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OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

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OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Proton conduction in tin phosphates and their application to electrochemical devices

Nagoya University
Graduate School of Environmental Studies

Masahiro Nagao

Contents

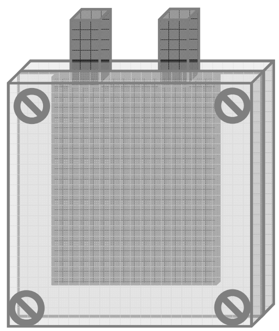
1. Development of proton conductor

H+

Applications using ionic conductors

Electrical charges are transported as the form of ions.

Fuel Cell

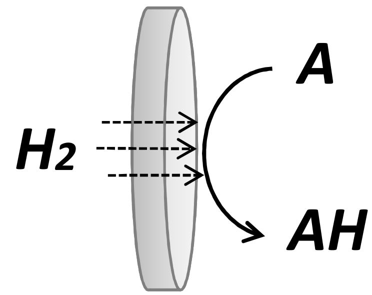


H^+, OH^-, CO^{3-}, O^{2-}

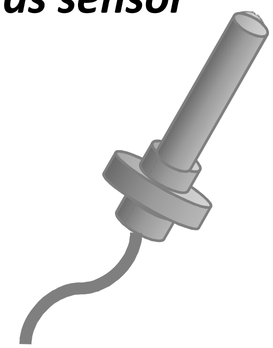
Battery

Li^+

Membrane reactor

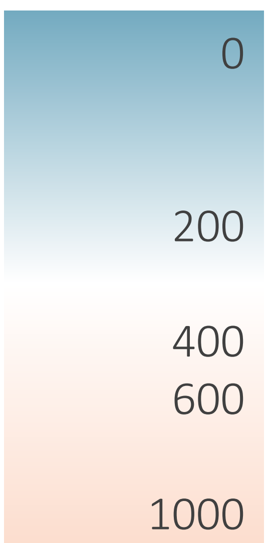


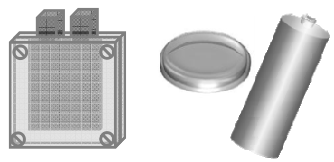
Gas sensor



H^+, O^{2-}

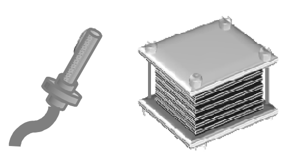
(°C)





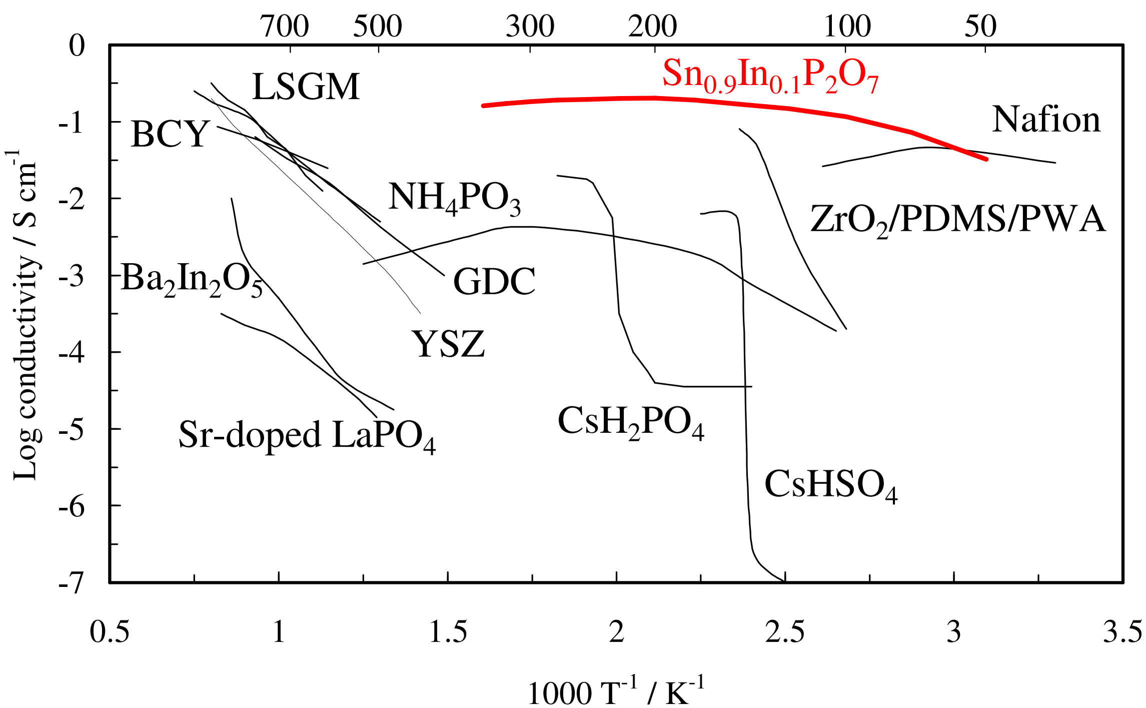
Ionic conductive liquids,
Polymers, Ionic-liquids

B L A N K

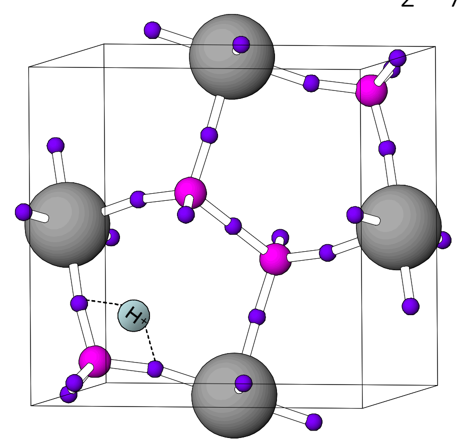


Molten salts
Ionic conductive ceramics

Ionic conductors



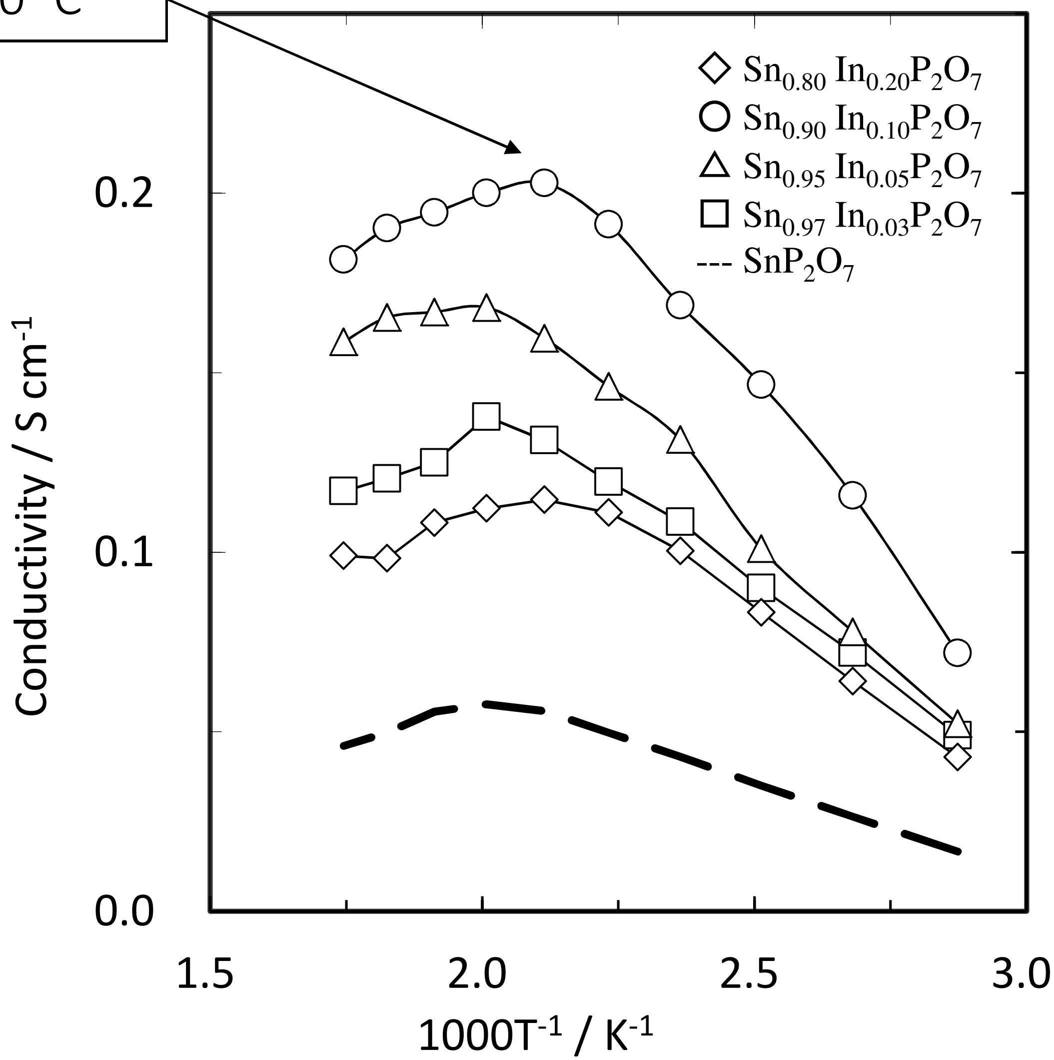
SnP_2O_7



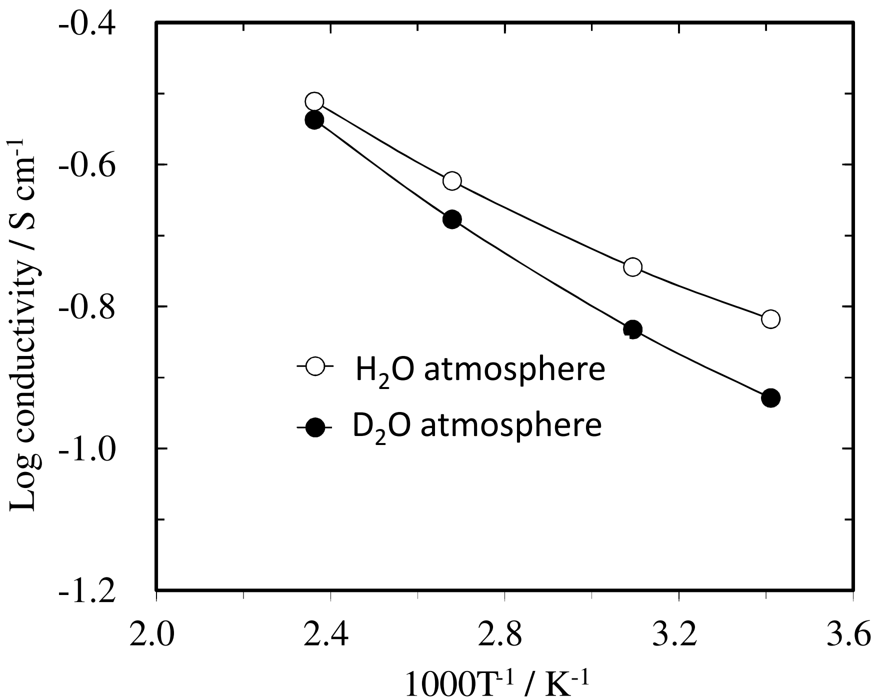
1) *Solid electrolyte*
2) *Conductive under unhumidified conditions*
3) *Stable under reducing conditions*

Conductivity of In^{3+} doped SnP_2O_7

0.2 Scm^{-1} @200°C



Charge carrier



Conductivity ratio

$\sigma_{H2O+} / \sigma_{D2O+} = 1.32$

(nearly $\sqrt{2}$)

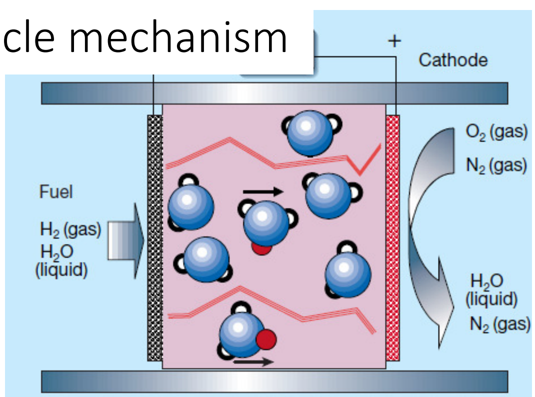
Conducting ions → ~~H_3O^+~~, H^+

Mass ratio

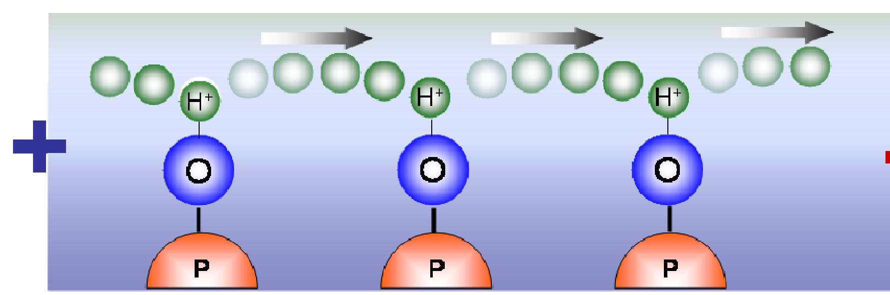
$M_{H3O+} : M_{D3O+} = 19 : 22$

$M_{H+} : M_{D+} = 1 : 2$

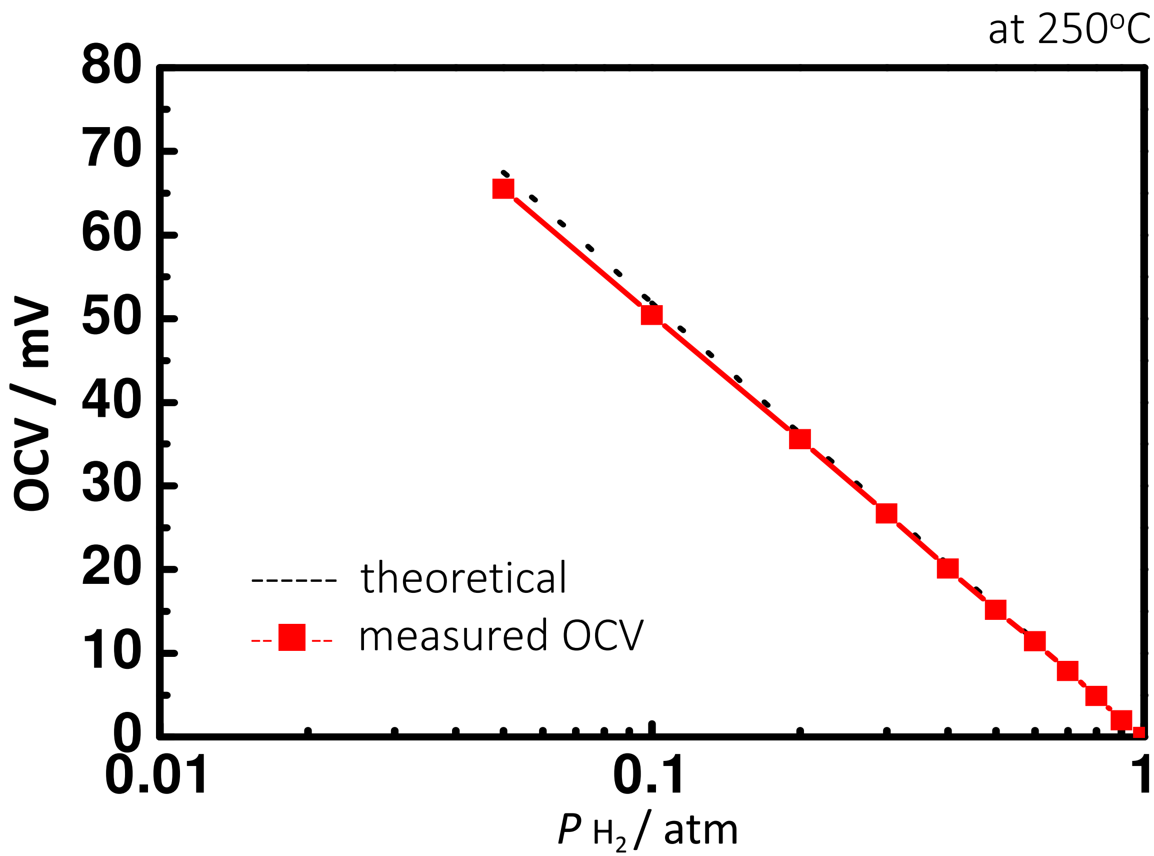
× vehicle mechanism

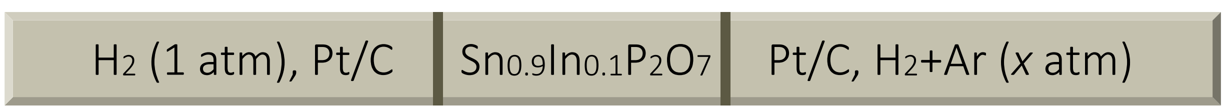


○ Grotthuss mechanism



ionic transport number



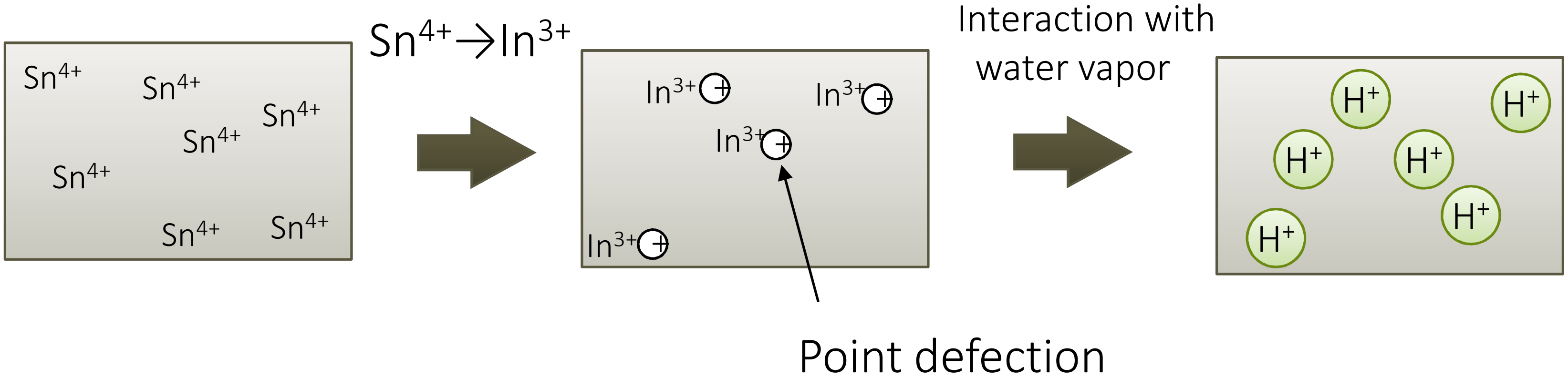


Ionic transport number : 0.97 → pure ionic conductor in H_2 atmosphere

introduction of protons

Increase of proton concentration by the doping

$$Sn^{4+} \Leftarrow In^{3+} + H^+$$



(1) *Substitution of* In^{3+} for Sn^{4+} *increase the h · concentration*

$$Sn^{4+} \rightarrow In^{3+} + h^{\cdot}$$

(2) H^+ *is introduced according to the interaction of* H_2O *with h ·*

$$H_2O\,(g) + h^{\cdot} \rightarrow H_i^+ + \tfrac{1}{2}\,O_2(g)$$

２． Application to the fuel cell

In^{3+} doping into Sn^{4+}

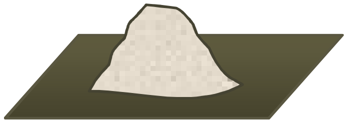
$SnO_2 + In_2O_3 + H_3PO_4 + H_2O$

stirred and heated at 300°C

Slurry with high viscosity

solid state reaction at 650°C for 2.5 hours

In^{3+} doped SnP_2O_7 powder



*P / (Sn + In) ratio = 2.0 (determined by XRF)

uniaxial hydrostatic press at 2,000kgcm^{-2}

pressed pellet

application to the fuel cell

0°C 100°C 200°C 600°C 1000°C

Ionic conductor

Nafion™ | H_3PO_4 ← **GAP** → Y-stabilized ZrO_2

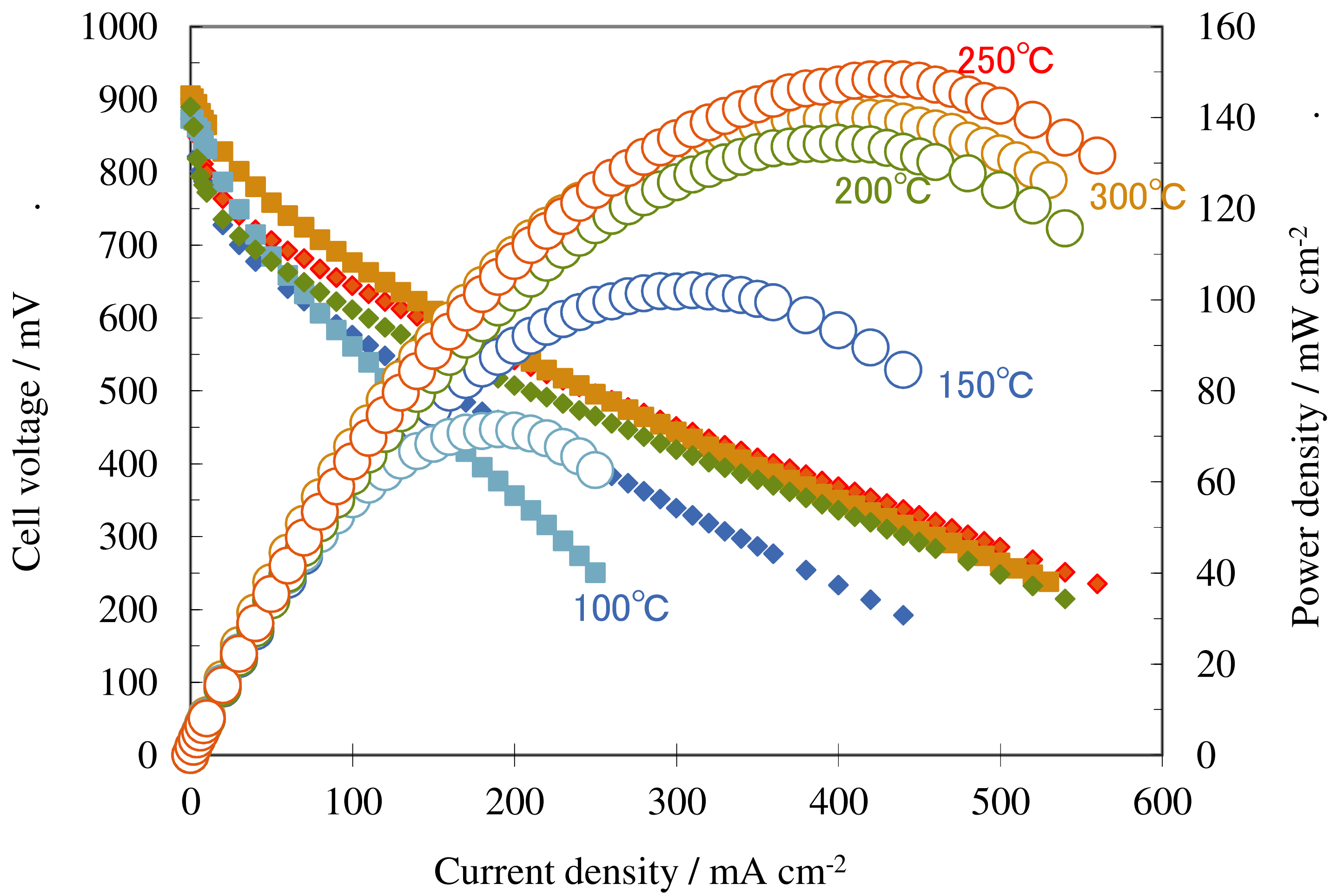
v.s. PEFC
- Platinum catalyst
- CO poisoning
- Smooth electrode reaction
- Highly purified and high-pressured H_2 storage
- Extreme humidification
- Variety of fuels (hydrocarbons, alcohols, ethers)

Intermediate temperature

v.s. SOFC
- Transition-metal(oxide) catalyst
- Cheap structural materials
- Extreme humidification
- Suitable for large size
- Careful start--stop operation

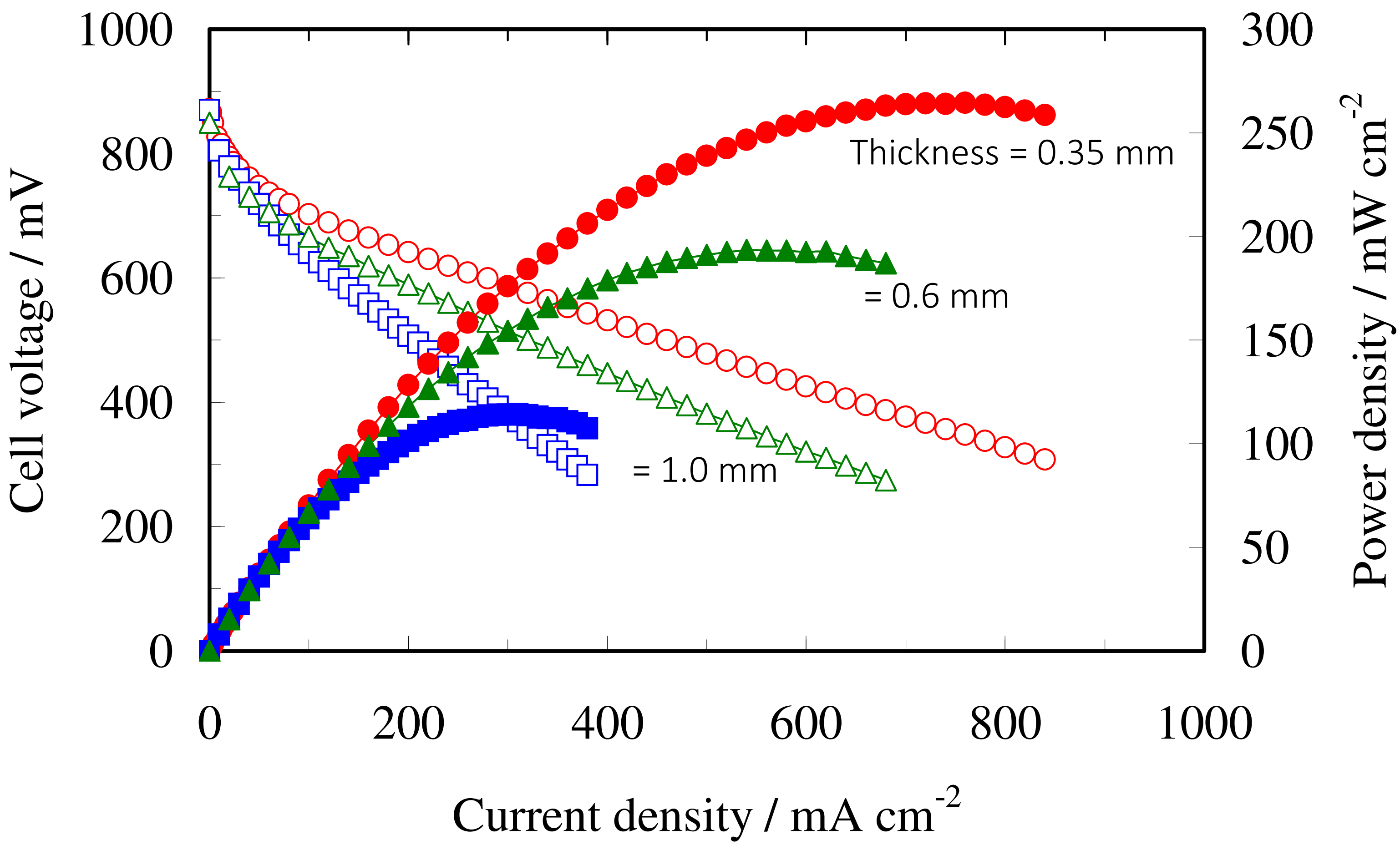
Fuel cell performance (temperature dependence)

Electrolyte thickness: 1.0 mm
Fuel: Hydrogen (30cc)

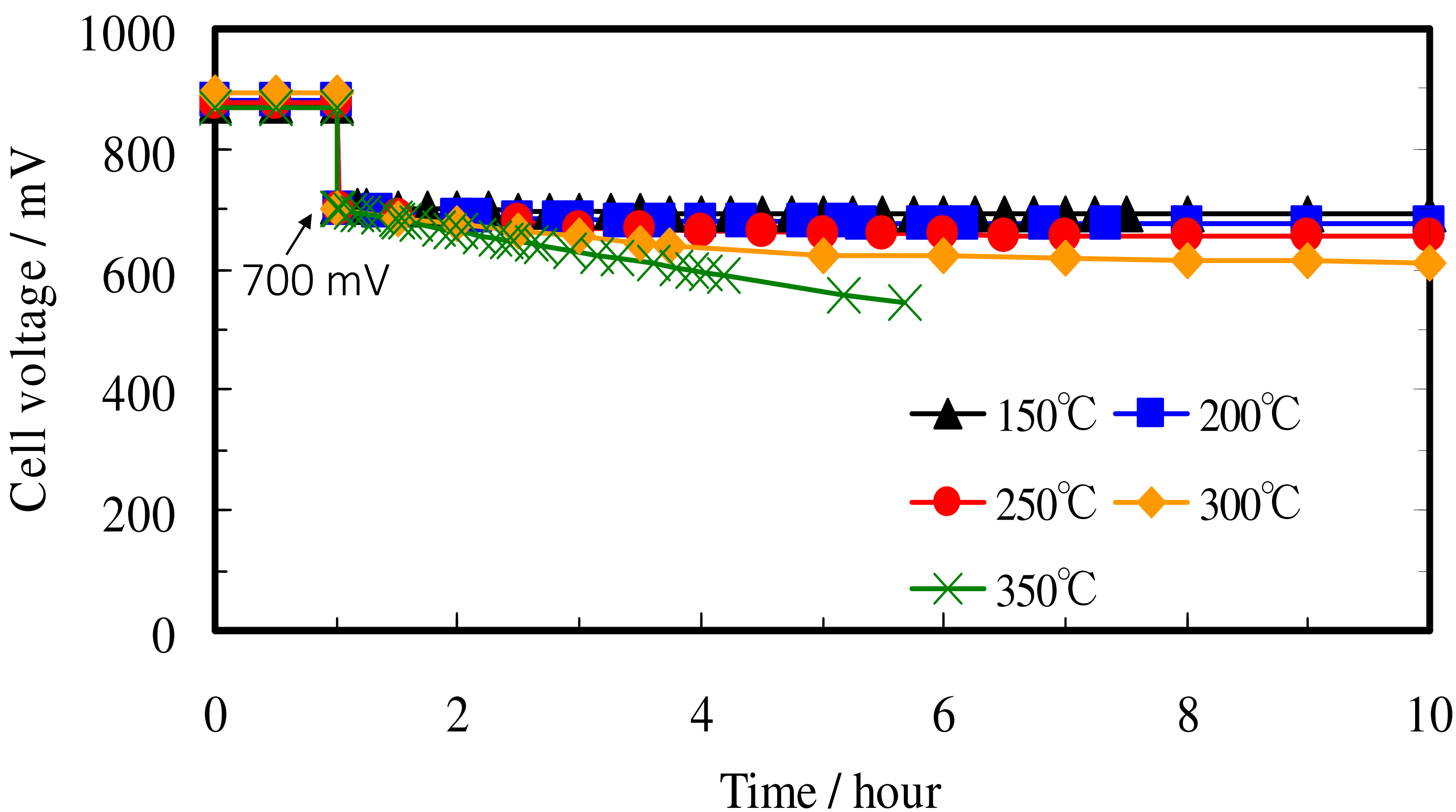


Fuel cell performance (dependence of electrolyte thickness)

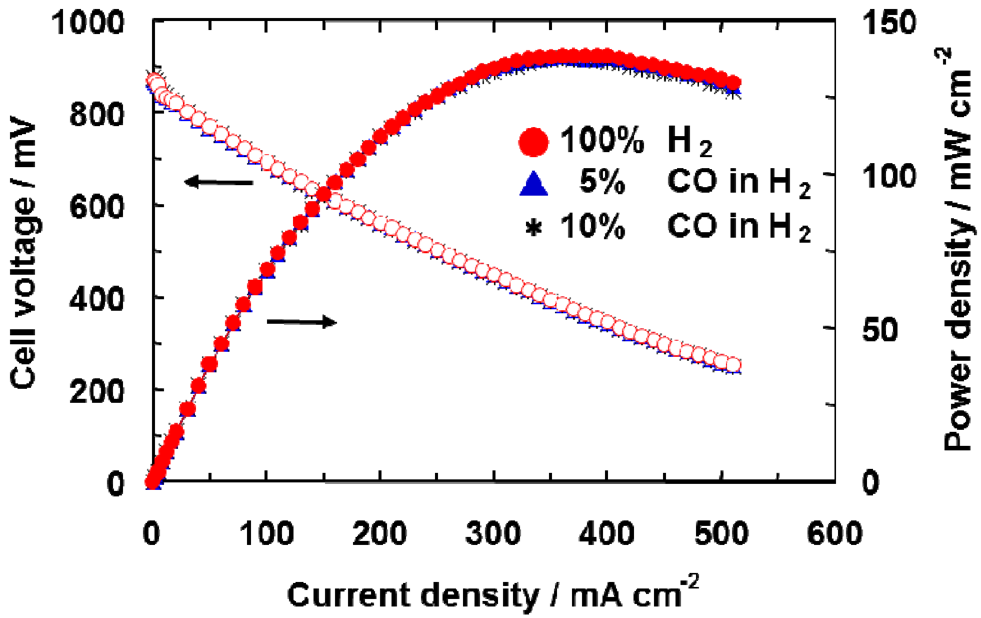
Temperature: 250°C
Fuel: Hydrogen (30cc)

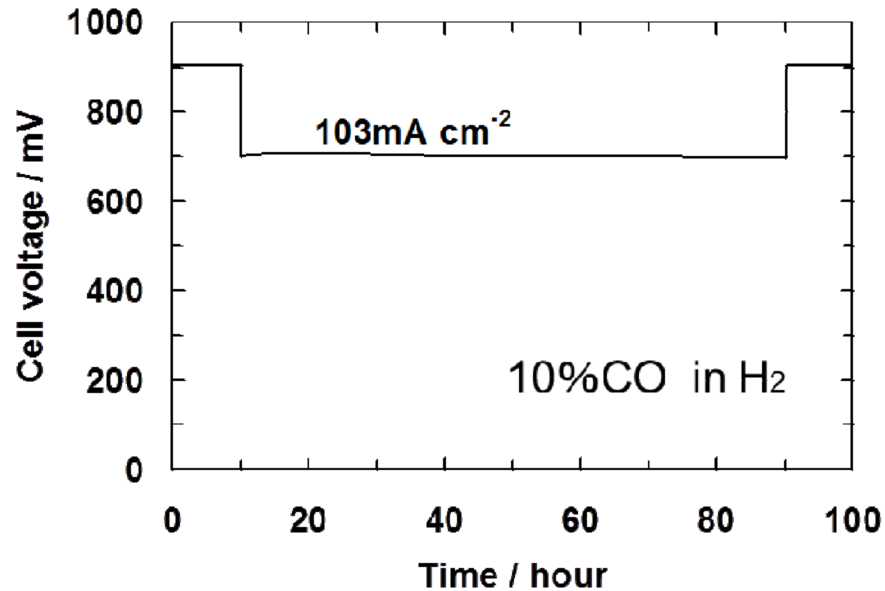


Stability test



CO tolerance on fuel cell performance





High tolerance and good stability toward CO

Other works

Cathode (ORR: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$)

Activation of ORR

- Increase of TPB by the composite of electrolyte and catalyst
- High dispersion of catalyst

Anode （HOR: $H_2 \rightarrow 2H^+ + 2e^-$）

non-platinum catalyst

- Mo_2C catalyst

Electrolyte

decrease of resistance

- Thin film by using binder

Fuel （Variety）

Electrochemically active gas or liquid

- methane, ethane, propane, butane, dimethyl ether
- methanol, (ethanol)

PAPERS

FUEL CELLS 10, 798-803, 2010

ELECTROCHEM. SOLID-STATE LETT. 12, B1-B4, 2009

SOLID STATE IONICS 179, 1446-1449, 2008
J. ELECTROCHEM. SOC. 154, B53-B56, 2007

JOURNAL OF POWER SOURCES 196, 6042-6047, 2011
ELECTROCHIMICA ACTA 55 8371-8375, 2010
ELECTROCHEM. SOLID-STATE LETT. 13, B8-B10, 2010

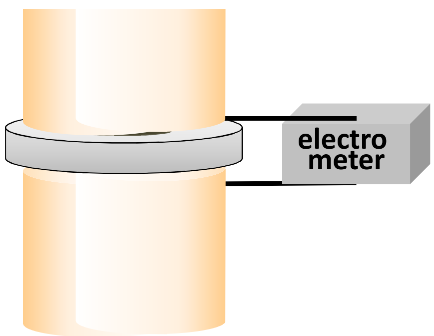
CHEM. COMMUN. *47, 5292-5294, 2011*
Angew. Chem. Int. Ed. 47, 7841-7844, 2008
J. ELECTROCHEM SOC. 155, B92-B95, 2008

３． Application to a NOx reactor

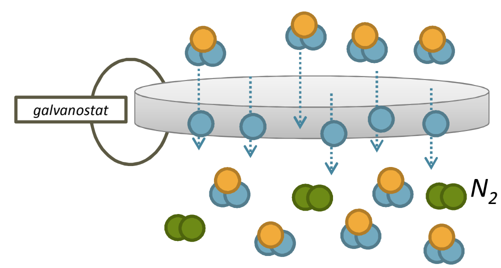
N_2

Other electrochemical devices

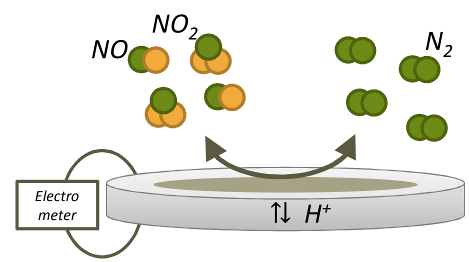
Application 1: Fuel cell



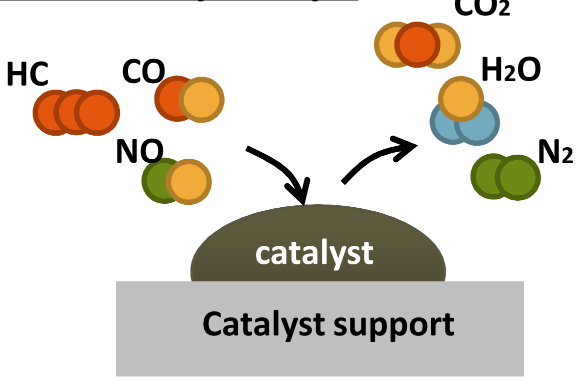
Application 2: Reactor



Application 3: Gas sensor

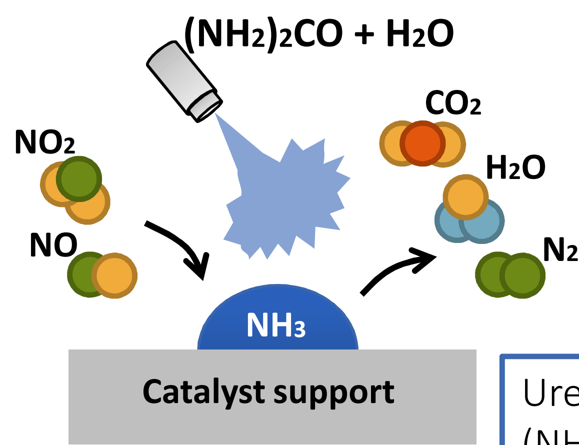


1. Three-way catalyst



*only for stoichiometric ratio

2. Urea SCR（selective catalytic reduction by urea）



Urea storage tank, infrastructure for urea supply, ammonia slip

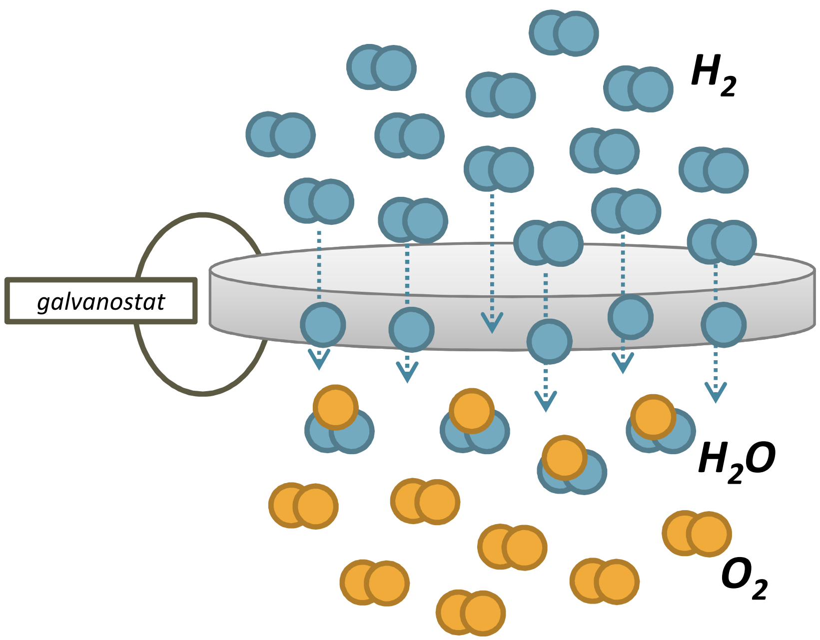
Urea SCR

$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$

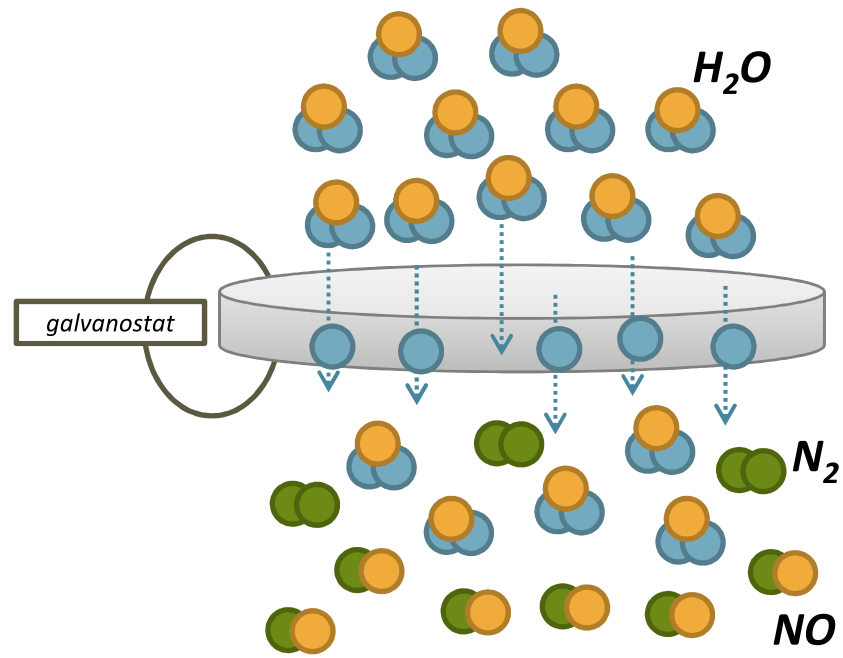
$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

New concept for NOx Reduction

Fuel cell



Reactor



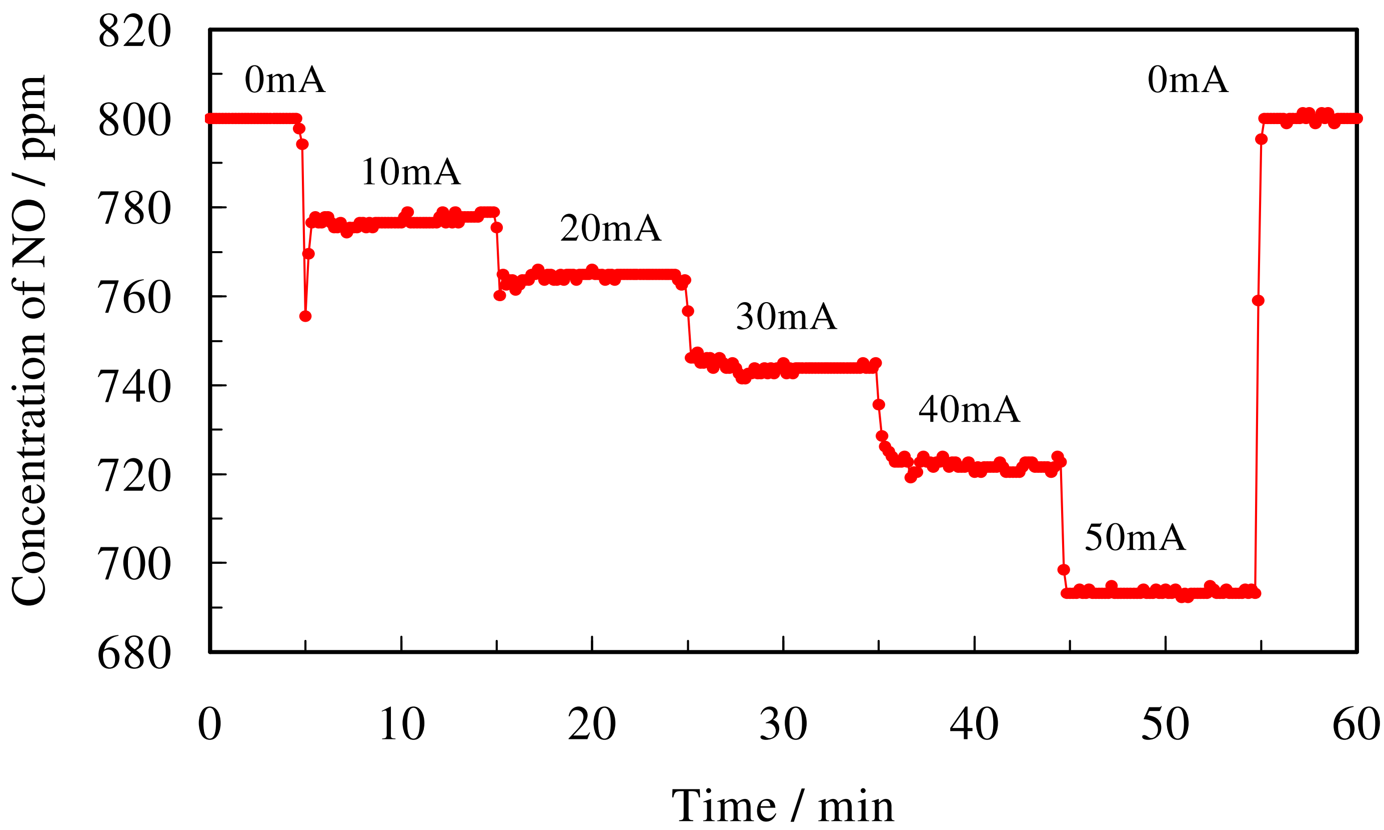
Electrochemical reduction

$$2H_2O \rightarrow 4H^+ + 2O_2 + 4e^-$$

$$2NO + 4H^+ + 4e^- \rightarrow N_2 + 2H_2O$$

NOx reduction by current（NOx conc. changes in outlet）

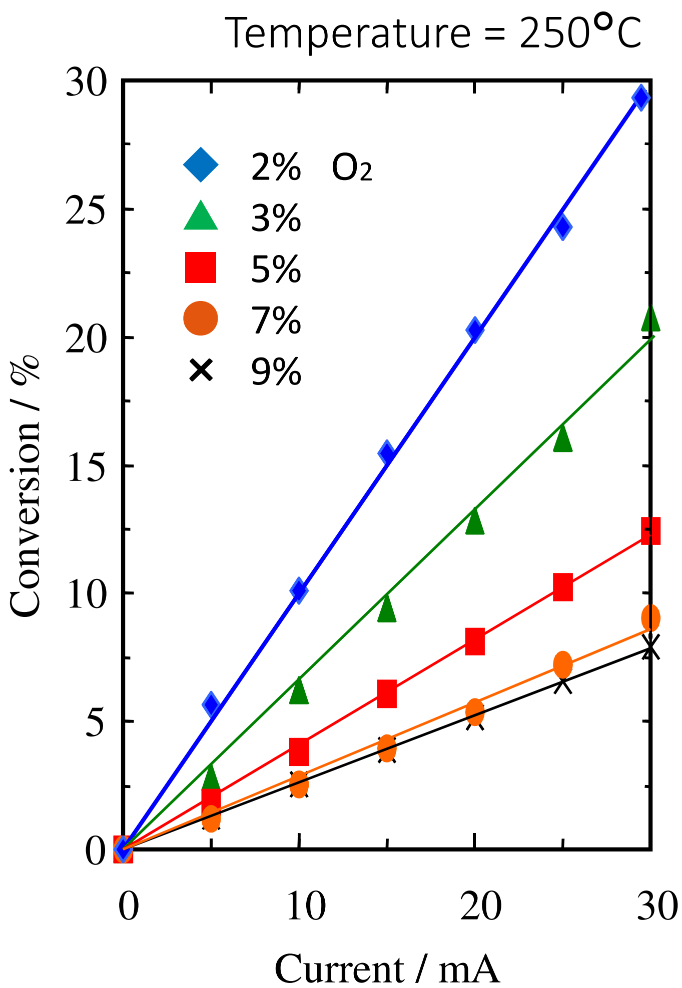
Temperature = 250°C
O_2 concentration = 5%

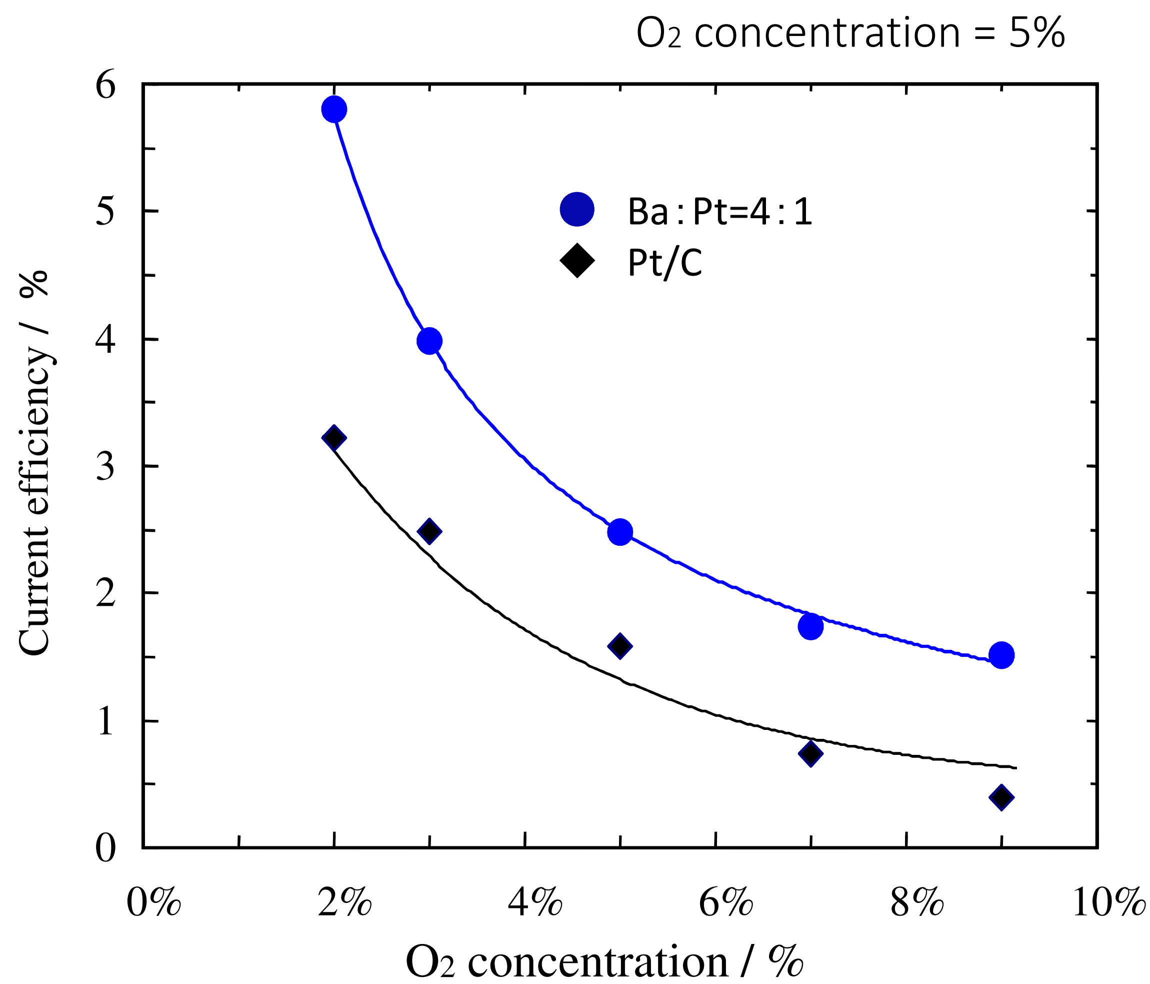


Counter $H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$

Working $NO + 2H^+ + 2e^- \rightarrow 1/2N_2 + H_2O$

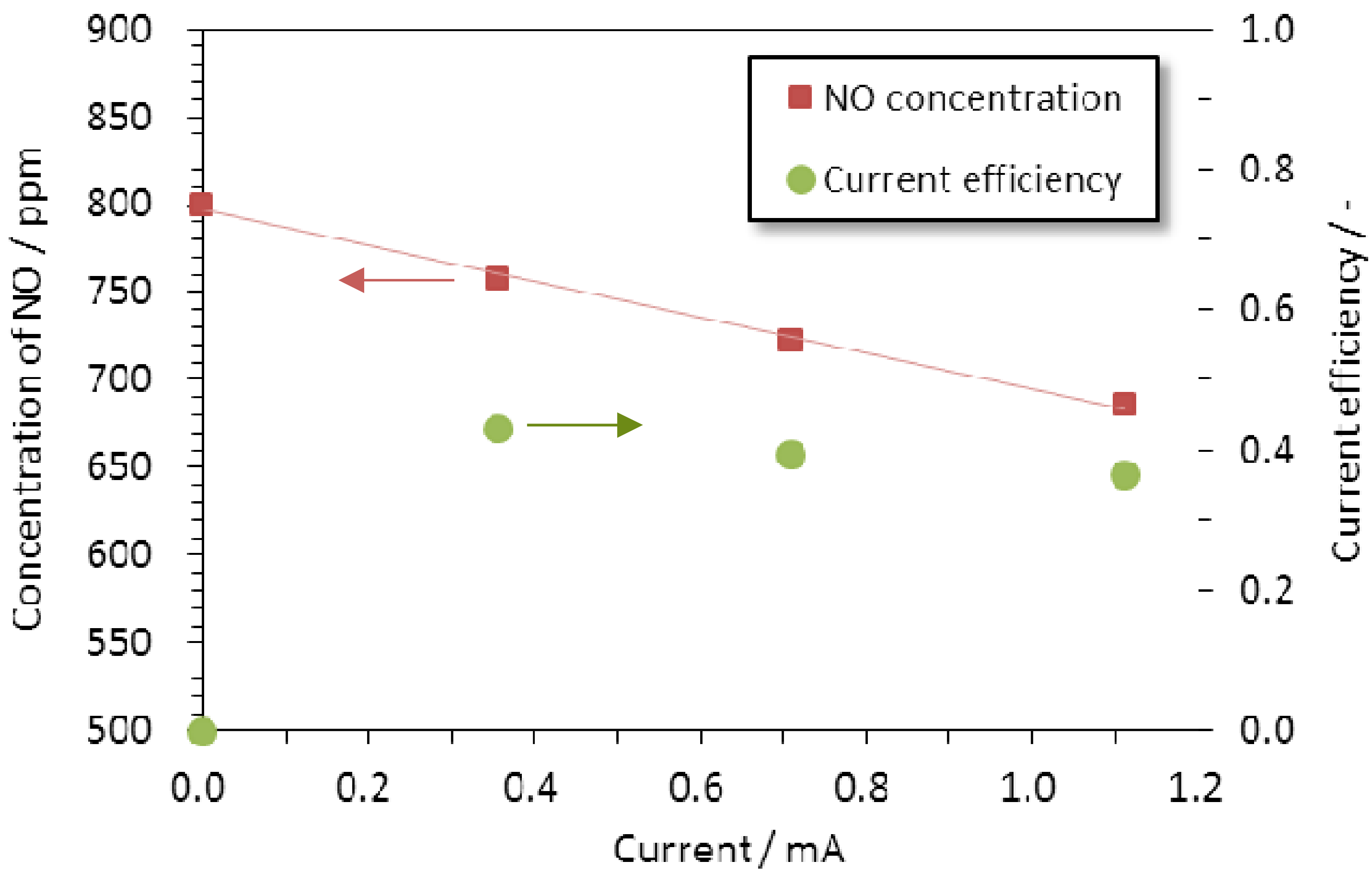
Current efficiency





NOx reduction by alternating current（NOx conc. changes in

Temperature = 150°C
Frequency = 0.01 Hz



Conclusion

- $Sn_{0.9}In_{0.1}P_2O_7$ showed high conductivity of 0.2 S cm^{-1} at 200--250 ℃ in unhumidified conditions.
- A fuel cell using $Sn_{0.9}In_{0.1}P_2O_7$ as the electrolyte (0.35 mm thick) showed high power density of 264 mW cm^{-2} at 250℃ in unhumidified conditions and had good stability for discharge properties below 350℃.
- The NOx reactor using $Sn_{0.9}In_{0.1}P_2O_7$ as the electrolyte showed a high conversion of NOx to nitrogen.
- The NOx were reduced by using alternating current at 0.01 Hz.

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Thank you for your attention.

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