Chemistry with a heart
TOKUYAMA

2011 AMFC WORKSHOP

Electrolyte Materials for AMFCs and AMFC Performance

May 8th 2011
Tokuyama Corporation
Kenji Fukuta

Location of Tokuyama Corporation

Application of Hydrocarbon IEM

Food And Pharmaceutical

* Demineralization of Cheese Whey
* Demineralization of Organic Acids and Amino Acids
* Desalination of Soy-Sauce
* Stabilization of Wine
* Demineralization and Purification of Pharmaceutical Intermediate

Electrodialyzers ACILYZER

Electronics

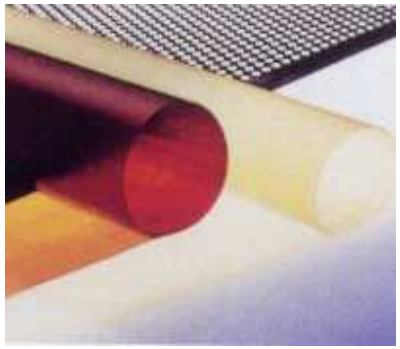
* Production of High Purity Chemicals
* Production of Ultra Pure Water
* Battery Diaphragm

NEOSEPTA®

EDCORE

NEOSEPTA®BIPOLAR

ACILYZER



Ion exchange Membrane NEOSEPTA

Environmental Conservation

* Desalination of Leachate
* Removal of Nitrate from Under-Ground Water

Others

* Production of Salt from Sea water
* Production of Drinking Water from Brackish Water
* Desalination of Deep Sea Water
* Acid Recovery from Waste Acid

Outline

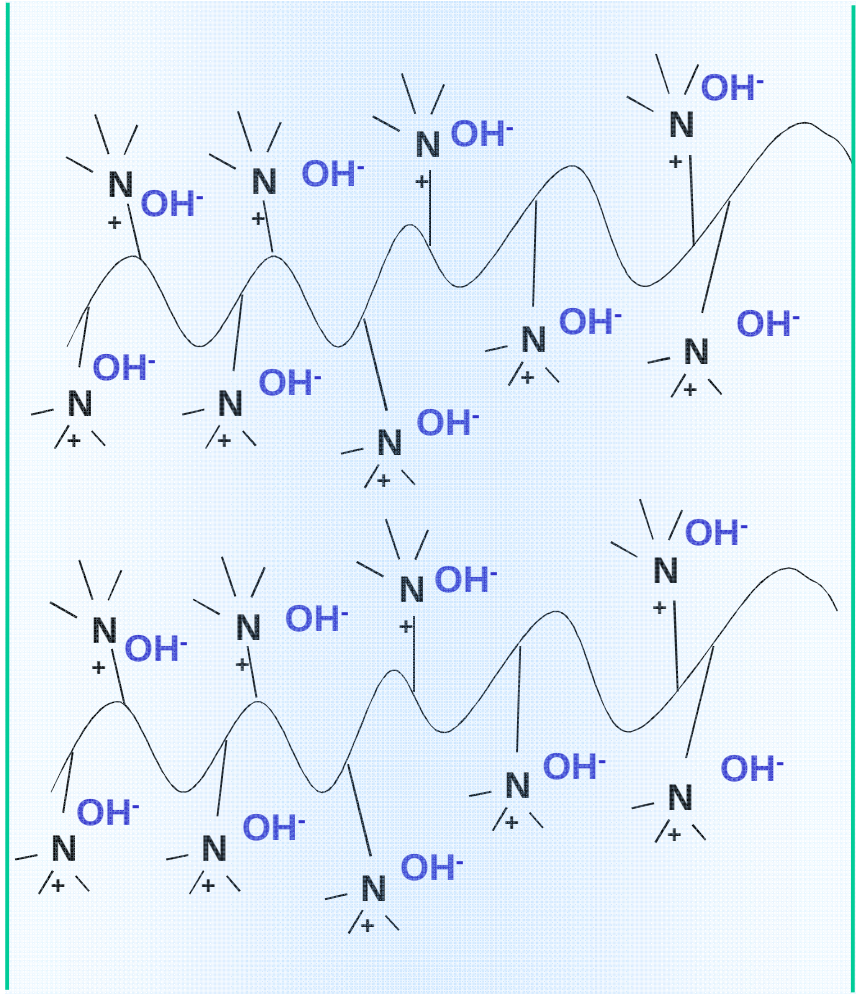
1. Tokuyama's Electrolyte Materials for AMFCs
- Anion exchange membrane
- Alkaline Ionomer

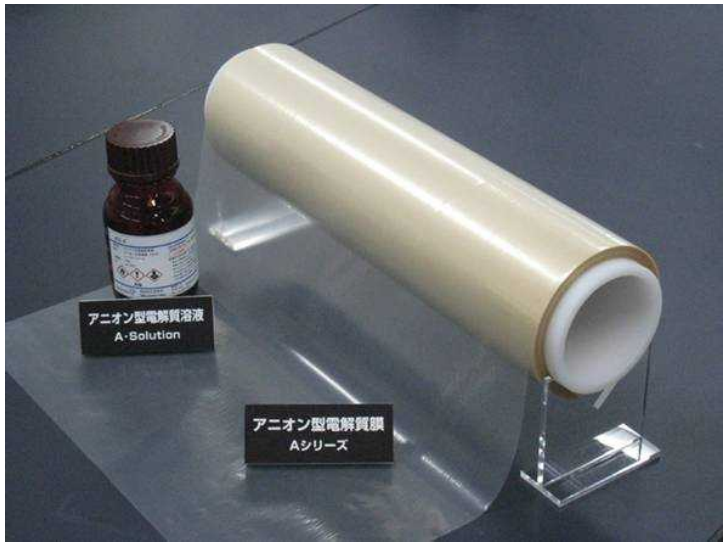
2. Performance of AMFCs
- Power density
- Characteristic behavior in AMFC
  - CO_2 problem
  - Water transport
- Durability

3. Summary

Tokuyama Anion exchange Membrane

Structural image



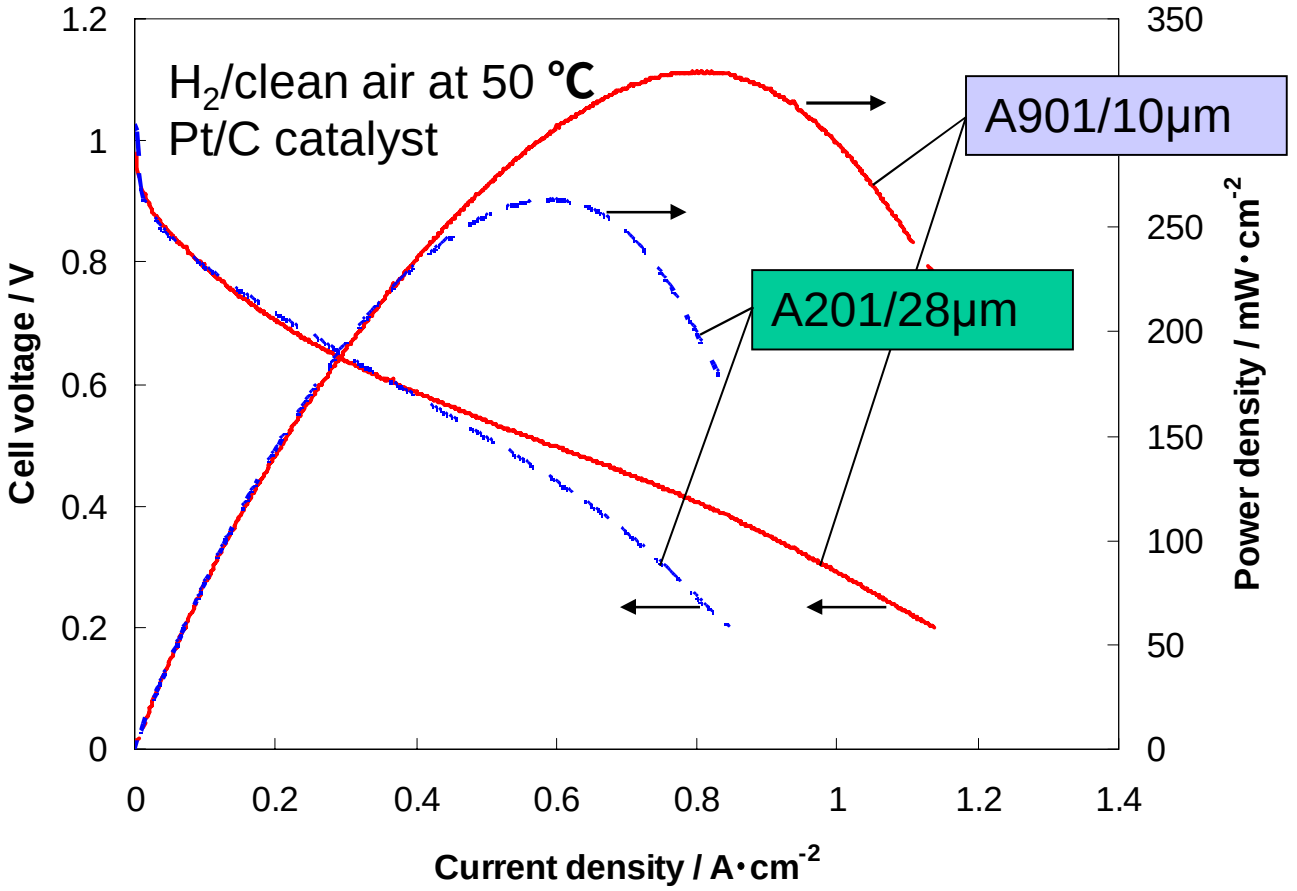


Properties of Anion Exchange Membranes

Properties		A201 (Tokuyama)	A901 (Tokuyama)	Fluorinated membrane (Cation Membrane)
Thickness	／μm	28	10	180
Ion-exchange capacity	／mmol･g^{-1}	1.8	1.8	1.0
Water content	／－	0.25	0.15	0.30
Ion conductance [1)]	／mS･cm^{-2}	11	29	4.2
Ion conductivity [1)]	／mS･cm^{-1}	42	38	84
Burst strength	／MPa	0.4	0.2	0.5
Dimensional change	wet⇔dry			
MD	／%	2	1	10
TD	／%	6	4	15

1) Two probe method for in plane conductivity measurement at 23 ℃, 90%RH under N_2 atmosphere, at OH- form

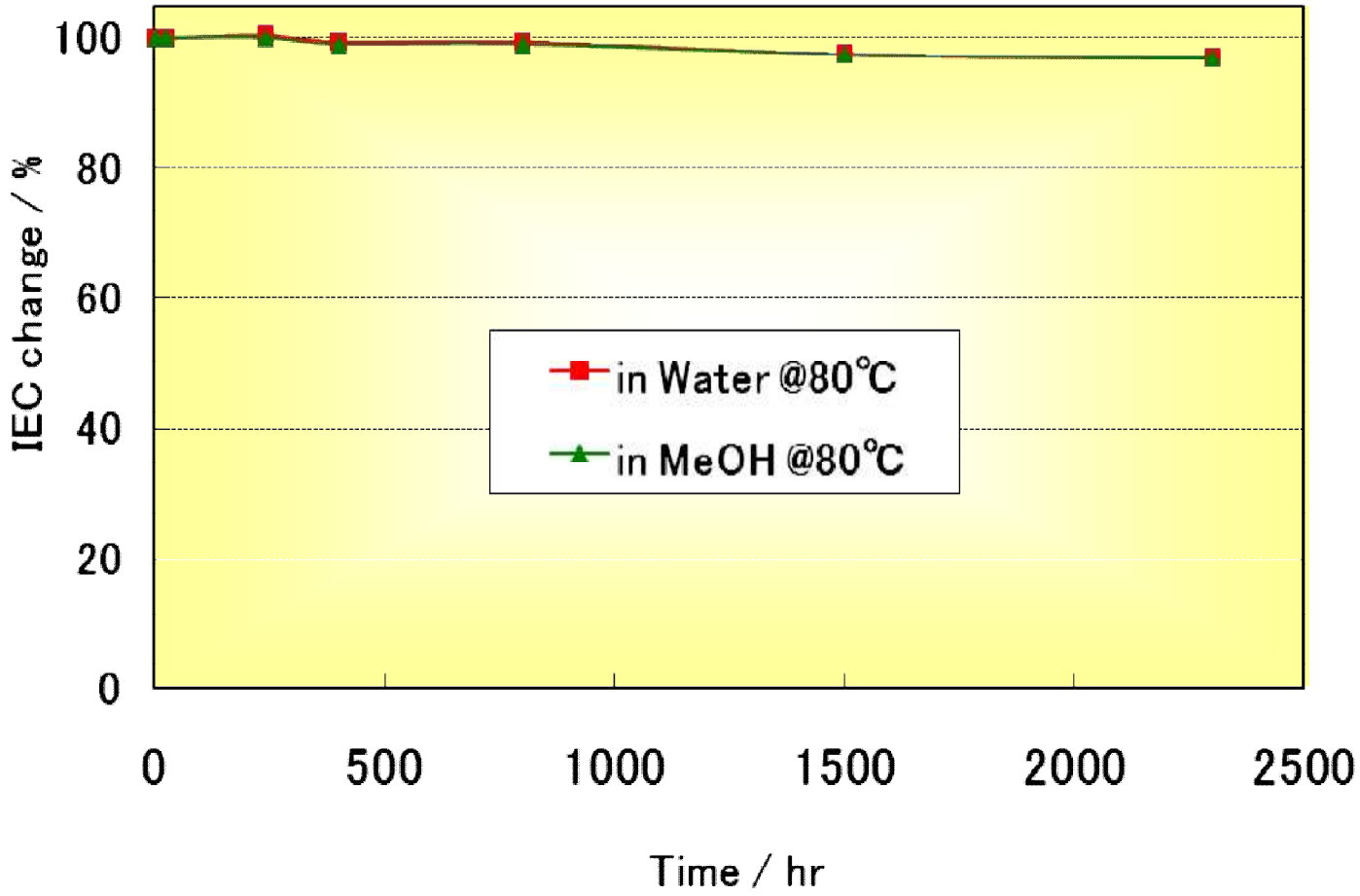
AMFC Performance with Different Membrane



【MEA composition】
Membrane ：A201 or A901
Ionomer ：AS－4
Pt amount ：0.5mg/cm²

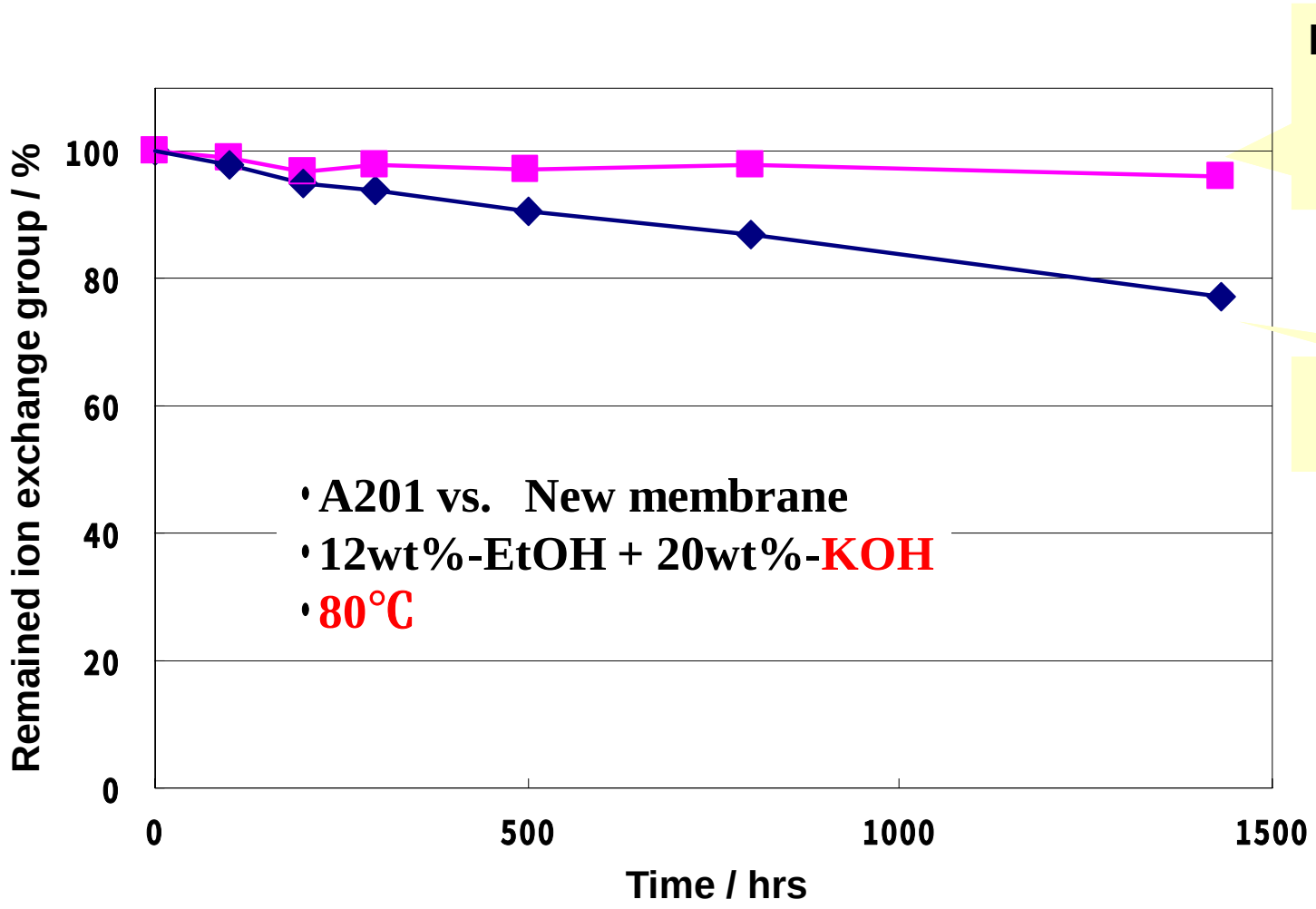
【measurement condition】
Cell temp. ：50℃
Anode ：95%RH H_2 0.5L/min (A201)、1.0L/min (A901)
Cathode ：95%RH clean air 1.0L/min (A201)、2.0L/min (A901)

Stability Test of Membrane (A201)



Membrane was ion-exchanged to OH^- form and stored in the air before durability test.
(maybe converted to HCO_3^- form)

Accelerated Durability Test

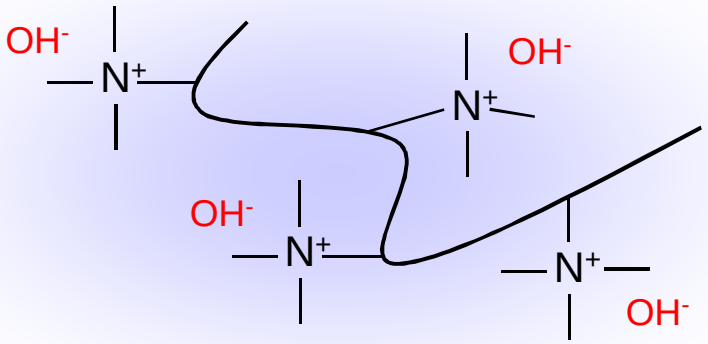


New membrane
- different ion-exchange group
- ～80℃

- A201
  ～70℃

Tokuyama Akaline Ionomers

Structural image



Linear hydrocarbon backbone with quaternary ammonium group

Needs for ionomers

- High ion conductivity
- Solubility into solvent at preparation of catalyst ink
- Non-solubility after preparation of catalyst layer
- Dispersivity in catalyst ink
- Durability

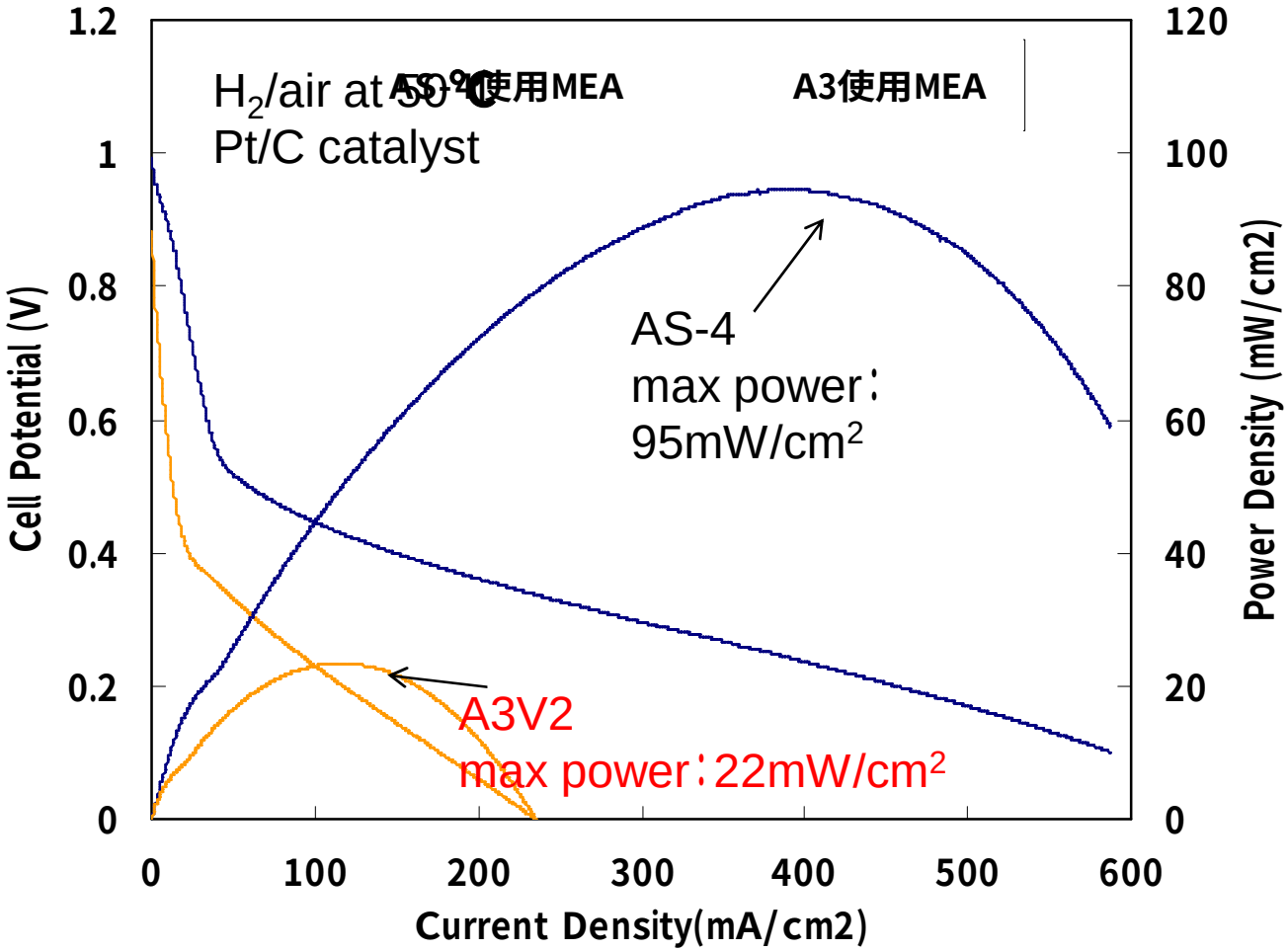
etc.

Properties of A-Ionomer Solution

State	Features	A3 ver.2	AS-4
solution	Polymer concentration／wt%	5	5
	Solvent	Tetrahydrofuran & 1-Propanol	1-Propanol
membrane (cast film)	Ion-exchange capacity／mmol･g^{-1}	0.7	1.4
	Ion conductivity／mS･cm^{-1} (HCO_3^- form)	2.6	13
	Solubility to solvent		
	Water	not soluble	not soluble
	MeOH	not soluble	not soluble
	EtOH	not soluble	not soluble

1)～3) Measured using cast film
2) Measured on alternative current(40℃, wet) ,at HCO_3^- form

AMFC Performance - Ionomer Type

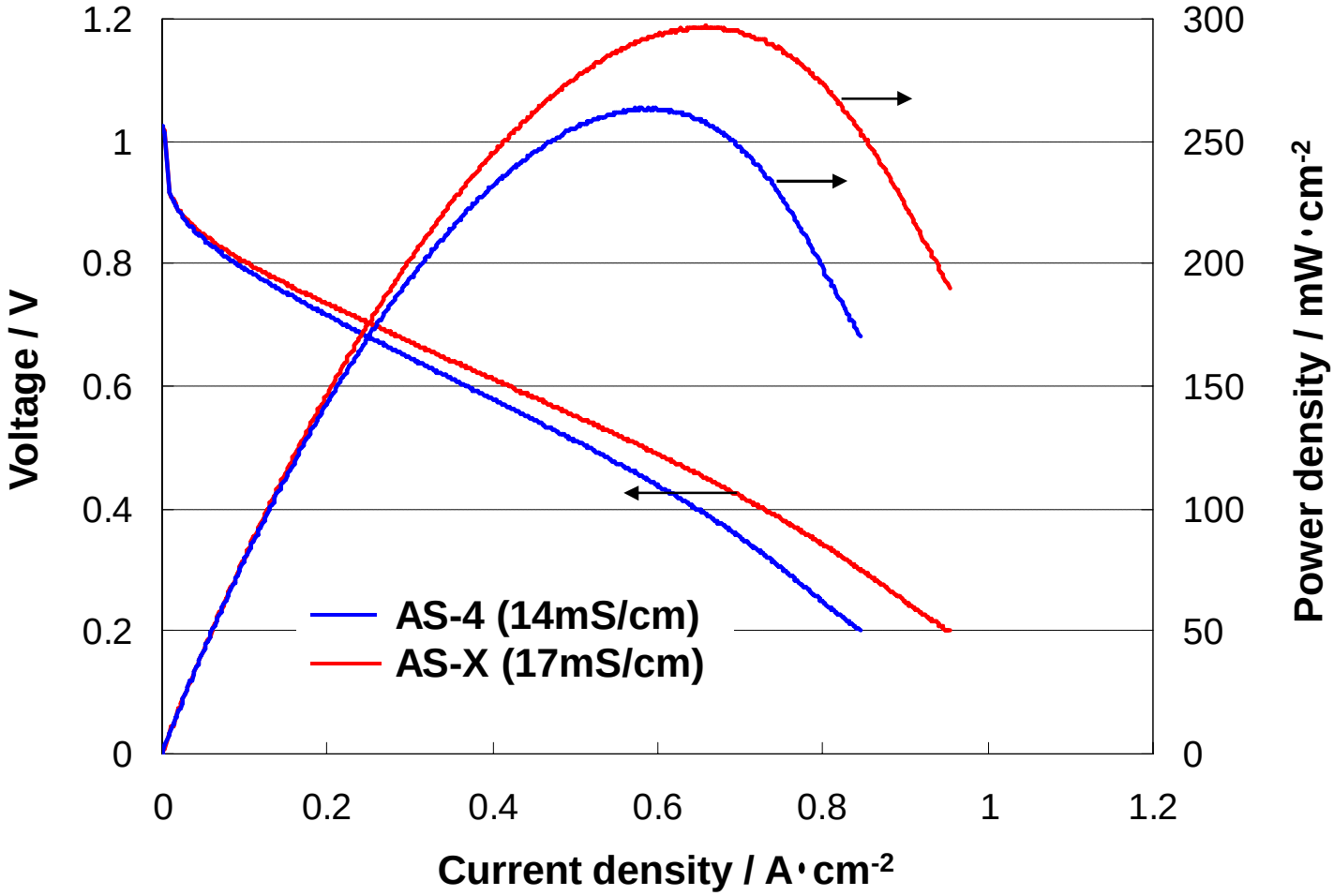


【MEA composition】
Membrane ：A801
Ionomer ：AS-4 or A3 ver.2
Pt amount ：0.5mg/cm^2

【measurement condition】
Cell temp. ：50℃
Anode ：95% RH H_2
Cathode ：95% RH air

Effect of improved ionomer

Ionomer	IEC (mmol/g)	Conductivity (mS/cm)
AS-4	1.4	14
AS-X	1.8	17



Outline

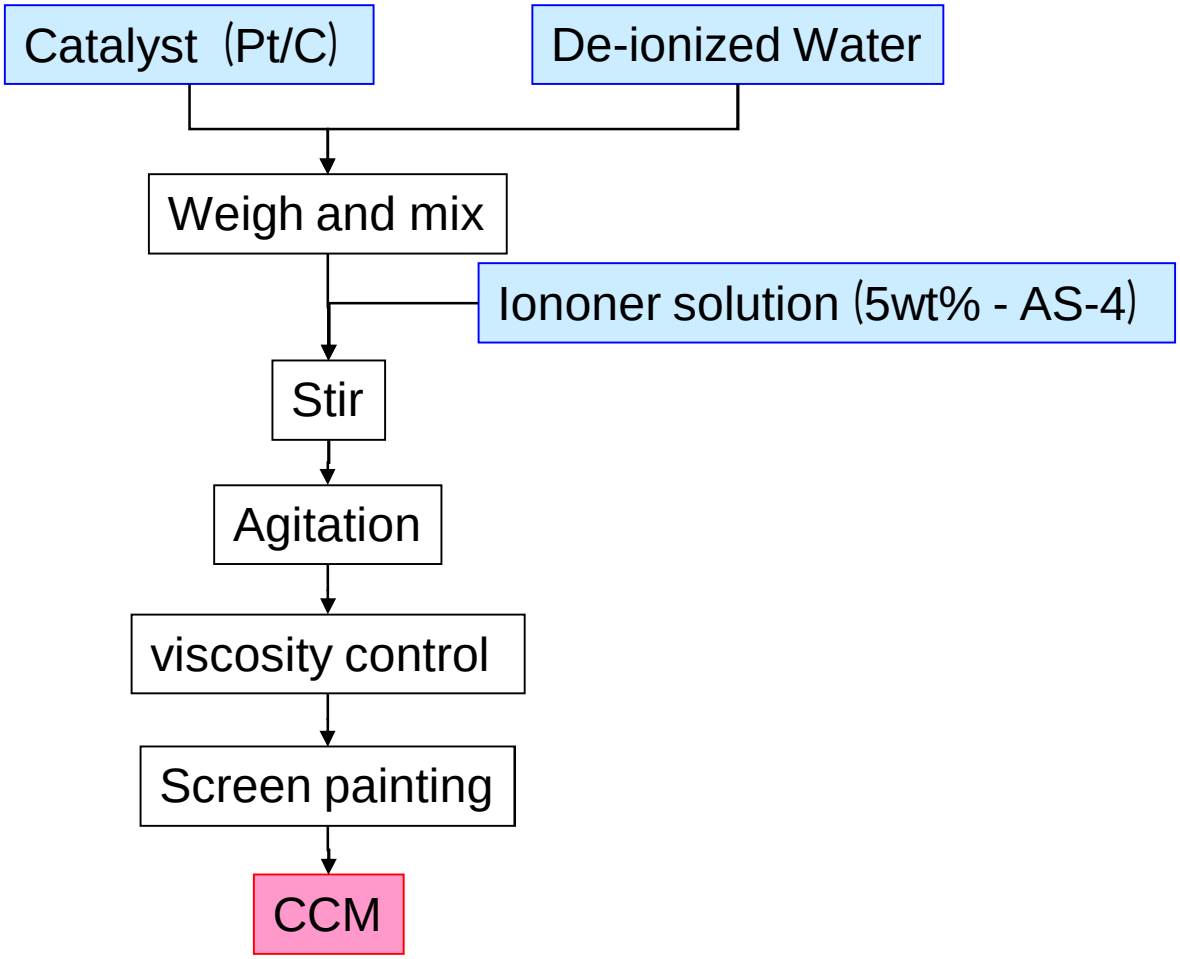
1. Tokuyama's Electrolyte Materials for AMFCs
- Anion exchange membrane
- Alkaline Ionomer

2. Performance of AMFCs
- **Power density**
- Characteristic behavior in AMFC
  - CO_2 problem
  - Water transport
- Durability

3. Summary

Fabrication of CCM

◎ Fabrication process （Catalyst：Iononer = 7:3）



Catalyst ink

CCM (5cm2)

Evaluation Procedure

Evaluation of I-V curves

- GDL : Toray TGP-H060 (without hydrophobic treatment)
- fuel : H_2 (95%RH, 1000mL/min)
- oxidant : clean-air (CO_2<0.1ppm, 95%RH, 2000mL/min)
  or O_2 (95%RH, 1000mL/min)
- Temperature : 50℃

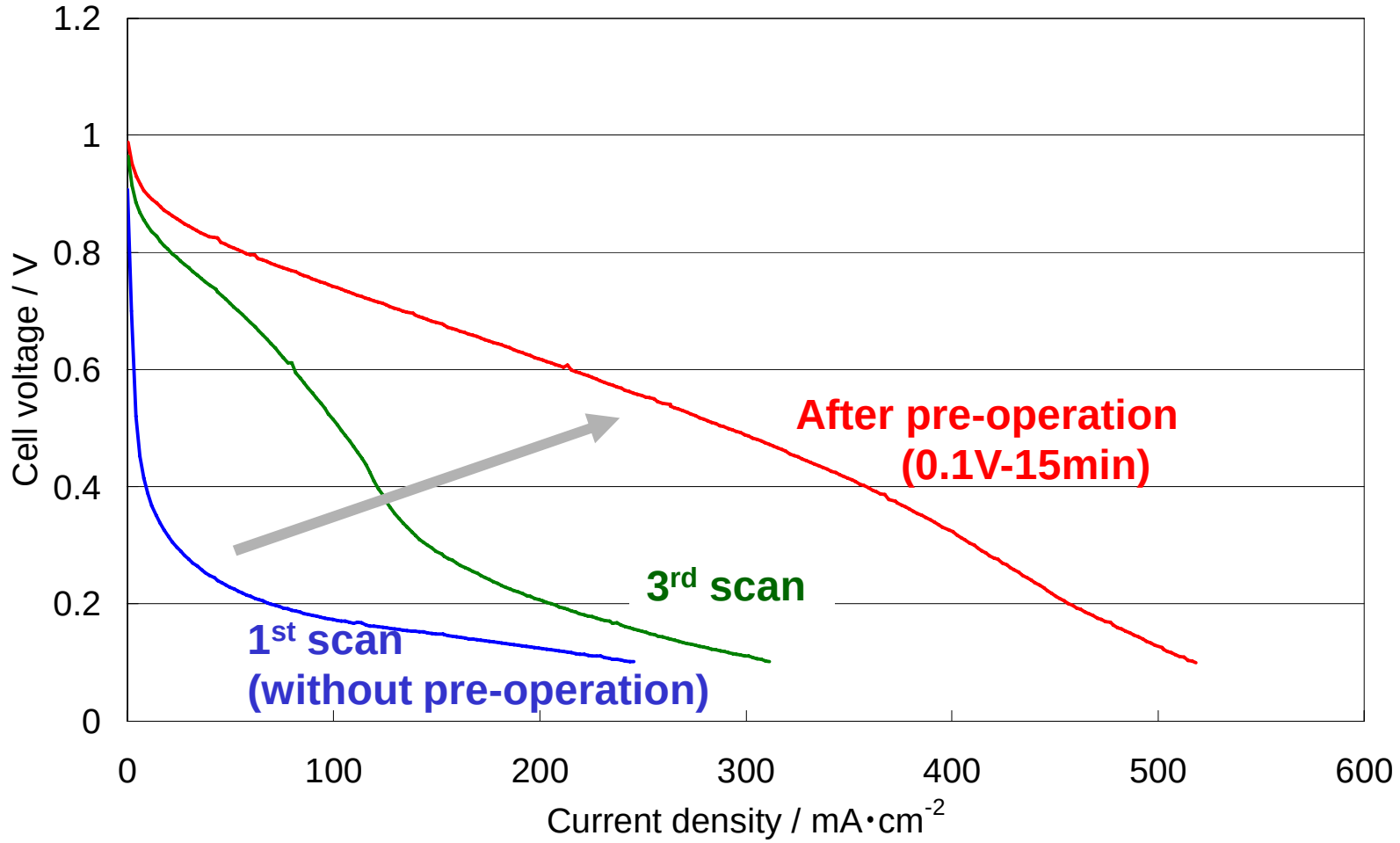
- evaluation step :
  MEA set into cell → pre-operation at 0.1V for 15min (for activation)
  → measurement of I-V curves

Optimized condition

- Pt/C:ionomer = 7:3 (in case of Pt/C(Pt;46wt%), at high flow rate)
- Maybe differ by catalyst and flow condition

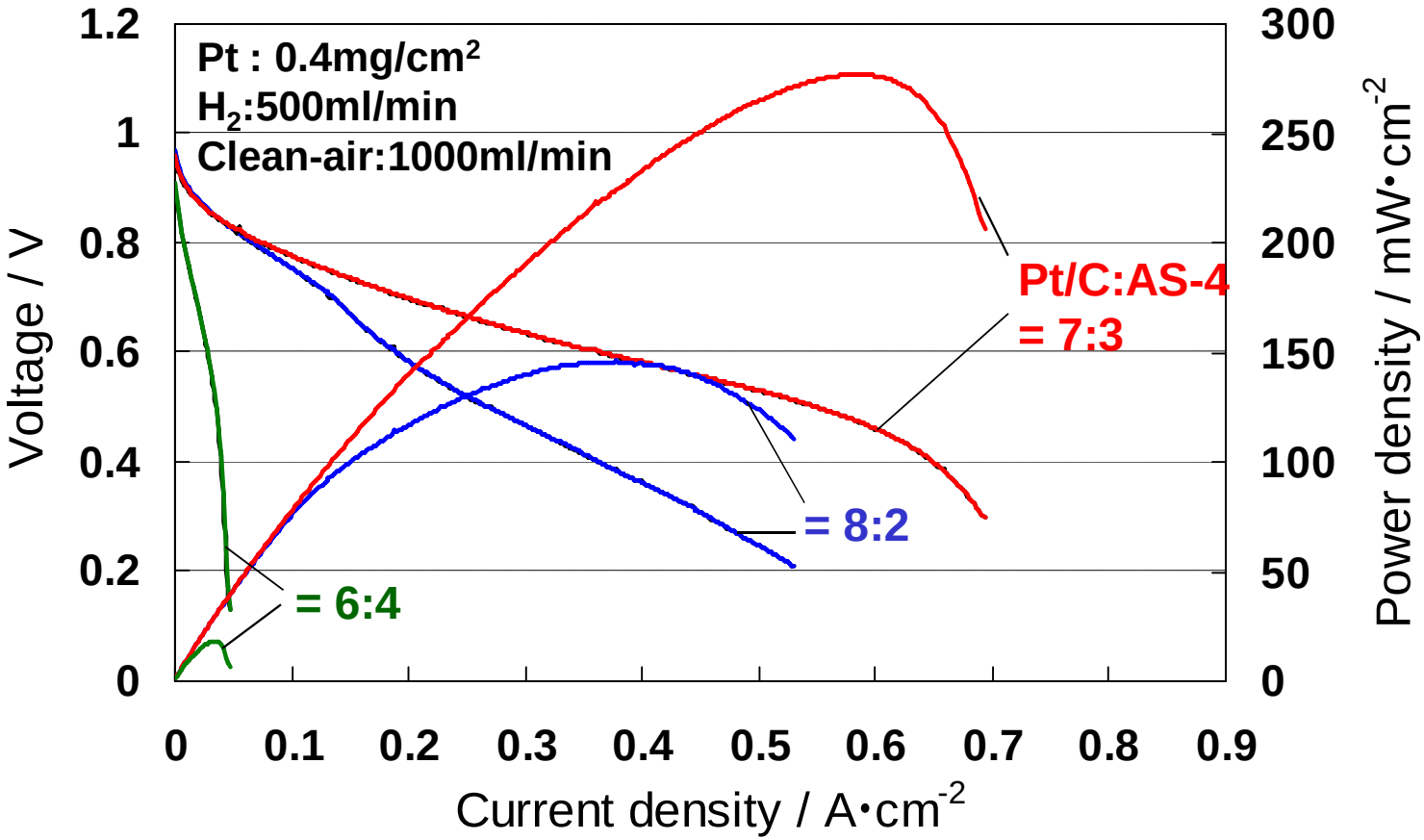
Effect of Pre-Activation

- HCO_3^- form membrane changes to OH^- form by the OH^- generated at cathode through pre-operation (self-purging), and it makes the performance higher.



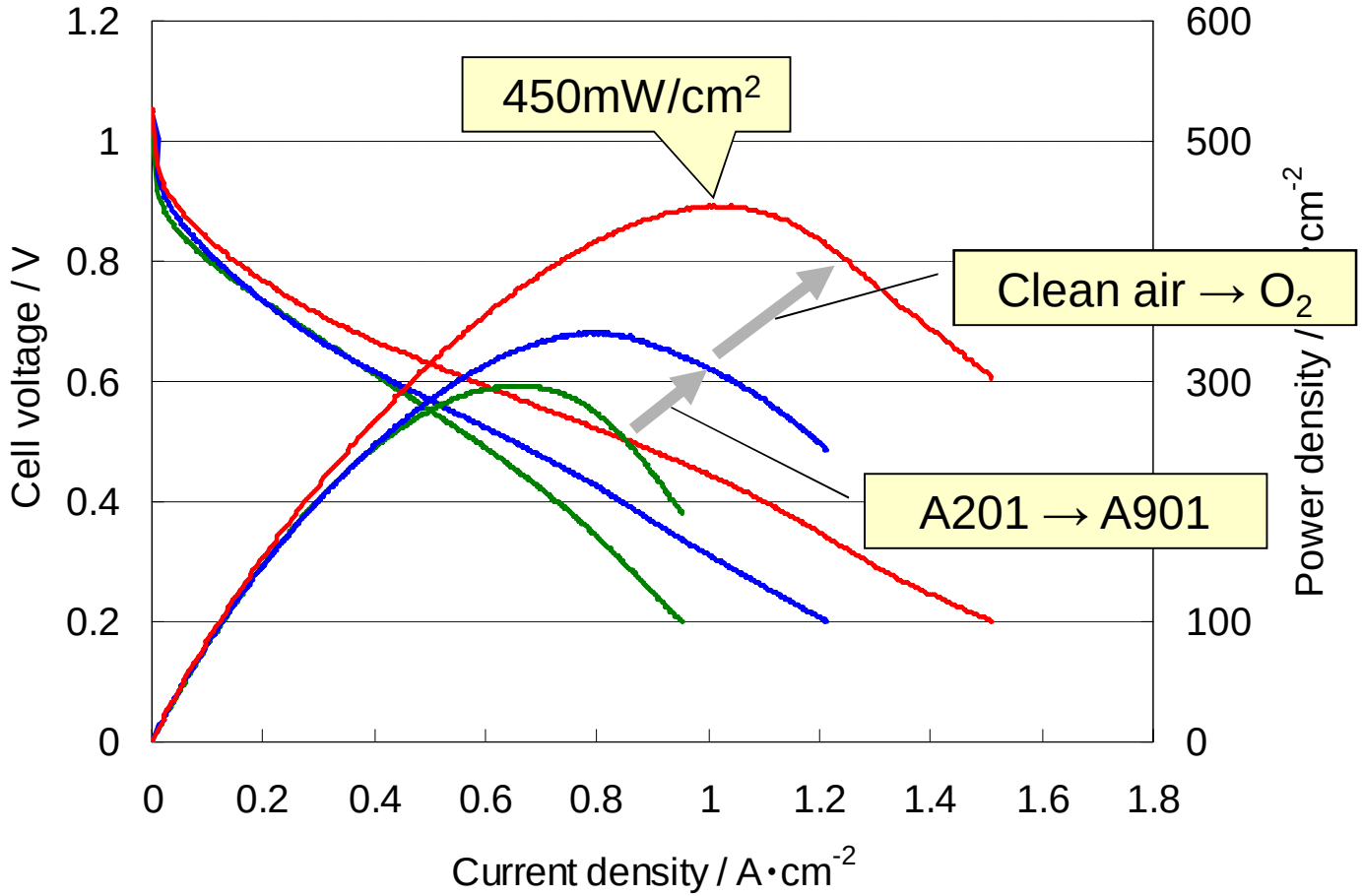
Influence of Ionomer Content

- Pt/C:AS-4 = 7:3 shows the best performance in this condition.
- Appropriate content should be differed by catalyst and operation condition.



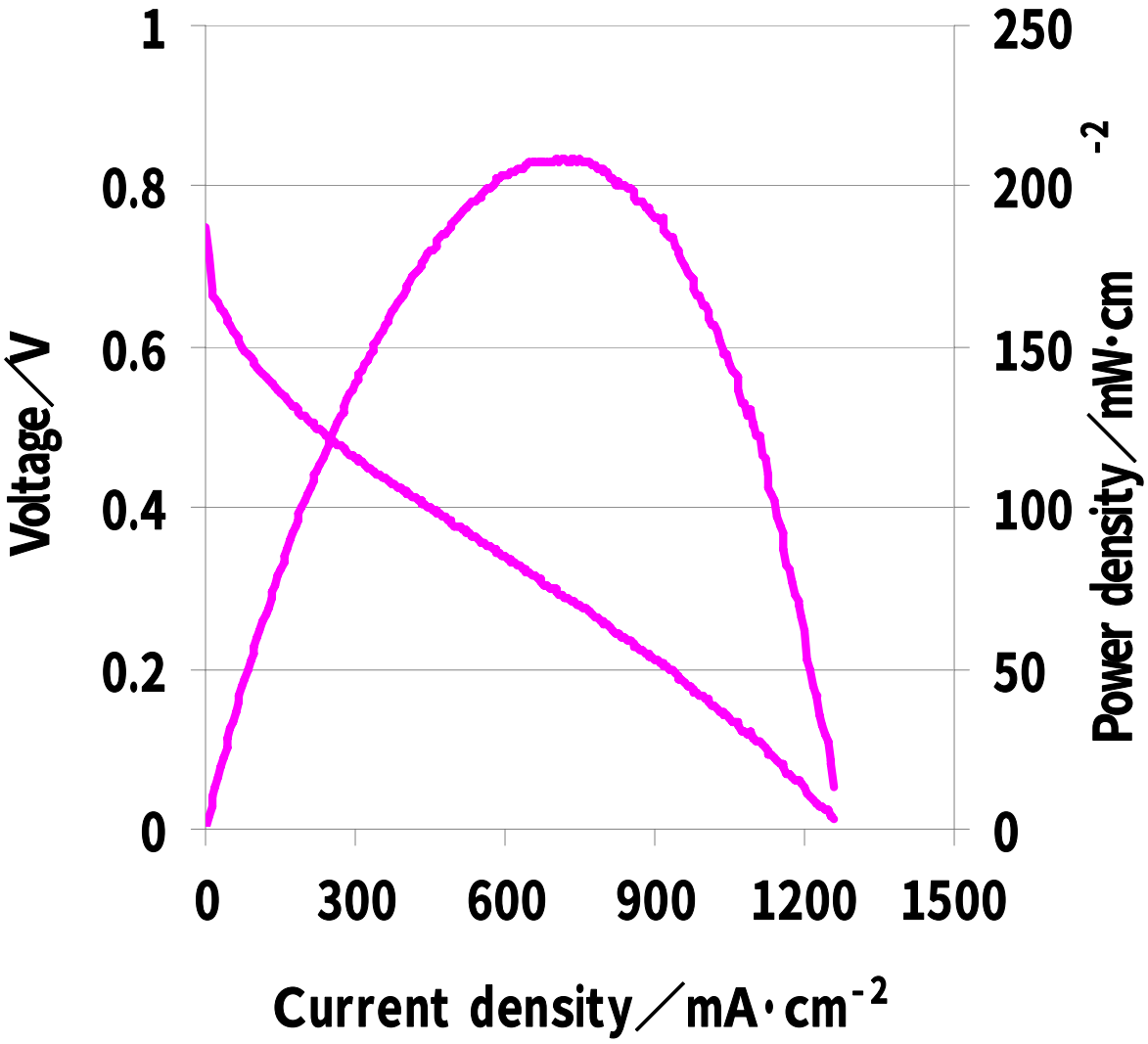
Optimized Performance at Tokuyama

Menbrane:A201 → A901, Ionomer:AS-4 → AS-X, Pt/C:AS-X=7/3, 0.5mg-Pt/cm^2



- **Best power density : 340mW/cm^2 (using clean air)**
- **450mW/cm^2 (using O_2)**

AMFC Performance (MeOH / KOH-Air)



- Membrane ：A201
- Catalyst ：Anode Pt-Ru/C 1.1mg/cm^2
  Cathode Pt/C 0.5mg/cm^2
- Ionomer ：AS-4
- Fuel ：3wt%-MeOH + 5wt%-KOH 10ml/min
- Oxidant ：95%RH Clean Air 4000ml/min
- Temp. ：80℃

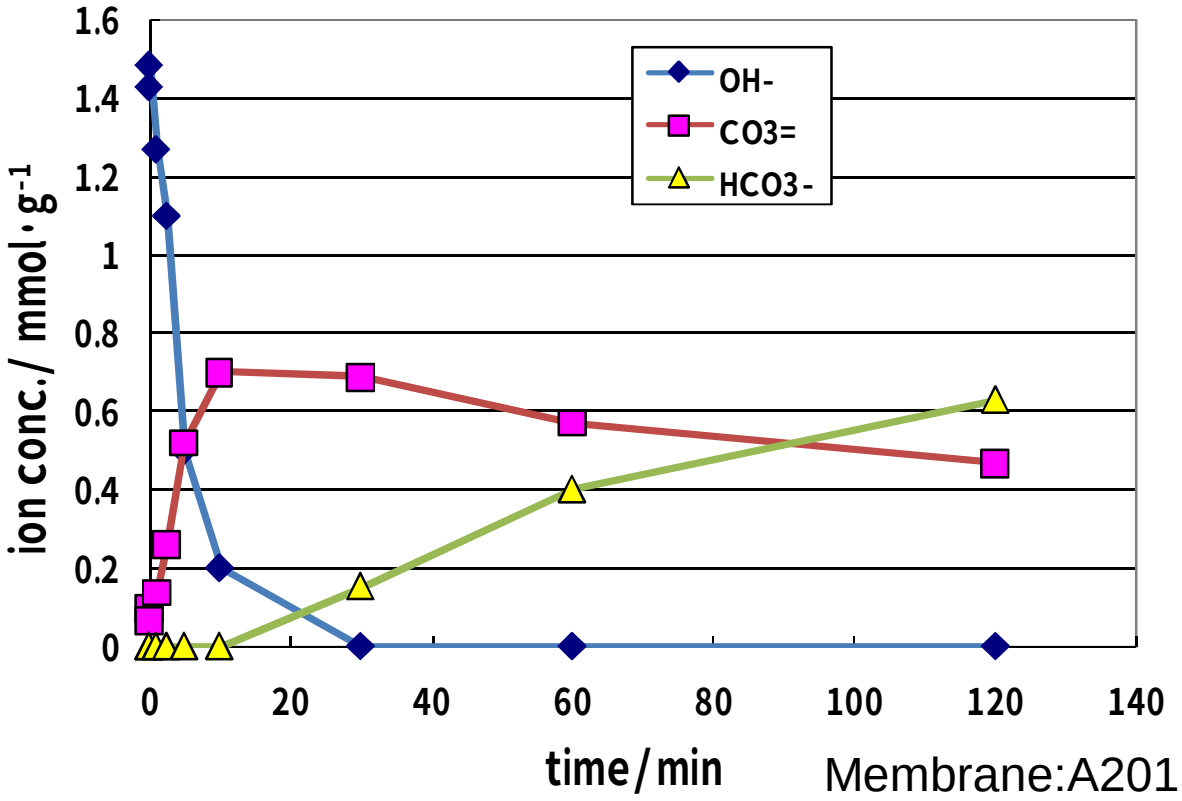
Outline

1. Tokuyama's Electrolyte Materials for AMFCs
   - Anion exchange membrane
   - Alkaline Ionomer
2. **Performance of AMFCs**
   - Power density
   - **Characteristic behavior in AMFC**
     - **CO_2 problem**
     - Water transport
   - Durability
3. Summary

CO_2 Absorption into Alkaline Membrane

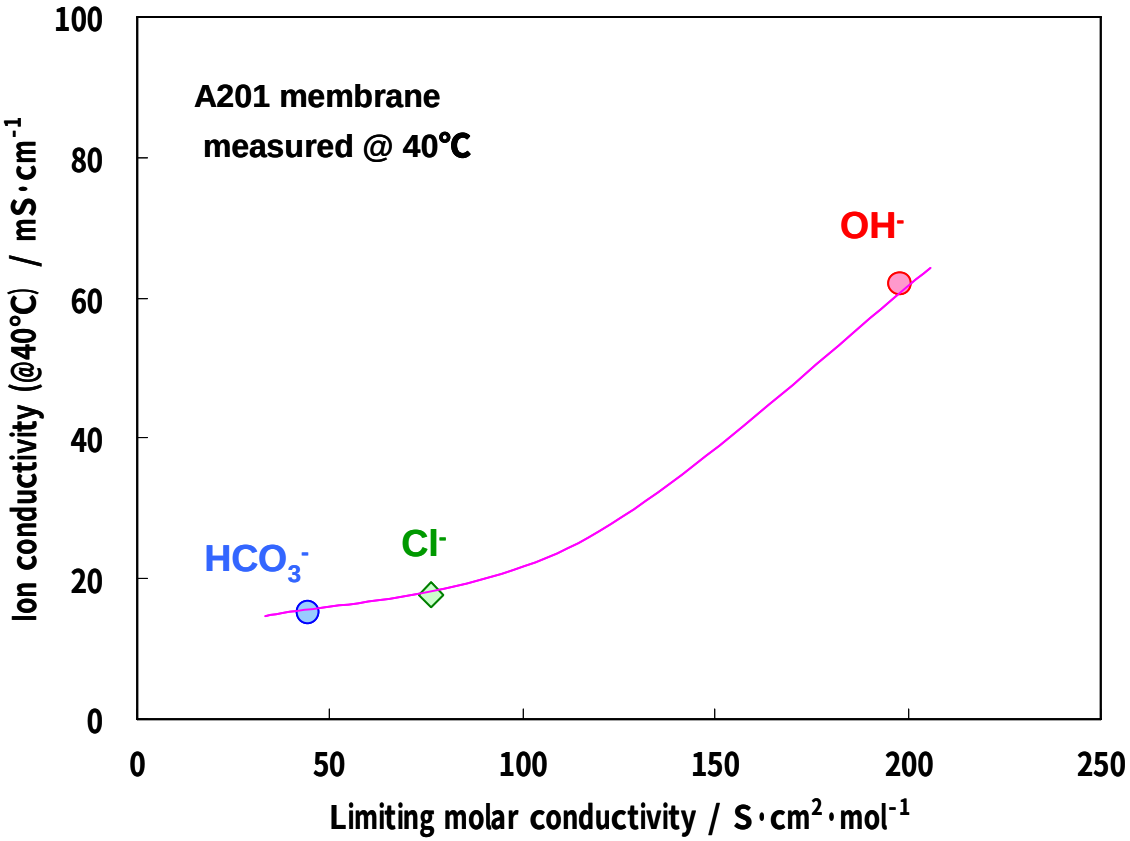
OH^- is changed to CO_3^{2-} in a few minutes, further to HCO_3^-.

Needs to know the effect of counter ion on the conductivity

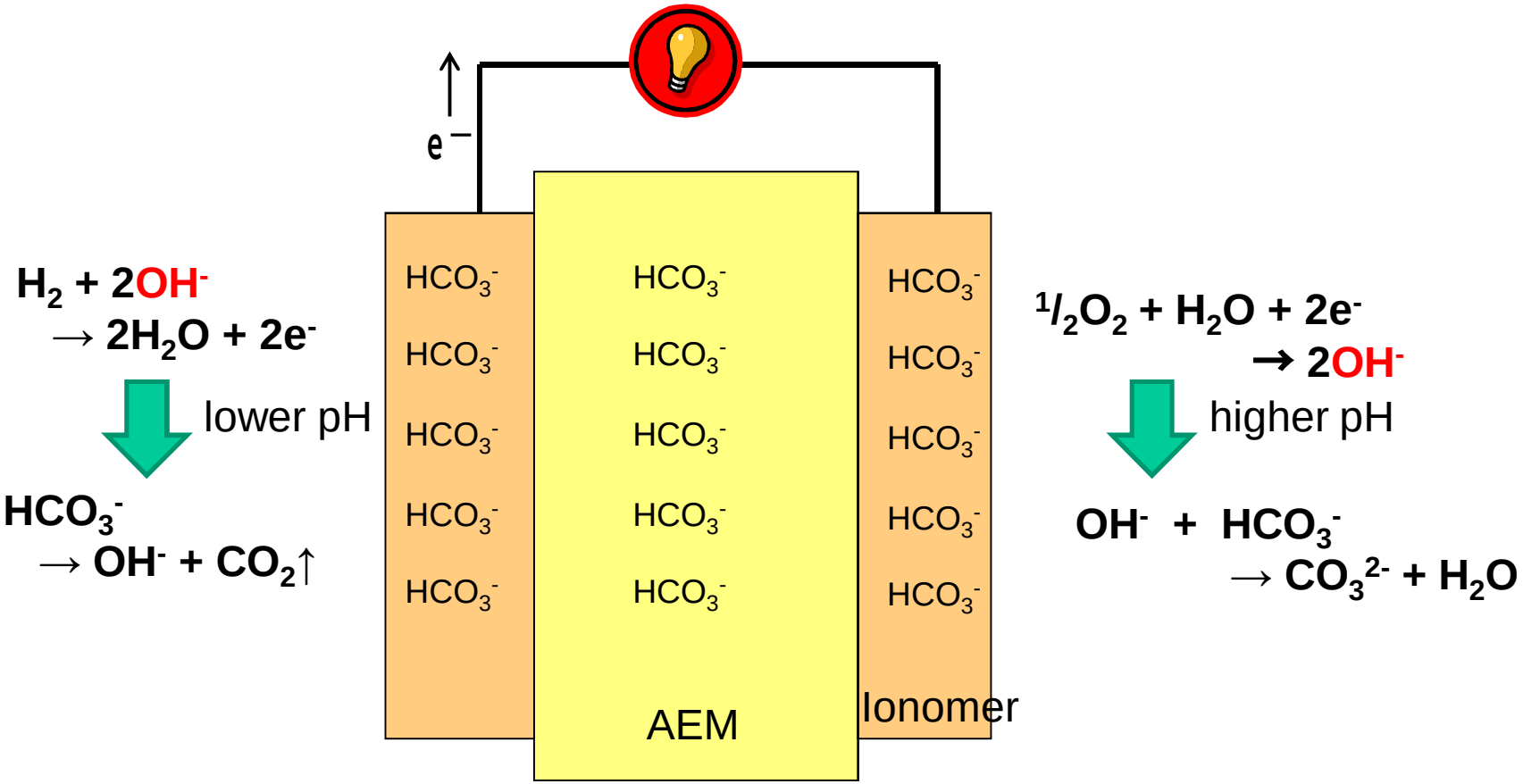


Effect of the counter anion

Membrane Conductivity depends on the mobility of counter anion .

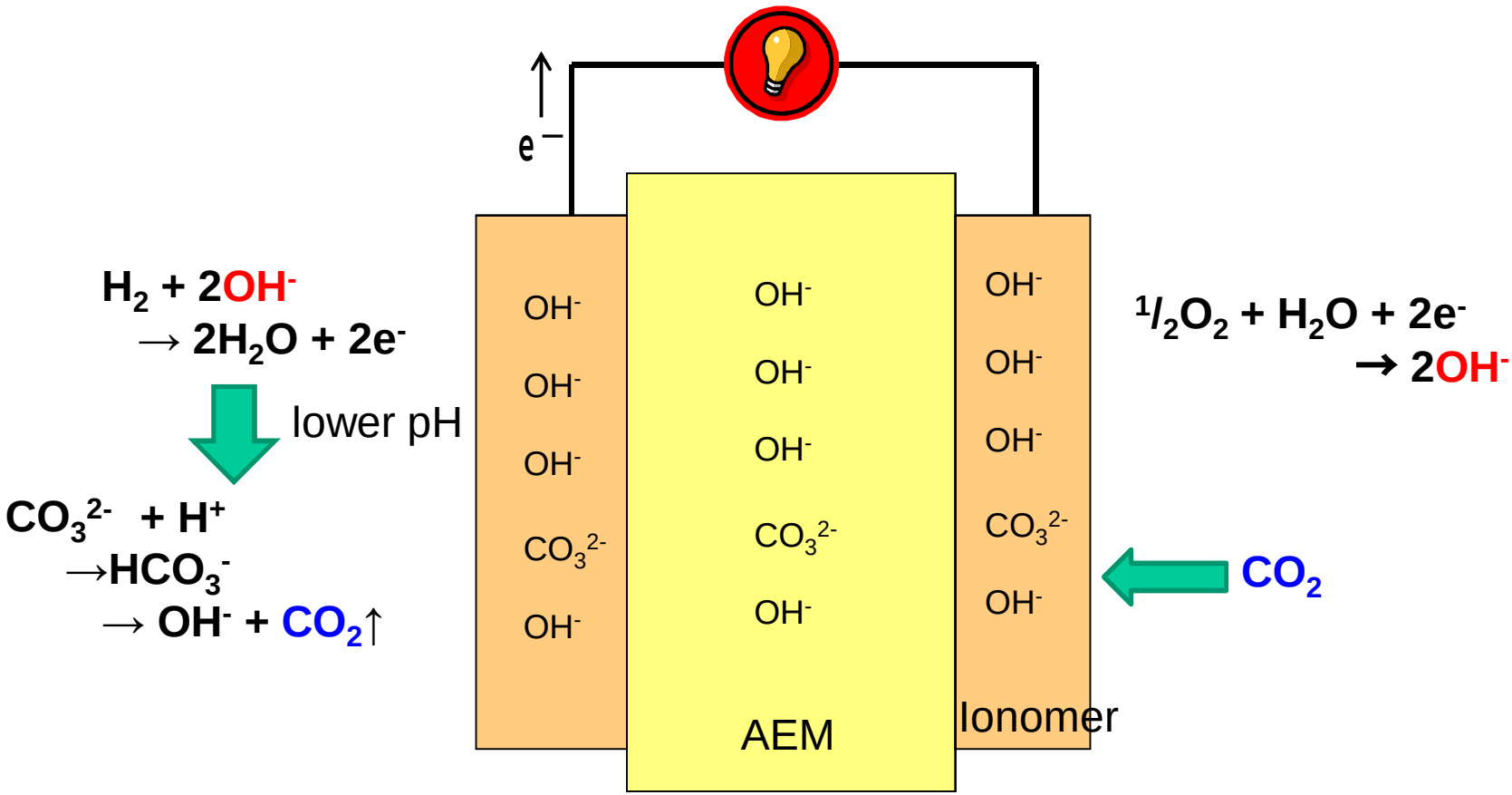


Self-Purging (Initial Stage)

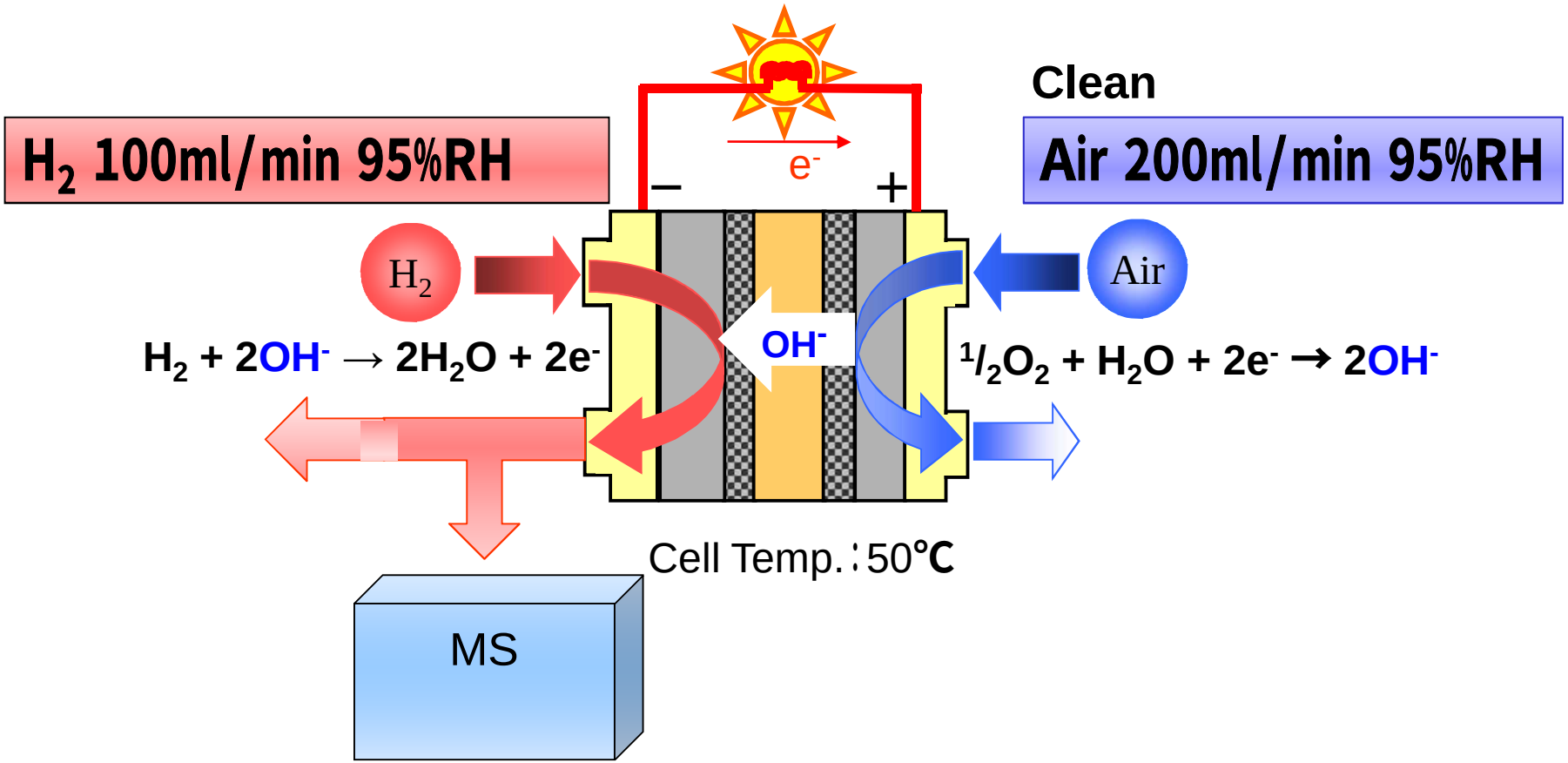


self-purge :
J.Varcoe et. al, ChemSusChem 2008, 1, 79–81

Self-Purging (Steady State)

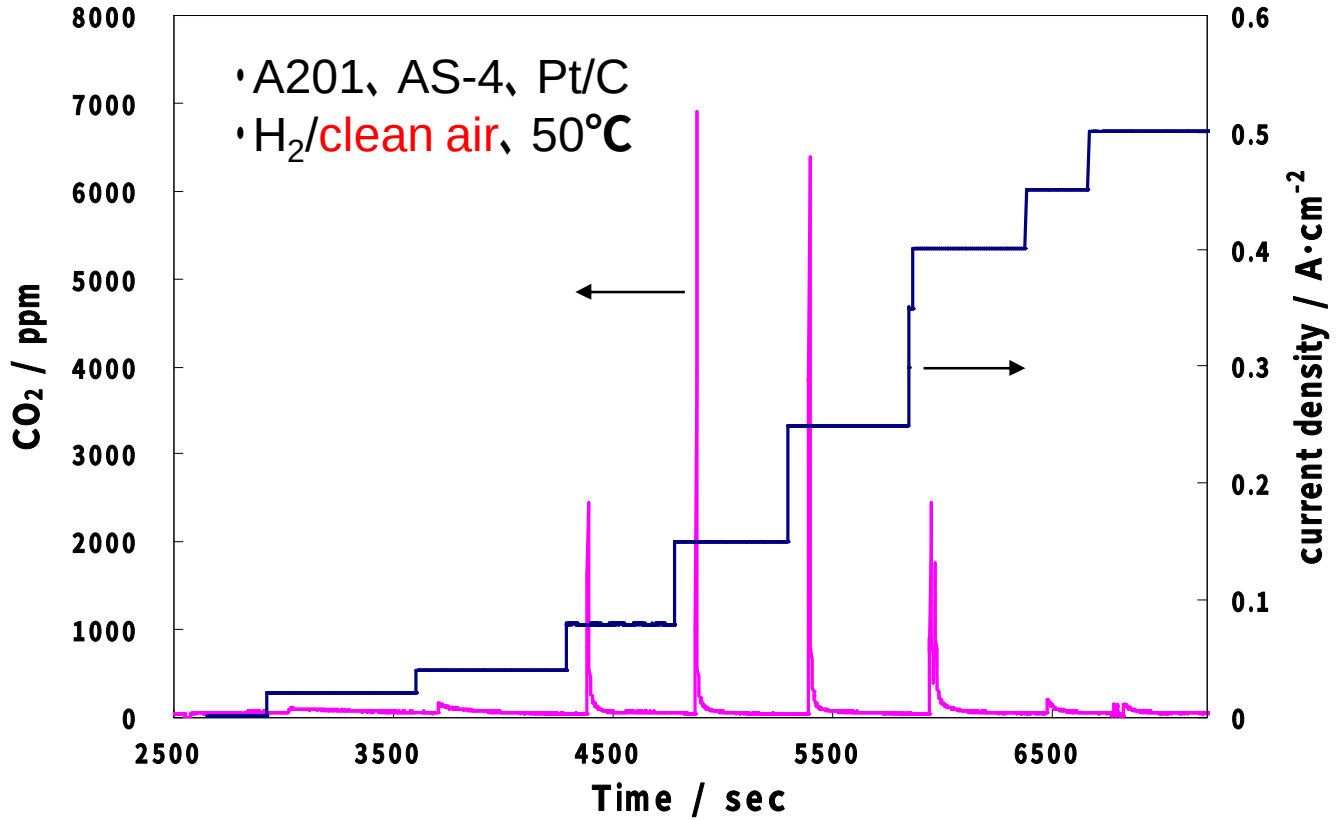


in-situ Analysis of CO_2



in-situ CO_2 measurement

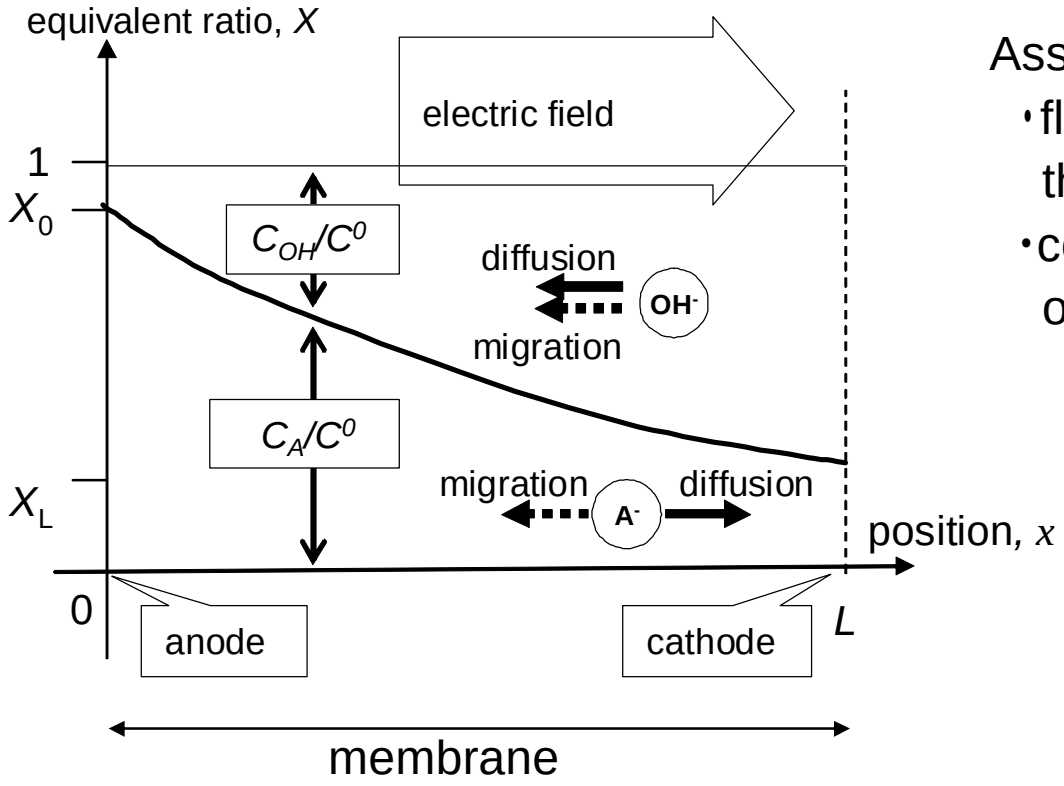
Observation of CO_2 Release from Anode



CO_2 is released quickly after increasing current density.
Released amount seems to depend on the current density.

⇒ Ref. Z. Siroma,et. al., *J. ElectroChem. Soc.*, 158, B682 (2011).

Modeling of CO_2 concentration profile

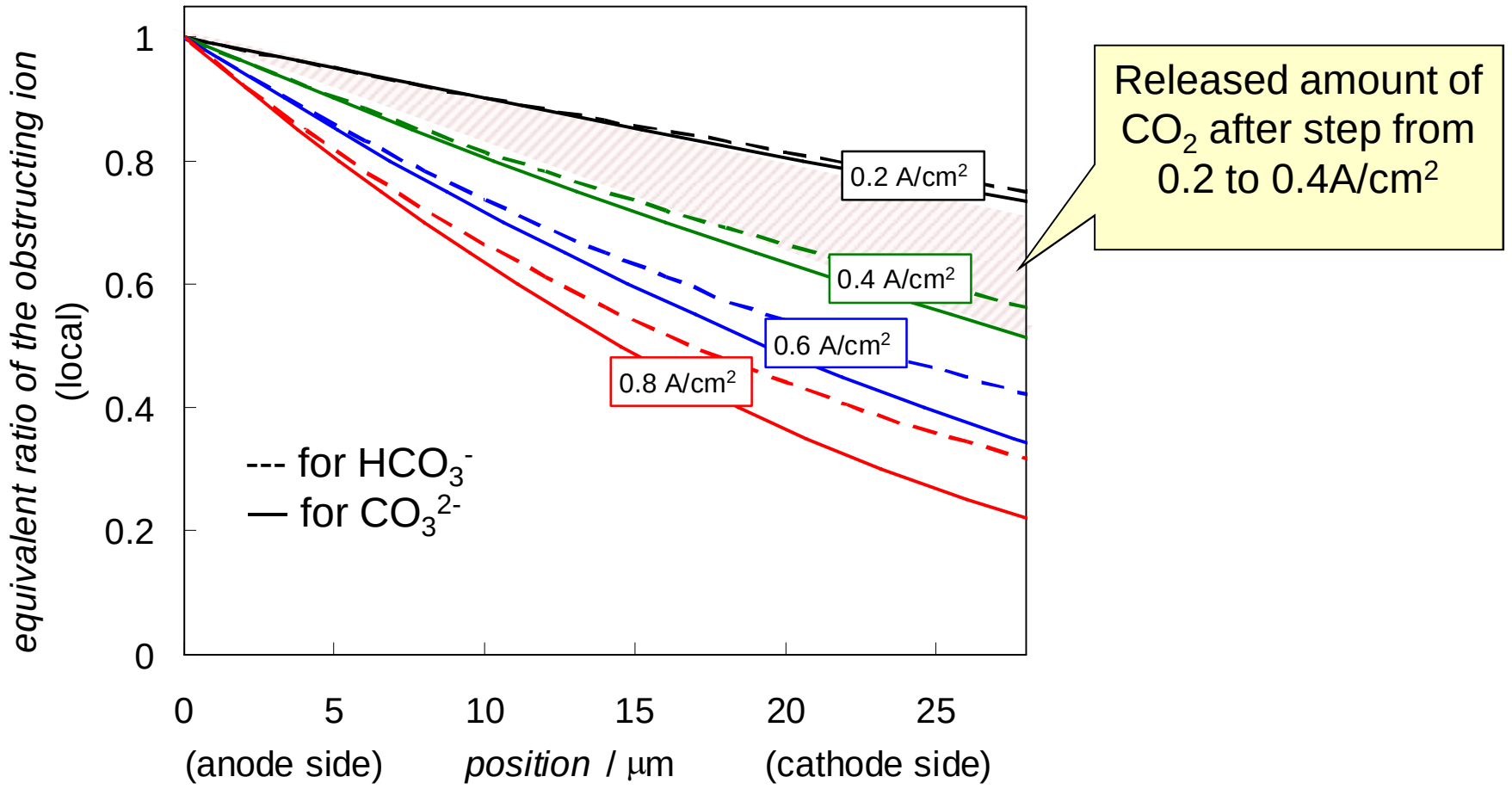


Assumption

- flux of carbonate ion is zero throughout the membrane
- concentration of OH- at the end of anode is fixed to zero

Z. Siroma,et. al., *J. ElectroChem. Soc.*, **158**, B682 (2011).

Calculated CO_2 concentration profile



Outline

1. Tokuyama's Electrolyte Materials for AMFCs
   - Anion exchange membrane
   - Alkaline Ionomer
2. **Performance of AMFCs**
   - Power density
   - **Characteristic behavior in AMFC**
     - CO_2 problem
     - **Water transport**
   - Durability
3. Summary

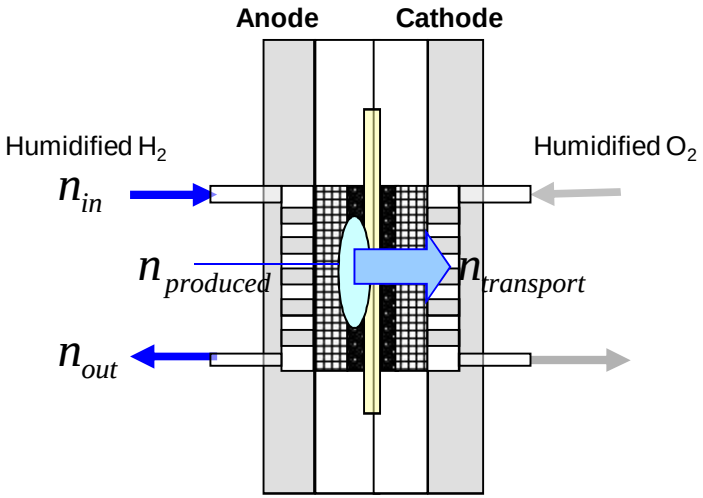
Water Transport Measurement

PENNSTATE Electrochemical Engine Center

- ✓ To learn how the water for ORR is supplied in AMFC
- ✓ To test the operation under the dry gas feeding condition

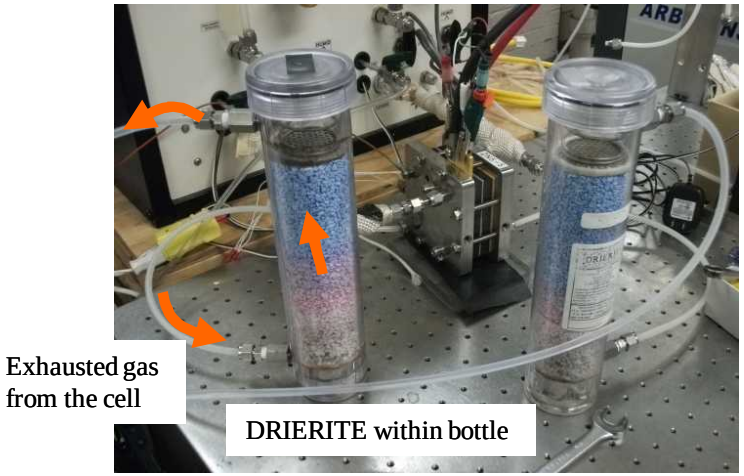
Net Water Flux from anode to cathode; $n_{transport}$

$$n_{transport} \quad n_{out} - n_{in} - n_{produced}$$



The Conditions for humidification in this study

Anode (H_2)	Cathode (O_2)
100	100
100	0 (dry gas)
0 (dry gas)	0(dry gas)



From the presentation at 219th ECS meeting (Montreal)

AMFC Performance with Dry Feed Conditions

- ✓ AMFC performance decreased with lowered humidity.
- ✓ The effect of cathode humidity was quite small.

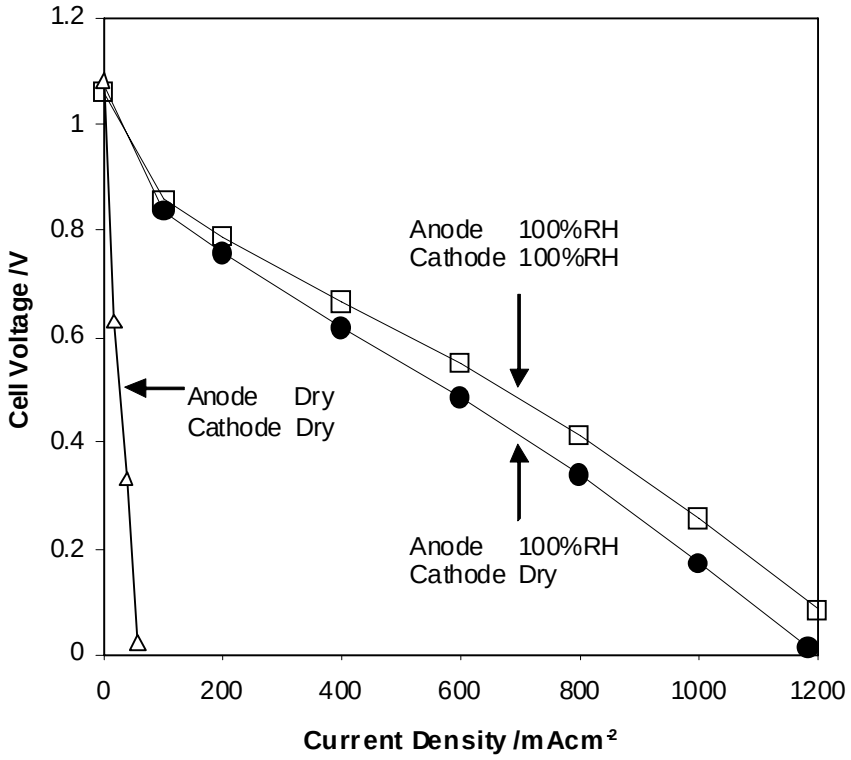


Fig.1 Polarization Curves under various humidified conditions
Anode feed: H_2 200mLmin^{-1}, Cathode feed: O_2 200mLmin^{-1} Cell Temperature 50°C

T. Isomura et.al., Abstract of 219th ECS meeting, #221(2011)

Net Water Flux from Anode to Cathode

- ✓ At 100%RH/100%RH, net water flux from anode to cathode was same as the theoretical amount of water required for ORR.
- ✓ It suggested that all the water required for ORR was supplied from anode.

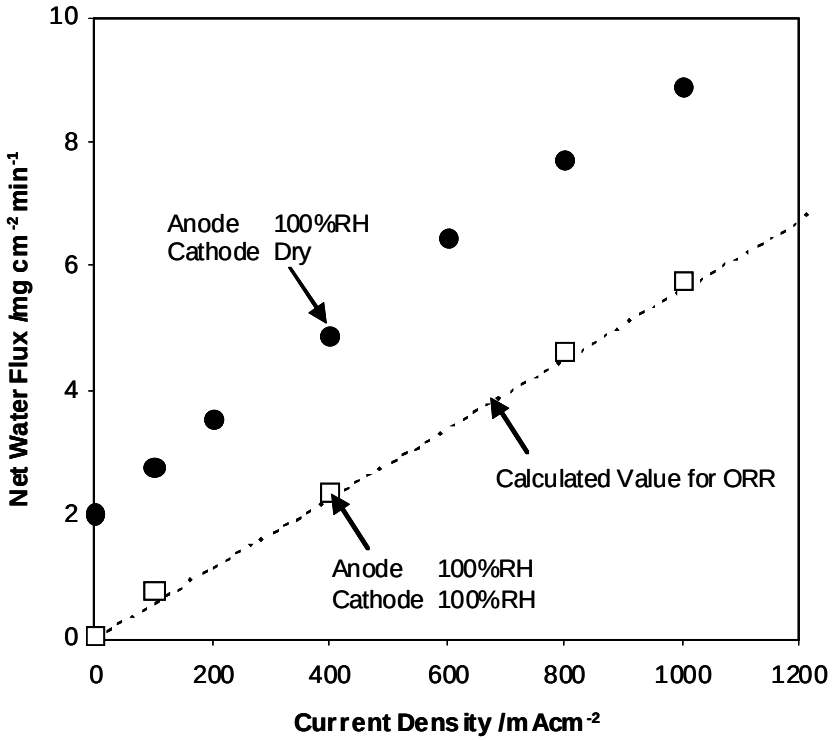


Fig.2 Net Water Flux from anode to cathode under various humidified conditions Dotted line shows calculated amount of water for ORR at cathode, Anode feed: H_2 200mLmin^{-1}, Cathode feed: O_2 200mLmin^{-1} Cell Temperature 50ºC

T. Isomura et.al., Abstract of 219th ECS meeting, #221(2011)

Outline

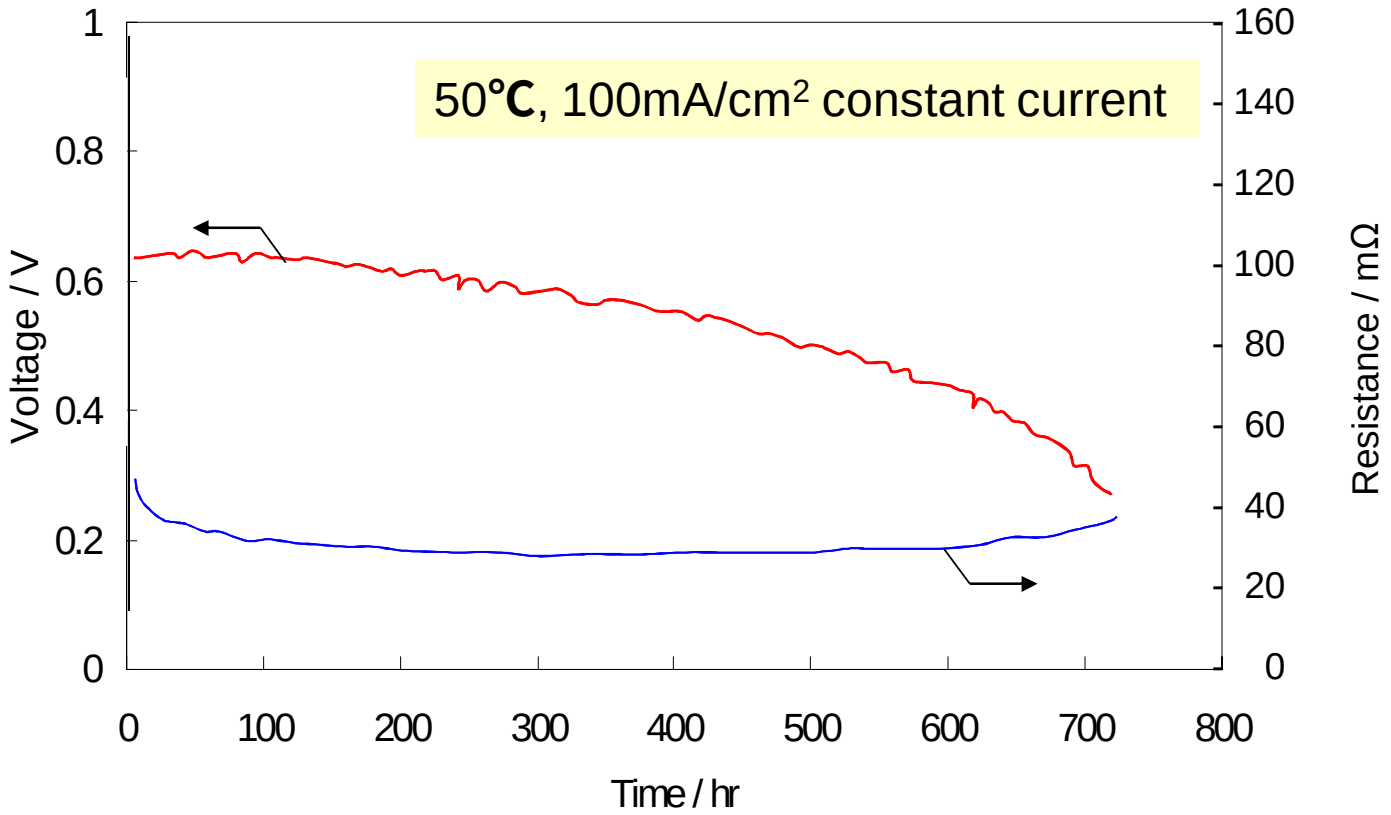
1. Tokuyama's Electrolyte Materials for AMFCs
- Anion exchange membrane
- Alkaline Ionomer

2. Performance of AMFCs
- Power density
- Characteristic behavior in AMFC
  - CO_2 problem
  - Water transport
- **Durability**

3. Summary

Durability Test

- With improved adhesion between membrane and catalyst layer, higher Pt loading seems to lead to better durability.
- Even after long-term operation, IEC of membrane has not changed.

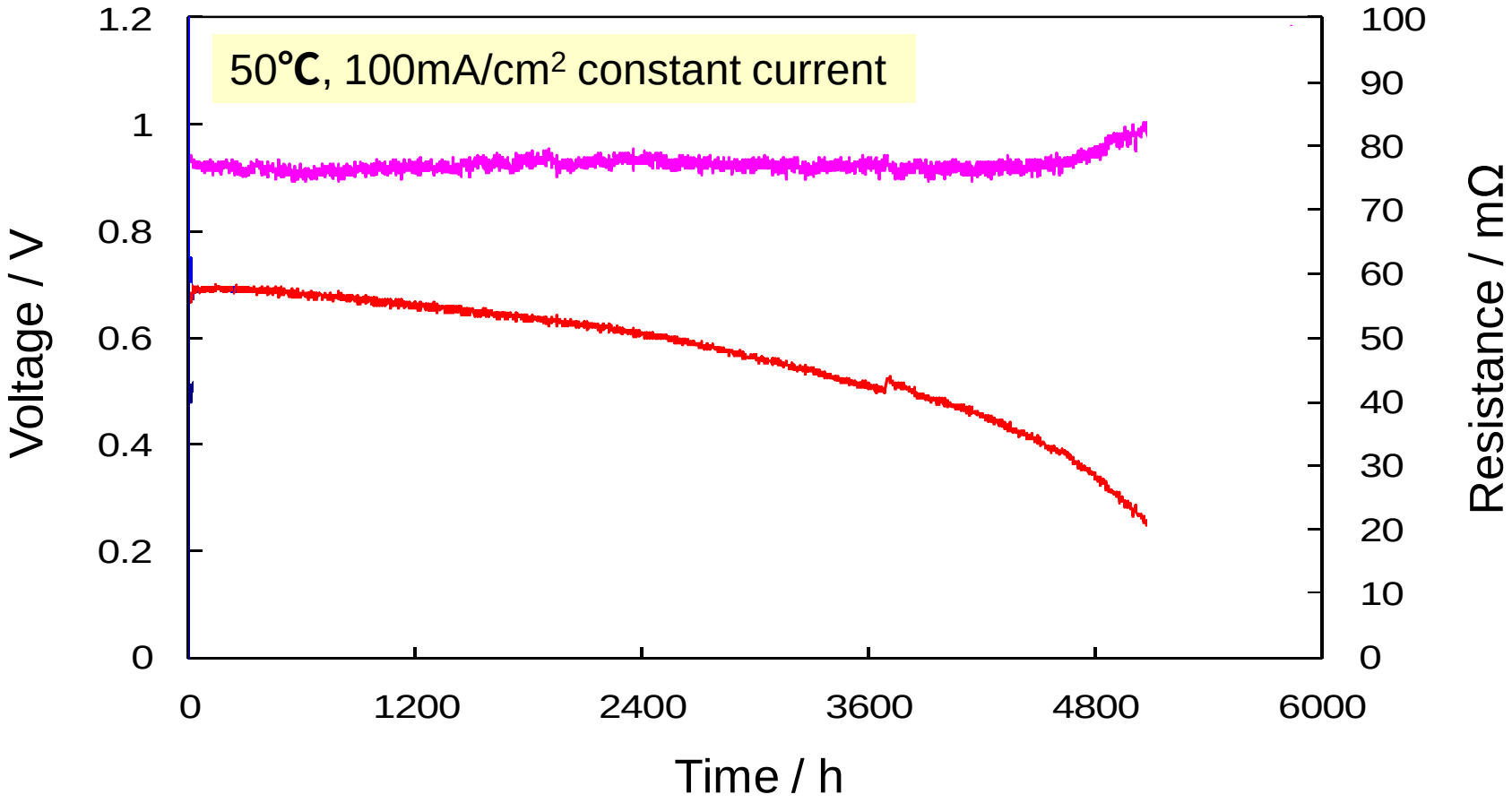


【MEA composition】
Membrane ：A201
Ionomer ：AS－4
Pt amount ：0.8mg/cm^2

【measurement condition】
Cell temp. ：50℃
Anode ：95%RH H_2 100ml/min
Cathode ：95%RH clean air 200ml/min (A201)

Improved Durability with Cross-Linked Ionomer

☐ With cross-linked Ionomer, which also has higher IEC, shows better durability.



Summary

☐ By improving properties of electrolyte materials, optimizing MEA construction and operating conditions, maximum power density was increased.
- around 500mW/cm^2 (H_2/O_2)
- around 350mW/cm^2 (H_2/clean air)

☐ CO2 in the air has large influence on the AMFC performance. To decrease the influence, AMFC operation at elevated temperature is effective, though it needs improved ionomer like cross-linked one.
- around 300mW/cm^2 (at 80℃, H_2/normal air) ・・・*not shown, unpublished date of PSU*

☐ Durability at sate of the art
- 700hrs at standard materials
- with cross-linked GDE : ＞4000hrs (50℃)
  ＞1200hrs (80℃) ・・・*not shown, unpublished date of PSU*

Issues for better performance

☐ Materials improvement : ion conductivity, thermal stability
☐ Decrease CO_2 influence : new concepts other than high temp. operation
☐ MEA fabrication in relation with operating conditions

Thank you !