Electrokinetics of a Concentration Fuel Cell in a Microchannel

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CEO Information

2003.6.4 (제403호)

SERI.org

산업판도를 바꿀 10대 미래기술

삼성경제연구소

1. System-On-Chip
2. Carbon Nanotube
3. 전자 종이 (Display)
4. Service Robot (가사, 의료)
5. 지능형 S/W (인공지능형)
6. Ad-hoc Network (홈시큐리티)
7. 양자 암호 (상거래)
8. 연료 전지 (2010년)
9. 프로테오믹스
10. 인공장기

Fuel Cell

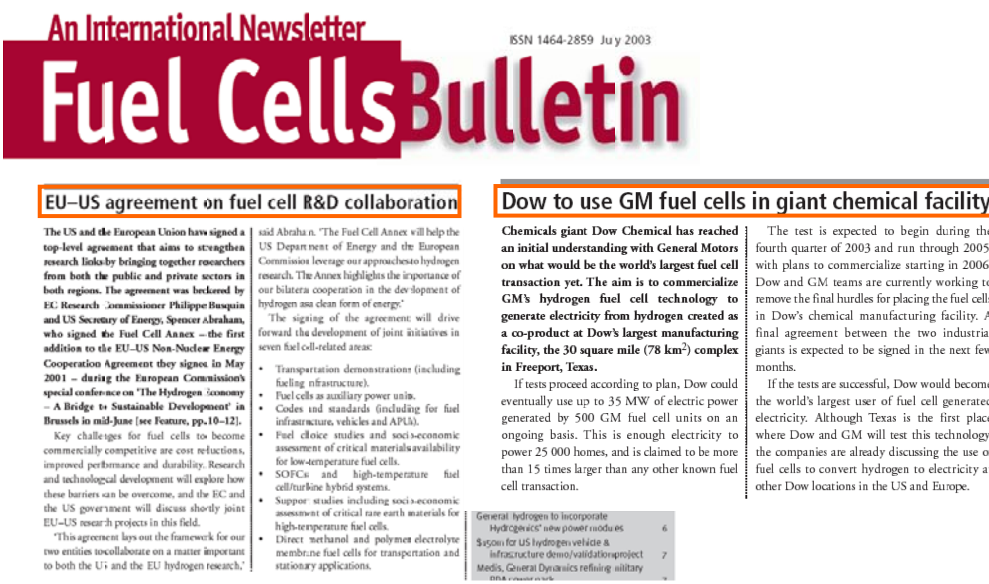
- Notebook PC for 40 hours without stop.
- Mobile utility charged by alcohol.

Nokia Cell. Phone eBay (US$25)

CONSEL (Germany) Suitcase, 7h×7ea, (2004)

NEC, Built in FC, 5h (2004), 40h in two year.

Rapid movement around the globe



An International Newsletter

ISSN 1464-2859 July 2003

Fuel Cells Bulletin

EU–US agreement on fuel cell R&D collaboration

The US and the European Union have signed a top-level agreement that aims to strengthen research links by bringing together researchers from both the public and private sectors in both regions. The agreement was brokered by EC Research Commissioner Philippe Busquin and US Secretary of Energy, Spencer Abraham, who signed the Fuel Cell Annex – the first addition to the EU–US Non-Nuclear Energy Cooperation Agreement they signed in May 2001 – during the European Commission's special conference on 'The Hydrogen Economy – A Bridge to Sustainable Development' in Brussels in mid-June [see Feature, pp.10–12].

Key challenges for fuel cells to become commercially competitive are cost reductions, improved performance and durability. Research and technological development will explore how these barriers can be overcome, and the EC and the US government will discuss shortly joint EU–US research projects in this field.

'This agreement lays out the framework for our two entities to collaborate on a matter important to both the US and the EU hydrogen research,' said Abraham. 'The Fuel Cell Annex will help the US Department of Energy and the European Commission leverage our approaches to hydrogen research. The Annex highlights the importance of our bilateral cooperation in the development of hydrogen as a clean form of energy.'

The signing of the agreement will drive forward the development of joint initiatives in seven fuel cell-related areas:

- Transportation demonstrations (including fueling infrastructure).
- Fuel cells as auxiliary power units.
- Codes and standards (including for fuel infrastructure, vehicles and APUs).
- Fuel choice studies and socio-economic assessment of critical materials availability for low-temperature fuel cells.
- SOFCs and high-temperature fuel cell/turbine hybrid systems.
- Support studies including socio-economic assessment of critical rare earth materials for high-temperature fuel cells.
- Direct methanol and polymer electrolyte membrane fuel cells for transportation and stationary applications.

Dow to use GM fuel cells in giant chemical facility

Chemicals giant Dow Chemical has reached an initial understanding with General Motors on what would be the world's largest fuel cell transaction yet. The aim is to commercialize GM's hydrogen fuel cell technology to generate electricity from hydrogen created as a co-product at Dow's largest manufacturing facility, the 30 square mile (78 km^2) complex in Freeport, Texas.

If tests proceed according to plan, Dow could eventually use up to 35 MW of electric power generated by 500 GM fuel cell units on an ongoing basis. This is enough electricity to power 25 000 homes, and is claimed to be more than 15 times larger than any other known fuel cell transaction.

The test is expected to begin during the fourth quarter of 2003 and run through 2005, with plans to commercialize starting in 2006. Dow and GM teams are currently working to remove the final hurdles for placing the fuel cells in Dow's chemical manufacturing facility. A final agreement between the two industrial giants is expected to be signed in the next few months.

If the tests are successful, Dow would become the world's largest user of fuel cell generated electricity. Although Texas is the first place where Dow and GM will test this technology, the companies are already discussing the use of fuel cells to convert hydrogen to electricity at other Dow locations in the US and Europe.

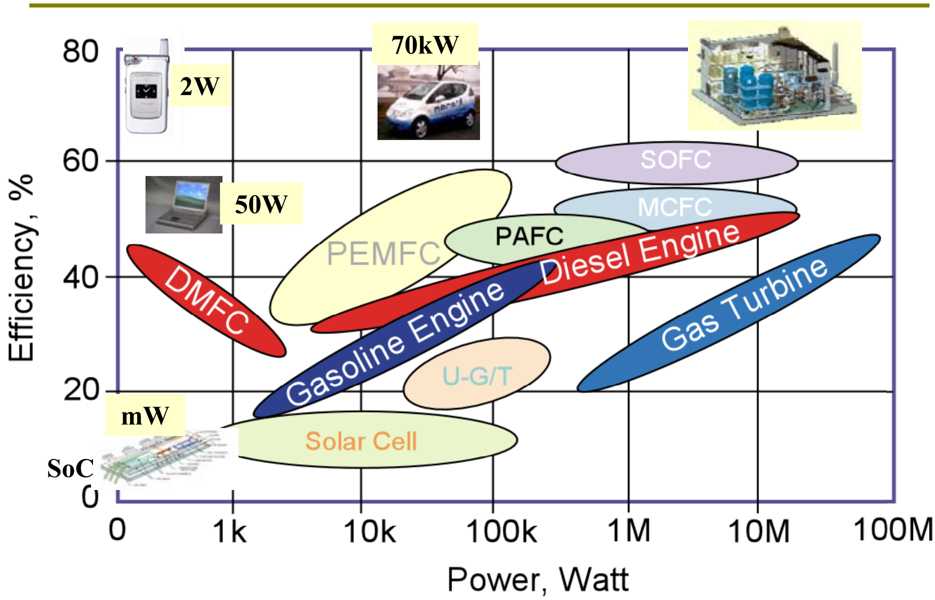
Rapid movement around the globe

Bush makes phone call powered by MTI MicroFuel fuel cell

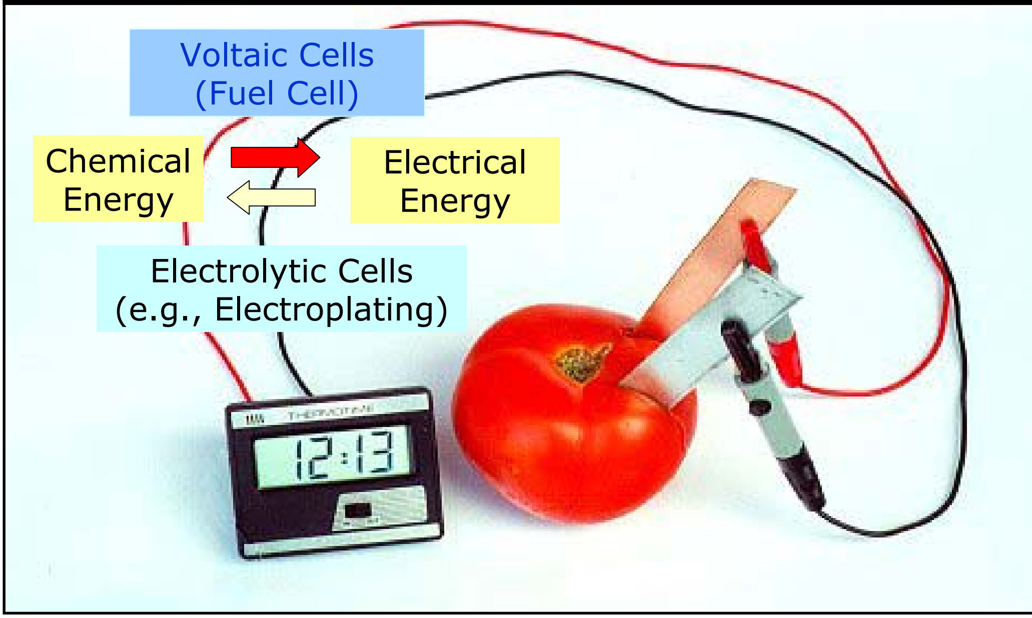
President Bush on Thursday stopped by a booth by MTI MicroFuel Cells Inc. of Albany in Washington, D.C., and made a cell phone call from a phone powered by MTI's *direct methanol micro fuel-cell* system, according to the company …

-Business Review-
Feb. 6, 2003

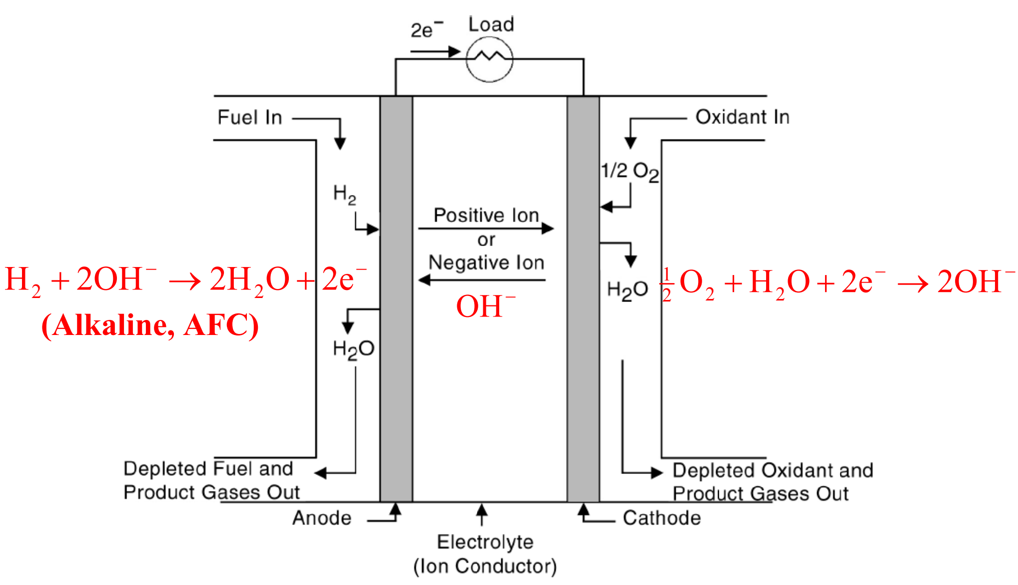
Fuel Cell: Efficiency



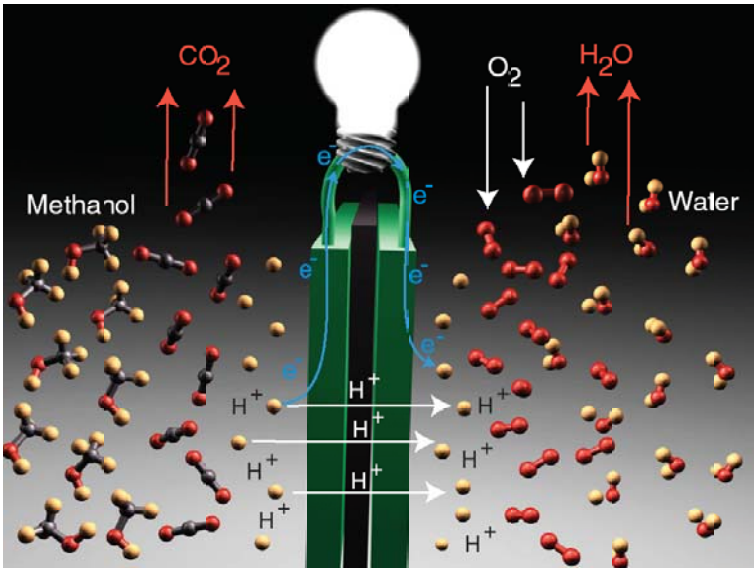
A Sample Voltaic Cell



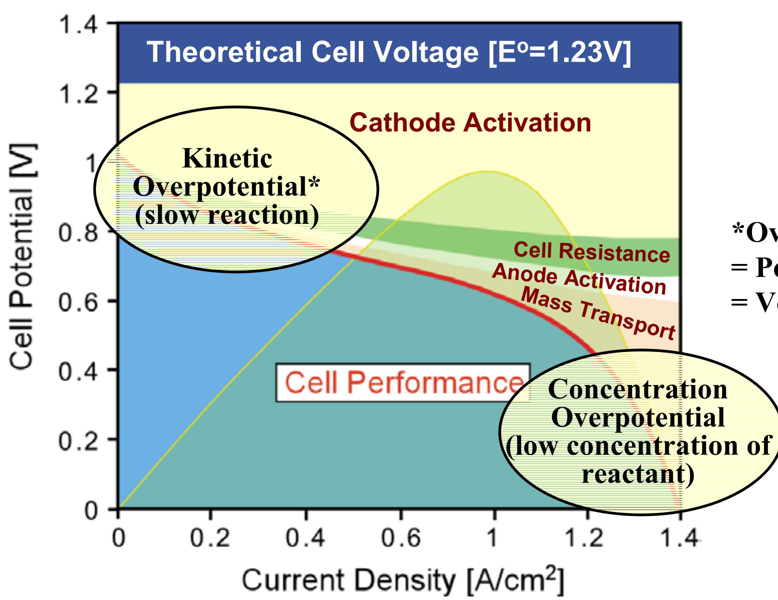
Fuel Cell Description



Direct Methanol Fuel Cell



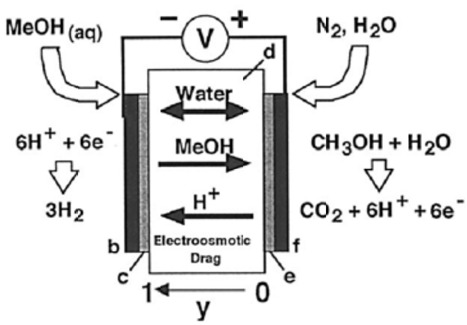
Characteristic Performance Curve



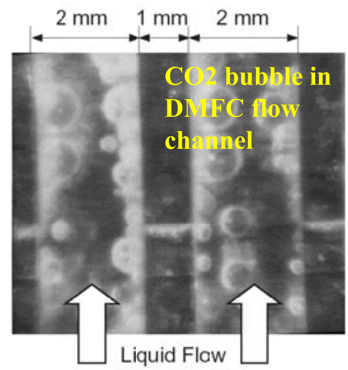
*Overpotential
= Polarization
= Voltage Loss

A few problems in fuel cell

- Methanol crossover through membrane.
- CO_2 bubble removal.



Ren et al. J. Electrochem. Soc. 147 (2000) 466.

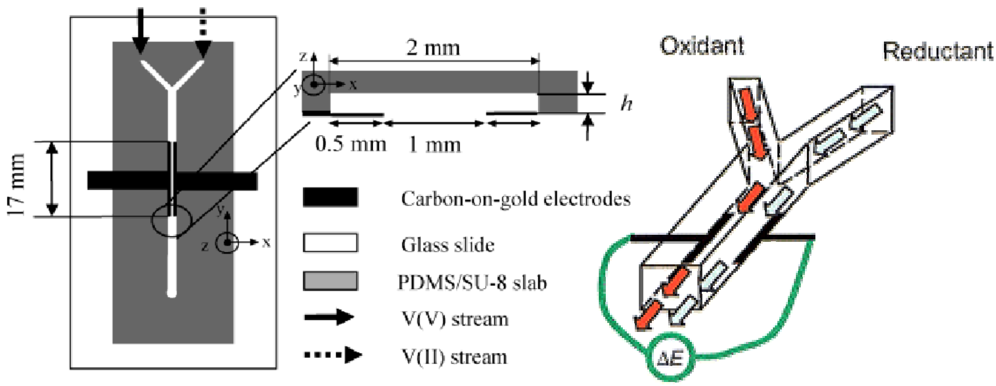


T. Schultz et al. Chem. Eng. Tech. 24 (2001) 12.

Fuel Cell in a Microchannel

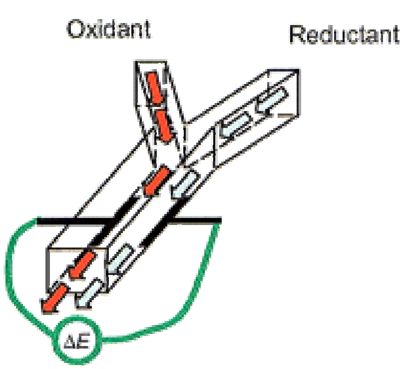
- Laminar Flow → Slow Mixing → Membrane is needless (Membraneless Fuel Cell).
- Fabrication by using the MEMS technology → miniaturization.
- Convenience in interfacing with μTAS.

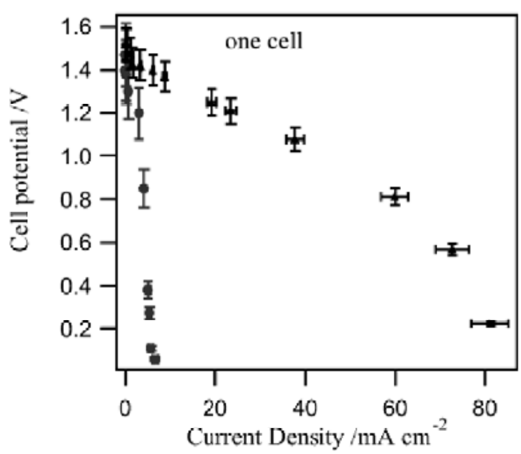
Membraneless Vanadium F.C.



R. Ferrigno, …, G.M. Whitesides "Membraneless Vanadium Redox Fuel Cell Using Laminar Flow," J. Am. Chem. Soc. 2002, 124, 12930.

Membraneless Vanadium F.C.

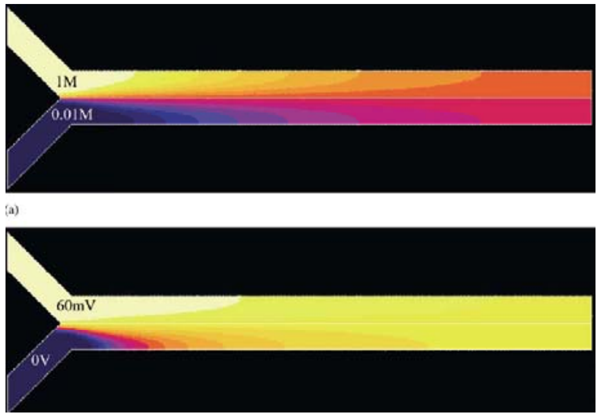




R. Ferrigno, …, G.M. Whitesides "Membraneless Vanadium Redox Fuel Cell Using Laminar Flow," J. Am. Chem. Soc. 2002, 124, 12930.

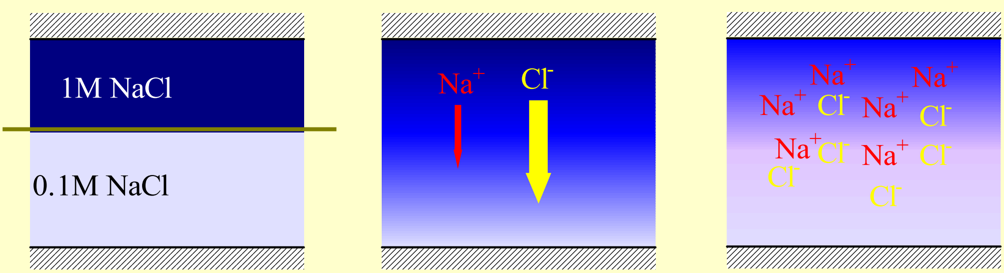
Concentration Fuel Cell

Beneficial usage of *liquid junction potential (LJP)*



R. Ferrigno, …, G.M. Whitesides "Membraneless Vanadium Redox Fuel Cell Using Laminar Flow," J. Am. Chem. Soc. 2002, 124, 12930.

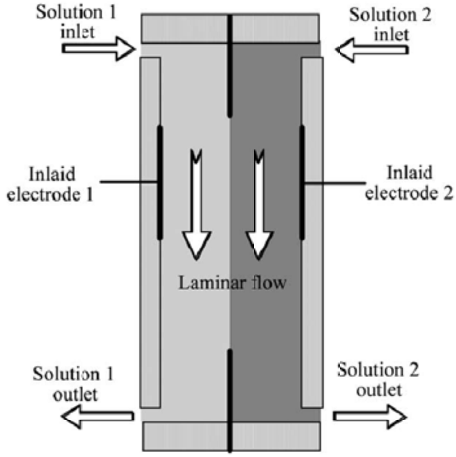
Liquid Junction Potential

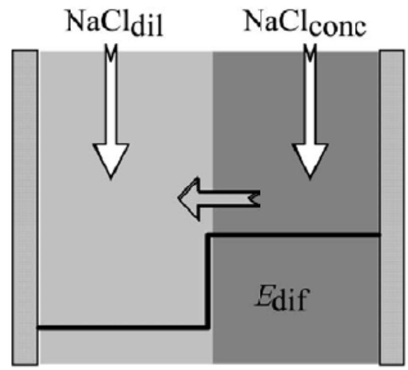


(a) isolated **(b) diffusion** **(c) Ion distribution**

Diffusivity difference of ionic species induces the *concentration polarization*.

Fuel Cell in Microchannel





G. Lagger et al. "Hydro-voltaic cells: Part I. Concentration cells," J. Electroanal. Chem. 545 (2003) 1.

Analysis of Concentration Fuel Cell

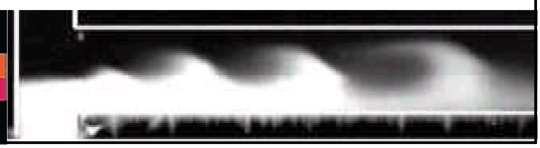
Objectives

- **Obtain the analytical formula for the LJP in a *finite* domain.**

  c.f. Planck's equation for the LJP

$$V_{LJP} = (t_2 - t_1)\frac{kT}{e}\ln\frac{c_{h0}}{c_{l0}}$$

- **Investigate the mechanism of the EOF instability.**



Basic Equations

- **Charge conservation:** $\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0$
- **Current:** $\mathbf{J}_i = -D_i \nabla c_i + z_i \omega_i F c_i \mathbf{E} + c_i \mathbf{u}$
- **Poisson equation:** $\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = \frac{F}{\varepsilon}(c_2 - c_1)$
- **Navier–Stokes equation**

$$\rho(\partial \mathbf{u} / \partial t + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \mu \nabla \mathbf{u} + \rho_c \mathbf{E}$$

Assumptions

- **Streamwise diffusion is negligible.**
- **Uniform velocity profile.**

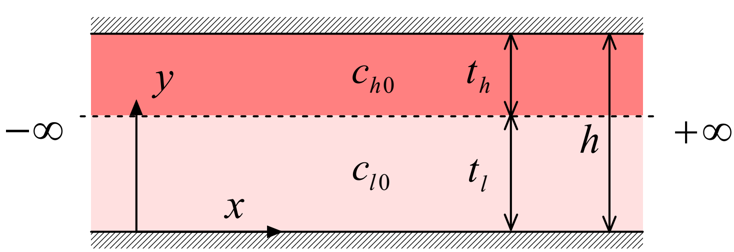
$$\cancel{\frac{\partial c_i}{\partial t}} + \mathbf{u}\cdot\nabla c_i = D_i\left\{\cancel{\frac{\partial^2 c_1}{\partial x^2}} + \frac{\partial^2 c_1}{\partial y^2} + \frac{z_i e}{kT}\left[\cancel{\frac{\partial}{\partial x}\left(c_i\frac{\partial \phi}{\partial x}\right)} + \frac{\partial}{\partial y}\left(c_i\frac{\partial \phi}{\partial y}\right)\right]\right\}$$

$$\longrightarrow \qquad U\frac{\partial c_i}{\partial x} = D_i\left\{\frac{\partial^2 c_i}{\partial y^2} + \frac{z_i e}{kT}\frac{\partial}{\partial y}\left(c_i\frac{\partial \phi}{\partial y}\right)\right\}$$

Coordinate Transform

$$U\frac{\partial c_i}{\partial x} = D_i\left\{\frac{\partial^2 c_i}{\partial y^2} + \frac{z_i e}{kT}\frac{\partial}{\partial y}\left(c_i\frac{\partial \phi}{\partial y}\right)\right\}$$

$$\xrightarrow{t = x/U} \qquad \frac{\partial c_i}{\partial t} = D_i\left\{\frac{\partial^2 c_i}{\partial y^2} + \frac{z_i e}{kT}\frac{\partial}{\partial y}\left(c_i\frac{\partial \phi}{\partial y}\right)\right\}$$

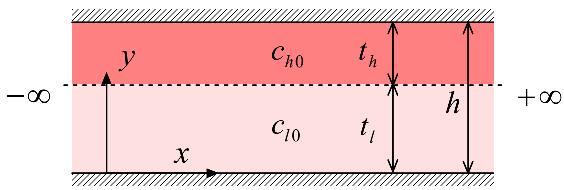


Reduced G.E., I.C. & B.C.

Governing equation

$$\frac{\partial c_i}{\partial t} = D_i \left\{ \frac{\partial^2 c_i}{\partial y^2} + \frac{z_i e}{kT} \frac{\partial}{\partial y} \left(c_i \frac{\partial \phi}{\partial y} \right) \right\}$$

$$\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = \frac{F}{\varepsilon}(c_2 - c_1)$$



Initial condition

$$c_{1,2} = \begin{cases} c_{l0}, & \text{if } \; y < t_l, \\ c_{h0}, & \text{if } \; y > t_l \end{cases}$$

Boundary conditions

$$\left.\frac{\partial c_{1,2}}{\partial y}\right|_{y=0} = \left.\frac{\partial c_{1,2}}{\partial y}\right|_{y=h} = 0$$

$$\left.\frac{\partial \varphi}{\partial \eta}\right|_{y=0} = \left.\frac{\partial \varphi}{\partial y}\right|_{y=h} = 0$$

Non-Dimensionalization

Introduce the following dimensionless variables

$$\tau = t/(h^2/D_{eq}), \quad \eta = y/h, \quad \varphi = \frac{e\phi}{kT}, \quad C_i = \frac{c_i}{c_{h0} - c_{l0}}$$

$$\frac{\partial C_1}{\partial \tau} = \frac{D_1}{D_{eq}} \left[\frac{\partial^2 C_1}{\partial \eta^2} + \frac{\partial}{\partial \eta} \left(C_1 \frac{\partial \varphi}{\partial \eta} \right) \right]$$

$$\frac{\partial C_2}{\partial \tau} = \frac{D_2}{D_{eq}} \left[\frac{\partial^2 C_2}{\partial \eta^2} - \frac{\partial}{\partial \eta} \left(C_2 \frac{\partial \varphi}{\partial \eta} \right) \right]$$

$$\frac{\partial^2 \varphi}{\partial \eta^2} = (\kappa h)^2 (C_2 - C_1)$$

$$D_{eq} = \frac{2 D_1 D_2}{D_1 + D_2}$$

$$\kappa = \sqrt{\frac{Fe(c_{h0} - c_{l0})}{\varepsilon k T}}$$

$$\sim 10^9 \, \mathrm{m}^{-1}$$

Charge Neutrality Assumption

- $\kappa \sim 10^9$, $h \sim 10^{-4}$ $\rightarrow$ $\kappa h \sim 10^5$

$$\frac{\partial^2 \varphi}{\partial \eta^2} = (\kappa h)^2 (C_2 - C_1) \longrightarrow C_1 \cong C_2 \equiv C$$

- Subtract the electromigration term

$$\left.\begin{aligned} \frac{\partial C_1}{\partial \tau} &= \frac{D_1}{D_{eq}}\left[\frac{\partial^2 C_1}{\partial \eta^2} + \frac{\partial}{\partial \eta}\left(C_1 \frac{\partial \varphi}{\partial \eta}\right)\right] \\ \frac{\partial C_2}{\partial \tau} &= \frac{D_2}{D_{eq}}\left[\frac{\partial^2 C_2}{\partial \eta^2} - \frac{\partial}{\partial \eta}\left(C_2 \frac{\partial \varphi}{\partial \eta}\right)\right] \end{aligned}\right\} \quad \frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \eta^2}$$

Electric Field and LJP

- Since $C_1 \cong C_2 \equiv C$

$$\frac{D_1}{D_{eq}}\left[\frac{\partial^2 C}{\partial \eta^2} + \frac{\partial}{\partial \eta}\left(C \frac{\partial \varphi}{\partial \eta}\right)\right] = \frac{D_1}{D_{eq}}\left[\frac{\partial^2 C}{\partial \eta^2} - \frac{\partial}{\partial \eta}\left(C \frac{\partial \varphi}{\partial \eta}\right)\right]$$

- Electric field and the LJP

$$\overline{E} = \frac{D_1 - D_2}{D_1 + D_2} \frac{1}{C} \frac{\partial C}{\partial \eta} = (t_1 - t_2) \frac{1}{C} \frac{\partial C}{\partial \eta}$$

$$\overline{V}_{LJP}(\tau) = (t_2 - t_1) \ln \frac{C_h(\tau)}{C_l(\tau)}$$

Analytical Solution of *C*

Diffusion equation with I.C. & B.C.

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \eta^2} \qquad C_{1,2} = \begin{cases} \dfrac{c_{l0}}{c_{h0} - c_{l0}}, & \text{if } \eta < \xi, \\ \dfrac{c_{h0}}{c_{h0} - c_{l0}}, & \text{if } \eta > \xi \end{cases}$$

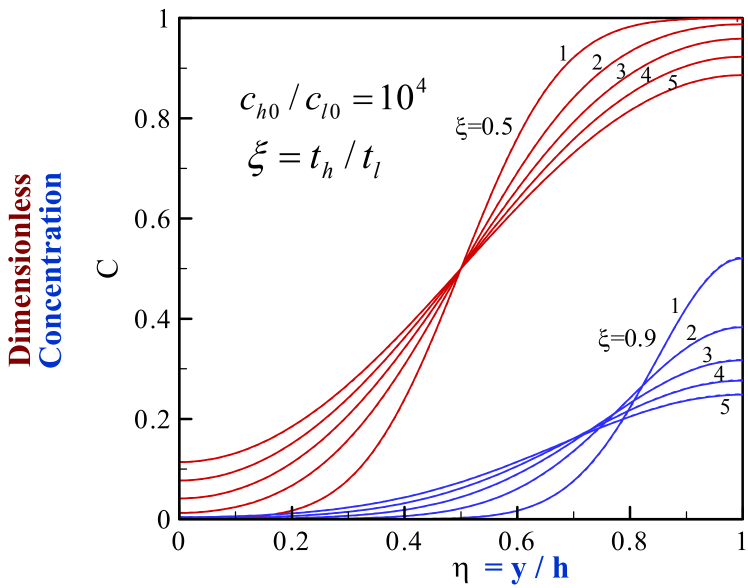
$$\left.\frac{\partial C_{1,2}}{\partial \eta}\right|_{\eta=0} = \left.\frac{\partial C_{1,2}}{\partial \eta}\right|_{\eta=1} = 0$$

$$\left.\frac{\partial \varphi}{\partial \eta}\right|_{\eta=0} = \left.\frac{\partial \varphi}{\partial \eta}\right|_{\eta=1} = 0$$

Eigenfunction expansion of *C*

$$C(\tau, \eta; \xi) = C_{h0} - \xi - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin n\pi\xi \exp(-n^2\pi^2\tau) \cos n\pi\eta}{n}$$

Evolution of Concentration



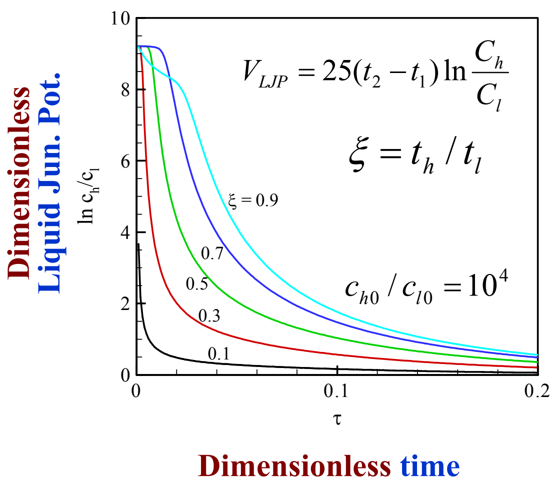
Liquid Junction Potential

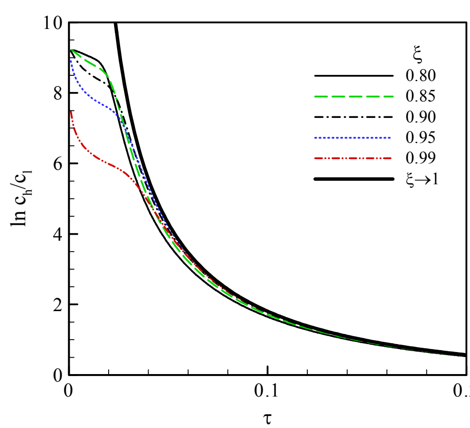
$$\overline{V}_{LJP}(\tau) = (t_2 - t_1)\ln\frac{C_h(\tau)}{C_l(\tau)}$$

$$C_l(\tau) = C_{h0} - \xi - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\sin n\pi\xi \exp(-n^2\pi^2\tau)}{n}$$

$$C_h(\tau) = C_{h0} - \xi - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n \sin n\pi\xi \exp(-n^2\pi^2\tau)}{n}$$

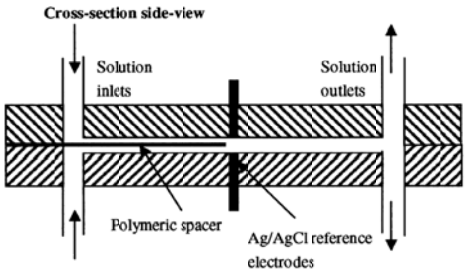
Liquid Junction Potential

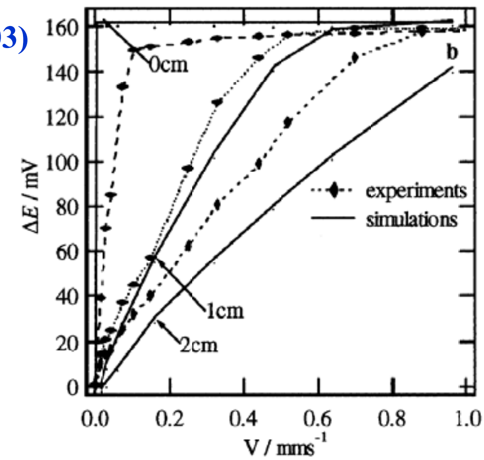




Comparison with Experiment (1)

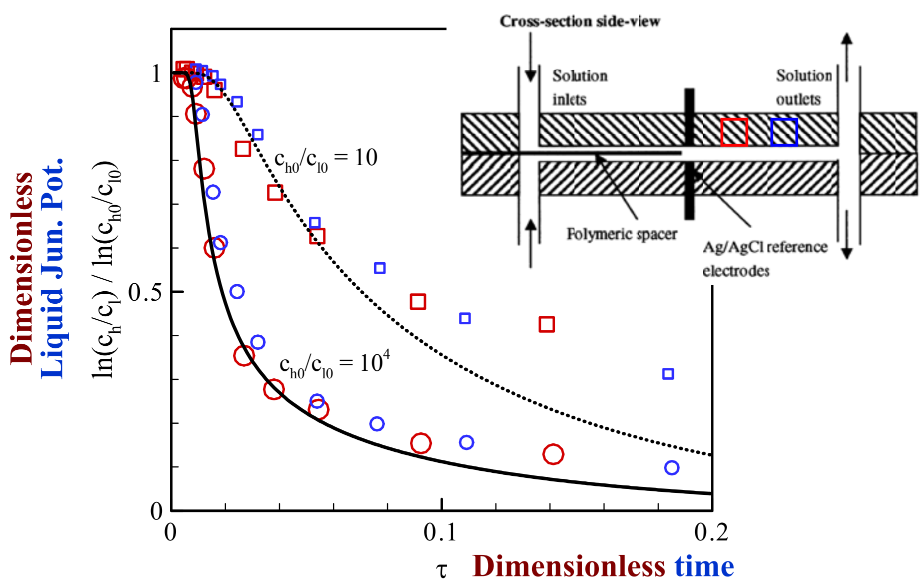
Experiment of Josserand et al. (2003)





Josserand et al. "Contact Galvani potential differences at liquid/liquid interfaces: Part II. Contact diffusion potentials in microsystems," J. Electroanal. Chem. 546 (2003) 1.

Comparison with Experiment (2)



Electric Field & Charge Density

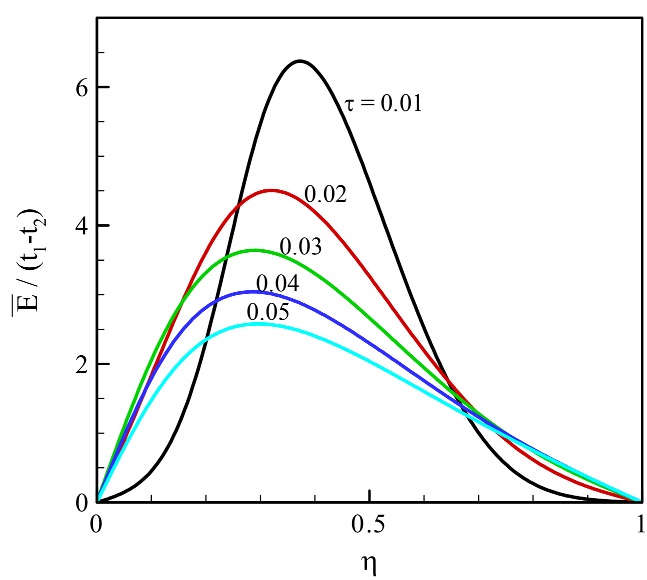
- **Electric field,** $\overline{E} = E(he/kT)$

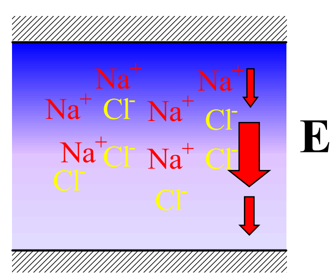
$$\overline{E} = \frac{D_1 - D_2}{D_1 + D_2}\frac{1}{C}\frac{\partial C}{\partial \eta} = (t_1 - t_2)\frac{1}{C}\frac{\partial C}{\partial \eta}$$

- **Charge density,** $\overline{\rho}_e = \rho_e(h^2\beta/\varepsilon)$

$$\overline{\rho}_e = -\frac{\partial \overline{E}}{\partial \eta} = (t_1 - t_2)\cdot\frac{\partial}{\partial \eta}\left(\frac{1}{C}\frac{\partial C}{\partial \eta}\right)$$

Electric Field

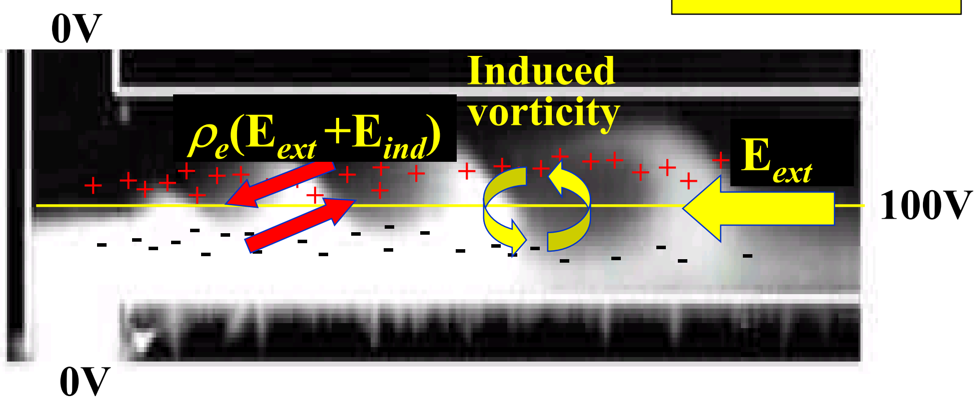




Mechanism of EOF instability?

Vorticity is generated due to concentration polarization.

$$\rho(\partial \mathbf{u}/\partial t + \mathbf{u}\cdot\nabla\mathbf{u}) = -\nabla p + \mu\nabla\mathbf{u} + \rho_e(\mathbf{E}_{ext} + \mathbf{E}_{ind})$$



Concluding Remarks

- **Liquid junction potential is well predicted by the simple analytical model.**
- **Analysis of the fuel-cell performance (*i-V* curve) is undergoing.**
- **Concentration polarization may induce the EOF instability; numerical analysis is undergoing.**