Charels Hatchett Award Hydrogen Webinar
7th, Dec., 2020,

Highly durable and active cathode catalysts for polymer electrolyte fuel cells using Nb-containing oxide supports

Katsuyoshi Kakinuma#
Fuel Cell Nanomaterials Center
University of Yamanashi

E-mail: kkakinuma@yamanashi.ac.jp

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- **Introduction**

  Electrocatalysts for PEFC

  Pt catalyst supported on ceramics support

- **Cell performance**

  Cell performance using Pt catalyst supported on ceramics support

  IV curve

  Durability (start up/shut down, load cycle)

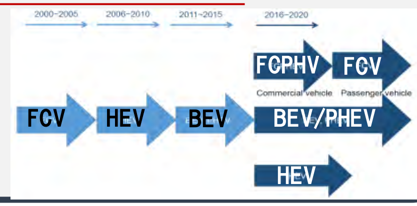
- **Design concept**

  Design concept the Pt catalyst supported on ceramics support and catalyst layer of Pt catalyst supported on ceramics support

- **Future plan**

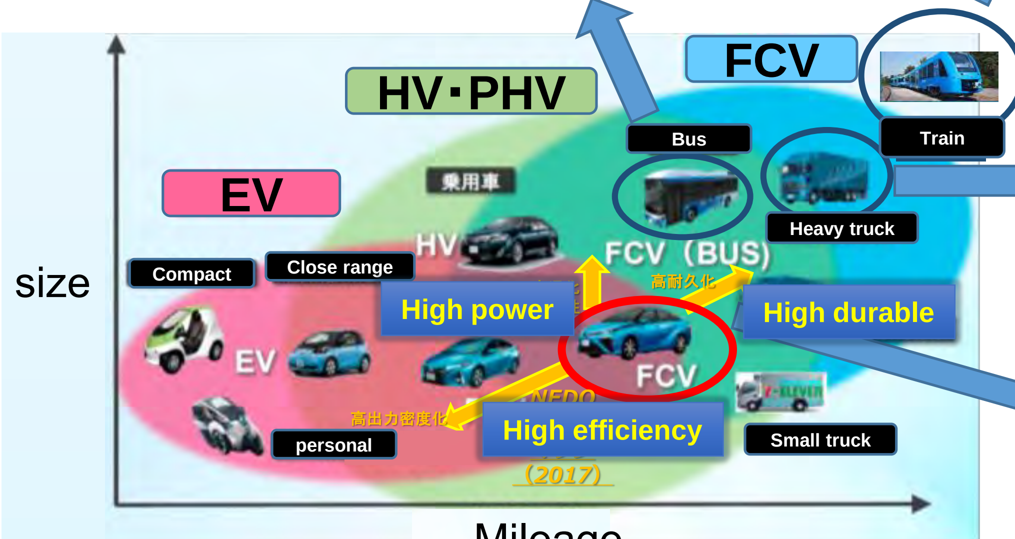
Toward the future FCV

China : 1271 sales @2017 (commercial vehicles)
One Billion target sales until 2030
Bus/Truck/Train ⇒ Vehicles



Germany : Train @2017
FCV @2018
Vehicles/Train

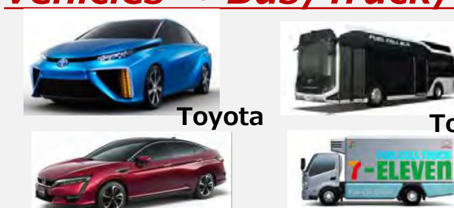
Train Daimler Stack Hydrogen tank



USA : 2313 sales @2017
Vehicles ⇒ Bus/Truck/Train

Toyota Toyota/Kenworth Honda Hyundai Nikola

Japan : 849 sales @2017
0.8 Billion target sales (until 2030)
Vehicles ⇒ Bus/Truck/Train



Toyota Toyota Honda Toyota

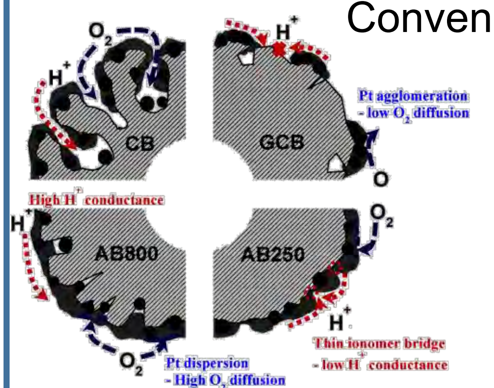
FCV has some priority in the vehicle size and mileage compared to the EV, HV and PHV.
In future, FCV system will be developed toward the high durability, high efficiency and high power.

Advantage and issues of current electrocatalysts

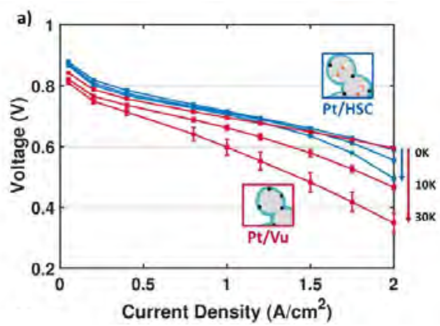
Typical electrocatalyst : **Pt catalyst supported on carbon**

Advantage

High electrical conductivity
High porosity
High BET surface area
Convenient surface morphology



J. Power Sources 315 (2016) 179-191

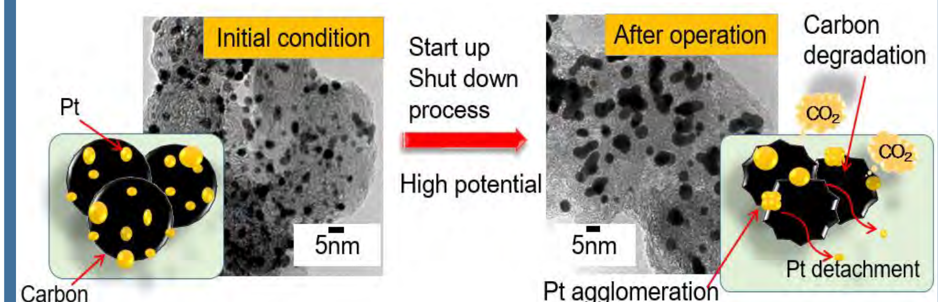


J. Electrochem. Soc. 166 (4) F198-F207 (2019)

Issue

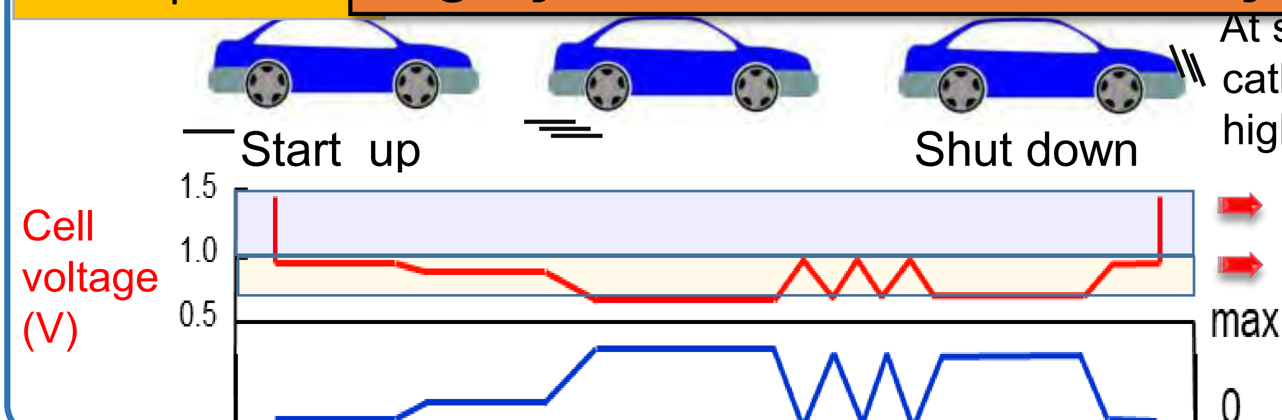
Intrinsic thermodynamic instability

$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ E = 0.207 V SHE



Highly durable cathode catalysts are required !

FCV operation



At start up / shut down operation, cathode catalysts are exposed to higher potential condition over 1.5V

- ➡ Carbon degradation
- ➡ Ostwald ripening

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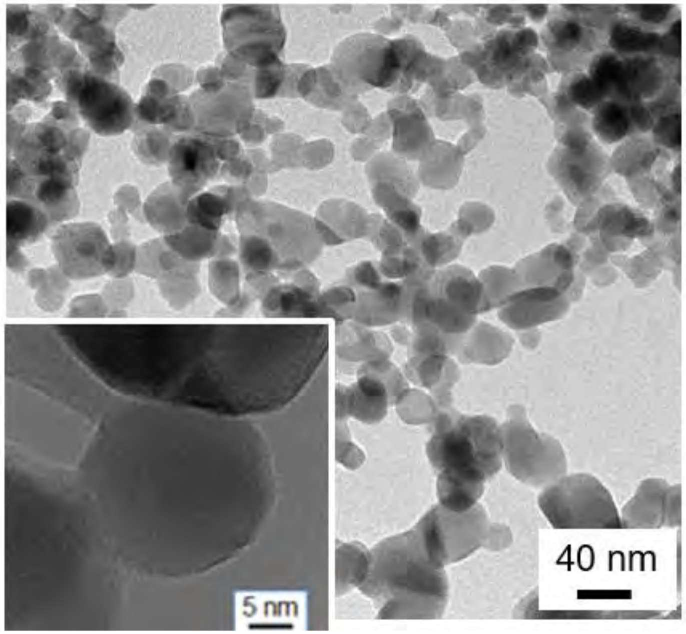
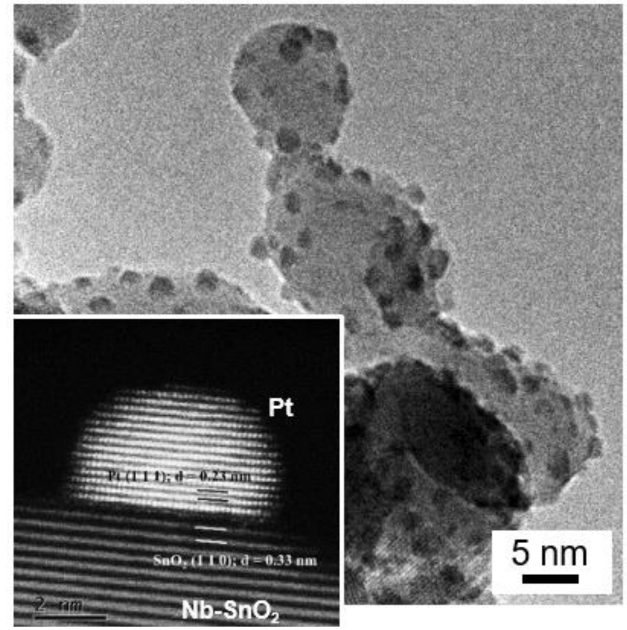
Alternative electrocatalyst : Pt/Nb-SnO_2 catalyst

Nb-SnO_2 support



Fused aggregate network microstructure

Pt/Nb-SnO_2 catalyst

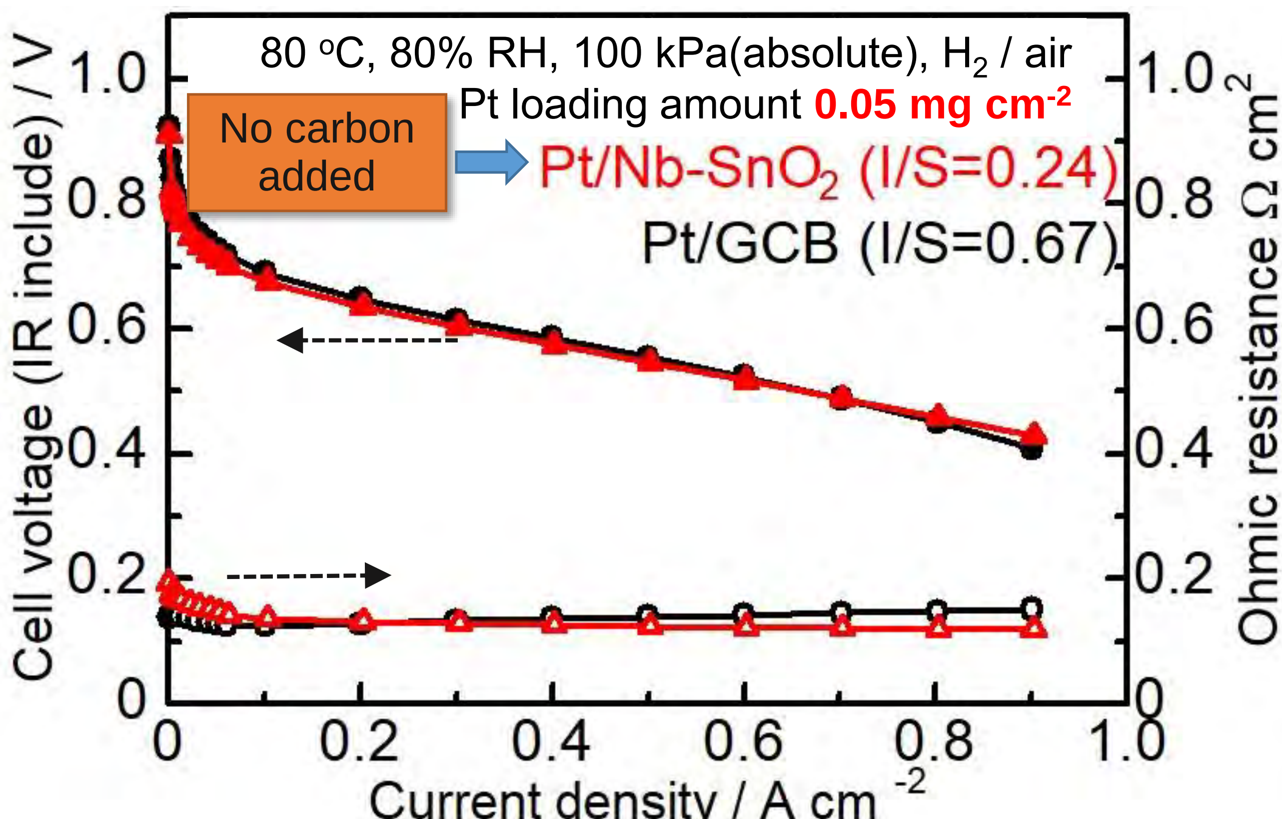


Pt orientation on the SnO_2 support

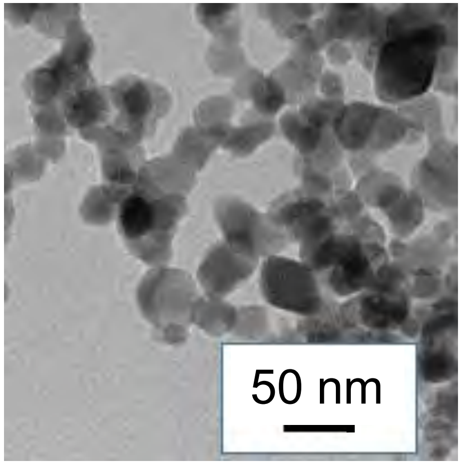
K.Kakinuma, M.Uchida et al. *Electrochim. Acta*, 56 (2011) 2881.
K.Kakinuma, M.Uchida et al. *Electrochim. Acta*, 110 (2013) 316.
K.Kakinuma, Y.Chino, Y.Senoo, M.Uchida, T.Kamino, H.Uchida, M.Watanabe *Electrochim. Acta*, 110 (2013) 316.

- ✔ High surface area → High Pt dispersion
- ✔ Fused aggregate network structure → High electronic conductivity and gas transport
- ✔ Chemical stability of the support → High durability
- ✔ Pt orientation on highly crystallized supports → Suppression of Pt migration

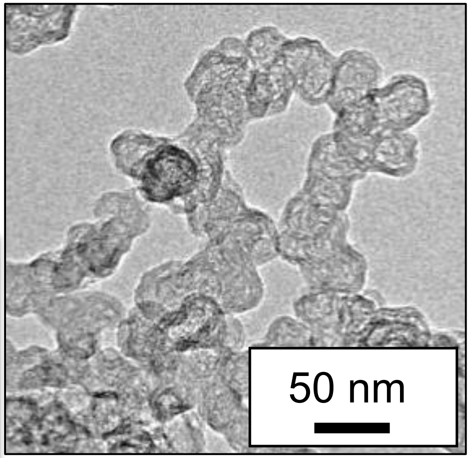
I-V performance of single cell using Pt/Nb-SnO_2 cathode catalyst layer



K. Kakinuma, R. Kobayashi, A. Iiyama, M. Uchida, *J. Electrochem. Soc.* 165 (2018) J3083.



Nb-SnO_2 nanoparticle
fused aggregate network microstructure



Carbon black

Single cell performance using Pt/Nb-SnO_2 cathode catalyst without carbon additives was equal to that using Pt/GCB. The Nb-SnO_2 support has a unique microstructure, the **fused aggregate network microstructure,** which reduces the contact resistance between each nanoparticle and increases the electrical conductivity.

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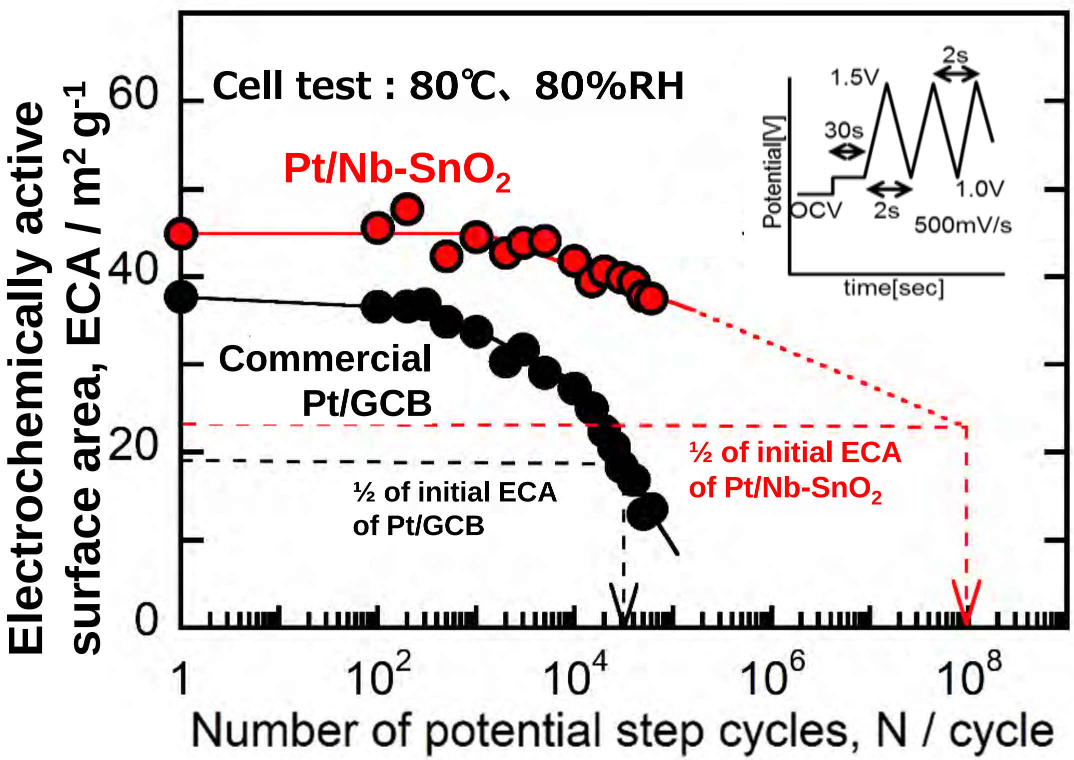
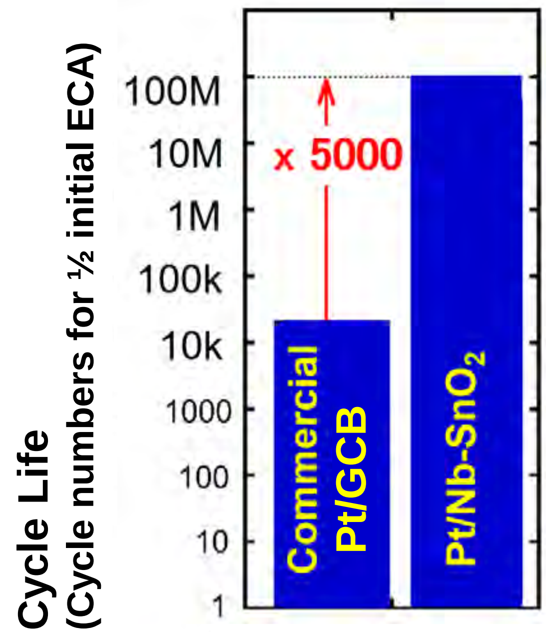
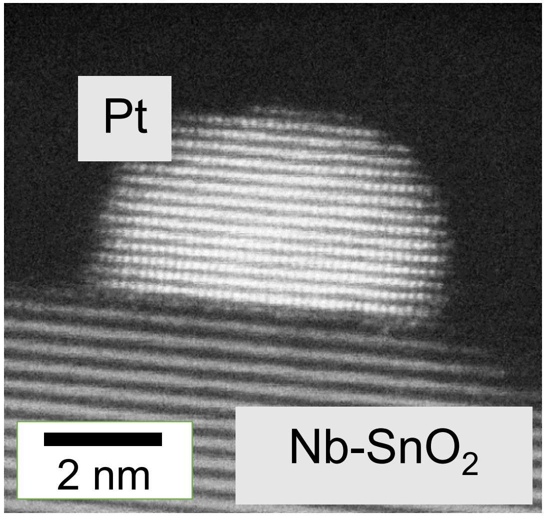
Start up / shut down durability of Pt/Nb-SnO_2



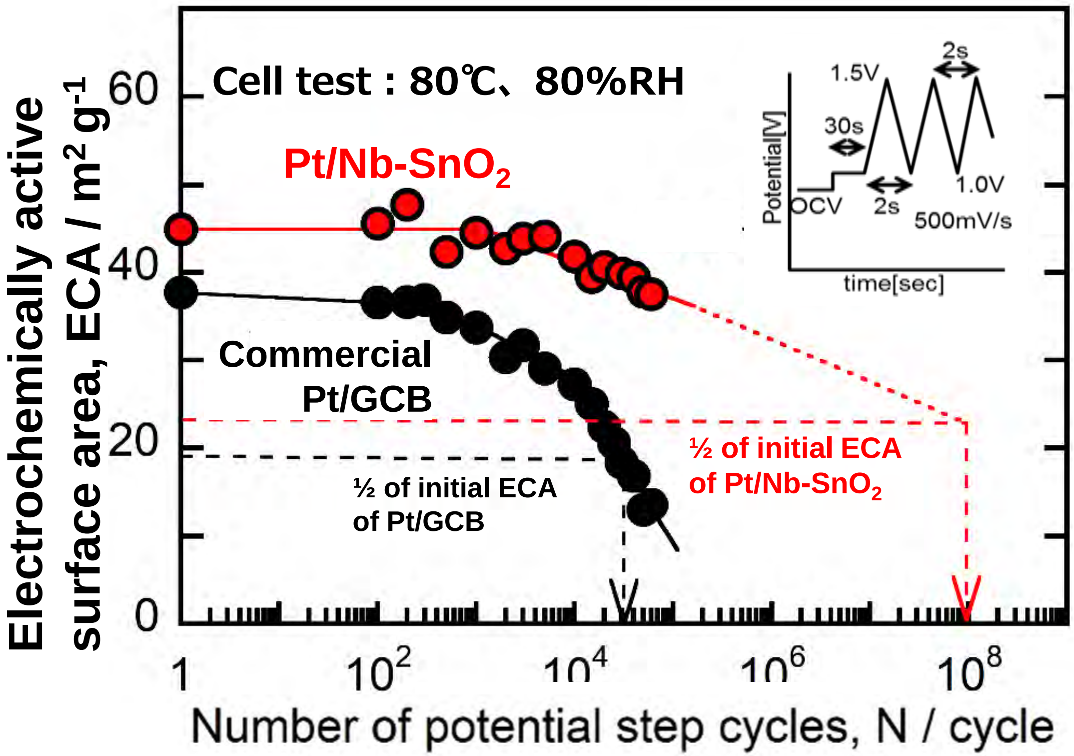
Y. Chino, K. Taniguchi, Y. Senoo, K. Kakinuma, M. Watanabe, M. Uchida, *J. Electrochem. Soc.* 162 (2015) 736.





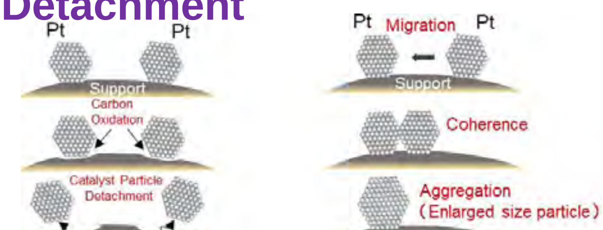
Startup / shutdown durability of Pt/Nb-SnO_2 catalyst layers is superior to that of Pt/GCB catalyst layers and relies on the strong bonding between Pt and Nb-SnO_2.

Start up / shut down durability of Pt/Nb-SnO_2



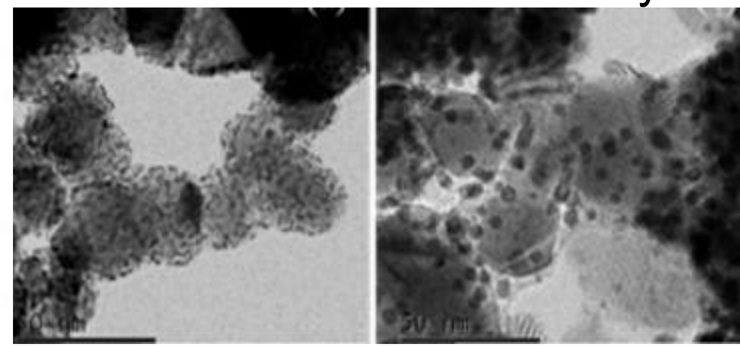
Y. Chino, K. Taniguchi, Y. Senoo, K. Kakinuma, M. Watanabe, M. Uchida, *J. Electrochem. Soc.* 162 (2015) 736.

Catalyst Particle Detachment **Aggregation**



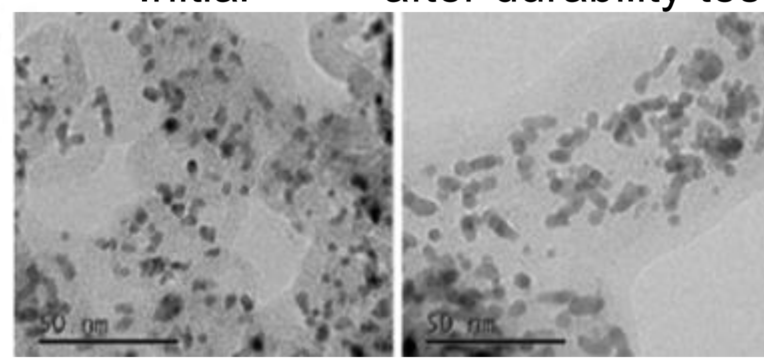
Pt/Nb-SnO_2

Initial after durability test



Pt/GCB

Initial after durability test



ECSA after 60000 cycles : 70% of initial value
(Pt/GCB: less than 40 % of initial value)

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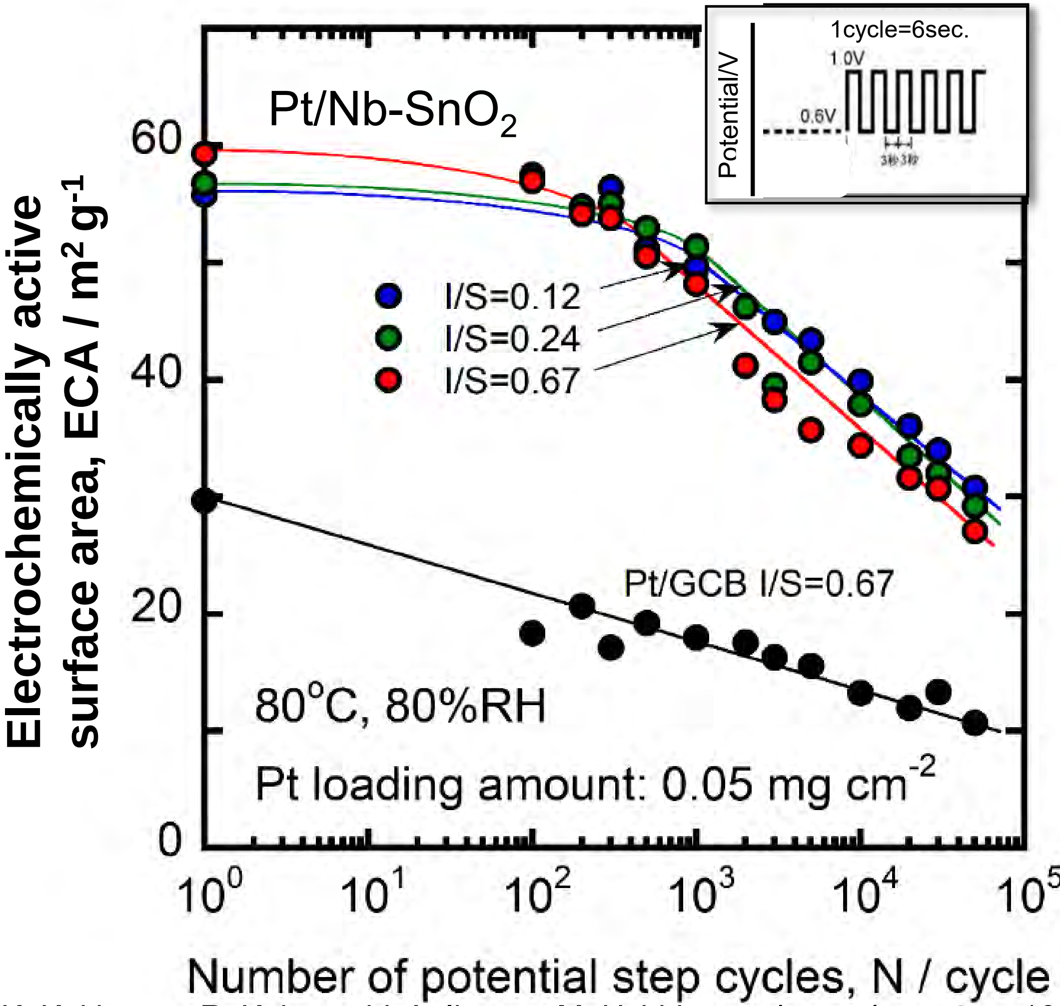
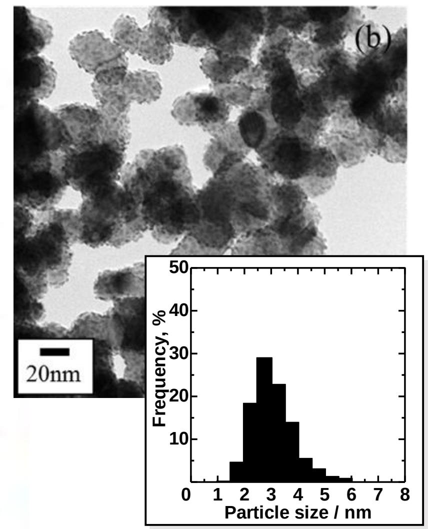
Load cycle durability of Pt/Nb-SnO_2

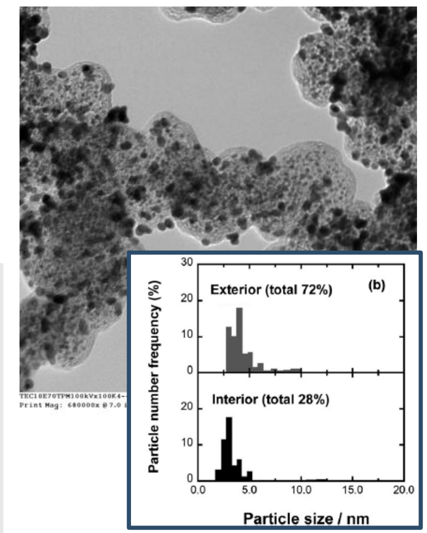


Pt/Nb-SnO_2

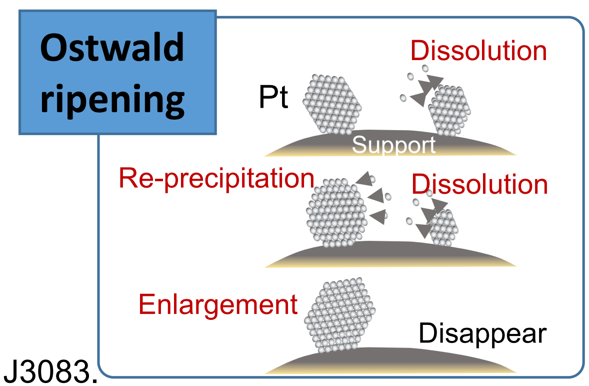


Pt : 3.1±0.8 nm

Pt/GCB



Pt : 4.7±1.8 nm



K. Kakinuma, R. Kobayashi, A. Iiyama, M. Uchida, *J. Electrochem. Soc.* 165 (2018) J3083.

Load cycle durability of Pt/Nb-SnO_2 catalyst layers is also superior to that of Pt/GCB catalyst layers.

Cross-section image of $Pt/Nb\text{-}SnO_2$ and Pt/GCB catalyst layers after load cycle test (50,000 cycles)

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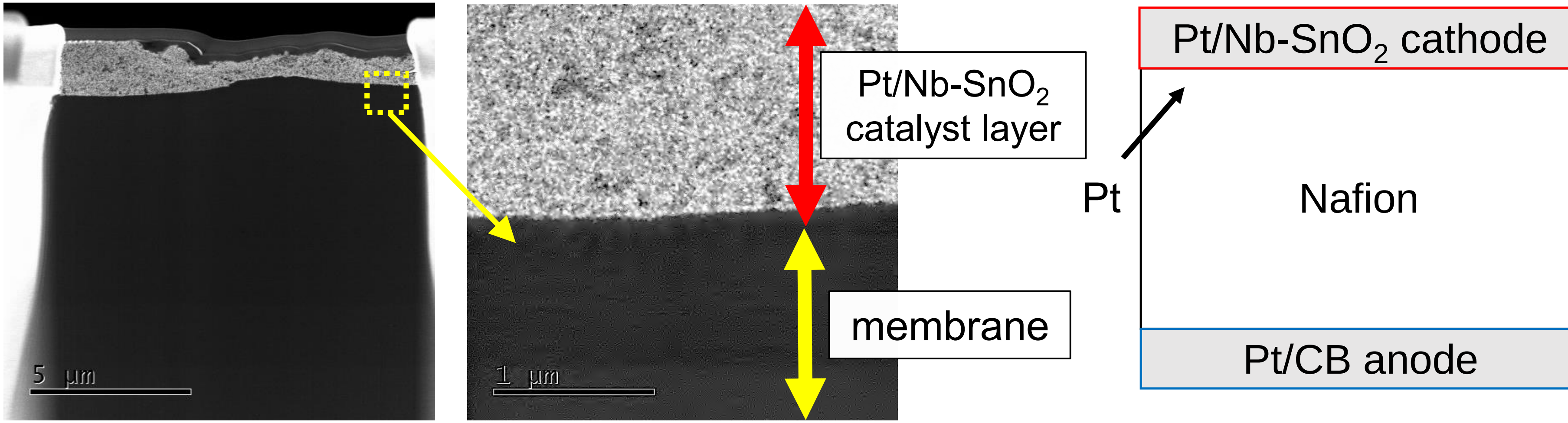
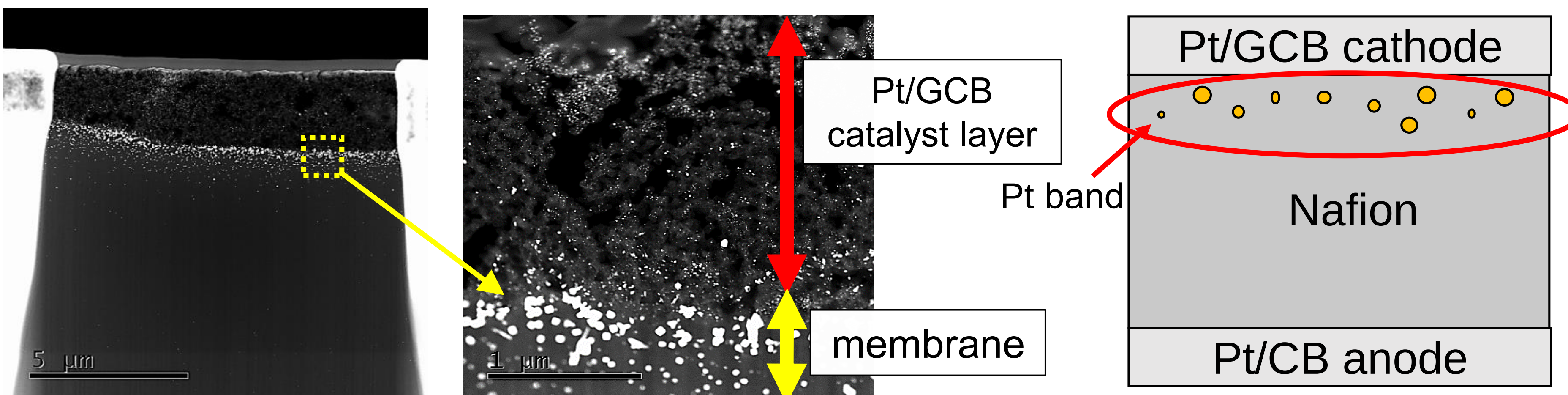
$Pt/Nb\text{-}SnO_2$ (I/S=0.12) 50,000 cycles



Pt/GCB (I/S = 0.70) 50,000 cycles



K. Kakinuma, R. Kobayashi, A. Iiyama, M. Uchida, *J. Electrochem. Soc.* 165 (2018) J3083.

Pt band was not detected in the Nafion membrane of the MEA using $Pt/Nb\text{-}SnO_2$ catalyst after load cycle testing.

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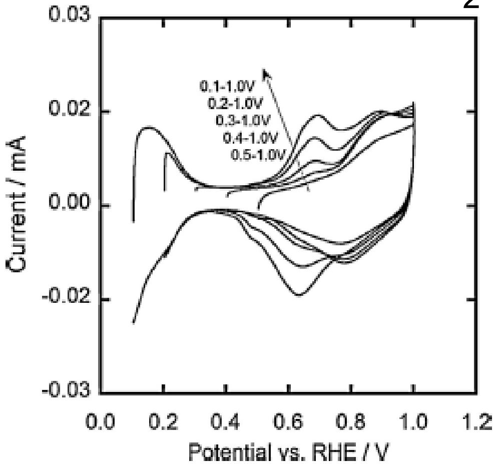
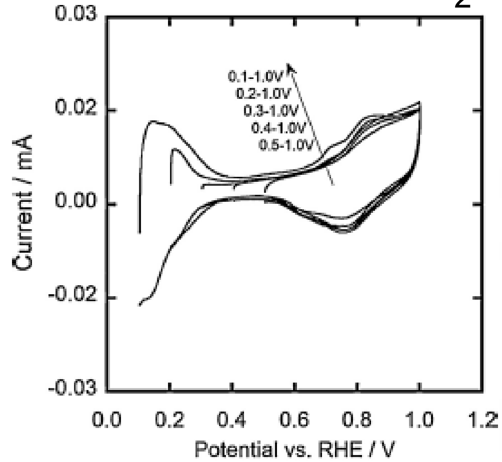
Evaluation of solubility of Pt/SnO_2

$Pt/Sb\text{-}SnO_2$

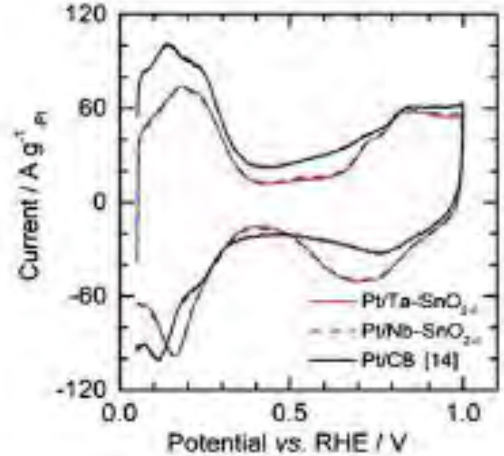


$Pt/Nb\text{-}SnO_2$



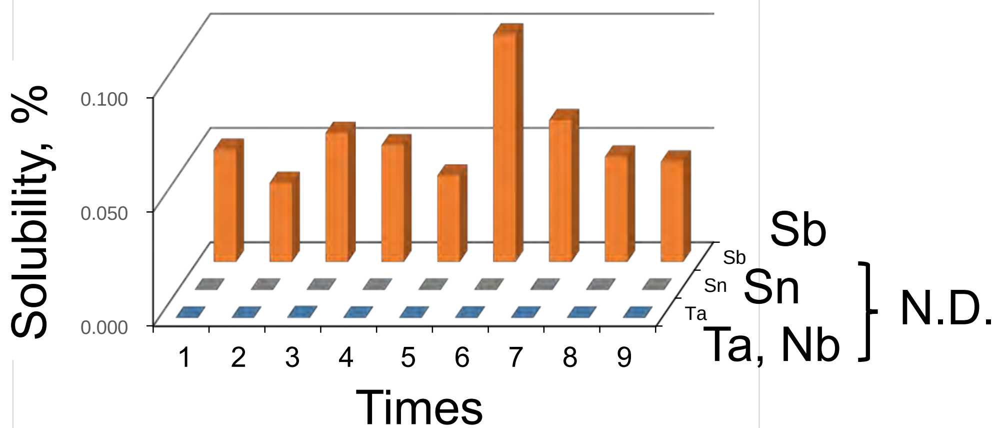
K.Kakinuma, Y.Chino, M. Uchida, T. kamino, H. Uchida, S. Deki, M. Watanabe
Electrochim. Acta 110 (2013) 316.

$Pt/Ta\text{-}SnO_2$



Y. Senoo, K. Taniguchi, K.Kakinuma, M. Uchida, H. Uchida, S. Deki, M. Watanabe
Electrochem. Commun. 51 (2015) 37.

Solubility in 1 N sulfuric acid (H_2SO_4) , 80^oC, 8 days



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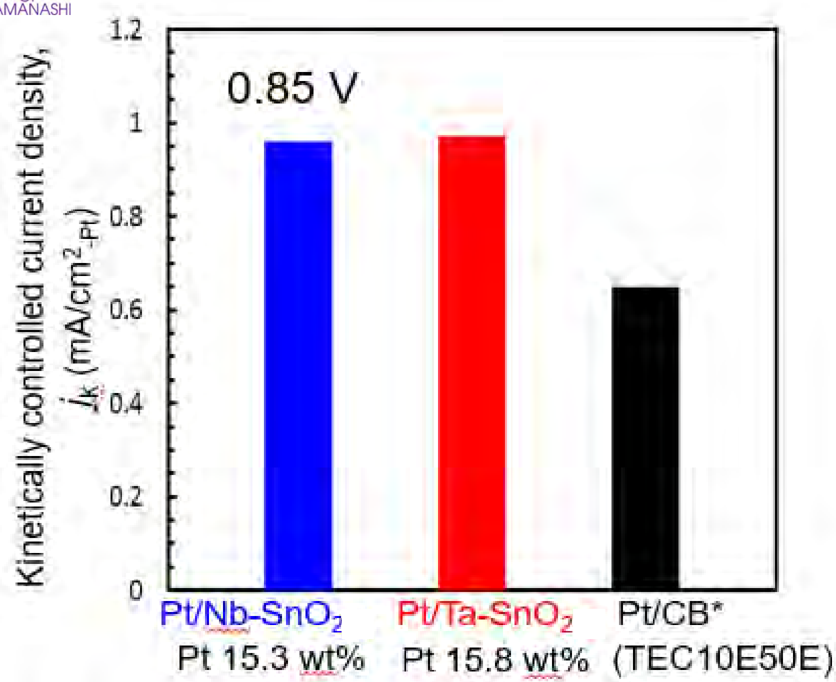
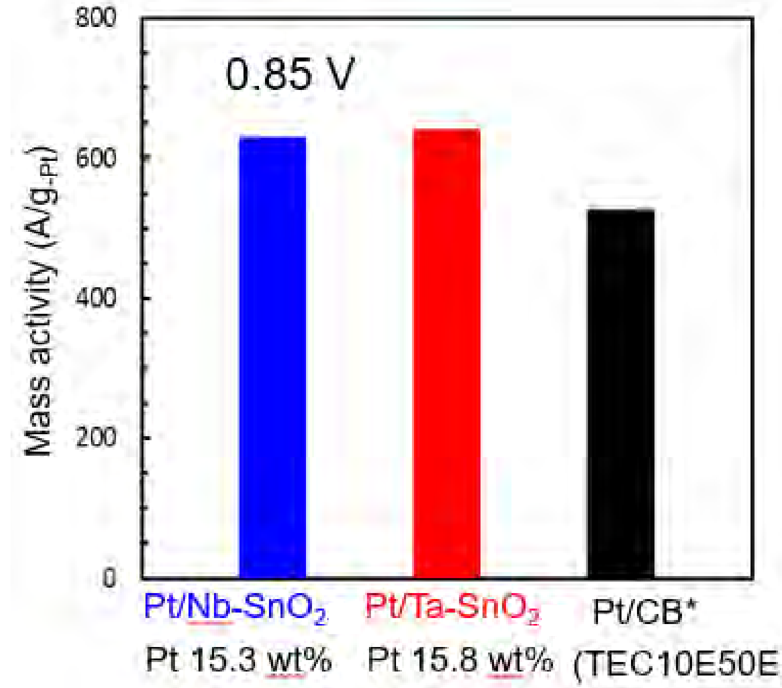
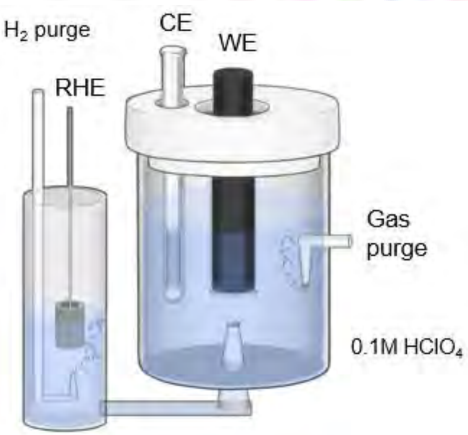
Evaluation of electrochemical activity of Pt/SnO_2







Temperature: 25^{o}C
Substrate: 5 mmφ(0.196cm^2)
Pt loading：11.0 μg cm^{-2}
Nafion coverage：0.05 μm

CE: counter electrode
WE: working electrode
RHE: reversible hydrogen electrode

K.Kakinuma, M.Uchida, T.Kamino, H.Uchida, M.Watanabe *Electrochim. Acta*, 56 (2011) 2881.

K.Kakinuma, Y.Chino, Y.Senoo, M.Uchida, T.Kamino, H.Uchida, M.Watanabe *Electrochim. Acta*, 110 (2013) 316.

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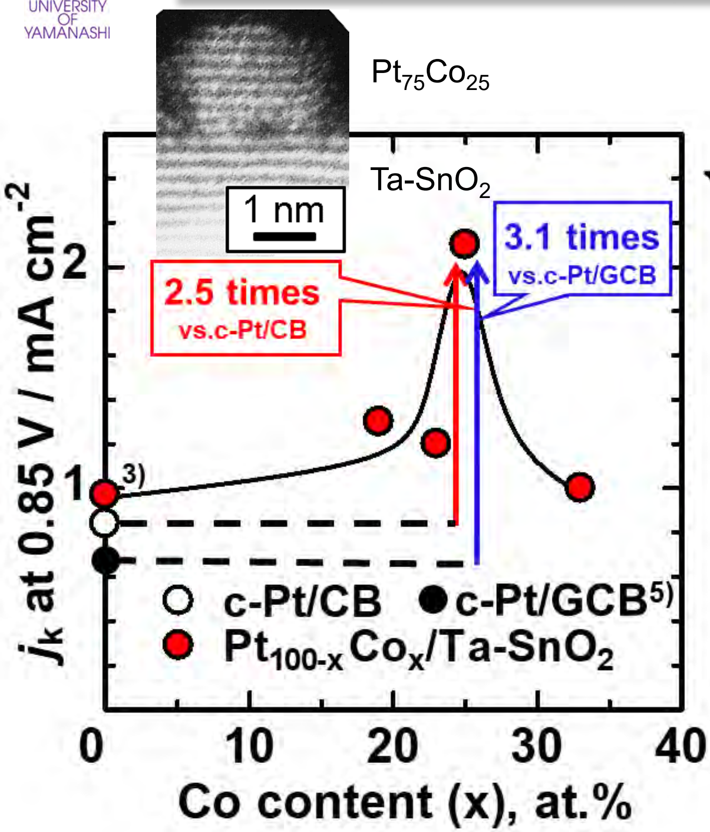
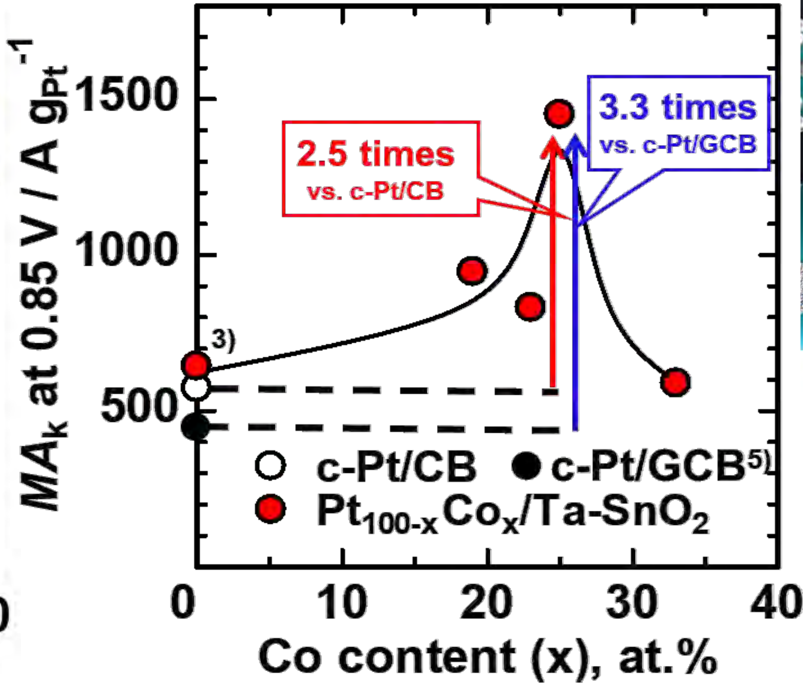
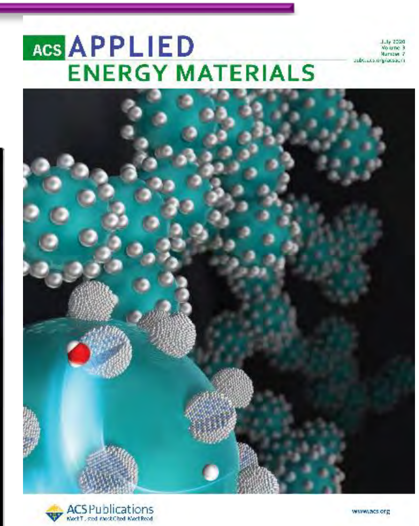
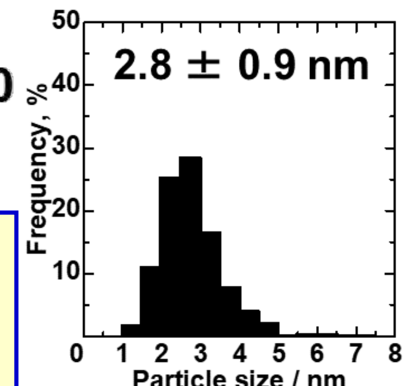
Evaluation of electrochemical activity of Pt alloy/SnO_2







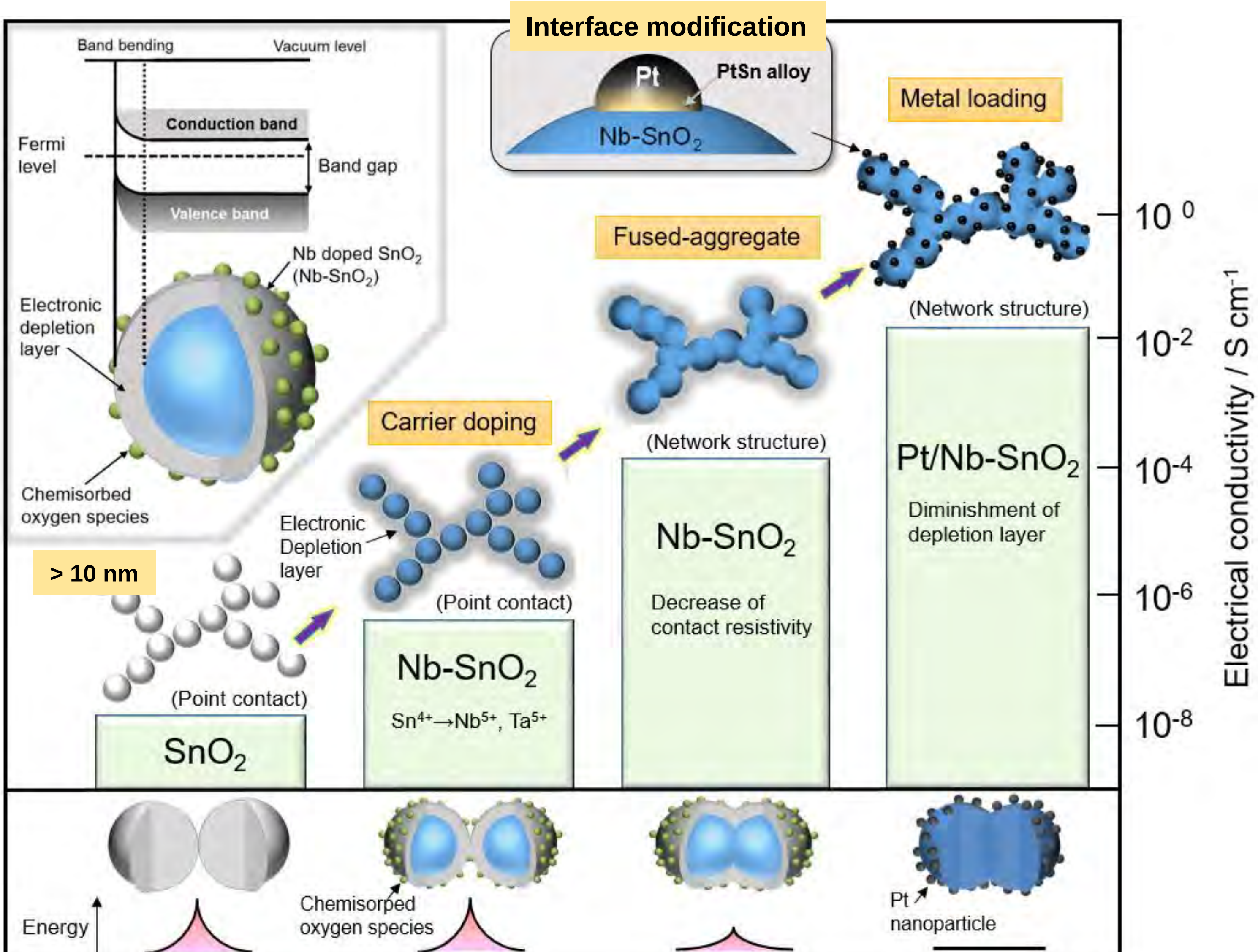
K.Kakinuma et al.
ACS Energy Mater.
3 (2020) 6922.



The relation ship between the kinetically controlled current density (j_k) and mass activity (MA_k) of $Pt_{100-x}Co_x/Ta-SnO_2$ shows a volcano curve.

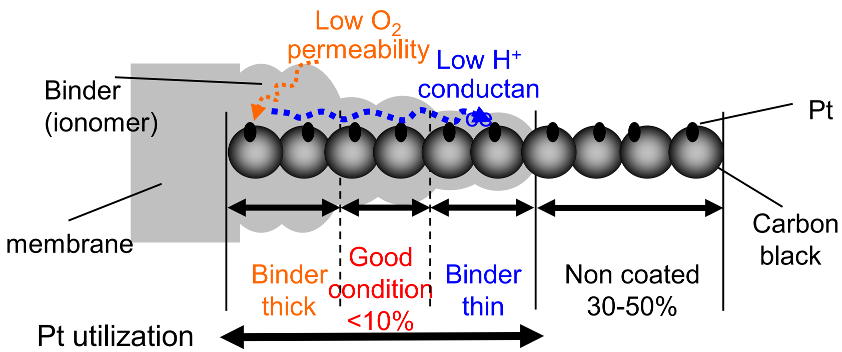
The maximum ORR activity reached ca. 3 times higher than that of commercial Pt/carbon.

Conclusion 1
The strategy to enhance the catalytic activity of Pt/SnO_2 catalyst

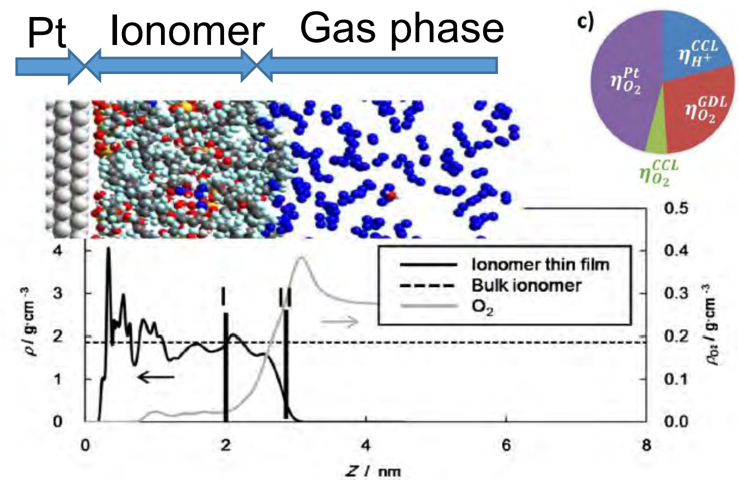


K.Kakinuma, et al. ACS Appl. Mater & Interfaces 11 (2019) 34957

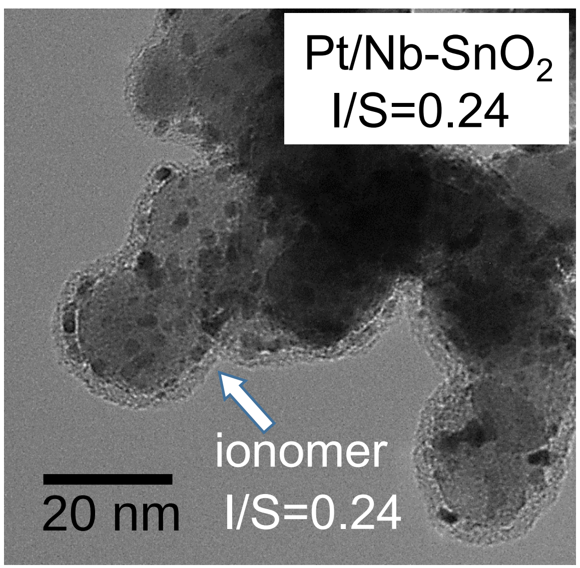
Design concept of Pt/SnO_2 catalyst layers - ionomer -

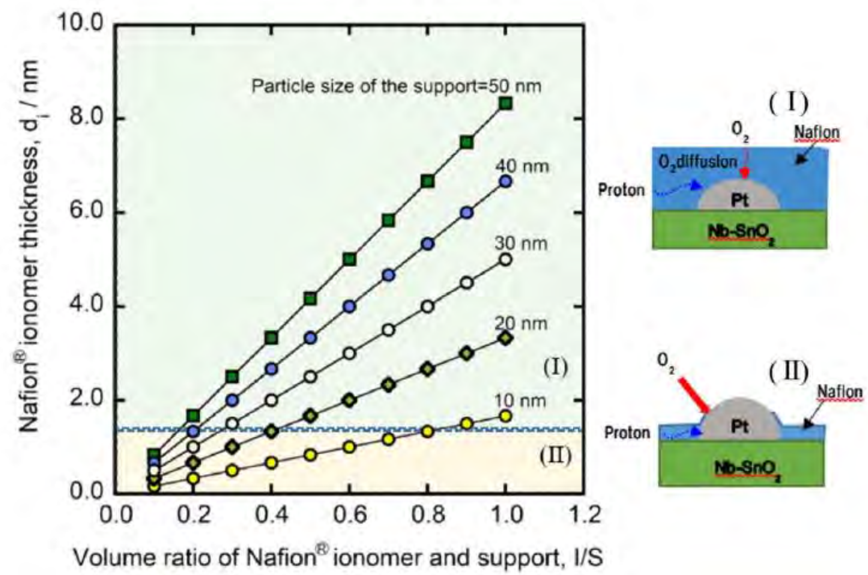


M. Lee, M. Uchida, H. Yano, D.A. Tryk, H. Uchida, M. Watanabe, Electrochimi. Acta, 55 (2010) 8504.



R.Jinnouchi, K.Kudo, N.Kitano, Y.Morimoto Electrochim. Acta, 188 (2016) 767, A. Kongkanand, M.F. MathiasJ. Phys. Chem. Lett. 7 (20106 1127.

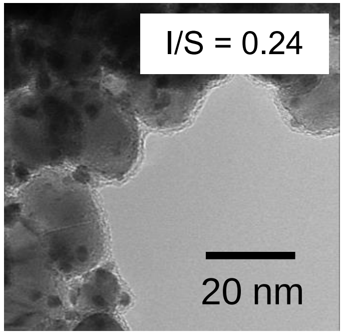


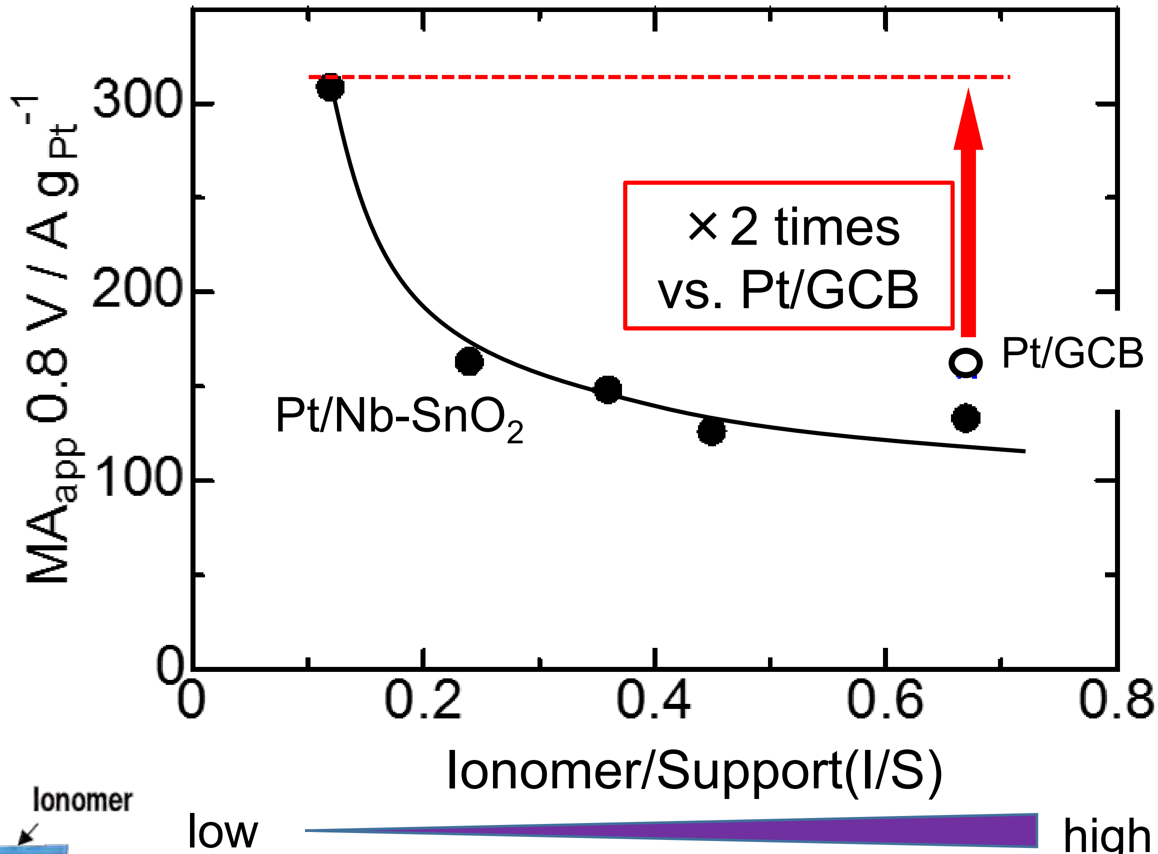


K. Kakinuma, R. Kobayashi, A. Iiyama, M. Uchida, *J. Electrochem. Soc.* 165 (2018) J3083.

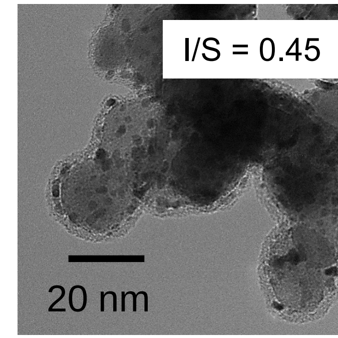
Mass activity of single cells using Pt/Nb-SnO_2 cathodes

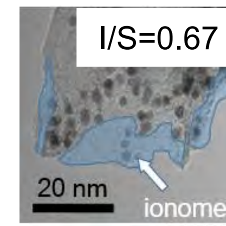
Pt/Nb-SnO_2



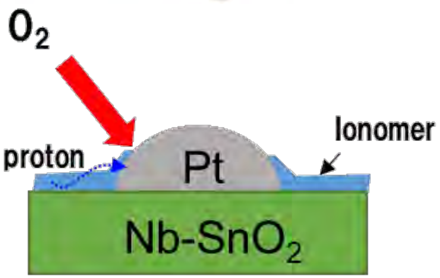


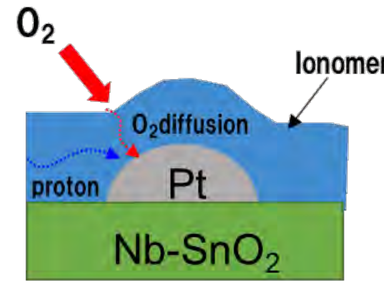
Pt/Nb-SnO_2





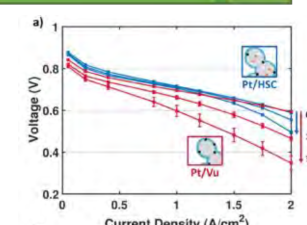
Pt/GCB





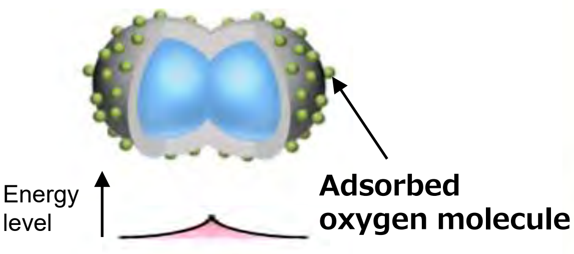
K. Kakinuma, R. Kobayashi, A. Iiyama, M. Uchida, *J. Electrochem. Soc.* 165 (2018) J3083.

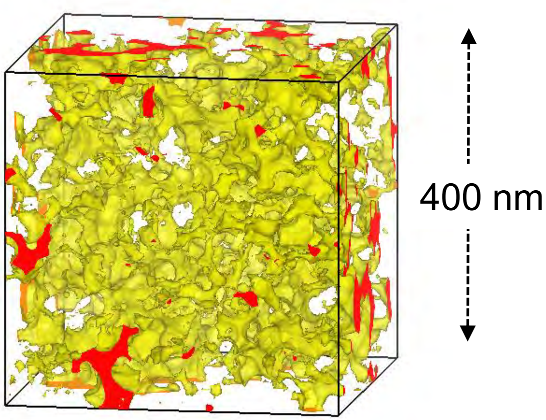
Mitigation of specific sulfonic acid adsorption
Decrease of gas diffusion resistance at Pt/ionomer interface



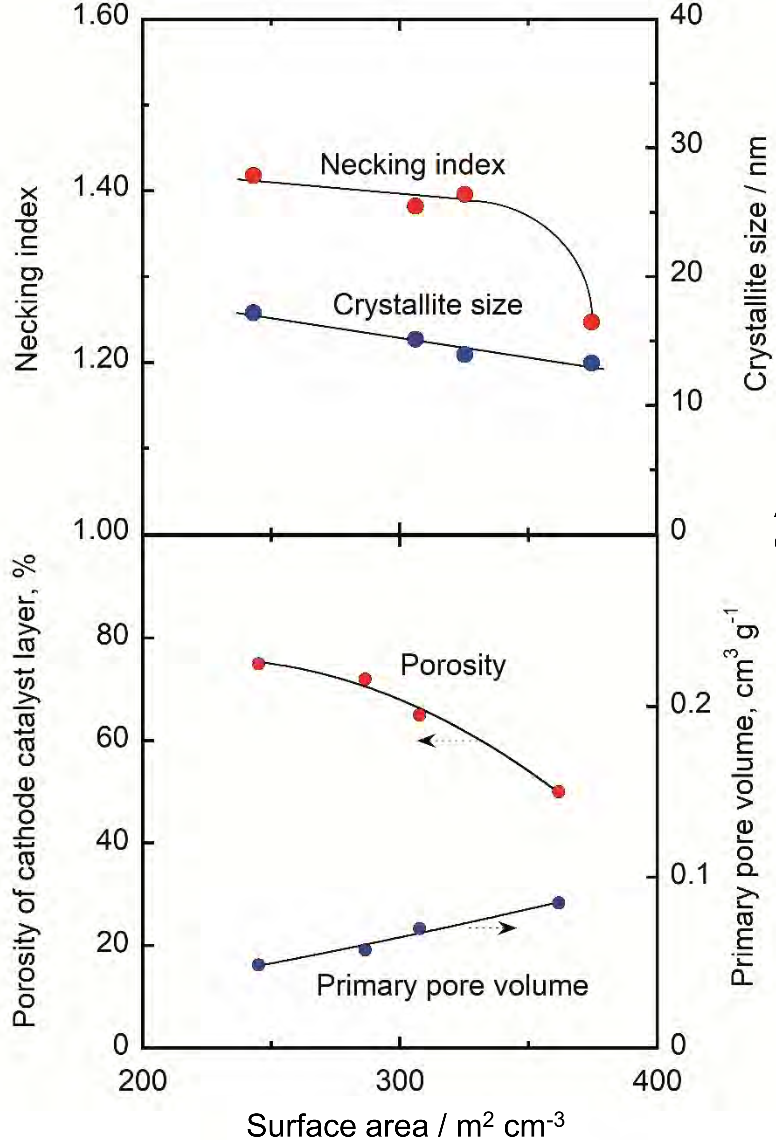
Porosity of Pt/SnO_2 catalyst layer

Primary pore volume (320 m² cm⁻³)

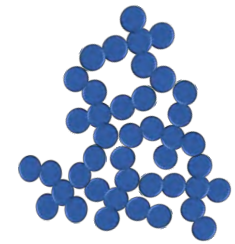




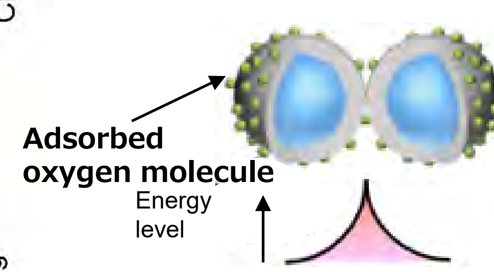
Pore (≧10 nm) distribution
Simulated by Rigaku

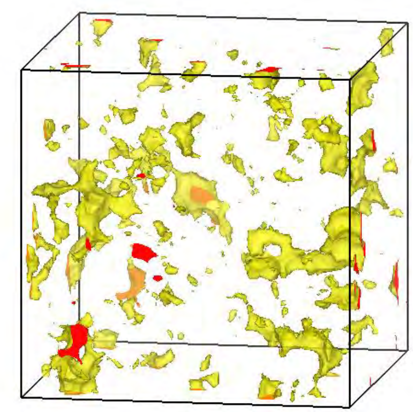


K.Kakinuma et al., Trans. Soc. Automotive Eng. Jpn. 50 (2019) 1549.



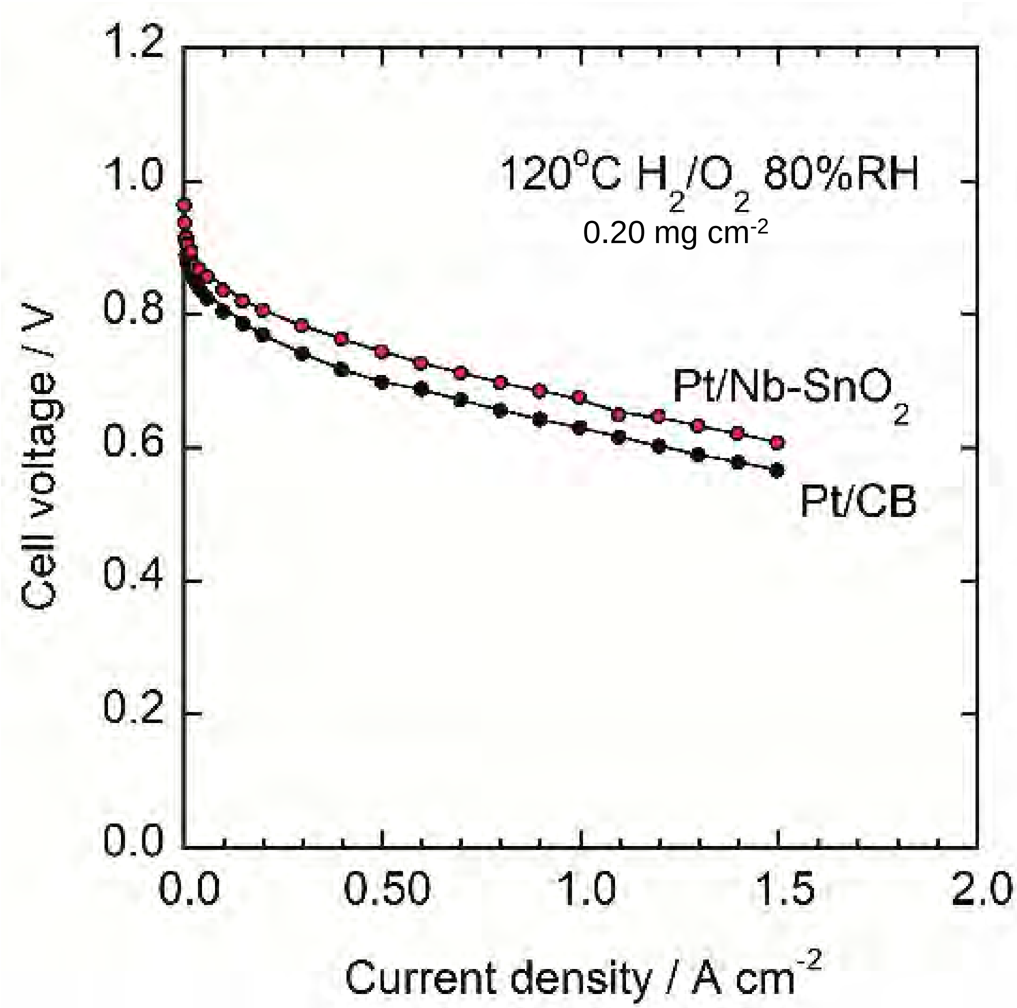
Primary pore volume (360 m² cm⁻³)





Pore (≧10 nm) distribution

120°C operation by Pt/Nb-SnO_2 catalysts



Operation at 120°C
High humidity & back pressure are required.

Single cell performances (power/durability) using Pt/Nb-SnO_2 catalyst layers is superior to those using current Pt supported on carbon (Pt/CB).

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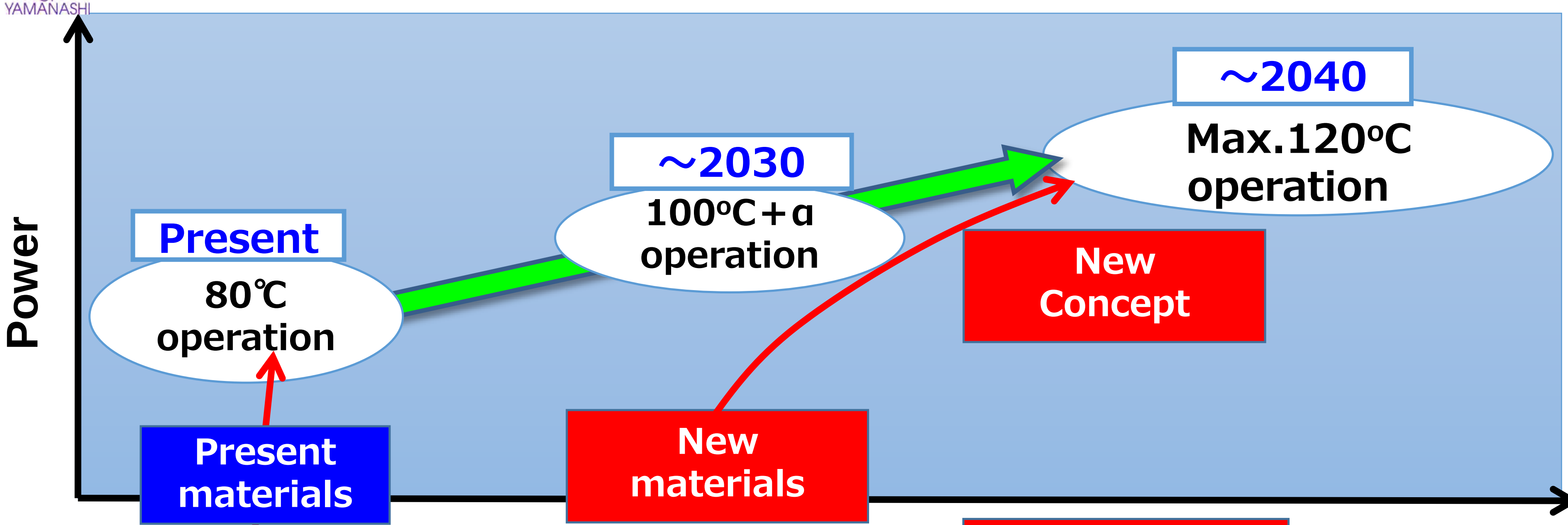
Conclusion 2
Toward the high power and durable PEFC



New materials

Pt nanowire
Fused-aggregated network
Conducting ceramic nanoparticles
Aromatic membrane with reinforce

Present concept

Pt alloy
Skin
Core-shell
carbon
Nafion

New concept

Pt/ceramic/ionomer interface control
high dimension fractal
Platinum anti-dissolution mechanism (PADM)
Atmospheric resistive switching mechanism (ARSM)

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Thank you very much
for your kind attention !