

Development of Ir-Based Electrocatalyst for Polymer Electrolyte Membrane Water Electrolysis

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Water Electrolysis

FC Catalyst Development Center

TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd.

Today's topics

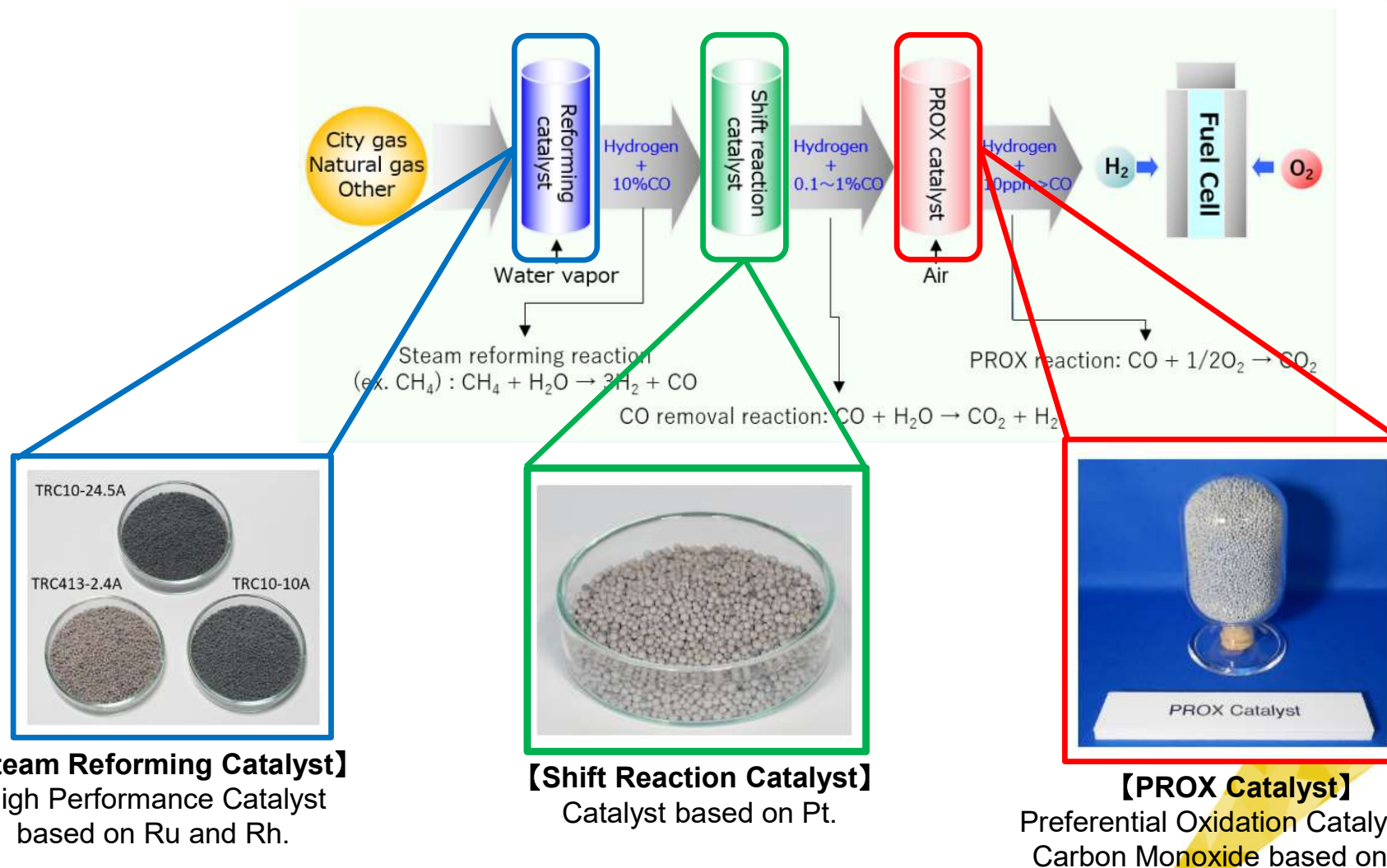
1. Introduction of TANAKA
2. Our Development History with Polymer Electrolyte Membrane Water Electrolysis(PEMWE)
3. Overview of Our Iridium-Based Catalyst (TEC77100, TEC77110)
4. Durability of TEC77100 and TEC77110
5. About New Catalyst
6. Summary

1. Introduction of TANAKA

Our Products for Carbon Neutral Society

① For Steam Reforming Process

Our products (catalyst) have been used at each step of the Steam Reforming Process.



【Steam Reforming Catalyst】
High Performance Catalyst
based on Ru and Rh.

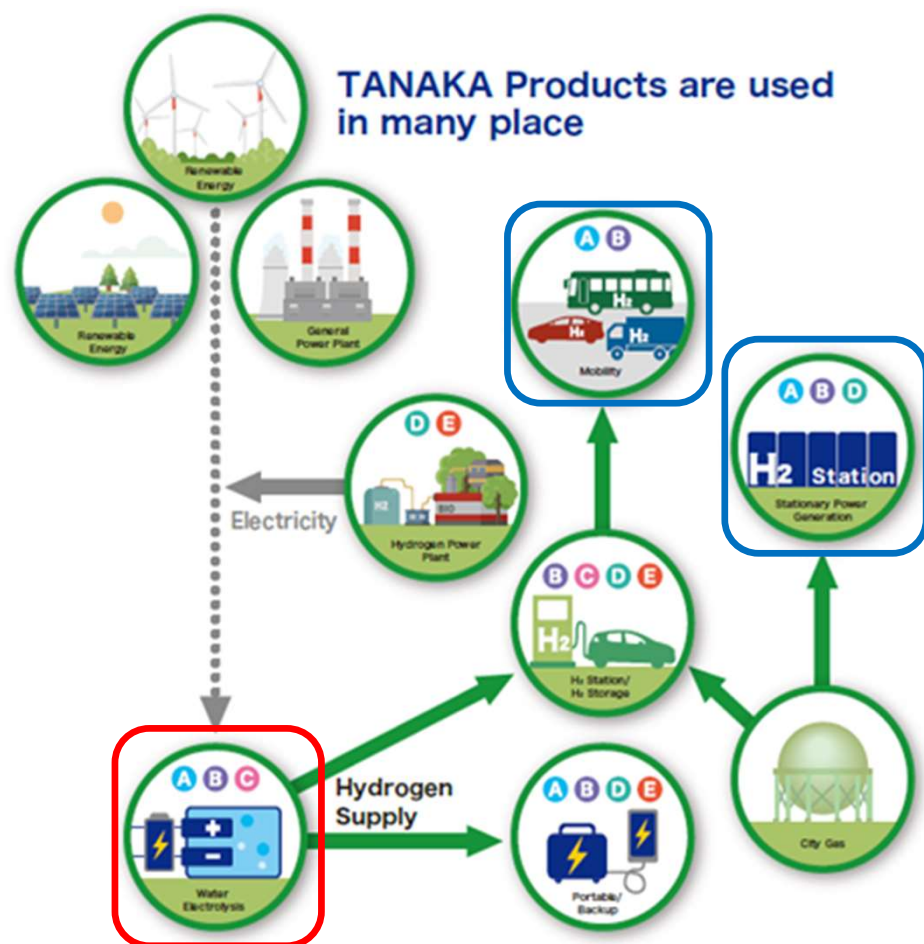
【Shift Reaction Catalyst】
Catalyst based on Pt.

【PROX Catalyst】
Preferential Oxidation Catalyst for
Carbon Monoxide based on Ru.

Our Products for Carbon Neutral Society

② Electrolyzer, Fuel Cells etc.

We also address the catalyst for PEMFC and PEMWE.



【Fuel Cell Catalyst】

Catalyst for Proton Exchange Membrane Fuel Cells (PEMFC)
Providing various line-up (Pt/C, PtCo/C, PtRu/C, etc.)

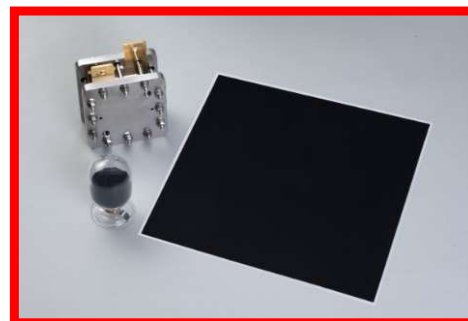
Pt/C catalyst



Used as a reference catalyst in papers, etc.

【Anode Catalyst for Electrolyzer】

Catalyst for Proton Exchange Membrane Water Electrolysis (PEMWE) based on Ir Oxide.

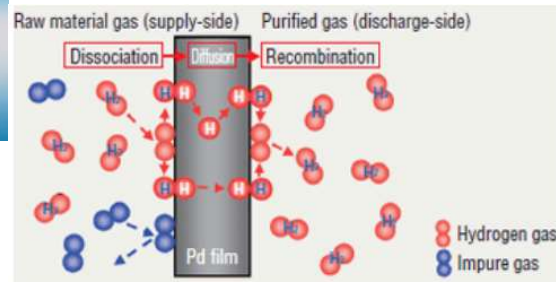


Our Products for Carbon Neutral Society

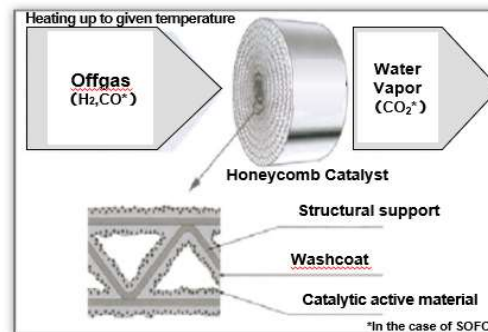
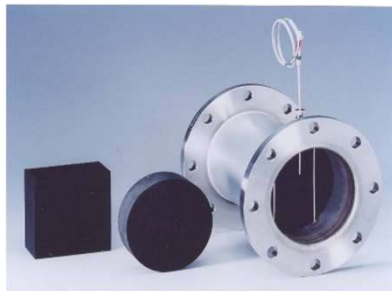
③ Others

【Hydrogen Permeable Films】

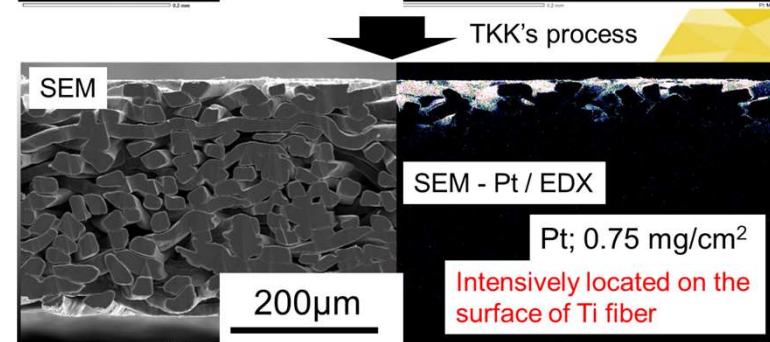
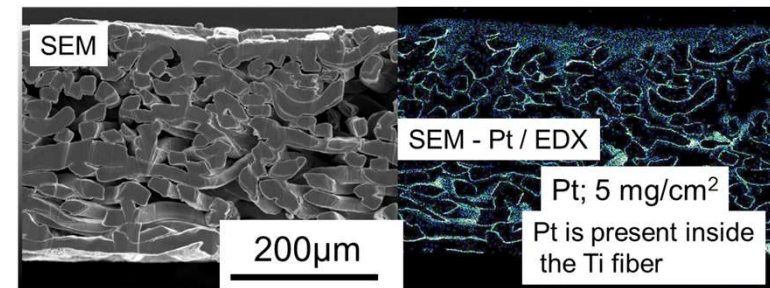
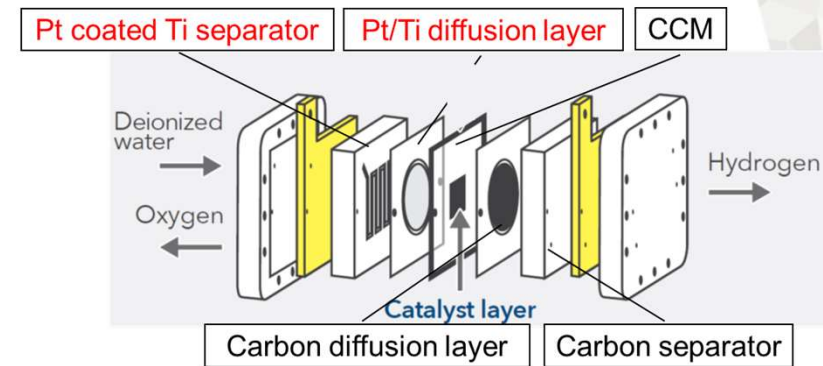
Pd and Pd-alloy films for hydrogen purification



【Exhaust Gas Purification Catalysts】

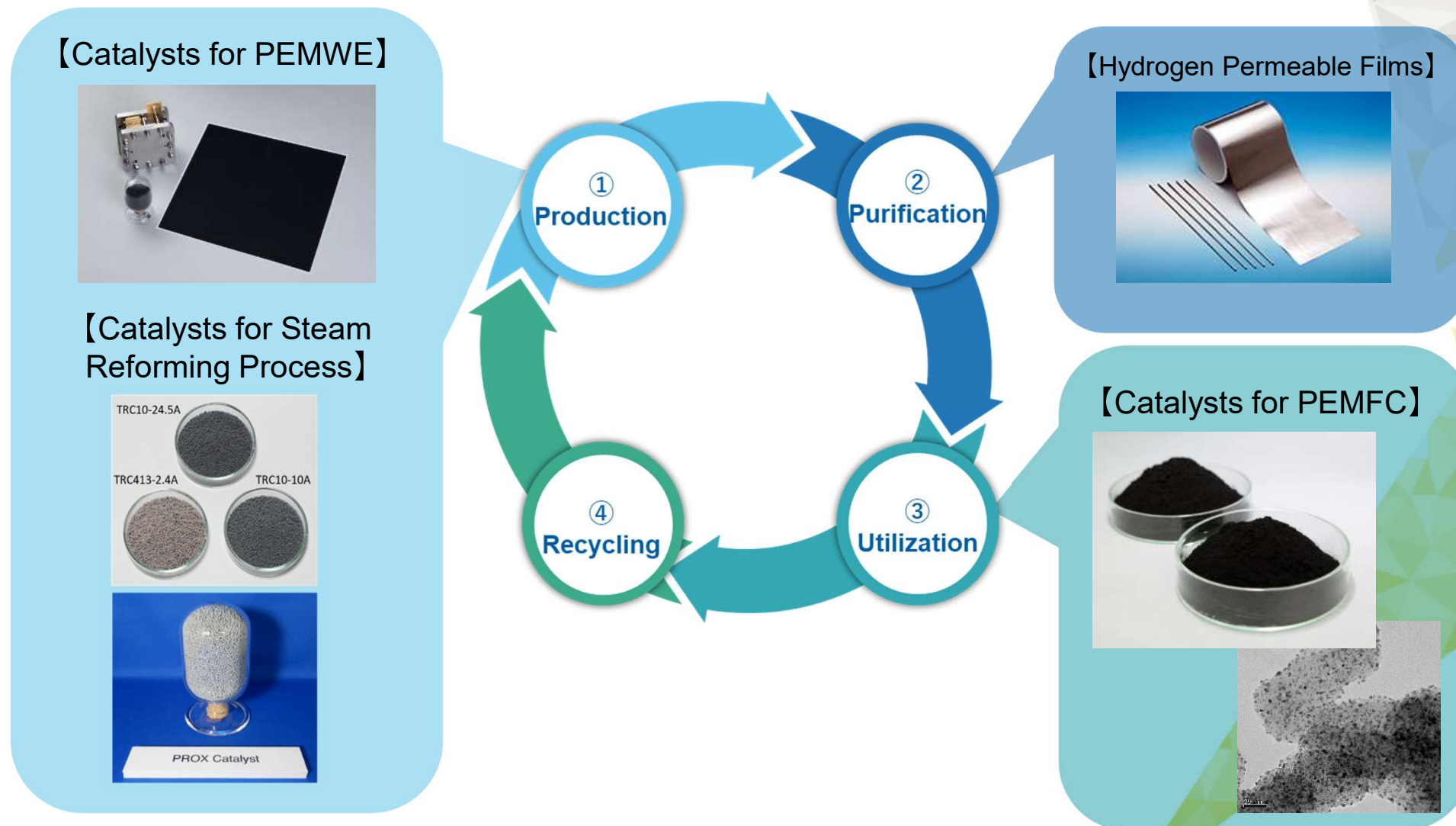


【Pt plating for Pt/Ti diffusion layer in PEMWE】



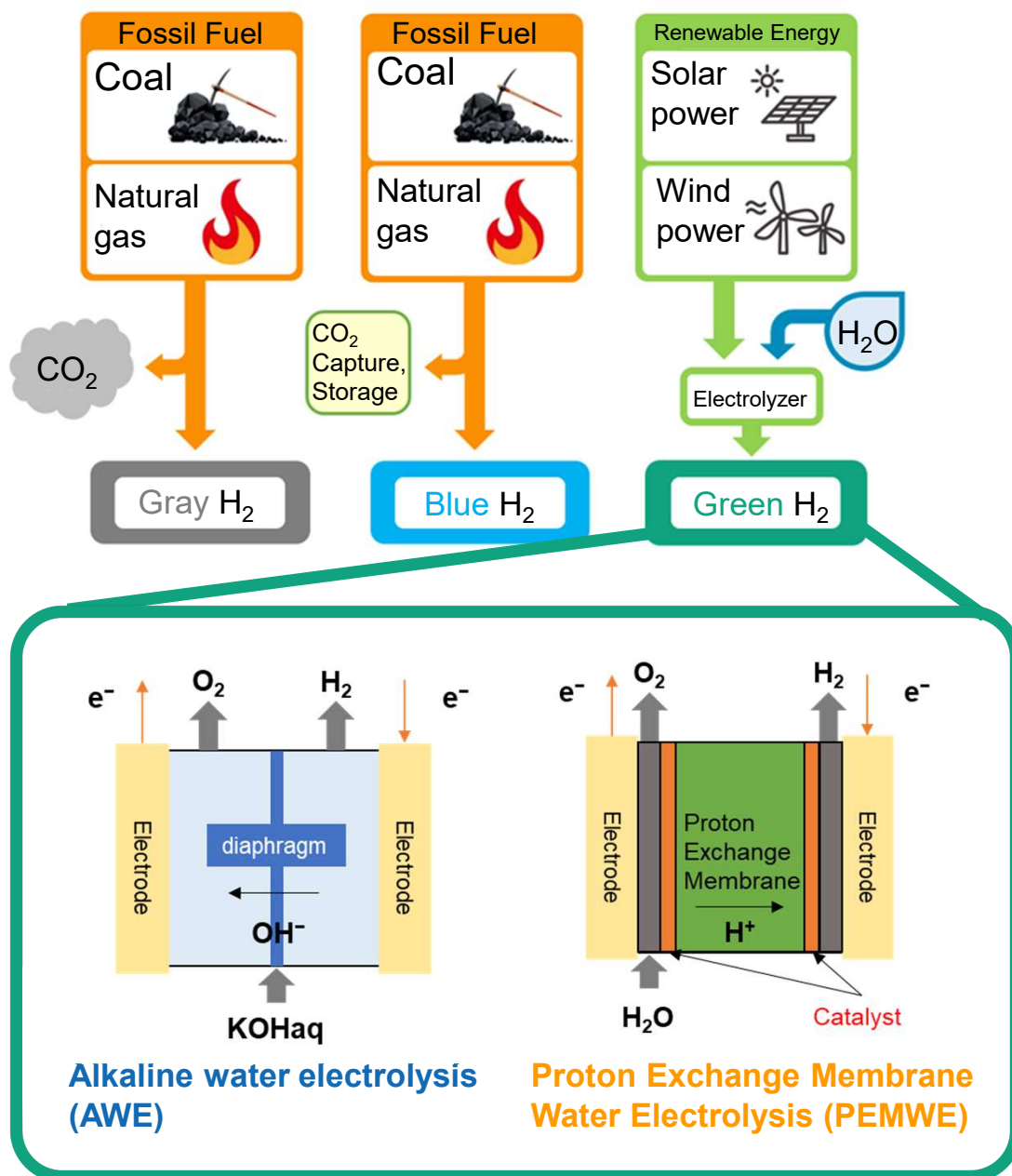
Our Strong point for Hydrogen Society -Summary-

We can address the whole process related to hydrogen production and utilization from production of hydrogen to recycling used materials.



2. Our Development History with Polymer Electrolyte Membrane Water Electrolysis (PEMWE)

Methods for electrocatalytic hydrogen production



Two types of Electrolyzers have been used commercially; AWE, PEMWE.

AWE

- The oldest type electrolyzer
- A certain level of performance
- Low ability to respond to power fluctuation, on-off mode

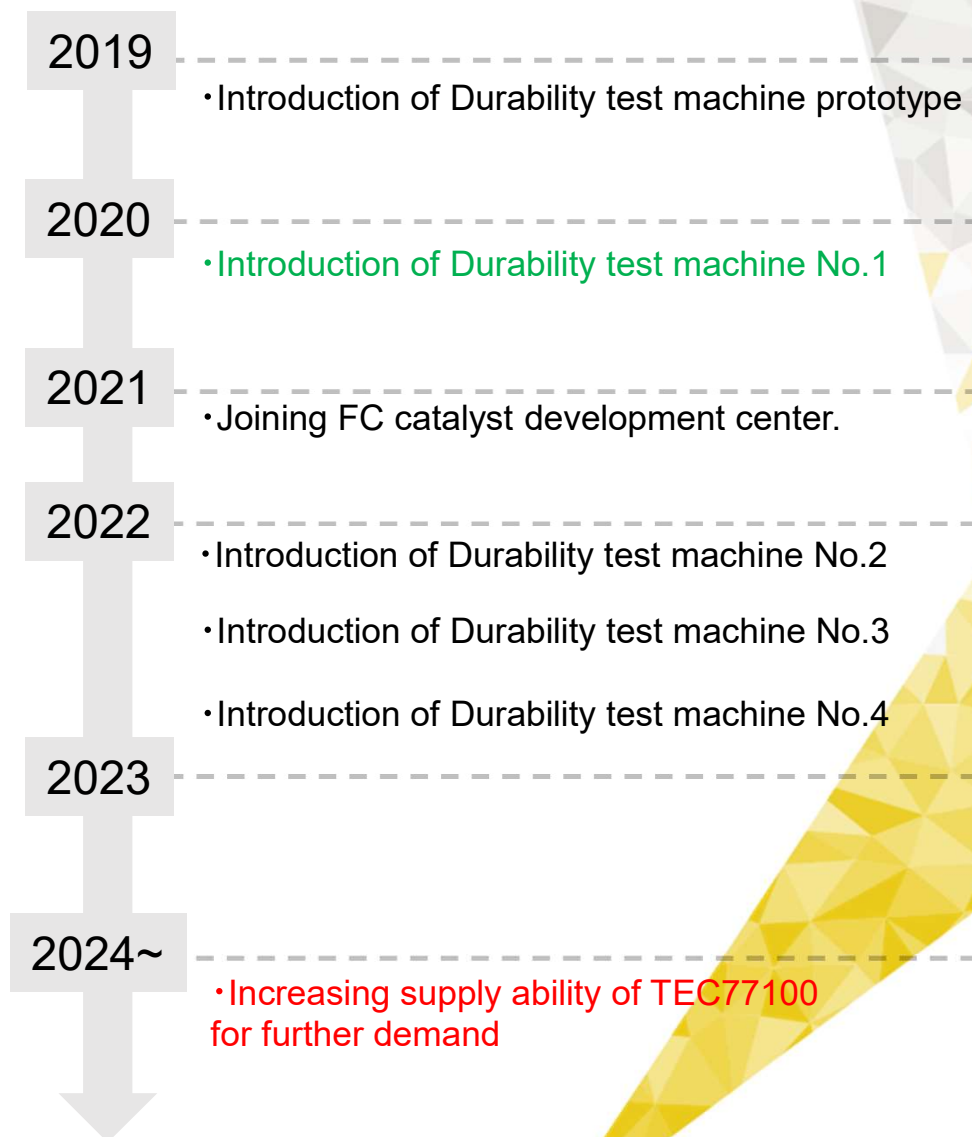
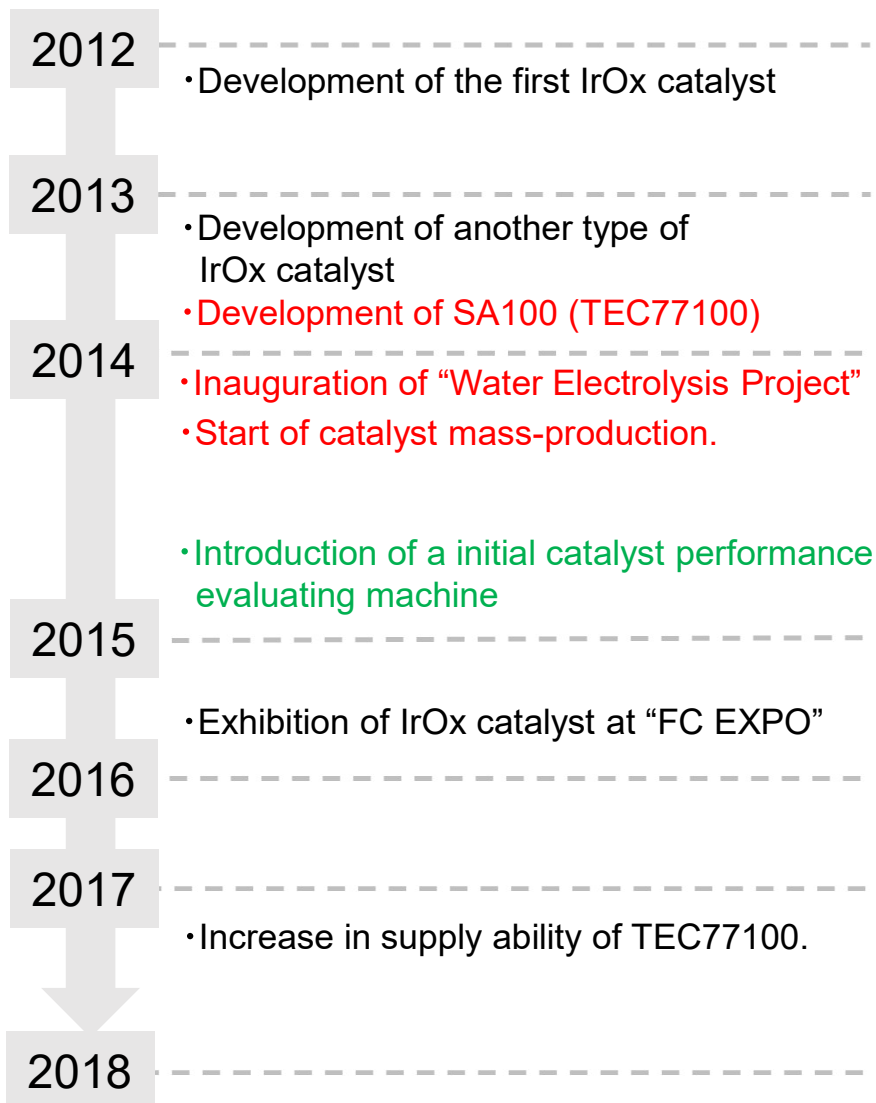
PEMWE

- Raw materials with higher cost
- High ability to respond to power fluctuation (High affinity with renewable energy source)

As a company addressing precious metals, we focus on PEMWE.

Our team's history

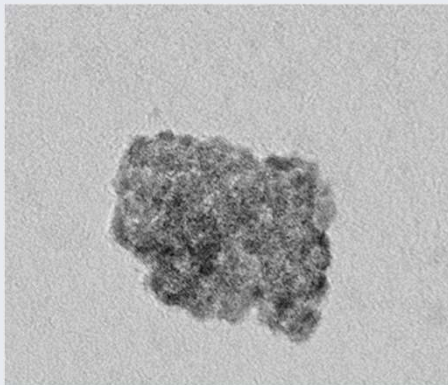
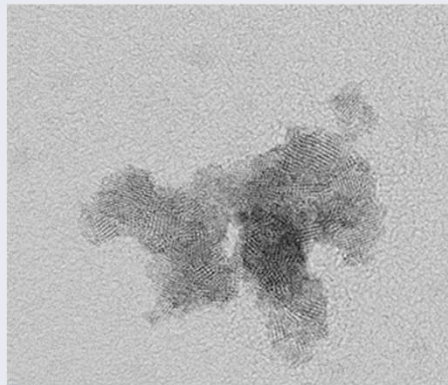
We've worked on PEMWE catalyst since 2012



3. Overview of Our Iridium-Based Catalyst (TEC77100, TEC77110)

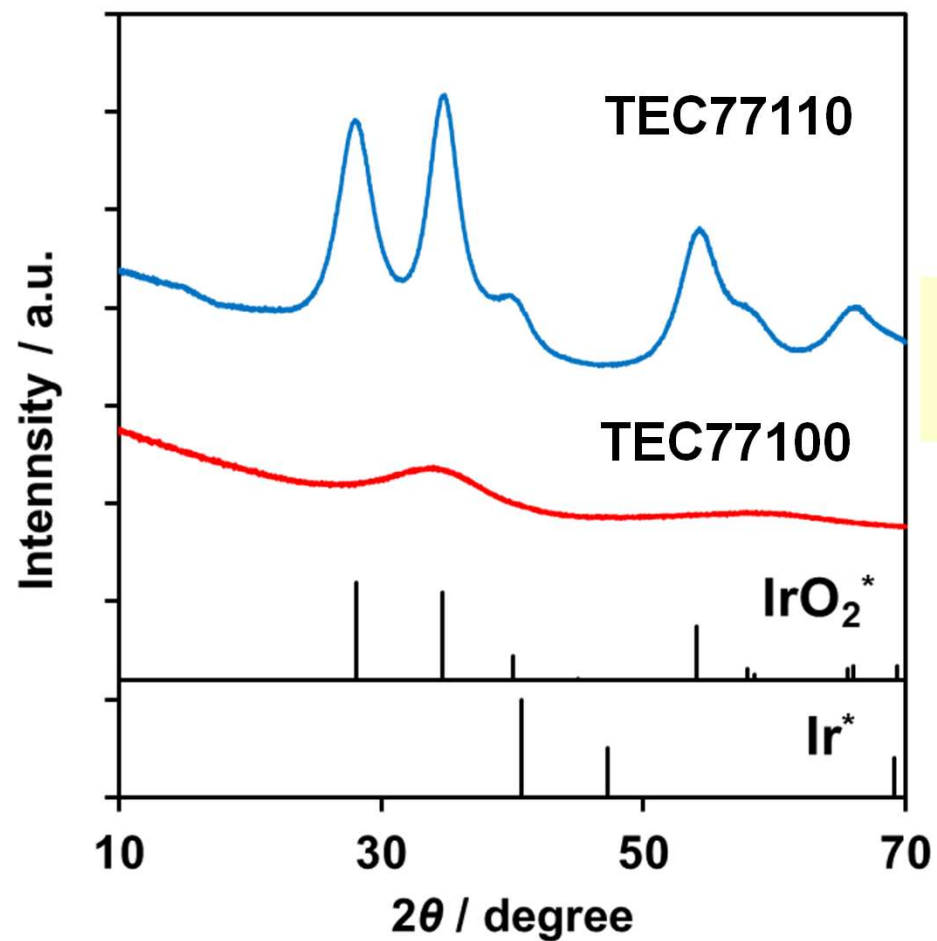
Overview

- Two types of Ir-based catalyst are lined up.

	TEC77100	TEC77110
Formula, Structure	$\text{IrOx} \cdot n\text{H}_2\text{O}$ Amorphous	IrO_2 Rutile type
Metal Loading	Ir 76%	Ir 86%
Surface Area (N_2 BET)	90 ~ 120 m^2/g	40 ~ 70 m^2/g
STEM Image example		

XRD patterns (crystal structure)

XRD patterns



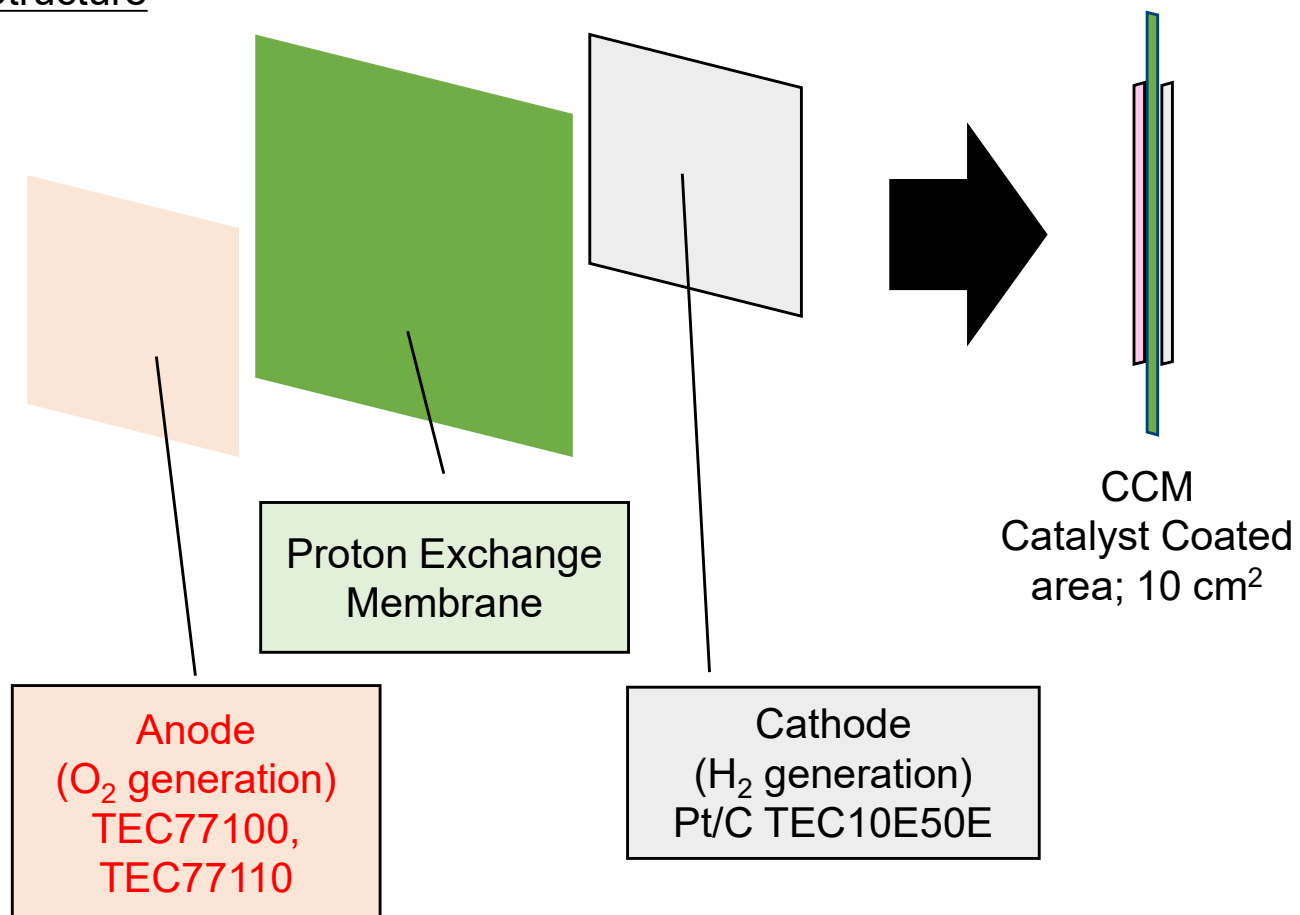
TEC77100 : amorphous type
TEC77110 : crystalline (rutile) type

*standard XRD patterns,
 IrO_2 #00-015-0870, Ir #00-006-0598

Our Standard CCM (Catalyst Coated Membrane) Structure

Catalyst performance is measured using CCM structure.
The catalyst layer is directly coated to membrane.

Structure



Preparation Process

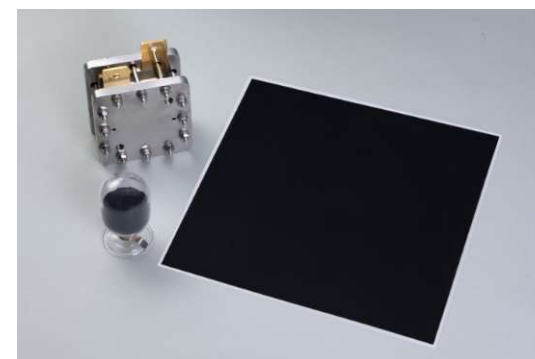
Ink preparation



Catalyst coating



Hot-press treatment



Conditions for Performance Evaluation

Pre-treatment & Initial performance evaluation

Temperature : 50°C

Method : Voltage sweeping

Range : 1.2–2.7 V^{*1}

Sweep speed : 2 mV s⁻¹

Times of sweeping : pre; 10 tms, initial performance ; 5 tms

Amount of water supply (anode)^{*2} : 50–60 mL min⁻¹

Amount of water supply (cathode) : none

^{*1} The maximum current is set to 55 A

^{*2} much more than the necessity

Durability test at constant current density^{*3}

Temperature : 50°C

Current density : 2 A cm⁻²

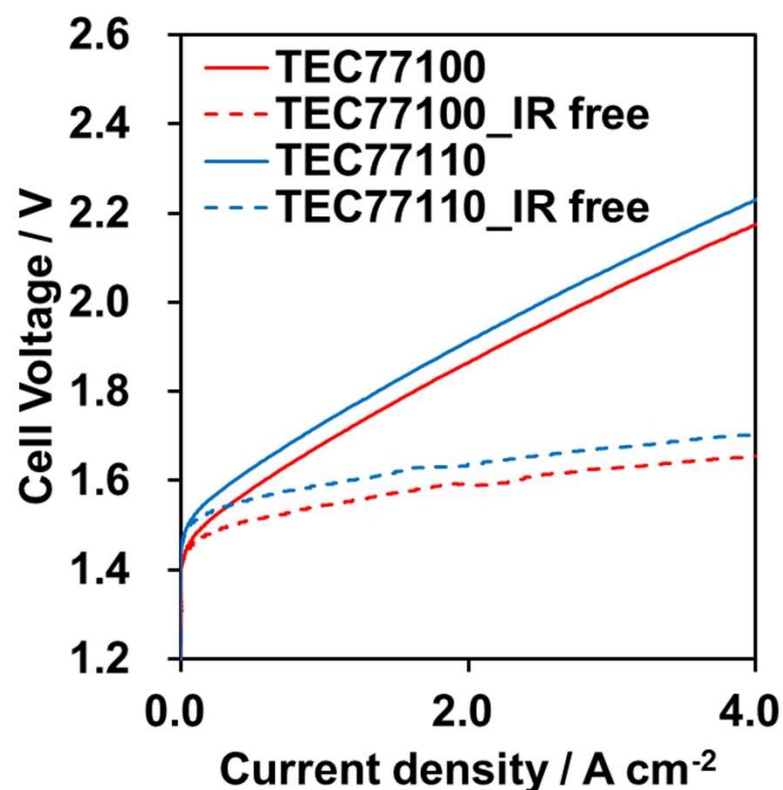
Amount of water supply (anode)^{*2} : 600 mL min⁻¹

Amount of water supply (cathode) : none

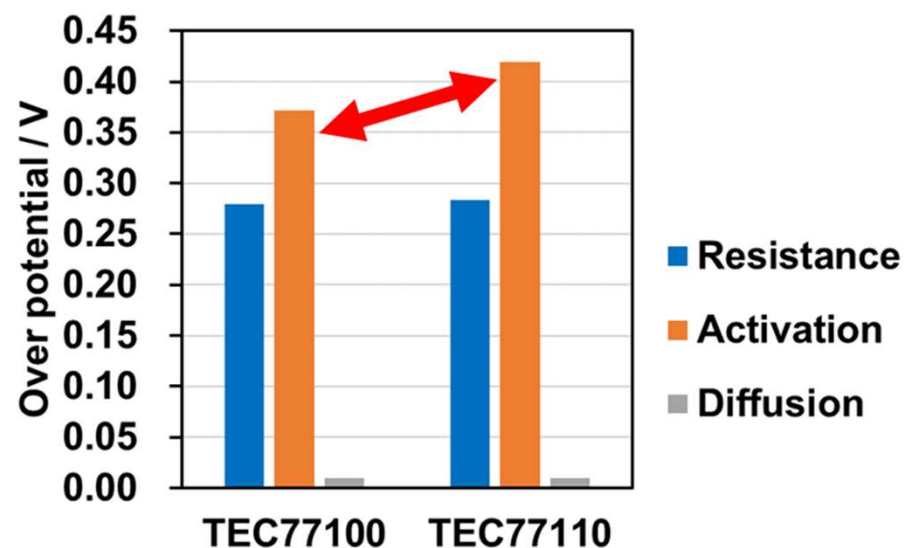
^{*3} IV curves were measured every 100 hrs.

Initial Performance (IV curves)

TEC77100 (amorphous type) has better initial performance than TEC77110 (rutile type). The difference between two catalysts may result from changes in crystal structure or in surface state rather than those in surface area.

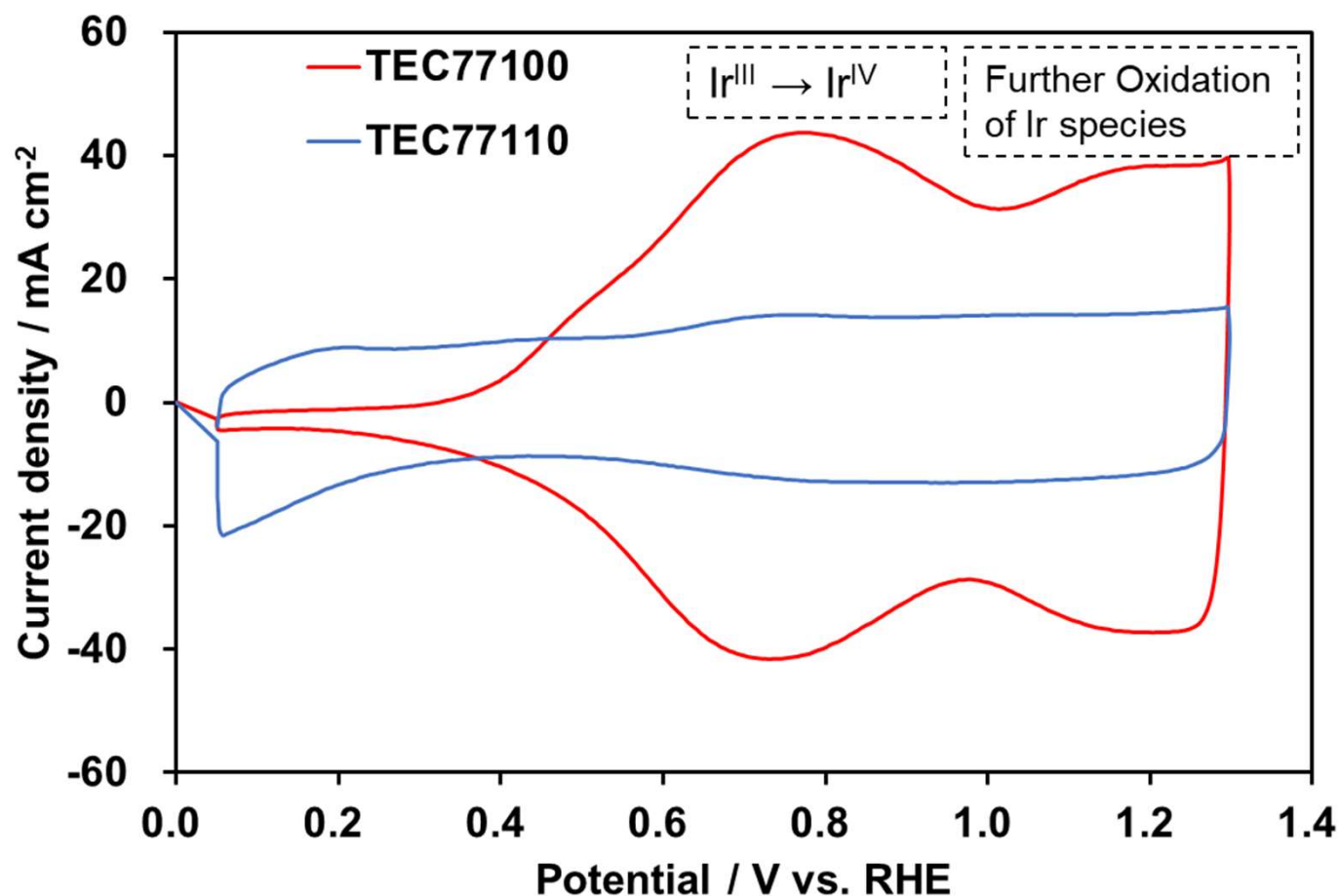


Examples of overvoltage isolation results @2 A cm⁻²



Initial performance (CV curves)

CV curves indicate that difference in the surface state between the two types of catalyst. TEC77100 has large current density derived from redox reaction of Iridium, which can affect the reaction mechanism of water oxidation.

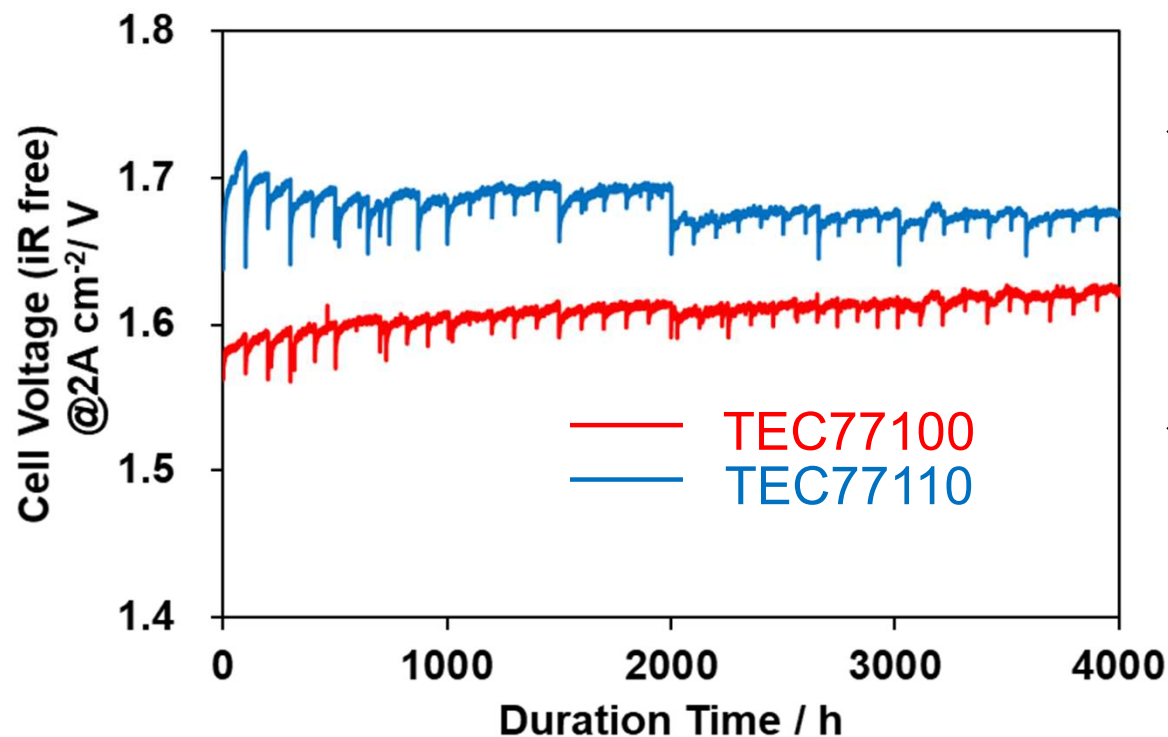


4. Durability of TEC77100 and TEC77110

Durability Tests 1

Cell Voltage Transition

TEC77110 has higher durability than TEC77100.
This can result from the difference in crystal structure.



◆CCM

- Anode; TEC77100, TEC77110
Ir 0.5 mg cm⁻²
- Cathode; TEC10E50E,
Pt 0.3 mg cm⁻²

◆Condition

- Constant Current Density 2A cm⁻²
- Temperature 50°C
- IV Curves Measurement every 100 h

	Degradation Rate / $\mu\text{V h}^{-1}$
TEC77100	7.4
TEC77110	-5.1

Durability Tests 2

CV curves transition

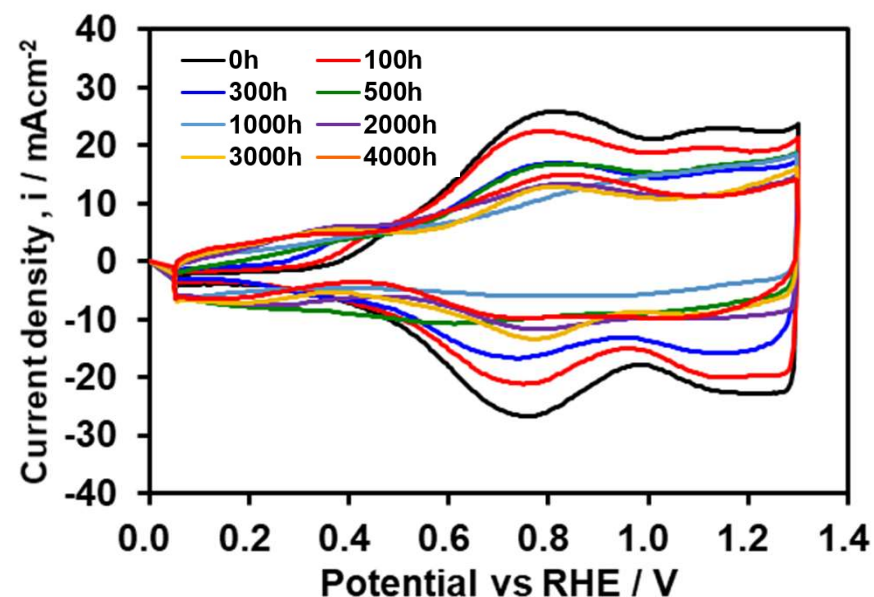
TEC77100 : CV curves drastically changed through durability testing.

TEC77110 : CV curves didn't apparently change.

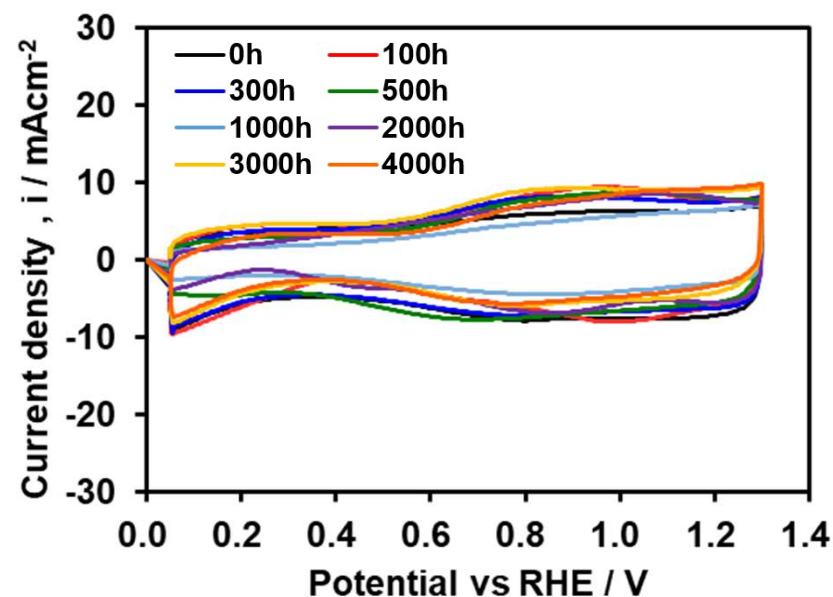
⇒ The surface state of TEC77100 changed through durability testing.

⇒ This is consistent with the cell voltage transition (degradation).

TEC77100



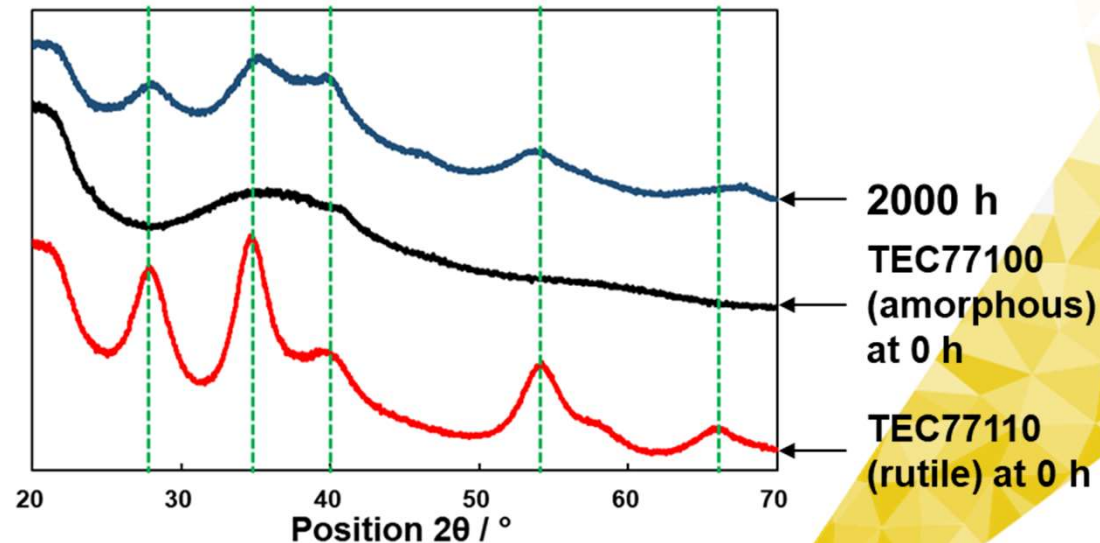
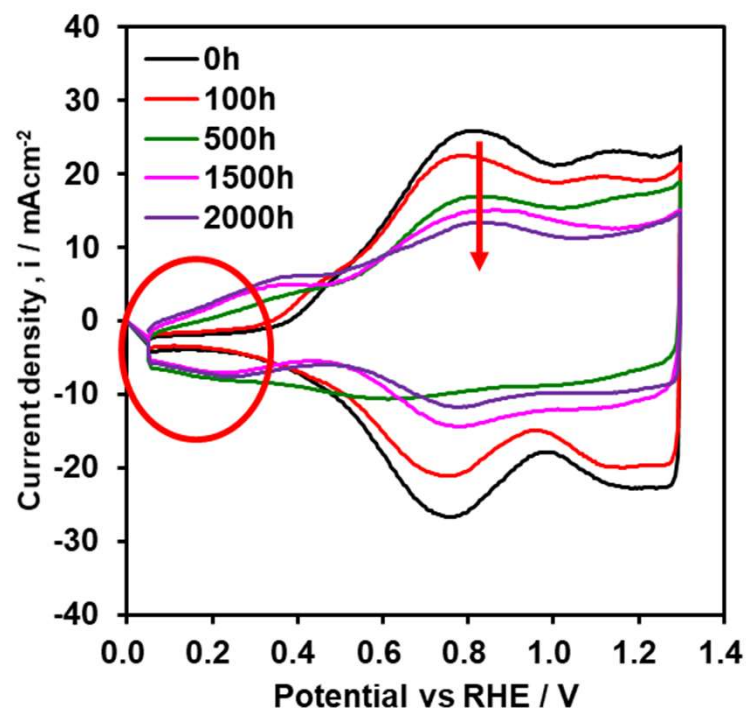
TEC77110



Estimation of Degradation mechanism of TEC77100

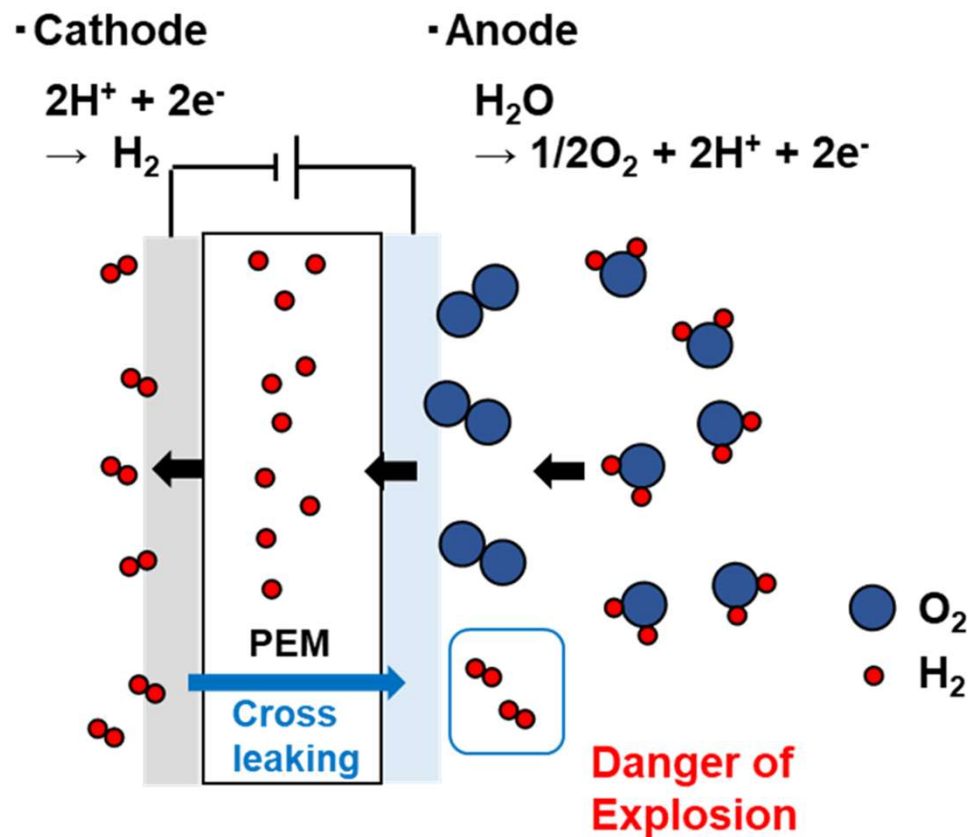
Aside from the change in the surface states, the crystal structure of TEC77100 also changed—the amorphous structure into the rutile structure.

⇒ This change in the crystal structure is consistent with the behavior of TEC77100's performance, which became closer to the performance of rutile-type TEC77110 during durability testing.



4. Durability of TEC77100 and TEC77110

Cross-leaking H₂



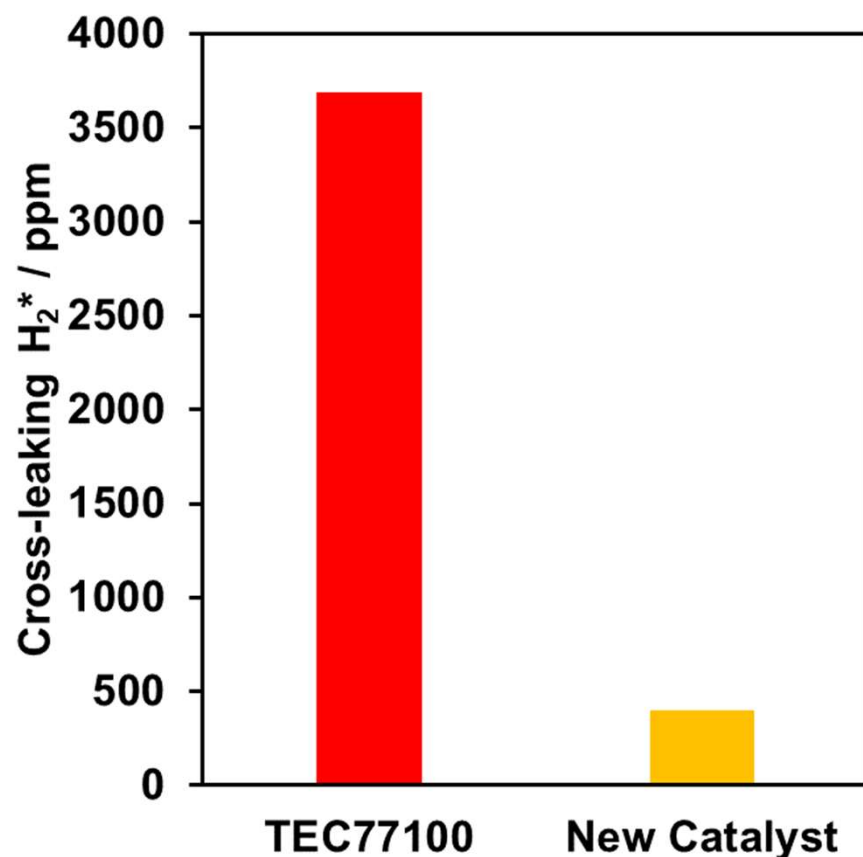
To acquire better PEMWE performance,
The thickness of membrane can get
thinner in the future

⇒ The amount of cross-leaking
hydrogen may get more and more.

⇒ **Danger of explosion**

Performance of new catalyst

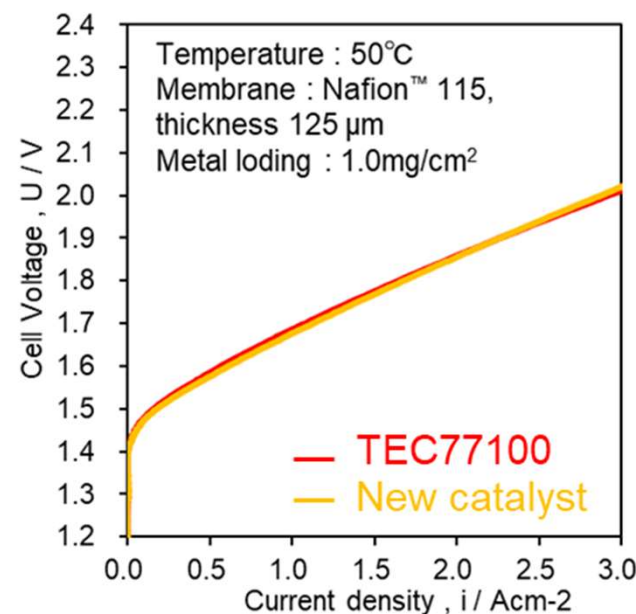
We developed the new catalyst, which could reduce the amount of cross-leaking hydrogen without adverse effects to the initial performance of the anode catalyst.



*measuring the concentration of H₂ in O₂ in the anode side
Average amount of our results.

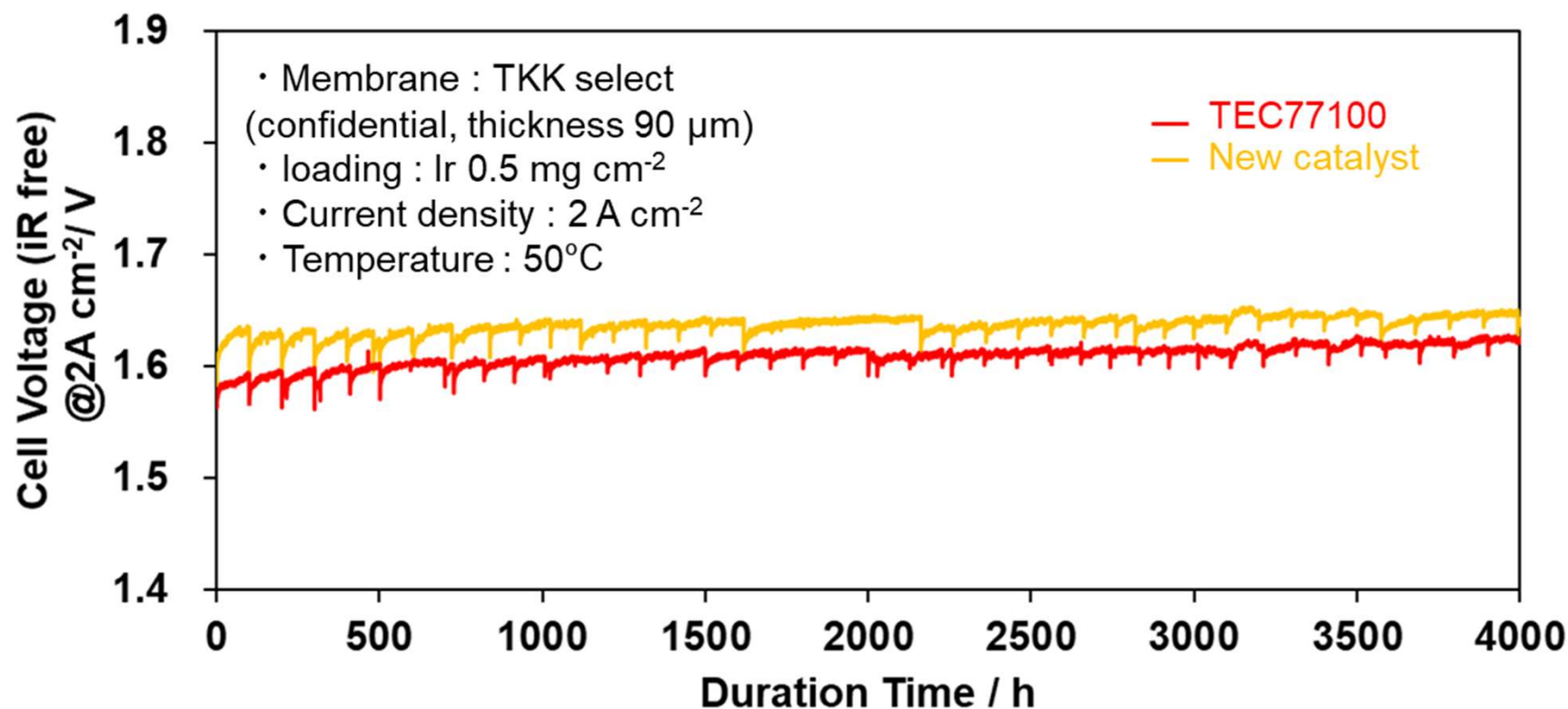
- Membrane : Nafion™ N212(thickness 50 μm)
- loading : Ir 0.5 mg cm⁻²
- Current density : 2 A cm⁻²
- Pressure : Atmospheric pressure
- Temperature : 50°C

<Ref.> Initial performance



Durability of new catalyst

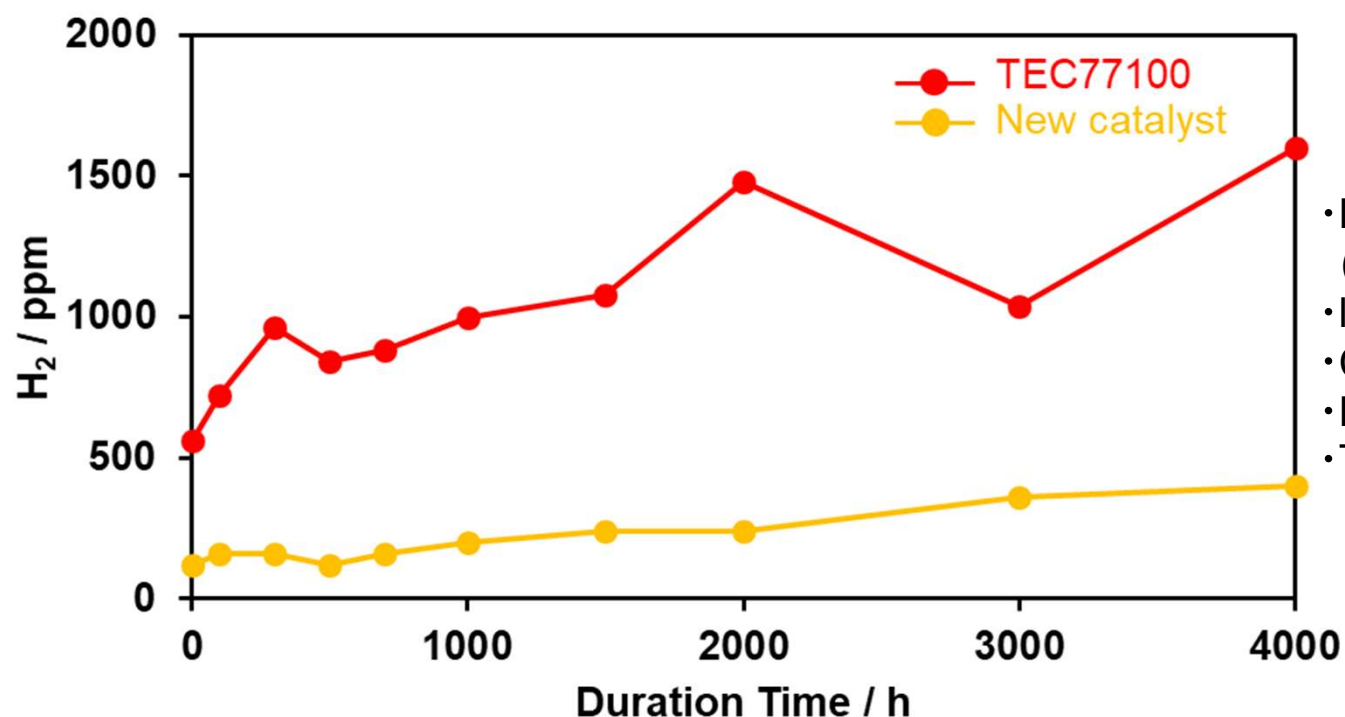
There are also no apparent adverse effects to the durability of catalyst.



	Degradation Rate / $\mu\text{V h}^{-1}$
TEC77100	7.4
New Catalyst	5.1

Durability of new catalyst

Even after long-term durability testing (–4000 h), the inhibitory effect to cross-leaking hydrogen highly maintained.



- Membrane : TTK select (confidential, thickness 90 μm)
- loading : Ir 0.5 mg cm^{-2}
- Current Density : 2 A cm^{-2}
- Pressure : Atmospheric pressure
- Temperature : 50°C

Summary

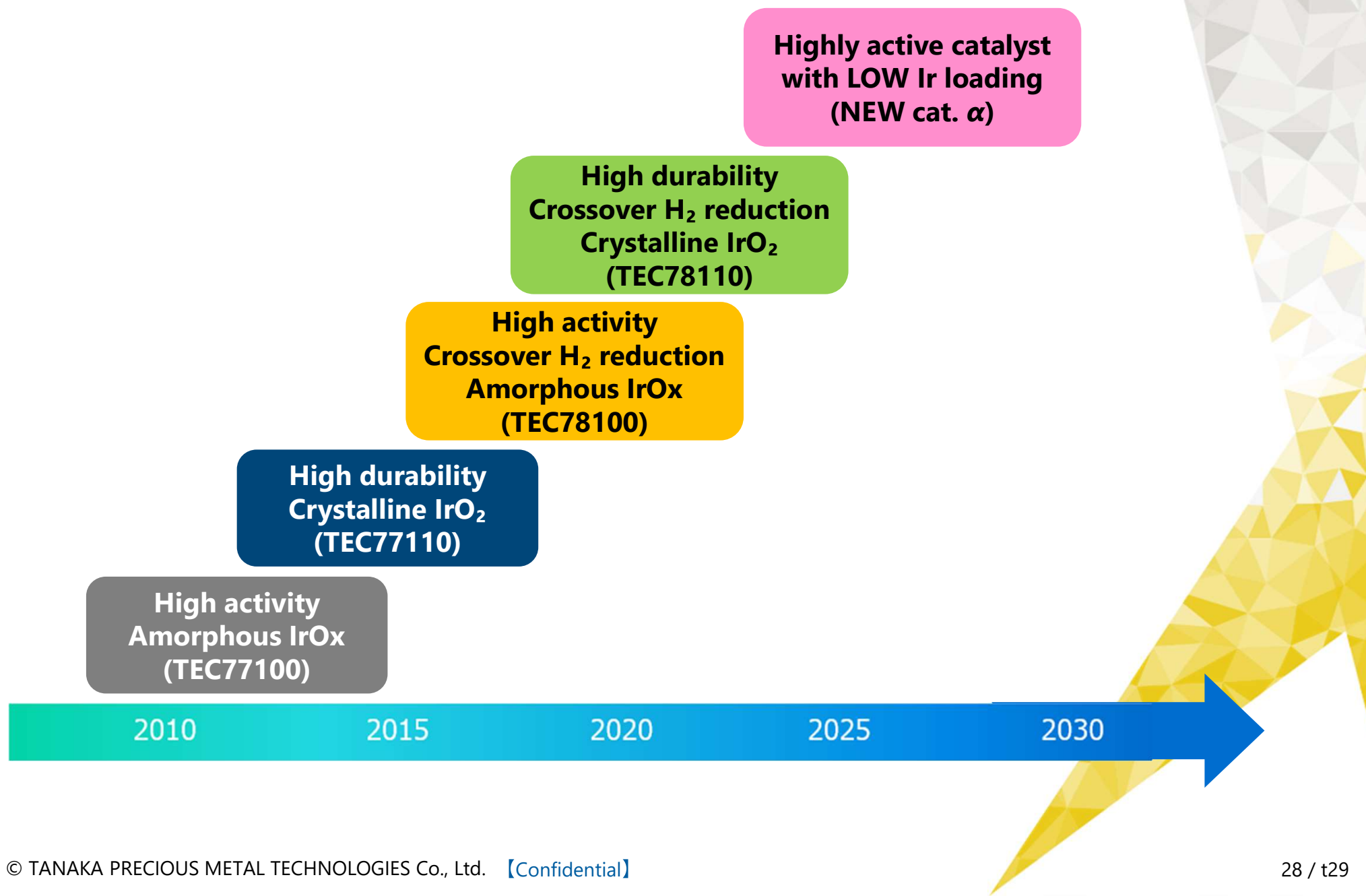
Summary

- We have developed the Ir-based catalyst (TEC77100, TEC77110).
- The differences between TEC77100 and TEC77110 in the initial performance and durability may result from changes in surface states or crystal structures.
- The degradation of amorphous type IrO_x can be mainly caused by the crystallization of IrO_x to rutile IrO_2 .
- To reduce the cross-leaking hydrogen, we have developed the new catalyst and confirmed its high initial activity and durability.

Future Prospects

- Development of catalysts with higher performance, durability.
- Investigation of possibility of “low-Ir catalyst” and “Ir-free catalyst”

Roadmap for the development of water electrocatalysts



With Precious Metals

Since our founding in 1885, we have continued to think on how to build a sustainable future, while Utilizing the limited resource that is precious metals.

As professionals in precious metals, we will continue to pursue the possibilities of precious metals.