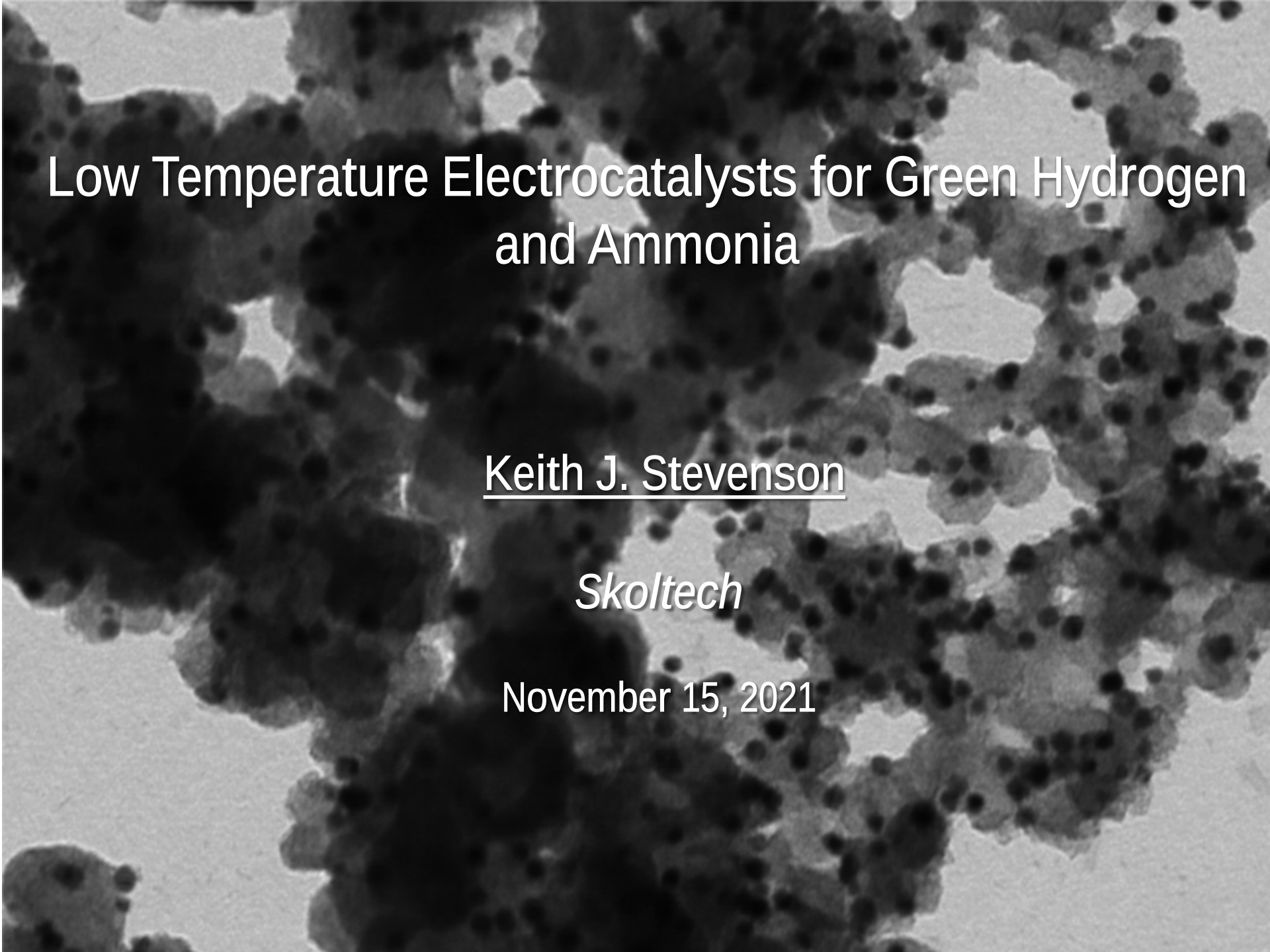


Low Temperature Electrocatalysts for Green Hydrogen and Ammonia

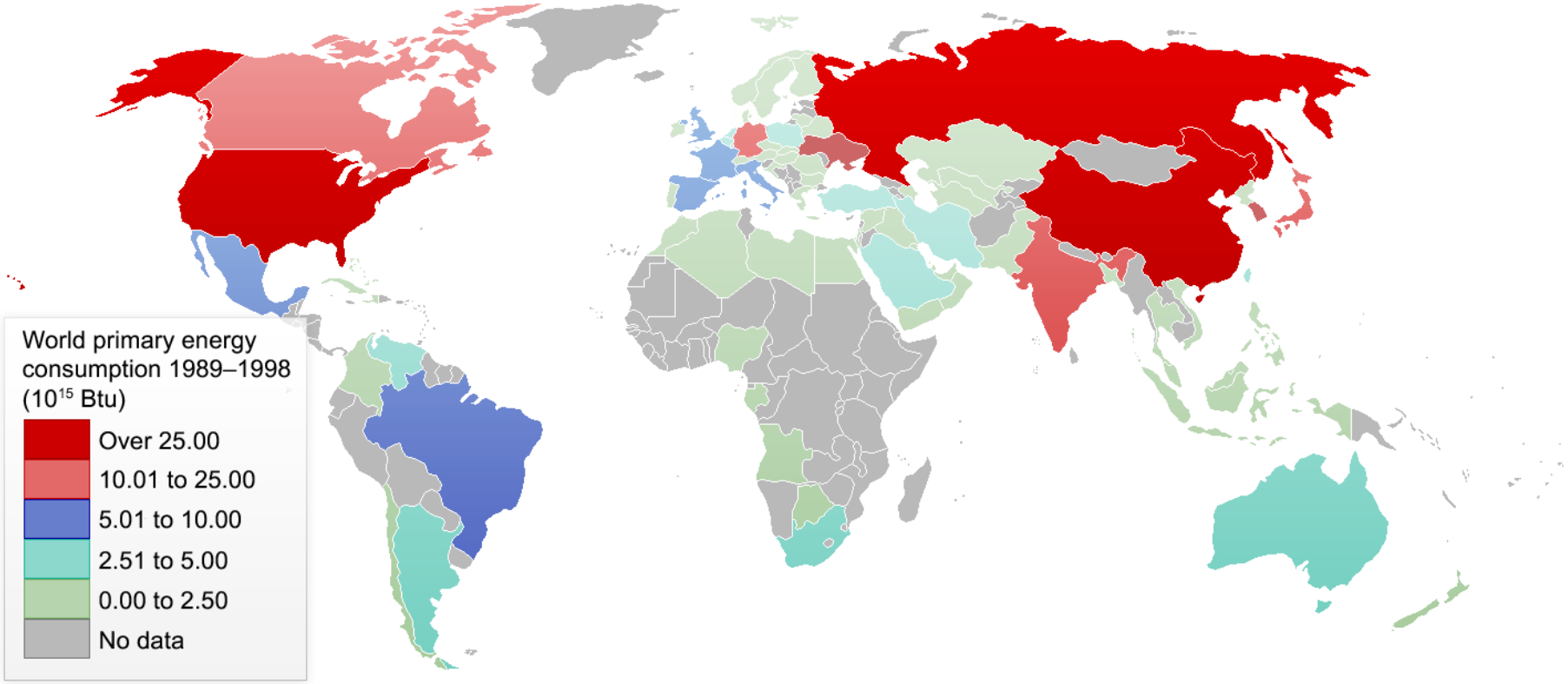
Keith J. Stevenson

Skoltech

November 15, 2021

World Energy Demand

Energy consumption predicted to increase 56% from 2010-2040



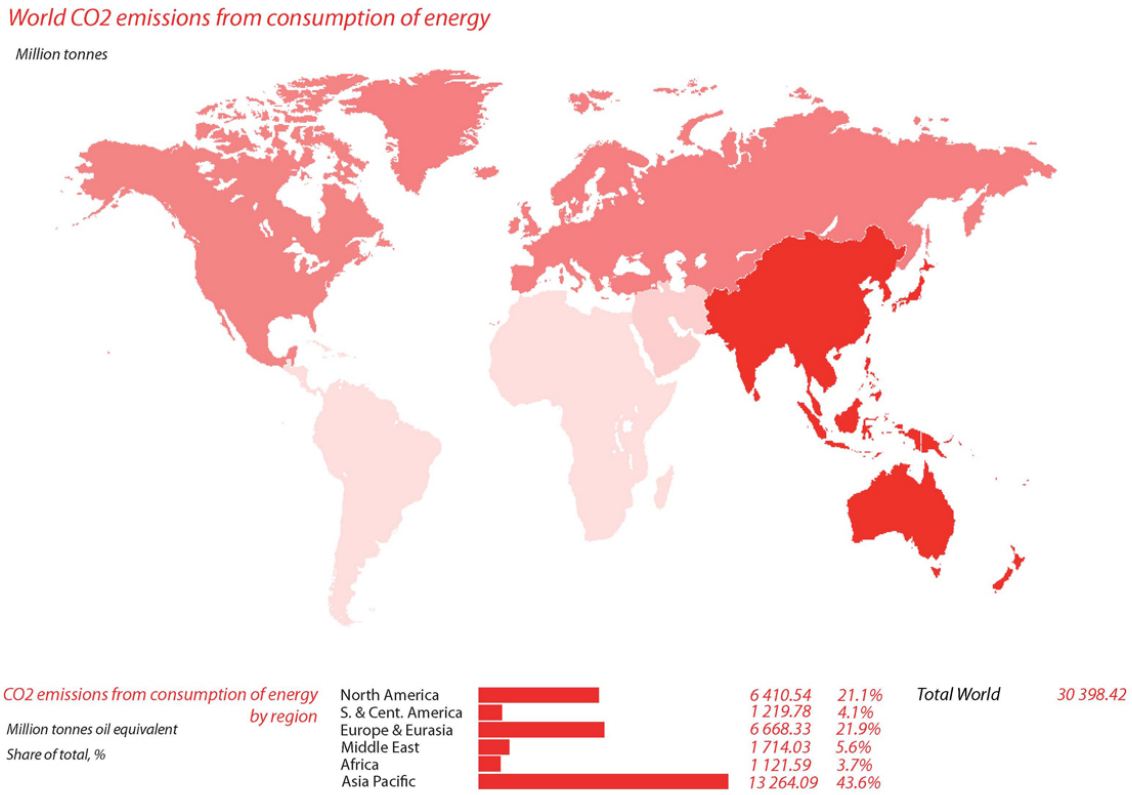
Require 30-40 TW to support >10 billion by 2050

http://www.kip.zcu.cz/kursy/svt/erasmus/8_2_ENERGY.html

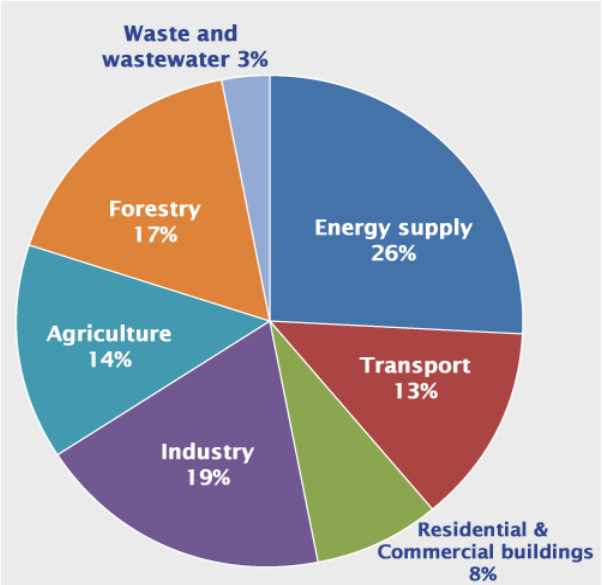
Global Greenhouse Gas Emissions

Emissions predicted to rise considerably

By Consumption



By Source

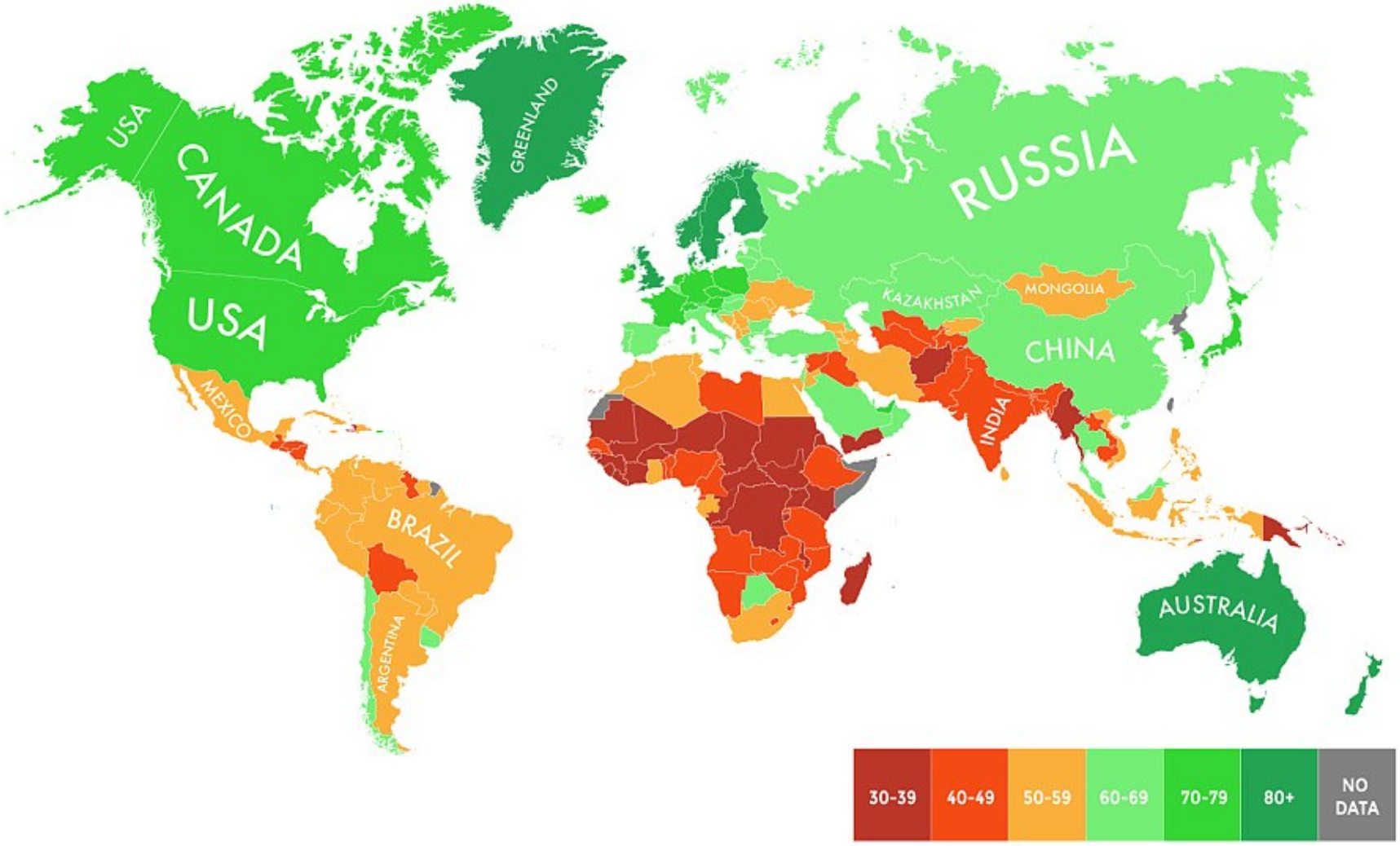


http://www.ftrctlb.com/node/382

IPCC, *Climate Change 2007: Synthesis Report*

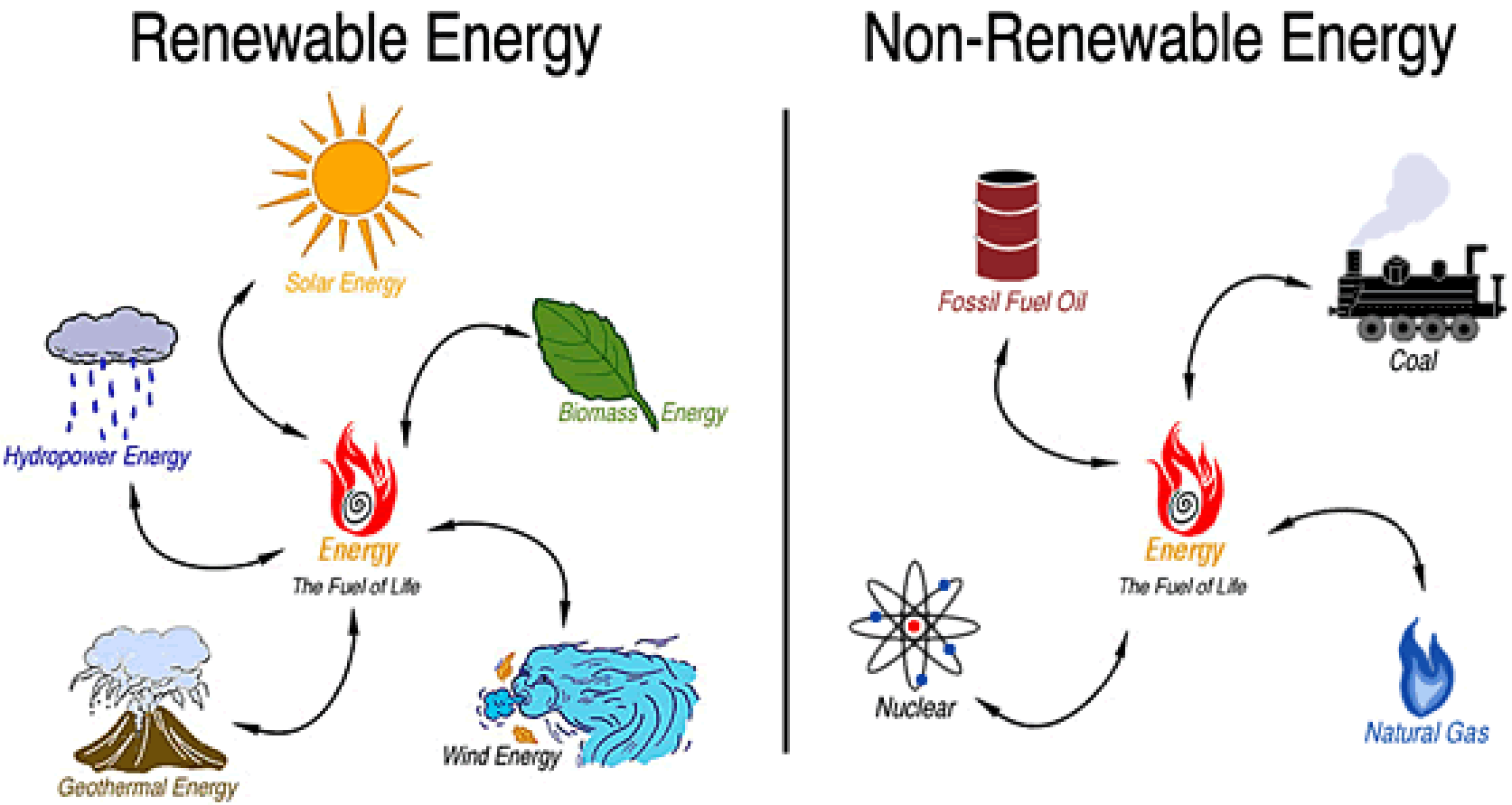
Countries Best to Cope With Climate Change

Ranked by “Vulnerability” and “Readiness”



http://www.dailymail.co.uk/sciencetech/article-2908213l

Alternative Energy Versus Conventional Energy



Closed Loop, Carbon Neutral Versus Open Loop, Carbon Emission

http://ecofriendlysolutionsindia.blogspot.ru/2013/03/conventional-alternative-energy-sources.html

Grand Challenges for Energy Sustainability

Carbon Free Energy

- Require 30-40 TW to support >10 billion by 2050.
- **Need new catalysts to support a mix of alternative energy sources.**

Main chemical transformations:

Methane Activation to Methanol: $CH_4 + ½O_2 \rightarrow CH_3OH$

Direct Methanol Fuel Cell: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

CO_2 (Photo)reduction to Methanol: $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$

H_2/O_2 Fuel Cell: $H_2 \rightarrow 2H^+ + 2e^-$; $O_2 + 4\,H^+ + 4e^- \rightarrow 2H_2O$

(Photo)chemical Water Splitting: $2H^+ + 2e^- \rightarrow H_2$; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

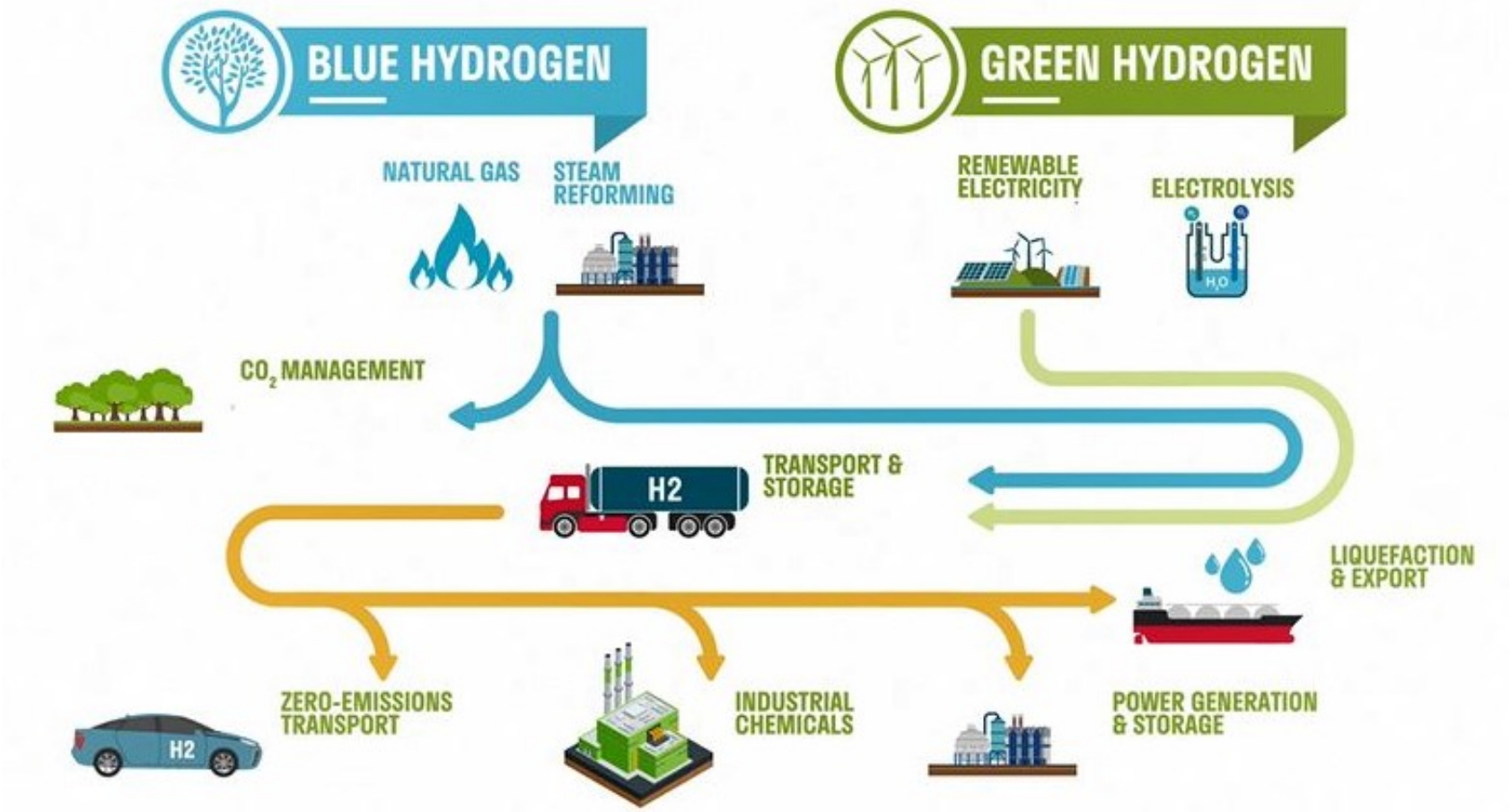
Dinitrogen to Ammonia: $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$; $N_2 + 6H_2O + 6e^- \rightarrow 2NH_3 + 6OH^-$

Strategy for Russia: Key Points from President Putin's Speeches 2021

Skoltech

- Reduce methane emission, eliminate gas flaring
- Energy efficiency across sectors
- CCUS from all sources
- Hydrogen as energy storage and source
- Establish carbon credits market
- Develop international monitoring system on GHG emissions using AI on data from satellites and ground measurements of CS
- Carbon sequestration in forests, capacity 2.5Bt CO2
- Russia is closer to 1990 baseline than others
- Nuclear power is green energy
- Green investments welcome in Russia

Sustainable Hydrogen



https://www.energy.gov/eere/fuelcells/h2scale

Holy Grail: Sustainable Hydrogen and Ammonia

$2H^+ + 2e^- \rightarrow H_2$;
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$3CH_4 + 6H_2O + 4N_2 \rightarrow 8NH_3 + 3CO_2$

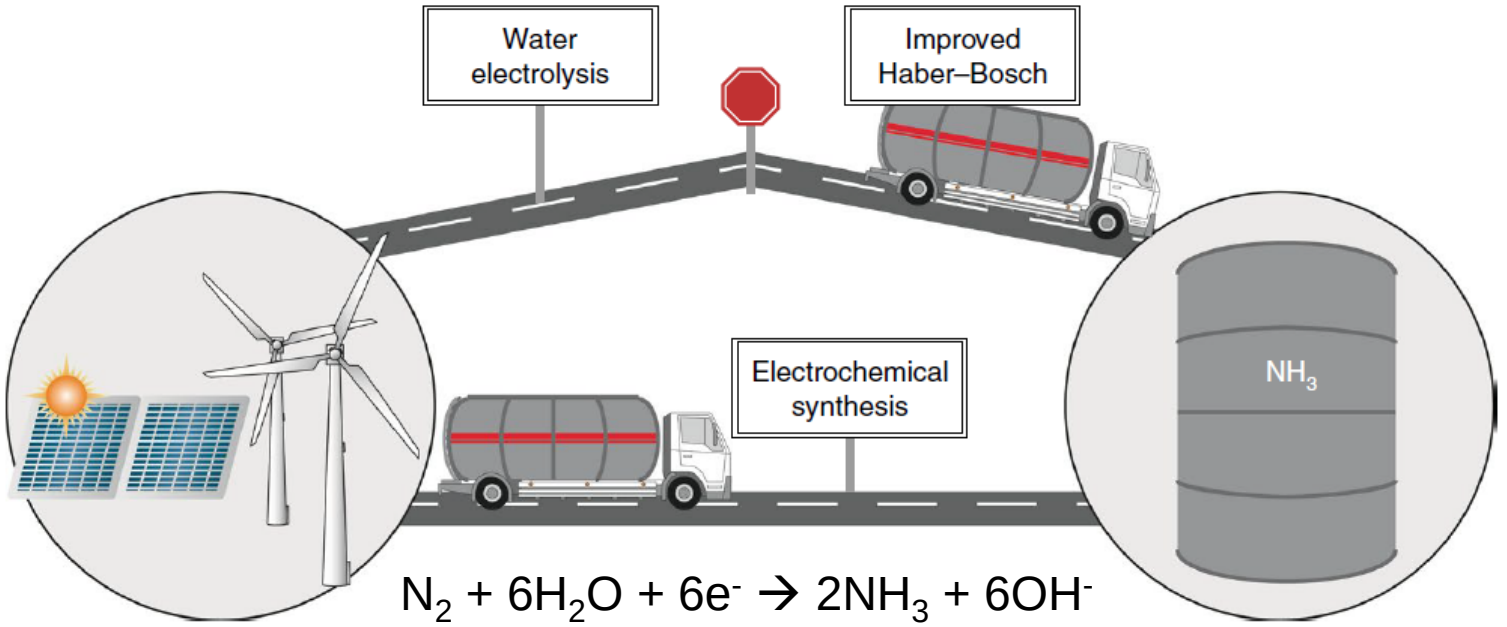
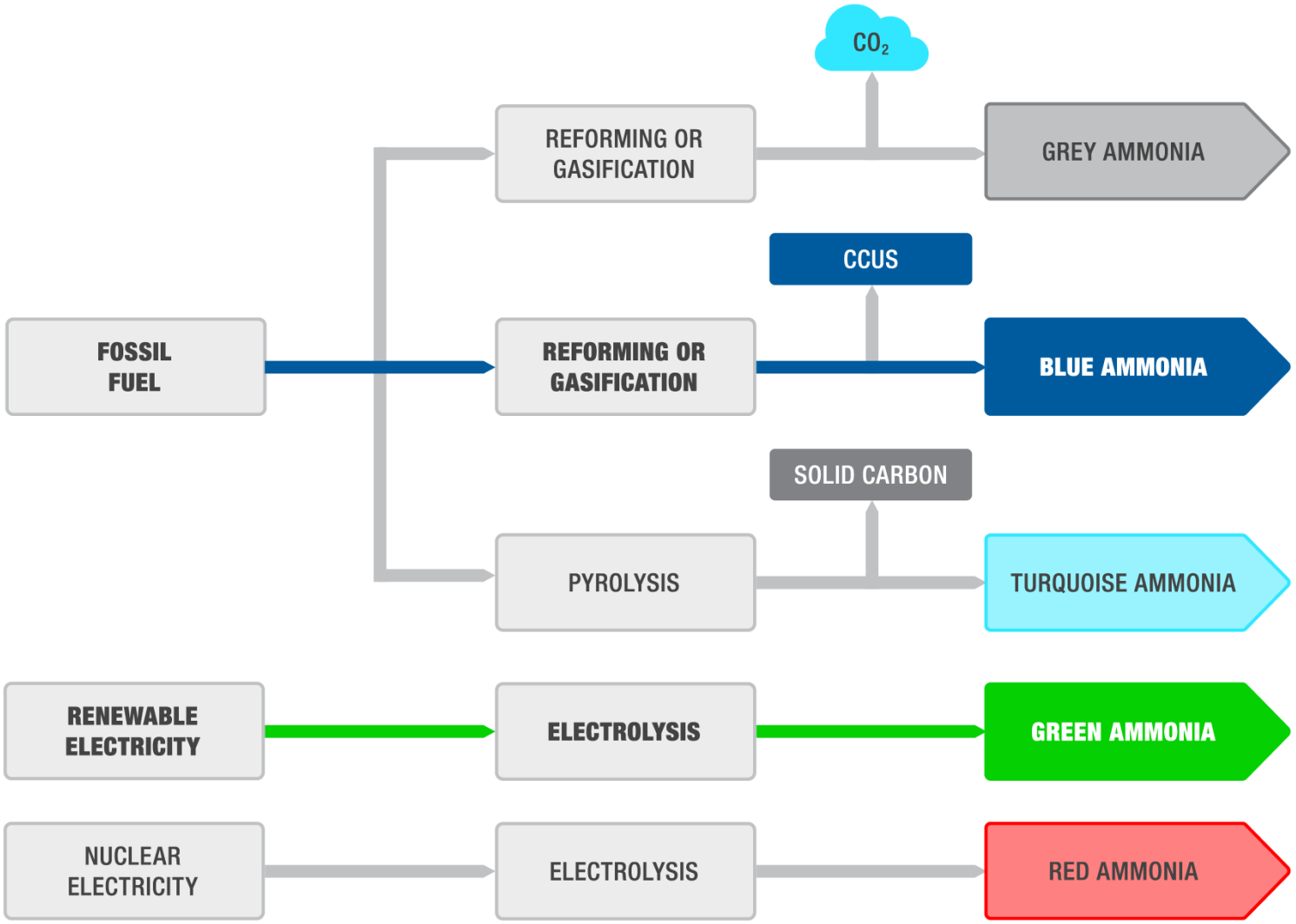
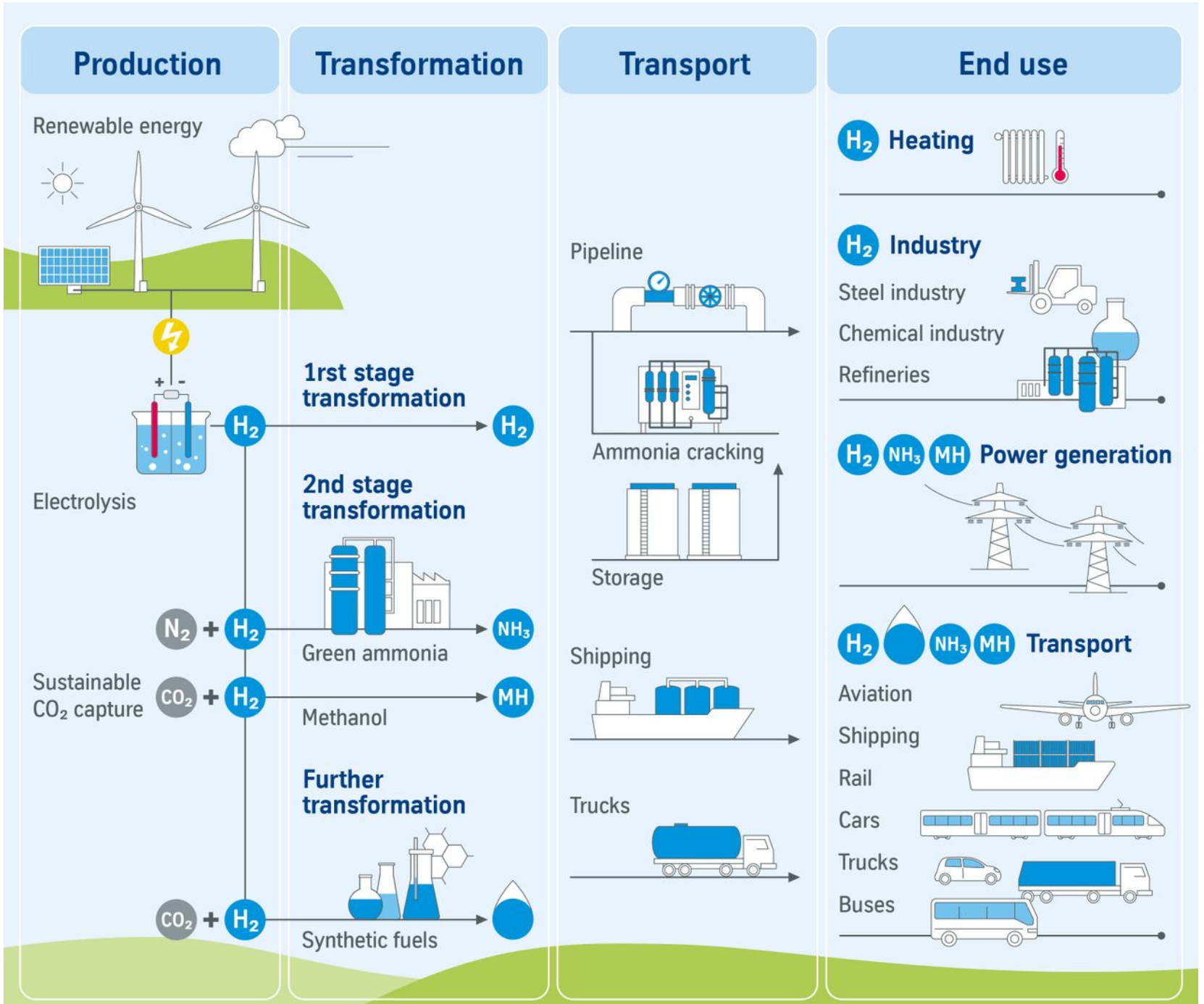


Fig. 1 | Pathways to renewable ammonia. Water electrolysis combined with the improved Haber–Bosch process (scenario A) and direct electrochemical synthesis (scenario B).

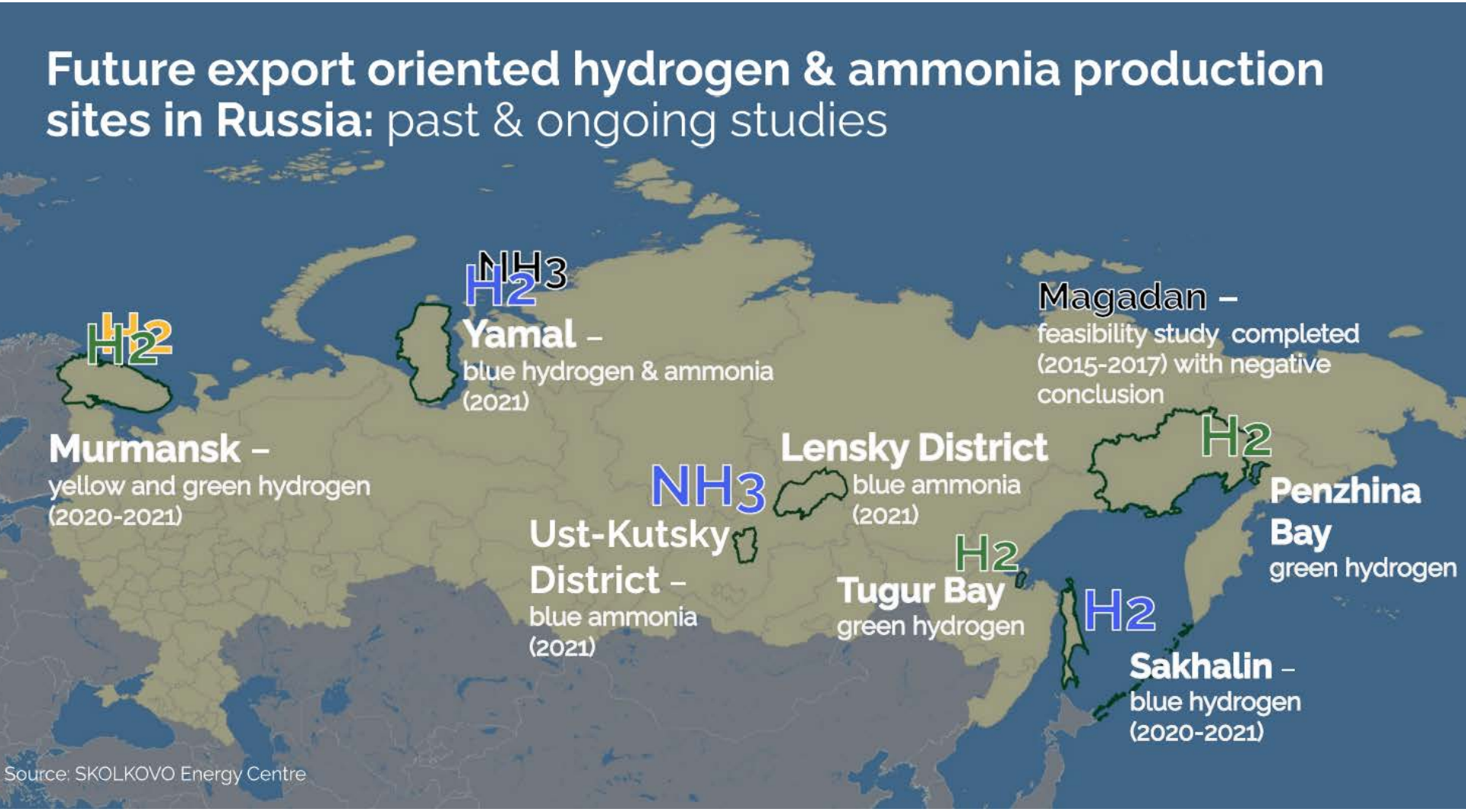
170 Million tons of NH_3 produced per year
1.5% of global total CO_2 emissions (2.9 ton CO_2 per NH_3)

NATURE CATALYSIS | VOL 2 | MAY 2019 | 377–380


CO_2
REFORMING OR GASIFICATION
GREY AMMONIA
CCUS
FOSSIL FUEL
REFORMING OR GASIFICATION
BLUE AMMONIA
SOLID CARBON
PYROLYSIS
TURQUOISE AMMONIA
RENEWABLE ELECTRICITY
ELECTROLYSIS
GREEN AMMONIA
NUCLEAR ELECTRICITY
ELECTROLYSIS
RED AMMONIA


Production
Transformation
Transport
End use
Renewable energy
Electrolysis
1rst stage transformation
H_2
H_2
2nd stage transformation
N_2 + H_2
NH_3
Green ammonia
Sustainable CO_2 capture
CO_2 + H_2
MH
Methanol
Further transformation
CO_2 + H_2
Synthetic fuels
Pipeline
Ammonia cracking
Storage
Shipping
Trucks
H_2 Heating
H_2 Industry
Steel industry
Chemical industry
Refineries
H_2 NH_3 MH Power generation
H_2 NH_3 MH Transport
Aviation
Shipping
Rail
Cars
Trucks
Buses

Russia Focused On Export of Hydrogen and Ammonia



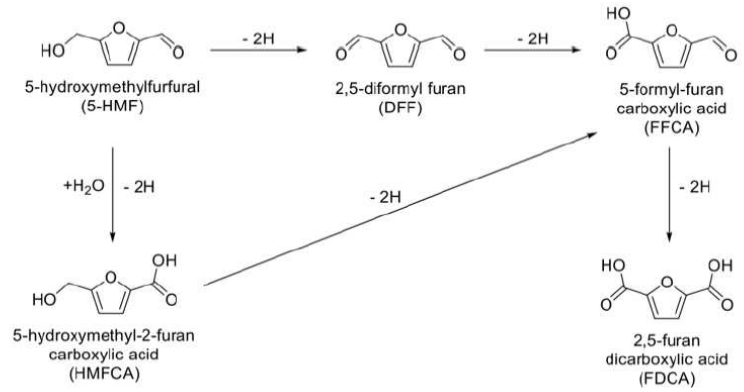
Low Temperature Electrocatalysis for Green Generation of Hydrogen and Ammonia

Areas of focus:

Room Temperature Electrocatalysis for (OER, HER)
Electrochemical Oxidation of Hydrogen carriers, (Urea, MeOH)
Electrochemical Reduction of Nitrogen to Ammonia
Electrochemical Valorization of Waste (HMF, Furfural, Glycerol, Ligin)
Electrochemical CO_2 Reduction to Ethylene?

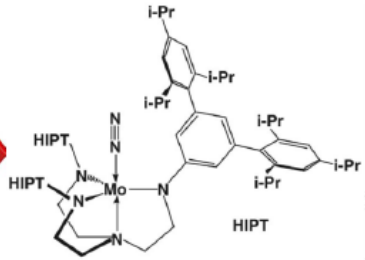
Alkaline Fuel Cells
Alkaline Electrolyzers

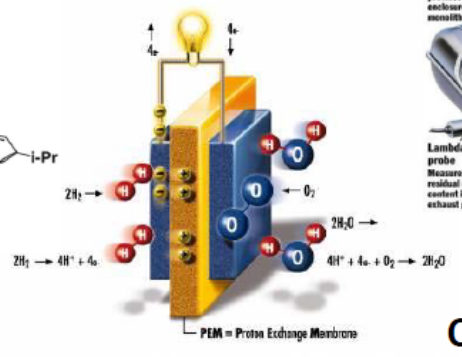
Skoltech CEST Faculty and Researchers
Stevenson, Abakumov, Nikitina, Levchenko, Akseynov, Artemov, etc

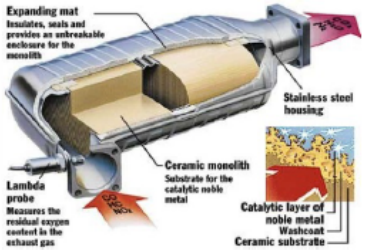


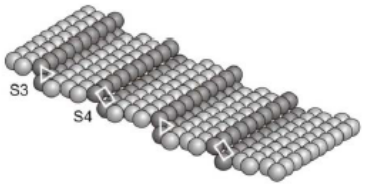
Scheme 1. Value-added products derived from the oxidative upgrading of HMF.

Five Broad Classes of Catalysts



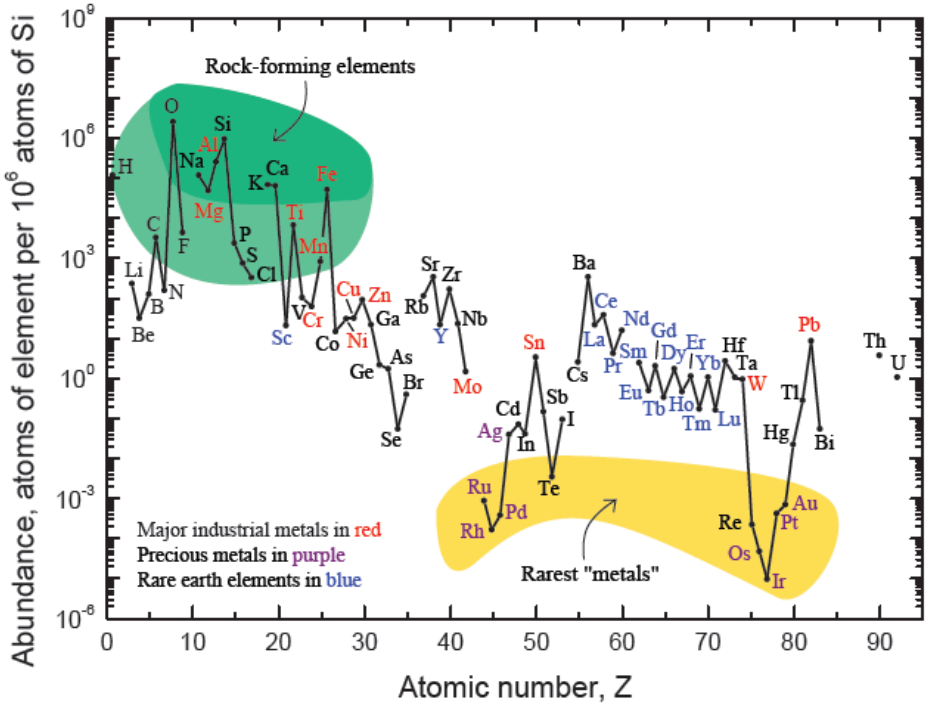






Biocatalysts	**Homogeneous Catalysts**	**Electrocatalysts**	**Conventional Heterogeneous Catalysts**	**Ultra-high Vacuum (UHV) Surface Science**
e.g. enzymes	e.g. transition metal complexes	e.g. Pt nanoparticles	e.g. Rh nanoparticles	e.g. Ru(109)
H_2O oxidation in photosynthesis	Fine chemicals Olefin metathesis	Fuel Cells Water electrolysis	Catalytic converters NH_3 synthesis	Fundamental studies Adsorption, desorption, reaction
H^+ and e^- transfers Ambient Temp Ambient Pressure Liquid (aqueous)	H^+/e^-, thermochemical Low-Intermediate T's Wide range P's Liquid (aq. or non-aq.)	H^+/e^-, thermochemical Wide range of Temps Wide range P's Liquid (aq. or non-aq.)	Thermochemical Wide range of Temps Wide range of P's Gas or liquid-phase	Thermochemical Wide range of Temps Very low P (vacuum) Gas-on-surface

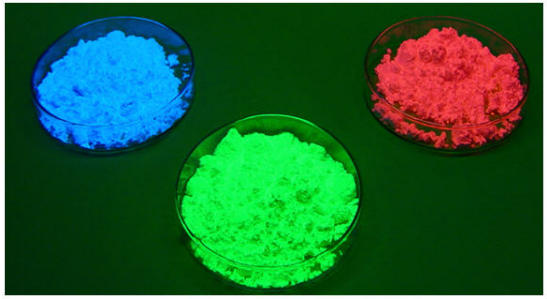
Use of Rare Elements in Modern Technologies



- Chemical catalysis
- Electronics
- Batteries, Fuel & Solar Cells
- Petroleum refining
- Catalytic convertors
- Metal refining
- Glass polishing

Anode for NMH batteries;
about 10 —15 kg La per vehicle

Permanent Nd magnets

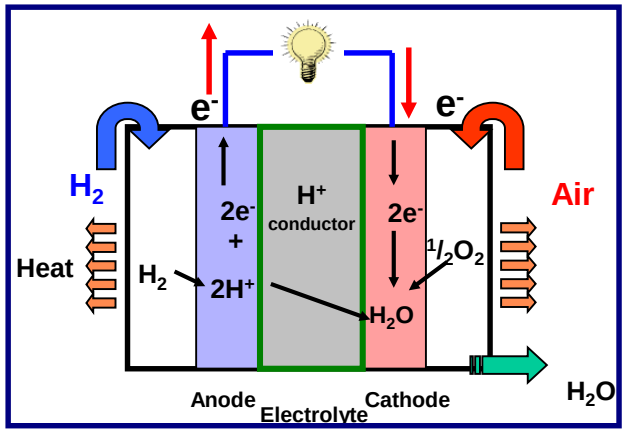


Tr, Eu, and Yt are the blue, green, and red phosphors used in many light bulbs, television, etc…

Electrochemical Energy Technologies

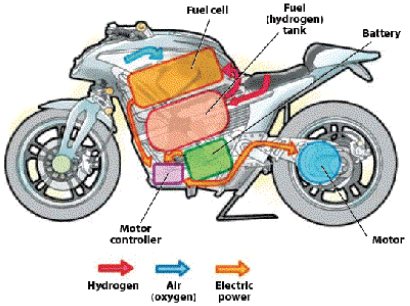
Fuel cells, batteries, supercapacitors (electrochemical)

Fuel Cell

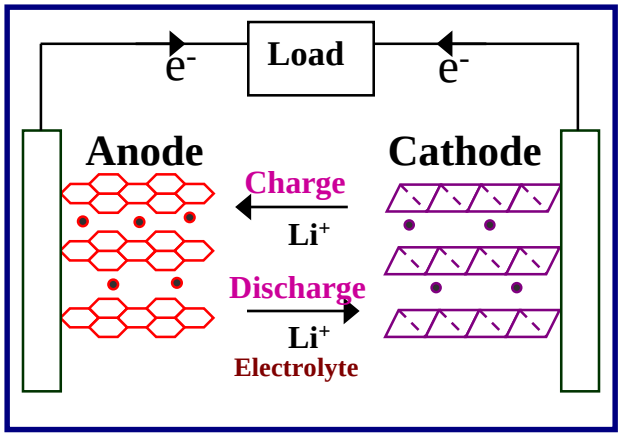


Conversion Device

Portable, transportation, & stationary



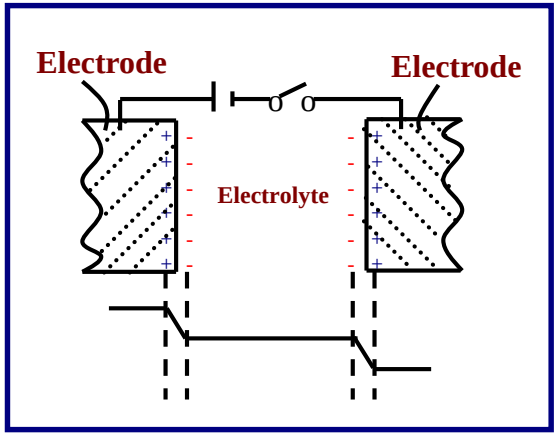
Battery



Storage Device

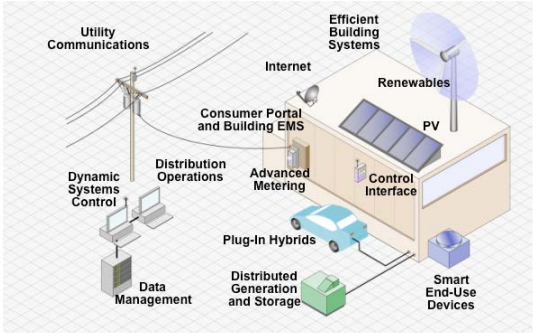
Portable & transportation

Supercapacitor



Storage Device

Portable & transportation



- **Chemical energy directly into electrical energy – clean energy technologies**

Electrochemical Power Sources Versus Combustion Engines

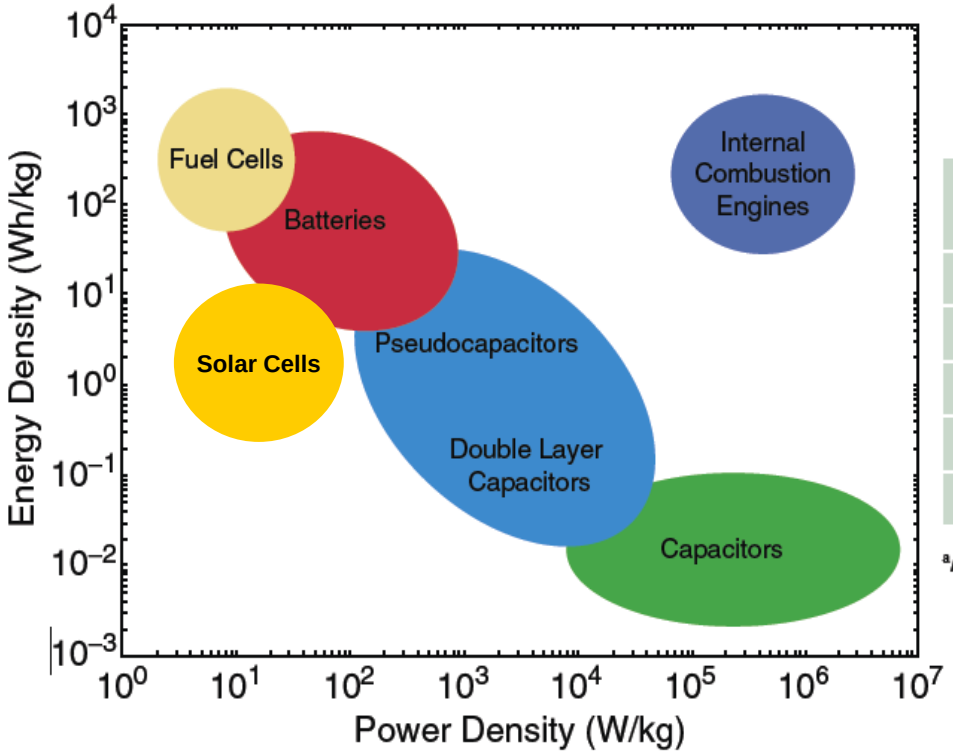


Table I: Energy Output of Electrochemical Devices and Petroleum.

Energy Source	Energy Output (kWh/kg)
Supercapacitors	0.01
Lithium battery	0.8
Hydrogen fuel cell	1.1
Gasoline	6.0[a]

[a]Assuming 30% combustion efficiency.

M. S. Whittingham, *MRS Bulletin* **2008**, *33*, 411.

Electrochemical Energy Storage Options

Secondary batteries

- Stationary electrode materials
- Mature technology (lead acid, NiCd, NiNH, NaS)
- Emerging technologies ($NaMCl_2$, Li-ion)
- New chemistries (Li-air, Li-S, Zn-air)

NGK 34 MW NAS alongside 51 MW Wind Farm

Source:http://www.ngk.co.jp/english/products/power/nas/

Redox flow batteries

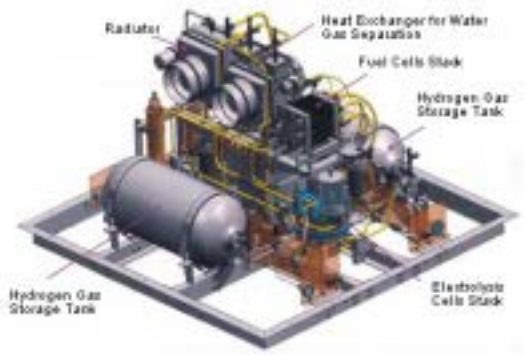
- Flowing electrode materials
- Mature technology (zinc-bromine, all-vanadium)
- Emerging technologies (cerium-zinc, iron-chromium)
- New chemistries (vanadium-bromine, soluble lead)

VRB (Prudent Energy) PacifiCorp (Moab, Utah) 2 MWh VRB-ESS

Source: http://www.pdenergy.com/

Regenerative fuel cells

- Gaseous electrode materials
- Emerging technologies (H_2-O_2 conventional and unitized)
- New chemistries (H_2-Br_2 , H_2-H_2O_2 , $NaBH_4$-H_2O_2)

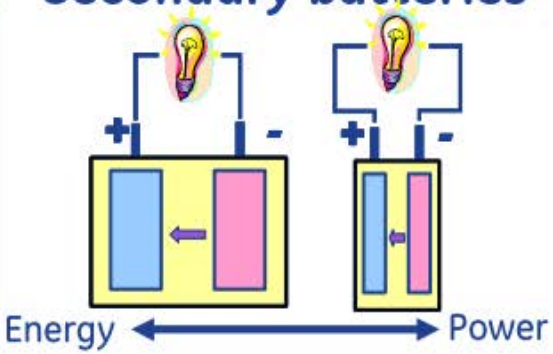


1kW-prototype Regenerative Fuel Cell System

Source: www.apg.jaxa.jp

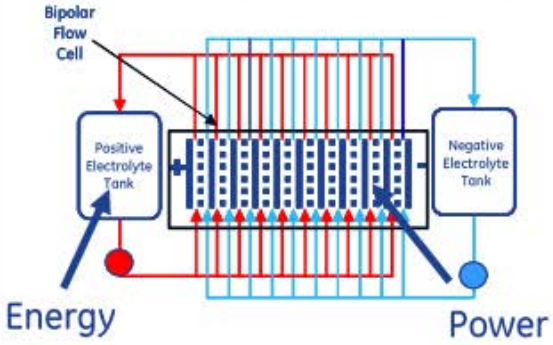
Electrochemical Energy Storage Comparison

Secondary batteries



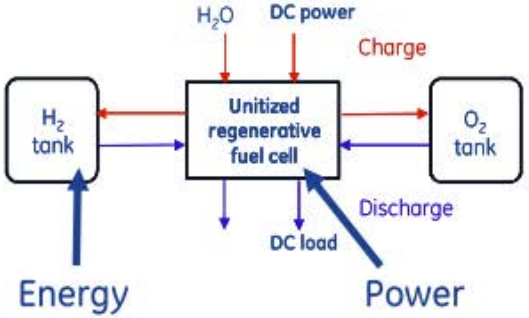
- No power-energy separation
- Moderate energy density (50 – 240 Wh/kg)
- High energy efficiency (65 – 90 %)
- Degradation mode – electrode
- Linear scalability (small cells)
- Moderate cost
- Mature technology

Redox flow batteries



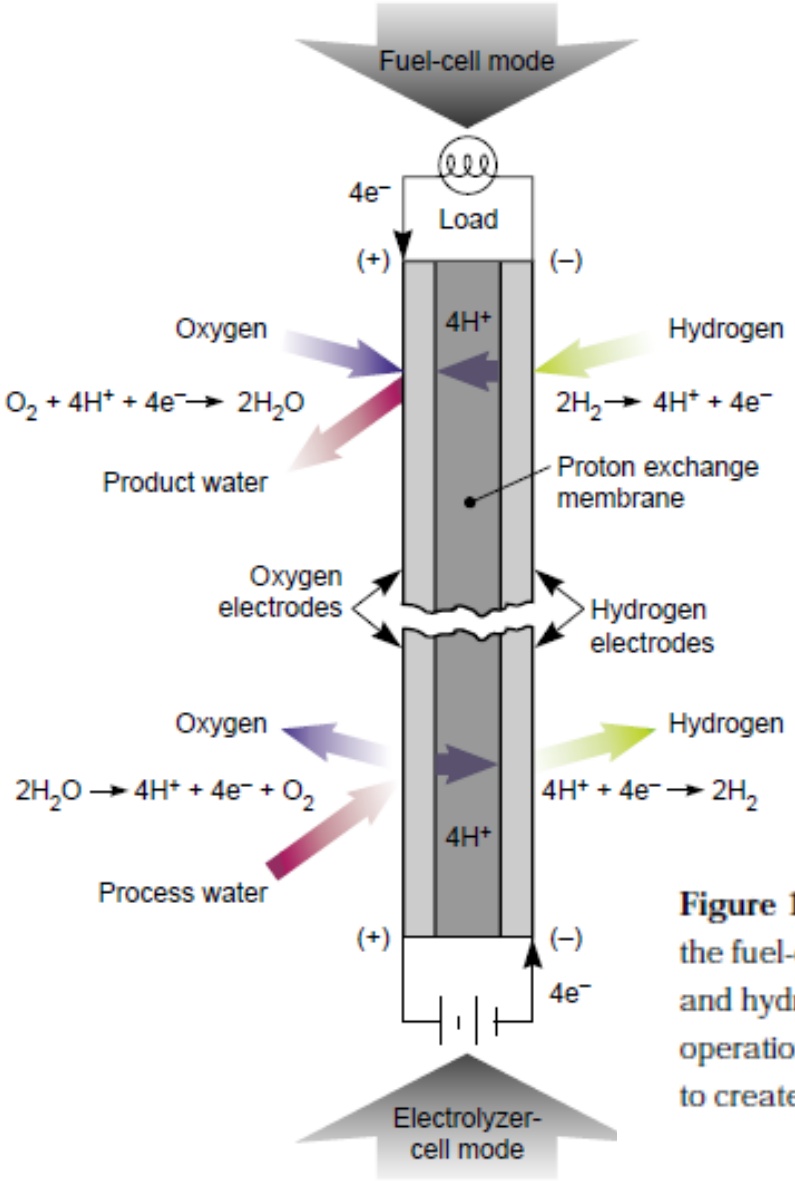
- Power and energy separated
- Low energy density (10 – 50 Wh/kg)
- High energy efficiency (65 – 78 %)
- Degradation mode – membrane
- Non-linear scalability (cell stacks)
- Low cost
- Emerging technology

Regenerative fuel cells



- Power and energy separated
- High energy density (450 – 500 Wh/kg)
- Low energy efficiency (35 – 50 %)
- Degradation mode – catalyst
- Non-linear scalability (cell stacks)
- High cost
- New technology

Unitized Regenerative Fuel Cell (URFC)



Desired for applications that require high energy density and low weight

- **Cars**
- **Solar powered aircraft**
- **Micro-spacecraft**
- **Load-leveling for wind turbines and Solar Cells**

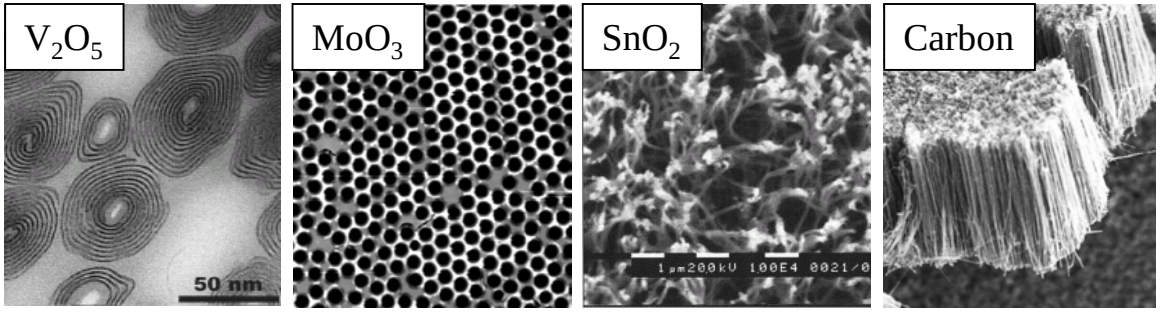
Figure 1. The electrochemistry of a unitized regenerative fuel cell. In the fuel-cell mode, a proton-exchange membrane combines oxygen and hydrogen to create electricity and water. When the cell reverses operation to act as an electrolyzer, electricity and water are combined to create oxygen and hydrogen.

Tailoring of Nanostructured Materials

Purposeful Tailoring of Structure, Shape, Composition, Orientation

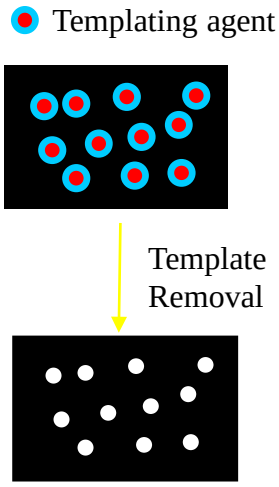
Desired Attributes

High Surface Area	**10-1000 m^2/g**
High Porosity	**50-97 %**
Low Density	**0.005-2 g/cm^3**



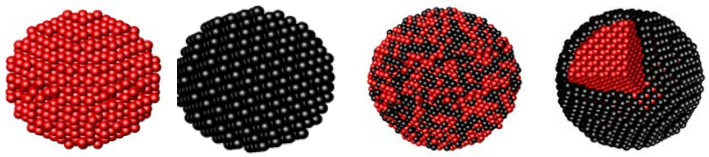
Templating & Structure Directing Agents

Catalyst particles (Iron, Cobalt, Gold)	Leiber, Smalley
Surfactants (alkylamines, block co-polymers)	Nesper, Turner
Membranes (Al_2O_3, polycarbonate,)	Martin, Caruso
Colloidal-crystals (latex, PS, SiO_2)	Stein, Bartlett, Dunn
Macromolecular (dendrimers)	Crooks, Chandler



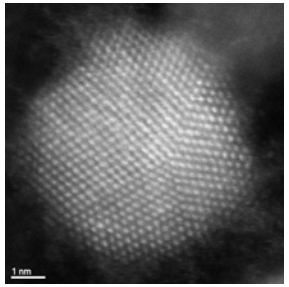
New Materials with Uncharacterized Structure/Property Relationships

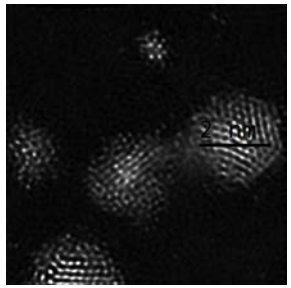
Catalyst Architectures

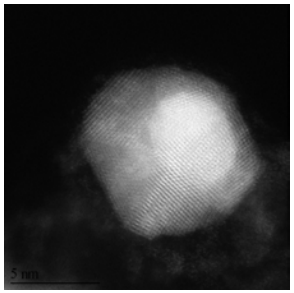


heterodimer alloy core@shell

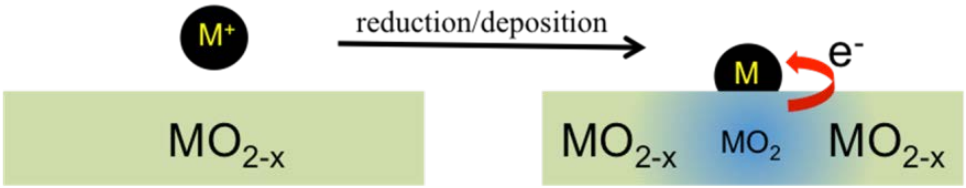
PtCu, PdCu, PdAg, PtPd, PdIr, PdMo

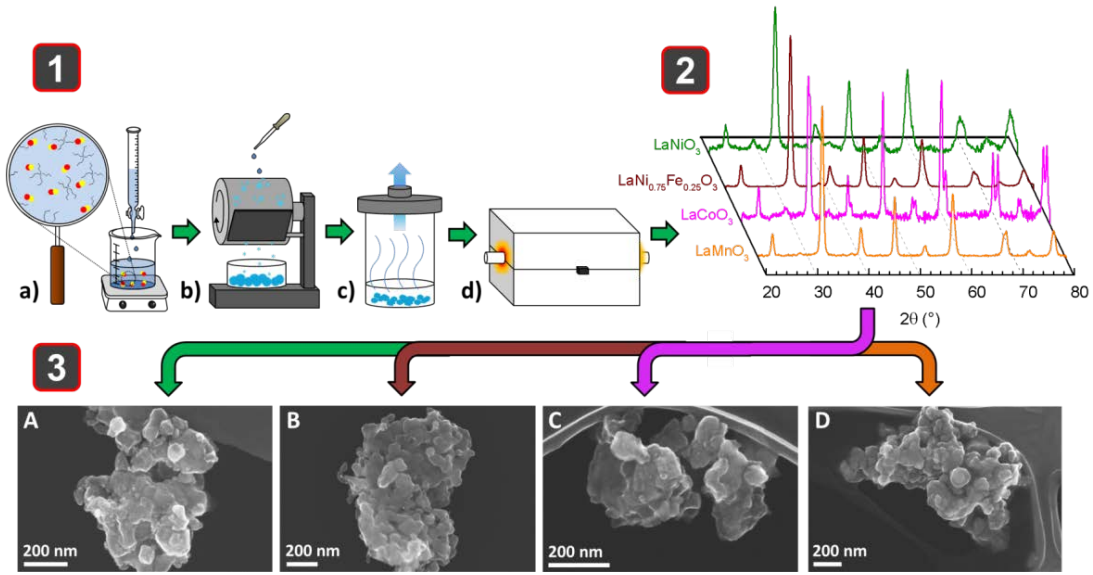




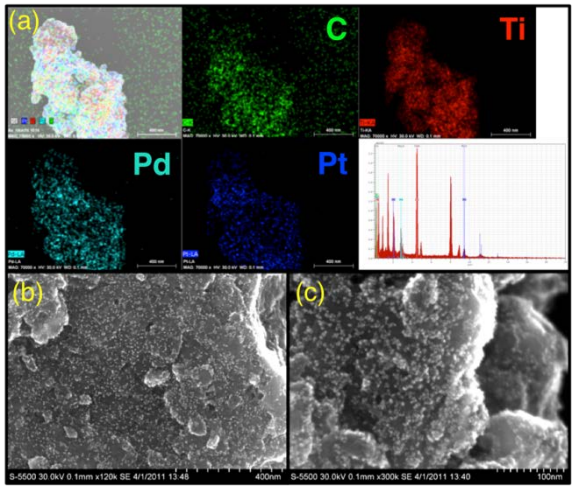


JACS **2012,** *134*(23), 9812 *J. Phys. Chem. C.* **2012**, *116*(20),11032





TiO_2(b), MnO_2, $LaMO_3$, MoS_2, Fe_3O_4



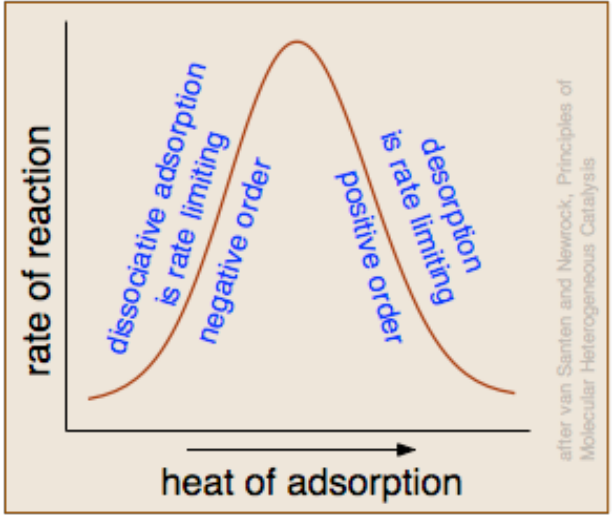
Chem. Commun. **2011**, *47*(44), 12104

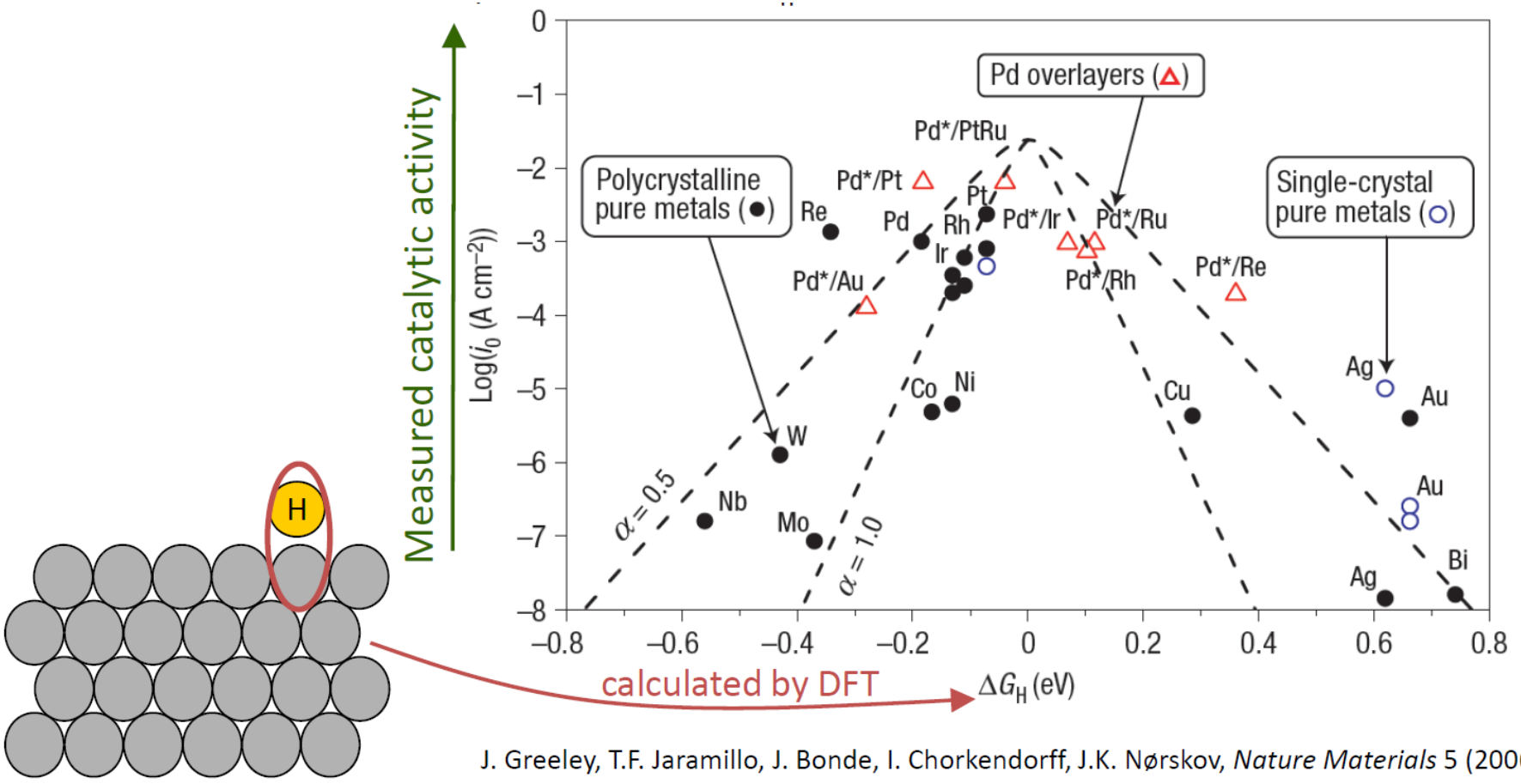
J. Phys. Chem. Lett. **2013**, *4,* 1254

J. Mater. Chem. A **2013,** *1*, 13443

Chem. Mater. **2014**, *26,* 3368

Activity Descriptors for Catalysis

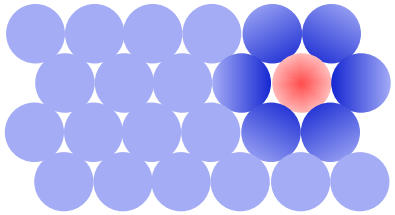




J. Greeley, T.F. Jaramillo, J. Bonde, I. Chorkendorff, J.K. Nørskov, *Nature Materials* 5 (2006) 909-913

Activity Enhancement Effects from Catalysts

Ligand Effects

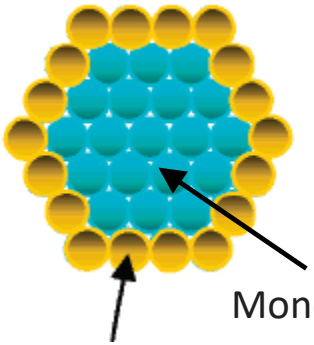


→ *Electron donation from dissimilar surface atoms*

Modify the binding energy of reaction intermediates

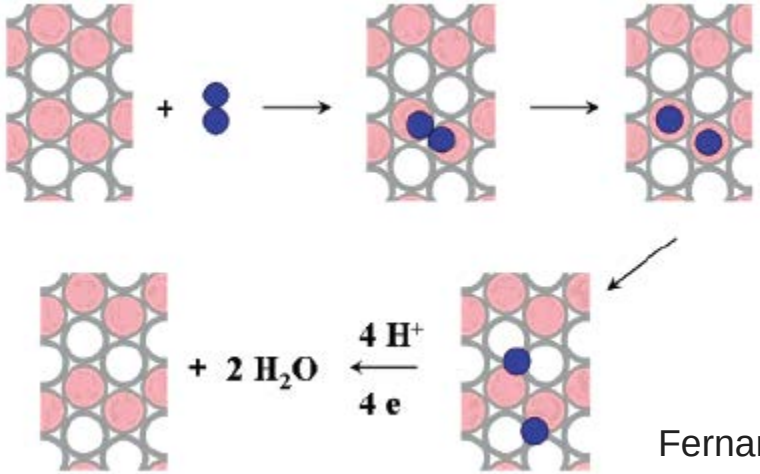
Geometric Effects

→ *Specific atomic arrangement of surface atoms*



J. Zhang. *J. Phys. Chem. B.* **2005.**

Ensemble Effects



→ Different atomic sites or clusters *cooperate to facilitate distinct reaction steps*

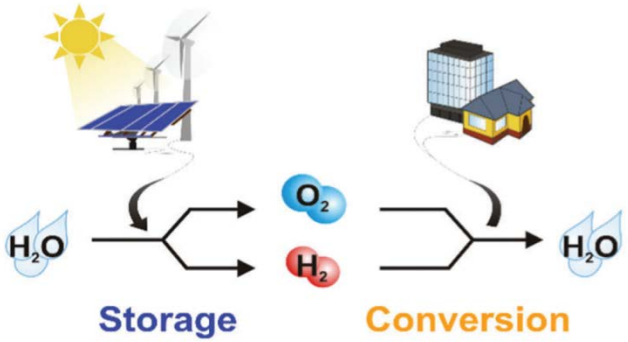
e.g. oxygen bond cleaving vs formation and desorption of water

Fernandez, Walsh & Bard *J. Am. Chem. Soc.* **2005.**

Oxygen Electrochemistry

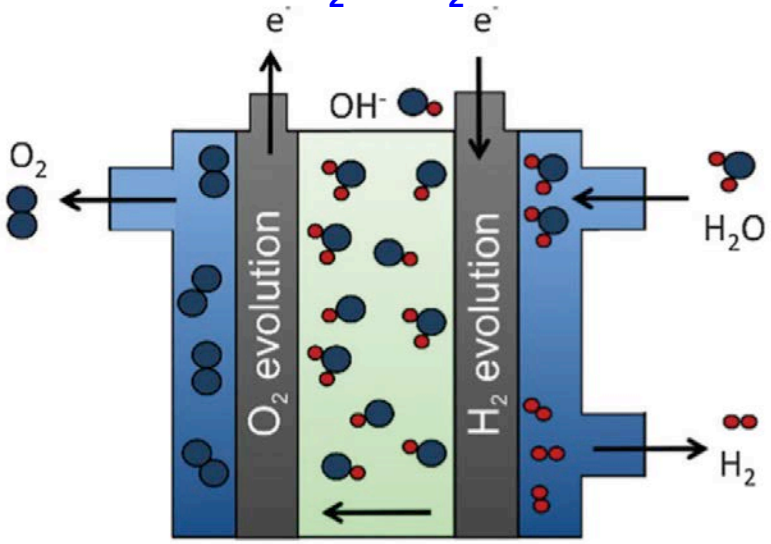
Oxygen Chemistry is Ubiquitous

- Electrolyzers for H_2 generation
- Metal-air batteries (Zn-air, Li-air)



oxygen evolution reaction (**OER**)

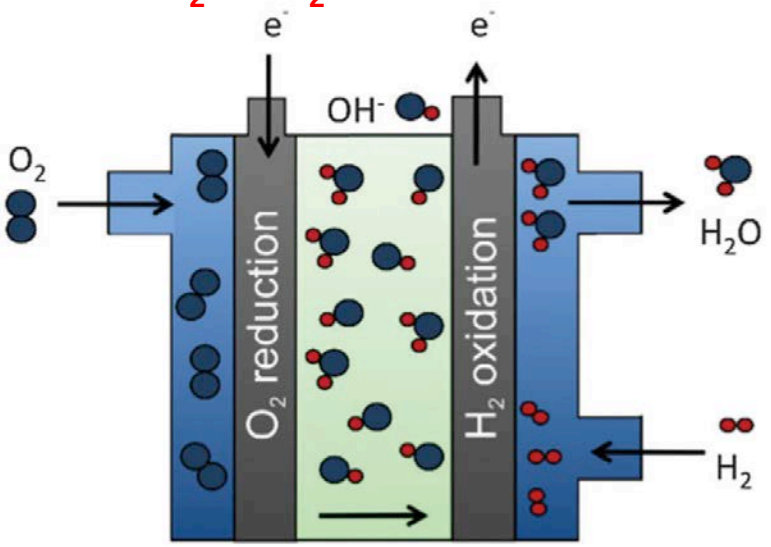
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$



Electrolyzer

oxygen reduction reaction (**ORR**)

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

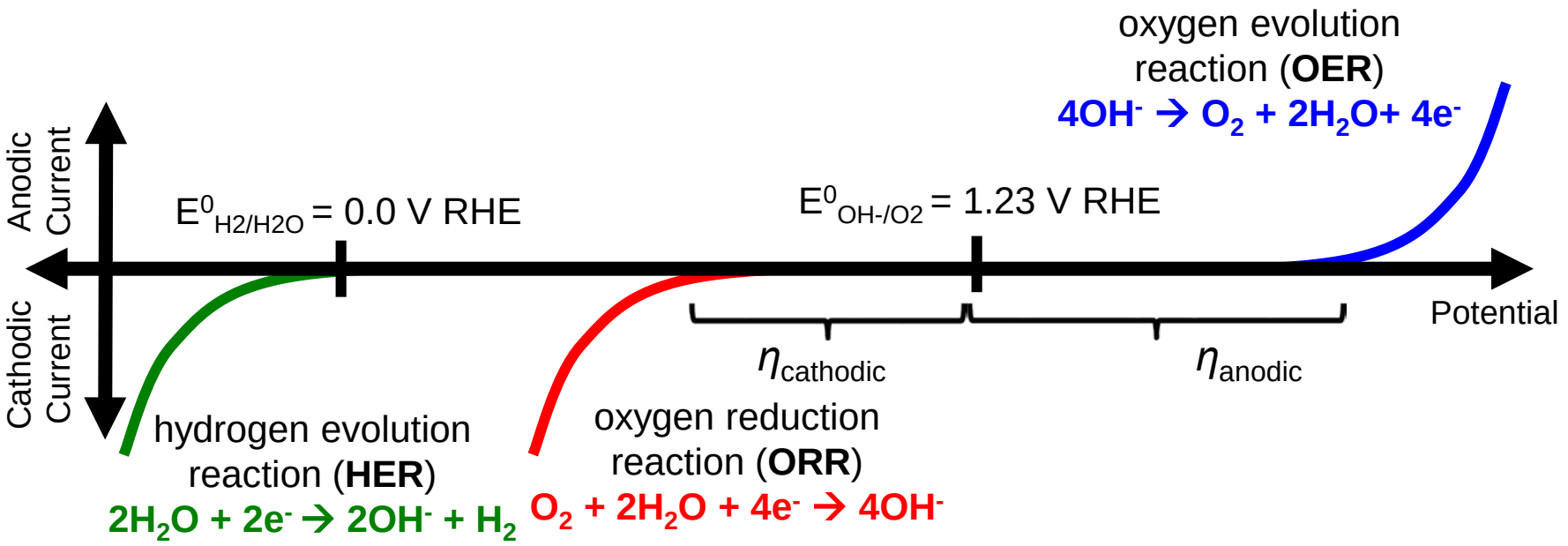


Fuel Cell

Hong, W. T.; Grimaud, A.; Suntivich, J.; Shao-Horn, Y. *Energy Environ. Sci.*, **2015**

OER and ORR
Thermodynamics vs Kinetics

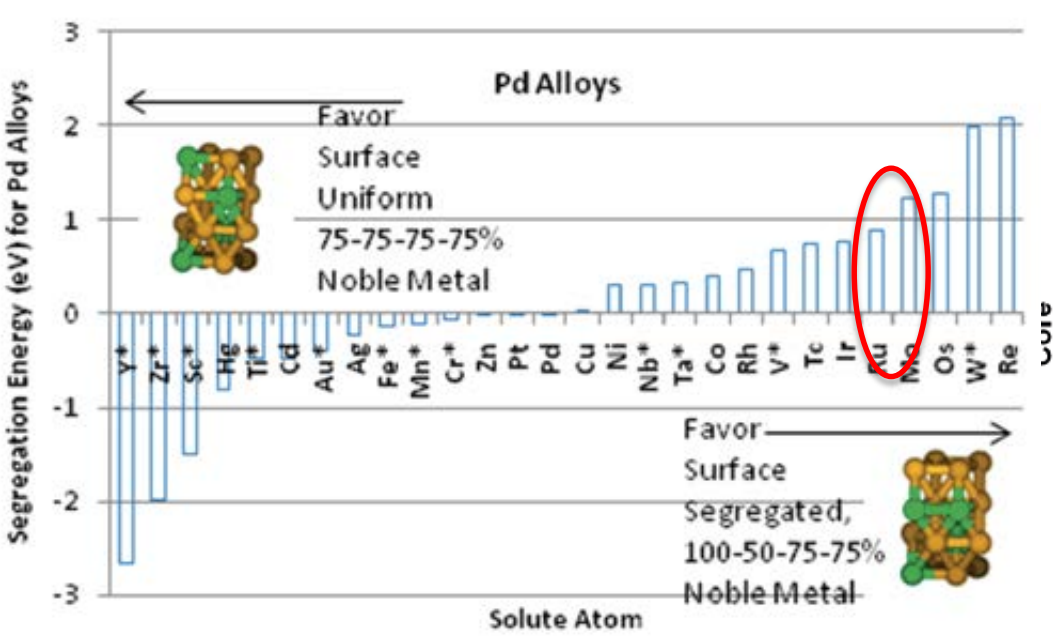
- "kinetically sluggish" reactions require large overpotentials ($\eta \geq 300$ mV)
- Large overpotentials result in lower power, device efficiency

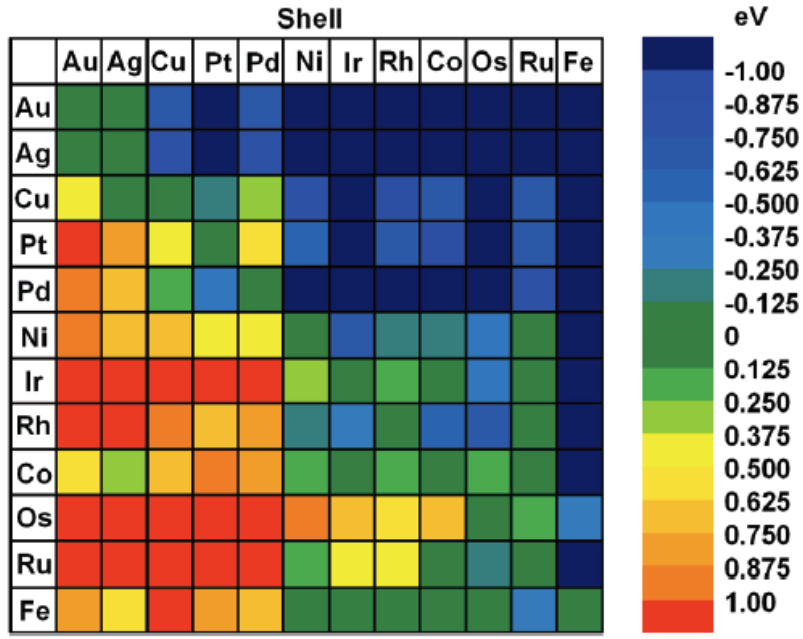


Catalyst materials

- Materials capable of both OER and ORR for regenerative fuel cells → '**bifunctional**' catalysts
- Alkaline electrolyte enables **non-precious metal oxides** → **Perovskites**

“Predictions” on Synthesis of Pd Alloy & Core@Shell Catalysts



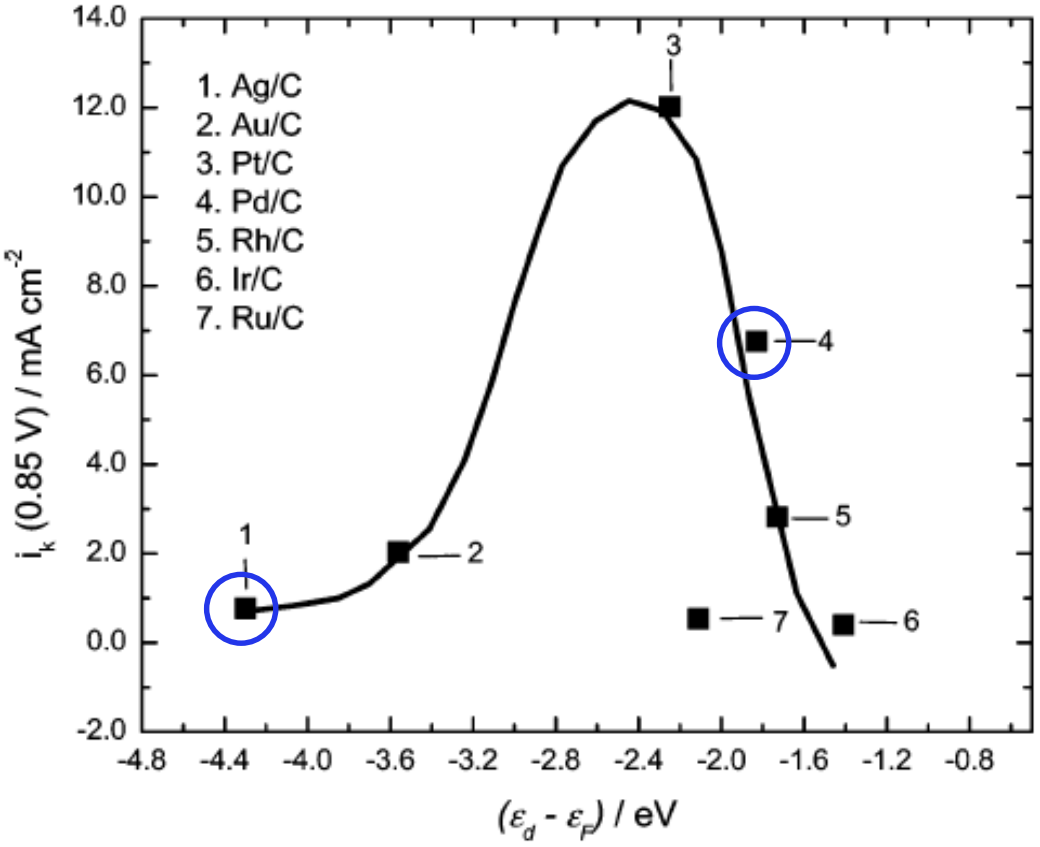


Calculations predict stability of Ir, Ru, Mo, W, Re@Pd core@shell structure And homogeneous alloy formation for PdAg & PdAu.

Yu & Goddard, *J. Phys. Chem. C*, **2010**, *114* , 11527.

Rationale for Choosing Pd-Ag Alloy

Volcano Dependence of Activity on DFT Calculated d-band Centers



F. H. B. Lima et al. *J. Phys. Chem. C.* **2007.**

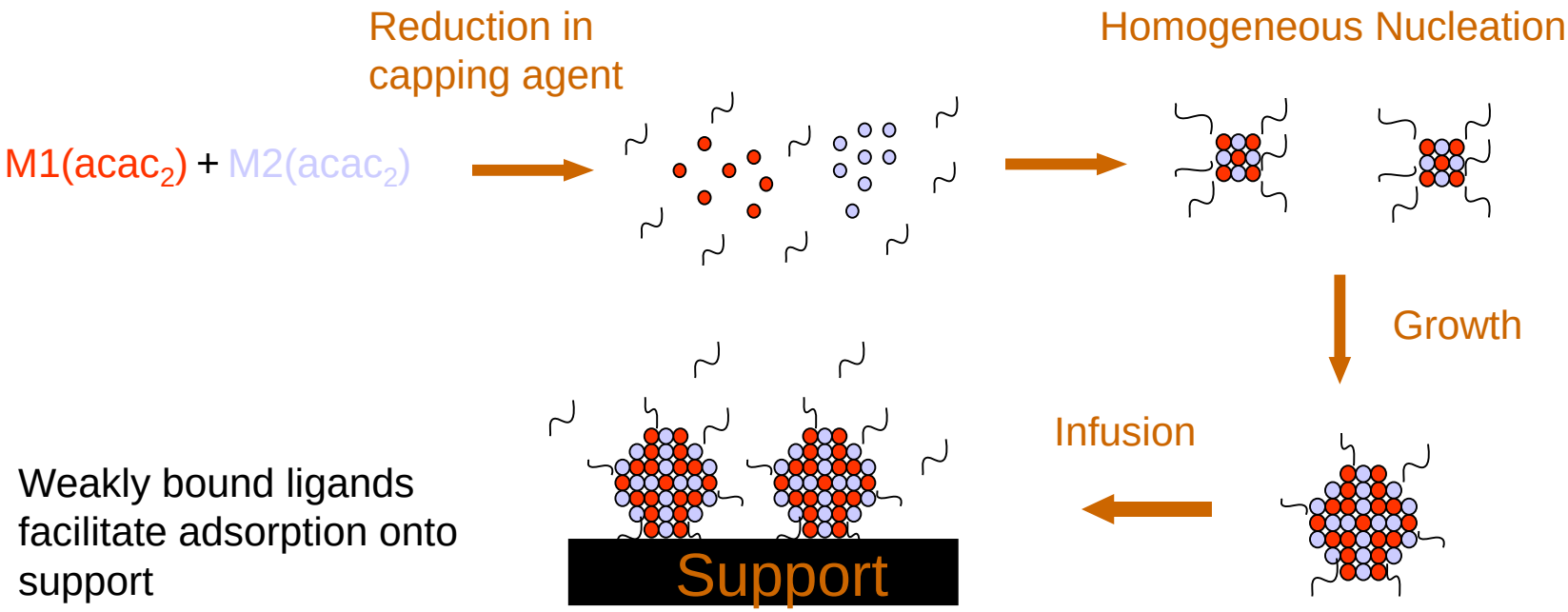
Ensemble Effect: Oxygen Binding on Ag is too weak, whereas too strong on Pd

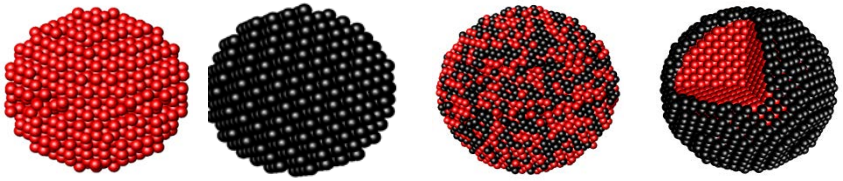
Economics: Pd ($630/troy oz) vs Ag ($30/troy oz)

Both Ag and Pd FCC metals → form solid solutions over compositional range

Challenge: Controlled synthesis of uniform alloys to take advantage of potential Pd-Ag synergy

Synthesis of Catalyst Architectures

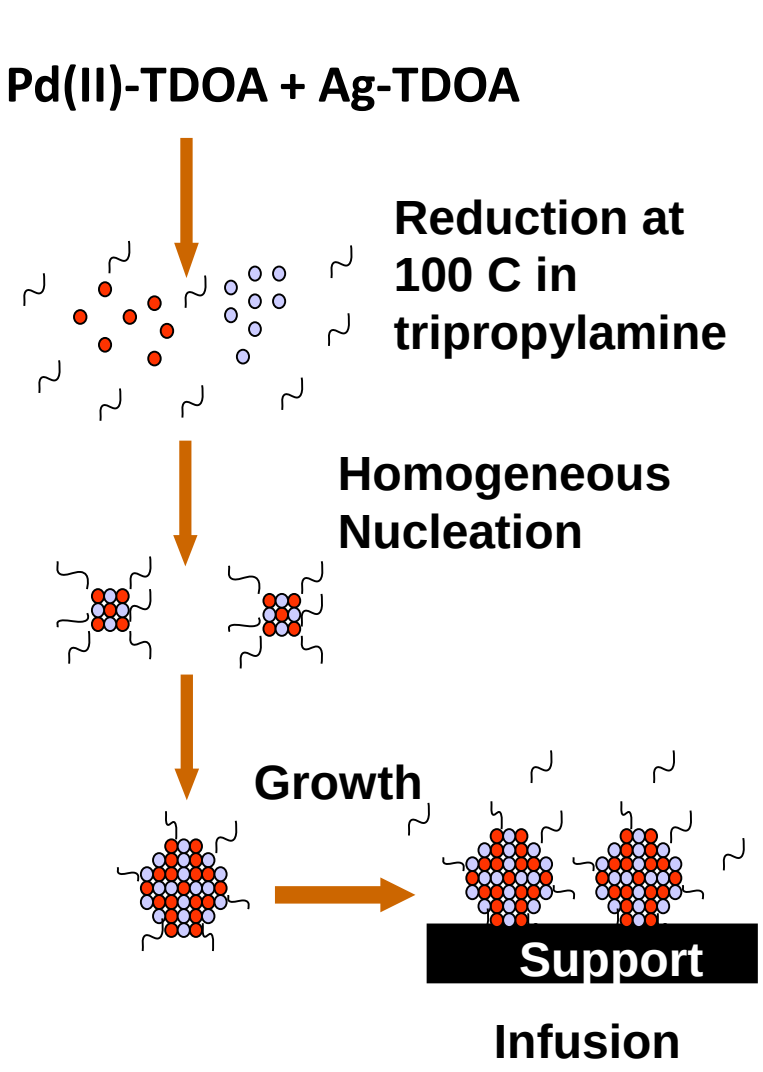




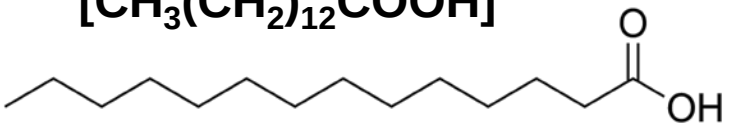
heterodimer alloy core@shell

How does size, shape, composition and morphology influence properties?

Synthesis of Ag-Rich Ag-Pd Alloy Catalysts



Tetradecanoic acid
[$CH_3(CH_2)_{12}COOH$]



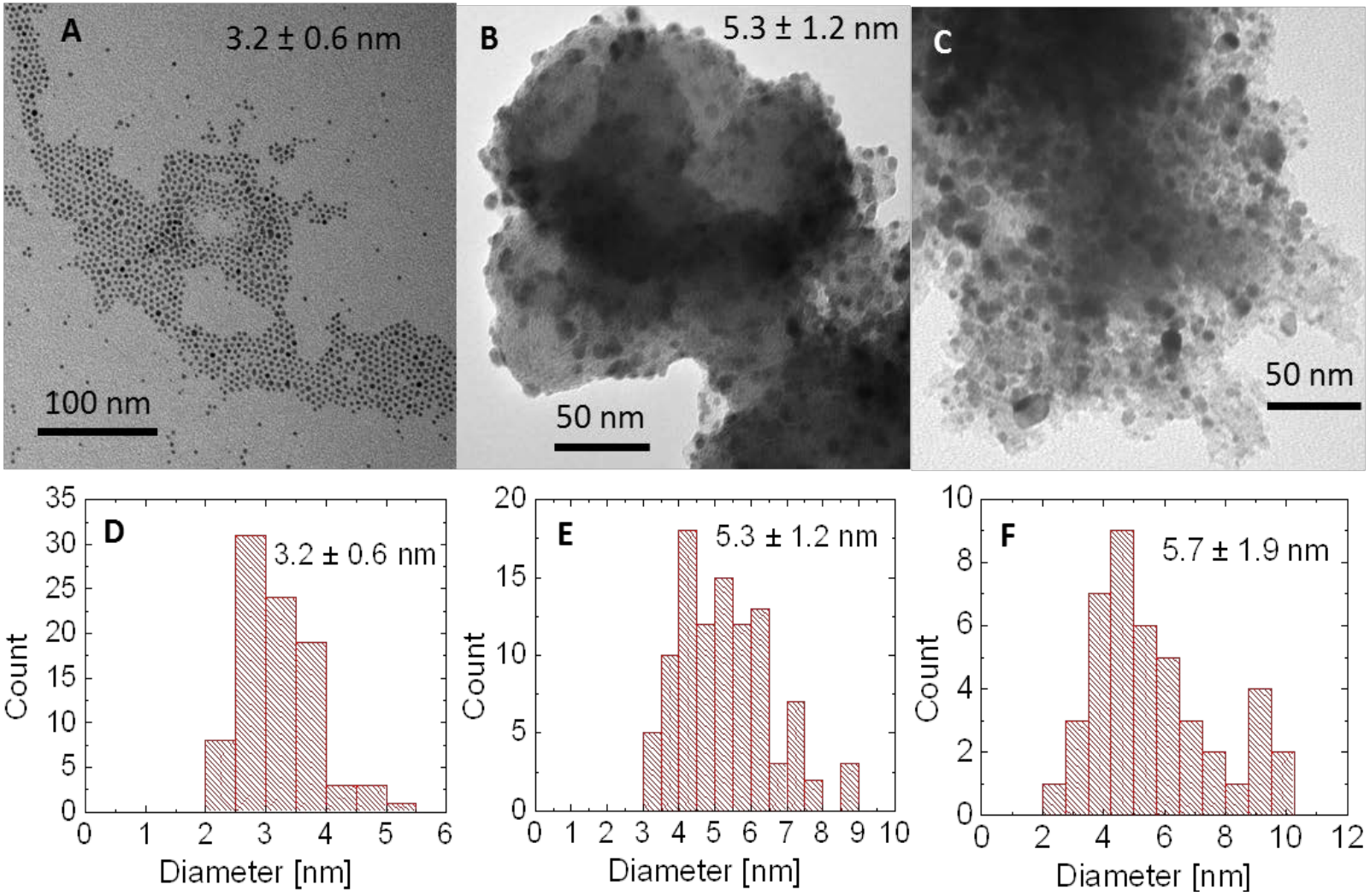
Ratio of Ag & Pd determines final alloy stoichiometry. Metal concentration always fixed at 1 mmol, theoretical reaction yield of ~105 mg.

- **Slow ramp to 100C, hold for 1 hr.**
- **React under Ar / N_2.**
- **Forms kinetic alloy**
- **Close to 100% yield**

Particles are 30% (by weight) ligand, results in ~130 mg yield per reaction.

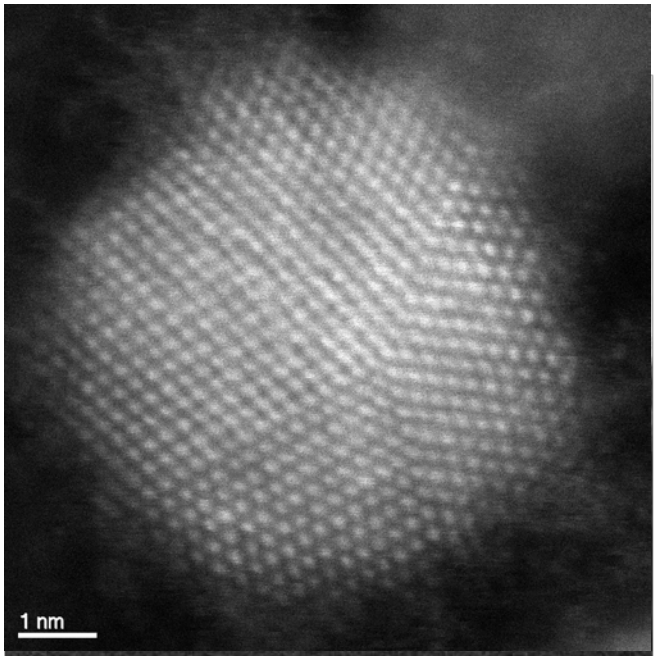
D. Slanac et al. *JACS* **2012.**

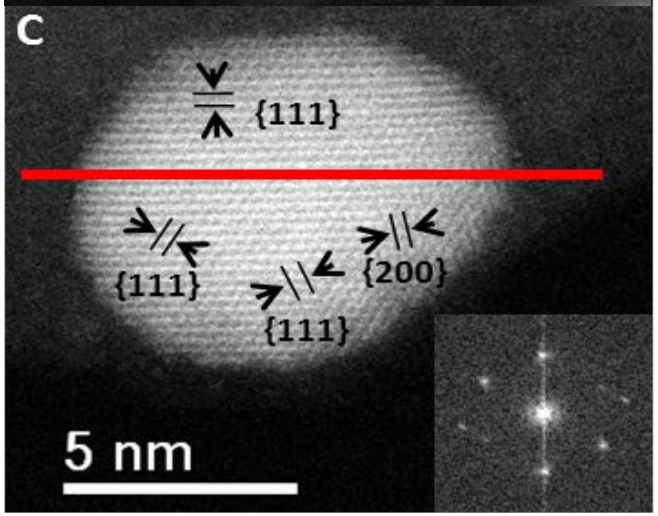
Homogeneous Ag-Pd Nanoalloys

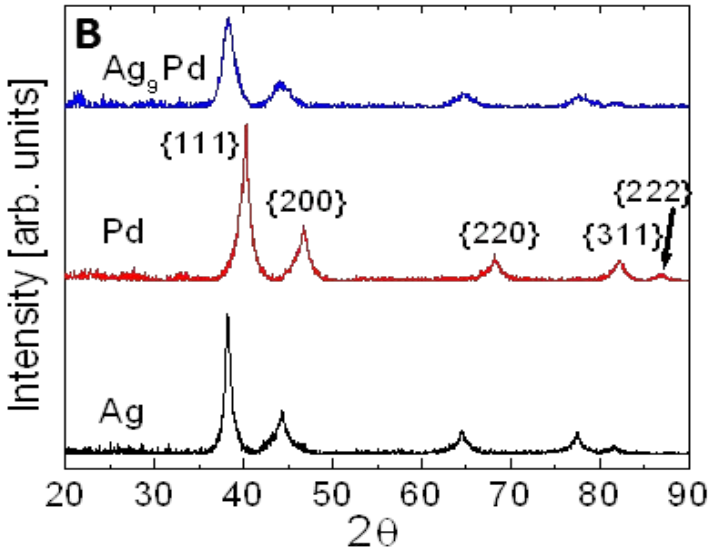


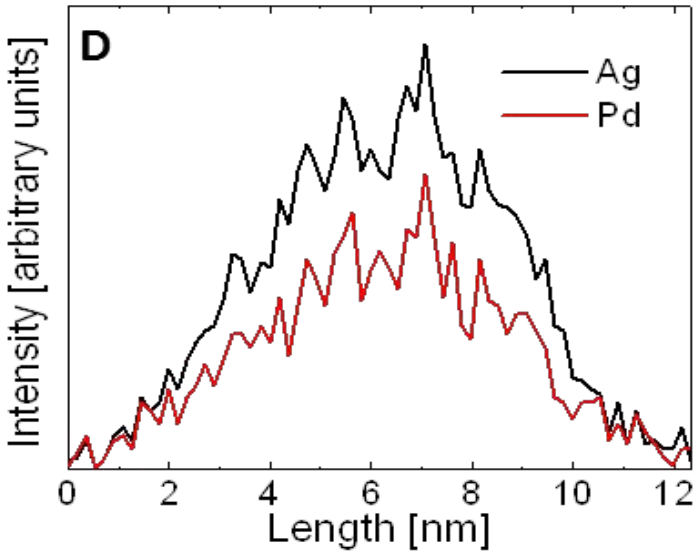
(A) as-synthesized Ag_9Pd nanoparticles, (B) Vulcan XC72 carbon supported Ag_9Pd particles after calcination at 450°C in N_2, and (C) commercial Pd/VC calcined at 450°C N_2. The alloy particles undergo slight sintering from 3.2 to 5.3 nm.

Homogeneous Ag-Pd Nanoalloys



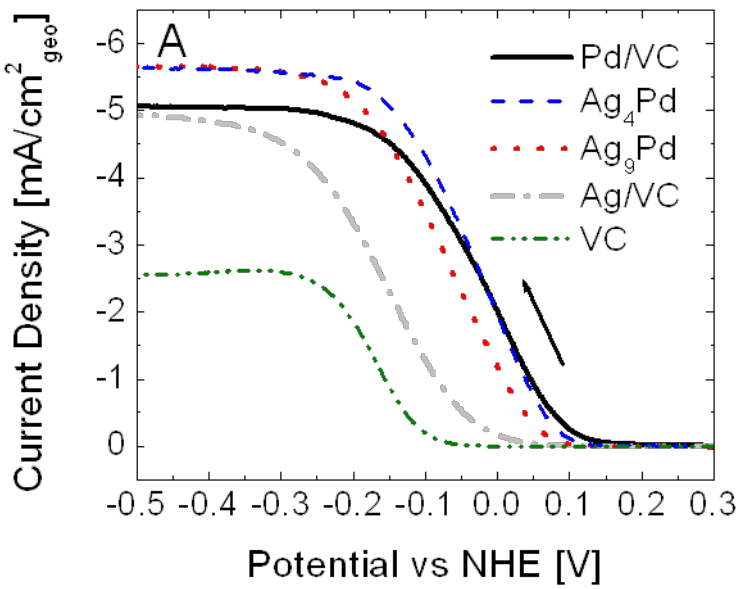


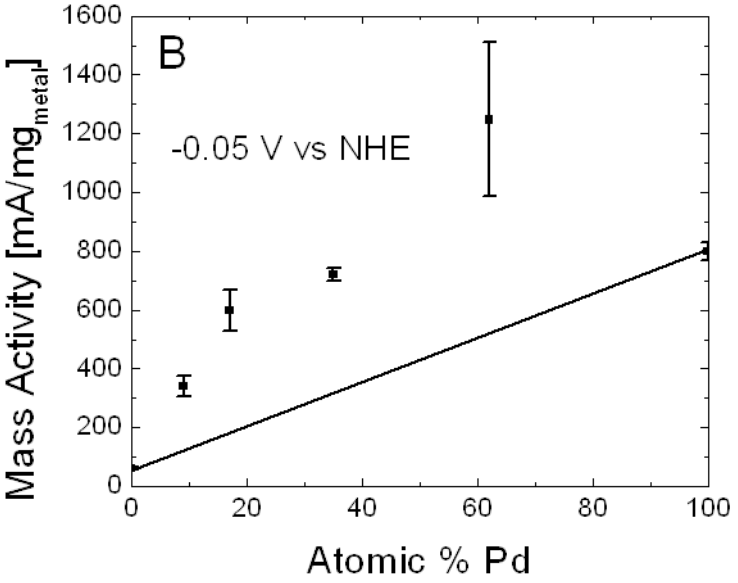


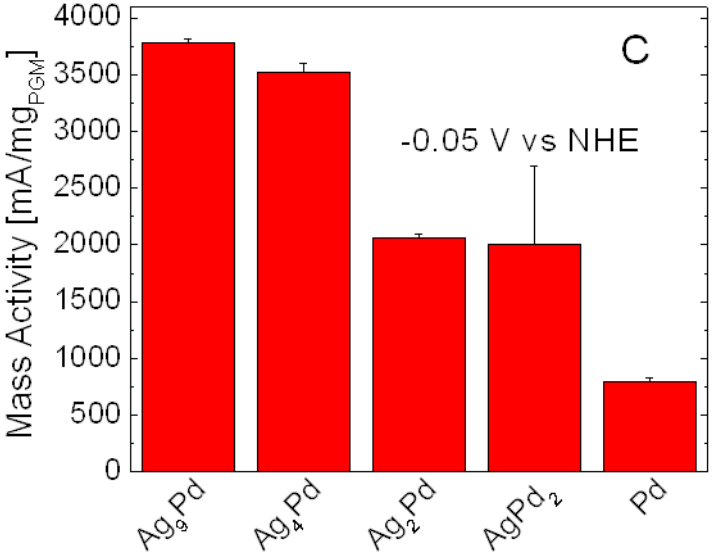


D. Slanac et al. *JACS* **2012.**

Activity Synergy from Ensemble and Ligand Effects







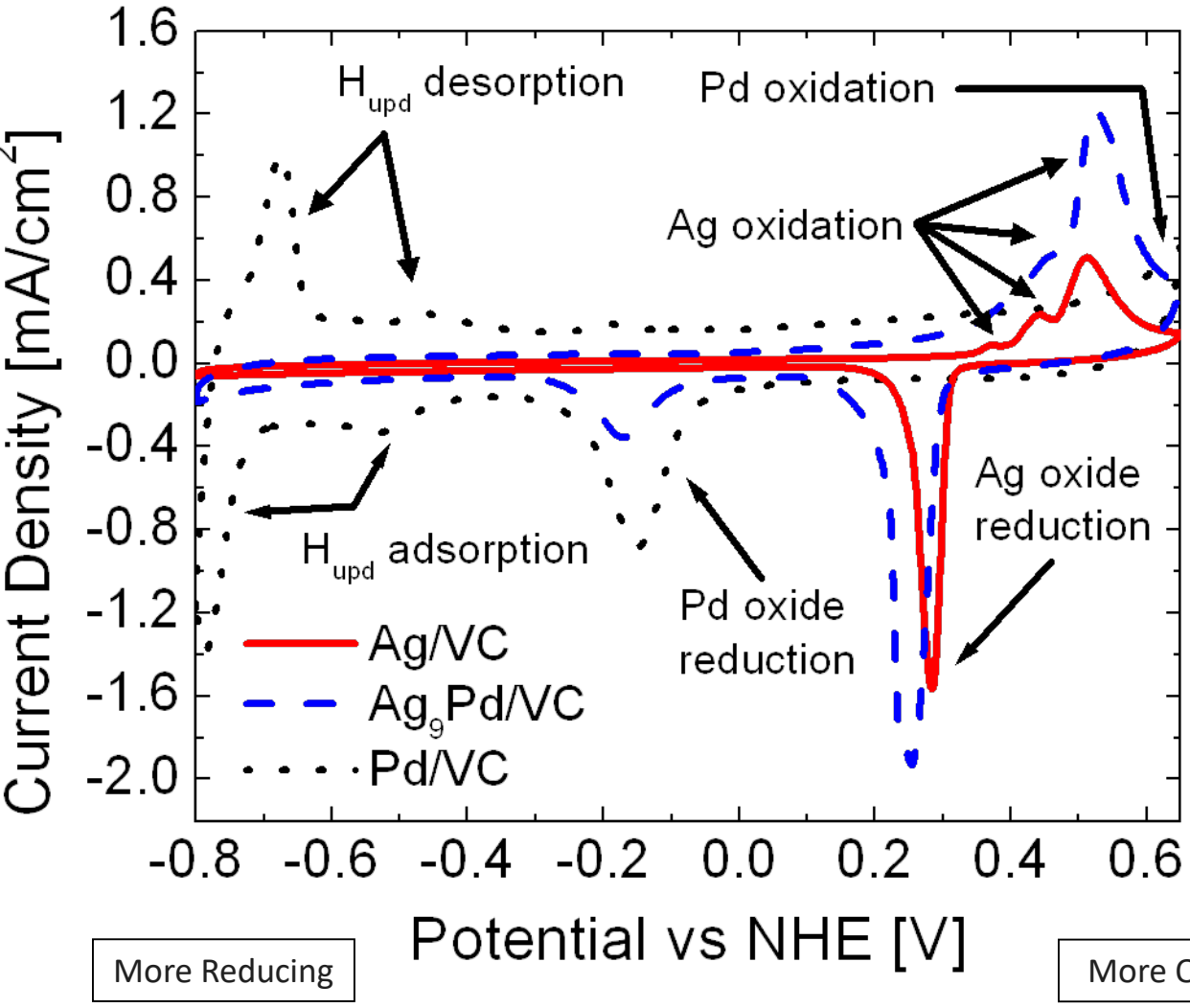
Total mass activity up to 4x over the expected linear combination of Ag and Pd

Pd helps O_2 bond breaking
Ag facilitates desorption of OH^-

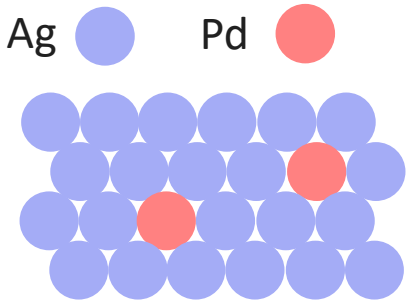
Per expensive Pd metal, ~4x activity enhancement

Electrochemical Evidence of Pd Single Atoms

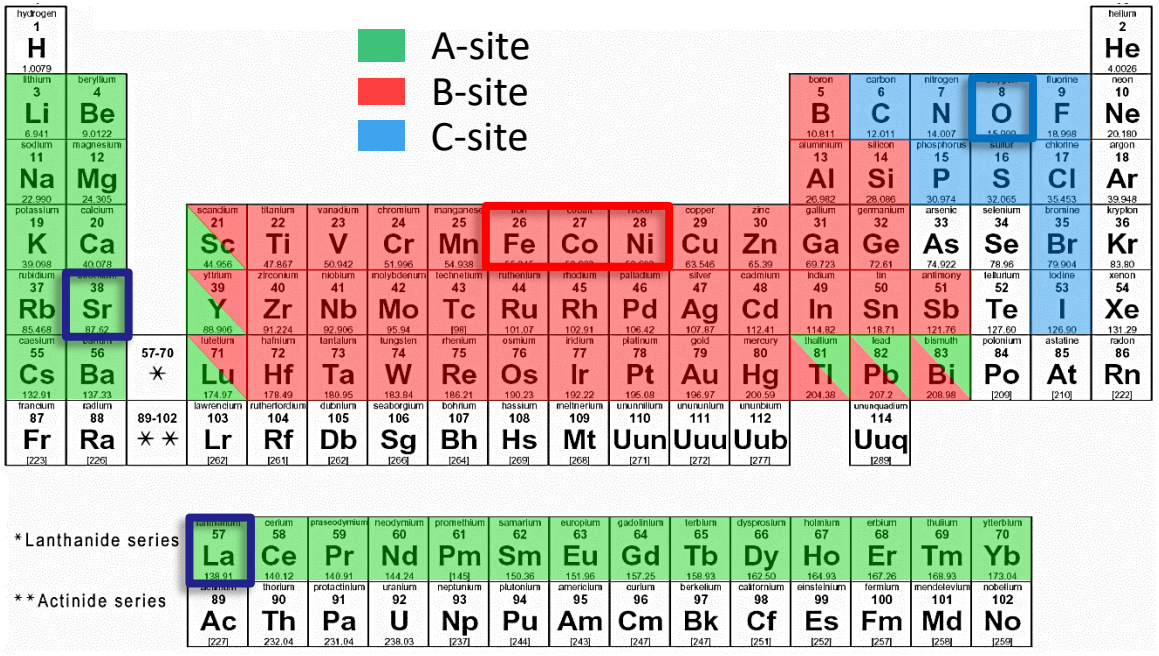
In Ar saturated 0.1M KOH

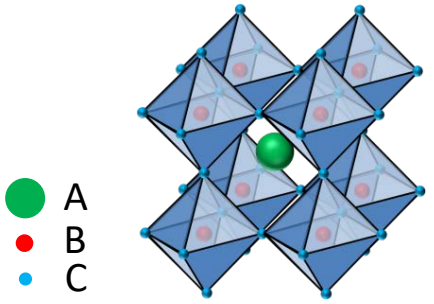


1. **Both Pd and Ag present in surface (reduction peaks)**
2. **No H_{upd} on alloy surface**
3. **Minimum of Pd dimers to give H_{upd}**
4. **Shift in metal ox/red peaks → ligand effect**
5. **Pd facilitates oxygen, binding, and Ag facilitates desorption**

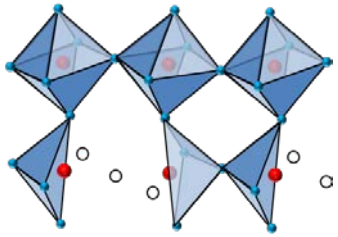


What is a Perovskite?

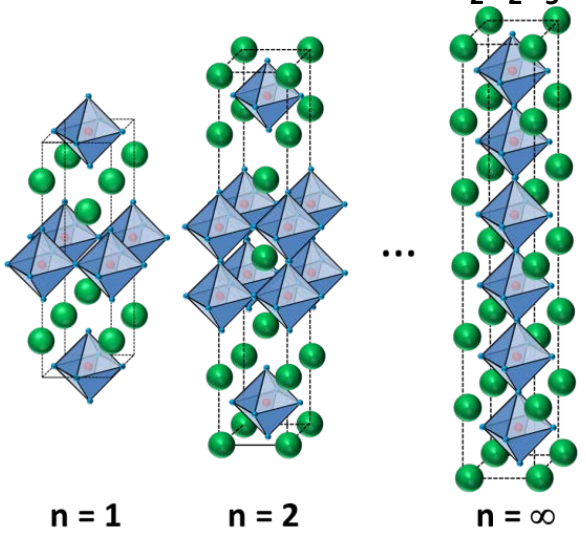




Perovskite: ABC_3



Brownmillerite: $A_2B_2C_5$



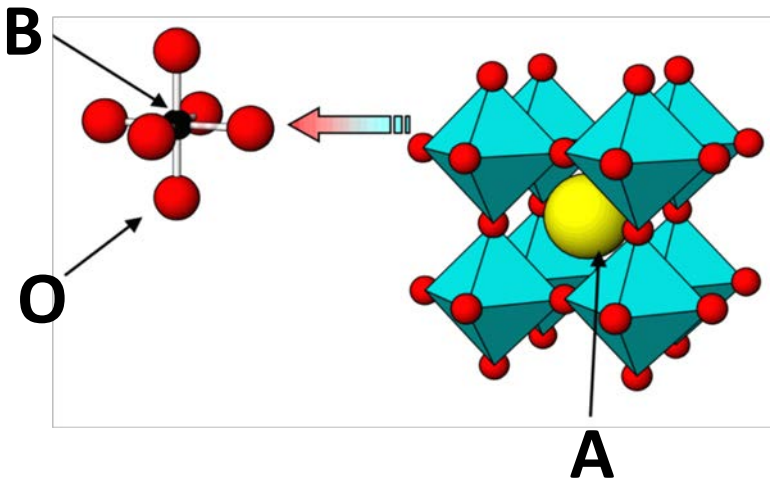
Ruddlesden-Popper: $(AC)(ABC_{3\pm\delta})_n$

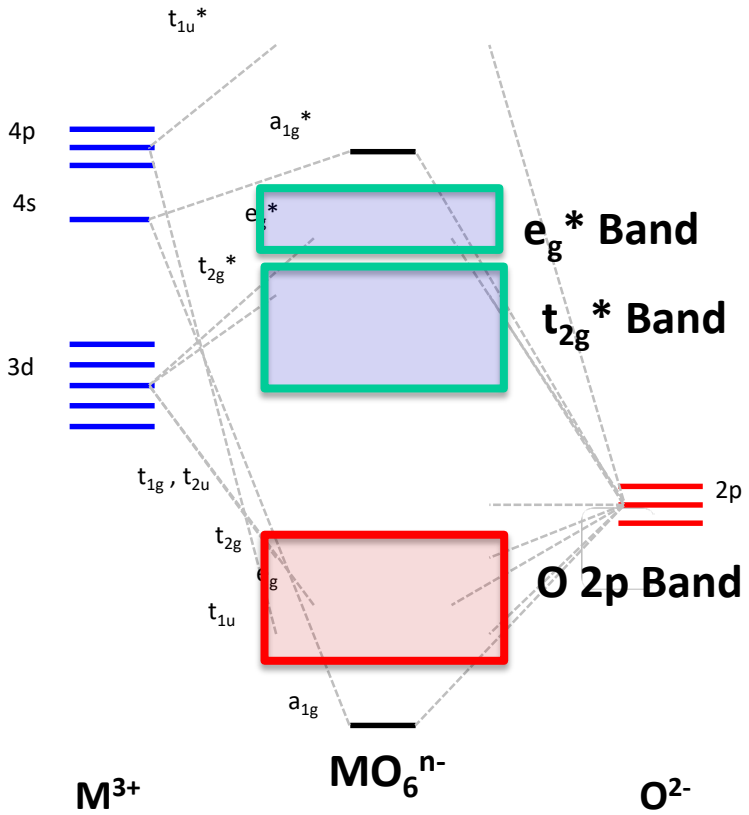
- Simple Cubic with formula ABC_3
- Generally **form at high temperatures** (>700° C), low S.A.
- Mixed ionic-electronic conductors
- Only B-Site is catalytically active

Background & Structure

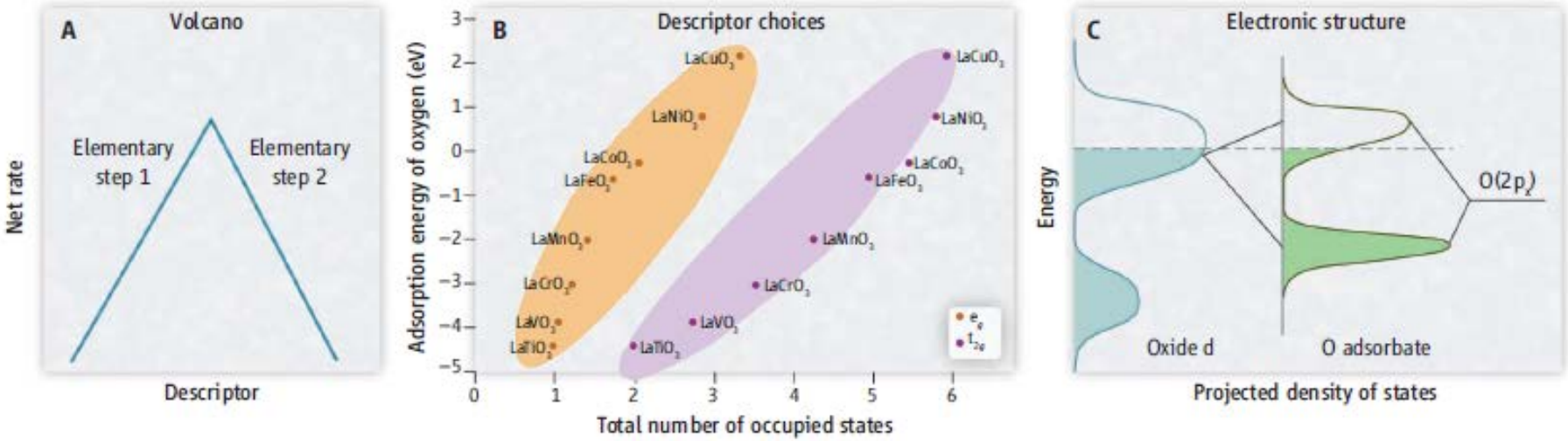
Perovskite-type oxide ABO_3

- B-site atom (1st row transition metal) in 6-fold octahedral coordination
- BO_6 units breaks *d* manifold degeneracy
- Cubic, hexagonal -> rhombohedral crystal structure, influenced by:
  - ionic sizes
  - B 3*d* – O 2*p* interactions
  - J-T distortions





Theory Guided Predictive Activity Descriptors

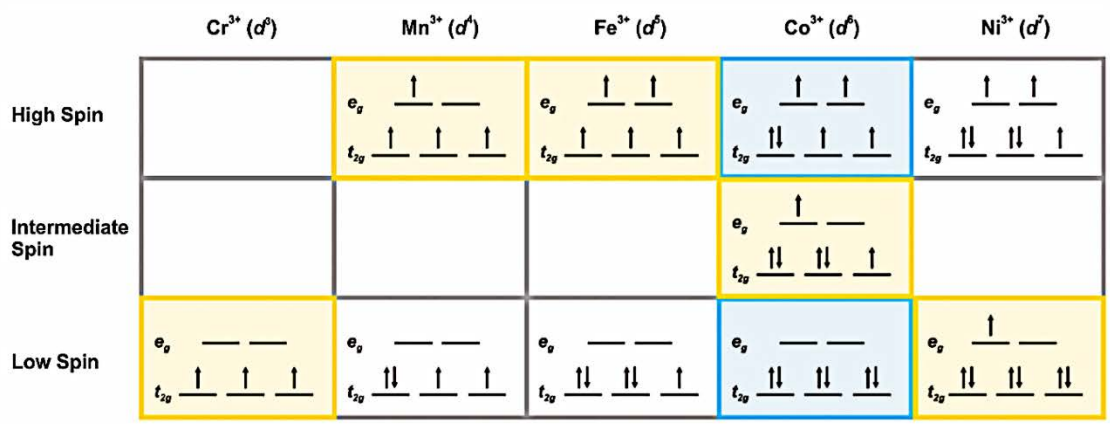


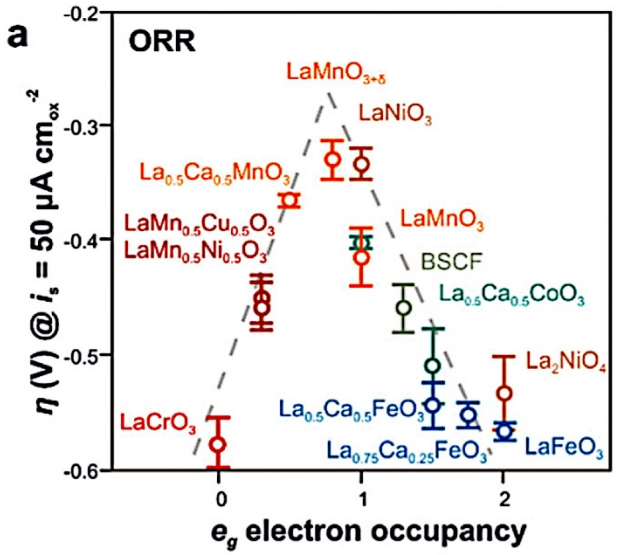
Optimizing Perovskites for the Water-Splitting Reaction
Aleksandra Vojvodic, *et al.*
Science **334**, 1355 (2011);

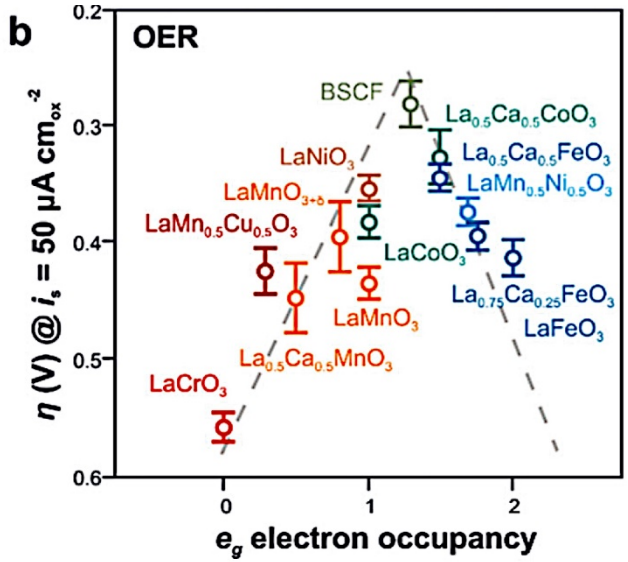
Catalyst Design Principles

e_g filling of 1 proposed as governing descriptor of OER/ORR activity – Sabatier principle

- Filling >1 → more antibonding → OH^- too weakly bound
- Filling <1 → more bonding → OH^- too strongly bound





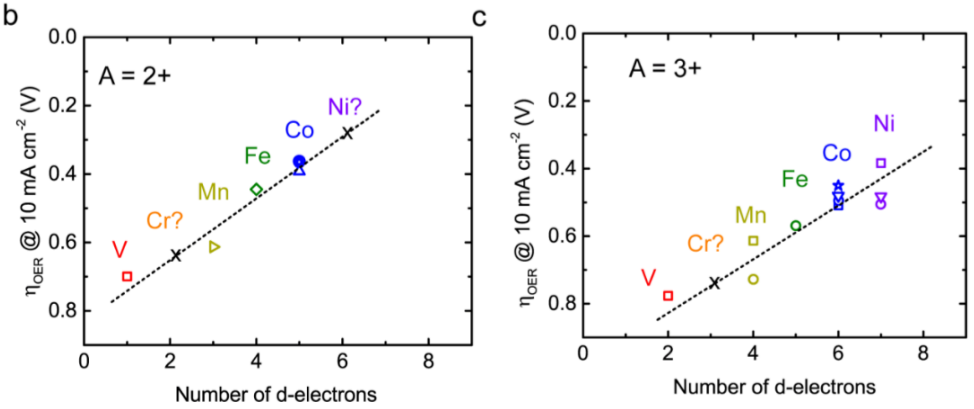


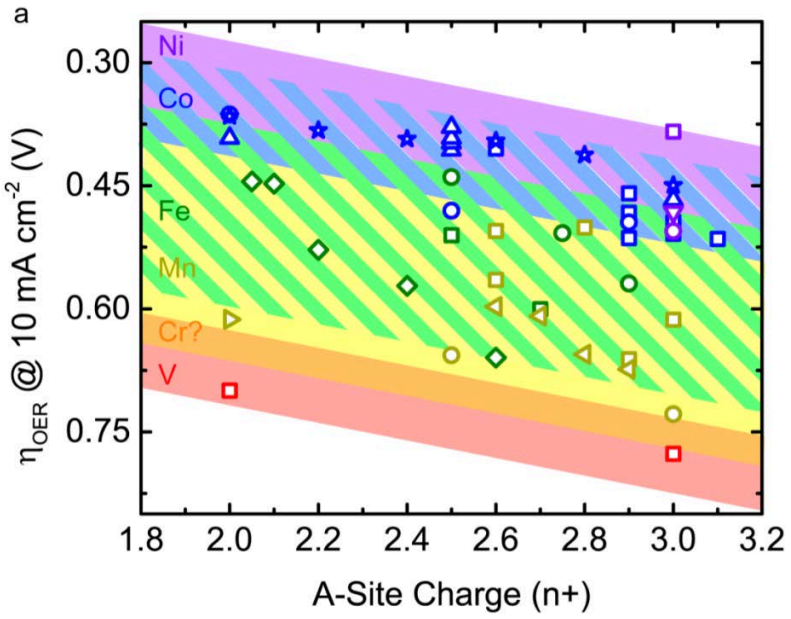
Hong, W. T.; Grimaud, A.; Suntivich, J.; Shao-Horn, Y. *Energy Environ. Sci.*, **2015**

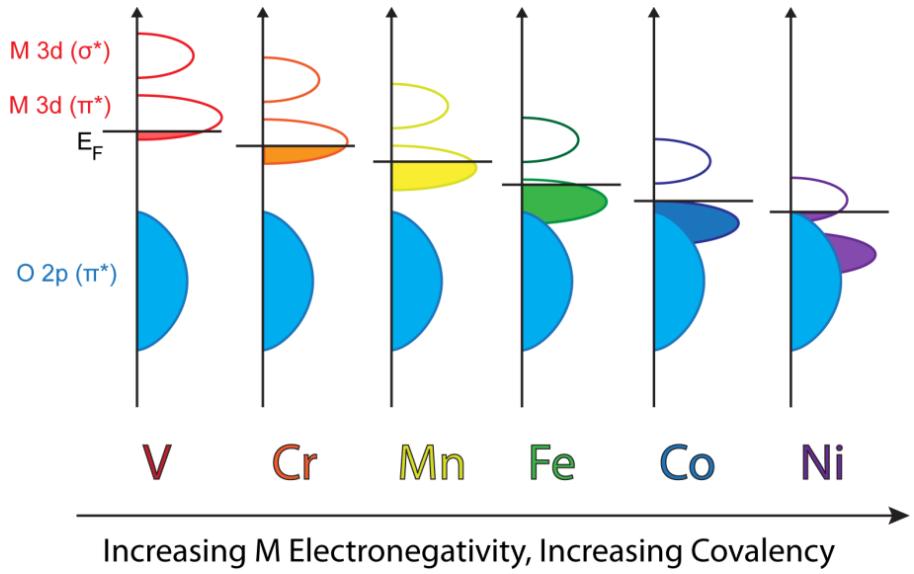
Catalyst Design Principles

More d electrons → greater activity

- More electronegative TM brings 3d electron energies down
- More covalent M – O bond

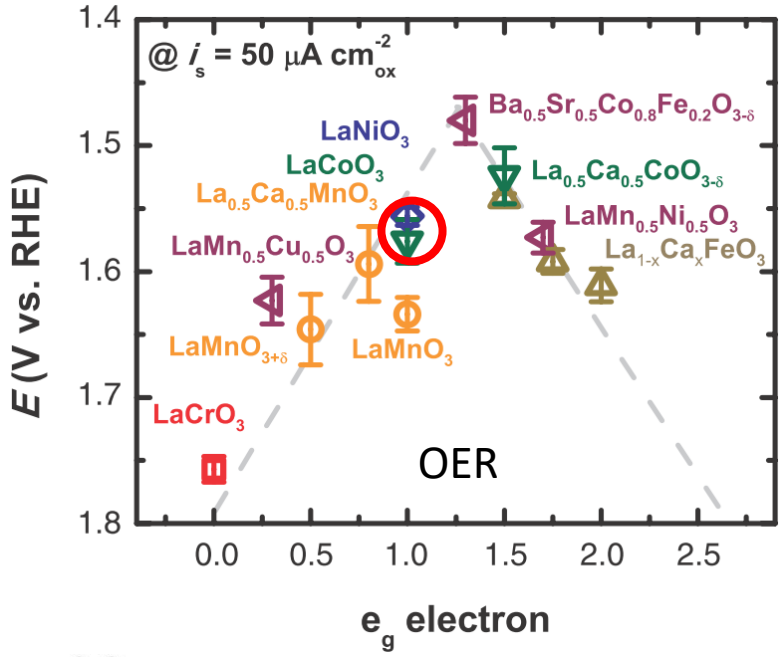


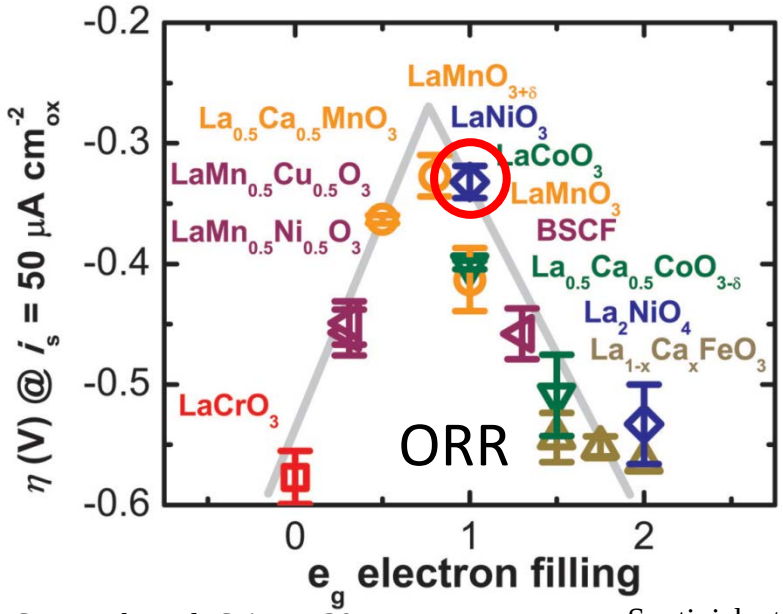




Rong, Kolpak, *ACS Catalysis* **2016**
Mefford et al. *Nature Comm.,* **2016**

Perovskite // Activity Relationships





e_g filling as catalytic descriptor

- same filling, different activity
- verify trend / reduce error

'Covalency' between M-O

Catalyze $k_{o/r1}$, $k_{o/r2}$ or k_d

<u>OER</u>

$H_2O + 2OH^- \rightarrow O_{ad} + 2H_2O + 2e^-$ k_{o1}

$O_{ad} + H_2O + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$ k_{o2}

<u>ORR</u>

$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ k_{r1}

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ k_{r2}

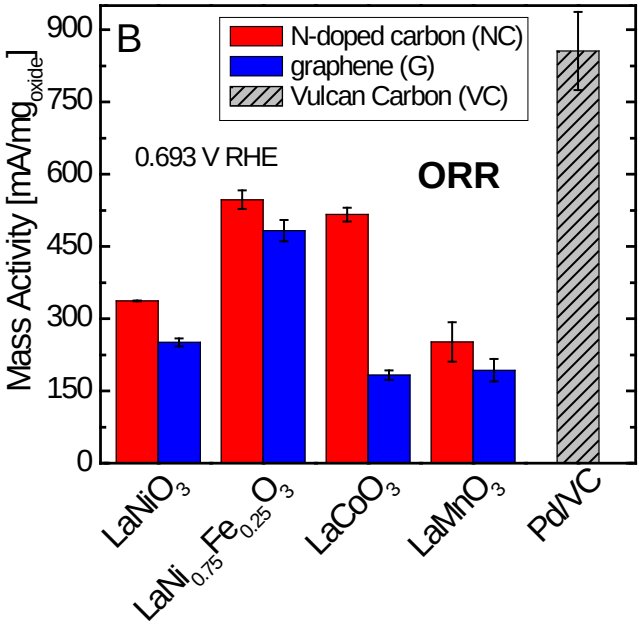
<u>Chemical Disproportionation</u>

$2HO_2^- \rightarrow 2OH^- + O_2$ k_d

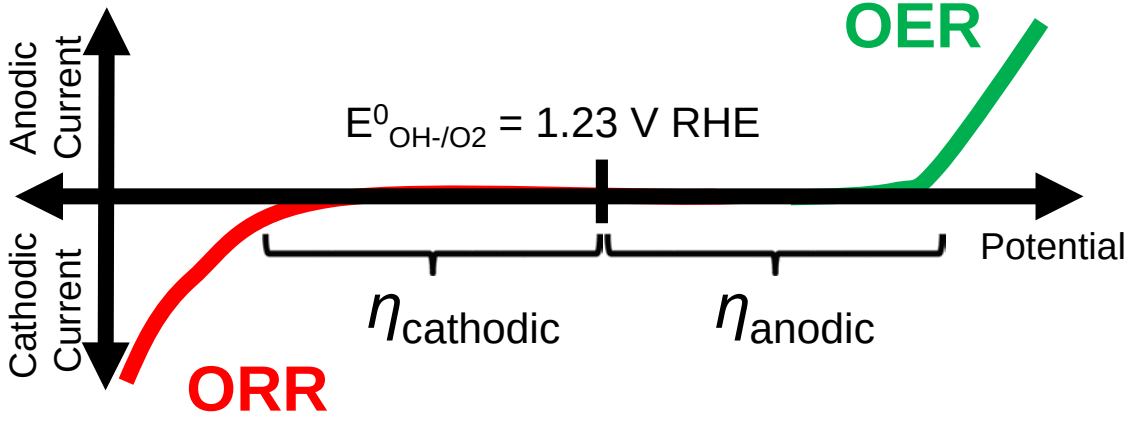
Suntivich et al. *Science* **2011**

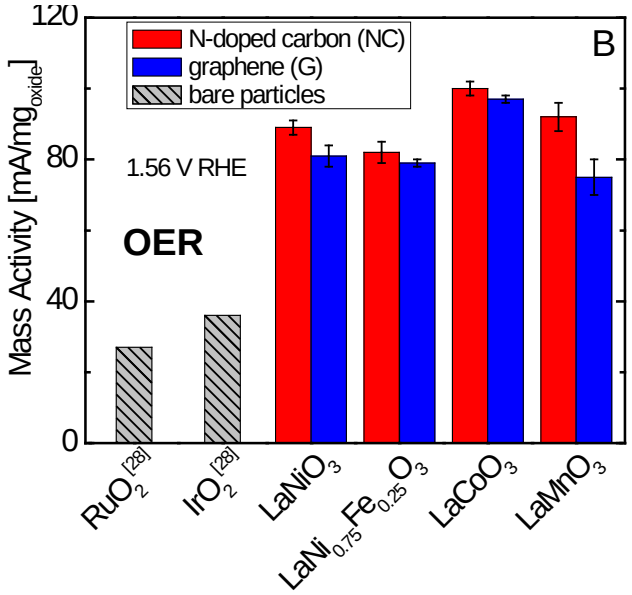
Suntivich et al. *Nature Materials* **2011**

Bifunctional Pervoskite Catalysts



- Support effects differ per reaction
- $LaNi_{0.75}Fe_{0.25}O_3$ is 90% more active than $LaNiO_3$



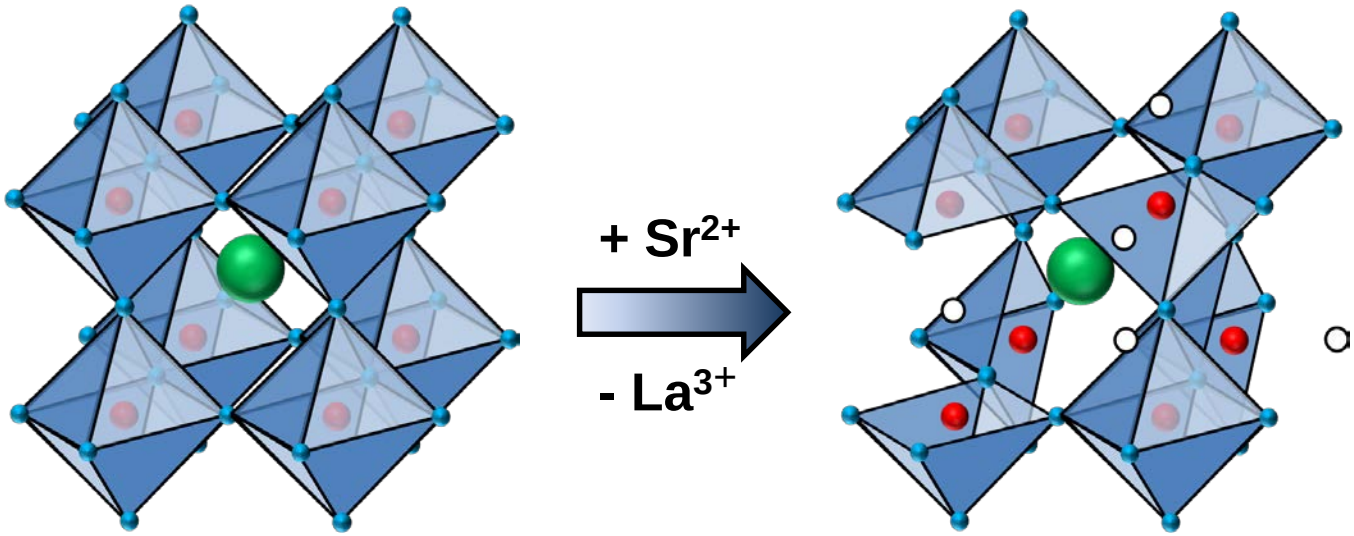


Material	ORR Potential (V) vs RHE @ j = -3 mA/cm^2	OER Potential (V) vs RHE @ j = 10 mA/cm^2	ΔE (V) Bifunctionality
$LaNiO_3$/NC	0.64	1.66	**1.02**
$LaNi_{0.75}Fe_{0.25}O_3$/NC	0.67	1.68	**1.01**
$LaCoO_3$/NC	0.64	1.64	**1.00**
20% Ir/C¥	0.69	1.61	**0.92**
20% Ru/C¥	0.73	1.62	**1.01**
20% Pt/C¥	0.86	2.02	**1.16**

Hardin, Mefford, et al. *Chem. Mater*. **2014**

¥ Jaramillo et al. *J. Am. Chem. Soc*. **2010**

Using Chemical Substitution to Control Oxygen Content in $La_{1-x}Sr_xCoO_{3-\delta}$

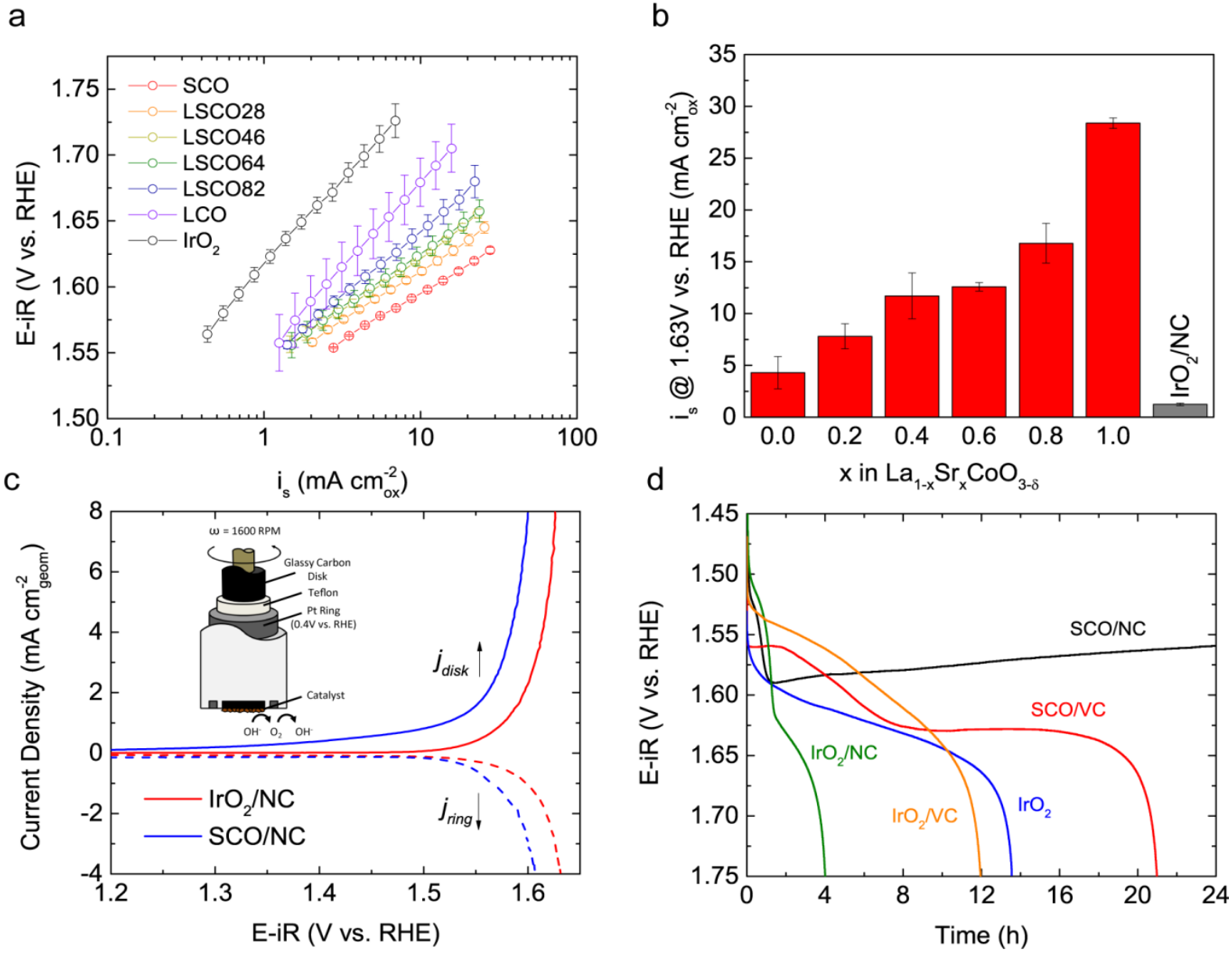


- Substituting Sr^{2+} for La^{3+} gives better control of oxygen content than thermal reduction processes
- Oxygen content is a function of both Sr^{2+} doping concentrations and charge compensation through an increase of Co oxidation state:

$$LaCo^{III}O_3 + xSr^{2+} - xLa^{3+} - \delta O^{2-} \rightarrow La_{1-x}Sr_xCo^{(III+x-\delta/2)}O_{3-\delta}$$

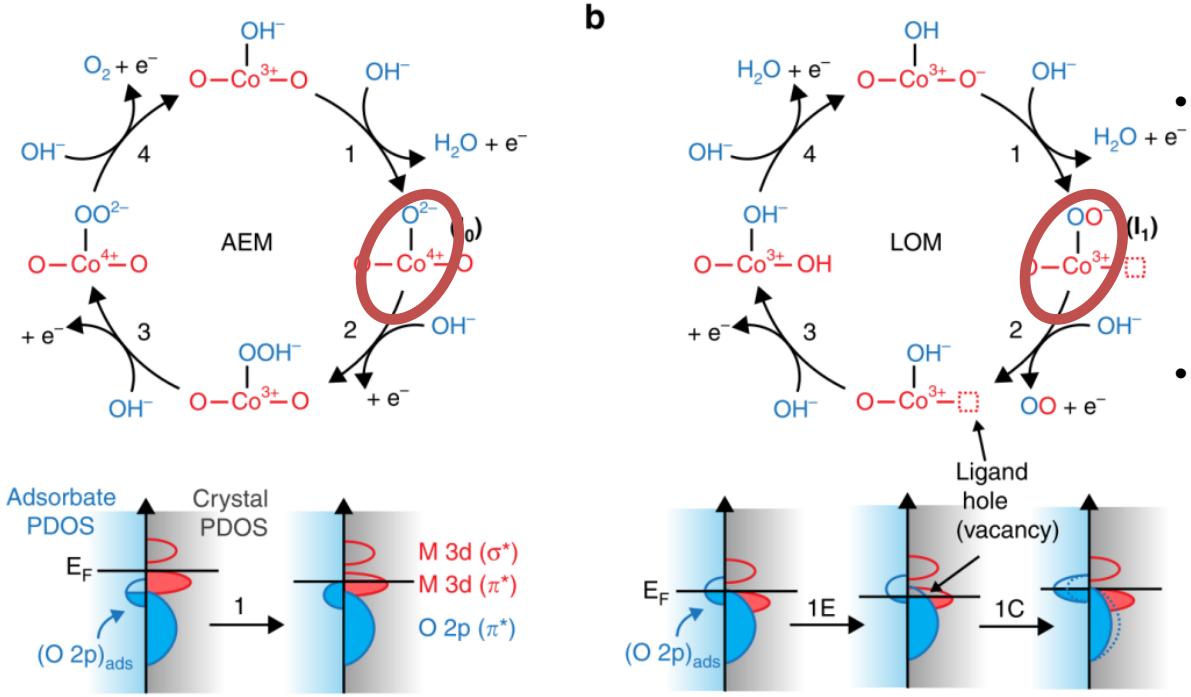
Yan, J.-Q., Zhou, J.-S. & Goodenough, J. B. Bond-length fluctuations and the spin-state transition in $LCoO_3$ (L=La, Pr, and Nd). *Phys. Rev. B* **69,** 134409 (2004).

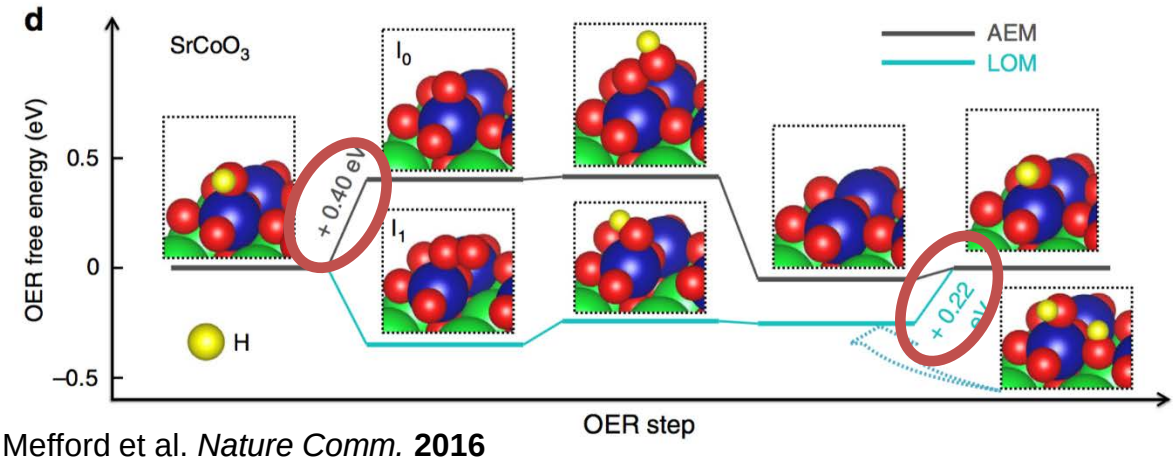
OER of LSCO Samples



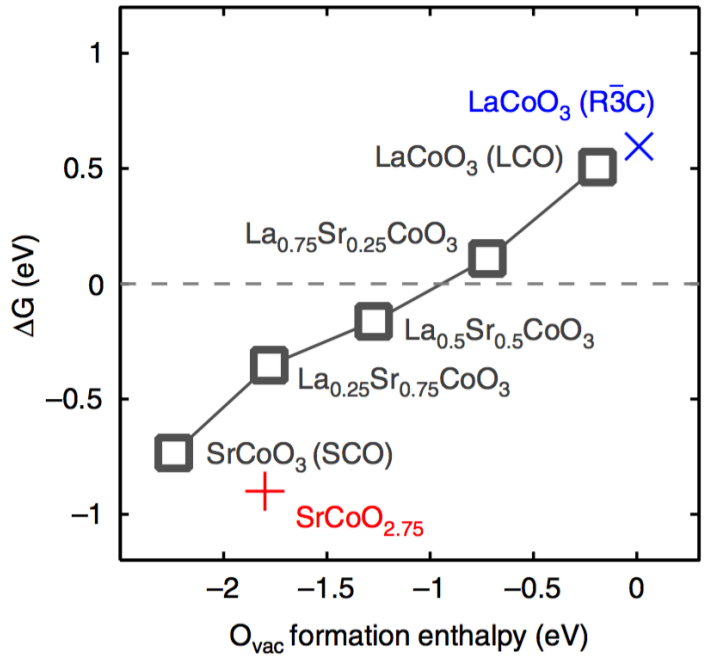
- **Increase in activity with increasing Sr content**

Lattice Oxygen Mediated Oxidation



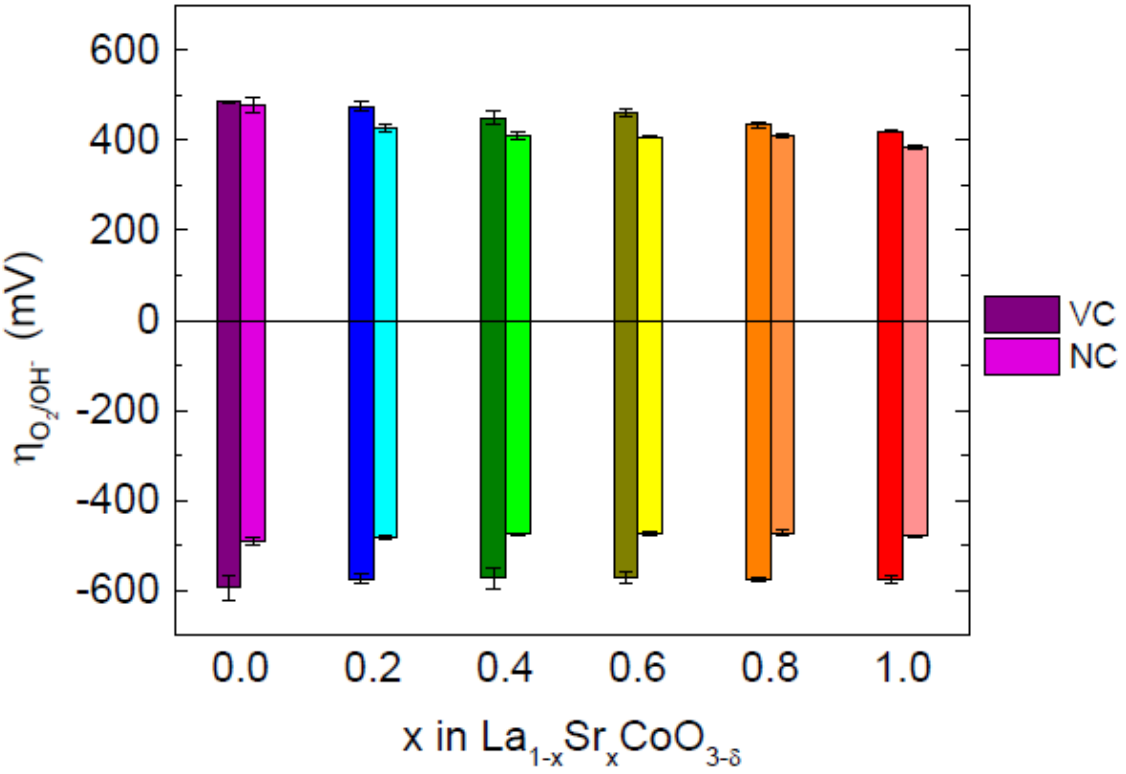


- New OER mechanism proposed, supported by DFT → lattice oxygen mediated (LOM)
  - Lower ΔG for RDS
  - Requires M-O bond covalency
- Labile lattice oxygen experimentally shown as indicator of M-O covalency



Mefford et al. *Nature Comm.* **2016**

Bifunctional OER and ORR $La_{1-x}Sr_xCoO_{3-\delta}$ Catalysts

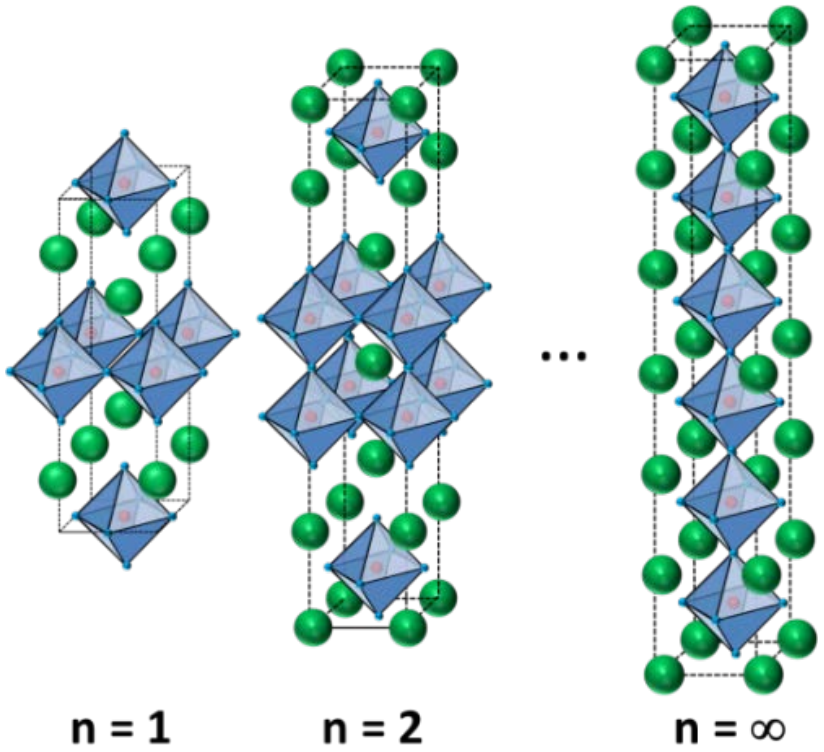


x	VC	NC
0	1.080	0.970
0.2	1.050	0.909
0.4	1.023	0.886
0.6	1.031	0.881
0.8	1.010	0.885
1	0.998	0.864

ORR @ i_k = -3 mA/cm^2_{geom}
OER @ i_k = 10 mA/cm^2_{geom}

Carbon is crucial in influencing oxygen electrocatalysis in bifunctional air electrodes, especially for the ORR!

What is a Ruddlesden-Popper?



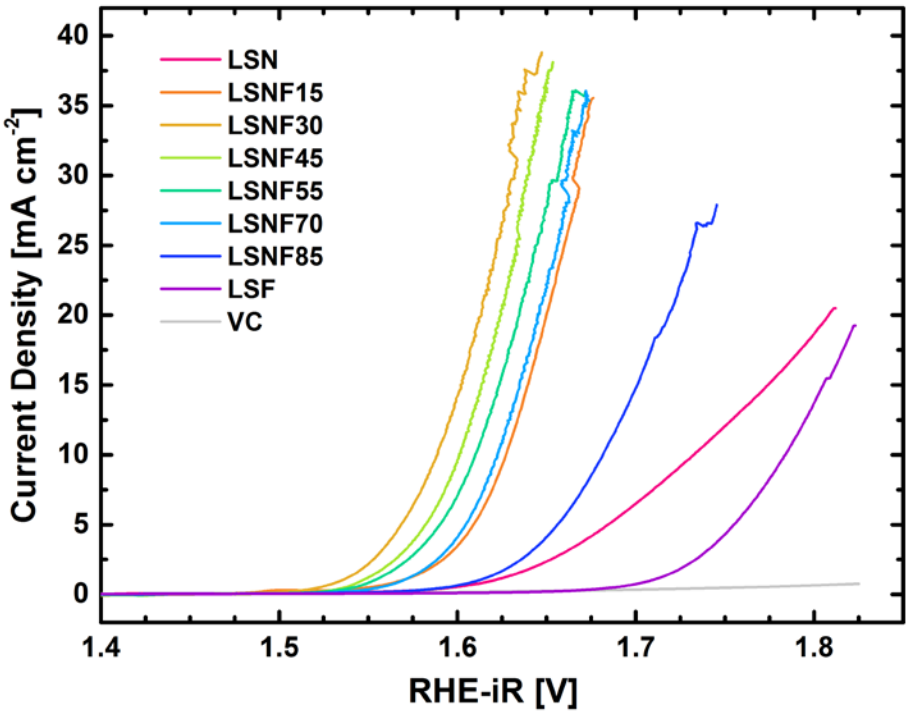
- Formula $(AO)(ABO_3)_n$
- *n* = perovskite layers (ABO_3) separated by a rock-salt (AO) interface
- As n → ∞, RP becomes pure ABO_3 perovskite
- Location of strained AO interfaces that support Sr^{2+} substitution of La^{3+} which is unstable in a pure perovskite phase

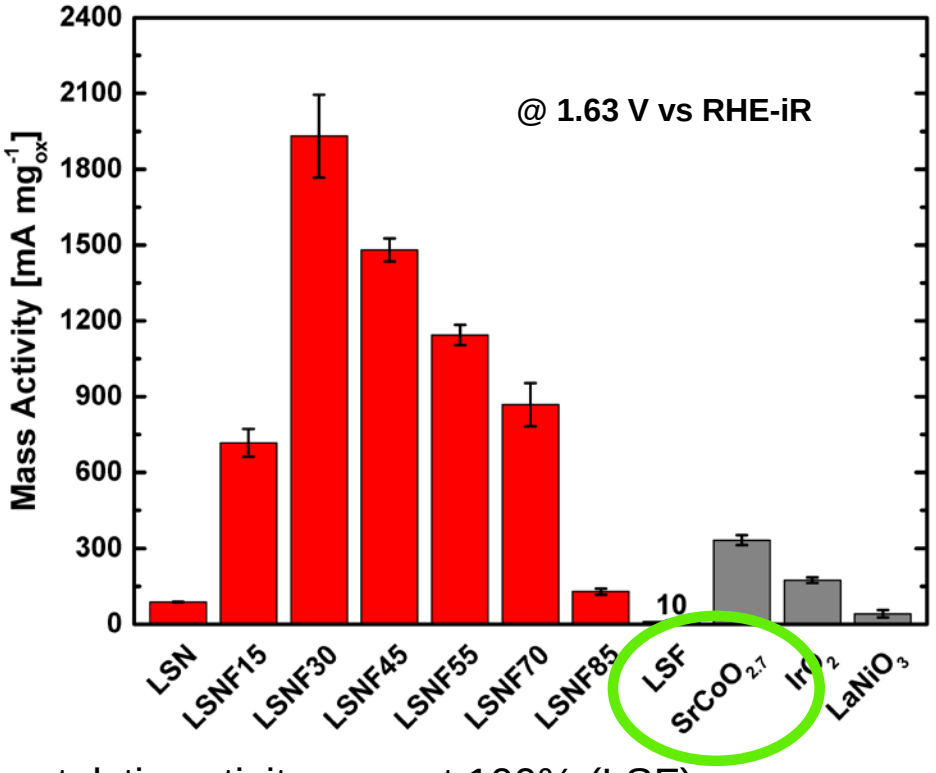
n	Formula	A = Ln^{3+}, B^{x+}	A= Sr^{2+}, B^{x+}
1	$A_2BO_{4\pm\delta}$	2	4
n	$(AO)(ABO_3)_n$	> 2.66	4
∞	ABO_3	3	4

Ruddlesden-Popper: $(AO)(ABO_{3\pm\delta})_n$

RP supports structural and electronic configurations not realizable in perovskites

OER Activity of Perovskites and RP





- All amounts of Fe substitution increase catalytic activity, except 100% (LSF)
- Most active composition being LSNF30 (32.7 mA cm$^{-2}_{ox}$)
- Polarization curves are averaged between anodic and cathodic scans to eliminate capacitive effects → **little to no hysteresis indicates catalyst stability**

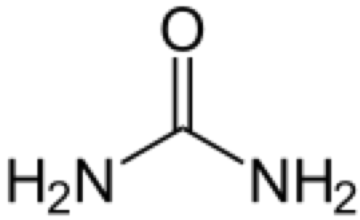
OER conditions: O_2 saturated 0.1 M KOH at 10 mV/s and 1600 rpm; 51 $\mu g_{tot}/cm^2$, 30 wt. % oxide on VC

Forslund, Hardin, et al. *Nature Comm.* **2018**

Urea Oxidation Reaction

At the Anode:

$$CO(NH_2)_{2(aq)} + 6OH^- \rightarrow N_{2(g)} + 5H_2O + CO_{2(g)} + 6e^-$$



Urea

At the Cathode:

$$6H_2O + 6e^- \rightarrow 3H_{2(g)} + 6OH^-$$

Overall:

$$CO(NH_2)_{2(aq)} + H_2O \rightarrow N_{2(g)} + 3H_{2(g)} + CO_{2(g)}$$

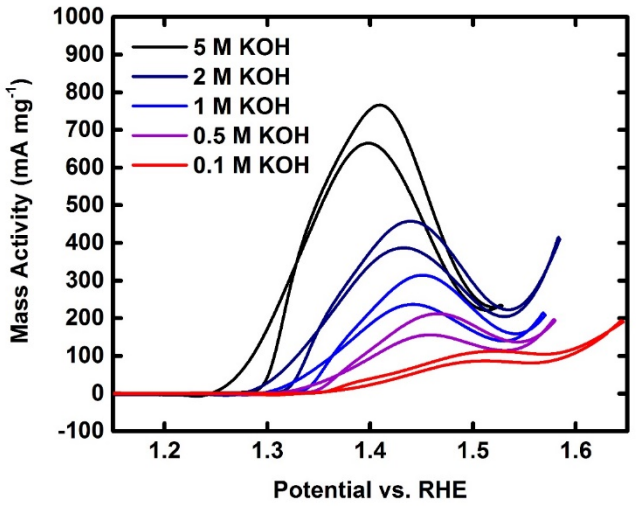
Ni metal in various morphologies used by many, EC' mechanism proposed

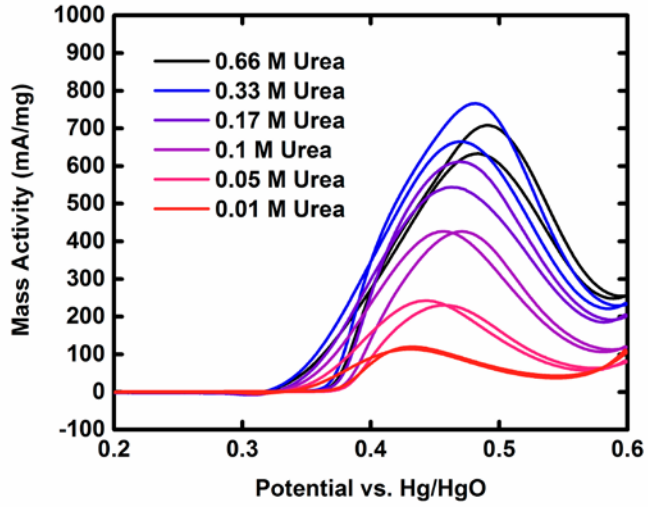
$$Ni(OH)_{2(s)} + OH^- \rightarrow NiOOH_{(s)} + H_2O + e^-$$

$$NiOOH_{(s)} + CO(NH_2)_{2(aq)} \rightarrow Ni(OH)_{2(s)} + N_{2(g)} + 3H_{2(g)} + CO_{2(g)}$$

Use a material where nickel is Ni^{3+} already

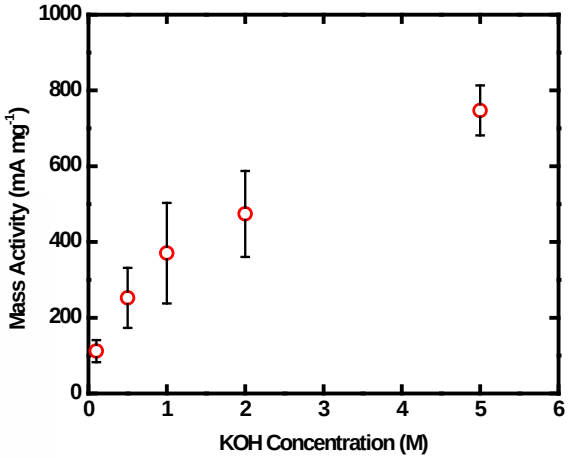
$LaNiO_3$ Catalytic Activity

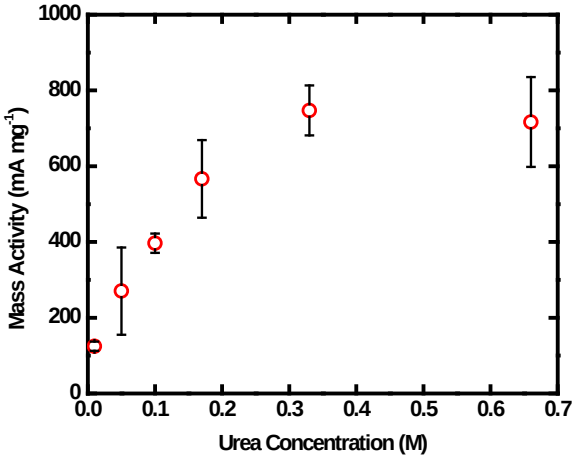




ACS Cat. **2016**, *6*, 5044

- Supported $LaNiO_3$ on Vulcan carbon (30 wt%) by ball-milling
- Suspended catalyst in EtOH with Na-substituted Nafion binder and drop cast onto 5 mm GCE
- Test at various concentrations of Ar- saturated KOH and urea at a scan rate of 10 mV s^{-1}

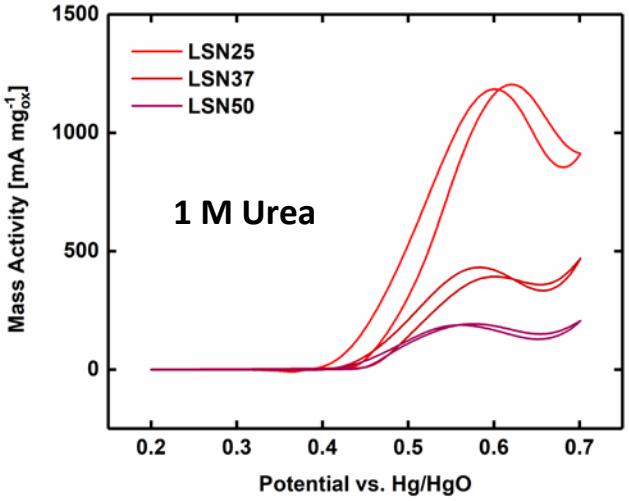


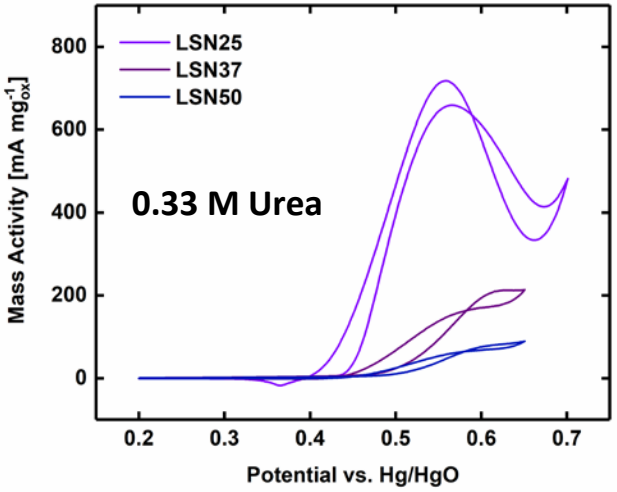


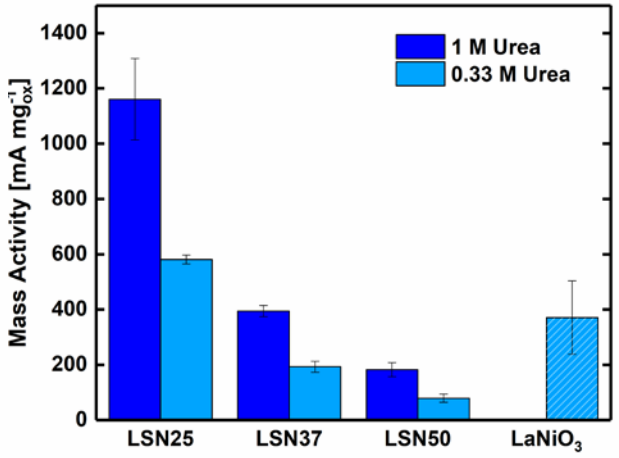
- Mass activity of 371 mA mg^{-1} 2.25 A $mg^{-1}cm^{-2}$ in 1M KOH compared to 830 mA $mg^{-1}cm^{-2}$ in 1M KOH for $NiMoO_4$
- Potential shifts cathodic with increasing KOH concentration but not with increasing urea concentration
  - Supports the EC' mechanism

Urea Oxidation On LSN RP

Tested in 0.33 M and 1 M urea, 1 M KOH at 10 mV s^{-1} on stationary glassy carbon





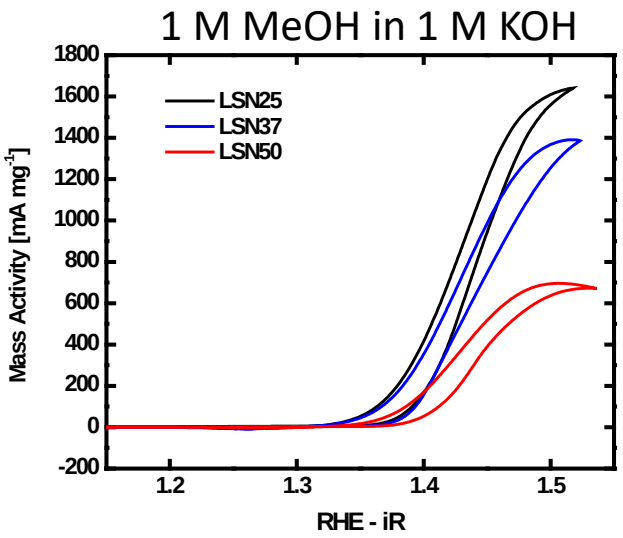


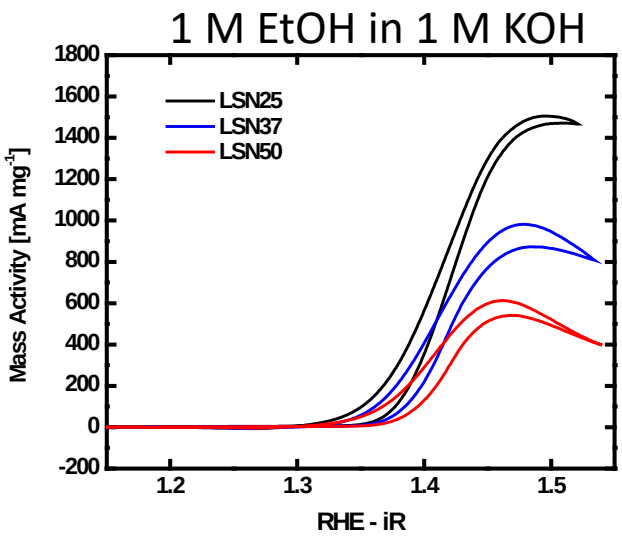
Increasing Ni oxidation state above Ni^{3+} leads to higher activities

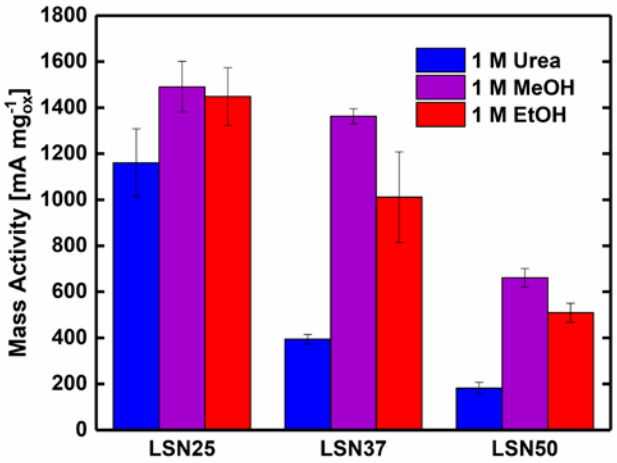
Material	Ni Oxidation State
LSN50	3
LSN37	3.25
LSN25	3.5

Forslund, R. et al. *ACS Catal.* **2019,** *9*(3), 2664–2673.

MeOH and EtOH Oxidation





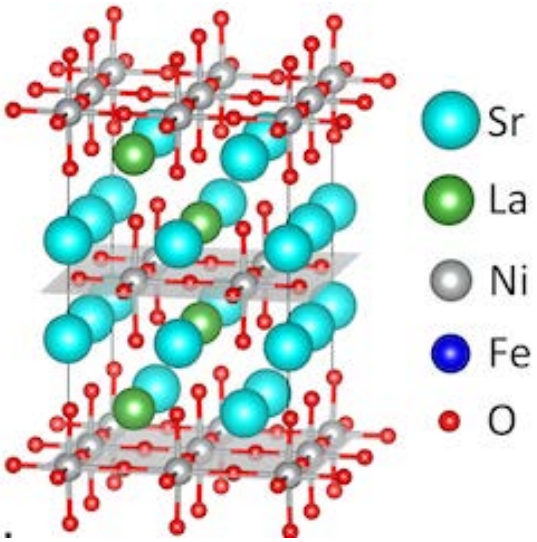


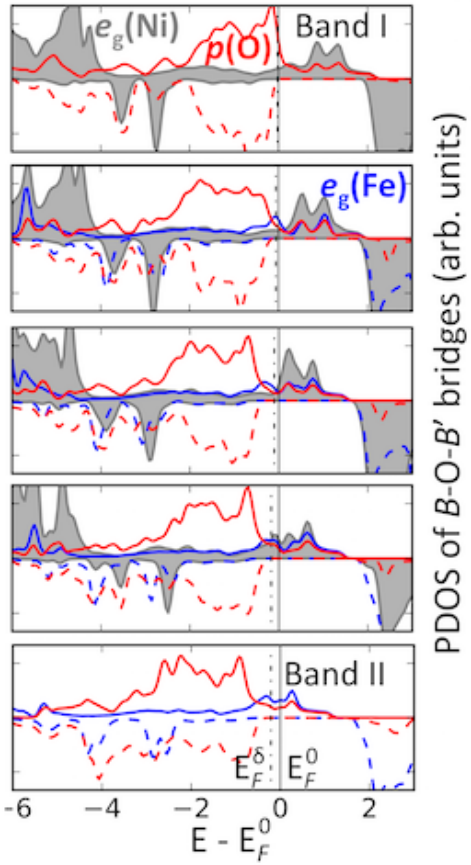
- **Activities for both ethanol and methanol oxidation are extremely high**
- **All three reactions have similar onset potentials**
  - **Corresponds with $Ni^{2+/3+}$ redox couple**
  - **Indicates that all three reactions (MeOH, EtOH, Urea) may follow the EC' mechanism**

Forslund, R. et al. *ACS Catal.* **2019,** *9*(3), 2664–2673.

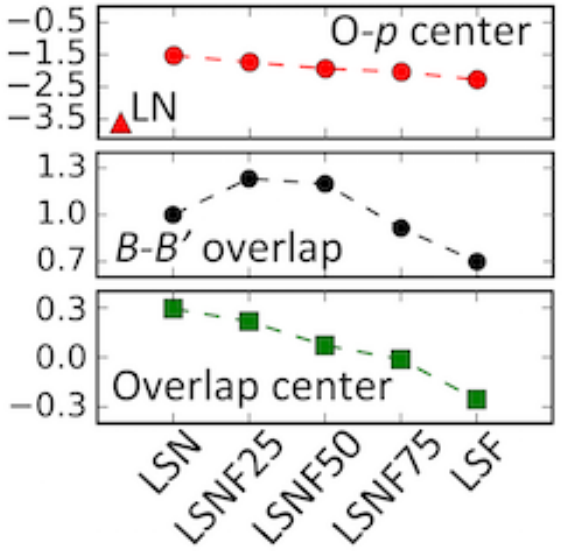
DFT+U Modeling On LSN RP

DFT+*U* to model PDOS of Ni-O-Fe bridges





Significant overlap of the Ni e_g^*, Fe e_g^*, and O 2p bands at E_F for all compositions

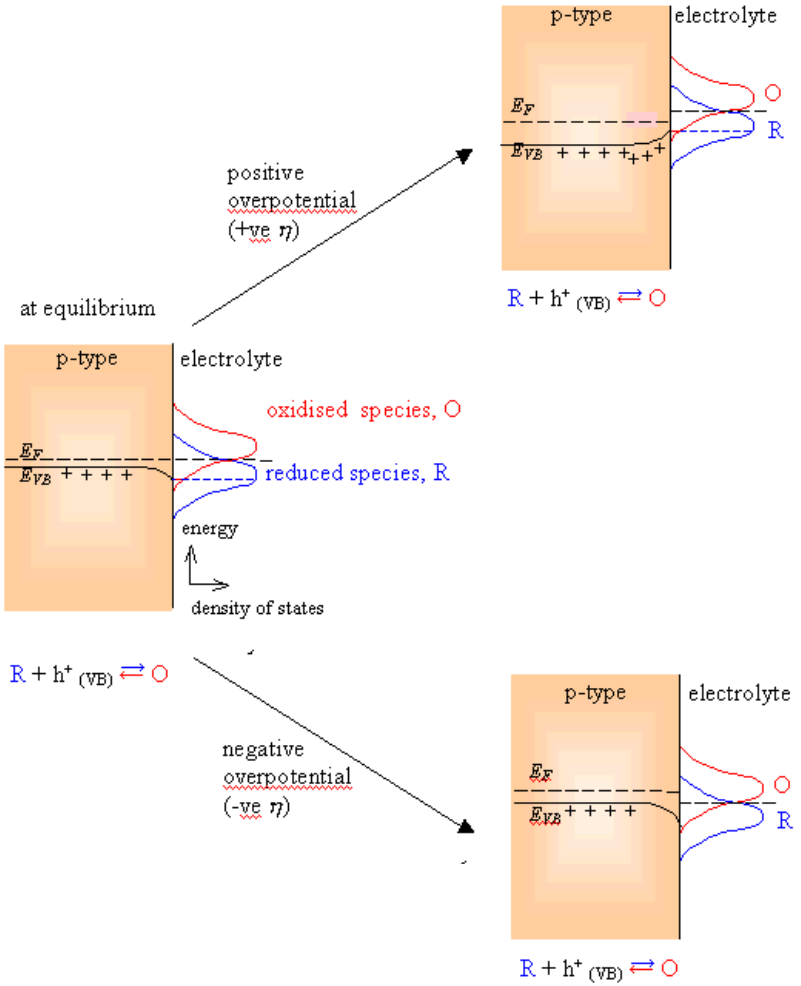


Larger bandwidth → higher density of occupied/unoccupied states around E_F → more surface redox reactions via only slight Fermi level shift → less energetic cost

e_g(Ni) and e_g(Fe) overlap with *p*(O) across the Fermi level: cross-gap hybridization

Forslund, Harding et al. *Nature Comm.* 2018 9(1) 3150.

Marcus-Gerischer Model of ET



*Electron transfer is fastest when the electron has the same energy in the electrode as it does in **Ox** at the point of transfer. So the rate will be proportional to the DOS.*

- Probe the relationship between electronic properties and reactivity
  - Semi-conductor properties of Perovskites
  - Density of States (DOS)
  - Effects of substitution and defects
- Correlation between electronic properties and electrochemical activity
  - Structural composition
  - Electron Transfer
  - Catalytic behavior towards OER and ORR and H_2O_2 decomposition, SM oxidations

$$i_{redn} \propto k^{-} W_{ox}(E) C_{ox}^{0} N_s(E)$$

McCreery, R.L., *J. Phys. Chem.*. 1994, *98*, 5314-5319.

Summary

New synthesis routes offer exquisite control of properties

- **Facile tuning of size, crystallinity, composition and morphology**
- **More precise and efficient synthesis of catalysts**
- **Reduces processing induced changes in material properties**

New materials require development of advanced tools for study and elucidation of structure-property-performance

- **Benchmarking of Homogeneous & Heterogeneous Catalysts**

Nano-sized, alloy and core@shell architechures show promise as advanced energy conversion catalysts

- **Need for predictive guidelines and theory**
- **Need for activity benchmarks and standards**

Explore creation of new compositions/architectures for catalysis, biosensing and environmental remediation

- **Promotion of catalyst synergism/bifunctionality**