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THE ROLE OF NIOBIUM IN FUEL CELLS AND HYDROGEN PRODUCTION TECHNOLOGIES

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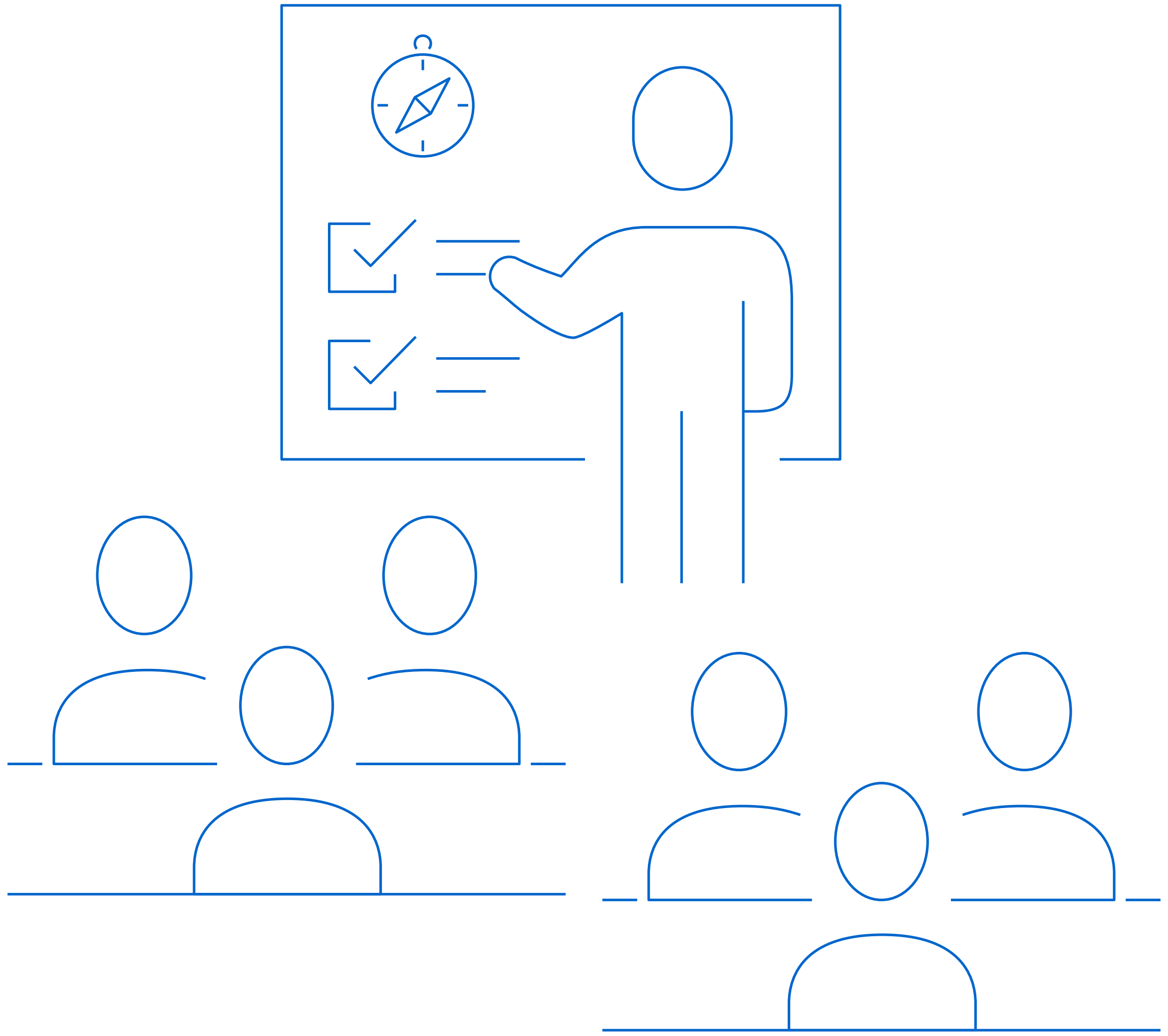
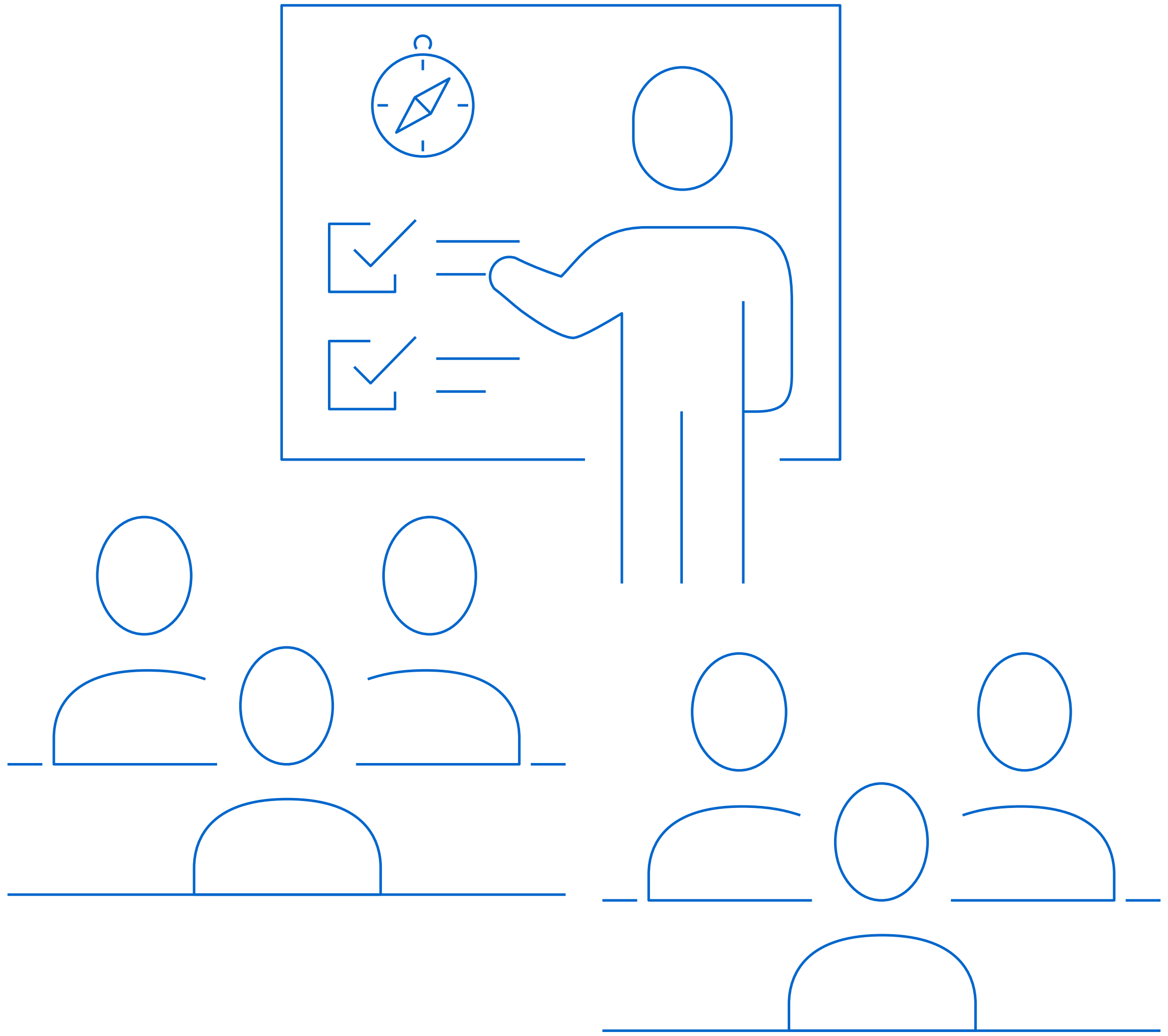
Senior Market Development Specialist

2020 CHARLES HATCHETT AWARD HYDROGEN SEMINAR



OVERVIEW

- HYDROGEN ECONOMY BACKGROUND
- NIOBIUM MARKET OPPORTUNITIES
- NIOBIUM ROLE ON GREEN HYDROGEN PRODUCTION
  - Photocatalytic Water Splitting
  - Water Electrolysis
- NIOBIUM ROLE ON HYDROGEN CONVERSION
  - PEM Fuel Cells
  - PGM Free and PGM Reduced Catalyst
  - Carbon Free Catalyst Supports



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WHY DO WE NEED HYDROGEN?

DECARBONIZING ENERGY MATRIX

Energy Density

Fuel	MJ/kg	kWh/kg
Hydrogen	**120**	**33.6**
Gasoline	46.4	12-14
Diesel	45.5	12-14
Natural Gas	53.6	14.7

Source: Wikipedia

Emissions

Fuel Source	Compounds
Hydrogen	**H_2O**
Gasoline	NO_x, CO/CO_2, unburned HCs
Diesel	NO_x, SO_x, CO/CO_2, PM, unburned HCs
Natural Gas	NO_x, CO/CO_2, unburned CH_4

Source: Wikipedia

HYDROGEN IS A CLEAN AND FULLY DECARBONIZED SOURCE OF ENERGY

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ENERGY TRANSITION – 7 ROLES OF HYDROGEN

DECARBONIZING ENERGY MATRIX

[1] Enabling large-scale renewables integration and power generation

[2] Distribute energy across sectors and regions

[3] Act as buffer to increase system resiliance

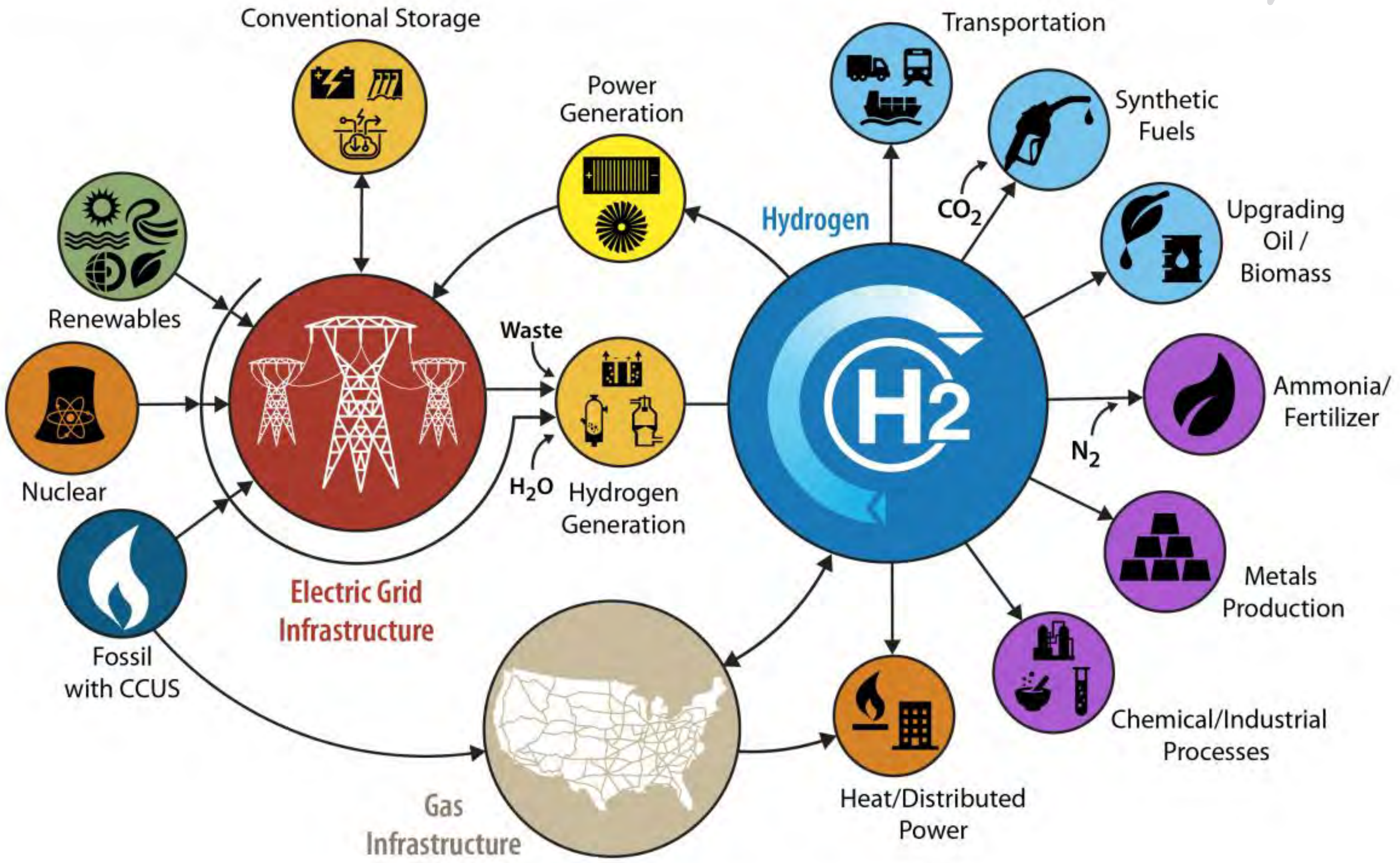
[4] Help decarbonize transportation

[5] Help decarbonize industrial energy use

[6] Help decarbonize buildings heat and power

[7] Serve as a renewable feedstock

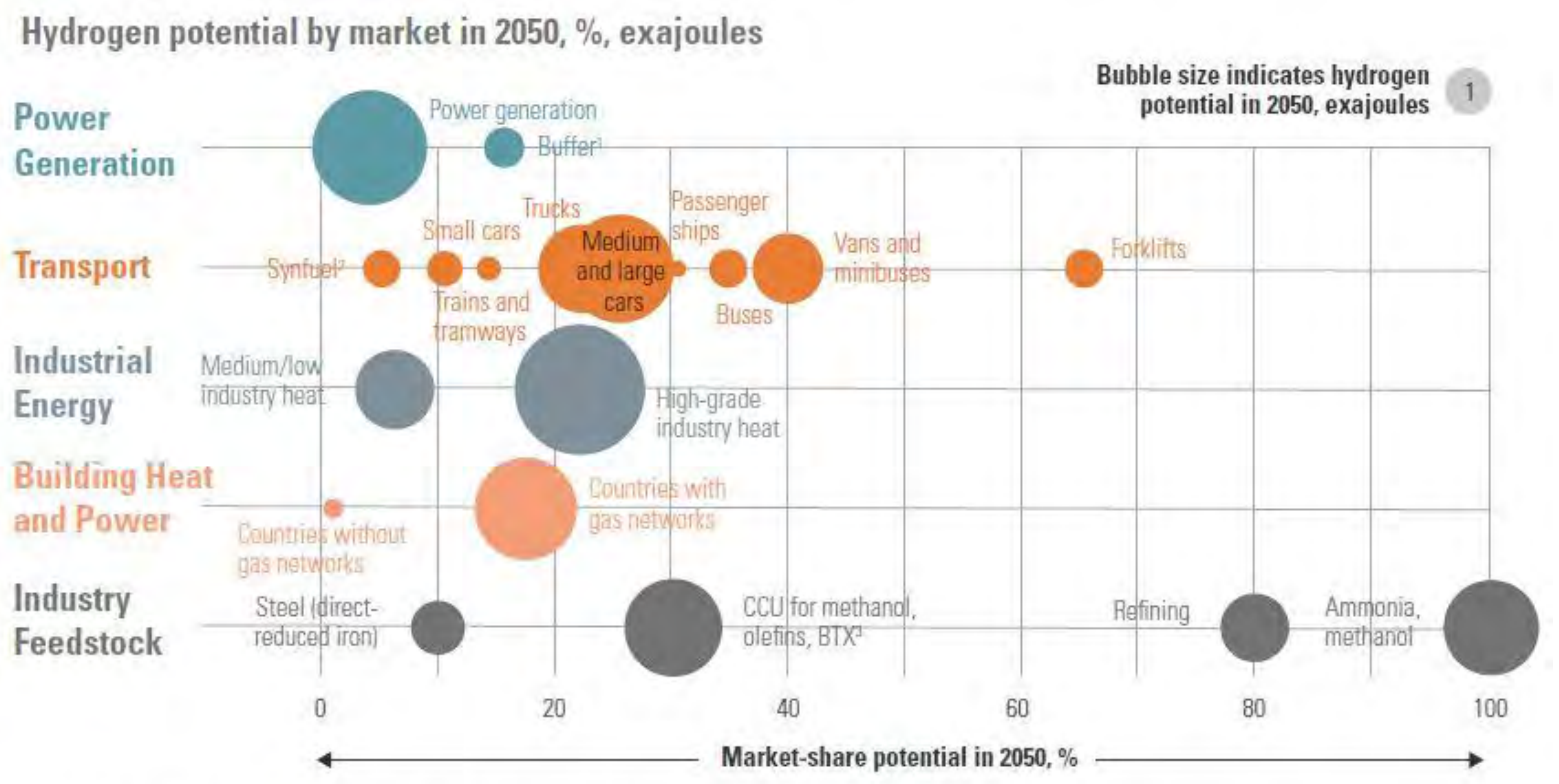
Source: McKinsey & Co.



Source: H2@Scale (DOE) https://www.energy.gov/eere/fuelcells/h2scale

HYDROGEN MARKET POTENTIAL – 2050, %

UTILIZATION PER BUSINESS SECTOR

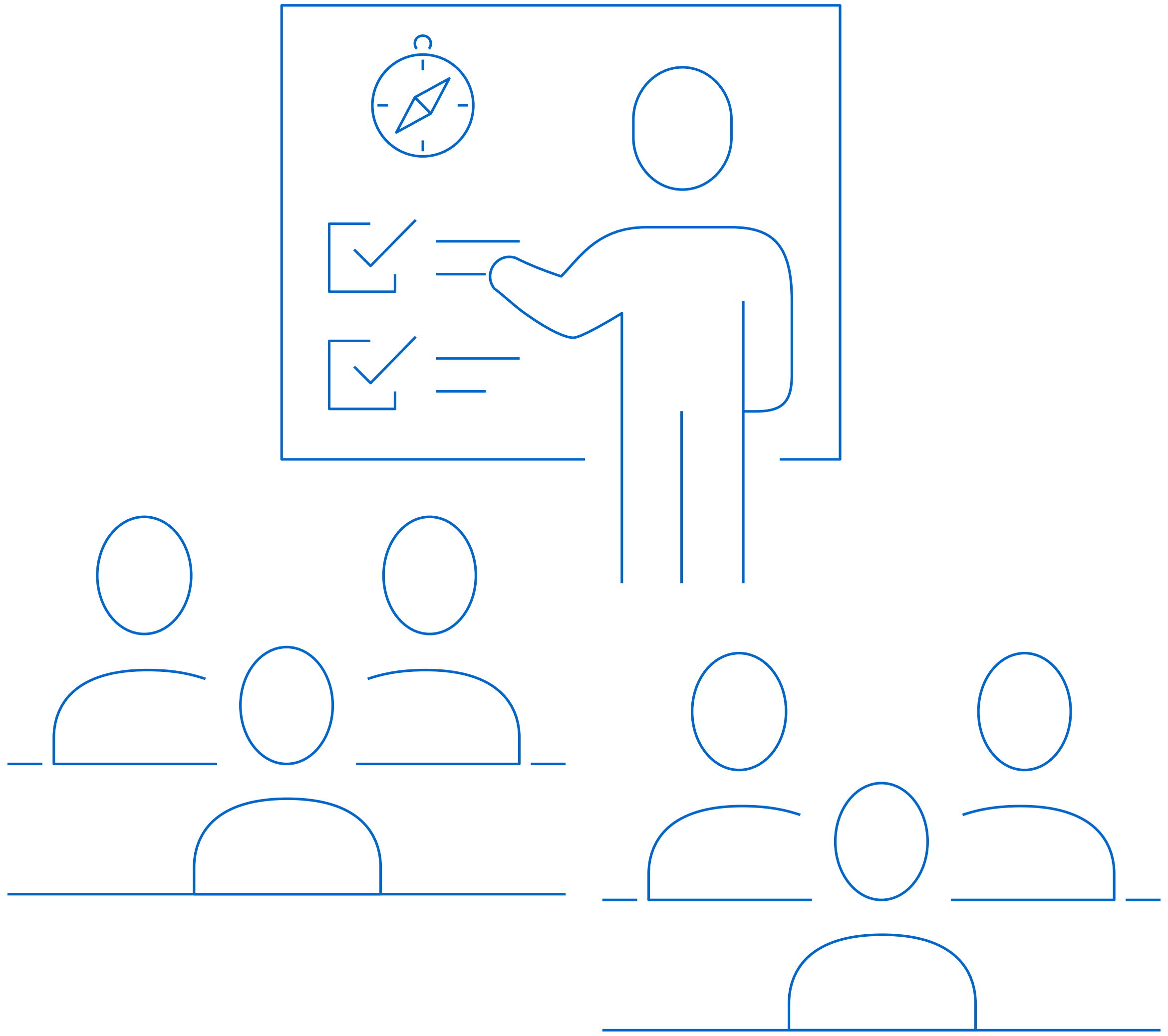


[1] % of total annual growth in hydrogen and variable renewable-power demand.

[2] For aviation and freight ships.

[3] Carbon capture and utilization; % of total methanol, olefin, and benzene, toluene, and xylene (BTX) production using olefins and captured carbon.

Source: McKinsey&Company



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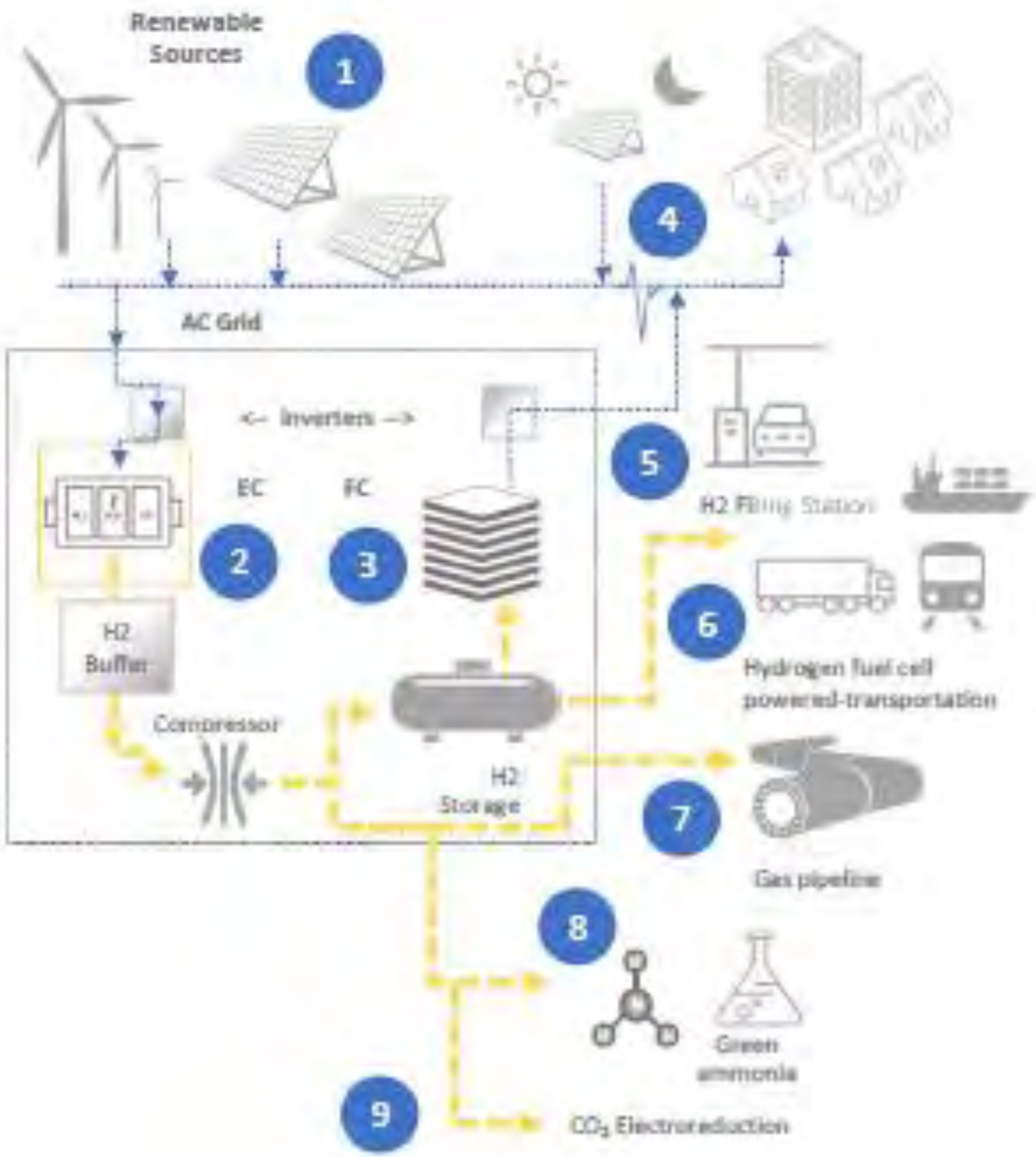
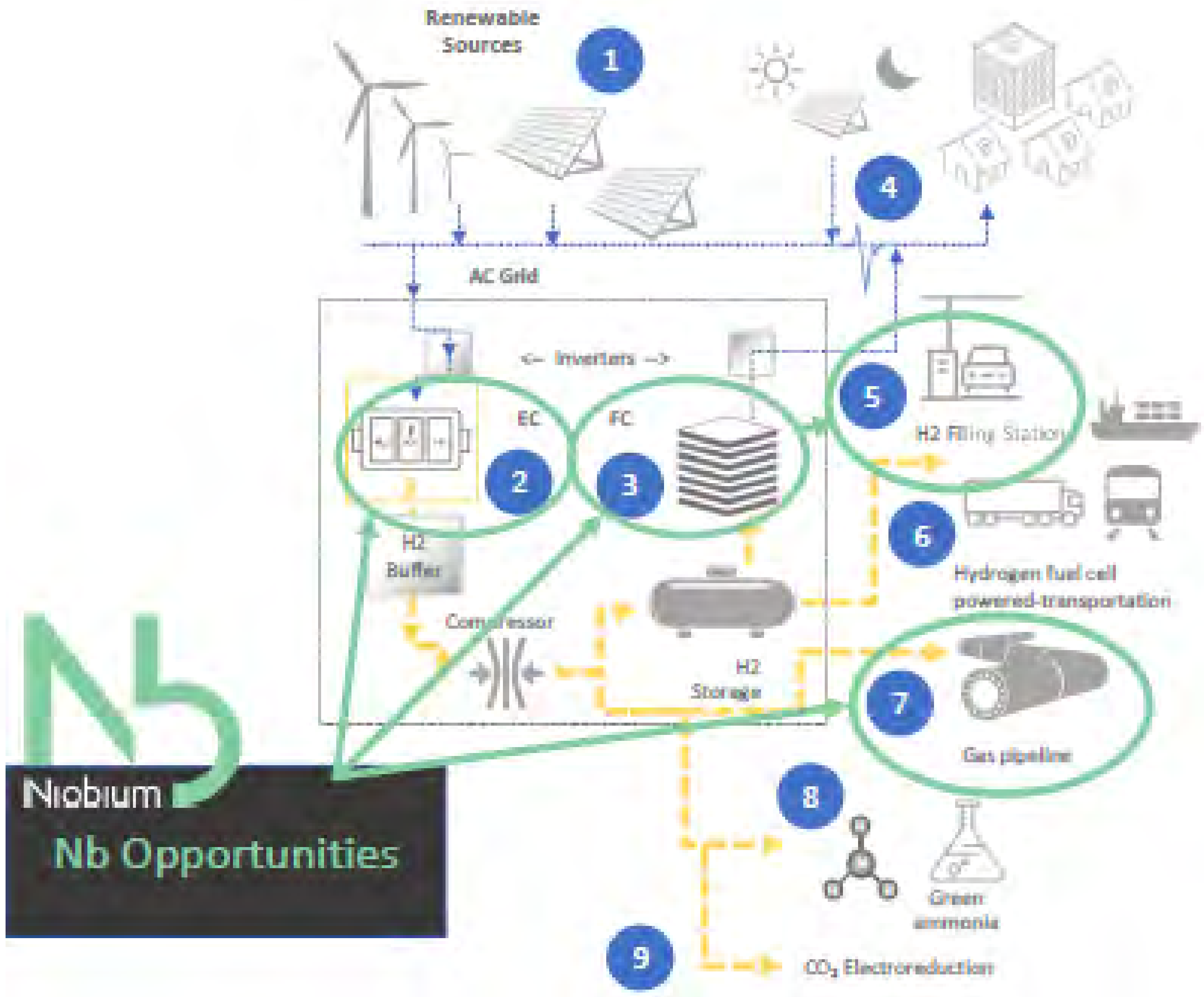
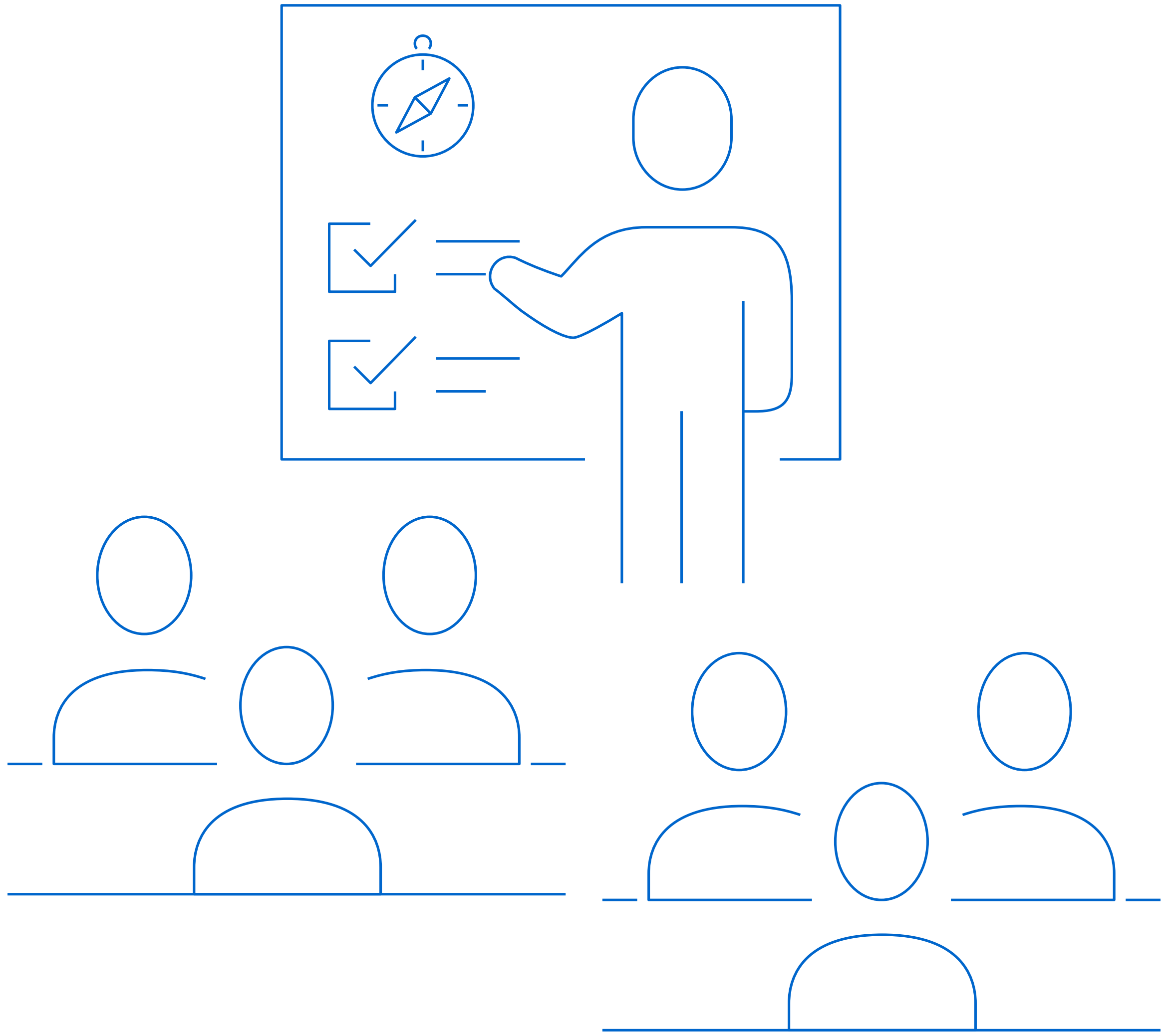
HYDROGEN ECONOMY INFRASTRUCTURE

MARKET OPPORTUNITIES FOR NIOBIUM





Courtesy from **Pajarito Powder LLC (Albuquerque, NM)**



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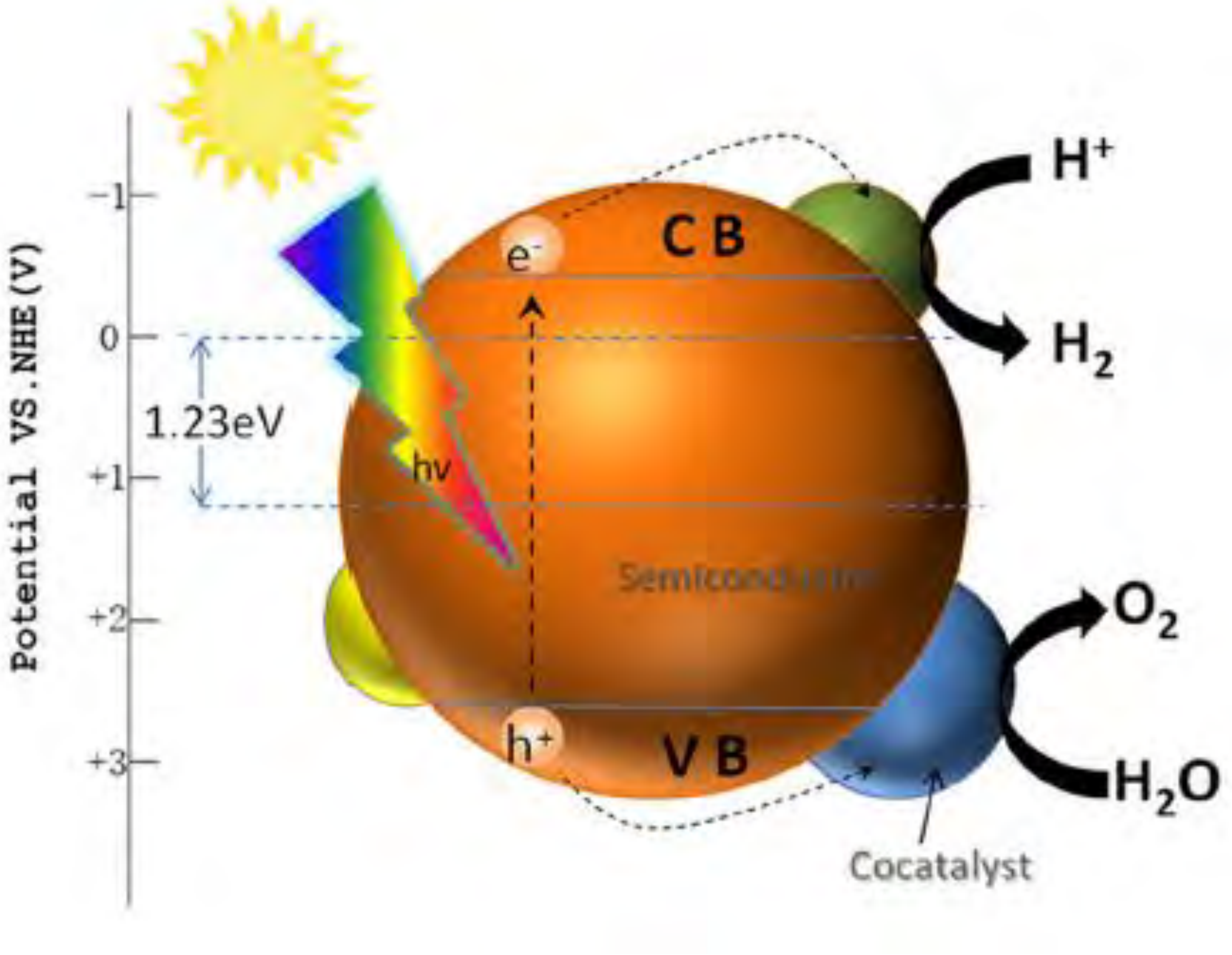
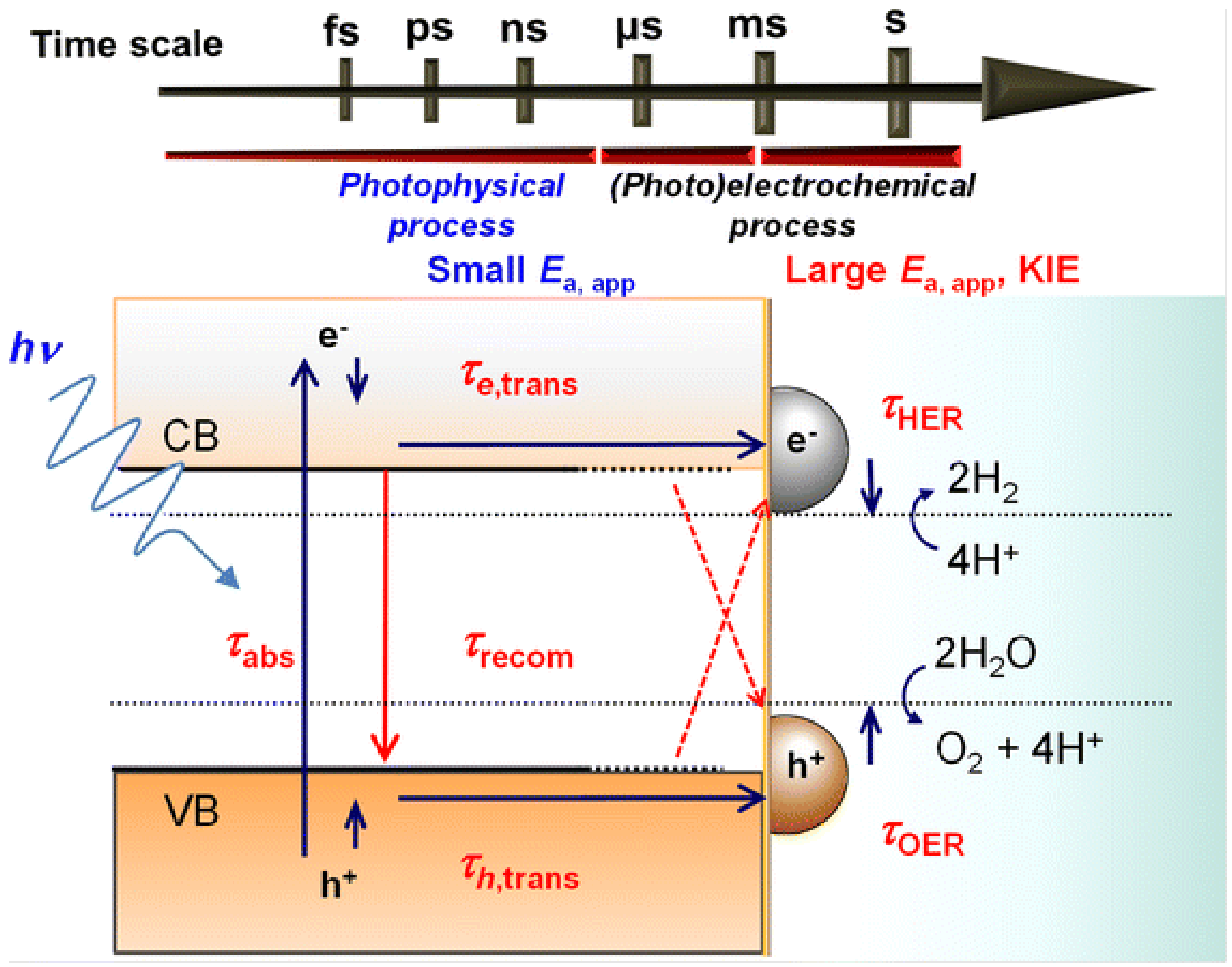
GREEN HYDROGEN PRODUCTION TECHNOLOGIES

PHOTOCATALYTIC WATER SPLITTING



$H_2O \rightarrow H_2 + ½ O_2 \quad \Delta E = -1.23$ eV

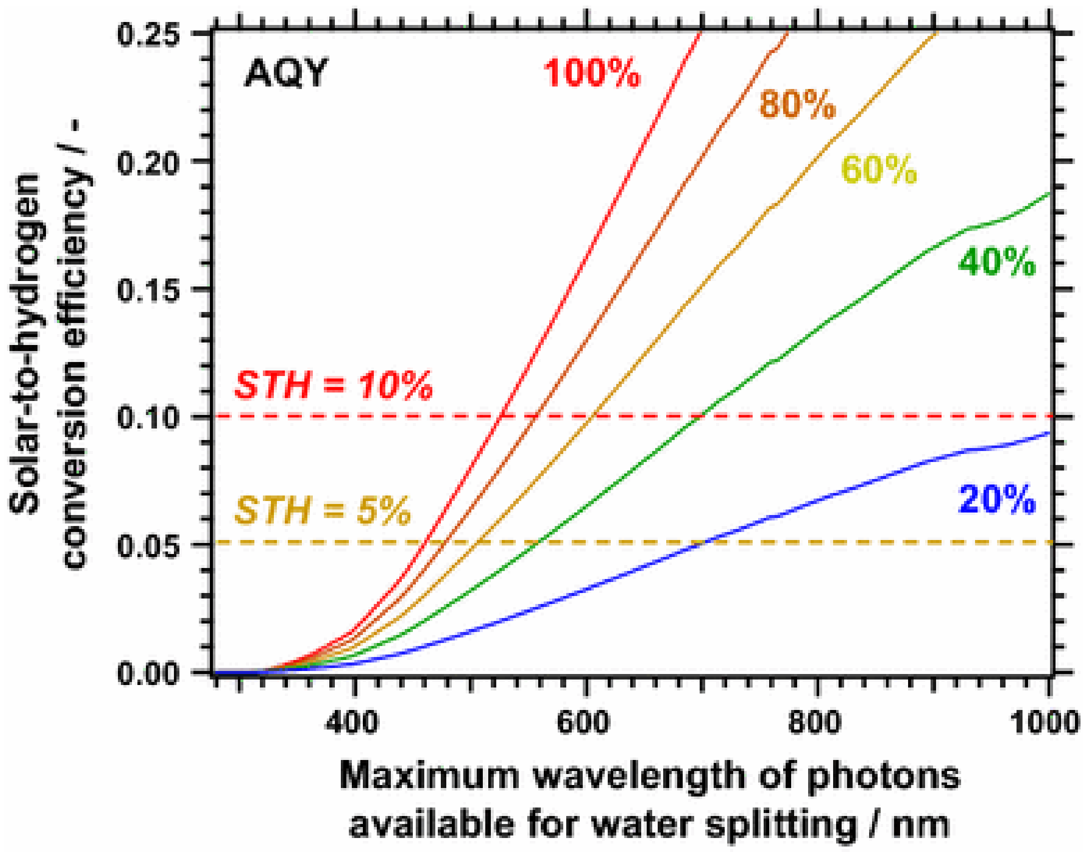


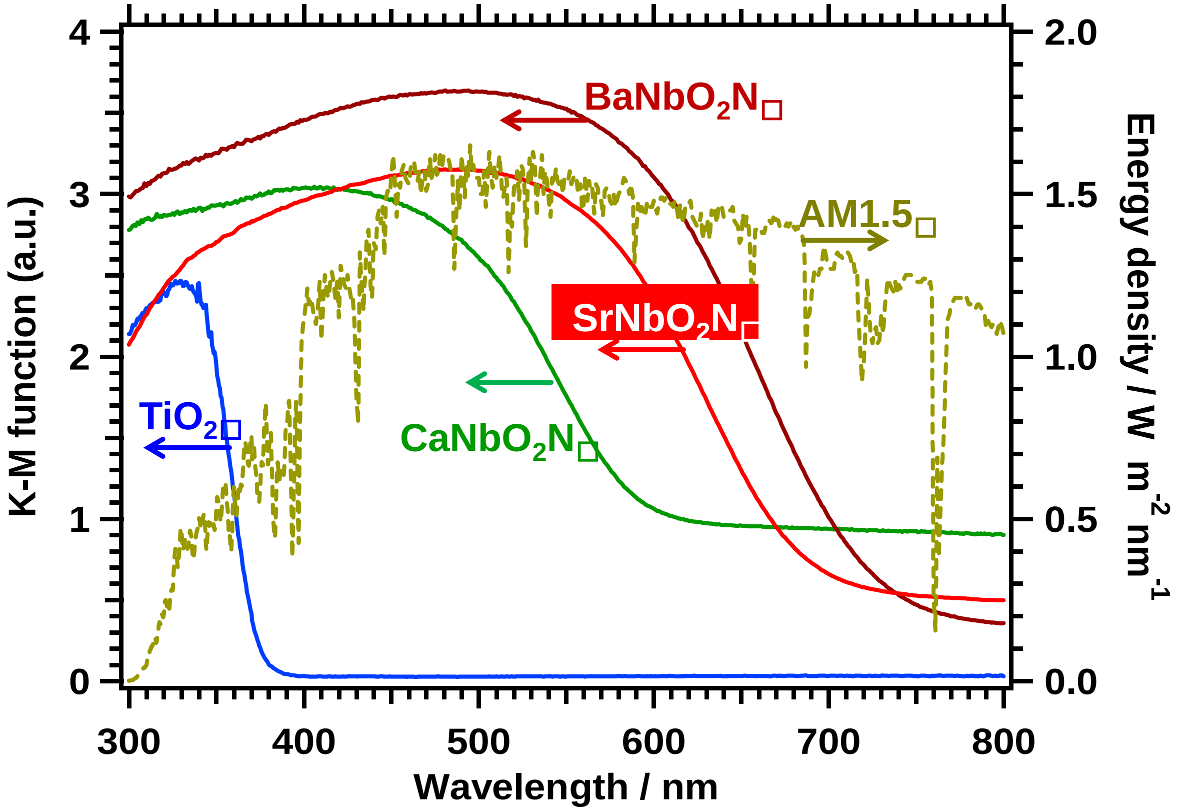
- **Charge carriers separation (*e^-/h^+*) drives water splitting efficiency**;
- Must occur under the **same timescales** of photoexcited carriers (e^-/h^+) **recombinations**
- Overall water splitting: **band-gap tuning; cocatalysts; nanostructuring**; etc.

Hisatomi et al, ***Catal Lett*** 145 (2015) 95

NIOBIUM BASED PHOTOCATALYTIC MATERIALS

WATER SPLITTING





NIOBATES –
→ $KCa_2Nb_3O_{10}$; $K_4Nb_6O_{17}$; NiO-$K_4Nb_6O_{17}$
(Band Gap: 3.0 – 3.5 eV)

LAYERED COMPOUNDS –
→ $Sr_2Nb_2O_7$; $Ca_2Nb_2O_7$
(Band Gap: 1.8 – 2.0 eV)

OXYNITRIDES PEROVSKITES and NITRIDES –
→ $CaNbO_2N$; $SrNbO_2N$; $BaNbO_2N$
→ NbN; Nb_3N_5
(Band Gap: ≤ 1.8 eV)

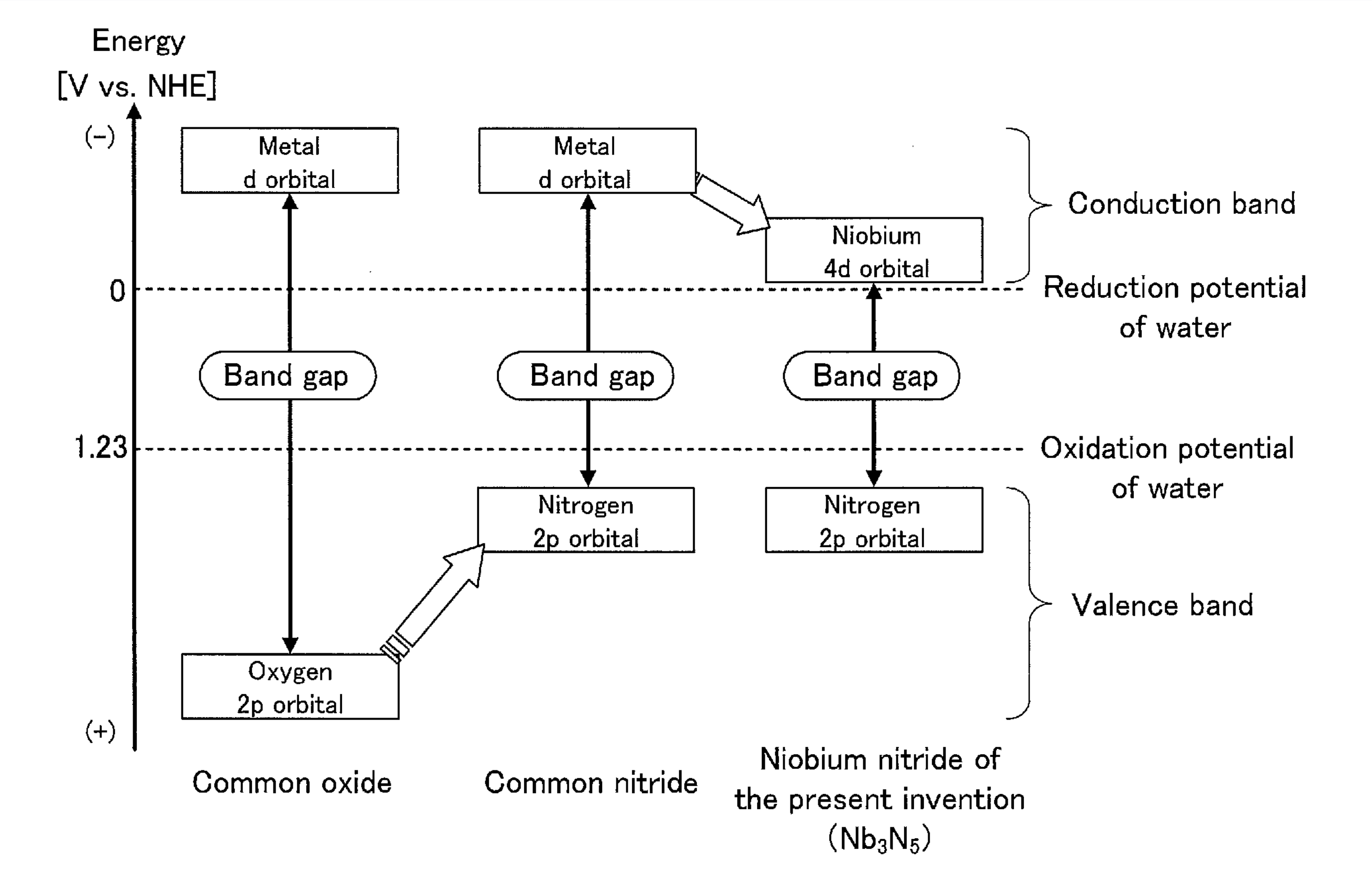
Hisatomi et al, ***Catal Lett*** 145 (2015) 95
Domen et al, ***J. Am. Chem. Soc***. 133 (32) (2011) 12334
Domen et al, ***ACS Appl. Energy Mater***. 2 (8) (2019) 5777

NIOBIUM BASED PHOTOCATALYTIC MATERIALS

WATER SPLITTING

BAND GAP TUNING TO H_2O OXI-REDUCTION POTENTIAL

Nb_2O_5 → NbN → **Nb_3N_5 (niobium (V) nitride) – thin films**



Suzuki et al, ***US Pat Appl 2014/0057187 A1*** to Panasonic

Sunlight Panels -
..announced by **Panasonic** to produce hydrogen from water splitting

Source: Nikkei Asian Review (11 July 2015)
https://asia.nikkei.com/Business/The-future-home-is-where-the-hydrogen-power-generator-is
https://worldindustrialreporter.com/panasonic-to-create-household-hydrogen-power-generators/

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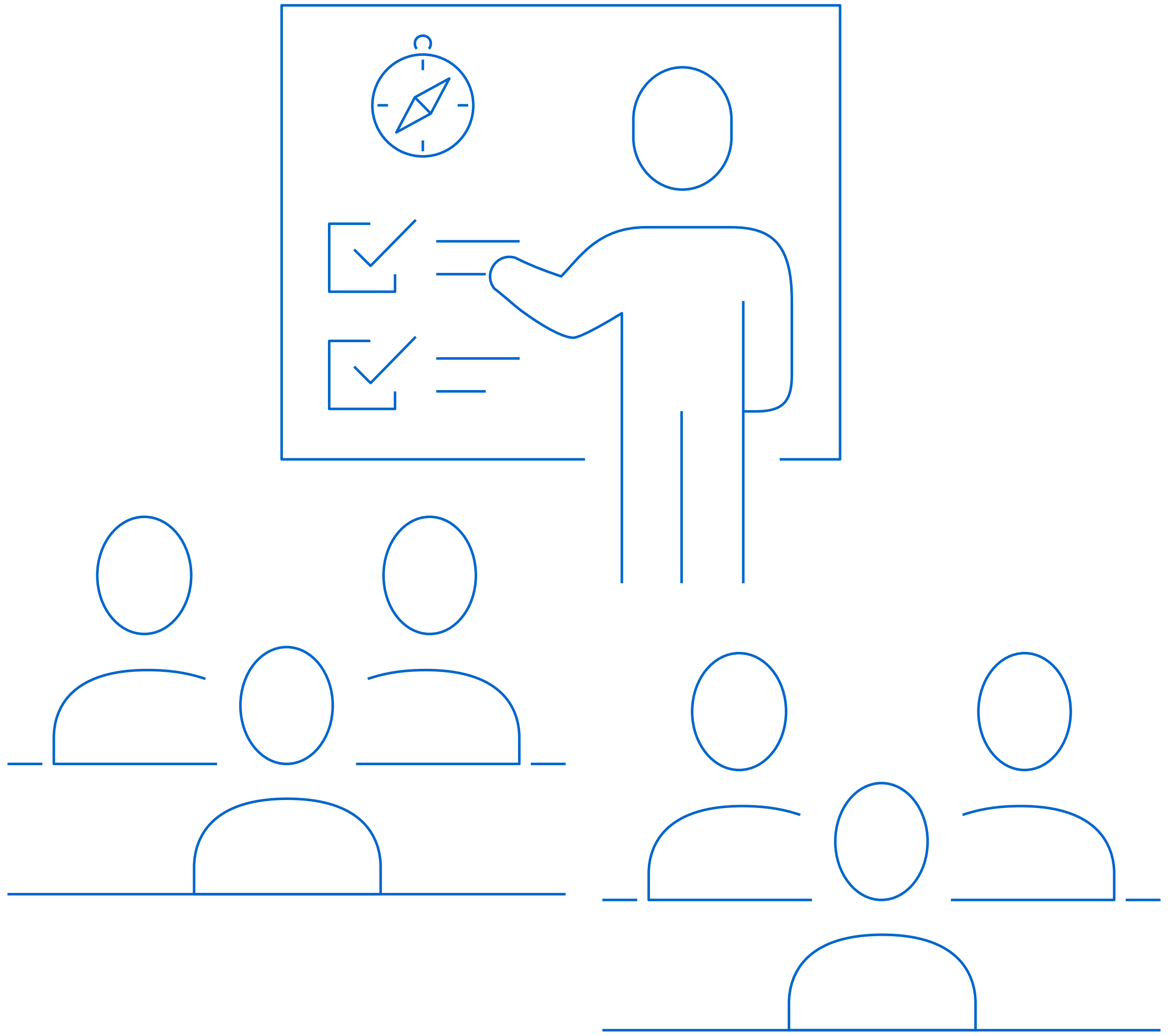

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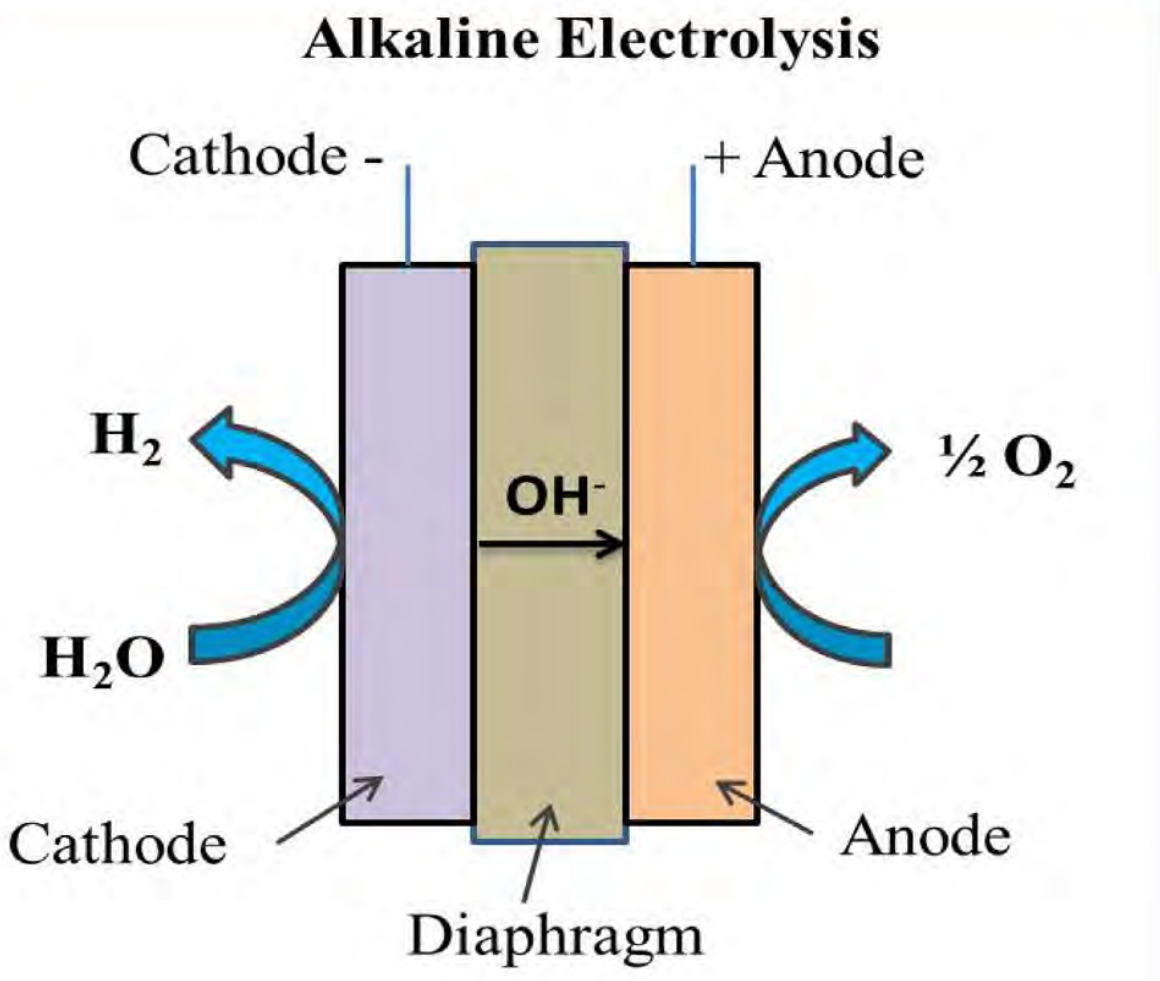
GREEN HYDROGEN PRODUCTION TECHNOLOGIES

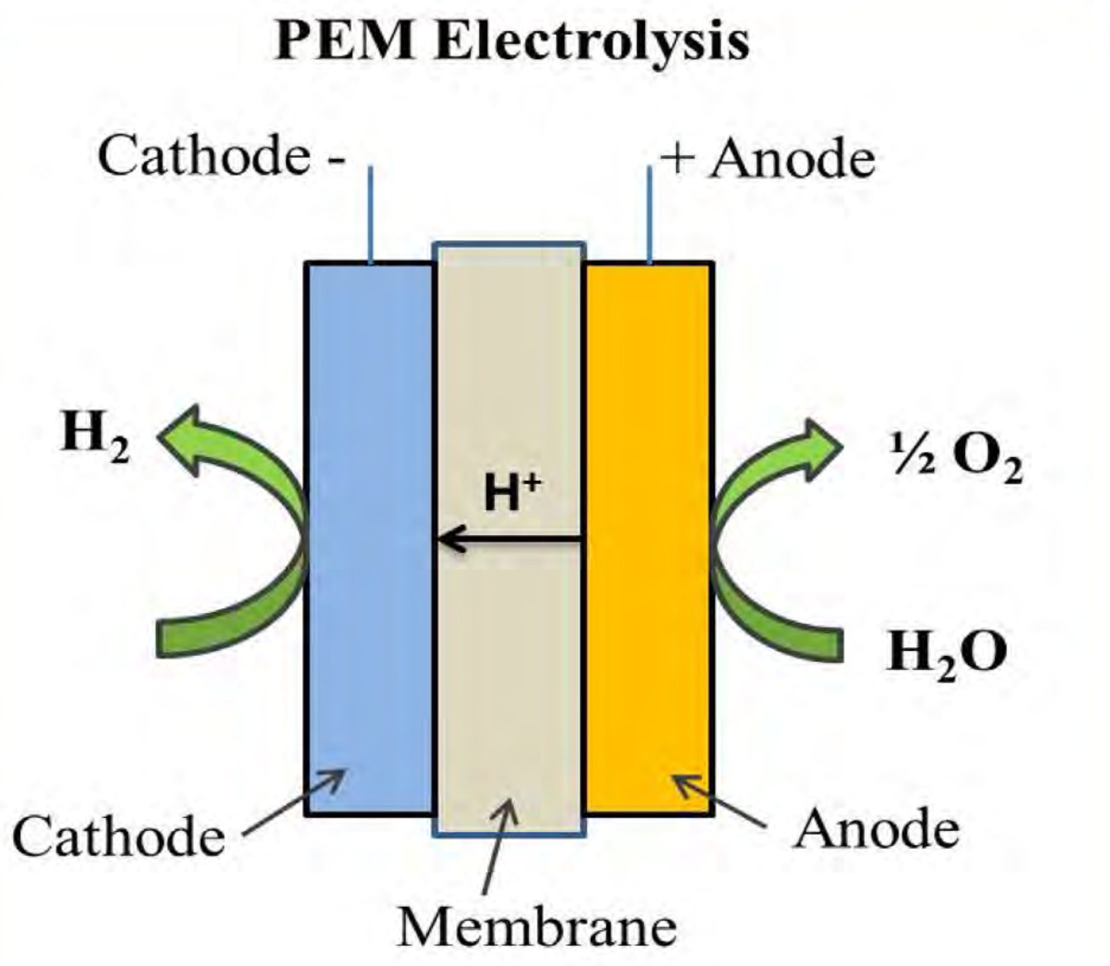
WATER ELECTROLYSIS



Anode: $2OH^- \rightarrow H_2O + \frac{1}{2} O_2 + 2e^-$

Cathode: $2 H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall cell: $H_2O \rightarrow H_2 + \frac{1}{2} O_2$



Anode: $H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Overall cell: $2H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Kumar et al, ***Mater Sci Energy Tech*** 2 (2019) 442

PEM WATER ELECTROLYSIS

CATALYSTS DEVELOPMENT CHALLENGES

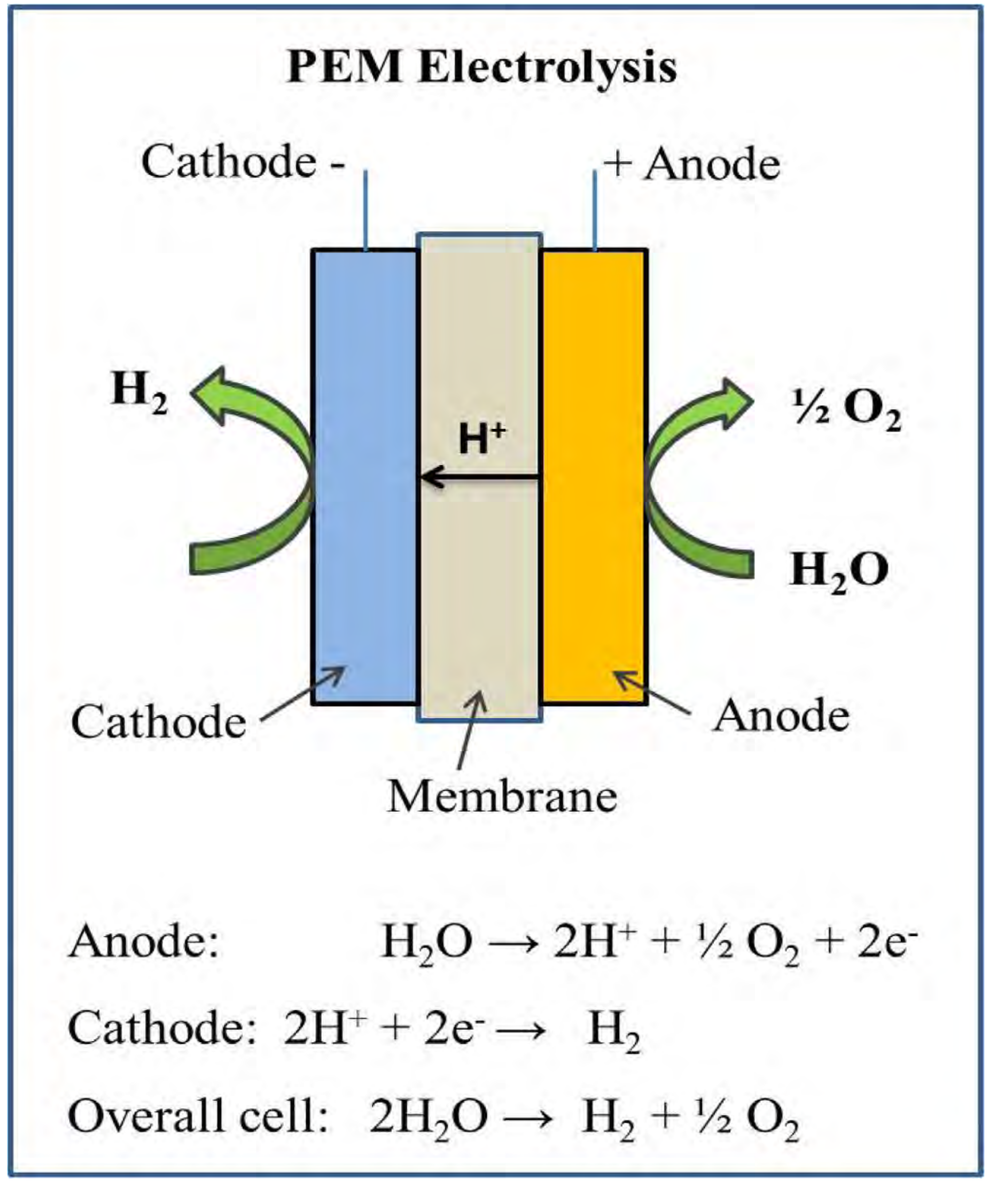


Table 4
Historical Results of Different Electrocatalysts in PEM Water Electrolysis.

anode catalyst	cathode catalyst	anode loading (mg/cm^2)	cathode loading (mg/cm^2)	membrane	Temp (°C)	Voltage at 1 A/cm^2	Ref.
Ir-Black	40% Pt/GNF	2.0	0.8	Nafion-115	90	1.67	[113]
Ir-Black	40% Pt/XC-72	2.0	0.8	Nafion-115	90	1.70	[113]
Ir-Black	Pt40/Vulcan XC-72	2.4	0.7	Nafion-115	90	1.66	[72]
Ir-Black	Pd40/Vulcan XC-72	2.4	0.7	Nafion-115	90	1.70	[72]
Ir-Black	Pt-black	2.0	0.8	Nafion-117	90	1.71	[156]
IrO_2	Pt-black	2.0	2.5	Nafion-115	80	1.60	[157]
RuO_2	40% Pt/C	10	0.4	Nafion-115	–	1.88	[158]
RuO_2	30% Pt/C	3.0	0.5	Nafion-112	80	1.65	[160]
RuO_2	30% Pt/C	1.5	0.5	Nafion-1035	80	1.63	[159]
IrO_2	30% Pt/C	1.5	0.5	Nafion-1035	80	1.67	[159]
IrO_2	60% Pt/C	3.0	0.5	Nafion-115	80	1.58	[161]
IrO_2	30% Pt/C	2.5	0.5	Nafion-115	80	1.7	[162]
Ir-Black	Pt/CNT	2.4	–	Nafion-115	90	1.72	[112]
$Ru_{0.7}Ir_{0.3}O_2$	40% Pt/C	2.5	0.5	Nafion-117	80	1.70	[154]
IrO_2/SnO_2	40% Pt/C	1.5	0.5	Nafion-212	80	1.57	[155]
RuO_2/SnO_2	40% Pt/C	30.	0.6	Nafion-115	80	1.723	[155]
RuO_2	40% Pt/C	3.0	0.6	Nafion-115	80	1.74	[155]
RuO_2	30%Pd/N-CNT	3.0	0.7	Nafion-115	80	1.84	[100]
RuO_2	30%Pd/P-CNPs	3.0	0.7	Nafion-115	80	2	[82]
RuO_2	30%Pd/PG	3.0	0.7	Nafion-115	80	1.95	[120]
RuO_2	30%Pd/PN-CNPs	3.0	0.7	Nafion-115	80	1.90	[163]
$Ru_{0.8}Pd_{0.2}O_2$	30% Pt/CB	3.0	0.7	Nafion-115	80	2.03	[164]
$Ir_{0.6}Ru_{0.4}O_2$	20% Pt/C	2.04	2.04	Nafion-115	80	1.56	[154]
RuO_2	46% Pt/C	1.0	0.2	Nafion-117	80	1.68	[165]
$Ru_{0.9}Ir_{0.1}O_2$	46% Pt/C	1.0	0.2	Nafion-117	80	1.75	[165]
$Ru_{0.7}Ir_{0.3}O_2$	46% Pt/C	1.6	0.2	Nafion-117	80	1.80	[165]
$Ru_{0.3}Ir_{0.7}O_2$	46% Pt/C	1.4	0.2	Nafion-117	80	1.74	[165]
IrO_2	46% Pt/C	1.2	0.2	Nafion-117	80	1.80	[165]

Kumar et al, ***Mater Sci Energy Tech*** 2 (2019) 442

- High utilization of costly precious metals as electrocatalysts: **Ir-based** (anode-OER) and **Pt-based** (cathode-HER)
- **Large hydrogen production scale** requires significant reduction of Ir (60-100 wt.%) and Pt (30-60 wt.%) amounts
- **Durable, acid resistant and kinetic performance** at lower PGM loadings

PEM WATER ELECTROLYSIS – ANODE CATALYST

OXYGEN EVOLUTION REACTION

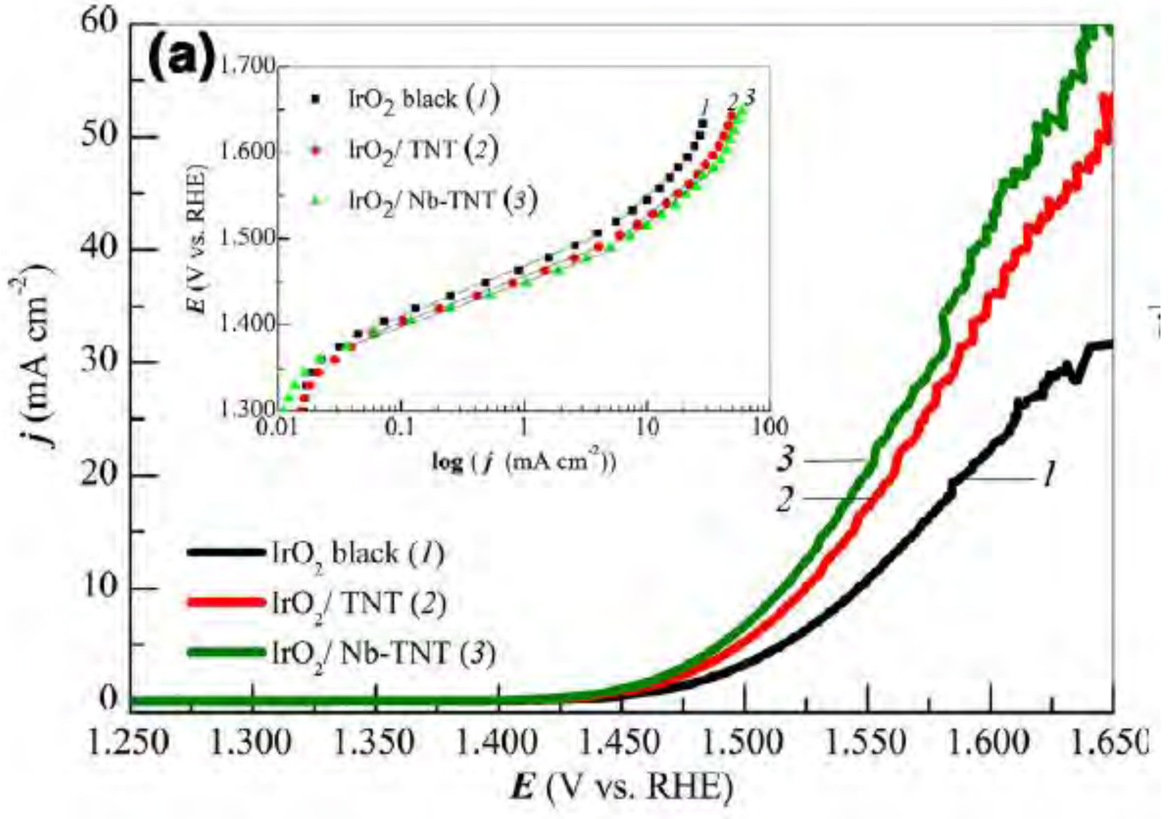
($H_2O \rightarrow 2H^+ + ½\ O_2 + 2\ e^-$)

Nb-TiO_2 supported IrO_2, $IrRuO_x$

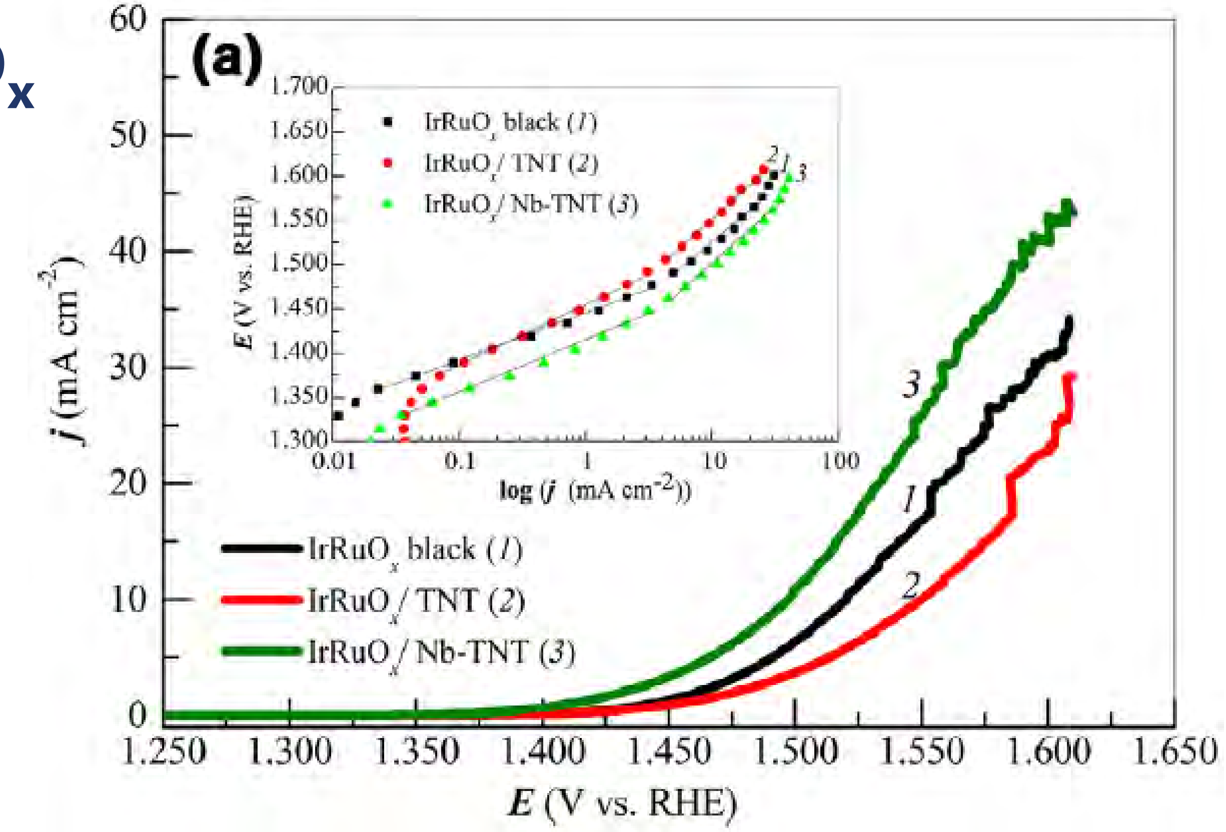
IrO_2 and IrRuOx (Ir:Ru 60:40 at.%) on TiO_2 and **Nb-doped TiO_2 nanotubes**

- \+ TNT – 145 $m^2.g^{-1}$
- \+ **3 wt.% Nb-TNT – 260 $m^2.g^{-1}$** (added corrosion resistance + **enhanced OER activity**)
- \+ **Nb(IV) species**, act as free electron donors to the conduction band of TiO_2
- \+ HSA Nb-doped TiO_2 support: ***IrO_2, $IrRuO_x$ better dispersion; stability and electronic conductivity***

IrO_2



$IrRuO_x$



***j-E* curves**, corrected by IR-drop, normalized by **electrode section**
(0.50 mol dm^{-3} H_2SO_4, 1 mV s^{-1}, T = 25 °C)

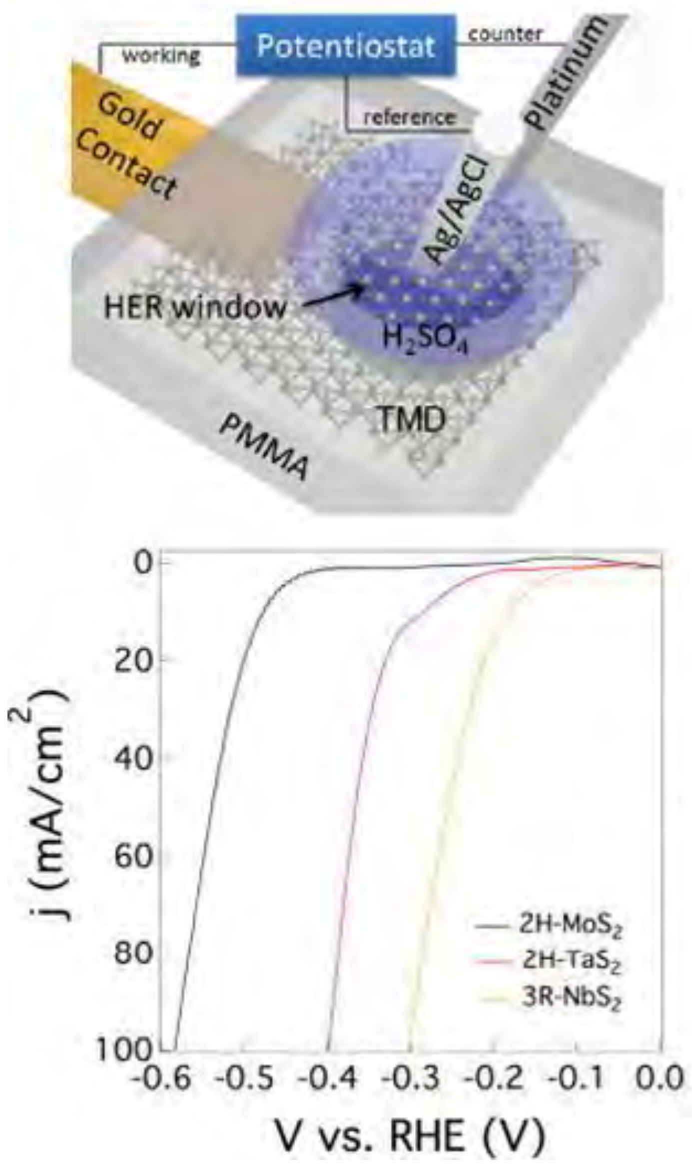
Genova-Koleva et al, ***J Energy Chem*** 34 (2019) 227

PEM WATER ELECTROLYSIS – CATHODE CATALYST

HYDROGEN EVOLUTION REACTION

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

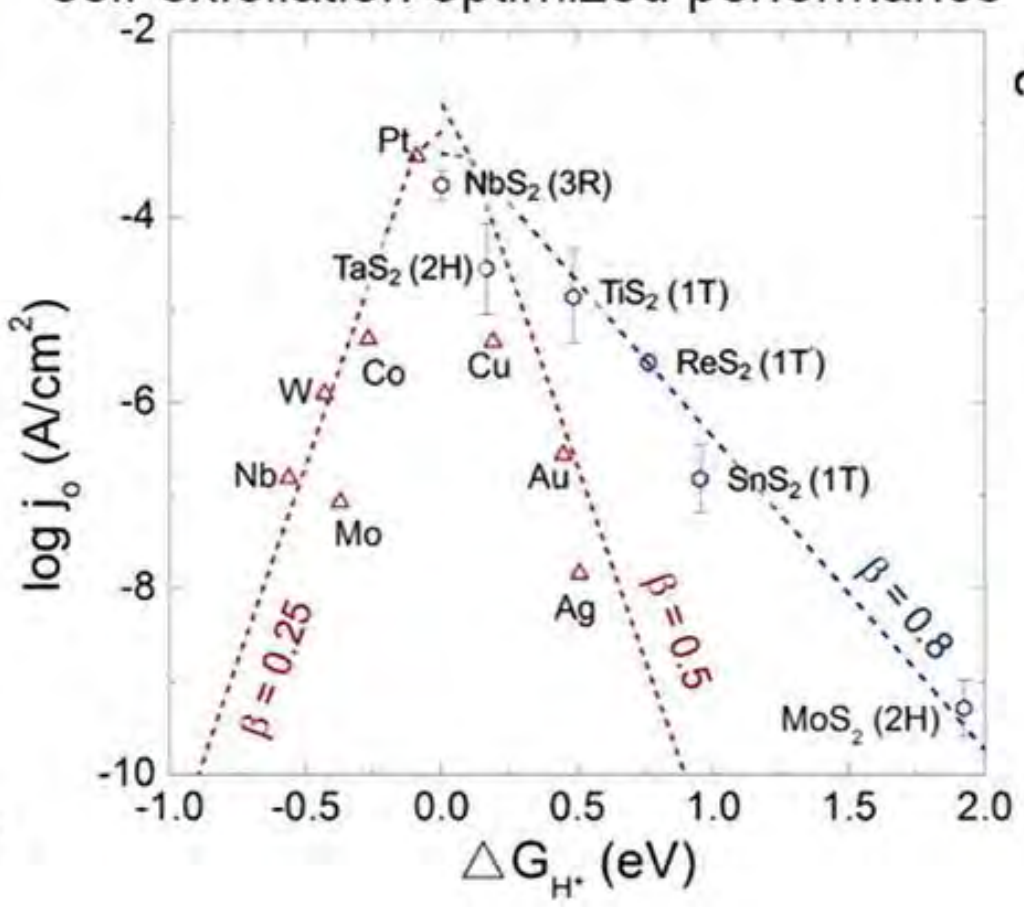
2D TMDs 3R-NbS_2 – Pt replacement

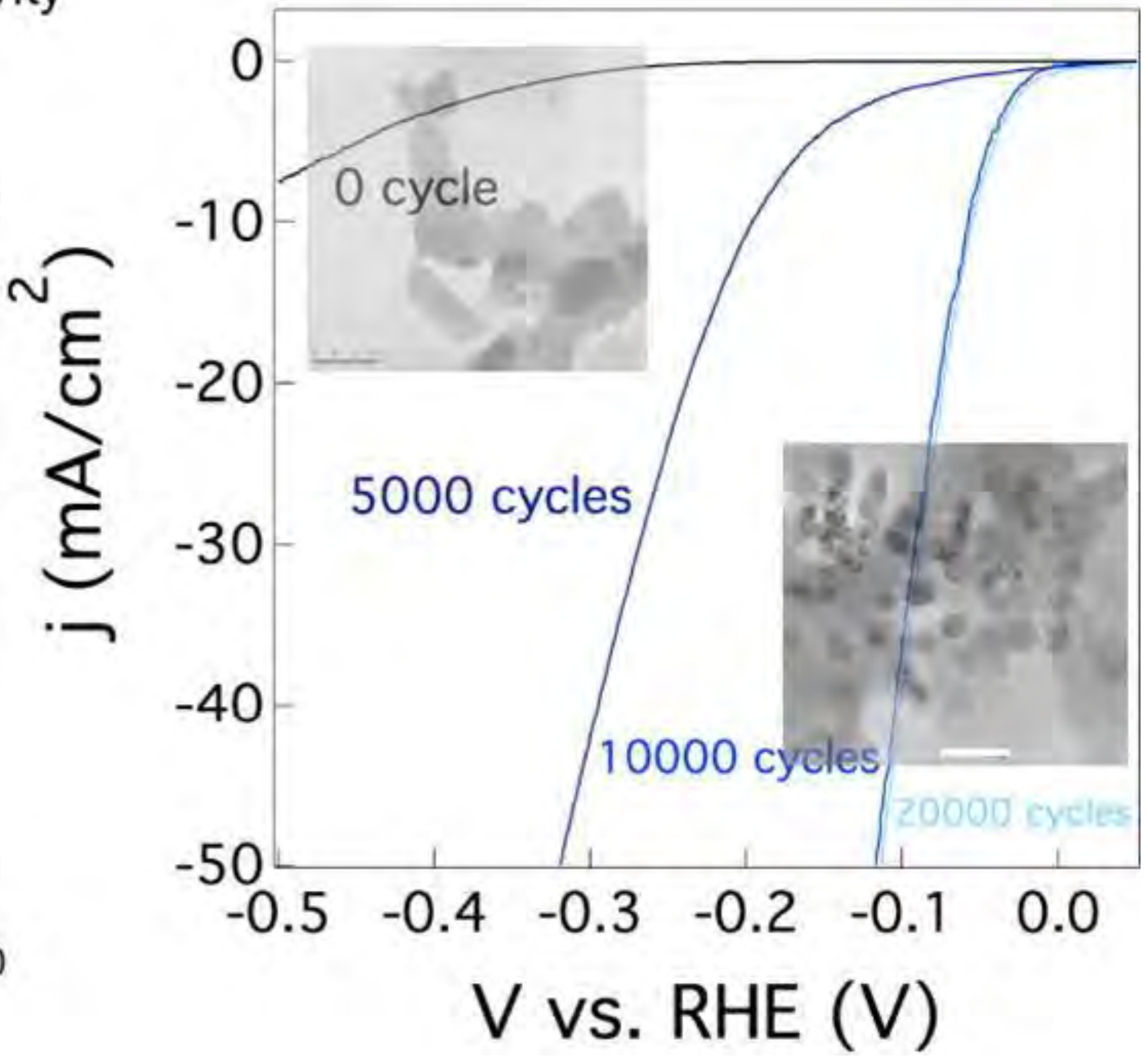


direct identification of basal plane activity

discovery of active 3R-NbS_2

self-exfoliation optimized performance





Volcano plot of transition metals vs. 2D TMDs – **3R-NbS_2 presents similar activity to Pt**

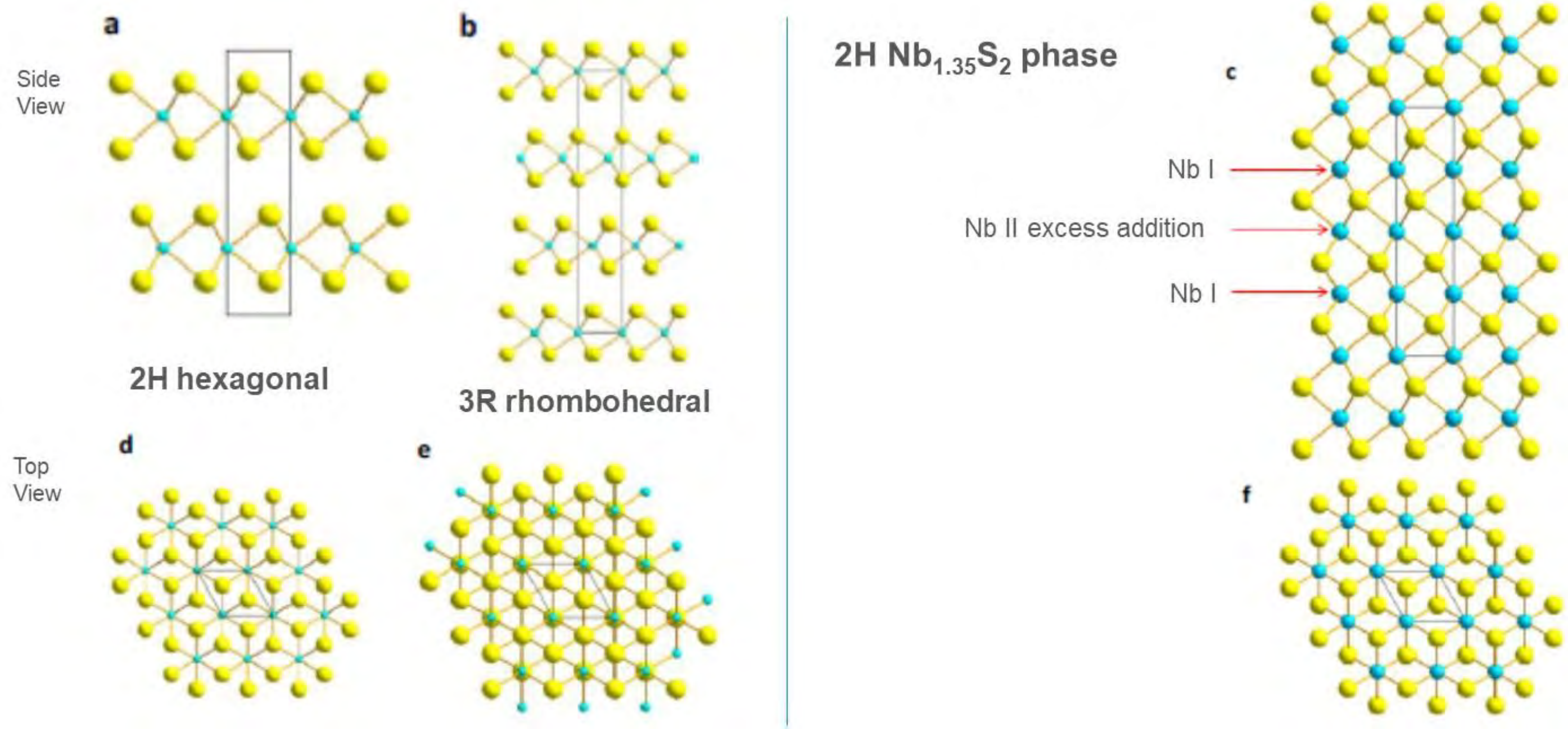
Zhang et al, ***Materials Today*** (2019) in press

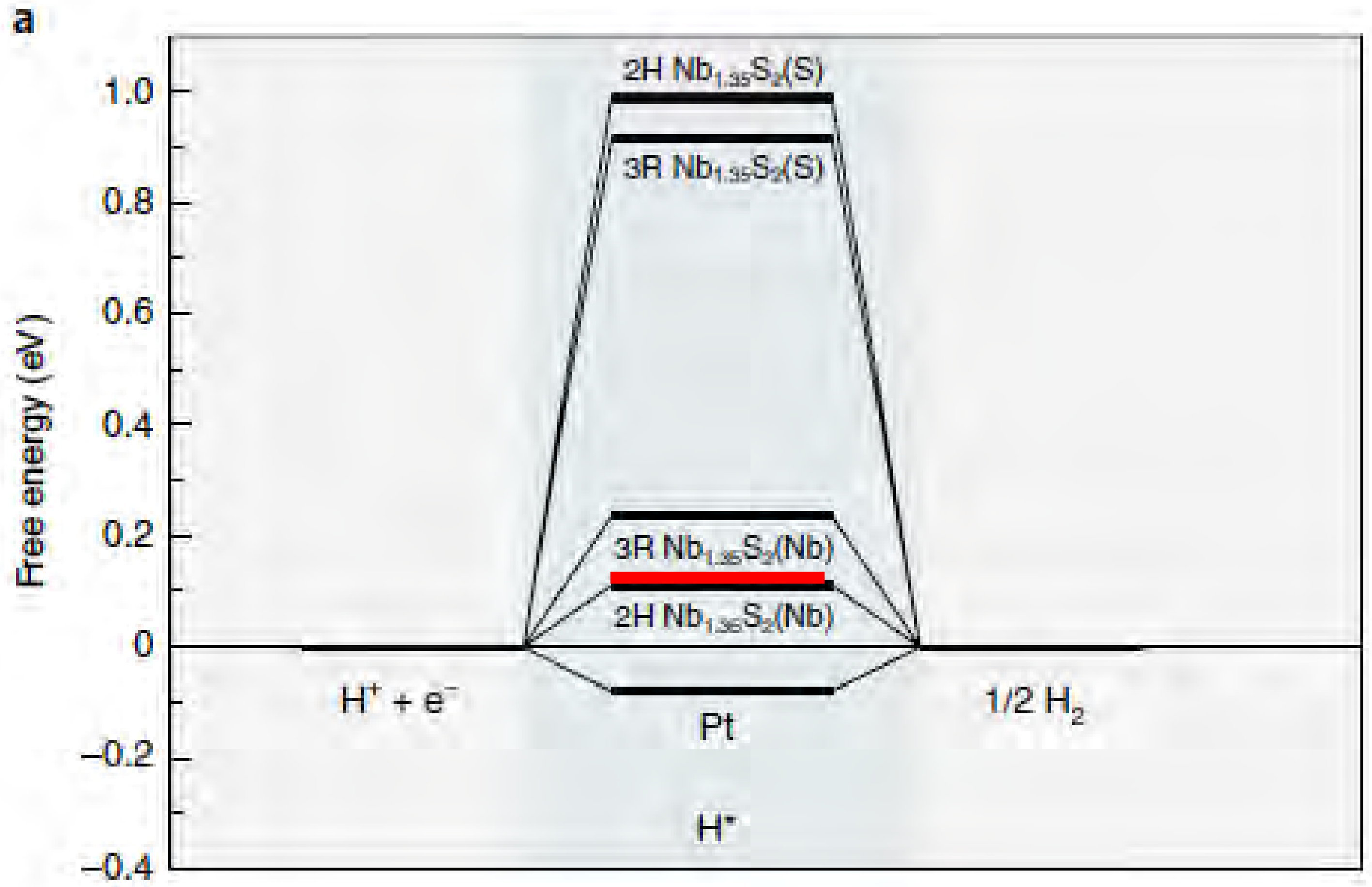
PEM WATER ELECTROLYSIS – CATHODE CATALYST

HYDROGEN EVOLUTION REACTION

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

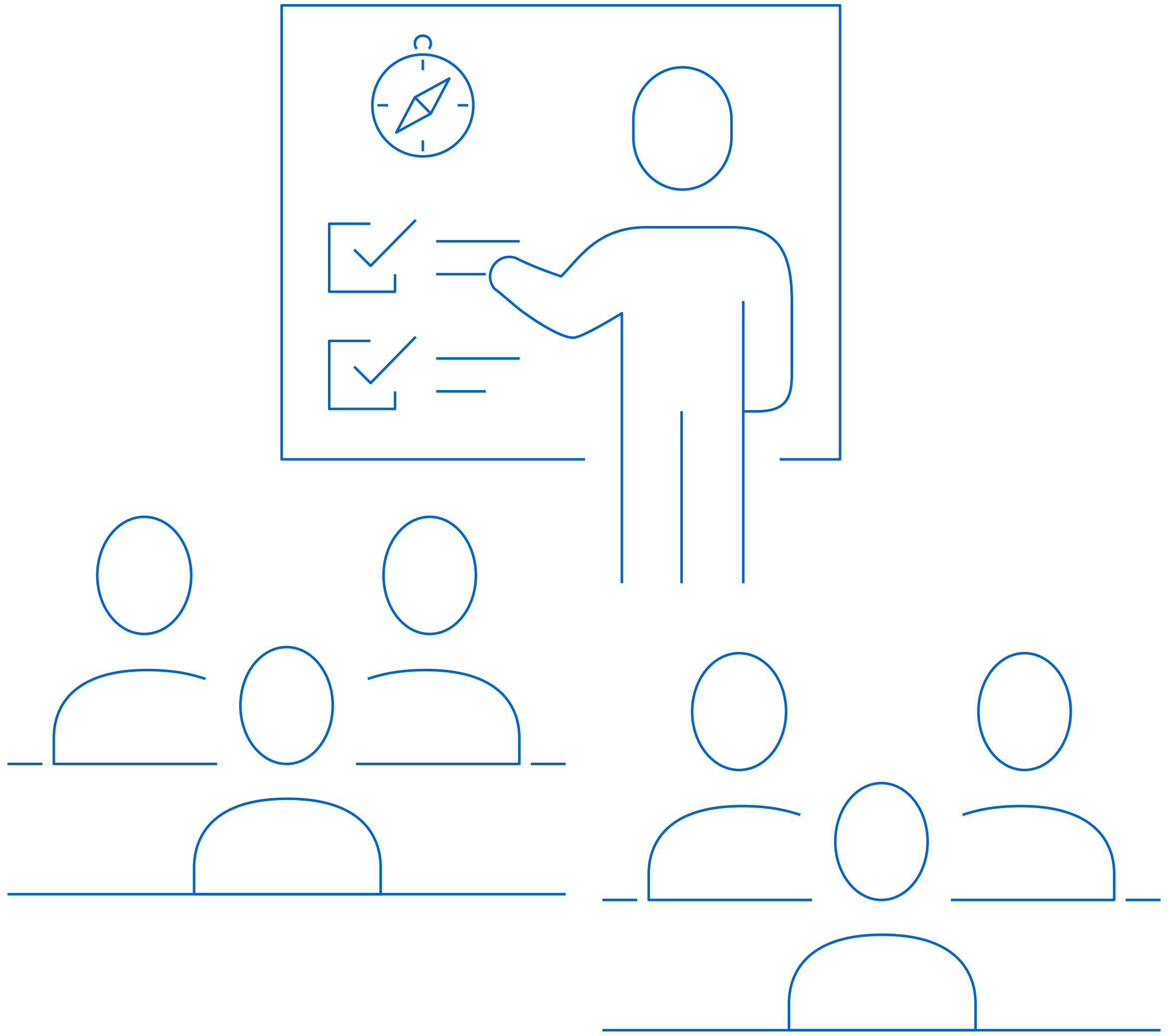
$2H\text{-}Nb_{1.35}S_2$ – Materials Engineering





$2H\text{-}Nb_{1.35}S_2$ is a HER catalyst as good as Platinum

Chhowalla et al, ***Nature Materials*** 18 (2019) 1309



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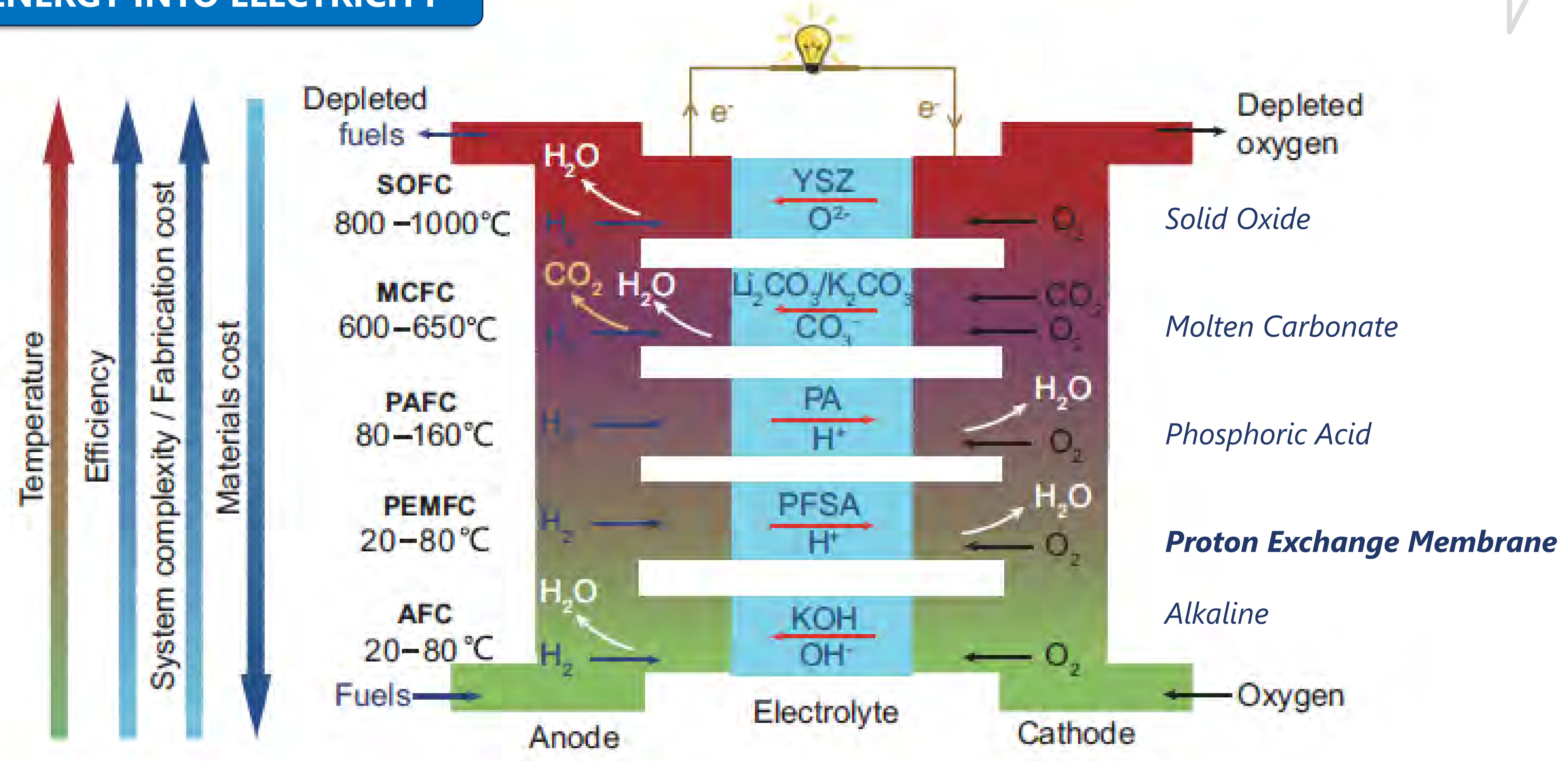
HYDROGEN CONVERSION TECHNOLOGY

FUEL CELLS TYPES

CHEMICAL ENERGY INTO ELECTRICITY

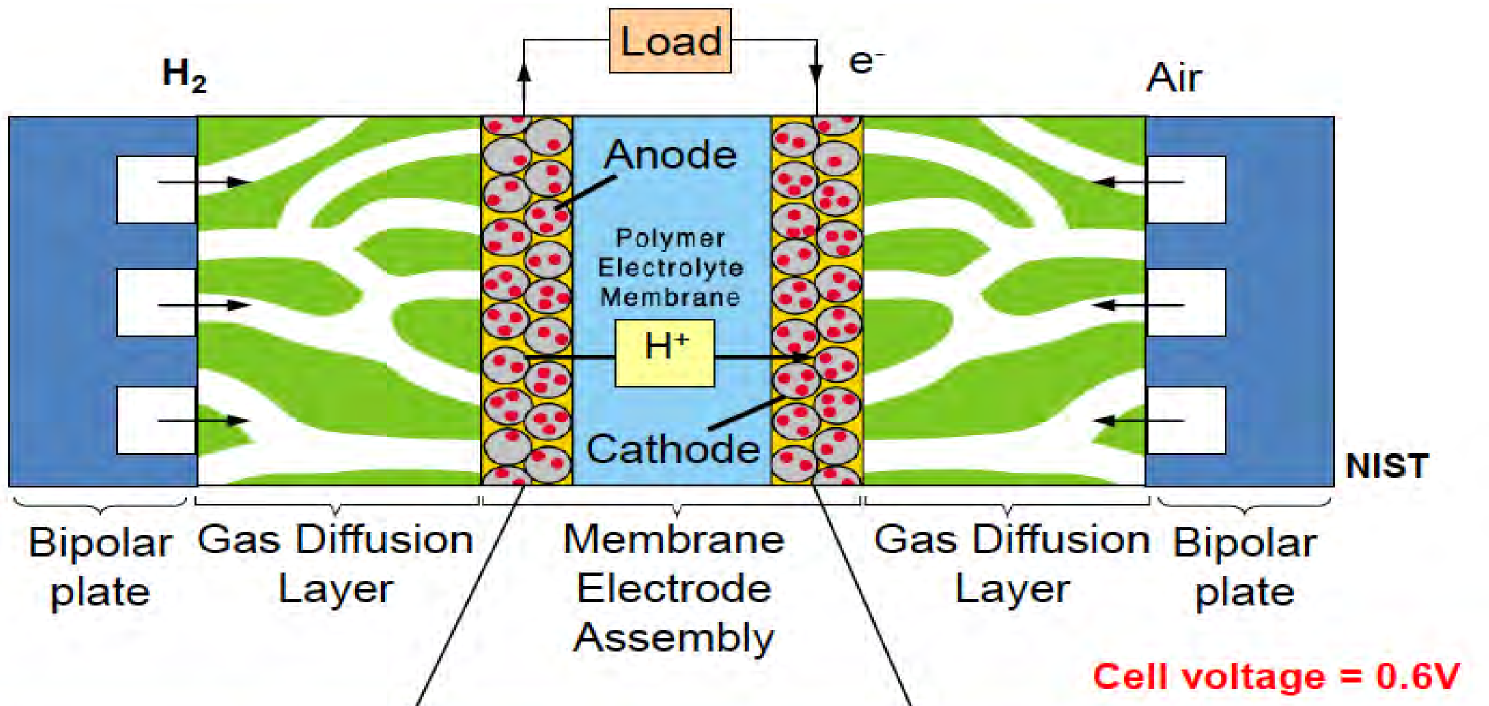


General Trends Relationship

Jiang et al, ***Natl Sci Rev 4 (2)*** (2017) 163

PROTON EXCHANGE MEMBRANE (PEM) FUEL CELLS

CATALYSTS DEVELOPMENT



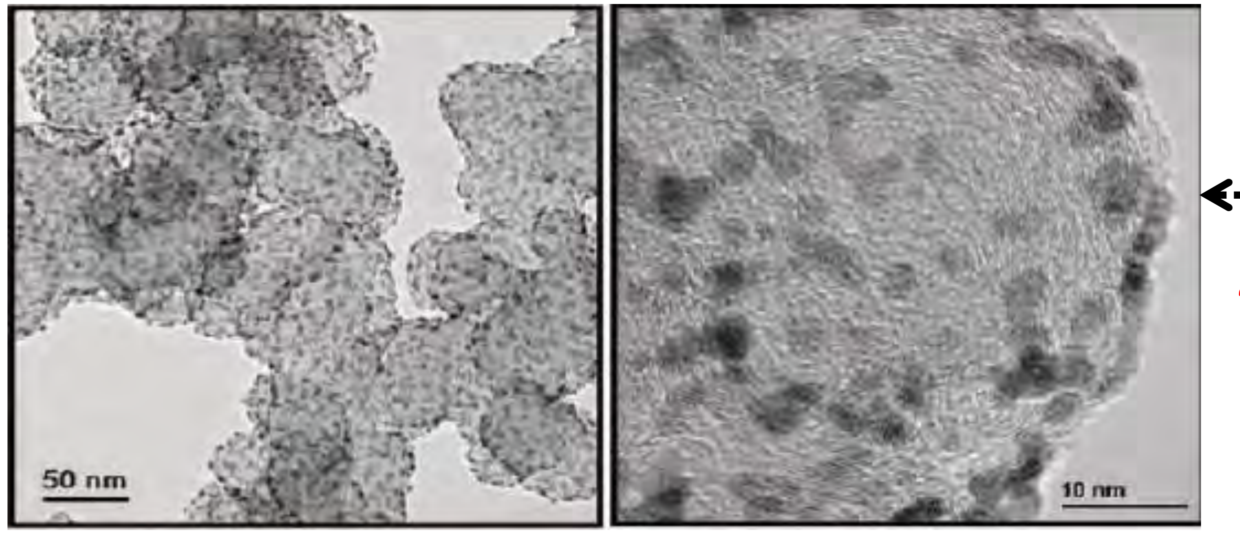
Anode Reaction

$2H_2 \rightarrow 4H^+ + 4e^-$

Cathode Reaction

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

Source: A. K. Prasad, U. Delaware



~ 40 wt.% Pt/C
ORR catalyst

Technical Challenges

- **Pt/C based catalysts** – cathode and anode
- **Cathode ORR activity is slow** - requires large amounts of costly and restricted Pt
- **Pt dissolution** and **carbon support corrosion** in acidic media
- **Anode/Cathode CO and S tolerance** from H_2 streams from steam reforming and air contamination

Development Strategies

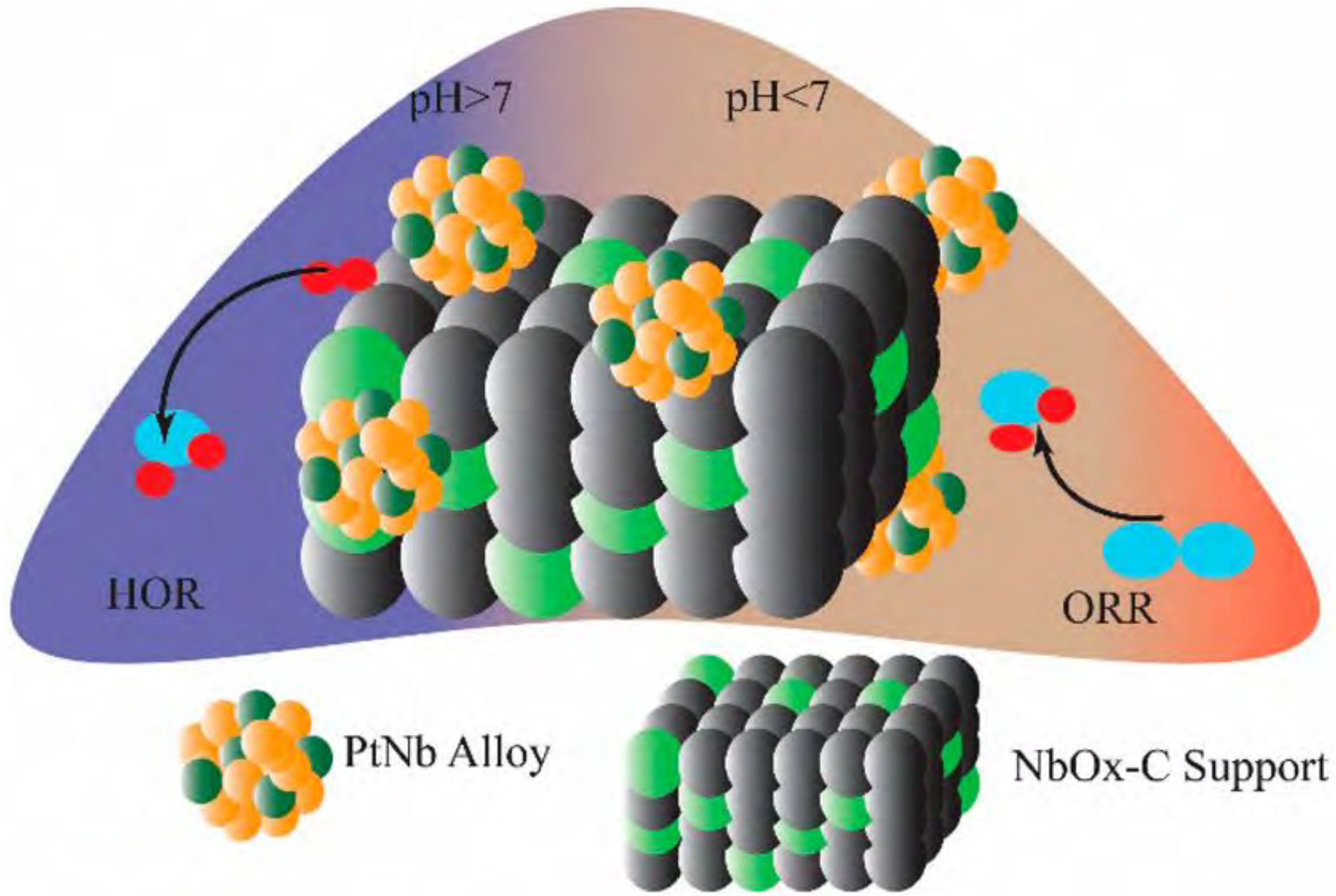
- **Pt Alloying –** e.g., Ni, Co, Ti, Fe**, Nb**, etc.
- **Pt-reduced or Pt-free**
- **Carbon support modification -** composites
- **Carbon-free supports –**TiO_2, SnO_2, **Nb_2O_5**, etc.

PEM FUEL CELLS – NIOBIUM FOR ELECTROCATALYSIS

NIOBIUM PRIME FEATURES

Nb PROPERTIES

- High oxophilicity
- Exceptional stability in acids
- Wide electrochemical window
- Multiplicity of oxidation states



Nb BENEFITS

- Pt ORR activity improved
- ORR catalyst durability enhanced
- Immunity to phosphate anion poisoning
- HOR activity enhanced
- Promote oxidative CO stripping

Mukerjee et al, ***ACS Catalysis*** 7 (2017) 4936

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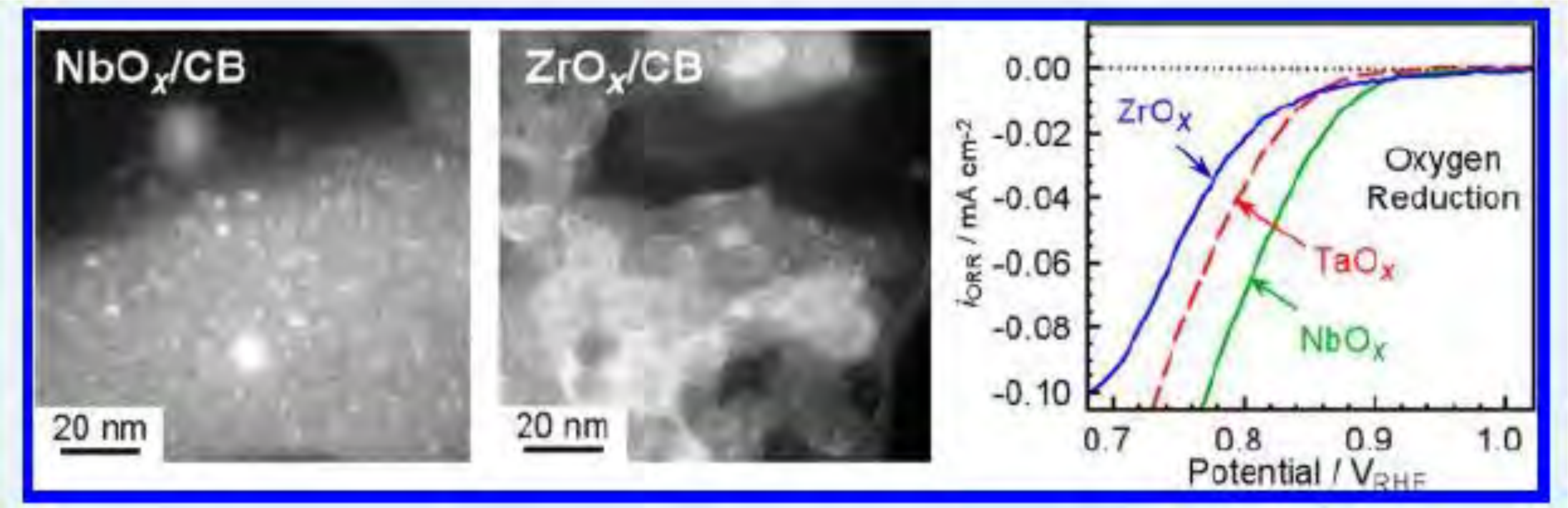
PEM FUEL CELLS – NIOBIUM FOR ELECTROCATALYSIS

PLATINUM FREE CATALYST

NbO_X Nanoparticles

Electrodeposited Ultrafine NbO_x Nanoparticles (2-3 nm) on Carbon Black



- Electrodeposition in nonaqueous metal ethoxide-based solutions at RT;
- High onset potential of NbO_x/CB (0.96 V_{RHE}) for ORR activity;
- High chemical stability;
- Highly dispersed nanoparticle structure with a mixture of fully oxide and suboxide states.

SEO et al, *ACS Catal* 3 (2013) 2181

PEM FUEL CELLS – NIOBIUM FOR ELECTROCATALYSIS

$Nb\text{-}TiO_x$ and $Nb\text{-}TiO_xN_y$ Electrodes

Pt/C electrodes
(1.03-1.05 V)

(Pt-substitute) →

PLATINUM FREE CATALYST

https://www.sdk.co.jp/english/news/2009/aanw_09_1098.html

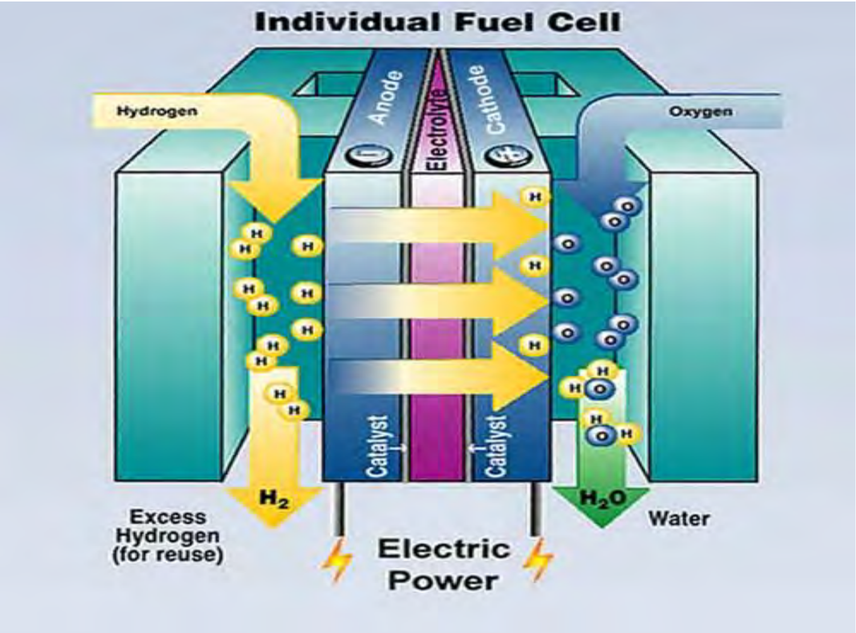
Showa Denko K.K. (Japan)

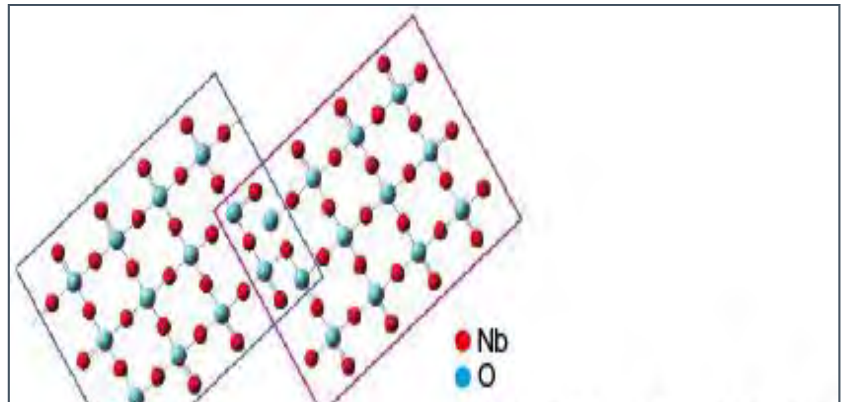
$Nb\text{-}TiO_x$ and $Nb\text{-}TiO_xN_y$ Electrodes

Open circuit voltage: 1.00 V or more

Durability: 500 hrs or more

Production cost: $6/kw





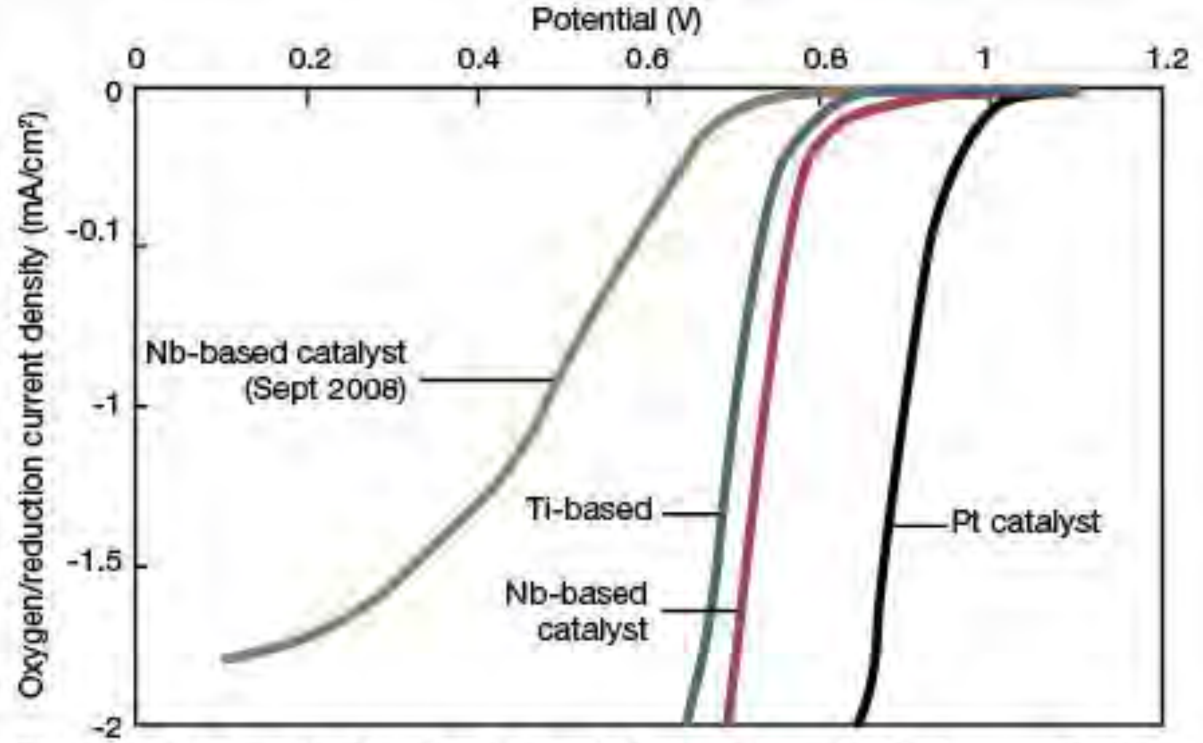


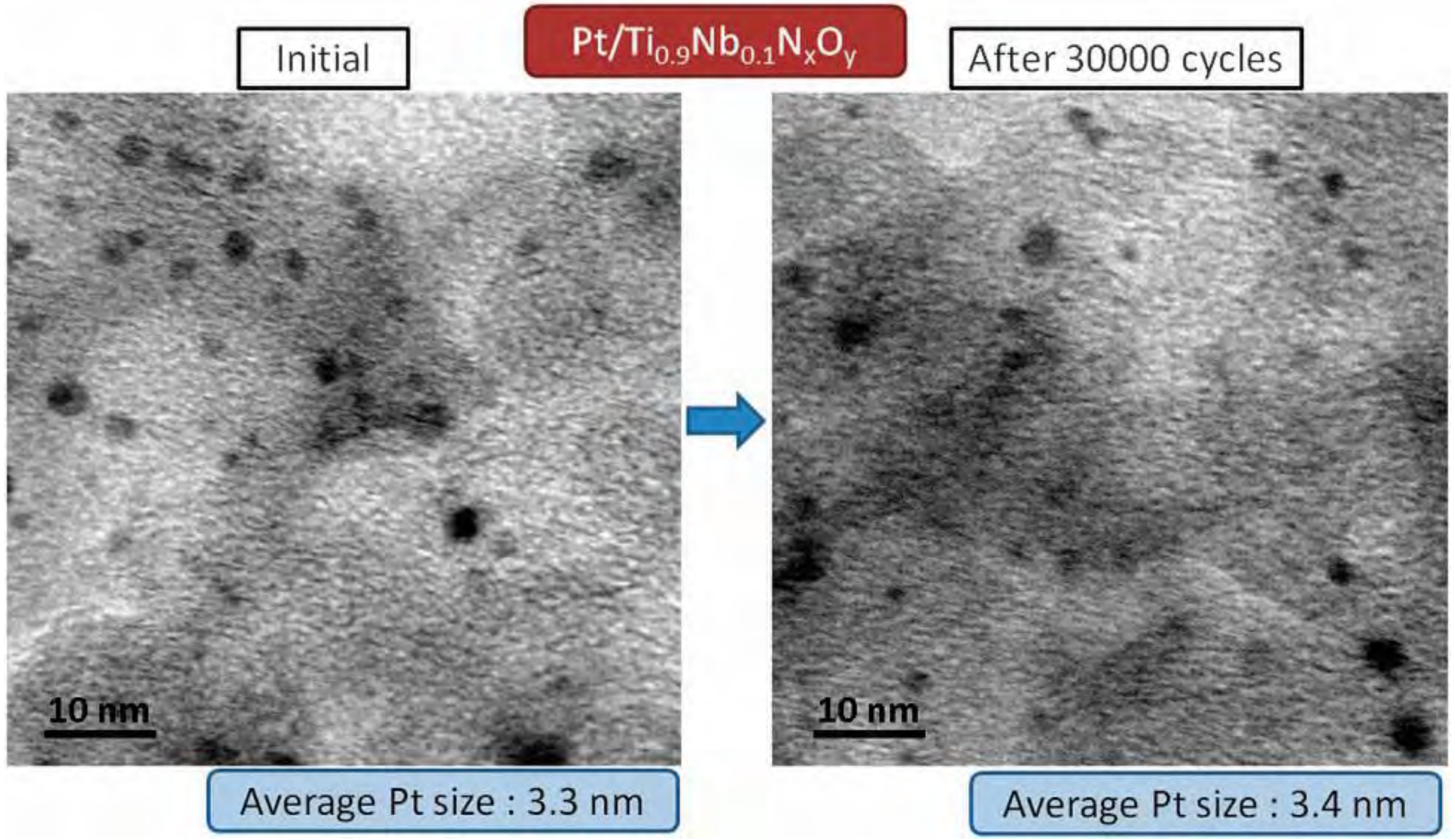
Fig 2 Oxidation/Reduction Potential on a Par with Platinum Both Ni- and Ti-oxide based catalysts have oxidation/reduction potentials of 1V or higher, about the same as Pt catalyst. The characteristics of the Nb-based catalyst have been improved significantly over the Sept 2008 level.

https://phys.org/news/2009-10-platinum-fuel-cell-technology.html

Hybrid & Electric Vehicle Progress, October 15, 2009

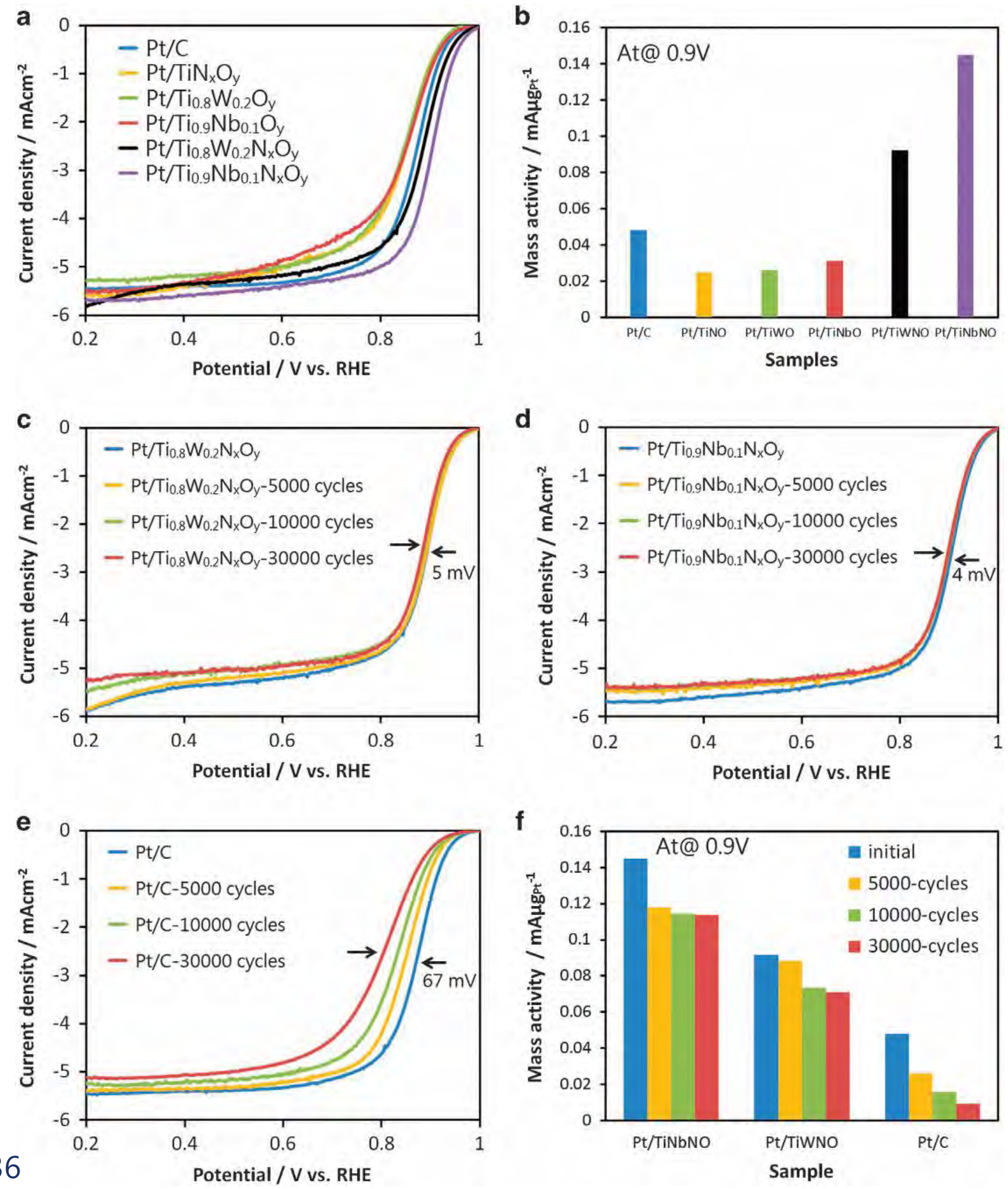
PEM FUEL CELLS – NIOBIUM FOR ELECTROCATALYSIS

Dual-doped Nb (W), N on TiO_x



1. **SMSI effect** leads to high **ORR activity** and stability:
   - Pt electronic state modification
   - Sintering resistance
2. **Dual-doping enhanced** the ***electronic conductivity***

CARBON FREE SUPPORT



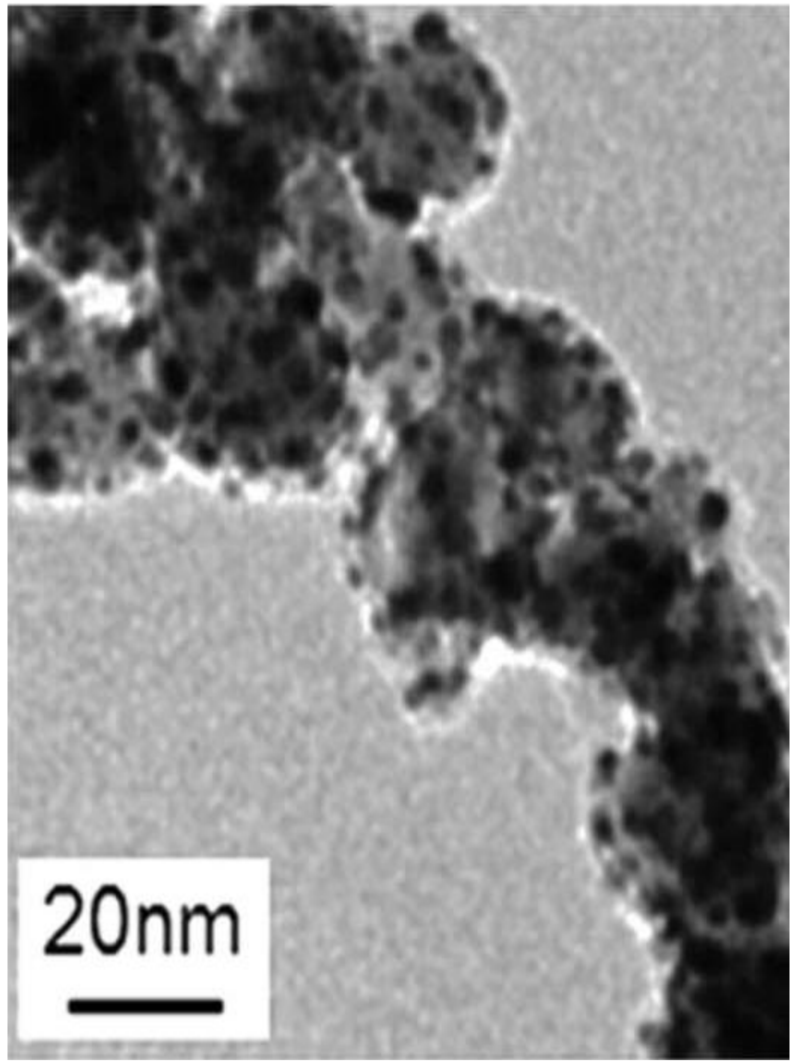
Hwang et al, ***NPG Asia Materials 9*** (2017) 4936

PEM FUEL CELLS – NIOBIUM FOR ELECTROCATALYSIS

CARBON FREE SUPPORT

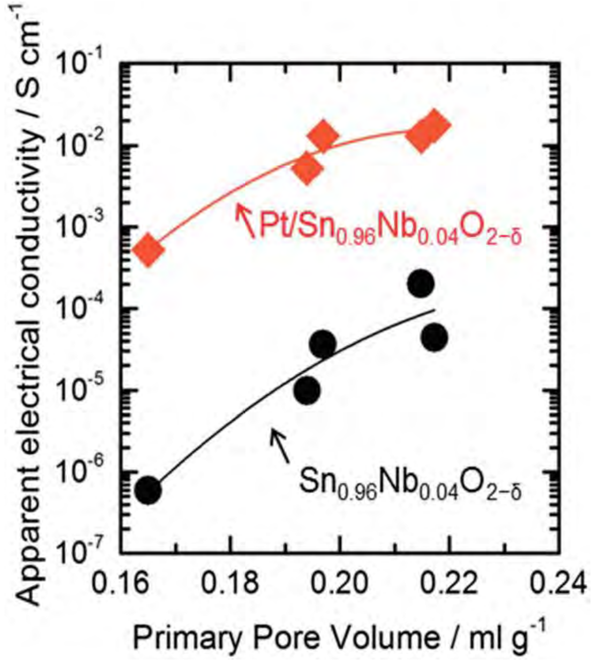
Nb-SnO_x catalyst support

Highly conductive Nb-doped $SnO_{2-\delta}$ nanoparticle supported Pt electrocatalyst



SENOO et al, *RSC Adv* 4 (2014) 32180

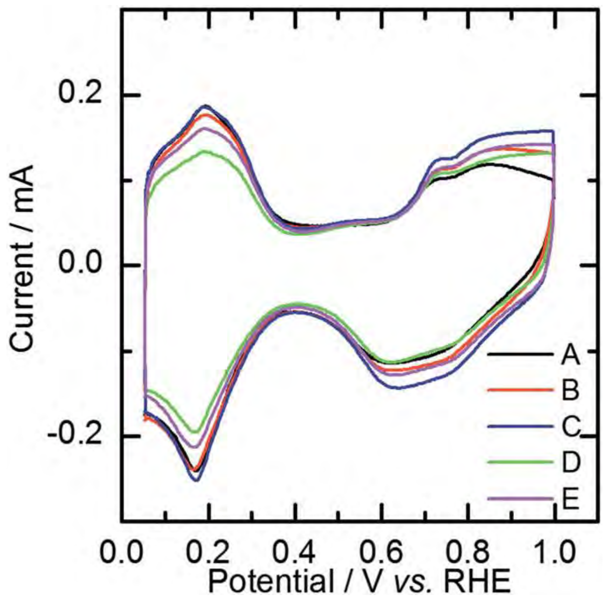
Sample	ESCA/ $m^2\ g^{-1}$	Current density/ $mA\ cm^{-2}$	Mass activity/ $A\ g^{-1}$
Pt/A	70.8	0.62	439
Pt/B	72.4	0.67	485
Pt/C	74.6	1.86	1387
Pt/D	59.4	1.79	1063
Pt/E	77.6	1.99	1544
Pt/CB Commercial	80.0	1.66	1328



Pt/$Sn_{0.96}Nb_{0.04}O_{2-\delta}$
(16.9 wt.% Pt)

Cyclic voltammograms
Sweep rate = 0.1 V s^{-1}
In N_2-saturaded
0.1 mol dm^{-3} $HClO_4$

Onset potential for ORR
0.98 V *vs.* RHE



CONCLUSIONS

Niobium is being increasing used for the synthesis of **advanced electrocatalysts** for **hydrogen production** (Photocatalytic Water Splitting and PEM-WE) **and conversion technologies** (PEM Fuel Cells), allowing:

- ✓ PGM-free and Carbon-free electrodes
- ✓ Higher resistance to corrosion in acidic media
- ✓ PGM higher dispersion and better use of active sites
- ✓ PGM sintering resistance
- ✓ ORR/HOR (PEM Fuel Cells) and OER/HER (PEM-WE) at low overpotentials

…

THANK YOU!

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