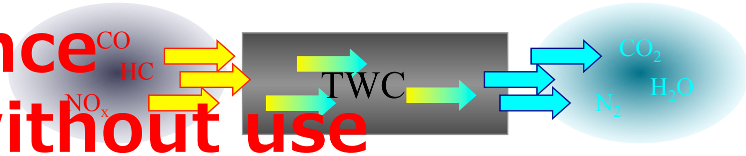
Elements Strategy Initiative for Catalysts and Batteries (ESICB)

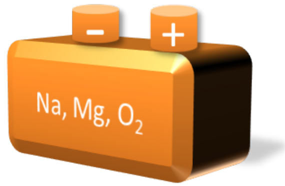
Tsunehiro Tanaka
Kyoto University

AIM of ESICB

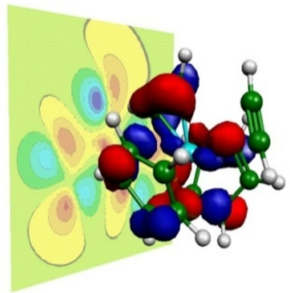


- **Development of high performance catalysts with less use of and without use of critical-elements**
- **Development of critical-elements-free rechargeable batteries of high performance**

Contribution to the realization of sustainable society



- **Elucidation of guidance principles and description of processes during catalysis and battery operation**



Deepening the science of interface and surface of complex and composite systems

- **Development of human resources for next generation**

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ESICB Elements Strategy Initiative for Catalysts & Batteries

Machida GL
Kumamoto University
Okada GL
KYUSHU UNIVERSITY
Komaba GL
TOKYO UNIVERSITY OF SCIENCE
NIMS
Tateyama
AIST
Otani
Nagoya Univ.
Satsuma
京都大学
KYOTO UNIVERSITY
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Tanaka Director
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Hagiwara
Yokohama Nat. Univ.
Dokko
Osaka Univ.
Morikawa
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Hokkaido Univ.
Shimizu
Taketsugu
Yamada Co-Director
THE UNIVERSITY OF TOKYO
Tsukuda GL
National Institutes of Natural Sciences
Institute for Molecular Science
Ehara GL

ESICB Organization

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Director
Catalysts
(Kyoto U.)

A. Yamada
Co-Director
Batteries
(U. Tokyo)

K. Ohta
Project
Manager
(Kyoto U.)

Group leaders

Fundamental

M. Ehara
Electronic Theory
(Inst. Mol. Sci.)

T. Tsukuda
Analysis & Evaluation
(U. Tokyo)

Material Synthesis

M. Machida
TW Catalysts
(Kumamoto U.)

S. Okada
Post LIB
(Kyushu U.)

S. Komaba
Na Batteries
(Tokyo U. Sci.)

Labs:40
Researchers : 120

Kyoto U., U.Tokyo
Inst. Mol. Sci.,
Kyushu U.,
Kumamoto U. ,
Tokyo U. Sci.,

Hokkaido U., NIMS,
Nagoya U., AIST,
Tohoku U., Osaka U.
Waseda U., Kobe U. ,
Nagoya Inst.Technol.,
Tokyo Metropolitan U.,
Yokohama Nat. U., etc.

Target elements

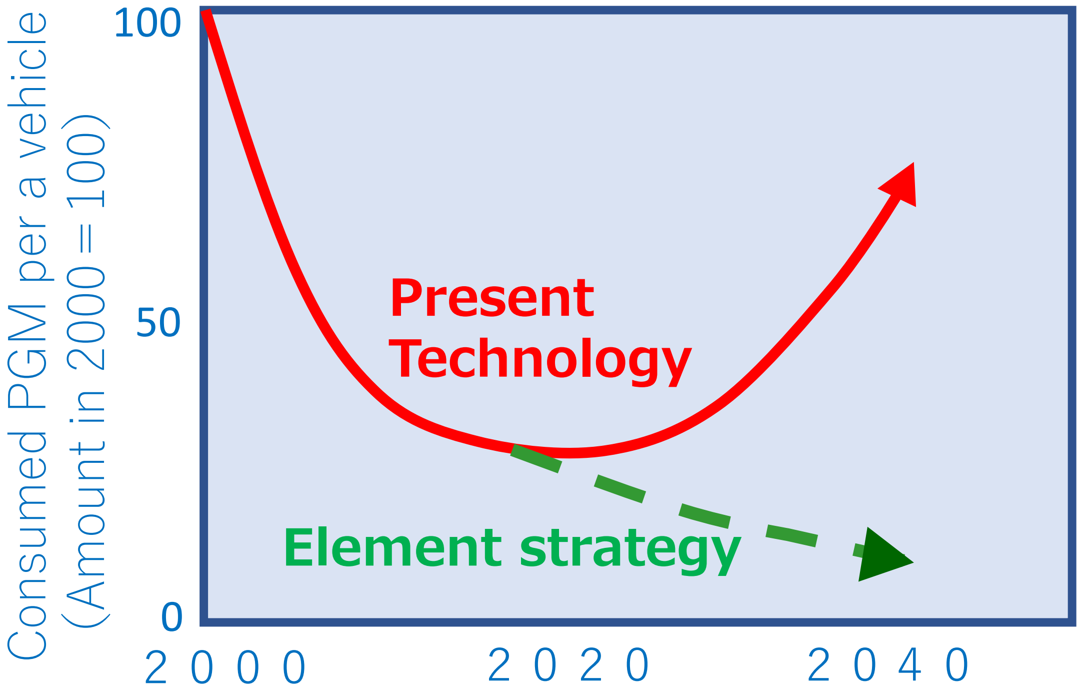
in catalysts and batteries

PGM (Platinum Group Metals) in automotive catalyst

Consumption of PGM for automotive catalyst（2012）

	Mining / ton	Demand / ton	Demand for Automobile / ton	(%)
Pt	190	240	100	(42)
Pd	205	300	210	(70)
Rh	23	30	25	(83)

PGM is essential for automotive catalyst for purification of exhaust gas
- A natural resources issue



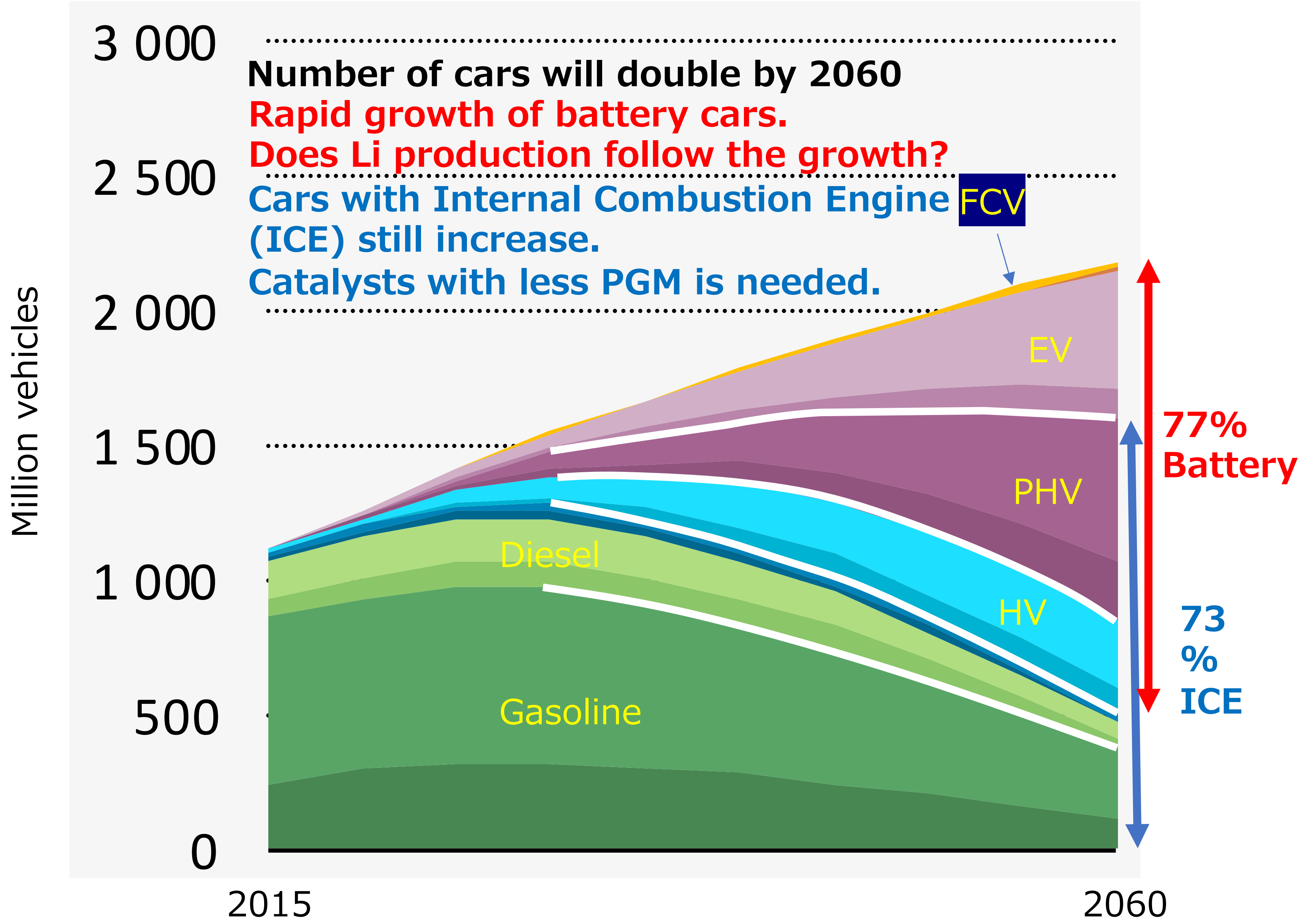
- Severe regulation
- Low temperature of exhaust gas

- Resulting in an increase in PGM use

Technology of less use of PGM or replacement is desired.

IEA forecast of stock-base vehicles -2060

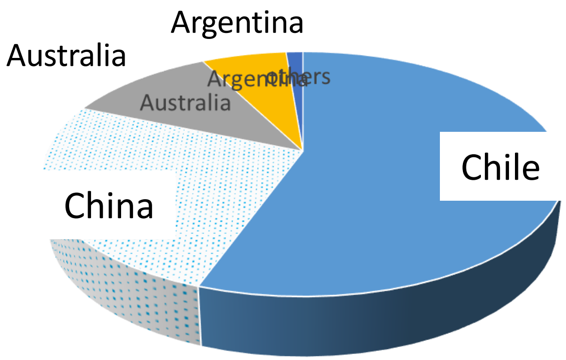
in 2017



Energy Technology Perspectives in 2017, International Energy Agency

Lithium Production

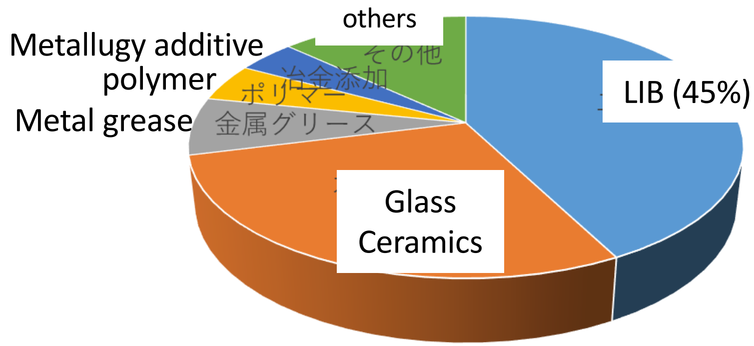
Estimated reserves of Li



84.6 million ton as LCE

Lithium element is uneven distributed.

Classified by use of Li



217 k ton as LCE in 2017

LCE: lithium carbonate equivalent

Ref. USGS, Industrial Minerals

・World production of lithium may not follow the estimated increase of battery cars although the lithium production will also increase.

- Production of 5 millions of battery electric cars is estimated in 2025, corresponding to the use of 150-250 k ton Li as LCE.

And price of lithium remarkably rises up, more than twice during last two years

Rechargeable Battery composed of abundant elements, alternative to LIB is desired.

Main research themes in ESICB

Catalyst

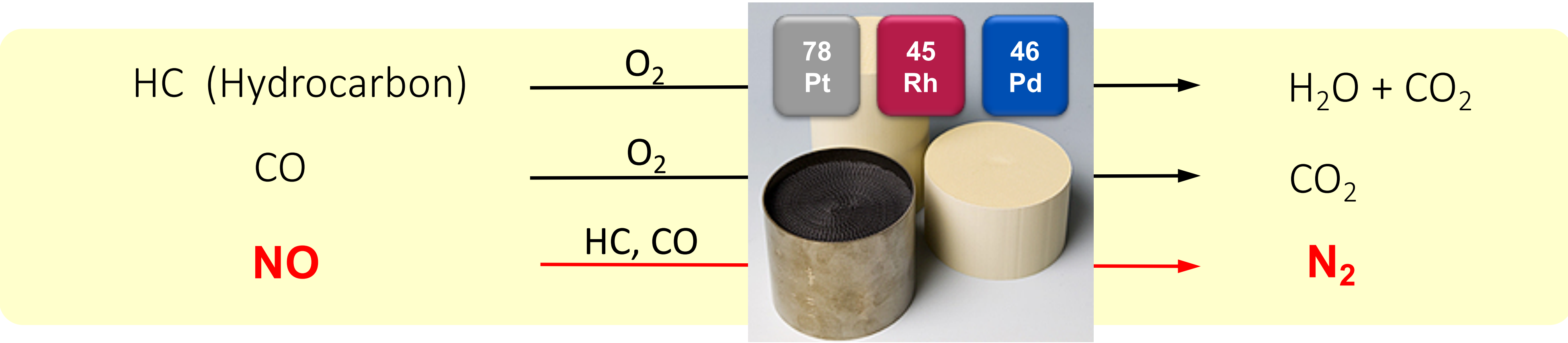
- Reduction of PGM use in TWC (three-way-catalyst) working at low temperature
- Realization of PGM-free TWC comparable to present PGM TWCs

Rechargeable battery

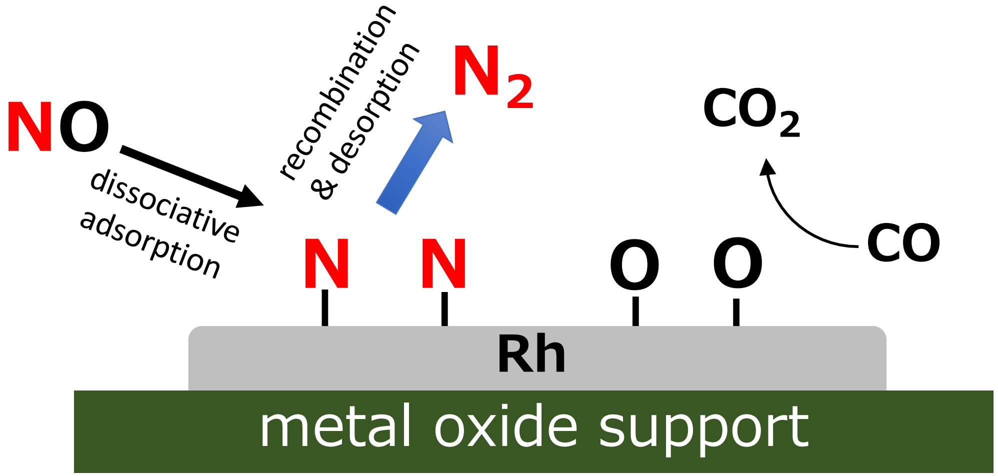
- Establishment of Na battery comparable to LIB
- Proposal of future rechargeable batteries

To save PGM in Three-Way-Catalysts

Purification of exhaust gas from gasoline engine

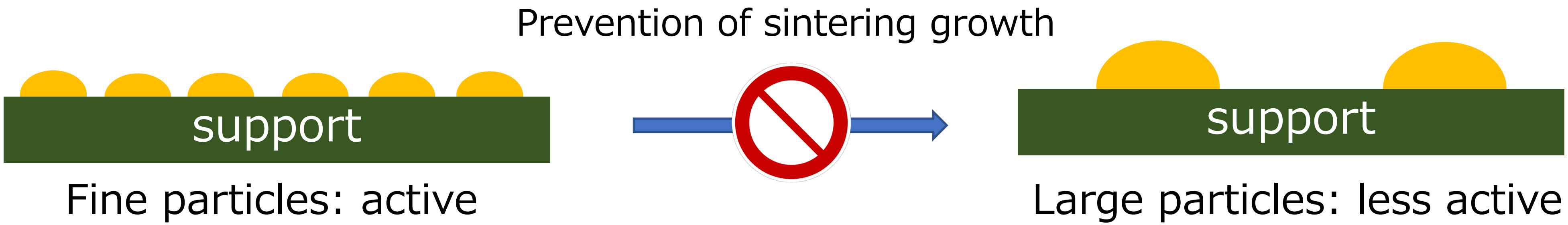


✓ deNOx takes place on PGM surface.



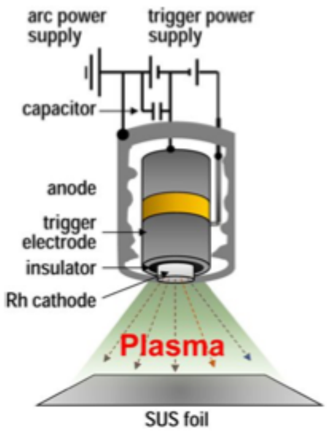
General policy to save PGM

✓ Stabilization of fine PGM nanoparticles and prevention of sintering of particles to **maintain high specific surface area** have been **the way to save PGM**.

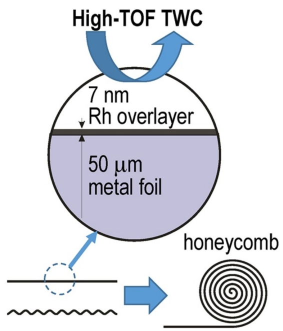


Rh nanofilm catalyst
– enhancement of activity of Rh metal

Collaboration between activity measurement and DFT calculations suggested that Rh(111) plane is the most active for NO reduction rather than nanoparticle with various planes.

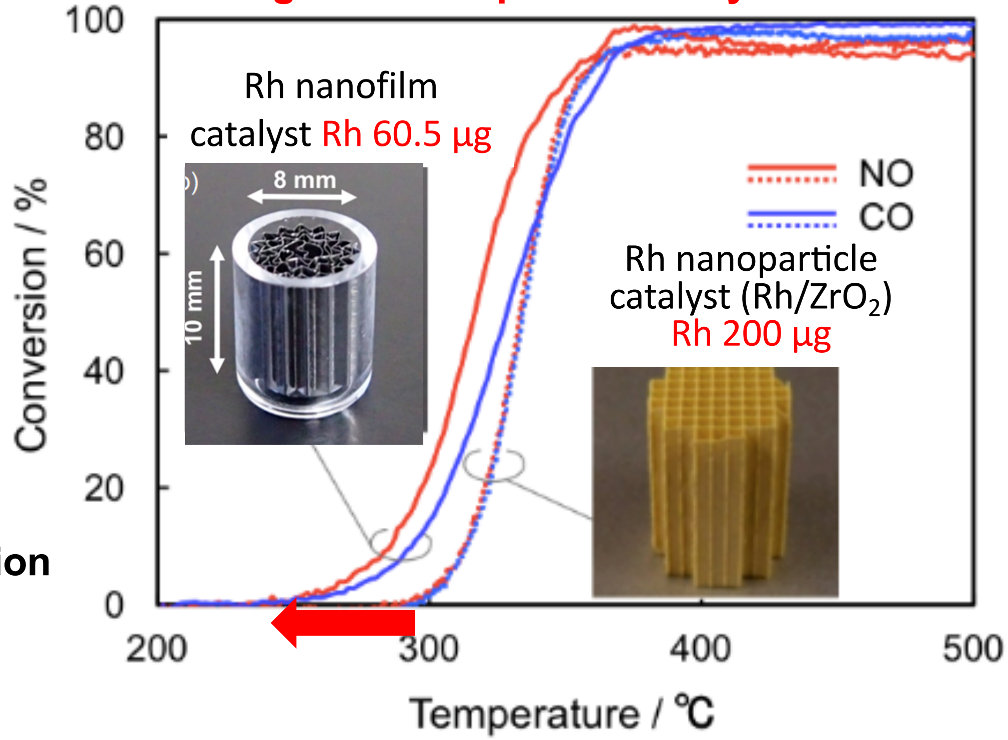


Pulsed AP deposition of Rh onto an SUS foil to create Rh(111) nanofilm

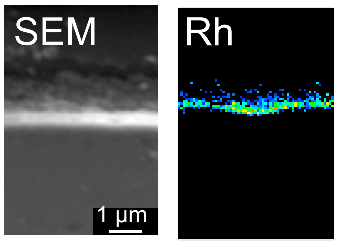


Miniature metal honeycomb fabrication

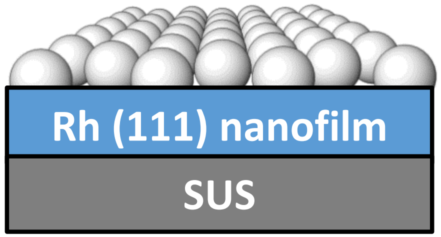
Light-off Temp. lowered by 50℃



1,000 shots of AP pulses



3 nm thickness

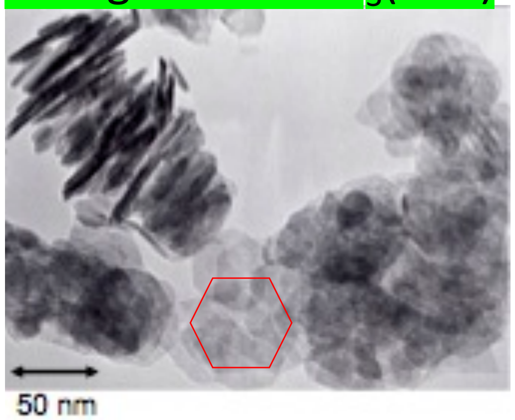


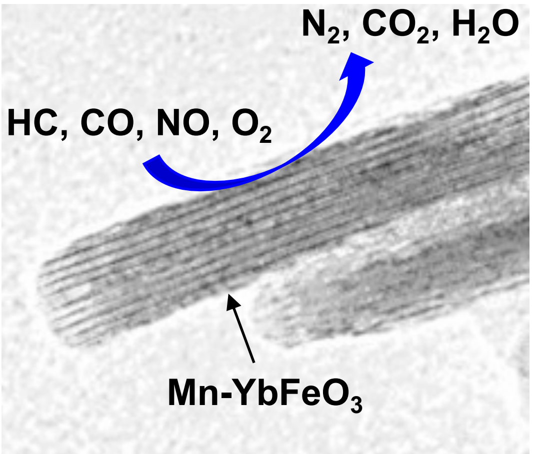
✓**Nanofilm catalyst with 1/3 lower Rh amount** shows higher activity at low temperature than conventional Rh catalyst.

H. Yoshida, K. Koizumi, M. Ehara, J. Ohyama, M. Machida et al., JPCC 2019, 123, 6080. JP2015-166264

Pd/Mn-modified *h*-$YbFeO_3$
– Activating MvK-type NO reduction

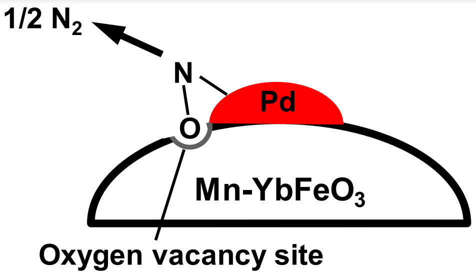
Hexagonal $YbFeO_3$(YFO)





Mn(III), Mn(IV)

$YbFeO_3$ is covered with Mn species in Mn-$YbFeO_3$

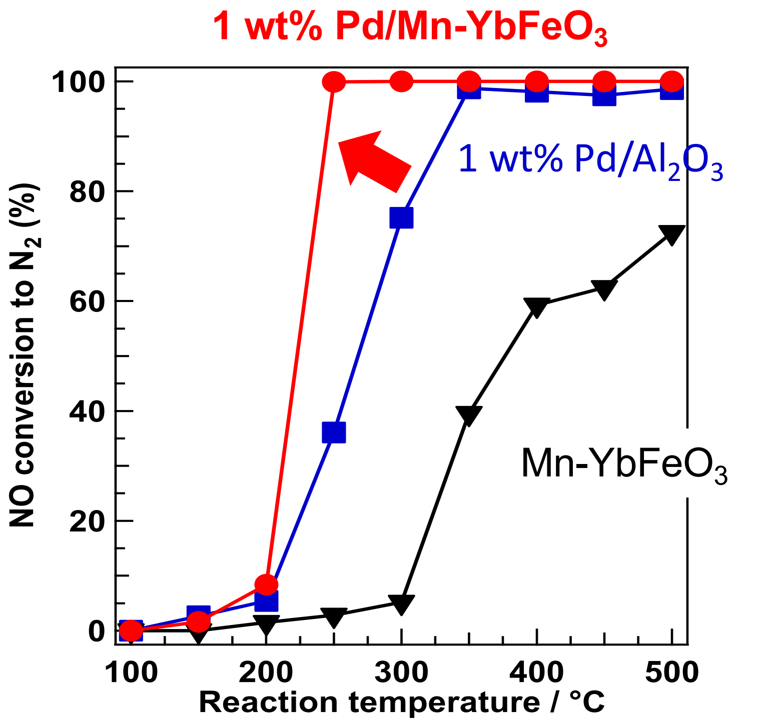


MvK-type NO reduction

$$CO + O_L \rightarrow CO_2 + V_O$$

$$2NO + 2V_O \rightarrow N_2 + 2O_L$$

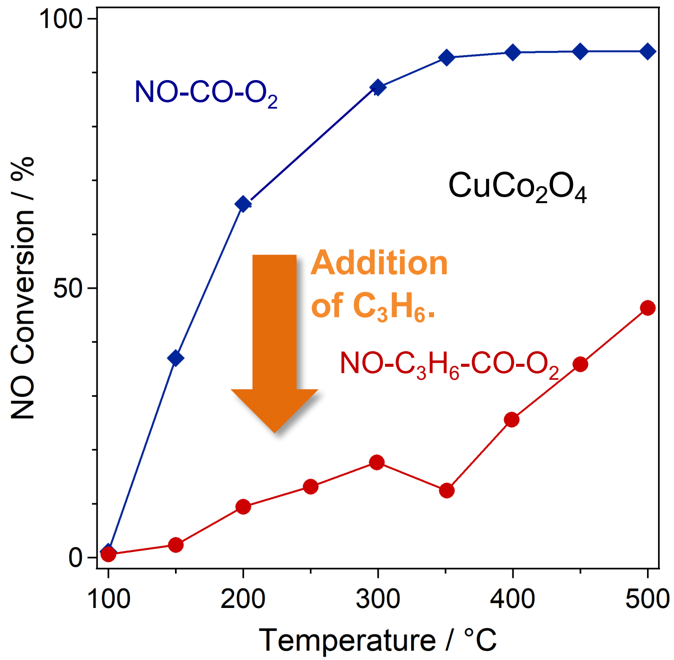
Pd works as a promoter

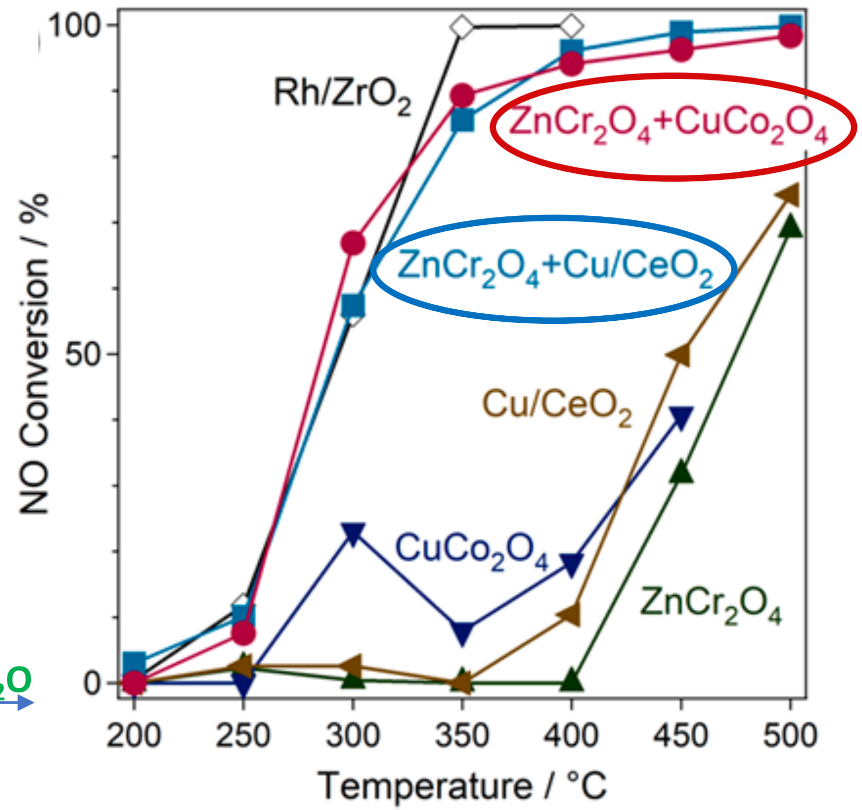


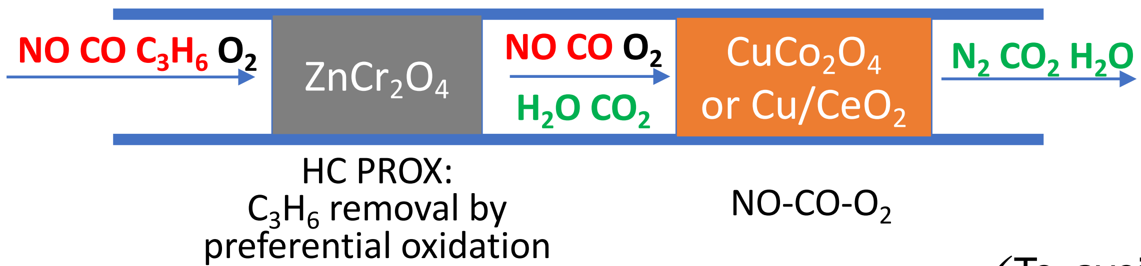
✓By utilizing MvK-type NO reduction mechanism over catalyst support (Mn-$YbFeO_3$), **PGM use can be reduced to 1/10.**

S. Hosokawa, K. Teramura, T. Tanaka et al, Catal. Sci. Technol. 2016, 6, 7868. PCT/JP2016/057771

Realization of PGM-free tandem catalyst: $ZnCr_2O_4$ + $CuCo_2O_4$, $ZnCr_2O_4$+Cu/CeO_2





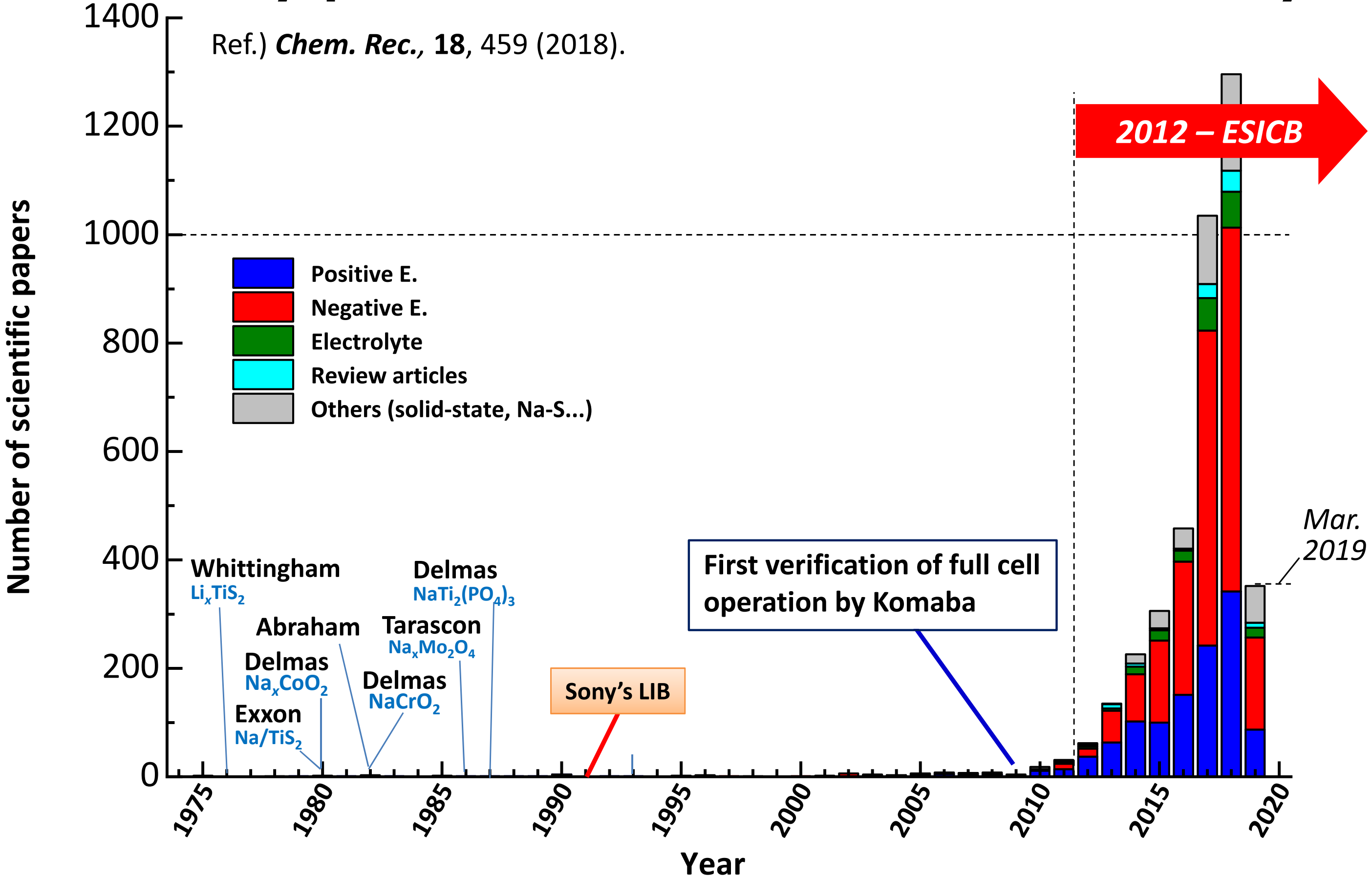


✓To avoid site-poisoning, **base metal oxide catalyst** for preferential oxidation of C_3H_6 was placed at upstream of Cu/CeO_2, resulting in **high activity comparable to Rh benchmarking catalyst.**

J. Ohyama, A. Satsuma et al., ACS Catal., 2019, 9, 2866. JP2018-098843

Positive electrode for sodium ion battery

Yearly publications related to Na battery

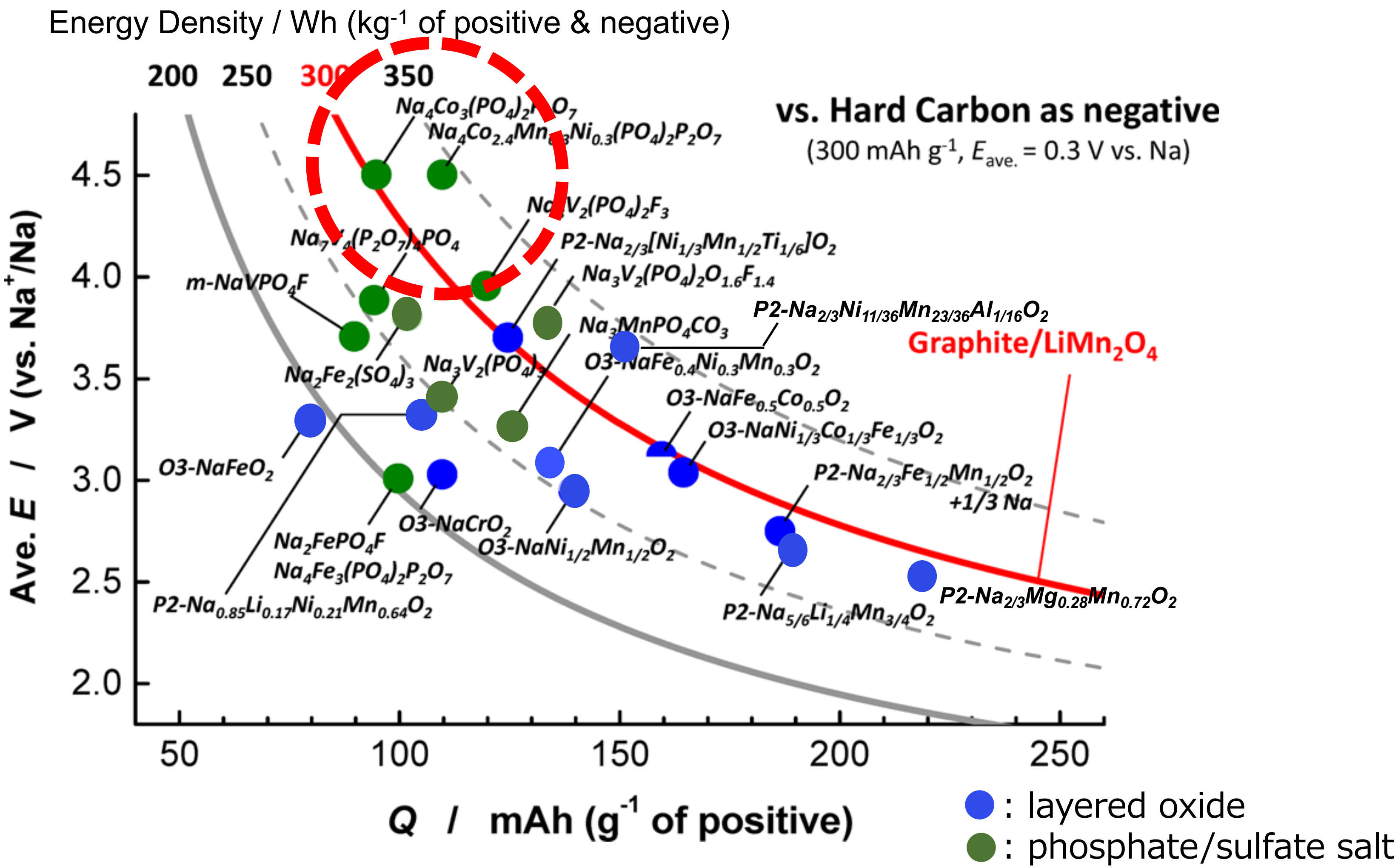


Discovering and searching for cathode materials
as well as development of ionic liquid for electrolyte

Na: disadvantage against Li:
Heavier atomic weight and more positive redox potential
Na: advantage:
High natural abundance and larger ionic radius

Variety of cathodes for Na battery

Effective cathode materials reported till 2015



ESICB's list of cathode materials is at the level of international database.

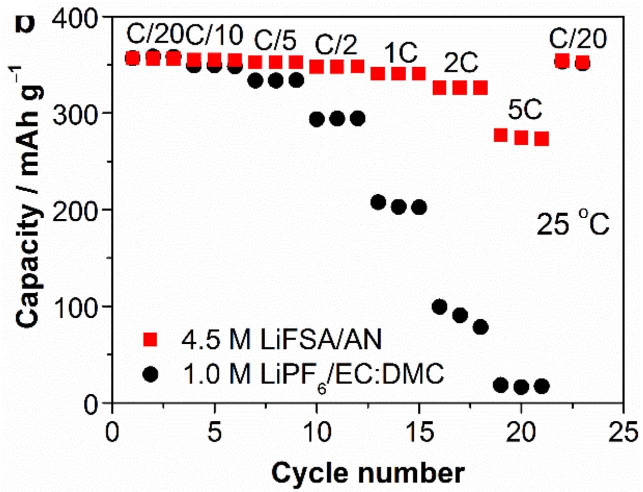
Revision of Fig. 26 in Yabuuchi, Kubota, Dahbi, Komaba, *Chem. Rev.*, 2014, 114, 11636

Unusual behavior of superconcentrated electrolytes
- The second start of highly concentrated electrolytes

4.5 M LiFSA/AN (acetonitrile)/ Li - Graphite anode

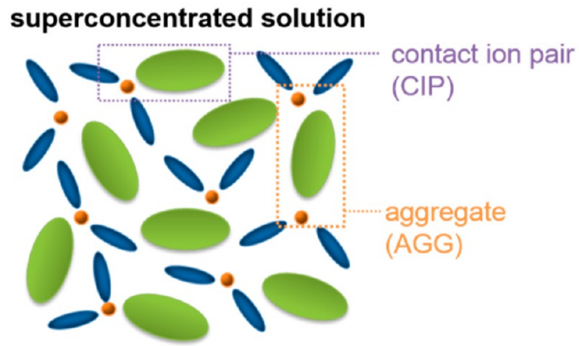
Molar ratio: Li/AN= 1/2

Performance of Li-graphite anode half cell



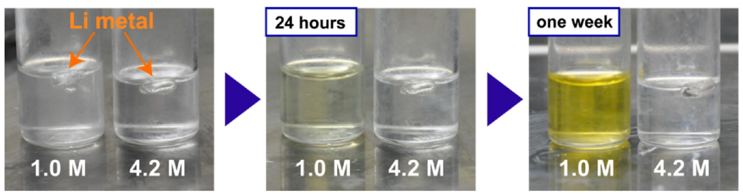
High rate and stable operation

CP-DFT-MD simulation



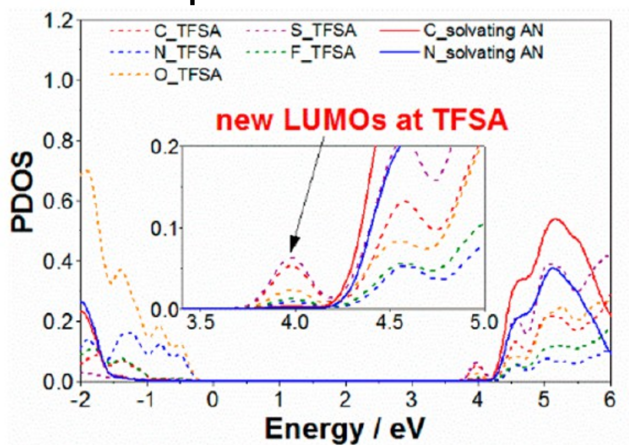
No free solvents or anions

Reactivity of Li and LiFSA/AN solutions



Enhancement of reductive stability of solvent

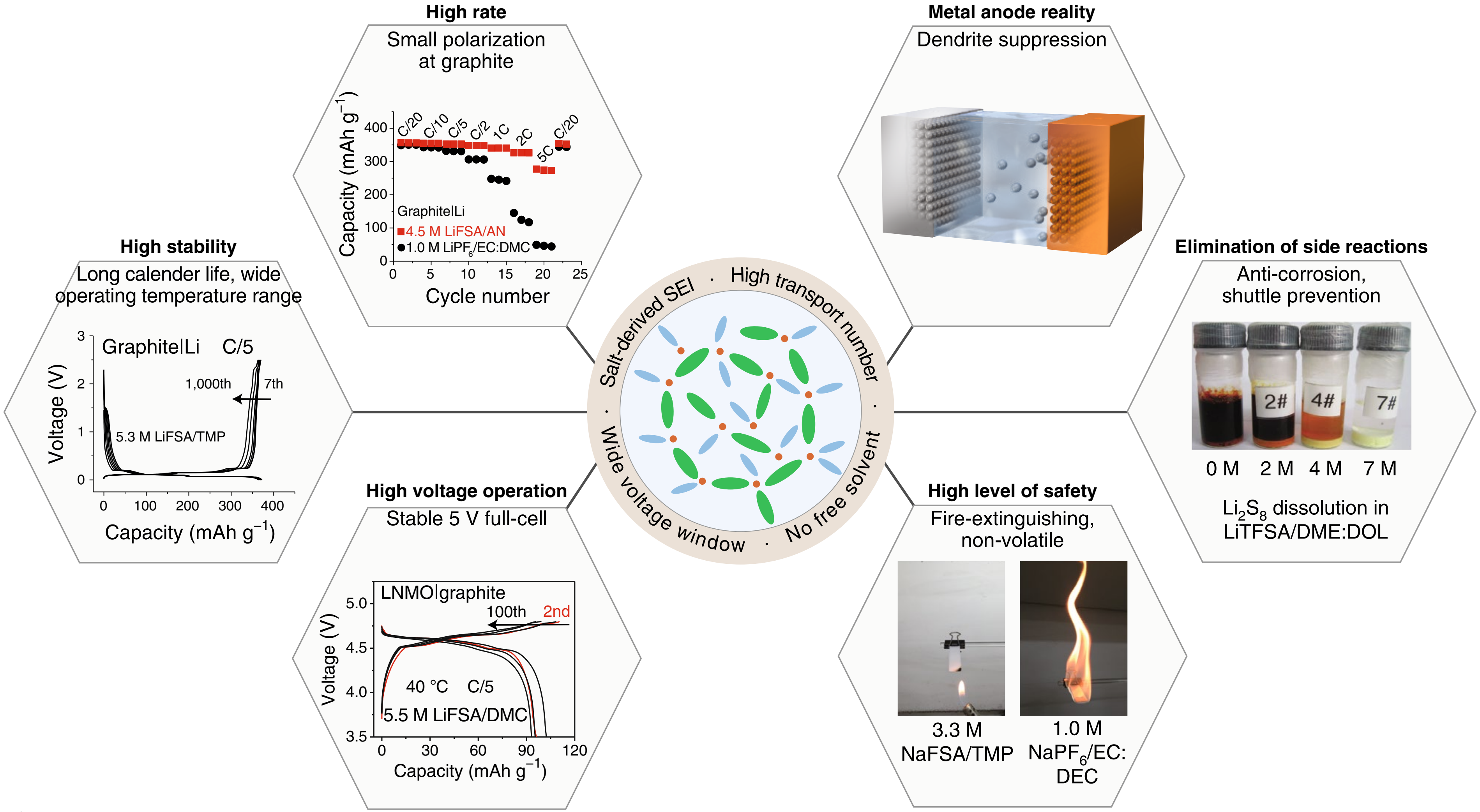
PDOS of superconcentrated solution



SEI film is formed by decomposition of anions

Y. Yamada, K. Sodeyama, Y. Tateyama, A. Yamada et al., J. Am. Chem. Soc., 2014, 136, 5039.

Superconcentrated electrolytes



Multiple functionality of superconcentrated electrolytes applicable to both Na and Li batteries

Publications and Patent Applications

Original papers

	Total publications	5＜I.F.＜10	10＜I.F.
2012	18	6	0
2013	97	20	4
2014	272	57	14
2015	200	41	16
2016	204	54	12
2017	245	58	11
2018	254	44	27

Patent applications

	Domestic	Inter-National
2012	2	0
2013	5	1
2014	4	1
2015	4	6
2016	6	1
2017	9	3
2018	4	5

Summary and vision for the future

Achievement

Catalysis

・Establishment of methodologies for reduction of PGM use in TWC
・Design of PGM-free TWC

Battery

・Proposal of sodium ion battery comparable to lithium ion battery
・Discovery of multiple functionality of superconcentrated electrolytes

Social implementation

Testing stage for practical use

・ 6 for catalyst and 7 for battery materials and technologies

Final stage of commercialization

・ 5 for catalyst and 4 for battery materials and technologies, and 4 softwares

Projects in the final term

Catalysis

・Realization of PGM-free TWC
・Development of TWC operatable at very low temperature

Battery

・Development of cathodes for high energy density
・Development of future battery; solid state Na battery, battery with aqueous electrolytes, etc.

Electrocatalysis

・Development of PGM-free/PGM less used cathodes of fuel cell
・Development of PGM-free OER and ORR electrocatalysts

Future vision of ESICB center at Kyoto University

・11ESICB unit will be continued after finishing the project. Upgrading the unit to independent center is planned.
・Strengthening the association among catalyst center at Kyoto and battery center at Tokyo tightly bound with the group of electronic theory at IMS