



Electrochemical Production of Chemicals

Applicability to CO2 Conversion

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December 10, 2012

Industrial scale electrochemistry

Present Industries

Chlor-Alkali production

Batteries

Water electrolysis

Desalination, etc.

PV, fuel cells

Metal extraction

Plating & Polishing

CO₂ related technologies

CO₂ reduction

Thermoelectrofuels

Electrofuels

Electrochemical governing factors

Faraday's law

$$W (g) = \frac{I(A) \times t(s) \times M \left(\frac{g}{mole}\right)}{z \times F \left(\frac{Coul}{mole}\right)}$$

Polarization

$$V = E_{eq} + \eta_{total}$$

$$\eta_{total} = \eta_a(i) + \eta_c(i) + i \times A \times R_{cell}$$

Energy efficiency

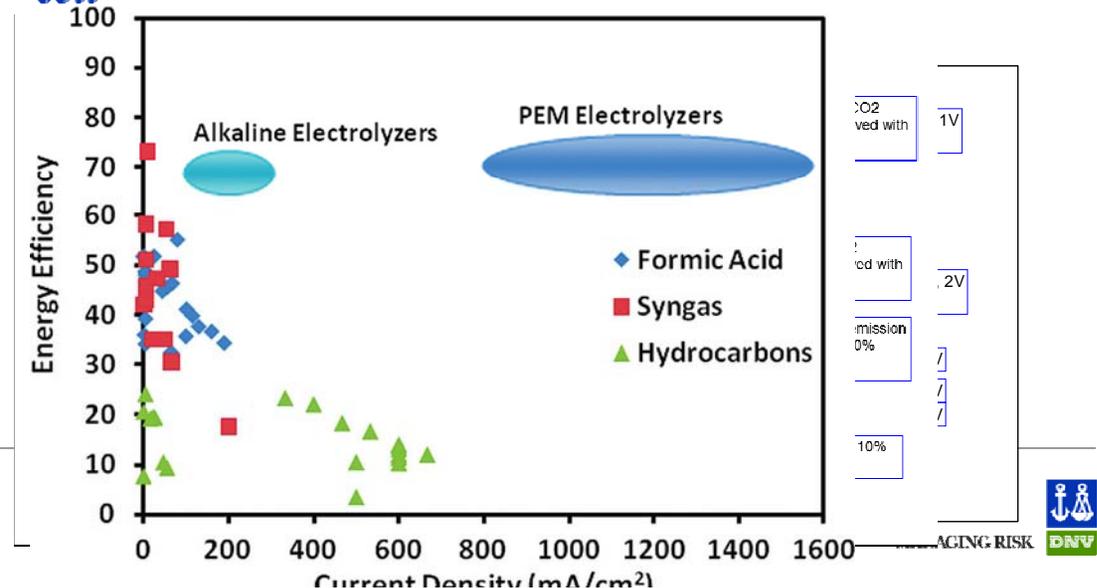
$$Energy\ Eff. = \frac{\sum_{i=1}^N (FE)_i E_i^{eq}}{V}$$

Faradaic/current efficiency (selectivity)

$$FE = \frac{i_n}{\sum_{n=1}^N i_n}$$

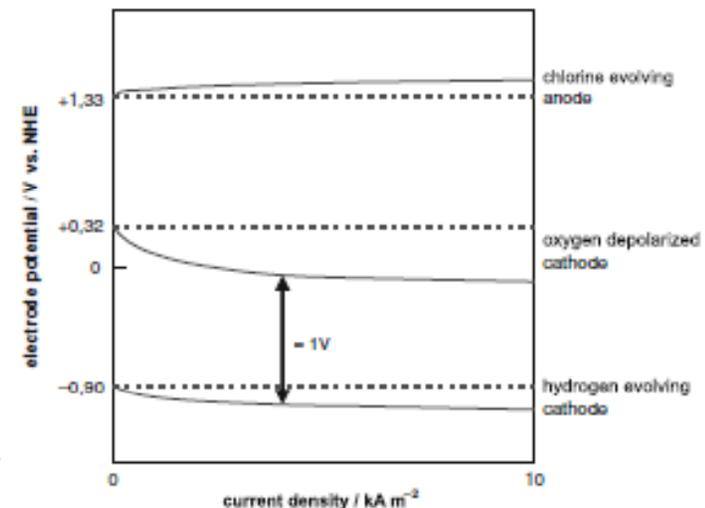
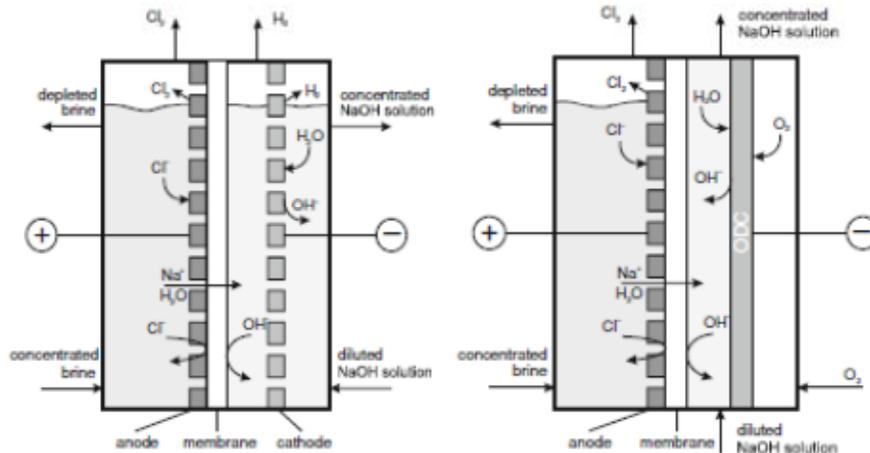
Energy consumption

$$\frac{Energy}{mass} = \frac{V \times z \times F \times t}{(FE) \times M}$$



The Chlor Alkali Process

- Three electrochemical processes (numbers from J. Appl. Elect., 2008)
 - Mercury (being phased out) – 3.1 to 3.4 MWh/t Cl_2
 - Diaphragm (asbestos and non-asbestos) – 3.2 to 3.8 MWh/t Cl_2
 - Membrane - 2.4 to 2.9 MWh/t Cl_2
- Long history
 - Over 100 years old
 - Energy reduction innovations occur even today (e.g., Oxygen depolarization cathodes)
 - Initial concept of ODC in 1950, but developments continued through 2000's.
 - Large surface area ($>2 \text{ m}^2$) and long life times possible (>3 years)
 - But energy reduction must consider other factors



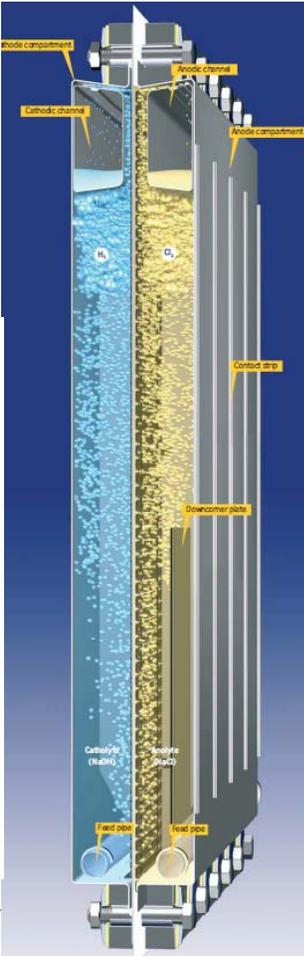
Technology Advances = Reduce Energy/Increase Efficiency

NAFION® Cation Ion Exchange Membrane Employed

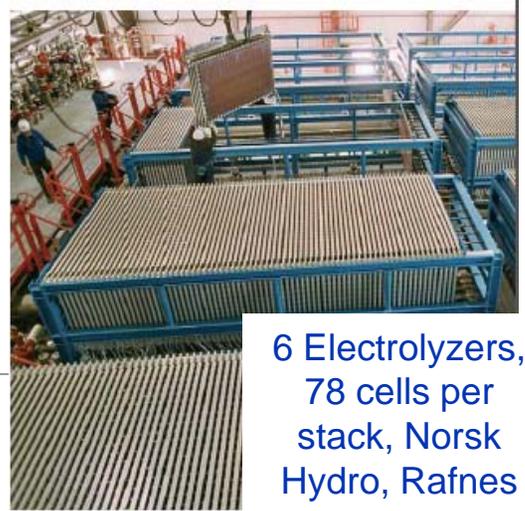
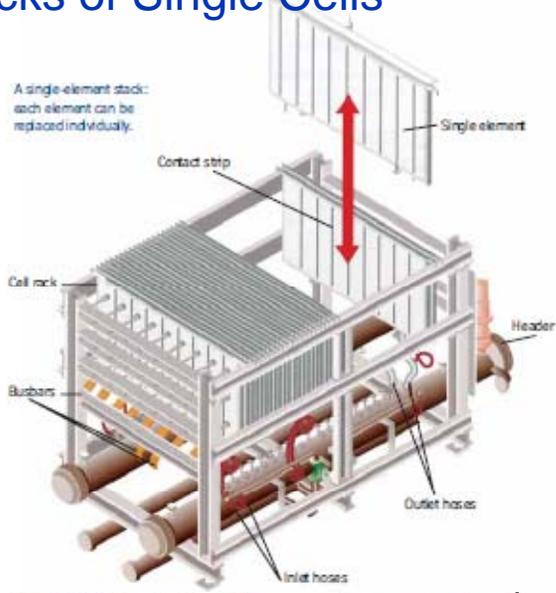
Mixed Metal Oxide Based Dimensionally Stable Anodes – long operating life

Operating data	
Current density	up to 7 kA/m ²
Power consumption	see graph
Cell temperature	88-90 °C
Service life	
anode coating	> 8 years
cathode coating	8 years
membranes	> 4 years
gaskets	> 4 years
compartments	> 20 years
Active area per element	2.72 m²

Optimized Single Cells



Modular – Skid Mounted Stacks of Single Cells



6 Electrolyzers, 78 cells per stack, Norsk Hydro, Rafnes

Comparison of Commercial Water Electrolyzers

Water to H₂ conversion efficiencies: 80 – 95%

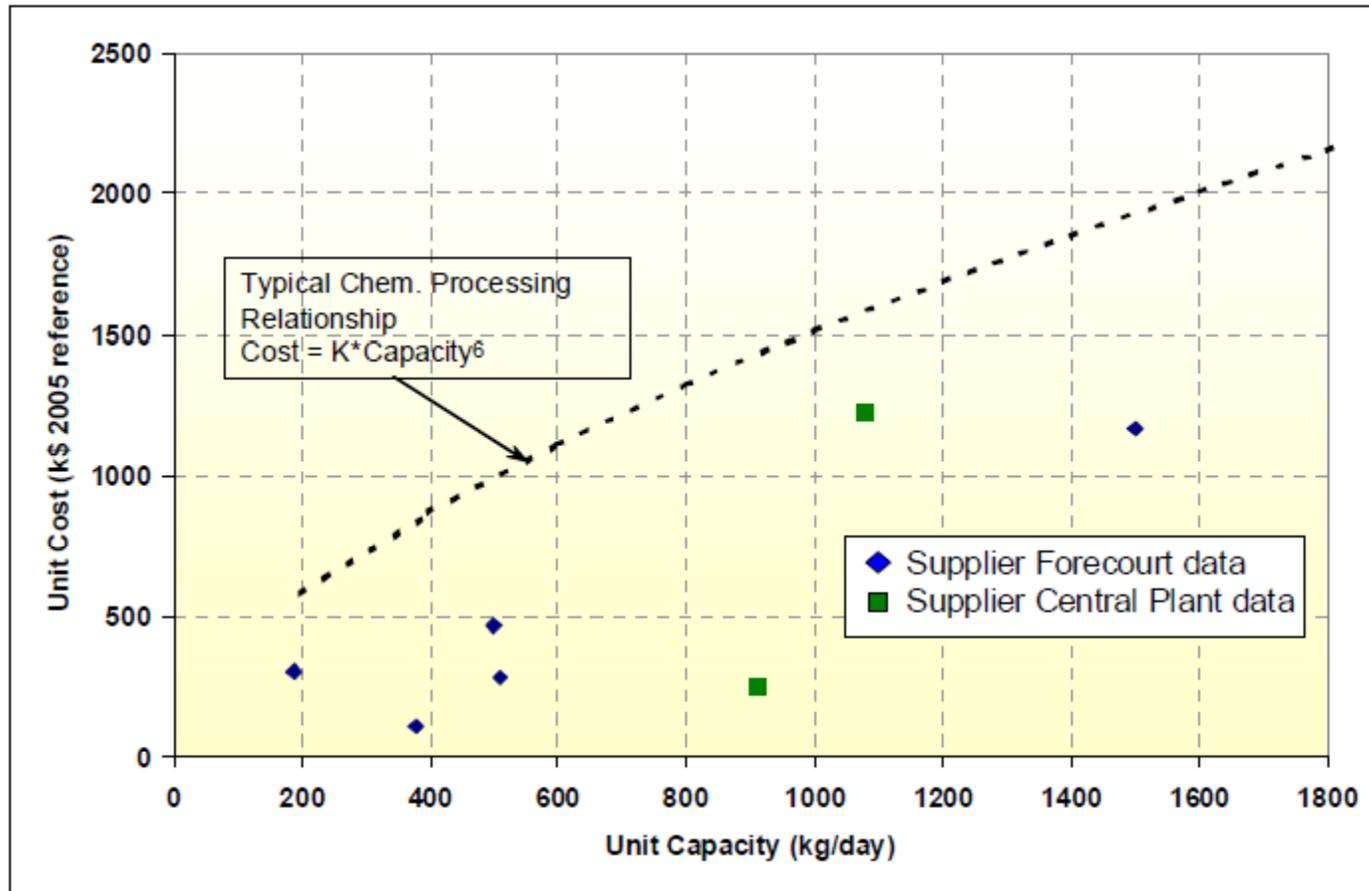
Energy Efficiencies (rectifier, electrolyzer, auxiliaries): 56 – 73%

H₂ purity: 99.8 – 99.998%

Manufacturer	Technology	← Operating Range Available Today →			
		System Energy Requirement (kWh/kg)	H ₂ Production Rate (kg/yr)	Power Required for Max. H ₂ Production Rate (kW)	H ₂ Product Pressure (psig)
Avalence	Unipolar Alkaline	56.4 – 60.5	320 – 3,600	2-25	Up to 10,000
Proton	PEM	62.3 – 70.1	400 - 7,900	3-63	~200
Teledyne	Bipolar Alkaline	59.0 – 67.9	2,200 - 33,000	17-240	60-115
Stuart	Bipolar Alkaline	53.4 – 54.5	2,400 - 71,000	15-360	360
Norsk Hydro	Bipolar Alkaline (high pressure)	53.4	7,900 - 47,000	48-290	~230
	Bipolar Alkaline (atmospheric)	53.4	39,000 - 380,000	240-2,300	0.3

Further requirements: Lower electric & capital, higher output pressure, larger sizes

Water electrolyzer capital costs



NREL report/BK-6A1-46676, 2009

Capital costs

- Chlor-alkali plants are capital intensive (\$200K/t/d to \$1M/t/d)
 - Includes auxiliary systems for treating and handling chemicals
 - Higher temperature (85 to 90 C) requires heating systems
 - Extremely corrosive (requiring expensive materials)
- Water electrolysis plants to produce hydrogen are less capital intensive depending on size
 - Room temperature
 - Less corrosive (depending on input electrolyte)
- CO₂ electrolysis plants may be in-between these two cases
 - We assume similarity to chlor-alkali plants in our analysis

CO₂ Recycling Plant

Desert

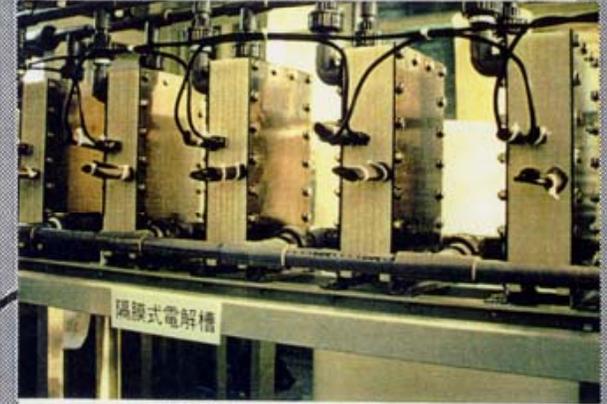


Electricity generation by solar cell operation.

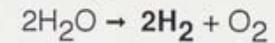
electric power



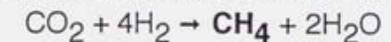
Coast close to the desert



Hydrogen production by electrolysis of seawater.



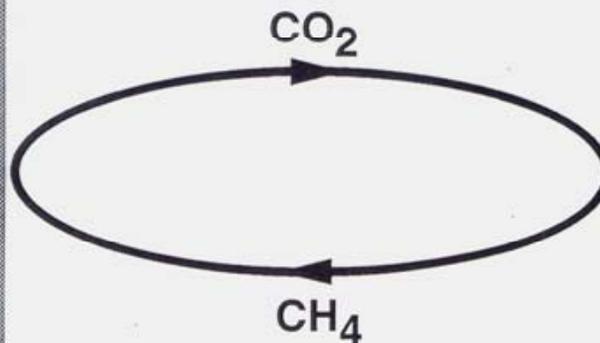
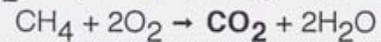
Methane formation by the reaction of hydrogen and carbon dioxide.



Energy consumer



CO₂ is spontaneously recovered.



1995 at Institute for Materials Research, Tohoku University

Pilot Plant of Industrial Scale

Hashimoto et al. (2003)

Hydrogen Production
by Seawater Electrolysis



Methane Production
by the reaction of
Carbon Dioxide with Hydrogen

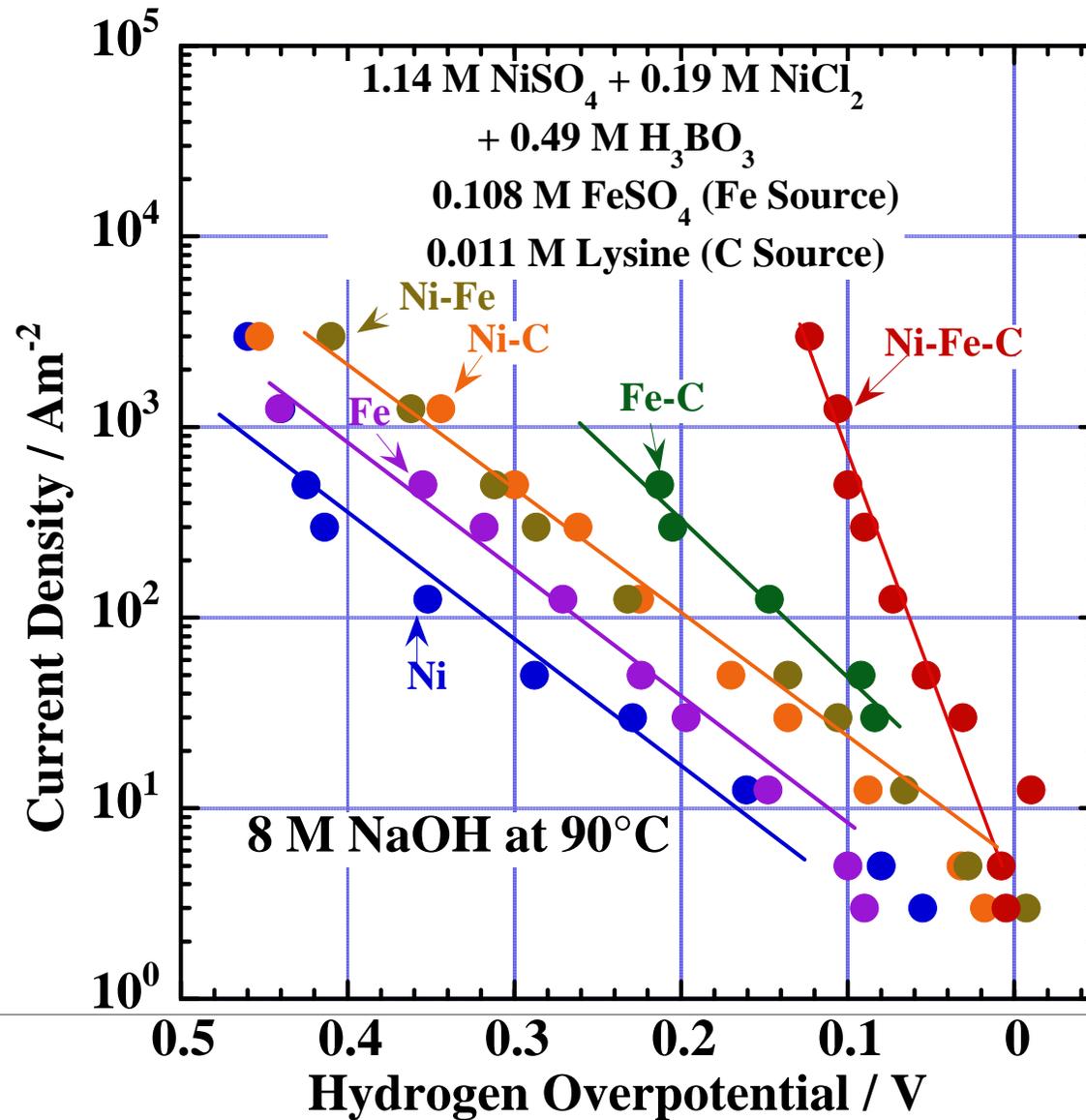


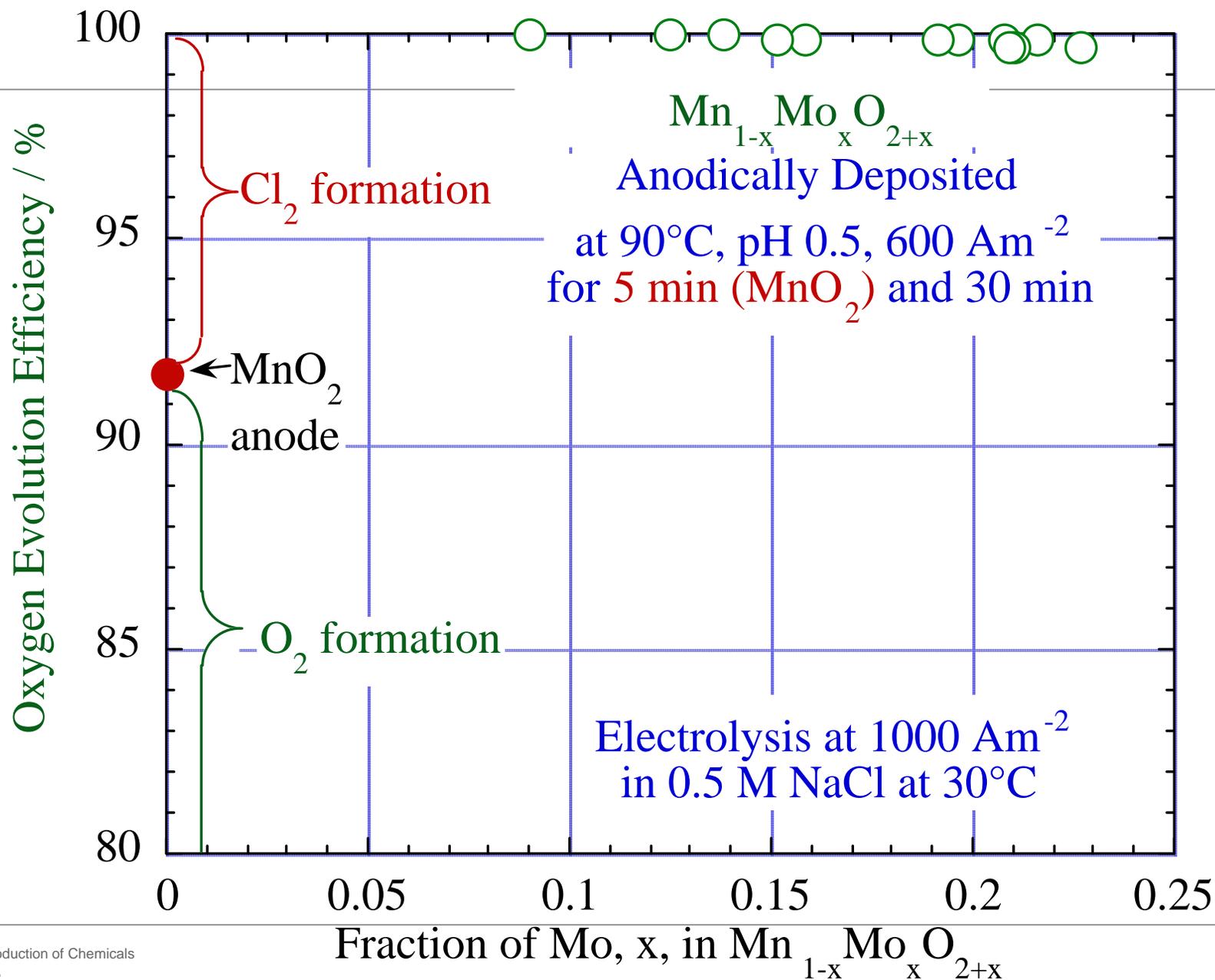
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2003 at Tohoku Institute of Technology

From Hashimoto et al.





CO₂ electrochemical conversion – a very brief history

- Long history of research
 - 1970's – oriented towards local power (U.S. Navy, NASA) - abandoned
 - 1980' and early 90's – fuel production (GRI funded efforts) - abandoned
 - 2000's – CO₂ reduction, renewable power usage orientation
- Focused on catalyst development and reaction mechanisms
 - Only a few full-cell studies
 - No engineering/economic requirements established
- First engineering/economic study of reactor performance by Oloman and Li (205 – 2008)
- More complete analyses for formic acid and CO by DNV group (2008 – now)
- Other reaction kinetics and scale up studies (e.g., Kenis et al.)

Many electrocatalysts

Group 1		CO ₂ Electrocatalysts															Group 18	
1																		2
H 1s																		He 1s ²
1.0079																		4.0026
	Group 2																	
3	4												5	6	7	8	9	10
Li 2s ¹	Be												B	C	N	O	F	Ne
6.941	9.012												10.81	12.011	14.0067	15.999	18.998	20.179
11	12																	
Na	Mg																	
22.989	24.305												26.982	28.086	30.974	32.06	35.453	39.948
		3	4	5	6	7	8	9	10	11	12							
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
39.098	40.08	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69		65.39	69.72	72.59	74.922	78.96	79.904	83.8	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
85.468	87.62	88.906	91.224	92.906	95.94	98	101.07	102.906	106.42	107.868	112.41	114.82	118.71	121.75	127.6	126.905	131.29	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	Ba	La ★	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
132.905	137.33	138.906	178.49	180.948	183.85	186.207	190.2	192.22	195.08	196.967	200.59	204.383	207.2	208.98	209	210	222	

From: Azuma et al., JES, 137 (6), 1772, (1990)
-2.2V vs. SCE, 0.05M KHCO₃, RT

Thermodynamics of CO₂ reduction

Thermodynamically, reduction of CO₂ should be as feasible as that of water

Practically, CO₂ reduction is governed by:

- Low kinetics
- Product economics

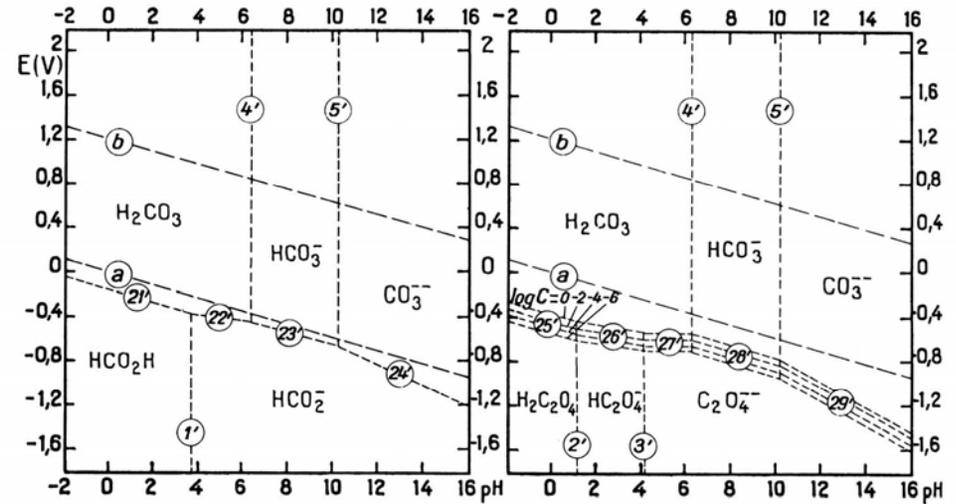


FIG. 3. Domains of relative predominance of carbon in the form of formate and carbonates, at 25°C.
 FIG. 4. Domains of relative predominance of carbon in the form of oxalates and carbonates, at 25°C.

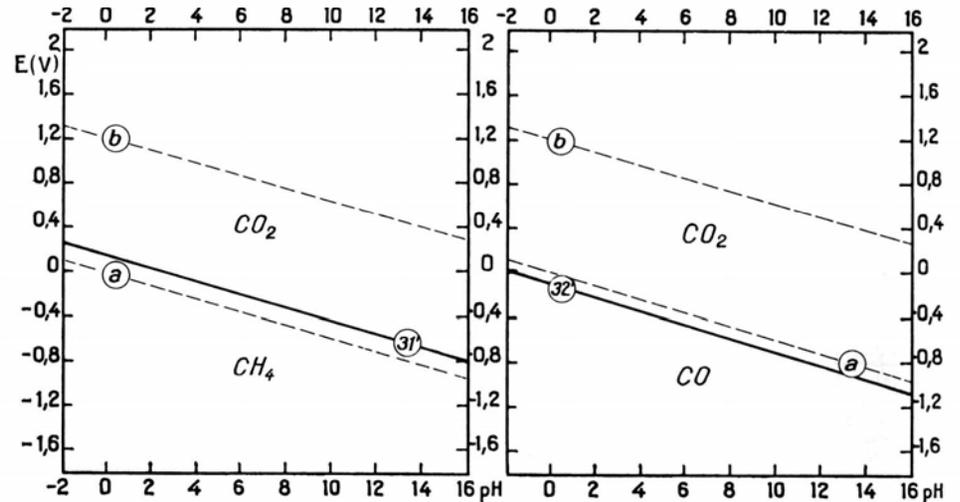
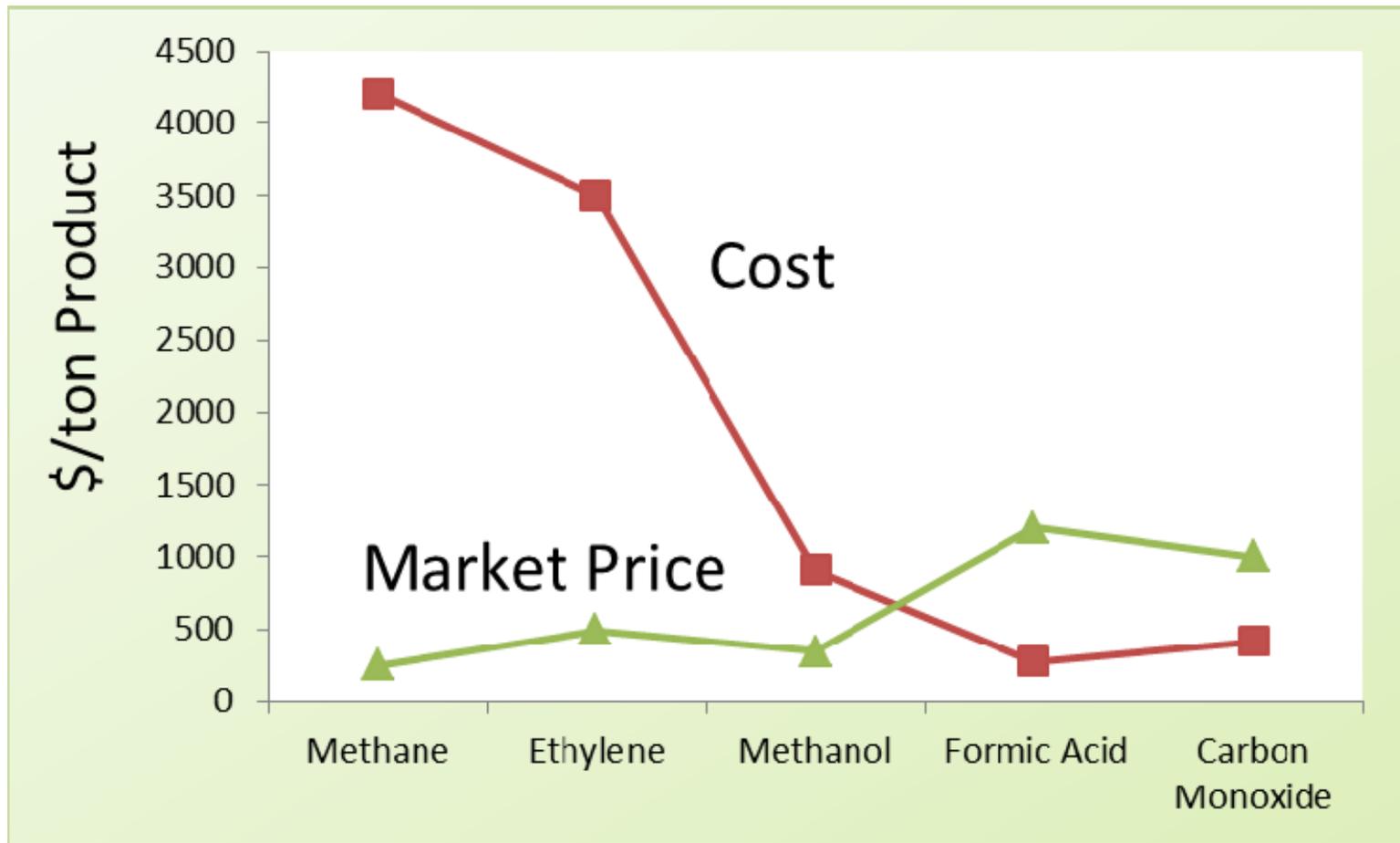


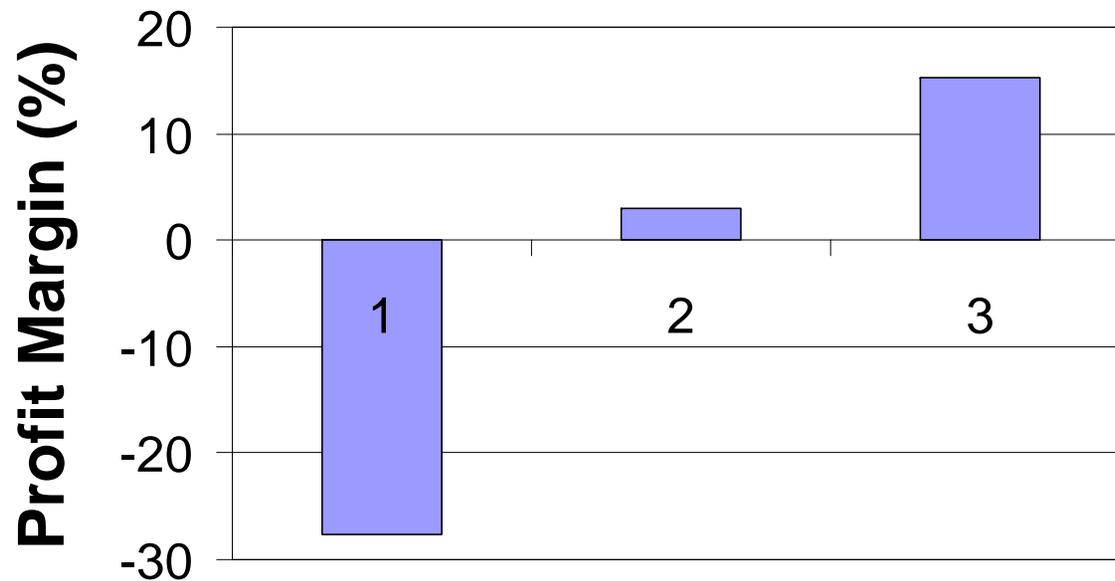
FIG. 5. Domains of relative predominance of the gaseous carbon derivatives CH₄ and CO₂ (stable equilibrium).
 FIG. 6. Domains of relative predominance of the gaseous carbon derivatives CO and CO₂ (unstable equilibrium).

Direct CO₂ Electrochemical Reduction – Approximate opex



Trade-offs in Technology Development

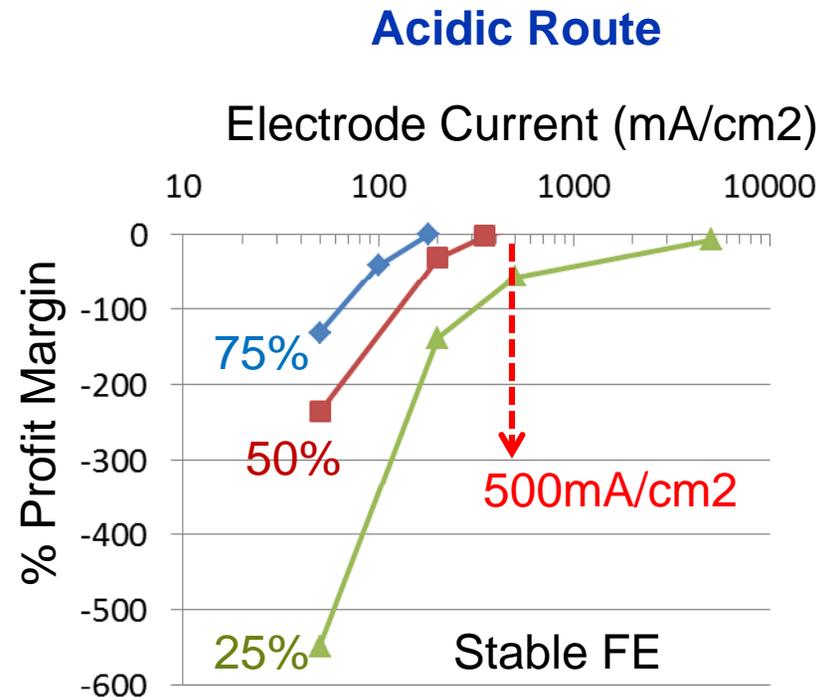
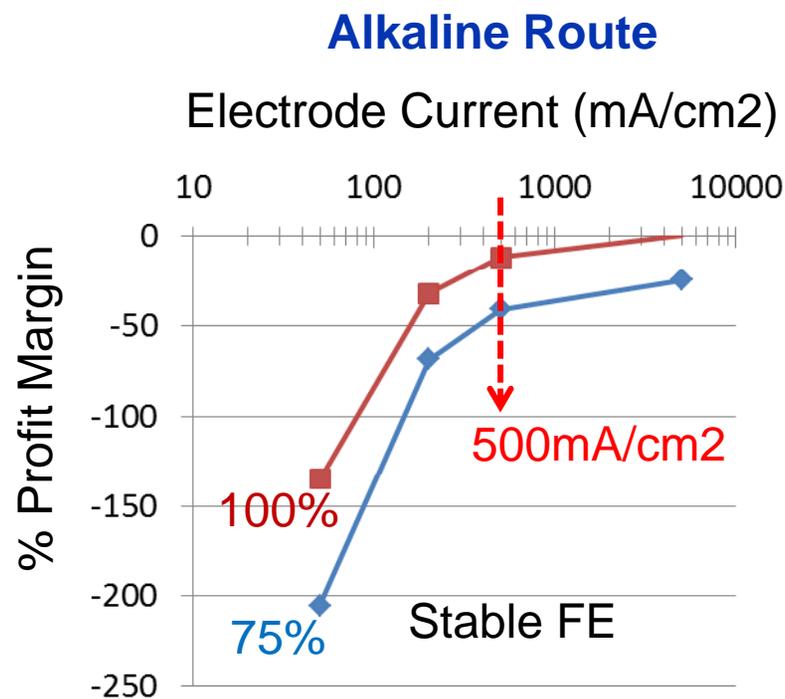
	Route	Energy (\$/ton)	Chemicals (\$/ton)	C.D. (mA/cm ²)
1	Alkaline anolyte	393	500	70
2	Acidic anolyte	560	3	40
3	Acidic anolyte – higher productivity goal	560	3	100



Formic Acid = 1,050 \$/ton
 Capacity = 90,000 ton/year
 20-year capitalization
 No carbon credit

Profit Margin - CAPEX and OPEX

- Alkaline route requires high current density and FE for profitability
- Acid route requires lower current density and lower stable FE
- Catalyst/Electrode development could increase current to 500 mA/cm²



Technology Development Targets

Economic Feasibility

Improved
50%

High Current Density
> 100 mA/cm²

Long Electrode Life
(1 – 2 years)



High Catalyst Selectivity
(FE > 70%)



Low Energy Consumption
(< 10 MWe/ton)



Low Chemical Consumption



Reduce corrosivity of chemicals

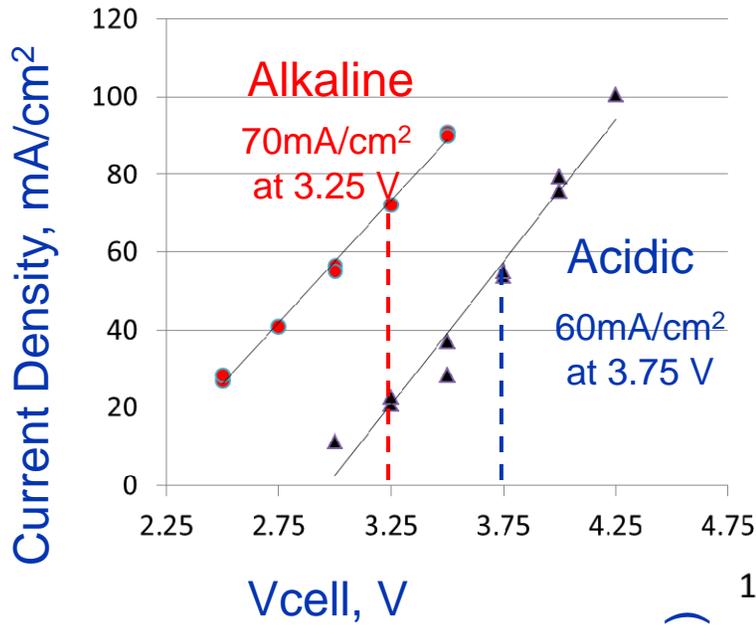
Electrode Fab.
True area
lifetime
(Cathode, Anode)

In-situ Catalyst
Reactivation

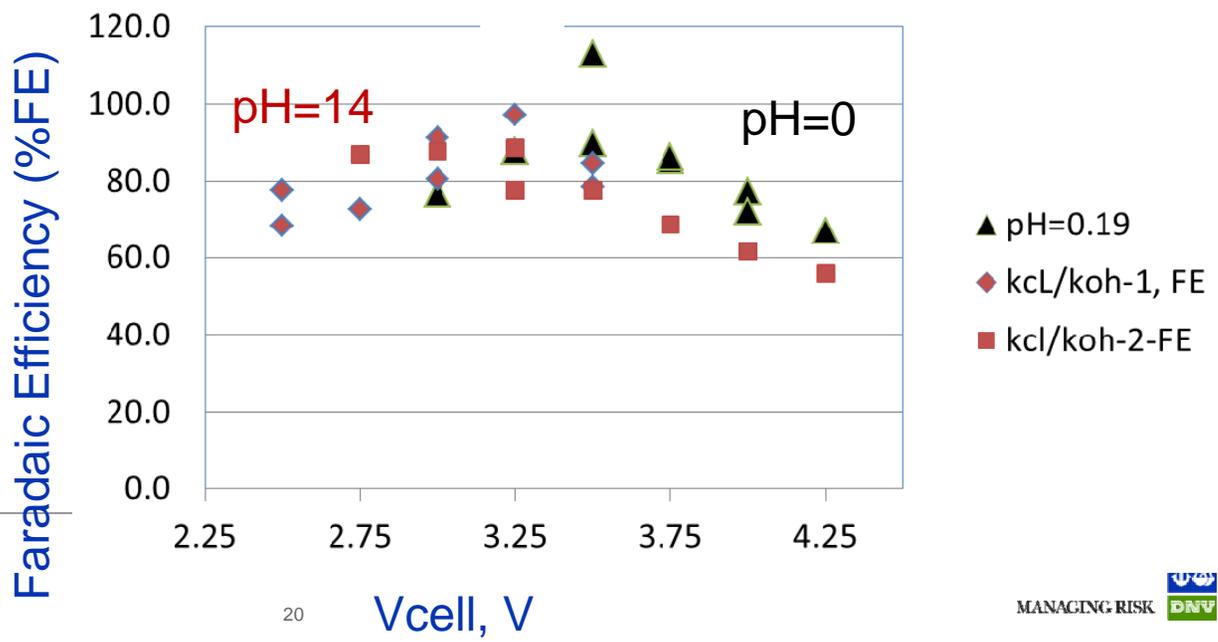
Novel Catalysts
Selectivity & Reactivity
(Cathode, Anode)

Chemical Routes

Optimal Value Comparison – Acidic and Alkaline Routes



Acidic route preferred because of Lower consumables

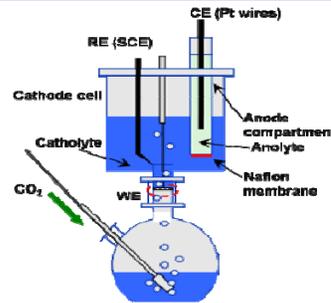


Multi-Scale Approach

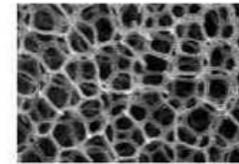
Lab Scale

Novel Cathode &
Anode catalysts

Reactivity &
Selectivity

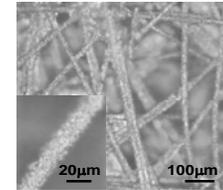


Macroporous
(>80%) Sn sponge



60–80 mA/cm², 40% FE,
constant over 1 day

Sn electrodeposited
carbon fiber

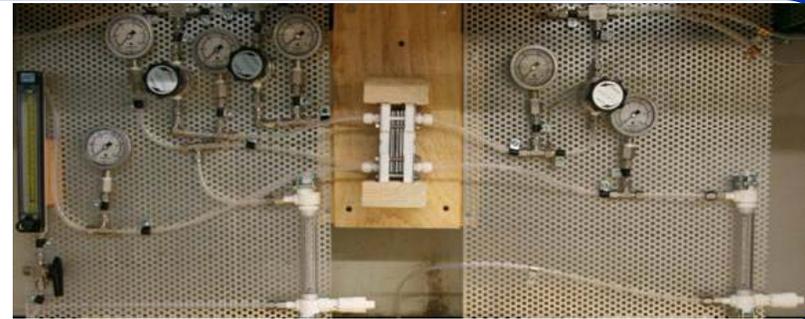


50–80 mA/cm², 70% FE,
decrease with time

Bench Scale

Continuous operation

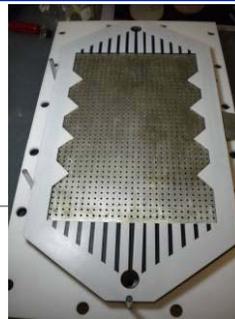
Electrodes, chemistry
Lifetime



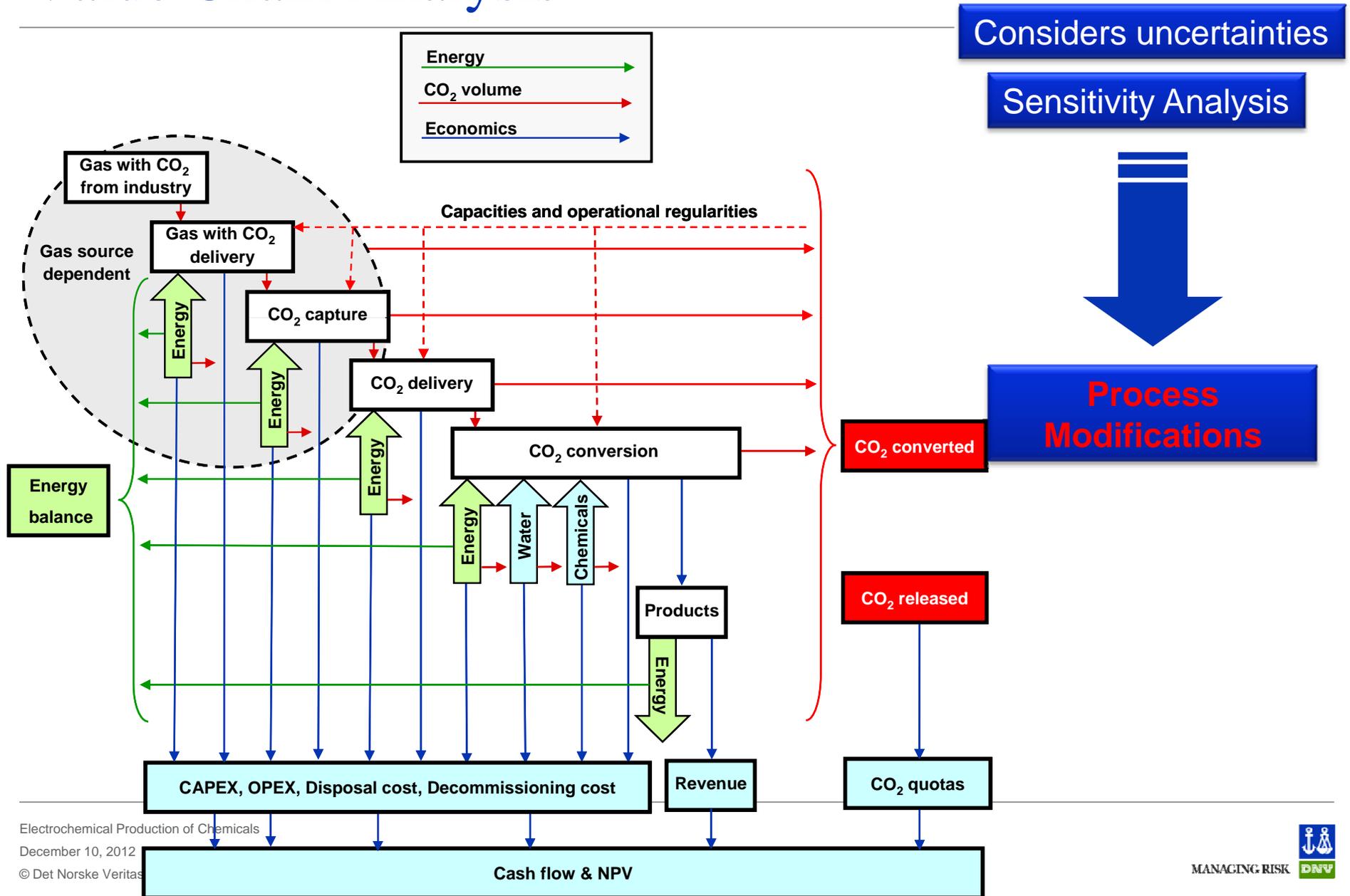
Demo Unit

Reactor Design

Mass Transfer



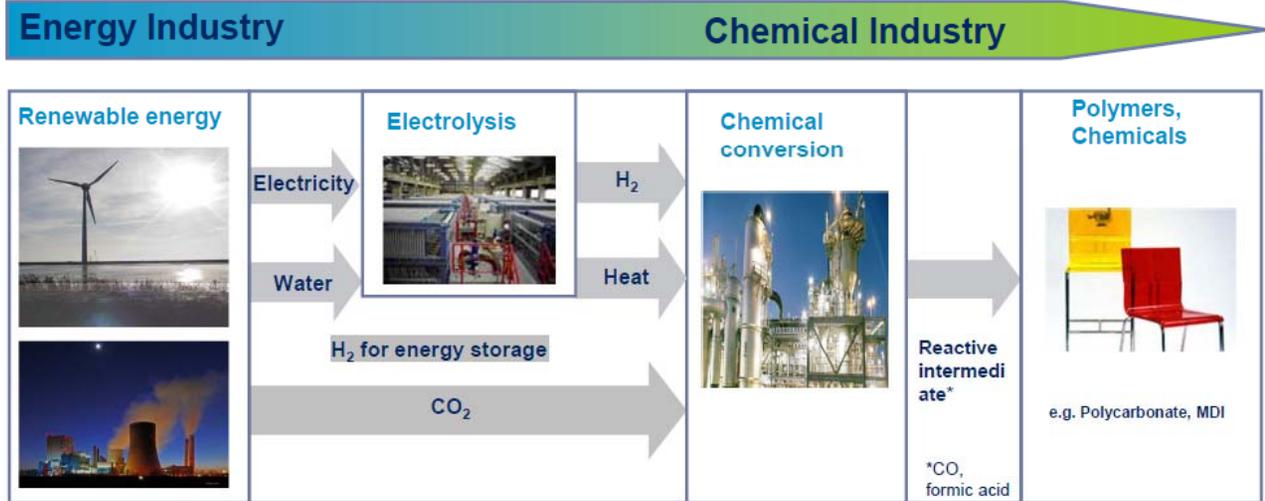
Value Chain Analysis



German Consortia Formed in 2010



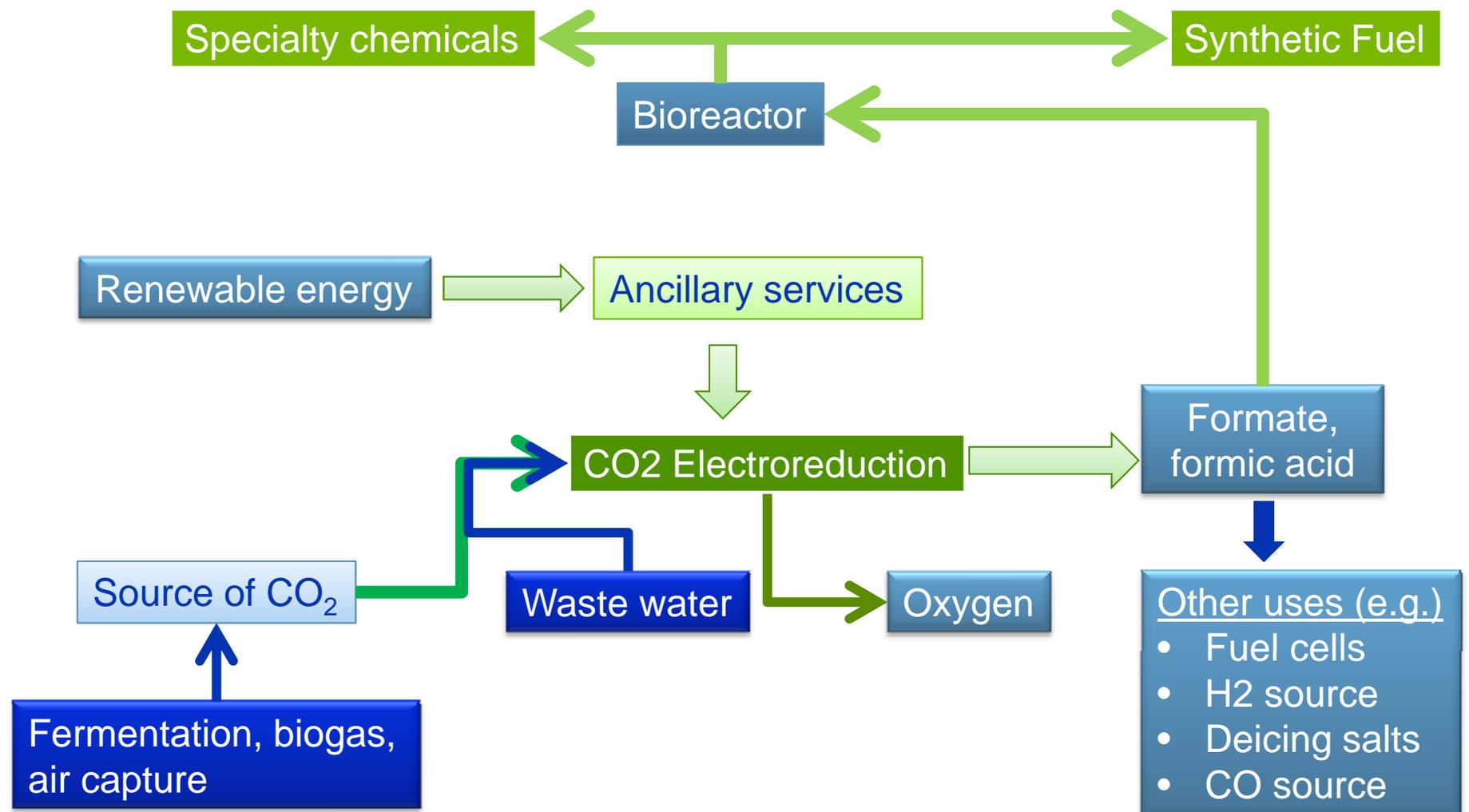
CO2RRECT – Wind Power to Polymer



VORWEG GEHEN SIEMENS Bayer Technology Services Bayer MaterialScience



A notional “Integrated CO₂ synthesis plant”



Summary

- Electrochemical reduction of CO₂ to formic acid or CO appears to be commercially feasible
 - Improvements in catalyst stability, current density, and reactor design are necessary
- Synthesis of fuels and fine chemicals from CO₂ should be considered as a combination of processes much like a refinery or petrochemical complex
- Multi-scale demonstration is a required step in continued improvement of processes
 - Chlor-alkali industry is still improving after 100+ years!
 - Economic and sustainability analyses are important

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