

燃料電池等利用の飛躍的拡大に向けた共通課題解決型 産学官連携研究開発事業

／研究開発項目Ⅱ 水素利用等高度化先端技術開発 ／プロトン交換膜型水電解装置用革新的低貴金属担持アノード触媒 の研究開発

委託：国立大学法人山梨大学
日本化学産業株式会社
石福金属興業株式会社

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水素・燃料電池ナノ材料研究センター
クリーンエネルギー研究センター

【研究開発の概要】

大規模かつ高効率に高純度水素を製造できるプロトン交換膜型水電解(PEM WE)システムでは、資源量の少ない酸化イリジウムがアノード(酸素発生極)に多く利用されています。本研究開発ではそのイリジウムの使用量の削減と電極性能の向上を目標に、新規な材料設計コンセプト“4 structure with synergy effect”のもとで、①イリジウム触媒の高活性化と使用量削減 ②新規イリジウム触媒の量合成を展開します。産業界等の要望も反映させつつ、PEM WE用革新的低貴金属担持酸素発生極触媒を開発します。

【研究開発の目標】

○中間目標 (2023年度末)

触媒・担体粒子の独自設計コンセプトにて新規触媒を合成し、 0.7 S cm^{-1} 以上の電気伝導度を達成しつつ、酸素発生活性が 17 A g^{-1} (@1.6 V) 以上を達成することを酸性電解液中で検証する。単セルにて 1.2 A cm^{-2} (1.6 V) を見通す。その単セルの目標値を 0.37 mg cm^{-2} (目付量)で見通す。触媒の劣化に関する主要因子の検討とメカニズムを検討し、劣化率(0.17%/1000 h)も見通す。これら新規触媒を7g/dayスケールにて合成する量産工程を検討する。

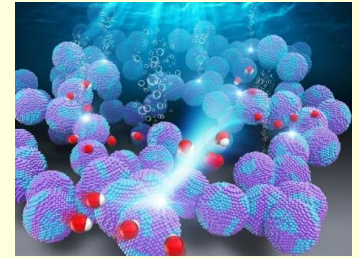
○最終目標 (2024年度末)

1.0 S cm^{-1} 以上の電気伝導度を達成しつつ、酸素発生活性が 25 A g^{-1} (@1.6 V) に到達することを酸性電解液中で検証する。単セルにて 1.7 A cm^{-2} (1.6 V)を見通す。その単セルの目標値を 0.25 mg cm^{-2} (目付量)で見通す。触媒の劣化に関する主要因子の検討とメカニズムの検討を継続し、劣化率(0.12%/1000 h)を見通す。これら新規触媒を10g/dayスケールにて合成する量産工程を検討する。

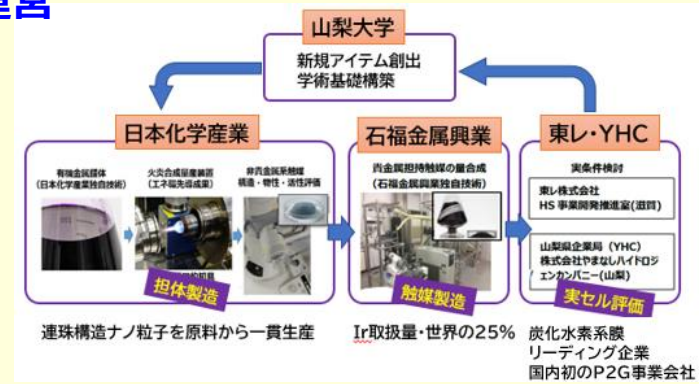
研究内容

ナノロッド/セラミック触媒

触媒/酸化物界面・電子状態制御
難溶性 & 高活性触媒粒子を設計
金属伝導 & 高物質輸送を実現



PJ運営



山梨大学・日本化学産業・石福金属興業 (委託)

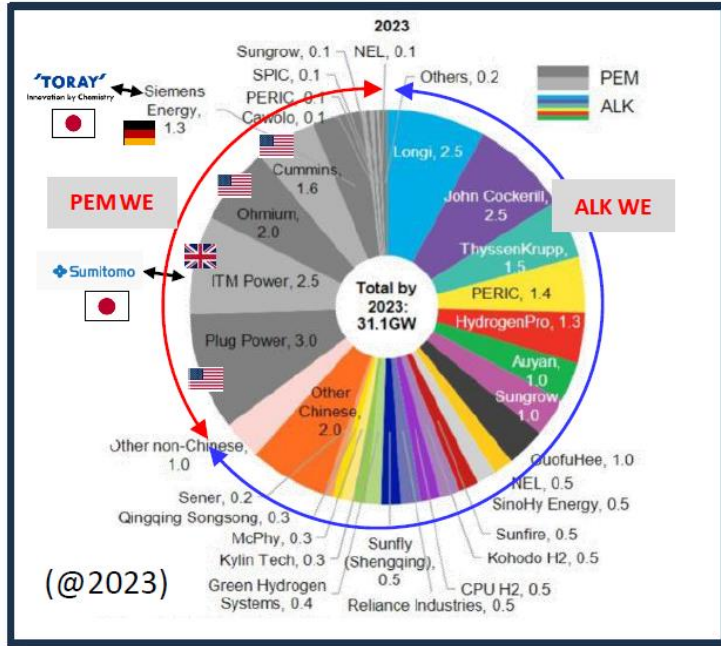
→触媒設計・評価・量合成

東レ・山梨企業局 (共同実施)

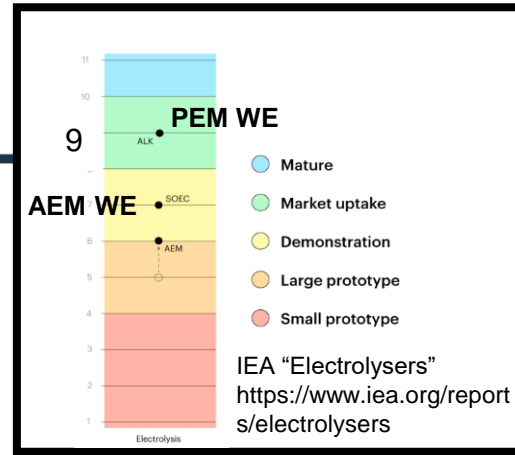
→実条件下での評価や産業界等の意見をフィードバック

Electrolyzer: present status and target (US\$ Billion)

Annual electrolyzer manufacturing capacity



TRL: Technology Readiness Level



1.12
2021

1.15
2022

2023

2024

2025

2026

2027

2028

2029

2030

2031

2032

Alkaline Electrolyzer PEM Solid Oxide Electrolyzer Others

Electrolyzer Market Size & Share | Growth Analysis, 2023-2032 (gminsights.com)

Source: www.gminsights.com

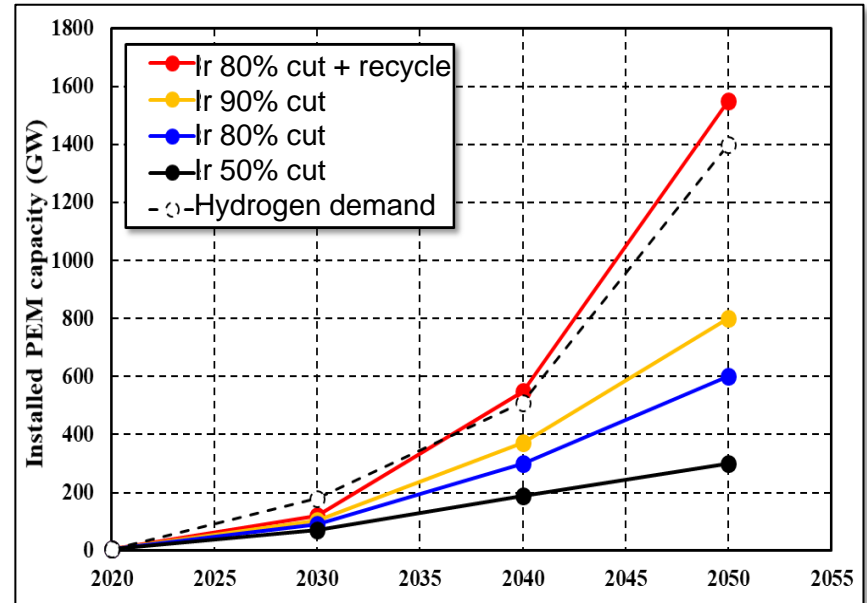
Ir loading amount should be reduced further toward the wide-spread use of PEM WE.

Ir supply and demand

Ir supply

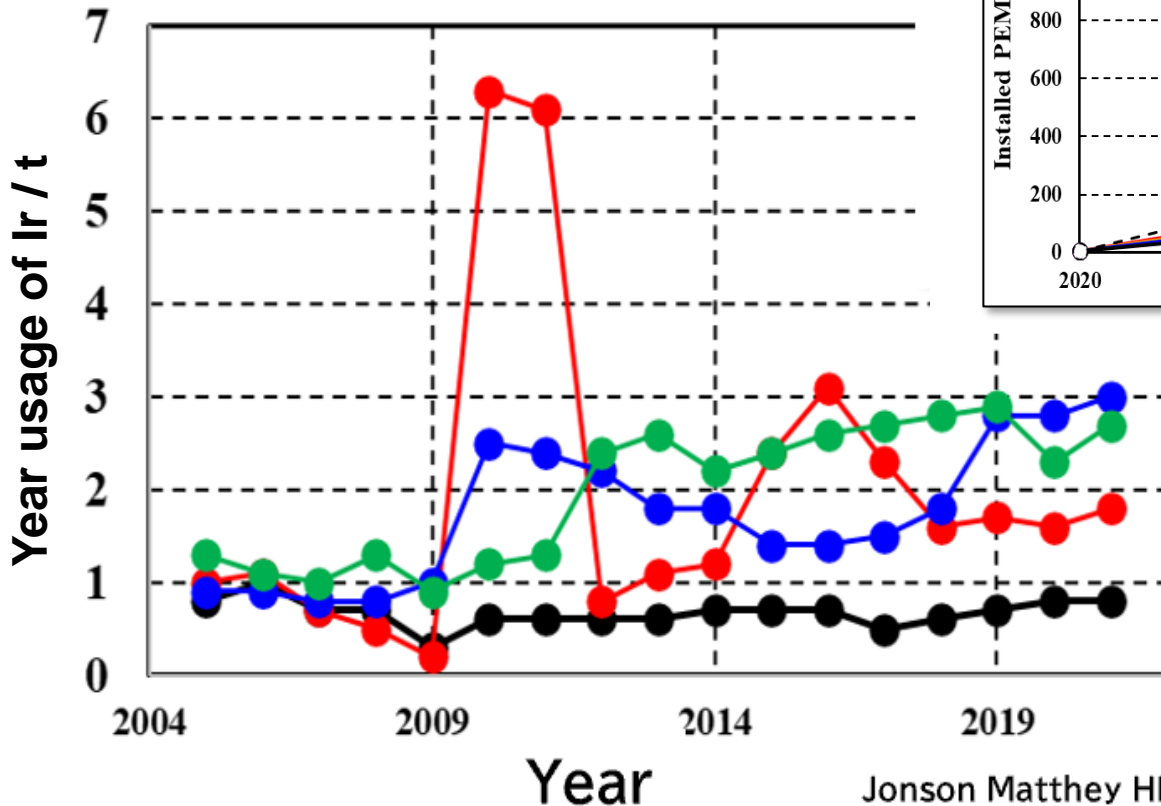
- ✓ Bi-product of platinum
- ✓ Generation ca. 8 t / year

Target of Ir loading amount



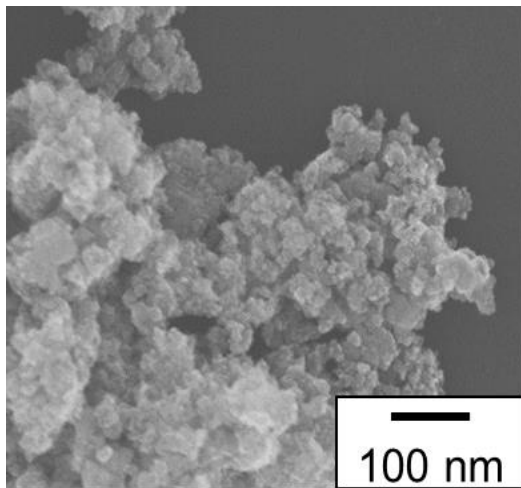
IEA "Electrolysers"
<https://www.iea.org/reports/electrolysers>

Electrochemical product
 Others
 Electricity
 Chemical product



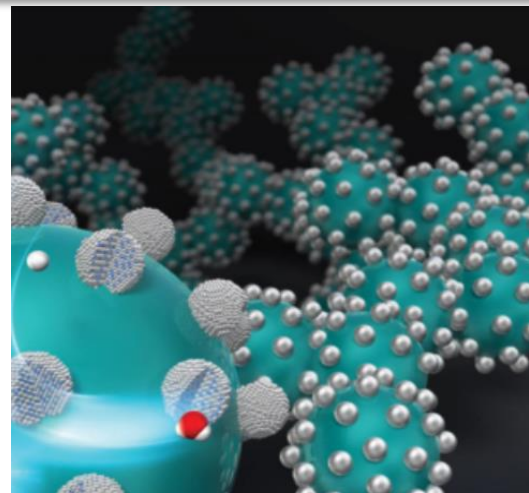
Jonson Matthey HP

Sub-micron sized IrO_x catalyst



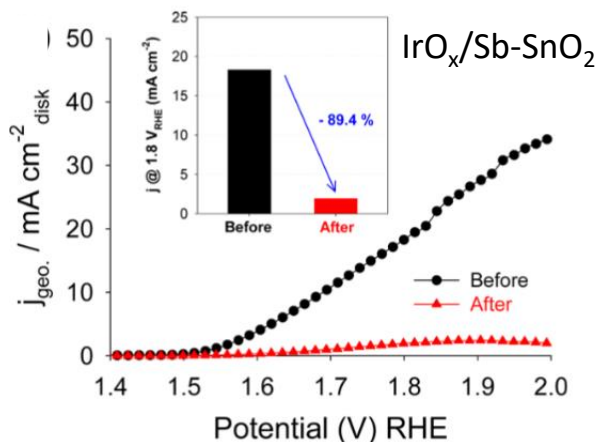
Commercial IrO_x
IrSrO_x, IrRuO_x

Nano-sized IrO_x catalyst

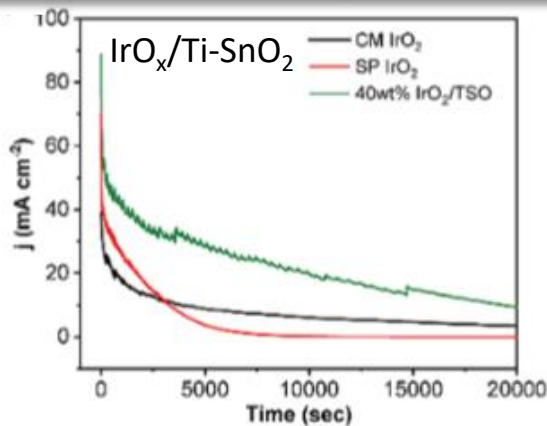


IrO_x system nanoparticles supported on unique conducting support

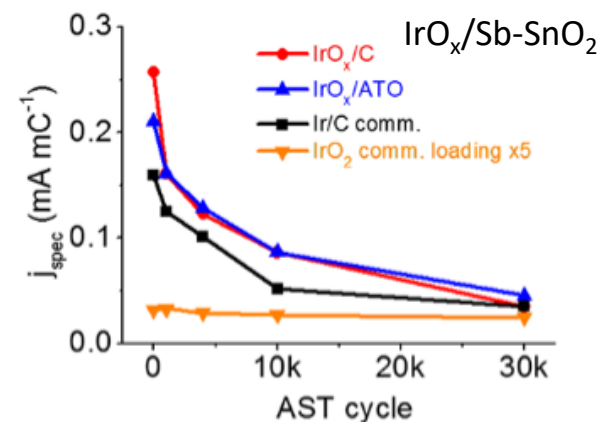
Nano-sized IrO_x dissolution



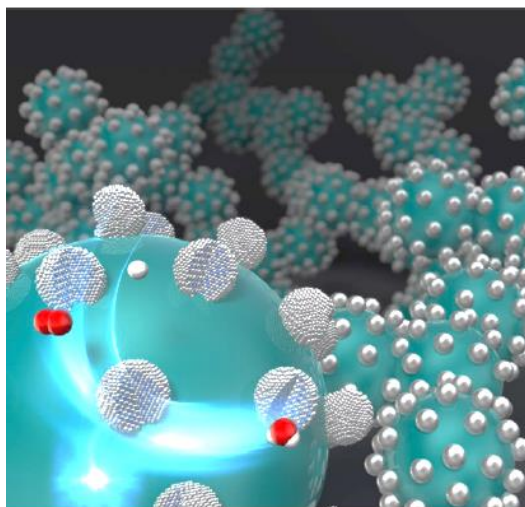
1.5-2.0 V 300 cycles in H₂SO₄ (pH 1).
J. Am. Chem. Soc. 138 (2016) 12552



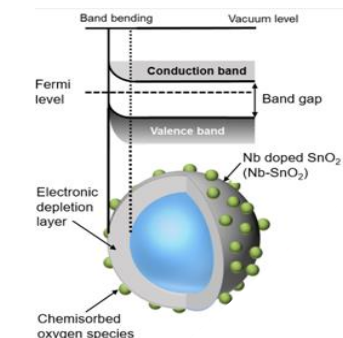
1.6 V in 0.5M-H₂SO₄
ACS Sustainable Chem. Eng. 11 (2023) 1121



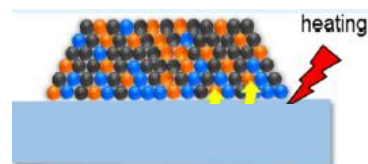
1.2-1.6 V cycles in 0.05M-H₂SO₄
ACS Catal. 9 (2019) 4688.



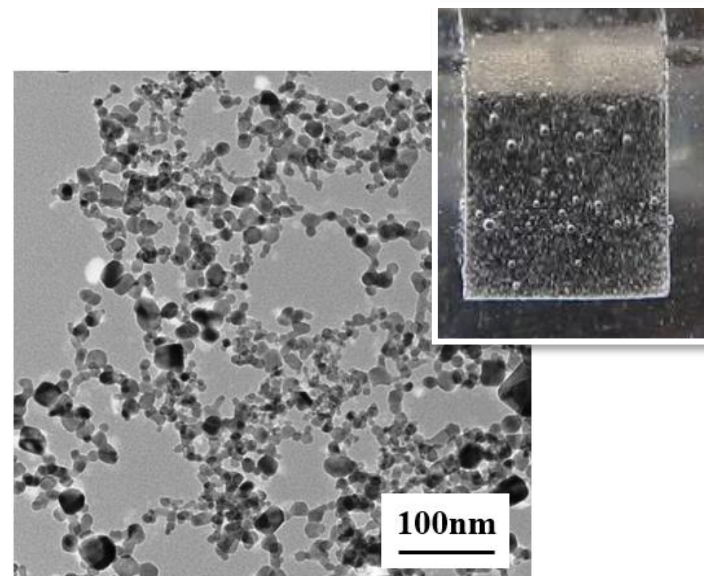
Ideal structure



Electronic structure



orientation

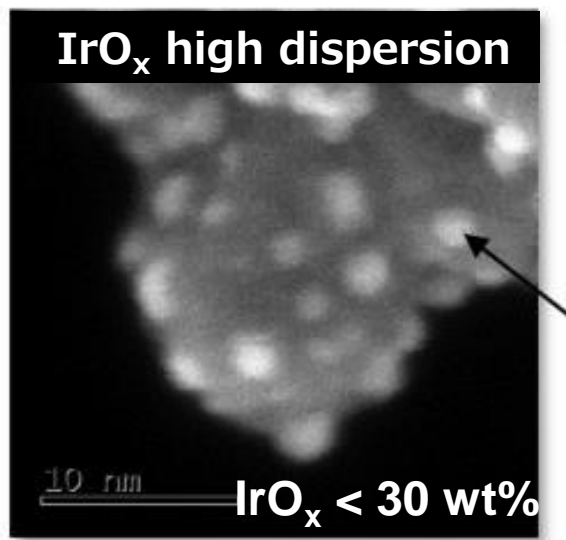
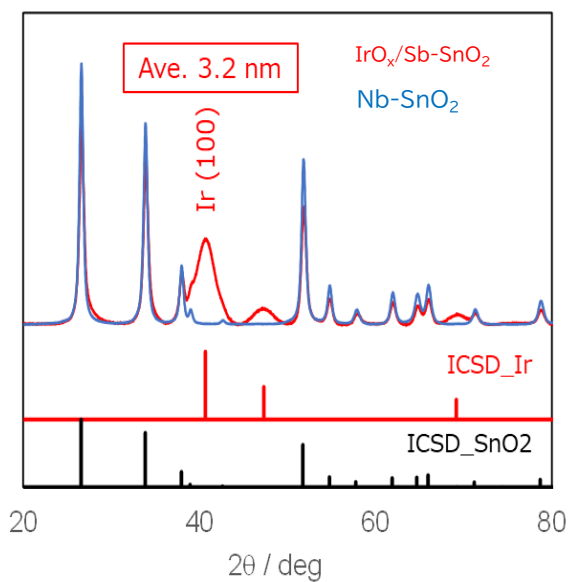
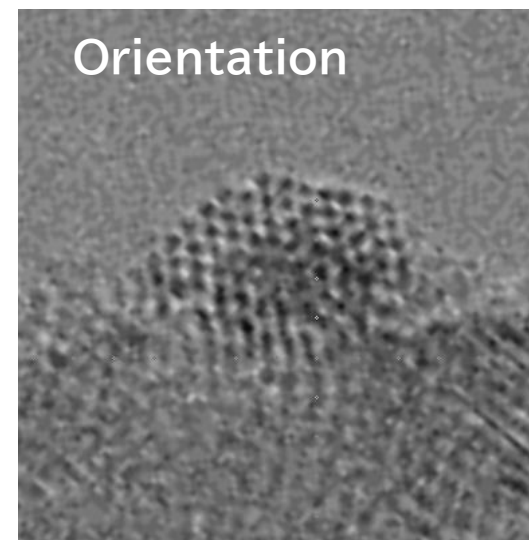
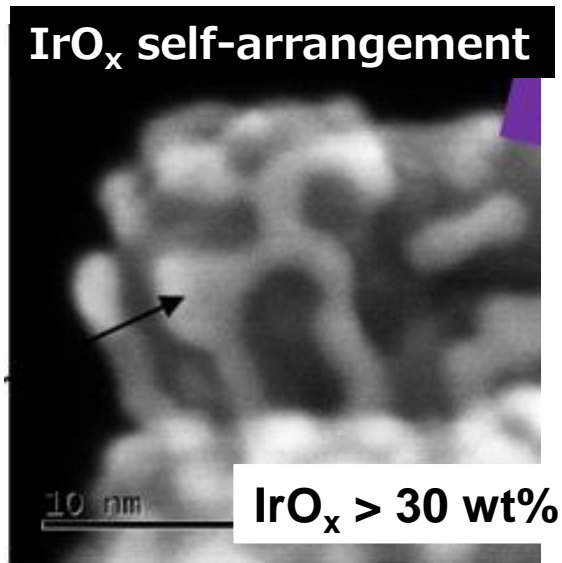
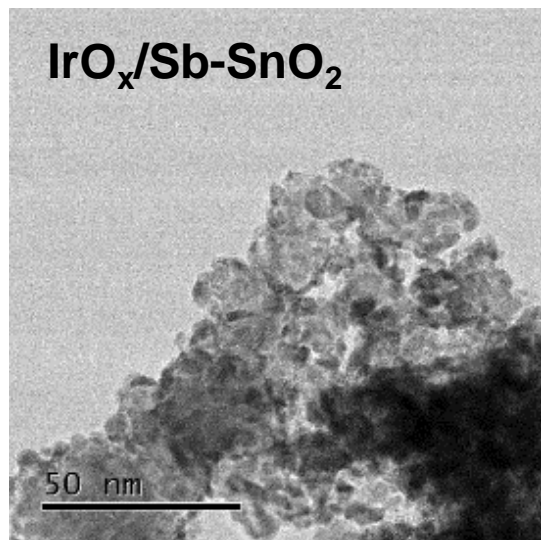


New support with **fused-aggregated network structure**

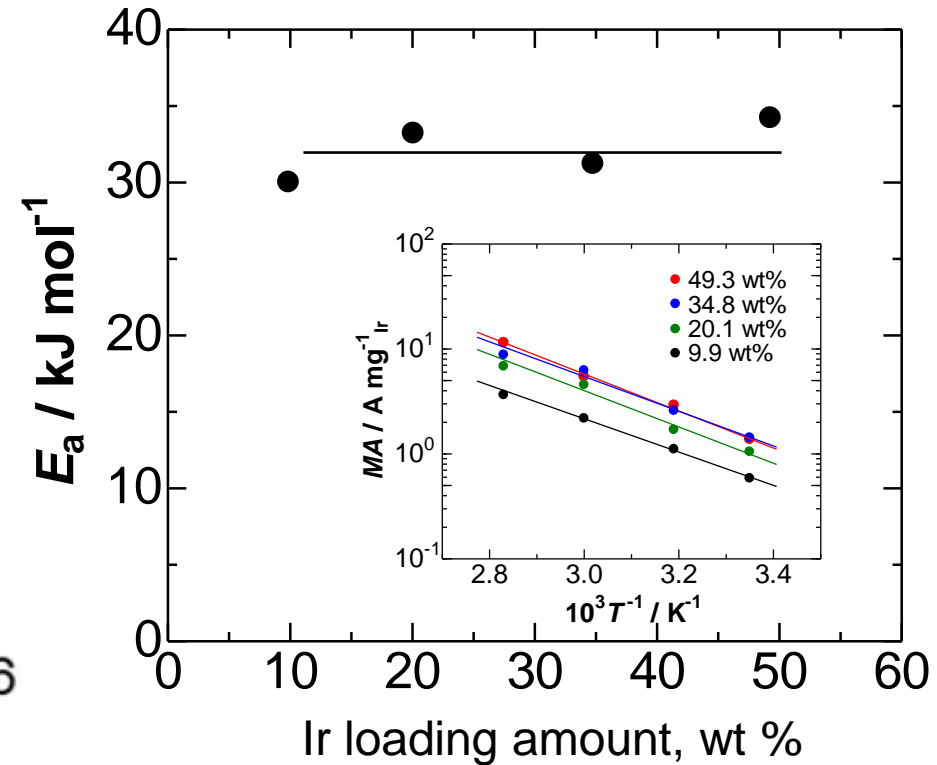
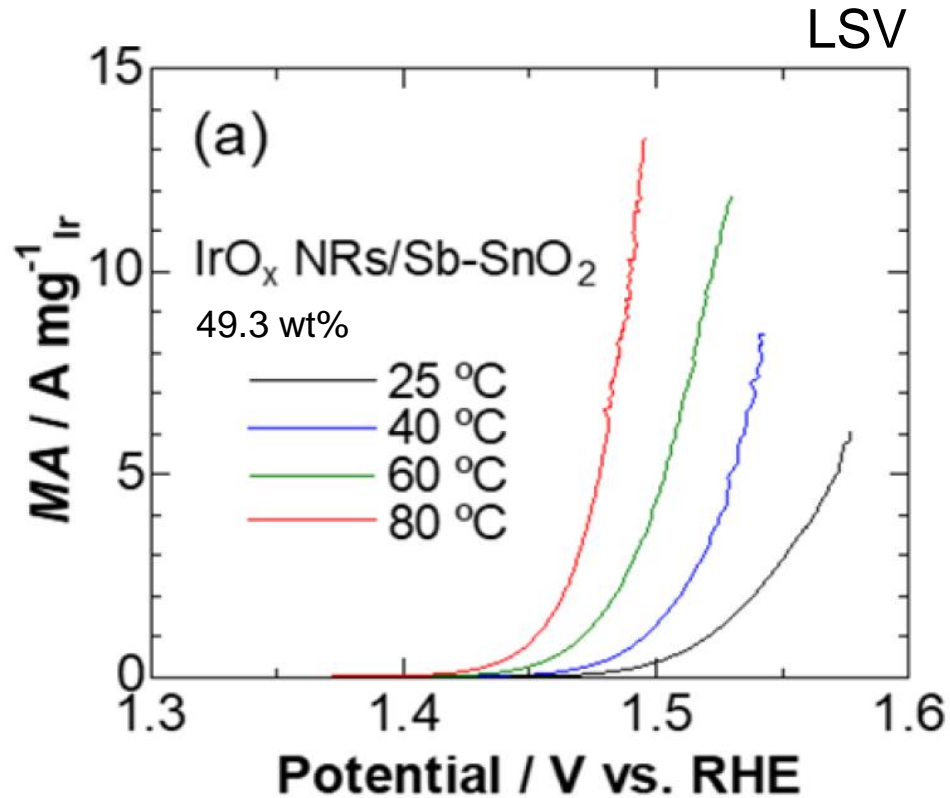
Point

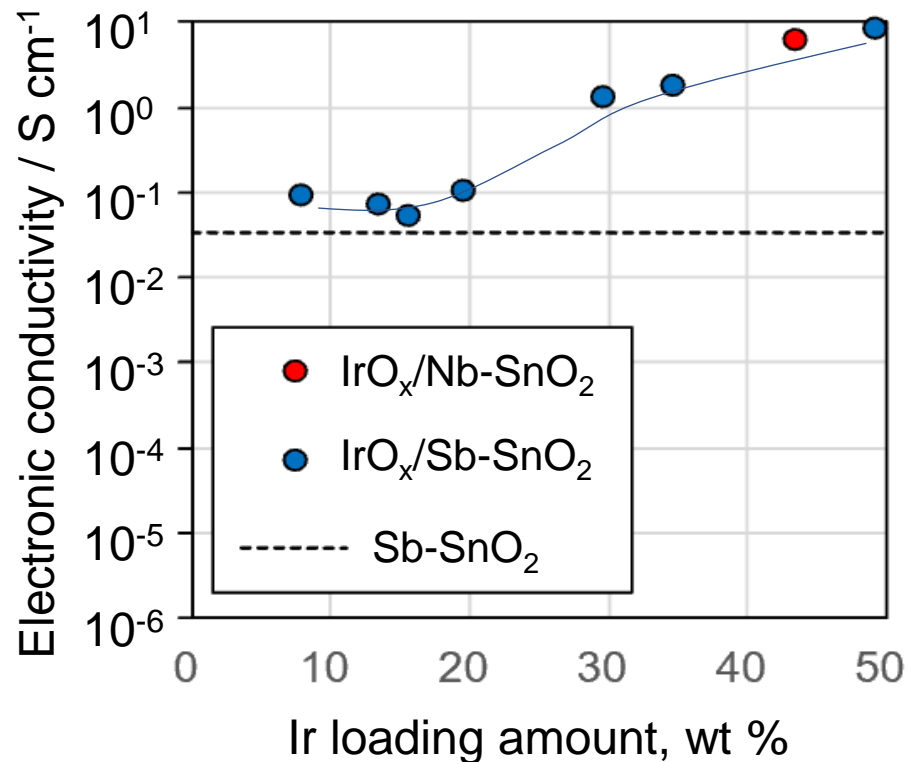
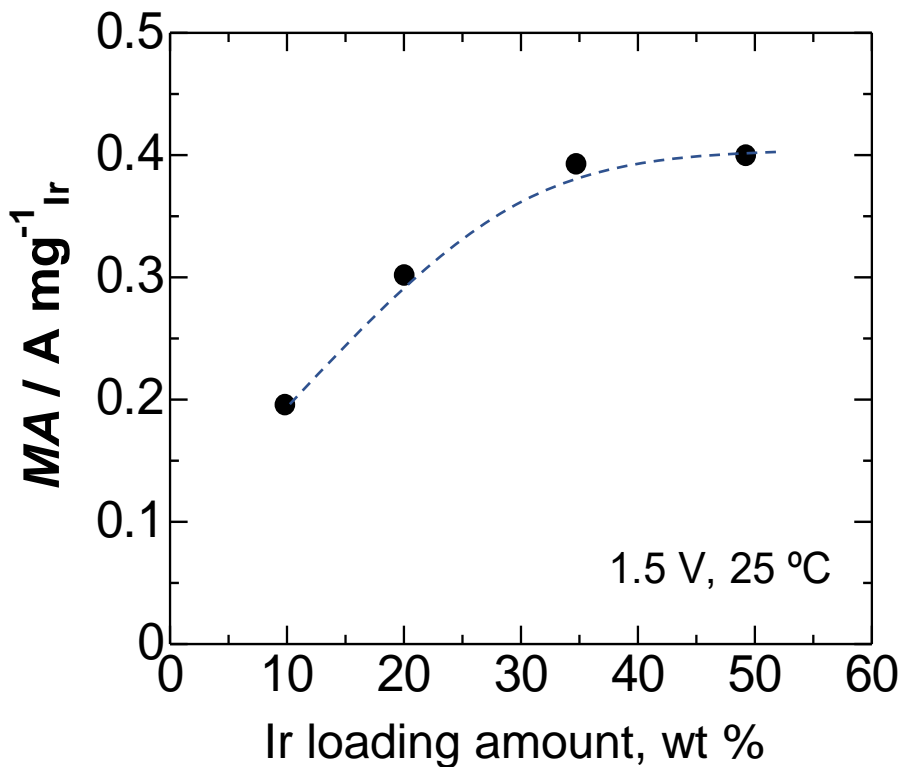
- Structure design and synergy effect -

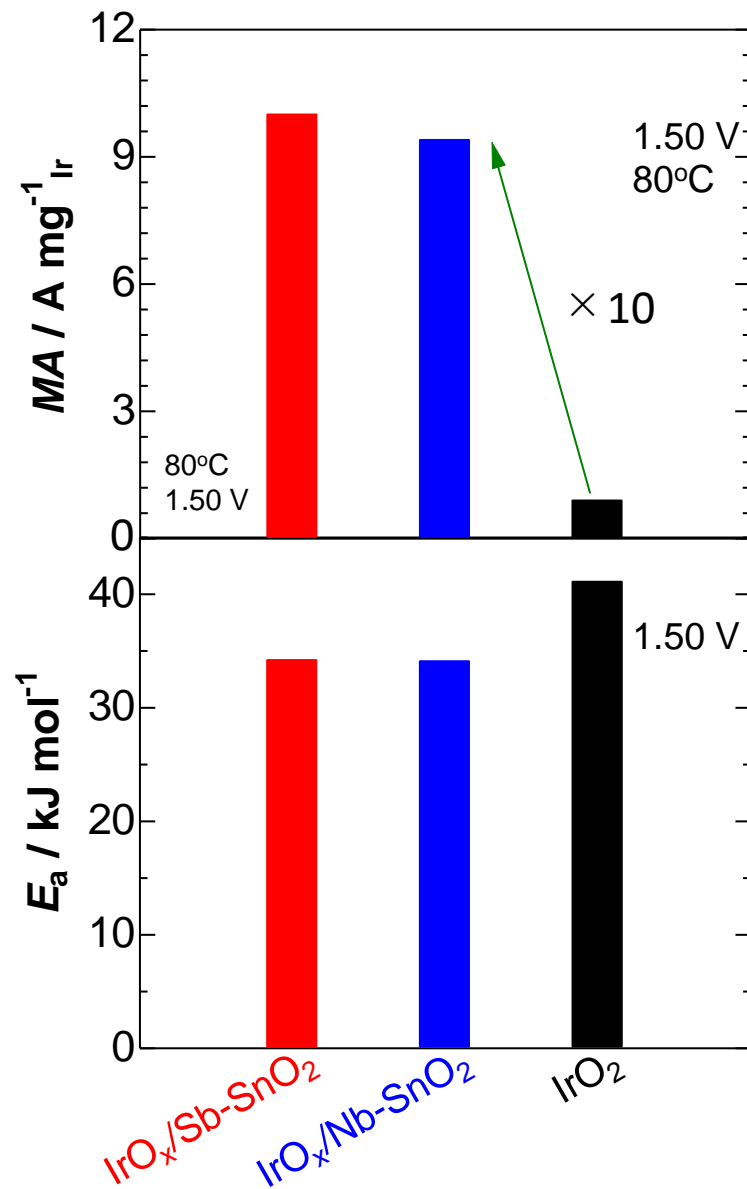
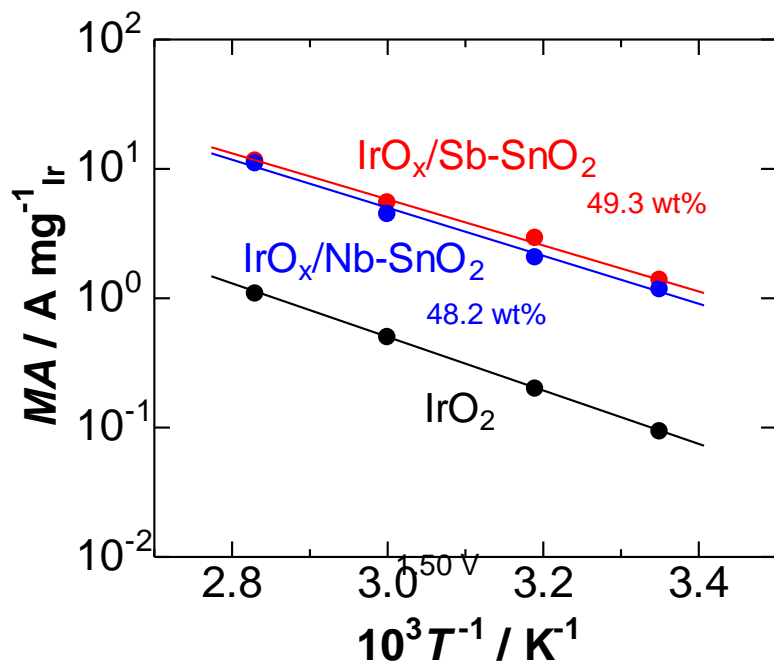
- | | | |
|-------------------------|------------------------------------|-------------------------------|
| A) Crystal structure | (high crystallized support) | Chemical stability |
| B) Interface structure | (orientation) | Catalytic activity/durability |
| C) Microstructure | (fused-aggregate network) | Gas transport |
| D) Electronic structure | (interaction around the interface) | Electronical conductivity |

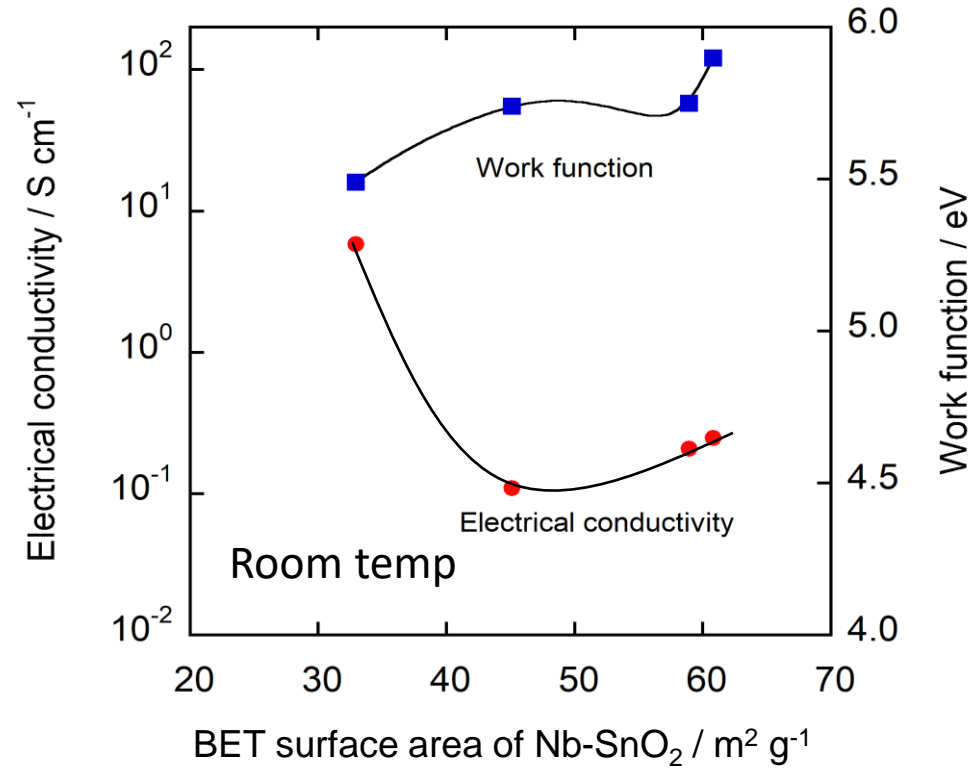
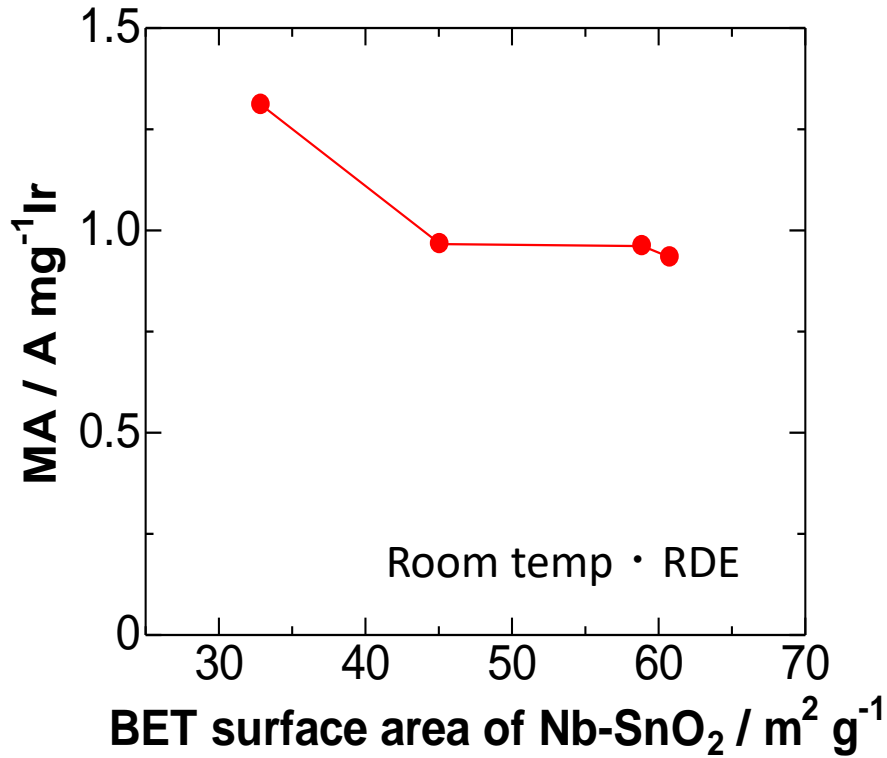


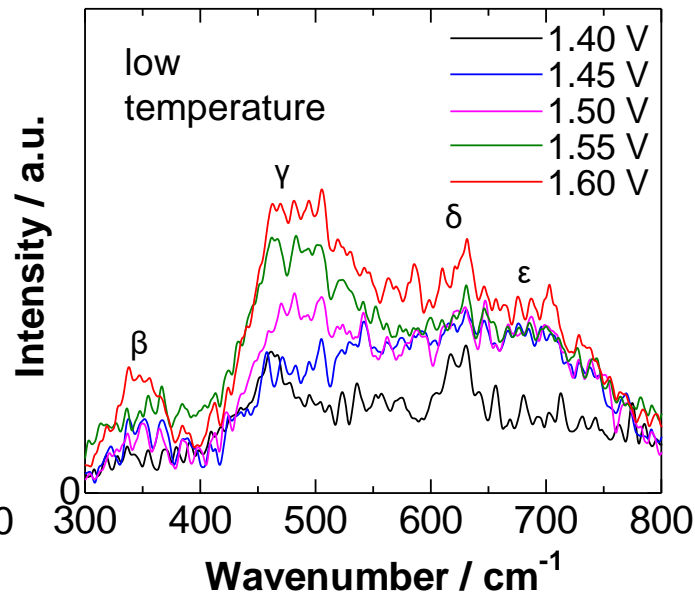
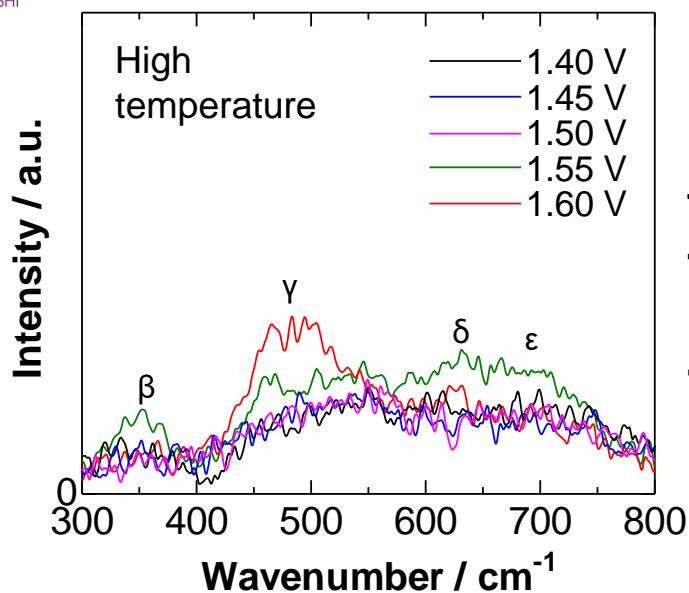
IrO_x, SnO₂
Crystal structure: Rutile type



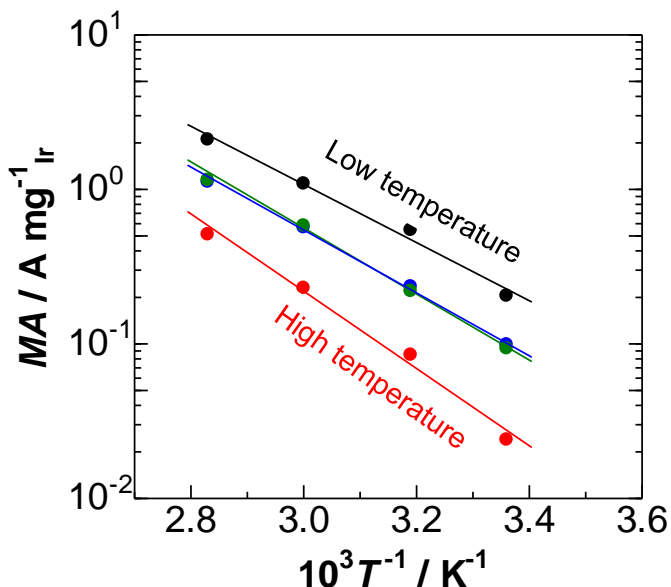
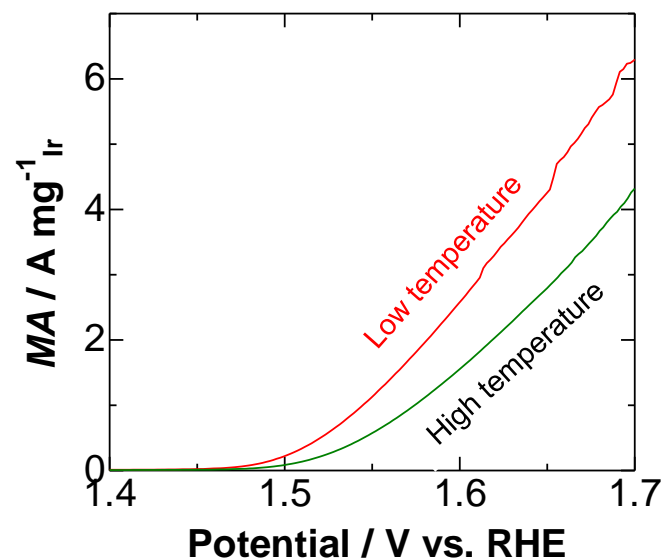


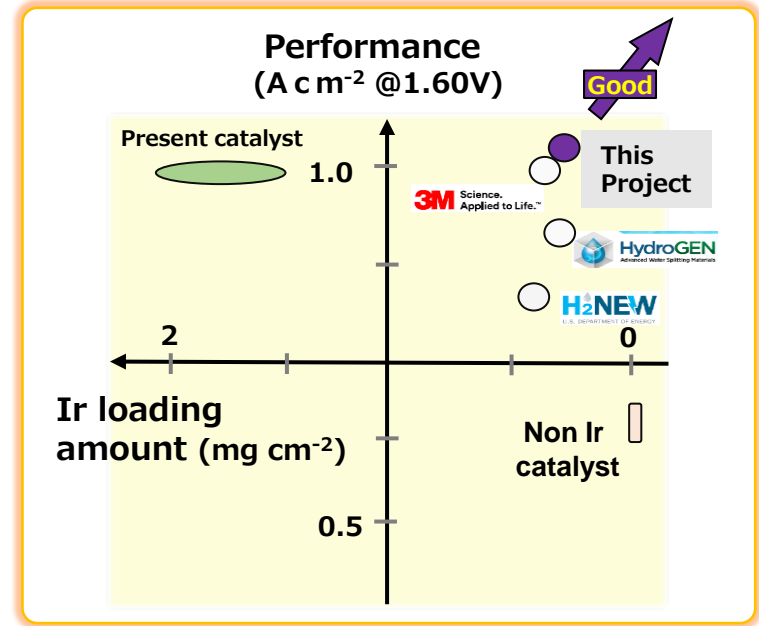
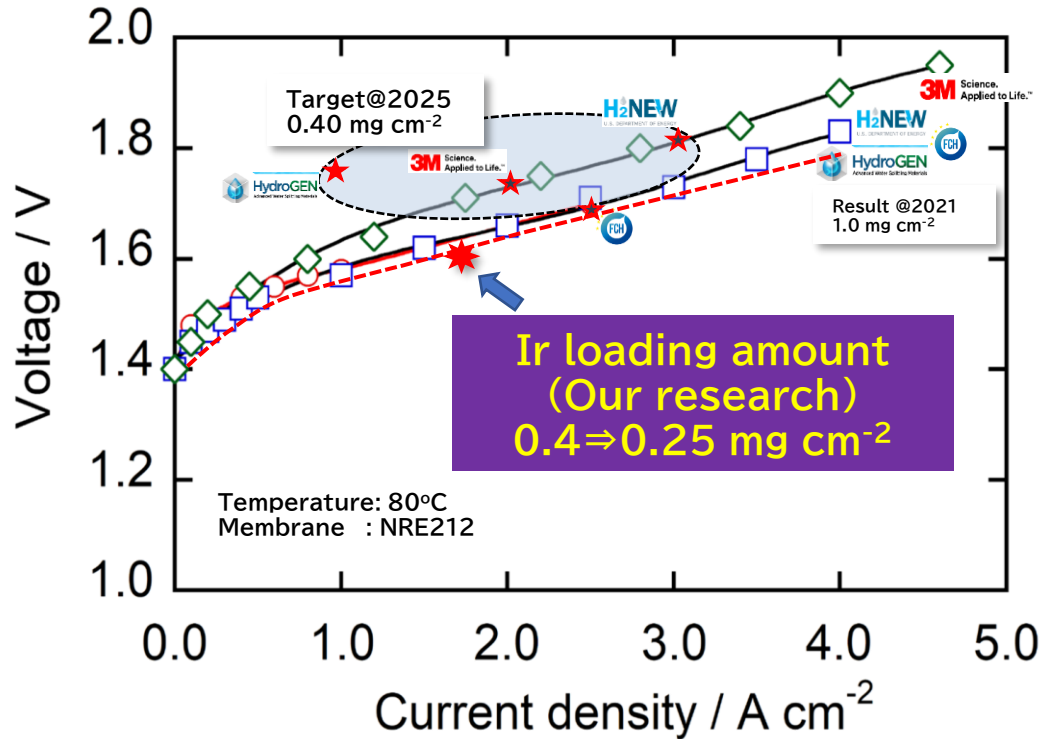






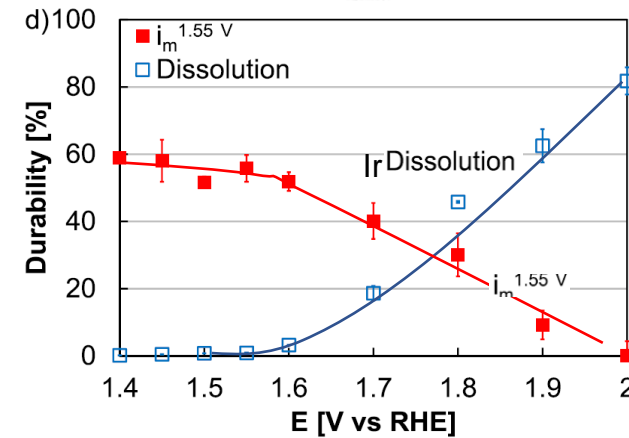
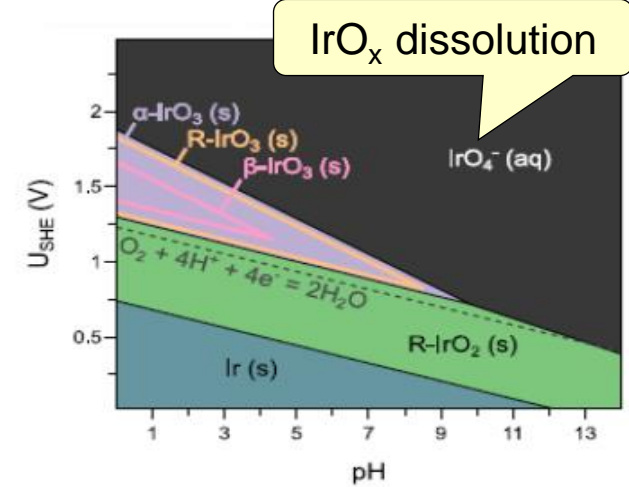
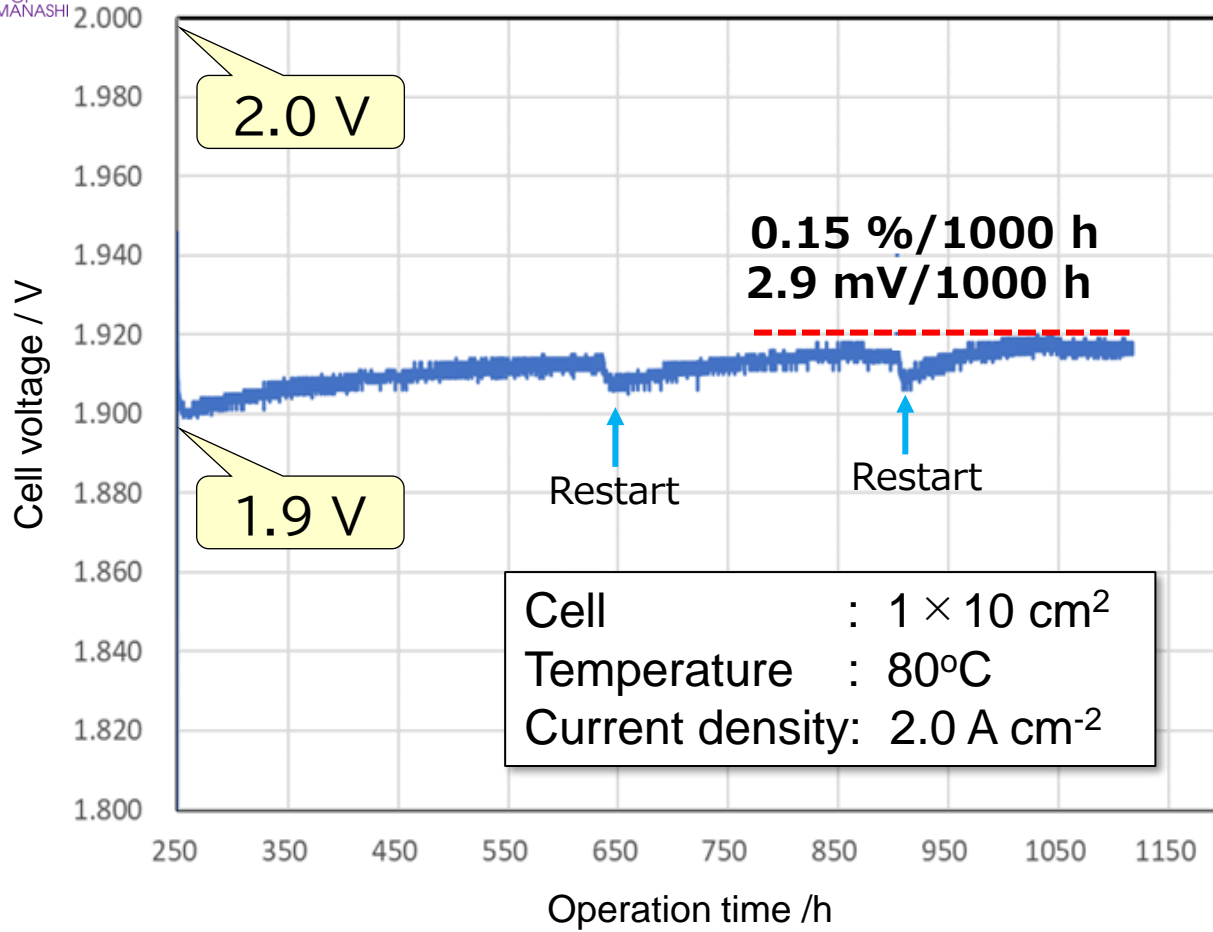
Peak label	Type of vibration
β	Ir-O bend
γ	Ir-O stretch
δ	Ir-O stretch
ε	Ir-O stretch



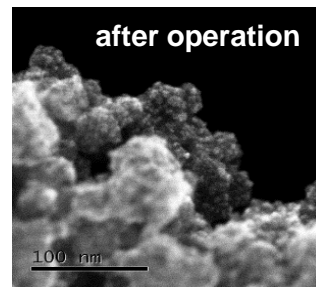
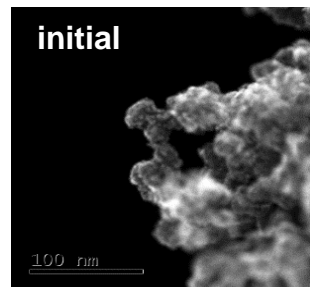


IEA : Energy Technology Perspectives 2020
https://iea.blob.core.windows.net/assets/7f8aed40-89af-4348-be19c8a67df0b9ea/Energy_Technology_Perspectives_2020_PDF.pdf
 Johnson Matthey : Iridium White Paper 2022
<https://matthey.com/documents/161599/3147297/JM+Iridium+White+Paper.pdf/27526faa-3b36-9160-6d9d-ac7a6dbb9d9f?t=1688641053268>

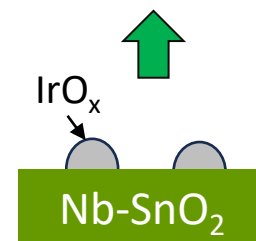
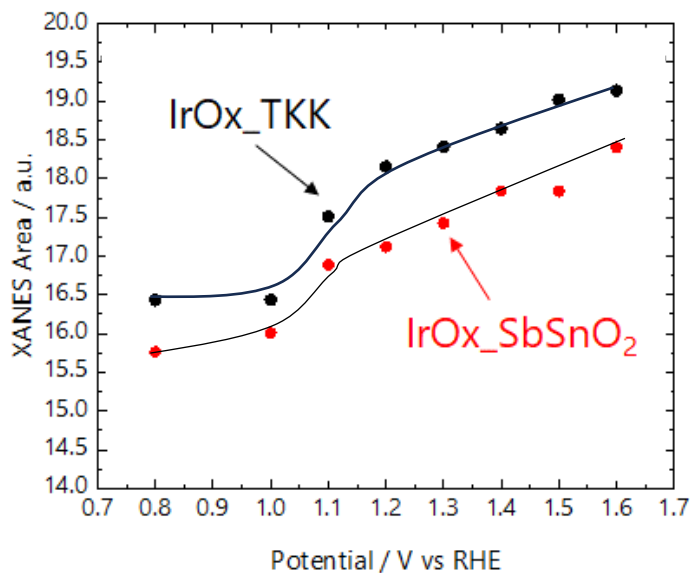
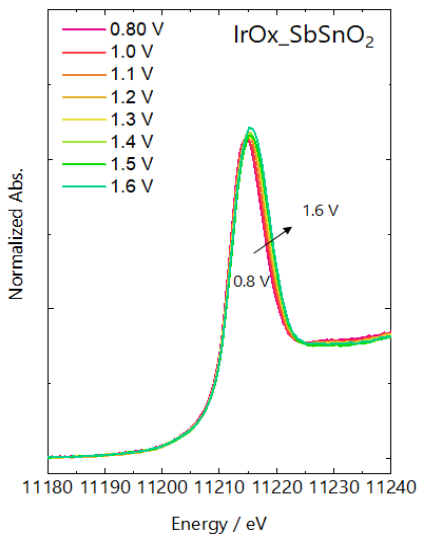
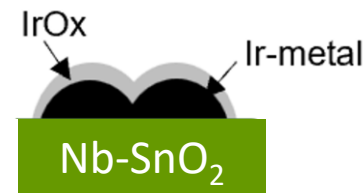
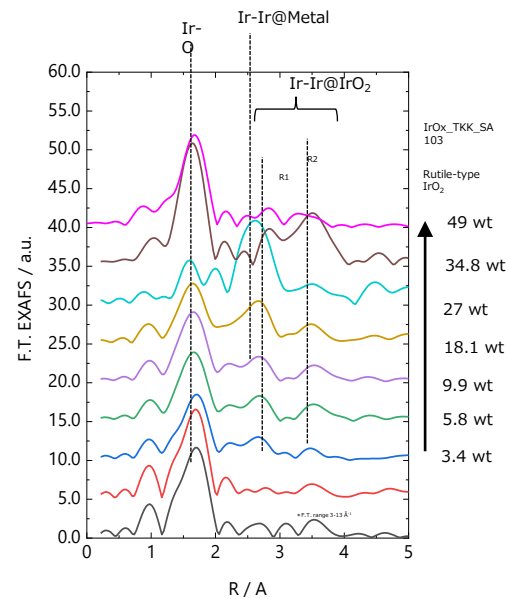
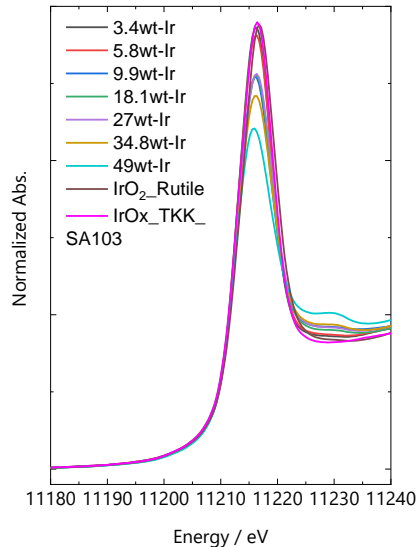
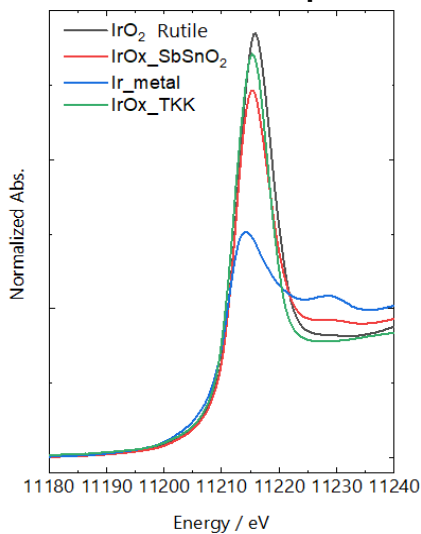
-Requirement and target-
 Ir loading amount: 0.25 mg cm⁻²
 Current density: ≥ 1.70 A cm⁻²
 (@ 1.60 V)

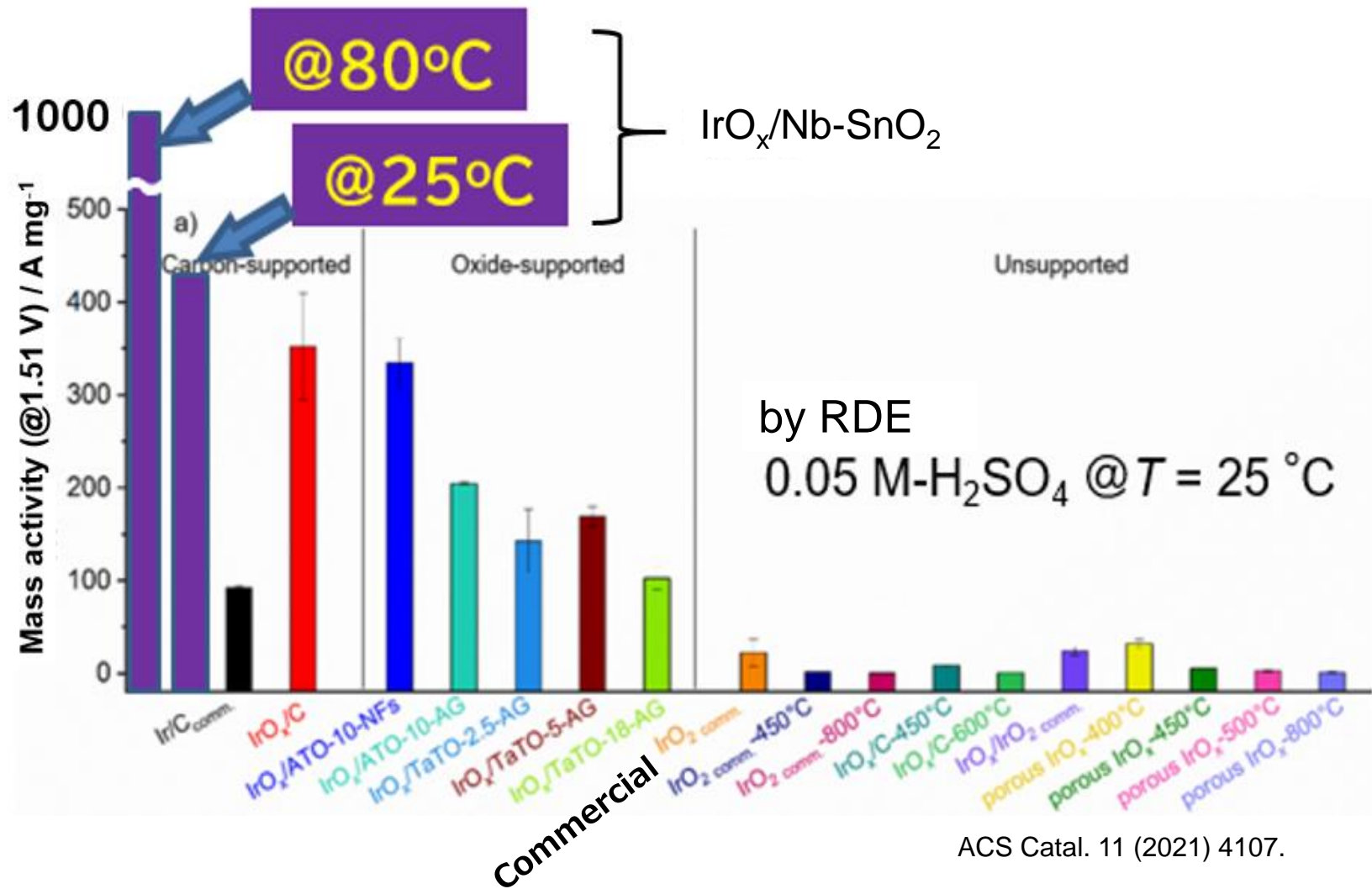


Chem. Mater. 32 (2022) 5854.

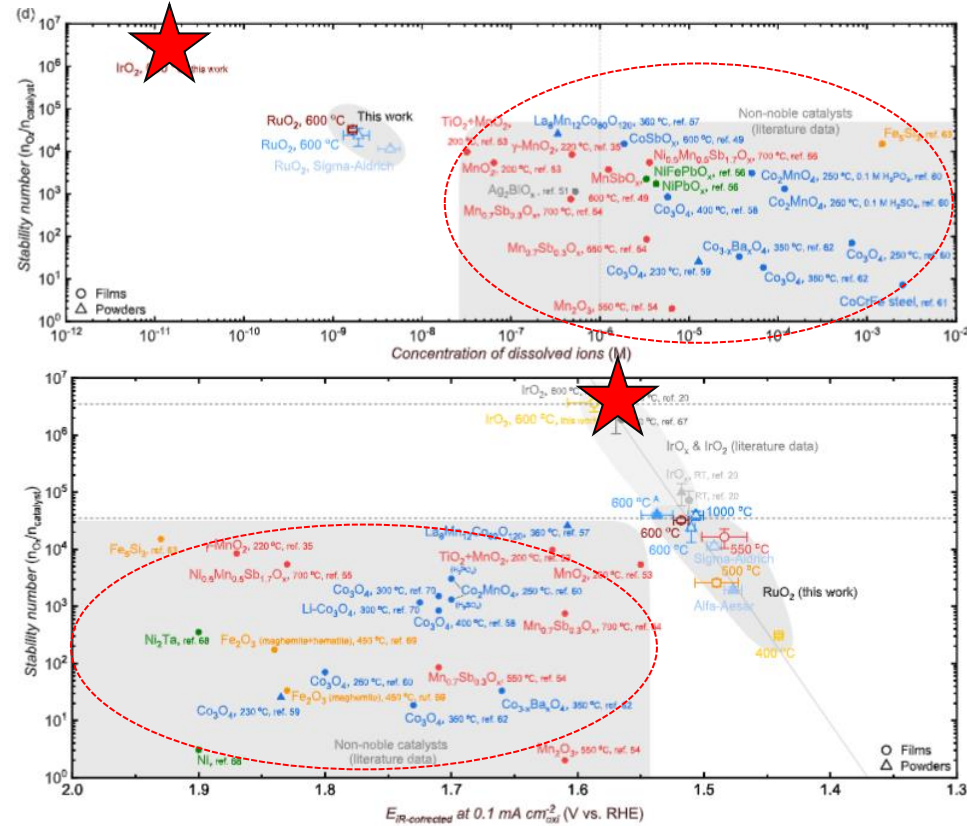


-Operando XAFS-



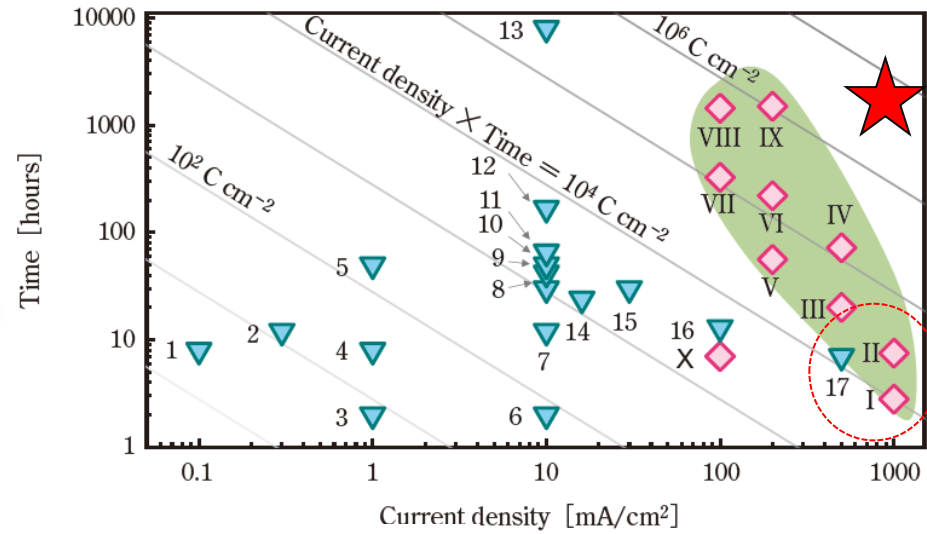


○ Ir related oxide



ACS Catal. 13 (2023) 14058.

○ Non-Ir oxide

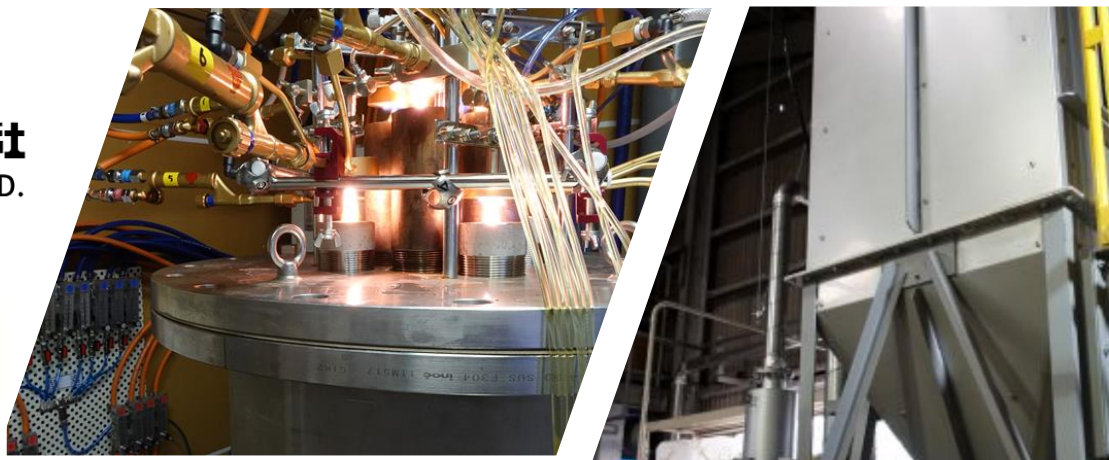


- 1 Activated MnO_x (*J. Am. Chem. Soc.* 2014)
- 2 Co-Fe Prussian blue (*J. Am. Chem. Soc.* 2016)
- 3 CoFeO_x (*Chem. Sci.* 2017)
- 4 CoPbO_x (*Chem. Sci.* 2017)
- 5 CoFePbO_x (*Chem. Sci.* 2017)
- 6 1T-MoS₂ (*Adv. Mater. Inter.* 2016)
- 7 Crystalline Co₃O₄ (*Chem. Mater.* 2017)
- 8 NiFeP (*Adv. Mater.* 2017)
- 9 Ni42 steel (*Catal. Sci. Technol.* 2018)
- 10 Co_{0.05}Fe_{0.95}O_x (*Chem. Commun.* 2019)
- 11 Ni₂Ta (*Inorg. Chem.* 2018)
- 12 Ni_{1.5}Mn_{1.5}Sb_{1.5}O₇ (*Energy Environ. Sci.* 2017)
- 13 γ -MnO₂ (*Angew. Chem. Int. Ed.* 2019)
- 14 F-Cu_{1.5}Mn_{1.5}O₄ (*Sci. Rep.* 2016)
- 15 Mn₂Sb_{1-x}O₂ (*ACS Catal.* 2018)
- 16 CoFePbO_x (*Nat. Catal.* 2019)
- 17 CoFePbO_x (*Nat. Catal.* 2019)

Nature Catal., 5 (2022) 109.

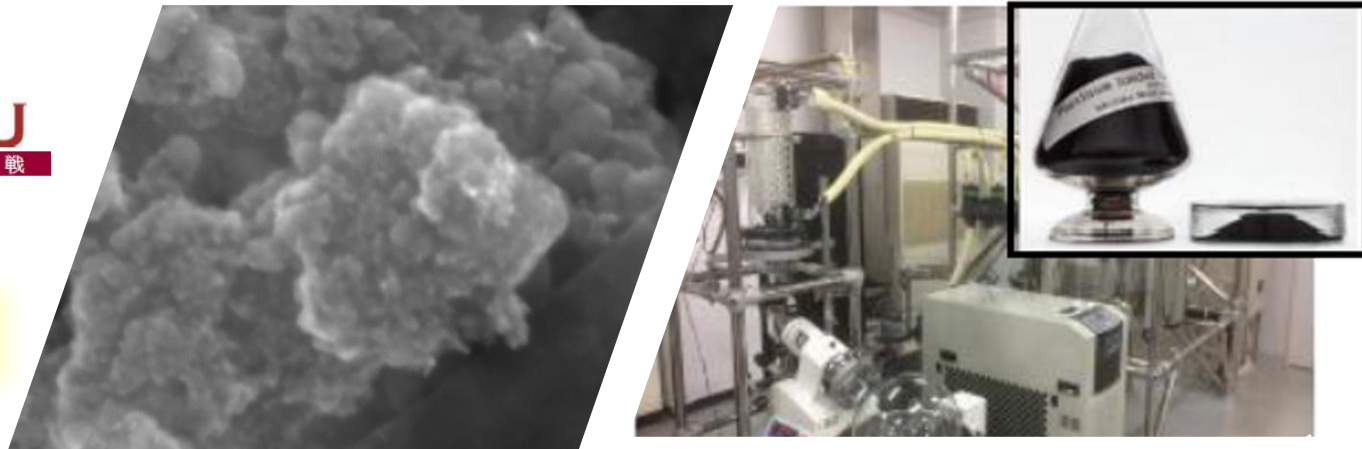
 **日本化学産業株式会社**
NIHON KAGAKU SANGYO CO.,LTD.

**Conducting ceramic
nano-particles support**



ISHIFUKU
貴金属へのあくなき挑戦

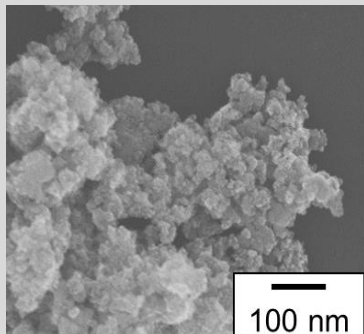
**Ir nano-particle
loading**



Mass product of IrO_x/Nb-SnO₂ (50 g/lot) will be supplied from ISHIFUKU soon.

Issue

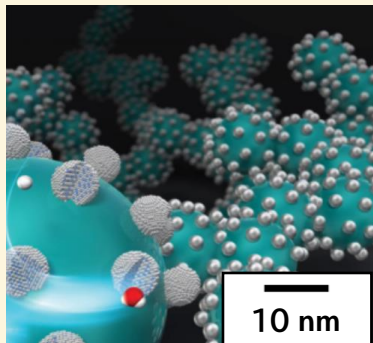
IrOx触媒の
OER活性向上と目付量削減



- ・Ir供給量の不足
- ・OER 活性向上
- ・化学的安定性

Point 1

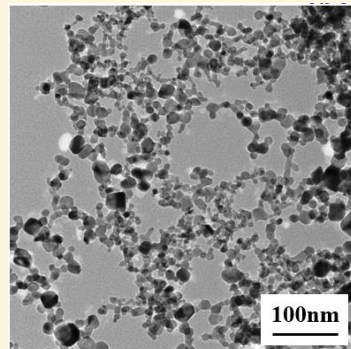
IrO_xナノ粒子利用



- ・質量活性の向上

Point 2

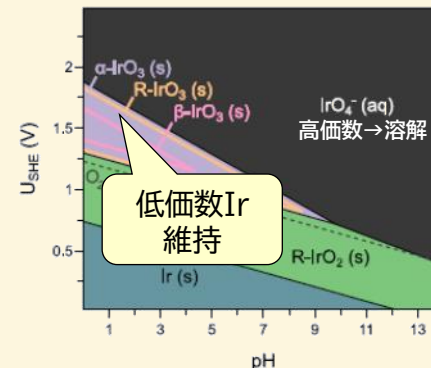
導電性セラミックナノ粒子



- ・連珠構造による多孔化
- ・導電性維持

Point 3

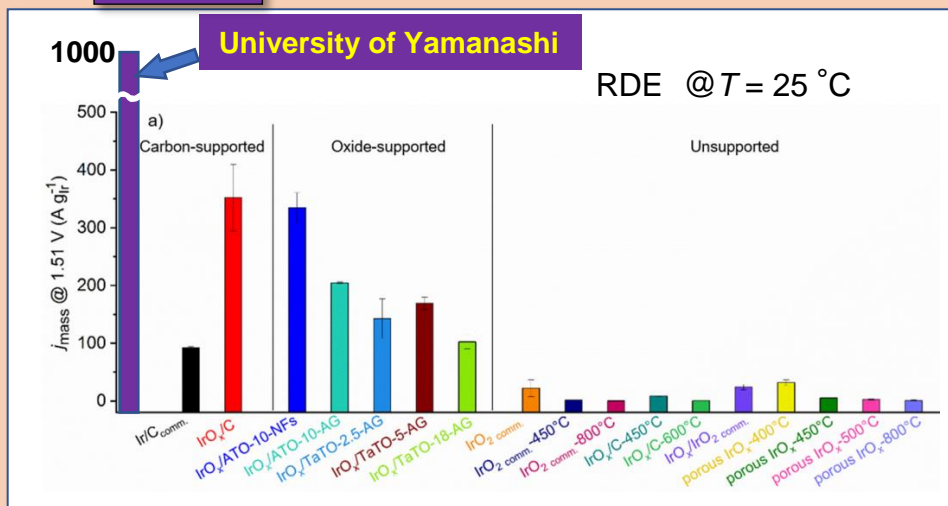
相互作用



- ・Irの溶解抑制
- ・電子状態制御

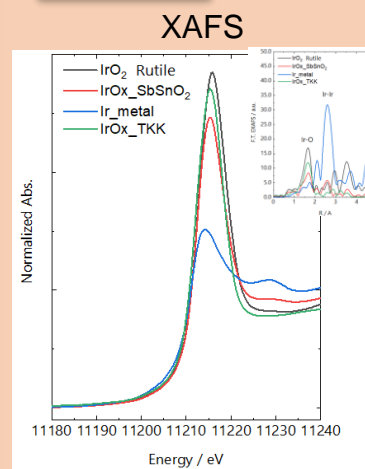
Result 1

OER活性の大幅向上

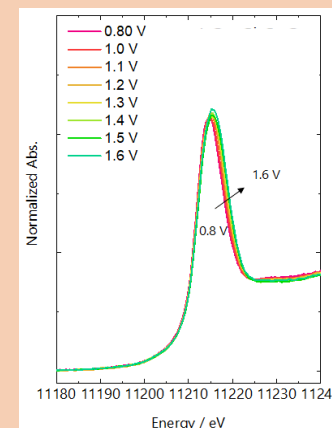


Result 2

低価数Irの維持による耐久向上



Operando XAFS



本研究は国立研究開発法人 新エネルギー・産業技術総合開発機構 (NEDO)の支援のもと行われました。関係各位に感謝申し上げます。



ご清聴ありがとうございました

