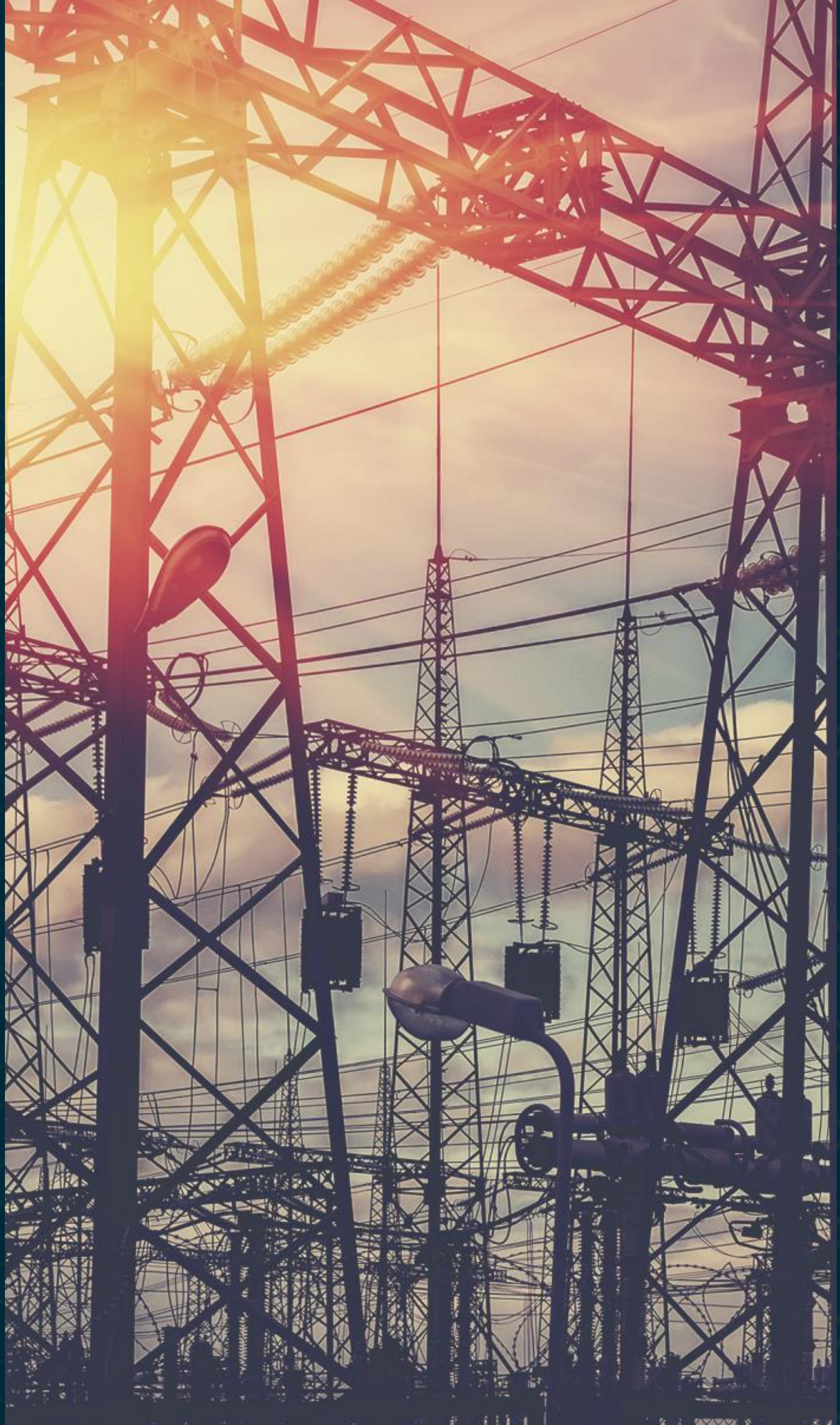
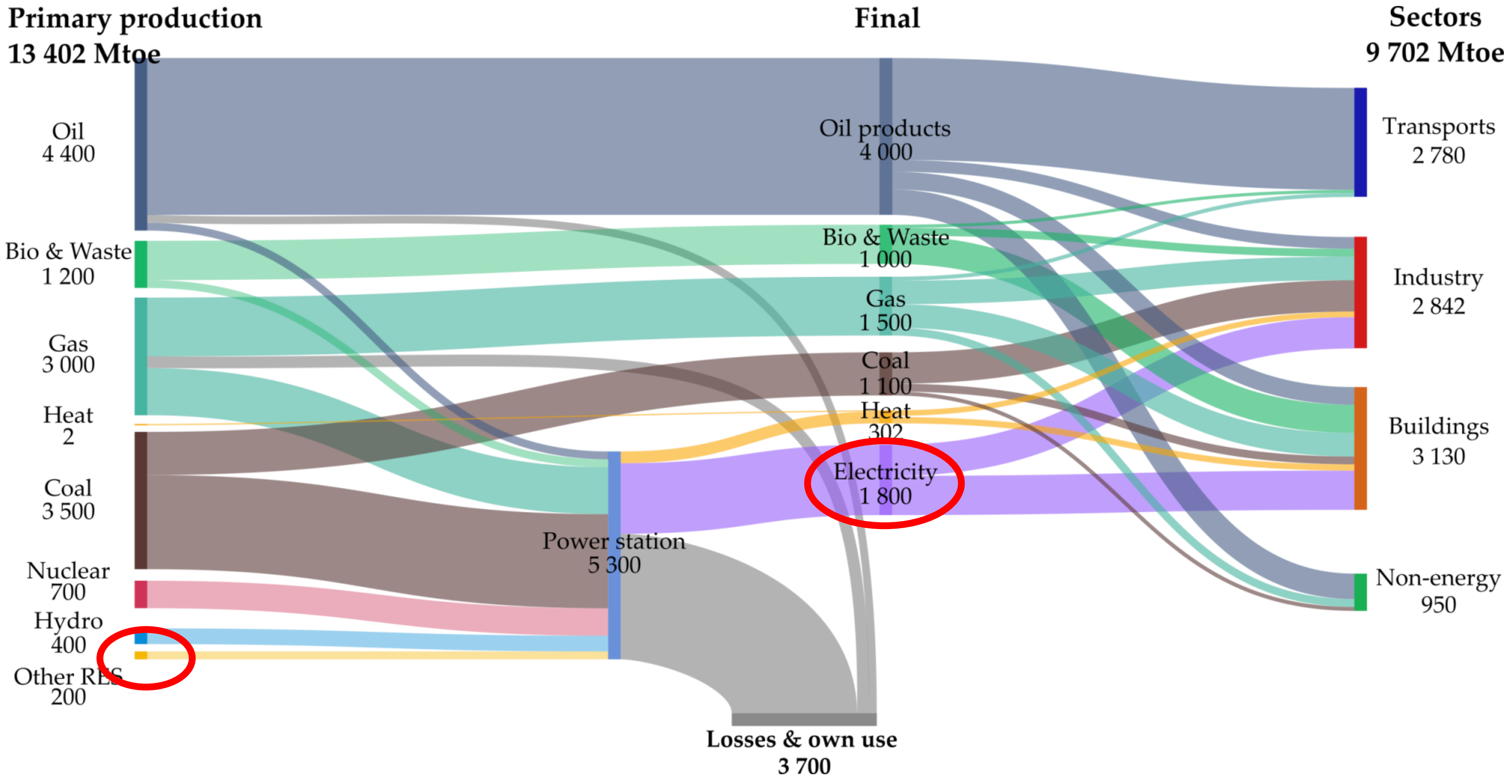
Lecture 9
Electrical grid
& electrical energy storage

PHY 555 – Energy & Environment

Erik Johnson, Mathieu de Naurois, Daniel Suchet



Today's menu – in and out the grid



Electricity
20% of final consumption

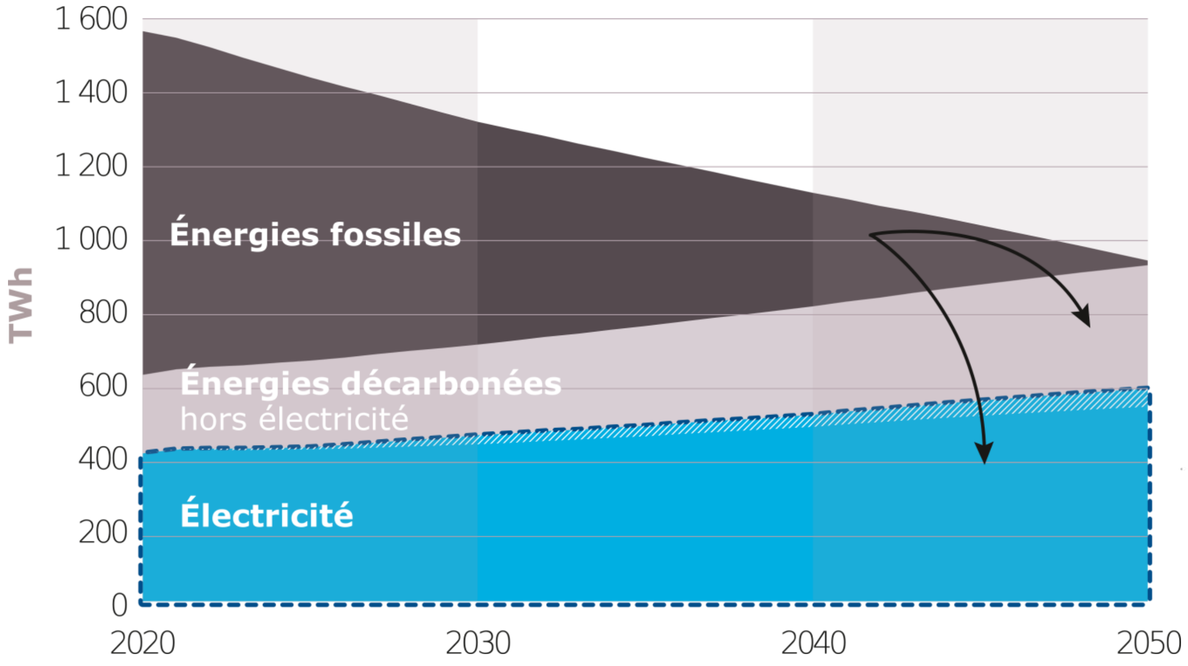
Grid stability with increasing renewables?

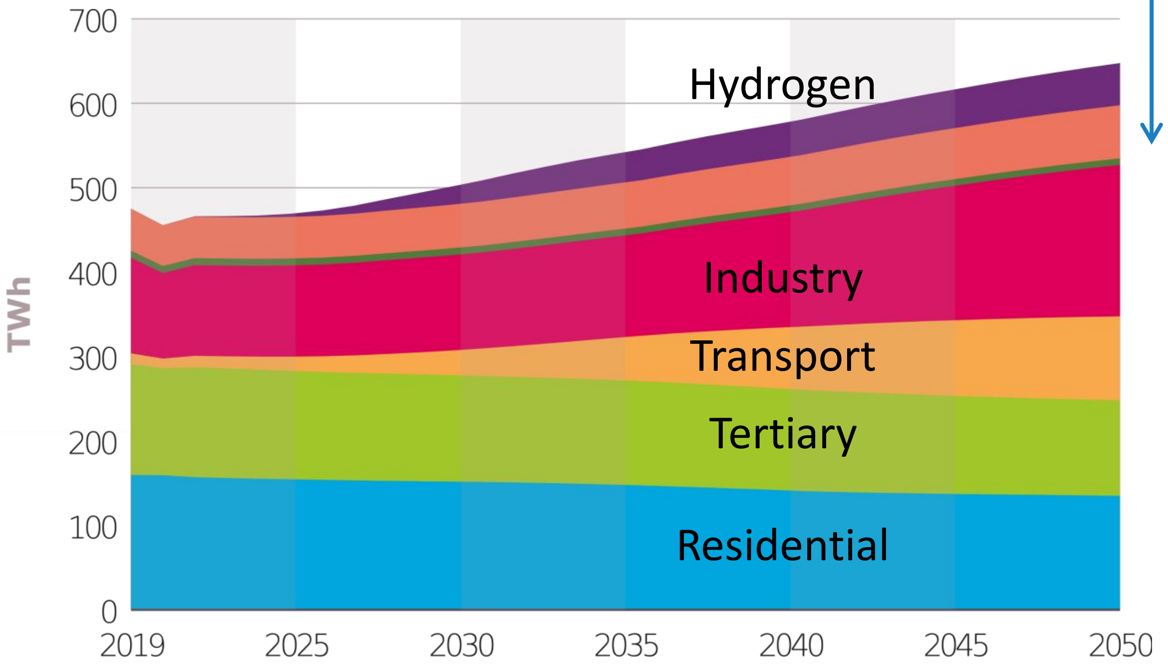
Can we electrify more applications?

Electricity storage?

An electric future?

Futurs
énergétiques
2050
Principaux résultats
Octobre 2021
RÉSUMÉ EXÉCUTIF



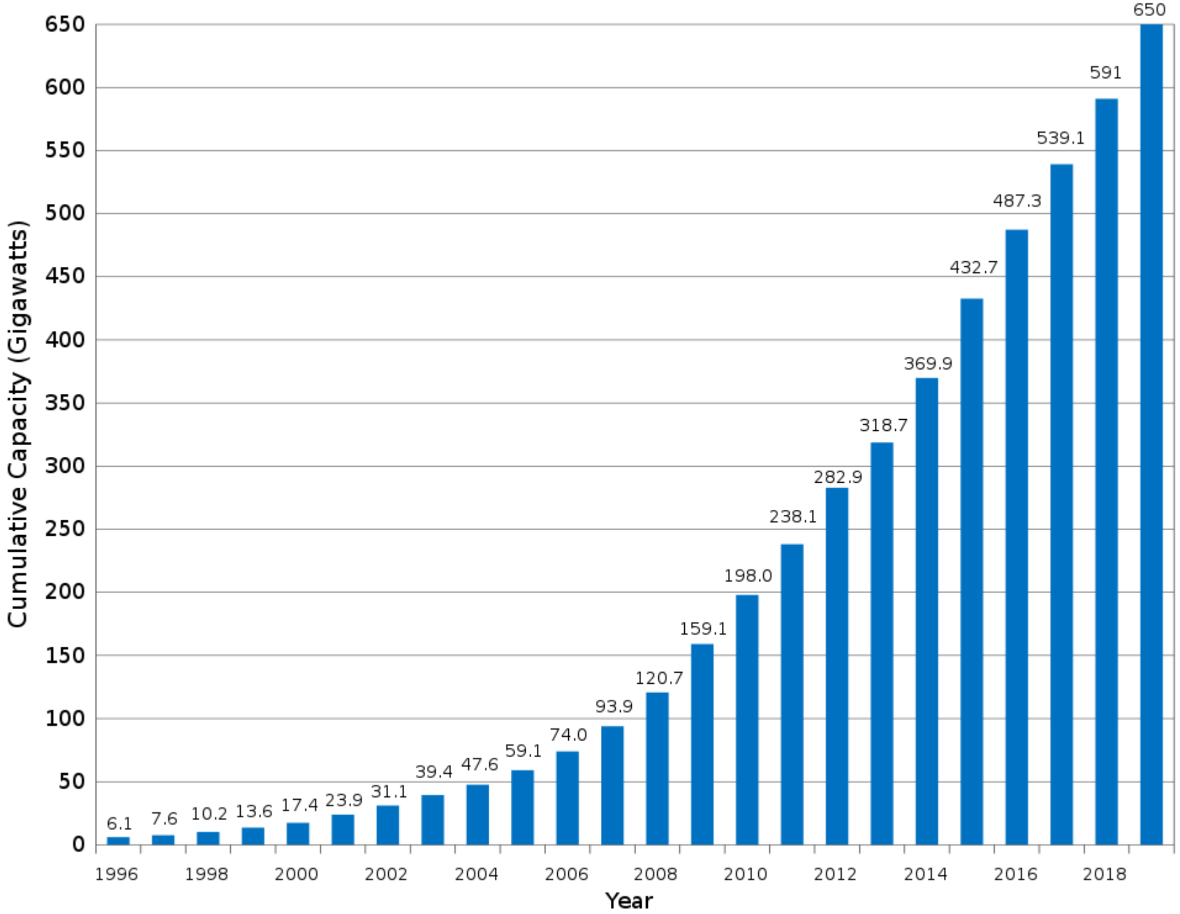


555
-
750
TWh

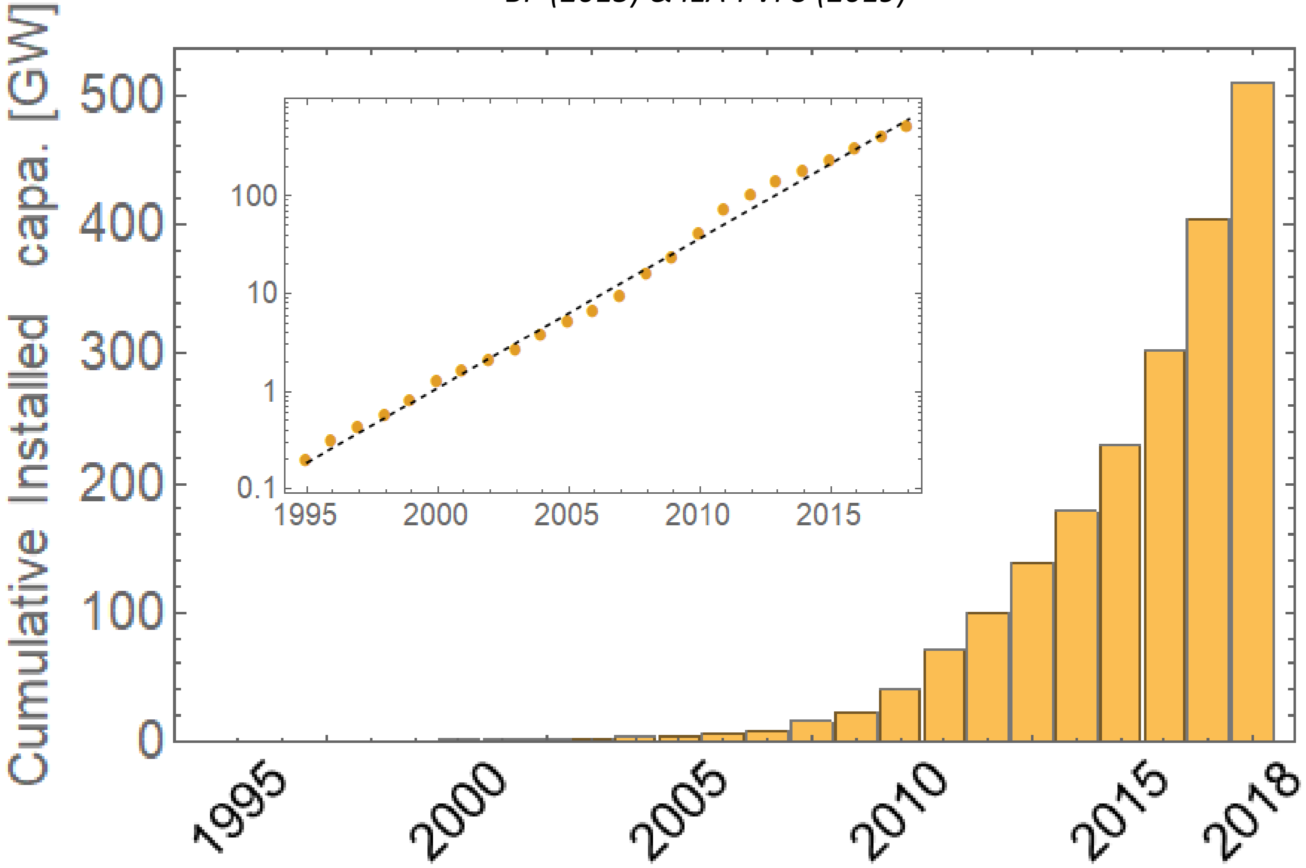
“The study concludes, without any ambiguity, that a sustained development of electric renewable energies in France is essential to meet its climate commitments.”

Renewable growth

Global Wind Power Cumulative Capacity (Data: GWEC)

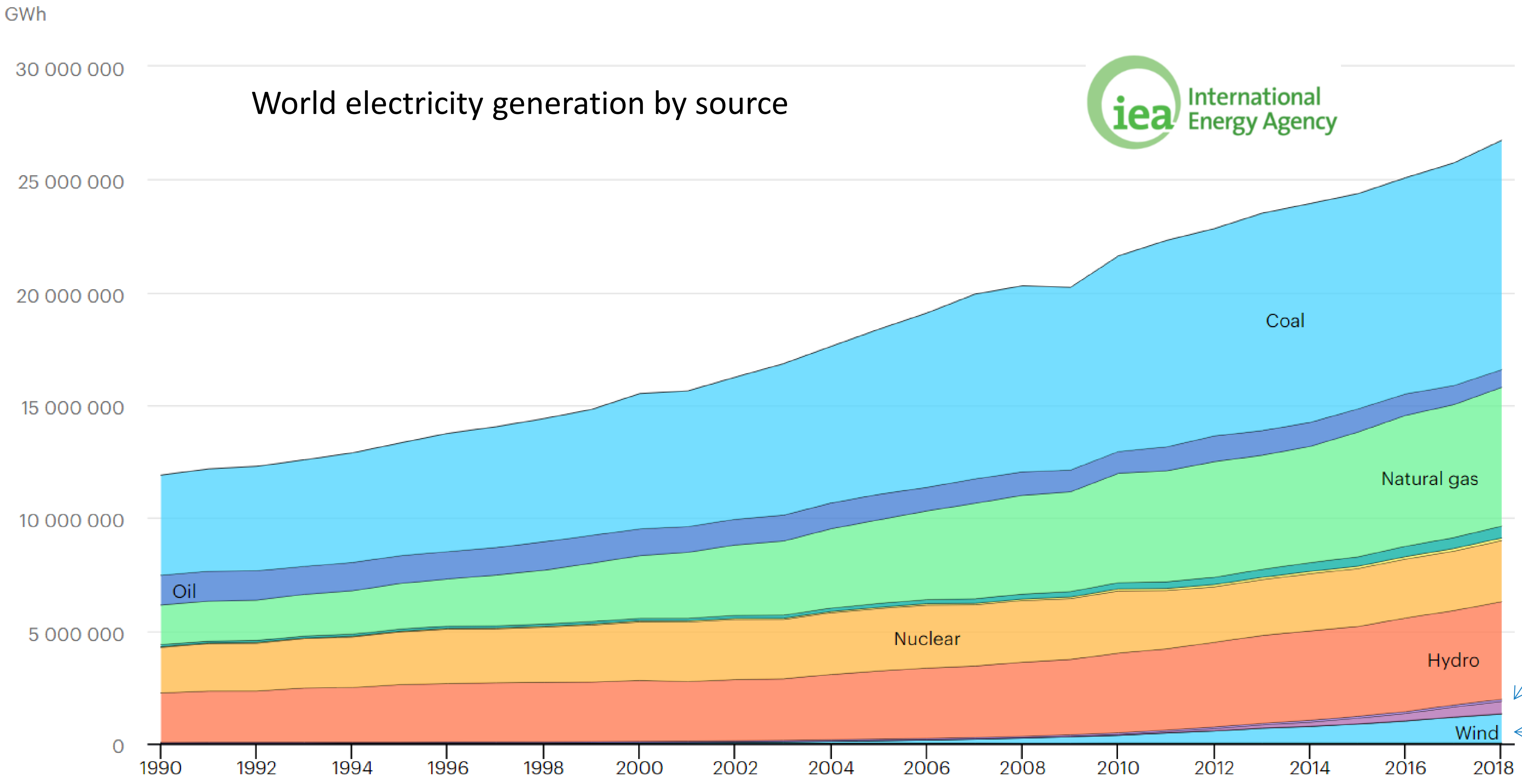


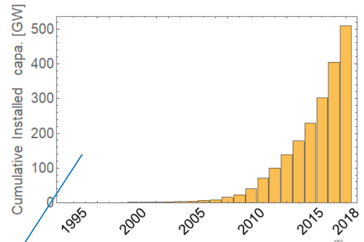
Global Solar Power Capactiy
BP (2015) & IEA-PVPS (2019)

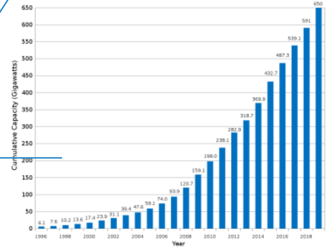


Note : hydro & biomass are also renewable, and produce much more, but behave like conventional sources

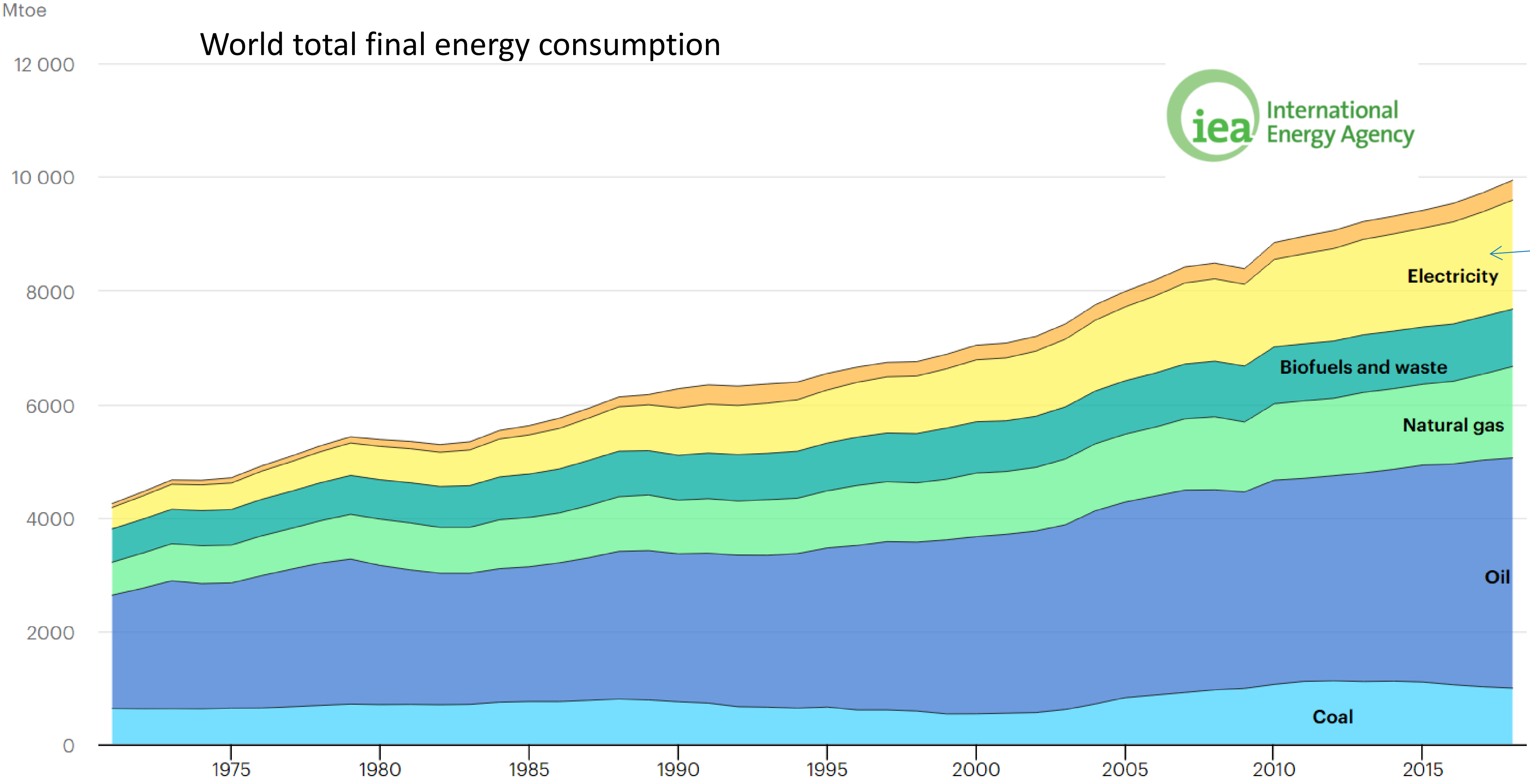
Zoom out

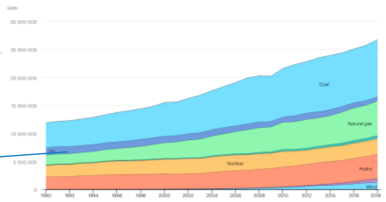

World electricity generation by source

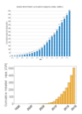




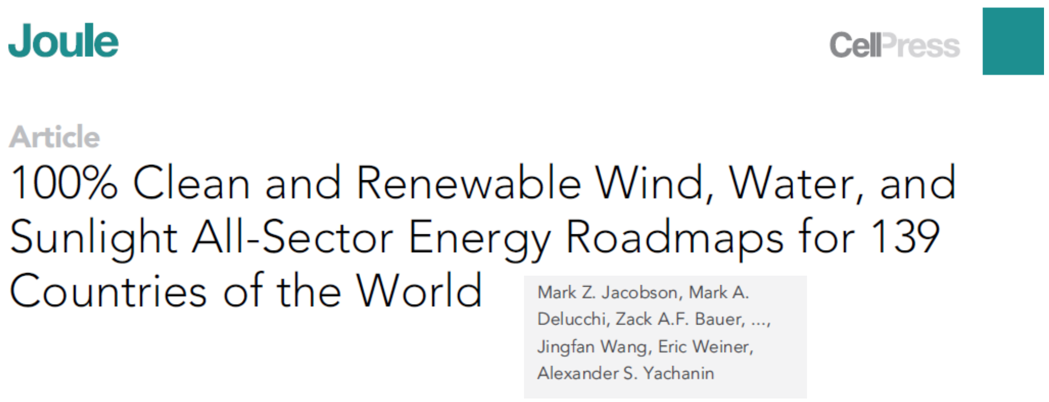
Zoom out again







Integrating renewables


Joule

CellPress

Article

100% Clean and Renewable Wind, Water, and Sunlight All-Sector Energy Roadmaps for 139 Countries of the World

Mark Z. Jacobson, Mark A. Delucchi, Zack A.F. Bauer, ..., Jingfan Wang, Eric Weiner, Alexander S. Yachanin

While social and political barriers exist, converting to 100% WWS using existing technologies is technically and economically feasible


Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

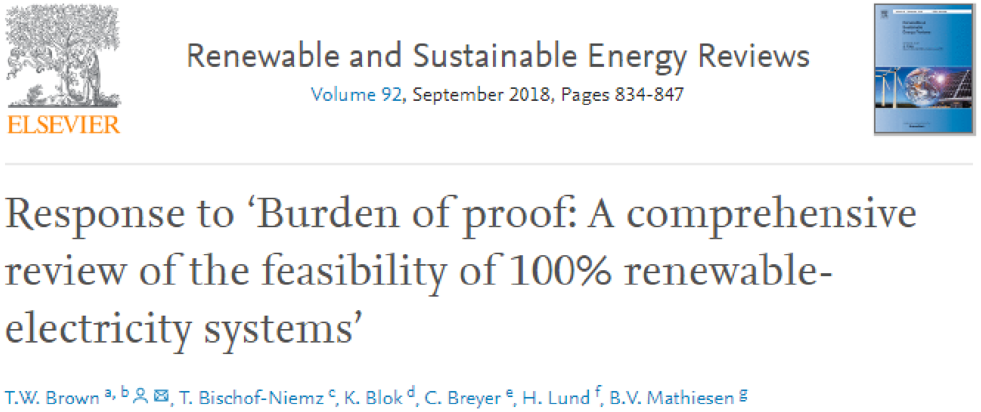
ELSEVIER

Burden of proof: A comprehensive review of the feasibility of 100% renewable-electricity systems

CrossMark

B.P. Heard[a,*], B.W. Brook[b], T.M.L. Wigley[a,c], C.J.A. Bradshaw[d]

Evaluated against these objective criteria, none of the 24 studies provides convincing evidence that these basic feasibility criteria can be met.


ELSEVIER

Renewable and Sustainable Energy Reviews

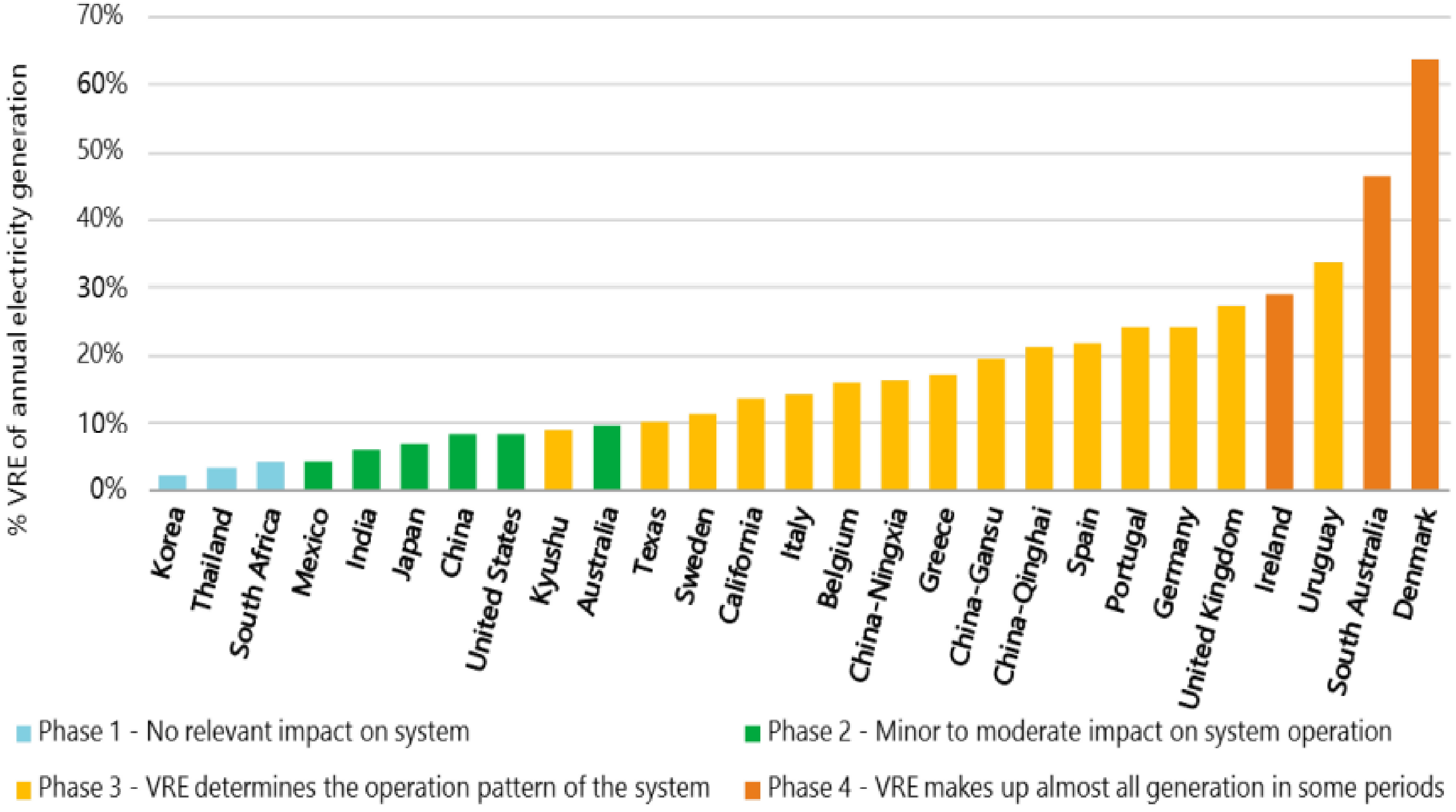
Volume 92, September 2018, Pages 834-847

Response to 'Burden of proof: A comprehensive review of the feasibility of 100% renewable-electricity systems'

T.W. Brown[a, b], T. Bischof-Niemz[c], K. Blok[d], C. Breyer[e], H. Lund[f], B.V. Mathiesen[g]

Based on a literature review we show that none of the issues raised in the article are critical for feasibility or viability.

Where do we stand



Source: IEA (2019a), *Status of Power System Transformation 2019: Power System Flexibility.*

France (RTE)

2022: 32 GW of wind and solar

Up to 50 GW : current infrastructures ok

Above 50 GW : structural changes required

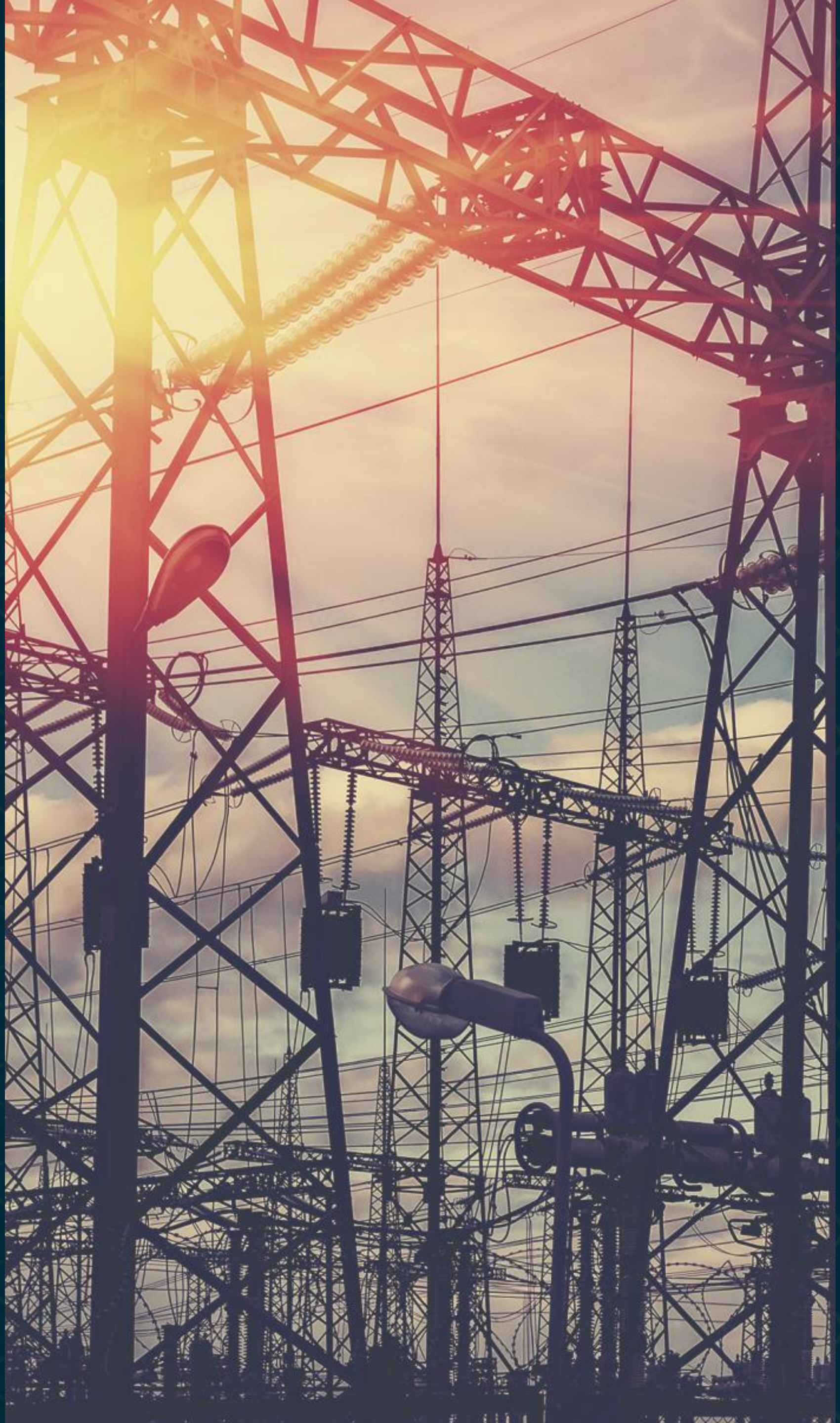
Lecture 9
Electrical grid
& electrical energy storage

I. The many time scales of grid stability
- **Introduction to the electrical grid**
- Time scales of grid stability
- Challenges raised by wind and solar integration

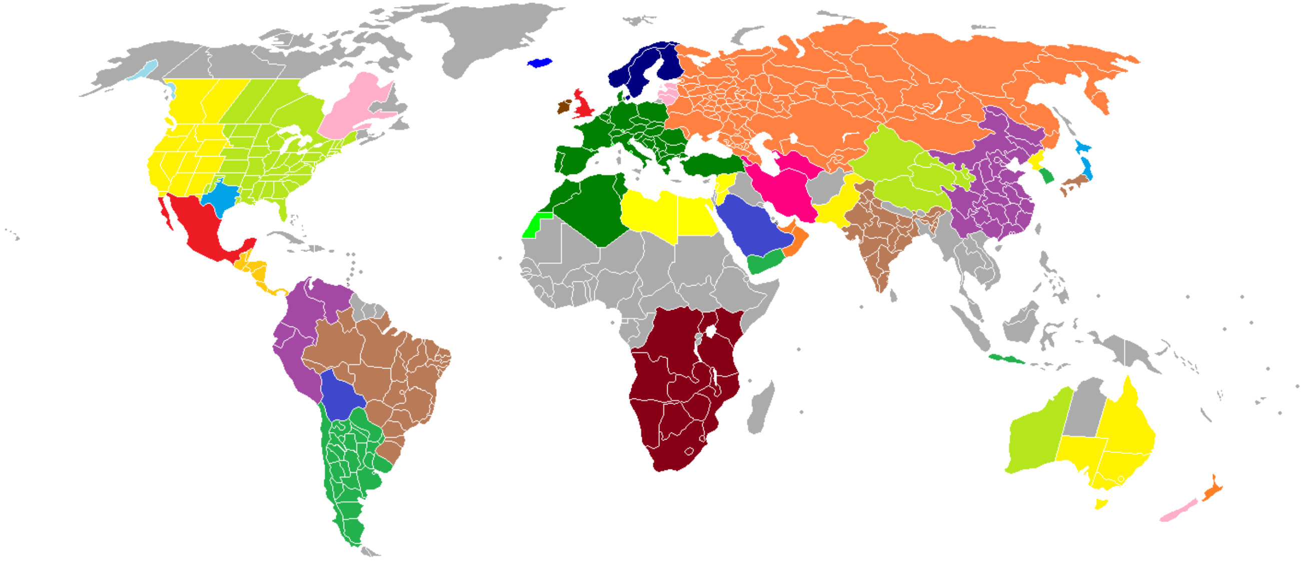
II. Power to X

III. Battery & electrical mobility

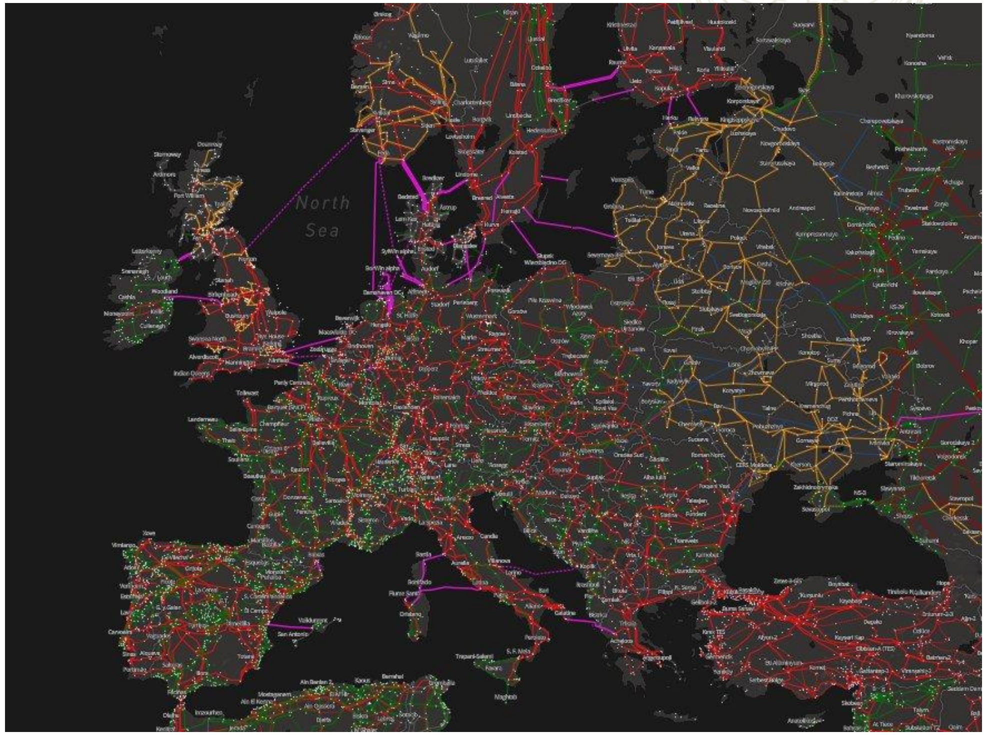
IV. Hydrogen



Welcome to the grid



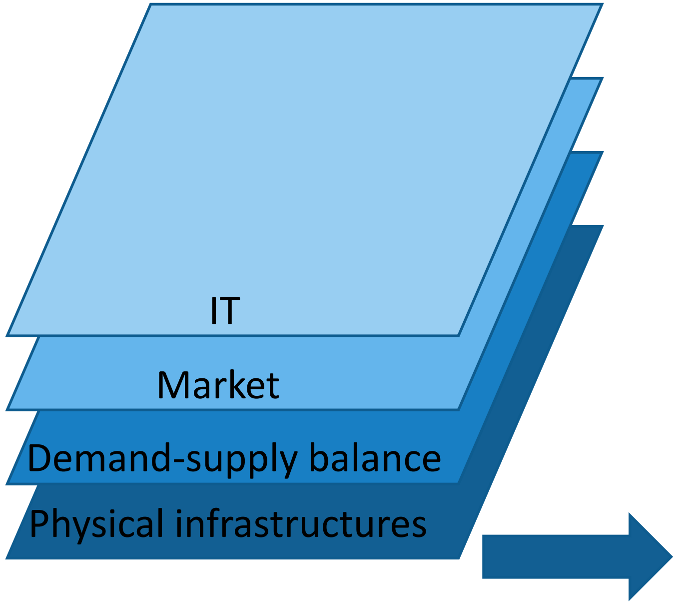
Wide area synchronous grid

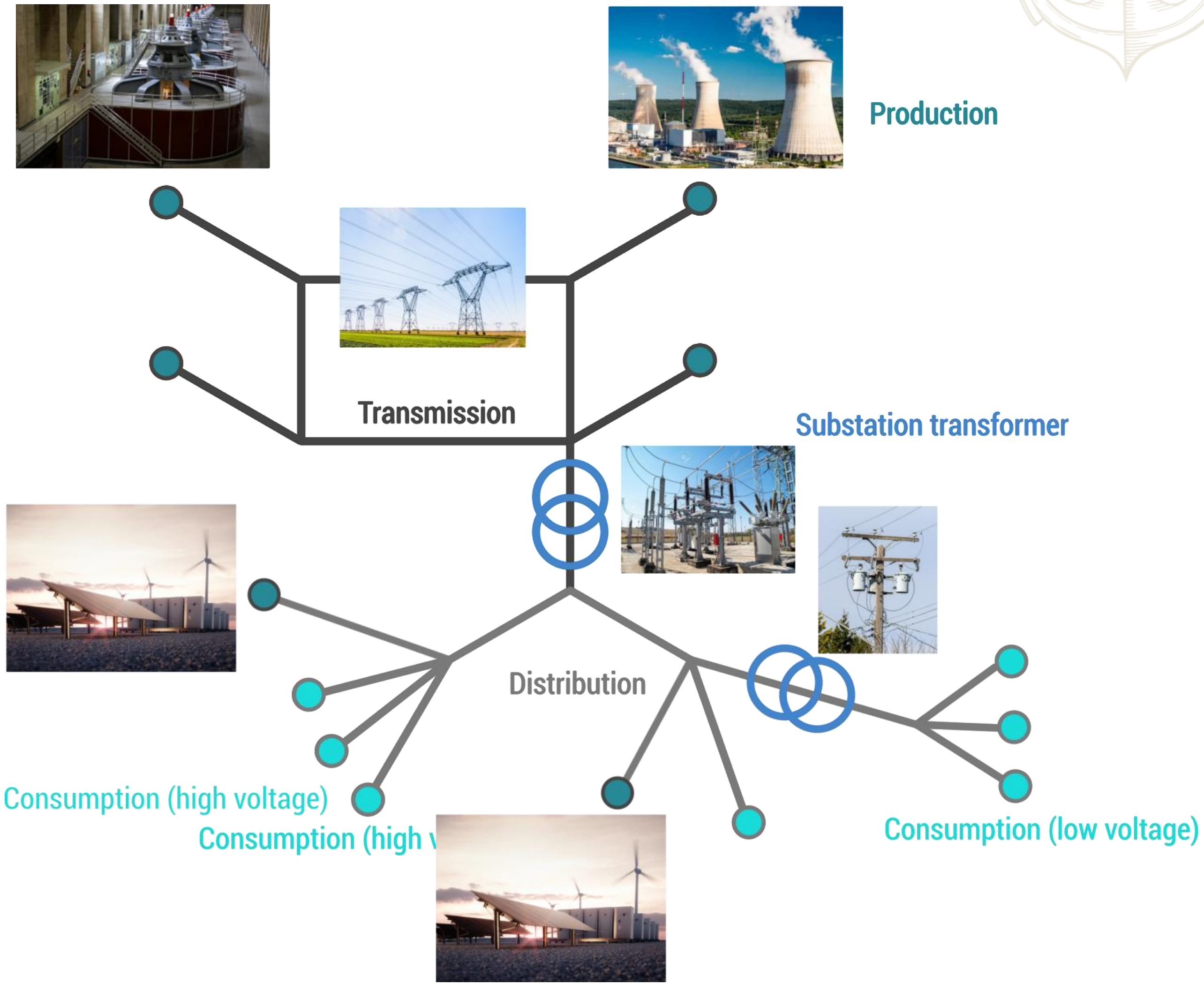


European grid:
36 countries
480 000 km
1100 GW

What is the grid?

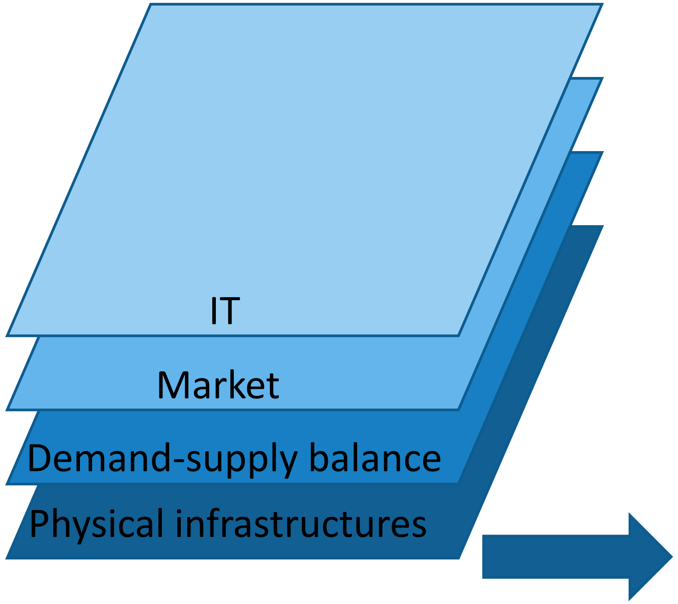
A multilayer system





What is the grid?

A multilayer system

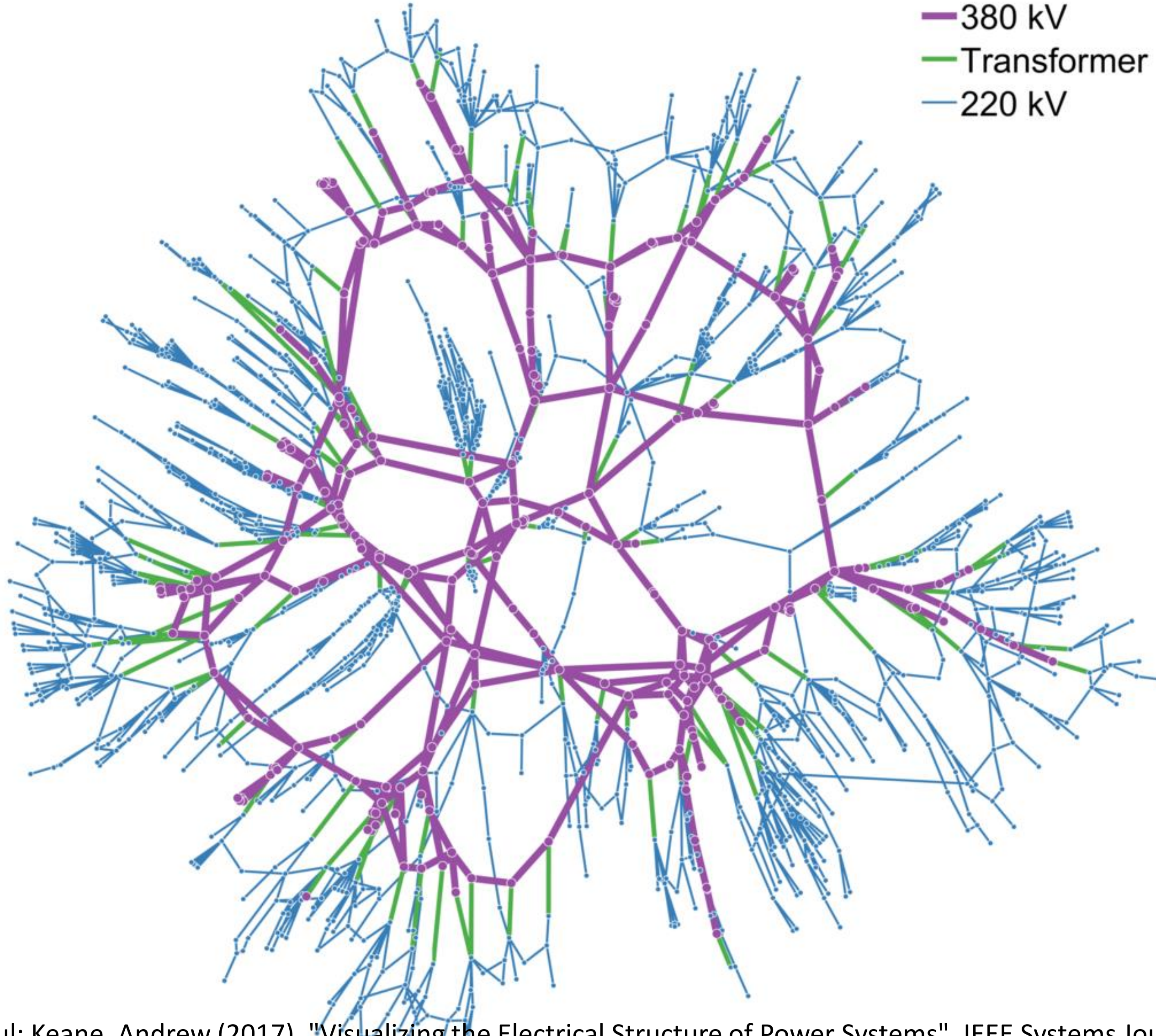


IT

Market

Demand-supply balance

Physical infrastructures



Meshed, redundant

Treelike

Cuffe, Paul; Keane, Andrew (2017). "Visualizing the Electrical Structure of Power Systems". IEEE Systems Journal. 11 (3)

Why is the grid?

- Not just an electron highway

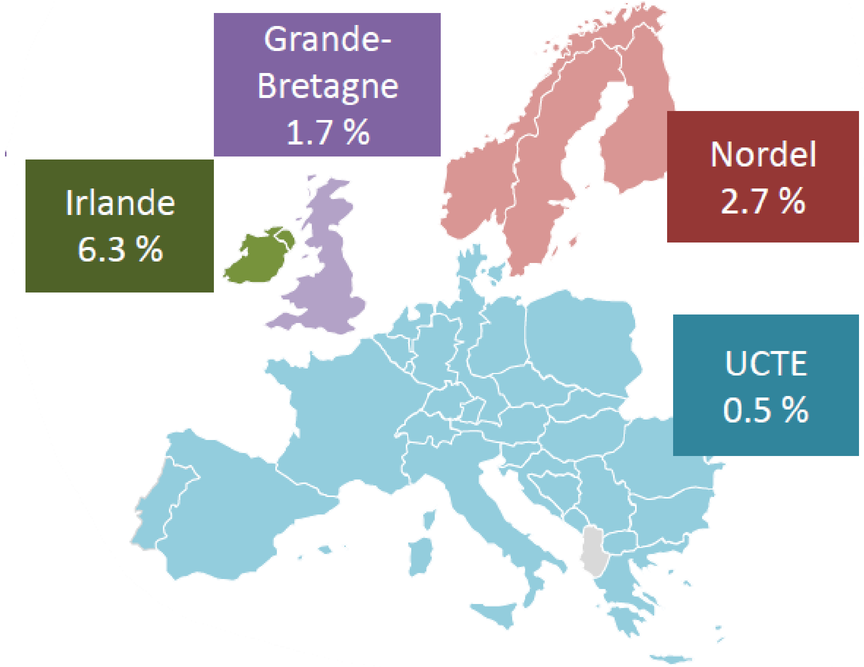
  Even if it’s pretty impressive…
  1.500.000 km de liaisons en France
    - 100.000 km de réseau de transport (63kV à 400kV, RTE)
    - 1.400.000 km de réseau distribution (220V à 20kV, Enediset autres)

- Mutualize resources

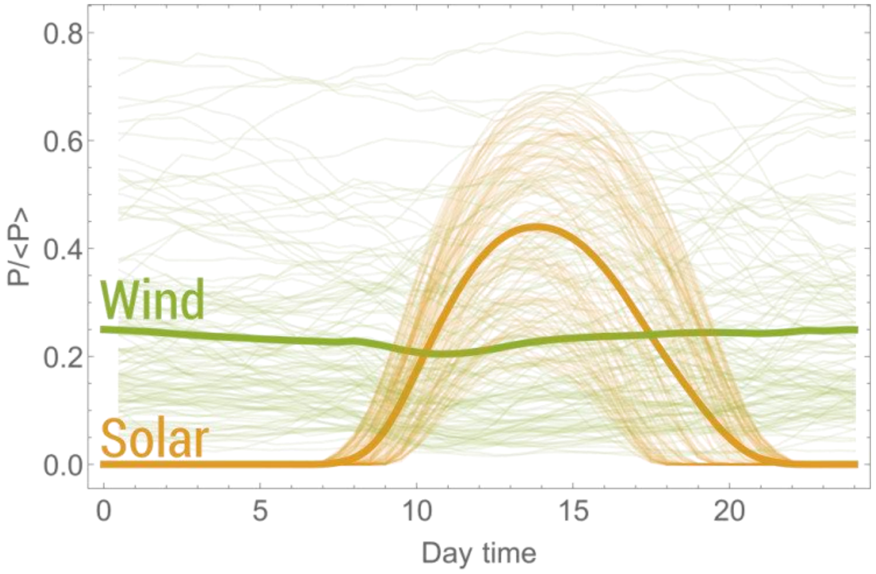
  Household max power (EDF contract) : 3, 6 or 9 kW
  Peak consumption : 1,5 kW/pers.

- Ensures power balance *at all times*

% of capacity kept for primary reserve



A key requirement : P = C

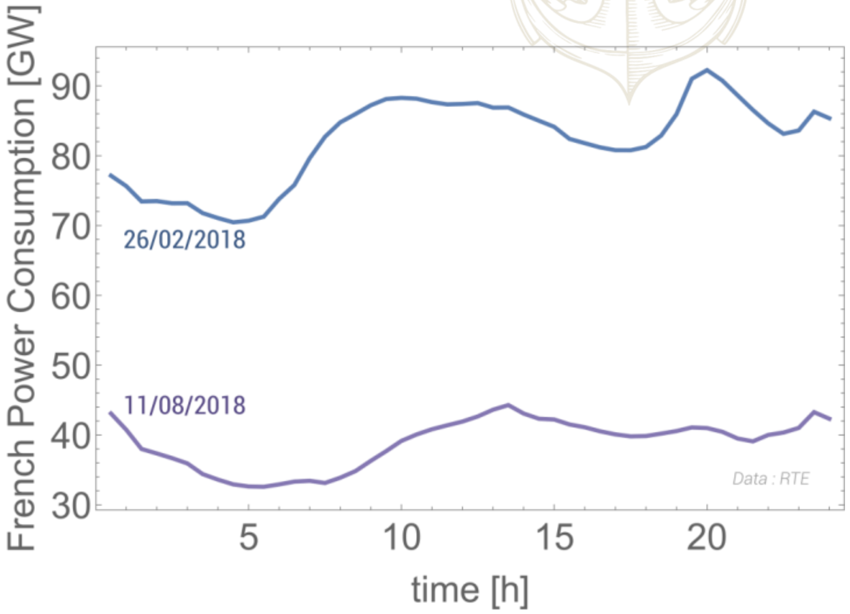


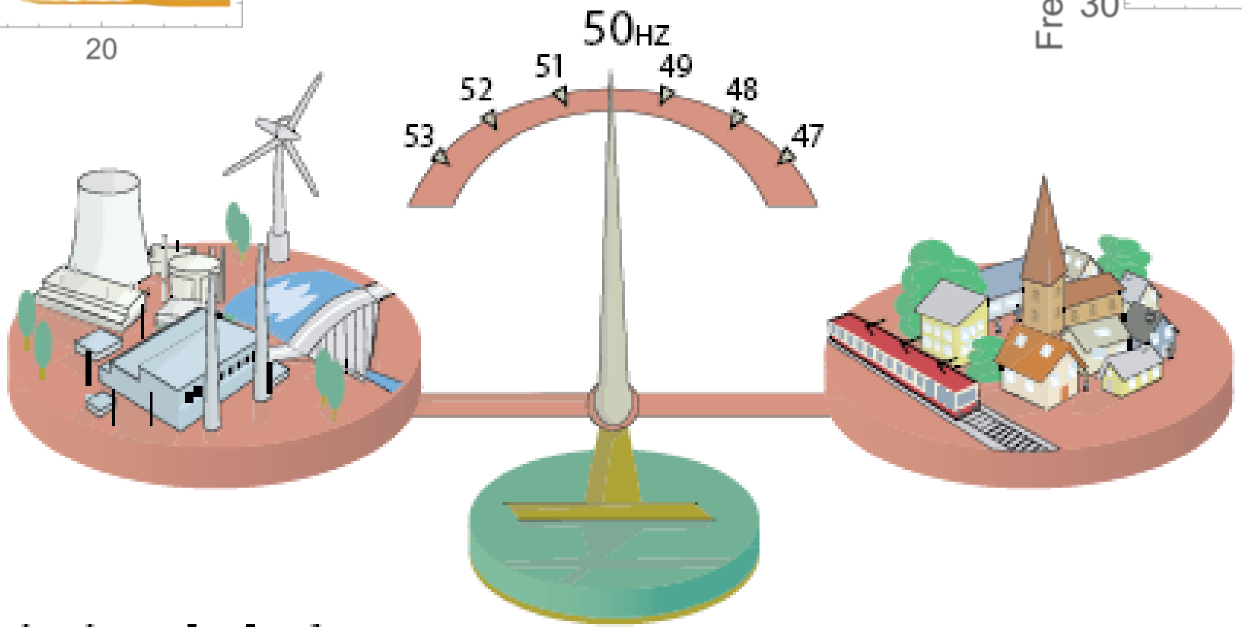
Production

=

Consumption

AT ALL TIMES





Power and frequency

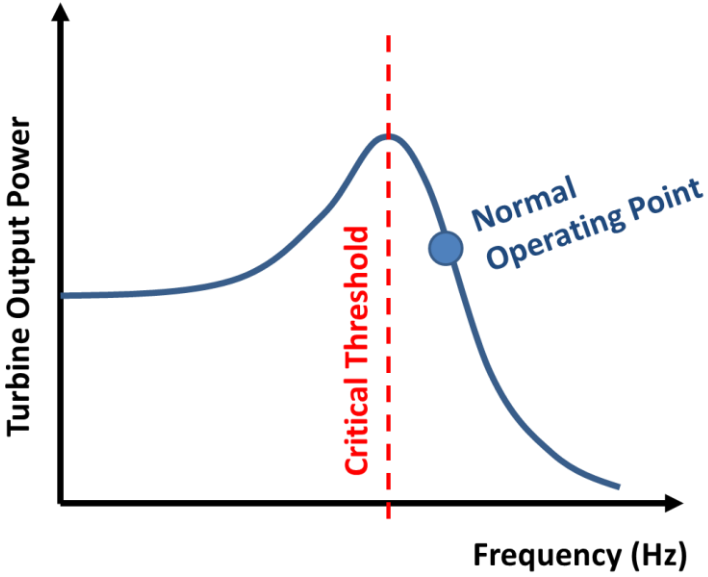
Why use a 50/60Hz AC system ?
AC allows tranformers
Too slow : flickering
Too fast : mechanical constraints

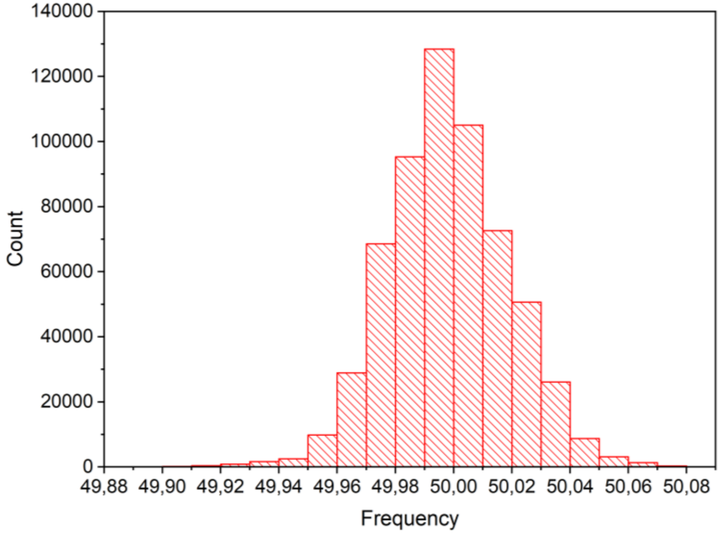
Why frequency should be kept steady ?
Power applications depend on frequency

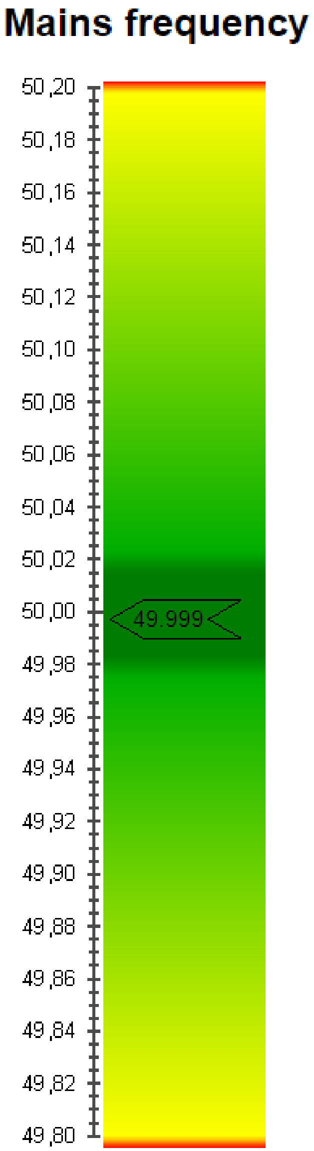
How come frequency monitors the system’s state ?
Energy conservation : power imbalance <-> frequency change

Turbine → $$E_C = \frac{1}{2} J\omega^2$$ → Grid

$$\frac{dE_C}{dt} = J\omega\frac{d\omega}{dt} = P_{\text{in}} - P_{\text{out}}$$







When everything goes wrong : a case study

"The sequence of events was triggered by a trip of [a transmission line with Switzerland] at 03:01, caused by a tree flashover. [...].

Other lines had taken over the load of the tripped line, as is always the case in similar situations. Due to its proximity, the other Swiss 380 kV line. was overloaded.

This overload was acceptable in such emergency circumstances, according to operational standards, only for a short period [of 15 minutes].

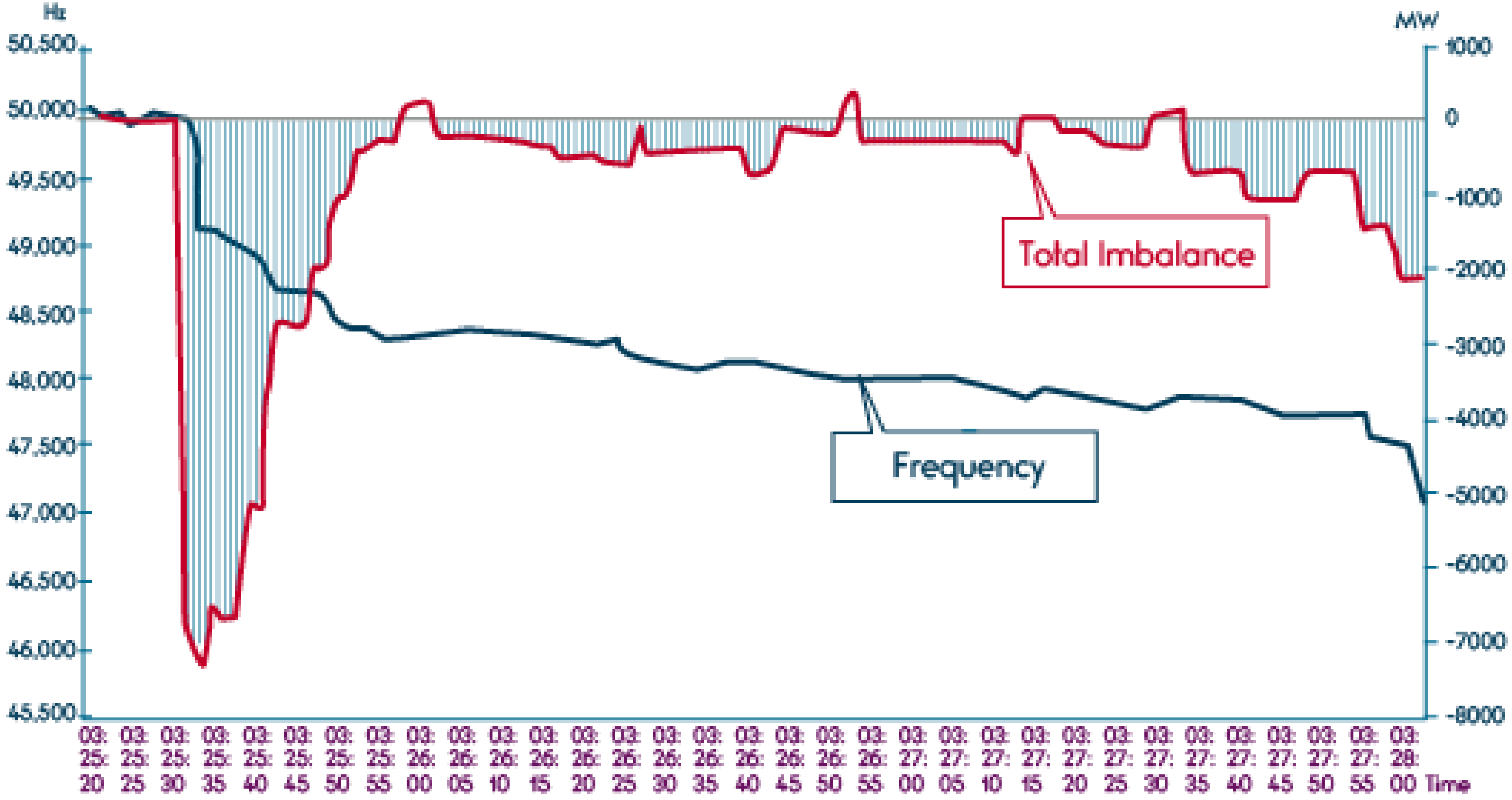
At 03:25, this second line also tripped after a tree flashover. This flashover was probably caused by the sag in the line, due to overheating of the conductors.

Having lost two important lines, the then created overloads on the remaining lines in the area became intolerable. By an almost simultaneous and automatic trip of the remaining interconnectors towards Italy, the Italian system was isolated from the European network about 12 seconds after the loss of the second line. [...]

[Despite all mitigation actions], the frequency continued to decrease and the system collapsed 2 minutes and 30 seconds after the separation of the country, when the frequency reached the threshold of 47,5 Hz."

UCTE, Final Report of the Investigation Committee on the 28 September 2003 Blackout in Italy

When everything goes wrong : a case study



UCTE, Final Report of the Investigation Committee on the 28 September 2003 Blackout in Italy

Lecture 9 – Grid and storage

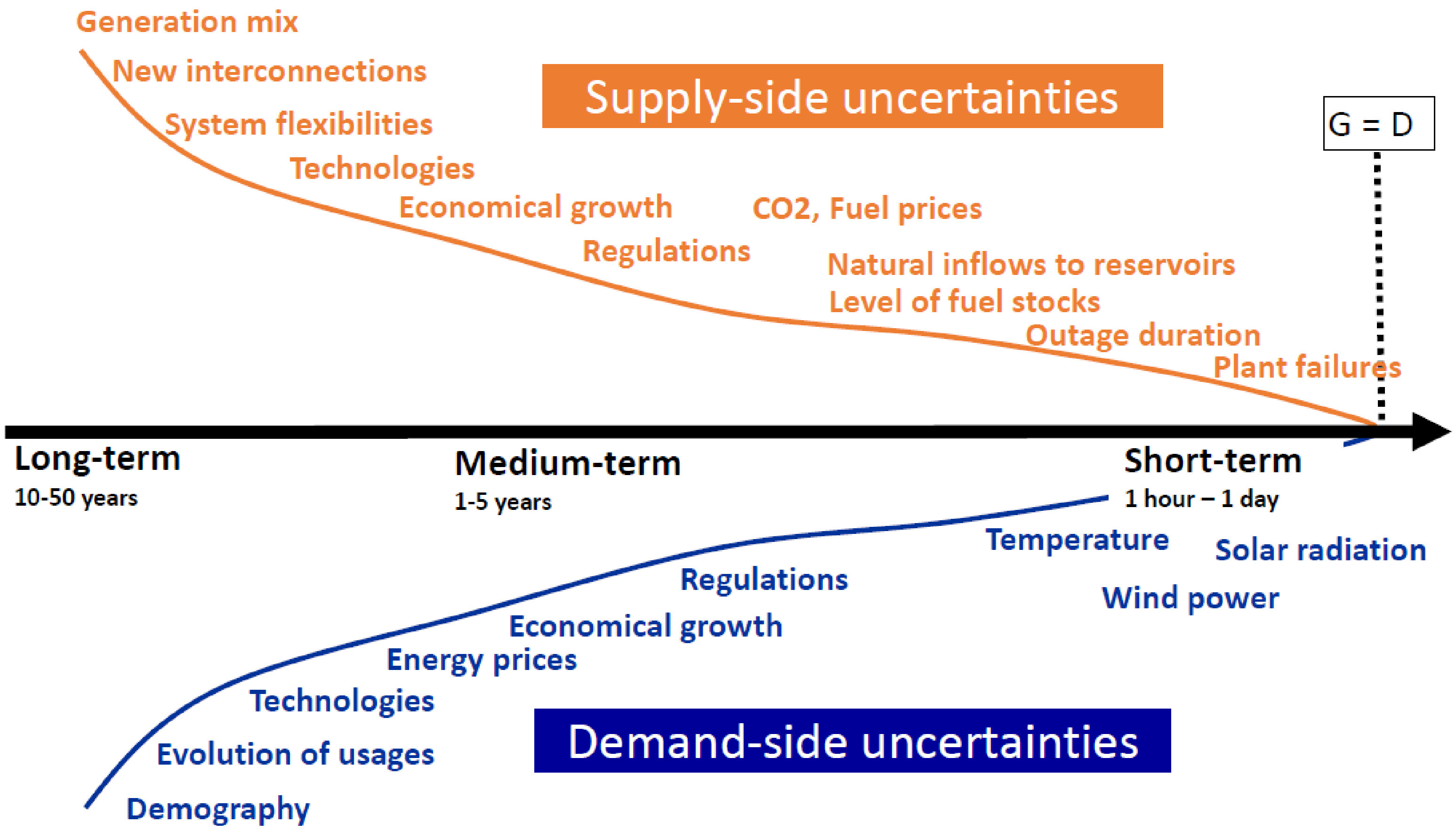
- The many time scales of grid stability
  - Introduction to the electrical grid
  - **Time scales of grid stability**
  - **Challenges raised by wind and solar integration**

- Power to X

- Battery & electrical mobility

- Hydrogen

Grid stability – time scales



Generation mix

New interconnections

System flexibilities

Technologies

Economical growth

Regulations

CO2, Fuel prices

Natural inflows to reservoirs

Level of fuel stocks

Outage duration

Plant failures

Supply-side uncertainties

G = D

Long-term
10-50 years

Medium-term
1-5 years

Short-term
1 hour – 1 day

Temperature

Solar radiation

Wind power

Regulations

Economical growth

Energy prices

Technologies

Evolution of usages

Demography

Demand-side uncertainties

Seconds: inertia

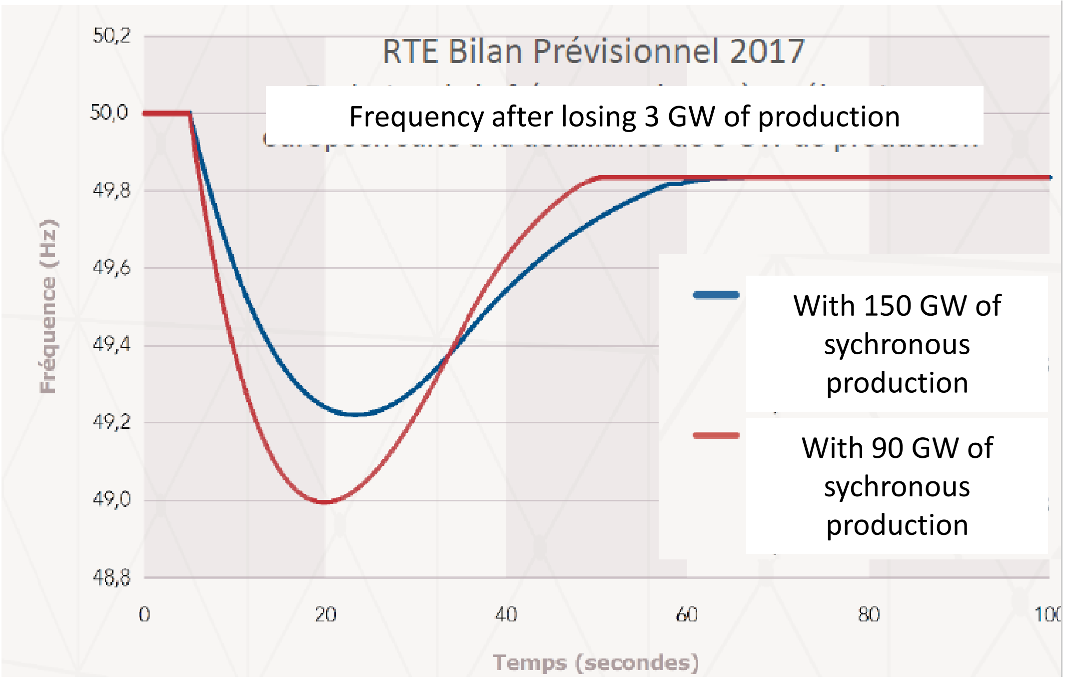
Turbine → $$E_C = \frac{1}{2} J\omega^2$$ → Grid

Moment of inertia $$J_{\text{cylinder}} = \frac{1}{2} m r^2$$

Energy conservation : power imbalance <-> frequency change

$$\frac{dE_C}{dt} = J\omega \frac{d\omega}{dt} = P_{\text{in}} - P_{\text{out}}$$

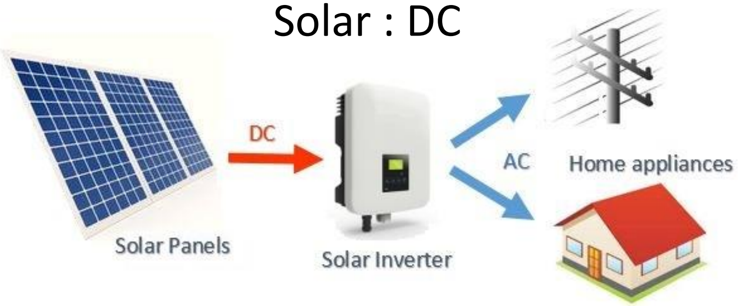
Rate of change of frequency (ROCOF)



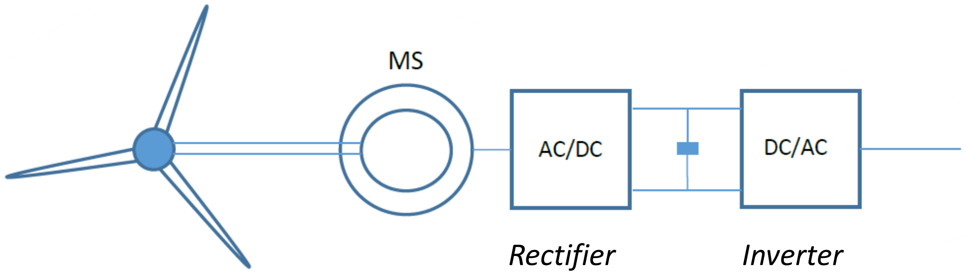
6 mHz/s when losing a 1300MW power plant on the European grid

Asynchronicity

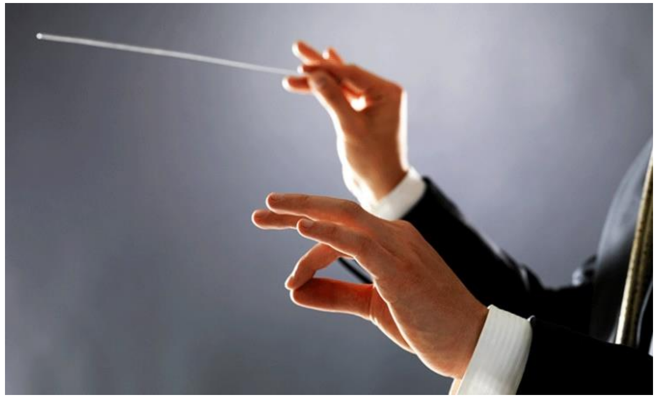
Solar : DC



Wind: AC at variable frequency (tip speed ratio)



Wind and solar provide asynchronous productions and do not contribute to the system's inertia

Grid forming inverters (power electronics)

Use generators as synchronous condensers

First flywheel + synchronous generator installed in Ireland (Siemens, 2021)

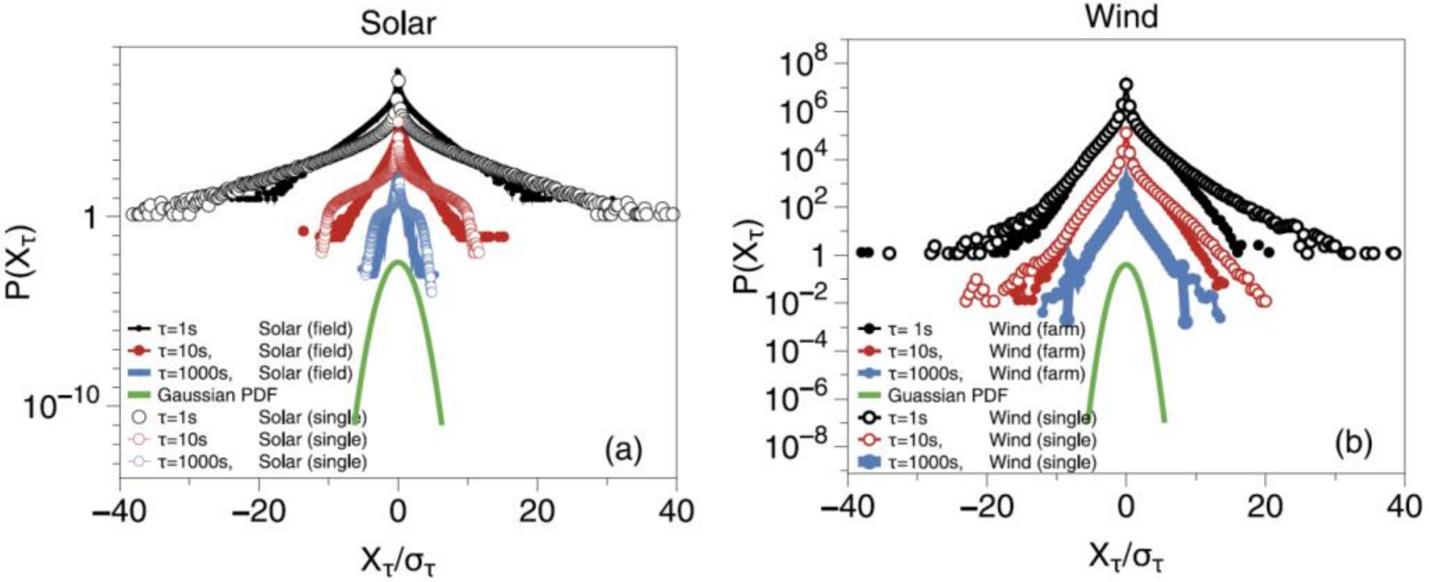
Keep
(or store)
a bit of power
to react when
frequency shifts

Intermittency

Intermittency : Rapid & abrupt variations of production

D. Suchet et al, *Energies* (2020).

Probability density function for $P(t+\tau) - P(t)$

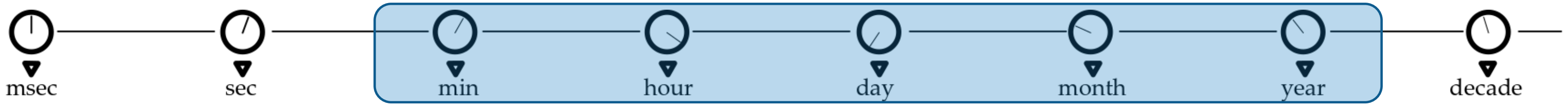


M. Anvari et al, *New J. Phys.* 18, 6 (2016).

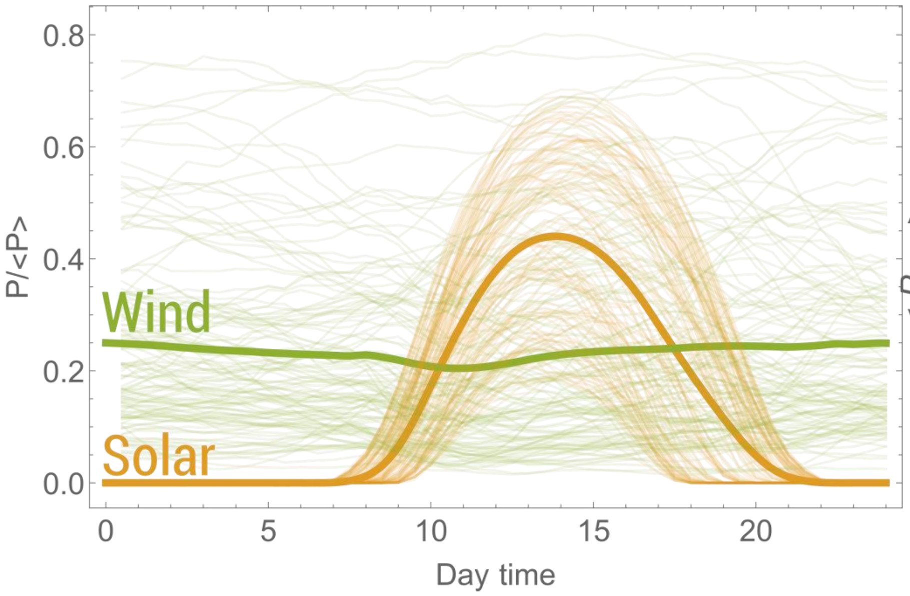
Consider the 1-second variation
20σ fluctuations occur :

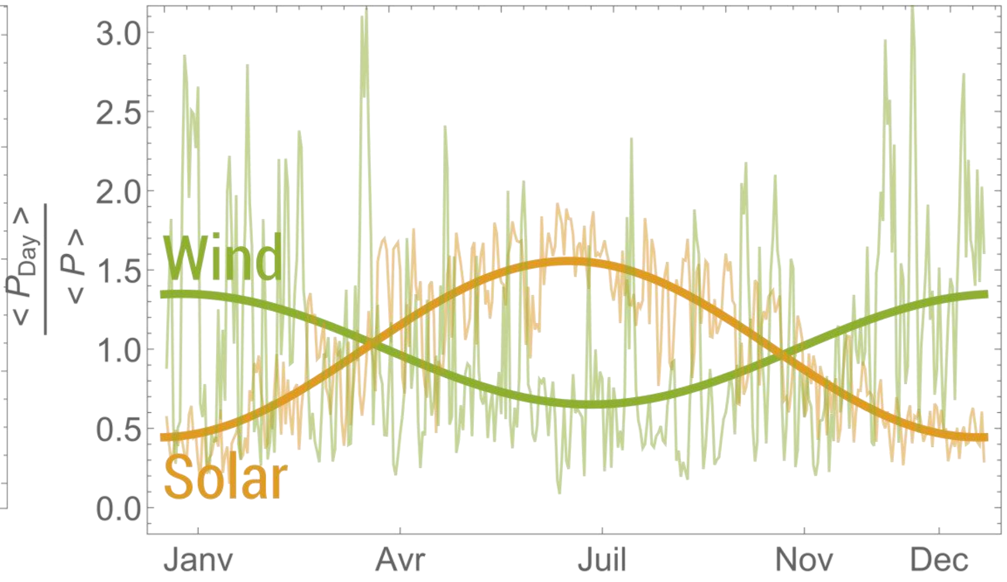
Gaussian : once every 3 millions years
Wind: once a month
PV : 1000 times a month

Variability

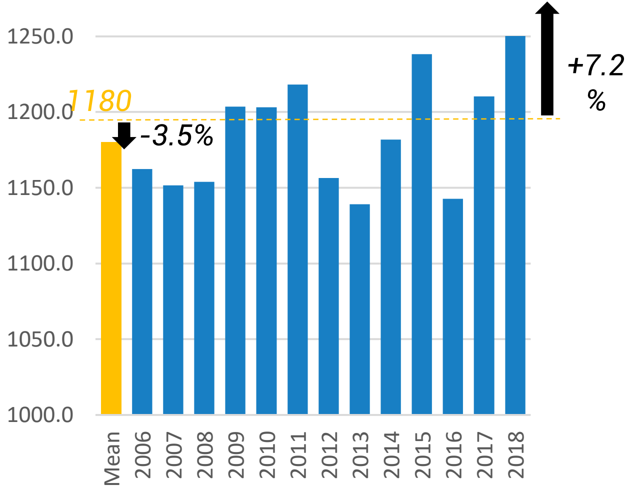


Hour to hour, day to day, season to season, year to year





Annual global horizontal irradiation (kWh/m^2)



Source: SIRTA observatorv. Palaiseau

Minutes: reserves

Primary reserve
Frequency Containment Reserve (FCR)

- Within 30 seconds, continues for up to 15 minutes.
- Automatic
- In Europe, FCR is aggregated among all countries, and calculated to handle the loss any two power plants (∼ 3 GW).
- Open to markets, based on weekly calls.

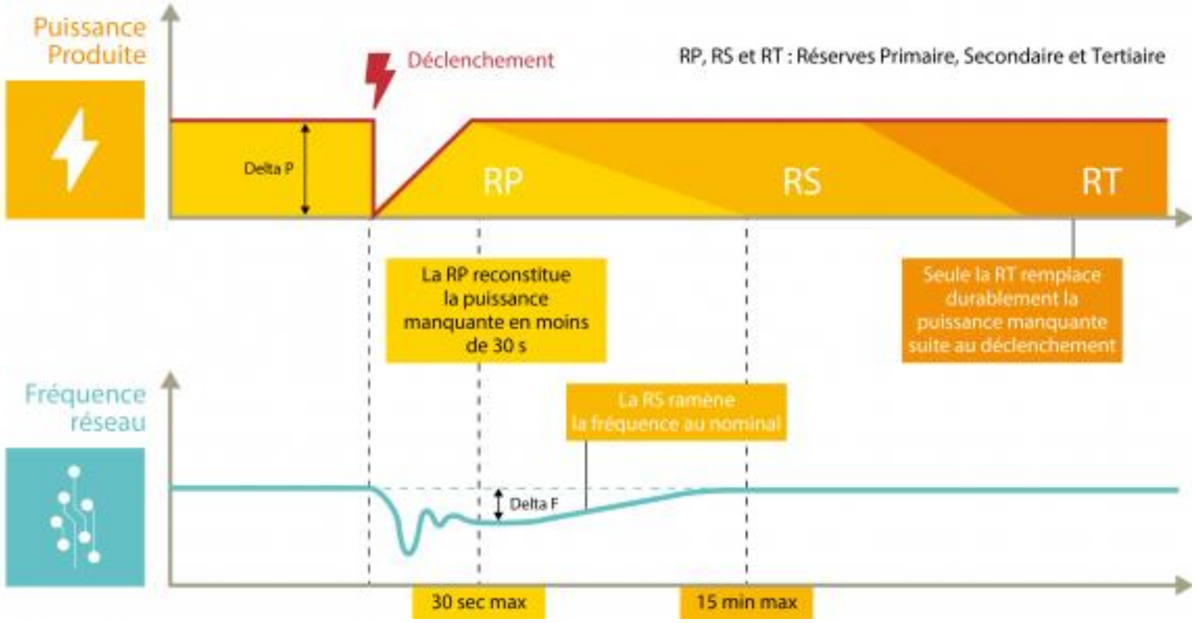
Secondary reserve
Auto. Frequency Restoration Reserve (a-FFR)

- within the first 10 minutes
- In Europe, a-FRR is specific to each country.
- In France, a-FFR = 500 MW to 1200 MW –
  any producer with a capacity >120 MW must contribute

Tertiary reserve
Manual Frequency Restoration Reserve (m-FFR)

- 30 or 60 minutes

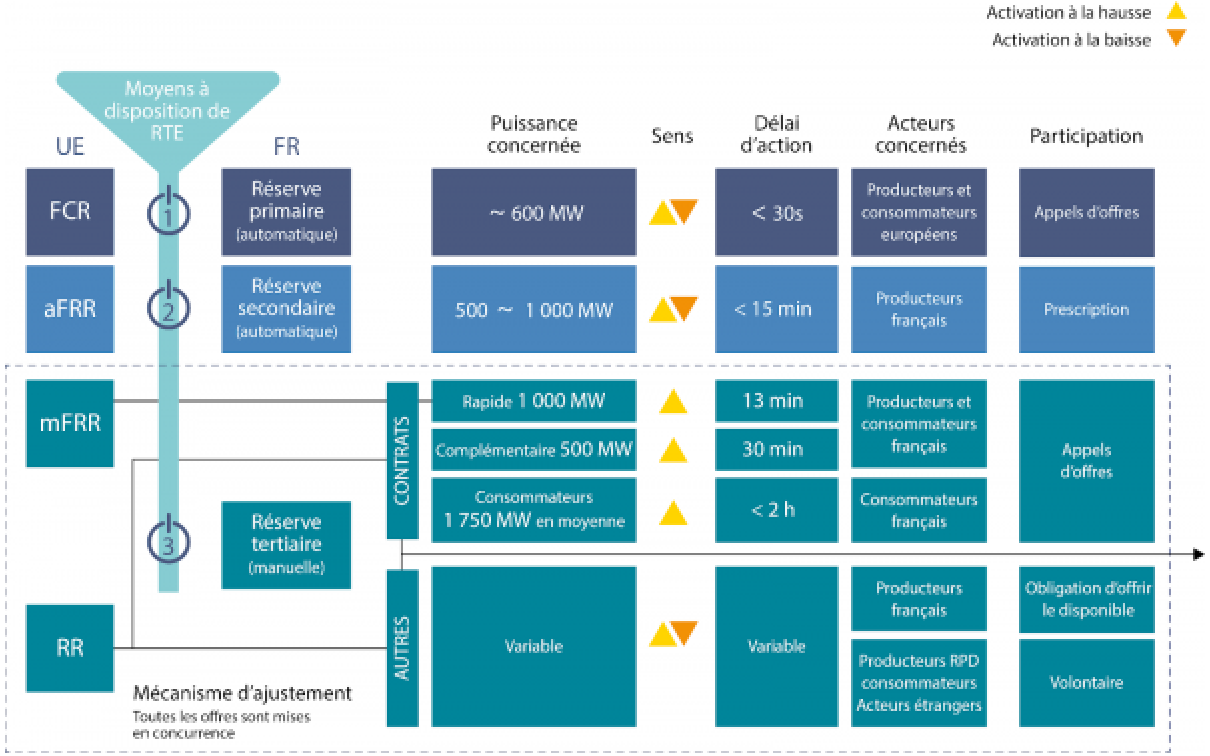
Minutes: reserves



La RP reconstitue la puissance manquante en moins de 30 s

La RS ramène la fréquence au nominal

Seule la RT remplace durablement la puissance manquante suite au déclenchement

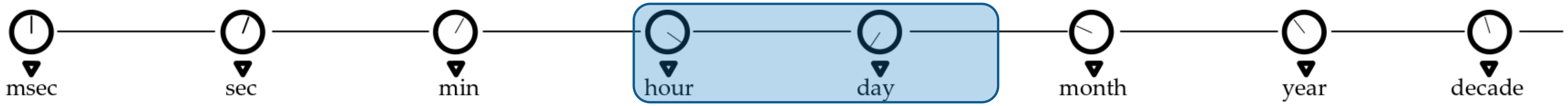


UE	FR		Puissance concernée	Sens	Délai d'action	Acteurs concernés	Participation
FCR	Réserve primaire (automatique)		~ 600 MW	▲▼	< 30s	Producteurs et consommateurs européens	Appels d'offres
aFRR	Réserve secondaire (automatique)		500 ~ 1 000 MW	▲▼	< 15 min	Producteurs français	Prescription
mFRR	Réserve tertiaire (manuelle)	CONTRATS	Rapide 1 000 MW	▲	13 min	Producteurs et consommateurs français	Appels d'offres
			Complémentaire 500 MW	▲	30 min		
			Consommateurs 1 750 MW en moyenne	▲	< 2 h	Consommateurs français	
RR		AUTRES	Variable	▲▼	Variable	Producteurs français	Obligation d'offrir le disponible
						Producteurs RPD consommateurs Acteurs étrangers	Volontaire

Mécanisme d'ajustement

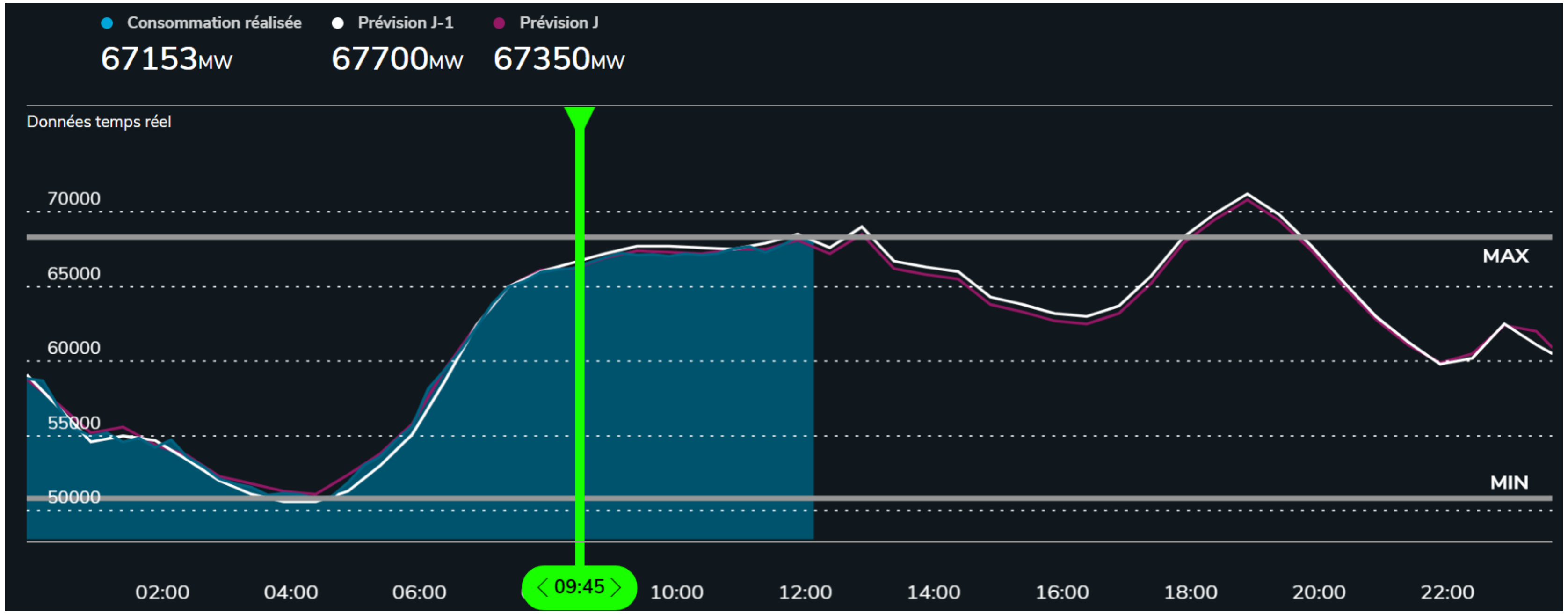
Toutes les offres sont mises en concurrence

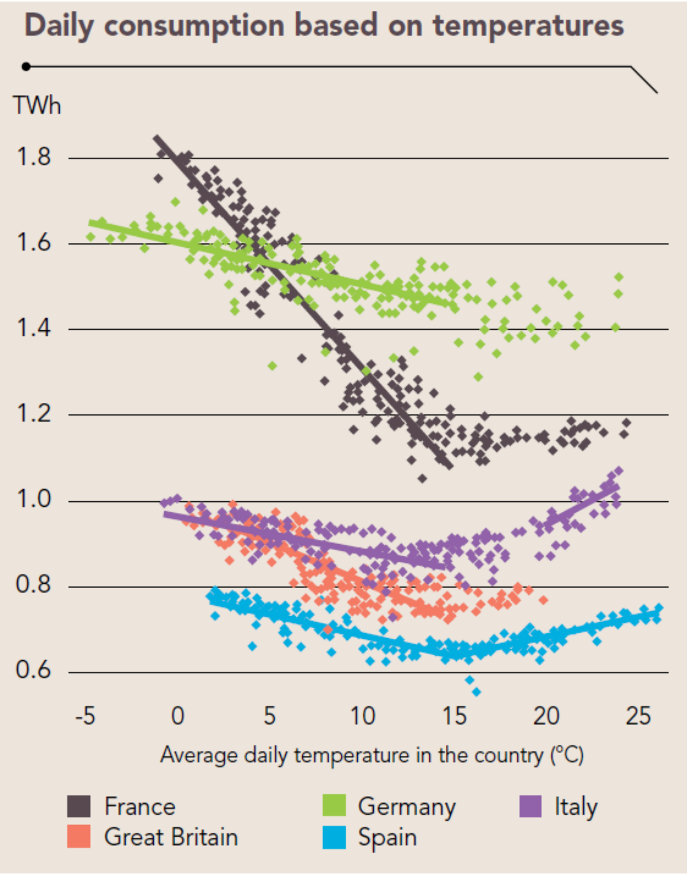
Days: previsions



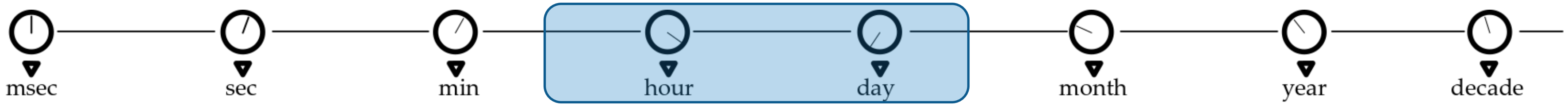
Up to long term previsions !

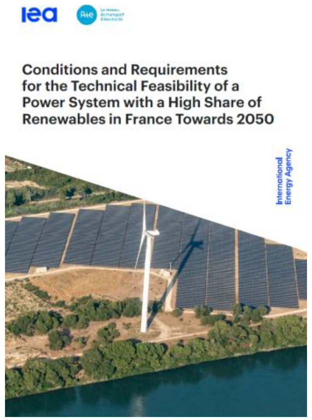
rte-france.com/eco2mix



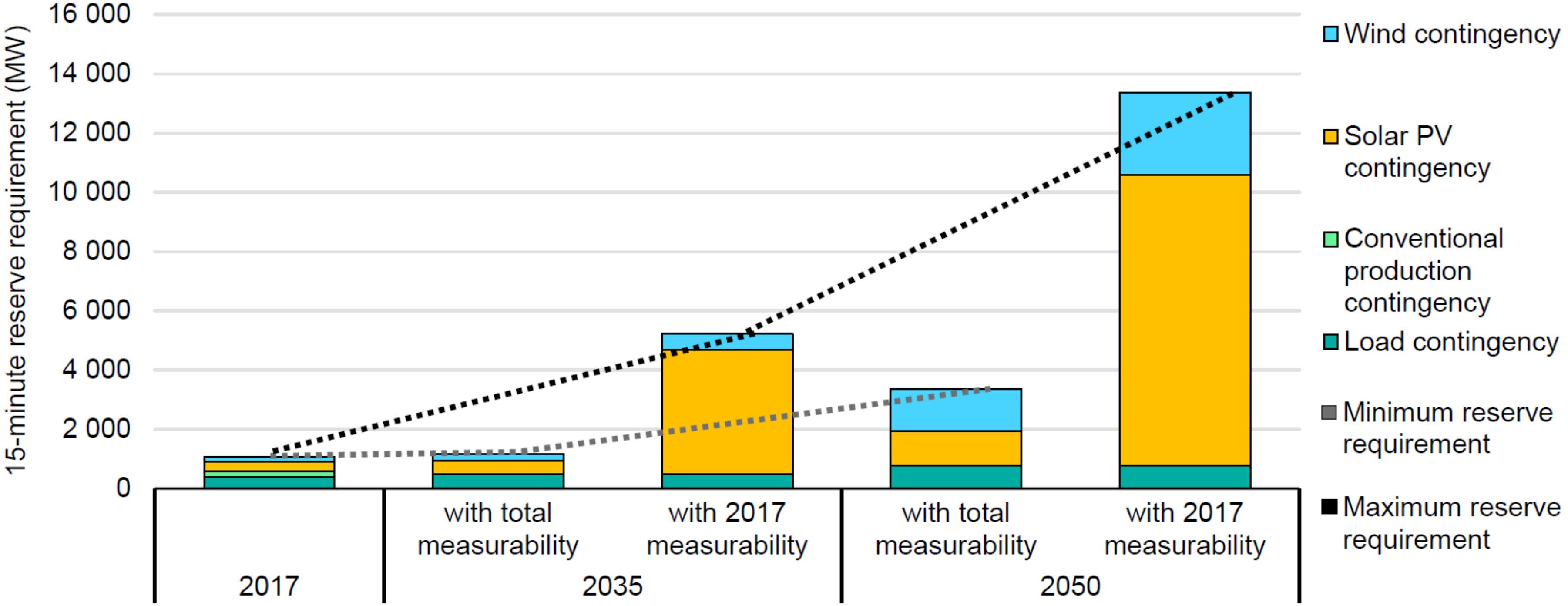


Predictibility




Conditions and Requirements for the Technical Feasibility of a Power System with a High Share of Renewables in France Towards 2050

More uncertainty → need more reserve to handle unexpected situations

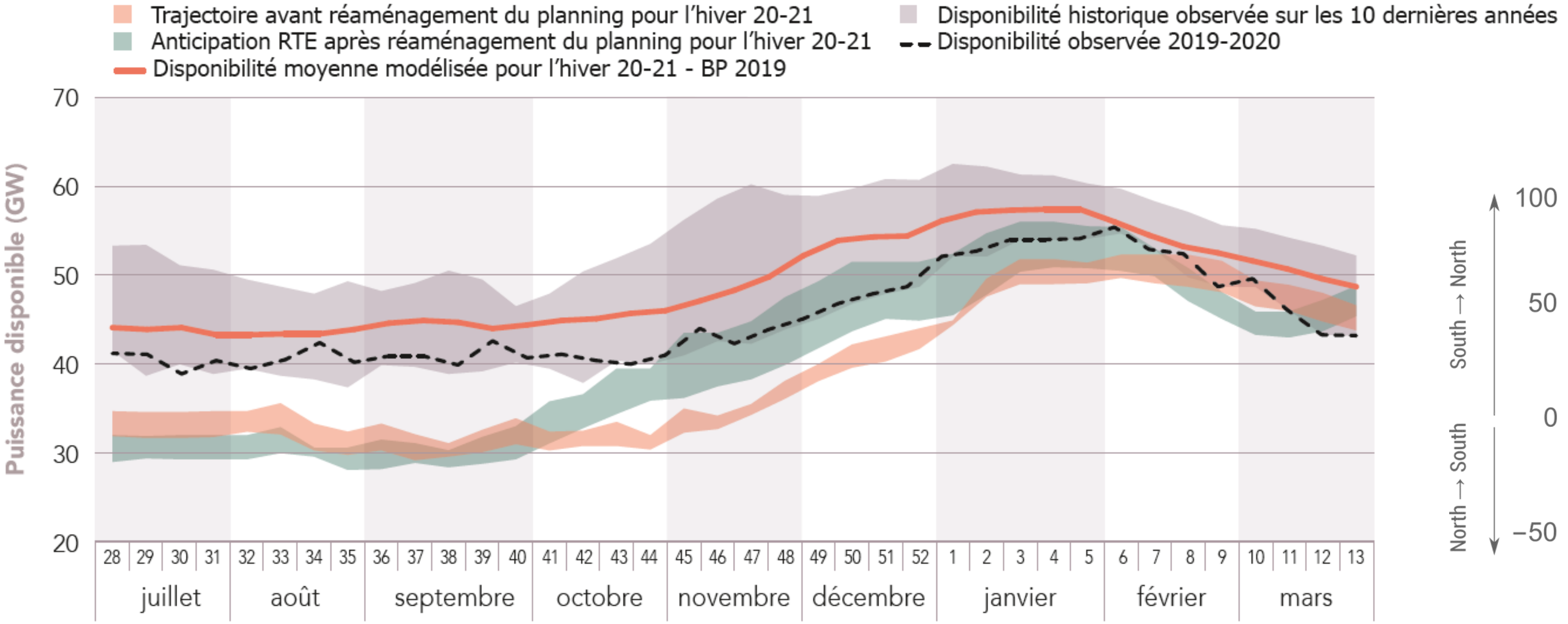


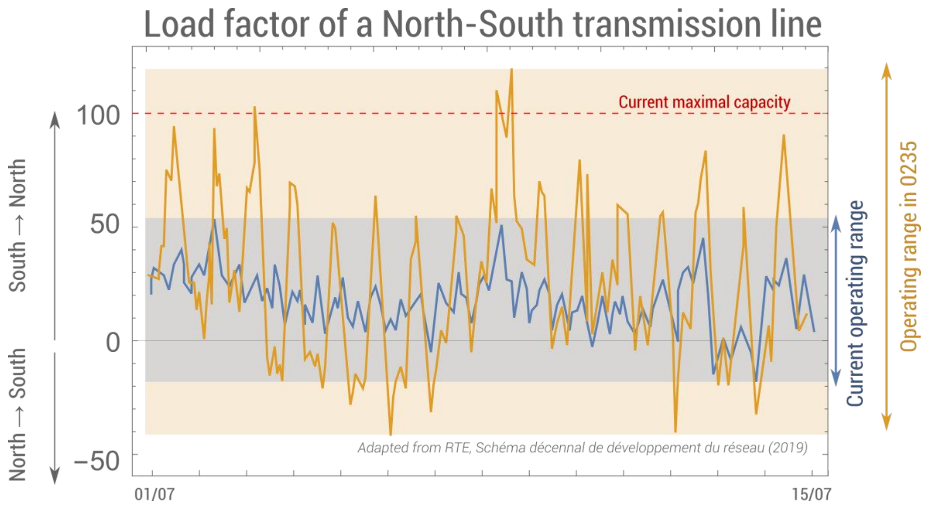
Longer time scales

Operation and maintenance

Development

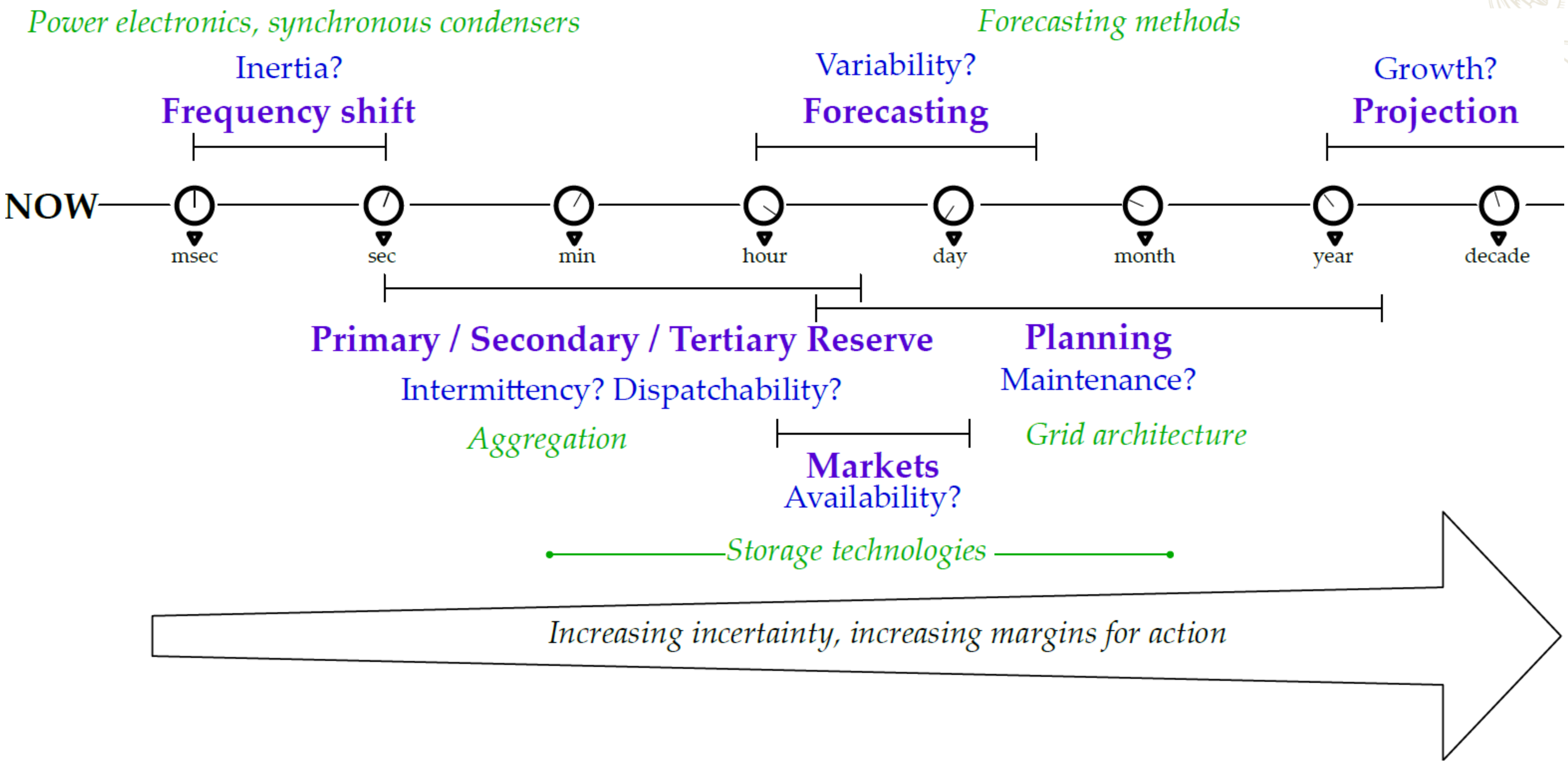
(demography, additionnal usages, behaviors, regulations…)





Adapted from RTE, Schéma décennal de développement du réseau (2019)

Timescales



Power electronics, synchronous condensers

Inertia?

Frequency shift

Forecasting methods

Variability?

Forecasting

Growth?

Projection

NOW

msec

sec

min

hour

day

month

year

decade

Primary / Secondary / Tertiary Reserve

Intermittency? Dispatchability?

Aggregation

Planning

Maintenance?

Grid architecture

Markets

Availability?

Storage technologies

Increasing incertainty, increasing margins for action

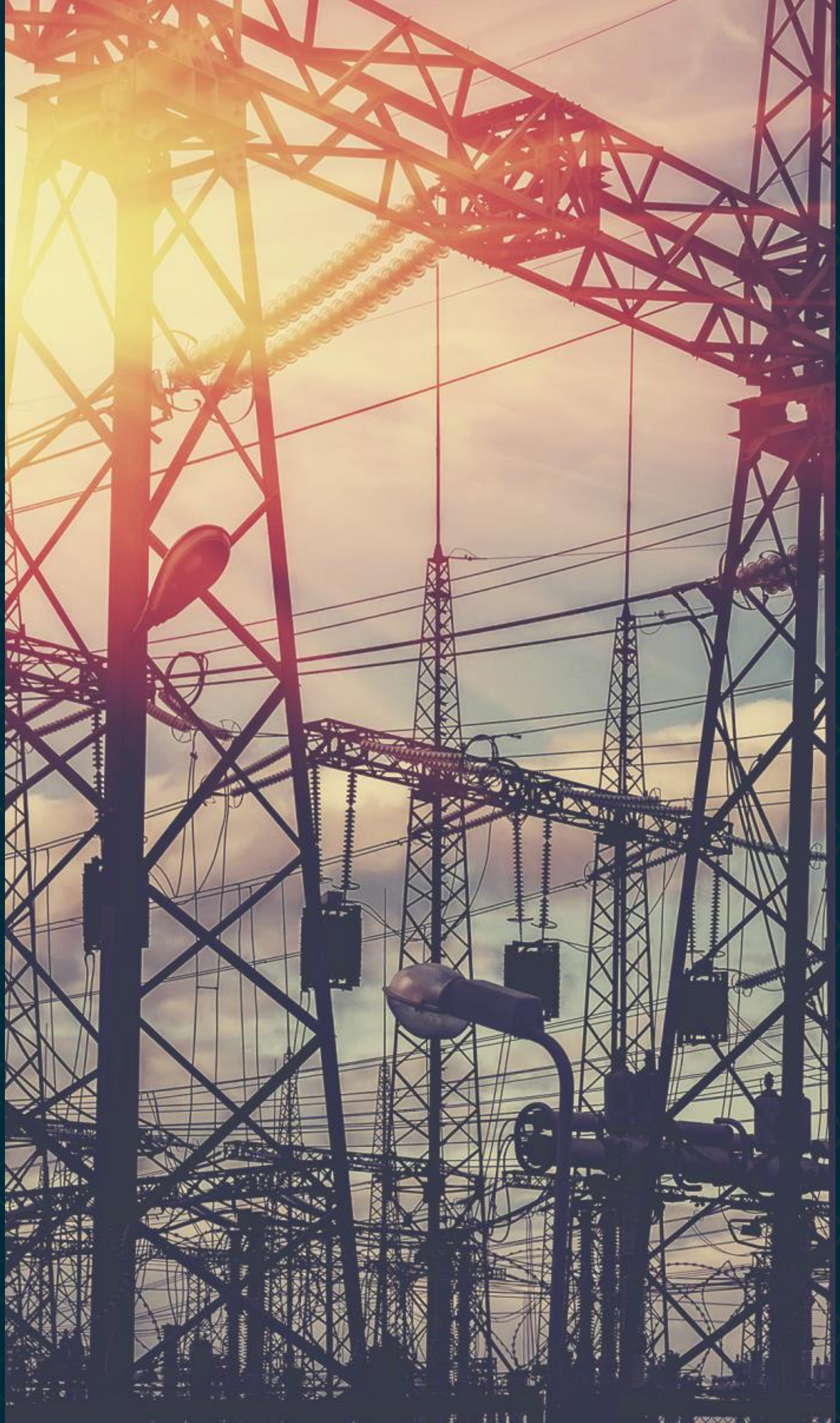
Lecture 9
Electrical grid
& electrical energy storage

I. The many time scales of grid stability
- Introduction to the electrical grid
- Time scales of grid stability
- Challenges raised by wind and solar integration

II. Power to X

III. Battery & electrical mobility

IV. Hydrogen

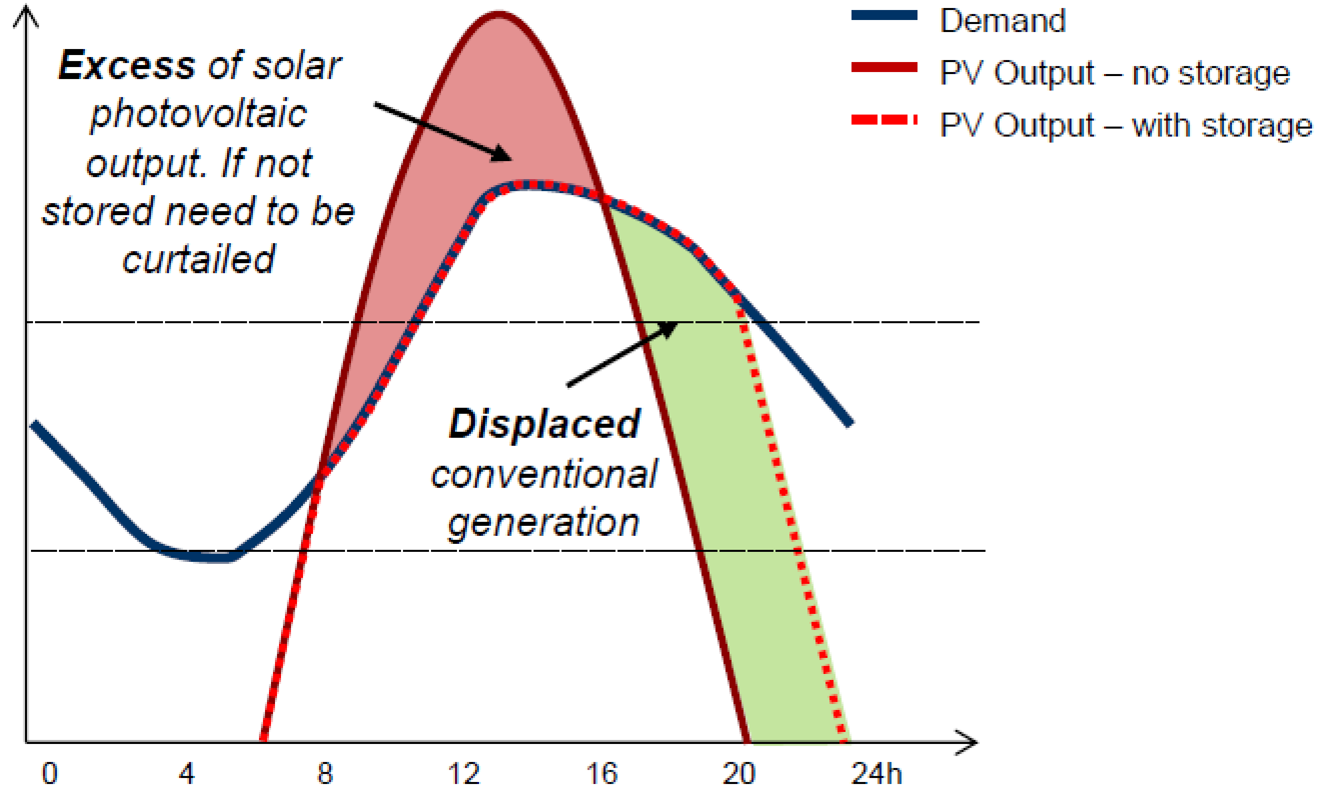


Storage technologies

General idea:

Stock power when overproducing

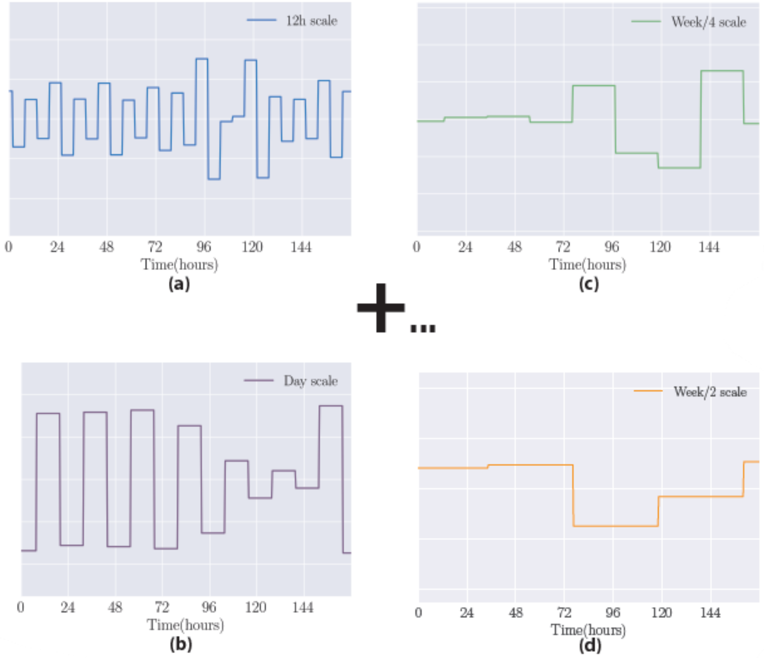
Tap storage when underproducing

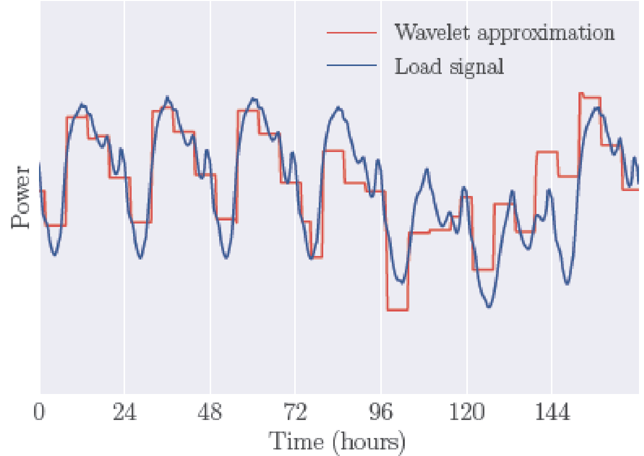


Remember !

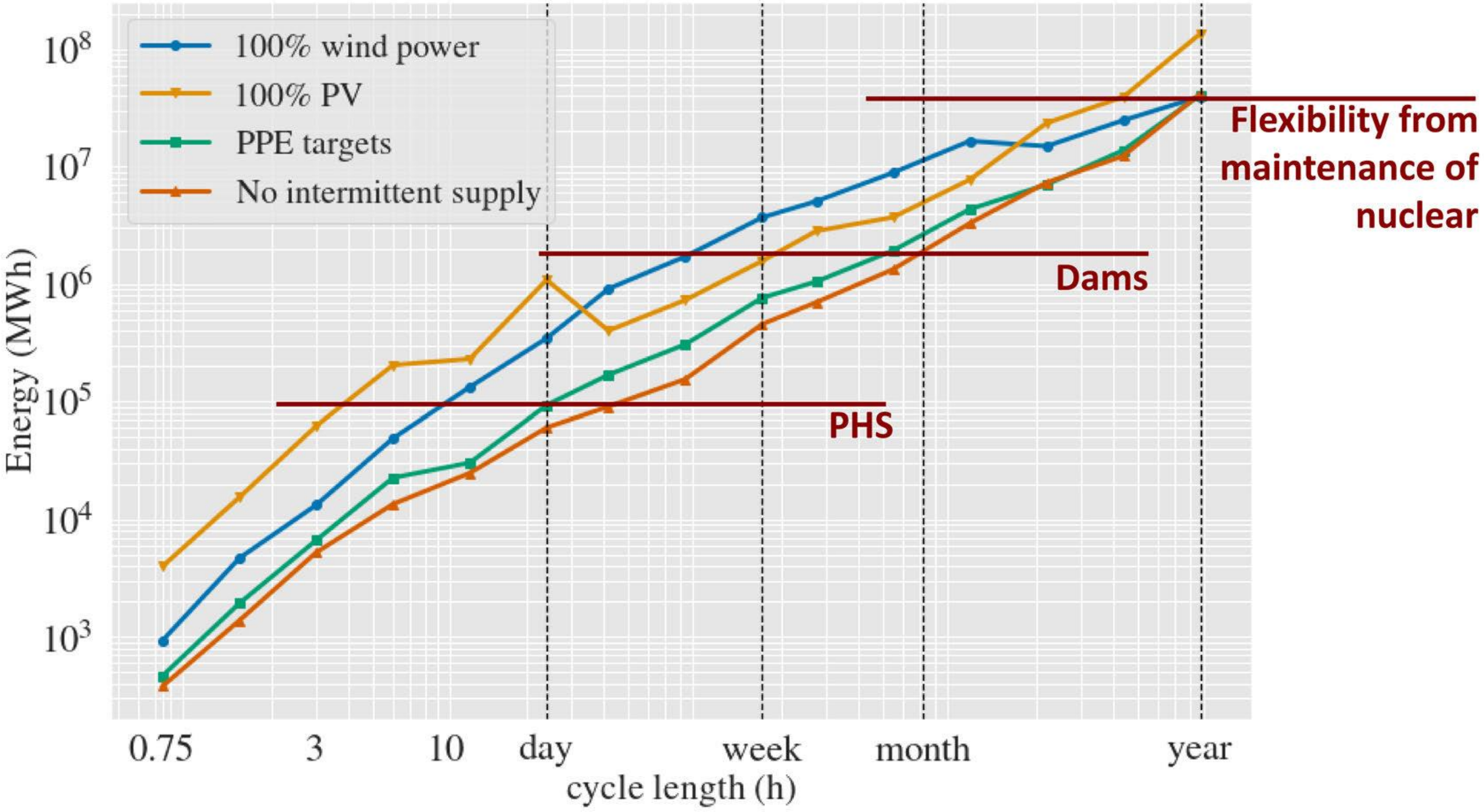
Many time scales

Storage requirements – wavelet analysis





A. Clerjon & F. Perdu, Energy Environ. Sci., 2019,12, 693-705



Power to X

How to store electricity when production is large and consumption is low

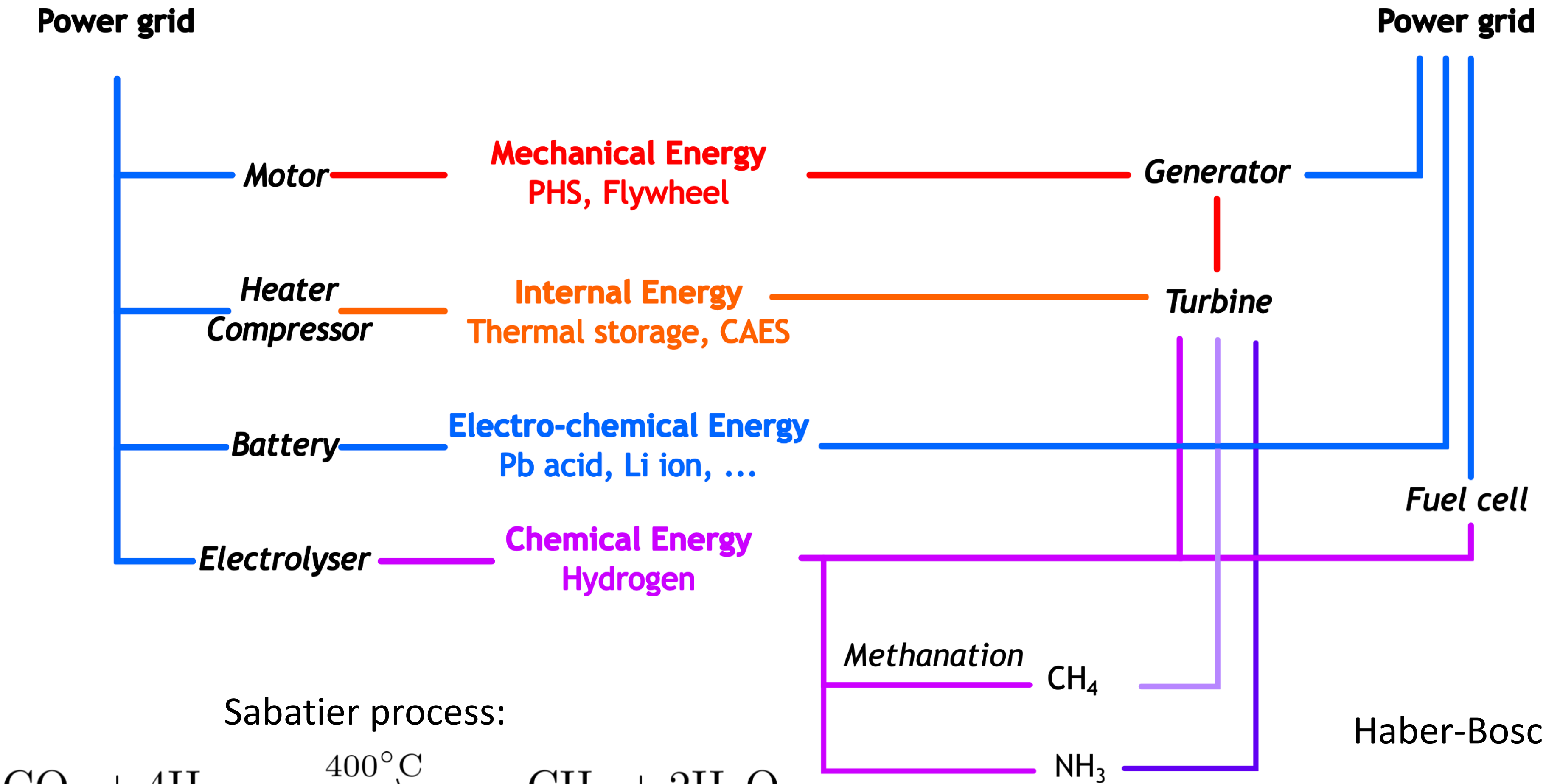
in prevision for low production, large consumption periods?

Can we use the (excess of) electricity production for other applications?

Basic indicators :

Efficiency	energy out / energy in
Self discharge / storage duration	How long can energy remain stored?
Lifetime / number of cycles	How long can the storage be used?
Storage capacity : Wh/kg or Wh/m^3	How much energy can be stored ?
Power rating : W/kg or W/m^3	How much power can the device handle?

Power to power



Power grid

Motor — **Mechanical Energy** PHS, Flywheel — *Generator*

Heater / *Compressor* — **Internal Energy** Thermal storage, CAES — *Turbine*

Battery — **Electro-chemical Energy** Pb acid, Li ion, …

Electrolyser — **Chemical Energy** Hydrogen

Fuel cell

Power grid

Methanation CH_4

NH_3

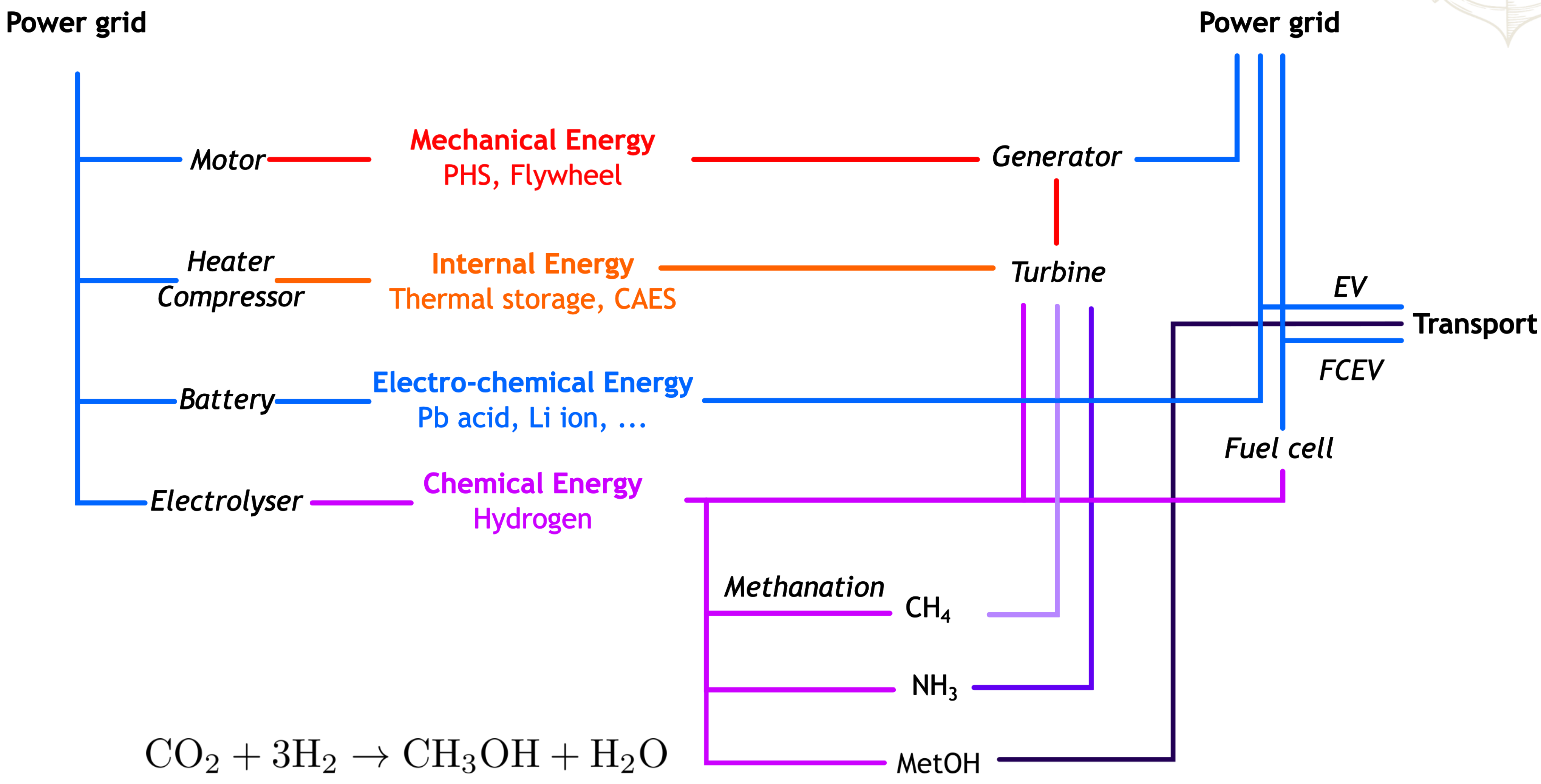
Sabatier process:

$$CO_2 + 4H_2 \xrightarrow[\text{pressure+catalyst}]{400^\circ C} CH_4 + 2H_2O$$

Haber-Bosch process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Power to mobility



Power grid

Motor

Mechanical Energy
PHS, Flywheel

Heater
Compressor

Internal Energy
Thermal storage, CAES

Battery

Electro-chemical Energy
Pb acid, Li ion, …

Electrolyser

Chemical Energy
Hydrogen

Methanation

CH_4

NH_3

MetOH

Generator

Turbine

Fuel cell

Power grid

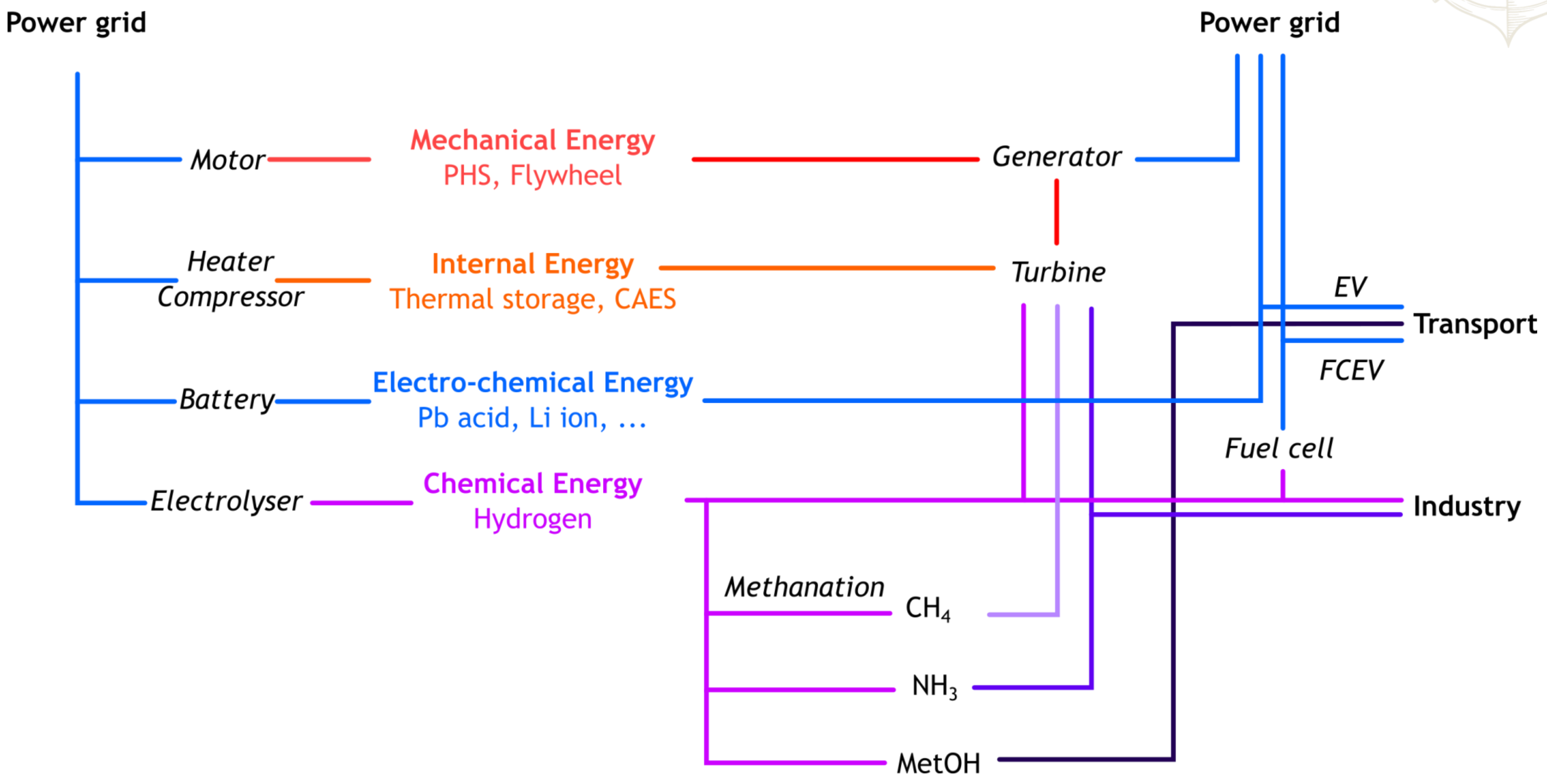
EV

Transport

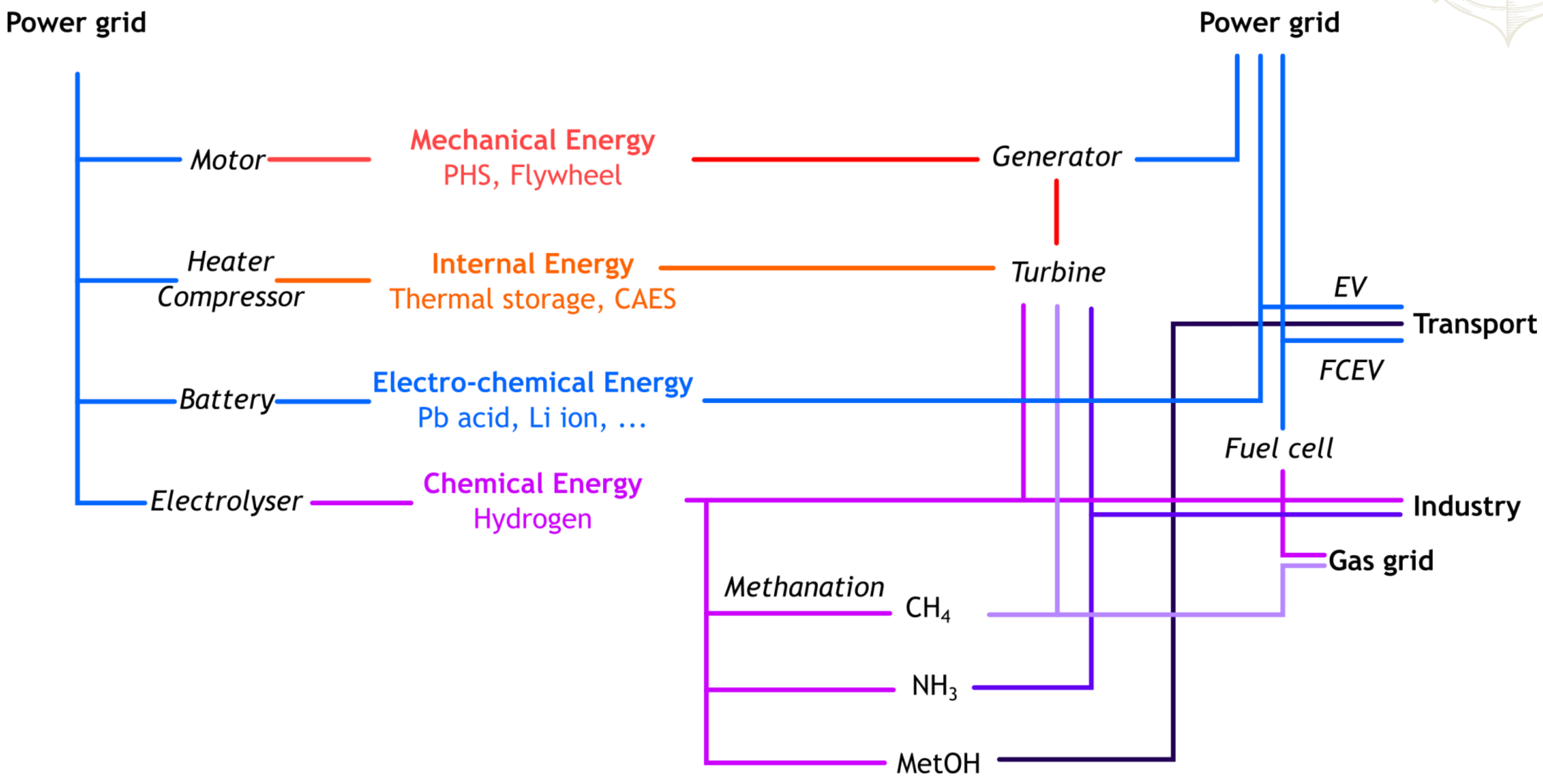
FCEV

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

Power to chemicals

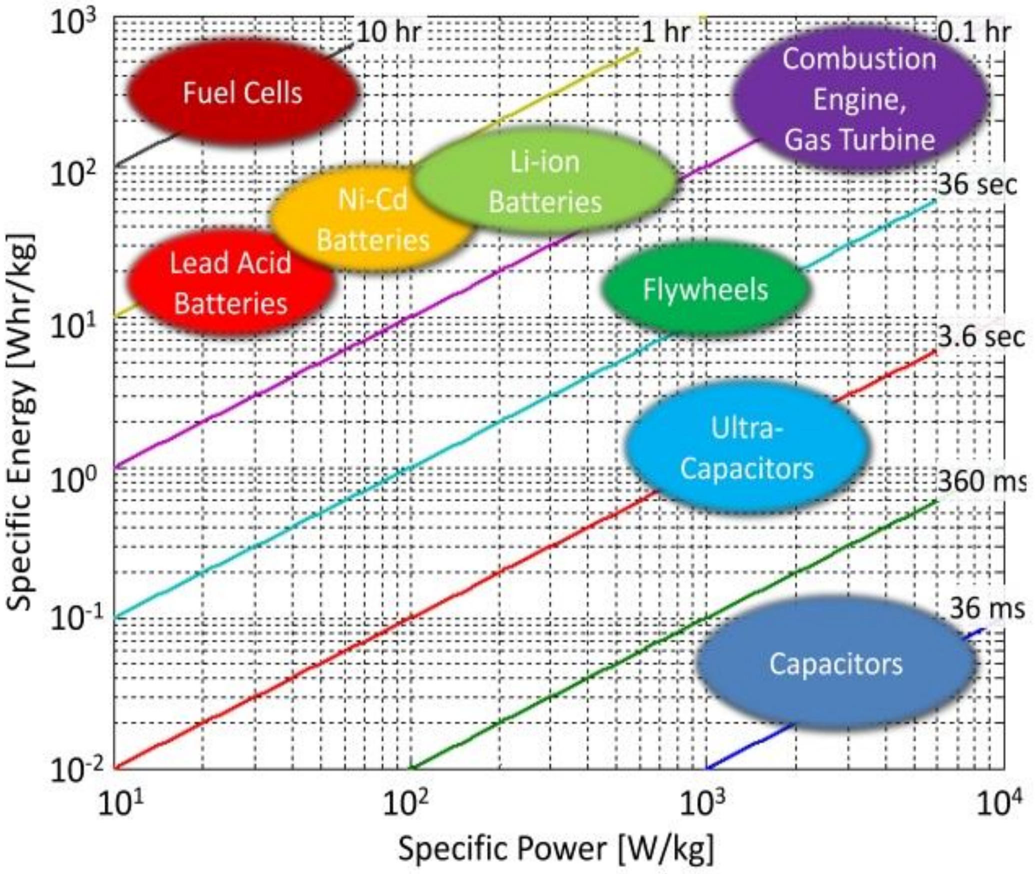


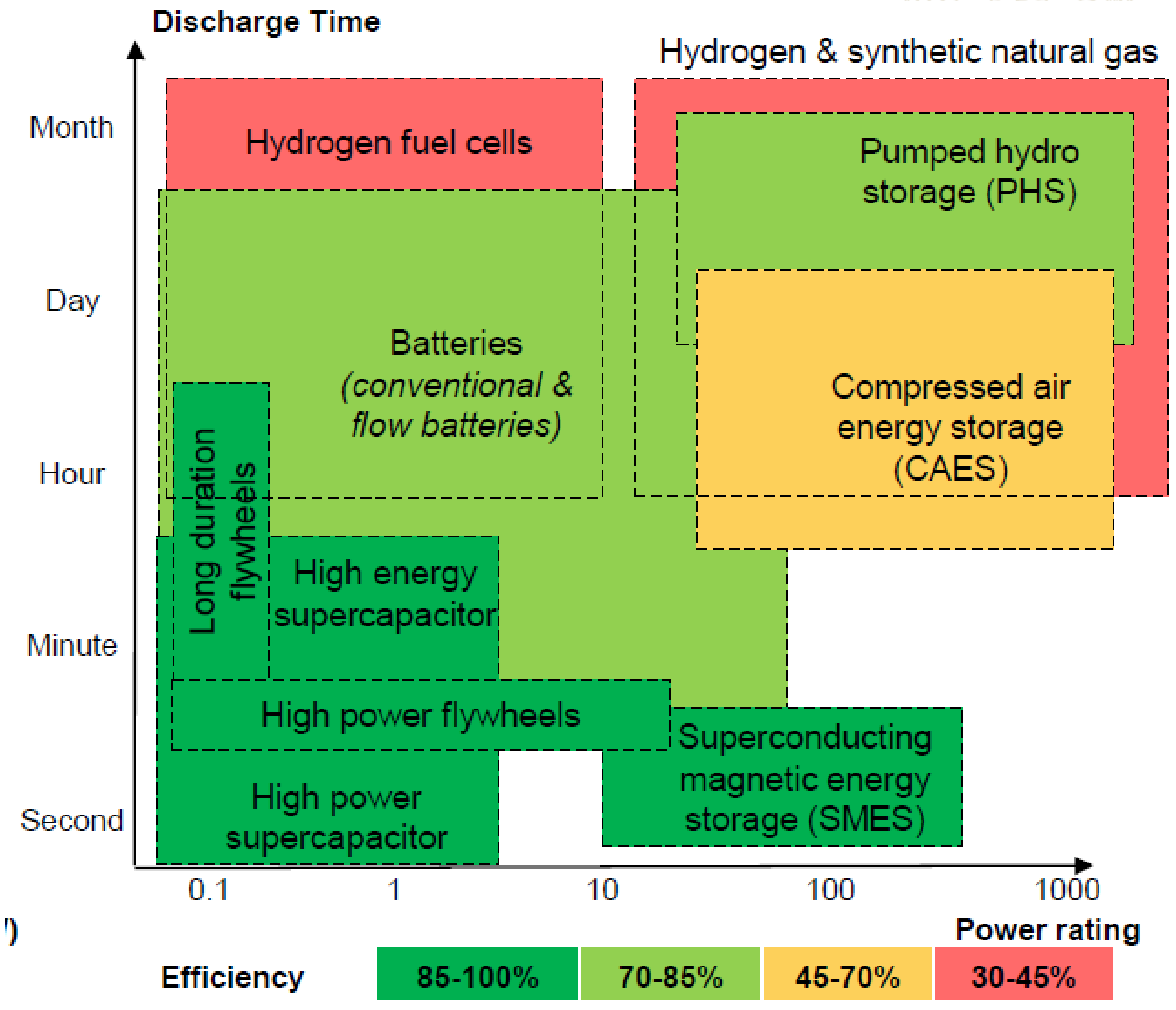
Power to gas


Power grid
Power grid
Motor
Mechanical Energy
PHS, Flywheel
Generator
Heater
Compressor
Internal Energy
Thermal storage, CAES
Turbine
EV
Transport
FCEV
Battery
Electro-chemical Energy
Pb acid, Li ion, …
Fuel cell
Electrolyser
Chemical Energy
Hydrogen
Industry
Gas grid
Methanation
CH_4
NH_3
MetOH

Which storage for which application?

Ragone chart:





2013 SBC Energy Institute

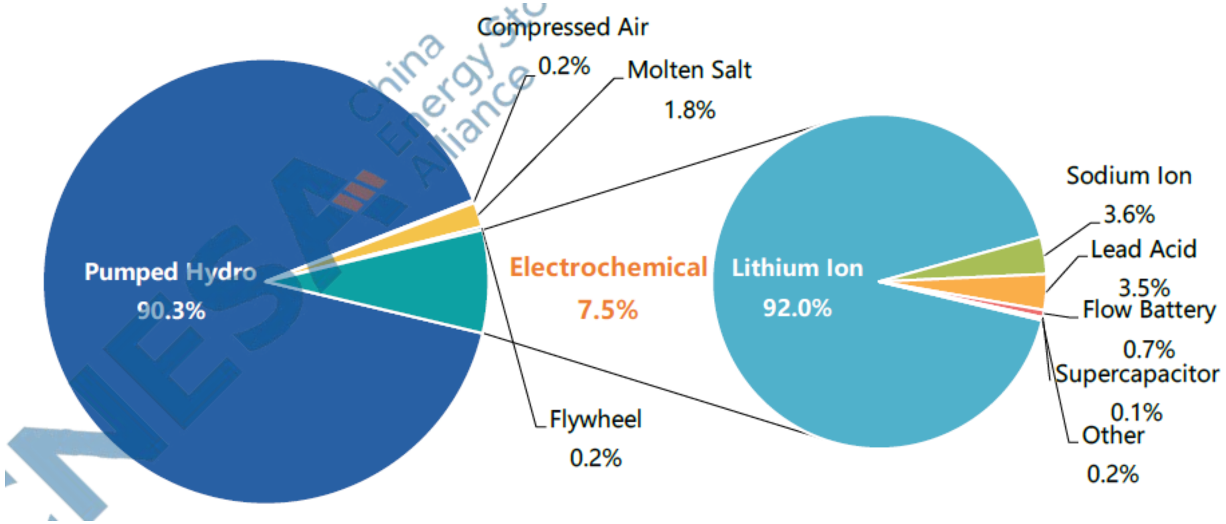
Storage technologies

	Power rating (MW)	Storage duration (h)	Cycling or lifetime	Self discharge [8] Per day	Energy density (Wh/l)	Power density (W/l)	Efficiency	Response time
PHS[1]	100 - 1,000	4 - 12h	30 - 60 years	~0	0.2 - 2	0.1 - 0.2	70-85%	Sec - Min
CAES[2]	10 - 1,000	2 - 30h	20 - 40 years	~0	2 - 6	0.2 - 0.6	40-75%	Sec - Min
Flywheels	0.001 - 1	Sec - hours	20,000 - 100,000	1.3 -100 %	20 - 80	5,000	70-95%	< sec
NaS battery[3]	10 - 100	1 min - 8h	2,500 - 4,500	0.05 - 20%	150 - 300	120 - 160	70-90%	< sec
Li-ion battery[4]	0.1 - 20	1 min - 8h	1,000 - 10,000	0.1 - 0.3%	200 - 400	1,300 - 10,000	85-98%	< sec
Flow battery[5]	0.1 - 100	1 - 0h	12,000 - 14,000	0.2%	20 - 70	0.5 - 2	60-85%	< sec
Supercapacitor	0.01 - 1	Ms - min	10,000- 100,000	20 - 40%	10 - 20	40,000 - 120,000	80-98%	< sec
SMES[6]	0.1 - 1	Ms - sec	100,000	10 - 15%	~6	~2,600	80-95%	< sec
Molten salt	1 - 150	Hours	30 years	n/a	70 - 210	n/a	80-90%	Min
Hydrogen	0.01 - 1,000	Min - weeks	5 - 30 years	0 - 4%	600 (200 bar)	0.2 - 20	25-45%	Sec - Min
SNG[7]	50 - 1,000	hours-weeks	30 years	negligible	1,800 (200 bar)	0.2 - 2	25-50%	Sec - Min

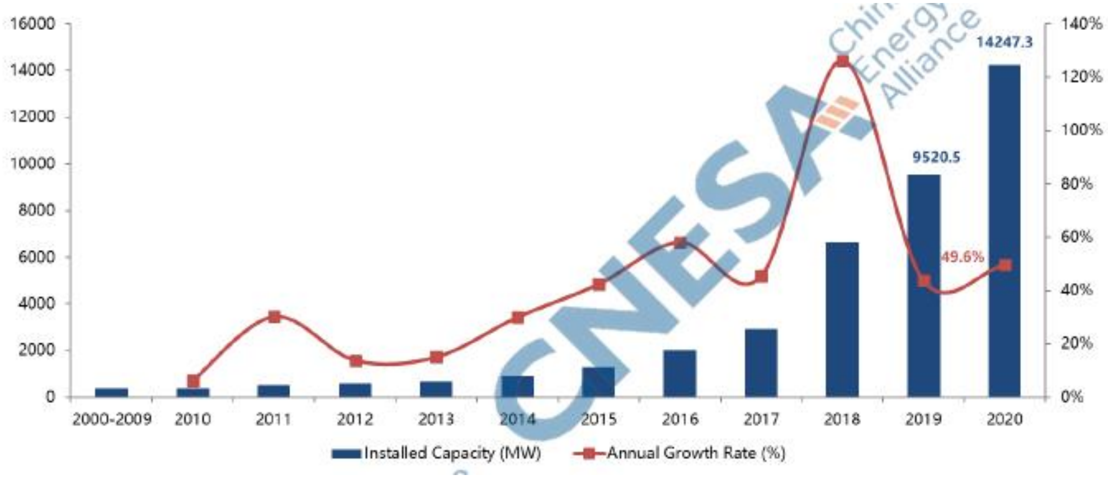
2013 SBC Energy Institute

Installed capacities (2023)

Global total storage capacity :
190 GW [2021]



2021 CNESA White Paper



Pump hydro storage

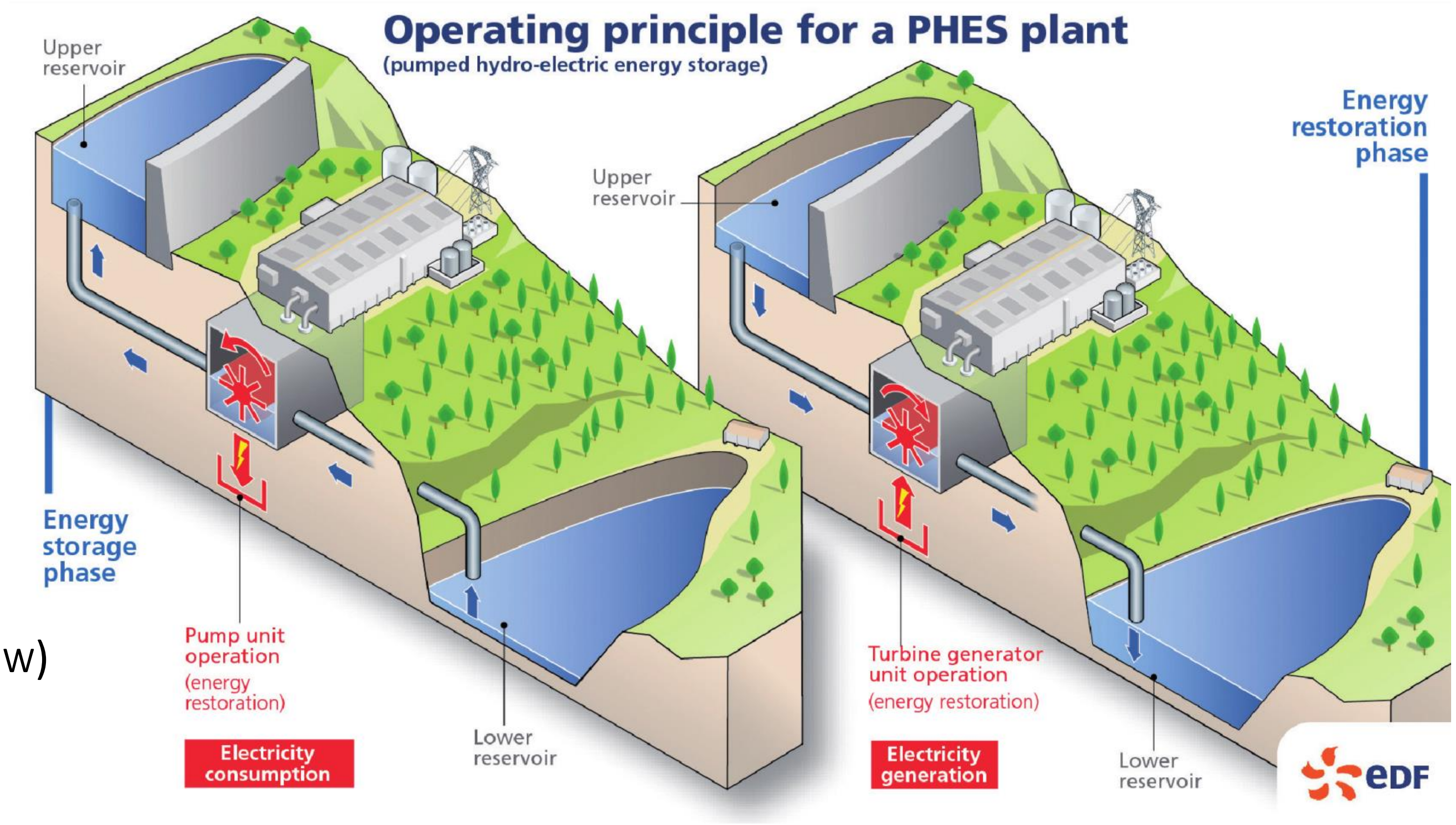
See PC 9

Over production :

Pump water up

Under production :

Turbine water down



Excellent efficiency (70-90%)

Low energy density (g h < 10 kJ/kg)

Large volume and power (Grandmaison : 300 GWh, 2GW)

Potential limited by available sites

France :

Installed capacity = 5 GW
Additionnal potential = 1-1,5 GW (ADEME)

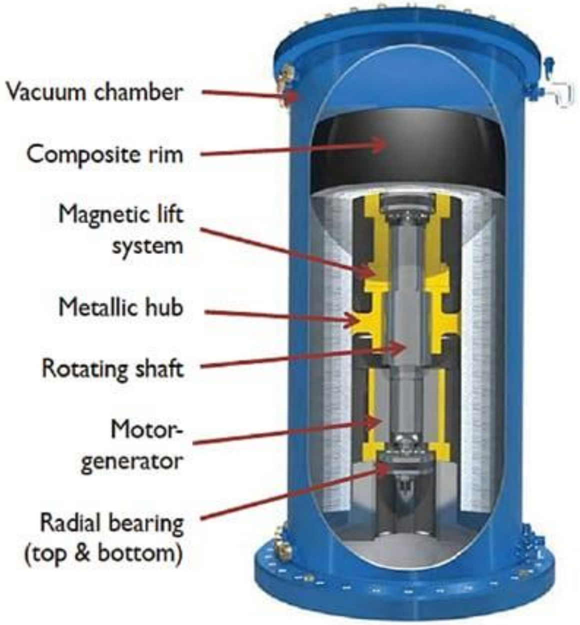
Flywheel

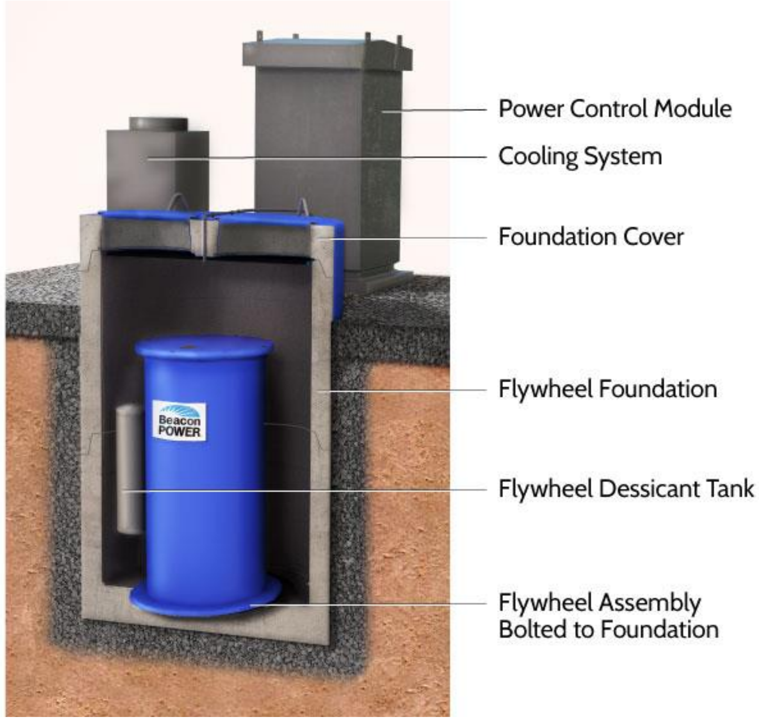
See PC 9

Storing energy as rotation speed

$$E_C = \frac{1}{2} J\omega^2 \qquad J_{\text{cylinder}} = \frac{1}{2} mr^2$$

High power, limited energy
Mechanical constraints (stress on material, bearings…)





Hazle Township, Pennsylvania
200 flywheels, 20 MW for frequency regulation

Beacon power system

Compressed air

Adiabatic: $T \sim T_0 \times r^{\frac{\gamma-1}{\gamma}}$

Isothermal: $W^{\text{isothermal}} = V\left(p_H \ln\frac{p_H}{p_0} - p_L \ln\frac{p_L}{p_0} - (p_H - p_L)\right)$

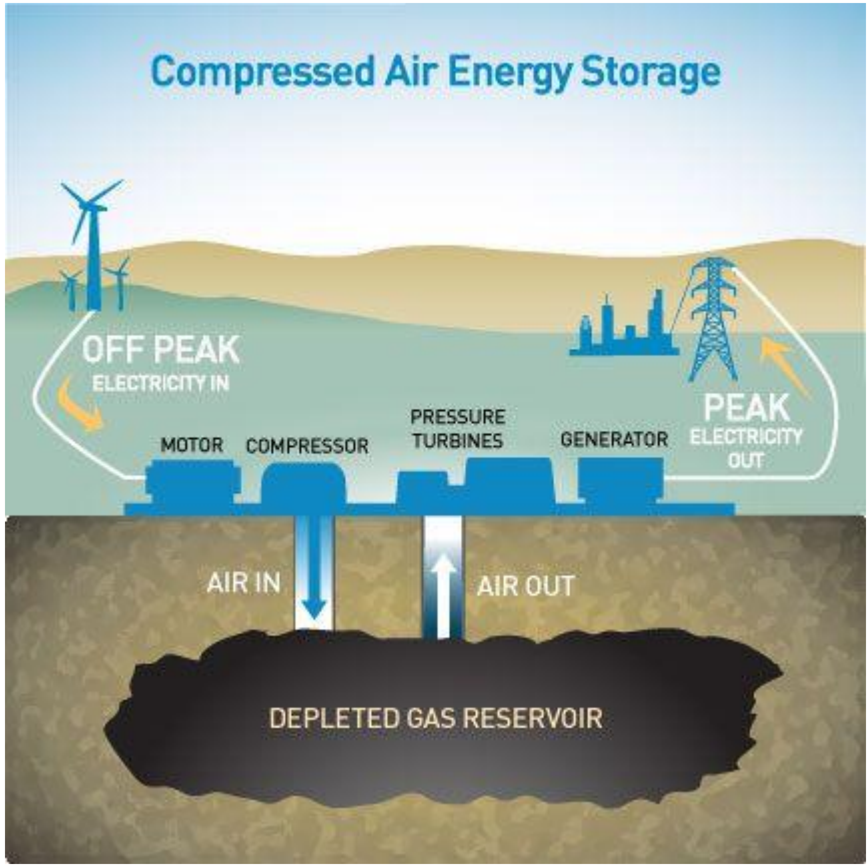
ΔN
p_0, T_0

N
V
p_L, T_0

N+ΔN
V
p_H, T_0

Couple with thermal storage

	Huntdorf, Germany	McIntosh, USA
Pressure	45 to 70 bar	45 to 76 bar
Volume	310 000 m³	560 000 m³
Power	290 MW	110 MW
Energy	1160 MWh (=4h)	2640 MWh (=24h)



Lecture 9
Electrical grid
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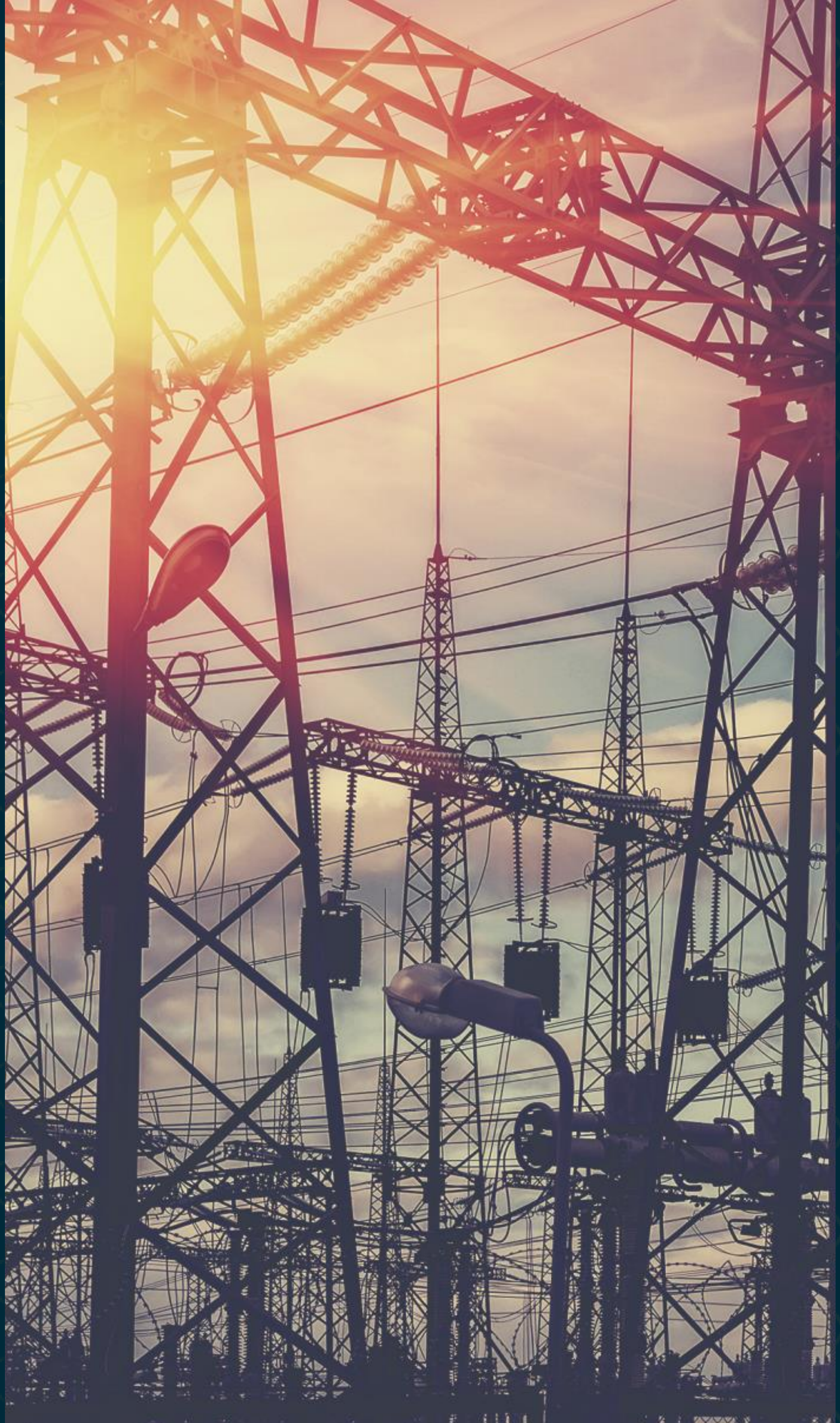


Batteries – driving force

“usual” chemical reaction

Spontaneous evolution:

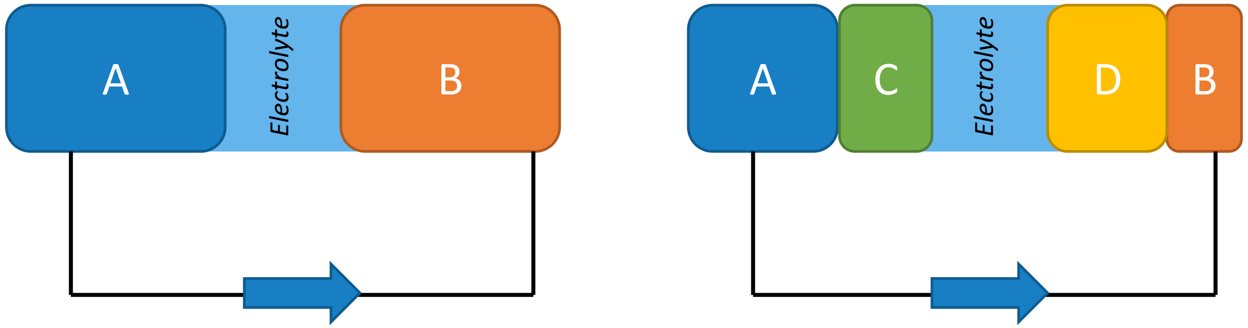
$$\Delta_r G < 0$$

$$aA + bB \rightarrow cC + dD$$

Battery: same reaction

ionic species can move through the electrolyte

but electrons have to go through an external circuit



Anode
Oxidation
Gives electrons

Cathode
Reduction
Receives electrons

Electron / ion duality

If electrons can’t flow (e.g. open circuit),
the chemical reaction stops

If ions can’t flow (e.g. contact issues…)
the electronic current stops

Batteries – Open circuit

Open circuit situation: no transport → independent of electrolyte

Open circuit voltage

$$U = -\frac{\Delta_r G}{z N_A e}$$

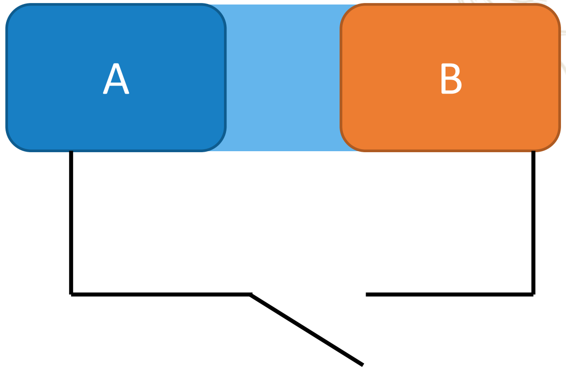
N_A e = 96 500 C/mol = Faraday’s constant

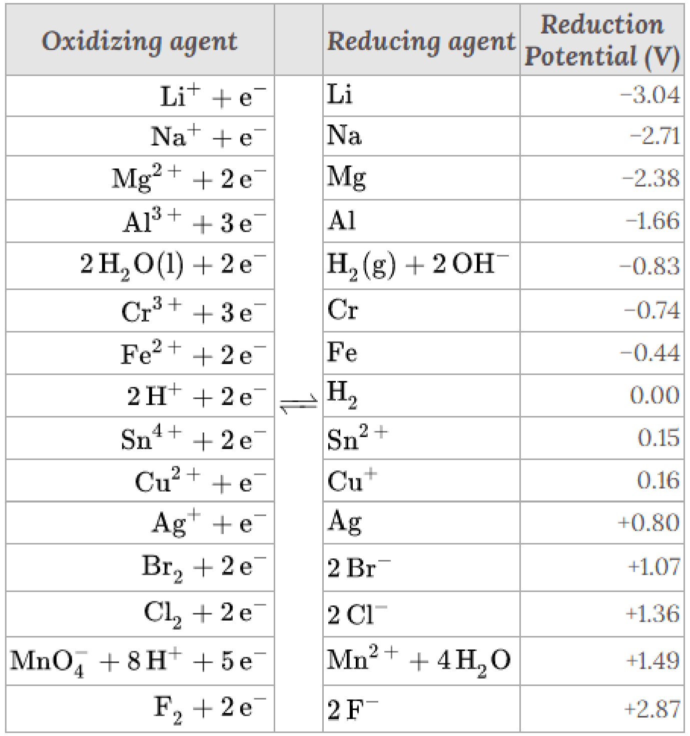
maximum theoretical specific energy (MTSE)

Real density = 20-25% of MTSE (electrolyte, casing…)

$$\mathrm{MTSE\ [kWh/kg]} = -\frac{\Delta_r G}{\mathrm{molar\ mass}} = 26.8\frac{zU}{\mathrm{molar\ mass}}$$

➡ Strong interest for Li !

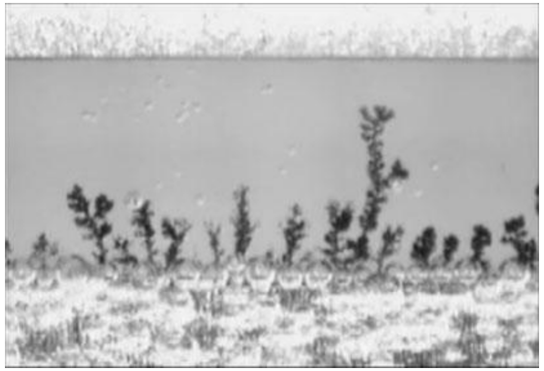


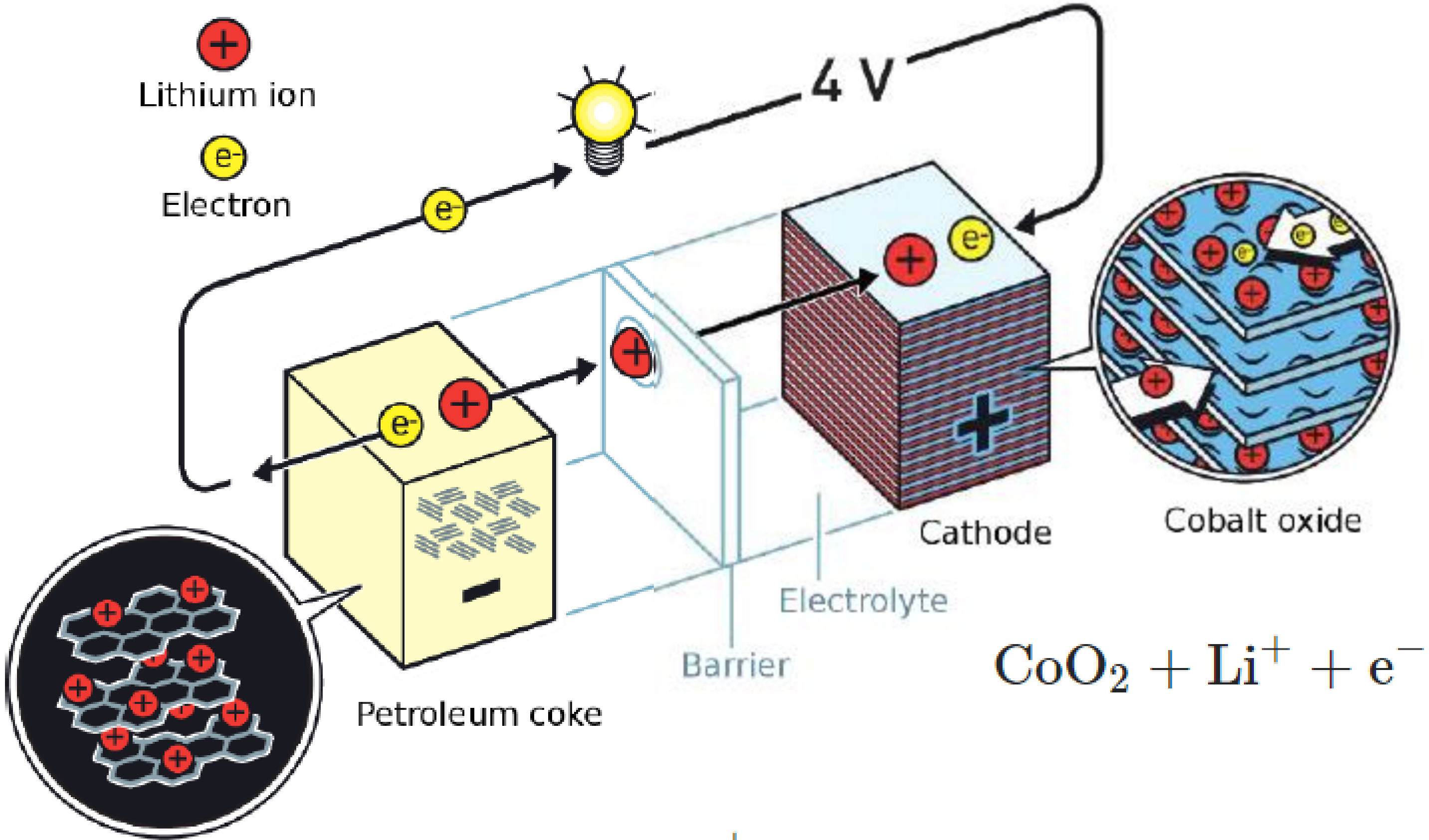


Oxidizing agent		Reducing agent	Reduction Potential (V)
$Li^+ + e^-$	$\rightleftharpoons$	Li	−3.04
$Na^+ + e^-$		Na	−2.71
$Mg^{2+} + 2e^-$		Mg	−2.38
$Al^{3+} + 3e^-$		Al	−1.66
$2H_2O(l) + 2e^-$		$H_2(g) + 2OH^-$	−0.83
$Cr^{3+} + 3e^-$		Cr	−0.74
$Fe^{2+} + 2e^-$		Fe	−0.44
$2H^+ + 2e^-$		H_2	0.00
$Sn^{4+} + 2e^-$		Sn^{2+}	0.15
$Cu^{2+} + e^-$		Cu^+	0.16
$Ag^+ + e^-$		Ag	+0.80
$Br_2 + 2e^-$		$2Br^-$	+1.07
$Cl_2 + 2e^-$		$2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^-$		$Mn^{2+} + 4H_2O$	+1.49
$F_2 + 2e^-$		$2F^-$	+2.87

Li-ion battery

Lithium !
Non aqueous electrolyte
Avoid metalic electrodes





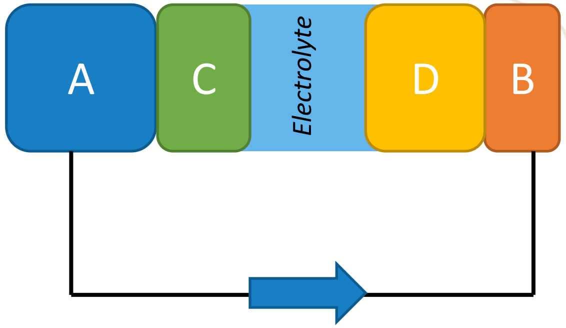
$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$

$$LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$$

John B. Goodenough, M. Stanley Whittingham, Akira Yoshino
“for the development of lithium-ion batteries”

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$$

Batteries – under operation



Gibbs energy depends on mixture concentration

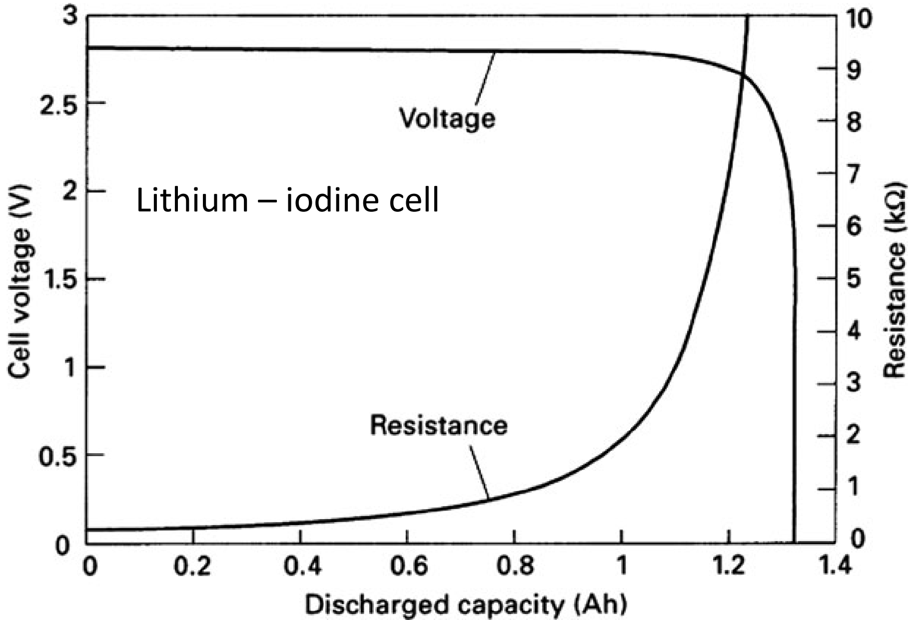
(a = activity = concentration in ideal case)

$$\Delta_r G = \Delta_r G^0 + RT \ln \frac{a_{\text{products}}}{a_{\text{reactants}}}$$

Nernst law

$$U = -\frac{\Delta_r G}{z N_A e} = U^0 - \frac{k_B T}{ze} \ln \frac{a_{\text{products}}}{a_{\text{reactants}}}$$

Voltage changes during cell operation



+ kinetic considerations (not addressed here)

A zoology of batteries

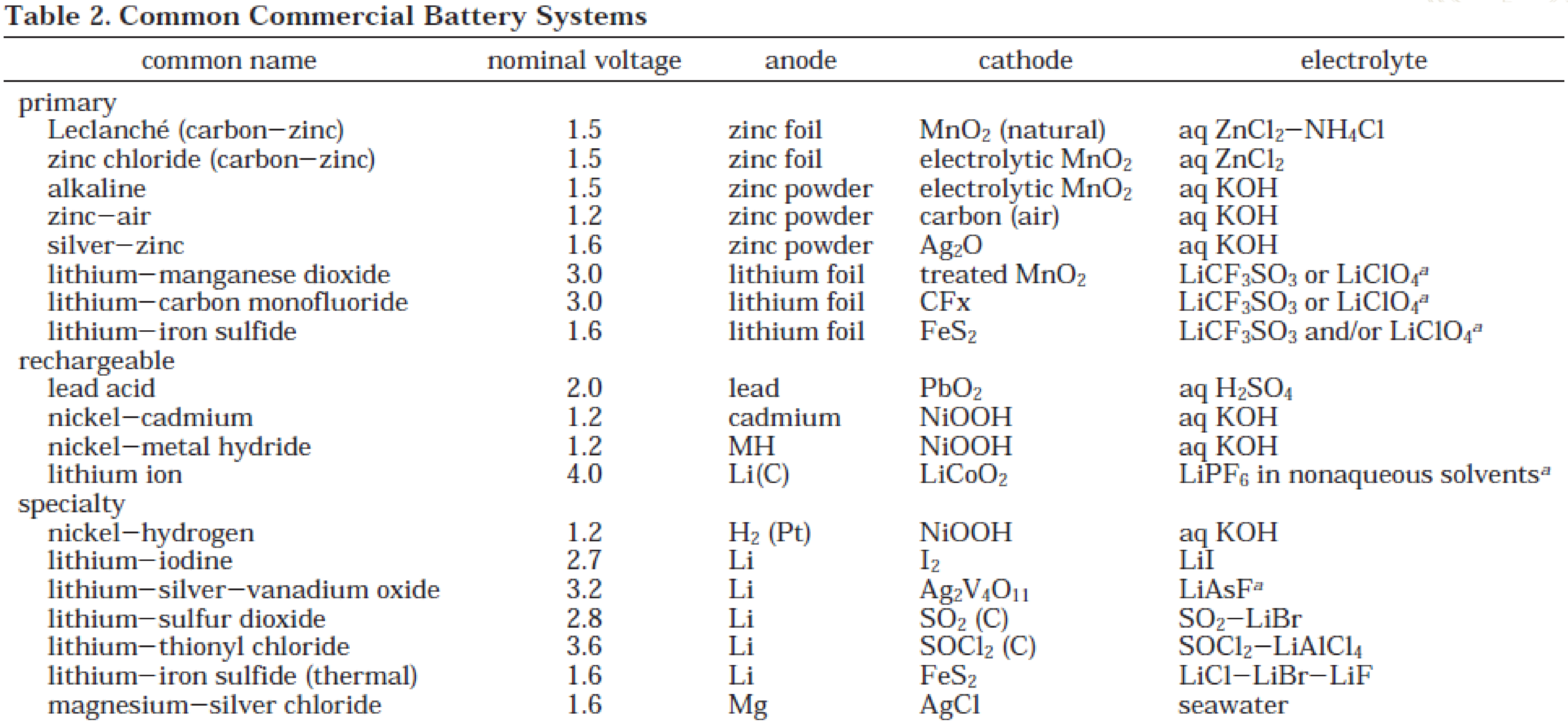


Table 2. Common Commercial Battery Systems

common name	nominal voltage	anode	cathode	electrolyte
primary				
Leclanché (carbon–zinc)	1.5	zinc foil	MnO_2 (natural)	aq $ZnCl_2$–NH_4Cl
zinc chloride (carbon–zinc)	1.5	zinc foil	electrolytic MnO_2	aq $ZnCl_2$
alkaline	1.5	zinc powder	electrolytic MnO_2	aq KOH
zinc–air	1.2	zinc powder	carbon (air)	aq KOH
silver–zinc	1.6	zinc powder	Ag_2O	aq KOH
lithium–manganese dioxide	3.0	lithium foil	treated MnO_2	$LiCF_3SO_3$ or $LiClO_4$[a]
lithium–carbon monofluoride	3.0	lithium foil	CFx	$LiCF_3SO_3$ or $LiClO_4$[a]
lithium–iron sulfide	1.6	lithium foil	FeS_2	$LiCF_3SO_3$ and/or $LiClO_4$[a]
rechargeable				
lead acid	2.0	lead	PbO_2	aq H_2SO_4
nickel–cadmium	1.2	cadmium	NiOOH	aq KOH
nickel–metal hydride	1.2	MH	NiOOH	aq KOH
lithium ion	4.0	Li(C)	$LiCoO_2$	$LiPF_6$ in nonaqueous solvents[a]
specialty				
nickel–hydrogen	1.2	H_2 (Pt)	NiOOH	aq KOH
lithium–iodine	2.7	Li	I_2	LiI
lithium–silver–vanadium oxide	3.2	Li	$Ag_2V_4O_{11}$	LiAsF[a]
lithium–sulfur dioxide	2.8	Li	SO_2 (C)	SO_2–LiBr
lithium–thionyl chloride	3.6	Li	$SOCl_2$ (C)	$SOCl_2$–$LiAlCl_4$
lithium–iron sulfide (thermal)	1.6	Li	FeS_2	LiCl–LiBr–LiF
magnesium–silver chloride	1.6	Mg	AgCl	seawater

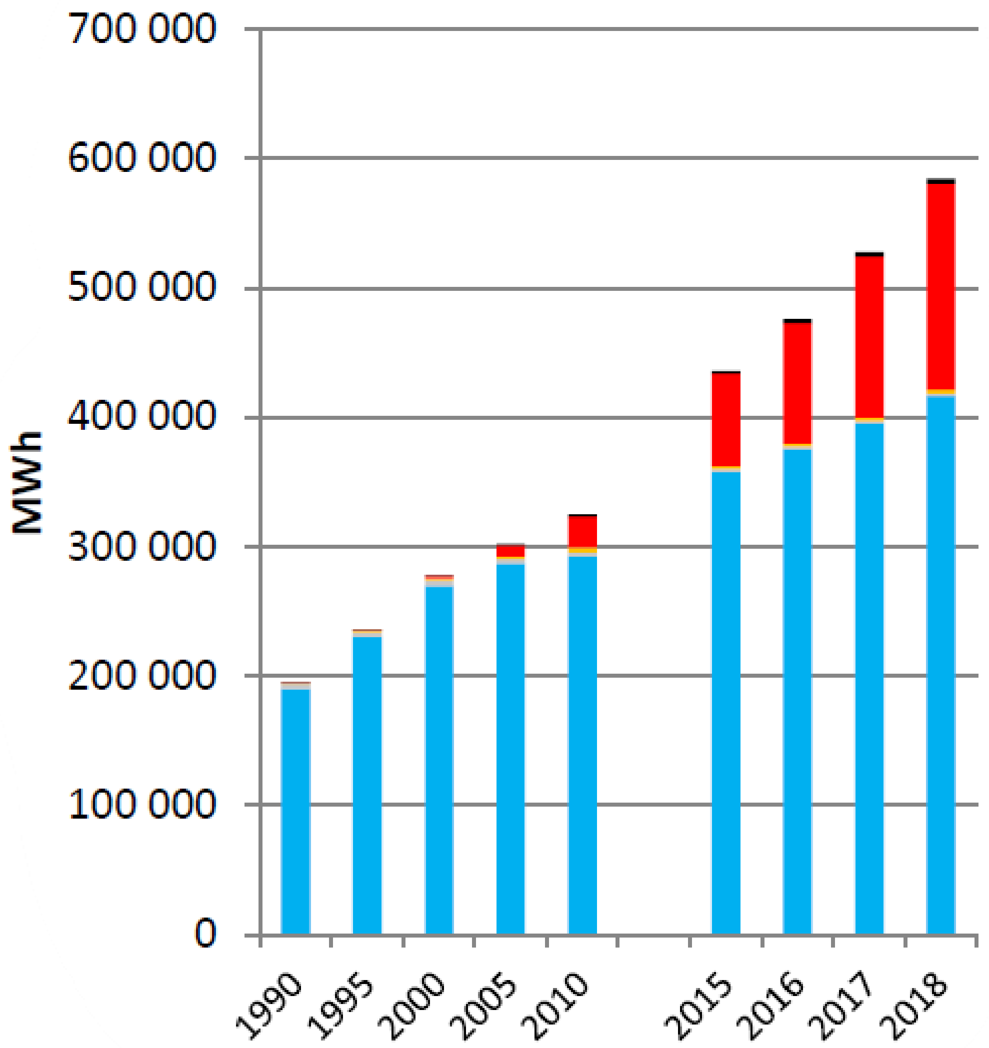
Chem. Rev. **2004,** 104, 4245-4269

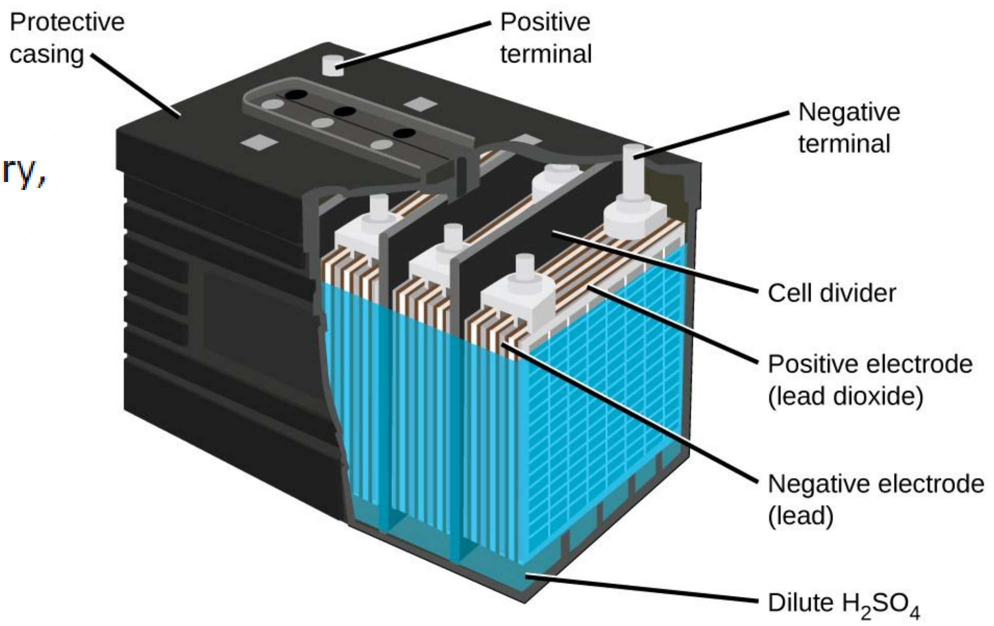
Usual battery technologies

	Sodium-sulfur (NaS)	Lithium-ion (Li-ion)	Nickel-cadmium (NiCd)	Lead-acid (LA)
Efficiency *%*	70 - 90	85 - 98	60 - 80	70 - 90
Self-discharge *% energy / day*	0.05 - 20	0.1 - 0.3	0.067 - 0.6	0.033 - 0.3
Cycle lifetime *cycles*	2,500 - 4,500	1,000 - 10,000	800 - 3,500	100 - 2,000
Expected lifetime *years*	5 - 15	5 - 15	5 - 20	3 - 20
Specific energy *Wh / kg*	150 - 240	75 - 200	50 - 75	30 - 50
Specific power *W / kg*	150 - 230	150 - 315	150 - 300	75 - 300
Energy density *Wh / Liter*	150 - 300	200 - 400	60 - 150	30 - 80
Other consideration *(environment & safety)*	Need to be maintained at temperatures of 300°C to 350°C, entailing safety issues and preventing suitability to small-scale applications	Lithium is highly reactive and flammable, and therefore requires recycling programs and safety measures	Cadmium is a toxic metal that needs to be recycled. NiCd also requires ventilation & air conditioning to maintain the temperature	Lead is toxic and sulfuric acid is highly corrosive, requiring recycling and neutralization. Air conditioning required to maintain stable temperature

2013 SBC Energy Institute

Battery market

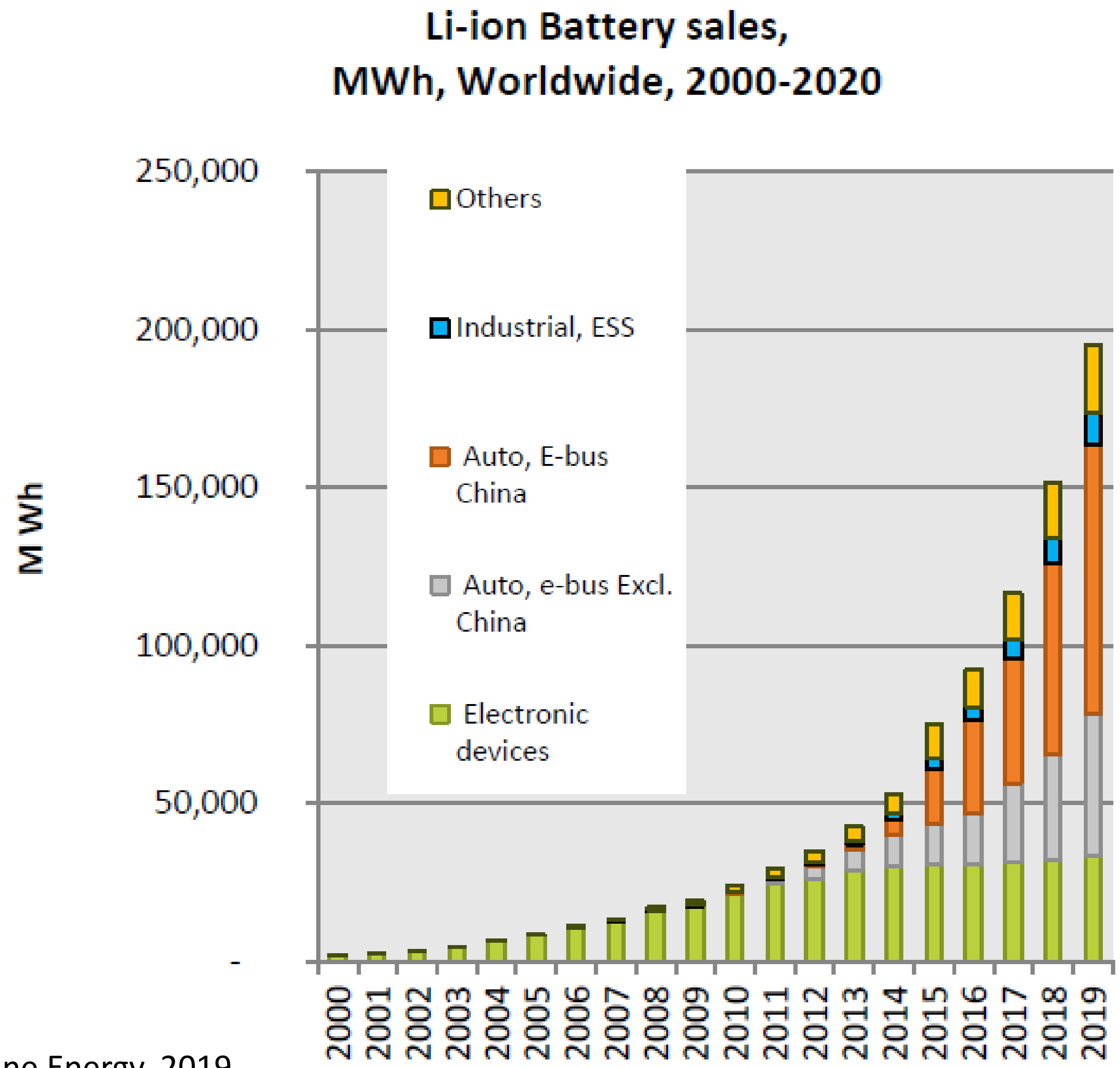


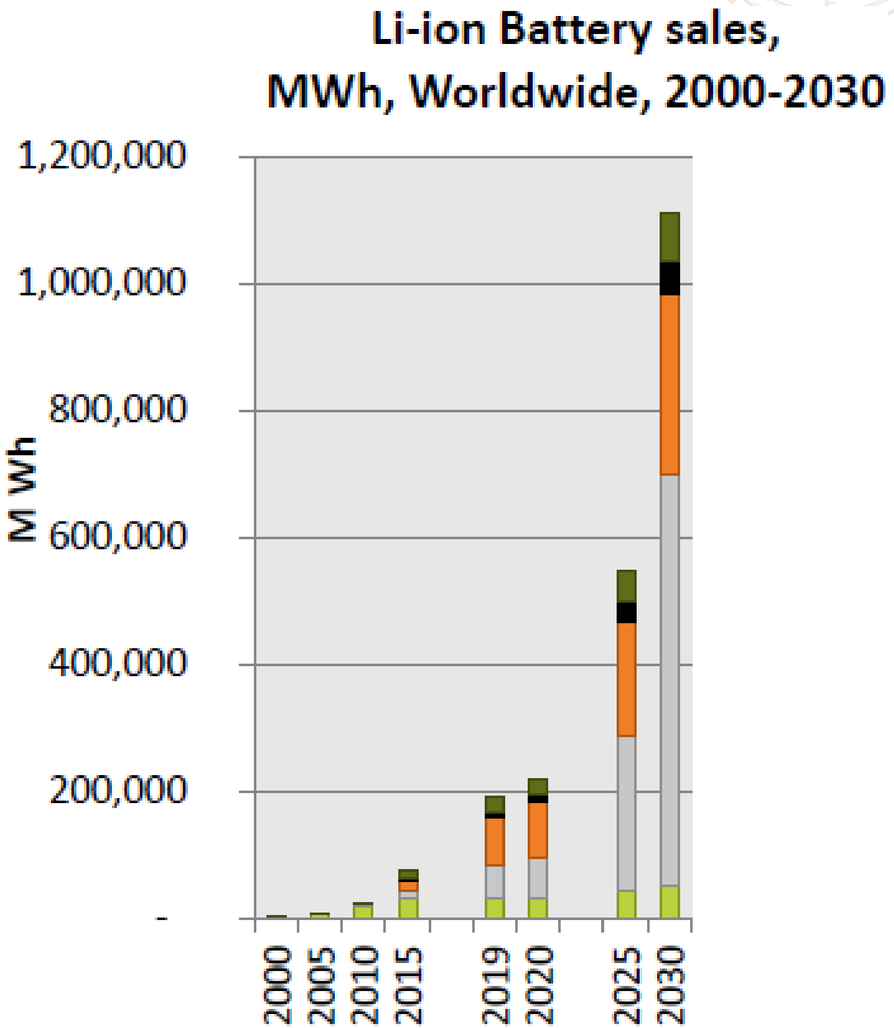


Reminder: Grandmaison : 300 GWh, 2GW

Avicenne Energy, 2019

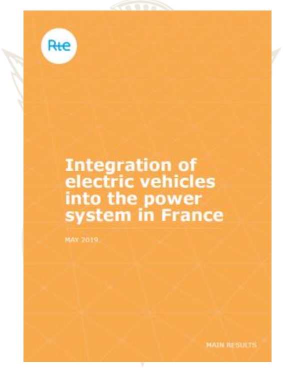
Focus on Li-ion batteries



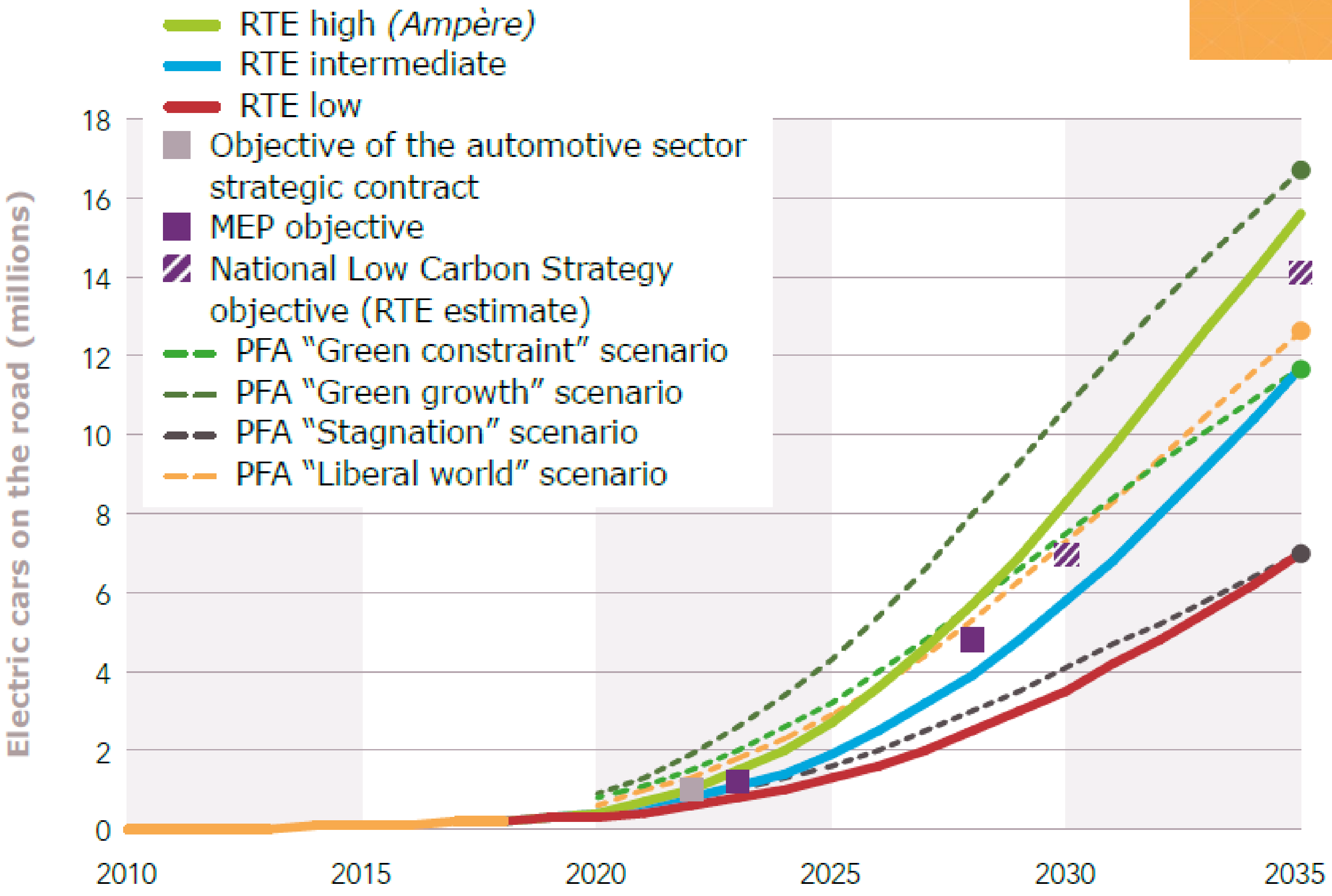


Avicenne Energy, 2019

E-mobility in France


Integration of electric vehicles into the power system in France

In 2020 in France
40 000 000 vehicles
~ 400 000 electric vehicles
1%

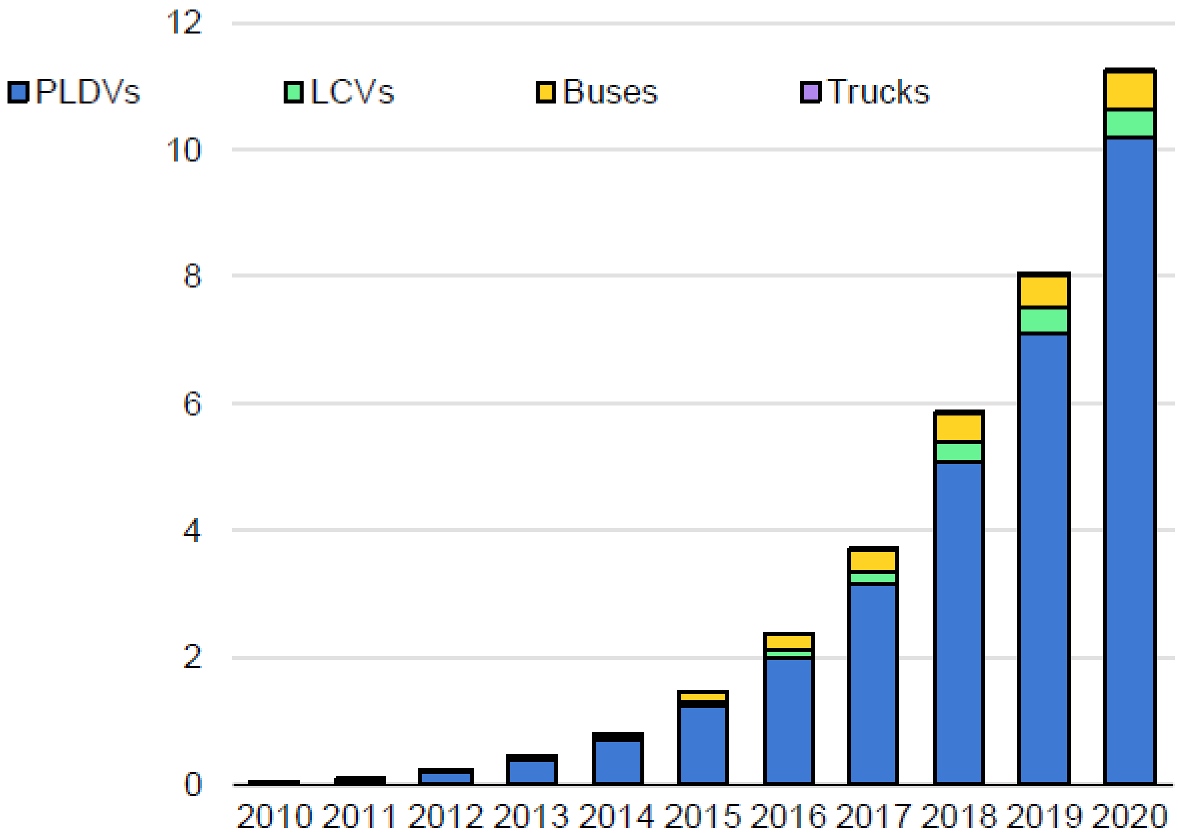


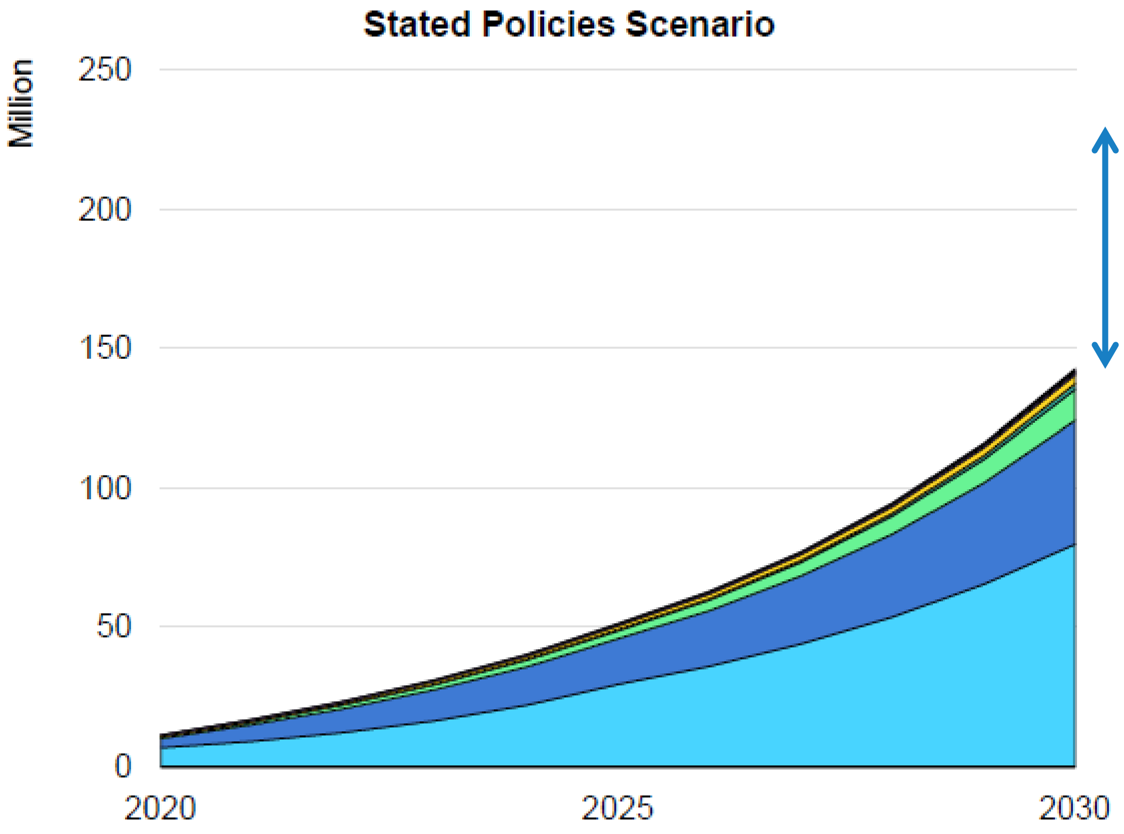
E-mobility in the world

Global EV Outlook 2021

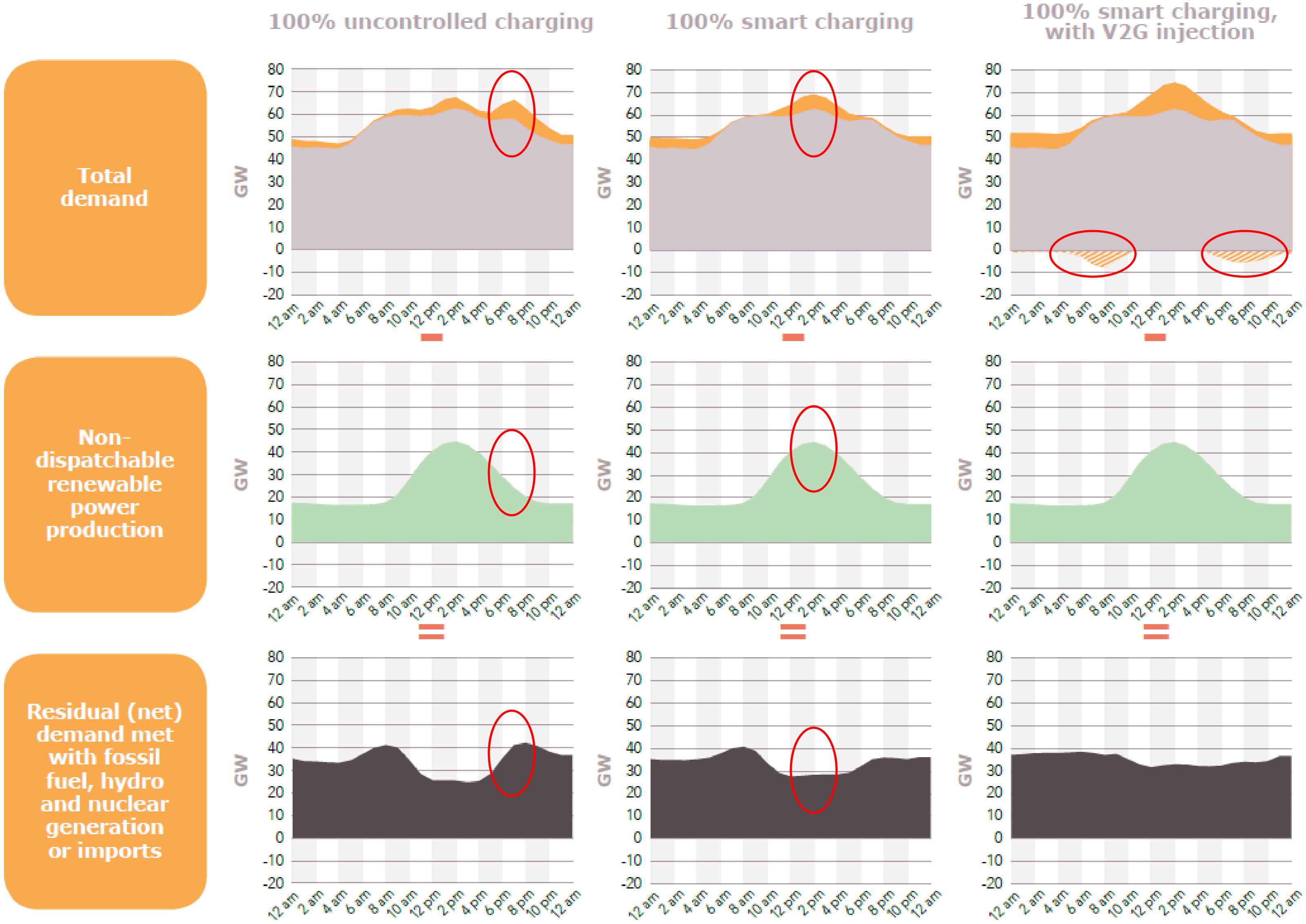
Accelerating ambitions despite the pandemic

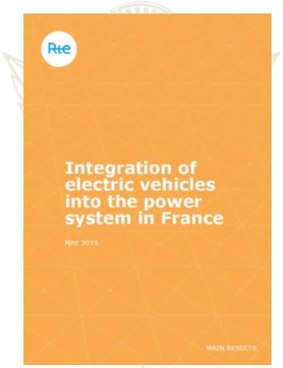
In 2020 in the World, similar statistics
1 000 000 000 vehicles
10 000 000 electric vehicles
1%





Integration strategies





400 000 EV

↓

15 000 000 EV

If uncontrolled charging:

- EV adds stress to the system
- daily operation more than holidays

Smart charging:

- Displace charging
- Not *required* (but useful) until 2035
- Required for larger developments

Vehicle to grid (V2G):

- Contribute to FCR and aFRR
- Not all vehicles

How many batteries ?

World : 10^9 vehicles, 50 kWh/vehicles = 50 TWh

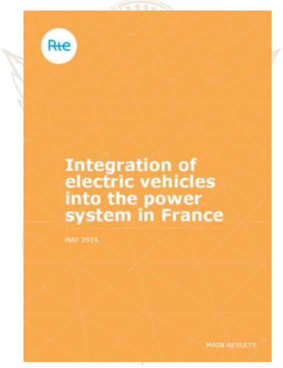
= 110 years of current Lead acid battery production

= 250 years of current Li-ion battery production

= 1 400 years of production by a Gigafactory

Courtesy to F. Perdu

Electric vehicle: CO$_2$ issues

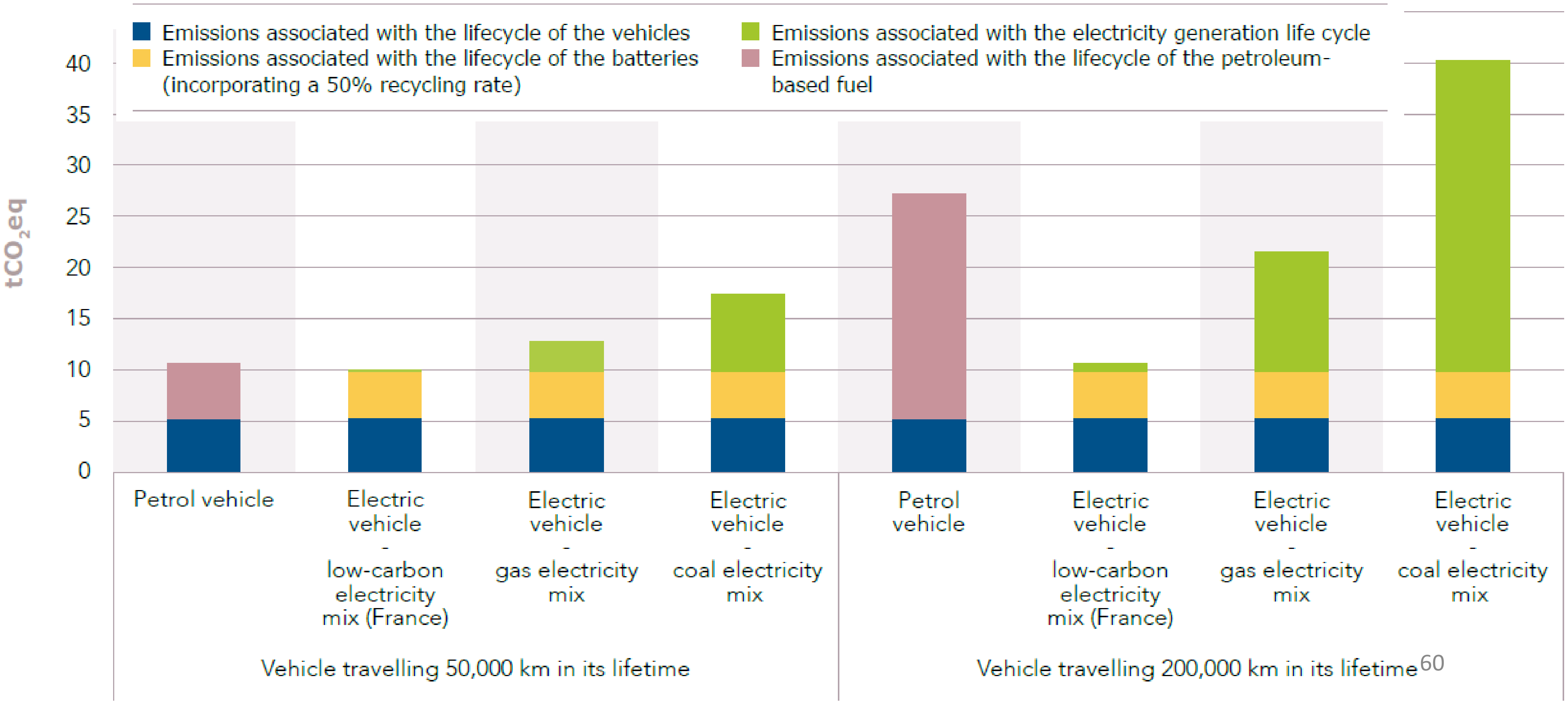


Integration of electric vehicles into the power system in France

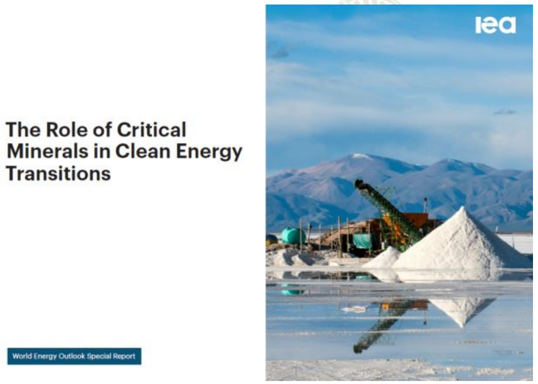
MAY 2019

MAIN RESULTS

7.3 The carbon benefit of e-mobility is still significant when the whole life cycle of the vehicle is included, even with batteries that are made in China…



Electric vehicle: material issues

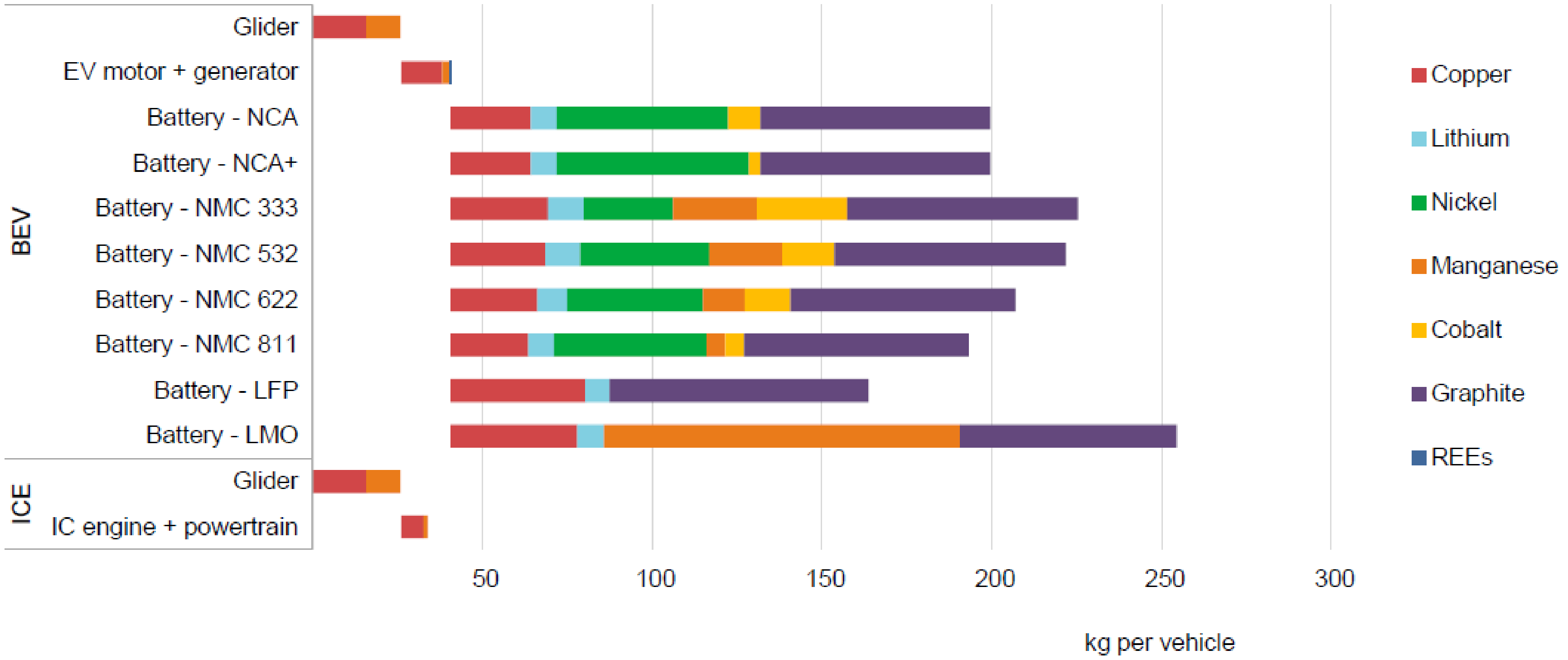


The Role of Critical Minerals in Clean Energy Transitions

World Energy Outlook Special Report

EVs use around six times more minerals than conventional vehicles

Typical use of minerals in an internal combustion engine vehicle and a battery electric vehicle



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Notes: For this figure, the EV motor is a permanent-magnet synchronous motor (neodymium iron boron [NdFeB]); the battery is 75 kilowatt hours (kWh) with graphite anodes.

Sources: Argonne National Laboratory (2020b, 2020a); Ballinger et al. (2019); Fishman et al. (2018b); Nordelöf et al. (2019); Watari et al. (2019).

Remember that
no solution is
perfect !

Lecture 9
Electrical grid
& electrical energy storage

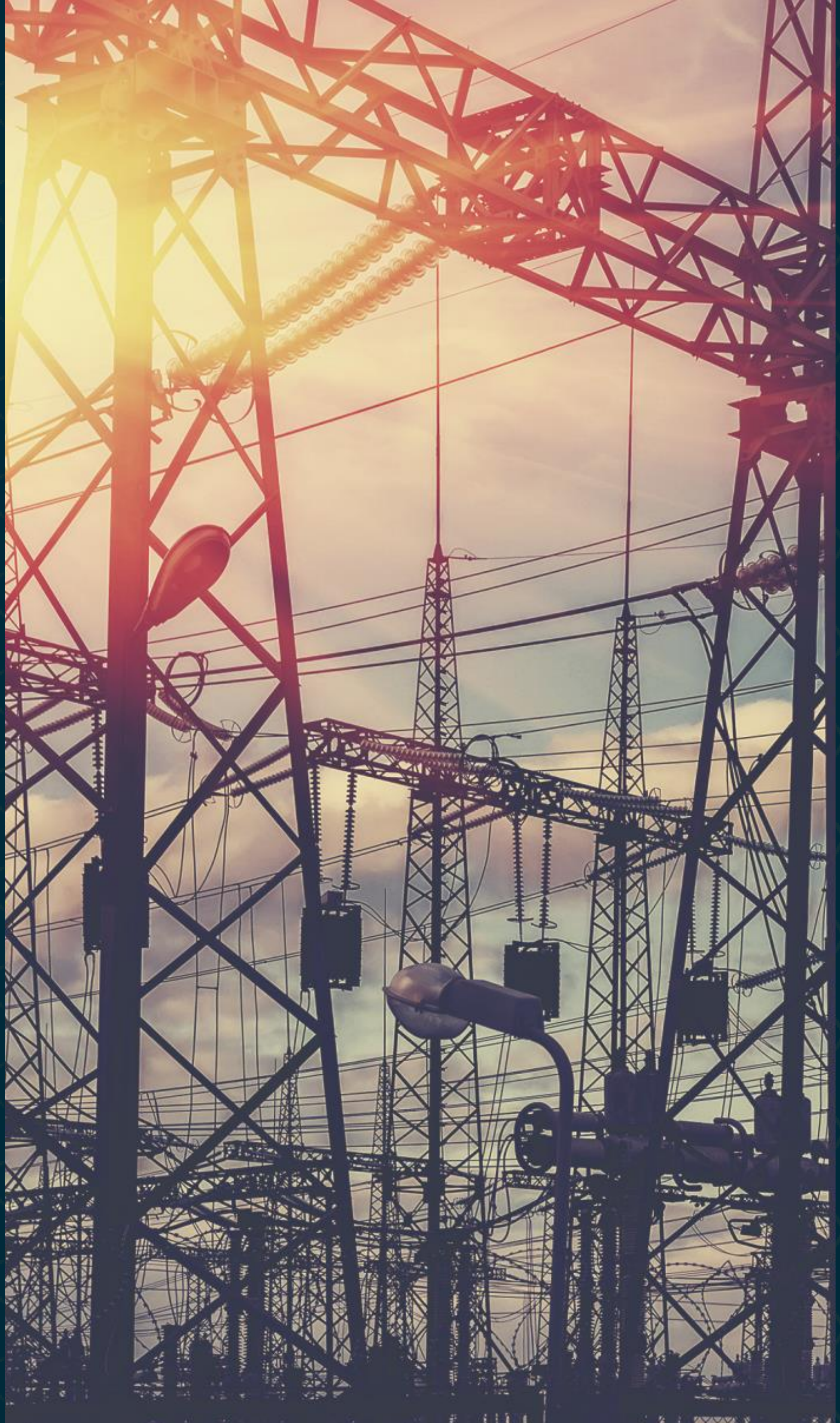
I. The many time scales of grid stability

- Introduction to the electrical grid
- Time scales of grid stability
- Challenges raised by wind and solar integration

II. Power to X

III. Battery & electrical mobility

IV. Hydrogen



Hydrogen properties

Own chemical properties (Sulfur removal in petroleum refinery…)

Produce new chemicals of interest (Ammonia, Methane, Methanol…)

Haber-Bosch process: $N_2 + 3H_2 \rightarrow 2NH_3$

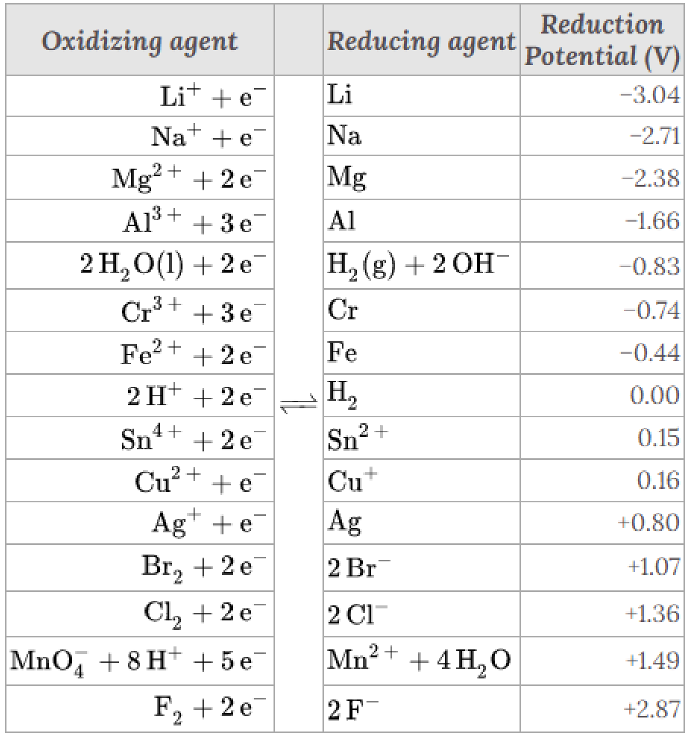
Sabatier process: $CO_2 + 4H_2 \xrightarrow[\text{pressure+catalyst}]{400^\circ C} CH_4 + 2H_2O$

Methanol production $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

→ *Synthetic fuels*

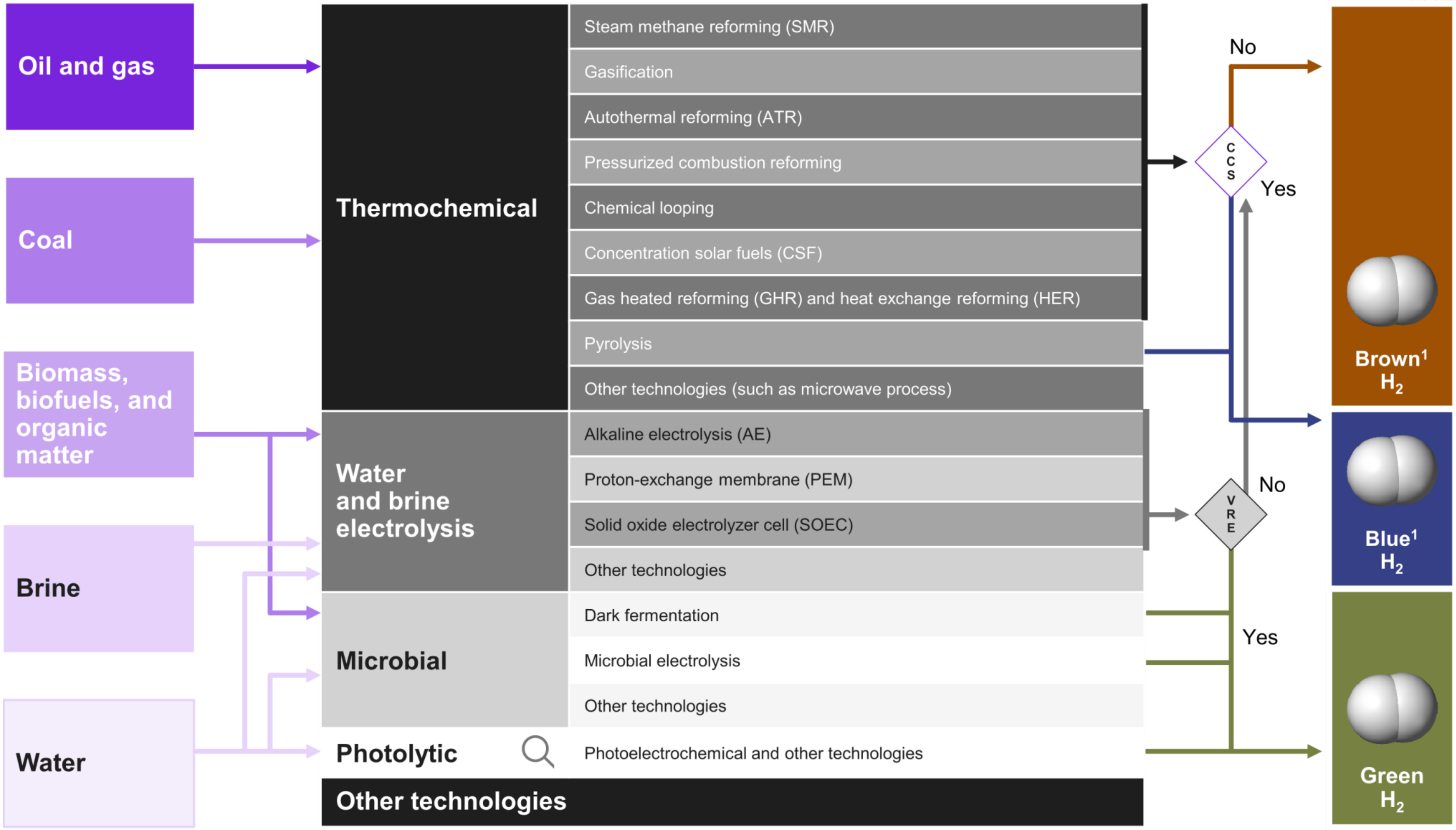
Energy $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$$\Delta G = -237\,\mathrm{kJ/mol}$$
$$\Delta H_{\mathrm{HHV}} = -286\,\mathrm{kJ/mol}$$



Oxidizing agent		*Reducing agent*	*Reduction Potential (V)*
$Li^+ + e^-$		Li	−3.04
$Na^+ + e^-$		Na	−2.71
$Mg^{2+} + 2\,e^-$		Mg	−2.38
$Al^{3+} + 3\,e^-$		Al	−1.66
$2\,H_2O(l) + 2\,e^-$		$H_2(g) + 2\,OH^-$	−0.83
$Cr^{3+} + 3\,e^-$		Cr	−0.74
$Fe^{2+} + 2\,e^-$		Fe	−0.44
$2\,H^+ + 2\,e^-$	$\rightleftharpoons$	H_2	0.00
$Sn^{4+} + 2\,e^-$		Sn^{2+}	0.15
$Cu^{2+} + e^-$		Cu^+	0.16
$Ag^+ + e^-$		Ag	+0.80
$Br_2 + 2\,e^-$		$2\,Br^-$	+1.07
$Cl_2 + 2\,e^-$		$2\,Cl^-$	+1.36
$MnO_4^- + 8\,H^+ + 5\,e^-$		$Mn^{2+} + 4\,H_2O$	+1.49
$F_2 + 2\,e^-$		$2\,F^-$	+2.87

Many ways of producing hydrogen



Oil and gas

Coal

Biomass, biofuels, and organic matter

Brine

Water

Thermochemical

- Steam methane reforming (SMR)
- Gasification
- Autothermal reforming (ATR)
- Pressurized combustion reforming
- Chemical looping
- Concentration solar fuels (CSF)
- Gas heated reforming (GHR) and heat exchange reforming (HER)
- Pyrolysis
- Other technologies (such as microwave process)

Water and brine electrolysis

- Alkaline electrolysis (AE)
- Proton-exchange membrane (PEM)
- Solid oxide electrolyzer cell (SOEC)
- Other technologies

Microbial

- Dark fermentation
- Microbial electrolysis
- Other technologies

Photolytic

- Photoelectrochemical and other technologies

Other technologies

CCS

No

Yes

VRE

No

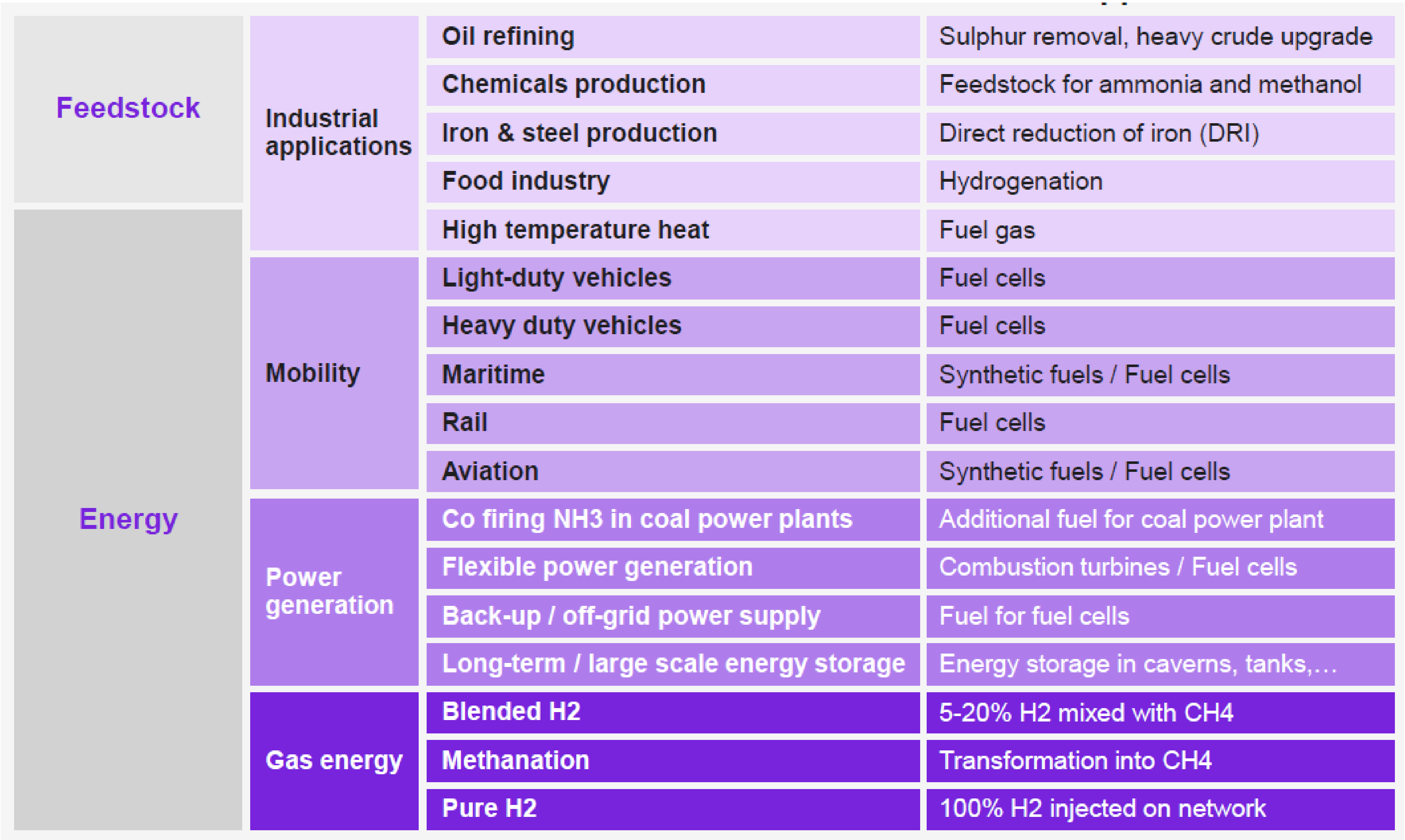
Yes

Brown[1] H_2

Blue[1] H_2

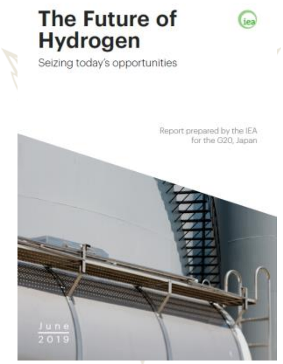
Green H_2

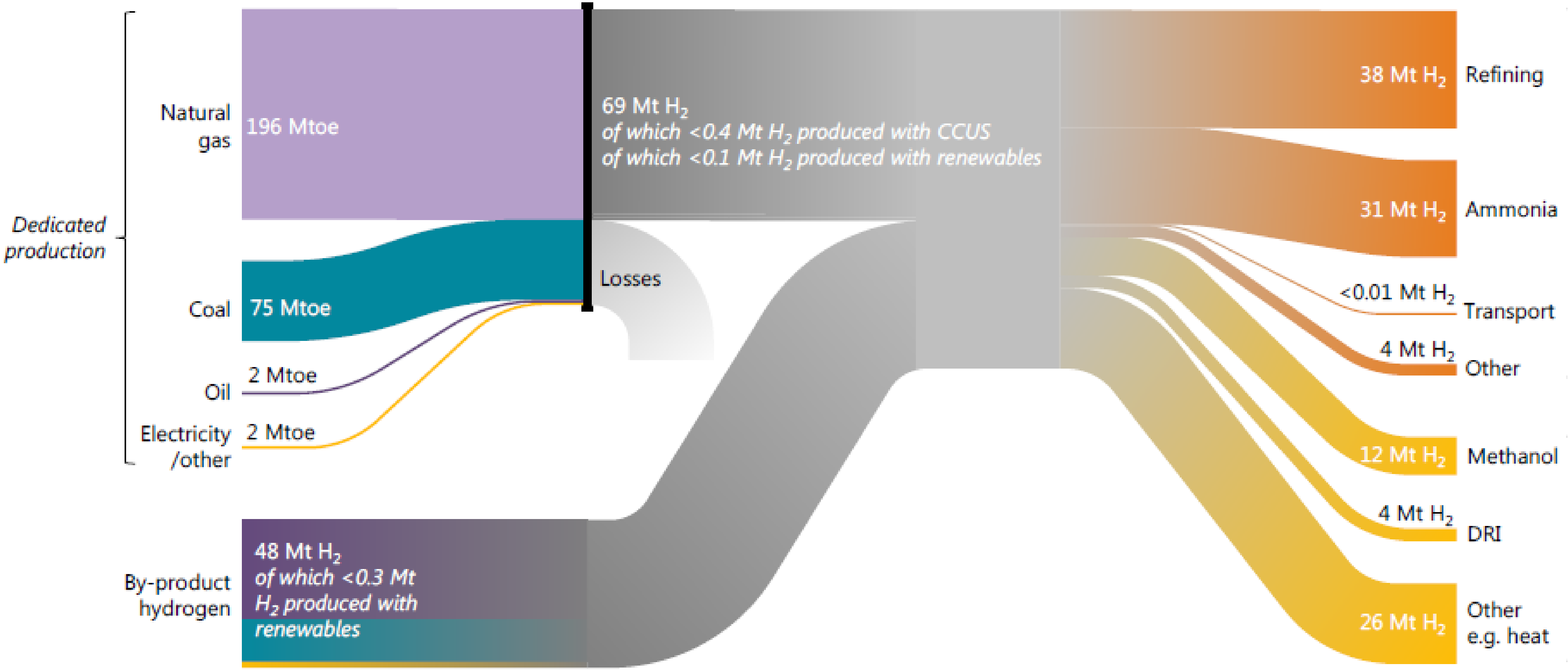
Many ways to use hydrogen



Feedstock	**Industrial applications**	**Oil refining**	Sulphur removal, heavy crude upgrade
		Chemicals production	Feedstock for ammonia and methanol
		Iron & steel production	Direct reduction of iron (DRI)
		Food industry	Hydrogenation
Energy		**High temperature heat**	Fuel gas
	Mobility	**Light-duty vehicles**	Fuel cells
		Heavy duty vehicles	Fuel cells
		Maritime	Synthetic fuels / Fuel cells
		Rail	Fuel cells
		Aviation	Synthetic fuels / Fuel cells
	Power generation	**Co firing NH3 in coal power plants**	Additional fuel for coal power plant
		Flexible power generation	Combustion turbines / Fuel cells
		Back-up / off-grid power supply	Fuel for fuel cells
		Long-term / large scale energy storage	Energy storage in caverns, tanks,…
	Gas energy	**Blended H2**	5-20% H2 mixed with CH4
		Methanation	Transformation into CH4
		Pure H2	100% H2 injected on network

Hydrogen today





Green hydrogen < 4% of hydrogen production

Main usage = chemical

Water electrolysis

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta G^0 = +237\,\mathrm{kJ/mol} \qquad \Delta H^0_{\mathrm{HHV}} = +286\,\mathrm{kJ/mol}$$

Need to provide ΔH energy in total,
with at least ΔG as work

Example: alkaline electrolyser

Anode

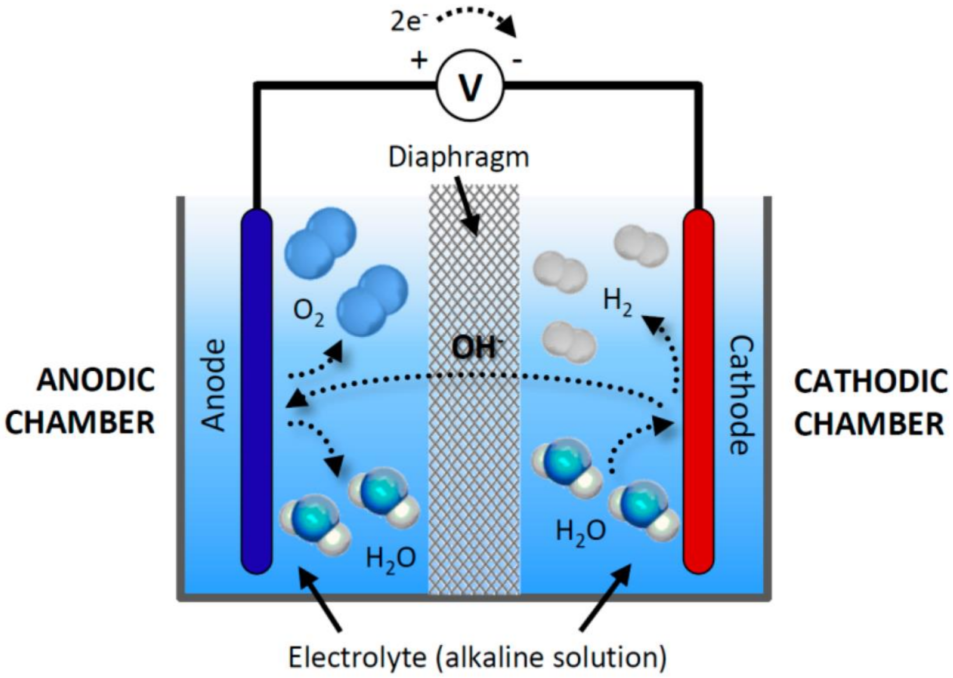
$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

Cathode

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

Minimal voltage

$$U \geq \frac{1}{2}\frac{\Delta G}{N_A e} = 1.23\mathrm{V}$$



Very similar to a battery
in reverse mode !

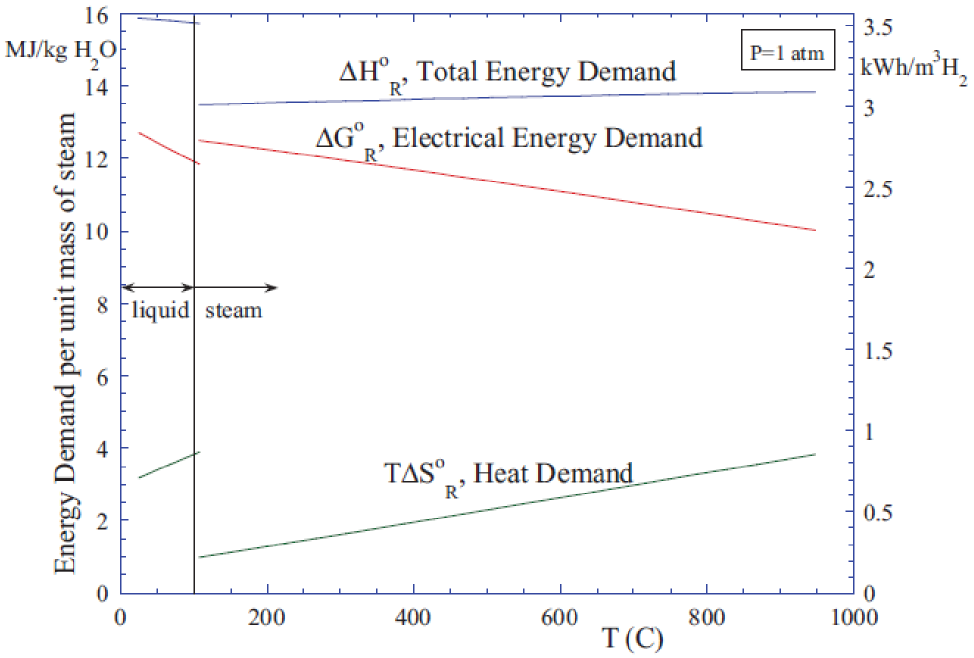
Water electrolysis in practice

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

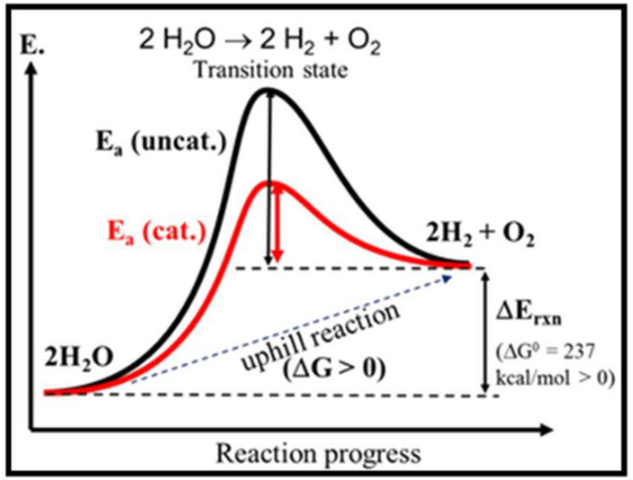
$$\Delta G^0 = +237\,\mathrm{kJ/mol}$$
$$\Delta H^0_{\mathrm{HHV}} = +286\,\mathrm{kJ/mol}$$

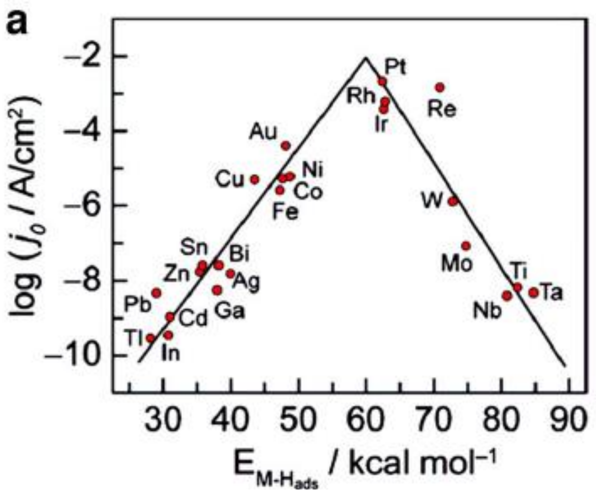
Need to provide ΔH energy in total,
with at least ΔG as work

Why high temperatures ?

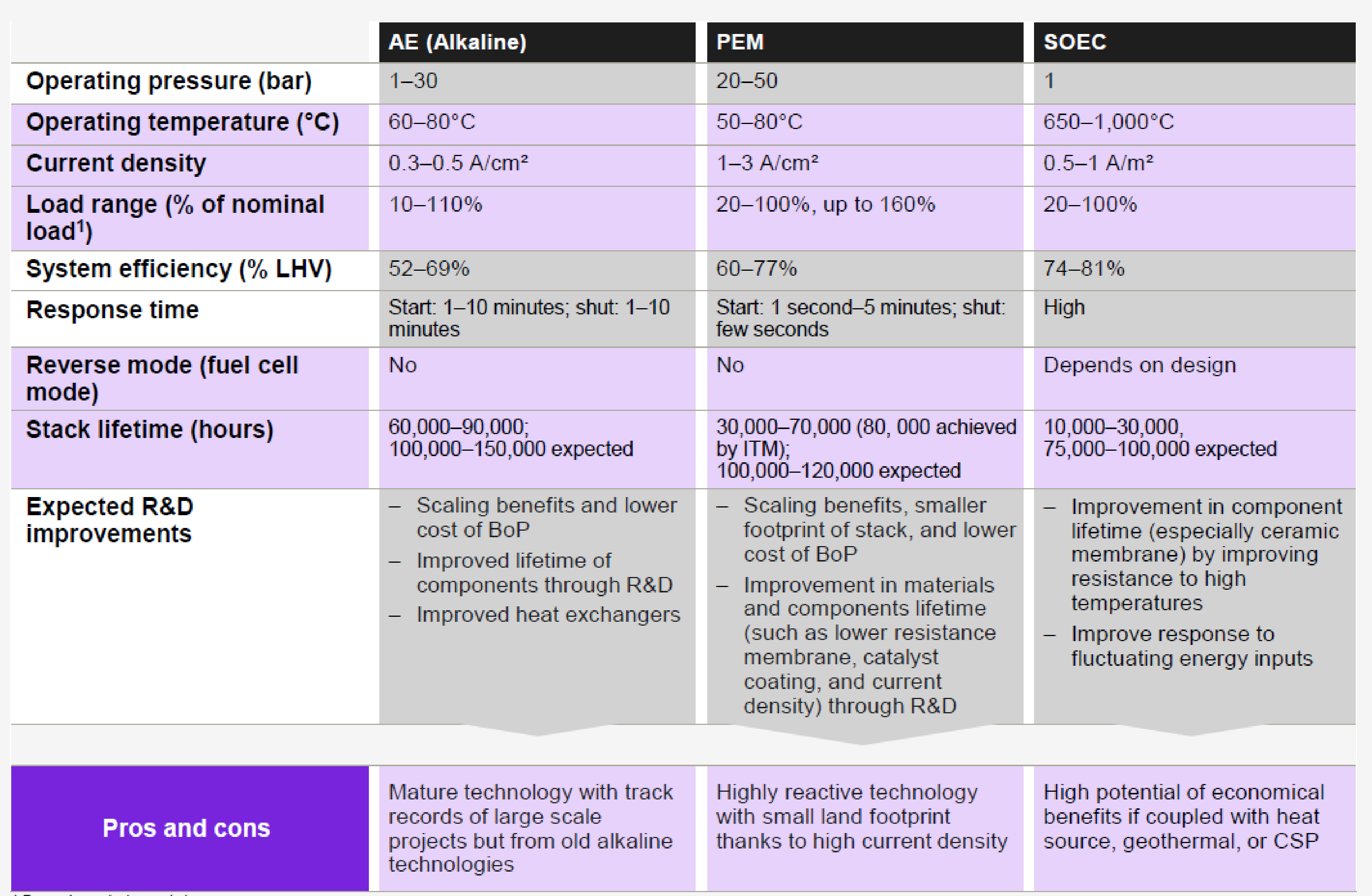


Why catalyst?





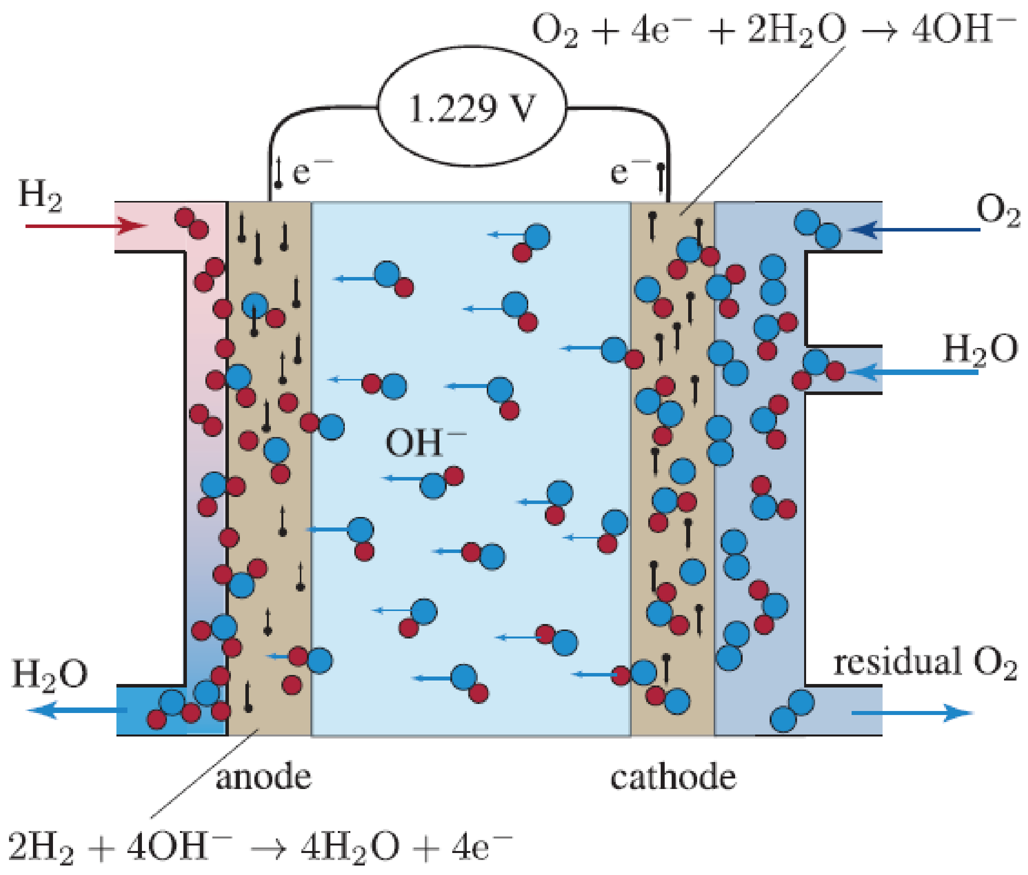
Electrolysers



	AE (Alkaline)	PEM	SOEC
Operating pressure (bar)	1–30	20–50	1
Operating temperature (°C)	60–80°C	50–80°C	650–1,000°C
Current density	0.3–0.5 A/cm²	1–3 A/cm²	0.5–1 A/m²
Load range (% of nominal load[1])	10–110%	20–100%, up to 160%	20–100%
System efficiency (% LHV)	52–69%	60–77%	74–81%
Response time	Start: 1–10 minutes; shut: 1–10 minutes	Start: 1 second–5 minutes; shut: few seconds	High
Reverse mode (fuel cell mode)	No	No	Depends on design
Stack lifetime (hours)	60,000–90,000; 100,000–150,000 expected	30,000–70,000 (80, 000 achieved by ITM); 100,000–120,000 expected	10,000–30,000, 75,000–100,000 expected
Expected R&D improvements	– Scaling benefits and lower cost of BoP – Improved lifetime of components through R&D – Improved heat exchangers	– Scaling benefits, smaller footprint of stack, and lower cost of BoP – Improvement in materials and components lifetime (such as lower resistance membrane, catalyst coating, and current density) through R&D	– Improvement in component lifetime (especially ceramic membrane) by improving resistance to high temperatures – Improve response to fluctuating energy inputs
Pros and cons	Mature technology with track records of large scale projects but from old alkaline technologies	Highly reactive technology with small land footprint thanks to high current density	High potential of economical benefits if coupled with heat source, geothermal, or CSP

Kerney energy transition institute

Fuel cell



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

$$\Delta G = -237\,\mathrm{kJ/mol}$$
$$\Delta H_{\mathrm{HHV}} = -286\,\mathrm{kJ/mol}$$

Fuel cell versus combustion

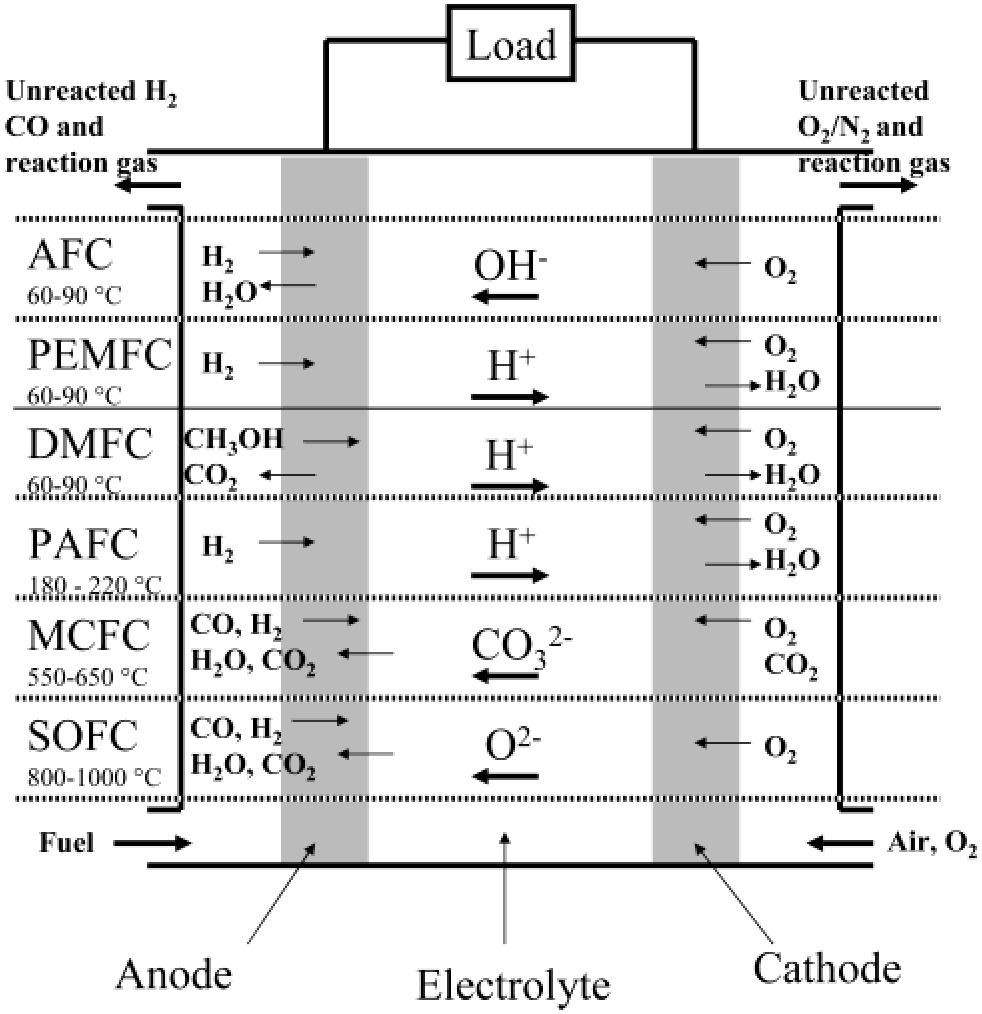
Energy transfered to (electro)chemical energy
not to thermal energy

Recover W = -ΔG rather than Q = -ΔH

Fuel cell versus battery

Fuel cell is not storing energy.
Reactants are stored elsewhere, and flow through the cell

Fuel cell technologies



Chem. Rev. **2004,** 104, 4245-4269

	Temperature	Slack size	Electrical performance (LHV)
Polymer electrolyte membrane (PEM)	<120°C	<1–100kW	**60%**
Alkaline (AFC)	<100°C	1-100kW	**60%**
Phosphoric acid (PAFC)	<150 – 200°C	5-400kW	**40%**
Molten carbonate (MCFC)	600-700°C	300kW – 3MW	**50%**
Solid oxide (SOFC)	500-1000°C	1kW-2MW	**60%**

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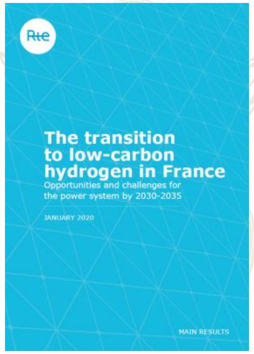
Hydrogen and the grid



RTE

The transition to low-carbon hydrogen in France

Opportunities and challenges for the power system by 2030-2035

JANUARY 2020

MAIN RESULTS

Short term :

Use REN to produce decarbonized H

→ Decarbonize current H usage

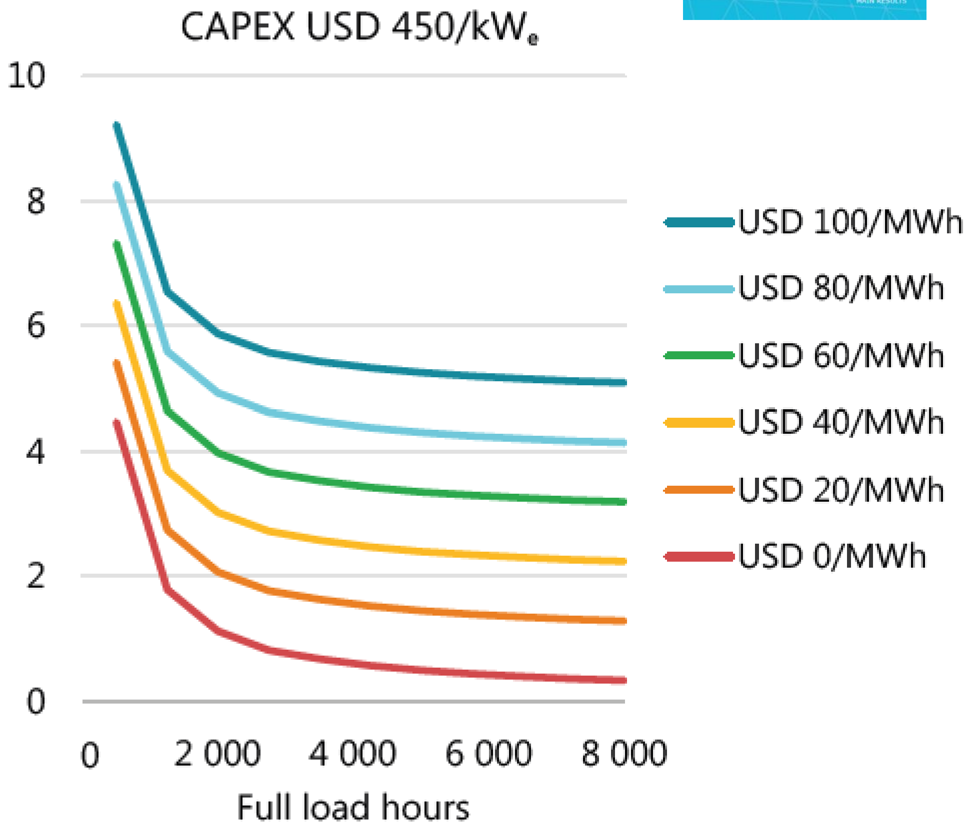
Middle term :

Use electrolysers to provide grid flexibility

Develop new H usage

Long term :

Seasonal storage via power to gas to power loop ?



electrolyser efficiency of 69% (LHV) and a discount rate of 8%.

IEA 2019, The Future of Hydorgen

Hydrogen and transports

Technical specificities?

power density, freezing point…

Costs?

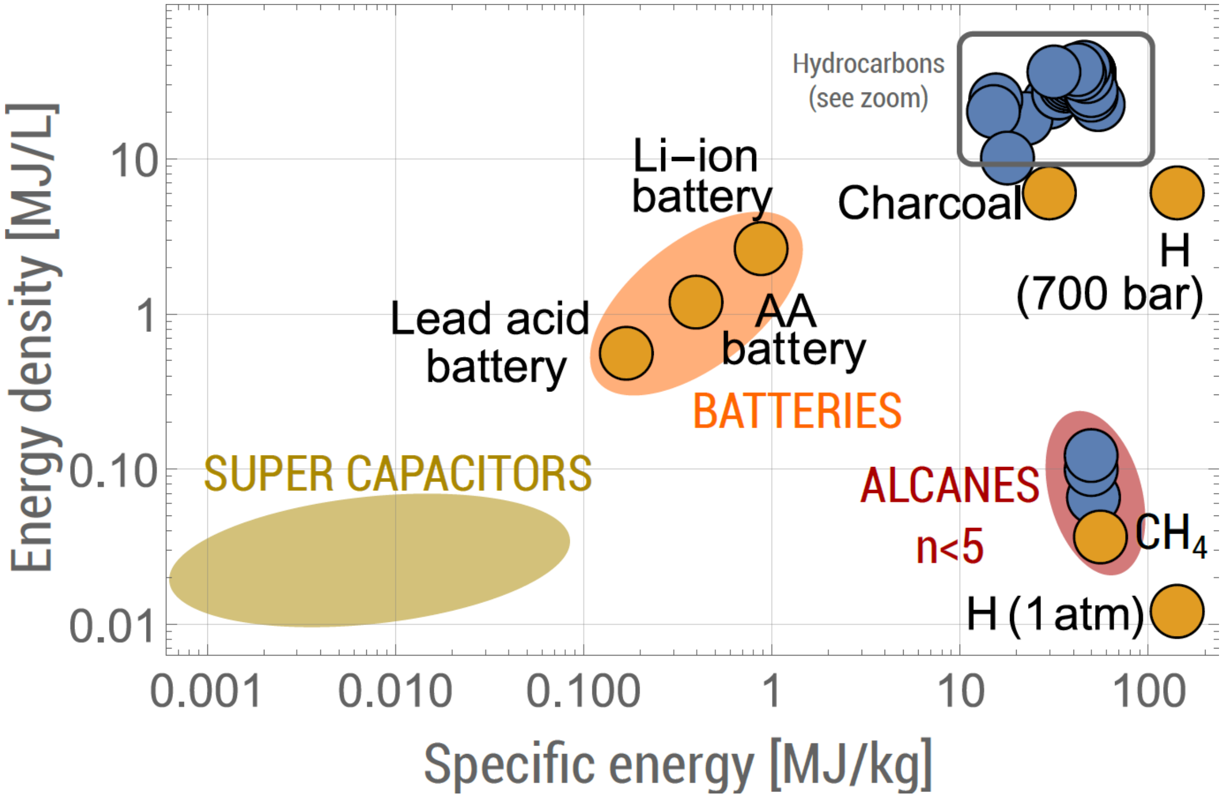
Overall efficiency, feedstock availability…

Supply chain?

Compatible with current infrastructures?

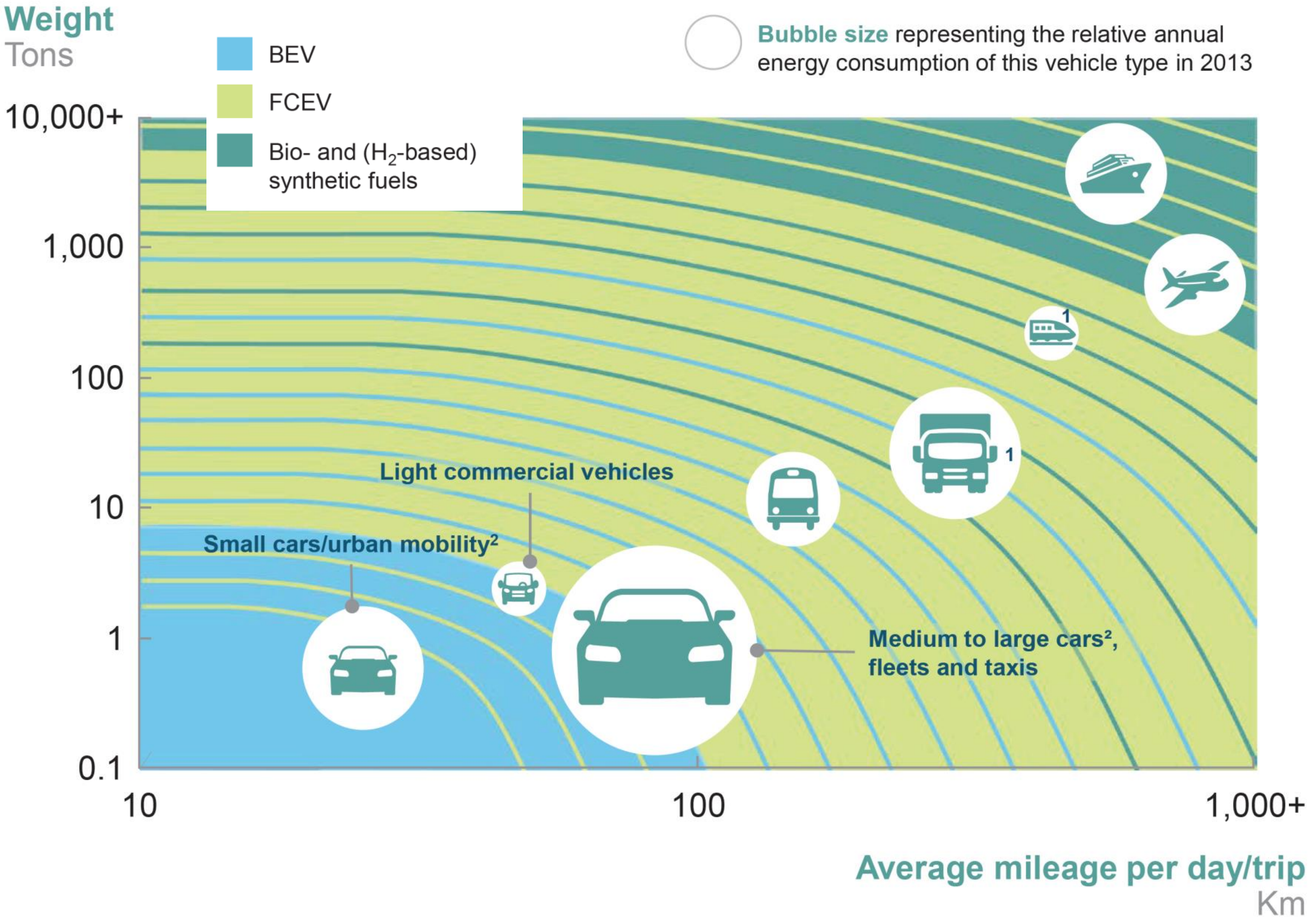
Environmental impacts?

Sustainability besides CO_2

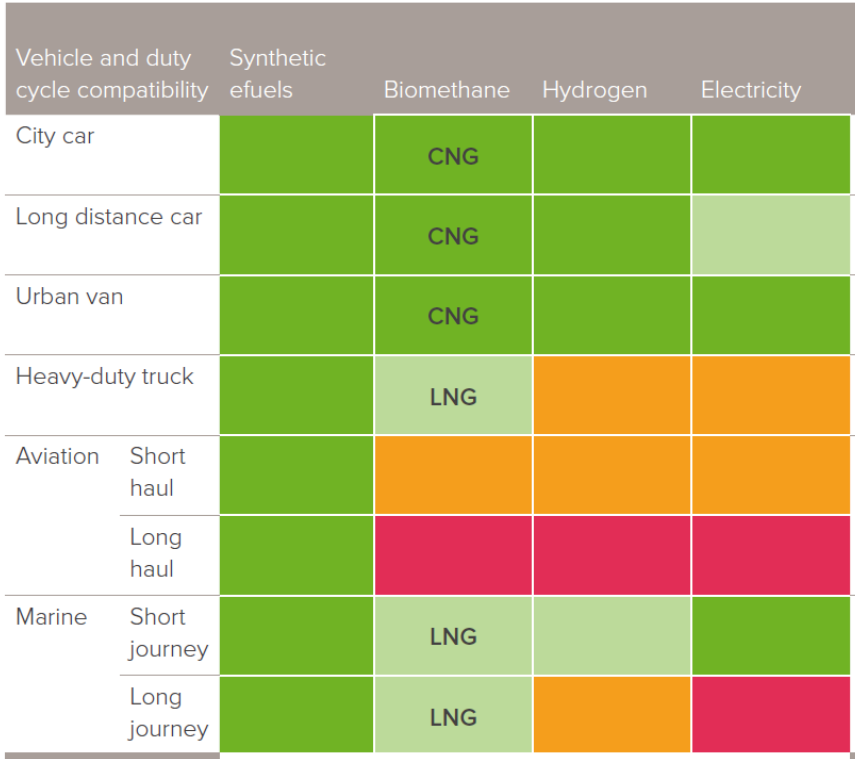


The Royal Society (2019), *Sustainablesyntheticcarbonbasedfuels for transport*

The right fuel for the right transport



“ How hydrogen empowers the energy transition”, Hydrogen Council January 2017

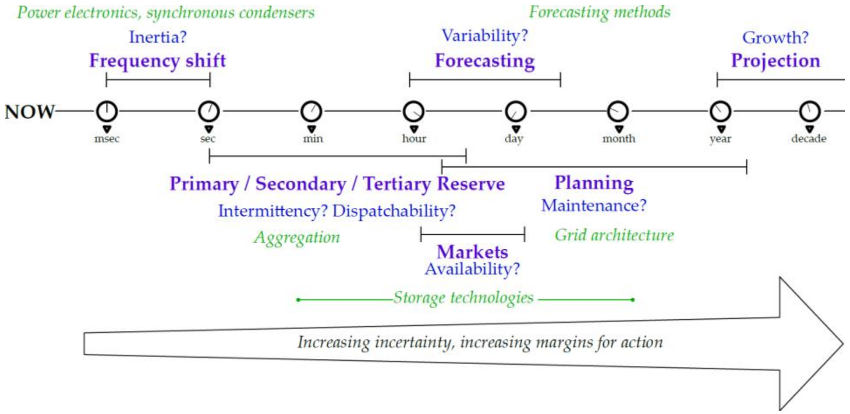


Vehicle and duty cycle compatibility		Synthetic efuels	Biomethane	Hydrogen	Electricity
City car		🟩	🟩 CNG	🟩	🟩
Long distance car		🟩	🟩 CNG	🟩	▨
Urban van		🟩	🟩 CNG	🟩	🟩
Heavy-duty truck		🟩	▨ LNG	🟧	🟧
Aviation	Short haul	🟩	🟧	🟧	🟧
	Long haul	🟩	🟥	🟥	🟥
Marine	Short journey	🟩	▨ LNG	▨	🟩
	Long journey	🟩	▨ LNG	🟧	🟥

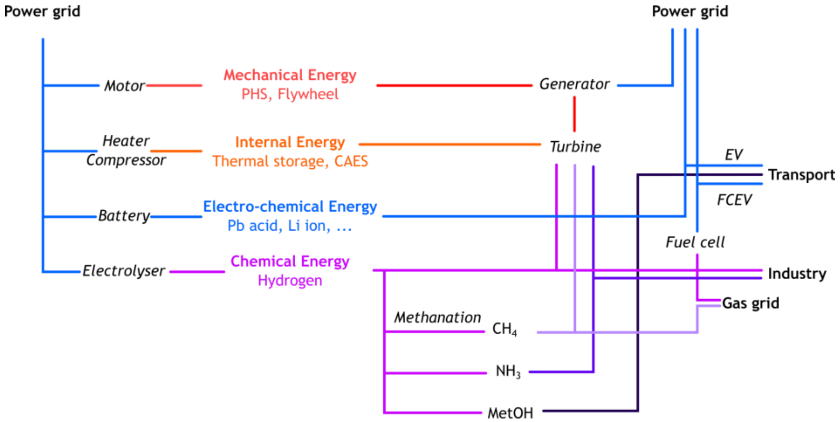
The Royal Society (2019), *Sustainablesyntheticcarbonbasedfuels for transport*

Take home message

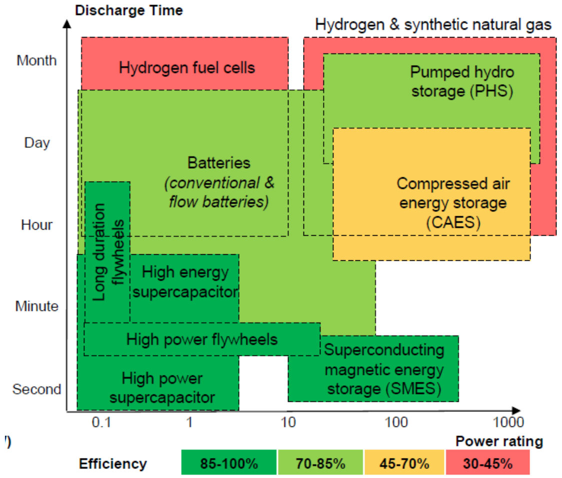
Grid stability timescales

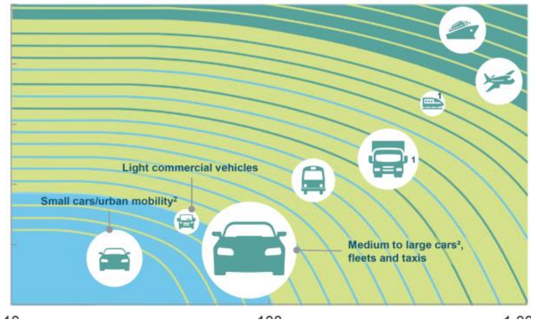


Power to X

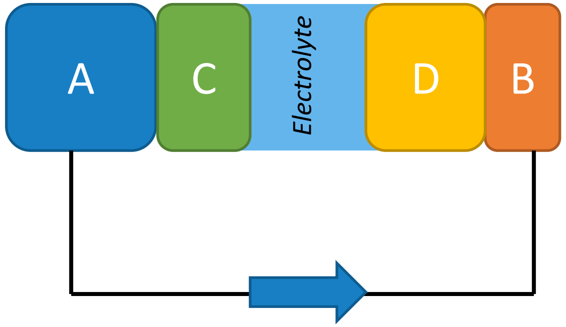


Different solutions for different problems



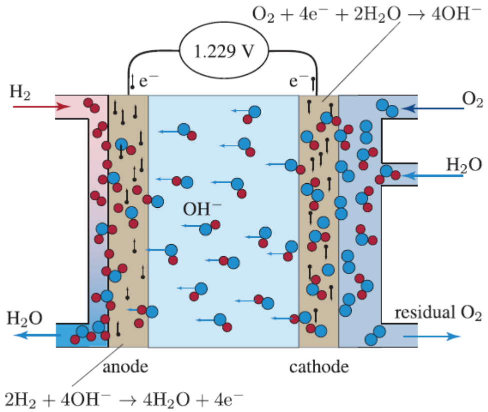


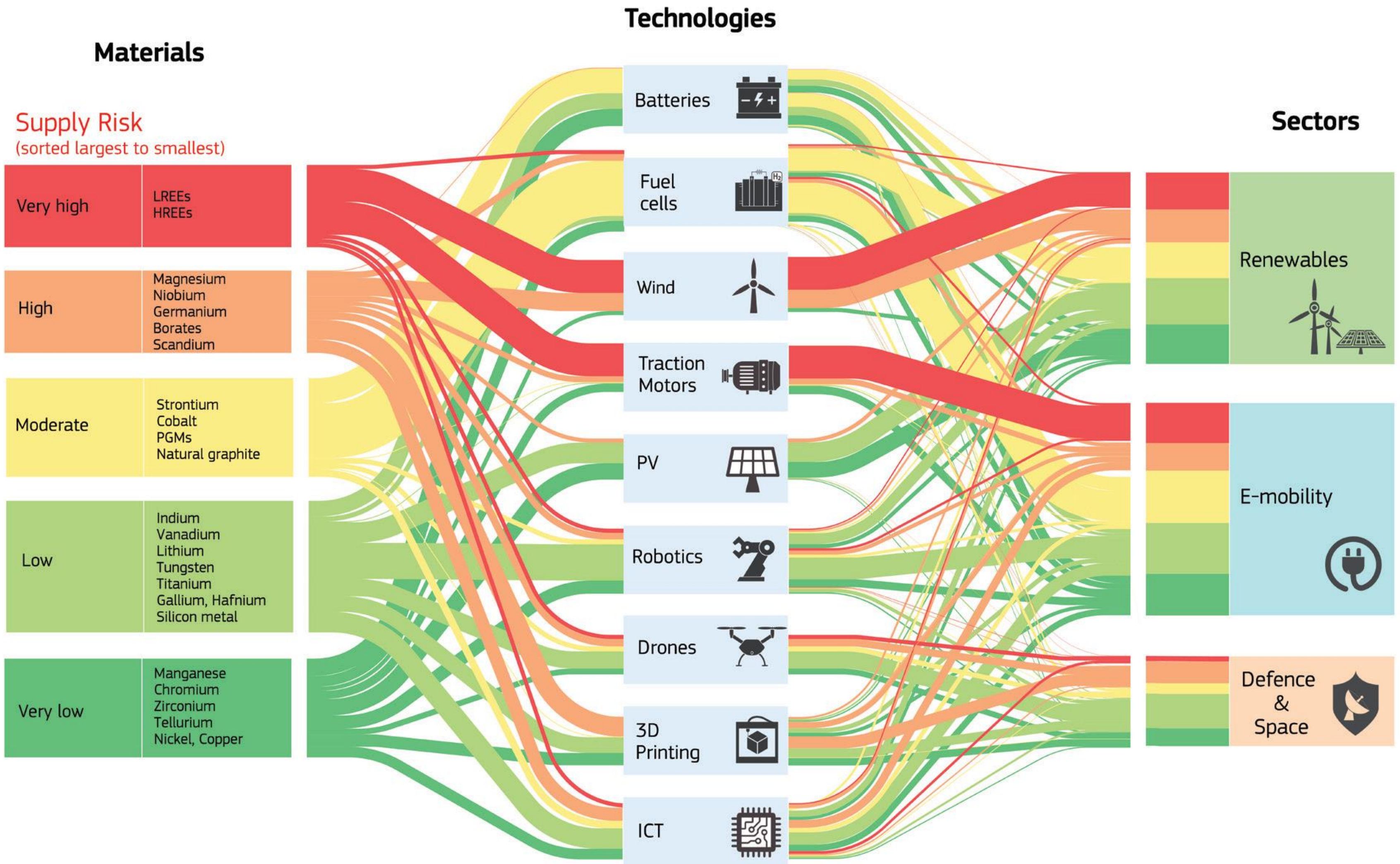
Battery & thermodynamics



$$U = -\frac{\Delta_r G}{z N_A e} = U^0 - \frac{k_B T}{ze} \ln \frac{a_{\text{products}}}{a_{\text{reactants}}}$$

Hydrogen & thermodynamics




Materials
Supply Risk
(sorted largest to smallest)
Very high
LREEs
HREEs
High
Magnesium
Niobium
Germanium
Borates
Scandium
Moderate
Strontium
Cobalt
PGMs
Natural graphite
Low
Indium
Vanadium
Lithium
Tungsten
Titanium
Gallium, Hafnium
Silicon metal
Very low
Manganese
Chromium
Zirconium
Tellurium
Nickel, Copper
Technologies
Batteries
Fuel cells
Wind
Traction Motors
PV
Robotics
Drones
3D Printing
ICT
Sectors
Renewables
E-mobility
Defence & Space