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Design and Analysis of MEMS-based direct methanol fuel cell

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Contents

Background

Due to the unique advantages, micro direct methanol fuel cells (µDMFCs) have been considered as the most promising candidates for the micro power sources of mobile devices.

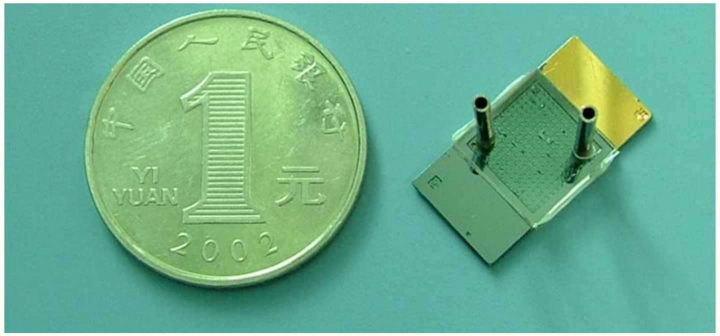
µDMFC for speaker and gadget charger, ***Sony (Japan)****, 2009*

µDMFC for cell phone, ***Motorola (USA)****, 2008*

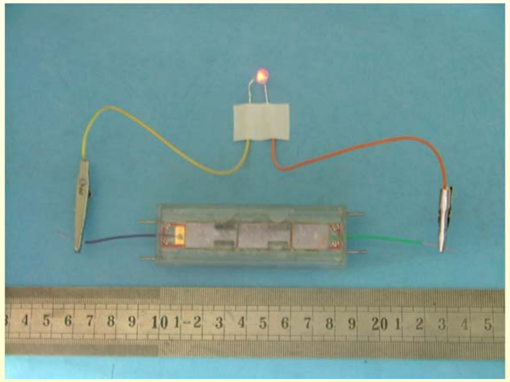
µDMFC for notebook, ***Ultracell (USA)****, 2007*

µDMFC for PDA, ***Hitachi (Japan)****, 2005*

MEMS Center, HIT

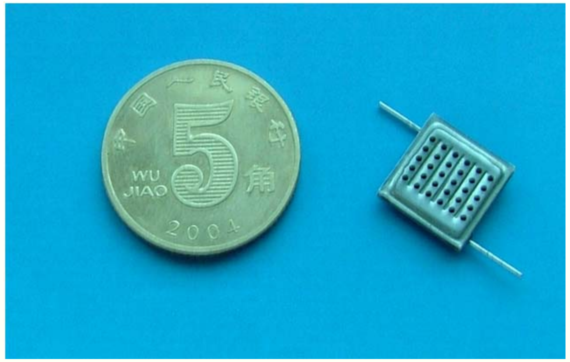


0.64cm^2，open circuit voltag:520mV，power density:5.9mW/cm^2

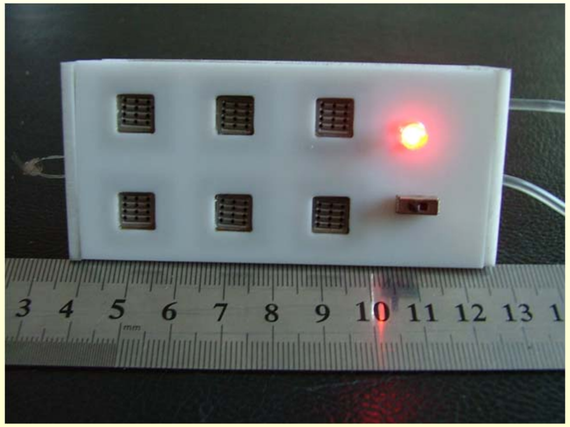


fuel cell stack，open voltage:2.75V，

power density:6.8mW。



Open voltage:650mV
power density:15.9mW/cm^2



Powered LED to work for 5h

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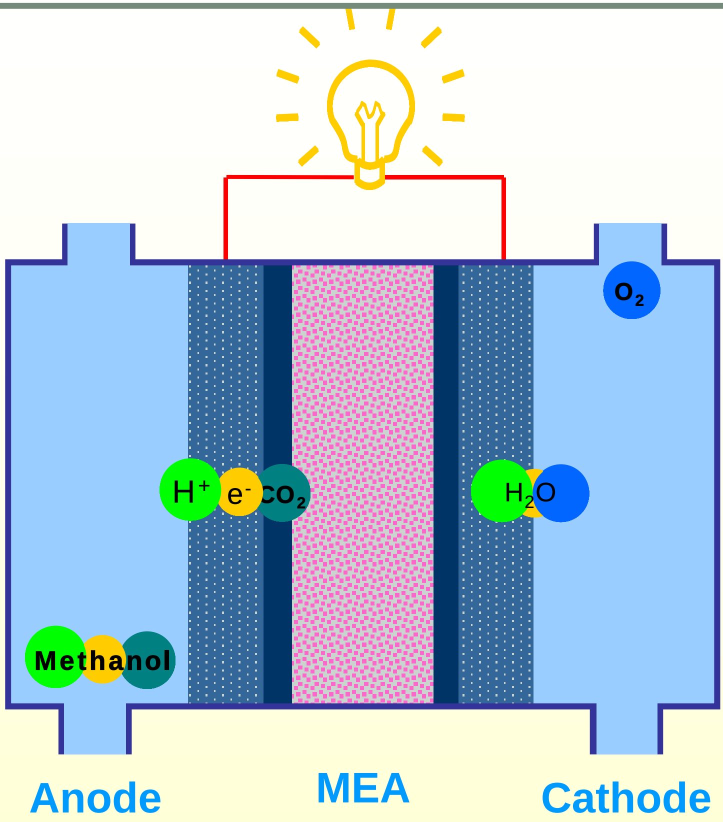
Principle



anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

overall: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$

- **（1） current collector material**
- **（2） structure design**
- **（3） mass transfer of MEA**
- **（4） theoretical analysis**

COMSOL Multiphysics

contents

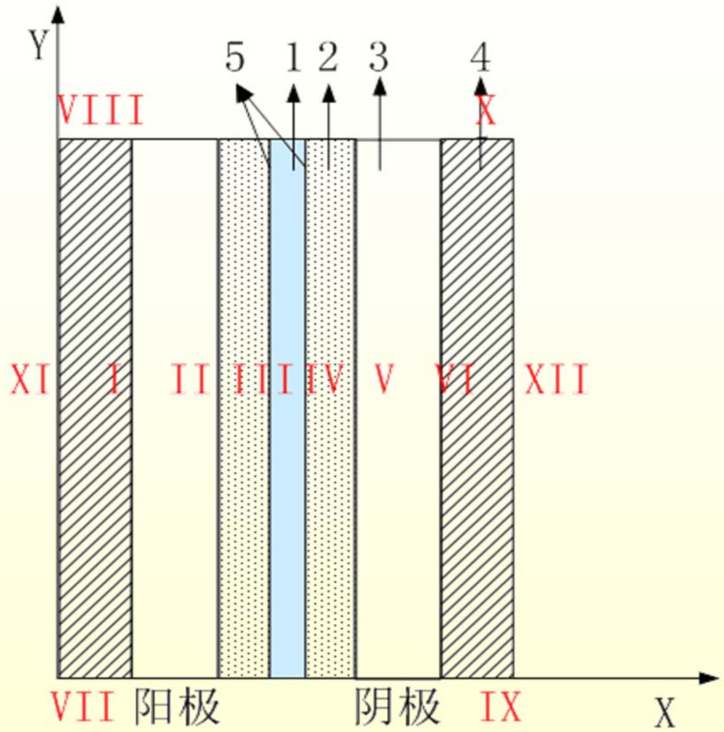
3. Application of COMSOL

- **3.1Two-dimensional,two-phase mass transport——mass transport， structure of DMFC**

- **3.2 μDMFC Three-dimensional model**
- **A novel cathode——structure， stability**

- A air-breathing cathode flow field——water-flooding
- Anode structure ——**optimize structure**

3.1A two-dimensional two-phase mass transport model：



1—质子交换膜　**2**—气体扩散层　**3**—流道

4—电流收集层　**5**—催化层

Mathematical model

- two-phase mass transport in the diffusion layer

• **continuous equation**

$$\begin{cases} \nabla\cdot(\rho_l \boldsymbol{u}_l) = S_l \\ \nabla\cdot(\rho_g \boldsymbol{u}_g) = S_g \end{cases}$$

•**momentum transport equation**

$$\begin{cases} \boldsymbol{u}_l = \dfrac{-Kk_{rl}}{\mu_l}\nabla p_l & k_{rl} = s^3 \\ \boldsymbol{u}_g = \dfrac{-Kk_{rg}}{\mu_g}\nabla p_g & k_{rg} = (1-s)^3 \end{cases}$$

• **Mass transport equation**

$$\begin{cases} \nabla\cdot\left(-D_{i,l}^{eff}\nabla C_{i,l} + C_{i,l}\boldsymbol{u}_l\right) = S_{i,l} & D_{i,l}^{eff} = D_{i,l}\varepsilon^{1.5}s^{1.5} \\ \nabla\cdot\left(-D_{i,g}^{eff}\nabla C_{i,g} + C_{i,g}\boldsymbol{u}_g\right) = S_{i,g} & D_{i,g}^{eff} = D_{i,g}\varepsilon^{1.5}(1-s)^{1.5} \end{cases}$$

•**pressure difference** $p_c = p_g - p_l = \sigma\cos\theta_c\left(\varepsilon / K\right)^{0.5} J(s)$

Leverette function $J(s) = \begin{cases} 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3 & 0 < \theta_c < 90^o \\ 1.417s - 2.120s^2 + 1.263s^3 & 90^o < \theta_c < 180^o \end{cases}$

Mathematical model

- **two-phase mass transport in anode channel**

  - **momentum transport equation** $$\frac{\partial(\phi\rho_l \boldsymbol{u}_l)}{\partial t}+\nabla\cdot(\phi\rho_l \boldsymbol{u}_l \boldsymbol{u}_l)=-\nabla p_l+\nabla\cdot(\phi\mu_l\nabla \boldsymbol{u}_l)+\phi\rho_l \boldsymbol{g}$$

    CO_2 **velocity——** $\boldsymbol{u}_g=\boldsymbol{u}_l+\boldsymbol{u}_{slip}$ $\quad \frac{3}{4}\frac{C_d}{d_b}\rho_l\left|\boldsymbol{u}_{slip}\right|\boldsymbol{u}_{slip}=-\nabla p_l \quad C_d=\frac{16}{\mathrm{Re}_b}$

  - **continuous equation** $$\begin{cases}\nabla\cdot(\phi\rho_l \boldsymbol{u}_l)=0\\ \frac{\partial((1-\phi)\rho_{CO_2})}{\partial t}+\nabla\cdot((1-\phi)\rho_{CO_2}\boldsymbol{u}_g)=0\end{cases}$$

  - **Mass transport of methanol ——** $\nabla\cdot(-D_{MeOH}^{eff}\nabla C_{MeOH}+C_{MeOH}\boldsymbol{u}_l)=0 \quad D_{MeOH}^{eff}=D_{MeOH}\phi^{1.5}$

- **two-phase mass transport in cathode channel**

  - **momentum transport equation——** $$\frac{\partial((1-\phi)\rho_g \boldsymbol{u}_g)}{\partial t}+\nabla\cdot((1-\phi)\rho_g \boldsymbol{u}_g \boldsymbol{u}_g)=-\nabla p_g+\nabla\cdot((1-\phi)\mu_g\nabla \boldsymbol{u}_g)+(1-\phi)\rho_g \boldsymbol{g}$$

    H_2O **velocity——** $\boldsymbol{u}_g=\boldsymbol{u}_l$

  - **continuous equation** $$\begin{cases}\nabla\cdot((1-\phi)\rho_g \boldsymbol{u}_g)=0\\ \frac{\partial(\phi\rho_{H_2O})}{\partial t}+\nabla\cdot(\phi\rho_{H_2O}\boldsymbol{u}_l)=0\end{cases}$$

  - **Mass transport of O_2——** $\nabla\cdot(-D_{O_2}^{eff}\nabla C_{O_2}+C_{O_2}\boldsymbol{u}_g)=0 \quad D_{O_2}^{eff}=D_{O_2}(1-\phi)^{1.5}$

Mathematical model

➢mass transport in PEM

- **Mass transport of methanol** (Concentration and electro-osmotic) ——

$$N_{MeOH,cross} = -D_{MeOH,mem}^{eff}\nabla C_{MeOH,mem} + n_d^m \frac{i}{F} = \frac{i_p}{6F}$$

- **Mass transport of H_2O**—— $N_{H_2O,cross} = n_d \dfrac{i}{F}$

➢The transportations of electron and proton

$$\nabla\cdot\left(\sigma_{s,eff}\nabla\phi_s\right) = 0 \qquad \nabla\cdot\left(\sigma_{m,eff}\nabla\phi_m\right) = 0$$

➢Electrochemical kinetics

- Anode——

$$i = i_m^{ref} s \left(\frac{C_{m,acl}}{C_m^{ref}}\right)^{\gamma} \exp\left(\frac{\alpha_a F}{RT_{acl}}\eta_a\right) \qquad \gamma = \begin{cases} 0 & C_{m,acl} > C_m^{ref} \\ 1 & C_{m,acl} \le C_m^{ref} \end{cases} \qquad C_m^{ref} = 0.1 mol/L$$

- Cathode——

$$i_c = i_{O_2}^{ref}(1-s)\frac{C_{O_2,ccl}}{C_{O_2}^{ref}}\exp\left(-\frac{\alpha_c F}{RT_{ccl}}\eta_c\right)$$

- Current density—— $i_p = i_c - i$

➢ Heat transfer

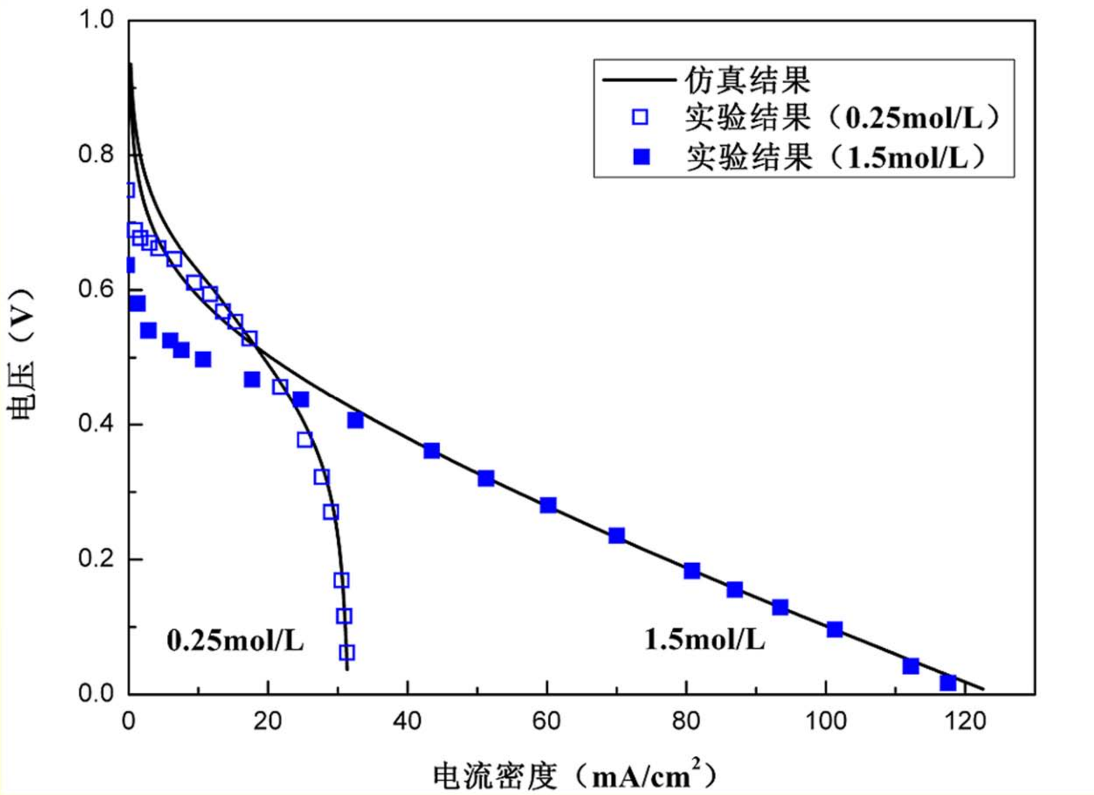
- Anode catalyst layer——

$$q_{acl} = i_a\left(\eta_a - \frac{\Delta H_a - \Delta G_a}{6F}\right)$$

- Cathode catalyst layer——

$$q_{ccl} = i_c\left(\eta_c - \frac{\Delta H_c - \Delta G_c}{4F}\right) - (i_c - i_a)\frac{\Delta H_a - \Delta G_a}{6F}$$

➢Comparison of the modeling results and experimental results



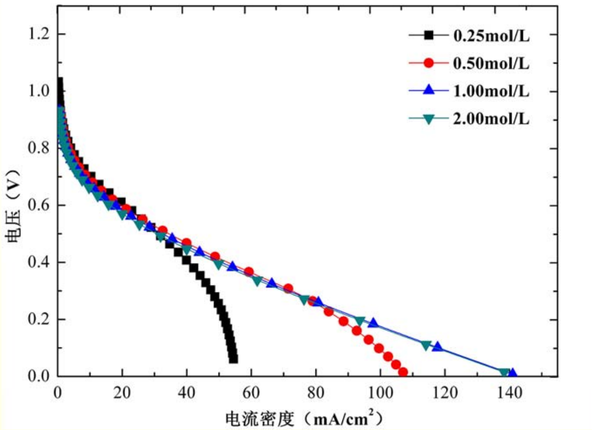
Model result

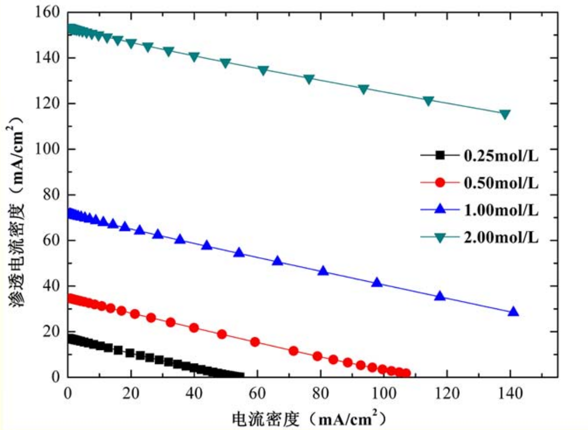
diffusion

electroosmosis

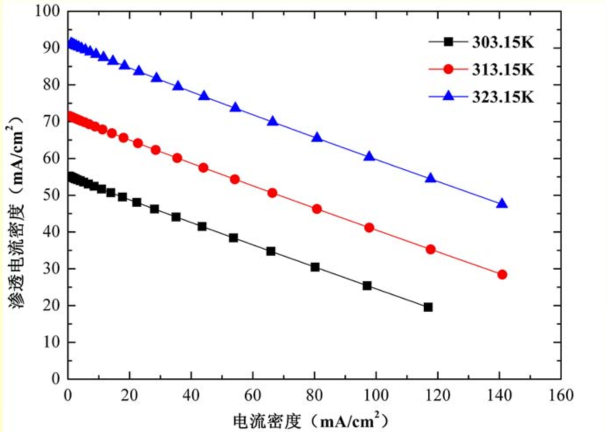
- ➢ effect of different methanol concentrations

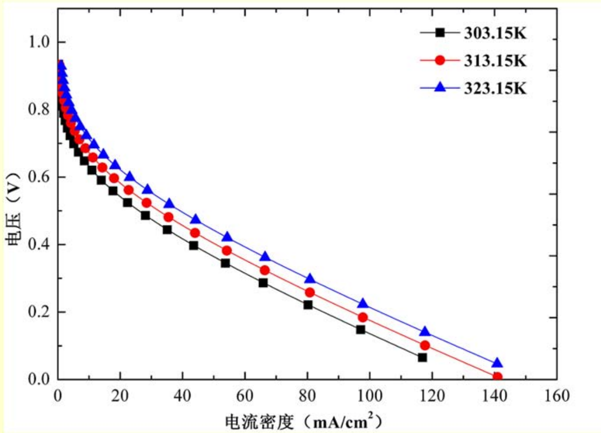
$$N_{MeOH,cross} = -D_{m,mem}^{eff} \nabla C_{m,mem} + n_d^m \frac{i}{F} = \frac{i_p}{6F}$$





- ➢ Effect of the operating temperature





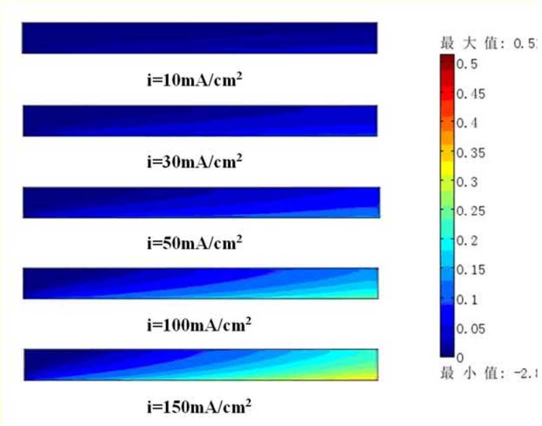
Model result

➢CO_2 content in anode flow field

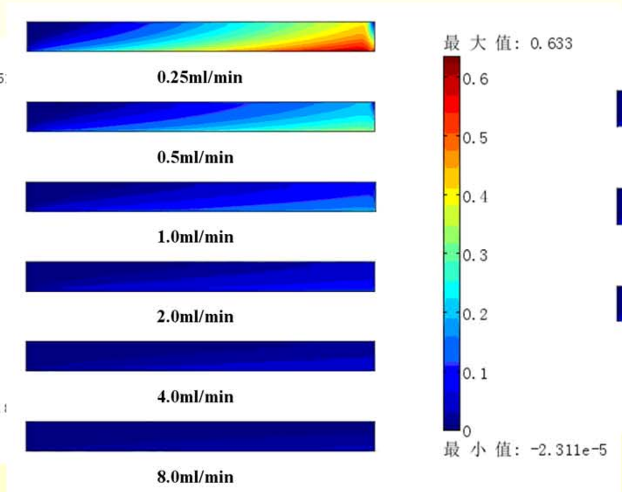
- **CO_2content increase with the current density and temperature**
- **The anode flow rates have the effect of the removal rate of the CO_2**
- **in accord with the results of Yang[1]and Liao[2]**

[1] H. Yang, T. S. Zhao, Q. Ye. J. Power Sources, 2005, 139: 79-90

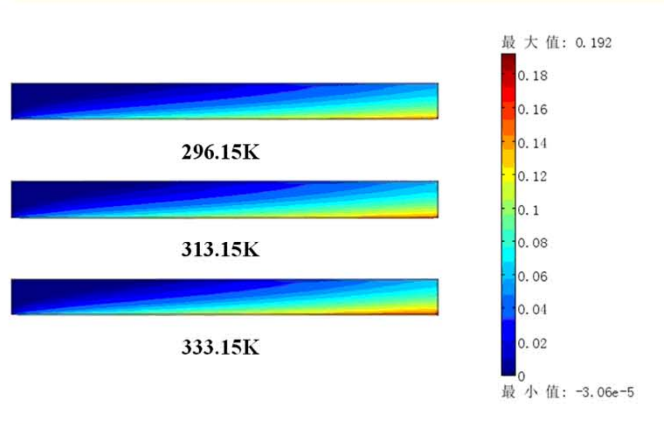
[2] Q. Liao, X. Zhu, X. Y. Zheng, et al. J. Power Sources, 2007, 171: 644-651



Current density



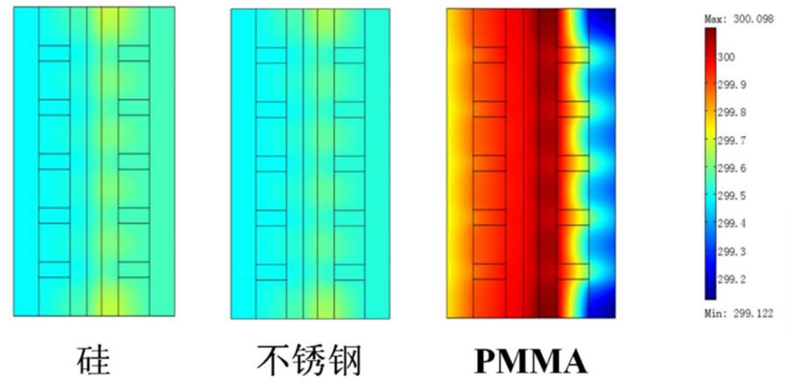
Flow rate



Temperature

Simulation Result

Temperature distribution in the μDMFC with different current collector materials : (a) silicon; (b) stainless steel; (c) PMMA.

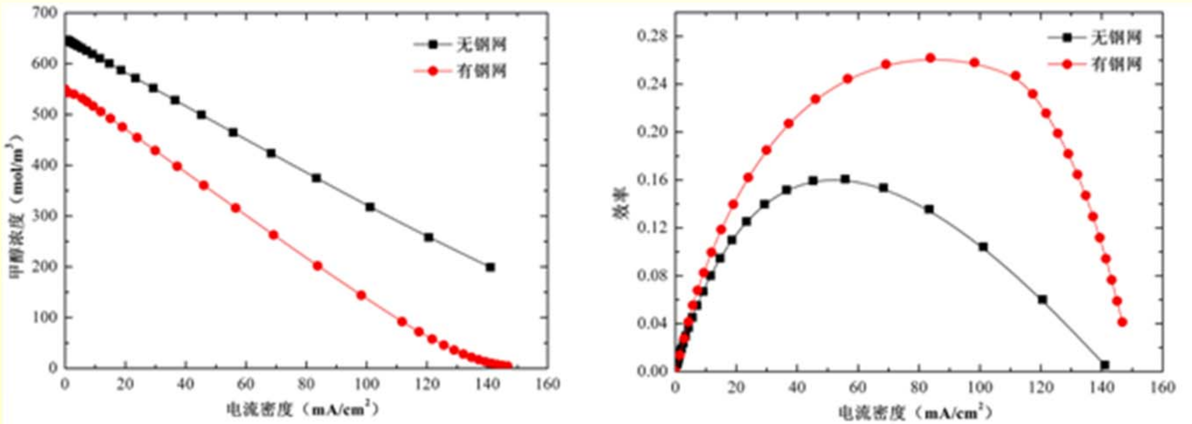


excellent qualities of the silicon and stainless steel in heat transfer, uniform temperature distributions were achieved in their corresponding cells

•stainless steel mesh

smaller methanol concentration in the anode catalyst layer, obtain the better performance

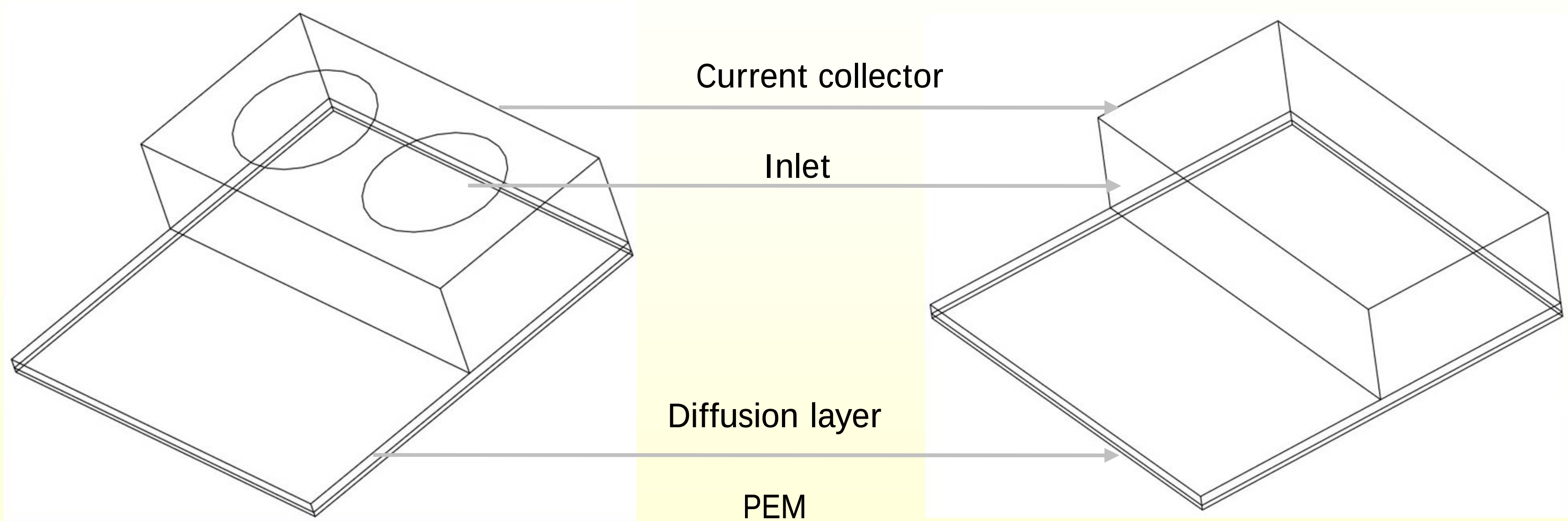
$$\eta = \eta_{th}\eta_{volt}\eta_{fuel} = \frac{\Delta G}{\Delta H} \times \frac{V_{cell}}{E_{cell}} \times \frac{i_a}{i_c} \times 100\%$$

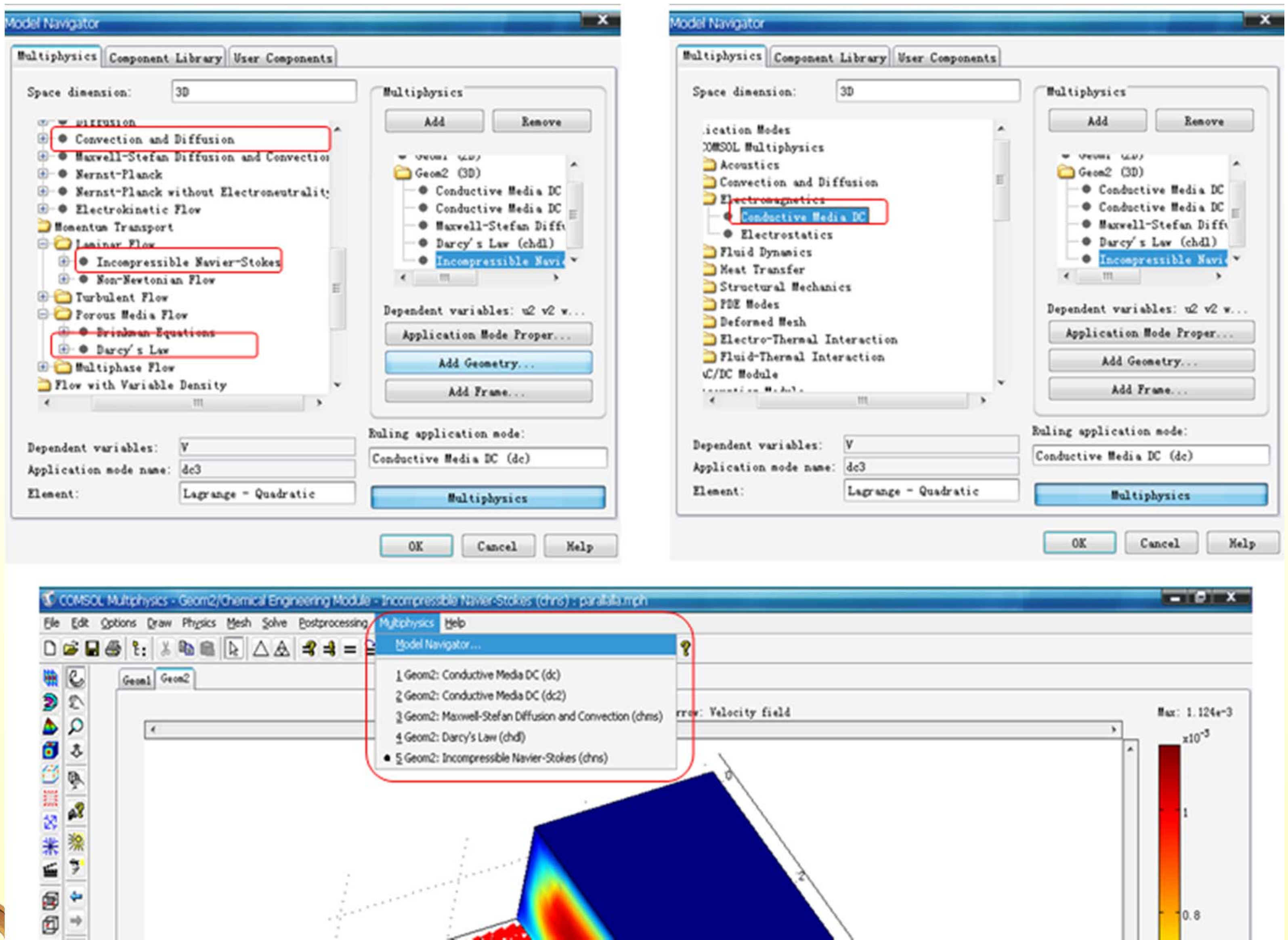


•Journal of Power Sources 195 (2010) 7338－7348 (IF=3.792)

3.2 µDMFC three-dimensional Model

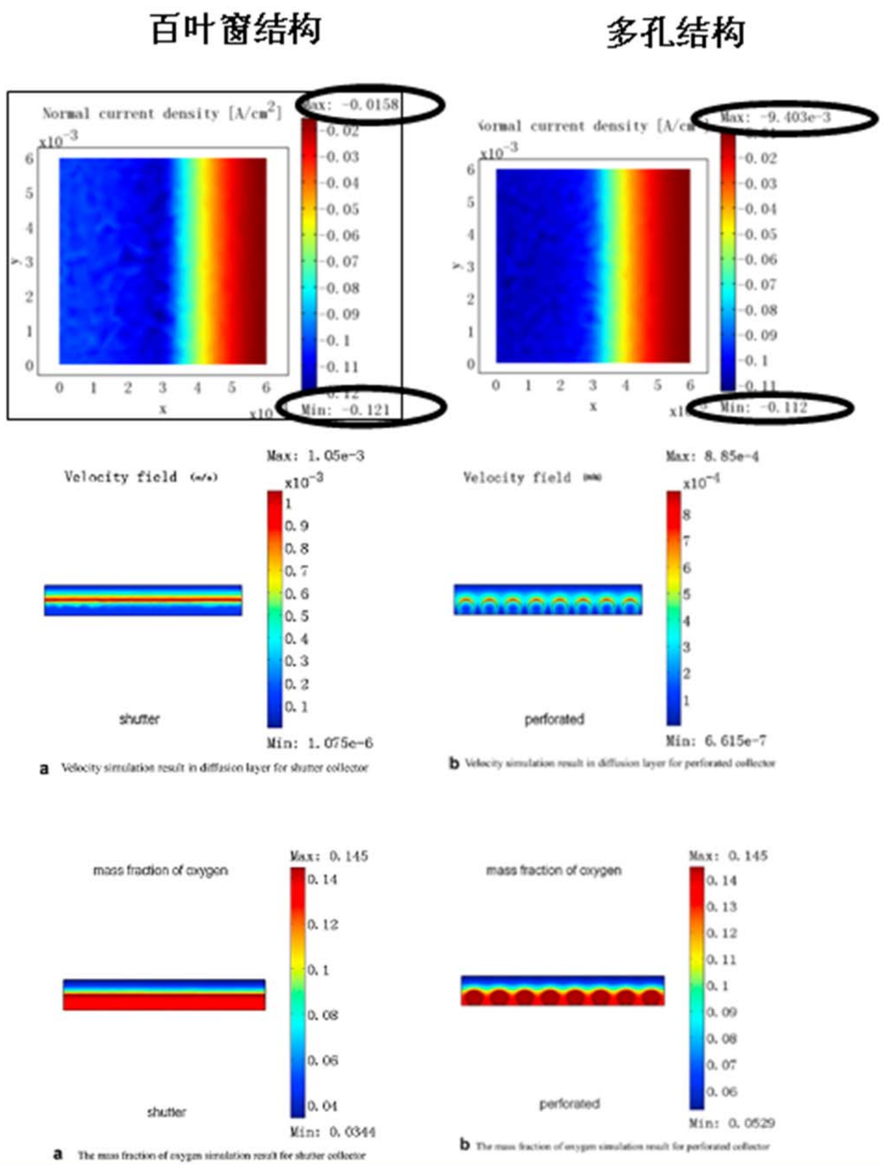
3.2.1An air-breathing direct methanol fuel cell with a novel cathode shutter current collector



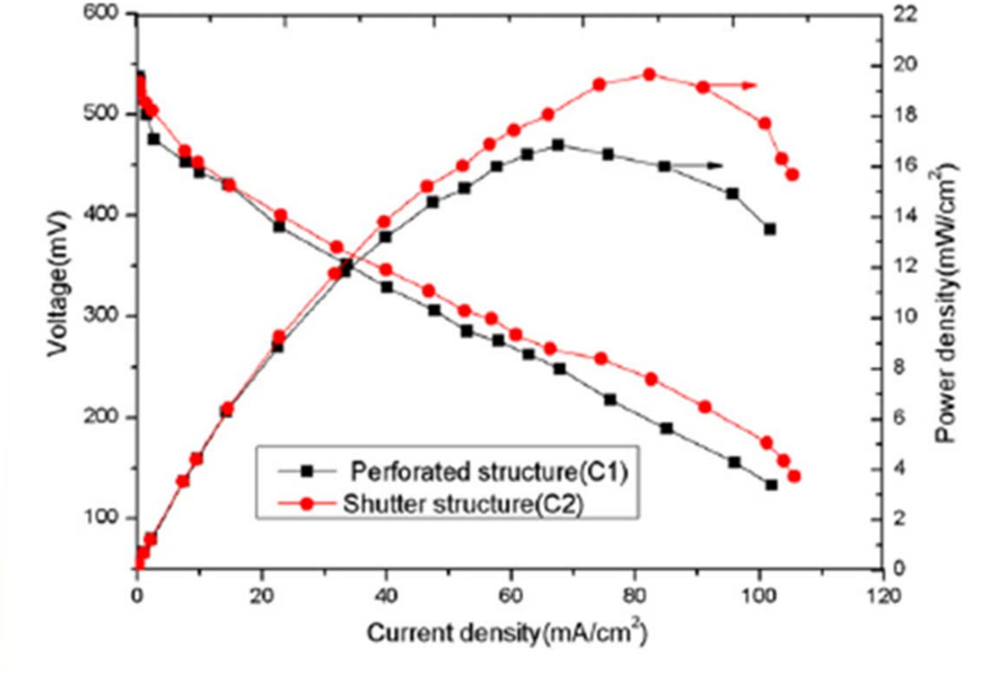

Model Navigator
Multiphysics
Component Library
User Components
Space dimension:
3D
Convection and Diffusion
Maxwell-Stefan Diffusion and Convection
Nernst-Planck
Nernst-Planck without Electroneutrality
Electrokinetic Flow
Momentum Transport
Incompressible Navier-Stokes
Non-Newtonian Flow
Turbulent Flow
Porous Media Flow
Darcy's Law
Multiphase Flow
Flow with Variable Density
Add
Remove
Geom2 (3D)
Conductive Media DC
Maxwell-Stefan Diffu
Darcy's Law (chdl)
Incompressible Navi
Dependent variables: u2 v2 w...
Application Mode Proper...
Add Geometry...
Add Frame...
Dependent variables:
Application mode name:
Element:
Lagrange - Quadratic
Ruling application mode:
Conductive Media DC (dc)
OK
Cancel
Help
Acoustics
Electromagnetics
Electrostatics
Fluid Dynamics
Heat Transfer
Structural Mechanics
PDE Modes
Deformed Mesh
Electro-Thermal Interaction
Fluid-Thermal Interaction
COMSOL Multiphysics - Geom2/Chemical Engineering Module - Incompressible Navier-Stokes (chns) : parallalla.mph
File Edit Options Draw Physics Mesh Solve Postprocessing Multiphysics Help
Model Navigator...
1 Geom2: Conductive Media DC (dc)
2 Geom2: Conductive Media DC (dc2)
3 Geom2: Maxwell-Stefan Diffusion and Convection (chms)
4 Geom2: Darcy's Law (chdl)
5 Geom2: Incompressible Navier-Stokes (chns)
Velocity field
Max: 1.124e-3

The velocity simulation results in diffusion layer with two types of collectors.

The mass fraction of oxygen simulation results with the two types of collector.



Test result



All experiments of the stack were performed with air self-breathing at room temperature on the cathode. Flow rates of 2 mL/min for 2 M methanol solution were supplied bya peristaltic pump.

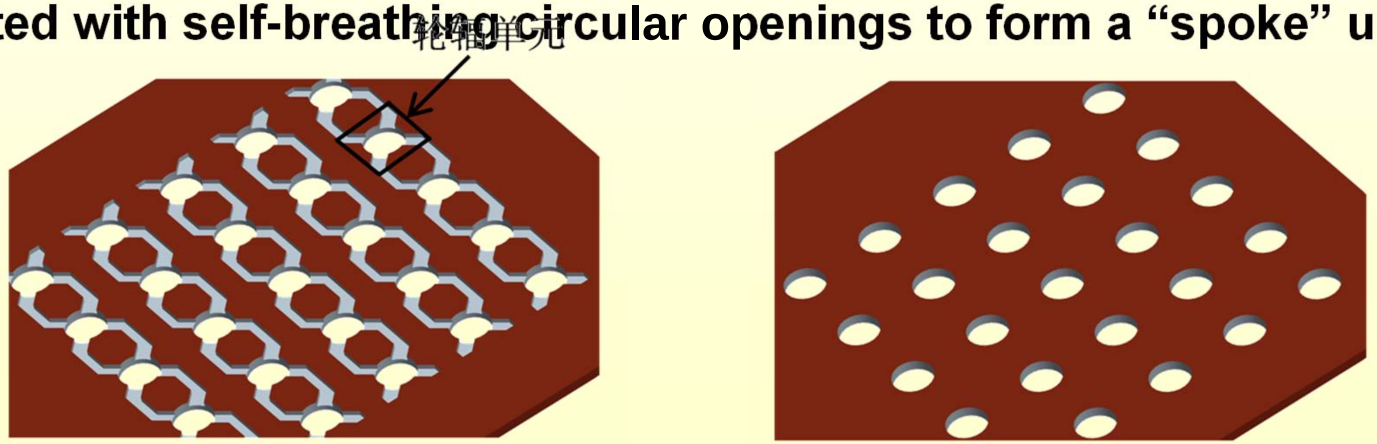
international journal of hydrogen energy 35 (2010) 5638-5646(IF=3.945)

3.2.2a three-dimensional two-phase-flow model for self-breathing μDMFCs

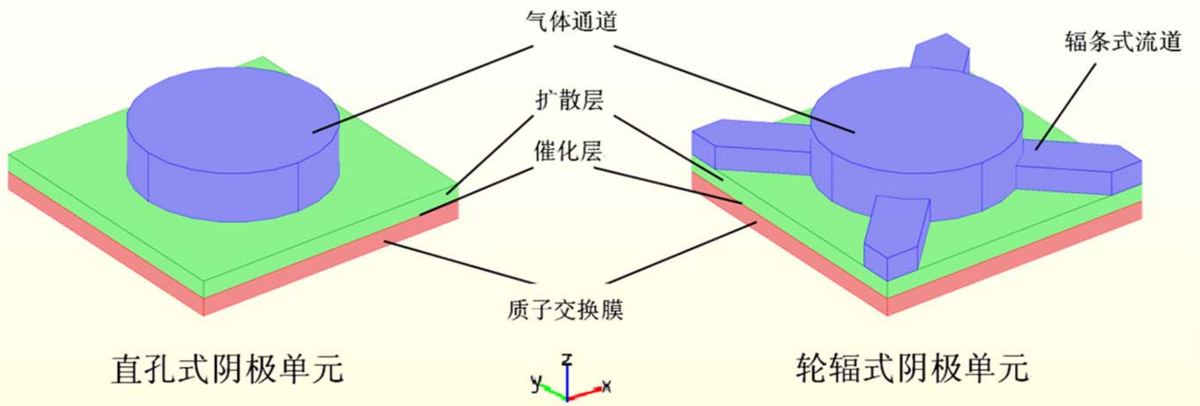
In order to ensure that the oxygen from air could enter the electrochemical reaction sufficiently and is well-distributed, the intension of this paper is to design a self-breathing μDMFC with a new cathode spoke structure

- structure

a similar back interface (air-contacting interface) structure to conventional perforated cathode, its front interface (electrode-contacting interface) is equipped with a certain number of blade-form channels which are connected with self-breathing circular openings to form a “spoke” unit.



➢Schematic of simulation domains of the three-dimensional model



➢Governing equations

- **electronic current** —— $-\nabla(-\sigma_{l,eff}\nabla\phi_l) = -S_a i_c$ $\qquad -\nabla(-\sigma_{s,eff}\nabla\phi_s) = S_a i_c$

- **Multicomponent mixed gas diffusion** —— $\pi_i = \{-\rho_g w_i \sum_{j=1}^{3} \frac{MD_{ij}}{M_j}(\nabla w_j + \frac{w_j}{M}\nabla M) + w_i \rho$

(Maxwell-Stefan)

➢ Governing equations

• **oxygen concentration ——** $\nabla \cdot (-D\nabla c_{O_2}) = R - \boldsymbol{u_g} \cdot \nabla c_{O_2}$

• **mass transport equation of the liquid-phase**

$$-\nabla \cdot (-\frac{\rho_l}{M_l}\frac{Kk_{rl}}{\mu_l}\sigma cos(\theta_c)(\frac{\varepsilon}{K})^{0.5}\nabla J(s)) + R_w = 0$$

• **The gas flow in the cathode flow channel is expressed by N-S equation:**

$$\rho_g \frac{\partial \boldsymbol{u_g}}{\partial t} - \nabla \cdot \mu_g(\nabla \boldsymbol{u_g} + (\nabla \boldsymbol{u_g})^T) + \rho_g(\boldsymbol{u_g} \cdot \nabla)\boldsymbol{u_g} + \nabla p_c = 0$$

• **The gas velocity in the diffusion layer** $\boldsymbol{u_g} = -\frac{Kk_{rg}}{\mu_g}\nabla p_g$

• **Butler-Volmer equation is used for explaining the relation between current and potential:**

$$i_c = i_0(\frac{c_{o_2}}{c_{o_2,ref}})\exp(-\frac{\alpha_c F(\phi_S - \phi_l)}{RT_0})$$

Result and discussion

➢ **compare of different cahtode**

•increases the efficiency of oxygen mass transport

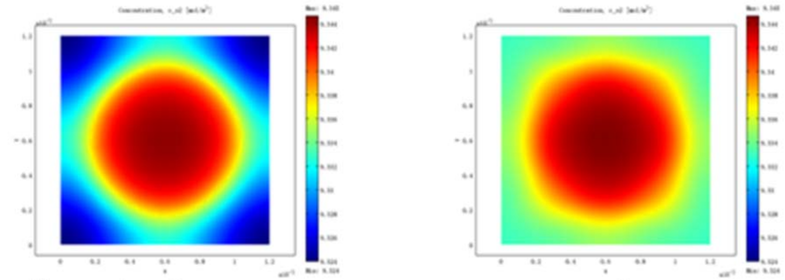
make the concentration more equal

•promotes the water transfer to PEM

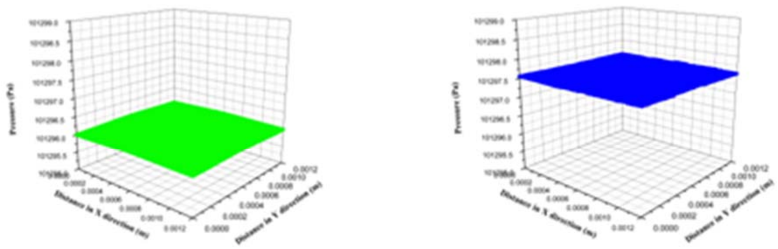
- **declining the inner resistance among PEM**

•Enchancing Electrocatalytic Activity

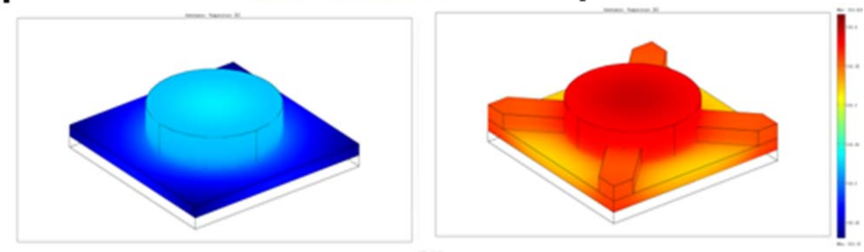
•Promoting the air vaporization



perforated (concentration) spoke



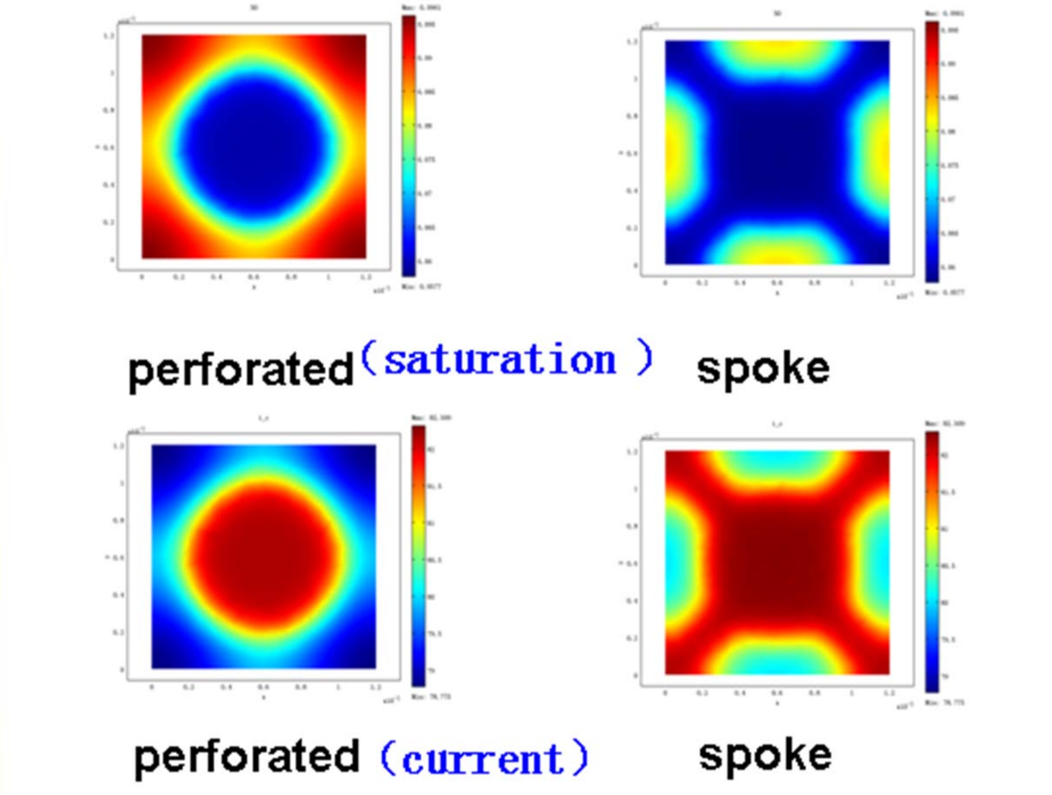
perforated (pressure) spoke



perforated (temperature) spoke

➢compare of different cahtode

- The latter shows a lower content than the former
- indicating a higher discharge capability

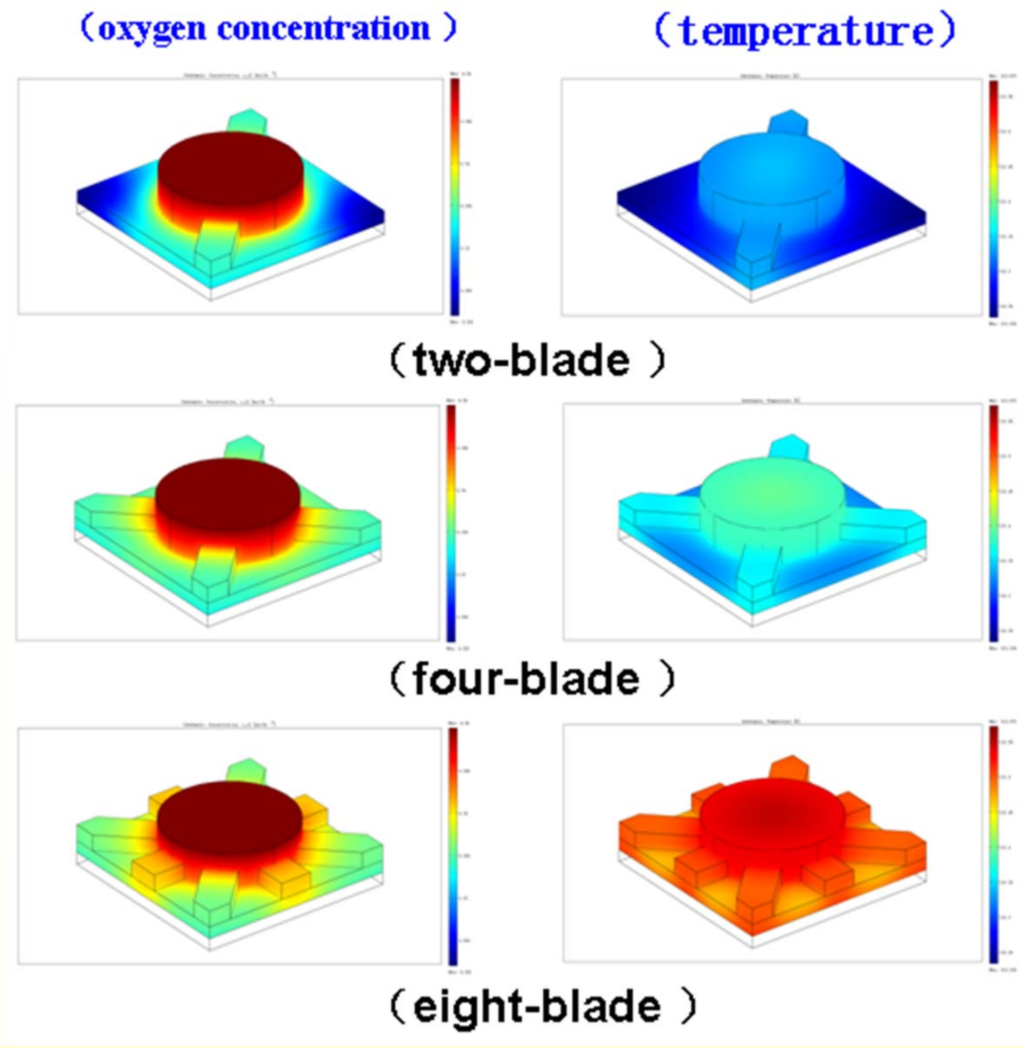


Model result

➤ different numbers of blades

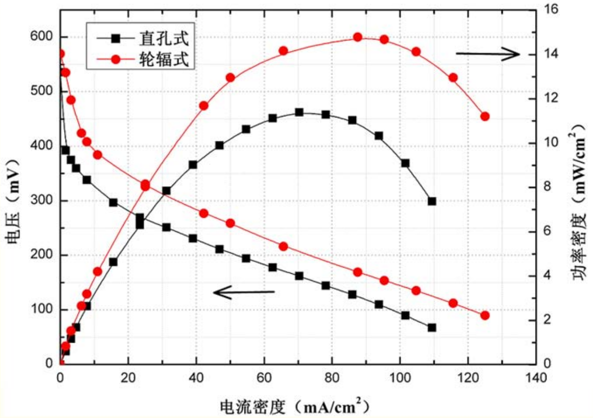
•**the eight-blade cathode shows the highest**

•**The distributions of the four-bladeand the eight-blade are relatively uniform**

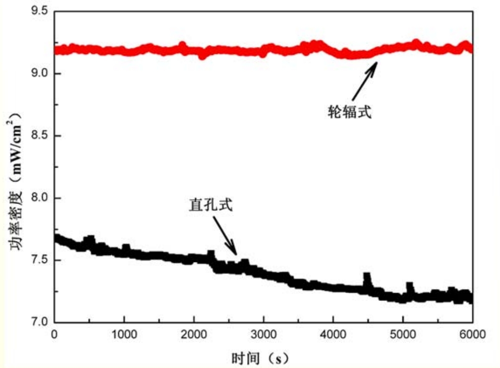


Test reult

- cathode structure



Performance comparison



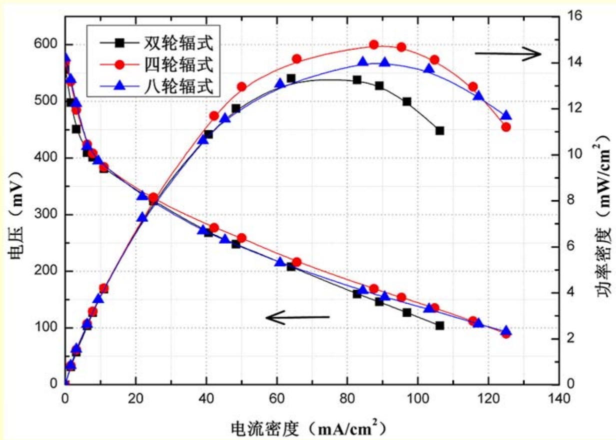
Durability

- number of blade

two-blade——13.33mW/cm²

four-blade——14.79mW/cm²

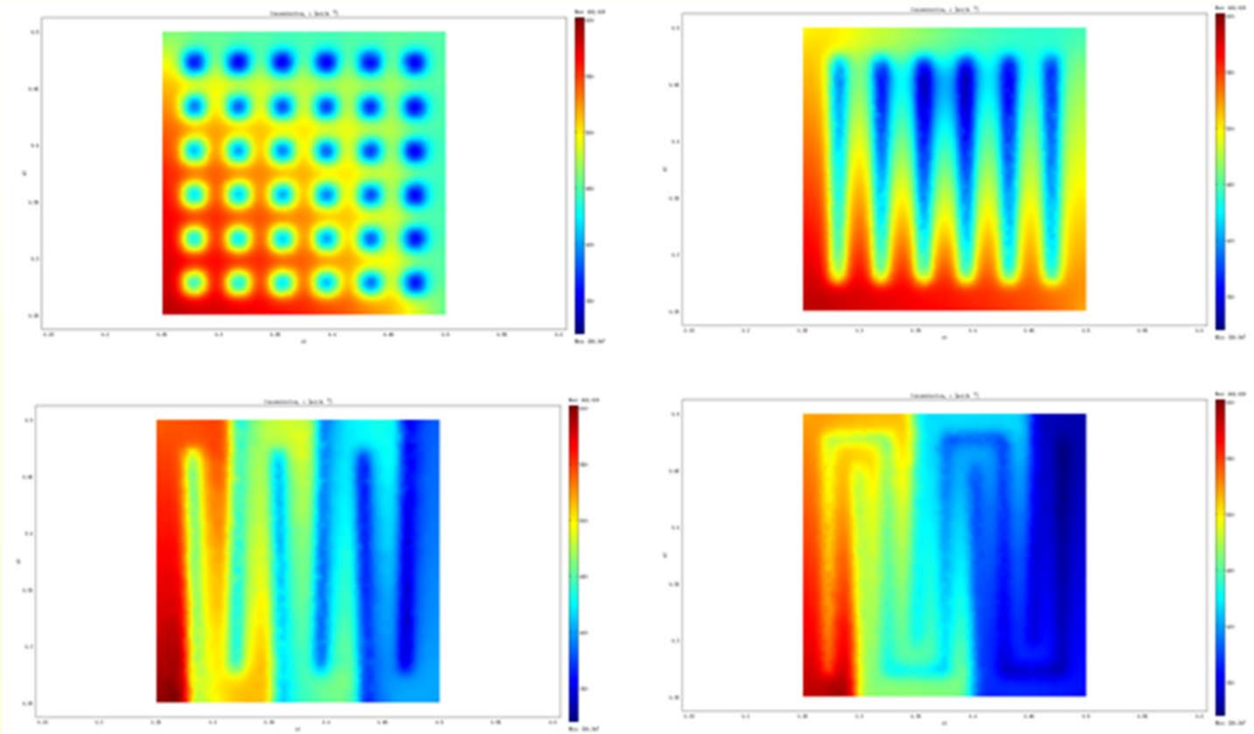
eight-blade——14.01mW/cm²

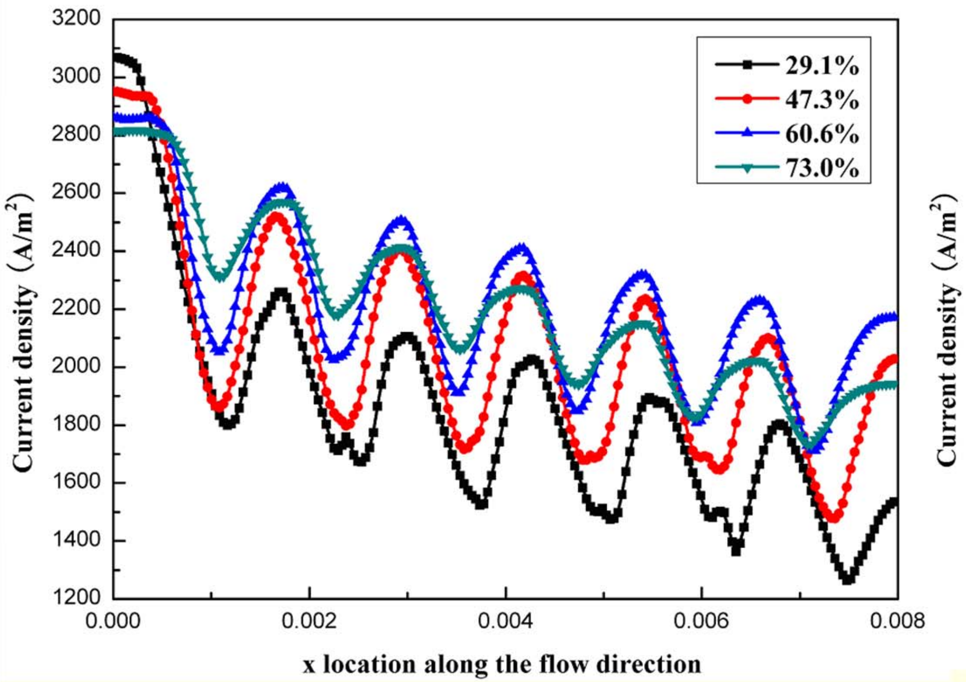


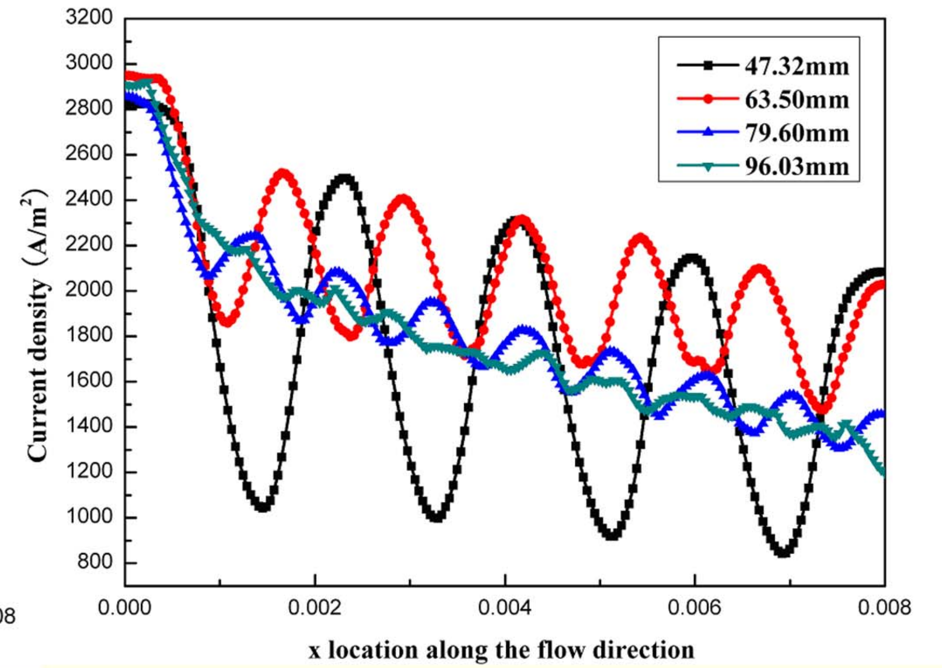
Performance comparison

Methanol concentration distributions at the catalyst layers under different flow fields are 586.58、585.29、602.03和590.93mol/m^3

single serpentine field flow has best performance

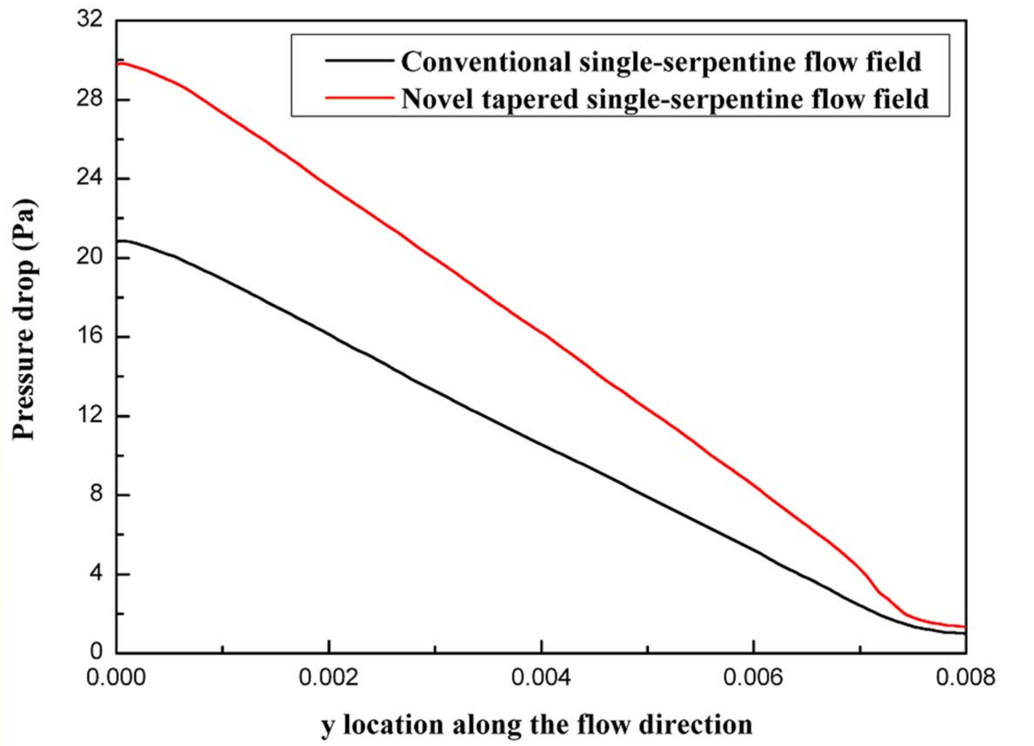




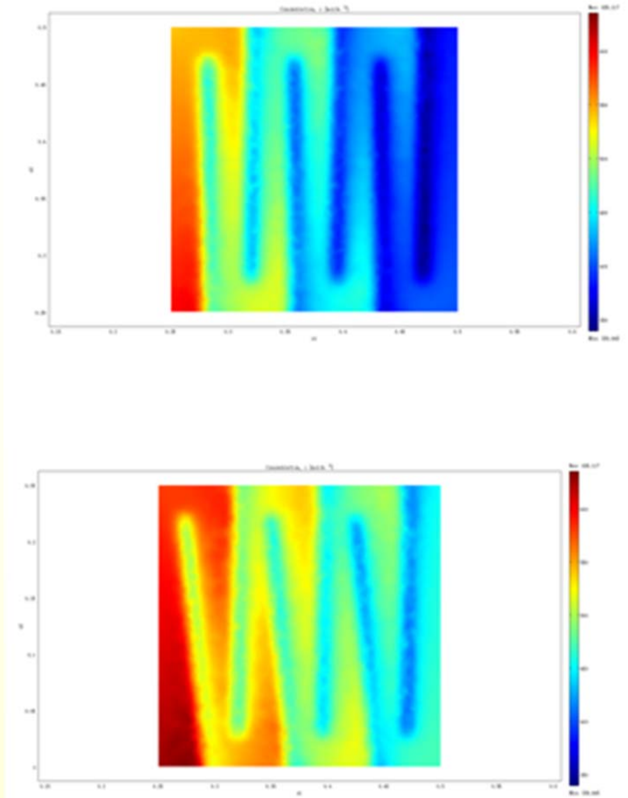


Current density distributions at the catalyst layers along x direction under the conditions of different open ratios.

Current density distributions at the catalyst layers along x direction under the conditions of different channel depth.



Comparison of the line pressure drop at the interfaces between the diffusion layers and two single-serpentine flow fields



Methanol concentration distributions

contents

4. summary

outlook:

- Methanol crossover
- Analyses of the fuel cell stack assembly pressure

THANKS!