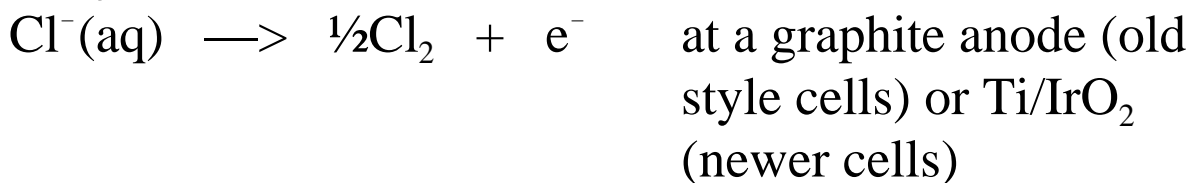# The chloralkali process

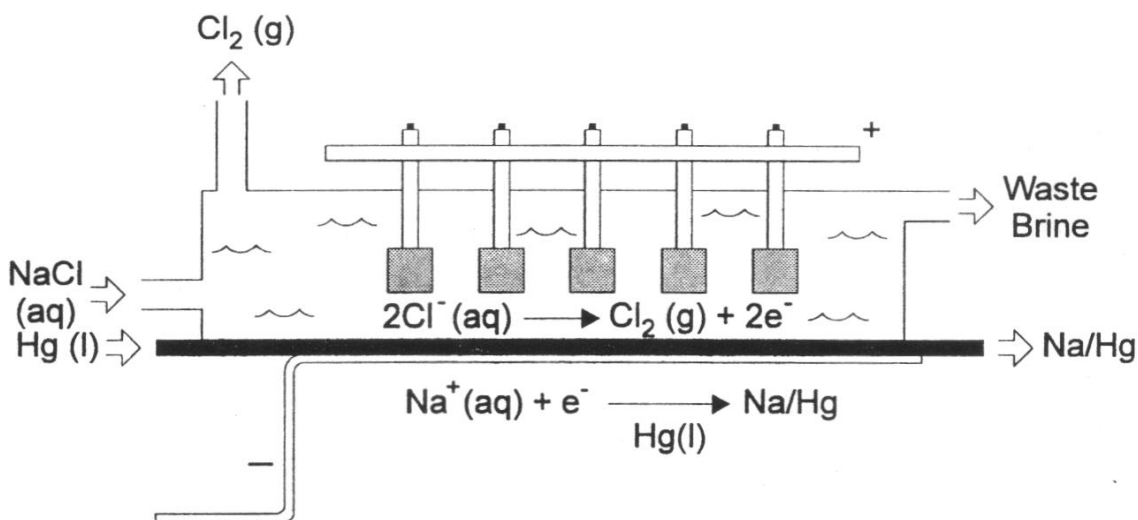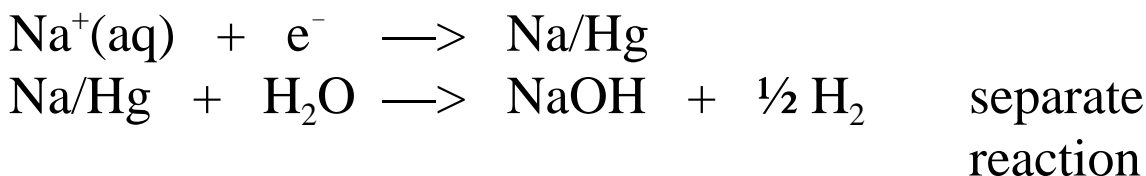$$2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$$

Economics of equal masses of NaOH and Cl_2 being produced; reintroduction of soda ash process for NaOH

Electrolysis: <u>Anode reaction</u>

$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2 + e^-$ at a graphite anode (old style cells) or Ti/IrO_2 (newer cells)

<u>Cathode reaction</u>: old style mercury cell

$Na^+(aq) + e^- \longrightarrow Na/Hg$

$Na/Hg + H_2O \longrightarrow NaOH + \frac{1}{2} H_2$ separate reaction


Flowing mercury cell for electrolyzing brine.

- Advantage of the old style cell: H_2 and Cl_2 formed in separate steps

- Disadvantage: cost of Hg and losses of Hg to the environment —> high concentrations of Hg in fish —> phase-out of this technology

- Newer technology: diaphragm or membrane separated cells to separate the $H_2(g)$ and $Cl_2(g)$ streams: use of Nafion as a cation exchange membrane (cations pass through; neutrals and anions are repelled). **Mercury free!**
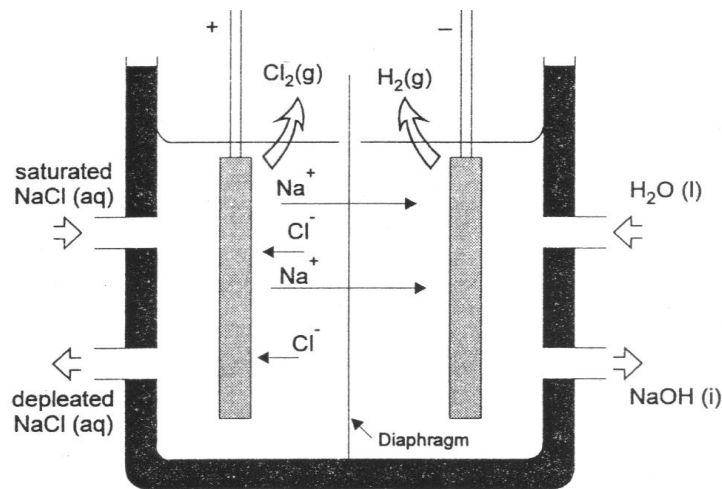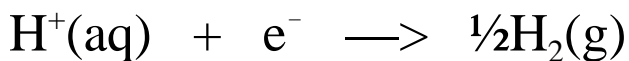

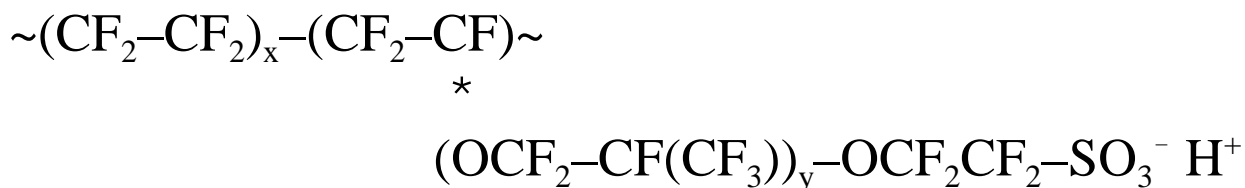Schematic of a diaphragm or membrane cell.

Anode reaction
$$Cl^-(aq) \longrightarrow \text{½}Cl_2(g) + e^-$$
Cathode reaction
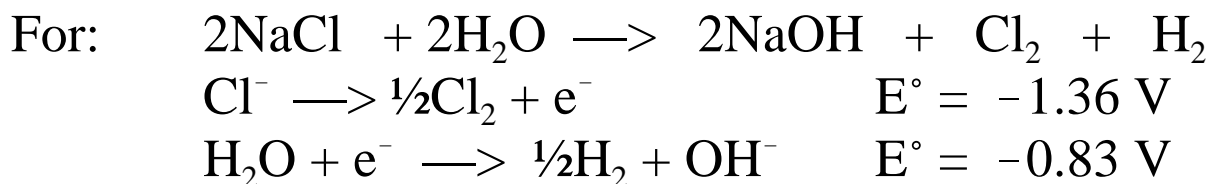$$H^+(aq) + e^- \longrightarrow \text{½}H_2(g)$$
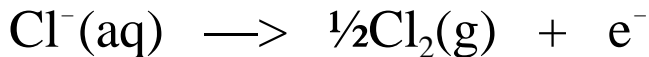
The asbestos diaphragm cell gives a lower quality NaOH; contaminated with NaCl because the diaphragm is not selectively permeable.

The Nafion membrane overcomes this limitation

$$\sim(CF_2-CF_2)_x-(CF_2-CF)\sim$$
$$*$$
$$(OCF_2-CF(CF_3))_y-OCF_2CF_2-SO_3^- \; H^+$$

- NaOH forms because Na^+ ions cross the ion exchange membrane to restore charge balance due to loss of H^+; **important property of ion exchange membranes**

Cell potential

For: $2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$
$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ $E° = -1.36\ V$
$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$ $E° = -0.83\ V$

Overall $E°(cell) = -2.19\ V$

Suppose you could use as the cathode:
$O_2 + 4e^- + 4H^+ \longrightarrow 4OH^-$ $E° = +0.40\ V$

Then the overall cell reaction would be:
$2NaCl + \frac{1}{2}O_2 + H_2O \longrightarrow 2NaOH + Cl_2$
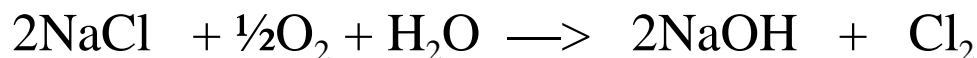
and the overall $E°(cell)$ would be reduced to $-0.96\ V$

Energy costs

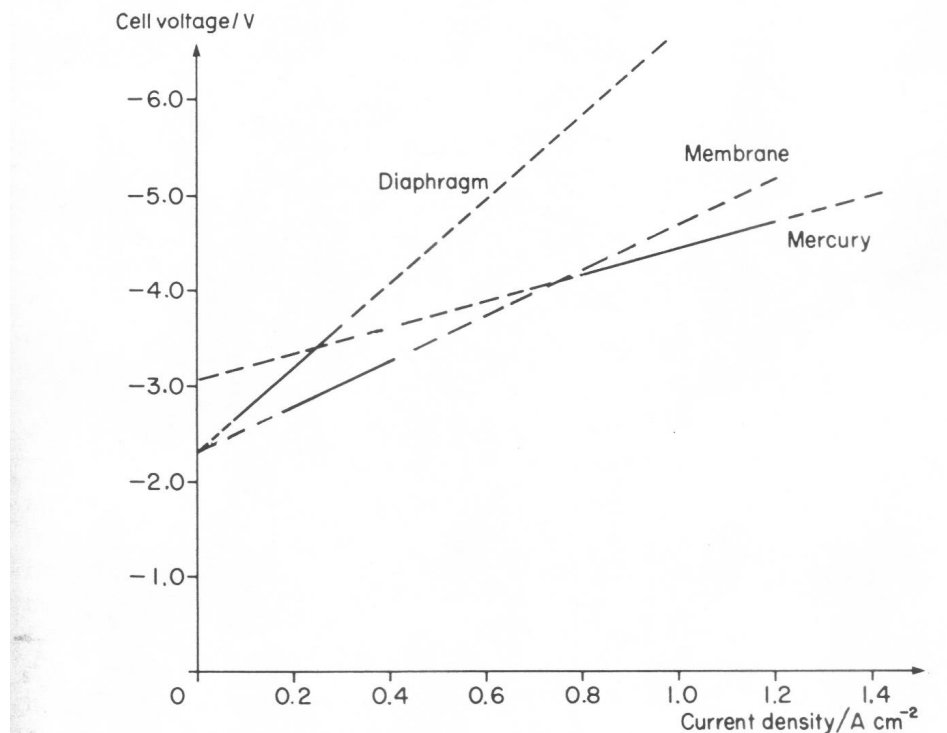Fig. 3.20 Cell voltage versus current-density plots for the three types of chlor-alkali cell
The full lines indicate the normal operating regions.

- the V *vs j* curves are linear because the major inefficiency in all cell types is due to iR_{cell}. The diaphragm has higher resistance than the Nafion membrane

- the mercury cell, for which the cathode reaction is:
  $$Na^+ \ + \ e^- \ \longrightarrow Na/Hg \qquad E = \ -1.85 \ V$$
  hence E at $j = 0$ is -3.2 V

- recall that energy costs scale linearly with V, but that high $j \longrightarrow$ greater rate of production. Compromise between throughput (return on capital) and operating costs

Table 3.5 Typical data for recent commercial chlor-alkali cells

	Mercury cell	Diaphragm cell	Membrane cell
Cell voltage/V	−4.4	−3.45	−2.95
Current density/A cm^{-2}	1.0	0.2	0.4
Current efficiency for Cl_2/%	97	96	98.5
Energy consumption/kWh per ton of NaOH			
(a) Electrolysis only	3150	2550	2400
(b) Electrolysis+evaporation to 50% NaOH	3150	3260	2520
Purity Cl_2/%	99.2	98	99.3
Purity H_2/%	99.9	99.9	99.9
O_2 in Cl_2/%	0.1	1–2	0.3
Cl^- in 50% NaOH/%	0.003	1–1.2	0.005
Sodium hydroxide concentration prior to evaporation/%	50	12	35
Mercury pollution considerations	Yes	No	No
Requirement for brine purification	Some	More stringent	Very extensive
Production rate per single cell/tons NaOH per year	5000	1000	100
Land area for plant.of 10^5 tons NaOH per year/m^2	3000	5300	2700

- E_{cell} > E°(calc) of 2.19 V

- high purity NaOH and better energy efficiency of membrane cell

- membrane cell requires higher purity NaCl to avoid membrane fouling: ***always a problem with divided cells!***

- Ti/IrO_2 anodes (superior to carbon) resist corrosion by Cl_2; a "dimensionally stabilized anode" (DSA)

Aluminum production: an example of electrowinning
- ore is bauxite Al_2O_3 which is purified, then electrolyzed using cryolite Na_3AlF_6 as the supporting electrolyte (Heroult-Hall process); 15 wt%, 1000°C
- Carbon anodes (powdered anthracite/pitch; compressed and baked); carbon cathodes (though they actually get covered with liquid Al metal)

- overall chemistry:

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

    exact Al species are not known

- pollution problems: HF; polycyclic aromatic hydrocarbons
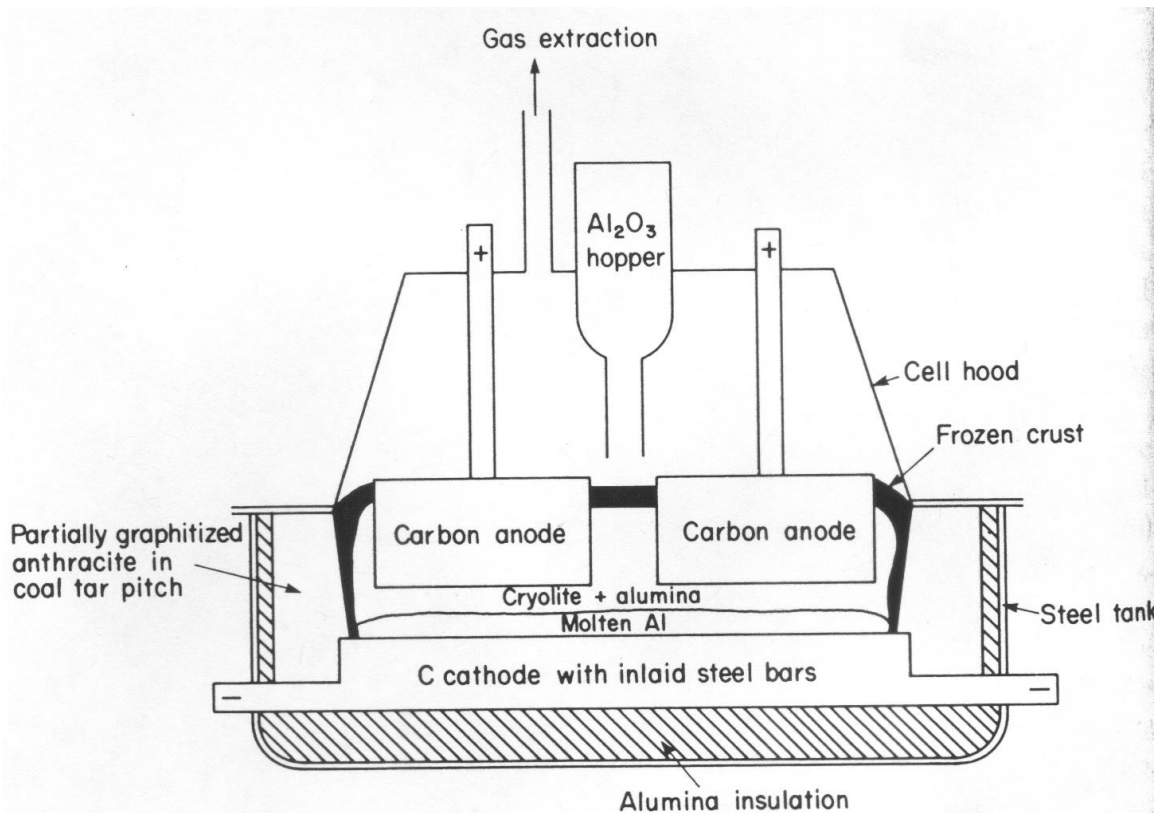

Fig. 4.1 Cell for the Hall–Heroult process for aluminium extraction.

Energetics and costs

- very high electricity requirement; ~ 15,000 kWh per tonne Al

- most Al reduction plants have their own hydroelectric supply (*e.g.*, Kitimat)

- thermodynamic cell potential is –1.18 V (it would be –2.2 V if O_2 were produced at the anode instead of CO_2)

Contributions to E_{cell}:	1.18 V
anode/cathode overvoltages	0.5 V (all at anode)*
iR drops (anode, cathode)	1.1 V
iR drop (electrolyte)	1.5 V
Total	4.3 V

*   typical problem when a gas is evolved; ohmic resistance of gas bubbles that have not disengaged the surface

- costs:

purified bauxite	30%
electricity	23
capital	17
labour	16
carbon anodes	7
other materials	7
Total	100%

Monsanto's adiponitrile process

- adiponitrile as an intermediate in the production of nylon[6.6], affording both adipic acid and hexamethylenediamine

- $2CH_2=CH-C\equiv N + 2H^+ + 2e^- \longrightarrow N\equiv C-(CH_2)_4-C\equiv N$

- mechanism is known in general outline, but not in every step
  $CH_2=CH-C\equiv N + e^- \longrightarrow [CH_2=CHCN]^{\cdot-}$ occurs first
  what is not clear is:
  1) the order of protonation and electron transfer steps
  2) whether electron transfer occurs from the cathode or from anionic intermediates in solution
  3) at what point the new C–C bond is formed. Here is one possibility

$CH_2=CHCN^{\cdot-} + CH_2=CH-CN \longrightarrow NC-CH^{\cdot}CH_2CH_2CH^-CN$

$$\downarrow H^+; e^-$$

$$N\equiv C-(CH_2)_4-C\equiv N$$
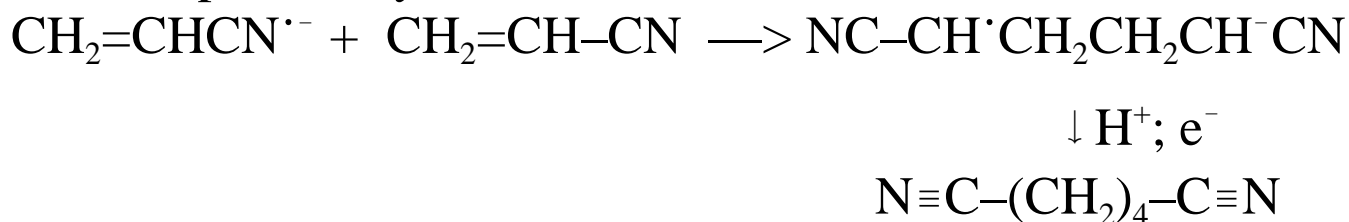
- Original adiponitrile process (Monsanto, 1965) used Pb cathode, PbO_2/AgOanode; cation exchange membrane; supporting electrolyte Et_4N^+ $EtOSO_3^-$. The anode reaction was O_2evolution from 5% H_2SO_4. Catholyte feed is acrylonitrile, which is 7% soluble in aq phase (adiponitrile dissolves into the excess acrylonitrile)

- More recent developments:
  - S   undivided cell (cheaper, simpler, easier extraction of products)
  - S   carbon steel anodes + corrosion inhibitors. Anode reaction is again O_2 evolution
  - S   Cd-plated carbon steel cathodes
  - S   in practice, there is a series of parallel carbon steel plates, one face of which is Cd plated. EDTA in the supporting electrolyte is found to suppress H_2 formation as a competing cathode reaction
  - S   15% Na_2HPO_4 as the supporting electrolyte (+ 0.4% of a complex quaternary ammonium salt)

- Energy aspects and costs

	Old style cell	New style cell
j, A cm^{-2}	0.45	0.20
Voltages		
reversible cell potential, V	-2.50	-2.50
overpotentials	-1.22	-1.87
electrolyte iR	-6.24	-0.47
membrane iR	-1.69	-
Total	-11.65	-3.84
Energy, kWh t^{-1}	6700	2500

Paired electrolysis: an electrochemist's dream

- The concept: to produce a useful product at each electrode *i.e.*, couple an oxidative reaction with a reductive reaction

- Better yet: use an undivided cell — therefore the product of reduction must not be reoxidizable and the product of oxidation must not be reducible

- The BASF process for phthalide and t-butylbenzaldehyde (agrochemical intermediates)

- Oxidative process: *p*-tert-butyltoluene –> *p*-tert-butylbenzaldehyde dimethylacetal
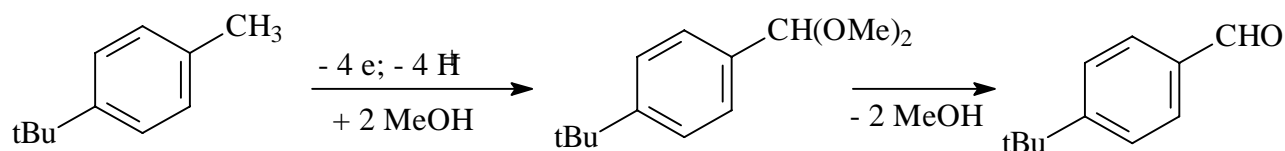
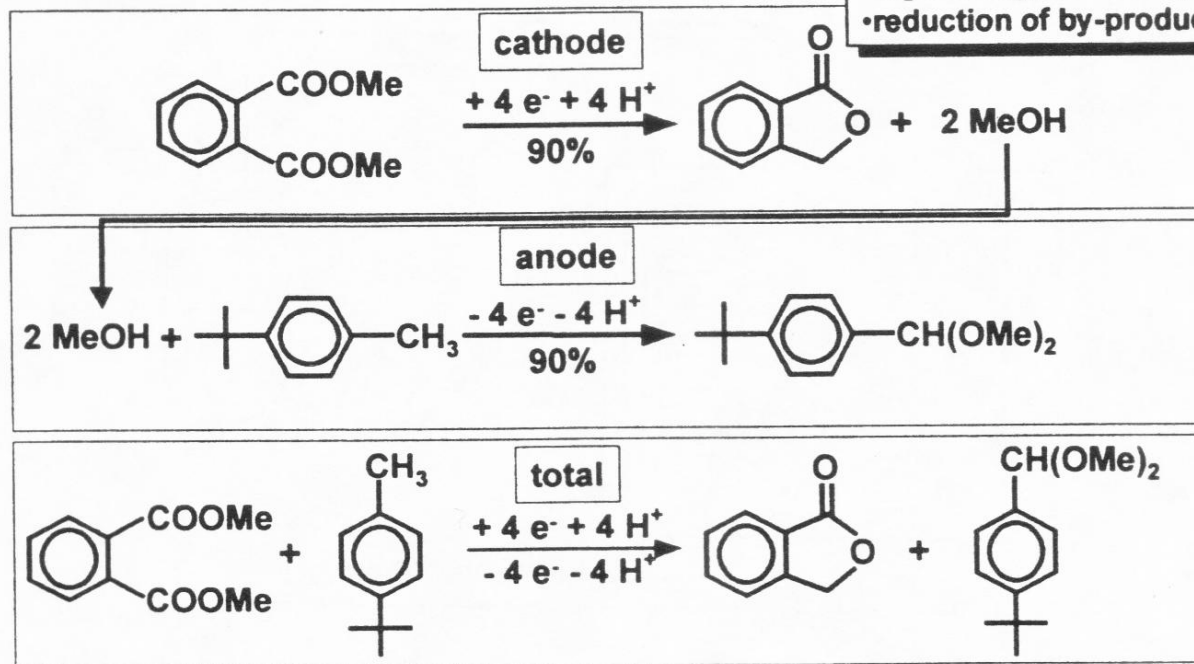- Reductive process: phthalic anhydride –> phthalide
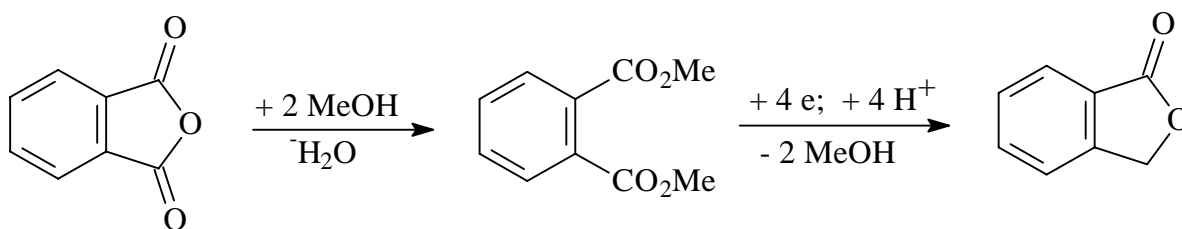
Phthalid/t-Butylbenzaldehyd

The First Commercial „Paired Electrosynthesis"

BASF

Green Context:
- high yield
- high atom efficiency
- high energy efficiency
- reduction of by-products

cathode: $+4\,e^- + 4\,H^+$, 90% → phthalide + 2 MeOH

anode: $2\,MeOH + $ (t-Bu-C6H4-CH3) $\xrightarrow[90\%]{-4\,e^- - 4\,H^+}$ t-Bu-C6H4-CH(OMe)$_2$

total: $\xrightarrow{+4\,e^- +4\,H^+ \ / \ -4\,e^- -4\,H^+}$

supporting electrolyte: MTBS; (Methyltributylammoniummethosulfat)

- From H. Pütter, *Electrochemistry Forum*, 2001