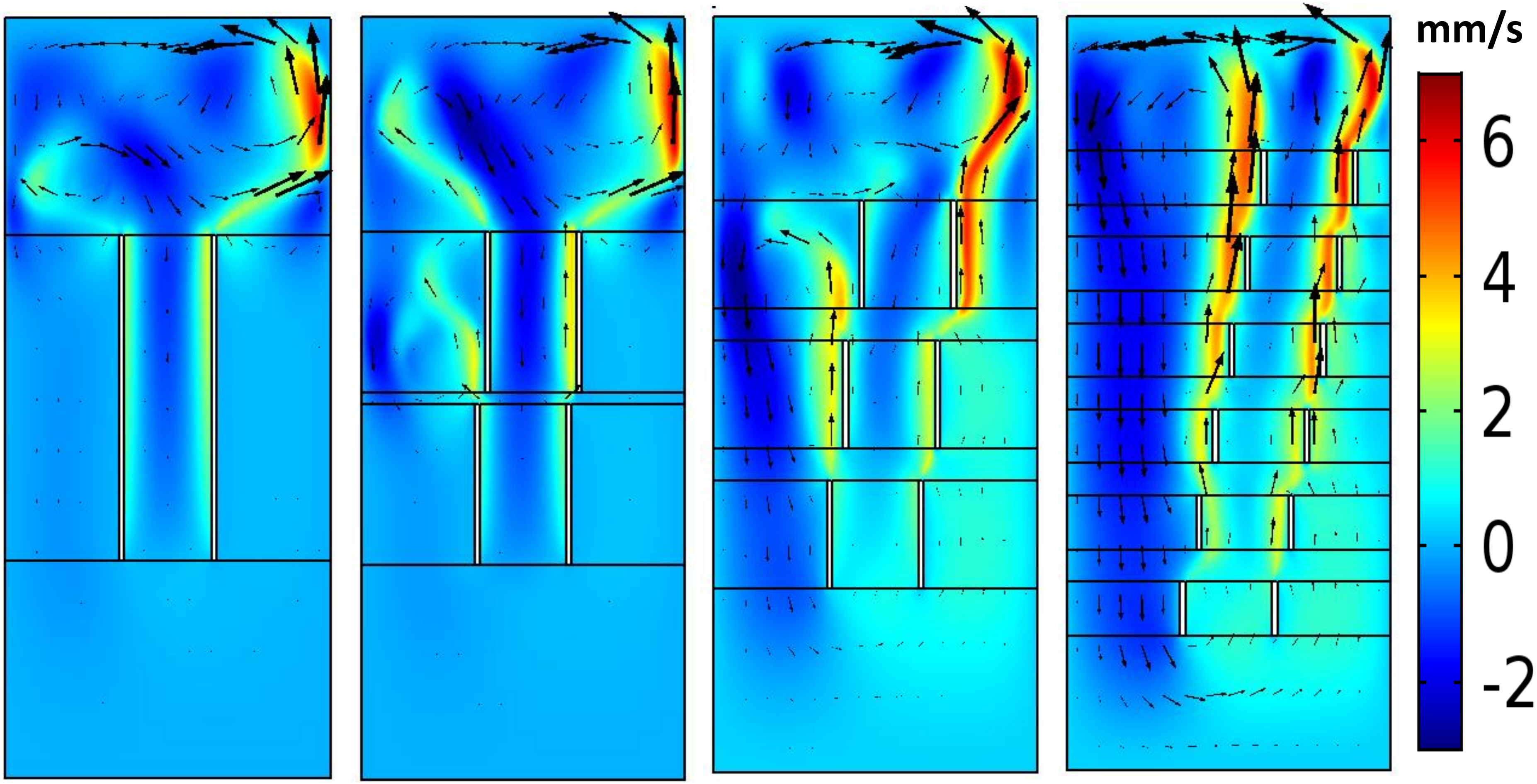




Model is able to predict the observe electrochemical behaviour !

Effect of Electrodes Splitting on Velocity Field

Charging: 20s

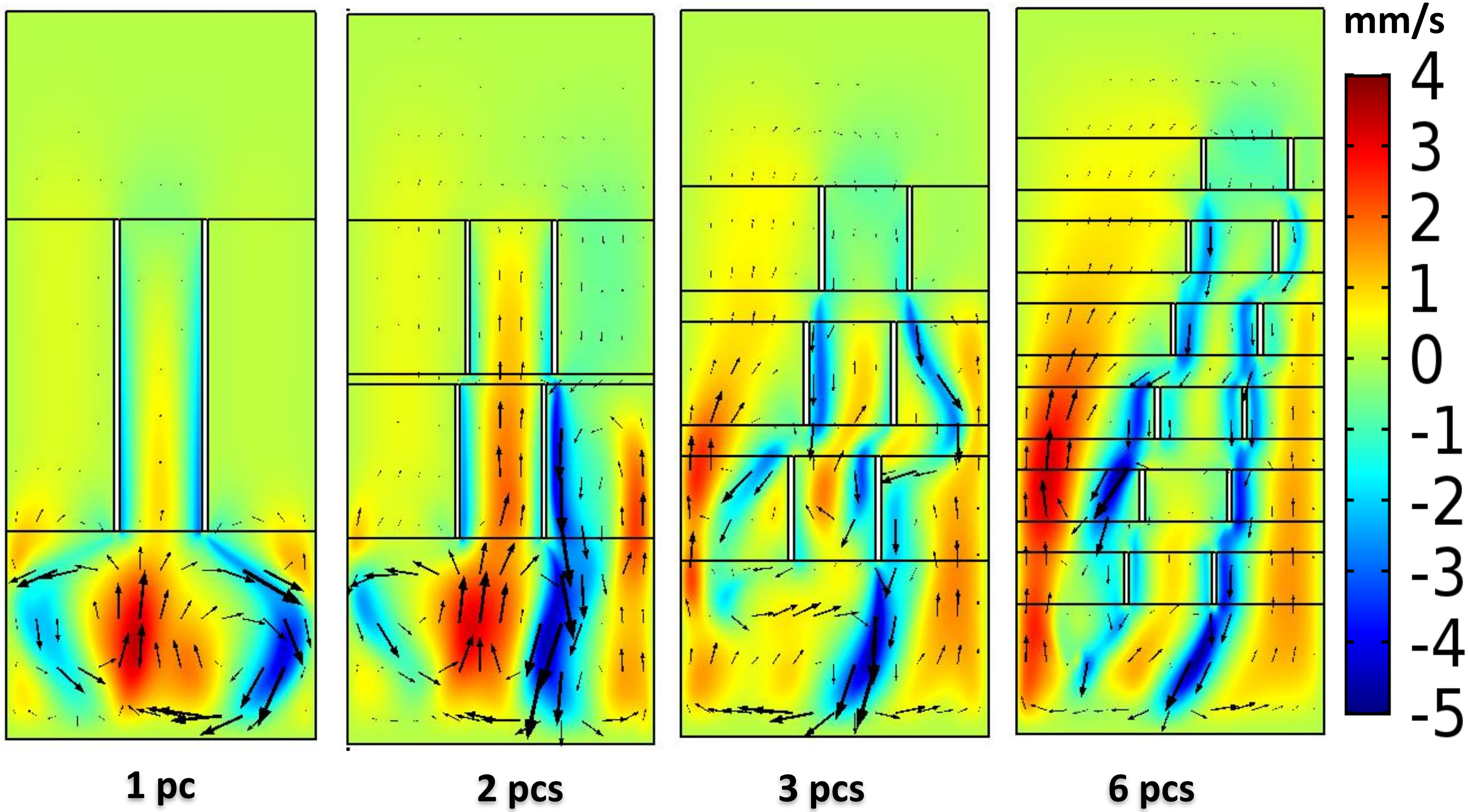


1 pc **2 pcs** **3 pcs** **6 pcs**

Splitting of electrodes improves electrolyte circulation!

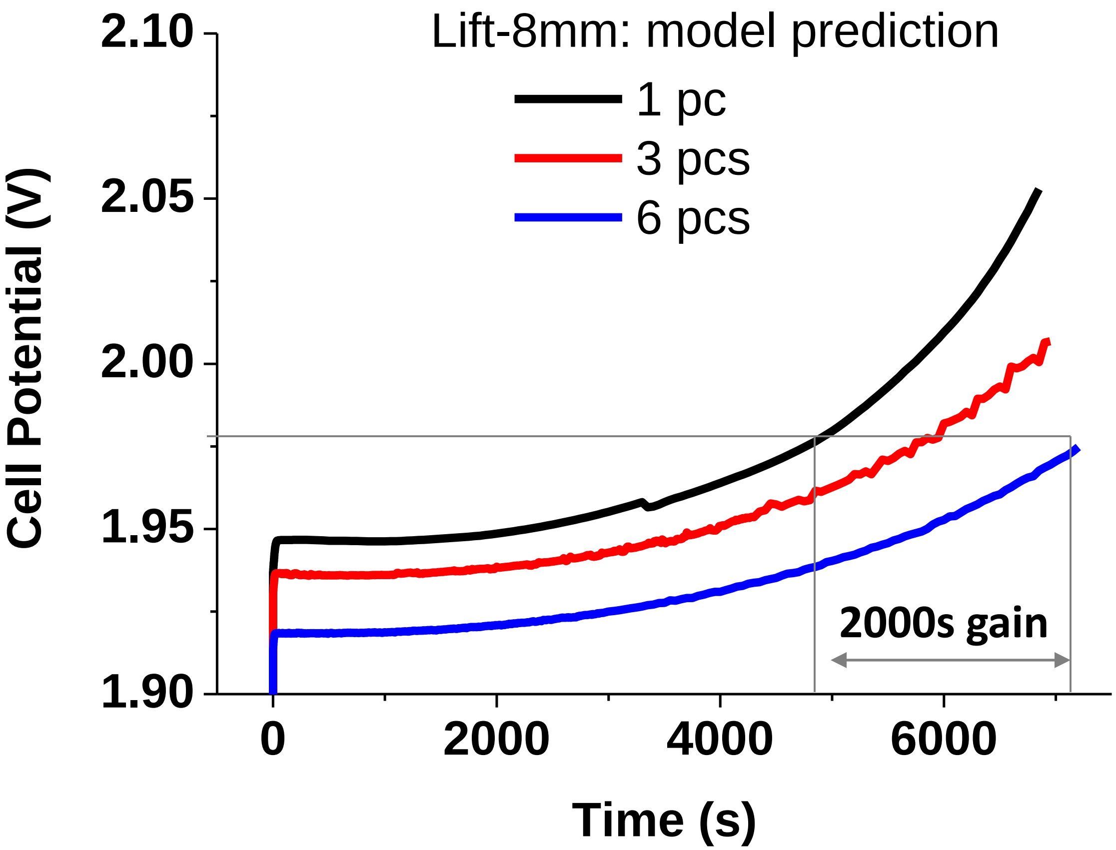
Effect of Electrodes Splitting on Velocity Field

Discharging: 20 s



Splitting of electrodes improves electrolyte circulation!

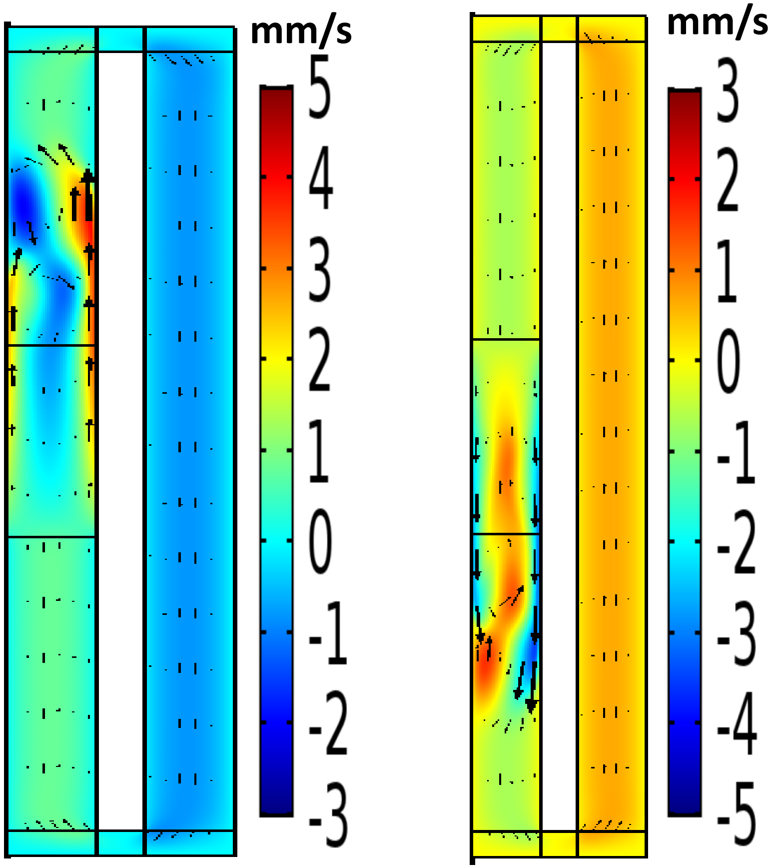
Effect of Electrodes Splitting and Staggering on Cell Performance



Splitting and staggering of electrodes into multiple pieces provides better mixing of electrolyte Compared to single piece of electrodes!

Effect of External Looping on cell Performance

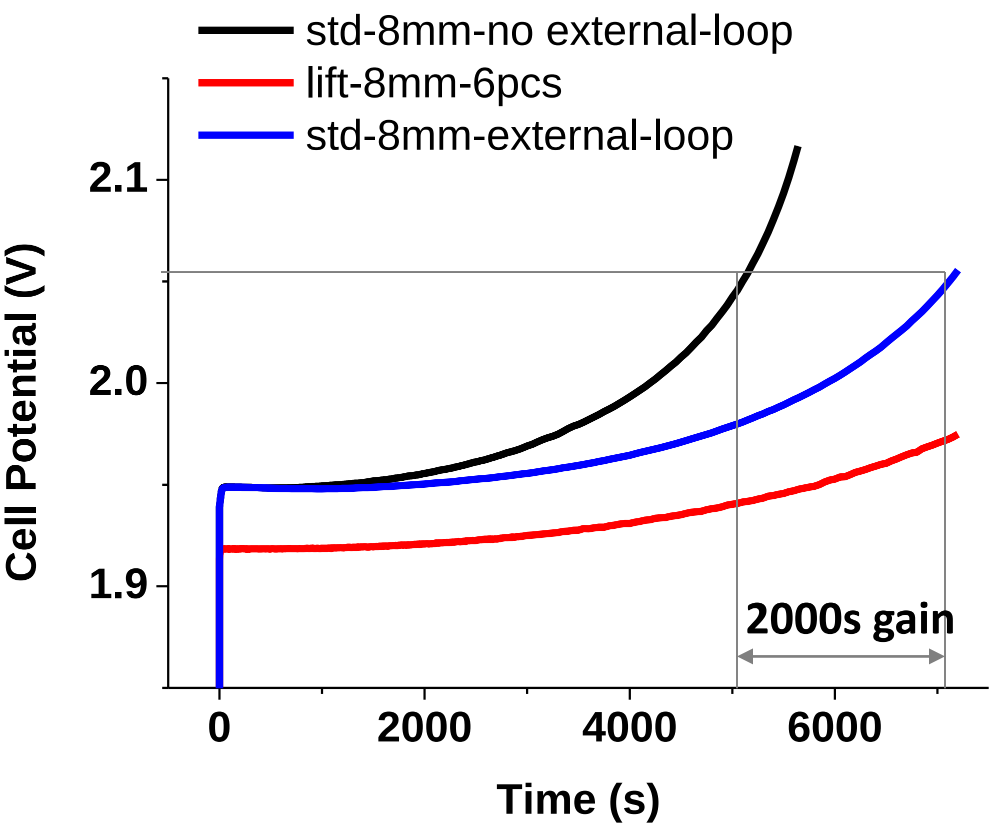
Velocity field



Charge

Discharge

Cell Potential



External looped cell improves mixing and it performs quite similar to the 6 pieces splitted electrodes design.

Conclusions

- ❑ Model is able to capture strong natural convection in the cell
- ❑ Flow predictions and PIV measurements show good qualitative agreements
- ❑ Electrochemical models and experimental data are in good agreement
- ❑ Splitting of electrodes into multiple pieces and external looing improves electrolyte mixing and provide charging for longer time

Thank you! ☺